Quantum Mechanics ①

Course Outline

1. Introduction and Motivation for Quantum Mechanics
2. Wave Mechanics and Schrödinger's Equation
3. Operator Methods and the Uncertainty Principle

3*. The Stern-Gerlach Experiment and Quantum No-Xerox Principle

4. Wave Mechanics in 3D : The Hydrogen Atom.

References

Gasiorowicz, and also the Feynman Lectures, Book 5

Introduction

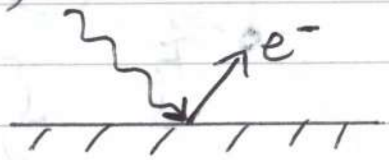
Quantum Mechanics makes use of the Planck constant, $\hbar = 1{\cdot}055 \times 10^{-34}$ Js. This is a fundamental constant.
Dimensionally : $[\hbar] = [J][s] = ML^2T^{-1}$

Also used are the speed of light, $c \approx 3 \times 10^{10}$ cm/s and G, Newton's Constant of Gravitation.

According to Maxwell's equations, light consists of radiation and behaves like waves. The fact that light is subject to refraction interference, diffraction and polarisation gives experimental evidence to support this. For monochromatic light :

$$\omega = c|\underline{k}| \quad , \quad \lambda = 2\pi/|\underline{k}|$$
$$\underline{E}, \underline{B} \propto \mathrm{Re}\left[\exp(i\underline{k}\cdot\underline{x} - i\omega t)\right]$$

The Photoelectric Effect (Hertz, 1887)



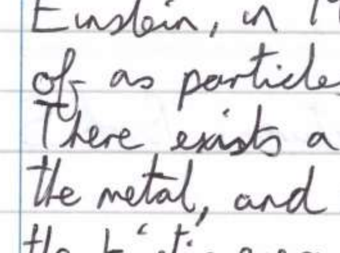
When light is shone onto the surface of a metal, electrons gain kinetic energy and are 'liberated' from the metal surface.

Note:

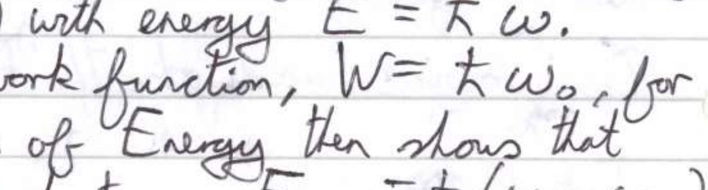
- This phenomenon only occurs when the frequency, ω, of the light exceeds a threshold frequency ω_0 which depends on the metal.
- The threshold frequency ω_0 is not dependent on the intensity, I, of light.
- The rate of emitted electrons is proportional to the intensity, I.

Einstein, in 1905, hypothesised that light should be thought of as particles (photons) with energy $E = \hbar\omega$. There exists a threshold work function, $W = \hbar\omega_0$, for the metal, and Conservation of Energy then shows that the kinetic energy of emitted electrons, $E_{KE} = \hbar(\omega - \omega_0)$, the correct linear relationship. Increasing the intensity of the light means increasing the number of photons and the rate of emissions.

Einstein's view of light as particles explains not only the Photoelectric effect, but other phenomena such as spectral lines.

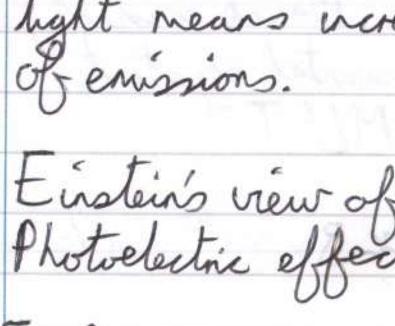


Radiation emissions from heated Hydrogen gas



Rutherford's Planetary Modell (1911)

Hydrogen



Rutherford's planetary model of the atom consists of an electron in a stable, circular orbit of radius r around a proton. The electron experiences electrostatic force F_c.

m_e - mass of an electron

m_p - mass of a proton

$\frac{m_e}{m_p} \approx \frac{1}{2000} \ll 1$ so gravitational effects on the electron are neglected.

Quantum Mechanics ①

e is the charge of an electron.

Coulomb's Law: $F_c = -\frac{e^2}{4\pi\varepsilon_0 r^2}$

Centripetal force: $F = -\frac{m_e V^2}{r}$

Angular momentum: $J = m_e V r$ $\Rightarrow r = \frac{4\pi\varepsilon_0}{m_e e^2} J$

Total Energy $E_{Total} = E_{KE} + E_{PE} = \frac{1}{2} m_e V^2 - \frac{e^2}{4\pi\varepsilon_0 r}$

$$E_{Total} = \left(-\frac{m_e e^4}{32\pi^2\varepsilon_0^2}\right)\frac{1}{J^2}$$

If J were continuous, then the line spectrum would be continuous which is not the case. Also, Maxwell predicts synchotron radiation, which would cause the orbit to lose energy making it unstable.

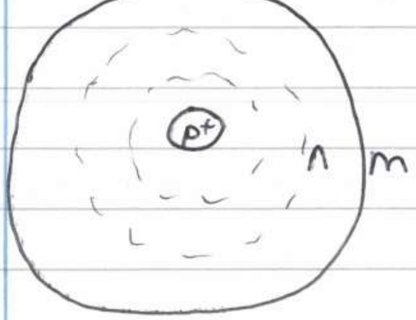
Bohr (1913)

Postulate I: The angular momentum, J, of the electron is quantised. $J = n\hbar$, for $n \in \mathbb{N}$.

Orbital radius: $r = \frac{4\pi\varepsilon_0}{m_e e^2}(n^2\hbar^2)$

$$E_{Total} = \left(-\frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2}\right)\frac{1}{n^2}$$

Postulate II: Energy states are stationary, or stable (called Stationary States)



$$E_m - E_n = \frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2}\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

$$R_\varphi = \frac{m_e e^4}{64\varepsilon_0^2\hbar^3 c} = 1.097\times10^7 \, m^{-1}$$

↑ The Rydberg Constant

Problems with Bohr's Postulates

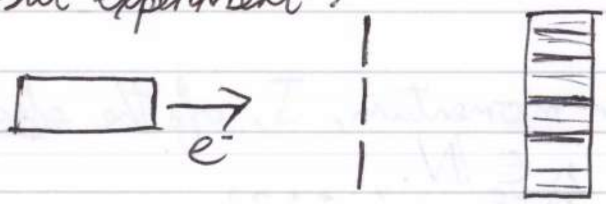
- Why should J be quantised? This is correct for Hydrogen but for no other atom.
- Why should states be stationary?
- No mechanics is involved; this is totally ad-hoc.

de Broglie then suggested that if light possessed both particle and wave properties, then matter might also.

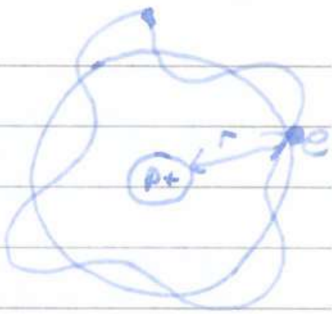
The de Broglie wavelength of a particle: $\lambda = \frac{2\pi\hbar}{p}$

$E = \sqrt{m^2c^4 + p^2c^2}$, $m_{photon} = 0$, $E_{photon} = pc = \hbar\omega$

Electrons can be made to diffract and interfere in the double slit experiment:



Quantum Mechanics ②



"Explanation" of Hydrogen Atom

$$2\pi r = n\lambda = n\frac{2\pi\hbar}{|p|}, \quad J = m_e v r = n\hbar$$

Machine Gun Diffraction

$m_{bullet} \approx 2\times10^{-3}\,kg$, $v \approx 800\,ms^{-1}$

$$\lambda_b = \frac{2\pi\hbar}{|p|} = \frac{2\pi\times1\times10^{-34}\,kg\,m^2s^{-1}}{2\times10^{-3}\times8\times10^{2}\,kg\,ms^{-1}} \approx 3\times10^{-34}\,m$$

To observe diffraction in machine gun bullets, we would need a slit size of 3×10^{-34} m, so this is unfeasible.

Electron Diffraction (1961 Claus Jonsson)

Slit size $0.3\times10^{-9}\,m$
Slit Separation $1\times10^{-9}\,m$

$m_e = 9\times10^{-31}\,kg$, $v = 0.5c$, $\lambda \approx 5\times10^{-12}\,m$

Notes

1. Diffraction is seen even when electrons are emitted singly.

2. We cannot predict where each electron will land, but we can predict the probability distribution given a large number of electrons.

Postulates of Quantum Mechanics

1. At any time, the particle state is described by a complex wavefunction $\Psi(x, t)$

2. The probability of finding the particle in volume dV is $|\Psi(x,t)|^2 dV$

3. "The particle must be somewhere". $\int_V |\Psi(\underline{x}, t)|^2 dV = 1$
(This is normalised. Any $N \in (0, \infty)$ will do)

4. The evolution of $\Psi(\underline{x}, t)$ is described by the Schrödinger Equation.
$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + U(\underline{x}) \Psi$$

5. The Schrödinger equation is first order in time and second order in space, and for non-relativistic particles (for relativistic particles, the Dirac equation)

Example (Free Particle)

The "Classical" picture is simply $E_T = KE + PE = \frac{1}{2}mv^2 + U(\underline{x})$
Conservation of energy $\Rightarrow \frac{dE_T}{dt} = 0$, $\dot{x} = v$, a constant

$i\hbar \frac{\partial \Psi}{\partial t} = -\hbar^2 \nabla^2 \Psi$. One solution is a plane wave: $\Psi(\underline{x}, t) = Ae^{i\underline{k}\cdot\underline{x} - i\omega t}$

$i\hbar A(-i\omega)\Psi = \frac{\hbar^2}{2m} |\underline{k}|^2 \Psi$, $\omega = \frac{\hbar}{2m} |\underline{k}|^2$
de Broglie : $\underline{p} = \hbar \underline{k}$, $E = \hbar\omega = \frac{|\underline{p}|^2}{2m}$

$\int_V |\Psi|^2 dV = \int_V |A|^2 dV \to \infty$, and the plane wave is Non-Normalisable.

