B7.3 FURTHER QUANTUM THEORY

OXFORD UNIVERSITY MATHEMATICS, PART B

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(based in part on notes by Prof. Lionel Mason)

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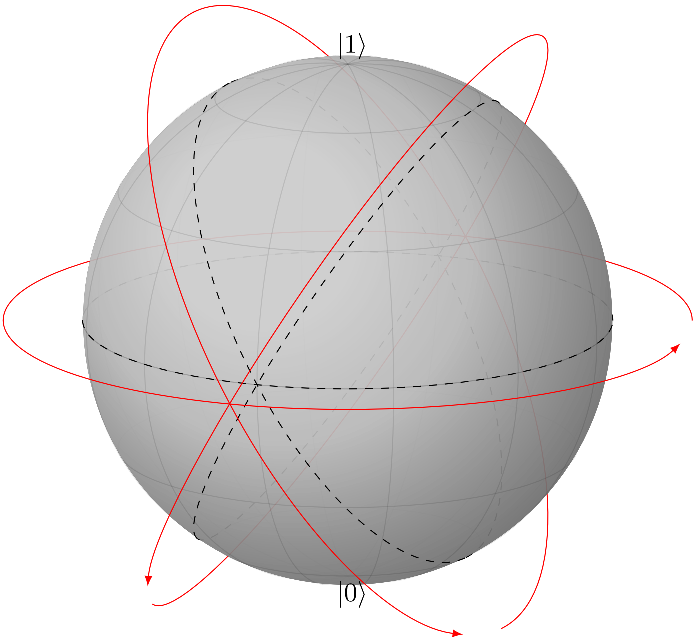

HT 2021

PART B
FURTHER QUANTUM THEORY

16 lectures HT 2021

Overview

Welcome to *B7.3 Further Quantum Theory*, part of the third year (Part B) of the Oxford University Mathematics course. This course is a continuation from the Part A long option *Quantum Theory*. In that first course, you have been introduced to many of the core concepts of quantum theory (often referred to as *quantum mechanics*, in reference to its status as an improvement upon the classical mechanics of particles that you've studied in your Dynamics course, as well as possibly *B7.1 Classical Mechanics*).

In this course we will be developing the subject more broadly and deeply, giving more time and emphasis to the abstract mathematical formalism of the theory as well as developing several important technical methods that are used to analyse quantum mechanical systems in practice. Along the way, a number of concepts from the theories of functional analysis, Lie groups, and representation theory will arise and be introduced, though you will not be expected to be familiar with these subjects in advance. Whenever possible I will point out places where the mathematically precise version of a statement exists but involves more machinery than we have available, before giving a simplified treatment that will serve our purposes.

Synopsis

- Abstract formulation of quantum mechanics in terms of linear operators on Hilbert spaces; Dirac notation; discrete and continuum states; time evolution and the propagator.
- Systems of several particles and Hilbert space tensor products; distinguishable and indistinguishable particles; Fermi-Dirac and Bose-Einstein statistics; Pauli exclusion principle; elementary aspects of quantum entanglement.
- Symmetries in quantum mechanics as unitary and anti-unitary operators; rotations, angular momentum, and spin; spin-$\frac{1}{2}$ and projective representations of $SO(3)$; addition of angular momentum; spin-statistics theorem.
- Approximation methods: Rayleigh-Schrödinger perturbation theory; variational methods; WKB approximation and Bohr-Sommerfeld quantisation.
- Time-dependence in the Heisenberg, Schrödinger, and interaction/Dyso pictures; time-dependent perturbation theory and the Feynman-Dyson expansion. (**Not Covered in 2021 - Not Examinable in 2021**)

- Elementary scattering theory.

Reading

You can never have enough quantum mechanics textbooks (I count around fifteen on my bookshelves right now). Accordingly, you should feel encouraged to look at a number of sources and find some that are written in a way that you find appealing. This said, the primary textbook references for this course are officially

- S. Weinberg, *Lectures on Quantum Mechanics* (CUP 2015).
- K. Hannabuss, *An Introduction to Quantum Theory* (OUP 1997).

The former probably more than the latter. We won't follow the notation of either of those references religiously. The following are also recommended for reference:

- E. Merzbacher, *Quantum Mechanics* (Wiley International 1970).
- D. Griffiths and D. Schroeter, *Introduction to Quantum Mechanics* (CUP 2018).
- J. Sakurai and J. Napolitano, *Modern Quantum Mechanics* (CUP 2017).

The latter two are standards, with Sakurai being a bit closer to the lecturer's style. The first is an older text that treats a number of topics in a bit more detail. In particular, the section on *Wave Packets and Free Particle Motion* in Merzbacher is nice, as well as the treatment of the WKB approximation.

Mathematical purists and rigour enthusiasts may want to take a peak at the (quite advanced) textbooks

- B. Hall, *Quantum Theory for Mathematicians* (Springer 2013).
- V. Moretti, *Fundamental Mathematical Structures of Quantum Theory* (Springer 2019).

These are both go far beyond the level of the present course, but (unlike the most of the other references) they were really written for mathematicians rather than physicists.

Note on these notes

These notes are meant to correspond to and supplement the recorded lectures for this course. They will be updated throughout the term with new Chapters added once the corresponding lectures are recorded. I also welcome feedback on the notes if there are typos or places where the text is unclear. Please send comments and corrections to `christopher.beem@maths.ox.ac.uk`.

Contents

Chapter 0

Review of Wave Mechanics, Standard Examples

The majority of your first course on quantum theory focused on the study of the Schrödinger equation (usually time-independent, but occasionally time-dependent) for single-particle wave functions in one, two, or occasionally three dimensions. These topics generally fall within the realm of what is called *wave mechanics*. We include in this (preparatory) section a brief recap of that formalism along with a review of some standard examples treated in this formalism that should be familiar from your previous course. In the remainder of this course we will freely refer back to these standard results. This is not meant to be a comprehensive review of the material from your part A course; and you should be prepared to refer to background material from that course as well. *The material in this section will not be the subject of any lectures.*

0.1 Review of wave mechanics

The primary object of wave mechanics is Schrödinger's *wave function* for a particle moving in, say, one dimension. This is a complex valued function of position x on the real line and time t, conventionally denoted $\Psi(x,t)$. The wave function is usually normalised to obey

$$\int_{-\infty}^{\infty} \mathrm{d}x\, |\Psi(x,t)|^2 = 1 \ . \tag{0.1}$$

The wave function encodes the probability density $\rho(x,t)$ for detecting the presence of the particle at a given point at a given time according to

$$\rho(x,t) = |\Psi(x,t)|^2 \ , \tag{0.2}$$

so the normalisation condition is just the condition that the total probability for finding the particle *somewhere* is one.

If a particle moves subject to an external potential energy function $V(x)$, then the wave function evolves according to the *time-dependent Schrödinger equation*, which says that

$$i\hbar \frac{\partial}{\partial t}\Psi(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) + V(x)\Psi(x,t) \ . \tag{0.3}$$

Here $\hbar$ is the reduced Planck constant, which is a fundamental unit of angular momentum (*i.e.*, it has units of $[mass] \times [length]^2 \times [time]^{-1}$).[1] It is a simple exercise to confirm that if $\Psi(x,t)$ evolves in time according to (0.3) then the normalisation condition (0.1) will hold for all time t if it holds at any given time t_0.

The differential operator in x acting on $\Psi(x,t)$ on the right hand side of this equation is the *Hamiltonian operator* for the theory. If we introduce the operators P and X acting on wave

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[1] In SI units, the reduced Planck constant is $\hbar \approx 1.0546 \times 10^{-34}\ kg \cdot m/s^2$. In a quantum mechanical world, it is often a better idea to use units in which $\hbar = 1$ (so-called natural units). For much of this course, $\hbar$ will behave more like a formal parameter.

function according to

$$P\Psi(x,t) = -i\hbar\frac{\partial}{\partial x}\Psi(x,t) \ , \qquad X\Psi(x,t) = x\Psi(x,t) \ , \tag{0.4}$$

then the Hamiltonian operator takes the form of the classical total energy operator (also the Hamiltonian of the corresponding classical system, if you have taken Part B Classical Mechanics),

$$H = \frac{P^2}{2m} + V(X) \ . \tag{0.5}$$

The time-dependent Schrödinger equation then takes the abstract form

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = H\Psi(x,t) \ . \tag{0.6}$$

In good cases, we look for separable solutions to this equation of the form

$$\Psi(x,t) = \psi_n(x)\exp\left(-\frac{iE_nt}{\hbar}\right) \ , \tag{0.7}$$

where E_n are identified with the *energies* of these solutions, and the $\psi_n(x)$ are *stationary state wave functions* that obey the *time-independent Schrödinger equation*,

$$H\psi_n(x) = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi_n(x) + V(x)\psi_n(x) = E_n\psi_n(x) \ . \tag{0.8}$$

We see that all of the time-dependence for stationary states is encapsulated by the time-dependent phase in (0.7). Then if the ψ_n form a *basis* for the space of possible wave functions at a fixed time, we can understand time-evolution in general by observing

$$\Psi(x,0) = \sum_n a_n\psi_n(x) \quad \Longrightarrow \quad \Psi(x,t) = \sum_n a_n \exp\left(-\frac{iE_nt}{\hbar}\right)\psi_n(x) \ . \tag{0.9}$$

This follows from the linearity of Schrödinger's equation.

By virtue of the structure outlined above, a major part of one's introduction to the world of quantum mechanics often involves learning a variety of standard examples where the stationary-state wave functions $\psi_n(x)$ can be understood completely. Below we review a few of these for ease of reference in the future.

Example 0.1.1 (Particle in a box)**.** When our particle is restricted to move in a fixed interval, say $x \in [0,a]$, this is referred to as the particle in a (one-dimensional) box. One can think of this as considering the general case of a particle on a real line with a potential $V(x)$ that is zero in the given interval and infinite outside of it.

The stationary state wave functions satisfy

$$-\frac{\hbar^2}{2m}\psi_n''(x) = E_n\psi_n(x) \ , \qquad \psi_n(0) = \psi_n(a) = 0 \ . \tag{0.10}$$

It follows that the stationary states and their energies are given by

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right) \ , \qquad E_n = \frac{\hbar^2n^2\pi^2}{a^2} \ . \tag{0.11}$$

The pre-factor is to render the stationary-state wave functions normalised. Indeed we have

$$\int_0^a \mathrm{d}x\ \overline{\psi_n(x)}\psi_m(x) = \delta_{n,m}\ . \tag{0.12}$$

Indeed, these sin functions form an orthonormal basis for the space of wave function on the interval in the sense of Fourier series, so the time-evolution of a general wave function can be understood by decomposing into its Fourier representation and introducing time-dependent phases depending on energies.

Example 0.1.2 (Harmonic Oscillator)**.** The next standard example is the harmonic osciillator, for which x is allowed to range over the entire real line but we have a potential function $V(x) = \frac{1}{2}m\omega^2x^2$. This is written so that the *classical* angular frequency of oscillator for the system would be ω.

Here the stationary state wave functions are given by

$$\psi_n(x) = \frac{1}{\sqrt{2^n\, n!}}\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}\exp\left(-\frac{m\omega x^2}{2\hbar}\right)H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right)\ , \tag{0.13}$$

where $H_n(x)$ is the Hermite polynomial,

$$H_n(x) = (-1)^n e^{x^2}\frac{\mathrm{d}^n}{\mathrm{d}x^n}\left(e^{x^2}\right)\ . \tag{0.14}$$

The analysis of this system is rendered must simpler by introducing the differential operators

$$\alpha_+ = \frac{1}{\sqrt{2m\hbar\omega}}(P + im\omega X)\ , \qquad \alpha_+ = \frac{1}{\sqrt{2m\hbar\omega}}(P - im\omega X)\ , \tag{0.15}$$

which obey a number of helpful relations,

$$\begin{aligned} \alpha_-\alpha_+ - \alpha_+\alpha_- =: [\alpha_-, \alpha_+] &= 1\ , & (0.16)\\ [H, \alpha_\pm] &= \hbar\omega\alpha_\pm\ , & (0.17)\\ H &= \hbar\omega(\alpha_\pm\alpha_\mp \pm \tfrac{1}{2})\ , & (0.18) \end{aligned}$$

In particular, the second relation implies that if $H\psi = E\psi$, then $H\alpha_\pm\psi = (E \pm \hbar\omega)\alpha_\pm\psi$, so the $\alpha_\pm$ differential operators move amongst stationary states in the space of wave functions.

Then the ground state wave function can be argued to obey $\alpha_-\psi_0 = 0$, which can be immediately solved to give the expression from (0.13) for $n = 0$, with energy $E_0 = \hbar\omega/2$ by virtue of (0.18). The higher energy states are obtained by the action of α_+,

$$\psi_n = \frac{(\alpha_+)^n}{\sqrt{n!}}\psi_0\ , \tag{0.19}$$

where the prefactor is such that the results are normalised when ψ_0 is normalised. These states then give the general result for the energy spectrum of the quantum harmonic oscillator,

$$H\psi_n = E_n\psi_n = \hbar\omega\left(n + \frac{1}{2}\right)\psi_n\ . \tag{0.20}$$

Example 0.1.3 (Hydrogenic atom)**.** Finally, there is the famous Hydrogen atom (or the Hydrogen-like or Hydrogenic atom if you allow general nuclear charge $Z > 0$). Here we have a three-dimensional problem with Coulomb potential,[2]

$$V(\mathbf{r}) = -\frac{Zq_e}{|\mathbf{r}|} \ . \tag{0.21}$$

A detailed analysis of the time-independent Schrödinger equation for this problem appeared in your Part A course, and we give a lightning review here. The stationary states are labelled by three *quantum numbers*, (n, ℓ, m), known as the principal quantum number, the orbital quantum number, and the magnetic quantum number, respectively. These are restricted according to $n = 1, 2, 3, \ldots$, $\ell = 0, 1, \ldots, n-1$, $m = -\ell, -\ell+1, \ldots, \ell-1, \ell$. The stationary state wave functions take the form

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n,\ell}(r) Y_{\ell,m}(\theta, \phi) = R_{n,\ell}(r) P_{\ell,m}(\cos\theta) e^{im\phi} \ . \tag{0.22}$$

The $Y_{\ell,m}(\theta, \phi)$ are spherical harmonic functions, which obey

$$\mathbf{L}^2 Y_{\ell,m}(\theta, \phi) = \hbar^2 \ell(\ell+1) Y_{\ell,m}(\theta, \phi) \ , \qquad L_3 Y_{\ell,m}(\theta, \phi) = \hbar m Y_{\ell,m}(\theta, \phi) \ , \tag{0.23}$$

where

$$\mathbf{L} = -i\hbar \left(\mathbf{x} \wedge \nabla\right) \ , \qquad L_3 = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) = -i\hbar \partial_\phi \ . \tag{0.24}$$

The $P_{\ell,m}(\cos\theta)$ are the *associated Legendre polynomials*. The radial wave function takes the form

$$R_{n,\ell}(r) = \exp\left(-\frac{Zr}{na_0} \right) f_{n,\ell}(r) \ , \tag{0.25}$$

where $f_{n,\ell}(r)$ is a polynomial of degree $n-1$. The energy, E_n, depends only on the principal quantum number and is given by

$$E_n = -\frac{\hbar^2 Z^2}{2ma_0^2 n^2} = -\frac{q_e^2 Z^2}{2a_0 n^2} \ . \tag{0.26}$$

In the first expression we used the *Bohr radius* $a_0 = \hbar^2/(mq_e^2)$. Note that the energy is always negative, so the exponential in (0.25) is decaying with r.

Unlike the previous two cases, the stationary state wave functions given here don't form a basis for all possible wave functions of the Hydrogen atom problem. Rather, they form a basis only for the *bound state wave functions*.[3] The possibility of additional wave functions for the Hydrogen atom that are not bound states is relevant in the context of *scattering theory*.

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[2] We adopt Gaussian units to avoid a factor of $\pi\epsilon_0$ in the denominator. Here q_e is the charge of the electron, often written as e in spite of the ambiguity with Euler's constant.

[3] We don't give a technical definition of bound state, but intuitively it corresponds to states where the electron stays localised in the neighborhood of the nucleus instead of running off to infinity.

Chapter 1

Postulates and Examples

To begin, we review the foundational postulates of quantum theory. You will have encountered these in perhaps a less detailed form, in *Part A Quantum Theory.* Here we will strive for a high degree of accuracy, while stopping short of a completely rigorous discussion that would require more substantial background in functional analysis. Where we gloss over technical subtleties there will (usually) be a footnote or comment to this effect. Interested students are encouraged to look in the books by Hall and Moretti for quite a bit more discussion.

After introducing the postulates, we will inspect two characteristic examples of quantum systems and observe how they are incorporated into the quantum theoretical framework. These will be the two-state *qubit* system and the system of a single particle moving on the one-dimensional real line.

1.1 Postulates of quantum theory

We adopt the abstract, algebraic formulation of quantum mechanics in terms of operators acting on Hilbert spaces. This is the main language of the subject, and was developed to a high degree of completeness by P. A. M. Dirac and John von Neumann; people often refer to these as the *Dirac-von Neumann axioms* of quantum theory. Many aspects of the original theory have come to be better understood mathematically since the inception of the framework, especially in connection with infinite-dimensional Hilbert spaces and their attendant subtleties. Here we will introduce, with comments, a set of working postulates/axioms for how physical systems should be described within the context of quantum mechanics. A high degree of familiarity with abstract linear algebra and metric/inner product spaces is assumed.

Postulate 1 (Space of states)**.** *The states of a physical system are represented by rays in a complex Hilbert space (often denoted $\mathcal{H}$).*

A complex Hilbert space is a complex vector space (often infinite dimensional) with an *Hermitian inner product*, *i.e.*, given $\phi, \psi \in \mathcal{H}$, and $\alpha \in \mathbb{C}$ we have,[4]

$$(\phi,\psi) = \overline{(\psi,\phi)} \ , \quad (\alpha\phi,\psi) = \overline{\alpha}(\phi,\psi) \ , \quad (\phi,\alpha\psi) = \alpha(\phi,\psi) \ . \tag{1.1}$$

If $\mathcal{H}$ is infinite dimensional, one also demands that the space be complete (limits of Cauchy sequences must exist) and separable (there exists a countable basis). We do not emphasise these subtleties in this course, but they are important for providing rigorous foundations to the subject.

A *ray* in $\mathcal{H}$ is the set of scalar multiples of a given non-zero vector. So given $\psi \in \mathcal{H}$, the vector $\alpha\psi \in \mathcal{H}$ represents the same physical state. We can promote this to an equivalence relation on non-zero vectors in $\mathcal{H}$:

$$\psi \sim \alpha\psi \quad \forall\, \alpha \in \mathbb{C}^{\times} \ . \tag{1.2}$$

The *space of quantum states* is then the quotient of the space of nonzero vectors in $\mathcal{H}$ by this equivalence relation, *i.e.*,

$$\{\text{Quantum States}\} \ = \ \left(\mathcal{H} - \{0\}\big/_{\sim}\right) \ \cong \ \mathbb{P}(\mathcal{H}) \ . \tag{1.3}$$

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[4] Observe that we adopt "physics conventions", in which the inner product is conjugate-linear in the *first* argument. In the mathematical literature it is more common to have the second entry be conjugate linear.

The latter equivalence identifies this space with the *projectivisation* of the Hilbert space. Often it is useful to adopt the convention of working with *normalised* state vectors (as in the discussion of wave functions in Chapter 0. This leaves an overall phase ambiguity, so we also have

$$\mathbb{P}(\mathcal{H}) \cong \left(\{\psi \in \mathcal{H} \mid (\psi, \psi) = 1\} \big/ \psi \sim e^{i\varphi}\psi \right) . \tag{1.4}$$

The two characterisations are completely equivalent, but by working with normalised vectors one can often simplify formlulæ.

Remark 1.1.1. The interplay between the physical space of states ($\mathbb{P}(\mathcal{H})$) and the larger Hilbert space $\mathcal{H}$ is the source of a variety of interesting facets of quantum theory. By working in Hilbert space, which in particular is a vector space, one makes manifest the important linear aspects of quantum theory. However, as we shall see in our discussion of symmetries and, in particular, of spin, it is sometimes important not lose sight of the true space of states being the projectivised Hilbert space.

Postulate 2 (Observables). *Observables of a physical system correspond to self-adjoint operators on the Hilbert space $\mathcal{H}$.*

Recall that the adjoint of a linear operator $A : \mathcal{H} \to \mathcal{H}$ is an operator $A^* : \mathcal{H} \to \mathcal{H}$ such that for any $\phi, \psi \in \mathcal{H}$ we have[5]

$$(\phi, A\psi) = (A^*\phi, \psi) . \tag{1.5}$$

A standard result that you have shown in *Part A Quantum Theory* is that the eigenvalues of a self-adjoint operator are necessarily real. There is also an important and, in the general case, difficult result that we will return to obliquely in the next lecture: the *spectral theorem for self-adjoint operators on a Hilbert space*. This says that in a suitable sense, a self-adjoint operator on a Hilbert space always admits a complete basis of eigenvectors, so for a general observable we can write

$$\psi = \sum_n c_n \psi_n , \tag{1.6}$$

where the ψ_n are eigenstates of the obsevable A,

$$A\psi_n = a_n \psi_n . \tag{1.7}$$

The set of eigenvalues $\{a_n\}$ is known as the *spectrum* of the operator A. The stationary states that solve the time-independent Schrödinger equation are just the eigenvectors for the Hamiltonian observable.

Postulate 3 (Measurement). *When measuring an observable A, the only possible results are the elements of the spectrum of A. The probability of a given result a is the squared norm of the orthogonal projection of the (normalised) initial state onto the a eigenspace $\mathcal{H}_a$.*

In the case when all eigenvalues of A are nondegenerate, this means that for a (normalised) state ψ as in (1.6), the probability of obtaining, say, a_i when measuring A is exactly $|c_i|^2$. More generally, suppose that for for some subset $\{\psi_{i\in I}\}$ of the A eigenbasis, the A eigenvalues are all degenerate

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[5] There is a subtlety here in the case of infinite-dimensional $\mathcal{H}$, which I mention here for completeness. General linear operators on an infinite-dimensional $\mathcal{H}$ are only *partially defined*, so their domain $D(A) \subsetneq \mathcal{H}$ (the exceptions are so-called *bounded operators*). The adjoint of an operator then has its own domain $D(A^*)$, and self-adjointness requires $D(A) = D(A^*)$ which is not automatic. For our purposes in this course, it will not be important to keep track of domains of the observables we study in any systematic way.

$a_{i\in I} = a$. Let Pr_a denote the orthogonal projection operator onto the a eigenspace $\mathcal{H}_a \subset \mathcal{H}$ for which the $\{\psi_{i\in I}\}$ form a basis, *i.e.*, the operator that acts on a state as given in (1.6) according to

$$Pr_a\psi = \sum_{i\in I} c_i\psi_i \ . \tag{1.8}$$

Then the probability of observing a when measuring A is given by

$$(Pr_a\psi, Pr_a\psi) = \left(\sum_{i\in I} c_i\psi_i, \sum_{i\in I} c_i\psi_i\right) = \sum_{i\in I} |c_i|^2 \ . \tag{1.9}$$

These probabilistic statements are compatible with the definition of the *expectation value* for the observable A in the state ψ,

$$\mathbb{E}_\psi(A) \equiv \langle A\rangle_\psi = (\psi, A\psi) = \sum_n a_n|c_n|^2 \ . \tag{1.10}$$

Similarly, we recall the *dispersion* of the observable A in the state ψ,

$$\Delta_\psi(A) = \mathbb{E}_\psi\left(\left(A - \langle A\rangle_\psi\right)^2\right) = \mathbb{E}_\psi\left(A^2 - \langle A\rangle_\psi^2\right) \ , \tag{1.11}$$

which agrees with the usual statistical notion of the variance of a random variable.[6]

Postulate 4 (Wave function collapse)**.** *Immediately following a measurement of the observable A that yields the result a, the state of the system is given by the orthogonal projection of the initial state onto the a eigenspace.*

This postulate is the subject to quite a bit of discussion under the headings of *interpretations of quantum mechanics* and *the measurement problem.* These discussions sometimes take a philosophical turn and will not be pursue in this course; indeed we will spend very little or no time discussing measurement. Some of the (more technical than interpretational) aspects of quantum measurement play an important role in quantum information theory, and if you're interested you might look into *C7.4 Introduction to Quantum Information.*

As a practical matter, the statement of wave function collapse has the reasonable consequence that if one measures an observable A and finds some value a, then immediately measuring A again will reproduce the result a (since the state of the system has been projected into the eigenspace where A evaluates to a identically).

Remark 1.1.2 (Compatible and Incompatible Measurements)*.* If two observables A and B commute, so $[A, B] = 0$, then there exists (in the same sense as in Postulate 2) a basis of states which are simultaneous eigenstates of A and B. In this case, one can unambiguously observe A and B simultaneously because the projection operators onto the appropriate eigenspaces commute. On the other hand, if $[A, B] \neq 0$ then measurement of A and B are incompatible, in the sense that if I measure A it will effect the outcome of a measurement of B and vice versa. In the special case of position and momentum operators, this idea is encapsulated in the Heisenberg uncertainty relation that you have seen in Part A.

Postulate 5 (Time evolution)**.** *The time development of a given state ψ is controlled by a special obervable called the Hamiltonian, usually denoted by H, according to the time-dependent Schrödinger*

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[6] In the above discussion, our formulæ were all tailored to the case of a normalised state vector ψ. For general ψ, one must divide through by a normalising factor.

equation,

$$i\hbar\frac{d}{dt}\psi = H\psi \ . \tag{1.12}$$

In general, H as an operator can depend explicitly on time $H = H(t)$, but this doesn't effect the form of the time-dependent Schrödinger equation. (In most of the examples we study this will not be the case; we study time-independent Hamiltonians.)

An important consequence of this equation (which you have seen before) is that the inner product (a.k.a., the *overlap*) between any two state vectors is preserved under time evolution,

$$\begin{aligned}\frac{d}{dt}(\phi,\psi) &= \left(\frac{d\phi}{dt},\psi\right) + \left(\phi,\frac{d\psi}{dt}\right) \ , \\ &= \left(\frac{H\phi}{i\hbar},\psi\right) + \left(\phi,\frac{H\psi}{i\hbar}\right) \ , \\ &= \frac{i}{\hbar}(H\phi,\psi) - \frac{i}{\hbar}(\phi,H\psi) \ , \\ &= 0 \ .\end{aligned} \tag{1.13}$$

In particular, for the case $\phi = \psi$ this implies that normalised states remain normalised under time evolution.

Let us define the operator $U(t_1;t_0) : \mathcal{H} \to \mathcal{H}$ that sends a state defined at time t_0, say $\psi(t_0)$, to its time evolution forward to time $t_1 > t_0$, which we call $\psi(t_1)$. Because (1.12) is linear, then $U(t_1;t_0)$ is itself a linear operator. We now have

$$\begin{aligned}(\phi(t_1),\psi(t_1)) &= (U(t_1;t_0)\phi(t_0), U(t_1;t_0)\psi(t_0)) \ , \\ &= (\phi(t_0), U(t_1;t_0)^* U(t_1;t_0)\psi(t_0)) \ , \\ &= (\phi(t_0),\psi(t_0)) \ .\end{aligned} \tag{1.14}$$

with the last equality a consequence of the time-independence of overlaps. So we have that the time-evolution operator $U(t_1;t_0)$ obeys the important relation

$$U(t_1,t_0)^* = U(t_1,t_0)^{-1} \ . \tag{1.15}$$

Such operators are called *unitary operators.*

Definition 1.1.1. *A* unitary operator *U on a Hilbert space is a linear map $U : \mathcal{H} \to \mathcal{H}$ that obeys*

$$U^*U = UU^* = \mathbb{1}_{\mathcal{H}} \ . \tag{1.16}$$

This is, equivalently, a surjective map from $\mathcal{H}$ to $\mathcal{H}$ obeying $U^*U = \mathbb{1}_{\mathcal{H}}$. The requirement to separately consider left- and right-composition by U^* or to demand surjectivity is associated with the subtleties of infinite-dimensional Hilbert space. In finite dimensional settings, this is the usual notion of a unitary matrix.

In the case where the Hamiltonian is time-independent, the time evolution operator will only depend on the time interval $t_1 - t_0$ and we can write $U(t_1 - t_0)$ instead. To understand time-evolution then amounts to identifying the basis of states that diagonalises the action of the Hamiltonian, *i.e.*, the stationary states obeying

$$H\psi_n = E_n\psi_n \ . \tag{1.17}$$

The time evolution operator $U(t_1 - t_0)$ can be understood very simply in the basis of stationary states, with its action given by

$$U(t_1 - t_0)\psi_n(x) = \exp\left(-\frac{iE_n(t_1 - t_0)}{\hbar}\right)\psi_n(x) \ , \tag{1.18}$$

from which the action on a general state can be deduced by linearity. We observe that we can write this operator as an exponentiation of the Hamiltonian operator,

$$U(t_1 - t_0) = \exp\left(-\frac{iH(t_1 - t_0)}{\hbar}\right) \ , \tag{1.19}$$

where the expression on the right has an obvious interpretation when applied to stationary states, and the more general case follows by linearity.

1.2 Qubit system as an instance of the framework

The simplest instances of quantum systems are those with *finite-dimensional Hilbert spaces.* The simplest non-trivial example is then when the Hilbert space has dimension two, in which case the system is often called a *qubit.*[7] Choosing an orthonormal basis we get an identification $\mathcal{H} \cong \mathbb{C}^2$ with inner product

$$(\mathbf{u}, \mathbf{v}) = \overline{\mathbf{u}} \cdot \mathbf{v} \ . \tag{1.20}$$

The space of quantum states in this case is just the complex projective line (*i.e.*, the Riemann sphere), $\mathbb{P}(\mathbb{C}^2) = \mathbb{CP}^1$. Topologically $\mathbb{CP}^1 \cong \mathbb{S}^2$, the two-sphere, so the space of quantum states of the qubit system is actually a sphere – this is known as the *Bloch sphere.*

Observables in this qubit system are 2×2 self-adjoint (*a.k.a.* Hermitian) matrices, a basis for which is as follows,

$$\sigma_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \ , \quad \sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \ , \quad \sigma_2 = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} \ , \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \ . \tag{1.21}$$

Here σ_0 is just the identity operator and so does not play much of a role as an observable. The σ_i, $i = 1, 2, 3$ are the so-called *Pauli matrices*, which obey the commutator algebra

$$[\sigma_1, \sigma_2] = 2i\sigma_3 \ , \qquad [\sigma_2, \sigma_3] = 2i\sigma_1 \ , \qquad [\sigma_3, \sigma_1] = 2i\sigma_2 \ . \tag{1.22}$$

In the given basis for $\mathcal{H}$, σ_3 is diagonalised with eigenvalues ±1 while σ_1 and σ_2 are not, and the nontrivial commutators imply that these are incompatible observables. By choosing a different basis one could diagonalise σ_1 or σ_2 instead, or an arbitrary linear combination of the σ_i. We will encounter more properties of these matrices when we revisit this Hilbert space in the context of our treatment of rotations and spin.

For a qubit, the possible time-evolution operators are elements of the two-dimensional unitary group $U(2)$ of 2×2 matrices whose transpose-conjugate (adjoint) is their inverse. It is interesting to consider the action of this group on the space of quantum states. In particular, note that there

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[7] Qubits play an important role as a building block of quantum computers. They stand in as the quantum mechanical of a classical bit, which is a degree of freedom that takes one of two values, conventionally called 0 and 1. Unlike classical bits, qubits can live in any linear superposition of their two basis states, which leads to their more powerful computational properties.

is a subgroup $U(1) \subset U(2)$ of matrices of the form

$$U = \begin{pmatrix} e^{i\varphi} & 0 \\ 0 & e^{i\varphi} \end{pmatrix} , \tag{1.23}$$

whose action on the space of quantum states is actually trivial (because states related by an overall phase are equivalent). Thus, we have that the action of $U(2)$ on the space $\mathbb{CP}^1$ factors through the quotient by this $U(1)$ subgroup, which happens to be the three-dimensional orthogonal group,

$$U(2)/U(1) \cong SO(3) \ . \tag{1.24}$$

There is an obvious action of $SO(3)$ on $\mathbb{CP}^1$ which is just the rigid rotations of the two-sphere, and indeed this is how this action arises (we won't prove it here). We are most familiar with $SO(3)$ in connection with rotations in three-dimensional space, and its appearence here is no accident, as we will see in more detail later in Chapter 6.

1.3 The one-dimensional particle as an instance of the formalism

The main instance of this formalism treated in *Part A Quantum Theory* arose in describing the movement of a single point-particle in $d = 1$, 2, or 3 dimensions. Here we restrict to $d = 1$. In this case, a state vectors is represented by a Schrödinger wave function $\psi : \mathbb{R} \to \mathbb{C}$, a complex function of position $x \in \mathbb{R}$. The Hermitian inner product of two state vectors is then given by

$$(\phi, \psi) = \int_{\mathbb{R}} \overline{\phi(x)} \psi(x) \, \mathrm{d}x \ . \tag{1.25}$$

Physical wave functions are required to be *normalisable*, so

$$(\psi, \psi) = \int_{\mathbb{R}} |\psi(x)|^2 \, \mathrm{d}x < \infty \ . \tag{1.26}$$

The Hilbert space of such a system is then, roughly speaking, the vector space of complex, square-integrable functions on $\mathbb{R}^d$. With some technical improvements,[8] this leads to the definition of the Hilbert space $\mathcal{H} \cong L^2(\mathbb{R})$ (here L is for Lebesgue and 2 indicates that it is the norm *squared* that appears in inner product).

The observables that we most frequently discuss in this setting are realised as differential operators on wave functions. In particular, the most natural observabes are the momentum and position operators P and X, which act according to

$$(P\psi)(x) = -i\hbar \left(\frac{\mathrm{d}\psi}{\mathrm{d}x} \right)(x) \ , \qquad (X\psi)(x) = x\psi(x) \ . \tag{1.27}$$

More generally, we can construct many self-adjoint differential operators as observables by composing the actions of P and X appropriately. (However, recall that because in general $(AB)^* = B^* A^*$, a generic composition of P's and X's will not be self-adjoint though P and X themselves are.) For

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[8] As you may know if you have taken *Part A Integration* of *B4.1 Functional Analysis*, to really define this space well one needs to form equivalence classes of functions that agree almost everywhere (*i.e.*, outside of sets of Lebesgue measure zero). This technical subtlety will not be important to us for the duration of this course.

example, the Hamiltonian in one dimension is usually taken to have its classical form

$$H = \frac{P^2}{2m} + V(X) \ , \tag{1.28}$$

for some function $V(x)$ that is (normally) bounded below. This acts on states-as-wave-functions according to

$$H\psi(x) = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}(x) + V(x)\psi(x) \ , \tag{1.29}$$

The stationary states, or H eigenstates, are those $\{\psi_n(x)\}$, that obey the wave-function version of the time-independent Schrödinger equation (see the review in Chapter 0),

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi_n}{\mathrm{d}x^2}(x) + V(x)\psi_n(x) = E_n\psi_n(x) \ , \tag{1.30}$$

for E_n in the spectrum of H. For examples like the harmonic oscillator, these form an orthonormal basis for $L^2(\mathbb{R})$.

Remark 1.3.1. Though X and P are intuitively two very natural observables for this system, note that the space of all square-integrable functions includes many functions which are not differentiable (or even continuous!) and many functions which, after multiplication by x, would no longer be square normalisable. This fact is indicative of the aforementioned subtlety that observables are often only defined on a (dense) subspace of the Hilbert space in the infinite-dimensional case. X and P also don't admit proper eigenfunctions in $\mathcal{H}$, an issue that we will return to in Chapter 2.

A class of observables that are better behaved, and which you in fact studied a bit in Part A in different terms, are the projection operators

$$\begin{aligned} Pr_E : \ \ \mathcal{H} &\longrightarrow \mathcal{H} \ , \\ \psi(x) &\longmapsto \mathbb{1}_E(x)\psi(x) \ , \end{aligned} \tag{1.31}$$

where $\mathbb{1}_E(x)$ is the indicator function for a measurable set $E \subset \mathbb{R}$. This operator is easily verified to be self-adjoint and a projection (in that $Pr_E \circ Pr_E = Pr_E$), which implies that its eigenvalues can only be zero or one. Indeed, by inspection one observes that a function can only be an eigenfunction if it is supported entirely within E (in which case it has eigenvalue one) or if it is supported entirely outside of E (in which case it has eigenvalue zero).

A measurement of Pr_E corresponds to asking the yes/no question "is the particle located within E?". The expectation value for this operator is given by

$$\mathbb{E}_\psi(Pr_E) = \int_{-\infty}^{\infty} \mathrm{d}x \, |\psi(x)|^2 \mathbb{1}_E(x) = \int_E \mathrm{d}x \, |\psi(x)|^2 \ , \tag{1.32}$$

which is exactly how in Part A you computed the probability that the particle was located in the region E. Here we see that this result is reproduced in a framework where one only asks questions of a system that can be encoded in an observable.

Chapter 2

Dirac's Formalism and Continuum Normalisation

The subject of this section is, in some sense, a matter of notational formalism. We will (re-)introduce the *bra-ket* formalism of Dirac for representing states and observables in quantum mechanical systems. In reality, Dirac's formalism (in the broadest sense) is more substantive than just a change of notation. The novelty arises when discussing observables with a *continuous spectrum.* This can happen only in infinite-dimensional Hilbert spaces.

