Commutators i.e. common set eigenf^{n}s

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

$= 0 \Rightarrow$ commute $\Leftrightarrow$ compatible, observables

$\neq 0 \Rightarrow$ not commute

$[\hat{p}_x, \hat{x}] = -i\hbar$ measured simultaneously can be known precisely

$[\hat{x}, \hat{p}] = i\hbar$ not com $\Rightarrow$ can't measure $\hat{p}_x$ & $\hat{x}$ simultaneously

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

$[\hat{p}_x, \hat{H}] = 0$ TDSE $\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$, Total E

TISE $\hat{H}(r)\phi_n(r) = E_n\phi_n(r)$

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

momentum eigenval $\hbar k$, e^{ikx}; energy eigenval $\hbar^2k^2/2m$

∞ square well

$\Psi(x) = 1/\sqrt{a}$

$E_n = \hbar^2\pi^2n^2/2ma^2$

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

$c_n = \int \phi_n^*\Psi$

$= \frac{\sqrt{2}}{a}\int_0^a \sin\left(\frac{m\pi x}{a}\right)dx$

$= \frac{\sqrt{2}}{a}\begin{cases} 0 & \text{even} \\ \frac{2a}{n\pi} & \text{odd}\end{cases}$

Prob of measuring $E_n = |c_n|^2$

Prob measuring momentum $|c(k)|^2 \; dk$, $e^{ik\cdot x}$

$\langle\Psi_1|\Psi_2\rangle = \int\Psi_1^*\Psi_2\,d^3r$

$\langle\Psi_1|\hat{A}|\Psi_2\rangle = \int\Psi_1^*\hat{A}\Psi_2\,d^3r$

$|\Psi\rangle = \sum_n c_n|\phi_n\rangle = \sum_n\langle\phi_n|\Psi\rangle|\phi_n\rangle$

$\langle\phi_m|\Psi\rangle = \sum_n c_n\langle\phi_m|\phi_n\rangle = \sum_n c_n\delta_{mn} = c_n$

Conjugate transpose / Hermitian

$|a\rangle = \langle a| = (a_1, a_2, \ldots)$

$\langle a|^+ = |a\rangle$ $\langle a|b\rangle = \langle b|a\rangle^*$

Prob finding particle at a point $\int|\Psi(r,t)|^2 d^3r$

1D: $P(x)dx = |\Psi(x,t)|^2dx$

3D: $P(r)d^3r = |\Psi(r,t)|^2d^3r$

3D Cartesian $d^3r = dx\,dy\,dz$

Spherical $d^3r = r^2\sin\theta\,dr\,d\theta\,d\phi$

Operator $\hat{A}\phi_n = a_n\phi$, Eigenf^n, Eigenval

Normalise wavef^n $\int|\Psi|^2dx = 1$

Hermitian operators: real eigenvalues, orthogonal eigenf^{n}s

$\int\phi_m^*\hat{A}\phi_n = a_n\int\phi_m^*\phi_n$

$\int(\hat{A}\phi_m)^*\phi_n = a_n\int\phi_m^*\phi_n$

$= a_m^*\phi_m^*$

$(a_n - a_m^*)\int\phi_m^*\phi_n = 0$

Expectation vals $\langle\hat{A}\rangle = \sum_n|c_n|^2a_n$

$\langle\hat{A}\rangle = \int\Psi^*\hat{A}\Psi$

posit^n $\langle\hat{x}\rangle = \int_0^a\Psi^*x\Psi\,dx$

momentum $\langle\hat{p}_x\rangle = -i\hbar\int_0^a\Psi^*\frac{\partial\Psi}{\partial x}dx$

$\hat{A}$ → syst → $|c_1|^2$: a_1, ϕ_1; $|c_2|^2$: a_2, ϕ_2; $|c_n|^2$: a_n, ϕ_n

spherical symmetric state $4\pi\int_0^\infty dr\,r^2|u|^2 = 1$

Uncertainty in measurement = width wave packet

$\Delta x = \sqrt{\langle\hat{x}^2\rangle}$

momentum: $\Delta p = \hbar\sqrt{9/2}$

Width Gaussian wavepacket Δt

$\Delta x(t) = \sqrt{\frac{1}{2a} + \frac{\hbar^2a\,t^2}{2m^2}}$

K.E. $\langle T\rangle = \iiint d^3r\,u\left(-\frac{\hbar^2}{2\mu}\nabla^2\right)u$

P.E. $\langle V\rangle = \iiint d^3r\,u\,V(r)u$

Later time

- wavef^n: $\Psi(x,t) = \sum c_nE_n\phi_ne^{-iE_nt/\hbar}$
- $\langle\hat{H}\rangle = \int_0^a dx\,\Psi^*\hat{H}\Psi \to = E_1c_1^2 + E_2c_2^2$

normalised $\Rightarrow$ orthog to each other

5 postulates QM

1. States are def by their wavef^n
2. Every observable has an operator
3. Only possible result of an eigenval measurement = relevant operator
4. QM is not deterministic
5. Btw measurements TDSE governs wavef^n evolut^n

OPERATORS

Differential $\hat{A} = d/dx$ Multiplicative $\hat{A} = x^2$

Parity $\hat{A}f(x) = f(-x)$ Linear $\hat{A}(c_1f_1 + c_2f_2) = c_1\hat{A}f_1 + c_2\hat{A}f_2$

momentum $\hat{p}_i = -i\hbar\nabla_i$, $\hat{p} = \sum_i\hat{p}_i$

Hermitian: $\int f_1^*(x)(\hat{A}f_2(x))dx = \int(\hat{A}f_1(x))^*f_2(x)dx$

$\Psi = \sum_n c_n\phi_n$ If Ψ & ϕ_n normalised $\sum|c_n|^2 = 1$

gives the "amount" of ϕ_n contained in Ψ

Prob obtaining a particular val $\hbar k$

$f(x) = \int dk\,F(k)e^{ikx}$ FT $F(k) = \frac{1}{2\pi}\int dx\,e^{-ikx}$

eigenf^n: $\Psi = \sum c_n\phi_n$

Prob measuring a_m is $|c_m|^2$

For continuous eigenvals FT

Prob measuring E_1 & E_2 $\Psi(x,0) = \frac{1}{\sqrt{2}}\phi_1 + \frac{1}{\sqrt{2}}\phi_2$

E_n & c_n $\Psi = \sum c_n\phi_n$

Prob: $\frac{1}{\sqrt{2}}\times\frac{1}{\sqrt{2}} = \frac{1}{2}$

time for wavepacket to ×2 (gaussian)

$\Delta x(t_0) = 1a$ $\Delta x(t_1) = 2a$

$\Delta x(t) = \sqrt{1/2a + \hbar^2at^2/2m}$

$t = \frac{\sqrt{3}m}{\hbar a}$

we want $\Delta x(t_1) = \sqrt{4/2a}$ ∴ $\frac{\hbar^2at^2}{2m} = \frac{3}{2a}$

∞ square well

Posit^n $\hat{r} = r$

Momentum $\hat{p} = -i\hbar\nabla$

KE → Classic $T = \frac{1}{2}mv^2 = \frac{p^2}{2m}$

→ Qntm $\hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2$

Potential E $\hat{V}(r) = V(r)$

Hamiltonian $\hat{H} = \hat{T} + \hat{V}$

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

Total E operator $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$

$-\frac{\hbar^2}{2m}\frac{\partial}{\partial x^2}\sin\left(\frac{n\pi x}{a}\right) = \frac{\hbar^2\pi^2n^2}{2ma}\sin\left(\frac{n\pi x}{a}\right)$

Eigenval $E_n = \hbar^2\pi^2n^2/2ma$

Eigenf^{n}s $\phi(n) \propto \sin(m\pi x/a)$ — wavef^n should be normalised

Find $\Delta\hat{H}$

Sketch $|c(k)|^2$ & $\langle p_x\rangle$ $|c(k)|^2\,dp = \hbar\,dk = \frac{\cos^2(ka/2)}{(\pi^2 - k^2a^2)^2}$

- symmetric $k=0$: consistent $\langle\hat{p}_x\rangle = 0$
- peaked $k = \pm\frac{\pi}{a}$: consistent $\langle\hat{p}_x^2\rangle = \pi^2\hbar^2/a^2$