Probability Current

How does probability density evolve with time? At time $t = 0$, with $\Psi_0(\underline{x}, 0)$, $\int_{\mathbb{R}^3} |\Psi(\underline{x}, 0)|^2 dV = 1$

Probability density $\rho(\underline{x}, t) = |\Psi(\underline{x}, t)|^2$, $\frac{\partial \rho}{\partial t} = \Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t}$

Schrödinger Equation : $i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + U\Psi$
$$\frac{\partial \rho}{\partial t} = \frac{i\hbar}{2m} (\Psi^* \nabla^2 \Psi - \Psi \nabla^2 \Psi^*) = \nabla \cdot \left[\frac{i\hbar}{2m}(\Psi^* \nabla \Psi - \Psi \nabla \Psi^*)\right]$$
$$= -\nabla \cdot \underline{j}$$
$\frac{\partial \rho}{\partial t} + \nabla \cdot \underline{j} = 0$, Conservation of probability

Quantum Mechanics (2)

Conservation of probability

$$\int_V \frac{\partial \rho}{\partial t}\, dV = \int_V -\nabla \cdot \underline{j}\, dV = -\int_{\partial V} \underline{j} \cdot d\underline{S}$$ ← Divergence Theor

Assertion : As $R \to \infty$, $\underline{j}(\underline{x}, 0) \to 0$ i.e. "probability doesn't leak

$$\lim_{R \to \infty} \int_{\partial V} \underline{j} \cdot d\underline{S} \Rightarrow 0$$

$$\int_V \frac{\partial \rho}{\partial t}\, dV = \frac{d}{dt} \int_V \rho(\underline{x}, t)\, dV$$

$\therefore$ If $\int_V \rho(\underline{x}, 0)\, dV = 1$, then the wavefunction is normalised for all time.

Quantum Mechanics ③

Superposition

i) If $\Psi(\underline{x}, t)$ is a normalisable solution to the Schrödinger equation, then so is $\alpha\Psi(\underline{x}, t)$, for $\alpha \in \mathbb{C}$.

ii) If Ψ_1, Ψ_2 are as above, then $\Psi = \alpha\Psi_1 + \beta\Psi_2$ is also a normalisable solution for $\alpha, \beta \in \mathbb{C}$.

Proof.

$\int_V |\Psi_i|^2 dV = N_i < \infty$, for $i = 1, 2$.

$|z_1 + z_2| \leq |z_1| + |z_2|$

$(|z_1| - |z_2|)^2 \geq 0 \Rightarrow 2|z_1||z_2| \leq |z_1|^2 + |z_2|^2, \ \forall z_1, z_2 \in \mathbb{C}$

$$\int_V |\Psi|^2 dV = \int_V |\alpha\Psi_1 + \beta\Psi_2|^2 \leq \int_V |\alpha\Psi_1|^2 + 2|\alpha\Psi_1||\beta\Psi_2| + |\beta\Psi_2|^2 dV$$
$$\leq \int_V 2|\alpha\Psi_1|^2 + 2|\beta\Psi_2|^2 dV < \infty$$

Expectation Values / Operator Methods

$\langle \cdot \rangle = \int_V \Psi^* \cdot \Psi \, dV$. In one dimension:

$\langle x \rangle = \int_{-\infty}^{\infty} x \, \rho(\underline{x}, t) \, dV$ = Average value of ρ

Momentum Operator : $\underline{p} = \frac{\hbar}{i} \nabla$

Energy Operator : $E = -\hbar^2 \nabla^2$??

Hilbert Space

Formally, in Quantum Mechanics, we are working within a Hilbert Space. This is an infinite dimensional complex vector space with a positive inner product, $\Psi > 0$, and if $\Psi_1 \propto \Psi_2$, then they describe the same state.

Solutions of the Schrödinger Equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + U(\underline{x}) \Psi \qquad \underline{p} = \hbar \underline{k}$$

Our plane solution $\Psi(\underline{x}, t) = A \exp[i\underline{k}\cdot\underline{x} - i\omega t]$ suggests a substitution of $\Psi(\underline{x}, t) = \chi(\underline{x}) \exp(-i\frac{Et}{\hbar})$ (separation of variables) where $-i\frac{Et}{\hbar} = -i\omega t$

$\Rightarrow -\frac{\hbar^2}{2m} \nabla^2 \chi + U(\underline{x}) \chi = E\chi$, the Time Independent Schrödinger Equation.

This is in Sturm-Liouville Form.

Quantum Mechanics ④ + ⑤

Time-Independent Schrödinger Equation : $-\frac{\hbar^2}{2m}\nabla^2\chi + U(\underline{x})\chi = E\chi$
This is a Sturm-Liouville problem with Eigenvalues corresponding to definite energy states, called "Stationary States".
$\omega = E/\hbar$. Note that $\rho(\underline{x}, t) = |\Psi|^2 = |\chi|^2$

The general solution to the time dependent Schrödinger equation is :
$\Psi(\underline{x}, t) = \sum_{n=1}^{\infty} a_n \chi_n(\underline{x}) \exp\left(-i\frac{E_n t}{\hbar}\right)$
$\Rightarrow \Psi$ is not a stationary solution.

Heisenberg Uncertainty Principle

$\Delta x \Delta p \geq \frac{\hbar}{2}$, where Δx and Δp are the variances of the position and momentum.

Classical vs. Quantum : A Free Particle

Classical : Fixed momentum $p = mv$, definite position $x = \frac{p}{m}(t - t_0)$

Quantum : Expected position and momentum, $\langle x \rangle, \langle p \rangle$

Particle in an Infinite Potential Well (1D)

$$u(x) = \begin{cases} 0 & 0 < x < a \\ \infty & \text{otherwise} \end{cases}$$

Stationary states : $-\frac{\hbar^2}{2m}\frac{\partial^2\chi}{\partial x^2} + U(x)\chi = E\chi$

$U_{outside} = \infty \Rightarrow \chi_{outside} \equiv 0$, otherwise $E = \infty$.
So we have zero probability of finding a particle outside the well

Inside : $U \equiv 0$, $-\frac{\hbar^2}{2m}\frac{\partial^2\chi}{\partial x^2} = E\chi$. Let $k = \sqrt{\frac{2mE}{\hbar^2}} > 0$.
$\frac{\partial^2\chi}{\partial x^2} = -k^2\chi$
$\chi(x) = A\sin kx + B\cos kx$

Boundary Conditions : $\chi(0) = \chi(a) = 0$

$\Rightarrow B = 0$, $A \sin ka = 0$, $ka = n\pi$, $n \in \mathbb{N}$ (but not zero!)

Normalisation $\Rightarrow$ $\chi_n(x) = \begin{cases} \sqrt{\frac{\pi}{a}} \sin kx & x \in [0, a] \\ 0 & \text{otherwise} \end{cases}$

$E_n = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{n\pi}{a}\right)^2$, $n \in \mathbb{N}$.

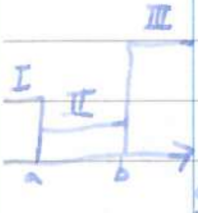
This is an example of quantised energy states (like the Bohr atom)

The lowest energy state, or ground state has $E_1 = \frac{\hbar^2 \pi^2}{2ma^2} > 0$

As $n \to \infty$, we recover the classical picture :

Quantum Mechanics ⑥

Prescription for solving 1D Quantum Mechanics Problems



Step 1: Solve the time independent Schrödinger equation in regions with different U.

If $E > U$, $k = \sqrt{\frac{2m(E+U)}{\hbar^2}} > 0$, $\frac{d^2\chi}{dx^2} = -k^2\chi$, $\chi = Ae^{ikx} + Be^{-ikx}$

If $E < U$, $K = \sqrt{\frac{2m(U-E)}{\hbar^2}} > 0$, $\frac{d^2\chi}{dx^2} = K^2\chi$, $\chi = Ae^{Kx} + Be^{-Kx}$

Sometimes, when $E < U$, normalisability $\Rightarrow A$ or $B = 0$

Step 2: Match solutions at discontinuities

Step 3: Find the spectrum of E as a function of U.

Continuity of Solutions

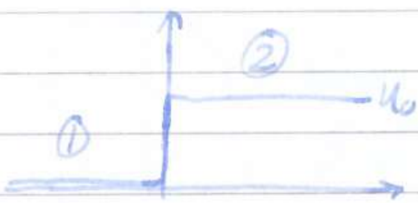
1. $U(x)$ smooth $\Rightarrow \chi$ is infinitely differentiable

2. $U(x)$ has an infinite discontinuity $\Rightarrow \chi$ is smooth but $\frac{d\chi}{dx}$ is not

3. $U(x)$ has a finite discontinuity $\Rightarrow \chi, \frac{d\chi}{dx}$ continuous but $\frac{d^2\chi}{dx^2}$ is not

$$-\int_{x_0-\varepsilon}^{x_0+\varepsilon} \frac{\hbar^2}{2m}\frac{d^2\chi}{dx^2}\,dx = \int_{x_0-\varepsilon}^{x_0+\varepsilon} (E\chi - U(x)\chi)\,dx \Rightarrow \left.\frac{d\chi}{dx}\right|_{x_0+\varepsilon} - \left.\frac{d\chi}{dx}\right|_{x_0-\varepsilon} = -\frac{2m}{\hbar^2}\int_{x_0-\varepsilon}^{x_0+\varepsilon} \chi(E-U_0$$

Example: Potential Step



$$U(x) = \begin{cases} U_0 & x > 0 \\ 0 & \text{otherwise} \end{cases}$$

First Case: $E > U_0$, $k = \sqrt{\frac{2mE}{\hbar^2}} > 0$, $U(x<0) = 0$

$\chi(x) = e^{ikx} + Re^{-ikx}$

"Reflectivity"

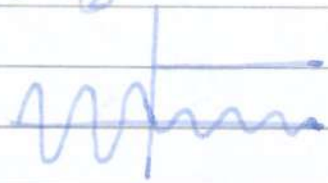
$u(x>0) = U_0$, $q = \sqrt{\frac{2m(E-U_0)}{\hbar^2}} > 0$

$\psi(x) = \vec{T} e^{iqx} + \cancel{e^{-iqx}}$ ← No left moving wave term

"Transmittivity"

Match at $x = 0$: $R = \frac{k-q}{k+q}$, $T = \frac{2k}{k+q}$. Here, R, T are real.

