# Quantum Mechanics Notes

## *The Basics of Quantum Mechanics*

*Schrödinger*

$$\underbrace{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}}_{\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}} + V(x)\psi = E\psi$$

spherical: $\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2$

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$

V is constant $\Rightarrow$

$\psi = e^{ikx} = \cos kx + i\sin kx$ $\qquad k = \left(\frac{2m(E-V)}{\hbar^2}\right)^{1/2}$

$\lambda = 2\pi/k$, & $E - V$ = kinetic energy $\therefore k = \left(\frac{2mE_k}{\hbar^2}\right)^{1/2}$

$E_k = \frac{k^2\hbar^2}{2m}$ & $E_k = p^2/2m$

$p = k\hbar$

$p = \frac{2\pi}{\lambda} \times \frac{h}{2\pi} = \frac{h}{\lambda}$.

*The Born Interpretation*

$\psi$ at a point x, has a probability for a particle being between x and x+dx proportional to $|\psi|^2$dx. Therefore,

$$N^2\int \psi^*\psi \, d\tau = 1$$

$$\Omega\psi = \omega\psi$$

$\Omega$ = eigenvalue and $\psi$ = eigenfunction.
When not an eigenfunction, must be a superposition or more than one wave function.

*Particle in a Box*

$\psi_n(x) = C\sin kx + D\cos kx$ $\qquad E_k = \frac{k^2\hbar^2}{2m}$

Boundary Conditions, $\psi = 0$ at $x = 0, L$.

$D = 0$.

$\psi(x) = C\sin kx$, $x = L$. $C = 0$ conflict with Born Int.

$0 = C\sin kL$, $\quad kL = n\pi$.

$\psi_n(x) = C\sin\frac{n\pi x}{L}$.

$$E_n = \frac{\left(\frac{n\pi}{L}\right)^2\hbar^2}{2m} = \frac{n^2h^2}{8mL^2}$$

$C = (2/L)^{1/2}$ by Normalisation.

Deriving Energies: $\quad L = n \times \frac{1}{2}\lambda \qquad \lambda = \frac{2L}{n}$.

$p = h/\lambda = \frac{nh}{2L}$.

$E_n = \frac{p^2}{2m}$, $= \frac{n^2h^2}{8mL^2}$.

Tunnelling – possibility of finding particle outside box classically forbidden.

*Vibrational Motion*

$V = \frac{1}{2}kx^2$.

$E_v = (v + \frac{1}{2})\hbar\omega \qquad \omega = \left(\frac{k}{m}\right)^{1/2}$

$\Delta E = \hbar\omega$. $\qquad E_0 = \frac{1}{2}\hbar\omega$.

Form:

$\psi(x) = N \times \underbrace{(\text{polynomial in } x)}_{\text{Hermite (orthogonal)}} \times \underbrace{(\text{Gaussian function})}_{e^{-x^2}}$

Error function, $\text{erf}\, z = 1 - \frac{2}{\pi^{1/2}}\int_z^\infty e^{-y^2}dy$.

$P = \int_z^\infty \psi_0^2\, dx = \alpha N^2 \int_1^\infty e^{-y^2}dy$

combined: used to give probability of error.

*Rotational Motion*

$$E = \frac{p^2}{2m}, \quad J = \pm pr \Rightarrow E = \frac{J^2}{2I}$$

ang mom

$$J_z = \pm \frac{hr}{\lambda} \qquad \lambda = \frac{2\pi r}{m_l}$$

$$J = \frac{m_l h}{2\pi} \qquad E = \frac{m_l^2 \hbar^2}{2I}$$

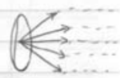
Cyclic boundary condition: $\psi(\phi + 2\pi) = \psi(\phi)$

Gives wavefunctions like:

$$\psi_{m_l}(\phi) = \frac{e^{im\phi}}{(2\pi)^{1/2}} \qquad m_l = \pm \frac{(2IE)^{1/2}}{\hbar}$$

$$E = l(l+1)\frac{\hbar^2}{2I} \qquad l, l-1 \dots; -l$$

$m_l = 2l + 1$.



*Spectroscopy*

$$\tilde{\nu} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

RITZ COMBINATION PRINCIPLE:

wavenumber at any spectral line is the difference b/w 2 terms – $T_n = \frac{R_H}{n^2}$.

$\therefore \quad \tilde{\nu} = T_{n'} - T_n$.

*Hydrogenics*

$$H = \hat{E}_{K,electron} + \hat{E}_{K,nucleus} + \hat{V}$$

$$= -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$R_{n,l}(r) = N_{n,l}\left(\frac{\rho}{n}\right)^l L_{n,l}\, e^{-\rho/2n} \qquad \rho = \frac{2Zr}{a_0}.$$

Ionisation Energy ← $E_n = -\frac{hcR_{atom}}{n^2}$ $\quad hcR_{atom} = \frac{Z^2\mu e^4}{32\pi^2\varepsilon_0^2\hbar^2} \qquad a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$

$$R_H = \frac{\mu_H}{m_e} R$$

Radial Distribution – independent of $\theta, \phi$.

$$P(r) = 4\pi r^2 \psi^2.$$

$$P(r) = r^2 R(r)^2.$$

Spin Orbit Coupling

Electron has spin angular momentum, and this generates a magnetic field.

Spin + orbit interactions – $j = l \pm ½$

Multiplicity = 2S + 1

## ***Postulates of Quantum Mechanics***

**1a:** the state of a system of N particles is fully described by a function $\psi(r_1, r_2, \dots r_N; t)$ – the wavefunction.

NOTES:

Spin omitted (for now).

**1b:** Born's Probabilistic Interpretation.

The probability that a system in a state $\psi$ will be found in the volume element $d\tau = dr_1\, dr_2 \dots dr_N$ is $\psi^*(r_1 \dots r_N, t)\, \psi(r_1 \dots r_N, t)\, d\tau$.

NOTES:

Statistical, even for 1 particle.

$P(x,t) = |\psi(x,t)|^2$ is the probability density.

Can deduce from here:

*Normalisation –*

$$\int_{\substack{all\\space}} |\psi(r_1...r_N, t)|^2 \; d\tau = 1$$

Conserves probability.

Physically acceptable $\psi$:

- Single valued.
- Continuous.
- Finite.

***Dirac's Bra-c-ket Notation –***

$$\int \psi^* \hat{A} \, \psi \, d\tau \equiv \langle \psi | \hat{A} | \psi \rangle$$
$$\int \psi^* \psi \, d\tau \equiv \langle \psi | \psi \rangle$$

(i.e. left hand side is conjugate wf

**2a:** in quantum mechanics, observables are represented mathematically by operators: corresponding to every classical observable A there is a corresponding operator Â which is linear and hermitian.
NOTES: e.g. x, $p_x$, E, etc.

**3:** Measurement. When a system is in a state described by $\psi$:

i) single measurement of an observable A always yields a single result – an eigenvalue $a_n$ of Â.

ii) Mean value of A equals the expectation value <Â>

*Define Expectation Value:*

$$\langle \hat{A} \rangle = \frac{\int \psi^* \hat{A} \psi \, d\tau}{\int \psi^* \psi \, d\tau} \equiv \int \psi^* \hat{A} \psi \, d\tau \qquad \text{[ if } \psi \text{ is normalised ]}$$

*Bra-c-ket:*

$$\langle \hat{A} \rangle = \langle \psi | \hat{A} | \psi \rangle \text{ if } \langle \psi | \psi \rangle = 1.$$

NOTES:
From (i) – Probability Distribution:

Common Sense, as mean A = sum over all n of $P_n a_n$.


