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A Brief Overview of 2nd Year Quantum Mechanics

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[1]Please email me any mistakes you see, or with feedback/comments.

Acknowledgements

This text draws heavily from Griffiths' *Introduction to Quantum Mechanics* (3rd ed.) and also from prof. Essler's notes, which can be found at `http://www-thphys.physics.ox.ac.uk/people/FabianEssler/QM/QM2022.pdf` at the time of writing. Prof Parameswaran's notes were also helpful, and can be found on Canvas.

About This Text

This text is intended to be used in conjunction with textbooks and lectures. I have included some worked examples that may or may not be problem sheet questions.

Contents

Part I

Quantum Mechanics Course

Chapter 1

Formalism & Basic Ideas

1.1 Bra-ket Notation

We use a convenient notation for vectors: a vector (ket) may be written $|\psi\rangle$. If it is in a space with basis $\{|n\rangle\}$, i.e. the nth basis vector is $|n\rangle$, we may write $|\psi\rangle = \sum_n c_n |n\rangle$. We expand a general vector in its basis as per usual. Its dual vector (bra) may be written as $\langle\psi| = \sum_n c_n^* \langle n|$. The inner product between two vectors $|\psi\rangle$ and $|\phi\rangle$ may be written $\langle\psi|\phi\rangle$. Recall the complex conjugate flips the order of the inner product: $\langle\psi|\phi\rangle^* = \langle\phi|\psi\rangle$.

1.2 Operators

Recall an operator is an object which maps elements of one space to the same space. We show an object is an operator by giving it a hat, like so: $\hat{A}$. Recall in linear algebra that operators may be represented, in general, as matrices. This breaks down a bit for infinite dimensional spaces, but the important features, like eigenvalues and eigenvectors, do indeed generalise.

1.3 Postulates

Quantum mechanics is built on a foundation of postulates. I will list them and then revisit each in turn. This section is intended purely as a summary: all will be explained in due course.

Postulate 1. *The state of a system can be represented as a vector in a Hilbert space*[1]

Postulate 2. *A space for a composite system may be represented as the tensor product*[2] *of the Hilbert spaces of each part.*

Postulate 3. *Observable quantities, i.e. ones you can take a measurement of (like position or momentum), are represented by hermitian operators. The possible results of measuring an observable are given by the eigenvalues of the corresponding hermitian operator. For a system in a normalised state $|\psi\rangle$, with an operator $\hat{A}$ with eigenvalues a_i and eigenvectors $\{|a_i\rangle\}$, the probability of measuring the quantity A as having the value a_j is given by $|\langle a_j|\psi\rangle|^2$*

Postulate 4. *Suppose a system has state $|\psi\rangle = \sum_n c_n |n\rangle$. If it is measured as being in state $|j\rangle$ then the system collapses, in the sense its state becomes $|\psi\rangle \to |j\rangle$. Repeated measurements will always show the system is in state $|j\rangle$.*

Postulate 5. *The time evolution of a system is given by the time-dependent Shrödinger Equation.*[3]

1.4 States & Vectors

A state is an object that encodes information about the physical state of a system. A system may have a number of different configurations. For example, let's imagine the system might be in the

[1] For our purposes, consider this a vector space, which may be infinite-dimensional, equipped with an inner product.
[2] Luckily, very limited understanding of tensors is needed for this course.
[3] In theory this can be derived, and is therefore not a postulate, but for our purposes we may as well take it as one.

state $|\uparrow\rangle$ or $|\downarrow\rangle$. The key concept is that we have no idea what state the system is in until we measure it. To be more precise, it doesn't even make sense to ask the question 'what state is the system in?' until it is measured. It simply does not occupy a single well-defined state. However, suppose we know that, upon measurement, there is some probability that we will measure it in state $|\uparrow\rangle$ and some other probability we measure it in $|\downarrow\rangle$. The use of vectors to describe states neatly and cleanly packages all of these concepts up. We can describe the system with the vector

$$|\psi\rangle = \alpha\,|\uparrow\rangle + \beta\,|\downarrow\rangle\,.$$

It is a postulate that the probability of observing the system's state as $|\uparrow\rangle$ is $\langle\uparrow|\psi\rangle = \alpha\alpha^* = |\alpha|^2$. Similarly, the probability of observing the system's state as $|\downarrow\rangle$ is $\langle\downarrow|\psi\rangle = \beta\beta^* = |\beta|^2$. This is how one obtains probabilities of outcomes of measurement from state vectors.
We say a state is *normalised* if the probabilities add to 1, such that $|\alpha|^2 + |\beta|^2 = 1$. In some sense, the system is in both states, but also in neither.

1.5 Observables

An observable is a quantity such as position, which might take the value 'here' or 'there', or energy, which might take the value 1J, 10J, etc. In general, it is represented by a hermitian operator. As an observable can in theory be measured, its value must be a real number - you cannot measure a physically relevant quantity and get a complex number.

1.5.1 Hermitian Operators

Hermitian operators have some important properties that make them suitable to describe observable properties.

Claim 1. *Hermitian operators have real eigenvalues.*

Claim 2. *Eigenvectors corresponding to different eigenvalues are orthogonal, and in the degenerate case one can find orthogonal eigenvectors by the Gram-Schmidt procedure.*

These will not be proven here, but proofs can be found in any text on linear algebra.
It is a postulate that the possible values of an observable quantity are the eigenvalues of its corresponding hermitian operator. You can see that the fact these are always real checks out nicely. Furthermore, the orthogonality of the eigenvectors means that they are linearly independent and therefore form a basis. This is useful as it means we can fully expand a general state of the system in terms of the possible states that measurement of a particular observable can take.

1.5.2 Discrete Spectra & the Hamiltonian

The operator corresponding to the energy of a system is called the Hamiltonian, denoted $\hat{H}$. This satisfies the relationship $\hat{H}\,|n\rangle = E_n\,|n\rangle$, where $\{|n\rangle\}$ are the energy levels of the system and E_n is the energy associated with the system being in the nth level. This is an example of a discrete spectrum, as there is a discrete set of eigenvalues, i.e. they take individual, separate values. There may or may not be infinitely many of them.
The Hamiltonian (in most cases) represents total energy, which usually is kinetic + potential energy, although this changes a bit when angular momentum or electromagnetic fields are involved. In the simple case of a particle free to move within a potential we may write

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

1.5.3 Functions of Operators

A function can be understood in terms of its Taylor (Maclaurin) expansion. As powers of operators are just repeated applications of them, functions of operators such as $V(\hat{x})$ are well defined.

There us a trick we can use to investigate unknown operators and objects in general in QM: sandwich the object in between an $\langle x|$ and a $|\psi\rangle$. Consider V having Taylor expansion $V(t) = \sum_n c_n t^n$:

$$\begin{aligned}\langle x| V(\hat{x}) |\psi\rangle &= \sum_n c_n \langle x| \hat{x}^n |\psi\rangle \\ &= \sum_n c_n x^n \langle x|\psi\rangle\end{aligned}$$

and as x is just a number we can move the bra and ket around:

$$= \langle x| \underbrace{\sum_n c_n x^n}_{V(x)} |\psi\rangle$$

Hence $\langle x| V(\hat{x}) |\psi\rangle = \langle x| V(x) |\psi\rangle$.

1.5.4 Continuous Spectra & the Position Basis

A useful observable of a system is position. For example, where a particle is located. We represent the one-dimensional position state as $|x\rangle$, where x is the position along some line. In analogy to an expansion over all discrete basis vectors, we expand a general state (in the basis of position eigenstates) like so[4]:

$$|\psi\rangle = \int_{-\infty}^{\infty} \psi(x) |x\rangle \, dx.$$

with the ket $|x\rangle$ satisfying the following relations:

$$\begin{aligned}\hat{x} |x\rangle &= x |x\rangle \qquad (x \text{ are the eigenvalues of the position operator}) \\ \langle x'|x\rangle &= \delta(x - x') \qquad (\text{orthonormality})\end{aligned}$$

such that $|\psi\rangle$ is normalised:

$$\begin{aligned}\langle\psi|\psi\rangle &= \iint_{-\infty}^{\infty} \psi(x)\psi^*(x') \langle x'|x\rangle \, dx'dx = 1 \\ \implies &\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1\end{aligned}$$

The quantity $\psi(x) = \langle x|\psi\rangle$ is called the wavefunction. Similar to the discrete case, we interpret $\langle x|\psi\rangle$ as a probability associated with the position x, but in this continuous case it is a probability density function:

$$P(x_2 > x > x_1) = \int_{x_1}^{x_2} |\langle x|\psi\rangle|^2 dx = \int_{x_1}^{x_2} \psi\psi^* dx$$

It is important to notice that the physically relevant quantity is not the wavefunciton itself, but the square modulus of the wavefunction. Therefore, any overall phase of the wavefunction will disappear.

1.5.5 Resolution of the Identity

It can be easily shown (by acting with it on any ket) that the quantities

$$\sum_i |i\rangle \langle i| = I \qquad (\text{energy basis}) \qquad\qquad \int |x\rangle \langle x| \, dx = I \qquad (\text{position basis})$$

(amongst others) are equivalent to the identity operator.[5] We can then insert an I anywhere and leave the expression unchanged.

[4] The integral is guaranteed to converge as we are working in a Hilbert space.

[5] I will omit the bounds of integration from these kinds of integrals, allowing them to be inferred from context.

1.5.6 Representing Operators

Recall that if one uses a basis of eigenstates of an operator, that operator will be diagonal with columns made of the eigenstates scaled by their eigenvalues. This carries over to bra-ket notation, although it looks a little different. An operator $\hat{Q}$ with discrete eigenvalues q_i and eigenstates $|q_i\rangle$ can be represented as

$$\hat{Q} = \sum_i q_i \, |q_i\rangle \, \langle q_i|$$

An operator with a continuum of eigenstates, e.g. $\hat{x}$ can be represented in the same way, although the sum becomes an integral:

$$\hat{x} = \int x \, |x\rangle \, \langle x| \, dx$$

Another perspective on this is take the operator, say $\hat{p}$, and insert an identity to the right. As the identity does nothing to the operator, we simply get

$$\int \hat{p} \, |p\rangle \, \langle p| \, dp = \int p \, |p\rangle \, \langle p| \, dp$$

1.5.7 Expected Values

Consider the quantity $Q = \langle \psi | \, \hat{A} \, | \psi \rangle$ for some operator $\hat{A}$. Inserting an identity operator in the A-basis:

$$\begin{aligned} \hat{A} \, |a_i\rangle &= a_i \, |a_i\rangle \\ Q &= \sum_i \langle \psi | \, \hat{A} \, |a_i\rangle \, \langle a_i | \psi \rangle \\ &= \sum_i a_i | \, \langle a_i | \psi \rangle \, |^2 \end{aligned}$$

As a_i is the ith possible outcome of measuring A, and $| \, \langle a_i | \psi \rangle \, |^2$ is the probability associated with this, then Q is an expected value:

$$\langle \psi | \, \hat{A} \, | \psi \rangle = \langle A \rangle$$

1.5.8 Compatible Observables

Consider two observables $\hat{A}, \hat{B}$. Suppose we would like to measure $\hat{A}$ followed by $\hat{B}$ afterwards on the same system, originally in state $|\psi\rangle$. If we measure the system as in the eigenstate $|a_i\rangle$ of $\hat{A}$ on the first measurement, the state collapses to $|a_i\rangle$ such that the measurement of $\hat{B}$ is performed on this collapsed state. If we want the probability the system is in eigenstate $|b_j\rangle$ of $\hat{B}$, the scenario looks like this:

$$P(a_i \to b_j) = | \, \langle b_j | a_i \rangle \, \langle a_i | \psi \rangle \, |^2$$

Now if we did the measurement the other way around:

$$P(b_j \to a_i) = | \, \langle a_i | b_j \rangle \, \langle b_j | \psi \rangle \, |^2$$

Which are not in general the same[6] unless the two operators commute, in which case $|a_i\rangle, |b_j\rangle$ are simultaneously eigenstates of both operators, and the first inner product is zero due to orthogonality. This makes sense as repeated measurements of a system in an eigenstate will always yield the same eigenstate. Hence, the probability of the system being in a different eigenstate is zero. If two operators commute, we say they are compatible, and otherwise they are incomptible.

[6] For a proof see Fabian Essler's notes.

1.5.9 Operators on Wavefunctions

Consider $\langle x \rangle = \langle \psi | \hat{x} | \psi \rangle$. Inserting an identity:

$$\begin{aligned}\langle x \rangle &= \int \langle \psi | \, \hat{x} \, | x \rangle \, \langle x | \psi \rangle \, dx \\ &= \int \psi^* x \psi dx.\end{aligned}$$

And we think of x as representing $\hat{x}$ when acting on ψ within an integral - instead of $|\psi\rangle$ outside of one. We call this an operator on wavefunctions.

1.5.10 Momentum Operator and its Basis

The operator $\hat{p}$ satisfies

$$\langle x | \, \hat{p} \, | \psi \rangle = -i\hbar \partial_x \, \langle x | \psi \rangle$$

And from this[7] identify the corresponding operator on wavefunctions as

$$\hat{p} \equiv -i\hbar \partial_x$$

We can expand in a basis of eigenstates of the momentum operator, $\hat{p}$. The eigenstates satisfy

$$\hat{p} \, |p\rangle = p \, |p\rangle$$

Applying $\langle x|$ to both sides:

$$\begin{aligned}&\langle x | \, \hat{p} \, | p \rangle = -i\hbar \partial_x \, \langle x | p \rangle = p \, \langle x | p \rangle \\ \implies &\langle x | p \rangle = A e^{\frac{ipx}{\hbar}}\end{aligned}$$

So the position wavefunction of the momentum eigenstates are plane waves. Let us now find the constant of proportionality. We would like the $\hat{p}$ eigenstates to be normalised in the same way as the $\hat{x}$ ones:

$$\langle p | p' \rangle = \delta(p - p')$$

Resolve the identity:

$$\begin{aligned}&= \int \langle p | x \rangle \, \langle x | p' \rangle \, dx \\ &= |A|^2 \int e^{-ipx/\hbar} e^{ip'x/\hbar} dx\end{aligned}$$

use $u = x/\hbar$:

$$= \hbar |A|^2 \underbrace{\int_{-\infty}^{\infty} e^{-iu(p-p')} du}_{= 2\pi\delta(p-p')}$$

as it can be shown that the integral is precisely the delta function we want up to a factor. Hence:

$$\langle x | p \rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{ipx}{\hbar}}$$

Lets look at the momentum wavefunction, by inserting an identity:

$$\begin{aligned}\psi_p &= \langle p | \psi \rangle \\ &= \int \langle p | x \rangle \, \langle x | \psi \rangle \, dx \\ &= \frac{1}{\sqrt{2\pi\hbar}} \int e^{-\frac{ipx}{\hbar}} \psi dx\end{aligned}$$

So the momentum wavefunction is related to the Fourier transform of the position wavefunction.

[7] Using the fact $|x\rangle$ can be taken out of the derivative, we can write $\langle x | \, \hat{p} \, | \psi \rangle = \langle x | - i\hbar \partial_x | \psi \rangle$

1.5.11 Operators in Different Bases

We would like to find a representation of the position operator in the momentum basis. We can do this change of basis as follows. Making use of the 'sandwiching' trick, and resolving the identity:

$$\begin{aligned}\langle p|\hat{x}|\psi\rangle &= \int \langle p|x\rangle \langle x|\hat{x}|\psi\rangle \, dx \\ &= \int \frac{e^{-ipx/\hbar}}{\sqrt{2\pi\hbar}} x\psi_x dx \\ &= i\hbar\partial_p \int \frac{e^{-ipx/\hbar}}{\sqrt{2\pi\hbar}} \psi_x dx \\ &= i\hbar\partial_p \int \langle p|x\rangle \langle x|\psi\rangle \, dx \\ &= i\hbar\partial_p \psi_p \\ &= \langle p|i\hbar\partial_p|\psi\rangle\end{aligned}$$

So $\hat{x}$ is associated with $i\hbar\partial_p$ in the momentum basis.

1.5.12 Canonical Commutation Relation

We can use the properties of the momentum operator to find an invaluable relationship between $\hat{x}$ and $\hat{p}$. Using the same 'sandwiching' trick as before:

$$\langle x|\,[\hat{x},\hat{p}]\,|\psi\rangle = \langle x|\,\hat{x}\hat{p}\,|\psi\rangle - \langle x|\,\hat{p}\hat{x}\,|\psi\rangle$$

Here we use a trick where we consider $\langle x|\,\hat{x}$ as $(\hat{x}^\dagger\,|x\rangle)^\dagger$, and the fact $\hat{x} = \hat{x}^\dagger$ as the position operator is hermitian. You can visualise this trick as replacing $\hat{x}$ with $\hat{x}^\dagger$ and acting to the left on the bra.

$$\begin{aligned}&= x\langle x|\,\hat{p}\,|\psi\rangle + i\hbar\partial_x \langle x|\,\hat{x}\,|\psi\rangle \\ &= -i\hbar x\partial_x \langle x|\psi\rangle + i\hbar\partial_x(x\langle x|\psi\rangle) \\ &= -i\hbar x\partial_x \langle x|\psi\rangle + i\hbar x\partial_x \langle x|\psi\rangle + i\hbar\langle x|\psi\rangle \\ &= \langle x|\,i\hbar\,|\psi\rangle\end{aligned}$$

Hence $[\hat{x},\hat{p}] = i\hbar$.

1.6 The Uncertainty Principle

This is a theorem which carries a huge amount of weight. It is important to know and understand the proof. There are many different ways of showing it, so here is my favourite.[8] Consider two operators $\hat{A},\hat{B}$. We can write the variance in $\hat{A}$ as follows:

$$(\Delta\hat{A})^2 = \langle\psi|\,(\hat{A} - \langle A\rangle)^2\,|\psi\rangle$$

As $\hat{A}$ is hermitian, we have

$$= \langle f|f\rangle$$

where $|f\rangle = (\hat{A} - \langle A\rangle)\,|\psi\rangle$. Analogously, let $|g\rangle = (\hat{B} - \langle B\rangle)\,|\psi\rangle$. Hence:

$$(\Delta\hat{A})^2(\Delta\hat{B})^2 = \langle f|f\rangle\langle g|g\rangle$$

Applying the Cauchy-Schwarz inequality:

$$\geq \langle f|g\rangle\langle g|f\rangle = |\langle f|g\rangle|^2$$

For any complex number $z = \mathrm{Re}(z) + i\mathrm{Im}(z)$, $|z|^2 = (\mathrm{Re}(z))^2 + (\mathrm{Im}(z))^2 \geq (\mathrm{Im}(z))^2$. Hence

$$\begin{aligned}(\Delta\hat{A})^2(\Delta\hat{B})^2 &\geq (\mathrm{Im}(\langle f|g\rangle))^2 \\ &= \left(\frac{1}{2i}(\langle f|g\rangle - \langle g|f\rangle)\right)^2\end{aligned}$$

[8] Adapted from Griffiths.

Expanding out $\langle f|g\rangle - \langle g|f\rangle$ you will find it equals $\langle[\hat{A},\hat{B}]\rangle$. Hence

$$\Delta\hat{A}\Delta\hat{B} \geq \frac{1}{2i}\langle[\hat{A},\hat{B}]\rangle$$

In the case of position and momentum we have

$$\Delta\hat{x}\Delta\hat{p} \geq \hbar/2$$

1.7 Interference

The single-particle double slit experiment is commonly used in pop science to demonstrate the wave nature of particles. Let us first look at interference of classical wave phenomena.
For a two-source scenario, let the amplitudes at some point be u_1, u_2. The intensity (the measurable quantity in this case) is defined as

$$\begin{aligned} I &= \langle(u_1+u_2)(u_1+u_2)^*\rangle_t \\ &= |u_1|^2 + |u_2|^2 + \underbrace{2\langle \mathrm{Re}(u_1 u_2^*)\rangle_t}_{\text{interference term}} \end{aligned}$$

In the quantum double slit experiment, the particle is allowed to travel through a system of two slits without measurement. For the particle after it has travelled through the slit system, the (non-normalised) state vector is in the following superposition:

$$|\psi\rangle = |L\rangle + |R\rangle$$

With components for the particle travelling through the left or right slit. Hence we can find the wavefuntion and therefore the probability density:

$$\begin{aligned} \psi &= \langle x|L\rangle + \langle x|R\rangle \\ \psi\psi^* &= |\langle x|L\rangle|^2 + |\langle x|R\rangle|^2 + \underbrace{2\mathrm{Re}(\langle x|L\rangle\langle x|R\rangle^*)}_{\text{interference term}} \end{aligned}$$

However, if we place a detector on the right slit, the state vector (again, after travelling through the system) has the form (for example)

$$|\psi\rangle = |R\rangle$$

So the probability density is $|\langle x|R\rangle|^2$, with no interference term.

1.8 Worked Example: Commutators and the Momentum Operator

Question 1. *Find* $[f(\hat{x}),\hat{p}]$.

We begin by using the sandwiching method, where we put the commutator between the following kets. Take note of where the function of $\hat{x}$ becomes a function of x: $\langle x|f(\hat{x})|\psi\rangle = \langle x|f(x)|\psi\rangle$.

$$\begin{aligned} \langle x|[f(\hat{x}),\hat{p}]|\psi\rangle &= \langle x|f(\hat{x})\hat{p}|\psi\rangle - \langle x|\hat{p}f(\hat{x})|\psi\rangle \\ &= \int \langle x|f(\hat{x})|x'\rangle\langle x'|\hat{p}|\psi\rangle\,dx' + i\hbar\partial_x\langle x|f(\hat{x})|\psi\rangle \\ &= -i\hbar f(x)\int \delta(x-x')\partial_{x'}\psi dx' + i\hbar\partial_x(f(x)\psi) \\ &= -i\hbar f(x)\partial_x\psi + i\hbar f(x)\partial_x\psi + i\hbar\psi\partial_x f \\ &= \langle x|i\hbar\partial_x f|\psi\rangle \end{aligned}$$

So the commutator has value $i\hbar\partial_x f$.

