

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, skipping a lot of the topics which, while important would not be strictly necessary or would need to be re-derived in the relativistic context, which 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

An Invitation

PART

I

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 these suggested different aspects of what would become the theory of quantum mechanics. It is usually wise to avoid going over the history of physics in great detail, otherwise we would waste a lot of time describing uninformative dead-ends. It is however 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 this was a widely successful theory. Capable to explaining several properties of chemical reactions, and being the basis of statistical mechanics and kinetic theory, which explained and superseded classical thermodynamics. The theory of the atom is so important that Richard P. Feynman (Fig.² 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.

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.³ 3) managed to show that cathode rays were in fact made up of tiny

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

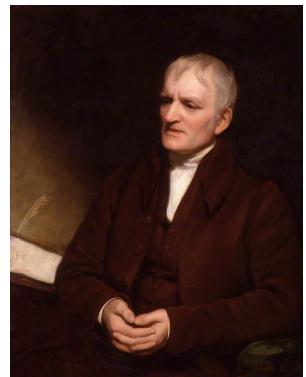


Figure 1. John Dalton FRS
Born: 1766 Eaglesfield, Great Britain
Died: 1844 Manchester, United Kingdom of Great Britain and Ireland



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

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

²Picture 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>

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

negatively charged particles around 1 800 times lighter than hydrogen. These rays are produced when a large potential difference is applied between two electrodes in a vacuum tube, Fig.⁴ 4.

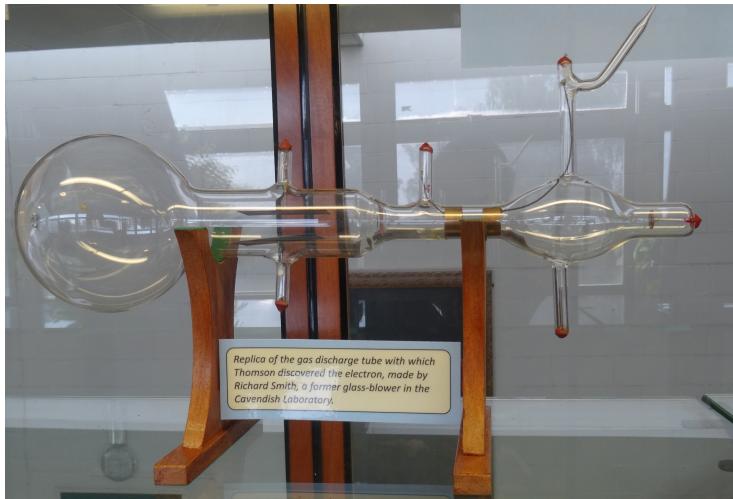


Figure 4. J. J. Thomson's experimental setup. There is a cathode on the right and anode on the centre with potential difference high enough that an electron is emitted from the cathode, it will traverse the whole tube hitting the glass on the left causing a bright glow. The plates on the centre left 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.

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, 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 are⁵

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

$$-e \approx -1.602 \times 10^{-19} \text{ C} \quad (1.2)$$

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.

Despite its success this model was short-lived. 10 years later Ernest Rutherford (Fig. ⁶ 5), a student of Thomson, was trying to measure the charge-to-mass ratio of alpha particles.

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

⁵We 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 $e = 1.602\ 176\ 634 \times 10^{-19} \text{ C}$, *exactly*.

⁶Picture 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>



Figure 3. Sir Joseph John Thomson OM FRS
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

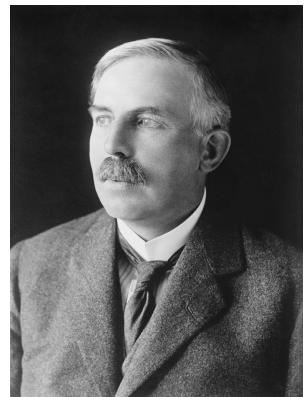


Figure 5. The Right Honourable Ernest Rutherford The Lord Rutherford of Nelson OM FRS HonFRSE
Born: 1871 Brightwater, Colony of New Zealand
Died: 1937 Cambridge, United Kingdom of Great Britain and Northern Ireland
Academic Advisor: Alexander Bickerton, J. J. Thomson

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.⁷ 6), and an undergraduate student, Ernest Marsden (Fig.⁸ 7), he wished to calculate its charge-to-mass ratio.

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

$$m_\alpha v_\alpha = mv + m_\alpha v'_\alpha \quad (1.3)$$

$$\frac{1}{2}m_\alpha v_\alpha^2 = \frac{1}{2}mv^2 + \frac{1}{2}m_\alpha v'^2 \quad (1.4)$$

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

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

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

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

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

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

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 $\sim 10^{-10} \text{ m}$.

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



Figure 6. Johannes Wilhelm “Hans” Geiger

Born: 1882 Neustadt an der Haardt, German Empire

Died: 1945 Potsdam, Allied-occupied Germany

Doctoral Advisor: Eilhard Wiedemann

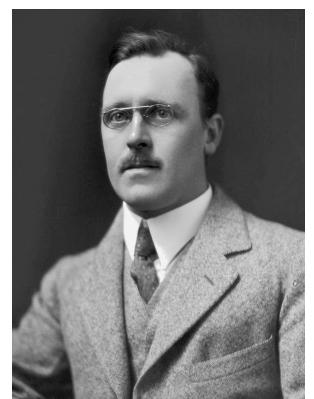


Figure 7. Sir Ernest Marsden

CMG CBE MC FRS

Born: 1889 Rishton, United Kingdom of Great Britain and Ireland

Died: 1970 Wellington, New Zealand

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

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

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. It however 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 give 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. ⁹ 8) realised the light from the sun wasn't exactly white but had dark lines at certain intervals. In 1814 Joseph von Fraunhofer (Fig. ¹⁰ 9) re-discovered them and studied them in greater detail which is why these dark lines are still called Fraunhofer lines, Fig. ¹¹ 10.

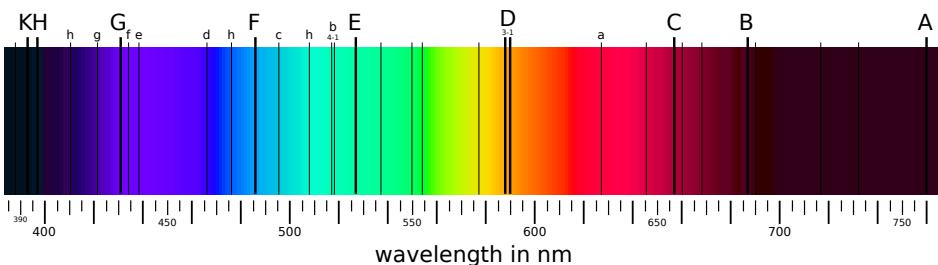


Figure 10. The dark lines in the solar spectrum in the visible range.

Over the next few decades, physicists continued to study these lines and related phenomena. What they found was beautifully summarised by Gustav Kirchhoff (Fig. ¹² 11) in his three laws of spectroscopy:

1. An incandescent material under high pressure emits a continuous spectrum.
2. A hot gas under low pressure emits a discrete spectrum with distinct bright emission lines.

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

¹⁰Picture 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>

¹¹Picture 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>

¹²Picture 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>

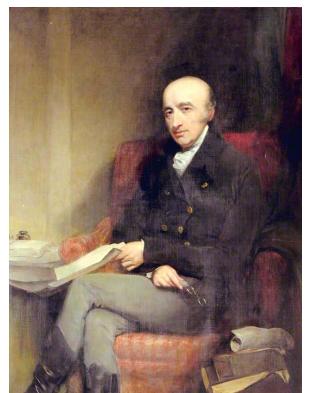


Figure 8. William Hyde Wollaston FRS

Born: 1766 East Dereham, Great Britain

Died: 1828 Chislehurst, United Kingdom of Great Britain and Ireland

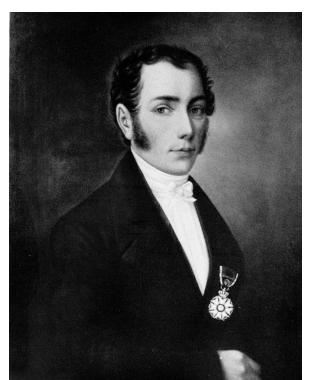


Figure 9. Joseph Fraunhofer, Ritter von Fraunhofer

Born: 1787 Straubing, Holy Roman Empire

Died: 1826 Munich, Kingdom of Bavaria

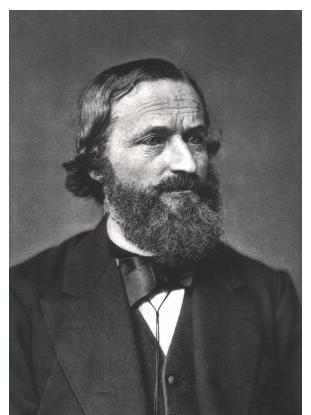


Figure 11. Gustav Robert Kirchhoff

Born: 1824 Königsberg, Kingdom of Prussia

Died: 1887 Berlin, German Empire

Academic Advisors: Carl Jacobi, Franz Ernst Neumann

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. 13 12), in 1890 Johannes Rydberg (Fig. 14 13) managed to derive an empirical formula for the frequencies of the hydrogen spectrum:

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

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

$$R \approx 3.290 \times 10^{15} \text{ Hz} \quad (1.9)$$

Further in 1908 Walther Ritz (Fig. 15 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. 16 15) offered an explanation for the case of the hydrogen atom. He was inspired by an earlier idea from John William Nicholson (Fig. 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, however, it was later discovered that hydrogen atoms indeed have only one electron. Bohr then proposed that there were special orbits such that the electron 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

$$m_e v r = n\hbar, \quad n = 1, 2, 3, \dots \quad (1.10)$$

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 or further away from the nucleus. He did not provide any mechanism that would ensure electrons were stable in these orbits. This is a significant departure from classical electrodynamics. Bohr’s guess is nonetheless almost right, even in the full quantum theory it will turn out that angular momentum is indeed quantised, just that the quantisation condition is a bit more complicated.

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

¹⁴Picture 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>

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

¹⁶Picture by The American Institute of Physics credits the photo to AB Lagerlöf & 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>



Figure 12. Johann Jakob Balmer
Born: 1825 Lausen, Switzerland
Died: 1898 Basel, Switzerland



Figure 13. Johannes "Janne" Robert Rydberg
Born: 1854 Halmstad, Sweden
Died: 1919 Lund, Sweden



Figure 14. Walther Heinrich Wilhelm Ritz
Born: 1878 Sion, Switzerland
Died: 1909 Göttingen, German Empire

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

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

which, together with the quantisation condition, yields

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

and therefore, the energy of each orbit is

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

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

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

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

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

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

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

which allows us to conclude

$$\Delta E = 2\pi\hbar\nu \quad (1.17)$$

And therefore the frequencies would be given by

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

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 radiation. This is a curious relation that would not be predicted by classical electrodynamics. It was first suggested by Max Planck (Fig.¹⁷ 17) in 1900 to explain the spectrum

¹⁷Picture 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>.



Figure 15. Niels Henrik David Bohr HE
Born: 1885 Copenhagen, Denmark
Died: 1962 Copenhagen, Denmark
Doctoral Advisor: Christian Christiansen

Figure 16. John William Nicholson FRS
Born: 1881 Darlington, United Kingdom of Great Britain and Ireland
Died: 1955

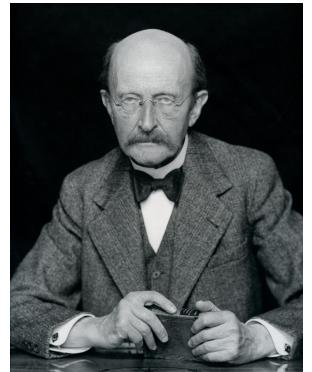


Figure 17. Max Karl Ernst Ludwig Planck
Born: 1858 Kiel, Duchy of Holstein
Died: 1947 Göttingen, Allied-occupied Germany
Doctoral Advisor: Alexander von Brill

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, it suffices to say the key difficulty was calculating the average energy of the radiation for a given temperature. J. Willard Gibbs (Fig. 18) are 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 $k_B \approx 1.381 \times 10^{-23} \text{ J K}^{-1}$ is the Boltzmann constant¹⁹. Therefore, if we allow for a continuum of energy in the emitted radiation its average energy would be

$$\bar{E} = \frac{\int_0^\infty dE E e^{-\frac{E}{k_B T}}}{\int_0^\infty dE e^{-\frac{E}{k_B T}}} = k_B T \quad (1.19)$$

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

$$\bar{E} = \frac{\sum_{n=0}^{\infty} nh\nu e^{-\frac{n h \nu}{k_B T}}}{\sum_{n=0}^{\infty} e^{-\frac{n h \nu}{k_B T}}} = \frac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1} \quad (1.20)$$

This new expression for the average energy does agree with the experimental data, the value for this new constant was measured to be

$$h \approx 6.626 \times 10^{-34} \text{ J s} \quad (1.21)$$

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. 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. Therefore we expected that the kinetic energy of the emitted electrons to be a function of the intensity of the radiation. What was instead observed is 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 cause additional electrons to be 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

[wikimedia.org/w/index.php?curid=153625300](https://commons.wikimedia.org/w/index.php?curid=153625300)

¹⁸Picture 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>

¹⁹In the modern SI system we use the value of this constant to *define* the Kelvin, therefore it is *exactly* given by $k_B = 1.380\ 649 \times 10^{-23} \text{ J K}^{-1}$

²⁰Picture 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>

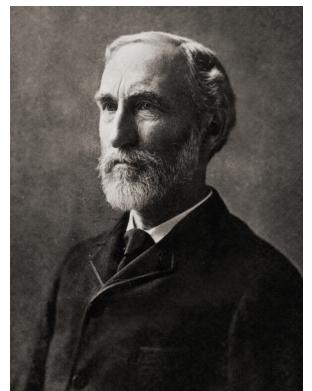


Figure 18. Josiah Willard Gibbs

Born: 1839 New Haven, United States of America

Died: 1903 New Haven, United States of America

Doctoral Advisor: Hubert Anson Newton

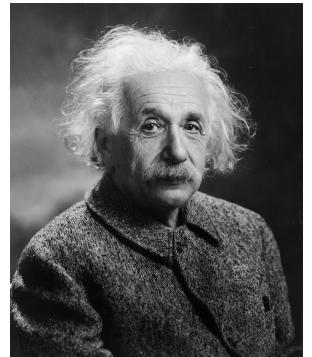


Figure 19. Albert Einstein

Born: 1879 Ulm, German Empire

Died: 1955 Princeton, United States of America

Doctoral Advisor: Alfred Kleiner

the Planck formula

$$E = h\nu \quad (1.22)$$

and increased intensity only meant that extra photons were created. Because the photons were small, only a single photon would hit each electron, the higher the frequency the higher the kinetic energy of the electron, 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

$$\hbar = \frac{h}{2\pi} \quad (1.23)$$

We therefore call \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:

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

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

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.²¹ 20). He noticed that we could use the relativistic connection between an electromagnetic wave's energy and liner momentum

$$E = pc \quad (1.25)$$

and the relationship between wavelength and frequency

$$\nu = \frac{c}{\lambda} \quad (1.26)$$

he could write a relationship between the photon's momentum and wavelength

$$p = \frac{h}{\lambda} \quad (1.27)$$

His 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

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

As a quick check he employed the usual definition of group velocity interms of the angular frequency $\omega = 2\pi\nu$ and wavenumber $k = 2\pi/\lambda$:

$$v = \frac{d\omega}{dk} = \frac{dE}{dp} \quad (1.29)$$



Figure 20. Louis Victor Pierre Raymond, Duc de Broglie
Born: 1892 Dieppe, France
Died: 1987 Louveciennes, France
Doctoral Advisor: Paul Langevin

²¹Picture 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>

then using the familiar formula²² $E = p^2/2m$ we get

$$v = \frac{p}{m} \quad (1.30)$$

as expected. Everything seemed consistent.

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

INSERT PICTURE

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

$$2\pi nr = \lambda = \frac{h}{p} \implies p = \frac{n\hbar}{r} \quad (1.31)$$

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 1801 double-slit experiment. The observed interference pattern was the only way we could explain this experiment. Let us apply the same reasoning for the electron²³.

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.

INSERT PICTURE

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

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

²³Despite 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 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.

from the straight-on trajectory. It is reasonable to expect a distribution such as the following.

INSERT PICTURE

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 $P_1(x)$.

INSERT PICTURE

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:

INSERT PICTURE

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

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

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 the following:

INSERT PICTURE

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 far more complicated. 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:

$$I = |h_1 + h_2|^2 \quad (2.2)$$

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. Depending on the distance between the slits the waves will have travelled a different distance and will be at a different phase when they hit the back wall, thereby exhibiting 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,

$$I = (h_1 + h_2)(h_1 + h_2)^* = |h_1|^2 + |h_2|^2 + 2 \operatorname{Re}\{h_1 h_2^*\} \quad (2.3)$$

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.

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 patterns 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 (CITE)

- 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 we summed complex waves and then took the mod-square.

INSERT PICTURE

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 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. We always observe a single electron.

Perhaps we try to see which slit the electron passed through? Well we could put some detector in place that would interact with the electron and tell us. Well, 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 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 imagined a dark street with intermitting light posts

INSERT PICTURE

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, nevertheless 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, and the maths are not complicated at all, they're just ordinary wave mechanics. Quantum mechanics is about giving up the impossible but realising that the possible can be done and with an astonishing accuracy.

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.

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 who seems to follow wave-like mechanics and whose mod-square gives the probability. In this chapter we will delve into these probability amplitudes, understanding what they represent and is the mathematics that describes them, ultimately arriving at the notion 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.

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

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 also have a magnetic moment. In 1921-1922 Otto Stern and Walther Gerlach tested this hypothesis and found truly unforeseen results.

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 μ is defined for an object such that the aligning torque as a result of an applied magnetic field B is

$$\tau = \mu \times B \quad (3.1)$$

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

$$\mu = IS\mathbf{n} \quad (3.2)$$

where \mathbf{n} is the normal vector to the loop whose direction is given by the right-hand rule.

INSERT PICTURE

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

$$\mathbf{F} = \nabla(\mu \cdot \mathbf{B}) \quad (3.3)$$

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

$$\mu = \frac{q}{2m}\mathbf{L} \quad (3.4)$$

where q is the total charge of the object, m its mass, and \mathbf{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 with 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 however is not feasible in practice because they will experience a Lorentz force due to their electric charge alone and it is hard to disentangle the two effects. 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 in practice it is easier to use silver atoms. In any case, this is the apparatus they concocted.

INSERT PICTURE

This will create a magnetic field is basically just pointing in the y direction and 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 y direction:

INSERT PICTURE

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

INSERT PICTURE

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.

3.3 Chaining Stern-Gerlach devices

Rather than just basking in our confusion let us try to regain some order and figure out what the hell could be going on here. We shall follow Feynman and consider a modified Stern-Gerlach device that recombines the beams at the end:

INSERT PICTURE

This device is much more complicated than the first one but will actually simplify our discussion. The main point here is that this modified apparatus splits the beams enough that we could include filters in the middle to block one of the two paths but not enough to ruin any interference effects which we know from Chapter 2 to be quite important. This way, after we recombine the beams its as if we had done nothing at all to the electrons.

Also remember that we will never discuss effects that come from the interaction between several electrons, we are discussing the experiment where we send an electron at a time and then tally how many went each way to calculate our probabilities.

With all that in mind let us put a filter to block any electrons that would have gone through the bottom path.

INSERT PICTURE

If we put a second Stern-Gerlach device what we see is the following

INSERT PICTURE

So there is some order in the universe. Even if it is weird that they are only either going up or down, if we filter for one type then they remain that type. This is often a very important step in quantum mechanical experiments which we usually call *state preparation*. Before the electron goes through any device we are ignorant about its spin but it is a normal kind of ignorance not due to quantum weirdness. However, after we have filtered the electrons we have gotten rid of our ignorance and any probability that remains must be inherent to nature rather than due to our ignorance.

But what about the spin component in the x direction? Well, it definitely should be zero right? If it wasn't then the dot product with the magnetic field would have been some intermediate value and we would get a continuous smear rather than the two points. Well let us rotate our device and see what happens:

INSERT PICTURE

We still get exactly the same answer. On the one hand, this is good, physics is still rotationally invariant. On the other hand it means the discreteness had nothing to do with the furnace, it seems to really be able to spit out electrons with spins pointing in any direction. It must be something about the interaction between the magnetic field and the electrons that forces them to orient the spin completely up or completely down.

Let us test this theory by adding a second device in the x direction, and in fact let us make this second device a classic one without recombining the beams for simplicity:

INSERT PICTURE

What we see is that every electron is deflected and once they are always maximally deflected either up or down. How strange, it really must be something in the interaction between the magnetic field and the electron which is different. We knew for a fact the spin was fully pointing up in the y direction and yet after the second device they come out fully pointing in the x direction.

We can also try to rotate the second device continuously so that they are no longer perpendicular:

INSERT PICTURE

We now find that the results are no longer 50-50. They are weighted, and continuously change from certainly spin-up for $\phi = 0$ and 50-50 for $\phi = \pi/2$, which makes some kind of sense given the results of the previous experiments, these weird flipping effects are at least continuous.

What if we put a third device? We need to recombine the beams in the second device to allow for a third device. We are also putting a filter in the second device to only allow electrons that went through the top beam in both x and y directions:

INSERT PICTURE

We return to a 50-50 split! The results of the first device are completely irrelevant, we can put a filter in any of the beams or even in no beam at all! If we measure the spin in the x direction we lose all knowledge we may have had about the spin in the y direction. But it gets much weirder than that. Let us make the third device also a recombination one, and let us put a filter on the top path:

INSERT PICTURE

That the electrons are split in half three times so 1/8th of them go through our contraption. Now let us remove the filter in the second device:

INSERT PICTURE

The second device is doing nothing, so we go back to the situation in Figure CITE, and *zero* electrons go through. 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 top beam then the right beam and then the bottom beam in Figure CITE are still being emitted from our furnace. Surely these must also go through Figure CITE. 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 putting a third field 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

Our goal is to re-write the ideas of the previous section in a more mathematical way. We will say that the electron is in the $|\uparrow y\rangle$ state if it went through the following device:

INSERT PICTURE

Similarly we say that it is in the $|\downarrow y\rangle$ state if it went through the following device:

INSERT PICTURE

Let us now add a device in the x direction that blocks spin-down electrons.

INSERT PICTURE

We shall denote by $\langle \uparrow x | \uparrow y \rangle$ the *amplitude* that it goes through this combined device (you read amplitudes from right to left, like Arabic). 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

$$\langle \uparrow y | \uparrow y \rangle = 1 \quad (3.5)$$

and

$$\langle \downarrow y | \uparrow y \rangle = 0 \quad (3.6)$$

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

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:

$$\langle \uparrow x | \uparrow y \rangle \langle \uparrow x | \uparrow y \rangle^* + \langle \downarrow x | \uparrow y \rangle \langle \downarrow x | \uparrow y \rangle^* = 1 \quad (3.7)$$

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:

$$\langle \uparrow x | \psi \rangle \langle \uparrow x | \psi \rangle^* + \langle \downarrow x | \psi \rangle \langle \downarrow x | \psi \rangle^* = 1 \quad (3.8)$$

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

Now let us move to the 3 device experiments, like,

INSERT PICTURE

whose amplitude is

$$\langle \downarrow y | \uparrow x \rangle \langle \uparrow x | \uparrow y \rangle \quad (3.9)$$

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

INSERT PICTURE

with amplitude

$$\langle \uparrow y | \uparrow x \rangle \langle \uparrow x | \uparrow y \rangle \quad (3.10)$$

The ratio

$$\frac{\langle \uparrow y | \uparrow x \rangle}{\langle \downarrow y | \uparrow x \rangle} \quad (3.11)$$

only depends on the details between the second and third device. 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. Let us consider the case when the middle device is not filtering at all:

INSERT PICTURE

Having the second device or not is exactly the same, this would be equivalent to having just the first and third devices

INSERT PICTURE

But let us think about what is happening in the second device. The electrons are being split into two beams, there are no other options. Therefore the previous result must be the sum of the electrons that went through the up beam and the electrons that went through the down beam. That is

$$\langle \chi | \psi \rangle = \langle \chi | \uparrow x \rangle \langle \uparrow x | \psi \rangle + \langle \chi | \downarrow x \rangle \langle \downarrow x | \psi \rangle \quad (3.12)$$

Note that we are *not* saying that each electron is going through each beam. That would correspond to adding the *probabilities* for the electron to go through either beam. We are instead adding the *probability amplitudes* as in Chapter 2. In this way we can preserve interference effects, *e.g.* what we described at the end of the previous section.

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

$$1 = \langle \uparrow y | \uparrow x \rangle \langle \uparrow x | \uparrow y \rangle + \langle \uparrow y | \downarrow x \rangle \langle \downarrow x | \uparrow y \rangle = \quad (3.13)$$

$$= \langle \uparrow x | \uparrow y \rangle^* \langle \uparrow x | \uparrow y \rangle + \langle \downarrow x | \uparrow y \rangle^* \langle \downarrow x | \uparrow y \rangle \quad (3.14)$$

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

$$\langle \uparrow y | \uparrow x \rangle = \langle \uparrow x | \uparrow y \rangle^* \quad (3.15)$$

$$\langle \uparrow y | \downarrow x \rangle = \langle \downarrow x | \uparrow y \rangle^* \quad (3.16)$$

and therefore

$$\langle \chi | \psi \rangle = \langle \psi | \chi \rangle^* \quad (3.17)$$

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

4 The physics of Hilbert spaces

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

$$\langle i | j \rangle = \delta_{ij} \quad (4.1)$$

$$\langle \chi | \psi \rangle = \sum_{\text{all } i} \langle \chi | i \rangle \langle i | \psi \rangle \quad (4.2)$$

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

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

Additionally, all amplitudes obey

$$\langle \chi | \psi \rangle = \langle \psi | \chi \rangle^* \quad (4.4)$$

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

$$\mathbf{e}_i \cdot \mathbf{e}_j = \delta_{ij} \quad (4.5)$$

Similarly the analogue of (4.2) is

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

where we have used the usual definition of vector components:

$$A_i = \mathbf{e}_i \cdot \mathbf{A} \quad (4.7)$$

Finally, the analogue of (4.4) is

$$\mathbf{A} \cdot \mathbf{B} = \mathbf{B} \cdot \mathbf{A} \quad (4.8)$$

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. 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.

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. That is 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 $|c\psi\rangle = c|\psi\rangle$ is also a vector, this operation obeys the following properties:
 - i. **Associativity:** $a(b|\psi\rangle) = (ab)|\psi\rangle$
 - ii. **Distributivity:** $(a+b)|\psi\rangle = a|\psi\rangle + b|\psi\rangle$ and $a(|\psi\rangle + |\chi\rangle) = a|\psi\rangle + b|\chi\rangle$
 - iii. **Existence of identity:** $1|\psi\rangle = |\psi\rangle$
2. **Inner Product:** The inner product is an operation that takes two vectors $|\psi\rangle$ and $|\chi\rangle$ and returns a complex number $(|\psi\rangle, |\chi\rangle)$. It obeys the following properties:
 - (a) **Complex commutativity:** $(|\psi\rangle, |\chi\rangle) = (|\chi\rangle, |\psi\rangle)^*$
 - (b) **Linearity:** $(|\psi\rangle, a|\chi\rangle + b|\phi\rangle) = a(|\psi\rangle, |\chi\rangle) + b(|\psi\rangle, |\phi\rangle)$
 - (c) **Positivity:** $(|\psi\rangle, |\psi\rangle) \geq 0$, equality if and only if $|\psi\rangle = 0$
3. **Norm:** The norm is defined as $\|\psi\| = \sqrt{(|\psi\rangle, |\psi\rangle)}$.
4. **Completeness:** Every Cauchy sequence converges in the Hilbert space. That is, every sequence $|\psi_1\rangle, |\psi_2\rangle, \dots$ that satisfies $\lim_{m,n \rightarrow \infty} \|\psi_n - \psi_m\| = 0$ is convergent in the Hilbert space.

^aIn the context of quantum mechanics, the scalars will always be complex numbers

^bWe 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—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. Namely, 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 are complicated by amplitudes simply add. We therefore interpret the vector addition of kets as representing a superposition of states.

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 scalar multiplication is necessary to allow for uneven superpositions were one of the states has a higher or lower probability than the other.

Additionally, in the double-slit experiment we saw that the relative phase of the two wave-amplitudes was what dictate if the interference was constructive or destructive or something in the middle. Therefore scalar multiplication must allow for complex numbers rather than just positive numbers to be able fully describe interference effects.

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 $\langle \psi | : \mathcal{H} \rightarrow \mathbb{C}$. $\langle \psi |$ 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:

$$\langle \psi | (\chi) \rangle \equiv \langle \psi | \chi \rangle \equiv (\psi, \chi) \quad (4.9)$$

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.

This construction allows us to interpret the inner product of two vectors: (ψ, χ) . 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 $|\langle \psi | \chi \rangle|^2 = |(\psi, \chi)|^2$. 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).

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:

$$(a |\chi\rangle + b |\phi\rangle, |\psi\rangle) = a^*(\chi, \psi) + b^*(\phi, \psi) \quad (4.10)$$

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

$$a|\psi\rangle + b|\chi\rangle \longleftrightarrow a^* \langle\psi| + b^* \langle\chi| \quad (4.11)$$

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

$$\langle\psi|\psi\rangle = 1 \quad (4.12)$$

These normalised vectors trivially satisfy the non-negativeness of the norm, as required in the definition of a Hilbert space. However, there is an ambiguity in this definition. If we multiplied the ket by a phase $|\psi\rangle \rightarrow e^{i\alpha}|\psi\rangle$ 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, for any $|\chi\rangle$. This suggest we should consider the kets $|\psi\rangle$ and $e^{i\alpha}|\psi\rangle$ to correspond to the same physical state, as they would yield exactly the same predictions. That is, we should consider the *physical state* as the equivalence class

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

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. That is even though

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

we cannot change the relative phase in this superposition:

$$a|\psi\rangle + b|\chi\rangle \not\sim a|\psi\rangle + e^{i\alpha}b|\chi\rangle \quad (4.15)$$

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, although 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.

Alternatively, you can 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

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

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

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

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

In either formulation, the Cauchy-Schwarz inequality ensures the assigned probabilities are always less than 1.

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

$$|\langle\psi|\chi\rangle|^2 \leq \langle\psi|\psi\rangle \langle\chi|\chi\rangle \quad (4.18)$$

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

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

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

$$4|\langle\psi|\chi\rangle| - 4\langle\psi|\psi\rangle \langle\chi|\chi\rangle \leq 0 \quad (4.20)$$

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

$$\langle p(s)|p(s)\rangle = 0 \implies |\psi\rangle + s_0\alpha|\chi\rangle = 0 \quad (4.21)$$

and therefore the vectors are linearly dependent. \square

^aIf $\langle\psi|\chi\rangle = 0$ 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

$$|\psi\rangle = \sum_i c_i |i\rangle \quad (4.22)$$

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

$$\psi_i \equiv \langle i|\psi\rangle \quad (4.23)$$

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:

$$|\psi\rangle = \sum_i |i\rangle \langle i|\psi\rangle \quad (4.24)$$

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

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

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

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

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

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

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

$$|i\rangle = \sum_j |j\rangle \langle j|i\rangle \quad (4.28)$$

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

$$P(\psi \rightarrow i) = |\langle i|\psi\rangle|^2 = |\psi_i|^2 = |c_i|^2 \quad (4.29)$$

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*.

Note however, that bases are not unique. We can always define a new basis $\{|\alpha\rangle\}$ via

$$|\alpha\rangle = \sum_i |i\rangle \langle i|\alpha\rangle \quad (4.30)$$

which allows us to write

$$\psi_\alpha = \langle \alpha|\psi\rangle = \sum_i \langle \alpha|i\rangle \langle i|\psi\rangle = \sum_i \langle \alpha|i\rangle \psi_i \quad (4.31)$$

Remember the Stern-Gerlach experiment, we could have chosen either the x or the y direction to define our basis without running into any inconsistencies.

We can also write bras in a basis:

$$\langle \psi | = \sum_i \langle \psi | i \rangle \langle i | \equiv \sum_i \psi_i^* \langle i | \quad (4.32)$$

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

$$\langle \psi | \chi \rangle = \sum_i \langle \psi | i \rangle \langle i | \chi \rangle = \sum_i \psi_i^* \chi_i \quad (4.33)$$

For this reason it is customary to think of kets as column vectors and bras as row vectors, the inner product then follows the ordinary rules of matrix multiplication. In this notation the map between kets and bras involves not just complex conjugation but also the matrix transpose, this operation is called *Hermitian conjugation* and will be very important in the next section.

Finally, note how in the definition of a Hilbert space or a basis 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.

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 do one better and also get rid of the $|\psi\rangle$ to write

$$\sum_i |i\rangle \langle i| = \mathbb{1} \quad (4.34)$$

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

$$A(a|\psi\rangle + b|\chi\rangle) = aA|\psi\rangle + bA|\chi\rangle \quad (4.35)$$

The example in (4.34) is the identity operator that obeys $\mathbb{1}|\psi\rangle = |\psi\rangle$.

We can also write them in a basis:

$$|\psi\rangle = A|\chi\rangle \implies \langle i|\psi\rangle = \langle i|A|\chi\rangle = \sum_j \langle i|A|j\rangle \langle j|\chi\rangle \equiv \sum_j A_{ij}\chi_j \quad (4.36)$$

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

$$A_{ij} = \langle i|A|j\rangle \quad (4.37)$$

This set of n^2 numbers (n being the dimension of the Hilbert space) 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 :

$$C |\psi\rangle = BA |\psi\rangle \quad (4.38)$$

the matrix elements of C are given by:

$$\sum_j \langle i | C | j \rangle \psi_j = \sum_{jk} \langle i | B | j \rangle \langle j | A | k \rangle \psi_k \implies C_{ij} = \sum_k B_{ik} A_{kj} \quad (4.39)$$

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 3-dimensional we can write:

$$\langle \psi | A | \chi \rangle = \begin{pmatrix} \psi_1^* & \psi_2^* & \psi_3^* \end{pmatrix} \begin{pmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{pmatrix} \begin{pmatrix} \chi_1 \\ \chi_2 \\ \chi_3 \end{pmatrix} \quad (4.40)$$

A very important consequence of these multiplication rules is that the order of operations matter, matrix multiplication is, in general, not commutative!

$$AB \neq BA \quad (4.41)$$

in fact we define the *commutator* to be the difference between the two orders:

$$[A, B] = AB - BA \quad (4.42)$$

This will be of crucial importance when we come to describe their physical significance.

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:

$$A_{\alpha\beta} = \sum_{ij} \langle \alpha | i \rangle A_{ij} \langle j | \alpha \rangle \quad (4.43)$$

Finally, before we move on to the physical interpretation, we can define the *adjoint* of an operator A^\dagger via²⁴

$$(|\psi\rangle, A^\dagger |\chi\rangle) \equiv (A |\psi\rangle, |\chi\rangle) = (|\chi\rangle, A |\psi\rangle)^* \quad (4.44)$$

therefore

$$\langle \psi | A^\dagger | \chi \rangle = \langle \chi | A | \psi \rangle^* \quad (4.45)$$

which means that, in terms of a basis:

$$A_{ij}^\dagger = A_{ji}^* \quad (4.46)$$

The adjoint of an operator corresponds to the Hermitian conjugation of their matrix elements. Mathematicians will make a distinction between the two actions, because, in the infinite dimensional context, there are some extra subtleties. However, I am a physicist so I will not pay any attention to these subtleties and will use the terms “adjoint” and “Hermitian conjugate” interchangeably.

