A3 QM (+ SO)

① Quantum Mechanics

swap { ③ Further Quantum Mechanics
② S7 Classical Mechanics }

④ Numerical Methods (not yet included)

① Quantum Mechanics (Basics)

Prob Amplitudes : $a_k = \langle k|\psi\rangle$ where $|\psi\rangle = \sum_i a_i |i\rangle$ (state vec) $\left(\sum_i |a_i|^2 = 1\right)$ (p.d.f. $P(x) = |\psi(x)|^2$)

Note that $A = A_1 + A_2$ (amplitudes)

★ $\text{Prob} = |A_1 + A_2|^2 \neq |A_1|^2 + |A_2|^2$ (interference)

Energy representation: $|\psi\rangle = \sum_i a_i |E_i\rangle$

Born rule $|\psi\rangle \xrightarrow[\text{energy measurement}]{} |E_i\rangle$ with $\text{Prob} = |\langle E_i|\psi\rangle|^2$ $(= |a_i|^2)$

(collapse of wavefunc.)

Operators

Hermitian : $(\langle\phi|Q|\psi\rangle)^* = \langle\psi|Q|\phi\rangle$ $(Q^\dagger = Q)$

. have real eigenvals & mutually orthogonal eigenvectors

correspond to observables in physics

Identity operator $I = \sum_i |i\rangle\langle i|$

Hamiltonian $H = \sum_i E_i |E_i\rangle\langle E_i|$

Functions of operators : $f(R) = \sum_i f(r_i)|r_i\rangle\langle r_i|$

→ same eigenkets but maps on r_i (eigvals)

Commutators $[A,B] \equiv AB - BA$

$\{A,B\} \equiv AB + BA$

Apart from linearity, useful quick rules:

$[AB, C] = [A,C]B + A[B,C]$

★ If B commutes with $[A,B]$

$[A, f(B)] = [A,B]\frac{df}{dB}$ (consider $f = f_0 + f_0'B + \frac{1}{2}f_0''B^2 + \dots$)

- If $[A,B]=0$, possible to find a complete set of mutual eigenkets of A & B.

Evolution in Time TDSE: $i\hbar\frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle$

consider TISE: $\underline{H|E_n\rangle = E_n|E_n\rangle} \rightarrow$ stationary state of well-defined energy which doesn't change.

consider $|\psi,t\rangle = \sum_n a_n(t)|E_n,t\rangle$

It can be shown that $\underline{|\psi,t\rangle = \sum_n a_n e^{-\frac{iE_nt}{\hbar}}|E_n,0\rangle}$

Ehrenfest Theorem: $i\hbar\frac{d}{dt}\langle\psi|Q|\psi\rangle = \langle\psi|[Q,H]|\psi\rangle$

$\rightarrow$ Good quantum numbers q_i are eigvals of Q_i where $[Q_i,H]=0$ (so $\langle Q_i\rangle = \text{const.}$)

Position (& Momentum) Representations

$|\psi\rangle = \int_{-\infty}^{\infty} dx\, \psi(x)|\psi\rangle$ with $\psi(x) = \langle x|\psi\rangle$ ← wavefunction in position space

And $\int dx\,|\psi(x)|^2 = 1$ Probability density function

$I = \int dx\,|x\rangle\langle x|$

Inner product: $\langle\phi|\psi\rangle = \int dx\,\langle\phi|x\rangle\langle x|\psi\rangle = \int dx\,\phi^*(x)\psi(x)$

Effect of an operator Q:

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

momentum operator (in position space) $\hat{p} = -i\hbar\nabla$

$[\hat{x},\hat{p}_x] = i\hbar$ (canonical commutation relation)

Uncertainty Principle

Start with $(\hat{A}+i\lambda\hat{B})|\psi\rangle \Rightarrow \langle\psi|(\hat{A}-i\lambda\hat{B})(\hat{A}+i\lambda\hat{B})|\psi\rangle \geq 0$

$\Rightarrow \langle\psi|\hat{A}^2|\psi\rangle\langle\psi|\hat{B}^2|\psi\rangle \geq \frac{1}{4}(\langle\psi|i[\hat{A},\hat{B}]|\psi\rangle)^2$

$$\langle\hat{A}^2\rangle\langle\hat{B}^2\rangle \geq \frac{1}{4}\langle i[\hat{A},\hat{B}]\rangle^2$$

$\hat{A},\hat{B}$ are Hermitian observables.

State of well-defined p: $\underline{\langle x|p\rangle = u_p(x) = Ae^{ipx/\hbar}}$ $\left(A = \frac{1}{\sqrt{2\pi\hbar}}\right)$

Generalisation in 3D

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

$$[\hat{x}_i, \hat{p}_j] = i\hbar\,\delta_{ij} \qquad \langle \underline{x} | \underline{p} \rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{i\underline{x}\cdot\underline{p}/\hbar}$$

TDSE: $i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V(\underline{x})\psi$

(in position basis)

Probability current

Density: $\rho(\underline{x}, t) = \psi^*(\underline{x}, t)\psi(\underline{x}, t) = |\psi(\underline{x}, t)|^2$

Probability conservation: $\frac{\partial \rho}{\partial t} + \underline{\nabla}\cdot\underline{J} = 0$ (continuity eqn.)

(using TDSE & TDSE*) $\rightarrow$ find $\boxed{\underline{J} = \frac{i\hbar}{2m}(\psi\nabla\psi^* - \psi^*\nabla\psi)}$

$\left(= \frac{\hbar}{2mi}(\psi^*\nabla\psi - \psi\nabla\psi^*)\right)$

Matching conditions at boundaries

$\psi(x_0)^- = \psi(x_0)^+$ always

$\frac{\partial \psi}{\partial x}(x_0)^- = \frac{\partial \psi}{\partial x}(x_0)^+$ finite jumps

$\frac{\partial \psi}{\partial x}(x_0)^+ - \frac{\partial \psi}{\partial x}(x_0)^- = \frac{2m}{\hbar^2} V(x_0)\,\psi(x_0)$ delta function jump at $x = x_0$. $V \sim \delta(x - x_0)$

Scattering (simple)

solving for k & k' at two sides:

match ψ & $\frac{\partial \psi}{\partial x}$: i.e. $\begin{cases} I + R = T \\ k(I - R) = k'T \end{cases}$ $(x = 0)$ (consider $\propto |\underline{J}|$)

