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Assignment-3

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Q1.

$$\hat{H}_p = q\mathcal{E}\hat{X}$$

$$\hat{H} = \hat{H}_0 + \hat{H}_p$$

$$= -\frac{\hbar}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2\hat{X}^2 + q\mathcal{E}\hat{X}$$

a) The eigenenergies of this Hamiltonian can be obtained exactly without resorting to any perturbative treatment. A variable change $y = x + \frac{q\mathcal{E}}{m\omega^2}$ leads

to $\rightarrow H = -\frac{\hbar^2}{2m}\frac{d^2}{dy^2} + \frac{1}{2}m\omega^2 y^2 - \frac{q^2\mathcal{E}^2}{2m^2\omega^2}$

This is the Hamiltonian of a harmonic oscillator from which a constant $\frac{q^2\mathcal{E}^2\omega^2}{2m^2}$ is subtracted.

The exact eigenenergies can thus be easily inferred as

$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega - \frac{q^2\mathcal{E}^2}{2m^2\omega^2}$$

b) Since the electric field is weak, we can treat $\hat{H}_p$ as a perturbation.

$$E_n^{(1)} = a\langle n|\hat{X}|n\rangle = 0$$

$$E_n^{(2)} = q^2\mathcal{E}^2\sum_{m\neq n}\frac{|\langle m|\hat{X}|n\rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

Since $E_n^{(0)} = \left(n+\frac{1}{2}\right)\hbar\omega$

$$\langle n+1|\hat{X}|n\rangle = \sqrt{n+1}\sqrt{\frac{\hbar}{2m\omega}}$$

$$E_n^{(0)} - E_{n-1}^{(0)} = \hbar\omega$$

$$\langle n-1|\hat{X}|n\rangle = \sqrt{n}\frac{\sqrt{\hbar}}{\sqrt{2m\omega}}$$

$$E_n^{(0)} - E_{n+1}^{(0)} = -\hbar\omega$$

$$E_n^{(2)} = q^2 \mathcal{E}^2 \left[\frac{|\langle n+1|\hat{x}|n\rangle|^2}{E_n^{(0)} - E_{n+1}^{(0)}} + \frac{|\langle n-1|\hat{x}|n\rangle|^2}{E_n^{(0)} - E_{n-1}^{(0)}} \right]$$

here Energy is given to 2^{nd} order by

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)}$$

$$= \left(n+\frac{1}{2}\right)\hbar\omega - \frac{q^2\mathcal{E}^2}{2m\omega^2}$$

$$|\psi_n^{(1)}\rangle = \frac{q\mathcal{E}}{\hbar\omega}\sqrt{\frac{\hbar}{2m\omega}}\left\{\sqrt{n}\,|n-1\rangle - \sqrt{n+1}\,|n+1\rangle\right\}$$

$|\psi_n\rangle$ is given to 1st order by →

$$|\psi_n\rangle = |n\rangle + \frac{q\mathcal{E}}{\hbar\omega}\sqrt{\frac{\hbar}{2m\omega}}\left\{\sqrt{n}\,|n-1\rangle - \sqrt{n+1}\,|n+1\rangle\right\}$$

Q2. $E_n = \dfrac{\hbar^2\pi^2 n^2}{8mL^2}$, $\psi_n(x) = \dfrac{1}{\sqrt{L}}\sin\left(\dfrac{n\pi x}{2L}\right)$

~~Acc~~ According to perturbation theory,

$$E_n = \frac{\hbar^2\pi^2 n^2}{8mL^2} + E_n^{(1)}$$

where $E_n^{(1)} = \langle\psi_n|V_p(x)|\psi_n\rangle$

$$= \frac{1}{L}\int_0^{2L} \sin^2\left(\frac{n\pi x}{2L}\right) V_p(x)\,dx$$

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a) $\int \cos n x \sin m x \, dx = -\frac{\cos(m-n)x}{2(m-n)} - \frac{\cos(m+n)x}{2(m+n)}$

$m \neq \pm n$

$V_p(x) = \lambda V_0 \sin\left(\frac{\pi x}{2L}\right)$

$$E_n^{(1)} = \frac{\lambda V_0}{L} \int_0^{2L} \sin^2\left(\frac{n\pi x}{2L}\right) \sin\left(\frac{\pi x}{2L}\right) dx$$

$$= \frac{\lambda V_0}{2L} \int_0^{2L} \left[1 - \cos\left(\frac{n\pi x}{L}\right)\right] \sin\left(\frac{\pi x}{2L}\right) dx$$

$$= \frac{\lambda V_0}{\pi} \left\{ -\cos\left(\frac{\pi x}{2L}\right) + \frac{\cos[(1-2n)\pi x/2L]}{2(1-2n)} + \frac{\cos[(1+2n)\pi x/2L]}{2(1+2n)} \right\}\Bigg|_0^{2L}$$

$$= \frac{2\lambda V_0}{\pi} \frac{4n^2}{4n^2-1}$$

$$E_n = \frac{\hbar^2 \pi^2 n^2}{8mL^2} + \frac{2\lambda V_0}{\pi} \frac{4n^2}{4n^2-1}$$

b) $V_p(x) = \lambda V_0 \delta(x-L)$

$$E_n^{(1)} = \frac{\lambda V_0}{L} \int_0^{2L} \sin^2\left(\frac{\pi n x}{2L}\right) \delta(x-L) \, dx$$

$$= \frac{\lambda V_0}{L} \sin^2\left(\frac{n\pi}{2}\right)$$

$$E_n = \frac{\hbar^2 \pi^2}{8mL^2} n^2 + \begin{cases} 0 & \text{if } n \text{ is even} \\ \lambda V_0 / L & \text{if } n \text{ is odd} \end{cases}$$

Q3. a) $H = \hat{H}_0 + \hat{H}_P$

$$= E_0 \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 8 & 0 & 0 \\ 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 7 \end{pmatrix}$$

$$+ E_0 \begin{pmatrix} \lambda & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2\lambda \\ 0 & 0 & -2\lambda & 0 \end{pmatrix}$$

Since $\hat{H}_0 \rightarrow$ diagonal, its eigenvalues are $\rightarrow$

$E_1^{(0)} = E_0$
$E_2^{(0)} = 8E_0$
$E_3^{(0)} = 3E_0$
$E_4^{(0)} = 7E_0$

& its eigenstates by $\rightarrow$

$$|\phi_1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$|\phi_2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}$$

$$|\phi_3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}$$

$$|\phi_4\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

b) Diagonalization of $\hat{H}$ →

$$\begin{vmatrix} (1+\lambda)E_0 - E & 0 & 0 & 0 \\ 0 & 8E_0 - E & 0 & 0 \\ 0 & 0 & 3E_0 - E & -2\lambda E_0 \\ 0 & 0 & -2\lambda E_0 & 7E_0 - E \end{vmatrix} = 0$$

$$(E_0 + \lambda E_0 - E)(8E_0 - E)\left[(3E_0 - E)(7E_0 - E) - 4\lambda^2 E_0^2\right] = 0$$

↳ gives exact eigenenergies

$$E_1 = (1+\lambda)E_0, \quad E_2 = 8E_0, \quad E_3 = (5 - 2\sqrt{1+\lambda^2})E_0$$

$$E_4 = (5 + 2\sqrt{1+\lambda^2})E_0$$

Since $\lambda \ll 1$, $\sqrt{1+\lambda^2} \simeq 1 + \frac{\lambda^2}{2}$

hence E_3 & E_4 are given to 2^{nd} order in λ by

$$E_3 \simeq (3 - \lambda^2)E_0$$
$$E_4 \simeq (7 + \lambda^2)E_0$$

c) From non-degenerate perturbation theory →

$$E_1^{(1)} = \langle \phi_1 | \hat{H}_p | \phi_1 \rangle = E_0 (1\ 0\ 0\ 0) \begin{pmatrix} \lambda & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2\lambda \\ 0 & 0 & -2\lambda & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$= \lambda E_0$$

|||^{ly}, we can verify $2^{nd}, 3^{rd}$ & 4^{th} eigenvalues have no 1st order corrections →

$$E_2^{(1)} = \langle \phi_2 | \hat{H}_p | \phi_2 \rangle = 0$$

$$E_3^{(1)} = \langle \phi_3 | \hat{H}_p | \phi_3 \rangle = 0$$

$$E_4^{(1)} = \langle \phi_4 | \hat{H}_p | \phi_4 \rangle = 0$$

$$E_1^{(2)} = \sum_{m=2,3,4} \frac{|\langle \phi_m | \hat{H}_p | \phi_1 \rangle|^2}{E_1^{(0)} - E_m^{(0)}} = 0$$

since $\langle \phi_2 | \hat{H}_p | \phi_1 \rangle = \langle \phi_3 | \hat{H}_p | \phi_1 \rangle = \langle \phi_4 | \hat{H}_p | \phi_1 \rangle = 0$

|||^{ly}, $$E_2^{(2)} = \sum_{m=1,3,4} \frac{|\langle \phi_m | \hat{H}_p | \phi_2 \rangle|^2}{E_2^{(0)} - E_m^{(0)}} = 0$$