There are a number of properties of Hermitian conjugation which are fairly easy to

²⁴This is one case where Dirac's notation is not very convenient.

prove (Exercise: try proving them without resorting to a basis!):

$$(AB)^\dagger = B^\dagger A^\dagger, \quad (A^\dagger)^\dagger = A, \quad (aA)^\dagger = a^* A^\dagger, \quad (A + B)^\dagger = A^\dagger + B^\dagger \quad (4.47)$$

Unitary operators A linear operator is unitary if it satisfies

$$U^{-1} = U^\dagger \quad (4.48)$$

Unitary operators are especially important because they define transformations in the states that leave amplitudes invariant. For concreteness, let U be a unitary operator, then we define the transformation for any ket $|\psi\rangle$ any $\langle\chi|$:

$$|\psi'\rangle = U|\psi\rangle, \quad \langle\chi'| = \langle\chi|U^\dagger \quad (4.49)$$

it is straightforward to show that any such transformation leaves all amplitudes invariant.

It may be tempting to interpret a change of basis as one of these transformations by defining $S_{\alpha i} = \langle\alpha|i\rangle$, and noticing that S as a matrix is unitary. There are however a couple of wrinkles with this idea. The key point is that S is not an operator that changes a ket, it only acts on the elements on a particular basis, the ket itself is supposed to be invariant, it is a *passive transformation*. The transformation given by a unitary operator U does map a ket in the Hilbert space to a different one, it is an *active transformation*.

The clearest difference between the two can be seen by how we take operators to transform. Under a change of basis we use (4.43) which can be written in matrix notation as

$$A \rightarrow SAS^\dagger \quad (4.50)$$

In a passive transformation the operator changes such that the matrix elements are kept invariant, that is, our goal is to achieve

$$\langle\chi'|A'|\psi'\rangle = \langle\chi|A|\psi\rangle \quad (4.51)$$

We just changed the labels but did nothing to the actual physical system.

For the unitary transformation we instead want to write

$$\langle\chi|A|\psi\rangle \rightarrow \langle\chi'|A|\psi'\rangle = \langle\chi|U^\dagger AU|\psi\rangle \quad (4.52)$$

so that

$$A \rightarrow U^\dagger AU \quad (4.53)$$

In an active transformation the matrix elements are *different*. The operator transformation law above is an *alternative* to changing the state²⁵. We never perform *both* the change in the state *and* the change in the operator. We just perform one of them. In equations, for an active transformation

$$\langle\chi'|A|\psi'\rangle = \langle\chi|A'|\psi\rangle \quad \text{but} \quad \langle\chi'|A'|\psi'\rangle \neq \langle\chi|A|\psi\rangle \quad (4.54)$$

Hermitian operators A linear operator is Hermitian if it satisfies

$$A = A^\dagger \quad (4.55)$$

²⁵Some authors define active and passive transformations in a different way, where by active they mean the version where we only change the kets and by passive the version where we only change the operators.

Hermitian operators are especially important because of the properties of their eigenvectors and eigenvalues. First, recall that an eigenvector $|a\rangle \neq 0$ of a linear operator A is defined such that

$$A|a\rangle = a|a\rangle \quad (4.56)$$

where $a \in \mathbb{C}$ is the eigenvalue²⁶. In particular, for Hermitian matrices we can prove the following theorem.

Theorem 4.2 (Spectral Theorem). The eigenvectors and eigenvalues of a Hermitian operator A on a finite dimensional Hilbert space, \mathcal{H} , satisfy the following properties:

1. The eigenvalues are all real and eigenvectors with different eigenvalues are always orthogonal
2. The eigenvectors can be made to form an orthonormal basis of \mathcal{H}
3. There is a unitary operator U and a diagonal operator D such that $A = UDU^{-1}$

Proof.

1. Let $|a\rangle$ and $|a'\rangle$ be two eigenvectors of A with eigenvalues a and a' , we can then write

$$a(|a'\rangle, |a\rangle) = (\langle a'|, A|a\rangle) = (A|a'\rangle, |a\rangle) = a'^*(\langle a'|, |a\rangle) \quad (4.57)$$

If $|a\rangle = |a'\rangle$, then we conclude $a = a^*$ and so the eigenvalues are real. If $|a\rangle \neq |a'\rangle$ then we conclude $(\langle a'|, |a\rangle) = 0$ and so the eigenvectors are orthogonal.

2. In order to show this we need to show that there are $n = \dim \mathcal{H}$ eigenvectors and that they can be made to be orthogonal. We shall proceed by induction.

Firstly, $A|a\rangle = a|a\rangle \implies (A - a\mathbb{1})|a\rangle = 0$. This equation can only have a non-trivial solution for $|a\rangle$ if the matrix $A_{ij} - a\delta_{ij}$ is not invertible, and this can only happen if its determinant vanishes: $\det(A_{ij} - a\delta_{ij}) = 0$. The determinant will be a polynomial of order n in a , by the fundamental theorem of algebra, there is at least one root. Hence there must be at least one eigenvalue and one eigenvector.

Now we assume that there are $m < n$ orthogonal eigenvectors of A , labelled $|a_i\rangle$. Now consider the set of vectors which are orthogonal to all $|a_i\rangle$, let us introduce an orthonormal basis for that set of vectors and call it $|b_a\rangle$. If $|b\rangle = \sum_a b_a |b_a\rangle$ be a generic vector in that space, then we can show $A|b\rangle$ is orthogonal to all $|a_i\rangle$:

$$(A|b\rangle, |a_i\rangle) = (\langle b|, A|a_i\rangle) = a_i(\langle b|, |a_i\rangle) = 0 \quad (4.58)$$

therefore we can expand $A|b\rangle$ in the basis $\{|b_a\rangle\}$ if we define A_{ba} such that $A|b_a\rangle = \sum_b A_{ba} |b_b\rangle$. These coefficients also form a Hermitian matrix but now in $n - m$ dimensions

$$A_{ba} = (\langle b|, A|b_a\rangle) = (A|b\rangle, |b_a\rangle) = A_{ab}^* \quad (4.59)$$

We can now apply the fundamental theorem of algebra again to show that there is some linear combination of the $|b_a\rangle$ such that they form an eigenvector, which, by construction, will be orthogonal to all the previous ones.

²⁶Unfortunately there is no agreed upon notation to distinguish operators and scalars, one must judge based on the context. We will often use uppercase for operators and lowercase for scalars but this will not be 100% consistent. When in doubt we will point it out in the text.

By induction we can find n orthonormal eigenvectors of A , which can be made into a basis of the Hilbert space.

3. If $|a_r\rangle$ is the r^{th} eigenvector of A , then we can construct a matrix U_{ir} with the i^{th} component of $|a_r\rangle$. Then the eigenvector condition can be written as

$$AU = UD \quad (4.60)$$

where $D = a_r \delta_{rs}$. The condition that the eigenvectors are orthonormal gives us that $U^\dagger U = \mathbb{1}$, so U is unitary. Acting with U^{-1} gives us $A = UDU^{-1}$.

□

For infinite dimensional Hilbert spaces the situation is more complicated. There are equivalent results to the finite dimensional case if one puts further assumptions on the operators (such as compactness or boundedness). However, many of the operators we will wish to deal with will not obey such requirements. There are however certain 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.

Assuming the spectral theorem works, then it will usually be convenient to use the eigenvectors of an important Hermitian operator as the basis of the Hilbert space. However, this may be tricky because of *degeneracies*, that is when there are several eigenvectors with the same eigenvalue. In that case, finding an orthonormal basis will be a bit more arbitrary. We can solve this by finding another Hermitian operator that commutes with A .

Theorem 4.3. Let A and B be two Hermitian 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 if and only if they commute.

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

$$AB|a\rangle = BA|a\rangle = Ba|a\rangle = aB|a\rangle \quad (4.61)$$

therefore the vector $B|a\rangle$ is also an eigenvector of A with eigenvalue a . If there are several vectors $|a_r\rangle$ with the same eigenvalue a then acting with B on any linear combination of these vectors will return a linear combination of those vectors. We can then apply the spectral theorem to this subspace and find a basis with eigenvectors of B . This means we can find an orthonormal basis of simultaneous eigenvectors 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

$$AB|ab\rangle = bA|ab\rangle = ba|ab\rangle = aB|ab\rangle = BA|ab\rangle \quad (4.62)$$

This finishes our proof. □

4.3 Hermitian operators as physical observables

Linear operators also have a very clear physical interpretation. Think of the following complicated sequence of Stern-Gerlach devices:

INSERT PICTURE

We could ask the question: what is the amplitude that a particle enters in state $|\psi\rangle$

goes through the complicated section and comes out as $|\chi\rangle$? The complicated action must be represented by an operator, call it A , so we should be able to write:

$$\langle \chi | A | \psi \rangle \quad (4.63)$$

This is one interpretation of operators, as literal actions we might perform on states²⁷.

There is however another interpretation that will be even more important. Imagine we want to perform a measurement on a physical state. Just like in Stern-Gerlach, the way to do so is to perform some action on a state that splits it into categories, *e.g.* going in the top beam means spin-up and going in the bottom beam means spin-down.

An additional requirement for these measurement actions is that once we have measured a certain property then if we measure it again, without acting on it in any other way in the meantime, we must obtain the same answer. In the Stern-Gerlach case, if we measured that an electron had spin-up in the y direction and then we measured spin in the y direction again we saw it was still spin-up; it only changed answers when we did something to it like measuring spin in the x direction. This requirement implies that there exists a certain class of states such that the act of measuring either leaves them unchanged or destroys them. In equations, calling A the measurement action and $|\psi\rangle$ one of these special state we must have

$$A |\psi\rangle = a |\psi\rangle \quad (4.64)$$

where a is either 0 or 1. But this is exactly the condition for $|\psi\rangle$ to be an eigenvector of A ! Eigenvectors of a measurement operator have definite values for the quantity being measured.

This operation answered only binary questions, *e.g.* “Does this state have spin-up in the y direction?”, but we can do better. Think of the original Stern-Gerlach experiment without recombining the beams. There we could tell whether it was spin up or down without including any filters. We just have to split the state into several categories and label them appropriately. The above argument for repeated measurements still applies, therefore eigenvectors of this operator still have definite answers for the quantity being measured. We can then label the eigenvectors by their eigenvalues. While mostly a matter of convention, this means that not only do eigenvectors have definite values for the quantity being measured, the outcome of that measurement is given by their eigenvalue. This eigenvalue is of course real for any physical quantity.

Finally, we can also show that these eigenvectors form a basis of the Hilbert space. Let us first assume the number of categories being measured is equal to the dimension of the Hilbert space. Further, we assume that the measurement always yields an answer, *i.e.* there is no state for which we don't assign a value. Then we can show that all eigenvectors are linearly independent. Imagine this wasn't true, then there would have to be an eigenvector $|s\rangle$ that could be written as a superposition of the others $|s\rangle = \sum_{i \neq s} |i\rangle$. However, if the action of the measurement is linear, then the superposition $\sum_{i \neq s} |i\rangle$ can yield any eigenvector $|i\rangle$ which does not equal $|s\rangle$, this violates the requirement that $|s\rangle$ has a definite answer for the measurement, therefore $|s\rangle$ must be linearly independent from the other eigenvectors. This implies that the eigenvectors of this measurement action form a basis. If we had fewer categories than number of dimensions of the Hilbert space that must mean that there is at least one category that has multiple linearly independent eigenvectors. We can just form an arbitrary basis of that subspace and still form a basis of the Hilbert

²⁷We are subtly assuming such an action acts *linearly* in the states. The only way to prove this is by comparing with experiment. We shall take it as an assumption that we will always be considering linear operators.

space with eigenvectors of the measurement operator.

All in all, if we are trying to measurement some physical quantity O then it has enough eigenvectors to form a basis of the Hilbert space $|\lambda_i\rangle$ and their eigenvalues λ_i are real. In this basis O is certainly diagonal:

$$O_{ij} = \lambda_i \delta_{ij} \quad (4.65)$$

This matrix is clearly Hermitian, therefore O is a Hermitian operator. By the spectral theorem, for any Hermitian operator we can run these steps backwards and find a eigenvectors with real eigenvalues that form a basis of the Hilbert space.

The conclusion is that any measurable quantity, called *observable*, can be represented by a Hermitian operator action on the Hilbert space of states. The outcome of measuring O on an eigenvector is the eigenvalue with definite result. For superpositions O is defined by linearity, the way to motivate this is to look at expectation values. By the Born rule, the probability of finding the system in state $|\lambda_i\rangle$ if we had prepared it in state $|\psi\rangle$ is $|\langle\lambda_i|\psi\rangle|^2$, therefore, the expectation value for the observable O is

$$\langle O \rangle = \sum_i \lambda_i |\langle\lambda_i|\psi\rangle|^2 = \sum_i \langle\psi|\lambda_i\rangle \lambda_i \langle\lambda_i|\psi\rangle = \sum_{ij} \langle\psi|\lambda_i\rangle O_{ij} \langle\lambda_j|\psi\rangle = \langle\psi|O|\psi\rangle \quad (4.66)$$

where in the last equality we used the fact the $\{|\lambda_i\rangle\}$ form an orthonormal basis of the Hilbert space. This motivates defining

$$O|\psi\rangle = \sum_i \lambda_i \psi_i |\lambda_i\rangle \quad (4.67)$$

where $\psi_i = \langle\lambda_i|\psi\rangle$ and $|\psi\rangle = \sum_i \psi_i |\lambda_i\rangle$. Therefore it is natural to assume that all observables are linear operators.

We can now also provide a new interpretation for the Born rule—the act of measuring O on $|\psi\rangle = \sum_i \psi_i |\lambda_i\rangle$ is λ_i with probability $|\psi_i|^2$. In the Stern-Gerlach example, the action of the observable is the splitting of the beams. The act of measuring, that projects/collapses a superposition onto a definite value is the act of filtering.

This is why Hermitian operators are so important, they correspond to the physical observables in our theory.

We can also define functions of observables by their action on eigenstates:

$$f(O)_{ij} = f(\lambda_i) \delta_{ij} \quad (4.68)$$

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

$$\langle f(O) \rangle \neq f(\langle O \rangle) \quad (4.69)$$

in particular

$$\langle O^2 \rangle \neq \langle O \rangle^2 \quad (4.70)$$

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

$$\Delta_\psi O = \sqrt{\langle (O - \langle O \rangle)^2 \rangle} \quad (4.71)$$

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 . Therefore, for all these vectors we can measure both quantities with definitive answers. We therefore 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:

$$\Delta_\psi A \cdot \Delta_\psi B \geq \frac{1}{2} |\langle [A, B] \rangle| \quad (4.72)$$

Proof. Let us define the following states

$$|A_\psi\rangle \equiv (A - \langle A \rangle) |\psi\rangle, \quad |B_\psi\rangle \equiv (B - \langle B \rangle) |\psi\rangle \quad (4.73)$$

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

$$\Delta_\psi A = \sqrt{\langle A_\psi | A_\psi \rangle}, \quad \Delta_\psi B = \sqrt{\langle B_\psi | B_\psi \rangle} \quad (4.74)$$

Using the Schwarz inequality, we can then write

$$\Delta_\psi A \cdot \Delta_\psi B \geq |\langle A_\psi | B_\psi \rangle| \quad (4.75)$$

For any complex number we have

$$|z| = \sqrt{\operatorname{Re}(z)^2 + \operatorname{Im}(z)^2} \geq \sqrt{\operatorname{Im}(z)^2} = |\operatorname{Im}(z)| = \left| \frac{1}{2i} (z - z^*) \right| = \frac{1}{2} |z - z^*| \quad (4.76)$$

therefore

$$\begin{aligned} \Delta_\psi A \cdot \Delta_\psi B &\geq \frac{1}{2} |\langle A_\psi | B_\psi \rangle - \langle B_\psi | A_\psi \rangle| = \\ &= \frac{1}{2} |\langle \psi | (AB - A\langle B \rangle - \langle A \rangle B + \langle A \rangle \langle B \rangle) | \psi \rangle - (A \leftrightarrow B)| = \\ &= \frac{1}{2} |\langle \psi | AB | \psi \rangle - \langle \psi | A | \psi \rangle \langle B \rangle - \langle A \rangle \langle \psi | B | \psi \rangle + \langle A \rangle \langle B \rangle \langle \psi | \psi \rangle - (A \leftrightarrow B)| = \\ &= \frac{1}{2} |\langle AB \rangle - \langle A \rangle \langle B \rangle - \langle A \rangle \langle B \rangle + \langle A \rangle \langle B \rangle - (A \leftrightarrow B)| = \\ &= \frac{1}{2} |\langle AB \rangle - \langle BA \rangle| = \\ &= \frac{1}{2} |\langle [A, B] \rangle| \end{aligned} \quad (4.77)$$

□

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. In fact, 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.

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, if we remember in the example from Chapter 2 we were measuring the position of an electron, and position is certainly a continuous variable. In fact, the first description of a quantum state was done in the position basis by Schrodinger, and more traditional approaches tend to start with that.

5.1 The wavefunction in position space

Let us take as our first example of a continuous basis the position. The components of a state in terms of a discrete basis were given by:

$$\psi_i = \langle i | \psi \rangle \quad (5.1)$$

Now, we shall make 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:

$$\psi(x) = \langle x | \psi \rangle \quad (5.2)$$

This representation of the state is so important it gets a special name: *wavefunction*. In fact it is so important that 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 instead must ask for probability of finding the particle in a certain *interval* of positions. Therefore we interpret $|\psi(x)|^2 dx$ as the probability of finding the particle between x and $x + dx$. The normalisation requirement will then read:

$$\int dx |\psi(x)|^2 = 1 \quad (5.3)$$

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 be the space of *square-integrable* functions usually denoted by L^2 . With inner product defined as:

$$\langle \psi | \chi \rangle = \int dx \psi^*(x) \chi(x) \quad (5.4)$$

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:

$$\langle X \rangle = \int dx x |\psi(x)|^2 \quad (5.5)$$

where we are denoting the position operator by X .

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

$$\langle x | X | \psi \rangle \equiv X \psi(x) \equiv x \psi(x) \quad (5.6)$$

What are the eigenvalues of such an operator? Despite its action on $\psi(x)$ being quite simple, generic functions are not eigenvalues of X because its action is not the multiplication by a number, it is the multiplication by a function. The eigenvalues of X will be some function which is so peaked at a particular value $x = y$ that multiplying by the function x will be the same as multiplying by the number y . In the bra-ket notation, the eigenstate of X with eigenvalue y in position basis is written as

$$\langle x|y \rangle \quad (5.7)$$

But this is just the inner product between two base states! Remember (4.1), When we are taking the inner product of two base states we get the Kronecker- δ . That is what we need to generalise to the continuous case. The definition in (4.3) is not readily generalisable, it is however equivalent to the following definition. We define δ_{ij} as the unique object such that

$$\sum_j \delta_{ij} \psi_j = \psi_i \quad (5.8)$$

Making the sum an integral we then define $\langle x|y \rangle \equiv \delta(x - y)$ as the unique object such that²⁸:

$$\int dx \delta(x - y) \psi(x) = \psi(y) \quad (5.9)$$

This object is called the *Dirac- δ* ²⁹ and is our continuous analogue of the Kronecker- δ .

Using only the definition above it is straightforward to prove the following properties:

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

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

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

$$\int dx \psi(x) \frac{1}{\epsilon \sqrt{2\pi}} e^{-\frac{x^2}{2\epsilon^2}} = \int dy \frac{1}{\sqrt{2\pi}} e^{-\frac{y^2}{2}} \psi(\epsilon y) \xrightarrow{\epsilon \rightarrow 0} \psi(0) \int dy \frac{1}{\sqrt{2\pi}} e^{-\frac{y^2}{2}} = \psi(0) \quad (5.11)$$

For finite ϵ we can graph this function:

INSERT PICTURE

As ϵ gets smaller and smaller we see that it gets more and more peaked around $x = 0$. In fact, for $x \neq 0$, we can see that

$$\lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon \sqrt{2\pi}} e^{-\frac{x^2}{2\epsilon^2}} = 0 \quad (5.12)$$

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

²⁸You might wonder we wrote $\delta(x - y)$ with a single argument rather than something like $\delta(x, y)$. It is however not too hard to show that the two definitions agree, you just have to do a variable change in the integral.

²⁹It 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.

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

$$\frac{1}{\epsilon\sqrt{2\pi}}e^{-\frac{x^2}{2\epsilon^2}} \Big|_{x=0} = \frac{1}{\epsilon\sqrt{2\pi}} \xrightarrow{\epsilon \rightarrow 0} \infty \quad (5.13)$$

The analogue of (4.3) becomes

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

which is clearly *not* an ordinary function.

The Dirac- δ only makes sense under an integral (or the promise of one), 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:

$$\int dx \delta(x)\delta(x) = \delta(0) = \infty \quad (5.15)$$

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

$$\langle x|x \rangle = \delta(0) = \infty \quad (5.16)$$

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

$$\int dx |x\rangle\langle x| = \mathbb{1} \quad (5.17)$$

since

$$\langle \psi|\chi \rangle = \int dx \psi^*(x)\chi(x) = \int dx \langle \psi|x \rangle \langle x|\chi \rangle \quad (5.18)$$

We shall instead fix the normalisation of $|x\rangle$ by the equation

$$\langle x|y \rangle = \delta(x - y) \quad (5.19)$$

with the definition (5.9).

We can then define the action of more generic operators via:

$$\langle \chi|A|\psi \rangle = \int dx dy \langle \chi|x \rangle \langle x|A|y \rangle \langle y|\psi \rangle = \int dx dy \chi^*(x)A(x,y)\psi(y) \quad (5.20)$$

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:

$$\langle x|D|\psi \rangle \equiv D\psi(x) \equiv \psi'(x) \quad (5.21)$$

This is certainly a linear action on our Hilbert space, so it should also be included in our definition of linear operators. However, 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 .

You may think I have gone completely mad. The Dirac- δ isn't even a function, how can

we possibly define its derivative? We just have to use its integral definition and integrate by parts:

$$\int dx \delta'(x) f(x) = - \int dx \delta(x) f'(x) = -f'(0) \quad (5.22)$$

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:

$$\delta(x) = \theta'(x) \quad (5.23)$$

where

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

We can then write

$$D\psi(x) = \frac{d\psi(x)}{dx} = \int dy \delta(x-y) \frac{d\psi(y)}{dy} = - \int \frac{d\delta(x-y)}{dy} \psi(y) \quad (5.25)$$

and therefore define

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

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 however seldom use this fact and instead more often write

$$D = \frac{d}{dx} \quad (5.27)$$

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 example from Chapter 2 suggest, the dynamics of the wavefunction will often resemble that of waves. As we are well aware, when wish to deal with wave phenomena it is a smart idea to Fourier transform³⁰, so let us study the wavefunction in the Fourier space.

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:

$$\tilde{\psi}(k) = \int dx e^{-ikx} \psi(x) \quad (5.28)$$

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

$$k = \frac{2\pi}{\lambda} \quad (5.29)$$

³⁰A wise lecturer once told me that if you don't know what to do in physics you Fourier transform and see what happens and that unblocked my first paper.

The inverse of the Fourier transform is then

$$\psi(x) = \int \frac{dk}{2\pi} e^{ikx} \tilde{\psi}(k) \quad (5.30)$$

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

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

$$\int dx e^{-ikx} \delta(x) = 1 \quad (5.31)$$

and therefore, the inverse Fourier transform of this expression gives

$$\int \frac{dk}{2\pi} e^{ikx} = \delta(x) \quad (5.32)$$

giving yet another representation for the Dirac- δ .

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

$$\begin{aligned} \langle \psi | \chi \rangle &= \int dx \psi^*(x) \chi(x) = \int dx \frac{dk dq}{(2\pi)^2} e^{ix(q-k)} \tilde{\psi}^*(k) \tilde{\chi}(q) = \\ &= \int \frac{dk dq}{(2\pi)^2} 2\pi \delta(q-k) \tilde{\psi}^*(k) \tilde{\chi}(q) = \\ &= \int \frac{dk}{2\pi} \tilde{\psi}^*(k) \tilde{\chi}(k) \end{aligned} \quad (5.33)$$

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:

$$\tilde{\psi}(k) \equiv \langle k | \psi \rangle = \int dx \langle k | x \rangle \langle x | \psi \rangle = \int dx \langle k | x \rangle \psi(x) \quad (5.34)$$

and therefore we conclude that

$$\langle k | x \rangle = e^{-ikx} \quad (5.35)$$

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

$$\langle k | q \rangle = \int dx \langle k | x \rangle \langle x | q \rangle = \int dx e^{ikx} e^{-iqx} = 2\pi \delta(k - q) \quad (5.36)$$

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:

$$\begin{aligned} \tilde{D}(k, q) \equiv \langle k | D | q \rangle &= \int dx dy \langle k | x \rangle \langle x | D | y \rangle \langle y | q \rangle = \int dx dy e^{-ikx} D(x, y) e^{iqy} = \\ &= - \int dx dy e^{-ikx} \frac{d\delta(x-y)}{dy} e^{iqy} = \int dx dy e^{-ikx} \delta(x-y) \frac{de^{iqy}}{dy} = \\ &= \int dx dy e^{-ikx} \delta(x-y) iq e^{iqy} = iq \int dx e^{ix(q-k)} = iq 2\pi \delta(q-k) \end{aligned} \quad (5.37)$$

Therefore

$$\langle k | D | \psi \rangle \equiv \tilde{D}\tilde{\psi}(k) = \int \frac{dq}{2\pi} \tilde{D}(k, q) \tilde{\psi}(q) = ik\tilde{\psi}(k) \quad (5.38)$$

so we usually write it more simply as

$$\tilde{D} = ik \quad (5.39)$$

Derivatives become just multiplication by ik . In fact this allows us to define the operator $K = -iD$ such that

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

which, in the position basis becomes

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

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.

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

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!)

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

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:

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

therefore

$$[X, K] = i \quad (5.45)$$

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

$$\Delta_\psi X \cdot \Delta_\psi K \geq \frac{1}{2} |\langle [X, K] \rangle| = \frac{1}{2} \quad (5.46)$$

This is a well known result in signal analysis and can be intuitively thought of in the following way. If we have a function with a very well defined value for K that means it is a wave

INSERT PICTURE

But this function is completely de-localised in space. Additionally, if we try to localise it in space

INSERT PICTURE

Now we don't have enough peaks to have an accurate value for the wavenumber.

We even saw this in the Fourier transform of the Dirac- δ which, as an eigenstate of

the position, has a completely determined value for the position. Its Fourier transform however is a constant, therefore in Fourier space it is equally likely to measure any value for the wavenumber.

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:

$$p = \frac{h}{\lambda} \quad (5.47)$$

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

$$P = \hbar K \quad (5.48)$$

where $\hbar = h/2\pi$ is the reduced Planck constant as before.

It is important to stress that there is no way to derive this relationship, it should be taken as a *fundamental postulate of quantum mechanics*. However, we need to verify it experimentally. How do we do so? Well, take a plane wave wavefunction:

$$\psi(x) = e^{ikx} \quad (5.49)$$

this 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 in 1923-27 Clinton Davisson and Lester Germer sent electrons through a crystal of nickel which exhibits a diffraction pattern. From this diffraction pattern they were able to measure the wavelength. 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

$$k = \frac{2\pi}{\lambda} \quad (5.50)$$

and the non-relativistic kinetic energy

$$E = \frac{p^2}{2m} \quad (5.51)$$

we get

$$\lambda = \frac{h}{\sqrt{2mE}} \quad (5.52)$$

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 relation³¹ is 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 ~ 1 kg, travelling at a velocity of ~ 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 ~ 1 m/s will have a wavelength of $\sim 7 \times 10^{-4}$ m, which is 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, in modern days the value of the Planck constant is not merely known approximately, it is *defined* to be *exactly*

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

This exact value is used to *define* the kilogram. This makes it seem that the value is completely arbitrary, after all we could simply choose a different value and get a slightly different definition for the kilogram. What is then the meaning for this value?

The value for the Planck constant was set to agree with a historical definition of the kilogram in terms of a reference weight. This reference weight was 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 the 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 bigger than quantum scales. The true value of \hbar is then not 10^{-34} it is³²

$$\hbar = 1 \quad (5.54)$$

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

$$P = K \quad (5.55)$$

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 these units energy, mass, frequency, momentum, wavenumber and temperature all have the same units, we still however need to fix one unit, 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

³¹And the related energy-frequency relationship which we will delve into in the next chapter

³²You 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.

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 eigenstates of the momentum obey

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

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

In position basis we can write

$$P = -i\hbar \frac{d}{dx} \quad (5.57)$$

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

$$[X, P] = i\hbar \quad (5.58)$$

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:

$$\Delta_\psi X \cdot \Delta_\psi P \geq \frac{\hbar}{2} \quad (5.59)$$

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. The whole construction relied on a phase space by specifying *both* position and momentum. They are the canonical variables of Hamiltonian mechanics. Even in Newtonian or Lagrangian mechanics we need to specify the position and velocity. Classical mechanics destroyed at its foundation.

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.

Quantum Dynamics

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. There are in fact two versions of the equations of motion: the wave mechanics of Schrodinger who puts time dependence on the states; and the matrix mechanics of Heisenberg who puts time dependence on the operators *i.e.* observables. In the coming chapter we will describe both versions and how they are ultimately equivalent. Along the way we will briefly delve into the matter of symmetries and the quantum mechanical version of Noether's theorem. Finally we will describe in detail the dynamics of the simplest 1-dimensional systems: a free particle; square potentials; and the harmonic oscillator.

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

6 The equations of motion

In classical mechanics there are several versions of the equations of motion. We can take the force vectors from Newton, Lagrange's variational principle, or Hamilton's canonical equations. This is also true of quantum mechanics: we have Schrodinger's wave mechanics, Heisenberg's matrix mechanics, and Dirac-Feynman's path integrals. What is interesting is that the first two versions were discovered independently and roughly at the same time, only later were they shown to be equivalent. Therefore the next two sections are written slightly differently, they can be read in any order. You can start with Section 6.1 or 6.2 as you please, both orders will make sense. I even encourage you to pick randomly by flipping a coin. You can also check out the following table to help you choose.

Schrodinger Picture	Heisenberg Picture
Time-dependent states	Time-dependent observables
Published 1926	Published 1925
Newton-like	Hamilton-like
Known paedophile	Known nazi collaborator

After this will shall discuss their equivalence and practical problem solving in quantum mechanics³³.

6.1 Schrodinger picture

Schrodinger asks a very intuitive question: how do the states depend on time? That is we are looking for an equation that relates $|\psi(t)\rangle$ to a, initial $|\psi(t_0)\rangle$. If probabilities are to be consistently attributed throughout this time evolution then the norms of the two kets must match:

$$\langle\psi(t)|\psi(t)\rangle = \langle\psi(t_0)|\psi(t_0)\rangle = 1 \quad (6.1)$$

this suggests looking for a unitary time evolution operator $U(t, t_0)$ such that

$$|\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle \quad (6.2)$$

³³We shall leave the path integral formulation for later as it is less useful for solving practical problems.

and

$$U(t, t_0)^\dagger U(t, t_0) = \mathbb{1} \quad (6.3)$$

we shall also impose that

$$U(t_2, t_0) = U(t_2, t_1)U(t_1, t_0) \quad (6.4)$$

to ensure that we can apply the time evolution operator repeatedly without running into inconsistencies.

We usually write equations of motion differentially so let us consider an infinitesimal time evolution, *i.e.* $t = t_0 + dt$. We can then expand:

$$U(t_0 + dt, t_0) = \mathbb{1} - i\Omega(t_0) dt + O(dt^2) \quad (6.5)$$

applying (6.3) we get

$$\begin{aligned} \mathbb{1} &= U(t_0 + dt, t_0)^\dagger U(t_0 + dt, t_0) = \\ &= (\mathbb{1} + i\Omega(t_0)^\dagger)(\mathbb{1} - i\Omega(t_0)) + O(dt^2) = \\ &= \mathbb{1} + i(\Omega(t_0)^\dagger - \Omega(t_0)) dt + O(dt^2) \end{aligned} \quad (6.6)$$

and therefore

$$\Omega(t_0) = \Omega(t_0)^\dagger \quad (6.7)$$

This operator $\Omega(t_0)$ we have introduced generates infinitesimal time translations. The unitarity of time evolution implies that it is Hermitian, and therefore it is, in principle at least, an observable. What does this mean for $|\psi(t)\rangle$? We can differentiate both sides of (6.2) to obtain

$$\frac{d}{dt} |\psi(t)\rangle = -i\Omega(t) |\psi(t)\rangle \quad (6.8)$$

So far, there is no physics, only mathematics and definitions. We have a differential equation for $|\psi(t)\rangle$ but it is in terms of an $\Omega(t)$ we do not understand, so we have not gained anything. Let us assume for a moment, for simplicity's sake, that Ω does not depend on t and is therefore constant in time. Given it is an observable we can go to its eigenbasis $\{|\omega\rangle\}$ and write:

$$\frac{d}{dt} |\omega(t)\rangle = -i\omega |\omega(t)\rangle \quad (6.9)$$

but this is trivially solved by:

$$|\omega(t)\rangle = e^{-i\omega t} |\omega(0)\rangle \quad (6.10)$$

The time evolution of the eigenvalues of Ω is very simple—they merely oscillate in time with angular frequency given by their eigenvalue ω . This in turn gives as an interpretation for Ω it is the *angular frequency operator*. We have waves in time why not in space as well? It is because the time evolution for states can be written in terms of these waves that this version of the equation of motion was originally given the monicker of *wave mechanics*.

Now we know how to measure ω but we still don't have an expression for it. Without it we still don't have a true equation of motion. In fact, it is not possible to derive such an expression. First recall Planck's relation between the energy and the frequency:

$$E = h\nu = \hbar\omega \quad (6.11)$$

remembering the relation between the conventional and angular frequency, $\nu = 2\pi\omega$. The same way we had to postulate the relationship between the wavenumber and the momentum, we now add the postulate that relates frequency and energy. To do so we promote E

and ω to operators and postulate that

$$H = \hbar\Omega \quad (6.12)$$

The energy operator H is commonly called the *Hamiltonian*, in analogy with the similar concept in the canonical formulation of classical mechanics. We have slightly altered our convention around operators and eigenvalues, the eigenvalues of H are denoted by E to avoid confusion with the Planck constant h .

Once again we reiterate that there is no way to derive this formula. It is a fundamental postulate of quantum mechanics that can only be verified by comparison with experiment. The most we can do is remember de Broglie's reasoning for the group velocity at the end of Chapter 1 that shows that the momentum-wavelength condition is consistent with the energy-frequency condition.