Finite potential Well

$E > V$ case $\quad \psi \sim e^{\pm ikx}$ oscillatory wave

$E < V$ case $\quad \psi \sim e^{-K|x|}$ decaying exponential

Parity

i.e. Suppose at $x > a \rightarrow u(x) = Ae^{-Kx}$

then $x < a \rightarrow u(x) = \begin{cases} Ae^{Kx} & \text{even parity} \\ -Ae^{Kx} & \text{odd parity} \end{cases}$

Infinite well

$$V = \begin{cases} 0 & |x| < a \\ \infty & |x| > a \end{cases}$$

$$\psi(x) = \begin{cases} \frac{1}{\sqrt{a}}\cos\left(\frac{(2r+1)\pi x}{2a}\right) & \text{even parity} \\ \frac{1}{\sqrt{a}}\sin\left(\frac{r\pi x}{a}\right) & \text{odd parity} \end{cases} \qquad \boxed{E_n = \frac{n^2\hbar^2\pi^2}{8ma^2}}$$

Quantum SHO (1D)

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \qquad \left(\ell = \sqrt{\frac{\hbar}{2m\omega}}\right)$$

Ladder operators: $\begin{cases} A = \dfrac{m\omega x + ip}{\sqrt{2m\hbar\omega}} \\ A^\dagger = \dfrac{m\omega x - ip}{\sqrt{2m\hbar\omega}} \end{cases}$

$H = \hbar\omega(A^\dagger A + \frac{1}{2})$ (can be shown)

And $\begin{cases} HA|E_n\rangle = (E_n - \hbar\omega)A|E_n\rangle \\ HA^\dagger|E_n\rangle = (E_n + \hbar\omega)A^\dagger|E_n\rangle \end{cases}$ (consider $HA = AH + [H, A]$)

Ladder operating rules: $\begin{cases} A|n\rangle = \sqrt{n}|n-1\rangle \\ A^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle \end{cases}$

$\{n\}$ are eigenstates of SHO.

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

$n = 0, 1, 2, \ldots$

· Ground state $|0\rangle$:

$$(m\omega x + \hbar\frac{\partial}{\partial x})\psi_0(x) = 0$$

$$\hookrightarrow \boxed{\psi_0(x) = \frac{1}{(2\pi\ell^2)^{1/4}} e^{-\frac{x^2}{4\ell^2}}} \quad \left(\ell \equiv \sqrt{\frac{\hbar}{2m\omega}}\right)$$

wavefunction at ground state.

☆ note $\begin{cases} A^\dagger = \dfrac{x}{2\ell} - \ell\dfrac{\partial}{\partial x} \\ A = \dfrac{x}{2\ell} + \ell\dfrac{\partial}{\partial x} \end{cases}$ $\rightarrow \underbrace{\psi_n(x)}_{\text{any wavefunc.}} = \frac{1}{\sqrt{n!}}\underbrace{\left(\frac{x}{2\ell} - \ell\frac{\partial}{\partial x}\right)}_{A^\dagger}{}^n \psi_0(x)$

i.e. $\psi_1(x) = \frac{1}{(2\pi\ell^2)^{\frac{1}{4}}}\frac{x}{\ell}e^{-\frac{x^2}{4\ell^2}}$ (odd)

↑ only difference from $\psi_0(x)$

$\begin{cases} x = \ell(A^\dagger + A) \\ p = \frac{i\hbar}{2\ell}(A^\dagger - A) \end{cases}$ ~~$x_{jk} = \ell(\sqrt{n_k}\,\delta_{j,k-1} + \sqrt{n_j}\,\delta_{j,k+1})$~~

$$x = \ell\begin{pmatrix} 0 & \sqrt{1} & & \cdots \\ \sqrt{1} & 0 & \sqrt{2} & \\ & \sqrt{2} & & \ddots \\ \vdots & & \ddots & \end{pmatrix} \qquad p = \frac{i\hbar}{2\ell}\begin{pmatrix} 0 & -\sqrt{1} & & \cdots \\ \sqrt{1} & 0 & -\sqrt{2} & \\ & \sqrt{2} & & \ddots \\ \vdots & & \ddots & \end{pmatrix}$$

(matrix explicit form) (off-diagonal)

Heisenberg Uncertainty $(\langle n|x^2|n\rangle)(\langle n|p^2|n\rangle) = \frac{E_n}{m\omega^2} mE_n = \frac{E_n^2}{\omega^2}$

(note $\langle x\rangle^2 = \langle p\rangle^2 = 0$) $\langle \Delta x^2\rangle\langle\Delta p^2\rangle = \hbar^2(n+\frac{1}{2})^2$

$\langle\Delta x\rangle\langle\Delta p\rangle = \hbar(n+\frac{1}{2}) \geq \frac{\hbar}{2}$ ✓.

Composite Systems

Generally, $|\psi\rangle = \sum_{ij} C_{ij} |a_i, b_j\rangle$ for two systems A, B with basis $\{a_i\}$, $\{b_j\}$.

Product state $|\psi\rangle = |A\rangle \otimes |B\rangle$

$\rightarrow$ then separable (uncorrelated)

$H_{AB} = H_A + H_B$ only

$[H_A, H_B] = 0$

TDSE:

$i\hbar\frac{\partial}{\partial t}|a,b\rangle = \underbrace{(H_a + H_b)}_{H_{AB}}|a,b\rangle$

Entangled state $|a,b\rangle = \sum_{a,b} C_{ab}|a\rangle|b\rangle$ generally

$H_{AB} = H_A + H_B + H_{int} \longrightarrow$ interaction Hamiltonian

$\boxed{\psi(x_A, x_B) \neq \psi_1(x_A)\psi_2(x_B) \text{ generally!}}$

$i\hbar\frac{\partial}{\partial t}|a,b\rangle = i\hbar\frac{\partial}{\partial t}(\sum_{a,b} C_{ab}|a\rangle|b\rangle)$

$\sum_{a,b} C_{ab}(H_A + H_B + H_{int})|a\rangle|b\rangle = \sum_{a,b} i\hbar\frac{\partial C_{ab}}{\partial t}|a\rangle|b\rangle + i\hbar\sum_{a,b} C_{ab}\frac{\partial}{\partial t}|a\rangle|b\rangle$

$\rightarrow i\hbar\sum_{a,b}\frac{\partial C_{ab}}{\partial t}|a\rangle|b\rangle = \sum_{ij} H_{int} C_{ab}|a\rangle|b\rangle = H_{int}|a,b\rangle$

$i\hbar\frac{\partial C_{ij}}{\partial t} = \sum_{ab} C_{ab}\langle i|\langle j| H_{int}|a\rangle|b\rangle$

Time evolutions of coefficients are driven by interaction H.