& $$E_3^{(2)} = \sum_{m=1,2,4} \frac{|\langle \phi_m | \hat{H}_p | \phi_3 \rangle|^2}{E_3^{(0)} - E_m^{(0)}}$$

$$= \frac{|\langle \phi_4 | \hat{H}_p | \phi_3 \rangle|^2}{E_3^{(0)} - E_4^{(0)}} = \frac{(-2\lambda E_0)^2}{(3-7)E_0} = -\lambda^2 E_0$$

since $\langle \phi_4 | \hat{H}_p | \phi_3 \rangle$

$$= E_0 (0\ 0\ 0\ 1) \begin{pmatrix} \lambda & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2\lambda \\ 0 & 0 & -2\lambda & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}$$

$$= -2\lambda E_0$$

lll^y since

$$\langle\phi_3|\hat{H}_p|\phi_4\rangle = E_0 \begin{pmatrix}0 & 0 & 1 & 0\end{pmatrix}\begin{pmatrix}\lambda & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & -2\lambda\\ 0 & 0 & -2\lambda & 0\end{pmatrix}\begin{pmatrix}0\\0\\0\\1\end{pmatrix}$$

$$= -2\lambda E_0$$

$$E_4^{(2)} = \sum_{m=1,2,3} \frac{|\langle\phi_m|\hat{H}_p|\phi_4\rangle|^2}{E_4^{(0)} - E_m^{(0)}}$$

$$= \frac{|\langle\phi_3|\hat{H}_p|\phi_4\rangle|^2}{E_4^{(0)} - E_3^{(0)}} = \frac{(-2\lambda E_0)^2}{(7-3)E_0} = \cancel{E_0}\,\lambda^2 E_0$$

$$E_1 = \cancel{E_0}\, E_1^{(0)} + E_1^{(1)} + E_1^{(2)} = (1+\lambda)E_0$$

$$E_2 = E_2^{(0)} + E_2^{(1)} + E_2^{(2)} = 5E_0$$

$$E_3 = E_3^{(0)} + E_3^{(1)} + E_3^{(2)} = (3-\lambda^2)E_0$$

$$E_4 = E_4^{(0)} + E_4^{(1)} + E_4^{(2)} = (7+\lambda^2)E_0$$

1st order corrections to eigenstates →

$$|\psi_n^{(1)}\rangle = \sum_{m\neq n} \frac{\langle\phi_m|\hat{H}_p|\phi_n\rangle|\phi_m\rangle}{E_m^{(0)} - E_n^{(0)}}$$

$$|\psi_1^{(1)}\rangle = \sum_{m=2,3,4} \frac{\langle\phi_m|\hat{H}_p|\phi_1\rangle|\phi_m\rangle}{E_m^{(0)} - E_1^{(0)}}$$

$$= \begin{pmatrix}0\\0\\0\\0\end{pmatrix}$$

lll^y $|\psi_2^{(1)}\rangle = \begin{pmatrix}0\\0\\0\\0\end{pmatrix}$, $|\psi_3^{(1)}\rangle = \sum_{m=1,2,4} \frac{\langle\phi_m|\hat{H}_p|\phi_3\rangle|\phi_m\rangle}{E_m^{(0)} - E_3^{(0)}}$

$$= \begin{pmatrix}0\\0\\0\\-\lambda/2\end{pmatrix}$$

$$|\psi_4^{(1)}\rangle = \sum_{m=1,2,3} \frac{\langle \phi_m | \hat{H}_p | \phi_4 \rangle}{E_m^{(0)} - E_4^{(0)}} |\phi_m\rangle$$

$$= \begin{pmatrix} 0 \\ 0 \\ 1 \\ \lambda/2 \end{pmatrix}$$

$$|\psi_n\rangle = |\phi_n\rangle + |\psi_n^{(1)}\rangle$$

$$|\psi_1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad |\psi_2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad |\psi_3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ -\lambda/2 \end{pmatrix}$$

$$|\psi_4\rangle = \begin{pmatrix} 0 \\ 0 \\ \lambda/2 \\ 1 \end{pmatrix}$$

Q4. energy & wave funct^n for an infinite, cubic potential well of side L are given by

$$E^{exact}_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

$$\phi_{n_x, n_y, n_z}(x, y, z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{\pi n_x x}{L}\right) \sin\left(\frac{\pi n_y y}{L}\right) \sin\left(\frac{\pi n_z z}{L}\right)$$

a) $$E^{exact}_{111} = \frac{3\pi^2 \hbar^2}{2mL^2}$$

$$\phi_{111}(x, y, z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{\pi y}{L}\right) \sin\left(\frac{\pi z}{L}\right)$$

The 1st excited state is 3-fold degenerate →

$\phi_{112}(x,y,z)$, $\phi_{121}(x,y,z)$, $\phi_{211}(x,y,z)$
correspond to the same energy $E_{112}^{exact} = E_{121}^{exact} = E_{211}^{exact}$
$= \frac{3\pi^2\hbar^2}{mL^2}$

b) 1st order correction to the ground state energy is given by →

$$E_1^{(1)} = \langle \phi_{111} | \hat{H}p | \phi_{111} \rangle$$
$$= 8V_0 \int_0^L \delta\left(x - \frac{L}{4}\right) \sin^2\left(\frac{\pi x}{L}\right) dx$$
$$\int_0^L \delta\left(y - \frac{3L}{4}\right) \sin^2\left(\frac{\pi y}{L}\right) dy$$
$$\int_0^L \delta\left(z - \frac{L}{4}\right) \sin^2\left(\frac{\pi z}{L}\right) dz$$
$$= 8V_0 \sin^2\frac{\pi}{4} \sin^2\frac{3\pi}{4} \sin^2\frac{\pi}{4} = V_0$$

$$E_0 = \frac{3\pi^2\hbar^2}{2mL^2} + V_0$$

c) To find the energy of the 1st excited state to 1st order, we need to use degenearate perturbation theory. The values of this energy are equal to $\frac{3\pi^2\hbar^2}{mL^2}$ plus the eigenvalue of the matrix →

$$\begin{pmatrix} V_{11} & V_{12} & V_{13} \\ V_{21} & V_{22} & V_{23} \\ V_{31} & V_{32} & V_{23} \end{pmatrix}$$

where $V_{nm} = \langle n | \hat{H}p | m \rangle$

$$|1\rangle = \phi_{211}(x,y,z) = \sqrt{\frac{8}{L^3}}\sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)\sin\left(\frac{\pi z}{L}\right)$$

$$|2\rangle = \phi_{121}(x,y,z) = \sqrt{\frac{8}{L^3}}\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi y}{L}\right)\sin\left(\frac{\pi z}{L}\right)$$

$$|3\rangle = \phi_{112}(x,y,z) = \sqrt{\frac{8}{L^3}}\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)\sin\left(\right.$$

$$V_{11} = 8V_0\int_0^L \delta\left(x-\frac{L}{4}\right)\sin^2\left(\frac{2\pi x}{L}\right)dx\int_0^L \delta\left(y-\frac{3L}{4}\right)\sin^2\left(\frac{\pi y}{L}\right)dy$$
$$\int_0^L \delta\left(z-\frac{L}{4}\right)\sin^2\left(\frac{\pi z}{L}\right)dz$$

$$= 8V_0\sin^2\frac{\pi}{2}\sin^2\frac{3\pi}{4}\sin^2\frac{\pi}{4} = 2V_0$$

$|||^{ly}$, $V_{12} = -2V_0$, $V_{13} = 2V_0$

$$V = 2V_0\begin{pmatrix} 1 & -1 & 1 \\ -1 & 1 & -1 \\ 1 & -1 & 1 \end{pmatrix}$$