2.1 States, dual states, and matrix elements

The basic notational device introduced by Dirac is the *bra-ket.* Here we represent vectors in a Hilbert space as *kets*,

$$\psi \in \mathcal{H} \quad \longleftrightarrow \quad |\psi\rangle \ . \tag{2.1}$$

Since a Hilbert space is equipped with an inner product, we can also assign to a given state a dual vector

$$\begin{aligned} \varphi_\psi \ &: \ \mathcal{H} \to \mathbb{C} \ , \\ &: \ \chi \mapsto (\psi, \chi) \ . \end{aligned} \tag{2.2}$$

Due to the sesquilinearity of the inner product on $\mathcal{H}$, this map is $\mathbb{C}$-conjugate-linear: $\varphi_{\lambda\psi} = \bar{\lambda}\varphi_\psi$ for $\lambda \in \mathbb{C}$. An important result in functional analysis is the following:

Theorem 2.1.1 (Riesz-Fréchet representation theorem)**.** *Let $\mathcal{H}$ be a Hilbert space. For every continuous linear functional $\varphi \in \mathcal{H}^*$, there exists a unique $\psi \in \mathcal{H}$ such that $\varphi = \varphi_\psi$ (using the notations above).*

We will not give a proof here. In the finite-dimensional setting, it is not a difficult result, but in the infinite-dimensional case it is not as obvious. Indeed, the presence of the adjective *continuous* in the above is relevant precisely in the case of infinite-dimensional $\mathcal{H}$ (all linear functionals are continuous in a finite dimensional Hilbert space). This theorem establishes a canonical *bijective, antilinear isometry* between $\mathcal{H}$ and $\mathcal{H}^*$.

In Dirac notation, we denote elements of the (continuous) dual space $\mathcal{H}^*$ by *bras*:

$$\varphi \in \mathcal{H}^* \quad \longleftrightarrow \quad \langle\varphi| \ . \tag{2.3}$$

As a somewhat abusive notational convention, we often use as the label for a *bra* the name of the state in $\mathcal{H}$ to which it corresponds under the Riesz-Fréchet isometry,

$$\varphi_\psi \quad \longleftrightarrow \quad \langle\psi| \ . \tag{2.4}$$

With these conventions in place, we denote the inner product between two states φ and ψ as a composite *bra-ket*, where the state and dual state are joined in the way that they visually want to be,

$$(\varphi, \psi) \quad \longleftrightarrow \quad \langle\varphi|\psi\rangle \ . \tag{2.5}$$

An operator A can act on kets from the left, whereupon it can be absorbed into the ket

$$A\left|\psi\right\rangle = \left|A\psi\right\rangle \ . \tag{2.6}$$

Similarly, operators act from the right upon bras, and are replaced by their adjoint when absorbed into the bra,

$$\left\langle\varphi\right| A = \left\langle A^*\varphi\right| \ . \tag{2.7}$$

Within an inner product, an operator can be moved around accordingly,

$$\langle\varphi|A\psi\rangle = \langle\varphi|A|\psi\rangle = \langle A^*\varphi|\psi\rangle \ . \tag{2.8}$$

The quantity $\langle\varphi|A|\psi\rangle$ will be referred to as the *matrix element* of A between φ and ψ.

2.2 Constructions with bra-kets

The bra-ket formalism is convenient for representing variious natural constructions utilising linear opearations on Hilbert spaces. For example, given the state $|\alpha\rangle$ and the dual-state $\langle\beta|$, we can construct the *outer product*,

$$\begin{aligned} \left|\alpha\right\rangle\left\langle\beta\right| \ : \ \mathcal{H} &\ \rightarrow\ \mathcal{H} \ , \\ \left|\psi\right\rangle &\ \mapsto\ \left|\alpha\right\rangle\left\langle\beta|\psi\right\rangle = \left(\left\langle\beta|\psi\right\rangle\right)\left|\alpha\right\rangle \ . \end{aligned} \tag{2.9}$$

So we can concatenate *bras* and *kets* in the visually obvious manner and get meaningful operations. Outer products also behave well under taking adjoints,

$$\left(\left|\alpha\right\rangle\left\langle\beta\right|\right)^* = \left|\beta\right\rangle\left\langle\alpha\right| \ . \tag{2.10}$$

Now let $\{\left|i\right\rangle \ , i \in I\}$ be a complete orthonormal basis for $\mathcal{H}$ (here I is some finite or countably infinite indexing set). Orthonormality means we have $\langle i|j\rangle = \langle j|i\rangle = \delta_{ij}$. We can then write an arbitrary vector in $\mathcal{H}$ uniquely as a (possibly infinite) linear combination of these basis vectors,

$$\left|\psi\right\rangle = \sum_{i\in I} c_i \left|i\right\rangle \ . \tag{2.11}$$

We can “measure” the components c_j for some $j \in I$ by acting with the *bra* corresponding to $|j\rangle$,

$$\langle j|\psi\rangle = \sum_{i\in I} c_i \left\langle j|i\right\rangle = \sum_{i\in I} c_i\delta_{ij} = c_j \ . \tag{2.12}$$

Using this, we see that we can build the operator that performs an orthogonal projection onto the one-dimensional subspace $\mathcal{H}_j$ spanned by the basis vector $|j\rangle$ by using the outer product $\left|j\right\rangle\left\langle j\right|$:[9]

$$\left|j\right\rangle\left\langle j|\psi\right\rangle = c_j \left|j\right\rangle \ . \tag{2.14}$$

More generally, for linear subspace $\mathcal{H}' \subseteq \mathcal{H}$ with orthonormal basis $\left|i'\right\rangle \ , i' \in I'$ we can form the

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[9] For the a general state vector ψ, not necessarily normalised, we have the orthogonal projection operator,

$$Pr_{\mathcal{H}_\psi} = \frac{\left|\psi\right\rangle\left\langle\psi\right|}{\langle\psi|\psi\rangle} \ . \tag{2.13}$$

manifestly self-adjoint, orthogonal projection operator from $\mathcal{H}$ onto $\mathcal{H}'$:

$$Pr_{\mathcal{H}'} = \sum_{i' \in I'} |i'\rangle \langle i'| \ . \tag{2.15}$$

In particular, for the case $\mathcal{H}' = \mathcal{H}$, we have an expression for the identity operator,

$$Pr_{\mathcal{H}} \equiv \mathbb{1}_{\mathcal{H}} = \sum_{i \in I} |i\rangle \langle i| \ . \tag{2.16}$$

This expression is often referred to as a *resolution of the identity* or *completeness relation*. Given a linear operator $A : \mathcal{H} \to \mathcal{H}$, we can then resolve it in terms of its matrix elements with respect to the given basis,

$$A = \mathbb{1}_{\mathcal{H}} A \mathbb{1}_{\mathcal{H}} = \sum_{i,j \in I} |i\rangle \langle i|A|j\rangle \langle j| = \sum_{i,j \in I} A_{ij} |i\rangle \langle j| \ . \tag{2.17}$$

where

$$A_{ij} = \langle i|A|j\rangle \ . \tag{2.18}$$

Finally, for A an observable if the states $\{|i\rangle\}$ are an orthonormal basis of A eigenstates obeying $A|i\rangle = a_i |i\rangle$ then we have matrix elements $A_{ij} = a_i \delta_{ij}$ and (2.17) becomes the *spectral decomposition* of A,

$$A = \sum_i a_i |i\rangle \langle i| \ . \tag{2.19}$$

In the case where $\mathcal{H}$ is finite-dimensional, this is all pretty familiar. The outer product $|i\rangle \langle j|$ corresponds to the matrix that is all zeroes except for having a one in the i'th row at the j'th column, and (2.17) describes the building up the operator A entry by entry as a matrix, while (2.19) corresponds to the matrix expression for A in the basis where A is diagonalised, which is the usual spectral decomposition of an Hermitian matrix. The resolution of the identity is just the expression for the identity operator as the identity matrix.

In terms of bra-kets, we can represent the expectation value of an observable as follows. If our basis $\{|i\rangle\}$ diagonalises the observable A as above, then we have

$$\begin{aligned} \mathbb{E}_\psi(A) = \mathbb{E}_\psi(A\mathbb{1}_{\mathcal{H}}) = &= \sum_{i \in I} \langle \psi|A|i\rangle \langle i|\psi\rangle \ , \\ &= \sum_{i \in I} a_i |\langle i|\psi\rangle|^2 \ , \end{aligned} \tag{2.20}$$

which matches the notion of expectation value for a random variable.

2.3 Continuous observables

We now come to the issue of observables with continuous spectrum. In finite dimensional Hilbert spaces the spectrum of any observble is discrete, so this is an issue of infinite-dimensional Hilbert spaces. Dirac suggested in his original treatise on the subject to extend his bra-ket formalism to this case in a natural, but mathematically tenuous, manner, and this is the method that is standard in the physics community. His approach can in retrospect be understood as being essentially an application of the *spectral theorem for self-adjoint operators* applied to infinite-dimensional Hilbert spaces. We will introduce this method in an operational sense.

To ground our discussion, let's return to our standard infinite-dimensional example: a particle moving on the real line, so with Hilbert space $L^2(\mathbb{R})$.[10] The two fundamental observables in this setting are the position and momentum operators. Let us first consider the position operator X. Now suppose we want to define an eigenstate $|\xi\rangle$ for this operator for $\xi \in \mathbb{R}$,[11]

$$X\,|\xi\rangle = \xi\,|\xi\rangle \ . \tag{2.21}$$

If we introduce a wave function $\psi_\xi(x)$ to represent such a state, it should satisfy the unlikely-looking identity

$$x\psi_\xi(x) = \xi\psi_\xi(x) \ . \tag{2.22}$$

For this to hold, it must be that $\psi_\xi(x) = 0$ for $x \neq \xi$, and indeed if this were an element of $L^2(\mathbb{R})$ that would mean it was the zero function, so certainly this can't correspond to a non-zero element of the Hilbert space. However, we propose to still introduce such an obejct, which we refer to as a *generalised eigenstate*. Note that since this generalised state is meant to represent a situation where the particle is *definitely at* $x = \xi$, it is reasonable to demand

$$\langle\xi|\psi\rangle = \psi(\xi) \ , \qquad \langle\psi|\xi\rangle = \overline{\psi(\xi)} \ . \tag{2.23}$$

This is actually an important idea: *the value of the wave function at a point $x = \xi$ is the overlap of the state in question with the generalised position eigenstate $|\xi\rangle$*. Expressing this in terms of wave functions, we have

$$\int\limits_{-\infty}^{\infty} \mathrm{d}x\,\overline{\psi_\xi(x)}\psi(x) = \psi(\xi) \ , \tag{2.24}$$

This is exactly the *sifting property* of (confusingly named) *Dirac δ-function*. Rather than a function, this is a *distribution*, meaning it is a linear functional on functions. You have met the Dirac $\delta-$function before in M4 Multivariable Calculus, and maybe also in ASO Integral Transforms. Indeed, we will identify

$$|\xi\rangle \quad\longleftrightarrow\quad \psi_\xi(x) = \delta(x-\xi) \ . \tag{2.25}$$

Note that while these generalised position eigenstates are not normalisable in the usual sense, they obey a *continuum normalisation condition*,

$$\langle\xi|\xi'\rangle = \int\limits_{-\infty}^{\infty} \mathrm{d}x\,\delta(x-\xi)\delta(x-\xi') = \delta(\xi-\xi') \ . \tag{2.26}$$

This is a fairly natural generalisation of the usual normalisation condition where we have a Kronecker δ, but with the Dirac δ instead.

Happily, it turns out that we can largely use these generalised position eigenstates in the same ways we would use ordinary basis states as discussed previously. Justification for this rests upon the functional analysis that we are sweeping under the rug,[12] but as we mentioned above, the quantum

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[10] A similar discussion here could take place for the particle moving on an interval $[0,1] \subset \mathbb{R}$, with Hilbert space $L^2([0,1])$. The free particle on the entire real line is even a bit more subtle.

[11] Here we begin to adopt a fairly standard notational choice: in the context of discussing a particular observable (in this case P), we denote states whose eigenvalue is some number (in this case $q \in \mathbb{R}$) by a *ket* whose label is *that same eigenvalue* (in this case $|q\rangle$). There is some danger of getting confused if not sufficiently diligent with this notational system, so be careful!

[12] There are a couple of realisations of these generalised eigenstates within a more rigorous framework. In one version of the spectral theorem for self-adjoint operators on infinite-dimensional Hilbert spaces, one constructs the Hilbert space of interest as a *direct integral* of smaller Hilbert spaces, and these generalised states are elements of the integrand of that direct integral. Alternatively, Hilbert spaces arising in quantum mechanics can be equipped with additional structure known as a *Gel'fand triple*. In this case the generalised states are elements of a larger space of

mechanical formalism (due to Dirac) actually predated the rigorous justification. In particular, we have a resolution of the identity in terms of these position eigenstates,

$$\mathbb{1}_{L^2(\mathbb{R})} = \int\limits_{-\infty}^{\infty} \mathrm{d}\xi \; |\xi\rangle \langle\xi| \;\; . \tag{2.27}$$

Acting on normalisable states (corresponding to authentic wave functions), we have

$$\begin{aligned} \mathbb{1}_{\mathcal{H}} |\psi\rangle &= \int\limits_{-\infty}^{\infty} \mathrm{d}\xi \; |\xi\rangle \langle\xi|\psi\rangle \;\; , \\ &= \int\limits_{-\infty}^{\infty} \mathrm{d}\xi \; |\xi\rangle \, \psi(\xi) \;\; , \\ &= |\psi\rangle \;\; , \end{aligned} \tag{2.28}$$

where the final equality gives us the continuum analogue of the decomposition of a general state in an orthonormal basis.

Generalising this resolution of the identity, if we integrate the (generalised) outer product $|\xi\rangle\langle\xi|$ over any Lebesgue measurable subset $E \subset \mathbb{R}$, we obtain the self-adjoint projection operator corresponding to multiplication by the indicator function $\mathbb{1}_E$ discussed in Chapter 1.3,

$$Pr_E = \int\limits_{E} \mathrm{d}\xi \; |\xi\rangle \langle\xi| \;\; , \qquad \langle x| P_E |\psi\rangle = \mathbb{1}_E(x)\psi(x) \;\; . \tag{2.29}$$

In a careful version of these constructions, it is this association of a self-adjoint projection operator to measurable subsets of $\mathbb{R}$ that is rigorously defined and guaranteed to exist by the spectral theorem; it is called a *projection valued measure.*

There is a similar story with the momentum operator $P = -i\hbar\frac{\mathrm{d}}{\mathrm{d}x}$. We introduce (generalised) momentum eigenstates $|p\rangle$,

$$P|p\rangle = p\,|p\rangle \;\; , \qquad p \in \mathbb{R} \;\; , \tag{2.30}$$

and if we denote the actual wave function associated to this state as $\psi_p(x)$, then we can easily solve the corresponding differential equation in a formal sense,

$$\begin{aligned} -i\hbar\,\psi_p'(x) &= p\psi_p(x) \;\; , \\ \psi_p(x) &= \mathcal{N} e^{\frac{ipx}{\hbar}} \;\; , \end{aligned} \tag{2.31}$$

where $\mathcal{N}$ is some normalisation factor. The problem is now clear: these wave functions are not square-normalisable at all (on the entire real line), so like in the position case, this is not giving us an element of $L^2(\mathbb{R})$, but rather something that can be interpreted as a distribution.

Using our previous insight about the relationship between wave functions and the generalised position eigenstates, we find the overlap equation

$$\langle x|p\rangle = \psi_p(x) = \mathcal{N} e^{\frac{ipx}{\hbar}} \;\; . \tag{2.32}$$

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distributions that form a part of that structure. You don't need to know any of this for the present course!

We can now compute the continuum normalisation condition for the momentum eigenstates,

$$\langle p|p'\rangle = \mathcal{N}^2 \int\limits_{-\infty}^{\infty} \mathrm{d}x\, e^{-\frac{ipx}{\hbar}} e^{\frac{ip'x}{\hbar}} = 2\pi\hbar\mathcal{N}^2 \int\limits_{-\infty}^{\infty} \mathrm{d}s\, e^{2\pi i(p-p')s} = 2\pi\hbar\mathcal{N}^2\delta(p-p') \ , \tag{2.33}$$

where in the last equation we have used the integral representation for the delta function. It is then natural to adopt the normalisation conventions $\mathcal{N} = (2\pi\hbar)^{-1/2}$ giving canonical continuum normalisation to the generalised momentum eigenstates. We then have an analogous resolution of the identity in terms of momentum states,

$$\mathbb{1}_{\mathcal{H}} = \int\limits_{-\infty}^{\infty} \mathrm{d}p\ |p\rangle\,\langle p| \ . \tag{2.34}$$

This formalism of position and momentum (generalised) bases for $L^2(\mathbb{R})$ gives us a nice new perspective on the quantum mechanics of a particle. To a given state vector $|\psi\rangle$, we can associated either its expression in *position space*,

$$\psi(x) = \langle x|\psi\rangle \ , \qquad |\psi\rangle = \int\limits_{-\infty}^{\infty} \mathrm{d}x\, \psi(x)\,|x\rangle \ , \tag{2.35}$$

or its expression in *momentum space*,

$$\widehat{\psi}(p) = \langle p|\psi\rangle \ , \qquad |\psi\rangle = \int\limits_{-\infty}^{\infty} \mathrm{d}p\, \widehat{\psi}(p)\,|p\rangle \ . \tag{2.36}$$

So there are actually (at least) two wave functions associated to the abstract state ψ. These are related by the Fourier transform,

$$\psi(x) \ = \ \langle x|\psi\rangle = \int\limits_{-\infty}^{\infty} \mathrm{d}p\ \langle x|p\rangle\,\langle p|\psi\rangle = \frac{1}{\sqrt{2\pi\hbar}} \int\limits_{-\infty}^{\infty} \mathrm{d}p\, e^{\frac{ipx}{\hbar}}\,\widehat{\psi}(p) \ . \tag{2.37}$$

$$\widehat{\psi}(p) \ = \ \langle p|\psi\rangle = \int\limits_{-\infty}^{\infty} \mathrm{d}x\ \langle p|x\rangle\,\langle x|\psi\rangle = \frac{1}{\sqrt{2\pi\hbar}} \int\limits_{-\infty}^{\infty} \mathrm{d}x\, e^{-\frac{ipx}{\hbar}}\,\psi(x) \ . \tag{2.38}$$

Indeed, the Fourier transform is a unitary map from $L^2(\mathbb{R})$ to itself (this is the Plancherel theorem), so the change from position to momentum representation is just a change of basis of sorts for our Hilbert space.

Remark 2.3.1. This formalism for generalised position eigenstates generalises immediately to the case of a particle moving in, say, $d = 2$ or $d = 3$ dimensions. There for $\mathbf{x} = (x_1, \ldots, x_d)$ we have the generalised eigenstates

$$X_i\,|\mathbf{x}\rangle = x_i\,|\mathbf{x}\rangle \ , \tag{2.39}$$

obeying the continuum normalisation condition,

$$\langle \mathbf{x}|\mathbf{x}'\rangle = \delta^d(\mathbf{x}-\mathbf{x}') \ , \tag{2.40}$$

and the corresponding resolution of the identity,

$$\mathbb{1}_{L^2(\mathbb{R}^d)} = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \mathrm{d}x_1 \cdots \mathrm{d}x_d \, |\mathbf{x}\rangle \langle \mathbf{x}| \ . \tag{2.41}$$

Similarly, we have generalised momentum eigenstates corresponding to non-normalisable plane-wave wave functions,

$$|\mathbf{p}\rangle \quad \longrightarrow \quad \psi_{\mathbf{p}}(\mathbf{x}) = \frac{1}{(2\pi\hbar)^{d/2}} e^{\frac{i\mathbf{p}\cdot\mathbf{x}}{\hbar}} \ , \tag{2.42}$$

obeying the same continuum normalisation condition and admitting the same type of resolution of the identity. d-dimensional wave functions in position space and momentum space are related now by the d-dimensional Fourier transform.

2.4 Application: free particle propagator

A nice application of what we've developed here is to introduce an important object in studying time-dependent quantum mechanical behaviours: the *propagator*. Intuitively, this is the quantity that tells you the quantum mechanical amplitude (square root of probability density) for a particle that starts at a given position to be detected at some other position at some definite time in the future. In terms of these generalised position eigenstates, this is formalised as

$$U(x_1, t_1; x_0, t_0) := \langle x_1 | U(t_1; t_0) | x_0 \rangle \ , \tag{2.43}$$

where $U(t_1; t_0)$ is the unitary time evolution operator. If one has the propagator under good control, then one can understand general time evolution as follows double integral

$$\begin{aligned} \langle \psi_1 | U(t_1, t_0) | \psi_0 \rangle &= \langle \psi_1 | \left(\int_{-\infty}^{\infty} \mathrm{d}x_1 \, |x_1\rangle \langle x_1| \right) U(t_1; t_0) \left(\int_{-\infty}^{\infty} \mathrm{d}x_0 \, |x_0\rangle \langle x_0| \right) |\psi_0\rangle \ , \\ &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \mathrm{d}x_1 \, \mathrm{d}x_0 \, \overline{\psi_1(x_1)} U(x_1, t_1; x_0, t_0) \psi_0(x_0) \ , \end{aligned} \tag{2.44}$$

In general, the propagator is not so easy to compute. Here we will do it for the case of the free particle in one dimension. The Hamiltonian is $H = P^2/2m$ and the (generalised) energy eigenstates are precisely the (generalised) momentum eigenstates:

$$H |p\rangle = E_p |p\rangle = \frac{p^2}{2m} |p\rangle \ . \tag{2.45}$$

As we know well, time evolution is then defined via phase multiplication on these states,

$$U(t_1, t_0) |p\rangle = \exp\left(\frac{-iE_p(t_1 - t_0)}{\hbar} \right) |p\rangle = \exp\left(\frac{-ip^2(t_1 - t_0)}{2m\hbar} \right) |q\rangle \ . \tag{2.46}$$

This means that the *momentum-space propagator* is very simple for the free particle,

$$\langle p_1 | \, U(t_1; t_0) \, |p_0\rangle =: \widehat{U}(p_1, t_1; p_0, t_0) = \delta(p_1 - p_0) \exp\left(-\frac{ip_0^2(t_1 - t_0)}{2m\hbar} \right) \ . \tag{2.47}$$

The position-space propagator is then obtained by a double Fourier transform,

$$U(x_1,t_1;x_0,t_0) = \langle x_1| \left(\int_{-\infty}^{\infty} dp_0 \, |p_0\rangle \langle p_0| \right) U(t_1;t_0) \left(\int_{-\infty}^{\infty} dp_1 \; |p_1\rangle \langle p_1| \right) |x_0\rangle \ , \tag{2.48}$$

$$= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dp_0 dp_1 \; \langle x_1|p_0\rangle \, \widehat{U}(p_1,t_1;p_0,t_0) \, \langle p_1|x_0\rangle \ , \tag{2.49}$$

$$= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dp_0 dp_1 \, \delta(p_1-p_0) \exp\left(\frac{ip_1x_1 - ip_0x_0}{\hbar} - \frac{ip_0^2(t_1-t_0)}{2m\hbar} \right) \ , \tag{2.50}$$

$$= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \mathrm{d}p \, \exp\left(\frac{ip(x_1-x_0)}{\hbar} - \frac{ip^2(t_1-t_0)}{2m\hbar} \right) \ , \tag{2.51}$$

$$= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \mathrm{d}p \, \exp\left(\frac{ip(x_1-x_0)}{\hbar} - \frac{ip^2(t_1-t_0)}{2m\hbar} \right) \ , \tag{2.52}$$

The last integral can be computed using results for *Fresnel integrals*,[13] which leaves us with

$$U(t_1,x_1;t_0,x_0) = \left(\frac{m}{2\pi i\hbar(t_1-t_0)} \right)^{\frac{1}{2}} \exp\left(-\frac{m(x_1-x_0)^2}{2i\hbar(t_1-t_0)} \right) \ . \tag{2.53}$$

It is interesting to observe that instantly when $t_1 > t_0$, the propagator is nonzero for arbitrarily large $x_1 - x_0$. This reflects the infinite uncertainty in momentum that is associated with the completely localised position eigenstate at time t_0. However, the phase in the exponential is also very large for large $x_1 - x_0$ and small $t_1 - t_0$, so when we average over positions (as we should if we start with a normalisable wave function) then there will be cancellations and the wave function will remain somewhat localised near its original support.

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[13] The general formula is

$$\int_{-\infty}^{\infty} \mathrm{d}x \, \exp\left(\frac{i}{2}ax^2 + ibx \right) = \left(\frac{2\pi i}{a} \right)^{\frac{1}{2}} \exp\left(-\frac{ib^2}{2a} \right) \ .$$

Chapter 3

Composite Systems, Tensor Products, Entanglement

It will prove important to be able to build up the description of a quantum system from those of more elementary subsystems with a smaller number of degrees of freedom. In this section we introduce the basic mathematical machinery for doing this (the Hilbert space tensor product), and look at a simple example of the phenomenon of quantum entanglement, which arises naturally as a consequence.

3.1 Hilbert space tensor product

Suppose we are presented with two non-interacting quantum systems that are to be subsumed into a single description. You might imagine two atoms (or collections of atoms) kept far enough apart so as to be non-interacting, or alternatively you might imagine a more general system of two particles that, in a first approximation, do not interact at all with one another and so can be treated separately. The two systems taken on their own will have their states encoded by Hilbert spaces $\mathcal{H}_1$ and $\mathcal{H}_2$, respectively, while as a composite system we should assign a single Hilbert space $\mathcal{H}_3$. How should this Hilbert space $\mathcal{H}_3$ behave? The following construction arises naturally from physical considerations:

- For state vectors $|\psi_1\rangle \in \mathcal{H}_1$ and $|\psi_2\rangle \in \mathcal{H}_2$, there should exist a definite state vector $|\psi_1 \otimes \psi_2\rangle \in \mathcal{H}_3$. Such a vector is called a *pure tensor*, or alternatively, *decomposable*.[14]
- By linearity, we should be able to take linear superpositions of these pure tensors. As a first approximation, we can consider the vector space $F(\mathcal{H}_1, \mathcal{H}_2)$ corresponding to all (finite) $\mathbb{C}$-linear combinations of these free tensors. This is known as the *free vector space on the set* $\mathcal{H}_1 \times \mathcal{H}_2$.
- The free vector space overcounts in some obvious ways, and we introduce a number of identifications:
  - $|\lambda\psi_1 \otimes \psi_2\rangle \sim \lambda\,|\psi_1 \otimes \psi_2\rangle \sim |\psi_1 \otimes \lambda\psi_2\rangle$ for $\lambda \in \mathbb{C}$.

    Since state vectors only encode physical states up to overall scalar multiplication, the consequence of rescaling either tensor factor should be no different from rescaling the vector as a whole.
  - $|(\psi_1 + \phi_1) \otimes \psi_2\rangle \sim |\psi_1 \otimes \psi_2\rangle + |\phi_1 \otimes \psi_2\rangle$.

    If system two is definitely in state $|\psi_2\rangle$, then when system one is in a superposition of two states, the total system is in the superposition of the corresponding two decomposable states where the second system remains in $|\psi_2\rangle$.
  - $|\psi_1 \otimes (\psi_2 + \phi_2)\rangle \sim |\psi_1 \otimes \psi_2\rangle + |\psi_1 \otimes \phi_2\rangle$.

    Same as above with the two systems switched.

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[14] When not using *bra-ket* notation, it is common to write this vector as $\psi_2 \otimes \psi_2$. We may also sometime use $|\psi_1, \psi_2\rangle$ or $|\psi_1\rangle \otimes |\psi_2\rangle$ interchangeably. Hopefully the situation will always be clear in context.

- The *vector space tensor product* is then defined as the quotient of the free vector space above by these equivalence relations,

$$\mathcal{H}_1 \otimes \mathcal{H}_2 := F(\mathcal{H}_1, \mathcal{H}_2)/\sim \ . \tag{3.1}$$

- An inner product on $\mathcal{H}_1 \otimes \mathcal{H}_2$ is inherited from those on $\mathcal{H}_1$ and $\mathcal{H}_2$ by defining for pure tensors

  $$\langle \psi_1 \otimes \psi_2 | \phi_1 \otimes \phi_2 \rangle = \langle \psi_1 | \phi_1 \rangle \langle \psi_2 | \phi_2 \rangle \ , \tag{3.2}$$

  and extending this to general elements by sesquilinearity. Note that this definition is compatible with the equivalence relations given above.

- The Hilbert space tensor product is obtained by taking the *completion* of this vector space tensor product with respect to the metric induced by the inner product. As usual, this is a technical detail that is relevant in the infinite dimensional case. It essentially means that we allow the possibility of taking infinite linear combinations of pure tensors whose norm is still finite. Finer aspects of this construction won't be important or examinable in this course, though we will see examples.

Remark 3.1.1 (Alternate construction of tensor product). There is an alternative, and in a sense much simpler, definition of the Hilbert space tensor product. Let $|\alpha_{i\in I}\rangle$ and $|\beta_{j\in J}\rangle$ denote bases for $\mathcal{H}_1$ and $\mathcal{H}_2$, respectively. Then $\mathcal{H}_1 \otimes \mathcal{H}_2$ can be identified with the Hilbert space with given basis $|\alpha_i \otimes \beta_j\rangle$ (again, in the infinite dimensional case one takes a completion which allows infinite linear combinations of these). To a purist, the first definition has the advantage being explicitly basis-independent. For practical purposes, this latter definition is often the most useful.

If we have a system described by a tensor product Hilbert space $\mathcal{H}_1 \otimes \mathcal{H}_2$, then operators and observables that are defined to act separately on $\mathcal{H}_1$ and $\mathcal{H}_2$ naturally extend to the tensor product. If $A_1 : \mathcal{H}_1 \to \mathcal{H}_1$ and $A_2 : \mathcal{H}_2 \to \mathcal{H}_2$, then we can define

$$\begin{aligned} A_1 \otimes A_2 : \mathcal{H}_1 \otimes \mathcal{H}_2 &\longrightarrow \mathcal{H}_1 \otimes \mathcal{H}_2 \\ |\psi_1 \otimes \psi_2\rangle &\longmapsto |A_1\psi_1 \otimes A_2\psi_2\rangle \ . \end{aligned} \tag{3.3}$$

In particular, when either A_1 or A_2 is the identity operator, then this gives operators that act on the tensor product only through the second or first tensor factor, respectively. Such operators naturally commute,

$$(A_1 \otimes \mathbb{1}_{\mathcal{H}_2})(\mathbb{1}_{\mathcal{H}_1} \otimes A_2) = (A_1 \otimes A_2) = (\mathbb{1}_{\mathcal{H}_1} \otimes A_2)(A_1 \otimes \mathbb{1}_{\mathcal{H}_2}) \ , \tag{3.4}$$

which is in correspondence with the physical criterion that making observations on one system should not impact another, in principle disjoint system.

We can similarly form the n-fold tensor product $\mathcal{H}_1 \otimes \mathcal{H}_2 \otimes \ldots \otimes \mathcal{H}_n$ with basis $\alpha_{i_1} \otimes \beta_{i_2} \otimes \ldots \otimes \gamma_{i_n}$ with i_j indexing a basis of $\mathcal{H}_j$. This is the Hilbert space for the composite of the n quantum mechanical systems described by $\mathcal{H}_i$, $i = 1, \ldots, n$. When the constituent Hilbert spaces are all identical to $\mathcal{H}$ we simply write $\otimes^n \mathcal{H}$ or $\mathcal{H}^{\otimes n}$.

A first important behaviour of Hilbert spaces under tensor product is that their dimensions (when finite) combine multiplicatively,

$$\dim(\mathcal{H}_1 \otimes \mathcal{H}_2) = \dim \mathcal{H}_1 \times \dim \mathcal{H}_2 \ . \tag{3.5}$$

This follows immediately from the second construction of the tensor product given above, where the number of basis elements clearly obeys this relation. It is worth pausing to compare this situation with what one encounters classically. If a two classical systems have configuration spaces of dimensions d_1 an d_2, say, then taken together their joint configuration space will be of dimension $d_1 + d_2$. In this sense, quantum mechanical state spaces get very big very fast compared to their classical analogues. Indeed, this is one of the properties that underlies the power of quantum computation.

There is a subspace of the tensor product Hilbert space that behaves a bit more classically: this is the subspace of pure tensors. Note that this is not a linear subspace of $\mathcal{H}_1 \otimes \mathcal{H}_2$, since the property of being a pure tensor is not preserved under addition. The dimensionality of the subspace of pure tensors does behave additively,

$$\dim(\mathcal{H}_1 \otimes \mathcal{H}_2)_{\text{decomposable}} = \dim \mathcal{H}_1 + \dim \mathcal{H}_2 - 1 \ , \tag{3.6}$$

where the correction by one comes from the equivalence of rescaling the two tensor factors in a pure tensor. Another way to see this result is to consider the relevant subspaces in projectivised Hilbert space. Here we have that subspace of decomposable states is of the form

$$\mathbb{P}(\mathcal{H}_1) \times \mathbb{P}(\mathcal{H}_2) \subset \mathbb{P}(\mathcal{H}_1 \otimes \mathcal{H}_2) \ . \tag{3.7}$$

The dimensionality of the let hand side is $\dim \mathcal{H}_1 + \dim \mathcal{H}_2 - 2$, and de-projectivising to recover the subspace of the Hilbert space adds one dimension. The embedding describing how the left hand side of (3.7) sits inside the right hand side is known as the *Segre embedding.*

3.2 Example: tensor product of qubits; entanglement

Let's consider the tensor product in the simplest case of combining several qubits (see Chapter 1.2). We recall that the qubit has Hilbert space $\mathcal{H} \cong \mathbb{C}^2$; let us now (adopting Dirac notation) denote a fixed orthonormal basis for the qubit by $|1\rangle$ and $|0\rangle$ such that $\sigma_3 |1\rangle = 1$ and $\sigma_3 |0\rangle = -1$.[15] We can then take as a basis for the tensor product $\mathbb{C}^2 \otimes \mathbb{C}^2 \cong \mathbb{C}^4$ the following pure tensors

$$|0 \otimes 0\rangle \ , \quad |0 \otimes 1\rangle \ , \quad |1 \otimes 0\rangle \ , \quad |1 \otimes 1\rangle \ . \tag{3.8}$$

Within this vector space, the most general state takes the form

$$a\,|0 \otimes 0\rangle + b\,|0 \otimes 1\rangle + c\,|1 \otimes 0\rangle + d\,|1 \otimes 1\rangle \ . \tag{3.9}$$

while the most general pure tensor takes the form

$$(\alpha\,|0\rangle + \beta\,|1\rangle) \otimes (\gamma\,|0\rangle + \delta\,|1\rangle) = \alpha\gamma\,|0 \otimes 0\rangle + \alpha\delta\,|0 \otimes 0\rangle + \beta\gamma\,|0 \otimes 0\rangle + \beta\delta\,|0 \otimes 0\rangle \tag{3.10}$$

One can check that a state of the form (3.9) can be written as in (3.10) if and only if $ad - bc = 0$, so indeed the set of pure states is a nonlinear subspace of $\mathcal{H}$ dimension $2 + 2 - 1 = 3$.

If we combine more qubits the dimension of the Hilbert space grows exponentially. In particular,

$$\otimes^n \mathbb{C}^2 \cong \mathbb{C}^{2^n} \ , \tag{3.11}$$

---

[15] These basis vectors are often denoted instead by $|\!\Uparrow\rangle$ and $|\!\Downarrow\rangle$ respectively due to their interpretation in terms of spins, and sometimes also $|+\rangle$ and $|-\rangle$. We may use either or both of these when we revisit this system in later chapters.

while the space of pure tensors is dramatically smaller (namely $2n-1$).

The two qubit system lets us introduce the simplest example of *quantum entanglement*. Suppose we have two qubit systems that are prepared (somehow) in the initial state[16]

$$|\mathrm{EPR}\rangle = \frac{|0\otimes 0\rangle - |1\otimes 1\rangle}{\sqrt{2}} ~. \tag{3.12}$$

Then suppose that Alice carries the first qubit with her to a faraway star system, while Bob remains on Earth with the second qubit. If Alice makes a measurement corresponding to the observable σ_3 on her qubit (so corresponding to the obsevable $\sigma_3\otimes\sigma_0$ on the tensor product Hilbert space), there is a 50% probability that she will find the value $+1$ and a 50% probability that she will find the value -1. In either case, she should find that the quantum state collapses according to the wave function collapse postulate,

$$\begin{aligned} &\text{Alice measures } +1 \quad \longrightarrow \quad |\psi\rangle = |1\otimes 1\rangle ~, \\ &\text{Alice measures } -1 \quad \longrightarrow \quad |\psi\rangle = |0\otimes 0\rangle ~. \end{aligned} \tag{3.13}$$

In each of the collapsed states, the results of a σ_3 measurement by Bob of his qubit (corresponding to the observable $\sigma_0\otimes\sigma_3$ on the combined system) should return a definite answer, with which answer is returned being dictated by the results of Alice's measurement. One might phrase this in a paradoxical-sounding way, as saying that when Alice makes her measurement, it instantaneously impacts the outcomes of Bob's experiment.