Chapter 2

The Schrödinger Equation

This equation dictates the time evolution of the state of a quantum system, a bit like $F = ma$. It has the following form:[1]

$$\boxed{i\hbar\partial_t |\psi\rangle = \hat{H} |\psi\rangle}$$

You will use it time and time again. It has the following form for bras:

$$\boxed{-i\hbar\partial_t \langle\psi| = \langle\psi| \hat{H}}$$

2.1 Ehrenfest's Theorem

This is a useful theorem about the time evolution of expected values. Consider an operator $\hat{A}$:

$$\begin{aligned}\frac{d}{dt}\langle\hat{A}\rangle &= \frac{d}{dt}\langle\psi|\hat{A}|\psi\rangle \\ &= \partial_t(\langle\psi|)\hat{A}|\psi\rangle + \langle\psi|\partial_t(\hat{A})|\psi\rangle + \langle\psi|\hat{A}\partial_t|\psi\rangle\end{aligned}$$

And using the Schrödinger equation:

$$\begin{aligned}&= \frac{\langle\psi|\hat{H}\hat{A}|\psi\rangle}{-i\hbar} + \langle\partial_t\hat{A}\rangle + \frac{\langle\psi|\hat{A}\hat{H}|\psi\rangle}{i\hbar} \\ &= \langle\partial_t\hat{A}\rangle + \frac{1}{i\hbar}\langle[\hat{A},\hat{H}]\rangle\end{aligned}$$

2.1.1 Deriving Newton's Law

For the case of the position operator, which is time-independent;

$$\frac{d}{dt}\langle\hat{x}\rangle = \frac{1}{i\hbar}\langle[\hat{x}, \frac{\hat{p}^2}{2m} + V(x)]\rangle$$

The position operator commutes with $V(x)$ as it's a function of x only, but doesn't commute with the momentum operator:

$$\begin{aligned}&= \frac{1}{2mi\hbar}\langle[\hat{x},\hat{p}\hat{p}]\rangle \\ &= \frac{1}{2mi\hbar}\langle[\hat{x},\hat{p}]\hat{p}\rangle + \frac{1}{2mi\hbar}\langle\hat{p}[\hat{x},\hat{p}]\rangle \\ &= \langle\hat{p}\rangle/m\end{aligned}$$

Hence $m\frac{d}{dt}\langle\hat{x}\rangle = \langle\hat{p}\rangle$ as expected. So far so good. We would like to reproduce $F = ma$ so we need the time derivative of $\langle\hat{p}\rangle$:

$$\begin{aligned}\frac{d}{dt}\langle\hat{p}\rangle &= \frac{1}{i\hbar}\langle[\hat{p},\hat{p}^2/2m + V]\rangle \\ &= \frac{1}{i\hbar}\langle[\hat{p},V]\rangle\end{aligned}$$

[1] This is known as the Time Dependent Schrödinger Equation, or TDSE.

As $\hat{p}$ commutes with functions of itself, we only need to consider V;

$$\begin{aligned}\langle x|[\hat{p},V]|\psi\rangle &= -i\hbar\partial_x \langle x|V|\psi\rangle + i\hbar V\partial_x\psi \\ &= Vi\hbar\partial_x\psi - i\hbar\partial_x(V\psi) \\ &= -i\hbar\psi\partial_x V \\ &= \langle x| - i\hbar\partial_x V|\psi\rangle\end{aligned}$$

Where our aforementioned 'sandwiching' trick has been used. Hence:

$$\frac{d}{dt}\langle\hat{p}\rangle = -\langle\partial_x V\rangle$$

From which it follows that

$$m\frac{d^2}{dt^2}\langle\hat{x}\rangle = -\langle\partial_x V\rangle$$

2.2 Time Evolution of Systems in Energy Eigenstates

As the Schrödinger equation links energy (the Hamiltonian) and time evolution, it would make sense if energy eigenstates get special treatment in quantum mechanics. Let us consider a basis of energy eigenstates $|n\rangle$, i.e. $\hat{H}|n\rangle = E_n|n\rangle$. What is the time evolution of a general state in this basis?

$$|\psi\rangle = \sum_n c_n|n\rangle$$

As the states form a basis the only way the system can time evolve is if the components of the different basis vectors change over time, i.e.:

$$|\psi(t)\rangle = \sum_n c_n(t)|n\rangle$$

Let us apply the TDSE to $|\psi\rangle$.

$$i\hbar\sum_n \dot{c}_n(t)|n\rangle = \hat{H}\sum_n c_n(t)|n\rangle = \sum_n c_n E_n|n\rangle$$

Now bra through with $\langle m| \neq \langle n|$, making use of orthogonality:

$$\begin{aligned} & i\hbar\dot{c}_m(t) = c_m(t)E_m \\ \implies\ & c_m(t) = c_m(0)e^{-iE_m t/\hbar} \\ \implies\ & |\psi(t)\rangle = \sum_n c_n(0)e^{-iE_n t/\hbar}|n\rangle\end{aligned}$$

So for a system initially in an energy eigenstate, say the mth one, then $c_n(0) = \delta_{mn}$:

$$|\psi(t)\rangle = e^{-iE_m t/\hbar}|m\rangle$$

Hence it remains in the original eigenstate, only gaining a phase which would disappear when the square modulus is taken. For this reason the probabilities associated with energy eigenstates are time independent, and they are therefore referred to as 'stationary states'.

2.3 Position Representation of the TDSE

It is useful to work with operators on wavefunctions instead of operators on kets in certain problems. We would like to translate the TDSE into this language. It is straightforward to do. We will introduce a slightly different notation, for which the reason will become clear shortly; let $\langle x|\psi\rangle = \Psi(x,t)$. Now

bra through with $\langle x|$:

$$\begin{aligned} i\hbar\partial_t \langle x|\psi\rangle &= \langle x|\hat{H}|\psi\rangle \\ i\hbar\partial_t\Psi &= \frac{1}{2m}\langle x|\hat{p}^2|\psi\rangle + \langle x|V|\psi\rangle \\ &= -\frac{i\hbar}{2m}\partial_x \langle x|\hat{p}|\psi\rangle + V\Psi \\ &= -\frac{i\hbar}{2m}\partial_x(-i\hbar\partial_x\Psi) + V\Psi \\ &= -\frac{\hbar^2}{2m}\partial_x^2\Psi + V\Psi \end{aligned}$$

So we have

$$\boxed{i\hbar\partial_t\Psi = -\tfrac{\hbar^2}{2m}\partial_x^2\Psi + V\Psi}$$

Note we can make use of the concept of operators on wavefuncitons to associate $\hat{H}$ with $-\frac{\hbar^2}{2m}\partial_x^2 + V$.

2.3.1 Solutions by Separation of Variables

The standard way of solving these linear PDEs is by separation of variables (SOV). Let us separate into $\Psi(x,t) = \psi(x)\phi(t)$ and sub in:

$$\begin{aligned} i\hbar\psi\dot{\phi} &= -\frac{\hbar^2}{2m}\phi\psi'' + V\psi\phi \\ \frac{i\hbar\dot{\phi}}{\phi} &= -\frac{\hbar^2}{2m}\frac{\psi''}{\psi} + V \end{aligned}$$

As the LHS is a function of t only and the RHS one of x only, they must both equal a constant, E:

$$\boxed{\left[-\tfrac{\hbar^2}{2m}\tfrac{d^2}{dx^2} + V\right]\psi = E\psi}$$

Which we can recognise as a generalisation of the eigenvalue equation $\hat{H}|n\rangle = E_n|n\rangle$. This equation is known as the time independent Schrödinger Equation (TISE). This shows that the separation constant E does indeed correspond to energy. It also shows, crucially, that **any ψ obtained by solution of the TISE is an eigenstate of the Hamiltonian; a stationary state.** Now let's consider the time dependent part:

$$\begin{aligned} i\hbar\dot{\phi} &= E\phi \\ \implies \phi(t) &= \phi(0)e^{-iEt/\hbar} \end{aligned}$$

For a set of energy levels E_n we can superpose solutions due to the linearity of the TDSE:

$$\Psi(x,t) = \sum_n c_n\psi_n(x)e^{-iE_nt/\hbar}$$

This is the most general solution.

2.4 The Schrödinger Equation in Three Dimensions

2.4.1 Generalisation of the Momentum Operator

A trivial generalisation of $\hat{p}$ is the association $\hat{p} = -i\hbar\nabla$. Momentum is separated into 3 components $\hat{p}_i$ which satisfy $[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$. The TISE becomes

$$\boxed{\left[-\tfrac{\hbar^2}{2m}\nabla^2 + V\right]\psi = E\psi}$$

2.4.2 Probability Current

Probabiliy has a density, namely $\rho = \Psi\Psi^*$, and in some sense the total probability is conserved by the fact it adds up to 1 - so we would like to derive a continuity equation for it. Due to our choice of the Hamiltonian this only applies to particles in potentials. We will use the following representations of the TDSE:

$$\begin{aligned} i\hbar\partial_t\Psi &= \hat{H}\Psi \\ -i\hbar\partial_t\Psi^* &= \hat{H}\Psi^* \end{aligned}$$

Start with the time derivative of the probability density:

$$\begin{aligned} \partial_t\rho &= \Psi\partial_t\Psi^* + \Psi^*\partial_t\Psi \\ &= \frac{1}{i\hbar}(\Psi^*\hat{H}\Psi - \Psi\hat{H}\Psi^*) \\ &= \frac{1}{i\hbar}\left(\Psi^*\left(\frac{(-i\hbar\nabla)^2}{2m} + V\right)\Psi - \Psi\left(\frac{(-i\hbar\nabla)^2}{2m} + V\right)\Psi^*\right) \\ &= \frac{\hbar}{2im}\left(\Psi\nabla^2\Psi^* - \Psi^*\nabla^2\Psi\right) \end{aligned}$$

Now we use the following vector identity you will find in your formula book:

$$\begin{aligned} \nabla\cdot(\varphi\mathbf{F}) &= \mathbf{F}\cdot(\nabla\varphi) + \varphi(\nabla\cdot\mathbf{F}) \\ \implies \varphi(\nabla\cdot\mathbf{F}) &= \nabla\cdot(\varphi\mathbf{F}) - \mathbf{F}\cdot(\nabla\varphi) \end{aligned}$$

Now use $\varphi = \Psi$, $\mathbf{F} = \nabla\Psi^*$:

$$\Psi\nabla^2\Psi^* = \nabla\cdot\Psi\nabla\Psi^* - \nabla\Psi^*\cdot\nabla\Psi$$

And with $\varphi = \Psi^*$, $\mathbf{F} = \nabla\Psi$:

$$\Psi^*\nabla^2\Psi = \nabla\cdot\Psi^*\nabla\Psi - \nabla\Psi\cdot\nabla\Psi^*$$

Subtracting the two equations:

$$\partial_t\rho = \nabla\cdot\left(\frac{\hbar}{2im}(\Psi\nabla\Psi^* - \Psi^*\nabla\Psi)\right)$$

A continuity equation takes the form $\partial_t\rho = -\nabla\cdot\mathbf{j}$ so we identify

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

Chapter 3

Exact Solutions to the Schrödinger Equation

In this chapter we present various important situations in which we can find exact solutions for the wavefunction. Such situations are rare and most scenarios require perturbative or other inexact methods. We will visit these later.

3.1 The Free Particle

In this case $V = 0$ and the TISE becomes

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

With solutions

$$\psi = Ae^{ix\sqrt{2mE}/\hbar} + Be^{-ix\sqrt{2mE}/\hbar}$$

Now we add on the time dependent part:

$$\Psi = Ae^{i(x\sqrt{2mE}/\hbar - Et/\hbar)} + Be^{i(-x\sqrt{2mE}/\hbar - Et/\hbar)}$$

So we if we make the identification $k^2 = 2mE/\hbar^2$ and $\omega = E/\hbar$ we have

$$\Psi = Ae^{i(kx-\omega t)} + Be^{-i(kx+\omega t)}$$

So the free 'particle' has properties of a wave! Note we can identify $E = \hbar\omega$ (Planck relation) and then

$$\begin{aligned} E &= \frac{\hbar^2 k^2}{2m} \\ k^2 &= 2m\omega/\hbar \end{aligned}$$

We can find, in some sense, the 'momentum' of the wave by looking at the group velocity, which represents the rate of transfer of information about the wave's localisation:

$$\begin{aligned} kdk &= mdw/\hbar \\ \Rightarrow mv_{\text{group}} &= \hbar k \\ p &= \hbar k \end{aligned}$$

This is the de Broglie relation.

3.1.1 Time Evolution of the Free Particle

If we prepare a particle with a specific wavefunction as an initial condition, the Schrödinger equation dictates this wavefunction will change with time.

Notice that any value of k, and therefore E, yields a valid solution to the TISE. As it is linear, the most general solution is a superposition; this takes the form of an integral rather than a sum as k is a continuous variable. Hence:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} c(k) e^{i(kx-\omega t)} dk$$

Where the numerical factor has been extracted from $c(k)$ to make the expression look more like a Fourier transform, and k has been allowed to run negative to leave only a single exponential.
But what is the function $c(k)$? We have

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} c(k) e^{ikx} dk$$

Which is simply the (inverse) Fourier transform of $c(k)$. Hence, we may freely invert the Fourier transform:

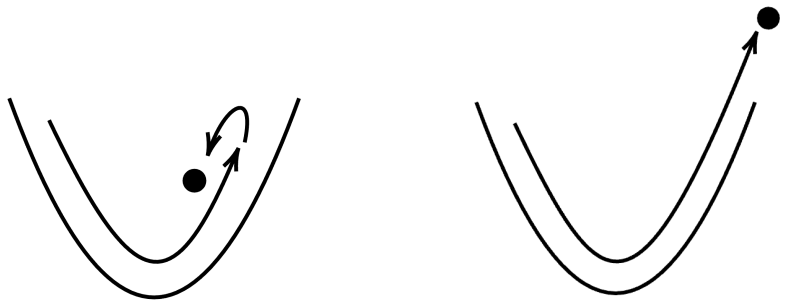
$$c(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0) e^{-ikx} dx$$

Hence, for a free particle, given some initial condition $\Psi(x,0)$, we can find the wavefunction at all future times $\Psi(x,t)$ by using the Fourier transform on the initial conditions.

3.2 Potential Wells in One Dimension

3.2.1 Bound and Scattering States

Consider a ball rolling down a hill. If it has enough kinetic energy to make it up the other side and actually escape the hill, the ball is in a scattering state. If it can't make it over and begins to roll down, it's in a bound state.



(a) Bound state (b) Scattering state

Figure 3.1: Particles with enough energy can escape a well; scattering states. Others, with less energy, are bound within.

3.2.2 Constraints on the Wavefunction

There are various constraints and boundary conditions that a wavefunction must satisfy. These are

1. ψ continuous
2. ψ normalised
3. ψ vanishes in regions of infinite V
4. ψ' discontinuous by a potential-dependent amount

We will now demonstrate the final two points. Consider the TISE:

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V\right]\psi = E\psi$$

just by looking at the equation[1] it is clear that as $V \to \infty$, $E \to \infty$ for a continuous[2] ψ unless $\psi \to 0$. Hence to maintain a finite (and therefore physical) energy we require that ψ vanishes in regions V is infinite.[3]
Now let us consider the discontinuity in the derivative of the wavefunction. If the potential is discontinuous at some point (we can arbitrarily make this the origin) We integrate the TISE over a very small surrounding region:

$$-\frac{\hbar^2}{2m}\int_{-\epsilon}^{\epsilon}\frac{d^2\psi}{dx^2}dx + \int_{-\epsilon}^{\epsilon}V\psi dx = E\int_{-\epsilon}^{\epsilon}\psi dx$$

The continuity of ψ means the RHS term goes to zero. Therefore the equation reads

$$\begin{aligned}\frac{\hbar^2}{2m}\left(\Delta\frac{d\psi}{dx}\right) &= \int_{-\epsilon}^{\epsilon}V\psi dx\\ \left(\Delta\frac{d\psi}{dx}\right) &= \frac{2m}{\hbar^2}\int_{-\epsilon}^{\epsilon}V\psi dx\end{aligned}$$

This specifies the discontinuity. Clearly if V jumps by a finite amount then the area of the infinitesimal sliver will go to zero. But if V jumps by an infinite amount, then there will be some area and the derivative will inherit a discontinuity.

3.2.3 Parity of Solutions

It can be proved that for an even potential, i.e. $V(x) = V(-x)$, solutions to the TISE are either even or odd. Consider replacing $x \to -x$: $\frac{d^2}{d(-x)^2} = \frac{d^2}{dx^2}$ so the TISE looks the same, but with $\psi(-x)$ instead:

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V\right]\psi(-x) = E\psi(-x)$$

So if $\psi(x)$ is a solution, so it $\psi(-x)$. There are now two possibilities. First, $\psi(x)$ could be linearly independent from $\psi(-x)$. Then we can construct even or odd solutions:

$$\begin{aligned}\psi_+ &= \psi(x)+\psi(-x)\\ \psi_- &= \psi(x)-\psi(-x)\end{aligned}$$

Alternatively, it could be linearly dependent:

$$\begin{aligned}&\psi(x) = A\psi(-x)\\ \Rightarrow\ &\psi(x) = A^2\psi(x)\\ &\Rightarrow A = \pm 1\end{aligned}$$

So either $\psi(x) = \psi(-x)$ or $\psi(x) = -\psi(-x)$; even and odd solutions. So for an even potential, wavefunctions have a well-defined parity.

3.2.4 Infinite Square Well

Consider the well defined by

$$V = \begin{cases}0 & 0 < x < a \quad \text{[region 1]}\\ \infty & \text{otherwise} \quad \text{[region 2]}\end{cases}$$

[1] Admittedly this is a non-rigorous approach.
[2] I.e. a finite ψ'.
[3] In a delta function potential, the region in question is a single point, and the probability of finding the particle at any single point is zero - consider integrating the probability density with both bounds being the same. Therefore in this case the potential doesn't go to zero and instead maintains continuity.

We tackle these problems by considering the TISE separately in different regions, and then imposing the aforementioned conditions on ψ. In region 1 we have

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = E\psi$$

With boundary conditions

$$\psi(0) = \psi(a) = 0$$

The solutions are

$$\psi = A\sin(kx) + B\cos(kx); \quad E = \frac{\hbar^2 k^2}{2m}$$

So applying the BCs, $B = 0$ and

$$\begin{aligned} k &= n\pi/a; n \in \mathbb{Z} \\ \Rightarrow E_n &= \frac{\hbar^2 n^2 \pi^2}{2ma^2} \end{aligned}$$

So the energies are quantised. The constant A can be determined by imposing the normalisation condition and is equal $\sqrt{2/a}$. Our final solution is

$$\psi_n = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$$

We can also set up the well with initial conditions, in which case we plug ψ_n into the general solution of the TDSE:

$$\begin{aligned} \Psi_n(x,t) &= \psi_n(x)e^{-iE_n t/\hbar} \\ \Psi(x,t) &= \sum_n c_n \psi_n(x) e^{-iE_n t/\hbar} \\ \Rightarrow \Psi(x,0) &= \sqrt{\frac{2}{a}}\sum_n c_n \sin\left(\frac{n\pi x}{a}\right) \end{aligned}$$

Which is a (sine) Fourier series, and the coefficients can be determined using the orthogonality of sine and cosine[4], then subbed back in to determine $\Psi(x,t)$.

3.2.5 Delta Function Well

$$V = -\underbrace{V_0}_{>0}\delta(x)$$

We will consider first the bound states, which in this case are[5] $E < 0$. We define region 1 to be $x < 0$ and region 2 to be $x > 0$. We have

$$\begin{cases} -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_1 = E\psi_1 \\ -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_2 = E\psi_2 \end{cases}$$

With solutions

$$\begin{cases} \psi_1 = Ae^{kx} + Be^{-kx} \\ \psi_2 = Ce^{kx} + De^{-kx} \end{cases}$$

[4] See mathematical methods course

[5] Bound states are usually defined as those with energy such that escape at infinity is impossible. In this case the potential goes to 0 at infinity so $E < 0$ is the bound state.

Where $k^2 = -2mE/\hbar^2$. To stop the wavefunction blowing up we have $B = C = 0$. So we have

$$\begin{cases} \psi_1 = Ae^{kx} \\ \psi_2 = De^{-kx} \\ \psi_1' = Ake^{kx} \\ \psi_2' = -Dke^{-kx} \end{cases}$$

Now we can calculate the discontiuity in the derivative:

$$\begin{aligned} \left(\Delta \frac{d\psi}{dx}\right) &= -\frac{2mV_0}{\hbar^2} \int_{-\epsilon}^{\epsilon} \delta(x)\psi dx \\ &= -\frac{2mV_0}{\hbar^2}\psi(0) \end{aligned}$$

Applying the BCs:

$$\begin{aligned} A = D &= \psi(0) \\ -k(A+D) &= -\frac{2mV_0}{\hbar^2}\psi(0) \\ \Rightarrow k &= \frac{mV_0}{\hbar^2} \\ \Rightarrow E &= -\frac{mV_0^2}{2\hbar^2} \end{aligned}$$

Now let's look at scattering ($E > 0$) states. The solutions now look like

$$\begin{cases} \psi_1 = Ae^{ikx} + Be^{-ikx} \\ \psi_2 = Ce^{ikx} + De^{-ikx} \end{cases}$$

with $k^2 = 2mE/\hbar$. Suppose we have a situation where particles are incident from $-\infty$. Also recall a factor of $e^{-iEt/\hbar}$ is multiplied on to each solution. This makes the solutions into plane waves, which means we can interpret A as incident amplitude, B as reflected amplitude C as transmitted amplitude and D as zero as there is no propagation right to left in region 2.