Examples of entanglement

$\{\overbrace{|\uparrow\rangle\otimes|\uparrow\rangle, \frac{1}{\sqrt{2}}(|\uparrow\rangle\otimes|\downarrow\rangle + |\downarrow\rangle\otimes|\uparrow\rangle), |\downarrow\rangle\otimes|\downarrow\rangle}^{① \text{ symmetric triplet}}\}$,

$\{\underbrace{\frac{1}{\sqrt{2}}(|\uparrow\rangle\otimes|\downarrow\rangle - |\downarrow\rangle\otimes|\uparrow\rangle)}_{② \text{ anti-symmetric singlet}}\}$

①, ② are entangled!

Symmetries & Transformations (Unitary Operators $U^\dagger = U^{-1}$)

$$\psi(\underline{x}-\underline{a}) = \langle \underline{x}-\underline{a}|\psi\rangle = \underbrace{\langle \underline{x}|\psi\rangle}_{\psi(\underline{x})} - \underline{a}\cdot\frac{\partial\psi}{\partial\underline{x}} + \frac{1}{2!}(\underline{a})^2\frac{\partial^2\psi}{\partial\underline{x}^2}) - \dots$$

Translation

$$= \exp(-\underline{a}\cdot\frac{\partial}{\partial\underline{x}})\,\psi(\underline{x})$$

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

$$= \underbrace{\boxed{\exp(-\frac{i\underline{a}\cdot\underline{P}}{\hbar})}}_{T(\underline{a})}\psi(\underline{x})$$

For Rotation $\rightarrow$ $\boxed{U(\underline{\alpha}) = \exp(-\frac{i\underline{\alpha}\cdot\underline{J}}{\hbar})}$ similarly $\quad \underline{J} = \hat{\underline{n}}J$

Parity operator : P, swap signs of all coordinates

$$\langle \underline{x}|P|\psi\rangle = P\psi(\underline{x}) = \psi(-\underline{x}) = \langle -\underline{x}|\psi\rangle$$

And $\langle \underline{x}|P^2|\psi\rangle = \langle\underline{x}|\psi\rangle = \psi(\underline{x})$ (no change)

$(P^2 = I)$

Mirror Operator : $\langle x, y|M|\psi\rangle = \langle y, x|\psi\rangle$

mirroring all amplitudes off the line $y=x$.

Angular momentum operator , ($\hat{J}$, $\hat{L}$ used interchangeably).

$\Rightarrow \hat{L}_i \equiv \varepsilon_{ijk}\hat{x}_j\hat{p}_k$ (ie. $\hat{L}_z = xp_y - yp_x$)

commutation: $[\hat{L}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}L_k$

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

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

generally $[\hat{L}_i, S] = 0$ for any operator S with scalar expval.

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

write an eigenstate of $\hat{L}^2$ & L_z as $|\beta, m\rangle$,

$$J_z J_\pm|\beta, m\rangle = (J_\pm J_z + [J_z, J_\pm])|\beta, m\rangle = (m\pm 1)J_\pm|\beta, m\rangle$$

so $J_\pm|\beta, m\rangle = \sqrt{\beta-(m\pm 1)m}\,|\beta, m\pm 1\rangle$ (ignore $\hbar$)

$(\beta = j(j+1))$

(by evaluating $\langle\beta, m|J_\mp J_\pm|\beta, m\rangle$)

for $\hat{L}^2$ eigval: $\beta = m_{max}(m_{max}+1) \equiv \boxed{j(j+1)}$ where $-j \le m \le j$

- m runs from: $(\underbrace{j, j-1, \dots, -j}_{2j+1 \text{ possibilities}})$ $\rightarrow$ integer or half-integer.

More useful to write eigenstate as $|j, m\rangle$

$m \rightarrow$ eigval of $\hat{J}_z$, $j \rightarrow$ eigval of $\hat{J}^2$ is $j(j+1)$.

<u>Summary</u>

$$\begin{cases} \hat{L}^2 |l, m\rangle = l(l+1)\hbar^2 |l, m\rangle \\ \hat{L}_z |l, m\rangle = m\hbar |l, m\rangle \\ \hat{L}_\pm |l, m\rangle = \hbar\sqrt{l(l+1) - m(m\pm1)}\, |l, m\pm1\rangle. \end{cases} \quad ☆$$

In angular variables: $\hat{L}^2 = -\hbar^2 \underbrace{\left\{ \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \right\}}_{\text{Angular part of } \nabla^2 \text{ in spherical.}}$

$\left(\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}\right)$

Solutions: $\underbrace{Y_{lm}(\theta, \phi)}_{\text{Spherical Harmonics}} = \langle\theta, \phi | l, m\rangle \propto \underbrace{P_{lm}(\cos\theta)}_{\text{associated Legendre Polynomials.}} e^{im\phi}$

- Here l, m are integer only (not half-integer) for single-valued.

Normalisation condition by $\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} |Y_{lm}(\theta, \phi)|^2 \sin\theta\, d\theta\, d\phi = 1$

$l=0 \quad Y_{00} = \frac{1}{\sqrt{4\pi}}$

$$l=1 \begin{cases} Y_{11} = -\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi} \\ Y_{10} = \sqrt{\frac{6}{8\pi}}\cos\theta \\ Y_{1-1} = \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\phi} \end{cases}$$

(overall phase conventional only)

<u>Rotational Spectra of simple diatomic molecules:</u> (dim-less)

$$H = \frac{\hbar^2}{2}\left(\frac{J_x^2}{I_x} + \frac{J_y^2}{I_y} + \frac{J_z^2}{I_z}\right) = \frac{\hbar^2}{2}\left(\frac{J^2}{I} + J_z^2\left(\frac{1}{I_z} - \frac{1}{I}\right)\right)$$

(let $I = I_x = I_y$, symmetric axis parallel to z-axis).

since $|m| < j$ for most cases $\Rightarrow$ $\boxed{E_j = \frac{\hbar^2}{2I}[j(j+1)]}$

<u>Spin</u>

(same formalism) $|s, m\rangle$, $-s \le m \le s$ (but s can be half-integers!)