This sounds odd, especially in view of Einstein's theory of relativity, which says that there should be no communication faster than the speed of light. Upon additional scrutiny, however, the situation is not quite so paradoxical; though the result of Alice's measurement means that the result of Bob's measurement can only take a particular value, Bob has no way of knowing what result Alice found. What we really get from the entangled state is a *perfect correlation* between the results of Alice and Bob's experiments.[17]

Note that by virtue of the significant difference in the growth rate between the dimensionality of the space of pure tensors and the dimensionality of the Hilbert spaces we get upon iterated tensor products, entangled states are by far the generic ones in composite quantum systems.

3.3 Example: multi-particle systems of distinguishable particles

Another incarnation of the tensor product arises when we consider systems of several elementary particles. If our particles move in d dimensional space, then the Hilbert space for the i'th particle will be identified as $\mathcal{H}_i \cong L^2(\mathbb{R}^d)$, and for n particles we are supposed to be interested in the Hilbert space

$$\mathcal{H} \cong L^2(\mathbb{R}^d)_1 \otimes L^2(\mathbb{R}^d)_2 \otimes \cdots \otimes L^2(\mathbb{R}^d)_n ~. \tag{3.14}$$

The result of the Hilbert space tensor product turns out to just be the space of square-normalizable wave functions of the n particle positions $\psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)$, *i.e.*,

$$\mathcal{H} \cong L^2(\mathbb{R}^{dn}) ~. \tag{3.15}$$

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[16] EPR here stands for Einstein-Podolsky-Rosen, the authors of a famous paper pointing out seemingly paradoxical properties of entangled quantum systems. This kind of a state is also sometimes called a *Bell pair*.

[17] There is a lot more to say here and we won't pursue it in this course. The actual EPR 'paradox' is related to a slightly different set of thought experiments involving Alice choosing one of several measurements to perform, which has a consequence for the resultant probability distribution for Bob's experiment after the fact. Rest assured, though, it still doesn't lead to a real paradox or any faster-than-light communication.

At a technical level, this is a case where the final step of *completing* the Hilbert space is relevant. We identify a pure tensor of single-particle wave functions with a separable n-particle wave function,

$$\psi_1(\mathbf{x}_1)\otimes\psi_1(\mathbf{x}_1)\otimes\cdots\otimes\psi_n(\mathbf{x}_n) \quad\longleftrightarrow\quad \psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)=\psi_1(\mathbf{x}_1)\psi_1(\mathbf{x}_1)\cdots\psi_n(\mathbf{x}_n)~. \tag{3.16}$$

While a general n-particle wave function certainly can't be written as a finite linear combination of separable wave functions of the above form, given a Hilbert space basis $\psi_i(\mathbf{x})$, $i=1,2,\ldots,\infty$ for $L^2(\mathbb{R}^d)$, then pure tensors formed from these basis elements form an orthonormal basis for $L^2(\mathbb{R}^{dn})$.

Remark 3.3.1. The technical subtlety associated with completion of the Hilbert space is, at least formally, evaded when we choose to work with our continuum basis of generalised position eigenstates. In this case, we introduce basis elements

$$|\mathbf{x}_1,\ldots,\mathbf{x}_n\rangle=|\mathbf{x}_1\rangle\otimes\cdots\otimes|\mathbf{x}_n\rangle~, \tag{3.17}$$

which obey

$$\langle\mathbf{x}_1,\ldots,\mathbf{x}_n|\mathbf{x}_1',\ldots,\mathbf{x}_n'\rangle=\delta^d(\mathbf{x}_1-\mathbf{x}_1')\cdots\delta^d(\mathbf{x}_n-\mathbf{x}_n')=\delta^{nd}((\mathbf{x}_1;\ldots;\mathbf{x}_n)-(\mathbf{x}_1';\ldots;\mathbf{x}_n'))~, \tag{3.18}$$

where in the last expression we are using the nd-dimensional Dirac delta function. Then the most general state takes the form

$$|\psi\rangle=\int_{\mathbb{R}^{nd}}d^d\mathbf{x}_1\cdots d^d\mathbf{x}_n\psi(\mathbf{x}_1,\ldots,\mathbf{x}_n)\,|\mathbf{x}_1,\ldots,\mathbf{x}_n\rangle~, \tag{3.19}$$

which is just an n-particle wave function in the usual sense as an element of $L^2(\mathbb{R}^{nd})$.

In view of what is to come in the next section, notice that for, say, the $n=2$ case of two particles, the basis elements $\psi_i(\mathbf{x}_1)\otimes\psi_j(\mathbf{x}_2)$ and $\psi_2(\mathbf{x}_1)\otimes\psi_j(\mathbf{x}_2)$ are inequivalent, and correspondingly, for a general two-particle wave function, $\psi(\mathbf{x}_1,\mathbf{x}_2)$ and $\psi(\mathbf{x}_2,\mathbf{x}_1)$ are unrelated. In words, the probability that particle one is in state i and particle two is in state j is not the same as particle one being in state j and two in state i. In this sense, this is a description of *distinguishable particles*, for which we know *a priori* what we mean by particle one and particle two.

Chapter 4

Identical particles and statistics

A curious consequence of the quantum mechanical picture of the world is that elementary particles of the same type (electrons, quarks, *etc.*) naturally come to be thought of as being *fundamentally indistinguishable*. To motivate this consider the following thought experiment.[18]

Suppose that at time $t = 0$ you have a pair of electrons whose positions are known well enough to distinguish them (*i.e.*, one is definitely in one half of the room and the other is definitely in the other half). After a period of time elapses, the wave function will have evolved so that both electrons could be anywhere in the room with some probability. At this point, we may make measurements to determine the positions of two electrons, but we will have no way to distinguish the two different electrons; in contrast to the classical case, we can't keep track of "electron one" by following it along its trajectory during the time interval – it had no definite trajectory when it was not being observed!

4.1 Indistinguishable particles and wave functions

We wish to address the consequences of indistinguishability on multi-particle wave functions, starting with the case of two particles. A two particle wave function is a (square-normalisable) function of two positions $\psi(\mathbf{x}_1, \mathbf{x}_2)$. If we now demand that the wave function represent indistinguishable particles, then it should assign the same probability (density) to find "particle one" at $\mathbf{x}_1$ and "particle two" at $\mathbf{x}_2$ as it does to finding "particle one" at $\mathbf{x}_2$ and "particle two" at $\mathbf{x}_1$.[19] In other words, the wave function should obey

$$|\psi(\mathbf{x}_2, \mathbf{x}_1)|^2 = |\psi(\mathbf{x}_1, \mathbf{x}_2)|^2 \quad \Longrightarrow \quad \psi(\mathbf{x}_2, \mathbf{x}_1) = \lambda\psi(\mathbf{x}_1, \mathbf{x}_2) \ , \tag{4.1}$$

where $\lambda = e^{i\varphi}$ is a *phase*. Iterating this relation we see that

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = \lambda^2\psi(\mathbf{x}_1, \mathbf{x}_2) \ , \tag{4.2}$$

so there are just two possibilities: $\lambda = \pm 1$.[20] In the case $\lambda = 1$ we are restricting ourselves to symmetric functions of the two particles' positions, while for $\lambda = -1$ we have anti-symmetric functions.

4.1.1 Permutations and Statistics

In the case of many particles, we have an obvious action of the symmetric group S_n on the space of n-particle wavefunctions,

$$\begin{array}{rcl} \big(S_n, L^2(\mathbb{R}^{nd})\big) & \longrightarrow & L^2(\mathbb{R}^{nd}) \\ (\pi, \psi(\mathbf{x}_1, \ldots, \mathbf{x}_n)) & \longmapsto & \psi(\mathbf{x}_{\pi(1)}, \ldots, \mathbf{x}_{\pi(n)}) \ . \end{array} \tag{4.3}$$

---

[18] It also turns out that the indistinguishability of elementary particles is a natural prediction of *quantum field theory*, which is the framework that synthesizes quantum theory with the special theory of relativity.

[19] Scare quotes because, of course, there is no unambiguous notion of particle one and particle two; this is just referring to the order of the arguments in the wave function.

[20] There is an oft-mentioned caveat here, which is that in two-dimensions there is a possibility for a more general phase λ, with the corresponding particles referred to as *anyons*. To see the possibility of this more general phase, it is necessary to be a bit more flexible about the description of the Hilbert space for several particles to allow multi-valued functions of positions. We will not pursue this here.

By the same argument as given above for the $n = 2$ case, indistinguishability requires that this action obeys

$$\psi(\mathbf{x}_{\pi(1)}, \ldots, \mathbf{x}_{\pi(n)}) = \lambda(\pi)\psi(\mathbf{x}_1, \ldots, \mathbf{x}_n) \ , \tag{4.4}$$

with $\lambda(\pi)$ a (now π-dependent) phase: $\lambda(\pi) = e^{i\varphi(\pi)}$. Composing the action of two permutations $\pi, \sigma \in S_n$ we find

$$\begin{aligned} \psi(\mathbf{x}_{(\pi\circ\sigma)(1)}, \ldots, \mathbf{x}_{(\pi\circ\sigma)(n)}) = \lambda(\pi)\psi(\mathbf{x}_{\sigma(1)}, \ldots, \mathbf{x}_{\sigma(n)}) &= \lambda(\pi)\lambda(\sigma)\psi(\mathbf{x}_1, \ldots, \mathbf{x}_n) \ , \\ &= \lambda(\pi\circ\sigma)\psi(\mathbf{x}_1, \ldots, \mathbf{x}_n) \ . \end{aligned} \tag{4.5}$$

So we have the rule $\lambda(\pi \circ \sigma) = \lambda(\pi)\lambda(\sigma)$.

Definition 4.1.1. *A* multiplicative character *of a group G is a group homomorphism from G into the circle group $U(1)$ (or more generally into the ring of units $k^\times$ of a field k).*

Thus, we have that the map $\lambda : S_n \to \mathbb{C}$ defines a multiplicative character for the permutation group S_n. It turns out that there are only two inequivalent multiplicative characters for S_n, as we shall now see.

First observe that any two elements of S_n that are conjugate to each other are mapped to the same value by a multiplicative character,

$$\lambda(\pi \circ \sigma \circ \pi^{-1}) = \lambda(\pi)\lambda(\sigma)\lambda(\pi^{-1}) = \lambda(\pi)\lambda(\sigma)\lambda(\pi)^{-1} = \lambda(\sigma) \ . \tag{4.6}$$

Now recall that in S_n, a *transposition* is a permutation that just swaps two elements of $\{1, \ldots, n\}$, say r and s, and is denoted $(r\,s)$. Such transpositions are all conjugate to one another:

$$(r\,s) = (1\,r)(2\,s)(1\,2)(2\,s)^{-1}(1\,r)^{-1} \ . \tag{4.7}$$

Thus we have that $\lambda((r\,s)) = \lambda((1\,2)) = \pm 1$, where our previous argument in the two-particle case implies the latter equality.

General permutations are generated by the composition of transpositions, and are unambiguously classified as either being *odd* or *even* according to whether they arise from an odd or even number of transpositions. Thus we have the following

Proposition 4.1.2. *Let $\lambda : S_n \to \mathbb{C}$ be a multiplicative character for the symmetric group. Then either $\lambda(\pi) \equiv 1$ or $\lambda(\pi) = \epsilon(\pi)$, where ϵ gives the signature of the permutation,*

$$\epsilon(\pi) := \begin{cases} 1 & \text{for } \pi \text{ even} \ , \\ -1 & \text{for } \pi \text{ odd} \ . \end{cases} \tag{4.8}$$

Thus the two possibilities for wave functions of indistinguishable particles are *totally symmetric* wave functions ($\lambda \equiv 1$) and *totally antisymmetric* wave functions ($\lambda = \epsilon$), generalising the two-particle case. For a given species of elementary (indistinguishable) particle, one of these two cases must apply. This leads to a binary classification of indistinguishable particles:

Definition 4.1.3. *Indistinguishable particles satisfying (4.4) are called* bosons *if the corresponding group character is the trivial one; these particles are said to obey* Bose-Einstein statistics*. Particles satisfying (4.4) with the nontrivial character (ϵ) are called* fermions*; these particles are said to obey* Fermi-Dirac statistics*.*

The known elementary fermions in nature are electrons, muons, τ-particles, and neutrinos, along with their anti-particles (collectively, *leptons*) as well as quarks. Also composite particles made up of an odd number of elementary fermions, such as protons and neutrons, are fermions.

The known elementary bosons in nature are photons, gluons, W- and Z-bosons, gravitons, and the Higgs boson. Also composite particles made up of an even number of elementary fermions, such as *mesons.*

An important fact that can be observed from nature is that the statistics of a particle is correlated with its *spin* (we will give a full treatment of spin in a later chapter). In fact, this empirical fact is also a mathematical theorem that can be proven within the context of *relativistic quantum field theory.*

Theorem 4.1.4 (Spin-statistics theorem in three dimensions)**.** *In a relativistic quantum theory in three spatial dimension, particles with integral spin must obey Bose-Einstein statistics. Particles with half-integral spin* ($n + \frac{1}{2}$ *for* $n \in \mathbb{N}$) *must obey Fermi-Dirac statistics.*

An analogous theorem holds in any number of spatial dimensions greater than three, where one must be a bit more precise about the meaning of integral/half-integral spin (spin is no longer charcterised by a single number in higher dimensions).

4.2 Bosonic and fermionic wave functions

It is useful to have some tools for producing and manipulating wave functions for particles obeying appropriate statistics. We first define projection operators onto the subspaces of completely symmetric and completely anti-symmetric (bosonic and fermionic, respectively) wave functions. In particular, for a general n-particle wave function ψ, define[21]

$$Pr_\lambda \psi = \frac{1}{n!} \sum_{\pi \in S_n} \lambda(\pi^{-1}) \psi(\mathbf{x}_{\pi(1)}, \ldots, \mathbf{x}_{\pi(n)}) \ , \tag{4.9}$$

where as before, λ is the identity for Bose-Einstein and is ϵ for Fermi-Dirac. We can think of this as *averaging over the action of the permutation group*, with the average weighted by the relevant group character. We easily prove the following:

Proposition 4.2.1. *For* $\sigma \in S_n$ *we have*

$$(Pr_\lambda \psi)(\mathbf{x}_{\sigma(1)}, \ldots, \mathbf{x}_{\sigma(n)}) = \lambda(\sigma)(Pr_\lambda \psi)(\mathbf{x}_1, \ldots, \mathbf{x}_n) \ . \tag{4.10}$$

and $Pr_\lambda^2 = Pr_\lambda$ *so* Pr_λ *is an orthogonal projection operator whose range consists of bosonic/fermionic wave functions.*

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[21] Since for our multiplicative characters $\lambda(\pi) = \pm 1 = \lambda(\pi^{-1})$, the π^{-1} argument could be replaced with a π. The expression here is the one that generalises to more complicated finite groups admitting more general multiplicative characters.

Proof. We proceed by direct calculation:

$$\begin{aligned}
(Pr_\lambda\psi)(\mathbf{x}_{\sigma(1)},\ldots,\mathbf{x}_{\sigma(n)}) &= \frac{1}{n!}\sum_{\pi\in S_n}\lambda(\pi^{-1})\psi\big(\mathbf{x}_{(\pi\circ\sigma)(1)},\ldots,\mathbf{x}_{(\pi\circ\sigma)(n)}\big)\ ,\\
&= \frac{1}{n!}\sum_{\pi\in S_n}\lambda(\sigma\circ(\pi\circ\sigma)^{-1})\psi\big(\mathbf{x}_{(\pi\circ\sigma)(1)},\ldots,\mathbf{x}_{(\pi\circ\sigma)(n)}\big)\ ,\\
&= \frac{1}{n!}\sum_{\tilde\pi\in S_n}\lambda(\sigma\circ\tilde\pi^{-1})\psi\big(\mathbf{x}_{\tilde\pi(1)},\ldots,\mathbf{x}_{\tilde\pi(n)}\big)\ ,\\
&= \lambda(\sigma)(Pr_\lambda\psi)(\mathbf{x}_1,\ldots,\mathbf{x}_n)\ .
\end{aligned}$$

to get to from the second to the third line we have used that for fixed $\sigma\in S_n$, as π ranges over S_n, so does $\tilde\pi=\pi\circ\sigma$ and so we can replace the latter by the former in the summation.

Using this we find

$$\begin{aligned}
Pr_\lambda(Pr_\lambda\psi)(\mathbf{x}_1,\ldots,\mathbf{x}_n) &= \frac{1}{n!}\sum_{\pi\in S_n}\lambda(\pi^{-1})(Pr_\lambda\psi)\big(\mathbf{x}_{\pi(1)},\ldots,\mathbf{x}_{\pi(n)}\big)\ ,\\
&= \frac{1}{n!}\sum_{\pi\in S_n}\lambda(\pi^{-1})\lambda(\pi)(Pr_\lambda\psi)(\mathbf{x}_1,\ldots,\mathbf{x}_n)\ ,\\
&= (Pr_\lambda\psi)(\mathbf{x}_1,\ldots,\mathbf{x}_n)\ ,
\end{aligned}$$

where we've used that $|S_n|=n!$. Finally, the orthogonality of the projection is equivalent to its self-adjointness. Self-adjointness can be shown by term-by-term change of variables in the inner product. We leave the details to the interested reader. The stated result then follows. ■

4.2.1 Two-particle projections

For the two-particle case $n=2$, where the space of distinguishable-particle wave functions is $L^2(\mathbb{R}^d\times\mathbb{R}^d)$ the two projectors we've just deinfed are just the symmetric and antisymmetric combinations:

$$Pr_1\psi(\mathbf{x}_1,\mathbf{x}_2)=\frac{\psi(\mathbf{x}_1,\mathbf{x}_2)+\psi(\mathbf{x}_2,\mathbf{x}_1)}{2}\ ,\qquad Pr_\epsilon\psi(\mathbf{x}_1,\mathbf{x}_2)=\frac{\psi(\mathbf{x}_1,\mathbf{x}_2)-\psi(\mathbf{x}_1,\mathbf{x}_2)}{2}\ . \tag{4.11}$$

In this case ($n=2$), all wave functions can be decomposed into symmetric and antisymmetric parts, so the full space of (distinguishable) two-particle wave functions can be decomposed into bosonic and fermionic wave functions. Alternatively, this can be phrased as the identity

$$Pr_1+Pr_\epsilon=\mathbb{1}_{L^2(\mathbb{R}^d\times\mathbb{R}^d)}\ , \tag{4.12}$$

which can be re-interpreted as the resolution of the identity for the permutation operator that exchanges $\mathbf{x}_1\leftrightarrow\mathbf{x}_2$.

Note that this is not the situation for larger values of n; there are wavefunctions that cannot be decomposed into just totally-symmetric and totally-antisymmetric parts. We will see a related phenomenon when we count bosonic and fermionic states associated to finite Hilbert spaces later in this Chapter.

4.2.2 n-particle projections

Though the general projection operator is a little complicated to perform in practice for general wave functions (it involves choosing a sufficiently efficient way to sum over permutations), there is a case where things can be phrased more compactly. This is where we start with a *separable* distinguishable-particle wave function:

$$\psi(\mathbf{x}_1,\ldots,\mathbf{x}_n) = \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\ldots\psi_n(\mathbf{x}_n)\ . \tag{4.13}$$

This is a particularly natural class of wavefunctions to consider when considering *non-interacting* identical particles, where we might chose the ψ_i to be stationary states of the one-particle Hamiltonian acting on $\mathbf{x}_i$ to get stationary states for the full n-particle system.

In the fermionic case, the projection can then be realised as the *Slater determinant*,

$$Pr_\epsilon\psi = \frac{1}{n!}\begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \ldots & \ldots & \psi_n(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \ldots & \ldots & \psi_n(\mathbf{x}_2) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \psi_1(\mathbf{x}_n) & \ldots & \ldots & \ldots & \psi_n(\mathbf{x}_n) \end{vmatrix}\ . \tag{4.14}$$

Since arbitrary states can be expressed as (infinite) linear combinations of separable states, all fermionic wave functions can be obtained as (infinite) linear combinations of these.

An analogous construction works for the bosonic case, though this uses the so-called *permanent* of a matrix, which is like the determinant but without the signs,

$$Pr_1\psi = \frac{1}{n!}\,\mathrm{perm}\begin{pmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \ldots & \ldots & \psi_n(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \ldots & \ldots & \psi_n(\mathbf{x}_2) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \psi_1(\mathbf{x}_n) & \ldots & \ldots & \ldots & \psi_n(\mathbf{x}_n) \end{pmatrix}\ . \tag{4.15}$$

As in the fermionic case, arbitary bosonic wave functions can be constructed from these permanent states.

4.3 Symmetric and anti-symmetric tensor products

Though the above focused on fermionic and bosonic *wave functions*, the (anti-)symmetrisation procedure we developed applies equally well to the case when we are taking tensor powers of some general Hilbert space $\mathcal{H}$ such as the qubit Hilbert space (or even a general vector space, for that matter). Here the n-fold tensor product of $\mathcal{H}$ admits a natural action of the symmetric group S_n just as was the case for wave functions. If we let $\{\psi_i\}$ denote a basis for $\mathcal{H}$, then we have

$$\begin{aligned} (S_n,\mathcal{H}^{\otimes n}) &\longrightarrow \mathcal{H}^{\otimes n} \\ (\pi,\psi_1\otimes\cdots\otimes\psi_n) &\longmapsto \psi_{\pi(1)}\otimes\cdots\otimes\psi_{\pi(n)}\ . \end{aligned} \tag{4.16}$$

where the action on pure tensors extends by linearity to all of $\mathcal{H}^{\otimes n}$. We can then define bosonic and fermionic projection operators analogous to the ones we used for wave functions above. Just like we had for separable wave functions, we can define the action of these projection operators in terms of the Slater determinant and the related permanent constructions, but now acting on pure tensors in $\mathcal{H}^{\otimes n}$ and then extended to the general case by linearity. We can correspondingly define bosonic and fermionic states in the n-fold tensor product of identical Hilbert spaces as the ranges of the corresponding orthogonal projectors:

Definition 4.3.1. *The n-*fold symmetric tensor product *of the Hilbert space $\mathcal{H}$ is the subspace of* *the n-fold tensor product $\mathcal{H}^{\otimes n}$ on which Pr_1 acts as the identity, or equivalently,*

$$\odot^n \mathcal{H} = \mathrm{Ran}_{\mathcal{H}^{\otimes n}} Pr_1 \ . \tag{4.17}$$

This is sometimes also denoted $\mathrm{Sym}^n\mathcal{H}$*, and these are states that are compatible with Bose-Einstein statistics.*

Definition 4.3.2. *The* n-fold antisymmetric tensor product *of the Hilbert space $\mathcal{H}$ is the subspace of the n-fold tensor product $\mathcal{H}^{\otimes n}$ on which Pr_ϵ acts as the identity, or alternatively,*

$$\wedge^n \mathcal{H} = \mathrm{Ran}_{\mathcal{H}^{\otimes n}} Pr_\epsilon \ . \tag{4.18}$$

This is sometimes called the exterior tensor product*, and these states are compatible with Fermi-Dirac statistics.*

From the standard properties of determinants, a Slater determinant state will vanish identically if two of the constituent ψ_i are proportional. This means that the basis of n-particle states we get by acting with the fermionic projection operator on a basis of pure tensors all come from states where each of the n particles is in a distinct basis state. This is often phrased in terms of the following,

The Pauli exclusion principle: *Two fermions cannot occupy the same state.*

Indeed, this leads to a significant reduction in the number of fermionic states that can be constructed from a given set of single-particle states. To see this more explicitly, let us count the bosonic and fermionic states that can be built from a given N-dimensional Hilbert space under interated symmetric and anti-symmetric tensor products. We have the following,

Lemma 4.3.3. *The space of fermionic n-particle states built from an N-dimensional single-particle Hilbert space $\mathcal{H}$ has dimension given by*

$$\dim\left(\wedge^n\mathcal{H}\right) = \binom{N}{n} \ . \tag{4.19}$$

Proof. We choose a basis for $\mathcal{H}$ and build a basis of states for the fermionic n-particle Hilbert space using Slater determinants where the ψ_i are elements of that basis. There are N choices for ψ_1, but since ψ_2 cannot be the same as ψ_1, there are $N-1$ choices for ψ_2 and so on. The final state is independent of the ordering of $\psi_1, \ldots, \psi_n$ so we have

$$\dim\left(\wedge^n\mathcal{H}\right) = \frac{N(N-1)\cdots(N-n+1)}{n!} = \frac{N!}{n!(N-n)!} = \binom{N}{n} \ . \tag{4.20}$$

■

Which leads to an immediate important observation:

Corollary 4.3.4. *At most N identical, non-interacting fermionic particles can coexist in a given N-dimensional single-particle Hilbert space $\mathcal{H}$.*

This will be an important restriction when we consider atomic structure in the presence of several electrons.

For completeness, we also consider the ccase of bosonic multi-particle states built from a given N-dimensional Hilbert space.

Lemma 4.3.5. *The space of bosonic n-particle states built from an N-dimensional single-particle Hilbert space $\mathcal{H}$ has dimension given by*

$$\dim\left(\odot^n\mathcal{H}\right)=\frac{(N+n-1)!}{(N-1)!\,n!}\ . \tag{4.21}$$

Proof. In order to prove this we introduce a generating function known as a *partition function* that has much wider applicability. In general a separable bosonic state can be represented as

$$Q_1\left(\psi_1^{\otimes k_1}\otimes\psi_2^{\otimes k_2}\cdots\psi_N^{\otimes k_N}\right)\ ,\qquad \sum k_i=n\ . \tag{4.22}$$

The overall order doesn't matter because of the symmetrisation, so we only pay attention to how many times each basis element appears. We therefore want to count the number of integer "partitions of n", $k_i\in\mathbb{N}$ such that the k_i add up to n. Let us replace the ψ_i by formal variables x_i, whereupon our problem becomes that of counting the number of distinct monomials of the form $x_1^{k_1}x_2^{k_2}\cdots x_N^{k_N}$ with the k_i addint up to n. If we further multiply each x_i by s, then the total power of s will be the sum of the k_i. If we form the sum over *all* $k_1,\ldots,k_N$, we obtain

$$\sum_{k_1,\ldots,k_N\in\mathbb{N}}(sx_1)^{k_1}(sx_2)^{k_2}\ldots(sx_N)^{k_N}=\prod_{j=1}^{N}\sum_{k_j\in\mathbb{N}}(sx_j)^{k_j}=\prod_{j=1}^{N}\frac{1}{1-sx_j}\ . \tag{4.23}$$

If we then set all the x_i to one, we obtain $1/(1-s)^N$ and the coefficient of s^n will simply count the number of terms where $\sum k_i=n$. The generalised binomial theorem then gives

$$\frac{1}{(1-s)^N}=\sum_{n\in\mathbb{N}}\binom{N+n-1}{n}s^n\ , \tag{4.24}$$

from which the result follows. ■

One can now observe that while for $n=2$ there is an accidental equality

$$\dim\mathcal{H}^{\otimes n}=N^n=\dim\wedge^n\mathcal{H}+\dim\odot^n\mathcal{H}\ ,\qquad n=2\ , \tag{4.25}$$

for more than two particles we have

$$\dim\mathcal{H}^{\otimes n}=N^n>\dim\wedge^n\mathcal{H}+\dim\odot^n\mathcal{H}\ ,\qquad n>2\ . \tag{4.26}$$

So for more than two particles, a general distinguishable multiparticle state cannot be decomposed into just bosonic and fermionic parts.

Chapter 5

Symmetries and One-Parameter Unitary Groups

We next turn our attention to the realisation of *symmetries* in quantum theories/systems. Before developing a formal theory of quantum symmetry, we will look at a simple example that illustrates the formalism and many of the key ideas.

5.1 An appetizer: spatial and time translations

Consider a free particle moving on the real line (so, as in Chapter 1.3, the Hilbert space is identified as $\mathcal{H} \cong L^2(\mathbb{R})$, and additionally the Hamiltonian is just $H = P^2/2m$). There is an intuitive sense in which *linear translations* in space should be symmetries of the theory. How does this manifest in the quantum mechanical formalism?

For $a \in \mathbb{R}$, we can define an operator $T(a) : \mathcal{H} \to \mathcal{H}$ that corrresponds to a translation of the entire system by a relative to a fixed reference frame. This will act on wavefunctions according to

$$(T(a)\psi)(x) = \psi(x-a) \ . \tag{5.1}$$

To see why the minus sign is there, note that the value of the transformed wavefunction at a will be the value of the original wave function at the origin. In terms of our generalised position eigenstates, we have[22]

$$T(a)\,|\xi\rangle = |\xi + a\rangle \ , \tag{5.2}$$

because a (generalised) eigenstate that was previously localised at $x = \xi$ should be localised at $x = \xi + a$ after translation. We see this is equivalent to (5.1) as follows,

$$\begin{aligned}
(T(a)\psi)(x) = \langle x|T(a)|\psi\rangle &= \int_{-\infty}^{\infty} \mathrm{d}\xi \ \langle x|T(a)|\xi\rangle \, \langle\xi|\psi\rangle \ , \\
&= \int_{-\infty}^{\infty} \mathrm{d}\xi \ \langle x|\xi + a\rangle \, \psi(\xi) \ , \\
&= \int_{-\infty}^{\infty} \mathrm{d}\xi \, \delta(x - \xi - a)\psi(\xi) \ , \\
&= \psi(x-a) \ .
\end{aligned} \tag{5.3}$$

We can make some immediate structural observations regarding the properties of these translation operators:

(1) $T(a)T(b) = T(a+b) \quad \forall \ a, b \in \mathbb{R}$

(2) $T(a)^{-1} = T(-a) \qquad \forall \ a \in \mathbb{R}$

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[22] Keeping track of the signs here is a good exercise in disambiguating generalised positions eigenstates from their wavefunctions

(3) $T(0) = \mathbb{1}$

We can also determine the adjoint of this translation operator by a change of variables in the integral expression for the inner product,

$$\langle\chi|T(a)\psi\rangle = \int_{-\infty}^{\infty} \mathrm{d}x\, \chi(x)\psi(x-a) = \int_{-\infty}^{\infty} \mathrm{d}x\, \chi(x+a)\psi(x) = \langle T(-a)\chi|\psi\rangle \ . \tag{5.4}$$

so we have

(4) $T(a)^* = T(-a) = T(a)^{-1}$

As in our discussion of time translation, this last condition identifies the operators $T(a)$ as unitary operators. The four properties that we have listed then precisely identify this structure as a *unitary representation of the additive group* $(\mathbb{R}, +)$ *on the Hilbert space* $\mathcal{H}$.

Definition 5.1.1. *The* unitary group $\mathsf{U}(\mathcal{H})$ *is the group of unitary operators on the Hilbert space* $\mathcal{H}$*. For the case of when* $\mathcal{H}$ *is finite-dimensional (say* $\dim(\mathcal{H}) = n$*, this can be identified with the usual matrix group* $U(n)$

Definition 5.1.2. *A* unitary representation *of a group* $\mathcal{G}$ *on a Hilbert space* $\mathcal{H}$ *is a group homomorphism* $U : \mathcal{G} \to \mathsf{U}(\mathcal{H})$*.*

In the case of infinite-dimensional $\mathcal{H}$, this is required to be a *strongly continuous homomorphism*, but we will not need to pay attention to that restriction in this course and so will not define it. (See, though, Def. 5.2.5 below for a related condition).

An important feature of the group of translations is that they can be taken arbitrarily small, in which case the translation operator should become arbitrarily close to the identity operator in an appropriate sense. We can observe how this transpires in terms of the action of translations on (differentiable) wave functions:[23]

$$\lim_{\epsilon\to 0}(T(\epsilon)\psi)(x) = \lim_{\epsilon\to 0}\psi(x-\epsilon) = \psi(x) - \epsilon\psi'(x) + O(\epsilon^2) \ . \tag{5.5}$$

We wish to interpret this result as defining an infinitesimal expansion of the translation operator itself,

$$T(\epsilon) = \mathbb{1} - \frac{i\epsilon}{\hbar}T_{\text{inf}} + O(\epsilon^2) \ , \qquad (T_{\text{inf}}\psi)(x) = -i\hbar\psi'(x) \ . \tag{5.6}$$

We have inserted conventional factors of i and $\hbar$ that alows us to make the identification of T_{inf} with the *momentum operator* P.

The relationship between translations and momentum is easier to tease out in momentum space.

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[23] The restriction to differentiable wave functions here is, once again, related to the infinite dimensionality of our Hilbert space, which means that the infinitesimal version of translation that we are defining is only partially defined on $L^2(\mathbb{R})$. Differentiable wave functions are dense in $L^2(\mathbb{R})$.

On generalised momentum eigenstates, we have

$$\begin{aligned}
T(a)\,|p\rangle &= \int_{-\infty}^{\infty} \mathrm{d}x\, T(a)\,|x\rangle\,\langle x|p\rangle &&= \int_{-\infty}^{\infty} \mathrm{d}x\ |x+a\rangle\, e^{\frac{ipx}{\hbar}}\ , \\
&= \int_{-\infty}^{\infty} \mathrm{d}x\ |x\rangle\, e^{\frac{ip(x-a)}{\hbar}} &&= e^{-\frac{ipa}{\hbar}} \int_{-\infty}^{\infty} \mathrm{d}x\ |x\rangle\, e^{\frac{ipx}{\hbar}}\ , \\
&= e^{-\frac{ipa}{\hbar}}\,|p\rangle &&= e^{-\frac{iPa}{\hbar}}\,|p\rangle\ ,
\end{aligned} \tag{5.7}$$

so on our (continuum) basis of generalised momentum eigenstates we have the operator relation

$$T(a) = \exp\left(-\frac{iPa}{\hbar}\right)\ , \tag{5.8}$$

from which we would formally deduce $T_{inf} = P$ just by taking the power series expansion of the exponential. We summarise this situation by saying that P is the *infinitesimal generator of translations*.[24] Note also that unitarity of $T(a)$ follows from self-adjointness of P and vice versa,

$$T(a)^* = \left(e^{-\frac{iPa}{\hbar}}\right)^* = \left(e^{\frac{iPa}{\hbar}}\right) = T(a)^{-1}\ . \tag{5.9}$$

What we've said so far makes no reference to translations being a *dynamical symmetry* of the system, *i.e.*, being a symmetry of the equations of motion (in our case, the time-dependent Schrödinger equation). Intuitively, this should depend on the potential $V(X)$ being constant (or zero), as otherwise the potential would violate translation invariance. To have translations as a dynamical symmetry, we would like to require that the symmetry transformation of the infinitesimal time evolution of a state vector is the same as the infinitesimal time evolution of the symmetry-transformed state vector, *i.e.*,

$$T(a)\,|H\psi\rangle = H\,|T(a)\psi\rangle\ , \tag{5.10}$$

which, by writing $|\psi\rangle = T(a)^*\,|\varphi\rangle$ for some $|\varphi\rangle$ we can equivalently characterise as

$$T(a)HT(a)^* = H\ . \tag{5.11}$$

Further looking at the case of infinitesimal translations, this gives the condition

$$\left(1 - \frac{i\epsilon}{\hbar}P + O(\epsilon^2)\right) H \left(1 + \frac{i\epsilon}{\hbar}P + O(\epsilon^2)\right) = H + \frac{i\epsilon}{\hbar}[H,P] + O(\epsilon^2) = H\ , \tag{5.12}$$

from which we deduce the requirement $[H,P] = 0$. Using our expression for finite translations as an exponentiated version of P, one can show that this vanishing commutator also implies the relation (5.11). And indeed, these will only hold for a Hamiltonian of the form $H = P^2/2m + V(X)$ only if $V(X)$ is a constant.[25]

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[24] If you are familiar with Noether's theorem from classical mechanics, then this should sound familiar as a counterpart of the fact that momentum is the conserved quantity associated with translation invariance, and it generates infinitesimal translations through the Poisson bracket.

[25] As a concrete example of this, in your first homework exercise, you will have shown that for the harmonic oscillator the finite spatial translation of the ground state is a coherent state, which is certainly no longer an energy eigenstate, let alone the ground state.

5.2 A general theory of quantum symmetries

What we've seen above gives us some insight into the general structure of symmetries in quantum systems. Now we'll look at this topic more abstractly.

5.2.1 A first attempt at generalisation

If we try to generalise a bit from what we've seen in our example, we might propose the following structures associated with the presence of a symmetry in a quantum system. It will turn out that these are not quite the complete story; we'll return to the correct formulation after some technical discussion.

- Symmetries should be implemented via unitary operators on $\mathcal{H}$, so as to preserve norms and overlaps.
- Symmetries naturally form a group—call it $\mathcal{G}$—and the operators implementing their action on $\mathcal{H}$ should form a unitary representation of that group,

$$U : \mathcal{G} \to \mathsf{U}(\mathcal{H}) \ , \qquad U(g_1)U(g_2) = U(g_1 g_2) \quad \forall\, g_1, g_2 \in \mathcal{G} \ . \tag{5.13}$$

- For continuous symmetries, infinitesimal transformations are realised by self-adjoint operators that generate finite transformations (parameterised by $s \in \mathbb{R}$) via exponentiation according to

$$U(g(s)) = \exp\left(-\frac{iGs}{\hbar}\right) \ , \quad G = G^*. \tag{5.14}$$

- For dynamical symmetries, we require

$$U(g)HU(g^{-1}) = H \qquad ([H,G]=0 \quad \text{for infinitesimal generators}) \ . \tag{5.15}$$

These properties do hold in quite a few examples of interest. For example, you should compare the above to our discussion of time evolution in Chapter 1. However, they are not the most general version of the story, and we have also been a bit cavalier about some technical details in our discussion of infinitesimal symmetries. We will address both of those issues below.

