

Quantum Mechanics Revision Notes

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Chapter 1

Failure of Classical Physics

1.1 Waves are particles

There is a plethora of evidence that *waves* can behave as particles, with the following properties:

$$\boxed{E = h\nu} \qquad \boxed{p = \frac{h}{\lambda}}$$

Black body radiation

Classically:

- For a cavity, the number of EM modes *per unit volume* with frequency between ν and $\nu + d\nu$ is given by

$$N(\nu) d\nu = \frac{8\pi\nu^2}{c^3} d\nu$$

Derive as follows:

- Let \underline{k} be the wavevector of our wave. Boundary conditions dictate that it must be quantised as $|\underline{k}| = \pi|\underline{p}|/L$, where \underline{p} is a vector with integer components in 3D space, and L is the dimension of the (square) cavity.
- In \underline{p} -space, the volume density of states is, by definition, 1 (because \underline{p} must have integer components). Therefore, the number of states in the range p to $p + dp$ is given by

$$dN(p) = N(p) dp = \frac{1}{8}4\pi p^2 dp$$

(Given that we are only interested in \underline{p} -vectors with positive components.

- Feeding this into the formula $|\underline{k}| = \pi|\underline{p}|/L$, taking into account *both* polarisation of EM waves, and dividing by L^3 to find the *density*, we obtain the relation above.

- Classically, the average energy of each harmonic mode (2 degrees of freedom) is $k_B T$ – so the *energy density* (ie: energy per unit volume) is given by the *Rayleigh-Jeans Law*:

$$\rho(\nu, T) = \frac{8\pi\nu^2}{c^3} k_B T$$

This, however, predicts that ρ increases without bound at high ν – the *ultraviolet catastrophe*.

- Planck hypothesised that the energy of each mode is not just kT , but is *quantised* in units of $h\nu$ – in other words, the average energy per mode is given by (note the *major* assumption that there is no zero-point energy – we say that this is the ‘energy of the vacuum’)

$$\bar{\epsilon} = \frac{\sum_{n=0}^{n=\infty} \overbrace{nh\nu e^{-nh\nu/k_B T}}^{\text{Boltzmann}}}{\underbrace{\sum_{n=0}^{n=\infty} e^{-nh\nu/k_B T}}_{\text{Partition func}}} = \frac{h\nu}{e^{h\nu/k_B T} - 1}$$

This expression can easily be obtained by noting that the denominator is an infinite geometric series ($\sum_{n=0}^{n=\infty} ar^n = a/(1-r)$) and that the top is the negative differential of the bottom, with respect to $\beta = k_B T$.

- We then get

$$\rho(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/k_B T} - 1}$$

This fits data, and reduces to Rayleigh-Jeans as $\nu \rightarrow 0$.

Conclusion:

The energy of each mode of electromagnetic radiation is quantised in units of $h\nu$

The X-rays are made out of photons with well-defined *momentum* given by

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

The Photoelectric Effect

When light falls on a metal, electrons emerge with different energies, which can be measured by making the metal the positive-end of an electrode, and varying V , the voltage across the electrode. The *stopping voltage*, V_{stop} is the voltage above which no electrons reach the cathode, and is proportional to the maximum kinetic energy of electrons that leave the metal (E_{max}).

The phenomenon is characterised by the following properties

- $E_{\text{max}} = h\nu - W$, where W is the *work function* of the metal (the minimum energy required to release an electron from the metal). Classically, one would expect the energy in the wave to vary with *intensity*, not frequency.
- The *number* of electrons emitted (the *saturation current*) is proportional to the intensity of light. Higher intensity means more packets.
- Electron emission is instantaneous – classically, one would expect a time delay to absorb enough energy to emit an electron.

These can be explained by the following conclusion:

Light *exists* as quantised packets, each of energy $h\nu$

The Compton Effect

In *Compton Scattering*, $X - Rays$ are fired onto a metal sample and scattered by electrons. It is found that the wavelength of the scattered X-Rays, λ' varies with ϕ , the angle between the new beam and the undeflected beam.

The correct relation between λ' and ϕ can be derived directly from conservation of momentum and energy as long as we assume that

Interference of light at low intensity

In a Young's Double Slit experiment at a very low intensity of light, we detect the light as *discrete photons*. However, the resulting pattern is what is expected of a double-slit pattern – each quantum particle interacts with both slits, and its trajectory is indeterminate – trying to identify which slit the electron passes through destroys the pattern.

1.2 Particles are waves

Evidence exists that suggests particles with momentum p have wave-like properties, with wavelength given by

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

and

angular momentum quantized in units of \hbar

Atomic structure & the de Broglie Hypothesis

Incandescent gasses have characteristic line spectra. The positive charge in the atom is known to be concentrated in the nucleus (α -scattering experiments), and the electrons orbit the nucleus. To explain why the electrons do not radiate and spiral in, Bohr suggested that

The electron's angular momentum L is *quantized* in units of \hbar

Starting from this assumption, he was able to recover the correct form for the line spectrum of hydrogen.

De Broglie hypothesised that

Particles behave with wave-like
 properties, with wavelength

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

This nearly justified one of Bohr's assumptions – for a stable orbit (a 'standing wave' around the nucleus), the circumference should be an *integer number* of de Broglie wavelengths:

$$2\pi r = n\lambda = \frac{nh}{p}$$

And angular momentum is therefore:

$$L = pr = n\hbar$$

As hypothesised by Bohr.

Electron & Molecular Diffraction

The Davidson-Germer experiment diffracted electrons through a crystalline array of atoms. The diffracted beam directions depended on the incident energy (and momentum).

Diffraction has since been shown to occur with many other particles, as heavy as fluorofullerene.

It is *experimental support* for the de Broglie hypothesis.

The Stern-Gerlach Experiment

- In the Stern-Gerlach experiment, a beam of *neutral* particles with *magnetic moment* μ are passed through a non-uniform electric field, that varies most rapidly in the positive z -direction (upwards).
- Classically, the orientation of the magnetic moments should be *random*, and the net force on any atom should vary continuously between $\pm\mu \left| \frac{\partial B_z}{\partial z} \right|$ – the emerging beam should be broadened in the z -direction to reflect this.
- In fact, the beam is split into a small number of *discrete* beams, indication that the *orientation* of magnetic moments is *quantized*.

This is *experimental support* for Bohr's Hypothesis.

Chapter 2

Basics

2.1 Basic postulates

Some of the basic postulates of Quantum Mechanics can be expressed as follows:

1. A particle is represented by a ‘wavefunction’, $\psi(x, t)$, which contains *all possible information* about the particle.
2. The *probability density* is given by

$$\rho(x, t) = |\psi(x, t)|^2$$

The probability that the position of the particle is between x and $x + dx$ is given by

$$P(x, t) dx = \rho(x, t) dx$$

The wavefunction needs to be normalised such that the probability of finding the particle in all space is 1. As such

$$\int_{-\infty}^{\infty} \rho(x, t) dx = 1$$

3. A *free particle* of mass m , momentum p and energy E is represented by a *plane wave* of the form

$$\Psi(x, t) = Ae^{i(kx - \omega t)} = Ae^{i\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right)} \quad (2.1)$$

The form of each term in the wavefunction arises from experimental evidence:

- **The De Broglie Hypothesis**, supported by the *Compton* and *Davidson-Germer* experiments, gives us $k = p/\hbar$
- **The photoelectric effect** gives rise to $\omega = E/\hbar$

2.2 Wavepackets

2.2.1 Introduction

The problem with this representation of a particle is that it $P(x, t)$ is completely *uniform* over all *space* – there is *no information* about the particle’s position.

If we want to know something about the particle’s position, ψ must to some degree be localised, such that $\psi(x, t) \rightarrow 0$ as $x \rightarrow \pm\infty$. This is achieved by the superposition of plane waves of different wavenumbers and frequencies

$$\psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(k) e^{i(kx - \omega t)} dk \quad (2.2)$$

For $t = 0$, this becomes a *Fourier Integral*.

2.2.2 Momentum Representation of a Wavepacket

Let us define

$$\Phi(p, t) = \frac{1}{\sqrt{\hbar}} = g(k, t) = g\left(\frac{p}{\hbar}, t\right)$$

We then have, in accordance with Equation 2.2:

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Phi(p, t) e^{i\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right)} dp$$

and

$$\Phi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Psi(x, t) e^{-i\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right)} dx$$

And, as above, the probability of finding the particle with momenta p to $p + dp$ is

$$P(p) = |\phi(p)| dp$$

Ψ and Φ are two different ways of representing the wavefunction fully – the in *position space* and *momentum space* respectively.

2.2.3 The Dispersion Relation for a Wavepacket

In general, ω in Equation 2.2 is related to k by a *dispersion relation*, $\omega = \omega(k)$.

For a wavepacket representing a particle, we know the following

- $E = \hbar\omega$
- $p = \hbar k$
- $E = p^2/2m$

The Dispersion Relation is therefore:

$$\omega = \frac{\hbar k^2}{2m} \quad (2.3)$$

The *group velocity* of a wavepacket is therefore:

$$v_g = \frac{d\omega}{dk} = \frac{\hbar k}{m} = \frac{p}{m} \quad (2.4)$$

2.2.4 Time Evolution of a general Wavepacket

Consider the following wavepacket:

$$\Psi(x, t) \propto \int_{-\infty}^{\infty} g(k) e^{i(kx - \omega(k)t)} dk$$

Where $\omega(k)$ is the dispersion relation

2.2.5 Time evolution of a wavepacket representing a particle

Because the dispersion relation is not linear, different components of the wavepacket (with different momenta) will travel at different speeds. As such, the wavepacket will change shape over time.

2.3 The Heisenberg Uncertainty Principle

Consider Ψ – the wavefunction itself has intrinsic positional uncertainty (since Ψ extends over a range of values of x), but there is also uncertainty in the momentum of the particle, because the wavefunction is made up of a number of plane waves, each with a different momentum.

These uncertainties are reciprocal, because of the properties of Fourier Transforms – the larger the one, the smaller the other.

Mathematically, the uncertainty in x is given by

$$\Delta(x) = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

Where

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\Psi(x)|^2 dx$$

For a *Gaussian Wavepacket*:

$$\Delta x \Delta p = \frac{\hbar}{2}$$

This is the *least* possible uncertainty attainable by any wavepacket (see Section 5.4.4).

2.4 Probability current

For the *probability density*, $\rho(\mathbf{r}, t)$ to remain *normalised* for all t , the *probability current* $\mathbf{j}(\mathbf{r}, t)$ must satisfy the *continuity equation*

$$\int_S \mathbf{j}(\mathbf{r}, t) \cdot d\mathbf{S} = -\frac{\partial}{\partial t} \int_V \rho(\mathbf{r}, t) dV$$

Where S is the surface bounding some V .

We can simplify as follows:

- Express $|\Psi|$ as $\Psi^* \Psi$, and evaluate the derivative.
- Get rid of the derivatives ∂t by using the time-dependent Schrodinger Equation (see section 3).
- Use Green's Second Theorem

$$\int_S [g(\nabla f) - f(\nabla g)] \cdot d\mathbf{S} = \int_V [g \nabla^2 f - f \nabla^2 g] dV$$

We then obtain the following expression:

$$\underline{\mathbf{j}}(\underline{\mathbf{r}}, t) = \frac{\hbar}{2mi} [\Psi^*(\underline{\mathbf{r}}, t) \nabla \Psi(\underline{\mathbf{r}}, t) - \Psi(\underline{\mathbf{r}}, t) \nabla \Psi^*(\underline{\mathbf{r}}, t)]$$

For stationary states:

$$\underline{\mathbf{j}}(\underline{\mathbf{r}}) = \frac{\hbar}{2mi} [\psi^*(\underline{\mathbf{r}}) \nabla \psi(\underline{\mathbf{r}}) - \psi(\underline{\mathbf{r}}) \nabla \psi^*(\underline{\mathbf{r}})]$$

Re-arranging:

$$\underline{\mathbf{j}}(\underline{\mathbf{r}}) = \frac{\hbar}{2mi} [\psi^*(\underline{\mathbf{r}}) \nabla \psi(\underline{\mathbf{r}}) - (\psi^*(\underline{\mathbf{r}}) \nabla \psi(\underline{\mathbf{r}}))^*]$$

$$\underline{\mathbf{j}} = \Re \left(\psi^* \frac{\hbar}{im} \nabla \psi \right) = \Re \left(\psi^* \frac{\hat{\mathbf{p}}}{m} \psi \right) \quad (2.5)$$

We note two important points:

- For a stationary state, the probability current \underline{j} is time-independent.
- From the equation above, we have $\nabla \cdot \underline{\mathbf{j}} = \cdot \rho$. However, we saw above that for a stationary state, $\cdot \rho = 0$, and so $\nabla \cdot \underline{\mathbf{j}} = 0$. In 1-Dimension, this means that

$$\frac{dj}{dx} = 0$$

Which means that the flux \underline{j} is independent of position as well. In more than 1 dimension, however, this is no longer the case.

2.5 Beams of particles

The plane wave

$$\Psi(x, t) = Ae^{i(kx - \omega t)}$$

is readily normalised if it only extends over a finite volume. Otherwise, it represents a particle of *well-defined momentum* but *completely unknown position*.

By choosing A properly, Ψ can be made to represent a *beam* of particles with momentum $\hbar k$.

2.5.1 Position representation

In the position representation of a beam

$$\int_{\text{unit length}} |\Psi|^2 dx = |A|^2$$

So $|A|^2$ is the *number of particles per unit length* (or volume in 3D) – the *particle number density*.