Note that $j_{①} = j_{②}$

Wavefunction  $E \gg U_0$, $q \to k$, $R \to 0$, $T \to 1$

<u>Second Case : $E < U_0$</u>

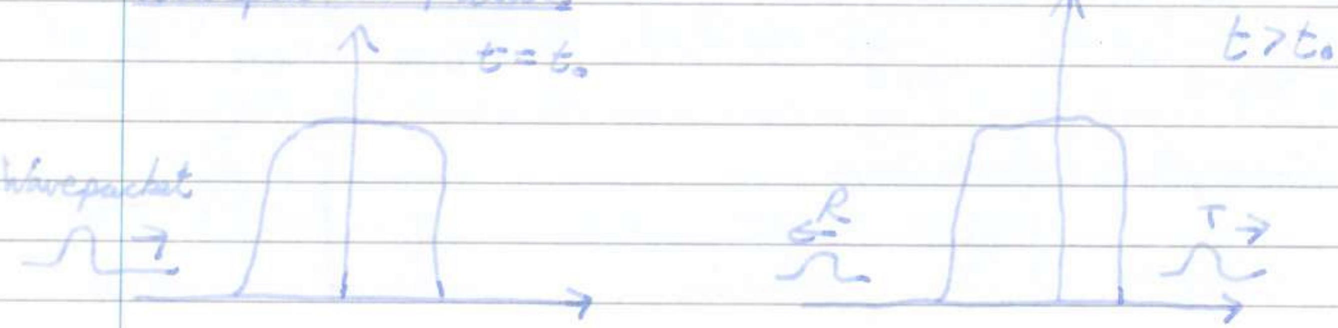
$u(x>0) = U_0$, $K = \sqrt{\frac{2m(U_0-E)}{\hbar^2}} > 0$, $\frac{d^2\psi}{dx^2} = K^2\psi$

$\psi(x) = \cancel{e^{Kx}} + Te^{-Kx}$, (use normalisability)

Matching solutions at $x = 0 \Rightarrow R = \frac{k-iK}{k+iK}$, $T = \frac{2k}{k+iK}$ $> \cancel{0}$

If $U(x)$ returns to zero, we get 

<u>Wavepacket Picture</u>



Arrange a wavepacket for the left-hand-side, then calculate T and R:

$|T|^2 = \lim_{t\to\infty} \int_0^\infty |\psi|^2 dx$

$|R|^2 = \lim_{t\to\infty} \int_{-\infty}^0 |\psi|^2 dx$

Quantum Mechanics (7)

Quantum Harmonic Oscillation

Classical Picture : Simple Harmonic motion , $u(x) = \frac{1}{2}m\omega^2x^2$

Newton : $F = m\frac{d^2x}{dt^2} = -\frac{du}{dx}$, $\ddot{x} = -\omega^2 x$

$x(t) = A\sin\omega t + B\cos\omega t$, period $\frac{2\pi}{\omega}$

Quantum : $-\frac{\hbar^2}{2m}\frac{\partial^2\chi}{\partial x^2} + \frac{1}{2}m\omega^2x^2\chi = E\chi$

Let $y = \sqrt{\frac{m\omega}{\hbar}}x$, $\mathcal{E} = \frac{2E}{\hbar\omega}$

$\Rightarrow -\frac{d^2\chi}{dy^2} + y^2\chi = \mathcal{E}\chi$

Use $\chi(y) = f(y)e^{-\frac{1}{2}y^2} \Rightarrow \frac{d^2f}{dy^2} - 2y\frac{df}{dy} + (\mathcal{E}-1)f = 0$

and let $f(y) = \sum_{n=0}^{\infty} a_n y^n$

$\Rightarrow a_{n+2} = \frac{2n-\mathcal{E}+1}{(n+1)(n+2)}a_n$

Normalisable Solution $\Rightarrow$ The series must terminate at some $N \geq 0$

For huge n, $\frac{a_{n+2}}{a_n} \approx 2/n$

$e^{y^2} = \sum_{n\geq 0,\text{even}} \frac{1}{(\frac{n}{2})!}y^n$, and for very large n, $\frac{(\frac{n}{2})!}{(\frac{n}{2}+1)!} \approx \frac{2}{n}$

So if our series does not terminate, $f(y) \approx e^{y^2}$, $\chi(y) \approx e^{\frac{1}{2}y^2}$ which is not normalisable.

So we impose the condition that $\exists N \geq 0 : a_n = 0 \;\forall n > N$

$\Rightarrow 2n - \mathcal{E} + 1 = 0$ where $2n = N$, $E_n = (N+\frac{1}{2})\hbar\omega$

Wavefunctions

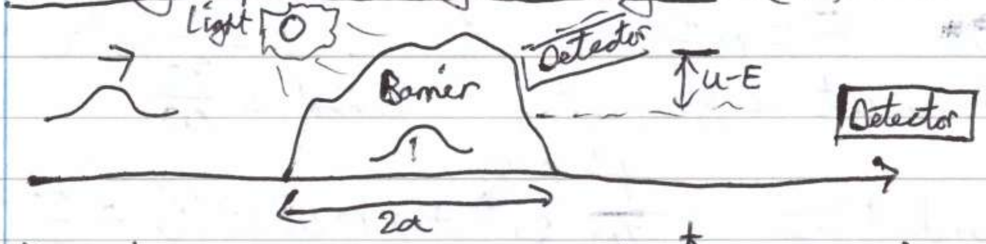
N	E_n	$\chi_n(x)$	Parity
0	$\frac{1}{2}\hbar\omega$	$e^{-\frac{1}{2}y^2}$	even
1	$\frac{3}{2}\hbar\omega$	$ye^{-\frac{1}{2}y^2}$	odd
2	$\frac{5}{2}\hbar\omega$	$(1-2y^2)e^{-\frac{1}{2}y^2}$	even

$\Delta E = \hbar\omega$

27/10/11

Quantum Mechanics 7

Catching a particle during tunneling? (*)



$\Delta x \ll 2a$

$K = \frac{2m}{\hbar^2}(U-E$

Heisenberg Uncertainty $\Delta x \Delta p \geq \frac{\hbar}{2} \Rightarrow \Delta p \gg \frac{\hbar}{4a}$

$\Rightarrow \Delta E \Rightarrow \frac{\Delta p^2}{2m} \gg \frac{\hbar^2}{32a^2 m}$

$|T|^2 = \frac{(2kK)^2}{(k^2+K^2)^2 \sinh^2 2Ka + (2kK)^2}$

$(U - E) \gg \Delta E \gg \frac{\hbar^2}{32a^2 m}$

$\frac{\hbar^2 K^2}{2m} \Rightarrow (Ka) \gg 1$ (2), $|T|^2 \approx \left(\frac{4kK}{k^2+K^2}\right)^2 e^{-4Ka}$ very small

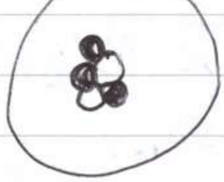
Suppose we use a light source to ~~do~~ try and detect a particle tunneling

$\lambda_{light} \ll 2a \qquad \Delta p = \frac{2\pi\hbar}{\lambda_{light}} \gg \frac{\hbar}{2a}$

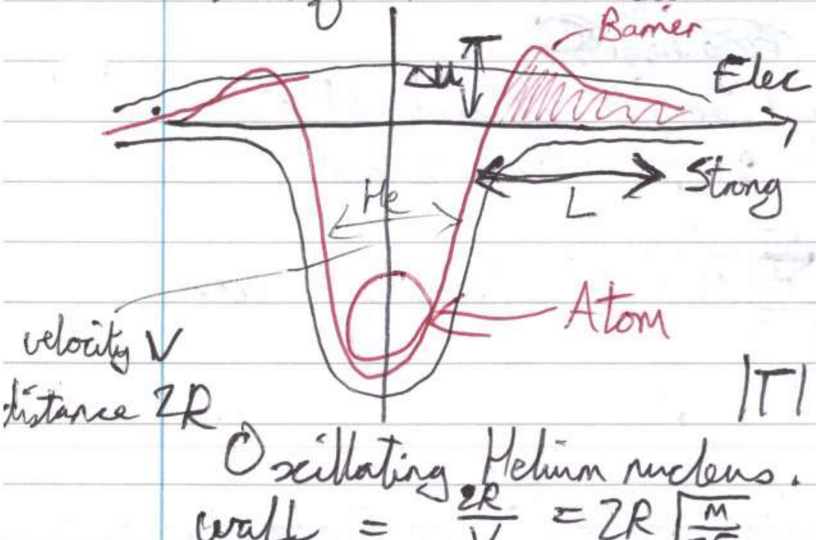
Radioactive Decay

Consider an isotope N_Z^A (A Atomic weight, Z Atomic number)

$A = \#p + \#n, \quad Z = \#p$



Atomic forces → Strong nuclear force (short range, strong, attractive)
→ Electrostatics (long range, repulsive, weak)



$U_T = U_{Strong} + U_{Electrostatic}$

— Total Potential

α emission

$N_Z^A \rightarrow N_{Z-2}^{A-4} + He_2^4$

$|T|^2 \xrightarrow{U_0 \gg E} e^{-\frac{2L}{\hbar}\sqrt{2m\Delta U}}$

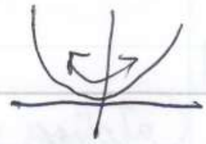
Oscillating Helium nucleus. Time between collisions with the potential wall $= \frac{2R}{V} = 2R\sqrt{\frac{m}{2E}}$

half life "lifetime" $\tau = 2R\sqrt{\frac{m}{2E}}|T|^{-2}$

U_{92}^{232} - 69 years $\quad Uuh_{116}^{293}$ - 61 ms

1

Quantum Harmonic Oscillation



Classical - SHM $\quad U(x) = \frac{1}{2} m\omega^2 x^2$

Newton's Law $\quad F = m\frac{d^2x}{dt^2} = -\frac{du}{dx}$, $\ddot{x} = -\omega^2 x$

$x(t) = A\sin\omega t + B\cos\omega t$, $\quad$ period $= \frac{2\pi}{\omega}$

Time Independent SE $\quad -\frac{\hbar^2}{2M}\frac{\partial^2\chi}{\partial x^2} + \frac{1}{2} m\omega^2 x^2 \chi = E\chi$

$y^2 = \frac{m\omega}{\hbar}x^2 \quad \varepsilon = \frac{2E}{\hbar\omega}$

$-\frac{d^2\chi}{dy^2} + y^2\chi = \varepsilon\chi$ (Hermite Polynomials)

χ normalisable $\Rightarrow \chi(y) \to 0$ as $y \to \pm\infty$

Minimum energy E, $\varepsilon = 1$ (gives the first normalisable solution) Cheat !!

$\chi(y) = e^{-\frac{1}{2}y^2}$ + a non-normalisable solution $\quad$ Cheat 2 !!

$\to$ Lowest energy state $E_0 = \frac{\hbar\omega}{2}$

General ε

Guess $\chi(y) = f(y)\, e^{-\frac{1}{2}y^2}$, gives $\frac{d^2f}{dy^2} - 2y\frac{df}{dy} + (\varepsilon - 1)f = 0$

Solution

$$f(y) = \sum_{n=0}^{\infty} a_n y^n$$

$\Rightarrow$ Recurrence relation $a_{n+2} = \frac{2n - \varepsilon + 1}{(n+1)(n+2)} a_n$

$a_0 \to$ even solutions $\quad U(x) = U(-x)$, even

$a_1 \to$ odd solutions

Normalisable $\to$ Our series must terminate at some $N > 0$.

