

Quantum Mechanics

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Will assume knowledge of :

- Ideas from QM1
- 2nd order differential equations
- Complex numbers
- Partial derivatives etc.

Part I

QM1 Recap

- Wave-particle duality, distinction depends on what is being measured, e.g. photons
 - particle; photoelectric effect
 - wave; electron diffraction
- Waves interfere or superpose - adding amplitudes rather than adding intensities as would be expected with particles
- Energy of quantum depends on its frequency;

$$E = hf \Rightarrow E = h\nu$$

Momentum of quantum depends on its wavelength, λ ;

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

where h =Planck's constant= 6.626×10^{-34} Js

1 Wave Picture of Matter

E+R ch3

Sine wave,

$$\psi(x, t) = A \sin(kx - \omega t)$$

(wave along the positive x-axis with time period $\frac{2\pi}{\omega}$)

Alternate form:

$$\begin{aligned}\psi(x, t) &= Ae^{i(kx - \omega t)} \\ &= A(\cos(kx - \omega t) + i \sin(kx - \omega t))\end{aligned}$$

where $k = \frac{2\pi}{\lambda}$, wavenumber, and $\omega = 2\pi f$, angular frequency.

$$E = \frac{h\omega}{2\pi} = \hbar\omega \quad p = \frac{h}{2\pi\lambda} = \hbar k$$

1.1 Probability Interpretation

Classical light is described by electromagnetic waves (Maxwell's equations)

e.g. E field along the x-axis $\underline{E}(x) = \underline{E}_0 \sin(kx - \omega t)$

Power of this wave is proportional to the $(amplitude)^2$

$$P \propto E_0^2 \text{ (Energy/sec perpendicular to the beam)}$$

Quantum mechanics however sees the beam of light as consisting of a finite number of particles, discrete photons, with energy = $\hbar\omega$,

$$\Rightarrow Power \propto n\hbar\omega$$

where n=number of particles detected per second.

To allow these two equations to match up and describe the same situation;

$$n \propto (amplitude)^2 \text{ of wavefunction describing photons}$$

This must also apply in quantum mechanics when n becomes very small, i.e. when $n \ll 1$, when the photons are detected separately. So this now works as an average power over a length of time when many photons are detected but quantum mechanics cannot predict the arrival of individual photons.

This invariably leads to a probabilistic interpretation,

$$(amplitude)^2 \text{ of the wave function} \propto \text{probability of a photon arriving per second}$$

1.2 Uncertainty in Quantum Mechanics

A sine wave has a definite momentum,

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

But the amplitude is the same for all values of x, so there is an equal probability of being anywhere in x, i.e. no information on the position of the particle.

A localized particle can be described with a wave packet.

Now there is a finite probability of finding the particle in Δx but zero elsewhere.

Here the wave packet has a wave of λ or k . This can be constructed by summing together a large number of sine and cosine waves of different wavelengths and amplitudes (Fourier Analysis). But now, by limiting the spacial range, some of the information regarding the momentum has been lost. So as $k \rightarrow \Delta k$,

$$p = \hbar k$$

Rigorous analysis of this shows that the limit is Heisenberg's Uncertainty principle,

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

The intrinsic quantum limit of to the information available arises from the wave picture, not dependent on the measurement technique.

Part II

The Schrödinger Equation

E+R pg 125-136

For a full description of an object with quantum mechanics, we need an equation of motion. This is analogous to the classical wave equation in 1 dimension,

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \psi}{\partial t^2}$$

where ψ is the classical wave-function. If this were describing a light wave, $v = c$ and ψ would be the equation of the electromagnetic or magnetic field. It's a 2nd order differential equation and can be derived from Newton's and Maxwell's equations.

The quantum mechanical version however cannot be derived from any more basic postulates as it is one of the fundamental postulates in quantum mechanics.

2 Plausibility Argument

To justify the form of Schrödinger's Equation (SE), it must satisfy a number of constraints.

1. Energy and momentum equations,

$$\begin{aligned} E &= mc^2 \\ p &= \hbar k \end{aligned} \tag{2.1}$$

Energy conservation at non-relativistic speeds,

$$\begin{aligned} E &= \frac{p^2}{2m} + V \\ \text{Total energy of system} &= E_k + E_p \end{aligned} \tag{2.2}$$

Differential equation must be linear to allow superposition if ψ_1 and ψ_2 are each solutions of SE, then

$$\psi = a\psi_1 + b\psi_2$$

(where a and b are constants) must be another solution. This leads to the property of superposition. Combine these two,

$$\frac{\hbar^2 k^2}{2m} + V = \hbar\omega \tag{2.3}$$

2. For a free particle, $v = v_0 = \text{constant}$, expect a $\sin + \cos$ wave solution with no preferred position as all positions are equivalent to each other.

So try free particle solution of the form,

$$\psi(x, t) = A(\cos(kx - \omega t) + \gamma \sin(kx - \omega t))$$

where $A, \gamma = \text{constants}$ to be determined.

Differentiate with respect to time,

$$\frac{\partial \psi}{\partial t} = A\omega(\sin(kx - \omega t) - \gamma \cos(kx - \omega t)) \tag{2.4}$$

$$\frac{\partial^2 \psi}{\partial t^2} = -Ak(\cos(kx - \omega t) - \gamma \sin(kx - \omega t)) \tag{2.5}$$

Comparing (4) and (5) with (3) suggests that the differential equation to contain $k^2 \omega$ terms,

$$\alpha \frac{\partial^2 \psi}{\partial x^2} + V_0 \psi = \beta \frac{\partial \psi}{\partial t} \quad (2.6)$$

where $\alpha, \beta = \text{constants}$ fixed by equation (3). This is very similar to the classical wave equation other than the classical wave equation has a 2nd order differential with respect to time where as the quantum wave equation has a 1st.

So sub (4), (5) into (6),

$$A(-\alpha k^2 + V_0)(\cos(kx - \omega t) + \gamma \sin(kx - \omega t)) = A\beta\omega(\sin(kx - \omega t) - \gamma \cos(kx - \omega t)) \quad (2.7)$$

This equation must be true for all values of x and t ,

$$\begin{aligned} \text{For, } kx - \omega t &= 0 \\ \Rightarrow \sin(kx - \omega t) &= 0 \\ -\alpha k^2 + V_0 &= -\beta\omega\gamma \end{aligned} \quad (2.8)$$

$$\begin{aligned} \text{For, } kx - \omega t &= \frac{\pi}{2} \\ \Rightarrow \cos(kx - \omega t) &= 0 \\ \Rightarrow (-\alpha k^2 + V_0)\gamma &= \beta\omega \end{aligned} \quad (2.9)$$

Divide (7)/(8)

$$\begin{aligned} \Rightarrow \frac{1}{\gamma} &= -\gamma \\ \gamma^2 &= -1, \gamma = \sqrt{-1} = \pm i \end{aligned}$$

The sign choice for γ is completely arbitrary, by convention $\gamma = +i$. So (4) becomes,

$$\begin{aligned} \psi(x, t) &= A(\cos(kx - \omega t) + i \sin(kx - \omega t)) \\ &= Ae^{i(kx - \omega t)} \end{aligned}$$

This is the equation for a free particle,

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

From (8)

$$-\alpha k^2 + V_0 = -i\beta\omega \quad \because \gamma = i$$

Match terms with (3)

$$\frac{\hbar^2 k^2}{2m} + V_0 = \hbar\omega$$

So for energy conservation $\alpha = -\frac{\hbar^2}{2m}$ and $\beta = i\hbar$.

Sub into (6)

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi = i\hbar \frac{\partial \psi}{\partial t}$$

This is the time dependent form of the Schrödinger Equation

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi = i\hbar \frac{\partial \psi}{\partial t}$$

This equation holds for all functions of the potential, V , and not just for the free particle with potential V_0 as was argued in the construction of the equation. This is a postulate that is agreed with by experimental data.

SE is a complex second order differential equation and the solution, $\psi(x, t)$ is generally also a complex function.

3 Interpretation in Terms of Real Measurements

The wave-function ψ is a complete description of the quantum object. It contains all the information that can be known about it subject to Heisenberg's Uncertainty Principle. ψ is complex and so cannot be measured experimentally. But we can apply mathematical operators to extract physical properties.

3.1 Probability Density Function (PDF)

Define $P(x, t)dx$ = probability of measuring the particle in the range $x \rightarrow x + dx$. $P(x, t)$ must obey certain conditions. It must be

- real
- non-negative
- normalized so that $P \geq 1$ does not occur.

In quantum mechanics,

$$\begin{aligned} P(x, t) &= |\psi|^2 = \psi^* \psi \\ \psi &= a + ib \quad \text{where } a, b \in \mathbb{R} \\ |\psi|^2 &= (a + ib)(a - ib) = a^2 + b^2 > 0, \in \mathbb{R} \\ \therefore |\psi|^2 &> 0, \in \mathbb{R} \end{aligned}$$

Normalization depends on the physical situation being described. The P over the whole of space must be =1 so that there is a 100% probability of measuring it somewhere.

$$\Rightarrow \int_{-\infty}^{\infty} |\psi|^2 dx = 1$$

Ex

$$\psi(x, t) = \begin{cases} A \cos(x) e^{-i \frac{Et}{\hbar}} & -\pi < x < \pi \\ 0 & \text{otherwise} \end{cases}$$

[If ψ_1 is a solution of SE then so is $\psi = A\psi_1$ (the original wave-function multiplied by a constant)]

$$\begin{aligned} \int_{-\pi}^{\pi} \left(A \cos(x) e^{-i \frac{Et}{\hbar}} \right) \left(A \cos(x) e^{i \frac{Et}{\hbar}} \right) dx &= 1 \\ |A|^2 \int_{-\pi}^{\pi} \cos^2(x) dx &= 1 \\ |A|^2 \frac{1}{2} \int_{-\pi}^{\pi} (1 + \cos(2x)) dx &= 1 \\ |A|^2 \pi &= 1 \\ A &= \frac{1}{\sqrt{\pi}} \quad (\text{Chosen } A \text{ to be real}) \\ \Rightarrow \psi(x, t) &= \begin{cases} \frac{1}{\sqrt{\pi}} \cos(x) e^{-i \frac{Et}{\hbar}} & -\pi < x < \pi \\ 0 & \text{otherwise} \end{cases} \end{aligned}$$

For a beam of particles, the normalization constant depends on the beam density.

3.2 Expectation Value

Quantum Mechanics cannot predict the outcome of a single measurement, it can only give a probability. We can calculate an average value over many repeated measurements. This is the expectation value. These repeated measurements must be of the exact same quantity so that the wave-function is identical.

$$\langle x \rangle = \int_{-\infty}^{\infty} xP(x,t)dx$$

This is simply the probability, P, weighted against the value of the displacement, x. In quantum mechanics,

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^* x \psi dx$$

$\langle x \rangle$ is the average, not a single measurement.

Ex

$$\begin{aligned} \psi &= A \cos(x) e^{-\frac{iEt}{\hbar}} \\ \Rightarrow \langle x \rangle &= \int_{-\pi}^{\pi} \left(A \cos(x) e^{-\frac{iEt}{\hbar}} \right)^* x \left(A \cos(x) e^{\frac{iEt}{\hbar}} \right) dx \\ &= A^2 \int_{-\pi}^{\pi} x \cos^2(x) dx = 0 \end{aligned}$$

Since $x \cos^2(x)$ is an odd function and the integration is symmetric about $x = 0$. This form is similar for other functions of x,

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{\infty} \psi^* x^2 \psi dx \\ \langle f(x) \rangle &= \int_{-\infty}^{\infty} \psi^* f(x) \psi dx \end{aligned}$$

However there are many quantities that might be needed, that cannot be written as functions of x, e.g the momentum, which would not be allowed by HUP if it dependent only on x. We can express these are mathematical operators,

$$\begin{aligned} \hat{O}f(x) &= g(x) \\ \text{eg } \frac{d}{dx} (x^2) &= 2x \end{aligned}$$

In quantum mechanics, an operator extracts physical information from the wave-function.

3.2.1 Momentum Operator:

$$\hat{P} = -i\hbar \frac{\partial}{\partial x}$$

Ex

Momentum of a free particle, $\psi = Ae^{i(kx - \omega t)}$,

$$\begin{aligned} \hat{P}\psi &= -i\hbar \frac{\partial}{\partial x} \left(Ae^{i(kx - \omega t)} \right) \\ &= -i\hbar ik Ae^{i(kx - \omega t)} \\ &= \hbar k Ae^{i(kx - \omega t)} \\ \Rightarrow \hat{P}\psi &= \text{constant} * \psi \quad \text{constant} = \hbar k \end{aligned}$$

Here the constant is equal to the momentum, $p = \hbar k$.

3.2.2 Total Energy Operator:

$$\hat{E} = i\hbar \frac{\partial}{\partial t}$$

EX

Total energy of a free particle,

$$\begin{aligned} \hat{E}\psi &= i\hbar \frac{\partial}{\partial t} \left(Ae^{i(kx-\omega t)} \right) \\ &= \hbar\omega Ae^{i(kx-\omega t)} \\ &= \hbar\omega\psi \\ \Rightarrow \hat{E}\psi &= \text{constant} * \psi, \quad \text{constant} = \hbar\omega \end{aligned}$$

3.2.3 Kinetic Energy Operator:

$$\begin{aligned} \hat{E}_k = \hat{T} &= \frac{\hat{P}^2}{2m} \\ &= \frac{1}{2m} \left(-i\hbar \frac{\partial}{\partial x} \right) \left(-i\hbar \frac{\partial}{\partial x} \right) \\ &= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \end{aligned}$$

EX

Kinetic energy of a free particle,

$$\begin{aligned} \frac{\hat{P}^2}{2m}\psi &= -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} \\ &= -\frac{\hbar^2}{2m} (-k^2)\psi = \frac{\hbar^2 k^2}{2m} \psi \\ \Rightarrow \hat{E}_k\psi &= \text{constant} * \psi \quad \text{constant} = \frac{\hbar^2 k^2}{2m} \end{aligned}$$

From these operators we can rewrite the Schrödinger Equation in a more compact form,

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi &= i\hbar \frac{\partial \psi}{\partial t} \\ \frac{\hat{P}^2}{2m}\psi + V\psi &= \hat{E}\psi \\ \hat{\mathcal{H}}\psi &= \hat{E}\psi \end{aligned}$$

where $\hat{\mathcal{H}}$ is the Hamiltonian operator.

A quantum mechanical operator extracts physical information from a wave-function.

e.g. for $\psi = Ae^{i(kx-\omega t)}$, $\hat{P}\psi = \hbar k\psi = p\psi$

$$\begin{aligned} \text{operator} \times (\text{function}) &= \text{constant} \times (\text{function}) \\ \hat{O}\psi_i &= a_i\psi_i \end{aligned}$$

Here, ψ_i is the eigenfunction of the operator $\hat{\mathcal{O}}$ corresponds to the observable \mathcal{O} , it represents a quantum eigenstate with a definite value for the observable \mathcal{O} . a_i is the eigenvalue of $\hat{\mathcal{O}}$, gives value of \mathcal{O} measured for the state ψ_i . The complete set of eigenvalues $a_i (i = 1, 2, 3, \dots, n)$ gives all the possible values of the observable \mathcal{O} that can be measured for this system.

So for example, $\psi = Ae^{i(kx - \omega t)}$ is an eigenfunction of the momentum operator \hat{P} and of the energy operator \hat{E} . These then produce the eigenvalues of $p = \hbar k$ and $E = \hbar\omega$.

3.3 Expectation Value for Operators

For any observable, \mathcal{O} , operator $\hat{\mathcal{O}}$ expectation value is given by

$$\langle \mathcal{O} \rangle = \int_{-\infty}^{\infty} \psi^* \hat{\mathcal{O}} \psi dx$$

So for the case where x is the observable, the operator is just x and the operation carried out would be $x\psi$ and $\hat{x} \equiv x$. Here however, when dealing with the operator expectation value, the order of the integral matters as,

$$\psi^* \hat{\mathcal{O}} \psi \neq \psi \hat{\mathcal{O}} \psi^* \neq \hat{\mathcal{O}} \psi \psi^*$$

The operator must be carried out on the original wave-function.

Ex

For the wave-function give by $\psi = \begin{cases} A \cos(x) e^{-i \frac{Et}{\hbar}} & -\pi \leq x \leq \pi \\ 0 & \text{otherwise} \end{cases}$

$$\begin{aligned} \langle \hat{E}_k \rangle &= \langle \frac{p^2}{2m} \rangle = \int_{-\pi}^{\pi} \hat{E}_k A \cos(x) e^{-i \frac{Et}{\hbar}} \psi^* \\ &= \int_{-\pi}^{\pi} (A \cos(x)) \left(\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} A \cos(x) \right) dx \\ &= \frac{\hbar^2}{2m} \int_{-\pi}^{\pi} A^2 \cos^2(x) dx \\ \langle \hat{E}_k \rangle &= \frac{\hbar^2}{2m} \end{aligned}$$

Part III

The Time Independent Schrödinger Equation

E+R pg 150-155

Often $V(x, t) = V(x)$ and so there is a static potential energy function. In this case, the full Schrödinger Equation can be simplified,

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

Try the solution $\Psi(x, t) = \Psi(x) \phi(t)$

$$\Rightarrow \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi + V \psi \right) \phi = \psi \left(i \hbar \frac{d\phi}{dt} \right)$$

Divide through by $\Phi = \psi\phi$

$$\Rightarrow \left(-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi \right) \frac{1}{\psi} = \frac{1}{\phi} \left(-i\hbar \frac{d\phi}{dt} \right) = G = \text{constant}$$

[LHS = only operators and functions of x, RHS = only operators and functions of t]

If $X(x) = T(t)$, then only true for all x and t if $X(x) = T(t) = \text{constant}$. So this 2nd order differential equation is now two ordinary differential equations which can be solved.

Time Dependant:

$$\begin{aligned} \frac{1}{\phi} i\hbar \frac{d\phi}{dt} &= G \\ i\hbar \frac{d\phi}{dt} &= G\phi \end{aligned}$$

But

$$\begin{aligned} \hat{E} &= i\hbar \frac{d\phi}{dt} = E\phi \\ \phi &= Ae^{-\frac{Et}{\hbar}} \text{ [This is the time dependant part of } \Phi(x, t)\text{]} \end{aligned}$$

Space Dependant:

$$\begin{aligned} \frac{1}{\psi} \left(-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi \right) &= G = E \\ -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi &= E\psi \text{ [This is the time indepentant form of } \Psi(x, t)\text{]} \end{aligned}$$

Solution $\psi(x)$ (spacial part of the wave-function) must be compared with $\phi(t)$ to get the full wave-function.

$$\Phi(x, t) = \psi(x)e^{-i\frac{Et}{\hbar}}$$

Time independent Schrödinger Equation is an ordinary differential equation and is REAL. Solution $\psi(x)$ may be real or complex.

4 Solutions of TISE - Potential Step

E+R pg 181-198

Form of $\psi(x)$ depends on the form of $V(x)$. The simplest case is when $V = V_0 = \text{constant}$ (free particle)

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V_0\psi &= E\psi \\ \frac{d^2\psi}{dx^2} &= -2m \left(\frac{E - V_0}{\hbar^2} \right) \psi \text{ [Simple harmonic oscillator equation]} \end{aligned}$$

This is a well know ODE with solutions of the form,

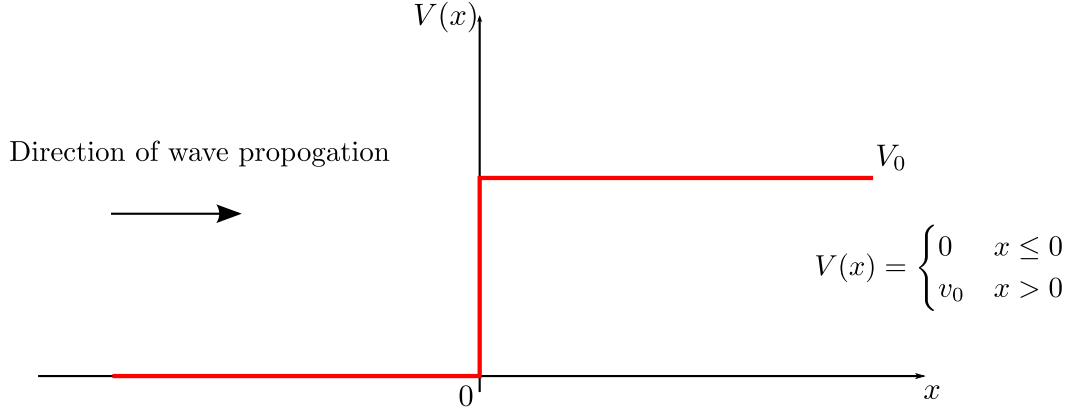
$$\psi = Ae^{ikx} + Be^{-ikx}, \quad k = \frac{\sqrt{2m(E - V_0)}}{\hbar}$$

$$\text{Equivalently } \psi = A \cos(kx) + B \sin(kx)$$

Solve TISE for various $V(x)$ which are not uniform,

$$\text{force} = \frac{dV}{dx} \neq 0$$

The simplest case is the potential step.