The particle flux (Equation 2.5) is then given by

$$j(x) = |A|^2 \frac{p}{m}$$

(In other words, the product of the number density and the velocity – as expected).

2.5.2 Momentum representation

Feeding the expression for Ψ into the momentum representation, we find that the time-independent momentum-representation of the beam is

$$\phi(p) \propto \delta(p - p_0)$$

The momentum is known *exactly* for the beam.

2.6 Practical stuff

- When trying to find the *minimum* uncertainty in a position measurement as a result of a wavepacket spreading, find an expression for the uncertainty in terms of the original uncertainty Δx_0 and differentiate.
- Alternatively, for the harmonic oscillator, write the expectation value of the energy as

$$\langle E \rangle = k \langle x^2 \rangle + \frac{\langle p \rangle^2}{2m}$$

And note that

- $\langle x^2 \rangle = (\Delta x)^2$, because $\langle x \rangle = 0$, since the potential is symmetric.
- $\langle p^2 \rangle = (\Delta p)^2$, because $\langle p \rangle = 0$, since the particle isn't drifting away.

Then, use the uncertainty relation to obtain Δp in terms of Δx , feed it into the expression for $\langle E \rangle$ above, and hence obtain an expression for Δx .

Chapter 3

The Schrödinger Equation

3.1 Derivation

By considering the form of the wavepacket in Equation 2.2, we can deduce that

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2}$$

If a potential $V(x, t)$ is present, though, and we move to 3D, this becomes:

$$i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}, t) + V(\mathbf{r}, t) \Psi(\mathbf{r}, t) \quad (3.1)$$

This can also be written using the Hamiltonian Operator (see below - Equation 3.4) as follows

$$i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = \widehat{H} \Psi(\mathbf{r}, t)$$

3.2 Stationary states

If V depends on \mathbf{r} only and does not change with time, then Equation 3.1 becomes separable, and this leads to a solution of the form

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r}) e^{-iEt/\hbar} \quad (3.2)$$

Where the positional wavefunction $\psi(\mathbf{r})$ satisfies

$$\widehat{H} \psi(\mathbf{r}) = E \psi(\mathbf{r}) \quad (3.3)$$

Where E is the *energy* of the particle and \widehat{H} is the *Hamiltonian Operator*, given by

$$\widehat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \quad (3.4)$$

3.3 Boundary Conditions

There are a number of Boundary Conditions that Quantum Mechanics imposes on ψ – our general method for finding ψ is simply to use a number of trial solutions, and to fit the boundary conditions.

- Boundary conditions on ψ
 - ψ must be *finite* everywhere. Otherwise, $|\psi|^2 \rightarrow \infty$, unphysically.
 - ψ must be *continuous*. Otherwise, the *particle flux* (Equation 2.5) would produce a singular, unphysical result (since it involves ψ').
- Boundary conditions on ψ'
 - ψ' must be finite, because ψ is finite.
 - If V is finite, and since ψ is finite the Schrödinger Equation in 1D implies that ψ'' must also be finite. This means that ψ' must be continuous, or else ψ'' would have an infinite singularity.
 - **HOWEVER**, if V is not finite, and tends to ∞ *discontinuously*, then $\psi'' \rightarrow \infty$, so ψ' is *discontinuous*.

To summarise

ψ is finite and continuous at all points, and differentiable at every point where V does not discontinuously tend to ∞ .

3.4 Solutions for Constant V

3.4.1 Plane wave solution

When dealing with unbound particles, we seek a plane wave solution. Feeding the trial solution into the Schrödinger Equation gives

$$\psi(x, t) = Ae^{i(kx - \omega t)}$$

Where

$$k = \pm \sqrt{\frac{2m[E - V(x)]}{\hbar^2}}$$

- For $E > V$ (ie: the particle's has real kinetic energy), ψ oscillates.
- For $E < V$, the kinetic energy is imaginary, and ψ decays exponentially. In that case, we write $\kappa = -ik$.

A general approach to solving the Schrödinger Equation for *any* potential V is simply to solve it in each region of constant V , and to match boundary conditions.

3.4.2 Non-plane wave solutions

For bound states, we need non-plane wave solutions, and we therefore use the most general solution of the equation (involving both the positive and negative exponential). The boundary conditions on the wave can then often we used to eliminate one of the exponentials.

Chapter 4

The Wave Approach to QM

4.1 Unbound states – scattering

We first consider a beam of particles, represented by a plane wave, travelling through some potential and being reflected/transmitted from an obstruction. Possible cases include a potential step, a potential barrier or a potential well.

In each case the strategy is the same:

- Find a plane-wave solution in each case. Note that reflected waves will have negative wavenumbers
- Match boundary conditions, bearing in mind that the wave at any point is given by the superposition of all the waves present there.

A few notes:

- Two kinds of reflection coefficients exist:
 - *Amplitude* reflection coefficients, \tilde{r} and \tilde{t} , are simply given by dividing the reflected amplitude over the incident amplitude.
 - *Flux* reflection coefficients, R and T are found by dividing the reflected *flux* (Equation 2.5) over the incident flux. If the wavenumber is the same in the incident and reflected regions, $T = \tilde{t}^2$, and $R = \tilde{r}^2$.

In all these problems, it is simplest to assume that the incident wave has an amplitude of 1, and it is useful to remember, in that case, that $T + R = 1$.

- Negative reflection coefficients indicate a phase change of π .

- In cases of, for example, a potential barrier, one *could* consider waves infinitely bouncing back and forth within the barrier – but it turns out to be just as general to consider *one* forward-going wave and *one* backward going wave.

- For a potential barrier, it is found that $T = 1$ when $k_2 a = n\pi$, in other words, when $a = n\lambda/2$ – at that point, the wave reflected from one side of the barrier and from the other side interfere destructively, resulting in $R = 0$.

- For a potential barrier, $V > E$, tunnelling occurs. If $\kappa_2 a$ is very large (very *high* or *thick* barrier), we are in the *weak tunnelling limit*, where we ignore all $e^{-\kappa_2 a}$ terms, and we have

$$T \approx \frac{16k_1^2 \kappa_2^2 e^{-2\kappa_2 a}}{(k_1^2 + \kappa_2^2)^2}$$

Note that

- This is a strong function of a , m and $V_0 - E$.
- A *single* evanescent wave carries no particle current, but a superposition of two opposite evanescent waves does. This is how tunnelling occurs.
- Note, in all cases, that the energy of the beam is not specified – a continuous range of energies is possible.

4.1.1 Applications of tunnelling

Field emission from a metal

- Electrons do not usually spontaneously escape from metals because of the potential step at the surface – the ‘work function’.
- However, if a strong applied electric field is applied, the potential barrier becomes $V = -eEx$, where x is the distance from the metal (the field cannot penetrate into the metal).
- This results in a barrier of finite width, and *tunnelling* occurs – field emission.

The Scanning Tunnelling Microscope

- Strong field occur between a metal surface and a very sharp metal tip, suitably biased – the resulting tunnelling current, I , can be monitored.
- The tip is scanned horizontally over the surface, and I is kept constant by moving the tip up and down with very sensitive piezo-electric actuators.
- Because I is constant, the tunnelling barrier must be constant, so the top follows a trace corresponding to a particular value of the electron wavefunction.
- The voltages controlling the tip are recorded, and allow a surface contour map to be generated, imaging the wavefunction density over the surface.
- Extremely high spatial resolution can be achieved ($\lesssim 0.1$ nm), imaging individual atoms.

Radioactive α -Decay

- In Rutherford scattering of α -particles from the U_{238} nucleus, 8.8 MeV particles are strongly back-scattered.
- This means that the Coulomb potential around the nucleus is at least 8.8 MeV high.

- However, in the radioactive decay of U_{238} , the emitted α -particles have energies less than this.
- The radioactive decay process occurs by tunnelling.

4.2 Bound states

Unbound particles can have any energy – but for bound particles, wavefunctions satisfying the Schrödinger Equation can only have particular energies (eigenvalues of the Hamiltonian).

A few general points:

- A particle bound in a *symmetric* potential V must be equally probably found at $\pm x$ – this means that

$$|\psi(-x)|^2 = |\psi(x)|^2 \Rightarrow \psi(-x) = e^{i\alpha}\psi(x)$$

By repeating the whole process the other way round, we obtain

$$\psi(x) = e^{i\alpha}\psi(-x)$$

Combining both

$$\psi(x) = [e^{i\alpha}]^2 \psi(x)$$

This means that

$$e^{i\alpha} = \pm 1$$

Going back to our original equation, we get that

$$\boxed{\psi(-x) = \hat{P}\psi(x) = \pm\psi(x)}$$

In other words, all the eigenstates have either even or odd parity.

- The *ground* state of a symmetric well *always* has **even** parity, because it results in less ‘curvature’ in the wavefunction, which in turn means that the Hamiltonian (involving ∇^2) is kept as small as possible.
- The correspondence principle can be shown to hold in all cases, both in position and in momentum space.

4.2.1 The Infinite Well

The energy of the states is

$$E = \frac{\hbar^2 n^2 \pi^2}{2ma^2}$$

Where a is the width of the well, and n is an integer, $n \geq 1$.

4.2.2 The δ -function potential

When faced with a δ -function potential:

- Integrate the Schrödinger Equation over the range $x_0 + \epsilon$ to $x_0 - \epsilon$.
- Any contribution on the RHS not involving the δ -function will vanish as $\epsilon \rightarrow 0$.
- The result will be an expression for the discontinuity in ψ' at x_0 , in terms of $\psi(x_0)$.

Thereafter, the tactic is to find trial solutions around the δ -function and then to match the boundaries using continuity of ψ and the discontinuity in ψ' found above.

4.2.3 Finite square well

For the finite square well, the ‘trial solution — boundary conditions’ approach can be used, and this leads to the following two equations:

$$Y = X \tan X$$

$$Y = -X \cot X$$

Where $X = ka/2$ and $Y = \kappa a/2$, and k and κ are the wavenumbers in the classically allowed and forbidden regions respectively.

From the form of κ and k , we can deduce that

$$X^2 + Y^2 = \frac{mV_0 a^2}{2\hbar^2}$$

Finding the intersection of this circle with the functions above gives the bound states, the energy of which can be recovered by using either the expression for k or κ .

4.2.4 The 1D Harmonic Oscillator

The energies of the oscillator are

$$E = \left(n + \frac{1}{2}\right) \hbar\omega$$

and their wavefunctions are

$$\psi_n = A_n H_n(q) e^{-q^2/2}$$

Where $q = x\sqrt{m\omega/\hbar}$ and the H are the *Hermite Polynomials*.

The constant ω is defined as

$$\omega = \sqrt{\frac{\alpha}{m}}$$

Where the potential is given by

$$V(x) = \frac{1}{2}\alpha x^2$$

4.2.5 Three Dimensions

The Harmonic Oscillator

In that case, each potential is harmonic, and the overall wavefunction is a product of three 1D wavefunctions. The energy is characterised by *three* quantum numbers, and is given by

$$E = (n_x + n_y + n_z + 3/2)\hbar\omega$$

The infinite well

If the infinite well has sides a , b and c , the total energy is given by

$$E = \frac{\pi^2 \hbar^2}{2m} \left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right]$$

Again, the wavefunction is a product of the 1D ones.

Chapter 5

The Basic Postulates & Operators

5.1 The Basic Postulates of QM

The basic postulates of QM are as follows:

1. The most complete knowledge that can be had of a system is represented by the state vector $|\chi\rangle$.
2. To every observable A , there corresponds a Hermitian operator \hat{A} . The results of the measurement of A must be one of the *eigenvalues* of \hat{A} .
3. If the eigenvalue a_i corresponds to eigenstate $|\psi_i\rangle$, then the probability of obtaining the result a_i when the system is in state $|\chi\rangle$ is $|\langle\psi_i|\chi\rangle|^2$.
4. As a result of a measurement of A in which the value a_i is obtained, the *state of the system is changed* to the corresponding eigenstate $|\psi_i\rangle$.
5. Between measurements, the state $|\chi\rangle$ evolves with time according to the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\chi\rangle = \hat{H} |\chi\rangle$$

5.2 Operators

A key part of these postulates is that observables are represented as *operators*. When measuring the value of the observable, the result is always an eigenvalue of the operator.

5.2.1 Dirac notation

When dealing with Hermitian operators, it is easiest to use *Dirac Notation*, in which

- $|\psi\rangle$ denotes “the state with wavefunction $\psi(x)$ ”.
- $\langle\psi|$ denotes “the state with the wavefunction $\psi^*(x)$ ”.
- The ‘inner product’ or ‘overlap integral’ is written

$$\langle\phi|\psi\rangle = \int_{-\infty}^{\infty} \phi^* \psi \, dx$$

5.2.2 Properties of Observables

A few key properties of operators corresponding to observables:

- They are *linear*, such that

$$\hat{A}(\alpha\Psi + \beta\Phi) = \alpha(\hat{A}\Psi) + \beta(\hat{A}\Phi)$$

- Operators *commute* over *addition*, but *not* over multiplication. The *commutator* of two operators as defined as

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

- Operators corresponding to observables are *Hermitian* – this means that

$$\hat{A} = \hat{A}^\dagger$$

Where \hat{A}^\dagger , the *Hermitian conjugate* of \hat{A} is defined by

$$\langle \phi | \hat{A} | \psi \rangle^* = \langle \psi | \hat{A}^\dagger | \phi \rangle$$

For *all* wavefunctions Φ and Ψ .