The diagonalization of this matrix gives a doubly degenerate eigenvalues & a non-degenerate eigenvalue

$$E_1^{(1)} = E_2^{(1)} = 0, \quad E_3^{(1)} = 6V_0$$

$$E_1 = E_2 = \frac{3\pi^2\hbar^2}{mL^2}, \quad E_3 = \frac{3\pi^2\hbar^2}{mL^2} + 6V_0$$

Q5. When the atom is placed in an external ~~el~~ electric field $\vec{\varepsilon} = \varepsilon(\vec{i}+\vec{j})$, the energy of interaction between the electron's dipole moment $(\vec{d} = -e\vec{r})$ & $\vec{\varepsilon}$ is given by $-\vec{d}\cdot\vec{\varepsilon} = e\varepsilon(x+y) = e\varepsilon r\sin\theta(\cos\phi + \sin\phi)$

On the other hand, when subjecting the atom to an external ~~E~~ B magnetic field $\vec{B} = B\hat{k}$, the linear momentum of the electron becomes $\vec{P} \rightarrow \vec{P} - \frac{e\vec{A}}{c}$, where

$\vec{A}$ is the vector potential corresponding to $\vec{B}$. So, when subjecting a hydrogen atom to both $\vec{\mathcal{E}}$ & $\vec{B}$, its hamiltonian is given by →

$$\hat{H} = \frac{1}{2\mu}\left(\vec{P} - \frac{e\vec{A}}{c}\right)^2 - \frac{e^2}{r} + e\mathcal{E} r\sin\theta\,(\cos\phi + \sin\phi)$$

$$= \frac{\vec{P}^2}{2\mu} - \frac{e^2}{r} - \frac{e}{2\mu c}\vec{B}\cdot\vec{L} + \frac{e}{2\mu c}A^2$$

$$+ e\mathcal{E} r\sin\theta\,(\cos\phi + \sin\phi)$$

Diagonalize the matrix →

$$\begin{bmatrix} \langle 1|\hat{H}_p|1\rangle & \langle 1|\hat{H}_p|2\rangle & \langle 1|\hat{H}_p|3\rangle & \langle 1|\hat{H}_p|4\rangle \\ \langle 2|\hat{H}_p|1\rangle & \langle 2|\hat{H}_p|2\rangle & \langle 2|\hat{H}_p|3\rangle & \langle 2|\hat{H}_p|4\rangle \\ \langle 3|\hat{H}_p|1\rangle & \langle 3|\hat{H}_p|2\rangle & \langle 3|\hat{H}_p|3\rangle & \langle 3|\hat{H}_p|4\rangle \\ \langle 4|\hat{H}_p|1\rangle & \langle 4|\hat{H}_p|2\rangle & \langle 4|\hat{H}_p|3\rangle & \langle 4|\hat{H}_p|4\rangle \end{bmatrix}$$

where $|1\rangle = |200\rangle$, $|2\rangle = |211\rangle$, $|3\rangle = |210\rangle$
$|4\rangle = |21-1\rangle$

$$\therefore \langle 2l'm'|\hat{H}_p|2lm\rangle = \frac{-eB}{2\mu c}m\hbar\,\delta_{l',l}\,\delta_{m',m}$$

$$+ e\mathcal{E}_0 \langle 2l'm'|r\sin\theta(\cos\phi + \sin\phi)|2lm\rangle$$

Since $x = r\sin\theta\cos\phi$ & $y = r\sin\theta\sin\phi$ are both odd, the only terms that survive among $\langle 2l'm'|x|2lm\rangle$ & $\langle 2l'm'|y|2lm\rangle$ are $\langle 200|x|21\pm1\rangle$, $\langle 200|y|21\pm1\rangle$, & their complex conjugates.
That is, x & y can couple only states of different parities ($l'-l = \pm1$) & whose azimuthal quantum nos satisfy this condition: $m'-m = \pm1$

So, we need to find only →

$$\langle 200|x|21\pm1\rangle = \int_0^{\infty} R_{20}^*(r) R_{21}(r) r^3 dr$$

$$\times \int Y_{00}^*(\Omega) \sin\theta \cos\phi \, Y_{1\pm1}(\Omega) d\Omega$$

$$\langle 200|y|21\pm1\rangle = \int_0^{+\infty} R_{20}^*(r) R_{21}(r) r^3 dr \times \int Y_{00}^*(\Omega) \sin\theta$$

$$\sin\phi \, Y_{1\pm1}(\Omega) d\Omega$$

Where $\int_0^{+\infty} R_{20}^*(r) R_{21}(r) r^3 dr = -3\sqrt{3} a_0$

$\hookrightarrow a_0 = \frac{\hbar^2}{m_e e^2}$

$$\sin\theta\cos\phi = \sqrt{\frac{2\pi}{3}} \left[Y_{1-1}(\Omega) - Y_{11}(\Omega) \right]$$

$$\sin\theta\sin\phi = i\sqrt{\frac{2\pi}{3}} \left[Y_{1-1}(\Omega) + Y_{11}(\Omega) \right]$$

$$\& \int Y_{l'm'}^*(\Omega) Y_{lm}(\Omega) d\Omega = \delta_{l',l} \delta_{m',m}$$

$$\int Y_{00}^*(\Omega) \sin\theta \cos\phi \, Y_{11}(\Omega) d\Omega = \frac{1}{\sqrt{4\pi}} \int \sin\theta\cos\phi \, Y_{11}(\Omega) d\Omega$$

$$= \frac{1}{\sqrt{6}} \int Y_{1-1}(\Omega) Y_{11}(\Omega) d\Omega$$

$$= \frac{-1}{\sqrt{6}}$$

$$\int Y_{00}^*(\Omega) \sin\theta \sin\phi \, Y_{11}(\Omega) d\Omega = \frac{i}{\sqrt{6}} \int Y_{11}(\Omega) Y_{11}(\Omega) d\Omega$$

$$= \frac{-i}{\sqrt{6}}$$

IIIly, $\int Y_{00}^*(\Omega) \sin\theta \cos\phi \, Y_{1-1}(\Omega) d\Omega$

$$= \frac{1}{\sqrt{6}}$$

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$$\int Y_{00}^{*}(\Omega) \sin\theta \sin\phi \, Y_{1-1}(\Omega) \, d\Omega = \frac{-i}{\sqrt{6}}$$

$$\langle 200 | x | 21 \pm 1 \rangle = \pm \frac{3}{\sqrt{2}} a_0$$

$$\langle 200 | y | 21 \pm 1 \rangle = \frac{3i}{\sqrt{2}} a_0$$

$$\langle 21 \pm 1 | x | 200 \rangle = \pm \frac{3}{\sqrt{2}} a_0$$

$$\langle 21 \pm 1 | y | 200 \rangle = \frac{-3i}{\sqrt{2}} a_0$$

$$\begin{pmatrix} 0 & \alpha + i\alpha & 0 & -\alpha + i\alpha \\ \alpha - i\alpha & -\beta & 0 & 0 \\ 0 & 0 & 0 & 0 \\ -\alpha - i\alpha & 0 & 0 & \beta \end{pmatrix}$$

where $\alpha = \frac{3e\mathcal{E}a_0}{\sqrt{2}}$, $\beta = \frac{e\hbar B}{2\mu c}$

diagonalization gives $\rightarrow$

$$\lambda_1 = -\sqrt{\frac{e^2\hbar^2 B^2}{4\mu^2 c^2} + 18 e^2 \mathcal{E}^2 a_0^2}$$

$$\lambda_2 = \lambda_3 = 0$$

$$\lambda_4 = \sqrt{\frac{e^2\hbar^2 B^2}{4\mu^2 c^2} + 18 e^2 \mathcal{E}^2 a_0^2}$$

for $n=2 \rightarrow$

$$E_{2_1}^{(1)} = \frac{-R}{4} - \sqrt{\frac{e^2\hbar^2B^2 + 18e^2\varepsilon^2a_0^2}{4\mu^2c^2}}$$

$$E_{2_2}^{(1)} = \frac{-R}{4}$$

$$E_{2_3}^{(1)} = \frac{-R}{4}, \quad E_{2_4}^{(1)} = \frac{-R}{4} + \sqrt{\frac{e^2\hbar^2B^2 + 18e^2\varepsilon^2a_0^2}{4\mu^2c^2}}$$

So, external electric & magnetic fields have lifted the degeneracy of $n=2$ level only partially.