5.2.2 Quantum symmetries and projective representations

The main shortcoming of the formulation above arises from having neglected the distinction between Hilbert space $\mathcal{H}$ and the true space of quantum states, $\mathbb{P}(\mathcal{H})$. *A priori*, one expects that a quantum symmetry need only be formulated as a map

$$\mathfrak{s} : \mathbb{P}(\mathcal{H}) \ \longrightarrow \ \mathbb{P}(\mathcal{H}) \ . \tag{5.16}$$

Rather than requiring that overlaps be preserved, it should be sufficient to require that *transition probabilities* are preserved, as these are the physically meaningful quantities. Let us denote a quantum state corresponding to the ray in $\mathcal{H}$ that passes through a vector ψ by $[\psi]$, so $[\psi] = [\lambda\psi]$ for $\lambda \in \mathbb{C}^\times$. For quantum states $[\psi], [\phi] \in \mathbb{P}(\mathcal{H})$, we then require equality of the transition probabilities:

$$\frac{|\,\langle\phi|\psi\rangle\,|^2}{\|\phi\|^2\|\psi\|^2} = \frac{|\,\langle\mathfrak{s}(\phi)|\mathfrak{s}(\psi)\rangle\,|^2}{\|\mathfrak{s}(\phi)\|^2\|\mathfrak{s}(\psi)\|^2} \ , \tag{5.17}$$

where in this expression ψ and ϕ could really be any representatives of the quantum states $[\psi]$ and $[\phi]$, respectively. (The transition probabilities are, as usual, independent of the choice of such representative.) Naively, this seems that it could be a weaker condition than the requirement that we have a unitary map on $\mathcal{H}$. This is indeed the case, but perhaps to a lesser extent than one might first think. The situation is explained by the following

Theorem 5.2.1 (Wigner)**.** *For any quantum symmetry $\mathfrak{s}$ defined as above on projective Hilbert space, there exists an operator $V(\mathfrak{s}) : \mathcal{H} \to \mathcal{H}$ that is compatible with $\mathfrak{s}$ that is either unitary or anti-unitary that induces $\mathfrak{s}$ when treated as a map of rays. When $\dim(\mathcal{H}) \geqslant 2$, the operator $V(\mathfrak{s})$ is unique up to an overall phase.*

(In the case that $\dim(\mathcal{H}) = 1$, $V(\mathfrak{s})$ can be chosen to be *either* unitary or anti-unitary for the same $\mathfrak{s}$; in higher dimensional Hilbert spaces it will be one or the other, with no choice involved other than the aforementioned phase.) We will set aside the topic of anti-unitary operators for the moment and focus on symmetries that are realised as unitary operators on $\mathcal{H}$.

Definition 5.2.2. *The* projective unitary group *of a Hilbert space $\mathcal{H}$ is the quotient*

$$\mathbb{P}\mathsf{U}(\mathcal{H}) = \mathsf{U}(\mathcal{H})/\{e^{i\theta}\mathbb{1}_{\mathcal{H}},\ \theta \in \mathbb{R}\}$$

of the group of unitary transformations on $\mathcal{H}$ by the normal subgroup consisting of multiplications by a constant phase.

What Wigner's theorem is telling us, given this definition, is that (neglecting the anti-unitary caveat) a quantum symmetry can be unambiguously lifted to an element of the projective unitary group for the corresponding Hilbert space.

Definition 5.2.3. *A* projective unitary representation *of a group $\mathcal{G}$ on a Hilbert space $\mathcal{H}$ is a group homomorphism $U : \mathcal{G} \to \mathbb{P}\mathsf{U}(\mathcal{H})$.*

What we should then be interested in are these projective unitary representations of a symmetry group $\mathcal{G}$. We can then lift these symmetries to actual unitary operators, but we have to choose phases. If we do this arbitrarily (choosing arbitrary phases for each $g \in \mathcal{G}$), then at the level of unitary operators the group law may not be defined, indeed we only expect

$$U(g_1)U(g_2) = e^{i\xi(g_1,g_2)}U(g_1g_2)\ , \qquad \xi(g_1,g_2) \in [0,2\pi)\ . \tag{5.18}$$

Associativity of the multiplication of operators on $\mathcal{G}$ gives a condition on these phases,[26]

$$\xi(g_1,g_2g_3) + \xi(g_2,g_3) = \xi(g_1,g_2) + \xi(g_1g_2,g_3) \mod 2\pi\ , \tag{5.19}$$

It follows immediately that we have the following

Proposition 5.2.4. *A* projective unitary representation *of a group $\mathcal{G}$ on a Hilbert space $\mathcal{H}$ is equivalently a map $U : \mathcal{G} \to \mathsf{U}(\mathcal{H})$ obeying (5.18) and (5.19).*

Indeed, this is sometimes used as the definition; physicists will say that "in quantum mechanics, the group law for symmetries only needs to be obeyed up to phase ambiguities". The phase ambiguities

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[26] Though it isn't important for us, this condition means that the map $\xi : \mathcal{G} \times \mathcal{G} \to U(1)$ is what's known as a *group 2-cocycle valued in $U(1)$*.

in the definitions of the operators $U(g_i)$ themselves means we can modify the phases in (5.18) by taking a map $\varphi : \mathcal{G} \to \mathbb{S}^1$ to produce an equivalent projective unitary representation but now with

$$\xi(g_1, g_2) \to \xi(g_1, g_2) + \varphi(g_1) + \varphi(g_2) \mod 2\pi \ . \tag{5.20}$$

Using this freedom to redefine phases, it turns out that in a large class of examples of continuous groups (when either $\mathcal{H}$ is finite-dimensional or, if infinite-dimensional, if $\mathcal{G}$ is what is called a *semi-simple* group), one can set the phases $\xi(g_1, g_2)$ to be zero for transformations that are suitably close to the identity, thus realising something that looks like a unitary representation for symmetries that are close to the identity. Globally there can be an obstruction to setting these phases to zero for all group multiplications; we will see an explicit example of this in the next chapter in the context of rotations.

5.2.3 One parameter unitary groups

In the discussion of translations some of the statements about the infinitesimal limit may have felt a bit sketchy. There is actually a powerful theorem that puts these statements on firm footing. We start with a definition:

Definition 5.2.5. *A* strongly continuous one-parameter unitary group *is a family $U(t)$ for $t \in \mathbb{R}$ of unitary operators on a Hilbert space $\mathcal{H}$ such that*

- $U(0) = \mathbb{1}_{\mathcal{H}}$,
- $\forall s, t \in \mathbb{R}$, $\quad U(t+s) = U(t)U(s)$,
- $\forall t \in \mathbb{R}$, $\quad \lim_{s \to t} U(s)\psi = U(t)\psi$.

The first two points defines a one-parameter unitary group, which you will recognise as being the same as a unitary representation of the additive group $(\mathbb{R}, +)$ as we had in the case of translations. The third point is the notion of *strong continuity.* We will not be very attentive to this continuity condition in this course; it will always hold in examples we consider.

Definition 5.2.6. *For $U(\cdot)$ a strongly continuous one-parameter unitary group, the* infinitesimal generator *of $U(\cdot)$ is the operator K defined by*[27]

$$K\psi = \lim_{t \to 0} \frac{1}{i} \frac{U(t)\psi - \psi}{t} \ . \tag{5.21}$$

It turns out that defined this way, K will be defined for a dense subset of $\mathcal{H}$ (or all of $\mathcal{H}$ in the finite-dimensional case). We then have the following:

Theorem 5.2.7 (Stone's Theorem on One-Parameter Unitary Groups)**.** *Let $U(\cdot)$ be a* strongly continuous *one-parameter unitary group, the infinitesimal generator K of the family is a self-adjoint operator, and for all t we have*

$$U(t) = \exp{(itK)} \ . \tag{5.22}$$

Conversely, every self-adjoint operator K generates a strongly continuous one-parameter unitary group this way.

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[27] This definition differs by a conventional minus sign and factor of $\hbar$ relative to what we used in the case of momentum and translations. In the quantum mechanical setting we will normally include those additional factors.

The exponential of K can be defined in terms of its action on a basis of (generalised) K-eigenstates. We won't study a proof of this theorem; instead it is meant to provide a justification for some of the more casual manipulations that arise when studying symmetries in what follows. It should be noted that even in the finite dimensional case this is a non-trivial theorem; it establishes a kind of differentiability for families of operators/matrices based only upon continuity.

We can observe now that the quantity $U(t_1 - t_0)$ that we considered in Chapter 1 and in the discussion of the propagator is precisely a one-parameter unitary group whose infinitesimal generator is the Hamiltonian. This is in the case when the Hamiltonian is time-independent. In the time-dependent case, one actually gets a unitary *groupoid*! But we won't discuss it here.

5.2.4 Anti-unitary operators

Now we return to the issue of anti-unitary operators, which appeared in the statement of Wigner's theorem.

Definition 5.2.8. *An* anti-unitary *operator on a Hilbert space $\mathcal{H}$ is a sujective linear map $A : \mathcal{H} \to \mathcal{H}$ obeying*

$$\langle A\phi | A\psi \rangle = \overline{\langle \phi | \psi \rangle} = \langle \psi | \phi \rangle \ . \tag{5.23}$$

We can see that an anti-unitary operator must be $\mathbb{C}$ anti-linear. The standard example of an anti-unitary operator on a complex Hilbert space is the complex conjugation operation, which takes states of the form

$$\psi = \sum_i c_i \psi_i \quad \longrightarrow \quad A\psi = \sum_i \overline{c_i} \psi_i \ , \tag{5.24}$$

for ψ_i and orthonormal basis. In the case of $L^2(\mathbb{R})$, you could think of the operation that takes the complex conjugate of a wave function.

An important observation is that if A is anti-unitary, then A^2 is unitary,

$$\left\langle A^2\phi \middle| A^2\psi \right\rangle = \langle A\psi | A\phi \rangle = \langle \phi | \psi \rangle \ . \tag{5.25}$$

This means that any symmetry that can be realised as the square of another symmetry will be realised unitarily on $\mathcal{H}$. In the case of continuous groups of symmetries, like translations and rotations, this lets us get away with ignoring anti-unitary symmetries all together. On a homework exercise, you will investigate the relationship between anti-unitary symmetries and time-reversal.

5.2.5 The form of quantum symmetries

We are now in position to formulate a more precise characterisation of the form that symmetries take in quantum mechanical systems.

- Symmetries are implemented via unitary or anti-unitary operators on $\mathcal{H}$.
- Symmetries naturally form a group and the operators implementing them form a projective representation of that group on $\mathcal{H}$.
- Continuous symmetries are generated, in the sense of Stone's theorem, by self-adjoint operators via exponentiation.
- For unitarily realised symmetries to be compatible with time evolution (dynamical symmetries), we require any of the following equivalent conditions

- $U(t)U(g) = U(g)U(t)$,
- $[H, U(g)] = 0$
- $[U(t), G] = 0$
- $[H, G] = 0$

Here $U(t) = \exp(-iHt/\hbar)$ is the time evolution operator while $U(g)$ is the unitary corresponding to an element $g \in \mathcal{G}$ of the symmetry group, and if $U(g)$ is part of a one-parameter group then it has infinitesimal generator G.

Chapter 6

Rotations, angular momentum, and their representations

In this chapter we will analyse an important instance of a symmetry realised in quantum systems: that of three-dimensional rotations. You know well from your geometry course (and perhaps elsewhere) that the proper rotation group in three dimensions is $\mathrm{SO}(3)$, which can be identified with the group of three-by-three orthogonal matrices with unit determinant. From the general formalism of the previous section, we expect that for a quantum system describing objects in three-dimensions, there should be a (projective) unitary representation of $\mathrm{SO}(3)$ on our Hilbert space. We will how this cashes out in practice by the end of the chapter.

6.1 Rotation group $\mathrm{SO}(3)$ and its infinitesimal generators

The three-dimensional orthogonal group $\mathrm{O}(3)$ is realised as a group of matrices acting on Cartesian coordinates as $x^i = (x^1, x^2, x^3)$ according to

$$x_i \longrightarrow \sum_{j=1}^{3} R_{ij} x_j \ , \qquad RR^{\mathsf{T}} = \mathbb{1}_{3\times 3} \ , \tag{6.1}$$

where $\mathbb{1}_{3\times 3}$ is the three-by-three identity matrix. The special orthogonal group $\mathrm{SO}(3)$ is the subgroup of $\mathrm{O}(3)$ for which $\det(R) = 1$; these correspond to rotations.

As with translations, rotations can be taken arbitrarily close to the identity. To capture this, let us consider a one-parameter family of rotation matrices $R(t)$ with $R(0) = \mathbb{1}_{3\times 3}$. (You may wish to think of this as the family or rotations about a fixed axis with t the angle of rotation.) If the matrix elements of R are differentiable functions of t, we can define the matrix elements of an infinitesimal rotation matrix ω according to

$$R_{ij}(\epsilon) = \delta_{ij} + \epsilon\omega_{ij} + O(\epsilon^2) \ . \tag{6.2}$$

Expanding the condition $R(\epsilon)R^{\mathsf{T}}(\epsilon) = \mathbb{1}_{3\times 3}$ to first order in ϵ gives

$$\omega_{ij} + \omega_{ji} = 0 \tag{6.3}$$

or in matrix notation $\omega + \omega^{\mathsf{T}} = 0$, *i.e.*, ω is a *skew symmetric* matrix. As you saw in your geometry course in prelims, it is natural to organise the components ω_{ij} of this matrix into a vector $\boldsymbol{\omega} = (\omega_1, \omega_2, \omega_3) = (\omega_{32}, \omega_{13}, \omega_{21})$ that encodes the axis about which the instantaneous rotation is taking place and its magnitude. The vector and matrix index labelling for these parameters are related according to

$$\omega_i = -\frac{1}{2}\sum_{j,k} \varepsilon_{ijk}\omega_{jk} \ , \qquad \omega_{ij} = -\sum_k \varepsilon_{ijk}\omega_k \ . \tag{6.4}$$

The first-order action of $R(\epsilon)$ on the coordinate x_i then is given by

$$\delta x_i = \sum_j \omega_{ij} x_j = \sum_j \varepsilon_{ijk}\omega_j x_k = (\boldsymbol{\omega} \wedge \mathbf{x})_i \ . \tag{6.5}$$

The group SO(3) is non-Abelian, so in general pairs of rotations do not commute, *i.e.*, $R_1R_2 \neq R_2R_1$. This lack of commutativity is encoded in the *group-theoretic commutator* $R_1R_2R_1^{-1}R_2^{-1}$, which is an element of SO(3) that will be the identity if and only if R_1 and R_2 commute. Let us consider this commutator at the level of infinitesimal rotations. If we take t and t' small (say both of order ϵ) in $R(t)$, $R'(t')$, then expanding the commutator to second order we have[28]

$$\begin{aligned} R(t)R'(t')R(t)^{-1}R'(t')^{-1} &= (\mathbb{1} + t\omega + \ldots)(\mathbb{1} + t'\omega' + \ldots)(\mathbb{1} - t\omega + \ldots)(\mathbb{1} - t'\omega' + \ldots) \ , \\ &= \mathbb{1} + tt'(\omega\omega' - \omega'\omega) + \ldots \ , \end{aligned} \tag{6.6}$$

so here the noncommutativity manifests in terms of the *matrix commutator* $[\omega, \omega'] = \omega\omega' - \omega'\omega$. Notice that

$$[\omega, \omega']_{ik} = \sum_j \omega_{ij}\omega'_{jk} - \omega'_{ij}\omega_{jk} = -\sum_l \varepsilon_{ikl}(\boldsymbol{\omega} \wedge \boldsymbol{\omega}')_l \ , \tag{6.7}$$

where to prove this it is useful to use the identity

$$\sum_k \varepsilon_{ijk}\varepsilon_{klm} = \delta_{il}\delta_{jm} - \delta_{im}\delta_{jl} \ . \tag{6.8}$$

Alternatively, if we tacitly use (6.4) to identify vectors with skew-symmetric matrices,

$$[\omega, \omega'] = (\omega \wedge \omega') \ . \tag{6.9}$$

The vector space of three-by-three skew-symmetric matrices endowed with the bilinear operation of the matrix commutator (observe that this preserves skew-symmetry) is known as the *Lie algebra* $\mathfrak{so}(3)$. In the theory of Lie groups, one finds that this matrix commutator encodes the full structure of the group SO(3) up to a single ambiguity, to which we will return later in our discussion of spin.

6.2 Rotations and wave functions

As our first example, we can define a natural action of the rotation group on wave functions in three dimensions, *i.e.*, on the Hilbert space $L^2(\mathbb{R}^3)$, according to

$$\psi(\mathbf{x}) \longmapsto (U(R)\psi)(\mathbf{x}) = \psi(R^{\intercal}\mathbf{x}) \ . \tag{6.10}$$

The appearance of the transpose (*i.e.*, inverse) in the argument is analogous to the minus sign that we included in our translation operator, and analogously to that case we have for generalised position eigenstates,

$$U(R)\,|\mathbf{x}\rangle = |R\mathbf{x}\rangle \ . \tag{6.11}$$

This corresponds to rotating the *system* in a fixed reference frame, which is sometimes called an *active transformation*, and it is the most natural way to think about symmetries in quantum mechanics when they are acting on the Hilbert space.

This action is manifestly complex linear. It is also unitary, since we have

$$\langle U(R)\psi | U(R)\psi\rangle = \int_{\mathbb{R}^3} |\psi(R^{\intercal}\mathbf{x})|^2\, \mathrm{d}^3\mathbf{x} = \int_{\mathbb{R}^3} |\psi|^2\, \mathrm{d}^3\mathbf{x} = \langle\psi|\psi\rangle \ , \tag{6.12}$$

where the change of variables $\mathbf{x} \to R\,\mathbf{x}$ introduces no Jacobian because R is an orthogonal matrix.

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[28] You can feel free to take this equation for granted, but deriving it while keeping second-order terms might be instructive.

Under composition, we see the importance of the transpose:[29]

$$\left(U(R_1)U(R_2)\psi\right)(\mathbf{x}) = \left(U(R_2)\psi\right)(R_1^{\intercal}\mathbf{x}) = \psi(R_2^{\intercal}R_1^{\intercal}\mathbf{x}) = \psi\left((R_1R_2)^{\intercal}\mathbf{x}\right) = \left(U(R_1R_2)\psi\right)(\mathbf{x})\ . \tag{6.13}$$

so our operators satisfy the group law,

$$U(R_1R_2) = U(R_1)U(R_2)\ , \tag{6.14}$$

and we have a unitary representation of SO(3).

Let us consider the infinitesimal action of rotations on wave functions. Using the expansion for rotation matrices in Eqn. (6.2), we have

$$\begin{aligned} \psi(R^{\intercal}(t)\mathbf{x}) &= \psi\left(\mathbf{x} - t\boldsymbol{\omega}\wedge\mathbf{x} + O(t^2)\right)\ , \\ &\approx \psi(\mathbf{x}) - t(\boldsymbol{\omega}\wedge\mathbf{x})\cdot\nabla\psi(\mathbf{x})\ , \\ &= \psi(\mathbf{x}) - t\,\boldsymbol{\omega}\cdot(\mathbf{x}\wedge\nabla\psi)\ , \\ &= \left(\mathbb{1}_{L^2(\mathbb{R})} - \frac{it}{\hbar}\boldsymbol{\omega}\cdot\mathbf{L}\right)\psi(\mathbf{x})\ . \end{aligned} \tag{6.15}$$

where $\mathbf{L}$ is the *orbital angular momentum* operator that you met in Part A, which we can rewrite in terms of position and momentum operators,

$$\mathbf{L} := \mathbf{X}\wedge\mathbf{P}\ . \tag{6.16}$$

You have seen in Part A, and one can compute explicitly, that the components L_i of the angular momentum operator obey the commutation relations

$$[L_i, L_j] = i\hbar\sum_k \varepsilon_{ijk}L_k\ . \tag{6.17}$$

For general vectors $\boldsymbol{\omega}$ and $\boldsymbol{\omega}'$, one then finds

$$[\boldsymbol{\omega}\cdot\mathbf{L}, \boldsymbol{\omega}'\cdot\mathbf{L}] = i\hbar(\boldsymbol{\omega}\wedge\boldsymbol{\omega}')\cdot\mathbf{L}\ , \tag{6.18}$$

or alternatively, in terms of the infinitesimal generators with extra constants included,

$$\left[-\frac{i}{\hbar}\boldsymbol{\omega}\cdot\mathbf{L}, -\frac{i}{\hbar}\boldsymbol{\omega}'\cdot\mathbf{L}\right] = -\frac{i}{\hbar}(\boldsymbol{\omega}\wedge\boldsymbol{\omega}')\cdot\mathbf{L}\ , \tag{6.19}$$

We observe that these exactly match the commutation relation (6.9) with the replacement

$$\omega \quad\longleftrightarrow\quad -\frac{i}{\hbar}\boldsymbol{\omega}\cdot\mathbf{L}\ , \tag{6.20}$$

where on the left hand side, ω represents a skew-symmetric matrix, and on the right hand side we have an operator on $L^2(\mathbb{R})$. We say that these operators furnish a *representation of the Lie algebra* $\mathfrak{so}(3)$ *on the Hilbert space* $L^2(\mathbb{R})$.

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[29] You might try rewrite the manipulations in Eqn. (6.13) using bra-ket notations for wave functions to get a feeling for the way the compositions here are behaving and the relation to the action on generalised position eigenstates.

6.3 General unitary representations

Now let us consider the general case of a unitary representation of the rotation group on a Hilbert space $\mathcal{H}$. We denote by $\mathbf{J}$ the infinitesimal generator of rotations, in the sense that for a one-parameter families of rotations $R(t)$ we have

$$U\left(R(\epsilon)\right) = \mathbb{1}_{\mathcal{H}} - \frac{i\epsilon\,\boldsymbol{\omega}\cdot\mathbf{J}}{\hbar} + O(\epsilon^2)\ . \tag{6.21}$$

We can compare the group-theoretic commutator of two rotations with the composition taken both before and after applying the map to $\mathsf{U}(\mathcal{H})$; we have the equation

$$U\left(R(t)\right)U\left(R'(t')\right)U\left(R(t)\right)^* U\left(R'(t')\right)^* = U\left(R(t)R'(t')R(t)^{-1}R'(t')^{-1}\right)\ , \tag{6.22}$$

where on the left we have the commutator of elements of $\mathsf{U}(\mathcal{H})$, and on the right we have the image in $\mathsf{U}(\mathcal{H})$ of the commutator of elements of $\mathrm{SO}(3)$. Letting each rotation be infinitesimal of the same order, we get, by comparing terms at second order,

$$[\boldsymbol{\omega}\cdot\mathbf{J}, \boldsymbol{\omega}'\cdot\mathbf{J}] = i\hbar(\boldsymbol{\omega}_{(1)}\wedge\boldsymbol{\omega}_{(2)})\cdot\mathbf{J} \tag{6.23}$$

which is exactly analogous to (6.19) with $\mathbf{L}$ replaced by $\mathbf{J}$. In components, this is

$$[J_i, J_j] = i\hbar\sum_k \varepsilon_{ijk}J_k\ . \tag{6.24}$$

This is an important result; whenever we have a representation of the rotation group on a Hilbert space, we get a trio of self-adjoint angular momentum operators, $\{J_i\}$, that obey the commutation relations (6.24). These generate the action of more general rotations via exponentiation in the sense of Stone's theorem.

6.4 Angular momentum multiplets

At an infinitesimal level, we have reduced the study of rotations in quantum systems to the study of *representations of the angular momentum operators*:

Definition 6.4.1. *A* representation of the angular momentum operators *is a Hilbert spaces $\mathcal{H}$ with an action of self-adjoint operators $J_i : \mathcal{H}\to\mathcal{H}$, $i = 1, 2, 3$, satisfying the commutation relations* (6.24)*.*

Remark 6.4.2. This is the equivalent to a representation of the Lie algebra $\mathfrak{so}(3)$ on $\mathcal{H}$. The difference is in the factor of $\hbar$ on the right hand side of (6.24), which can be removed by an appropriate rescaling of the J_i. Also in some cases it is conventional for a representation of $\mathfrak{so}(3)$ to use anti-self adjoint operators, in which case a factor of i is included as well.

Definition 6.4.3. *An* irreducible representation *of the angular momentum operators is a representation of the angular momentum operators for which there is no a proper subspace $\mathcal{H}'\subset\mathcal{H}$ with $J_i : \mathcal{H}'\to\mathcal{H}'$,* i.e., *$\mathcal{H}$ contains no proper sub-representation of the angular momentum operators.*

In *Part A Quantum Theory*, in the context of discussing orbital angular momentum for three-dimensional wave functions, you identified the structure of general irreducible representations of the angular momentum operators. Here we will recall the story.

We define the *total angular momentum operator* $\mathbf{J}^2 = \mathbf{J} \cdot \mathbf{J}$. A short calculation shows that

$$[\mathbf{J}^2, J_i] = 0 \ , \tag{6.25}$$

so the action of the J_i operators preserves eigenspaces of $\mathbf{J}^2$. Since $\mathbf{J}^2$ is self-adjoint, we can choose a basis of its eigenstates, and so if $\mathcal{H}$ is irreducible then $\mathbf{J}^2$ must just act by a multiple of the identity on $\mathcal{H}$. We can give a completely explicit description of all finite-dimensional, irreducible representations if we furthermore diagonalis e J_3.

Theorem 6.4.4. *The irreducible representations of the angular momentum operators are labeled by a half-integer* $j = 0, \frac{1}{2}, 1, \ldots \in \frac{1}{2}\mathbb{N}$ *known as the* spin *of the representation. Denote the Hilbert space admitting such a representation by* $\mathcal{H}_{\text{spin}\, j}$. *The dimension of* $\mathcal{H}_{\text{spin}\, j}$ *is* $2j+1$ *and* $\mathbf{J}^2$ *acts with eigenvalue* $\hbar^2 j(j+1)$.

There is an orthonormal basis of $\mathcal{H}_{\text{spin}\, j}$ *consisting of eigenvectors* $|j,m\rangle$ *of* J_3 *with* $J_3 |j,m\rangle = \hbar m |j,m\rangle$ *for* $m = -j, -j+1, \ldots j-1, j$.

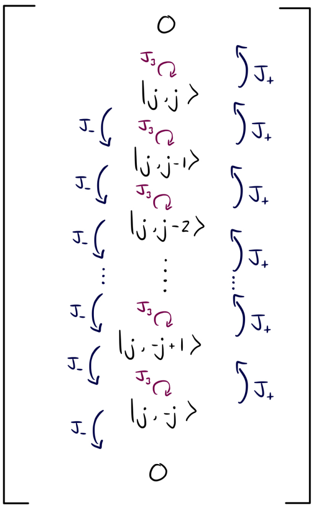

Figure 1. Depiction of irreducible representation of the angular momentum operators.

Proof. We introduce the ladder operators

$$J_\pm = J_1 \pm i J_2 \ , \tag{6.26}$$

which commute with $\mathbf{J}^2$. We also can check

$$[J_3, J_\pm] = \pm \hbar J_\pm \ . \tag{6.27}$$

This gives them the interpretation as raising and lowering operators for eigenvectors $|j,m\rangle$ of J_3 (with eigenvalue $\hbar m$, say):

$$J_3 \left(J_\pm |j,m\rangle \right) = \pm \hbar J_\pm |j,m\rangle + J_\pm J_3 |j,m\rangle = \hbar(m \pm 1) \left(J_\pm |j,m\rangle \right) \ . \tag{6.28}$$

Thus $J_\pm |j,m\rangle$ is a multiple of an eigenvector for J_3 with eigenvalue $\hbar(m \pm 1)$. The following then shows that the values for $|m|$ must be bounded.

Lemma 6.4.5. *Let* $\mathbf{J}^2 |\psi\rangle = \lambda\hbar^2 |\psi\rangle$ *and* $J_3 |\psi\rangle = \hbar m |\psi\rangle$*. Then for all* $\varphi \in \mathcal{H}$*,*

$$\langle J_\pm\varphi|J_\pm\psi\rangle = \hbar^2 (\lambda - m(m \pm 1)) \langle\varphi|\psi\rangle \qquad \textit{and} \qquad \|J_\pm\psi\|^2 = \hbar^2 (\lambda - m(m \pm 1)) \|\psi\|^2 \ . \tag{6.29}$$

Proof. Observe from the angular momentum commutation relations that

$$J_+J_- = \mathbf{J}^2 - J_3^2 + \hbar J_3 \, , \qquad J_-J_+ = \mathbf{J}^2 - J_3^2 - \hbar J_3 \ , \tag{6.30}$$

so the identities follow from

$$\langle J_-\varphi|J_-\psi\rangle = \langle\varphi|J_+J_-\psi\rangle = \left\langle\varphi\middle|(\mathbf{J}^2 - J_3^2 + \hbar J_3)\psi\right\rangle \ , \tag{6.31}$$

and using the eigenvalue relations (and similarly for the J_+ plus version of (6.31)). ■

Thus, given that λ is fixed on an irreducible representation, $|m|$ cannot be too large as otherwise the norm squared of these states would eventually become negative. The only way that $|m|$ can avoid becoming arbitrarily large in the negative direction is if for some smallest value m_-, $J_- \left|\psi_{m_-}\right\rangle = 0$ where $J_3 \left|\psi_{m_-}\right\rangle = \hbar m_- \left|\psi_{m_-}\right\rangle$, which requires $\lambda = m_-(m_- - 1)$. The only way that $|m|$ can avoid becoming arbitrarily large in the positive direction is if analogously for some largest value m_+, $J_+ \left|\psi_{m_+}\right\rangle = 0$, so $\lambda = m_+(m_+ + 1)$. To realise both situations at once, we need

$$\lambda = j(j+1) \ , \qquad m_- = -j \ , \qquad m_+ = j \ . \tag{6.32}$$

By construction $m_+ - m_- = 2j$ must be an integer (since starting with the $\left|\psi_{m_-}\right\rangle$ and acting repeatedly with J_+ we must arrive eventually as $\left|\psi_{m_+}\right\rangle$. Hence the constraints on the eigenvalues stated in the theorem.

To finish we require that the J_3 eigenvalues be nondegenerate. This follows from irreducibility. Suppose that there are two linearly independent eigenvectors $|j, m; 1\rangle$ and $|j, m; 2\rangle$ that, without loss of generality, can be taken to be mutually orthogonal. Then it follows from the expressions above that $J_\pm^n |j, m; 1\rangle$ and $J_\pm^n |j, m; 2\rangle$ are orthogonal. Thus there will be two nontrivial J_i-invariant subspaces spanned by $J_\pm^n |j, m; 1\rangle$ and by $J_\pm^n |j, m; 2\rangle$, contradicting irreducibility. ■

We finish this discussion with a few additional comments:

- If we are working in a definite irreducible representation of spin j, we might sometimes simply denote the state kets $|m\rangle$ to encode the J_3 eigenvalue.
- The basis $|j, m\rangle$ of $\mathcal{H}_{spin\, j}$ is unique up to an *overall phase* for the entire representation if we impose the normalisation conditions

  $$|j, m \pm 1\rangle = \frac{J_\pm |j, m\rangle}{\hbar\sqrt{j(j+1) - m(m \pm 1)}} \ . \tag{6.33}$$

  This definition ensures in particular that the states $|j, m\rangle$ all have the same norm, so if we choose a particular state, say $|j, j\rangle$, to be unit normalised and construct the rest of the representation by the action of J_-, then all of these states will be unit normalised.
- Important examples of representations with integer spin were given in *Part A Quantum Theory* in terms of spherical harmonics. These are angular momentum representations realised

using the orbital angular momentum operators $\mathbf{L}$, which can be written in spherical polar coordinates as

$$L_\pm = i\hbar e^{\pm i\phi}\left(\cot\theta\frac{\partial}{\partial\phi} \pm i\frac{\partial}{\partial\theta}\right) \ , \qquad L_3 = -i\hbar\frac{\partial}{\partial\phi} \ . \tag{6.34}$$

The total spin j is usually denoted by ℓ in this context. The wave functions $\Psi_\ell^m(\phi,\theta)$ corresponding to the basis states $|\ell,m\rangle$ take the form

$$Y_\ell^m(\phi,\theta) = P_\ell^m(\cos\theta)e^{im\phi} \ , \tag{6.35}$$

where $P_\ell^m(x)$ are associated Legendre functions. The requirement that ℓ and m be integral follows from the need for $e^{im\phi}$ to be single valued.

6.5 Spin 1/2

We saw that while half-integral spin is acceptable in the context of formal representations of the angular momentum operators, it doesn't arise in the context of orbital angular for three-dimensional wave functions. Let us investigate the simplest case of spin $j = 1/2$.

The discussion above gives an explicit realisation of this representation,

$$\mathcal{H}_{\text{spin }\frac{1}{2}} \cong \mathbb{C}^2 = \text{Span}\left\{\, \left|\tfrac{1}{2},\tfrac{1}{2}\right\rangle, \left|\tfrac{1}{2},-\tfrac{1}{2}\right\rangle \,\right\} \ . \tag{6.36}$$

Of course this is just our old friend the qubit. The above action of $J_\pm$ and hence J_1 and J_2 is determined by (6.33) for which in this case the denominator is just $\hbar$, and the eigenvalue condition determines J_3. Thus, in this basis we have

$$\mathbf{J} = \frac{\hbar}{2}\boldsymbol{\sigma} \tag{6.37}$$

where $\boldsymbol{\sigma} = (\sigma_1,\sigma_2,\sigma_3)$ are the same Pauli spin matrices we met in our qubit discussion. Now let us consider a general rotation by some angle θ about an axis designated by the unit vector $\mathbf{n}$; we denote this by $R_\mathbf{n}(\theta)$. By Stone's theorem, this should be realised on our two-dimensional Hilbert space by the unitary matrix

$$U(R_\mathbf{n}(\theta)) =: U_\mathbf{n}(\theta) = \exp\left(-\frac{i\theta}{\hbar}\mathbf{n}\cdot\mathbf{J}\right) = \exp\left(-\frac{i\theta}{2}\mathbf{n}\cdot\boldsymbol{\sigma}\right) \ . \tag{6.38}$$

An explicit computation of this matrix exponential yields an expression for the matrix that should represent the rotation,

$$U_\mathbf{n}(\theta) = \cos\left(\frac{\theta}{2}\right)\mathbb{1}_{2\times 2} - i\sin\left(\frac{\theta}{2}\right)\mathbf{n}\cdot\boldsymbol{\sigma} \ . \tag{6.39}$$

By letting $\mathbf{n}$ range over the unit sphere in three dimensions and letting θ run from 0 to 2π, this gives a parameterisation of the most general element of SU(2). However, compared to rotations this is double counting! Rotating by θ around the axis defined by $\mathbf{n}$ is the same as rotating by $2\pi - \theta$ around the axis defined by $-\mathbf{n}$. Equivalently, for fixed $\mathbf{n}$, we see that setting $\theta = 2\pi$ doesn't give us back the identity, but rather minus the identity. It is only upon taking $\theta = 4\pi$ that our unitary matrix returns to the identity. So there is a two-to-one correspondence between the elements of SU(2) and the inequivalent rotations, *i.e.*, the elements of SO(3).

What we're encountering is precisely a situation where our symmetry group (SO(3)) is implemented via a projective unitary representation that is not strictly a unitary representation of the group we started with. We can see this in terms of the group law. Consider the rotation $R_\mathbf{n}(\pi)$ that performs a half rotation about the axis $\mathbf{n}$. Then performing this twice we have have

$$U\left(R_{\mathbf{n}}(\pi)\right) U\left(R_{\mathbf{n}}(\pi)\right) = U_{\mathbf{n}}(2\pi) = -\mathbb{1}_{2\times 2}\ . \tag{6.40}$$

whereas if we compose the rotations before taking the map to unitary matrices, we have

$$U\left(R_{\mathbf{n}}(\pi) R_{\mathbf{n}}(\pi)\right) = U(R_{\mathbf{n}}(2\pi)) = U(R_{\mathbf{n}}(0)) = \mathbb{1}_{2\times 2}\ . \tag{6.41}$$

The sign difference is precisely the type of "extra phase" that is allowed for projective representations!

It turns out that this example is indicative of the general story for half-integer-spin representations. These are projective unitary representations of SO(3) that do not lift to unitary representations of SO(3). Rather, they correspond to unitary representations of SU(2), where the relation between the two groups is by a quotient,

$$\mathbb{P}\mathrm{SU}(2) := \mathrm{SU}(2)/\{\pm\mathbb{1}\} \cong \mathrm{SO}(3)\ . \tag{6.42}$$

In the case of orbital angular momentum, there is *manifestly* a representation of the honest rotation group via the action on wave functions; consequently only integer spin can occur.