- Some properties of Hermitian operators:

$$- (\hat{C}^\dagger)^\dagger = \hat{C}$$

$$- (\hat{A} + \hat{B})^\dagger = \hat{A}^\dagger + \hat{B}^\dagger$$

$$- (\hat{A}\hat{B}\hat{C}\dots\hat{Z})^\dagger = \hat{Z}^\dagger \dots \hat{C}^\dagger \hat{B}^\dagger \hat{A}^\dagger$$

- If \hat{A} and \hat{B} are Hermitian, then $\hat{A}\hat{B}$ is not necessarily Hermitian, but

$$\hat{C} = \hat{A}\hat{B} + \hat{B}\hat{A}$$

is.

- If \hat{A} and \hat{B} are Hermitian, then $\hat{A}\hat{B} - \hat{B}\hat{A} = i[\hat{A}, \hat{B}]$ is not necessarily Hermitian, but

$$i[\hat{A}, \hat{B}]$$

is.

- If $\hat{A}|\psi\rangle = |\phi\rangle$, then $\langle \psi | \hat{A}^\dagger = \langle \phi |$

- Operators corresponding to observables have *real eigenvalues*, because the observables are *real quantities*. This follows from the hermiticity of the operators.
- Operators corresponding to observables have *orthogonal eigenfunctions*, provided that the eigenfunctions are not degenerate. We also normalise the eigenfunctions ϕ_i such that

$$\langle \phi_i | \phi_j \rangle = \delta_{ij}$$

If the eigenfunctions *are* degenerate, we can *make* them orthogonal using the Gram-Schmidt orthogonalisation process. Consider eigenfunctions ϕ_1 and ϕ_2 , both with the same eigenvalue a , but not necessarily orthogonal. We can construct an eigenvector ϕ that *will* be orthogonal to ϕ_1 as follows:

$$\phi = \alpha\phi_1 + \beta\phi_2$$

where

$$\frac{\alpha}{\beta} = -\frac{\langle \phi_1 | \phi_2 \rangle}{\langle \phi_1 | \phi_1 \rangle}$$

- The set of eigenfunctions of a Hermitian operator is *complete*. In other words, if the ϕ_i are the orthogonal and normalised eigenfunctions, and $|\psi\rangle$ is a wavefunction spanning the same space, we can write

$$|\psi\rangle = \sum_i c_i |\phi_i\rangle$$

where

$$c_i = \langle \phi_i | \psi \rangle$$

- Note that this idea can, and indeed must, be extended to operators with an infinite number of eigenvalues and eigenvectors – for example, the position operator.

5.3 Expectation values

Consider a wavefunction ψ , and an operator \hat{A} . ψ can clearly be expressed in terms of the eigenfunctions, ϕ_i of \hat{A} – $\psi = \sum_i c_i \phi_i$.

It then stands to reason that if we make a measurement of A when the particle is in state ψ , the *expected* value the measurement will be equal to the product of each eigenvalue with the probability of obtaining it. This is given by

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

5.4 The Generalised Uncertainty Principle

5.4.1 Compatible Observables

Consider two observables A and B that commute (ie: $[\hat{A}, \hat{B}] = 0$). Let the orthogonal eigenfunctions of \hat{A} be ϕ_i , with corresponding eigenvalues a_i . Degeneracy or not, these eigenfunctions can be chosen to be orthogonal.

Now, consider

$$\hat{A}(\hat{B}\phi_i) = \hat{B}(\hat{A}\phi_i) = a_i(\hat{B}\phi_i)$$

So we see that $\hat{B}\phi_i$ is also an eigenfunction of \hat{A} .

However, this means that $\widehat{\mathbf{B}}\phi_i$ must be proportional to ϕ_i (or at least to one of the ϕ_i that has an the eigenvalue a_i).

In other words, $\widehat{\mathbf{A}}$ and $\widehat{\mathbf{B}}$ have simultaneous eigenstates. This means that

If two observables *commute*, they share eigenfunctions, and one such eigenfunction has definite, precise values of the two operators *simultaneously*. The two operators are *compatible*.

5.4.2 Incompatible Observables

Now, consider two operators $\widehat{\mathbf{A}}$ and $\widehat{\mathbf{B}}$ that *do not* commute. We define the operator $\widehat{\mathbf{A}}_d$, which defines the *deviation* of A from its mean value \bar{A} :

$$\widehat{\mathbf{A}}_d = \widehat{\mathbf{A}} - \bar{A}$$

$$\widehat{\mathbf{A}}_d^2 = (\widehat{\mathbf{A}} - \bar{A})^2 = \widehat{\mathbf{A}}^2 - 2\bar{A}\widehat{\mathbf{A}} + \bar{A}^2$$

So:

$$\begin{aligned} \langle \widehat{\mathbf{A}}_d^2 \rangle &= \langle \widehat{\mathbf{A}}^2 \rangle - \overbrace{2\bar{A}\langle \widehat{\mathbf{A}} \rangle}^{=2\bar{A}\bar{A}} \\ \langle \widehat{\mathbf{A}}_d^2 \rangle &= \langle \widehat{\mathbf{A}}^2 \rangle - \bar{A}^2 = (\Delta A)^2 \end{aligned}$$

A similar operator $\widehat{\mathbf{B}}_d$ can be constructed for $\widehat{\mathbf{B}}$.

Now, consider the state vector $|\phi\rangle$ obtained from any state vector $|\psi\rangle$ as follows

$$|\phi\rangle = (\widehat{\mathbf{A}}_d + i\lambda\widehat{\mathbf{B}}_d)|\psi\rangle$$

Where λ is an arbitrary real number.

And consider the inner product $\langle\phi|\phi\rangle$, which *must* be positive:

$$\begin{aligned} \langle\phi|\phi\rangle &= \langle\psi|(\widehat{\mathbf{A}}_d - i\lambda\widehat{\mathbf{B}}_d)(\widehat{\mathbf{A}}_d + i\lambda\widehat{\mathbf{B}}_d)|\psi\rangle \\ &= (\Delta A)^2 + \lambda^2(\Delta B)^2 + \lambda\langle i[\widehat{\mathbf{A}}_d, \widehat{\mathbf{B}}_d] \rangle \\ &\geq 0 \end{aligned}$$

Now:

- $\widehat{\mathbf{A}}$ and $\widehat{\mathbf{A}}^2$ are Hermitian, which implies that $\widehat{\mathbf{A}}_d$ is Hermitian. This means that $\langle A \rangle_d^2 = \Delta A$ *must* be real, and that $(\Delta A)^2$ must be real and positive.

- Likewise, $(\Delta B)^2$ *must* be real and positive.
- We also showed above that $i[\widehat{\mathbf{A}}, \widehat{\mathbf{B}}]$ is Hermitian, so $\langle i[\widehat{\mathbf{A}}, \widehat{\mathbf{B}}] \rangle$ is also real.

Since all the coefficients of Quadratic 5.1 are real, but we also require the quadratic to be ≥ 0 , we must have $b^2 - 4ac \leq 0$. This means that

$$\langle i[\widehat{\mathbf{A}}_d, \widehat{\mathbf{B}}_d] \rangle^2 - 4(\Delta A)^2(\Delta B)^2 \leq 0$$

Finally, we note that

$$[\widehat{\mathbf{A}}_d, \widehat{\mathbf{B}}_d] = [\widehat{\mathbf{A}}, \widehat{\mathbf{B}}]$$

As such, we have that

$$\Delta A \cdot \Delta B \geq \frac{1}{2} \left| \langle i[\widehat{\mathbf{A}}, \widehat{\mathbf{B}}] \rangle \right|$$

This is the *generalised uncertainty principle*.

5.4.3 Conjugate Observables

Conjugate pairs of Observables, p_i and q_i are determined from the Lagrangian

$$L = T - V$$

where

$$p_i = \frac{\partial L}{\partial q_i}$$

In QM, it is a fundamental assumption that these are replaced by operators, according to

$$q_i \rightarrow \widehat{\mathbf{q}}_i \text{ and } p_i \rightarrow \widehat{\mathbf{p}}_i = \frac{\hbar}{i} \frac{\partial}{\partial q_i}$$

Examples of conjugate observables are position/momentum and angle/angular momentum.

For conjugate observables A and B , it is always the case that

$$[\widehat{\mathbf{A}}, \widehat{\mathbf{B}}] = i\hbar$$

and we then get the familiar uncertainty principle

$$\Delta p_i \Delta q_i \leq \frac{1}{2} \hbar$$

5.4.4 Minimum Uncertainty States The Momentum Operator

It is reasonably clear from the analysis above that if we want the uncertainty to be kept to a minimum, we require the inner product $\langle \phi | \phi \rangle$ to vanish. Therefore

$$|\phi\rangle = \left(\widehat{\mathbf{A}}_d + i\lambda \widehat{\mathbf{B}}_d \right) |\psi\rangle = 0$$

This gives a differential equation for ψ :

$$\left[(x - \bar{x}) + i\lambda \left(\frac{\hbar}{i} \frac{\partial}{\partial x} - \bar{p} \right) \right] \psi(x) = 0$$

$$\frac{\partial \psi}{\partial x} = \left[-\frac{x - \bar{x}}{\hbar\lambda} + i\frac{\bar{p}}{\hbar} \right] \psi(x)$$

This has, as a solution, the standard Gaussian wavepacket

$$\psi(x) = C e^{-(x-\bar{x})^2/2\hbar\lambda} e^{i\bar{p}x/\hbar}$$

For which $\Delta x = \sqrt{\frac{\hbar\lambda}{2}}$ $\Delta p = \sqrt{\frac{\hbar}{2\lambda}}$

5.5 Examples of operators

The Hamiltonian Operator

We saw above that the Hamiltonian Operator is given by

$$\widehat{\mathbf{H}} = -\frac{\hbar^2}{2m} \nabla^2 + V(r)$$

We also interpreted the two parts of the operator to represent the *kinetic energy* and *potential energy* of the particle, so we obtain two new operators:

- The *Kinetic Energy* operator, $\widehat{\mathbf{T}}$, is given by

$$\widehat{\mathbf{T}} = -\frac{\hbar^2}{2m} \nabla^2 = \frac{\widehat{\mathbf{p}}^2}{2m}$$

- The *Potential Energy* operator, $\widehat{\mathbf{V}}$, is simply a number

$$\widehat{\mathbf{V}} = V(r)$$

Classically, the relation between kinetic energy and momentum is given by $T = p^2/2m$. Given the form of T in Quantum Mechanics, we can conjecture that the equivalent momentum operator in QM is

$$\widehat{\mathbf{p}} = -i\hbar\nabla$$

The Parity Operator

The Parity Operator simply inverts the wavefunction through the origin

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

The Translation and Rotation Operators

The Translation Operator, $\widehat{\mathbf{D}}_\epsilon$, produces a shift ϵ along Ox :

$$\widehat{\mathbf{D}}_\epsilon f(x) = f(x + \epsilon)$$

For *small* ϵ :

$$\widehat{\mathbf{D}}_\epsilon = 1 + i\epsilon \frac{\widehat{\mathbf{p}}_x}{\hbar}$$

The Rotation Operator, $\widehat{\mathbf{R}}_\epsilon$, produces a rotation ϵ about Oz :

$$\widehat{\mathbf{R}}_\epsilon f(\phi) = f(\phi + \epsilon)$$

The Position Operator

The *position operator*, $\widehat{\mathbf{x}}$, is simply a number, x – the position of the particle. The eigenfunctions of the operator are Dirac Delta functions, at the point x . This means that, if we want, for example, to find the probability that the particle is at a position x_0 , we simply use Postulate 3:

$$\text{Probability} = |\langle \delta(x - x_0) | \psi \rangle|^2 = |\psi(x_0)|^2$$

Which is consistent with our previous interpretation of the wavefunction.

5.6 Ladder Operators

Suppose that two operators, X and N , have the commutation relation

$$[N, X] = cX$$

We can then derive a number of useful results

Ladder action

Let $|\phi\rangle$ be an eigenstate of N with eigenvalue α , and consider N acting on $X|\phi\rangle$:

$$\begin{aligned} NX|\phi\rangle &= (XN + [N, X])|\phi\rangle \\ &= (XN + cX)|\phi\rangle \\ &= X\alpha|\phi\rangle + cX|\phi\rangle \\ &= (\alpha + c)X|\phi\rangle \end{aligned}$$

In other words, the operator X has changed our eigenstate to another eigenstate with eigenvalue c higher than the previous one.

Lowering operator

Now, consider X^\dagger

$$([N, X^\dagger])^\dagger = (NX^\dagger - X^\dagger N)^\dagger = XN^\dagger - N^\dagger X$$

Now, if N is a Hermitian operator, this gives

$$([N, X^\dagger])^\dagger = XN - NX = -cX$$

Taking the Hermitian Conjugate of both sides

$$[N, X^\dagger] = -cX^\dagger$$

And this operator will therefore *lower* the eigenvalue by C .

In other words, if X is a *raising operator* for the Hermitian operator N , then X^\dagger is a *lowering operator* for N .

We can use these as follows:

- The ladder operators themselves reveal the spacing between the energy levels.
- Extra information about the states (eg: they must have a minimum value) allows us to find the eigenstates.