Consider huge n. $\frac{a_{n+2}}{a_n} \approx \frac{2}{n}$ when n is large.

if $g(y) \equiv e^{y^2} = \sum_{n=0}^{\infty} \frac{1}{(\frac{n}{2})!} y^n$ for only n even

At very large n $\quad \frac{(\frac{n}{2})!}{(\frac{n}{2}+1)!} \approx \frac{2}{n}$

If $f(y) \approx e^{y^2}$, $\chi(y) \approx e^{\frac{1}{2}y^2}$, not normalisable

$\Rightarrow$ Impose condition, $\exists N > 0 : a_n = 0 \ \forall n > N$.

$\Rightarrow 2n - \varepsilon + 1 = 0$, $2n = N \Rightarrow E_n = (N + \frac{1}{2})\hbar\omega$

Spectrum

Quantum Mechanics (2)

Observables and Operators

"Observables" are measurable quantities.

For a classical particle, we have:

- position, $\underline{x}$ — momentum $\underline{p}$
- Energy $E = KE + PE = \frac{|\underline{p}|^2}{2m} + U(\underline{x})$ — Angular momentum $\underline{L} = \underline{x} \times \underline{p}$

- The evolution of measurable quantities is "deterministic", i.e. the state of the particle is uniquely determined, for any time, by x_0, p_0 (measured to arbitrary accuracy) and Newton's Laws.

Quantum Measurables

The state of a quantum particle is specified by $\Psi(\underline{x}, t)$, and given some initial state $\Psi(x_0, t_0)$, $\Psi(\underline{x}, t > t_0)$ is uniquely determined by the Schrödinger equation.

Quantum "observables" correspond to operators e.g. momentum.
The expectation value of an operator: $\quad \underline{p} = -i\hbar\nabla$

$$\langle \hat{O} \rangle = \int_V dV\, \Psi^* \hat{O} \Psi$$

Given $f : \mathbb{R}^3 \to \mathbb{C}$, $\hat{O} f = g : \mathbb{R}^3 \to \mathbb{C}$

Linear operators are used i.e. $\hat{O}(\alpha f + \beta g) = \alpha \hat{O} f + \beta \hat{O} g$ for $\alpha, \beta \in \mathbb{C}$

If $\hat{O} f(x) = \lambda f(x)$, then $f(x)$, λ are an eigenfunction and eigenvalue of $\hat{O}$. For our operators, eigenvalues are always real.
If there is more than one eigenfunction for any λ, then λ is a degenerate eigenvalue.

The outcome of any measurement of any observable $\hat{O}$ is always an eigenvalue of $\hat{O}$. Our operators $\hat{O}$ are always Hermitian.

Any state Ψ can be expanded as a set of eigenfunctions:
Discrete systems $\Psi(\underline{x}) = \sum_n a_n u_n(\underline{x})$
Continuous systems $\Psi(\underline{x}) = \int dm\, c(m)\, u_m(\underline{x})$

The probability of measuring an eigenvalue λ_n associated with an eigenfunction u_n is $|a_n|^2$ (discrete) or $\int_{\Delta m} |c(m)|^2 dm$ (continuous

Examples

① Momentum, $\hat{\underline{p}} = -i\hbar\nabla$. Momentum eigenfunctions are plane wave solutions $A\exp(i\underline{k}\cdot\underline{x})$. These are not normalisable and eigenstates are always continuous.

② Energy, $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U(\underline{x})$
We can write the Schrödinger Equation as $\hat{H}\Psi = E\Psi$ and obtain $\hat{H}\chi = E\chi$, with the $\chi(x)$ stationary states.

Boundstates are the stationary states with $E < U$

In 1D, $U(\underline{x}) = 0$, we have degeneracy as there are eigenfunctions $\chi_k(x)\, e^{ikx}$ and $\chi_k(x)\, e^{-ikx}$ for the same E

Quantum Mechanics (9)

Quantum Operators

(3) Position, $\hat{x}$:
Let $\psi_{\underline{x}_0}(\underline{x})$ be an eigenfunction of $\hat{x}$ with eigenvalue x_0.
$\hat{\underline{x}}\,\psi_{\underline{x}_0}(\underline{x}) = \underline{x}_0\,\psi_{\underline{x}_0}(\underline{x})$

Assertion (1D) : $\psi_{x_0}(x) = \delta(x - x_0)$
Formally, $x\,\delta(x - x_0) = x_0\,\delta(x - x_0)$

Completeness : $\psi(x) = \int_{-\infty}^{\infty} f(x_0)\,\delta(x - x_0)\,dx_0$
$\hat{x}\,\psi(x) = \int_{-\infty}^{\infty} f(x_0)\,\delta(x - x_0)\,x_0\,dx_0 = x\,f(x)$
$f(x) = \psi(x)$, $\hat{x}\,\psi(x) = x\,\psi(x)$

Norm $|\psi_{x_0}(x)|^2 = \delta(x - x_0)^2$
$\int_{-\infty}^{\infty} \delta(x - x_0)^2\,dx$ is not defined, so $\delta(x - x_0)$ is not normalisabl

(4) Parity Operator $\hat{P}$
1D : $\hat{P} f(x) = f(-x)$ 2D : $\hat{P} f(x,y) = f(-x,y)$ for examp
3D : $\hat{P} f(\underline{x}) = f(-\underline{x})$
Clearly, odd and even functions are eigenfunctions of $\hat{P}$ with eigenvalues ± 1. Note also that $\hat{P}^2 f(x) = f(x)$.

Properties/Definition of Hermitian Operators

A linear operator $\hat{O}$ is said to be Hermitian, if, for any 2 complex valued functions f, g, which obey appropriate boundary conditions (normalisability for Quantum Mechanics)

$$\int_V f^* \hat{O} g \, dV = \int_V (\hat{O} f)^* g \, dV$$

If $\hat{O}_1, \hat{O}_2$ are Hermitian, so is $\hat{O}_1 + \hat{O}_2$, $\hat{O}_1^{\,2}$, but not, in general $\hat{O}_1\hat{O}_2$.

Reality of Eigenvalues / Orthogonality of Eigenfunctions

Suppose $\hat{O}$ is Hermitian with discrete eigenvalues $\{\lambda_n\}$ with associated eigenfunctions $\{u_n\}$, $n = 1, 2, \ldots$

$\hat{O}\, u_n(\underline{x}) = \lambda_n u_n(\underline{x})$. Consider u_m, u_n:

$$\int_V u_m^* \hat{O} u_n \, dV = \int_V (\hat{O} u_m)^* u_n \, dV$$

If $m=n$, $(\lambda_m - \lambda_m)^* \int_V |u_m|^2 dV = 0$

$\Rightarrow \lambda_m - \lambda_m^* = 0$, λ_m is real for any m.

If $m \neq n$, $(\lambda_n - \lambda_m) \int_V u_m^* u_n \, dV = 0$

If the eigenvalues are not degenerate, then $\lambda_n - \lambda_m \neq 0$ and $\int_V u_m^* u_n \, dV = 0$, so u_m, u_n are orthogonal.

If u_m is normalised, we say that the u_m are orthonormal and

$$\int_V u_m^* u_n \, dV = \delta_{mn}$$

Note that if $\hat{O}$ has degeneracy, then at least one λ has more than one eigenfunction, then we can always orthogonalise using Gram-Schmidt so that $\int u_i^* u_j \, dV = \delta_{ij}$

Completeness

$$\Psi(\underline{x}) = \sum_n c_n u_n(\underline{x})$$

Inner Product (Scalar Product)

Define $\langle u_m, u_n \rangle = \int_V u_m^* u_n \, dV$

$$u_m \cdot \Psi(\underline{x}) = \int_V u_m^* \sum_{n=0}^{\infty} c_n u_n(\underline{x}) \, dV = c_n \delta_{mn} = c_m$$

Wavefunction Normalisation

$$\langle \Psi(\underline{x}), \Psi(\underline{x}) \rangle = \int_V \left(\sum_{n=0}^{\infty} c_n u_n\right)^* \left(\sum_{n=0}^{\infty} c_n u_n\right) dV = \sum_{m=0}^{\infty} |c_m|^2 = 1$$

Quantum Mechanics (10)

For a discrete set of eigenfunctions $u_n(\underline{x})$, we have
$\Psi(\underline{x}) = \sum_{n=0}^{\infty} c_n u_n(\underline{x})$. $\int_V u_n^* u_m \, dV = \delta_{mn}$

For a continuous set of eigenfunctions:
$\Psi(\underline{x}) = \int c(k) \, u(k, \underline{x}) \, dk$, $\int_V u^*(k_1, \underline{x}) \, u(k_2, \underline{x}) \, dV = \delta(k_1 -$

1. 1D Momentum Operator

$\hat{p} = -i\hbar \frac{d}{dx}$ gives a continuous set of eigenfunctions.

$$\int_{-\infty}^{\infty} f^*(x) \left(-i\hbar \frac{d}{dx}\right) g(x) \, dx = \int_{-\infty}^{\infty} \left(-i\hbar \frac{d}{dx} f(x)\right)^* g(x) \, dx$$
(integration by parts)

$k = p/\hbar$. Recall that $u_p(x) = \frac{1}{\sqrt{2\pi}} e^{ikx}$
$$\Psi(x) = \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi}} c(k) \, e^{ikx} \, dk$$

$$\langle u_p(k, x), u_{p'}(k', x) \rangle = \int_{-\infty}^{\infty} \frac{1}{2\pi} e^{ix(k'-k)} \, dx = \delta(k - k')$$

2. Hamiltonian Operator

The Hamiltonian Operator may give a discrete or continuous set of eigenfunctions depending on $U(\underline{x})$.

In 1D, $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x)$

$\langle f, \hat{H} g \rangle = \langle \hat{H} f, g \rangle$ (integration by parts, twice)

3. Position Operator

$\hat{x} f(x) = x f(x)$

4. Parity Operator $\hat{P}$

$\hat{P}g(x) = g(-x)$ Prove $\langle \hat{P}f, g \rangle = \langle f, \hat{P}g \rangle$ by change of variables.