4.1 Case when $V_0 < E$ 

This constitutes two regions of potential joined by a step at $x = 0$. This is not a physically realistic situation but a simplification. Here $0 < V_0 < E$, where E is the energy of the particle coming from the left. Classically, the particle would be transmitted as $E > V_0$ so would continue towards $x \rightarrow \infty$; only being slowed down. However,

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

4.1.1 Solve TISE for $V_0 < E$

We already know the solution for $V = 0$ and for $V = V_0$ separately as these are just TISE with a constant potential energy function.

$$x \leq 0, V = 0, \psi_1(x) = Ae^{ik_1x} + Be^{-ik_1x} \quad k_1 = \frac{\sqrt{2mE}}{\hbar}$$

$$x > 0, V = V_0, \psi_2(x) = Ce^{ik_2x} + De^{-ik_2x} \quad k_2 = \frac{\sqrt{2m(E - V_0)}}{\hbar}$$

By definition, $V_0 < E$, so $k_2 < k_1$. So $\hbar k_2 < \hbar k_1$, which means the momentum after $x = 0$ is less than before so the particle slows down when it hits the potential barrier.

Need physical boundary conditions to find A, B, C and D;

1. De^{-ik_2x} would represent a traveling reflected wave from the right hand side, though there is nothing to be reflected from, so can argue that this wave would not exist, so $D = 0$,

$$\Rightarrow \psi_2 = Ce^{ik_2x}$$

2. Continuity considerations at boundary, $x = 0$,

(a) Wave-function must be continuous else $p \propto \frac{d\psi}{dx} \rightarrow \infty$

(b) Wave-function must have a continuous gradient $\frac{d\psi}{dx}$, else kinetic energy $\propto \frac{d^2\psi}{dx^2} \rightarrow \infty$

At $x = 0$

$$(a) \psi_1(0) = \psi_2(0)$$

$$A + B = C$$

$$(b) \frac{d}{dx}\psi_1(0) = \frac{d}{dx}\psi_2(0)$$

$$ik_1(A + B) = ik_2C$$

$$A - B = \frac{k_2}{k_1}C$$

$$\Rightarrow 2A = \left(1 + \frac{k_2}{k_1}\right)C, \quad C = \frac{2k_1}{k_1 + k_2}A$$

$$\Rightarrow B = C - A = \left(\frac{2k_1}{k_1 + k_2} - 1\right)A, \quad B = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)A$$

In general, A, B and C must all have non zero values so have some transmission and some reflection of the wave at the step, unlike the classical particle which would be 100% transmitted if $E > V_0$. But this is similar to a classical WAVE where reflection and refraction both occur at the boundary. So QM particle exhibits wave like properties.

4.2 Transmission and Reflection Coefficients

T = probability of transmission (beyond $x > 0$)

R = probability of reflection

Flux = number density in the beam \times velocity. Number density $\propto |\psi|^2 = \psi^* \psi$, velocity $\propto k$.

$$\Rightarrow \text{Flux} \propto k|\psi|^2$$

Transmitted probability,

$$T = \frac{\text{Transmitted flux}}{\text{Incident flux}} \quad (4.1)$$

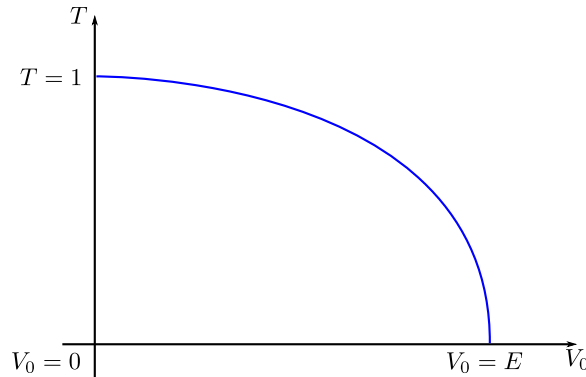
$$T = \frac{k_2|C|^2}{k_1|A|^2} = \frac{k_2}{k_1} \left(\frac{2k_1}{k_1 + k_2}\right)^2 = \frac{4k_1k_2}{(k_1 + k_2)^2} \quad (\text{For THIS particle})$$

Reflected probability,

$$R = \frac{\text{Reflected flux}}{\text{Incident flux}} \quad (4.2)$$

$$R = \frac{k_1|B|^2}{k_1|A|^2} = \frac{|B|^2}{|A|^2} = \left(\frac{k_1 - k_2}{k_1 + k_2}\right)^2 \quad (\text{For THIS particle})$$

The net flux is conserved, so $\sum(T + R) = 1$



If $V_0 = 0$, then $k_2 = k_1$, then $T = 1$ and $R = 0$ (this is the case when there is no step)

If $V_0 = E$, then $k_2 = 0$, then $T = 0$ and $R = 1$ (full reflection)

4.3 Case when $V_0 > E$

Classically, the particle would be reflected 100% of the time with perfect certainty. The region $x > 0$ would be energetically forbidden (E_p barrier $> E_k$ of incident particle)

4.3.1 Solve TISE for $V_0 > E$

$$x \leq 0, V = 0, \psi_1(x) = Ae^{ik_1x} + Be^{-ik_1x} \quad k_1 = \frac{\sqrt{2mE}}{\hbar}$$

$$x > 0, V = V_0, \psi_2(x) = Ce^{-ik_2x} + De^{-ik_2x} \quad k_2 = \frac{\sqrt{2m(E - V_0)}}{\hbar}$$

This is identical to the situation where $V_0 < E$. Now however, when $V_0 > E$,

$$k_2 = \frac{\sqrt{2m(E - V_0)}}{\hbar} = a + ib$$

. So the wavenumber is imaginary. So rewrite this as,

$$k_2 = \frac{-\sqrt{2m(V_0 - E)}}{\hbar}$$

$$k_2 = iK, \quad \text{where } K = \frac{\sqrt{2m(V_0 - E)}}{\hbar} \in \mathbb{R} > 0$$

$$\Rightarrow \psi_2(x) = Ce^{-Kx} + De^{Kx}$$

Generally, the wave function of a particle in any region that is energetically forbidden has this real exponential form (not oscillatory). Use boundary conditions to determine the integration constants A, B, C and D.

As $x \rightarrow \infty$, $e^{Kx} \rightarrow \infty$. But $\psi_2(x)$ must remain finite because $|\psi|^2 \propto \text{probability}$. So put $D = 0$.

$$\Rightarrow \psi_2(x) = Ce^{-Kx}$$

1. This time $D \neq 0$
2. Continuity considerations at the step $x = 0$ are the same. ψ is continuous,
At $x = 0$

$$(a) \psi_1(0) = \psi_2(0)$$

$$A + B = C$$

$$(b) \frac{d}{dx}\psi_1(0) = \frac{d}{dx}\psi_2(0)$$

$$ik_1(A - B) = -KC$$

$$\Rightarrow 2A = \left(1 + \frac{iK}{k_1}\right)C$$

$$\Rightarrow 2B = \left(1 - \frac{iK}{k_1}\right)C$$

Reflection coefficient

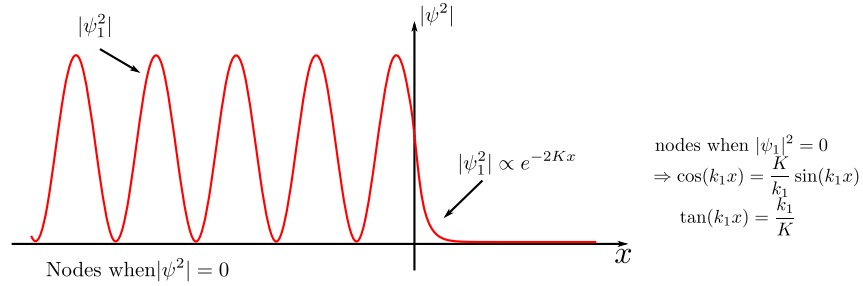
$$R = \left|\frac{B}{A}\right|^2 = \left|\frac{1 - \frac{iK}{k_1}}{1 + \frac{iK}{k_1}}\right|^2 = 1, \quad \Rightarrow T = 0$$

So for the quantum particle, we also get 100% reflection, the same as for a classical particle. C , however, is non zero, so $\psi_2 \neq 0$ in the region $x > 0$. So there is a finite probability of measuring the particle in the region $x > 0$ where it is energetically forbidden to be.

Rewrite ψ_1 as,

$$\begin{aligned}\psi_1 &= \frac{C}{2} \left(1 + \frac{iK}{k_1} \right) e^{ik_1 x} + \frac{C}{2} \left(1 - \frac{iK}{k_1} \right) e^{-ik_1 x} \\ &= C \left(\cos(k_1 x) - \frac{K}{k_1} \sin(k_1 x) \right)\end{aligned}$$

This is a standing wave solution from interference of incident wave with the reflected wave



Due to full destructive interference between incident and reflected wave because the amplitudes of the two waves are the same $|A| = |B|$. In the region $x > 0$, $|\psi|^2 \propto e^{-2Kx}$. This falls by a factor of $e \approx 2.7$ in distance, $x = \frac{1}{2K}$ (penetration distance).

If the particle was observed in this energetically forbidden region, then energy would not be conserved and the kinetic energy would be greater than the potential energy at this point. In order to observe the particle in this position, $x > 0$, then a spatial resolution of $\Delta p \geq \frac{\hbar}{2\Delta x} \approx \hbar k$

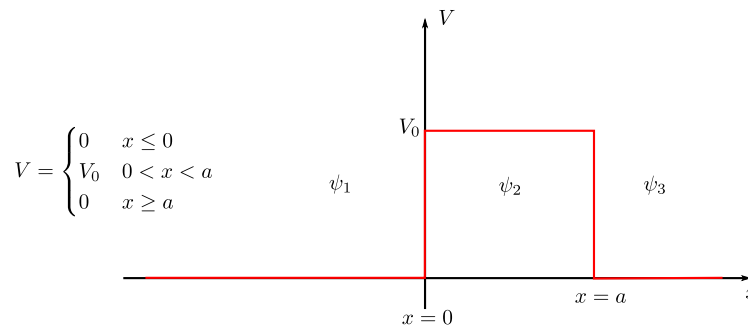
$$\Rightarrow \Delta E \approx \frac{\Delta p^2}{2m} \gtrsim \frac{\hbar^2}{2m} \frac{2m(V_0 - E)}{\hbar^2} = V_0 - E$$

So if the measurement resolution of the location of the particle $x > 0$, is high enough to determine its position, then the resolution of the energy measurement decreases so that $V_0 - E$ cannot be measured so the energy violation cannot be measured directly either.

Characteristic Quantum Result: ψ appears to violate energy conservation, but quantum uncertainty prohibits unphysical behavior being measured. But there are measurable physical quantities.

5 Solutions to TISE - Quantum Tunneling

E+R pg 199-209



Consider the case when $V_0 > E$. For a classical particle, incident from the left, the region $x > 0$ is energetically forbidden so 100% probability that it is reflected and 0% transmitted.

Solve TISE for three regions and two boundaries. Write down free particle solution for each separate region,

$$\begin{aligned} x \leq 0, \quad \psi_1 &= Ae^{ikx} + Be^{-ikx}, \quad k = \frac{\sqrt{2mE}}{\hbar} \\ 0 < x < a, \quad \psi_2 &= Ce^{iKx} + De^{Kx}, \quad K = \frac{\sqrt{2m(V_0 - E)}}{\hbar} \in \mathbb{R}, > 0 \\ x \geq a, \quad \psi_3 &= Fe^{ikx}, \quad (\text{same } k \text{ since } V = 0) \end{aligned}$$

Note: x cannot $\rightarrow \infty$ in $0 \leq x \leq a$, so $D \neq 0$ but ψ_3 has no e^{-ikx} term since no reflection beyond $x = a$.

Boundary Conditions: Continuity ψ, ψ' at $x = 0$ and $x = a$,

$$\begin{aligned} x = 0, \quad \psi_1(0) &= \psi_2(0), \quad \frac{d\psi_1(0)}{dx} = \frac{d\psi_2(0)}{dx} \\ x = a, \quad \psi_1(a) &= \psi_2(a), \quad \frac{d\psi_1(a)}{dx} = \frac{d\psi_2(a)}{dx} \end{aligned}$$

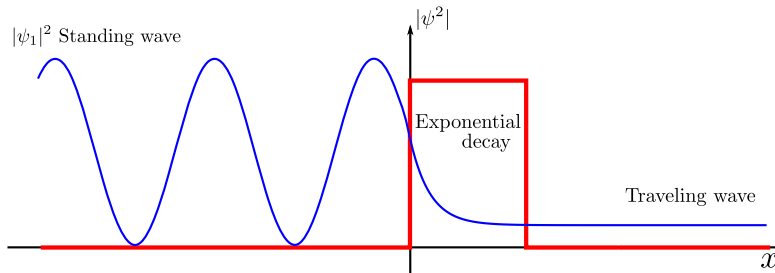
The probability of the particle tunneling through the barrier to $x \rightarrow \infty$.

$$\text{Transmission Coefficient} = T = \frac{k|F|^2}{k|A|^2} = \frac{|F|^2}{|A|^2} = \left| \frac{F}{A} \right|^2$$

For a very high ($V_0 \gg E$, k large) or very wide ($a \gg \frac{1}{k}$) barrier ,

$$T = \frac{16E}{V_0} \left(1 - \frac{E}{V_0} \right) e^{-2Ka}, \quad (ka \ll 1)$$

This is non zero, so there is a finite tunneling probability, though this is generally a small number.



$|\psi_1|^2 \neq 0$ at nodes since $R < 1$, incomplete interference.

$$|\psi_3|^2 = |Fe^{ikx}|^2 = |F|^2 = \text{constant}$$

Can measure the particle in $x > a$ but cannot resolve the particle inside the barrier.

For macroscopic objects, e.g.; $m = 1\text{kg}$, $v = 1\text{ms}^{-1}$, $E = \frac{1}{2}mv^2 = \frac{1}{2}J$, $V_0 = 1J$, $a = 1\text{cm}$,

$$\begin{aligned} \Rightarrow K &= \frac{\sqrt{2m(V_0 - E)}}{\hbar} = \frac{1}{\hbar} \\ &= 10^{34}\text{m}^{-1} \end{aligned}$$

$$\begin{aligned}
e^{ika} &\approx e^{-(2 \times 10^{34}) \times 10^{-2}} = e^{-2 \times 10^{32}} \\
&= 10^{\frac{-2 \times 10^{32}}{\ln 10}} \\
&\approx 0
\end{aligned}$$

So for the macroscopic scale, we don't get quantum tunneling.

For the atomic scale, $m = 9.1 \times 10^{-31} \text{kg}$, $E = 1 \text{eV}$, $V_0 = 10 \text{eV}$, $a = 1 \text{\AA} = 10^{-10} \text{m}$

$$\Rightarrow T = 7\%$$

So there is still a small but finite number for the atomic scale.

So far we have considered only free particles that are unbound ($\Delta x = \infty$),

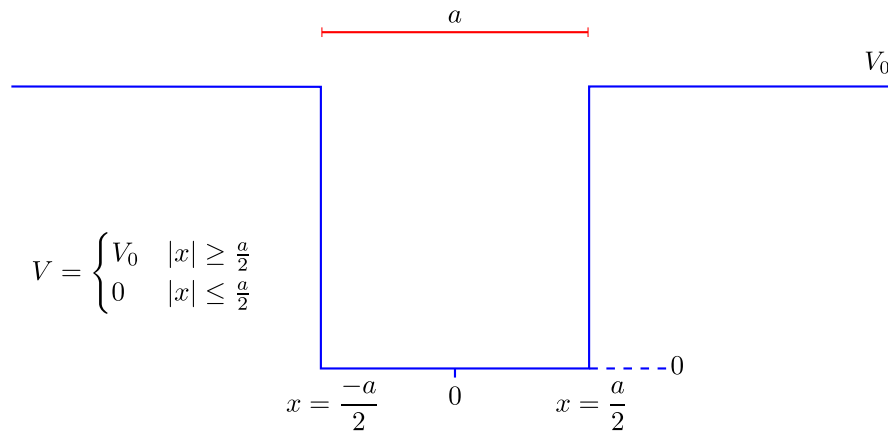
- k depends on V , $k \propto \frac{1}{\lambda} \propto \sqrt{E - V_0}$.
- any sudden change in potential (weather up or down) will cause both the possibility of reflection and transmission.
- the wave function inside an energetically forbidden region is a real exponential $\neq 0$ ($\psi \in \mathbb{R} \neq 0$).
- as a consequence, a particle can tunnel through a forbidden region or barrier and be observed on the other side.

6 Bound State Particles

Consider a particle in a finite region $\Delta x < \infty$, this leads to several new quantum phenomena. This will be considered for the simplified one dimensional situation.

6.1 Square Well Potential

E+R pg 209-221



If $E < V_0$, then the particle is bound as the energy is classically forbidden outside the well and so the wave-function would quickly tend to zero in this region. First consider the infinite square well, where $V_0 = \infty$ which is the simplest case. When $V = \infty$, the only solution $\neq 0$ is inside the well, i.e. the particle is not found anywhere $|x| > \frac{a}{2}$.

6.1.1 Solve TISE

$$\psi = A \sin(kx) + B \cos(kx)$$

Boundary Conditions

- ψ continuous at edge of the well
- $\psi = 0$ outside the well

$$\Rightarrow x = -\frac{a}{2}$$

$$\begin{aligned} 0 &= A \sin\left(-k\frac{a}{2}\right) + B \cos\left(-k\frac{a}{2}\right) \\ &= -A \sin\left(k\frac{a}{2}\right) + B \cos\left(k\frac{a}{2}\right) \end{aligned} \quad (6.1)$$

$$\Rightarrow x = \frac{a}{2}$$

$$0 = A \sin\left(k\frac{a}{2}\right) + B \cos\left(k\frac{a}{2}\right) \quad (6.2)$$

In this case, because $V = \infty$, ψ' is not required to be continuous at the edges of the well as it is unphysical to have an infinite potential, so the normal rules do not apply.

$$(10) + (11) \quad B \cos\left(k\frac{a}{2}\right) = 0 \quad (6.3)$$

$$(10) - (11) \quad A \sin\left(k\frac{a}{2}\right) = 0 \quad (6.4)$$

Try $A = B = 0 \Rightarrow \psi = 0$ so no particle. So either

$$A = 0 \quad \cos\left(k\frac{a}{2}\right) = 0 \quad (6.5)$$

OR

$$B = 0 \quad \sin\left(k\frac{a}{2}\right) = 0 \quad (6.6)$$

$$(14) \rightarrow \psi = \cos\left(k\frac{a}{2}\right) \quad k\frac{a}{2} = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2} \dots$$

$$(15) \rightarrow \psi = \sin\left(k\frac{a}{2}\right) \quad k\frac{a}{2} = \pi, 2\pi, 3\pi \dots$$

So we are left with two sets of solutions.

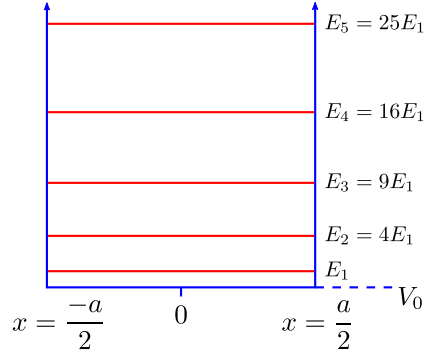
$$1. \psi_n = B_n \cos(k_n x) \quad \text{with } k_n = \frac{n\pi}{a}, \quad n = 1, 3, 5 \dots$$

$$2. \psi_n = A_n \sin(k_n x) \quad \text{with } k_n = \frac{n\pi}{a}, \quad n = 2, 4, 6 \dots$$

So there is an infinite number of possible solutions. n is the quantum number, labels solution (eigenstate). Corresponding energy eigenvalues;

$$\begin{aligned} E_n &= \frac{(\hbar k_n)^2}{2m} \\ &= \frac{n^2 \pi^2 \hbar^2}{2ma^2} \quad n = 1, 2, 3 \dots \end{aligned}$$

This means that the energy is not a continuous variable, but has distinct discrete values. So solving TISE has led to energy quantization, only discrete energy values are allowed.