3.2.6 Transmission and Reflection Coefficients

Consider the scattering situation where we have two regions where the wavenumber may be different, i.e. k_1, k_2. Assuming waves are incident from left to right, the solutions in general will look like

$$\begin{cases} \psi_1 = A_i e^{ik_1 x} + A_r e^{-ik_1 x} \\ \psi_2 = A_t e^{ik_2 x} \end{cases}$$

Transmission and reflection coefficients take the form of *probabilities* of transmission and reflection. They are defined in terms of probability current:

$$\begin{aligned} T &= \frac{|\mathbf{j}_t|}{|\mathbf{j}_i|} \\ R &= \frac{|\mathbf{j}_r|}{|\mathbf{j}_i|} \end{aligned}$$

We can convert the definition of probability current from the previous chapter into a one-dimensional version:

$$j = \frac{i\hbar}{2m}(\Psi \partial_x \Psi^* - \Psi^* \partial_x \Psi)$$

The wavefunctions that we want are

$$\begin{aligned} \Psi_i &= A_i e^{i(k_1 x - Et/\hbar)} \\ \Psi_r &= A_r e^{i(-k_1 x - Et/\hbar)} \\ \Psi_t &= A_t e^{i(k_2 x - Et/\hbar)} \end{aligned}$$

After some algebra we get

$$j_i = \frac{\hbar k_1 |A_i|^2}{m}$$
$$j_r = -\frac{\hbar k_1 |A_r|^2}{m}$$
$$j_t = \frac{\hbar k_2 |A_t|^2}{m}$$

Now depending on the conditions on ψ, we may get different results for the coefficients as they depend on the amplitudes; different conditions yield different equations for the amplitudes. For a finite step potential, both ψ and ψ' will be continuous and the coefficients will be

$$T = \frac{4k_1 k_2}{(k_1 + k_2)^2}$$
$$R = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2$$

For the delta function potential we covered previously, we have that $k_1 = k_2 = k$. The continuity of ψ yields

$$A_i + A_r = A_t$$

And the derivative's discontinuity yields

$$ik(A_i - A_r) - \frac{2mV_0}{\hbar^2}\psi(0) = ikA_t$$

Let $K = \frac{2mV_0}{\hbar^2}$ and notice $\psi(0) = A_t$. Then we get

$$A_i - A_r = A_t(1 - iK/k)$$

Which gives

$$T = \frac{1}{1 + (K/2k)^2}$$
$$R = \frac{1}{1 + (2k/K)^2}$$

And in both cases $T + R = 1$ as expected.

3.2.7 Finite Square Well

The situation is

$$V = \begin{cases} 0 & |x| < a \quad \text{[region 1]} \\ V_0 & \text{otherwise} \quad \text{[region 2]} \end{cases}$$

We would like to consider first the bound states, i.e. $E < V_0$. The solution in region 1 is the same as in the infinite case:

$$\psi_1 = A\sin(k_1 x) + B\cos(k_1 x); \quad E = \frac{\hbar^2 k_1^2}{2m}$$

In region 2 we have

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_2 + V_0\psi_2 = E\psi_2$$

$$\psi_2'' = \underbrace{-\frac{2m(E - V_0)}{\hbar^2}}_{=k_2^2 > 0}\psi_2$$

Hence the solutions are exponentials:

$$\psi_2 = \begin{cases} Ce^{k_2 x} + De^{-k_2 x} & x < -a \\ Ee^{k_2 x} + Fe^{-k_2 x} & x > a \end{cases}$$

To stop ψ_2 blowing up at ∞ we require $D = E = 0$:

$$\psi = \begin{cases} Ce^{k_2 x} & x < -a \\ A\sin(k_1 x) + B\cos(k_1 x) & |x| < a \\ Fe^{-k_2 x} & x > a \end{cases}$$

$$\psi' = \begin{cases} Ck_2 e^{k_2 x} & x < -a \\ Ak_1\cos(k_1 x) - Bk_1\sin(k_1 x) & |x| < a \\ -Fk_2 e^{-k_2 x} & x > a \end{cases}$$

As the potential has only a finite jump, ψ' is continuous at $x = \pm a$. Recall ψ is always continuous too. Imposing these boundary conditions yields the following system of equations:

$$\begin{cases} e^{-k_2 a}(C + F) = 2B\cos(k_1 a) \\ e^{-k_2 a}(F - C) = 2A\sin(k_1 a) \\ \frac{k_1}{k_2} e^{-k_2 a}(F + C) = 2B\sin(k_1 a) \\ \frac{k_1}{k_2} e^{-k_2 a}(C - F) = 2A\cos(k_1 a) \end{cases}$$

Recall that solutions of the TISE with an even potential, such as this one, are even or odd - let's look for these solutions. $A = 0$ yields the even solutions, implying

$$k_2 = k_1 \tan(k_1 a)$$

While $B = 0$ yields odd solutions, giving

$$k_2 = -k_1 \cot(k_1 a)$$

Note that

$$k_2^2 = \frac{2mV_0}{\hbar^2} - k_1^2$$

So the equations become

$$k_1 \tan(k_1 a) = \sqrt{\frac{2mV_0}{\hbar^2} - k_1^2}$$
$$k_1 \cot(k_1 a) = -\sqrt{\frac{2mV_0}{\hbar^2} - k_1^2}$$

It can be shown[6] that there is always at least one bound state solution. Notice also that despite $E < V_0$, which would mean that classically the particle could not escape the well, the wavefunction is non zero outside the walls of the well. This is the phenomenon of quantum tunneling.

3.3 The Harmonic Oscillator

This is one of the most important situations that can arise in all of physics. It is important to know and understand it well. We will begin with the Hamiltonian for the quantum harmonic oscillator (QHO):

$$\boxed{\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2}$$

[6] See Griffiths.

3.3.1 Ladder Operators

We will now make an inspired guess at two operators which, as you will see, will allow us to find the eigenfunctions of the Hamiltonian and the corresponding energies.

$$\hat{a}_+ = \frac{1}{\sqrt{2m\omega\hbar}}(m\omega\hat{x} - i\hat{p})$$
$$\hat{a}_- = \frac{1}{\sqrt{2m\omega\hbar}}(m\omega\hat{x} + i\hat{p})$$

Notice that $\hat{a}_\pm = \hat{a}_\mp^\dagger$. These operators have the following useful property:

$$\begin{aligned}
\hat{a}_\pm\hat{a}_\mp &= \frac{1}{2m\omega\hbar}(m\omega\hat{x} \mp i\hat{p})(m\omega\hat{x} \pm i\hat{p}) \\
&= \frac{1}{2m\omega\hbar}((m\omega\hat{x})^2 + \hat{p}^2 \pm im\omega(\hat{x}\hat{p} - \hat{p}\hat{x})) \\
&= \frac{1}{2m\omega\hbar}((m\omega\hat{x})^2 + \hat{p}^2 \pm im\omega[\hat{x}, \hat{p}]) \\
&= \frac{1}{2m\omega\hbar}((m\omega\hat{x})^2 + \hat{p}^2 \mp m\omega\hbar) \\
&= \frac{\hat{H}}{\hbar\omega} \mp \frac{1}{2} \\
\Rightarrow \hat{H} &= \left(\hat{a}_\pm\hat{a}_\mp \pm \frac{1}{2}\right)\hbar\omega
\end{aligned}$$

3.3.2 Eigenfunctions and Eigenvalues

We claim that if $|\psi\rangle$ satisfies the TISE with eigenvalue E, i.e. $H|\psi\rangle = E|\psi\rangle$, then $\hat{a}_\pm|\psi\rangle$ also satisfies it with eigenvalue $E \pm \hbar\omega$. This can be seen as follows.

$$\begin{aligned}
\hat{H}\hat{a}_\pm|\psi\rangle &= \hbar\omega\left(\hat{a}_\pm\hat{a}_\mp \pm \frac{1}{2}\right)\hat{a}_\pm|\psi\rangle \\
&= \hbar\omega\hat{a}_\pm\hat{a}_\mp\hat{a}_\pm|\psi\rangle \pm \frac{\hbar\omega}{2}\hat{a}_\pm|\psi\rangle \\
&= \hbar\omega\hat{a}_\pm\left(\frac{\hat{H}}{\hbar\omega} \pm \frac{1}{2}\right)|\psi\rangle \pm \frac{\hbar\omega}{2}\hat{a}_\pm|\psi\rangle \\
&= \hat{a}_\pm E|\psi\rangle \pm \hbar\omega\hat{a}_\pm|\psi\rangle \\
&= (E \pm \hbar\omega)\hat{a}_\pm|\psi\rangle
\end{aligned}$$

So $\hat{a}_+$ increases the energy and $\hat{a}_-$ decreases it, like stepping up and down the rungs of a ladder. However, this cannot go down forever, as at some point one would reach oscillations with negative energy which are un-physical. There must be a lowest energy state. Let's find it, find the corresponding wavefunction, and then check the energy. Consider the fact that the inner product of two vectors is ≥ 0:

$$\begin{aligned}
\langle\psi|\hat{a}_+\hat{a}_-|\psi\rangle &= \langle\psi|\frac{\hat{H}}{\hbar\omega} - \frac{1}{2}|\psi\rangle \\
&= \frac{E}{\hbar\omega} - \frac{1}{2} \geq 0 \\
\Rightarrow E &\geq \frac{\hbar\omega}{2}
\end{aligned}$$

So we have a lowest eigenvalue. Hence there exists an eigenstate with lowest energy, satisfying

$$\begin{aligned}
\hat{a}_-|0\rangle &= 0 \\
\Rightarrow \frac{1}{\sqrt{2m\hbar\omega}}(mw\hat{x} + i\hat{p})|0\rangle &= 0
\end{aligned}$$

To convert this into an equation for the wavefunction, we bra through with an $\langle x|$ which yields

$$\frac{1}{\sqrt{2m\hbar\omega}}\left(m\omega x + \hbar\frac{d}{dx}\right)\psi_0 = 0$$

This is a differential equation that is easily solvable for the ground state wavefunction:

$$\begin{aligned}\psi_0' &= -(m\omega x/\hbar)\psi_0 \\ \Rightarrow \psi_0 &= Ae^{-\frac{m\omega}{2\hbar}x^2}\end{aligned}$$

The normalisation constant is calculated as usual with $\langle 0|0\rangle = 1$ and comes out to be $\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}$. Let's check the energy by plugging into the TISE:

$$\begin{aligned}E\psi_0 &= -\frac{\hbar^2}{2m}\psi_0'' + \frac{1}{2}m\omega^2x^2\psi_0 \\ \psi_0'' &= \frac{m\omega}{\hbar}\psi_0\left(\frac{m\omega x^2}{\hbar} - 1\right) \\ \Rightarrow E\psi_0 &= \frac{\hbar\omega}{2}\psi_0\end{aligned}$$

So this is indeed the minimum energy state. To get all other wavefunctions, simply operate on ψ_0 with $\hat{a}_+$ repeatedly. We can see that the energy of the nth state is $\hbar\omega(n + 1/2)$ as the energy is increased by $\hbar\omega$ in each step. There is one final problem to resolve; we have seen how $\hat{a}_\pm$ generates states with higher or lower eigenvalues, so it seems to be the case that acting on a state with $\hat{a}_\pm$ should also yield higher and lower *states* as well:

$$\hat{a}_\pm |n\rangle = c_\pm |n \pm 1\rangle$$

Now all that remains is to find the constants of proportionality. We do this by considering the inner product:

$$\begin{aligned}|c_\pm|^2 &= \langle n|\hat{a}_\mp\hat{a}_\pm|n\rangle \\ &= \langle n|\frac{\hat{H}}{\hbar\omega} \pm \frac{1}{2}|n\rangle \\ &= n + \frac{1}{2} \pm \frac{1}{2}\end{aligned}$$

So $c_+ = \sqrt{n+1}$ and $c_- = \sqrt{n}$.

3.3.3 What Oscillates?

It is not clear what is actually doing the oscillation. It is enlightening to look at the expected value of position, in the nth level:

$$\langle\hat{x}\rangle = \langle n(t)|\hat{x}|n(t)\rangle$$

By adding the raising and lowering operators, we can rewrite $\hat{x}$ as

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}_+ + \hat{a}_-)$$

Also, the states $|n\rangle$ only solve the TISE. To make them solutions of the TDSE, we need to add on the factor of $e^{-iE_nt/\hbar}$.

$$\langle\hat{x}\rangle = \sqrt{\frac{\hbar}{2m\omega}}\,\langle n|(\hat{a}_+ + \hat{a}_-)|n\rangle = 0$$

So it seems that the harmonic oscillator isn't doing any... oscillating. It turns out this is a feature of the eigenstates; they don't resemble the characteristic oscillatory states of a classical oscillator. However, it is possible to prepare states, known as coherent states, that oscillate in a 'nice' way. It

is also possible to see the oscillatory behaviour from general superpositions of states:

$$\begin{aligned}
\psi(t) &= \sum_j c_j e^{-i\omega(n+1/2)t} \left|j\right\rangle \\
\langle\hat{x}\rangle &= \langle\psi(t)|\hat{x}|\psi(t)\rangle \\
&= \sqrt{\frac{\hbar}{2m\omega}} \sum_j \sum_k c_j^* c_k e^{i\omega(j+1/2)t} e^{-i\omega(k+1/2)t} \left\langle j\right|(\hat{a}_+ + \hat{a}_-)\left|k\right\rangle \\
&= \sqrt{\frac{\hbar}{2m\omega}} \sum_j \sum_k c_j^* c_k e^{-i\omega t(j-k)} \left\langle j\right| \left(\sqrt{k+1}\left|k+1\right\rangle + \sqrt{k}\left|k-1\right\rangle\right) \\
&= \sqrt{\frac{\hbar}{2m\omega}} \sum_j \sum_k c_j^* c_k e^{-i\omega t(j-k)} (\sqrt{k+1}\delta_{j,k+1} + \sqrt{k}\delta_{j,k-1}) \\
&= \sqrt{\frac{\hbar}{2m\omega}} \left[\sum_j c_j^* c_{j-1} e^{-i\omega t}\sqrt{j} + \sum_k c_{k-1}^* c_k e^{i\omega t}\sqrt{k}\right] \\
&= \sqrt{\frac{\hbar}{2m\omega}} \sum_j \sqrt{j}(c_j^* c_{j-1} e^{-i\omega t} + c_{j-1}^* c_j e^{i\omega t})
\end{aligned}$$

Notice $c_j^* c_{j-1} e^{-i\omega t} + c_{j-1}^* c_j e^{i\omega t} = 2\mathrm{Re}(c_j c_{j-1}^* e^{i\omega t})$ and therefore let $c_j c_{j-1}^* = \alpha_j e^{i\phi_j}$:

$$\begin{aligned}
c_j^* c_{j-1} e^{-i\omega t} + c_{j-1}^* c_j e^{i\omega t} &= 2\alpha_j \cos(\omega t + \phi_j) \\
\Rightarrow \langle\hat{x}\rangle &= \sqrt{\frac{2\hbar}{m\omega}} \sum_j \sqrt{j}\alpha_j \cos(\omega t + \phi_j)
\end{aligned}$$

Hence we see oscillatory behaviour.

Chapter 4

Transformations and the Heisenberg Picture

This chapter is intended to give a very brief introduction to the relationship between operators and transformations, such as rotations or translations. The transformations we consider may be thought of as being carried out on the state itself, rather than the co-ordinate system: for example, in a translation we would move the system rather than the origin of our co-ordinates. We begin with one-dimensional translations.

4.1 Translations and the Momentum Operator

We introduce a translation operator $\hat{T}(\epsilon)$ that satisfies $\hat{T}(\epsilon)\,|x\rangle = |x+\epsilon\rangle$, i.e. translation by a small amount ϵ.

4.1.1 Translations on the Wavefunction

$$\hat{T}(\epsilon)\,|\psi(x)\rangle = |\psi'\rangle$$

It should be clear that if we move the system by ϵ, the translated wavefunction should look the same at the new point as the original did at the original point, i.e. $\psi'(x+\epsilon) = \psi(x)$ where $\langle x|\hat{T}(\epsilon)|\psi\rangle = \psi'(x)$. We can use this to prove the following property of $\hat{T}(\epsilon)$.

$$\begin{aligned}&\psi'(x+\epsilon) = \psi(x)\\ &\Rightarrow \psi'(x) = \psi(x-\epsilon)\end{aligned}$$

Notice we can express the RHS in bra-ket notation

$$\begin{aligned}\psi(x-\epsilon) &= \int \delta(x'-(x-\epsilon))\psi(x')dx'\\ &= \int \langle x-\epsilon|x'\rangle\,\langle x'|\psi\rangle\,dx'\\ &= \langle x-\epsilon|\psi\rangle\end{aligned}$$

So we have the equation

$$\begin{aligned}&\langle x|\hat{T}(\epsilon)|\psi\rangle = \langle x-\epsilon|\psi\rangle\\ &\Rightarrow \langle x|\,\hat{T}(\epsilon) = \langle x-\epsilon|\\ &\Rightarrow \hat{T}^{\dagger}(\epsilon)\,|x\rangle = |x-\epsilon\rangle\end{aligned}$$

Consider the inverse translation, satisfying $\hat{T}^{-1}(\epsilon)\,|x\rangle = |x-\epsilon\rangle$ (i.e. translation by $-\epsilon$). We therefore have

$$\hat{T}^{\dagger}(\epsilon) = \hat{T}^{-1}(\epsilon)$$

i.e. $\hat{T}(\epsilon)$ is a unitary operator.

4.1.2 Relationship with the Momentum operator

Consider a very small translation by ϵ. We propose $\hat{T}(\epsilon)$ has the form $I + G$ where G is some small matrix. We know $\psi'(x) = \psi(x - \epsilon)$, so we may Taylor expand for small epsilon:

$$\begin{aligned}
\langle x|\hat{T}(\epsilon)|\psi\rangle &= \psi'(x) = \psi(x-\epsilon) \\
&\approx \psi(x) - \epsilon\partial_x\psi \\
&= \langle x|I + G|\psi\rangle \\
&= \psi(x) + \langle x|G|\psi\rangle \\
\Rightarrow G &= -\epsilon\partial_x\psi \\
G &= -\frac{i\epsilon}{\hbar}\hat{p}
\end{aligned}$$

Hence $\hat{T}(\epsilon) = I - \frac{i\epsilon}{\hbar}\hat{p}$ for a very small translation. We can make any translation by successively doing a large number of these infinitesimal translations: let d be the total shift caused by N infinitesimal translations such that $d = N\epsilon$. Then we have

$$\hat{T}(d) = \lim_{N\to\infty}\left(I - \frac{id}{N\hbar}\hat{p}\right)^N$$

Which is precisely the limit definition of a matrix exponential - therefore we have

$$\hat{T}(d) = e^{-\frac{id\hat{p}}{\hbar}}$$

4.2 Rotations and the Angular Momentum Operator

The rotation operator, for a rotation by small angle ϵ about the z axis satisfies

$$R(\epsilon, z)|x, y, z\rangle = |x\cos(\epsilon) - y\sin(\epsilon), x\sin(\epsilon) + y\cos(\epsilon), z\rangle$$

Which can be deduced by considering the action of a rotation matrix on $\mathbf{r}$.

4.2.1 Rotations on the Wavefunction

In the same vein as the position operator we require the rotated wavefunction at rotated point is the same as the original at the original point:

$$\begin{aligned}
&\psi'(x', y', z') = \psi(x, y, z) \\
\Rightarrow\ &\psi'(x, y, z) = \psi(x\cos(\epsilon) + y\sin(\epsilon), -x\sin(\epsilon) + y\cos(\epsilon), z)
\end{aligned}$$

Where the second equality comes from undoing the transformation with an inverse rotation matrix. We now have the equation

$$\begin{aligned}
&\langle x|R(\epsilon, z)|\psi\rangle = \langle x\cos(\epsilon) + y\sin(\epsilon), -x\sin(\epsilon) + y\cos(\epsilon), z|\psi\rangle \\
\Rightarrow\ &R^\dagger(\epsilon, z)|x\rangle = |x\cos(\epsilon) + y\sin(\epsilon), -x\sin(\epsilon) + y\cos(\epsilon), z\rangle \\
&\Rightarrow R^\dagger(\epsilon, z) = R^{-1}(\epsilon, z)
\end{aligned}$$

So R is unitary.

4.2.2 Relationship with the Angular Momentum Operator

Now we use the fact the rotations are infinitesimal, use small angle approximations and Taylor expand:

$$\begin{aligned}
\psi'(x, y, z) &= \psi(x + y\epsilon, -x\epsilon + y, z) \\
&\approx \psi(x, y, z) + y\epsilon\partial_x\psi - x\epsilon\partial_y\psi
\end{aligned}$$

Now compare with the proposed form $R(\epsilon, z) = I + G$:

$$\langle x|I + G|\psi\rangle = \psi(x, y, z) + \langle x|G|\psi\rangle$$
$$\Rightarrow G = -\frac{\epsilon}{i\hbar}(\hat{y}\hat{p}_x - \hat{x}\hat{p}_y)$$

As you will see later, this is related to the angular momentum operator:

$$R(\epsilon, z) = I - \frac{i\epsilon}{\hbar}\hat{L}_z$$

We can now apply a large number $N = \theta/\epsilon$ to reach any angle θ:

$$R(\theta, z) = \lim_{N\to\infty}\left(I - \frac{i\theta}{N\hbar}\hat{L}_z\right)^N$$

Which is of course a matrix exponential

$$R(\theta, z) = e^{-\frac{i\theta\hat{L}_z}{\hbar}}$$

4.3 Time Translations and the Hamiltonian

By considering the Schrödinger equation

$$\boxed{i\hbar\partial_t|\psi(t)\rangle = \hat{H}|\psi(t)\rangle}$$

We can see that $|\psi(t)\rangle$ can be created by action on $|\psi(0)\rangle$ by the following operator, like so:

$$|\psi(t)\rangle = e^{-\frac{i\hat{H}t}{\hbar}}|\psi(0)\rangle$$

And hence we define the time evolution operator:

$$\hat{U}(t) = e^{-\frac{i\hat{H}t}{\hbar}}$$

As $\hat{H}$ is hermitian, $\hat{U}^\dagger(t)$ is simply given by

$$\hat{U}^\dagger(t) = e^{\frac{i\hat{H}t}{\hbar}}$$

And hence $\hat{U}(t)$ is unitary as $\hat{U}(t)\hat{U}^\dagger(t) = I$.

