A Primer on Quantum Mechanics

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Preface

At the turn of the 20th century there were two revolutions that shook the foundations of what is now called classical physics: relativity and quantum mechanics. Of these two the latter is several orders of magnitude more revolutionary.

It may be true that relativity shook a lot of the biases of Newtonian physics. Time was no longer absolute but instead it was the speed of light that was absolute. Simultaneity is relative and only time-like separated events have a causal order. With general relativity gravity ceases to be a force and becomes attached to the geometry of spacetime which therefore becomes dynamical and changing. Seems pretty revolutionary.

Nevertheless, the basic structure of physics was left unchanged: we have to set up initial conditions such as the particles initial position and velocity, and then we solve its equations of motion fully deterministically. Sure, we might have to deal with fields instead of particles, and perhaps even spacetime curvature. But, even with time being relative, even with dynamical spacetime curvature, the fundamental equations can be summarised as an (admittedly terribly complicated) initial value problem. Further, the act of measuring can be assumed to be negligible and doesn't need to be included in the fundamental description of the theory. Measuring the position of Mercury with a telescope for sure won't change its trajectory, and despite the incredible amounts of noise and the precision required for the experiment, the same is true for gravitational waves. And finally, we can measure any two observables with arbitrary precision, knowing Mercury's position has no bearing on how precisely we know it's velocity.

For quantum mechanics, none of the above is true. The theory at its most fundamental is probabilistic, we cannot determine the outcomes of experiments with certainty, only their probabilities. Measuring an observable disturbs the system under study significantly and greatly affects the outcomes of future measurements. Some observables cannot be known with infinite precision at the same time, there is an absolute and fundamental limit to the combined precision of certain measurements.

These features are so untenable, so vile, that in the century since its discovery many and many physicists have tried to find flaws in quantum mechanics. Surely our description is incomplete or flawed in some way, right? For over a century people have been so sceptical of quantum mechanics that they still try to find loopholes and interpretations and alternatives, desperately trying to show that it is somehow wrong or incomplete. And yet, despite its abhorrent features, Quantum Mechanics holds supreme, predicting the results of the experiment with an astonishing level of accuracy.

The computer you are probably reading this on relies on transistors which themselves rely on quantum mechanics. The smell of the mug of tea, or coffee, or hot chocolate you are probably holding also relies on quantum mechanical processes in your nose. Every time you witness a chemical reaction you are witnessing quantum mechanics. Quantum mechanics is everywhere, it is the language of Nature. Whether we like it or not, it is here to stay. Now it is your time to learn it.

Despite all of this, quantum mechanics can be understood. In fact, it is not even that complicated to understand. The complicated part is to do away with our intuition entirely and treat it as a wholly new thing. It is not quantum mechanics which is confusing it is our biases as to how Nature should work that make it confusing.

The approach in these notes will be quite unconventional. Rather than following the traditional approach of Schrodinger and his wavefunctions we will instead follow a route closer to Dirac and Feynman, first treating discrete systems and only later dealing with the continuous case. After dealing with the quantum kinematics we delve into the dynamics keeping Schrodinger and Heisenberg's approach on equal footing, immediately using them to understand how symmetries can help us solve quantum mechanical problems. We then go on to solve several of the simplest 1-dim examples: the free particle, piecewise constant potentials, and the harmonic oscillator. After this we tackle the topic of central potentials and rotational symmetry in 3 dimensions, introducing the quantum version of angular momentum, both orbital and spin. We end with a treatment of the measurement problem, following Sidney Coleman's perspective that it is not quantum mechanics that needs interpretation but classical mechanics that needs to be interpreted within the framework of quantum mechanics.

This text was written to cover the bare minimum of quantum mechanics necessary to start learning quantum field theory. We have skipped a lot of the topics which, while important, would either not be strictly necessary or would need to be re-derived in the relativistic context. This is why we have omitted time-independent perturbation theory, which is usually covered in the first course on quantum mechanics. What is covered should be sufficient for a 1-semester course on quantum mechanics if supplemented with an introduction to time-independent perturbation theory.

The mathematical pre-requisites are linear algebra, complex and vector calculus, and Fourier analysis. Distribution theory and group theory are welcome but not essential. Physically we will very often rely on the Hamiltonian formalism of classical mechanics and Poisson brackets, and it is also assumed one has seen classical wave mechanics, including diffraction and evanescent waves. Electromagnetism will be occasionally useful but the necessary tools and concepts will be introduced as needed.

João F. Melo, 2025

PART I

Chapter 1. The puzzles with atomic theory
Chapter 2. Are electrons particles or waves?

An Invitation

As with any subject, the history of the discovery of quantum mechanics is complex. There were many hints that there was something deeply wrong with classical mechanics, from the spectrum of black body radiation to the emission spectra of atoms. All of which suggested different aspects of what would become the theory of quantum mechanics. It is usually wise to avoid the history of physics in great detail, otherwise we would waste a lot of time describing uninformative dead-ends. Nevertheless, it is worth it to know what were the problems our theory is meant to solve, to have something to aim for. That is the objective of these two chapters. We will narrow our focus on the nature of the atom and the electron as these not only highlight some key features of quantum mechanics but they will be fully explained by the end of this volume. The same would not be true of the theory of photons and radiation as that requires more advanced techniques beyond the scope of this text.

1 The puzzles with atomic theory

From the ancient Greek ἄτομον meaning "uncuttable", the atom has been theorised as the fundamental, indivisible, constituent of matter for millennia. These ideas became scientific in 1804 when John Dalton (Fig. 1.1) proposed the law of multiple proportions, realising that in chemical reactions the ratios between the different elements involved were small whole numbers. This suggests that each element corresponds to a different atom, and each molecule to a specific arrangement of these atoms. Although a topic of great contention, by the end of the 19th century the atomic theory was widely successful, being capable to explaining several properties of chemical reactions and classical thermodynamics, serving as the basis for statistical mechanics and kinetic theory. The theory of the atom is so important that Richard P. Feynman (Fig. 1.2) in his famous lectures stated

> If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generations of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis (or the atomic fact, or whatever you wish to call it) that *all things are made of atoms—little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another.*

Nevertheless, as with many other things, the turn of the century proved to be quite challenging.

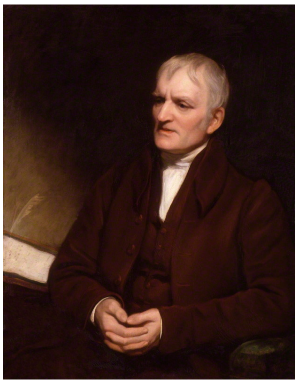

Figure 1.1. **John Dalton** FRS[1]
Born: 1766 Eaglesfield, Kingdom of Great Britain
Died: 1844 Manchester, United Kingdom of Great Britain and Ireland

Figure 1.2. **Richard Phillips Feynman**[2]
Born: 1918 New York City, United States of America
Died: 1988 Los Angeles, United States of America
Doctoral Advisor: John Archibald Wheeler

1.1 The electron and the nucleus

The first hint was the discovery that the atom is in fact *not* indivisible. In 1897, J. J. Thomson (Fig. 1.3) managed to show that cathode rays were in fact made up of tiny negatively charged particles around 1 800 times lighter than hydrogen. These rays are

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[1] Picture by Thomas Phillips - National Portrait Gallery, London, Public Domain, https://commons.wikimedia.org/w/index.php?curid=11727058

[2] Picture by The Nobel Foundation - http://www.nobelprize.org/nobel_prizes/physics/laureates/1965/feynman-bio.html, PD-Sweden, https://en.wikipedia.org/w/index.php?curid=34664654

produced when a large potential difference is applied between two electrodes in a vacuum tube, Fig. 1.4.

Figure 1.3. Sir **Joseph John Thomson** OM FRS[3]
Born: 1856 Manchester, United Kingdom of Great Britain and Ireland
Died: 1940 Cambridge, United Kingdom of Great Britain and Northern Ireland
Academic Advisor: Lord Rayleigh

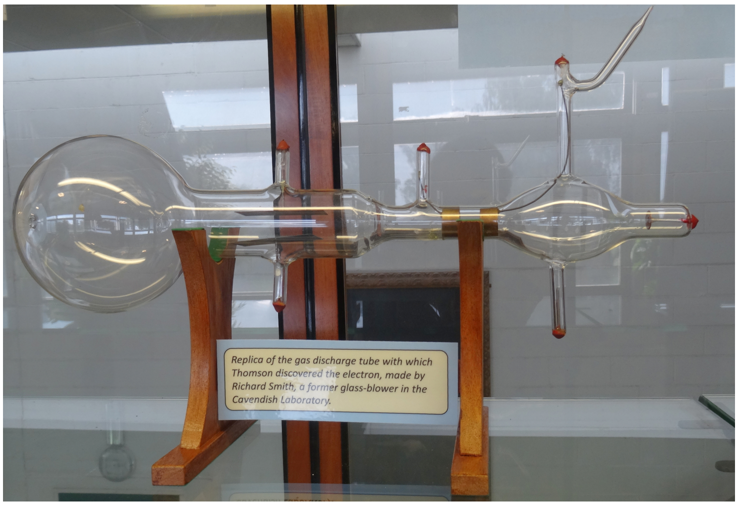

Figure 1.4. J. J. Thomson's experimental setup. There is a cathode on the right and anode on the centre with potential difference high enough that an electron is emitted from the cathode, it will traverse the whole tube hitting the glass on the left causing a bright glow. The plates on the centre left also have a potential difference among them that creates an electric field which deflects the electron. By measuring the amount of deflection We can determine the charge-to-mass ratio of the electron.[4]

Beyond being far smaller than atoms, these particles had the same mass-to-charge ratio no matter the material that made up the electrodes or the trace gas in the tube. Furthermore, in 1899 Thomson showed the particles produced by shining ultraviolet light on a metal, called the *photoelectric effect*, had exactly the same properties. They must be universal constituents of atoms themselves. Due to their electric charge and their role in ordinary electric current, they were named *electrons*. The approximate values for its charge and mass are[5]

$$m_e \approx 9.109 \times 10^{-31}\ \text{kg} \approx 511\ \text{keV}/c^2 \tag{1.1}$$

$$-e \approx -1.602 \times 10^{-19}\ \text{C} \tag{1.2}$$

The atom was not indivisible after all as it must contain electrons in it. Because atoms are neutral, Thomson envisioned the atom as a sphere made up of a positively charged fluid inside which resided the electrons, bound by electromagnetic forces. Most of the mass of the atom lay in this fluid whose properties were unknown. This model had the immediate success of being able to explain ions as atoms that either were stripped of electrons or gained extra electrons.

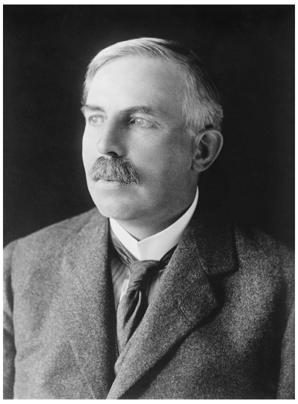

Figure 1.5. The Right Honourable **Ernest Rutherford** The Lord Rutherford of Nelson OM FRS HonFRSE[6]
Born: 1871 Brightwater, Colony of New Zealand
Died: 1937 Cambridge, United Kingdom of Great Britain and Northern Ireland
Academic Advisor: Alexander Bickerton, J. J. Thomson

Despite its success this model was short-lived. 10 years later Ernest Rutherford (Fig.

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[3] Picture by Not Mentioned - FirstWorldWar.com, Public Domain, https://commons.wikimedia.org/w/index.php?curid=2969861

[4] Picture by Rolf Kickuth - Own work, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=103442270

[5] We define e to be positive so that the charge of the electron is $-e$. Further, because every charge comes in integer multiples of the electron charge, the modern SI unit system defines the Coulomb via the value of the charge of the electron. So, in fact, we can say that $e = 1.602\ 176\ 634 \times 10^{-19}$ C, *exactly*.

[6] Picture by Bain News Service, publisher. Restored by: Bammesk - Library of Congress Catalog: https://lccn.loc.gov/2014716719. Image download: https://cdn.loc.gov/service/pnp/ggbain/36500/36570v.jpg. Original url: https://www.loc.gov/pictures/item/2014716719/. Public Domain, https://commons.wikimedia.org/w/index.php?curid=112190894

1.5), a student of Thomson, was trying to measure the charge-to-mass ratio of alpha particles. These were had been discovered by Rutherford himself in 1899 as the product of the decay of certain radioactive materials. In 1906 he had managed to deduce they were essentially helium stripped of two electrons (at the time they did not know how many electrons atoms had), and in 1908 together with a post-doc, Hans Geiger (Fig. 1.6), and an undergraduate student, Ernest Marsden (Fig. 1.7), he wished to calculate its charge-to-mass ratio.

Figure 1.6. **Johannes Wilhelm "Hans" Geiger**[7]
Born: 1882 Neustadt an der Haardt, German Empire
Died: 1945 Potsdam, Allied-occupied Germany
Doctoral Advisor: Eilhard Wiedemann

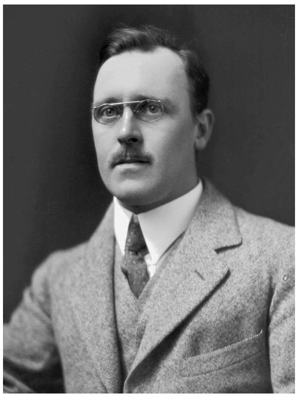

Figure 1.7. Sir **Ernest Marsden** CMG CBE MC FRS[8]
Born: 1889 Rishton, United Kingdom of Great Britain and Ireland
Died: 1970 Wellington, New Zealand

The issue with this experiment was that these alpha particles kept being deflected by the air, which rendered the experiment useless. This was a big puzzle because they though alpha particles would have been big enough to avoid these problems. To set things right they tried to scatter alpha particles off of a thin sheet of gold. This way they could test how far would alpha particles travel through matter and how its scattering would depend on the material and its thickness. The results of the experiment were so confusing that Rutherford suggest looking for large angle scattering even if they were not expecting any. What they witnessed was that some of the alpha particles were not only scattered at large angles but were reflected backwards! Rutherford himself commented on the surprising results by saying "It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you.".

Let us put some equations to this scattering experiment so see what kind of particles could be responsible for such a reflection. Let m_α be the mass of the alpha particle, v_α and v'_α its initial and final velocities, m and v the mass and final velocity of the particle that was hit. Conservation of momentum and energy gives us

$$m_\alpha v_\alpha = mv + m_\alpha v'_\alpha \tag{1.3}$$

$$\frac{1}{2}m_\alpha v_\alpha^2 = \frac{1}{2}mv^2 + \frac{1}{2}m_\alpha {v'_\alpha}^2 \tag{1.4}$$

Eliminating v we get a quadratic equation for v'_α/v_α, the two solutions are $v_\alpha = v'_\alpha$ which is not relevant and

$$v'_\alpha = -v_\alpha \frac{m - m_\alpha}{m + m_\alpha} \tag{1.5}$$

The only way that the final velocity can be negative is if the particle that was hit was heavier than the alpha particle itself. The electron would not do. We also have a constraint on the size of these particles. In order for reflection to happen we would need a turning point where all of the kinetic energy of the alpha particle was converted to potential electrostatic energy. The charge of the alpha particle is $+2e$, taking the charge of the scattering particle to be Ze we must then have

$$\frac{1}{2}m_\alpha v_\alpha^2 = \frac{1}{4\pi\epsilon_0}\frac{2e \cdot Ze}{r} \tag{1.6}$$

Plugging in the mass of the alpha particle, and considering the incident velocity was $v_\alpha \approx 2.09 \times 10^7$ m s^{-1} we find

$$r = \frac{Ze^2}{\pi\epsilon_0 m_\alpha v_\alpha^2} \approx 3Z \times 10^{-16} \text{ m} \tag{1.7}$$

which, even for fairly large Z, like $Z \sim 100$, is still orders of magnitude smaller than the size of a gold atom which is $\sim 10^{-10}$ m.

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[7] Picture by Unknown author - http://wal.nbed.nb.ca/sciencesettechnologies/pierrebrideau/geiger.jpg, Public Domain, https://commons.wikimedia.org/w/index.php?curid=34187140

[8] Picture by S P Andrew Ltd. - http://mp.natlib.govt.nz/detail/?id=27055&l=en, Public Domain, https://commons.wikimedia.org/w/index.php?curid=34174345

Whatever was scattering the alpha particles must have a mass similar or larger than atoms but be several orders of magnitude smaller in size. Rutherford concluded that this was a hitherto unknown nucleus of the atoms. This nucleus would be positively charged, contain most of the mass of the atom, but be very very small. The electrons would then orbit this nucleus like planets orbit the sun. Most of the atom would just be empty space. The Thomson model with the positive charge evenly dispersed throughout the atom cannot explain these scattering experiments.

This new model also came with new successful predictions. The charge of the nucleus was much better at organising the elements in the periodic table than the mass of the atoms, this came to be known as the *atomic number* and uniquely determines the element. Even so, it came with a bitter prediction. Electrons in orbit are constantly accelerating, but accelerating electric charges emit radiation, called *bremsstrahlung*, losing energy in the process. Classical electrodynamics predicts that this style of atoms is hopelessly unstable, even the hydrogen atom would be predicted to decay in $\sim 10^{-11}$ s. Such an emission of radiation is wholly incompatible with observations. Something is afoot.

1.2 Atomic spectroscopy

The above issue was largely theoretical. We knew that there were nuclei and electrons, and we also knew that nuclei were much smaller than the full atom. Our issue is when we apply the ideas of classical electrodynamics we get nonsensical answers. In these conditions, what is needed is experimental data that would hopefully gives us hints to resolve the theoretical conundrum. The relevant piece of data turns out to be from *spectroscopy*.

The story of spectroscopy begins in 1802 when William Hyde Wollaston (Fig. 1.8) realised the light from the sun wasn't exactly white but had dark lines at certain intervals. In 1814 Joseph von Fraunhofer (Fig. 1.9) re-discovered them and studied them in greater detail which is why these dark lines are still called Fraunhofer lines, Fig. 1.10.

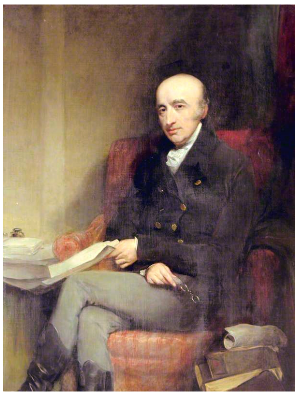

Figure 1.8. **William Hyde Wollaston** FRS[9]
Born: 1766 East Dereham, Kingdom of Great Britain
Died: 1828 Chislehurst, United Kingdom of Great Britain and Ireland

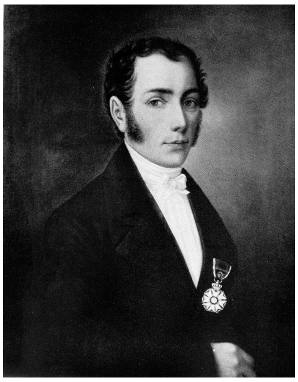

Figure 1.9. **Joseph Fraunhofer**, Ritter von Fraunhofer[10]
Born: 1787 Straubing, Holy Roman Empire of the German Nation
Died: 1826 Munich, Kingdom of Bavaria

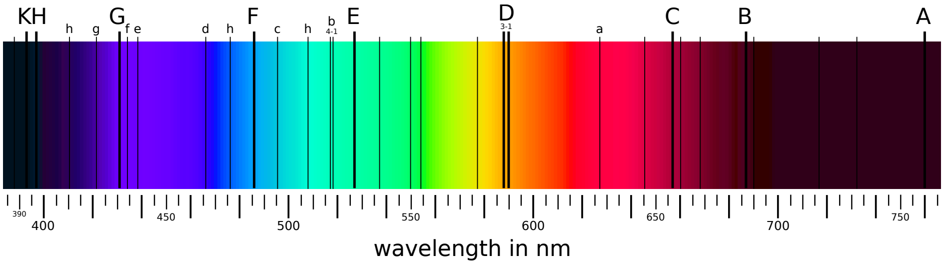

Figure 1.10. The dark lines in the solar spectrum in the visible range.[11]

Over the next few decades, physicists continued to study these lines and related phenomena. What they found was beautifully summarised by Gustav Kirchhoff (Fig. 1.11) in his three laws of spectroscopy:

1. An incandescent material under high pressure emits a continuous spectrum.

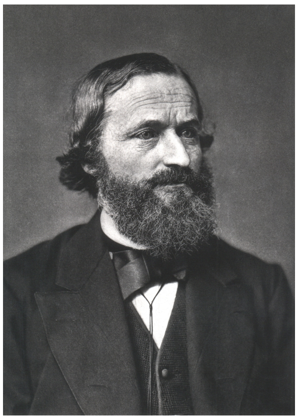

Figure 1.11. **Gustav Robert Kirchhoff**[12]
Born: 1824 Königsberg, Kingdom of Prussia
Died: 1887 Berlin, German Empire
Academic Advisors: Carl Jacobi, Franz Ernst Neumann

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[9] Picture by John Jackson - Scan from Platinum Metals Review, 2003, page 176, Public Domain, https://commons.wikimedia.org/w/index.php?curid=3508688

[10] Picture by Unknown author - Scanned from "Die großen Deutschen im Bilde" (1936) by Michael Schönitzer, Public Domain, https://commons.wikimedia.org/w/index.php?curid=5017460

[11] Figure by Fraunhofer_lines.jpg: nl: Gebruiker:MaureenV Spectrum-sRGB.svg: Phrood commonswiki Fraunhofer_lines_DE.svg: *Fraunhofer_lines.jpg: Saperaud 19:26, 5. Jul. 2005. derivative work: Cepheiden (talk)derivative work: Cepheiden (talk) - Fraunhofer_lines.jpg Spectrum-sRGB.svg Fraunhofer_lines_DE.svg, Public Domain, https://commons.wikimedia.org/w/index.php?curid=7003857

[12] Picture by Unknown author - Portrait of Gustav Kirchhoff, Smithsonian libraries (SIL-SIL14-k002-03) (image), Public Domain, https://commons.wikimedia.org/w/index.php?curid=1774907

2. A hot gas under low pressure emits a discrete spectrum with distinct bright emission lines.

3. A continuous spectrum source viewed through a cool, low-density gas exhibits a continuous spectrum with discrete gaps of dark lines.

Additionally, it was discovered that each element had its own distinct spectrum, and the emission or absorption spectrum was precisely the same. That is the bright emission lines had precisely the same frequency as the dark absorption lines. These spectra were as fingerprints for the elements and widely used to identify the composition of the atmospheres of distant stars.

However, it was like these spectra were written in a forgotten language. No one knew why or how these gases could emit/absorb at these specific frequencies. Nevertheless, some progress was made. Based on an early result by Johann Balmer (Fig. 1.12), in 1890 Johannes Rydberg (Fig. 1.13) managed to derive an empirical formula for the frequencies of the hydrogen spectrum:

$$\nu = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \tag{1.8}$$

where ν is the frequency, $n,\ m$ two integers, and R is the *Rydberg frequency*

$$R \approx 3.290 \times 10^{15}\ \text{Hz} \tag{1.9}$$

In 1908 Walther Ritz (Fig. 1.14) managed to generalise this idea by realising that the frequencies were always differences between elementary "terms", but he gave no interpretation as to what these terms were meant to represent.

Finally, in 1913 Niels Bohr (Fig. 1.15) offered an explanation for the case of the hydrogen atom. He was inspired by an earlier idea from John William Nicholson (Fig. 1.16) who attempted to connect the frequency of the electron's orbit to the frequency of the emitted radiation. The discreteness of the observed frequencies would then imply a discreteness to the angular momentum of the electron. The error in Nicholson's model was proposing that electrons would come in pairs to avoid collapsing to the nucleus. This hypothesis was disproven by a later discovery that hydrogen atoms indeed have only one electron. Bohr then proposed that there were special orbits such that the electron orbit would be stable and not emit any radiation. These orbits would correspond to angular momentum, quantised in units of a fundamental constant $\hbar$ (pronounced "h-bar") such that

$$m_e v r = n\hbar, \quad n = 1, 2, 3, \ldots \tag{1.10}$$

where v is the velocity of the electron and r the distance from the nucleus.

The only way the electron could emit radiation was by transitioning between these stable orbits, either by emitting or absorbing radiation of the corresponding energy, depending on whether it was going from an orbit closer to or further away from the nucleus. He did not provide any mechanism that would ensure these orbits were stable, which is a significant departure from classical electrodynamics. Bohr's guess is fact almost right. Even in the full quantum theory it will turn out that angular momentum is indeed quantised, it's just that the quantisation condition is a bit more complicated.

Figure 1.12. **Johann Jakob Balmer**[13]
Born: 1825 Lausen, Swiss Confederation
Died: 1898 Basel, Swiss Confederacy

Figure 1.13. **Johannes "Janne" Robert Rydberg**[14]
Born: 1854 Halmstad, United Kingdoms of Sweden and Norway
Died: 1919 Lund, Kingdom of Sweden

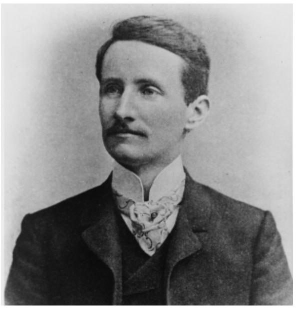

Figure 1.14. **Walther Heinrich Wilhelm Ritz**[15]
Born: 1878 Sion, Swiss Confederacy
Died: 1909 Göttingen, German Empire

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[13] Picture by Johann Jakob Balmer - Reproduction of a public domain painting, Public Domain, `https://commons.wikimedia.org/w/index.php?curid=1580258`

[14] Picture by sv: Per Bagge (1866-1936) - Original photograph in the collections of sv: Akademiska Föreningens Arkiv & Studentmuseum (The Archives and Museum of the Academic Society) in Lund, Sweden. Public Domain, `https://commons.wikimedia.org/w/index.php?curid=41525001`

[15] By Unknown author, Public Domain, `https://commons.wikimedia.org/w/index.php?curid=86166792`

He then proceed recklessly, assuming that the orbit was in equilibrium we needed a balance between the centrifugal force and the centripetal electrostatic force

$$\frac{m_e v^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2} \tag{1.11}$$

which, together with the quantisation condition, yields

$$v = \frac{e^2}{4\pi\epsilon_0 n\hbar} \quad r = \frac{4\pi\epsilon_0 n^2\hbar^2}{m_e e^2} \tag{1.12}$$

and therefore, the energy of each orbit is

$$E = \frac{1}{2}m_e v^2 - \frac{e^2}{4\pi\epsilon_0 r} = -\frac{e^4 m_e}{32\pi^2\epsilon_0^2 n^2\hbar^2} \tag{1.13}$$

The energy in the emitted or absorbed radiation would correspond to the difference in these discrete energy levels

$$\Delta E = E_m - E_n = \frac{e^4 m_e}{32\pi^2\epsilon_0^2\hbar^2}\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \tag{1.14}$$

All we have left to do is connect these energy differences to the frequency of the emitted radiation. To do so, he took the case when $n \gg 1$ and $m = n + 1$. For such large n the allowed orbits form almost a continuum and we would expect classical electrodynamics to hold. The frequency of the emitted radiation should then essentially be the frequency of the electron in its orbit, and because $n \approx m$ there is little ambiguity as to which orbit should be used for defining this frequency. We then have

$$\nu = \frac{v}{2\pi r} = \frac{e^4 m_2}{32\pi^3\epsilon_0^2 n^3\hbar^3} \tag{1.15}$$

Additionally, for $n \gg 1$ and $m = n + 1$ we can write

$$\Delta E \approx \frac{e^4 m_e}{16\pi^2\epsilon_0^2\hbar^2 n^3} \tag{1.16}$$

which allows us to conclude

$$\Delta E = 2\pi\hbar\nu \tag{1.17}$$

And therefore the frequencies would be given by

$$\nu = \frac{e^4 m_e}{64\pi^3\epsilon_0^2\hbar^3}\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \tag{1.18}$$

This is exactly the formula that Rydberg predicted, but it seems we haven't gained much. Sure, it's no longer trial-and-error but there is no justification for the quantisation of angular momentum and without an independent way to set $\hbar$ we haven't even been able to predict the Rydberg frequency. The latter of these issues was actually resolved before Bohr suggested his model, in fact, the solution was one of the key motivations for his work.

The key lies in (1.17) that relates the energy difference to the frequency of the emitted

Figure 1.15. Niels Henrik David Bohr HE[16]
Born: 1885 Copenhagen, Denmark
Died: 1962 Copenhagen, Denmark
Doctoral Advisor: Christian Christiansen

Figure 1.16. John William Nicholson FRS
Born: 1881 Darlington, United Kingdom of Great Britain and Ireland
Died: 1955

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[16] Picture by The American Institute of Physics credits the photo to AB Lagrelius & Westphal, which is the Swedish company used by the Nobel Foundation for most photos of its book series Les Prix Nobel. - Niels Bohr's Nobel Prize biography, from 1922, Public Domain, `https://commons.wikimedia.org/w/index.php?curid=288274`

radiation. This is a curious relation that would not be predicted by classical electrodynamics. It was first suggested by Max Planck (Fig. 1.17) in 1900 to explain the spectrum of black body radiation. By black body we mean something which absorbs all radiation that hits it, without reflecting any; it emits a continuous spectrum of radiation like what is described by Kirchhoff's first law of spectroscopy. It would take us too far afield to fully describe the problem, but it suffices to say the key difficulty was calculating the average energy of the radiation for a given temperature. J. Willard Gibbs (Fig. 1.18) showed that for a system in thermal equilibrium at a given temperature T the probability that it has an energy E is proportional to $\exp(-E/k_B T)$ where $k_B \approx 1.381 \times 10^{-23}$ J K^{-1} is the Boltzmann constant[17]. Therefore, if we allow for a continuum of energy in the emitted radiation its average energy would be

$$\bar{E} = \frac{\displaystyle\int_0^\infty \mathrm{d}E\, E\ \mathrm{e}^{-\frac{E}{k_B T}}}{\displaystyle\int_0^\infty \mathrm{d}E\, \mathrm{e}^{-\frac{E}{k_B T}}} = k_B T \tag{1.19}$$

which does not agree with the experimentally observed radiation. Planck instead assumed there was some constant h (now called the Planck constant) such that the energy in the radiation had to be an integer multiple of $h\nu$, where ν is the frequency. The average energy would then be given by

$$\bar{E} = \frac{\displaystyle\sum_{n=0}^{\infty} nh\nu\ \mathrm{e}^{-\frac{nh\nu}{k_B T}}}{\displaystyle\sum_{n=0}^{\infty} \mathrm{e}^{-\frac{nh\nu}{k_B T}}} = \frac{h\nu}{\mathrm{e}^{\frac{h\nu}{k_B T}} - 1} \tag{1.20}$$

This new expression for the average energy does agree with the experimental data as long as the value for this new constant is taken to be

$$h \approx 6.626 \times 10^{-34}\ \mathrm{J\ s} \tag{1.21}$$

Planck did not have any justification for this assumption of energy quantisation, later calling it "an act of desperation". He interpreted the quantisation condition to apply to the black body itself rather than the radiation.

Albert Einstein (Fig. 1.19) would take a step further in trying to explain the photoelectric effect. As mentioned earlier, this is the emission of electrons by a metal when being hit by UV radiation. Classically, the energy of the radiation is independent of the frequency, but instead a function of its intensity. We therefore expected that the kinetic energy of the emitted electrons was going to be a function of the intensity of the radiation. What was instead observed was that the kinetic energy of the electrons was a linear function of the frequency and independent of the intensity. Increasing the intensity of the light did not give extra energy to the electrons but instead merely caused additional electrons to be

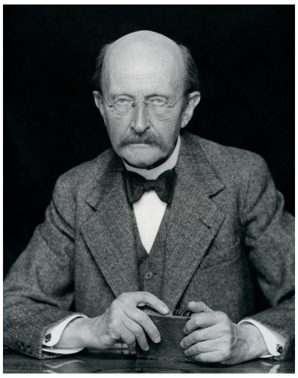

Figure 1.17. **Max Karl Ernst Ludwig Planck**[18]
Born: 1858 Kiel, Duchy of Holstein
Died: 1947 Göttingen, Allied-occupied Germany
Doctoral Advisor: Alexander von Brill

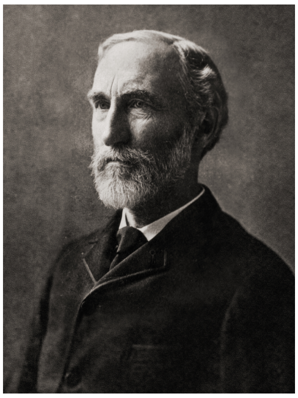

Figure 1.18. **Josiah Willard Gibbs**[19]
Born: 1839 New Haven, United States of America
Died: 1903 New Haven, United States of America
Doctoral Advisor: Hubert Anson Newton

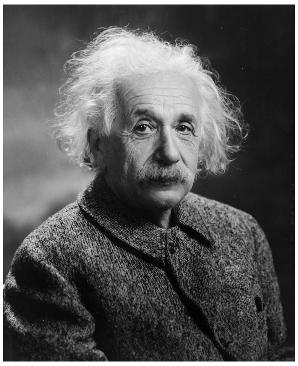

Figure 1.19. **Albert Einstein**[20]
Born: 1879 Ulm, German Empire
Died: 1955 Princeton, United States of America
Doctoral Advisor: Alfred Kleiner

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[17] In the modern SI system we use the value of this constant to *define* the Kelvin, therefore it is *exactly* given by $k_B = 1.380\ 649 \times 10^{-23}$ J K^{-1}

[18] Picture by Hugo Erfurth - This file was derived from: Max Planck by Hugo Erfurth 1938cr.jpg. Original source: `https://www.dhm.de/lemo/bestand/objekt/max-planck`. Public Domain, `https://commons.wikimedia.org/w/index.php?curid=153625300`

[19] Picture by Unknown. Uploaded by Serge Lachinov - Frontispiece of The Scientific Papers of J. Willard Gibbs, in two volumes, eds. H. A. Bumstead and R. G. Van Name, (London and New York: Longmans, Green, and Co., 1906), Public Domain, `https://commons.wikimedia.org/w/index.php?curid=7919387`

[20] Picture by Photograph by Oren Jack Turner, Princeton, N.J. - This image is available from the United States Library of Congress's Prints and Photographs division under the digital ID cph.3b46036. This tag does not indicate the copyright status of the attached work. A normal copyright tag is still required. See Commons:Licensing. Public Domain, `https://commons.wikimedia.org/w/index.php?curid=254353`

emitted.

Einstein managed to explain this phenomenon by assuming that light was made of particles, called *photons*, rather than waves. The energy of each photon would be given by the Planck formula

$$E = h\nu \tag{1.22}$$

and increased intensity only meant that extra photons were created. Because the photons were small, only a single photon could hit a given electron. The higher the frequency the higher the kinetic energy of that electron. On the other hand, the higher the intensity the more photons and the more electrons are emitted. Exactly as verified experimentally.

Connecting back to Bohr's model of the atom, we see that this particle description of electromagnetic radiation would agree with his energy-frequency relation if we took

$$\hbar = \frac{h}{2\pi} \tag{1.23}$$

We call Bohr's $\hbar$ the *reduced Planck constant*, it will very often be more convenient than the original Planck constant h. Plugging this definition into (1.18) we obtain the following expression for the Rydberg frequency:

$$R = \frac{e^4 m_e}{8\epsilon_0^2 h^3} \tag{1.24}$$

you can plug in the values for all the constants and check everything is consistent.

This is as far as Bohr came. With the independent verification for the Planck constant he could predict the Rydberg formula from first principles, at the cost of assuming an ad-hoc quantisation of angular momentum. The next step would be taken by Louis de Broglie (Fig. 1.20). He noticed he could use the relativistic expression relating an electromagnetic wave's energy to its linear momentum

Figure 1.20. **Louis Victor Pierre Raymond**, Duc de Broglie[21]
Born: 1892 Dieppe, French Republic
Died: 1987 Louveciennes, French Republic
Doctoral Advisor: Paul Langevin

$$E = pc \tag{1.25}$$

and the relationship between wavelength and frequency

$$\nu = \frac{c}{\lambda} \tag{1.26}$$

to write a relationship between the photon's momentum and wavelength

$$p = \frac{h}{\lambda} \tag{1.27}$$

The next step was to generalise this relationship. After all, if light can be a particle and a wave, why can't the electron? If the electron were a wave, then its frequency and wavelength would be given by

$$\nu = \frac{E}{h} \quad \text{and} \quad \lambda = \frac{h}{p} \tag{1.28}$$

where E and p are the electron's energy and momentum, respectively.

As a quick check he employed the usual definition of group velocity in terms of the

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[21] Picture by Unknown author - `http://www.physics.umd.edu/courses/Phys420/Spring2002/Parra_Spring2002/HTMPages/whoswho.htm`, Public Domain, `https://commons.wikimedia.org/w/index.php?curid=622169`

angular frequency $\omega = 2\pi\nu$ and wavenumber $k = 2\pi/\lambda$:

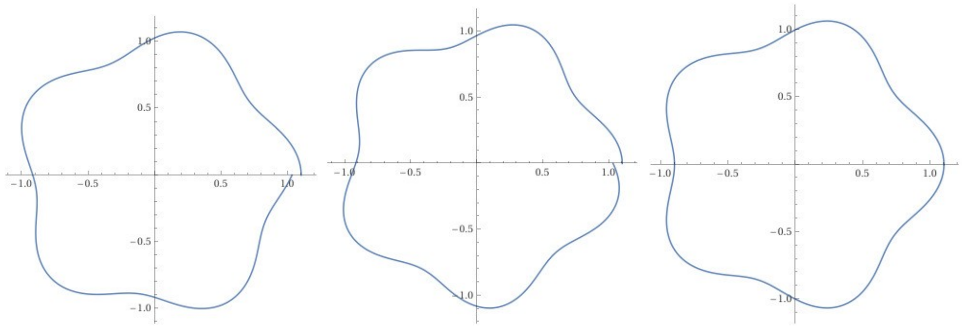
$$v = \frac{\mathrm{d}\omega}{\mathrm{d}k} = \frac{\mathrm{d}E}{\mathrm{d}p} \tag{1.29}$$

then using the familiar formula[22] $E = p^2/2m$ we get

$$v = \frac{p}{m} \tag{1.30}$$

as expected. Everything seemed consistent.

If you switch to interpret the electron as a wave then it must go a whole number of wavelengths as it goes once around the orbit, otherwise this wave wouldn't be single-valued (Fig. 1.21).



(a) λ too big (b) λ too small (c) λ just right

Figure 1.21. De Broglie's atomic model. If the wavelength is not quite what is predicted by the quantisation condition, the electron wave doesn't loop back on itself properly as a single-valued function would.

This means that the length of the orbit $2\pi r$ must be an integer multiple of the wavelength λ. In terms of the momentum we find

$$2\pi n r = \lambda = \frac{h}{p} \implies p = \frac{n\hbar}{r} \tag{1.31}$$

which is precisely the quantisation of angular momentum that Bohr predicted!

It seems like this wave picture of the electron together with a particle picture of light is able to explain the atomic spectra we observe. Truly it seems like everything is the opposite of what it should be.

2 Are electrons particles or waves?

In the last chapter it seemed like the only way we could explain atomic spectra and the photoelectric effect was to take a wave-like view of the electron and a particle-like view of light. Which is it, are they particles or waves? The original experiment that demonstrated that light was a wave was Thomas Young's (Fig. 2.1) 1801 double-slit experiment. The only way we could explain the observed interference pattern was if light was a wave. Let us apply the same reasoning for the electron[24].

Figure 2.1. **Thomas Young** FRS[23]
Born: 1773 Milverton, Kingdom of Great Britain
Died: 1829 London, United Kingdom of Great Britain and Ireland

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[22] He actually used the relativistic version of this expression, but that is a needless complication.

[23] Picture by Henry Perronet Briggs - `http://rstb.royalsocietypublishing.org/content/370/1666/20140308`, CC BY-SA 4.0, `https://commons.wikimedia.org/w/index.php?curid=109315084`

[24] Despite being one of the first results of quantum mechanics, the theory of the photon is quite complicated and will be beyond the scope of this volume. The main issue is that photons are routinely absorbed

2.1 An experiment with particles

First, let us run this experiment with particles. As an example of particles, think of small bullets. We have a source of these bullets, a back wall that collects the bullets, and a wall in between with two narrow slits. For simplicity, we shall assume that both the bullets and the walls are indestructible. We will also assume that we cannot control whatever is the source of the bullets, you can think of it as a very lousy gun firing bullets in every direction.

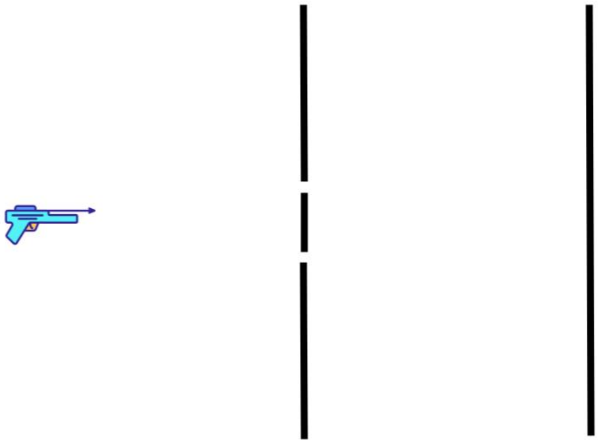

Figure 2.2. Double slit experiment with particles

The slits should be only very slightly wider than the bullets. So if they are fired straight-on they can pass but even a slight deviation will cause a collision with the walls and mess up the trajectory. For simplicity, assume that these collisions are elastic, that there is no air resistance and that the bullets are all fired with the same speed. This means that, no matter the trajectory, the energy imparted by each bullet on the back wall is the same.

What do we see on the back wall? Well, we don't know exactly what will happen for each bullet because its trajectory is random. However, trajectories which land very far away from the position of the slits are less likely than ones that are only slight deviations from the straight-on trajectory. It is reasonable to to expect a distribution such as Fig 2.3.

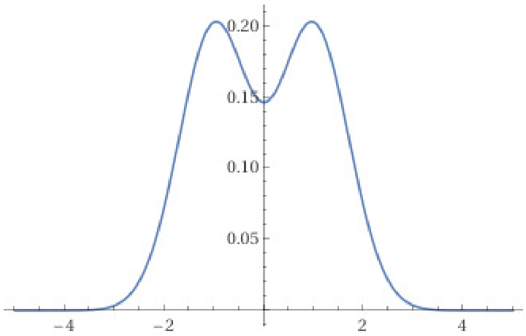

Figure 2.3. Outcome of the double slit experiment with particles. We are depicting the sum of two Gaussian distributions, one centred at $x = -1$ and the other centred at $x = 1$ both with unit standard deviation.

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and emitted, therefore we need to describe them using a formalism that is able to create and annihilate particles. Non-relativistic electrons and atoms do not have this issue so they will be the focus of this text.

One very important point is that we will *not* observe this distribution immediately. The back wall will receive one bullet at a time in discrete indivisible lumps. You never get half a bullet. What you see is that over time, after sending many bullets, we can plot the number of bullets that land in a given location and infer the probability distribution $P(x)$ from above. The overall normalisation is arbitrary, we can set it to 1 so that we are seeing the probability distribution itself.

Further, we can construct this full probability distribution from the probability distributions associated with the single-slit experiments. Imagine covering up slit 2, we then are sure that the particle goes through slit 1 and we observe a certain probability distribution $P_1(x)$.

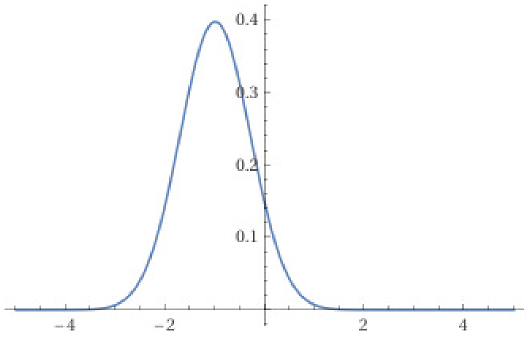

Figure 2.4. Outcome of the single slit experiment with particles where we cover up the second slit.

We could repeat the experiment by covering up slit 1, and measuring $P_2(x)$, which is the same as $P_1(x)$ but translated in the x axis:

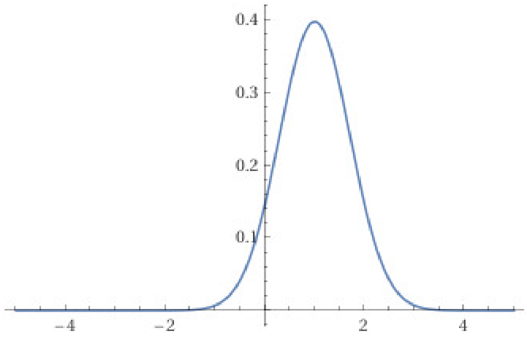

Figure 2.5. Outcome of the single slit experiment with particles where we cover up the first slit.

The crucial fact is that, when both slits are open, each bullet definitely passes through exactly one of them. it cannot be divided so it cannot pass through both at the same time. Therefore, from the perspective of each bullet, it's irrelevant as to whether the slit it didn't pass through was open or closed. Assuming half the bullets go through slit 1 and half the bullets go through slit 2 we must conclude that

$$P(x) = \frac{1}{2}P_1(x) + \frac{1}{2}P_2(x) \tag{2.1}$$

which is exactly what we observe.

To summarise, if electrons are particles we expect the following properties to be true:

- The energy transmitted to the back wall comes in discrete and indivisible lumps.

You either get the full energy or none of it, we would not be able to observe half an electron.

- These discrete lumps land with a certain probability distribution $P(x)$ given by the (normalised) sum of the probability distributions $P_1(x)$ and $P_2(x)$ obtained by covering one slit at a time.

2.2 An experiment with waves

Now let us run the experiment with waves, like water waves or sound waves. The walls are set up in the same way but we are instead sending plane waves with a constant frequency and amplitude. The height of these waves is given by (the real part of) h_1, where h_1 is the *complex amplitude* who also carries information about the phase of the wave. The energy transmitted to the back wall is given by the intensity of the wave I which equals the mod-square of the amplitude $I = |h|^2$. What we observe is depicted in Fig. 2.6.

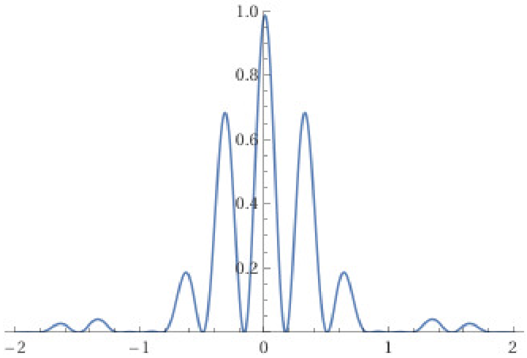

Figure 2.6. Outcome of the double slit experiment for waves. We see the complicated interference pattern that results in a sequence of maxima and minima of intensity.

Now the outcome is continuous. You can dial down the amplitude of the initial wave as much as you want but it only scales down the observed pattern on the back wall. We see that pattern all at once, no lumps of energy.

The observed pattern is also far more complicated than in the particle version of the experiment. It can be derived in the following way. If the slits are narrow enough, we can use the Huygens–Fresnel principle we can treat each slit as a source of a spherical wave. Let us denote the wave emitted from slit 1 as h_1, and the wave emitted from slit 2 as h_2. The waves then add together such that the total wave is given by $h = h_1 + h_2$. However, the energy transmitted to the back wall is given by the intensity of the wave obtained from the mod-square of the complex wave:

$$I = |h_1 + h_2|^2 \tag{2.2}$$

The pattern we see depends on the relative phases/signs of h_1 and h_2. When both are in phase, *i.e.* if they are both at a maximum or both at a minimum, they will have the same sign and will add together. When they are out of phase, *i.e.* if one is at a maximum and the other at a minimum, they will cancel each other. Because the slits have some non-zero separation, the waves from each slit will travel slightly different distances before hitting the back wall. This difference in distance yields a difference in phase resulting in this *interference pattern*.

Crucially, this pattern is *not* the sum of what we would obtain from covering one slit at a time. If we cover slit 2 so that the wave only passes through slit 1 then the energy transmitted is $I_1 = |h_1|^2$ and similarly for covering slit 1. However,

$$I = (h_1 + h_2)(h_1 + h_2)^* = |h_1|^2 + |h_2|^2 + 2\,\mathrm{Re}\{h_1 h_2^*\} \tag{2.3}$$

which is *not* just $I_1 + I_2$, it has an extra term, the *interference term*, which is only there when the waves can path through *both* slits.

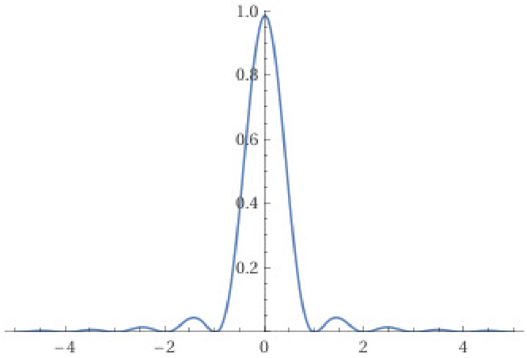

Figure 2.7. Outcome of the single slit experiment for waves. It is similar but slightly more complicated than the single slit experiment for particles. The key feature is that adding two of these cannot reproduce the effects depicted in Fig. 2.6

In summary, if electrons were waves we would observe the following:

- The energy transmitted to the back wall is continuous. If we dial down the wave source we merely scale the total output down.
- The pattern observed exhibits interference, being different from the sum of the patters observed when either of the slits is closed. The waves pass through both slits at once, we must sum the complex waves first and then take the mod-square.

2.3 An experiment with electrons

So what happens for an electron? We observe the following:

- The energy transmitted to the back wall comes in discrete and indivisible lumps. You either get the full energy or none of it, we would not be able to observe half an electron.
- The probability observed exhibits interference, being different from the sum of the patterns observed when either of the slits is closed. It is the same pattern that was observed when the we summed complex waves and then took the mod-square.

This wasn't one of the options? How on earth did this happen? Somehow electrons are neither particles nor waves but something else entirely? This experiment was repeated again and again. But the outcome is the same. We get one electron at a time, at a random location and the probability is given by an interference pattern that looks as if we summed complex waves and took the mod-square to get the probability.

This doesn't make any sense. Surely if the electrons come in lumps then they must pass through exactly one of the slits right? But the total probability is *not* the sum of

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[25] Picture by Roger Bach, Damian Pope, Sy-Hwang Liou and Herman Batelaan See Roger Bach et al 2013 New J. Phys. 15 033018DOI 10.1088/1367-2630/15/3/033018 - `https://iopscience.iop.org/article/10.1088/1367-2630/15/3/033018/data`, CC BY 3.0, `https://commons.wikimedia.org/w/index.php?curid=132124128`

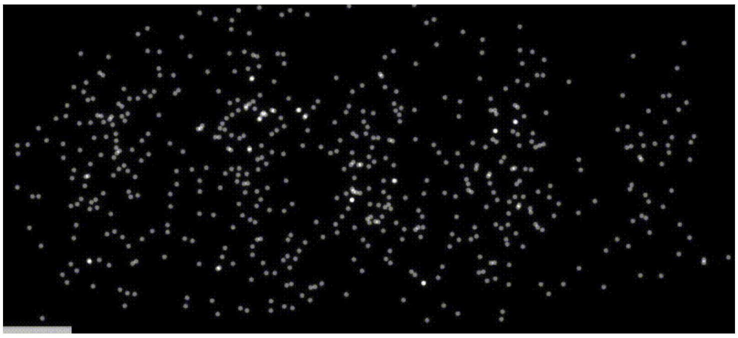

Figure 2.8. Outcome of the electron slit experiment with electrons. We are seeing an intermediate result of the experiment to emphasise the discreteness of the outcomes. We can nevertheless start to see the interference lines similar to the wave experiment[25]

the probabilities observed when we close a slit at a time. So maybe they slip apart and somehow go through both slits at the same time? But that also can't be because we never observe half an electron. Even if we put the back wall really close to the slits we always observe a single electron.

Perhaps we could try to see which slit the electron passed through? Perhaps we could put some detector in place that would interact with the electron and tell us, the electron has an electric charge so maybe a light source will do. But electrons are small and light, even a very meek light source will disturb the electron and change the observed pattern. We could try to dim the light as much as we can but we run into the same issue. As we saw previously, light is also made up of particles, the photons. Dimming the light source will not change the energy of each photon, just the number of photons emitted. So the energy transmitted to each electron will be exactly the same, when dimming it we just send fewer photons and so there will be some electrons which are not hit by any photon and pass undisturbed. There are three options:

1. Electron is detected going through slit 1. Pattern: P_1
2. Electron is detected going through slit 2. Pattern: P_2
3. Electron is not detected. Pattern: I

You can try to concoct further and further ways to try to figure out which slit the electron went through without destroying the interference pattern but to no avail. As far as we know it is impossible. We know we fire a single electron, and we know it hits the back wall, we do not know its trajectory we don't even know if has a trajectory at all.

Werner Heisenberg (Fig. 2.9) imagined a dark street with intermitting light posts. We can see the person only when they're bellow one of the light posts, we can assume they went through the middle but there's no way to check what trajectory they took. In the quantum mechanics case we go further, we claim it's *impossible* to know.

This might seem quite discouraging, but there is a silver lining. Even if we don't know what trajectory an individual electron takes and where it's going to land, the probability distribution is perfectly predictable. The maths aren't even that complicated, it's just ordinary wave mechanics. In quantum mechanics we have to give up and take some questions as impossible to answer. But those questions which we can answer, we do so with an incredible accuracy.

Figure 2.9. **Werner Karl Heisenberg** ForMemRS[26]
Born: 1901 Würzburg, German Empire
Died: 1976 Munich, Federal Republic of Germany
Doctoral Advisor: Arnold Sommerfeld

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[26] Picture by Bundesarchiv, Bild 183-R57262 / Unknown author / CC-BY-SA 3.0, CC BY-SA 3.0 de, `https://commons.wikimedia.org/w/index.php?curid=5436254`

So what are electrons: waves or particles? Well they're neither, they obey the following properties:

- They come in discrete and indivisible lumps, we sometimes call those lumps *quanta*
- The probability they are detected in a given location is given by the square of the complex modulus of a function which seems to follow the laws of wave mechanics. We call that complex function whose mod-square gives the probability a *probability amplitude*
- If we try to detect where an electron is we inevitably disturb it and ruin any interference pattern previously observed

The goal of the following chapters is to clarify and quantify this behaviour.

PART

II

Chapter 3. The Stern-Gerlach experiment
Chapter 4. Hilbert spaces
Chapter 5. Quantum mechanics for continuous variables

Quantum Kinematics

In the previous chapter we described the outcomes of the double-slit experiment for electrons. The chief concept was that of the probability amplitude whose mod-square gives the probability and that seems to follow wave-like mechanics. In this chapter, we will delve into these probability amplitudes, understanding what they represent and how to describe them, ultimately arriving at the mathematics of Hilbert spaces. To make matters simpler, rather than pursuing the direction of wave mechanics we will instead start by considering a different system which only has a discrete set of outcomes: spin in the Stern-Gerlach experiment. Only after the discrete case is fully understood will we delve into the continuous wave mechanics.

3 The Stern-Gerlach experiment

Somewhat anachronistically let us continue our exploration of the properties of the electron. In the last chapter we found out it was neither a particle nor a wave but a secret third option. The question now is, does it have internal structure? Because if so then it can possibly spin about some internal axis. Given it has an electric charge, if it also has an internal angular momentum, then it will have a magnetic moment. In 1921-1922 Otto Stern (Fig. 3.1) and Walther Gerlach (Fig. 3.2) tested this hypothesis and found truly unforeseen results.

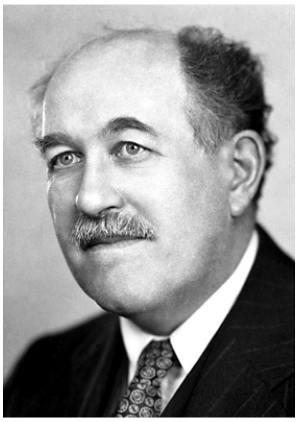

Figure 3.1. Otto Stern[27]
Born: 1888 Sohrau, German Empire
Died: 1969 Berkeley, United States of America
Doctoral Advisor: Otto Sackur

Figure 3.2. Walther Gerlach
Born: 1889 Biebrich, German Empire
Died: 1979 Munich, Federal Republic of Germany
Academic Advisor: Friedrich Paschen

3.1 A review of the magnetic moment in classical electrodynamics

Before we delve into the experiment itself a review of some concepts in classical electrodynamics is in order. The magnetic moment $\boldsymbol{\mu}$ is defined for an object such that the aligning torque as a result of an applied magnetic field $\boldsymbol{B}$ is

$$\boldsymbol{\tau} = \boldsymbol{\mu} \times \boldsymbol{B} \tag{3.1}$$

For a small loop of current I and area S it equals

$$\boldsymbol{\mu} = IS\boldsymbol{n} \tag{3.2}$$

where $\boldsymbol{n}$ is the normal vector to the loop whose direction is given by the right-hand rule, Fig. 3.3.

If the applied magnetic field is constant then despite there being an aligning torque there is no resulting force, if, however, the field varies in space we get a resulting force given by

$$\boldsymbol{F} = \boldsymbol{\nabla}(\boldsymbol{\mu} \cdot \boldsymbol{B}) \tag{3.3}$$

Finally consider an extended object of constant mass and charge rotating. Its rotation creates an electric current and hence a magnetic moment. Integrating (3.2) we find

$$\boldsymbol{\mu} = \frac{q}{2m}\boldsymbol{L} \tag{3.4}$$

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[27] Picture by Nobelprize.org - `http://nobelprize.org/nobel_prizes/physics/laureates/1943/stern-bio.html`, Public Domain, `https://commons.wikimedia.org/w/index.php?curid=6196370`

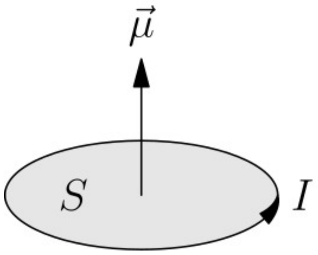

Figure 3.3. Illustration of the magnetic moment $\boldsymbol{\mu}$ of a loop of current I with area S.[28]

where q is the total charge of the object, m its mass, and $\boldsymbol{L}$ its angular momentum.

The fact that the magnetic moment is proportional to the angular momentum will still hold in quantum mechanics. However, the proportionality constant between the two will not match the classical prediction. For the electron, for instance, it will be off by a factor of 2, meaning that it has a magnetic moment twice as strong as the classical prediction. In order to derive this discrepancy one will need a relativistic understanding of quantum mechanics which will not be presented in this volume. Additionally it will turn out that evidence of the spin angular momentum of the electron is not actually evidence of internal structure. Quantum particles can have an intrinsic angular momentum even if they are fundamental. Neither of these details will be crucial for the following discussion, but needed mention for the sake of honesty.

3.2 The original Stern-Gerlach experiment

Using the knowledge above, what we need to do in order to test whether an given particle has a magnetic moment is to put them in a strongly varying magnetic field. Doing the experiment with electrons is not feasible in practice because they will experience a Lorentz force due to their electric charge alone. Cancelling this Lorentz force or disentangling the two effects is prohibitively difficult. The original Stern-Gerlach experiment was done with silver atoms to get around this issue. For simplicity's sake I will refer to the particles sent as electrons as it does not affect the main point I am trying to make. Just bear in mind that the actual experiment used silver atoms. The apparatus they concocted is illustrated in Fig. 3.4. It creates a magnetic field that is basically just pointing in the vertical direction and which is stronger at the tip of the top magnet.

Given we are not preparing the incoming beam in any special way, we expect its magnetic moment vectors to be pointing randomly in every direction. Looking at (3.3) we see that the intensity of the force will depend on the dot product of the moment and the magnetic field. An electron whose moment is completely aligned with the magnetic field will be deflected strongest and one whose magnetic moment is aligned perpendicularly with the field will not be deflected at all. Given they will have random alignments we expect a smear in the vertical direction, as depicted by (4) from Fig. 3.4

Observing a smear like this rather than a single dot in the centre would prove that the electrons have an internal angular momentum, which we call *spin*. What we observe however is neither of the two options but instead (5) from Fig. 3.4. It seems as if an electron does have spin, and therefore a magnetic moment, but that it is somehow either fully up or fully down, rather than a continuous of possibilities. The quantum realm really is bizarre.

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[28] Figure by Glosser.ca - Own work, CC BY-SA 3.0, `https://commons.wikimedia.org/w/index.php?curid=18933480`

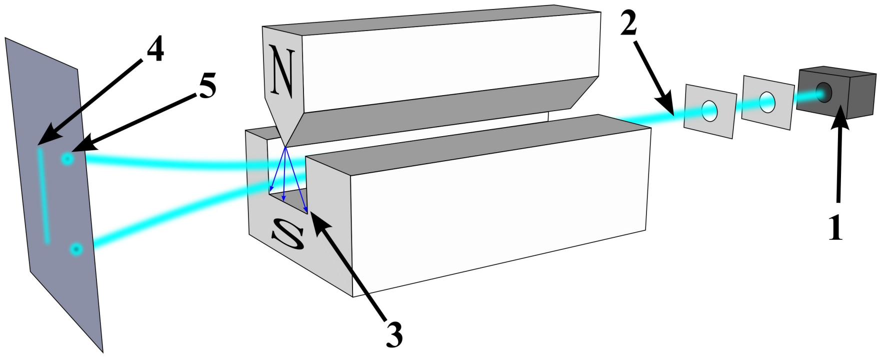

Figure 3.4. Illustration of the Stern-Gerlach experiment. (1) is the furnace producing silver atoms. (2) is the beam of silver atoms with random spin orientations. (3) is the inhomogeneous magnetic field that causes a deflection due to the spin angular momentum. (4) is the classically predicted result. (5) is the actual result of the experiment.[29]

3.3 Chaining Stern-Gerlach devices

So far we have no idea what is going on. In order to glean some structure out of these baffling results we will have to play with the experiment a little bit. Our first step will be to introduce a modified version of our Stern-Gerlach device that recombines the beams at the end, as sketched in Fig. 3.5.

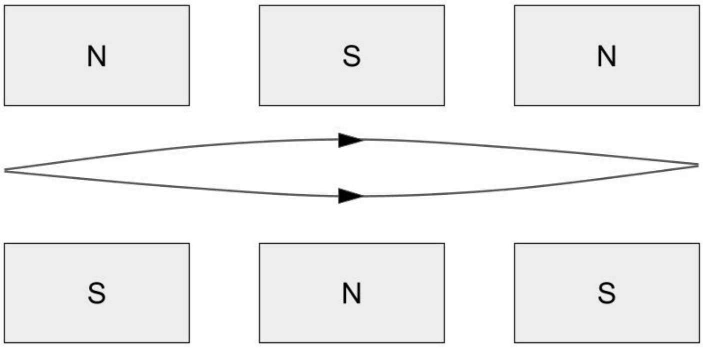

Figure 3.5. A modified version of the Stern-Gerlach experiment in which the beams recombine at the end.

At first sight it appears it does nothing, it splits and then recombines the beams and we end up with the same result as we started. The crucial aspect of this version of the experiment is that it allows us to include filters that block one of the two beams before they are allowed to recombine, Fig. 3.6

If we do nothing else we just notice that only half of the electrons come through, which isn't a lot of information. However, we can tack on an ordinary Stern-Gerlach apparatus at the end and see that all of the electrons that go through have the same spin, Fig. 3.7

There are two very important points with these experiments. Firstly, it is crucial that we not separate the beams too much in the modified device. Our goal is that the recombined beam is *exactly* the same as the incoming beam. But we know from the previous chapters

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[29] Figure by Tatoute - Own work, CC BY-SA 4.0, `https://commons.wikimedia.org/w/index.php?curid=34095239`

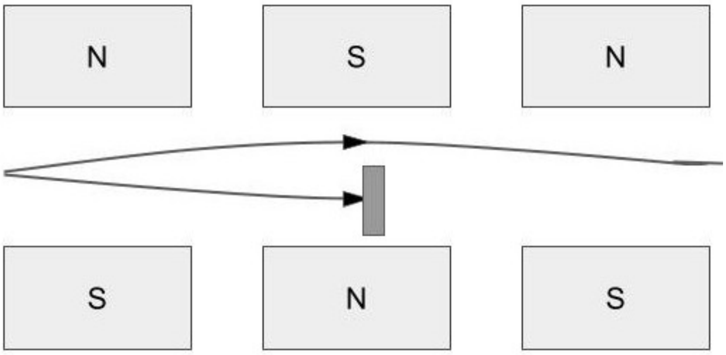

Figure 3.6. A modified Stern-Gerlach apparatus with a filter.

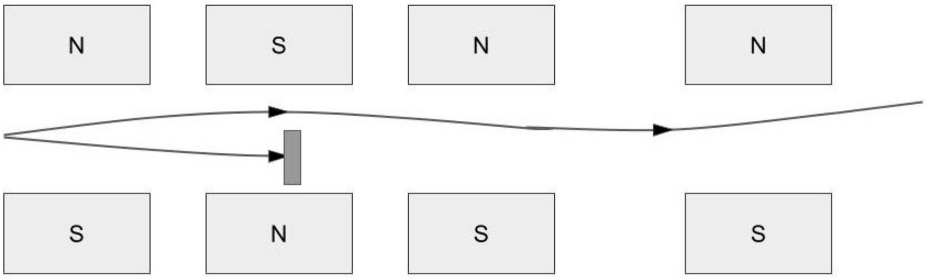

Figure 3.7. Checking the filter works as expected.

that there are interference effects between the two paths, which would be ruined if the beams were separated too much. We want just enough separation to include filters, but not too much to ruin interference.

Secondly, none of the effects described above or below rely on the interaction between different electrons. We can run the experiment with a very low intensity beam, sending one electron at a time, and the results would remain unchanged. Any weirdness, including interference effects between different possible paths, must come from a behaviour intrinsic to the electron, rather than due to some complicated interaction between distinct electrons.

With all of this in mind, let us play with our various Stern-Gerlach devices. To simplify our notation I will depict an ordinary Stern-Gerlach device by a box labelled "SG" followed by an indication of the orientation as in Fig. 3.8.

Figure 3.8. Simplified notation for an ordinary Stern-Gerlach device oriented along the y direction. The top beam corresponds to the positive y direction, and the bottom beam corresponds to the negative y direction.

A modified Stern-Gerlach device will be labelled "mSG", followed by an indication of the orientation, and an indication of the filters applied: a + sign, means only the beams in the positive direction were allowed to pass through (alternatively, that we put a filter in the negative direction); a − sign means that only the beams in the negative direction were un-blocked; and a ± sign means that no filters were applied so that both positive and negative direction beams were allowed. An example is depicted in Fig. 3.9

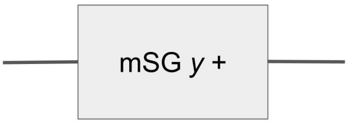

Figure 3.9. Simplified notation for an modified Stern-Gerlach device oriented along the y direction with a filter blocking the beam in the negative y direction, so that only the spins along the positive y direction were allowed to pass.

For example, the situation depicted in Fig. 3.7 would be depicted as in Fig. 3.10.

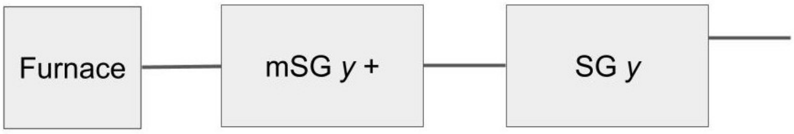

Figure 3.10. Simplified version of Fig. 3.7

Another advantage of this notation is that we are not drawing the precise path we think the electron went through. From the double slit experiment we know we should be wary of thinking of electrons as travelling through a specific slit, so we shouldn't really think that an electron goes through any single beam. We only know the end result.

Armed with these tools let's explore and play with spins. The first thing we might want to try is to rotate the devices. After all, we expected the spins to come out of the furnace randomly oriented, perhaps it's the furnace itself that has a preferred direction. What happens if we rotated the original device so that now it was aligned with the x direction, as in Fig. 3.11?

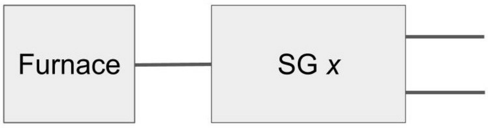

Figure 3.11. Rotated Stern-Gerlach experiment

We once more get only two discrete outcomes. The results of the experiment do not depend on the relative orientation between the apparatus and the furnace, so it cannot be some weird property of the furnace. This is very strange indeed, the force should be proportional to the dot product between the magnetic moment and the magnetic field, but in every direction we obtain that the magnetic moment was fully aligned with the field. Naively this would be impossible, the magnetic moment cannot be aligned with all directions without being zero, and yet, that is what we observe experimentally.

What if we put them in sequence? As in, filtering so that we know we only have spins pointing in the positive y direction, and then measuring the spin in the x direction, as depicted in Fig. 3.12. In this case we still get a 50/50 chance of the magnetic moment being purely aligned or anti-aligned with the x direction. This is pure madness, if there was some component of $\boldsymbol{\mu}$ in the x direction then the inner product with a $\boldsymbol{B}$ aligned with the y direction cannot be maximal. And yet, this is what we observe.

We can also try to have these two devices at an angle ϕ rather than being completely perpendicular, Fig. 3.13.

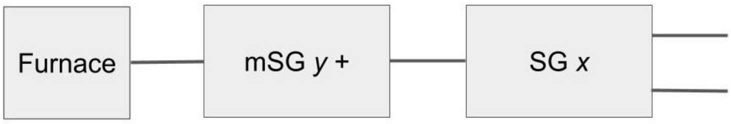

Figure 3.12. Measuring the spin in the x direction after having filtered in the y direction.

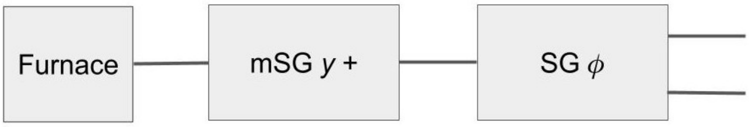

Figure 3.13. Two devices at an angle ϕ.

We still obtain a random result but it is not 50/50. The ratio between the two beams interpolates between Fig. 3.10 and Fig. 3.12 in a continuous manner. The results are weird but at least there is some continuity.

Now let us consider a three device set up, where we first filter in the $y+$ direction, then we filter in the $x+$ direction, and we finish by checking the spin in the y direction at the end, Fig. 3.14.

Figure 3.14. Three device experiment. Despite having filtered for the $y+$ direction, the end result is completely random.

Despite having filtered so that only electrons with moment in the positive y direction came through, at the end the result is completely random! Measuring the spin in the x direction totally ruined our previous measurements in the y direction. But it gets worse, imagine we removed the filter in the middle device?

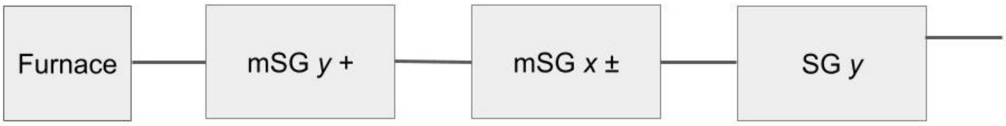

Figure 3.15. By removing the filter in the middle device, the electrons at the end are all deflected in the positive y direction.