5.6.1 The Harmonic Oscillator

We can put this all to good use to work out the energy levels of the Harmonic Oscillator, with Hamiltonian

$$\widehat{H} = \widehat{T} + \widehat{V} = \frac{\widehat{p}^2}{2m} + \frac{m\omega^2\widehat{x}^2}{2}$$

The Operators

Consider

$$\begin{aligned} \widehat{a} &= \sqrt{\frac{1}{\omega\hbar}} \left(\sqrt{\widehat{V}} + i\sqrt{\widehat{T}} \right) \\ \widehat{a} &= \sqrt{\frac{m\omega}{2\hbar}} \widehat{x} + i\frac{\widehat{p}}{\sqrt{2m\hbar\omega}} \end{aligned}$$

Now

$$[\widehat{H}, \widehat{a}] = -\hbar\omega$$

\widehat{a} therefore acts as a lowering operator, and \widehat{a}^\dagger as a raising operator.

The Energy Spectrum

The ‘extra bit of information’ we have here is that the energy of the oscillator must be positive, because $\langle \widehat{p}^2 \rangle$ and $\langle \widehat{x}^2 \rangle$ must be positive, which means that $\langle \widehat{H} \rangle \geq 0$. As such, there must be a *lowest energy* ground state satisfying

$$\widehat{a}|\phi_0\rangle = 0$$

Otherwise,

$$\widehat{a}|\phi_0\rangle$$

would be a lower energy state.

Now, we note that we can prove

$$[\widehat{a}, \widehat{a}^\dagger] = 1$$

$$\widehat{H} = \frac{1}{2}\hbar\omega \left(\widehat{a}\widehat{a}^\dagger + \widehat{a}^\dagger\widehat{a} \right) = \hbar\omega \left(\widehat{a}^\dagger\widehat{a} + \frac{1}{2} \right)$$

As such

$$\widehat{H}|\phi_0\rangle = \frac{1}{2}\hbar\omega|\phi_0\rangle$$

The excited states are obtained by operating repeatedly with the raising operator – we found that each is $\hbar\omega$ higher than the previous one. This gives the energy spectrum

$$E_n = (n + \frac{1}{2})\hbar\omega$$

The Wavefunctions

To find the ground state wavefunction, simply write the equation $\hat{\mathbf{a}}|\phi_0\rangle$ in full, and solve the resulting differential equation.

To find higher wavefunctions, remember that

$$|\phi_n\rangle = C_n(\hat{\mathbf{a}}^\dagger)^n|\phi_0\rangle$$

and find C_n recursively by finding an expression for $|\phi_n\rangle$ in terms of $|\phi_{n-1}\rangle$, and using the fact that $\langle\phi_n|\phi_n\rangle = 1$.

Chapter 6

Time Dependence

6.1 Measurements

We mentioned above that a measurement of a given observable A produces a value a_i , one of the eigenvalues of \hat{A} , and collapses the wavefunction into the corresponding eigenfunction ψ_i .

This eigenfunction ψ_i can be expressed in terms of the eigenfunctions of the Hamiltonian (the energy eigenfunctions):

$$\psi_i = \sum_i b_i \phi_i$$

And we know that between measurements, the wavefunction evolves according to the time-dependent Schrodinger equation. This means that *each* of the eigenfunctions of the Hamiltonian (which, we know, are time-independent stationary states of the Schrödinger equation – see section 3.2) have a time dependence $e^{-iE_it/\hbar}$.

In other words:

$$\Psi_i(t) = \sum_i b_i \Phi_i(0) e^{-iE_it/\hbar}$$

So we see that, in general, an eigenfunction of an observable is not necessarily a stationary state. The state of the system remains a superposition of energy eigenstates with the *same relative amplitudes* but *different relative phases*.

6.2 Ehrenfest's Theorem

We know that the expectation value for an observable A for a system in state $\Psi(x, t)$ is given by

$$\langle A \rangle = \langle \Psi | \hat{A} | \Psi \rangle$$

We can find an expression that describes how this changes with time

$$\begin{aligned} \frac{d\langle A \rangle}{dt} &= \frac{d}{dt} \int dx \langle \Psi | \hat{A} | \Psi \rangle \\ &= \int dx \left[\frac{\partial \Psi^*}{\partial t} \hat{A} \Psi + \Psi^* \frac{\partial \hat{A}}{\partial t} \Psi + \Psi^* \hat{A} \frac{\partial \Psi}{\partial t} \right] \\ &= \int dx \left[\frac{\partial \Psi^*}{\partial t} \hat{A} \Psi + \Psi^* \hat{A} \frac{\partial \Psi}{\partial t} \right] + \left\langle \frac{\partial \hat{A}}{\partial t} \right\rangle \end{aligned}$$

Use time dependent S.E.

$$\frac{d\langle A \rangle}{dt} = \frac{1}{\hbar} \langle i [\hat{H}, \hat{A}] \rangle + \left\langle \frac{\partial \hat{A}}{\partial t} \right\rangle$$

This last result is *Ehrenfest's Theorem* – a QM Equation of Motion.

For *observables*, \hat{A} has no explicit time-dependence, and so

$$\frac{d\langle A \rangle}{dt} = \frac{1}{\hbar} \langle i [\hat{H}, \hat{A}] \rangle$$

6.2.1 Classical limit

We consider the classical limit of Ehrenfest's Theorem in the case of two operators:

Position – \hat{x}

Since $\hat{V} = V$ and $\hat{x} = x$ commute (they're just numbers), we have that¹

$$[\hat{H}, \hat{x}] = \frac{1}{2m} [\hat{p}^2, \hat{x}] = -2i\hbar p$$

Therefore:

$$\frac{d\langle \hat{x} \rangle}{dt} = \frac{\langle \hat{p} \rangle}{m}$$

To be compared with the classical result

$$\frac{dx}{dt} = \frac{p}{m}$$

Momentum – \hat{p}

In this case \hat{p} obviously commutes with \hat{p}^2 , but not with V . So:

$$[\hat{H}, \hat{p}] = [\hat{V}, \hat{p}] = i\hbar \frac{dV}{dx}$$

(Using the definition of \hat{p} , and assuming it acts on an arbitrary function $f(x)$, in the last step).

As such

$$\frac{d\hat{p}}{dt} = \left\langle -\frac{dV}{dx} \right\rangle = \langle F(x) \rangle$$

Classically, we would have

$$\frac{d\hat{p}}{dt} = F(\langle x \rangle)$$

The two expressions are not generally equivalent. However, if we perform a Taylor expansion of $F(x)$ about $\langle \hat{x} \rangle$ and find its expected value, we find that they *are* the same as long as we can ignore the quantum uncertainty Δx . This is true in, for example, particle accelerators, where Δx is much smaller than any scale over which we would expect the fields to change, and we would expect to recover the classical equations.

¹The trick to simplify $[\hat{p}^2, \hat{x}]$ is to write it as $\hat{p}\hat{p}\hat{x} + \hat{p}\hat{x}\hat{p} - \hat{x}\hat{p}\hat{p}$.

6.3 Conserved Quantities

We note that if $[\hat{H}, \hat{A}] = 0$, $\frac{d\langle A \rangle}{dt} = 0$.

This means that any operator that commutes with the Hamiltonian is a *constant of the motion*.

Similarly, if Ψ is a stationary state, all observables have time-independent values.

6.3.1 Parity

We note that the parity operator, \hat{P} , has two eigenvalues – +1 and –1 (clearly, those are the only ones, since $\hat{P}^2 = \hat{I}$).

We also note that \hat{P} always commutes with \hat{p} , and commutes with V if $V(x) = V(-x)$. Therefore, \hat{P} commutes with \hat{H} , and is a conserved quantity, if the potential itself is symmetric.

This means that a particle with a given energy in a symmetric potential will *always* retain the same parity as time passes.

More generally, this is because \hat{H} is invariant under \hat{P} . In fact, for every *symmetry property* of \hat{H} , there exists a *symmetric operator* which commutes with \hat{H} .

An example of this is *translational invariance* – if $dV/dx = 0$, then $[\hat{H}, \hat{p}_x] = 0$ (this can be shown in a rather roundabout way using the Taylor expansion of the translation operator above).

6.4 The Time-Energy Uncertainty Relation

This is very different from the general uncertainty relations we have discussed thus far – time is not a dynamical variable, represented by an operator – it cannot be “measured”. Also, it does not appear in the Lagrangian formulations. It is simply a parameter identifying the *instant* at which the property of the system is measured.

Chapter 7

3 Dimensions

7.1 Angular Momentum

Angular momentum in QM is defined, as in classical mechanics, by $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$. Its components are therefore

$$\hat{L}_i = \hat{\mathbf{j}}\hat{p}_k - \hat{\mathbf{k}}\hat{p}_j$$

Where i, j and k are *any* cyclic permutation of x, y and z .

The operator for the square of the total orbital angular momentum $\hat{\mathbf{L}}$ is

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

7.2 Commutation relations

The following can be proved:

$$[\hat{x}_\alpha, \hat{p}_\beta] = i\hbar\delta_{\alpha\beta}$$

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

$$[\hat{L}^2, \hat{L}_\alpha] = 0$$

Where α and β are any of x, y and z , and i, j and k are *any* cyclic permutation of x, y and z .

It follows that the magnitude of L and *one* of L_x, L_y and L_z can be known simultaneously (ie: are compatible observables) – no two components of the angular momentum can be precisely known simultaneously. By convention, we choose to accurately specify the z -component.

Other commutation relations, which might or might not be useful:

$$[\hat{L}_x, \hat{\mathbf{x}}] = [\hat{L}_x, \hat{p}_x] = 0$$

$$[\hat{L}_x, \hat{y}] = i\hbar\hat{x}$$

$$[\hat{L}_x, \hat{p}_y] = i\hbar\hat{p}_z$$

$$[\hat{L}_x, \hat{r}^2] = [\hat{L}_x, \hat{p}^2] = 0$$

Chapter 8

Angular Momentum

8.1 Orbital Angular Momentum Eigenvalues

Ladder operators

Consider the following operator

$$\hat{\mathbf{L}}_+ = \hat{\mathbf{L}}_x + i\hat{\mathbf{L}}_y$$

We note that

$$[\hat{\mathbf{L}}_z, \hat{\mathbf{L}}_+] = \hbar\hat{\mathbf{L}}_+$$

As such, $\hat{\mathbf{L}}_+$ is a *ladder operator* for angular momentum

Separation of Eigenvalues

We therefore know that the eigenvalues of $\hat{\mathbf{L}}_z$ are separated by \hbar . Let's call these eigenvalues $m_\ell\hbar$, and the eigenstates $|\phi_{m_\ell}\rangle$.

Total angular momentum

Now, $\hat{\mathbf{L}}^2$ and $\hat{\mathbf{L}}_z$ commute, so they will have simultaneous eigenstates.

However, $\hat{\mathbf{L}}^2$ also commutes with $\hat{\mathbf{L}}_y$ and $\hat{\mathbf{L}}_x$, and therefore also commutes with $\hat{\mathbf{L}}_\pm$. This means that $\hat{\mathbf{L}}^2$ and $\hat{\mathbf{L}}_\pm$ have simultaneous eigenstates. As such, $\hat{\mathbf{L}}_\pm |\phi_{m_\ell}\rangle$ has the same eigenvalue of $\hat{\mathbf{L}}^2$ as $|\phi_{m_\ell}\rangle$.¹

¹To prove, let $|\phi_{m_\ell}\rangle$ have eigenvalue $\Lambda\hbar^2$ of $\hat{\mathbf{L}}^2$, and note that $\hat{\mathbf{L}}^2\hat{\mathbf{L}}_\pm|\phi_{m_\ell}\rangle = \hat{\mathbf{L}}_\pm\hat{\mathbf{L}}^2|\phi_{m_\ell}\rangle = \Lambda\hbar^2\hat{\mathbf{L}}_\pm|\phi_{m_\ell}\rangle$

This means that *all* the $|\phi_{m_\ell}\rangle$ have the *same* eigenvalue of $\hat{\mathbf{L}}^2$ – call it $\Lambda\hbar^2$.

We will now label our states

$$|\phi_{\Lambda, m_\ell}\rangle$$

Restraining condition

Obviously, L_z must be smaller or equal to L , so

$$\langle \hat{\mathbf{L}}_z \rangle \leq \langle \hat{\mathbf{L}}^2 \rangle$$

And so, we must have

$$m_\ell^2 \leq \Lambda$$

Furthermore, if $\lambda < \sqrt{\Lambda}$ is the largest possible value of m_ℓ , then, by symmetry, the smallest value must be $-\lambda$.

The Eigenvalues m_ℓ of $\hat{\mathbf{L}}_z$

Using the ladder operators, this means that m_ℓ must have values

$$m_\ell = \lambda, \lambda - 1, \dots, 1 - \lambda, -\lambda$$

The number of eigenvalues is $2n + 1$ and *must* be an integer. For this to happen, we must have

$$\lambda = \ell \text{ or } \ell + \frac{1}{2}$$

Where ℓ is an integer.

For *orbital* angular momentum, it will be shown that only the $\lambda = \ell$ case is possible.