$\Psi(x)$ can be expressed as $\alpha^+ u^+(x) + \alpha^- u^-(x)$, a two state system

Measurement in QM

i) The state of a system is described by $\Psi(\underline{x}, t)$

ii) Observables correspond to Hermitian operators $\hat{O}$

iii) Completeness $\Psi(\underline{x}, t) = \sum_{n=0}^{\infty} c_n(t) u_n(\underline{x})$

Measurement of $\hat{O}$, on Ψ returns an eigenvalue λ_n of $\hat{O}$ with probability $|c_n|^2$. After the measurement Ψ "collapses" into the $u_n(\underline{x})$ associated with the measured λ_n. Making a measurement means that the measurer "interacts" with the wavefunction, changing it into one of the eigenfunctions of $\hat{O}$.

Subsequent evolution of Ψ is determined by the Schrödinger Equation.

Expectation Values

$$\langle \hat{O} \rangle_\Psi = \sum_{n=0}^{\infty} (\text{eigenvalue } \lambda_n) \times (\text{probability of measuring } \lambda_n)$$

$$\langle \hat{O} \rangle_\Psi = \sum_{n=0}^{\infty} \lambda_n |c_n|^2 = \langle \Psi, \hat{O}\Psi \rangle$$

$\langle \hat{O} \rangle$ does not have to return an eigenvalue.

Quantum Mechanics (11)

Commutators and Uncertainty

Consider operators $\hat{O}_1$, $\hat{O}_2$ corresponding to 2 observables. Now, if Ψ is an eigenfunction of both $\hat{O}_1$, $\hat{O}_2$:

$$\hat{O}_1 \Psi = \lambda \Psi, \quad \hat{O}_2 \Psi = \gamma \Psi, \quad \hat{O}_1 \hat{O}_2 \Psi = \lambda \gamma \Psi = \gamma \lambda \Psi = \hat{O}_2 \hat{O}_1 \Psi$$

$[\hat{O}_1, \hat{O}_2] = \hat{O}_1 \hat{O}_2 - \hat{O}_2 \hat{O}_1$, the commutator of $\hat{O}_1$, $\hat{O}_2$

$[\hat{O}_1, \hat{O}_2] = -[\hat{O}_2, \hat{O}_1]$

If $\alpha \in \mathbb{C}$, $[\hat{O}_1, \alpha] = 0$

If Ψ is an eigenfunction of $\hat{O}_1$, $\hat{O}_2$ then $[\hat{O}_1, \hat{O}_2]\Psi = 0$. If Ψ can be expanded in both eigenfunctions of $\hat{O}_1$, $\hat{O}_2$, and $[\hat{O}_1, \hat{O}_2]\Psi = 0$, then $\hat{O}_1$, $\hat{O}_2$ share the same eigenfunctions, and we say that $\hat{O}_1$, $\hat{O}_2$ commute.

Theorem

If $[\hat{O}_1, \hat{O}_2]$ commute, and the eigenvalues of $\hat{O}_1$ are not degenerate, then the eigenfunctions of $\hat{O}_1$ are also eigenfunctions of $\hat{O}_2$.

Proof

Consider u_m, u_n, eigenfunctions of $\hat{O}_1$.

$$\int_{-\infty}^{\infty} u_m^* [\hat{O}_1, \hat{O}_2] u_n \, dx = 0$$

$$\Rightarrow \int_{-\infty}^{\infty} (u_m^* \hat{O}_1 \hat{O}_2 u_n - u_m^* \hat{O}_2 \hat{O}_1 u_n) \, dx = 0$$

$$\Rightarrow (\lambda_m - \lambda_n) \int u_m^* \hat{O}_2 u_n \, dx = 0$$

$m \neq n \Rightarrow \hat{O} u_n = \mu u_n$, and the u_n are simultaneous eigenfunctions of $\hat{O}_1$, $\hat{O}_2$.

Example : Commuting Operators

1D : Consider $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x)$ with $U(x) = U(-x)$.

$\hat{H}\chi_E(x) = E\chi_E(x)$, $\hat{H}\chi_E(-x) = E\chi_E(-x)$

$\hat{P} f(x) = f(-x)$

$$[\hat{P}, \hat{H}]\chi_E = \hat{P}\hat{H}\chi_E(x) - \hat{H}\hat{P}\chi_E(x)$$
$$= \hat{P}E\chi_E(x) - \hat{H}\chi_E(-x) = 0$$

For an unknown Ψ, making a first measurement using $\hat{O}_1$, we measure λ_n with probability $|c_n|^2$, if $\Psi \Rightarrow u_n$.
Making a further measurement using $\hat{O}_2$, we measure r_n with probability 1 if $[\hat{O}_1, \hat{O}_2] = 0$, so these measurements do not interfere.

Example : Non-Commuting Operators

$$[\hat{x}, \hat{p}]f = x\left(-i\hbar\frac{d}{dx}\right)f - \left(-i\hbar\frac{d}{dx}\right)(xf)$$
$$= -i\hbar x\frac{df}{dx} + i\hbar f + i\hbar x\frac{df}{dx} = i\hbar f = i\hbar \mathbb{1} f$$

identity operator

Uncertainty

We define $\Delta\hat{O}$, the uncertainty of $\hat{O}$, to be
$\Delta\hat{O} = \hat{O} - \langle\hat{O}\rangle\mathbb{1}$
$\langle(\Delta\hat{O})^2\rangle = \langle\hat{O}^2 + \langle\hat{O}\rangle^2 - 2\hat{O}\langle\hat{O}\rangle\rangle = \langle\hat{O}^2\rangle - \langle\hat{O}\rangle^2$

Consider normalised Ψ, where $\hat{O}\Psi = \lambda\Psi$
$\langle\hat{O}^2\rangle = \int_V \Psi^* \hat{O}^2 \Psi \, dV = \lambda^2 \int_V |\Psi|^2 dV = \lambda^2$
$\langle\hat{O}\rangle^2 = \left(\int_V \Psi^* \hat{O} \Psi \, dV\right)^2 = \left(\lambda \int_V |\Psi|^2 dV\right) = \lambda^2$
$\Rightarrow \langle(\Delta\hat{O})^2\rangle_\Psi = 0$ for an eigenfunction of $\hat{O}$, Ψ.

Quantum Mechanics (11)

If $[\hat{O}_1, \hat{O}_2] = 0$, then also $\langle(\Delta\hat{O}_2)^2\rangle_\psi = 0$ as ψ is also an eigenfunction of $\hat{O}_2$.

$[\hat{O}_1, \hat{O}_2] \neq 0$ means that there is a residual uncertainty when measuring $\hat{O}_1, \hat{O}_2$.

e.g. $[\hat{x}, \hat{p}] = i\hbar$, the Heisenberg Uncertainty Principle.

15/11/11

Quantum Mechanics (12)

Last time

$[\hat{x}, \hat{p}] = i\hbar \Rightarrow$ Uncertainty Principle

We want to show $\langle(\Delta\hat{x})^2\rangle\langle(\Delta\hat{p})^2\rangle \geq \frac{\hbar^2}{4}$

Let $[\hat{O}_1, \hat{O}_2] \neq 0$. Define $\hat{A} = \Delta\hat{O}_1 = \hat{O}_1 - \langle\hat{O}_1\rangle$, $\hat{B} = \Delta\hat{O}_2 = \hat{O}_2 - \langle\hat{O}_2\rangle$

Consider $\phi = \hat{A}\Psi + i\lambda\hat{B}\Psi$, $\lambda \in \mathbb{R}$. $\int|\Psi|^2 dx = 1$

$$I(\lambda) = \int_{-\infty}^{\infty} \phi^*\phi \, dx \quad \begin{matrix}\geq 0 \\ < \infty\end{matrix}$$

$$= \int_{-\infty}^{\infty} (\hat{A}\Psi + i\lambda\hat{B}\Psi)^*(\hat{A}\Psi + i\lambda\hat{B}\Psi)\, dx$$

$$= \int_{-\infty}^{\infty} \overset{①}{(\hat{A}\Psi)^*(\hat{A}\Psi)} + \lambda^2\overset{②}{(\hat{B}\Psi)^*(\hat{B}\Psi)} + i\lambda\overset{③}{[(\hat{A}\Psi)^*(\hat{B}\Psi) - (\hat{B}\Psi)^*(\hat{A}\Psi)]}$$

Use the fact that $\hat{A}, \hat{B}$ are Hermitian.

① $= \int_{-\infty}^{\infty} \Psi^* \hat{A}^2 \Psi \, dx$ ② $= \int_{-\infty}^{\infty} \Psi^* \hat{B}^2 \Psi \, dx$

③ $= i\lambda \int_{-\infty}^{\infty} \Psi^* (\hat{A}\hat{B} - \hat{B}\hat{A})\Psi \, dx = i\lambda \int_{-\infty}^{\infty} \Psi^* [\hat{A}, \hat{B}]\Psi \, dx$

$\langle \hat{A}^2 \rangle = \langle (\Delta\hat{O}_1)^2 \rangle (\in \mathbb{R}) = \alpha \qquad [\hat{A}, \hat{B}] = [\hat{O}_1, \hat{O}_2]$

$\langle \hat{B}^2 \rangle = \langle (\Delta\hat{O}_2)^2 \rangle (\in \mathbb{R}) = \beta$

$$I(\lambda) = \alpha + \lambda^2\beta + \cancel{I(\lambda)}\, i\lambda \int_{-\infty}^{\infty} dx \, \Psi^* [\hat{O}_1, \hat{O}_2]\Psi \geq 0$$

Choose $\hat{O}_1 = \hat{x}$, $\hat{O}_2 = \hat{p}$, $[\hat{x}, \hat{p}] = i\hbar$

$I(\lambda) = \alpha + \lambda^2\beta - \lambda\hbar \geq 0$

Minimum $\frac{dI}{d\lambda} = 0 \Rightarrow \lambda_{min} = \frac{\hbar}{2\beta}$

Hence $I(\lambda_{min}) = \alpha + \left(\frac{\hbar}{2\beta}\right)^2\beta - \frac{\hbar}{2\beta} \geq 0 \Rightarrow \alpha\beta \geq \frac{\hbar^2}{4}$

$$\langle(\Delta\hat{x})^2\rangle\langle(\Delta\hat{p})^2\rangle \geq \frac{\hbar^2}{4}$$

Heuristically: "$\Delta x \, \Delta p \gtrsim \frac{\hbar}{2}$"

In general if $i[\hat{O}_1, \hat{O}_2] \neq 0$ but is Hermitian, then

$$\langle(\Delta\hat{O}_1)^2\rangle\langle(\Delta\hat{O}_2)^2\rangle \geq \frac{1}{4}\langle i[\hat{O}_1, \hat{O}_2]\rangle$$

Gaussian Wave Packet Redux

The Gaussian Wave Packet is a state that minimises uncertainty.