All in all, in the same way that in the quantum world wavenumber was the same as momentum, so too are energy and angular frequency entirely the same phenomenon. We can now write, in full generality Schrodinger's equation of motion for quantum states:

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle \quad (6.13)$$

Despite us still not having given an expression for the Hamiltonian, its interpretation as energy allows us to use analogies with classical theories to guess Hamiltonians. It is exactly the same as with Newton's second law. Without an independent expression for the forces it has no value, we need independent laws for the forces in order to give predictive power to Newton's second law. Our interpretation of the Hamiltonian as energy gives us an interpretational tool to help us find those independent laws. Given a Hamiltonian, then Schrodinger's equation has full predictive power. For example, for a single particle in a potential, we would write the classical Hamiltonian as a sum of the kinetic and potential energies:

$$H = \frac{p^2}{2m} + V(x) \quad (6.14)$$

so it is not too much of a stretch to guess that a quantum particle subject to a potential would have a Hamiltonian operator given by

$$H = \frac{P^2}{2m} + V(X) \quad (6.15)$$

where X and P are the position and momentum operators respectively.

In the position basis, *i.e.* in terms of Schrodinger's wavefunctions, we can then write the Schrodinger equation as

$$i\hbar \frac{\partial}{\partial t} \psi(x, t) = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \psi(x, t) \quad (6.16)$$

which is how Schrodinger originally wrote it, and is the starting point of the more traditional treatments of quantum mechanics. This is a partial differential equation of second order in space but first order in time. Despite being first order in time it is *not* a heat equation. The factor of i in the time derivative is rather crucial and it ensures that solutions to the Schrodinger equation are wave-like. In that regard it behaves more like a hyperbolic wave equation.

We shall close this section with a final look at the unitarity condition (6.3). When we first introduced it, we were considering it as a *global* statement—the total probability must

be conserved. However, in the position basis we can write a more detailed *local* statement. The probability density at a given point in space and time is given by $|\psi(x, t)|^2$ how does this density evolve in time?

$$\frac{\partial}{\partial t} |\psi(x, t)|^2 = \frac{\partial \psi}{\partial t} \psi^* + \psi \frac{\partial \psi^*}{\partial t} \quad (6.17)$$

using (6.16) we find

$$\begin{aligned} \frac{\partial}{\partial t} |\psi(x, t)|^2 &= -\frac{i}{\hbar} \left(-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi \right) \psi^* + \frac{i}{\hbar} \psi \left(-\frac{\hbar^2}{2m} \frac{\partial^2 \psi^*}{\partial x^2} + V(x)\psi^* \right) = \\ &= \frac{\partial}{\partial x} \left(\frac{i\hbar}{2m} \left(\frac{\partial \psi}{\partial x} \psi^* - \psi \frac{\partial \psi^*}{\partial x} \right) \right) \end{aligned} \quad (6.18)$$

This last expression looks an awful lot like a continuity equation if we define the *probability current*

$$\mathbf{j} = \frac{i\hbar}{2m} \left(\frac{\partial \psi^*}{\partial x} \psi - \psi^* \frac{\partial \psi}{\partial x} \right) \quad (6.19)$$

so that we can write

$$\frac{\partial}{\partial t} |\psi|^2 + \frac{\partial \mathbf{j}}{\partial x} = 0 \quad (6.20)$$

In higher dimensions \mathbf{j} becomes a vector given by:

$$\mathbf{j} = \frac{i\hbar}{2m} (\psi \nabla \psi^* - \psi^* \nabla \psi) \quad (6.21)$$

and the continuity equation becomes

$$\frac{\partial}{\partial t} |\psi|^2 + \nabla \cdot \mathbf{j} = 0 \quad (6.22)$$

These are exactly like the continuity equation that expresses local conservation of charge. In that case, it expresses that the only way that charge density can change is if there is some electric current. For the quantum mechanical case we see that it is not only the *total* probability which is conserved. We also have a continuity equation relating the *local* change in probability density to the divergence of what we interpret as a *probability current*. This slightly stronger statement will often come in handy when solving practical problems.

6.2 Heisenberg picture

From Heisenberg's point of view, physics should deal first and foremost with what can be measured. The quantum state is not measurable, it is merely a mathematical tool to describe the probability amplitudes. What can be measured are observables. How do these depend on time?

As we promised, Heisenberg's equations of motion are based on the Hamiltonian formulation of mechanics, so let us briefly review it. In this formalism, the equations of motion are given by

$$\frac{dx}{dt} = \frac{dH}{dp} \quad \frac{dp}{dt} = -\frac{dH}{dx} \quad (6.23)$$

where x and p and the particle's position and respective canonical momentum and $H(x, p)$ is the Hamiltonian, which equals the total energy of the particle written in terms of the

position and momentum, *e.g.* for a particle in a potential

$$H(x, p) = \frac{p^2}{2m} + V(x) \quad (6.24)$$

Trying to convert these equations into quantum operator equations seems rather challenging. It is not clear at all *a priori* how one might take a derivative with respect to an operator. We can however re-write these equations in terms of *Poisson brackets* whose algebraic structure is much more amenable to generalisation. The classical Poisson bracket is defined for two functions $f(x, p)$ and $g(x, p)$ as³⁴:

$$\{f, g\} = \frac{\partial f}{\partial x} \frac{\partial g}{\partial p} - \frac{\partial f}{\partial p} \frac{\partial g}{\partial x} \quad (6.25)$$

for multiple particles or higher dimensions you sum over all degrees of freedom.

In terms of the Poisson bracket we can write an equation of motion for a generic function on phase space $f(x, p)$:

$$\frac{df}{dt} = \{f, H\} \quad (6.26)$$

it is straightforward to show that this reproduces (6.23) in the case when $f = x$ or $f = p$ respectively.

One can also trivially show that

$$\{x, p\} = 1 \quad (6.27)$$

Finally we have the following algebraic properties of the Poisson bracket which are straightforward to demonstrate:

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:** $\{f, \{g, h\}\} + \{g, \{h, f\}\} + \{h, \{f, g\}\} = 0$

In fact, just using these algebraic properties and the canonical Poisson bracket relation (6.27) is sufficient to define the Poisson bracket uniquely. Not only that, these algebraic relations pose no immediate puzzle as to how they could be realised in the quantum world. In fact, we shall now prove that the algebraic properties of the Poisson bracket when applied to non-commuting observables necessarily imply that the Poisson bracket is proportional to their commutator.

To prove this, let us calculate $\{A_1 A_2, B_1 B_2\}$ 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

³⁴The notation for Poisson brackets, despite standard in the classical mechanics literature, may be confused with that of the anti-commutator: $\{A, B\} = AB + BA$. We shall only use Poisson brackets in this section, in following sections the curly brackets will always denote an anti-commutator.

said Poisson bracket merely by resorting to its algebraic properties.

$$\begin{aligned} \{A_1 A_2, B_1 B_2\} &= \{A_1, B_1 B_2\} A_2 + A_1 \{A_2, B_1 B_2\} = \\ &= (\{A_1, B_1\} B_2 + B_1 \{A_1, B_2\}) A_2 + A_1 (\{A_2, B_1\} B_2 + B_1 \{A_2, B_2\}) = \\ &= \{A_1, B_1\} B_2 A_2 + B_1 \{A_1, B_2\} A_2 + A_1 \{A_2, B_2\} B_2 + A_1 B_1 \{A_2, B_2\} \end{aligned} \quad (6.28)$$

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

$$\begin{aligned} \{A_1 A_2, B_1 B_2\} &= \{A_1 A_2, B_1\} B_2 + B_1 \{A_1 A_2, B_2\} = \\ &= \{A_1, B_1\} A_2 B_2 + A_1 \{A_2, B_1\} B_2 + B_1 \{A_1, B_2\} A_2 + B_1 A_1 \{A_2, B_2\} \end{aligned} \quad (6.29)$$

equating these two results

$$\{A_1, B_1\} (A_2 B_2 - B_2 A_2) = (A_1 B_1 - B_1 A_1) \{A_2, B_2\} \quad (6.30)$$

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

$$\{A, B\} \propto AB - BA \quad (6.31)$$

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

Our goal is just to find the proportionality constant. To do so just recall (5.58)

$$[X, P] = i\hbar \quad (6.32)$$

and compare with (6.27). They are the same up to a factor of $i\hbar$. That is we shall assume

$$i\hbar \{A, B\} = [A, B] \quad (6.33)$$

The factor of i is crucially important. It ensures the Poisson bracket of two Hermitian operators is itself Hermitian. This is because the commutator of two Hermitian operators is in fact anti-Hermitian

$$[A, B]^\dagger = [B^\dagger, A^\dagger] = [B, A] = -[A, B] \quad (6.34)$$

The factor of \hbar gives us another interpretation for the Planck constant, it connects the quantum and classical Poisson brackets.

To write the equations of motion for a generic observable A we construct an analogue of (6.26). We turn functions in phase space to operators in Hilbert space and the Poisson bracket is replaced by a commutator divided by $i\hbar$. All in all, this allows us to write the *Heisenberg equations of motion*

$$i\hbar \frac{dA}{dt} = [A, H] \quad (6.35)$$

It is important to be honest about the above reasoning. It wasn't a strictly rigorous derivation. We proceeded by analogy, comparison and consistency relations. They are reasonable, but the only way to verify is by comparing with experiment.

The expression itself is deceptively simple. If we pick a simple Hamiltonian:

$$H = \frac{P^2}{2m} + V(X) \quad (6.36)$$

Then the Heisenberg equations of motion for X and P will take on a very familiar form³⁵:

$$\dot{X} = \frac{P}{m} \quad (6.37)$$

$$\dot{P} = -V'(X) \quad (6.38)$$

but remember these are *not* your usual classical equations of motion. These are equations for *operators* for whom the product isn't commutative. Your intuition from classical mechanics will not hold unless we can find a particularly simple basis. In fact Heisenberg's original method for solving for quantum dynamics was finding a simple (*i.e.* diagonal) basis for his matrices (*i.e.* operators), and only then solving the equations of motion. This is why this method is often called *matrix mechanics*.

Nevertheless we can use the classical-like expressions for the equations of motion to derive *Ehrenfest's theorem*, that states the expectation values of quantum observables obey classical equations of motion. We just have to take the expectation value of (6.38).

$$\begin{cases} \dot{X} = \frac{P}{m} \\ \dot{P} = -V'(X) \end{cases} \implies \begin{cases} \langle \dot{X} \rangle = \frac{\langle P \rangle}{m} \\ \langle \dot{P} \rangle = -\langle V'(X) \rangle \end{cases} \implies \begin{cases} \langle \dot{X} \rangle = \frac{\langle P \rangle}{m} \\ \langle \dot{P} \rangle = -V'(\langle X \rangle) \end{cases} \quad (6.39)$$

The first implication is trivial but the last one is not. We are exchanging the derivative with the expectation value (usually involving an integral). Only if the potential V is nice enough will we be able to do that exchange. And this is not just mathematical pedantry. For some physical applications, such as cold atoms, it is a good approximation to take the potential as a Dirac- δ , which is definitely not nice enough for the above reasoning. In that case Ehrenfest's theorem may not apply.

6.3 A unifying picture

In the previous two sections we constructed two different versions of time-dependent quantum systems. The Schrodinger picture has operators, A_S which are constant in time and kets, $|\psi(t)\rangle_S$ which evolve unitarily in time determined by the Hamiltonian:

$$A_S(t) = A_S(t_0) = A_S \quad i\hbar \frac{d}{dt} |\psi(t)\rangle_S = H_S |\psi(t)\rangle_S \quad (6.40)$$

The Heisenberg picture has kets $|\psi\rangle_H$ which are constant in time, and operators $A_H(t)$ which evolve according to the Heisenberg equation of motion, constructed in analogy with the Poisson brackets

$$i\hbar \frac{d}{dt} A_H(t) = [A_H, H_H] \quad |\psi(t)\rangle_H = |\psi(t_0)\rangle_H = |\psi\rangle_H \quad (6.41)$$

³⁵If you are concerned about the $V'(X)$ because we are taking a derivative wrt to an operator, just remember how we defined functions of observables—by their action on an eigenbasis. You can then construct the function V' in the usual way and just apply that to the eigenvalues.

Despite their aesthetic differences they are in fact one and the same. Just two alternative pictures of the same quantum system. To make this connection we shall assume that both pictures agree at time $t = t_0$ that is

$$A_H(t_0) = A_S \quad |\psi(t_0)\rangle_S = |\psi\rangle_H \quad (6.42)$$

Because the Hamiltonian commutes with itself it also easy to show that

$$H_H = H_S = H \quad (6.43)$$

for all times.

For simplicity, let us first assume that the Hamiltonian has no explicit time dependence. Then it is straightforward to solve both the Schrodinger and the Heisenberg equations:

$$|\psi(t)\rangle_S = e^{-\frac{i}{\hbar}Ht} |\psi(t_0)\rangle_S \quad (6.44)$$

$$A_H(t) = e^{\frac{i}{\hbar}Ht} A_H(t_0) e^{-\frac{i}{\hbar}Ht} \quad (6.45)$$

To see the equivalence between the two pictures we can look at the time dependence of the generic matrix element $\langle \chi | A | \psi \rangle$. We can then write:

$$\begin{aligned} \langle \chi(t) |_S A_S(t) | \psi(t) \rangle_S &= \langle \chi(t_0) |_S e^{\frac{i}{\hbar}Ht} A_S(t_0) e^{-\frac{i}{\hbar}Ht} |\psi(t_0)\rangle_S = \\ &= \langle \chi(t_0) |_H e^{\frac{i}{\hbar}Ht} A_H(t_0) e^{-\frac{i}{\hbar}Ht} |\psi(t_0)\rangle_H = \\ &= \langle \chi(t) |_H A_H(t) |\psi(t)\rangle_H \end{aligned} \quad (6.46)$$

Thereby demonstrating the two pictures give exactly the same expression for the matrix element at all instances in time. We must therefore conclude that they must be equivalent.

To show this is also true for Hamiltonians which depend explicitly on time, we use the time evolution operator $U(t, t_0)$ defined by the following differential equation

$$i\hbar \frac{d}{dt} U(t, t_0) = H U(t, t_0) \quad (6.47)$$

with the boundary condition

$$U(t_0, t_0) = 1 \quad (6.48)$$

Using the Hermiticity of H and (6.6) it is easy to show that U defined in this way is unitary. In terms of this operator the solution to Schrodinger's and Heisenberg's equations of motion is then given by

$$|\psi(t)\rangle_S = U(t, t_0) |\psi(t_0)\rangle_S \quad (6.49)$$

$$A_H(t) = U(t, t_0)^\dagger A_H(t_0) U(t, t_0) \quad (6.50)$$

From here it is easy to again show that the time evolution of the matrix elements is the same in both pictures.

All in all, we have these two alternative pictures for the time evolution of quantum systems, both equally valid and giving equivalent answers. Which one is better? As usual it depends on which questions we're trying to answer.

At its most complex Schrodinger's picture will involve some PDEs where the solutions will be some vector who is a function of all the continuous variables. Functions and vectors are much easier to deal with than operators so in many applications Schrodinger's picture will be the most straightforward. Additionally, for the case when the Hamiltonian is time

independent it will be very helpful to go to the eigenbasis of the Hamiltonian. The equation for finding the eigenstates of the Hamiltonian is the following:

$$H |\psi\rangle = E |\psi\rangle \quad (6.51)$$

or in position space reads

$$\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \psi(x, t) = E \psi(x, t) \quad (6.52)$$

which is so similar to the Schrodinger equation of motion it is commonly called the *time independent Schrodinger equation* or TISE for short. So, even we want to use the Heisenberg picture we will very often start by solving the TISE as if we were in the Schrodinger picture.

The real advantage of the Heisenberg picture is the easy comparison with classical mechanics. For example, proving Ehrenfest's theorem was trivial in the Heisenberg picture and takes a bit more work in the Schrodinger picture. When we have lots of symmetries, dealing with operators directly will also often lead to very slick algebraic reasonings which would be very opaque in the Schrodinger picture. When those methods work (like we will see for the harmonic oscillator and the angular momentum) they are far quicker than solving a complicated PDE. For more generic cases using Schrodinger's equation is easier.

In the future we will use whatever picture is best for the problem at hand. In fact, if that is convenient we might swap pictures mid way through a problem. As with everything in Physics everything is fair game, use whatever works.

Now that we have a complete picture for the time evolution on either states or operators we can prove one final uncertainty relation—the one involving time and energy. At first this might seem impossible, time in quantum mechanics has not been promoted to an operator like position, it is instead an external label. Therefore it seems like we can't apply the generalised Heisenberg uncertainty principle. However, if we're a bit clever we can use the uncertainty relation between H and a generic observable A :

$$\Delta_\psi H \Delta_\psi A \geq \frac{1}{2} |\langle [H, A] \rangle| \geq \frac{\hbar}{2} \left| \left\langle \frac{dA}{dt} \right\rangle \right| \quad (6.53)$$

If we define

$$\Delta_{\psi,At} \equiv \frac{\Delta_\psi A}{\left| \frac{d\langle A \rangle}{dt} \right|} \quad (6.54)$$

then we can write, assuming the expectation value commutes with the derivative

$$\Delta_\psi H \Delta_{\psi,At} \geq \frac{\hbar}{2} \quad (6.55)$$

which is the time-energy uncertainty relation.

Notice, however, the meaning of $\Delta_{\psi,At}$. It is the time it takes for the expectation value of A to change by one standard deviation. Rather than relating the uncertainty in energy to the uncertainty in time, it relates the uncertainty in energy to the time it takes for the system in study to change significantly. It not only depends on the state $|\psi\rangle$ as usual but it now also depends on the specific observable A you are using. This change might be faster for one observable than another. If, however, the uncertainty in energy is small then this time interval must be large, *i.e.* all observables must change very gradually. In the limit when we are dealing with an energy eigenstate then the expectation values cannot change at all. Conversely, if at least one observable changes very dramatically then we must have a very large uncertainty in energy.

6.4 Symmetries and conserved quantities

One of the seminal results of classical dynamics is Noether's theorem relating symmetries to conserved quantities. You will be pleased to find out that this fact carries through rather straightforwardly to quantum dynamics.

Firstly, what is a symmetry in the quantum context? We shall define symmetry to mean any transformation of the states which leaves all transition probabilities invariant:

$$|\psi\rangle \rightarrow |\psi'\rangle \quad \text{such that} \quad |\langle\psi|\chi\rangle|^2 = |\langle\psi'|\chi'\rangle|^2 \quad (6.56)$$

This may seem rather abstract but there is a general theorem by Eugene Wigner that states that any such transformation that does not reverse the direction of time³⁶ can be represented by a linear and unitary operator:

$$|\psi\rangle \rightarrow |\psi'\rangle = U|\psi\rangle \quad \text{such that} \quad UU^\dagger = \mathbb{1} \quad (6.57)$$

As per usual with these kinds of actions we can instead keep the kets invariant and just change the operators via

$$A \rightarrow A' = U^\dagger AU \quad (6.58)$$

Additionally we shall also impose that the relation (6.56) is valid at all instances in time, *i.e.*

$$|\langle\psi(t)|\chi(t)\rangle|^2 = |\langle\psi'(t)|\chi'(t)\rangle|^2 \quad (6.59)$$

for all t .

This implies that³⁷

$$U|\psi(t)\rangle = U(t, t_0)U|\psi(t_0)\rangle \quad (6.60)$$

Taking time derivatives and using Shrodinger's equation it is straightforward to see that we must therefore impose that

$$[H, U] = 0 \iff U^\dagger HU = H \quad (6.61)$$

so that the Hamiltonian is itself unchanged by the symmetry transformation.

This is already close to our desired result. Unitary matrices are also diagonalisable, at least in the finite dimensional case. Therefore, the above invariance of the Hamiltonian means we can simultaneously diagonalise both H and U . This in turn means we can classify eigenstates of H by their transformation properties. In other words, if we want to find energy eigenstates (which is typically quite hard) we can start by looking at states for which U acts diagonally (which is typically a lot easier). This may seem rather trivial but applying the symmetries first and only then trying to solve the TISE is typically much easier.

Example. The parity transformation is usually defined such that $P : \mathbf{x} \rightarrow -\mathbf{x}$. In the quantum mechanical setup, we shall then define the parity transformation by its action on the position operator

$$P^\dagger X P = -X \quad (6.62)$$

Using the fact the canonical commutator between X and P is a number we find that

³⁶The symmetry that corresponds to time reversal is instead *anti*-linear and *anti*-unitary.

³⁷Apologies for the confusion between the symmetry transformation U and the time evolution operator $U(t, t_0)$. They will only mix in this single equation.

the momentum transforms as

$$\mathbf{P}^\dagger \mathbf{P} \mathbf{P} = -\mathbf{P} \quad (6.63)$$

Therefore, parity is a symmetry of the Hamiltonian

$$H = \frac{P^2}{2m} + V(X) \quad (6.64)$$

if the potential is a symmetric function, *i.e.* $V(x) = V(-x)$.

If instead we consider its action on a wavefunction we find

$$\mathbf{P}\psi(x) = \psi(-x) \quad (6.65)$$

Additionally, applying it twice takes us back to the same situation, we therefore write

$$\mathbf{P}^2 = \mathbb{1} \quad (6.66)$$

Assuming that $\psi(x)$ is an eigenstate of \mathbf{P} with eigenvalue η we can write

$$\psi(x) = \mathbf{P}^2\psi(x) = \eta^2\psi(x) \quad (6.67)$$

and therefore $\eta = \pm 1$ are the only allowed eigenvalues of \mathbf{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 :

$$\mathbf{P}\psi(x) = \psi(-x) = \pm\psi(x) \quad (6.68)$$

Despite that success, U is unitary rather than Hermitian so it will not directly correspond to a physical observable which could possibly be our candidate for conserved quantity. To find this conserved quantity and prove the quantum version of Noether's theorem we must consider continuous symmetries. For those symmetries we can write

$$U(\epsilon) = \mathbb{1} - i\epsilon Q + O(\epsilon^2) \quad (6.69)$$

where Q is some ϵ -independent operator. Applying the same reasoning we applied for the time evolution operator in (6.6) we conclude that

$$Q^\dagger = Q \quad (6.70)$$

The operator Q that generates infinitesimal symmetries is Hermitian, and therefore corresponds to an observable.

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

$$U(\theta) = U(\theta/N)^N = \left(\mathbb{1} - i\frac{\theta}{N} Q \right)^N \xrightarrow{N \rightarrow \infty} e^{-i\theta Q} \quad (6.71)$$

Where in taking the limit we used the definition of the exponential³⁸. We see that Q generates the whole symmetry, not just the infinitesimal limit.

Combining (6.58) and (6.71) for small θ we find:

$$A' = U^\dagger A U = e^{i\theta Q} A e^{-i\theta Q} \approx A + i\theta [Q, A] + O(\theta^2) \quad (6.72)$$

³⁸This is slightly non trivial because Q is an operator rather than a number. However, because Q is Hermitian we can just go to its eigenbasis and then the operator can be replaced by the eigenvalue.

Therefore, the action of the infinitesimal symmetry on an operator corresponds to the commutator with the symmetry generator.

To get Noether’s theorem we just have to apply this expression to the Hamiltonian.

$$H = U^\dagger H U \implies [Q, H] = 0 \quad (6.73)$$

so the symmetry generator must also commute with the Hamiltonian.

Applying the Heisenberg equation of motion we therefore conclude that, in the Heisenberg picture,

$$\frac{dQ}{dt} = 0 \quad (6.74)$$

which is our conservation law. Even in the Schrodinger picture, any matrix element with the symmetry generator will be conserved.

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.

Additionally, because the conserved charge Q is Hermitian and commutes with the Hamiltonian, we can simultaneously diagonalise them. This means that we 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 $U : x \rightarrow x + a$ where a is some continuous parameter. In quantum mechanics we therefore define:

$$U(a)^\dagger X U(a) = X + a \quad (6.75)$$

Taking a to be small and using (6.72) we find

$$ia[Q, X] = a \implies [X, Q] = i \quad (6.76)$$

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

$$\psi(x + a) = e^{-\frac{i}{\hbar} Pa} \psi(x) = e^{a \frac{d}{dx}} \psi(x) \quad (6.77)$$

7 The “free” particle

In the next few chapters we will consider several simple 1-dimensional examples of quantum systems, to get acquainted with some key quantum phenomena and tools. We begin with the simplest of them all, a free particle, whose Hamiltonian is simply given by:

$$H = \frac{P^2}{2m} \quad (7.1)$$

Using our symmetry language from the previous section, we see that this Hamiltonian is translation invariant. Therefore we should look at eigenstates of the operator P .

$$P |p\rangle = p |p\rangle \quad (7.2)$$

The energy of these eigenstates is simply given by

$$H|p\rangle = \frac{p^2}{2m}|p\rangle \implies E_p = \frac{p^2}{2m} \quad (7.3)$$

In the position basis, this states look like:

$$\psi_p(x, t) = \langle x | e^{-\frac{i}{\hbar}E_p t} | p \rangle = e^{\frac{i}{\hbar}(px - E_p t)} \quad (7.4)$$

As expected, free particles correspond to plane waves. We in fact already knew this, we used this result when we tried to justify the Planck relation $E = \hbar\omega$. But here is precisely our issue—plane waves are *not* normalisable! In fact we should write something like

$$\psi_p(x, t) = C e^{\frac{i}{\hbar}(px - E_p t)} \quad (7.5)$$

for some unknown constant C because we do not have a priori 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, for physical states we really struggle to interpret this non-normalisability. 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

$$\psi(x) = 0 \quad \text{if } x > a \quad \text{or} \quad x < -a \quad (7.6)$$

Assuming that the wavefunction is continuous³⁹ it is perfectly reasonable to use the following Dirichlet boundary conditions

$$\psi(x) = 0 \quad \text{for } x = \pm a \quad (7.7)$$

All in all, in the position basis, we wish to solve the following equation:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} = E\psi(x) \quad (7.8)$$

subject to the boundary conditions in (7.7).

The general solution to this equation is given by a linear combination of exponentials

$$\psi(x) = A e^{ikx} + B e^{-ikx} \quad (7.9)$$

where

$$E = \frac{\hbar^2 k^2}{2m} \quad (7.10)$$

³⁹This 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.

We now just have to impose the boundary conditions. They correspond to the following conditions:

$$\begin{cases} \psi(a) = 0 \\ \psi(-a) = 0 \end{cases} \iff \begin{cases} Ae^{ika} + Be^{-ika} = 0 \\ Ae^{-ika} + Be^{ika} = 0 \end{cases} \quad (7.11)$$

The first of these can be solved to give

$$B = -Ae^{2ika} \quad (7.12)$$

so that

$$\psi(x) = A\left(e^{ikx} - e^{-ik(x-2a)}\right) = 2iAe^{ika} \sin(k(x-a)) = C \sin(k(x-a)) \quad (7.13)$$

where we put all of the constants in front into a single constant C to be determined when we normalise our wavefunction. Imposing that

$$\int_{-a}^a dx |\psi(x)|^2 = 1 \quad (7.14)$$

we find

$$|C| = \frac{1}{\sqrt{a}} \quad (7.15)$$

Imposing the second boundary condition gives us

$$\sin(2ka) = 0 \implies k = \frac{\pi n}{2a} \quad n \in \mathbb{Z} \quad (7.16)$$

With these boundary conditions our wavenumber comes in discrete multiples! This is a key feature of quantum mechanics, its boundary conditions often yield discrete outcomes.

All in all, our solution will be

$$\psi(x) = \frac{1}{\sqrt{a}} \sin\left(\frac{\pi n}{2a}(x-a)\right) \quad (7.17)$$

whose energy is given by

$$E_n = \frac{\hbar^2 \pi^2 n^2}{8a^2 m} \quad (7.18)$$

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

$$\begin{aligned} \psi(-x) &= \frac{1}{\sqrt{a}} \sin\left(\frac{\pi n}{2a}(-x-a)\right) = -\frac{1}{\sqrt{a}} \sin\left(\frac{\pi n}{2a}(x+a)\right) = \\ &= -\frac{1}{\sqrt{a}} \sin\left(\frac{\pi n}{2a}(x-a) + \pi n\right) = -(-1)^n \frac{1}{\sqrt{a}} \sin\left(\frac{\pi n}{2a}(x-a)\right) = \\ &= (-1)^{n+1} \psi(x) \end{aligned} \quad (7.19)$$

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^2 , 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 perfectly normalisable and were 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:

$$P\psi(x) = -i\hbar \frac{\partial\psi(x)}{\partial x} = -\frac{i\hbar\pi n}{2a\sqrt{a}} \cos\left(\frac{\pi n}{2a}(x-a)\right) \quad (7.20)$$

which is *not* a multiple of $\psi(x)$.

And our situation is worse, we can compute the expectation value of the momentum as

$$\begin{aligned} \langle P \rangle &= \int_{-a}^a dx \psi^*(x) \left(-i\hbar \frac{\partial\psi(x)}{\partial x} \right) = \\ &= -\frac{i\hbar\pi n}{2a^2} \int_{-a}^a dx \sin\left(\frac{\pi n}{2a}(x-a)\right) \cos\left(\frac{\pi n}{2a}(x-a)\right) = \\ &= -\frac{i\hbar\pi n}{4a^2} \int_{-a}^a dx \sin\left(\frac{\pi n}{a}(x-a)\right) = 0 \end{aligned} \quad (7.21)$$

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. By imposing that the wavefunction vanishes outside our box it is equivalent to having an infinite potential outside the box

$$V(x) = \begin{cases} 0 & -a < x < a \\ \infty & \text{otherwise} \end{cases} \quad (7.22)$$

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 e^{ikx} and e^{-ikx} , *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

$$\psi(x + L) = \psi(x) \quad (7.23)$$

These boundary conditions are equivalent to considering a particle on a circle of radius $R = L/2\pi$.

INSERT PICTURE

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 eigenstate of P with eigenvalue p :

$$\psi_p(x) = C e^{\frac{i}{\hbar} px} \quad (7.24)$$

we then impose (7.23)

$$e^{\frac{i}{\hbar} p(x+L)} = e^{\frac{i}{\hbar} px} \implies e^{\frac{i}{\hbar} pL} = 1 \implies p = \frac{2\pi\hbar n}{L} = \frac{\hbar n}{R} \quad n \in \mathbb{Z} \quad (7.25)$$

The energy is given by

$$E = \frac{p^2}{2m} = \frac{\hbar^2 n^2}{2mL^2} = \frac{\hbar^2 n^2}{2mR^2} \quad (7.26)$$

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 \hbar/L or equivalently \hbar/R ,

It is trivial to show that

$$\int_0^L dx |\psi_p(x)|^2 = |C|^2 L \quad (7.27)$$

therefore our normalised wavefunctions will be

$$\psi_p(x) = \frac{e^{2\pi i n \frac{x}{L}}}{\sqrt{L}} = \frac{e^{i n \frac{x}{R}}}{\sqrt{2\pi R}} \quad (7.28)$$

identifying the angle around the circle as $\theta = x/R$ we can also write them as

$$\psi_p(\theta) = \frac{e^{i n \theta}}{\sqrt{2\pi R}} \quad (7.29)$$

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

$$L = |n|\lambda \quad (7.30)$$

therefore $|n|$ complete waves fit into the circle. In fact, this was the original motivation for de Broglie, he wanted to use this quantisation condition to explain the discrete spectrum of the Hydrogen atom. He thought of the electron as orbiting the nucleus the same way planets orbit the Sun, then this condition could explain why electrons couldn’t have orbits of any shape, they could only fit in discrete levels. Although 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 $R \rightarrow \infty$ 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 or 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 \hbar/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. In order to have the particle contained in a range of positions we must therefore 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 $f(p)$:

$$\psi(x, t) = \int \frac{dp}{\hbar} f(p) e^{\frac{i}{\hbar}(px - E_p t)} \quad (7.31)$$

This is called a *wavepacket*.

Imposing that this wavepacket is correctly normalised requires

$$\begin{aligned} 1 &= \int dx |\psi(x)|^2 = \\ &= \int dx \frac{dp dq}{h^2} f^*(p) f(q) e^{\frac{it}{\hbar}(E_p - E_q)} e^{\frac{ix}{\hbar}(q-p)} \\ &= \int \frac{dp dq}{h^2} f^*(p) f(q) e^{\frac{it}{\hbar}(E_p - E_q)} 2\pi\delta\left(\frac{q-p}{\hbar}\right) \\ &= \int \frac{dp dq}{h} f^*(p) f(q) e^{\frac{it}{\hbar}(E_p - E_q)} \delta(q-p) \\ &= \int \frac{dp}{h} |f(p)|^2 \end{aligned} \quad (7.32)$$

The wavepacket approach is the most mathematically rigorous, 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 :

$$f(p) = \sqrt{\frac{h}{\sigma\sqrt{2\pi}}} \exp\left(-\frac{(p-p_0)^2}{4\sigma^2}\right) \quad (7.33)$$

INSERT PLOT

To show that the above choice of f is indeed correctly normalised we just have to use the expression for the Gaussian integral

$$\int dx e^{-a(x-x_0)^2} = \sqrt{\frac{\pi}{a}} \quad (7.34)$$

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

$$\tilde{\psi}(p, t) = \int dx e^{-\frac{i}{\hbar}px} \psi(x, t) = f(p) e^{-\frac{i}{\hbar}E_p t} \quad (7.35)$$

We can now compute various averages of position and momentum to see what this wavepacket represents.

$$\begin{aligned} \langle P \rangle &= \int \frac{dp}{h} p |f(p)|^2 = \\ &= \int \frac{dp}{h} p \frac{h}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(p-p_0)^2}{2\sigma^2}\right) = \\ &= \frac{1}{\sigma\sqrt{2\pi}} \int dq (q + p_0) \exp\left(-\frac{q^2}{2\sigma^2}\right) = \\ &= p_0 \end{aligned} \quad (7.36)$$

where we have used (7.34) and that

$$\int dx x e^{-ax^2} = 0 \quad (7.37)$$

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 $\Delta_\psi P$. First we compute

$$\begin{aligned} \langle P^2 \rangle &= \int \frac{dp}{h} p^2 |f(p)|^2 = \\ &= \int \frac{dp}{h} p^2 \frac{h}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(p-p_0)^2}{2\sigma^2}\right) = \\ &= \frac{1}{\sigma\sqrt{2\pi}} \int dq (q + p_0)^2 \exp\left(-\frac{q^2}{2\sigma^2}\right) = \\ &= p_0^2 + \sigma^2 \end{aligned} \quad (7.38)$$

where we used (7.34), (7.37) and

$$\int dx x^2 e^{-ax^2} = \frac{\sqrt{\pi}}{2a^{3/2}} \quad (7.39)$$

so that

$$\Delta_\psi P = \sqrt{\langle (P - \langle P \rangle)^2 \rangle} = \sqrt{\langle P^2 \rangle - \langle P \rangle^2} = \sigma \quad (7.40)$$

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

$$X\tilde{\psi}(p, t) = i\hbar \frac{\partial \tilde{\psi}(p, t)}{\partial p} \quad (7.41)$$

we then obtain

$$\begin{aligned} \langle X \rangle &= \int \frac{dp}{\hbar} f^*(p) e^{\frac{i}{\hbar} E_p t} i\hbar \frac{\partial}{\partial p} \left(f(p) e^{-\frac{i}{\hbar} E_p t} \right) = \\ &= \int dp \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(p-p_0)^2}{2\sigma^2}\right) i\hbar \left(-\frac{p-p_0}{2\sigma^2} - \frac{ipt}{\hbar m}\right) = \\ &= \int dq \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{q^2}{2\sigma^2}\right) i\hbar \left(-\frac{q}{2\sigma^2} - \frac{i(q+p_0)t}{\hbar m}\right) = \\ &= \frac{p_0 t}{m} \end{aligned} \quad (7.42)$$

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

$$\begin{aligned} \langle X^2 \rangle &= \int \frac{dp}{\hbar} f^*(p) e^{\frac{i}{\hbar} E_p t} (-\hbar^2) \frac{\partial^2}{\partial p^2} \left(f(p) e^{-\frac{i}{\hbar} E_p t} \right) = \\ &= -\hbar^2 \int \frac{dp}{\hbar} f^*(p) e^{\frac{i}{\hbar} E_p t} \frac{\partial}{\partial p} \left(\left(-\frac{p-p_0}{2\sigma^2} - \frac{ipt}{\hbar m}\right) f(p) e^{-\frac{i}{\hbar} E_p t} \right) = \\ &= -\hbar^2 \int dp \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(p-p_0)^2}{2\sigma^2}\right) \left(-\frac{1}{2\sigma^2} - \frac{it}{\hbar m} + \left(-\frac{p-p_0}{2\sigma^2} - \frac{ipt}{\hbar m}\right)^2\right) = \\ &= \hbar^2 \int dq \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{q^2}{2\sigma^2}\right) \left(\frac{1}{2\sigma^2} + \frac{it}{\hbar m} - \left(\frac{q}{2\sigma^2} + \frac{i(q+p_0)t}{\hbar m}\right)^2\right) = \\ &= \hbar^2 \int dq \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{q^2}{2\sigma^2}\right) \left(\frac{1}{2\sigma^2} + \frac{it}{\hbar m} - q^2 \left(\frac{1}{2\sigma^2} + \frac{it}{\hbar m}\right)^2 + \frac{p_0^2 t^2}{\hbar^2 m^2}\right) = \\ &= \frac{\hbar^2}{2\sigma^2} + \frac{i\hbar t}{m} + \frac{p_0^2 t^2}{m^2} - \hbar^2 \sigma^2 \left(\frac{1}{2\sigma^2} + \frac{it}{\hbar m}\right)^2 = \\ &= \frac{p_0^2 t^2}{m^2} + \frac{\hbar^2}{4\sigma^2} + \frac{t^2 \sigma^2}{m^2} \end{aligned} \quad (7.43)$$

This was a bit trickier but now we can reap the benefits of our hard work. The uncertainty in X is given by

$$\Delta_\psi X = \sqrt{\frac{\hbar^2}{4\sigma^2} + \frac{t^2 \sigma^2}{m^2}} \quad (7.44)$$

which, in contrast with the uncertainty in P grows with time!