$S^2 |s, m\rangle = \hbar^2 s(s+1) |s, m\rangle$

$S_z |s, m\rangle = \hbar m |s, m\rangle$

$S_\pm |s, m\rangle = \hbar\sqrt{s(s+1) - m(m\pm1)}\, |s, m\pm1\rangle$

Spin ½ case: $S_z|\frac{1}{2}, \pm\frac{1}{2}\rangle = \pm\frac{1}{2}\hbar|\frac{1}{2}, \pm\frac{1}{2}\rangle$

$S_\pm|\frac{1}{2}, \pm\frac{1}{2}\rangle \Rightarrow$ find matrix elements.

$$\begin{cases} S_x = \frac{1}{2}(S_+ + S_-) \\ S_y = \frac{1}{2i}(S_+ - S_-) \end{cases} \Longrightarrow \text{Pauli matrices: } S_i = \frac{\hbar}{2}\sigma_i$$

$$[\sigma_i, \sigma_j] = 2i\,\varepsilon_{ijk}\sigma_k$$

$$\{\sigma_i, \sigma_j\} = 2\delta_{ij}$$

Suppose eigenstates of S_z are $|+\rangle$ & $|-\rangle$

$(\frac{\hbar}{2})$, $(-\frac{\hbar}{2})$

· Any general state: $|\psi\rangle = a|+\rangle + b|-\rangle$ (spinor)

If making a measurement along $\underline{n} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$

$$\underline{n}\cdot\underline{\sigma} = \begin{pmatrix} \cos\theta & \sin\theta e^{-i\phi} \\ \sin\theta e^{i\phi} & -\cos\theta \end{pmatrix}$$

$\hookrightarrow$ eigenvectors: $|+,\theta\rangle = \sin\frac{\theta}{2} e^{i\phi/2}|-\rangle + \cos\frac{\theta}{2} e^{-i\phi/2}|+\rangle$

(certain $\frac{\hbar}{2}$ or $-\frac{\hbar}{2}$) $|-,\theta\rangle = \cos\frac{\theta}{2} e^{i\phi/2}|-\rangle - \sin\frac{\theta}{2} e^{-i\phi/2}|+\rangle$

Spin-1 system.

$S_+|-1\rangle = \sqrt{2}|0\rangle$ $S_+|0\rangle = \sqrt{2}|1\rangle$

$S_-|1\rangle = \sqrt{2}|0\rangle$ $S_-|0\rangle = \sqrt{2}|-1\rangle$

$$S_x = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \quad S_y = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} \quad S_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

in basis of $\{|1\rangle, |0\rangle, |-1\rangle\}$

Stern-Gerlach

mag. moment $\underline{\mu} = \gamma\underline{S}$ $\gamma = \frac{ge}{2m}$ gyromagnetic ratio

$$H = -\underline{\mu}\cdot\underline{B} = -\gamma\underline{S}\cdot\underline{B} \rightarrow E_\pm = -\frac{2\mu}{\hbar}\left(\pm\frac{\hbar}{2}\right)B = \mp\mu B$$

Precession in magnetic field

Suppose at $t=0$ → spinor: $|\psi,0\rangle = a_-|-\rangle + a_+|+\rangle$

$$|\psi,t\rangle = a_- e^{-iE_-t/\hbar}|-\rangle + a_+ e^{-iE_+t/\hbar}|+\rangle$$

Suppose initially $|\psi,0\rangle = |+,n\rangle$ (certain yield $\frac{\hbar}{2}$ parallel to $\underline{n}$)

Then $|\psi,t\rangle = \sin\frac{\theta}{2} e^{i\phi/2}|-\rangle + \cos\frac{\theta}{2} e^{-i\phi/2}|+\rangle$

where $\phi = \frac{2E_+t}{\hbar} = \omega t \rightarrow \omega = -\frac{2\mu B}{\hbar}$

Combining angular momentum

$j_1, j_2 \Rightarrow$ (assume $j_1 > j_2$)	J_{tot}	No. of states (deg.)
	$j_1 + j_2$	$2(j_1+j_2)+1$
	$j_1 + j_2 - 1$	$2(j_1+j_2-1)+1$
	$\dots$	$\dots$
	$j_1 - j_2$	$2(j_1-j_2)+1$
	All	$(2j_1+1)(2j_2+1)$

i.e. $\underbrace{\frac{1}{2}}_{j_1}, \underbrace{\frac{1}{2}}_{j_2}$ $\quad j=1$ or 0

deg. $3 \oplus 1 = 2 \otimes 2 = \underline{4}$ possible states

$\underline{|j, m\rangle}$:

$|1,1\rangle = |+\rangle|+\rangle$

$|1,0\rangle = \frac{1}{\sqrt{2}}(|-\rangle|+\rangle + |+\rangle|-\rangle)$

$|1,-1\rangle = |-\rangle|-\rangle$

$|0,0\rangle = \frac{1}{\sqrt{2}}(|-\rangle|+\rangle - |+\rangle|-\rangle)$

Hydrogenic Atom (1-electron in r^{-1} potential)

reduced mass $\mu = \frac{m_e m_n}{m_e + m_n} \sim m_e$ (for $m_n \gg m_e$)

$$H \equiv \underbrace{\frac{\hat{P}_r^2}{2\mu}}_{\text{translational KE}} + \underbrace{\frac{\hat{L}^2}{2\mu r^2}}_{\text{angular KE}} - \underbrace{\frac{Ze^2}{4\pi\varepsilon_0 r}}_{\text{Coulomb potential}}$$

Good quantum numbers : $|n, l, m\rangle \equiv |n,l\rangle|l,m\rangle$

n → principal; l → total angular momentum; m → z-component of ang. mom.

$$\hat{L}^2|n,l,m\rangle = l(l+1)|n,l,m\rangle .$$

Thus TISE becomes (for radial eigenval. eqn)

$$\left(-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \left(\frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\right) R_{nl}(r) = E_{nl} R_{nl}(r)$$