$\Psi(x) = \left(\frac{1}{\pi}\right)^{\frac{1}{4}} e^{-\frac{x^2}{2}}$

$\langle \hat{x} \rangle = \int dx\, \Psi^* x \Psi^* = \sqrt{\frac{1}{\pi}} \int_{-\infty}^{\infty} x e^{-x^2} dx = 0$

$\langle \hat{p} \rangle = 0$ by symmetry.

$\langle \hat{x}^2 \rangle = \sqrt{\frac{1}{\pi}} \int_{-\infty}^{\infty} dx\, x^2 e^{-x^2} = \frac{1}{2}$

$\langle \hat{p}^2 \rangle = \sqrt{\frac{1}{\pi}} \int_{-\infty}^{\infty} (-\hbar^2) e^{-\frac{x^2}{2}} \frac{\partial^2}{\partial x^2} e^{-\frac{x^2}{2}} dx = \frac{1}{2}\hbar^2$

$\langle (\Delta \hat{x})^2 \rangle \langle (\Delta \hat{p})^2 \rangle = \frac{\hbar^2}{4}$

What about the Energy-Time Uncertainty Relationship?

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

"To measure some state's energy to accuracy ΔE, we need at least $\Delta t \geq \frac{\hbar}{2\Delta E}$" WRONG!!!

Reason: There is no operator with $i\hbar \frac{\partial}{\partial t}$, "$\hat{t}$" does not exist.

* Correct Interpretation * Given some $\hat{H}$ (with discrete spectrum), ΔE, and some initial state Ψ_E, then after some time Δt, the state ceases "to look like" Ψ_E.

$\Delta E \, \Delta t \approx \hbar$

depends on "look like"

* Non-relativistic QM * not invariant under $t \to -t$

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

$t \to -t$, $\frac{\partial}{\partial t} \to -\frac{\partial}{\partial t}$, $\Psi(x,t) \to \Psi(x,-t)$ *

15/4/11

Quantum Mechanics (12)

Schrödinger Equation in 3D (Spherically Symmetric Potential)

Time independant : $-\frac{\hbar^2}{2m}\nabla^2\Psi + U(\vec{x})\Psi = E\Psi$

3D Cartesian : $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

$U(\vec{x}) \to U(r)$, $r = \sqrt{x^2+y^2+z^2}$

Spherical Coordinates

$x = r\cos\varphi \sin\theta$ $\quad r \in [0, \infty)$

$y = r\sin\varphi \sin\theta$ $\quad \theta \in [0, \pi]$

$z = r\cos\theta$ $\quad \varphi \in [0, 2\pi)$

Laplacian : $\nabla^2 f = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial f}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 f}{\partial\varphi^2}$

$U(r,\theta,\varphi) = U(r)$

$\Psi_0(r,\theta,\varphi) = \Psi(r)$ Spherically Symmetric Solutions ("S" states)

$\frac{\partial}{\partial r} \to \frac{d}{dr}$

$$\nabla^2\chi(r) = \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\chi}{dr}\right) = \frac{2}{r}\frac{d\chi}{dr} + \frac{d^2\chi}{dr^2}$$

$$-\frac{\hbar^2}{2m}\left(\frac{2}{r}\frac{d\chi}{dr} + \frac{d^2\chi}{dr^2}\right) + U(r)\chi(r) = E\chi(r)$$

We impose normalisability : $\int_{\mathbb{R}^3}|\chi|^2 dV = \int_0^{2\pi}d\varphi\int_{-1}^{1}d(\cos\theta)\int_{-\infty}^{\infty}r^2|\chi|^2 dr$

$$\int_{\mathbb{R}^3}|\chi|^2 dV = 4\pi\int_{-\infty}^{\infty}r^2|\chi|^2 dr < \infty$$

Implies that $\chi(r) \to 0$ as $r \to \infty$, and $\chi(r)$ is bounded as $r \to 0$. Note $\left(\frac{2}{r}\frac{d\chi}{dr} + \frac{d^2\chi}{dr^2}\right) = \frac{1}{r}\frac{d^2}{dr^2}(r\chi)$

$S = r\chi(r)$

$$-\frac{\hbar^2}{2m}\frac{1}{r}\frac{d^2S}{dr^2} + U(r)\frac{S}{r} = E\frac{S}{r}$$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2S}{dr^2} + U(r)S = ES$$

Boundary $0 \le r < \infty$

$\chi(r)$ finite at $r = 0$. L'Hôpital : $\lim_{r\to 0}\frac{S(r)}{r} = \lim_{r\to 0}\frac{dS}{dr}$

Provided $S'(r)$ is finite as $r \to 0$, $S(r) \to 0$ as $r \to 0$

7/11/11

Quantum Mechanics (13)

We consider solutions to the Schröödinger equation in 3D with spherically symmetric potentials. We consider "S-states" with

$\psi(r, \theta, \varphi) = \chi(r)$

$\sigma(r) = r\chi(r)$ gives $-\frac{\hbar^2}{2m}\frac{d^2\sigma}{dr^2} + U(r)\,\sigma(r) = E\,\sigma(r)$

$0 \leq r < \infty$

$\chi(r) = O\left(\frac{1}{r^2}\right)$ as $r \to \infty \Rightarrow \sigma(r) \to 0$

$\chi(r)$ finite as $r \to 0 \Rightarrow \sigma(0) = 0$, $\sigma'(0)$ finite.

Normalisability $\int_0^\infty |\sigma|^2\,dr < \infty \Rightarrow \int_0^\infty r^2 |\chi|^2\,dr < \infty$

Bound state solutions $E < U_{max}$

Method $U(r) \to U(-r)$. We will solve the Schröödinger equation for potential $U(r) = U(-r)$, for $r \in (-\infty, \infty)$ (giving parity states).

Boundary condition $\sigma(0) = 0 \Rightarrow$ odd parity states are solutions.

Examples

(1) Spherical Box $U(r) = \begin{cases} 0 & 0 \leq r \leq \frac{a}{2} \\ \infty & r > \frac{a}{2} \end{cases}$

Odd solutions. $\sigma_1(r) = r\chi_1(r) = \sqrt{\frac{2}{a}}\sin\left(\frac{2\pi r}{a}\right)$, $E_1 = \frac{2\hbar^2\pi^2}{ma^2}$

$\sigma_2(r) = r\chi_2(r) = \sqrt{\frac{2}{a}}\sin\left(\frac{4\pi r}{a}\right)$, $E_2 = \frac{8\hbar^2\pi^2}{ma^2}$

Simple Spherically Symmetric Harmonic Oscillator

$U(r) = \frac{1}{2}m\omega^2 r^2, \quad 0 \leq r < \infty$

Spectrum $E_N = (N + \frac{1}{2})\hbar\omega = \frac{3}{2}\hbar\omega, \frac{7}{2}\hbar\omega, \ldots$ (odd states only)

Wavefunctions, $y = \sqrt{\frac{m\omega}{\hbar}}\,r$, $\sigma_1 = y e^{-\frac{y^2}{2}}$

The Hydrogen Atom !! (Angular momentum operator)

$U(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$ Coulomb Potential

as $r \to \infty$, $U(r) \to 0$

$\Rightarrow$ "$E = 0$" is such that a particle at rest has 0 energy.

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(r,\theta,\varphi) + U(r)\Psi(r,\theta,\varphi) = E\Psi(r,\theta,\varphi)$$

$$-\frac{\hbar^2}{2m}\left(\frac{2}{r}\frac{\partial\Psi}{\partial r} + \frac{\partial^2\Psi}{\partial r^2}\right) - \frac{1}{2mr}\underbrace{\left[\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right) + \frac{\hbar^2}{\sin^2\theta}\frac{\partial^2\Psi}{\partial\varphi^2}\right]}_{-\hat{L}^2\Psi}$$

$$-\frac{e^2}{4\pi\varepsilon_0 r}\Psi(r,\theta,\varphi) = E\Psi(r,\theta,\varphi)$$

$\hat{L}^2$: total angular momentum operator

General Solution $\Psi(r,\theta,\varphi) = \chi_{En}(r)\,Y_{lm}(\theta,\varphi)$

- n is the principal quantum number
- L is the total Angular momentum number $\rightarrow$ $\begin{pmatrix} s & p & d & f & \\ l=0 & 1 & 2 & 3 & \text{etc} \end{pmatrix}$
- m is the magnetic Quantum number

S-states (those were $\hat{L}^2\Psi = 0$)

Define $\nu^2 = -\frac{2mE}{\hbar^2} > 0$, $\beta = \frac{e^2 m_e}{2\pi\varepsilon_0\hbar^2} > 0$

Look for Bound States $E < 0$

$$\frac{d^2\chi}{dr^2} + \frac{1}{r}\left(2\frac{d}{dr} + \beta\right)\chi - \nu^2\chi = 0$$

As $r \to \infty$, $\frac{d^2\chi}{dr^2} \approx \nu^2\chi$

As $r \to \infty$, $\chi(r) \approx e^{\pm\nu r}$, so we take $e^{-\nu r}$

We guess (ansatz) $\chi(r) = f(r)e^{-\nu r}$

$$\frac{d^2f}{dr^2} + \frac{2}{r}(1-\nu r)\frac{df}{dr} + \frac{1}{r}(\beta - 2\nu)f = 0$$

Unlike with simple harmonic motion in 1D, $r=0$ is not an ordinary point, but it is a regular singular point, so we can find a solution $f(r)$ such that $f(r) = r^s\sum_{n=0}^{\infty} a_n r^n$

We want to find S such that the lowest power r term vanishes.

$$\sum_n (s+n)(s+n-1)a_n r^{n+s-2} + 2(1-\nu r)\sum(s+n)a_n r^{n+s-2} + (\beta-2\nu)\sum_n a_n r^{n+s-1} = 0$$

Coefficient for lowest power r: $s(s-1) + 2s = 0$

(Indicial equation) Independent of ν, β

17/11/11

Quantum Mechanics (13)

2 roots, $s = 0, -1$.

For $s = -1$, $\chi(r \to 0) \sim \frac{1}{r} e^{-\nu r}$ (does not obey our boundary conditions)

$$f(r) = \sum_{n=0}^{\infty} a_n r^n \qquad a_n = \frac{(2\nu n - \beta)}{n(n+1)} a_{n-1}$$

[N.B. For Simple Harmonic oscillation $a_n = f(n) a_{n-2} \Rightarrow$ odd, even series.