From (ii) – must expand $\psi$ in terms of eigenfunctions of Â.

$$\psi = \sum_n c_n f_n$$

$$\hat{A}\mathbf{f}_n = a_n f_n$$

$$\langle \hat{A} \rangle = \int \psi^* \hat{A} \psi \, d\tau = \sum_{n,m} c_n{}^* c_m \int f_n{}^* \hat{A} f_m \, d\tau = \sum_n |c_n|^2 \, a_n$$

i.e. $P_n = |c_n|^2$

Probability $P_n$ that particular value $a_n$ is measures is $|c_n|^2$, where $c_n$ is the coefficient of eigenfunction $f_n$ of Â (in the expansion).

Dispersion in distribution of measurements is characterised by:
Root mean square deviation (RMS) $\Delta A$ =

$$(\Delta A)^2 = \langle (\hat{A} - \langle \hat{A} \rangle)^2 \rangle = \langle (\hat{A}^2 - 2\hat{A} \langle \hat{A} \rangle + \langle \hat{A} \rangle^2 ) \rangle$$
$$(\Delta A)^2 = \langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2$$

<u>Special Case –</u>
$\psi$ is an eigenfunction of $\hat{A}$, so $\hat{A}\psi = a\psi$. $\langle \hat{A} \rangle$ is:

$$\langle \hat{A} \rangle = \int \psi^* \hat{A} \psi \, d\tau = a_\varepsilon \int \psi^* \psi \, d\tau = a_\varepsilon$$

$P_n = 1$ or $0$ ($n=\varepsilon$ or $n \neq \varepsilon$), then dispersion free – single measure value, $a_\varepsilon$. $\langle \hat{A} \rangle = a_\varepsilon$, $\langle \hat{A}^2 \rangle = a_\varepsilon^2$, $\Delta A = 0$.
Thus, if $\psi$ is an eigenfunction of $\hat{A}$ then observable A will always yield the same result.

**<u>2b:</u>** Choice of Operators.

| OBSERVABLE | OPERATOR |
|---|---|
| Position, x | $\hat{x}$ |
| Linear momentum, $p_x$ | $\hat{p}_x = -i\hbar \dfrac{\partial}{\partial x}$ |
| Total Energy, E | $\hat{E} = i\hbar \dfrac{\partial}{\partial t}$ |

All linear and hermitian.

***Linearity –***

Operator is linear if:
$$A(a\varphi_1 + b\varphi_2) = aA\varphi_1 + bA\varphi_2$$

Examples:
$x$ <u>is</u> linear as $x(a\varphi_1 + b\varphi_2) = xa\varphi_1 + xb\varphi_2$
$\sqrt{\ }$ is <u>not</u> linear as $(a\varphi_1 + b\varphi_2)^{1/2} \neq (a\varphi_1)^{1/2} + (b\varphi_2)$

| LINEAR | NOT LINEAR |
|---|---|
| $\frac{\partial}{\partial x}$ | $*$ |
| $i\frac{\partial}{\partial x}$ | $+k$ |

***Hermiticity –***
$\hat{A}$ is Hermitian if: $\langle m | \hat{A} | n \rangle = \langle n | \hat{A} | m \rangle^*$
EXAMPLES:

$$\langle \varphi_1 | A | \varphi_2 \rangle = \langle \varphi_2 | A | \varphi_1 \rangle^*$$

EXAMPLES:

$x$: $\langle \varphi_1 | x | \varphi_2 \rangle \Rightarrow \int \varphi_1^* x \varphi_2 = \left[ \int \varphi_1 x^* \varphi_2^* \right]^*$
$= \left[ \int \varphi_2^* x \varphi_1 \right]^* = \langle \varphi_2 | x | \varphi_1 \rangle^*$
$\therefore$ <u>$x$ is Hermitian</u>

$i\frac{\partial}{\partial x}$: $i\int_{-\infty}^{\infty} \varphi_1^* \varphi_2' = i\left[ \cancel{\varphi_1^* \varphi_2} \right]_{-\infty}^{\infty} - i\int_{-\infty}^{\infty} \varphi_1'^* \varphi_2$
$\Rightarrow -i\int_{-\infty}^{\infty} \varphi_1'^* \varphi_2 = i\left( \int_{-\infty}^{\infty} \varphi_1' \varphi_2^* \right)^*$
$\Rightarrow i\int_{-\infty}^{\infty} \left( \frac{\partial}{\partial x} \varphi_1 \right)^* \varphi_2(x) = \langle \varphi_2 | i\frac{\partial}{\partial x} | \varphi_1 \rangle^*$
<u>$i\frac{\partial}{\partial x}$ is Hermitian.</u>

$\frac{\partial^2}{\partial x^2}$: $\int \varphi_1^* \frac{\partial^2}{\partial x^2} \varphi_2 = \int \varphi_1^* \frac{\partial}{\partial x} \varphi_2' = \varphi_1^* \varphi_2' - \int \varphi_1'^* \varphi_2'$
$= \left[ \cancel{\varphi_1^* \varphi_2'} \right]_{-\infty}^{\infty} - \left[ \cancel{\varphi_1'^* \varphi_2} \right]_{-\infty}^{\infty} + \int \varphi_1''^* \varphi_2$
$\rightarrow \varphi_2 \left( \frac{\partial^2}{\partial x^2} \varphi_1^* \right) = \langle \varphi_2 | \frac{\partial^2}{\partial x^2} | \varphi_1 \rangle^*$
<u>$\frac{\partial^2}{\partial x^2}$ is Hermitian.</u>

$$\frac{\partial}{\partial x} \quad \int_{-\infty}^{\infty} \psi_1^* \psi_2' = \left[\cancel{\psi_1^* \psi_2}\right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \psi_1^* \psi_2$$

$$= -\left(\int_{-\infty}^{\infty} \psi_2^* \psi_1'\right)^* = \underbrace{-}_{\text{NOT Hermitian}} \langle \psi_2 | \tfrac{\partial}{\partial x} | \psi_1 \rangle^*$$

(all Hermitian)

Note: $x,\ i\frac{\partial}{\partial x},\ \frac{\partial^2}{\partial x^2}$ — ALL OBSERVABLES

$\frac{\partial}{\partial x}$ — Not an observable

The eigenvalues of Hermitian Operators are real:

$$\hat{A}|n\rangle = a_n|n\rangle \qquad \langle n|n\rangle = 1$$

Then,

$$\langle n|\hat{A}|n\rangle = \langle n|a_n|n\rangle = a_n\langle n|n\rangle = a_n$$

But,

$$\underbrace{\langle n|\hat{A}|n\rangle}_{a_n} = \langle n|\hat{A}|n\rangle^* = a_n^* \quad (\text{By Hermiticity})$$

$$a_n = a_n^*$$

*Orthonormality –*

$\langle \varphi_1|\varphi_2\rangle = 0$ – orthogonal.

$\langle \varphi_1|\varphi_1\rangle = 1$ – normalised.

Both above $\Rightarrow$ orthonormal.