6.1.2 Infinite Square Potential Well

For an infinite well, there are infinite values of energy levels. For square well $E_n \propto n^2$.

The ground-state (lowest energy of the system) has $n = 1$,

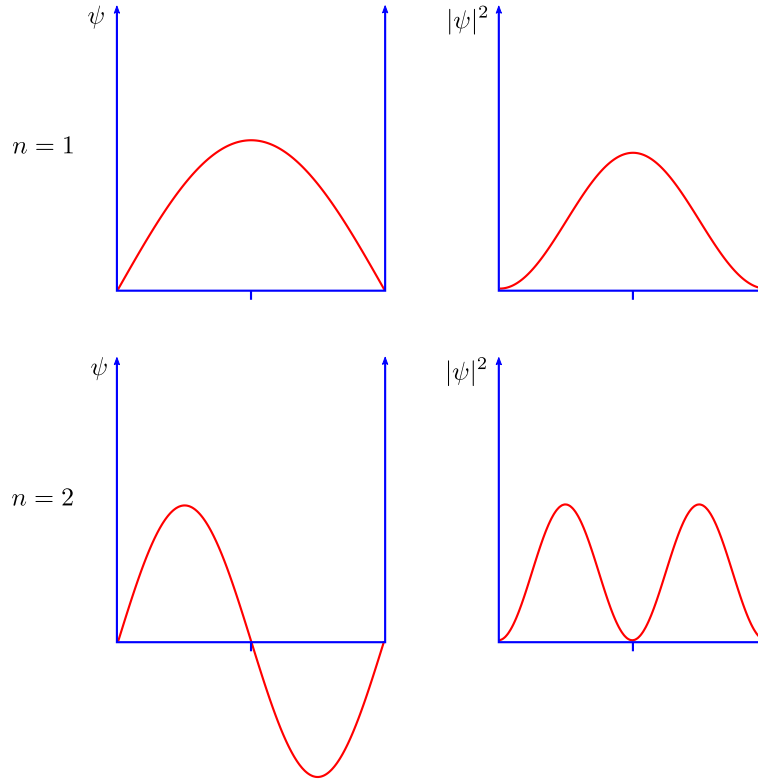
$$\Rightarrow E_1 = \frac{\pi^2 \hbar^2}{2ma^2} > 0 \quad \text{zero point energy}$$

For Heisenberg Uncertainty Principle, if $\Delta x < \infty$ (bound), then $\Delta p > 0$, so $p \neq 0$ and thus $E \neq 0$, zero point energy. So any bound state has a non-zero lowest energy.

6.1.3 Wave-functions

$$k_n = \frac{n\pi}{a}, \quad k = \frac{2\pi}{\lambda}, \quad a = \frac{n\lambda}{2}$$

So there are an infinite number of HALF wavelengths inside the well, this just restates the boundary conditions that the wave-function must go to zero at the edges of the well.



Two sets of solutions have different parities (symmetry about $x = 0$)

$$\begin{aligned} \psi_n &= B_n \cos(k_n x) & \psi(x) &= \psi(-x) & \text{even parity for odd } n \\ \psi_n &= A_n \sin(k_n x) & \psi(x) &= -\psi(-x) & \text{odd parity for even } n \end{aligned}$$

$|\psi|^2$ is always even parity, given that the potential is symmetric about $x = 0$.

6.2 Finite Square Potential Well

E+R pg 209-214 and
Appendix H

Solve TISE for each of the three regions and two boundaries. Now the wave-function is non-zero in the two energetically forbidden regions, and there are two boundary conditions for each edge of the well;

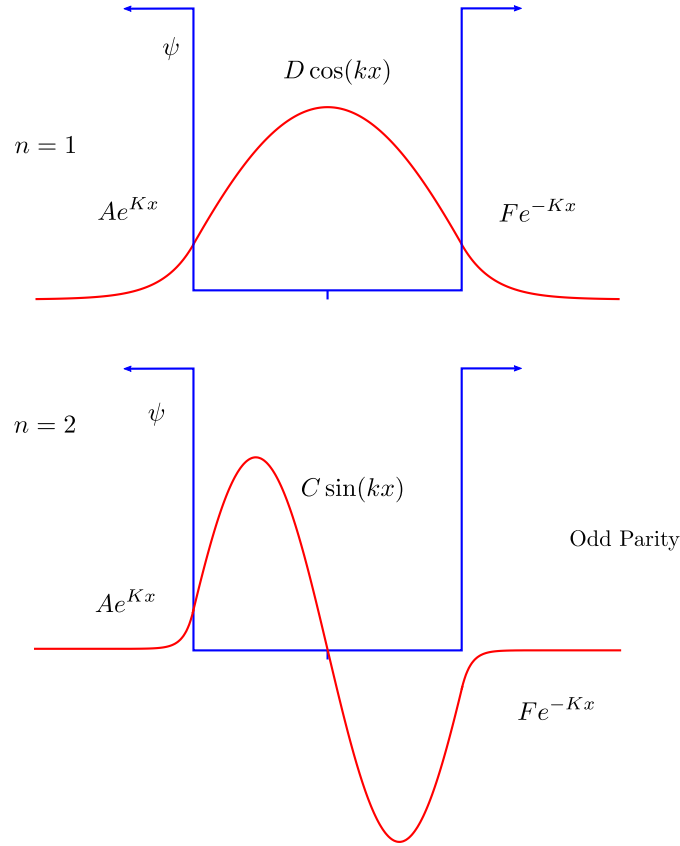
$$\psi_1(0) = \psi_2(0)$$

and

$$\frac{d\psi_1(0)}{dx} = \frac{d\psi_2(0)}{dx}$$

Also $\psi \rightarrow 0$ at either side as $x \rightarrow \infty$, since $V_0 < E$.

Again there are two sets of solutions with opposite parity.



As $V_0 = \infty \rightarrow V_0 = \text{finite}$, ψ “spreads out” into the walls of the well. So there is now a less than integer number of half wavelengths inside the well. λ has effectively increased, so the energy has decreased. So the corresponding energy levels in infinite and finite square wells will not be the same. Finite well energy level $<$ infinite well energy level.

To get the energy eigenvalues, we need to solve the other half of the boundary condition equations,

$$\begin{aligned} \tan\left(\frac{ka}{2}\right) &= \frac{K}{k} && \text{Even parity} \\ \cot\left(\frac{ka}{2}\right) &= -\frac{K}{k} && \text{Odd parity} \end{aligned}$$

There exists no analytical technique to solve these equations, so we need a numerical method or graphical technique. Rewrite E , V_0 ,

$$\begin{aligned} \Rightarrow \tan\left(\frac{a}{\hbar} \sqrt{\frac{mE}{2}}\right) &= \sqrt{\frac{V_0 - E}{E}} && \text{OR} \\ \Rightarrow -\cot\left(\frac{a}{\hbar} \sqrt{\frac{mE}{2}}\right) &= \sqrt{\frac{V_0 - E}{E}} \end{aligned}$$

For convenience, change the variables,

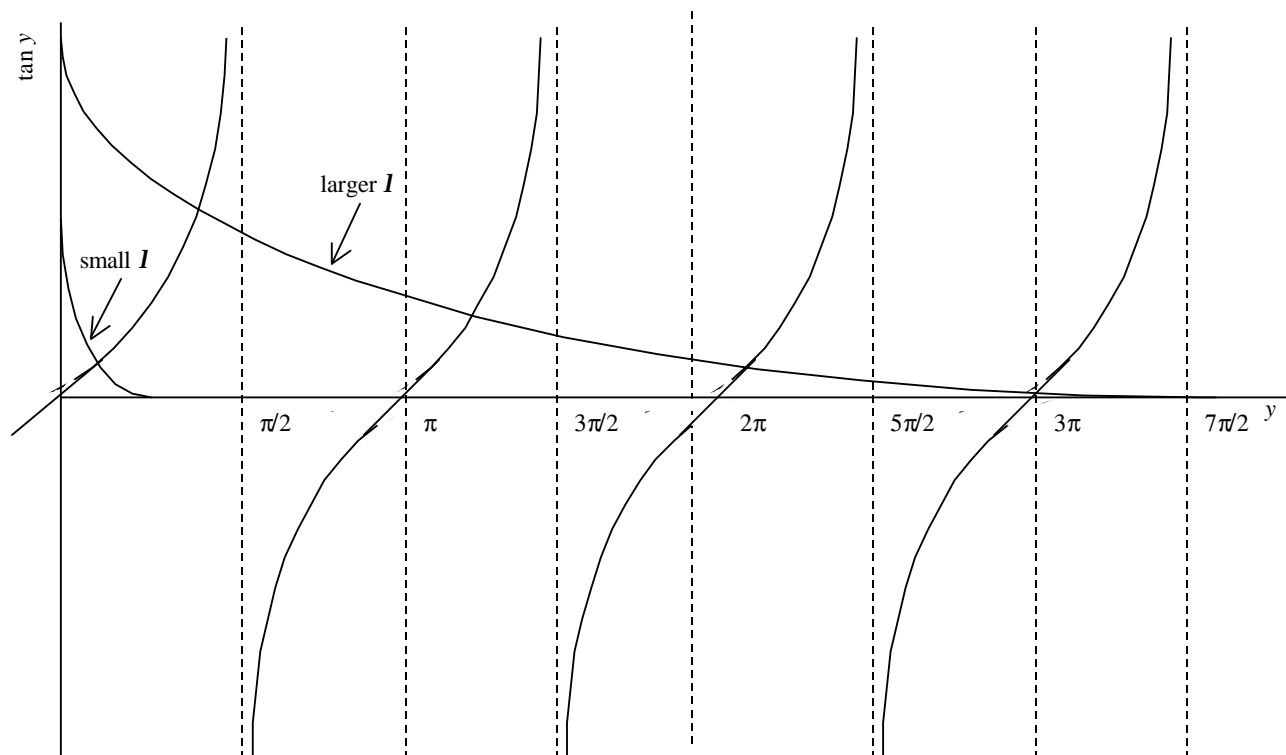
$$\begin{aligned} y &= \frac{a}{\hbar} \sqrt{\frac{mE}{2}} = \frac{ka}{2} \\ \lambda &= \frac{mV_0 a^2}{2\hbar^2} = \text{constant} \end{aligned}$$

Note $\lambda > y^2$, when $V_0 > E$,

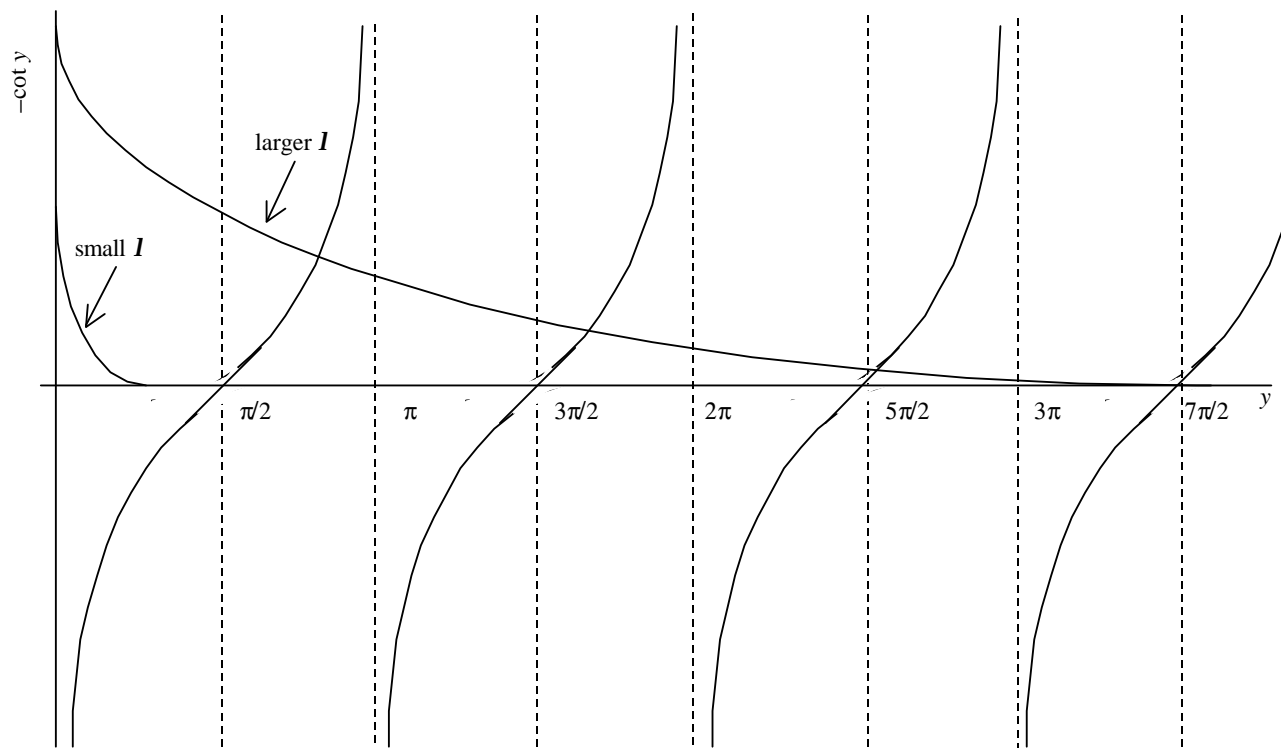
$$\begin{aligned}\Rightarrow \tan(y) &= \frac{\sqrt{\lambda - y^2}}{y} & \text{OR} \\ \Rightarrow -\cot(y) &= \frac{\sqrt{\lambda - y^2}}{y}\end{aligned}$$

Plot LHS and RHS as graphs as functions of y . The locations where the two curves intersect gives the solutions of y . As y is a function of E , this gives E . When $\lambda \rightarrow \infty$ (so $V_0 \rightarrow \infty$) the intersections tend to values of $\frac{\tan}{\cot}$ at the poles (asymptotes), i.e. at $\pm\infty$.

“Even” solutions of finite well



“Odd” solutions of finite well



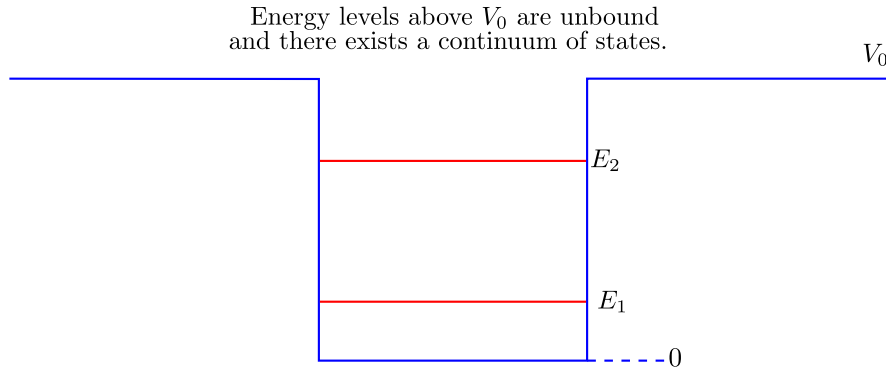
So

$$\begin{aligned} y &= \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2} \dots & \text{even} \\ y &= \pi, 2\pi, 3\pi \dots & \text{odd} \end{aligned}$$

So $k = \frac{n\pi}{a}$ as expected from the previous infinite well case. For V_0 finite, λ is finite, the intersections occur at smaller y -values, so the energy levels are lower for finite well.

When λ is finite, there are only a finite number of solutions as there are only a finite number of intersections with $y^2 < \lambda$ i.e. $E < V_0$. So there are a finite number of energy levels in a finite well. For $E > V_0$, the particle would be unbound from the well.

As V_0 is reduced, the higher energy levels are lost (as they are unbound) but there is always at least one bound state so long as $V_0 > 0$, ground state, $n = 1$, with even parity.



6.3 Simple Harmonic Oscillator Potential Well

E+R pg 209-214 and
Appendix I

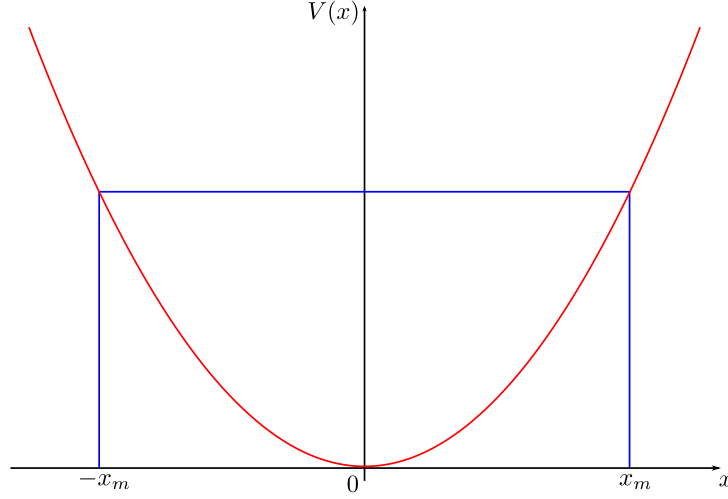
The SHO is an important potential and is physically more realistic than the square well as it does not have any abrupt step in potential/ Classically, the simple harmonic oscillator is formed by displacing mass m , by a distance x , from the equilibrium given there is a restoring force proportional to the displacement, $-cx$,

$$\begin{aligned} F &= m\ddot{x} = -cx \\ \ddot{x} &= -\frac{c}{m}x = -\omega^2 x \quad \omega = \sqrt{\frac{c}{m}} \text{ (angular frequency)} \end{aligned}$$

In quantum mechanics, the force is linked to the displacement by,

$$\begin{aligned} F &= -\frac{dV}{dx} = -cx \\ V &= \int cxdx = \frac{1}{2}cx^2 = \frac{1}{2}\omega^2 x^2 m \end{aligned}$$

This is a quadratic equation for the potential. So the shape of the simple harmonic oscillator is a parabolic well.