At $t = 0$ the uncertainty in X is minimal, and in fact

$$\Delta_\psi X \Delta_\psi P = \frac{\hbar}{2} \quad (7.45)$$

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

$$x_0 + \delta x + t(v_0 + \delta v) - (x_0 - \delta x + t(v_0 - \delta v)) = 2\delta x + 2t\delta v \quad (7.46)$$

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 (6.20). 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

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0 \quad (7.47)$$

where $\mathbf{j} \equiv \rho \mathbf{v}$ and \mathbf{v} is the velocity of the particles at point \mathbf{x} .

We can interpret \mathbf{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 \mathbf{j} has units $\text{m}^{-2} \text{ s}^{-1}$.

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In 1 dimension, we can instead write

$$\frac{\partial \rho}{\partial t} + \frac{\partial j}{\partial x} = 0 \quad (7.48)$$

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 (6.20) and (6.22) 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 (6.20) 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

$$|\psi(x, t)|^2 = |C|^2 \quad (7.49)$$

which is a constant, and

$$j = \frac{i\hbar}{2m} \left(\frac{\partial \psi^*}{\partial x} \psi - \psi^* \frac{\partial \psi}{\partial x} \right) = \frac{p}{m} |C|^2 \quad (7.50)$$

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 (6.20). Moreover, instead of discussing total probabilities for a given process, say a scattering of an electron off 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 be 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:

$$V(x) = \begin{cases} 0 & x < 0 \\ V & x > 0 \end{cases} \quad (8.1)$$

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

$$\psi(x) = Ae^{ikx} + Be^{-ikx}, \quad x < 0 \quad (8.2)$$

where A and B are two complex constants. The energy of these solutions is given by

$$E = \frac{\hbar^2 k^2}{2m} \quad (8.3)$$

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

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + V\psi(x) = E\psi(x) \iff -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} = (E - V)\psi(x) \quad (8.4)$$

therefore the solutions will be exactly the same as for the free particles⁴⁰, with the exchange $E \rightarrow E - V$:

$$\psi(x) = Ce^{iqx} + De^{-iqx}, \quad x > 0 \quad (8.5)$$

where, once more, C and D are some complex constants. The energy will be given by

$$E - V = \frac{\hbar^2 q^2}{2m} \quad (8.6)$$

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

⁴⁰This is why we will focus on piecewise constant potentials, the solution is always just a sum of plane waves.

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 $x \rightarrow \infty$, 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 (6.19) (remembering to multiply by $\exp(-\frac{i}{\hbar}Et)$ to capture the time dependence) we find

$$j(x) = \begin{cases} \frac{\hbar k}{m} (|A|^2 - |B|^2) & x < 0 \\ \frac{\hbar q}{m} |C|^2 & x > 0 \end{cases} \quad (8.7)$$

we therefore define the *incoming flux*

$$j_{\text{inc}} \equiv \frac{\hbar k}{m} |A|^2 \quad (8.8)$$

the *reflected flux*

$$j_{\text{ref}} \equiv \frac{\hbar k}{m} |B|^2 \quad (8.9)$$

and the *transmitted flux*

$$j_{\text{trans}} \equiv \frac{\hbar q}{m} |C|^2 \quad (8.10)$$

It is straightforward to show that the particle density is a constant in time, therefore the fluxes must match at $x = 0$ which means

$$j_{\text{inc}} - j_{\text{ref}} = j_{\text{trans}} \implies j_{\text{inc}} = j_{\text{ref}} + j_{\text{trans}} \quad (8.11)$$

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

$$P_{\text{ref}} = \frac{j_{\text{ref}}}{j_{\text{inc}}} = \frac{|B|^2}{|A|^2} \quad (8.12)$$

and the probability that a particle is transmitted is similarly given by

$$P_{\text{trans}} = \frac{j_{\text{trans}}}{j_{\text{inc}}} = \frac{|C|^2 q}{|A|^2 k} \quad (8.13)$$

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 $x = 0$:

$$\begin{aligned} -\frac{\hbar^2}{2m} \int_{-\epsilon}^{\epsilon} dx \frac{\partial^2 \psi(x)}{\partial x^2} &= \int_{-\epsilon}^{\epsilon} dx (E - V(x)) \psi(x) \\ -\frac{\hbar^2}{2m} \left(\frac{\partial \psi(x)}{\partial x} \Big|_{x=\epsilon} - \frac{\partial \psi(x)}{\partial x} \Big|_{x=-\epsilon} \right) &= \int_{-\epsilon}^{\epsilon} dx (E - V(x)) \psi(x) \end{aligned} \quad (8.14)$$

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 continuous⁴¹. 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

$$\begin{cases} \psi(0) \text{ continuous} \\ \psi'(0) \text{ continuous} \end{cases} \implies \begin{cases} A + B = C \\ ikA - ikB = iqC \end{cases} \implies \begin{cases} B = \frac{k-q}{k+q}A \\ C = \frac{2k}{k+q}A \end{cases} \quad (8.15)$$

Plugging these results into (8.12) and (8.13) we find

$$P_{\text{ref}} = \left(\frac{k-q}{k+q} \right)^2 \quad (8.16)$$

$$P_{\text{trans}} = \frac{4kq}{(k+q)^2} \quad (8.17)$$

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

$$k = \frac{\sqrt{2mE}}{\hbar} \quad (8.18)$$

$$q = \frac{\sqrt{2m(E-V)}}{\hbar} \quad (8.19)$$

Instead of thinking of incoming energy, we can also use incoming momentum and write q as a function of k

$$q = \sqrt{k^2 - \frac{2mV}{\hbar}} \quad (8.20)$$

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 $E \rightarrow V$ then $q \rightarrow 0$ which means $P_{\text{ref}} \rightarrow 1$ and $P_{\text{trans}} \rightarrow 0$. If the particle has basically no energy above the potential then it is almost

⁴¹If 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.

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*:

$$q^2 = \frac{2m(E - V)}{\hbar^2} < 0 \quad (8.21)$$

This means that our solution for $x > 0$ is not an outgoing particle but a decaying exponential. Defining $\eta = -iq$ we have

$$\psi(x) = Ce^{-\eta x} \quad x > 0 \quad (8.22)$$

for

$$\eta = \frac{\sqrt{2m(V - E)}}{\hbar} \quad (8.23)$$

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

$$B = \frac{k + i\eta}{k - i\eta} A \quad (8.24)$$

$$C = \frac{2k}{k - i\eta} A \quad (8.25)$$

The calculations for the fluxes however is quite different because B and C are no longer real.

$$j_{\text{ref}} = \frac{\hbar k}{2m} B^* B = \frac{\hbar k}{2m} |A|^2 \frac{k + i\eta}{k - i\eta} \frac{k - i\eta}{k + i\eta} = \frac{\hbar k}{2m} |A|^2 = j_{\text{inc}} \quad (8.26)$$

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 show that the transmitted flux vanishes

$$j_{\text{trans}} = \frac{i\hbar}{2m} \left(\frac{\partial \psi^*}{\partial x} \psi - \psi^* \frac{\partial \psi}{\partial x} \right) = 0 \quad (8.27)$$

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

$$V(x) = \begin{cases} V & -a < x < a \\ 0 & \text{otherwise} \end{cases} \quad (8.28)$$

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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

$$\psi(x) = \begin{cases} e^{ikx} + Re^{-ikx} & x < -a \\ Ae^{iqx} + Be^{-iqx} & -a < x < a \\ Te^{ikx} & x > a \end{cases} \quad (8.29)$$

where

$$k = \frac{\sqrt{2mE}}{\hbar} \quad (8.30)$$

$$q = \frac{\sqrt{2m(E-V)}}{\hbar} \quad (8.31)$$

depending on the sign of $E - V$, the wavenumber in the middle region, q might be positive or negative.

We have chosen to only have incoming particles from the left, and therefore not included a term $\propto e^{-ikx}$ 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 ratio of the velocities as we did in (8.13). The probabilities for reflection and transmission are therefore given by

$$P_{\text{ref}} = |R|^2 \quad (8.32)$$

$$P_{\text{trans}} = |T|^2 \quad (8.33)$$

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

$$e^{-ika} + Re^{ika} = Ae^{-iqa} + Be^{iqa} \quad (8.34)$$

$$ik(e^{-ika} - Re^{ika}) = iq(Ae^{-iqa} - Be^{iqa}) \quad (8.35)$$

$$Ae^{iqa} + Be^{-iqa} = Te^{ika} \quad (8.36)$$

$$iq(Ae^{iqa} - Be^{-iqa}) = ikTe^{ika} \quad (8.37)$$

Solving this linear system of equations is straightforward if a bit tedious, the solution is

$$A = \frac{k(q+k)e^{-i(q+k)a}}{2kq\cos(2qa) - i(q^2+k^2)\sin(2qa)} \quad (8.38)$$

$$B = \frac{k(q-k)e^{i(q-k)a}}{2kq\cos(2qa) - i(q^2+k^2)\sin(2qa)} \quad (8.39)$$

$$R = \frac{i(q^2-k^2)e^{-2ika}\sin(2qa)}{2kq\cos(2qa) - i(q^2+k^2)\sin(2qa)} \quad (8.40)$$

$$T = \frac{2kqe^{-2ika}}{2kq\cos(2qa) - i(q^2+k^2)\sin(2qa)} \quad (8.41)$$

From here we can compute the probabilities of reflection and transmission

$$P_{\text{ref}} = |R|^2 = \frac{(q^2-k^2)^2 \sin^2(2qa)}{4k^2q^2 \cos^2(2qa) + (q^2+k^2)^2 \sin^2(2qa)} \quad (8.42)$$

$$P_{\text{trans}} = |T|^2 = \frac{4k^2q^2}{4k^2q^2 \cos^2(2qa) + (q^2+k^2)^2 \sin^2(2qa)} \quad (8.43)$$

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 $q \rightarrow k$ 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 $E \rightarrow V$ then $q \rightarrow 0$ 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

$$E = V + \frac{n^2\pi^2\hbar^2}{8ma^2} \quad (8.44)$$

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

$$\eta \equiv -iq = \frac{\sqrt{2m(V-E)}}{\hbar} \quad (8.45)$$

we can write down the new coefficients

$$A = \frac{k(\eta - ik)e^{-ika}e^{\eta a}}{2k\eta \cosh(2\eta a) - i(k^2 - \eta^2)\sinh(2\eta a)} \quad (8.46)$$

$$B = \frac{k(\eta + ik)e^{-ika}e^{-\eta a}}{2k\eta \cosh(2\eta a) - i(k^2 - \eta^2)\sinh(2\eta a)} \quad (8.47)$$

$$R = \frac{-i(\eta^2 + k^2)e^{-2ika}\sinh(2\eta a)}{2k\eta \cosh(2\eta a) - i(k^2 - \eta^2)\sinh(2\eta a)} \quad (8.48)$$

$$T = \frac{2k\eta e^{-2ika}}{2k\eta \cosh(2\eta a) - i(k^2 - \eta^2)\sinh(2\eta a)} \quad (8.49)$$

and the new probabilities

$$P_{\text{ref}} = \frac{(\eta^2 + k^2)^2 \sinh^2(2\eta a)}{4k^2\eta^2 + (k^2 + \eta^2)^2 \sinh^2(2\eta a)} \quad (8.50)$$

$$P_{\text{trans}} = \frac{4k^2\eta^2}{4k^2\eta^2 + (k^2 + \eta^2)^2 \sinh^2(2\eta a)} \quad (8.51)$$

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

$$\Delta X \gtrsim 2a \quad (8.52)$$

but this implies an uncertainty in momentum of

$$\Delta P \gtrsim \frac{\hbar}{2a} \quad (8.53)$$

and therefore an uncertain in energy of

$$\Delta E \gtrsim \frac{\hbar^2}{8ma^2} \quad (8.54)$$

Additionally, in order to be sure we observe negative energy this uncertainty would have to be less than $V - E$ and therefore

$$\frac{\hbar^2\eta^2}{2m} \gtrsim \Delta E \gtrsim \frac{\hbar^2}{8ma^2} \quad (8.55)$$

combining these two we find we would need, at the very least,

$$2\eta a \gtrsim 1 \quad (8.56)$$

However, in the limit $2\eta a \gg 1$ we have

$$P_{\text{trans}} \approx \frac{16\eta^2 k^2}{(k^2 + \eta^2)^2} e^{-4\eta a} \quad (8.57)$$

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

$$\log P_{\text{trans}} = \text{const} - 2\eta L \quad (8.58)$$

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

$$\log P_{\text{total}} \approx \sum \log P_{\text{slice}} = -2 \sum L_{\text{slice}} \eta_{\text{slice}} \approx -2 \int dx \eta(x) \quad (8.59)$$

where

$$\eta(x) = \frac{\sqrt{2m(V(x) - E)}}{\hbar} \quad (8.60)$$

All in all we wish to write something on the lines of

$$P_{\text{total}} = C \exp\left(-\frac{2}{\hbar} \int dx \sqrt{2m(V(x) - E)}\right) \quad (8.61)$$

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 below zero so that we are considering a potential well? In this section we shall consider the potential

$$V(x) = \begin{cases} -V_0 & -a < x < a \\ 0 & \text{otherwise} \end{cases} \quad (8.62)$$

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

$$\lambda = -ik = \frac{\sqrt{-2mE}}{\hbar} \quad (8.63)$$

such that the generic solution for $|x| > a$ will be

$$\psi(x) = Ae^{-\lambda x} + Be^{\lambda x} \quad (8.64)$$

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.*

$$\psi(x) = \begin{cases} Ae^{\lambda x} & x < -a \\ Be^{-\lambda x} & x > a \end{cases} \quad (8.65)$$

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

$$\psi(x) = Ce^{-iqx} + De^{-iqx} \quad \text{for } -a < x < a \quad (8.66)$$

where

$$q = \frac{\sqrt{2m(E + V_0)}}{\hbar} \quad (8.67)$$

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 6.4, 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

$$\psi(x) = \psi(-x) \quad (8.68)$$

Imposing this condition on (8.65) and (8.66) we find

$$A = B \quad C = D \quad (8.69)$$

which allows us to write (we have relabelled $C \rightarrow C/2$ for convenience)

$$\psi(x) = \begin{cases} Ae^{-\lambda|x|} & |x| > a \\ C \cos(qx) & |x| < a \end{cases} \quad (8.70)$$

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

$$Ae^{-\lambda a} = C \cos(qa) \quad (8.71)$$

$$-\lambda Ae^{-\lambda a} = -Cq \sin(qa) \quad (8.72)$$

Dividing these two equations we find

$$\lambda = q \tan(qa) \quad (8.73)$$

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

$$q^2 + \lambda^2 = \frac{2mV_0}{\hbar^2} \quad (8.74)$$

we can see that the allowed energies correspond to the intersection of the function

$$f(z) = z \tan z \quad (8.75)$$

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 $V_0 \rightarrow \infty$ 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

$$E + V_0 \approx \frac{\hbar^2\pi^2(2n-1)^2}{8ma^2} \quad (8.76)$$

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.*

$$(n-1)\pi < z < \left(n - \frac{1}{2}\right)\pi \quad (8.77)$$

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

$$\psi(x) = -\psi(-x) \quad (8.78)$$

therefore we must impose

$$A = -B \quad C = -D \quad (8.79)$$

which allows us to write (once again relabelling C to something more convenient)

$$\psi(x) = \begin{cases} \text{sgn}(x)Ae^{-\lambda|x|} & |x| > a \\ C \sin(qx) & |x| < a \end{cases} \quad (8.80)$$

The continuity relations will look like

$$Ae^{-\lambda a} = C \sin(qa) \quad (8.81)$$

$$-\lambda Ae^{-\lambda a} = Cq \cos(qa) \quad (8.82)$$

Once again diving the two gives

$$\lambda = -q \cot(qa) \quad (8.83)$$

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

$$f(z) = -z \cot z \quad (8.84)$$

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 cotangent function has its first zero at $z = \pi/2$ we conclude there are only parity-odd eigenfunctions if

$$\frac{2mV_0a^2}{\hbar^2} > \frac{\pi^2}{4} \quad (8.85)$$

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 $V_0 \rightarrow \infty$ 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:

$$E + V_0 \approx \frac{\hbar^2 \pi^2 (2n)^2}{8ma^2} \quad (8.86)$$

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 $x \rightarrow -\infty$. 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

$$\psi_{\pm}(x) = \psi(x) \pm \psi(-x) = \begin{cases} e^{ikx} + (R \pm T)e^{-ikx} & x < -a \\ (A \pm B)e^{ikx} + (B \pm A)e^{-ikx} & -a < x < a \\ \pm e^{-ikx} + (T \pm R)e^{ikx} & x > a \end{cases} \quad (8.87)$$

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

$$R + T = e^{-2ika} \frac{ik - q \tan(qa)}{ik + q \tan(qa)} \quad (8.88)$$

$$R - T = -e^{-2ika} \frac{q + ik \tan(qa)}{q - ik \tan(qa)} \quad (8.89)$$

which makes it easy to show that

$$|R \pm T|^2 = 1 \quad (8.90)$$

and therefore, these coefficients are just phases.

Our scenario is then the following. We have an incoming wavefunction of $e^{-i|x|}$ or $-\text{sgn}(x)e^{-i|x|}$, 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 $(R + T)e^{ik|x|}$ or $-\text{sgn}(x)(R - T)e^{ik|x|}$, 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 $\lambda = -ik$. Our solution (ignoring the middle bit) will then look like

$$\psi_{\pm}(x) = \begin{cases} e^{-\lambda x} + (R \pm T)e^{\lambda x} & x < -a \\ \pm e^{\lambda x} + (T \pm R)e^{-\lambda x} & x > a \end{cases} \quad (8.91)$$

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

$$\psi_{\pm}(x) = \begin{cases} \frac{1}{R \pm T} e^{-\lambda x} + e^{\lambda x} & x < -a \\ \frac{\pm 1}{R \pm T} e^{\lambda x} \pm e^{-\lambda x} & x > a \end{cases} \quad (8.92)$$

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 $\lambda = -ik$ the expressions (8.88) and (8.89) blow up if

$$\lambda = q \tan(qa) \quad (8.93)$$

$$\lambda = -q \cot(qa) \quad (8.94)$$

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. Exper-

imentally 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 system⁴².

Our goal in this chapter to find the spectrum of the following Hamiltonian

$$H = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 X^2 \quad (9.1)$$

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.

9.1 Solving the differential equation

The TISE in the position basis for the harmonic oscillator looks like

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + \frac{1}{2}m\omega^2 x^2 \psi(x) = E\psi(x) \quad (9.2)$$

We can simplify this equation by defining new variables

$$y = \sqrt{\frac{m\omega}{\hbar}} x \quad (9.3)$$

$$\mathcal{E} = \frac{2E}{\hbar\omega} \quad (9.4)$$

⁴²A 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.

in terms of which the equation becomes

$$\frac{d^2\psi(y)}{dy^2} + (\mathcal{E} - y^2)\psi(y) = 0 \quad (9.5)$$

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

$$\frac{d^2\psi(y)}{dy^2} - y^2\psi(y) \approx 0 \quad (9.6)$$

which is approximately solved by

$$\psi(y) \approx Ae^{-y^2/2} + Be^{y^2/2} \quad (9.7)$$

Note that this isn't an exact solution of (9.6), it is only an approximate solution in the large y limit, in fact

$$\frac{d^2\psi(y)}{dy^2} = Ay^2e^{-y^2/2} + By^2e^{y^2/2} - Ae^{-y^2/2} + Be^{y^2/2} \quad (9.8)$$

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

$$\psi(y) \rightarrow Ae^{-y^2/2} \quad (9.9)$$

as $y^2 \rightarrow \infty$.

All in all this motivates peeling off this exponential behaviour and defining

$$\psi(y) \equiv h(y)e^{-y^2/2} \quad (9.10)$$

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

$$h''(y) - 2yh'(y) + (\mathcal{E} - 1)h(y) = 0 \quad (9.11)$$

Let us try a power series solution for $h(y)$:

$$h(y) = \sum_{n=1}^{\infty} a_n y^n \quad (9.12)$$

plugging this in we find the following recursion relation for the coefficients a_n

$$(n+2)(n+1)a_{n+2} = (2n+1 - \mathcal{E})a_n \quad (9.13)$$

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

$n \rightarrow \infty$. In this limit, the recursion relation is given approximately by

$$a_{n+2} = \frac{2}{n} a_n \quad (9.14)$$

This can be approximately solved using factorials

$$a_n \approx \frac{C}{(n/2)!} \quad (9.15)$$

as can be seen from

$$\frac{(n/2)!}{(n/2 + 1)!} = \frac{1}{n/2 + 1} \approx \frac{2}{n} \quad (9.16)$$

In that case, asymptotically, $h(y)$ would be given by

$$h(y) \rightarrow \sum_n C \frac{y^n}{(n/2)!} = \sum_{n'} C \frac{y^{2n'}}{n'!} = C e^{y^2} \quad (9.17)$$

But this is bad, it means

$$\psi(y) \rightarrow C e^{y^2/2} \quad (9.18)$$

which is again not normalisable!

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

$$2n + 1 - \mathcal{E} = 0 \quad (9.19)$$

In turn this implies that the only allowed energies are

$$\mathcal{E}_n = 2n + 1 \implies E_n = \hbar\omega \left(n + \frac{1}{2} \right) \quad (9.20)$$

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 $n \rightarrow j$)

$$a_{j+2} = 2 \frac{j-n}{(j+2)(j+1)} a_j \quad (9.21)$$

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

$$H_0(y) = 1 \quad (9.22)$$

$$H_1(y) = 2y \quad (9.23)$$

$$H_2(y) = 4y^2 - 2 \quad (9.24)$$

$$H_3(y) = 8y^3 - 12y \quad (9.25)$$

$$H_4(y) = 16y^4 - 48y^2 + 12 \quad (9.26)$$

$$H_5(y) = 32y^5 - 160y^3 + 120y \quad (9.27)$$

notice how even-numbered polynomials only involve even powers of y and similarly for the odd-numbered ones.

There are many important properties of these polynomials but the most important one is their orthogonality

$$\int dy e^{-y^2} H_n(y) H_m(y) = 2^n n! \sqrt{\pi} \delta_{nm} \quad (9.28)$$

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

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right) e^{-\frac{m\omega x^2}{2\hbar}} \quad (9.29)$$

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

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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 than at the middle where 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

$$\frac{dX}{dt} = \frac{P}{m} \quad (9.30)$$

$$\frac{dP}{dt} = -m\omega^2 X \quad (9.31)$$

These are simple but they are not diagonal. It would be 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

$$A = \alpha X + \beta P \quad (9.32)$$

such that its Heisenberg evolution is given by

$$\frac{dA}{dt} = \lambda A \quad (9.33)$$

To find α , β , and λ we impose (9.31):

$$\frac{dA}{dt} = \alpha \frac{dX}{dt} + \beta \frac{dP}{dt} = \alpha \frac{P}{m} - \beta m\omega^2 X \quad (9.34)$$

equating with (9.33) we get

$$\begin{cases} -\beta m\omega^2 = \lambda\alpha \\ \frac{\alpha}{m} = \lambda\beta \end{cases} \implies \begin{cases} \lambda^2 = -\omega^2 \\ \beta = \frac{\alpha}{m\lambda} \end{cases} \quad (9.35)$$

In particular λ is pure imaginary and we can write

$$\frac{dA^\pm}{dt} = \pm i\omega A^\pm \quad (9.36)$$

where

$$A^\pm = \alpha \left(X \mp \frac{i}{m\omega} P \right) \quad (9.37)$$

These operators have a particularly simple time dependence:

$$A^\pm(t) = e^{\pm i\omega t} A^\pm(0) \quad (9.38)$$

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

$$[A^-, A^+] = \alpha^2 \left(-\frac{i}{m\omega} [X, P] + \frac{i}{m\omega} [P, X] \right) = \frac{2\alpha^2 \hbar}{m\omega} \quad (9.39)$$

We define the normalisation by setting this commutator to 1, correspond to the choice

$$\alpha = \frac{m\omega}{2\hbar} \quad (9.40)$$

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:

$$a = \sqrt{\frac{m\omega}{2\hbar}} \left(X + \frac{i}{m\omega} P \right) \quad (9.41)$$

which obey

$$[a, a^\dagger] = 1 \quad (9.42)$$

and whose time dependence in the Heisenberg picture is given by

$$a(t) = a(0)e^{-i\omega t} \quad (9.43)$$

We can also invert this definition to write X and P in terms of a and a^\dagger :

$$X = \sqrt{\frac{\hbar}{2m\omega}} (a + a^\dagger) \quad (9.44)$$

$$P = -i\sqrt{\frac{\hbar m\omega}{2}} (a - a^\dagger) \quad (9.45)$$

and plug these expressions back into the Hamiltonian to find

$$H = \frac{\hbar\omega}{2} (aa^\dagger + a^\dagger a) = \hbar\omega \left(a^\dagger a + \frac{1}{2} \right) \quad (9.46)$$

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

$$[H, a] = -\hbar\omega a \quad [H, a^\dagger] = \hbar\omega a^\dagger \quad (9.47)$$

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 :

$$H|E\rangle = E|E\rangle \quad (9.48)$$

then the state $a|E\rangle$ will also be an energy eigenstate but with energy $E - \hbar\omega$

$$Ha|E\rangle = ([H, a] + aH)|E\rangle = (E - \hbar\omega)a|E\rangle \quad (9.49)$$

Similarly, the ket $a^\dagger|E\rangle$ will have energy $E + \hbar\omega$

$$Ha^\dagger|E\rangle = ([H, a^\dagger] + a^\dagger H)|E\rangle = (E + \hbar\omega)a^\dagger|E\rangle \quad (9.50)$$

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

$$a|0\rangle = 0 \quad (9.51)$$

thereby terminating our cascade and finding the lowest energy eigenvalue. This is the *ground state* and it has energy

$$H|0\rangle = \hbar\omega \left(a^\dagger a + \frac{1}{2} \right) |0\rangle = \frac{\hbar\omega}{2} |0\rangle \quad (9.52)$$

The remaining energy eigenstates can be found by repeated application of a^\dagger :

$$|n\rangle = C(a^\dagger)^n |0\rangle \quad (9.53)$$

with energy

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right) \quad (9.54)$$

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

$$\begin{aligned} \langle n|n\rangle &= |C|^2 \langle 0| a^n (a^\dagger)^n |0\rangle = \\ &= |C|^2 \langle 0| a^{n-1} (1 + a^\dagger a) (a^\dagger)^{n-1} |0\rangle = \\ &= 2|C|^2 \langle 0| a^{n-1} (a^\dagger)^{n-1} |0\rangle + |C|^2 \langle 0| a^{n-1} (a^\dagger)^2 a (a^\dagger)^{n-2} |0\rangle = \dots \\ &= n|C|^2 \langle 0| a^{n-1} (a^\dagger)^{n-1} |0\rangle + |C|^2 \langle 0| a^{n-1} (a^\dagger)^n a |0\rangle = \\ &= n|C|^2 \langle 0| a^{n-1} (a^\dagger)^{n-1} |0\rangle = \dots \\ &= n!|C|^2 \langle 0|0\rangle \end{aligned} \quad (9.55)$$

therefore, if $|0\rangle$ is correctly normalised we should choose $C = \frac{1}{\sqrt{n!}}$ and hence define the normalised energy eigenstates via

$$|n\rangle = \frac{1}{\sqrt{n!}} (a^\dagger)^n |0\rangle \quad (9.56)$$

In particular we can use this definition to show that

$$a^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle \quad \text{and} \quad a |n\rangle = \sqrt{n} |n-1\rangle \quad (9.57)$$

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

$$\langle x| a |0\rangle = 0 \implies \left(x + \frac{\hbar}{m\omega} \frac{d}{dx} \right) \psi_0(x) = 0 \quad (9.58)$$

where $\psi_0(x) = \langle x|0\rangle$. This is an easily solvable first order differential equation

$$\psi_0(x) = B e^{-\frac{m\omega x^2}{2\hbar}} \quad (9.59)$$

to find B we just impose that $\langle 0|0\rangle = 1$ or equivalently

$$1 = \int dx |\psi_0(x)|^2 = \int dx |B|^2 e^{-\frac{m\omega x^2}{\hbar}} = |B|^2 \sqrt{\frac{\pi\hbar}{m\omega}} \quad (9.60)$$

Therefore we must impose $B = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}$:

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}} \quad (9.61)$$

For higher n we have

$$\begin{aligned} \psi_n(x) &= \frac{1}{\sqrt{n!}} \left(\frac{m\omega}{\pi\hbar}\right) \left(\frac{m\omega}{2\hbar}\right)^{n/2} \left(x - \frac{\hbar}{m\omega} \frac{d}{dx}\right)^n e^{-\frac{m\omega x^2}{2\hbar}} = \\ &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} \left(y - \frac{d}{dy}\right)^n e^{-y^2/2} \end{aligned} \quad (9.62)$$

where we, once again, defined for convenience

$$y = \sqrt{\frac{m\omega}{\hbar}} x \quad (9.63)$$

This is of course some polynomial of degree n multiplied by $e^{-y^2/2}$. We can use the Rodrigues's formula

$$H_n(y) = e^{y^2/2} \left(y - \frac{d}{dy}\right)^n e^{-y^2/2} \quad (9.64)$$

to once again identify the Hermite polynomials. We then obtain

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n\left(\sqrt{\frac{m\omega}{\hbar}} x\right) e^{-\frac{m\omega x^2}{2\hbar}} \quad (9.65)$$

as expected.

Central Potentials and Angular Momentum

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.