Q6. a) Diagonalization of $\hat{H}_0 \rightarrow$
eigenstate

$$|\phi_1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad |\phi_2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \quad |\phi_3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}$$

$$|\phi_4\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

Unperturbed energies values by non-degenerate value $E_1^{(0)} = 15E_0$ & a 3-fold degenerate value $E_2^{(0)} = E_3^{(0)} = E_4^{(0)} = 3E_0$

Exact eigenvalue of $\hat{H}$ obtained by diagonalizing $\hat{H}$.
let $\lambda = \frac{1}{100}$

$$\begin{vmatrix} 15E_0 - E & 0 & 0 & 0 \\ 0 & 3E_0 - E & \lambda E_0 & 0 \\ 0 & \lambda E_0 & 3E_0 - E & 0 \\ 0 & 0 & 0 & 3E_0 - E \end{vmatrix} = 0$$

$$(15E_0 - E)(3E_0 - E)\left[(3E_0 - E)^2 - \lambda^2 E_0^2\right] = 0$$

↳ gives exact values of eigenenergies →

$E_1 = 15E_0$, $E_2 = 3E_0$, $E_3 = (3-\lambda)E_0$, $E_4 = (3+\lambda)E_0$

b) $E_1 = 15E_0 + \langle \phi_1 | \hat{H}_1 | \phi_1 \rangle$

$$= 15E_0 + \frac{E_0}{100}(1\ 0\ 0\ 0)\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & \lambda E_0 & 0 \\ 0 & \lambda E_0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

non-degenerate state's energy ← $E_1 = 15E_0$

For degenerate states, $V = \begin{pmatrix} V_{11} & V_{12} & V_{13} \\ V_{21} & V_{22} & V_{23} \\ V_{31} & V_{32} & V_{33} \end{pmatrix}$

↳ Diagonalize

$V_{11} = \langle \phi_2 | \hat{H}_p | \phi_2 \rangle$

$$= (0\ 1\ 0\ 0)\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & \lambda E_0 & 0 \\ 0 & \lambda E_0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} = 0$$

$$V_{12} = \langle \phi_2 | \hat{H}_p | \phi_3 \rangle = (0\ 1\ 0\ 0)\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & \lambda E_0 & 0 \\ 0 & \lambda E_0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}$$

$$= \lambda E_0$$

$V_{13} = \langle \phi_2 | \hat{H}_P | \phi_4 \rangle = (0\ 1\ 0\ 0) \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & \lambda E_0 & 0 \\ 0 & \lambda E_0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$

$= 0$

$III^{ly} \rightarrow$

$V_{21} = \langle \phi_3 | \hat{H}_P | \phi_2 \rangle = \lambda E_0$

$V_{22} = \langle \phi_3 | \hat{H}_P | \phi_3 \rangle = 0$

$V_{23} = \langle \phi_3 | \hat{H}_P | \phi_4 \rangle = 0$

$V_{31} = \langle \phi_4 | \hat{H}_P | \phi_2 \rangle = 0$

$V_{32} = \langle \phi_4 | \hat{H}_P | \phi_3 \rangle = 0$

$V_{33} = \langle \phi_4 | \hat{H}_P | \phi_4 \rangle = 0$

$V = \begin{pmatrix} 0 & \lambda E_0 & 0 \\ \lambda E_0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ → Diagonalization leads to

$E_2^{(1)} = 0$

$E_3^{(1)} = \lambda E_0$

$E_4^{(1)} = -\lambda E_0$

$E_2 = E_2^{(0)} + E_2^{(1)} = 3E_0$

$E_3 = E_3^{(0)} + E_3^{(1)} = (3-\lambda) E_0$

$E_4 = E_4^{(0)} + E_4^{(1)} = (3+\lambda) E_0$

Q7. a) $\psi_0(x, \alpha) = A e^{-\alpha|x|}$

Normaliz-ation → $\langle \psi_0 | \psi_0 \rangle = A^2 \int_{-\infty}^{0} e^{2\alpha x} dx + A^2 \int_0^{\infty} e^{-2\alpha x} dx$

$= 2A^2 \int_0^{\infty} e^{-2\alpha x} dx = \frac{A^2}{\alpha}$

$\therefore A = \sqrt{\alpha}$

$\int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$

$$\langle \psi_0 | V(x) | \psi_0 \rangle = \frac{1}{2} m\omega^2 A^2 \int_{-\infty}^{\infty} x^2 e^{-2\alpha|x|}\, dx$$

$$= m\omega^2 A^2 \int_0^{\infty} x^2 e^{-2\alpha x}\, dx = \frac{m\omega^2}{4\alpha^2}$$

$$-\frac{\hbar^2}{2m}\langle \psi_0 | \frac{d^2}{dx^2} | \psi_0 \rangle = -\frac{\hbar^2}{2m} A^2 \int_{-\infty}^{\infty} e^{-\alpha|x|} \frac{d^2 e^{-\alpha|x|}}{dx^2}\, dx$$

$$= -\frac{\hbar^2}{m} A^2 \int_0^{\infty} e^{-\alpha x} \frac{d^2 e^{-\alpha x}}{dx^2}\, dx$$

$$= -\frac{\hbar^2 \alpha^2}{m} A^2 \int_0^{\infty} e^{-2\alpha x}\, dx = -\frac{\hbar^2 \alpha^2}{2m}$$

↓

incorrect way to calculate this as it leads to a $-$ve K.E since the 1st derivative of $\psi_0(x)$ is discontinuous at $x=0$

So, correct way to find K.E term →

$$-\frac{\hbar^2}{2m}\langle \psi_0 | \frac{d^2}{dx^2} | \psi_0 \rangle = \frac{\hbar^2}{2m} A^2 \int_{-\infty}^{\infty} \left| \frac{d e^{-\alpha|x|}}{dx} \right|^2 dx$$

$$= \frac{\hbar^2 \alpha^2}{2m} A^2 \int_{-\infty}^{\infty} e^{-2\alpha|x|}\, dx$$

$$= \frac{\hbar^2 \alpha^2}{2m}$$

since $A^2 \int_{-\infty}^{\infty} e^{-2\alpha|x|}\, dx = 1$

The above 2 expressions differ as the correct expression for $\frac{d\psi(x)}{dx}$ is $\rightarrow$

$$\frac{d\psi_0(x)}{dx} = \frac{A\,d e^{-\alpha|x|}}{dx}$$

$$= -\alpha\psi_0(x)\frac{d|x|}{dx}$$

$$= -\alpha\psi_0(x)\begin{cases} -1 & x<0 \\ 1 & x>0 \end{cases}$$

$$\frac{d\psi_0(x)}{dx} = -\alpha\left[\Theta(x) - \Theta(-x)\right]\psi_0(x)$$

$\Theta \rightarrow$ heaviside function

$$\Theta = \begin{cases} 0 & x<0 \\ 1 & x>0 \end{cases}$$

2^{nd} derivative of $\psi_0(x)$ contains delta funct^n

$$\frac{d^2\psi_0(x)}{dx^2} = \frac{d}{dx}\left\{-\alpha\left[\Theta(x) - \Theta(-x)\right]\psi_0(x)\right\}$$

& since $\frac{d\Theta(x)}{dx} = \delta(x)$

$$\left[\Theta(x) - \Theta(-x)\right]^2 = 1$$

since $\delta(x) = \delta(-x)$

$$\frac{d^2\psi_0(x)}{dx^2} = \alpha^2\left[\Theta(x) - \Theta(-x)\right]^2\psi_0(x) - \alpha\left[\delta(x) + \delta(-x)\right]\psi_0(x)$$

$$= \alpha^2\psi_0(x) - 2\alpha\psi_0(x)\delta(x)$$

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$\therefore$ $\frac{-\hbar^2}{2m} \langle \psi_0 | \frac{d^2}{dx^2} | \psi_0 \rangle$

$$= -\frac{\hbar^2}{2m} \int_{-\alpha}^{\alpha} \psi_0^*(x) \frac{d^2 \psi_0(x)}{dx^2} \, dx$$

$$= \frac{-\hbar^2}{2m} \alpha^2 + \frac{\hbar^2}{m} \alpha |\psi_0(0)|^2 = \frac{+\hbar^2 \alpha^2}{2m}$$

$$E_0(\alpha) = \frac{\hbar^2}{2m}\alpha^2 + \frac{m\omega^2}{4\alpha^2}$$

Minimizing gives $\rightarrow$ $0 = \frac{\delta E_0(\alpha)}{\delta \alpha}$

$$\Rightarrow \alpha_0^2 = \frac{m\omega}{\sqrt{2}\hbar}$$

$$E_0(\alpha_0) = \frac{\hbar^2}{2m} \frac{m\omega}{\sqrt{2}\hbar} + \frac{m\omega^2}{4} \frac{\sqrt{2}\hbar}{m\omega} = \frac{\hbar\omega}{\sqrt{2}}$$