$\Delta A^2 = \int\Psi^*(\hat{A} - \langle\hat{A}\rangle)^2\Psi = \langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2$

results look like: $\Delta^2x = a^2\left(\frac{1}{12} - \frac{1}{2\pi^2}\right)$ ∴ $\Delta x = 0.18a$

$\Delta x\,\Delta p = 0.57\hbar \Rightarrow$ not consistent with uncertainty princ

In 3rd measurement: ϕ_1: β_1 prob 4/13, β_2 prob 9/13

$\phi_1 = \sqrt{\frac{1}{13}}(2x_1 + 3x_2)$ ϕ_2: β_1 prob 9/13, β_2 prob 4/13

$\phi_2 = \sqrt{\frac{1}{13}}(3x_1 - 2x_2)$

Probs some val: Total prob $= \frac{4}{13}\times\frac{4}{13} + \frac{9}{13}\times\frac{9}{13}$

Prove normalised $\int\phi_n^*\phi_n = 1$ orthogonal $\int\phi_n^*\phi_m = \int\phi_n\phi_m^* = 0$

Normalise $\Psi(r) = A\exp(-r/a_0)$ H in 3D $A = \sqrt{1/\pi a_0^3}$

$\iiint\Psi^2r^2\sin\theta\,dr\,d\theta\,d\phi$

Angular momentum

Classic $\underline{L} = \underline{r}\times\underline{p}$ QM $\hat{\underline{L}} = \hat{\underline{r}}\times\hat{\underline{p}}$

$\begin{vmatrix} i & j & k \\ x & y & z \\ p_x & p_y & p_z\end{vmatrix}$

angular momentum, posit^n, momentum particle

$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$

$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z$

$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$

square magnitude tot angular mom $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$

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

$[a,b] = -[b,a]$

Note: $\hat{L}_x$ & $\hat{L}_y$ are non commuting $\Rightarrow [\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$

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

$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x$ only terms that don't commute $\hat{p}_x : [\hat{x}, \hat{p}_x] = i\hbar$

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

$[\hat{L}^2, \hat{L}_x] = 0$ $L_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$

$[L_z, L_z] = L_zL_z - L_zL_z = 0$

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

$[\hat{L}_+, \hat{L}_-] = 2\hbar\hat{L}_z$

Prove total E ($\hat{H}$) & momentum $\hat{p}$ can be measured simultaneously

i.e. commute / compatible

$\hat{p} = i\hbar\frac{d}{dx}$ Commutator $[\hat{p}, \hat{H}] = \frac{i\hbar^3}{2m}\left(\frac{d}{dx}\frac{d^2}{dx^2} - \frac{d^2}{dx^2}\frac{d}{dx}\right) = 0$

$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$ apply to arbitrary f^n: $-i\hbar\left(\frac{d}{dx}V(x) - V(x)\frac{d}{dx}\right)$

$\frac{d}{dx}(V(x)f(x)) - V(x)\frac{d}{dx}f(x) = \frac{dV}{dx}f(x)$

$[\hat{p}, \hat{H}] = -i\hbar\,dV/dx$ if $V(x)$ cnst $\Rightarrow \frac{dV}{dx} = 0 \Rightarrow$ commute ✓

Ladder operators

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

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

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

$\beta_{n+1} = \beta_n + \hbar$, β_n, $\beta_{n-1} = \beta_n - \hbar$

$\hat{L}_+|\phi_{max}\rangle = 0$

$\hat{L}_-|\phi_{min}\rangle = 0$

$\hat{L}_+\hat{L}_-|\phi_{max}\rangle = 0$

$\hat{L}_-\hat{L}_+ = \hat{L}^2 + \hat{L}_z^2 - \hbar\hat{L}_z$ ↓ similar ans

$\Rightarrow(\hat{L}^2 + \hat{L}_z^2 - \hbar\hat{L}_z)|\phi_{max}\rangle = 0$ $\alpha = \beta_{min}(\beta_{min} - \hbar)$

$(\alpha - \beta_{max}^2 - \hbar\beta_{max})|\phi_{max}\rangle = 0$ $\beta_{min} = -\beta_{max}$

$\alpha = \beta_{max}(\beta_{max} + \hbar)$ $\alpha = \beta_{min}(\beta_{min} - \hbar) = \beta_{max}(\beta_{max} + \hbar)$

neighbouring β on ladder differ by $\hbar$ $\beta_{max} - \beta_{min} = n\hbar$

Prove $L_-|\phi_n\rangle = (\beta_n - \hbar)|\phi_n\rangle$

$\hat{L}_z|\phi_n\rangle = \beta_n|\phi_n\rangle$

$L_-L_z|\phi_n\rangle = \beta_n\hat{L}_-|\phi_n\rangle$

$L_-L_z = \hbar L_- + L_zL_-$

$L_-L_z|\phi_n\rangle = \hbar\hat{L}_-|\phi_n\rangle + \hat{L}_z\hat{L}_-|\phi_n\rangle$

$L_z(L_-\phi_n) = (\beta - \hbar)\hat{L}_-|\phi_n\rangle$

$L_-|\phi_n\rangle$ in an eigenf^n of L_z with eigenval $(\beta_n - \hbar)$

Stern-Gerlach: measures z component for angular momentum

$Y_{\ell m}(\theta,\phi)$: common eigenf^{n}s $\hat{L}^2$ & $\hat{L}_z$ ⇒ Solut^n spherical harm

$\hat{L}^2|Y_{\ell m}(\theta,\phi)\rangle = \ell(\ell+1)\hbar|Y_{\ell m}(\theta,\phi)\rangle$

$\hat{L}_z|Y_{\ell m}(\theta,\phi)\rangle = m\hbar|Y_{\ell m}(\theta,\phi)\rangle$

eigenvals $\hat{L}^2 \to \ell(\ell+1)$, ℓ = integer

$\hat{L}_z \to m\hbar$, $-\ell < m$ = integer $< \ell$

ℓ	Magnitude L	Possible L_z vals
0	0	
1	$\sqrt{2}\hbar$	$-\hbar, 0, \hbar$
2	$\sqrt{6}\hbar$	$-2\hbar, -\hbar, 0, \hbar, 2\hbar$
1/2	$\sqrt{3}/2\,\hbar$	$-\hbar/2, \hbar/2$

½ integer ≠ orbital angular momentum

r, θ, ϕ

$\hat{L} = \hat{r}\times\hat{p} = -i\hbar\,r\times\nabla$

$\nabla = e_r\frac{\partial}{\partial r} + e_\theta\frac{1}{r}\frac{\partial}{\partial\theta} + e_\phi\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}$

$\hat{L} = -i\hbar\left(e_\phi\frac{\partial}{\partial\theta} - e_\theta\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\right)$

$\hat{L}_z = -i\hbar\,\partial/\partial\phi$

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

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

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

$\hat{L}_+ = \hbar\exp(i\phi)\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)$

$\hat{L}_- = \hbar\exp(-i\phi)\left(-\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)$

$\exp(i\phi) = \cos\phi + i\sin\phi$

$\hat{S}$ spin angular momentum

$[S_x, S_y] = i\hbar S_z$

Component	Eigenval	Eigenvector
S_x	$+\hbar/2$	$\frac{1}{\sqrt{2}}\binom{1}{1}$
S_x	$-\hbar/2$	$\frac{1}{\sqrt{2}}\binom{1}{-1}$
S_y	$+\hbar/2$	$\frac{1}{\sqrt{2}}\binom{1}{i}$
S_y	$-\hbar/2$	$\frac{1}{\sqrt{2}}\binom{1}{-i}$
S_z	$+\hbar/2$ $m_s = \frac{1}{2}$	$\binom{1}{0}$ ↑
S_z	$-\hbar/2$ $m_s = -\frac{1}{2}$	$\binom{0}{1}$ ↓

Pauli matrices $\hat{S}_i = \frac{\hbar}{2}\sigma_i$

$\sigma_x = \begin{pmatrix}0&1\\1&0\end{pmatrix}$ $\sigma_y = \begin{pmatrix}0&-i\\i&0\end{pmatrix}$ $\sigma_z = \begin{pmatrix}1&0\\0&-1\end{pmatrix}$