4.3.1 The Schrödinger and Heisenberg Pictures

There are two ways to consider the time evolution of an observable in quantum mechanics. The fist is the familiar picture, where bras and kets are time dependent and operators are time independent:

$$\langle\hat{O}_S\rangle = \langle\psi(t)|\hat{O}_S|\psi(t)\rangle$$

And the kets evolve as dictated by the Schrödinger equation. This is the Schrödinger picture. However, we could also write the bra and ket in terms of the time evolution operator:

$$\langle\hat{O}_S\rangle = \langle\psi(0)|\hat{U}^\dagger(t)\hat{O}_S\hat{U}(t)|\psi(0)\rangle$$

In this case we could consider the bras and kets time independent and the object $\hat{U}^\dagger(t)\hat{O}_S\hat{U}(t) = \hat{O}_H$ as a time-dependent operator. This is the Heisenberg picture. Using the fact $\hat{O}_S$ doesn't depend on time, we can derive the time evolution relationship of these operators too:

$$\partial_t\hat{O}_H = (\partial_t\hat{U}^\dagger)\hat{O}_S\hat{U} + \hat{U}^\dagger\hat{O}_S(\partial_t\hat{U})$$
$$\partial_t\hat{U}^\dagger = \frac{i}{\hbar}\hat{H}\hat{U}^\dagger$$
$$\partial_t\hat{U} = -\frac{i}{\hbar}\hat{H}\hat{U}$$
$$\Rightarrow \partial_t\hat{O}_H = \frac{i}{\hbar}(\hat{H}\hat{U}^\dagger\hat{O}_S\hat{U} - \hat{U}^\dagger\hat{O}_S\hat{H}\hat{U})$$

As $\hat{U}$ is a function of $\hat{H}$ only, it commutes with $\hat{H}$ and thus we can write

$$\partial_t\hat{O}_H = \frac{i}{\hbar}[\hat{H}, \hat{O}_H]$$

This is the Heisenberg equation of motion.

4.4 Invariance

Consider a transformation $\hat{\tau}$. If a system is invariant under $\hat{\tau}$ then measuring the energy of a system in state $|\psi\rangle$ should give the same result as that of a system in state $\hat{\tau}|\psi\rangle$. So if $|\psi\rangle$ is an eigenstate of the Hamiltonian then $\hat{\tau}|\psi\rangle$ should also be, with the same eigenvalue E:

$$\begin{aligned} \hat{H}|\psi\rangle &= E|\psi\rangle \\ \Rightarrow \hat{\tau}\hat{H}|\psi\rangle &= E\hat{\tau}|\psi\rangle \end{aligned}$$

And also

$$\hat{H}\hat{\tau}|\psi\rangle = E\hat{\tau}|\psi\rangle$$

By subtracting the last two equations it can be seen that $[\hat{\tau}, \hat{H}] = 0$. So for a system to be invariant under a transformation, said transformation must commute with the Hamiltonian.

4.5 Worked Example: Reflection Operator

Question 2. *Let $\hat{P}_{x_0}$ be the operator that reflects about a point x_0. Show that*

1. *the transformed wavefunction ψ' satisfies $\psi'(x) = \psi(2x_0 - x)$*
2. $\hat{P}_{x_0}|x_0 + x\rangle = |x_0 - x\rangle$
3. $\hat{P}_{x_0}\hat{x}\hat{P}_{x_0} = 2x_0 I - \hat{x}$
4. $\hat{P}_{x_0}\hat{p}\hat{P}_{x_0} = -\hat{p}$

Draw a number line and convince yourself that when a point x is reflected about x_0 it goes to $2x_0 - x$. The transformed wavefunction at the transformed point should equal the original wavefunction at the original point, as we have seen already in this chapter: $\psi'(2x_0 - x) = \psi(x)$ from which the first part follows immediately. To show the second part holds is also simple: we already know $\hat{P}_{x_0}|x\rangle = |2x_0 - x\rangle$, and the answer follows a simple replacement of x with $x_0 - x$. For the third part, begin by inserting an identity after the expression:

$$\begin{aligned} \hat{P}_{x_0}\hat{x}\hat{P}_{x_0} &= \int \hat{P}_{x_0}\hat{x}\hat{P}_{x_0}|x\rangle\langle x|\,dx \\ &= \int \hat{P}_{x_0}\hat{x}|2x_0 - x\rangle\langle x|\,dx \end{aligned}$$

Now $|2x_0 - x\rangle$ is still a position eigenstate so the $\hat{x}$ operator acts on it as you would expect:

$$\begin{aligned} &= \int (2x_0 - x)\hat{P}_{x_0}|2x_0 - x\rangle\langle x|\,dx \\ &= \int (2x_0 - x)|x\rangle\langle x|\,dx \end{aligned}$$

What could this operator be? Let's make an 'informed' guess of $2x_0 I - \hat{x}$. Inserting an identity:

$$\begin{aligned} 2x_0 I - \hat{x} &= \int (2x_0 I - \hat{x})|x\rangle\langle x|\,dx \\ &= \int (2x_0 - x)|x\rangle\langle x|\,dx \end{aligned}$$

So the expressions are equal, and we 'guessed' correctly. This isn't a great argument, so maybe send me an email if you come up with a better one. Anyway, for the last part we need to prove an

intermediary result. Consider the following

$$\begin{aligned}
\langle x|\hat{P}_{x_0}|\psi\rangle &= \langle x|\psi'\rangle \\
&= \psi'(x) \\
&= \psi(2x_0 - x) \\
&= \int \delta(x' - (2x_0 - x)) \langle x'|\psi\rangle \, dx' \\
&= \int \langle 2x_0 - x|x'\rangle \langle x'|\psi\rangle \, dx' \\
&= \langle 2x_0 - x|\psi\rangle
\end{aligned}$$

So clearly $\langle x| \hat{P}_{x_0} = \langle 2x_0 - x|$. Now let's use the sandwiching method again:

$$\begin{aligned}
\langle x|\hat{P}_{x_0}\hat{p}\hat{P}_{x_0}|\psi\rangle &= \langle 2x_0 - x|\hat{p}\hat{P}_{x_0}|\psi\rangle \\
&= -i\hbar \frac{\partial}{\partial(2x_0 - x)} \langle 2x_0 - x|\hat{P}_{x_0}|\psi\rangle \\
&= -i\hbar \frac{dx}{d(2x_0 - x)} \partial_x \langle x|\psi\rangle \\
&= \langle x|i\hbar\partial_x|\psi\rangle
\end{aligned}$$

Which clearly demonstrates the fourth part of the question.

Chapter 5

Angular Momentum

5.1 Orbital Angular Momentum

Angular momentum is defined as $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. We can use an analogous definition here, with components 1, 2 and 3 corresponding to x, y, z:

$$\hat{L}_i = \epsilon_{ijk} \hat{x}_j \hat{p}_k$$

Now consider the commutator

$$\begin{aligned}
[\hat{L}_x, \hat{L}_y] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] \\
&= [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] \\
&= \hat{y}[\hat{p}_z, \hat{z}]\hat{p}_x + \hat{x}[\hat{z}, \hat{p}_z]\hat{p}_y \\
&= i\hbar(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) \\
&= i\hbar\hat{L}_z
\end{aligned}$$

By cyclically permuting the components we can derive the general relationship

$$[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k$$

Let $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$. It can be shown (tediously)[1] that $[\hat{L}^2, \mathbf{L}] = 0$, i.e. $\hat{L}^2$ commutes with all components. Hence it is possible to find simultaneous eigenstates of $\hat{L}^2$ and $\hat{L}_z$.

5.1.1 Ladder Operators

We begin by defining the following operators:

$$\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y$$

It should be clear that $\hat{L}_\pm^\dagger = \hat{L}_\mp$. Some useful relationships for you to prove are

$$\begin{aligned}
[\hat{L}_z, \hat{L}_\pm] &= \pm\hbar\hat{L}_\pm \\
[\hat{L}^2, \hat{L}_\pm] &= 0
\end{aligned}$$

Hence, consider the following. If $|\psi\rangle$ is an eigenstate of $\hat{L}^2$, i.e. $\hat{L}^2|\psi\rangle = \lambda|\psi\rangle$:

$$\begin{aligned}
&[\hat{L}^2, \hat{L}_\pm]|\psi\rangle = \hat{L}^2\hat{L}_\pm|\psi\rangle - \hat{L}_\pm\hat{L}^2|\psi\rangle = 0 \\
&\Rightarrow \lambda\hat{L}_\pm|\psi\rangle = \hat{L}^2\hat{L}_\pm|\psi\rangle
\end{aligned}$$

So $\hat{L}_\pm|\psi\rangle$ is also an eigenstate of $\hat{L}^2$ with the same eigenvalue. Now consider the second commutator equation. Let $|\psi\rangle$ satisfy $\hat{L}_z|\psi\rangle = \mu|\psi\rangle$:

$$\begin{aligned}
&[\hat{L}_z, \hat{L}_\pm]|\psi\rangle = \hat{L}_z\hat{L}_\pm|\psi\rangle - \hat{L}_\pm\hat{L}_z|\psi\rangle = \pm\hbar\hat{L}_\pm|\psi\rangle \\
&\hat{L}_z\hat{L}_\pm|\psi\rangle = \mu\hat{L}_\pm|\psi\rangle \pm \hbar\hat{L}_\pm|\psi\rangle = (\mu \pm \hbar)\hat{L}_\pm|\psi\rangle
\end{aligned}$$

[1] See Griffiths.

So if $|\psi\rangle$ is an eigenstate of $\hat{L}_z$ with eigenvalue μ then $\hat{L}_\pm |\psi\rangle$ is also an eigenstate with eigenvalue $\mu \pm \hbar$.
Notice that we can therefore use these ladder operators to increase the eigenvalue of $\hat{L}_z$, but at some point it will be possible to reach a state with z-component greater than the total. Therefore, we must reach a highest rung of the ladder. Similarly, we can't go down forever as we would eventually reach a value with a greater magnitude than the total (it would of course be negative). It is not required for this course to derive the eigenvalues of $\hat{L}_z, \hat{L}^2$, but the derivation can be found in Griffiths. I will quote what you need to know:

1. Simultaneous eigenstates of $\hat{L}_z, \hat{L}^2$ can be written as $|l, m\rangle$ which satisfy the following eigenvalue equations:
   - $\hat{L}_z |l, m\rangle = \hbar m |l, m\rangle$
   - $\hat{L}^2 |l, m\rangle = \hbar^2 l(l+1) |l, m\rangle$
2. m goes from $-l$ to l in integer steps.
3. l may be an integer or half-integer, i.e. 0, 0.5, 1, etc. This will be revisited later, as it turns out we can exclude the half integers.

As we did with the harmonic oscillator, we can investigate how an eigenstate changes when it is operated on by $\hat{L}_\pm$:

$$\begin{aligned}\hat{L}_\pm |l, m\rangle &= c_\pm |l, m \pm 1\rangle \\ |c_\pm|^2 &= \langle l, m | \hat{L}_\mp \hat{L}_\pm | l, m\rangle\end{aligned}$$

Consider $\hat{L}_\mp \hat{L}_\pm$:

$$\begin{aligned}\hat{L}_\mp \hat{L}_\pm &= (\hat{L}_x \mp i\hat{L}_y)(\hat{L}_x \pm i\hat{L}_y) \\ &= \hat{L}_x^2 + \hat{L}_y^2 \pm i[\hat{L}_x, \hat{L}_y] \\ &= \hat{L}^2 - \hat{L}_z^2 \mp \hbar \hat{L}_z\end{aligned}$$

Subbing this in we get

$$\begin{aligned}|c_\pm|^2 &= \langle l, m | \hat{L}^2 - \hat{L}_z^2 \mp \hbar \hat{L}_z | l, m\rangle \\ &= \hbar^2 l(l+1) - \hbar^2 m^2 \mp \hbar^2 m \\ \Rightarrow c_\pm &= \hbar\sqrt{l(l+1) - m(m \pm 1)}\end{aligned}$$

5.1.2 Matrix Representation

We can easily work out the matrices that represent the angular momentum operators. We will consider the $l = 1$ case. By making the association

$$\begin{aligned}|1, 1\rangle &\equiv \begin{pmatrix}1\\0\\0\end{pmatrix} \\ |1, 0\rangle &\equiv \begin{pmatrix}0\\1\\0\end{pmatrix} \\ |1, -1\rangle &\equiv \begin{pmatrix}0\\0\\1\end{pmatrix}\end{aligned}$$

We can consider the eigenvalue equations of $\hat{L}_z$ to find its form:

$$\hat{L}_z \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \hbar \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$
$$\hat{L}_z \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = 0$$
$$\hat{L}_z \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = -\hbar \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

Hence we have

$$\hat{L}_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Now consider the eigenvalue equations of $\hat{L}_\pm$:

$$\hat{L}_+ \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = 0$$
$$\hat{L}_+ \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = \hbar\sqrt{2} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$
$$\hat{L}_+ \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \hbar\sqrt{2} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$
$$\hat{L}_- \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \hbar\sqrt{2} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$
$$\hat{L}_- \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = \hbar\sqrt{2} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$
$$\hat{L}_- \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = 0$$

Which yields

$$\hat{L}_+ = \hbar\sqrt{2} \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix}$$
$$\hat{L}_- = \hbar\sqrt{2} \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

Now we use $\hat{L}_x = (\hat{L}_+ + \hat{L}_-)/2$, $\hat{L}_y = (\hat{L}_+ - \hat{L}_-)/2i$ to obtain

$$\hat{L}_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$
$$\hat{L}_y = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$

5.1.3 Angular Momentum in Position Basis

We begin from the equation $\hat{L}_i = \epsilon_{ijk}\hat{x}_j\hat{p}_k$, and using our position basis representations for $\hat{x}$ and $\hat{p}$:

$$\hat{L}_i = -i\hbar\epsilon_{ijk}x_j\partial_{x_k}$$

If you would like, you can work through a lot of algebra to convert these expressions into spherical co-ordinates. As I am currently typing this while on holiday in Greece, and would therefore like to minimise the amount of misery I have to go through to create these notes, I will simply quote the results here.

$$\begin{aligned}
\hat{L}_x &= -i\hbar\left(-\sin\phi\partial_\theta - \cot\theta\cos\phi\partial_\phi\right)\\
\hat{L}_y &= -i\hbar\left(\cos\phi\partial_\theta - \cot\theta\sin\phi\partial_\phi\right)\\
\hat{L}_z &= -i\hbar\partial_\phi\\
\hat{L}^2 &= -\hbar^2\left(\frac{\partial_\theta(\sin\theta\partial_\theta)}{\sin\theta} + \frac{\partial_\phi^2}{\sin^2\theta}\right)
\end{aligned}$$

5.1.4 Eigenfunctions

In the position basis, the simultaneous eigenfunctions of $\hat{L}_z$ and $\hat{L}^2$ satisfy

$$\begin{aligned}
\hat{L}^2 Y_l^m &= \hbar^2 l(l+1)Y_l^m\\
\hat{L}_z Y_l^m &= \hbar m Y_l^m
\end{aligned}$$

You are required to know the form of these eigenfunctions, known as spherical harmonics, for $l = 0, 1$:

$$\begin{aligned}
Y_{00} &\propto 1\\
Y_{10} &\propto \cos\theta\\
Y_{1\pm1} &\propto \mp e^{\pm i\phi}\sin\theta
\end{aligned}$$

You can work out the normalisation by integrating over the spherical coordinates.

5.1.5 Integer or Half-Integer Eigenvalues

I previously stated m goes from $-l$ to l in integer steps, which corresponds to successive $\hat{L}_z$ eigenvalues differing by $\hbar$. However, notice that if it takes N integer steps to get from $-l$ to l, we have $l-(-l) = N \Rightarrow l = N/2$. As N is an integer, then l (and thus m) may be an integer or half-integer. However, m being a half integer is actually forbidden in this case, which we can see by considering the situation physically. Consider the eigenfunction equation for the spherical harmonics:

$$\hat{L}_z Y_l^m = \hbar m Y_l^m$$

And now use the position representation of $\hat{L}_z$:

$$\begin{aligned}
-i\hbar\partial_\phi Y_l^m &= \hbar m Y_l^m\\
\Rightarrow Y_l^m &= Ae^{im\phi}
\end{aligned}$$

where A is some constant that may be a function of θ. Notice that if we rotate ϕ through 2π, we expect Y_l^m to remain the same:

$$e^{2\pi im} = e^0 = 1$$

Which implies m must be an integer. As the case $l = m$ is allowed, this also restricts l to being an integer. We shall see that in the spin case no such constraint exists.

5.2 Spin

It can be shown through experiment that particles have intrinsic angular momentum, known as spin. Intrinsic, in this context, means that spin is not a function of other properties, like how orbital angular momentum is a function of $\mathbf{r}$ and $\mathbf{p}$, and therefore of r, θ, ϕ. Let's see what we can find out about this quantity. We introduce the operators $\hat{S}_z$ and $\hat{S}^2$ in analogy to $\hat{L}_z$ and $\hat{L}^2$. The algebra is the same:

$$
\begin{aligned}
[\hat{S}_i, \hat{S}_j] &= i\hbar\epsilon_{ijk}\hat{S}_k \\
\hat{S}_z \left|s, m\right\rangle &= \hbar m \left|s, m\right\rangle \\
\hat{S}^2 \left|s, m\right\rangle &= \hbar^2 s(s+1) \left|s, m\right\rangle \\
\hat{S}_\pm \left|s, m\right\rangle &= \hbar\sqrt{s(s+1) - m(m\pm 1)} \left|s, m\pm 1\right\rangle
\end{aligned}
$$

Again, m goes from $-s$ to s in integer steps. However, as spin is intrinsic, we cannot find eigenfunctions in terms of r, θ, ϕ, and therefore can't impose the same constraint as we did before, namely that m must only be an integer; in this case s may be an integer or half integer (as we saw before with l). It turns out that the value of s is constant for each type of particle. Electrons are the simplest case, and they have $s = 1/2$.

5.2.1 Spin 1/2

As $s = 1/2$ and m goes from $-s$ to s in integer steps, we have $m = -1/2$ and $m = 1/2$ as the two possible eigenvalues of $\hat{S}_z$. We denote the corresponding eigenstates as

$$
\begin{aligned}
\left|\uparrow\right\rangle &= \left|\frac{1}{2}, \frac{1}{2}\right\rangle \\
\left|\downarrow\right\rangle &= \left|\frac{1}{2}, -\frac{1}{2}\right\rangle
\end{aligned}
$$

Which we refer to as spin up and down respectively. We would like to find the matrix representation of the spin operators. Let's begin by making the association $\begin{pmatrix}1\\0\end{pmatrix} \to \left|\uparrow\right\rangle$ and $\begin{pmatrix}0\\1\end{pmatrix} \to \left|\downarrow\right\rangle$. We know the action of $\hat{S}_\pm$ on these states:

$$
\begin{aligned}
\hat{S}_+ \begin{pmatrix}1\\0\end{pmatrix} &= 0 \\
\hat{S}_+ \begin{pmatrix}0\\1\end{pmatrix} &= \hbar \begin{pmatrix}1\\0\end{pmatrix} \\
\hat{S}_- \begin{pmatrix}1\\0\end{pmatrix} &= \hbar \begin{pmatrix}0\\1\end{pmatrix} \\
\hat{S}_- \begin{pmatrix}0\\1\end{pmatrix} &= 0
\end{aligned}
$$

Which lets us construct $\hat{S}_\pm$:

$$
\begin{aligned}
\hat{S}_+ &= \hbar \begin{pmatrix}0 & 1\\0 & 0\end{pmatrix} \\
\hat{S}_- &= \hbar \begin{pmatrix}0 & 0\\1 & 0\end{pmatrix}
\end{aligned}
$$

Now use the fact that $\hat{S}_x = (\hat{S}_+ + \hat{S}_-)/2$ and $\hat{S}_y = (\hat{S}_+ - \hat{S}_-)/2i$:

$$
\begin{aligned}
\hat{S}_x &= \hbar/2 \begin{pmatrix}0 & 1\\1 & 0\end{pmatrix} \\
\hat{S}_y &= i\hbar/2 \begin{pmatrix}0 & -1\\1 & 0\end{pmatrix}
\end{aligned}
$$

Also from the eigenvalue equations we know the forms of $\hat{S}_z$ and $\hat{S}^2$:

$$\hat{S}_z = \hbar/2 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$
$$\hat{S}^2 = 3\hbar^2/4 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Now suppose we would like to measure the spin along the x (say) direction. To investigate this, we need to find the eigenvalues and states of the corresponding observable, in this case $\hat{S}_x$. You can check that the eigenvectors are $\frac{1}{\sqrt{2}}(|\uparrow\rangle \pm |\downarrow\rangle)$ with eigenvalues $\pm\hbar/2$. Hence, measuring the spin component in the x direction throws the system into a superposition state where we no longer have any information about its spin in the z direction: it could be up or down, with equal likelihood.

5.3 Particles in Electric and Magnetic Fields I

Considering only the particle's spin as contributing to the magnetic moment, we will assume the magnetic moment is proportional to the spin. This is indeed the case for a classical particle, so we will take the liberty to write

$$\boldsymbol{\mu} = \gamma \hat{\mathbf{S}}$$

5.3.1 Larmor Precession

From your EM course you should know that the potential energy of a magnetic dipole in a B-field is $U = -\boldsymbol{\mu} \cdot \mathbf{B}$. We can use this as our Hamiltonian, assuming the particle to be at rest:

$$\hat{H} = -\gamma \hat{\mathbf{S}} \cdot \mathbf{B}$$

Without loss of generality take the field to be in the z direction. Hence:

$$\hat{H} = -\gamma B \hat{S}_z = -\frac{\gamma B \hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Now let's say the system is in a general state $|\psi(t)\rangle = a(t)\,|\uparrow\rangle + b(t)\,|\downarrow\rangle$. We can use the Schrödinger equation to get:

$$i\hbar\partial_t \begin{pmatrix} a \\ b \end{pmatrix} = -\frac{\gamma B \hbar}{2} \begin{pmatrix} a \\ -b \end{pmatrix}$$

From which we obtain

$$|\psi(t)\rangle = \begin{pmatrix} a_0 e^{i\gamma B t/2} \\ b_0 e^{-i\gamma B t/2} \end{pmatrix}$$

Notice that the normalisation of $|\psi(t)\rangle$ gives the constraint $a_0^2 + b_0^2 = 1$ so without loss of generality we can let $a_0 = \sin(\alpha/2), b_0 = \cos(\alpha/2)$ for some α. We are now in a position to find quantities of interest $\langle \hat{S}_x \rangle$ and $\langle \hat{S}_y \rangle$. Working through the algebra yields

$$\langle \hat{S}_x \rangle = \frac{\hbar}{2} \sin(\alpha) \cos(\gamma B t)$$
$$\langle \hat{S}_y \rangle = -\frac{\hbar}{2} \sin(\alpha) \sin(\gamma B t)$$
$$\langle \hat{S}_z \rangle = \frac{\hbar}{2} \cos(\alpha)$$

In some sense then, the spin precesses around the z axis at an angle α to it.