$$E_0(\alpha_0) = 0.707 \hbar\omega$$

This result was inaccurate due to the cusp at $x=0$

b) Normalization constant $A = \left(\frac{A\alpha^3}{\pi^2}\right)^{1/4}$

$$E_0(\alpha) = \langle \psi_0(\alpha) | \hat{H} | \psi_0(\alpha) \rangle$$

$$= A^2 \int_{-\alpha}^{\alpha} \frac{1}{x^2+\alpha} \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m\omega^2 x^2 \right) \frac{1}{x^2+\alpha} \, dx$$

$$= \frac{-A^2\hbar^2}{2m} \int_{-\alpha}^{\alpha} \frac{6x^2 - 2\alpha}{(x^2+\alpha)^4} dx + \frac{1}{2} m\omega^2 A^2 \int_{-\alpha}^{\alpha} \frac{x^2}{(x^2+\alpha)^2} dx$$

$$E_0(\alpha) = \frac{\hbar^2}{4m\alpha} + \frac{1}{2}m\omega^2\alpha$$

$\hookrightarrow$ minimization leads to $E_0(\alpha_0) = \frac{\hbar\omega}{\sqrt{2}}$

as $\frac{\partial E(\alpha)}{\partial\alpha} = 0 \Rightarrow \alpha_0 = \frac{\hbar}{\sqrt{2}m\omega}$

$$E_0(\alpha_0) = \frac{\hbar\omega}{\sqrt{2}}$$

$\hookrightarrow$ Answer is similar to part (a) due to the fact that $\frac{A}{x^2+a}$ is not a good approximation to exact wavefunctⁿ which has a Gaussian form.

Q8. $E_n^{exact} = \frac{\pi^2\hbar^2 n^2}{2mL^2}$

a) let the parabolic trial functⁿ $\rightarrow$

$$\psi_0(x) = x(L-x)$$

$$E_0 = \frac{\langle\psi_0|\hat{H}|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle}$$

$$\langle\psi_0|\psi_0\rangle = \int_0^L \psi_0^2(x)\,dx$$

$$= \int_0^L x^2(L^2 - 2Lx + x^2)\,dx = \frac{L^5}{30}$$

$$\langle\psi_0|\hat{H}|\psi_0\rangle = \frac{\hbar^2}{2m}\int_0^L \left(\frac{d\psi_0(x)}{dx}\right)^2 dx$$

$$= \frac{\hbar^2}{2m}\int_0^L (L^2 - 4Lx + 4x^2)\,dx = \frac{\hbar^2 L^3}{6m}$$

Ground state energy →

$$E_0^{VM} = \frac{\langle \psi_0 | \hat{H} | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle} = 10\frac{\hbar^2}{2mL^2}$$

accurate result as $E_0^{VM} = \frac{10}{\pi^2} E^{exact}$

b) Trial wavefunct^n → $\psi_1(x) = x\left(x - \frac{L}{2}\right)(x - L)$

$\psi_1(x)$ → satisfies all conditions of properties of exact wave funct^n of 1st excited state → has one node at $x = L/2$ & must be odd w.r.t $x = L/2$ ⇒ this property makes it orthogonal to the ground state which is even about $L/2$. ∴, the funct^n vanishes at $x = 0, L/2, L$ & must be atleast cubic.

To find E_1^{VM}, we need → $\langle \psi_1 | \psi_1 \rangle$

$$\langle \psi_1 | \psi_1 \rangle = \int_0^L \psi_1^2(x)\,dx = \int_0^L x^2\left(x - \frac{L}{2}\right)^2 (x-L)^2\,dx$$

$$= \frac{1}{840} L^7$$

$$\langle \psi_1 | \hat{H} | \psi_1 \rangle = \frac{\hbar^2}{2m}\int_0^L \left(\frac{d\psi_1(x)}{dx}\right)^2 dx$$

$$= \frac{\hbar^2}{2m}\int_0^L \left(3x^2 - 3Lx + \frac{L^2}{2}\right)^2 dx$$

$$= \frac{\hbar^2 L^5}{40m}$$

$$E_1^{VM} = \frac{\langle \psi_1 | \hat{H} | \psi_1 \rangle}{\langle \psi_1 | \psi_1 \rangle} = \frac{42\hbar^2}{2mL^2}$$

Since $E_1^{exact} = \frac{(2\pi)^2 \hbar^2}{2mL^2}$

$$E_1^{VM} = 42 E_1^{exact} / (2\pi)^2$$

E_1^{VM} is higher than E_1^{exact} by 6%

Q9. For a potential well $\rightarrow$

$$E_n^{exact} = \frac{\pi^2 \hbar^2}{2mL^2} n^2, \quad \phi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

a) $E_n^{(1)} = \langle \phi_n | V_p | \phi_n \rangle$

$$= \frac{2}{L} V_0 \int_0^{L/2} \sin^2\left(\frac{n\pi x}{L}\right) dx$$

$$= \frac{1}{L} V_0 \int_0^{L/2} \left[1 - \cos\left(\frac{2n\pi x}{L}\right)\right] dx = \frac{V_0}{2}$$

energy is given to 1st-order perturbation ~~theory~~ by $\rightarrow$

$$E_n^{PT} = \frac{\pi^2 \hbar^2}{2mL^2} n^2 + \frac{V_0}{2}$$

b) $\int_0^L p(E_n, x)\, dx = n\pi\hbar$

$$\int_0^L p(E_n, x)\, dx = \sqrt{2m(E_n - V_0)} \int_0^{L/2} dx + \sqrt{2mE_n} \int_{L/2}^{L} dx$$

$$= \frac{L}{2} \sqrt{2m} \left(\sqrt{E_n - V_0} + \sqrt{E_n}\right) = n\pi\hbar$$

$$\sqrt{E_n - V_0} + \sqrt{E_n} = \frac{2n\pi\hbar}{L\sqrt{2m}}$$

$$2\sqrt{E_n(E_n - V_0)} = \alpha_n - 2E_n + V_0$$

$$\alpha_n = 2n^2\pi^2\hbar^2/mL^2$$

Squaring both sides & solving for E_n gives →

$$E_n = \frac{\alpha_n}{4} + \frac{V_0}{2} + \frac{V_0^2}{4\alpha_n}$$

$$E_n^{WKB} = \frac{\pi^2\hbar^2 n^2}{2mL^2} + \frac{V_0}{2} + \frac{mL^2V_0^2}{8\pi^2\hbar^2} \cdot \frac{1}{n^2}$$

Since $n >> 1$ & V_0 is very small →
we get → $E_n^{WKB} \simeq E_n^{PT} = \frac{\pi^2\hbar^2 n^2}{2mL^2} + \frac{V_0}{2}$

↳ which is same as the one derived from a 1st order perturbative treatment.

Q10. a) Ground state wave funct^n → no nodes
vanish at $z=0$
be finite as $z \to +\infty$

∴, $\psi_0(z,\alpha) = Aze^{-\alpha z}$ → satisfies these conditions
α → parameter
A → normalization constant
$A = 2\alpha^{3/2}$

$$\psi_0(z,\alpha) = 2\sqrt{\alpha^3}\, ze^{-\alpha z}$$

energy is given by →

$$E_0^{VM}(\alpha) = 4\alpha^3 \int_0^\infty ze^{-\alpha z}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dz^2} + mgz\right)ze^{-\alpha z}dz$$

$$= \frac{4\alpha^3\hbar^2}{2m}\int_0^\infty (2\alpha z - \alpha^2 z^2)e^{-2\alpha z}dz$$

$$+ 4\alpha^3 mg \int_0^{\infty} z^3 e^{-2\alpha z}\, dz$$

$$= \frac{2\alpha^3 \hbar^2}{m}\left(\frac{1}{2\alpha} - \frac{1}{4\alpha}\right) + 4mg\,\alpha^3 \frac{3}{8\alpha^4}$$

$$E_0^{VM}(\alpha) = \frac{\hbar^2 \alpha^2}{2m} + \frac{3}{2\alpha} mg$$

↳ Minimization of $E_0(\alpha)$ gives →

$$E_0^{VM}(\alpha_0) = \frac{3}{2}\left(\frac{9}{2}\right)^{1/3}\left(\frac{1}{2} mg^2 \hbar^2\right)^{1/3}$$

b) $\int_0^{E/mg} p\, dz = \left(n + \frac{3}{4}\right)\hbar\pi$

The potential ~~occurs~~ has 1 rigid wall at $x=0$ & turning pt occurs at $E = mgz$ & $z = E/mg$

$$E = \frac{p^2}{2m} + mgz \quad , \quad p(E,z) = \sqrt{2mE}\sqrt{1 - mgz/E}$$

$$\therefore \int_0^{E/mg} p(E_n, z)\, dz = \sqrt{2mE}\int_0^{E/mg}\sqrt{1 - \frac{mg}{E}z}\, dz$$

$$= \sqrt{2mE}\,\frac{2E}{3mg} = \sqrt{\frac{8E^3}{9mg^2}}$$

$$\int_0^{E/mg} p\, dz = \left(n + \frac{3}{4}\right)\pi\hbar$$

$$= \sqrt{\frac{8E^3}{9mg^2}}$$

WKB approximation → $E_n^{WKB} = \left[\frac{9\pi^2}{8} mg^2 \pi^2 \hbar^2 \left(n + \frac{3}{4}\right)^2\right]^{1/3}$