Again, this is an infinite and symmetric well, so we would expect an infinite number of solutions with energy quantization, and that the eigenfunctions have even or odd parity. k (hence $\frac{1}{\lambda}$) varies across the well as $\sqrt{E - V}$ changes. The classical oscillator would be limited to the width of the well at the given energy level,

$$\begin{aligned} E = V &= \frac{1}{2}m\omega^2 x^2 \\ \Rightarrow x_m &= \pm \sqrt{\frac{2E}{m\omega^2}} \end{aligned}$$

Quantum effects, however, mean that the quantum particle is not confined strictly to the potential well, but will be able to penetrate slightly into the wall. But the wave-function tends to zero rapidly as $|x| \rightarrow \infty$. TISE then,

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

In this case, there are no regions of flat potential (free particle solution) and so the full solution of TISE must be performed. See appendix I in E+R for solution. Change in spatial variable to

$$u = x \sqrt{\frac{m\omega}{\hbar}}$$

then the eigenfunctions are,

$$\psi_n(u) = h_n(u) E^{-\frac{u^2}{2}}$$

where h_n is a Hermite polynomial ($n = 0, 1, 2, 3, \dots$). The first few (unnormalized) solutions are,

$$\begin{aligned} \psi_0(u) &= e^{-\frac{u^2}{2}} \\ \psi_1(u) &= u e^{-\frac{u^2}{2}} \\ \psi_2(u) &= (2u^2 - 1) e^{-\frac{u^2}{2}} \end{aligned}$$

This satisfies the infinite number of bound states of even and odd parity penetrating into the potential

wall. Check by substituting into TISE,

$$\begin{aligned}
 \psi_0 &= e^{-\frac{x^2}{2}} = e^{-\frac{m\omega x^2}{2\hbar}} \\
 \frac{d\psi_0}{dx} &= -\frac{m\omega x}{\hbar} e^{-\frac{m\omega x^2}{2\hbar}} \\
 \frac{d^2\psi_0}{dx^2} &= -\frac{m\omega}{\hbar} e^{-\frac{m\omega x^2}{2\hbar}} - \frac{m^2\omega^2 x^2}{\hbar^2} e^{-\frac{m\omega x^2}{2\hbar}} \\
 &= \left(-\frac{m\omega}{\hbar} - \frac{m^2\omega^2 x^2}{\hbar^2} \right) e^{-\frac{m\omega x^2}{2\hbar}}
 \end{aligned}$$

$$\begin{aligned}
 \text{TISE} \Rightarrow -\frac{\hbar^2}{2m} \left(-\frac{m\omega}{\hbar} - \frac{m^2\omega^2 x^2}{\hbar^2} \right) e^{-\frac{m\omega x^2}{2\hbar}} \psi_0 + \frac{1}{2}m\omega^2 x^2 \psi_0 &= E_0 \psi_0 \\
 \frac{1}{2}\hbar\omega \psi_0 &= E_0 \psi_0
 \end{aligned}$$

So the ground state of the energy of the simple harmonic oscillator is given by,

$$E = \frac{1}{2}\hbar\omega$$

this is the zero point energy.

$$\begin{aligned}
 n=0, \quad E_0 &= \frac{1}{2}\hbar\omega \\
 n=1, \quad E_1 &= \frac{3}{2}\hbar\omega \\
 n=2, \quad E_2 &= \frac{5}{2}\hbar\omega \\
 &\vdots \\
 n=n, \quad E_n &= \left(n + \frac{1}{2} \right) \hbar\omega
 \end{aligned}$$

for the simple harmonic oscillator. The energy levels are now evenly spaced with a linear dependence on n , with the spacing being $\hbar\omega$,

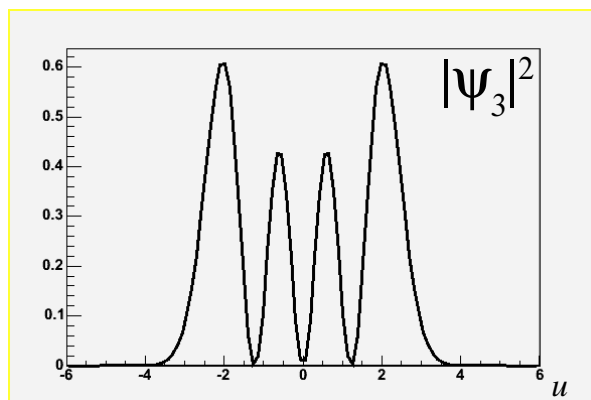
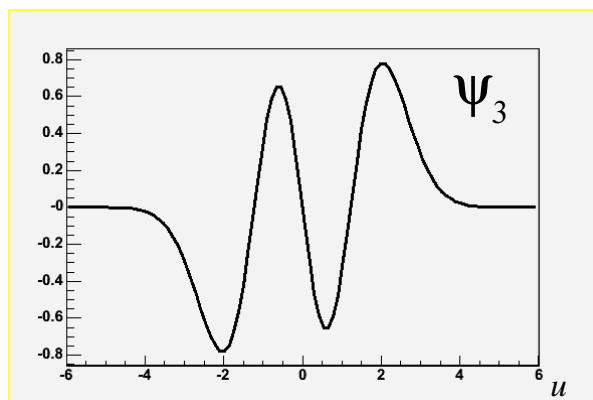
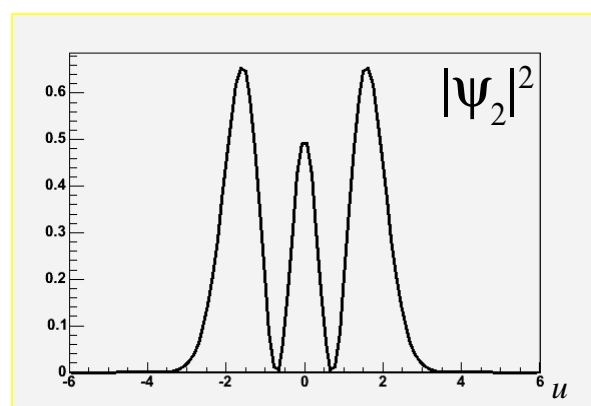
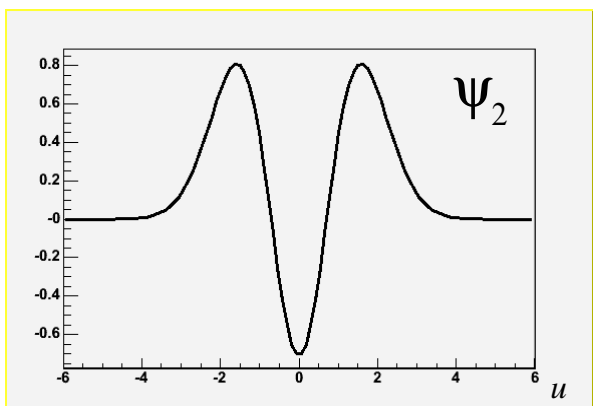
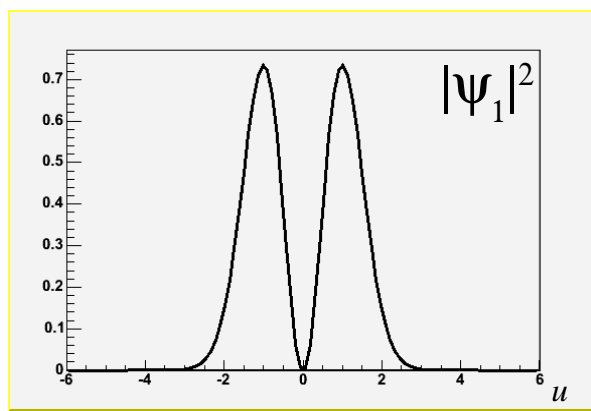
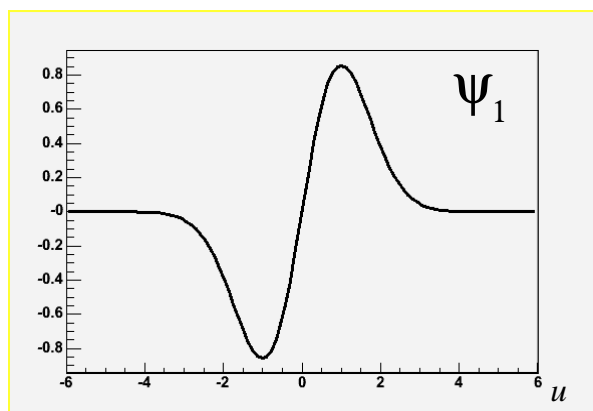
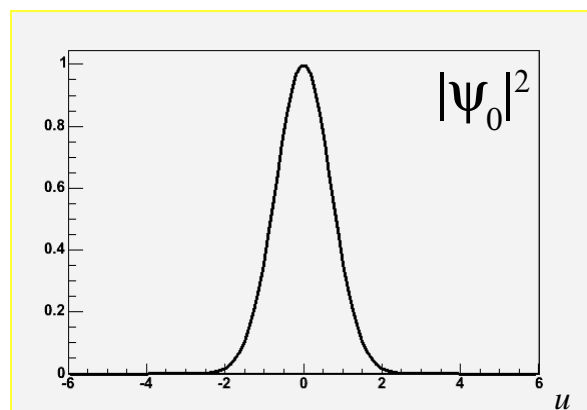
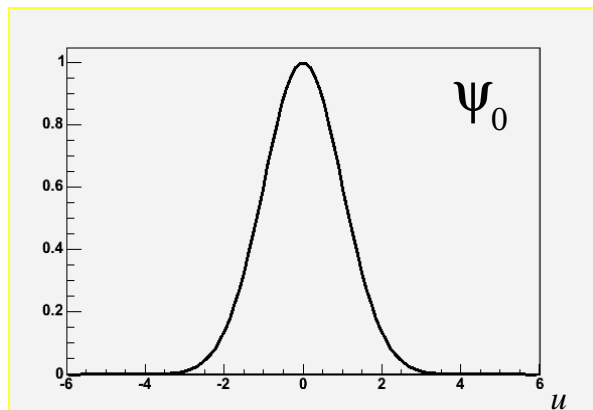
$$E_{n+1} - E_n = \hbar\omega$$

which is the energy of the photon. The probability function, $|\psi|^2$, varies with location across the well. Classically, the PDF is smooth with peaks at the edges of the range. At large values of n , the individual peaks and troughs cannot be resolved at the classical situation is reached.

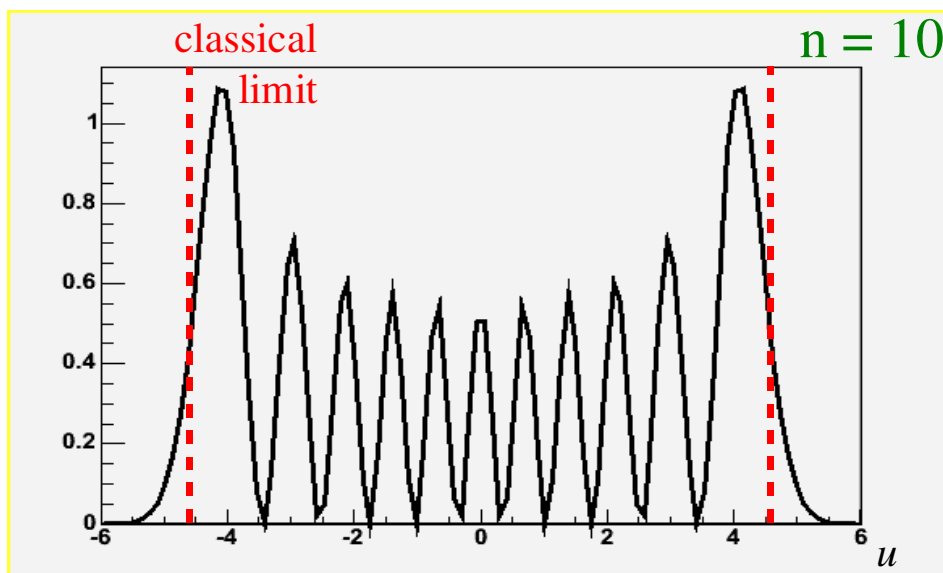
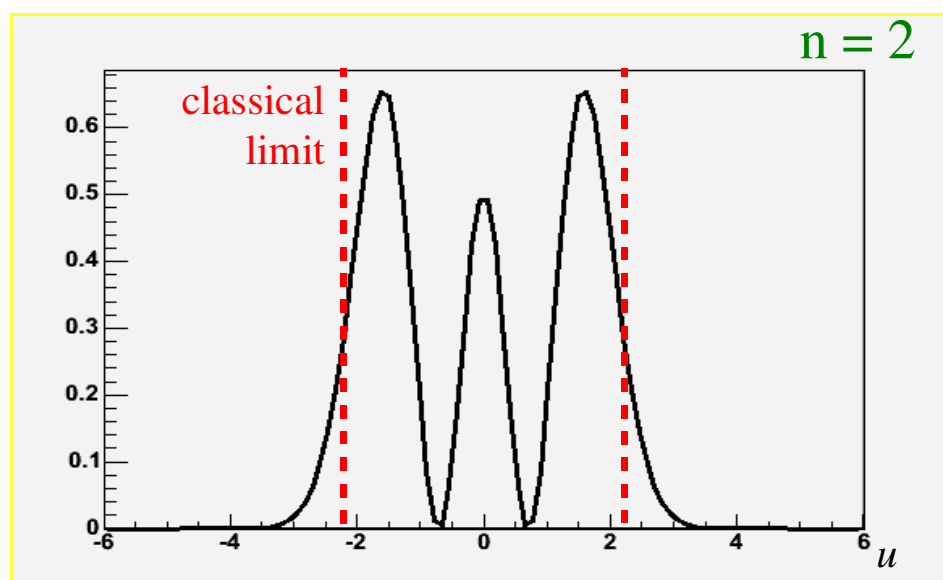
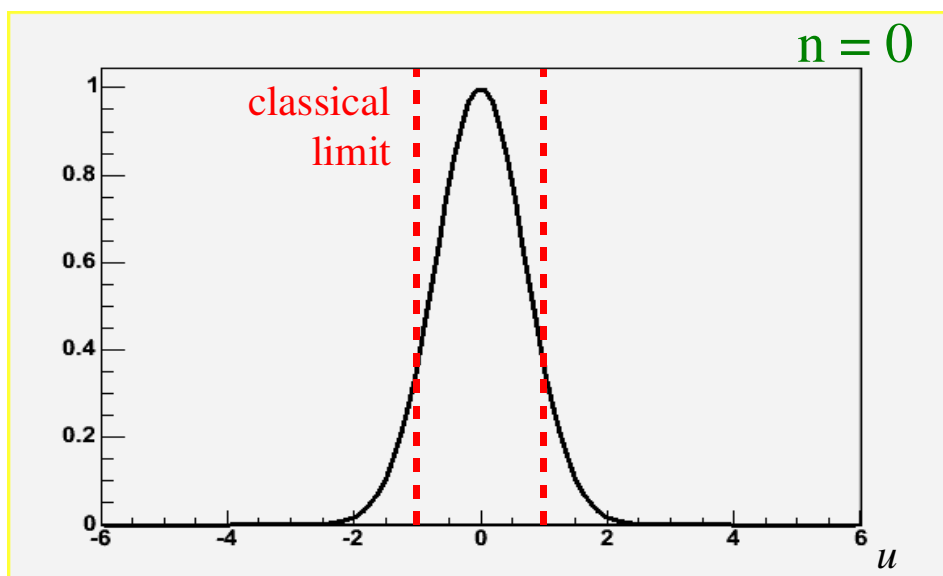
So as $n \rightarrow \infty$, quantum \rightarrow classical

This is an example of the CORRESPONDENCE PRINCIPLE.

SHO Wavefunctions and Probability Densities



SHO Probability Densities vs order of solution



Part IV

Time Dependence, Superposition and Measurement

7 Time Dependence

E+R pg 166-167

If $\psi_n(x)$ is a solution of TISE (spacial wave-function) then the full wave-function,

$$\Psi(x, t) = \psi_n(x) e^{-\frac{E_n t}{\hbar}}$$

where E_n is the energy eigenvalue. This is the solution of the full SE,

$$\begin{aligned} |\Psi|^2 &= \left(\psi_n^* e^{i \frac{E_n t}{\hbar}} \right) \left(\psi_n e^{-i \frac{E_n t}{\hbar}} \right) \\ &= \psi_n^* \psi_n = |\psi|^2 \end{aligned}$$

which has no time dependence. This is true when the wave-function is an eigenfunction of the Hamiltonian.

Consider the mixed state,

$$\begin{aligned} \Phi(x, t) &= \Psi_m(x, t) + \Psi_n(x, t) \\ |\Phi|^2 &= |\Psi_m + \Psi_n|^2 \\ &= \Psi_m^* \Psi_m + \Psi_n^* \Psi_n + \underbrace{\Psi_m^* \Psi_n + \Psi_n^* \Psi_m}_{\text{interference terms}} \\ &= |\Psi_m|^2 + |\Psi_n|^2 + \Psi_m^* \Psi_n e^{-i \frac{(E_n - E_m)t}{\hbar}} + \Psi_n^* \Psi_m e^{-i \frac{(E_n - E_m)t}{\hbar}} \\ &= |\Psi_m|^2 + |\Psi_n|^2 + \mathbb{R} \left\{ \Psi_m^* \Psi_n e^{-i \frac{(E_n - E_m)t}{\hbar}} \right\} \\ &= |\Psi_m|^2 + |\Psi_n|^2 + 2 \Psi_m^* \Psi_n \cos \left(\frac{\Delta E t}{\hbar} \right) \end{aligned}$$

$\Delta E = E_n - E_m$, and assuming that $\Psi_m^* \Psi_m$ is real, if its not then also term $\propto \sin \left(\frac{\Delta E t}{\hbar} \right)$. So the probability density oscillates between states with an angular frequency,

$$\omega = \frac{\Delta E}{\hbar}$$

$\Phi(x, t) = \Psi_m(x, t) + \Psi_n(x, t)$ is called a superposition states. If both Ψ_m and Ψ_n are solutions of the full SE, the linearity means that Φ must also be a solution for the same potential function, V . But

$$\phi(x) = \psi_m(x) + \psi_n(x)$$

is NOT a solution of TISE because

$$\begin{aligned} \hat{\mathcal{H}}\phi &= \hat{\mathcal{H}}(\psi_m + \psi_n) \\ &= E_m \psi_m + E_n \psi_n \neq \psi_n E (\psi_m + \psi_n) \end{aligned}$$

since $E_m \neq E_n$. $\Phi(x, t)$ is not an eigenfunction of $\hat{\mathcal{H}}$, so does not have a definite value of E .

8 Superposition

If $\Phi_i(x, t)$ ($i = 1, 2, 3, \dots$) form a complete set of solutions of SE, (for certain $V(x, t)$) then the general solution can be expressed as

$$\Phi(x, t) = \sum_{i=1}^n C_i \Psi_i(x, t)$$

with C_i ($i = 1, 2, 3, \dots$) being a constant coefficient which are in general complex. Any valid wavefunction can be written in this way. In general, Φ is not an eigenfunction of $\hat{\mathcal{H}}$ or other operators, so have to have no definite value for the energy or other observables. So what is the result of a measurement of energy etc?

8.0.1 More on Eigenfunctions and Eigenvalues

If $\hat{A}\psi_i = a_i\psi_i$ for the operator \hat{A} corresponding to the observable A , then the value of this observable is given by the eigenvalue a_i for the particle in state ψ_i . State ψ_i has a well defined value of A . A complete set of eigenfunctions ψ_i ($i = 1, 2, 3, \dots$), gives all possible results of measuring this observable, for this system, for this state. Other values are not allowed (quantization).

\therefore all eigenvalues, a_i , must be real.

8.1 Hermitian Operators

Definition Hermitian operators satisfy the conditions

$$\int_{-\infty}^{\infty} \psi_b^* \hat{O} \psi_a dx = \int_{-\infty}^{\infty} \psi_a (\hat{O} \psi_b)^* dx$$

This is in one dimension, but is the same for the general situation in all space, for any two wavefunctions ψ_a and ψ_b .

Suppose ψ_a is an eigenfunction: $\hat{O}\psi_a = a\psi_a$, then

$$\begin{aligned} \int \psi_a^* \hat{O} \psi_a dx &= \int \psi_a (\hat{O} \psi_a)^* dx \\ \int \psi_a^* a \psi_a dx &= \int \psi_a (a \psi_a)^* dx \\ a \int \psi_a^* \psi_a dx &= a^* \int \psi_a \psi_a^* dx \\ \Rightarrow a &= a^* \quad \therefore a \in \mathbb{R} \end{aligned}$$

So Hermitian operators produce eigenvalues that are always real. This condition is required as they

produce a physical, measurable property. Suppose also that ψ_b is another eigenfunction $\hat{O}\psi_b = b\psi_b$,

$$\begin{aligned}\int \psi_b^* \hat{O} \psi_a dx &= \int \psi_a (\hat{O} \psi_b)^* dx \\ \int \psi_b^* a \psi_a dx &= \int \psi_a (b \psi_b)^* dx \\ a \int \psi_b^* \psi_a dx &= b \int \psi_a \psi_b^* dx \\ (a - b) \int \psi_b^* \psi_a dx &= 0 \\ \text{If } a \neq b, \quad \int \psi_b^* \psi_a dx &= 0 \\ \text{If } a = b, \quad \int \psi_a^* \psi_a dx &= 1\end{aligned}$$

In general,

$$\int_{-\infty}^{\infty} \psi_b^* \psi_a = \begin{cases} 0 & \text{if } a \neq b \\ 1 & \text{if } a = b \end{cases} = \delta_{ab} \text{ (Kronecker Delta)}$$

Therefore Hermitian operators are orthogonal. In quantum mechanics, Hermitian operators represent physical observables, real eigenvalues give the measured value of the observable, and the orthogonal eigenfunctions present a basis to write any wave-function Φ as superposition,

$$\Phi = \sum_{i=1}^n C_i \Psi_i$$

8.2 Expectation Value for Superposition States

$$\begin{aligned}\phi &= \sum_{i=1}^n C_i \Psi_i \\ \langle o \rangle &= \int \psi^* \hat{O} \psi dx = \int \phi^* \hat{O} \phi dx \\ &= \int \left(\sum_{i=1}^n C_i \psi_i \right)^* \hat{O} \left(\sum_{j=1}^n C_j \psi_j \right) dx \\ &= \int \sum_{i=1}^n C_i^* \psi_i^* \sum_{j=1}^n C_j a_j \psi_j dx \\ &= \sum_{i=1}^n \sum_{j=1}^n C_i^* C_j a_j \int \psi_j^* \psi_i dx \\ &= \sum_{i=1}^n \sum_{j=1}^n C_i^* C_j a_j \delta_{ij} \\ &= \sum_{i=j=1}^n C_i^* C_j a_j = \sum_{j=1}^n |C_j|^2 a_j\end{aligned}$$

When $i \neq j$, the values of $\delta_{ij} = 0$ so the sum collapses for all values other than when $i = j$.