5.3.2 Stern-Gerlach Apparatus

Consider that if the potential is $U = -\boldsymbol{\mu} \cdot \mathbf{B}$ and $\mathbf{F} = -\nabla U$, then there will be a force on the particle equal to $\mathbf{F} = \nabla(\gamma \hat{\mathbf{S}} \cdot \mathbf{B})$. As you can see, in the case of a uniform field we have zero force. However, in the case of an inhomogeneous field, we might have a force - let's explore the simplest case; a strong field in the z direction with a small linear inhomogeneity:

$$\mathbf{B} = (B_0 + \alpha z)\hat{\mathbf{k}}$$

This had better be a physically possible field, so let's check if it works with Maxwell's equations:

$$\begin{aligned} &\nabla \cdot \mathbf{B} = 0 \\ &\Rightarrow \alpha = 0 \\ &\Rightarrow \mathbf{B} = B_0 \hat{\mathbf{k}} \end{aligned}$$

So this gives us a homogeneous field in the z direction: exactly what we didn't want. To fix this we will have to also add a small inhomogeneity in the x direction:

$$\mathbf{B} = -\alpha x \hat{\mathbf{i}} + (B_0 + \alpha z)\hat{\mathbf{k}}$$

And you can check this satisfies the no magnetic monopoles law. In this case then the force is

$$\mathbf{F} = \gamma\alpha(-\hat{S}_x \hat{\mathbf{i}} + \hat{S}_z \hat{\mathbf{k}})$$

Over time Larmor precession ensures that $\langle \hat{S}_x \rangle$ averages to zero, leaving only a force in the z direction of magnitude $\gamma\alpha\langle \hat{S}_z \rangle$. Hence, a particle in the state $|\uparrow\rangle$ will experience a force in the opposite direction to one in $|\downarrow\rangle$. We can use the SGA as a spin filter, and to measure components of spin in a given direction.

5.3.3 Stern-Gerlach Filters at an Angle

If we would like to measure spin along some arbitrary axis $\mathbf{n} = (0, \sin\theta, \cos\theta)$, then we simply have to find the eigenstates of $\mathbf{n} \cdot \hat{\mathbf{S}}$, i.e. the component of the spin along the axis. In the spin 1/2 case, we have

$$\mathbf{n} \cdot \hat{\mathbf{S}} = \frac{\hbar}{2} \begin{pmatrix} \cos\theta & -i\sin\theta \\ i\sin\theta & -\cos\theta \end{pmatrix}$$

And so the eigenvalues are $\pm\hbar/2$ as we would expect, and the eigenvectors are

$$\begin{aligned} |\uparrow, \theta\rangle &= \begin{pmatrix} \cos(\theta/2) \\ i\sin(\theta/2) \end{pmatrix} = \cos(\theta/2)\,|\uparrow\rangle + i\sin(\theta/2)\,|\downarrow\rangle \\ |\downarrow, \theta\rangle &= \begin{pmatrix} i\sin(\theta/2) \\ \cos(\theta/2) \end{pmatrix} = i\sin(\theta/2)\,|\uparrow\rangle + \cos(\theta/2)\,|\downarrow\rangle \end{aligned}$$

Where $|\uparrow, \theta\rangle$ and $|\downarrow, \theta\rangle$ correspond to the eigenvalues of $\pm\hbar/2$ respectively. We can see that after the particle goes through the filter, the probability of measuring $\hbar/2$ along the z direction, e.g. by way of a z-oriented SGA after the angled one, would be

$$P(\hbar/2 \text{ in } z \text{ direction}) = |\,\langle\uparrow \mid \uparrow, \theta\rangle\,|^2 = \cos^2(\theta/2)$$

5.4 Worked Example: Angular Wavefunction

Question 3. *The angular part of a system's wavefunction is*

$$\langle\theta, \phi|\psi\rangle \propto \sqrt{2}\cos\theta + \sin\theta e^{-i\phi} - \sin\theta e^{i\phi}$$

What are the possible results of measurement of $\hat{L}_z$ and $\hat{L}^2$, and their probabilities?

Rewriting in terms of the spherical harmonics we have

$$\langle\theta, \phi|\psi\rangle \propto \sqrt{\frac{8\pi}{3}} Y_1^0 + \sqrt{\frac{8\pi}{3}} Y_1^1 + \sqrt{\frac{8\pi}{3}} Y_1^{-1}$$

$\hat{L}^2$ has eigenvalue $\hbar^2 l(l+1)$ and this wavefunction has a single l value, namely 1, so the possible outcome of measuring $\hat{L}^2$ is $2\hbar^2$ with probability 1. As the wavefunction weights the different values of m equally, and $\hat{L}_z$ has eigenvalues $\hbar m$, the possible outcomes are $\pm\hbar, 0$ with equal probability 1/3.

Chapter 6

The Hydrogen Atom

We would like to know two things:

1. wavefunction of the electron, so we can predict where it may or may not be
2. allowed energies (eigenvalues).

What follows is the 'best'[1] derivation I settled on, which you will need to memorise for the exam. It is mostly lifted from Griffiths. We consider not just hydrogen, but hydrogen-like ions, i.e. nuclei of nuclear charge Z with a single electron.

6.1 Derivation

We begin with the Hamiltonian. As usual, we have kinetic + potential energy, but we have to consider both the energy of the nucleus and the electron:

$$\hat{H} = \frac{\hat{\mathbf{p}}_n^2}{2m_n} + \frac{\hat{\mathbf{p}}_e^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0|\mathbf{x}_n - \mathbf{x}_e|}$$

We would like to rewrite this Hamiltonian in terms of centre of mass (CM) coordinates; these are the position of the CM ($\mathbf{x}_{CM}$) and the radial separation $\mathbf{r} = \mathbf{x}_n - \mathbf{x}_e$. After some manipulation which I am quite confident you will not be required to reproduce, and switching to the position representation, we arrive at

$$\left[-\frac{\hbar^2}{2M}\nabla_{CM}^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Ze^2}{4\pi\epsilon_0 r}\right]\psi = (E_{CM} + E_r)\psi$$

Where μ is the reduced mass, M is the total mass ($m_n + m_e$), E_{CM} is the energy associated with CM motion and E_r is the energy associated with relative motion. Now as the nucleus is heavy relative to the electron, lets ignore all the CM motion in this equation and focus on the relative motion:

$$\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Ze^2}{4\pi\epsilon_0 r}\right]\psi = E\psi$$

Where I have relabeled E_r as E. Now lets use the first of many convenient ansatzes: we will write ψ in terms of some radial wavefunction $R(r)$ and the spherical harmonics, which as you know are functions of θ and ϕ. This is a simple separation of variables.

$$\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Ze^2}{4\pi\epsilon_0 r}\right]RY_l^m = ERY_l^m$$

We can also rewrite the Laplace operator in the following form:

$$\nabla_r^2 \circ = \frac{1}{r}\partial_r^2(r\circ) - \frac{\hat{L}^2}{\hbar^2 r^2}\circ$$

[1] By 'best' I mean the one which requires the least memorisation while still being somewhat rigorous.

Where the $\circ$ indicates where the function the operator is applied to should go. We now have

$$-\frac{\hbar^2}{2\mu r}\partial_r^2(rRY_l^m) + \frac{\hat{L}^2(RY_l^m)}{2\mu r^2} - \frac{Ze^2}{4\pi\epsilon_0 r}RY_l^m = ERY_l^m$$

Recall the eigenfunctions of $\hat{L}^2$ are the spherical harmonics:

$$\hat{L}^2 Y_l^m = \hbar^2 l(l+1)Y_l^m$$

So we have

$$-\frac{\hbar^2 Y_l^m}{2\mu r}\frac{d^2(rR)}{dr^2} + \frac{\hbar^2 l(l+1)RY_l^m}{2\mu r^2} - \frac{Ze^2}{4\pi\epsilon_0 r}RY_l^m = ERY_l^m$$

Let's cancel the spherical harmonics. Also, introduce a change of variables $u = rR$:

$$-\frac{\hbar^2}{2\mu}\frac{d^2u}{dr^2} + \frac{\hbar^2 l(l+1)u}{2\mu r^2} - \frac{Ze^2 u}{4\pi\epsilon_0 r} = Eu$$

Now we use another substitution, in which we write the energy as related to some wavenumber in the usual way, although negative as we expect the energies to be negative (energy needs to be put in to ionise the atom).

$$E = -\frac{\hbar^2 k^2}{2\mu}$$

Leaving us with

$$\frac{d^2u}{dr^2} - \frac{l(l+1)u}{r^2} + \frac{\mu Ze^2 u}{2\pi\epsilon_0\hbar^2 r} = k^2 u$$

Now two further substitutions. One to introduce a length scale ($\rho = kr$) and one to clean up the mess of constants ($\rho_0 = \mu Ze^2/2\pi\epsilon_0\hbar^2 k$). Notice that $d^2/dr^2 = k^2 d^2/d\rho^2$:

$$\frac{d^2u}{d\rho^2} = u\left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]$$

Let us investigate small and large-ρ behaviour. At large ρ we have

$$u'' \approx u$$
$$\Rightarrow u = Ae^{-\rho} + Be^{\rho}$$

And we have $B = 0$ as we want the wavefunction to die away at large ρ. Now for small ρ:

$$u'' \approx \frac{ul(l+1)}{\rho^2}$$
$$\Rightarrow u = C\rho^{l+1} + D\rho^{-l}$$

And $D = 0$ as the wavefunciton needs to not diverge for small ρ. Hence we propose u has the form $u = e^{-\rho}\rho^{l+1}v(\rho)$. After tedious algebra, you will find

$$u'' = e^{-\rho}\rho^{l+1}\left[v\left(\frac{l(l+1)}{\rho^2} - \frac{2(l+1)}{\rho} + 1\right) + 2v'\left(\frac{l+1}{\rho} - 1\right) + v''\right]$$

So let's sub this into our differential equation for u. We will get

$$\rho v'' + 2v'(l+1-\rho) + v(\rho_0 - 2(l+1)) = 0$$

Now we need to find v. Let's use an infinite series ansatz:

$$v = \sum_{j=0}^{\infty} c_j \rho^j$$
$$\Rightarrow \frac{dv}{d\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1}$$
$$\frac{d^2v}{d\rho^2} = \sum_{j=0}^{\infty} j(j-1)c_j\rho^{j-2} = \sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^{j-1}$$

Where the last sum was re-indexed. Hence

$$\sum_{j=0}^{\infty}\left[j(j+1)c_{j+1}\rho^j + 2(l+1-\rho)jc_j\rho^{j-1} + c_j(\rho_0 - 2(l+1))\rho^j\right] = 0$$

As the series equals 0, the like powers of ρ must also sum to zero. This leads to

$$\begin{aligned} 0 &= j(j+1)c_{j+1} + 2(l+1)(j+1)c_{j+1} - 2jc_j + c_j(\rho_0 - 2(l+1)) \\ \Rightarrow c_{j+1} &= c_j\frac{2j + 2(l+1) - \rho_0}{(j+1)(j+2(l+1))} \end{aligned}$$

Now notice that for large j, the coefficients approach $c_{j+1}/c_j \approx 2/j$. This is the same ratio between coefficients as in the following:

$$\sum_{j=0}^{\infty}\frac{(2\rho)^j}{j!} = e^{2\rho}$$

Which is an exponential increase, not a decrease: so as we add more terms in the series, v gets closer to a diverging function of ρ. This is not what we want; the series must terminate at some $j = N$ such that $c_N = 0$ but $c_{N-1} \neq 0$. Note that c_0 can't be 0 as then there would be no series at all. We may rewrite the coefficient relationship like so:

$$c_j = c_{j-1}\frac{2(j+l) - \rho_0}{j(j+2l+1)}$$

Now notice to also satisfy our termination criteria we have

$$N + l = \frac{\rho_0}{2}$$

Let's define $N + l = n$. Because N is an integer from 1 to ∞ and l is an integer from 0 to ∞, n is an integer from 1 to ∞. As $N = n - l$ is definitely an integer > 0 as discussed previously, and $l \geq 0$, we have that $n > l$, which implies l goes from 0 to $n - 1$. Anyway:

$$\begin{aligned} 2n = \rho_0 &= \frac{\mu Ze^2}{2\pi\epsilon_0\hbar^2 k} \\ \Rightarrow k &= \frac{\mu Ze^2}{4\pi\epsilon_0\hbar^2 n} \\ \Rightarrow E_n &= -\frac{1}{n^2}\left[\frac{\mu}{2\hbar^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2\right] \end{aligned}$$

These are our energy eigenvalues; the allowed energies of hydrogen-like ions. We also have a length scale, defined by $1/k$. We usually use the $n = 1$ version of this, which is called the Bohr radius a_B for $Z = 1$ and $\mu = m_e$, or a_Z in general. This is given by

$$\begin{aligned} a_Z &= \frac{4\pi\epsilon_0\hbar^2}{\mu Ze^2} = \frac{1}{nk} \\ a_B &= \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \end{aligned}$$

Now we have our eigenvalues, let's move onto the wavefunction. We can see that v, and therefore u, and therefore R, depend on n and l. For $n = 1$, $l = 0$ and we have a single wavefunction to consider, $R_{nl} = R_{10}$. I could find the others as well but it's really tedious and you probably won't be asked to do this, it's better to just memorise the first few that the syllabus mentions. Anyway, $N = n = 1$ so the series of v is only a constant, which we forget about as we will normalise the whole thing anyway, leaving $u \propto \rho e^{-\rho}$ or $R_{10} \propto e^{-r/a_Z}$. As $m = 0$ and Y_0^0 is a constant the first wavefunction is still proportional to this exponential, and the constant can be worked out through normalisation. You can find the rest of the wavefunctions in Griffiths.

6.2 Ground State Wavefunction

For future reference, the normalised ground state wavefunction of a hydrogenic ion with nuclear charge Z is

$$\psi_{100} = \frac{1}{\sqrt{\pi a_z^3}} e^{-r/a_z}$$

6.3 Degeneracy

A quick note on degeneracy: for each level, there may be n different values of l ($l = 0$ to $n-1$) that correspond to the same energy. Each l has a further $2l+1$ ($-l$ to l) allowed m values, leading to a total of

$$\sum_{l=0}^{n-1} (2l+1) = n^2$$

unique states that correspond to the same energy E_n.

Chapter 7

Composite Systems

7.1 Algebra

7.1.1 Notation

Suppose we have two particles, labelled 1 and 2. These particles may be in one of two states, also labelled 1 or 2. Particle 1's states, namely $|1,1\rangle, |1,2\rangle$ live in a separate (vector) space of states from $|2,1\rangle, |2,2\rangle$, particle 2's states: it doesn't make sense for a single particle to be in a superposition of both particle one and two states. If our system is contains the two particles, say with 1 in $|1,1\rangle$ and 2 in $|2,1\rangle$, we write the state of the system as a whole as $|1,1\rangle |2,1\rangle$ or $|1,1\rangle \otimes |2,1\rangle$. Formally, this object is in a tensor product space of the two independent spaces, but don't worry about this too much.

7.1.2 Scalar Products

The main idea with composite systems is that parts from one space only combine with parts of that same space. The scalar product works like this:

$$(\langle 1,m| \langle 2,n|)(|1,p\rangle |2,q\rangle) = \langle 1,m|1,p\rangle \langle 2,n|2,q\rangle$$

7.1.3 Operators

Operators also only act on the ket from the space they are in:

$$\hat{O}_1(|1,p\rangle \otimes |2,q\rangle) = (\hat{O}_1 |1,p\rangle) \otimes |2,q\rangle$$
$$\hat{O}_2(|1,p\rangle \otimes |2,q\rangle) = |1,p\rangle \otimes (\hat{O}_2 |2,q\rangle)$$

7.1.4 Integrals and the Position Representation

Integrals are evaluated over all position spaces. For example, consider the integral associated with the identity operator in the position representation:

$$I = \int\int |x_1, x_2\rangle \langle x_1, x_2| \, dx_1 dx_2$$

7.2 Composite Hamiltonian and Schrödiger Equation

The Hamiltonian is (predictably) the kinetic and potential terms for each particle, plus a possible interaction potential:

$$\hat{H} = \frac{\hat{\mathbf{p}}_1^2}{2m_1} + \frac{\hat{\mathbf{p}}_2^2}{2m_2} + V_1(\hat{\mathbf{x}}_1) + V_2(\hat{\mathbf{x}}_2) + V_{int}(\hat{\mathbf{x}}_1, \hat{\mathbf{x}}_2)$$

This leads to a TDSE of the form

$$i\hbar\partial_t \psi(\mathbf{x}_1, \mathbf{x}_2, t) = \left[-\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2 + V_1(\mathbf{x}_2) + V_2(\mathbf{x}_2) + V_{int}(\mathbf{x}_1, \mathbf{x}_2) \right] \psi(\mathbf{x}_1, \mathbf{x}_2, t)$$

7.3 Independent Particles

An important case is when $V_{int} = 0$ and therefore $\hat{H} = \hat{H}_1 + \hat{H}_2$. In this case, the wavefunction can be separated into independent components: $\psi(\mathbf{x}_1, \mathbf{x}_2) = \phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2)$

7.4 Product States and Entanglement

7.4.1 Product States

Consider a state $|\psi\rangle = c_{11}c_{21}\,|1,1\rangle\,|2,1\rangle + c_{11}c_{22}\,|1,1\rangle\,|2,2\rangle + c_{12}c_{21}\,|1,2\rangle\,|2,1\rangle + c_{12}c_{22}\,|1,2\rangle\,|2,2\rangle$. This is known as a product state, as it may be written as a (tensor) product of states from the two different parts: $|\psi\rangle = (c_{11}\,|1,1\rangle + c_{12}\,|1,2\rangle)(c_{21}\,|2,1\rangle + c_{22}\,|2,2\rangle)$. Notice that if we measure the state of particle 1, there will be no effect on the state of particle 2. We can see this through a simple application of Bayes' theorem. Let's say we would like to measure the probability that particle 2 (p2) is in state 1 given that we have already measured particle 1 (p1) as being in state 2. Bayes' theorem tell us

$$P(\text{p2 in state 1 given p1 in state 2})P(\text{p1 in state 2}) = P(\text{p1 in state 2 AND p2 in state 1})$$

We know the RHS $= |c_{12}c_{21}|^2$ and also

$$\begin{aligned} P(\text{p1 in state 2}) &= P(\text{p1 in state 2 AND p2 in state 1}) + P(\text{p1 in state 2 AND p2 in state 2}) \\ &= |c_{12}c_{21}|^2 + |c_{12}c_{22}|^2 \end{aligned}$$

so we can write

$$P(\text{p2 in state 1 given p1 in state 2}) = \frac{|c_{12}c_{21}|^2}{|c_{12}c_{21}|^2 + |c_{12}c_{22}|^2} = \frac{1}{1 + \frac{|c_{22}|^2}{|c_{21}|^2}}$$

Notice the expression after the last equality is independent of particle 1; we have measured particle 1's state, and this had no effect on the state of particle 2. This property is true of all product states.

7.5 Entangled States

Consider the state $|\psi\rangle = c_{11}c_{22}\,|1,1\rangle\,|2,2\rangle + c_{12}c_{21}\,|1,2\rangle\,|2,1\rangle$. This state cannot be factorised into a product of two states of different particles. Notice if we measure particle 1 as being in state 2 first, the superposition collapses to $|\psi\rangle = |1,2\rangle\,|2,1\rangle$ as there is no chance subsequent measurements would show it to be in state 1[1]. Hence if we were to measure particle 2, now, we would always find it in state 1. Contrast this with the situation where particle 1 is measured as being in state 1 first: the superposition collapses to $|\psi\rangle = |1,1\rangle\,|2,2\rangle$ and we will now always measure particle 2 as being in state 2. These kinds of states are called entangled states, and measurements on one part of the system will be correlated with measurements on other parts.

7.6 Combining Two Spin 1/2 Systems

Recall that the state of a single system with spin may be written as $|s, m\rangle$. We can then write the state of a two component system as $|s_1m_1\rangle\,|s_2m_2\rangle$ or for compactness $|s_1m_1s_2m_2\rangle$. There will be an $\hat{S}_z$ operator for each space, which we denote $\hat{S}_z^{(1)}, \hat{S}_z^{(2)}$. Therefore, the operator representing total spin component in the z direction will be $\hat{S}_z = \hat{S}_z^{(1)} + \hat{S}_z^{(2)}$. Lets apply this to our general two particle spin state:

$$\begin{aligned} \hat{S}_z\,|s_1m_1s_2m_2\rangle &= (\hat{S}_z^{(1)}\,|s_1m_1\rangle) \otimes |s_2m_2\rangle + |s_1m_1\rangle \otimes (\hat{S}_z^{(2)}\,|s_2m_2\rangle) \\ &= \hbar(m_1 + m_2)\,|s_1m_1s_2m_2\rangle \end{aligned}$$

So we expect m to simply add.

[1] Remember, this is a postulate.