The second device is doing nothing, so we go back to the situation in Fig. 3.10, and *zero* electrons go through the bottom beam. How can this be? We have *removed* a filter and *fewer* electrons go through? This is pure madness. Surely the 1/8th electrons that went through the $y+$ beam then the $x+$ beam and then the $y-$ beam in Fig. 3.14 are still being emitted from our furnace. Surely these must also go through Fig. 3.10. How can we loose *all* electrons?

Well, if we think of electrons as definitely going through each of the beams then this is impossible. The only possible conclusion is that the electron does *not* go through a single beam but instead goes through both. Exactly like the double slit experiment.

In fact, we see this exact behaviour with polarising filters and light. If you have two perpendicular filters they perfectly block the incoming light but put a third filter at an intermediate angle then some light does get through. It doesn't seem weird in this case because we think of light as a wave and this is normal behaviour for waves.

Once more we must arrive at the conclusion that electrons behave neither as particles nor as waves but as a secret third option: quanta.

3.4 The properties of probability amplitudes

We have some intuition and some results, but we need to do some mathematics with it. We will say that the electron is in the $|\uparrow y\rangle$ state if it went through the device in Fig. 3.16.

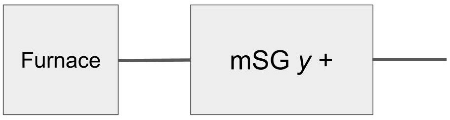

Figure 3.16. Preparing a $|\uparrow y\rangle$ state.

Similarly we say that it is in the $|\downarrow y\rangle$ state if it went through the device in Fig. 3.17.

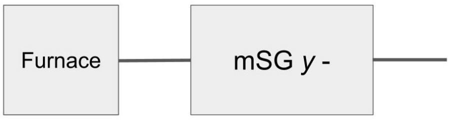

Figure 3.17. Preparing a $|\downarrow y\rangle$ state.

If add a device in the x direction that blocks spin-down electrons, as in Fig. 3.18, we denote by $\langle\uparrow x|\uparrow y\rangle$ the *amplitude* that it goes through this combined device, so that the probability that the electrons go through is $|\langle\uparrow x|\uparrow y\rangle|^2$. You read amplitudes right to left as in Arabic.

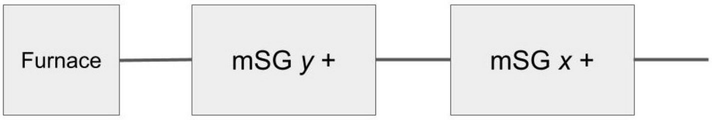

Figure 3.18. Chain of devices yielding the amplitude $\langle\uparrow x|\uparrow y\rangle$.

In general $\langle\psi|\chi\rangle$ is the amplitude that an electron prepared in the $|\chi\rangle$ state goes through a device which only lets electrons in the $|\psi\rangle$ state go through. The corresponding probability is given by $|\langle\psi|\chi\rangle|^2$ as described in the previous chapter. The central problem of quantum mechanics will be to calculate these amplitudes and probabilities.

From the first few experiments we can immediately conclude that

$$\langle\uparrow y|\uparrow y\rangle = 1 \tag{3.5}$$

and

$$\langle\downarrow y|\uparrow y\rangle = 0 \tag{3.6}$$

That is, if we prepare an electron in the $|\uparrow y\rangle$ state it remains in that state, and also that it then definitely is not in the $|\downarrow y\rangle$ state.

We don't yet have the tools to calculate amplitudes such as $\langle \uparrow x | \uparrow y \rangle$, but we can make some progress. First note that there are only two options for the second device, it's either up or down. So the sum of the probability that the electron comes out as up in the second device plus the probability that it comes out as down should add to one. In equations:

$$\langle \uparrow x | \uparrow y \rangle^* \langle \uparrow x | \uparrow y \rangle + \langle \downarrow x | \uparrow y \rangle^* \langle \downarrow x | \uparrow y \rangle = 1 \tag{3.7}$$

where we have written $|\langle \uparrow x | \uparrow y \rangle|^2 = \langle \uparrow x | \uparrow y \rangle^* \langle \uparrow x | \uparrow y \rangle$ for future convenience.

Of course (3.7) would also be true for $|\downarrow y\rangle$ instead of $|\uparrow y\rangle$. In fact, no matter the initial state, it will still be true that there are only two options on the second device, so the probability will have to add up to 1:

$$\langle \uparrow x | \psi \rangle^* \langle \uparrow x | \psi \rangle + \langle \downarrow x | \psi \rangle^* \langle \downarrow x | \psi \rangle = 1 \tag{3.8}$$

This seemingly trivial statement will be quite helpful in the future.

Now let us move to the 3 device experiments, like Fig. 3.19 whose amplitude is

$$\langle \downarrow y | \uparrow x \rangle \langle \uparrow x | \uparrow y \rangle \tag{3.9}$$

Figure 3.19. Chain of 3 devices yielding the amplitude $\langle \downarrow y | \uparrow x \rangle \langle \uparrow x | \uparrow y \rangle$.

In this notation, we can also show that amplitudes are only dependent of the initial state, not on the previous history. Consider the setup in Fig. 3.20 with amplitude

$$\langle \uparrow y | \uparrow x \rangle \langle \uparrow x | \uparrow y \rangle \tag{3.10}$$

Figure 3.20. Chain of 3 devices yielding the amplitude $\langle \uparrow y | \uparrow x \rangle \langle \uparrow x | \uparrow y \rangle$.

The ratio

$$\frac{\langle \uparrow y | \uparrow x \rangle}{\langle \downarrow y | \uparrow x \rangle} \tag{3.11}$$

only depends on the details between the second and third devices. It is completely independent on which state the first device picked.

We can also derive a statement similar to (3.8) in the 3 device setup. Recall Fig. 3.15 where the middle device is not filtering at all, which is equivalent to having just the first and third devices, like in Fig. 3.10. The only way we could explain these results was through interference effects between the two beams. However, there are still only two options in the middle device of Fig. 3.15. If the electrons were being completely jumbled and having totally random trajectories the filtering would not have worked as advertised. Therefore, even if we cannot just add the probabilities we can still add the amplitudes for each beam in the middle device. In fact, the whole point of introducing amplitudes was because we could add them up and still take interference into account.

In general, the amplitude between any two states $|\psi\rangle$ and $|\chi\rangle$ must be precisely the same as the sum of the amplitudes of putting a middle device filtering for $|\uparrow x\rangle$ or $|\downarrow x\rangle$. That is,

$$\langle\chi|\psi\rangle = \langle\chi|\uparrow x\rangle \langle\uparrow x|\psi\rangle + \langle\chi|\downarrow x\rangle \langle\downarrow x|\psi\rangle \tag{3.12}$$

States such as $\{|\uparrow x\rangle, |\downarrow x\rangle\}$ that obey (3.8) and (3.12) are said to be *base states*. Additionally if they obey equations like (3.5) and (3.6) we say they are *orthonormal*. If this language is reminding you of vector language it should! That is precisely what we are building towards.

Finally let us put together (3.7) and (3.12). Take (3.12) where both $|\chi\rangle$ and $|\psi\rangle$ are taken to be $|\uparrow y\rangle$. The LHS is $\langle\uparrow y|\uparrow y\rangle$ which is clearly 1, therefore we obtain

$$\begin{aligned} 1 &= \langle\uparrow y|\uparrow x\rangle \langle\uparrow x|\uparrow y\rangle + \langle\uparrow y|\downarrow x\rangle \langle\downarrow x|\uparrow y\rangle = && (3.13)\\ &= \langle\uparrow x|\uparrow y\rangle^* \langle\uparrow x|\uparrow y\rangle + \langle\downarrow x|\uparrow y\rangle^* \langle\downarrow x|\uparrow y\rangle && (3.14)\end{aligned}$$

To derive this we did not use the fact the x and y directions are perpendicular. This equation must then be true for all possible relative orientations between x and y, and therefore we must conclude that

$$\begin{aligned} \langle\uparrow y|\uparrow x\rangle &= \langle\uparrow x|\uparrow y\rangle^* && (3.15)\\ \langle\uparrow y|\downarrow x\rangle &= \langle\downarrow x|\uparrow y\rangle^* && (3.16)\end{aligned}$$

and therefore

$$\langle\chi|\psi\rangle = \langle\psi|\chi\rangle^* \tag{3.17}$$

This final equation is the result of imposing that probabilities add up to 1, without it we would not be able to consistently assign probabilities.

4 The physics of Hilbert spaces

Figure 4.1. Leopold Kronecker[30]
Born: 1823 Liegnitz, Kingdom of Prussia
Died: 1891 Berlin, German Empire
Doctoral Advisors: Johann Encke, Peter Gustav Lejeune Dirichlet

In the previous chapter we derived three key properties of probability amplitudes. Firstly there exists as set of states $\{|i\rangle\}$ that form an *orthonormal basis* such that

$$\begin{aligned} \langle i|j\rangle &= \delta_{ij} && (4.1)\\ \langle\chi|\psi\rangle &= \sum_{\text{all } i} \langle\chi|i\rangle \langle i|\psi\rangle && (4.2)\end{aligned}$$

where δ_{ij} is the Kronecker-delta symbol defined as

$$\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases} \tag{4.3}$$

named after Leopold Kronecker (Fig. 4.1).

Additionally, we showed that all amplitudes obey

$$\langle\chi|\psi\rangle = \langle\psi|\chi\rangle^* \tag{4.4}$$

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[30] Picture by Unknown author - http://www.britannica.com/EBchecked/media/28346/Kronecker-1865, Public Domain, https://commons.wikimedia.org/w/index.php?curid=33753789

These equations are very reminiscent of equations we get in linear algebra. Consider the vector space $\mathbb{R}^n$ with an orthonormal basis $\{\boldsymbol{e}_i\}$. The analogue of (4.1) is

$$\boldsymbol{e}_i \cdot \boldsymbol{e}_j = \delta_{ij} \tag{4.5}$$

Similarly the analogue of (4.2) is

$$\boldsymbol{A} \cdot \boldsymbol{B} = \sum_{i=1}^{n} (\boldsymbol{e}_i \cdot \boldsymbol{A})(\boldsymbol{e}_i \cdot \boldsymbol{B}) = \sum_{i=1}^{n} A_i B_i \tag{4.6}$$

where we have used the usual definition of vector components:

$$A_i = \boldsymbol{e}_i \cdot \boldsymbol{A} \tag{4.7}$$

Finally, the analogue of (4.4) is

$$\boldsymbol{A} \cdot \boldsymbol{B} = \boldsymbol{B} \cdot \boldsymbol{A} \tag{4.8}$$

which looks slightly different because $\mathbb{R}^n$ only deals with real variables.

These similarities motivate us to think of the states $|\psi\rangle$ as vectors in a complex vector space with an inner product. These quantum mechanical state-vectors are commonly called 'kets'. It turns out that the correct mathematical structure to describe quantum system is the *Hilbert space*, named after the mathematician David Hilbert (Fig. 4.2). As usual in physics we can never fully *prove* that this is the correct mathematical structure. What we do is motivate its main properties and check if the definition and its consequences agrees with experiment. In the rest of this chapter we will examine the physical interpretation of the definition of Hilbert spaces, the properties of linear operators on those spaces, and finally how observers are represented by this mathematical structure.

Figure 4.2. David Hilbert[31]
Born: 1862 Königsberg, Kingdom of Prussia
Died: 1943 Göttingen, German Reich
Doctoral Advisor: Ferdinand von Lindemann

4.1 The definition of a Hilbert space

The full mathematical definition of a Hilbert space is as follows:

Definition 4.1 (Hilbert Space)**.** A Hilbert space $\mathcal{H}$ is a (complex) vector space with an inner product such that the norm defined by that inner product turns $\mathcal{H}$ into a complete metric space. This means it obeys the following properties:

1. **Vector Space**: A vector space is a set which is closed under vector addition and scalar[a] multiplication.
    (a) **Vector Addition**: If $|\psi\rangle$ and $|\chi\rangle$ are vectors then so is $|\phi\rangle = |\psi\rangle + |\chi\rangle$, this operation obeys the following properties:
        i. **Commutativity**: $|\psi\rangle + |\chi\rangle = |\chi\rangle + |\psi\rangle$
        ii. **Associativity**: $|\psi\rangle + (|\chi\rangle + |\phi\rangle) = (|\psi\rangle + |\chi\rangle) + |\phi\rangle$
        iii. **Existence of identity**[b]: $|\psi\rangle + 0 = |\psi\rangle$
        iv. **Existence of inverse**: $|\psi\rangle + (-|\psi\rangle) = 0$
    (b) **Scalar Multiplication**: If $|\psi\rangle$ is a vector and c a scalar then $|\chi\rangle = c\,|\psi\rangle$ is also a vector, this operation obeys the following properties:
        i. **Associativity**: $a(b\,|\psi\rangle) = (ab)\,|\psi\rangle$

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[31] Picture by Unknown author - Possibly Reid, Constance (1970) Hilbert, Berlin, Heidelberg: Springer Berlin Heidelberg Imprint Springer, p.·230 ISBN: 978-3-662-27132-2., Public Domain, `https://commons.wikimedia.org/w/index.php?curid=36302`

   ii. **Distributivity**: $(a+b)\left|\psi\right\rangle = a\left|\psi\right\rangle + b\left|\psi\right\rangle$ and $a(\left|\psi\right\rangle + \left|\chi\right\rangle) = a\left|\psi\right\rangle + b\left|\chi\right\rangle$
   iii. **Existence of identity**: $1\left|\psi\right\rangle = \left|\psi\right\rangle$

2. **Inner Product**: The inner product is an operation that takes two vectors $\left|\psi\right\rangle$ and $\left|\chi\right\rangle$ and returns a complex number $(\left|\psi\right\rangle, \left|\chi\right\rangle)$. It obeys the following properties:
   (a) **Complex commutativity**: $(\left|\psi\right\rangle, \left|\chi\right\rangle) = (\left|\chi\right\rangle, \left|\psi\right\rangle)^*$
   (b) **Linearity**: $(\left|\psi\right\rangle, a\left|\chi\right\rangle + b\left|\phi\right\rangle) = a(\left|\psi\right\rangle, \left|\chi\right\rangle) + b(\left|\psi\right\rangle, \left|\phi\right\rangle)$
   (c) **Positivity**: $(\left|\psi\right\rangle, \left|\psi\right\rangle) \geqslant 0$, equality if and only if $\left|\psi\right\rangle = 0$
3. **Norm**: The norm is defined as $\|\left|\psi\right\rangle\| = \sqrt{(\left|\psi\right\rangle, \left|\psi\right\rangle)}$.
4. **Completeness**: Every Cauchy sequence converges in the Hilbert space. That is, every sequence $\left|\psi_1\right\rangle, \left|\psi_2\right\rangle, \ldots$ that satisfies $\lim\limits_{m,n\to\infty} \|\left|\psi\right\rangle_n - \left|\psi\right\rangle_m\| = 0$ is convergent in the Hilbert space.

---

[a] In the context of quantum mechanics, the scalars will always be complex numbers

[b] We will not make a distinction between the scalar 0 and the vector 0. This is a slightly sloppy notation but entirely standard in the physics literature.

Let us examine the physical consequence of all these axioms in turn.

Linearity and superpositions Let us return to the example of the double-slit experiment—by measuring which slit the electron went through we change the final distribution. A similar phenomenon was also observed in the Stern-Gerlach experiment from Fig. 3.14—when we filtered in the middle device we changed the state and allowed additional electrons to go through.

The only way we can reconcile the outcome of these experiments is if we say that the electron goes through *both* slits/beams at the same time. It cannot be in just one of them otherwise measuring which slit/beam the electron traversed we would not change its state. We call this phenomenon *superposition* and it is a fundamental property of quantum systems.

Despite the counter-intuitive features of superposition we were still able to make concrete predictions. For instance, in the double-slit experiment, we were able to predict the interference pattern by adding the probability amplitudes. In fact, that was the very motivation for introducing probability amplitudes. The actual probabilities combine in a complicated manner but amplitudes simply add. The same way that probability amplitudes simply add for superpositions, we will interpret the addition of two kets as a superposition between the corresponding states.

Going further, when we chained Stern-Gerlach devices at arbitrary angles we saw that sometimes the results were uneven. It still behaved as a superposition but the probabilities weren't 50-50. In terms of amplitudes we could depict this by adding but with different weights given to each state. Thus, not only is the addition of two kets representing superpositions, but we can also use scalar multiplication to encode uneven superpositions, where one of the states has a higher or lower probability than the other.

What is more, in the double-slit experiment we saw that the relative phase of the two wave-amplitudes was what dictated if the interference was constructive or destructive or something in the middle. This means that, if we are to describe interference effects, we must allow for complex scalar multiplication.

All in all, general linear combinations of kets are the mathematical way to represent superpositions between the corresponding states. Scalar multiplication then encodes interference and/or uneven superpositions.

Inner product and amplitudes To interpret the inner product we first need to introduce the concept of the dual space.

> **Definition 4.2** (Dual Vector Space). Given a vector space $\mathcal{H}$ its dual vector space $\mathcal{H}^*$ is the vector space of linear functions $\langle\psi| : \mathcal{H} \to \mathbb{C}$. $\langle\psi|$ is then called a dual vector.

In the context of quantum mechanics it is customary to call these dual vectors 'bras'. Because our Hilbert space is supplied with an inner product there is a natural identification between bras and kets given by:

$$\langle\psi|\left(|\chi\rangle\right) \equiv \langle\psi|\chi\rangle \equiv \left(|\psi\rangle, |\chi\rangle\right) \tag{4.9}$$

The number $\langle\psi|\chi\rangle$ is often called the bra(c)ket, motivating the nomenclature bra/ket for (dual) vectors, this nomenclature and notation is due to Paul Dirac (Fig. 4.3).

This construction allows us to interpret the inner product of two vectors: $(|\psi\rangle, |\chi\rangle)$. If we prepared the system to be in state $|\chi\rangle$ (think filtering only spin-up in the first Stern-Gerlach device) and then we tried measuring whether it was in state $|\psi\rangle$ (think filtering through a second Stern-Gerlach device) we would find that this would happen with probability $|\langle\psi|\chi\rangle|^2 = |(|\psi\rangle, |\chi\rangle)|^2$. Our previous notation for the amplitude was implicitly using the action of the dual vectors to write the inner product in a simpler notation. It certainly obeys (4.4), and we will see below that this inner product will also obey (4.1) and (4.2).

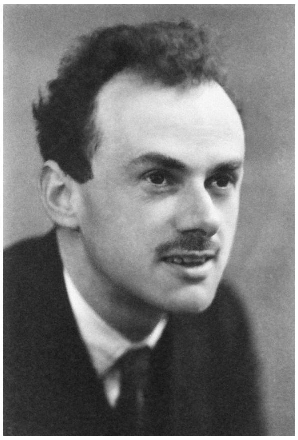

Figure 4.3. **Paul Adrien Maurice Dirac** OM FRS[32]
Born: 1902, Bristol, United Kingdom of Great Britain and Ireland
Died: 1984, Tallahassee, United States of America
Doctoral Advisor: Ralph H. Fowler

There is an important subtlety with Dirac's bra-ket notation. The inner product is only linear in the second argument, it is in fact anti-linear in the first argument:

$$\left(a|\chi\rangle + b|\phi\rangle, |\psi\rangle\right) = a^*\left(|\chi\rangle, |\psi\rangle\right) + b^*\left(|\phi\rangle, |\psi\rangle\right) \tag{4.10}$$

This means that the dual to a linear combination of vectors involves the complex conjugate of the coefficients, that is:

$$a|\psi\rangle + b|\chi\rangle \longleftrightarrow a^*\langle\psi| + b^*\langle\chi| \tag{4.11}$$

This subtlety would not have been apparent in the bra-ket notation. When it becomes relevant we will return to the more mathematical inner product notation: (,).

Normalisability and positivity In order for probabilities to add up to 1 we have so far only considered *normalised* vectors, that is, ones that obey

$$\langle\psi|\psi\rangle = 1 \tag{4.12}$$

These normalised vectors trivially satisfy the non-negativeness of the norm, as required in the definition of a Hilbert space.

But there is an ambiguity in this definition. If we multiplied the ket by a phase $|\psi\rangle \to \mathrm{e}^{\mathrm{i}\alpha}|\psi\rangle$ then it would still be normalised. Further, even though amplitudes would change, the probabilities $|\langle\chi|\psi\rangle|^2$ would be identical after this transformation. This suggest we should consider the kets $|\psi\rangle$ and $\mathrm{e}^{\mathrm{i}\alpha}|\psi\rangle$ to correspond to the same physical state, as they would yield exactly the same predictions.

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[32] Picture by Nobel Foundation - http://nobelprize.org/nobel_prizes/physics/laureates/1933/dirac.html, Public Domain, https://commons.wikimedia.org/w/index.php?curid=624401

We should then consider the physical state as the *equivalence class*

$$|\psi\rangle \sim \mathrm{e}^{\mathrm{i}\alpha}|\psi\rangle \quad \text{for} \quad \alpha \in \mathbb{R} \tag{4.13}$$

sometimes called a *ray* in the Hilbert space.

But be very careful, *relative phases* still matter, so you must be careful when doing linear combinations of vectors. Even though

$$a|\psi\rangle + b|\chi\rangle \sim \mathrm{e}^{\mathrm{i}\alpha}(a|\psi\rangle + b|\chi\rangle) \tag{4.14}$$

we cannot change the relative phase in this superposition:

$$a|\psi\rangle + b|\chi\rangle \nsim a|\psi\rangle + \mathrm{e}^{\mathrm{i}\alpha}b|\chi\rangle \tag{4.15}$$

the physical predictions of the LHS and RHS are distinct.

If for any reason you are handed a vector which is not normalised you can always multiply it by a scalar to ensure $\langle\psi|\psi\rangle = 1$. However, you can only do this if $\langle\psi|\psi\rangle > 0$, otherwise there is no complex scalar that you could multiply this vector to normalise it. Vectors with negative norm cannot correspond to physical states and therefore should be excluded from consideration. The zero-vector is also not normalisable but is useful for mathematical manipulations, even if it will also not correspond to any physical state. The other way vectors can be non-normalisable is if their norm is infinity. Although these vectors are still unphysical, it is still possible to make sense of them by only talking about ratios of amplitudes which might still be well defined. We will see examples of these kinds of states when we discuss Hilbert spaces with continuous labels.

Figure 4.4. **Augustin Louis**, baron Cauchy FRS FRSE[33]
Born:1789 Paris, Kingdom of France
Died: 1857 Sceaux, French Empire

Figure 4.5. **Karl Hermann Amandus Schwarz**[34]
Born: 1843 Hermsdorf, Kingdom of Prussia
Died: 1921 Berlin, German Republic
Doctoral Advisor: Karl Weierstrass, Ernst Kummer

You can also just deal with non-normalised vectors (with non-negative norm). You just have to modify how you calculate probabilities from inner products. Rather than $|\langle\chi|\psi\rangle|^2$ the probability would be given by

$$P(\psi \to \chi) = \frac{|\langle\chi|\psi\rangle|^2}{\langle\psi|\psi\rangle\langle\chi|\chi\rangle} \tag{4.16}$$

In this expression the importance of positivity is even starker. If any of these vectors had negative norm the probability would have come out negative.

Using non-normalised vectors the equivalence class is greater, rather than being restricted to phases you are now allowed to multiply by any complex number

$$|\psi\rangle \sim c|\psi\rangle \quad \text{for} \quad c \in \mathbb{C} \tag{4.17}$$

Confusingly, this equivalence class is also called a ray in the Hilbert space.

In either formulation, the Cauchy-Schwarz inequality ensures the assigned probabilities are always less than 1. This inequality was first discovered by Augustin Louis-Cauchy (Fig. 4.4) but the modern proof is due to Hermann Schwarz (Fig. 4.5).

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[33] Picture by Public domain - Library of Congress Prints and Photographs Division. From an illustration in: Das neunzehnte Jahrhundert in Bildnissen / Karl Werckmeister, ed. Berlin: Kunstverlag der photographische gesellschaft, 1901, vol. V, no. 581., Public Domain, `https://commons.wikimedia.org/w/index.php?curid=7059486`

[34] Picture by Louis Zipfel / Adam Cuerden - This image is from the collection of the ETH-Bibliothek and has been published on Wikimedia Commons as part of a cooperation with Wikimedia CH. Corrections and additional information are welcome. Public Domain, `https://commons.wikimedia.org/w/index.php?curid=142940682`

Theorem 4.1 (Cauchy-Schwarz Inequality). For any vectors $|\psi\rangle$ and $|\chi\rangle$ in the Hilbert space, the following inequality holds:

$$|\langle\psi|\chi\rangle|^2 \leqslant \langle\psi|\psi\rangle \langle\chi|\chi\rangle \tag{4.18}$$

with equality if and only if the vectors are linearly dependent: $|\psi\rangle = a\,|\chi\rangle$.

Proof. Let us define the following vector $|p(s)\rangle = |\psi\rangle + s\alpha\,|\chi\rangle$ where $s \in \mathbb{R}$, and α is defined such that $|\alpha| = 1$ and $\alpha\,\langle\psi|\chi\rangle = |\langle\psi|\chi\rangle|$[a]. We then have

$$\begin{aligned}\langle p(s)|p(s)\rangle &= (\langle\psi| + s\alpha^* \langle\chi|)(|\psi\rangle + s\alpha\,|\chi\rangle) = \\ &= \langle\psi|\psi\rangle + s\alpha^* \langle\chi|\psi\rangle + s\alpha\,\langle\psi|\chi\rangle + s^2|\alpha|\,\langle\chi|\chi\rangle = \\ &= \langle\psi|\psi\rangle + 2s|\langle\psi|\chi\rangle| + s^2\,\langle\chi|\chi\rangle \end{aligned} \tag{4.19}$$

Unless $|\chi\rangle = 0$ (in which case the proof is trivial), this is a second degree polynomial in s. Because $\langle p(s)|p(s)\rangle$ must be non-negative for all s, this polynomial can at most have one root for real s, therefore its discriminant must be non-positive which implies

$$4|\langle\psi|\chi\rangle| - 4\,\langle\psi|\psi\rangle\,\langle\chi|\chi\rangle \leqslant 0 \tag{4.20}$$

which is our desired conclusion.
Additionally, note that if we have an equality, then $\langle p(s)|p(s)\rangle = (\|\psi\| + s\|\chi\|)^2$. If $s_0 = -\|\psi\|/\|\chi\|$ then

$$\langle p(s)|p(s)\rangle = 0 \implies |\psi\rangle + s_0\alpha\,|\chi\rangle = 0 \tag{4.21}$$

and therefore the vectors are linearly dependent. ☐

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[a] If $\langle\psi|\chi\rangle = 0$ then we can take $\alpha = 1$.

Bases and completeness A basis of a Hilbert space is a set of linearly independent vectors $\{|i\rangle\}$ such that any vector $|\psi\rangle \in \mathcal{H}$ can be uniquely written as

$$|\psi\rangle = \sum_i c_i\,|i\rangle \tag{4.22}$$

However, before we defined Hilbert space we defined basis states as those that satisfy (4.1) and (4.2). We will now show that if any two of (4.1), (4.2), and (4.22) are true then they imply the third is also true.

For convenience we will denote

$$\psi_i \equiv \langle i|\psi\rangle \tag{4.23}$$

Proving (4.1) and (4.2) imply (4.22). Because $\langle\chi|$ in (4.2) is arbitrary we can just remove it to write an equation between kets rather than numbers:

$$|\psi\rangle = \sum_i |i\rangle\,\langle i|\psi\rangle \tag{4.24}$$

which is (4.22) with $c_i = \psi_i$.

We can also easily show that the $\{|i\rangle\}$ are linearly independent. If they weren't we could write

$$|i\rangle = \sum_j c_j^{(i)}\,|j\rangle \tag{4.25}$$

however, by acting with $\langle k|$ on the left we get

$$\langle k|i\rangle = \delta_{ki} = \sum_j c_j^{(i)} \langle k|j\rangle = \sum_j c_j^{(i)} \delta_{kj} = c_k^{(i)} \implies c_k^{(i)} = \delta_{ik} \tag{4.26}$$

and therefore the $\{|i\rangle\}$ are linearly independent.

Proving (4.1) and (4.22) imply (4.2). Take (4.2) with $\langle\chi| = \langle i|$ and $|\psi\rangle = |j\rangle$. We then get

$$\sum_k \langle i|k\rangle \langle k|j\rangle = \sum_k \delta_{ik}\delta_{kj} = \delta_{ij} = \langle i|j\rangle \tag{4.27}$$

Because (4.22) is linear, it is straightforward to generalise the above for any vectors, thereby proving (4.2).

Proving (4.2) and (4.22) imply (4.1). We once more remove $\langle\chi|$ from (4.2) to write it as an equality between kets and then we choose $|\psi\rangle = |i\rangle$ to write

$$|i\rangle = \sum_j |j\rangle \langle j|i\rangle \tag{4.28}$$

because the $\{|i\rangle\}$ are linearly independent, it should not be possibly to write $|i\rangle$ as a linear combination of $|j\rangle$ as above. The only possibility is that (4.1) is true.

All in all, this justifies why we were calling $\{|i\rangle\}$ 'base states'. Any state in the Hilbert space can be written as a superposition of base states. The coefficients of this expansion also have a clear interpretation. Imagine we prepared our quantum system in the state $|\psi\rangle$ and later we tried measuring which of the states $\{|i\rangle\}$ our system was in. According to our previous interpretation we will find that the state $|\psi\rangle$ is in the state $|i\rangle$ with a probability given by

$$P(\psi \to i) = |\langle i|\psi\rangle|^2 = |\psi_i|^2 = |c_i|^2 \tag{4.29}$$

The coefficients in the expansion in base states give us the probability amplitude of finding our system in each of the states. This relationship is known as the *Born rule*, after Max Born (Fig. 4.6).

Figure 4.6. Max Born[35]
Born: 1882 Breslau, German Empire
Died: 1970 Göttingen, Federal Republic of Germany
Doctoral Advisor: Carl Runge

Note how in the above we never used the fact that there were a finite number of base vectors, or equivalently that the Hilbert space had finite dimension. In fact, in most physical applications we will need to consider infinite dimensional Hilbert spaces. This is one of the reasons we had to specify the Hilbert space had to be complete. For a finite dimensional Hilbert space with complex scalars, it becomes essentially $\mathbb{C}^n$ which is very obviously complete. However, for the infinite dimensional case, without completeness it would be quite hard to deal with expressions such as (4.22). One of the interpretations of the completeness property, is that it allow us to use expansions in terms of base vectors (and consequently the Born rule) even in the infinite dimensional case without having to worry too much about it. However, we are physicists after all so we won't worry too much about these mathematical technicalities.

An important point is that bases are not unique. Let us take two orthonormal bases $\{|a_i\rangle\}$ and $\{|b_i\rangle\}$, where $i = 1, \ldots, n = \dim\mathcal{H}$. We can then write

$$|\psi\rangle = \sum_i \psi_i^a |a_i\rangle = \sum_i \psi_i^b |b_i\rangle \tag{4.30}$$

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[35] Public Domain, `https://commons.wikimedia.org/w/index.php?curid=137838`

Using the orthonormality of the two bases we can relate the coefficients of $|\psi\rangle$ in both bases

$$\psi_i^b = \sum_j \psi_j^a \langle b_i | a_j \rangle \tag{4.31}$$

This equivalence is similar to how in the Stern-Gerlach experiment we could have used either $\{|\uparrow x\rangle, |\downarrow x\rangle\}$ or $\{|\uparrow y\rangle, |\downarrow y\rangle\}$. In order to relate two different bases you just need the $n \times n$ set of numbers $\langle b_i | a_j \rangle$. In particular these numbers also dictate how to relate the elements of the two bases

$$|a_i\rangle = \sum_j |b_j\rangle \langle b_j | a_i \rangle \tag{4.32}$$

Notice how the transformation of the kets is opposite to that of the basis elements. In tensor language, we would say that the kets transform *contravariantly*, whereas the basis elements transform *covariantly*.

We can also write bras in a basis:

$$\langle \psi | = \sum_i \langle \psi | a_i \rangle \langle a_i | \equiv \sum_i \psi_i^{a*} \langle a_i | \tag{4.33}$$

Its components are just the complex conjugate of the components of the corresponding kets. We can therefore write the inner product as

$$\langle \psi | \chi \rangle = \sum_i \langle \psi | a_i \rangle \langle a_i | \chi \rangle = \sum_i \psi_i^{a*} \chi_i^a \tag{4.34}$$

and their transformation under a change of basis as

$$\psi_i^{b*} = \sum_j \psi_j^{a*} \langle b_i | a_j \rangle^* = \sum_j \psi_j^{a*} \langle a_i | b_j \rangle \tag{4.35}$$

which transform covariantly.

All of these expressions motivate a matrix understanding of bras and kets. Kets can be viewed as column vectors and bras as row vectors. The change of basis is done by using the following matrix

$$S_{ij}^{ba} \equiv \langle b_i | a_j \rangle \tag{4.36}$$

so that

$$|b^i\rangle = \sum_j |a^j\rangle S_{ij}^{ba*} = \sum_j |a^j\rangle \left[S^{ba}\right]^\dagger{}_{ji} \tag{4.37}$$

$$\psi_i^b = \sum_j S_{ij}^{ba} \psi_j^a \tag{4.38}$$

$$\psi_i^{b*} = \sum_j \psi_j^{a*} S_{ij}^{ba*} = \sum_j \psi_j^{a*} \left[S^{ba}\right]^\dagger{}_{ji} \tag{4.39}$$

just as we would expect from matrix algebra. We have denoted by † the combined action of taking the complex conjugate and the matrix transpose. This is often called *Hermitian conjugate*, after Charles Hermite (Fig. 4.7). We are also denoting matrices with square brackets to distinguish from the linear operators defined in the next section.

In particular, in this notation, we can show the change of basis matrix $\left[S^{ba}\right]$ is uni-

Figure 4.7. Charles Hermite FRS FRSE[36]
Born: 1822 Dieuze, Kingdom of France
Died: 1901 Paris, French Republic
Doctoral Advisor: Eugène Charles Catalan

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[36] Picture by Eugène Pirou / Paul Dujardin - Correspondance d'Hermite et de Stieltjes, Paris, Gauthier-Villars, 1905., Public Domain, `https://commons.wikimedia.org/w/index.php?curid=120343802`

tary[37],

$$\sum_k \left[S^{ba}\right]_{ik} \left[S^{ba}\right]^{\dagger}_{kj} = \sum_k \langle b_i|a_k\rangle \langle b_j|a_k\rangle^* = \sum_k \langle b_i|a_k\rangle \langle a_k|b_j\rangle = \delta_{ij} \tag{4.40}$$

This property of unitarity is what ensures the new basis is also orthonormal. In general a change of basis matrix need only be invertible, but if it is not unitary, the new basis is not properly normalised.

4.2 Linear operators on a Hilbert space

Previously, we removed $\langle\chi|$ from (4.2) to write an equation between kets rather than amplitudes. We can actually to one better and also get rid of the $|\psi\rangle$ to write

$$\sum_i |i\rangle\langle i| = \mathbb{1} \tag{4.41}$$

This is our first example of a *linear operator* acting on our Hilbert space, *i.e.* a function $A : \mathcal{H} \to \mathcal{H}$ such that[38]

$$A(a\,|\psi\rangle + b\,|\chi\rangle) = aA\,|\psi\rangle + bA\,|\chi\rangle \tag{4.42}$$

The example in (4.41) is the identity operator that obeys $\mathbb{1}\,|\psi\rangle = |\psi\rangle\,,\ \forall\,|\psi\rangle \in \mathcal{H}$.

We will have more to say about the physical interpretation of these operators in the rest of this chapter, but, for the moment, you can think about them as any sort of manipulation you can perform on quantum states. Like combining any of the various kinds of SG devices we introduced in the previous chapter. The assumption of linearity will be crucial to avoid destroying the structure of the Hilbert space. Much later on in Chapter 14 we will see how linearity will be what ensures quantum mechanics is local.

As with the kets, we can write operators in a given basis:

$$|\psi\rangle = A\,|\chi\rangle \implies \langle i|\psi\rangle = \langle i|\,A\,|\chi\rangle = \sum_j \langle i|\,A\,|j\rangle\,\langle j|\chi\rangle \equiv \sum_j A_{ij}\chi_j \tag{4.43}$$

where we have defined the *matrix elements* of the operator A:

$$A_{ij} = \langle i|\,A\,|j\rangle \tag{4.44}$$

This set of n^2 numbers completely determines the action of A on any ket. The name “matrix elements” comes from the repeated action of operators. Let A and B be two operators and define C as the action of A and then B:

$$C\,|\psi\rangle = BA\,|\psi\rangle \tag{4.45}$$

the matrix elements of C are given by:

$$\sum_j \langle i|\,C\,|j\rangle\,\psi_j = \sum_{jk} \langle i|\,B\,|k\rangle\,\langle k|\,A\,|j\rangle\,\psi_j \implies C_{ij} = \sum_k B_{ik}A_{kj} \tag{4.46}$$

which means they follow the matrix multiplication rule. This also agrees with our previous convention of denoting kets as column vectors and bras as row vectors, given operators act on kets from the right and bras act on operators from the left. *E.g.* if the Hilbert space is

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[37] Recall that a unitary matrix is one that satisfies $[M][M]^\dagger = [M]^\dagger[M] = [\mathbb{1}]$.

[38] In this text we will mostly reserve uppercase letters for operators and lowercase letters for scalars. Nevertheless, neither we nor the literature is 100% consistent on this distinction so always pay attention to the context to figure out whether it's an operator or a scalar.

3-dimensional we can write:

$$\langle\psi| A |\chi\rangle = \begin{pmatrix}\psi_1^* & \psi_2^* & \psi_3^*\end{pmatrix}\begin{pmatrix}A_{11} & A_{12} & A_{13}\\ A_{21} & A_{22} & A_{23}\\ A_{31} & A_{32} & A_{33}\end{pmatrix}\begin{pmatrix}\chi_1\\ \chi_2\\ \chi_3\end{pmatrix} \tag{4.47}$$

A very important consequence of these multiplication rules is that the order of operations matters. Matrix multiplication is, in general, not commutative!

$$AB \neq BA \tag{4.48}$$

We can even define the *commutator* to be the difference between the two orderings:

$$[A, B] \equiv AB - BA \tag{4.49}$$

which, in general, does not vanish.

We can also derive a formula for the change of basis of an operator by demanding that the amplitude $\langle\psi| A |\chi\rangle$ is unchanged under the change of basis:

$$A^b_{ij} = \sum_{kl} \langle b_i|a_k\rangle A^a_{kl} \langle a_l|b_j\rangle = \sum_{kl} S^{ba}_{ik} A^a_{kl} S^{ba*}_{jl} \tag{4.50}$$

or in matrix notation

$$\left[A^b\right] = \left[S^{ba}\right]\left[A^a\right]\left[S^{ba}\right]^\dagger \tag{4.51}$$

The fact that a change of basis is represented by a matrix may entice you to define an operator that performs the act changing a basis, but this cannot be done. Under a change of basis the kets are *the same*, it is only the components that change. We are not mapping kets to other kets like with a linear operator. The transformation laws for the components were derived precisely under the assumption that the kets were left unchanged. The same was true for the operators. In Section 4.4 we will delve more into actual transformations that change the kets, and how they differ from changes in the basis.

Another crucial concept with regards to linear operators is the *adjoint* defined via[39]

$$\left(|\psi\rangle, A^\dagger |\chi\rangle\right) \equiv (A|\psi\rangle, |\chi\rangle) = (|\chi\rangle, A|\psi\rangle)^* \tag{4.52}$$

therefore

$$\langle\psi| A^\dagger |\chi\rangle = \langle\chi| A |\psi\rangle^* \tag{4.53}$$

which means that, in terms of a basis:

$$A^\dagger_{ij} = A^*_{ji} \tag{4.54}$$

This is precisely the Hermitian conjugation we mentioned in the previous section. The fact that in terms of the components the adjoint is the same as Hermitian conjugate is why we used the same notation for both. In rigour they are not exactly the same operation, especially for the infinite dimensional case. In the physics literature it is commonplace to not bother with this distinction and use the terms "adjoint" and "Hermitian conjugate" interchangeably, which I will also do.

There are a number of properties of the adjoint which are fairly easy to prove (Exercise:

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[39] This is one case where Dirac's notation is not very convenient.

try proving them without resorting to a basis!):

$$(AB)^\dagger = B^\dagger A^\dagger, \quad (A^\dagger)^\dagger = A, \quad (aA)^\dagger = a^* A^\dagger, \quad (A+B)^\dagger = A^\dagger + B^\dagger \tag{4.55}$$

Using these concepts we can define the following special categories of operators

Unitary An operator U is unitary iff $UU^\dagger = U^\dagger U = \mathbb{1}$, or alternatively $U^\dagger = U^{-1}$.

Hermitian An operator O is Hermitian (also called self-adjoint) iff $O^\dagger = O$.

Normal An operator N is normal iff $\left[N, N^\dagger\right] = 0$.

It is trivial to see that both unitary and Hermitian operators are normal. In terms of components these definitions agree with the usual definitions of unitary, Hermitian, and normal matrices.

We will see in the following sections how Hermitian operators will encode physical observables, and how unitary operators encode probability preserving transformations. Normal operators on the other hand are useful because of their spectral properties, *i.e.* the properties of their eigenvalues and eigenvectors, which are the numbers λ and kets $|\lambda\rangle$ that obey

$$N|\lambda\rangle = \lambda|\lambda\rangle \tag{4.56}$$

Theorem 4.2 (Spectral Theorem)**.** A linear operator N on a finite dimensional Hilbert space is normal iff there exists an orthonormal basis of its eigenvectors.

The proof is a bit long, so it is relegated to Appendix A. Beyond the actual result, the most important detail is that the proof heavily relies on sticking to a finite dimensional Hilbert space. Under additionally assumptions, such as compactness or boundedness, we can extend these results to infinite dimensional case. However, for a lot of physical applications those assumptions are actually not true. Nevertheless, there are a few tricks that can be employed, if one is comfortable with leaving strict mathematical rigour, that will allow us to ignore that the spectral theorem is quite different for infinite dimensional Hilbert spaces.

In any case, we will usually want to pick an orthonormal basis that diagonalises some normal operators of interest (usually unitary or Hermitian). But, diagonalising one normal operator does not mean we have diagonalised all other normal operators; in fact, the following theorem shows that we can only diagonalise two normal operators simultaneously if they commute.

Theorem 4.3. Let A and B be two normal operators for which the spectral theorem applies. Then we can find an orthonormal basis for the Hilbert space made up of eigenvectors of both operators iff they commute.

Proof. Let $|a\rangle$ be an eigenvector of A. We can then write

$$AB|a\rangle = BA|a\rangle = Ba|a\rangle = aB|a\rangle \tag{4.57}$$

therefore the vector $B|a\rangle$ is also an eigenvector of A with eigenvalue a. If there are no degeneracies, *i.e.* if for each eigenvalue of A there is only a single eigenvector with that eigenvalue, then that means $B|a\rangle \propto |a\rangle$ and we are done. The orthonormal basis made up of eigenvectors of A will also be an orthonormal basis made up of eigenvectors of B.

If there are several kets $|a_r\rangle$ with the same eigenvalue a, then we have to be a bit

more careful, as acting with B on one of these kets may yield a linear combination of any of the other kets with the same eigenvalue, which means they may not be simultaneous eigenvectors of B. However, acting with B on any linear combination of $|a_r\rangle$ will necessarily output a linear combination of these $|a_r\rangle$. This means we can apply the spectral theorem to this subspace and find an orthonormal basis of this subspace made up of eigenvectors of B. Because every $|a_r\rangle$ is an eigenvector of A with the *same* eigenvalue, then every vector in this subspace will be a valid eigenvector of A, including the orthonormal basis of eigenvectors of B. Applying this procedure to every eigenvalue of A allows us to find an orthonormal basis of the Hilbert space of simultaneous eigenvalues of A and B.
Conversely, if there are simultaneous eigenvectors of A and B, call them $|ab\rangle$ then we can show that A and B commute

$$AB\,|ab\rangle = bA\,|ab\rangle = ba\,|ab\rangle = aB\,|ab\rangle = BA\,|ab\rangle \tag{4.58}$$

By linearity, if A and B commute on every basis vector they must commute on any vector. This finishes our proof. ☐

4.3 Hermitian operators as physical observables

At this point in our construction of a framework for quantum mechanics we have states which dictate probability amplitudes, and we have operators that encode actions on those states. However, we do not have observables, *i.e.* measurable quantities that characterise our system, like energy or position of a particle. That is the topic of this section. The ultimate conclusion will be that Hermitian operators are how we can encode these observables.

In order to figure out how to encode observables into our framework we must use one of the big lessons of the quantum revolution: you cannot neglect the action of measurement. This means that we must encode the measurement apparatus into the very framework of the theory. Long gone are the days where measuring a certain quantity had a negligible influence on the system under study. Quantum systems are frequently so small that the interaction of the measurement apparatus cannot be neglected. This poses a conundrum, measurement apparatuses are themselves quantum systems, but we need them to build up our theory, and that theory is needed for us to know how these measurement apparatuses work. This circularity is the source of the common confusions and misunderstandings with quantum mechanics and it will take until Chapter 15 for us to fully address it. In the mean time, we will be physicists and take a “shut up and calculate” approach, and not worry too much about these technicalities.

Let’s build intuition using the Stern-Gerlach experiment. We measured spins in two different ways, with the ordinary and the modified SG devices. Let us first think of the modified device. The way it worked is that we sent a particle in, it did something to the state, and we either had a particle come out or not.

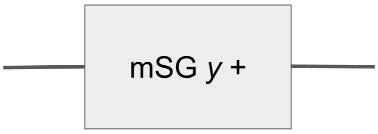

Figure 4.8. Example of a device which only lets through incoming particles with spin-up in the y direction.

For some states the outcome was definite. For the device in Fig 4.8, if we sent an

$|\uparrow y\rangle$ state then it always passed through, whereas if we had sent a $|\downarrow y\rangle$ state it would never pass through. For other states the outcome was uncertain, if we send a $|\uparrow x\rangle$ state there would be a 50/50 change of the particle passing through. Note that this isn't any ignorance due to the furnace, we can prepare the state so that we are certain it's a $|\uparrow x\rangle$, (*e.g.* by first filtering with another modified SG device) and the result from Fig 4.8 would still be uncertain[40]. However, we know exactly what the probability that the state $|\uparrow x\rangle$ is let through, it's given by the Born rule $|\langle\uparrow y|\uparrow x\rangle|^2$.

In any case, no matter the initial state, the end result is always a particle which is definitely spin-up. Once we check what the spin is, repeated measurements would yield the same answer. This motivates us to write the action of this device as a projection operator

$$\mathit{\Pi} = |\uparrow y\rangle\langle\uparrow y| \tag{4.59}$$

Using this operator we can calculate the probability of the state $|\psi\rangle$ being spin-up by computing $\langle\psi|\,\mathit{\Pi}\,|\psi\rangle$. The only subtlety is that if we want the state after the measurement we would need to rescale it to ensure it remains appropriately normalised[41]. Barring this normalisation subtlety, this action of projection ensures that repeated measurements yield the same answer. The special states that have definite answers now appear as eigenstates of this operator. There are two of them in this case: $|\uparrow y\rangle$ with eigenvalue 1, and $|\downarrow y\rangle$ with eigenvalue 0.

But this is not all we can do. After all, in the original Stern-Gerlach experiment we were able to just fully measure spin in the y direction. The outcome was still discrete (we will deal with continuous observables in the next chapter), but the result wasn't just yes/no, we knew whether the particle had spin-up, spin-down, or, in fact, we would even have been able to tell if it had different values for the spin. Like before, there were special states which had a definite value of spin, and generic ones for which the value of the spin was uncertain. But, regardless of the initial state, once we measured the spin, that was it, future experiments would continue to yield that same value.

Let us imagine our experiment had a set of possible values $\{\lambda_i\}$ for some observable O. We will now show that for each of those possible values λ_i we can find one more states $|\lambda_i, r\rangle$ which definitely yield the value λ_i when measured. The label r is accounting for the possibility that there are multiple states that definitely yield the value λ_i, *i.e.* that there are degeneracies. Further, we will be able to show we can organise those $|\lambda_i, r\rangle$ into an orthonormal basis of the Hilbert space. Assuming that the values λ_i are real, because we are measuring them with in an actual real laboratory, this will then allow us to argue that we can represent O with a Hermitian operator. Along the way, all we will need to assume is that any state in a superposition of $|\lambda_i, r\rangle$ with different λ_i can yield any option λ_i with probability given by the Born rule, and that repeated measurements yield the same value.

Firstly, let us argue that for each possible value λ_i there is at least one definite-value-state that yields that value. There are two ways that statement could be false: either no state yields that value, or some states yield that value but the outcome is not definite. In the first case, then λ_i is *not* a possible value for O because it is impossible to obtain it, so we should remove it from the set. In the second case we use the repeated measurement hypothesis. Take one state that can yield λ_i but not with certainty, after the act of

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[40] You might wonder if there is still some chance of this probability being a product of some classical ignorance. Perhaps there are other variables beyond spin that would need fixing before we knew the answer. Alas, this is not the case, any such hidden variables theory would have to be non-local as demonstrated by Bell's theorem in Chapter 14

[41] Properly setting up a quantum system that reproduces this sort of action is quite tricky and not fully understood, an introduction to this topic is given in Chapter 15

measurement whatever state comes out must yield the value λ_i with certainty upon repeated measurements. This is exactly the definite-value-state we were looking for.

Now we will argue that the states $|\lambda_i, r\rangle$ can form an orthonormal basis of the Hilbert space. First, let us consider the case when there are no degeneracies so that each value λ_i corresponds to exactly one state $|\lambda_i\rangle$ that definitely yields that value. If these states weren't linearly independent, then we could write one as a linear combination of the others, *e.g.* $|\lambda_s\rangle = \sum_{i\neq s} |\lambda_i\rangle$. But this is just a superposition, which, by construction, does *not* have well defined outcomes. This is a contradiction, so we conclude these states must be linearly independent. Further, to avoid contradictions within the Born rule the states $|\lambda_i\rangle$ must be orthogonal, otherwise we would stay that there is a probability $|\langle\lambda_j|\lambda_i\rangle|^2$ for the state $|\lambda_i\rangle$ to yield the value λ_j, which would also contradict the definite-value assumption.

If, as argued above, the states $|\lambda_i\rangle$ are all orthogonal and linearly independent, then, at most, there are as many values λ_i as there are dimensions in the Hilbert space. If those two numbers match then we are done, the states $|\lambda_i\rangle$ form an orthonormal basis of the Hilbert space. If there are fewer λ_i than dimensions of the Hilbert space then either there are degeneracies, or some states do not yield any of the values $\{\lambda_i\}$ upon measured. Whatever result those states yield must be added to the set, including for instance the value 0 if the state is destroyed, *i.e.* if it becomes the 0-vector. After we have added the missing possibilities we either end up with degeneracies or we have exactly as many λ_i as dimensions of the Hilbert space.

Now let us consider the case when there are degeneracies. The above argument for linear independence and orthogonality still hold for states corresponding to different values λ_i, but do *not* hold for the states $|\lambda_i, r\rangle$ with the same λ_i but different r. Additionally, we will add every possibly outcome to the set $\{\lambda_i\}$ so that every state must yield one of those values. In particular, this implies that any state can be written as a superposition of $|\lambda_i, r\rangle$, that is what is implied by the Born rule. So we can definitely construct a basis from $\{|\lambda_i, r\rangle\}$ the only question is orthonormality.

Take a the span of $\{|\lambda_i, r\rangle\}$ with the same λ_i but different r. All of these states must definitely yield the value λ_i, no matter how the superposition is constructed, given the Born rule gives probability 0 for all other values λ_j. We can just take this subspace and do Gram-Schmidt to find an orthonormal basis of this subspace. Doing this for every value λ_i, together with the above arguments for the orthogonality of kets belonging to different values yields our desired orthonormal basis.

All in all, we can find an orthonormal basis of the Hilbert space made up of states with a definite value for O. The considerations of repeated measurements suggest we should build our observable action from the projectors $|\lambda_i\rangle\langle\lambda_i|$[42]. In a generic state $|\psi\rangle$ we don't know what value it will have, but we know the probability of obtaining each value, so we can calculate the expectation value of O in the state $|\psi\rangle$

$$\langle O\rangle = \sum_i \lambda_i |\langle\lambda_i|\psi\rangle|^2 = \sum_i \lambda_i \langle\psi|\lambda_i\rangle \langle\lambda_i|\psi\rangle = \langle\psi| \left(\sum_i \lambda_i |\lambda_i\rangle\langle\lambda_i|\right) |\psi\rangle \tag{4.60}$$

This motivates defining the observable as

$$O \equiv \sum_i \lambda_i |\lambda_i\rangle\langle\lambda_i| \tag{4.61}$$

This certainly gives the correct value for the definite states, which now arise as the eigen-

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[42] We're dropping the label r for ease of notation, this doesn't affect the conclusions, we would just have to add sums over r in many of the following equations.

states of the operator O, and it also gives the correct value for the expectation values in generic superpositions. We haven't completely proved this definition will work for *every* case but we have hopefully provided sufficient motivation. As with everything in physics, we need to make motivated assumptions which then must be compared with experimental results.

All in all, we have concluded that our observables can be represented with operators, such that we can form an orthonormal basis from its eigenstates all of which with real eigenvalues. This means these operators are Hermitian, $O^\dagger = O$. If the spectral theorem holds then checking for Hermiticity is enough to guarantee the above properties of unitary diagonalisation with real eigenvalues. Checking whether an operator is Hermitian is much easier than diagonalising it, so it is customary to flip this argument on its head and just define observables in quantum mechanics as Hermitian operators. This is why Hermitian operators are so important, they correspond to the physical observables in our theory.

In the infinite dimensional case, all of this is a bit trickier, especially when dealing with continuous variables. Nevertheless, remember that all of this is merely so that we can say things about observables in some generality. An actual observable is something we measure, Hermitian operators are at best *candidates* for observables. It will always be a case-by-case analysis. This is why we will not worry too much about these subtleties with the spectrum of Hermitian operators in the continuum. Nevertheless it will still come back to bite us when we discuss the free particle in Chapter 7.

Before we move on to unitary operators, let us consider functions of observables. These can be defined by their action on eigenvalues:

$$f(O) = \sum_i f(\lambda_i) \, |\lambda_i\rangle\langle\lambda_i| \tag{4.62}$$

Don't forget that the act of taking a function does not commute with the act of taking the expectation value:

$$\langle f(O) \rangle \neq f(\langle O \rangle) \tag{4.63}$$

in particular

$$\left\langle O^2 \right\rangle \neq \langle O \rangle^2 \tag{4.64}$$

which allows us to define the standard deviation/uncertainty of the measurement of an observable on a given state:

$$\Delta O = \sqrt{\left\langle (O - \langle O \rangle)^2 \right\rangle} \tag{4.65}$$

This uncertainty is *not* an artefact of our measurement apparatus. Even in an idealised measurement, there is a fundamental quantum statistical uncertainty in our measurement of the quantity O. Some states simply have a range of possible values for O, regardless of how we try to measure it.

If two observables A and B commute then we can find a basis such that all the basis vectors will be eigenvectors of both A and B. This means that for all these vectors we can measure both quantities with definitive answers. We call two observables that obey such a relation *compatible*.

If, however, these two observables A and B don't commute, it turns out to be *impossible* to measure both quantities. Measuring one of them will inevitably ruin any measurement of the other. The quantitative version of this statement is the *Heisenberg uncertainty principle*, first discovered for the case of position and momentum but later generalised for any two non-commuting observables.

Theorem 4.4 (Heisenberg Uncertain Principle)**.** For two observables A and B which do not commute, their uncertainties obey:

$$\Delta A \cdot \Delta B \geqslant \frac{1}{2}|\langle [A,B] \rangle| \tag{4.66}$$

Proof. Let us define the following states

$$|A_\psi\rangle \equiv (A - \langle A \rangle)|\psi\rangle\,, \quad |B_\psi\rangle \equiv (B - \langle B \rangle)|\psi\rangle \tag{4.67}$$

then we can write (exploiting the fact $A - \langle A \rangle$ is also Hermitian, and similarly for B)

$$\Delta A = \sqrt{\langle A_\psi | A_\psi \rangle}, \quad \Delta B = \sqrt{\langle B_\psi | B_\psi \rangle} \tag{4.68}$$

Using the Cauchy-Schwarz inequality, we can then write

$$\Delta A \cdot \Delta B \geqslant |\langle A_\psi | B_\psi \rangle| \tag{4.69}$$

For any complex number we have

$$|z| = \sqrt{\mathrm{Re}(z)^2 + \mathrm{Im}(z)^2} \geqslant \sqrt{\mathrm{Im}(z)^2} = |\mathrm{Im}(z)| = \left|\frac{1}{2\mathrm{i}}(z - z^*)\right| = \frac{1}{2}|z - z^*| \tag{4.70}$$

therefore

$$\begin{aligned}
\Delta A \cdot \Delta B \geqslant & \frac{1}{2}|\langle A_\psi | B_\psi \rangle - \langle B_\psi | A_\psi \rangle| = \\
=& \frac{1}{2}|\langle \psi | (AB - A\langle B \rangle - \langle A \rangle B + \langle A \rangle \langle B \rangle)|\psi\rangle - (A \leftrightarrow B)| = \\
=& \frac{1}{2}|\langle \psi | AB | \psi \rangle - \langle \psi | A | \psi \rangle \langle B \rangle - \langle A \rangle \langle \psi | B | \psi \rangle + \langle A \rangle \langle B \rangle \langle \psi | \psi \rangle - (A \leftrightarrow B)| = \\
=& \frac{1}{2}|\langle AB \rangle - \langle A \rangle \langle B \rangle - \langle A \rangle \langle B \rangle + \langle A \rangle \langle B \rangle - (A \leftrightarrow B)| = \\
=& \frac{1}{2}|\langle AB \rangle - \langle BA \rangle| = \\
=& \frac{1}{2}|\langle [A,B] \rangle|
\end{aligned} \tag{4.71}$$

□

If we are silly enough to try to measure non-commuting observables the product of their variance is controlled by the commutator. If we measure observable A very precisely then we must have a very large variance for observable B and vice versa. Indeed, the fact we couldn't measure spin in the x and y simultaneously is evidence that the spin operator in the x direction does not commute with the spin operator in the y direction. A fact we will derive later on.

4.4 Unitary operators as probability preserving transformations

When we discussed normal operators we also defined two special cases: Hermitian and unitary operators. In the previous section we saw how Hermitian operators encode physical observables. In this section we will see how unitary operators encode probability preserving transformations. These will be crucial when we come to discuss symmetries of quantum systems.

Let us take a unitary operator U, we can apply it to *every* operator in the Hilbert space:

$$|\psi\rangle \to |\psi'\rangle = U|\psi\rangle \tag{4.72}$$

Despite this transformation potentially changing every ket in the Hilbert space, every *amplitude* is left invariant

$$\langle\chi'|\psi'\rangle = \langle\chi| U^\dagger U |\psi\rangle = \langle\chi|\psi\rangle \tag{4.73}$$

Therefore, the transformation defined by the unitary operator U, does not change the probability structure of the Hilbert space. We call this a *probability preserving transformation.*

In fact, Eugene Wigner (Fig. 4.9) showed in 1931 that there was some uniqueness to this correspondence in what has become known as *Wigner's theorem.*

Figure 4.9. Wigner Jenő Pál aka Eugene Paul Wigner[43]
Born: 1902, Budapest, Austro-Hungarian Monarchy
Died: 1995 Princeton, United States of America
Doctoral Advisor: Michael Polanyi

Theorem 4.5 (Wigner's theorem)**.** Any invertible transformation of the kets in a Hilbert space $|\psi\rangle \to |\psi'\rangle$ which leaves the transition probabilities $|\langle\chi|\psi\rangle|^2$ invariant can be represented by an operator which is either:

- Linear and unitary. That is one which obeys $U(a|\psi\rangle + b|\chi\rangle) = aU|\psi\rangle + bU|\chi\rangle$ and $(U|\psi\rangle, U|\chi\rangle) = (|\psi\rangle, |\chi\rangle)$.
- Anti-linear and anti-unitary. That is one which obeys $U(a|\psi\rangle + b|\chi\rangle) = a^*U|\psi\rangle + b^*U|\chi\rangle$ and $(U|\psi\rangle, U|\chi\rangle) = (|\psi\rangle, |\chi\rangle)^*$

The latter option, of anti-linear and anti-unitary operators, turns out to always involve a reversal in the direction of time. We will not consider that option in this volume and therefore restrict ourselves to the linear and unitary case. The proof of this theorem is presented in Appendix B.

One very important point about these transformations is that changing a basis is *not* an example of a unitary transformation. Under a change of basis the kets are *unchanged* it is merely their components that change, whereas under (4.72) the kets *do* change. A stark difference can be seen in how matrix elements of operators transform. Under (4.72) we have

$$\langle\chi| A |\psi\rangle \to \langle\chi'| A |\psi'\rangle = \langle\chi| U^\dagger A U |\psi\rangle \tag{4.74}$$

Once again, note how matrix elements *change* under a unitary transformation, whereas if we had just changed bases these would be left invariant.

But (4.74) motivates a different way to look at unitary transformations. Given probability amplitudes are left invariant, the only thing that changes is the matrix elements. Therefore, instead of applying the transformation to the kets we could apply them to the operators:

$$A \to A' = U^\dagger A U \tag{4.75}$$

such that

$$\langle\chi| A |\psi\rangle \to \langle\chi| A' |\psi\rangle = \langle\chi| U^\dagger A U |\psi\rangle \tag{4.76}$$

exactly like before. This point of view is called *passive*, whereas the version where you change the kets but keep the operators fixed is called *active.*

Contrast (4.75) and (4.51), the † is on different places in either case. The way an operator transforms under a unitary transformation or a change of basis is precisely the opposite. This specific difference is because under a unitary transformation you *either* change the kets *or* you change the operators, not both. Whereas under a change of basis

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[43] Picture by Nobel foundation - `http://nobelprize.org/nobel_prizes/physics/laureates/1963/wigner-bio.html`, Public Domain, `https://commons.wikimedia.org/w/index.php?curid=6141135`

you must change *both* the ket components *and* the operator components in order to ensure every matrix element stays invariant.

However, there is a way in which the two can appear related, which is also the motivation behind the active/passive nomenclature. Imagine A was Hermitian, and further imagine that we were using the eigenkets of A as basis $\{|a_i\rangle\}$. In the active version of the unitary transformation, while the state kets transform via

$$|\psi\rangle \to U\,|\psi\rangle \tag{4.77}$$

our basis of eigenkets of A does *not* transform.

$$|a_i'\rangle = |a_i\rangle \tag{4.78}$$

This is because A has not transformed, so its eigenkets will be the same as before.

In the passive point of view, the state kets are left invariant, but A will transform

$$A \to A' = U^\dagger A U \tag{4.79}$$

which means the eigenkets of the new operator A' will now have to be

$$|a_i'\rangle = U^\dagger\,|a_i\rangle \tag{4.80}$$

because

$$A'\,|a_i'\rangle = U^\dagger A U U^\dagger\,|a_i\rangle = U^\dagger A\,|a_i\rangle = a_i U^\dagger\,|a_i\rangle = a_i\,|a_i'\rangle \tag{4.81}$$

Even though the state kets were left invariant, because A transformed the eigenkets also transformed. If we insisted on using eigenkets of A as our basis we would see our basis transform under the *inverse* of the unitary transform.

This is why we called the two points of view active and passive. In the active point of view we are moving the kets and leaving the basis unchanged. In the passive point of view we are leaving the kets where they were, but changing the basis in the opposite direction. Making an analogy with rotations in classical physics, in the active point of view we are rotating the actual object while keeping the axes fixed, and the passive point of view we are leaving the object where it was but moving the axes in the opposite direction.

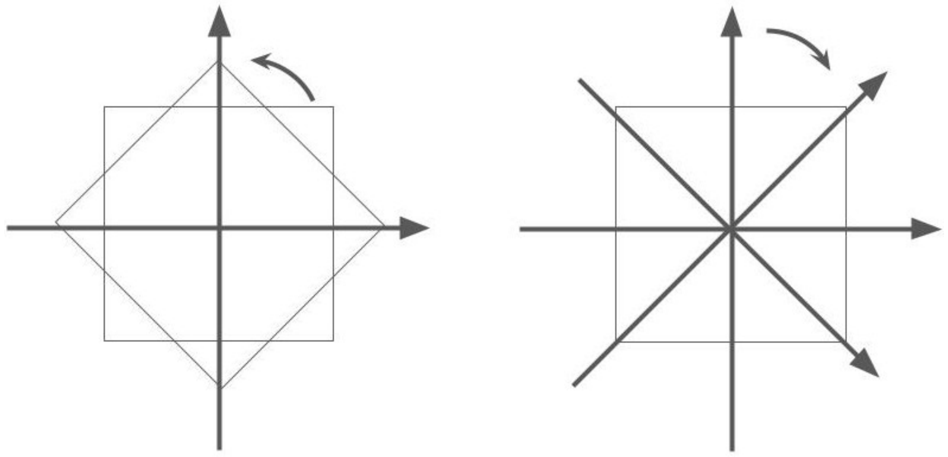

Figure 4.10. On the left we have an active rotation: the square is rotated 45º anti-clockwise while the axes are fixed. On the right we have a passive rotation: the square is kept fixed but the axes rotate 45º clockwise. The end result is equivalent

There are two limitations to this analogy. Firstly, in the passive point of view we actually do change something about the system: the operators. And in fact, these are our observables so we're not truly leaving the object where it is. Secondly, we are only changing the basis with the inverse transformation because we want to. Nothing is stopping us from using whatever basis we wanted, we don't have to use the eigenkets of A as a basis. The passive point of view is *not* reducing the unitary transformation to a change of basis.

This section may have been a bit abstract but these kinds of unitary transformations are ubiquitous in quantum mechanics. They can represent spatial translation, rotations, parity, or even some internal symmetry like isospin. We will see later that time translation is also encoded as a unitary transformation, which is what will allow us to write equations of motion for quantum mechanics.

5 Quantum mechanics for continuous variables

While the theory discussed above in principle applies for infinite dimensional cases we have always assumed that the bases could be written with a discrete label. However, in many physical applications this will not be the case. For example, in Chapter 2 we were measuring the position of an electron, which certainly seems to be a continuous variable. This chapter will focus on how to deal with these continuous observables like position or momentum.

5.1 The wavefunction in position space

The components of a state in terms of a discrete basis were given by:

$$\psi_i = \langle i|\psi\rangle \tag{5.1}$$

Now, we shall swap i by the position x of the particle, and make it continuous. Because of this change, the components ψ_i can no longer be written as column vectors, they instead become functions:

$$\psi(x) = \langle x|\psi\rangle \tag{5.2}$$

This representation of the state is so important it gets a special name: *wavefunction*. In fact, it is not unusual to use the word wavefunction as synonymous with quantum state, even when we are not in the position basis.

Previously we interpreted $|\psi_i|^2$ as the probability of finding the state $|\psi\rangle$ in state $|i\rangle$ after a measurement. As is standard in probability theory, when we are dealing with continuous variables, we instead deal with *probability densities*. This is because the probability of finding a particle at position x *exactly* will be zero for well-behaved probability distributions. We must instead ask for probability of finding the particle in a certain *interval* of positions. We then interpret $|\psi(x)|^2\,\mathrm{d}x$ as the probability of finding the particle between x and $x + \mathrm{d}x$. The normalisation requirement will then read:

$$\int \mathrm{d}x\, |\psi(x)|^2 = 1 \tag{5.3}$$

We have purposefully left the limits of the integral unfixed. In certain applications they will be finite, in others we will wish to integrate over the whole real line. In either case we see that our Hilbert space will the be the space of *square-integrable* functions usually denoted by $L^2(a, b)$, where (a, b) denote the limits of the integral. The inner product is defined as:

$$\langle\psi|\chi\rangle = \int \mathrm{d}x\, \psi^*(x)\chi(x) \tag{5.4}$$

You can check that this space satisfies all of the requirements of a Hilbert space.

The only thing left to do is to figure out how operators act in this basis. Let us first think of position. Intuitively it is clear that the expectation value for the position of a particle should be:

$$\langle X\rangle = \int \mathrm{d}x\, x|\psi(x)|^2 \tag{5.5}$$

where we are denoting the position operator by X.

With the above expression in mind we can *define* the position operator by:

$$\langle x| X |\psi\rangle \equiv X\psi(x) \equiv x\psi(x) \tag{5.6}$$

it is not too hard to show that this operator is Hermitian, which means it is a good candidate for an observable.

And what are the eigenvectors of this operator? Its action on generic $\psi(x)$ is quite simple but not simple enough. In order for a function to classify as an eigenvector of X, the action of X on that function must be the multiplication by a *number*, but x is a function rather than a fixed number. Intuitively, these eigenvectors must be functions so peaked at a particular value of $x = y$ that multiplying by the function x is the same as multiplying by the number y.

An easier way to understand these eigvenctors is by using bras and kets. In this notation, the eigenvector of X with eigenvalue y can be written in the position basis as

$$\langle x|y\rangle \tag{5.7}$$

which is just the inner product between two base states! According to (4.1), when we are taking the inner product of two base states we get the Kronecker-δ. We just need to generalise it to the continuous case.

We might not be able readily generalise (4.3), but we can notice that it is equivalent to defining δ_{ij} as the unique object such that

$$\sum_j \delta_{ij}\psi_j = \psi_i \tag{5.8}$$

Making the sum an integral we then define $\langle x|y\rangle \equiv \delta(x-y)$ as the unique object such that[44]:

$$\int \mathrm{d}x\, \delta(x-y)\psi(x) = \psi(y) \tag{5.9}$$

This object is called the *Dirac-*δ[45] and is our continuous analogue of the Kronecker-δ.

It is straightforward to prove the following properties:

1. $\delta(ax) = \dfrac{1}{|a|}\delta(x) \implies \delta(-x) = \delta(x)$
2. $f(x)\delta(x) = f(0)\delta(x)$

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[44] You might wonder we we wrote $\delta(x-y)$ with a single argument rather than something like $\delta(x, y)$. It is not too hard to show that the two definitions agree, you just have to do a change of variables in the integral.

[45] It is also sometimes referred to as the δ-function. However, as we will see shortly, it is in fact *not* a function. We will therefore avoid such nomenclature.

3. $\delta(g(x)) = \sum_{x_0|g(x_0)=0} \frac{1}{|g'(x_0)|}\delta(x-x_0) \implies \delta(x^2-a^2) = \frac{1}{2|a|}(\delta(x-a)+\delta(x-a))$

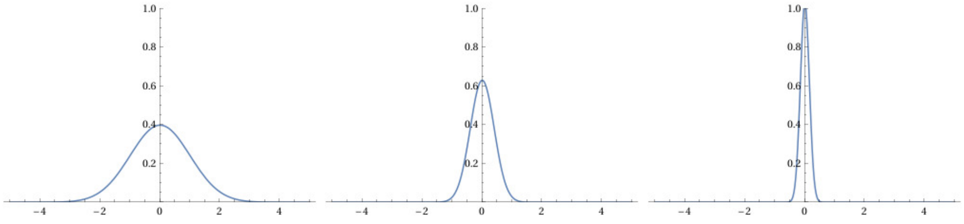
Additionally, we can capture the intuitive idea that the eigenstates of position should be sharply peaked by realising that we can represent the Dirac-δ by the following limit:

$$\delta(x) = \lim_{\epsilon\to 0}\frac{1}{\epsilon\sqrt{2\pi}}\mathrm{e}^{-\frac{x^2}{2\epsilon^2}} \tag{5.10}$$

to show this we just need to consider the following integral:

$$\int \mathrm{d}x\,\psi(x)\frac{1}{\epsilon\sqrt{2\pi}}\mathrm{e}^{-\frac{x^2}{2\epsilon^2}} = \int \mathrm{d}y\,\frac{1}{\sqrt{2\pi}}\mathrm{e}^{-\frac{y^2}{2}}\psi(\epsilon y) \xrightarrow{\epsilon\to 0} \psi(0)\int \mathrm{d}y\,\frac{1}{\sqrt{2\pi}}\mathrm{e}^{-\frac{y^2}{2}} = \psi(0) \tag{5.11}$$

For finite ϵ we can graph this function and see that as ϵ gets smaller and smaller we see that it gets more and more peaked around $x=0$, Fig. 5.1.