Here we have only 1 series. As $n \to \infty$ $\frac{a_n}{a_{n-2}} \to \frac{2\nu}{n}$

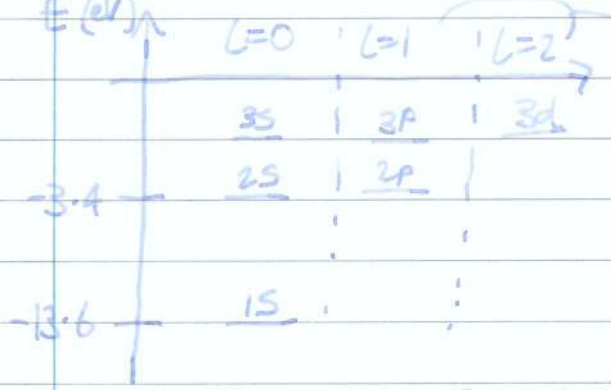
As with simple harmonic oscillation, if the series does not terminate then since $e^{2\nu r} = \sum \frac{(2\nu)^n}{n!} r^n \Rightarrow \left(\frac{(2\nu)^n}{n!}\right) \div \left(\frac{(2\nu)^{n-1}}{(n-1)!}\right) = \frac{2\nu}{n}$

$\chi(r) = f(r) e^{-\nu r} \to e^{\nu r}$ for large n, but this is not normalisable!

So $\exists N > 0$ such that $a_n = 0 \ \forall n > N$.

Using our recurrence relations, we have $2\nu N = \beta$

$$E_n = -\frac{\hbar^2}{2m}\nu^2 = -\frac{\hbar^2}{2m}\left(\frac{e^2 m_e}{4\pi\epsilon_0 \hbar^2}\right)\left(\frac{1}{N^2}\right) \quad \text{for } N = 1, 2, 3, \ldots$$



$\to \hat{L}^2\psi \neq 0$

Wavefunctions (for S states)

$\nu = \frac{\beta}{2N}$, $\frac{a_n}{a_{n-1}} = -2\nu\left(\frac{N-n}{n^2+n}\right)$

$N=1$, $a_0 = 1$, $\chi_1(r) = e^{-\nu r}$

$N=2$, $a_0 = 1$, $a_1 = -\nu$ $\quad \chi_2(r) = (1-\nu r)e^{-\nu r}$

$N=3$, $\quad \chi_3(r) = (1 - 2\nu r + \frac{2}{3}(\nu r)^2) e^{-\nu r}$

$$\chi_N(r) = \underbrace{f_N(r)}_{\text{Laguerre Polynomials}} e^{-\nu r}$$

22/11/11

Quantum Mechanics

Angular Momentum (Operator methods)

Classical Mechanics

$\vec{L} = \vec{x} \times \vec{p}$

Quantum Mechanics

$\hat{L} = \hat{x} \times \hat{p}$ "Give them hats" "Promote $\vec{x} \to \hat{x}$, $\vec{p} \to \hat{p}$"

Then $\hat{L}$ is the angular momentum operator.

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

$L_x = -i\hbar \left(\hat{y} \frac{\partial}{\partial z} - \hat{z} \frac{\partial}{\partial y} \right)$ etc

What are the properties of QM angular momentum operator?

- Hermitian
- They do not commute with each other

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

Different components of the angular momentum cannot be measured simultaneously to arbitrary accuracy. ($[\hat{x}, \hat{p}] = i\hbar$)

Some Operator identities

1. $[\hat{A} - \hat{B}, \hat{C}] = [\hat{A}, \hat{C}] - [\hat{B}, \hat{C}]$
2. $[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$
3. If $\hat{C}$ commutes $\hat{A}$, $\hat{B}$, then
   $[\hat{A}, \hat{B}\hat{C}] = \hat{C}[\hat{A}, \hat{B}] = [\hat{A}, \hat{B}]\hat{C}$
4. Jacobi Identity:
   $[\hat{A}, [\hat{B}, \hat{C}]] + [\hat{B}, [\hat{C}, \hat{A}]] + [\hat{C}, [\hat{A}, \hat{B}]] = 0$

$$[\hat{L}_x, \hat{L}_y] = [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z]$$
$$= {}_{①}[\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] - \cancel{[\hat{y}\hat{p}_z, \hat{x}\hat{p}_z]} - \cancel{[\hat{z}\hat{p}_y, \hat{z}\hat{p}_x]} + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z]_{②}$$

$[\hat{x}_i, \hat{x}_j] = 0$

$[\hat{p}_i, \hat{p}_j] = 0$ $[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$

$\cancel{[\hat{L}_x, \hat{L}_y]}$ ① $[\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] = \hat{y}\hat{p}_x[\hat{p}_z, \hat{z}]$

② $[\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] = \hat{x}\hat{p}_y[\hat{z}, \hat{p}_z]$

$$[\hat{L}_x, \hat{L}_y] = \hat{y}\hat{p}_x[\hat{p}_z, \hat{z}] + \hat{x}\hat{p}_y[\hat{z}, \hat{p}_z]$$

$$= i\hbar(\hat{p}_y\hat{x} - \hat{y}\hat{p}_x) = i\hbar\hat{L}_z$$

<u>Total Angular Momentum</u>

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

$\hat{L}^2$ is Hermitian. $\quad [\hat{L}_i, \hat{L}^2] = 0$

For the x component:

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

$= i\hbar(\hat{L}_z\hat{L}_y + \hat{L}_y\hat{L}_z)$

$[\hat{L}_x, \hat{L}_z^2] = -i\hbar(\hat{L}_y\hat{L}_z + \hat{L}_z\hat{L}_y)$

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

<u>Levi-Civita Symbol</u> ε_{ijk} $\quad$ ¡NO SC!

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

Commutator of $\hat{L}$ and $\hat{x}, \hat{p}$:

$[\hat{L}_i, \hat{x}_m] = \varepsilon_{ijk}\hat{x}_j\hat{p}_k\hat{x}_m - \varepsilon_{ijk}\hat{x}_m\hat{x}_j\hat{p}_k$

$([\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij})$ $\quad = \varepsilon_{ijk}\hat{x}_j(\hat{x}_m\hat{p}_k - i\hbar\delta_{mk}) - \varepsilon_{ijk}\hat{x}_m\hat{x}_j\hat{p}_k$

$= -i\hbar\varepsilon_{ijm}\hat{x}_j = i\hbar\varepsilon_{imj}\hat{x}_j$

It can be shown that $[\hat{L}_i, \hat{x}_j^2] = 2i\hbar\varepsilon_{ijk}\hat{x}_j\hat{x}_k$

$\Rightarrow [\hat{L}_i, \hat{x}_1^2 + \hat{x}_2^2 + \hat{x}_3^2] = 0$

$[\hat{L}_i, \hat{p}_j] = i\hbar\varepsilon_{ijk}\hat{p}_k$, $[\hat{L}_i, \hat{p}_j^2] = 2i\hbar\varepsilon_{ijk}\hat{p}_j\hat{p}_k$

$\Rightarrow [\hat{L}_i, \hat{p}_1^2 + \hat{p}_2^2 + \hat{p}_3^2] = 0$

22/11/11

Quantum Mechanics

Angular momentum with spherically symmetric potentials

Classically, $\frac{dL}{dt} = 0$, $U(r, \theta, \varphi) = U(r)$

Constants of motion in classical mechanics usually lead to observables in Quantum Mechanics which commute with $\hat{H}$.

$\hat{H} = \frac{\hat{p}^2}{2m} + U(\hat{r})$, $\hat{r} = \sqrt{\hat{x}^2 + \hat{y}^2 + \hat{z}^2}$

Using commutator relations: $[\hat{H}, \hat{L}] = [\frac{1}{2m}|\hat{p}|^2 + U(\hat{r}), \hat{L}] = 0$

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

$\hat{H}$, $\hat{L}^2$ and any one of $\hat{L}_x, \hat{L}_y, \hat{L}_z$ must form a set of three mutually commuting observables

$\Rightarrow$ We can find simultaneous eigenfunctions for all 3.

We ~~can~~ only choose $\hat{L}_z$ because it doesn't commute with $\hat{L}_y, \hat{L}_x$.

$\hat{L}_x = i\hbar(\cos\varphi \cot\theta \frac{\partial}{\partial\varphi} + \sin\varphi \frac{\partial}{\partial\theta})$

$\hat{L}_y = i\hbar(\sin\varphi \cot\theta \frac{\partial}{\partial\varphi} - \cos\varphi \frac{\partial}{\partial\theta})$

$\hat{L}_z = -i\hbar \frac{\partial}{\partial\varphi}$

24/11/11

Quantum Mechanics (15)

Last time

$\hat{H}, \hat{\underline{L}}^2, \hat{L}_z$ mutually commute. We wish to find simultaneous eigenfunctions for all 3 operators. We start by looking for simultaneous eigenfunctions for $\hat{\underline{L}}^2, \hat{L}_z$

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

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$$

$\exists\, Y(\theta,\varphi)$ such that $\hat{L}_z Y(\theta,\varphi) = m\hbar\, Y(\theta,\varphi)$

$\hat{\underline{L}}^2 Y(\theta,\varphi) = \lambda\hbar\, Y(\theta,\varphi)$, $\lambda \geq 0$

We guess $Y(\theta,\varphi) = A(\theta)e^{im\varphi}$

$\hat{L}_z Y(\theta,\varphi) = -i\hbar\frac{\partial}{\partial\varphi}\left[A(\theta)e^{im\varphi}\right] = m\hbar\, Y(\theta,\varphi)$

Periodicity: $Y(\theta,\varphi) = Y(\theta,\varphi+2\pi) \Rightarrow e^{im2\pi} = 1$

So $m \in \mathbb{Z}$. (Bohr Quantisation, $J = m\hbar$) $\boxed{\text{N.B. } m \text{ can also be } \tfrac{1}{2} \text{ integer valued}}$

Total Angular Momentum

Substitute $Y(\theta,\varphi) = A(\theta)e^{im\varphi}$

$\hat{\underline{L}}^2 Y(\theta,\varphi) = \lambda\hbar^2 Y(\theta,\varphi)$. We obtain

$$\left[-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial A}{\partial\theta}\right) + \frac{m^2}{\sin^2\theta}A(\theta) = \lambda A(\theta)\right]e^{im\varphi}$$ ← Associated Legendre Equation

Non-singular (normalisable) solution: Legendre Polynomial

$A(\theta) = (\sin\theta)^{|m|}\left(\frac{d}{d\cos\theta}\right)^{|m|}P_l(\cos\theta) = P_{l,m}(\cos\theta)$ ~~Assoc~~

$\hat{\underline{L}}^2 Y(\theta,\varphi) = l(l+1)\hbar^2 Y(\theta,\varphi)$, $\lambda = l(l+1) \geq 0 \Rightarrow l \geq 0$

$A(\theta) \Rightarrow A_{l,m}(\theta)$, $Y(\theta,\varphi) \rightarrow Y_{l,m}(\theta,\varphi)$ (Spherical Harmonics)