7.6.1 Singlet and Triplet States

Let's look at the specific case of spin 1/2. Our states are

$$\left|\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}\right\rangle \equiv |\uparrow\uparrow\rangle \quad (m=1)$$
$$\left|\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{-1}{2}\right\rangle \equiv |\uparrow\downarrow\rangle \quad (m=0)$$
$$\left|\frac{1}{2}\frac{-1}{2}\frac{1}{2}\frac{1}{2}\right\rangle \equiv |\downarrow\uparrow\rangle \quad (m=0)$$
$$\left|\frac{1}{2}\frac{-1}{2}\frac{1}{2}\frac{-1}{2}\right\rangle =\equiv |\downarrow\downarrow\rangle \quad (m=-1)$$

We would expect that the combined m goes from $-s$ to s (where s is the s-number for the composite system) in integer steps, but clearly something isn't quite right; there are two states with $m = 0$ where there should only be one. Recall that using the raising operator on the highest state will give 0, and likewise the lowering operator gives 0 when acting on the lowest state. We can define the relevant operators for our composite system:

$$\hat{S}_\pm = \hat{S}^{(1)}_\pm + \hat{S}^{(2)}_\pm$$

Applying these to $|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$ shows that these are indeed the highest and lowest states:

$$\hat{S}_+ |\uparrow\uparrow\rangle = (\underbrace{\hat{S}^{(1)}_+ |\uparrow\rangle}_{=0}) \otimes |\uparrow\rangle + |\uparrow\rangle \otimes (\underbrace{\hat{S}^{(2)}_+ |\uparrow\rangle}_{=0}) = 0$$
$$\hat{S}_- |\downarrow\downarrow\rangle = (\underbrace{\hat{S}^{(1)}_- |\downarrow\rangle}_{=0}) \otimes |\downarrow\rangle + |\downarrow\rangle \otimes (\underbrace{\hat{S}^{(2)}_- |\downarrow\rangle}_{=0}) = 0$$

But notice what happens if we apply the lowering operator on $|\uparrow\uparrow\rangle$[2]:

$$\begin{aligned}\hat{S}_- |\uparrow\uparrow\rangle &= (\hat{S}^{(1)}_- |\uparrow\rangle) \otimes |\uparrow\rangle + |\uparrow\rangle \otimes (\hat{S}^{(2)}_- |\uparrow\rangle) \\ &= \hbar(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle)\end{aligned}$$

You can check by applying $\hat{S}_z$ to this state that you get $m = 0$, implying this is our correct $m = 0$ state. You can also check that if you use the lowering operator on this state again you will arrive at $|\downarrow\downarrow\rangle$ (up to a factor which is irrelevant due to normalisation). We have states that go from -1 to 1 in integer steps: these states therefore correspond to $s = 1$ and our job is done. However, we originally started with four basis states and have reduced these down to three. What happened to the fourth state? It turns out that there is also an $s = 0$ state, where the spins 'cancel out'. This state is $\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$, and you can check that applying the raising and lowering operators yields 0. This is indeed the only state, and as it goes from 0 to 0, s is indeed 0. So we have the following correctly normalised states:

$$\text{Triplet state } (s=1) \begin{cases} |\uparrow\uparrow\rangle \\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |\downarrow\downarrow\rangle \end{cases}$$
$$\text{Singlet state } (s=0) \left\{ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \right.$$

[2] You could also get the same result by applying the raising operator on $|\downarrow\downarrow\rangle$.

Part II

Further Quantum Mechanics Course

Chapter 8

Time-Independent Perturbation Theory

8.1 Non-Degenerate Perturbation Theory

8.1.1 First Order

Suppose we have a Hamiltonian $\hat{H}$ that has been *perturbed* slightly from a value $\hat{H}^0$:

$$\hat{H} = \hat{H}^0 + \lambda\delta\hat{H}$$

Where λ is a small number and $\delta\hat{H}$ is the correction. Suppose further that we know the eigenvalues (let them be E_n^0) and orthogonal eigenstates (let them be $|n^0\rangle$) that satisfy the original TISE in $\hat{H}^0$:

$$\hat{H}^0 |n^0\rangle = E_n^0 |n^0\rangle$$

And finally let us assume we can expand the eigenstates and eigenvalues of our corrected Hamiltonian $\hat{H}$ as a series in λ of smaller and smaller corrections to these original eigenstates:

$$|n\rangle = |n^0\rangle + \lambda |n^1\rangle + \lambda^2 |n^2\rangle + ...$$
$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + ...$$

Then the situation satisfies

$$(\hat{H}^0 + \lambda\delta\hat{H})(|n^0\rangle + \lambda |n^1\rangle + \lambda^2 |n^2\rangle + ...) = (E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + ...)(|n^0\rangle + \lambda |n^1\rangle + \lambda^2 |n^2\rangle + ...)$$

Let's expand this to order λ^2:

$$\hat{H}^0 |n^0\rangle + \lambda(\delta\hat{H} |n^0\rangle + \hat{H}^0 |n^1\rangle) + \lambda^2(\hat{H}^0 |n^2\rangle + \delta\hat{H} |n^1\rangle) = E_n^0 |n^0\rangle + \lambda(E_n^1 |n^0\rangle + E_n^0 |n^1\rangle) + \lambda^2(E_n^0 |n^2\rangle + E_n^1 |n^1\rangle + E_n^2 |n^0\rangle)$$

Now we can compare the order λ terms:

$$\delta\hat{H} |n^0\rangle + \hat{H}^0 |n^1\rangle = E_n^1 |n^0\rangle + E_n^0 |n^1\rangle$$

Let's bra through with $\langle n^0|$:

$$\langle n^0|\delta\hat{H}|n^0\rangle + \underbrace{\langle n^0| \hat{H}^0}_{E_n^0\langle n^0|} |n^1\rangle = E_n^1 + E_n^0 \langle n^0|n^1\rangle$$

Which leaves us with an expression for the 1st order correction to the energy:

$$E_n^1 = \langle n^0|\delta\hat{H}|n^0\rangle$$

Let's now find the 1st order correction to the kets. Let's bra through the order λ expression with $\langle m^0|, m \neq n$ instead. Remember due to orthogonality $\langle m^0|n^0\rangle = 0$:

$$\langle m^0|\delta\hat{H}|n^0\rangle + \underbrace{\langle m^0| \hat{H}^0}_{E_m^0\langle m^0|} |n^1\rangle = E_n^0 \langle m^0|n^1\rangle$$

Rearranging, the components of our first order correction satisfy

$$\Rightarrow \langle m^0|n^1\rangle = \frac{\langle m^0|\delta\hat{H}|n^0\rangle}{E_n^0 - E_m^0}$$
$$\Rightarrow |n^1\rangle = \sum_{m\neq n} \frac{\langle m^0|\delta\hat{H}|n^0\rangle}{E_n^0 - E_m^0}|m^0\rangle$$

Notice this is not valid in the degenerate case, i.e. $E_n^0 = E_m^0$. We will revisit this later. It should be noted that the normalisation condition $\langle n|n\rangle = 1$ causes $|n^k\rangle, k > 0$ to have no $|n^0\rangle$ component. In other words, $\langle n^0|n^k\rangle = 0$. Try and prove this yourself; you can find it in a footnote in Griffiths if you can't.

8.1.2 Second Order

Let us now compare order λ^2 terms from our previous expansion:

$$\hat{H}^0|n^2\rangle + \delta\hat{H}|n^1\rangle = E_n^0|n^2\rangle + E_n^1|n^1\rangle + E_n^2|n^0\rangle$$

Let's bra though with $\langle n^0|$:

$$\underbrace{\langle n^0|\hat{H}^0}_{=E_n^0\langle n^0|}|n^2\rangle + \langle n^0|\delta\hat{H}|n^1\rangle = E_n^2$$

Where $\langle n^0|n^k\rangle = 0, k > 0$ was used - use it again to eliminate the first term on the LHS. Hence, subbing in our previous result for $|n^1\rangle$:

$$E_n^2 = \sum_{m\neq n} \frac{|\langle m^0|\delta\hat{H}|n^0\rangle|^2}{E_n^0 - E_m^0}$$

8.2 Degenerate Perturbation Theory

Consider an energy E^0 common to two states:

$$\hat{H}^0|a^0\rangle = E^0|a^0\rangle$$
$$\hat{H}^0|b^0\rangle = E^0|b^0\rangle$$

Recall that any linear combination of these eigenstates is itself an eigenstate: let's construct one.

$$|z^0\rangle = \alpha|a^0\rangle + \beta|b^0\rangle$$
$$\hat{H}^0|z^0\rangle = E^0|z^0\rangle$$

This means we can use $|z\rangle$ instead of $|n\rangle$ in our 1st order expansion:

$$\delta\hat{H}|z^0\rangle + \hat{H}^0|z^1\rangle = E^1|z^0\rangle + E^0|z^1\rangle$$

And bra through with $|a^0\rangle$:

$$\langle a^0|\delta\hat{H}|z^0\rangle + \underbrace{\langle a^0|\hat{H}^0}_{E^0\langle a^0|}|z^1\rangle = E^1\underbrace{\langle a^0|z^0\rangle}_{\alpha} + E^0\langle a^0|z^1\rangle$$

The 2nd term on the LHS cancels the 2nd term on the RHS leaving

$$\alpha E^1 = \alpha\underbrace{\langle a^0|\delta\hat{H}|a^0\rangle}_{\delta\hat{H}_{aa}} + \beta\underbrace{\langle a^0|\delta\hat{H}|b^0\rangle}_{\delta\hat{H}_{ab}}$$

If we bra through with $|b^0\rangle$ instead we get

$$\beta E^1 = \alpha\underbrace{\langle b^0|\delta\hat{H}|a^0\rangle}_{\delta\hat{H}_{ba}} + \beta\underbrace{\langle b^0|\delta\hat{H}|b^0\rangle}_{\delta\hat{H}_{bb}}$$

We can arrange these equations into an eigenvalue equation:

$$\underbrace{\begin{pmatrix} \delta\hat{H}_{aa} & \delta\hat{H}_{ab} \\ \delta\hat{H}_{ba} & \delta\hat{H}_{bb} \end{pmatrix}}_{\delta\hat{H}_d} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

Here $\delta\hat{H}_d$ is a small part of the larger $\delta\hat{H}$ matrix corresponding to the degenerate region of vectors in its space. The crucial idea here is that **perturbation lifts the degeneracy**. Let's imagine that the perturbation is not active, and therefore there are two states with the same energy. These states may be chosen at will from the space of linear combinations of the relevant eigenstates, as any state within that space is also an eigenstate. Then, let's apply the perturbation fully: the energy splits into positively and negatively corrected energies, and the states we chose from the space also receive a correction. Now, let's reverse the process, and start switching off the perturbation. The correction to the states reduces until they become two uncorrected states that live in the space again. Are these two states the ones we chose? No - they can't be, because the perturbation will apply a correction that turns them all into the same corrected state, no matter which ones we chose initially. This means no information about the states we chose from the space originally is carried over to the perturbed states - so they can't 'remember' what they were originally when the perturbation is removed! Therefore, they must settle into two 'special' states, which of course still live in the space. These are called 'good' states, and are given by the eigenvectors of $\delta\hat{H}_d$, and the positive and negative 1st order corrections to the energy are the eigenvalues.

8.3 Worked Example: Hamiltonian Matrix

Question 4. $\hat{H} = \begin{pmatrix} A_1 + \epsilon B_1 & \epsilon B_2 \\ \epsilon B_2 & A_2 \end{pmatrix}$. *Find the allowed energies to 1st order in ϵ in the case $A_1 \neq A_2$ and $A_1 = A_2$.*

We begin by identifying $\hat{H}^0$ and $\delta\hat{H}$:

$$\hat{H}^0 = \begin{pmatrix} A_1 & 0 \\ 0 & A_2 \end{pmatrix}$$
$$\delta\hat{H} = \begin{pmatrix} \epsilon B_1 & \epsilon B_2 \\ \epsilon B_2 & 0 \end{pmatrix}$$

Let's start with the non-degenerate case. Our unperturbed states are $|1^0\rangle = (1,0), |2^0\rangle = (0,1)$ with unperturbed energies $E_1^0 = A_1, E_2^0 = A_2$ respectively. To find the correction we use 1st order perturbation theory:

$$\begin{aligned} E_1^1 &= \langle 1^0|\delta\hat{H}|1^0\rangle \\ &= \epsilon(1,0)\begin{pmatrix} B_1 & B_2 \\ B_2 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \epsilon B_1 \\ E_2^1 &= \langle 2^0|\delta\hat{H}|2^0\rangle \\ &= \epsilon(0,1)\begin{pmatrix} B_1 & B_2 \\ B_2 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0 \end{aligned}$$

So the allowed energies to first order are $E_1 = A_1 + \epsilon B_1, E_2 = A_2$. Let's move on to the degenerate case. In this case the whole $\hat{H}^0$ is degenerate so $\delta\hat{H}_d$ will be the whole $\delta\hat{H}$ matrix. To find the energy corrections we just need to find the eigenvalues. These come out as being

$$\lambda_\pm = \frac{\epsilon}{2}(B_1 \pm \sqrt{B_1^2 + 4B_2})$$

And the energies are of course

$$E_\pm = A_1 + \lambda_\pm$$

8.4 Worked Example: QHO Perturbation I

Question 5. *The harmonic oscillator of frequency ω is perturbed by $\delta\hat{H} = \epsilon\hat{x}^2$. For $l = \sqrt{\hbar/2m\omega}$:*

1. *What is the exact change in the ground-state energy? Expand this change in powers of ϵ up to order ϵ^2.*
2. *Show that the 1st order energy change agrees with the exact result.*
3. *Show that the first order change to the ground state is $|b\rangle = -(\epsilon l^2/\sqrt{2}\hbar\omega)\,|2^0\rangle$.*
4. *Show that second order perturbation theory yields a change $E_0^2 = -\epsilon^2\hbar/4m^2\omega^3$ in agreement with the exact result.*

Let's begin by writing down the Hamiltonian.

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 + \epsilon\hat{x}^2$$

And notice that this is still a QHO Hamiltonian:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\Omega^2\hat{x}^2$$
$$\Omega = \sqrt{\omega^2 + 2\epsilon/m}$$

Hence the ground state energy is $E_0 = \frac{1}{2}\hbar\Omega$. Let's binomially expand:

$$\begin{aligned} E_0 &= \frac{1}{2}\hbar\omega(1 + 2\epsilon/m\omega^2)^{1/2} \\ &\approx \frac{1}{2}\hbar\omega(1 + \epsilon/m\omega^2 - \epsilon^2/2m^2\omega^4) \\ &= \frac{1}{2}\hbar\omega + \frac{\hbar\epsilon}{2m\omega} - \frac{\hbar\epsilon^2}{4m^2\omega^3} \\ &= \frac{1}{2}\hbar\omega + l^2\epsilon - \frac{\epsilon^2 l^4}{\hbar\omega} \end{aligned}$$

Now let's find the 1st order energy change. We need to evaluate

$$E_0^1 = \langle 0^0|\epsilon\hat{x}^2|0^0\rangle$$

As these states are harmonic oscillator states, we should convert $\hat{x}^2$ into a form involving raising and lowering operators. You can check that

$$\begin{aligned} \hat{x} &= l(a_+ + a_-) \\ \Rightarrow \hat{x}^2 &= l^2(\hat{a}_+^2 + \hat{a}_-^2 + \hat{a}_+\hat{a}_- + \hat{a}_-\hat{a}_+) \end{aligned}$$

But remember that $\hat{a}_\pm\hat{a}_\mp = \frac{\hat{H}}{\hbar\omega} \mp \frac{1}{2}$:

$$\hat{x}^2 = l^2\left(\hat{a}_+^2 + \hat{a}_-^2 + \frac{2\hat{H}}{\hbar\omega}\right)$$

So

$$\begin{aligned} E_0^1 &= \epsilon l^2\,\langle 0^0|\hat{a}_+^2 + \hat{a}_-^2 + \frac{2\hat{H}}{\hbar\omega}|0^0\rangle \\ &= \epsilon l^2\,\langle 0^0|\,(\sqrt{2}\,|2^0\rangle + |0^0\rangle) \\ &= l^2\epsilon \end{aligned}$$

In agreement with the 1st order result.
Now let's find the change in the ground state:

$$\begin{aligned}
|b\rangle &= \sum_{j=1}^{\infty} \frac{\langle j^0|\epsilon\hat{x}^2|0^0\rangle\,|j^0\rangle}{\frac{\hbar\omega}{2} - \left(j\hbar\omega + \frac{\hbar\omega}{2}\right)} \\
&= -\frac{\epsilon l^2}{\hbar\omega}\sum_{j=1}^{\infty} \frac{\langle j^0|\hat{a}_+^2 + \hat{a}_-^2 + \frac{2\hat{H}}{\hbar\omega}|0^0\rangle\,|j^0\rangle}{j} \\
&= -\frac{\epsilon l^2}{\hbar\omega}\sum_{j=1}^{\infty} \frac{\langle j^0|\left(\sqrt{2}\,|2^0\rangle + |0^0\rangle\right)|j^0\rangle}{j} \\
&= -(\epsilon l^2/\sqrt{2}\hbar\omega)\,|2^0\rangle
\end{aligned}$$

Now finally, the second order energy change:

$$\begin{aligned}
E_0^2 &= \sum_{j=1}^{\infty} \frac{|\,\langle j^0|\epsilon\hat{x}^2|0^0\rangle\,|^2}{\frac{\hbar\omega}{2} - \left(j\hbar\omega + \frac{\hbar\omega}{2}\right)} \\
&= -\frac{1}{\hbar\omega}\frac{(\epsilon l^2\sqrt{2})^2}{2} \\
&= -\frac{\epsilon^2 l^4}{\hbar\omega}
\end{aligned}$$

In agreement with the exact result.

8.5 Worked Example: QHO Perturbation II

Question 6. *The harmonic oscillator of frequency ω is perturbed by $\delta\hat{H} = \epsilon\hat{x}^4$. For $l = \sqrt{\hbar/2m\omega}$, show that the first order energy correction of the nth state is*

$$E_n^1 = 3\epsilon l^4(2n^2 + 2n + 1)$$

From the previous question we have $\hat{x}^2 = l^2\left(\hat{a}_+^2 + \hat{a}_-^2 + \frac{2\hat{H}}{\hbar\omega}\right)$. Consider $E_n^1 = \langle n^0|\epsilon\hat{x}^4|n^0\rangle$. Recall $\hat{x}$ is hermitian; we can therefore split the $\hat{x}^4$ into two $\hat{x}^2$ and act on the bra with one of them. As the expression is symmetric we can write

$$\begin{aligned}
E_n^1 &= \epsilon|\hat{x}^2\,|n^0\rangle\,|^2 \\
&= \epsilon l^4\left|\left(\hat{a}_+^2 + \hat{a}_-^2 + \frac{2\hat{H}}{\hbar\omega}\right)|n^0\rangle\right|^2 \\
&= \epsilon l^4|\sqrt{(n+1)(n+2)}\,|(n+2)^0\rangle + \sqrt{n(n-1)}\,|(n-2)^0\rangle + 2(n+1/2)\,|n^0\rangle\,|^2 \\
&= \epsilon l^4((n+1)(n+2) + n(n-1) + (2n+1)^2) \\
&= 3\epsilon l^4(2n^2 + 2n + 1)
\end{aligned}$$

Chapter 9

Selection Rules

This brief chapter will cover an important trick for simplifying integrals you'll have to do in this part of the course. I apologise for the poor quality of this part as I never really understood what this was all about - you'll have to find somewhere else to learn this from if you're in the same boat. Anyway, here's my limited knowledge of selection rules.

9.1 Matrix Elements

9.1.1 Converting Bra-kets to Integrals

Let's begin by considering the quantity $\langle n'l'm'|f(\hat{\mathbf{x}})|nlm\rangle$. We can resolve the identity over the spherical co-ordinates:

$$= \int \langle n'l'm'|r,\theta,\phi\rangle \langle r,\theta,\phi|f(\hat{\mathbf{x}})|nlm\rangle \, drd\theta d\phi$$

Recall that $\langle x| V(\hat{\mathbf{x}}) |\psi\rangle = \langle x| V(\mathbf{x}) |\psi\rangle$. This allows us to move the function out of the ket sandwich:

$$= \int \psi'^* f(r,\theta,\phi) \langle r,\theta,\phi|nlm\rangle \, drd\theta d\phi$$
$$= \int \psi'^* f(r,\theta,\phi)\psi drd\theta d\phi$$

9.1.2 Z-Direction

Lets take $f(\hat{\mathbf{x}}) = \hat{z}$. This yields the integral

$$\int R_{n'l'}(Y_{l'}^{m'})^*(r^3 \sin\theta\cos\theta)R_{nl}Y_l^m drd\theta d\phi$$

We are interested in when this integral is zero. This will never happen due to the radial integral, so we can safely ignore it. You can check Prof. Parameswaran's notes to see a summary of how to use parity to get the rule that l changes by at most one and never zero. Also, by considering the form of the spherical harmonics (there's a useful table on Wikipedia) you can see that the ϕ integral takes the form

$$\int_0^{2\pi} e^{-i(m_f - m_i)\phi} d\phi$$

Which is non-zero only if $m_f = m_i$

9.2 Angular Momentum

It should be memorised that photons have $l_{ph} = 1$ and $m_{ph} = \pm 1$. Hence if a photon travelling along the z axis is absorbed, the m value of the atom must change by at most 1, and there is no change if the photon is absorbed after travelling along any direction in the $x - y$ plane. Also, as l

corresponds to the maximum possible value of angular momentum in the z-direction, it is possible (by considering a photon travelling along the z-axis) to see that this number in the composite system can change by at most $\pm l_{ph}$ depending in whether the photon's angular momentum axis is aligned or anti-aligned with the atom's. However if the photon travels along some other axis, the l value could change by less than l_{ph} as the component aligned with the atom's angular momentum axis could cause partial cancellation. Therefore the final l value for the atom that absorbed the photon satisfies $|l-1| \leq l_f \leq l+1$. In this case a change in l of zero is allowed, but it is *dis*allowed by considering matrix elements so is not relevant here.

9.3 Worked Example: Matrix Elements

Question 7. *With $|nlm\rangle$ a stationary state of Hydrogen, which of these are non-zero?*

1. $\langle 100|z|200\rangle$
2. $\langle 100|z|210\rangle$
3. $\langle 100|z|211\rangle$
4. $\langle 100|z|300\rangle$
5. $\langle 100|z|310\rangle$
6. $\langle 100|z|320\rangle$
7. $\langle 100|x|200\rangle$
8. $\langle 100|x|210\rangle$
9. $\langle 100|x|211\rangle$

Note $z = r\cos\theta, x = r\sin\theta\cos\phi$.