(a) $\epsilon = 1$ (b) $\epsilon = 0.4$ (c) $\epsilon = 0.15$

Figure 5.1. Plots of (5.10) for different values of the parameter ϵ. We can see how as $\epsilon \to 0$ the function is more sharply peaked around $x = 0$.

In fact, for $x \neq 0$, we can see that

$$\lim_{\epsilon\to 0}\frac{1}{\epsilon\sqrt{2\pi}}\mathrm{e}^{-\frac{x^2}{2\epsilon^2}} = 0 \tag{5.12}$$

therefore $\delta(x) = 0$ for $x \neq 0$.

However, the limit diverges for $x = 0$:

$$\left.\frac{1}{\epsilon\sqrt{2\pi}}\mathrm{e}^{-\frac{x^2}{2\epsilon^2}}\right|_{x=0} = \frac{1}{\epsilon\sqrt{2\pi}} \xrightarrow{\epsilon\to 0} \infty \tag{5.13}$$

The analogue of (4.3) becomes

$$\delta(x) = \begin{cases} 0 & x \neq 0 \\ \infty & x = 0 \end{cases} \tag{5.14}$$

which is clearly *not* an ordinary function.

The Dirac-δ only makes sense under an integral (or the promise of one), because that is when we can apply its defining property (5.9). Objects like this that only make sense under an integral are described by the *theory of distributions*. We won't get into too many details regarding this mathematics except to point out one must be careful when manipulating the Dirac-δ to avoid getting nonsensical results. For example, the square of a Dirac-δ does not make sense:

$$\int \mathrm{d}x\,\delta(x)\delta(x) = \delta(0) = \infty \tag{5.15}$$

Consequently, the Dirac-δ is *not* square-integrable. But this means the kets $|x\rangle$ are not even in the Hilbert space! They are not normalisable:

$$\langle x|x\rangle = \delta(0) = \infty \tag{5.16}$$

This is precisely the sorts of issues we can run into with infinite dimensional Hilbert spaces. X is a perfectly sensible Hermitian operator, however, its eigenvectors (if you can call them that) are not in the Hilbert space. Our candidate for the position operator seems to not be unitarily diagonalisable.

This seems worse than it actually is. What it means physically is that we can never truly prepare eigenstates of position, they are not physically attainable states. Nevertheless, we can still use normalisable wavefunctions $\psi(x)$ without any issues, and we still have access to the expression

$$\int \mathrm{d}x\, |x\rangle\langle x| = \mathbb{1} \tag{5.17}$$

since

$$\langle\psi|\chi\rangle = \int \mathrm{d}x\, \psi^*(x)\chi(x) = \int \mathrm{d}x\, \langle\psi|x\rangle\, \langle x|\chi\rangle \tag{5.18}$$

So, even if $|x\rangle$ are not in the Hilbert space, we can still deal with them. For instance, despite not being square-integrable we can still consistently fix their normalisation via the equation

$$\langle x|y\rangle = \delta(x-y) \tag{5.19}$$

with the definition (5.9).

Using these tricks we can deal with more generic operators via expressions like:

$$\langle\chi|\, A\, |\psi\rangle = \int \mathrm{d}x\, \mathrm{d}y\, \langle\chi|x\rangle\, \langle x|\, A\, |y\rangle\, \langle y|\psi\rangle = \int \mathrm{d}x\, \mathrm{d}y\, \chi^*(x)A(x,y)\psi(y) \tag{5.20}$$

Linear operators can then be identified as *integral operators*. But this doesn't seem completely generic. Take for example the action of taking a derivative:

$$\langle x|\, D\, |\psi\rangle \equiv D\psi(x) \equiv \psi'(x) \tag{5.21}$$

This is certainly a linear action on our Hilbert space, so it should also be included in our definition of linear operators, but it seems like it acts in a completely different way. Nevertheless, there is a way to relate the two if we define derivatives of the Dirac-δ.

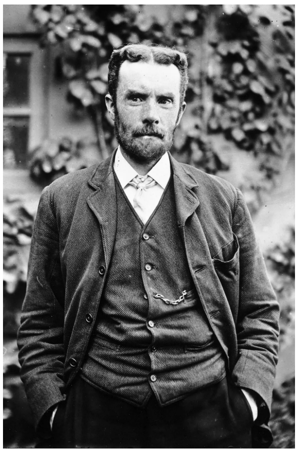


Figure 5.2. Oliver Heaviside FRS[46]
Born: 1850 Camden Town, United Kingdom of Great Britain and Ireland
Died: 1925 Torquay, United Kingdom of Great Britain and Northern Ireland

You may think I have gone completely mad. The Dirac-δ isn't even a function, how can we possibly define its derivative? The trick is to use integration by parts:

$$\int \mathrm{d}x\, \delta'(x)f(x) = -\int \mathrm{d}x\, \delta(x)f'(x) = -f'(0) \tag{5.22}$$

where we have discarded the boundary term because $\delta(x) = 0$ for $x \neq 0$. This is a perfectly well defined object, or at least as well defined as the Dirac-δ itself. This way of taking derivatives via integration by parts is called *distributional derivative* and will allow us to take derivatives of basically any function at all. In fact, another way of defining the Dirac-δ is as the distributional derivative of the Heaviside step function, named after Oliver Heaviside (Fig. 5.2):

$$\delta(x) = \theta'(x) \tag{5.23}$$

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[46] Picture by Unknown author - IET Archive, Public Domain, https://commons.wikimedia.org/w/index.php?curid=13673594

where

$$\theta(x) = \begin{cases} 0 & x < 0 \\ \frac{1}{2} & x = 0 \\ 1 & x > 0 \end{cases} \tag{5.24}$$

We can then write

$$D\psi(x) = \frac{\mathrm{d}\psi(x)}{\mathrm{d}x} = \int \mathrm{d}y\, \delta(x-y)\frac{\mathrm{d}\psi(y)}{\mathrm{d}y} = -\int \frac{\mathrm{d}\delta(x-y)}{\mathrm{d}y}\psi(y) \tag{5.25}$$

and therefore define

$$\langle x| D |y\rangle \equiv D(x,y) = -\frac{\mathrm{d}\delta(x-y)}{\mathrm{d}y} \tag{5.26}$$

Using derivatives of the Dirac-δ we can see that we can write any differential operator as an integral operator. So our definition of linear operators as integral operators was in fact fully generic. We will seldom use this fact and instead more often write

$$D = \frac{\mathrm{d}}{\mathrm{d}x} \tag{5.27}$$

for simplicity. It is nevertheless important to note our understanding from the discrete case still holds.

5.2 The wavefunction in Fourier space

As the name and the double-slit experiment from Chapter 2 suggest, the dynamics of the wavefunction will often resemble that of waves. As you may be well aware, when wish to deal with wave phenomena it is a smart idea to Fourier transform, so let us study the wavefunction in Fourier space. These tools were first developed by Joseph Fourier[47] (Fig. 5.3) to help solve the heat equation.

Figure 5.3. **Jean Baptiste Joseph Fourier**[48]
Born: 1768 Auxerre, Kingdom of France
Died: 1830 Paris, Kingdom of France
Academic Advisors: Jean-Baptiste Biot, Joseph-Louis Lagrange

There are a number of conventions for Fourier transforms around, we shall adopt the following. The Fourier transform of the function $\psi(x)$ is given by:

$$\tilde{\psi}(k) = \int \mathrm{d}x\, \mathrm{e}^{-\mathrm{i}kx}\psi(x) \tag{5.28}$$

The variable k is called the wavenumber and is related to the wavelength by

$$k = \frac{2\pi}{\lambda} \tag{5.29}$$

The inverse of the Fourier transform is then

$$\psi(x) = \int \frac{\mathrm{d}k}{2\pi}\mathrm{e}^{\mathrm{i}kx}\tilde{\psi}(k) \tag{5.30}$$

In this way integrals in Fourier space always carry factors of 2π.

In particular the Fourier transform of a Dirac-δ is given by

$$\int \mathrm{d}x\, \mathrm{e}^{-\mathrm{i}kx}\delta(x) = 1 \tag{5.31}$$

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[47] Not to be confused with Charles Fourier, the socialist philosopher who coined the term "feminism". As far as I could verify there seems to be no relation between them except having coincidentally identical surnames.

[48] Picture by Julien-Léopold Boilly - This file was derived from: Fourier2.jpg. Restored by: Bammesk. Original source: https://www.gettyimages.com.au/license/169251384https://wellcomecollection.org/works/b4qh352u, Public Domain, https://commons.wikimedia.org/w/index.php?curid=114366437

and therefore, the inverse Fourier transform of this expression gives

$$\int \frac{\mathrm{d}k}{2\pi} \mathrm{e}^{\mathrm{i}kx} = \delta(x) \tag{5.32}$$

giving yet another representation for the Dirac-δ.

Finally, we can also write the inner product in this space

$$\begin{aligned} \langle\psi|\chi\rangle = \int \mathrm{d}x\, \psi^*(x)\chi(x) &= \int \mathrm{d}x\, \frac{\mathrm{d}k\,\mathrm{d}q}{(2\pi)^2} \mathrm{e}^{\mathrm{i}x(q-k)} \tilde{\psi}^*(k)\tilde{\chi}(q) = \\ &= \int \frac{\mathrm{d}k\,\mathrm{d}q}{(2\pi)^2} 2\pi\delta(q-k)\tilde{\psi}^*(k)\tilde{\chi}(q) = \\ &= \int \frac{\mathrm{d}k}{2\pi} \tilde{\psi}^*(k)\tilde{\chi}(k) \end{aligned} \tag{5.33}$$

where in going to the second line we used (5.32) with the roles of k and x interchanged.

All of these results are exactly what you would expect from a change of basis from $\{|x\rangle\}$ to $\{|k\rangle\}$. We define:

$$\tilde{\psi}(k) \equiv \langle k|\psi\rangle = \int \mathrm{d}x\, \langle k|x\rangle \langle x|\psi\rangle = \int \mathrm{d}x\, \langle k|x\rangle\, \psi(x) \tag{5.34}$$

which gives us

$$\langle k|x\rangle = \mathrm{e}^{-\mathrm{i}kx} \tag{5.35}$$

The states $\{|k\rangle\}$ have a slightly different normalisation than $\{|x\rangle\}$ due to our factors of 2π in the definition of the Fourier transform.

$$\langle k|q\rangle = \int \mathrm{d}x\, \langle k|x\rangle \langle x|q\rangle = \int \mathrm{d}x\, \mathrm{e}^{\mathrm{i}kx}\mathrm{e}^{-\mathrm{i}qx} = 2\pi\delta(k-q) \tag{5.36}$$

The way to remember these factors is to keep in mind that the measure in Fourier space is $\mathrm{d}k\,/2\pi$ rather than just $\mathrm{d}k$.

One of the big advantages of the Fourier basis is that derivatives act much more simply. Keeping in mind our expression (5.26) for the action of a derivative we can write:

$$\begin{aligned} \tilde{D}(k,q) \equiv \langle k|\, D\, |q\rangle = \int \mathrm{d}x\,\mathrm{d}y\, \langle k|x\rangle \langle x|\, D\, |y\rangle \langle y|q\rangle &= \int \mathrm{d}x\,\mathrm{d}y\, \mathrm{e}^{-\mathrm{i}kx} D(x,y) \mathrm{e}^{\mathrm{i}qy} = \\ = -\int \mathrm{d}x\,\mathrm{d}y\, \mathrm{e}^{-\mathrm{i}kx} \frac{\mathrm{d}\delta(x-y)}{\mathrm{d}y} \mathrm{e}^{\mathrm{i}qy} &= \int \mathrm{d}x\,\mathrm{d}y\, \mathrm{e}^{-\mathrm{i}kx} \delta(x-y) \frac{\mathrm{d}\mathrm{e}^{\mathrm{i}qy}}{\mathrm{d}y} = \\ = \int \mathrm{d}x\,\mathrm{d}y\, \mathrm{e}^{-\mathrm{i}kx}\delta(x-y)\mathrm{i}q\mathrm{e}^{\mathrm{i}qy} = \mathrm{i}q \int \mathrm{d}x\, \mathrm{e}^{\mathrm{i}x(q-k)} &= \mathrm{i}q2\pi\delta(q-k) \end{aligned} \tag{5.37}$$

where in the second line we integrated by parts, using the fact that $\delta(x-y)$ vanishes for $x \neq y$ to discard the boundary term. In the last line we first integrated over y using the definition of the Dirac-δ, and then we integrated over x using (5.32) with the roles of k and x interchanged.

Therefore

$$\langle k|\, D\, |\psi\rangle \equiv \tilde{D}\tilde{\psi}(k) = \int \frac{\mathrm{d}q}{2\pi} \tilde{D}(k,q)\tilde{\psi}(q) = \mathrm{i}k\tilde{\psi}(k) \tag{5.38}$$

so we usually write it more simply as

$$\tilde{D} = \mathrm{i}k \tag{5.39}$$

Derivatives become just multiplication by $\mathrm{i}k$. In fact this allows us to define the operator $K = -\mathrm{i}D$ such that

$$\langle k| K |\psi\rangle \equiv K\tilde{\psi}(k) = k\psi(k) \tag{5.40}$$

which, in the position basis becomes

$$\langle x| K |\psi\rangle = -\mathrm{i}\frac{\mathrm{d}\psi(x)}{\mathrm{d}x} \tag{5.41}$$

The reason for defining this operator is that D is *not* a Hermitian operator but K *is*. This is trivially seen by the representation in Fourier space but we can also show this in the position basis with a little more work.

$$\begin{aligned}\langle\psi| K^\dagger |\chi\rangle = \int \mathrm{d}x\,(K\psi(x))^*\chi(x) = \int \mathrm{d}x\,\mathrm{i}\frac{\mathrm{d}\psi^*(x)}{\mathrm{d}x}\chi(x) = \\ = \int \mathrm{d}x\,\psi^*(x)\left(-\mathrm{i}\frac{\mathrm{d}\chi(x)}{\mathrm{d}x}\right) = \langle\psi| K |\chi\rangle\end{aligned} \tag{5.42}$$

where in going to the last line we integrated by parts, discarding the boundary term as both $\psi(x)$ and $\chi(x)$ are square-integrable and therefore must vanish at infinity.

Similarly, the position operator X can be written in the Fourier basis in the following way (check!)

$$\langle k| X |\psi\rangle = i\frac{\mathrm{d}\tilde{\psi}(k)}{\mathrm{d}k} \tag{5.43}$$

We have two observables, the position and the wavenumber. Could we measure them simultaneously? The only way to find out is by calculating their commutator, $[X, K]$. Let us do so in the position basis:

$$[X,K]\psi(x) = XK\psi(x) - KX\psi(x) = -\mathrm{i}x\frac{\mathrm{d}\psi(x)}{\mathrm{d}x} + \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}x}(x\psi(x)) = \mathrm{i}\psi(x) \tag{5.44}$$

therefore

$$[X,K] = \mathrm{i} \tag{5.45}$$

which is non-zero! We cannot measure both X and K with absolute precision. In fact, we can use the Heisenberg uncertainty principle to write

$$\Delta X \cdot \Delta K \geqslant \frac{1}{2}|\langle[X,K]\rangle| = \frac{1}{2} \tag{5.46}$$

This is a well known result in signal analysis and can be intuitively though of in the following way. If we have a function with a very well defined value for K that means it is a wave like Fig. 5.4. But this function is completely de-localised in space!

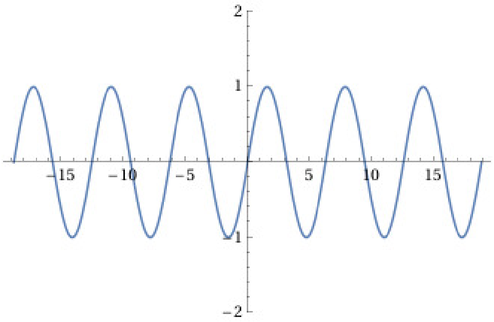

Figure 5.4. Sinusoidal wave: the wave number is known precisely but the position is not.

But if we try to localise it in space, like in Fig. 5.5, we no longer have enough peaks to have an accurate value for the wavenumber.

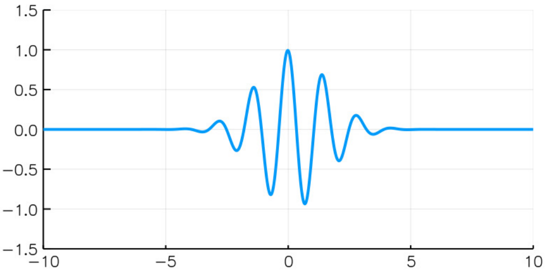

Figure 5.5. Localised wavepacket: the position is known precisely but the wavenumber is not.

We even saw this in the Fourier transform of the Dirac-δ. As an eigenstate of the position it has a completely determined value for the position, but its Fourier transform is a constant! It is equally likely to measure any value of the wavenumber, it is completely de-localised in Fourier space.

Figure 5.6. **Clinton Joseph Davisson**[49]
Born: 1881 Bloomington, United States of America
Died: 1958 Charlottesville, United States of America
Doctoral Advisor: Owen Richardson

Figure 5.7. **Lester Halbert Germer**[50]
Born: 1896 Chicago, United States of America
Died: 1971 Shawangunk Ridge, United States of America
Doctoral Advisor: Clinton Davisson

5.3 Momentum in quantum mechanics

We have explored how position is represented in quantum mechanics but what about momentum? Somewhat disappointingly, there is no way to derive how momentum appears in quantum systems, we have to just postulate it and see the consequences. The way to do it is to unearth the proposal by Louis de Broglie all the way from Chapter 1 that related the momentum and wavelength of the electron:

$$p = \frac{h}{\lambda} \tag{5.47}$$

where h is the Planck constant. Recalling the relationship between wavelength and wavenumber (5.29), and promoting the wavenumber to the operator defined earlier (5.41) we postulate that the momentum operator is given by

$$P = \hbar K \tag{5.48}$$

where $\hbar = h/2\pi$ is the reduced Planck constant as before. This relationship *cannot* be derived theoretically. It must be taken as a *fundamental postulate of quantum mechanics.*

Despite not having a theoretical derivation, it still needs experimental verification. To do so, take a plane wave wavefunction:

$$\psi(x) = \mathrm{e}^{\mathrm{i}kx} \tag{5.49}$$

which is an eigenstate of K with eigenvalue k. If we found a way to measure both its momentum and its wavenumber we could verify (5.48). But we already have such an experiment: the double-slit experiment from Chapter 2!

Historically, rather than doing the double-slit interference experiment, Clinton Davisson (Fig. 5.6) and Lester Germer (Fig. 5.7) sent electrons through a crystal of nickel which

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[49] Picture by Nobel foundation - http://nobelprize.org/nobel_prizes/physics/laureates/1937/davisson-bio.html, Public Domain, https://commons.wikimedia.org/w/index.php?curid=6186817

[50] Picture by Credit Line: AIP Emilio Segrè Visual Archives - https://repository.aip.org/islandora/object/nbla%3A297939, Copyrighted free use, https://commons.wikimedia.org/w/index.php?curid=148262492

exhibits a diffraction patter. From this diffraction pattern they were able to measure the wavelength of the incoming wavefunction. To measure the momentum they just had to measure the energy of the beam of electrons. More specifically, combining the relation between the wavenumber and the wavelength

$$k = \frac{2\pi}{\lambda} \tag{5.50}$$

and the non-relativistic kinetic energy

$$E = \frac{p^2}{2m} \tag{5.51}$$

we get

$$\lambda = \frac{h}{\sqrt{2mE}} \tag{5.52}$$

And lo and behold this is precisely the wavelength measured by Davisson and Germer.

To fully establish this law we not only need to measure the relationship for an electron but for all kinds of particles to really ensure $\hbar$ is a constant of Nature. This is also verified experimentally.

It appears then that the Planck constant and de Broglie's guess were not just some temporary crutches on the road to quantum mechanics. This relation[51] is instead a deep fundamental fact of nature. Let us plug in some numbers to get our heads around this. If we take an object with mass $\sim$ 1 kg, travelling at a velocity of $\sim$ 1 m/s, then the wavelength associated with this particle is $\sim 7 \times 10^{-34}$ m. Which is quite small! This smallness explains why in day-to-day life we never experience wave-like phenomena, the wavelength is so small that it becomes completely negligible. Only for atom sized and smaller objects will the wavelength be more significant. For example, an electron travelling at $\sim$ 1 m/s will have a wavelength of $\sim 7 \times 10^{-4}$ m, a much more reasonable length scale.

The reasoning above is the usual story told about the Planck constant and, while largely correct, is missing a subtlety. The value for the Planck constant is completely arbitrary. It entirely depends on the system of units in use. In fact, nowadays, the value of the Planck constant is not merely known approximately, it is *defined* to be *exactly*

$$h = 6.626\ 070\ 15 \times 10^{-34} \text{ J s} \tag{5.53}$$

which is then used to *define* the kilogram. Choosing a different value would have resulted in a different definition of the kilogram, the physics would be unchanged.

But why did we pick $6.626\ 070\ 15 \times 10^{-34}$ J s? This value was chosen to agree with a historical definition of the kilogram in terms of a reference weight. This reference weight was itself chosen so that 1 litre of water at room temperature weighed 1 kilogram. This historical definition is actually more enlightening. It was chosen to be a sensible mass scale for human beings. 1 litre is a very normal amount of water to carry around, so we all know how much a kilogram weights. Our weight is itself a few dozen kilograms. And this is also true for the second and the metre. The second is a very natural amount of time to count in, and human beings are between 1 and 2 metres tall. They are all set to be convenient numbers for everyday use by humans.

The smallness of the Planck scale then appears to not be a statement about Nature but a statement about us. It is not that atoms are small, we are the ones who are big! It doesn't tell us that quantum objects are small, it tells us that we the humans are much

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[51] And the related energy-frequency relationship which we will delve into in the next chapter

bigger than quantum scales. The *true* value of $\hbar$ is not $\sim 10^{-34}$ it is[52]

$$\hbar = 1 \tag{5.54}$$

The de Broglie relation then tells us that momentum *is* wavenumber. The two aren't just related, they're one and the same.

$$P = K \tag{5.55}$$

The units in which $\hbar = 1$ (and $c = 1$ and $k_B = 1$) are called "natural units" and are the most common units in use in active research. In this context energy, mass, frequency, momentum, wavenumber and temperature all have the same units. We still need to fix one of them, usually chosen to be a unit of energy like the electron-Volt. Interestingly, this is also true for the SI units. Every unit is defined in terms of a fundamental constant except for the second, which is defined in terms of the frequency of a transition in Cesium atoms, a phenomenological time scale rather than a fundamental constant of nature. In this volume we will keep using SI units to avoid confusion, but in future volumes we will resort to natural units.

Now we bring the conclusions from the previous section into the momentum notation. Instead of Fourier space, we very often call it *momentum space*. The eingenstates of the momentum obey

$$\langle p|q\rangle = 2\pi\hbar\ \delta(p-q) = h\ \delta(p-q) \tag{5.56}$$

therefore our momentum integrals will have a factor of $2\pi\hbar = h$ rather than just 2π.

In position basis we can write

$$P = -\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}x} \tag{5.57}$$

The same way that we showed that K was Hermitian we can show that P is Hermitian.

The commutator between X and P is then

$$[X, P] = \mathrm{i}\hbar \tag{5.58}$$

Previously it was no puzzle at all that we could not measure position and wavenumber at the same time. This is a well known result from signal processing. But now, we are claiming that we cannot know both the position and *momentum* of a particle at the same time. This was the original version of the Heisenberg uncertainty principle:

$$\Delta X \cdot \Delta P \geqslant \frac{\hbar}{2} \tag{5.59}$$

If we know exactly where a particle is then we are very uncertain about how fast it's moving and vice-versa. This is not just weird, it goes against the very fabric of classical mechanics. In order to solve the equations of motion we had to specify *both* the position and the momentum/velocity of the particle. Without knowing both, we cannot construct a phase space or solve the equations of motion (in whatever formulation you prefer). This uncertainty principle destroys classical mechanics at its heart.

And yet, this is what experiment tells us. No matter how hard we try, we cannot fix both the position and momentum. We must choose. And despite these difficulties, we can still construct equations of motion which agree with classical results in the appropriate limits.

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[52] You may wonder why we choose $\hbar = 1$ rather than $h = 1$. They are of course the same up to factors of 2π. Setting $\hbar = 1$ is essentially working with radians which are mathematically more convenient.

5.4 * The quantum Poisson bracket

More than anything, the Heisenberg uncertainty principles seems to really put the nail in the coffin of classical mechanics. The whole foundation of the theory relies on fixing both the position and momentum/velocity in order to solve the second order equations of motion. And while it is true that quantum mechanics fundamentally breaks with classical physics there is in fact a deep connection between the two, but in order to see that we must view classical mechanics from the canonical perspective championed by William Rowan Hamilton (Fig. 5.8).

Figure 5.8. Sir **William Rowan Hamilton** FRAS[53]
Born: 1805 Dublin, United Kingdom of Great Britain and Ireland
Died: 1865 Dublin, United Kingdom of Great Britain and Ireland
Academic Advisor: John Brinkley

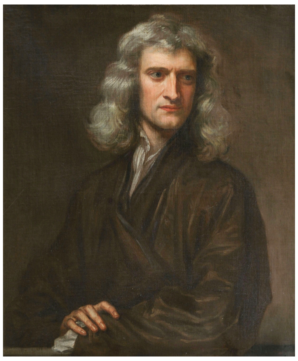

Figure 5.9. Sir **Isaac Newton** FRS[54]
Born: 1643 Woolsthorpe-by-Colsterworth, Kingdom of England
Died: 1727 Kensington, Kingdom of Great Britain
Academic Advisors: Isaac Barrow, Benjamin Pulleyn

The standard way we introduce the classical equations of motion is through the three laws of motion handed to us by Isaac Newton (Fig. 5.9) in 1687, the chief of which is the second law which states that the acceleration of a particle is proportional to the force applied

$$\ddot{x} = \frac{F}{m} \tag{5.60}$$

In this law m is a property of the particle and F an input specific to the physical system under study.

The canonical (also called Hamiltonian) point of view is to modify these equations so that they only involve first order time derivatives. We take the momentum $p = m\dot{x}$ as an independent dynamical variable and our equations of motion become

$$\dot{p} = F \tag{5.61}$$

$$\dot{x} = \frac{p}{m} \tag{5.62}$$

If the force was conservative so that,

$$F = -\frac{\mathrm{d}V}{\mathrm{d}x} \tag{5.63}$$

then we can write the equations of motion in terms of the total energy

$$H = T + V = \frac{p^2}{2m} + V(x) \tag{5.64}$$

as

$$\dot{p} = -\frac{\mathrm{d}H}{\mathrm{d}x} \tag{5.65}$$

$$\dot{x} = \frac{\mathrm{d}H}{\mathrm{d}p} \tag{5.66}$$

These are the canonical equations of motion. We have denoted the total energy by H rather than E for two reasons. First, to emphasise it must be written as a function of x and p, rather than x and $\dot{x}$. It is to be taken as a function of *phase space*, *i.e.* the space $\{x, p\}$, rather than the coordinate space $\{x\}$. Additionally, there are some fringe cases where the H that gives the correct equations of motion differs from the total energy, although we will mostly not be too concerned with these details[55]. For these reasons we not only use the

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[53] Picture by William_Rowan_Hamilton_portrait_oval.png: Unknown William_Rowan_Hamilton_portrait_oval_2.png: Unknown derivative work: Quibik (talk) - William_Rowan_Hamilton_portrait_oval.png William_Rowan_Hamilton_portrait_oval_2.png, Public Domain, https://commons.wikimedia.org/w/index.php?curid=11336587

[54] Picture by Godfrey Kneller - File:Portrait of Sir Isaac Newton, 1689.jpg from https://exhibitions.lib.cam.ac.uk/linesofthought/artifacts, Public Domain, https://commons.wikimedia.org/w/index.php?curid=132521185

[55] You can nevertheless find in depth discussions on all of this in Goldstein's book "Classical Mechanics"

letter H but call it *Hamiltonian*.

In this formalism it is even more apparent how radical is the idea that you cannot know both x and p at the same time. Without it we cannot even define the space our functions are supposed to live in. Despite this we actually need just a few extra steps to make the connection to the quantum world. The first of which is to introduce the Poisson bracket, named after Siméon Denis Poisson (Fig. 5.10). Its input are two functions on phase space, and its output is another function in phase space defined as

$$\{f, g\} = \frac{\partial f}{\partial x}\frac{\partial g}{\partial p} - \frac{\partial f}{\partial p}\frac{\partial g}{\partial x} \tag{5.67}$$

In particular, the Poisson brackets of the canonical coordinates x and p is

$$\{x, p\} = 1, \quad \{x, x\} = 0, \quad \{p, p\} = 0 \tag{5.68}$$

Crucially, it then allows us to write a generalised form of the canonical equations of motion. The time dependence of any function on phase space $f(x, p.t)$ (where we have allowed some explicit time dependence beyond the implicit time dependence through $x(t)$ and $p(t)$) is governed by

$$\frac{\mathrm{d}f}{\mathrm{d}t} = \frac{\partial f}{\partial t} + \{f, H\} \tag{5.69}$$

The Poisson bracket satisfies the following properties:

1. **Action on constant**: $\{f, a\} = 0$ for a a constant
2. **Anticommutativity**: $\{f, g\} = -\{g, f\}$
3. **Bilinearity**: $\{af + bg, h\} = a\{f, h\} + b\{g, h\}$ and $\{f, ag + bh\} = a\{f, g\} + b\{f, h\}$ for $a,\ b$ two constants
4. **Leibniz rule**: $\{fg, h\} = \{f, h\}g + f\{g, h\}$
5. **Jacobi identity**: $\{f, \{g, h\}\} + \{g, \{h, f\}\} + \{h, \{f, g\}\} = 0$

The final two properties named after the famed mathematicians Gottfried Leibniz and Carl Jacobi of two every different epochs.

Moreover, these properties, together with (5.68), *uniquely* determine the Poisson bracket. That is, if we assume the properties above and (5.68) then we can derive (5.67). You just need to show that

$$\begin{aligned}\left\{x^a p^b, x^c p^d\right\} &= ad\ x^{a+c-1}p^{b+d-1} - bc\ x^{a+c-1}p^{b+d-1} = \\ &= \frac{\partial\left(x^a p^b\right)}{\partial x}\frac{\partial\left(x^c p^d\right)}{\partial p} - \frac{\partial\left(x^a p^b\right)}{\partial p}\frac{\partial\left(x^c p^d\right)}{\partial x}\end{aligned} \tag{5.70}$$

using only properties (1)-(5) above together with (5.68). Then we can use linearity to extend the result to analytic functions.

Figure 5.10. Siméon Denis Poisson FRS FRSE[56]
Born: 1781 Pithiviers, Kingdom of France
Died: 1840 Sceaux, Kingdom of France
Academic Advisors: Joseph-Louis Lagrange, Pierre-Simon Laplace

Figure 5.11. Gottfried Wilhelm Leibniz[57]
Born: 1646 Leipzig, Holy Roman Empire of the German Nation
Died: 1716 Hanover, Holy Roman Empire of the German Nation
Doctoral Advisor: B. L. von Schwendendörffer

Figure 5.12. Jacques Simon Jacobi aka Carl Gustav Jacob Jacobi aka Carolus Gustavus Jacobus Jacobi[58]
Born: 1804 Potsdam, Holy Roman Empire of the German Nation
Died: 1851 Berlin, Kingdom of Prussia
Doctoral Advisors: Enno Dirksen

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[56] Picture by François-Séraphin Delpech / After Nicolas Eustache Maurin - `http://www.sil.si.edu/digitalcollections/hst/scientific-identity/CF/display_results.cfm?alpha_sort=Phttp://www.sil.si.edu/digitalcollections/hst/scientific-identity/fullsize/SIL14-P005-06a.jpg`, Public Domain, `https://commons.wikimedia.org/w/index.php?curid=378439`

[57] Picture by Christoph Bernhard Francke - Herzog Anton Ulrich-Museum, online, Public Domain, `https://commons.wikimedia.org/w/index.php?curid=53159699`

[58] Picture by Unknown author - `http://www.sil.si.edu/digitalcollections/hst/scientific-identity/explore.htm` (reworked), Public Domain, `https://commons.wikimedia.org/w/index.php?curid=140344`

Introducing the Poisson bracket might seem an unnecessary complication but it is just what we need to make the connection with quantum mechanics. In particular, we have now abstracted the equations of motion into an algebraic structure. In the usual formulation of the equations of motion we have to differentiate with respect to x and/or p, which is not an easy idea to apply to quantum operators. However, the algebraic point of view of Poisson brackets seems much more amenable to generalisation. Our goal will be to find a quantum analogue of the Poisson bracket.

We want this quantum Poisson bracket to obey some version of the properties (1)-(5) above, but now applied to Hermitian operators on a Hilbert space whose product isn't commutative. This simple change—allowing non-commutative observables—will necessarily imply that the quantum version of the Poisson bracket must be proportional to the commutator.

To prove this, let us calculate $\{A_1A_2, B_1B_2\}$ where A_1, A_2, B_1 and B_2 are now non-commuting Hermitian operators rather than functions on phase space. We shall calculate said Poisson bracket merely by resorting to its algebraic properties.

$$\begin{aligned}\{A_1A_2, B_1B_2\} =& \{A_1, B_1B_2\}A_2 + A_1\{A_2, B_1B_2\} = \\ =& (\{A_1, B_1\}B_2 + B_1\{A_1, B_2\})A_2 + A_1(\{A_2, B_1\}B_2 + B_1\{A_2, B_2\}) = \\ =& \{A_1, B_1\}B_2A_2 + B_1\{A_1, B_2\}A_2 + A_1\{A_2, B_2\}B_2 + A_1B_1\{A_2, B_2\}\end{aligned} \tag{5.71}$$

where in the first line we used the Leibniz rule in the first argument, and in the second line we used the Leibniz rule in the second argument. We could however do the reverse, first applying the Leibniz rule in the second argument and only then applying it in the first argument. We then get

$$\begin{aligned}\{A_1A_2, B_1B_2\} =& \{A_1A_2, B_1\}B_2 + B_1\{A_1A_2, B_2\} = \\ =& \{A_1, B_1\}A_2B_2 + A_1\{A_2, B_1\}B_2 + B_1\{A_1, B_2\}A_2 + B_1A_1\{A_2, B_2\}\end{aligned} \tag{5.72}$$

equating these two results

$$\{A_1, B_1\}(A_2B_2 - B_2A_2) = (A_1B_1 - B_1A_1)\{A_2, B_2\} \tag{5.73}$$

This would of course be completely trivial if the operators were classical functions of phase space whose product is commutative. For our non-commuting operators this is not the case. In fact, the only way it can be true for arbitrary operators A_1, A_2, B_1 and B_2 is if

$$\{A, B\} \propto AB - BA \tag{5.74}$$

Which shows that the quantum Poisson bracket must be proportional to the commutator. It is straightforward to show that the commutator obeys all of the necessary algebraic properties of a Poisson bracket.

Now we get to the whole point of this section. The canonical Poisson bracket between the position and momentum

$$\{x, p\} = 1 \tag{5.75}$$

in the quantum world must become

$$[X, P] = \text{const} \tag{5.76}$$

If this constant were 0, then we would necessarily have commuting observables and we would be back to classical mechanics. The fact that quantum mechanics involves non-commuting observables means that, in particular, X and P *must* be a non-commuting pair. What seemed like a radical departure from classical mechanics is in fact a necessary consistency condition when we apply the algebra of classical physics to non-commutative observables. There is no way out, position and momentum *cannot* commute unless all observables do so as well.

Given both X and P are Hermitian and the commutator is anti-symmetric, the constant of proportionality between Poisson brackets and commutators must be purely imaginary, and so we can write

$$[X, P] = \mathrm{i}\hbar \tag{5.77}$$

The Planck constant now appears as the constant of proportionality between the Poisson bracket and the commutator.

We can even show that this commutation relation necessarily implies the usual expression for the momentum operator in the position basis. We just need to sandwich (5.77) between two position eigenstates:

$$\langle x| [X, P] |y\rangle = \langle x| \mathrm{i}\hbar |y\rangle \tag{5.78}$$

$$\langle x| (XP - PX) |y\rangle = \mathrm{i}\hbar \langle x|y\rangle \tag{5.79}$$

$$(x - y) \langle x| P |y\rangle = \mathrm{i}\hbar\delta(x - y) \tag{5.80}$$

Using the following property of the derivative of the Dirac-δ (which can be straightforwardly proven using its definition)

$$x\frac{\mathrm{d}}{\mathrm{d}x}\delta(x) = -\delta(x) \tag{5.81}$$

we conclude

$$\langle x| P |y\rangle = -\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}x}\delta(x - y) = \mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}y}\delta(x - y) \tag{5.82}$$

Remembering (5.26) and (5.27) we can write

$$P = -\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}x} \tag{5.83}$$

exactly as intended. A more careful version of this result is known as the Stone–von Neumann theorem after Marshall H. Stone (Fig. 5.13) and John von Neumann (Fig. 5.14).

It seems as if the de Broglie relation could be derived after all. All we had to do is apply the classical Poisson bracket algebra structure to non-commutative Hermitian operators on a Hilbert space. However, we have merely shifted the burden of proof. The idea that we can apply the Poisson bracket algebra is just as unjustified as the original de Broglie relation. The main advantage of this approach is the connection with classical mechanics. From the quantum Poisson bracket logic, the Heisenberg uncertainty principle is a *consequence* of classical mechanics, rather than standing in opposition to it. Additionally, the connection between classical Poisson brackets and quantum commutators, while being quite subtle in a lot of circumstances, still provides a very useful rule of thumb when constructing physical theories.

Figure 5.13. **Marshall Harvey Stone**
Born: 1903 New York City, United States of America
Died: 1989 Madras, Republic of India
Doctoral Advisors: G. D. Birkhoff

Figure 5.14. Margittai **Neumann János Lajos** aka John von Neumann[59]
Born: 1903 Budapest, Austro-Hungarian Monarchy
Died: 1957 Washington, United States of America
Doctoral Advisor: Lipót Fejér

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[59] Picture by LANL - http://www.lanl.gov/history/atomicbomb/images/NeumannL.GIF (archive copy at the Wayback Machine), Attribution, https://commons.wikimedia.org/w/index.php?curid=3429594

Quantum Dynamics

PART

III

Chapter 6. The equations of motion
Chapter 7. The “free” particle
Chapter 8. Square potentials
Chapter 9. The harmonic oscillator

We have unravelled a lot of the structure of quantum mechanics, but so far we have only considered the stationary case. We still have yet to discuss anything regarding time dependent systems. We begin by motivating and describing the main formulations for the equations of motion of quantum mechanical systems, including the quantum version of Noether's theorem and the classical limit. Finally we will describe in detail the dynamics of the simplest 1-dimensional systems: a free particle; square potentials; and the harmonic oscillator.

6 The equations of motion

Just how we cannot really derive Newton's laws of motion there is no way to mathematically derive the equations governing the time dependence of quantum systems from first principles. Our goal in this chapter will therefore be to adequately motivate these equations so that they are at least plausible. The first key input is that time evolution should preserve probabilities, which necessarily means it must be representable by a unitary transformation. The second input is the Planck relation between the energy and frequency, which will allow us to write the equation of motion in terms of the total energy. Alternatively, we could use the connection between the Poisson bracket and the commutator discussed in Section 5.4, which gives a slightly different but mathematically equivalent formulation. Finally we will delve into the topic of symmetries and discuss how to connect with classical mechanics.

6.1 Unitary time evolution

Suppose that the system under study is represented by the ket $|\psi_0\rangle$ at time t_0. At some time $t > t_0$ we can generically expect the system to be represented by a different ket $|\psi(t)\rangle$. We shall assume that time is a continuous parameter so that

$$\lim_{t \to t_0} |\psi(t)\rangle = |\psi_0\rangle \tag{6.1}$$

Our goal is to find $|\psi(t)\rangle$.

Certainly, if $|\psi_0\rangle$ is correctly normalised, we should expect the same to be true for $|\psi(t)\rangle$, *i.e.*

$$\langle\psi_0|\psi_0\rangle = 1 = \langle\psi(t)|\psi(t)\rangle \tag{6.2}$$

Further, we do not want t_0 or any other time to be special. Said in other words, we want our theory to have a symmetry under time translations. It seems therefore at least plausible that the probability structure of our Hilbert space should not change with time, *i.e.* we want

$$|\langle\psi_0|\chi_0\rangle|^2 = |\langle\psi(t)|\chi(t)\rangle|^2 \tag{6.3}$$

Wigner's theorem then dictates that time evolution must be represented by a *linear unitary* operator $U(t, t_0)$

$$|\psi(t)\rangle = U(t, t_0)\,|\psi_0\rangle \tag{6.4}$$

such that

$$U(t,t_0)^\dagger U(t,t_0) = \mathbb{1} \tag{6.5}$$

$$U(t,t_0)(a\,|\psi_0\rangle + b\,|\chi_0\rangle) = a\,|\psi(t)\rangle + b\,|\chi(t)\rangle \tag{6.6}$$

This is of course an assumption. We are assuming that time translations acts linearly and unitarily. Like any assumptions in physical theories they must be tested against experiment and discarded if proven wrong. Testing these particular assumptions directly is quite tricky, however, one example will be given much later in Chapter 14, where we will see how linearity is intimately connected to locality. Any non-linear time evolution would almost certainly lead to non-local phenomena, which, as of yet, has not been observed. If we assume linearity then (6.2) is sufficient to ensure said linear operator is unitary.

The final property we wish to impose is *composition*. Imagine we had three time instances $t_0 < t_1 < t_2$. It seems perfectly reasonable that evolving from t_0 to t_1 and then from t_1 to t_2 should be the same as evolving directly from t_0 to t_2. In equations this reads,

$$U(t_2,t_0) = U(t_2,t_1)U(t_1,t_0) \tag{6.7}$$

This property together with the initial condition (6.1) gives us

$$U(t,t) = \mathbb{1} \tag{6.8}$$

for any t. These two properties, together with the invertibility of $U(t,t_0)$ ensure that time translations are a *group*. But worry not, we shall not require any knowledge of group theory for the remainder of this text.

At last we can exploit the fact time is a continuous parameter to consider $t = t_0 + \mathrm{d}t$ where $\mathrm{d}t$ is infinitesimal, and write

$$U(t,t_0) = \mathbb{1} - \mathrm{i}\mathit{\Omega}(t_0)\,\mathrm{d}t + O(\mathrm{d}t^2) \tag{6.9}$$

Checking (6.8) is trivial, having both arguments identical is the same as setting $\mathrm{d}t = 0$. We can also easily check (6.7):

$$\begin{aligned}
&U(t_0 + \mathrm{d}t_1 + \mathrm{d}t_2\,, t_0 + \mathrm{d}t_1)U(t_0 + \mathrm{d}t_1\,, t_0) = \\
=&(\mathbb{1} - \mathrm{i}\mathit{\Omega}(t_0 + \mathrm{d}t_1)\,\mathrm{d}t_2)(\mathbb{1} - \mathrm{i}\mathit{\Omega}(t_0)\,\mathrm{d}t_1) + O\big(\mathrm{d}t_1{}^2\,, \mathrm{d}t_2{}^2\,, \mathrm{d}t_1\,\mathrm{d}t_2\big) = \\
=&\mathbb{1} - \mathrm{i}\mathit{\Omega}(t_0)(\mathrm{d}t_1 + \mathrm{d}t_2) + O\big(\mathrm{d}t_1{}^2\,, \mathrm{d}t_2{}^2\,, \mathrm{d}t_1\,\mathrm{d}t_2\big) = \\
=&U(t_0 + \mathrm{d}t_1 + \mathrm{d}t_2\,, t_0)
\end{aligned} \tag{6.10}$$

where in going to the third line we have used the fact that $\mathit{\Omega}(t_0 + \mathrm{d}t_1) = \mathit{\Omega}(t_0) + O(\mathrm{d}t_1)$.

Unitarity on the other hand is not satisfied automatically up to $O(\mathrm{d}t^2)$, instead it will impose some restrictions on $\mathit{\Omega}$. In particular, imposing unitary yields

$$\begin{aligned}
\mathbb{1} &= U(t,t_0)^\dagger U(t,t_0) = (\mathbb{1} - \mathrm{i}\mathit{\Omega}(t_0)\,\mathrm{d}t)^\dagger(\mathbb{1} - \mathrm{i}\mathit{\Omega}(t_0)\,\mathrm{d}t) + O(\mathrm{d}t^2) \\
\mathbb{1} &= \mathbb{1} - \mathrm{i}(\mathit{\Omega}(t_0) - \mathit{\Omega}(t_0)^\dagger)\,\mathrm{d}t + O(\mathrm{d}t^2)
\end{aligned} \tag{6.11}$$

and therefore

$$\mathit{\Omega}(t_0) = \mathit{\Omega}(t_0)^\dagger \tag{6.12}$$

This means that the operator $\mathit{\Omega}$ *must* be Hermitian.

Putting this all together allows us to write a differential equation for $U(t,t_0)$.

$$U(t+\mathrm{d}t\,,t_0)=U(t+\mathrm{d}t\,,t)U(t,t_0)=(\mathbb{1}-\mathrm{i}\Omega(t)\,\mathrm{d}t)U(t,t_0) \tag{6.13}$$

where in the first equality we used the composition property, and in the second we used the fact that $\mathrm{d}t$ is infinitesimal. We can then write

$$U(t+\mathrm{d}t\,,t_0)-U(t,t_0)=-\mathrm{i}\Omega(t)\,\mathrm{d}t\,U(t,t_0) \implies \mathrm{i}\frac{\partial}{\partial t}U(t,t_0)=\Omega(t)U(t,t_0) \tag{6.14}$$

This is sometimes called the Schrodinger equation for the time evolution operator.

We cannot really solve this differential equation without explicit knowledge of $\Omega(t)$, but can still go over a few distinct cases.

Ω is time independent In this case the solution to (6.14) is given by

$$U(t,t_0)=\exp(-\mathrm{i}\Omega(t-t_0)) \tag{6.15}$$

where the exponential of an operator is defined by its Taylor series

$$\exp A\equiv\sum_{n=0}^{\infty}\frac{A^n}{n!} \tag{6.16}$$

It is straightforward to check (6.15) satisfies (6.14) by differentiating the Taylor series term by term. Alternatively, we can use the composition property repeatedly to write

$$U(t,t_0)=\lim_{N\to\infty}\left(\mathbb{1}-\mathrm{i}\Omega\frac{t-t_0}{N}\right)^N=\exp(-\mathrm{i}\Omega(t-t_0)) \tag{6.17}$$

Ω is time dependent and the $\Omega(t)$ at different times commute This case is very similar to the above. The solution is simply

$$U(t,t_0)=\exp\left(-\mathrm{i}\int_{t_0}^{t}\mathrm{d}t'\,\Omega(t')\right) \tag{6.18}$$

Just replace $\Omega(t-t_0)$ with $\int_{t_0}^{t}\mathrm{d}t'\,\Omega(t')$ into the Taylor series of the exponential to verify the validity of this solution.

Ω is time dependent,but the $\Omega(t)$ at different times don't commute This case is the most complicated out of the previous ones. Although we will not need this solution in this volume we present it for completeness' sake

$$U(t,t_0)=\mathbb{1}+\sum_{n=1}^{\infty}(-\mathrm{i})^n\int_{t_0}^{t}\mathrm{d}t_1\int_{t_0}^{t_1}\mathrm{d}t_2\cdots\int_{t_0}^{t_{n-1}}\mathrm{d}t_n\,\Omega(t_1)\Omega(t_2)\cdots\Omega(t_n) \tag{6.19}$$

This expression is called the *Dyson series* after Freeman Dyson (Fig. 6.1), who first used it in the context of time-dependent perturbation theory. The crux is that the limits of integration ensure the Ω are *time-ordered*, such that the earlier times are on the right.

Figure 6.1. **Freeman John Dyson** FRS[60]
Born: 1923 Crowthorne, United Kingdom of Great Britain and Ireland
Died: 2020 Plainsboro Township, United States of America
Academic Advisor: Hans Bethe

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[60] Picture by ioerror - Flickr, CC BY-SA 2.0, https://commons.wikimedia.org/w/index.php?curid=71877726

Taking the derivative yields

$$\begin{aligned}\frac{\partial}{\partial t}U(t,t_0) &= \sum_{n=1}^{\infty}(-\mathrm{i})^n \int_{t_0}^{t}\mathrm{d}t_2\cdots\int_{t_0}^{t_{n-1}}\mathrm{d}t_n\,\Omega(t)\Omega(t_2)\cdots\Omega(t_n) = \\ &= -\mathrm{i}\Omega(t)\left(\mathbb{1}+\sum_{n=2}^{\infty}(-\mathrm{i})^{n-1}\int_{t_0}^{t}\mathrm{d}t_2\cdots\int_{t_0}^{t_{n-1}}\mathrm{d}t_n\,\Omega(t_2)\cdots\Omega(t_n)\right) = \\ &= -\mathrm{i}\Omega(t)U(t,t_0) \end{aligned} \tag{6.20}$$

precisely as desired, and without having to pass any Ω through each other.

6.2 The Hamiltonian

In order to actually determine the time evolution of quantum systems we need an independent way to set Ω. However, there are two ways to do so: the wave mechanics of Schrodinger, and the matrix mechanics of Heisenberg. The former is the active point of view where the unitary time evolution acts on the kets leaving the operators unchanged. The latter is the passive point of view where the states are fixed, and the observables evolve with time.

Of course the two points of view must ultimately give the same answers. But, as is usual in physics, even if the answers are the same, our work in obtaining said answers is certainly not the same. To emphasise the equal merit of the two approaches this section is written a bit differently, the parts of it can be read in any order, and I encourage you to leave up to chance. Just beware that the Heisenberg picture will rely on the ideas of Section 5.4 so if you skipped that section you should read the Schrodinger picture first. If you don't want to leave it to chance you can use the following table to pick a favourite:

Schrodinger Picture	**Heisenberg Picture**
Time-dependent states	Time-dependent observables
Published 1926	Published 1925
Newton-like	Hamilton-like
Paedophile	Nazi collaborator

In practical calculations we should always use whatever picture is most convenient for the problem at hand. To avoid confusion it is customary to use subscript 'S' for kets and operators in the Schrodinger picture and subscript 'H' for kets and operators in the Heisenberg picture. Whenever there is little chance for confusion we will omit those subscripts to avoid clutter.

Schrodinger picture We begin by converting (6.14) into a differential equation in terms of the time-dependent states, rather than the unitary operator directly. Using the definition

$$|\psi(t)\rangle = U(t,t_0) \tag{6.21}$$

together with (6.14) we find

$$\mathrm{i}\frac{\mathrm{d}\,|\psi(t)\rangle}{\mathrm{d}t} = \mathrm{i}\frac{\partial U(t,t_0)}{\partial t}\,|\psi_0\rangle = \Omega(t)U(t,t_0)\,|\psi_0\rangle = \Omega(t)\,|\psi(t)\rangle \tag{6.22}$$

To make it easier let us consider time-independent Ω. In that case, and because Ω is Hermitian we can find an orthogonal basis of eigenvectors $\{|\omega_i\rangle\}$. Expanding our initial state $|\psi_0\rangle$ in this basis

$$|\psi_0\rangle = \sum_i c_i\,|\omega_i\rangle \tag{6.23}$$

we can easily find the solution to (6.22) by directly applying (6.15):

$$\begin{aligned}|\psi(t)\rangle &= \mathrm{e}^{-\mathrm{i}\Omega(t-t_0)}\sum_i c_i\,|\omega_i\rangle = \\ &= \sum_i c_i\mathrm{e}^{-\mathrm{i}\Omega(t-t_0)}\,|\omega_i\rangle = \\ &= \sum_i c_i\mathrm{e}^{-\mathrm{i}\omega_i(t-t_0)}\,|\omega_i\rangle \end{aligned} \tag{6.24}$$

Every term in this sum gains a phase which oscillates at a specific angular frequency ω_i. The individual eigenkets are just multiplied by a phase which does not affect the physical state, but superpositions of these eigenkets physically change as the balance between the the different terms is affected.

Crucially, this expansion allows us to interpret the operator Ω as a *frequency operator*. Telling us about the oscillation in time of our physical state. Now we can recover Planck's relation all the way from Chapter 1 that connects frequency to the energy of radiation. Generalising we therefore postulate that the operator Ω is proportional to the Hamiltonian

$$\hbar\Omega = H \tag{6.25}$$

This was the first quantum mechanical equation to be discovered. Now it appears as a fundamental postulate dictating the time evolution of physical systems. Just like the de Broglie relation between momentum and wavenumber it cannot be derived. It is a postulate which requires experimental verification. This time the work has already been done, Planck's success in describing black body radiation and Einstein's success with the photoelectric effect are both direct verifications of this formula.

In terms of the Hamiltonian we can write the differential equation for the time dependence of states in a more familiar form

$$\mathrm{i}\hbar\frac{\mathrm{d}\,|\psi(t)\rangle}{\mathrm{d}t} = H\,|\psi(t)\rangle \tag{6.26}$$

This is the *Schrodinger equation* and is one of the cornerstones of quantum mechanics.

You may find it odd that we call it "Hamiltonian" rather than just "energy", this is for two main reasons. Firstly, as detailed in Section 5.4, the classical Hamiltonian is written as a function of x and p rather than x and $\dot{x}$, the former makes more sense in the quantum world and that is a point worth emphasising. Secondly, when the Hamiltonian depends on time, energy will not be conserved and is in fact not necessarily very well defined, but the Hamiltonian will still dictate the time dependence of the system. We will therefore mostly reserve the word "energy" for the eigenvalues of H, but bear in mind this isn't a strict definition.

Some of you might be skeptical we have done very much at all. We didn't know what Ω was, but we don't necessarily have a way of knowing what H is, they're merely written in different units. And while this is true, and in general we can only fix H through experiment, this interpretation is still helpful. Firstly, there is an interpretative power in saying that the total energy of a system is what dictates its time evolution, that interpretation on its own is valuable. Secondly, it allows us to easily make good educated guesses for H. In particular, if the system has a classical limit, it's a good idea to try the classical Hamiltonian but with x and p promoted to the operators X and P. This will of course not work for systems without a clear classical analogue. For example, for a single particle subjected to a potential, we can guess that

$$H = \frac{P^2}{2m} + V(X) \tag{6.27}$$

which yields the following Schrodinger equation in the position basis

$$\mathrm{i}\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x)\psi(x,t) \tag{6.28}$$

which is the original (and most famous) version of the Schrodinger equation. Most of this volume will be concerned with solving ever more complicated examples of this equation.

A particular advantage of the Schrodinger equation is that it is a partial differential equation with wave-like solutions[61]. The tools needed to solve this type of equations are not too distinct from the tools used in classical wave mechanics. Hence why this picture of quantum mechanics is often called *wave mechanics*. Nevertheless, this formulation sometimes can hide some of the algebraic structure of the Hilbert space under functional analysis and it might not be the most appropriate tool in some specific circumstances.

In most practical applications however, we rarely solve (6.26) or (6.28) directly. If the Hamiltonian is time independent it is much more fruitful to first use its Hermiticity to find the basis provided by its eigenvectors. The equation we then want to solve is

$$H\left|E_n\right\rangle = E_n\left|E_n\right\rangle \tag{6.29}$$

or in position basis

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi_n(x)}{\mathrm{d}x^2} + V(x)\psi_n(x) = E_n\psi_n(x) \tag{6.30}$$

These are known as the *time-independent Schrodinger equation*, or TISE for short. After we have solve either of them and have found the eigenvectors and corresponding eigenvalues it is easy to determine the time variation of any state, it is simply given by

$$\left|\psi(t)\right\rangle = \sum_n c_n \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}E_n(t-t_0)}\left|E_n\right\rangle \tag{6.31}$$

where the c_n are the coefficients of the initial state in the energy basis

$$c_n = \left\langle E_n | \psi_0 \right\rangle \tag{6.32}$$

Heisenberg picture We begin by converting (6.14) into a differential equation in terms of the time-dependent observables, rather than the unitary operator directly. Recalling the action of a unitary operator on a state (4.75) we define

$$O(t) = U(t,t_0)^\dagger O_0 U(t,t_0) \tag{6.33}$$

together with (6.14) we find

$$\begin{aligned}\frac{\mathrm{d}O(t)}{\mathrm{d}t} &= \frac{\partial U(t,t_0)^\dagger}{\partial t} O_0 U(t,t_0) + U(t,t_0)^\dagger O_0 \frac{\partial U(t,t_0)}{\partial t} = \\ &= (-\mathrm{i}\Omega U(t,t_0))^\dagger O_0 U(t,t_0) + U(t,t_0)^\dagger O_0 (-\mathrm{i}\Omega U(t,t_0)) = \\ &= \mathrm{i}\big(U(t,t_0)^\dagger \Omega O_0 U(t,t_0) - U(t,t_0)^\dagger O_0 \Omega U(t,t_0)\big)\end{aligned} \tag{6.34}$$

---

[61] Despite being first-order in time derivatives the factor of i means that it behaves more like a hyperbolic PDE rather than a parabolic PDE like the heat equation

where in going to the last line we used the fact that Ω is Hermitian. Now we use the fact U is unitary to insert two factors of $\mathbb{1} = UU^\dagger$ (and omitting the argument of U for ease of notation)

$$\begin{aligned} \mathrm{i}\frac{\mathrm{d}O(t)}{\mathrm{d}t} &= U^\dagger O_0 U U^\dagger \Omega U - U^\dagger \Omega U U^\dagger O_0 U = \\ &= O(t) U^\dagger \Omega U - U^\dagger \Omega U O(t) \end{aligned} \tag{6.35}$$

where in the last line we have used the definition of $O(t)$. For simplicity, let us assume that Ω is time independent, in which case U and Ω commute and we can write $U^\dagger \Omega U = \Omega$. All in all, we get

$$\mathrm{i}\frac{\mathrm{d}O(t)}{\mathrm{d}t} = O(t)\Omega - \Omega O(t) = [O(t), \Omega] \tag{6.36}$$

This expression is very reminiscent of (5.69), the only difference is that we have not included an explicit time dependence in O. Applying the correspondence between Poisson brackets and commutators postulated in (5.77) gives us

$$\mathrm{i}\hbar\frac{\mathrm{d}O(t)}{\mathrm{d}t} = [O(t), H] \tag{6.37}$$

This is the *Heisenberg equation of motion*, and comparing with the above we find

$$\hbar\Omega = H \tag{6.38}$$

which is just like the Planck relation all the way from Chapter 1.

The Heisenberg equation of motion is quite tricky to solve because Hermitian operators are not particularly convenient objects to manipulate in practice. In particular, it is often not very clear what initial conditions we should impose. The fact these operators can be represented as matrices is why this picture of quantum dynamics is often called *matrix mechanics*[62] However, its resemblance with the classical equations of motion and its algebraic nature sometimes allows for slick tricks that can solve specific systems in a particularly efficient way. This will be the case for the simple harmonic oscillator as we will see in Chapter 9.

For example, consider a single particle subjected to a potential $V(x)$. The Hamiltonian for this system is

$$H = \frac{P^2}{2m} + V(X) \tag{6.39}$$

Now let us determine the equations of motion for X and P. First for the position

$$\frac{\mathrm{d}X}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar}[X, H] = -\frac{\mathrm{i}}{2\hbar m}\left[X, P^2\right] = -\frac{\mathrm{i}}{2\hbar m}(P[X,P] + [X,P]P) = \frac{P}{m} \tag{6.40}$$

where we have used the canonical commutator $[X, P] = \mathrm{i}\hbar$. Now for the momentum we have

$$\frac{\mathrm{d}P}{\mathrm{d}t} = -\frac{\mathrm{i}}{\hbar}[P, H] = -\frac{\mathrm{i}}{\hbar}[P, V(X)] \tag{6.41}$$

---

[62] In fact Heisenberg had never heard of matrices when he wrote his equation! He instead did it the other way around deriving matrix multiplication from quantum mechanics.

to calculate this last commutator it is easier to go to the position basis

$$\begin{aligned}[P, V(X)]\psi(x) &= -\mathrm{i}\hbar\frac{\mathrm{d}}{\mathrm{d}x}(V(x)\psi(x)) - V(x)\left(-\mathrm{i}\hbar\frac{\mathrm{d}\psi(x)}{\mathrm{d}x}\right) = \\ &= -\mathrm{i}\hbar V'(x)\psi(x) - \mathrm{i}\hbar V(x)\psi'(x) + \mathrm{i}\hbar V(x)\psi'(x) = \\ &= -\mathrm{i}\hbar V'(x)\psi(x) \end{aligned} \tag{6.42}$$

Putting everything together we get

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \frac{P}{m} \tag{6.43}$$

$$\frac{\mathrm{d}P}{\mathrm{d}t} = -V'(X) \tag{6.44}$$

which are just the classical equations of motion! Albeit in terms of operators rather than functions in phase space.

This result is only valid in the Heisenberg picture, but if we take expectation values then it must hold in either picture.

$$\frac{\mathrm{d}\langle X\rangle}{\mathrm{d}t} = \frac{\langle P\rangle}{m} \tag{6.45}$$

$$\frac{\mathrm{d}\langle P\rangle}{\mathrm{d}t} = -\langle V'(X)\rangle \tag{6.46}$$

This result is known as Ehrenfest's theorem after Paul Ehrenfest (Fig. 6.2). Note how easy it was to prove this in the Heisenberg picture, in the Schrodinger picture this would have been far more complicated. Also, you must be careful, to write $\langle V'(X)\rangle$ rather than $V'(\langle X\rangle)$ as these two are not generically identical.

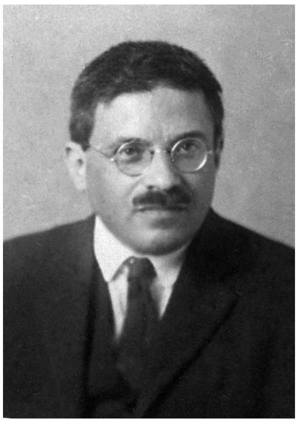

Figure 6.2. **Paul Ehrenfest**[63]
Born: 1880 Vienna, Austro-Hungarian Monarchy
Died: 1933 Amsterdam, Kingdom of the Netherlands
Doctoral Advisor: Ludwig Boltzmann

6.3 Symmetries and conservation laws

Both symmetries and conservations laws have always been fundamental tools in tackling any problem in Physics. But they gained special importance in 1918 when Emmy Noether (Fig. 6.3) proved her eponymous theorem. This theorem demonstrated that any continuous symmetry necessarily has an associated conservation law. Symmetry under spatial translations is what gives us conservation of linear momentum, rotational symmetry corresponds to angular momentum conservation, and time translations to conservation of energy, just to name a few. Her theorem originally was only valid for classical mechanics but it can be generalised also to quantum mechanics, and even better, the proof is actually simpler in quantum mechanics!

Let us begin by clarifying what do we mean when we say "symmetry". The idea is to have some map between the kets in our Hilbert space

$$|\psi\rangle \rightarrow |\psi'\rangle \tag{6.47}$$

such that the physics before and after the transformation are in some sense the same. There are a few key properties we demand of these transformations to ensure this.

Figure 6.3. **Amalie Emmy Noether**[64]
Born: 1882 Erlangen, German Empire
Died: 1935 Bryn Mawr, United States of America
Doctoral Advisor: Paul Gordan

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[63] Picture by Unknown author - Portraits from the Dibner Library of the History of Science and Technology (reworked), Public Domain, https://commons.wikimedia.org/w/index.php?curid=140762

[64] Picture by Unknown author Publisher: Mathematical Association of America [3], Brooklyn Museum [4], Agnes Scott College [5], [6] - Emmy Noether (1882-1935), Archived, Public Domain, https://commons.wikimedia.org/w/index.php?curid=158126186

Firstly, we impose that the transition probabilities are invariant:

$$|\langle\chi|\psi\rangle|^2 = |\langle\chi'|\psi'\rangle|^2 \tag{6.48}$$

Wigner's theorem then guarantees that it can be represented by a linear and unitary operator or by an anti-linear and anti-unitary one. The latter case always involves a reversal of the temporal direction so we will not discuss it for the time being. Therefore, our prospective symmetry transformation will be a linear and unitary operator:

$$|\psi'\rangle = U\,|\psi\rangle \tag{6.49}$$

Or alternatively, in the passive point of view, the kets are left invariant and the operators transform as

$$A \to A' = U^\dagger A U \tag{6.50}$$

Additionally, if this is to truly help us solve the Schrodinger equation, this symmetry transformation shouldn't interfere with our time evolution. In particular, applying U then evolving in time, then reversing with $U^\dagger$, should be the same as just evolving in time once:[65]

$$U(t,t_0)\,|\psi(t)\rangle = U^\dagger U(t,t_0)U\,|\psi_0\rangle \Longleftrightarrow UU(t,t_0)\,|\psi_0\rangle = U(t,t_0)U\,|\psi_0\rangle \tag{6.51}$$

Taking derivatives and recalling the Schrodinger equation then gives us

$$[U,H] = 0 \tag{6.52}$$

We conclude that the unitary operator that represents a symmetry must commute with the Hamiltonian.

In the passive picture, where the kets are left unchanged and the operators change as

$$A \to A' = U^\dagger A U \tag{6.53}$$

the condition (6.52) becomes

$$H' = U^\dagger H U = H \tag{6.54}$$

i.e. the Hamiltonian must be invariant under the symmetry transformation.

This is already quite a powerful result, even before specializing to the case of continuous symmetries. The spectral theorem applies to all normal operators, which includes both Hermitian operators like H and unitary operators like U. The condition that they commute then ensures we can simultaneously diagonalise both H and U. Even without a conservation law it is frequently quite useful to first diagonalise U and only then try to diagonalise H.

> **Example.** The parity transformation is defined as the map $\mathsf{P} : \boldsymbol{x} \to -\boldsymbol{x}$. In the quantum mechanical setup, we shall then define the parity transformation by its action on the position operator
>
> $$\mathsf{P}^\dagger X\ \mathsf{P} = -X \tag{6.55}$$
>
> Given the commutator between X and P is a number we can write the transformation of the momentum as
>
> $$\mathsf{P}^\dagger P\ \mathsf{P} = -P \tag{6.56}$$

---

[65] Apologies for the confusion between the symmetry operator U and the time evolution operator $U(t,t_0)$, this is the only equation with both quantities.

and therefore, parity is a symmetry of the Hamiltonian

$$H = \frac{P^2}{2m} + V(X) \tag{6.57}$$

if the potential is a symmetric function, *i.e.* $V(X) = V(-X)$.
Now let us find its eigenvectors. The action of parity on a wavefunction is simply

$$\mathsf{P}\psi(x) = \psi(-x) \tag{6.58}$$

Assuming that $\psi(x)$ is an eigenstate of P with eigenvalue η and using the fact $\mathsf{P}^2 = \mathbb{1}$ we get

$$\psi(x) = \mathsf{P}^2\psi(x) = \eta^2\psi(x) \tag{6.59}$$

and therefore $\eta = \pm 1$ are the only allowed eigenvalues of P.
We can then conclude that the wavefunctions corresponding to eigenvalues of H can be constructed to be either even or odd functions of x:

$$\mathsf{P}\psi(x) = \psi(-x) = \pm\psi(x) \tag{6.60}$$

As with the classical version of Noether's theorem, it is *continuous* symmetries specifically that have an associated conserved quantity. For those cases we can write

$$U(\epsilon) = \mathbb{1} - \mathrm{i}\epsilon Q + O\big(\epsilon^2\big) \tag{6.61}$$

where Q is some ϵ-independent operator. Applying the same reasoning we applied for the time evolution operator in (6.11) we conclude that

$$Q^\dagger = Q \tag{6.62}$$

The operator Q that generates infinitesimal symmetries is Hermitian, which means it is a physical observer and a good candidate for our conserved quantity.

If we take $\epsilon = \theta/N$ for some finite θ which is N independent and N an integer and then apply the transformation N times we find

$$U(\theta) = U(\theta/N)^N = \left(\mathbb{1} - \mathrm{i}\frac{\theta}{N}Q\right)^N \xrightarrow{N\to\infty} \mathrm{e}^{-\mathrm{i}\theta Q} \tag{6.63}$$

Where in taking the limit we used the definition of the exponential. This is perfectly analogous to (6.15). In particular, we see that Q generates the whole symmetry, not just the infinitesimal limit[66].

Using the passive point of view, combining (6.53) and (6.63) for small θ we find:

$$A' = U^\dagger A U = \mathrm{e}^{\mathrm{i}\theta Q} A \mathrm{e}^{-\mathrm{i}\theta Q} \approx A + \mathrm{i}\theta[Q, A] + O\big(\theta^2\big) \tag{6.64}$$

Therefore, the action of the infinitesimal symmetry on an operator corresponds to the commutator with the symmetry generator. Which, once again is precisely the same result as we saw in the Heisenberg picture for time translations.

To get Noether's theorem we just have to apply this expression to the Hamiltonian.

$$H = U^\dagger H U \implies [Q, H] = 0 \tag{6.65}$$

---

[66] If the symmetry transformation depended on several continuous parameters then the situation would be more complicated and would require the machinery of Lie groups and algebras, which is beyond the scope of this text.

so the symmetry generator must also commute with the Hamiltonian.

Applying the Heisenberg equation of motion we therefore conclude that, in the Heisenberg picture,

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = 0 \tag{6.66}$$

which is our conservation law. Taking expectation values we can write a result that is also valid in the Schrodinger picture

$$\frac{\mathrm{d}\left\langle Q\right\rangle}{\mathrm{d}t} = 0 \tag{6.67}$$

In quantum mechanics the relation between symmetries and conserved quantities is even closer than in classical physics. The infinitesimal symmetry operator, *i.e.* the symmetry *generator*, is itself a conserved quantity. We very often call Q a conserved *charge*, in analogy with electrical charge conservation, even in the general case.

As an almost trivial example, if the Hamiltonian is time independent then it commutes with itself. Also, it is the Hamiltonian that generates time translations. Therefore invariance under time translations implies conservation of the Hamiltonian, *i.e.* energy.

Additionally, because the conserved charge Q is Hermitian and commutes with the Hamiltonian, we can simultaneously diagonalise them. This means that we can restrict our analysis to energy eigenstates which have well defined values for the conserved charge. In practice finding eigenstates of Q first is often much easier than trying to diagonalise H right away.