Identify $|C_i|^2$ = probability of measuring observable o to have a value of a_i for the state ϕ . Eigenfunction value $\langle o \rangle$ = weighted average.

$$\begin{aligned} &= \sum_{i=1}^n \left[\begin{array}{c} \text{probability of} \\ \text{measuring this value} \end{array} \times \text{value} \right] \\ &= \sum_{i=1}^n [|C_i|^2 \times a_i] \end{aligned}$$

Also note that

$$\int_{-\infty}^{\infty} \phi^* \phi dx = \sum_{i=1}^n |C_i|^2 = 1 = \text{total probability}$$

Ex

$\phi = \sqrt{\frac{2}{a}} \cos\left(\frac{\pi x}{a}\right)$ is a free particle normalized over the space $-\frac{a}{2}$ to $\frac{a}{2}$. ϕ is an eigenfunction of kinetic energy,

$$\hat{E}_k = \frac{\hat{P}}{2m} \phi = \frac{\pi^2 \hbar^2}{2ma^2} \phi$$

But this state, ϕ , is not an eigenfunction of momentum since the cosine becomes sine and the original wave-function is lost,

$$\hat{P} = -i\hbar \frac{d}{dx}$$

Write ϕ as the superposition in terms of \hat{P} eigenfunction

$$\begin{aligned} \psi_+ &= \frac{1}{\sqrt{a}} e^{i\pi x}, & \hat{P}\psi_+ &= \frac{\pi\hbar}{a} \psi_+ \\ \psi_- &= \frac{1}{\sqrt{a}} e^{-i\pi x}, & \hat{P}\psi_- &= \frac{-\pi\hbar}{a} \psi_- \end{aligned}$$

these are also normalized over the space $-\frac{a}{2}$ to $\frac{a}{2}$.

$$\begin{aligned} \Rightarrow \phi &= \sqrt{\frac{2}{a}} \left(\frac{e^{i\frac{\pi x}{2}} + e^{-i\frac{\pi x}{2}}}{2} \right) \\ &= \frac{1}{\sqrt{2}} \psi_+ + \frac{1}{\sqrt{2}} \psi_- = C_+ \psi_+ + C_- \psi_- \quad C_+ = C_- = \frac{1}{\sqrt{2}} \end{aligned}$$

For the state ϕ , the probability measurement of the momentum value

$$\begin{aligned} p_+ &\Rightarrow |C_+|^2 = \frac{1}{2} \\ p_- &\Rightarrow |C_-|^2 = \frac{1}{2} \end{aligned}$$

So the particle is equally likely to be moving along the \pm x-axis with $|p| = \frac{\pi\hbar}{a}$, $E_k = \frac{\pi^2 \hbar^2}{2ma^2}$

$$\langle p \rangle = |C_+|^2 p_+ + |C_-|^2 p_- = 0$$

8.2.1 Calculating Coefficients C_i in General

$$\phi = \sum_{i=1}^n C_i \psi_i$$

$$\begin{aligned}
 \int \psi_j^* \phi dx &= \sum_{i=1}^n C_i \int \psi_j^* \psi_i dx \\
 &= \sum_{i=1}^n C_i \delta_{ij} = C_j \\
 C_j &= \int_{-\infty}^{\infty} \psi_j^* \phi dx \quad (\text{overlap integral})
 \end{aligned}$$

So for a given state ϕ , eigenfunction ψ_i ($i = 1, 2, 3, \dots, n$), the coefficients C_i ($i = 1, 2, 3, \dots, n$) can be calculated. Hence the probabilities $|C_i|^2$ ($i = 1, 2, 3, \dots, n$) of measuring the observable, o , having the value a_i for the state ϕ_i where

$$\hat{O}\psi_i = a_i\psi_i$$

9 Measurement and Collapse of Wave-functions

Consider repeat measurements on many particles, each in the same state described by ϕ . We will get different results for each measurement corresponding to the different eigenvalues, $a_1, a_2, a_3 \dots a_n$ with probabilities $|C_1|^2, |C_2|^2, |C_3|^2 \dots |C_n|^2$. Quantum mechanics does not predict definite results of single measurements, but the average is

$$\langle \mathcal{O} \rangle = \sum_{i=1}^n |C_i|^2 a_i$$

This can be predicted and compared to experimental measurements. If instead a single particle is measured, there will be a definite result, a_j , probability is given by $|C_j|^2$ for the observable, \mathcal{O} . Suppose, the, the same observable is measured again immediately after the first. We would expect the get the same result for the same particle. We would expect the same value for \mathcal{O} with a probability of 1 (certainty).

The particle has some definite value, a_j , for the observable \mathcal{O} . So now the particle must be described by a different wave-function (not ϕ) so that it is an eigenfunction of the operator for the observable \mathcal{O} . After the first measurement, the particle is in an eigenstate of \mathcal{O} with eigenvalue, a_j , i.e. the wave-function is ψ_j . This process is called the collapse of the wave-function from $\phi \rightarrow \psi_j$. Collapse is discontinuous and irreversible process and cause the loss of all history of the previous state ϕ .

EX

Initial state $\phi = \sqrt{\frac{2}{a}} \cos\left(\frac{\pi x}{a}\right)$, which is an eigenstate of E_k but not p), where the momentum eigenstates are $= \frac{1}{\sqrt{2}}\psi_+ + \frac{1}{\sqrt{2}}\psi_-$

$$\psi_{\pm} = \frac{1}{\sqrt{a}} e^{\pm \frac{i\pi x}{a}}$$

Eigenvalues $P_{\pm} = \pm \frac{\pi\hbar}{a}$

Measure the momentum for this particle gives the result $p_+ = +\frac{\pi\hbar}{a}$ (probability = $\frac{1}{2}$) When the wave-function collapses, $\phi \rightarrow \psi_+ = \frac{1}{\sqrt{a}} e^{\frac{i\pi x}{a}}$,

$$\psi_+ = \left(\cos\left(\frac{\pi x}{a}\right) - i \sin\left(\frac{\pi x}{a}\right) \right) \frac{1}{\sqrt{a}} \neq \phi$$

The collapse of the wave-function does not follow SE. It is a separate postulate of QM. Interpretation of this postulate is still controversial and leads to a purely philosophical debate,

1. Is superposition time independent of states or just our knowledge of it?

- Can observe quantum interference easily which leads to the superposition of the real state.
2. Is the result of a measurement on superposition unknown or actually indeterminate beforehand?
- Quantum mechanics says indeterminate. Experimental verification by Alan Aspect and from “Bell’s inequalities”.
3. What is “measurement”? and when does the collapse actually “occur”?
- Schrödinger’s Cat thought experiment lets us consider the situation
 - Unpredictable, unstable nuclear decay can be detected. This causes the death of the cat. So the fate of the cat is determined by the state of the nucleus. This happens in a box whereby the experimenters do not know the state of the system. So before the box is opened, the cat is in a superposition of the alive and dead states.
 - Common usage is the Copenhagen Interpretation which basically says “ignore the philosophy and use it as a tool”.

10 Commutation

A wave-function can be an eigenfunction of more than one operator, e.g.

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

is an eigenfunction of momentum, $\hat{P} = -i\hbar \frac{\partial}{\partial x}$, with eigenvalue $p = \hbar k$, and of energy, $\hat{E} = i\hbar \frac{\partial}{\partial t}$ with eigenvalue $E = \hbar\omega$. So we could know precisely the value of the momentum and the energy at the same time, without uncertainty. But some combinations of observables cannot be known simultaneously, e.g.

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

which is one form of the Heisenberg Uncertainty Principle. Commutation refers to the order in which operators or functions are acted. Most numbers, functions etc commute,

$$\begin{aligned} 2 \times 3 &= 3 \times 2 \\ xy &= yx \\ &\vdots \end{aligned}$$

But in general, this is not true of operators, they don’t all commute,

$$x \frac{d}{dx} \psi \neq \frac{d}{dx} (x\psi)$$

In general

$$\begin{aligned} \hat{A}\hat{B}\psi &\neq \hat{B}\hat{A}\psi \\ (\hat{A}\hat{B} - \hat{B}\hat{A})\psi &\neq 0 \end{aligned}$$

$(\hat{A}\hat{B} - \hat{B}\hat{A})$ is called the commutator of operators A and B and is rewritten as $[\hat{A}, \hat{B}] \psi \neq 0$. For the general situation, with wave-function ψ , $[\hat{A}, \hat{B}] \neq 0$. \hat{A} and \hat{B} do not commute. For most pairs of operators this is true.

10.1 Simultaneous Eigenfunctions

\hat{A} and \hat{B} are said to share a complete set of simultaneous eigenfunctions if,

$$\begin{aligned}\hat{A}\psi_i &= a_i\psi_i \\ \hat{B}\psi_i &= b_i\psi_i\end{aligned}$$

for all $i = 1, 2, 3 \dots n$. Operators that have this property, that share simultaneous eigenfunctions, do commute,

$$\begin{aligned}[\hat{A}, \hat{B}] &= 0 \\ (\hat{A}\hat{B} - \hat{B}\hat{A})\psi_i &= [\hat{A}, \hat{B}]\psi_i \\ &= \hat{A}b_i\psi_i - \hat{B}a_i\psi_i \\ &= 0\end{aligned}$$

since numbers commute. This is true for the general function $\phi = \sum_{i=1}^n C_i\psi_i$

$$[\hat{A}, \hat{B}]\phi = \sum_{i=1}^n C_i [\hat{A}, \hat{B}]\psi_i = 0 \Rightarrow [\hat{A}, \hat{B}] = 0$$

Therefore \hat{A} and \hat{B} commute. The converse argument is also true, any two operators that commute also share simultaneous eigenfunction. This can be proved.

This result has a consequence in terms of measuring the observables. The initial state

$$\phi = \sum_{i=1}^n C_i\psi_i$$

Measuring the observable A gives a result, a_j , with the probability $|C_j|^2$. This causes the state to collapse to ψ_j . now take a second measurement of the observable B . This now has the definite value b_j , with a probability of 1 because ψ_j is an eigenfunction of B . This second measurement will have no effect on the wave-function ψ_j and the state is left unchanged for the second measurement. So if \hat{A} and \hat{B} commute, then \hat{A} and \hat{B} share a complete set of eigenfunctions and the precise values of the observables a and b can be known precisely at the same time.

Consider the case where \hat{A} and \hat{B} do not commute, e.g.

$$\begin{aligned}[\hat{x}, \hat{P}]\psi &= \left[x, -i\hbar \frac{\partial}{\partial x}\right]\psi \\ &= i\hbar \left(x \frac{\partial}{\partial x}\psi - \frac{\partial}{\partial x}(x\psi)\right) \\ &= i\hbar \left(x \frac{\partial}{\partial x}\psi - x \frac{\partial}{\partial x}\psi - \psi\right) \\ &= i\hbar\psi \neq 0\end{aligned}$$

This result is true for any function, so $[\hat{x}, \hat{P}] = i\hbar \neq 0$ and so \hat{x} and \hat{P} do not commute. So \hat{x} and \hat{P} do not share a complete set of eigenfunctions so we cannot know the value of x and p precisely at the same time. This leads to an uncertainty product relationship..

10.1.1 Root Mean Squared

Define the statistical root mean squared of the uncertainty on the observable A ,

$$\begin{aligned}(\Delta A)^2 &= \langle (A - \langle A \rangle)^2 \rangle \\ &= \langle A^2 \rangle - \langle A \rangle^2\end{aligned}$$

It can be shown that

$$(\Delta A)^2(\Delta B)^2 \geq \frac{1}{4} \left| \langle [\hat{A}, \hat{B}] \rangle \right|^2$$

e.g.

$$\begin{aligned}(\Delta x)^2(\Delta p)^2 &= \frac{1}{4} |i\hbar|^2 = \frac{\hbar^2}{4} \\ \Delta x \Delta p &= \frac{\hbar}{2}\end{aligned}$$

This is the Heisenberg Uncertainty Principle. It is generally true that for any two pairs of operators that do not commute, there exists an uncertainty product, e.g.

$$\begin{aligned}[\hat{E}, \hat{t}] \psi &= \left[i\hbar \frac{\partial}{\partial t}, t \right] \psi = i\hbar \psi \\ \Delta E \Delta t &\geq \frac{\hbar}{2}\end{aligned}$$

This relationship relates to the decay time interval Δt . The uncertainty in the energy released by

$$\Delta E \geq \frac{\hbar}{2\Delta t}$$

Ex

Spectral line width - consider an excited atom which decays and emits a gamma photon γ with energy E . The lifetime, τ , is related to

$$N(t) = N(0)e^{-\frac{t}{\tau}}$$

Let $\Delta t = \tau$, then $\Delta E \geq \frac{\hbar}{2\tau}$. If $\tau = 10^{-7}$ s, then $\Delta E \geq \frac{\hbar}{2 \times 10^{-7}} \approx 3 \times 10^{-9}$ eV

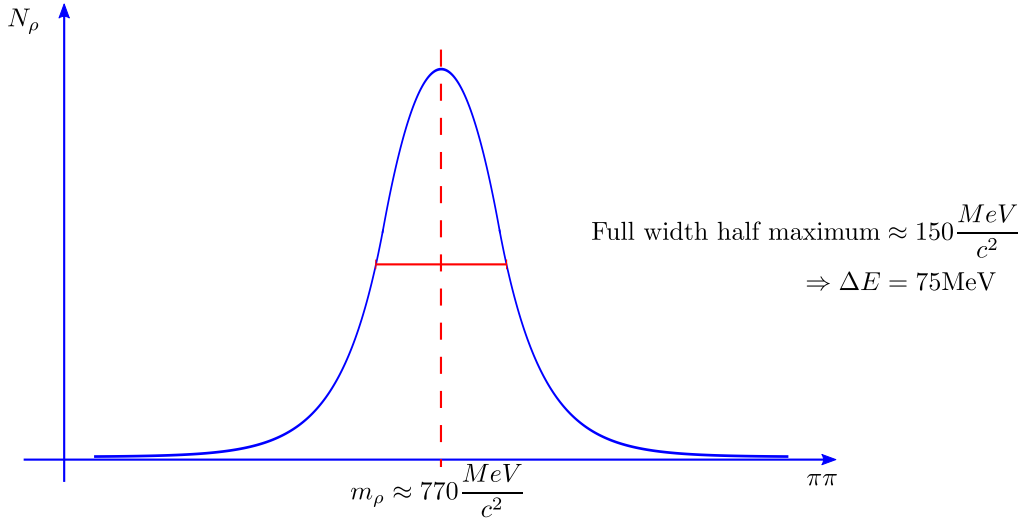
This gives us the intrinsic quantum limit to the resolution on the line width, $\frac{\Delta E}{E}$. The practice experimental limit is usually much greater than this but this gives the absolute minimum resolution for a perfect experiment.

Ex

Particle decay width - rho meson

$$\rho \rightarrow \pi + \pi$$

(fast decay governed by the strong force)> The ρ mass can be reconstructed from the energy of the two pions, this gives the invariant mass of the rho meson.



$$\begin{aligned}
 \Delta E &= 75 MeV/c^2 \\
 \Rightarrow \Delta t \Delta E &\geq \frac{\hbar}{2} \\
 \Rightarrow \tau_\rho &= \Delta t \approx \frac{\hbar}{2\Delta E} \approx 4 \times 10^{-24} s
 \end{aligned}$$

This is the same order of magnitude as the time taken for light to travel a distance equal to the radius of the rho meson.

Part V

3-Dimensional Quantum Mechanics

11 Some Obvious Generalizations

So far we have considered only the one dimensional simplification of the Schrödinger Equation. In three dimensions, $\underline{r} = (x, y, z)$ or (r, θ, ϕ) . This leads to some emergence of new quantum phenomena.

11.1 Operators

11.1.1 Momentum Operator

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}, \hat{p}_y = -i\hbar \frac{\partial}{\partial y}, \hat{p}_z = -i\hbar \frac{\partial}{\partial z}$$

Define $\underline{\hat{P}} = (\hat{P}_x, \hat{P}_y, \hat{P}_z) = -i\hbar \underline{\nabla}$

11.1.2 Kinetic Energy Operator

$$\frac{\hat{P}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2$$

Hence in three dimensional the SE becomes

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

This is the full time dependent case where V and Ψ are functions of (x, y, z, t) . If $V = V(\underline{r})$, independent of t , the the three dimensional TISE becomes

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\underline{r}) + V(\underline{r})\psi(\underline{r}) = E\psi(\underline{r})$$

with $\Psi(\underline{r}, t) = \psi(\underline{r})e^{-\frac{iEt}{\hbar}}$

11.1.3 Momentum Eigenfunctions

$$\hat{P}_y e^{ik_y y} = \hbar k_y e^{ik_y y}$$

In three dimensions, momentum eigenfunction is the product of the three one dimensional forms,

$$\begin{aligned} p &= A e^{ik_x x} e^{ik_y y} e^{ik_z z} \\ &= A e^{i(k_x x + k_y y + k_z z)} \\ &= A e^{i(\underline{k} \cdot \underline{r})} \end{aligned}$$

where $\underline{k} = (k_x, k_y, k_z)$ which is called the wave vector and is the equivalent of the wave number from one dimension.

$$\hat{P} e^{i\underline{k} \cdot \underline{r}} = \hbar \underline{k} e^{i\underline{k} \cdot \underline{r}}$$

So the eigenvalue is $\underline{P} = \hbar \underline{k}$, which is itself a vector.

11.2 Uncertainty Relationships in 3D

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

This applies in each dimension separately,

$$\begin{aligned} [\hat{y}, \hat{P}_y] &= i\hbar, & [\hat{z}, \hat{P}_z] &= i\hbar \\ \Delta y \Delta p_y &\geq \frac{\hbar}{2}, & \Delta z \Delta p_z &\geq \frac{\hbar}{2} \end{aligned}$$

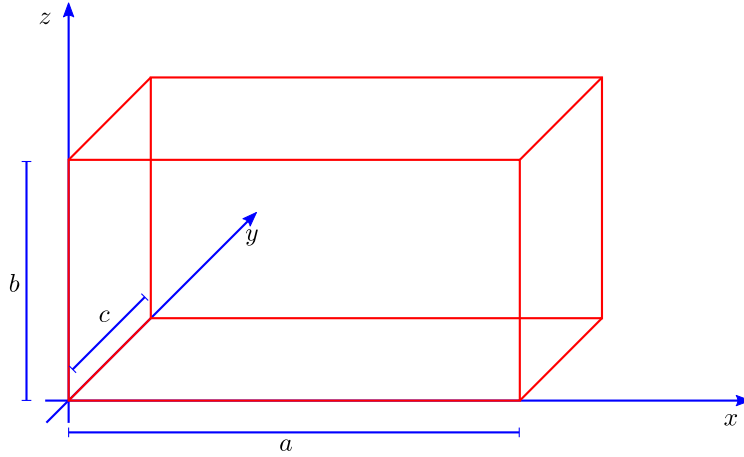
But now there is the possibility of interaction across dimensions. These same patters do not hold across dimensions, and so there is no uncertainty product,

$$\begin{aligned} [\hat{x}, \hat{P}_y] &= 0 \\ [\hat{z}, \hat{P}_x] &= 0 \\ &\vdots \end{aligned}$$

So we can know the position and momentum along perpendicular directions at the same time, just not parallel directions.