$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \frac{3}{4}\hbar^2\begin{pmatrix}1&0\\0&1\end{pmatrix}$

eigenvals: $s(s+1)\hbar$, $s = \frac{1}{2}$

eigenvectors: $\hat{S}_x, \hat{S}_y, \hat{S}_z$ with eigenval $\frac{3}{4}\hbar^2$

electrons = spin half particle $s = 1/2$, $m_s = \pm 1/2$

$|\Psi\rangle = \binom{a}{b}$ in terms of S_x. If measurement made in x component of spin ang momentum, what are prob of measuring $+\hbar/2$ & $-\hbar/2$? $\hat{S}_x \to \frac{1}{\sqrt{2}}\binom{1}{1} = |\phi_1\rangle$

$\frac{1}{\sqrt{2}}\binom{1}{-1} = |\phi_2\rangle$

$c_1 \langle\phi_1|\Psi\rangle = \frac{1}{\sqrt{2}}(1\;1)\binom{a}{b} = \frac{a+b}{\sqrt{2}}$

$c_2 \langle\phi_2|\Psi\rangle = \frac{1}{\sqrt{2}}(1\;-1)\binom{a}{b} = \frac{a-b}{\sqrt{2}}$

$\langle\Psi|\Psi\rangle = (a^*\;b^*)\binom{a}{b} = |a|^2 + |b|^2 = 1$ normalise

Prob $\to +\frac{\hbar}{2} \Rightarrow c_1 = \left|\frac{a+b}{\sqrt{2}}\right|^2 = \frac{|a|^2 + |b|^2 + as^* + a^*b}{2}$

$\to -\frac{\hbar}{2} \Rightarrow c_2 = \left|\frac{a-b}{\sqrt{2}}\right|^2 = \frac{1}{2}\,\mathrm{Re}(as^*)^2$

$= \mathrm{Re}(as^*)$

Two distinguishable particles non-interacting in external field → indep

Potential E $V(r_1, r_2) = V_1 + V_2$

$\phi(r_1, r_2) = u_a(r_1)u_b(r_2)$

state of a particle 1, "u_b" of "2"

Hamiltonian $\hat{H} = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V_1 + V_2$

TISE: $\left[-\frac{\hbar^2}{2m_1}\frac{1}{u_a}\nabla_1^2u_a + \frac{1}{u_a}V_1(r_1)u_a\right]$ + $\left[-\frac{\hbar^2}{2m_1}\frac{1}{u_b}\nabla_2^2u_b + \frac{1}{u_b}V_2(r_2)u_b\right] = E$

each bracket = cnst, $\sum$cnst $= E_1 + E_2 = E_{TOT}$ } separates into 2 TISE$_s$ $[\;] = E_1u_a$, $[\;] = E_2u_b$

Apply H, ground state: Find E eigenvals: $\hat{H} = \hat{T}_1 + \hat{T}_2$, $= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x_2^2}$, $E_n = n^2\hbar^2\pi^2/2ma^2$

$u_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$, $E_n = n^2\hbar^2\pi^2/2ma^2$

Find spatial part eigenf^n + Eigenval + degeneracy: correspond to 1 or more diff state, ground & 1st excited state

- Distinguishable particles

$u_{ab}(x_1, x_2) = u_a(x_1)u_b(x_2)$

$E_{ab} = E_a + E_b = (n_a^2 + n_b^2)\frac{\hbar^2\pi^2}{2ma^2}$

- Ground state $a = b = 1$: $u_{11}(x_1, x_2) = \frac{2}{a}\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{a}\right)$, $n_a = n_b = 1$, $E_1 = 2\hbar^2\pi^2/2ma^2$

non-degenerate

- 1st excited state: $n_a = 1, n_b = 2$: $u_{12}(x_1, x_2) = \frac{2}{a}\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{2\pi x_2}{a}\right)$

or $n_a = 2, n_b = 1$ $E_{12} = 5\hbar^2\pi^2/2ma^2$

$u_{21}(x_1, x_2) = \frac{2}{a}\sin\left(\frac{2\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{a}\right)$, $E_{21} = 5\hbar^2\pi^2/2ma^2$

exchanging particle labels changes E eigenf^n but not energy eigenval ⇒ 1st state double degenerate

Fermions indist. $u_-(x_1, x_2) = \frac{1}{\sqrt{2}}[u_a(x_1)u_b(x_2) - u_a(x_2)u_b(x_1)]$

$a = b = 1 \Rightarrow u_- = 0$: does not exist (Pauli exclus^n)

- Ground state $u_{-,\text{ground}} = \frac{1}{\sqrt{2}}[u_1(x_1)u_2(x_2) - u_1(x_2)u_2(x_1)]$

$= \frac{1}{\sqrt{2}}\left[\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{2\pi x_2}{a}\right) - \sin\left(\frac{\pi x_2}{a}\right)\sin\left(\frac{2\pi x_1}{a}\right)\right]$

$E_{\text{ground}} = 5\hbar^2\pi^2/2ma^2$

interchanging particles gives $-u_-$, ground

$|u_{-,\text{ground}}|^2 = |-u_{\text{ground}}|^2$

∴ % locating particle unchanged ⇒ non-degen

Distinguishable particles $u_g(x_1, x_2) = u_1(x_1)u_1(x_2)$ & $\hat{T}_1u_1(x_1) = E_1u_1(x_1)$

∴ $\hat{H}u_{\text{ground}}(x_1, x_2) = (\hat{T}_1 + \hat{T}_2)u_1(x_1)u_1(x_2)$

$= u_1(x_2)\hat{T}_1u_1(x_1) + u_1(x_1)\hat{T}_2u_1(x_2)$

$= (E_1 + E_2)u_1(x_1)u_1(x_2) = E_{\text{ground}}u_1(x_1)u_1(x_2)$

$E_{\text{ground}} = 2E_1 = 2\hbar^2\pi^2/2ma^2$

Bosons identical $u_g = u_1(x_1)u_1(x_2)$ (follow same logic as above)

Fermions identical $u_{-,g} = \frac{1}{\sqrt{2}}[u_1(x_1)u_2(x_2) - u_1(x_2)u_2(x_1)]$

$\hat{T}_1u_1(x_1) = E_1u_1(x_1)$, $\hat{T}_2u_2(x_2) = E_2u_2(x_2)$ } $\hat{H}u_{-,g}(x_1, x_2) = (\hat{T}_1 + \hat{T}_2)u_{-,\text{ground}}(x_1, x_2)$

$= \frac{u_2(x_2)}{\sqrt{2}}\hat{T}_1u_1(x_1) + \frac{u_1(x_1)}{\sqrt{2}}\hat{T}_2u_2(x_2) - \frac{u_1(x_2)}{\sqrt{2}}\hat{T}_1u_2(x_1) - \frac{u_2(x_1)}{\sqrt{2}}\hat{T}_2u_1(x_2)$

$= (E_1 + E_2)\frac{u_1(x_1)u_2(x_2)}{\sqrt{2}} - (E_2 + E_1)\frac{u_1(x_2)u_2(x_1)}{\sqrt{2}}$

$= (E_1 + E_2)u_{-,\text{ground}} = E_{\text{ground}}u_{-,\text{ground}}$

∴ $E_{\text{ground}} = E_1 + E_2 = 5\frac{\hbar^2\pi^2}{2ma^2}$

Bosons indist. $u_+(x_1, x_2) = A[u_a(x_1)u_b(x_2) + u_a(x_2)u_b(x_1)]$

- Ground state $a = b = 1$ with normalisat^n cnst $A = 1/2$ ← symmetric wavef^n with $u_a = u_b$: $u_+ = A[u_au_a + u_au_a]$, $= 4|A|^2 = 1$ ∴ $A = 1/2$

$u_{+,\text{ground}} = \frac{1}{2}[u_1(x_1)u_1(x_2) + u_1(x_2)u_1(x_1)]$

$= u_1(x_1)u_1(x_2) = \frac{2}{a}\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{a}\right)$