Remark 6.5.1. There is a beautiful observation to make here that I cannot help but include for your entertainment (I hope). As was observed above, we have a realisation of SU(2) by a choice of unit vector in $\mathbb{R}^3$ and an angle $\theta \in 2\pi$. This gives us a realisation of SU(2) as a *circle fibration over the two-sphere* (you can imagine a circle corresponding to the choice of angle sitting over each point on the two-sphere corresponding to the choice of unit vector). This is what's known as the *Hopf fibration*, which realises the three sphere $S^3 \cong \mathrm{SU}(2)$ as a circle fibration over S^2. The rotation group $SO(3)$ then gets identified as the quotient space $S^3/\mathbb{Z}_2$, with $\mathbb{Z}_2$ acting as the antipodal map.

Chapter 7

Intrinsic Spin and Addition of Angular Momentum

When we consider a quantum particle or system that has some internal structure, the action of the rotation group can be more complicated than what we have seen before with wave functions. We could describe such a system in terms of its center of mass, which will be labelled by a point in $\mathbb{R}^3$, as well as some internal structure whose quantum mechanical configurations are encoded in a Hilbert space $\mathcal{H}_{\text{internal}}$. The full Hilbert space for such a structured particle will then given by

$$\mathcal{H} = L^2(\mathbb{R}^3) \otimes \mathcal{H}_{\text{internal}} \ . \tag{7.1}$$

We will then have a (projective) unitary representation of SO(3) on this Hilbert space generated by some *total angular momentum operators* $\mathbf{J}$. At the infinitesimal level, we know that $\mathbf{J}$ will act on the center of mass wave function as the orbital angular momentum operator $\mathbf{L}$, while we can introduce operators $\mathbf{S}$ that describe the action on $\mathcal{H}_{\text{internal}}$,

$$\mathbf{J} = \mathbf{L} \otimes \mathbb{1}_{\mathcal{H}_{\text{internal}}} + \mathbb{1}_{L^2(\mathbb{R})} \otimes \mathbf{S} \ , \tag{7.2}$$

where the $\mathbf{J}$ and $\mathbf{L}$ operators commute, and we also have

$$[S_i, S_j] = i\hbar \sum_k \varepsilon_{ijk} S_k \ . \tag{7.3}$$

In the case of elementary particles, we can expect $\mathcal{H}_{\text{internal}}$ to support an irreducible angular momentum representation; otherwise we would think of the different subrepresentations as corresponding to (detectably!) different versions of the elementary particle, and therefore we would call them different elementary particles. If a particle has $\mathcal{H}_{\text{spin}\, j}$ as its internal Hilbert space with the attendant operators $\mathbf{S}$ describing rotations, then we say the particle itself has *intrinsic spin* j, though often we simply shorten this to say the particle has spin j. This intrinsic spin is the quantity that was referred to in the spin statistics theorem of Chapter 4.

7.1 Addition of angular momentum

If we want to understand the full action of rotations on a system with both orbital angular momentum and intrinsic spin, then we will will have to understand the action of the total angular momentum operators in a system where we initially understand the action of the components $\mathbf{L}$ and $\mathbf{S}$. Similarly, if we have a system of n particles each of which has some angular momentum operator $\mathbf{J}_i$ acting on its single-particle Hilbert space, then we will want to understand the total angular momentum[30] $\mathbf{J} = \mathbf{J}_{(1)} + \ldots + \mathbf{J}_{(n)}$ acting on the composite Hilbert space starting with an understanding of the individual angular momentum representations. This procedure is, in the physics literature, usually referred to as the *addition of angular momentum.* We first pose the problem in the context of there being two constituent representations of angular momentum.

Problem 7.1.1. *Consider the Hilbert space* $\mathcal{H} \cong \mathcal{H}_1 \otimes \mathcal{H}_2$ *where* $\mathcal{H}_i$ *supports an irreducible representation of the angular momentum operators* $\mathbf{J}^{(i)}$ *with spin* j_i. *We have* $\dim \mathcal{H} = (2j_1+1)(2j_2+1)$.

---

[30] Here and in what follows we drop the explicit tensor notation for these sums of operators acting on different tensor factors of a composite Hilbert space.

How does this composite system decompose into irreducible representations of the total angular momentum operator $\mathbf{J} = \mathbf{J}^{(1)} + \mathbf{J}^{(2)}$*?*

The answer is given by the following

Proposition 7.1.2. *Under the action of the total angular momentum, the tensor product* $\mathcal{H} \cong \mathcal{H}_1 \otimes \mathcal{H}_2$ *of irreducible representations with spins* j_1 *and* j_2*, respectively, decomposes into irreducible representations according to*

$$\mathcal{H}_1 \otimes \mathcal{H}_2 = \bigoplus_{J=|j_1-j_2|}^{j_1+j_2} \mathcal{H}_{\text{spin } J} \ . \tag{7.4}$$

Thus we can find an orthonormal basis for this tensor product that we denote by $|J, M\rangle$ *with* $J = |j_1 - j_2|, |j_1 - j_2| + 1, \ldots, j_1 + j_2 - 1, j_1 + j + 2$ *and* $M = -J, -J+1, \ldots, J-1, J$ *obeying,*[31]

$$(\mathbf{J}^{(1)})^2 \, |J, M\rangle \ = \ \hbar^2 j_1(j_1+1) \, |J, M\rangle \ , \qquad \mathbf{J}^2 \, |J, M\rangle \ = \ \hbar^2 J(J+1) \, |J, M\rangle \ , \tag{7.5}$$

$$(\mathbf{J}^{(2)})^2 \, |J, M\rangle \ = \ \hbar^2 j_2(j_2+1) \, |J, M\rangle \ , \qquad J_3 \, |J, M\rangle \ = \ \hbar \, M \, |J, M\rangle \ . \tag{7.6}$$

Proof. In what follows we assume, without loss of generality, that $j_1 \geqslant j_2$.

We proceed inductively, first finding the representation of highest total spin $\mathcal{H}_{\text{spin}\,(j_1+j_2)}$ inside $\mathcal{H}$, then proceeding to find the representation of next highest total spin inside the orthogonal complement $\mathcal{H}^{\perp}_{\text{spin}\,(j_1+j_2)} \subset \mathcal{H}$, and so on.

We will write our pure-tensor basis vectors as $|m_1; m_2\rangle$,[32] which as a reminder, obey

$$\begin{aligned} (\mathbf{J}^{(1)})^2 \, |m_1; m_2\rangle &= \hbar^2 j_1(j_1+1) \, |m_1; m_2\rangle \ , \qquad (J^{(1)})_3 \, |m_1; m_2\rangle = \hbar \, m_1 \, |m_1; m_2\rangle \ , \\ (\mathbf{J}^{(2)})^2 \, |m_1; m_2\rangle &= \hbar^2 j_2(j_2+1) \, |m_1; m_2\rangle \ , \qquad (J^{(2)})_3 \, |m_1; m_2\rangle = \hbar \, m_2 \, |m_1; m_2\rangle \ . \end{aligned} \tag{7.7}$$

These are evidently already eigenvectors of $J_3 = (J^{(1)})_3 + (J^{(2)})_3$, with eigenvalues $M = m_1 + m_2$. There is a unique state with maximum $M = j_1 + j_2$, which we must be able to identify with the "top" state in a spin $j_1 + j_2$ representation; we can therefore identify

$$|j_1 + j_2, j_1 + j_2\rangle \ = \ |j_1; j_2\rangle \ . \tag{7.8}$$

The rest of the spin $j_1 + j_2$ representation can be recovered by acting with the total lowering operator $J_- = J_-^{(1)} + J_-^{(2)}$. Normalising these using (6.33), we obtain the states $|j_1 + j_2, M\rangle$ that still have total spin $J = j_1 + j_2$, but now have J_3 eigenvalue M. These constitute a complete spin $J = j_1 + j_2$ representation inside $\mathcal{H}$.

Next we consider the states with $M = j_1 + j_2 - 1$. There are two linearly independent such states, $|j_1 - 1; j_2\rangle$ and $|j_1; j_2 - 1\rangle$. One combination of these occurs in the spin $j_1 + j_2$ representation defined above. Taking a vector in the orthogonal complement, we get a state vector that must be the top state in a spin $j_1 + j_2 - 1$ representation, since acting with a raising operator must give zero, else this would be part of the previous spin $j_1 + j_2$ representation. We therefore denote a normalised element of this orthogonal complement by $|j_1 + j_2 - 1, j_1 + j_2 - 1\rangle$. Again acting with $J_-^{(1)} + J_-^{(2)}$ on this state generates a full irreducible subrepresentation, this time of spin $j_1 + j_2 - 1$.

---

[31] Occasionally, these states are written $|j_1, j_2; J, M\rangle$ to make manifest the constituent spins that are being combined. We will leave these implicit to avoid overly burdensome notation whenever possible.

[32] As with the previous basis states, these will sometimes be labelled $|j_1, m_1; j_2, m_2\rangle$ to indicate the constituent spins. We will avoid this when possible.

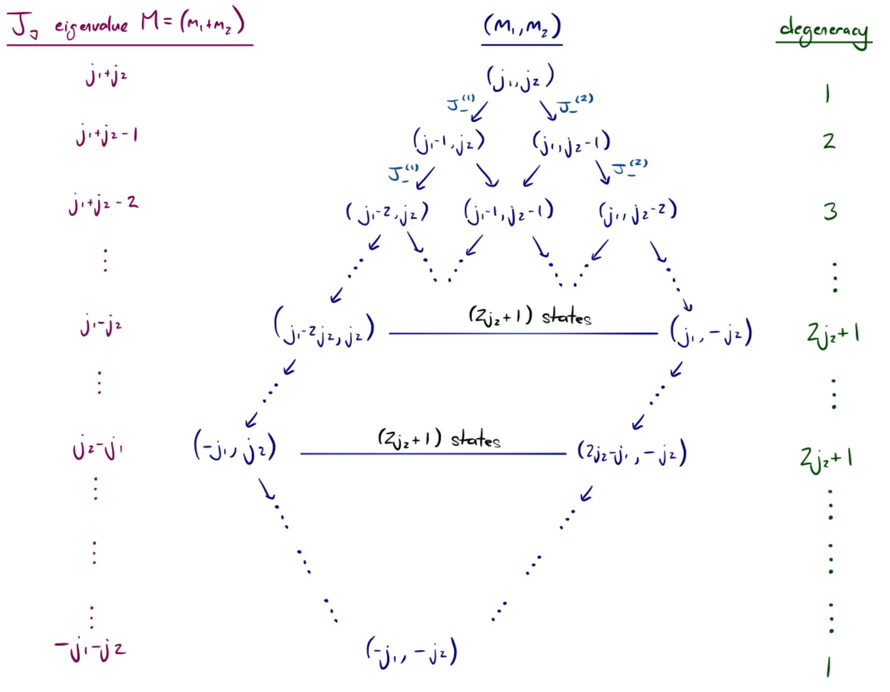

Figure 2. Depiction of states in the tensor product of irreducible representations of angular momentum with spins j_1 and j_2, where we assume $j_1 \geqslant j_2$.

If $j_2 = \frac{1}{2}$, then the degeneracy for M eigenvalues with $j_1 + j_2 - 1 \geqslant M \geqslant -(j_1 + j_2 - 1)$ is just two, corresponding to the $m_2 = \pm\frac{1}{2}$ states, and so must be spanned by the corresponding M-eigenstates of the two multiplets we have just found. In this case we would be done.

If $j_2 > \frac{1}{2}$, then the degeneracy for the $M = j_1 + j_2 - 2$ eigenvalue is three with $(m_1, m_2) = (j_1, j_2 - 2), (j_1 - 1, j_2 - 1)$ or $(j_1 - 2, j_2)$. Thus, as before, there is a nontrivial orthogonal normalised vector $|j_1 + j_2 - 2, j_1 + j_2 - 2\rangle$ orthogonal to those $M = j_1 + j_2 - 2$ eigenvalues of total spin $j_1 + j_2$ and $j_1 + j_2 - 1$, unique up to a phase. This gives rise to a spin $j_1 + j_2 - 2$ representation by lowering.

In general, the degeneracy of the M-eigenstates is $1 + j_1 + j_2 - |M|$ for $|M| \geqslant j_1 - j_2$, but is $2j_2 + 1$ otherwise as it cannot exceed the number of choices $2j_2 + 1$ for m_2 (see Figure 7.1). So we can carry on by induction, generating a new multiplet at each stage, until we eventually produce all the angular momentum multiplets with spins from $J = j_1 - j_2$ to $J = j_1 + j_2$, as required. This gives a total of $2j_2 + 1$ irreducible representations ($2j_2 + 1$ being the maximal degeneracy of the M eigenvalue, realised for $|M| \leqslant j_1 - j_2$). ■

Before moving on, we'll look at the simplest example of addition of angular momentum: the tensor product of two spin 1/2 systems.

Example 7.1.3 (Two qubits)**.** We can be very explicit in examining the two-qubit system,

$$\mathcal{H} = \mathcal{H}_{\text{spin } \frac{1}{2}}^{\otimes 2} \,. \tag{7.9}$$

If we now adopt the basis for the qubit from the last chapter, we have as our basis for the tensor product Hilbert space $\left|\pm\frac{1}{2};\pm\frac{1}{2}\right\rangle$, with the signs chosen independently. To make things easier on the eyes, we will adopt the notation $|\pm\pm\rangle$. If we organise these by J_3 eigenvalue $M = m_1 + m_2$, we have

$$\begin{array}{rccc} M = +1: & & |{+}{+}\rangle & \\ M = 0: & |{+}{-}\rangle & & |{-}{+}\rangle \\ M = -1: & & |{-}{-}\rangle & \end{array} \tag{7.10}$$

Starting with the top state, we produce the following states in the spin-one sub-representation of this system,

$$|1,1\rangle = |{+}{+}\rangle \ , \quad |1,0\rangle = \frac{|{+}{-}\rangle + |{-}{+}\rangle}{\sqrt{2}} \ , \quad |1,-1\rangle = |{-}{-}\rangle \ . \tag{7.11}$$

There is an additional spin-zero state (so a rotationally-invariant state),

$$|0,0\rangle = \frac{|{+}{-}\rangle - |{-}{+}\rangle}{\sqrt{2}} \ . \tag{7.12}$$

It may be worth remarking that the spin-one representation consists of bosonic (symmetric) states, while the spin-zero representation is the one fermionic (anti-symmetric) state in this tensor product. Indeed, the total angular momentum operators can be seen by inspection to commute with the action of permutations on the n-fold tensor product of identical representations of angular momentum, which means that the bosonic and fermionic subspaces will always transform amongst themselves under rotations.

Example 7.1.4 (Everything from spin one half)**.** The previous example suggests a general construction of the spins j representation for any j using spins 1/2 representations as building blocks. Consider the n-fold symmetric tensor product of the qubit Hilbert space $\odot^n\mathcal{H}_{\text{spin }\frac{1}{2}}$. By our results in Chapter 4, this has dimension

$$\dim\left(\odot^n\mathcal{H}_{\text{spin }\frac{1}{2}}\right) = n+1 \ . \tag{7.13}$$

If we consider the state $|{+}+\cdots+\rangle$, this has

$$J_3^{(tot)}\,|{+}+\cdots+\rangle = \tfrac{1}{2}\hbar n\,|{+}+\cdots+\rangle \ , \tag{7.14}$$

so this must be an element of a representation with spin greater than or equal to $n/2$. But based on the dimensionality of the Hilbert space, this can only be a representation of spin $n/2$ exactly, and indeed it is clear that this state is the top state of its angular momentum representation.

Thus, if you like, you can think of any irreducible representation of angular momentum in terms of an appropriate number of identical (bosonic) qubits. This can prove a useful mental model for these representations.

7.2 Clebsch-Gordan coefficients

Equation (7.4) tells us in general terms how the tensor product of irreducible angular momentum representations will transform under the total angular momentum. However, to work with these composite systems and do calculations in practice, one needs to be able to concretely construct and manipulate the elements of the different irreducible representations appearing in that direct sum. This means having expressions for the precise linear combinations of the states $|m_1;m_2\rangle$ that constitute the states $|J,M\rangle$ and *vice versa*. To this end we make the following definition.

Definition 7.2.1. *The* Clebsch-Gordan coefficients $C_{j_1\,j_2}(J,M;m_1,m_2)$ *are defined by*

$$|J,M\rangle = \sum_{\substack{m_1,m_2\\ m_1+m_2=M}} C_{j_1j_2}(J,M;m_1,m_2)\,|m_1;m_2\rangle\ , \tag{7.15}$$

so these are the coefficients of the expansion of our orthonormal basis of states in the (J,M) *basis in terms of those in the separable,* (m_1,m_2) *basis.*

The coefficients defined as such are not uniquely well-defined, because there is some choice over overall phases in the states for each irreducible representation involved. However, this freedom can be fixed by requiring that the Clebsch-Gordan coeffiecients be real along with an additional convention.

Because both bases are orthonormal, we can deduce a number of useful expressions involving the Clebsch-Gordan coefficients. For example, we can realise them explicitly in terms of inner products of the form

$$C_{j_1j_2}(J,M;m_1,m_2) = \langle m_1;m_2|J,M\rangle\ . \tag{7.16}$$

If we make the conventional choice mentioned above to ensure reality of the Clebsch-Gordan coefficients, then we will also have

$$C_{j_1j_2}(J,M;m_1,m_2) = \langle J,M|m_1;m_2\rangle\ . \tag{7.17}$$

The completeness relation for our Hilbert space leads to the following identity,

$$\begin{aligned} 1 &= \langle J,M|J,M\rangle \\ &= \sum_{\substack{m_1,m_2\\ m_1+m_2=M}} \langle J,M|m_1;m_2\rangle\,\langle m_1;m_2|J,M\rangle \\ &= \sum_{\substack{m_1,m_2\\ m_1+m_2=M}} |C_{j_1j_2}(J,M;m_1,m_2)|^2 \end{aligned} \tag{7.18}$$

Let's see how this works in a couple of simple examples.

Example 7.2.2. Let $j_2=\frac{1}{2}$ with $j_1\neq 0$ an arbitrary spin. Then we have as usual for the highest spins state overall $\left|j_1+\frac{1}{2},j_1+\frac{1}{2}\right\rangle = \left|j_1;\frac{1}{2}\right\rangle$. Acting with the total lowering operators we get

$$\begin{aligned} \left|j_1+\tfrac{1}{2},j_1-\tfrac{1}{2}\right\rangle &= \frac{1}{\hbar\sqrt{2j_1+1}}J_-\left|j_1+\tfrac{1}{2},j_1+\tfrac{1}{2}\right\rangle\ , \\ &= \frac{1}{\hbar\sqrt{2j_1+1}}\left(J_-^{(1)}+J_-^{(2)}\right)\left|j_1;\tfrac{1}{2}\right\rangle\ , \\ &= \frac{1}{\sqrt{2j_1+1}}\left(\sqrt{2j_1}\left|j_1-1;\tfrac{1}{2}\right\rangle + \left|j_1;-\tfrac{1}{2}\right\rangle\right)\ . \end{aligned} \tag{7.19}$$

We can identify the most general (normalised) orthogonal complement in the $M=j_1-\frac{1}{2}$ eigenspace as

$$\left|j_1-\tfrac{1}{2},j_1-\tfrac{1}{2}\right\rangle \sim \frac{1}{\sqrt{2j_1+1}}\left(\left|j_1-1;\tfrac{1}{2}\right\rangle - \sqrt{2j_1}\left|j_1;-\tfrac{1}{2}\right\rangle\right)\ . \tag{7.20}$$

At this point we can use some of our freedom in introducing phases to fix the overall phase of this state. Demanding that the Clebsch-Gordan coefficients (so the coefficients of the expansion) be real gives us

$$\left|j_1-\tfrac{1}{2},j_1-\tfrac{1}{2}\right\rangle = \pm\frac{1}{\sqrt{2j_1+1}}\left(\sqrt{2j_1}\left|j_1;-\tfrac{1}{2}\right\rangle - \left|j_1-1;\tfrac{1}{2}\right\rangle\right) \ . \tag{7.21}$$

To fix the final sign ambiguity, one may adopt a standard convention known as the *Condon-Shortley convention*. This amounts to declaring that

$$C_{j_1j_2}(J,J;j_1,J-j_1) > 0 \ . \tag{7.22}$$

In the above, this selects the plus sign, and with that highest state fixed, we can produce the rest of the spin $j_1-\frac{1}{2}$ multiplet by acting with J_-. (Note that this convention depends on the order of the two constituent spins j_1 and j_2.)

One can read off the Clebsch-Gordan coefficients from the resulting expressions for our states, *e.g.*, from (7.19) and (7.21) we have

$$\begin{aligned}
C_{j_1\,\frac{1}{2}}\left(j_1+\tfrac{1}{2},j_1+\tfrac{1}{2};j_1,\tfrac{1}{2}\right) &= 1 \ ,\\
C_{j_1\,\frac{1}{2}}\left(j_1+\tfrac{1}{2},j_1-\tfrac{1}{2};j_1,-\tfrac{1}{2}\right) &= \frac{1}{\sqrt{2j_1+1}} \ ,\\
C_{j_1\,\frac{1}{2}}\left(j_1+\tfrac{1}{2},j_1-\tfrac{1}{2};j_1-1,\tfrac{1}{2}\right) &= \sqrt{\tfrac{2j_1}{2j_1+1}} \ ,\\
C_{j_1\,\frac{1}{2}}\left(j_1-\tfrac{1}{2},j_1-\tfrac{1}{2};j_1,-\tfrac{1}{2}\right) &= \sqrt{\tfrac{2j_1}{2j_1+1}} \ ,\\
C_{j_1\,\frac{1}{2}}\left(j_1-\tfrac{1}{2},j_1-\tfrac{1}{2};j_1-1,\tfrac{1}{2}\right) &= \frac{-1}{\sqrt{2j_1+1}} \ .
\end{aligned} \tag{7.23}$$

You can look up tables of Clebsch-Gordan coefficients in textbooks and online, but you should learn to love them and practice deriving some!

7.3 Angular momenta of hydrogen energy levels

An important instance of this general story arises in the analysis of atoms. Let us start with a single-electron atom (a.k.a., a Hydrogen-like atom). We model this as an electron moving in an external Coulomb potential, and you have studied the corresponding stationary state wave functions in Part A. However, the electron is a fermionic particle with intrinsic spin 1/2, so we should really think of its Hilbert space as being the tensor product

$$\mathcal{H}_{\text{electron}} \cong L^2(\mathbb{R}^3)\otimes\mathcal{H}_{\text{spin}\,1/2} \ . \tag{7.24}$$

A general state in the electron Hilbert space will then consist of *two wavefunctions*, one for each of the possible internal spin states

$$|\psi\rangle = \psi_+(\mathbf{x})\left|+\tfrac{1}{2}\right\rangle + \psi_-(\mathbf{x})\left|-\tfrac{1}{2}\right\rangle \ , \tag{7.25}$$

where $\left|\pm\frac{1}{2}\right\rangle$ are the $m_s=\pm\frac{1}{2}$ intrinsic spin eigenstates for, say, the S_3 operator. Thus $\psi_+(\mathbf{r})$ gives the wave function for the situation that the electron has $m_s=\frac{1}{2}$ spin and $\psi_-(\mathbf{r})$ gives the wave function for the situation that the electron has $m_s=-\frac{1}{2}$ spin. In non-relativistic quantum mechanics, the Schrödinger equation doesnt mix the two m-values, so the component wave functions $\psi_\pm(\mathbf{x})$ must both individually satisfy the same Schrodinger equation.[33]

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[33] In a relativistic setting, the usual Schrödinger equation is replaced by the *Dirac equation*, which does mix up the different spin states. This is beyond the scope of our course.

If we then take the $\psi_\pm(\mathbf{x})$ to be one of the stationary state wave functions that you have met in your previous course, we end up with states that we write as

$$|n,\ell,m_\ell;m_s\rangle = f_{n\ell}(r)Y_\ell^{m_\ell}(\theta,\phi)\,|m_s\rangle \ , \tag{7.26}$$

where on the right we have brought out the explicit wave function part in front and left only the intrinic spin state in the ket. Here, as elsewhere, the $Y_\ell^{m_\ell}(\theta,\phi)$ are the spherical harmonics with eigenvalues $\hbar^2\ell(\ell+1)$ for $\mathbf{L}^2$ and $\hbar m_\ell$ for L_3, and $f_{n\ell}(r)$ is a (particular) polynomial in r of degree $n-1$ multiplied by $\exp(-Zr/na_0)$. These states simultaneously diagonalise $\mathbf{L}^2$, $\mathbf{S}^2$, L_3, S_3, and H, with energy

$$E_n = \frac{E_0}{n^2}\ , \quad E_0 = -\frac{Z^2q_e^2}{2a_0}\ . \tag{7.27}$$

The energy eigenstates depend only on the *principal quantum number*, n, and for a given n there are states with $\ell = 0,\ldots,n-1$, and for each ℓ there are $2\ell+1$ different values of m_ℓ. Each such wave function also occurs twice, once for each of the two values of m_s. Adding everything up, there is a degeneracy of $2n^2$ for the energy level E_n.

Now for various purposes it proves useful to adopt a basis of states that diagonalises the total angular momentum operator $\mathbf{J}^2$ (where $\mathbf{J} = \mathbf{L}+\mathbf{S}$). Following our previous discussion of addition of angular momentum, we can find a basis of states that does this with eigenvalue $j(j+1)\hbar^2$, where $j = \ell\pm\frac{1}{2}$ (or $j=\frac{1}{2}$ if $\ell = 0$). These are given by the linear combinations,

$$|n,\ell,j,m_j\rangle = \sum_{\substack{m_\ell,m_s\\ m_\ell+m_s=m_j}} C_{\ell,\frac{1}{2}}(j,m_j;m_\ell,m_s)\,|n,\ell,m_\ell;m_s\rangle \ . \tag{7.28}$$

where $C_{\ell,\frac{1}{2}}(j,m_j;m_\ell,m_s)$ are of course the Clebsch-Gordan coefficients. This gives us a basis of stationary states that are eigenvectors for H, $\mathbf{L}^2$, $\mathbf{J}^2$, and J_3, the latter with eigenvalue m_j, but not for L_3 and S_3.

There is a standard nomenclature for the electron states in this form. The set of states with given values of n, ℓ, and j are known as $n\ell_j$ orbitals. For historical reasons, instead of writing the numerical value for $\ell = 0,1,2,3,4,\ldots$, one normally substitutes the letters $s,p,d,f,g,\ldots$ respectively (continuing alphabetically). Each such orbital contains $2j+1$ states with $m_j = -j,-j+1,\ldots,j-1,j$. So, for example:

- For all n we have the $\ell = 0$ states, *i.e.*, s states, which appear only in the orbital $ns_{\frac{1}{2}}$ with the two states corresopnding to $m_j = m_s = \pm\frac{1}{2}$.
- For $n\geqslant 2$ we can have $\ell = 1$, the p orbitals, which arise in the configuration $np_{\frac{1}{2}}$ with two states or $np_{\frac{3}{2}}$ with four states, giving a total of 6 states for the np states.
- In general, we have orbits $n\ell_{\ell\pm\frac{1}{2}}$ with $n\geqslant \ell+1$, and a similar counting for the $n\ell$ type of energy level gives a total of $2(\ell-\frac{1}{2})+1+2(\ell+\frac{1}{2})+1 = 4\ell+2$ states.

Remark 7.3.1. We have here reorganised the Hydrogen stationary states so as to diagonalise the total angular momentum operator; it may not yet be clear that this is a superior basis to choose. We will see in some examples in the next chapter that when we start considering *corrections* to the Hydrogen atom Hamiltonian arising from more subtle physical effects, these will often lead to a preference for one basis over another.

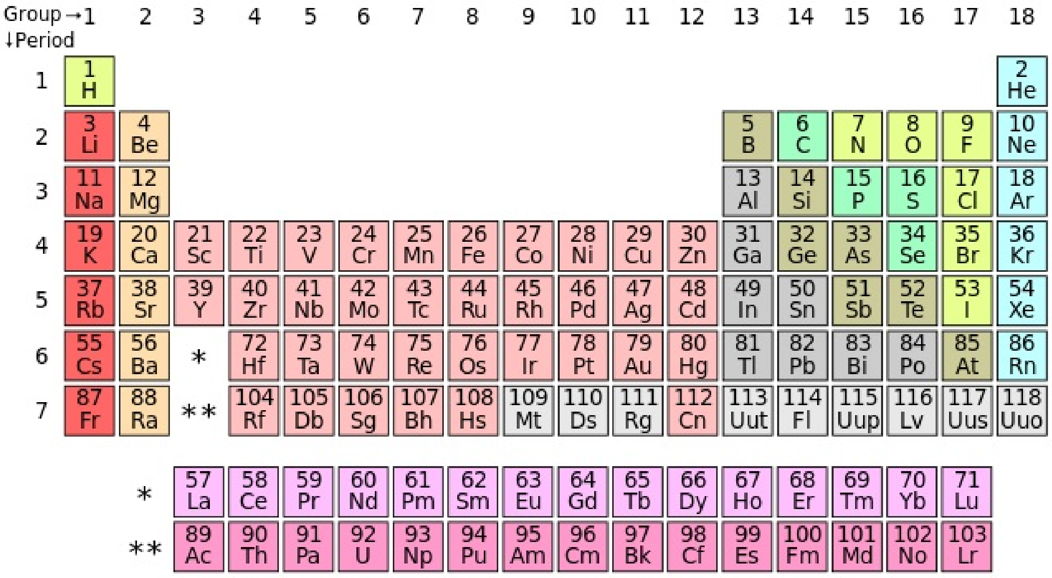

Figure 3. Periodic table of the elements.[34]

7.4 Fermionic statistics and the periodic table

Finally, let us combine the fermionic nature of electrons with the structure of angular momentum representations for the Hydrogen-like atom's energy eigenstates to develop a qualitative understanding of the periodic table of the elements.

As a first approximation to describing an atom with n electrons, we might model the n electrons to be non-interacting amongst themselves, so the n-particle energy eigenstates will simply be built from single electron energy eigenstates. But by the Pauli exclusion principle, as soon as, say, the two states in the $1s$ orbital are filled, a third electron will be required to lie in the first excited state (in the $2s$ or $2p$ orbital).[35] It turns out that although the model of non-interacting fermions is good for the first few energy levels, more elaborate calculations that incorporate, *e.g.*, shielding of nuclear charge by the inner orbits, affect the overall energy levels of the different orbitals and gives the following ordering from lowest energy to highest, with levels on the same line being approximately equal:

$$\begin{array}{lllll c}
\multicolumn{5}{c}{\text{orbital labels}} & \text{number of states} \\
1s, & & & & & 2 \\
2s, & 2p, & & & & 2+6=8 \\
3s, & 3p, & & & & 2+6=8 \\
4s, & 3d, & 4p & & & 2+10+6=18 \\
5s, & 4d, & 5p & & & 2+10+6=18 \\
6s, & 4f, & 5d, & 6p, & & 2+14+10+6=32 \\
7s, & 5f, & 6d, & 7p, & \ldots & \ldots
\end{array} \tag{7.29}$$

and so on. (We ignore the so-called *fine structure* separation for different j-values in a given orbital at this level of approximation; we will return to it in the next chapter on perturbation theory.) The point here is that for the larger ℓ orbits, the electrons in the smaller ℓ orbits are shielding the

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[35] We are being a bit careless with our language here; really we are dealing with antisymmetrised wave functions and there is no distinguishable "third electron". For the purposes of thinking about energy eigenstates the sloppier terminology will suffice.

nuclear charge, reducing the attraction towards the nucleus and hence raising the energy level of the outer orbits.

This already gives a reasonably good understanding of the periodic table of the elements. This is ordered by the charge of the nucleus and hence number of electrons. The elements in the same column are grouped by their physical and chemical properties. As can be seen the lengths of the rows line up precisely with the numbers of states in the different orbitals given above. Most notable are those on the far right, the noble gases. These are the most stable unreactive elements and are those for whom the orbitals of a given energy are full. This is because chemical bonds arise from sharing electrons between different atoms. However, the noble gases find it hard to accept new electrons because a new electron would have to go into a higher energy orbital than the existing one, and the existing electrons are tightly bound so they don't like to leave. On the left hand side are elements with one electron sitting alone in a higher orbital. This electron can be lost easily because it has more energy. Such an element is said to have valency one. Similarly, an element on the left of a noble gas has one space left in its orbital, and so easily accepts an electron and is said to have valency -1, and so on. The qualitative theory of chemical bonding all comes down to this valency in which stable molecules have net valency zero (*i.e.*, H_2O with $+1$ for each Hydrogen atom and -2 for the Oxygen atom).

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[35] Periodic table (polyatomic) by DePiep- Own work. Licensed under Creative Commons Attribution-Share Alike 3.0 via Wikimedia Commons, https://commons.wikimedia.org/wiki/File:Periodic_table_(polyatomic).svg.

Chapter 8

Rayleigh-Schrödinger Perturbation Theory

We now turn to an important practical and conceptual question in quantum thoery, which is how to approximate the energy levels of systems that are *close to* being described by a system that we can solve. We will say a little (but not a lot) more below about what we mean by "close", but intuitively, we can imagine, for example, modelling an atom with several electrons as being approximated by such an atom where the elecrons are assumed to not interact amongst themselves (except through fermionic statistics), as in our discussion of the periodic table in the previous Chapter. Alternatively, when we consider a Hydrogen-like, single-electron atom in the real world, we think of it as being well-described by the usual Hamiltonian with Coulomb potential, but there are actually small corrections to this due to the effects of (for example) special relativity.

8.1 Formal perturbation theory

First we'll introduce the basic idea. We imagine a scenario in which the Hamiltonian (for now we take this to be time-independent) of a quantum system can be written as a perturbation of a reference Hamiltonian $H^{(0)}$ taking the form

$$H = H^{(0)} + \delta H \ . \tag{8.1}$$

We have in mind (though it need not be the case to develop the abstract formalism) that $H^{(0)}$ is a Hamiltonian whose spectral problem we have understood exactly, such as that of the harmonic oscillator or the Hydrogen atom (restricting to bound states). Now we want to consider δH as being small in an appropriate sense, and we make this explicit by writing

$$\delta H = \epsilon H^{(1)} \ , \tag{8.2}$$

where ϵ is a small parameter, either in the sense of being numerically small (with H' being somehow fixed in size and so not scaling like an inverse power of ϵ), or more accurately for our immediate purposes, in the sense of being *formally small.* So we will take our energy levels and stationary states to be formal series expansions in this parameter ϵ,

$$\begin{aligned} \psi_\epsilon &= \psi^{(0)} + \epsilon\psi^{(1)} + \epsilon^2\psi^{(2)} + \ldots + \epsilon^n\psi^{(n)} + \ldots \ , \\ E_\epsilon &= E^{(0)} + \epsilon E^{(1)} + \epsilon^2 E^{(2)} + \ldots + \epsilon^n E^{(n)} + \ldots \ , \end{aligned} \tag{8.3}$$

and ask that these satisfy the time-independent Schrödinger equation as formal series,

$$H\psi_\epsilon = E_\epsilon\psi_\epsilon \ , \qquad \text{order by order in } \epsilon \ . \tag{8.4}$$

The issue of normalisation for this formal solution can be a little bit subtle, since the normalisation of our formal solution will itself be a formal series in ϵ. It turns out that a convenient normalisation is, rather than demanding ψ_ϵ be unit normalised, to require

$$\left\langle \psi^{(0)} \middle| \psi_\epsilon \right\rangle = 1 \ , \tag{8.5}$$

which is equivalent to

$$\langle\psi^{(0)}|\psi^{(n)}\rangle = \delta_{n,0} \ . \tag{8.6}$$

You may find it useful to think about how one should go about enforcing this normalisation if given a formal solution with an arbitrary normalisation.

If we write out the the formal series in (8.4) then we have

$$\begin{aligned}\left(H^{(0)}+\epsilon H^{(1)}\right)\left(\psi^{(0)}+\epsilon\psi^{(1)}+\epsilon^2\psi^{(2)}+\ldots\right) &= \\ \left(E^{(0)}+\epsilon E^{(1)}+\epsilon^2 E^{(2)}+\ldots\right)&\left(\psi^{(0)}+\epsilon\psi^{(1)}+\epsilon^2\psi^{(2)}+\ldots\right)\ ,\end{aligned} \tag{8.7}$$

and equating coefficients of order ϵ^n then gives the infinite sequence of relations

$$H^{(0)}\psi^{(n)}+H^{(1)}\psi^{(n-1)}=\sum_{m=0}^{n}E^{(m)}\psi^{(n-m)}\ . \tag{8.8}$$

The first of these relations, where $n=0$ (by convention we let $\psi^{(-1)}=0$) just tells us that zeroeth term in each expansion corresponds to an eigenstate and energy level of the unperturbed system,

$$H^{(0)}\psi^{(0)}=E^{(0)}\psi^{(0)}\ . \tag{8.9}$$

We will turn to an analysis of higher order terms momentarily. However, first we should make a short comment about how we should interpret this formal series.

Remark 8.1.1 (Analytic considerations). The analytic status of these formal series solutions is an interesting subject. Natural questions include whether we can assign some numerical value to ϵ so that the resultant series expansions for the energies and the eigenstates converge, and if so what the radius of convergence might be. The following theorem due to Kato gives some sense of under what conditions we get convergence.