The eigenfunctions for different eigenvalues of Hermitian Operators are orthogonal, i.e. if $\hat{A}\,|\,f_n\rangle = a_n\,|\,f_n\rangle$ and $\hat{A}\,|\,f_m\rangle = a_m\,|\,f_m\rangle$, where $a_m \neq a_n$, then $\langle f_m\,|\,f_n\rangle = 0$.

$$\hat{A}|m\rangle = a_m|m\rangle \quad \& \quad \hat{A}|n\rangle = a_n|n\rangle$$

$a_m \neq a_n$ (def) & $\hat{A}$ Hermitian

$$\langle n|\hat{A}|m\rangle = \langle n|a_m|m\rangle = a_m\langle n|m\rangle \quad ①$$

$$\langle m|\hat{A}|n\rangle = \langle m|a_n|n\rangle = a_n\langle m|n\rangle \quad ②$$

$$\langle m|\hat{A}|n\rangle^* = a_n^*\langle m|n\rangle^* = a_n\langle n|m\rangle \quad ③$$

① − ③

$$\underbrace{\langle n|\hat{A}|m\rangle - \langle m|\hat{A}|n\rangle^*}_{0 \text{ by Hermiticity}} = \underbrace{(a_m - a_n)}_{\neq 0 \text{ by hypothesis}} \underbrace{\langle n|m\rangle}_{\therefore \text{ must } = 0.}$$

$$\langle n|m\rangle = 0$$

Note: if $a_m = a_n$, can choose $\langle n|m\rangle = 0$

if $n = m \Rightarrow$ Normalised $\langle n|m\rangle = 1$

ORTHONORMAL

***Time Dependence and Stationary States***

Classical Observable → Quantum Operator.

e.g. Kinetic Energy,

$$T = ½\,m\,(p_x^2 + p_y^2 + p_z^2) \Rightarrow \hat{T} = ½\,m\,(\hat{p}_x^{\,2} + \hat{p}_y^{\,2} + \hat{p}_z^{\,2})$$

$$\therefore \hat{T} = \frac{-\hbar^2}{m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = \frac{-\hbar^2}{m}\nabla^2$$

Potential Energy,

$$V = V(x,y,z), \text{ so } \hat{V} = V(\hat{x}, \hat{y}, \hat{z})$$

Total Energy = T + V, ➔ $H(x,p_x)$ [ Hamilton's Function ]

Also note that the total energy operator from $P_{2b}$ is $\hat{E} = i\hbar\frac{\partial}{\partial t}$.

$$H\psi(r_i,t) = i\hbar\frac{\partial}{\partial t}\psi(r_i,t)$$ - Time Dependent Schrodinger Equation, TDSE.

H is independent of time (in conservative systems), so always separable solutions to the TDSE of the form:

$$\psi(r^N;t) = \phi_n(r^N)f(t)$$

Note that
$$i\hbar\frac{\partial f}{\partial t} = E_n f(t) \Rightarrow f(t) \propto e^{-iE_nt/\hbar},$$

Hence, $$\psi(r^N,t) = e^{-iE_nt/\hbar}\phi_n(r^N)$$

Since $$\frac{1}{\phi_n(r^N)}\hat{H}\phi_n(r^N) = \frac{i\hbar}{f(t)}\frac{\partial f(t)}{\partial t} = E_n \text{ (constant)}$$

$$H\phi(r^N) = E_n\phi_n(r^N) \quad \text{– Time Independent S.E.}$$

A system in a state described by this is said to be in a stationary state.

Its energy is a precise quantity ($P_3$) and no measurable property of the system changes with time, i.e. <A>(t) = <A>(0) where <A>(t) is the expectation value of operator A at time t.
Proof:

$$\begin{aligned}\langle A\rangle(t) &= \int\psi^*(r^N,t)\hat{A}\psi(r^N,t)\,d\tau \\ &= \int e^{-iE_nt/\hbar}\phi_n(r^N)^*\hat{A}(e^{-iE_nt/\hbar}\phi_n(r^N))d\tau \\ &= \int\phi_n^*(r^N)\hat{A}\phi_n(r^N)\,d\tau \\ &= \langle\hat{A}\rangle(0)\end{aligned}$$

NOTES:
This resolves the “radiation paradox” of old Quantum Mechanics. Stationary State ➔ still not solved the TDSE. Need $\phi_n$ from TISE.

A common relation that is useful is:

TDSE: Prove $\frac{d}{dt}\langle A\rangle = \frac{i}{\hbar}\langle[H,A]\rangle$

Use: $$i\hbar\frac{\partial}{\partial t}\psi(x,t) = H\psi(x,t) \quad (1)$$

$$\langle A\rangle = \langle\psi|A|\psi\rangle = \int_{-\infty}^{\infty}\psi(x,t)^* A\,\psi(x,t)\,dx$$

$$\frac{d}{dt}\langle\psi|A|\psi\rangle = \langle\frac{d\psi}{dt}|A|\psi\rangle + \langle\psi|\cancel{\frac{dA}{dt}}^{0}|\psi\rangle + \langle\psi|A|\frac{d\psi}{dt}\rangle$$

From (1) $$\frac{d|\psi\rangle}{dt} = \frac{H|\psi\rangle}{i\hbar} \quad \& \quad \frac{d\langle\psi|}{dt} = \frac{-\langle H\psi|}{i\hbar}$$

$$\Rightarrow \frac{-1}{i\hbar}\langle H\psi|A|\psi\rangle + \frac{1}{i\hbar}\langle\psi|A|H\psi\rangle$$

$$= \frac{-1}{i\hbar}\langle\psi|HA|\psi\rangle + \frac{1}{i\hbar}\langle\psi|AH|\psi\rangle$$

$$= \frac{i}{\hbar}\langle[H,A]\rangle$$

To use this, it is necessary to understand what a commutator is.

## ***Commutators, Complementary Observables, and the Heisenberg Uncertainty Principle***

ABf ≠ BAf in general, where A and B are operators.

**Define:**
Commutator [A,B] of A & B:

$$[A,B] = AB - BA$$

Compared the effects on a ghost function, e.g.
$[x, p_x]\,f = (xp_x - p_xx)\,f = -i\hbar\,(x(d/dx) - (d/dx)x)\,f = -i\hbar\,(x(df/dx) - (d/dx)(xf)) = i\hbar f$
Therefore $\mathbf{[x,p_x] = i\hbar}$.

If [A,B] = 0, they are said to commute. For example, $[y,p_x] = 0$ (independent x,y).

NOTES:

- $[B,A] = -[A,B]$
- $[A,\alpha B] = \alpha[A,B]$
- $[A,B+C] = [A,B] + [A,C]$
- $[A,BC] = [A,B]C + B[A,C]$

*Uses:*
From $P_3$, $A\psi = a\psi$ and $B\psi = b\psi$. This implies precise measurement of A and B, therefore [A,B] = 0 ➔ precise value for each observable can be known simultaneously.
If [A,B] = 0, then there is an eigenfunction of A which is simultaneously an eigenfunction of B.

If $[A,B] \neq 0$, it is NOT generally possible to measure the observables precisely and simultaneously.

These observables are said to be complementary or conjugate.

EXAMPLES:

$$[H,x] = \frac{1}{2m}[p_x^2,x] = \frac{1}{2m}(p_x[p_x,x] + p_x[p_x,x])$$
$$= \frac{1}{2m}(-2p_x i\hbar)$$
$$= \frac{-ip_x\hbar}{m}$$

$$[H,p_x] = [V(x),p_x] = -i\hbar\left[V(x).\frac{\partial}{\partial x} - \frac{\partial}{\partial x}V(x)\right]f$$
$$= -i\hbar\left(V(x)\frac{\partial f}{\partial x} - \frac{\partial(V(x)f)}{\partial x}\right)$$
$$= -i\hbar\left(V(x)\frac{\partial f}{\partial x} - \left[V(x)\frac{\partial f}{\partial x} + f\frac{\partial V(x)}{\partial x}\right]\right)$$
$$= i\hbar\frac{\partial V}{\partial x}$$

***Heisenberg's Uncertainty Principle:***

$$\Delta A \Delta B \geq \tfrac{1}{2}\,|\langle[A,B]\rangle|$$

Where,
$(\Delta A)^2 = \langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2$
e.g. $[x,p_x] = i\hbar$, ➔ $\langle[x,p_x]\rangle = i\hbar$, so $|\langle[x,p_x]\rangle| = \hbar$
Hence, $\Delta x\Delta p_x \geq \hbar/2$

## ***Applications of Quantum Mechanics***

***1 D free particle (no Potential)***

$$H = \frac{p_x^2}{2m} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

TISE, $H\phi = E\phi \Rightarrow$

(1) $\frac{\partial^2\phi(x)}{dx^2} + k^2\phi(x) = 0 \qquad k = \frac{\sqrt{2mE}}{\hbar}$

2° differential eqn: 2 solutions.