$E_{\text{ground}} = 2\hbar^2\pi^2/2ma^2$ → non-degen

- 1st ex st: $A = 1/\sqrt{2}$ ← $\int d^2u_a^2u_b^2 = |A|^2\int d^2[u_au_b \pm u_au_b]^*[u_au_b \pm u_au_b] = 1$

$u_{+,1^{st}\text{exc}} = \frac{1}{\sqrt{2}}[u_1(x_1)u_2(x_2) + u_1(x_2)u_2(x_1)] = \frac{1}{\sqrt{2}}\frac{2}{a}\left[\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{2\pi x_2}{a}\right) + \sin\left(\frac{\pi x_2}{a}\right)\sin\left(\frac{2\pi x_1}{a}\right)\right]$

$E_{1^{st}\text{exc}} = 5\hbar^2\pi^2/2ma^2$

interchanging particle labels does not change $u_{+,1^{st}\text{excite}} \Rightarrow 1^{st}$ ex st non-degen

Indistinguishable particles: Hermitian operator unchanged $\hat{H}(1,2) = \hat{H}(2,1)$

Particle exchange operator $\hat{P}_{12}$ $\hat{P}_{12}\hat{H}(1,2)\phi(1,2) = \hat{H}(2,1)\phi(2,1) = \alpha\phi(2,1)$

$\hat{H}(2,1)\phi(2,1) = \alpha\phi(2,1)$

$= \alpha\hat{P}_{12}\phi(1,2)$

Show exchange operator is Hermitian if $\langle\phi|\hat{P}_{12}\phi\rangle = \langle\hat{P}_{12}\phi|\phi\rangle$

$\hat{P}_{12}$: $\hat{A}(1,2)\phi(1,2) = \alpha\phi(1,2)$, $\hat{P}_{12}\hat{A}(1,2)\phi(1,2) = \alpha\phi(2,1)$

$\langle\phi|\hat{P}_{12}\phi\rangle = \int dr$

acts on $\phi(1,2)$ of $\hat{A}(1,2)$ → labels are interchanged

$= \alpha\phi(2,1)$

$= \hat{A}(2,1)\phi(2,1)$

$= \hat{A}(1,2)\hat{P}_{12}(1,2)$

$\hat{P}_{12}\phi(1,2) = \phi(2,1)$

$[\hat{P}_{12}, \hat{A}(1,2)] = 0$ ⇐ $\hat{P}_{12}\hat{A}(1,2)\phi(1,2) - \hat{A}(1,2)\hat{P}_{12}\phi(1,2) = 0$

∴ $\hat{P}$ compatible with any Hermitian op $\hat{A}$

∴ an eigenf^n $\phi(1,2)$ of $\hat{A}(1,2)$ must be solut^n eigenval eq^n

$\hat{P}_{12}\phi(1,2) = p\phi(1,2)$

$\phi(1,2) = \hat{P}_{12}\phi(2,1) = p^2\phi(1,2)$

$\therefore p^2 = 1 \to p = \pm 1$

$\phi(1,2) = \pm\phi(2,1)$ symmetric / anti-sym

Sym	Anti-sym
$\phi(1,2) = \phi(2,1)$	$\phi(1,2) = -\phi(2,1)$
$S = 0, 1, 2$	$S = 1/2, 3/2, \ldots$
Bose-Einstein: photons, phonons, pi-mesons, cooper pairs	Fermi-Dirac: electrons, protons, neutrons
$u_+(1,2) = \frac{1}{\sqrt{2}}[u_a(1)u_b(2) + u_a(2)u_b(1)]$	$u_-(1,2) = \frac{1}{\sqrt{2}}[u_a(1)u_b(2) - u_a(2)u_b(1)]$ normalised

Pauli exclus^n: 2 ferm^{n}s cannot exist same single state

Fermi-D: occupat^n ferm^n state either zero or unity

Bose Einstein: if state exists $(u_a(1,2) \neq 0$ if $u_a = u_b)$ no limit n^o particles in same qntm state

Two particles, no external field

Potential E only $\propto r = r_1 - r_2$

Hamiltonian $\hat{H} = -\sum_i\frac{\hbar^2}{2m_i}\nabla_i^2 + V(r_1, r_2, \ldots r_n)$

$\hat{H} = \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + V(r_1, r_2)$

Treat centre-of mass & relative mot^n separately $M = m_1 + m_2$

Centre of mass coord $\underline{R} = \frac{m_1r_1 + m_2r_2}{m_1 + m_2} = \frac{m_1}{M}r_1 + \frac{m_2}{M}r_2$

Velocity centre mass $\underline{v} = \frac{d\underline{R}}{dt} = \frac{m_1}{M}v_1 + \frac{m_2}{M}v_2$

Momentum c of m $\underline{P} = M\underline{V}$ $= \underline{p}_1 + \underline{p}_2$

Relative mot^n particle reduced mass $\mu = \frac{m_1m_2}{M}$

velocity $\underline{v} = dr/dt = v_1 - v_2$

momentum $\underline{p} = \mu\underline{v} = \frac{m_1m_2}{M}(v_1 - v_2) = \frac{m_2p_1 - m_1p_2}{M}$

$\underline{P} = \underline{p} + \frac{m_1}{M}\underline{P}$, $\underline{p}_2 = -\underline{p} + \frac{m_2}{M}\underline{P}$

hamiltonian $\hat{H} = \frac{m_1 + m_2}{2M^2}\hat{P}^2 + \frac{1}{2}\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\hat{p}^2 + V(r)$

$= \frac{\hat{P}^2}{2M} + \frac{\hat{p}^2}{2\mu} + V(r)$

$\hat{H} = \hat{H}_{cm} + \hat{H}_{RM}$

$-\frac{\hbar^2}{2M}\nabla_R^2$, $-\frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)$

$\phi(R, r) = U(R)\,u(r)$

TISE → CM $-\frac{\hbar^2}{2M}\nabla_R^2U = E_RU$

→ RM $-\frac{\hbar^2}{2\mu}\nabla^2u + V(r)u = E_ru$

spherical symmetric state $4\pi\int_0^\infty dr\,r^2|u|^2 = 1$

Central potentials: $V(r) \propto$ distance origin, 3D Schrod → separates

general potential E polar coords $r = (r, \theta, \phi)$

TISE: $-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial u}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial u}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2u}{\partial\phi^2}\right] + V(r)u = Eu$

$u = RY \to r^2/RY$

we look for separable solut^{n}s $[u(r,\theta,\phi) = R(r)\,Y(\theta,\phi)]$

$\left[\frac{-\hbar^2}{2\mu}\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + r^2V(r) - r^2E\right] - \frac{\hbar^2}{2\mu}\left[\frac{1}{Y}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{Y}\frac{1}{\sin^2\theta}\frac{\partial^2Y}{\partial\phi^2}\right] = 0$

for only r & $\theta\phi$: each bracket must be cnst to hold in all points in space $[\;] = -\lambda$

$-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left(V(r) + \frac{\hbar^2\lambda}{2\mu r^2}\right)R = ER$

$-\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)$

$-\frac{1}{\sin^2\theta}\frac{\partial^2Y}{\partial\phi^2} = \lambda Y$

radial dependence, found solving; becomes $\hbar\ell(\ell+1)/2\mu r^2$

Angular momentum operator $\hat{L}^2$

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

$\hat{L}^2|Y_{\ell m}(\theta,\phi)\rangle = \ell(\ell+1)\hbar^2|Y_{\ell m}(\theta,\phi)\rangle$

degenerate solut^n: m & ℓ

discrepancy error → reduced mass, $\lambda = \ell(\ell+1)$

Hydrogen atom

Electrostatic potential energy btw e & proton $V(r) = -e^2/4\pi\epsilon_0r$

Energy eigenvals $E_n = -\frac{1}{n^2}\left(\frac{\mu e^4}{32\pi^2\epsilon_0^2\hbar^2}\right)$ [eV]

n: principal qnt n^o, l: angular momentum, m: magnetic $|m| \le \ell$

$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$ Bohr radius

$\to n = 1, \ell = 0, m = 0$

$R(r) \propto \exp(-r/a_0)$

$Y_{00} = \sqrt{1/4\pi}$, $u_{100} = A\exp(-r/a_0)$

Normalisat^n cnst A: $\iiint r^2\sin\theta\,dr\,d\theta\,d\phi\,|u|^2 = 1$

Eigenval $E_1 = -13.6$eV Binding energy $= E_1$

positron $m_p = m_e$

wavelength btw Balmer line $\frac{1}{\lambda} = \frac{\mu}{m_e}R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$