> **Example.** Let us take spatial translations as an example of a continuous symmetry. Classically the translation operation would correspond to $U : x \to x + a$ where a is some continuous parameter. In quantum mechanics we therefore define:
>
> $$U(a)^\dagger X\ U(a) = X + a \tag{6.68}$$
>
> Taking a to be small and using (6.64) we find
>
> $$\mathrm{i}a[Q, X] = a \implies [X, Q] = \mathrm{i} \tag{6.69}$$
>
> which means that the conserved charge associated with translations is just the linear momentum P, up to a factor of $\hbar$. This is exactly the same result as can be found from classical mechanics and lends further weight to the validity of our definition of the operator P. In terms of a wavefunction we then have
>
> $$\psi(x + a) = \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}Pa}\psi(x) = \mathrm{e}^{a\frac{\mathrm{d}}{\mathrm{d}x}}\psi(x) \tag{6.70}$$

There is one final conservation law worth discussing which doesn't come directly from Noether's theorem: conservation of probability. This is a consequence of the unitarity of the time evolution operator, and, while important, may seem a bit trivial. If our initial ket is appropriately normalised the evolved ket will also be. However, in the position basis we can actually write down a *local* version of this conservation of probability, and that one is quite useful.

In the position basis, the total normalisation of the wavefunction is given by

$$1 = \int \mathrm{d}x\, |\psi(x, t)|^2 \tag{6.71}$$

Just be looking at this integral it is very intuitive to define the local probability *density* as

$$\rho(x, t) = |\psi(x, t)|^2 \tag{6.72}$$

Although its integral over all of space is constant in time, this local probability density isn't. However, its time derivative is simple to compute using the Schrodinger equation

$$\begin{aligned}\frac{\partial\rho(x,t)}{\partial t} =&\frac{\partial\psi^*(x,t)}{\partial t}\psi(x,t)+\psi^*(x,t)\frac{\partial\psi(x,t)}{\partial t} =\\ =&-\frac{\mathrm{i}}{\hbar}\Bigg(\frac{\hbar^2}{2m}\frac{\partial^2\psi^*(x,t)}{\partial x^2}\psi(x,t)-V(x)|\psi(x,t)|^2-\\ &-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2}\psi^*(x,t)+V(x)|\psi(x,t)|^2\Bigg) =\\ =&\frac{\mathrm{i}\hbar}{2m}\frac{\partial}{\partial x}\left(\psi^*(x,t)\frac{\partial\psi(x,t)}{\partial x}-\frac{\partial\psi^*(x,t)}{\partial x}\psi(x,t)\right) =\\ =&-\frac{\hbar}{m}\frac{\partial}{\partial x}\operatorname{Im}\left(\psi^*(x,t)\frac{\partial\psi(x,t)}{\partial x}\right)\end{aligned} \tag{6.73}$$

Defining the *probability current* as

$$j(x,t)=\frac{\hbar}{m}\operatorname{Im}\left(\psi^*(x,t)\frac{\partial\psi(x,t)}{\partial x}\right) \tag{6.74}$$

we can write the *continuity equatioon*

$$\frac{\partial\rho}{\partial t}+\frac{\partial j}{\partial x}=0 \tag{6.75}$$

This is an equation giving us a *local* conservation of probability.

The name "continuity equation" and "probability current" make a bit more sense if we go to 3-dim notation, where we define

$$\boldsymbol{j}(\boldsymbol{x},t)=\frac{\hbar}{m}\operatorname{Im}\left(\psi^*(\boldsymbol{x},t)\boldsymbol{\nabla}\psi(\boldsymbol{x},t)\right) \tag{6.76}$$

and the local conservation of probability becomes

$$\frac{\partial\rho}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{j}=0 \tag{6.77}$$

Now it looks just like the usual continuity equation like the ones dictating the conservation of mass in a fluid or electric charge. The current j can then be interpreted as the *probability flow* and is a very useful concept to have in mind. This can also be seen by integrating the probability current over all of space

$$\begin{aligned}\int \mathrm{d}x\, j(x,t) =& -\frac{\mathrm{i}\hbar}{2m}\int \mathrm{d}x\left(\psi^*(x,t)\frac{\partial\psi(x,t)}{\partial x}-\frac{\partial\psi^*(x,t)}{\partial x}\psi(x,t)\right)-\\ =& -\frac{\mathrm{i}\hbar}{m}\int \mathrm{d}x\,\psi^*(x,t)\frac{\partial\psi(x,t)}{\partial x}=\frac{\langle P\rangle}{m}\end{aligned} \tag{6.78}$$

Therefore the integral of the probability current gives a sort of "average velocity" of our particle.

6.4 * The classical limit

Before we move on toward finding the dynamics of specific quantum systems, we should address the thorny matter of recovering classical physics. That question has two parts, the first and most complicated one being recovering definite answers to all observables from a probabilistic Hilbert space. That question is quite hard, and considered by some to not be wholly settled. We therefore defer dealing with it until Chapters 14 and 15. The second part of recovering classical mechanics is much simpler and will be the focus of this section: how do we recover Newton's laws from the Schrodinger equation?

We begin by expressing the wavefunction in terms of its amplitude and phase

$$\psi(x,t) = \sqrt{\rho(x,t)}\mathrm{e}^{\mathrm{i}\frac{S(x,t)}{\hbar}} \tag{6.79}$$

where $\rho = |\psi|^2$ is the probability density defined above, and $S(x,t)$ is some real function of the position and time. We have included a factor of $\hbar$ in the exponential for future convenience.

We have a good interpretation for the mod of the wavefunction, but what about its phase? We just need to plug our ansatz (6.79) into the definition of the probability current (6.74).

$$\begin{aligned}\psi^* \frac{\partial \psi}{\partial x} &= \sqrt{\rho}\mathrm{e}^{-\mathrm{i}\frac{S}{\hbar}} \left(\frac{\partial \sqrt{\rho}}{\partial x} + \frac{\mathrm{i}}{\hbar}\sqrt{\rho}\frac{\partial S}{\partial x} \right) \mathrm{e}^{\mathrm{i}\frac{S}{\hbar}} \\ &= \sqrt{\rho}\frac{\partial \sqrt{\rho}}{\partial x} + \frac{\mathrm{i}}{\hbar}\rho\frac{\partial S}{\partial x}\end{aligned} \tag{6.80}$$

and therefore

$$j = \frac{\hbar}{m}\,\mathrm{Im}\left(\psi^* \frac{\partial \psi}{\partial x}\right) = \frac{\rho}{m}\frac{\partial S}{\partial x} \tag{6.81}$$

If the integral over all of space of j was some notion of “average velocity”, we could tentatively claim that j (like in a fluid) is the probability density times some local velocity. The derivative of the phase seems to represent a sort of “local velocity”. Remember, however, that you cannot know the position and velocity of a particle at the same time. So take this interpretation with a grain of salt.

Nevertheless, we can use our new form of j to write the continuity equation in terms of ρ and S:

$$\frac{\partial \rho}{\partial t} + \frac{1}{m}\frac{\partial \rho}{\partial x}\frac{\partial S}{\partial x} + \frac{\rho}{m}\frac{\partial^2 S}{\partial x^2} = 0 \tag{6.82}$$

this will come in handy shortly.

Now we plug in our ansatz (6.79) into the Schrodinger equation (6.28) to obtain

$$\begin{aligned}&-\frac{\hbar^2}{2m}\left(\frac{\partial^2 \sqrt{\rho}}{\partial x^2} + \frac{2\mathrm{i}}{\hbar}\frac{\partial \sqrt{\rho}}{\partial x}\frac{\partial S}{\partial x} + \frac{\mathrm{i}}{\hbar}\sqrt{\rho}\frac{\partial^2 S}{\partial x^2} - \frac{\sqrt{\rho}}{\hbar^2}\left(\frac{\partial S}{\partial x}\right)^2 \right) + V(x)\sqrt{\rho} = \\ &= \mathrm{i}\hbar\left(\frac{\partial \sqrt{\rho}}{\partial t} + \frac{\mathrm{i}\sqrt{\rho}}{\hbar}\frac{\partial S}{\partial t} \right)\end{aligned} \tag{6.83}$$

Now we expand the derivatives of $\sqrt{\rho}$ on the second and third terms of the LHS and on the first term of the RHS to notice they form exactly the continuity equation as written in (6.82), we can therefore cancel them and simplify the above expression to

$$\frac{\partial S}{\partial t} + \frac{1}{2m}\left(\frac{\partial S}{\partial x}\right)^2 + V(x) - \frac{\hbar^2}{2m}\frac{\partial^2 \sqrt{\rho}}{\partial x^2}\frac{1}{\sqrt{\rho}} = 0 \tag{6.84}$$

We have managed to reduce the complex Schrodinger equation into two real equations: (6.82) involving the mod-square and (6.84) involving the phase. So far our treatment is exact and no approximations have been made.

If you are a classical mechanics guru, you will have noticed that the first three terms of (6.84) are precisely the *Hamilton-Jacobi equation*. Yet another way to formulate the classical equations of motion. Incidentally this is precisely the reason for the factor of $\hbar$ in the phase of the wavefunction, it allows us to write the classical Hamilton-Jacobi equation without any factors of $\hbar$. This immediately suggests that getting rid of the last term in (6.84) is the classical limit.

An easier way to understand what is going on is to define

$$W = S + Et \tag{6.85}$$

for some constant E. In terms of which we can write (6.84) as (ignoring the last term)

$$\frac{1}{2m}\left(\frac{\partial W}{\partial x}\right)^2 + V(x) = E \Longleftrightarrow H\left(x, \frac{\partial W}{\partial x}\right) = E \tag{6.86}$$

where we have noticed that the LHS is just the classical Hamiltonian where instead of momentum we insert $\partial W/\partial x$. If we take this seriously and define our momentum as

$$p = \frac{\partial W}{\partial x} \tag{6.87}$$

then the time evolution equations become

$$H(x,p) = E \tag{6.88}$$

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}\left(\rho \frac{p}{m}\right) = 0 \tag{6.89}$$

These are exactly what we expect from a classic fluid flow with energy E and momentum p. Each individual point x will behave just like a classical particle. The initial position and momentum determine the initial energy, we then evolve the position by using $\dot{x} = p/m$ and evolve the momentum by demanding that $H(x,p) = E$. For a classical trajectory with a time independent Hamiltonian the energy is conserved and this whole procedure is perfectly consistent[67].

All in all, neglecting the last term in (6.84) has given us a classical trajectory. The thorny issue is that we know that in quantum mechanics we cannot fully determine the position and momentum with absolute certainty. How did we get around this?

Imagine we had an initial condition where ρ vanished outside some small region. If we also are to have the momentum reasonably well determined then there must be a sufficient number of wavelengths inside this region to allow us to accurately compute the wavenumber/momentum. This in turn requires that the phase of the wavefunction varies much more rapidly than the density, which is precisely the approximation we employed to neglect the last term in (6.84). More precisely, neglecting the last term in (6.84) assumes

$$\left(\frac{\partial S}{\partial x}\right)^2 \gg \frac{\partial^2 \sqrt{\rho}}{\partial x^2} \frac{\hbar^2}{\sqrt{\rho}} \tag{6.90}$$

Clearly if ρ is *too* peaked around that small region, then necessarily its derivatives will be large and this inequality won't hold. This is precisely what we expected from the Heisenberg uncertainty principle, if we try to have the position too localised then the RHS of (6.90) will be too large and our approximation will be rubbish.

The key here is to lower our standards. Let's us re-examine (6.90) using more macro-

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[67] If you are wondering what became of S and W, the solution to the Hamilton-Jacobi equation is given by setting S equal the classical action evaluated on a solution to the equations of motion. In this context W is called *Hamilton's characteristic function*. You can find more details about this on Goldstein's "Classical Mechanics– textbook.

scopic ideas, the LHS is just our momentum squared, the RHS is the variation in $\sqrt{\rho}$ in units of $\sqrt{\rho}$ times $\hbar^2$. Roughly we then have

$$p^2 \gg \frac{\text{Change in } \sqrt{\rho}}{\Delta x^2} \cdot \hbar^2 \tag{6.91}$$

For macroscopic objects we can just use the values of the SI units to get a ballpark of how tight this inequality is. What helps is the factor of $\hbar^2$ on the RHS, which is really really small in SI units. Even for the fairly large changes in ρ needed for an appropriately localised particle we can have pretty normal momenta *and* satisfy (6.90) no problem. For macroscopic objects, not only is the Heisenberg uncertainty principle not an issue, but we have managed to show that the time evolution is precisely what would be predicted by classical mechanics.

You may have noticed how the strict classical limit would have been obtained by taking $\hbar \to 0$. This also helps understand how we can fix both position and momentum, in the limit $\hbar \to 0$ the commutator of X and P vanishes and so they can be simultaneously diagonalised. It might be a very useful rule of thumb but one must be careful to not take it too seriously. It only worked because we made very judicious choices for S, if we had chosen a different factor of $\hbar$ then taking the limit $\hbar \to 0$ would not have recovered classical physics. The inequality in (6.90) is more precise and would work no matter the dimensions we chose.

7 The “free” particle

In the next few chapters we will consider several simple 1-dimensional examples of quantum systems, to get acquaintated with some key quantum phenomena and tools. We begin with the simplest of them all, a free particle, whose Hamiltonian is simply given by:

$$H = \frac{P^2}{2m} \tag{7.1}$$

Using our symmetry language, we see that this Hamiltonian is translation invariant. Therefore we should look at eigenstates of the operator P.

$$P\left|p\right\rangle = p\left|p\right\rangle \tag{7.2}$$

The energy of these eigenstates is simply given by

$$H\left|p\right\rangle = \frac{p^2}{2m}\left|p\right\rangle \implies E_p = \frac{p^2}{2m} \tag{7.3}$$

In the position basis, this states look like:

$$\psi_p(x,t) = \left\langle x\right| \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}E_p}\left|p\right\rangle = \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(px - E_p t)} \tag{7.4}$$

Free particles in quantum mechanics are plane waves, but that has an issue—plane waves are *not* normalisable! In fact we should write something like

$$\psi_p(x,t) = C\mathrm{e}^{\frac{\mathrm{i}}{\hbar}(px - E_p t)} \tag{7.5}$$

for some unknown constant C because *a priori* we do not have any way of fixing this normalisation.

We were somewhat comfortable with using non-normalisable basis states like $|x\rangle$ or $|p\rangle$, mostly because we were just using them for intermediate calculations and definitions. But we now wish to represent a physical free particle, and in this case non-normalisability is a much bigger issue. In the remainder of this chapter we will describe several options to get around this non-normalisability, some more popular than others.

7.1 A particle in a box

The issue that made our wavefunctions non-normalisable was the fact we were integrating over the infinite volume of space. It stands to reason this problem would be resolved if instead of considering $x \in \mathbb{R}$ we took some finite interval $x \in [-a, a]$. The question is what boundary conditions to impose at $x = \pm a$. Intuitively, the particle should never be found outside of this interval so it is reasonable to assume that

$$\psi(x) = 0 \quad \text{if} \quad x > a \quad \text{or} \quad x < -a \tag{7.6}$$

Assuming that the wavefunction is continuous[68] it is perfectly reasonable to use the following Dirichlet boundary conditions

$$\psi(x) = 0 \quad \text{for} \quad x = \pm a \tag{7.7}$$

named after Lejeune Dirichlet who successfully used them to solve partial differential equations.

All in all, in the position basis, we wish to solve the following equation:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = E\psi(x) \tag{7.8}$$

subject to the boundary conditions in (7.7).

The general solution to this equation is given by a linear combination of exponentials

$$\psi(x) = A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx} \tag{7.9}$$

where

$$E = \frac{\hbar^2 k^2}{2m} \tag{7.10}$$

We now just have to impose the boundary conditions. They correspond to the following conditions:

$$\begin{cases} \psi(a) = 0 \\ \psi(-a) = 0 \end{cases} \iff \begin{cases} A\mathrm{e}^{\mathrm{i}ka} + B\mathrm{e}^{-\mathrm{i}ka} = 0 \\ A\mathrm{e}^{-\mathrm{i}ka} + B\mathrm{e}^{\mathrm{i}ka} = 0 \end{cases} \tag{7.11}$$

The first of these can be solved to give

$$B = -A\mathrm{e}^{2\mathrm{i}ka} \tag{7.12}$$

so that

$$\psi(x) = A\left(\mathrm{e}^{\mathrm{i}kx} - \mathrm{e}^{-\mathrm{i}k(x-2a)}\right) = 2\mathrm{i}A\mathrm{e}^{\mathrm{i}ka}\sin(k(x-a)) = C\sin(k(x-a)) \tag{7.13}$$

Figure 7.1. **Johann Peter Gustav Lejeune Dirichlet**[69]
Born: 1805 Düren, French Republic
Died: 1859 Göttingen, Kingdom of Hanover
Academic Advisors: Siméon Poisson, Joseph Fourier, Carl Gauss

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[68] This assumption is not true in general and usually merits more justification. In our case, by just considering $x \in [-a, a]$ in effect, positions outside this interval don't *exist*. We could in fact impose different boundary conditions if we so wished. Continuity was used to merely motivate our choice.

[69] Picture by Unknown author - Unknown source, Public Domain, `https://commons.wikimedia.org/w/index.php?curid=90476`

where we put all of the constants in front into a single constant C to be determined when we normalise our wavefunction. Imposing that

$$\int_{-a}^{a} \mathrm{d}x \, |\psi(x)|^2 = 1 \tag{7.14}$$

we find

$$|C| = \frac{1}{\sqrt{a}} \tag{7.15}$$

Imposing the second boundary condition gives us

$$\sin(2ka) = 0 \implies k = \frac{\pi n}{2a} \quad n \in \mathbb{Z} \tag{7.16}$$

With these boundary conditions our wavenumber comes in discrete multiples! This is a key feature of quantum mechanics, boundary conditions often yield discrete outcomes.

All in all, our solution will be

$$\psi(x) = \frac{1}{\sqrt{a}} \sin\Big(\frac{\pi n}{2a}(x-a)\Big) \tag{7.17}$$

whose energy is given by

$$E_n = \frac{\hbar^2 \pi^2 n^2}{8a^2 m} \tag{7.18}$$

which is also quantised, but now in multiples of n^2.

Note that although every $n \in \mathbb{Z}$ is a valid solution, the wavefunctions for n and $-n$ only differ by a sign, hence a phase. They therefore correspond to the same physical state. We should only consider $n \in \mathbb{Z}^+$ as distinct physical solutions.

INSERT PLOT OF THE NORMALISED SOLUTION FOR THE FIRST FEW VALUES OF N

Also note how, for a given n the solution is either even or odd. In fact

$$\begin{aligned}\psi(-x) &= \frac{1}{\sqrt{a}} \sin\Big(\frac{\pi n}{2a}(-x-a)\Big) = -\frac{1}{\sqrt{a}} \sin\Big(\frac{\pi n}{2a}(x+a)\Big) = \\ &= -\frac{1}{\sqrt{a}} \sin\Big(\frac{\pi n}{2a}(x-a) + \pi n\Big) = -(-1)^n \frac{1}{\sqrt{a}} \sin\Big(\frac{\pi n}{2a}(x-a)\Big) = \\ &= (-1)^{n+1} \psi(x)\end{aligned} \tag{7.19}$$

For n odd the solution is even, and for n even the solution is odd.

This is exactly what we expected from symmetry considerations. The Hamiltonian is independent of X and even in P, therefore it is parity invariant. Additionally, our boundary conditions are symmetric in x so they don't spoil our symmetry. Hence, we expect our energy eigenstates to either be even or odd functions of x so that parity acts diagonally, and this is precisely what we observe.

So far these functions seem perfectly acceptable. They are normalisable solutions to Schrodinger's equation without a potential. However, these are poor candidates for free particles. Chiefly, they are *not* eigenstates of the momentum operator:

$$P\psi(x) = -\mathrm{i}\hbar \frac{\partial \psi(x)}{\partial x} = -\frac{\mathrm{i}\hbar\pi n}{2a\sqrt{a}} \cos\Big(\frac{\pi n}{2a}(x-a)\Big) \tag{7.20}$$

which is *not* a multiple of $\psi(x)$.

And our situation is worse, we can compute the expectation value of the momentum as

$$\begin{aligned}\langle P\rangle &= \int_{-a}^{a} \mathrm{d}x\, \psi^*(x)\Big(-\mathrm{i}\hbar\frac{\partial\psi(x)}{\partial x}\Big) = \\ &= -\frac{\mathrm{i}\hbar\pi n}{2a^2}\int_{-a}^{a}\mathrm{d}x\,\sin\Big(\frac{\pi n}{2a}(x-a)\Big)\cos\Big(\frac{\pi n}{2a}(x-a)\Big) = \\ &= -\frac{\mathrm{i}\hbar\pi n}{4a^2}\int_{-a}^{a}\mathrm{d}x\,\sin\Big(\frac{\pi n}{a}(x-a)\Big) = 0 \end{aligned} \tag{7.21}$$

Not only, are our solutions not momentum eigenstates but the expectation value of the momentum vanishes!

We can trace these issues back to our boundary conditions. Imposing that the wavefunction vanishes outside our box is equivalent to having an infinite potential outside the box

$$V(x) = \begin{cases} 0 & -a < x < a \\ \infty & \text{otherwise} \end{cases} \tag{7.22}$$

This breaks translation invariance badly, which is why the energy eigenstates were no longer momentum eigenstates. Looking at our wavefunction we see that it is a linear combination of $\mathrm{e}^{\mathrm{i}kx}$ and $\mathrm{e}^{-\mathrm{i}kx}$, *i.e.* a superposition of particles with momentum $p = +\hbar k$ and $p = -\hbar k$, which clearly does not have a well defined momentum.

The fact that the average momentum is zero is because the motion of the particle with momentum $p = +\hbar k$ is cancelled by the one with momentum $p = -\hbar k$. You can think of our solution as a superposition of two particles who keep bouncing back and forth between the walls of the box, their momenta being perfect opposites of each other, giving an overall vanishing momenta. What you shouldn’t do is think of this as a static particle in the box, the expectation value of P^2 is $2mE$ which is *not* zero, so our solution isn’t one with zero momentum, the particles in the superposition are moving around, it just so happens that their momenta perfectly cancel.

Ultimately, using fixed Dirichlet-type boundary conditions is not a good way to model a free particle. The reason we have went into so much detail of this model is that it is in fact a decent first approximation for a potential well, which we will cover in more detail later on.

7.2 A particle in a circle

If our issue was that we broke translation invariance then how about trying boundary conditions who keep translation invariance but still ensure that our wavefunction is only integrated over a finite range in position? One way to do that is to impose *periodic* boundary conditions

$$\psi(x+L) = \psi(x) \tag{7.23}$$

These boundary conditions are equivalent to considering a particle on a circle of radius $R = L/2\pi$.

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Thinking of this as a circle makes it more intuitive that we have not broken translation invariance. Despite the circle having finite length we can still go around it as much as we like. In fact, we can now satisfy our boundary conditions with a single eigenstate of the momentum operator, rather than requiring a superposition. Taking an an eigenstate of P with eigenvalue p:

$$\psi_p(x) = C\mathrm{e}^{\frac{\mathrm{i}}{\hbar}px} \tag{7.24}$$

we then impose (7.23)

$$e^{\frac{i}{\hbar}p(x+L)} = e^{\frac{i}{\hbar}px} \implies e^{\frac{i}{\hbar}pL} = 1 \implies p = \frac{2\pi\hbar n}{L} = \frac{hn}{L} \quad n \in \mathbb{Z} \tag{7.25}$$

The energy is given by

$$E = \frac{p^2}{2m} = \frac{h^2 n^2}{2mL^2} = \frac{\hbar^2 n^2}{2mR^2} \tag{7.26}$$

This energy precisely matches what we obtained for the particle in a box if $L = 2a$, *i.e.* if the total interval the particle can occupy is the same. The main difference is that now the particle has a well defined value for the momentum which is an integer multiple of h/L or equivalently $\hbar/R$,

It is trivial to show that

$$\int_0^L \mathrm{d}x\, |\psi_p(x)|^2 = |C|^2 L \tag{7.27}$$

therefore our normalised wavefunctions will be

$$\psi_p(x) = \frac{e^{2\pi i n \frac{x}{L}}}{\sqrt{L}} = \frac{e^{i n \frac{x}{R}}}{\sqrt{2\pi R}} \tag{7.28}$$

identifying the angle around the circle as $\theta = x/R$ we can also write them as

$$\psi_p(\theta) = \frac{e^{in\theta}}{\sqrt{2\pi R}} \tag{7.29}$$

We can sketch (the real part of) these wavefunctions

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We see that the momentum quantisation condition means that they fit nicely with $|n|$ oscillations as we go once around the circle. In fact, using de Broglie’s relation between momentum and wavelength we see that

$$L = |n|\lambda \tag{7.30}$$

therefore $|n|$ complete waves fit into the circle. In fact, this was the original motivation for de Broglie. His idea was to think of electrons orbiting the Hydrogen nucleus in the same way planets orbit the sun. If they were also wave-like then only an integer number of wavelengths could fit without that electron wave being discontinuous. Even if the specific planetary model of the atom wasn’t quite right, the relation between the wavelength and the momentum was.

One additional difference from the box scenario is that positive and negative values of n are distinct solutions. They correspond to particles travelling to the left or the right. They will have the same energy but opposite momentum. Previously, any solution would have to include both.

For large values of R we see that the discrete splitting in momentum and energy eigenvalues gets smaller. In the limit $R \to \infty$ we approach the continuous spectrum we had when x could take on any value. However, we can clearly see that the normalisation of the wavefunction goes to zero, showcasing the original issue of non-normalisability.

In conclusion, periodic boundary conditions are much better for modelling free particles than Dirichlet boundary conditions. They allow us to keep translation invariance while still having a finite size for our spatial dimension, and therefore allowing for normalisable wavefunctions. This is an important lesson that will be relevant all the way to quantum field theory. If you have an infinity that you wish to regularise, in our case the integral over all of space of $|\psi|^2$, you should be careful to introduce a cut-off that does not break any important symmetries. In our case, we cut off large values of x in two ways, one which broke translation invariance and one that didn't. The second one had physics which were far similar to the original case we wished to study. The only price we had to pay is that we are no longer allowed to have any continuous value for the momentum, we are restricted to integer multiples of h/L. This also means that instead of dealing with momentum integrals we deal with discrete sums. In many physical applications choosing periodic boundary conditions will be the best way forward.

7.3 Wavepackets

Another perspective is that our issue was that we were picking a state with definite momentum. By the Heisenberg uncertainty principle it must have a completely indefinite position, *i.e.* the particle is spread all over space. This is not only not exactly what we usually mean by particle, but is also clearly not regular. Of course that a particle which is evenly spread through all of space will not be normalisable. If we are to have the particle contained in a range of positions we must introduce some uncertainty in the momentum. After all, in real experiments we will never be able to determine the momentum with absolute precision so including some uncertainty in the momentum is perfectly reasonable.

To include some uncertainty in the momentum we integrate (7.5) over the momentum with some weight function $f(p)$:

$$\psi(x,t) = \int \frac{\mathrm{d}p}{h} f(p) \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(px - E_p t)} \tag{7.31}$$

This is called a *wavepacket.*

Imposing that this wavepacket is correctly normalised requires

$$1 = \int \mathrm{d}x\, |\psi(x)|^2 = \int \frac{\mathrm{d}p}{h} |f(p)|^2 \tag{7.32}$$

This wavepacket approach is the most mathematically rigorous and if one wishes to do rigorous proofs it is often the only option. However, it is quite cumbersome, and, despite its physical motivation, it has some properties that are not very convenient.

Firstly, given ψ is no longer an eigenstate of the momentum, it will therefore also not be an eigenstate of the energy. Very often looking for the energy spectrum is precisely our goal. Using wavepackets it will quite tough to extract that information.

To see the second downside it is convenient to pick a specific profile for $f(p)$. Let us pick a Gaussian peaked at $p = p_0$ with width σ:

$$f(p) = \sqrt{\frac{h}{\sigma\sqrt{2\pi}}} \exp\left(-\frac{(p-p_0)^2}{4\sigma^2}\right) \tag{7.33}$$

named after the proliferous Carl Friedrich Gauss (Fig. 7.2).

INSERT PLOT

To show that the above choice of f is indeed correctly normalised we just have to use

Figure 7.2. Johann Carl Friedrich Gauß aka Carolus Fridericus Gauss[70]
Born: 1777 Brunswick, Holy Roman Empire of the German Nation
Died: 1855 Göttingen, Kingdom of Hanover
Doctoral Advisor: Johann Friedrich Pfaff

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[70] Picture by Christian Albrecht Jensen - http://archiv.bbaw.de/archiv/archivbestaende/abteilung-sammlungen/gesamtbestand-des-kunstbesitzes/gelehrtengemaelde/gelehrtengemalde-seiten/ZIMM-0001.html, Public Domain, https://commons.wikimedia.org/w/index.php?curid=6886354

the expression for the Gaussian integral

$$\int \mathrm{d}x\, \mathrm{e}^{-a(x-x_0)^2} = \sqrt{\frac{\pi}{a}} \tag{7.34}$$

The normalisation of our f is different from what you may recognise from probability theory. This is because the probability density is given by $|f(p)|^2$ rather than $f(p)$ itself.

To examine this Gaussian wavepacket it is more helpful to Fourier transform into momentum space

$$\tilde{\psi}(p,t) = \int \mathrm{d}x\, \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}px}\psi(x,t) = f(p)\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}E_p t} \tag{7.35}$$

Additionally, beyond (7.34) we will need the following Gaussian integrals:

$$\int \mathrm{d}x\, x\, \mathrm{e}^{-ax^2} = 0 \tag{7.36}$$

which is trivial because the Gaussian is even and x is odd, and

$$\int \mathrm{d}x\, x^2\, \mathrm{e}^{-ax^2} = \frac{\sqrt{\pi}}{2a^{3/2}} \tag{7.37}$$

which can be derived by taking derivatives wrt a in (7.34).

All of the expectation values computed below will require some elbow grease with changes of variables and reducing to the three Gaussian integrals above. The reader is encouraged to try and do the computations themself, but we will not go into too much detail to simplify the discussion.

We can now compute various averages of position and momentum to see what this wavepacket represents.

$$\langle P \rangle = \int \frac{\mathrm{d}p}{h} p|f(p)|^2 = \cdots = p_0 \tag{7.38}$$

where to derive this we needed (7.34) and (7.36).

This result is reassuring, we chose a Gaussian profile peaked at p_0 so the average momentum better be p_0. We can also compute the uncertainty ΔP. First we compute

$$\langle P^2 \rangle = \int \frac{\mathrm{d}p}{h} p^2|f(p)|^2 = \cdots = p_0^2 + \sigma^2 \tag{7.39}$$

where now all three (7.34), (7.36) and (7.37) are necessary.

In total

$$\Delta P = \sqrt{\left\langle (P - \langle P \rangle)^2 \right\rangle} = \sqrt{\langle P^2 \rangle - \langle P \rangle^2} = \sigma \tag{7.40}$$

which justifies our calling σ the width.

So far we have only justified our notation and nomenclature for $f(p)$, to get some physics we must also compute the equivalent quantities for X. To compute these we use the fact

$$X\tilde{\psi}(p,t) = \mathrm{i}\hbar \frac{\partial \tilde{\psi}(p,t)}{\partial p} \tag{7.41}$$

we then obtain

$$\langle X \rangle = \int \frac{\mathrm{d}p}{h} f^*(p)\mathrm{e}^{\frac{\mathrm{i}}{\hbar}E_p t}\mathrm{i}\hbar \frac{\partial}{\partial p}\left(f(p)\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}E_p t} \right) = \cdots = \frac{p_0 t}{m} \tag{7.42}$$

This is precisely what we would have expected from Ehrenfest's theorem, the average position of the particle travels with velocity p_0/m.

Finally, we can compute the uncertainty in X. First we compute (beware, this is the trickiest)

$$\langle X^2 \rangle = \int \frac{\mathrm{d}p}{h} f^*(p) \mathrm{e}^{\frac{\mathrm{i}}{\hbar}E_p t}(-\hbar^2)\frac{\partial^2}{\partial p^2}\left(f(p)\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}E_p t}\right) = \cdots = \frac{p_0^2 t^2}{m^2} + \frac{\hbar^2}{4\sigma^2} + \frac{t^2\sigma^2}{m^2} \tag{7.43}$$

Now we can reap the benefits of our hard work. The uncertainty in X is given by

$$\Delta X = \sqrt{\frac{\hbar^2}{4\sigma^2} + \frac{t^2\sigma^2}{m^2}} \tag{7.44}$$

which, in contrast with the uncertainty in P grows with time!

At $t = 0$ the uncertainty in X is minimal, and in fact

$$\Delta X \Delta P = \frac{\hbar}{2} \tag{7.45}$$

which saturates the Heisenberg uncertainty bound. This was precisely the motivation for picking this waveform, it is the best we can possibly do according to the Heisenberg uncertainty principle. We still have one free parameter, σ, but we can see that by decreasing σ and thereby making our knowledge of the momentum more precise we increase the uncertainty in the position, at least at $t = 0$.

The state of affairs at $t = 0$ is then basically optimal. We have a wavefunction which is peaked at some value of the momentum and is also reasonably peaked at some value of the position. We can't have both arbitrarily peaked, but this is as good as we'll get.

Nevertheless, the weakness of this wavepacket is in the time dependence of ΔX. As time goes on, the uncertainty increases, not only does our wavefunction, on average travel with velocity p_0/m but it also spreads out becoming more evenly distributed over time. We loose whatever spatial localisation we started with, loosing our intuitive picture of a reasonably well localised particle travelling with a given velocity.

INSERT PLOT OF THE TIME EVOLUTION OF THE POSITION WAVEFUNCTION

This can be understood intuitively. At a given point in time our particle is at position $x_0 \pm \delta x$ and moving with velocity $v_0 \pm \delta v$. The worst case scenario would be if it is at position $x_0 + \delta x$ moving with velocity $v_0 + \delta v$, or at position $x_0 - \delta x$ moving with velocity $v_0 - \delta v$. The uncertainty after some time t will be

$$x_0 + \delta x + t(v_0 + \delta v) - (x_0 - \delta x + t(v_0 - \delta v)) = 2\delta x + 2t\delta v \tag{7.46}$$

so our uncertainty increases with time.

Together with the greater computational complexity, the fact we loose our spacial localisation makes this method even less appealing. Nevertheless it might be the only option in some more rigorous approaches.

7.4 A continuous beam of particles

The final approach we shall consider is the simplest and therefore the one we will chiefly use in this volume—just use non-normalisable states. But how can we fix the value of C in (7.5)? The trick is to recover our continuity equation for probability (6.75). Let us for a momentum consider a classical beam of N particles. Calling ρ the number of particles per unit volume and assuming no particles can get created or destroyed we can write a continuity equation for the number of particles

$$\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{j} = 0 \tag{7.47}$$

where $\boldsymbol{j} \equiv \rho \boldsymbol{v}$ and $\boldsymbol{v}$ is the velocity of the particles at point $\boldsymbol{x}$.

We can interpret $\boldsymbol{j}$ as the flux, as it gives the number of particles that strike a cross-sectional area per unit time. Indeed its units match up, ρ has units m^{-3} and therefore $\boldsymbol{j}$ has units $\mathrm{m}^{-2}\ \mathrm{s}^{-1}$.

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In 1 dimension, we can instead write

$$\frac{\partial \rho}{\partial t} + \frac{\partial j}{\partial x} = 0 \tag{7.48}$$

the particle density ρ will have units m^{-1} and j will have units s^{-1}. The flux will now represent the number of particles that pass through a point in our 1 dimensional line per unit time.

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Comparing with (6.75) and (6.77) we see that we can re-interpret $|\psi(x,t)|^2$ as the particle density ρ. Of course, $|\psi(x,t)|^2$ is actually representing a probability, but if we had normalised it to N rather than 1 then it could have potentially represented the particle density. The fact that globally the integral of $|\psi(x,t)|^2$ blows up is perhaps less concerning for local questions. If we had a uniform particle density and an infinite spatial volume, the integral of ρ would indeed blow us because N would be infinite. Nevertheless, the continuity equation would still apply. Quantum mechanically, we can also check that to prove (6.75) we used the Schrodinger equation but did not need to assume the solution was normalisable, only the local properties of the Schrodinger equation mattered. In fact we can check (7.5) satisfies the continuity equation

$$|\psi(x,t)|^2 = |C|^2 \tag{7.49}$$

which is a constant, and

$$j = \frac{\mathrm{i}\hbar}{2m}\left(\frac{\partial \psi^*}{\partial x}\psi - \psi^*\frac{\partial \psi}{\partial x}\right) = \frac{p}{m}|C|^2 \tag{7.50}$$

which does not depend on x. Additionally, we can even see that $j = \rho v$ if we define $v \equiv p/m$, exactly what we expected classically.

It seems that we can therefore restrict ourselves to asking local questions, and if we're careful we might get away with using non-normalisable states. If we need to impose unitarity, *i.e.* conservation of probability, we can just use the local continuity equation (6.75). Moreover, instead of discussion total probabilities for a given process, say a scattering of an electron of an atom, we can talk of *ratios* of probabilities, *i.e.* if we have a beam of many electrons, what fraction of them are scattered by a given angle? For those kinds of questions it will usually convenient to pick $C = 1$, *i.e.* a beam with 1 particle per unit length/volume, but we should remind ourselves that we are only computing ratios, even if we conveniently pick a denominator of 1.

This approach is by far the least rigorous of the ones we discussed, the price we pay for that lack of rigour is that we are very heavily restricted on the kinds of questions we can even ask. Nevertheless, there are quite a few problems of great physical importance, *e.g.* scattering, for which these are exactly the interesting questions. In those cases this approach is the best one because it provides the simplest calculations.

8 Square potentials

So far we have only considered free particles but real quantum systems also include potentials. In this chapter we shall focus on the simplest possible potentials—those that are piecewise constant. We begin by considering what happens to particles that hit a barrier, uncovering one of the most famous phenomena of quantum mechanics—tunnelling. Then we will describe bound states in a finite potential well, seeing how boundary conditions are key to discreteness in energy spectra. Finally, we shall connect the two calculations by showing that divergences in scattering amplitudes give us bound state energies.

Throughout this chapter we shall focus on energy eigenstates so that the time dependence is trivial. Therefore we shall chiefly resort to the time-independent Schrodinger equation and use the language of wave mechanics.

8.1 A particle hitting a wall

The first example we shall consider is a wall, that is, we want to solve the (time-independent) Schrodinger equation for the following potential:

$$V(x) = \begin{cases} 0 & x < 0 \\ V & x > 0 \end{cases} \tag{8.1}$$

or equivalently, $V(x) = \theta(x)$.

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For $x < 0$, the potential vanishes so the generic solution is just the plane wave solutions we discussed in the previous chapter

$$\psi(x) = A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx}, \quad x < 0 \tag{8.2}$$

where A and B are two complex constants. The energy of these solutions is given by

$$E = \frac{\hbar^2 k^2}{2m} \tag{8.3}$$

Of course this energy allows for k to be positive or negative corresponding to the A, and B terms above. We will define k to always be positive to distinguish between the two coefficients. This means that the A term corresponds to a particle moving to the right and the B term corresponds to a particle moving to the left.

For $x > 0$ now the potential is not zero, therefore we are solving the equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V\psi(x) = E\psi(x) \Longleftrightarrow -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = (E-V)\psi(x) \tag{8.4}$$

therefore the solutions will be exactly the same as for the free particles[71], with the exchange $E \to E - V$:

$$\psi(x) = C\mathrm{e}^{\mathrm{i}qx} + D\mathrm{e}^{-\mathrm{i}qx}, \quad x > 0 \tag{8.5}$$

where, once more, C and D are some complex constants. The energy will be given by

$$E - V = \frac{\hbar^2 q^2}{2m} \tag{8.6}$$

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[71] This is why we will focus on piecewise constant potentials, the solution is always just a sum of plane waves.

Let us consider initially the $E > V$ case so that q is real. We then have the same situation as for $x < 0$, q can be either positive or negative, corresponding to the C and D terms. We shall define q to be positive to distinguish between them. This means that the C term corresponds to a particle moving to the right and the D term corresponds to a particle moving to the left.

INSERT PICTURE WITH ARROWS EXPLAINING WHAT EACH TERM IS DOING

What we have left to do now is fix A, B, C, and D. Let us think about the physics we are trying to describe. Our goal is to send a particle from left, let it hit our barrier and see what happens. The A term will of course represent our *incoming* particles. The B term describes particles moving to the left in the $x < 0$ region, this would correspond to *reflected* particles. The C term represents particles who continue to move to the right after hitting the barrier, therefore it represents *transmitted* particles. Finally the D term represents particles who are moving to the left but in the $x > 0$ region, these are *incoming* particles but from $x \to \infty$, we do not wish to consider the case where there are incoming particles from the right so we will set $D = 0$.

To obtain the probabilities for reflection and transmission you might wish to take ratios between B, C, and A; this is however a bit too quick. The issue with our current scenario is that $q \neq k$ so particles after the barrier are moving with different speeds, hence, comparing the densities at a given point will not be a fair measure of the number of particles. To really capture the fraction of particles which are reflected/transmitted we should instead compute the fluxes which do take into account the speed of the particles. Plugging in (8.2) and (8.5) into (6.74) (remembering to multiply by $\exp\left(-\frac{i}{\hbar}Et\right)$ to capture the time dependence) we find

$$j(x) = \begin{cases} \frac{\hbar k}{m}\left(|A|^2 - |B|^2\right) & x < 0 \\ \frac{\hbar q}{m}|C|^2 & x > 0 \end{cases} \tag{8.7}$$

we therefore define the *incoming flux*

$$j_{\text{inc}} \equiv \frac{\hbar k}{m}|A|^2 \tag{8.8}$$

the *reflected flux*

$$j_{\text{ref}} \equiv \frac{\hbar k}{m}|B|^2 \tag{8.9}$$

and the *transmitted flux*

$$j_{\text{trans}} \equiv \frac{\hbar q}{m}|C|^2 \tag{8.10}$$

It is straightforward to show that the particle density is a constant in time, therefore the fluxes must match at $x = 0$ which means

$$j_{\text{inc}} - j_{\text{ref}} = j_{\text{trans}} \implies j_{\text{inc}} = j_{\text{ref}} + j_{\text{trans}} \tag{8.11}$$

this equation captures the fact we cannot loose any particles; every incoming particle is either reflected or transmitted.

With all of this in mind we can identity the probability that a particle is reflected as the fracton of particles which is reflected

$$P_{\text{ref}} = \frac{j_{\text{ref}}}{j_{\text{inc}}} = \frac{|B|^2}{|A|^2} \tag{8.12}$$

and the probability that a particle is transmitted is similarly given by

$$P_{\text{trans}} = \frac{j_{\text{trans}}}{j_{\text{inc}}} = \frac{|C|^2 q}{|A|^2 k} \tag{8.13}$$

Here we see the importance of considering the fluxes, the probability of transmission involves the ratio of the two wavenumbers, *i.e.* velocities. This is the correct expression because it is the fluxes which are conserved as can be seen from (8.11).

To find B and C we need to match the solutions at $x = 0$, however, our potential is discontinuous so it bears discussing if and why our wavefunction should be continuous at $x = 0$. Let us integrate the Schrodinger equation in a small interval around $x = 0$:

$$\begin{aligned} -\frac{\hbar^2}{2m}\int_{-\epsilon}^{\epsilon} \mathrm{d}x\, \frac{\partial^2\psi(x)}{\partial x^2} &= \int_{-\epsilon}^{\epsilon} \mathrm{d}x\,(E - V(x))\psi(x) \\ -\frac{\hbar^2}{2m}\left(\left.\frac{\partial\psi(x)}{\partial x}\right|_{x=\epsilon} - \left.\frac{\partial\psi(x)}{\partial x}\right|_{x=-\epsilon}\right) &= \int_{-\epsilon}^{\epsilon} \mathrm{d}x\,(E - V(x))\psi(x) \end{aligned} \tag{8.14}$$

The potential $V(x)$ might be discontinuous, but it is finite, this means that the RHS of the above vanishes. Therefore the derivative of $\psi(x)$ is continuous[72]. Given that the derivative of the wavefunction is continuous then the wavefunction itself must also be continuous.

Applying continuity in $\psi(x)$ and $\psi'(x)$ at $x = 0$ we find

$$\begin{cases} \psi(0) \text{ continuous} \\ \psi'(0) \text{ continuous} \end{cases} \implies \begin{cases} A + B = C \\ \mathrm{i}kA - \mathrm{i}kB = \mathrm{i}qC \end{cases} \implies \begin{cases} B = \frac{k-q}{k+q}A \\ C = \frac{2k}{k+q}A \end{cases} \tag{8.15}$$

Plugging these results into (8.12) and (8.13) we find

$$P_{\text{ref}} = \left(\frac{k-q}{k+q}\right)^2 \tag{8.16}$$

$$P_{\text{trans}} = \frac{4kq}{(k+q)^2} \tag{8.17}$$

Let us analyse our results. Firstly, it is fairly trivial to verify that $P_{\text{ref}} + P_{\text{trans}} = 1$ reassuring ourselves that we probably didn't make any big mistake. Nevertheless, we are already seeing some behaviour which is distinct from classical physics. If we sent a classical particle through a potential with enough energy to clear the potential barrier it would go straight through, even if its kinetic energy, and hence velocity, would be lower. We see that in quantum mechanics this is not true, even with enough energy to clear the potential the particle still has some probability of being reflected.

Further, you should not view q as an independent variable. It is a function of the incoming energy and the height of the potential. In particular we can write

$$k = \frac{\sqrt{2mE}}{\hbar} \tag{8.18}$$

$$q = \frac{\sqrt{2m(E-V)}}{\hbar} \tag{8.19}$$

Instead of thinking of incoming energy, we can also use incoming momentum and write q

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[72] If the potential had a divergence, *e.g.* a Dirac-δ, then the RHS would not vanish, and there would be a discontinuity in the derivative.

as a function of k

$$q = \sqrt{k^2 - \frac{2mV}{\hbar}} \tag{8.20}$$

Inserting any of these expression into (8.17) is not very instructive but it is worth keeping it in mind which variables are independent.

To our heads around this, let us think of some limits. Firstly, if $E \gg V$ then $q \approx k$ and the probability of reflection approaches 0. It is as if the incoming particle does not feel the barrier and goes straight through. If instead $E \to V$ then $q \to 0$ which means $P_{\text{ref}} \to 1$ and $P_{\text{trans}} \to 0$. If the particle has basically no energy above the potential then it is almost surely reflected back and has very little chance of making it through. The intermediate cases are governed by our exact expressions (8.17).

What if the particle we sent didn't have enough energy to clear the potential, *i.e.* if $E < V$? Classically, the particle would always be reflected, the region $x > 0$ would be forbidden. Nonetheless, this is not what happens in the quantum realm, for $E < V$ the outgoing momentum q is *complex*:

$$q^2 = \frac{2m(E - V)}{\hbar^2} < 0 \tag{8.21}$$

This means that our solution for $x > 0$ is not an outgoing particle but a decaying exponential. Defining $\eta = -\mathrm{i}q$ we have

$$\psi(x) = C\mathrm{e}^{-\eta x} \quad x > 0 \tag{8.22}$$

for

$$\eta = \frac{\sqrt{2m(V - E)}}{\hbar} \tag{8.23}$$

Despite the particle not having enough energy to clear the potential there is still a probability that the particle is found *after* the barrier. This probability decays exponentially quickly but is sizeable for a length $\sim \eta^{-1}$. This behaviour is unexplainable with classical physics, it would correspond to a negative kinetic energy, pure nonsense. Still there is a classical analogue of this situation. Even if we send light beyond its angle of total reflection there will still be a exponentially decaying electromagnetic field beyond the interface of the two mediums. This is called the *evanescent wave* and is perfectly ordinary behaviour for waves. Our quantum "paradoxes" arise when we use wave mechanics to describe particle motion.

Our equations that relate A, B, and C were algebraic in nature so they apply just as well

$$B = \frac{k + \mathrm{i}\eta}{k - \mathrm{i}\eta} A \tag{8.24}$$

$$C = \frac{2k}{k - \mathrm{i}\eta} A \tag{8.25}$$

The calculations for the fluxes however is quite different because B and C are no longer real.

$$j_{\text{ref}} = \frac{\hbar k}{2m} B^* B = \frac{\hbar k}{2m} |A|^2 \frac{k + \mathrm{i}\eta}{k - \mathrm{i}\eta} \frac{k - \mathrm{i}\eta}{k + \mathrm{i}\eta} = \frac{\hbar k}{2m} |A|^2 = j_{\text{inc}} \tag{8.26}$$

Even if there is a probability for the particle to be found after the barrier the reflected flux is *equal* to the incident flux.

Relatedly, it is not too hard to how that the transmitted flux vanishes

$$j_{\text{trans}} = \frac{\mathrm{i}\hbar}{2m}\left(\frac{\partial\psi^*}{\partial x}\psi - \psi^*\frac{\partial\psi}{\partial x}\right) = 0 \tag{8.27}$$

because the wavefunction for $x > 0$ is real.

Here we see the limitations of using non-normalisable states, despite having a non-zero wave function beyond the boundary and therefore presumably a non-zero probability of finding the particle there, the fluxes describe total reflection. They predict no transmitted particles at all. After all, our interpretation for the fluxes was predicated on the free particle wavefunction, it is not surprising that they would fail when applied to a different case. However, we cannot just use the Born rule because our wavefunctions are not normalisable. In order to calculate the probability of finding a particle in the forbidden region we would have to use something like wavepackets.

But not all is lost, in real experiments, potential barriers will have some finite thickness. In that case, after the barrier we would presumably have free particle plane waves again and be able to use fluxes. This is the situation we will discuss next.

8.2 Tunnelling through a constant barrier

Let us consider the following potential, as the simplest model for a potential barrier with finite thickness

$$V(x) = \begin{cases} V & -a < x < a \\ 0 & \text{otherwise} \end{cases} \tag{8.28}$$

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Once again, we want to send particles from the left and see what happens. Following the discussion from the last section we shall look for solutions of the form

$$\psi(x) = \begin{cases} \mathrm{e}^{\mathrm{i}kx} + R\mathrm{e}^{-\mathrm{i}kx} & x < -a \\ A\mathrm{e}^{\mathrm{i}qx} + B\mathrm{e}^{-\mathrm{i}qx} & -a < x < a \\ T\mathrm{e}^{\mathrm{i}kx} & x > a \end{cases} \tag{8.29}$$

where

$$k = \frac{\sqrt{2mE}}{\hbar} \tag{8.30}$$

$$q = \frac{\sqrt{2m(E-V)}}{\hbar} \tag{8.31}$$

depending on the sign of $E - V$, the wavenumber in the middle region, q might be real or imaginary.

We have chosen to only have incoming particles from the left, and therefore not included a term $\propto \mathrm{e}^{-ikx}$ in the $x > a$ region. Additionally, to simplify calculations we have chosen the density of incoming particles to be unity. Finally, because the potential vanishes for $x > a$ as well as for $x < -a$ the velocity of incoming and transmitted particles is the same, which means we will not have to deal with the ration of the velocities as we did in (8.13). The probabilities for reflection and transmission are therefore given by

$$P_{\text{ref}} = |R|^2 \tag{8.32}$$

$$P_{\text{trans}} = |T|^2 \tag{8.33}$$

To fix R, T, A, and B we will need four conditions. Using similar arguments to the ones in the last section we conclude that despite the discontinuities in the potential the wavefunction and its derivatives need to be continuous at $x = \pm a$, which will give us the four matching conditions we were looking for

$$\mathrm{e}^{-\mathrm{i}ka} + R\mathrm{e}^{\mathrm{i}ka} = A\mathrm{e}^{-\mathrm{i}qa} + B\mathrm{e}^{\mathrm{i}qa} \tag{8.34}$$

$$\mathrm{i}k\big(\mathrm{e}^{-\mathrm{i}ka} - R\mathrm{e}^{\mathrm{i}ka}\big) = \mathrm{i}q\big(A\mathrm{e}^{-\mathrm{i}qa} - B\mathrm{e}^{\mathrm{i}qa}\big) \tag{8.35}$$

$$A\mathrm{e}^{\mathrm{i}qa} + B\mathrm{e}^{-\mathrm{i}qa} = T\mathrm{e}^{\mathrm{i}ka} \tag{8.36}$$

$$\mathrm{i}q\big(A\mathrm{e}^{\mathrm{i}qa} - B\mathrm{e}^{-\mathrm{i}qa}\big) = \mathrm{i}kT\mathrm{e}^{\mathrm{i}ka} \tag{8.37}$$

Solving this linear system of equations is straightforward if a bit tedious, the solution is

$$A = \frac{k(q+k)\mathrm{e}^{-\mathrm{i}(q+k)a}}{2kq\cos(2qa) - \mathrm{i}(q^2+k^2)\sin(2qa)} \tag{8.38}$$

$$B = \frac{k(q-k)\mathrm{e}^{\mathrm{i}(q-k)a}}{2kq\cos(2qa) - \mathrm{i}(q^2+k^2)\sin(2qa)} \tag{8.39}$$

$$R = \frac{\mathrm{i}(q^2-k^2)\mathrm{e}^{-2\mathrm{i}ka}\sin(2qa)}{2kq\cos(2qa) - \mathrm{i}(q^2+k^2)\sin(2qa)} \tag{8.40}$$

$$T = \frac{2kq\mathrm{e}^{-2\mathrm{i}ka}}{2kq\cos(2qa) - \mathrm{i}(q^2+k^2)\sin(2qa)} \tag{8.41}$$

From here we can compute the probabilities of reflection and transmission

$$P_{\mathrm{ref}} = |R|^2 = \frac{(q^2-k^2)^2\sin^2(2qa)}{4k^2q^2\cos^2(2qa) + (q^2+k^2)^2\sin^2(2qa)} \tag{8.42}$$

$$P_{\mathrm{trans}} = |T|^2 = \frac{4k^2q^2}{4k^2q^2\cos^2(2qa) + (q^2+k^2)^2\sin^2(2qa)} \tag{8.43}$$

which sum to 1 as they should.

These expressions are more complicated than we had previously but we can still draw some important conclusions. Firstly, if $E \gg V$ then $q \to k$ and the probability of reflection goes to zero, this is exactly the behaviour we had previously, for large enough energies the particles doesn't notice the barrier. For $E \to V$ then $q \to 0$ and the probability of transmission goes to zero, once more as we lower the energy to be closer to the height of the potential we get closer to total reflection.

Additionally, for $\sin(2qa) = 0$ the probability of reflection vanishes and we obtain total transmission. This is called *transmission resonance* and is in fact observed in the scattering of low energy electrons from a gas of noble atoms such as neon or argon. For our case it happens at energies given by

$$E = V + \frac{n^2\pi^2\hbar^2}{8ma^2} \tag{8.44}$$

where $n \in \mathbb{Z}$. Note how these energies are highly dependent on the specifics of our potential. We have to really fine tune our incoming energy/momentum to observe this transmission resonance.

Finally, let us consider energies lower than the potential barrier $E < V$. Our intermediate wavenumber becomes complex, giving rise to real wavefunctions inside the potential, however, now a sum of decaying and rising exponentials. Defining as before

$$\eta \equiv -\mathrm{i}q = \frac{\sqrt{2m(V-E)}}{\hbar} \tag{8.45}$$

we can write down the new coefficients

$$A = \frac{k(\eta - \mathrm{i}k)\mathrm{e}^{-\mathrm{i}ka}\mathrm{e}^{\eta a}}{2k\eta\cosh(2\eta a) - \mathrm{i}(k^2 - \eta^2)\sinh(2\eta a)} \tag{8.46}$$

$$B = \frac{k(\eta + \mathrm{i}k)\mathrm{e}^{-\mathrm{i}ka}\mathrm{e}^{-\eta a}}{2k\eta\cosh(2\eta a) - \mathrm{i}(k^2 - \eta^2)\sinh(2\eta a)} \tag{8.47}$$

$$R = \frac{-\mathrm{i}(\eta^2 + k^2)\mathrm{e}^{-2\mathrm{i}ka}\sinh(2\eta a)}{2k\eta\cosh(2\eta a) - \mathrm{i}(k^2 - \eta^2)\sinh(2\eta a)} \tag{8.48}$$

$$T = \frac{2k\eta\mathrm{e}^{-2\mathrm{i}ka}}{2k\eta\cosh(2\eta a) - \mathrm{i}(k^2 - \eta^2)\sinh(2\eta a)} \tag{8.49}$$

and the new probabilities

$$P_{\text{ref}} = \frac{(\eta^2 + k^2)^2\sinh^2(2\eta a)}{4k^2\eta^2 + (k^2 + \eta^2)^2\sinh^2(2\eta a)} \tag{8.50}$$

$$P_{\text{trans}} = \frac{4k^2\eta^2}{4k^2\eta^2 + (k^2 + \eta^2)^2\sinh^2(2\eta a)} \tag{8.51}$$

Now, despite using non-normalisable states we have managed to calculate the probability that a quantum particle traverses a barrier even if the incoming energy is lower than the height of the potential. This phenomenon of crossing a classically forbidden region is called *tunnelling* and is one of the key features of quantum mechanics. Examples of tunnelling nature are the emission of alpha particles who would be trapped by a large potential barrier and cold emission of electrons in a metal. Neither of these is well described by our simple constant potential model, but both correspond to particles that traverse a potential barrier higher than their kinetic energy would have allowed.

Despite the experimental success you might still be uneasy. After all, there is a very good reason those regions were classically forbidden—energy conservation. How can our results be consistent with energy conservation? We can look to the uncertainty principle to get a heuristic picture of how this comes about. In order to measure negative kinetic energies we would need to localise the particle with an accuracy

$$\Delta X \gtrsim 2a \tag{8.52}$$

but this implies an uncertainty in momentum of

$$\Delta P \gtrsim \frac{\hbar}{2a} \tag{8.53}$$

and therefore an uncertain in energy of

$$\Delta E \gtrsim \frac{\hbar^2}{8ma^2} \tag{8.54}$$

Additionally, in order to be sure we observe negative energy this uncertainty would have to be less than $V - E$ and therefore

$$\frac{\hbar^2\eta^2}{2m} \gtrsim \Delta E \gtrsim \frac{\hbar^2}{8ma^2} \tag{8.55}$$

combining these two we find we would need, at the very least,

$$2\eta a \gtrsim 1 \tag{8.56}$$

However, in the limit $2\eta a \gg 1$ we have

$$P_{\text{trans}} \approx \frac{16\eta^2 k^2}{(k^2+\eta^2)^2} \mathrm{e}^{-4\eta a} \tag{8.57}$$

which decays exponentially! Even moderate values for $2\eta a$ would yield a completely negligible transmission probability. So, in order to have enough precision to actually detect a particle with negative energy directly the probability for that event is vanishingly small. What we are instead able to observe is the frequency of particles that escape even when they classically shouldn't. Even then this exponential suppression is the origin of the long half lives of these kinds of decays.

Our result only applies for a constant potential, but we can actually use a heuristic argument to obtain a more generalised expression. First note that the dependence on a of (8.57) is only through the exponential, the pre-factor being just a function of the incoming energy. This allows us to write

$$\log P_{\text{trans}} = \text{const} - 2\eta L \tag{8.58}$$

where we wrote $L = 2a$ as the width of the barrier. For a generic barrier shape we can approximate it as many thin square barriers

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Assuming that the probability of going through each slice is independent, the total probability of going through the whole barrier will be given the product of the probabilities of going through each individual slice. We can therefore write, up to a constant

$$\log P_{\text{total}} \approx \sum \log P_{\text{slice}} = -2 \sum L_{\text{slice}} \eta_{\text{slice}} \approx -2 \int \mathrm{d}x\, \eta(x) \tag{8.59}$$

where

$$\eta(x) = \frac{\sqrt{2m(V(x)-E)}}{\hbar} \tag{8.60}$$

All in all we wish to write something on the lines of

$$P_{\text{total}} = C \exp\left(-\frac{2}{\hbar} \int \mathrm{d}x\, \sqrt{2m(V(x)-E)}\right) \tag{8.61}$$

Now of course our "derivation" was not very rigorous at all. Crucially, we had to assume that the length of each slice was small, but in order to apply (8.57) we need $\eta a \gg 1$ so in fact we need $\eta \gg a^{-1}$; this in particular means we have no hope of trusting our approximation when $V(x) \sim E$ *i.e.* near the edges of our barrier.

Despite all of those objections (8.61) will turn out to be basically correct, its the true justification comes via the semi-classical approximation methods developed by Harold Jeffreys and later independently rediscovered by Gregor Wentzel, Hendrik Anthony Kramers, and Léon Brillouin, usually called the WKBJ approximation.

8.3 Bound states in a potential well

So far we have restricted our attention to potential barriers, *i.e.* to $V > 0$. What happens we let V drop bellow zero so that we are considering a potential well? In this section we shall consider the potential

$$V(x) = \begin{cases} -V_0 & -a < x < a \\ 0 & \text{otherwise} \end{cases} \tag{8.62}$$

where $V_0 > 0$.

For $E > 0$ the conclusions from the previous section continue to hold with no changes at all. Our analysis was only dependent on the sign of $E - V$ not on the sign of V itself. The only distinction is that now we won't be able to have $V > E > 0$ to observe tunnelling.

The main difference is that now we are allowed to consider $E < 0$. In that case it is k that will become complex, so we define

$$\lambda = -\mathrm{i}k = \frac{\sqrt{-2mE}}{\hbar} \tag{8.63}$$

such that the generic solution for $|x| > a$ will be

$$\psi(x) = A\mathrm{e}^{-\lambda x} + B\mathrm{e}^{\lambda x} \tag{8.64}$$

Asymptotically we no longer have free particles, we instead have growing/decaying real exponentials. In fact, it is not too hard to show that the flux vanishes for any $|x| > a$. Consequently, we must consider normalisable wavefunctions as we don't have the particle beam interpretation to help us. This implies we can only have decaying exponentials, *i.e.*

$$\psi(x) = \begin{cases} A\mathrm{e}^{\lambda x} & x < -a \\ B\mathrm{e}^{-\lambda x} & x > a \end{cases} \tag{8.65}$$

Therefore, our particle almost certainly lies between $x = -a$ and $x = a$. For this reason these states are called *bound states.*

In the region the potential is non-zero q will be real and therefore our wavefunction will be given by

$$\psi(x) = C\mathrm{e}^{-\mathrm{i}qx} + D\mathrm{e}^{-\mathrm{i}qx} \quad \text{for} \quad -a < x < a \tag{8.66}$$

where

$$q = \frac{\sqrt{2m(E + V_0)}}{\hbar} \tag{8.67}$$

To fix these four constants we will need to impose continuity of the wavefunction and its derivative at $x = \pm a$, and at the end we normalise it. We can however make our lives easier if we exploit parity. Our potential is invariant under parity and therefore so is our Hamiltonian. Using the results from Section 6.3, we know that we can restrict our attention to eigenstates of parity, *i.e.* to wavefunctions which are even or odd functions of x. Let us consider these two cases in turn.

Parity-even wavefunctions Let us look for energy eigenstates among parity-even wavefunctions, *i.e.* ones that satisfy

$$\psi(x) = \psi(-x) \tag{8.68}$$

Imposing this condition on (8.65) and (8.66) we find

$$A = B \quad C = D \tag{8.69}$$

which allows us to write (we have relabelled $C \to C/2$ for convenience)

$$\psi(x) = \begin{cases} A\mathrm{e}^{-\lambda|x|} & |x| > a \\ C\cos(qx) & |x| < a \end{cases} \tag{8.70}$$

Because we are dealing with an even-parity wavefunction we only need to impose continuity conditions at one of the points, taking $x = a$ we obtain

$$\begin{aligned} A\mathrm{e}^{-\lambda a} =& C\cos(qa) && (8.71) \\ -\lambda A\mathrm{e}^{-\lambda a} =& -Cq\sin(qa) && (8.72) \end{aligned}$$

Dividing these two equations we find

$$\lambda = q\tan(qa) \tag{8.73}$$

Using the fact both λ and q are merely functions of E and V_0 we can interpret this as an equation for the allowed energy levels for the parity-even eigenfunctions. Despite the simplicity of our potential this is a transcendental equation with no closed form solution. We can however glean some properties of the solutions by looking at graphs.

Re-writing (8.67) as

$$q^2 + \lambda^2 = \frac{2mV_0}{\hbar^2} \tag{8.74}$$

we can see that the allowed energies correspond to the intersection of the function

$$f(z) = z\tan z \tag{8.75}$$

with a circle of radius $2mV_0a^2/\hbar^2$. Where in our old variables $z = qa$ and $f(z) = \lambda a$.

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It is clear from the fact the circle has a finite radius that for any given V_0 there will be a finite set of discrete solutions. Further, because $z\tan z$ intersects the origin and then grows monotonically, no matter how small the radius of the circle is, there will always be at least one intersection. The number of additional solutions will depend on our parameters. In particular, the way we have set up our graph, the only thing that varies is the radius of the circle, which increases with both V_0 and a. Therefore we conclude that both a deeper and/or a wider potential well would have more possible energy eigenvalues. Specifically, in the limit $V_0 \to \infty$ keeping a fixed, the intersections will basically be at the point where $\tan z$ diverges, *i.e.* $z \approx (n - 1/2)\pi$ for $n \in \mathbb{Z}$. In this limit, the energies of course will blow up, but the difference between the energy and the bottom of the potential remains constant

$$E + V_0 \approx \frac{\hbar^2\pi^2(2n-1)^2}{8ma^2} \tag{8.76}$$

which are the energy levels for our particle in the box! The reason we only get the odd levels is because we are only looking at parity even wavefunctions. We see here that our particle in a box was much closer to a potential well than to a free particle.

We can also have an approximate location for the intersections. The n^{th} intersection will have to occur in between a zero of $\tan z$ and the next divergence, *i.e.*

$$(n-1)\pi < z < \left(n - \frac{1}{2}\right)\pi \tag{8.77}$$

To obtain the full solutions we would have to plug in the relation between A and C and then normalise the wavefunction. We will not bother because it is not very instructive. The most important result is the energy levels rather than accurate probabilities for the position of the particle. We will nevertheless remark on a tunnelling-adjacent phenomenon. For negative energies, classically, we would have expected that the particle would have been fully trapped between $x = -a$ and $x = a$, however, solving for A and C gives non-zero solutions for both, which means the particle has a non-zero probability to be found *outside* the well. Just as with tunnelling this probability is exponentially small.

Parity-odd solutions The procedure is very similar to the parity-even case. We are now looking for wavefunctions that obey

$$\psi(x) = -\psi(-x) \tag{8.78}$$

therefore we must impose

$$A = -B \quad C = -D \tag{8.79}$$

which allows us to write (once again relabelling C to something more convenient)

$$\psi(x) = \begin{cases} \mathrm{sgn}(x) A \mathrm{e}^{-\lambda|x|} & |x| > a \\ C \sin(qx) & |x| < a \end{cases} \tag{8.80}$$

The continuity relations will look like

$$A\mathrm{e}^{-\lambda a} = C \sin(qa) \tag{8.81}$$

$$-\lambda A\mathrm{e}^{-\lambda a} = Cq \cos(qa) \tag{8.82}$$

Once again diving the two gives

$$\lambda = -q \cot(qa) \tag{8.83}$$

This is still a transcendental equation which we can only solve graphically. We can still use (8.74) to give our solution as an intersection of a circle of radius $2mV_0a^2/\hbar^2$ with the function

$$f(z) = -z \cot z \tag{8.84}$$

where $z = qa$ and $f(z) = \lambda a$.

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The main difference with the previous case is that $f(z)$ starts out negative, so the first intersection can only occur after the first zero of $\cot z$. This means that there is a minimum radius for the circle below which there is no parity-odd solution. Given the cotagent function has its first zero at $z = \pi/2$ we conclude there are only parity-odd eigenfunctions if

$$\frac{2mV_0a^2}{\hbar^2} > \frac{\pi^2}{4} \tag{8.85}$$

If the potential is too shallow or too narrow we will only have parity-even eigenfunctions.

The rest of the analysis is very similar, we can even take the $V_0 \to \infty$ limit to find the solutions we were missing for the particle in the box limit. The divergences of cot happen for $z = n\pi$, which gives us:

$$E + V_0 \approx \frac{\hbar^2\pi^2(2n)^2}{8ma^2} \tag{8.86}$$

Only even integers contribute.

8.4 * Bound states from poles in scattering amplitudes

In the previous section, the use of parity eigenfunctions was quite helpful in finding the bound state energies. Nevertheless, for the scattering experiments we did not use parity eigenfunctions, we instead were considering sending particles from $x \to -\infty$. Let us see what we can learn from using parity eigenfunctions.

Parity eigenfunction solutions can be constructed from linear combinations of (8.29). Namely, denoting ψ_+ to be the parity-even solution and ψ_- to be the parity-odd solution we can write

$$\psi_\pm(x) = \psi(x) \pm \psi(-x) = \begin{cases} \mathrm{e}^{\mathrm{i}kx} + (R \pm T)\mathrm{e}^{-\mathrm{i}kx} & x < -a \\ (A \pm B)\mathrm{e}^{\mathrm{i}kx} + (B \pm A)\mathrm{e}^{-\mathrm{i}kx} & -a < x < a \\ \pm\mathrm{e}^{-\mathrm{i}kx} + (T \pm R)\mathrm{e}^{\mathrm{i}kx} & x > a \end{cases} \tag{8.87}$$

In this basis we no longer have the easy interpretation of reflection and transmission amplitudes. Nevertheless, some straightforward (if fiddly) trigonometric manipulations allow us to simplify the sum and difference of R and T to

$$R + T = \mathrm{e}^{-2\mathrm{i}ka} \frac{\mathrm{i}k - q\tan(qa)}{\mathrm{i}k + q\tan(qa)} \tag{8.88}$$

$$R - T = -\mathrm{e}^{-2\mathrm{i}ka} \frac{q + \mathrm{i}k\tan(qa)}{q - \mathrm{i}k\tan(qa)} \tag{8.89}$$

which makes it easy to show that

$$|R \pm T|^2 = 1 \tag{8.90}$$

and therefore, these coefficients are just phases.

Our scenario is then the following. We have an incoming wavefunction of $\mathrm{e}^{-\mathrm{i}|x|}$ or $-\mathrm{sgn}(x)\mathrm{e}^{-\mathrm{i}|x|}$, respectively parity-even and parity-odd. That is, in order to have a parity eigenfunction we need to have incoming particles coming from both direction, with either sign.

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Our outgoing wavefunctions are given by $(R+T)\mathrm{e}^{\mathrm{i}k|x|}$ or $-\mathrm{sgn}(x)(R-T)\mathrm{e}^{\mathrm{i}k|x|}$, respectively parity-even and parity-odd. Which also involve outgoing particles in both directions.

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However, as expected, the outgoing wavefunction keeps its parity, that is, if we send a parity-even/odd wavefunction we will witness an outgoing parity-even/odd wavefunction. The coefficients $R \pm T$ therefore characterise the *phase shift* between the incoming and outgoing wavefunctions. The idea that the scattering experiment can be described by phase shifts in the appropriate basis will continue to be important in more general circumstances.