The Eigenvalues Λ of $\widehat{\mathbf{L}}^2$

We can write $\widehat{\mathbf{L}}^2$ in terms of the raising and lowering operators

$$\begin{aligned}\widehat{\mathbf{L}}_- \widehat{\mathbf{L}}^+ &= \widehat{\mathbf{L}}^2 - \widehat{\mathbf{L}}_z^2 - \hbar \widehat{\mathbf{L}}_z \\ \widehat{\mathbf{L}}^2 &= \widehat{\mathbf{L}}_- \widehat{\mathbf{L}}_+ + \hbar \widehat{\mathbf{L}}_z + \widehat{\mathbf{L}}_z^2\end{aligned}$$

Now, consider the state $|\phi_{\Lambda, m_\ell} = \ell\rangle - \widehat{\mathbf{L}}_+ \widehat{\mathbf{L}}_+ |\phi_{\Lambda, m_\ell} = \ell\rangle$ acting on that state should give 0, so

$$\Lambda \hbar^2 = \widehat{\mathbf{L}}^2 |\phi_{\Lambda, m_\ell} = \ell\rangle = 0 + \hbar \ell \hbar + (\ell \hbar)^2$$

And therefore

$$\Lambda = \ell(\ell + 1)$$

To summarise:

The eigenstates of both $\widehat{\mathbf{L}}_z$ and $\widehat{\mathbf{L}}^2$ are denoted

$$|\ell, m_\ell\rangle$$

The corresponding eigenvalues are given by

$$\widehat{\mathbf{L}}^2 |\ell, m_\ell\rangle = \ell(\ell + 1)\hbar^2 |\ell, m_\ell\rangle$$

$$\widehat{\mathbf{L}}_z |\ell, m_\ell\rangle = m_\ell \hbar |\ell, m_\ell\rangle$$

Where

$$m_\ell = -\ell, -\ell + 1, \dots, -1, 0, 1, \dots, \ell - 1, \ell$$

$$\ell \text{ is 0 or an integer}$$

Notes:

- We can think of this as the eigenvalues of $\widehat{\mathbf{L}}^2$ restricting the length of the L -vector in space, and eigenvalues of $\widehat{\mathbf{L}}_z$ restricting its direction.
- Note that L_x and L_y are still completely unknown.
- The states with $\ell = 0, 1, 2, 3, 4, \dots$ are called s-, p-, d-, f-, g-, ... states respectively.
- For the s state, *all* the components of angular momentum are simultaneously 0.

8.2 Eigenstates

Effect of Raising and Lowering Operators

We have, so far, derived that

$$\widehat{\mathbf{L}}_+ |\ell, m_\ell\rangle = D_{\ell, m_\ell} |\ell, m_\ell + 1\rangle$$

$$\widehat{\mathbf{L}}_- |\ell, m_\ell\rangle = C_{\ell, m_\ell} |\ell, m_\ell - 1\rangle$$

We can work out what C and D are as follows:

- Take the Hermitian Conjugate of both the equations above, and then apply to the original equations, from the left.
- Simplify using the following identity

$$\widehat{\mathbf{L}}^2 = \widehat{\mathbf{L}}_+ \widehat{\mathbf{L}}_- - \hbar \widehat{\mathbf{L}}_z + \widehat{\mathbf{L}}_z^2$$

(Prove by expanding $\widehat{\mathbf{L}}_+ \widehat{\mathbf{L}}_-$).

- Assume $|\ell, m_\ell\rangle$ and $|\ell, m_\ell - 1\rangle$ are normalised, and that C and D are real.

This gives

$$C_{\ell, m_\ell} = \hbar \sqrt{\ell(\ell + 1) - m_\ell(m_\ell - 1)}$$

$$D_{\ell, m_\ell} = \hbar \sqrt{\ell(\ell + 1) - m_\ell(m_\ell + 1)}$$

The Operators in Spherical Polars

In 3D spherical polars

$$\widehat{\mathbf{p}} = \frac{\hbar}{i} \nabla = \frac{\widehat{\mathbf{p}}_r}{i} \frac{\partial}{\partial r} \mathbf{r} + \frac{1}{r} \frac{\widehat{\mathbf{p}}_\theta}{i} \frac{\partial}{\partial \theta} \boldsymbol{\theta} + \frac{\widehat{\mathbf{p}}_\phi}{i} \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \boldsymbol{\phi}$$

We can use these to explicitly find the forms of each component of $\widehat{\mathbf{L}}$, in terms of the angular $\widehat{\mathbf{p}}$ operators, the form of which we can obtain from the Hamiltonian above:

$$\widehat{\mathbf{L}}_z = -i\hbar \frac{\partial}{\partial \phi}$$

$$\widehat{\mathbf{L}}_x = i\hbar \left(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right)$$

$$\widehat{\mathbf{L}}_y = i\hbar \left(-\cos\phi \frac{\partial}{\partial\theta} + \cot\theta \sin\phi \frac{\partial}{\partial\phi} \right)$$

The ladder operators then become

$$\widehat{\mathbf{L}}_{\pm} = \hbar e^{\pm i\phi} \left(\pm \frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right)$$

All these operators depend on θ and ϕ only – so all the angular momentum eigenfunctions $|\ell, m_\ell\rangle$ will be functions of these angles only – say $Y_{\ell, m_\ell}(\theta, \phi)$.

The Eigenfunctions

We find the eigenfunctions in two parts

The ϕ part The eigenvalue equation for $\widehat{\mathbf{L}}_z$ is

$$\widehat{\mathbf{L}}_z Y_{\ell, m_\ell}(\theta, \phi) = \hbar m_\ell Y_{\ell, m_\ell}(\theta, \phi)$$

Using the operator derived above

$$-i\hbar \frac{\partial}{\partial\phi} = \hbar m_\ell Y_{\ell, m_\ell}(\theta, \phi)$$

Which means that

$$Y_{\ell, m_\ell}(\theta, \phi) = F_{\ell, m_\ell}(\theta) e^{im_\ell\phi}$$

Note that *this* is what forces the m_ℓ to be integers for orbital angular momentum – we require a rotation of 2π about the z axis to leave the wavefunction unchanged.

The θ part As earlier, $\widehat{\mathbf{L}}_+$ has to give 0 when it acts on the highest eigenstate of $\widehat{\mathbf{L}}_z$ (the one with $m_\ell = \ell$). So

$$\hbar e^{i\phi} \left(\frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right) |\ell, \ell\rangle = 0$$

This gives

$$\sin\theta \frac{dF_{\ell, \ell}}{d\theta} = \ell \cos\theta F_{\ell, \ell}$$

Which gives

$$F_{\ell, \ell}(\theta) \propto (\sin\theta)^\ell$$

To obtain lower eigenfunctions, we successively apply the lowering operator.

The resulting eigenfunctions must be normalised to unity when integrated over all angles

$$\int_0^{2\pi} \int_0^\pi |Y_{\ell, m_\ell}|^2 \sin\theta d\theta d\phi = 1$$

To summarise

The eigenfunctions of $\widehat{\mathbf{L}}_z$, the *Spherical Harmonics*, Y_{ℓ, m_ℓ} have the form

$$Y_{\ell, m_\ell} = F_{\ell, m_\ell}(\theta) e^{im_\ell\phi}$$

Where the θ -part F_{ℓ, m_ℓ} is given by

$$F_{\ell, \ell} \propto (\sin\theta)^\ell$$

$$F_{\ell, m_\ell-1} \propto \frac{dF_{\ell, m_\ell}}{d\theta} + m_\ell \cot\theta F_{\ell, m_\ell}(\theta)$$

8.3 Bits and bobs

Note the following properties of the spherical harmonics

$$Y_{\ell, -m_\ell} = (-1)^{m_\ell} Y_{\ell, m_\ell}^*(\theta, \phi) = Y_{\ell, m_\ell}(\theta, \pi - \phi)$$

$$Y_{\ell, m_\ell}(\pi - \theta, \pi + \phi) = (-1)^\ell Y_{\ell, m_\ell}(\theta, \phi)$$

Parity

In 3D, the parity operator inverts the wavefunction through the origin:

$$\widehat{\mathbf{P}}\psi(\mathbf{r}) = \psi(-\mathbf{r})$$

$$\widehat{\mathbf{P}}\psi(r, \theta, \phi) = \psi(r, \pi - \theta, \pi + \phi)$$

From the second property above, therefore

$$\widehat{\mathbf{P}}Y_{\ell, m_\ell} = (-1)^\ell Y_{\ell, m_\ell}$$

The eigenstates of $\widehat{\mathbf{L}}^2$ and $\widehat{\mathbf{L}}_z$ are all either even or odd, depending on whether ℓ is even or odd...

Conservation of Angular Momentum

As we showed above, the rotation operator, for a small rotation ϵ about the z -axis is given by

$$\widehat{\mathbf{R}}_\epsilon \psi(r, \theta, \phi) = \psi(r, \theta, \phi + \epsilon) = \psi + \epsilon \frac{\partial \psi}{\partial \phi}$$

But using the form of $\widehat{\mathbf{L}}_z$:

$$\widehat{\mathbf{R}}_\epsilon = 1 + \frac{i\epsilon}{\hbar} \widehat{\mathbf{L}}_z$$

Thus, if the system is rotationally invariant, then $\widehat{\mathbf{R}}_\epsilon$ will commute with the Hamiltonian and so will $\widehat{\mathbf{L}}_z$ – angular momentum is then a *conserved quantity*.

Particle Flux

Using the expression for ∇ in spherical polars

$$\nabla = \left(\frac{\partial}{\partial r} \underline{\mathbf{r}} + \frac{1}{r} \frac{\partial}{\partial \theta} \underline{\boldsymbol{\theta}} + \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \underline{\boldsymbol{\phi}} \right)$$

We can work out the particle flux for the spherical harmonics. We find that

- For those spherical harmonics with $m_\ell = 0$ (ie: zero z -component of angular momentum), there is *no* particle flux, even though the total momentum is non-zero. This is because the momentum is only in the x and y direction, but is completely indeterminate, and so cancels to 0.
- For other spherical harmonics, we find a net current around the z -axis, as indeed expected.

Energy

The energy of the particular eigenstates depends on the system under consideration – we will consider the example of the rigid rotor and of the hydrogen atom later on.

8.4 The Stern-Gerlach Experiment

Classically, an electron moving in a circular orbit of radius r with speed v has orbital period $T = 2\pi r/v$

and angular momentum $L = m_e v r$. It is effectively a loop of area $A = \pi r^2$ carrying a current $I = -e/T$, and so it has a magnetic moment of

$$\mu = -\frac{eL}{2m_e}$$

But we now know that L_z is quantified, as $L_z = m_\ell \hbar$. So

$$\mu_z = -\frac{e\hbar}{2m_e} m_\ell$$

So this means that the z -component of the magnetic field is quantized in units of

$$\mu_B = \frac{e\hbar}{2m_e} \text{ – the Bohr magneton}$$

It is now clear, in the Stern-Gerlach experiment, why a discrete number of beams emerge – taking the z -axis to lie along the B-field gradient, there is a quantized number of values the magnetic moment was able to have.

Chapter 9

Spin

9.1 Experimental Evidence

We saw above that the splitting of beams in the Stern-Gerlach experiment was due to quantisation of angular momentum. There are $2\ell + 1$ possible values of m_ℓ , and since ℓ must be in *integer* for orbital angular momentum, this should produce an ODD number of beams.

However, there are some experiments where an *even* number of beams is produced – there seems to be a non-orbital magnetic moment in some atoms. We call this *SPIN*.

Spin has *no classical counterpart*. If we try and view spin as a rotation of the electron about its axis, not only do we end up with nonsensical numbers, but we also defeat the purpose of introducing spin, because we would still require quantisation in *integer* units of \hbar .

9.2 Eigenvalues and Eigenvectors

Every statement made above about angular momentum also applies to spin.

The eigenfunctions, however, require a somewhat different treatment, because they *do not* involve any *spatial* coordinates – spin cannot be described in terms of matter moving through space.

It turns out that it emerges naturally from the **Dirac Equation** – a *relativistic* wave equation, and it turns out that spin can be represented by

‘bolting on’ a spin wavefunction, $|S\rangle$, to the spatial wavefunction.

Spatial operators (like L) *only* act on the *spatial* wavefunction, whereas spin operators (denoted S) *only* acts on the *spin* wavefunction.

To summarise:

The eigenstates of both \widehat{S}_z and \widehat{S}^2 are denoted

$$|S\rangle$$

The corresponding eigenvalues are given by

$$\widehat{S}^2 |S\rangle = s(s+1)\hbar^2 |S\rangle$$

$$\widehat{S}_z |S\rangle = m_s \hbar |S\rangle$$

Where

$$m_s = -s, -s+1, \dots, -1, 0, 1, \dots, s-1, s$$

s is 0, an integer **or a half-integer**

For $s = \frac{1}{2}$, the $m_s = \pm \frac{1}{2}$ states are usually denoted $|\chi_+\rangle$ and $|\chi_-\rangle$. They are called ‘up’ and ‘down’ spin states, even though in truth, they point at $\approx 55^\circ$ to the horizontal.

Ladder operators work as before.

9.3 Uncertainties

Measurement of \widehat{S}_z when the spin part of the system is in one of the eigenstates of \widehat{S}_z gives the corresponding eigenvalue with 0 uncertainty.

When the system is in one of the x or y eigenstates, the *expected* value of \widehat{S}_z is 0, but the *uncertainty* is $\frac{\hbar}{2}$ (use ladder operators to prove).

9.4 Spin in any direction

Spin in *any* direction can be expressed as a linear combination of up and down spin:

$$|\alpha\rangle = c_1 |\chi_+\rangle + c_2 |\chi_-\rangle$$

And the vector spin operator is given by

$$\widehat{\mathbf{S}} = (\widehat{S}_x, \widehat{S}_y, \widehat{S}_z)$$

We can find $\langle \widehat{\mathbf{S}} \rangle$ by explicitly evaluating $\langle \alpha | \widehat{\mathbf{S}} | \alpha \rangle$, and we obtain

$$\langle \widehat{\mathbf{S}} \rangle = \frac{\hbar}{2} [(c_2^* c_1 + c_1^* c_2) \mathbf{i} + i(c_2^* c_1 - c_1^* c_2) \mathbf{j} + (c_1^* c_1 + c_2^* c_2) \mathbf{k}]$$

Let the spin be pointing in the \mathbf{n} direction.