Chapter 10. Spherical symmetry
 Chapter 11. Solving the radial equation
 Chapter 12. Spin

10 Spherical symmetry

In this chapter we will study particles subjected to a central potential, *i.e.* ones whose potential is given by $V(\mathbf{x}) = V(r)$ where $r^2 = |\mathbf{x}|^2 = x^2 + y^2 + z^2$. 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:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \quad (10.1)$$

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, \mathbf{X} and \mathbf{P} . Fourier transforms are now written as

$$\tilde{\psi}(\mathbf{k}) = \int d^3x e^{-i\mathbf{k}\cdot\mathbf{x}} \psi(\mathbf{x}) \quad (10.2)$$

with inverse given by

$$\psi(\mathbf{x}) = \int \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k}\cdot\mathbf{x}} \tilde{\psi}(\mathbf{k}) \quad (10.3)$$

The Dirac- δ is now defined via

$$\int d^3x f(\mathbf{x})\delta^{(3)}(\mathbf{x} - \mathbf{x}') = f(\mathbf{x}') \quad (10.4)$$

You can think of this Dirac- δ as the product of the Dirac- δ s for the individual directions

$$\delta^{(3)}(\mathbf{x}) = \delta(x)\delta(y)\delta(z) \quad (10.5)$$

It can also be represented in terms of Fourier modes as

$$\delta^{(3)}(\mathbf{x}) = \int \frac{d^3k}{(2\pi)^3} e^{ik \cdot x} \quad (10.6)$$

The de Broglie relation between wavenumber and momentum will now imply that the momentum in the position basis acts like the gradient operator:

$$\mathbf{P} = -i\hbar\nabla \quad (10.7)$$

therefore, the commutator between the position and momentum gives

$$[X_i, P_j] = i\hbar\delta_{ij} \quad (10.8)$$

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

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(\mathbf{x}) + V(r)\psi(\mathbf{x}) = E\psi(\mathbf{x}) \quad (10.9)$$

where ∇^2 is the 3-dimensional Laplacian:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (10.10)$$

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

$$H = \frac{\mathbf{P}_e^2}{2m_e} + \frac{\mathbf{P}_N^2}{2m_N} + V(\mathbf{X}_e - \mathbf{X}_N) \quad (10.11)$$

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:

$$\mathbf{X}_{\text{rel}} \equiv \mathbf{X}_e - \mathbf{X}_N \quad \mathbf{X}_{\text{CM}} = \frac{m_e \mathbf{X}_e + m_N \mathbf{X}_N}{m_e + m_N} \quad (10.12)$$

and similarly a relative and centre of mass momentum variables

$$\mathbf{P}_{\text{rel}} \equiv \mu \left(\frac{\mathbf{P}_e}{m_e} - \frac{\mathbf{P}_N}{m_N} \right) \quad \mathbf{P}_{\text{CM}} = \mathbf{P}_e + \mathbf{P}_N \quad (10.13)$$

where

$$\mu \equiv \frac{m_e m_N}{m_e + m_N} \quad (10.14)$$

It is straightforward to then verify that

$$H = \frac{\mathbf{P}_{\text{rel}}^2}{2\mu} + \frac{\mathbf{P}_{\text{CM}}^2}{2(m_e + m_N)} + V(\mathbf{X}_{\text{rel}}) \quad (10.15)$$

You can also verify that the new position and momentum variables satisfy the usual relation:

$$\begin{cases} \mathbf{P}_e = -i\hbar \nabla_e \\ \mathbf{P}_N = -i\hbar \nabla_N \end{cases} \implies \begin{cases} \mathbf{P}_{\text{rel}} = -i\hbar \nabla_{\text{rel}} \\ \mathbf{P}_{\text{CM}} = -i\hbar \nabla_{\text{CM}} \end{cases} \quad (10.16)$$

which in turn means they obey the canonical commutation relations, and additionally, the two sets of variables completely commute

$$[\mathbf{P}_{\text{rel}}, \mathbf{X}_{\text{CM}}] = [\mathbf{X}_{\text{rel}}, \mathbf{P}_{\text{CM}}] = 0 \quad (10.17)$$

Therefore the Hamiltonian fully commutes with \mathbf{P}_{CM} , so eigenstates of H can also be taken to be eigenstates of \mathbf{P}_{CM} , and therefore we can write

$$\psi(\mathbf{x}_{\text{CM}}, \mathbf{x}_{\text{rel}}) = e^{\frac{i}{\hbar} \mathbf{P}_{\text{CM}} \cdot \mathbf{x}_{\text{CM}}} \psi(\mathbf{x}_{\text{rel}}) \quad (10.18)$$

where $\psi(\mathbf{x}_{\text{rel}})$ 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

$$E_{\text{tot}} = E + \frac{\mathbf{P}_{\text{CM}}^2}{2(m_e + m_N)} \quad (10.19)$$

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.* ${}^1\text{H}$, with a single proton in the nucleons, and ${}^2\text{H}$ with a proton and a neutron, usually called *deuterium*. These have quite different nucleon masses: $m_{{}^1\text{H}} \approx 1836m_e$ and $m_{{}^2\text{H}} \approx 3670m_e$; and consequently slightly different reduced masses: $\mu_{{}^1\text{H}} \approx 0.99945m_e$ and $\mu_{{}^2\text{H}} = 0.99973m_e$. 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

$$x = r \sin \theta \cos \phi \quad y = r \sin \theta \sin \phi \quad z = r \cos \theta \quad (10.20)$$

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

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad (10.21)$$

So that the TISE looks like

$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi(r, \theta, \phi)}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi(r, \theta, \phi)}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi(r, \theta, \phi)}{\partial \phi^2} \right] + V(r)\psi(r, \theta, \phi) = E\psi(r, \theta, \phi) \quad (10.22)$$

This looks rather complicated but we can try separation of variables to solve it. That is we look for solutions of the type:

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi) \quad (10.23)$$

in terms of which (10.22) becomes

$$\begin{aligned} & \frac{1}{R(r)} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) - \frac{2\mu r^2}{\hbar^2} (V(r) - E) = \\ &= -\frac{1}{Y(\theta, \phi)} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} \right) \end{aligned} \quad (10.24)$$

The LHS only depends on r and the RHS only depends on θ and ϕ ; therefore they must both equal some constant λ :

$$\frac{1}{R(r)} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) - \frac{2\mu r^2}{\hbar^2} (V(r) - E) = \lambda \quad (10.25)$$

$$-\frac{1}{Y(\theta, \phi)} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} \right) = \lambda \quad (10.26)$$

Bearing in mind that the integration measure in polar coordinates is

$$d^3x = r^2 \sin \theta dr d\theta d\phi \quad (10.27)$$

the condition that $\psi(r, \theta, \phi)$ is square integrable becomes, in terms of the new variables

$$\int_0^\infty dr r^2 |R(r)|^2 < \infty \quad \text{and} \quad \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta |Y(\theta, \phi)|^2 < \infty \quad (10.28)$$

we sometimes also write

$$d^2\Omega = d\phi d\theta \sin \theta \quad (10.29)$$

as the differential *solid angle* for simplicity.

Let us focus on the angular equation:

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} + \lambda Y(\theta, \phi) = 0 \quad (10.30)$$

To solve this equation we once again try separation of variables:

$$Y(\theta, \phi) = P(\theta)\Phi(\phi) \quad (10.31)$$

plugging this in we find:

$$\frac{1}{P(\theta)} \left(\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{dP(\theta)}{d\theta} \right) + \lambda \sin^2 \theta P(\theta) \right) = -\frac{1}{\Phi(\phi)} \frac{d^2 \Phi(\phi)}{d\phi^2} \quad (10.32)$$

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:

$$\frac{1}{P(\theta)} \left(\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{dP(\theta)}{d\theta} \right) + \lambda \sin^2 \theta P(\theta) \right) = m^2 \quad (10.33)$$

$$-\frac{1}{\Phi(\phi)} \frac{d^2 \Phi(\phi)}{d\phi^2} = m^2 \quad (10.34)$$

The condition for square integrability in these variables becomes

$$\int_0^{2\pi} d\phi |\Phi(\phi)|^2 < \infty \quad \text{and} \quad \int_0^\pi d\theta \sin \theta |P(\theta)|^2 < \infty \quad (10.35)$$

The solution to the ϕ equation is quite straightforward:

$$\Phi(\phi) = C e^{\pm im\phi} \quad (10.36)$$

and from this we obtain our first quantisation condition. In spherical coordinates single-valued functions must be periodic under $\phi \rightarrow \phi + 2\pi$, 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

$$z = \cos \theta \quad (10.37)$$

in terms of which the equation becomes

$$\frac{d}{dz} \left((1-z^2) \frac{dP(z)}{dz} \right) + \lambda P(z) - \frac{m^2}{1-z^2} P(z) = 0 \quad (10.38)$$

Let us first examine the $m = 0$ case and try a power series solution

$$P(z) = \sum_{n=0}^{\infty} a_n z^n \quad (10.39)$$

We can then plug this in to derive a recurrence relation among these coefficients

$$(n+2)(n+1)a_{n+2} = (n^2 + n - \lambda)a_n \quad (10.40)$$

Similarly to what we did for the harmonic oscillator let us examine the large n behaviour:

$$\frac{a_{n+2}}{a_n} \rightarrow 1 \quad (10.41)$$

This means that for large n , the series comes a polynomial in z plus

$$C \sum_n z^n = \frac{C}{1-z} \quad (10.42)$$

but this is singular at $z = 1$, or equivalently $\theta = 0$. In fact, this solution is not square

integrable!

$$\int_0^\pi d\theta \sin \theta |P(\theta)|^2 = \int_{-1}^1 dz |P(z)|^2 \quad (10.43)$$

but

$$\int_{-1}^1 dz \frac{1}{|1-z|^2} \quad (10.44)$$

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

$$\lambda = \ell(\ell + 1) \quad (10.45)$$

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

$$\frac{d}{dz} \left((1 - z^2) \frac{dP_\ell(z)}{dz} \right) + \ell(\ell + 1) P_\ell(z) = 0 \quad (10.46)$$

and the first few are given by

$$P_0(z) = 1 \quad (10.47)$$

$$P_1(z) = z \quad (10.48)$$

$$P_2(z) = \frac{1}{2}(3z^2 - 1) \quad (10.49)$$

$$P_3(z) = \frac{1}{2}(5z^3 - 3z) \quad (10.50)$$

$$P_4(z) = \frac{1}{8}(35z^4 - 30z^2 + 3) \quad (10.51)$$

where they are conventionally normalised such that

$$\int_{-1}^1 dz P_\ell(z) P_{\ell'}(z) = \frac{1}{\ell + \frac{1}{2}} \delta_{\ell\ell'} \quad (10.52)$$

From the Legendre polynomials it is not too hard to obtain the solution for generic m . Firstly, we notice that

$$P_\ell^m(z) = (-1)^m (1 - z^2)^{m/2} \frac{d^m}{dz^m} P_\ell(z) \quad (10.53)$$

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

$$|m| \leq \ell \quad (10.54)$$

We can therefore write the full solution for the angular equation:

$$Y_\ell^m(\theta, \psi) \propto P_\ell^{|m|}(\cos \theta) e^{im\phi} \quad (10.55)$$

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

$$P_\ell^{-|m|}(z) = (-1)^{|m|} \frac{(\ell - |m|)!}{(\ell + |m|)!} P_\ell^{|m|}(z) \quad (10.56)$$

we can write the normalised spherical harmonics as

$$Y_\ell^m(\theta, \psi) = \sqrt{\frac{\ell + \frac{1}{2}}{2\pi} \frac{(\ell - m)!}{(\ell + m)!}} e^{im\phi} P_\ell^m(\cos \theta) \quad (10.57)$$

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

$$\hat{x} = \frac{x}{r} \quad (10.58)$$

we can write

$$1 = \hat{x}^2 = \hat{x}^2 + \hat{y}^2 + \hat{z}^2 \quad (10.59)$$

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

$$P_\ell(\alpha \hat{x}, \alpha \hat{y}, \alpha \hat{z}) = \alpha^\ell P_\ell(\hat{x}, \hat{y}, \hat{z}) \quad (10.60)$$

For example we can write

$$P_2(\hat{z}) = \frac{1}{2}(3\hat{z}^2 - 1) = \frac{1}{2}(3\hat{z}^2 - \hat{x}^2 - \hat{y}^2 - \hat{z}^2) = \hat{z}^2 - \frac{1}{2}(\hat{x}^2 + \hat{y}^2) \quad (10.61)$$

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:

$$x_\pm = x \pm iy = r \sin \theta e^{\pm i\phi} \quad (10.62)$$

this allows us to write (for $m > 0$)

$$(1 - \hat{z}^2)^{|m|/2} e^{\pm im\phi} = (\sin \theta)^{|m|} e^{\pm im\phi} = \hat{x}_\pm^m \quad (10.63)$$

Therefore the spherical harmonics are homogeneous polynomials of degree ℓ in the variables \hat{x}_\pm and \hat{z} . Where the number ν_\pm of factors \hat{x}_\pm must be such that

$$m = \nu_+ - \nu_- \quad (10.64)$$

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

$$\nabla^2(r^\ell Y_\ell^m) = 0 \quad (10.65)$$

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 $\ell \leq 2$.

$\ell = 0$: 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

$$Y_0^0 = \frac{1}{\sqrt{4\pi}} \quad (10.66)$$

$\ell = 1$: 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

$$Y_1^1 = -\sqrt{\frac{3}{8\pi}} \hat{x}_+ = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi} \quad (10.67)$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \hat{z} = \sqrt{\frac{3}{4\pi}} \cos \theta \quad (10.68)$$

$$Y_1^{-1} = \sqrt{\frac{3}{8\pi}} \hat{x}_- = \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi} \quad (10.69)$$

$\ell = 2$: 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:

$$\nabla^2(r^2 Y_2^0) = \nabla^2(Ax_+ x_- + Bz^2) = \nabla^2(A(x^2 + y^2) + Bz^2) = 4A + 2B \quad (10.70)$$

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

$$Y_2^2 = \sqrt{\frac{15}{32\pi}} \hat{x}_+^2 = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{2i\phi} \quad (10.71)$$

$$Y_2^1 = -\sqrt{\frac{15}{8\pi}} \hat{x}_+ \hat{z} = -\sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\phi} \quad (10.72)$$

$$Y_2^0 = \sqrt{\frac{5}{16\pi}} (2\hat{z} - \hat{x}_+ \hat{x}_-) = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1) \quad (10.73)$$

$$Y_2^{-1} = \sqrt{\frac{15}{8\pi}} \hat{x}_- \hat{z} = \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{-i\phi} \quad (10.74)$$

$$Y_2^{-2} = \sqrt{\frac{15}{32\pi}} \hat{x}_-^2 = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{-2i\phi} \quad (10.75)$$

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

$$\int d^2\Omega Y_\ell^m(\theta, \phi)^* Y_{\ell'}^{m'}(\theta, \phi) = \delta_{\ell\ell'} \delta_{mm'} \quad (10.76)$$

additionally they change by a factor of $(-1)^\ell$ under parity:

$$Y_\ell^m(\pi - \theta, \pi + \phi) = (-1)^\ell Y_\ell^m(\theta, \phi) \quad (10.77)$$

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. The 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

$$\mathbf{L} = \mathbf{X} \times \mathbf{P} \quad (10.78)$$

which in the position basis becomes

$$\mathbf{L} = -i\hbar \mathbf{x} \times \nabla \quad (10.79)$$

We can also write these using Einstein summation convention and the Levi-Civita symbol

$$L_i = \epsilon_{ijk} X_j P_k = -i\hbar \epsilon_{ijk} x_j \frac{\partial}{\partial x_k} \quad (10.80)$$

where

$$\epsilon_{ijk} = \begin{cases} 1 & \text{even permutation of } 123 \\ -1 & \text{odd permutation of } 123 \\ 0 & \text{otherwise} \end{cases} \quad (10.81)$$

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 \mathbf{L} with the position and momentum:

$$[L_i, X_j] = \epsilon_{ikl} X_k [P_l, X_j] = -i\hbar \epsilon_{ikl} X_k \delta_{lj} = i\hbar \epsilon_{ijk} X_k \quad (10.82)$$

$$[L_i, P_j] = \epsilon_{ikl} [X_k, P_j] P_l = i\hbar \epsilon_{ikl} \delta_{kj} P_l = i\hbar \epsilon_{ijk} P_k \quad (10.83)$$

where we have used (10.8).

Using these results we can also compute the commutator between different components of the angular momentum

$$[L_i, L_j] = \epsilon_{jkl} [L_i, X_k P_l] = \epsilon_{jkl} ([L_i, X_k] P_l + X_k [L_i, P_l]) \quad (10.84)$$

$$= i\hbar \epsilon_{jkl} (\epsilon_{ikm} X_m P_l + X_k \epsilon_{ilm} P_m) \quad (10.85)$$

using the following identity

$$\epsilon_{ijk} \epsilon_{lmk} = \delta_{il} \delta_{jm} - \delta_{im} \delta_{jl} \quad (10.86)$$

we find

$$[L_i, L_j] = i\hbar (X_m P_l (\delta_{ji} \delta_{lm} - \delta_{jm} \delta_{li}) - X_k P_m (\delta_{ji} \delta_{km} - \delta_{jm} \delta_{ki})) \quad (10.87)$$

$$= i\hbar (X_i P_j - X_j P_i) \quad (10.88)$$

however, using (10.86) we find

$$\epsilon_{ijk} L_k = \epsilon_{ijk} \epsilon_{klm} X_l P_m = (\delta_{il} \delta_{jm} - \delta_{im} \delta_{jl}) X_l P_m = X_i P_j - X_j P_i \quad (10.89)$$

therefore we conclude that

$$[L_i, L_j] = i\hbar\epsilon_{ijk}L_k \quad (10.90)$$

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 \mathbf{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 $\hat{\mathbf{v}}$ and then rotating about an angle β around an axis $\hat{\mathbf{u}}$ is not the same as doing it in the reverse order:

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Although as we will see later, despite appearances \mathbf{L} is *not* the generator of rotations.

In any case we can write the above commutation relations in a more generic way, let \mathbf{V} be a stand-in for \mathbf{X} , \mathbf{P} or \mathbf{L} ⁴³. Then we can summarise the above commutation relations as

$$[L_i, V_j] = i\hbar\epsilon_{ijk}V_k \quad (10.91)$$

Then, if \mathbf{U} is another vector which satisfies the same commutation relation (could be equal to \mathbf{V} or it could be different), then the following will hold for the inner product of the two

$$[L_i, V_j U_j] = V_j [L_i, U_j] + [L_i, V_j] U_j = i\hbar\epsilon_{ijk}(V_j U_k + V_k U_j) = 0 \quad (10.92)$$

where in the last equality we used the antisymmetry of the Levi-Civita symbol.

In particular this means we can write

$$[\mathbf{L}, \mathbf{X}^2] = [\mathbf{L}, \mathbf{P}^2] = [\mathbf{L}, \mathbf{L}^2] = 0 \quad (10.93)$$

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 \mathbf{X}^2 and \mathbf{P}^2 , therefore we conclude

$$[\mathbf{L}, H] = 0 \quad (10.94)$$

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 \mathbf{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 \mathbf{L}^2 and L_z , *i.e.* states $|\lambda, m\rangle$ that satisfy

$$\mathbf{L}^2 |\lambda, m\rangle = \hbar^2 \lambda |\lambda, m\rangle \quad (10.95)$$

$$L_z |\lambda, m\rangle = \hbar m |\lambda, m\rangle \quad (10.96)$$

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:

$$L_{\pm} = L_x \pm iL_y \quad (10.97)$$

The reason we call these “ladder” operators is because of their commutation relations with

⁴³In fact, this will work for any vector constructed from \mathbf{X} and \mathbf{P}

L_z and \mathbf{L}^2

$$[L_z, L_{\pm}] = [L_z, L_x] \pm i[L_z, L_y] = i\hbar L_y \pm \hbar L_x = \pm \hbar(L_x \pm iL_y) = \pm \hbar L_{\pm} \quad (10.98)$$

$$[\mathbf{L}^2, L_{\pm}] = [\mathbf{L}^2, L_x] \pm i[\mathbf{L}^2, L_y] = 0 \quad (10.99)$$

Using these we can calculate the action of \mathbf{L}^2 and L_z on the state $L_{\pm} |\lambda, m\rangle$

$$\mathbf{L}^2 L_{\pm} |\lambda, m\rangle = L_{\pm} \mathbf{L}^2 |\lambda, m\rangle = \hbar^2 \lambda L_{\pm} |\lambda, m\rangle \quad (10.100)$$

$$L_z L_{\pm} |\lambda, m\rangle = (L_{\pm} L_z \pm \hbar L_{\pm}) |\lambda, m\rangle = \hbar(m \pm 1) L_{\pm} |\lambda, m\rangle \quad (10.101)$$

which means the state $L_{\pm} |\lambda, m\rangle$ is an eigenstate of \mathbf{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 \mathbf{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:

$$\langle \mathbf{L}^2 \rangle = \langle L_x^2 \rangle + \langle L_y^2 \rangle + \langle L_z^2 \rangle \geq \langle L_z^2 \rangle \quad (10.102)$$

therefore⁴⁴

$$\langle \lambda, m | \mathbf{L}^2 | \lambda, m \rangle = \hbar^2 \lambda \geq \langle \lambda, m | L_z^2 | \lambda, m \rangle = \hbar^2 m^2 \implies m^2 \leq \lambda \quad (10.103)$$

This means there must be a state $|\lambda, m_{\max}\rangle$ such that

$$L_+ |\lambda, m_{\max}\rangle = 0 \quad (10.104)$$

and a state $|\lambda, m_{\min}\rangle$ such that

$$L_- |\lambda, m_{\min}\rangle = 0 \quad (10.105)$$

Using the fact that

$$L_{\pm} L_{\mp} = (L_x \pm iL_y)(L_x \mp iL_y) = L_x^2 + L_y^2 \mp i[L_x, L_y] = \mathbf{L}^2 - L_z^2 \pm \hbar L_z \quad (10.106)$$

We can calculate m_{\min} and m_{\max} in terms of λ :

$$\mathbf{L}^2 |\lambda, m_{\max}\rangle = (L_- L_+ + L_z^2 + \hbar L_z) |\lambda, m_{\max}\rangle = \hbar^2 m_{\max}(m_{\max} + 1) |\lambda, m_{\max}\rangle \quad (10.107)$$

$$\mathbf{L}^2 |\lambda, m_{\min}\rangle = (L_+ L_- + L_z^2 - \hbar L_z) |\lambda, m_{\min}\rangle = \hbar^2 m_{\min}(m_{\min} - 1) |\lambda, m_{\min}\rangle \quad (10.108)$$

but both of these should have the same eigenvalue of \mathbf{L}^2 : $\hbar^2 \lambda$; we therefore conclude that

$$\lambda = m_{\max}(m_{\max} + 1) = m_{\min}(m_{\min} - 1) \quad (10.109)$$

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

$$m_{\max} = -m_{\min} = \ell \quad (10.110)$$

Therefore, the eigenvalues of L_z are $\hbar m$ where m goes between $-\ell$ and ℓ in integer

⁴⁴Note that L_z is Hermitian, therefore m is real.

steps. This in turn implies that there is some integer N such that

$$\ell = -\ell + N \implies \ell = \frac{N}{2} \quad (10.111)$$

so ℓ must be either a integer or a half-integer!

All in all, the eigenstates of \mathbf{L}^2 and L_z can be labelled by two numbers ℓ and m such that

$$\mathbf{L}^2 |\ell, m\rangle = \hbar^2 \ell(\ell+1) |\ell, m\rangle \quad \text{and} \quad L_z |\ell, m\rangle = \hbar m |\ell, m\rangle \quad (10.112)$$

and

$$\ell = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots \quad m = -\ell, -\ell+1, \dots, \ell-1, \ell \quad (10.113)$$

The number ℓ is sometimes called the total angular momentum quantum number, but beware, it is *not* true that ℓ is the eigenvalue of $|\mathbf{L}|$, instead the eigenvalue of $|\mathbf{L}|$ 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 $L_{\pm} |\ell, m\rangle$ in terms of $|\ell, m \pm 1\rangle$. First we note that $L_+^\dagger = L_-$, then we write

$$1 = \langle \ell, m \pm 1 | \ell, m \pm 1 \rangle = |C_{\pm}|^2 \langle \ell, m | L_{\pm}^\dagger L_{\pm} | \ell, m \rangle = |C_{\pm}|^2 \langle \ell, m | L_{\mp} L_{\pm} | \ell, m \rangle \quad (10.114)$$

$$= |C_{\pm}|^2 \langle \ell, m | (\mathbf{L}^2 - L_z^2 \mp \hbar L_z) | \ell, m \rangle = |C_{\pm}|^2 \hbar^2 (\ell(\ell+1) - m(m \pm 1)) \quad (10.115)$$

therefore we conclude

$$L_{\pm} |\ell, m\rangle = C_{\pm}^{-1} |\ell, m \pm 1\rangle = \hbar \sqrt{\ell(\ell+1) - m(m \pm 1)} |\ell, m \pm 1\rangle \quad (10.116)$$

These states have non-negative norm if and only if $-\ell \leq m \leq \ell$ which is another to prove the bound on m .

10.4 Eigenstates of \mathbf{L}^2 and L_z in spherical coordinates

The notation for the eigenvalues of \mathbf{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 \mathbf{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 $f(\mathbf{x})$ on the right to make the action of the derivatives clearer)

$$\mathbf{L}^2 f(\mathbf{x}) = L_i L_i f(\mathbf{x}) = -\hbar^2 \epsilon_{ijk} \epsilon_{ilm} x_j \frac{\partial}{\partial x_k} \left(x_l \frac{\partial f(\mathbf{x})}{\partial x_m} \right) \quad (10.117)$$

applying (10.86) we get

$$\mathbf{L}^2 f(\mathbf{x}) = -\hbar^2 \left(x_j \frac{\partial}{\partial x_k} \left(x_j \frac{\partial f(\mathbf{x})}{\partial x_k} \right) - x_j \frac{\partial}{\partial x_k} \left(x_k \frac{\partial f(\mathbf{x})}{\partial x_j} \right) \right) \quad (10.118)$$

using the fact

$$\frac{\partial x_i}{\partial x_j} = \delta_{ij} \quad (10.119)$$

we find

$$\mathbf{L}^2 f(\mathbf{x}) = -\hbar^2 \left(x_j x_j \frac{\partial^2 f(\mathbf{x})}{\partial x_k \partial x_k} - 2x_j \frac{\partial f(\mathbf{x})}{\partial x_j} - x_j x_k \frac{\partial^2 f(\mathbf{x})}{\partial x_j \partial x_k} \right) \quad (10.120)$$

The first term is easy to identify because $r^2 = x_j x_j$ and in Cartesian coordinates

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{\partial^2}{\partial x_j \partial x_j} \quad (10.121)$$

therefore

$$x_j x_j \frac{\partial^2 f(\mathbf{x})}{\partial x_k \partial x_k} = r^2 \nabla^2 f(\mathbf{x}) \quad (10.122)$$

The other terms are a bit trickier, we first have to write

$$x_j \frac{\partial}{\partial x_j} \left(x_k \frac{\partial f(\mathbf{x})}{\partial x_k} \right) = x_j \frac{\partial f(\mathbf{x})}{\partial x_j} + x_j x_j \frac{\partial^2 f(\mathbf{x})}{\partial x_j \partial x_k} \quad (10.123)$$

so that we can have

$$-2x_j \frac{\partial f(\mathbf{x})}{\partial x_j} - x_j x_k \frac{\partial^2 f(\mathbf{x})}{\partial x_j \partial x_k} = -x_j \frac{\partial f(\mathbf{x})}{\partial x_j} - x_j \frac{\partial}{\partial x_j} \left(x_k \frac{\partial f(\mathbf{x})}{\partial x_k} \right) \quad (10.124)$$

finally we identify

$$x_j \frac{\partial f(\mathbf{x})}{\partial x_j} = r \frac{\partial f(\mathbf{x})}{\partial r} \quad (10.125)$$

so that we can conclude

$$-2x_j \frac{\partial f(\mathbf{x})}{\partial x_j} - x_j x_k \frac{\partial^2 f(\mathbf{x})}{\partial x_j \partial x_k} = -r \frac{\partial f(\mathbf{x})}{\partial r} - r \frac{\partial}{\partial r} \left(r \frac{\partial f(\mathbf{x})}{\partial r} \right) = -\frac{\partial}{\partial r} \left(r^2 \frac{\partial f(\mathbf{x})}{\partial r} \right) \quad (10.126)$$

Putting all of this together allows us to write

$$\mathbf{L}^2 f(\mathbf{x}) = -\hbar^2 \left(r^2 \nabla^2 f(\mathbf{x}) - \frac{\partial}{\partial r} \left(r^2 \frac{\partial f(\mathbf{x})}{\partial r} \right) \right) \quad (10.127)$$

This expression is rather useful, we can use to immediately conclude two things. Firstly, we can write

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{\mathbf{L}^2}{\hbar^2 r^2} \quad (10.128)$$

which allows us to write the TISE in spherical coordinates as

$$-\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi(\mathbf{x})}{\partial r} \right) + \frac{1}{2\mu r^2} \mathbf{L}^2 \psi(\mathbf{x}) + V(r) \psi(\mathbf{x}) = E \psi(\mathbf{x}) \quad (10.129)$$

If $\psi(\mathbf{x})$ is chosen to be an eigenstate of \mathbf{L}^2 with eigenvalue $\hbar^2 \ell(\ell+1)$ we get

$$-\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi(\mathbf{x})}{\partial r} \right) + \frac{\hbar^2}{2\mu r^2} \ell(\ell+1) \psi(\mathbf{x}) + V(r) \psi(\mathbf{x}) = E \psi(\mathbf{x}) \quad (10.130)$$

which is the same as (10.25) with $\lambda = \ell(\ell+1)$.

In fact, comparing with (10.21) we can see that

$$\mathbf{L}^2 = -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \quad (10.131)$$

This means that the spherical harmonics are eigenstates of the total angular momentum

$$\mathbf{L}^2 Y_\ell^m(\theta, \psi) = \hbar^2 \ell(\ell+1) Y_\ell^m(\theta, \psi) \quad (10.132)$$

Additionally, one can write

$$\begin{aligned} \frac{\partial}{\partial \phi} &= \frac{\partial x}{\partial \phi} \frac{\partial}{\partial x} + \frac{\partial y}{\partial \phi} \frac{\partial}{\partial y} + \frac{\partial z}{\partial \phi} \frac{\partial}{\partial z} = \\ &= -r \sin \theta \sin \phi \frac{\partial}{\partial x} + r \sin \theta \cos \phi \frac{\partial}{\partial y} = -y \frac{\partial}{\partial x} + x \frac{\partial}{\partial y} = \\ &= \frac{i}{\hbar} L_z \end{aligned} \quad (10.133)$$

therefore

$$L_z Y_\ell^m(\theta, \phi) = -i\hbar \frac{\partial Y_\ell^m(\theta, \phi)}{\partial \phi} = \hbar m Y_\ell^m(\theta, \phi) \quad (10.134)$$

Therefore the eigenstates $|\ell, m\rangle$ of \mathbf{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 , \mathbf{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

$$Y_\ell^{1/2}(\theta, \phi + 2\pi) = -Y_\ell^{1/2}(\theta, \phi) \quad (10.135)$$

which would not lead to a single-valued wavefunction⁴⁵. 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.

⁴⁵You 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

$$-\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + \frac{\hbar^2}{2\mu r^2} \ell(\ell+1) R(r) + V(r) R(r) = ER(r) \quad (11.1)$$

subject to the normalisability requirement

$$\int_0^\infty dr r^2 |R(r)|^2 < \infty \quad (11.2)$$

If we define a new variable

$$u(r) = rR(r) \quad (11.3)$$

then this equation will look exactly like the Schrodinger equation in 1 dimension:

$$-\frac{\hbar^2}{2\mu} \frac{d^2 u(r)}{dr^2} + \left(V(r) + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} \right) u(r) = Eu(r) \quad (11.4)$$

with an effective potential

$$V_{\text{eff}}(r) = V(r) + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} \quad (11.5)$$

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

$$\int_0^\infty dr |u(r)|^2 < \infty \quad (11.6)$$

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 $r \rightarrow 0$ we have, approximately, for $r \approx 0$

$$-\frac{d^2 u(r)}{dr^2} + \frac{\ell(\ell+1)}{r^2} u(r) \approx 0 \quad (11.7)$$

which has two solutions

$$u(r) \propto r^{\ell+1} \quad \text{and} \quad u(r) \propto r^{-\ell} \quad (11.8)$$

For $\ell \geq 1$ 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 $u(r) = \text{const}$ 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

$$\begin{aligned} & \int_0^\infty dr f^*(r) \left(-\frac{\hbar^2}{2\mu} \frac{d^2 g(r)}{dr^2} + \left(V(r) + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} \right) g(r) \right) = \\ &= \int_0^\infty dr \left(-\frac{\hbar^2}{2\mu} \frac{d^2 f^*(r)}{dr^2} + \left(V(r) + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} \right) f^*(r) \right) g(r) \end{aligned} \quad (11.9)$$

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)

$$\begin{aligned} \int_0^\infty dr f^*(r) \frac{d^2 g(r)}{dr^2} &= \left[f^*(r) \frac{dg}{dr} \right]_0^\infty - \int_0^\infty dr \frac{df^*(r)}{dr} \frac{dg(r)}{dr} = \\ &= \left[f^*(r) \frac{dg}{dr} - \frac{df^*}{dr} g(r) \right]_0^\infty + \int_0^\infty dr \frac{d^2 f^*(r)}{dr^2} g(r) \end{aligned} \quad (11.10)$$

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

$$\int_0^\infty dr \frac{1}{r^2} = \infty \quad (11.11)$$

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

$$u(r) \xrightarrow{r \rightarrow 0} C r^{\ell+1} \quad (11.12)$$

for some constant C^{46} .

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:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \quad (11.13)$$

where e is the charge of the proton, and ϵ_0 is the vacuum permittivity.

The equation we wish to solve is

$$-\frac{\hbar^2}{2\mu} \frac{d^2 u(r)}{dr^2} + \left(-\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} \right) u(r) = Eu(r) \quad (11.14)$$

⁴⁶Incidentally, 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

$$u(r) \propto r^{\ell+1} \quad \text{as } r \rightarrow 0 \quad (11.15)$$

Before we attempt to solve this equation it is helpful to introduce new variables to get rid of all of the annoying constants⁴⁷

$$\kappa \equiv \sqrt{-\frac{2mE}{\hbar^2}} \quad (11.16)$$

$$\xi \equiv \frac{\mu e^2}{2\pi\epsilon_0\hbar^2\kappa} \quad (11.17)$$

$$\rho \equiv \kappa r \quad (11.18)$$

such that the equation looks like

$$\frac{d^2u(\rho)}{d\rho^2} = \left(1 - \frac{\xi}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right)u(\rho) \quad (11.19)$$

The same we did for the harmonic oscillator we begin by stripping off the asymptotic behaviour. Looking at $r \rightarrow \infty$ we see that the constant term in the brackets in the RHS dominates, yielding

$$\frac{d^2u(\rho)}{d\rho^2} \approx u(\rho) \quad (11.20)$$

which has as solutions

$$u(\rho) = Ae^{-\rho} + Be^{\rho} \quad (11.21)$$

The second of these is clearly not square integrable, so we throw it out.

Stripping the $\rho \rightarrow 0$ and the $\rho \rightarrow \infty$ asymptotics we define

$$u(\rho) \equiv \rho^{\ell+1}F(\rho)e^{-\rho} \quad (11.22)$$

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

$$\frac{d^2F(\rho)}{d\rho^2} + 2\left(\frac{\ell+1}{\rho} - 1\right)\frac{dF(\rho)}{d\rho} + \frac{\xi - 2(\ell+1)}{\rho}F(\rho) = 0 \quad (11.23)$$

Following our harmonic oscillator footsteps we try a power series solution

$$F(\rho) = \sum_{j=0}^{\infty} a_j \rho^j \quad (11.24)$$

and derive a recurrence relation for the coefficients a_j

$$(j+2(\ell+1))(j+1)a_{j+1} = (2(j+\ell+1) - \xi)a_j \quad (11.25)$$

This relation determines all coefficients in terms of a_0 .

⁴⁷In the definition of κ we have anticipated that we looking for bound states with negative E .

Looking at the large j limit we see that⁴⁸

$$\frac{a_{j+1}}{a_j} \rightarrow \frac{2}{j+1} \quad (11.26)$$

which is solved by

$$a_j \approx \frac{2^j}{j!} a_0 \quad (11.27)$$

but this means

$$F(\rho) \sim c_0 e^{2\rho} \quad (11.28)$$

and therefore

$$u(\rho) \sim \rho^{\ell+1} e^\rho \quad (11.29)$$

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 $N \geq 0$ such that

$$2(N + \ell + 1) = \xi_N \quad (11.30)$$

thereby giving quantisation in the energy:

$$E_N = -\frac{\hbar^2 \kappa_N}{2\mu} = -\frac{\mu e^4}{8\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{\xi_N^2} = -\frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{(N + \ell + 1)^2} \quad (11.31)$$

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*

$$n \equiv N + \ell + 1 \quad (11.32)$$

In terms of this n the functions $F(\rho)$ will be polynomials of order $n - \ell - 1$, and the energies given by

$$E_n = -\frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2} = \frac{E_1}{n^2} \quad (11.33)$$

where in the last equality we wrote them in terms of the ground state energy,

$$E_1 = -\frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \approx -13.6 \text{ eV} \quad (11.34)$$

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 $N \geq 0$ we conclude $n \geq \ell + 1$ and therefore, for a given n , we have $0 \leq \ell \leq n - 1$. Additionally, for each value for n and ℓ there are $2\ell + 1$ allowed values for m . Therefore

⁴⁸We 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

$$\sum_{\ell=0}^{n-1} (2\ell + 1) = 2 \frac{n(n-1)}{2} + n = n^2 \quad (11.35)$$

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*

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137} \quad (11.36)$$

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

$$E_n = -\frac{\alpha^2 \mu c^2}{2} \frac{1}{n^2} \quad (11.37)$$

where we identify

$$\mu c^2 \approx m_e c^2 \approx 511 \text{ keV} \quad (11.38)$$

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. levels.