What is more interesting is that, we can use the expressions (8.88) and (8.89) to actually derive the *bound state* energies! To do, we first analytically continue our solution to imaginary k, defining $\lambda = -\mathrm{i}k$. Our solution (ignoring the middle bit) will then look like

$$\psi_\pm(x) = \begin{cases} \mathrm{e}^{-\lambda x} + (R \pm T)\mathrm{e}^{\lambda x} & x < -a \\ \pm\mathrm{e}^{\lambda x} + (T \pm R)\mathrm{e}^{-\lambda x} & x > a \end{cases} \tag{8.91}$$

but this involves growing exponentials! It seems like it is not a solution at all. Nonetheless, we can use a trick to obtain the correct bound state solution. Just multiply the wavefunction by $(R{\pm}T)^{-1}$. After all, we are always allowed to multiply a wavefunction by a phase factor without changing the physics. We then obtain

$$\psi_\pm(x) = \begin{cases} \frac{1}{R\pm T}\mathrm{e}^{-\lambda x} + \mathrm{e}^{\lambda x} & x < -a \\ \frac{\pm 1}{R\pm T}\mathrm{e}^{\lambda x} \pm \mathrm{e}^{-\lambda x} & x > a \end{cases} \tag{8.92}$$

But, if $R \pm T$ would blow up, then the growing exponentials would be multiplied by zero, leading to normalisable wavefunctions. In fact, we can check that for $\lambda = -\mathrm{i}k$ the expressions (8.88) and (8.89) blow up if

$$\lambda = q\tan(qa) \tag{8.93}$$

$$\lambda = -q\cot(qa) \tag{8.94}$$

which are precisely the bound state energy equations for parity-even and parity-odd eigenfunctions!

This is a very simple example of a general phenomena. Poles in scattering amplitudes correspond to bound states. In fact, in particle physics one often only has access to the scattering amplitudes and we look for bound states by trying to find these poles. Experimentally this is born out by finding *resonances* in the scattering of certain particles. In fact, this is how the Z and the Higgs boson were discovered.

INSERT PLOTS FROM BOTH EXPERIMENTS

9 The harmonic oscillator

In many ways the harmonic oscillator is the most important physical system. Firstly, it is exactly solvable, both in classical and quantum mechanics alike we can solve for the motion of the harmonic oscillator exactly without having to resort to approximations or numerics. Secondly, it is a good approximation for any physical system near a stable equilibrium. This means that a large class of physical systems can be studied via perturbations of the harmonic oscillator, making the exact results an important basis for many applications. Finally it is the basis for most field theories. Although it is beyond the scope of these notes, the beginnings of quantum field theories and particle physics will rely on mathematics which are based on the harmonic oscillator. In fact, it is often said that a quantum field is merely a collection of interacting harmonic oscillators. Although not quite true it still highlights the importance of this system[73].

Our goal in this chapter to find the spectrum of the following Hamiltonian

$$H = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 X^2 \tag{9.1}$$

where ω classically would correspond to the natural angular frequency for the oscillations. This will also bear out in the quantum scenario but for the time being can be taken as just a free parameter dictating the strength of the oscillator.

This problem is so crucial that we will in fact solve it twice. We will first use Schrodinger-like methods similar to those employed in the previous chapter to just outright solve the differential equation that (9.1) gives in the position basis. This highlights important features of the solutions and exemplifies useful methods for solving the Schrodinger equation. After this we will re-derive all of our results using Heisenberg-like methods. The harmonic oscillator is simple enough that there exists a slick purely algebraic derivation of its spectrum. In turn this will introduce the language of raising and lowering operators which will be crucial throughout all of quantum physics.

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[73] A former lecturer of mine used to joke that physicists only know how to solve two problems: the free particle and the harmonic oscillator. All others have to either be reduced to one of these or treated perturbatively.

9.1 Solving the differential equation

The TISE in the position basis for the harmonic oscillator looks like

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}+\frac{1}{2}m\omega^2x^2\psi(x)=E\psi(x) \tag{9.2}$$

We can simplify this equation by defining new variables

$$y=\sqrt{\frac{m\omega}{\hbar}}x \tag{9.3}$$

$$\mathcal{E}=\frac{2E}{\hbar\omega} \tag{9.4}$$

in terms of which the equation becomes

$$\frac{\mathrm{d}^2\psi(y)}{\mathrm{d}y^2}+\left(\mathcal{E}-y^2\right)\psi(y)=0 \tag{9.5}$$

To solve this equation we will first try to look at the large y limit. In this limit, the $\mathcal{E}$ term is negligible, so we find

$$\frac{\mathrm{d}^2\psi(y)}{\mathrm{d}y^2}-y^2\psi(y)\approx 0 \tag{9.6}$$

which is approximately solved by

$$\psi(y)\approx A\mathrm{e}^{-y^2/2}+B\mathrm{e}^{y^2/2} \tag{9.7}$$

Note that this isn't an exact solution of (9.6), it is only an approximate solution in the large y limit, in fact

$$\frac{\mathrm{d}^2\psi(y)}{\mathrm{d}y^2}=Ay^2\mathrm{e}^{-y^2/2}+By^2\mathrm{e}^{y^2/2}-A\mathrm{e}^{-y^2/2}+B\mathrm{e}^{y^2/2} \tag{9.8}$$

which does satisfy (9.6) if the last two terms are negligible.

However, the B term grows exponentially, therefore it cannot correspond to a normalisable wavefunction. We must therefore take $B=0$ and have only that

$$\psi(y)\to A\mathrm{e}^{-y^2/2} \tag{9.9}$$

as $y^2\to\infty$.

All in all this motivates peeling off this exponential behaviour and defining

$$\psi(y)\equiv h(y)\mathrm{e}^{-y^2/2} \tag{9.10}$$

Note that even if our motivation for this exponential behaviour involved some approximations, this definition is *exact*. We are not making any approximations in the definition of $h(y)$. This method of peeling the asymptotic behaviour is very common when solving differential equations. In terms of $h(y)$ we have

$$h''(y)-2yh'(y)+(\mathcal{E}-1)h(y)=0 \tag{9.11}$$

Let us try a power series solution for $h(y)$:

$$h(y)=\sum_{n=1}^{\infty}a_ny^n \tag{9.12}$$

plugging this in we find the following recursion relation for the coefficients a_n

$$(n+2)(n+1)a_{n+2} = (2n+1-\mathcal{E})a_n \tag{9.13}$$

Given a_0 and a_1, this recursion relation completely determines $h(y)$. The fact we have to fix two coefficients comes from the fact we are solving a second order differential equation. Further notice how odd powers of y are completely independent from the even powers of y. This is to be expected from the parity invariance of the Hamiltonian. We can split our solutions into parity-even ones, only involving even powers of y, and parity-odd ones, only involving odd powers of y.

For arbitrary $\mathcal{E}$ let us examine the asymptotic behaviour of this series, *i.e.* the limit $n \to \infty$. In this limit, the recursion relation is given approximately by

$$a_{n+2} = \frac{2}{n} a_n \tag{9.14}$$

This can be approximately solved using factorials

$$a_n \approx \frac{C}{(n/2)!} \tag{9.15}$$

as can be seen from

$$\frac{(n/2)!}{(n/2+1)!} = \frac{1}{n/2+1} \approx \frac{2}{n} \tag{9.16}$$

In that case, asymptotically, $h(y)$ would be given by

$$h(y) \to \sum_n C \frac{y^n}{(n/2)!} = \sum_{n'} C \frac{y^{2n'}}{n'!} = C\mathrm{e}^{y^2} \tag{9.17}$$

But this is bad, it means

$$\psi(y) \to C\mathrm{e}^{y^2/2} \tag{9.18}$$

which is again not normalisable! It's that pesky B term that we were trying to get rid of. We got it back because the equation for h was exact, we *had* to find it once more. Now we must get rid of it.

The only way out of this conundrum is if the series terminates at some a_n. This would impede us from using this asymptotic and obtaining exponential growth. In order for this series to terminate, there must be an $n \in \mathbb{Z}$ such that

$$2n + 1 - \mathcal{E} = 0 \tag{9.19}$$

In turn this implies that the only allowed energies are

$$\mathcal{E}_n = 2n+1 \implies E_n = \hbar\omega\left(n + \frac{1}{2}\right) \tag{9.20}$$

Note that the equation (9.11) has solutions for any $\mathcal{E} \in \mathbb{R}$, the restriction to $\mathcal{E}_n$ comes from further demanding the solution falls off at infinity quickly enough to be normalisable. Once again it is the boundary conditions that give us quantisation

INSERT PICTURE WITH THE SOLUTION FOR E SLIGHTLY ABOVE AND SLIGHTLY BELOW THE ALLOWED VALUE

There are two features of this energy quantisation condition which are very worth emphasising. Firstly, even the ground state as energy $E_0 = \frac{1}{2}\hbar\omega$. This *zero-point energy* is a common feature of quantum mechanics, and ultimately is the source of one of the unsolved problems in physics, the *cosmological constant problem*, where the naive expectation for the zero-point energy in quantum fields is 120 orders of magnitude off from the measured value. In more mundane scenarios, this zero-point energy is the origin of the fact that helium remains liquid even close to absolute zero (at normal pressures), its zero point energy is enough to preclude its freezing.

Secondly, the difference between two energy eigenvalues is always an integer multiple of $\hbar\omega$. This fact was the original motivation for the introduction of the Planck constant. In order to explain black-body radiation Max Planck supposed the light inside the box was composed of a large number of oscillators whose energies would be $\hbar\omega$. We have now re-derived this fact which was originally just an incredible guess.

To obtain the eigenfunctions we insert the quantised energies into our recursion relation, finding (after relabelling our dummy variable $n \to j$)

$$a_{j+2} = 2\frac{j-n}{(j+2)(j+1)}a_j \tag{9.21}$$

The solution being polynomials of degree n. Luckily for us they have a special name, they are called *Hermite polynomials*. They are normalised such that the coefficient of the x^n term is 2^n and are denoted by $H_n(y)$. The first five are given by

$$H_0(y) = 1 \tag{9.22}$$

$$H_1(y) = 2y \tag{9.23}$$

$$H_2(y) = 4y^2 - 2 \tag{9.24}$$

$$H_3(y) = 8y^3 - 12y \tag{9.25}$$

$$H_4(y) = 16y^4 - 48y^2 + 12 \tag{9.26}$$

$$H_5(y) = 32y^5 - 160y^3 + 120y \tag{9.27}$$

notice how even-numbered polynomials only involve even powers of y and similarly for the odd-numered ones.

There are many important properties of these polynomials but the most important one is their orthogonality

$$\int \mathrm{d}y\, \mathrm{e}^{-y^2} H_n(y)H_m(y) = 2^n n!\sqrt{\pi}\ \delta_{nm} \tag{9.28}$$

The fact they are orthogonal was to be expected because they arise from eigenfunctions of a Hermitian operator H with distinct eigenvalues. The specific normalisation allows us to write the normalised wavefunctions as

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) \mathrm{e}^{-\frac{m\omega x^2}{2\hbar}} \tag{9.29}$$

with energy $E_n = \hbar\omega(n + 1/2)$.

INSERT PLOTS OF A FEW EIGENFUNCTIONS

Looking at the graphs a couple of qualitative features are clear. The ground state is just a Gaussian centred on the equilibrium point. Higher order eigenfunctions will oscillate giving rather complex patterns of where the particle is most likely to be. Nevertheless, note that both $\langle X\rangle = 0$ and $\langle P\rangle = 0$, which is what we expect classically from a particle oscillating in a quadratic potential. Additionally, notice that once more, the quantum particle has a non-zero probability of being found in the classically forbidden region. Even if this probability is exponentially suppressed.

Finally, if we plot the wavefunction for very high n we get

INSERT PICTURE

On average, we see that the particle is more likely to be found near the turning points. This would also be true classically, as the particle is turning it slows down, so if you take a photo at a random time you are much more likely to find it near those points that at the middle were it is moving quite fast. This highlights another common feature of quantum mechanics, for larger energies we approach classical behaviour.

9.2 Raising and lowering operators

The method of the previous section was quite successful but took some hard work. There is however a trick if we use the Heisenberg picture. The Heisenberg equations of motion for X and P are

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \frac{P}{m} \tag{9.30}$$

$$\frac{\mathrm{d}P}{\mathrm{d}t} = -m\omega^2 X \tag{9.31}$$

These are simple but they are are not diagonal. It would extremely convenient if we managed to find a linear combination of X and P such that these equations of motion were diagonal. Let us define a new operator

$$A = \alpha X + \beta P \tag{9.32}$$

such that its Heisenberg evolution is given by

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \lambda A \tag{9.33}$$

To find α, β, and λ we impose (9.31):

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \alpha\frac{\mathrm{d}X}{\mathrm{d}t} + \beta\frac{\mathrm{d}P}{\mathrm{d}t} = \alpha\frac{P}{m} - \beta m\omega^2 X \tag{9.34}$$

equating with (9.33) we get

$$\begin{cases} -\beta m\omega^2 = \lambda\alpha \\ \frac{\alpha}{m} = \lambda\beta \end{cases} \implies \begin{cases} \lambda^2 = -\omega^2 \\ \beta = \frac{\alpha}{m\lambda} \end{cases} \tag{9.35}$$

In particular λ is pure imaginary and we can write

$$\frac{\mathrm{d}A^\pm}{\mathrm{d}t} = \pm\mathrm{i}\omega A^\pm \tag{9.36}$$

where

$$A^\pm = \alpha\left(X \mp \frac{\mathrm{i}}{m\omega}P\right) \tag{9.37}$$

These operators have a particularly simple time dependence:

$$A^\pm(t) = \mathrm{e}^{\pm\mathrm{i}\omega t}A^\pm(0) \tag{9.38}$$

The normalisation, as is usual with these sorts of problems is free to choose. The conventional choice for α can be motivated by looking at the commutator

$$\left[A^-, A^+\right] = \alpha^2\left(-\frac{\mathrm{i}}{m\omega}[X,P] + \frac{\mathrm{i}}{m\omega}[P,X]\right) = \frac{2\alpha^2\hbar}{m\omega} \tag{9.39}$$

We define the normalisation by setting this commutator to 1, correspond to the choice

$$\alpha = \frac{m\omega}{2\hbar} \tag{9.40}$$

With this choice it is straightforward to see that $A^- = (A^+)^\dagger$. Because these are not Hermitian operators they won't correspond to observables so we won't try to diagonalise them and so we don't need a distinction between the operator and its eigenvalue. Therefore we can use the more conventional notation of lower case for these operators:

$$a = \sqrt{\frac{m\omega}{2\hbar}}\left(X + \frac{\mathrm{i}}{m\omega}P\right) \tag{9.41}$$

which obey

$$\left[a, a^\dagger\right] = 1 \tag{9.42}$$

and whose time dependence in the Heisenberg picture is given by

$$a(t) = a(0)\mathrm{e}^{-\mathrm{i}\omega t} \tag{9.43}$$

We can also invert this definition to write X and P in terms of a and $a^\dagger$:

$$X = \sqrt{\frac{\hbar}{2m\omega}}\left(a + a^\dagger\right) \tag{9.44}$$

$$P = -\mathrm{i}\sqrt{\frac{\hbar m\omega}{2}}\left(a - a^\dagger\right) \tag{9.45}$$

and plug these expressions back into the Hamiltonian to find

$$H = \frac{\hbar\omega}{2}\left(aa^\dagger + a^\dagger a\right) = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right) \tag{9.46}$$

where in the last equality we used (9.42). With this expression you can already see the $\frac{1}{2}\hbar\omega$ zero-point energy. We haven't proved that this is the energy of the ground state, but you can already see that term.

Using the above expressions it is also straightforward to show that

$$[H, a] = -\hbar\omega a \quad \left[H, a^\dagger\right] = \hbar\omega a^\dagger \tag{9.47}$$

these commutation relations are the key to finding the spectrum. Diagonalising the Heisenberg equations of motion was merely a motivation to find operators which would obey these commutation relations with the Hamiltonian. For, imagine $|E\rangle$ is an eigenstate of the Hamiltonian with energy E:

$$H|E\rangle = E|E\rangle \tag{9.48}$$

then the state $a|E\rangle$ will also be an energy eigenstate but with energy $E - \hbar\omega$

$$Ha|E\rangle = ([H,a] + aH)|E\rangle = (E - \hbar\omega)a|E\rangle \tag{9.49}$$

Similarly, the ket $a^\dagger |E\rangle$ will have energy $E + \hbar\omega$

$$Ha^\dagger |E\rangle = \left(\left[H, a^\dagger\right] + a^\dagger H\right) |E\rangle = (E + \hbar\omega)a^\dagger |E\rangle \tag{9.50}$$

The operators a and $a^\dagger$ respectively, lower and raise the energy of a given eigenstate by $\hbar\omega$. For this reason they are called *ladder operators* or simply raising and lowering operators. From one eigenstate we can apply a or $a^\dagger$ repeatedly to find other eigenstates.

But we have an issue, if we have a given energy eigenstate $|E\rangle$ then by applying a over and over again we can find eigenstates with arbitrarily low energy. This is very bad physically. If the Hamiltonian is unbounded below then a particle in any state could emit infinite energy as it cascades down the ladder. This is clearly untenable so we must have that there is a state $|0\rangle$ such that

$$a|0\rangle = 0 \tag{9.51}$$

thereby terminating our cascade and finding the lowest energy eigenvalue. This is the *ground state* and it has energy

$$H|0\rangle = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right)|0\rangle = \frac{\hbar\omega}{2}|0\rangle \tag{9.52}$$

The remaining energy eigenstates can be found by repeated application of $a^\dagger$:

$$|n\rangle = C\left(a^\dagger\right)^n |0\rangle \tag{9.53}$$

with energy

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \tag{9.54}$$

which is our energy spectrum from before. Now we managed to find it from purely algebraic means, no differential equations in sight. It is also clear from this approach that the quantisation of the energy eigenvalues came from the fact the Hamiltonian must be bounded below.

We can also find the correct normalisation for these states

$$\begin{aligned}
\langle n|n\rangle &= |C|^2 \langle 0| a^n \left(a^\dagger\right)^n |0\rangle = \\
&= |C|^2 \langle 0| a^{n-1}\left(1 + a^\dagger a\right)\left(a^\dagger\right)^{n-1} |0\rangle = \\
&= 2|C|^2 \langle 0| a^{n-1}\left(a^\dagger\right)^{n-1} |0\rangle + |C|^2 \langle 0| a^{n-1}\left(a^\dagger\right)^2 a\left(a^\dagger\right)^{n-2} |0\rangle = \dots \\
&= n|C|^2 \langle 0| a^{n-1}\left(a^\dagger\right)^{n-1} |0\rangle + |C|^2 \langle 0| a^{n-1}\left(a^\dagger\right)^n a|0\rangle = \\
&= n|C|^2 \langle 0| a^{n-1}\left(a^\dagger\right)^{n-1} |0\rangle = \dots \\
&= n!|C|^2 \langle 0|0\rangle
\end{aligned} \tag{9.55}$$

therefore, if $|0\rangle$ is correctly normalised we should choose $C = \frac{1}{\sqrt{n!}}$ and hence define the normalised energy eigenstates via

$$|n\rangle = \frac{1}{\sqrt{n!}}\left(a^\dagger\right)^n |0\rangle \tag{9.56}$$

In particular we can use this definition to show that

$$a^\dagger |n\rangle = \sqrt{n+1}\,|n+1\rangle \quad \text{and} \quad a|n\rangle = \sqrt{n}\,|n-1\rangle \tag{9.57}$$

We have managed to find the whole energy spectrum in a purely algebraic fashion, no position basis or Schrodinger equation in sight. However, we can easily convert to the position basis and find our previous wavefunctions. First, we find the ground state by imposing

$$\langle x| a |0\rangle = 0 \implies \left(x + \frac{\hbar}{m\omega}\frac{\mathrm{d}}{\mathrm{d}x}\right)\psi_0(x) = 0 \tag{9.58}$$

where $\psi_0(x) = \langle x|0\rangle$. This is an easily solvable first order differential equation

$$\psi_0(x) = B\mathrm{e}^{-\frac{m\omega x^2}{2\hbar}} \tag{9.59}$$

to find B we just impose that $\langle 0|0\rangle = 1$ or equivalently

$$1 = \int \mathrm{d}x\, |\psi_0(x)|^2 = \int \mathrm{d}x\, |B|^2\mathrm{e}^{-\frac{m\omega x^2}{\hbar}} = |B|^2\sqrt{\frac{\pi\hbar}{m\omega}} \tag{9.60}$$

Therefore we must impose $B = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$:

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\mathrm{e}^{-\frac{m\omega x^2}{2\hbar}} \tag{9.61}$$

For higher n we have

$$\begin{aligned}\psi_n(x) &= \frac{1}{\sqrt{n!}}\left(\frac{m\omega}{\pi\hbar}\right)\left(\frac{m\omega}{2\hbar}\right)^{n/2}\left(x - \frac{\hbar}{m\omega}\frac{\mathrm{d}}{\mathrm{d}x}\right)^n \mathrm{e}^{-\frac{m\omega x^2}{2\hbar}} = \\ &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{1}{\sqrt{2^n n!}}\left(y - \frac{\mathrm{d}}{\mathrm{d}y}\right)^n \mathrm{e}^{-y^2/2}\end{aligned} \tag{9.62}$$

where we, once again, defined for convenience

$$y = \sqrt{\frac{m\omega}{\hbar}}x \tag{9.63}$$

This is of course some polynomial of degree n multiplied by $\mathrm{e}^{-y^2/2}$. We can use the Rodrigues's formula

$$H_n(y) = \mathrm{e}^{y^2/2}\left(y - \frac{\mathrm{d}}{\mathrm{d}y}\right)^n \mathrm{e}^{-y^2/2} \tag{9.64}$$

to once again identify the Hermite polynomials. We then obtain

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{1}{\sqrt{2^n n!}}H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right)\mathrm{e}^{-\frac{m\omega x^2}{2\hbar}} \tag{9.65}$$

as expected.

PART

IV

Central Potentials and Angular Momentum

Chapter 10. Spherical symmetry
Chapter 11. Solving the radial equation
Chapter 12. Spin

So far we have focused on 1-dimensional quantum systems, even though the real world is in fact 3-dimensional. Indeed we were entirely missing the physics of rotations and spherical symmetry. We will now look into spherically symmetric quantum systems in 3 spatial dimensions. In particular, we will focus our attention on a single particle subjected to a central potential, *i.e.* one that only depends on the distance to some central point, usually taken as the origin of our frame of reference. Along the way we shall uncover the physics of angular momentum, both orbital and spin, leading to an explanation of the Stern-Gerlach experiment that kicked off our journey.

10 Spherical symmetry

In this chapter we will study particles subjected to a central potential, *i.e.* ones whose potential is given by $V(\boldsymbol{x}) = V(r)$ where $r^2 = |\boldsymbol{x}|^2 = x^2 + y^2 + z^2$. These potentials are special because they exhibit spherical symmetry and will therefore serve as an entry-way to the quantum physics of angular momentum. The canonical example of this type of potentials is the Coulomb potential that an electron experiences in a Hydrogen atom:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \tag{10.1}$$

where $-e$ is the charge of the electron, and ϵ_0 is the vacuum permittivity.

We begin by briefly describing the minor changes that are needed to describe 3-dimensional quantum systems. Then we follow a structure similar to what we used to study the harmonic oscillator. We first use analytic methods to separate the radial and angular components of the wavefunction and solve the angular equations to arrive at the spherical harmonics. Then we use algebraic methods to get at the same separation of variables and interpret the spherical harmonics as eigenfunctions of the angular momentum operator. Interestingly we shall see a small discrepancy between the two methods—the algebraic method allows for half-integer angular momentum which cannot be described using spherical harmonics. In Chapter 12 we shall return to this disparity and see what physics lies there.

10.1 Quantum mechanics in 3 dimensions

Most of the changes needed to describe 3 spatial dimensions are rather trivial, in 3D the position and momentum are vectors, $\boldsymbol{X}$ and $\boldsymbol{P}$. Fourier transforms are now written as

$$\tilde{\psi}(\boldsymbol{k}) = \int \mathrm{d}^3x \, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}} \psi(\boldsymbol{x}) \tag{10.2}$$

with inverse given by

$$\psi(\boldsymbol{x}) = \int \frac{\mathrm{d}^3k}{(2\pi)^3} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}} \tilde{\psi}(\boldsymbol{k}) \tag{10.3}$$

The Dirac-δ is now defined via

$$\int \mathrm{d}^3x\, f(\boldsymbol{x})\delta^{(3)}(\boldsymbol{x}-\boldsymbol{x}') = f(\boldsymbol{x}') \tag{10.4}$$

You can think of this Dirac-δ as the product of the Dirac-δs for the individual directions

$$\delta^{(3)}(\boldsymbol{x}) = \delta(x)\delta(y)\delta(z) \tag{10.5}$$

It can also be represented in terms of Fourier modes as

$$\delta^{(3)}(\boldsymbol{x}) = \int \frac{\mathrm{d}^3k}{(2\pi)^3}\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}} \tag{10.6}$$

The de Broglie relation between wavenumber and momentum will now imply that the momentum in the position basis acts like the gradient operator:

$$\boldsymbol{P} = -\mathrm{i}\hbar\boldsymbol{\nabla} \tag{10.7}$$

therefore, the commutator between the position and momentum gives

$$[X_i, P_i] = \mathrm{i}\hbar\delta_{ij} \tag{10.8}$$

where $i, j = 1, 2, 3$. This is exactly what we would have expected from analogy with the Poisson bracket.

The (time-independent) Schrodinger equation therefore becomes

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(\boldsymbol{x}) + V(r)\psi(\boldsymbol{x}) = E\psi(\boldsymbol{x}) \tag{10.9}$$

where ∇^2 is the 3-dimensional Laplacian:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{10.10}$$

You may noticed we have slightly changed our notation and used μ for the mass rather than m, there are two reasons for this. Firstly, m is conventionally used to denote the quantum number for the z component of the angular momentum. I do recognise this is a rather weak excuse because mass was m before that quantum number. A much better reason is that μ is *not* the mass of the particle, it is in fact the *reduced mass* of the two-body problem, in perfect analogy with the classical definition. Before we proceed let us examine how that bears out in the quantum context.

Central potentials (and in fact most potentials) actually arise from an interaction between two particles, which, because of translation invariance, will only depend on the difference between their positions

$$H = \frac{\boldsymbol{P}_e^2}{2m_e} + \frac{\boldsymbol{P}_N^2}{2m_N} + V(\boldsymbol{X}_e - \boldsymbol{X}_N) \tag{10.11}$$

where the labels e and N refer to “electron” and “nucleon” which would be the case in the Hydrogen atom.

We can now introduce a relative and centre of mass position variables:

$$\boldsymbol{X}_{\mathrm{rel}} \equiv \boldsymbol{X}_e - \boldsymbol{X}_N \quad \boldsymbol{X}_{\mathrm{CM}} = \frac{m_e\boldsymbol{X}_e + m_N\boldsymbol{X}_N}{m_e + m_N} \tag{10.12}$$

and similarly a relative and centre of mass momentum variables

$$\boldsymbol{P}_{\text{rel}} \equiv \mu\left(\frac{\boldsymbol{P}_e}{m_e} - \frac{\boldsymbol{P}_N}{m_N}\right) \qquad \boldsymbol{P}_{\text{CM}} = \boldsymbol{P}_e + \boldsymbol{P}_N \tag{10.13}$$

where

$$\mu \equiv \frac{m_e m_N}{m_e + m_N} \tag{10.14}$$

It is straightforward to then verify that

$$H = \frac{\boldsymbol{P}_{\text{rel}}^2}{2\mu} + \frac{\boldsymbol{P}_{\text{CM}}^2}{2(m_e + m_N)} + V(\boldsymbol{X}_{\text{rel}}) \tag{10.15}$$

You can also verify that the new position and momentum variables satisfy the usual relation:

$$\begin{cases} \boldsymbol{P}_e = -\mathrm{i}\hbar\boldsymbol{\nabla}_e \\ \boldsymbol{P}_N = -\mathrm{i}\hbar\boldsymbol{\nabla}_N \end{cases} \implies \begin{cases} \boldsymbol{P}_{\text{rel}} = -\mathrm{i}\hbar\boldsymbol{\nabla}_{\text{rel}} \\ \boldsymbol{P}_{\text{CM}} = -\mathrm{i}\hbar\boldsymbol{\nabla}_{\text{CM}} \end{cases} \tag{10.16}$$

which in turn means they obey the canonical commutation relations, and additionally, the two sets of variables completely commute

$$[\boldsymbol{P}_{\text{rel}}, \boldsymbol{X}_{\text{CM}}] = [\boldsymbol{X}_{\text{rel}}, \boldsymbol{P}_{\text{CM}}] = 0 \tag{10.17}$$

Therefore the Hamiltonian fully commutes with $\boldsymbol{P}_{\text{CM}}$, so eigenstates of H can also be taken to be eigenstates of $\boldsymbol{P}_{\text{CM}}$, and therefore we can write

$$\psi(\boldsymbol{x}_{\text{CM}}, \boldsymbol{x}_{\text{rel}}) = \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\boldsymbol{p}_{\text{CM}}\cdot\boldsymbol{x}_{\text{CM}}}\psi(\boldsymbol{x}_{\text{rel}}) \tag{10.18}$$

where $\psi(\boldsymbol{x}_{\text{rel}})$ obeys 10.9 if we drop the 'rel' label. The internal energy described by 10.9 is related to the total energy given by 10.11 via

$$E_{\text{tot}} = E + \frac{\boldsymbol{p}_{\text{CM}}^2}{2(m_e + m_N)} \tag{10.19}$$

It seems like a lot of work to justify a simple notational difference but it has experimentally observed consequences. We shall later derive the spectrum of the Hydrogen atom, but it will depend on both the charge and the reduced mass. However, there are several isotopes of Hydrogen, *e.g.* ^{1}H, with a single proton in the nucleons, and ^{2}H with a proton and a neutron, usually called *deuterium*. These have quite different nucleon masses: $m_{^1\text{H}} \approx 1836 m_e$ and $m_{^2\text{H}} \approx 3670 m_e$; and consequently slightly different reduced masses: $\mu_{^1\text{H}} \approx 0.99945 m_e$ and $\mu_{^2\text{H}} = 0.99973 m_e$. However small, this difference has been detected experimentally.

10.2 Spherical harmonics

As is standard in spherically symmetric problems it is convenient to introduce spherical polar coordinates given by

$$x = r\sin\theta\cos\phi \quad y = r\sin\theta\sin\phi \quad z = r\cos\theta \tag{10.20}$$

where $r > 0$, $0 < \phi < 2\pi$, $0 < \theta < \pi$.

INSERT PICTURE WITH DEFINITION OF SPHERICAL COORDINATES

In these coordinates the Laplacian is given by

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{10.21}$$

So that the TISE looks like

$$\begin{aligned}-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi(r,\theta,\phi)}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi(r,\theta,\phi)}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi(r,\theta,\phi)}{\partial\phi^2}\right]+\\ + V(r)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi) \end{aligned}\tag{10.22}$$

This looks rather complicated but we can try separation of variables to solve it. That is we look for solutions of the type:

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\psi) \tag{10.23}$$

in terms of which (10.22) becomes

$$\begin{aligned}\frac{1}{R(r)}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R(r)}{\mathrm{d}r}\right) - \frac{2\mu r^2}{\hbar^2}(V(r)-E) =\\ = -\frac{1}{Y(\theta,\phi)}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}\right)\end{aligned} \tag{10.24}$$

The LHS only depends on r and the RHS only depends on θ and ϕ; therefore they must both equal some constant λ:

$$\frac{1}{R(r)}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R(r)}{\mathrm{d}r}\right) - \frac{2\mu r^2}{\hbar^2}(V(r)-E) = \lambda \tag{10.25}$$

$$-\frac{1}{Y(\theta,\phi)}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2}\right) = \lambda \tag{10.26}$$

Bearing in mind that the integration measure in polar coordinates is

$$\mathrm{d}^3x = r^2\sin\theta\,\mathrm{d}r\,\mathrm{d}\theta\,\mathrm{d}\psi \tag{10.27}$$

the condition that $\psi(r,\theta,\phi)$ is square integrable becomes, in terms of the new variables

$$\int_0^\infty \mathrm{d}r\, r^2|R(r)|^2 < \infty \quad \text{and} \quad \int_0^{2\pi}\mathrm{d}\phi\int_0^\pi \mathrm{d}\theta\sin\theta|Y(\theta,\phi)|^2 < \infty \tag{10.28}$$

we sometimes also write

$$\mathrm{d}^2\Omega = \mathrm{d}\phi\,\mathrm{d}\theta\sin\theta \tag{10.29}$$

as the differential *solid angle* for simplicity.

Let us focus on the angular equation:

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y(\theta,\phi)}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y(\theta,\phi)}{\partial\phi^2} + \lambda Y(\theta,\phi) = 0 \tag{10.30}$$

To solve this equation we once again try separation of variables:

$$Y(\theta,\phi) = P(\theta)\Phi(\phi) \tag{10.31}$$

plugging this in we find:

$$\frac{1}{P(\theta)}\left(\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}P(\theta)}{\mathrm{d}\theta}\right)+\lambda\sin^2\theta P(\theta)\right)=-\frac{1}{\Phi(\phi)}\frac{\mathrm{d}^2\Phi(\phi)}{\mathrm{d}\phi^2} \tag{10.32}$$

and once more we notice that the LHS depends only on θ and the RHS depends only on ϕ to conclude that they must both equal a constant which we write:

$$\frac{1}{P(\theta)}\left(\sin\theta\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}P(\theta)}{\mathrm{d}\theta}\right)+\lambda\sin^2\theta P(\theta)\right)=m^2 \tag{10.33}$$

$$-\frac{1}{\Phi(\phi)}\frac{\mathrm{d}^2\Phi(\phi)}{\mathrm{d}\phi^2}=m^2 \tag{10.34}$$

The condition for square integrability in these variables becomes

$$\int_0^{2\pi}\mathrm{d}\phi\,|\Phi(\phi)|^2<\infty \quad \text{and} \quad \int_0^{\pi}\mathrm{d}\theta\sin\theta|P(\theta)|^2<\infty \tag{10.35}$$

The solution to the ϕ equation is quite straightforward:

$$\Phi(\phi)=C\mathrm{e}^{\pm\mathrm{i}m\phi} \tag{10.36}$$

and from this we obtain our first quantisation condition. In spherical coordinates single-valued functions must be periodic under $\phi\to\phi+2\pi$, the only way this can be true for our solutions is if m is an integer.

To solve the θ equation we first do a change of variables by defining

$$z=\cos\theta \tag{10.37}$$

in terms of which the equation becomes

$$\frac{\mathrm{d}}{\mathrm{d}z}\left((1-z^2)\frac{\mathrm{d}P(z)}{\mathrm{d}z}\right)+\lambda P(z)-\frac{m^2}{1-z^2}P(z)=0 \tag{10.38}$$

Let us first examine the $m=0$ case and try a power series solution

$$P(z)=\sum_{n=0}^{\infty}a_n z^n \tag{10.39}$$

We can then plug this in to derive a recurrence relation among these coefficients

$$(n+2)(n+1)a_{n+2}=(n^2+n-\lambda)a_n \tag{10.40}$$

Similarly to what we did for the harmonic oscillator let us examine the large n behaviour:

$$\frac{a_{n+2}}{a_n}\to 1 \tag{10.41}$$

This means that for large n, the series comes a polynomial in z plus

$$C\sum_n z^n=\frac{C}{1-z} \tag{10.42}$$

but this is singular at $z=1$, or equivalently $\theta=0$. In fact, this solution is not square integrable!

$$\int_0^\pi \mathrm{d}\theta \sin\theta |P(\theta)|^2 = \int_{-1}^1 \mathrm{d}z\, |P(z)|^2 \tag{10.43}$$

but

$$\int_{-1}^1 \mathrm{d}z \, \frac{1}{|1-z|^2} \tag{10.44}$$

is infinite!

The only option is to do what we did for the harmonic oscillator and demand that the series terminates. This means that there exists an integer $\ell \in \mathbb{Z}_0^+$ such that

$$\lambda = \ell(\ell+1) \tag{10.45}$$

Once again it is the boundary conditions that give us quantised quantities. Firstly periodicity in ϕ and then regularity in θ.

The polynomial solutions for $\lambda = \ell(\ell+1)$ and $m = 0$, are called *Legendre polynomials*, and are denoted by $P_\ell(z)$. They obey

$$\frac{\mathrm{d}}{\mathrm{d}z}\left(\left(1-z^2\right)\frac{\mathrm{d}P_\ell(z)}{\mathrm{d}z}\right) + \ell(\ell+1)P_\ell(z) = 0 \tag{10.46}$$

and the first few are given by

$$P_0(z) = 1 \tag{10.47}$$

$$P_1(z) = z \tag{10.48}$$

$$P_2(z) = \frac{1}{2}\left(3z^2-1\right) \tag{10.49}$$

$$P_3(z) = \frac{1}{2}\left(5z^3-3z\right) \tag{10.50}$$

$$P_4(z) = \frac{1}{8}\left(35z^4-30z^2+3\right) \tag{10.51}$$

where they are conventionally normalised such that

$$\int_{-1}^1 \mathrm{d}z\, P_\ell(z)P_{\ell'}(z) = \frac{1}{\ell+\frac{1}{2}}\delta_{\ell\ell'} \tag{10.52}$$

From the Legendre polynomials it is not too hard to obtain the solution for generic m. Firstly, we notice that

$$P_\ell^m(z) = (-1)^m\left(1-z^2\right)^{m/2}\frac{\mathrm{d}^m}{\mathrm{d}z^m}P_\ell(z) \tag{10.53}$$

solves (10.38) for $m > 0$. These are called *associated Legendre functions*. Then we notice that (10.38) only involves m^2 so the solution for positive and negative m must be the same. Notice how if we take more than ℓ derivatives we get zero, therefore we conclude that

$$|m| \leqslant \ell \tag{10.54}$$

We can therefore write the full solution for the angular equation:

$$Y_\ell^m(\theta,\psi) \propto P_\ell^{|m|}(\cos\theta)\mathrm{e}^{\mathrm{i}m\phi} \tag{10.55}$$

The normalised Y_ℓ^m are called *spherical harmonics* and dictate the angular dependence of a wavefunction subjected to a central potential.

Using the standard convention that for negative m we write the associated Legendre functions as

$$P_\ell^{-|m|}(z) = (-1)^{|m|}\frac{(\ell-|m|)!}{(\ell+|m|)!}P_\ell^{|m|}(z) \tag{10.56}$$

we can write the normalised spherical harmonics as

$$Y_\ell^m(\theta,\psi) = \sqrt{\frac{\ell+\frac{1}{2}}{2\pi}\frac{(\ell-m)!}{(\ell+m)!}}\mathrm{e}^{\mathrm{i}m\phi}P_\ell^m(\cos\theta) \tag{10.57}$$

Deriving the normalisation factor is quite tricky. Additionally, it is quite laborious to apply the recurrence relation to find P_ℓ first and then apply a number of derivatives to find the final answer. There is however a very simple trick to obtain the spherical harmonics using only simple calculations.

First, we notice that (10.40) comes in steps of 2. That is, we either only have even powers of $\cos\theta$ or only odd powers of $\cos\theta$. Defining the normalised unit vectors as

$$\hat{\boldsymbol{x}} = \frac{\boldsymbol{x}}{r} \tag{10.58}$$

we can write

$$1 = \hat{\boldsymbol{x}}^2 = \hat{x}^2 + \hat{y}^2 + \hat{z}^2 \tag{10.59}$$

but in polar coordinates $\hat{z} = \cos\theta$, we had just omitted the hat earlier for brevity. This means that despite P_ℓ being a polynomial with many different powers of $\hat{z}$ we can actually make it a homogenous polynomial of order ℓ in $\hat{x}$, $\hat{y}$, $\hat{z}$ by using (10.59) repeatedly, that is we can make such that

$$P_\ell(\alpha\hat{x},\alpha\hat{y},\alpha\hat{z}) = \alpha^\ell P_\ell(\hat{x},\hat{y},\hat{z}) \tag{10.60}$$

For example we can write

$$P_2(\hat{z}) = \frac{1}{2}\big(3\hat{z}^2-1\big) = \frac{1}{2}\big(3\hat{z}^2-\hat{x}^2-\hat{y}^2-\hat{z}^2\big) = \hat{z}^2 - \frac{1}{2}\big(\hat{x}^2+\hat{y}^2\big) \tag{10.61}$$

This argument clearly also applies to the m^{th} derivative of P_ℓ. But it seems like we run into an issue with the factor of $(1-z^2)^{m/2}$ in (10.53). There is however a solution. We introduce new variables:

$$x_\pm = x \pm \mathrm{i}y = r\sin\theta\mathrm{e}^{\pm\mathrm{i}\phi} \tag{10.62}$$

this allows us to write (for $m > 0$

$$(1-\hat{z}^2)^{|m|/2}\mathrm{e}^{\pm\mathrm{i}m\phi} = (\sin\theta)^{|m|}\mathrm{e}^{\pm\mathrm{i}m\phi} = \hat{x}_\pm^m \tag{10.63}$$

Therefore the spherical harmonics are homogeneous polynomials of degree ℓ in the variables $\hat{x}_\pm$ and $\hat{z}$. Where the number $\nu_\pm$ of factors $\hat{x}_\pm$ must be such that

$$m = \nu_+ - \nu_- \tag{10.64}$$

We're not done yet but we are close. If Y_ℓ^m is a homogeneous polynomial of degree ℓ in $\hat{x}_\pm$ and $\hat{z}$, then $r^\ell Y_\ell^m$ must be a homogeneous polynomial in $x_\pm$ and z. Using (10.21) and (10.30) with $\lambda = \ell(\ell+1)$ we find that

$$\nabla^2(r^\ell Y_\ell^m) = 0 \tag{10.65}$$

And now we have our algorithm for finding Y_ℓ^m. We first fix ℓ and m; then we find the most generic homogeneous polynomial of degree ℓ in $\hat{x}_\pm$ and $\hat{z}$ such that $m = \nu_+ - \nu_-$; then we impose (10.65); finally we normalise. As an example let us apply this method to find all spherical harmonics with $\ell \leqslant 2$.

$\ell = 0$: Y_0^0 cannot have any factors at all of $\hat{x}_\pm$ or $\hat{z}$ therefore it must be a constant. We trivially find

$$Y_0^0 = \frac{1}{\sqrt{4\pi}} \tag{10.66}$$

$\ell = 1$: Each Y_1^m must have a single factor of $\hat{x}_\pm$ or $\hat{z}$. In particular Y_1^1 must be proportional to $\hat{x}_+$; Y_1^0 to $\hat{z}$; and Y_1^{-1} to $\hat{x}_-$. Therefore, after normalising we find

$$Y_1^1 = -\sqrt{\frac{3}{8\pi}}\hat{x}_+ = -\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi} \tag{10.67}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\hat{z} = \sqrt{\frac{3}{4\pi}}\cos\theta \tag{10.68}$$

$$Y_1^{-1} = \sqrt{\frac{3}{8\pi}}\hat{x}_- = \sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi} \tag{10.69}$$

$\ell = 2$: Each Y_2^m must have exactly two factors of $\hat{x}_\pm$ or $\hat{z}$. For $Y_2^{\pm 2}$ it is straightforward, they must be proportional to $\hat{x}_\pm^2$. Similarly $Y_2^{\pm 1} \propto \hat{x}_\pm \hat{z}$. For Y_2^0 it is a little bit more involved because both $\hat{x}_+\hat{x}_-$ and $\hat{z}$ work. We therefore impose (10.65) on an arbitrary linear combination of the two:

$$\nabla^2(r^2 Y_2^0) = \nabla^2(Ax_+x_- + Bz^2) = \nabla^2(A(x^2+y^2) + Bz^2) = 4A + 2B \tag{10.70}$$

therefore we conclude $B = -2A$, and that $Y_2^0 \propto \hat{x}_+\hat{x}_- - 2\hat{z} = 1 - 3\cos^2\theta$. All in all, after normalising we find

$$Y_2^2 = \sqrt{\frac{15}{32\pi}}\hat{x}_+^2 = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\phi} \tag{10.71}$$

$$Y_2^1 = -\sqrt{\frac{15}{8\pi}}\hat{x}_+\hat{z} = -\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\phi} \tag{10.72}$$

$$Y_2^0 = \sqrt{\frac{5}{16\pi}}(2\hat{z} - \hat{x}_+\hat{x}_-) = \sqrt{\frac{5}{16\pi}}\big(3\cos^2\theta - 1\big) \tag{10.73}$$

$$Y_2^{-1} = \sqrt{\frac{15}{8\pi}}\hat{x}_-\hat{z} = \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{-i\phi} \tag{10.74}$$

$$Y_2^{-2} = \sqrt{\frac{15}{32\pi}}\hat{x}_-^2 = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-2i\phi} \tag{10.75}$$

As usual, the phases are completely arbitrary and dependent on convention. The ones we chose were for convenience in the next section.

INSERT PLOTS OF THE SPHERICAL HARMONICS

The spherical harmonics are not only normalised by they are orthogonal

$$\int d^2\Omega\, Y_\ell^m(\theta,\phi)^* Y_{\ell'}^{m'}(\theta,\phi) = \delta_{\ell\ell'}\delta_{mm'} \tag{10.76}$$

additionally they change by a factor of $(-1)^\ell$ under parity:

$$Y_\ell^m(\pi-\theta, \pi+\phi) = (-1)^\ell Y_\ell^m(\theta,\phi) \tag{10.77}$$

10.3 Orbital angular momentum

In the previous section we derived the spherical harmonics as the solution to the angular part of the time-independent Schrodinger equation after separation by parts. We found that the solutions were indexed by two integers, their quantisation being a consequence of the single-valuedness and square-integrability of the wavefunction in spherical polar coordinates. Now we are going to re-derive those results in a purely algebraic manner. They key is to bring up the concept of *angular momentum*. After all, it is usually a convenient concept to use when solving rotationally invariant problems.

In classical mechanics the angular momentum was defined as the vector product between the position and momentum, it is therefore reasonable to define a quantum angular momentum operator via

$$\boldsymbol{L} = \boldsymbol{X} \times \boldsymbol{P} \tag{10.78}$$

which in the position basis becomes

$$\boldsymbol{L} = -\mathrm{i}\hbar \boldsymbol{x} \times \boldsymbol{\nabla} \tag{10.79}$$

We can also write these using Einstein summation convention and the Levi-Civita symbol

$$L_i = \epsilon_{ijk} X_j P_k = -\mathrm{i}\hbar \epsilon_{ijk} x_j \frac{\partial}{\partial x_k} \tag{10.80}$$

where

$$\epsilon_{ijk} = \begin{cases} 1 & \text{even permutation of 123} \\ -1 & \text{odd permutation of 123} \\ 0 & \text{otherwise} \end{cases} \tag{10.81}$$

Using either of these expressions it is not too hard to show that this operator is indeed Hermitian, therefore corresponding to a physical observable.

We can now compute the commutators of $\boldsymbol{L}$ with the position and momentum:

$$[L_i, X_j] = \epsilon_{ikl} X_k [P_l, X_j] = -\mathrm{i}\hbar \epsilon_{ikl} X_k \delta_{lj} = \mathrm{i}\hbar \epsilon_{ijk} X_k \tag{10.82}$$

$$[L_i, P_j] = \epsilon_{ikl} [X_k, P_j] P_l = \mathrm{i}\hbar \epsilon_{ikl} \delta_{kj} P_l = \mathrm{i}\hbar \epsilon_{ijk} P_k \tag{10.83}$$

where we have used (10.8).

Using these results we can also compute the commutator between different components of the angular momentum

$$[L_i, L_j] = \epsilon_{jkl} [L_i, X_k P_l] = \epsilon_{jkl} ([L_i, X_k] P_l + X_k [L_i, P_l]) \tag{10.84}$$

$$= \mathrm{i}\hbar \epsilon_{jkl} (\epsilon_{ikm} X_m P_l + X_k \epsilon_{ilm} P_m) \tag{10.85}$$

using the following identity

$$\epsilon_{ijk} \epsilon_{lmk} = \delta_{il} \delta_{jm} - \delta_{im} \delta_{kl} \tag{10.86}$$

we find

$$[L_i, L_j] = \mathrm{i}\hbar (X_m P_l (\delta_{ji} \delta_{lm} - \delta_{jm} \delta_{li}) - X_k P_m (\delta_{ji} \delta_{km} - \delta_{jm} \delta_{ki})) \tag{10.87}$$

$$= \mathrm{i}\hbar (X_i P_j - X_j P_i) \tag{10.88}$$

however, using (10.86) we find

$$\epsilon_{ijk} L_k = \epsilon_{ijk} \epsilon_{klm} X_l P_m = (\delta_{il} \delta_{jm} - \delta_{im} \delta_{jl}) X_l P_m = X_i P_j - X_j P_i \tag{10.89}$$

therefore we conclude that

$$[L_i, L_j] = \mathrm{i}\hbar\epsilon_{ijk}L_k \tag{10.90}$$

The components of the angular momentum don't commute with each other! By the Heisenberg uncertainty principle we conclude that it is not possible to fully specify the vector $\boldsymbol{L}$. If we specify any one component, say L_z then we cannot have absolute precision in L_y or L_x. This is ultimately due to the fact that rotations do not commute, that is, rotating by an angle α around an axis $\hat{\boldsymbol{v}}$ and then rotating about an angle β around an axis $\hat{\boldsymbol{u}}$ is not the same as doing it in the reverse order:

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Although as we will see later, despite appearances $\boldsymbol{L}$ is *not* the generator of rotations.

In any case we can write the above commutation relations in a more generic way, let $\boldsymbol{V}$ be a stand-in for $\boldsymbol{X}$, $\boldsymbol{P}$ or $\boldsymbol{L}$[74]. Then we can summarise the above commutation relations as

$$[L_i, V_j] = \mathrm{i}\hbar\epsilon_{ijk}V_k \tag{10.91}$$

Then, if $\boldsymbol{U}$ is another vector which satisfies the same commutation relation (could be equal to $\boldsymbol{V}$ or it could be different), then the following will hold for the inner product of the two

$$[L_i, V_jU_j] = V_j[L_i, U_j] + [L_i, V_j]U_j = \mathrm{i}\hbar\epsilon_{ijk}(V_jU_k + V_kU_j) = 0 \tag{10.92}$$

where in the last equality we used the antisymmetry of the Levi-Civita symbol.

In particular this means we can write

$$\left[\boldsymbol{L}, \boldsymbol{X}^2\right] = \left[\boldsymbol{L}, \boldsymbol{P}^2\right] = \left[\boldsymbol{L}, \boldsymbol{L}^2\right] = 0 \tag{10.93}$$

We can draw two conclusions from this fact. Firstly, even though the individual components do not commute with each other, the square of the angular momentum commutes with *every* component. This means we are able to know the *total* angular momentum and any one of its components, even if we cannot determine it exactly.

Secondly, for a central potential, the Hamiltonian H is a function of only $\boldsymbol{X}^2$ and $\boldsymbol{P}^2$, therefore we conclude

$$[\boldsymbol{L}, H] = 0 \tag{10.94}$$

We have recovered the classical fact that the angular momentum is conserved if the potential is spherically symmetric. Additionally, this means that we simultaneously diagonalise the Hamiltonian H, the total angular momentum $\boldsymbol{L}^2$, and any one component of the angular momentum, usually chosen to be L_z. In particular, if we wish to find the energy eigenstates we can first find the eigenstates of $\boldsymbol{L}^2$ and L_z, *i.e.* states $|\lambda, m\rangle$ that satisfy

$$\boldsymbol{L}^2 |\lambda, m\rangle = \hbar^2\lambda |\lambda, m\rangle \tag{10.95}$$

$$L_z |\lambda, m\rangle = \hbar m |\lambda, m\rangle \tag{10.96}$$

where the factors of $\hbar$ are just for convenience to make λ and m dimensionless.

To find these eigenvalues and eigenvectors we introduce ladder operators, like we did for the harmonic oscillator:

$$L_\pm = L_x \pm \mathrm{i}L_y \tag{10.97}$$

The reason we call these "ladder" operators is because of their commutation relations with

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[74] In fact, this will work for any vector constructed from $\boldsymbol{X}$ and $\boldsymbol{P}$

L_z and $\boldsymbol{L}^2$

$$[L_z, L_\pm] = [L_z, L_x] \pm \mathrm{i}[L_z, L_y] = \mathrm{i}\hbar L_y \pm \hbar L_x = \pm\hbar(L_x \pm \mathrm{i}L_y) = \pm\hbar L_\pm \tag{10.98}$$

$$\big[\boldsymbol{L}^2, L_\pm\big] = \big[\boldsymbol{L}^2, L_x\big] \pm \mathrm{i}\big[\boldsymbol{L}^2, L_y\big] = 0 \tag{10.99}$$

Using these we can calculate the action of $\boldsymbol{L}^2$ and L_z on the state $L_\pm |\lambda, m\rangle$

$$\boldsymbol{L}^2 L_\pm |\lambda, m\rangle = L_\pm \boldsymbol{L}^2 |\lambda, m\rangle = \hbar^2\lambda L_\pm |\lambda, m\rangle \tag{10.100}$$

$$L_z L_\pm |\lambda, m\rangle = (L_\pm L_z \pm \hbar L_\pm)|\lambda, m\rangle = \hbar(m \pm 1)L_\pm |\lambda, m\rangle \tag{10.101}$$

which means the state $L_\pm |\lambda, m\rangle$ is an eigenstate of $\boldsymbol{L}^2$ and L_z, respectively with eigenvalues $\hbar^2\lambda$ and $\hbar(m \pm 1)$.

Acting with the operators $L_\pm$ does not change the eigenvalue of $\boldsymbol{L}^2$ but it raises/lowers the eigenvalue of L_z by $\pm\hbar$. However, this ladder of states must terminate. This is because the angular momentum along the z direction cannot be greater than the total angular momentum. To be precise, we can look at expectation values:

$$\langle \boldsymbol{L}^2 \rangle = \langle L_x^2 \rangle + \langle L_y^2 \rangle + \langle L_z^2 \rangle \geqslant \langle L_z^2 \rangle \tag{10.102}$$

therefore[75]

$$\langle \lambda, m| \boldsymbol{L}^2 |\lambda, m\rangle = \hbar^2\lambda \geqslant \langle \lambda, m| L_z^2 |\lambda, m\rangle = \hbar^2 m^2 \implies m^2 \leqslant \lambda \tag{10.103}$$

This means there must be a state $|\lambda, m_{\max}\rangle$ such that

$$L_+ |\lambda, m_{\max}\rangle = 0 \tag{10.104}$$

and a state $|\lambda, m_{\min}\rangle$ such that

$$L_- |\lambda, m_{\min}\rangle = 0 \tag{10.105}$$

Using the fact that

$$L_\pm L_\mp = (L_x \pm \mathrm{i}L_y)(L_x \mp \mathrm{i}L_y) = L_x^2 + L_y^2 \mp \mathrm{i}[L_x, L_y] = \boldsymbol{L}^2 - L_z^2 \pm \hbar L_z \tag{10.106}$$

We can calculate $m_{\min}$ and $m_{\max}$ in terms of λ:

$$\boldsymbol{L}^2 |\lambda, m_{\max}\rangle = (L_- L_+ + L_z^2 + \hbar L_z)|\lambda, m_{\max}\rangle = \hbar^2 m_{\max}(m_{\max} + 1)|\lambda, m_{\max}\rangle \tag{10.107}$$

$$\boldsymbol{L}^2 |\lambda, m_{\min}\rangle = (L_+ L_- + L_z^2 - \hbar L_z)|\lambda, m_{\min}\rangle = \hbar^2 m_{\min}(m_{\min} - 1)|\lambda, m_{\max}\rangle \tag{10.108}$$

but both of these should have the same eigenvalue of $\boldsymbol{L}^2$: $\hbar^2\lambda$; we therefore conclude that

$$\lambda = m_{\max}(m_{\max} + 1) = m_{\min}(m_{\min} - 1) \tag{10.109}$$

this has two possible solutions, either $m_{\max} = m_{\min} - 1$ which is absurd because it would imply the maximum value of m is below its minimum, or

$$m_{\max} = -m_{\min} = \ell \tag{10.110}$$

Therefore, the eigenvalues of L_z are $\hbar m$ where m goes between $-\ell$ and ℓ in integer

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[75] Note that L_z is Hermitian, therefore m is real.

steps. This in turn implies that there is some integer N such that

$$\ell = -\ell + N \implies \ell = \frac{N}{2} \tag{10.111}$$

so ℓ must be either a integer or a half-integer!

All in all, the eigenstates of $\boldsymbol{L}^2$ and L_z can be labelled by two numbers ℓ and m such that

$$\boldsymbol{L}^2 \left|\ell, m\right\rangle = \hbar^2 \ell(\ell+1) \left|\ell, m\right\rangle \quad \text{and} \quad L_z \left|\ell, m\right\rangle = \hbar m \left|\ell, m\right\rangle \tag{10.112}$$

and

$$\ell = 0,\ \frac{1}{2},\ 1,\ \frac{3}{2}, \dots \qquad m = -\ell,\ -\ell+1, \dots,\ \ell-1,\ \ell \tag{10.113}$$

The number ℓ is sometimes called the total angular momentum quantum number, but beware, it is *not* true that ℓ is the eigenvalue of $|\boldsymbol{L}|$, instead the eigenvalue of $|\boldsymbol{L}|$ is $\sqrt{\ell(\ell+1)}$ which is larger than ℓ unless $\ell = 0$. This also means that the angular momentum can never fully point in the z-direction. This is a direct consequence of the Heisenberg uncertainty principle, if the angular momentum would point fully in the z-direction then we would be able to know all of the other components with absolute precision, which is not possible. The difference between ℓ and $\sqrt{\ell(\ell+1)}$ allows for the necessary leeway to abide by the uncertainty principle.

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Before we proceed to write these eigenstates in spherical coordinates, let us fully write $L_\pm \left|\ell, m\right\rangle$ in terms of $\left|\ell, m \pm 1\right\rangle$. First we note that $L_+^\dagger = L_-$, then we write

$$\begin{aligned} 1 = \left\langle \ell, m \pm 1 \middle| \ell, m \pm 1 \right\rangle = |C_\pm|^2 \left\langle \ell, m\right| L_\pm^\dagger L_\pm \left|\ell, m\right\rangle = |C_\pm|^2 \left\langle \ell, m\right| L_\mp L_\pm \left|\ell, m\right\rangle \quad (10.114)\\ = |C_\pm|^2 \left\langle \ell, m\right| \left(\boldsymbol{L}^2 - L_z^2 \mp \hbar L_z\right) \left|\ell, m\right\rangle = |C_\pm|^2 \hbar^2 (\ell(\ell+1) - m(m \pm 1)) \quad (10.115) \end{aligned}$$

therefore we conclude

$$L_\pm \left|\ell, m\right\rangle = C_\pm^{-1} \left|\ell, m \pm 1\right\rangle = \hbar \sqrt{\ell(\ell+1) - m(m \pm 1)} \left|\ell, m \pm 1\right\rangle \tag{10.116}$$

These states have non-negative norm if and only if $-\ell \leqslant m \leqslant \ell$ which is another to prove the bound on m.

10.4 Eigenstates of $\boldsymbol{L}^2$ and L_z in spherical coordinates

The notation for the eigenvalues of $\boldsymbol{L}^2$ and L_z was identical to the one used for the parameters in the spherical harmonics. This is not a coincidence, in this section we will show that the spherical harmonics are the eigenstates of $\boldsymbol{L}^2$ and L_z when written in the position basis using spherical coordinates.

Using (10.80) we find (where we have included a function $f(\boldsymbol{x})$ on the right to make the action of the derivatives clearer)

$$\boldsymbol{L}^2 f(\boldsymbol{x}) = L_i L_i f(\boldsymbol{x}) = -\hbar^2 \epsilon_{ijk} \epsilon_{ilm} x_j \frac{\partial}{\partial x_k} \left(x_l \frac{\partial f(\boldsymbol{x})}{\partial x_m} \right) \tag{10.117}$$

applying (10.86) we get

$$\boldsymbol{L}^2 f(\boldsymbol{x}) = -\hbar^2 \left(x_j \frac{\partial}{\partial x_k} \left(x_j \frac{\partial f(\boldsymbol{x})}{\partial x_k} \right) - x_j \frac{\partial}{\partial x_k} \left(x_k \frac{\partial f(\boldsymbol{x})}{\partial x_j} \right) \right) \tag{10.118}$$

using the fact

$$\frac{\partial x_i}{\partial x_j} = \delta_{ij} \tag{10.119}$$

we find

$$\boldsymbol{L}^2 f(\boldsymbol{x}) = -\hbar^2 \left(x_j x_j \frac{\partial^2 f(\boldsymbol{x})}{\partial x_k \partial x_k} - 2x_j \frac{\partial f(\boldsymbol{x})}{\partial x_j} - x_j x_k \frac{\partial^2 f(\boldsymbol{x})}{\partial x_j \partial x_k} \right) \tag{10.120}$$

The first term is easy to identify because $r^2 = x_j x_j$ and in Cartesian coordinates

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial x^2} = \frac{\partial^2}{\partial x_j \partial x_j} \tag{10.121}$$

therefore

$$x_j x_j \frac{\partial^2 f(\boldsymbol{x})}{\partial x_k \partial x_k} = r^2 \nabla^2 f(\boldsymbol{x}) \tag{10.122}$$

The other terms are a bit trickier, we first have to write

$$x_j \frac{\partial}{\partial x_j} \left(x_k \frac{\partial f(\boldsymbol{x})}{\partial x_k} \right) = x_j \frac{\partial f(\boldsymbol{x})}{\partial x_j} + x_j x_j \frac{\partial^2 f(\boldsymbol{x})}{\partial x_j \partial x_k} \tag{10.123}$$

so that we can have

$$-2x_j \frac{\partial f(\boldsymbol{x})}{\partial x_j} - x_j x_k \frac{\partial^2 f(\boldsymbol{x})}{\partial x_j \partial x_k} = -x_j \frac{\partial f(\boldsymbol{x})}{\partial x_j} - x_j \frac{\partial}{\partial x_j} \left(x_k \frac{\partial f(\boldsymbol{x})}{\partial x_k} \right) \tag{10.124}$$

finally we identify

$$x_j \frac{\partial f(\boldsymbol{x})}{\partial x_j} = r \frac{\partial f(\boldsymbol{x})}{\partial r} \tag{10.125}$$

so that we can conclude

$$-2x_j \frac{\partial f(\boldsymbol{x})}{\partial x_j} - x_j x_k \frac{\partial^2 f(\boldsymbol{x})}{\partial x_j \partial x_k} = -r \frac{\partial f(\boldsymbol{x})}{\partial r} - r \frac{\partial}{\partial r} \left(r \frac{\partial f(\boldsymbol{x})}{\partial r} \right) = -\frac{\partial}{\partial r} \left(r^2 \frac{\partial f(\boldsymbol{x})}{\partial r} \right) \tag{10.126}$$

Putting all of this together allows us to write

$$\boldsymbol{L^2} f(\boldsymbol{x}) = -\hbar^2 \left(r^2 \nabla^2 f(\boldsymbol{x}) - \frac{\partial}{\partial r} \left(r^2 \frac{\partial f(\boldsymbol{x})}{\partial r} \right) \right) \tag{10.127}$$

This expression is rather useful, we can use to immediately conclude two things. Firstly, we can write

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{\boldsymbol{L}^2}{\hbar^2 r^2} \tag{10.128}$$

which allows us to write the TISE in spherical coordinates as

$$-\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi(\boldsymbol{x})}{\partial r} \right) + \frac{1}{2\mu r^2} \boldsymbol{L}^2 \psi(\boldsymbol{x}) + V(r)\psi(\boldsymbol{x}) = E\psi(\boldsymbol{x}) \tag{10.129}$$

If $\psi(\boldsymbol{x})$ is chosen to be an eigenstate of $\boldsymbol{L}^2$ with eigenvalue $\hbar^2 \ell(\ell+1)$ we get

$$-\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi(\boldsymbol{x})}{\partial r} \right) + \frac{\hbar^2}{2\mu r^2} \ell(\ell+1) \psi(\boldsymbol{x}) + V(r)\psi(\boldsymbol{x}) = E\psi(\boldsymbol{x}) \tag{10.130}$$

which is the same as (10.25) with $\lambda = \ell(\ell+1)$.

In fact, comparing with (10.21) we can see that

$$\boldsymbol{L}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) \tag{10.131}$$

This means that the spherical harmonics are eigenstates of the total angular momentum

$$\boldsymbol{L}^2 Y_\ell^m(\theta,\psi) = \hbar^2\ell(\ell+1)Y_\ell^m(\theta,\psi) \tag{10.132}$$

Additionally, one can write

$$\begin{aligned}\frac{\partial}{\partial\phi} &= \frac{\partial x}{\partial\phi}\frac{\partial}{\partial x} + \frac{\partial y}{\partial\phi}\frac{\partial}{\partial y} + \frac{\partial z}{\partial\phi}\frac{\partial}{\partial z} = \\ &= -r\sin\theta\sin\phi\frac{\partial}{\partial x} + r\sin\theta\cos\phi\frac{\partial}{\partial y} = -y\frac{\partial}{\partial x} + x\frac{\partial}{\partial y} = \\ &= \frac{\mathrm{i}}{\hbar}L_z\end{aligned} \tag{10.133}$$

therefore

$$L_z Y_\ell^m(\theta,\phi) = -\mathrm{i}\hbar\frac{\partial Y_\ell^m(\theta,\phi)}{\partial\phi} = \hbar m Y_\ell^m(\theta,\phi) \tag{10.134}$$

Therefore the eigenstates $|\ell,m\rangle$ of $\boldsymbol{L}^2$ and L_z, when written in the position basis are precisely the spherical harmonics we derived earlier. The method of separation of variables is equivalent to the simultaneous diagonalisation of H, $\boldsymbol{L}^2$ and L_z.

There is, however, one crucial difference. When we solved the angular equation to obtain the spherical harmonics we only found *integer* m and ℓ. On the other hand, the algebraic arguments from the previous section also allowed for half-integer m and ℓ. These half-integer solutions cannot correspond to a single-valued function of θ and ϕ, in for example, if $m = \frac{1}{2}$ we would have

$$Y_\ell^{1/2}(\theta,\phi+2\pi) = -Y_\ell^{1/2}(\theta,\phi) \tag{10.135}$$

which would not lead to a single-valued wavefunction[76]. At this point, the only logical conclusion is to take these half-integer states as spurious and remove them from consideration. We will return to this in Chapter 12 where we will make use of these half-integer states.

11 Solving the radial equation

Either by separation of variables or by finding the angular momentum eigenstates all we have left to do to find the energy eigenvalues is to solve the radial equation. In this chapter we will begin with some generic properties valid for any potential, including how it can be reduced to a 1-dimensional problem and the small r behaviour. Then we focus on a particular example—the Coulomb potential felt by an electron in a Hydrogen atom. We will find that the energy levels derived from there are more degenerate than we would have otherwise predicted, this is due to a non-trivial additional symmetry which can provide a slicker (if less intuitive) derivation of the energy spectrum.

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[76] You might wonder why I didn't mention the normalisability. In fact, the argument for integer ℓ using normalisability of the θ integration set $m = 0$, however, if ℓ is half-integer we never hit $m = 0$ so the argument doesn't apply.

11.1 The effective potential

The equation we wish to solve is

$$-\frac{\hbar^2}{2\mu r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}R(r)}{\mathrm{d}r}\right)+\frac{\hbar^2}{2\mu r^2}\ell(\ell+1)R(r)+V(r)R(r)=ER(r) \tag{11.1}$$

subject to the normalisability requirement

$$\int_0^\infty \mathrm{d}r\, r^2|R(r)|^2<\infty \tag{11.2}$$

If we define a new variable

$$u(r)=rR(r) \tag{11.3}$$

then this equation will look exactly like the Schrodinger equation in 1 dimension:

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2u(r)}{\mathrm{d}r^2}+\left(V(r)+\frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\right)u(r)=Eu(r) \tag{11.4}$$

with an effective potential

$$V_{\text{eff}}(r)=V(r)+\frac{\hbar^2\ell(\ell+1)}{2\mu r^2} \tag{11.5}$$

which includes a centrifugal barrier

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The normalisation condition in terms of $u(r)$ is also exactly what you would expect from a particle in 1 dimension

$$\int_0^\infty \mathrm{d}r\,|u(r)|^2<\infty \tag{11.6}$$

From this form of the equation two things are immediately clear. Firstly, the advantage of spherical symmetry is to effectively reduce our problem to a 1-dimensional one. This is what makes spherical symmetry so much easier to tackle analytically. Secondly, in general, the energy levels will depend on ℓ as it appears in the effective potential. They will, however, be independent of m. This is a consequence of spherical symmetry, our energy levels only depend on the *total* angular momentum, not on any one component of it. We therefore expect a degeneracy of $2\ell+1$ for each energy level.

The main difference from a truly 1-dimensional problem is the boundary at $r=0$, so let us focus on that parameter region. Assuming that $V(r)$ does not diverge faster than r^{-2} as $r\to 0$ we have, approximately, for $r\approx 0$

$$-\frac{\mathrm{d}^2u(r)}{\mathrm{d}r^2}+\frac{\ell(\ell+1)}{r^2}u(r)\approx 0 \tag{11.7}$$

which as two solutions

$$u(r)\propto r^{\ell+1}\quad\text{and}\quad u(r)\propto r^{-\ell} \tag{11.8}$$

For $\ell\geqslant 1$ we must discard the second solution as it will not be square-integrable. However, for $\ell=0$ it appears that the second solution is perfectly fine. This is a bit too quick, for although $u(r)=$const would be square-integrable it would not lead to a Hermitian Hamiltonian.

In order that the effective 1-dim Hamiltonian is Hermitian we must have

$$\int_0^\infty \mathrm{d}r\, f^*(r)\left(-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2 g(r)}{\mathrm{d}r^2} + \left(V(r) + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\right)g(r)\right) = \\ = \int_0^\infty \mathrm{d}r\left(-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2 f^*(r)}{\mathrm{d}r^2} + \left(V(r) + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\right)f^*(r)\right)g(r) \tag{11.9}$$

for $f(r)$ and $g(r)$ two square integrable functions on $r \in (0, \infty)$. This cannot be true if either of the functions does not vanish at $r = 0$.

Firstly, we can focus on the kinetic term (ignoring the overall $-\hbar^2/2\mu$ factor)

$$\int_0^\infty \mathrm{d}r\, f^*(r)\frac{\mathrm{d}^2 g(r)}{\mathrm{d}r^2} = \left[f^*(r)\frac{\mathrm{d}g}{\mathrm{d}r}\right]_0^\infty - \int_0^\infty \mathrm{d}r\,\frac{\mathrm{d}f^*(r)}{\mathrm{d}r}\frac{\mathrm{d}g(r)}{\mathrm{d}r} = \\ = \left[f^*(r)\frac{\mathrm{d}g}{\mathrm{d}r} - \frac{\mathrm{d}f^*}{\mathrm{d}r}g(r)\right]_0^\infty + \int_0^\infty \mathrm{d}r\,\frac{\mathrm{d}^2 f^*(r)}{\mathrm{d}r^2}g(r) \tag{11.10}$$

The boundary condition would clearly be satisfied if both functions approach zero at the origin. However, if one has a behaviour $\sim r^\alpha$, for some $\alpha > 0$ and the other approaches a non-zero constant, then the boundary condition would not be satisfied. The Hamiltonian is only Hermitian if all allowed functions vanish at the origin.

Secondly we can look at the potential term. No integration by parts is necessary, but the integral must converge. This is in fact not trivial, because

$$\int_0^\infty \mathrm{d}r\,\frac{1}{r^2} = \infty \tag{11.11}$$

Therefore, the functions f and g must be able to curb this divergence in the centrifugal barrier. This can only happen if they vanish at $r = 0$ at least as fast as r.

All in all, we see that we should discard the $u(r) \propto r^{-\ell}$ solution and instead demand that

$$u(r) \xrightarrow{r\to 0} C\, r^{\ell+1} \tag{11.12}$$

for some constant C[77].