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Ground state energy $\rightarrow E_0^{WKB} = \frac{3}{4}(3\pi^2)^{1/3}\left(\frac{1}{2}mg^2\hbar^2\right)^{1/3}$

c) $V(z) = mgz$; $E_0^{exact} = 2.338\left(\frac{1}{2}mg^2\hbar^2\right)^{1/3}$

$$E_0^{VM} = \frac{3}{2}\left(\frac{9}{2}\right)^{1/3} \frac{E_0^{exact}}{2.338} \simeq 1.059 E_0^{exact}$$

$$E_0^{WKB} = \frac{3}{4}(3\pi^2)^{1/3} \frac{E_0^{exact}}{2.338} \simeq 0.992 E_0^{exact}$$

VM overestimates the energy by a 5.9% error
WKB method underestimates it by a 0.8% error.

Q11. In the absence of the field, the energy levels of $|2,1,m\rangle$ states are 3-fold degenerate: $|2,1,-1\rangle$, $|2,1,0\rangle$ & $|2,1,1\rangle$ & correspond to same energy $E_2 = \frac{-R}{4}$, $R = 13.6 eV$ is the Rydberg constant.
When the quadrupole field is turned on & since φ_{-2}, φ_0 & φ_2 are small.

$$\hat{H}_P = \varphi_{-2} r^2 Y_{2-2}(\Omega) + \varphi_0 r^2 Y_{20}(\Omega) + \varphi_2 r^2 Y_{22}(\Omega)$$

is a perturbation:

$$\begin{pmatrix} \langle 2,1,-1|\hat{H}_P|2,1,-1\rangle & \langle 2,1,-1|\hat{H}_P|2,1,0\rangle & \langle 2,1,-1|\hat{H}_P|2,1,1\rangle \\ \langle 2,1,0|\hat{H}_P|2,1,-1\rangle & \langle 2,1,0|\hat{H}_P|2,1,0\rangle & \langle 2,1,0|\hat{H}_P|2,1,1\rangle \\ \langle 2,1,1|\hat{H}_P|2,1,-1\rangle & \langle 2,1,1|\hat{H}_P|2,1,0\rangle & \langle 2,1,1|\hat{H}_P|2,1,1\rangle \end{pmatrix}$$

$$\langle n,l|r^2|n,l\rangle = \int_0^{\infty} r^4 |R_{nl}|^2 dr = \frac{1}{2} n^2\left(5n^2+1-3l(l+1)\right) a_0^2$$

where $\langle 2,1,m'|\hat{H}_P|2,1,m\rangle = \langle 2,1|r^2|2,1\rangle \langle 1,m'|\varphi_{-2}Y_{2-2} + \varphi_0 Y_{20} + \varphi_2 Y_{22}|1,m\rangle$

hence $\langle 2,1|r^2|2,1\rangle = 30 a_0^2$

$$\langle l',m'|Y_{2\mu}|l,m\rangle = \sqrt{\frac{5}{4\pi}}\sqrt{\frac{2l+1}{2l'+1}}\langle l,2;0,0|l',0\rangle \langle l,2;m,\mu|l',m'\rangle$$

$$\langle 1,-1|Y_{2-2}|1,1\rangle = \langle 1,1|Y_{22}|1,-1\rangle = -\sqrt{\frac{3}{10\pi}}$$

$$\langle 1,-1|Y_{20}|1,-1\rangle = \langle 1,1|Y_{20}|1,1\rangle = -\frac{1}{\sqrt{20\pi}}$$

$$\langle 1,0|Y_{20}|1,0\rangle = \frac{1}{\sqrt{5\pi}}$$

obtained from $\rightarrow$

$$\langle l,2;m,0|l,m\rangle = \frac{[3m^2 - l(l+1)]}{\sqrt{l(2l-1)(l+1)(2l+3)}}$$

$$\langle l,2;m,\mp 2,\pm 2|l,m\rangle = \sqrt{\frac{3(l\pm m-1)(l\pm m)(l\mp m+1)(l\mp m+2)}{2l(2l-1)(l+1)(2l+3)}}$$

Matrix $\rightarrow$ $30a_0^2 \begin{pmatrix} -\frac{\varphi_0}{\sqrt{20\pi}} & 0 & -\varphi_2\sqrt{\frac{3}{10\pi}} \\ 0 & \frac{\varphi_0}{\sqrt{5\pi}} & 0 \\ -\varphi_2\sqrt{\frac{3}{10\pi}} & 0 & -\frac{\varphi_0}{\sqrt{20\pi}} \end{pmatrix}$

its diagonalization gives $\rightarrow$

$$E_1^{(1)} = -\frac{30 a_0^2}{\sqrt{10\pi}}\left(\frac{\varphi_0}{\sqrt{2}} \mp \varphi_2\sqrt{3}\right).$$

$$E_2^{(1)} = \frac{30\phi_0 a_0^2}{\sqrt{5\pi}}$$

$$E_3^{(1)} = \frac{30 a_0^2}{\sqrt{10\pi}} \left(-\frac{\phi_0}{\sqrt{2}} + \phi_2\sqrt{3} \right)$$

1st order perturbation theory, energies of p-level given by →

$$E_{21} = \frac{-R}{4} - \frac{30 a_0^2}{\sqrt{10\pi}} \left(\frac{\phi_0}{\sqrt{2}} + \phi_2\sqrt{3} \right)$$

$$E_{22} = \frac{-R}{4} + 30\,\frac{\phi_0 a_0^2}{\sqrt{5\pi}}$$

$$E_{23} = \frac{-R}{4} + \frac{30 a_0^2}{\sqrt{10\pi}} \left(\frac{-\phi_0}{\sqrt{2}} + \phi_2\sqrt{3} \right)$$

Q12. a) $\vec{\mu}_1 = \frac{2\mu_0 \vec{S}_1}{\hbar}$, $\mu_2 = \frac{2\mu_0 \vec{S}_2}{\hbar}$

$$\mu_0 = \frac{\hbar e}{2 m_p c}$$

$$\hat{H}_0 = -(\vec{\mu}_1 + \vec{\mu}_2)\cdot\vec{B} = -\frac{2\mu_0}{\hbar}(\vec{S}_1 + \vec{S}_2)\cdot\vec{B}$$

$$= -\frac{2\mu_0 B}{\hbar}\hat{S}_z$$

$$|\chi_1\rangle = |1,1\rangle = \left|\tfrac{1}{2},\tfrac{1}{2};\tfrac{1}{2},\tfrac{1}{2}\right\rangle$$

$$|\chi_2\rangle = |1,-1\rangle = \left|\tfrac{1}{2},\tfrac{1}{2};\tfrac{-1}{2},\tfrac{-1}{2}\right\rangle$$

$$|\chi_3\rangle = |1,0\rangle = \frac{1}{\sqrt{2}}\left[\left|\tfrac{1}{2},\tfrac{1}{2};\tfrac{1}{2},\tfrac{-1}{2}\right\rangle + \left|\tfrac{1}{2},\tfrac{1}{2};\tfrac{-1}{2},\tfrac{1}{2}\right\rangle \right]$$

$$|\chi_4\rangle = |0,0\rangle = \frac{1}{\sqrt{2}}\left\{ \left|\tfrac{1}{2},\tfrac{1}{2};\tfrac{1}{2},\tfrac{-1}{2}\right\rangle - \left|\tfrac{1}{2},\tfrac{1}{2};\tfrac{-1}{2},\tfrac{1}{2}\right\rangle \right\}$$