Restriction: For every l value, $|m| \leq l$. In other words, there is a $2l+1$ degeneracy in m.

$$Y_{l,m}(\theta,\varphi) = (-1)^m \left[\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}\right]^{\frac{1}{2}} P_{l,m}(\cos\theta)\, e^{im\varphi}$$

$m \geq 0$, $\quad P_{l,m}(\cos\theta) = (-1)^{l+m} \frac{(l+m)!}{(l-m)!} \frac{(\sin\theta)^{-m}}{2^l l!} \left(\frac{d}{d\cos\theta}\right)^{l-m} (1-\cos^2\theta)^l$

$m < 0$ $\quad P_{l,-m} = (-1)^m \frac{(l-m)!}{(l+m)!} P_{l,m}$

We have orthonormality : $\int_{S_2} d\Omega\, Y^*_{lm} Y_{l'm'} = \delta_{ll'}\delta_{mm'}$

Some eigenfunctions : $Y_{0,0} = \frac{1}{\sqrt{4\pi}}$, $Y_{2,2} = \sqrt{\frac{15}{32\pi}}\, e^{2i\varphi} \sin^2\theta$

$\Psi(\theta,\varphi) = \sum_l \sum_{m=-l}^{l} c_{lm} Y_{lm}$ where $c_{lm} = \langle Y_{lm}, \Psi(\theta,\varphi)\rangle$
(as the eigenfunctions are complete)

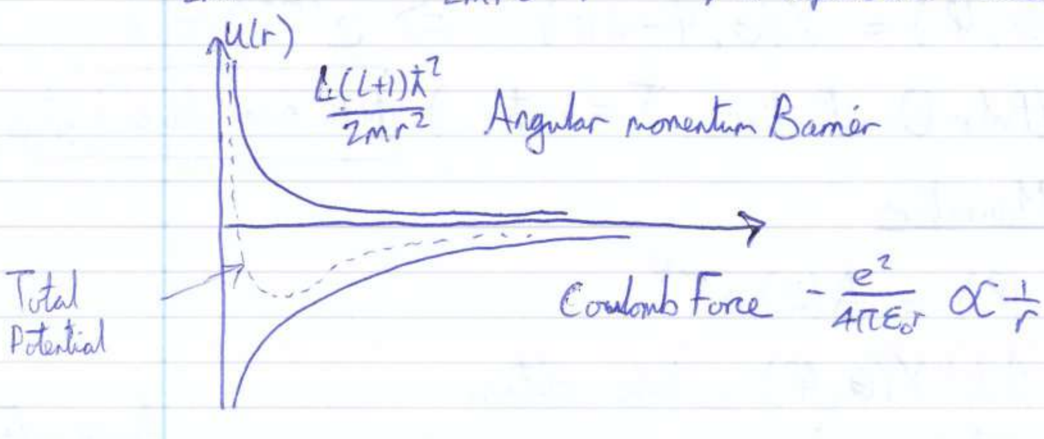
The Hydrogen Atom in Full

$$\hat{H}_{Total} = -\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right) - \frac{e^2}{4\pi\varepsilon_0 r} + \frac{\hat{L}^2}{2mr^2}$$

Simultaneous eigenfunctions: $\Psi(r,\theta,\varphi) = \chi(r)\, \underbrace{Y_{lm}(\theta,\varphi)}$

Eigenfunction for $\hat{L}^2$, $\hat{L}_z$

$\frac{\hat{L}^2}{2mr^2}\Psi = \frac{l(l+1)\hbar^2}{2mr^2}\Psi$, a repulsive Force



<u>Step 1</u> Find the solution as $r \to \infty$ $\qquad \nu^2 = -\frac{2mE}{\hbar^2}$

Normalisability $\Rightarrow \chi(r\to\infty) = e^{-\nu r}$ $\qquad \beta = \frac{e^2 m_e}{2\pi\varepsilon_0\hbar^2}$

<u>Step 2</u> Guess $\chi(r) = f(r)\, e^{-\nu r}$

We then look for a power series solution for f.

$$\frac{d^2 f}{dr^2} + \frac{2}{r}(1-\nu r)\frac{df}{dr} + \frac{1}{r}(\beta - 2\nu) f = \frac{l(l+1)}{r^2} f$$

We try $f(r) = r^s \sum_{n=0}^{\infty} a_n r^n$

Indicial Equation : $l(l+1) = s(s+1)$

roots : $s = l, -l-1$. We take $s = l$ for a normalisable solution.

/11 # Quantum Mechanics (15)

Step 3

Find a recurrence relation. $a_n = \frac{2\nu(n+L)-\beta}{n(n+2L+1)} a_{n-1}$

We recover spherically symmetric states for $L=0$ (s states)

Step 4

Show that the series terminates (Exactly the same as the s-states solution)

$\frac{a_n}{a_{n-1}} \to \frac{2\nu}{n}$. $\exists N > 0$ such that $a_n = 0$ for $n > N$.

$\Rightarrow 2\nu(N+L) - \beta = 0$

$q \equiv N+1$
$L < q$

Step 5 Find the energy spectrum.

$E_q = \left(-\frac{e^4 m_e}{32\pi^2 \varepsilon_0^2 \hbar^2}\right)\frac{1}{q^2}$, $q = 1,2,3,\ldots$ the same as before.

Step 6

$\chi_q(r) = L_q(\nu r)e^{-\nu r}$ (Laguerre Polynomial)

$\Psi_{q,L,m}(r,\theta,\varphi) = L_q(\nu r)\, e^{-\nu r}\, Y(\theta,\varphi)$

$\hat{H}\Psi_{q,L,m} = E_q \Psi_{q,L,m}$, $\hat{L}_z \Psi_{q,L,m} = m\hbar \Psi_{q,L,m}$

$\hat{\underline{L}}^2 \Psi_{q,L,m} = L(L+1)\hbar^2 \Psi_{q,L,m}$

$q = 1,2,3\ldots$ Principal Quantum Number

$L = 0,1,2,\ldots$ Total Angular Momentum quantum number, $L < q$

$m = -L, -L+1, \ldots, 0, 1, 2, \ldots, L$ magnetic angular momentum quantum number

Degeneracy: For each q, $D(q) = \sum_{L=0}^{q-1}(2L+1) = q^2$

29/11/11

Quantum Mechanics 16

Vector / Matrix Analogy

Choose a basis $\underline{A} = a_1 \underline{e_1} + a_2 \underline{e_2}$, $a_1 = \underline{e_1} \cdot \underline{A}$, $a_2 = \underline{e_2} \cdot \underline{A}$

$\{\underline{e_1}', \underline{e_2}'\}$ is related to $\{\underline{e_1}, \underline{e_2}\}$ by $\underline{e_i}' = R_{ij} \underline{e_j}$ (SC !!!)

Quantum Mechanics and Vectors

(wavefunction)

Quantum Mechanical Physical states can be described by an N-dimensio[nal]

complex vector. $\Psi = \sum_{i=1}^{N} \alpha_i e_i$, $\alpha_i \in \mathbb{C}$

$O_{ij} = O_{ji}^*$

An Hermitian Operator $\hat{O}\Psi \Rightarrow \Psi'$ has an Hermitian matrix O_{ij} $(N \times N)$

Real eigenvalues λ_i, $\det(O_{ij} - \lambda_i I) = 0 \leftarrow$ zero

If the λ_i are distinct, then we have non-degeneracy.

If the λ_i are not distinct, we have degeneracy.

Orthogonality $\underline{e_i} \cdot \underline{e_j} = \delta_{ij}$

Inner product $\Psi \cdot \phi = \Psi^{\dagger} \phi$

O can be diagonalised. Eigenvectors $\Leftrightarrow$ Eigenfunctions

2 state systems

A Quantum cat can be happy or sad.

$\underline{e}_{\smile} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ $\underline{e}_{\frown} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

$\Psi_{cat} = \alpha_{\smile} \underline{e}_{\smile} + \alpha_{\frown} \underline{e}_{\frown}$ $|\alpha_{\smile}|^2 + |\alpha_{\frown}|^2 = 1$

$P_{\smile} = |\alpha_{\smile} \underline{e}_{\smile}|^2 = |\alpha_{\smile}|^2$, $P_{\frown} = |\alpha_{\frown} \underline{e}_{\frown}|^2 = |\alpha_{\frown}|^2$

$\Psi_{cat}' = A' \Psi_{cat}$

$A_{ij} \Psi_j = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \left(\alpha_{\smile} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \alpha_{\frown} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right)$

$= \Psi_j'$

Doing something to the cat.

Let P_{ij} be some Hermitian operator (corresponding to the cat being fed)

$P\Psi_{\frown} = \Psi_{\smile}$, $P\Psi_{\smile} = \Psi_{\frown}$

$P_{ij} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ (Hermitian)

Opening the box $\iff$ Making a measurement

$\Psi_{cat} = \alpha_{\smile} \underline{e}_{\smile} + \alpha_{\frown} \underline{e}_{\frown}$ Collapses the wavefunction

<u>Ammonia</u> NH_3

"Up"

"Down"

<u>Hamiltonian Matrix</u> H_{ij} (Generates motion)

$\Psi_i'(t+\Delta t) = U_{ij}(t+\Delta t, t)\Psi_j(t)$

Evolution Operator

$\Delta t \to 0$, $U_{ij}(t,t) = 1$

$U_{ij}(t+\Delta t, t) = U_{ij}(t,t) - \frac{i}{\hbar} H_{ij}\Delta t$

$\frac{\Psi_i(t+\Delta t) - \Psi_i(t)}{\Delta t} = -\frac{i}{\hbar} H_{ij}\Psi_j(t)$

$i\hbar \frac{d\Psi_i}{dt} = H_{ij}\Psi_j(t)$ Generalisation of the Schrödinger Equation

H_{ij} is Hermitian. $H_{ij}U_j = E_{(i)}U_i \longleftarrow$ Eigenvectors (stationary states)

Energy of eigenvector i

A special basis is the energy basis with stationary states as a basis

<u>Evolution of states of Ψ in time</u>

Let $\Psi = \begin{pmatrix} \alpha_1(t) \\ \alpha_2(t) \\ \vdots \end{pmatrix}_E$ $\quad i\hbar \frac{d\Psi_i}{dt} = H_{ij}\Psi_j$

29/11/11

Quantum Mechanics ⑯

$$a_i(t) = a_i(0)\exp\left[-\frac{i}{\hbar}E_i t\right]$$

$$\Psi(t) = \sum_{i=1}^{N} a_i(0)\exp\left[-\frac{i}{\hbar}E_i t\right]$$

Knowing the Hamiltonian allows the equation to be solved.