Interestingly, we see that our trick to derive the spherical harmonics as homogeneous polynomials actually applies to all energy eigenfunctions near $r = 0$. That is, any eigenfunction of both the energy and angular momentum is a homogeneous polynomial of degree ℓ near the origin.

11.2 The spectrum of the Hydrogen atom

Now we apply our knowledge to a particular example which is both exactly solvable and experimentally relevant, the Coulomb potential:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \tag{11.13}$$

where e is the charge of the proton, and ϵ_0 is the vacuum permittivity.

The equation we wish to solve is

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2 u(r)}{\mathrm{d}r^2} + \left(-\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\right)u(r) = Eu(r) \tag{11.14}$$

---

[77] Incidentally, this also puts a limit on how singular $V(r)$ can be at the origin. The worst case scenario is if both f and g have $\ell = 0$ so that they each approach r near the origin. In this case if $V(r) \sim r^\alpha$ then the exponent must obey $\alpha > -3$ to ensure the integral converges.

subject to the boundary condition

$$u(r) \propto r^{\ell+1} \quad \text{as} \quad r \to 0 \tag{11.15}$$

Before we attempt to solve this equation it is helpful to introduce new variables to get rid of all of the annoying constants[78]

$$\kappa \equiv \sqrt{-\frac{2mE}{\hbar^2}} \tag{11.16}$$

$$\xi \equiv \frac{\mu e^2}{2\pi\epsilon_0\hbar^2\kappa} \tag{11.17}$$

$$\rho \equiv \kappa r \tag{11.18}$$

such that the equation looks like

$$\frac{\mathrm{d}^2u(\rho)}{\mathrm{d}\rho^2} = \left(1 - \frac{\xi}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right)u(\rho) \tag{11.19}$$

The same we did for the harmonic oscillator we begin by stripping off the asymptotic behaviour. Looking at $r \to \infty$ we see that the constant term in the brackets in the RHS dominates, yielding

$$\frac{\mathrm{d}^2u(\rho)}{\mathrm{d}\rho^2} \approx u(\rho) \tag{11.20}$$

which has as solutions

$$u(\rho) = A\mathrm{e}^{-\rho} + B\mathrm{e}^{\rho} \tag{11.21}$$

The second of these is clearly not square integrable, so we throw it out.

Stripping the $\rho \to 0$ and the $\rho \to \infty$ asymptotics we define

$$u(\rho) \equiv \rho^{\ell+1}F(\rho)\mathrm{e}^{-\rho} \tag{11.22}$$

Remember that exactly like with the harmonic oscillator, this definition is *exact*. The approximations were merely used to motivate this expression.

Plugging this definition in we find

$$\frac{\mathrm{d}^2F(\rho)}{\mathrm{d}\rho^2} + 2\left(\frac{\ell+1}{\rho} - 1\right)\frac{\mathrm{d}F(\rho)}{\mathrm{d}\rho} + \frac{\xi - 2(\ell+1)}{\rho}F(\rho) = 0 \tag{11.23}$$

Following our harmonic oscillator footsteps we try a power series solution

$$F(\rho) = \sum_{j=0}^{\infty} a_j\rho^j \tag{11.24}$$

and derive a recurrence relation for the coefficients a_j

$$(j + 2(\ell+1))(j+1)a_{j+1} = (2(j+\ell+1) - \xi)a_j \tag{11.25}$$

This relation determines all coefficients in terms of a_0.

---

[78] In the definition of κ we have anticipated that we looking for bound states with negative E.

Looking at the large j limit we see that[79]

$$\frac{a_{j+1}}{a_j} \to \frac{2}{j+1} \tag{11.26}$$

which is solved by

$$a_j \approx \frac{2^j}{j!} a_0 \tag{11.27}$$

but this means

$$F(\rho) \sim c_0 \mathrm{e}^{2\rho} \tag{11.28}$$

and therefore

$$u(\rho) \sim \rho^{\ell+1} \mathrm{e}^{\rho} \tag{11.29}$$

which is not normalisable.

We once again see that if we do not impose that the series terminates we end up recovering the non-normalisable solution we had thrown out. The only resolution is if there exists an integer $N \geqslant 0$ such that

$$2(N+\ell+1) = \xi_N \tag{11.30}$$

thereby giving quantisation in the energy:

$$E_N = -\frac{\hbar^2 \kappa_N}{2\mu} = -\frac{\mu e^4}{8\pi^2\epsilon_0^2\hbar^2}\frac{1}{\xi_N^2} = -\frac{\mu e^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{(N+\ell+1)^2} \tag{11.31}$$

This appears to depend on both N and ℓ but this is an illusion, *e.g.* the $N=1$, $\ell=2$ state will have the same energy as the $N=2$, $\ell=1$ state. It is therefore more conventional to define the *principal quantum number*

$$n \equiv N+\ell+1 \tag{11.32}$$

In terms of this n the functions $F(\rho)$ will be polynomials of order $n-\ell-1$, and the energies given by

$$E_n = -\frac{\mu e^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2} = \frac{E_1}{n^2} \tag{11.33}$$

where in the last equality we wrote them in terms of the ground state energy,

$$E_1 = -\frac{\mu e^4}{32\pi^2\epsilon_0^2\hbar^2} \approx -13.6 \text{ eV} \tag{11.34}$$

We have now fully recovered Bohr's energy levels from first principles. We see that quantisation of the angular momentum was important but that the quantum number related to that quantisation does not appear in the energy levels. The reason for this discrepancy was the incorrect use of forces in Bohr's derivation, thereby adding some Newtonian arguments in an otherwise quantum system.

For each energy level E_n there are multiple allowed values of ℓ, in particular because $N \geqslant 0$ we conclude $n \geqslant \ell+1$ and therefore, for a given n, we have $0 \leqslant \ell \leqslant n-1$. Additionally, for each value for n and ℓ there are $2\ell+1$ allowed values for m. Therefore

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[79] We keep the $+1$ in the denominator just for simplicity, it of course will not change the conclusions as it is negligible for large j.

the total number of states with energy E_n is given by

$$\sum_{\ell=0}^{n-1}(2\ell+1) = 2\frac{n(n-1)}{2} + n = n^2 \tag{11.35}$$

this is far larger than what would be expected from rotational symmetry alone. This is because the Coulomb potential is very special, as we will see in the next section there is an additional symmetry that is behind this large degeneracy.

Before we proceed we will write the energy spectrum in yet another way by introducing the *fine structure constant*

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137} \tag{11.36}$$

This dimensionless constant can be interpreted as the true measure of the strength of the electromagnetic interaction, as it is dimensionless, only involving fundamental constants. Using this constant we can write

$$E_n = -\frac{\alpha^2\mu c^2}{2}\frac{1}{n^2} \tag{11.37}$$

where we identify

$$\mu c^2 \approx m_e c^2 \approx 511\ \text{keV} \tag{11.38}$$

as the relativistic rest energy of the electron, which is much larger than E_1. It is the suppression by α^2 that connects the relativistic particle physics energies to the much smaller energies of atomic physics.

We can also write down the wavefunctions exactly. First we note that the degree $n-\ell-1$ polynomials $F(\rho)$ are known by mathematitians as the *associated Laguerre Polynomials* denoted by

$$F(\rho) = L^{2\ell+1}_{n-\ell-1}(2\rho) \tag{11.39}$$

They are normalised such that

$$\int_0^\infty \mathrm{d}x\, \mathrm{e}^{-x} x^k L^k_n(x) L^k_m(x) = \frac{(n+k)!}{n!}\delta_{mn} \tag{11.40}$$

and even have an exact formula

$$L^k_n(x) = \sum_{m=0}^{n}(-1)^m \frac{(n+k)!}{(n-m)!(k+m)!m!}x^m \tag{11.41}$$

The first few are given by

$$L^k_0(x) = 1 \tag{11.42}$$

$$L^k_1(x) = -x + k + 1 \tag{11.43}$$

$$L^k_2(x) = \frac{1}{2}\big(x^2 - 2(k+2)x + (k+1)(k+2)\big) \tag{11.44}$$

Note that even though the energy levels are independent of ℓ, the radial part of the wavefunction surely isn't. Let us focus on the ground state, it has $n = 1$ by definition, the only allowed value for ℓ is therefore 0, which also implies $m = 0$. Therefore

$$F(\rho) = L^1_0(2\rho) = 1 \implies u(\rho) = \rho\mathrm{e}^{-\rho} \implies R(r) = C\mathrm{e}^{-\kappa r} \tag{11.45}$$

We can determine C by imposing normalisation

$$\int_0^\infty \mathrm{d}r\, r^2 |R(r)|^2 = \int_0^\infty \mathrm{d}r\, |C|^2 r^2 \mathrm{e}^{-2\kappa r} = |C|^2 \frac{1}{4\kappa^3} = 1 \tag{11.46}$$

Defining the *Bohr radius* as

$$a_0 \equiv \frac{4\pi\epsilon_0 \hbar^2}{e^2 \mu} = \frac{\hbar}{\mu c \alpha} \tag{11.47}$$

and remembering $Y_0^0 = 1/\sqrt{4\pi}$ we can write

$$\psi(r,\theta,\phi) = \frac{1}{\sqrt{\pi a_0^3}} \mathrm{e}^{-r/a_0} \tag{11.48}$$

This gives the interpretation for the Bohr radius, it sets the size of the ground state of the Hydrogen atom. In SI units it is approximately

$$a_0 \approx 5.29 \times 10^{-11} \text{ m} \tag{11.49}$$

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The other wavefunctions are harder to plot, we can however write the fully normalised expression for any $n,\ \ell,\ m$.

$$\psi_{n\ell m}(\boldsymbol{x}) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} \exp\left(-\frac{r}{na_0}\right) \left(\frac{2r}{na_0}\right)^\ell L_{n-\ell-1}^{2\ell+1}\left(\frac{r}{na_0}\right) Y_\ell^m(\theta,\phi) \tag{11.50}$$

Ignoring the spherical harmonics, the first few radial wavefunctions, denoted by $R_{n\ell}(r)$ are given by

$$R_{10}(r) = \frac{1}{2a_0^{3/2}} \mathrm{e}^{-r/a_0} \tag{11.51}$$

$$R_{20}(r) = \frac{1}{\sqrt{2}} a_0^{-3/2} \left(1 - \frac{r}{2a_0}\right) \mathrm{e}^{-r/2a_0} \tag{11.52}$$

$$R_{21}(r) = \frac{1}{2\sqrt{6}} a_0^{-5/2} r \mathrm{e}^{-r/2a_0} \tag{11.53}$$

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Visualising the full wavefunctions is a bit trickier. We can draw density plots where the brightness is proportional to $|\psi|^2$, or draw the curves of constant density.

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11.3 * The Runge-Lenz vector

In the previous section we obtain the spectrum of the Hydrogen atom by solving a differential equation. However, at the end we found the degeneracy of the spectrum was far higher than what we would have expected. This is because there is an additional conserved quantity, the *Runge-Lenz vector*

$$\boldsymbol{R} \equiv -\frac{e^2}{4\pi\epsilon_0} \frac{\boldsymbol{X}}{|\boldsymbol{X}|} + \frac{1}{2\mu}(\boldsymbol{P} \times \boldsymbol{L} - \boldsymbol{L} \times \boldsymbol{P}) \tag{11.54}$$

where we have defined $|\boldsymbol{X}| = \sqrt{\boldsymbol{X} \cdot \boldsymbol{X}}$.

This is a well known object in classical orbital mechanics. Classically it points from the centre of the force to the periapsis, *i.e.* the point of closest approach in the orbit. It can be used to show that the classical orbits in a Newtonian potential are closed curves.

More precisely, we have taken an average between $\boldsymbol{P} \times \boldsymbol{L}$ and $-\boldsymbol{L} \times \boldsymbol{P}$ (which are classically the same) to ensure this operator is Hermitian

$$\boldsymbol{R}^\dagger = \boldsymbol{R} \tag{11.55}$$

First we need to show that this vector actually is conserved, *i.e.* that

$$[H, \boldsymbol{R}] = 0 \tag{11.56}$$

For this we need to remember that $[\boldsymbol{L}, H] = 0$, and to compute the commutator of $\boldsymbol{P}$ and the Hamiltonian:

$$[H, P_i] = \left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{|\boldsymbol{X}|}, P_i\right] \tag{11.57}$$

this is easy to compute in the position basis

$$\left[\frac{1}{|\boldsymbol{X}|}, P_i\right]\psi(\boldsymbol{x}) = -\mathrm{i}\hbar\left(\frac{1}{r}\frac{\partial\psi(\boldsymbol{x})}{\partial x_i} - \frac{\partial}{\partial x_i}\left(\frac{\psi(\boldsymbol{x})}{r}\right)\right) = -\mathrm{i}\hbar\frac{\psi(\boldsymbol{x})}{r^2}\frac{\partial r}{\partial x_i} = -\mathrm{i}\hbar\frac{x_i}{r^3}\psi(\boldsymbol{x}) \tag{11.58}$$

therefore

$$[H, P_i] = \mathrm{i}\hbar\frac{e^2}{4\pi\epsilon_0}\frac{X_i}{|\boldsymbol{X}|^3} \tag{11.59}$$

We will also need

$$\begin{aligned}
\left[H, \frac{X_i}{|\boldsymbol{X}|}\right] &= \frac{P_j}{2\mu}\left[P_j, \frac{X_i}{|\boldsymbol{X}|}\right] + \left[P_j, \frac{X_i}{|\boldsymbol{X}|}\right]\frac{P_j}{2\mu} = \\
&= \frac{P_j}{2\mu}\left(-\mathrm{i}\hbar\delta_{ij}\frac{1}{|\boldsymbol{X}|} + X_i\left[P_j, \frac{1}{|\boldsymbol{X}|}\right]\right) + \left(-\mathrm{i}\hbar\delta_{ij}\frac{1}{|\boldsymbol{X}|} + X_i\left[P_j, \frac{1}{|\boldsymbol{X}|}\right]\right)\frac{P_j}{2\mu} = \\
&= \frac{P_j}{2\mu}\left(-\mathrm{i}\hbar\delta_{ij}\frac{1}{|\boldsymbol{X}|} + X_i\mathrm{i}\hbar\frac{X_j}{|\boldsymbol{X}|^3}\right) + \left(-\mathrm{i}\hbar\delta_{ij}\frac{1}{|\boldsymbol{X}|} + X_i\mathrm{i}\hbar\frac{X_j}{|\boldsymbol{X}|^3}\right)\frac{P_j}{2\mu} = \\
&= \frac{\mathrm{i}\hbar}{2\mu}\left[P_j\left(\frac{X_iX_j}{|\boldsymbol{X}|^3} - \frac{\delta_{ij}}{|\boldsymbol{X}|}\right) + \left(\frac{X_iX_j}{|\boldsymbol{X}|^3} - \frac{\delta_{ij}}{|\boldsymbol{X}|}\right)P_j\right]
\end{aligned} \tag{11.60}$$

We can also use the commutator $[L_i, P_j] = \mathrm{i}\hbar\epsilon_{ijk}P_k$ to write

$$\begin{aligned}
R_i &= -\frac{e^2}{4\pi\epsilon_0}\frac{X_i}{|\boldsymbol{X}|} + \frac{1}{2\mu}(\epsilon_{ijk}P_jL_k - \epsilon_{ijk}L_jP_k) = \\
&= -\frac{e^2}{4\pi\epsilon_0}\frac{X_i}{|\boldsymbol{X}|} + \frac{1}{2\mu}(\epsilon_{ijk}P_jL_k - \epsilon_{ijk}(P_kL_j + \mathrm{i}\hbar\epsilon_{jkl}P_l)) = \\
&= -\frac{e^2}{4\pi\epsilon_0}\frac{X_i}{|\boldsymbol{X}|} + \frac{1}{\mu}\epsilon_{ijk}P_jL_k - \frac{\mathrm{i}\hbar}{\mu}P_i
\end{aligned} \tag{11.61}$$

Now we are ready to show this vector is conserved:

$$\begin{aligned}
[H, R_i] &= -\frac{e^2}{4\pi\epsilon_0}\left[H, \frac{X_i}{|\boldsymbol{X}|}\right] + \frac{1}{\mu}\epsilon_{ijk}[H, P_j]L_k - \frac{\mathrm{i}\hbar}{\mu}[H, P_i] = \\
&= \frac{\mathrm{i}\hbar e^2}{4\pi\epsilon_0\mu}\left(\frac{P_j}{2}\left(\frac{\delta_{ij}}{|\boldsymbol{X}|} - \frac{X_iX_j}{|\boldsymbol{X}|^3}\right) + \left(\frac{\delta_{ij}}{|\boldsymbol{X}|} - \frac{X_iX_j}{|\boldsymbol{X}|^3}\right)\frac{P_j}{2} + \epsilon_{ijk}\frac{X_j}{|\boldsymbol{X}|^3}L_k - \mathrm{i}\hbar\frac{X_i}{|\boldsymbol{X}|^3}\right) =
\end{aligned}$$

$$
\begin{aligned}
&= \frac{\mathrm{i}\hbar e^2}{4\pi\epsilon_0\mu}\left(\frac{P_j}{2}\left(\frac{\delta_{ij}}{|\boldsymbol{X}|}-\frac{X_iX_j}{|\boldsymbol{X}|^3}\right)+\left(\frac{\delta_{ij}}{|\boldsymbol{X}|}-\frac{X_iX_j}{|\boldsymbol{X}|^3}\right)\frac{P_j}{2}+\frac{X_j}{|\boldsymbol{X}|^3}(X_iP_j-X_jP_i)-\mathrm{i}\hbar\frac{X_i}{|\boldsymbol{X}|^3}\right)= \\
&= \frac{\mathrm{i}\hbar e^2}{4\pi\epsilon_0\mu}\left(\frac{P_j}{2}\left(\frac{\delta_{ij}}{|\boldsymbol{X}|}-\frac{X_iX_j}{|\boldsymbol{X}|^3}\right)-\left(\frac{\delta_{ij}}{|\boldsymbol{X}|}-\frac{X_iX_j}{|\boldsymbol{X}|^3}\right)\frac{P_j}{2}-\mathrm{i}\hbar\frac{X_i}{|\boldsymbol{X}|^3}\right)= \\
&= \frac{\mathrm{i}\hbar e^2}{4\pi\epsilon_0\mu}\left(\left[\frac{P_j}{2},\frac{\delta_{ij}}{|\boldsymbol{X}|}-\frac{X_iX_j}{|\boldsymbol{X}|^3}\right]-\mathrm{i}\hbar\frac{X_i}{|\boldsymbol{X}|^3}\right)= \\
&= -\frac{\mathrm{i}\hbar e^2}{8\pi\epsilon_0\mu}\left(\left[P_j,\frac{X_iX_j}{|\boldsymbol{X}|^3}\right]+\mathrm{i}\hbar\frac{X_i}{|\boldsymbol{X}|^3}\right) \qquad (11.62)
\end{aligned}
$$

The final commutator is not too hard to calculate in the position basis

$$\left[P_j,\frac{X_iX_j}{|\boldsymbol{X}|^3}\right]\psi(\boldsymbol{x}) = -\mathrm{i}\hbar\frac{\partial}{\partial x_j}\left(\frac{x_ix_j}{r^3}\right)\psi(\boldsymbol{x}) = -\mathrm{i}\hbar\frac{x_i}{r^3}\psi(\boldsymbol{x}) \qquad (11.63)$$

This finally gives us that

$$[H,\boldsymbol{R}] = 0 \qquad (11.64)$$

Usually we find conserved quantities by finding symmetries. In this case it is true that there is some symmetry involved by it is not very intuitive. Suffice to say that it has some relation to a 4-dimensional rotation. Interestingly, as we will see shortly, the commutators of $\boldsymbol{R}$ involve the Hamiltonian. These kinds of symmetries are called *dynamical symmetries* and they allow us to determine the energy levels in a purely algebraic way. Classically, we could see that this symmetry is not related to a *cyclic coordinate*, *i.e.* a coordinate such that the symmetry acts as a translation along that direction. All in all, these dynamical symmetries are much less intuitive and much harder to spot but they are a powerful tool to explain the energy levels and their degeneracy.

Firstly, we can calculate the commutator between the components of $\boldsymbol{R}$. It is rather lengthy but the manipulations are very similar to what we used above to prove that $[H,\boldsymbol{R}] = 0$, so we will not repeat them here. The main tools are the commutators between $\boldsymbol{X}$, $\boldsymbol{P}$, and $\boldsymbol{L}$; the fact $\boldsymbol{L}$ commutes with any function of $|\boldsymbol{X}|$; and the orthogonality relations $\boldsymbol{X}\cdot\boldsymbol{L} = 0$ and $\boldsymbol{L}\cdot\boldsymbol{P} = 0$. The end result is

$$[R_i, R_i] = -\frac{2\mathrm{i}\hbar}{\mu}\epsilon_{ijk}HL_k \qquad (11.65)$$

This commutator involves the angular momentum and the Hamiltonian, we say that the algebra is not closed. We can see the Hamiltonian in the RHS, making this symmetry dynamical. We can also compute the commutator between the Runge-Lenz vector and the angular momentum

$$[L_i, R_j] = \mathrm{i}\hbar\epsilon_{ijk}R_k \qquad (11.66)$$

which is the expected result for a vector made up from $\boldsymbol{X}$ and $\boldsymbol{P}$.

Comparing these two relations we see that, even though the components of $\boldsymbol{R}$ do not form a closed algebra, the set of $\left\{L_i, R_j/\sqrt{-H}\right\}$ do form a closed algebra. Indeed we can introduce

$$\boldsymbol{A}_\pm \equiv \frac{1}{2}\left(\boldsymbol{L} \pm \sqrt{\frac{\mu}{-2H}}\boldsymbol{R}\right) \qquad (11.67)$$

whose commutators yield

$$[A_{\pm i}, A_{\pm j}] = \mathrm{i}\hbar\epsilon_{ijk}A_{\pm j} \tag{11.68}$$

$$[A_{\pm i}, A_{\mp j}] = 0 \tag{11.69}$$

which are very familiar! They are the same commutation relations that the angular momentum obeys. This also allows us to see the symmetry behind the conservation of the Runge-Lenz vector. Roughly each $\boldsymbol{A}_\pm$ has the same algebra as angular momentum so they have something to do with 3-dimensional rotations; in fact two sets of 3-dimensional rotations can be combined into a single rotation in 4-dimensions. This is all rather abstract and conveys the weirdness of this symmetry.

Using exactly the same process as we did for the angular momentum we can form eigenstates of these operators. In particular we know that $\boldsymbol{A}_\pm^2$ has eigenvalues $\hbar^2 a_\pm(a_\pm+1)$ for $a_\pm$ an integer of half-integers. In fact, we can do better by writing

$$\boldsymbol{A}_\pm^2 = \frac{1}{4}\Big(\boldsymbol{L}^2 - \frac{\mu}{2H}\boldsymbol{R}^2\Big) \tag{11.70}$$

where we have used the fact $\boldsymbol{L}\cdot\boldsymbol{R} = \boldsymbol{R}\cdot\boldsymbol{L} = 0$. This is the same for both combinations so we actually have $a_+ = a_- = a$.

All we have left to do is compute $\boldsymbol{R}^2$. This is our last lengthy algebraic computation, using all of the commutators we by now are very familiar with, the end result is

$$\boldsymbol{R}^2 = \frac{e^4}{16\pi^2\epsilon_0^2} + \frac{2H}{\mu}\big(\boldsymbol{L}^2 + \hbar^2\big) \tag{11.71}$$

Plugging this in we get

$$\boldsymbol{A}_\pm^2 = \frac{1}{4}\bigg(\boldsymbol{L}^2 - \frac{\mu}{2H}\frac{e^4}{16\pi^2\epsilon_0^2} - \big(\boldsymbol{L}^2 + \hbar^2\big)\bigg) = -\frac{\mu}{8H}\frac{e^4}{16\pi^2\epsilon_0^2} - \frac{\hbar^2}{4} \tag{11.72}$$

Plugging in the eigenvalues we obtain

$$\hbar^2 a(a+1) = -\frac{\mu}{8E}\frac{e^4}{16\pi^2\epsilon_0^2} - \frac{\hbar^2}{4} \tag{11.73}$$

which can be simplified to

$$E = -\frac{\mu e^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{(2a+1)^2} \tag{11.74}$$

which agrees with our previous answer if $n = 2a+1$.

We now have a full explanation for the degeneracy. Each operator $A_{\pm 3}$ can take the values $-a, -a+1, \ldots, a$, and because there are two of them we will have $(2a+1)^2 = n^2$ states with the same energy. This is exactly the result we had previously.

We didn't have to solve any differential equation, but computing all of the commutators wasn't exactly trivial. Additionally, this method only works for the Coulomb potential and the harmonic oscillator. Any other central potential will not have an equivalent of the Runge-Lenz vector and its spectrum will depend on ℓ. It is nice to know where the extra degeneracy comes from but the methods of the previous section are more easily applicable to more generic cases.

12 Spin

Our achievements in the last chapter are nothing short of a tremendous success. Deriving the discrete spectrum of the Hydrogen atom was one of the earliest goals of quantum mechanics. The fact we managed to explain it from first principles without any hiccoughs is astonishing. Early attempts needed some ad-hoc quantisation of angular momentum, only very crudely motivated with a naive application of the De Broglie relation between wavelength and momentum.

There is however one flaw in our theory. From the algebra of angular momentum we saw that we could have either integer or half-integer ℓ. However, when written in terms of spherical harmonics we see that half-integer ℓ do not lead to single-valued wavefunctions. There is no algebraic way to derive this restriction. What is the meaning of these half-integer angular momentum states?

In this chapter we will see that these half-integer states can be fully realised by introduce the concept of *spin* angular momentum. We will examine the specific case of spin-1/2 which describes an electron. Finally we shall study how electrons behave under a magnetic field thereby explaining the outcomes of the Stern-Gerlach experiment from first principles.

12.1 Rotations Vs Translations around a circle

The key idea that we were missing in the previous chapters is that, despite appearances, $\boldsymbol{L}$ is *not* the generator of rotations. It is instead the generator of translations around a circle. To explain the difference it is easier to look at pictures

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For objects with some kind of internal structure it is clear that the two actions are distinct. Let us first show that $\boldsymbol{L}$ generates these translations around a circle.

First recall that the generator of translations is given by the linear momentum; that is for an infinitesimal translations $\boldsymbol{\delta a}$ we have that

$$U(\boldsymbol{\delta a}) = \mathbb{1} - \frac{\mathrm{i}}{\hbar}\boldsymbol{\delta a}\cdot\boldsymbol{P} + O(\boldsymbol{\delta a}^2) \tag{12.1}$$

is such that

$$U(\boldsymbol{\delta a})^\dagger \boldsymbol{X} U(\boldsymbol{\delta a}) = \boldsymbol{X} + \boldsymbol{\delta a} \tag{12.2}$$

Then let us think about what it means to translate along a circle. We can first approximate the circle by a polygon with N sides

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In which case the translation around this polygon involves N displacements by vectors $\boldsymbol{a}_1, \dots, \boldsymbol{a}_N$ such that $\boldsymbol{a}_1 + \cdots + \boldsymbol{a}_N = 0$, if we take $N \to \infty$ this approaches the circle. Let us now focus on a single of these displacements in the limit where $N \to \infty$ so that they are infinitesimal. We start at position $\boldsymbol{x}$ making an angle α along the circle and we end at position $\boldsymbol{x} + \boldsymbol{\delta a}$ making an angle $\alpha + \delta\alpha$ along the circle. If $\boldsymbol{n}$ is the unit normal to the circle then it is clear that $\boldsymbol{\delta a} = \delta\alpha\, \boldsymbol{n} \times \boldsymbol{x}$.

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The unitary operator that describes this translation is

$$U(\boldsymbol{\delta a}) = \mathbb{1} - \frac{\mathrm{i}}{\hbar}\delta\alpha(\boldsymbol{n}\times\boldsymbol{X})\cdot\boldsymbol{P} + O(\boldsymbol{\delta a}^2) = \mathbb{1} - \frac{\mathrm{i}}{\hbar}\delta\alpha\, \boldsymbol{n}\cdot(\boldsymbol{X}\times\boldsymbol{P}) + O(\boldsymbol{\delta a}^2) \tag{12.3}$$

This shows that $\boldsymbol{L} = \boldsymbol{X}\times\boldsymbol{P}$ indeed generates translations around a circle.

What is then the generator of true rotations? The analysis of rotational symmetry is a fruitful and complex topic, here we shall focus on infinitesimal rotations for simplicity.

In geometric terms, the action of rotating a vector $\boldsymbol{v}$ along the axis $\boldsymbol{\delta\alpha}$ by an angle $|\boldsymbol{\delta\alpha}|$ can be written as

$$\boldsymbol{v} \to \boldsymbol{v}' = \boldsymbol{v} + \boldsymbol{\delta\alpha} \times \boldsymbol{v} + O(\boldsymbol{\delta\alpha}^2) \tag{12.4}$$

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We denote the generator of true rotations by $\boldsymbol{J}$ such that the unitary operator that describes rotations is written as

$$U(\boldsymbol{\delta\alpha}) = \mathbb{1} - \frac{\mathrm{i}}{\hbar}\boldsymbol{\delta\alpha} \cdot \boldsymbol{J} + O(\boldsymbol{\delta\alpha}^2) \tag{12.5}$$

Any vector operator $\boldsymbol{V}$ must then obey the following commutation relations with $\boldsymbol{J}$:

$$U(\boldsymbol{\delta\alpha})^\dagger\ \boldsymbol{V}\ U(\boldsymbol{\delta\alpha}) = \boldsymbol{V} + \boldsymbol{\delta\alpha} \times \boldsymbol{V} + O(\boldsymbol{\delta\alpha}^2) \tag{12.6}$$

plugging in (12.5) we obtain

$$\frac{\mathrm{i}}{\hbar}[\boldsymbol{\delta\alpha} \cdot \boldsymbol{J}, \boldsymbol{V}] = \boldsymbol{\delta\alpha} \times \boldsymbol{V} \tag{12.7}$$

which implies

$$[J_i, V_j] = \mathrm{i}\hbar\epsilon_{ijk}V_k \tag{12.8}$$

which is very reminiscent of the commutation relations between $\boldsymbol{L}$ and the vectors made from $\boldsymbol{X}$ and $\boldsymbol{P}$.

Purely geometrically, the order in which we apply rotations matters.

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We can therefore derive the commutation relations between the components of $\boldsymbol{J}$ by looking at the difference between first rotating by $\boldsymbol{\delta\alpha}$ and then rotating by $\boldsymbol{\delta\beta}$:

$$\boldsymbol{V} \to \boldsymbol{V} + \boldsymbol{\delta\alpha} \times \boldsymbol{V} \to \boldsymbol{V} + \boldsymbol{\delta\alpha} \times \boldsymbol{V} + \boldsymbol{\delta\beta} \times \boldsymbol{V} + \boldsymbol{\delta\beta} \times (\boldsymbol{\delta\alpha} \times \boldsymbol{V}) \tag{12.9}$$

and performing these rotations in the reverse order

$$\boldsymbol{V} \to \boldsymbol{V} + \boldsymbol{\delta\beta} \times \boldsymbol{V} \to \boldsymbol{V} + \boldsymbol{\delta\beta} \times \boldsymbol{V} + \boldsymbol{\delta\alpha} \times \boldsymbol{V} + \boldsymbol{\delta\alpha} \times (\boldsymbol{\delta\beta} \times \boldsymbol{V}) \tag{12.10}$$

The difference between the two is given by

$$\begin{aligned}
&U(\boldsymbol{\delta\beta})^\dagger \big(U(\boldsymbol{\delta\alpha})^\dagger\ \boldsymbol{V}\ U(\boldsymbol{\delta\alpha})\big)U(\boldsymbol{\delta\beta}) - U(\boldsymbol{\delta\alpha})^\dagger \big(U(\boldsymbol{\delta\beta})^\dagger\ \boldsymbol{V}\ U(\boldsymbol{\delta\beta})\big)U(\boldsymbol{\delta\alpha}) = \\
=&\boldsymbol{\delta\beta} \times (\boldsymbol{\delta\alpha} \times \boldsymbol{V}) - \boldsymbol{\delta\alpha} \times (\boldsymbol{\delta\beta} \times \boldsymbol{V}) = (\boldsymbol{\delta\beta} \times \boldsymbol{\delta\alpha}) \times \boldsymbol{V} = \\
=&U(\boldsymbol{\delta\beta} \times \boldsymbol{\delta\alpha})^\dagger\ \boldsymbol{V}\ U(\boldsymbol{\delta\beta} \times \boldsymbol{\delta\alpha}) - \boldsymbol{V}
\end{aligned} \tag{12.11}$$

we therefore conclude that

$$[U(\boldsymbol{\delta\alpha}), U(\boldsymbol{\delta\beta})] = U(\boldsymbol{\delta\beta} \times \boldsymbol{\delta\alpha}) - \mathbb{1} \tag{12.12}$$

plugging in the definition of $\boldsymbol{J}$ we get

$$-\frac{\mathrm{i}}{\hbar^2}[\boldsymbol{\delta\alpha} \cdot \boldsymbol{J}, \boldsymbol{\delta\beta} \cdot \boldsymbol{J}] = -\frac{\mathrm{i}}{\hbar}(\boldsymbol{\delta\beta} \times \boldsymbol{\delta\alpha}) \cdot \boldsymbol{J} \tag{12.13}$$

and therefore

$$[J_i, J_j] = \mathrm{i}\hbar\epsilon_{ijk}J_k \tag{12.14}$$

which are the same commutation relations we had for the components of $\boldsymbol{L}$.

This operator $\boldsymbol{J}$ is the true generator of rotations. Its commutation relations are very similar to $\boldsymbol{L}$ but it is possible that the two are not the same. We call their difference *spin* and define it as:

$$\boldsymbol{S} \equiv \boldsymbol{J} - \boldsymbol{L} \tag{12.15}$$

so that we can say that the total angular momentum $\boldsymbol{J}$ is the sum of the orbital angular momentum $\boldsymbol{L}$ and the spin angular momentum $\boldsymbol{S}$ in analogy with the classical case.

Using the fact $\boldsymbol{L}$ is a vector, we have $[J_i, L_j] = \mathrm{i}\hbar\epsilon_{ijk}L_k$, and therefore the commutator between the components of $\boldsymbol{S}$ are

$$\begin{aligned}[S_i, S_j] = [J_i - L_i, J_j - L_j] = [J_i, J_j] - [J_i, L_j] - [L_i, J_j] + [J_i, J_j] = \\ = \mathrm{i}\hbar\epsilon_{ijk}(J_k - L_k + L_k + L_k) = \mathrm{i}\hbar\epsilon_{ijk}S_k\end{aligned} \tag{12.16}$$

which are the commutation relations we have come to expect from angular momentum operators. It suggests that we can indeed interpret $\boldsymbol{S}$ as some form of angular momentum.

However, using the fact both $[J_i, X_k] = \mathrm{i}\hbar\epsilon_{ijk}X_k$ and $[L_i, X_k] = \mathrm{i}\hbar\epsilon_{ijk}X_k$ we find

$$[S_i, X_j] = 0 \tag{12.17}$$

and similarly for the linear momentum $\boldsymbol{P}$.

This tells us that this operator has nothing to do with the location or momentum of the particle. It must describe some internal rotation. Nevertheless, the commutation relations are exactly the same as $\boldsymbol{L}$ therefore the algebraic derivation of the eigenstates goes through without changes. We can construct states $|s, m_s\rangle$ such that

$$\boldsymbol{S}^2 |s, m_s\rangle = \hbar^2 s(s+1) |s, m_s\rangle \tag{12.18}$$

$$S_z |s, m_s\rangle = \hbar m_s |s, m_s\rangle \tag{12.19}$$

$$S_\pm |s, m_s\rangle = \hbar\sqrt{s(s+1) - m_s(m_s \pm 1)}\, |s, m_s \pm 1\rangle \tag{12.20}$$

where $S_\pm \equiv S_x \pm \mathrm{i}S_y$ and the numbers s and m_s are such that

$$s = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots \quad \text{and} \quad m_s = -s, -s+1, \ldots, s-1, s \tag{12.21}$$

The question now if we can also discard the half-integer spin states or not. More specifically, if we could attribute $\boldsymbol{S}$ to the motion of internal degrees of freedom, so that it is merely a sum of the orbital angular momenta of internal constituents with positions s $\boldsymbol{X}_a$ and momenta $\boldsymbol{P}_a$; we would be able to write:

$$\boldsymbol{S} \overset{?}{=} \sum_a \boldsymbol{X}_a \times \boldsymbol{P}_a \tag{12.22}$$

But then if this were indeed true, we would be able to write the states $|s, m_s\rangle$ in the position basis where the $\boldsymbol{X}_a$ act as multiplication by $\boldsymbol{x}_a$. In that case they would obey an equation similar to (10.30) and therefore we would be forced to write them in terms of single-valued spherical harmonics. We would therefore only be allowed to include integer values for s.

This is not what we observe experimentally. There are several examples of particles which can only be described using half-integer spin. The electron and the proton for example are observed to have spin-1/2; $\varDelta$ baryons are observed to have spin-3/2. This is evidence that there must be some *intrinsic* spin angular momentum which goes beyond the motion of individual constituents. The electron, for example, as far as we currently understand it seems to be fundamental. The proton is in turn made of of quarks and gluons and its total spin would be a sum of the spins of quarks and gluons and the orbital angular momentum due to their internal motion.

We see therefore that half-integer spin (and consequently half-integer total angular momentum j) is allowed. In quantum mechanics even fundamental particles are allowed to have spin angular momentum. Because we do not have a wavefunction representation of these fundamental spin states there is no way we could demand single-valuedness and no reason to exclude these half-integer spin states. An important addition to this is that particles (fundamental or not) always have a specific and immutable spin. Electrons and protons are *always* observed to have spin-1/2; they are never observed to have other values of spin.

12.2 Spin-1/2

In this section we will examine in detail the states with spin-1/2. You might wonder why we are going to such depth for this specific case. There are three main reasons: pedagogical, experimental, and mathematical. Firstly, it is very simple, it is in fact the simplest non-trivial example of a quantum system that is still experimentally relevant; in fact it was our starting point and it is worth revisiting now that we have the knowledge to describe it more rigorously. Secondly, it is very important for experiments. Many particles have spin-1/2 like the electron, the proton, and the neutron; it is crucial to understand this case in depth if we wish to understand these particles. Finally there is a beautiful mathematical reason which we won't delve into, all other spin states can be built up from the spin-1/2 states. In group theory language they furnish the *fundamental representation.* So, with enough mathematics by studying spin-1/2 we are actually studying all spin.

The spin-1/2 eigentates, have $s = 1/2$ and $m_s = \pm 1/2$ in the notation of the previous section. There are only two of them and for simplicity they are usually called "spin-up", $|\uparrow\rangle$, or "spin-down", $|\downarrow\rangle$, depending on the sign of m_s:

$$|\uparrow\rangle = \left|\frac{1}{2}, \frac{1}{2}\right\rangle \tag{12.23}$$

$$|\downarrow\rangle = \left|\frac{1}{2}, -\frac{1}{2}\right\rangle \tag{12.24}$$

Of course spin-1/2 particles can be in a superposition of these states, these states can then be viewed as the orthonormal basis for the 2-dimensional Hilbert space of spin-1/2 states. We can represent a generic state in this Hilbert space by a 2-component column vector χ, called a *spinor*:

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_- \tag{12.25}$$

where

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{12.26}$$

and

$$a = \langle\uparrow|\chi\rangle \quad \text{and} \quad b = \langle\downarrow|\chi\rangle \tag{12.27}$$

The normalisation condition in terms of these spinors is

$$1 = |a|^2 + |b|^2 = \begin{pmatrix} a^* & b^* \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \chi^\dagger \chi \tag{12.28}$$

The spin operators will then be represented by 2×2 matrices, let us calculate their matrix elements. Firstly, we have

$$S_z \left|\uparrow\right\rangle = +\frac{\hbar}{2} \left|\uparrow\right\rangle \tag{12.29}$$

$$S_z \left|\downarrow\right\rangle = -\frac{\hbar}{2} \left|\downarrow\right\rangle \tag{12.30}$$

therefore, the matrix representation of this operator will be

$$S_z = \begin{pmatrix} \left\langle\uparrow\right| S_z \left|\uparrow\right\rangle & \left\langle\uparrow\right| S_z \left|\downarrow\right\rangle \\ \left\langle\downarrow\right| S_z \left|\uparrow\right\rangle & \left\langle\downarrow\right| S_z \left|\downarrow\right\rangle \end{pmatrix} = \begin{pmatrix} \frac{\hbar}{2} & 0 \\ 0 & -\frac{\hbar}{2} \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{12.31}$$

We can do the same procedure for the raising operator:

$$S_+ \left|\uparrow\right\rangle = 0 \tag{12.32}$$

$$S_+ \left|\downarrow\right\rangle = \hbar \left|\uparrow\right\rangle \tag{12.33}$$

which gives

$$S_+ = \begin{pmatrix} \left\langle\uparrow\right| S_+ \left|\uparrow\right\rangle & \left\langle\uparrow\right| S_+ \left|\downarrow\right\rangle \\ \left\langle\downarrow\right| S_+ \left|\uparrow\right\rangle & \left\langle\downarrow\right| S_+ \left|\downarrow\right\rangle \end{pmatrix} = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \tag{12.34}$$

And for the lowering operator

$$S_- \left|\uparrow\right\rangle = \hbar \left|\downarrow\right\rangle \tag{12.35}$$

$$S_- \left|\downarrow\right\rangle = 0 \tag{12.36}$$

which gives

$$S_- = \begin{pmatrix} \left\langle\uparrow\right| S_- \left|\uparrow\right\rangle & \left\langle\uparrow\right| S_- \left|\downarrow\right\rangle \\ \left\langle\downarrow\right| S_- \left|\uparrow\right\rangle & \left\langle\downarrow\right| S_- \left|\downarrow\right\rangle \end{pmatrix} = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{12.37}$$

We can combine these last two to find out the matrix elements of S_x and S_y:

$$S_x = \frac{1}{2}(S_+ + S_-) = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{12.38}$$

$$S_y = \frac{1}{2\mathrm{i}}(S_+ - S_-) = \frac{\hbar}{2}\begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \tag{12.39}$$

We can combine all of these results into a single equation

$$\boldsymbol{S} = \frac{\hbar}{2}\boldsymbol{\sigma} \tag{12.40}$$

where $\boldsymbol{\sigma}$ are the *Pauli matrices*:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{12.41}$$

They obey the following commutation and anti-commutation relations, as can be easily checked explicitly

$$[\sigma_i, \sigma_j] = 2\mathrm{i}\epsilon_{ijk}\sigma_k \tag{12.42}$$

$$\{\sigma_i, \sigma_j\} = 2\delta_{jk}\mathbb{1} \tag{12.43}$$

We can also check very straightforwardly that,

$$\boldsymbol{S}^2 = S_x^2 + S_y^2 + S_z^2 = \frac{3}{4}\hbar\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{12.44}$$

as we expected from spin-1/2 states.

In more realistic scenarios the spinors χ would also have to include the values of other quantum numbers, *e.g.* they could depend on the position. But they are already fit to explore certain questions. For example, take a generic spinor $\chi = a\chi_+ + b\chi_-$, if we chose to measure S_z, by the Born rule, we would obtain the value $\hbar/2$ with probability $|a|^2$ or the value $-\hbar/2$ with probability $|b|^2$. What would be the outcome if we chose to measure S_x? We first need to find the eigenspinors of S_x. The characteristic equation is

$$\begin{vmatrix} -\lambda & \frac{\hbar}{2} \\ \frac{\hbar}{2} & -\lambda \end{vmatrix} = 0 \implies \lambda^2 = \frac{\hbar^2}{4} \implies \lambda = \pm\frac{\hbar}{2} \tag{12.45}$$

so the possible outcomes are the same as for S_z which is to be expected.

The eigenspinors are obtained in the usual way

$$\frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \pm\frac{\hbar}{2}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} \implies \begin{pmatrix} \beta \\ \alpha \end{pmatrix} = \pm\begin{pmatrix} \alpha \\ \beta \end{pmatrix} \tag{12.46}$$

therefore the normalised eigenspinors of S_x are

$$\chi_+^x = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{and} \quad \chi_-^x = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \tag{12.47}$$

Therefore the probability of measuring spin ±$\hbar/2$ in the x-direction is

$$\left|\chi_\pm^{x\,\dagger}\chi\right|^2 = \frac{|a \pm b|^2}{2} \tag{12.48}$$

If for example we had prepared the state to have spin-up in the z-direction we would have a 50/50 change of measuring each outcome in the x-direction. This is exactly the behaviour we observed at the beginning with our Stern-Gerlach devices!

Now imagine we wished to measure spin in a direction $\boldsymbol{n} = (\cos\phi, \sin\phi, 0)$. Then we need to diagonalise the operator

$$S_z\cos\phi + S_y\sin\phi = \frac{\hbar}{2}\begin{pmatrix} 0 & \mathrm{e}^{-\mathrm{i}\phi} \\ \mathrm{e}^{\mathrm{i}\phi} & 0 \end{pmatrix} \tag{12.49}$$

It is not too hard to show that its eigenvectors are

$$\chi_+^\phi = \frac{1}{\sqrt{2}}\begin{pmatrix} \mathrm{e}^{-\mathrm{i}\phi/2} \\ \mathrm{e}^{\mathrm{i}\phi/2} \end{pmatrix} \quad \text{and} \quad \chi_-^\phi = \frac{1}{\sqrt{2}}\begin{pmatrix} \mathrm{e}^{-\mathrm{i}\phi/2} \\ -\mathrm{e}^{\mathrm{i}\phi/2} \end{pmatrix} \tag{12.50}$$

with eigenvalues $+\hbar/2$ and $-\hbar/2$ respectively.

The probability of measuring spin-up in this direction if we had prepared the state in the spin-up in the z-direction is

$$\left|\chi_+^{\phi\,\dagger}\chi_+\right|^2 = \left|\frac{1}{\sqrt{2}}\begin{pmatrix} \mathrm{e}^{\mathrm{i}\phi/2} & \mathrm{e}^{-\mathrm{i}\phi/2} \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix}\right|^2 = \frac{1}{2} \tag{12.51}$$

This is to be expected, we get 50/50 chance for any direction perpendicular to the one we measured earlier. A more interesting case is if we had prepared the state to be spin-up in the x-direction:

$$\left|\chi_+^{\phi\,\dagger}\chi_+^x\right|^2 = \left|\frac{1}{2}\begin{pmatrix}\mathrm{e}^{\mathrm{i}\phi/2} & \mathrm{e}^{-\mathrm{i}\phi/2}\end{pmatrix}\begin{pmatrix}1\\1\end{pmatrix}\right|^2 = \left|\left(\mathrm{e}^{\mathrm{i}\phi/2}+\mathrm{e}^{-\mathrm{i}\phi/2}\right)\right|^2 = \cos^2\left(\frac{\phi}{2}\right) \tag{12.52}$$

At $\phi = 0$ we recover our earlier result that the spin was definitely $+\hbar/2$ along the x-direction. For $\phi = \pi/2$, *i.e.* if we are measuring in the y-direction we get probability 1/2; and of course for $\phi = \pi$ we are measuring in fact whether it was spin-down in the x-direction so the probability is 0. All of this we managed to glean experimentally. Now we have a way to predict the outcome for generic angles. What was once complex and nearly inscrutable is now almost trivial.

12.3 Spins in a magnetic field: Stern-Gerlach explained

In the previous sections we have repeatedly stated that several particles (fundamental or not) are observed to have spin angular momentum. In the rest of this chapter we will explore how these measurements can be made. We begin with the experiment that started our journey: the Stern-Gerlach experiment. Now we can finally have a first-principles understanding of it.

From the force (3.3) we can deduce a potential energy in the usual way given by:

$$V = -\boldsymbol{\mu}\cdot\boldsymbol{B} \tag{12.53}$$

Classically, for an electron with spin angular momentum $\boldsymbol{S}$ we would expect that its magnetic momentum is given by (3.2) with $\boldsymbol{L}\to\boldsymbol{S}$ and $q = -e$. However, as mentioned in Chapter 3 this turns out to be wrong in quantum mechanics. It is still true that the magnetic moment is proportional to the spin, but it's proportionality constant isn't $q/2m$. In general we therefore write

$$\boldsymbol{\mu} = \gamma\boldsymbol{S} \tag{12.54}$$

where γ is called the *gyromagnetic ratio.*

For the electron in particular we have

$$\gamma = -\frac{eg_e}{2m_e} \tag{12.55}$$

where

$$g_e = 2.002\ 319\ 304\ 360\ 92(36) \tag{12.56}$$

is sometimes known as the *g-factor*. We have written that many significant figures to highlight the precision of our knowledge. Dirac's relativistic equation for the electron is able to predict that $g_e = 2$ the decimal figures come from quantum field theory corrections. This number is the best agreement between theory and experiment in all of science. Other particles will have different g-factors, the proton for example has $g_p \approx 5.6$.

Using the Pauli matrices, we may sometimes write the magnetic moment of the electron as

$$\boldsymbol{\mu} = -\frac{g_e}{2}\mu_B\boldsymbol{\sigma} \tag{12.57}$$

where

$$\mu_B = \frac{e\hbar}{2m_e} \approx 9.274\times 10^{-24}\ \mathrm{J\ T^{-1}} \approx 5.788\times 10^{-5}\ \mathrm{eV\ T^{-1}} \tag{12.58}$$

is the *Bohr magneton*. Because $g_e \approx 2$, we can write

$$\boldsymbol{\mu} \approx -\mu_B \boldsymbol{\sigma} \tag{12.59}$$

making apparent that μ_B sets the scale for the magnetic moment of the electron.

We wish to study the effect of the coupling between the spin and the magnetic field. To avoid extraneous effects due to the coupling between the orbital angular momentum and the magnetic field it is usually best to consider neutral particles. Stern and Gerlach for instance used silver atoms which have spin-1/2. All in all we wish the examine the following Hamiltonian

$$H = \frac{P^2}{2m} - \gamma \boldsymbol{S} \cdot \boldsymbol{B} \tag{12.60}$$

Note that the magnetic field is external, it is not an observable represented by a Hermitian operator. Think of it as the potential V, if it is constant then it is a number, but it might depend on the position $\boldsymbol{X}$ making it an operator.

For our purposes it will be easier to work in the Heisenberg picture. First let us examine the time dependence of the spin vector:

$$\mathrm{i}\hbar \frac{\mathrm{d}\boldsymbol{S}}{\mathrm{d}t} = [\boldsymbol{S}, H] \tag{12.61}$$

using (12.16) and the fact $[S_i, P_j] = 0$ we find

$$\mathrm{i}\hbar \frac{\mathrm{d}S_i}{\mathrm{d}t} = -\gamma B_j [S_i, S_j] = -\gamma B_j \mathrm{i}\hbar \epsilon_{ijk} S_k \tag{12.62}$$

writing in vector notation once more we find

$$\frac{\mathrm{d}\boldsymbol{S}}{\mathrm{d}t} = \gamma \boldsymbol{S} \times \boldsymbol{B} \tag{12.63}$$

which is exactly what we would have expected classically from the torque given by (3.1). This is not too surprising, after all, Heisenberg's equation is always closer to classical mechanics.

Let us consider the case when the magnetic field is constant and, wlog, assume that it is pointing along the z-direction. We therefore have

$$\frac{\mathrm{d}S_x}{\mathrm{d}t} = \gamma S_y B_z \tag{12.64}$$

$$\frac{\mathrm{d}S_y}{\mathrm{d}t} = -\gamma S_x B_z \tag{12.65}$$

$$\frac{\mathrm{d}S_z}{\mathrm{d}t} = 0 \tag{12.66}$$

which is solved by

$$\boldsymbol{S}(t) = \begin{pmatrix} S_x(0)\cos(\gamma B_z t) + S_y(0)\sin(\gamma B_z t) \\ S_y(0)\cos(\gamma B_z t) - S_x(0)\sin(\gamma B_z t) \\ S_z(0) \end{pmatrix} \tag{12.67}$$

We see that the spin *precesses* around the magnetic field[80]

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[80] If you are finding it hard to interpret this Heisenberg picture result just take the expectation value which will then agree with the Schrodinger picture. We can then port our conclusions over to say that the expectation value of the spin operator $\langle \boldsymbol{S} \rangle$ precesses around the magnetic field vector $\boldsymbol{B}$.

This is called *Larmor precession* and the frequency of this oscillation is the *Larmor frequency*

$$\omega_L = \gamma|B| \tag{12.68}$$

Now we wish to consider how the position of the particles evolves over time. If $\boldsymbol{B}$ is a constant then $\boldsymbol{X}$ and $\boldsymbol{P}$ commute with the potential (12.53) and the position and momentum evolve just as with free particles. This is exactly what we observed classically, only a spatially varying magnetic field could produce an overall force. It is not too hard to show that the Heisenberg equation and the canonical commutation relations imply

$$m\frac{\mathrm{d}^2\boldsymbol{X}}{\mathrm{d}t^2} = \gamma\boldsymbol{\nabla}(\boldsymbol{S}\cdot\boldsymbol{B}) \tag{12.69}$$

which is what we expected from analogy with classical physics.

In order to measure the spin in the z-direction we ideally would like the magnetic field to roughly be $\boldsymbol{B} \sim \alpha z\boldsymbol{e_z}$ but this would not obey the electromagnetic law $\boldsymbol{\nabla}\cdot\boldsymbol{B} = 0$. In order to have the z-component to be what we want we need to add a similar component in another direction which would ruin our measurement. What we can do is instead consider the following magnetic field:

$$\boldsymbol{B} = -\alpha\boldsymbol{e_x} + (B_0 + \alpha z)\boldsymbol{e_z} \tag{12.70}$$

Then if B_0 is sufficiently strong then the spin vector will precess very rapidly around the z-axis. The spin in the x-direction would then average to zero and therefore, in the timescale needed for the position to change appreciably, the resulting force in the x-direction would be zero. The same would not happen for the z-direction. We can therefore approximately write

$$m\frac{\mathrm{d}^2\boldsymbol{X}}{\mathrm{d}t^2} \approx \gamma S_z\alpha\boldsymbol{e_z} \tag{12.71}$$

Additionally, given the components S_x and S_y average to zero in the timescales we are interested in we can restrict our attention to eigenstates of $\boldsymbol{S}^2$ and S_z. Taking the expectation value in the states $|s, m_s\rangle$ we then find

$$m\frac{\mathrm{d}^2\langle\boldsymbol{X}\rangle}{\mathrm{d}t^2} \approx \alpha\gamma\hbar m_s\boldsymbol{e_z} \tag{12.72}$$

We see that if we send particles of spin-s through a region with magnetic field (12.70) they will be deflected according to their value of m_s, the eigenvalue of S_z. They will split into $2s+1$ distinct beams, demonstrating the discreteness of the spectrum of the spin operator.

12.4 Hydrogen atoms in a magnetic field: the Paschen-Back effect

You might be slightly disappointed by our the previous section. It seems that in practice we can only measure the spin of neutral particles, like atoms, and not electrons. This is, fortunately, not the case. There are indirect ways of measuring the spin of the electron one of these is by studying the change in the energy levels of a Hydrogen atom when subjected to a constant external magnetic field.

In particular we will subject the Hydrogen atoms to a constant and strong magnetic field. The reason for choosing a strong magnetic field is to ensure it dominates over the relativistic corrections to the spectrum of Hydrogen[81]. If the magnetic field was too weak

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[81] These are the origin of the famed *fine structure* of Hydrogen, called that because it is suppressed by a power of α^2 relative to the results in the previous chapter

then we would have to include these relativistic effects before considering the effects of the magnetic field itself. In practice it means we shall only consider fields of order $|\boldsymbol{B}| \gtrsim 5$ T. We shall also neglect effects quadratic in the magnetic field $\sim B^2$, sometimes called the *diamagnetic* terms, which restrict us to fields $|\boldsymbol{B}| \lesssim 10$ T.

All in all, the Hamiltonian we wish to consider is the following

$$H = \frac{\boldsymbol{P}^2}{2\mu} - \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\boldsymbol{X}|} + \frac{e}{2m_e}\boldsymbol{B}\cdot(\boldsymbol{L} + g_e\boldsymbol{S}) \tag{12.73}$$

where we have also added the orbital contribution to the magnetic moment, whose gyromagnetic ratio equals the classical value.

It is incredibly easy to find the eigenstates of this Hamiltonian. Because both $\boldsymbol{J}$ and $\boldsymbol{S}$ commute with the first two terms we can simultaneously diagonalise the Coulomb Hamiltonian and the additional magnetic term. In fact, we can, without loss of generality, define the z-direction such that $\boldsymbol{B} = B\boldsymbol{e_z}$ and therefore the states $|n, \ell, m_\ell, s, m_s\rangle$ we found earlier are also eigenstates of the magnetic term leading to

$$E_{\text{tot}} = E_n + \mu_B B(m_\ell + g_e m_s) \tag{12.74}$$

where E_n is given by (11.37).

The application of $\boldsymbol{B}$ has lifted the degeneracy for different values of m_ℓ and m_s. This shift in the energies for strong magnetic fields is called the *Paschen-Back effect*[82]. We can now use this splitting to determine the spin of the electron directly. For example, looking at ground state with $\ell = 0$ we see that it is split into $2s+1$ levels according to the value of m_s, the fact we observe it splitting into two levels demonstrates that the electron has spin-1/2. Further we can examine the details of this splitting to measure the value of g_e.

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Note that we have not fully lifted the degeneracy present earlier. For example, a state $m_\ell = 1$ and $m_s = -1/2$ has the same energy as a state with $m_\ell = 0$ and $m_s = 1/2$ (and the same value of n and ℓ).

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13 * Spontaneous emission of radiation

In the last few chapters we have worked hard to, among other things, obtain the energy levels for the hydrogen atom, both isolated and subjected to a strong magnetic field. However, we have not described how we could experimentally verify these results. At most we could have appealed to the early quantum ideas that the system could go from an excited state to a state with lower energy by emitting a photon of the corresponding energy, and doing the opposite transition by absorbing a photon. In this chapter we will describe these processes, finally providing a first principles derivation of atomic spectra.

We shall begin by considering electromagnetic interactions in greater generality, highlighting the role of the potentials and gauge symmetry via the Aharonov-Bohm effect. Then we will use the rotating wave approximation to describe the absorption of radiation. Finally, we will employ a trick, originally due to Einstein, to use the rate of absorption and some simple thermodynamics to obtain the rate of spontaneous and stimulated emission of radiation.

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[82] In many textbooks it is instead known as the Zeeman effect. Historically however, Pieter Zeeman measured the effect of weak magnetic fields which is quite different (and much more involved) than what we have described here. It was Friedrich Paschen and Ernst Back that first examined the strong field regime.

13.1 Electromagnetic interactions and the Aharonov-Bohm effect

Classically, a particle with charge q subjected to an electric field $\boldsymbol{E}$ and a magnetic field $\boldsymbol{B}$ will experience the Lorentz force

$$\boldsymbol{F} = q(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B}) \tag{13.1}$$

where $\boldsymbol{v}$ is the particle's velocity.

Alternatively, we can re-derive the equations of motion implied by the Lorentz force using the following Hamiltonian:

$$H = \frac{1}{2m}(\boldsymbol{p} - q\boldsymbol{A})^2 + q\varphi \tag{13.2}$$

where φ and $\boldsymbol{A}$ are the electromagnetic potentials from which we can obtain the electric and magnetic fields via

$$\boldsymbol{E} = -\boldsymbol{\nabla}\varphi - \frac{\partial \boldsymbol{A}}{\partial t} \tag{13.3}$$

$$\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A} \tag{13.4}$$

It is therefore straightforward to suggest that a quantum particle with charge q when subjected to external electromagnetic fields will be described by the Hamiltonian[83]

$$H = \frac{1}{2m}(\boldsymbol{P} - q\boldsymbol{A})^2 + q\varphi \tag{13.5}$$

or in position basis

$$H = \frac{1}{2m}(-\mathrm{i}\hbar\boldsymbol{\nabla} - q\boldsymbol{A}(t, \boldsymbol{x}))^2 + q\varphi(t, \boldsymbol{x}) \tag{13.6}$$

This is the Hamiltonian we will study in the coming chapters, but, before we proceed, we need to remark on a curious aspect of the quantum mechanical electromagnetic interaction. Classically we introduced the electromagnetic potentials φ and $\boldsymbol{A}$ purely for mathematical convenience. They obey simpler equations than the electric and magnetic fields and allow for a simple expression for the Hamiltonian. The force a particle experiences and any physically measurable quantities can be written purely in terms of the electric and magnetic fields $\boldsymbol{E}$ and $\boldsymbol{B}$. In fact, the electromagnetic potentials are not uniquely determined, we can define new potentials φ' and $\boldsymbol{A'}$ given by

$$\varphi' = \varphi - \frac{\partial \Lambda}{\partial t} \tag{13.7}$$

$$\boldsymbol{A'} = \boldsymbol{A} + \boldsymbol{\nabla}\Lambda \tag{13.8}$$

with Λ an arbitrary function of space and time. These new potentials yield exactly the same electric and magnetic fields as the old ones. This fact is known as *gauge invariance* and demonstrates that there is a redundancy in our definitions of the electromagnetic potentials.

This gauge invariance is also manifested in the quantum mechanical theory if, together with the transformation of the potentials, we also transform the wavefunction as

$$\psi'(t, \boldsymbol{x}) = \mathrm{e}^{\mathrm{i}q\Lambda/\hbar}\psi(t, \boldsymbol{x}) \tag{13.9}$$

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[83] We could have also allowed for a coupling between the intrinsically quantum mechanical spin and the magnetic field by adding a term equal to $-\gamma\boldsymbol{S}\cdot\boldsymbol{B}$.

Since this is only a phase factor it seems as if the two wavefunctions define the same physical state. This is however a bit too quick because, even though we cannot measure *overall* phases we can still measure *relative* phases. In fact, Yakir Aharonov and David Bohm managed to show that we can measure these relative phases even in regions where both $\boldsymbol{E}$ and $\boldsymbol{B}$ vanish!

Let us then consider the case when $\boldsymbol{B} = 0$ and $\boldsymbol{E} = 0$. We can use our gauge freedom to therefore set $\varphi = 0$ and $\boldsymbol{\nabla} \cdot \boldsymbol{A} = 0$. The Schrodinger equation then looks like

$$\mathrm{i}\hbar \frac{\partial \psi}{\partial t} = \frac{1}{2m}(-\mathrm{i}\hbar\boldsymbol{\nabla} - q\boldsymbol{A})^2\psi \tag{13.10}$$

We can simplify this problem by writing

$$\psi = \mathrm{e}^{\mathrm{i}g}\psi' \tag{13.11}$$

where

$$g(\boldsymbol{x}) = \frac{q}{\hbar}\int_F^{\boldsymbol{x}} \mathrm{d}\boldsymbol{x}' \cdot \boldsymbol{A}(\boldsymbol{x}') \tag{13.12}$$

and F is some arbitrary reference point. Because $\boldsymbol{\nabla} \times \boldsymbol{A} = 0$ as long as we are considering a simply connected region g will indeed only be a function of $\boldsymbol{x}$ and will not depend on path taken from F to $\boldsymbol{x}$.

We therefore write

$$\boldsymbol{\nabla}\psi = \mathrm{e}^{\mathrm{i}g}\boldsymbol{\nabla}\psi' + \mathrm{e}^{\mathrm{i}g}(\mathrm{i}\boldsymbol{\nabla}g)\psi' \tag{13.13}$$

using the fact $\boldsymbol{\nabla}g = \frac{q}{\hbar}\boldsymbol{A}$ we get

$$(-\mathrm{i}\hbar\boldsymbol{\nabla} - q\boldsymbol{A})\psi = -\mathrm{i}\hbar\mathrm{e}^{\mathrm{i}g}\boldsymbol{\nabla}\psi' \tag{13.14}$$

and therefore

$$(-\mathrm{i}\hbar\boldsymbol{\nabla} - q\boldsymbol{A})^2\psi = -\hbar^2\mathrm{e}^{\mathrm{i}g}\nabla^2\psi' \tag{13.15}$$

plugging this into (13.10) we find

$$\mathrm{i}\hbar\frac{\partial \psi'}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi' \tag{13.16}$$

So that ψ' behaves like a free particle! With this result we have a very simple prescription for solving the Schrodinger equation in a region where $\boldsymbol{E} = \boldsymbol{B} = 0$, just solve the free particle problem and then tack on the phase $\mathrm{e}^{\mathrm{i}g}$.

Now consider the following setup: we have a very long solenoid of radius a carrying a steady electric current I

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We want the solenoid to be long enough such that the magnetic field inside the solenoid is uniform and the field outside is zero. Nevertheless, the gauge potential outside this solenoid is *not* zero. In fact, in the Coulomb gauge $\boldsymbol{\nabla} \cdot \boldsymbol{A} = 0$, we have

$$\boldsymbol{A} = \frac{\Phi}{2\pi r}\boldsymbol{e}_{\Phi} \tag{13.17}$$

where $\Phi = \pi a^2 B$ is the magnetic flux through the solenoid and r is the cylindrical distance from the centre of the solenoid. This vector potential obeys $\boldsymbol{\nabla} \times \boldsymbol{A} = 0$ as desired.

What Yakir Aharonov and David Bohm imagined was sending two electron beams, each passing through opposite sides of the solenoid.

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The beams would be kept well away from the solenoid so that they would only experience $\boldsymbol{B} = 0$. However, they would still experience non-zero $\boldsymbol{A}$ and they would pick up phases equal to

$$g = \frac{q}{\hbar}\int \mathrm{d}\boldsymbol{x}\cdot\boldsymbol{A} = \frac{q\Phi}{2\pi\hbar}\int (r\boldsymbol{e}_\phi\,\mathrm{d}\phi)\cdot\left(\frac{1}{r}\boldsymbol{e}_\phi\right) = \pm\frac{q\Phi}{2\hbar} \tag{13.18}$$

Where we put $\mathcal{P}$ in the incoming beam, use cylindrical coordinates, and then ϕ runs from 0 to π for one of the beams, and from 0 to $-\pi$ for the other.

You may be concerned that the solenoid breaks the simple connectedness needed for the definition of g. However, each beam only goes through half of the space, and each half is simple connected, therefore g is well defined for each beam[84].

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The phase each beam has is not measurable, but their relative phase is! We predict that the beams would have a relative phase of $q\Phi/\hbar$, we can then use interference to measure this relative phase. It was quite challenging to really ensure the electrons were going through a region with vanishing fields but this was finally done using superconducting rings in 1986 (CITE).

We see that our classical expectations were mistaken, we can measure the effects of electromagnetic interactions even in regions where $\boldsymbol{E} = \boldsymbol{B} = 0$. Note however that we cannot measure $\boldsymbol{A}$ directly, only the flux was measurable, thereby maintaining the gauge invariance of our theory. Nevertheless we see that a theory which focuses solely on the electric and magnetic fields is doomed, we must include the potentials (and their gauge redundancy) if we want to describe nature.

13.2 Absorption of monochromatic radiation

Our goal is to calculate the probability of an atom absorbing incoming radiation. This at first hand seems prohibitively complicated because incoming radiation will necessarily be time-dependent. Our Hamiltonian will therefore have an explicit time dependence so we cannot use the TISE to simplify our calculations. Nevertheless there are a couple of simplifying assumptions that will make our problem tractable. The first of these is to assume the incoming radiation is monochromatic, therefore, the electric and magnetic fields will be given by (the real part of)

$$\boldsymbol{E} = \boldsymbol{E}_0 \mathrm{e}^{\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-\omega t)} \quad \text{and} \quad \boldsymbol{B} = \frac{1}{c}\left(\hat{\boldsymbol{k}}\times\boldsymbol{E}_0\right)\mathrm{e}^{\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-\omega t)} \tag{13.19}$$

where $\omega = c|\boldsymbol{k}|$. Right away this will mean the time-dependence of the Hamiltonian will be harmonic which is simpler.

The second assumption is an educated guess. We shall assume that the frequency is close to the difference between two levels, that is

$$\hbar\omega \approx E_n - E_m \tag{13.20}$$

The will see later the crucial role this approximation will have in dealing with the explicit time-dependence.

To simplify further we note that the wavelength will be much larger than the typical

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[84] If you are still concerned you can check the original paper where they provide a full analytic solution to they Schrodinger equation without resorting to this trick and the results match.

length scales of hydrogen atom, set by the Bohr radius a_0[85]

$$\frac{\lambda}{a_0} = \frac{2\pi c}{\omega a_0} = \frac{2\pi m_e c^2 \alpha}{\hbar\omega} \approx \frac{4\pi}{\alpha}\frac{n^2 m^2}{n^2 - m^2} \tag{13.21}$$

where we have used the expressions (11.47) for the Bohr radius and (11.37) for the energy levels. Now we note that for $n > m$ and $n, m \geqslant 1$ we have $\frac{n^2m^2}{n^2-m^2} \geqslant 1$ which gives us

$$\frac{\lambda}{a_0} \gtrsim \frac{4\pi}{\alpha} \approx 1722 \gg 1 \tag{13.22}$$

We conclude that, when the frequency is close to the difference between two energy levels, the wavelength is much larger than the typical lengths scales of the atom. It is therefore a decent approximation to neglect the spatial dependence of the incoming radiation, and assume it is constant in space.

For a constant magnetic field we can look to the Paschen-Back effect for an estimate of the contribution to the energy

$$\Delta E_{\text{mag}} \sim \mu_B |\boldsymbol{B}_0| = \frac{e\hbar|\boldsymbol{B}_0|}{2m_e} \sim \frac{e\hbar|\boldsymbol{E}_0|}{2m_e c} \tag{13.23}$$

We can also do the same for the electric field. The potential for a constant electric field is just

$$\varphi = \boldsymbol{E} \cdot \boldsymbol{X} \tag{13.24}$$

therefore the contribution to the energy due to the electric field is roughly

$$\Delta E_{\text{electric}} \sim e a_0 |\boldsymbol{E}_0| = \frac{e|\boldsymbol{E}_0|\hbar}{m_e c\alpha} \tag{13.25}$$

Hence we conclude

$$\Delta E_{\text{mag}} \sim \alpha \Delta E_{\text{electric}} \tag{13.26}$$

which means the contribution of the magnetic field is suppressed by a factor of α relative to the contribution of the electric field. We will therefore approximate and neglect the magnetic field entirely.

All in all, the Hamiltonian we wish to consider is

$$H(t) = H_0 + \Delta H(t) \tag{13.27}$$

where H_0 is the Coulomb Hamiltonian and

$$\Delta H(t) = e\boldsymbol{E}_0 \cdot \boldsymbol{X} \cos(\omega t) \tag{13.28}$$

We are looking for the probability for the electron in a state with energy E_m to absorb a photon and end in state E_n. Of course, for the Hydrogen atom there is a large degeneracy, there are a lot of states with either energy unless $m = 1$ in which case the original state is the ground state. However, this angular variables will not matter too much so we'll omit the angular labels for simplicity, and just say $|\psi_n\rangle$ is one of the states with energy E_n.