Theorem 8.1.2. *If there exist real constants* $a,b\geqslant 0$ *such that for any* ψ *in the domain of* $H^{(0)}$, *we have*

$$\|H^{(1)}\psi\|\leqslant a\|\psi\|+b\|H^{(0)}\psi\|\ , \tag{8.10}$$

then the formal series for ψ_ϵ *and* E_ϵ *will have a finite radius of convergence.*

Estimating this radius of convergence is a more subtle issue. Observe that for the case of a finite dimensional Hilbert space, this is always satisfied since all of the quantities appearing in (8.10) will be bounded. In the infinite dimensional case, the simplest scenario is again when the left hand side is simply bounded for all $\psi\in\mathcal{H}$; in such a case there is always a positive radius of convergence.

The cases that are most often of interest in a physical setting are of the more complicated variety, where $\mathcal{H}$ is infinite dimensional and the operators in question lead to unbounded left hand side of (8.10). In these cases establishing the bound in question might be a difficult problem. However, even when the series have zero radius of convergence, these expansions can often be interpreted as asymptotic series, and can be used to do computations that give good agreement with experiment (sometimes extraordinarily good agreement) with experiment by simply truncating the formal series after a fixed number of terms. In our applications this will be our *modus operandi.*

8.2 First order perturbation theory (nondegenerate)

Now we return to our equation in (8.8) and look at the first correction term ($m=1$),

$$H^{(1)}\psi^{(0)}+H^{(0)}\psi^{(1)}=E^{(1)}\psi^{(0)}+E^{(0)}\psi^{(1)}\ . \tag{8.11}$$

Rewriting this gives

$$\left(H^{(0)}-E^{(0)}\right)\psi^{(1)}=-\left(H^{(1)}-E^{(1)}\right)\psi^{(0)}\ . \tag{8.12}$$

We want this equation to determine both $E^{(1)}$ and $\psi^{(1)}$, given the unperturbed (zeroeth order) information. For now we assume that $E^{(0)}$ is a nondegenerate energy level, so $\psi^{(0)}$ is the only state vector (up to rescaling) with eigenvalue $E^{(0)}$. An important fact is that we can determine the energy correction $E^{(1)}$ without worrying about $\psi^{(1)}$. To do this, we take the inner product of both sides of equation (8.12) with the state vector $\psi^{(0)}$,

$$\left\langle\psi^{(0)}\middle|\left(H^{(0)}-E^{(0)}\right)\middle|\psi^{(1)}\right\rangle=-\left\langle\psi^{(0)}\middle|\left(H^{(1)}-E^{(1)}\right)\middle|\psi^{(0)}\right\rangle\ . \tag{8.13}$$

The left hand side vanishes, since $H^{(0)}$ can act to the left and just give $E^{(0)}$, and we get the equation for our energy correction

$$E^{(1)}=\left\langle\psi^{(0)}\middle|H^{(1)}\middle|\psi^{(0)}\right\rangle\ . \tag{8.14}$$

This simple expression is extremely important and extremely powerful; in a slogan it tells us that the leading correction to the energy of a stationary state is given by the expectation value of the perturbation in that state.

We can then consider the problem of determining $\psi^{(1)}$. We will find an expression for the expansion of this correction vector in terms of a basis of stationary state vectors for the unperturbed Hamiltonian, which we denote by $\{\psi_n^{(0)}\}$ where

$$H^{(0)}\left|\psi_n^{(0)}\right\rangle=E_n^{(0)}\left|\psi_n^{(0)}\right\rangle\ . \tag{8.15}$$

We label these states so that the state whose perturbation we are studying is the m'th state ($n=m$), with energy $E_m^{(0)}$. We write such an expansion of the correction vector using a resolution of the identity,

$$\psi_m^{(1)}=\sum_{n\neq m}\left\langle\psi_n^{(0)}\middle|\psi_m^{(1)}\right\rangle\psi_n^{(0)}\ . \tag{8.16}$$

where $n=m$ is not included in the sum due to our normalisation condition. Now we can compute these overlaps by taking the inner product of both sides of (8.12) with $\psi_n^{(0)}$, which yields

$$\begin{aligned}
\left\langle\psi_n^{(0)}\middle|\left(H^{(0)}-E_m^{(0)}\right)\middle|\psi_m^{(1)}\right\rangle &= -\left\langle\psi_n^{(0)}\middle|\left(H^{(1)}-E_m^{(1)}\right)\middle|\psi_m^{(0)}\right\rangle\ ,\\
\Longrightarrow\qquad \left(E_n^{(0)}-E_m^{(0)}\right)\left\langle\psi_n^{(0)}\middle|\psi_m^{(1)}\right\rangle &= -\left\langle\psi_n^{(0)}\middle|H^{(1)}\middle|\psi_m^{(0)}\right\rangle\ ,\\
\Longrightarrow\qquad \left\langle\psi_n^{(0)}\middle|\psi_m^{(1)}\right\rangle &= \frac{\left\langle\psi_n^{(0)}\middle|H^{(1)}\middle|\psi_m^{(0)}\right\rangle}{E_m^{(0)}-E_n^{(0)}}\ .
\end{aligned} \tag{8.17}$$

This allows us to give the expansion of the first order correction vector in our orthonormal basis with explicit coefficients.

Remark 8.2.1. There is a nice way of thinking about the expression for the first state correction that is a bit slicker and offers a useful heuristic. Formally, we would like to take (8.12) and solve for $\psi^{(1)_m}$ by inverting the operator appearing on the left hand side,

$$\psi_m^{(1)}=-\frac{1}{H^{(0)}-E_m^{(0)}}\left(H^{(1)}-E^{(1)_m}\right)\psi_m^{(0)}\ . \tag{8.18}$$

However, we know that the operator $H^{(0)} - E_m^{(0)}$ is *not* invertible since it has a kernel (spanned by $\psi_m^{(0)}$ in this non-degenerate case). A related fact is that the range of this operator doesn't include all of $\mathcal{H}$; $\psi_m^{(0)}$ is absent, and indeed it is the only one of our basis vectors that is absent. Consequently, we can only define this inverse operator on the subspace of $\mathcal{H}$ that is orthogonal to $\psi_m^{(0)}$, and it is defined only up to the possible addition of multiples of $\psi_m^{(0)}$. The first of these requirements gives us a solvability condition that is exactly our condition that determines $E_m^{(1)}$. The second requires us to adopt a convention, which is exactly our normalisation condition for the formal solution. With both of those issues square away, we get an expression for $\psi_m^{(1)}$ upon inserting a resolution of the identity for the Hilbert space $\mathcal{H}^\perp$ that is orthogonal to $\psi_m^{(0)}$, which must act as the identity given that we have ensured that the state vector to the right is orthogonal to $\psi_m^{(0)}$,

$$\begin{aligned} \psi_m^{(1)} &= \frac{-1}{H^{(0)} - E_m^{(0)}} \sum_{n \neq m} \left| \psi_n^{(0)} \right\rangle \left\langle \psi_n^{(0)} \right| \left(H^{(1)} - E_m^{(1)} \right) \left| \psi_m^{(0)} \right\rangle \ , \\ &= \sum_{n \neq m} \left(\frac{\left\langle \psi_n^{(0)} \right| H^{(1)} \left| \psi_m^{(0)} \right\rangle}{E_m^{(0)} - E_n^{(0)}} \right) \left| \psi_n^{(0)} \right\rangle \ . \end{aligned} \tag{8.19}$$

In passing to the second line we have defined the action of the inverted operator using our usual rule that on eigenvectors of an observable A with eigenvalue a, we let a function of the observable $f(A)$ act by $f(a)$. We see that this procedure neatly reproduces the more piecemeal analysis carried out above.

Example 8.2.2 (The Helium atom ground state)**.** Consider an atom with two electrons (so probably Helium), and for now imagine that we can ignore spin (so treat electrons as if they were spin zero). The Hamiltonian of such an atom will be given by

$$H = H_1 + H_2 + H_{\text{int}} \ , \tag{8.20}$$

where

$$H_i = -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Z q_e^2}{|\mathbf{r}_i|} \ , \ i = 1, 2, \quad H_{\text{int}} = \frac{q_e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \ . \tag{8.21}$$

Here the nuclear charge Z would be two for Helium, H_1 and H_2 are the standard single-electron Hamiltonians, and H_{int} is *interaction Hamiltonian* that encodes the repulsion between the two electrons. If the Hamiltonian were $H_1 + H_2$, this would just be the tensor product of two copies of the Hydrogen atom, so we would have separable energy eigenstates of the form

$$\psi_{n_1, n_2}(\mathbf{x}_1, \mathbf{x}_2) = \psi_{n_1}(\mathbf{x}_1) \psi_{n_2}(\mathbf{x}_2) \ . \tag{8.22}$$

In particular, the ground state is non-degenerate and given by

$$\begin{aligned} \psi_{1,1}(\mathbf{x}_1, \mathbf{x}_2) &= \left(\frac{Z^3}{\pi a_0^3} \right)^{\frac{1}{2}} \exp\left(-\frac{Z r_1}{a_0} \right) \times \left(\frac{Z^3}{\pi a_0^3} \right)^{\frac{1}{2}} \exp\left(-\frac{Z r_2}{a_0} \right) \ , \\ &= \left(\frac{Z^3}{\pi a_0^3} \right) \exp\left(-\frac{Z(r_1 + r_2)}{a_0} \right) \ . \end{aligned} \tag{8.23}$$

Though it is by no means clear that the interaction Hamiltonian is *small*, we can nevertheless proceed with a formal perturbative analysis setting $\delta H = H_{\text{int}}$. The first order correction to the ground state energy using our machinery from above is then given by the expectation value,

$$E_1^{(1)} = \left\langle \psi^{(0)} \middle| H^{(1)} \middle| \psi^{(0)} \right\rangle = \left(\frac{Z^3}{\pi a_0^3} \right)^2 \int\limits_{\mathbb{R}^6} \frac{q_e^2 \exp\left(\frac{-2Z(r_1+r_2)}{a_0} \right)}{|\mathbf{x}_1 - \mathbf{x}_2|} \, \mathrm{d}^3\mathbf{x}_1 \, \mathrm{d}^3\mathbf{x}_2 \ . \tag{8.24}$$

Evaluating integrals like these is, unfortunately, largely unavoidable when it comes time to turn the abstract algebra of perturbation theory into actual numbers for systems like the Helium atom. We can perform this integral by first noting that by spherical symmetry we can take $\mathbf{x}_1$ to point in the $\hat{\mathbf{z}}$ direction (picking up a factor of 4π from the solid angle for $\mathbf{x}_1$). Introducing spherical polar oordinates for $\mathbf{x}_2$, we then have $\mathbf{x}_1 \cdot \mathbf{x}_2 = r_1 r_2 \cos\theta$ and so $|\mathbf{x}_1 - \mathbf{x}_2| = (r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta)^{1/2}$. The ϕ integral for $\mathbf{x}_2$ is trivial and gives an extra factor of 2π. The remaining integral becomes

$$\left(\frac{8Z^6 q_e^2}{a_0^6} \right) \int\limits_0^\infty \int\limits_0^\infty \int\limits_0^\pi \exp\left(\frac{-2Z(r_1+r_2)}{a_0} \right) \frac{r_1^2 r_2^2 \sin\theta}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta}} \, \mathrm{d}\theta \, \mathrm{d}r_1 \, \mathrm{d}r_2 \ . \tag{8.25}$$

The angular integral can be done immediately,

$$\begin{aligned}
\int\limits_0^{2\pi} \frac{\sin\theta \, \mathrm{d}\theta}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta}} &= \frac{1}{r_1 r_2} \left(r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta \right)^{\frac{1}{2}} \Big|_0^\pi \ . && (8.26) \\
&= \frac{1}{r_1 r_2} \left((r_1 + r_2) - |r_1 - r_2| \right) \ , && (8.27) \\
&= \begin{cases} \frac{2}{r_1} & r_1 > r_2 \ , \\ \frac{2}{r_2} & r_2 > r_1 \ . \end{cases} && (8.28)
\end{aligned}$$

By symmetry the integration regions where $r_1 > r_2$ and that with $r_2 > r_1$ contribute equally, so we can write the resulting radial integral as

$$E_1^{(1)} = \left(\frac{32 Z^6 q_e^2}{a_0^6} \right) \int\limits_0^\infty \int\limits_{r_2}^\infty \exp\left(-\frac{2Z(r_1+r_2)}{a_0} \right) r_1 r_2^2 \, \mathrm{d}r_1 \, \mathrm{d}r_2 \ . \tag{8.29}$$

This leaves radial integrations, and these can be performed with the help of the following useful integral identity

Lemma 8.2.3. *For any non-negative integer n, we have*

$$\int\limits_R^\infty e^{-kr} r^n \, \mathrm{d}r = \frac{n! \exp(-kR)}{k^{n+1}} \sum_{j=0}^n \frac{(kR)^j}{j!} \ . \tag{8.30}$$

This is proved by induction on n by differentiating with respect to k.

Applying this lemme a few times, we end up with the result

$$E_1^{(1)} = \frac{5}{8} \frac{Z q_e^2}{a_0} \ . \tag{8.31}$$

Selecting $Z = 2$ as is appropriate for Helium and performing a crude truncation of the perturbation series to first order, this gives an estimation for the ground state energy as

$$E_1 \approx E_1^{(0)} + E_1^{(1)} = -\frac{2q_e^2}{a_0}\left(2 - \frac{5}{8}\right) = -\frac{2.75q_e^2}{a_0} \ . \tag{8.32}$$

The experimental result for the Helium atom's ground state energy is

$$E_1^{(\exp)} \approx -\frac{2.92q_e^2}{a_0} \ . \tag{8.33}$$

Though we don't have systematic control of higher order corrections, we can see that our estimate with a coefficient of 2.75 is much closer to the experimental value than the zeroeth order estimate with a coefficient of 4.

An interesting interpretation of this result is that the corrected energy is as it would be for non-interacting electrons if the nuclear charge Z were equal to 11/8 instead of two. One could imagine modelling the effect of extra electrons as "shielding" some of the electric charge of the nucleus that the other electrons experience, but otherwise having no interactive effect. We will see in a later Chapter when discussing variational methods that such an approach can be made quite effective.

8.3 First order perturbation theory (degenerate)

In general we need to be wary of the case where the energy level whose corrections we are considering is degenerate in the unperturbed theory. For example, we may be considering a Hydrogen-like ion where the energy levels all have some degeneracy, some quite a bit, as described in the previous chapter. In this case, the analysis of the previous section is a bit too naive.

This becomes apparent when we consider the determination of the first correction to a given degenerate energy level. Suppose that both $\psi^{(0)}$ and $\varphi^{(0)}$ have unperturbed energy $E^{(0)}$. Taking the inner product of both sides of (8.11) with both $\psi^{(0)}$ and $\varphi^{(0)}$ we find

$$E^{(1)} = \left\langle \psi^{(0)} \middle| H^{(1)} \middle| \psi^{(0)} \right\rangle \ , \qquad 0 = \left\langle \varphi^{(0)} \middle| H^{(1)} \middle| \psi^{(0)} \right\rangle \ , \tag{8.34}$$

The first of these amounts to our previous determination of the energy correction, but the second is a condition that may or may not be satisfied depending on whether we've been lucky in our choice of basis vectors $\psi^{(0)}$ and $\varphi^{(0)}$. Indeed, the issue here is that there is an ambiguity in the basis that we choose for the degenerrate $E^{(0)}$ eigenspace, but after perturbation there is a preferred choice of basis. This resolution proceeds as follows.

Theorem 8.3.1. *Let $\varphi_1, \ldots, \varphi_d$ be an orthonormal basis for the $E^{(0)}$ eigenspace of $H^{(0)}$. Then (8.12) can be solved if and only if $E^{(1)}$ and $\psi^{(0)}$ are chosen so that $E^{(1)}$ is a solution to*

$$\det\left(\left\langle \varphi_r \middle| H^{(1)} \middle| \varphi_s \right\rangle - E^{(1)}\delta_{rs}\right) = 0 \ , \tag{8.35}$$

and $\psi^{(0)} = \sum_{r=1}^{d} c_r \varphi_r$ is the corresponding eigenvector

$$\sum_s \left\langle \varphi_r \middle| H^{(1)} \middle| \varphi_s \right\rangle c_s = E^{(1)} c_r \ . \tag{8.36}$$

In a slogan, this says that before setting up the first order perturbation problem, one should choose a basis for the degenerate $E^{(0)}$ eigenspace that diagonalises the action of the restriction of $H^{(1)}$ to that subspace. In this basis, the rules are the same as in the non-degenerate setting.

Proof. This follows directly from the requirement that we avoid the potential contradictions arising as in (8.34). We can also argue more abstractly in terms of the formulation from Remark 8.2.1. We need to be able to solve (8.12), but again $H^{(0)} - E^{(0)}$ has a (now d-dimensional) kernel and is not invertible, so the right hand side could fail to be in the range of $H^{(0)} - E^{(0)}$. A useful fact is then the following:

Proposition 8.3.2. *The range of a self-adjoint operator on a Hilbert space $\mathcal{H}$ coincides with the orthogonal complement of its kernel.*

Proof. We first establish that $\mathrm{Ran}(A) \subseteq \ker(A)^{\perp}$. Let $\psi \in \mathrm{Ran}A$, so we can write $\psi = A\psi'$. Then we have for any $\varphi \in \ker(A)$,

$$\langle\varphi|\psi\rangle = \langle\varphi|A\psi'\rangle = \langle A\varphi|\psi'\rangle = 0 \ , \tag{8.37}$$

which gives our inclusion.

Now we establish that $\ker(A)^{\perp} \subseteq \mathrm{Ran}(A)$. First, note that for $\varphi \in \mathrm{Ran}(A)^{\perp}$, we have that for all $\psi \in \mathcal{H}$, we have

$$0 = \langle\varphi|A\psi\rangle = \langle A\varphi|\psi\rangle \ , \tag{8.38}$$

so $A\varphi$ must be the zero vector, and thus $\varphi \in \ker(A)$ and so $\mathrm{Ran}(A)^{\perp} \subseteq \ker(A)$. We will use without proof a fact from functional analysis, which is that for any self-adjoint operator on a Hilbert space, $(\mathrm{Ran}(A)^{\perp})^{\perp} = \mathrm{Ran}(A)$.[36] Thus taking complements of this second inclusion, we have $\ker(A)^{\perp} \subseteq \mathrm{Ran}(A)^{\perp\perp} = \mathrm{Ran}(A)$. With both inclusions in place, we get the stated identification. ■

Thus, to be able to define an inverse action of our operator $H^{(0)} - E^{(0)}$ what we need is that the the right hand side of (8.12) is orthogonal to the operator's kernel. Taking the inner product with any one of the φ_r we find,

$$0 = \left\langle \varphi_r \middle| \left(H^{(1)} - E^{(1)}\right) \middle| \psi^{(0)} \right\rangle = \sum_s \left\langle \varphi_r \middle| H^{(1)} \middle| \varphi_s \right\rangle c_s - E^{(1)}\delta_{rs}c_s \ , \tag{8.39}$$

where $\psi^{(0)}$ is expanded in terms of the φ_i as in the statement of the theorem. This is precisely the condition that $E^{(1)}$ be an eigenvalue of the matrix with matrix elements $\langle \varphi_r | H^{(1)} | \varphi_s \rangle$ with $\psi^{(0)}$ (thought of as an element of the d-dimensional $E^{(0)}$ eigenspace) the corresponding eigenvector. ■

In practice, what one should usually do is to choose the basis $\varphi_1, \ldots, \varphi_d$ to already diagonalise the restriction to the $E^{(0)}$ eigenspace of the perturbation $H^{(1)}$, and use these as our unperturbed state vectors when we set up our formal perturbation problem. Suppose we set $\psi^{(0)} = \varphi_1$. Then we have for the first correction to such an eigenstate,

$$\psi^{(1)} = \sum_{E_n^{(0)} \neq E^{(0)}} \left(\frac{\left\langle \psi_n^{(0)} \middle| H^{(1)} \middle| \psi^{(0)} \right\rangle}{E^{(0)} - E_n^{(0)}} \right) \left| \psi_n^{(0)} \right\rangle + \sum_{\substack{j=1 \\ j \neq i}}^{d} \lambda_j \left| \varphi_j \right\rangle \ , \tag{8.40}$$

where we have introduced parameters λ_i corresponding to the ambiguity in defining the pre-image of the right hand side of (8.12) due to the enlarged kernel of $H^{(0)} - E^{(0)}$. At this stage these parameters are genuinely ambiguous. You will see on the third problem sheet that these parameters can be fixed upon continuing to higher orders in perturbation theory.

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[36] This is a familiar fact that the iterated orthogonal complement is the identity for finite-dimensional inner product spaces; the novelty here is that in infinite dimensions it isn't necessarily true, but it is still true for ranges of self-adjoint operators on Hilbert spaces.

Example 8.3.3 (Strong field Zeeman effect)**.** A simple example of degenerate perturbation theory arises in what is known as the Zeeman effect (or Zeeman splitting) for Hydrogen-like atoms. If we apply a constant magnetic field $\mathbf{B}$ to such an atom, there will be a correction to the Hamiltonian given by,[37]

$$\delta H = \frac{q_e}{2m_e c}\mathbf{B}\cdot(\mathbf{L}+g_e\mathbf{S})\ , \tag{8.41}$$

where $g_e \approx 2$ is a numerical constant known as the *gyromagnetic ratio* of the electron. Without loss of generality, we will take $\mathbf{B}$ to be oriented in the x_3-direction.

When considering the effect of this perturbation, we must account for the degeneracy of the Hydrogen energy levels, and as we understood in the previous chapter, there are at least two natural bases for the degenerate energy eigenspaces of the Hydrogen atom, depending on whether we want to diagonalise the total angular momentum ($|n,\ell,j,m_j\rangle$ states) or the x_3 component of both orbital and spin angular momentum ($|n,\ell,m_\ell;m_s\rangle$ states). For this perturbation, then, we should use the latter states since they are actually already simultaneous eigenvectors of L_3 and S_3.

If we restrict to states with principle quantum number n (so unperturbed energy E_n), then the first order corrections are given by

$$E^{(1)}_{n,\ell,m_\ell,m_s} = \langle n,\ell,m_\ell;m_s|\delta H|n,\ell,m_\ell;m_s\rangle = \frac{q_e B}{2m_e c}\left(m_\ell + g_e m_s\right)\ . \tag{8.42}$$

The above example is a bit artificial as an example of perturbation theory, because the $|n,\ell,m_\ell;m_s\rangle$ states actually are *exact eigenstates* of the perturbed Hamiltonian, as they diagonalise the J_3 and S_3 operators appearing in δH on the nose. Correspondingly, you should be able to convince yourself that the correction (8.40) to the energy eigenstates vanishes exactly. Therefore this analysis is valid for *large* values of B. In fact, it is *only* value for sufficiently large values of B, because for small B there are competing corrections that need to be accounted for.

8.4 Higher order perturbation theory

We will briefly comment on the extension to higher orders in the perturbative expansion. To begin, let us just proceed directly to second order, where the $O(\epsilon^2)$ term in (8.7) amounts to the equation

$$H^{(0)}\psi^{(2)} + H^{(1)}\psi^{(1)} = E^{(0)}\psi^{(2)} + E^{(1)}\psi^{(1)} + E^{(2)}\psi^{(0)}\ . \tag{8.43}$$

We reorganise this suggestively as

$$\left(H^{(0)} - E^{(0)}\right)\psi^{(2)} = -\left(H^{(1)} - E^{(1)}\right)\psi^{(1)} + E^{(2)}\psi^{(0)}\ , \tag{8.44}$$

which again tells us that to be able to determine $\psi^{(2)}$ we have to find the pre-image under $H^{(0)}-E^{(0)}$ of the vector on the right hand side. If for now we assume that the unperturbed energy level in question is non-degenerate, then like above our first task will be to establish a solvability condition that the right hand side is orthogonal to the kernel of $H^{(0)}-E^{(0)}$, which is to say that it is orthogonal to $\psi^{(0)}$. This determines $E^{(2)}$:

$$E^{(2)} = \left\langle \psi^{(0)}\middle|\left(H^{(1)} - E^{(1)}\right)\middle|\psi^{1}\right\rangle = \left\langle \psi^{(0)}\middle|H^{(1)}\middle|\psi^{1}\right\rangle\ , \tag{8.45}$$

---

[37] We won't worry about how the precise form of this correction comes about.

which, plugging in our expression for $\psi^{(1)}$, gives

$$E^{(2)} = \sum_{\psi_n^{(0)} \neq \psi^{(0)}} \frac{\left\langle \psi^{(0)} \middle| H^{(1)} \middle| \psi_n^{(0)} \right\rangle \left\langle \psi_n^{(0)} \middle| H^{(1)} \middle| \psi^{(0)} \right\rangle}{E^{(0)} - E_n^{(0)}} = \sum_n \frac{\left| \left\langle \psi_n^{(0)} \middle| H^{(1)} \middle| \psi^{(0)} \right\rangle \right|^2}{E^{(0)} - E_n^{(0)}} \ . \tag{8.46}$$

Let us make a few comments.

- If ψ^0 was the ground state, then the denominator in (8.46) is always negative and so the second order energy correction is necessarily negative.
- This formula is especially useful if $H^{(1)}\psi^{(0)}$ is itself an energy eigenstate, so that we only get one nonvanishing term in the sum due to the orthogonality of the different energy eigenstates.
- If energy levels are well separated, then we expect the terms corresponding to mixing with nearby energy eigenstates to dominate the correction due to suppression in the denominator by energy difference.

Continuing in the non-degenerate case and considering the second-order correction to the state (subject to our normalisation condition),

$$\psi^{(2)} = \sum_{\psi_n^{(0)} \neq \psi^{(0)}} \left\langle \psi_n^{(0)} \middle| \psi^{(2)} \right\rangle \psi_n^{(0)} \ , \tag{8.47}$$

we can solve for the coefficients using (8.43) and find

$$\begin{aligned} \psi^{(2)} = \sum_{\psi_{n,m}^{(0)} \neq \psi^{(0)}} & \frac{\left\langle \psi_n^{(0)} \middle| H^{(1)} \middle| \psi_m^{(0)} \right\rangle \left\langle \psi_m^{(0)} \middle| H^{(1)} \middle| \psi^{(0)} \right\rangle}{\left(E_n^{(0)} - E^{(0)}\right)\left(E_m^{(0)} - E^{(0)}\right)} \psi_n^{(0)} - \\ & \sum_{\psi_n^{(0)} \neq \psi^{(0)}} \frac{\left\langle \psi_n^{(0)} \middle| H^{(1)} \middle| \psi^{(0)} \right\rangle \left\langle \psi^{(0)} \middle| H^{(1)} \middle| \psi^{(0)} \right\rangle}{\left(E_n^{(0)} - E^{(0)}\right)^2} \psi_n^{(0)} \ . \end{aligned} \tag{8.48}$$

Clearly, at this point (and even more at higher orders) things get quite cluttered in these general expressions.

Often it is more important to have expressions for higher order corrections to energy levels than it is to have the high order expressions for the state vectors. From our general perturbative expension, this would naively require obtaining $\psi^{(k-1)}$ if we want to compute $E^{(k)}$ because expanding $H_\epsilon \psi_\epsilon = E_\epsilon \psi_\epsilon$ to order k gives from the coefficient of ϵ^k

$$H^{(0)}\psi^{(k)} + H^{(1)}\psi^{(k-1)} = E^{(0)}\psi^{(k)} + E^{(1)}\psi^{(k-1)} + \ldots + E^{(k)}\psi^{(0)} \ , \tag{8.49}$$

and taking the inner product with $\psi^{(0)}$ (imposing the solvability condition in the nondegenerate case), using $\left\langle \psi^{(0)} \middle| \psi^{(l)} \right\rangle = 0$ that follows from the normalization condition, we obtain

$$E^{(k)} = \left\langle \psi^{(0)} \middle| H^{(1)} \middle| \psi^{(k-1)} \right\rangle \ , \tag{8.50}$$

In fact, one can avoid calculating all the way up to $\psi^{(k-1)}$ using a clever trick that draws out relations between the different perturbative corrections.

Lemma 8.4.1. *As a formal expansion in* ϵ_1 *and* ϵ_2*, we have*

$$\left\langle \psi_{\epsilon_1} \middle| H^{(1)} \middle| \psi_{\epsilon_2} \right\rangle = \frac{E_{\epsilon_1} - E_{\epsilon_2}}{\epsilon_1 - \epsilon_2} \left\langle \psi_{\epsilon_1} | \psi_{\epsilon_2} \right\rangle \ . \tag{8.51}$$

Proof. We have $H_{\epsilon_1} - H_{\epsilon_2} = (\epsilon_1 - \epsilon_2) H^{(1)}$ so we can compute,

$$\begin{aligned} \langle \psi_{\epsilon_1} | H_{\epsilon_1} - H_{\epsilon_2} | \psi_{\epsilon_2} \rangle &= \langle \psi_{\epsilon_1} | H_{\epsilon_1} | \psi_{\epsilon_2} \rangle - \langle \psi_{\epsilon_1} | H_{\epsilon_2} | \psi_{\epsilon_2} \rangle \ , & (8.52) \\ (\epsilon_1 - \epsilon_2) \left\langle \psi_{\epsilon_1} \middle| H^{(1)} \middle| \psi_{\epsilon_2} \right\rangle &= E_{\epsilon_1} \langle \psi_{\epsilon_1} | \psi_{\epsilon_2} \rangle - E_{\epsilon_2} \langle \psi_{\epsilon_1} | \psi_{\epsilon_2} \rangle \ . & (8.53) \end{aligned}$$

which leads to the conclusion. ■

Note that $E_{\epsilon_1} - E_{\epsilon_2}$ is proportional to $\epsilon_1 - \epsilon_2$, so the right hand side can still be taken as a formal expansion in the two variables.

By expanding both sides of (8.51), and considering each monomial in the ϵ's, we generate various identities for the perturbative corrections. Indeed, our first naive higher order formula (8.50) represents the coefficient of ϵ_2^{k-1}. However, we can be a bit more efficient if we are clever.

Corollary 8.4.2. $E^{(2k+1)}$ *can be expressed in terms of only the* $\psi^{(r)}$ *with* $r \leqslant k$ *and and their matrix elements with respect to* $H^{(1)}$*.*

Proof. The coefficient on the right hand side of (8.51) can be expanded as

$$\begin{aligned} \frac{E_{\epsilon_1} - E_{\epsilon_2}}{\epsilon_1 - \epsilon_2} &= \sum_{n=1}^{\infty} \frac{{\epsilon_1}^n - {\epsilon_2}^n}{\epsilon_1 - \epsilon_2} E^{(n)} & (8.54) \\ &= \sum_{n=1}^{\infty} E^{(n)} \left(\sum_{j=0}^{n-1} {\epsilon_1}^j {\epsilon_2}^{n-1-j} \right) \ , & (8.55) \end{aligned}$$

so at order ${\epsilon_1}^k {\epsilon_2}^k$ we have $E^{(2k+1)}$. This is then equal to the coefficient of ${\epsilon_1}^k {\epsilon_2}^k$ in the expansion of

$$\frac{\left\langle \psi_{\epsilon_1} \middle| H^{(1)} \middle| \psi_{\epsilon_2} \right\rangle}{\left\langle \psi_{\epsilon_1} | \psi_{\epsilon_2} \right\rangle} \ . \tag{8.56}$$

That term clearly depends only on $\psi^{(r)}$ for $r \leqslant k$. ■

The simplest example of this gives us an economical expression for the third order energy correction,

$$E^{(3)} = \left\langle \psi^{(1)} \middle| H^{(1)} \middle| \psi^{(1)} \right\rangle - E^{(1)} \left\langle \psi^{(1)} \middle| \psi^{(1)} \right\rangle \ , \tag{8.57}$$

which we could calculate using only the results of first-order computations.

Chapter 9

Variational Methods

It isn't uncommon to encounter a system that is not particularly close to being solvable, rendering perturbation theory at least unreliable and at worst completely unhelpful. There are an important class of techniques that go by the name of *variational methods* that can be applied quite generally in these circumstances, though they often require a bit of creativity to exploit well. In this chapter we present the essential idea behind these methods and study (again!) the Helium atom as a nice example.

9.1 Rayleigh quotients for observables

The basic tool behind our variational methods will be the so-called *Rayleigh quotient.*

Definition 9.1.1 (Rayleigh Quotient)**.** *The (real) function*

$$\begin{aligned} f_A : \mathcal{H} &\longrightarrow \mathbb{R}\ , \\ \psi &\longmapsto \mathbb{E}_\psi(A) = \frac{\langle\psi|A|\psi\rangle}{\langle\psi|\psi\rangle}\ . \end{aligned} \tag{9.1}$$

is known as the Rayleigh quotient *for A.*

It may seem a bit overwrought to introduce a name for what is already the expectation value as we have defined it before. For us, the point is to accentuate the fact that this is now being thought of as a (smooth) function on $\mathcal{H}$, which is not necessarily how we thought about expectation values previously.

A key property of the Rayleigh quotient is that stationary values/vectors for $f_A(\psi)$ are precisely eigenvalue/vectors for A, as can be seen from the following.

Theorem 9.1.2. *Given a subspace $\mathcal{K} \subseteq \mathcal{H}$, then*

$$\frac{\mathrm{d}}{\mathrm{d}t} f_A(\psi + t\varphi)\bigg|_{t=0} = 0\ , \quad \forall \varphi \in \mathcal{K} \quad \Longleftrightarrow \quad \langle\varphi|A - f_A(\psi)|\psi\rangle = 0 \quad \forall\varphi \in \mathcal{K}\ , \tag{9.2}$$

which in particular, for $\mathcal{K} = \mathcal{H}$, implies that

$$\left(A - f_A(\psi)\right)|\psi\rangle = 0\ . \tag{9.3}$$

This latter statement says that the critical points of $f_A(\psi)$ are precisely the eigenvectors of A and the critical values are the eigenvalues of A.

Proof. For $\varphi \in \mathcal{K}$, $i\varphi \in \mathcal{K}$, so we require both

$$\frac{\mathrm{d}}{\mathrm{d}t} f_A(\psi + t\varphi) = 0 \qquad \text{and} \qquad \frac{\mathrm{d}}{\mathrm{d}t} f_A(\psi + it\varphi) = 0\ . \tag{9.4}$$

The first of these gives

$$
\begin{aligned}
0 &= \left.\frac{\mathrm{d}}{\mathrm{d}t}\frac{\langle\psi+t\varphi|A|\psi+t\varphi\rangle}{\langle\psi+t\varphi|\psi+t\varphi\rangle}\right|_{t=0} ,\\
&= \left.\frac{\mathrm{d}}{\mathrm{d}t}\frac{\langle\psi|A|\psi\rangle+t\,\langle\varphi|A|\psi\rangle+t\,\langle\psi|A|\varphi\rangle+O(t^2)}{\langle\psi|\psi\rangle+t\,\langle\varphi|\psi\rangle+t\,\langle\psi|\varphi\rangle+O(t^2)}\right|_{t=0} ,\\
&= \frac{\langle\varphi|A|\psi\rangle+\langle\psi|A|\varphi\rangle}{\langle\psi|\psi\rangle} - \frac{\langle\psi|A|\psi\rangle\left(\langle\varphi|\psi\rangle+\langle\psi|\varphi\rangle\right)}{\langle\psi|\psi\rangle^2} ,\\
&= 2\Re\left(\frac{\langle\varphi|(H-f_A(\psi))|\psi\rangle}{\langle\psi|\psi\rangle}\right) .
\end{aligned}
$$

This implies the real part of the desired equation, and if we repeat the argument with $\varphi\to i\varphi$ we get the imaginary part as well, and thus deduce that for states that are stationary against adding vectors $\varphi\in\mathcal{K}$,

$$\langle\varphi|(A-f_A(\psi))|\psi\rangle = 0 . \tag{9.5}$$

Thus $(A-f_A(\psi))\,|\psi\rangle\in\mathcal{K}^{\perp}$ so if we set $\mathcal{K}=\mathcal{H}$, then $\mathcal{K}^{\perp}=\{0\}$ and so

$$(A-f_A(\psi))\,|\psi\rangle = 0 \tag{9.6}$$

as desired. ■

Remark 9.1.3. Since $f_A(\psi)$ is independent of rescaling $\psi\to\lambda\psi$, the Rayleigh quotient is really a function on the projectivised Hilbert space whose critical points correspond to energy eigenstates. We could also just as well take variations over, say, the unit sphere in Hilbert space, *i.e.*, the states with norm one.

9.2 The virial theorem

We can obtain useful, general information about energy eigenstates by considering variations within one-parameter families of states. An example is the following important theorem.

Theorem 9.2.1 (Virial theorem)**.** *Assume the Hamiltonian for a quantum mechanical system whose Hilbert space is identified with a space of wave functions in d dimensions has the conventional form $H=T+V$ with*

$$T=\frac{\mathbf{P}^2}{2m}=-\frac{\hbar^2}{2m}\nabla^2 , \qquad V=V(\mathbf{X}) . \tag{9.7}$$

Then for any stationary state ψ with $H\psi=E\psi$, the following condition holds,

$$2\mathbb{E}_\psi(T)=\mathbb{E}_\psi(\mathbf{x}\cdot\nabla V) . \tag{9.8}$$

If V is homogeneous of degree N, i.e., *$V(\lambda\mathbf{x})=\lambda^N V(\mathbf{x})$, then*

$$\mathbb{E}_\psi(T)=\frac{N}{N+2}E , \qquad \mathbb{E}_\psi(V)=\frac{2}{N+2}E . \tag{9.9}$$

Proof. The idea is to perform a variational analysis of the family of wave functions of the form $\psi_\lambda(\mathbf{x})=\lambda^{d/2}\psi(\lambda\mathbf{x})$ for a given reference wave function $\psi(\mathbf{x})$. The factor of $\lambda^{d/2}$ is included to ensure that all of these wave functions are normalised equally; this is only done for convenience so that in computing Rayleigh quotients we can ignore the denominator.