We can also write down the wavefunctions exactly. First we note that the degree $n-\ell-1$ polynomials $F(\rho)$ are known by mathematicians as the *associated Laguerre Polynomials* denoted by

$$F(\rho) = L_{n-\ell-1}^{2\ell+1}(2\rho) \quad (11.39)$$

They are normalised such that

$$\int_0^\infty dx e^{-x} x^k L_n^k(x) L_m^k(x) = \frac{(n+k)!}{n!} \delta_{mn} \quad (11.40)$$

and even have an exact formula

$$L_n^k(x) = \sum_{m=0}^n (-1)^m \frac{(n+k)!}{(n-m)!(k+m)!m!} x^m \quad (11.41)$$

The first few are given by

$$L_0^k(x) = 1 \quad (11.42)$$

$$L_1^k(x) = -x + k + 1 \quad (11.43)$$

$$L_2^k(x) = \frac{1}{2}(x^2 - 2(k+2)x + (k+1)(k+2)) \quad (11.44)$$

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

$$F(\rho) = L_0^1(2\rho) = 1 \implies u(\rho) = \rho e^{-\rho} \implies R(r) = C e^{-\kappa r} \quad (11.45)$$

We can determine C by imposing normalisation

$$\int_0^\infty dr r^2 |R(r)|^2 = \int_0^\infty dr |C|^2 r^2 e^{-2\kappa r} = |C|^2 \frac{1}{4\kappa^3} = 1 \quad (11.46)$$

Defining the *Bohr radius* as

$$a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{e^2\mu} = \frac{\hbar}{\mu c \alpha} \quad (11.47)$$

and remembering $Y_0^0 = 1/\sqrt{4\pi}$ we can write

$$\psi(r, \theta, \phi) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \quad (11.48)$$

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

$$a_0 \approx 5.29 \times 10^{-11} \text{ m} \quad (11.49)$$

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The other wavefunctions are harder to plot, we can however write the fully normalised expression for any n, ℓ, m .

$$\psi_{n\ell m}(\mathbf{r}) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} \exp\left(-\frac{r}{na_0}\right) \left(\frac{2r}{na_0}\right)^\ell L_{n-\ell-1}^{2\ell+1}\left(\frac{r}{na_0}\right) Y_\ell^m(\theta, \phi) \quad (11.50)$$

Ignoring the spherical harmonics, the first few radial wavefunctions, denoted by $R_{n\ell}(r)$ are given by

$$R_{10}(r) = \frac{1}{2a_0^{3/2}} e^{-r/a_0} \quad (11.51)$$

$$R_{20}(r) = \frac{1}{\sqrt{2}} a_0^{-3/2} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} \quad (11.52)$$

$$R_{21}(r) = \frac{1}{2\sqrt{6}} a_0^{-5/2} r e^{-r/2a_0} \quad (11.53)$$

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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*

$$\mathbf{R} \equiv -\frac{e^2}{4\pi\epsilon_0} \frac{\mathbf{X}}{|\mathbf{X}|} + \frac{1}{2\mu} (\mathbf{P} \times \mathbf{L} - \mathbf{L} \times \mathbf{P}) \quad (11.54)$$

where we have defined $|\mathbf{X}| = \sqrt{\mathbf{X} \cdot \mathbf{X}}$.

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 $\mathbf{P} \times \mathbf{L}$ and $-\mathbf{L} \times \mathbf{P}$ (which are classically the same) to ensure this operator is Hermitian

$$\mathbf{R}^\dagger = \mathbf{R} \quad (11.55)$$

First we need to show that this vector actually is conserved, *i.e.* that

$$[H, \mathbf{R}] = 0 \quad (11.56)$$

For this we need to remember that $[\mathbf{L}, H] = 0$, and to compute the commutator of \mathbf{P} and the Hamiltonian:

$$[H, P_i] = \left[-\frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{X}|}, P_i \right] \quad (11.57)$$

this is easy to compute in the position basis

$$\left[\frac{1}{|\mathbf{X}|}, P_i \right] \psi(\mathbf{x}) = -i\hbar \left(\frac{1}{r} \frac{\partial \psi(\mathbf{x})}{\partial x_i} - \frac{\partial}{\partial x_i} \left(\frac{\psi(\mathbf{x})}{r} \right) \right) = -i\hbar \frac{\psi(\mathbf{x})}{r^2} \frac{\partial r}{\partial x_i} = -i\hbar \frac{x_i}{r^3} \psi(\mathbf{x}) \quad (11.58)$$

therefore

$$[H, P_i] = i\hbar \frac{e^2}{4\pi\epsilon_0} \frac{X_i}{|\mathbf{X}|^3} \quad (11.59)$$

We will also need

$$\begin{aligned} \left[H, \frac{X_i}{|\mathbf{X}|} \right] &= \frac{P_j}{2\mu} \left[P_j, \frac{X_i}{|\mathbf{X}|} \right] + \left[P_j, \frac{X_i}{|\mathbf{X}|} \right] \frac{P_j}{2\mu} = \\ &= \frac{P_j}{2\mu} \left(-i\hbar \delta_{ij} \frac{1}{|\mathbf{X}|} + X_i \left[P_j, \frac{1}{|\mathbf{X}|} \right] \right) + \left(-i\hbar \delta_{ij} \frac{1}{|\mathbf{X}|} + X_i \left[P_j, \frac{1}{|\mathbf{X}|} \right] \right) \frac{P_j}{2\mu} = \\ &= \frac{P_j}{2\mu} \left(-i\hbar \delta_{ij} \frac{1}{|\mathbf{X}|} + X_i i\hbar \frac{X_j}{|\mathbf{X}|^3} \right) + \left(-i\hbar \delta_{ij} \frac{1}{|\mathbf{X}|} + X_i i\hbar \frac{X_j}{|\mathbf{X}|^3} \right) \frac{P_j}{2\mu} = \\ &= \frac{i\hbar}{2\mu} \left[P_j \left(\frac{X_i X_j}{|\mathbf{X}|^3} - \frac{\delta_{ij}}{|\mathbf{X}|} \right) + \left(\frac{X_i X_j}{|\mathbf{X}|^3} - \frac{\delta_{ij}}{|\mathbf{X}|} \right) P_j \right] \end{aligned} \quad (11.60)$$

We can also use the commutator $[L_i, P_j] = i\hbar \epsilon_{ijk} P_k$ to write

$$\begin{aligned} R_i &= -\frac{e^2}{4\pi\epsilon_0} \frac{X_i}{|\mathbf{X}|} + \frac{1}{2\mu} (\epsilon_{ijk} P_j L_k - \epsilon_{ijk} L_j P_k) = \\ &= -\frac{e^2}{4\pi\epsilon_0} \frac{X_i}{|\mathbf{X}|} + \frac{1}{2\mu} (\epsilon_{ijk} P_j L_k - \epsilon_{ijk} (P_k L_j + i\hbar \epsilon_{jkl} P_l)) = \\ &= -\frac{e^2}{4\pi\epsilon_0} \frac{X_i}{|\mathbf{X}|} + \frac{1}{\mu} \epsilon_{ijk} P_j L_k - \frac{i\hbar}{\mu} P_i \end{aligned} \quad (11.61)$$

Now we are ready to show this vector is conserved:

$$\begin{aligned} [H, R_i] &= -\frac{e^2}{4\pi\epsilon_0} \left[H, \frac{X_i}{|\mathbf{X}|} \right] + \frac{1}{\mu} \epsilon_{ijk} [H, P_j] L_k - \frac{i\hbar}{\mu} [H, P_i] = \\ &= \frac{i\hbar e^2}{4\pi\epsilon_0 \mu} \left(\frac{P_j}{2} \left(\frac{\delta_{ij}}{|\mathbf{X}|} - \frac{X_i X_j}{|\mathbf{X}|^3} \right) + \left(\frac{\delta_{ij}}{|\mathbf{X}|} - \frac{X_i X_j}{|\mathbf{X}|^3} \right) \frac{P_j}{2} + \epsilon_{ijk} \frac{X_j}{|\mathbf{X}|^3} L_k - i\hbar \frac{X_i}{|\mathbf{X}|^3} \right) = \end{aligned}$$

$$\begin{aligned}
&= \frac{i\hbar e^2}{4\pi\epsilon_0\mu} \left(\frac{P_j}{2} \left(\frac{\delta_{ij}}{|\mathbf{X}|} - \frac{X_i X_j}{|\mathbf{X}|^3} \right) + \left(\frac{\delta_{ij}}{|\mathbf{X}|} - \frac{X_i X_j}{|\mathbf{X}|^3} \right) \frac{P_j}{2} + \frac{X_j}{|\mathbf{X}|^3} (X_i P_j - X_j P_i) - i\hbar \frac{X_i}{|\mathbf{X}|^3} \right) = \\
&= \frac{i\hbar e^2}{4\pi\epsilon_0\mu} \left(\frac{P_j}{2} \left(\frac{\delta_{ij}}{|\mathbf{X}|} - \frac{X_i X_j}{|\mathbf{X}|^3} \right) - \left(\frac{\delta_{ij}}{|\mathbf{X}|} - \frac{X_i X_j}{|\mathbf{X}|^3} \right) \frac{P_j}{2} - i\hbar \frac{X_i}{|\mathbf{X}|^3} \right) = \\
&= \frac{i\hbar e^2}{4\pi\epsilon_0\mu} \left(\left[\frac{P_j}{2}, \frac{\delta_{ij}}{|\mathbf{X}|} - \frac{X_i X_j}{|\mathbf{X}|^3} \right] - i\hbar \frac{X_i}{|\mathbf{X}|^3} \right) = \\
&= -\frac{i\hbar e^2}{8\pi\epsilon_0\mu} \left(\left[P_j, \frac{X_i X_j}{|\mathbf{X}|^3} \right] + i\hbar \frac{X_i}{|\mathbf{X}|^3} \right)
\end{aligned} \tag{11.62}$$

The final commutator is not too hard to calculate in the position basis

$$\left[P_j, \frac{X_i X_j}{|\mathbf{X}|^3} \right] \psi(\mathbf{x}) = -i\hbar \frac{\partial}{\partial x_j} \left(\frac{x_i x_j}{r^3} \right) \psi(\mathbf{x}) = -i\hbar \frac{x_i}{r^3} \psi(\mathbf{x}) \tag{11.63}$$

This finally gives us that

$$[H, \mathbf{R}] = 0 \tag{11.64}$$

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 \mathbf{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 \mathbf{R} . It is rather lengthy but the manipulations are very similar to what we used above to prove that $[H, \mathbf{R}] = 0$, so we will not repeat them here. The main tools are the commutators between \mathbf{X} , \mathbf{P} , and \mathbf{L} ; the fact \mathbf{L} commutes with any function of $|\mathbf{X}|$; and the orthogonality relations $\mathbf{X} \cdot \mathbf{L} = 0$ and $\mathbf{L} \cdot \mathbf{P} = 0$. The end result is

$$[R_i, R_j] = -\frac{2i\hbar}{\mu} \epsilon_{ijk} H L_k \tag{11.65}$$

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

$$[L_i, R_j] = i\hbar \epsilon_{ijk} R_k \tag{11.66}$$

which is the expected result for a vector made up from \mathbf{X} and \mathbf{P} .

Comparing these two relations we see that, even though the components of \mathbf{R} do not form a closed algebra, the set of $\{L_i, R_j/\sqrt{-H}\}$ do form a closed algebra. Indeed we can introduce

$$\mathbf{A}_\pm \equiv \frac{1}{2} \left(\mathbf{L} \pm \sqrt{\frac{\mu}{-2H}} \mathbf{R} \right) \tag{11.67}$$

whose commutators yield

$$[A_{\pm i}, A_{\pm j}] = i\hbar\epsilon_{ijk}A_{\pm k} \quad (11.68)$$

$$[A_{\pm i}, A_{\mp j}] = 0 \quad (11.69)$$

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 \mathbf{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 \mathbf{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

$$\mathbf{A}_{\pm}^2 = \frac{1}{4} \left(\mathbf{L}^2 - \frac{\mu}{2H} \mathbf{R}^2 \right) \quad (11.70)$$

where we have used the fact $\mathbf{L} \cdot \mathbf{R} = \mathbf{R} \cdot \mathbf{L} = 0$. This is the same for both combinations so we actually have $a_+ = a_- = a$.

All we have left to do is compute \mathbf{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

$$\mathbf{R}^2 = \frac{e^4}{16\pi^2\epsilon_0^2} + \frac{2H}{\mu} (\mathbf{L}^2 + \hbar^2) \quad (11.71)$$

Plugging this in we get

$$\mathbf{A}_{\pm}^2 = \frac{1}{4} \left(\mathbf{L}^2 - \frac{\mu}{2H} \frac{e^4}{16\pi^2\epsilon_0^2} - (\mathbf{L}^2 + \hbar^2) \right) = -\frac{\mu}{8H} \frac{e^4}{16\pi^2\epsilon_0^2} - \frac{\hbar^2}{4} \quad (11.72)$$

Plugging in the eigenvalues we obtain

$$\hbar^2 a(a+1) = -\frac{\mu}{8E} \frac{e^4}{16\pi^2\epsilon_0^2} - \frac{\hbar^2}{4} \quad (11.73)$$

which can be simplified to

$$E = -\frac{\mu e^4}{32\pi^2\epsilon_0^2\hbar^2} \frac{1}{(2a+1)^2} \quad (11.74)$$

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 $-a, -a+1, \dots, a$, 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, \mathbf{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 \mathbf{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 $\delta\mathbf{a}$ we have that

$$U(\delta\mathbf{a}) = \mathbb{1} - \frac{i}{\hbar} \delta\mathbf{a} \cdot \mathbf{P} + O(\delta\mathbf{a}^2) \quad (12.1)$$

is such that

$$U(\delta\mathbf{a})^\dagger \mathbf{X} U(\delta\mathbf{a}) = \mathbf{X} + \delta\mathbf{a} \quad (12.2)$$

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 $\mathbf{a}_1, \dots, \mathbf{a}_N$ such that $\mathbf{a}_1 + \dots + \mathbf{a}_N = 0$, if we take $N \rightarrow \infty$ this approaches the circle. Let us now focus on a single of these displacements in the limit where $N \rightarrow \infty$ so that they are infinitesimal. We start at position \mathbf{x} making an angle α along the circle and we end at position $\mathbf{x} + \delta\mathbf{a}$ making an angle $\alpha + \delta\alpha$ along the circle. If \mathbf{n} is the unit normal to the circle then it is clear that $\delta\mathbf{a} = \delta\alpha \mathbf{n} \times \mathbf{x}$.

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The unitary operator that describes this translation is

$$U(\delta\mathbf{a}) = \mathbb{1} - \frac{i}{\hbar} \delta\alpha (\mathbf{n} \times \mathbf{X}) \cdot \mathbf{P} + O(\delta\mathbf{a}^2) = \mathbb{1} - \frac{i}{\hbar} \delta\alpha \mathbf{n} \cdot (\mathbf{X} \times \mathbf{P}) + O(\delta\mathbf{a}^2) \quad (12.3)$$

This shows that $\mathbf{L} = \mathbf{X} \times \mathbf{P}$ 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 \mathbf{v} along the axis $\delta\alpha$ by an angle $|\delta\alpha|$ can be written as

$$\mathbf{v} \rightarrow \mathbf{v}' = \mathbf{v} + \delta\alpha \times \mathbf{v} + O(\delta\alpha^2) \quad (12.4)$$

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We denote the generator of true rotations by \mathbf{J} such that the unitary operator that describes rotations is written as

$$U(\delta\alpha) = \mathbb{1} - \frac{i}{\hbar} \delta\alpha \cdot \mathbf{J} + O(\delta\alpha^2) \quad (12.5)$$

Any vector operator \mathbf{V} must then obey the following commutation relations with \mathbf{J} :

$$U(\delta\alpha)^\dagger \mathbf{V} U(\delta\alpha) = \mathbf{V} + \delta\alpha \times \mathbf{V} + O(\delta\alpha^2) \quad (12.6)$$

plugging in (12.5) we obtain

$$\frac{i}{\hbar} [\delta\alpha \cdot \mathbf{J}, \mathbf{V}] = \delta\alpha \times \mathbf{V} \quad (12.7)$$

which implies

$$[J_i, V_j] = i\hbar\epsilon_{ijk}V_k \quad (12.8)$$

which is very reminiscent of the commutation relations between \mathbf{L} and the vectors made from \mathbf{X} and \mathbf{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 \mathbf{J} by looking at the difference between first rotating by $\delta\alpha$ and then rotating by $\delta\beta$:

$$\mathbf{V} \rightarrow \mathbf{V} + \delta\alpha \times \mathbf{V} \rightarrow \mathbf{V} + \delta\alpha \times \mathbf{V} + \delta\beta \times \mathbf{V} + \delta\beta \times (\delta\alpha \times \mathbf{V}) \quad (12.9)$$

and performing these rotations in the reverse order

$$\mathbf{V} \rightarrow \mathbf{V} + \delta\beta \times \mathbf{V} \rightarrow \mathbf{V} + \delta\beta \times \mathbf{V} + \delta\alpha \times \mathbf{V} + \delta\alpha \times (\delta\beta \times \mathbf{V}) \quad (12.10)$$

The difference between the two is given by

$$\begin{aligned} & U(\delta\beta)^\dagger (U(\delta\alpha)^\dagger \mathbf{V} U(\delta\alpha)) U(\delta\beta) - U(\delta\alpha)^\dagger (U(\delta\beta)^\dagger \mathbf{V} U(\delta\beta)) U(\delta\alpha) = \\ &= \delta\beta \times (\delta\alpha \times \mathbf{V}) - \delta\alpha \times (\delta\beta \times \mathbf{V}) = (\delta\beta \times \delta\alpha) \times \mathbf{V} = \\ &= U(\delta\beta \times \delta\alpha)^\dagger \mathbf{V} U(\delta\beta \times \delta\alpha) - \mathbf{V} \end{aligned} \quad (12.11)$$

we therefore conclude that

$$[U(\delta\alpha), U(\delta\beta)] = U(\delta\beta \times \delta\alpha) - \mathbb{1} \quad (12.12)$$

plugging in the definition of \mathbf{J} we get

$$-\frac{i}{\hbar^2} [\delta\alpha \cdot \mathbf{J}, \delta\beta \cdot \mathbf{J}] = -\frac{i}{\hbar} (\delta\beta \times \delta\alpha) \cdot \mathbf{J} \quad (12.13)$$

and therefore

$$[J_i, J_j] = i\hbar\epsilon_{ijk}J_k \quad (12.14)$$

which are the same commutation relations we had for the components of \mathbf{L} .

This operator \mathbf{J} is the true generator of rotations. Its commutation relations are very

similar to \mathbf{L} but it is possible that the two are not the same. We call their difference *spin* and define it as:

$$\mathbf{S} \equiv \mathbf{J} - \mathbf{L} \quad (12.15)$$

so that we can say that the total angular momentum \mathbf{J} is the sum of the orbital angular momentum \mathbf{L} and the spin angular momentum \mathbf{S} in analogy with the classical case.

Using the fact \mathbf{L} is a vector, we have $[J_i, L_j] = i\hbar\epsilon_{ijk}L_k$, and therefore the commutator between the components of \mathbf{S} are

$$\begin{aligned} [S_i, S_j] &= [J_i - L_i, J_j - L_j] = [J_i, J_j] - [J_i, L_j] - [L_i, J_j] + [J_i, J_j] = \\ &= i\hbar\epsilon_{ijk}(J_k - L_k + L_k + L_k) = i\hbar\epsilon_{ijk}S_k \end{aligned} \quad (12.16)$$

which are the commutation relations we have come to expect from angular momentum operators. It suggests that we can indeed interpret \mathbf{S} as some form of angular momentum.

However, using the fact both $[J_i, X_k] = i\hbar\epsilon_{ijk}X_k$ and $[L_i, X_k] = i\hbar\epsilon_{ijk}X_k$ we find

$$[S_i, X_j] = 0 \quad (12.17)$$

and similarly for the linear momentum \mathbf{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 \mathbf{L} therefore the algebraic derivation of the eigenstates goes through without changes. We can construct states $|s, m_s\rangle$ such that

$$\mathbf{S}^2 |s, m_s\rangle = \hbar^2 s(s+1) |s, m_s\rangle \quad (12.18)$$

$$S_z |s, m_s\rangle = \hbar m_s |s, m_s\rangle \quad (12.19)$$

$$S_{\pm} |s, m_s\rangle = \hbar \sqrt{s(s+1) - m_s(m_s \pm 1)} |s, m_s \pm 1\rangle \quad (12.20)$$

where $S_{\pm} \equiv S_x \pm iS_y$ and the numbers s and m_s are such that

$$s = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots \quad \text{and} \quad m_s = -s, -s+1, \dots, s-1, s \quad (12.21)$$

The question now if we can also discard the half-integer spin states or not. More specifically, if we could attribute \mathbf{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 \mathbf{x}_a and momenta \mathbf{P}_a ; we would be able to write:

$$\mathbf{S} \stackrel{?}{=} \sum_a \mathbf{X}_a \times \mathbf{P}_a \quad (12.22)$$

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 \mathbf{X}_a act as multiplication by 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; Δ 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 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 eigenstates, 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 :

$$|\uparrow\rangle = \left| \frac{1}{2}, \frac{1}{2} \right\rangle \quad (12.23)$$

$$|\downarrow\rangle = \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \quad (12.24)$$

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*:

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_- \quad (12.25)$$

where

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (12.26)$$

and

$$a = \langle \uparrow | \chi \rangle \quad \text{and} \quad b = \langle \downarrow | \chi \rangle \quad (12.27)$$

The normalisation condition in terms of these spinors is

$$1 = |a|^2 + |b|^2 = \begin{pmatrix} a^* & b^* \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \chi^\dagger \chi \quad (12.28)$$

The spin operators will then be represented by 2×2 matrices, let us calculate their matrix elements. Firstly, we have

$$S_z |\uparrow\rangle = +\frac{\hbar}{2} |\uparrow\rangle \quad (12.29)$$

$$S_z |\downarrow\rangle = -\frac{\hbar}{2} |\downarrow\rangle \quad (12.30)$$

therefore, the matrix representation of this operator will be

$$S_z = \begin{pmatrix} \langle \uparrow | S_z | \uparrow \rangle & \langle \uparrow | S_z | \downarrow \rangle \\ \langle \downarrow | S_z | \uparrow \rangle & \langle \downarrow | S_z | \downarrow \rangle \end{pmatrix} = \begin{pmatrix} \frac{\hbar}{2} & 0 \\ 0 & -\frac{\hbar}{2} \end{pmatrix} = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (12.31)$$

We can do the same procedure for the raising operator:

$$S_+ |\uparrow\rangle = 0 \quad (12.32)$$

$$S_+ |\downarrow\rangle = \hbar |\uparrow\rangle \quad (12.33)$$

which gives

$$S_+ = \begin{pmatrix} \langle \uparrow | S_+ | \uparrow \rangle & \langle \uparrow | S_+ | \downarrow \rangle \\ \langle \downarrow | S_+ | \uparrow \rangle & \langle \downarrow | S_+ | \downarrow \rangle \end{pmatrix} = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad (12.34)$$

And for the lowering operator

$$S_- |\uparrow\rangle = \hbar |\downarrow\rangle \quad (12.35)$$

$$S_- |\downarrow\rangle = 0 \quad (12.36)$$

which gives

$$S_- = \begin{pmatrix} \langle \uparrow | S_- | \uparrow \rangle & \langle \uparrow | S_- | \downarrow \rangle \\ \langle \downarrow | S_- | \uparrow \rangle & \langle \downarrow | S_- | \downarrow \rangle \end{pmatrix} = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \quad (12.37)$$

We can combine these last two to find out the matrix elements of S_x and S_y :

$$S_x = \frac{1}{2}(S_+ + S_-) = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (12.38)$$

$$S_y = \frac{1}{2i}(S_+ - S_-) = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (12.39)$$

We can combine all of these results into a single equation

$$\mathbf{S} = \frac{\hbar}{2} \boldsymbol{\sigma} \quad (12.40)$$

where $\boldsymbol{\sigma}$ are the *Pauli matrices*:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (12.41)$$

They obey the following commutation and anti-commutation relations, as can be easily checked explicitly

$$[\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k \quad (12.42)$$

$$\{\sigma_i, \sigma_j\} = 2\delta_{jk}\mathbb{1} \quad (12.43)$$

We can also check very straightforwardly that,

$$\mathbf{S}^2 = S_x^2 + S_y^2 + S_z^2 = \frac{3}{4}\hbar \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (12.44)$$

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

$$\begin{vmatrix} -\lambda & \frac{\hbar}{2} \\ \frac{\hbar}{2} & -\lambda \end{vmatrix} = 0 \implies \lambda^2 = \frac{\hbar^2}{4} \implies \lambda = \pm \frac{\hbar}{2} \quad (12.45)$$

so the possible outcomes are the same as for S_z which is to be expected.

The eigenspinors are obtained in the usual way

$$\frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \pm \frac{\hbar}{2} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \implies \begin{pmatrix} \beta \\ \alpha \end{pmatrix} = \pm \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad (12.46)$$

therefore the normalised eigenspinors of S_x are

$$\chi_+^x = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{and} \quad \chi_-^x = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad (12.47)$$

Therefore the probability of measuring spin $\pm\hbar/2$ in the x -direction is

$$|\chi_{\pm}^x| \cdot |\chi_{\pm}^x| = \frac{|a \pm b|^2}{2} \quad (12.48)$$

If for example we had prepared the state to have spin-up in the z -direction we would have a 50/50 chance 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 $\mathbf{n} = (\cos \phi, \sin \phi, 0)$. Then we need to diagonalise the operator

$$S_z \cos \phi + S_y \sin \phi = \frac{\hbar}{2} \begin{pmatrix} 0 & e^{-i\phi} \\ e^{i\phi} & 0 \end{pmatrix} \quad (12.49)$$

It is not too hard to show that its eigenvectors are

$$\chi_+^\phi = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\phi/2} \\ e^{i\phi/2} \end{pmatrix} \quad \text{and} \quad \chi_-^\phi = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\phi/2} \\ -e^{i\phi/2} \end{pmatrix} \quad (12.50)$$

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

$$|\chi_+^\phi| \cdot |\chi_+^\phi| = \left| \frac{1}{\sqrt{2}} \begin{pmatrix} e^{i\phi/2} & e^{-i\phi/2} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right|^2 = \frac{1}{2} \quad (12.51)$$

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:

$$\left| \chi_+^{\phi\dagger} \chi_+^x \right|^2 = \left| \frac{1}{2} \left(e^{i\phi/2} e^{-i\phi/2} \right) \begin{pmatrix} 1 \\ 1 \end{pmatrix} \right|^2 = \left| \left(e^{i\phi/2} + e^{-i\phi/2} \right) \begin{pmatrix} 1 \\ 1 \end{pmatrix} \right|^2 = \cos^2 \left(\frac{\phi}{2} \right) \quad (12.52)$$

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:

$$V = -\boldsymbol{\mu} \cdot \mathbf{B} \quad (12.53)$$

Classically, for an electron with spin angular momentum \mathbf{S} we would expect that its magnetic momentum is given by (3.2) with $\mathbf{L} \rightarrow \mathbf{S}$ 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 its proportionality constant isn't $q/2m$. In general we therefore write

$$\boldsymbol{\mu} = \gamma \mathbf{S} \quad (12.54)$$

where γ is called the *gyromagnetic ratio*.

For the electron in particular we have

$$\gamma = -\frac{e g_e}{2m_e} \quad (12.55)$$

where

$$g_e = 2.002\ 319\ 304\ 360\ 92(36) \quad (12.56)$$

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

$$\boldsymbol{\mu} = -\frac{g_e}{2} \mu_B \boldsymbol{\sigma} \quad (12.57)$$

where

$$\mu_B = \frac{e\hbar}{2m_e} \approx 9.274 \times 10^{-24} \text{ J T}^{-1} \approx 5.788 \times 10^{-5} \text{ eV T}^{-1} \quad (12.58)$$

is the *Bohr magneton*. Because $g_e \approx 2$, we can write

$$\boldsymbol{\mu} \approx -\mu_B \boldsymbol{\sigma} \quad (12.59)$$

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 to examine the following Hamiltonian

$$H = \frac{P^2}{2m} - \gamma \boldsymbol{S} \cdot \boldsymbol{B} \quad (12.60)$$

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 \mathbf{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:

$$i\hbar \frac{d\boldsymbol{S}}{dt} = [\boldsymbol{S}, H] \quad (12.61)$$

using (12.16) and the fact $[S_i, P_j] = 0$ we find

$$i\hbar \frac{dS_i}{dt} = -\gamma B_j [S_i, S_j] = -\gamma B_j i\hbar \epsilon_{ijk} S_k \quad (12.62)$$

writing in vector notation once more we find

$$\frac{d\boldsymbol{S}}{dt} = \gamma \boldsymbol{S} \times \boldsymbol{B} \quad (12.63)$$

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

$$\frac{dS_x}{dt} = \gamma S_y B_z \quad (12.64)$$

$$\frac{dS_y}{dt} = -\gamma S_x B_z \quad (12.65)$$

$$\frac{dS_z}{dt} = 0 \quad (12.66)$$

which is solved by

$$\boldsymbol{S}(t) = \begin{pmatrix} S_x(0) \cos(\gamma B_z t) + S_y(0) \sin(\gamma B_z t) \\ S_y(0) \cos(\gamma B_z t) - S_x(0) \sin(\gamma B_z t) \\ S_z(0) \end{pmatrix} \quad (12.67)$$

We see that the spin *precesses* around the magnetic field⁴⁹

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⁴⁹If 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*

$$\omega_L = \gamma|B| \quad (12.68)$$

Now we wish to consider how the position of the particles evolves over time. If \mathbf{B} is a constant then \mathbf{X} and \mathbf{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

$$m \frac{d^2 \mathbf{X}}{dt^2} = \gamma \nabla (\mathbf{S} \cdot \mathbf{B}) \quad (12.69)$$

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 $\mathbf{B} \sim \alpha z \mathbf{e}_z$ but this would not obey the electromagnetic law $\nabla \cdot \mathbf{B} = 0$. 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:

$$\mathbf{B} = -\alpha \mathbf{e}_x + (B_0 + \alpha z) \mathbf{e}_z \quad (12.70)$$

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

$$m \frac{d^2 \mathbf{X}}{dt^2} \approx \gamma S_z \alpha \mathbf{e}_z \quad (12.71)$$

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 \mathbf{S}^2 and S_z . Taking the expectation value in the states $|s, m_s\rangle$ we then find

$$m \frac{d^2 \langle \mathbf{X} \rangle}{dt^2} \approx \alpha \gamma \hbar m_s \mathbf{e}_z \quad (12.72)$$

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 Hydrogen⁵⁰. If the magnetic field was too weak

⁵⁰These 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 $|\mathbf{B}| \gtrsim 5$ T. We shall also neglect effects quadratic in the magnetic field $\sim B^2$, sometimes called the *diamagnetic* terms, which restrict us to fields $|\mathbf{B}| \lesssim 10$ T.

All in all, the Hamiltonian we wish to consider is the following

$$H = \frac{P^2}{2\mu} - \frac{1}{4\pi\epsilon_0} \frac{e^2}{|X|} + \frac{e}{2m_e} \mathbf{B} \cdot (\mathbf{L} + g_e \mathbf{S}) \quad (12.73)$$

where we have also added the orbital contribution to the magnetic moment, whose gyro-magnetic ratio equals the classical value.

It is incredibly easy to find the eigenstates of this Hamiltonian. Because both \mathbf{J} and \mathbf{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 $\mathbf{B} = Be_z$ and therefore the states $|n, \ell, m_\ell, s, m_s\rangle$ we found earlier are also eigenstates of the magnetic term leading to

$$E_{\text{tot}} = E_n + \mu_B B(m_\ell + g_e m_s) \quad (12.74)$$

where E_n is given by (11.37).

The application of \mathbf{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*⁵¹. 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.

⁵¹In 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 \mathbf{E} and a magnetic field \mathbf{B} will experience the Lorentz force

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (13.1)$$

where \mathbf{v} is the particle's velocity.

Alternatively, we can re-derive the equations of motion implied by the Lorentz force using the following Hamiltonian:

$$H = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + q\varphi \quad (13.2)$$

where φ and \mathbf{A} are the electromagnetic potentials from which we can obtain the electric and magnetic fields via

$$\mathbf{E} = -\nabla\varphi - \frac{\partial\mathbf{A}}{\partial t} \quad (13.3)$$

$$\mathbf{B} = \nabla \times \mathbf{A} \quad (13.4)$$

It is therefore straightforward to suggest that a quantum particle with charge q when subjected to external electromagnetic fields will be described by the Hamiltonian⁵²

$$H = \frac{1}{2m}(\mathbf{P} - q\mathbf{A})^2 + q\varphi \quad (13.5)$$

or in position basis

$$H = \frac{1}{2m}(-i\hbar\nabla - q\mathbf{A}(t, \mathbf{x}))^2 + q\varphi(t, \mathbf{x}) \quad (13.6)$$

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 \mathbf{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 \mathbf{E} and \mathbf{B} . In fact, the electromagnetic potentials are not uniquely determined, we can define new potentials φ' and \mathbf{A}' given by

$$\varphi' = \varphi - \frac{\partial\Lambda}{\partial t} \quad (13.7)$$

$$\mathbf{A}' = \mathbf{A} + \nabla\Lambda \quad (13.8)$$

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

$$\psi'(t, \mathbf{x}) = e^{iq\Lambda/\hbar}\psi(t, \mathbf{x}) \quad (13.9)$$

⁵²We could have also allowed for a coupling between the intrinsically quantum mechanical spin and the magnetic field by adding a term equal to $-\gamma\mathbf{S} \cdot \mathbf{B}$.

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 \mathbf{E} and \mathbf{B} vanish!

Let us then consider the case when $\mathbf{B} = 0$ and $\mathbf{E} = 0$. We can use our gauge freedom to therefore set $\varphi = 0$ and $\nabla \cdot \mathbf{A} = 0$. The Schrodinger equation then looks like

$$i\hbar \frac{\partial \psi}{\partial t} = \frac{1}{2m} (-i\hbar \nabla - q\mathbf{A})^2 \psi \quad (13.10)$$

We can simplify this problem by writing

$$\psi = e^{ig}\psi' \quad (13.11)$$

where

$$g(\mathbf{x}) = \frac{q}{\hbar} \int_F^{\mathbf{x}} d\mathbf{x}' \cdot \mathbf{A}(\mathbf{x}') \quad (13.12)$$

and F is some arbitrary reference point. Because $\nabla \times \mathbf{A} = 0$ as long as we are considering a simply connected region g will indeed only be a function of \mathbf{x} and will not depend on path taken from F to \mathbf{x} .