(Laguerre eqn.)

where $\psi(r,\theta,\phi) = R_{nl}(r)\, Y_{lm}(\theta,\phi)$

$$\langle r,\theta,\phi|n,l,m\rangle = \langle r|n,l\rangle\langle\theta,\phi|l,m\rangle$$

- Radial eigenfunctions : Laguerre polynomials of (n,l). (Associated)

$$\boxed{E_{nl} = -\overset{\overset{\sim 1}{\uparrow}}{\left(\frac{\mu}{m_e}\right)} \frac{Z^2 E_R}{n^2}}$$

$E_R = \frac{m_e e^4}{32\pi^2 \varepsilon_0^2 \hbar^2} \approx 13.6\,eV$
(Rydberg constant)

where $n = 1, 2, 3, 4, \cdots$
$0 \leq l \leq n-1$
$-l \leq m \leq l \quad \cdots$

Bohr radius $\boxed{a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2}}$ $\quad a_Z = \frac{a_0}{Z}\left(\frac{m_e}{\mu}\right)$

Example eigenfunctions $\quad |n, l\rangle = |1, 0\rangle; |2, 0\rangle, |2, 1\rangle \ldots$

$1, 0, 0$ $\left(\frac{1}{\sqrt{\pi a_Z^3}} e^{-\frac{r}{a_Z}}\right)$ ☆
(n, l, m)

$2, 0, 0$ $\quad \frac{1}{4\sqrt{2\pi a_Z^3}}\left(2 - \frac{Z}{a_Z}\right) e^{-\frac{r}{2a_Z}}$

$\vdots$

Fine structure constant

$\Rightarrow \alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} = \boxed{\frac{\hbar}{m_e c a_0}}$ $\quad$ ☆ $\boxed{R = \frac{1}{2} m_e \alpha^2 c^2}$

Can write $\boxed{E_n = -\frac{1}{2}\mu \alpha^2 c^2 \frac{Z^2}{n^2}}$ ☆ (on data sheet)

degeneracy

$n=1$	$l=0$	$m=0$	1
$n=2$	$l=0, 1$	$m=0$	4
		$m=-1, 0, 1$	
$n=3$	$l=0$	$m=0$	9
	1	$m=-1, 0, 1$	
	2	$m=-2, -1, 0, 1, 2$	
$\vdots$			

- n-th level is n^2 - degenerate

For calculating $\langle r^n \rangle$, note that $\int_0^\infty dr\, r^n e^{-r} = r! = \Gamma(r+1)$
(factorial integral)

Hamiltonian for a particle under magnetic field

$H = \frac{(\underline{p} - q\underline{A})^2}{2m}$ $\quad \nabla \times \underline{A} = \underline{B}$

Convenient choice of $\underline{A}$: $\quad \underline{A} = \frac{1}{2}\underline{B} \times \underline{x}$

(ignore terms of A^2, too weak)

$$H \approx \frac{p^2}{2m} - \frac{q}{4m}\Big(\underbrace{(\underline{B}\times\underline{x})\cdot\underline{p} + \underline{p}\cdot(\underline{B}\times\underline{x})}_{=2(\underline{x}\times\underline{p})\cdot\underline{B} = 2\underline{L}\cdot\underline{B}}\Big)$$

$$H = \frac{p^2}{2m} - \underbrace{\frac{q}{2m}\underline{L}}_{\mu}\cdot\underline{B}$$ for weak magnetic coupling.

$$\mu_B = \frac{e\hbar}{2m_e}$$ → (Bohr magneton)

<u>Heisenberg picture</u> (operators evolve)

$$|\psi(t)\rangle = \underbrace{U}_{e^{-\frac{i}{\hbar}\hat{H}t}}|\psi(0)\rangle$$: $[H, U] = 0$ energy conserved.

$\langle\psi(t)|A|\psi(t)\rangle$ → Schrödinger

$\langle\psi(0)|\underbrace{U^{\dagger}AU}_{A(t)}|\psi(0)\rangle$ → Heisenberg

$$i\hbar\frac{d}{dt}\langle A\rangle = \langle[A, H]\rangle$$ (Ehrenfest)

If H are constant in time → $i\hbar\frac{\partial\hat{A}}{\partial t} = [\hat{A}, \hat{H}]$

③ Further Quantum Mechanics

Time-independent PT

Assume
$$\begin{cases} H = H_0 + \delta H \\ E = E_n + \delta E_n + \dots \\ |\psi\rangle = |E_n\rangle + |\delta E_n\rangle + \cdots \end{cases}$$

Need $(H_0 + \delta H)(|E_n\rangle + |\delta E_n\rangle + \dots) = (E_n + \delta E_n + \delta^2 E_n + \cdots)(|E_n\rangle + |\delta E_n\rangle + \dots)$

match ↳
$$\begin{cases} \delta E_n^{(1)} = \langle E_n | \delta H | E_n \rangle & (\text{take } \langle E_n|) \\ |\delta E_n^{(1)}\rangle = \sum_{m \neq n} \underbrace{\frac{\langle E_m | \delta H | E_n\rangle}{E_n - E_m}}_{\langle E_m | \delta E_n\rangle} |E_m\rangle & (\text{take } \langle E_m|) \end{cases}$$

find this

2nd-order: $\delta E_n^{(2)} = \langle E_n | \delta H | \delta E_n^{(1)}\rangle = \sum_{m \neq n} \frac{|\langle E_m | \delta H | E_n\rangle|^2}{E_n - E_m}$

Deg. PT

- Diagonalize the matrix δH in its deg. subspace
- Eigenvalues will be the 1st-order energy deviation

$$\delta E_{n'}^{(1)} = \langle n' | \delta H | n' \rangle$$

↳ new eigenbasis where δH is diagonal

Hydrogen Atom under influence of B field

$$H = \frac{1}{2m}(\underline{p} - q\underline{A})^2 + q\phi \quad \text{where} \begin{cases} \underline{B} = \nabla \times \underline{A} & (\text{magnetic}) \\ \underline{E} = -\nabla\phi - \partial_t \underline{A} & (\text{electric}) \end{cases}$$

Gauge invariance: $\begin{cases} \underline{A} \to \underline{A} + \nabla\chi \\ \phi \to \phi - \partial_t \chi \end{cases}$ leaves $\underline{B}, \underline{E}$ invariant.