Now suppose that $\psi(\mathbf{x})$ is a (normalised) stationary state; then the Rayleigh quotient of $\psi_\lambda(\mathbf{x})$ must be stationary as a function of λ at $\lambda = 1$,

$$\frac{\mathrm{d}}{\mathrm{d}\lambda} f_H(\psi_\lambda)\bigg|_{\lambda=1} = 0 \ . \tag{9.10}$$

Proceeding by direct computation, we have by the chain rule $\nabla\psi_\lambda(\mathbf{x}) = \lambda^{\frac{d+2}{2}} (\nabla\psi)(\lambda\mathbf{x})$, which gives us for the Rayleigh quotient,

$$\begin{aligned} f_H(\psi_\lambda) &= \int\limits_{\mathbb{R}^d} \left(\frac{-\hbar^2\lambda^{d+2}}{2m} |(\nabla\psi)(\lambda\mathbf{x})|^2 + \lambda^d V(\mathbf{x})|\psi(\lambda\mathbf{x})|^2 \right) \mathrm{d}^d\mathbf{x} \ , \\ &= \int\limits_{\mathbb{R}^d} \left(\frac{-\lambda^2\hbar^2}{2m} |\nabla'\psi(\mathbf{x}')| + V(\lambda^{-1}\mathbf{x}')|\psi(\mathbf{x}')|^2 \right) \mathrm{d}^d\mathbf{x}' \ , \\ &= \lambda^2\mathbb{E}_\psi(T) + \mathbb{E}_\psi(V(\lambda^{-1}\mathbf{x})) \ . \end{aligned} \tag{9.11}$$

In the passing to the second line we have defined $\mathbf{x}' = \lambda\mathbf{x}$. With this, (9.10) gives the condition

$$0 = 2\mathbb{E}_\psi(T) + \frac{\mathrm{d}}{\mathrm{d}\lambda}\mathbb{E}_\psi(V(\lambda^{-1}\mathbf{x}))\bigg|_{\lambda=1} = 2\mathbb{E}_\psi(T) - \mathbb{E}_\psi(\mathbf{x}\cdot\nabla V(\mathbf{x})) \ , \tag{9.12}$$

which reproduces (9.8). For V homogeneous of degree N, $\mathbf{x}\cdot\nabla V = NV$ and we get the simpler result

$$2\mathbb{E}_\psi(T) = N\,\mathbb{E}_\psi\left(V(\mathbf{x})\right) \ . \tag{9.13}$$

We also have for an energy eigenstate

$$E = \mathbb{E}_\psi(T) + \mathbb{E}_\psi(V(\mathbf{x})) \ , \tag{9.14}$$

and putting these together gives

$$\mathbb{E}_\psi(T) = \frac{N}{N+2}E \ , \qquad \mathbb{E}_\psi(V) = \frac{2}{N+2}E \ , \tag{9.15}$$

as required. ■

Remark 9.2.2. We offer some additional comments here.

- We see here that the Coulomb potential where $N = -1$, we must have $E < 0$ as $V < 0$ and $\mathbb{E}_\psi(V)$ is twice the size of $\mathbb{E}_\psi(T)$.
- For the harmonic oscillator, kinetic and potential energies are equal and balanced $\mathbb{E}_\psi(V) = \mathbb{E}_\psi(T) = \frac{1}{2}E$.
- This *quantum virial theorem* has a classical counterpart, which is the original virial theorem. The classical theorem has to do with time-averages of energies along classical trajectories.

9.3 Approximating the ground state

The flagship application of variational methods in quantum theory is to the study of the ground state and ground state energy of complicated quantum systems. To this end, one observes the following.

Proposition 9.3.1. *If f_H is bounded below and achieves its minimum, $E_0 := \inf_{\mathbb{P}(\mathcal{H})} f_H$, then E_0 is the ground state energy (minimum eigenvalue) and any state ψ for which $f_H(\psi) = E_0$ is indeed a ground state.*

Proof. f_H is automatically stationary at its minimum, and this will necessarily correspond to an eigenstate. Its eigenvalue will be the minimal one because the other eigenvalues are realised as values of f_H as well. ■

Conversely, when a system does have a normalisable ground state ψ_0, the function f_H achieves its lower bound at ψ_0.

Though this is a relatively simple observation, this result is actually very powerful. The idea is that we can try to find an approximate ground state by finding the minumum $E_{0,\text{approx}}$ of f_H restricted to some well-chosen subset of $\mathcal{H}$. We are guaranteed that $E_{0,\text{approx}} \geqslant E_0$ by the above, so this procedure produces rigorous upper bounds for E_0. If we are lucky and clever, these upper bounds will also be good approximations (though to estimate errors would be beyond the scope of the discussion here).

Example 9.3.2 (Helium again)**.** We return to the two-electron Helium atom, with Hamiltonian

$$H = \frac{\mathbf{P}_1^2}{2m} + \frac{\mathbf{P}_2^2}{2m} - 2q_e^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{q_e^2}{|\mathbf{x}_1 - \mathbf{x}_2|} = T + V + \delta H \ , \tag{9.16}$$

where

$$T = \frac{\mathbf{P}_1^2}{2m} + \frac{\mathbf{P}_2^2}{2m} \ , \quad V = -2q_e^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \ , \quad \delta H = \frac{q_e^2}{|\mathbf{x}_1 - \mathbf{x}_2|} \ . \tag{9.17}$$

As we saw previously, we can try to treat δH as a small correction and use first-order perturbation theory to get decent results for the ground state energy. However, the approximation in that case seemed quite uncontrolled; δH doesn't actually seem particularly negligible compared to other terms in the potential. This is a perfect case in which to attempt a variational estimate, and indeed we can do quite well.

Proposition 9.3.3. *The Helium ground state energy E_0 is bounded above according to*

$$E_0 \leqslant -\left(\frac{27}{16}\right)^2 \frac{q_e^2}{a_0} \ . \tag{9.18}$$

This should be compared to our estimate of $-\frac{11}{4}\frac{q_e^2}{a_0}$ from first-order perturbation theory; the variational upper bound is well below the first order estimate, and indeed is within three percent of the experimental value.

Proof. We derive this using a one-parameter family of wavefunctions like we did with the virial theorem. To choose our *variational Ansatz*, we use a physical argument. The idea is that if we want to model the dynamics of two electrons in the Helium atom as being non-interacting, we should adjust the effective value of the nuclear charge to account for screening, *i.e.*, each electron should on average see less than the full charge of the nucleus since the other electron is producing an electric field with the opposite sign. In other circumstances, this kind of an approximation is sometimes called a *mean field approximation*, and it can be quite effective.

To put this idea into practice, we adopt trial wave functions of the form

$$\psi_Z(\mathbf{x}_1,\mathbf{x}_2) = \left(\frac{Z^3}{\pi a_0^3}\right)\exp\left(-\frac{Z(r_1+r_2)}{a_0}\right) \ , \tag{9.19}$$

where Z is the parameter we will minimise over. This is the exact ground state for the effective Hamiltonian

$$H_Z = \frac{\mathbf{P}_1^2}{2m} + \frac{\mathbf{P}_2^2}{2m} - Zq_e^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right) = T + \frac{Z}{2}V \ , \tag{9.20}$$

satisfying $H_Z\psi_Z = E_Z\psi_Z$ with $E_Z = -Z^2q_e^2/a_0$, so indeed these are the ground state wave functions for systems of non-interacting electrons with an adjustable nuclear charge. We then want to minimise the Rayleigh quotient associated to the true Hamiltonian H evaluated on these states as a function of Z, so we need to compute

$$f_H(\psi_Z) = \mathbb{E}_{\psi_Z}(T) + \frac{2}{Z}\mathbb{E}_{\psi_Z}\left(\frac{ZV}{2}\right) + \mathbb{E}_{\psi_Z}\left(\delta H\right) \ . \tag{9.21}$$

The first two terms can be evaluated using the virial theorem with respect to the effective Hamiltonian H_Z, which gives us

$$\mathbb{E}_{\psi_Z}(T) = -E_Z = \frac{Z^2q_e^2}{a_0} \ , \qquad \mathbb{E}_{\psi_Z}\left(\frac{ZV}{2}\right) = 2E_Z = -\frac{2Z^2q_e^2}{a_0} \ . \tag{9.22}$$

The last term in (9.21) is precisely what we computed in our first-order perturbation theory calculation previously, and gives

$$\langle\psi_Z|\delta H|\psi_Z\rangle = q_e^2\left\langle\psi_Z\middle|\frac{1}{|\mathbf{x}_1-\mathbf{x}_2|}\middle|\psi_Z\right\rangle = \frac{5}{8}\frac{Zq_e^2}{a_0} \ . \tag{9.23}$$

Putting everything together, we have

$$f_H\left(\psi_Z\right) = \frac{q_e^2}{a_0}\left(Z^2 - \frac{27}{8}Z\right) = \frac{q_e^2}{a_0}\left[\left(Z-\frac{27}{16}\right)^2 - \left(\frac{27}{16}\right)^2\right] \ . \tag{9.24}$$

As a function of Z, this is minimised at $Z = \frac{27}{16}$, reflecting the extent to which each electron shields the charge of the nucleus to the other. From this we extract the upper bound

$$E_0 \leqslant f_H(\psi_{\frac{27}{16}}) = -\frac{q_e^2}{a_0}\left(\frac{27}{16}\right)^2 \ . \tag{9.25}$$

■

As we noted above, this is not only an upper bound but turns out to be a very good estimate for the ground state energy (compare the coefficient $(27/16)^2 \approx 2.85$ to the experimental value 2.92). The accuracy can be improved by considering a more general Ansatz for trial wave functions—indeed, an accuracy to within three parts in 10^8 has been obtained for this calculation using a family of *393 basis functions.*

The above result represents a marked improvement over what we got using elementary perturbation theory. The fact that we do better is not a coincidence at all. Indeed, we have the following.

Proposition 9.3.4. *Let $H = H_0+\delta H$ as before and let the family of states $\{\psi_\lambda\}$ over which we will minimise be chosen so that $\psi_0^{(0)}$ (the ground state of H_0) is contained in the family. Let $E_0^{(0)} + E_0^{(1)}$*

be the first order perturbation theoretic estimate of the ground state energy found before. Then for $E_{\text{var}} = \inf_{\{\psi_\lambda\}} f_H$ *we have*

$$E_0^{(0)} + E_0^{(1)} \geqslant E_{\text{var}} \geqslant E_{\text{ground}} \ . \tag{9.26}$$

Proof. Recall that $E_0^{(1)} = \left\langle \psi_0^{(0)} \middle| \delta H \middle| \psi_0^{(0)} \right\rangle$ so that

$$E_0^{(0)} + E_0^{(1)} = \left\langle \psi_0^{(0)} \middle| H_0 + \delta H \middle| \psi_0^{(0)} \right\rangle = f_H\left(\psi_0^{(0)}\right) \ , \tag{9.27}$$

and since $\psi_0^{(0)} \in \{\psi_\lambda\}$, this is an upper bound for the infimum of f_H on $\{\psi_\lambda\}$. ■

9.4 Approximating excited states

Though the ground state energy tends to be of particular interest, we may also want to approximate the energies of excited states. If we were to have perfect knowledge of the first k eigenstates $\psi_0, \dots \psi_{k-1}$, with energies $E_0, E_1, \dots, E_{k-1}$, say, then it would be straightforward to use the same variational ideas as we did above to approximate the $k+1$st state. Letting $\mathcal{H}_k = \text{Span}\{\psi_0, \dots, \psi_{k-1}\}$, we would have

Proposition 9.4.1. *If* $\inf_{\mathcal{H}_k^\perp} f_H$ *is attained for some* $\psi_k \in \mathcal{H}_k^\perp$*, then this is the* $k+1$*st lowest energy eigenstate, and* $f_H(\psi_k) \geqslant E_j$*,* $j = 0, \dots, k-1$*.*

Proof. Since $H : \mathcal{H}_k \to \mathcal{H}_k$, self adjointness implies that $H : \mathcal{H}_k^\perp \to \mathcal{H}_k^\perp$. Applying the main variational result for f_H on $\mathcal{H}_k^\perp$ gives that if f_H achieves its infimum at ψ_k, then $(H - f_H(\psi_k))\,|\psi_k\rangle = 0$ and ψ_k is the eigenstate with the lowest eigenvalue in $\mathcal{H}_k^\perp$. Since the lowest k eigenvalues are in $\mathcal{H}_k$, this must be the $k+1$st. ■

If we only had this result, we would be in the unfortunate situation of needing to have an exact result for lower lying states before approximating the higher ones. It turns out that we can proceed without knowledge of the first k eigenvectors/eigenvalues using the following important theorem.

Theorem 9.4.2 (Min-max)**.** *If the infimum*

$$\inf\left\{\max\{f_H(\psi) \ , \quad \psi \in \mathcal{K} \ , \quad \dim \mathcal{K} = k\}\right\} \tag{9.28}$$

is attained, where the infimum is taken over k*-dimensional subspaces* $\mathcal{K} \subset \mathcal{H}$*, then it is the* k*th lowest eigenvalue and the state on which it is attained the corresponding eigenvector.*

We will give the proof for the case where $\mathcal{H}$ has a basis of normalisable energy eigenstates. In the general case (involving generalised eigenstates), both the statement of the theorem and the proof become slightly more technical.

Proof. Let $E_0 \leqslant E_1 \leqslant E_2 \leqslant \dots$ be the ordered energy eigenvalues and let $\psi_0, \psi_1, \dots$ be the corresponding energy eigenstates. Let $\mathcal{H}_{k-1} = \text{Span}\{\psi_0, \dots, \psi_{k-2}\}$. Now for any k-dimensional subspace $\mathcal{K} \subset \mathcal{H}$, we will have $\dim\left(\mathcal{K} \cap \mathcal{H}_{k-1}^\perp\right) \geqslant 1$, so we can find a (normalised) vector $\psi \in \mathcal{K}$ that can be expressed in terms of the ψ_n for $n \geqslant k-1$.

$$\psi = \sum_{n=k-1}^{\dim \mathcal{H}} a_n \psi_n \ , \qquad \sum_{n=k-1}^{\dim \mathcal{H}} |a_n|^2 = 1 \ . \tag{9.29}$$

For which we have

$$f_H(\psi) = \sum_{n=k-1}^{d} |a_n|^2 E_n \geqslant \sum_{n=k-1}^{d} |a_n|^2 E_{k-1} = E_{k-1} \ , \tag{9.30}$$

so $\max_{\psi\in\mathcal{K}}\{f_H(\psi)\} \geqslant E_{k-1}$.

On the other hand, for $\mathcal{K} = \mathrm{span}\{\psi_0, \psi_1, \dots, \psi_{k-1}\}$ we have that $\max_{\psi\in\mathcal{K}} f_H(\psi) = E_{k-1}$, and the result follows. ■

Thus, the maximum value of f_H on $\mathcal{K}$ is an upper bound for E_{k-1}, and by varying the possible choices of $\mathcal{K}$ we can try to improve the bound. Indeed, this leads to a nice approximation scheme. To do so, we choose trial subspaces $\mathcal{K}$ (perhaps varying with respect to some parameters), and for a given trial subspace of dimension k, the maximum of f_H will be the largest eigenvalue of the restriction/projection of H to $\mathcal{K}$. So we can produce bounds (and potentially estimates) for E_{k-1} by solving finite-dimensional eigenvalue problems.

Chapter 10

WKB Approximation

We now come to a much different kind of approximation, the *semi-classical approximation* for stationary state wave functions. This is also known as the WKB approximation, in honour of the physicists Wentzel-Kramers-Brillouin who developed it in the mid 1920's. Unlike the approximation methods of the previous chapters, which were formulated in the abstract language of Hilbert spaces and observables, the semi-classical approximation that we will consider here is very much tailored to the study of wave functions in particular. Indeed, there is an entire branch of the analysis of PDEs known as *semi-classical analysis* that is closely related to the methods presented here.

We begin with a somewhat informal derivation of what we will momentarily come to understand as the zeroeth order WKB approximation. Recall that the momentum operator acts on wave functions according to

$$P\psi(x) = -i\hbar\psi'(x) \ . \tag{10.1}$$

Now for a given potential energy function $V(x)$ and a given energy E, the *classical* momentum of a particle with that energy at a given x (assuming $E > V(x)$) would be given by

$$p(x) = \sqrt{2m(E - V(x))} \ . \tag{10.2}$$

One might imagine then that a wave function for a state with energy E would obey something like an equation of the form

$$P\psi(x) \overset{?}{=} p(x)\psi(x) \ , \tag{10.3}$$

which is then a first order ODE that can be solved as

$$\psi(x) \overset{?}{=} \exp\left(\pm\frac{i}{\hbar}\int\limits_{x_0}^{x} p(s)\,\mathrm{d}s\right) \ . \tag{10.4}$$

In general, this analysis is obvioiusly flawed; in particular, when we evaluate the kinetic energy operator $P^2/2m$ on such a wave function, the second action of P will not only bring down another copy of $p(x)$ but will also differentiate $p(x)$. Consequently, this analysis exactly valid only when $p(x)$ is a constant, in which case we just have a plane wave solution as a generalised momentum/energy eigenstate.

Nevertheless, there is some appeal to the idea that the operator P should more or less look like the classical momentum as a function of x, at least in some kind of limit. Indeed, if there is a limiting situation in which quantum mechanics starts to systematically reduce to classical mechanics, you might very well expect such a relation to hold. It turns out there is such a limit, which is known as the *semi-classical limit*, and the above *ad hoc* wave function is just the first approximation in a systematic expansion.

10.1 The semi-classical expansion and WKB approximation

The starting point for making the previous procedure more systematic is to rewrite a stationary state wave function in terms of (the exponential of) its logarithm,

$$\psi(x) = \exp\left(\frac{iS(x)}{\hbar}\right) . \tag{10.5}$$

In light of the heuristic discussion before, we anticipate that the phase S might be related to the integral of the classical momentum in some regime. The time-independent Schrödinger equation in terms of this polar expression takes the form (after dividing through by $\psi(x)$ and rearranging some terms),[38]

$$S'(x)^2 - i\hbar S''(x) = 2m(E - V(x)) = p^2(x) . \tag{10.6}$$

The key assumption that we make at this point is that *as an expansion in* $\hbar$, we have

$$S(x) = S^{(0)}(x) + \hbar S^{(1)}(x) + \ldots . \tag{10.7}$$

This is sometimes referred to as a *semi-classical expansion*, since the parameter $\hbar$ can be thought of as characterising a scale where quantum effects become important, so the $\hbar \to 0$ limit should in some sense be a classical limit.[39]

Solving order by order in $\hbar$, we find that the first two terms in the semi-classical expansion of (10.6) and are given by

$$\begin{aligned} S_0'(x)^2 &= p(x)^2 , & (10.8)\\ 2S_0'(x)S_1'(x) &= iS_0''(x) . & (10.9) \end{aligned}$$

The first equation (10.8) can be solved to give

$$S_0(x) = \pm \int_{x_0}^{x} p(s)\,\mathrm{d}s , \tag{10.10}$$

where, as before, p represents the classical momentum as a function of position (and, implicitly, energy). This reproduces our heuristic result (10.4), as promised. Continuing to the first correction (10.9), we compute

$$iS_1'(x) = -\frac{p'(x)}{2p(x)} , \tag{10.11}$$

which we can integrate to find

$$iS_1(x) = -\log\left(\sqrt{p(x)}\right) . \tag{10.12}$$

The WKB approximation refers to the situation where we truncate the series at this order, giving

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[38] This equation is an instance of the so-called *Riccati equation* for $S'(x)$.

[39] In a physical context, one must be wary about the notion of taking $\hbar \to 0$, since $\hbar$ is a dimensionful parameter with units of angular momentum; one should instead want to take an appropriate collection of other dimensionful parameters in the problem and form a dimensionless combination involving $\hbar$ that can then be taken to zero by scaling the other variables relative to $\hbar$. For our analysis here it won't be important to keep track of this issue and we will instead treat $\hbar$ as a small parameter; this is what is most often done in the mathematical treatment of this subject.

us the approximate *WKB wave functions*

$$\psi_\pm(x) = \frac{1}{\sqrt{p(x)}} \exp\left(\pm \frac{i}{\hbar} \int\limits_{x_0}^{x} p(s)\, \mathrm{d}s \right) . \tag{10.13}$$

In general, this is a local approximation for the wave function and we need to be careful about what happens in the various regions of space, as we will see in a bit. However, there is a simple example where the analysis to this point is entirely sufficient to proceed.

Example 10.1.1. Consider the case of infinite potential barriers at, say, $x = a$ and $x = b$ with $a < b$, and assume $E > V(x)$ for $x \in (a, b)$. We then have a WKB wave function that should take the form

$$\psi_{\mathrm{WKB}}(x) = C_+\psi_+(x) + C_-\psi_-(x) , \qquad a \leqslant x \leqslant b , \tag{10.14}$$

and we need to impose the boundary conditions $\psi(a) = \psi(b) = 0$. Letting $x_0 = a$ in our expressions (10.13), the boundary condition at $x = a$ requires that we set $C_+ + C_- = 0$, so we have

$$\psi_{\mathrm{WKB}}(x) = \frac{C}{\sqrt{p(x)}} \sin\left(\frac{1}{\hbar} \int\limits_{a}^{x} p(s)\, \mathrm{d}s \right) . \tag{10.15}$$

Then the requirement $\psi(b) = 0$ gives the *quantisation condition*,

$$\frac{1}{\hbar} \int\limits_{a}^{b} p(x)\, \mathrm{d}x = n\pi , \qquad n = 1, 2, 3, \ldots . \tag{10.16}$$

For the case of constant potential $V = V_0$, this gives exactly the correct energy levels,

$$\sqrt{2m(E - V_0)}(b - a) = n\pi\hbar \quad \Longrightarrow \quad E = V_0 + \frac{n^2\pi^2\hbar^2}{2m(b-a)^2} . \tag{10.17}$$

Indeed, the WKB wave functions are exactly the correct stationary state wave functions for the constant potential case. In the case of a non-constant potential, (10.16) gives an approximation to the energy levels of the system.

For more general potentials (see Figure 4, for example), for a fixed value of E, $E - V(x)$ will become negative for some values of x. These regions in space are referred to as the *classically forbidden regions*, and as $p^2/2m = E - V < 0$, for these regions the “classical momentum” becomes pure imaginary. Assume that, as in the figure, $E - V(x) \geqslant 0$ on the interval $[a, b]$ with $b > a$, and is negative outside and vanishing at a and b. These two points are referred to as the *classical turning points*, since in a classical trajectory these would indeed be the points where the particle turned from moving right to moving left and vice versa.

In the classically forbidden regions, as the classical momentum becomes pure imaginary, we instead define the real quantity

$$q(x) = \sqrt{2m(V(x) - E)} , \tag{10.18}$$

which is a kind of analogue of the classical momentum in the forbidden region. We then solve (10.8)

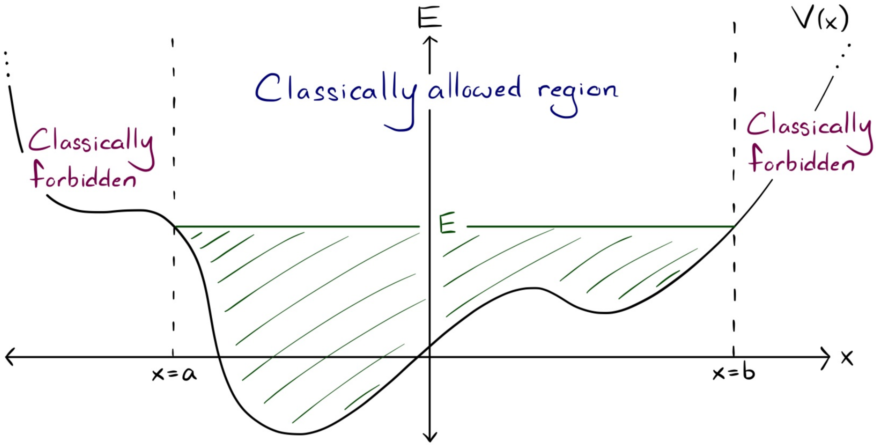

Figure 4. Example of a general potential with a single classically allowed region (between $x = a$ and $x = b$). A WKB wave function for this type of potential (and energy level as drawn) will be defined in three separate regions and subjected to connection conditions at the classical turning points $x = a$ and $x = b$.

with an *imaginary* $S(x)$,

$$S(x) = \pm i \int_{x_0}^{x} \sqrt{2m\,(V(s) - E)}\,\mathrm{d}s = \pm i \int_{x_0}^{x} q(s)\,\mathrm{d}s\ . \tag{10.19}$$

The $O(\hbar)$ term then proceeds analogously, and we arrive at the semiclassical WKB wave functions for classically forbidden regions,

$$\psi_{\pm}^{\text{forbidden}}(x) = \frac{1}{\sqrt{q(x)}} \exp\left(\pm \frac{1}{\hbar} \int_{x_0}^{x} q(s)\,\mathrm{d}s \right)\ , \tag{10.20}$$

which instead of being oscillatory are exponentially growing or decaying as a function of x. (Note that in a given classical forbidden region, $q(s)$ is strictly positive, so the integral is monotonically growing with x.)

10.2 WKB Connection Formulæ

In order for our solution to be normalisable, the solution in the left-most classically forbidden region must be exponentially growing with x (so decaying as $x \to -\infty$), and in the right-most forbidden region myst be exponentially decaying with x. Therefore, we would aim to have a solution of the form[40]

$$\psi(x)=\begin{cases}\frac{C_I}{\sqrt{q(x)}}\exp\left(-\frac{1}{\hbar}\int_x^a q(s)\,\mathrm{d}s\right)\ , & x<a\ ,\\ \frac{C_+}{\sqrt{p(x)}}\exp\left(\frac{i}{\hbar}\int_a^x p(s)\,\mathrm{d}s\right)+\frac{C_-}{\sqrt{p(x)}}\exp\left(-\frac{i}{\hbar}\int_a^x p(s)\,\mathrm{d}s\right)\ , & a<x<b\ ,\\ \frac{\tilde{C}_+}{\sqrt{p(x)}}\exp\left(\frac{i}{\hbar}\int_x^b p(s)\,\mathrm{d}s\right)+\frac{\tilde{C}_-}{\sqrt{p(x)}}\exp\left(-\frac{i}{\hbar}\int_x^b p(s)\,\mathrm{d}s\right)\ , & a<x<b\ ,\\ \frac{C_{II}}{\sqrt{q(x)}}\exp\left(-\frac{1}{\hbar}\int_b^x q(s)\,\mathrm{d}s\right)\ , & x>b\ .\end{cases} \tag{10.21}$$

There is an issue in deciding how to *connect* the exponentially increasing/decreasing solutions across the classical turning points at a and b to the oscillatory WKB wave functions in the classically allowed region. Indeed, all of our WKB wave functions actually diverge at a and b due to the denominator, which vanishes when $E=V(x)$. This is a breakdown in the WKB approximation in the vicinity of classical turning points.

To illuminate the situation, we perform an additional analysis in a *small neighbourhood of the classical turning point.* For $x\approx b$, say, we approximate the potential (assuming it is sufficiently smooth) according to

$$V(x)\approx V(b)+(x-b)V'(b)\ , \tag{10.22}$$

where in this case $V'(b)$ is positive. We then consider the Schrödinger eqaution for this approximation. Setting $y=x-b$ and $\tilde{\psi}(y)=\psi(x)$, we have

$$-\frac{\hbar^2}{2m}\tilde{\psi}''(y)=\left(E-V(b)-yV'(b)\right)\tilde{\psi}(y)=-yV'(b)\tilde{\psi}(y)\ . \tag{10.23}$$

Introducing a further variable $z=\left(2mV'(b)/\hbar^2\right)^{1/3}y$ and defining $\phi(z)=\tilde{\psi}(y)$, this becomes a famous ordinary differential equation, the *Airy equation*,

$$\phi''(z)=z\phi(z)\ . \tag{10.24}$$

We will take for granted the following integral expressions for a basis of solutions of the Airy equation (you can try to confirm for yourself that these solve the Airy equation by differentiating under the integral).

$$\begin{aligned}Ai(z)&=\frac{1}{\pi}\int_0^\infty\cos\left(\frac{t^3}{3}+zt\right)\,\mathrm{d}t\ ,\\ Bi(z)&=\frac{1}{\pi}\int_0^\infty\left(\sin\left(\tfrac{t^3}{3}+zt\right)+\exp\left(-\tfrac{t^3}{3}+zt\right)\right)\,\mathrm{d}t\ ,\end{aligned} \tag{10.25}$$

What's important for our purposes is the large $|z|$ asymptotics of these functions, which take the

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[40] Notice the somewhat strategic choice of limits of integration we have adopted. We have also given two versions of the wave function in the classically allowed region, one adapted for comparing to the left-most forbidden region and the other adapted for comparing to the right-most forbidden region.

form (again, feel free to take this for granted),

$$Ai(z) \sim \frac{\exp\left(-\frac{2}{3}z^{\frac{3}{2}}\right)}{2\sqrt{\pi}z^{\frac{1}{4}}}\ , \qquad Bi(z) \sim \frac{\exp\left(\frac{2}{3}z^{\frac{3}{2}}\right)}{\sqrt{\pi}z^{\frac{1}{4}}}\ , \qquad z \gg 1\ , \tag{10.26}$$

$$Ai(z) \sim \frac{\cos\left(\frac{2}{3}(-z)^{\frac{3}{2}} - \frac{\pi}{4}\right)}{\sqrt{\pi}(-z)^{\frac{1}{4}}}\ , \quad Bi(z) \sim \frac{\cos\left(\frac{2}{3}(-z)^{\frac{3}{2}} + \frac{\pi}{4}\right)}{\sqrt{\pi}(-z)^{\frac{1}{4}}}\ , \quad z \ll -1\ , \tag{10.27}$$

We see that it is $Ai(z)$ that behaves like a decaying exponential for large positive z, while $Bi(z)$ instead behaves like a growing exponential. This suggests that we should want to use the $Ai(z)$ solution to interpolate between the forbidden and allowed regions.[41]

Indeed, if we consider the forbidden-region decaying exponential WKB wave function in the right region and use the same approximation (10.22) for the potential near $x = b$, then we find

$$\begin{aligned}\frac{C_{II}}{\sqrt{q(x)}}\exp\left(-\frac{1}{\hbar}\int\limits_b^x q(s)\,\mathrm{d}s\right) &\approx \frac{C_{II}}{(2mV'(b)y)^{\frac{1}{4}}}\exp\left(-\left(\frac{2mV'(b)}{\hbar^2}\right)^{\frac{1}{2}}\int\limits_0^x s^{\frac{1}{2}}\,\mathrm{d}s\right)\ ,\\ &= \frac{C_{II}\exp\left(-\frac{2}{3}z^{\frac{3}{2}}\right)}{(2mV'(b)\hbar)^{\frac{1}{6}}z^{\frac{1}{4}}}\ ,\\ &\approx \kappa C_{II}Ai(z)\ .\end{aligned} \tag{10.28}$$

where $\kappa = 2\sqrt{\pi}/(2mV'(b)\hbar)^{\frac{1}{6}}$ is a numerical constant that we could also have absorbed into our overall constant. So this matches precisely the asymptotics of the $Ai(z)$ precisely up to a numerical factor! This allows us to indeed use $Ai(z)$ to interpolate from the forbidden to allowed region, and then in the allowed region we will have to match to an appropriate combination of oscillatory WKB wave functions.

To this end, we observe that in the allowed region we have, under the approximation (10.22) for $x \approx b$,

$$\begin{aligned}\frac{2C_{II}}{\sqrt{p(x)}}\cos\left(\frac{1}{\hbar}\int\limits_x^b p(s)\,\mathrm{d}s - \frac{\pi}{4}\right) &\approx \frac{2C_{II}}{(-2mV'(b)y)^{\frac{1}{4}}}\cos\left(\left(\frac{2mV'(b)}{\hbar^2}\right)^{\frac{1}{2}}\int\limits_y^0 (-s)^{\frac{1}{2}}\,\mathrm{d}s - \frac{\pi}{4}\right)\\ &= \frac{2C_{II}\cos\left(\frac{2}{3}(-z)^{\frac{3}{2}} - \frac{\pi}{4}\right)}{(2mV'(b)\hbar)^{\frac{1}{6}}(-z)^{\frac{1}{4}}}\ ,\\ &\approx \kappa C_{II}Ai(z)\ .\end{aligned} \tag{10.29}$$

We conclude that to interpolate with the $Ai(z)$ Airy function, we should choose $\tilde{C}_\pm$ in the allowed region so that they combine to give the first expression in (10.29). An analogous treatment at the turning point $x = a$ implies that the allowed-region WKB wave function on the right hand side of that turning point should be given by

$$\psi(x) = \frac{2C_I}{\sqrt{p(x)}}\cos\left(\frac{1}{\hbar}\int\limits_a^x p(s)\,\mathrm{d}s - \frac{\pi}{4}\right)\ . \tag{10.30}$$

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[41] In a careful treatment, we should further subdivide our space to include turning point regions where we use this Airy approximation, and these should overlap with the regions where the WKB wave functions are valid. This level of detail is important for an estimation of the size of errors in the WKB approximation, but will not be necessary for us.

The resulting connection formulæ are summed up in the following.

Proposition 10.2.1. *For continuation to the exponentially decreasing solution past the turning point at b we must have*

$$\tilde{C}_+ = C_{II}\mathrm{e}^{-\frac{\pi i}{4}} \ , \quad \tilde{C}_- = C_{II}\mathrm{e}^{\frac{\pi i}{4}} \quad \Longrightarrow \quad \psi(x) = \frac{2C_{II}}{\sqrt{p(x)}}\cos\left(\frac{1}{\hbar}\int\limits_x^b p(s)\,\mathrm{d}s - \frac{\pi}{4}\right) \ , \tag{10.31}$$

Similarly, for continuation to the solution that exponentially decays as $x \to -\infty$ past the turning point at a we must have

$$C_+ = C_I\mathrm{e}^{-\frac{\pi i}{4}} \ , \quad C_- = C_I\mathrm{e}^{\frac{\pi i}{4}} \quad \Longrightarrow \quad \psi(x) = \frac{2C_I}{\sqrt{p(x)}}\cos\left(\frac{1}{\hbar}\int_a^x p(x)\,\mathrm{d}s - \frac{\pi}{4}\right) \ , \tag{10.32}$$

Remark 10.2.2. Though not important in this particular analysis, one does run into situations where one wants to match onto the exponentially *growing* solution on the other side of the classical turning point. In this case, we have by an analogous analysis that if the wave functions in the forbidden regions are of the form

$$\psi_I(x) = \frac{D_I\exp\left(\frac{1}{\hbar}\int_x^a q(s)\,\mathrm{d}s\right)}{\sqrt{q(x)}} \ , \qquad \psi_{II}(x) = \frac{D_{II}\exp\left(\frac{1}{\hbar}\int_b^x q(s)\,\mathrm{d}s\right)}{\sqrt{q(x)}} \ , \tag{10.33}$$

then the matching must be done with the $Bi(z)$ Airy function and one has in the classically allowed region

$$\tilde{C}_+ = \frac{D_{II}}{2}\mathrm{e}^{\frac{\pi i}{4}} \ , \quad \tilde{C}_- = \frac{D_{II}}{2}\mathrm{e}^{-\frac{\pi i}{4}} \quad \Longrightarrow \quad \psi(x) = \frac{D_{II}}{\sqrt{p(x)}}\cos\left(\frac{1}{\hbar}\int\limits_x^b p(s)\,\mathrm{d}s + \frac{\pi}{4}\right) \ , \tag{10.34}$$

for matching to the right and

$$C_+ = \frac{D_I}{2}\mathrm{e}^{\frac{\pi i}{4}} \ , \quad C_- = \frac{D_I}{2}\mathrm{e}^{-\frac{\pi i}{4}} \quad \Longrightarrow \quad \psi(x) = \frac{D_I}{\sqrt{p(x)}}\cos\left(\frac{1}{\hbar}\int_a^x p(x)\,\mathrm{d}s + \frac{\pi}{4}\right) \ , \tag{10.35}$$

for matching to the left. Taken together, this full set of connection formulæ allow us to match an arbitrary solution across turning points.

Remark 10.2.3. An imporant feature of this result is that, when all is said and done, we can forget about the Airy functions and the interpolation region; the relation between the coefficients in the allowed and forbidden regions is fixed *universally* subject to only the assumption that the potential is smooth at the turning points.