1. $\propto \int_0^\pi \cos\theta\sin\theta d\theta = 0$
2. $\neq 0$
3. $\propto \int_0^\pi \cos\theta\sin\theta d\theta = 0$
4. $\propto \int_0^\pi \cos\theta\sin\theta d\theta = 0$
5. $\neq 0$
6. $\propto \int_0^\pi (3\sin\theta\cos^3\theta - \sin\theta\cos\theta) d\theta = 0$
7. $\propto \int_0^{2\pi} \cos\phi d\phi = 0$
8. $\propto \int_0^{2\pi} \cos\phi d\phi = 0$
9. $\neq 0$

Chapter 10

Particles in Electric and Magnetic Fields II

10.1 Minimal Coupling

The Hamiltonian for a particle of charge q in a magnetic vector potential $\mathbf{A}$ and electric potential ϕ is

$$\hat{H} = \frac{1}{2m}(\hat{\mathbf{p}} - q\mathbf{A})^2 + q\phi$$

10.1.1 Fields and Gauge Invariance

Recall from EM the forms of the electric and magnetic fields:

$$\mathbf{B} = \nabla \times \mathbf{A}$$
$$\mathbf{E} = -\nabla\phi - \partial_t \mathbf{A}$$

A gauge transformation is one that satisfies

$$\mathbf{A} \to \mathbf{A}' = \mathbf{A} + \nabla\Lambda$$
$$\phi \to \phi' = \phi - \partial_t \Lambda$$

For a scalar field Λ. You can check by substitution that such a transformation leaves $\mathbf{E}$ and $\mathbf{B}$ unchanged. If we transform the potentials, and therefore $\hat{H}$, in this way, and simultaneously transform the wavefunction as

$$\Psi \to \Psi' = e^{iq\Lambda/\hbar}\Psi$$

Then the TDSE is still satisfied: $i\hbar\partial_t\Psi' = H'\Psi'$. This phase factor disappears when calculating probabilities so different choices of gauge correspond to the same physical state. We can also recover the Lorentz force equation from this Hamiltonian. You can check in the lecture notes that one can arrive at the following expression by employing Ehrenfest's theorem:

$$m\frac{d\langle\mathbf{v}\rangle}{dt} = q\left\langle \mathbf{E} + \frac{\mathbf{v}\times\mathbf{B} - \mathbf{B}\times\mathbf{v}}{2} \right\rangle$$

10.2 Aharonov-Bohm Effect

Consider the following situation: we send electrons through two slits, then they pass around a solenoid in the middle. In the ideal case the $\mathbf{B}$ field is 0 outside the solenoid; the $\mathbf{A}$ field, however, is not.

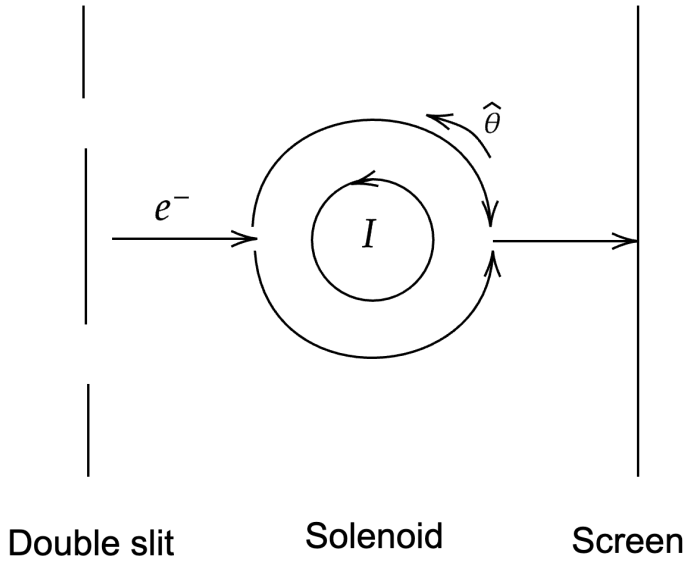


Figure 10.1: Setup of the experiment described by Aharonov and Bohm.

10.2.1 Calculation of the Vector Potential

Let's use some results from EM. First:

$$\mathbf{B} = \nabla \times \mathbf{A}$$
$$\Rightarrow \oint_C \mathbf{A} \cdot d\mathbf{l} = \Phi$$

Where C is the circular path marked by the outside of the solenoid, in the direction of $\hat{\boldsymbol{\theta}}$. Due to symmetry $\mathbf{A}$ does not vary over C, so the integral can be evaluated:

$$2\pi RA = \Phi$$
$$\Rightarrow \mathbf{A} = \frac{\Phi \hat{\boldsymbol{\theta}}}{2\pi R}$$

Finally, in the region outside the solenoid we want $\mathbf{B} = 0$ so $\mathbf{A}$ is curl-free, and thus can be written as the gradient of a potential, which without loss of generality we may write as $\mathbf{A} = \nabla g \frac{\hbar}{q}$. Notice that this implies an integral form for g, namely[1]

$$g(\mathbf{r}) = \frac{q}{\hbar} \int_{\mathbf{r}_{\text{ref}}}^{\mathbf{r}} \mathbf{A}(\mathbf{r}') \cdot d\mathbf{r}'$$

10.2.2 TDSE Under a Change of Variables

Consider the ansatz

$$\Psi = e^{ig}\Psi'$$

It turns out this ansatz simplifies the TDSE. After lots of algebra and vector identities, you can show the TDSE with Ψ becomes

$$-\frac{\hbar^2}{2m}\nabla^2\Psi' = i\hbar\partial_t\Psi'$$

Which implies that we can treat the situation as if it were a free particle by considering Ψ', then tack on the e^{ig} at the end to get the actual wavefunction.

[1] This is of course similar to the integral form of the electric potential.

10.2.3 Phase Differences

Considering the integral form of g, we have along the top path $d\mathbf{r}' = -Rd\theta\hat{\boldsymbol{\theta}}$, and hence evaluating the integral we get

$$g_{top} = -\frac{q\Phi}{2\hbar}$$

For the bottom path $d\mathbf{r}' = Rd\theta\hat{\boldsymbol{\theta}}$, so we get

$$g_{bottom} = \frac{q\Phi}{2\hbar}$$

and hence there is an extra constant phase difference of $\frac{q\Phi}{\hbar}$ added to the phase difference from the two-slit interference, which shifts the interference pattern by a constant amount.

10.3 Uniform Magnetic Field: Laundau Levels

Remember we are free to choose any gauge we like; lets choose $\mathbf{A} = (0, Bx, 0)$ which you can verify produces a uniform field in the z-direction. Let's assume the particle has no motion out of the $x-y$ plane. When thinking about the classical analogue, the particle would be doing circular motion in the plane instead of spiralling out of it. Anyway, the Hamiltonian becomes

$$\begin{aligned}\hat{H} &= \frac{1}{2m}(-i\hbar\partial_x\hat{\mathbf{i}} - i\hbar\partial_y\hat{\mathbf{j}} - qBx\hat{\mathbf{j}})^2 \\ &= \frac{1}{2m}((i\hbar\partial_x)^2 + (i\hbar\partial_y + qBx)^2)\end{aligned}$$

Now lets use the ansatz $\psi(x, y) = e^{iky}\phi(x)$.

$$\begin{aligned}Ee^{iky}\phi(x) &= \frac{1}{2m}(-\hbar^2 e^{iky}\phi'' + \phi(i\hbar\partial_y + qBx)e^{iky}(-\hbar k + qBx)) \\ &= \frac{1}{2m}(-\hbar^2 e^{iky}\phi'' + \phi(-\hbar k e^{iky} + qBxe^{iky})(-\hbar k + qBx)) \\ &= \frac{e^{iky}}{2m}(-\hbar^2\phi'' + \phi(qBx - \hbar k)^2) \\ \Rightarrow E\phi &= \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{(qBx - \hbar k)^2}{2m}\right)\phi \\ &= \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{q^2B^2}{2m}\left(x - \frac{\hbar k}{qB}\right)^2\right)\phi\end{aligned}$$

Notice the RHS looks like a displaced harmonic oscillator with Hamiltonian

$$\hat{H} = -\frac{\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega(x - x_0)^2$$

Where in this case

$$\begin{aligned}\omega &= \left(\frac{qB}{m}\right)^2 \\ x_0 &= \frac{\hbar k}{qB}\end{aligned}$$

As the Hamiltonian is just a displaced oscillator, the eigenvalues are those of an oscillator: $E_n = (n + 1/2)\hbar\omega$. The eigenfunctions are also those of an oscillator, although displaced by x_0. Note that the energy doesn't depend on k, so the system is infinitely degenerate as any choice of k yields the same energy.

10.4 Hydrogen in a Uniform Magnetic Field: Zeeman Effect

Consider the minimal coupling Hamiltonian with a gauge $\mathbf{A} = \frac{1}{2}\mathbf{B} \times \mathbf{r}$, where $\mathbf{B} = B\hat{\mathbf{k}}$. Let's expand it:

$$\begin{aligned}\hat{H} &= \underbrace{\frac{\hat{\boldsymbol{p}}^2}{2m}}_{\hat{H}^0} + \frac{q^2|\mathbf{A}|^2}{2m} - \frac{q}{m}\hat{\boldsymbol{p}} \cdot \mathbf{A} \\ &= \hat{H}^0 + \frac{q^2|\mathbf{A}|^2}{2m} - \frac{q}{2m}\hat{\boldsymbol{p}} \cdot (\mathbf{B} \times \mathbf{r})\end{aligned}$$

Notice we have treated everything that isn't the free particle as a perturbation. Now let's use a vector identity:

$$\begin{aligned}&= \hat{H}^0 + \frac{q^2|\mathbf{A}|^2}{2m} - \frac{q}{2m}\mathbf{B} \cdot (\mathbf{r} \times \hat{\boldsymbol{p}}) \\ &= \hat{H}^0 + \frac{q^2|\mathbf{A}|^2}{2m} - \frac{q}{2m}\mathbf{B} \cdot \hat{\boldsymbol{L}}\end{aligned}$$

We also can find the value of $|\mathbf{A}|^2$ from its definition:

$$\hat{H} = \hat{H}^0 + \underbrace{\frac{q^2B^2(x^2+y^2)}{8m}}_{\text{small, can ignore}} - \frac{q}{2m}\mathbf{B} \cdot \hat{\boldsymbol{L}}$$

So our perturbation is effectively

$$\delta\hat{H} = -\frac{q}{2m}\underbrace{\mathbf{B} \cdot \hat{\boldsymbol{L}}}_{B\hat{L}_z}$$

Now we would like to know the corrections to the energy that this produces. This is a degenerate problem: our original states are $|nlm\rangle$ and there is therefore degeneracy due to multiple values of m, l for each energy. We may as well see if these are good states:

$$\begin{aligned}\delta\hat{H}\,|nlm\rangle &= -\frac{qB}{2m_e}\hat{L}_z\,|nlm\rangle \\ &= -\frac{qB\hbar m}{2m_e}\,|nlm\rangle\end{aligned}$$

So it turns out they were the good states all along, and as the corrections are given by the eigenvalue, the hydrogen energies are changed by the amount $-\frac{qB\hbar m}{2m_e}$.

10.5 Hydrogen in a Uniform Electric Field: Stark Effect

10.5.1 Ground State: Quadratic Stark Effect

In this section we consider the effect on the ground state energy of a hydrogen atom in a uniform electric field. This is done with perturbation theory. Recall that an electric field appears in the Hamiltonian as a $+q\phi$ term, where ϕ is the potential. If $\mathbf{E} = E\hat{\mathbf{k}}$, you can check that $\phi = -Er\cos\theta$ and hence our perturbation is $\delta\hat{H} = -eEr\cos\theta$. We can plug this into our formula for 1st order energy correction: $E_1^1 = -eE\,\langle 100|r\cos\theta|100\rangle$. Notice:

$$\langle 100|r\cos\theta|100\rangle \propto \int_0^\pi \cos\theta\sin\theta d\theta = 0$$

So there is no change at 1st order. Let's look at 2nd order.

$$E_1^2 = -\sum_{n,l,m\neq 1,0,0} \frac{\langle 100|eEr\cos\theta|nlm\rangle}{E_1^0 - E_n^0}$$

Somewhere in the depths of Binney and Skinner you can find a way to evaluate this integral, but it is needlessly convoluted and I haven't got the patience to try and understand it and then transcribe it here. It will probably not come up, as it only tests your ability to do a ridiculous integral and not any actual physics, and if it does you will be guided through it. Anyway that aside, the integral (allegedly) evaluates to

$$E_1^2 = -\frac{9e^2E^2a_B^2}{4R}$$

Where R is the Rydberg.

10.5.2 Excited States: Linear Stark Effect

We'll consider the 1st excited state, $n = 2$. This is a degenerate perturbation theory problem as we have 4 degenerate states: $|200\rangle, |21-1\rangle, |210\rangle, |211\rangle$ to which we associate $(1,0,0,0), (0,1,0,0), (0,0,1,0), (0,0,0,1)$ respectively. To get the 1st order energy correction we need the matrix elements of $\delta\hat{H}_d$, and to get those we need the integral

$$-eE\underbrace{\langle 2l'm'|r\cos\theta|2lm\rangle}_{M}$$

Notice we can get rid of a load of cases by considering the selection rules:

$$M \propto \int_0^{2\pi} (e^{i\phi})^{m-m'} d\phi$$

Which $= 0$ for $m \neq m'$ and $= 2\pi$ for $m = m'$. Also consider the case $l, m = l', m'$. If we look at the list of spherical harmonics, we can see that there are three cases to consider:

$$\begin{aligned} M &\propto \int_0^{\pi} \sin^3\theta\cos\theta d\theta \\ &\propto [\sin^4\theta]_0^{\pi} = 0 \end{aligned}$$

or

$$\begin{aligned} M &\propto \int_0^{\pi} \cos^3\theta\sin\theta d\theta \\ &\propto [\cos^4\theta]_0^{\pi} = 0 \end{aligned}$$

or

$$M \propto \int_0^{\pi} \cos\theta\sin\theta d\theta = 0$$

So in all cases they equal zero. This leaves just two non-zero matrix elements: $\langle 200|r\cos\theta|210\rangle$ and its conjugate. Let's step through the integrals.

$$\begin{aligned} M &= (2\pi)\int_0^{\pi} \frac{1}{2\sqrt{\pi}}\frac{\sqrt{3}}{2\sqrt{\pi}}\sin\theta\cos^2\theta d\theta \int_0^{\infty} r^3 \left(\frac{a_z^{-3/2}}{\sqrt{2}}\left(1-\frac{r}{2a_z}\right)e^{-r/2a_z}\right)\left(\frac{a_z^{-3/2}}{2\sqrt{6}}\frac{r}{a_z}e^{-r/2a_z}\right)dr \\ &= \frac{1}{8}\int_0^{\pi}\sin\theta\cos^2\theta d\theta \int_0^{\infty}\left(\frac{r}{a_z}\right)^4\left(1-\frac{r}{2a_z}\right)e^{-r/a_z}dr \end{aligned}$$

Now let $\rho = r/a_z$, so $dr = a_z d\rho$:

$$\begin{aligned} &= \frac{a_z}{12}\int_0^{\infty}\rho^4\left(1-\frac{\rho}{2}\right)e^{-\rho}d\rho \\ &= \frac{a_z}{12}(-36) = -3a_z \end{aligned}$$

Hence we have the matrix

$$\delta\hat{H}_d = 3eEa_z \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

Which has eigenvectors $\frac{(-1,0,1,0)}{\sqrt{2}}, \frac{(1,0,1,0)}{\sqrt{2}}, (0,0,0,1), (0,1,0,0)$ with eigenvalues$-3eEa_z, 3eEa_z, 0, 0$ respectively. These are our energy corrections.

Chapter 11

The Variational Method

I will start by proving an important theorem and then go into more detail on what it implies.

11.1 The Variational Theorem

Suppose we have a set of orthonormal energy eigenstates. $|n\rangle$, $n = 0, 1, ...$ such that $E_0 \leq E_1 \leq ....$ By expanding in these states $|\psi\rangle = \sum_m c_m |m\rangle$ we can show

$$\sum_m |c_m|^2 = \langle\psi|\psi\rangle = 1$$

due to normalisation. This holds for any state $|\psi\rangle$. Now, lets consider some 'trial state' $|\psi_t\rangle$ (the meaning of this will become clear soon) and find the expected value of the Hamiltonian in this state:

$$\begin{aligned}\langle\psi_t|\hat{H}|\psi_t\rangle &= \sum_m \sum_n c_m^* c_n \langle m|\hat{H}|n\rangle \\ &= \sum_m |c_m|^2 E_m\end{aligned}$$

Now let's add and subtract $E_0 \sum_m |c_m|^2$, so we add zero:

$$= \underbrace{E_0 \sum_m |c_m|^2}_{E_0} + \underbrace{\sum_m |c_m|^2 (E_m - E_0)}_{\geq 0}$$

As the energy increases in each level. So overall we have $\langle\psi_t|\hat{H}|\psi_t\rangle \geq E_0$.

11.2 So What?

This means that if we have a situation where we don't know the wavefunction but would like to know the ground state energy, we can make a guess at the form of the wavefunction by way of a trial wavefunction ψ_t. This will have some parameter in it that we can minimize the quantity $\langle\psi_t|\hat{H}|\psi_t\rangle$ with respect to. When we have minimised this quantity, we have an upper bound for the ground state energy.

Chapter 12

Time-Dependent Hamiltonians

12.1 Sudden Limit - Fast Hamiltonians

In this case the Hamiltonian undergoes an instantaneous change after a certain time, say $t = 0$, but the Hamiltonians either side of $t = 0$ are time-independent. This will yield two sets of energy eigenstates. As the ground state for the initial Hamiltonian may not be the ground state for the final one, there may be a chance the system is excited by the change.

12.2 Adiabatic Limit - Slow Hamiltonians

The idea here is that if the Hamiltonian changes slowly enough, and if the system is in the nth eigenstate, it will remain there after the change. There is a proof for this in Prof. Parameswaran's notes but I am confident such a proof will not be examined.

12.3 Time-Dependent Perturbation Theory - Small Hamiltonians

This method applies to Hamiltonians of the form $\hat{H} = \hat{H}^0 + V(t)$, where $V(t)$ is a small time-dependent perturbation. We expand $|\psi\rangle$ as normal, but let the coefficients of the expansion be time-dependent:

$$|\psi(t)\rangle = \sum_n c_n(t) e^{-iE_n t/\hbar} |n\rangle$$

Where $\hat{H}^0 |n\rangle = E_n |n\rangle$. Applying the TDSE:

$$\begin{aligned}
\hat{H} |\psi\rangle &= i\hbar \partial_t |\psi\rangle \\
&= i\hbar \sum_n |n\rangle \left(e^{iE_n t/\hbar} \dot{c}_n - \frac{iE_n}{\hbar} c_n e^{-iE_n t/\hbar} \right) \\
&= \sum_n i\hbar e^{-iE_n t/\hbar} \dot{c}_n |n\rangle + \sum_n c_n e^{-iE_n t/\hbar} E_n |n\rangle \\
&= \sum_n c_n e^{-iE_n t/\hbar} (E_n + V) |n\rangle \\
\Rightarrow \sum_n i\hbar e^{-iE_n t/\hbar} \dot{c}_n |n\rangle &= \sum_n c_n e^{-iE_n t/\hbar} V |n\rangle
\end{aligned}$$

Now let's bra through with $\langle m|, m \neq n$:

$$\begin{aligned}
i\hbar e^{-iE_m t/\hbar} \dot{c}_m &= \sum_n c_n e^{-iE_n t/\hbar} \langle m|V|n\rangle \\
\Rightarrow \dot{c}_m &= \frac{1}{i\hbar} \sum_n c_n e^{-i(E_n - E_m)t/\hbar} \langle m|V|n\rangle
\end{aligned}$$

As V is a 1st order correction to the Hamiltonian, the quantity $\frac{1}{i\hbar}e^{-i(E_n-E_m)t/\hbar}\langle m|V|n\rangle = \epsilon M_{mn}$ is a 1st order (order ϵ) matrix element. We can also expand c_m to 1st order:

$$c_m = c_m^{(0)} + \epsilon c_m^{(1)} + ...$$

Subbing this in:

$$\dot{c}_m^{(0)} + \epsilon\dot{c}_m^{(1)} = \sum_n (c_n^{(0)} + \epsilon c_n^{(1)})\epsilon M_{mn}$$

Comparing 0th order terms gives $\dot{c}_m^{(0)} = 0 \Rightarrow c_m^{(0)} = \text{const} = c_m^{(0)}(0)$. At $t = 0$ assume perturbation is off so $\epsilon = 0$. This means $c_m^{(0)} = c_m(0)$. Now let's compare 1st order terms:

$$\dot{c}_m^{(1)} = \sum_n M_{mn}c_n(0)$$

Let the system be in the eigenstate $|i\rangle$ at $t = 0$. So $c_n = \delta_{in}$. Hence $\dot{c}_m^{(1)} = M_{mi}$ and to 1st order we have an expression for $\dot{c}_m$:

$$\dot{c}_m = \dot{c}_m^{(0)} + \epsilon\dot{c}_m^{(1)} = \epsilon M_{mi} = \frac{1}{i\hbar}e^{-i(E_i-E_m)t/\hbar}\langle m|V|i\rangle$$

12.3.1 Time-Periodic Perturbations and Fermi's Golden Rule

Integrating both sides, and looking for the coefficient of landing in a particular final state f:

$$c_f = \frac{1}{i\hbar}\int_0^t e^{-i(E_i-E_f)t'/\hbar}\langle f|V|i\rangle\, dt'$$

Now let's let $\omega_{fi} = \frac{E_f-E_i}{\hbar}$. Also, let V be a time-periodic perturbation, i.e. $V = V_0e^{-i\omega t}$:

$$\begin{aligned}
c_f &= \frac{1}{i\hbar}\int_0^{t'} e^{i(\omega_{fi}-\omega)t'}\langle f|V_0|i\rangle\, dt' \\
&= -\frac{1}{\hbar}\left[\frac{e^{i(\omega_{fi}-\omega)t'}\langle f|V_0|i\rangle}{\omega_{fi}-\omega}\right]_0^t \\
&= -\frac{\langle f|V_0|i\rangle}{\hbar(\omega_{fi}-\omega)}(e^{i(\omega_{fi}-\omega)t} - 1) \\
\Rightarrow |c_f|^2 &= \frac{|\langle f|V_0|i\rangle|^2}{\hbar^2}\frac{\sin^2((\omega_{fi}-\omega)t/2)}{((\omega_{fi}-\omega)/2)^2}
\end{aligned}$$

The function $\frac{\sin^2((\omega_{fi}-\omega)t/2)}{((\omega_{fi}-\omega)/2)^2}$ is sharply peaked at $\omega = \omega_{fi}$, and its integral over that peak[1] equals $2\pi t$. Hence we can approximate it with a delta function:

$$|c_f|^2 = |\langle f|V_0|i\rangle|^2\frac{2\pi t\delta(\omega-\omega_{fi})}{\hbar^2}$$

Then the probability per unit time, or the *transition rate*, is

$$r_\omega = |\langle f|V_0|i\rangle|^2\frac{2\pi\delta(\omega-\omega_{fi})}{\hbar^2}$$

We discussed the case of the perturbation being made up of a single frequency, ω. However if it is made up of a range of frequencies density $\rho(\omega)$, then the transition rate would be the integral over all of them with the density function:

$$r = |\langle f|V_0|i\rangle|^2\frac{2\pi\rho(\omega_{fi})}{\hbar^2}$$

For a density of states g this yields

$$r = |\langle f|V_0|i\rangle|^2\frac{2\pi g(E_f)}{\hbar}$$

With one less factor of $\hbar$ as $dE = \hbar d\omega$.