(2) $\phi_+(x) = e^{+ikx}$ & $\phi_-(x) = e^{-ikx}$

Physically, $\hat{p}_x\phi_\pm(x) = \pm p\phi_\pm(x) \quad (p = \hbar k)$
momentum $\hbar k$ ($\rightleftarrows \pm$)

NOTES:
$[H,p_x] = \frac{1}{2m}[p_x,p_x] = 0$ – eigenfunctions of H & $p_x$ simultaneously ($\phi_+$ & $\phi_-$)

Note that general solution to (1) is a linear combination:

$$\phi(x) = A'\phi_+(x) + B'\phi_-(x)$$
$$\& \quad p_x\phi(x) = p[A'\phi_+ - B'\phi_-]$$

General interpretation using $P_3$ is that there is always dispersion-free energy for the above, but the relative probability of finding the particle moving in a given direction with momentum ±hk is $|A'|^2|B'|^2$

General Solution to the Schrödinger Equation from the above (2) & (3):

$$\phi(x) = A'e^{ipx/\hbar} + B'e^{-ipx/\hbar}$$
$$= A\cos\left(\frac{px}{\hbar}\right) + B\sin\left(\frac{px}{\hbar}\right)$$
$$A = A' + B'$$
$$B = i(A' - B')$$

Compare to classical standing waves,

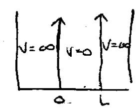
$$\cos(2\pi x/\lambda) + \sin(2\pi x/\lambda)$$

Therefore $2\pi/\lambda = p/\hbar$, ➔ $\boldsymbol{\lambda = h/p}$ [ De Broglie Relation ]

***Quantisation – Particle in a Box***

$d = 1$, $\hat{H} = \frac{p_x^2}{2m} + V(x)$ with

$$V(x) = \begin{cases} 0 : & 0 < x < L \\ \infty : & x < 0, x > L \end{cases}$$




Outside the Box: $\phi(x) = 0$ – no particle here.
Inside the Box: $V(x) = 0$ so TISE same as free particle above. Solution as above is:

$$\phi(x) = A\cos(px/\hbar) + B\sin(px/\hbar)$$

$\psi(x)$ is continuous, therefore Boundary Condition: $\phi(0) = 0 = \phi(L)$.
Hence,
$\phi(0) = 0$ ➔ $A = 0$.
$\phi(L) = 0$ ➔ $B \sin({}^{pL}/_{\hbar}) = 0$.
Thus,
${}^{pL}/_{\hbar} = n\pi$, where n = 1,2,3…
Also, $p = \sqrt{(2mE)}$:

$$E_n = \frac{n^2\hbar^2}{8mL^2}, \; n = 1,2,3\ldots$$

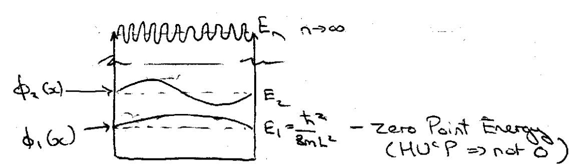
Quantisation arose from the Boundary Condition. Quantum number n is established.

$$H\,\phi_n(x) = E_n\,\phi_n(x).$$
$$\phi_n(x) = B\sin(n\pi x/L) \text{ for } 0 \le x \le L$$
$$\phi_n(x) = 0 \text{ for } x \le L, \text{ or } x \ge L$$

B, such that $\phi_n(x)$ is normalised, is found by:

$$\int_0^L |\phi_n(x)|^2\,dx = 1$$
$$\therefore B = \sqrt{\frac{2}{L}}$$

Pictorially,




Probability Density $|\phi_n(x)|^2$ → tends to classical limit (**Correspondence Principle**)

*Energy Level Separation:*

$$\Delta E = E_{n+1} - E_n = \frac{(2n+1)h^2}{8mL^2}$$

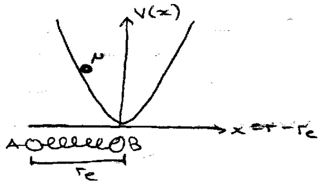
So, $\Delta E \rightarrow 0$ as $L \rightarrow \infty$

*Extra Dimensions:*

$$d = 2,\ E_n = \frac{h^2}{8m}\left[\frac{n_1^{\ 2}}{Lx^2} + \frac{n_2^{\ 2}}{Ly^2}\right]$$

$Lx = Ly$ ➔ square box. $n_1 = n_2$ is single degenerate, while $n_1 \neq n_2$ is doubly degenerate. Degeneracy is a consequence of symmetry.

***Harmonic Oscillator***




$V(x) = \frac{1}{2}kx^2$
$F = -V'(x) = -kx$

$k$ = force constant $\equiv V''(0)$
as $V(x) = V(0) + x\cancel{V'(0)}_{0} + \frac{1}{2}x^2\cancel{V''(0)}_{k}$

Classically, $E = T + V = p_x^2/2\mu + \frac{1}{2}kx^2$
Quantum Mechanics:

$$E = \frac{-h^2}{2\mu}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2$$

$$H\psi = E\psi \Rightarrow \left(\frac{-\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2\right)\psi(x) = E\psi(x) \quad (S.E)$$

Crude Solve:

$x \rightarrow \pm\infty \Rightarrow V(x) \rightarrow \infty$
$P = |\psi(x)|^2 \rightarrow 0$
$\therefore \psi(x) \rightarrow 0$

Simple function that decays to 0 as $x \rightarrow \pm\infty$ – Gaussian.

$$\psi(x) = e^{-\alpha x^2/2}$$

Test: $\psi'(x) = -\alpha x e^{-\alpha x^2/2} = -\alpha x \psi(x)$
$\psi''(x) = (\alpha^2 x^2 - \alpha)\psi(x)$

$$\therefore \left(\frac{-\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2\right)\psi(x) = \left[\frac{-\hbar^2}{2\mu}(\alpha^2x^2 - \alpha) + \frac{1}{2}kx^2\right]\psi(x) = E\psi(x)$$

Satisfied for all x if both:

$$\frac{\hbar^2\alpha^2}{2\mu} = \frac{1}{2}k$$

and

$$\frac{\hbar^2\alpha}{2\mu} = E$$

$$\therefore \alpha = \frac{\sqrt{\mu k}}{\hbar} \quad \& \quad E = \frac{1}{2}\hbar\sqrt{\frac{k}{\mu}} = \frac{1}{2}\hbar\omega$$

Hence, $\psi_0(x) = N_0 e^{-\alpha x^2/2}$
$E_0 = \frac{1}{2}\hbar\omega$ (Ground Vib state)

Normalise,

$$\int_{-\infty}^{\infty} dx\ \psi_0^{\ 2}(x) = 1$$

i.e. $N_0^2 \int_{-\infty}^{\infty} dx\ e^{-\alpha x^2} \Rightarrow N_0 = \left(\frac{\alpha}{\pi}\right)^{1/4}$

For remaining solutions try:

$$\psi_n(x) = P_n(x)e^{-\alpha x^2/2}$$

$P_n(x)$ = polynomial in x.