12 3D Infinite Square Potential Well - Particle in a Box

Consider a particle confined to a three dimensional right rectangular box,



$$V(\underline{r}) = \begin{cases} 0 & \begin{cases} 0 \leq x \leq a \\ 0 \leq y \leq b \\ 0 \leq z \leq c \end{cases} \\ \infty & \text{outside the box} \end{cases}$$

Outside the box, $V = \infty \rightarrow \psi(\underline{r}) = 0$ everywhere

Inside the box, $\psi(\underline{r})$ is a solution of 3D TISE,

$$\begin{aligned} -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) &= E\psi \\ -\frac{\hbar^2}{2m} \nabla^2 &= E\psi \end{aligned}$$

Solve using SEPARATION OF VARIABLES. Try solution of the form

$$\psi(x, y, z) = X(x)Y(y)Z(z)$$

Substitute this guess into TISE, so that the partial differential equation becomes three ordinary differential equations,

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2 X}{dx^2} &= E_x X & 0 \leq x \leq a \\ -\frac{\hbar^2}{2m} \frac{d^2 Y}{dy^2} &= E_y Y & 0 \leq y \leq b \\ -\frac{\hbar^2}{2m} \frac{d^2 Z}{dz^2} &= E_z Z & 0 \leq z \leq c \end{aligned}$$

where $E = E_x + E_y + E_z$. Each of these is the same as for the one dimensional well, so the solutions are known. Apply boundary conditions, which gives the solutions,

$$\begin{aligned} X(x) &= A_x \sin\left(\frac{n_x \pi x}{a}\right) & (n_x = 1, 2, 3 \dots) & E_x = \frac{n_x^2 \pi^2 \hbar^2}{2ma^2} \\ Y(y) &= A_y \sin\left(\frac{n_y \pi y}{b}\right) & (n_y = 1, 2, 3 \dots) & E_y = \frac{n_y^2 \pi^2 \hbar^2}{2mb^2} \\ Z(z) &= A_z \sin\left(\frac{n_z \pi z}{c}\right) & (n_z = 1, 2, 3 \dots) & E_z = \frac{n_z^2 \pi^2 \hbar^2}{2mc^2} \end{aligned}$$

Therefore the 3D solution is given by,

$$\psi = XYZ = A \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

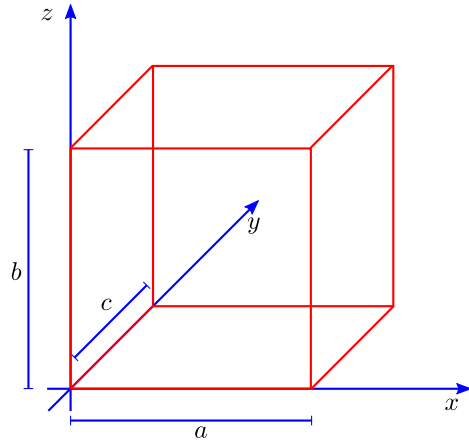
with

$$E = E_x + E_y + E_z = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

12.1 Regular Cube

Consider the symmetric box (cube) with $a = b = c$, then

$$E = \frac{\pi^2 \hbar^2}{2ma^2} (n_x^2 + n_y^2 + n_z^2)$$



$$V(\underline{r}) = \begin{cases} 0 & \begin{cases} 0 \leq x \leq a \\ 0 \leq y \leq b \\ 0 \leq z \leq c \end{cases} \\ \infty & \text{outside the box} \end{cases}$$

13 Energy Degeneration

Use the particle in a symmetrical cube as an example. Different combinations of n_x, n_y, n_z can give the same value for the energy eigenvalue of the particle. This is called the degeneracy, when there is more than one distinct eigenfunctions that share the same numerical eigenvalue.

Energy Level	n_x	n_y	n_z	E (in units of $\frac{\pi^2 \hbar^2}{2ma^2}$)	Degeneracy Value
Ground State	1	1	1	3	1
1st Excited state	2	1	1	6	3
	1	2	1	6	
	1	1	2	6	
2nd Excited State	2	2	1	9	3
	2	1	2	9	
	1	2	2	9	

This effect of degeneracy emerges when there is any form of symmetry in the potential function of the system. Similarly, whenever energy degeneracy is seen, there must be symmetry present in the potential function. Degeneracy is closely related to the modeling of physical systems, such as the hydrogen atoms.

14 Angular Momentum

This is another case of new phenomena that emerges when the higher dimensions are included, it cannot exist in 1D or 2D, it is an intrinsically 3D property. Classically,

$$\underline{L} = \underline{r} \times \underline{p} \quad \begin{cases} \underline{L}_x = yp_z - zp_y \\ \underline{L}_y = zp_x - xp_z \\ \underline{L}_z = xp_y - yp_x \end{cases}$$

So the quantum mechanical operator is a combination of the position and linear momentum operators,

$$\begin{aligned} \hat{L}_x &= -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \\ \hat{L}_y &= -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \\ \hat{L}_z &= -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \end{aligned}$$

There also exists an operator for the (angular momentum)²,

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

So there are 4 quantum mechanical operators for the angular momentum of a particle in three dimensions. This starts from the premise that the position and the momentum are both known well, so that they can be combined to form the angular momentum. however this is expressly forbidden in quantum mechanics, due to the uncertainty product that relates them $\Delta x \Delta p \geq \frac{\hbar}{2}$. Look at the operators and their commutation,

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &= \hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x \\ &= -\hbar^2 \left[\left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) - \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \right] \\ &= -\hbar^2 \left(y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right) \\ &= -\hbar^2 \hat{L}_z \end{aligned}$$

So

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &= -\hbar^2 \hat{L}_z \\ [\hat{L}_y, \hat{L}_z] &= -\hbar^2 \hat{L}_x \\ [\hat{L}_z, \hat{L}_x] &= -\hbar^2 \hat{L}_y \end{aligned}$$

So in general, the angular momentum operators do not commute, so we can know the precise value of only one component of \underline{L} . We cannot know $\underline{L} = (L_x, L_y, L_z)$ fully.

Analyze (angular momentum)² operator.

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

Since any operator always commutes with itself,

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

Use commutator identity mentioned previously,

$$\begin{aligned} [\hat{A}\hat{B}, \hat{C}] &= \hat{A} [\hat{B}, \hat{C}] + [\hat{A}, \hat{C}] \hat{B} \\ \Rightarrow [\hat{L}_x^2, \hat{L}_z] &= \hat{L}_x [\hat{L}_x, \hat{L}_z] + [\hat{L}_x, \hat{L}_z] \hat{L}_x \\ &= \hat{L}_x (-i\hbar \hat{L}_y) + (-i\hbar \hat{L}_y) \hat{L}_x \\ &= -i\hbar (\hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x) \end{aligned}$$

Similarly

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

So

$$[\hat{L}^2, \hat{L}_z] = 0 + 0 = 0$$

Similarly

$$[\hat{L}^2, \hat{L}_z] = [\hat{L}^2, \hat{L}_y] = 0$$

So the (angular momentum)² commutes with all three components of the angular momentum separately. Therefore we can know the precise value of the (angular momentum)² AND one component only of angular momentum simultaneously. By convention, we chose to know the z component, along with \hat{L}^2 . In other words, we can know the magnitude of the angular momentum, $|\underline{L}| = \sqrt{L^2}$, but not the direction of this magnitude.

15 Quantum Mechanics in Spherical Polar Co-ordinates

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$$\begin{aligned} x &= r \sin(\theta) \cos(\phi) \\ y &= r \sin(\theta) \sin(\phi) \\ z &= r \cos(\theta) \end{aligned}$$

θ is called the polar angle and ϕ is the azimuthal angle. Using these, the equations for the angular momentum can be rewritten,

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

The rotation about the z-axis is independent of θ so the z-component is simple.

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} \right]$$

15.1 Eigenfunctions of $\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$

These have the form,

$$\begin{aligned}\Phi_m &= Ae^{im\phi} \\ L_z \hat{\Phi}_m &= -i\hbar \frac{\partial}{\partial \phi} (Ae^{im\phi}) = m\hbar \Phi_m\end{aligned}$$

Φ_m is an eigenfunction L_z with an eigenvalue $m\hbar$. The angle ϕ has a periodicity of 2π . This leads to quantization and normalization conditions. The period $= 2\pi$ but $\phi + 2\pi = \phi$. So

$$\begin{aligned}\Phi(\phi + 2\pi) &= \Phi(\phi) \\ Ae^{im\phi} &= Ae^{im(\phi + 2\pi)} \\ \Rightarrow e^{2\pi im} &= 1 \\ \cos(2m\pi) + i\sin(2m\pi) &= 1 \quad \therefore m \in \mathbb{Z}, -\infty < m < \infty\end{aligned}$$

This is the boundary condition. The normalization condition is derived from,

$$\begin{aligned}\int_0^{2\pi} \Phi_m^2 d\phi &= 1 \\ \int_0^{2\pi} A^2 d\phi &= 1 \\ A &= \frac{1}{\sqrt{2\pi}}\end{aligned}$$

So the eigenfunctions of \hat{L}_z are

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

where $m \in \mathbb{Z}$ with eigenfunctions $L_z = m\hbar$. As m can only take integer values, the value of the eigenvalues L_z are quantized in units of \hbar .

15.2 Eigenvalues of (Angular Momentum)²

Can show that L^2 eigenvalues have the form,

$$L^2 = l(l+1)\hbar^2$$

where l is the quantum number, $l \in \mathbb{Z} \geq 0$. The quantum number l and m are related, so write m as m_l . Logically, then,

$$L_z^2 \leq L^2$$

So

$$(m_l \hbar)^2 \leq l(l+1)\hbar^2$$

But both l and m are required to be integers, so the maximum value of $|m_l|$ is $|m_l| = l$ (because the next integer value $m_l = l+1 \rightarrow m_l^2 = (l+1)^2 > l(l+1)$ which doesn't satisfy the condition so must be incorrect). So the condition becomes

$$|m_l| \leq l$$

ie $m_l = -l, (-l+1), \dots, 0, \dots, (l-1), l$. Note that $|m_l| \leq l$ implies that

$$\begin{aligned}L_z^2 &< L^2 \\ L_z^2 &\neq L^2 \text{ (unless } l = 0\text{)}\end{aligned}$$

So the angular momentum cannot be aligned directly along the z-axis. This is because of the uncertainty product in angular momentum, as in this case, all of the information about the angular momentum would be known as, $L_x = L_y = 0$.

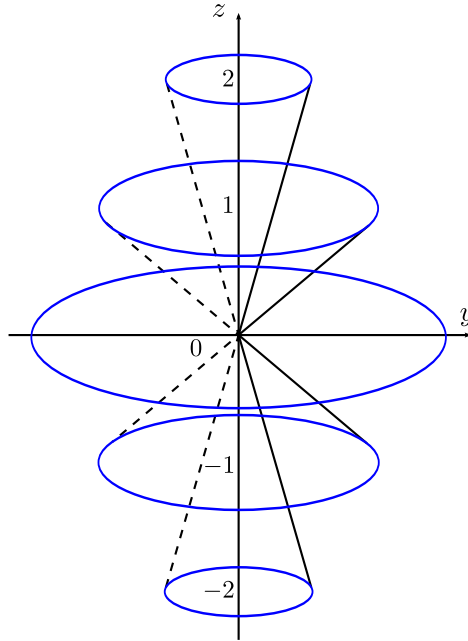
15.3 Visualization

Ex

Let $l = 2$, so $L^2 = 2(2+1)\hbar^2 = 6\hbar^2$ and $|L| = \sqrt{6}\hbar$. Also

$$\begin{aligned} m_l &= -2, -1, 0, 1, 2 \\ L_z &= -2\hbar, -\hbar, 0, \hbar, 2\hbar \end{aligned}$$

The length of the vector can then be known, but the location around the contour cannot be known.



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15.3.1 Reduced Mass

A hydrogen atom has electrons, with mass m , and a very heavy nucleus (proton) with mass M with a separation r which are both orbiting a common center of mass. Kinematically this is the same as an electron of reduced mass μ orbiting a fixed nucleus (mass ∞) at the same distance r , where

$$\mu = \frac{mM}{m+M}$$

This is the same as the classical situation.

15.4 Single Electron Atoms

Coulomb potential causes an attraction between the electron and the nucleus,

$$V(r) = \frac{q_1 q_2}{4\pi\epsilon_0 r} \quad F(r) = \frac{q_1 q_2}{4\pi\epsilon_0 r^2}$$

where $q_1 = Ze$ (Z is the atomic number, 1 for hydrogen) and $q_2 = -e$. This coulomb potential is an example of a radial or central potential as it depends only on the separation,

$$V(r) = V(r)$$

so it is independent of θ and ϕ .

TISE for an electron on an atom, therefore, is

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}\right)\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

For the specific hydrogen atom case, Z would equal 1. The Laplacian operator in spherical polar co-ordinates is given by

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2(\theta)} \frac{\partial^2}{\partial \phi^2}$$

Though this equation for ∇^2 is more complicated than for Cartesian co-ordinates, this form allows the equation to be solved by separation of variables. Something that is not possible when in Cartesian. Using this method, the result is that eigenfunctions are found with the form

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

which is composed of a radial part and an angular part. The solution of TISE also gives values for the energy eigenvalues. These are a set of distinct energy eigenvalues of the form

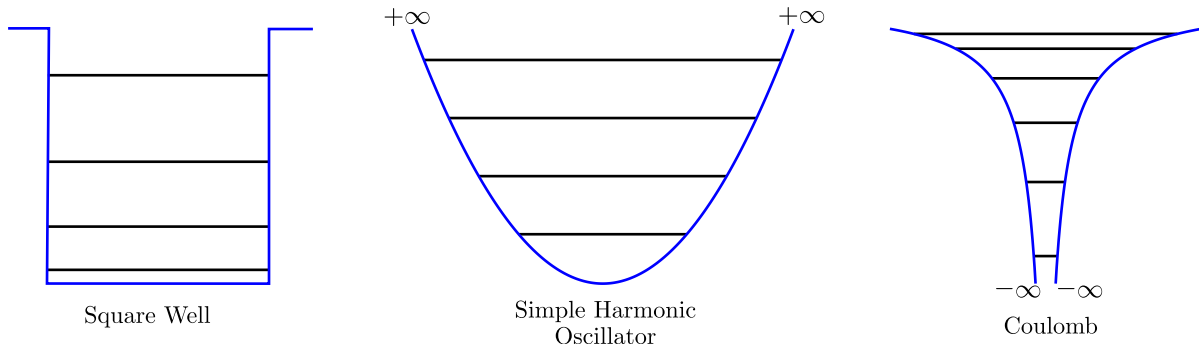
$$\begin{aligned} E_n &= \frac{-\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} \\ E_n &\propto -\frac{1}{n^2} \quad n \in \mathbb{Z} \end{aligned}$$

So the electron is bound to the nucleus with discrete quantized energy levels $E_n \propto -\frac{1}{n^2}$. For $Z = 1$ (hydrogen atom),

$$E_n = \frac{-13.6\text{eV}}{n^2}$$

The value of E_n is negative because the potential is defined to be $V = 0$ at $r = \infty$, so any value of r less than ∞ will produce a value of potential that is less than 0. There exists an infinite number of bound states but the energy separation tends to zero as $r \rightarrow \infty$. $E = 13.6\text{eV}$ is the ionization energy for the electron in the ground state of the hydrogen atom.

15.4.1 Comparison of 3 Infinite Potential Wells



1D	Square Well	$V \propto r^0$	$E \propto n^2$	$n = 1, 2, 3, \dots$
1D	SHO	$V \propto r^2$	$E \propto (n + \frac{1}{2})$	$n = 0, 1, 2, \dots$
3D	Coulomb	$V \propto r^{-1}$	$E \propto -\frac{1}{n^2}$	$n = 1, 2, 3, \dots$

Part VI

Single Electron Wave-functions

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16 Atomic Quantum Numbers and Polar Co-ordinates

The most important quantum number is the one used here, called n , the principle quantum number (sometimes also called the radial quantum number or the shell quantum number). n alone determines the energy level $E_n \propto -\frac{1}{n^2}$. All eigenstates of the electron within the atom with the same n quantum number have the same value. This is because of the energy degeneracy, and arises due to the very symmetrical system in which the electrons are confined, ie a spherical potential, $V(r)$. The radius (or $\langle r \rangle$) of the atom increases along with the energy as the n value increases. The solution of TISE also restricts the angular momentum quantum number such that

$$l < n \quad (l \neq n)$$

so

$$0 \leq l < n$$

So for the three atomic quantum numbers, n, l, m are all integers

- $n > 0$, determines the energy $E_n \propto -\frac{1}{n^2}$ and the radius
- $0 \leq l < n$, determines the magnitude of the orbital angular momentum $|L| = \sqrt{l(l+1)}\hbar$
- $-l \leq m_l \leq l$, determines the component of the orbital angular momentum about the z-axis $L_z = m_l \hbar$

Set n, l, m_l as the labels for the electron eigenstates in the atom.

$$\psi(r, \theta, \phi) = R_{n,l}(r)Y_{l,m}(\theta, \phi)$$

$R_{n,l}(r)$ is the radial component that depends on the principle quantum number, n , and the angular momentum quantum number, l , and is a function only of the radial distance.

$Y_{l,m}(\theta, \phi)$ is the angular component that depends on the angular momentum quantum number and the m number and is a function of the angles θ and ϕ .

16.1 Radial Wave-function

This depends on the quantum numbers n and l .

$$R_{n,l}(r) = e^{-\frac{Zr}{na_0}} \left(\frac{Zr}{a_0}\right)^l G_{n,l}\left(\frac{Zr}{a_0}\right)$$

where

- $a_0 = \frac{4\pi\epsilon_0\hbar}{\mu e^2} \approx 0.529 \times 10^{-10}\text{m} \approx \frac{\text{\AA}}{2}$ this is referred to as the Bohr radius, and is the “radius” of a ground state hydrogen atom.

- $G_{n,l}\left(\frac{Zr}{a_0}\right)$ is a polynomial function of the order $n - (l + 1)$
- $e^{-\frac{Zr}{na_0}}$ tends to zero as r increases to infinity since n is on the denominator of the exponential. This means as the energy levels increase, ie n increases, the average radius increases as the exponential penetrates further into the potential wall.

The first few unnormalized states are given by,

$$\begin{aligned}R_{1,0} &\propto e^{-\frac{Zr}{a_0}} \\R_{2,0} &\propto \left(1 - \frac{Zr}{2a_0}\right) e^{-\frac{Zr}{2a_0}} \\R_{2,1} &\propto \frac{Zr}{a_0} e^{-\frac{Zr}{2a_0}}\end{aligned}$$

Hence we can evaluate the radial probability density functions,

$$P(r)dr = |R_{nl}|^2 \times 4\pi r^2 dr$$

The final term comes from the area of the sphere,

$$\int_0^{2\pi} r d\phi \int_0^\pi r \sin \theta d\theta dr$$

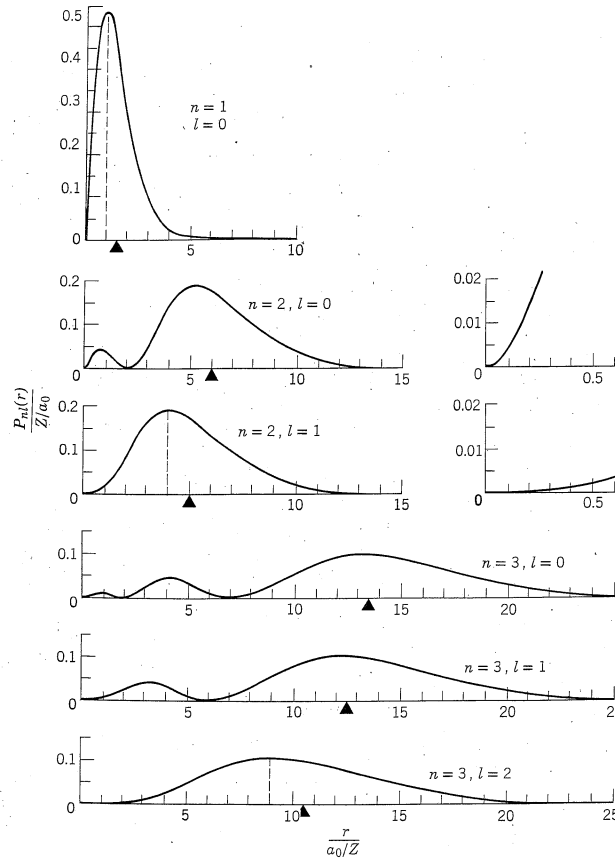


Figure 7-5 The radial probability density for the electron in a one-electron atom for $n = 1, 2, 3$ and the values of l shown. The triangle on each abscissa indicates the value of \bar{r}_{nl} as given by (7-29). For $n = 2$ the plots are redrawn with abscissa and ordinate scales expanded by a factor of 10 to show the behavior of $P_{nl}(r)$ near the origin. Note that in the three cases for which $l = l_{\max} = n - 1$ the maximum of $P_{nl}(r)$ occurs at $r_{\text{Bohr}} = n^2 a_0 / Z$, which is indicated by the location of the dashed line.