$E_1^{(0)} = -2\mu_0 B$, $E_2^{(0)} = 2\mu_0 B$, $E_3^{(0)} = E_4^{(0)} = 0$

$|\chi_3\rangle$ & $|\chi_4\rangle$ → doubly degenerate
while
$|\chi_1\rangle$ & $|\chi_2\rangle$ are not

B) $\hat{H}_{P_{ij}} = \langle \chi_i | \hat{H}_P | \chi_j \rangle$

$i, j = 1, 2, 3, 4$

$\vec{r} = d\vec{k}$, $\vec{\mu_1} \cdot \vec{r} = 2\mu_0 d \hat{S}_{1z} / \hbar$

$\vec{\mu_2} \cdot \vec{r} = 2\mu_0 d \hat{S}_{2z} / \hbar$

$$\therefore \hat{H}_P = \frac{1}{r^3}\left[\vec{\mu_1} \cdot \vec{\mu_2} - 3\frac{(\vec{\mu_1} \cdot \vec{r})(\vec{\mu_2} \cdot \vec{r})}{r^2}\right]$$

$$= \frac{4\mu_0^2}{d^3 \hbar^2}\left[\vec{S_1} \cdot \vec{S_2} - 3\hat{S}_{1z}\hat{S}_{2z}\right]$$

$$\hat{H}_P |S, S_z\rangle = \frac{2\mu_0^2}{d^3}\left[S(S+1) - \frac{3}{2} - 3\left(S_z^2 - \frac{1}{2}\right)\right]|S, S_z\rangle$$

$$= \frac{2\mu_0^2}{d^3}\left[S(S+1) - 3S_z^2\right]|S, S_z\rangle$$

$S = 1$, $S_z = -1, 0, 1$ → triplet state
$S = 0$, $S_z = 0$ → singlet

Matrix elements of $\hat{H}_P$ →

$$E_1^{(1)} = \langle \chi_1 | \hat{H}_p | \chi_1 \rangle = \frac{-2\mu_0^2}{d^3}$$

$$E_2^{(1)} = \langle \chi_2 | \hat{H}_p | \chi_2 \rangle = -\frac{2\mu_0^2}{d^3}$$

$$E_3^{(1)} = \langle \chi_3 | \hat{H}_p | \chi_3 \rangle = \frac{4\mu_0^2}{d^3}$$

$$E_4^{(1)} = \langle \chi_4 | \hat{H}_p | \chi_4 \rangle = 0$$

$$\langle \chi_i | \hat{H}_p | \chi_j \rangle = 0 \text{ for } i \neq j$$

Energies $\rightarrow$ $E_n = E_n^{(0)} + E_n^{(1)}$

$$\therefore E_1 = -2\mu_0 B - \frac{2\mu_0^2}{d^3}$$

$$E_2 = 2\mu_0 B - \frac{2\mu_0^2}{d^3}, \quad E_3 = \frac{4\mu_0^2}{d^3}, \quad E_4 = 0$$

So, dipole-dipole magnetic interaction have lifted the degeneracy of energy levels in 2-proton system.

Q13. $E_n = \dfrac{\hbar^2 \pi^2 n^2}{8mL^2}$, $\psi_n(x) = \dfrac{1}{\sqrt{L}} \begin{cases} \cos\left(\dfrac{n\pi x}{2L}\right), & n = 1, 3, 5, \ldots \\ \sin\left(\dfrac{n\pi x}{2L}\right), & n = 2, 4, 6, \ldots \end{cases}$

When the spin of the particle is considered, its wave function is the product of a special part $\psi_n(x)$ & a spin part $|\chi_\pm\rangle$:

$$\psi_n^{\pm}(x) = |\chi_\pm\rangle \psi_n(x)$$

$$= |\chi_\pm\rangle \begin{cases} \frac{1}{\sqrt{L}} \cos\left(\frac{n\pi x}{2L}\right), & n = 1, 3, 5, \dots \\ \frac{1}{\sqrt{L}} \sin\left(\frac{n\pi x}{2L}\right), & n = 2, 4, 6, \dots \end{cases}$$

$$|\chi_+\rangle = \left|\frac{1}{2}, \frac{1}{2}\right\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$|\chi_-\rangle = \left|\frac{1}{2}, \frac{-1}{2}\right\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\hat{H}_p = -\vec{\mu}\cdot\vec{B} = B\mu_0 \begin{cases} \sigma_z, & -L \le x \le 0 \\ \sigma_x, & 0 \le x \le L \end{cases}$$

Where $\vec{\mu} = \frac{2\mu_0 \vec{S}}{\hbar} = \mu_0 \vec{\sigma}$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\begin{pmatrix} \langle \psi_n^- | \hat{H}_p | \psi_n^- \rangle & \langle \psi_n^- | \hat{H}_p | \psi_n^+ \rangle \\ \langle \psi_n^+ | \hat{H}_p | \psi_n^- \rangle & \langle \psi_n^+ | \hat{H}_p | \psi_n^+ \rangle \end{pmatrix}$$

$$\langle \psi_n^- | \hat{H}_p | \psi_n^- \rangle = \int_{-L}^{0} |\psi_n(x)|^2 \langle \chi_- | \hat{H}_p | \chi_- \rangle dx$$

$$+ \int_0^L |\psi_n(x)|^2 \langle \chi_- | \hat{H}_p | \chi_- \rangle dx$$

$$= \mu_0 B\left[\langle \chi_- | \sigma_z | \chi_- \rangle \int_{-L}^{0} |\psi_n(x)|^2 dx + \langle \chi_- | \sigma_x | \chi_- \rangle \int_0^L |\psi_n(x)|^2 dx\right]$$

Using $\int_{-L}^{0} |\psi_n(x)|^2 dx = \int_0^L |\psi_n(x)|^2 dx = \frac{1}{2}$

& since

$$\langle \chi_- | \sigma_z | \chi_- \rangle = (0\ 1)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$= -1$$

$$\langle \chi_- | \sigma_x | \chi_- \rangle = (0\ 1)\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = 0$$

$$\langle \psi_n^- | \hat{H}_p | \psi_n^- \rangle = -\frac{\mu_0 B}{2}$$

Following this procedure, we can find the remaining matrix elements →

$$\frac{\mu_0 B}{2}\begin{pmatrix} -1 & 1 \\ 1 & 1 \end{pmatrix}$$

Its diagonalization →

$$\left(-\frac{\mu_0 B}{2} - E^{(1)}\right)\left(\frac{\mu_0 B}{2} - E^{(1)}\right) - \left(\frac{\mu_0 B}{2}\right)^2 = 0$$

$$E^{(1)} = \frac{\pm \mu_0 B}{\sqrt{2}}$$

Energy of n^{th} excited state to 1st-order degenerate perturbation theory is given by →

$$E_n = \frac{\hbar^2 \pi^2 n^2}{8mL^2} \pm \frac{\mu_0 B}{\sqrt{2}}$$

The magnetic field has completely removed the degeneracy of the energy spectrum of this particle

Q14. a) The ground state wave function of this potential must be selected from the harmonic oscillator wave functions that vanish at $x=0$. Only odd wave functions vanish at $x=0$ →

$$\psi_0(x,0) = x e^{-\alpha x^2}$$

$$\langle \psi_0 | \psi_0 \rangle = \int_0^{\infty} x^2 e^{-2\alpha x^2} dx = \frac{1}{8\alpha}\sqrt{\frac{\pi}{2\alpha}}$$

$$\langle \psi_0 | \frac{1}{2} m\omega^2 x^2 | \psi_0 \rangle = \frac{1}{2} m\omega^2 \int_0^{\infty} x^4 e^{-2\alpha x^2} dx$$

$$= \frac{3m\omega^2}{64\alpha^2}\sqrt{\frac{\pi}{2\alpha}}$$

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$$\langle\psi_0|\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}|\psi_0\rangle = \frac{\hbar^2}{2m}\int_0^{\alpha}(3\alpha x^2 - 2\alpha^2 x^4)\, e^{-2\alpha x^2}dx$$

$$= \frac{3\hbar^2}{16m}\sqrt{\frac{\pi}{2\alpha}}$$

Ground state energy →

$$E_0(\alpha) = \frac{\langle\psi_0(\alpha)|\hat{H}|\psi_0(\alpha)\rangle}{\langle\psi_0|\psi_0\rangle}$$

$$= \frac{3\hbar^2}{2m}\alpha + \frac{3m\omega^2}{8a}$$

Minimizing $E_0(\alpha)$ w.r.t α gives →

$$\alpha_0 = \frac{m\omega}{2\hbar}$$

$$E_0(\alpha_0) = \frac{3}{2}\hbar\omega$$

b) This potential has a single rigid wall at $x=0$.