$R = m_ee^4/32\pi^2\epsilon_0^2\hbar hc\,[m^{-1}]$

$S = S_1 + S_2$ $M_s = 1$ & $S = 0$

Total spin operator $\hat{S}^2 = (\hat{S}_1 + \hat{S}_2)\cdot(\hat{S}_1 + \hat{S}_2) = \hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1\cdot\hat{S}_2$

$\hat{S}_1\cdot\hat{S}_2 = S_{1x}S_{2x} + S_{1y}S_{2y} + S_{1z}S_{2z}$

Eigenf^n 2 fermions with $s_i = \frac{1}{2}$: $\alpha_i = \binom{1}{0}$, $\beta_i = \binom{0}{1}$

$\hat{S}_{zi}\alpha_i = \frac{\hbar}{2}\binom{1}{0}\binom{1}{0} = \frac{\hbar}{2}\alpha_i$ & $\hat{S}_{zi}\beta_i = -\frac{\hbar}{2}\beta_i$

Two non-interacting indisting spin ½ ferm^n: spin eigf^{n}s

$S = 1 \Rightarrow 3$ spin eigf^n: $M_s = -1, 0, 1$

$\chi_{11}(1,2) = \alpha_1\alpha_2$, $\chi_{1-1}(1,2) = \beta_1\beta_2$, $\chi_{10}(1,2) = \frac{1}{\sqrt{2}}[\ldots + \alpha_2\beta_1]$ 2 identical $s = \frac{1}{2}$ ferm^{n}s

$S = 0 \Rightarrow M_s = 0$: $\chi_{00}(1,2) = \frac{1}{\sqrt{2}}[\alpha_1\beta_2 - \alpha_2\beta_1]$

Space & Spin dependent eigenf^n $\phi(1,2) = u(1,2)\,\chi(1,2)$

$\hat{S}^2\chi_{SM_S}(1,2) = S(S+1)\hbar^2\chi_{SM_S}(1,2)$

$\hat{S}_z\chi_{SM_S}(1,2) = M_S\hbar\chi_{SM_S}(1,2)$

spin magnetic qntm n^o: $M_s = -S, -S+1, \ldots S$

2 ways to generate antisym eigf^n $\phi(1,2)$ required for ferm^{n}s → Triplet state ↑↑ → Singlet state ↓↓

Triplet state ↑↑

exchange force
(1/2) ← → (1/2)
repel each other; short separat°s
property anti-sy space eigenf°

$u(1,2)$ antisym, $X(1,2)$ sym

$u_-(1,2) = \frac{1}{\sqrt{2}}[u_a(1)u_b(2) - u_a(2)u_b(1)]$

$\chi_{11}(1,2) = \alpha_1\alpha_2$ $\quad r_1 \approx r_2 \Rightarrow u_a(1)u_b(2) \approx u_a(2)u_b(1)$

$\chi_{1-1}(1,2) = \beta_1\beta_2$ $\quad \Rightarrow u_-(1,2) \approx 0$, $\varnothing(1,2) \approx 0$

$\chi_{10}(1,2) = \frac{1}{\sqrt{2}}[\alpha_1\beta_2 + \alpha_2\beta_1]$ fermi°s with aligned spins have small % of being found in the same reg° of space

Singlet stt ↑↓

exchange force
(1/2) → ← (1/2)
attract each other; short separat°s

$u(1,2)$ sym, $X(1,2)$ antisym

$u_+(1,2) = \frac{1}{\sqrt{2}}[u_a(1)u_b(2) + u_a(2)u_b(1)]$

$\chi_{00}(1,2) = \frac{1}{\sqrt{2}}[\alpha_1\beta_2 - \alpha_2\beta_1]$

$r_1 \approx r_2$, $\varnothing(1,2) \neq 0 \Rightarrow$ ferm° with anti-parallel spins have bigger % of being found same reg° space

Find expectat° val square separat° distance btw two partic ← orthonormal state

$\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2\langle x_1 x_2 \rangle$

distinguishable $u(x_1, x_2) = u_a(x_1)u_b(x_2)$

$\langle x_1^2 \rangle = \iint u_a^* u_b^* x_1^2 u_a u_b \, dx_1 dx_2$

orth: $= \int u_a^* x_1^2 u_a \, dx_1 \int |u_b|^2 dx_2$

$= \int u_a^* x_1^2 u_a \, dx_1 = \langle x^2 \rangle_a \cdot 1$

$\langle x_2^2 \rangle = \iint u_a^* u_b^* x_2^2 u_a u_b \, dx_1 dx_2 = \langle x^2 \rangle_b$

$\langle x_1 x_2 \rangle = \int u_a^* x_1 u_a \, dx_1 \int u_b^* x_2 u_b \, dx_2 = \langle x \rangle_a \langle x \rangle_b$

$\langle (x_1 - x_2)^2 \rangle_{disting} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b$

bosons/ferm°s $u_\pm = \frac{1}{\sqrt{2}}[u_a u_b \pm u_a u_b]$

$\int dx_i \, u_a^*(x_i) u_b(x_i) = \delta_{ab}$

$\langle x_1^2 \rangle = \iint u_\pm^* x_1^2 u_\pm \, dx_1 dx_2$

$= \frac{1}{2}\begin{bmatrix} \int x_1^2 |u_a(x_1)|^2 dx_1 \int |u_b(x_2)|^2 dx_2 \\ + \int x_1^2 |u_b(x_1)|^2 dx_1 \int |u_a(x_2)|^2 dx_2 \\ \pm \int x_1^2 u_a(x_1)^* u_b(x_1) dx_1 \int u_b(x_2)^* u_a(x_2) dx_2 \\ \pm \int x_1^2 u_b(x_1)^* u_a(x_1) dx_1 \int u_a(x_2)^* u_b(x_2) dx_2 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} \langle x^2 \rangle_a + \langle x^2 \rangle_b \\ \pm 0 \pm 0 \end{bmatrix} = \frac{1}{2}[\langle x^2 \rangle_a + \langle x^2 \rangle_b]$

$\sim \langle x_2^2 \rangle = \frac{1}{2}[\langle x^2 \rangle_b + \langle x^2 \rangle_a]$

$\langle x_1 x_2 \rangle = \iint u_\pm^* x_1 x_2 u_\pm \, dx_1 dx_2 = \langle x \rangle_a \langle x \rangle_b \pm \langle a|x|b\rangle \langle b|x|a\rangle$

$= \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2$

$\Rightarrow \langle (x_1 - x_2)^2 \rangle_\pm = \langle (x_1 - x_2)^2 \rangle_{disting} \mp 2|\langle x \rangle_{ab}|^2$

identical [bosons tend to be [close together; ferm°s further apart] exchange force

Note: $\langle (x_1 - x_2)^2 \rangle_\pm = \langle (x_1 - x_2)^2 \rangle_{disting}$ if $\langle x \rangle_{ab} = \int x u_a(x)^* u_b(x) dx = 0 \Leftrightarrow$ no overlap btw u_a & u_b

particles far enough apart ⇒ treat as indistinguishable

Find ground state wavef° 2 non-interact fermi°s in

(↑↑) Total spin $S = 1$; overall eigf° $\varnothing(1,2) = u_-(1,2)\chi_{1m_s}(1,2)$

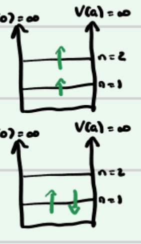
Ground state corresponds 1 electron $n=1$ & other e in $n=2$; $M_s = -1, 0, 1$

$u_{-,ground} = \frac{1}{\sqrt{2}}[u_1(x_1)u_2(x_2) - u_1(x_2)u_2(x_1)]$

(↑↓) $S = 0$ $\quad \varnothing(1,2) = u_+(1,2)\chi_{00}(1,2)$

Ground state: $a = b = 1$ $\quad \chi_{00}(1,2) = \frac{1}{\sqrt{2}}[\alpha_1\beta_2 - \alpha_2\beta_1]$