- The average radius increases for higher values of n . The ground state ($n = 1$) peaks at $r = a_0$ (Bohr radius) and then the excited states with $l = n - 1$ peak at $r = n^2 a_0$.
- $P(r = 0) = 0$ due to the $4\pi r^2$ factor, but only for $l = 0$ does $R_{nl}(r = 0) \neq 0$.
- The exponential factor tends to zero as the radius increases to infinity as the wave-function penetrates into the wall of the potential barrier.
- The number of nodes in the probability above $r = 0$ is $n - (l + 1)$

These characteristics determine much of the chemistry of the atom as they control the location of the electrons in this single electron atom.

16.2 Angular Wave-function

$$Y_{l,m}(\theta, \phi) = (\text{polynomial in } \sin \theta \text{ or } \cos \theta) \times e^{im\phi}$$

These go by the name “spherical harmonic” functions and are eigenfunctions of the \hat{L}^2 operator. The angular probability density depends only on θ since $|e^{im\phi}|^2 = 1$.

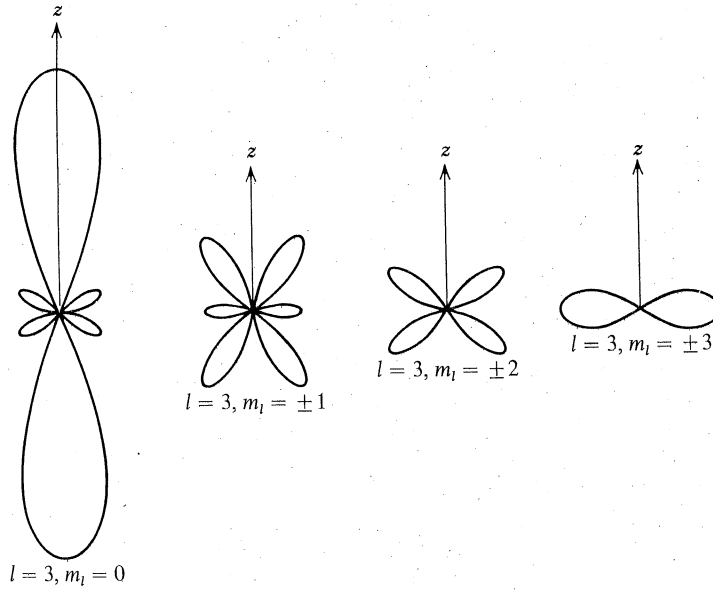
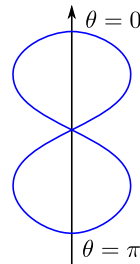


Figure 7-8 Polar diagrams of the directional dependence of the one-electron atom probability densities for $l = 3$; $m_l = 0, \pm 1, \pm 2, \pm 3$.

EX

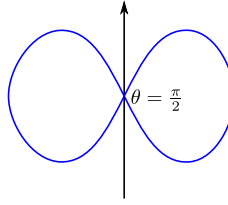
1. $l = 0, m_l = 0 \Rightarrow Y_{0,0}(\theta, \phi) = 1$ is a spherical symmetry without dependence on the angle.
2. $l = 1, m_l = 0 \Rightarrow Y_{1,0}(\theta, \phi) = \cos(\theta)e^{i\theta \times 0} = \cos(\theta)$

Probability peaks along the z-axis $\theta = 0, \theta = \pi$ because $L_z = 0$. (L_z is angular momentum about the z-axis)



3. $l = 1, m_l = \pm 1 \Rightarrow Y_{1,\pm 1}(\theta, \phi) = \sin(\theta)e^{\pm i\theta}$

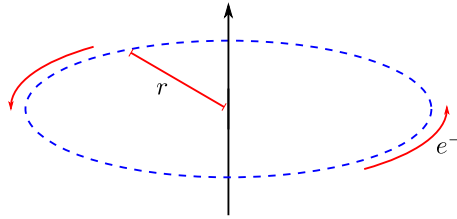
Probability peaks at $\theta = \frac{\pi}{2}$ since $|L_z| = \hbar$



The time independent Schrödinger equation predicts energy and angular momentum properties of an atomic electron. The energies are measured with spectroscopy techniques, the results of which agree closely with the predictions made by quantum mechanical calculations.

17 Magnetic Dipole Moment

An arbitrary electric charge is equivalent to a current loop. This generates a magnetic dipole moment, μ .



$$\begin{aligned}\mu &= \text{current} \times \text{area} \\ &= \frac{-e}{\left(\frac{2\pi r}{v}\right)} \times \pi r^2 \\ &= \frac{-ver}{2}\end{aligned}$$

Also, the angular momentum,

$$\begin{aligned}\underline{L} &= \underline{r} \times \underline{p} \\ |\underline{L}| &= rmv \\ \Rightarrow \mu &= -\frac{eL}{2m}\end{aligned}$$

This is for, for example, an electron orbiting around a nucleus. Rewrite this as,

$$\underline{\mu_l} = -\frac{g_l \mu_B}{\hbar} \underline{L}$$

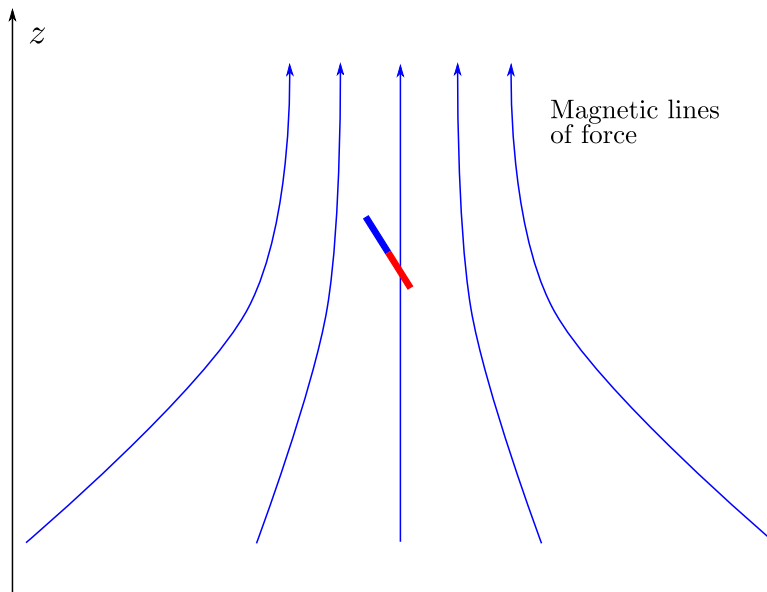
where l denotes the orbital angular momentum, $\mu_B = \frac{e\hbar}{2m} = 0.927 \times 10^{-23} \text{ Am}^2$ (this is the Bohr magneton and is the typical unit used for the magnetic dipole moment of an atom), $g_l = 1$ (this is the orbital g factor for consistency with equation later on).

This was a purely classical electromagnetic argument, but the quantum mechanical analysis gives the same equation. In quantum mechanics, we can know the precise values of the magnitude and the z

component of the dipole moment.

$$\begin{aligned}
 \text{Magnitude} \quad |\mu_l| &= \frac{g_l \mu_B}{\hbar} \sqrt{l(l+1)} \hbar \\
 &= g_l \mu_B \sqrt{l(l+1)} \\
 z \text{ component} \quad (\mu_l)_z &= -\frac{g_l \mu_B}{\hbar} m_l \hbar \\
 &= -g_l \mu_B m_l
 \end{aligned}$$

To measure the magnetic dipole, a non-uniform magnetic field is needed.



If the field lines were uniform, the force felt by the north and south poles would be equal and opposite and so a torque would exist about the center of the bar magnet, but there would exist no linear translation. Since the field is non-uniform, the north pole feels a greater force than the south pole.

$$\begin{aligned}
 \text{Potential energy} \quad V &= -\mu B \\
 &= g_l \mu_B m_l B
 \end{aligned}$$

If B_z varies along the z axis, then

$$F_z = -\frac{\partial V}{\partial z} = -g_l \mu_B m_l \frac{\partial B_z}{\partial z}$$

This then gives a means to measure m_l and hence get L_z of the electron.

17.1 Stern-Gerlach Experiment (1922)

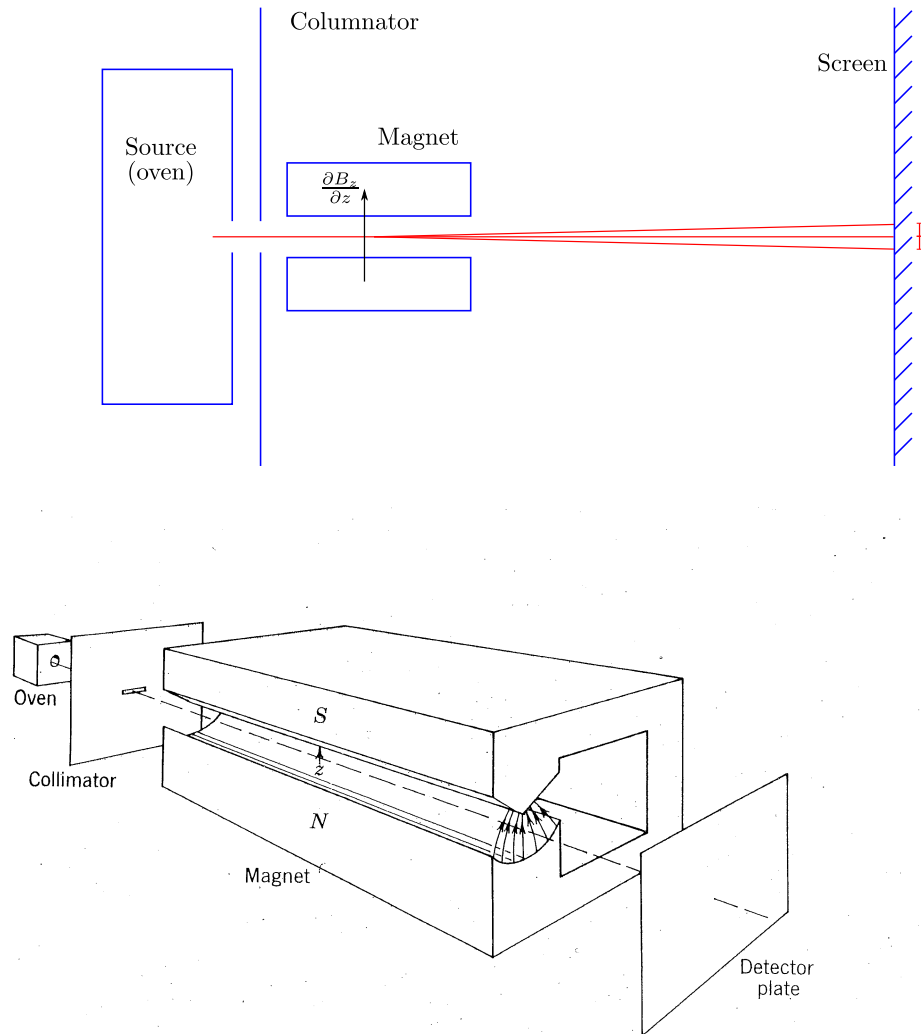


Figure 8-5 The Stern-Gerlach apparatus. The field between the two magnet pole pieces is indicated by the field lines drawn at the near end of the magnet. The field intensity increases most rapidly in the positive z direction (upward).

Predicted Results

For classical (unquantified) system, the angular momentum would be expected to be continuous with a range of L_z values,

$$-L \leq L_z \leq L$$

This would give a range of all possible results when measured, so a stripe would be seen on the screen. For the quantized quantum mechanical system, there are only certain discrete values of L_z , e.g. if $L = 1$, then $L_z = -\hbar, 0, \hbar$ so there would exist only three different spots on the screen from these

possible values of the angular momentum. Generally there are $2l + 1$ values of m_l so the expected number of spots to be seen would be $2l + 1$. Since l is an integer, and odd number of spots should be seen.

Measured Results

Consider the simplest case of a hydrogen atom in its ground state energy level, so $n = 1$, $l = 0$, $m_l = 0$, $L_z = 0$. Expected results would be $\mu_z = 0$ so no deflections and only one spot. But this is not what was measured. The result observed was *two* spots with an equal deflection in the positive and negative directions corresponding to $\mu_z = \pm\mu_B$.

17.2 Conclusion

Angular momentum *is* quantized so no stripe is observed, but Schrödinger equation does not correctly predict μ_z .

17.3 Spin

The explanation of this observed effect is that the electron has an intrinsic angular momentum, called spin. This has similar quantum mechanical properties to the orbital angular momentum. This is impossible to visualize as the electron is believed to have no physically dimensional extent so cannot have a property related to rotation, However it is a property that all electrons possess.

In quantum mechanics we can know,

$$\begin{array}{ll} \text{Magnitude} & |\underline{S}| = \sqrt{S(S+1)}\hbar \\ z\text{-component} & S_z = m_s\hbar \end{array}$$

where $|m_s| \leq S$ and is quantized in steps of 1. This leads to the spin magnetic dipole moment,

$$(\mu_s)_z = -g_s\mu m_s$$

This leads to the conclusion that, because there are only two spots and so there must be two possible values of the spin with an integer step between them, that $m_s = \pm\frac{1}{2}$ and so $S_z = \pm\frac{1}{2}\hbar$. This leads to the zero possibility of an electron ever having zero spin. These two states are often called spin up and spin down, and are the only spin states for a half spin particle.

Also, to get the observed deflection, $g_s = 2 = 2g_l$. This spin property is not predicted by the Schrödinger equation but is compatible with it. However it is predicted from relativistic quantum mechanics via the Dirac equation. This form *requires* two components of the electron wave function relating to the spin up and spin down states. It also *requires* that $g_s = 2$ (as predicted from the Stern-Gerlach experiment). Finally, it also includes two further components of the wave-function that relate to the equivalent two spin possibilities of the positron (anti-electron) which has the same $\frac{1}{2}$ spin characteristics as the electron.

18 Total Angular Momentum

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An atomic electron has both intrinsic (spin) and orbital angular momentum. These can be combined into the total angular momentum,

$$\underline{J} = \underline{S} + \underline{L}$$

Associated with this property, there are similar total angular momentum operators, $\hat{J}_x, \hat{J}_y, \hat{J}_z, \hat{J}^2$ and quantum numbers j and m_j .

$$\begin{array}{ll} \text{Magnitude} & |\underline{J}| = \sqrt{j(j+1)}\hbar \\ z\text{-component} & J_z = m_j\hbar \end{array}$$

where $-j \leq m_j \leq j$ with quantization into unit steps. The z -components are scalars, so $J_z = L_z + S_z$ and so $m_j = m_l + m_s$.

For the $s = \frac{1}{2}$ case, the vector addition is simple as there are only two possible values of j ,

$$\begin{array}{ll} \text{Either} & j = l + s \quad (\underline{L}, \underline{S} \text{ are parallel}) \\ \text{Or} & j = l - s \quad (\underline{L}, \underline{S} \text{ are anti-parallel}) \end{array}$$

So

$$j = l \pm \frac{1}{2}$$

(if $l = 0$ then only $j = \frac{1}{2}$ is possible as $j > 0$)

Ex

Electron in one of the $l = 1$ atomic states.

$$\begin{array}{ll} \text{So when } s = +\frac{1}{2} & j = 1 + \frac{1}{2} = \frac{3}{2} \\ & |\underline{J}| = \sqrt{\frac{3}{2} \times \frac{5}{2}}\hbar = \frac{\sqrt{15}}{2}\hbar \\ & m_j = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2} \end{array} \quad \begin{array}{ll} \text{Or when } s = -\frac{1}{2} & j = 1 - \frac{1}{2} = \frac{1}{2} \\ & |\underline{J}| = \sqrt{\frac{1}{2} \times \frac{3}{2}}\hbar = \frac{\sqrt{3}}{2}\hbar \\ & m_j = -\frac{1}{2}, \frac{1}{2} \end{array}$$

In general, the multiplicity of $m_j = 2j + 1$. Since $m_j = m_l + m_s$, if a value of m_l is already known, some of the values of m_j might be ruled out.

19 Pauli Exclusion Principle

There are two distinct types of quantum particle,

- Bosons
- Fermions

Bosons

Bosons are particles with integer spin, $s = 0, 1, 2, 3 \dots$, $s \in \mathbb{Z}$, e.g. photon, pion, ${}^4\text{He}$ nucleus, W^\pm , Z^0 . Importantly, for bosons, an unlimited number of them can occupy the same quantum state simultaneously. This leads to important phenomena like lasers, super-conductivity, super-fluidity, Bose-Einstein condensates etc.

Fermions

Fermions are half integer spin particles, $s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \dots$, $s \in \frac{\mathbb{Z}}{2}$, e.g. electron, proton, quark, ${}^3\text{He}$ nucleus etc. The Pauli exclusion principle states that no two fermions can occupy the same quantum state simultaneously. Alternatively, no two fermions can share exactly the same set of quantum numbers. This is essential for multi-electron atoms as it means the electrons cannot all occupy the ground state, and so leads to the field of chemistry.

20 Atomic Quantum Numbers

We now need 4 quantum numbers to specify the eigenstate of the electron,

$$n, l, m_l, m_s$$

$m_s = \pm \frac{1}{2}$, gives the z -component of the spin angular momentum.

Alternative set of 4 quantum numbers,

$$n, l, j, m_j$$

j, m_j give the magnitude and z -component of the total angular momentum. The first set is fine for single electron atoms, but this leads to ambiguity when multi-electrons are considered. So the second set is used to reduce ambiguity and simplify definitions.

Part VII

Multi-Electron Atoms

The Pauli Exclusion Principle requires that, when more than one electron is present, they occupy different eigenstates. For the ground state atom, the lowest states are occupied first, that is, the lowest n -value and lowest l -value are filled first. As more eigenstates are filled, the different elements with different chemical properties are formed.

$n = 1$	$l = 0$	$m_l = 0$	$m_s = \pm \frac{1}{2}$	2 states (H, He)
$n = 2$	$l = 0$	$m_l = 0$	$m_s = \pm \frac{1}{2}$	8 states (Li → Na)
	$l = 1$	$m_l = 0, \pm 1$	$m_s = \pm \frac{1}{2}$	
$n = 3$	$l = 0$	$m_l = 0$	$m_s = \pm \frac{1}{2}$	18 states (Na →)
	$l = 1$	$m_l = 0, \pm 1$	$m_s = \pm \frac{1}{2}$	
	$l = 2$	$m_l = 0, \pm 1, \pm 2$	$m_s = \pm \frac{1}{2}$	

The energy levels are disrupted for $n = 3$ due to the effect of the other electrons in the atom and so the higher level energy states do not follow this simple hydrogen atom model.

The even spots observed in the Stern-Gerlach experiment is due to the contribution when there is an odd number of electrons since this case is when there is an unpaired electron.

20.1 Spectroscopic Notation

It is conventional to write the atomic quantum numbers in the form

$$n[l]_j$$

where n and j are numerals, but $[l]$ is a letter code to signify the value of l ,

$l = 0$	s	(strong)
$l = 1$	p	(primary)
$l = 2$	d	(diffuse)
$l = 3$	f	(fine)

e.g.

$$1s_{\frac{1}{2}}, \quad n=1, l=0, j=\frac{1}{2}, \left(m_j = \pm\frac{1}{2}\right)$$

$$2s_{\frac{3}{2}}, \quad n=2, l=1, j=\frac{3}{2}, \left(m_j = \pm\frac{1}{2}, \pm\frac{3}{2}\right)$$

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20.2 Selection Rules for Atomic Transitions

Atomic electrons can transition between one state and another, emitting or absorbing a photon of energy equal to the difference between the energy levels. This is the field of spectroscopy. Only certain transitions are allowed, obeying certain selection rules:

- Δl must be ± 1 AND
- Δj must be 0 or ± 1

These rules arise from the photon properties and conservation laws,

- $\Delta j = 0, \pm 1$ because a photon is a spin $s = 1$ particle, so carries a unit angular momentum, so to conserve angular momentum, the atom must change by one unit. So either $\Delta j = \pm 1$ or $j = 0$ and m_j changes by one unit, eg $m_j = -\frac{1}{2} \leftrightarrow m_j = +\frac{1}{2}$, this is when the spin flips.
- $\Delta l = \pm 1$ comes from the property of parity. The photon has a negative intrinsic parity which must be conserved. So when the photon is emitted or absorbed, the parity of the atom must change. Atomic parity $= (-1)^l$ (from symmetry of angular wave-function, $Y_{l,m}$) So $\Delta l = \pm 1$ changes parity.