Aharonov-Bohm Effect

$\underline{A} \neq 0$, $\underline{B} = 0$ → still physical as $\Phi = \oint_C \underline{A} \cdot d\underline{l}$ affects position of interference fringes.

(Based on interference of matter waves in such a region).

External Magnetic field PT

$$\delta H = -\frac{q}{m}\,\underline{P}\cdot\underline{A} + \frac{q^2}{2m}|\underline{A}|^2 \qquad \left(\text{choose } \underline{A} = \tfrac{1}{2}\underline{B}\times\underline{r}\right)$$

$$= -\frac{q}{2m}\,\underline{B}\cdot\underline{L} + \frac{q^2B^2}{8m}(x^2+y^2) \qquad (\text{no } z \text{ component for } \underline{r})$$

$$\underline{B} = B\hat{z}$$

Diamagnetic Response: $l=0 \rightarrow \langle \underline{B}\cdot\underline{L}\rangle = B\langle L_z\rangle = 0$

use 2nd quad. term $\rightarrow \delta E_n^{(1)} = \frac{q^2B^2}{8m}\langle x^2+y^2\rangle$

diamagnetic susceptibility $\chi_M = -\frac{d^2 E_n^{(1)}}{dB^2} = -\frac{q^2}{4m}\underbrace{\langle x^2+y^2\rangle}_{\frac{2}{3}\langle r^2\rangle} = -\frac{q^2}{6m}\langle r^2\rangle$

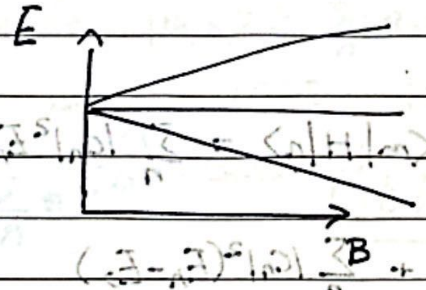
Paramagnetism? (Zeeman effect)

$l\neq 0 \rightarrow (l=1 \text{ i.e.})\quad \delta H = -\frac{qB}{2m_e}(\underbrace{L_z}_{\text{orbital}} + \underbrace{\hat{\sigma}_z}_{\text{spin}})$

degeneracy $\Rightarrow$ go to diagonal basis $L_z|n,l,m\rangle = \hbar m|n,l,m\rangle$

$$\delta E_n^{(1)} = \langle n_1,l_1,m_1|\delta H|n_2,l_2,m_2\rangle = -\frac{\hbar qB}{2m_e}(m+2S_z)$$

(L_z eigval.) (mass of electron)



External Electric field PT

$$\delta H = eEz = eEr\cos\theta$$

Quadratic Stark Effect (ground state) $n=1$

$n=1,\ l=0,\ m=0 \rightarrow \langle 1,0,0|\delta H|1,0,0\rangle \propto \int_0^\pi \cos\theta\sin\theta\, d\theta = 0$

$\delta E_1^{(1)} = 0$

2nd order needed:

$$\delta E_1^{(2)} = \sum_{m=2}^{\infty}\frac{|\langle m,1,0|\delta H|1,1,0\rangle|^2}{-\frac{R}{m^2}+\frac{R}{1^2}} = -\underbrace{\frac{9}{4}}_{\text{by evaluating integral}}\cdot\frac{e^2E^2a_0^2}{R}$$

Polarizability $\chi_e = -\frac{d^2\delta E_1^{(2)}}{dE^2} = \frac{9}{2}\frac{e^2a_0^2}{R}$

Linear Stark Effect (n=2, degenerate PT)

same energies for $|2,0,0\rangle, |2,1,0\rangle, |2,1,-1\rangle, |2,1,1\rangle$
(n,l,m)

only non-zero terms is $\langle 2,0,0|\delta H|2,1,0\rangle$ by integral
$= \langle 2,1,0|\delta H|2,0,0\rangle = -3eEa_0 \equiv V$ → sign!

$$\delta H = \begin{bmatrix} 0 & V & & \\ V & 0 & & \\ & & 0 & \\ & & & 0 \end{bmatrix}$$

diagonalize → eigvecs: energy shifts: $\left(+\left(-\frac{R}{2^2}\right)\right)$

$$\begin{cases} \frac{1}{\sqrt{2}}(|2,0,0\rangle + |2,1,0\rangle) & V \\ \frac{1}{\sqrt{2}}(|2,0,0\rangle - |2,1,0\rangle) & -V \\ |2,1,-1\rangle & 0 \\ |2,1,1\rangle & 0 \end{cases}$$

Variational Principle

$$\langle\psi|H|\psi\rangle = \sum_m\sum_n c_m^* c_n \langle m|H|n\rangle = \sum_n |c_n|^2 E_n$$

$$= E_0 \underbrace{\sum_n |c_n|^2}_{1} + \underbrace{\sum_n |c_n|^2(E_n - E_0)}_{\geq 0}$$

$= E_0 +$ positive term

$\langle\psi|H|\psi\rangle \geq E_0$

$\frac{d\langle H\rangle}{da} = 0$ (g.s.)
↳ optimal value for parameter in an ansatz!

Time-dependent Hamiltonian

Characteristic timescale: $\tau_H = \frac{\hbar}{\Delta E}$ ← energy difference of two levels.

Sudden limit

$\Delta t \ll T_H$ not enough time for the system to modify its wavefunction.

$$H(t) = \begin{cases} H_i & t<0 \\ H_f & t>0 \end{cases}$$

$(t>0)$ $|\psi, t\rangle = \sum_n a_n e^{-iE_n t/\hbar} |n\rangle$ for $H_f|n\rangle = E_n|n\rangle$

with $a_n = \langle n| \underbrace{\psi(t=0^-)}_{\text{ket before the sudden change}}\rangle$

Adiabatic limit

$\Delta t \gg T_H$

Adiabatic principle: the system remains in the said eigenstate if it is already in an eigenstate, under slow time evolution. (only phase evolution) (Contrary to sudden limit where it is possible to jump to other states)

Proof of adiabatic theorem

write $|\psi, t\rangle = \sum_n a_n(t) e^{-\frac{i}{\hbar}\int_0^t dt' E_n(t') dt'} |n(t)\rangle$.