- The spin $|\alpha\rangle$ will be an eigenvector of a measurement of spin that direction (ie: $\mathbf{n} \cdot \widehat{\mathbf{S}}$) with eigenvalue $\pm \frac{1}{2}$ (assuming $s = \frac{1}{2}$).
- To find an expression for an arbitrary spin $|\chi\rangle$ in terms of $|\chi_+\rangle$ and $|\chi_-\rangle$, we can use the above, or simply solve the equation $\mathbf{n} \cdot \widehat{\mathbf{S}} |\chi\rangle = \pm \frac{1}{2} \hbar |\chi\rangle$.

9.5 Combining Orbital & Spin Angular Momentum

9.5.1 Introduction

The *total angular momentum*, J , consists of both orbital and spin angular momentum. The operator is therefore given by

$$\widehat{\mathbf{J}} = \widehat{\mathbf{L}} + \widehat{\mathbf{S}}$$

Because the spin operators do not affect the spatial ones, and vice versa, it doesn't matter what order one applies $\widehat{\mathbf{L}}$ and $\widehat{\mathbf{S}}$ in, so $\widehat{\mathbf{L}}$ and $\widehat{\mathbf{S}}$ commute.

Using this fact, we can show that the usual commutation relations apply to the components of $\widehat{\mathbf{J}}$, and this means that everything we've done so far applies. So:

The eigenstates of both \widehat{J}_z and \widehat{J}^2 (which are compatible observables) are denoted

$$|j, m_j\rangle$$

The corresponding eigenvalues are given by

$$\widehat{J}^2 |j, m_j\rangle = j(j+1)\hbar^2 |j, m_j\rangle$$

$$\widehat{J}_z |j, m_j\rangle = j_s \hbar |j, m_j\rangle$$

Where

$$m_j = -j, -j+1, \dots, -1, 0, 1, \dots, j-1, j$$

j is an integer or a half-integer

9.5.2 The values of J

Spins add vectorially, so taking the z component, we clearly have

$$m_j = m_l + m_s$$

Therefore, the *maximum* and *minimum* values of m_j are given by

$$m_{j,\max} = m_{l,\max} + m_{s,\max} = \ell + s$$

$$m_{j,\min} = |\ell - s|$$

(In the first case, the spins are 'maximally aligned', and in the second, they are 'maximally anti-aligned').

Therefore,

$$j = (\ell + s), (\ell + s - 1), \dots, |\ell - s| + 1, |\ell - s|$$

9.5.3 Combined wavefunctions

If m_j and j are *definitely* known for a particular particle, then the orbital part of its wavefunction will be a linear combination of all the possible individual orbital and spin angular momentum eigenfunctions that would lead to those values of j and m_j .

To find them:

- First, construct one definite wavefunction, for which there is no linear combination – just one possibility for both angular and orbital angular momentum eigenfunctions.
- Use the lowering operator, $\hat{J}_- = \hat{L}_- + \hat{S}_-$, to find the eigenfunction which is the next m_j down, as follows:
 - Apply the operator in its \hat{J} form on the LHS.
 - Apply it in its \hat{L} and \hat{S} form on the RHS.
 - Deduce the next wavefunction down.
- For other values of j , use the fact that all wavefunctions *must* be orthogonal, and apply that condition with an already-determined wavefunction that contains the same constituent parts.

Which means that \hat{J}_z will be a *constant of the motion* – angular momentum is conserved.

9.6 Conservation of total angular momentum

The rotation operator for a small angle ϵ around the z -axis is given by

$$\hat{R}_{\epsilon,L} = \left(1 + \frac{i\epsilon}{\hbar} \hat{L}_z \right)$$

Assuming a similar expression for spin, and ignoring terms in ϵ^2 , then the operator for *overall rotation* in both spin and spatial coordinates is

$$\hat{R}_\epsilon = 1 + \frac{i\epsilon}{\hbar} \hat{J}_z$$

If \hat{H} is invariant under such rotations, then it obviously commutes with \hat{R}_ϵ , so $[\hat{H}, \hat{R}_\epsilon] = 0$, which implies that

$$[\hat{H}, \hat{J}_z] = 0$$

Chapter 10

Central Potentials

10.1 Conservation of angular momentum

If we consider a Hamiltonian in which the potential, V , is a function of r only, we find, as before

$$[\widehat{H}, \widehat{L}_\alpha] = 0$$

$$[\widehat{H}, \widehat{L}^2] = 0$$

This follows from the fact that the angular momentum operators are functions of angle only, and therefore commute with any function of r , and the fact they commute with the \widehat{p} operators.

This means that angular momentum is a *conserved quantity*.

10.2 Quantum numbers

It also means, however, that \widehat{L}^2 , \widehat{L}_z and \widehat{H} must have a common set of eigenstates, and their eigenvalues can be specified simultaneously. Furthermore, since the angular momentum operators depend only on angle, and the hamiltonian operator depends only on r (for central potentials), the common eigenstates will be of the form

$$\psi(r, \theta, \phi) = R(r)Y_{\ell, m_\ell}(\theta, \phi)$$

Notes:

- The angular motion is quantized by ℓ and m_ℓ .

- The r -motion, however, will also be quantized, and will contribute to determining the energy of the state – let the quantum number n label the radial motion.
- For a central potential, E cannot depend on m_ℓ , because its value depends on the choice of z -axis, which does not affect the Hamiltonian (which depends only on r). So E depends on n and ℓ .
- The radial part affects the energy, so we can label it $R_{n, \ell}(r)$.

10.3 Separation of Variables

∇^2 , in the Schrödinger Equation, contains both radial and angular parts, and to separate these requires tedious calculations.

The result of these calculations gives

$$-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{\widehat{L}^2 \psi}{2mr^2} + V(r)\psi = E\psi$$

Feeding in $\psi(r, \theta, \phi) = R(r)Y(\theta, \psi)$ into this, we get

$$\boxed{-\frac{\hbar^2}{2m} \frac{d^2U}{dr^2} + \left(\frac{\hbar^2 \ell(\ell+1)}{2mr^2} + V(r) \right) U = EU}$$

Where

$$\boxed{U(r) = rR(r)}$$

This is just a 1D “radial” Schrödinger Equation in r , with an extra contribution to the potential of

the form $\langle L^2 \rangle / 2mr^2$ – which corresponds to the “centrifugal potential” term in the radial equation of a classical orbit.

For small r , and as long as $V(r)$ doesn’t diverge as fast as r^{-2} , the centrifugal potential dominates, and the wavefunction looks like $R \propto r^\ell$. We see that only for $\ell = 0$ (s-state) can the wavefunction be nonzero at the origin.

10.4 Normalisation & Probabilities

The normalisation of any wavefunction will be such that

$$\int_0^\infty \int_0^{2\pi} \int_0^\pi |\psi(r, \theta, \phi)|^2 r^2 \sin \theta \, d\theta \, d\phi \, dr = 1$$

In the case where the wavefunction is separated into an angular and a radial part ($\psi = RY$), the probability of finding the particle between spherical shells of radius r and $r + dr$ is simply

$$P(r) \, dr = r^2 |R(r)|^2 \, dr$$

Note that this is *no* factor of 4π , because the spherical harmonics are already normalised over all angular integrations.

10.5 Practical tips

When considering a spherically symmetric potential in 3D therefore, simply use the ‘1D radial equation’ above to reduce the problem to a 1-dimensional one. But note

- If considering the ground state, remember to set $\ell = 0$.
- Remember that the 1D equation solves for rR , *not* R . As such, $R = U/r$. Therefore, at $r = 0$, we *must* have $U = 0$, or else the limit is undefined or the wavefunction unphysically tends to infinity.

Chapter 11

Two-Particle Systems

Many systems involve *two* particles – for example, the hydrogenic atom involves the orbiting electron *and* the nucleus.

will affect the coordinates of *b*, or vice-versa, so

$$[\underline{r}_a, \underline{p}_b] = 0 = [\underline{r}_b, \underline{p}_a]$$

11.1 Position Probabilities

If we consider both particles, Ψ must be written in terms of *both* the spatial coordinates

$$|\Psi\rangle = \Psi(\underline{r}_a, \underline{r}_b, t)$$

(ignoring spin for the time being).

The probability of finding particle *a* in a volume $d^3\underline{r}_a$ around \underline{r}_a and particle *b* in a volume $d^3\underline{r}_b$ around \underline{r}_b is

$$|\Psi(\underline{r}_a, \underline{r}_b, t)|^2 d^3\underline{r}_a d^3\underline{r}_b$$

The probability for particle *a* without regard to position *b* is obtain by integrating the wavefunction over all possible values positions of particle *b*:

$$P(\underline{r}_a, t) d^3\underline{r}_a = \left[\int |\Psi(\underline{r}_a, \underline{r}_b, t)|^2 d^3\underline{r}_b \right] d^3\underline{r}_a$$

11.2 Observables

The observables relating to each particle correspond to operators acting *only* on the relevant \underline{r} -dependence of $|\Psi\rangle$.

The usual commutation relations apply for observables for any one particle. Furthermore, it is obvious that no momentum operator pertaining to *a*

11.3 The Hamiltonian

In the presence of a potential, the Hamiltonian is

$$\widehat{H} = \frac{\underline{p}_a^2}{2m_a} + \frac{\underline{p}_b^2}{2m_b} + V(\underline{r}_a, \underline{r}_b)$$

V includes any external potential as well as any arising from their mutual interaction. Often, V is a function *only* of the separation between the two particles

$$V(\underline{r}_a, \underline{r}_b) = V(|\underline{r}_a - \underline{r}_b|) = V(r)$$

11.4 Conservation of Total Momentum

The total momentum operator is

$$\underline{P} = \underline{p}_a + \underline{p}_b$$

We can show that (α and β are any of x , y and z)

- $[\widehat{P}_\alpha, \widehat{r}_\beta] = 0$, where \underline{r} is the *separation* between the two particles.
- $[\widehat{P}_\alpha, \widehat{p}_{a,\beta}^2] = [\widehat{P}_\alpha, \widehat{p}_{b,\beta}^2] = 0$, because each of \widehat{p}_a and \widehat{p}_b commute with \widehat{p}_a^2 and \widehat{p}_b^2 , so \widehat{P} does also.

Together, these two facts tell us that

$$\left[\widehat{\mathbf{H}}_\alpha, \widehat{\mathbf{P}}_\beta \right]$$

In other words, $\widehat{\mathbf{P}}$ is a *conserved quantity* – just as expected from classical physics, since there is only the “internal force”, and no “external force”.

However, note that $\widehat{\mathbf{p}}_a$ and $\widehat{\mathbf{p}}_b$ do not individually commute with \mathbf{r} , and therefore not with $V(\mathbf{r})$, and therefore not with $\widehat{\mathbf{H}}$. The momenta are *not* conserved.

11.5 Centre of Mass Motion

The position of the centre of mass for a two-particle system is

$$\mathbf{R} = \frac{m_a \mathbf{r}_a + m_b \mathbf{r}_b}{m_a + m_b}$$

Consider the commutator of $\widehat{\mathbf{R}}$ with the two-particle Hamiltonian. It can be shown that

$$\left[\widehat{\mathbf{R}}, \widehat{\mathbf{H}} \right] = \frac{\left[\widehat{\mathbf{r}}_a, \widehat{\mathbf{p}}_a^2 \right] + \left[\widehat{\mathbf{r}}_b, \widehat{\mathbf{p}}_b^2 \right]}{2(m_a + m_b)}$$

Expanding the vectors out, we find that

$$\left[\widehat{\mathbf{r}}_a, \widehat{\mathbf{p}}_a^2 \right] = 2i\hbar \widehat{\mathbf{p}}_a$$

and that a similar expression applies for b .

Therefore, we have

$$\left[\widehat{\mathbf{R}}, \widehat{\mathbf{H}} \right] = i\hbar \frac{\widehat{\mathbf{P}}}{M}$$

Where \mathbf{P} is the total angular momentum, and M is the total mass.

Using the Ehrenfest Theorem, we therefore have

$$\frac{d \langle \widehat{\mathbf{R}} \rangle}{dt} = \frac{\langle \widehat{\mathbf{P}} \rangle}{M}$$

Which is, indeed, as expected, since the velocity of the centre of mass is \mathbf{P}/M .

11.6 Separation of CoM Motion and Relative Motion

We will attempt to re-write the Hamiltonian in terms of new variables – \mathbf{R} , representing the position of the centre of mass and defined above, and \mathbf{r} , representing the separation between particles (also defined above).

Now

$$\begin{aligned} \left(\frac{\partial}{\partial x_a} \right)_{x_b} &= \left(\frac{\partial R_x}{\partial x_a} \right)_{x_b} \frac{\partial}{\partial R_x} + \left(\frac{\partial r_x}{\partial x_a} \right)_{x_b} \frac{\partial}{\partial r_x} \\ &= \frac{m_a}{M} \frac{\partial}{\partial R_x} - \frac{\partial}{\partial r_x} \end{aligned}$$

So we can say that

$$\widehat{\mathbf{p}}_a = \frac{m_a}{M} \widehat{\mathbf{P}} - \widehat{\mathbf{p}}_r$$

And likewise for b .