Gives second order differential equations for $P_n(x)$ when subbed into the Schrodinger Equation. The solutions are called Hermite Polynomials.

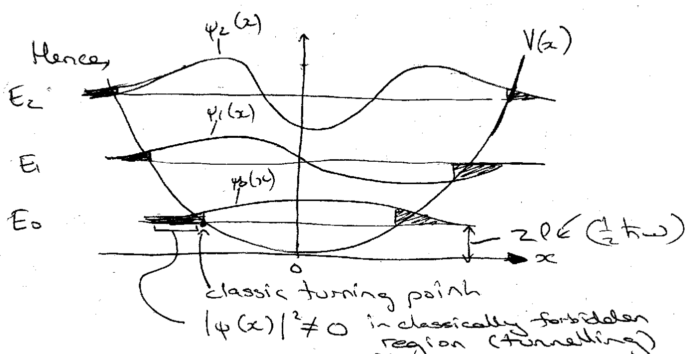
$P_n(x) = H_n(\sqrt{\alpha}\, x)$

Eigenvalues $E_n = (n+½)\hbar\omega$ , n = 0,1,2…

| | |
|---|---|
| $H_0(\sqrt{\alpha}\, x) = 1$ | [ even in x ] |
| $H_1(\sqrt{\alpha}\, x) = 2\sqrt{\alpha}\, x$ | [ odd in x ] |
| $H_2(\sqrt{\alpha}\, x) = 4\alpha x^2 - 2$ | [ even in x ] |

… etc.

Hence,




$$\psi_n(x) = N_n H_n(\sqrt{\alpha}\, x)\, e^{-\alpha x^2/2}$$

$$E_n = (n+\tfrac{1}{2})\hbar\omega \quad n = 0, 1, 2 \ldots$$

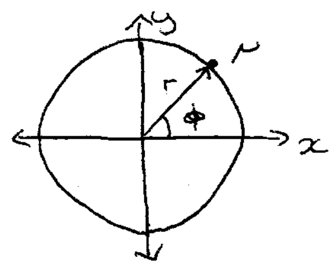
***Particle on a Ring***

To get H:

Transform to polar cords.

Fix r, look at angular component of H.

Transforming to polar coordinates:




$$\left.\frac{\partial}{\partial x}\right)_y = \left.\frac{\partial r}{\partial x}\right)_y \left.\frac{\partial}{\partial r}\right)_\phi + \left.\frac{\partial \phi}{\partial x}\right)_y \left.\frac{\partial}{\partial \phi}\right)_r$$

$$\left.\frac{\partial}{\partial y}\right)_x = \left.\frac{\partial r}{\partial y}\right)_x \left.\frac{\partial}{\partial r}\right)_\phi + \left.\frac{\partial \phi}{\partial y}\right)_x \left.\frac{\partial}{\partial \phi}\right)_r$$

where, $x = r\cos\phi$ $\quad \left.\frac{\partial r}{\partial x}\right)_y = \cos\phi,\ \left.\frac{\partial r}{\partial y}\right)_x = \sin\phi$

$y = r\sin\phi$ $\quad \left.\frac{\partial \phi}{\partial x}\right)_y = -\frac{\sin\phi}{r}\ \ \left.\frac{\partial \phi}{\partial y}\right)_x = \frac{\cos\phi}{r}$

Hence,

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}\right)$$

Fixing r means that $\frac{\partial^2}{\partial r^2}$ & $\frac{1}{r}\frac{\partial}{\partial r}$ can be dropped. $\psi = \psi(\phi)$: $d\psi/dr = 0 = d^2\psi/dr^2$.

Thus,

$$\hat{H} = \frac{-\hbar^2}{2\mu r^2}\frac{\partial^2}{\partial \phi^2} = \frac{-\hbar^2}{2I}\frac{\partial^2}{\partial \phi^2} \qquad I = \mu r^2$$

$$\hat{H} = \frac{\hat{L}_z^2}{2I} \qquad \hat{L}_z = -i\hbar\frac{\partial}{\partial \phi} \quad \text{operator for z-ang momentum}$$

$$[\hat{H}, \hat{L}_z] = \hat{H}\hat{L}_z - \hat{L}_z\hat{H} = \frac{1}{2I}(\hat{L}_z^3 - \hat{L}_z^3) = 0$$

Therefore eigenfunctions of H can be chosen to be eigenfunctions of $L_z$.

$$L_z \psi_m(\phi) = -i\hbar \frac{\partial}{\partial\phi}\psi_m(\phi) = m\hbar\psi_m(\phi)$$

subject to:

$$\psi_m(\phi+2\pi) = \psi_m(\phi)$$

Then,

$$\frac{\partial}{\partial\phi}\psi_m(\phi) = im\,\psi_m(\phi)$$

$$\psi_m(\phi) = N_m e^{im\phi}$$

$$\psi_m(\phi+2\pi) = e^{im2\pi}\psi_m(\phi)$$

$$e^{im2\pi} = 1 \Rightarrow m = \text{integer}: 0, \pm1, \pm2 \ldots$$

&

$$\int_0^{2\pi} d\phi\, |\psi_m(\phi)|^2 = N_m^2\, 2\pi = 1 \Rightarrow N_m = \frac{1}{\sqrt{2\pi}},\ \forall m$$

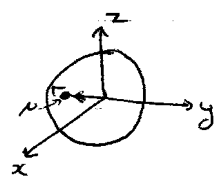
Therefore normalised eigenfunctions of H = $\frac{1}{2I}L_z^{\,2}$ which satisfy the boundary condition are:

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

$$L_z\psi_m(\phi) = m\hbar\psi_m(\phi)$$

$$\hat{H}\psi_m(\phi) = \frac{m^2\hbar^2}{2I}\psi_m(\phi) = E_m\psi_m(\phi)$$

NB: $E_m = \frac{m^2\hbar^2}{2I}$ is doubly degenerate for | m | > 0.




***Particle on a Sphere***

Transform to polar cords.
Consider angular parts.
Separate θ/φ dependence.

$$\hat{H} = \frac{-\hbar^2}{2\mu}\nabla^2 \qquad \begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta \end{aligned}$$

$$\left.\frac{\partial}{\partial x}\right)_{y,z} = \left.\frac{\partial r}{\partial x}\right)_{y,z}\left(\frac{\partial}{\partial r}\right)_{\theta,\phi} + \left.\frac{\partial\theta}{\partial x}\right)_{y,z}\left.\frac{\partial}{\partial\theta}\right)_{r,\phi} + \left.\frac{\partial\phi}{\partial x}\right)_{y,z}\left.\frac{\partial}{\partial\phi}\right)_{r,\theta} \text{ etc.}$$

gives

$$\frac{-\hbar^2}{2\mu}\nabla^2 = \frac{-\hbar^2}{2\mu}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

Set $\psi = \psi(\theta,\phi) \Rightarrow \frac{\partial\psi}{\partial r} = 0$, $\frac{\partial^2\psi}{\partial r^2} = 0$

$$\frac{1}{2I}L_z^{\,2}$$

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \quad \& \quad I = \mu r^2$$

NOTES:

$E = L^2/2I$ classically

$L^2 = L.L = L_x^2 + L_y^2 + L_z^2$ (i.e. not $L_z^2$)

$H \propto L^2 \Rightarrow$ finding eigenfunctions/values of $\hat{L}^2$

Separating variables,

$\frac{\partial}{\partial\phi}$ commutes w/ $\sin\theta, \frac{1}{\sin\theta}, \frac{\partial}{\partial\theta}$ & itself,

$$\therefore \underbrace{[\hat{L}^2, \hat{L}_z]}_{\text{simultaneous eigenfn's.}} = 0 \qquad (\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi})$$

(1) $L^2\psi(\theta,\phi) = \lambda\hbar^2\psi(\theta,\phi)$ & ($\lambda$ = dimensionless constant)
(2) $L_z\psi(\theta,\phi) = m\hbar\psi(\theta,\phi)$.