Remark 10.2.4. There is another way of deducing these connection formulæ that is quite elegant, though the justification is not entirely transparent. The idea is to *analytically continue* the WKB wave functions around the classical turning point, avoiding the singularity, and matching on either side. In other words, for (say) the turning point at $x = a$, set $x - a = \rho\mathrm{e}^{i\phi}$, with ρ sufficiently large that the WKB approximation can plausibly stays reliable. Starting with the exponential solution in the forbidden region, we continue along the path in the upper half plane ($\phi \in (0, \pi)$) and this produces the coefficient C_- near a; the C_+ term is instead obtained by analytic continuation in the lower half plane ($\phi \in (\pi, 2\pi)$). In this treatment, the important phase shift by $\pi/4$ arises from the analytic continuation of the $1/\sqrt{p} \simeq (x - a)^{-\frac{1}{4}}$ factor. A similar analysis follows at $x = b$.

10.3 Bohr-Sommerfeld quantisation

We produced two expressions for the WKB wave function in the classically allowed region by matching to the appropriate exponential wave functions in both forbidden regions. The requirement that these two expressions agree gives the *Bohr-Sommerfeld quantisation rule*, which generalises the quantisation condition from our example to the case with finite potential in the classically forbidden regions.

Corollary 10.3.1 (Bohr-Sommerfeld quantisation rule)**.** *Normalisable semiclassical solutions satisfying the connection formulæ at classical turning points exist if and only if*

$$\int_a^b p(x)\,\mathrm{d}x = \left(n+\frac{1}{2}\right)\pi\hbar\ . \tag{10.36}$$

Proof. Equating the two expressions for the allowed-region WKB wave function we have

$$\frac{C_I}{\sqrt{p}}\cos\left(\frac{1}{\hbar}\int_a^x p(s)\,\mathrm{d}s-\frac{\pi}{4}\right)=\frac{C_{II}}{\sqrt{p}}\cos\left(\frac{1}{\hbar}\int_x^b p\,\mathrm{d}s-\frac{\pi}{4}\right)\ . \tag{10.37}$$

Rewriting

$$\frac{1}{\hbar}\int_x^b p(s)\,\mathrm{d}s-\frac{\pi}{4}=\frac{1}{\hbar}\int_a^b p(s)\,\mathrm{d}s-\frac{1}{\hbar}\int_a^x p(s)\,\mathrm{d}s-\frac{\pi}{4}\ , \tag{10.38}$$

and using evenness of cos, we have that one of the following must hold

$$\begin{aligned} C_I &= +C_{II}\ , & \frac{1}{\hbar}\int_a^b p(x)\,\mathrm{d}x &= \frac{\pi}{2}+2\pi n\ , & n&=0,1,2,\ldots\\ C_I &= -C_{II}\ , & \frac{1}{\hbar}\int_a^b p(x)\,\mathrm{d}x &= \frac{3\pi}{2}+2\pi n\ , & n&=0,1,2,\ldots \end{aligned} \tag{10.39}$$

which, allowing for either sign, gives the expected condition

$$\int_a^b p(x)\,\mathrm{d}x = \left(n+\frac{1}{2}\right)\pi\hbar\ , \qquad n=0,1,2,\ldots\ . \tag{10.40}$$

The correction factor of 1/2 coming from the connection conditions is known as the *Maslov correction.* ■

This condition is capable of giving surprisingly good answers. For example, it is *exact* for the simple harmonic oscillator.

A frequent interpretation/application of (10.36) arises from expressing the same quantity as an area integral. Indeed, if we identify the region $A(E)\subset\mathbb{R}^2_{x,p}$ where $p^2\leqslant 2m(E-V(x))$, then we estimate the *number of quantum states* corresponding to the classical states whose trajectories are confined to this region in phase space by

$$\#\ \text{states}(E) \approx n(E) = \frac{1}{\pi\hbar}\int_{a(E)}^{b(E)} p\,\mathrm{d}x = \frac{1}{2\pi\hbar}\iint_{A(E)} \mathrm{d}p\,\mathrm{d}x\ , \tag{10.41}$$

where the final equality involves a factor of two because the area of the region includes both the area above the x-axis and the area below it. Since wave functions decay exponentially fast outside the region, this number can also be thought of as an estimate of the number of states whose wave functions are supported in $A(E)$.

This formula is often summarised by saying that there is, roughly, a quantum state for each $2\pi\hbar$ unit of area in phase space; this can be generalised to systems in higher dimensions, in which case there is roughly one quantum state for each $(2\pi\hbar)^d$ unit of volume in phase space.

10.4 The radial WKB approximation

The WKB method we've been studying is particularly suited to the case of one-dimensional systems. We can easily extend this to three dimensional problems in the case where spherically symmetry allows us to restrict to definite angular momentum eigenstates and then solve a one-dimensional radial problem. Indeed, with central potential $V(\mathbf{x}) = V(r)$, we have for $\psi(\mathbf{x}) = R(r)Y_\ell^m(\theta,\phi)$ the radial (time-independent) Schrödinger equation,

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}(rR)\right] + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}R(r) = (E - V(r))\,R(r)\ , \tag{10.42}$$

which can be rewritten as a one-dimensional Schrödinger equation for $rR(r)$ (with a modified potential for nonzero angular momentum),

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2}(rR) = \left(E - V(r) - \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right)(rR)\ . \tag{10.43}$$

Consequently we have radial WKB wave functions given by

$$R_\pm(r) = \frac{1}{rp(r)^{\frac{1}{2}}}\exp\left(\pm\frac{i}{\hbar}\int^r p(r)\right)\ , \tag{10.44}$$

where

$$p(r)^2 = 2m\left(E - V(r) - \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right)\ . \tag{10.45}$$

In the case where $V(r)$ is a strictly increasing function of r (such as the harmonic oscillator or the Hydrogen atom), there is an important distinction between the case where $\ell = 0$ (spherically symmetric states), for which there is no inner turning point, and the case where $\ell \neq 0$, for which for any energy there will be an inner turning point as long as the potential diverges less-than-quadratically with radius at the origin. (See Figure 5.)

The semiclassical wave function must still satisfy the connection condition of 10.2.1 at $r = r_{\text{outer}}$. However, there is a new ingredient in the case when $\ell = 0$, which is that for $R(r)$ to be bounded, $rR(r)$ should vanish at the origin. As a result, we will have the sin combination of $R_\pm$ wave

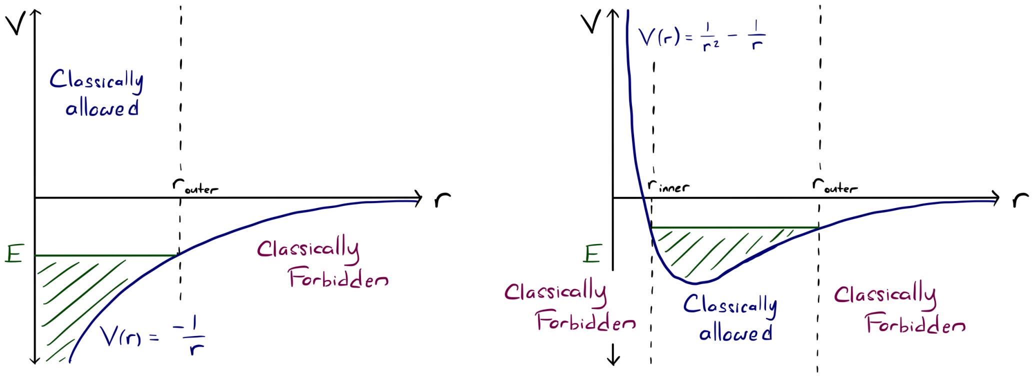

Figure 5. Radial potentials (in this case similar to the Coulomb potential) with and without “centrifugal” term from angular momentum. In the case without, there is a single classical turning point at r_{outer}, while for the case with angular momentum there is also an inner turning point at r_{inner}.

functions, and we have

$$R(r) = \frac{C}{rp(r)^{\frac{1}{2}}} \sin\left(\frac{1}{\hbar}\int_0^r p(s)\,\mathrm{d}s\right) = \frac{\tilde{C}}{rp(r)^{\frac{1}{2}}} \cos\left(\frac{1}{\hbar}\int_r^{r_{\text{outer}}} p(s)\,\mathrm{d}s - \frac{\pi}{4}\right) , \tag{10.46}$$

and to match both expressions we need

$$\frac{1}{\hbar}\int_0^{r_{\text{outer}}} p(s)\,\mathrm{d}s = \left(n + \frac{3}{4}\right)\pi , \qquad n = 0, 1, 2, \ldots \; . \tag{10.47}$$

For the Hydrogen atom, this yields good estimates for the energies of s-orbitals, as you will see on Problem Sheet 4.

Remark 10.4.1. For states with nonzero angular momentum, one has an inner turning point so there is a naive quantisation condition of the usual form,

$$\frac{1}{\hbar}\int_{r_{\text{inner}}}^{r_{\text{outer}}} p(s)\,\mathrm{d}s = \left(n + \frac{1}{2}\right)\pi , \qquad n = 0, 1, 2, \ldots \; . \tag{10.48}$$

There is a subtlety here, because the resulting exponentially decaying WKB wave function in the interior forbidden region won’t actually be bounded at $r = 0$ due to the enhanced singularity in the effective potential. There is a curious correction known as the *Langer correction* that can be implemented to improve errors arising from this problem at the origin, and you will encounter this as well in Problem Sheet 4.

Chapter 11

One Dimensional Scattering

We have spent most of our time in this course discussing normalisable stationary states, their properties, and the methods used to calculate them. In the application of quantum theory to the real world, there is another large and important subject that has something of a different flavour: the theory of *scattering.*

The basic formulation of the problem is as follows: we imagine that there is some “stuff” that is localised in space, and we want to predict what will happen if we throw some probe particle at the stuff. (Alternatively, one might be interested in observing the result of such throwing-a-particle-at-stuff experiments and reconstructing a microscopic model of the stuff. This is referred to as an *inverse scattering problem.*) The scattering problem arises in both classical dynamics and in quantum mechanics, but of course here we consider the quantum version. In this case one wants to assess the *probability amplitude* for various configurations of outgoing scattered particles.

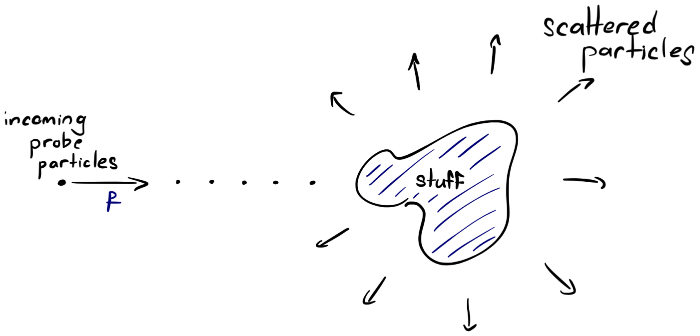

Figure 6. Cartoon representation of a scattering problem.

In the classical setting, we would specify the asymptotic trajectory (say, momentum and impact parameter) of the incoming probe particle in the far past (as you will recall from your study of hyperbolic orbits in the Kepler problem in prelims Dynamics) and predict the subsequent trajectory and, in particular, the late-time trajectory when the particle escapes back to infinity.

In the quantum mechanical setting, there is some subtlety in how we realise this intuitive scattering question within our mathematical formalism. The general treatment is quite technical. In this chapter we consider a simplified version of the story, where space is one-dimensional.

11.1 Left-right asymmetric scattering

We consider a situation as depicted in Figure 7, where the potential takes constant values outside of a bounded *interaction region.* The idea is then that particles will propagate freely in the L and R regions, so we can consider particles incident from, say, the left and ask for their amplitude to be either reflected back to the left or transmitted through the interaction region out to the right.

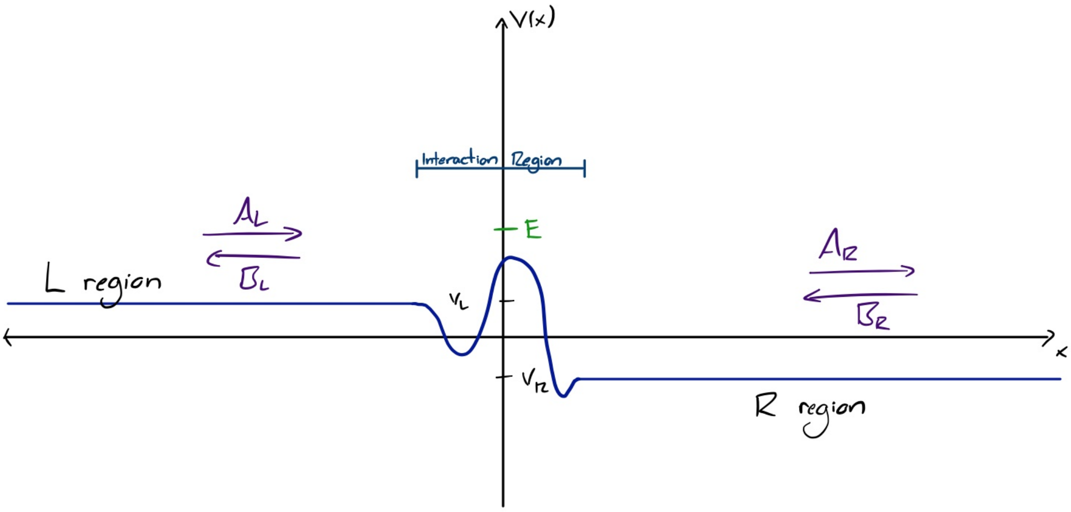

Figure 7. One-dimensional scattering with a localised interaction region.

To really model the process described above, we would need to perform a time-dependent analysis in which our initial state is a kind of a wave packet localised in the L region and moving to the right, and then we would ask for the late time behaviour of that state.

Fortunately, it turns out that we can treat this as a time independent problem. We consider (generalised) energy eigenstates with energy $E > V_{L,R}$, which will necessarily look like plane waves in the L and R regions,

$$\begin{aligned} &\text{for } x \in L\ , \quad \psi(x) = \psi_L(x) = A_L e^{ik_L x} + B_L e^{-ik_L x}\ , \qquad \hbar k_L = p_L\ , \qquad \frac{p_L^2}{2m} = E - V_L\ , \\ &\text{for } x \in R\ , \quad \psi(x) = \psi_R(x) = A_R e^{ik_R x} + B_R e^{-ik_R x}\ , \qquad \hbar k_R = p_R\ , \qquad \frac{p_R^2}{2m} = E - V_R\ . \end{aligned} \tag{11.1}$$

The $A_{L,R}$ terms correspond to the particle having positive momentum, while the $B_{L,R}$ terms describe negative momentum. In the "interaction region" the potential is nontrivial, and it may be difficult to produce an exact expression for the stationary state wave functions there, but on general grounds we konw there will be a two-dimensional space of such wave functions at fixed energy that will interpolate between the plane wave behaviour to the left and the right. Matching onto the solutions in the L and R regions, the form of these solutions will imply a linear relationship between the coefficients (A_L, B_L) and (A_R, B_R), which we encode in a (energy-dependent) matrix M,

$$\begin{pmatrix} A_L \\ B_L \end{pmatrix} = M \begin{pmatrix} A_R \\ B_R \end{pmatrix}\ . \tag{11.2}$$

Here we will focus on the case of *scattering from the left*, which we encode by setting $B_R = 0$, as this would represent some amplitude for the particle to be arriving from the right. In this case, we define the following physically important quantities.

Definition 11.1.1. *The* reflection coefficient R *and the* transmission coefficient T *are defined (as a function of energy) for one-dimensional scattering as described above by*

$$R = \frac{|B_L|^2}{|A_L|^2}\ , \qquad T = \frac{k_R |A_R|^2}{k_L |A_L|^2}\ . \tag{11.3}$$

These coefficients obey an important conservation condition related to their probabilistic interpretation.

Proposition 11.1.2. *The reflection and transmission coefficients are related according to*

$$R + T = 1 \ . \tag{11.4}$$

We interpret R as the probability that a particle incident from the left with energy E will be reflected off of the potential, and T to be the probability that the particle is transmitted through the potential.

Proof. The simple relation follows from the probability conservation condition for stationary states,

$$\partial_x j(x) = 0 \ , \qquad j(x) = \frac{\hbar}{2mi}\left(\overline{\psi(x)}\partial_x\psi(x) - \psi(x)\partial_x\overline{\psi}(x)\right) \ . \tag{11.5}$$

You have encountered this rule in your part A course, and it follows as an immediate consequence of the time-independent Schrödinger equation. Applying this to stationary *scattering states* as above, we have

$$j(x) = \begin{cases} \frac{p_L}{m}|A_L|^2 - \frac{p_L}{m}|B_L|^2 \ , & x \in L \ , \\ \frac{p_R}{m}|A_R|^2 - \frac{p_R}{m}|B_R|^2 \ , & x \in R \ . \end{cases} \tag{11.6}$$

Conservation of the probability current then equates the value of $j(x)$ on either side of the interaction region and gives

$$\frac{p_L}{m}|A_L|^2 + \frac{p_R}{m}|B_R|^2 = \frac{p_L}{m}|B_L|^2 + \frac{p_R}{m}|A_R|^2 \ . \tag{11.7}$$

setting $B_R = 0$ and dividing through by the left hand side gives $R + T = 1$. ■

Remark 11.1.3. Equation (11.7) is often understood in slightly different terms by making a somewhat different (and non-canonical) interpretation of these generalised energy eigenstates. If we say that a wave function of the form

$$\psi(x) = Ae^{\frac{ipx}{\hbar}} \ , \tag{11.8}$$

describes an *ensemble of particles* (sometimes people say a *beam of particles*) travelling with momentum p and density $|A|^2$, then the flow rate of these particles will be given by $\frac{p}{m}|A|^2$. In these terms, our probability current j is reinterpreted as an actual flow rate of particles, and the conservation rule becomes a conservation condition for the number of particles in a given region in a steady state: the rate of particles entering into the interaction region (left hand side) is equal to the rate of particles exiting (right hand side).

Remark 11.1.4. It is a remarkable (and not all that obvious) fact that the time-independent analysis given here is sufficient to make predictions about what happens in a more physical scattering setup when one starts with a wave packet approaching the interaction region from the left. The idea is that one can decompose a wave packet in, say, the L in term so of the scattering states (rather than the usual plane waves of Fourier analysis), and then the time evolution of the wave packet will proceed analogously to what we say in our discussion of the propagator in Chapter 2. Because the scattering states know about the structure of the interaction region, as the wave packet evolves the it will arrive from the left at the interaction region, do something in the interaction region, and ultimately there will be a reflected and a transmitted wave packed emitted to the left and right, respectively. Importantly, the relative amplitudes will be controlled by R and T (up to the issue of there being a spread of energies in the wave packet). A careful analysis of this story goes well beyond our treatment here, but the important conclusion is that this time-independent analysis capture the real physics of the situation!

11.2 Local potential scattering and the S matrix

To have a one-dimensional analogue of higher-dimensional scattering off of a localised potential, it is natural to impose that $V_L = V_R$. (In higher dimensions, if the potential is localised in one region then you can go *around* the potential and so the asymptotic value of the potential should be the same in every direction.) In this case, the conservation condition takes the even nicer form

$$|A_L|^2 + |B_R|^2 = |B_L|^2 + |A_R|^2 \ . \tag{11.9}$$

From a physical point of view (rather than that of solving ODEs), we should be inclined to think of the problem as being that of determining B_R and A_L (the amplitudes of the outgoing parts of the wave function) given A_L and B_R (the amplitudes of the incident parts of the wave function). As long as the upper left-hand component M_{11} of the matrix M, we can find such a relation:

$$\begin{pmatrix} A_R \\ B_L \end{pmatrix} = S \begin{pmatrix} A_L \\ B_R \end{pmatrix} \ , \qquad S = \begin{pmatrix} \frac{1}{M_{11}} & -\frac{M_{12}}{M_{11}} \\ \frac{M_{21}}{M_{11}} & \frac{\det M}{M_{11}} \end{pmatrix} \ . \tag{11.10}$$

By virtue of (11.9), the matrix S is a norm-preserving endomorphism of $\mathbb{C}^2$ and so a *unitary* 2×2 matrix. Indeed, this is a baby version an important object, the *unitary S-matrix*, which encodes the relationship between incoming and outgoing scattering wavefunctions. (This is an object of significant importance in relativistic quantum field theory and high energy particle physics, where scattering experiments are the main tool of the trade.)

We can then recognise the R and T coefficients in terms of the S matrix coefficients,

$$T = |S_{11}|^2 \ , \qquad R = |S_{21}|^2 \ , \tag{11.11}$$

and the condition $R + T = 1$ is a simple consequence of unitarity of S.

Remark 11.2.1. We specialised to scattering from the left, but we could also consider scattering from the right, in which case $A_L = 0$. Then the corresponding reflection and transmission coefficients would be given by $T_{\text{right}} = |S_{22}|^2$ and $R_{\text{right}} = |S_{12}|^2$, which obey an analogous conservation condition.

11.3 Piecewise constant potentials

A (somewhat contrived) class of examples that can be solved exactly, and consequently form a nice test environment for our methods, are the *piecewise constant* potentials (see Figure 8). For these we have a set of junction points $-\infty = a_0 < a_1 < \cdots < a_{n-1} < a_n = \infty$ and set

$$V(x) = V_i \ , \quad x \in (a_{i-1}, a_i) \ , \tag{11.12}$$

where in these conventions we have $V_L = V_0$ and $V_R = V_n$. Then our wave function will be piecewise a linear combination of plane waves or exponentials,

$$\psi(x) = \psi_i(x) = A_j e^{ik_j x} + B_j e^{-ik_j x} \ , \qquad x \in [a_{j-1}, a_j] \ . \tag{11.13}$$

(If in some region we have $E < V_j$, then we will define $k_j = i\mu_j$ with $\mu_j > 0$. Then the plane wave $e^{ik_j x}$ becomes a dying exponential $e^{-\mu_j x}$ while $e^{-ik_j x}$ becomes a growing exponential $e^{\mu_j x}$.)

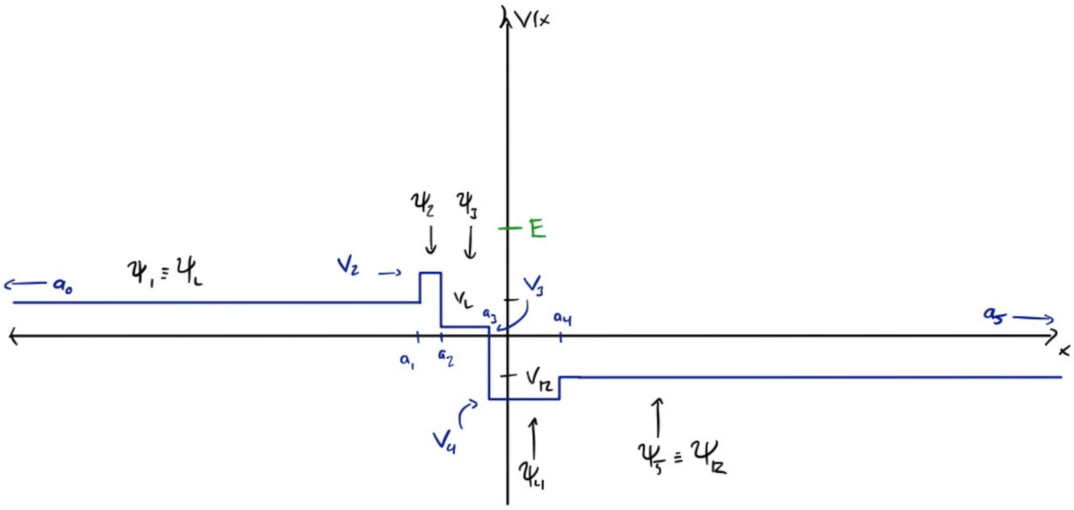

Figure 8. Scattering off of a piecewise constant potential.

The boundary conditions (continuity of ψ and ψ') at $x = a_i$ require

$$
\begin{aligned}
\psi_j(a_j) = \psi_{j+1}(a_j) \;\Rightarrow &\qquad A_j \mathrm{e}^{ik_j a_j} + B_j \mathrm{e}^{-ik_j a_j} = A_{j+1}\mathrm{e}^{ik_{j+1}a_j} + B_{j+1}\mathrm{e}^{-ik_{j+1}a_j} \ , \\
\psi_j'(a_j) = \psi_{j+1}'(a_j) \;\Rightarrow &\; k_j\left(A_j \mathrm{e}^{ik_j a_j} - B_j \mathrm{e}^{-ik_j a_j}\right) = k_{j+1}\left(A_{j+1}\mathrm{e}^{ik_{j+1}a_j} - B_{j+1}\mathrm{e}^{-ik_{j+1}a_j}\right) \ ,
\end{aligned}
\tag{11.14}
$$

and this condition can be solved to express the coefficients (A_j, B_j) in terms of (A_{j+1}, B_{j+1}). We encode the relation in a matrix M_j:

$$
M_j = \frac{1}{2k_j}\begin{pmatrix} s_j \mathrm{e}^{-id_j a_j} & d_j \mathrm{e}^{-is_j a_j} \\ d_j \mathrm{e}^{is_j a_j} & s_j \mathrm{e}^{id_j a_j} \end{pmatrix} \ , \qquad s_j = k_j + k_{j+1} \ , \quad d_j = k_j - k_{j+1} \ . \tag{11.15}
$$

We then have for our total scattering process, $M = M_1 M_2 \cdots M_{n-1}$

Example 11.3.1 (Single barrier scattering and tunnelling)**.** The simplest case of a piecewise constant scattering problem is that of scattering off of a rectangular barrier. In this case there are just two junction points, and as in Figure 9, for ease of notation we will set $a_1 = 0$, $a_2 = a$, $V_L = V_R = 0$, $V_1 = V$. For scattering from the left (in which case $B_R = 0$) we can write

$$
\begin{pmatrix} A_L \\ B_L \end{pmatrix} = M_1 M_2 \begin{pmatrix} A_R \\ 0 \end{pmatrix} \ , \tag{11.16}
$$

So ultimately we are interested in the left-hand column of the M matrix. Now specialising our general expression for the matrices M_j to our case, we have

$$
M_1 = \frac{1}{2k}\begin{pmatrix} s & d \\ d & s \end{pmatrix} \ , \quad M_i = \frac{1}{2k'}\begin{pmatrix} se^{ida} & -de^{-isa} \\ -de^{isa} & se^{-ida} \end{pmatrix} \ , \quad s = k + k' \ , \quad d = k - k' \ , \tag{11.17}
$$

which when composed gives us

$$
M = \frac{1}{s^2 - d^2}\begin{pmatrix} s^2 e^{ida} - d^2 e^{isa} & sd(e^{-ida} - e^{-isa}) \\ sd(e^{ida} - e^{isa}) & s^2 e^{-ida} - d^2 e^{-isa} \end{pmatrix} \ . \tag{11.18}
$$

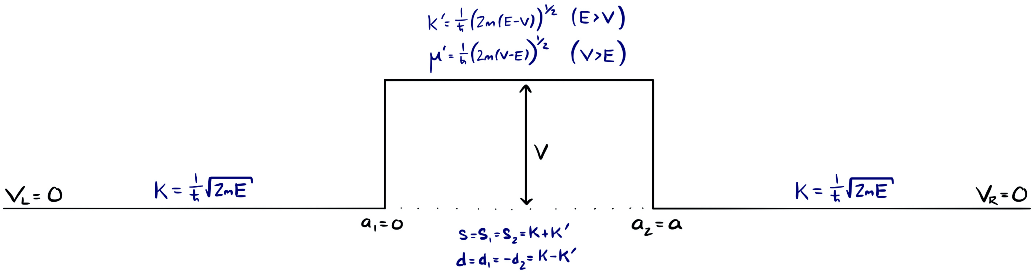

Figure 9. Scattering from a rectangular barrier.

With some massaging we compute the full S matrix, which is given by

$$
\begin{aligned}
S &= \frac{1}{d^2 e^{ias} - s^2 e^{iad}} \begin{pmatrix} d^2 - s^2 & ds(e^{-iad} - e^{-ias}) \\ ds(e^{iad} - e^{-ias}) & d^2 - s^2 \end{pmatrix} , \\
&= \frac{1}{2ikk' \cos(k'a) + (k^2 + k'^2)\sin(k'a)} \begin{pmatrix} 2ikk' e^{-ika} & (k^2 - k'^2)\sin(ak')e^{-2ika} \\ (k^2 - k'^2)\sin(ak') & 2ikk' e^{-ika} \end{pmatrix} .
\end{aligned}
\tag{11.19}
$$

From this we extract the reflection and transmission coefficients,

$$
\begin{aligned}
T &= \frac{4k^2 k'^2}{(k^2 + k'^2)^2 \sin^2(k'a) + 4k^2 k'^2 \cos^2(k'a)} , \\
R &= \frac{(k^2 - k'^2)^2 \sin^2(k'a)}{(k^2 + k'^2)^2 \sin^2(k'a) + 4k^2 k'^2 \cos^2(k'a)} .
\end{aligned}
\tag{11.20}
$$

As sanity checks, we can observe that as $k' \to k$ (so no barrier), $(T, R) \to (1, 0)$, and as $k' \to \infty$ (infinite barrier), $(T, R) \to (0, 1)$, and also that the unitarity condition $T + R = 1$ does indeed hold here.

To treat the case where $E < V$ transparently, we make the replacement $k' = i\mu'$ with $\mu' > 0$. Being careful with signs coming from imaginary arguments in trigonometric functions, we have

$$
\begin{aligned}
T &= \frac{4k^2 \mu'^2}{(k^2 - \mu'^2)^2 \sinh^2(\mu'a) + 4k^2 \mu'^2 \cosh^2(\mu'a)} , \\
R &= \frac{(k^2 + \mu'^2)^2 \sinh^2(\mu'a)}{(k^2 - \mu'^2)^2 \sinh^2(\mu'a) + 4k^2 \mu'^2 \cosh^2(\mu'a)} .
\end{aligned}
\tag{11.21}
$$

The most striking result here (though it was clear from the setting up of our problem that this would be the case) is that $T \neq 0$ when $E < V$. This is the phenomenon of *quantum tunnelling*, wherein a particle can transmit through a barrier that would classically block it completely; this behaviour have important technological applications, such as in scanning tunnelling microscopes.

Example 11.3.2 (Bound states and poles)**.** A close relative of our previous example is scattering from a rectangular potential *well*, as in Figure 10. In the first instance, we can simply repurpose our S matrix from the previous example, where now we will have $k' > k$, but otherwise everything will be the same as in (11.19).

The novel feature of this example is that in addition to the scattering states we've been studying,

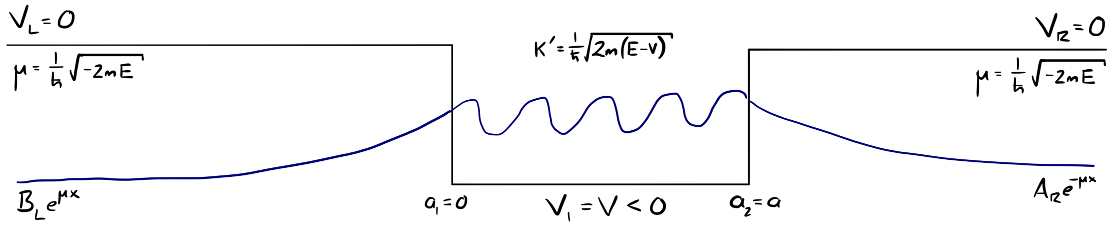

Figure 10. Bound state in a rectangular well.

there are also bound states with $V < E < 0$; the bound state wave functions will be of the form

$$\psi_{\text{bound}}(x) = \begin{cases} B_L e^{\mu x} \ , & x < 0 \ , \\ A_1 e^{ik'x} + B_1 e^{-ik'x} \ , & 0 < x < a \ , \\ A_R e^{-\mu x} \ , & x > a \ , \end{cases} \tag{11.22}$$

We observe that this is a wave function of precisely the type we considered for scattering states but with the replacement $k = i\mu$, $\mu = \sqrt{-2mE}$ just as in the previous example but now for the wavefunctions in the left and right regions.

Now the bound states correspond to solutions with $A_L = B_R = 0$, which by (11.10) requires that the S matrix become singular. Indeed, upon making the replacement $k \to i\mu$ the (now somewhat formal, as there is no scattering) S matrix takes the form

$$S = \frac{1}{2\mu k' \cos(k'a) + (\mu^2 - k'^2)\sin(k'a)} \begin{pmatrix} 2\mu k' \mathrm{e}^{\mu a} & (\mu^2 + k'^2)\sin(ak')\mathrm{e}^{2\mu a} \\ (\mu^2 + k'^2)\sin(ak') & 2\mu k' \mathrm{e}^{\mu a} \end{pmatrix} \ , \tag{11.23}$$

and each term becomes singular precisely when

$$2\mu k' \cos(k'a) + (\mu^2 - k'^2)\sin(k'a) = 0 \ . \tag{11.24}$$

Looking back to (11.2) the condition to be able to find a solution with $A_L = B_R = 0$ requires precisely that $M_{11} = 0$, and it is the M_{11} denominator in each entry of the S-matrix that is being set to zero by the condition above. For your own entertainment, you may wish to observe that if instead we take $k \to -i\mu$, then the *same bound states* are responsible for the S matrix developing a kernel.

Remark 11.3.3. What we've observed here is a shadow of a much more general phenomenon in quantum mechanical scattering, where information about bound states can be extracted from the analytic structure (zeroes and poles) of the continuation of scattering data to complex kinematical variables (in this case the asymptotic momentum).

Chapter 12

Epilogue

In this final chapter (with no corresponding lecture), we gesture towards some of the topics that, unfortunately, can't be made to fit into an eight week course but are equally deserving of discussion. I hope you might look into them independently if you have some interest.

Time dependent phenomena and methods

In almost the entirety of this course (with the exception of the discussion of the propagator early on) we have aggressively maintained a focus on aspects of the quantum theory that could be studied through time-independent methods. Of course, the world is dynamical and it is often useful to have more intrinsically time-dependent tools at one's disposal. Some key words in these areas are:

- **Pictures of time evolution.** Using the unitary time evolution operator $U(t_1; t_0)$, one can recast the subject of time evolution as applying to the *operators* of quantum theory rather than the states (this is called the *Heisenberg picture* of time evolution). One can go further and evolve states and operators using different time evolution operators (one involving interactions and one corresponding to free propagation). This leads to the *interaction picture.* This formalism is especially important in perturbative scattering theory.
- **Time-dependent perturbation theory.** A realistic, and therefore important, situation to deal with is when a system is perturbed in a manner that is explicitly time-dependent. This could mean that the "underlying" Hamiltonian is time-dependent (say, because you are on the surface of the Earth which is exposed to electromagnetic radiation from the sun periodically), or that we have an underlying time-independent system which we momentarily disturb in a dynamical way (say, by momentarily hitting a Hydrogen atom with a laser beam). This gives rise to slightly different questions than those we addressed in our analysis of perturbation theory. For example, at what rate will the time-dependent perturbation mediate transitions between some given eigenstates of the original system? If you shine a laser at a gas of Hydrogen atoms, how frequently do you expect to ionise the atoms (knock electrons out of bound states into scattering states)? In the case where the time-dependent effect is small, these problems can be treated by a generalisation of perturbation theory to a time-dependent context.

Remark 12.0.4. **Please observe that aspects of these subjects are present on the course synopsis, but as they did not fall within the material covered in the lectures this year you will not be responsible for them in exams.**

Higher-dimensional scattering

In more than one spatial dimension, the particulars of scattering gets quite a bit more complicated. In particular, the issue of angular dependence takes center stage: given particles incident on a local potential with a fixed momentum, how likely are they to be scattered in any particular direction? This is encoded in something called a differential cross section, and higher-dimensional scattering theory is largely tied up with calculating these cross sections.

The Feynman path integral

An influential "third way" of thinking about quantum theory (in contrast to the algebraic approach of Heisenberg or the differential equation approach of Schrödinger) was supplied by Richard Feynman in a 1948 paper (building on earlier work by himself and others, including Dirac). The idea, roughly, is if we want to compute the propagator,

$$U(x_f,t_f;x_i,t_i)=\langle x_f|U(t_f;t_i)|x_i\rangle \ . \tag{12.1}$$

then by repeated insertions of resolutions of the identity separated by very short time evolutions, one arrives at a picture where one should *sum over all possible trajectories* of the particle between the initial and final position. This sum over histories is encoded in the *Feynman path integral*, which is denoted as follows

$$U(x_f,t_f;x_i,t_i)=\int\limits_{x(t_i)=x_i}^{x(t_f)=x_f}[\mathcal{D}x]\mathrm{e}^{\frac{i}{\hbar}S[x(t)]} \ . \tag{12.2}$$

The beautiful result of Feynman's derivation is that the weight with which each trajectory contributes is the (imaginary exponential of) the *classical action* of that trajectory. The integration measure (denoted by $[\mathcal{D}x]$) is a subtle thing to make rigorous sense out of, nevertheless the intuition gained from this formulation has proven invaluable for quantum physicists. Indeed, from this perspective, the WKB approximation that we studied in Chapter 9.4 amounts to performing a stationary-phase approximation for the path integral!

You can learn all about path integrals in, for example, **C7.1 Theoretical Physics**.

Entanglement and quantum information theory

We only touched ever-so-briefly upon the issue of quantum entanglement. A more detailed study of the manipulation of finite quantum systems leads to the subject of quantum computing and quantum information theory, in which entanglement is leveraged to perform computational tasks that would seem impossible using conventional classical methods. You can learn all about this in **C7.4 Introduction to Quantum Information**.