We will now employ a trick which is very common for time-dependent problems, we strip out the time-dependence of a part of the Hamiltonian which is easy to solve, in our

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[85] Recall (11.50) which tells us that the wavefunctions of the hydrogen atom all decay as $\exp(-r/na_0)$.

case H_0. We will therefore use the ansatz

$$|\mathit{\Psi}(t)\rangle = c_m(t)\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}E_m t}\,|\psi_m\rangle + c_n(t)\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}E_n t}\,|\psi_n\rangle \tag{13.29}$$

plugging this into the time-dependent Schrodinger equation

$$\frac{\partial\,|\mathit{\Psi}(t)\rangle}{\partial t} = H(t)\,|\mathit{\Psi}(t)\rangle \tag{13.30}$$

we find

$$\mathrm{i}\hbar\dot{c}_m(t)\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}E_m t}\,|\psi_m\rangle + \mathrm{i}\hbar\dot{c}_n(t)\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}E_n t}\,|\psi_n\rangle = \Delta H(t)\,|\mathit{\Psi}(t)\rangle \tag{13.31}$$

Acting with $\langle\psi_n|$ and $\langle\psi_m|$ in turn we get two coupled equations

$$\begin{aligned}\mathrm{i}\hbar\dot{c}_m(t) =& c_m(t)\,\langle\psi_m|\,\Delta H(t)\,|\psi_m\rangle + c_n(t)\mathrm{e}^{-\mathrm{i}\omega_{nm}t}\,\langle\psi_m|\,\Delta H(t)\,|\psi_n\rangle &(13.32)\\ \mathrm{i}\hbar\dot{c}_n(t) =& c_m(t)\mathrm{e}^{\mathrm{i}\omega_{nm}t}\,\langle\psi_n|\,\Delta H(t)\,|\psi_m\rangle + c_n(t)\,\langle\psi_n|\,\Delta H(t)\,|\psi_n\rangle &(13.33)\end{aligned}$$

where we have defined the natural frequency of the transition

$$\omega_{nm} \equiv \frac{E_n - E_m}{\hbar} \tag{13.34}$$

In order to solve the equations we need the matrix elements of $\Delta H(t)$. First we note that the diagonal matrix element vanishes. This is because the H_0 is parity-invariant, therefore the $|\psi_n\rangle$ are eigenstates of parity, but $\boldsymbol{X}$ is parity-odd. In more detail,

$$\mathsf{P}\,|\psi_n\rangle = (-1)^{\ell}\,|\psi_n\rangle \implies \langle\psi_n|\,\boldsymbol{X}\,|\psi_n\rangle = (-1)^{2\ell}\,\langle\psi_n|\,\mathsf{P}^\dagger\boldsymbol{X}\mathsf{P}\,|\psi_n\rangle = -\,\langle\psi_n|\,\boldsymbol{X}\,|\psi_n\rangle \tag{13.35}$$

which means

$$\langle\psi_n|\,\Delta H(t)\,|\psi_n\rangle = e\cos(\omega t)\boldsymbol{E}_0\cdot\langle\psi_n|\,\boldsymbol{X}\,|\psi_n\rangle = 0 \tag{13.36}$$

A similar argument will tell us that the off-diagonal element will also vanish if both $|\psi_n\rangle$ and $|\psi_m\rangle$ have the same parity. If they have opposite parity we will, for convenience, define the *Rabi frequency*

$$\mathit{\Omega} \equiv \frac{e}{\hbar}\boldsymbol{E}_0\cdot\langle\psi_m|\,\boldsymbol{X}\,|\psi_n\rangle \tag{13.37}$$

which is real because $\boldsymbol{X}$ is Hermitian which implies $\langle\psi_m|\,\boldsymbol{X}\,|\psi_n\rangle = \langle\psi_n|\,\boldsymbol{X}\,|\psi_m\rangle$. In particular this frequency is proportional to the magnitude of the electric field.

All in all, the equations we have to solve are

$$\begin{aligned}\mathrm{i}\dot{c}_m(t) =& c_n(t)\mathrm{e}^{-\mathrm{i}\omega_{nm}t}\mathit{\Omega}\cos(\omega t) = c_n(t)\frac{\mathit{\Omega}}{2}\left(\mathrm{e}^{\mathrm{i}(\omega-\omega_{nm})t} + \mathrm{e}^{-\mathrm{i}(\omega+\omega_{nm})t}\right) &(13.38)\\ \mathrm{i}\dot{c}_n(t) =& c_m(t)\mathrm{e}^{\mathrm{i}\omega_{nm}t}\mathit{\Omega}\cos(\omega t) = c_m(t)\frac{\mathit{\Omega}}{2}\left(\mathrm{e}^{\mathrm{i}(\omega+\omega_{nm})t} + \mathrm{e}^{-\mathrm{i}(\omega-\omega_{nm})t}\right) &(13.39)\end{aligned}$$

which is still a bit too hard to solve analytically. However, we can use the approximation that the external frequency ω is close to the difference between two energy levels ω_{nm} in particular this means

$$|\omega - \omega_{nm}| \ll \omega + \omega_{nm} \tag{13.40}$$

Therefore the terms with the exponential with $\omega + \omega_{nm}$ oscillate much faster than the ones with $\omega - \omega_{nm}$. If we look at the longer timescales $\sim |\omega - \omega_{nm}|^{-1}$ we can simply neglect the terms with $\omega + \omega_{nm}$ as they will average out to zero. This is known as the *rotating wave approximation* and is what allowed Isidor Isaac Rabi to find the solution to this problem without resorting to perturbation theory, In this approximation we finally have a set of equations we can solve

$$\mathrm{i}\dot{c}_m(t) = c_n(t)\frac{\mathit{\Omega}}{2}\mathrm{e}^{\mathrm{i}\delta t} \tag{13.41}$$

$$\mathrm{i}\dot{c}_n(t) = c_m(t)\frac{\mathit{\Omega}}{2}\mathrm{e}^{-\mathrm{i}\delta t} \tag{13.42}$$

where

$$\delta \equiv \omega - \omega_{nm} \tag{13.43}$$

tells us how far we are from the natural frequency.

It is fairly straightforward to solve these equations, we just need boundary conditions. We want the probability for absorption so we set

$$c_m(0) = 1 \tag{13.44}$$

$$c_n(0) = 0 \tag{13.45}$$

which give us the solutions

$$c_m(t) = \mathrm{e}^{\mathrm{i}\delta t/2}\left(\cos\left(\frac{\sqrt{\mathit{\Omega}^2+\delta^2}}{2}t\right) - \frac{\mathrm{i}\delta}{\sqrt{\mathit{\Omega}^2+\delta^2}}\sin\left(\frac{\sqrt{\mathit{\Omega}^2+\delta^2}}{2}t\right)\right) \tag{13.46}$$

$$c_n(t) = -\mathrm{i}\mathrm{e}^{-\mathrm{i}\delta t/2}\frac{\mathit{\Omega}}{\sqrt{\mathit{\Omega}^2+\delta^2}}\sin\left(\frac{\sqrt{\mathit{\Omega}^2+\delta^2}}{2}t\right) \tag{13.47}$$

The probability of the system being in the excited state, *i.e.* the probability of absorption is

$$\begin{aligned} P_{\mathrm{abs}}(t) = |c_n(t)|^2 &= \frac{\mathit{\Omega}^2}{\mathit{\Omega}^2+\delta^2}\sin^2\left(\frac{\sqrt{\mathit{\Omega}^2+\delta^2}}{2}t\right) = \\ = |c_n(t)|^2 &= \frac{\mathit{\Omega}^2}{2(\mathit{\Omega}^2+\delta^2)}\left(1-\cos\left(\sqrt{\mathit{\Omega}^2+\delta^2}t\right)\right) \end{aligned} \tag{13.48}$$

Under this perturbation the system will oscillate between the two states with frequency $\sqrt{\mathit{\Omega}^2+\delta^2}$, the higher the difference from the natural frequency the faster the oscillations. These are the *Rabi oscillations* or *Rabi flopping.* For $\delta = 0$ the probability of absorption is highest and we obtain

$$P_{\mathrm{abs}}(t) = \sin^2\left(\frac{\mathit{\Omega}}{2}t\right) \tag{13.49}$$

This fact explains the absorption spectra, although it is true that the system will oscillate between the two states and we don't have perfect absorption we still see that the probability of absorption is higher if $\delta = 0$, which is sufficient to cause the dark lines in the spectrum. If we do want to ensure absorption we can send radiation for a time $\Delta t = \pi/\mathit{\Omega}$, which is known as a *$\pi$-pulse.* If $\delta \neq 0$ then we can never quite attain this certainty.

In the next section we will also need the expression for when the incident electric field is very weak so that $\mathit{\Omega} \ll \delta \ll 1$ we get

$$P_{\mathrm{abs}}(t) \approx \frac{\mathit{\Omega}^2}{\delta^2}\sin^2\left(\frac{\delta}{2}t\right) \tag{13.50}$$

In this limit we can use the following expression for the Dirac-δ

$$\delta(x) = \lim_{\epsilon\to 0}\frac{\epsilon}{\pi}\frac{\sin^2\left(\frac{x}{\epsilon}\right)}{x^2} \tag{13.51}$$

to write

$$\frac{P_{\text{abs}}(t)}{t} \xrightarrow{t\to\infty} \frac{\pi}{2}\Omega^2\ \delta(\omega-\omega_{nm}) \tag{13.52}$$

This is a special case of *Fermi's golden rule* which applies more generally in the first order time-dependent perturbation theory for harmonic perturbations. It makes the need for $\omega = \omega_{nm}$ much clearer but only applies for very weak electric fields and at late times. The expression (13.49) is better for studying the resonance itself.

13.3 Emission and absorption rates in a thermal bath of photons

In the previous section we were able to study absorption of monochromatic radiation in great detail, we didn't have to assume the electric field was weak but we did have to assume the drive frequency was close to the natural frequency. This is sufficient for explaining the absorption spectrum but is not sufficient to explain the emission spectrum. A full derivation of spontaneous emission would need a theory of photons which is rather complicated because the number of photons isn't conserved, which is the whole point, we want to study the spontaneous creation of a photon. There is however a trick due to Einstein. Instead of considering emission of a single photon we subject the atom to a thermal bath of photons. Then we can use some simple thermodynamics and detailed balance to set the rate of emission in terms of the rate of absorption. To obtain this result we need three ingredients:

1. The absorption rate of an ensemble of photons
2. The energy density of these photons in the Gibbs ensemble
3. The detailed balance equation

Absorption in an ensemble of photons In an ensemble of photons we will have many frequencies at play which precludes the simple application of the results from the previous section. We can however make statements about the *ensemble averages.* We shall denote ensemble averages by an overline to distinguish from the quantum mechanical expectation values. In particular, we will need the average of the product of the electric field at two points in time, *i.e.* the 2-point correlator:

$$\overline{E_i(t_1)E_j(t_2)} \tag{13.53}$$

Assuming we are in thermal equilibrium these averages must be time-translation invariant. Therefore this correlator can only depend on $t_1 - t_2$. Similarly, assuming there is no preferred direction, *i.e.* that the system is rotationally invariant, it must be proportional to δ_{ij}. Taking a Fourier transform we must have[86]

$$\overline{E_i(t_1)E_j(t_2)} = \delta_{ij}\int_{-\infty}^{\infty}\frac{\mathrm{d}\omega}{2\pi}F(\omega)\mathrm{e}^{-\mathrm{i}\omega(t_1-t_2)} \tag{13.54}$$

Given the LHS is real and symmetric under the exchange of t_1 and i with t_2 and j we must have

$$F(\omega) = F(-\omega) = F(\omega)^* \tag{13.55}$$

We can also write this correlator in terms of the energy density in the radiation field. First recall that the energy density in the electromagnetic fields is

$$\rho = \frac{1}{2}\left(\epsilon_0\boldsymbol{E}^2 + \frac{\boldsymbol{B}^2}{\mu_0}\right) \tag{13.56}$$

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[86] We are using a different sign in the exponential than usual for momentary convenience. Because $F(\omega) = F(-\omega)$ this has no material effect.

In radiation we have $\boldsymbol{E}^2 = \boldsymbol{B}^2/c^2$, and also $1/\mu_0 = c^2\epsilon_0$ so that

$$\rho = \frac{1}{2}\left(\epsilon_0 \boldsymbol{E}^2 + c^2\epsilon_0 \frac{\boldsymbol{E}^2}{c^2}\right) = \epsilon_0 \boldsymbol{E}^2 \tag{13.57}$$

therefore, the ensemble average of this energy density is

$$\rho = \epsilon_0 \overline{\boldsymbol{E}(t)^2} = 3\epsilon_0 \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} F(\omega) = 3\epsilon_0 \int_0^{\infty} \frac{\mathrm{d}\omega}{\pi} F(\omega) \tag{13.58}$$

We can therefore relate the energy density between angular frequencies ω and $\omega + \mathrm{d}\omega$, $\rho(\omega)\,\mathrm{d}\omega$, to the Fourier transform of the 2-point correlator

$$\rho(\omega)\,\mathrm{d}\omega = \frac{3}{\pi}\epsilon_0 F(\omega)\,\mathrm{d}\omega \tag{13.59}$$

which allows us to write the correlator in terms of this energy density

$$\overline{E_i(t_1)E_j(t_2)} = \frac{\delta_{ij}}{6\epsilon_0}\int_{-\infty}^{\infty} \mathrm{d}\omega\, \rho(|\omega|)\mathrm{e}^{-\mathrm{i}\omega(t_1-t_2)} \tag{13.60}$$

The perturbation Hamiltonian is still given by

$$\Delta H(t) = e\boldsymbol{E}(t)\cdot\boldsymbol{X} \tag{13.61}$$

so equation (13.36) will still hold and we still will not have any diagonal terms. We can therefore, still write

$$\mathrm{i}\hbar\dot{c}_m(t) = c_n(t)\mathrm{e}^{-\mathrm{i}\omega_{nm}t}\left\langle\psi_m\right|\Delta H(t)\left|\psi_n\right\rangle \tag{13.62}$$

$$\mathrm{i}\hbar\dot{c}_n(t) = c_m(t)\mathrm{e}^{\mathrm{i}\omega_{nm}t}\left\langle\psi_n\right|\Delta H(t)\left|\psi_m\right\rangle \tag{13.63}$$

Without the assumption of monochromatic waves we cannot solve these equations exactly. We can however assume the electric field is very weak and solve them perturbatively to obtain

$$c_n(t) \approx c_n(0) - \frac{\mathrm{i}}{\hbar}c_m(0)\int_0^t \mathrm{d}t'\,\left\langle\psi_n\right|\Delta H(t')\left|\psi_m\right\rangle \mathrm{e}^{\mathrm{i}\omega_{nm}t'} + O\big(\boldsymbol{E}^2\big) \tag{13.64}$$

and similarly for $c_m(t)$.

Therefore, the probability of absorption will, approximately, be

$$\begin{aligned} P_{\mathrm{abs}}(t) = |c_n(t)|^2 &= \frac{1}{\hbar^2}\int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2\, \mathrm{e}^{\mathrm{i}\omega_{nm}(t_1-t_2)}\left\langle\psi_n\right|\Delta H(t_1)\left|\psi_m\right\rangle\left\langle\psi_n\right|\Delta H(t_2)\left|\psi_m\right\rangle^* = \\ &= \frac{e^2}{\hbar^2}\left\langle\psi_n\right|X_i\left|\psi_m\right\rangle\left\langle\psi_m\right|X_j\left|\psi_n\right\rangle\int_0^t \mathrm{d}t_1\int_0^t \mathrm{d}t_2\,\mathrm{e}^{\mathrm{i}\omega_{nm}(t_1-t_2)}E_i(t_1)E_j(t_2) \end{aligned} \tag{13.65}$$

And now we take the ensemble average

$$\begin{aligned} \overline{P_{\mathrm{abs}}(t)} &= \frac{e^2}{\hbar^2}\left\langle\psi_n\right|X_i\left|\psi_m\right\rangle\left\langle\psi_m\right|X_j\left|\psi_n\right\rangle\int_0^t \mathrm{d}t_1\int_0^t \mathrm{d}t_2\,\mathrm{e}^{\mathrm{i}\omega_{nm}(t_1-t_2)}\overline{E_i(t_1)E_j(t_2)} = \\ &= \frac{e^2}{6\epsilon_0\hbar^2}\left|\left\langle\psi_n\right|\boldsymbol{X}\left|\psi_m\right\rangle\right|^2\int_0^t \mathrm{d}t_1\int_0^t \mathrm{d}t_2\,\mathrm{e}^{\mathrm{i}\omega_{nm}(t_1-t_2)}\int \mathrm{d}\omega\,\rho(|\omega|)\mathrm{e}^{-\mathrm{i}\omega(t_1-t_2)} = \\ &= \frac{e^2}{6\epsilon_0\hbar^2}\left|\left\langle\psi_n\right|\boldsymbol{X}\left|\psi_m\right\rangle\right|^2\int \mathrm{d}\omega\,\rho(|\omega|)\left|\int_0^t \mathrm{d}t_1\,\mathrm{e}^{\mathrm{i}(\omega_{nm}-\omega)t_1}\right|^2 = \end{aligned}$$

$$= \frac{2e^2}{3\epsilon_0\hbar^2}|\langle\psi_n|\,\boldsymbol{X}\,|\psi_m\rangle|^2 \int \mathrm{d}\omega\,\rho(|\omega|)\frac{\sin^2\left(\frac{\omega_{nm}-\omega}{2}t\right)}{(\omega_{nm}-\omega)^2} \tag{13.66}$$

We can now use (13.51) to obtain the average rate of absorption at late times

$$\begin{aligned}\frac{\overline{P_{\text{abs}}(t)}}{t} \xrightarrow{t\to\infty} & \frac{e^2}{3\epsilon_0\hbar^2}|\langle\psi_n|\,\boldsymbol{X}\,|\psi_m\rangle|^2 \int \mathrm{d}\omega\,\pi\rho(|\omega|)\delta(\omega_{nm}-\omega) = \\ =& \frac{\pi e^2}{3\epsilon_0\hbar^2}|\langle\psi_n|\,\boldsymbol{X}\,|\psi_m\rangle|^2\rho(\omega_{nm}) \end{aligned} \tag{13.67}$$

For the case of monochromatic radiation with just an electric field we have

$$\rho(\omega_{mn}) = \frac{1}{2}\epsilon_0\boldsymbol{E}_0^2\delta(\omega-\omega_{mn}) \tag{13.68}$$

plugging this in we recover (13.52).

Calculating the energy density We have written our results as a function of the energy density $\rho(\omega)$, if we are to proceed we will need to know this function. Let us assume our radiation bath is in a box of sides L with periodic boundary conditions. In this case, the allowed wavenumbers are

$$\boldsymbol{k} = \frac{2\pi}{L}\boldsymbol{n} \tag{13.69}$$

where $\boldsymbol{n}$ is a vector whose components are arbitrary (possibly distinct) integers. The angular frequency can then be written in terms of this $\boldsymbol{n}$:

$$\omega = \frac{2\pi}{L}c|\boldsymbol{n}| \tag{13.70}$$

The total number of modes is given by

$$N_{\text{tot}} = \sum_{\boldsymbol{n}} 2 \tag{13.71}$$

where the factor of 2 comes from the two distinct polarisations of light, *e.g.* left and right circular polarisation. If the box is sufficiently large we can approximate this sum as an integral and write the total number of modes as

$$N_{\text{tot}} \approx \int \mathrm{d}^3n\,2 = L^3\int\frac{\mathrm{d}^3k}{(2\pi)^3}2 = \frac{8\pi L^3}{(2\pi)^3}\int_0^\infty \mathrm{d}k\,k^2 = \frac{L^3}{\pi^2c^3}\int_0^\infty \mathrm{d}\omega\,\omega^2 \tag{13.72}$$

therefore the number of modes with frequency between ω and $\omega+\mathrm{d}\omega$ is

$$N(\omega)\,\mathrm{d}\omega = \frac{L^3}{\pi^2c^3}\omega^2\,\mathrm{d}\omega \tag{13.73}$$

The energy density in the radiation with frequencies between ω and $\omega+\mathrm{d}\omega$ is therefore

$$\rho(\omega)\,\mathrm{d}\omega = \overline{E(T)}\frac{N(\omega)\,\mathrm{d}\omega}{L^3} = \overline{E(T)}\frac{\omega^2}{\pi^2c^3}\,\mathrm{d}\omega \tag{13.74}$$

All we need to calculate is the ensemble average of the energy, $\overline{E(T)}$, but this is easy enough.

Each independent polarisation of light obeys a separate homogeneous wave equation

$$\frac{\partial^2E_\pm}{\partial t^2} - c^2\nabla^2E_\pm = 0 \tag{13.75}$$

which, Fourier space will look like

$$\frac{\partial^2 \tilde{E}_\pm}{\partial t^2} + c^2 \boldsymbol{k}^2 \tilde{E}_\pm = 0 \tag{13.76}$$

For each value of $\omega = |\boldsymbol{k}|c$ the wave equation is exactly the same as the equation of motion for a harmonic oscillator. As we derived in Chapter 9 the energy of a quantum harmonic oscillator (ignoring the zero-point energy) is $E_n = n\hbar\omega$. Additionally, in the Gibbs ensemble the probability that a system in the ensemble has energy E is proportional to $\exp\left(-\frac{E}{k_B T}\right)$. All in all, this means the average energy is given by

$$\overline{E(T)} = \frac{\sum_{n=0}^{\infty} \mathrm{e}^{-\frac{n\hbar\omega}{k_B T}} n\hbar\omega}{\sum_{n=0}^{\infty} \mathrm{e}^{-\frac{n\hbar\omega}{k_B T}}} = \frac{\hbar\omega}{\mathrm{e}^{\frac{\hbar\omega}{k_B T}} - 1} \tag{13.77}$$

Plugging this into (13.74) gives us

$$\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{\mathrm{e}^{\frac{\hbar\omega}{k_B T}} - 1} \tag{13.78}$$

This is the *Planck distribution*, it was the first ever correct prediction of quantum mechanics.

Detailed balance In thermal equilibrium, the number of electrons making the transition from $n \to m$ from higher to lower energy must be exactly the same as the number of electrons making the transition $m \to n$ from lower to higher energy. Let A_n^m be the rate at which electrons will spontaneously decay from the state n to m by emitting a photon of energy $\hbar\omega_{nm}$; let $B_m^n \rho(\omega_{nm})$ be the rate of absorbing a photon and transitioning from m to n, we have included a factor of the energy density of photons because this rate will have to be proportional to how many photons are available to be absorbed; further let us consider the possibility that the presence of photons might *stimulate* the emission of a related photon with rate $B_n^m \rho(\omega_{nm})$ also proportional to the energy density of photons. These quantities are known as *Einstein coefficients.*

In thermal equilibrium all of these rates must match:

$$N_n(A_n^m + B_n^m \rho(\omega_{nm})) = N_m B_m^n \rho(\omega_{nm}) \tag{13.79}$$

where N_n is the number of atoms in state n, and similarly for N_m. Additionally, in the Gibbs ensemble, we have

$$\frac{N_m}{N_n} = \exp\left(\frac{\hbar\omega_{nm}}{k_B T}\right) \tag{13.80}$$

where for this equation to be valid it is important that N_n is the number of atoms in the state n rather than the number of atoms with energy E_n to avoid issues with degeneracies.

Putting everything together we find

$$A_n^m = \left(\frac{N_m}{N_n} B_m^n - B_n^m\right)\rho(\omega_{nm}) = \frac{\hbar\omega_{nm}^3}{\pi^2 c^3} \frac{1}{\mathrm{e}^{\frac{\hbar\omega_{nm}}{k_B T}} - 1} \left(\mathrm{e}^{\frac{\hbar\omega_{nm}}{k_B T}} B_m^n - B_n^m\right) \tag{13.81}$$

In order for this to be true for all temperatures T we must have

$$B_n^m = B_m^n \quad \text{and} \quad A_n^m = \frac{\hbar\omega_{nm}^3}{\pi^2 c^3} B_m^n \tag{13.82}$$

Just by knowing the rate of absorption of photons we can calculate the rate for both stimulated and spontaneous emission. In particular note how we could not have equilibrium if we did not account for both stimulated and spontaneous emission of radiation.

From (13.67) we can find the coefficient B_m^n:

$$B_m^n = \frac{\pi e^2}{3\epsilon_0 \hbar^2} \left|\langle\psi_n|\, \boldsymbol{X}\, |\psi_m\rangle\right|^2 \tag{13.83}$$

and therefore we obtain the rate of spontaneous emission of radiation as

$$A_n^m = \frac{e^2\omega_{nm}^3}{3\pi c^3 \epsilon_0 \hbar} \left|\langle\psi_n|\, \boldsymbol{X}\, |\psi_m\rangle\right|^2 \tag{13.84}$$

This is a remarkable result because we managed to use thermodynamics to push the bounds of what we could calculate with our formalism. The result we derived above agrees precisely with the first principles calculation from the full quantum electrodynamics theory of photons. In that calculation we would be able to conclude that spontaneous emission is actually stimulated emission but due to the vacuum fluctuations, a level of detail we do not have access. Nevertheless we were able to fully explain the emission and absorption spectra which started our quantum journey.

Measurements and Interpretations

PART

V

Chapter 14. The failure of hidden variables
Chapter 15. The dynamics of measurements

Our story so far has been one of astonishing success. After all our hard work were finally able to explain all of the initial puzzles with quantum mechanics: the black-body spectrum, the nature of spin, the stability of hydrogen atom and its emission and absorption spectra. Not to mention the countless other successful predictions that we have not yet delved into. It is not an exaggeration to say that quantum mechanics is one of (if the not *the*) most successful scientific theories of all time.

Despite all of these successes, there are many people who are uncomfortable with quantum mechanics. Famously, despite his importance in the early days of quantum theory, Albert Einstein himself stated that "God does not play dice with the Universe". Even Niels Bohr, who strongly argued with Einstein, advocating in favour of the quantum mechanical world-view, still attributed a fundamental role to classical systems in his famed Copenhagen interpretation of quantum mechanics. It is often said that quantum mechanics needs to be "interpreted".

These ideas seem, at least to me, downright absurd. Quantum mechanics doesn't *need* to be interpreted any more than any other scientific theory. It doesn't make sense to bring classical physics into the foundations of quantum mechanics. Quantum mechanics should be fundamental, classicality should be some limit to be derived from the more fundamental theory. It would be like asking to explain general relativity using Newtonian concepts, clearly a ridiculous proposition. If anyone is uncomfortable with the probabilistic nature of quantum physics then that is a "them" problem, not an issue with quantum mechanics. For this reason, we have so far taken the "shut up and calculate" approach, don't worry about the philosopher's qualms with probability, just compute what the experimentalist should see and compare with what they do see. If it works good, job well done.

This is, however, a bit too quick. There *is* an issue with the way quantum mechanics is usually formulated. The core of the problem is our description of the process of measurement. We say that if we prepared the system in state

$$|\psi\rangle = \sum_n c_n |n\rangle \tag{13.85}$$

where say $|n\rangle$ are energy eigenstates, $H|n\rangle = E_n |n\rangle$. Then we would say that the probability of measuring the energy and obtaining the result E_n is given by the Born rule

$$P(\psi \to n) = |c_n|^2 \tag{13.86}$$

Crucially, subsequent measurements of the energy would also yield E_n as an answer. It is no longer probabilistic. We say that after the measurement the state *collapsed*

$$|\psi\rangle \to |n\rangle \tag{13.87}$$

But a measurement is just a, possibly quite complicated, action on a state. And we know how states evolve with time—they obey the Schrodinger equation

$$\mathrm{i}\hbar \frac{\partial}{\partial t} |\psi\rangle = H |\psi\rangle \tag{13.88}$$

but there is no Hamiltonian capable to describing (13.87)! The collapse implied by the consistency of repeated measurements is not *unitary*.

This seems bad but doesn't quite examine the full extent of the problem. Maybe the collapse is just some effective description, useful in practice but in theory fully unitary. The full issue arises when we remember *why* we care about unitarity—it needed is to conserve probability. This was the very foundation of our quantum mechanical theory. We introduced Hilbert spaces as a way to encode the linear structure of probability amplitudes, and we introduced probability amplitudes because they were linear, in contrast to the probabilities themselves. But the *definition* of probability amplitudes is that under a measurement the probability of obtaining a certain result is given by the Born rule (13.86), which is exactly what gave us the non-unitary collapse.

It seems like we need unitarity because we have probability amplitudes, but the definition of those probability amplitudes implies non-unitary evolution. This is bad, it seems like a circular contradiction. We call this contradiction the *measurement problem*, our goal in the coming Chapters is resolve this inconsistency. Note that the issue is not with "interpretations". In fact, in some way there can *never* be an issue with interpretations. Because if the only issue is its interpretation, then I would say there is no issue at all. Pick whatever words makes you feel better and move on. The real issue is that it seems like the postulates of quantum mechanics are self-contradicting and that is truly concerning.

In the following chapters we shall examine the measurement problem, coming to the somewhat controversial conclusion that there *is* a solution within the standard formalism of quantum mechanics, regardless of whatever interpretation you prefer. Firstly, we will rule out one potential solution to the issue: hidden variables. We show that any hidden variables theory must be non-local, whereas quantum mechanics itself *is* local, the latter conclusion hinging heavily on the linearity of quantum mechanics. Then we tackle measurements as a phenomenon to be understood. We begin by showcasing the link between linearity and always observing definite results, including an argument as why the Born rule is unique. Finally, we delve into the role of the environment by examining decoherence.

14 The failure of hidden variables

The very first thing you might suggest to solve the measurement problem (and the philosophical qualms with probability), is the possibility of *hidden variables*. That is, we posit that quantum mechanics is *not* fundamental, that is is somehow incomplete. In this framework here are hidden variables that we do not understand yet which would be completely deterministic. The probabilistic nature of quantum mechanics, rather than fundamental is just due to our ignorance of these hidden variables, in very much the same way that the determinist Newton's equations can still yield a random coin toss if we are ignorant of the precise initial conditions and forces acting on the coin. Even non-commutativity is easily explained by interfering measurements. For example, the order in which we measure the spin in the x or z directions changes the outcome because measuring S_x will change the hidden variables in an unknown way, and that would change the outcome of subsequent measurements.

For a long time it seemed like this would be perfectly possible, but John Bell in 1964 showed that no such hidden variables theory could be local *and* reproduce all predictions from quantum mechanics. Better yet, this wasn't just some theoretical construction, there were distinct experimental predictions from local hidden variables and quantum mechanics. Verifying these results is what gave Alain Aspect, John F. Clauser, and Anton Zeilinger the 2022 Nobel Prize in Physics "for experiments with entangled photons, establishing the violation of Bell inequalities and pioneering quantum information science". These results completely doom any hidden variables theory, if they are non-local then they would have no hope of recovering relativistic physics.

Our goal in this chapter is two-fold: examining why local hidden variables theories fail, and examining why quantum mechanics can be local while recoving the experimental observations.

14.1 The EPR paradox

The first to suggest that there might be an issue with locality in quantum mechanics were Albert Einstein, Boris Podolsky, and Nathan Rosen in 1935. Their initial article was about position and momentum but David Bohm provided a sharper argument using two spin-1/2 particles. In either case, the crux of the argument relies on the phenomenon of *entanglement* which happens when the outcomes of experiments performed on two different particles are correlated.

In order to describe entanglement we need a new-ish mathematical tool, *tensor producs*.

Definition 14.1 (Tensor Product)**.** If you have a Hilbert space $\mathcal{H}_A$ with basis $\{|i_A\rangle\}$ and another Hilbert space $\mathcal{H}_B$ with basis $\{|\alpha_B\rangle\}$, then we define the tensor product $\mathcal{H}_A \otimes \mathcal{H}_B$ such that.

1. Its elements are given by $|\psi\rangle = \sum_{i,\alpha} \psi_{i\alpha} |i_A\rangle \otimes |\alpha_B\rangle$
2. The inner product is given by $(|\chi\rangle, |\psi\rangle) = \sum_{ij\alpha\beta} \chi^*_{i\alpha}\psi_{j\beta}(|i_A\rangle, |j_A\rangle)(|\alpha_B\rangle, |\beta_B\rangle)$

This might seem unfamiliar but we have actually already encountered tensor products. They essentially correspond to having multiple labels on a state-vector. For example, the energy eigenstates of the Hydrogen atom are labelled $|n, \ell, m\rangle$ which could be thought of as $|n, \ell, m\rangle = |n\rangle \otimes |\ell\rangle \otimes |m\rangle$. It is standard practice to omit the $\otimes$ and just write $|\psi\rangle \otimes |\chi\rangle = |\psi\rangle |\chi\rangle$, or even $|\psi, \chi\rangle$. These simpler notations often make manipulations with tensor products very intuitive.

Just to give another perspective we can write the tensor product of two finite vectors in components.

$$\begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix} \otimes \begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix} = \begin{pmatrix} v_1u_1 \\ v_1u_2 \\ v_1u_3 \\ v_2u_1 \\ v_2u_2 \\ v_2u_3 \\ v_3u_1 \\ v_3u_2 \\ v_3u_3 \end{pmatrix} \tag{14.1}$$

In general if $\dim \mathcal{H}_A = d_A$ and $\dim \mathcal{H}_B = d_B$ then $\dim(\mathcal{H}_A \otimes \mathcal{H}_B) = d_A d_B$.

Very importantly, there are states in the tensor product Hilbert space which cannot be written as the tensor product of states in the smaller Hilbert spaces. *I.e.* there are $|\psi_{AB}\rangle \in \mathcal{H}_A \otimes \mathcal{H}_B$ such that there are no $|\chi_A\rangle \in \mathcal{H}_A$ and $|\phi_B\rangle \in \mathcal{H}_B$ such that

$$|\psi_{AB}\rangle = |\chi_A\rangle \otimes |\phi_B\rangle \tag{14.2}$$

very often we will need to take linear combinations of tensor product states.

States which can be written as (14.2) are called *separable*, otherwise we say that the states are *entangled*. In this latter case measurements on the A components will be correlated with measurements on the B components.

What EPR (and Bohm) envisioned was preparing the following state made of two spin-1/2 particles

$$|\mathrm{EPR}\rangle = \frac{1}{\sqrt{2}}(|\uparrow_A\downarrow_B\rangle - |\downarrow_A\uparrow_B\rangle) \tag{14.3}$$

This preparation is perfectly feasible experimentally as this is a rotationally invariant state (You can check that it is written the same way regardless of choosing eigenstates of S_z or S_x or any other direction).

Then we send each particle to two observers, Alice and Bob, who will measure their spin. Crucially, they will be so far away that it would be impossible to send any signal between then without breaking the speed of light barrier.

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If relativity is to hold, then the results of these two experiments cannot influence one another. However, if Alice measures spin-up she knows *instantly*, that Bob must have measured spin-down. Even though they cannot communicate, when they compare their results they will see that the spins were *always* perfectly anti-correlated. Einstein called this "spooky action at a distance" claiming this was proof quantum mechanics must be somehow incomplete.

The solution EPR (and Bohm) proposed was that there could be some hidden variables we didn't have access to which would fix the true value of the spin locally when the particles were produced. Then there is no "spooky action at a distance" required. The situation would be perfectly identical to me giving my two gloves in closed boxes to two different people. When Alice, say, opens the box and sees a left-hand glove she *instantly* knows that Bob has the right-hand glove. There is no "spooky action at a distance", it's correlation which was set-up locally.

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What we will see in the next section is that this solution cannot be. There are subtle differences between the classical and the quantum versions of this experiment which can be, and have been, verified. Luckily for us, it turns out that quantum mechanics *is* local, without requiring "spooky action at a distance".

14.2 Hidden variables cannot be local

We will describe three ways in which local hidden variables disagree with quantum mechanics (and Nature). Each of these would be sufficient to demonstrate this fact but we shall present all three for completeness. The first was originally proposed by Daniel Greenberger, Michael Horne, and Anton Zeilinger in 1989 and is much simpler than the others, serving as a warm-up. The second was the original derivation due to John Bell. The final is more generic and was the one which was first verified experimentally, it was first described by John Clauser, Michael Horne, Abner Shimony, and Richard Holt in 1969.

The GHZ experiment The GHZ version of the EPR paradox involves three spin-1/2 particles prepared in the following state

$$|\mathrm{GHZ}\rangle = \frac{1}{\sqrt{2}}(|\uparrow_A\uparrow_B\uparrow_C\rangle - |\downarrow_A\downarrow_B\downarrow_C\rangle) \tag{14.4}$$

We then send each particle very far away to three different observers Alice, Bob and Charlie who each measure the spin of their respective particles. They are far enough that no subluminal signal could be sent in between their measurements.

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Each observer has two options, they are allowed to either measure the spin in the x or the y direction[87] and they do not communicate the choice beforehand.

The outcome of these measurements is random. Sometimes, they get spin up, sometimes they get spin down. However, when they compare their notes they discover correlations between their measurements. In particular, whenever two of them measured the spin in the y direction and the other measured the spin in the x direction, the product of their answers is $+1$.

We can check this prediction using quantum mechanics, remembering the usual results from the definition of the Pauli matrices

$$\sigma_x \left|\uparrow\right\rangle = \left|\downarrow\right\rangle , \; \sigma_x \left|\downarrow\right\rangle = \left|\uparrow\right\rangle , \; \sigma_y \left|\uparrow\right\rangle = \mathrm{i} \left|\downarrow\right\rangle , \; \sigma_y \left|\downarrow\right\rangle = -\mathrm{i} \left|\uparrow\right\rangle \tag{14.5}$$

to obtain

$$\begin{aligned}\sigma_x^A \otimes \sigma_y^B \otimes \sigma_y^C \left|\mathrm{GHZ}\right\rangle =& \frac{1}{\sqrt{2}}\left(\sigma_x^A \left|\uparrow_A\right\rangle \otimes \sigma_y^B \left|\uparrow_B\right\rangle \otimes \sigma_y^C \left|\uparrow_C\right\rangle - \sigma_x^A \left|\downarrow_A\right\rangle \otimes \sigma_y^B \left|\downarrow_B\right\rangle \otimes \sigma_y^C \left|\downarrow_C\right\rangle\right) = \\ =& \frac{1}{\sqrt{2}}(\left|\downarrow_A\right\rangle \otimes \mathrm{i} \left|\downarrow_B\right\rangle \otimes \mathrm{i} \left|\downarrow_C\right\rangle - \left|\uparrow_A\right\rangle \otimes (-\mathrm{i} \left|\uparrow_B\right\rangle) \otimes (-\mathrm{i} \left|\uparrow_C\right\rangle)) = \\ =& \frac{1}{\sqrt{2}}(- \left|\downarrow_A \downarrow_B \downarrow_C\right\rangle + \left|\uparrow_A \uparrow_B \uparrow_C\right\rangle) = \left|\mathrm{GHZ}\right\rangle\end{aligned} \tag{14.6}$$

and similarly for the other two combinations.

If we believe local hidden variables, then the spins were determined at the creation of this state without needed any superluminal communication. Calling the true value for the spin of the A particle in the x direction s_x^A, and similarly for the other particles we can therefore conclude from the above that

$$s_x^A s_y^B s_y^C = s_y^A s_x^B s_y^C = s_y^A s_y^B s_x^C = +1 \tag{14.7}$$

multiplying these three expressions and remembering that every spin can only be ± 1, which means $\left(s_y^B\right)^2 = \left(s_y^A\right)^2 = \left(s_y^C\right)^2 = +1$, we conclude

$$s_x^A s_x^B s_x^C = +1 \tag{14.8}$$

But this is *not* the prediction from quantum mechanics:

$$\begin{aligned}\sigma_x^A \otimes \sigma_x^B \otimes \sigma_x^C \left|\mathrm{GHZ}\right\rangle =& \frac{1}{\sqrt{2}}\left(\sigma_x^A \left|\uparrow_A\right\rangle \otimes \sigma_x^B \left|\uparrow_B\right\rangle \otimes \sigma_x^C \left|\uparrow_C\right\rangle - \sigma_x^A \left|\downarrow_A\right\rangle \otimes \sigma_x^B \left|\downarrow_B\right\rangle \otimes \sigma_x^C \left|\downarrow_C\right\rangle\right) = \\ =& \frac{1}{\sqrt{2}}(\left|\downarrow_A \downarrow_B \downarrow_C\right\rangle - \left|\uparrow_A \uparrow_B \uparrow_C\right\rangle) = - \left|\mathrm{GHZ}\right\rangle\end{aligned} \tag{14.9}$$

We see that *local* hidden variables cannot reproduce the results from quantum mechanics.

Bell's inequalities Now we go back to the EPR case. For clarity, we have two particles in the state

$$\left|\mathrm{EPR}\right\rangle = \frac{1}{\sqrt{2}}(\left|\uparrow_A \downarrow_B\right\rangle - \left|\downarrow_A \uparrow_B\right\rangle) \tag{14.10}$$

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[87] For simplicity we will rescale the spin variables so that the outcomes are ± 1 rather than $\pm \hbar/2$. Our observables are therefore the Pauli matrices $\boldsymbol{\sigma}$.

and two observers, Alice and Bob, which are sufficiently far away to preven subluminal communication.

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We will allow them to measure spin in any direction. The hidden variables position is that at the furnace each particle had a definite spin which is a function of the direction to be measured $\hat{\boldsymbol{a}}$ and the hidden variables λ (it could be a set of variables for all we know, this is merely a compact notation). We call those functions $s^A(\hat{\boldsymbol{a}},\lambda)$ and $s^B(\hat{\boldsymbol{a}},\lambda)$, and note they can only take the values ± 1. If both observers measure the spin in the same direction $\hat{\boldsymbol{a}}$ then we get opposite results, that is, $s^A(\hat{\boldsymbol{a}},\lambda) = -s^B(\hat{\boldsymbol{a}},\lambda)$. So we will simplify and define $s(\hat{\boldsymbol{a}},\lambda) \equiv s^A(\hat{\boldsymbol{a}},\lambda)$.

The values of λ is fixed, but we are ignorant of them, so we must introduce a probability distribution $p(\lambda)$ such that $p(\lambda) \geqslant 0$ and $\int \mathrm{d}\lambda\, p(\lambda) = 1$. The expectation value of the product of the spins in two arbitrary directions $\hat{\boldsymbol{a}}$ and $\hat{\boldsymbol{b}}$ is then given by

$$\Big\langle \left(\boldsymbol{\sigma}^A \cdot \hat{\boldsymbol{a}}\right)\Big(\boldsymbol{\sigma}^B \cdot \hat{\boldsymbol{b}}\Big)\Big\rangle = -\int \mathrm{d}\lambda\, p(\lambda) s(\hat{\boldsymbol{a}},\lambda) s(\hat{\boldsymbol{b}},\lambda) \tag{14.11}$$

In quantum mechanics we use the definition of the Pauli matrices to write

$$\boldsymbol{\sigma}\cdot\hat{\boldsymbol{a}} = \begin{pmatrix} \hat{a}_3 & \hat{a}_1 - \mathrm{i}\hat{a}_2 \\ \hat{a}_1 + \mathrm{i}\hat{a}_2 & -\hat{a}_3 \end{pmatrix} \tag{14.12}$$

which will give us

$$\begin{aligned}
&\langle \mathrm{EPR}|\left(\boldsymbol{\sigma}^A\cdot\hat{\boldsymbol{a}}\right)\Big(\boldsymbol{\sigma}^B\cdot\hat{\boldsymbol{b}}\Big)|\mathrm{EPR}\rangle = \\
=&\frac{1}{2}\Big(\langle\uparrow_A|\boldsymbol{\sigma}^A\cdot\hat{\boldsymbol{a}}|\uparrow_A\rangle\langle\downarrow_B|\boldsymbol{\sigma}^B\cdot\hat{\boldsymbol{b}}|\downarrow_B\rangle + \langle\uparrow_A|\boldsymbol{\sigma}^A\cdot\hat{\boldsymbol{a}}|\downarrow_A\rangle\langle\uparrow_B|\boldsymbol{\sigma}^B\cdot\hat{\boldsymbol{b}}|\uparrow_B\rangle - \\
&- \langle\uparrow_A|\boldsymbol{\sigma}^A\cdot\hat{\boldsymbol{a}}|\downarrow_A\rangle\langle\downarrow_B|\boldsymbol{\sigma}^B\cdot\hat{\boldsymbol{b}}|\uparrow_B\rangle - \langle\downarrow_A|\boldsymbol{\sigma}^A\cdot\hat{\boldsymbol{a}}|\uparrow_A\rangle\langle\uparrow_B|\boldsymbol{\sigma}^B\cdot\hat{\boldsymbol{b}}|\downarrow_B\rangle\Big) = \\
=&\frac{1}{2}\Big(-\hat{a}_3\hat{b}_3 - \hat{a}_3\hat{b}_3 - (\hat{a}_1 - \mathrm{i}\hat{a}_2)(\hat{b}_1 + \mathrm{i}\hat{b}_2) - (\hat{a}_1 + \mathrm{i}\hat{a}_2)(\hat{b}_1 - \mathrm{i}\hat{b}_2)\Big) = \\
=&-\hat{\boldsymbol{a}}\cdot\hat{\boldsymbol{b}}
\end{aligned} \tag{14.13}$$

So far, there is no issue with finding hidden variables than can reproduce these results, but this is not the case when we consider three possible directions, $\hat{\boldsymbol{a}}$, $\hat{\boldsymbol{b}}$ and $\hat{\boldsymbol{c}}$. Using (14.11) we can write

$$\Big\langle \left(\boldsymbol{\sigma}^A\cdot\hat{\boldsymbol{a}}\right)\Big(\boldsymbol{\sigma}^B\cdot\hat{\boldsymbol{b}}\Big)\Big\rangle - \big\langle \left(\boldsymbol{\sigma}^A\cdot\hat{\boldsymbol{a}}\right)\left(\boldsymbol{\sigma}^B\cdot\hat{\boldsymbol{c}}\right)\big\rangle = -\int \mathrm{d}\lambda\, p(\lambda)\Big(s(\hat{\boldsymbol{a}},\lambda)s(\hat{\boldsymbol{b}},\lambda) - s(\hat{\boldsymbol{a}},\lambda)s(\hat{\boldsymbol{c}},\lambda)\Big) \tag{14.14}$$

Now, since $s(\hat{\boldsymbol{b}}.\lambda) = \pm 1$ we have $s(\hat{\boldsymbol{b}}.\lambda)^2 = +1$, and therefore we can write

$$\Big\langle \left(\boldsymbol{\sigma}^A\cdot\hat{\boldsymbol{a}}\right)\Big(\boldsymbol{\sigma}^B\cdot\hat{\boldsymbol{b}}\Big)\Big\rangle - \big\langle \left(\boldsymbol{\sigma}^A\cdot\hat{\boldsymbol{a}}\right)\left(\boldsymbol{\sigma}^B\cdot\hat{\boldsymbol{c}}\right)\big\rangle = -\int \mathrm{d}\lambda\, p(\lambda) s(\hat{\boldsymbol{a}},\lambda)s(\hat{\boldsymbol{b}},\lambda)\Big(1 - s(\hat{\boldsymbol{b}},\lambda)s(\hat{\boldsymbol{c}},\lambda)\Big) \tag{14.15}$$

The absolute value of an integral is less or equal than the integral of the absolute value, and $|s(\hat{\boldsymbol{a}}.\lambda)| = |s(\hat{\boldsymbol{b}}.\lambda)| = +1$, so we have

$$\begin{aligned}
\Big|\Big\langle \left(\boldsymbol{\sigma}^A\cdot\hat{\boldsymbol{a}}\right)\Big(\boldsymbol{\sigma}^B\cdot\hat{\boldsymbol{b}}\Big)\Big\rangle - \big\langle \left(\boldsymbol{\sigma}^A\cdot\hat{\boldsymbol{a}}\right)\left(\boldsymbol{\sigma}^B\cdot\hat{\boldsymbol{c}}\right)\big\rangle\Big| \leqslant& \int \mathrm{d}\lambda\, p(\lambda)\Big(1 - s(\hat{\boldsymbol{b}},\lambda)s(\hat{\boldsymbol{c}},\lambda)\Big) = \\
=&1 + \big\langle \left(\boldsymbol{\sigma}^A\cdot\hat{\boldsymbol{c}}\right)\left(\boldsymbol{\sigma}^B\cdot\hat{\boldsymbol{c}}\right)\big\rangle
\end{aligned} \tag{14.16}$$

This is the *Bell inequality* and must be obeyed by any local hidden variables theory.

However, quantum mechanics does *not* obey Bell's inequality for all $\hat{\boldsymbol{a}}$, $\hat{\boldsymbol{b}}$, $\hat{\boldsymbol{c}}$. In particular, take

$$\hat{\boldsymbol{a}} \cdot \hat{\boldsymbol{b}} = 0 \quad \text{and} \quad \hat{\boldsymbol{c}} = \frac{\hat{\boldsymbol{a}} + \hat{\boldsymbol{b}}}{\sqrt{2}} \tag{14.17}$$

we then have, using (14.13)

$$\left| \langle \text{EPR}| \big(\boldsymbol{\sigma}^A \cdot \hat{\boldsymbol{a}}\big) \Big(\boldsymbol{\sigma}^B \cdot \hat{\boldsymbol{b}}\Big) |\text{EPR}\rangle - \langle \text{EPR}| \big(\boldsymbol{\sigma}^A \cdot \hat{\boldsymbol{a}}\big) \big(\boldsymbol{\sigma}^B \cdot \hat{\boldsymbol{c}}\big) |\text{EPR}\rangle \right| = \frac{1}{\sqrt{2}} \tag{14.18}$$

but

$$1 + \langle \text{EPR}| \big(\boldsymbol{\sigma}^A \cdot \hat{\boldsymbol{c}}\big) \big(\boldsymbol{\sigma}^B \cdot \hat{\boldsymbol{c}}\big) |\text{EPR}\rangle = 1 + \frac{1}{\sqrt{2}} \tag{14.19}$$

which is larger than (14.18)! Therefore quantum mechanics violates Bell's inequalities, and cannot be described by a local hidden variables theory.

The CHSH inequality The last example is a bit more general than the previous two (although we will still use the EPR state). Take two observers, Alice and Bob, who can each choose to measure one of two observables A_1 or A_2, and B_1 or B_2. Each of these observables can only take the values ±1. We will required that the two measurements are spacelike separated so that

$$[A_i, B_j] = 0 \quad \text{for} \quad i, j = 1, 2 \tag{14.20}$$

but no assumptions on $[A_1, A_2]$ or $[B_1, B_2]$.

Our goal is to ask about the expectation value of a new observable

$$C = (A_1 + A_2)B_1 + (A_1 - A_2)B_2 \tag{14.21}$$

If we have hidden variables we can replace all observables with their corresponding value

$$c = (a_1 + a_2)b_1 + (a_1 - a_2)b_2 \tag{14.22}$$

which are all possibly quite complicated functions of the hidden variables.

Since $a_i = \pm 1$ we have two options

- $a_1 + a_2 = 0 \implies a_1 - a_2 = \pm 2$
- $a_1 - a_2 = 0 \implies a_1 + a_2 = \pm 2$

additionally, $b_i = \pm 1 \implies |b_i| = \pm 1$, therefore

$$-2 \leqslant c \leqslant 2 \tag{14.23}$$

This is the *CHSH inequality.*

In quantum mechanics we cannot give values to both A_1 *and* A_2, nor can we fix both B_1 *and* B_2, so we must be a bit more cautious. However, because the eigenvalues are ±1 it is still true that $A_i^2 = B_i^2 = \mathbb{1}$. Therefore, after some algebra we can find

$$C^2 = 4\mathbb{1} - [A_1, A_2][B_1, B_2] \tag{14.24}$$

Even without fixing $[A_1, A_2]$ we can still write

$$|\langle [A_1, A_2] \rangle| \leqslant |\langle A_1 A_2 \rangle| + |\langle A_2 A_1 \rangle| \leqslant 2 \tag{14.25}$$

and similarly for $[B_1, B_2]$. We can conclude that

$$8 \leqslant \left\langle C^2 \right\rangle \leqslant 8 \tag{14.26}$$

and using $\left\langle C^2 \right\rangle \geqslant \langle C \rangle^2$ we write

$$2\sqrt{2} \leqslant \langle C \rangle \leqslant 2\sqrt{2} \tag{14.27}$$

which is a larger interval than what is allowed by local hidden variables! This new inequality is known as the *Cirel'son bound* (somtimes also transliterated as Tsirelson) after Boris S. Cirel'son (or Tsirelson).

In the EPR state we can saturate this bound if we choose

$$\begin{aligned} A_1 &= \sigma_z && (14.28) \\ B_1 &= \frac{1}{\sqrt{2}}(\sigma_x + \sigma_z) && (14.29) \\ A_2 &= \sigma_x && (14.30) \\ B_2 &= \frac{1}{\sqrt{2}}(-\sigma_x + \sigma_z) && (14.31) \end{aligned}$$

Once more demonstrating the inability of local hidden variables to describe the results from quantum mechanics.

14.3 Quantum mechanics is local

In the previous section we saw three examples of why hidden variables theories cannot both be local and reproduce the results from the experiment. Quantum mechanics can of course reproduce the results from experiment, but is it local?

Let us focus on the EPR case when we have only two observers. Our Hilbert space is then the tensor product of two other Hilbert spaces: $\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B$. Now imagine Alice wants to compute the expectation value of some local observable O_A. By local we mean that it does not effect the B variables at all, so we can write it as

$$O = O_A \otimes \mathbb{1}_B \tag{14.32}$$

the expectation value of this observable in a generic state

$$|\psi\rangle = \sum_{i\alpha} \psi_{i\alpha} |i_A\rangle |\alpha_B\rangle \tag{14.33}$$

is given by

$$\langle\psi|O|\psi\rangle = \sum_{ij\alpha\beta} \psi^*_{i\alpha}\psi_{j\beta} \langle i_A| O_A |j_A\rangle \langle\alpha_B|\beta_B\rangle \tag{14.34}$$

assuming the bases are orthonormal we find

$$\langle\psi|O|\psi\rangle = \sum_{ij\alpha} \psi^*_{i\alpha}\psi_{j\alpha} \langle i_A| O_A |j_A\rangle \tag{14.35}$$

Once again notice this expectation value does *not* look like the expectation value on some state $|\chi\rangle$ purely on $\mathcal{H}_A$:

$$\langle\chi|O_A|\chi\rangle = \sum_{ij} \chi^*_i\chi_j \langle i_A| O_A |j_A\rangle \tag{14.36}$$

unless $\psi_{ia} = \chi_i \phi_a$ in which case

$$|\psi\rangle = |\chi\rangle \otimes |\phi\rangle \tag{14.37}$$

i.e. unless the state was separable.

The existence of entangled states leaves us in a bind. It seems like we cannot just compute things in $\mathcal{H}_A$ without knowing what is happening in $\mathcal{H}_B$, which would entail some sort on non-locality. Luckily this is not the case, we just have to extend slightly our notion of physical state.

Looking back at (14.35) the repeated α index really resembles a trace of some operator. In fact, we can construct an operator from $|\psi\rangle$:

$$\rho = |\psi\rangle\langle\psi| \tag{14.38}$$

such that (check!)

$$\langle\psi|O|\psi\rangle = \mathrm{Tr}(\rho O) \tag{14.39}$$

This operator is known as the *density matrix*[88].

Even though we cannot define a state-vector on $\mathcal{H}_A$ we are still able to define a density matrix on $\mathcal{H}_A$ by taking a *partial trace*

$$\rho_A \equiv \mathrm{Tr}_B\, \rho \equiv \sum_{ij\alpha} \psi^*_{i\alpha}\psi_{j\alpha} \left|i_A\right\rangle \left\langle j_A\right| \tag{14.40}$$

It is straightforward to verify that

$$\langle O_A \rangle = \mathrm{Tr}_A(\rho_A O_A) \tag{14.41}$$

This means the density matrix is able to recover all of the expectation values that the ket would compute, but it can do more and also describe subsystems without needing to reference the full Hilbert space. It seems these density matrices can be generalisations of state vectors. We just need to find their key properties if we are to provide an independent definition.

From the original ρ three properties are immediately clear:

1. Hermiticity: $\rho^\dagger = (|\psi\rangle\langle\psi|)^\dagger = |\psi\rangle\langle\psi| = \rho$
2. Positive definite: $\langle\phi|\rho|\phi\rangle = \langle\phi|\psi\rangle \left\langle\psi\right| \left|\psi\right\rangle = |\langle\phi|\psi\rangle|^2 \geqslant 0$
3. Unit trace: $\mathrm{Tr}\,\rho = \langle\psi|\psi\rangle = 1$

We can also show this properties hold for the subsystem ρ_A:

1. Hermiticity: $\rho_A^\dagger = \sum_{ij\alpha}(\psi^*_{i\alpha}\psi_{j\alpha}\left|i_A\right\rangle\left\langle j_B\right|)^\dagger = \sum_{ij\alpha}\psi_{i\alpha}\psi^*_{j\alpha}\left|j_A\right\rangle\left\langle i_A\right| = \rho_A$
2. Positive definite:

$$\langle\phi|\rho_A|\phi\rangle = \sum_{ijkl\alpha}\psi^*_{i\alpha}\psi_{j\alpha}\phi^*_k\phi_l \left\langle k_A|i_A\right\rangle\left\langle j_A|l_A\right\rangle = \sum_{ij\alpha}\psi^*_{i\alpha}\psi_{j\alpha}\phi^*_i\phi_j = \sum_\alpha\left|\sum_i \psi_{i\alpha}\phi_i\right|^2 \geqslant 0$$

3. Unit trace: $\mathrm{Tr}\,\rho_A = \sum_{ij\alpha}\psi_{i\alpha}\psi^*_{j\alpha}\left\langle i_A|j_A\right\rangle = \sum_{i\alpha}|\psi_{i\alpha}|^2 = \langle\psi|\psi\rangle = 1$

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[88] The name "density" was given for very obscure reasons, in statistical mechanics it appears in some equations where the phase space density would have appeared in classical physics.

Additionally note that density matrices are invariant under changes of phase of the vectors, the usual phase ambiguity is gone. We therefore generalise the notion of physical state into the following definition:

Definition 14.2. A physical state is represented by a density matrix ρ which an linear operator on a Hilbert space, $\mathcal{H}$, that satisfied two properties

1. **Positive definite**[a]**:** $\langle\psi|\rho|\psi\rangle \geqslant 0 \quad \forall\, |\psi\rangle \in \mathcal{H}$
2. **Unit trace:** $\operatorname{Tr}\rho = 1$

---

[a] Note that positive definiteness implies Hermiticity so we don't have to specify them separately.

If the density matrix can be written as $\rho = |\psi\rangle\langle\psi|$ then we say that the state is *pure*, otherwise we say that it is *mixed*. Additionally we can go back to the notion of entanglement we introduced earlier. If the state in the full Hilbert space is separable (and pure), then the state in the reduced Hilbert spaces is also pure. If, however, the original state was not separable, then the reduced density matrices will be mixed.

We introduced density matrices to be able to deal with subsystems but their Hermiticity suggests an alternative interpretation. Let $|p_i\rangle$ be the eigenvectors of ρ, with eigenvalues $p_i \geqslant 0$. Because ρ is Hermitian, they necessarily form an orthonormal basis, so we can then write

$$\rho = \sum_i p_i\, |p_i\rangle\langle p_i| \tag{14.42}$$

An expectation value in this basis looks like

$$\operatorname{Tr}(\rho O) = \sum_i p_i\, \langle p_i|O|p_i\rangle \tag{14.43}$$

Additionally, the unit trace condition gives

$$\operatorname{Tr}\rho = \sum_i p_i = 1 \tag{14.44}$$

These expressions are the same as if we were ignorant as to what the true state of the system was and only new it could be any of states $|p_i\rangle$ with probability p_i. The density matrix can therefore also encode *classical* ignorance about the true state of the system.

This interpretation motivates the definition of *von Neumann entropy*

$$S(\rho) = -\operatorname{Tr}(\rho \log \rho) \tag{14.45}$$

which, in the basis (14.42), looks like

$$S(\rho) = -\sum_i p_i \log p_i \tag{14.46}$$

if we define $0 \log 0 = 0$. Because $p_i \geqslant 0$ and $\sum_i p_i = 1$, all of the terms in the sum are positive. Further, either one of the p_i is 1 and all the others 0, in which case ρ is pure; or none of the p_i equals 1, and ρ is mixed. We conclude

$$S(\rho) = 0 \quad \text{iff} \quad \rho = |\psi\rangle\langle\psi| \quad \text{for some} \quad |\psi\rangle \in \mathcal{H} \tag{14.47}$$

The two ideas of density matrices, as classical ignorance or as a way to describe subsystems are in fact mathematically equivalent. Let us enlarge the Hilbert space by taking two copies of it, $\mathcal{H} \to \mathcal{H} \otimes \mathcal{H}$. We can then define the vector

$$|\Psi\rangle = \sum_i \sqrt{p_i}\, |p_i\rangle \otimes |p_i\rangle \tag{14.48}$$

such that the original density matrix is reduction of the matrix

$$\rho = |\Psi\rangle\langle\Psi| \tag{14.49}$$

by tracing out one of the copies. This process is called *purification*, it is certainly not a unique procedure, but it showcases any density matrix can be seen as a subsystem of a pure state in a larger Hilbert spae.

We can finally go back to the EPR example and talk about locality. The density matrix representing the full pure state on $\mathcal{H}_A \otimes \mathcal{H}_B$ is

$$\rho = |\text{EPR}\rangle\langle\text{EPR}| = \frac{1}{2}(|{\uparrow_A}{\downarrow_B}\rangle\langle{\uparrow_A}{\downarrow_B}| + |{\downarrow_A}{\uparrow_B}\rangle\langle{\downarrow_A}{\uparrow_B}| - |{\uparrow_A}{\downarrow_B}\rangle\langle{\downarrow_A}{\uparrow_B}| - |{\downarrow_A}{\uparrow_B}\rangle\langle{\uparrow_A}{\downarrow_B}|) \tag{14.50}$$

Tracing over $\mathcal{H}_B$ we find the reduced density matrix Alice has access to is

$$\rho_A = \frac{1}{2}(|{\uparrow_A}\rangle\langle{\uparrow_A}| + |{\downarrow_A}\rangle\langle{\downarrow_A}|) \tag{14.51}$$

which is exactly what we expected, a 50-50 change of observing spin-up or spin-down.

Now let us imagine Bob performs his measurement. He will observe the state $|{\uparrow_A}{\downarrow_B}\rangle$ with 50% probability or the state $|{\downarrow_A}{\uparrow_B}\rangle$ with 50% probability. These probabilities are now just classical ignorance about the outcome of the measurement. Therefore, the total density matrix after Bob does his measurement is

$$\rho_{\text{measured}} = \frac{1}{2}(|{\uparrow_A}{\downarrow_B}\rangle\langle{\uparrow_A}{\downarrow_B}| + |{\downarrow_A}{\uparrow_B}\rangle\langle{\downarrow_A}{\uparrow_B}|) \tag{14.52}$$

tracing over $\mathcal{H}_B$ we again find

$$\rho_A = \frac{1}{2}(|{\uparrow_A}\rangle\langle{\uparrow_A}| + |{\downarrow_A}\rangle\langle{\downarrow_A}|) \tag{14.53}$$

The density matrix that Alice has access to is the same whether or not Bob performed his measurement. Despite there being non-local correlations between $\mathcal{H}_A$ and $\mathcal{H}_B$, the local measurements are none the wiser. We cannot use these correlations for any kind of superluminal communication. Remember the reason why relativity forbids superluminal communication—the order between spacelike events is not unique. We cannot have a causal connection between two events if their order is reversed. In this case we see that the order of events does not matter for the local observations. From Alice's perspective there is no way to tell whether Bob has done his measurement or not. Bob's measurement might change the global state but it does not change the local state that Alice can probe. Quantum mechanics *is* local.

In general, take a density matrix

$$\rho = \sum_i p_i\, |p_i\rangle\langle p_i| \tag{14.54}$$

if we measure a certain observable O with eigenvectors $|\lambda_a\rangle$ then we will obtain the result λ_a with probability

$$P(|\lambda_a\rangle) = \sum_i p_i |\langle p_i|\lambda_a\rangle|^2 \tag{14.55}$$

because p_i is the probability that we were in state $|p_i\rangle$ and $|\langle p_i|\lambda_a\rangle|^2$ is the probability we end up in state $|\lambda_a\rangle$ if we were in state $|p_i\rangle$. The density matrix after measurement is then

$$\begin{aligned}\rho' &= \sum_a P(|\lambda_a\rangle)\,|\lambda_a\rangle\langle\lambda_a| = \sum_{ai} |\langle\lambda_a|p_i\rangle|^2 p_i\,|\lambda_a\rangle\langle\lambda_a| = \\ &= \sum_a |\lambda_a\rangle\langle\lambda_a| \left(\sum_i p_i\,|p_i\rangle\langle p_i|\right) |\lambda_a\rangle\langle\lambda_a| = \sum_a |\lambda_a\rangle\,\langle\lambda_a|\,\rho\,|\lambda_a\rangle\,\langle\lambda_a| \end{aligned} \tag{14.56}$$

Very crucially this is a linear action.

Additionally, if the Hamiltonian is given by H, then the states $|p_i\rangle$ evolve as

$$|p_i(t)\rangle = \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}Ht}\,|p_i(0)\rangle \tag{14.57}$$

and therefore the density matrix evolves as

$$\rho(t) = \sum_i p_i\,|p_i(t)\rangle\langle p_i(t)| = \sum_i p_i \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}Ht}\,|p_i(0)\rangle\langle p_i(0)|\,\mathrm{e}^{\frac{\mathrm{i}}{\hbar}Ht} \tag{14.58}$$

which is also linear. We can also write as a differential equation

$$\mathrm{i}\hbar\frac{\partial\rho}{\partial t} = -[\rho, H] \tag{14.59}$$

which is the *quantum Liouville equation*. Note how this is *not* the Heisenberg equation, there is a minus sign which is different. The density matrix is a special operator when it comes to time evolution because it isn't an observable, it is the state.

No matter whether we are performing measurements or regular Hamiltonian time evolution, the change in the density matrix is always linear. We can therefore write generically, in a basis

$$\rho'_{ij} = \sum_{kl} K_{ik,jl}\rho_{kl} \tag{14.60}$$

where $K_{ik,jl}$ is the *kernel* and obeys

$$\sum_i K_{ik,il} = 1 \tag{14.61}$$

to ensure ρ' has unit trace.

If the Hilbert space is made up of two isolated subsystems then, even if the density matrix isn't separable, the measurement and Hamiltonian actions will be, so we can write

$$K_{i\alpha k\gamma,j\beta l\delta} = K^A_{ij,kl}K^B_{\alpha\gamma,\beta\delta} \tag{14.62}$$

The density matrix of subsystem A is

$$\rho^A_{ij} = \sum_\alpha \rho_{i\alpha,j\alpha} \tag{14.63}$$

which evolves as

$$\rho^A_{ij} \to \sum_{kl\alpha\gamma\delta} K^A_{ik,jl}K^B_{\alpha\gamma,\alpha\delta}\rho_{k\gamma,l\delta} = \sum_{kl} K^A_{ik,jl}\rho^A_{kl} \tag{14.64}$$

where we have used

$$\sum_\alpha K^B_{\alpha\gamma,\alpha\delta} = 1 \tag{14.65}$$

which follows from (14.61)

We see that what we observed in the EPR state is generic. The evolution if $\mathcal{H}_A$ is always independent of whatever was done in $\mathcal{H}_B$, as long as they are far enough away that the Hamiltonian and measurements factorise. This is a generic way to see that quantum mechanics *is* local. Unless there is some direct coupling in the Hamiltonian there is no way for $\mathcal{H}_A$ to influence $\mathcal{H}_B$.

The previous result hinges very heavily on the linear structure of quantum mechanics. Any changes to quantum mechanics that introduce any sort of non-linearity risk having to contend with the possibility of superluminal communication. Linearity and locality are very intimately linked.

15 The dynamics of measurements

The first solution we came up with to resolve the measurement problem was to posit quantum mechanics was somehow incomplete, that there were hidden variables we didn't control who could explain all of the weird phenomena with just classical ignorance rather than fundamental probabilities. No matter how attractive such as solution may seem in the previous chapter we have thoroughly ruled out such a hypothesis. To explain the experimental observations any such hidden variables theory would necessarily have to be non-local, which is not compatible with relativity. Quantum mechanics on the other hand is perfectly capable of describing experiment without introducing any non-localities, the crux being the linear structure of Hilbert spaces.

How can we then resolve the measurement problem? One possibility would be if we could somehow derive the Born rule, then perhaps we could at least get rid of the circularity. This, at first, seems impossible. The Born rule was at the heart of quantum mechanics, we introduced Hilbert spaces to codify the mathematical properties of probability amplitudes. The state arose as a mere abstraction of a probability amplitude to allow us to work in an unspecified basis.

In truth, however, we only used those properties as *motivation* for the introduction of a Hilbert space. We didn't *prove* that the observed properties of probability amplitudes necessarily imply Hilbert spaces. What we did was get at a couple of fundamental properties and then *postulate* quantum mechanics could be described by state-vectors in a Hilbert space and verified we could use that mathematical structure to encode the results we had obtained earlier. From this latter point of view, the Born rule arose as an ad hoc late addition to interpret inner products. Sure, it was helpful in motivating unitary time evolution but, at the end of the day, we also had to just *postulate* the Schrodinger equation. We could even have entirely sidestepped this unitary time evolution motivation and just used the quantum Poisson bracket to get the Heisenberg equation and then used the map between the two pictures to get the Schrodinger equation.

From this latter point of view, it might be eminently reasonable to abandon the postulate of the Born rule and see whether we can re-derive it from the other postulates. This is precisely our first objective, we will be able to derive the need for a fundamental probability structure and motivate the Born rule from the linearity of superpositions and the postulate that observables are linear Hermitian operators who have well defined values for their eigenstates. After this we will tackle the dynamics of measurement, uncovering the role of the environment in dampening the non-diagonal terms in our system's density matrix, a phenomenon known as *decoherence*. We first show a simple example to give the idea, then we give a more general argument showcasing this phenomenon under certain physical assumptions.

15.1 Linearity and the Born rule

Let us revisit our description of the Stern-Gerlach experiment. Under a magnetic field

$$\boldsymbol{B} = -\alpha \boldsymbol{e_x} + (B_0 + \alpha z)\boldsymbol{e_z} \tag{15.1}$$

where B_0 is quite strong, the trajectory of the particle will approximately be given by

$$\frac{\mathrm{d}^2 \langle \boldsymbol{X} \rangle}{\mathrm{d}t^2} \approx \alpha\gamma \langle S_z \rangle \boldsymbol{e_z} \tag{15.2}$$

This equation predicts that if we send a particle in the state $|\uparrow\rangle$ it will be deflected upwards and if we send a particle in the state $|\downarrow\rangle$ then it will be deflected downwards.

This is however not the full story. We haven't yet described how we can tell which way the particle went. The actual experiment also involves a particle detector, for example it could be a screen that reacts when a particle hits it in a given location, giving some visual cue the experimentalist can observe. A particle with definite position $\boldsymbol{x}$ (or suitably peaked around that value) at the point it hits the screen will cause a dot on that position.

INSERT PICTURE

The detector itself is just a complicated quantum mechanical system. Let us call $|D_\emptyset\rangle$ the state corresponding to no dot on the detector and $|D_{\boldsymbol{x}}\rangle$ the state corresponding to a dot on position $\boldsymbol{x}$ of the detector. If we have an incoming particle with initial position $\boldsymbol{x}_i$, in the spin-up state, the initial state of the full system, before the particle hits the detector is

$$|\boldsymbol{x}_i, \uparrow, D_\emptyset\rangle \tag{15.3}$$

This particle will be deflected upwards as dictated by (15.2), let us call the final position when it hits the detector $\boldsymbol{x}_\uparrow$. Then the final state, at the moment the particle hits the detector is

$$\left|\boldsymbol{x}_\uparrow, \uparrow, D_{\boldsymbol{x}_\uparrow}\right\rangle \tag{15.4}$$

Similarly, if the initial state was instead

$$|\boldsymbol{x}_i, \downarrow, D_\emptyset\rangle \tag{15.5}$$

the final state will be

$$\left|\boldsymbol{x}_\downarrow, \downarrow, D_{\boldsymbol{x}_\downarrow}\right\rangle \tag{15.6}$$

where $\boldsymbol{x}_\uparrow$ is the final position of the particle, as dictated by (15.2).