[1] See complex analysis short option.

12.4 Worked Example: Sudden Beta Decay

Question 8. *H^3 suddenly undergoes beta decay and becomes $(He^3)^+$. Assuming the electron is in the ground state of H^3 initially, what is the probability it remains in the ground state of $(He^3)^+$ after the change?*

The probability P we want satisfies

$$\begin{aligned}\sqrt{P} &= \langle 100^{He}|100^{H}\rangle \\ &= \frac{1}{\pi(a_B a_2)^{3/2}}\int_0^\infty r^2 e^{-r(1/a_B+1/a_2)}dr\int_0^{2\pi}\int_0^{\pi}\sin\theta d\theta d\phi\end{aligned}$$

Now let $\rho = r(1/a_B + 1/a_2)$. Then:

$$\begin{aligned}\sqrt{P} &= \frac{4}{((\frac{1}{a_B}+\frac{1}{a_2})\sqrt{a_B a_2})^3}\int_0^\infty \rho^2 e^{-\rho}d\rho \\ &= \frac{8}{\left(\sqrt{\frac{a_2}{a_B}}+\sqrt{\frac{a_B}{a_2}}\right)^3}\end{aligned}$$

Recall $a_2 = a_B/2$. Then we have $P = 64/(\frac{1}{\sqrt{2}}+\sqrt{2})^6 \approx 0.7$

12.5 Worked Example: QHO Perturbation III

Question 9. *A harmonic oscillator of mass m and frequency ω is initially (at $t=-\infty$) in its ground state. A perturbation $\epsilon\hat{x}e^{-t^2/\tau^2}$ is applied. Find the probability P that the oscillator transitions to the first excited state, at late times ($t=\infty$).*

The quantity we want is $P = |c_1(t)|^2$. The relevant formula is

$$\dot{c}_1 = \frac{1}{i\hbar}e^{-i(E_0-E_1)t/\hbar}\langle 1|\epsilon\hat{x}e^{-t^2/\tau^2}|0\rangle$$

Plugging in the energies and wavefunctions:

$$\begin{aligned}&= \frac{\epsilon}{i\hbar}e^{i\omega t-\frac{t^2}{\tau^2}}\sqrt{\frac{m\omega}{\pi\hbar}}\sqrt{\frac{2m\omega}{\hbar}}\int_{-\infty}^{\infty}x^2 e^{-\frac{m\omega}{\hbar}x^2}dx \\ &= \frac{\epsilon}{i\hbar}\sqrt{\frac{\hbar}{2m\omega}}e^{i\omega t-\frac{t^2}{\tau^2}}\end{aligned}$$

Now we integrate to find c_1 at late times:

$$c_1 = \frac{\epsilon}{i\hbar}\sqrt{\frac{\hbar}{2m\omega}}\int_{-\infty}^{\infty}e^{i\omega t-\frac{t^2}{\tau^2}}dt$$

Let $T = t/\tau$:

$$c_1 = \frac{\epsilon\tau}{i\hbar}\sqrt{\frac{\hbar}{2m\omega}}\int_{-\infty}^{\infty}e^{i\omega T\tau-T^2}dT$$

Complete the square in the exponent:

$$\begin{aligned}c_1 &= \frac{\epsilon\tau}{i\hbar}\sqrt{\frac{\hbar}{2m\omega}}\int_{-\infty}^{\infty}e^{-(T-i\tau\omega/2)^2-(\tau\omega/2)^2}dT \\ &= \frac{\epsilon\tau}{i\hbar}\sqrt{\frac{\hbar}{2m\omega}}e^{-(\tau\omega/2)^2}\underbrace{\int_{-\infty}^{\infty}e^{-(T-i\tau\omega/2)^2}dT}_{=\sqrt{\pi}}\end{aligned}$$

See complex analysis for details on how to evaluate that last integral. Then we are done:

$$P = \frac{\pi\epsilon^2\tau^2}{2m\omega\hbar}e^{-\tau^2\omega^2/2}$$

Chapter 13

Identical Particles

In this course we deal exclusively with non-interacting particles. As you will recall from the composite systems chapter, this implies that the system's wavefunction can be decomposed by separation of variables into wavefunctions of the system's parts. In other words:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)$$

But there's a problem. As the particles are identical, then swapping them over should leave all physically measurable quantities invariant. This corresponds to the fact

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\psi(\mathbf{r}_2, \mathbf{r}_1)|^2$$

Which of course means that ψ can only gain a phase under a swap of the particles:

$$\psi(\mathbf{r}_2, \mathbf{r}_1) = e^{i\alpha}\psi(\mathbf{r}_1, \mathbf{r}_2)$$

Now let's swap them again:

$$\begin{aligned}\psi(\mathbf{r}_1, \mathbf{r}_2) &= (e^{i\alpha})^2\psi(\mathbf{r}_1, \mathbf{r}_2) \\ \Rightarrow e^{i\alpha} &= \pm 1\end{aligned}$$

So whatever our composite wavefunction is, it must either stay the same or change sign under swaps of the two particles. Let's test this on our wavefunction from before:

$$\begin{aligned}\psi(\mathbf{r}_1, \mathbf{r}_2) &= \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \\ \psi(\mathbf{r}_2, \mathbf{r}_1) &= \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)\end{aligned}$$

This does not differ from the original by at most a sign, so this wavefunction is not allowed. The way we solve it is by so-called symmetrisation and anti-symmetrisation. The TISE is a linear differential equation, so we can linearly superpose solutions. Lets construct symmetric solutions;

$$\psi_+(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}(\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1))$$

Now when we swap the particles, the wavefunction is exactly the same. Particles with wavefunctions like this are **bosons**. We can also construct antisymmetric solutions:

$$\psi_-(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}(\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1))$$

Where we have the second case, that the wavefunction picks up a minus sign under a swap. These particles are **fermions**.

13.1 Pauli Exclusion Principle

Let's see what happens if we have a wavefunction for a pair of fermions that we have placed in the same physical location such that $\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}$.

$$\psi(\mathbf{r}, \mathbf{r}) = \frac{1}{\sqrt{2}}(\phi_1(\mathbf{r})\phi_2(\mathbf{r}) - \phi_1(\mathbf{r})\phi_2(\mathbf{r})) = 0$$

So the wavefunction goes to zero, hence the probability of finding two fermions in the same place is zero. It's a bit more subtle than that, and in fact you can overlap fermions if you give them different spins. The formal statement of the Pauli Exclusion Principle is that two identical fermions cannot occupy the same quantum state.

13.2 Exchange Interactions

We've seen that fermions can't be in the same place (if everything else in their state is the same). Let's look at quantifying how they stay apart in practice. We'll do this by first looking at

$$\langle(\hat{x}_1 - \hat{x}_2)^2\rangle = \langle\hat{x}_1^2\rangle + \langle\hat{x}_2^2\rangle - 2\langle\hat{x}_1\hat{x}_2\rangle$$

We'll do this in one dimension for simplicity but the argument equally applies to three. Anyway. First the distinguishable case, where the wavefunction is a simple separation of variables: $\psi_d = \phi_1(x_1)\phi_2(x_2)$. We have

$$\langle\hat{x}_1^2\rangle = \int \phi_1^* x_1^2 \phi_1 dx_1 \underbrace{\int \phi_2^* \phi_2 dx_2}_{=1}$$

So it equals the expected value of $\hat{x}_1^2$ when in the single particle state ϕ_1, which we denote $\langle\hat{x}_1^2\rangle_1$. Similarly you can show that $\langle\hat{x}_2^2\rangle = \langle\hat{x}_2^2\rangle_2$. Finally:

$$\langle\hat{x}_1\hat{x}_2\rangle = \int \phi_1^* x_1 \phi_1 dx_1 \int \phi_2^* x_2 \phi_2 dx_2 = \langle\hat{x}_1\rangle_1\langle\hat{x}_2\rangle_2$$

So overall for distinguishable particles we have

$$\langle(\hat{x}_1 - \hat{x}_2)^2\rangle = \langle\hat{x}_1^2\rangle_1 + \langle\hat{x}_2^2\rangle_2 - 2\langle\hat{x}_1\rangle_1\langle\hat{x}_2\rangle_2$$

Or, as the coordinate number doesn't matter (even though they're distinguishable, they will have the same physical constraints, so all that matters is the state the expected value is taken with respect to) we may as well write

$$\langle(\hat{x}_1 - \hat{x}_2)^2\rangle = \langle\hat{x}^2\rangle_1 + \langle\hat{x}^2\rangle_2 - 2\langle\hat{x}\rangle_1\langle\hat{x}\rangle_2$$

Now let's look at identical particles.

$$\begin{aligned}\langle\hat{x}_1^2\rangle &= \int \psi_\pm^* x_1^2 \psi_\pm dx_1 dx_2 \\ &= \frac{1}{2}\int x_1^2(\phi_1^*(x_1)\phi_2^*(x_2) \pm \phi_1^*(x_2)\phi_2^*(x_1))(\phi_1(x_1)\phi_2(x_2) \pm \phi_1(x_2)\phi_2(x_1))dx_1 dx_2\end{aligned}$$

$$\begin{aligned}&= \frac{1}{2}\Big(\int \phi_1^*(x_1)x_1^2\phi_1(x_1)dx_1 \underbrace{\int \phi_2^*(x_2)\phi_2(x_2)dx_2}_{=1} \pm \int \phi_1^*(x_1)x_1^2\phi_2(x_1)dx_1 \underbrace{\int \phi_1(x_2)\phi_2^*(x_2)dx_2}_{=0} \\ &\pm \int \phi_1(x_1)x_1^2\phi_2^*(x_1)dx_1 \underbrace{\int \phi_1^*(x_2)\phi_2(x_2)dx_2}_{=0} + \int \phi_2^*(x_1)x_1^2\phi_2(x_1)dx_1 \underbrace{\int \phi_1^*(x_2)\phi_1(x_2)dx_2)}_{=1}\end{aligned}$$

$$= \frac{1}{2}(\langle\hat{x}_1^2\rangle_1 + \langle\hat{x}_1^2\rangle_2)$$

Where the integrals that are zero or one are such due to orthonormality of the wavefunctions. Similarly for $\langle\hat{x}_2^2\rangle$:

$$\langle\hat{x}_2^2\rangle = \frac{1}{2}(\langle\hat{x}_2^2\rangle_1 + \langle\hat{x}_2^2\rangle_2)$$

Now let's look at $\langle \hat{x}_1 \hat{x}_2 \rangle$:

$$\langle \hat{x}_1 \hat{x}_2 \rangle = \frac{1}{2}(\int \phi_1^*(x_1) x_1 \phi_1(x_1) dx_1 \int \phi_2^*(x_2) x_2 \phi_2(x_2) dx_2$$
$$\pm \int \phi_1^*(x_1) x_1 \phi_2(x_1) dx_1 \int \phi_1(x_2) x_2 \phi_2^*(x_2) dx_2 \pm \int \phi_1(x_1) x_1 \phi_2^*(x_1) dx_1 \int \phi_1^*(x_2) x_2 \phi_2(x_2) dx_2$$
$$+ \int \phi_2^*(x_1) x_1 \phi_2(x_1) dx_1 \int \phi_1^*(x_2) x_2 \phi_1(x_2) dx_2)$$

Let's introduce the notation for these so-called 'overlap integrals':

$$\int \phi_i^*(x_k) x_k \phi_j(x_k) dx_k = \langle \hat{x}_k \rangle_{ij}$$

So we have

$$\langle \hat{x}_1 \hat{x}_2 \rangle = \frac{1}{2}(\langle \hat{x}_1 \rangle_1 \langle \hat{x}_2 \rangle_2 \pm \langle \hat{x}_1 \rangle_{12} \langle \hat{x}_2 \rangle_{21} \pm \langle \hat{x}_1 \rangle_{21} \langle \hat{x}_2 \rangle_{12} + \langle \hat{x}_1 \rangle_2 \langle \hat{x}_2 \rangle_1)$$

We can further simplify by noticing that $\langle \hat{x}_1^2 \rangle_i = \langle \hat{x}_2^2 \rangle_i = \langle \hat{x}^2 \rangle_i$, $\langle \hat{x}_1 \rangle_i = \langle \hat{x}_2 \rangle_i = \langle \hat{x} \rangle_i$ and $\langle \hat{x}_1 \rangle_{ij} = \langle \hat{x}_2 \rangle_{ij} = \langle \hat{x} \rangle_{ij}$ as the particles are identical. Hence:

$$\langle (\hat{x}_1 - \hat{x}_2)^2 \rangle = \langle \hat{x}^2 \rangle_1 + \langle \hat{x}^2 \rangle_2 - 2\langle \hat{x} \rangle_1 \langle \hat{x} \rangle_2 \mp 2\langle \hat{x} \rangle_{12} \langle \hat{x} \rangle_{21}$$

Which is related to the distinguishable case by

$$\langle (\hat{x}_1 - \hat{x}_2)^2 \rangle_{\text{ident.}} = \langle (\hat{x}_1 - \hat{x}_2)^2 \rangle_d \mp 2\langle \hat{x} \rangle_{12} \langle \hat{x} \rangle_{21}$$

So bosons (the upper signs) tend to be closer together than fermions (the lower signs), compared to distinguishable particles. Notice that the overlap integral vanishes unless the two wavefunctions overlap (are both non-zero over some common part of their domain). This means that for non-overlapping wavefunctions, the two identical particles behave as they are distinguishable!

13.3 Space and Spin

We need to bring spin into the picture. First, recall that bosons have symmetric states and fermions have antisymmetric states. Spin states can be symmetric and antisymmetric too, and together with the wavefunction form part of an 'overall' state of a particle. If we want to construct a state for bosons, we need either both spin and space states to be symmetric or both to be antisymmetric so that the overall state is symmetric. For fermions, they need to be one of each. For spin 1/2 particles, the symmetric states are the triplet states, and the antisymmetric state is the singlet state. Convince yourself of this by swapping the particles in these states, as we did before with the wavefunction. We write such an overall state as $|\psi\rangle = |\text{space}\rangle \otimes |\text{spin}\rangle$.

13.4 Worked Example: Particles in a Box

Question 10. *Two non-interacting particles of mass m are confined to a 1D box of length L.*

1. *Suppose the particles are identical spin-zero bosons. What is the wavefunction if the system is in an eigenstate with total energy*
   (a) $\frac{\hbar^2 \pi^2}{mL^2}$
   (b) $\frac{5\hbar^2 \pi^2}{2mL^2}$
2. *Now repeat with the particles being spin 1/2 fermions.*

As the particles are non-interacting, the energy is the sum of the individual particle in a box energies:

$$E = \frac{\hbar^2 \pi^2}{2mL^2}(n_1^2 + n_2^2)$$

We also know the wavefunction of the nth level is

$$\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

So for part 1a, the un-normalised wavefunction would be

$$\psi = \psi_1(x_1)\psi_1(x_2)$$

And for part b, clearly one particle is in $n = 1$ and one in $n = 2$. So we need to make a symmetric wavefunction:

$$\psi = \psi_1(x_1)\psi_2(x_2) + \psi_1(x_2)\psi_2(x_1)$$

For the fermion case in part a, we have a symmetric space part so we need an antisymmetric spin part:

$$\psi = \psi_1(x_1)\psi_1(x_2) \otimes |\text{singlet}\rangle$$

And for part b, we could construct an antisymmetric space and symmetric spin wavefunction:

$$\psi = (\psi_1(x_1)\psi_2(x_2) - \psi_1(x_2)\psi_2(x_1)) \otimes |\text{triplet}\rangle$$

For any triplet state. Or, we could construct a symmetric space and antisymmetric spin one:

$$\psi = (\psi_1(x_1)\psi_2(x_2) + \psi_1(x_2)\psi_2(x_1)) \otimes |\text{singlet}\rangle$$

Chapter 14

Helium

14.1 Gross Structure Hamiltonian

Helium's Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_1 - \mathbf{r}_2|}$$

Notice that the nuclear charge is $+2e$ and the final term is the electron-electron interaction term.

14.2 Singlet and Triplet Configurations

As electrons are fermions, their overall wavefunction must be antisymmetric. This means that if they are both in the $n = 1$ state (symmetric), then they must be in the singlet configuration (antisymmetric). The next excited state is one electron in $n = 1$ and one in $n = 2$. We are free to construct either a symmetric of antisymmetric space part, and then fix the spin to ensure the overall antisymmetry. Supposing we chose a symmetric space part, we would have to chose the singlet configuration. The symmetric space part would also make the particles behave like bosons (at least where exhange interactions are concerned) and be somewhat closer together. This would give them a higher interaction energy. If we choose an antisymmetric space part, we must then choose a triplet state for the spin part. This configuration (orthohelium) will be somewhat lower in energy than the singlet (parahelium) configuration.

14.3 Ground State: Variational Method

Recall that if we ignore the interaction term, we can use separation of variables and write the wavefunction as a product of hydrogenic wavefunctions:

$$\begin{aligned}\psi_0 &= \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) \\ &= \frac{Z^3}{\pi a_B^3} e^{-Z(r_1+r_2)/a_B}\end{aligned}$$

Where in this case $Z = 2$. This doesn't give a great approximation of the experimentally measured energy, so a better option would be to treat Z as a variational parameter and optimise with respect to it to get an upper bound for the ground state energy. This is motivated by the fact that the nuclear charge is partially shielded from one electron by the other electron, so the effective Z will not be exactly 2. Let's rewrite the Hamiltonian in terms of Z:

$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\right)$$

Notice that the terms $-\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$ constitute two copies the Hamiltonian of a hydrogen-like ion with atomic number Z. The expected value of this part would be the expected

value of energy of a hydrogen-like ion, times 2, i.e. $2Z^2R$ with $R = -13.605693\text{eV}$. If we take the expected value of the whole we therefore get

$$\langle \hat{H} \rangle = 2Z^2R + \frac{(Z-2)e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r_1} + \frac{1}{r_2} \right\rangle + \langle V_{ee} \rangle$$

$\langle V_{ee} \rangle$ is the expected value of the interaction energy. You can find a step-by-step guide to evaluate the required integral in Griffiths. The result is $\langle V_{ee} \rangle = -\frac{5ZR}{4}$. We also need to find the value of $\left\langle \frac{1}{r_1} + \frac{1}{r_2} \right\rangle$, which is thankfully straightforward to evaluate:

$$\begin{aligned}\left\langle \frac{1}{r_1} + \frac{1}{r_2} \right\rangle &= \frac{Z^6}{\pi^2 a_B^6} \int\int\int\int\int\int r_1^2 \sin\theta_1 r_2^2 \sin\theta_2 e^{-2Z(r_1+r_2)/a_B} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) dr_1 d\theta_1 d\phi_1 dr_2 d\theta_2 d\phi_2 \\ &= \frac{16Z^6}{a_B^6} \left(\int\int r_1^2 r_2 e^{-2Z(r_1+r_2)/a_B} dr_1 dr_2 + \int\int r_1 r_2^2 e^{-2Z(r_1+r_2)/a_B} dr_1 dr_2 \right)\end{aligned}$$

The two integrals are equal due to symmetry, so we remove a copy and double the result:

$$= \frac{32Z^6}{a_B^6} \int r_1 e^{-2Zr_1/a_B} dr_1 \int r_2^2 e^{-2Zr_2/a_B} dr_2$$

Let $x = 2Zr_1/a_B, y = 2Zr_2/a_B$. Then:

$$= \frac{32Z^6}{a_B^6} \left(\frac{a_B}{2Z} \right)^5 \underbrace{\int_0^\infty x e^{-x} dx}_{=1} \underbrace{\int_0^\infty y^2 e^{-y} dy}_{=2}$$

So overall we have

$$\left\langle \frac{1}{r_1} + \frac{1}{r_2} \right\rangle = \frac{2Z}{a_B}$$

Then our expression we need to minimise is $\langle \hat{H} \rangle = 2Z^2R + \frac{e^2(Z^2-2Z)}{2\pi\epsilon_0 a_B} - \frac{5ZR}{4}$. This can be simplified further to

$$\langle \hat{H} \rangle = (-2Z^2 + 6.75Z)R$$

Optimising we get $Z = 1.6875$ and hence our upper bound on the ground state energy is

$$E \geq 5.6953125R = -77.49\text{eV}$$

The experimentally measured value is -78.975eV, so we're pretty close!

14.4 Ground & Excited States: Perturbation Theory

Let's begin by ignoring the electron-electron interactions. Then, we can separate variables, using the product of hydrogenic wavefunctions. Again, the ground state has unperturbed energy of $2Z^2R$, i.e. $8R$. We then treat the electron interaction term as a perturbation and we can get the energy corrections of any state:

$$E_n^1 = \langle nlm | \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} | nlm \rangle$$

You can find a step-by-step evaluation of this integral in Griffiths (for the ground state), and the final result is $-\frac{5R}{2}$. Hence we get, to first order, the energy of the ground state as

$$E = 5.5R = -74.83\text{eV}$$

So, pretty close to the experimental value.