$u_+(1,2) = \frac{1}{2}[u_1(x_1)u_1(x_2) + u_1(x_2)u_1(x_1)] = u_1(x_1)u_1(x_2)$ finite



Given χ Find S & M_s

$\chi_{11}(1,2)\alpha_1\alpha_2 \Rightarrow \hat{S}^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2(\hat{S}_{x_1}\hat{S}_{x_2} + \hat{S}_{y_1}\hat{S}_{y_2} + \hat{S}_{z_1}\hat{S}_{z_2})$

$\hat{S}_1^2 = \hat{S}_{x_1}^2 + \hat{S}_{y_1}^2 + \hat{S}_{z_1}^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

$\hat{S}_1^2 \alpha_1 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{3}{4}\hbar^2 \alpha_1$ $\quad \alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

$\hat{S}_1^2 \alpha_1\alpha_2 = (\hat{S}_1^2\alpha_1)\alpha_2 = \frac{3}{4}\hbar^2 \alpha_1\alpha_2$ $\quad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

$\hat{S}_2^2 \alpha_1\alpha_2 = \frac{3}{4}\hbar^2 \alpha_1\alpha_2$

$\hat{S}_{x_1}\hat{S}_{x_2}\alpha_1\alpha_2 = \hat{S}_{x_1}\alpha_1 \hat{S}_{x_2}\alpha_2 = \frac{\hbar^2}{4}\beta_1\beta_2$

$\hat{S}_{y_1}\hat{S}_{y_2} = -\frac{\hbar^2}{4}\beta_1\beta_2$ $\quad \hat{S}_{z_1}\hat{S}_{z_2} = \frac{\hbar^2}{4}\alpha_1\alpha_2$

$\Rightarrow \hat{S}^2 \alpha_1\alpha_2 = \frac{3}{4}\hbar^2\alpha_1\alpha_2 + \frac{3}{4}\hbar^2\alpha_1\alpha_2 + 2\frac{\hbar^2}{4}(\beta_1\beta_2 - \beta_1\beta_2 + \alpha_1\alpha_2)$

$= S(S+1)\hbar^2\alpha_1\alpha_2 \Rightarrow S = 1$

$\hat{S}_{\pm i} = \hat{S}_{x_i} \pm i\hat{S}_y = \frac{\hbar}{2}\left[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \pm i\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\right] = \frac{\hbar}{2}\left[\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \pm \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\right]$

$\hat{S}_{+i} = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$ Effect $\hat{S}_{\pm i}$ single spin particle: $\hat{S}_{+i}\alpha_i = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix}\hbar = 0$: top ladder

$\hat{S}_{-i} = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$ $\quad \hat{S}_{-i}\alpha_i = \hbar\begin{pmatrix} 0 \\ 1 \end{pmatrix} \alpha\beta_i$ $\quad (\hat{S}_{-1}\alpha_1)\alpha_2$

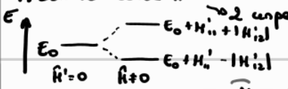
Two particle state → $\hat{S}_+\chi_{11}(1,2) = (\hat{S}_{+1} + \hat{S}_{+2})\alpha_1\alpha_2 = +(\hat{S}_{+2}\alpha_2)\alpha_1 = 0$

$\hat{S}_-\chi_{11} = \hbar(\beta_1\alpha_2 + \alpha_1\beta_2)\alpha\chi_{10}(1,2)$ $\quad$ +1, 0, -1

Degenerate perturbat° theory

Problems arise if $E_{0n} - E_{0k} < \langle \varnothing_{0k}|\hat{H}|\varnothing_{0n}\rangle$ → 2 unperturbed eigenval are degen

2 degen states $|\varnothing_{01}\rangle$ $|\varnothing_{02}\rangle$ $\quad \hat{h}_0|\varnothing_{01}\rangle = E_0|\varnothing_{01}\rangle$ ① $\quad \hat{h}_0|\varnothing_{02}\rangle = E_0|\varnothing_{02}\rangle$



$E = E_0 + H_{11}' \pm |H_{12}'|$

PERTURBAT° BREAKS DEGEN $|\varnothing_{01}\rangle$ & $|\varnothing_{02}\rangle$ $\quad$ E corresponds 2 or more different quantum states

H degen states ⇒ $|\varnothing\rangle = \sum_{m=1}^{n} a_m|\varnothing_m\rangle$

We look for solut°s of $(\hat{h}_0 + \hat{H}')|\varnothing\rangle = E|\varnothing\rangle$ ② in the form $|\varnothing\rangle = a_1|\varnothing_{01}\rangle + a_2|\varnothing_{02}\rangle$ ③

2 → 3 with ①

$\begin{vmatrix} H_{11}' - \Delta E & \cdots & H_{1n}' \\ H_{21} & H_{22}' - \Delta E & \vdots \\ \vdots & & \\ H_{n1}' & \cdots & H_{nn}' - \Delta E \end{vmatrix} = 0$

$(E_0 - E)a_1|\varnothing_{01}\rangle + (E_0 - E)a_2|\varnothing_{02}\rangle + a_1\hat{H}'|\varnothing_{01}\rangle + a_2\hat{H}'|\varnothing_{02}\rangle = 0$

normalised $\langle \varnothing_{01}|\varnothing_{01}\rangle = 1$; orthog $\langle \varnothing_{01}|\varnothing_{02}\rangle = 0$; close with $\langle \varnothing_{01}|$ & $\langle \varnothing_{02}|$

$H_{d\beta}' = \langle \varnothing_{0\alpha}|\hat{H}|\varnothing_{0\beta}\rangle$

$\Delta E = E - E_0$

$(E_0 + H_{11}' - E)a_1 + H_{12}'a_2 = 0$
$H_{21}'a_1 + (E_0 + H_{22}' - E)a_2 = 0$
$H_{d\beta}' = \langle \varnothing_{0\alpha}|\hat{H}'|\varnothing_{0\beta}\rangle$

$\begin{pmatrix} (E_0 + H_{11}') - E & H_{12}' \\ H_{21}' & (E_0 + H_{22}') - E \end{pmatrix}\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 0$

$H_{21}' = (H_{12}')^*$ ↓ standard matrix eigenval pb

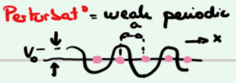
$\begin{vmatrix} (E_0 + H_{11}') - E & H_{12}' \\ H_{21}' & (E_0 + H_{22}') - E \end{vmatrix} = 0 \Rightarrow E = E_0 + H_{11}' \pm |H_{12}'|$ simplest case $H_{11}' = H_{22}'$

1D "solid" of length L; unperturbed $V = 0$ states will be free electron states 1D

$|\varnothing_{0k}\rangle = \sqrt{\frac{1}{L}}\exp(ikx)$ ← "box" normalisat°

$E_{0k} = \hbar^2k^2/2m$ $\quad |\varnothing_k\rangle$ & $|\varnothing_{-k}\rangle$ same E ⇒ degen

Perturbat°: weak periodic potential $\hat{H}' = V_0\cos\left(\frac{2\pi x}{a}\right)$ (V_0: strength; a: repeat distance: ion core separat°)



Eigenvals: 'nearly free e model'

$H_{kk}' = H_{k'k'}' = \frac{V_0}{L}\int_0^L \cos\left(\frac{2\pi x}{a}\right)dx = 0$

$H_{kk'}' = \frac{1}{L}\int_0^L \exp(-ikx)V_0\cos\left(\frac{2\pi x}{a}\right)\exp(ik'x)dx$

$\begin{cases} = \frac{V_0}{2} & \text{if } k - k' = \pm 2\pi/a \\ = 0 & \text{otherwise} \end{cases}$

$E_{0k} = \frac{\hbar^2k^2}{2m}$ → unperturbed state $k = \frac{\pi}{a}$ degen with state $k' = -\frac{\pi}{a}$