(2) & $L_z = i\hbar\frac{\partial}{\partial\phi} \Rightarrow \frac{\partial}{\partial\phi}\psi(\theta,\phi) = im\,\psi(\theta,\phi)$

$\therefore \quad \psi(\theta,\phi) = \Theta(\theta)e^{im\phi}$

$\Theta$ is a function of $\theta$ but not $\phi$
has separable form, since $[L^2, L_z] = 0$.

$\psi(\theta,\phi) = \Theta(\theta)e^{im\phi}$ into (1) gives:

$$\hat{L}^2\psi(\theta,\phi) = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\Theta(\theta)e^{im\phi}$$
$$= -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} - \frac{m^2}{\sin^2\theta}\right)\Theta(\theta)e^{im\phi}$$
$$= \lambda\hbar^2\,\Theta(\theta)e^{im\phi}$$
$$\Rightarrow -\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} - \frac{m^2}{\sin^2\theta}\right)\Theta(\theta) = \lambda\Theta(\theta)$$

Ordinary Differential Equation for (H)($\theta$), the Legendre Equation.

Solutions are associated Legendre functions,

$$\Theta(\theta) = P_l^m(\cos\theta)$$

eigenvalues ($\lambda$) are

$$\lambda = l(l+1). \qquad \text{for } l = |m|, |m|+1, |m|+2 \text{ etc}$$

i.e. $m = -l, -(l-1), \ldots 0, \ldots (l-1), l$.

This gives the spherical harmonics:

$$\underbrace{\psi(\theta,\phi) = Y_{lm}(\phi,\theta)}_{\text{spherical harmonic}} = \underbrace{N_{l,m}}_{\text{norm. const.}}\,\underbrace{P_l^m(\cos\theta)}_{\text{Legendre function}}\,e^{im\phi}$$

$$\int_0^{2\pi}d\phi\int_0^{\pi}d\theta\,\sin\theta\;Y_{l,m}(\theta,\phi)^*Y_{l,m}(\theta,\phi) = 1$$

Which satisfy:

$$\hat{L}^2 Y_{l,m}(\theta,\phi) = \hbar^2 l(l+1)Y_{l,m}(\theta,\phi)$$
$$\hat{L}_z Y_{l,m}(\theta,\phi) = \hbar m\,Y_{l,m}(\theta,\phi)$$

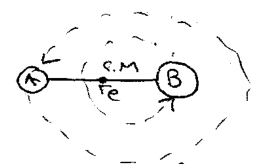
$l = 0, 1, 2\ldots$ ANG. MOM. Q. NO.

$m = -l, -(l+1), \ldots +l$ $\quad [2l+1]$ values

ANG. MOM. PROJECTION Q. NO.

***Molecular Rotation***

Equivalent to free motion of particle with reduced mass on surface of a sphere (radius $r_e$).




Therefore H = $\dfrac{1}{2I}J^2$ [ J not L – convention for molecular systems ]

$$\hat{H}\varphi = E\varphi \quad \frac{J^2}{2I},\ Y_{J,M}(\theta,\phi) \rightarrow \frac{\hbar^2 J(J+1)}{2I}$$

i.e. $E_J = BhcJ(J+1)$ [ rotational energy levels ]
$B = h/(8\pi^2 Ic)$ [ units $m^{-1}$ or $cm^{-1}$ ]

$J = 0,1,2 \ldots$
$M = -J, -(J-1) \ldots J.$ [ projection of momentum along z ]
This is (2J+1) degenerate.

***Atomic Orbitals***
First, it is useful to refine our units onto the atomic scale:

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

Let $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$ (1), $E_h = \frac{e^2}{4\pi\varepsilon_0 a_0}$. (2)

Convert lengths: $x \rightarrow a_0 x'$, $y \rightarrow a_0 y'$ etc.

$$\Rightarrow H = \frac{-\hbar^2}{2m}\frac{\nabla'^2}{a_0^2} - \frac{e^2}{4\pi\varepsilon_0 a_0 r'}$$

Apply (2): $H = \frac{-\hbar^2 \nabla'^2}{2m a_0^2} - \frac{E_h}{r'}$

Apply (1) for $a_0$: $H = \frac{-\hbar^2}{2m}\frac{\nabla'^2}{a_0}\left(\frac{m e^2}{4\pi\varepsilon_0\hbar^2}\right) - \frac{E_h}{r'}$

Apply (2) again: $H = -\frac{\nabla'^2 E_h}{2} - \frac{E_h}{r'}$

$\Rightarrow \frac{H}{E_h} = -\frac{1}{2}\nabla'^2 - \frac{1}{r'}$    $\varepsilon$ in Hartree's
$r' \Rightarrow a_0$ in Bohr radii

In atomic units,

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r}$$

$[H, L^2] = [H, L_z] = 0$

$$= -\frac{1}{2}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2} r - \frac{\hat{L}^2}{r^2}\right] - \frac{1}{r}$$

(1) $\hat{H}\varphi_{nlm}(r,\theta,\phi) = E_n \varphi_{nlm}(r,\theta,\phi)$    $n = 1, 2, 3$
(2) $\hat{L}^2 \varphi_{nlm}(r,\theta,\phi) = l(l+1)\varphi_{nlm}(r,\theta,\phi)$    $l = 0, 1, 2 \ldots (n-1)$
(3) $\hat{L}_z \varphi_{nlm}(r,\theta,\phi) = m\varphi_{nlm}(r,\theta,\phi)$    $m = -l, -(l-1), \ldots 0, \ldots +l$

From (2) and (3), any atomic orbital can be written as separable:

$$\varphi_{nlm}(r,\theta,\phi) = R_{nl}(r)\,Y_{lm}(\theta,\phi)$$

Sub this into (1):

$$\hat{H}\varphi_{nlm}(r,\theta,\phi) = \left[-\frac{1}{2}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2} r - \frac{\hat{L}^2}{r^2}\right) - \frac{1}{r}\right] R_{nl}(r)\,Y_{lm}(\theta,\phi)$$

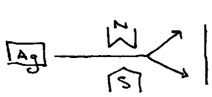
ordinary differential eqn:

$$= \left[-\frac{1}{2}\left(\frac{1}{r}\frac{\partial^2}{\partial r^2} r - \frac{l(l+1)}{r^2}\right) - \frac{1}{r}\right] R_{nl}(r)\,Y_{lm}(r,\theta,\phi)$$

$$= E_n R_{nl}(r)\,Y_{lm}(r,\theta,\phi) \quad \rightarrow E_n$$

This is the “associated Laguerre Equation”. $E_n = -1/(2n^2)$ Hartree, n = 1,2,3 …

## ***Electron Spin***




Stern & Gerlach (1922) passed beam of Ag atoms through an inhomogeneous magnetic field (i.e. a field gradient was present ➔ force). Beam split in two. Ag ($5s^1$). If S = ½, then $m_s$ = ± ½ … 2 components with different energies in a magnetic field.