We therefore write

$$\nabla \psi = e^{ig} \nabla \psi' + e^{ig} (i\nabla g) \psi' \quad (13.13)$$

using the fact $\nabla g = \frac{q}{\hbar} \mathbf{A}$ we get

$$(-i\hbar \nabla - q\mathbf{A})\psi = -i\hbar e^{ig} \nabla \psi' \quad (13.14)$$

and therefore

$$(-i\hbar \nabla - q\mathbf{A})^2 \psi = -\hbar^2 e^{ig} \nabla^2 \psi' \quad (13.15)$$

plugging this into (13.10) we find

$$i\hbar \frac{\partial \psi'}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi' \quad (13.16)$$

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 $\mathbf{E} = \mathbf{B} = 0$, just solve the free particle problem and then tack on the phase e^{ig} .

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 $\nabla \cdot \mathbf{A} = 0$, we have

$$\mathbf{A} = \frac{\Phi}{2\pi r} \mathbf{e}_\phi \quad (13.17)$$

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 $\nabla \times \mathbf{A} = 0$ 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 $\mathbf{B} = 0$. However, they would still experience non-zero \mathbf{A} and they would pick up phases equal to

$$g = \frac{q}{\hbar} \int d\mathbf{x} \cdot \mathbf{A} = \frac{q\Phi}{2\pi\hbar} \int (re_\phi d\phi) \cdot \left(\frac{1}{r} \mathbf{e}_\phi \right) = \pm \frac{q\Phi}{2\hbar} \quad (13.18)$$

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 beam⁵³.

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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 $\mathbf{E} = \mathbf{B} = 0$. Note however that we cannot measure \mathbf{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)

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k} \cdot \mathbf{x} - \omega t)} \quad \text{and} \quad \mathbf{B} = \frac{1}{c} (\hat{\mathbf{k}} \times \mathbf{E}_0) e^{i(\mathbf{k} \cdot \mathbf{x} - \omega t)} \quad (13.19)$$

where $\omega = c|\mathbf{k}|$. 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

$$\hbar\omega \approx E_n - E_m \quad (13.20)$$

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

⁵³If you are still concerned you can check the original paper where they provide a full analytic solution to the Schrodinger equation without resorting to this trick and the results match.

length scales of hydrogen atom, set by the Bohr radius a_0 ⁵⁴

$$\frac{\lambda}{a_0} = \frac{2\pi c}{\omega a_0} = \frac{2\pi m_e c^2 \alpha}{\hbar \omega} \approx \frac{4\pi}{\alpha} \frac{n^2 m^2}{n^2 - m^2} \quad (13.21)$$

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 $n, m \geq 1$ we have $\frac{n^2 m^2}{n^2 - m^2} \geq 1$ which gives us

$$\frac{\lambda}{a_0} \gtrsim \frac{4\pi}{\alpha} \approx 1722 \gg 1 \quad (13.22)$$

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

$$\Delta E_{\text{mag}} \sim \mu_B |\mathbf{B}_0| = \frac{e\hbar|\mathbf{B}_0|}{2m_e} \sim \frac{e\hbar|\mathbf{E}_0|}{2m_e c} \quad (13.23)$$

We can also do the same for the electric field. The potential for a constant electric field is just

$$\varphi = \mathbf{E} \cdot \mathbf{X} \quad (13.24)$$

therefore the contribution to the energy due to the electric field is roughly

$$\Delta E_{\text{electric}} \sim e a_0 |\mathbf{E}_0| = \frac{e |\mathbf{E}_0| \hbar}{m_e c \alpha} \quad (13.25)$$

Hence we conclude

$$\Delta E_{\text{mag}} \sim \alpha \Delta E_{\text{electric}} \quad (13.26)$$

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

$$H(t) = H_0 + \Delta H(t) \quad (13.27)$$

where H_0 is the Coulomb Hamiltonian and

$$\Delta H(t) = e \mathbf{E}_0 \cdot \mathbf{X} \cos(\omega t) \quad (13.28)$$

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

⁵⁴Recall (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

$$|\Psi(t)\rangle = c_m(t)e^{-\frac{i}{\hbar}E_m t} |\psi_m\rangle + c_n(t)e^{-\frac{i}{\hbar}E_n t} |\psi_n\rangle \quad (13.29)$$

plugging this into the time-dependent Schrodinger equation

$$\frac{\partial |\Psi(t)\rangle}{\partial t} = H(t) |\Psi(t)\rangle \quad (13.30)$$

we find

$$i\hbar\dot{c}_m(t)e^{-\frac{i}{\hbar}E_m t} |\psi_m\rangle + i\hbar\dot{c}_n(t)e^{-\frac{i}{\hbar}E_n t} |\psi_n\rangle = \Delta H(t) |\Psi(t)\rangle \quad (13.31)$$

Acting with $\langle\psi_n|$ and $\langle\psi_m|$ in turn we get two coupled equations

$$i\hbar\dot{c}_m(t) = c_m(t) \langle\psi_m| \Delta H(t) |\psi_m\rangle + c_n(t) e^{-i\omega_{nm}t} \langle\psi_m| \Delta H(t) |\psi_n\rangle \quad (13.32)$$

$$i\hbar\dot{c}_n(t) = c_m(t) e^{i\omega_{nm}t} \langle\psi_n| \Delta H(t) |\psi_m\rangle + c_n(t) \langle\psi_n| \Delta H(t) |\psi_n\rangle \quad (13.33)$$

where we have defined the natural frequency of the transition

$$\omega_{nm} \equiv \frac{E_n - E_m}{\hbar} \quad (13.34)$$

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 \mathbf{X} is parity-odd. In more detail,

$$\mathbf{P}|\psi_n\rangle = (-1)^\ell |\psi_n\rangle \implies \langle\psi_n| \mathbf{X} |\psi_n\rangle = (-1)^{2\ell} \langle\psi_n| \mathbf{P}^\dagger \mathbf{X} \mathbf{P} |\psi_n\rangle = -\langle\psi_n| \mathbf{X} |\psi_n\rangle \quad (13.35)$$

which means

$$\langle\psi_n| \Delta H(t) |\psi_n\rangle = e \cos(\omega t) \mathbf{E}_0 \cdot \langle\psi_n| \mathbf{X} |\psi_n\rangle = 0 \quad (13.36)$$

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*

$$\Omega \equiv \frac{e}{\hbar} \mathbf{E}_0 \cdot \langle\psi_m| \mathbf{X} |\psi_n\rangle \quad (13.37)$$

which is real because \mathbf{X} is Hermitian which implies $\langle\psi_m| \mathbf{X} |\psi_n\rangle = \langle\psi_n| \mathbf{X} |\psi_m\rangle$. In particular this frequency is proportional to the magnitude of the electric field.

All in all, the equations we have to solve are

$$i\dot{c}_m(t) = c_n(t) e^{-i\omega_{nm}t} \Omega \cos(\omega t) = c_n(t) \frac{\Omega}{2} \left(e^{i(\omega-\omega_{nm})t} + e^{-i(\omega+\omega_{nm})t} \right) \quad (13.38)$$

$$i\dot{c}_n(t) = c_m(t) e^{i\omega_{nm}t} \Omega \cos(\omega t) = c_m(t) \frac{\Omega}{2} \left(e^{i(\omega+\omega_{nm})t} + e^{-i(\omega-\omega_{nm})t} \right) \quad (13.39)$$

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

$$|\omega - \omega_{nm}| \ll \omega + \omega_{nm} \quad (13.40)$$

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

$$i\dot{c}_m(t) = c_n(t) \frac{\Omega}{2} e^{i\delta t} \quad (13.41)$$

$$i\dot{c}_n(t) = c_m(t) \frac{\Omega}{2} e^{-i\delta t} \quad (13.42)$$

where

$$\delta \equiv \omega - \omega_{nm} \quad (13.43)$$

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

$$c_m(0) = 1 \quad (13.44)$$

$$c_n(0) = 0 \quad (13.45)$$

which give us the solutions

$$c_m(t) = e^{i\delta t/2} \left(\cos\left(\frac{\sqrt{\Omega^2 + \delta^2}}{2}t\right) - \frac{i\delta}{\sqrt{\Omega^2 + \delta^2}} \sin\left(\frac{\sqrt{\Omega^2 + \delta^2}}{2}t\right) \right) \quad (13.46)$$

$$c_n(t) = -ie^{-i\delta t/2} \frac{\Omega}{\sqrt{\Omega^2 + \delta^2}} \sin\left(\frac{\sqrt{\Omega^2 + \delta^2}}{2}t\right) \quad (13.47)$$

The probability of the system being in the excited state, *i.e.* the probability of absorption is

$$\begin{aligned} P_{\text{abs}}(t) &= |c_n(t)|^2 = \frac{\Omega^2}{\Omega^2 + \delta^2} \sin^2\left(\frac{\sqrt{\Omega^2 + \delta^2}}{2}t\right) = \\ &= |c_n(t)|^2 = \frac{\Omega^2}{2(\Omega^2 + \delta^2)} \left(1 - \cos\left(\sqrt{\Omega^2 + \delta^2}t\right)\right) \end{aligned} \quad (13.48)$$

Under this perturbation the system will oscillate between the two states with frequency $\sqrt{\Omega^2 + \delta^2}$, 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

$$P_{\text{abs}}(t) = \sin^2\left(\frac{\Omega}{2}t\right) \quad (13.49)$$

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 $\Delta t = \pi/\Omega$, which is known as a *π -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 $\Omega \ll \delta \ll 1$ we get

$$P_{\text{abs}}(t) \approx \frac{\Omega^2}{\delta^2} \sin^2\left(\frac{\delta}{2}t\right) \quad (13.50)$$

In this limit we can use the following expression for the Dirac- δ

$$\delta(x) = \lim_{\epsilon \rightarrow 0} \frac{\epsilon}{\pi} \frac{\sin^2\left(\frac{x}{\epsilon}\right)}{x^2} \quad (13.51)$$

to write

$$\frac{P_{\text{abs}}(t)}{t} \xrightarrow{t \rightarrow \infty} \frac{\pi}{2} \Omega^2 \delta(\omega - \omega_{nm}) \quad (13.52)$$

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:

$$\overline{E_i(t_1)E_j(t_2)} \quad (13.53)$$

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 have⁵⁵

$$\overline{E_i(t_1)E_j(t_2)} = \delta_{ij} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} F(\omega) e^{-i\omega(t_1-t_2)} \quad (13.54)$$

Given the LHS is real and symmetric under the exchange of t_1 and i with t_2 and j we must have

$$F(\omega) = F(-\omega) = F(\omega)^* \quad (13.55)$$

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

$$\rho = \frac{1}{2} \left(\epsilon_0 \mathbf{E}^2 + \frac{\mathbf{B}^2}{\mu_0} \right) \quad (13.56)$$

⁵⁵We 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 $\mathbf{E}^2 = \mathbf{B}^2/c^2$, and also $1/\mu_0 = c^2\epsilon_0$ so that

$$\rho = \frac{1}{2} \left(\epsilon_0 \mathbf{E}^2 + c^2 \epsilon_0 \frac{\mathbf{E}^2}{c^2} \right) = \epsilon_0 \mathbf{E}^2 \quad (13.57)$$

therefore, the ensemble average of this energy density is

$$\rho = \epsilon_0 \overline{\mathbf{E}(t)^2} = 3\epsilon_0 \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} F(\omega) = 3\epsilon_0 \int_0^{\infty} \frac{d\omega}{\pi} F(\omega) \quad (13.58)$$

We can therefore relate the energy density between angular frequencies ω and $\omega + d\omega$, $\rho(\omega) d\omega$, to the Fourier transform of the 2-point correlator

$$\rho(\omega) d\omega = \frac{3}{\pi} \epsilon_0 F(\omega) d\omega \quad (13.59)$$

which allows us to write the correlator in terms of this energy density

$$\overline{E_i(t_1)E_j(t_2)} = \frac{\delta_{ij}}{6\epsilon_0} \int_{-\infty}^{\infty} d\omega \rho(|\omega|) e^{-i\omega(t_1-t_2)} \quad (13.60)$$

The perturbation Hamiltonian is still given by

$$\Delta H(t) = e \mathbf{E}(t) \cdot \mathbf{X} \quad (13.61)$$

so equation (13.36) will still hold and we still will not have any diagonal terms. We can therefore, still write

$$i\hbar \dot{c}_m(t) = c_n(t) e^{-i\omega_{nm}t} \langle \psi_m | \Delta H(t) | \psi_n \rangle \quad (13.62)$$

$$i\hbar \dot{c}_n(t) = c_m(t) e^{i\omega_{nm}t} \langle \psi_n | \Delta H(t) | \psi_m \rangle \quad (13.63)$$

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

$$c_n(t) \approx c_n(0) - \frac{i}{\hbar} c_m(0) \int_0^t dt' \langle \psi_n | \Delta H(t') | \psi_m \rangle e^{i\omega_{nm}t'} + O(\mathbf{E}^2) \quad (13.64)$$

and similarly for $c_m(t)$.

Therefore, the probability of absorption will, approximately, be

$$\begin{aligned} P_{\text{abs}}(t) &= |c_n(t)|^2 = \frac{1}{\hbar^2} \int_0^t dt_1 \int_0^t dt_2 e^{i\omega_{nm}(t_1-t_2)} \langle \psi_n | \Delta H(t_1) | \psi_m \rangle \langle \psi_n | \Delta H(t_2) | \psi_m \rangle^* = \\ &= \frac{e^2}{\hbar^2} \langle \psi_n | X_i | \psi_m \rangle \langle \psi_m | X_j | \psi_n \rangle \int_0^t dt_1 \int_0^t dt_2 e^{i\omega_{nm}(t_1-t_2)} E_i(t_1) E_j(t_2) \end{aligned} \quad (13.65)$$

And now we take the ensemble average

$$\begin{aligned} \overline{P_{\text{abs}}(t)} &= \frac{e^2}{\hbar^2} \langle \psi_n | X_i | \psi_m \rangle \langle \psi_m | X_j | \psi_n \rangle \int_0^t dt_1 \int_0^t dt_2 e^{i\omega_{nm}(t_1-t_2)} \overline{E_i(t_1) E_j(t_2)} = \\ &= \frac{e^2}{6\epsilon_0 \hbar^2} |\langle \psi_n | \mathbf{X} | \psi_m \rangle|^2 \int_0^t dt_1 \int_0^t dt_2 e^{i\omega_{nm}(t_1-t_2)} \int d\omega \rho(|\omega|) e^{-i\omega(t_1-t_2)} = \\ &= \frac{e^2}{6\epsilon_0 \hbar^2} |\langle \psi_n | \mathbf{X} | \psi_m \rangle|^2 \int d\omega \rho(|\omega|) \left| \int_0^t dt_1 e^{i(\omega_{nm}-\omega)t_1} \right|^2 = \end{aligned}$$

$$= \frac{2e^2}{3\epsilon_0\hbar^2} |\langle \psi_n | \mathbf{X} | \psi_m \rangle|^2 \int d\omega \rho(|\omega|) \frac{\sin^2(\frac{\omega_{nm}-\omega}{2}t)}{(\omega_{nm}-\omega)^2} \quad (13.66)$$

We can now use (13.51) to obtain the average rate of absorption at late times

$$\begin{aligned} \frac{\overline{P_{\text{abs}}(t)}}{t} &\xrightarrow{t \rightarrow \infty} \frac{e^2}{3\epsilon_0\hbar^2} |\langle \psi_n | \mathbf{X} | \psi_m \rangle|^2 \int d\omega \pi \rho(|\omega|) \delta(\omega_{nm} - \omega) = \\ &= \frac{\pi e^2}{3\epsilon_0\hbar^2} |\langle \psi_n | \mathbf{X} | \psi_m \rangle|^2 \rho(\omega_{nm}) \end{aligned} \quad (13.67)$$

For the case of monochromatic radiation with just an electric field we have

$$\rho(\omega_{mn}) = \frac{1}{2} \epsilon_0 \mathbf{E}_0^2 \delta(\omega - \omega_{mn}) \quad (13.68)$$

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

$$\mathbf{k} = \frac{2\pi}{L} \mathbf{n} \quad (13.69)$$

where \mathbf{n} is a vector whose components are arbitrary (possibly distinct) integers. The angular frequency can then be written in terms of this \mathbf{n} :

$$\omega = \frac{2\pi}{L} c |\mathbf{n}| \quad (13.70)$$

The total number of modes is given by

$$N_{\text{tot}} = \sum_{\mathbf{n}} 2 \quad (13.71)$$

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

$$N_{\text{tot}} \approx \int d^3n 2 = L^3 \int \frac{d^3k}{(2\pi)^3} 2 = \frac{8\pi L^3}{(2\pi)^3} \int_0^\infty dk k^2 = \frac{L^3}{\pi^2 c^3} \int_0^\infty d\omega \omega^2 \quad (13.72)$$

therefore the number of modes with frequency between ω and $\omega + d\omega$ is

$$N(\omega) d\omega = \frac{L^3}{\pi^2 c^3} \omega^2 d\omega \quad (13.73)$$

The energy density in the radiation with frequencies between ω and $\omega + d\omega$ is therefore

$$\rho(\omega) d\omega = \overline{E(T)} \frac{N(\omega) d\omega}{L^3} = \overline{E(T)} \frac{\omega^2}{\pi^2 c^3} d\omega \quad (13.74)$$

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

$$\frac{\partial^2 E_{\pm}}{\partial t^2} - c^2 \nabla^2 E_{\pm} = 0 \quad (13.75)$$

which, Fourier space will look like

$$\frac{\partial^2 \tilde{E}_\pm}{\partial t^2} + c^2 \mathbf{k}^2 \tilde{E}_\pm = 0 \quad (13.76)$$

For each value of $\omega = |\mathbf{k}|c$ 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 $\exp(-\frac{E}{k_B T})$. All in all, this means the average energy is given by

$$\overline{E(T)} = \frac{\sum_{n=0}^{\infty} e^{-\frac{n\hbar\omega}{k_B T}} n\hbar\omega}{\sum_{n=0}^{\infty} e^{-\frac{n\hbar\omega}{k_B T}}} = \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} \quad (13.77)$$

Plugging this into (13.74) gives us

$$\rho(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} \quad (13.78)$$

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 $n \rightarrow m$ from higher to lower energy must be exactly the same as the number of electrons making the transition $m \rightarrow n$ 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:

$$N_n(A_n^m + B_n^m \rho(\omega_{nm})) = N_m B_m^n \rho(\omega_{nm}) \quad (13.79)$$

where N_n is the number of atoms in state n , and similarly for N_m . Additionally, in the Gibbs ensemble, we have

$$\frac{N_m}{N_n} = \exp\left(\frac{\hbar\omega_{nm}}{k_B T}\right) \quad (13.80)$$

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

$$A_n^m = \left(\frac{N_m}{N_n} B_m^n - B_n^m \right) \rho(\omega_{nm}) = \frac{\hbar\omega_{nm}^3}{\pi^2 c^3} \frac{1}{e^{\frac{\hbar\omega_{nm}}{k_B T}} - 1} \left(e^{\frac{\hbar\omega_{nm}}{k_B T}} B_m^n - B_n^m \right) \quad (13.81)$$

In order for this to be true for all temperatures T we must have

$$B_n^m = B_m^n \quad \text{and} \quad A_n^m = \frac{\hbar\omega_{nm}^3}{\pi^2 c^3} B_m^n \quad (13.82)$$

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 :

$$B_m^n = \frac{\pi e^2}{3\epsilon_0 \hbar^2} |\langle \psi_n | \mathbf{X} | \psi_m \rangle|^2 \quad (13.83)$$

and therefore we obtain the rate of spontaneous emission of radiation as

$$A_n^m = \frac{e^2 \omega_{nm}^3}{3\pi c^3 \epsilon_0 \hbar} |\langle \psi_n | \mathbf{X} | \psi_m \rangle|^2 \quad (13.84)$$

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

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 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

$$|\psi\rangle = \sum_n c_n |n\rangle \quad (13.85)$$

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

$$P(\psi \rightarrow n) = |c_n|^2 \quad (13.86)$$

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*

$$|\psi\rangle \rightarrow |n\rangle \quad (13.87)$$

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

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = H |\psi\rangle \quad (13.88)$$

but there is no Hamiltonian capable of 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 is needed 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 to 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 make 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 to 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 it 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 recovering 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 products*.

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.

$$\begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix} \otimes \begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix} = \begin{pmatrix} v_1 u_1 \\ v_1 u_2 \\ v_1 u_3 \\ v_2 u_1 \\ v_2 u_2 \\ v_2 u_3 \\ v_3 u_1 \\ v_3 u_2 \\ v_3 u_3 \end{pmatrix} \quad (14.1)$$

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

$$|\psi_{AB}\rangle = |\chi_A\rangle \otimes |\phi_B\rangle \quad (14.2)$$

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

$$|\text{EPR}\rangle = \frac{1}{\sqrt{2}}(|\uparrow_A\downarrow_B\rangle - |\downarrow_A\uparrow_B\rangle) \quad (14.3)$$

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 them 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

$$|\text{GHZ}\rangle = \frac{1}{\sqrt{2}}(|\uparrow_A\uparrow_B\uparrow_C\rangle - |\downarrow_A\downarrow_B\downarrow_C\rangle) \quad (14.4)$$

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 direction⁵⁶ 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

$$\sigma_x |\uparrow\rangle = |\downarrow\rangle, \quad \sigma_x |\downarrow\rangle = |\uparrow\rangle, \quad \sigma_y |\uparrow\rangle = i|\downarrow\rangle, \quad \sigma_y |\downarrow\rangle = -i|\uparrow\rangle \quad (14.5)$$

to obtain

$$\begin{aligned} \sigma_x^A \otimes \sigma_y^B \otimes \sigma_y^C |\text{GHZ}\rangle &= \frac{1}{\sqrt{2}} (\sigma_x^A |\uparrow_A\rangle \otimes \sigma_y^B |\uparrow_B\rangle \otimes \sigma_y^C |\uparrow_C\rangle - \sigma_x^A |\downarrow_A\rangle \otimes \sigma_y^B |\downarrow_B\rangle \otimes \sigma_y^C |\downarrow_C\rangle) = \\ &= \frac{1}{\sqrt{2}} (|\downarrow_A\rangle \otimes i|\downarrow_B\rangle \otimes i|\downarrow_C\rangle - |\uparrow_A\rangle \otimes (-i|\uparrow_B\rangle) \otimes (-i|\uparrow_C\rangle)) = \\ &= \frac{1}{\sqrt{2}} (-|\downarrow_A\downarrow_B\downarrow_C\rangle + |\uparrow_A\uparrow_B\uparrow_C\rangle) = |\text{GHZ}\rangle \end{aligned} \quad (14.6)$$

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

$$s_x^A s_y^B s_y^C = s_y^A s_x^B s_y^C = s_y^A s_y^B s_x^C = +1 \quad (14.7)$$

multiplying these three expressions and remembering that every spin can only be ± 1 , which means $(s_y^B)^2 = (s_y^A)^2 = (s_y^C)^2 = +1$, we conclude

$$s_x^A s_x^B s_x^C = +1 \quad (14.8)$$

But this is *not* the prediction from quantum mechanics:

$$\begin{aligned} \sigma_x^A \otimes \sigma_x^B \otimes \sigma_x^C |\text{GHZ}\rangle &= \frac{1}{\sqrt{2}} (\sigma_x^A |\uparrow_A\rangle \otimes \sigma_x^B |\uparrow_B\rangle \otimes \sigma_x^C |\uparrow_C\rangle - \sigma_x^A |\downarrow_A\rangle \otimes \sigma_x^B |\downarrow_B\rangle \otimes \sigma_x^C |\downarrow_C\rangle) = \\ &= \frac{1}{\sqrt{2}} (|\downarrow_A\downarrow_B\downarrow_C\rangle - |\uparrow_A\uparrow_B\uparrow_C\rangle) = -|\text{GHZ}\rangle \end{aligned} \quad (14.9)$$

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

$$|\text{EPR}\rangle = \frac{1}{\sqrt{2}} (|\uparrow_A\downarrow_B\rangle - |\downarrow_A\uparrow_B\rangle) \quad (14.10)$$

⁵⁶For 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 σ .

and two observers, Alice and Bob, which are sufficiently far away to prevent 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 $\hat{\mathbf{a}}$ 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 $s^A(\hat{\mathbf{a}}, \lambda)$ and $s^B(\hat{\mathbf{a}}, \lambda)$, and note they can only take the values ± 1 . If both observers measure the spin in the same direction $\hat{\mathbf{a}}$ then we get opposite results, that is, $s^A(\hat{\mathbf{a}}, \lambda) = -s^B(\hat{\mathbf{a}}, \lambda)$. So we will simplify and define $s(\hat{\mathbf{a}}, \lambda) \equiv s^A(\hat{\mathbf{a}}, \lambda)$.

The values of λ is fixed, but we are ignorant of them, so we must introduce a probability distribution $p(\lambda)$ such that $p(\lambda) \geq 0$ and $\int d\lambda p(\lambda) = 1$. The expectation value of the product of the spins in two arbitrary directions $\hat{\mathbf{a}}$ and $\hat{\mathbf{b}}$ is then given by

$$\langle (\sigma^A \cdot \hat{\mathbf{a}})(\sigma^B \cdot \hat{\mathbf{b}}) \rangle = - \int d\lambda p(\lambda) s(\hat{\mathbf{a}}, \lambda) s(\hat{\mathbf{b}}, \lambda) \quad (14.11)$$

In quantum mechanics we use the definition of the Pauli matrices to write

$$\sigma \cdot \hat{\mathbf{a}} = \begin{pmatrix} \hat{a}_3 & \hat{a}_1 - i\hat{a}_2 \\ \hat{a}_1 + i\hat{a}_2 & -\hat{a}_3 \end{pmatrix} \quad (14.12)$$

which will give us

$$\begin{aligned} & \langle \text{EPR} | (\sigma^A \cdot \hat{\mathbf{a}})(\sigma^B \cdot \hat{\mathbf{b}}) | \text{EPR} \rangle = \\ &= \frac{1}{2} \left(\langle \uparrow_A | \sigma^A \cdot \hat{\mathbf{a}} | \uparrow_A \rangle \langle \downarrow_B | \sigma^B \cdot \hat{\mathbf{b}} | \downarrow_B \rangle + \langle \uparrow_A | \sigma^A \cdot \hat{\mathbf{a}} | \downarrow_A \rangle \langle \uparrow_B | \sigma^B \cdot \hat{\mathbf{b}} | \uparrow_B \rangle - \right. \\ & \quad \left. - \langle \uparrow_A | \sigma^A \cdot \hat{\mathbf{a}} | \downarrow_A \rangle \langle \downarrow_B | \sigma^B \cdot \hat{\mathbf{b}} | \uparrow_B \rangle - \langle \downarrow_A | \sigma^A \cdot \hat{\mathbf{a}} | \uparrow_A \rangle \langle \uparrow_B | \sigma^B \cdot \hat{\mathbf{b}} | \downarrow_B \rangle \right) = \\ &= \frac{1}{2} \left(-\hat{a}_3 \hat{b}_3 - \hat{a}_3 \hat{b}_3 - (\hat{a}_1 - i\hat{a}_2)(\hat{b}_1 + i\hat{b}_2) - (\hat{a}_1 + i\hat{a}_2)(\hat{b}_1 - i\hat{b}_2) \right) = \\ &= -\hat{\mathbf{a}} \cdot \hat{\mathbf{b}} \end{aligned} \quad (14.13)$$

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, $\hat{\mathbf{a}}$, $\hat{\mathbf{b}}$ and $\hat{\mathbf{c}}$. Using (14.11) we can write

$$\langle (\sigma^A \cdot \hat{\mathbf{a}})(\sigma^B \cdot \hat{\mathbf{b}}) \rangle - \langle (\sigma^A \cdot \hat{\mathbf{a}})(\sigma^B \cdot \hat{\mathbf{c}}) \rangle = - \int d\lambda p(\lambda) (s(\hat{\mathbf{a}}, \lambda) s(\hat{\mathbf{b}}, \lambda) - s(\hat{\mathbf{a}}, \lambda) s(\hat{\mathbf{c}}, \lambda)) \quad (14.14)$$

Now, since $s(\hat{\mathbf{b}}, \lambda) = \pm 1$ we have $s(\hat{\mathbf{b}}, \lambda)^2 = +1$, and therefore we can write

$$\langle (\sigma^A \cdot \hat{\mathbf{a}})(\sigma^B \cdot \hat{\mathbf{b}}) \rangle - \langle (\sigma^A \cdot \hat{\mathbf{a}})(\sigma^B \cdot \hat{\mathbf{c}}) \rangle = - \int d\lambda p(\lambda) s(\hat{\mathbf{a}}, \lambda) s(\hat{\mathbf{b}}, \lambda) (1 - s(\hat{\mathbf{b}}, \lambda) s(\hat{\mathbf{c}}, \lambda)) \quad (14.15)$$

The absolute value of an integral is less or equal than the integral of the absolute value, and $|s(\hat{\mathbf{a}}, \lambda)| = |s(\hat{\mathbf{b}}, \lambda)| = +1$, so we have

$$\begin{aligned} & \left| \langle (\sigma^A \cdot \hat{\mathbf{a}})(\sigma^B \cdot \hat{\mathbf{b}}) \rangle - \langle (\sigma^A \cdot \hat{\mathbf{a}})(\sigma^B \cdot \hat{\mathbf{c}}) \rangle \right| \leq \int d\lambda p(\lambda) (1 - s(\hat{\mathbf{b}}, \lambda) s(\hat{\mathbf{c}}, \lambda)) = \\ &= 1 + \langle (\sigma^A \cdot \hat{\mathbf{c}})(\sigma^B \cdot \hat{\mathbf{c}}) \rangle \end{aligned} \quad (14.16)$$

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 $\hat{a}, \hat{b}, \hat{c}$. In particular, take

$$\hat{a} \cdot \hat{b} = 0 \quad \text{and} \quad \hat{c} = \frac{\hat{a} + \hat{b}}{\sqrt{2}} \quad (14.17)$$

we then have, using (14.13)

$$\left| \langle \text{EPR} | (\sigma^A \cdot \hat{a}) (\sigma^B \cdot \hat{b}) | \text{EPR} \rangle - \langle \text{EPR} | (\sigma^A \cdot \hat{a}) (\sigma^B \cdot \hat{c}) | \text{EPR} \rangle \right| = \frac{1}{\sqrt{2}} \quad (14.18)$$

but

$$1 + \langle \text{EPR} | (\sigma^A \cdot \hat{c}) (\sigma^B \cdot \hat{c}) | \text{EPR} \rangle = 1 + \frac{1}{\sqrt{2}} \quad (14.19)$$

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

$$[A_i, B_j] = 0 \quad \text{for } i, j = 1, 2 \quad (14.20)$$

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

$$C = (A_1 + A_2)B_1 + (A_1 - A_2)B_2 \quad (14.21)$$

If we have hidden variables we can replace all observables with their corresponding value

$$c = (a_1 + a_2)b_1 + (a_1 - a_2)b_2 \quad (14.22)$$

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

$$-2 \leq c \leq 2 \quad (14.23)$$

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

$$C^2 = 4\mathbb{1} - [A_1, A_2][B_1, B_2] \quad (14.24)$$

Even without fixing $[A_1, A_2]$ we can still write

$$|\langle [A_1, A_2] \rangle| \leq |\langle A_1 A_2 \rangle| + |\langle A_2 A_1 \rangle| \leq 2 \quad (14.25)$$

and similarly for $[B_1, B_2]$. We can conclude that

$$8 \leq \langle C^2 \rangle \leq 8 \quad (14.26)$$

and using $\langle C^2 \rangle \geq \langle C \rangle^2$ we write

$$2\sqrt{2} \leq \langle C \rangle \leq 2\sqrt{2} \quad (14.27)$$

which is a larger interval than what is allowed by local hidden variables! This new inequality is known as the *Cirel'son bound* (sometimes also transliterated as Tsirelson) after Boris S. Cirel'son (or Tsirelson).

In the EPR state we can saturate this bound if we choose

$$A_1 = \sigma_z \quad (14.28)$$

$$B_1 = \frac{1}{\sqrt{2}}(\sigma_x + \sigma_z) \quad (14.29)$$

$$A_2 = \sigma_x \quad (14.30)$$

$$B_2 = \frac{1}{\sqrt{2}}(-\sigma_x + \sigma_z) \quad (14.31)$$

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

$$O = O_A \otimes \mathbb{1}_B \quad (14.32)$$

the expectation value of this observable in a generic state

$$|\psi\rangle = \sum_{i\alpha} \psi_{i\alpha} |i_A\rangle |\alpha_B\rangle \quad (14.33)$$

is given by

$$\langle \psi | O | \psi \rangle = \sum_{ij\alpha\beta} \psi_{i\alpha}^* \psi_{j\beta} \langle i_A | O_A | j_A \rangle \langle \alpha_B | \beta_B \rangle \quad (14.34)$$

assuming the bases are orthonormal we find

$$\langle \psi | O | \psi \rangle = \sum_{ij\alpha} \psi_{i\alpha}^* \psi_{j\alpha} \langle i_A | O_A | j_A \rangle \quad (14.35)$$

Once again notice this expectation value does *not* look like the expectation value on some state $|\chi\rangle$ purely on \mathcal{H}_A :

$$\langle \chi | O_A | \chi \rangle = \sum_{ij} \chi_i^* \chi_j \langle i_A | O_A | j_A \rangle \quad (14.36)$$

unless $\psi_{ia} = \chi_i \phi_a$ in which case

$$|\psi\rangle = |\chi\rangle \otimes |\phi\rangle \quad (14.37)$$

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 of 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 $|\psi\rangle$:

$$\rho = |\psi\rangle\langle\psi| \quad (14.38)$$

such that (check!)

$$\langle\psi|O|\psi\rangle = \text{Tr}(\rho O) \quad (14.39)$$

This operator is known as the *density matrix*⁵⁷.