We can also send in a superposition of spin-up and spin-down states with definite initial position $\boldsymbol{x}_i$.

$$|\psi_i\rangle = a\,|\boldsymbol{x}_i, \uparrow, D_\emptyset\rangle + b\,|\boldsymbol{x}_i, \downarrow, D_\emptyset\rangle \tag{15.7}$$

The time evolution is a linear action, therefore the final state will be given by

$$|\psi_f\rangle = a\left|\boldsymbol{x}_\uparrow, \uparrow, D_{\boldsymbol{x}_\uparrow}\right\rangle + b\left|\boldsymbol{x}_\downarrow, \downarrow, D_{\boldsymbol{x}_\downarrow}\right\rangle \tag{15.8}$$

What do we see on the detector screen?

Let us define an operator $D_\uparrow$ that tells us whether or not the detector has detected spin-up, we define its action as

$$D_\uparrow |D_{\boldsymbol{x}}\rangle = |D_{\boldsymbol{x}}\rangle \quad \text{for} \quad \boldsymbol{x} = \boldsymbol{x}_\uparrow \tag{15.9}$$

$$D_\uparrow |D_{\boldsymbol{x}}\rangle = 0 \quad \text{otherwise} \tag{15.10}$$

The superposition $|\psi_f\rangle$ is not an eigenstate of this operator so we do not know if it has spin-up.

Similarly, we can define $D_\downarrow$ that tells us whether the detector has detected spin-down:

$$D_\downarrow |D_{\boldsymbol{x}}\rangle = |D_{\boldsymbol{x}}\rangle \quad \text{for} \quad \boldsymbol{x} = \boldsymbol{x}_\downarrow \tag{15.11}$$

$$D_\downarrow |D_{\boldsymbol{x}}\rangle = 0 \quad \text{otherwise} \tag{15.12}$$

Once more the state $|\psi_f\rangle$ is not an eigenstate of this operator so we do not know if it has spin-down.

We can also define a operator $D_{\uparrow\vee\downarrow}$ which tells us whether we have spin-up *or* spin-down, defined by

$$D_{\uparrow\vee\downarrow} |D_{\boldsymbol{x}}\rangle = |D_{\boldsymbol{x}}\rangle \quad \text{for} \quad \boldsymbol{x} = \boldsymbol{x}_\uparrow \tag{15.13}$$

$$D_{\uparrow\vee\downarrow} |D_{\boldsymbol{x}}\rangle = |D_{\boldsymbol{x}}\rangle \quad \text{for} \quad \boldsymbol{x} = \boldsymbol{x}_\downarrow \tag{15.14}$$

$$D_{\uparrow\vee\downarrow} |D_{\boldsymbol{x}}\rangle = 0 \quad \text{otherwise} \tag{15.15}$$

This is a "definiteness" operator, which tells us whether or not we have detected a state with definite spin. A state that ends up in a position $\boldsymbol{x}$ which is neither $\boldsymbol{x}_\uparrow$ nor $\boldsymbol{x}_\downarrow$ would have eigenvalue 0. If we do observe a definite spin state then this operator yields 1, *i.e.* yes.

Acting on $|\psi_f\rangle$ we have

$$D_{\uparrow\vee\downarrow} |\psi_f\rangle = |\psi_f\rangle \tag{15.16}$$

This superposition is not definitely 'spin-up' nor is it definitely 'spin-down', but it is definitely 'spin-up or spin-down'. The linearity of superpositions implies that any superposition of spin-up and spin-down states is still a state which is for sure definitely 'spin-up or spin-down'. We never observe something else.

More generally, let us call $|i\rangle$ the set of states which has a definite result for a given observable O

$$O |i\rangle = \lambda_i |i\rangle \tag{15.17}$$

The observable which tells us whether we have observed a definite result of O is defined by

$$D |i\rangle = |i\rangle \tag{15.18}$$

$$D |\psi\rangle = 0 \quad \text{otherwise} \tag{15.19}$$

Because O is an observable and therefore Hermitian, the states $|i\rangle$ form a basis. Therefore for an arbitrary state in this Hilbert space we have

$$D |\psi\rangle = D \sum_i c_i |i\rangle = \sum_i c_i D |i\rangle = \sum_i |i\rangle = |\psi\rangle \tag{15.20}$$

which means D is the identity operator! Therefore, any state in the Hilbert space has a definite result for O. The results and discussion from the Stern-Gerlach case are generic.

What we have assumed is that superpositions are linear combinations of the base states, that observables are represented by Hermitian operators, and that eigenstates of these observables have definite values. These postulates when combined give us that we always observe definite results. Note this very subtle point, we don't always observe the *same* value. It is not true that $|\psi_f\rangle$ always yields spin-up for example. What is true is that we always observe a definite answer, we get spin-up *or* spin-down, not anything else.

Do what *do* we observe? We have several options but no way to determine which ones we do observe. Without hidden variables we do not have a way to predict which option happens, in fact, quantum mechanics tells us it is impossible, it's random. What we can predict are the *probabilities* of obtaining each outcome. In practice the way we measure these probabilities is by taking N copies of the same state (or more precisely N copies of identically prepared states) and measure the relative *frequencies* of each outcome for large enough N. If the state we want to examine is generically given by

$$|\psi\rangle = \sum_i c_i |i\rangle \tag{15.21}$$

then the state in the combined system of the N copies is

$$|\Psi\rangle = |\psi\rangle \otimes |\psi\rangle \otimes \cdots = \sum_{i_1 i_2 \dots i_N} c_{i_1} c_{i_2} \cdots c_{i_N} |i_1 i_2 \dots i_N\rangle \tag{15.22}$$

If the states $|i\rangle$ for an orthonormal basis then

$$\langle i_1 i_2 \dots i_N | j_1 j_2 \dots j_N \rangle = \delta_{i_1 j_1} \delta_{i_2 j_2} \cdots \delta_{i_N j_N} \tag{15.23}$$

the state $|\Psi\rangle$ is normalised if $\sum_i |c_i|^2 = 1$.

We define the frequency operator on the basis $|i_1 i_2 \dots i_N\rangle$ such that

$$P_n |i_1 i_2 \dots i_N\rangle = \frac{N_n}{N} |i_1 i_2 \dots i_N\rangle \tag{15.24}$$

where N_n is how many indices $i_1,\ i_2,\ \dots,\ i_N$ are equal to n.

Our goal is to show that

$$\left\| \left(P_n - |c_n|^2 \mathbb{1} \right) |\Psi\rangle \right\|^2 = \frac{|c_n|^2 \left(1 - |c_n|^2 \right)}{N} \tag{15.25}$$

which shows that in the limit $N \to \infty$ the state $|\Psi\rangle$ is an eigenstate of the frequency operator with eigenvalue $|c_n|^2$, as predicted by the Born rule.

Assuming that P_n is linear we have

$$P_n |\Psi\rangle = \sum_{i_1 i_2 \dots i_N} c_{i_1} c_{i_2} \cdots c_{i_N} P_n |i_1 i_2 \dots i_N\rangle = \sum_{i_1 i_2 \dots i_N} c_{i_1} c_{i_2} \cdots c_{i_N} \frac{N_n}{N} |i_1 i_2 \dots i_N\rangle \tag{15.26}$$

To make calculations simpler we introduce a compound index I to replace the set of indices $i_1 i_2 \dots i_N$, and we introduce $N_{I,n}$ to be how many of the indices $i_1 i_2 \dots i_N$ in I are equal to n. Of course for any I we will have

$$\sum_n N_{I,n} = N \tag{15.27}$$

In this notation we write

$$|\Psi\rangle = \sum_I \left(\prod_n c_n^{N_{I,n}} \right) |I\rangle \tag{15.28}$$

and therefore

$$P_n |\Psi\rangle = \sum_I \left(\prod_m c_m^{N_{I,m}} \right) \frac{N_{I,n}}{N} |I\rangle \tag{15.29}$$

which gives us

$$\left\| \left(P_n - |c_n|^2 \mathbb{1} \right) |\Psi\rangle \right\|^2 = \sum_I \left(\prod_m |c_m|^{N_{I,m}} \right)^2 \left(\frac{N_{I,n}}{N} - |c_n|^2 \right)^2 \tag{15.30}$$

Instead of summing over I we can sum over N_1, N_2, etc. The number of Is with $N_{I,n} = N_n$ for a given set of $N_1, N_2, \ldots$ is just the binomial coefficient

$$\frac{N!}{N_1! N_2! \cdots} \tag{15.31}$$

therefore

$$\left\| \left(P_n - |c_n|^2 \mathbb{1} \right) |\Psi\rangle \right\|^2 = \sum_{N_1 N_2 \ldots} \left(\prod_m |c_m|^{2N_m} \right) \left(\frac{N_n}{N} - |c_n|^2 \right)^2 \frac{N!}{N_1! N_2! \cdots} \tag{15.32}$$

where the sum is constrained by $N_1 + N_2 + \cdots = N$. Now we use the binomial theorem to write

$$\sum_{N_1 N_2 \ldots} \left(\prod_m |c_m|^{2N_m} \right) \frac{N!}{N_1! N_2! \cdots} = \left(\sum_m |c_m|^2 \right)^N \tag{15.33}$$

we can also write

$$|c_n|^2 \frac{\partial}{\partial |c_n|^2} \left(\prod_m |c_m|^{2N_m} \right) = N_n \tag{15.34}$$

and putting the two togehter we find

$$\begin{aligned} \left\| \left(P_n - |c_n|^2 \mathbb{1} \right) |\Psi\rangle \right\|^2 =& \left(\frac{1}{N} |c_n|^2 \frac{\partial}{\partial |c_n|^2} - |c_n|^2 \right)^2 \left(\sum_m |c_m|^2 \right)^N = \\ =& \left(\frac{1}{N^2} \left(|c_n|^2 \frac{\partial}{\partial |c_n|^2} \right)^2 - \frac{2}{N} |c_n|^4 \frac{\partial}{\partial |c_n|^2} + |c_n|^4 \right) \left(\sum_m |c_m|^2 \right)^N = \\ =& N(N-1) \frac{|c_n|^4}{N^2} \left(\sum_m |c_m|^2 \right)^{N-2} + N \frac{|c_n|^2}{N^2} \left(\sum_m |c_m|^2 \right)^{N-1} - \\ & - 2N \frac{|c_n|^4}{N} \left(\sum_m |c_m|^2 \right)^{N-1} + |c_n|^4 \left(\sum_m |c_m|^2 \right)^N \end{aligned} \tag{15.35}$$

using $\sum_i |c_i|^2 = 1$ we find

$$\left\| \left(P_n - |c_n|^2 \mathbb{1} \right) |\Psi\rangle \right\|^2 = \frac{|c_n|^2 \left(1 - |c_n|^2 \right)}{N} \tag{15.36}$$

as desired.

This result is exactly what we needed. We just assumed linearity, hermiticity and that eigenstates have definite values, and we obtained that the frequency operator has as eigenvalues exactly what we wished from the Born rule. There are however complaints about this procedure, firstly it's frequencist in nature which is not what a lot of statisticians prefer. Secondly, the limit $N \to \infty$ is dubious. Without invoking the Born rule we cannot actually interpret the action of P_n on $|\Psi\rangle$, it's definitely *close* to an eigenstate with eigenvalues $|c_n|^2$, but it's not quite there. Further, although there are constructions for $N = \infty$ there are also objections to those constructions. It's not just that the Hilbert space is infinite dimensional, it's that we taking infinitely many copies of a possibly infinite dimensional Hilbert space. This infinity is sometimes a bit too big and breaks the mathematics in a fundamental way[89].

In case you are a more serious mathematician than I am and these issues are too serious for you to be convinced, there is an alternative—Gleason's theorem. This theorem states that the *unique* probability distribution one can assign to projection operators $|i\rangle\langle i|$ is given by

$$P_i = \mathrm{Tr}(\rho\,|i\rangle\langle i|) \tag{15.37}$$

where ρ obeys the axioms of a density matrix. Although it doesn't have the flavour and intuitiveness of the frequencist argument, this theorem is more mathematically robust, showing that the Born rule is unique.

All in all, we see that linearity, hermiticity and the eigenstate postulate determine that we always observe definite results, even for superpositions. Further, we can use these postulates to derive the probability of obtaining each outcome and it uniquely gives us the Born rule. Because we have ruled out hidden variables these probabilities are to be understood as a fundamental indeterminacy of nature.

15.2 Decoherence: a simple example

The ideas of the previous section are good but they are not enough. For one, we were always working in a given basis. But the definiteness operator is the identity which is the same in every basis. Why are $|\uparrow\rangle$ and $|\downarrow\rangle$ special? At first sight the state

$$\frac{1}{\sqrt{2}}(|\uparrow\rangle + |\downarrow\rangle) \tag{15.38}$$

is an equally valid pure state in the Hilbert space. Why is the basis $\{|\uparrow\rangle, |\downarrow\rangle\}$ special? Additionally, we have no understanding of the dynamics of measurement. Does collapse actually happen? If so, how does it work, who gets to collapse states, and in what basis does the state collapse into?

To illustrate these issues, it is worth going over a famous scenario concocted by Erwin Schrodinger in 1935. He imagined a closed box containing both a cat and a device consisting of a tiny amount of a radioactive source and some poison. If the radioactive source decays then the poison will be triggered and the cat will die. If the radioactive source doesn't decay then the poison will not be triggered and the cat doesn't die.

INSERT PICTURE

If we wait for a time equal to the half-life of the radioactive source, the state that system will be in is given by

$$|\mathrm{source}\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |0\rangle) \tag{15.39}$$

where $|1\rangle$ is the initial excited state and $|0\rangle$ is the final ground state. If the state is $|1\rangle$ the cat is alive, if the state is $|0\rangle$ the cat is dead, so the conclusion is that the cat is in a superposition between alive and dead

$$|\mathrm{cat}\rangle = \frac{1}{\sqrt{2}}(|\mathrm{alive}\rangle + |\mathrm{dead}\rangle) \tag{15.40}$$

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[89] A similar issue arises for quantum field theories, which essentially assign a harmonic oscillator (which is infinitely dimensional) to every point in spacetime

This conclusion is so bizarre that Schrodinger called it “completely burlesque”. We never observe macroscopic systems to be in such superpositions. Of course, if someone, say Alice, were to open the box then they would be able to measure and collapse the cat’s state into “alive” or “dead”. But who gets to collapse the superposition? Could Bob not say that instead Alice was in a superposition

$$|\text{Alice}\rangle \propto |\text{cat alive}\rangle\,|\text{Alice sees cat alive}\rangle + |\text{cat dead}\rangle\,|\text{Alice sees cat dead}\rangle \tag{15.41}$$

correlated with the state of the cat?

In the early days of quantum mechanics people tried to make measurements obey different laws than quantum systems. Some of them attributed special behaviour to consciousness. The Copenhagen interpretation championed by Niels Bohr posited that large systems had to be described classically and that it was the interaction between a quantum and a classical system is what caused the collapse. Both of these options seem untenable for modern readers. We want classicality to be an emergent phenomenon from quantum mechanics. It cannot be fundamentally separate.

The answer to all of these puzzles lies in the role of the environment. After all, our quantum systems are not isolated, they are subject to an environment. If nothing else the black body radiation from the cosmic microwave background. Every system is in fact an open system, the total Hilbert space is then $\mathcal{H} = \mathcal{H}_S \otimes \mathcal{H}_E$. Assuming the full system is described by a pure state $|\psi\rangle \in \mathcal{H}$ we are looking after the time evolution of the system density matrix

$$\rho_S = \text{Tr}_E\,|\psi\rangle\langle\psi| \tag{15.42}$$

The full state $|\psi\rangle$ evolves unitarily as given by the Hamiltonian of the full system, however, the evolution of ρ_S might not be unitary.

Let us assume the system starts out separable

$$|\psi(0)\rangle = |\phi_S\rangle \otimes |\chi_E\rangle \tag{15.43}$$

where $|\phi_S\rangle \in \mathcal{H}_S$ and $|\chi_E\rangle \in \mathcal{H}_E$. This means the initial system density matrix is pure

$$\rho_S(0) = |\phi_S\rangle\langle\phi_S| \tag{15.44}$$

The state of the full system at time t is given by

$$|\psi(t)\rangle = U(t)\,|\psi(0)\rangle \tag{15.45}$$

therefore, the system density matrix is

$$\begin{aligned}\rho_S(t) =& \text{Tr}_E(|\psi(t)\rangle\langle\psi(t)|) = \text{Tr}_E(U(t)\,|\psi(0)\rangle\langle\psi(0)|\,U(t)^\dagger) = \\ =& \sum_\alpha \langle\alpha_E|\,U(t)\,|\psi(0)\rangle\,\langle\psi(0)|\,U(t)^\dagger\,|\alpha_E\rangle\end{aligned} \tag{15.46}$$

where $\{|\alpha_E\rangle\}$ is a basis of $\mathcal{H}_E$.

If we define the *Kraus* operators $M_\alpha(t) : \mathcal{H}_S \to \mathcal{H}_S$

$$M_\alpha(t) = \langle\alpha_E|\,U(t)\,|\chi\rangle = \text{Tr}_E(U(t)\,|\chi\rangle\langle\alpha_E|) \tag{15.47}$$

we can write the time evolution of the system density matrix as

$$\rho_S(t) = \sum_\alpha M_\alpha(t)\rho_S(0)M_\alpha(t)^\dagger \tag{15.48}$$

which is in general not a unitary transformation (although it *is* linear!).

If the Hamiltonian does not actually couple the two systems so that

$$H = H_S \otimes \mathbb{1}_E + \mathbb{1}_S \otimes H_E \tag{15.49}$$

we have

$$U(t) = U_S(t) \otimes U_E(t) \tag{15.50}$$

which gives

$$\begin{aligned}\rho_S(t) =& \sum_\alpha M_\alpha(t)\rho_S(0)M_\alpha(t)^\dagger = \sum_\alpha \langle\alpha_E|\, U_E(t)\,|\chi\rangle\, U_S(t)\rho_S(0)U_S(t)^\dagger\, \langle\chi|\, U_E(t)^\dagger\,|\alpha_E\rangle = \\ =& U_S(t)\rho_S(0)U_S(t)^\dagger \sum_\alpha \langle\chi|\, U_E(t)\,|\alpha_E\rangle\, \langle\alpha_E|\, U_E(t)^\dagger\,|\chi\rangle = \\ =& U_S(t)\rho_S(0)U_S(t)^\dagger\, \langle\chi|\, U_E(t)U_E(t)^\dagger\,|\chi\rangle = \\ =& U_S(t)\rho_S(0)U_S(t)^\dagger\, \langle\chi|\chi\rangle = \\ =& U_S(t)\rho_S(0)U_S(t)^\dagger\end{aligned} \tag{15.51}$$

which is unitary!

We see that the if the systems starts in a pure state and doesn't interact with the environment then it will remain a pure state evolving unitarily. Any loss of unitarity that would make ρ_S mixed must be a consequence of the interactions between the system and the environment. This time evolution is in general quite complicated. In this section we will examine a simple toy model with a 2-level system and 3-level environment. In the next section we will describe the more physically relevant cases in greater generality.

Let us suppose our system is the spin-1/2 Hilbert space with $|{\uparrow}\rangle$ and $|{\downarrow}\rangle$ and the environment is three dimensional with basis $|0\rangle$, $|1\rangle$, $|2\rangle$. Let us suppose we set up the Hamiltonian and interaction between the two systems such that the unitary time evolution is given by (Exercise: determine the action on $|1\rangle$ and $|2\rangle$ such that this is indeed unitary):

$$U\,|{\uparrow}\rangle \otimes |0\rangle = |{\uparrow}\rangle \otimes \left(\sqrt{1-p}\,|0\rangle + \sqrt{p}\,|1\rangle\right) \tag{15.52}$$

$$U\,|{\downarrow}\rangle \otimes |0\rangle = |{\downarrow}\rangle \otimes \left(\sqrt{1-p}\,|0\rangle + \sqrt{p}\,|2\rangle\right) \tag{15.53}$$

In other words, the environment starts in the ground state $|0\rangle$ and after interacting with the system it has a probability p of transitioning to $|1\rangle$ if the system was spin-up or to $|2\rangle$ if the system was spin-down, it therefore has probability $1-p$ of staying in $|0\rangle$.

Let us suppose the initial state is

$$|\psi\rangle = (a\,|{\uparrow}\rangle + b\,|{\downarrow}\rangle) \otimes |0\rangle \tag{15.54}$$

where $|a|^2 + |b|^2 = 1$, so that the initial system density matrix is

$$\rho_S(0) = \begin{pmatrix} |a|^2 & ab^* \\ a^*b & |b|^2 \end{pmatrix} \tag{15.55}$$

The Kraus operators for this time evolution are

$$M_0 = \langle 0|\, U \,|0\rangle = \sqrt{1-p}\; \mathbb{1}_S \tag{15.56}$$

$$M_1 = \langle 1|\, U \,|0\rangle = \sqrt{p}\, |{\uparrow}\rangle\!\langle{\uparrow}| \tag{15.57}$$

$$M_2 = \langle 2|\, U \,|0\rangle = \sqrt{p}\, |{\downarrow}\rangle\!\langle{\downarrow}| \tag{15.58}$$

Therefore, the system density matrix at later times is given by

$$\rho_S(t) = \begin{pmatrix} |a|^2 & (1-p)ab^* \\ (1-p)a^*b & |b|^2 \end{pmatrix} \tag{15.59}$$

We see that the off-diagonal terms are suppressed under this time evolution. This behaviour becomes even more clear under repeated applications of this time evolution. If we define the rate of change as $\Gamma/\delta t$, after a time $t = N\delta t$, the off-diagonal terms become

$$(1-p)^N = \left(1 - \Gamma\frac{t}{N}\right)^N \to \mathrm{e}^{-\Gamma t} \tag{15.60}$$

and therefore

$$\rho_S(t) \to \begin{pmatrix} |a|^2 & \mathrm{e}^{-\Gamma t}ab^* \\ \mathrm{e}^{-\Gamma t}a^*b & |b|^2 \end{pmatrix} \to \begin{pmatrix} |a|^2 & 0 \\ 0 & |b|^2 \end{pmatrix} \tag{15.61}$$

This damping of the off-diagonal terms of the system density matrix will turn out to be generic and not a consequence of our specific toy model. This is known as *decoherence* because the final density matrix is mixed or *phase-damping* because the final density matrix is real.

There are two main lessons to take away from this example. Firstly, the fact we ended up with a diagonal density matrix was because of our judicious choice of basis such that U did not change the system states. It is the shape of these interactions that dictates what is the basis in which the density matrix will become diagonal. In more realistic scenarios, the fact that U is *local* will mean it is a function of $\boldsymbol{X}$ and therefore in the position basis it will not change the system. This is ultimately why in the Stern-Gerlach we preferred $|\boldsymbol{x}_\uparrow\rangle$ and $|\boldsymbol{x}_\downarrow\rangle$ or in the Schrodinger's cat we wanted $|\text{alive}\rangle$ or $|\text{dead}\rangle$, these are eigenstates of position, which are unchanged by the interactions with the environment. The cross terms between these states will evolve with time and generically be dampened. Decoherence solves the basis problem.

The second lesson is due to the final form of the density matrix. It looks like

$$\rho_S \to |a|^2\, |{\uparrow}\rangle\!\langle{\uparrow}| + |b|^2\, |{\downarrow}\rangle\!\langle{\downarrow}| \tag{15.62}$$

which looks like a classical ensemble between the states $|{\uparrow}\rangle$ and $|{\downarrow}\rangle$ with relative probabilities dictated by the Born rule. This is exactly what the outcome of a measurement process should be! If we wish to include the apparatus in our description we would write something like

$$\rho_S \to |a|^2\, |{\uparrow}, D_{\boldsymbol{x}_\uparrow}\rangle\!\langle{\uparrow}, D_{\boldsymbol{x}_\uparrow}| + |b|^2\, |{\downarrow}, D_{\boldsymbol{x}_\uparrow}\rangle\!\langle{\downarrow}, D_{\boldsymbol{x}_\uparrow}| \tag{15.63}$$

The two possibilities are completely disconnected. They will never re-cohere. We can therefore simplify and just use one of the branches the one we, as a quantum system ourselves, become correlated with

$$\rho_S \to |a|^2\, |{\uparrow}, D_{\boldsymbol{x}_\uparrow}\rangle\!\langle{\uparrow}, D_{\boldsymbol{x}_\uparrow}| + |b|^2\, |{\downarrow}, D_{\boldsymbol{x}_\uparrow}\rangle\!\langle{\downarrow}, D_{\boldsymbol{x}_\uparrow}| \to |{\uparrow}, D_{\boldsymbol{x}_\uparrow}\rangle\!\langle{\uparrow}, D_{\boldsymbol{x}_\uparrow}| \tag{15.64}$$

The collapse becomes just a way to simplify our calculations once decoherence has occurred. It is only an approximation to say they are fully disconnected but a useful one. We could if we liked, keep the other branches, but these cannot be influenced experimentally so it is often too much trouble. Some people like to think they're real, others prefer to say they are not. The distinction is irrelevant, it is a matter of interpretation. What matters is the outcome of decoherence as a way to explain the effective description of collapse of the wavefunction.

There is one important misconception worth addressing before proceeding to the general case. We have *not* derived the Born rule. Although the end result of the decoherence looks like a classical ensemble, without the Born rule we could not interpret it as such. We needed the Born rule to interpret the tracing out of the environment. It is Gleason's theorem and linearity which gives us the Born rule, as a fundamental probability measure to be assigned to states in the Hilbert space. Decoherence merely gives a way to dynamically realise these probabilities in a way we can interact with.

15.3 * Decoherence in greater generality

Our goal in this final section is to demonstrate the phenomenon of decoherence in greater generality. The calculation is quite technical and lengthy but the detail will make it very clear what are the physical assumptions needed to observe decoherence. In particular, we will consider an environment which is thermal and much larger than the system under study. We will also assume that the coupling between the two is weak. These are physically well motivated and will allow us to perform explicit computations.

Under these assumptions, the time scales of interest will be much larger than the time it takes for correlations between the environment and the system to dissipate, which will allow us to write a differential time-evolution equation for the density matrix of the system, the *Lindblad equation* in terms of its Hamiltonian and some additional *jump operators* related to the interaction terms between the system and the environment. The presence of these operators will generalise the usual Hamiltonian evolution of the density matrix beyond just a unitary transformation. Generically, there will be a special basis in which the jump operators are diagonal, and in that basis decoherence will happen suppressing the off-diagonal terms of the density matrix.

Now for the calculation. The setup is that we have a total quantum system $\mathcal{H}_T$ which is composed of a system of interest $\mathcal{H}_S$ and an environment $\mathcal{H}_E$ which we wish to trace out.

INSERT PICTURE

The evolution of the total density matrix, ρ_T is given by

$$\mathrm{i}\hbar\frac{\partial\rho_T}{\partial t} = [H_T, \rho_T] \tag{15.65}$$

but we are only interested in the evolution of the system density matrix, ρ_S defined as

$$\rho_S = \mathrm{Tr}_E\,\rho_T \tag{15.66}$$

We will write the total Hamiltonian as follows

$$H_T = H_S \otimes \mathbb{1}_E + \mathbb{1}_S \otimes H_E + \epsilon H_{SE} \tag{15.67}$$

where H_S is the Hamiltonian of the system, H_E is the Hamiltonian of the environment, and H_{SE} is the interaction Hamiltonian between the two, ϵ is a parameter controlling the strength of this interaction. If ϵ were zero then the evolution of either subsystem would be unitary, we will want non-vanishing ϵ but we will assume it is small to simplify our calculations. Further we will write

$$H_{SE} = \sum_i S_i \otimes E_i \tag{15.68}$$

where S_i are operators on $\mathcal{H}_S$ and E_i are operators on $\mathcal{H}_E$.

A last bit of notation, for an operator A_T on $\mathcal{H}_T$ we define

$$\hat{A}_T(t) = \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(H_S\otimes\mathbb{1}_E + \mathbb{1}_S\otimes H_E)t} A_T \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}(H_S\otimes\mathbb{1}_E + \mathbb{1}_S\otimes H_E)t} \tag{15.69}$$

to strip out the unimportant time-evolution due to the isolated parts of the Hamiltonians.

Using this notation we can write

$$\mathrm{i}\hbar\frac{\partial\hat{\rho}_T}{\partial t} = \epsilon\Big[\hat{H}_{SE}(t), \hat{\rho}_T(t)\Big] \tag{15.70}$$

We can turn this equation into an integral one (note that $\hat{A}(0) = A(0)$ for any operator)

$$\hat{\rho}_T(t) = \rho_T(0) - \frac{\mathrm{i}\epsilon}{\hbar}\int_0^t \mathrm{d}s \,\Big[\hat{H}_{SE}(s), \hat{\rho}_T(s)\Big] \tag{15.71}$$

and then plug this expression back into the differential version

$$\frac{\partial\hat{\rho}_T}{\partial t} = -\frac{\mathrm{i}\epsilon}{\hbar}\Big[\hat{H}_{SE}(t), \rho_T(0)\Big] - \frac{\epsilon^2}{\hbar^2}\int_0^t \mathrm{d}s \,\Big[\hat{H}_{SE}(t), \Big[\hat{H}_{SE}(s), \hat{\rho}_T(s)\Big]\Big] \tag{15.72}$$

and once more

$$\frac{\partial\hat{\rho}_T}{\partial t} = -\frac{\mathrm{i}\epsilon}{\hbar}\Big[\hat{H}_{SE}(t), \rho_T(0)\Big] - \frac{\epsilon^2}{\hbar^2}\int_0^t \mathrm{d}s \,\Big[\hat{H}_{SE}(t), \Big[\hat{H}_{SE}(s), \hat{\rho}_T(t)\Big]\Big] + O\big(\epsilon^3\big) \tag{15.73}$$

from this point onward we will neglect terms of order $O\big(\epsilon^3\big)$.

In terms of the system density matrix we have

$$\frac{\partial\hat{\rho}_S}{\partial t} = -\frac{\mathrm{i}\epsilon}{\hbar}\operatorname{Tr}_E\Big[\hat{H}_{SE}(t), \rho_T(0)\Big] - \frac{\epsilon^2}{\hbar^2}\int_0^t \mathrm{d}s \operatorname{Tr}_E\Big[\hat{H}_{SE}(t), \Big[\hat{H}_{SE}(s), \hat{\rho}_T(t)\Big]\Big] \tag{15.74}$$

which is still not the equation we are looking after because it still depends on the total density matrix. We want a closed form expression for the evolution of ρ_S.

Assuming that the initial total density matrix is separable, $\rho_T(0) = \rho_S(0)\otimes\rho_E(0)$, and that the environment density matrix is thermal so that $\rho_E(0) \propto \exp(-H_E/k_B T)$ we can show the first term in (15.74) vanishes. First note that it equals

$$\operatorname{Tr}_E\Big[\hat{H}_{SE}(t), \rho_T(0)\Big] = \sum_i \Big(\hat{S}_i(t)\rho_S(0)\operatorname{Tr}_E\Big(\hat{E}_i(t)\rho_E(0)\Big) - \rho_S(0)\hat{S}_i(t)\operatorname{Tr}_E\Big(\rho_E(0)\hat{E}_i(t)\Big)\Big) \tag{15.75}$$

Because $\rho_E(0)$ is thermal, we have $[H_E, \rho_E(0)] = 0$, using the cyclicity of the trace, we have

$$\operatorname{Tr}_E\Big(\hat{E}_i(t)\rho_E(0)\Big) = \operatorname{Tr}_E\left(E_i\rho_E(0)\right) \equiv \langle E_i\rangle \tag{15.76}$$

Without loss of generality we can assume $\langle E_i\rangle = 0$, because we can always shift

$$H_S \to H_S + \epsilon\sum_i \langle E_i\rangle S_i \quad\text{and}\quad H_{SE} \to \sum_i S_i\otimes\left(E_i - \langle E_i\rangle\right) \tag{15.77}$$

to ensure it is the case. All in all, the first term in (15.74) vanishes, and we can therefore write

$$\frac{\partial \hat{\rho}_S}{\partial t} = -\frac{\epsilon^2}{\hbar^2} \int_0^t \mathrm{d}s \, \mathrm{Tr}_E \left[\hat{H}_{SE}(t), \left[\hat{H}_{SE}(s), \hat{\rho}_T(t) \right] \right] \tag{15.78}$$

We're close but we need one further crucial assumption, we will assume the environment is so vast that any correlations between the system and the environment are lost after a time τ_{corr}. This is perfectly compatible with weak coupling, because a small ϵ will mean that the time-scale for the evolution of the system τ_{sys} is much larger than the time it takes for the system to uncorrelate $\tau_{\text{sys}} \gg \tau_{\text{corr}}$. This is quite a strong assumption but it is what will allow us to fully trace out the dynamics of the environment. This is where the size of the environment comes into play, for the toy model in the previous section we were not careful about this when we applied the Kraus operators repeatedly, if we instead reapplied the unitary evolution and then traced out the environment we would have obtained a different answer. All in all, this means we shall assume

$$\hat{\rho}_T(t) = \hat{\rho}_S(t) \otimes \hat{\rho}_E(t) \tag{15.79}$$

Changing variables $s \to t - s$ we can write

$$\frac{\partial \hat{\rho}_S}{\partial t} = -\frac{\epsilon^2}{\hbar^2} \int_0^t \mathrm{d}s \, \mathrm{Tr}_E \left[\hat{H}_{SE}(t), \left[\hat{H}_{SE}(t-s), \hat{\rho}_S(t) \otimes \hat{\rho}_E(t) \right] \right] \tag{15.80}$$

now we expand the commutators to write

$$\begin{aligned} \frac{\partial \hat{\rho}_S}{\partial t} = -\frac{\epsilon^2}{\hbar^2} \int_0^t \mathrm{d}s \, \mathrm{Tr}_E \Big(& \hat{H}_{SE}(t)\hat{H}_{SE}(t-s)(\hat{\rho}_S(t) \otimes \hat{\rho}_E(t)) - \\ & -\hat{H}_{SE}(t)(\hat{\rho}_S(t) \otimes \hat{\rho}_E(t))\hat{H}_{SE}(t-s) - \\ & -\hat{H}_{SE}(t-s)(\hat{\rho}_S(t) \otimes \hat{\rho}_E(t))\hat{H}_{SE}(t) + \\ & +(\hat{\rho}_S(t) \otimes \hat{\rho}_E(t))\hat{H}_{SE}(t-s)\hat{H}_{SE}(t) \Big) \end{aligned} \tag{15.81}$$

To proceed we need an expression for $\hat{S}_i(t)$, its definition is

$$\hat{S}_i(t) = \mathrm{e}^{\frac{\mathrm{i}}{\hbar} H_S t} S_i \mathrm{e}^{-\frac{\mathrm{i}}{\hbar} H_S t} \tag{15.82}$$

which can be written differentially as

$$\frac{\partial \hat{S}_i}{\partial t} = \frac{\mathrm{i}}{\hbar} \left[H_S, \hat{S}_i \right] \tag{15.83}$$

Defining an operator inner product

$$(A, B) \equiv \mathrm{Tr}\big(A^\dagger B\big) \tag{15.84}$$

we can show that the action of the commutator is Hermitian if H_S is Hermitian

$$\begin{aligned} (A, [H_S, B]) &= \mathrm{Tr}\big(A^\dagger [H_S, B]\big) = \\ &= \mathrm{Tr}\big(A^\dagger H_S B - A^\dagger B H_S\big) = \\ &= \mathrm{Tr}\big(A^\dagger H_S B - H_S A^\dagger B\big) = \\ &= \mathrm{Tr}\Big((H_S A)^\dagger B - (A H_S)^\dagger B\Big) = \end{aligned}$$

$$\begin{aligned} &= \mathrm{Tr}\Big(([H_S, A])^\dagger B\Big) = \\ &= ([H_S, A], B) \end{aligned} \tag{15.85}$$

Therefore we can find eigen-operators $S_i(\omega)$ such that

$$[H_S, S_i(\omega)] = -\hbar\omega S_i(\omega) \tag{15.86}$$

and that we can expand

$$S_i = \sum_\omega S_i(\omega) \tag{15.87}$$

In this basis we can write

$$\hat{H}_{SE}(t) = \sum_{\omega,i} \mathrm{e}^{-\mathrm{i}\omega t} S_i(\omega) \otimes \hat{E}_i(t) = \sum_{\omega,i} \mathrm{e}^{\mathrm{i}\omega t} S_i^\dagger(\omega) \otimes \hat{E}_i^\dagger(t) \tag{15.88}$$

where in the last equality we used the fact $\hat{H}_{SE}$ is Hermitian.

Applying the decomposition in terms of $S_i(\omega)$ for $\hat{H}_{SE}(t-s)$, and in terms of $S_i^\dagger(\omega')$ for $\hat{H}_{SE}(t)$ in the first and third terms, doing the opposite for the second and forth terms; using the cyclicity of the trace; and some elbow grease we find

$$\begin{aligned} \hbar\frac{\partial\hat{\rho}_S}{\partial t} = \sum_{\omega,\omega',i,j} \Big(& \mathrm{e}^{-\mathrm{i}(\omega-\omega')t} \varGamma_{ij}(\omega, t) \Big[S_i(\omega)\hat{\rho}_S(t), S_j^\dagger(\omega')\Big] + \\ & + \mathrm{e}^{\mathrm{i}(\omega-\omega')t} \varGamma_{ji}^*(\omega, t) \Big[S_i(\omega), \hat{\rho}_S(t) S_j^\dagger(\omega')\Big]\Big) \end{aligned} \tag{15.89}$$

where

$$\varGamma_{ij}(\omega, t) = \frac{\epsilon^2}{\hbar} \int_0^t \mathrm{d}s\, \mathrm{e}^{\mathrm{i}\omega s}\, \mathrm{Tr}_E \left(\hat{E}_j^\dagger(t) \hat{E}_i(t-s) \hat{\rho}_E(t)\right) \tag{15.90}$$

using the cyclicity of the trace and the fact $[\rho_E(0), H_E] = 0$ which implies $\hat{\rho}_E(t) = \rho_E(0)$ we find

$$\varGamma_{ij}(\omega, t) = \frac{\epsilon^2}{\hbar} \int_0^t \mathrm{d}s\, \mathrm{e}^{\mathrm{i}\omega s}\, \mathrm{Tr}_E \left(\hat{E}_j^\dagger(s) E_i \rho_E(0)\right) \tag{15.91}$$

We will now use our final approximation. We are interested in times much larger than the time it takes for correlations between the system and environment to die down and also much larger than the relaxation time of the environment. Both of which are sensible in the small ϵ regime. But in this limit, unless $\omega = \omega'$ the oscillations will cancel each other. We will therefore take $\omega = \omega'$ and let $t \to \infty$ in the definition of $\varGamma_{ij}(\omega, t)$ to write

$$\hbar\frac{\partial\hat{\rho}_S}{\partial t} = \sum_{\omega,i,j} \left(\varGamma_{ij}(\omega) \Big[S_i(\omega)\hat{\rho}_S(t), S_j^\dagger(\omega)\Big] + \varGamma_{ji}^*(\omega) \Big[S_i(\omega), \hat{\rho}_S(t) S_j^\dagger(\omega)\Big]\right) \tag{15.92}$$

where

$$\varGamma_{ij}(\omega) = \frac{\epsilon^2}{\hbar} \int_0^\infty \mathrm{d}s\, \mathrm{e}^{\mathrm{i}\omega s}\, \mathrm{Tr}_E \left(\hat{E}_j^\dagger(s) E_i \rho_E(0)\right) \tag{15.93}$$

which is finally a closed form time-evolution equation for ρ_S.

We can find a more useful formulation of this equation if we decompose $\varGamma_{ij}(\omega)$ into

$$\pi_{ij}(\omega) \equiv -\frac{\mathrm{i}}{2}\big(\varGamma_{ij}(\omega) - \varGamma_{ij}^*(\omega)\big) \tag{15.94}$$

$$\gamma_{ij}(\omega) \equiv \varGamma_{ij}(\omega) + \varGamma_{ij}^*(\omega) = \frac{\epsilon^2}{\hbar^2} \int_{-\infty}^\infty \mathrm{d}s\, \mathrm{e}^{\mathrm{i}\omega s}\, \mathrm{Tr}_E \left(\hat{E}_j^\dagger(s) E_i \rho_E(0)\right) \tag{15.95}$$

Removing the hats to go back to the usual Schrodinger picture time dependence we find

$$\hbar\frac{\partial\rho_S}{\partial t} = -\mathrm{i}[H'_S,\rho_S(t)] + \sum_{\omega,i,j}\gamma_{ij}(\omega)\left(S_i(\omega)\rho_S(t)S_j^\dagger(\omega) - \frac{1}{2}\left\{S_j^\dagger(\omega)S_i(\omega),\rho_S(t)\right\}\right) \tag{15.96}$$

where

$$H'_S = H_S + \sum_{\omega,i,j}\pi_{ij}(\omega)S_j^\dagger(\omega)S_i(\omega) \tag{15.97}$$

is the system Hamiltonian, taking into account a change in the system's energy levels due to the environment, this last term is sometimes called the *Lamb shift*.

Finally, the matrix γ_{ij} can be diagonalised, allowing us to write

$$\hbar\frac{\partial\rho_S}{\partial t} = -\mathrm{i}[H'_S,\rho_S(t)] + \sum_{\omega,i}\left(L_i(\omega)\rho_S(t)L_i^\dagger(\omega) - \frac{1}{2}\left\{L_i^\dagger(\omega)L_i(\omega),\rho_S(t)\right\}\right) \tag{15.98}$$

which is the *Lindblad equation*. The operators L_i are sometimes called the *jump operators*, as we can see they provide a non-unitary jump between energy levels due to the interaction with the environment. For simplicity we can lump the i and the ω dependence into a single index, a, and write

$$\hbar\frac{\partial\rho_S}{\partial t} = -\mathrm{i}[H'_S,\rho_S(t)] + \sum_{a}\left(L_a\rho_S(t)L_a^\dagger - \frac{1}{2}\left\{L_a^\dagger L_a,\rho_S(t)\right\}\right) \tag{15.99}$$

It was a lot of work but we finally have an equation for the system density matrix in terms of its Hamiltonian (with some additions due to the environment which nonetheless keep its unitarity), and the jump operators which are linear combinations of the operators S_i controlling the interaction between the system and the environment.

To see decoherence happening we need to find operators L_a that would trigger a measurement like action. Assume we are trying to measure some observable O with eigenvectors $|\alpha\rangle$. Then the outcome of the measurement should be a density matrix roughly of the form

$$\rho_S \sim P_\alpha\,|\alpha\rangle\!\langle\alpha| \tag{15.100}$$

we are not going to impose this limit, but we observe that this at least should be a solution. Said another way, we have no hope of describing a measurement if the above expression isn't a solution to the Lindblad equation. In order for that to happen the L_a must be linear combinations of the projection operators $|\alpha\rangle\!\langle\alpha|$.

$$L_a = \sum_{i\omega} l_{a\alpha}\,|\alpha\rangle\!\langle\alpha| \tag{15.101}$$

This is where the special basis arises, this statement is essentially demanding that L_a are diagonal in the basis provided by $|\lambda_\alpha\rangle$. In real life the logic is the opposite, L_a are whatever they are with the interaction between the system and the environment, but we can find a basis such that (15.101) is true[90]. For instance, for local interactions, we will usually have to work in the position basis. Thereby removing the possibility of observing linear combinations of $|\text{alive}\rangle$ and $|\text{dead}\rangle$.

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[90] If the L_a are Hermitian then this is trivial because we can always diagonalise them. Otherwise it may be a bit more subtle, it may be that the interactions between the system and the environment are not going to cause a measurement-like evolution.

Neglecting the system Hamiltonian for simplicity we can write

$$\hbar\frac{\partial\rho_S}{\partial t} = \sum_{\alpha\beta} C_{\alpha\beta}\left(|\alpha\rangle\langle\alpha|\,\rho_S(t)\,|\beta\rangle\langle\beta| - \frac{\delta_{\alpha\beta}}{2}\{|\alpha\rangle\langle\alpha|\,,\rho_S(t)\}\right) \tag{15.102}$$

where

$$C_{\alpha\beta} = \sum_a l_{a\alpha} l_{a\beta} \tag{15.103}$$

Using the ansatz

$$\rho_S(t) = \sum_{\alpha\beta} f_{\alpha\beta}(t)\,|\alpha\rangle\langle\alpha|\,\rho(0)\,|\beta\rangle\langle\beta| \tag{15.104}$$

with the initial condition $f_{\alpha\beta}(0) = 1$ we find

$$\frac{\mathrm{d}f_{\alpha\beta}}{\mathrm{d}t} = \lambda_{\alpha\beta} f_{\alpha\beta} \tag{15.105}$$

where

$$\lambda_{\alpha\beta} = C_{\alpha\beta} - \frac{1}{2}(C_{\alpha\alpha} + C_{\beta\beta}) = -\frac{1}{2}\sum_a (l_{a\alpha} - l_{a\beta})^2 \tag{15.106}$$

The solution to this equation is of course

$$f_{\alpha\beta}(t) = \mathrm{e}^{\lambda_{\alpha\beta} t} \tag{15.107}$$

therefore we can write

$$\rho_S(t) = \sum_{\alpha\beta} \mathrm{e}^{\lambda_{\alpha\beta} t}\,|\alpha\rangle\langle\alpha|\,\rho(0)\,|\beta\rangle\langle\beta| \tag{15.108}$$

In the generic case where there are no degeneracies and

$$l_{a\alpha} = l_{a\beta} \implies \alpha = \beta \tag{15.109}$$

all the terms with $\alpha \neq \beta$ in (15.108) have a negative definite exponent. The only terms which do not vanish for late times are the diagonal terms giving us

$$\rho_S(t) \to \sum_{\alpha} |\alpha\rangle\langle\alpha|\,\rho(0)\,|\alpha\rangle\langle\alpha| \tag{15.110}$$

habemus decoherence

It was a lengthy derivation but its length is counterbalanced by its generality and clarity in the assumptions. We had to assume several things about the dynamics of the environment, the size of the environment, and the interaction between the system and the environment. All of these assumptions are physically well motivated but they provide ways out of decoherence, to allow us to experimentally test when it occurs and doesn't occur. We see that for generic measurements, the action of a large thermal-like environment will be to suppress the non-diagonal terms at late times, in the basis where the interactions between the system and the environment are diagonal. The end result being a classical ensemble of non-interacting branches, with probabilities given by the Born rule. We have provided a dynamical description of measurements, thereby explaining hoe the fundamental probabilities implied by Gleason's theorem are realised in nature.

Afterword

It was a challenging journey through the quantum realm. From our humble beginnings trying to understand atomic spectra, we stumbled upon a strange world. A world of probability amplitudes rather than deterministic outcomes. A world where particles and waves are one and the same, where even fundamental particles with no internal structure can have a spin angular momentum in a way which is impossible to describe using motion of its constituents. A world where potential barriers are mere suggestions and particles can tunnel right through regions where classical conservation of energy would forbid them.

In the end we managed to explain all of the phenomena which troubled us. We explained the spectrum of hydrogen, including its interaction with radiation. We explained the origin of spin-1/2 and how it interacts with magnetic fields. And we even managed to resolve the apparent inconsistencies with quantum mechanics, ruling out the possibility of a a more fundamental deterministic theory, showing quantum mechanics is local, but probabilistic and that measurements come from complex interactions with a large environment.

And yet, the story of quantum mechanics is far from over. We briefly mentioned and used symmetries but there is a much richer story to be unfolded there. The story of parity and time-reversal and how it was shown those are *not* symmetries of nature. How discrete translations in a crystal lattice can explain a lot of the phenomena of ordinary materials. And in the continuum there is much more to be uncovered in the structure of rotational symmetry, how it can constrain which decays can and can't happen and its role in classifying particles. The mathematics of rotation is foundational to the study of other continuous symmetries like isospin, so crucial in the early days of particle physics.

Sometimes we were also forced to employ approximations. When studying radiation and when dealing with decoherence we assumed there was a small parameter to expand in. These are both examples of *perturbation theory*, crucial in studying many quantum systems. Beyond that, there are many other methods to *approximately* solve complicated quantum setups. From semi-classical methods to adiabatic approximations, there is a lot of physics to be uncovered near the systems we can solve exactly.

All of this without mentioning the origin of the potential! We just assumed a classical Coulomb potential for the hydrogen atom, but that comes from Maxwell's equations. A complete quantum theory should also include a quantum version of electrodynamics and a theory of the photon. That path leads inevitably to relativity and quantum field theory which are the underpinnings of our current best understanding of fundamental physics.

There is a long way to go still but you now have the tools to understand the true language of Nature—Quantum Mechanics.

Appendices

Appendix A. Proof of the spectral theorem
Appendix B. Proof of Wigner's theorem

A Proof of the spectral theorem

Theorem A.1 (Spectral Theorem). A linear operator N on a finite dimensional Hilbert space is normal iff there exists an orthonormal basis of its eigenvectors.

Proof. For simplicity we will omit the square brackets from the matrix notation. To distinguish between the operator and the matrix representation in a given basis we will merely use a superscript identifying the basis.
Firstly, if there is a unitary basis of eigenvectors $|\lambda_i\rangle$, then, in that basis, the operator N is diagonal, because

$$\langle\lambda_j|\, N\,|\lambda_i\rangle = \lambda_i\delta_{ij} \implies N^\lambda = \begin{pmatrix} \lambda_1 & & \\ & \lambda_2 & \\ & & \ddots \end{pmatrix} \tag{A.1}$$

And therefore

$$N^a = S^{a\lambda}N^\lambda S^{a\lambda\dagger} \tag{A.2}$$

that is, there is a unitary change of basis such that the matrix representing the operator is diagonal. We usually say that the operator is *unitarily diagonalisable*. Conversely, if there is such a basis, then well the basis elements are orthonormal and all eigenvectors. Therefore having an orthonormal basis of eigenvectors is equivalent to being unitarily diagonalisable.
Let us first assume that N has an orthonormal basis of eigenvectors, we therefore have

$$N^a = S^{a\lambda}N^\lambda S^{a\lambda\dagger} \tag{A.3}$$

$$N^{a\dagger} = S^{a\lambda}N^{\lambda\dagger} S^{a\lambda\dagger} \tag{A.4}$$

where N^λ is a diagonal matrix. Using the fact $S^{a\lambda}$ is unitary, we have

$$\left[N^a, N^{a\dagger}\right] = S^{a\lambda}N^\lambda N^{\lambda\dagger}S^{a\lambda\dagger} - S^{a\lambda}N^{\lambda\dagger}N^\lambda S^{a\lambda\dagger} \tag{A.5}$$

$$= S^{a\lambda}\left[N^\lambda, N^{\lambda\dagger}\right]S^{a\lambda\dagger} = 0 \tag{A.6}$$

where the last equality follows from the fact all diagonal matrices commute. We have therefore shown that if a matrix has an orthonormal basis of eigenvectors it must be normal.
Showing the converse is a bit trickier, but we will proceed from induction. Firstly, note that this statement is trivial for a 1-dim Hilbert space. Now we shall assume it holds for an $(n-1)$-dim Hilbert space and show it must hold for an n-dim Hilbert space.
Firstly, we know that N has at least one eigenvector. This is because

$$N\,|\lambda\rangle = \lambda\,|\lambda\rangle \implies \det(N - \lambda\mathbb{1}) = 0 \tag{A.7}$$

The latter equation is a polynomial of degree n so the fundamental theorem of algebra states that it has at least one solution, which means N has at least one eigenvalue. We can also show that $|\lambda\rangle$ is also an eigenvector of $N^\dagger$ but with eigenvalue λ^*. Just consider the vector

$$|\omega\rangle = \left(N^\dagger - \lambda^* \mathbb{1}\right)|\lambda\rangle \tag{A.8}$$

it is straightforward to show that its norm vanishes

$$\begin{aligned}\|\omega\| &= \langle\lambda|\,(N - \lambda\mathbb{1})\left(N^\dagger - \lambda^*\mathbb{1}\right)|\lambda\rangle && \text{(A.9)}\\ &= \langle\lambda|\left(N^\dagger - \lambda^*\mathbb{1}\right)(N - \lambda\mathbb{1})\,|\lambda\rangle = 0 && \text{(A.10)}\end{aligned}$$

where in going to the last line we used the fact N was normal to swap the order of N and $N^\dagger$. All in all we must have

$$|\omega\rangle = 0 \implies N^\dagger|\lambda\rangle = \lambda^*|\lambda\rangle \tag{A.11}$$

which is what we wanted to show.

Now let us consider a different orthornomal basis $\{|b_i\rangle\}$ such that $|b_1\rangle = |\lambda\rangle$. We can then define the following operator

$$U_1 = \sum_i |b_i\rangle\!\langle a_i| \tag{A.12}$$

such that

$$\begin{aligned}U_1|a_1\rangle &= |b_1\rangle = |\lambda\rangle && \text{(A.13)}\\ U_1^\dagger|\lambda\rangle &= U_1^\dagger|b_1\rangle = |a_1\rangle && \text{(A.14)}\end{aligned}$$

Importantly, this operator is unitary

$$U_1U_1^\dagger = \sum_{ij}|b_i\rangle\langle a_i|a_j\rangle\langle b_j| = \sum_i |b_i\rangle\!\langle b_i| = \mathbb{1} \tag{A.15}$$

We will also need the following operator

$$N_1 = U_1^\dagger N U_1 \tag{A.16}$$

which obeys

$$N_1|a_1\rangle = U_1^\dagger N U_1|a_1\rangle = U_1^\dagger N|\lambda\rangle = \lambda|a_1\rangle \tag{A.17}$$

and is normal

$$\begin{aligned}\left[N_1, N_1^\dagger\right] &= U_1^\dagger N U_1 U_1^\dagger N^\dagger U_1 - U_1^\dagger N^\dagger U_1 U_1^\dagger N U_1 && \text{(A.18)}\\ &= U_1^\dagger N N^\dagger U_1 - U_1^\dagger N^\dagger N U_1 = U_1^\dagger\left[N, N^\dagger\right]U_1 = 0 && \text{(A.19)}\end{aligned}$$

where in the last line we used the fact that N is normal.

Because N_1 is also normal, $|a_1\rangle$ is also an eigenvector of $N_1^\dagger$ but with eigenvalue λ_1^*. Using this fact and the orthonormality of the basis $\{|a_i\rangle\}$ we get

$$\begin{aligned}\langle a_j|\,N_1\,|a_1\rangle &= \lambda_1\langle a_j|a_1\rangle = \lambda_1\delta_{1j} && \text{(A.20)}\\ \langle a_1|\,N_1\,|a_j\rangle &= \langle a_j|\,N_1^\dagger\,|a_1\rangle^* = \lambda_1\delta_{1j} && \text{(A.21)}\end{aligned}$$

which means we can write

$$N_1^a = \begin{pmatrix} \lambda_1 & 0 \cdots 0 \\ 0 & \\ \vdots & N' \\ 0 & \end{pmatrix} \tag{A.22}$$

The submatrix N' is $(n-1)\times(n-1)$. And we can show that if N_1 is normal then so is N'.

$$\left[N_1^a, N_1^{a\dagger}\right] = \begin{pmatrix} \lambda_1 & 0 \cdots 0 \\ 0 & \\ \vdots & N' \\ 0 & \end{pmatrix}\begin{pmatrix} \lambda_1^* & 0 \cdots 0 \\ 0 & \\ \vdots & N'^\dagger \\ 0 & \end{pmatrix} - \begin{pmatrix} \lambda_1^* & 0 \cdots 0 \\ 0 & \\ \vdots & N'^\dagger \\ 0 & \end{pmatrix}\begin{pmatrix} \lambda_1 & 0 \cdots 0 \\ 0 & \\ \vdots & N' \\ 0 & \end{pmatrix} = \tag{A.23}$$

$$= \begin{pmatrix} 0 & 0 \cdots 0 \\ 0 & \\ \vdots & \left[N', N'^\dagger\right] \\ 0 & \end{pmatrix} = 0 \tag{A.24}$$

Therefore, by our induction hypothesis we have that N' can be unitarily diagonalisable. Calling S' the matrix that diagonalises N',

$$S'^\dagger N' S' = D' \tag{A.25}$$

one can check that the matrix

$$S = \begin{pmatrix} 1 & 0 \cdots 0 \\ 0 & \\ \vdots & S' \\ 0 & \end{pmatrix} \tag{A.26}$$

is unitary.

$$SS^\dagger = \begin{pmatrix} 1 & 0 \cdots 0 \\ 0 & \\ \vdots & S' \\ 0 & \end{pmatrix}\begin{pmatrix} 1 & 0 \cdots 0 \\ 0 & \\ \vdots & S'^\dagger \\ 0 & \end{pmatrix} = \begin{pmatrix} 1 & 0 \cdots 0 \\ 0 & \\ \vdots & S'S'^\dagger \\ 0 & \end{pmatrix} = \mathbb{1} \tag{A.27}$$

Additionally we have that

$$S^\dagger N_1^a S = \begin{pmatrix} \lambda_1 & 0 \cdots 0 \\ 0 & \\ \vdots & D' \\ 0 & \end{pmatrix} \tag{A.28}$$

which is diagonal. Therefore

$$(U_1^a S)^\dagger N^a (U_1^a S) \tag{A.29}$$

is diagonal which means N is unitarily diagonalisable, which concludes our proof. □

B Proof of Wigner's theorem

Theorem B.1 (Wigner's theorem)**.** Any invertible transformation of the kets in a Hilbert space $|\psi\rangle \to |\psi'\rangle$ which leaves the transition probabilities $|\langle\chi|\psi\rangle|^2$ invariant can be represented by an operator which is either:

- Linear and unitary. That is one which obeys $U(a|\psi\rangle + b|\chi\rangle) = aU|\psi\rangle + bU|\chi\rangle$ and $(U|\psi\rangle, U|\chi\rangle) = (|\psi\rangle, |\chi\rangle)$.
- Anti-linear and anti-unitary. That is one which obeys $U(a|\psi\rangle + b|\chi\rangle) = a^*U|\psi\rangle + b^*U|\chi\rangle$ and $(U|\psi\rangle, U|\chi\rangle) = (|\psi\rangle, |\chi\rangle)^*$

Proof. Let $\{|i\rangle\}$ be an orthonormal basis for the Hilbert space, we will begin this proof by showing that the set of the transformed basis kets $\{|i'\rangle\}$ is also an orthonormal basis.

From the assumption that probabilities are preserved we have

$$|\langle i'|j'\rangle|^2 = |\langle i|j\rangle|^2 = \delta_{ij} \tag{B.1}$$

But, from the positivity of the norm we know that $\langle i'|i'\rangle$ must be real and non-negative, so the above relationship actually fixes its value as 1. This allows us to write

$$\langle i'|j'\rangle = \delta_{ij} \tag{B.2}$$

From the fact that there are n transformed kets and that they are linearly independent, we immediately conclude that $\{|i'\rangle\}$ is an orthonormal basis if the Hilbert space is finite dimensional. However, we can use the fact the transformation is assumed to be invertible to show that same fact without relying on finite dimensionality.

Let us assume there is a non-zero $|\psi'\rangle$ orthogonal to all $\{|i'\rangle\}$. Now consider its inverse transformed ket $|\psi''\rangle$, this obeys

$$|\langle i|\psi''\rangle|^2 = |\langle i'|\psi'\rangle|^2 = 0 \tag{B.3}$$

but $\{|i\rangle\}$ is an orthonormal basis of the Hilbert space, so the above result implies $|\psi''\rangle$ is the zero vector, which then necessarily implies that $|\psi'\rangle$ is the zero-vector to ensure $|\langle\psi'|\chi'\rangle|^2 = 0$ for any $|\chi\rangle$. This contradicts our initial assumption and so we must have that $\{|i'\rangle\}$ is an orthonormal basis of the Hilbert space.

As with physical states there is a fundamental arbitrariness in the phases of the transformed kets because multiplication by a phase would leave invariant the transition probabilities. So we will now set up a phase convention to help us in the remainder of our proof.

Let us pick one basis element, say $|1\rangle$ and construct the following kets

$$|\eta_i\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |i\rangle) \tag{B.4}$$

The transformed kets can be expanded in the transformed basis

$$|\eta_i'\rangle = \sum_j c_{ij}|i'\rangle \tag{B.5}$$

From the invariance of the transition of probabilities we conclude that

$$|c_{i1}|^2 = |\langle 1'|\eta_i'\rangle|^2 = |\langle 1|\eta_i\rangle|^2 = \frac{1}{2} \tag{B.6}$$

$$|c_{ii}|^2 = |\langle i'|\eta_i'\rangle|^2 = |\langle i|\eta_i\rangle|^2 = \frac{1}{2} \tag{B.7}$$

$$|c_{ij}|^2 = |\langle j'|\eta_i'\rangle|^2 = |\langle j|\eta_i\rangle|^2 = 0 \quad \text{if} \quad j \neq 1, i \tag{B.8}$$

For any i we can shift the phases of the two kets $|\eta_i'\rangle$ and $|i'\rangle$ to ensure both coefficients c_{ii} and c_{i1} are real and positive. We can then write, without loss of generality

$$|\eta_i'\rangle = \frac{1}{\sqrt{2}}(|1'\rangle + |i'\rangle) \tag{B.9}$$

Now comes the key step in the proof. We have defined the transformation for the $|\eta_i\rangle$ in terms of the transformation of the basis, but we have not done that for arbitrary kets $|\psi'\rangle$. This is our current goal. Let us take an arbitrary ket

$$|\psi\rangle = \sum_i c_i\,|i\rangle \tag{B.10}$$

the transformed ket can be written as an expansion of the transformed basis

$$|\psi'\rangle = \sum_i c_i'\,|i'\rangle \tag{B.11}$$

but the coefficients may be different. If the coefficients were the same then we knew the transformation was linear, but we will see that there is a way around this. Using the invariance of the transition probabilities we have

$$|c_i'|^2 = |\langle i'|\psi'\rangle|^2 = |\langle i|\psi\rangle|^2 = |c_i|^2 \tag{B.12}$$

but we can also use the overlaps with $|\eta_i\rangle$

$$\begin{cases} |\langle \eta_i|\psi\rangle|^2 = \frac{1}{2}|c_1 + c_i|^2 \\ |\langle \eta_i'|\psi'\rangle|^2 = \frac{1}{2}|c_1' + c_i'|^2 \end{cases} \Longrightarrow \; |c_1 + c_i|^2 = |c_1' + c_i'|^2 \tag{B.13}$$

Taking the ratio of (B.13) and (B.12) we get

$$\begin{gathered} \left|1 + \frac{c_1}{c_k}\right|^2 = \left|1 + \frac{c_1'}{c_k'}\right|^2 \\ 1 + \frac{c_1}{c_k} + \frac{c_1^*}{c_k^*} + \frac{|c_1|^2}{|c_k|^2} = 1 + \frac{c_1'}{c_k'} + \frac{c_1'^*}{c_k'^*} + \frac{|c_1'|^2}{|c_k'|^2} \end{gathered} \tag{B.14}$$

using (B.12) again we find

$$\mathrm{Re}\left\{\frac{c_1}{c_k}\right\} = \mathrm{Re}\left\{\frac{c_1'}{c_k'}\right\} \tag{B.15}$$

which together with (B.12) then implies

$$\mathrm{Im}\left\{\frac{c_1}{c_k}\right\} = \pm\,\mathrm{Im}\left\{\frac{c_1'}{c_k'}\right\} \tag{B.16}$$

In order to satisfy these two constraints we only have two options, either

$$\frac{c_1}{c_k} = \frac{c'_1}{c'_k} \tag{B.17}$$

or

$$\frac{c_1^*}{c_k^*} = \frac{c'_1}{c'_k} \tag{B.18}$$

The first option will turn out to correspond to linear and unitary operators, whereas the second to anti-linear and anti-unitary operators. It is the fact that probabilities are mod-square of amplitudes that allow for these two options. This is the crux of the proof, the rest is just some bookkeeping to ensure we must take the same option for every component and for every ket.

First we need to show that we cannot have (B.27) for some components and (B.28) for others. Let us assume that

$$\frac{c_i}{c_1} = \frac{c'_i}{c'_1} \tag{B.19}$$

but that

$$\frac{c_j^*}{c_1^*} = \frac{c'_j}{c'_1} \tag{B.20}$$

for some $i \neq 1$, $j \neq 1$ and $i \neq j$. If any of those ratios were real then the two cases would be indistinguishable. In order to check whether or not we are allowed to make different choices for different components let us assume both ratios are complex.

Consider the ket

$$|\phi\rangle = \frac{1}{\sqrt{3}}(|1\rangle + |i\rangle + |j\rangle) \tag{B.21}$$

because these coefficients are real, it doesn't matter which option we pick, the ratios between the components of the transformed ket must be the same as before, we must therefore have

$$|\phi'\rangle = \frac{\alpha}{\sqrt{3}}(|1'\rangle + |i'\rangle + |j'\rangle) \tag{B.22}$$

where $|\alpha| = 1$. Matching $|\langle\phi|\psi\rangle|^2$ with $|\langle\phi'|\psi'\rangle|^2$ gives us

$$\left|1 + \frac{c_i}{c_1} + \frac{c_j}{c_1}\right|^2 = \left|1 + \frac{c'_i}{c'_1} + \frac{c'_j}{c'_1}\right|^2 \tag{B.23}$$

using our assumptions regarding the ratios gives us

$$\left|1 + \frac{c_i}{c_1} + \frac{c_j}{c_1}\right|^2 = \left|1 + \frac{c_i}{c_1} + \frac{c_j^*}{c_1^*}\right|^2 \tag{B.24}$$

expanding this out then allows to write

$$\mathrm{Re}\left\{\frac{c_i c_j^*}{c_1 c_1^*}\right\} = \mathrm{Re}\left\{\frac{c_i c_j}{c_1 c_1}\right\} \tag{B.25}$$

once again we can expand this by isolating each ratio and write

$$\mathrm{Im}\left\{\frac{c_i}{c_1}\right\}\mathrm{Im}\left\{\frac{c_j}{c_1}\right\} = 0 \tag{B.26}$$

which implies that one of the two ratios is real, and is a contradiction! If we try to make a different choice for different components it turns out that it can only be consistent if one of those ratios is secretly real, for whom the choices are equivalent and so we actually didn't make different choices at all. This means that we either have

$$|\psi\rangle = \sum_i c_i |i\rangle \to |\psi'\rangle = \sum_i c_i |i'\rangle \tag{B.27}$$

or

$$|\psi\rangle = \sum_i c_i |i\rangle \to |\psi'\rangle = \sum_i c_i^* |i'\rangle \tag{B.28}$$

The only thing we have left is to show that you must make the same choice for *all* kets. For that we will need to consider three distinct kets.

$$|\phi\rangle = \sum_i a_i |i\rangle\,, \quad |\chi\rangle = \sum_i b_i |i\rangle \quad \text{and} \quad |\psi\rangle = \sum_i c_i |i\rangle \tag{B.29}$$

and let us take (B.27) to apply to $|\phi\rangle$ and (B.28) to apply to $|\chi\rangle$. Once again we need to ensure that these two really are distinct options, so we must assume that not all a_i and not all b_i have the same phase, because otherwise they'd be a phase away from being real and then both options would be the same.

The invariance of the transition probabilities gives us

$$|\langle\chi|\phi\rangle|^2 = \left|\sum_i b_i^* a_i\right|^2 = |\langle\chi'|\phi'\rangle|^2 = \left|\sum_i b_i a_i\right|^2 \tag{B.30}$$

expanding this out gives

$$\begin{aligned} \sum_{ij} b_i^* a_i b_j a_j^* = \sum_{ij} b_i a_i b_j^* a_j^* \iff \\ \iff \sum_{ij} a_i a_j^* \operatorname{Im}\{b_i b_j^*\} = 0 \implies \\ \implies \sum_{ij} \operatorname{Im}\{a_i a_j^*\} \operatorname{Im}\{b_i b_j^*\} = 0 \end{aligned} \tag{B.31}$$

This relation is nice and symmetrical, giving a consistency condition for two kets having different choices between (B.27) and (B.28). Additionally, it is a non-trivial consistency condition if not all a_i and not all b_i have the same phase, which is precisely what we ruled out earlier.

Now if we add the third ket $|\psi\rangle$ it either obeys (B.27) or (B.28), and therefore it must be different choice to at least one of $|\phi\rangle$ or $|\chi\rangle$, which would mean it must obey either

$$\sum_{ij} \operatorname{Im}\{c_i c_j^*\} \operatorname{Im}\{b_i b_j^*\} = 0 \tag{B.32}$$

or

$$\sum_{ij} \operatorname{Im}\{c_i c_j^*\} \operatorname{Im}\{a_i a_j^*\} = 0 \tag{B.33}$$

However, we can show that we can always find a ket such that neither of those two relations are valid.

If there is a pair i, j such that both $a_i a_j^*$ and $b_i b_j^*$ are not real, then we can just choose all cs to vanish except for c_i and c_j and pick those two to have different phases. If $a_i a_j^*$ isn't real but $b_i b_j^*$ is, then there must be some pair k, l such that $b_k b_l^*$ is complex (remember that we cannot have them all be real). If $a_k a_l^*$ is also complex then we can pick all cs to vanish except c_k and c_l and pick those two to have different phases.

If $a_k a_l^*$ is real then we must pick all cs to vanish except c_i, c_j, c_k, and c_l and pick different phases for all of them.
All in all, we can always find a ket $|\psi\rangle$ that would break the necessary consistency conditions. Therefore, we must conclude that we cannot have different choices between (B.27) and (B.28) for different kets.
Our proof is essentially done. Let us denote the action of this transformation by

$$|\psi'\rangle = U|\psi\rangle \tag{B.34}$$

Then if we pick (B.27) we have

$$\begin{aligned} U(\alpha|\psi\rangle + \beta|\chi\rangle) = U\sum_i (\alpha a_i + \beta b_i)|i\rangle = \sum_i (\alpha a_i + \beta b_i) U|i\rangle = \\ = \alpha U|\psi\rangle + \beta U|\chi\rangle \end{aligned} \tag{B.35}$$

which means it is linear. Using the fact the transformed basis is orthonormal we can also show that

$$(U|\psi\rangle, U|\chi\rangle) = \sum_{ij} a_i^* b_j (U|i\rangle, U|j\rangle) = \sum_{ij} a_i^* b_j = (|\psi\rangle, |\chi\rangle) \tag{B.36}$$

which means it is unitary.
On the other hand, if we pick (B.28) we have

$$\begin{aligned} U(\alpha|\psi\rangle + \beta|\chi\rangle) = U\sum_i (\alpha a_i + \beta b_i)|i\rangle = \sum_i (\alpha^* a_i^* + \beta^* b_i^*) U|i\rangle = \\ = \alpha^* U|\psi\rangle + \beta^* U|\chi\rangle \end{aligned} \tag{B.37}$$

which means it is anti-linear. And also

$$(U|\psi\rangle, U|\chi\rangle) = \sum_{ij} a_i b_j^* (U|i\rangle, U|j\rangle) = \sum_{ij} a_i b_j^* = (|\psi\rangle, |\chi\rangle)^* \tag{B.38}$$

which means it is anti-unitary. ☐