1925 – splittings in atomic spectra. $e^-$ had intrinsic angular momentum of ½ ħ.
1930 – Dirac. Obtained wave equation for $e^-$ by combining Quantum Mechanics and Special Relativity. Equation predicted s = ½, confirming the above.

$$\mu = \underbrace{-}_{\text{motion of -ve charge}} \underbrace{g_e}_{=2\ (\text{Dirac})} \underbrace{\mu_B}_{=\frac{e\hbar}{2m_e}\ (\text{Bohr Magneton})} \underbrace{\frac{s}{\hbar}}_{\text{spin angular momentum}}$$

$$E = -\mu \cdot B$$

If B is in the z-direction, $s.B = s_z B_z$, ➔

$$\left.\begin{array}{ll} \uparrow & s_z/\hbar = +1/2 : E(m_s = +1/2) \\ \downarrow & s_z/\hbar = -1/2 : E(m_s = -1/2) \end{array}\right\} \text{2 different energies}$$

***Spin Wavefunctions***

<u>Single electron:</u>

$$|s = 1/2, m_s = +1/2 > = |\alpha> \quad \uparrow$$
$$|s = 1/2, m_s = -1/2 > = |\beta> \quad \downarrow$$

Satisfy usual angular momentum eigenvalue equations:

$$s^2 |s, m_s> = \hbar^2 s(s+1) |s, m_s> \quad s = 1/2$$
$$s_z |s, m_s> = \hbar m_s |s, m_s> \quad m_s = \pm 1/2$$

Also,

$$<\alpha|\alpha> = 1 = <\beta|\beta> \quad \text{Normalised over spin coordinates}$$
$$<\alpha|\beta> = 0 = <\beta|\alpha> \quad \text{orthogonal.}$$

eigenfunction of Hermitian operator $\hat{s}_z$ w/ different eigenvalues

<u>Two electrons:</u>
Only linear combinations of following possibilities –

| | | $m_1$ | $m_2$ | $M_s$ |
|---|---|---|---|---|
| ↑↑ | $\|\alpha_1, \alpha_2>$ | 1/2 | 1/2 | 1 |
| ↑↓ | $\|\alpha_1, \beta_2>$ | 1/2 | -1/2 | 0 |
| ↓↑ | $\|\beta_1, \alpha_2>$ | -1/2 | 1/2 | 0 |
| ↓↓ | $\|\beta_1, \beta_2>$ | -1/2 | -1/2 | -1 |

Possible values of $M_s = m_1 + m_2$ are:
$M_s$ = 1,0,-1 (S=1) and $M_s$ = 0 (S=0).
$M_S$ = S, S-1, .. –S ➔ (2S+1) = 3 (triplet).
$M_S$ = S, S-1, .. –S ➔ (2S+1) = 1 (singlet).

But what are corresponding 2 electron spin wavefunctions, $| s, m_s >$ ?

$$| S = 1, M_s = +1 > = | \alpha_1 \alpha_2 >$$

(as this is the only way to get $M_s$ = +1).
Similarly,

$$| S = 1, M_s = -1 > = | \beta_1 \beta_2 >$$

($M_s$ = -1).

Both of these S=1 wavefunctions are symmetric wrt interchange of the 2 electrons ($e_1 \leftrightarrow e_2$).
Hence, the remaining S=1, $M_s$=0 component of the triplet states must be symmetric too [ $M_s$ quantum number depends on where *we choose* to put the z-axis, which clearly cannot affect the exchange symmetry of a triplet state ].

Hence, only possibility for:

| S = 1, $M_s$ = 0 > = symmetric combination of $\frac{1}{\sqrt{2}}(|\alpha_1\beta_2> + |\beta_1\alpha_2>)$, where the term outside the brackets is a Normalisation Constant.
Similarly,

| S = 0, $M_s$ = 0 > = $\frac{1}{\sqrt{2}}(|\alpha_1\beta_2> - |\beta_1\alpha_2>)$, which has antisymmetric exchange symmetry.

### *Pauli Exclusion Principle*

Suppose quantum system contains two indistinguishable particles 1 and 2 such that:

$$\psi = \psi(1,2)$$

i.e. $\psi$ is a function of all space and spin coordinates.

Let $P_{12}\psi(1,2) = \psi(2,1) = e^{i\alpha}\psi(1,2)$

equiv. to $\psi(1,2)$ as $|\psi(1,2)|^2 = |\psi(2,1)|^2$ ∵ indistinguishable.

multiplicative phase factor ($\alpha$ is real) which satisfies $|e^{i\alpha}|^2 = 1$

Repeat operation:

$P_{12}^{\,2}\psi(1,2) = \psi(1,2) = e^{2i\alpha}\psi(1,2)$

$\Rightarrow e^{2i\alpha} = 1$ & $\therefore e^{i\alpha} = +1$ or $-1$.

So, either symmetric : $e^{i\alpha} = 1$.
or antisymmetric : $e^{i\alpha} = -1$.
(wrt to exchange).

$\psi(2,1) = \pm\psi(1,2)$

(s) = bosons.
- integer spin
- obey Bose-Einstein statistics.

(a) = fermions.
- half-odd-integer spin
- obey Fermi-Dirac statistics.

*Corollary 1: Exclusion Principle in Orbital Space.*
No 2 electrons can have the same set of 4 quantum number ($n,l,m_l,m_s$) within the orbital approximation.
Combination with the Aufbau Principle gives the Periodic Table.
Reason:

$$\psi(2,1) = \psi_{n,l,ml,ms}(2)\,\psi_{n,l,ml,ms}(1) = \psi_{n,l,ml,ms}(1)\,\psi_{n,l,ml,ms}(2) = +\psi(1,2)$$

But electrons are fermions so $\psi(1,2) = -\psi(2,1)$.

*Corollary 2: Exclusion Principle in Real Space.*
2 electrons in a triplet state (S=1) cannot be at the same point in space.

$$\psi(1,2) = \psi_{space} \times \psi_{spin}$$

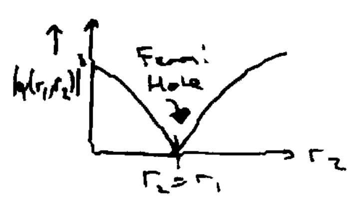
$$\underbrace{\psi(1,2)}_{\text{antisymmetric wrt } e_1 \leftrightarrow e_2} = \psi(r_1,r_2) \times \underbrace{\frac{1}{\sqrt{2}}(|\alpha_1\beta_2> + |\beta_1\alpha_2>)}_{\text{Symmetric wrt } e_1 \leftrightarrow e_2}$$

Thus, $\psi_{space}$ must be antisymmetric wrt $e_1 \leftrightarrow e_2$.

$$\psi(r_2,r_1) = -\psi(r_1,r_2)$$

Setting $r_2 = r_1 = r$:

$$\psi(r,r) = -\psi(r,r)$$



Therefore $\psi(r,r) = 0$ and $|\psi(r,r)|^2 = 0$, so get a "Fermi Hole".

Basis of Hund's 1st Rule: triplet states are lower in energy than singlet states, all other things – including the electron configurations – being equal.

## ***The Variational Method***

How to find good approximate solutions to problems that can't be solved exactly.