By using these expressions to write $\widehat{\mathbf{p}}_a^2$ and $\widehat{\mathbf{p}}_b^2$ in terms of $\widehat{\mathbf{P}}$ and $\widehat{\mathbf{p}}_r$, we can write the Hamiltonian as follows

$$\widehat{\mathbf{H}} = \frac{\widehat{\mathbf{P}}^2}{2M} + \left(\frac{\widehat{\mathbf{p}}_r^2}{2\mu} + V(r) \right) = \widehat{\mathbf{H}}_{\text{CoM}} + \widehat{\mathbf{H}}_r$$

Where μ is the reduced mass – $\mu^{-1} = m_a^{-1} + m_b^{-1}$.

Substituting $\psi(\mathbf{R}, \mathbf{r}) = U(\mathbf{R})u(\mathbf{r})$, and feeding into the Schrödinger Equation, we obtain

$$\frac{1}{U} \widehat{\mathbf{H}}_{\text{CoM}} U + \frac{1}{u} \widehat{\mathbf{H}}_r u = E$$

In other words, the equation becomes *separable*, with each part equal to a constant, and we get the following two equations

$$\frac{\widehat{\mathbf{P}}^2}{2M} U(\mathbf{R}) = E_{\text{CoM}} U(\mathbf{R})$$

$$\left(\frac{\widehat{\mathbf{p}}_r^2}{2\mu} + V(|\mathbf{r}|) \right) u(\mathbf{r}) = E_r u(\mathbf{r})$$

With a total energy of

$$E = E_{\text{CoM}} + E_r$$

- The first equation describes the motion of a free particle of mass M .

- The second equation describes the motion of a *single* particle, mass μ , moving in a potential $V(r)$ (a problem which we have already solved).
- The energy eigenvalues are therefore

$$E = \frac{P^2}{2M} + E_{n\ell}$$

Where P is the eigenvalue of $\hat{\underline{P}}$.

The overall wavefunction then has separated form

$$\psi(\underline{\mathbf{r}}_a, \underline{\mathbf{r}}_b) = \psi(\underline{\mathbf{R}}, \underline{\mathbf{r}}) = e^{i\frac{\underline{\mathbf{P}}\underline{\mathbf{R}}}{\hbar}} \psi_{n,\ell,m_\ell}(\underline{\mathbf{r}})$$

11.7 Combining spins

Spins for two particles can be combined, using precisely the same results as those derived earlier for the combination of orbital and spin angular momentum.

For two particles of spin s_1 and s_2 , the total spin, S , will, once again, range as follows:

$$S = (s_1 + s_2), (s_1 + s_2) - 1, \dots, |s_1 - s_2| + 1, |s_1 - s_2|$$

Once again, the eigenfunctions are found by finding all the possible combinations, and using the ladder operators.

Chapter 12

Examples of real systems

12.1 The rigid rotor

A *rigid rotor* is a particle of mass m fixed to the origin O by a rigid light rod of length a . A diatomic molecule can be considered as two rigid rotors rotating about the common centre of mass.

Now, the kinetic energy of the rigid rotor is

$$E = \frac{1}{2}I\omega^2$$

(No potential energy term for the free rotation). In each case, $L = I\omega$, so

$$E = \frac{L^2}{2I}$$

With the known angular momentum eigenstates, this gives the allowed energy levels:

$$E_\ell = \frac{\ell(\ell+1)\hbar^2}{2I} \text{ degeneracy of } 2\ell+1$$

(The degeneracy is obtained from the number of possible m_ℓ for every ℓ).

12.2 The Harmonic Oscillator

12.3 The Hydrogenic Atom

In the hydrogenic atom

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

And the radial equation becomes:

$$-\frac{\hbar^2}{2m} \frac{d^2 U_{n,\ell}}{dr^2} + \left(\frac{\hbar^2 \ell(\ell+1)}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r} \right) U_{n,\ell} = E_{n,\ell} U_{n,\ell}$$

We can solve this as follows

1. Re-write in dimensionless form, by substituting

$$A = \frac{2m}{\hbar^2} \frac{Ze^2}{4\pi\epsilon_0} \quad \kappa^2 = -\frac{2mE_{n,\ell}}{\hbar^2}$$

so that

$$\frac{d^2 U_{n,\ell}}{dr^2} - \left(\frac{\ell(\ell+1)}{r^2} - \frac{A}{r} + \kappa^2 \right) U_{n,\ell} = 0$$

2. Consider the solution for $r \rightarrow \infty$.
3. Consider the solution for $r \rightarrow 0$.
4. Try a solution consisting of the product of the last two multiplied by a polynomial

$$U_{n,\ell}(r) = e^{-\kappa r} r^{\ell+1} G(r)$$

This results in the *associated Laguerre Equation*.

5. Substitute a polynomial solutions.
6. Require the series to terminate so that it can be physically acceptable. Do this by finding c_{p+1}/c_p as $p \rightarrow \infty$, and not that it diverges as $e^{2\kappa r}$.
7. The termination requires that

$$\frac{A}{2\kappa} = n$$

and

$$p + \ell + 1 = n$$

where n is the *principal quantum number*, an *integer* larger than 0.

8. The fact that p must be larger than 0 implies that $\ell \leq n - 1$.
9. We can then find an expression for the energy of each state.

To summarise:

The stationary states are labelled by the principal (n), orbital (ℓ) and magnetic (m_ℓ) quantum numbers, which specify three compatible observables \widehat{H} , \widehat{L}^2 and \widehat{L}_z .

$$n \geq 1$$

$$\ell = 0, 1, 2, \dots, n - 1$$

$$m_\ell = -\ell, -\ell + 1, \dots, -1, 0, 1, \dots, \ell - 1, \ell$$

All the quantum numbers are integer. The energy of each state is determined by n alone

$$E_n = -\frac{Z^2 e^4 m}{2(4\pi\epsilon_0)^2 \hbar^2} \frac{1}{n^2} = -\frac{\hbar^2}{2m} \frac{Z^2}{a_0^2} \frac{1}{n^2}$$

And the degeneracy of each state is therefore

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

(The additional factor 2 arises because of spin).

lar momentum for each of these orbitals will be 0.

Such wavefunctions are useful in certain situations

- Isolated atoms involve electrons moving in the central Coulomb potential of the nucleus – angular momentum is conserved, and we can use the standard orbitals.
- In a molecule or solid, the potential is no longer central – it is perturbed by the potential of neighbouring atoms.
- Solving Schrödinger's Equation for these is hard, though a natural starting point to discuss the true wavefunctions is to use wavefunctions that conform to the local cartesian symmetry of the potential – *hybridised orbitals*.

A number of symmetries are possible.

Hybridisation

- All the wavefunctions corresponding to a given n have degenerate energies, any linear combination of them is also an eigenstate of \widehat{H} .
- We can therefore combine our existing orbitals into any number of new ones, pointing in any number of arbitrary directions.
- These are called *hybridised orbitals*.
- The results are still eigenstates of \widehat{H} (and of \widehat{L}^2 , if only orbitals of equal ℓ are combined), but are no longer eigenstates of \widehat{L}_z . In fact, the expectation value of each component of angu-

Chapter 13

Identical Particles

13.1 Exchange Symmetry

- For an N -particle system, the Hamiltonian and N -particle wavefunction would take the forms

$$\begin{aligned}\widehat{H}_N &= \widehat{H}(\mathbf{r}_1, \mathbf{p}_1; \dots; \mathbf{r}_N, \mathbf{p}_N) \\ \psi_N &= \psi(\mathbf{r}_1, \dots, \mathbf{r}_N) \\ \widehat{H}_N |\psi_N\rangle &= E_N |\psi_N\rangle\end{aligned}$$

Where E_N is the eigenenergy of the entire N -particle system.

- The *particle exchange operator*, \widehat{P}_{ij} has the effect of swapping the two particles i and j .
- We prove that \widehat{P}_{ij} is Hermitian as follows

$$\begin{aligned}- \widehat{P}_{ij} |\Psi_N\rangle &= \langle \Psi_N | \widehat{P}_{ij}^\dagger = \Psi_{N,\text{exchanged}} \\ - \langle \Psi_N | \widehat{P}_{ij}^\dagger \widehat{P}_{ij} | \Psi_N \rangle &= \\ \langle \Psi_{N,\text{exchanged}} | \Psi_{N,\text{exchanged}} \rangle &= 1\end{aligned}$$

– Since $\langle \Psi_N | \Psi_N \rangle = 1$, this implies that $\widehat{P}_{ij}^\dagger \widehat{P}_{ij} = \widehat{I}$.

– But applying \widehat{P}_{ij} twice has no effect, so $\widehat{P}_{ij}^2 = \widehat{I}$

– Therefore, $\widehat{P}_{ij}^\dagger = \widehat{P}_{ij}$

- If two particles are *identical*, the Hamiltonian cannot depend on which particle is labelled what – therefore, \widehat{H}_N is invariant under particle exchange:

$$\widehat{P}_{ij} \widehat{H}_N = \widehat{H}_N$$

This can be seen as the definition of indistinguishable particles...

- For identical particles, particle exchange cannot affect the overall particle density – so

$$|\Psi|^2 = |\widehat{P}_{ij} \Psi|^2$$

And so

$$|\Psi\rangle = e^{i\phi} \widehat{P}_{ij} |\Psi\rangle$$

But since i and j are identical, we can imagine starting from a system with i and j interchanged, and we would also expect

$$\widehat{P}_{ij} |\Psi\rangle = e^{i\phi} |\Psi\rangle$$

Therefore

$$|\Psi\rangle = e^{2i\phi} |\Psi\rangle$$

Which means that $e^{i\phi} = \pm 1$. Therefore

The wavefunction Ψ_N , including two identical particles i and j , must be an eigenstate of \widehat{P}_{ij} with eigenvalues $\eta = \pm 1$

- If two particles are indistinguishable, no measurement of an operator \widehat{A} can distinguish between the them. Therefore, $\widehat{A} |\Psi_N\rangle = \widehat{A} \widehat{P}_{ij} |\Psi_N\rangle$. So

$$[\widehat{A}, \widehat{P}_{ij}] = 0$$

Exchange-symmetry is compatible with *any* observable. η is a conserved quantity.

Even if measurements are made, this is the case. Every eigenfunction of an operator that forms part of a state $|\psi\rangle$ must have the same exchange symmetry eigenvalue η as $|\psi\rangle$. We can see this by writing the expansion of $|\psi\rangle$ and applying \widehat{P}_{ij} separately to each eigenfunction and to $|\psi\rangle$ itself, and writing both results as a series expansion.

13.2 The Spin-Statistics Theorem

The spin-statistics Theorem comes from relativistic quantum field theory

If identical particles have *integer* spin quantum number s , their overall wavefunctions must be *symmetric* under exchange ($\eta = 1$) – these are called ***bosons***.

If identical particles have *half-integer* spin quantum number s , the wavefunctions must be *antisymmetric* under exchange ($\eta = -1$) – these are called ***fermions***.

13.3 Non-interacting particles

For an N -particle system, the potential of each particle i in general depends on the position of every other particle j , and on any external potential. Let's denote the hamiltonian for particle i by \hat{h}_i , and that for the whole system by \hat{H}_N .

We have

$$\hat{h}_i = \hat{T}_i + V_{\text{ext}}(\mathbf{r}_i) + \sum_{j \neq i} NV_i |\mathbf{r}_i - \mathbf{r}_j|$$

However, the term if we assume that the particles *do not* interact, and that the term in red above can be ignored, we then have

$$\hat{H}_N = \sum_j^N \left(\hat{T}_j + V_{\text{ext}}(\mathbf{r}_j) \right)$$

And the whole wavefunction, Ψ_N can be constructed from the individual solutions of $\hat{h}_i u_i = E_i u_i$.

13.4 N particles

13.4.1 Distinguishable

If the particles are distinguishable and different, then their Hamiltonians, and eigenstates and

eigenenergies, will be different.

The overall wavefunction if the particles are in states α, β , etc. . . is then

$$\Psi_N = u_{1\alpha}(1)u_{2\beta}(2) \cdots u_{N\kappa}(N)$$

And this has eigenenergy

$$E_N = E_{1\alpha} + E_{2\beta} + \cdots + E_{N\kappa}$$

We can split each of the u wavefunctions into their spatial and spin parts

$$u_{i\gamma}(i) = \phi_{ig}(\mathbf{r}_i) |\chi_i\rangle$$

Now, the probability of finding particle i at any point \mathbf{r}_i is then

$$\begin{aligned} P(\mathbf{r}_i) &= \int (\phi_{1a}(\mathbf{r}_1)\phi_{2b}(\mathbf{r}_2) \cdots)^* \\ &\quad (\phi_{1a}(\mathbf{r}_1)\phi_{2b}(\mathbf{r}_2) \cdots) [d\mathbf{r}_1 d\mathbf{r}_2 \cancel{d\mathbf{r}_i}] \\ &= |\phi_{ik}(\mathbf{r}_i)|^2 \end{aligned}$$

In other words, the particle behaves as if the other ones weren't there – the motion of the particles is *uncorrelated*.

13.4.2 Indistinguishable

For *identical particles*, we can drop the numerical eigenfunction subscripts above, because the particles are all identical, and so are their eigenstates. However, because the particles are *identical*, Φ_N must be symmetric or antisymmetric under particle exchange.