Ex

$1s_{\frac{1}{2}} \rightarrow 2p_{\frac{1}{2}}$	$\Delta l = 1, \Delta j = 0$	✓
$1s_{\frac{1}{2}} \rightarrow 2p_{\frac{3}{2}}$	$\Delta l = 1, \Delta j = 1$	✓
$2s_{\frac{1}{2}} \rightarrow 1s_{\frac{1}{2}}$	$\Delta l = 0, \Delta j = 0$	×
$3d_{\frac{5}{2}} \rightarrow 2p_{\frac{3}{2}}$	$\Delta l = -1, \Delta j = -1$	✓

Appendix

A Operators

Momentum

$$\begin{aligned}\hat{p}_x &= -i\hbar \frac{\partial}{\partial x} \\ \hat{\mathbf{p}} &= -i\hbar \underline{\nabla}\end{aligned}$$

Hamiltonian

$$\begin{aligned}\hat{\mathcal{H}}_x &= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \\ \hat{\mathcal{H}} &= -\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z)\end{aligned}$$

Energy

$$\hat{E} = i\hbar \frac{\partial}{\partial t}$$

Angular Momentum

$$\begin{aligned}\hat{L}_x &= -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \\ \hat{L}_y &= -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \\ \hat{L}_z &= -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)\end{aligned}$$

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

Ladder Operator Solution of the Harmonic Oscillator

Solving the Schrödinger equation for the harmonic oscillator potential is straightforward but slightly long-winded. However, it is possible to find the energy eigenvalues without actually solving the differential equation. The method is quite simple, and a nice introduction to more sophisticated approaches to quantum mechanics, so this handout is provided for anyone who is interested. The method described here will not be needed for any assessment in this course though.

We start from the time-independent Schrödinger equation in operator form:

$$\hat{H}\psi = E\psi,$$

where E is the energy eigenvalue and \hat{H} is the hamiltonian:

$$\begin{aligned}\hat{H} &= \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2 \\ &= \left(\frac{\hat{p}^2}{2m\omega} + \frac{1}{2}m\omega x^2 \right) \omega.\end{aligned}$$

We see that this contains 2 quadratic terms. For 2 numbers b and c we could write:

$$b^2 + c^2 = (b + ic)(b - ic).$$

Since operators do not in general commute, for 2 operators \hat{B} and \hat{C} we instead find:

$$\begin{aligned}(\hat{B} + i\hat{C})(\hat{B} - i\hat{C}) &= \hat{B}^2 + \hat{C}^2 + i(\hat{C}\hat{B} - \hat{B}\hat{C}) \\ \therefore \hat{B}^2 + \hat{C}^2 &= (\hat{B} + i\hat{C})(\hat{B} - i\hat{C}) + i[\hat{B}, \hat{C}].\end{aligned}$$

So, using this we rewrite the hamiltonian as:

$$\hat{H} = \left(\frac{\hat{p}^2}{2m\omega} + \frac{1}{2}m\omega x^2 \right) \omega = \left(\frac{\hat{p}}{\sqrt{2m\omega}} + ix\sqrt{\frac{m\omega}{2}} \right) \left(\frac{\hat{p}}{\sqrt{2m\omega}} - ix\sqrt{\frac{m\omega}{2}} \right) \omega + \frac{i}{2}[\hat{p}, x]\omega.$$

We know that $[\hat{p}, x] = -i\hbar$, so if we introduce 2 new operators:

$$\begin{aligned}\hat{A}^\dagger &= \frac{\hat{p}}{\sqrt{2m\omega}} + ix\sqrt{\frac{m\omega}{2}}, \\ \hat{A} &= \frac{\hat{p}}{\sqrt{2m\omega}} - ix\sqrt{\frac{m\omega}{2}},\end{aligned}$$

we can rewrite the hamiltonian in a compact form:

$$\hat{H} = \hat{A}^\dagger \hat{A} \omega + \frac{\hbar\omega}{2}.$$

We need just one more thing: the commutators of A , A^\dagger with each other and the hamiltonian. A little algebra gives us:

$$\begin{aligned}[\hat{A}, \hat{A}^\dagger] &= i[\hat{p}, x] = \hbar, \\ [\hat{H}, \hat{A}] &= [\omega \hat{A}^\dagger \hat{A}, \hat{A}] + [\frac{\hbar\omega}{2}, \hat{A}] \\ &= \omega(\hat{A}^\dagger [\hat{A}, \hat{A}] + [\hat{A}^\dagger, \hat{A}]\hat{A}) \\ &= -\hbar\omega \hat{A}, \\ [\hat{H}, \hat{A}^\dagger] &= \hbar\omega \hat{A}^\dagger.\end{aligned}$$

Calculating the Transmission Coefficient for a Potential Barrier

Consider a simple barrier potential:

$$\begin{aligned} V(x) &= 0 & x < 0 \\ &= V_0 & 0 \leq x \leq a \\ &= 0 & x > a \end{aligned}$$

For a particle approaching the barrier from $x < 0$, with $E < V_0$, we may write the equations and solutions in the three regions as:

$$\begin{aligned} x < 0 : \quad & \frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \Rightarrow \psi = Ae^{ikx} + Be^{-ikx} \\ 0 \leq x \leq a : \quad & \frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V_0\psi = E\psi \Rightarrow \psi = Ce^{-Kx} + De^{Kx} \\ x > a : \quad & \frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \Rightarrow \psi = Fe^{ikx} \end{aligned}$$

where

$$k = \frac{\sqrt{2mE}}{\hbar}, \quad K = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

We are interested in the transmission coefficient:

$$T = \frac{\text{transmitted flux}}{\text{incident flux}} = \frac{v|F|^2}{v|A|^2}$$

So to obtain this we need to relate A to F .

The various normalisation constants are related by the requirements that ψ and ψ' must be continuous across the two boundaries:

$$x = 0 : \text{Continuity of } \psi \Rightarrow A + B = C + D \quad (1)$$

$$\text{Continuity of } \psi' \Rightarrow ik(A - B) = -K(C - D)$$

$$\Rightarrow A - B = \frac{iK}{k}(C - D) \quad (2)$$

$$x = a : \text{Continuity of } \psi \Rightarrow Ce^{-Ka} + De^{Ka} = Fe^{ika} \quad (3)$$

$$\text{Continuity of } \psi' \Rightarrow -K(Ce^{-Ka} - De^{Ka}) = ikFe^{ika}$$

$$\Rightarrow \frac{-ik}{K}Fe^{ika} = (Ce^{-Ka} - De^{Ka}) \quad (4)$$

The conditions at $x = 0$ allow us to write A in terms of C and D . Adding (1) and (2) we obtain:

$$A = \frac{C}{2k}(k + iK) + \frac{D}{2k}(k - iK) \quad (5)$$

The conditions at $x = a$ meanwhile allow us to write C and D in terms of F . By adding and subtracting (4) to/from (3) we obtain:

$$D = \frac{1}{2} F e^{ika} e^{-Ka} \left(1 + \frac{ik}{K} \right) = \frac{F}{2K} (K + ik) e^{ika} e^{-Ka}$$

$$C = \frac{1}{2} F e^{ika} e^{Ka} \left(1 - \frac{ik}{K} \right) = \frac{F}{2K} (K - ik) e^{ika} e^{Ka}$$

and substituting these into (5) gives:

$$A = \frac{F}{4kK} (K - ik)(k + iK) e^{ika} e^{Ka} + \frac{F}{4kK} (K + ik)(k - iK) e^{ika} e^{-Ka}$$

$$A = \frac{F}{4kK} \left(i(K - ik)^2 e^{Ka} - i(K + ik)^2 e^{-Ka} \right) e^{ika}$$

$$A = \frac{iF}{4kK} \left((K - ik)^2 e^{Ka} - (K + ik)^2 e^{-Ka} \right) e^{ika}$$

We can therefore calculate the transmission coefficient T :

$$T = \frac{F^* F}{A^* A} = \frac{16k^2 K^2}{\left((K + ik)^2 e^{Ka} - (K - ik)^2 e^{-Ka} \right) \left((K - ik)^2 e^{Ka} - (K + ik)^2 e^{-Ka} \right)}$$

However, the expression is a lot simpler if we consider the case $Ka \gg 1$ (so very high or very thick barrier). In this case the relation between A and F simplifies to:

$$A = \frac{iF}{4kK} (K - ik)^2 e^{Ka} e^{ika}$$

giving:

$$T = \frac{F^* F}{A^* A} = \frac{16k^2 K^2}{(K + ik)^2 e^{Ka} (K - ik)^2 e^{Ka}} = \frac{16k^2 K^2}{(K^2 + k^2)^2} e^{-2Ka}$$

and substituting for k and K we finally obtain:

$$T = 16 \frac{E}{V_0} \left(1 - \frac{E}{V_0} \right) e^{-2Ka}$$

Solution of Time-Independent Schrödinger Equation for a Finite One-Dimensional Square-Well Potential

A particle of mass m is confined inside a finite one-dimensional potential well of width a , with $V = 0$ inside the well ($-a/2 < x < a/2$) and $V = V_0 = \text{constant}$ outside the well ($|x| \geq a/2$). The potential V_0 is finite, but the energy of the particle $E < V_0$ so that it is bound.

The method of solution of the Time-Independent Schrödinger Equation follows the same steps as the other examples covered in the lectures, but the algebra is a little longer.

First write the general solution in each of the three regions.

$$\begin{aligned} x \leq -a/2 : \quad V(x) &= V_0, & \psi_1(x) &= Ae^{Kx} + Be^{-Kx}, \\ -a/2 < x < a/2 : \quad V(x) &= 0, & \psi_2(x) &= C \sin(kx) + D \cos(kx), \\ x \geq a/2 : \quad V(x) &= V_0, & \psi_3(x) &= Fe^{-Kx} + Ge^{Kx}, \end{aligned}$$

where $k = \sqrt{2mE}/\hbar$ and $K = \sqrt{2m(V_0 - E)}/\hbar$.

The choice of the trigonometric form of the solution inside the well is because a bound standing-wave solution is expected. Outside the well exponentially decaying solutions are expected. These choices are for convenience, to keep the algebra as straightforward as possible.

Now apply conditions to determine the coefficients.

The wavefunction must remain finite everywhere.

As $x \rightarrow -\infty$, $e^{-Kx} \rightarrow \infty$, and so $B = 0$ to keep ψ_1 finite.

As $x \rightarrow +\infty$, $e^{Kx} \rightarrow \infty$, and so $G = 0$ to keep ψ_3 finite.

At the two well boundaries, $x = \pm a/2$, the wavefunction must be continuous.

$$\begin{aligned} \text{At } x = -a/2 : \quad \psi_1(-a/2) &= \psi_2(-a/2) \\ \therefore Ae^{-Ka/2} &= C \sin(-ka/2) + D \cos(-ka/2) \\ \therefore -C \sin(ka/2) + D \cos(ka/2) &= Ae^{-Ka/2}. \end{aligned} \tag{1}$$

$$\begin{aligned} \text{At } x = +a/2 : \quad \psi_2(a/2) &= \psi_3(a/2) \\ \therefore C \sin(ka/2) + D \cos(ka/2) &= Fe^{-Ka/2}. \end{aligned} \tag{2}$$

At the two well boundaries the first derivative of the wavefunction, $\psi' = d\psi/dx$, must be continuous.

$$\begin{aligned} \text{At } x = -a/2 : \quad \psi'_1(-a/2) &= \psi'_2(-a/2) \\ \therefore KAe^{-Ka/2} &= kC \cos(-ka/2) - kD \sin(-ka/2) \\ \therefore C \cos(ka/2) + D \sin(ka/2) &= (K/k)Ae^{-Ka/2}. \end{aligned} \tag{3}$$

$$\begin{aligned} \text{At } x = +a/2 : \quad \psi'_2(a/2) &= \psi'_3(a/2) \\ \therefore kC \cos(ka/2) - kD \sin(ka/2) &= -KF e^{-Ka/2} \\ \therefore C \cos(ka/2) - D \sin(ka/2) &= -(K/k)F e^{-Ka/2}. \end{aligned} \tag{4}$$

Equations (1)-(4) must be satisfied simultaneously.

Combine them in pairs to form four alternative equations.

$$(2) - (1) \rightarrow 2C \sin(ka/2) = (F - A) e^{-Ka/2} \tag{5}$$

$$(3) + (4) \rightarrow 2C \cos(ka/2) = -(K/k)(F - A) e^{-Ka/2} \tag{6}$$

$$(2) + (1) \rightarrow 2D \cos(ka/2) = (F + A) e^{-Ka/2} \tag{7}$$

$$(3) - (4) \rightarrow 2D \sin(ka/2) = (K/k)(F + A) e^{-Ka/2} \tag{8}$$

Equations (5)-(8) must be satisfied simultaneously.

For equations (5) and (6) **both** to be true requires

$$\textbf{EITHER :} \quad C = 0 \quad \textbf{and} \quad A = F \quad (9a)$$

$$\textbf{OR :} \quad \cot(ka/2) = -K/k \quad (9b)$$

Condition (9b) comes from dividing equation (6) by equation (5).

For equations (7) and (8) **both** to be true requires

$$\textbf{EITHER :} \quad D = 0 \quad \textbf{and} \quad A = -F \quad (10a)$$

$$\textbf{OR :} \quad \tan(ka/2) = K/k \quad (10b)$$

Condition (10b) comes from dividing equation (8) by equation (7).

Therefore, to satisfy the boundary conditions, one of the conditions (9a) or (9b) must be true, **and** simultaneously one of the conditions (10a) or (10b) must be true.

If both (9a) and (10a) are true, then $C = D = 0$ and so $\psi_2 = 0$, which means that there is no particle inside the well. This is not an acceptable solution.

If both (9b) and (10b) are true, then

$$\begin{aligned} \tan(ka/2) &= -\cot(ka/2) \\ \therefore \tan^2(ka/2) &= -1, \end{aligned}$$

which is impossible, because both k and a are real numbers.

So conditions (9b) and (10b) **cannot** be simultaneously true.

Therefore there are two possibilities. **Either** conditions (9a) **and** (10b) are both true, **or** conditions (9b) **and** (10a) are both true. These generate two different sets of solutions for the finite square-well potential.

In the **first** set of solutions, $C = 0$ and $A = F$, so $\psi_2(x) = D \cos(kx)$ and $\psi_1(x) = \psi_3(-x)$.

These solutions are symmetric about the centre of the well ($x = 0$) and so have **even** parity.

The energy eigenvalues for these solutions can be found using equation (10b).

In the **second** set of solutions, $D = 0$ and $A = -F$, so $\psi_2(x) = C \sin(kx)$ and $\psi_1(x) = -\psi_3(-x)$.

These solutions are antisymmetric about the centre of the well ($x = 0$) and so have **odd** parity.

The energy eigenvalues for these solutions can be found using equation (9b).

Methods for solving equations (9b) and (10b), and the properties of the resulting wavefunctions, will be discussed further in the lectures.

Properties of Commutators

Although in the lectures our main interest in commutators of 2 operators will be whether they are zero or non-zero (whether the operators commute or not), it can be useful, even for this limited purpose, to be able to do some algebra with them. We will use this later when we look at angular momentum, for example.

There are a few algebraic properties of commutators which can be useful. Starting from the definition of the commutator of 2 operators:

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

we can obtain the following:

$$\begin{aligned} [\hat{B}, \hat{A}] &= \hat{B}\hat{A} - \hat{A}\hat{B} \\ &= -[\hat{A}, \hat{B}], \end{aligned}$$

and, of course

$$[\hat{A}, \hat{A}] = 0.$$

Also,

$$\begin{aligned} [\hat{A}, \hat{B} + \hat{C}] &= \hat{A}(\hat{B} + \hat{C}) - (\hat{B} + \hat{C})\hat{A} \\ &= \hat{A}\hat{B} - \hat{B}\hat{A} + \hat{A}\hat{C} - \hat{C}\hat{A} \\ &= [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}], \end{aligned}$$

$$\begin{aligned} [\hat{A}\hat{B}, \hat{C}] &= \hat{A}\hat{B}\hat{C} - \hat{C}\hat{A}\hat{B} \\ &= \hat{A}\hat{B}\hat{C} - \hat{A}\hat{C}\hat{B} + \hat{A}\hat{C}\hat{B} - \hat{C}\hat{A}\hat{B} \\ &= \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}, \end{aligned}$$

and

$$[\hat{A}, [\hat{B}, \hat{C}]] + [\hat{B}, [\hat{C}, \hat{A}]] + [\hat{C}, [\hat{A}, \hat{B}]] = 0.$$

These relations can be useful where you know the commutator(s) of 2 (or more) operators and need to find whether particular combinations of them commute or not, allowing you to express the unknown commutator as a combination of known ones.

Significance of Commuting Operators

We showed in the lecture that if 2 operators shared a complete set of eigenfunctions, i.e. if every wavefunction can be written as a linear combination of functions which are eigenfunctions of both operators, then the two operators will commute:

$$\left[\hat{A}, \hat{B} \right] \Psi = 0 \quad \text{for any function } \Psi$$

The significance of the two operators sharing such a set of eigenfunctions is that it is possible to know precise values for both observables at the same time.

What we did not show was the converse: the fact that the two operators commute means that they must have a set of common eigenfunctions. The argument is slightly more subtle than the previous one.

Consider two commuting operators \hat{A} and \hat{B} . Let \hat{A} have a complete set of eigenfunctions ψ_n . Now let us evaluate the commutator applied to one of these eigenfunctions:

$$\begin{aligned} \left[\hat{A}, \hat{B} \right] \psi_n &= \hat{A}\hat{B}\psi_n - \hat{B}\hat{A}\psi_n = 0 \\ \therefore \hat{A}\hat{B}\psi_n &= \hat{B}\hat{A}\psi_n \\ \hat{A}(\hat{B}\psi_n) &= a_n\hat{B}\psi_n \end{aligned}$$

Therefore $\hat{B}\psi_n$ is an eigenfunction of \hat{A} with eigenvalue a_n .

There are now 2 cases we should consider:

1. The eigenfunctions ψ_n of \hat{A} are non-degenerate, i.e. all of the eigenvalues are different.

In this case it follows that since $\hat{B}\psi_n$ is an eigenfunction of \hat{A} with the same eigenvalue, a_n , as ψ_n , $\hat{B}\psi_n$ must be the same eigenfunction as ψ_n itself. However, it could be ψ_n multiplied by a constant, as that would not affect the eigenvalue equation. So in general:

$$\hat{B}\psi_n = \text{constant} \times \psi_n$$

Thus ψ_n is also an eigenfunction of \hat{B} , and so the operators \hat{A} and \hat{B} do have a set of common eigenfunctions.

2. Some of the eigenfunctions ψ_n are degenerate, i.e. have same eigenvalue.

Let us say that ψ_j and ψ_k have the same eigenvalue, a :

$$\begin{aligned} \hat{A}\psi_j &= a\psi_j \\ \hat{A}\psi_k &= a\psi_k \end{aligned}$$

Then the statement

$$\hat{A}(\hat{B}\psi_j) = a\hat{B}\psi_j$$

does not imply that $\hat{B}\psi_j = \text{constant} \times \psi_j$, i.e. ψ_j need not be an eigenfunction of \hat{B} .

What it does mean is

$$\hat{B}\psi_j = c_j\psi_j + c_k\psi_k$$

i.e. that $\hat{B}\psi_j$ must be a linear combination of the eigenfunctions of \hat{A} with this eigenvalue. However, since any linear combination of these eigenfunctions is an equally good eigenfunction of \hat{A} , we may simply find the combinations of ψ_j and ψ_k which *are* eigenfunctions of \hat{B} and use these as eigenfunctions of \hat{A} in place of ψ_j and ψ_k .

Hence the fact that the two operators commute does indeed mean that the eigenfunctions of one operator are eigenfunctions of the other, i.e. that they share a set of eigenfunctions.