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_o$$

Where $\psi$ = trial wavefunction and $E_o$ = exact ground state energy.

$$\psi = \sum_i c_i \psi_i \quad \text{(expansion theorem)}$$

where,

$$H\psi_i = E_i\psi_i \quad \& \quad \langle\psi_i|\psi_j\rangle = \delta_{ij} \leftarrow \text{orthonormal: } (=1 \text{ if } i=j,\ =0 \text{ otherwise})$$

$$\therefore \langle\psi|H|\psi\rangle = \sum_{ij} c_i^* \langle\psi_i|H^*|\psi_j\rangle c_j$$

$$= \sum_{ij} c_i^* \langle\psi_i|E_j|\psi_j\rangle c_j = \sum_{ij} E_j \langle\psi_i|\psi_j\rangle c_i^* c_j$$

$$= \sum_{ij} E_j \delta_{ij} c_i^* c_j = \sum_j E_j c_j^* c_j = \sum_j E_j |c_j|^2$$

$$\geq E_o \sum_j |c_j|^2 \quad (\text{as } E_j \geq E_o)$$

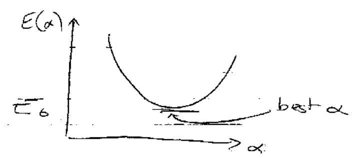
& similarly,

$$\langle\psi|\psi\rangle = \sum_{ij} c_i^* \langle\psi_i|\psi_j\rangle c_j = \sum_j |c_j|^2$$

So,

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq \frac{E_o \sum_j |c_j|^2}{\sum_j |c_j|^2} = E_o$$

Suppose we have a trial wavefunction $\psi_\alpha$ that depends on a parameter $\alpha$. Find the best $\alpha$ (most accurate wavefunction) by minimising:




i.e. $\frac{dE(\alpha)}{d\alpha} = 0$

*Example – Quartic Oscillator*

$$H = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^4$$

Similar to Harmonic Oscillator, so try that wavefunction as trial:

$$\psi_\alpha(x) = e^{-\alpha x^2/2} \quad \text{(not Normalised)}$$

$$\Rightarrow \psi_\alpha''(x) = (\alpha^2 x^2 - \alpha)\psi_\alpha(x)$$

$$\Rightarrow H\psi_\alpha(x) = \left[\frac{-\hbar^2}{2\mu}(\alpha^2 x^2 - \alpha) + \frac{1}{2}kx^4\right]\psi_\alpha(x)$$

$$\therefore \langle\psi_\alpha|H|\psi_\alpha\rangle = \frac{\hbar^2\alpha}{2\mu}I_0 - \frac{\hbar^2\alpha^2}{2\mu}I_2 + \frac{1}{2}kI_4$$

$$\& \quad \langle\psi_\alpha|\psi_\alpha\rangle = I_0$$

Where,

$$I_{2n} = \int_{-\infty}^{\infty} dx\, x^{2n} e^{-\alpha x^2} = \frac{1.3.5\ (2n-1)}{(2\alpha)^n}\sqrt{\frac{\pi}{\alpha}}$$

Hence,

$$E(\alpha) = \frac{\langle\varphi_\alpha|H|\varphi_\alpha\rangle}{\langle\varphi_\alpha|\varphi_\alpha\rangle} = \frac{\hbar^2\alpha}{2\mu} - \frac{\hbar^2\alpha^2}{2\mu}\frac{I_2}{I_0} + \frac{1}{2}k\frac{I_4}{I_0}$$

$$= \frac{\hbar^2\alpha}{2\mu} - \frac{\hbar^2\alpha^2}{2\mu}\cdot\frac{1}{2\alpha} + \frac{k}{2}\cdot\frac{3}{4\alpha^2}$$

$$= \frac{\hbar^2}{4\mu}\alpha + \frac{3k}{8}\alpha^{-2}$$

$$\frac{dE(\alpha)}{d\alpha} = \frac{\hbar^2}{4\mu} - \frac{3k}{4}\alpha^{-3} = 0 \quad \text{when} \quad \alpha = \left[\frac{3k\mu}{\hbar^2}\right]^{1/3}$$

$$\Rightarrow E_{best} = \frac{\hbar^2}{4\mu}\alpha_{best} + \frac{3k}{8}\alpha_{best}^{-2}$$

$$= \frac{\hbar^2}{4\mu}\left(\frac{3k\mu}{\hbar^2}\right)^{1/3} + \frac{3k}{8}\left(\frac{\hbar^2}{3k\mu}\right)^{2/3}$$

$$\text{i.e. } E_{best} = \frac{3}{8}\left(\frac{3\hbar^4 k}{\mu^2}\right)^{1/3}$$

*Example 2 – Secular Equations*

Given: $\varphi = \phi_1 c_1 + \phi_2 c_2$

$\phi_1$ & $\phi_2$ orthonormal, $c_1$ & $c_2$ real &

$\langle\phi_1|H|\phi_1\rangle = \alpha_1$, $\langle\phi_2|H|\phi_2\rangle = \alpha_2$

$\langle\phi_1|H|\phi_2\rangle = \beta \quad (<0)$

$$\langle\varphi|H|\varphi\rangle = \langle c_1\phi_1 + c_2\phi_2|H|c_1\phi_1 + c_2\phi_2\rangle$$
$$= c_1^2\langle\phi_1|H|\phi_1\rangle + c_1c_2\langle\phi_1|H|\phi_2\rangle + c_2c_1\langle\phi_2|H|\phi_1\rangle + c_2^2\langle\phi_2|H|\phi_2\rangle$$
$$= c_1^2\alpha_1 + 2c_1c_2\beta + c_2^2\alpha_2$$

$\langle\varphi|\varphi\rangle = c_1^2 + c_2^2$ (by orthonormality of $\phi_1, \phi_2$)

$$\therefore E = \frac{c_1^2\alpha_1 + 2c_1c_2\beta + c_2^2\alpha_2}{c_1^2 + c_2^2}$$

$$\frac{\partial E}{\partial c_1} = 0 = \frac{\partial E}{\partial c_2}$$

$$\frac{\partial E}{\partial c_1} = \frac{2c_1\alpha_1 + 2c_2\beta}{c_1^2 + c_2^2} - \frac{2c_1}{c_1^2 + c_2^2}E = 0$$

when $2c_1(\alpha_1 - E) + 2c_2\beta = 0$

$$\frac{\partial E}{\partial c_2} = \frac{2c_1\beta + 2c_2\alpha}{c_1^2 + c_2^2} - \frac{2c_2}{c_1^2 + c_2^2}E$$

$= 0$ when $2c_1\beta + 2c_2(\alpha - E) = 0$

Variational Principle:

$$\left.\begin{aligned}(\alpha_1 - E)c_1 + \beta c_2 &= 0\\ \beta c_1 + (\alpha_2 - E)c_2 &= 0\end{aligned}\right\}\ \text{Secular Eqns}$$

$$\Rightarrow \begin{pmatrix}\alpha_1 - E & \beta\\ \beta & \alpha_2 - E\end{pmatrix}\begin{pmatrix}c_1\\ c_2\end{pmatrix} = \begin{pmatrix}0\\ 0\end{pmatrix}$$

homogeneous $\Rightarrow$ set to zero for non-trivial $c_1$ & $c_2$

$$\begin{vmatrix} \alpha_1 - E & \beta \\ \beta & \alpha_2 - E \end{vmatrix} = (\alpha_1 - E)(\alpha_2 - E) - \beta^2$$

$$= E^2 - (\alpha_1 + \alpha_2)E + \alpha_1\alpha_2 - \beta^2 = 0$$

$\Rightarrow$

$$E_\pm = \tfrac{1}{2}(\alpha_1 + \alpha_2) \pm \tfrac{1}{2}\sqrt{(\alpha_1+\alpha_2)^2 - 4(\alpha_1\alpha_2 - \beta^2)}$$

$$= \tfrac{1}{2}(\alpha_1 + \alpha_2) \pm \sqrt{(\alpha_1 - \alpha_2)^2 + 4\beta^2}$$

When $\alpha_1 = \alpha_2 = \alpha$

$$\Rightarrow E_\pm = \alpha \pm |\beta|$$

$c_2 = -c_1$ when $E = E_+$

Normalise, $\langle \psi | \psi \rangle = c_1^2 + c_2^2 = 1$

$$\Rightarrow c_1 = \frac{1}{\sqrt{2}} = -c_2$$

$$\Rightarrow \psi_+ = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$$

Similarly $E = E_- \Rightarrow c_2 = +c_1$

$$\Rightarrow \psi_- = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$$