↳ sub into TDSE: $i\hbar \frac{\partial}{\partial t}|\psi, t\rangle = H(t)|\psi, t\rangle$

$$\sum_n e^{-\frac{i}{\hbar}\int_0^t dt' E_n(t') dt'} \left[i\hbar \dot{a}_n |n(t)\rangle + a_n E_n(t)|n(t)\rangle + i\hbar a_n \frac{\partial |n(t)\rangle}{\partial t} \right]$$

$$= \sum_n e^{-\frac{i}{\hbar}\int_0^t dt' E_n(t') dt'} a_n(t) \underbrace{E_n(t)|n(t)\rangle}_{H(t)|n(t)\rangle}$$

Take $\langle m(t)|$

$$\Rightarrow \dot{a}_m = -\sum_n a_n e^{\frac{i}{\hbar}\int_0^t dt' (E_m(t') - E_n(t'))} \langle m|\partial_t|n\rangle$$

Determine $\langle m|\partial_t|n\rangle$ $\quad \partial_t|n\rangle = \lim_{\delta t \to 0} \frac{|\delta E_n^{(1)}\rangle}{\delta t} = \sum_{m \neq n} \frac{\langle m|\frac{\partial H}{\partial t}|n\rangle}{E_n - E_m}|m\rangle$

Hence split: $\dot{a}_m = \partial_t a_m = -\langle m|\partial_t|m\rangle a_m$

(RHS) $$+ \underbrace{\sum_{n\neq m} a_n e^{\frac{i}{\hbar}\int_0^t dt' (E_m(t') - E_n(t'))} \times \left(\frac{\langle m|\frac{\partial H}{\partial t}|n\rangle}{E_n - E_m} \right)}_{\to 0 \text{ for } \Delta t \gg T_H}$$

avg. zero for rapid phase variations

$$\Rightarrow \boxed{\partial_t a_m = -\langle m|\partial_t|m\rangle a_m}$$

under adiabatic limit.

$\langle m|\partial_t|m\rangle = -i\chi_m(t)$ → purely imaginary

$$\Rightarrow \quad a_m(t) = a_m(0)\underbrace{e^{i\int_0^t \chi_m(t')dt'}}_{\text{Berry phase}}$$

Berry phase ('normally' not observable)

Energy in timedependent systems $\quad E(t) = \langle\psi(t)|H(t)|\psi(t)\rangle$

Take ∂_t : $\boxed{\partial_t E(t) = \langle\psi(t)|[\partial_t H(t)]|\psi(t)\rangle}$

(other two terms cancel, from TDSE)

Time-dependent PT

Assume fixed eigenvals & eigenkets fixed.

$$|\psi,t\rangle = \sum_n c_n e^{-iE_nt/\hbar}|n\rangle$$

Now $\delta H = \delta H(t)$ → time dependent

Consider: (TDSE) $\quad i\hbar\frac{\partial}{\partial t}|\psi,t\rangle = (H_0+\delta H)|\psi,t\rangle$

$$\sum_n e^{-iE_nt/\hbar}\{i\hbar\partial_t c_n + \cancel{E_nc_n}\}|n\rangle = \sum_n e^{-iE_nt/\hbar}c_n\{\cancel{H_0}+\delta H\}|n\rangle$$

(Take $\langle m|$): $\quad \partial_t c_m = -\frac{i}{\hbar}\sum_n e^{i(E_m-E_n)t/\hbar}\langle m|\delta H|n\rangle c_n$

Suppose initially system in state i, $c_n = \delta_{ni}$

$$\dot{c}_m \approx -\frac{i}{\hbar}e^{i(E_m-E_i)t/\hbar}\langle m|\delta H|i\rangle \quad (+O(\delta H^2))$$

Can be integrated in time.

Periodic perturbation

If $\delta H = Ve^{-i\omega t}$ $\quad$ Let $\omega_{fi} = \frac{E_f-E_i}{\hbar}$

$$\dot{c}_f = -\frac{i}{\hbar}\langle f|V|i\rangle e^{i(\omega_{fi}-\omega)t}$$

Integrate → $\quad c_f = -\frac{1}{\hbar}\langle f|V|i\rangle\frac{e^{i(\omega_{fi}-\omega)t}-1}{(\omega_{fi}-\omega)}$

$$|c_f|^2 = \frac{1}{\hbar^2}|\langle f|V|i\rangle|^2\underbrace{\frac{\sin^2((\omega_{fi}-\omega)t/2)}{[(\omega_{fi}-\omega)/2]^2}}_{=2\pi t\,\delta(\omega_{fi}-\omega)}$$

Transition rate : $\frac{2\pi}{\hbar^2}|\langle f|V|i\rangle|^2 \delta(\omega_{fi}-\omega)$

$\Downarrow$

Fermi's Golden Rule $\boxed{\frac{2\pi}{\hbar^2}|\langle f|V|i\rangle|^2 \rho(\omega_{fi})}$ (Integrate over range of frequencies)

Note that $\rho(\omega_{fi})\, d\omega_{fi} = \frac{1}{\hbar} g(E_f = E_i + \hbar\omega)\, dE_f$

$\therefore g(E_f = E_i + \hbar\omega) = \hbar\rho(\omega_{fi})$

In energy terms: $\boxed{\frac{2\pi}{\hbar}|\langle f|V|i\rangle|^2 g(E_f)}$

$\delta H \begin{cases} Ve^{-i\omega t} & \rightarrow \text{ up in energy} \\ Ve^{i\omega t} & \rightarrow \text{ down } \ldots \end{cases}$ (for $\omega > 0$, $E_f - E_i = \hbar\omega > 0$)

Radiative Transitions

dipole approx. : ① E-field dominates (electron speed $\ll c$) ② E-field nearly constant over a small-size atom.

model an uniform oscillating E-field $\delta H = Ve^{\mp i\omega t}$ with $V = e\mathcal{E}z$

Transition rate : $\frac{2\pi}{\hbar^2} e^2 \mathcal{E}^2 |\langle f|z|i\rangle|^2 \rho(\omega_{fi})$

for stimulated emission & absorption.

(z can be x, y in other direction cases)

Selection Rules :-

- Need more than $\omega = \omega_{fi}$ matching.
- Require $\langle f|z|i\rangle \neq 0$.