For these state $k - k' = \frac{2\pi}{a}$ i.e. $H_{kk'}' = H_{k'k}' = \frac{V_0}{2}$

| | becomes $\begin{vmatrix} E_0 - E & V_0/2 \\ V_0/2 & E_0 - E \end{vmatrix} = 0 \xrightarrow{\text{solut°}} E = E_0 \pm V_0/2$

perturbat° lifts degeneracy e with $|k| = \pi/a$

↓ extend nearly-degen sts

$k = \frac{\pi}{a} + \delta k : |\varnothing_{01}\rangle$ $\quad k' = -\frac{\pi}{a} + \delta k : |\varnothing_2\rangle$

$E_{01} = \frac{\hbar^2}{2m}\left(\left(\frac{\pi}{a}\right)^2 + \delta k^2 + \frac{2\pi\delta k}{a}\right)$ ⇒ $E_{01} = \bar{E}_0 + \frac{\hbar^2\pi\delta k}{ma}$

$E_{02} = \frac{\hbar^2}{2m}\left(\left(\frac{\pi}{a}\right)^2 + \delta k^2 - \frac{2\pi\delta k}{a}\right)$ ⇒ $E_{02} = \bar{E}_0 + \frac{\hbar^2\pi\delta k}{ma}$

$\underbrace{\frac{\hbar^2}{2m}\left(\left(\frac{\pi}{a}\right)^2 + \delta k^2\right)}_{E_0}$

$H_{11}' = H_{22}' = 0$
$H_{12}' = H_{21}' = V_0/2$

$\begin{vmatrix} (E_{01} + H_{kk}') - E & H_{kk'}' \\ H_{kk}' & (E_{02} + H_{k'k'}') - E \end{vmatrix} = 0$

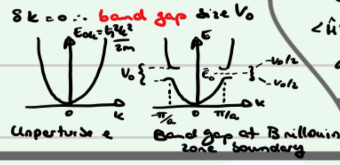
$\begin{vmatrix} \frac{\hbar^2\pi\delta k}{ma} - (E - \bar{E}_0) & V_0/2 \\ V_0/2 & -\frac{\hbar^2\pi\delta k}{ma} - (E - \bar{E}_0) \end{vmatrix} = 0$

⇓

$E = \bar{E}_0 \pm \sqrt{\left(\frac{\hbar^2\pi\delta k}{ma}\right)^2 + \frac{V_0^2}{4}}$

Perturbat° affects states over range of δk where $\hbar^2\pi\delta k/ma$ is small compared $V_0/2$ i.e. perturbat° has a negligible effect on states not close to $k = \pm\pi/a$

$\delta k = 0$ ∴ band gap size V_0



Unperturbed e $\quad$ Band gap at Brillouin zone boundary

Non-degen perturbat° theory

$\hat{h}_0|\varnothing_{0n}\rangle = E_{0n}|\varnothing_{0n}\rangle$

$\hat{H} = \hat{H}_0 + \lambda\hat{H}'$ unperturbed; λ cast we eventually $= 1$

$E_n = E_{0n} + \lambda E_{1n} + \lambda^2 E_{2n} + \cdots$

$|\varnothing_n\rangle = |\varnothing_{0n}\rangle + \lambda|\varnothing_{1n}\rangle + \lambda^2|\varnothing_{2n}\rangle + \cdots$

$H'(x) = \delta V'$ (0.4a, 0.6a → x)

Unperturbed system

$\varnothing_{0n}(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$

$E_{0n} = \hbar^2\pi^2n^2/2ma^2$

1st order perturbat°

$E_{1n} = \frac{2}{a}\int_{0.4a}^{0.6a}\sin\left(\frac{n\pi x}{a}\right)V'\sin\left(\frac{n\pi x}{a}\right)dx$

Energy perturbed system (to 1st order)

$E_n = E_{0n} + E_{1n}$

$n = 1$, $E_{11} = 0.39V'$

Ground state: $E_1 = \frac{\hbar^2\pi^2}{2ma^2} + 0.39V'$

$n = 2$, $E_{12} = 0.03V'$

1st excit state: $E_2 = \frac{2\hbar^2\pi^2}{2ma^2} + 0.03V'$

1st order correct°: 1st order terms

λ^1 terms: $\hat{H}|\varnothing_{(n-1)}\rangle + \hat{H}_0|\varnothing_{n}\rangle = \sum_{i=0}^{2} E_{in}|\varnothing_{(n-i)}\rangle$

1st order correct°

$|\varnothing_{1n}\rangle = \sum_k a_{nk}|\varnothing_{0k}\rangle$ $\quad a_{nk} = \langle \varnothing_{0m}|\hat{H}'|\varnothing_{0n}\rangle/(E_{0n} - E_{0m})$

$(\hat{H}' - E_{1n})|\varnothing_{0n}\rangle = \sum_k a_{nk}(E_{0n} - E_{0k})|\varnothing_{0k}\rangle$

1D $E_{1n} = \int \varnothing_{0n}^* \hat{H}'\varnothing_{0n} \, dx$

3D $E_{1n} = \iiint \varnothing_{0n}^* \hat{H}'\varnothing_{0n} \, d^3r$

$|\varnothing_n\rangle = |\varnothing_{0n}\rangle + \sum_{k \neq n}\frac{\langle \varnothing_{0k}|\hat{H}'|\varnothing_{0n}\rangle}{E_{0n} - E_{0k}}|\varnothing_{0k}\rangle$ (1st order)

set $\lambda = 1$

$E_n = E_{0n} + \underbrace{\langle \varnothing_{0n}|\hat{H}'|\varnothing_{0n}\rangle}_{1^{st}\text{ order}} + \underbrace{\sum_{k \neq n}\frac{\langle \varnothing_{0n}|\hat{H}'|\varnothing_{0k}\rangle\langle \varnothing_{0k}|\hat{H}'|\varnothing_{0n}\rangle}{E_{0n} - E_{0k}}}_{2^{nd}\text{ order}} + \cdots$

1st order correct°: E state 1s H atom in E field of magnitude ε

1st order correct°: $E_{1n} = \langle \varnothing_{0n}|\hat{H}'|\varnothing_{0n}\rangle$

$|\varnothing_{0n}\rangle = 1^{st}$ state H atom: $\varnothing_{0n} = \sqrt{\frac{1}{\pi a_0^3}}\exp(-r/a_0)$

Perturbat° $\hat{H}' = V = e\varepsilon r\cos\theta$

$E_1 = \frac{1}{\pi a_0^3}\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} e\varepsilon r\cos\theta \, r^2\sin\theta \, dr\,d\theta\,d\phi = 0 \Rightarrow$ 1st order correct° is zero

Variational method

1st order perturbat° theory insufficient → stationary state

Variational method: does not presuppose knowledge solut° for simpler pb; particularly useful for calc ground state E

- Start TISE: $\hat{H}\varnothing_n = E_n\varnothing_n$ $\quad E_1 < E_2 < \cdots$ $\quad \Psi = \sum_n c_n\varnothing_n$
- Normalisat° $\langle \Psi|\Psi\rangle = \langle \sum_m c_m\varnothing_m|\sum_n c_n\varnothing_n\rangle$

$= \sum_m\sum_n c_m^* c_n \underbrace{\langle \varnothing_m|\varnothing_n\rangle}_{=\delta_{mn}} = \sum_n |c_n|^2 = 1$

- Expectat° val: $\langle \hat{H}\rangle = \langle \Psi|\hat{H}|\Psi\rangle$

$= \sum_m\sum_n c_m^* c_n E_n \underbrace{\langle \varnothing_m|\varnothing_n\rangle}_{=\delta_{mn}}$

$\langle \hat{H}\rangle = \langle \Psi|\hat{H}|\Psi\rangle \geq E_1$ ← ground state E $\quad = \sum_n |c_n|^2 E_n \geq E_1\sum_n |c_n|^2 = E_1$

minimise $\langle \hat{H}\rangle$ → best E_1 approx

know operator $\hat{H}$ → guess ground state wavef° → ground state E ↺ improve wavef° (V method) End with an upper bound on ground state energy E_1

Ground state hydrogen atom

Ground state $\ell = 0 \Rightarrow \Psi = \Psi(r) \neq 0$

Trial wavef° satisfies BC: $\Psi = ce^{-\alpha r}$ (α: variational param; c: normalisat° cnst)