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*

$$\rho_A \equiv \text{Tr}_B \rho \equiv \sum_{ij\alpha} \psi_{i\alpha}^* \psi_{j\alpha} |i_A\rangle \langle j_A| \quad (14.40)$$

It is straightforward to verify that

$$\langle O_A \rangle = \text{Tr}_A(\rho_A O_A) \quad (14.41)$$

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: $\langle\phi|\rho|\phi\rangle = \langle\phi|\psi\rangle \langle\psi|\phi\rangle = |\langle\phi|\psi\rangle|^2 \geq 0$
3. Unit trace: $\text{Tr } \rho = \langle\psi|\psi\rangle = 1$

We can also show these properties hold for the subsystem ρ_A :

1. Hermiticity: $\rho_A^\dagger = \sum_{ij\alpha} (\psi_{i\alpha}^* \psi_{j\alpha} |i_A\rangle \langle j_B|)^\dagger = \sum_{ij\alpha} \psi_{i\alpha} \psi_{j\alpha}^* |j_A\rangle \langle i_A| = \rho_A$

2. Positive definite:

$$\langle\phi|\rho_A|\phi\rangle = \sum_{ijkl\alpha} \psi_{i\alpha}^* \psi_{j\alpha} \phi_k^* \phi_l \langle k_A|i_A\rangle \langle j_A|l_A\rangle = \sum_{ij\alpha} \psi_{i\alpha}^* \psi_{j\alpha} \phi_i^* \phi_j = \sum_{\alpha} \left| \sum_i \psi_{i\alpha} \phi_i \right|^2 \geq 0$$

3. Unit trace: $\text{Tr } \rho_A = \sum_{ij\alpha} \psi_{i\alpha} \psi_{j\alpha}^* \langle i_A|j_A\rangle = \sum_{i\alpha} |\psi_{i\alpha}|^2 = \langle\psi|\psi\rangle = 1$

⁵⁷The 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 is a linear operator on a Hilbert space, \mathcal{H} , that satisfies two properties

1. **Positive definite**^a: $\langle \psi | \rho | \psi \rangle \geq 0 \quad \forall |\psi\rangle \in \mathcal{H}$
2. **Unit trace**: $\text{Tr } \rho = 1$

^aNote 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 $p_i \geq 0$. Because ρ is Hermitian, they necessarily form an orthonormal basis, so we can then write

$$\rho = \sum_i p_i |p_i\rangle\langle p_i| \quad (14.42)$$

An expectation value in this basis looks like

$$\text{Tr}(\rho O) = \sum_i p_i \langle p_i | O | p_i \rangle \quad (14.43)$$

Additionally, the unit trace condition gives

$$\text{Tr } \rho = \sum_i p_i = 1 \quad (14.44)$$

These expressions are the same as if we were ignorant as to what the true state of the system was and only knew 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*

$$S(\rho) = -\text{Tr}(\rho \log \rho) \quad (14.45)$$

which, in the basis (14.42), looks like

$$S(\rho) = -\sum_i p_i \log p_i \quad (14.46)$$

if we define $0 \log 0 = 0$. Because $p_i \geq 0$ 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

$$S(\rho) = 0 \quad \text{iff} \quad \rho = |\psi\rangle\langle\psi| \quad \text{for some } |\psi\rangle \in \mathcal{H} \quad (14.47)$$

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, $\mathcal{H} \rightarrow \mathcal{H} \otimes \mathcal{H}$. We can then define the vector

$$|\Psi\rangle = \sum_i \sqrt{p_i} |p_i\rangle \otimes |p_i\rangle \quad (14.48)$$

such that the original density matrix is reduction of the matrix

$$\rho = |\Psi\rangle\langle\Psi| \quad (14.49)$$

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 space.

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

$$\rho = |\text{EPR}\rangle\langle\text{EPR}| = \frac{1}{2}(|\uparrow_A\downarrow_B\rangle\langle\uparrow_A\downarrow_B| + |\downarrow_A\uparrow_B\rangle\langle\downarrow_A\uparrow_B| - |\uparrow_A\downarrow_B\rangle\langle\downarrow_A\uparrow_B| - |\downarrow_A\uparrow_B\rangle\langle\uparrow_A\downarrow_B|) \quad (14.50)$$

Tracing over \mathcal{H}_B we find the reduced density matrix Alice has access to is

$$\rho_A = \frac{1}{2}(|\uparrow_A\rangle\langle\uparrow_A| + |\downarrow_A\rangle\langle\downarrow_A|) \quad (14.51)$$

which is exactly what we expected, a 50-50 chance 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

$$\rho_{\text{measured}} = \frac{1}{2}(|\uparrow_A\downarrow_B\rangle\langle\uparrow_A\downarrow_B| + |\downarrow_A\uparrow_B\rangle\langle\downarrow_A\uparrow_B|) \quad (14.52)$$

tracing over \mathcal{H}_B we again find

$$\rho_A = \frac{1}{2}(|\uparrow_A\rangle\langle\uparrow_A| + |\downarrow_A\rangle\langle\downarrow_A|) \quad (14.53)$$

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

$$\rho = \sum_i p_i |p_i\rangle\langle p_i| \quad (14.54)$$

if we measure a certain observable O with eigenvectors $|\lambda_a\rangle$ then we will obtain the result λ_a with probability

$$P(|\lambda_a\rangle) = \sum_i p_i |\langle p_i | \lambda_a \rangle|^2 \quad (14.55)$$

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

$$\begin{aligned}\rho' &= \sum_a P(|\lambda_a\rangle) |\lambda_a\rangle\langle\lambda_a| = \sum_{ai} |\langle\lambda_a|p_i\rangle|^2 p_i |\lambda_a\rangle\langle\lambda_a| = \\ &= \sum_a |\lambda_a\rangle\langle\lambda_a| \left(\sum_i p_i |p_i\rangle\langle p_i| \right) |\lambda_a\rangle\langle\lambda_a| = \sum_a |\lambda_a\rangle\langle\lambda_a| \rho |\lambda_a\rangle\langle\lambda_a|\end{aligned}\quad (14.56)$$

Very crucially this is a linear action.

Additionally, if the Hamiltonian is given by H , then the states $|p_i\rangle$ evolve as

$$|p_i(t)\rangle = e^{-\frac{i}{\hbar}Ht} |p_i(0)\rangle \quad (14.57)$$

and therefore the density matrix evolves as

$$\rho(t) = \sum_i p_i |p_i(t)\rangle\langle p_i(t)| = \sum_i p_i e^{-\frac{i}{\hbar}Ht} |p_i(0)\rangle\langle p_i(0)| e^{\frac{i}{\hbar}Ht} \quad (14.58)$$

which is also linear. We can also write as a differential equation

$$i\hbar \frac{\partial \rho}{\partial t} = -[\rho, H] \quad (14.59)$$

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

$$\rho'_{ij} = \sum_{kl} K_{ik,jl} \rho_{kl} \quad (14.60)$$

where $K_{ik,jl}$ is the *kernel* and obeys

$$\sum_i K_{ik,il} = 1 \quad (14.61)$$

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

$$K_{i\alpha k\gamma, j\beta l\delta} = K_{ij,kl}^A K_{\alpha\gamma,\beta\delta}^B \quad (14.62)$$

The density matrix of subsystem A is

$$\rho_{ij}^A = \sum_\alpha \rho_{i\alpha,j\alpha} \quad (14.63)$$

which evolves as

$$\rho_{ij}^A \rightarrow \sum_{kl\alpha\gamma\delta} K_{ik,jl}^A K_{\alpha\gamma,\alpha\delta}^B \rho_{k\gamma,l\delta} = \sum_{kl} K_{ik,jl}^A \rho_{kl}^A \quad (14.64)$$

where we have used

$$\sum_\alpha K_{\alpha\gamma,\alpha\delta}^B = 1 \quad (14.65)$$

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 a 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

$$\mathbf{B} = -\alpha \mathbf{e}_x + (B_0 + \alpha z) \mathbf{e}_z \quad (15.1)$$

where B_0 is quite strong, the trajectory of the particle will approximately be given by

$$\frac{d^2 \langle \mathbf{X} \rangle}{dt^2} \approx \alpha \gamma \langle S_z \rangle \mathbf{e}_z \quad (15.2)$$

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 \mathbf{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 $|D_x\rangle$ the state corresponding to a dot on position x of the detector. If we have an incoming particle with initial position \mathbf{x}_i , in the spin-up state, the initial state of the full system, before the particle hits the detector is

$$|\mathbf{x}_i, \uparrow, D_\emptyset\rangle \quad (15.3)$$

This particle will be deflected upwards as dictated by (15.2), let us call the final position when it hits the detector \mathbf{x}_\uparrow . Then the final state, at the moment the particle hits the detector is

$$|\mathbf{x}_\uparrow, \uparrow, D_{\mathbf{x}_\uparrow}\rangle \quad (15.4)$$

Similarly, if the initial state was instead

$$|\mathbf{x}_i, \downarrow, D_\emptyset\rangle \quad (15.5)$$

the final state will be

$$|\mathbf{x}_\downarrow, \downarrow, D_{\mathbf{x}_\downarrow}\rangle \quad (15.6)$$

where \mathbf{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 \mathbf{x}_i .

$$|\psi_i\rangle = a |\mathbf{x}_i, \uparrow, D_\emptyset\rangle + b |\mathbf{x}_i, \downarrow, D_\emptyset\rangle \quad (15.7)$$

The time evolution is a linear action, therefore the final state will be given by

$$|\psi_f\rangle = a |\mathbf{x}_\uparrow, \uparrow, D_{\mathbf{x}_\uparrow}\rangle + b |\mathbf{x}_\downarrow, \downarrow, D_{\mathbf{x}_\downarrow}\rangle \quad (15.8)$$

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

$$D_\uparrow |D_x\rangle = |D_x\rangle \quad \text{for } \mathbf{x} = \mathbf{x}_\uparrow \quad (15.9)$$

$$D_\uparrow |D_x\rangle = 0 \quad \text{otherwise} \quad (15.10)$$

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:

$$D_\downarrow |D_x\rangle = |D_x\rangle \quad \text{for } x = x_\downarrow \quad (15.11)$$

$$D_\downarrow |D_x\rangle = 0 \quad \text{otherwise} \quad (15.12)$$

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

$$D_{\uparrow\vee\downarrow} |D_x\rangle = |D_x\rangle \quad \text{for } x = x_\uparrow \quad (15.13)$$

$$D_{\uparrow\vee\downarrow} |D_x\rangle = |D_x\rangle \quad \text{for } x = x_\downarrow \quad (15.14)$$

$$D_{\uparrow\vee\downarrow} |D_x\rangle = 0 \quad \text{otherwise} \quad (15.15)$$

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 x which is neither x_\uparrow nor 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

$$D_{\uparrow\vee\downarrow} |\psi_f\rangle = |\psi_f\rangle \quad (15.16)$$

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

$$O |i\rangle = \lambda_i |i\rangle \quad (15.17)$$

The observable which tells us whether we have observed a definite result of O is defined by

$$D |i\rangle = |i\rangle \quad (15.18)$$

$$D |\psi\rangle = 0 \quad \text{otherwise} \quad (15.19)$$

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

$$D |\psi\rangle = D \sum_i c_i |i\rangle = \sum_i c_i D |i\rangle = \sum_i |i\rangle = |\psi\rangle \quad (15.20)$$

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

$$|\psi\rangle = \sum_i c_i |i\rangle \quad (15.21)$$

then the state in the combined system of the N copies is

$$|\Psi\rangle = |\psi\rangle \otimes |\psi\rangle \otimes \dots = \sum_{i_1 i_2 \dots i_N} c_{i_1} c_{i_2} \dots c_{i_N} |i_1 i_2 \dots i_N\rangle \quad (15.22)$$

If the states $|i\rangle$ for an orthonormal basis then

$$\langle i_1 i_2 \dots i_N | j_1 j_2 \dots j_N \rangle = \delta_{i_1 j_1} \delta_{i_2 j_2} \dots \delta_{i_N j_N} \quad (15.23)$$

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

$$P_n |i_1 i_2 \dots i_N\rangle = \frac{N_n}{N} |i_1 i_2 \dots i_N\rangle \quad (15.24)$$

where N_n is how many indices i_1, i_2, \dots, i_N are equal to n .

Our goal is to show that

$$\left\| \left(P_n - |c_n|^2 \mathbb{1} \right) |\Psi\rangle \right\|^2 = \frac{|c_n|^2 (1 - |c_n|^2)}{N} \quad (15.25)$$

which shows that in the limit $N \rightarrow \infty$ 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

$$P_n |\Psi\rangle = \sum_{i_1 i_2 \dots i_N} c_{i_1} c_{i_2} \dots c_{i_N} P_n |i_1 i_2 \dots i_N\rangle = \sum_{i_1 i_2 \dots i_N} c_{i_1} c_{i_2} \dots c_{i_N} \frac{N_n}{N} |i_1 i_2 \dots i_N\rangle \quad (15.26)$$

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

$$\sum_n N_{I,n} = N \quad (15.27)$$

In this notation we write

$$|\Psi\rangle = \sum_I \left(\prod_n c_n^{N_{I,n}} \right) |I\rangle \quad (15.28)$$

and therefore

$$P_n |\Psi\rangle = \sum_I \left(\prod_m c_m^{N_{I,m}} \right) \frac{N_{I,n}}{N} |I\rangle \quad (15.29)$$

which gives us

$$\left\| \left(P_n - |c_n|^2 \mathbb{1} \right) |\Psi\rangle \right\|^2 = \sum_I \left(\prod_m |c_m|^{N_{I,m}} \right)^2 \left(\frac{N_{I,n}}{N} - |c_n|^2 \right)^2 \quad (15.30)$$

Instead of summing over I we can sum over N_1, N_2 , etc. The number of I s with $N_{I,n} = N_n$ for a given set of N_1, N_2, \dots is just the binomial coefficient

$$\frac{N!}{N_1! N_2! \dots} \quad (15.31)$$

therefore

$$\left\| \left(P_n - |c_n|^2 \mathbb{1} \right) |\Psi\rangle \right\|^2 = \sum_{N_1 N_2 \dots} \left(\prod_m |c_m|^{2N_m} \right) \left(\frac{N_n}{N} - |c_n|^2 \right)^2 \frac{N!}{N_1! N_2! \dots} \quad (15.32)$$

where the sum is constrained by $N_1 + N_2 + \dots = N$. Now we use the binomial theorem to write

$$\sum_{N_1 N_2 \dots} \left(\prod_m |c_m|^{2N_m} \right) \frac{N!}{N_1! N_2! \dots} = \left(\sum_m |c_m|^2 \right)^N \quad (15.33)$$

we can also write

$$|c_n|^2 \frac{\partial}{\partial |c_n|^2} \left(\prod_m |c_m|^{2N_m} \right) = N_n \quad (15.34)$$

and putting the two together we find

$$\begin{aligned} \left\| \left(P_n - |c_n|^2 \mathbb{1} \right) |\Psi\rangle \right\|^2 &= \left(\frac{1}{N} |c_n|^2 \frac{\partial}{\partial |c_n|^2} - |c_n|^2 \right)^2 \left(\sum_m |c_m|^2 \right)^N = \\ &= \left(\frac{1}{N^2} \left(|c_n|^2 \frac{\partial}{\partial |c_n|^2} \right)^2 - \frac{2}{N} |c_n|^4 \frac{\partial}{\partial |c_n|^2} + |c_n|^4 \right) \left(\sum_m |c_m|^2 \right)^N = \\ &= N(N-1) \frac{|c_n|^4}{N^2} \left(\sum_m |c_m|^2 \right)^{N-2} + N \frac{|c_n|^2}{N^2} \left(\sum_m |c_m|^2 \right)^{N-1} - \\ &\quad - 2N \frac{|c_n|^4}{N} \left(\sum_m |c_m|^2 \right)^{N-1} + |c_n|^4 \left(\sum_m |c_m|^2 \right)^N \end{aligned} \quad (15.35)$$

using $\sum_i |c_i|^2 = 1$ we find

$$\left\| \left(P_n - |c_n|^2 \mathbb{1} \right) |\Psi\rangle \right\|^2 = \frac{|c_n|^2 (1 - |c_n|^2)}{N} \quad (15.36)$$

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 frequentist in nature which is not what a lot of statisticians prefer. Secondly, the limit $N \rightarrow \infty$ 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're 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 way⁵⁸.

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

$$P_i = \text{Tr}(\rho |i\rangle\langle i|) \quad (15.37)$$

where ρ obeys the axioms of a density matrix. Although it doesn't have the flavour and intuitiveness of the frequentist 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

$$\frac{1}{\sqrt{2}}(|\uparrow\rangle + |\downarrow\rangle) \quad (15.38)$$

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 Schrödinger 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

$$|\text{source}\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |0\rangle) \quad (15.39)$$

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

$$|\text{cat}\rangle = \frac{1}{\sqrt{2}}(|\text{alive}\rangle + |\text{dead}\rangle) \quad (15.40)$$

⁵⁸A 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

$$|\text{Alice}\rangle \propto |\text{cat alive}\rangle |\text{Alice sees cat alive}\rangle + |\text{cat dead}\rangle |\text{Alice sees cat dead}\rangle \quad (15.41)$$

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

$$\rho_S = \text{Tr}_E |\psi\rangle\langle\psi| \quad (15.42)$$

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

$$|\psi(0)\rangle = |\phi_S\rangle \otimes |\chi_E\rangle \quad (15.43)$$

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

$$\rho_S(0) = |\phi_S\rangle\langle\phi_S| \quad (15.44)$$

The state of the full system at time t is given by

$$|\psi(t)\rangle = U(t) |\psi(0)\rangle \quad (15.45)$$

therefore, the system density matrix is

$$\begin{aligned} \rho_S(t) &= \text{Tr}_E(|\psi(t)\rangle\langle\psi(t)|) = \text{Tr}_E(U(t)|\psi(0)\rangle\langle\psi(0)|U(t)^\dagger) = \\ &= \sum_{\alpha} \langle\alpha_E|U(t)|\psi(0)\rangle\langle\psi(0)|U(t)^\dagger|\alpha_E\rangle \end{aligned} \quad (15.46)$$

where $\{|\alpha_E\rangle\}$ is a basis of \mathcal{H}_E .

If we define the *Kraus* operators $M_\alpha(t) : \mathcal{H}_S \rightarrow \mathcal{H}_S$

$$M_\alpha(t) = \langle\alpha_E|U(t)|\chi\rangle = \text{Tr}_E(U(t)|\chi\rangle\langle\alpha_E|) \quad (15.47)$$

we can write the time evolution of the system density matrix as

$$\rho_S(t) = \sum_{\alpha} M_{\alpha}(t) \rho_S(0) M_{\alpha}(t)^{\dagger} \quad (15.48)$$

which is in general not a unitary transformation (although it *is* linear!).

If the Hamiltonian does not actually couple the two systems so that

$$H = H_S \otimes \mathbb{1}_E + \mathbb{1}_S \otimes H_E \quad (15.49)$$

we have

$$U(t) = U_S(t) \otimes U_E(t) \quad (15.50)$$

which gives

$$\begin{aligned} \rho_S(t) &= \sum_{\alpha} M_{\alpha}(t) \rho_S(0) M_{\alpha}(t)^{\dagger} = \sum_{\alpha} \langle \alpha_E | U_E(t) | \chi \rangle U_S(t) \rho_S(0) U_S(t)^{\dagger} \langle \chi | U_E(t)^{\dagger} | \alpha_E \rangle = \\ &= U_S(t) \rho_S(0) U_S(t)^{\dagger} \sum_{\alpha} \langle \chi | U_E(t) | \alpha_E \rangle \langle \alpha_E | U_E(t)^{\dagger} | \chi \rangle = \\ &= U_S(t) \rho_S(0) U_S(t)^{\dagger} \langle \chi | U_E(t) U_E(t)^{\dagger} | \chi \rangle = \\ &= U_S(t) \rho_S(0) U_S(t)^{\dagger} \langle \chi | \chi \rangle = \\ &= U_S(t) \rho_S(0) U_S(t)^{\dagger} \end{aligned} \quad (15.51)$$

which is unitary!

We see that if the system 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):

$$U |\uparrow\rangle \otimes |0\rangle = |\uparrow\rangle \otimes \left(\sqrt{1-p} |0\rangle + \sqrt{p} |1\rangle \right) \quad (15.52)$$

$$U |\downarrow\rangle \otimes |0\rangle = |\downarrow\rangle \otimes \left(\sqrt{1-p} |0\rangle + \sqrt{p} |2\rangle \right) \quad (15.53)$$

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

$$|\psi\rangle = (a |\uparrow\rangle + b |\downarrow\rangle) \otimes |0\rangle \quad (15.54)$$

where $|a|^2 + |b|^2 = 1$, so that the initial system density matrix is

$$\rho_S(0) = \begin{pmatrix} |a|^2 & ab^* \\ a^*b & |b|^2 \end{pmatrix} \quad (15.55)$$

The Kraus operators for this time evolution are

$$M_0 = \langle 0 | U | 0 \rangle = \sqrt{1-p} \mathbb{1}_S \quad (15.56)$$

$$M_1 = \langle 1 | U | 0 \rangle = \sqrt{p} |\uparrow\rangle\langle\uparrow| \quad (15.57)$$

$$M_2 = \langle 2 | U | 0 \rangle = \sqrt{p} |\downarrow\rangle\langle\downarrow| \quad (15.58)$$

Therefore, the system density matrix at later times is given by

$$\rho_S(t) = \begin{pmatrix} |a|^2 & (1-p)ab^* \\ (1-p)a^*b & |b|^2 \end{pmatrix} \quad (15.59)$$

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

$$(1-p)^N = \left(1 - \Gamma \frac{t}{N}\right)^N \rightarrow e^{-\Gamma t} \quad (15.60)$$

and therefore

$$\rho_S(t) \rightarrow \begin{pmatrix} |a|^2 & e^{-\Gamma t} ab^* \\ e^{-\Gamma t} a^* b & |b|^2 \end{pmatrix} \rightarrow \begin{pmatrix} |a|^2 & 0 \\ 0 & |b|^2 \end{pmatrix} \quad (15.61)$$

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 \mathbf{X} and therefore in the position basis it will not change the system. This is ultimately why in the Stern-Gerlach we preferred $|\mathbf{x}_\uparrow\rangle$ and $|\mathbf{x}_\downarrow\rangle$ 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 damped. Decoherence solves the basis problem.

The second lesson is due to the final form of the density matrix. It looks like

$$\rho_S \rightarrow |a|^2 |\uparrow\rangle\langle\uparrow| + |b|^2 |\downarrow\rangle\langle\downarrow| \quad (15.62)$$

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

$$\rho_S \rightarrow |a|^2 |\uparrow, D_{x_\uparrow}\rangle\langle\uparrow, D_{x_\uparrow}| + |b|^2 |\downarrow, D_{x_\downarrow}\rangle\langle\downarrow, D_{x_\downarrow}| \quad (15.63)$$

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

$$\rho_S \rightarrow |a|^2 |\uparrow, D_{x_\uparrow}\rangle\langle\uparrow, D_{x_\uparrow}| + |b|^2 |\downarrow, D_{x_\downarrow}\rangle\langle\downarrow, D_{x_\downarrow}| \rightarrow |\uparrow, D_{x_\uparrow}\rangle\langle\uparrow, D_{x_\uparrow}| \quad (15.64)$$

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.

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The evolution of the total density matrix, ρ_T is given by

$$i\hbar \frac{\partial \rho_T}{\partial t} = [H_T, \rho_T] \quad (15.65)$$

but we are only interested in the evolution of the system density matrix, ρ_S defined as

$$\rho_S = \text{Tr}_E \rho_T \quad (15.66)$$

We will write the total Hamiltonian as follows

$$H_T = H_S \otimes \mathbb{1}_E + \mathbb{1}_S \otimes H_E + \epsilon H_{SE} \quad (15.67)$$

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

$$H_{SE} = \sum_i S_i \otimes E_i \quad (15.68)$$

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

$$\hat{A}_T(t) = e^{\frac{i}{\hbar}(H_S \otimes \mathbb{1}_E + \mathbb{1}_S \otimes H_E)t} A_T e^{-\frac{i}{\hbar}(H_S \otimes \mathbb{1}_E + \mathbb{1}_S \otimes H_E)t} \quad (15.69)$$

to strip out the unimportant time-evolution due to the isolated parts of the Hamiltonians.

Using this notation we can write

$$i\hbar \frac{\partial \hat{\rho}_T}{\partial t} = \epsilon [\hat{H}_{SE}(t), \hat{\rho}_T(t)] \quad (15.70)$$

We can turn this equation into an integral one (note that $\hat{A}(0) = A(0)$ for any operator)

$$\hat{\rho}_T(t) = \rho_T(0) - \frac{i\epsilon}{\hbar} \int_0^t ds [\hat{H}_{SE}(s), \hat{\rho}_T(s)] \quad (15.71)$$

and then plug this expression back into the differential version

$$\frac{\partial \hat{\rho}_T}{\partial t} = -\frac{i\epsilon}{\hbar} [\hat{H}_{SE}(t), \rho_T(0)] - \frac{\epsilon^2}{\hbar^2} \int_0^t ds [\hat{H}_{SE}(t), [\hat{H}_{SE}(s), \hat{\rho}_T(s)]] \quad (15.72)$$

and once more

$$\frac{\partial \hat{\rho}_T}{\partial t} = -\frac{i\epsilon}{\hbar} [\hat{H}_{SE}(t), \rho_T(0)] - \frac{\epsilon^2}{\hbar^2} \int_0^t ds [\hat{H}_{SE}(t), [\hat{H}_{SE}(s), \hat{\rho}_T(s)]] + O(\epsilon^3) \quad (15.73)$$

from this point onward we will neglect terms of order $O(\epsilon^3)$.

In terms of the system density matrix we have

$$\frac{\partial \hat{\rho}_S}{\partial t} = -\frac{i\epsilon}{\hbar} \text{Tr}_E [\hat{H}_{SE}(t), \rho_T(0)] - \frac{\epsilon^2}{\hbar^2} \int_0^t ds \text{Tr}_E [\hat{H}_{SE}(t), [\hat{H}_{SE}(s), \hat{\rho}_T(s)]] \quad (15.74)$$

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

$$\text{Tr}_E [\hat{H}_{SE}(t), \rho_T(0)] = \sum_i (\hat{S}_i(t) \rho_S(0) \text{Tr}_E (\hat{E}_i(t) \rho_E(0)) - \rho_S(0) \hat{S}_i(t) \text{Tr}_E (\rho_E(0) \hat{E}_i(t))) \quad (15.75)$$

Because $\rho_E(0)$ is thermal, we have $[H_E, \rho_E(0)] = 0$, using the cyclicity of the trace, we have

$$\text{Tr}_E (\hat{E}_i(t) \rho_E(0)) = \text{Tr}_E (E_i \rho_E(0)) \equiv \langle E_i \rangle \quad (15.76)$$

Without loss of generality we can assume $\langle E_i \rangle = 0$, because we can always shift

$$H_S \rightarrow H_S + \epsilon \sum_i \langle E_i \rangle S_i \quad \text{and} \quad H_{SE} \rightarrow \sum_i S_i \otimes (E_i - \langle E_i \rangle) \quad (15.77)$$

to ensure it is the case. All in all, the first term in (15.74) vanishes, and we can therefore write

$$\frac{\partial \hat{\rho}_S}{\partial t} = -\frac{\epsilon^2}{\hbar^2} \int_0^t ds \text{Tr}_E \left[\hat{H}_{SE}(t), [\hat{H}_{SE}(s), \hat{\rho}_T(t)] \right] \quad (15.78)$$

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

$$\hat{\rho}_T(t) = \hat{\rho}_S(t) \otimes \hat{\rho}_E(t) \quad (15.79)$$

Changing variables $s \rightarrow t - s$ we can write

$$\frac{\partial \hat{\rho}_S}{\partial t} = -\frac{\epsilon^2}{\hbar^2} \int_0^t ds \text{Tr}_E \left[\hat{H}_{SE}(t), [\hat{H}_{SE}(t-s), \hat{\rho}_S(t) \otimes \hat{\rho}_E(t)] \right] \quad (15.80)$$

now we expand the commutators to write

$$\begin{aligned} \frac{\partial \hat{\rho}_S}{\partial t} = & -\frac{\epsilon^2}{\hbar^2} \int_0^t ds \text{Tr}_E \left(\hat{H}_{SE}(t) \hat{H}_{SE}(t-s) (\hat{\rho}_S(t) \otimes \hat{\rho}_E(t)) - \right. \\ & - \hat{H}_{SE}(t) (\hat{\rho}_S(t) \otimes \hat{\rho}_E(t)) \hat{H}_{SE}(t-s) - \\ & - \hat{H}_{SE}(t-s) (\hat{\rho}_S(t) \otimes \hat{\rho}_E(t)) \hat{H}_{SE}(t) + \\ & \left. + (\hat{\rho}_S(t) \otimes \hat{\rho}_E(t)) \hat{H}_{SE}(t-s) \hat{H}_{SE}(t) \right) \end{aligned} \quad (15.81)$$

To proceed we need an expression for $\hat{S}_i(t)$, its definition is

$$\hat{S}_i(t) = e^{\frac{i}{\hbar} H_S t} S_i e^{-\frac{i}{\hbar} H_S t} \quad (15.82)$$

which can be written differentially as

$$\frac{\partial \hat{S}_i}{\partial t} = \frac{i}{\hbar} [H_S, \hat{S}_i] \quad (15.83)$$

Defining an operator inner product

$$(A, B) \equiv \text{Tr}(A^\dagger B) \quad (15.84)$$

we can show that the action of the commutator is Hermitian if H_S is Hermitian

$$\begin{aligned} (A, [H_S, B]) &= \text{Tr}(A^\dagger [H_S, B]) = \\ &= \text{Tr}(A^\dagger H_S B - A^\dagger B H_S) = \\ &= \text{Tr}(A^\dagger H_S B - H_S A^\dagger B) = \\ &= \text{Tr}((H_S A)^\dagger B - (A H_S)^\dagger B) = \end{aligned}$$

$$\begin{aligned}
&= \text{Tr} \left(([H_S, A])^\dagger B \right) = \\
&= ([H_S, A], B)
\end{aligned} \tag{15.85}$$

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

$$\hat{H}_{SE}(t) = \sum_{\omega, i} e^{-i\omega t} S_i(\omega) \otimes \hat{E}_i(t) = \sum_{\omega, i} e^{i\omega t} S_i^\dagger(\omega) \otimes \hat{E}_i^\dagger(t) \tag{15.88}$$

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

$$\begin{aligned}
\hbar \frac{\partial \hat{\rho}_S}{\partial t} = & \sum_{\omega, \omega', i, j} \left(e^{-i(\omega-\omega')t} \Gamma_{ij}(\omega, t) \left[S_i(\omega) \hat{\rho}_S(t), S_j^\dagger(\omega') \right] + \right. \\
& \left. + e^{i(\omega-\omega')t} \Gamma_{ji}^*(\omega, t) \left[S_i(\omega), \hat{\rho}_S(t) S_j^\dagger(\omega') \right] \right) \tag{15.89}
\end{aligned}$$

where

$$\Gamma_{ij}(\omega, t) = \frac{\epsilon^2}{\hbar} \int_0^t ds e^{i\omega s} \text{Tr}_E \left(\hat{E}_j^\dagger(t) \hat{E}_i(t-s) \hat{\rho}_E(t) \right) \tag{15.90}$$

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

$$\Gamma_{ij}(\omega, t) = \frac{\epsilon^2}{\hbar} \int_0^t ds e^{i\omega s} \text{Tr}_E \left(\hat{E}_j^\dagger(s) E_i \rho_E(0) \right) \tag{15.91}$$

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 $t \rightarrow \infty$ in the definition of $\Gamma_{ij}(\omega, t)$ to write

$$\hbar \frac{\partial \hat{\rho}_S}{\partial t} = \sum_{\omega, i, j} \left(\Gamma_{ij}(\omega) \left[S_i(\omega) \hat{\rho}_S(t), S_j^\dagger(\omega) \right] + \Gamma_{ji}^*(\omega) \left[S_i(\omega), \hat{\rho}_S(t) S_j^\dagger(\omega) \right] \right) \tag{15.92}$$

where

$$\Gamma_{ij}(\omega) = \frac{\epsilon^2}{\hbar} \int_0^\infty ds e^{i\omega s} \text{Tr}_E \left(\hat{E}_j^\dagger(s) E_i \rho_E(0) \right) \tag{15.93}$$

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 $\Gamma_{ij}(\omega)$ into

$$\pi_{ij}(\omega) \equiv -\frac{i}{2} (\Gamma_{ij}(\omega) - \Gamma_{ij}^*(\omega)) \tag{15.94}$$

$$\gamma_{ij}(\omega) \equiv \Gamma_{ij}(\omega) + \Gamma_{ij}^*(\omega) = \frac{\epsilon^2}{\hbar^2} \int_{-\infty}^\infty ds e^{i\omega s} \text{Tr}_E \left(\hat{E}_j^\dagger(s) E_i \rho_E(0) \right) \tag{15.95}$$

Removing the hats to go back to the usual Schrodinger picture time dependence we find

$$\hbar \frac{\partial \rho_S}{\partial t} = -i[H'_S, \rho_S(t)] + \sum_{\omega, i, j} \gamma_{ij}(\omega) \left(S_i(\omega) \rho_S(t) S_j^\dagger(\omega) - \frac{1}{2} \{ S_j^\dagger(\omega) S_i(\omega), \rho_S(t) \} \right) \quad (15.96)$$

where

$$H'_S = H_S + \sum_{\omega, i, j} \pi_{ij}(\omega) S_j^\dagger(\omega) S_i(\omega) \quad (15.97)$$

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

$$\hbar \frac{\partial \rho_S}{\partial t} = -i[H'_S, \rho_S(t)] + \sum_{\omega, i} \left(L_i(\omega) \rho_S(t) L_i^\dagger(\omega) - \frac{1}{2} \{ L_i^\dagger(\omega) L_i(\omega), \rho_S(t) \} \right) \quad (15.98)$$

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

$$\hbar \frac{\partial \rho_S}{\partial t} = -i[H'_S, \rho_S(t)] + \sum_a \left(L_a \rho_S(t) L_a^\dagger - \frac{1}{2} \{ L_a^\dagger L_a, \rho_S(t) \} \right) \quad (15.99)$$

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

$$\rho_S \sim P_\alpha |\alpha\rangle\langle\alpha| \quad (15.100)$$

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 $|\alpha\rangle\langle\alpha|$.

$$L_a = \sum_{i\omega} l_{a\alpha} |\alpha\rangle\langle\alpha| \quad (15.101)$$

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 true⁵⁹. 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 $|\text{dead}\rangle$.

⁵⁹If 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

$$\hbar \frac{\partial \rho_S}{\partial t} = \sum_{\alpha\beta} C_{\alpha\beta} \left(|\alpha\rangle\langle\alpha| \rho_S(t) |\beta\rangle\langle\beta| - \frac{\delta_{\alpha\beta}}{2} \{|\alpha\rangle\langle\alpha|, \rho_S(t)\} \right) \quad (15.102)$$

where

$$C_{\alpha\beta} = \sum_a l_{a\alpha} l_{a\beta} \quad (15.103)$$

Using the ansatz

$$\rho_S(t) = \sum_{\alpha\beta} f_{\alpha\beta}(t) |\alpha\rangle\langle\alpha| \rho(0) |\beta\rangle\langle\beta| \quad (15.104)$$

with the initial condition $f_{\alpha\beta}(0) = 1$ we find

$$\frac{df_{\alpha\beta}}{dt} = \lambda_{\alpha\beta} f_{\alpha\beta} \quad (15.105)$$

where

$$\lambda_{\alpha\beta} = C_{\alpha\beta} - \frac{1}{2} (C_{\alpha\alpha} + C_{\beta\beta}) = -\frac{1}{2} \sum_a (l_{a\alpha} - l_{a\beta})^2 \quad (15.106)$$

The solution to this equation is of course

$$f_{\alpha\beta}(t) = e^{\lambda_{\alpha\beta} t} \quad (15.107)$$

therefore we can write

$$\rho_S(t) = \sum_{\alpha\beta} e^{\lambda_{\alpha\beta} t} |\alpha\rangle\langle\alpha| \rho(0) |\beta\rangle\langle\beta| \quad (15.108)$$

In the generic case where there are no degeneracies and

$$l_{a\alpha} = l_{a\beta} \implies \alpha = \beta \quad (15.109)$$

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

$$\rho_S(t) \rightarrow \sum_{\alpha} |\alpha\rangle\langle\alpha| \rho(0) |\alpha\rangle\langle\alpha| \quad (15.110)$$

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 how 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 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.