① By angular momentum conservation

combined system: $\begin{cases} |l_1 - l_2| \le l_{tot} \le l_1 + l_2 \\ m_{tot} = m_1 + m_2 \end{cases}$

② photon: $l_{ph} = 1$, $m_{ph} = \pm 1$ ($\neq 0$ since photon massless) no stationary photon

in z-axis $\begin{cases} |l_i - 1| \le l_f \le l_i + 1 \\ m_f = m_i \pm 1 \end{cases}$

in other directions: $\begin{cases} |l_i - 1| \le l_f \le l_i + 1 \text{ (same)} \\ m_f = m_i,\ m_i \pm 1 \end{cases}$

(Note: $l_f = l_i$ not allowed actually, because zero matrix elements).

② By dipole matrix elements (better, more general)

Looking for $\neq 0$ elements!

- Rotational invar. & Parity

$$\underset{\text{inversion}}{I}\begin{cases} \mathbf{r} \to -\mathbf{r} \\ \theta \to \pi-\theta \\ \phi \to \phi+\pi \end{cases} \qquad Y_{lm}(\theta,\phi) \to Y_{lm}(\pi-\theta, \phi+\pi) = (-1)^{l}\, Y(\theta,\phi)$$

Thus $\langle f|V|i\rangle = (-1)^{l_f + l_i + 1} \langle f|V|i\rangle$

(with l_f from $\langle f|$, l_i from $|i\rangle$, 1 from (V))

Need $l_f + l_i + 1$ be even for non-zero $\langle f|V|i\rangle$.

$$\boxed{\Delta l = \pm 1, \ \Delta l \neq 0}$$

- Integral in ϕ: $\langle f|V|i\rangle \propto \int_0^{2\pi} d\phi\, e^{-im_f\phi} \begin{Bmatrix} x \\ y \\ z \end{Bmatrix} e^{im_i\phi}$

$\Uparrow$ Based on polarisation of incident light

Polarisation in z: need $m_f = m_i$

in x, y: need $m_f - m_i = \pm 1$

For Photon propagating:

$$\text{in}\begin{cases} \hat{z} & (x,y) & \boxed{\Delta m = \pm 1} \to \text{left-hand \& right-hand polarisation of light} \\ \hat{x}, \hat{y} & (y,z), (x,z) & \boxed{\Delta m = 0, \pm 1} \to \text{Linear polarisation of light} \end{cases}$$

$\underbrace{\hat{x},\hat{y}}_{\text{photon travelling direction}}$ $\underbrace{(y,z),(x,z)}_{\text{Polarisation directions}}$

Indistinguishable Particles

$|\psi(x_1, x_2)|^2 = |\psi(x_2, x_1)|^2$ (swapping labels don't affect prob.)

$\psi(x_1, x_2) = e^{i\phi}\, \psi(x_2, x_1)$

$\psi(x_1, x_2) = e^{2i\phi}\, \psi(x_1, x_2)$

$$\to e^{2i\phi} = 1 \Rightarrow \underline{e^{i\phi} = \pm 1} \begin{cases} \psi(x_2, x_1) = +\psi(x_1, x_2) & \text{(bosons)} \\ \psi(x_2, x_1) = -\psi(x_1, x_2) & \text{(fermions)} \end{cases}$$

$$\Psi(\underline{r_1}, \underline{r_2}) = \frac{1}{\sqrt{2}}\left(\phi_1(\underline{r_1})\phi_2(\underline{r_2}) - \phi_1(\underline{r_2})\phi_2(\underline{r_1})\right)$$

If $\phi_1 = \phi_2$

$\rightarrow \underline{\Psi(\underline{r_1}, \underline{r_2}) = 0}$

Pauli-exclusion: ~~set~~ $\cancel{x_1 = x_2 \rightarrow \Psi(x_1, x_1) = -\Psi(x_1, x_1) = 0}$

$\rightarrow$ No two fermions occupy the same state.

for fermions: product space is anti-symmetric

either: $S \times A$

or $A \times S$

A $\downarrow$ position wavefunction

S $\downarrow$ spin

$$\left\{\begin{array}{l} |\uparrow\uparrow\rangle \\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |\downarrow\downarrow\rangle \end{array}\right. \text{ sym.}$$

$$\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \text{ asy.}$$

Helium Atom

$$H = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z}{|\underline{x_1}|} + \frac{Z}{|\underline{x_2}|} - \frac{1}{|\underline{x_1} - \underline{x_2}|}\right)$$

$(Z=2)$

electron-electron interaction.

$\rightarrow$ P.T. for $\delta H = \frac{e^2}{4\pi\varepsilon_0|\underline{x_1} - \underline{x_2}|}$ is bad.

$\rightarrow$ Use trial wavefunction $\Psi_{Z^*}(r) = \frac{Z^{*\frac{3}{2}}}{\sqrt{\pi}\, a_0^{3/2}} e^{-\frac{Z^* r}{a_0}}$

(var. method)

Z^*: effective charge.

Virial theorem: $\left\{\begin{array}{l} PE = 2E_{tot} \\ KE = -E_{tot} \end{array}\right.$

original (ignore all electron-electron int.) $\approx -2RZ^2$ (bad)

Now with Z^* effective charge:

$$E(Z^*) = KE_{Z^*} + PE_{Z^*} + \langle \text{int.} \rangle$$

$$KE_{Z^*} = 2RZ^{*2}$$

$$PE_{Z^*} = -4RZZ^*$$

$$\langle \text{int.} \rangle = \left\langle \frac{e^2}{4\pi\varepsilon_0|\underline{x_1} - \underline{x_2}|} \right\rangle_{Z^*} = \frac{5}{4}RZ^* \quad \text{(given)}$$

$$E(Z^*) = -2R\left(2ZZ^* - Z^{*2} - \frac{5}{8}Z^*\right)$$

$$\frac{dE_{Z^*}}{dZ^*} = 0 \quad \rightarrow \quad Z^* = Z - \frac{5}{16} = 2 - \frac{5}{16} \approx 1.6875$$

(And take $Z = 2$)

$Z^* < 2$ (screening by electron

$\underline{E_{tot} \approx -77.5\text{ eV}}$ $(\gtrsim E_{0\,\text{actual}})$

By var. Principle