Normalisat° $\langle \Psi|\Psi\rangle = c^2\int_0^\infty e^{-2\alpha r}4\pi r^2 dr = 1 \Rightarrow c = \left(\frac{\alpha^3}{\pi}\right)^{1/2}$

Hydrogen: $\hat{H} = \frac{-\hbar^2}{2\mu}\nabla^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$

Expectat° val potential E: $\langle \Psi|V|\Psi\rangle = -c^2\int_0^\infty e^{-\alpha r}\frac{1}{4\pi\varepsilon_0}e^{-\alpha r}4\pi r^2 dr$

$= -\frac{\alpha^3}{\pi}\frac{e^2}{\varepsilon_0}\int_0^\infty re^{-2\alpha r}dr = \frac{-e^2}{4\pi\varepsilon_0}\alpha$

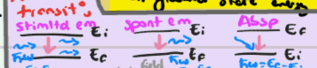
$\langle \Psi|\hat{T}|\Psi\rangle = -\frac{\hbar^2}{2\mu}c^2 4\pi\int_0^\infty dr \, e^{-\alpha r}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)e^{-\alpha r} = \frac{\hbar^2}{2\mu}\alpha^2$

$\langle \Psi|\hat{H}|\Psi\rangle = \frac{\hbar^2}{2\mu}\alpha^2 - \frac{e^2}{4\pi\varepsilon_0}\alpha$

Minimise w.r.t α: $\frac{d}{d\alpha}\langle \Psi|\hat{H}|\Psi\rangle = 0 \Rightarrow \alpha = e^2\mu/4\pi\varepsilon_0\hbar^2$

∴ Upper bound ground state energy: $E_1 = -\frac{1}{2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\frac{\mu}{\hbar^2} = -13.6\,eV$

Atomic transit°s



stimltd em; spont em; Absp

$\hbar\omega = E_i - E_f$; $\hbar\omega = E_i - E_f$; $\hbar\omega = E_f - E_i$

time & space varying e field: $\varepsilon = \varepsilon_0\cos(k \cdot r - \omega t)$ (ε_0: e field amplitude; k: wavevector radiat°, $|k| = 2\pi/\lambda$; ω: angular freq of radiat°, $\omega = c|k|$)

Ground state in 1D triangular well

$\begin{cases} V(x) = \infty & \text{for } x < 0 \\ V(x) = V_0x/a & \text{for } x > 0 \end{cases}$

$\Psi(x) = Axe^{-\lambda x}$ $\quad \hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{V_0x}{a}$, $x > 0$

normalisat° $\langle \Psi|\Psi\rangle = 1 = \int_0^\infty Axe^{-\lambda x}Axe^{-\lambda x}dx \Rightarrow A = 4\lambda^3$

$\hat{H}\Psi = -\frac{\hbar^2}{2m}A(-2\lambda + \lambda^2x)e^{-\lambda x} + A\frac{V_0}{a}x^2e^{-\lambda x}$

Expect° val

$\langle \hat{H}\rangle = \langle \hat{T}\rangle + \langle \hat{V}\rangle = \langle \Psi|\hat{H}|\Psi\rangle = \frac{A^2}{8\lambda}\left(\frac{\hbar^2}{m} + \frac{3V_0}{a}\right) \xrightarrow{\text{normalisat°}} \langle \hat{H}\rangle = \frac{\hbar^2\lambda^2}{2m} + \frac{3V_0}{2a}\frac{1}{\lambda}$

$\langle \hat{T}\rangle = \langle \Psi|\hat{T}|\Psi\rangle = \int(Axe^{-\lambda x})\left[-\frac{\hbar^2}{2m}\left(2\frac{\lambda}{x} + \lambda^2\right)\right](Axe^{-\lambda x}) = A^2\frac{\hbar^2}{2m}\left(\frac{1}{4\lambda}\right)$

$\langle \hat{V}\rangle = \langle \Psi|\hat{V}|\Psi\rangle = \int(Axe^{-\lambda x})\left[\frac{V_0}{a}x\right](Axe^{-\lambda x}) = A^2\frac{V_0}{a}\frac{3}{8\lambda}$

minimising $\frac{d\langle \hat{H}\rangle}{d\lambda} = \left(\frac{\hbar^2\lambda}{m} - \frac{3V_0}{2a}\frac{1}{\lambda^2}\right) = 0$ $\quad \langle \hat{H}\rangle_{min} = \frac{\hbar^2\lambda_{min}^2}{2m} + \frac{3V_0}{2a}\frac{1}{\lambda}$

$\lambda^3 = 3mV_0/2\hbar a$ $\quad \lambda_{min} = \sqrt[3]{\frac{3mV_0}{2\hbar a}}$

Ground stt E: $E_g \leq \langle \hat{H}_{min}\rangle \begin{cases} = \frac{3V_0}{4a}\sqrt{\frac{3mV_0}{2a}}\hbar + \sqrt{\frac{6V_0}{4am}} \\ \leq \sqrt{\frac{6V_0}{4am}} \end{cases}$

Ground state 1D harmonic oscillator

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

Gaussian trial wavf° $\Psi(x) = Ae^{-bx^2}$

Normalisat° $A^2\int_{-\infty}^{\infty}e^{-2bx^2}dx = A^2\left(\frac{\pi}{2b}\right)^{1/2} = 1$ ⇓ $A = \left(\frac{2b}{\pi}\right)^{1/4}$

Expectat° val $\langle \hat{H}\rangle = \langle \hat{T}\rangle + \langle \hat{V}\rangle$

$\langle \hat{T}\rangle = -\frac{\hbar^2}{2m}A^2\int_{-\infty}^{\infty}e^{-bx^2}\frac{d^2}{dx^2}(e^{-bx^2})dx = \hbar^2b/2m$

$\langle \hat{V}\rangle = \frac{1}{2}m\omega^2A^2\int_{-\infty}^{\infty}e^{-2bx^2}x^2dx = m\omega^2/8b$

$\langle \hat{H}\rangle = \frac{\hbar^2b}{2m} + \frac{m\omega^2}{8b}$

Minimise w.r.t b: $\frac{d\langle \hat{H}\rangle}{db} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} = 0$ ⇓ $b = m\omega/2\hbar$

Ground state $E_g \leq \langle \hat{H}_{min}\rangle = \frac{1}{2}\hbar\omega$

$\Psi(x) = Ae^{-bx^2} = \left(\frac{m\omega}{\hbar\pi}\right)^{1/4}\exp\left(-\frac{m\omega x^2}{2\hbar}\right)$: exact

Ground state 1D: $V(x) = -\alpha\delta(x)$

$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - \alpha\delta(x)$ $\quad \Psi(x) = Ae^{-bx^2}$

$\delta = \begin{cases} 0 & \text{if } x \neq 0 \\ \infty & \text{if } x = 0 \end{cases}$ $\quad \int_{-\infty}^{\infty}\delta(x)dx = 1$

$A = \left(\frac{2b}{\pi}\right)^{1/4}$ $\quad \langle \hat{T}\rangle = \frac{\hbar^2b}{2m}$ $\quad \langle \hat{V}\rangle = -\alpha A^2\int_{-\infty}^{\infty}e^{-2bx^2}\delta(x)dx$

$\langle \hat{H}\rangle = \langle \hat{T}\rangle + \langle \hat{V}\rangle = \frac{\hbar^2b}{2m} - \alpha\left(\frac{2b}{\pi}\right)^{1/2}$

$\frac{d\langle \hat{H}\rangle}{db} = 0 \Rightarrow b = \frac{2m^2\alpha^2}{\pi\hbar^4}$ s.t. $\langle \hat{H}\rangle_{min} = \frac{-m\alpha^2}{\pi\hbar^2}$

negative sign indicates bound state

$E_{ground} \leq \langle \hat{H}\rangle_{min} = -m\alpha^2/\pi\hbar^2$

use of trial Gaussian wavef° overestimates ground stt E because $\pi > 2$ i.e. less negative

FINISH
A4 - sect 6

Square magnitude tot ang momentum

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

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