The simple product of appropriate eigenstates, however, does *not* satisfy this condition – Φ_N must therefore be formed from *linear combinations* of various products of the eigenstates

Fermions – antisymmetric Ψ_N

The most general linear combination of products of N single-particle wavefunctions $u_{\kappa}(i)$ which is *antisymmetric* under exchange of *any* two particles is given by the *Slater Determinant*

$$\Psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_\alpha(1) & u_\alpha(2) & u_\alpha(3) & \cdots & u_\alpha(N) \\ u_\beta(1) & u_\beta(2) & u_\beta(3) & \cdots & u_\beta(N) \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ u_\kappa(1) & u_\kappa(2) & u_\kappa(3) & \cdots & u_\kappa(N) \end{vmatrix}$$

This does, indeed, have the required property that interchanging two particle labels interchanges two columns, and therefore changes the sign of the determinant.

If any two of the particles are chosen to be in the same state (ie: $\alpha = \beta$), then two rows of the determinant are the same, and Ψ_N immediately goes to 0.

This means that

No two identical Fermions can be in the same single-particle state – they cannot have the same set of quantum numbers.

This is the ***Pauli Exclusion Principle***

Bosons – symmetric Ψ_N

All we need to do in the Bosonic case is to make every sign in the expression for the Slater Determinant positive instead of alternately positive or negative, and the result is symmetric.

We note that the Pauli Exclusion Principle does not apply to Bosons – in fact, every particle can be in the same single-particle state, which is indeed what happens in *Bose-Einstein Condensation*.

13.5 $N = 2$

Things become rather complicated for $N > 2$ – however, a number of comments can be made about the case $N = 2$

• Fermionic case

- The particles can be in the same *spatial* states, or in different *spatial* states.

- If they are in the *same* spatial states, the spatial part of the wavefunction will be *symmetric*, so this forces the spin part to be *antisymmetric*.

- If they are in *different* spatial states, the spatial part can be either symmetric or antisymmetric, and the spin part must have opposite exchange symmetry.

- The way to find the wavefunctions in this case is to list every possible eigenstate (spatial & spin parts included) and find linear combinations of them by calculating Slater Determinants (or by inspection).

- Sometimes, Slater Determinants cannot be separated into a spatial and a spin part, but linear combinations of these problematic states usually can be.

• Bosonic case

- Very similar considerations apply.

- For example, if we have spin-0 bosons, the spin-part of the wavefunction *must* be symmetric (because *must* particles must have the same spin – 0), and the spatial part therefore *must* also be symmetric.

13.5.1 Diatomic molecules

Diatomic molecules are good examples of two ‘effectively non-interacting particles’. Notes:

- Only the rotational parts of the wavefunctions must be taken into consideration, because r is fixed.
- The nuclei are well separated, and there is only a negligibly weak interaction between their spins.
- Exchange symmetry, on this case, is equivalent to parity inversion. But we know that the spherical harmonics behave as follows under parity inversion:

$$\hat{P}Y_{\ell, m_\ell} = (-1)^\ell Y_{\ell, m_\ell}$$

So the *spatial* wavefunction is exchange-symmetric for even ℓ , and exchange-antisymmetric for odd ℓ .

Hydrogen

The nuclei are protons – spin- $\frac{1}{2}$ fermions – so the spin wavefunctions are just the exchange-symmetric singlet and the exchange symmetric triplet states.

Since the protons are *fermions*, the overall wavefunction must be *antisymmetric*.

There are therefore two distinct populations

Para- H_2 consists of the anti-symmetric spin singlet, has $S = 0$, and needs to have an angular part with even ℓ .

Ortho- H_2 consists of the symmetric spin triplet, has $S = 1$, and needs to have an angular part with odd ℓ .

The latter population is three times more likely than the former, at high temperatures.

Deuterium

The nuclei now consist of a proton and a neutron. The resulting *deuteron* is a spin-1-boson. This means that

- There are now six symmetric spin wavefunctions (a sextet) and three anti-symmetric one (a triplet).
- The overall wavefunction now has to be symmetric.

There are, once again, two distinct populations, as above. The ‘*para*’ population has an anti-symmetric spin wavefunction, and the ‘*ortho*’ population has symmetric spin wavefunction.

13.6 Correlation and Exchange Forces

For *distinguishable particles*, the overall wavefunction is the simple product of the single-particle wavefunctions, and so the probability of finding the particles in the same place is simply given by the product of the moduli of the two spatial wavefunctions squared.

However, for *identical* particles, Φ must be either symmetric or antisymmetric:

- If Φ is antisymmetric, then the probability of finding the two particles at the same place is 0. There is “effective repulsion” between them.
- If Φ is symmetric, then the probability of finding the two particles at the same place is *larger* than it would be in the indistinguishable case – the two particles seem to “attract”

This is a significant effect even in quasi-classical systems.

In the case of two spin- $\frac{1}{2}$ particles, either with ‘up’ or ‘down’ spin:

- For the *triplet* spin state, $S = 1$, with “parallel” spins, the spin wavefunction is exchange symmetric, and so the spatial wavefunction *must* be antisymmetric. Therefore,

Parallel $\frac{1}{2}$ -spins “repel”

- Similarly, for the *singlet* spin state, $S = 0$, with “anti-parallel” spins, the spatial wavefunction must be symmetric and so

Anti-parallel $\frac{1}{2}$ -spins “attract”

13.7 Interacting Particles

13.7.1 Exchange energy

If the two particles do not mutually interact, their correlated motion makes no difference to the energies of the 2-particle states – if we turn the interaction on, things are different. For example, for electrons:

- The further apart the electrons are, the lesser the Coulomb energy.
- Therefore, the correlated states (anti-parallel spins) is *higher* in energy than the parallel-spins case.
- The difference in energy is called the *exchange energy*.
- All other things being equal, the exchange interactions produces an energetic preference for

the spins to line up – this lies at the root of ferromagnetism in atoms and solids.

13.7.2 Energy Spectra

However, the Coulomb Interaction sometimes significantly alters the overall Hamiltonian, and the single-particle wavefunctions are no longer true eigenstates.

A good example of this is the He atom. Without interaction, everything we discussed so far applies.

Switching on interactions, however, the spin-state affects the overall energy, so we have two distinct populations:

- **Para-helium**

- The spatial wavefunction must be symmetric.
- The closeness of the electrons considerably raises the energies of the eigenstates.
- The (1s, 2p) state is slightly higher than the (1s, 2s) state, because of “spin-orbit interactions” (whatever they might be).

- **Ortho-helium**

- The spatial wavefunction must be anti-symmetric.
- (1s, 1s) is not possible.
- However, (1s, 2s) and (1s, 2p) are slightly lower than in Para-helium, because the exchange-correlation keeps the electrons further apart. In the (1s, 2s) cases, the difference in energy is the exchange energy.

As a result, their atomic absorption and emission spectra (which depend on transitions between the levels) are entirely different.

13.8 Practical tips

- When finding degeneracies, we can proceed in two ways:

- One way is to consider the possible spin wavefunctions (eg: the triplet and singlet states for a spin- $\frac{1}{2}$ Fermion), and then separately consider the possible symmetric and anti-symmetric wavefunctions that could go with them.

- Another (usually more sensible) way is

- * Consider the spatial degeneracy (ie: the number of ways the spatial wavefunction can be constructed).

For example, for two particles each of which can be in two states spatial, the spatial degeneracy is 3 (see next point).

- * Consider the spin degeneracy

For example, for two spin- $\frac{1}{2}$ particles, the spin degeneracy is 3 (see next point).

and multiply them together.

If the actual wavefunctions need to be found, find Slater Determinants for every possible combination.

- In the second method above, when considering spatial combinations, it is important to *separately* consider cases in which the spatial states are *the same* and those in which they are *different*, for two reasons:

- In the case of *Fermions*, the spatial states might restrict the permitted spin states. For example, if the spatial states of the two particles are identical, then only those non-identical spin states are allowed.

- In all cases, the similarity or otherwise of the spatial states will affect the number of spin states allowed. Consider:

- * If the two spatial states are *identical*, then it doesn't matter whether the spins are $\uparrow\downarrow$ or $\downarrow\uparrow$ – the overall wavefunction will still end up the same, because the spatial parts are identical. This therefore removes one's degree of degeneracy.

- * However, if the particles were in different spatial states, then this would definitely make a difference, because there would be a number of different products in the wavefunctions.
- To determine whether a multiparticle system (eg: an atom) is Fermionic or Bosonic, imagine two identical such systems, and imagine swapping each of the constituent particles one-by-one. The change in the wavefunction at each ‘swap’ is obvious from whether these individual particles are Fermionic or Bosonic. By looking at the final overall change in wavefunction (ie: once *all* constituent particles – and therefore the whole system – has been swapped), one can easily say whether the system is Fermionic or Bosonic.

Chapter 14

Matrix Methods

14.1 Introduction

We define the *matrix* of an operator $\hat{\mathbf{A}}$ as follows:

$$A_{mn} = \langle \phi_m | \hat{\mathbf{A}} | \phi_n \rangle$$

Where the ϕ are some complete set of eigenfunctions, but *no necessarily* those of $\hat{\mathbf{A}}$.

Any wavefunction can then be represented as a column vector – an expansion in terms of the said eigenfunctions.

The eigenvalues of the operator are then simply given by the eigenvalues of the matrix, and this can be used to find the eigenvectors.

14.2 Orbital angular momentum

For example, with $\ell = 1$

$$L_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$L_+ = \hbar \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix}$$

$$L_- = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \end{pmatrix}$$

14.3 Spin angular momentum

When spin is represented as a column vector with respect to $|\chi_+\rangle$ and $|\chi_-\rangle$, these vectors are called *spinors*.

The *Pauli matrices* are as follows:

$$S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

We usually write this

$$\hat{\mathbf{S}} = \frac{1}{2} \hbar \hat{\boldsymbol{\sigma}}$$

Where the σ are the Pauli matrices.

And

$$S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

Chapter 15

Heat capacities, etc...

One of the main ways Quantum effects can be observed at a macroscopic level is through the heat capacities of various things:

- As $T \rightarrow \infty$, $C \rightarrow Nk_B$, the classical limit.
- $C_{\text{vib}} \rightarrow 0$ as $T \rightarrow 0$ – this is consistent with the Third Law of Thermodynamics.

15.1 Vibrational Specific Heat of Diatomic molecules

A diatomic molecule is modelled as two masses, m_1 and m_2 , connected by a spring. The system can be modelled as a single harmonic oscillator oscillating with the reduced mass.

Classically, each degree of freedom (KE and PE) of the oscillator should have $\frac{1}{2}k_B T$ of energy, and so the vibrational heat capacity (dE/dT for N molecules should be Nk_B (a constant).

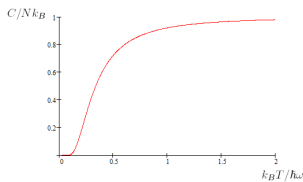
Quantum mechanically, we expect the average energy of each molecule (we're not working with degrees of freedom anymore) to be

$$\langle E \rangle = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

Which gives a specific heat capacity of

$$C_{\text{vib}} = N \frac{d\langle E \rangle}{dT} = Nk_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2}$$

A plot of C/Nk_B against $k_B T/\hbar\omega$ gives



Note a few interesting things:

15.2 Rotational Specific Heat of Diatomic molecules

A diatomic molecule can be modelled as a rigid rotor, for which we saw the energy levels were

$$E_\ell = \frac{\ell(\ell + 1)\hbar^2}{2I}$$

each with degeneracy $2\ell + 1$.

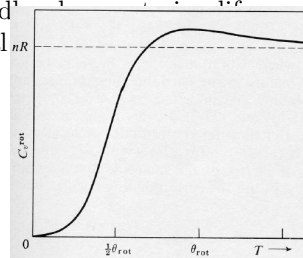
The mean rotational kinetic energy per molecule at T is therefore

$$\langle E \rangle = \frac{\sum_{\ell=0}^{\infty} E_\ell (2\ell + 1) e^{-\beta E_\ell}}{\sum_{\ell=0}^{\infty} (2\ell + 1) e^{-\beta E_\ell}}$$

Which we can re-write by expressing temperature in units of $\theta_{\text{rot}} = \hbar^2/2Ik_B$:

$$\langle E \rangle = \theta_{\text{rot}} k_B \frac{\sum_{\ell=0}^{\infty} \ell(\ell + 1)(2\ell + 1) e^{\ell(\ell+1)\theta_{\text{rot}}/T}}{\sum_{\ell=0}^{\infty} (2\ell + 1) e^{\ell(\ell+1)\theta_{\text{rot}}/T}}$$

This, sadly, doesn't look like



A few notes:

- As expected, $C_{\text{rot}} \rightarrow 0$ as $T \rightarrow 0$.
- $C_{\text{rot}} \rightarrow nR = Nk_B$ as $T \rightarrow \infty$, as expected for *two* degrees of freedom.
- C_{rot} turns on at about $\theta_{\text{rot}}/2$.

In general, rotational modes “turn on” at *much* lower temperatures than vibrational modes.

15.3 Identical Particles and Rotational Heat Capacities

Whether molecules are in their ‘para’ or ‘ortho’ forms considerably restricts the energies that the molecule can take, and therefore considerably alters the variation of heat capacity with temperature.

A few notes:

- At high temperature ($T \gg \theta_{\text{rot}}$), many rotational levels are populated and so the equilibrium fractions of ortho- and para- reflect their spin degeneracies.
- As T falls, the population fractions change in true equilibrium, as the relative probabilities of each rotational state changes (the higher the energy, the lesser the probability).
- At very low spins, the lowest levels will be occupied (para- H_2 and ortho- D_2). As T subsequently rises fast, the curve corresponds to these pure chemicals.