$$\int_0^a p\,dx = \left(n+\frac{3}{4}\right)\pi\hbar$$

Turning pt occurs at $x=a$ with $E = \frac{1}{2}m\omega^2 a^2$

$$\& \quad a = \sqrt{2E/m\omega^2}$$

$$\int_0^a p\,dx = \int_0^a \sqrt{2mE - m^2\omega^2 x^2}\,dx = m\omega\int_0^a \sqrt{a^2 - x^2}\,dx$$

put $x = a\sin\theta$

$$\int_0^a \sqrt{a^2 - x^2}\, dx = a^2 \int_0^{\pi/2} \cos^2\theta \, d\theta$$

$$= \frac{a^2}{2} \int_0^{\pi/2} (1+\cos 2\theta)\, d\theta$$

$$= \frac{\pi a^2}{4}$$

hence, $\displaystyle\int_0^a p\,dx = m\omega \frac{\pi a^2}{4} = \frac{\pi E}{2\omega}$

$\displaystyle\int_0^a p\,dx = \left(n + \frac{3}{4}\right)\pi\hbar$, i.e,

$$\frac{\pi E}{2\omega} = \left(n+\frac{3}{4}\right)\pi\hbar$$

$$E_n^{WKB} = \left(2n + \frac{3}{2}\right)\hbar\omega \ , \ n = 0, 1, 2, 3, \ldots$$

$$E_0^{WKB} = \frac{3}{2}\hbar\omega$$

Q15. $\hat{H} = \hat{H}_0 + \hat{H}_p = \hat{H}_0^A + \hat{H}_0^B + \hat{H}_p$

$$\hat{H}_p = \frac{e^2}{R} + \frac{e^2}{|\vec{R} + \vec{r}_A - \vec{r}_B|} - \frac{e^2}{|\vec{R}+\vec{r}_A|} - \frac{e^2}{|\vec{R}-\vec{r}_B|}$$

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$$\hat{H}_p = \frac{e^2}{R^3}\left[\vec{r}_A \cdot \vec{r}_B - \frac{3(\vec{r}_A \cdot \vec{R})(\vec{r}_B \cdot \vec{R})}{R^2}\right]$$

$$\vec{R} = \hat{R}_z$$

$$\hat{H}_p = \frac{e^2}{R^3}\left[\hat{X}_A \hat{X}_B + \hat{Y}_A \hat{Y}_B - 2\hat{Z}_A \hat{Z}_B\right]$$

$$E_0 = E_0^A + E_0^B = 2E_{100} = -\frac{e^2}{a_0}.$$

$$|\phi_0\rangle = |\phi_0^A\rangle |\phi_0^B\rangle = |100\rangle_A |100\rangle_B$$

The 1st-order reaction to the molecule' energy,

$E^{(1)} = \langle \phi_0 | \hat{H}_p | \phi_0 \rangle$ is given by →

$$E^{(1)} = \frac{e^2}{R^3}\Big(\langle \phi_0^A | \hat{X}_A | \phi_0^A \rangle \langle \phi_0^B | \hat{X}_B | \phi_0^B \rangle$$

$$+ \langle \phi_0^A | \hat{Y}_A | \phi_0^A \rangle \langle \phi_0^B | \hat{Y}_B | \phi_0^B \rangle$$

$$- 2\left(\langle \phi_0^A | \hat{Z}_A | \phi_0^A \rangle \langle \phi_0^B | \hat{Z}_B | \phi_0^B \rangle\right)$$

Since the operators $\hat{X}, \hat{Y}$ & $\hat{Z}$ are odd & the states $|\phi_0^A\rangle$ & $|\phi_0^B\rangle$ are spherically symmetric, then all the terms are zero.

$\therefore E^{(1)} = 0$

$$E^{(2)} = \sum_{nlm n'l'm' \neq 1,0,0} \frac{|\langle n,l,m, n',l',m' | \hat{H}_p | \phi_0 \rangle|^2}{2E_{100} - E_n - E_{n'}}$$

$\langle n, l, m, n', l', m' | \hat{H}_p | \phi_0 \rangle$

$= \frac{e^2}{R^3} (\langle n, l, m | X_A | 1,0,0 \rangle_A \langle n', l', m' | X_B | 1,0,0 \rangle_B$

$+ \langle n, l, m | Y_A | 1,0,0 \rangle_A \langle n', l', m' | X_B | 1,0,0 \rangle_B$

$- 2 \langle n, l, m | Z_A | 1,0,0 \rangle_A \langle n', l', m' | Z_B | 1,0,0 \rangle_B)$

$$E^{(2)} \leq \frac{1}{2(E_{100} - E_{200})} \sum_{n,l,m,n',l',m' \neq 1,0,0} | \langle n,l,m; n', l', m' | \hat{H}_p | \phi_0 \rangle |^2$$

$$\sum_{n,l,m,n',l',m'} | \langle n,l,m; n', l', m' | \hat{H}_p | \phi_0 \rangle |^2$$

$$= \sum_{n,l,m,n',l',m'} \langle 1,0,0; 1,0,0 | \hat{H}_p | n,l,m,n',l',m' \rangle \langle n,l,m; n', l', m' | \hat{H}_p | 1,0,0; 1,0,0 \rangle$$

$$= \langle 1,0,0; 1,0,0 | (\hat{H}_p)^2 | 1,0,0; 1,0,0 \rangle$$

$$= \frac{e^4}{R^6} \langle 1,0,0; 1,0,0 | (X_A X_B + Y_A Y_B - 2 Z_A Z_B)^2 | 1,0,0; 1,0,0 \rangle$$

The cross terms are zero due to spherical symmetry.

$$\langle X_A Y_A \rangle_A = \langle X_A Z_A \rangle_A = \langle Y_A Z_A \rangle_A$$
$$= \langle X_B Y_B \rangle_B = \cdots \langle Y_B Z_B \rangle_B = 0$$

$$\langle X_A^2 \rangle_A = \langle Y_A^2 \rangle_A = \langle Z_A^2 \rangle_A = \langle X_B^2 \rangle_B$$

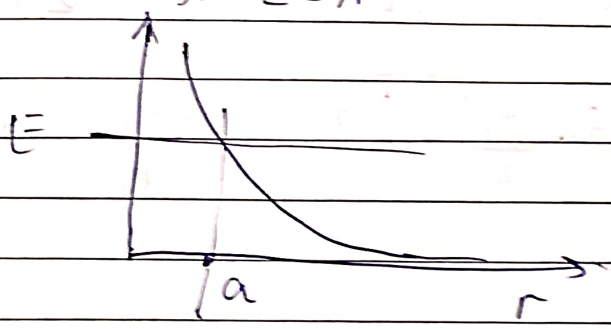
$$= \langle x_B^2 \rangle_B = \langle z_B^2 \rangle_B = a_0^2$$

$$\langle C \rangle_A = \langle \phi_0^A | C | \phi_0^A \rangle$$

$$\langle D \rangle_B = \langle \phi_0^B | D | \phi_0^B \rangle$$

$$\langle 1,0,0;1,0,0 | (x_A x_B + y_A y_B - 2 z_A z_B)^2 | 1,0,0;1,0,0 \rangle = 6a_0^4$$

$$V(r) = Ze^2/r$$



$$E^{(2)} \le \frac{\langle 1,0,0;1,0,0 | (\hat{H}_P)^2 | 1,0,0;1,0,0 \rangle}{2(E_{100} - E_{200})}$$

$$= \frac{3e^4 a_0^4}{R^6} \cdot \frac{1}{E_{100} - E_{200}}$$

$$E^{(2)} \le -\frac{8e^2 a_0^5}{R^6}$$

$$E_2 \le 2E_{100} - \frac{8e^2 a_0^5}{R^6} \cancel{\Rightarrow E_2 \le -e^2}$$

$$\Rightarrow E_2 \le \frac{-e^2}{a_0}\left(1 + \frac{8a_0^6}{R^6}\right)$$

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Q16: To penetrate inside the nucleus, the proton has to overcome the repulsive coulomb force of the nucleus. That is, it has to tunnel through the coulomb barrier, $V(r) = Ze^2/r$.

$$T = e^{-2\gamma}$$

$$\gamma = \frac{1}{\hbar}\int_a^0 \sqrt{2m(V(r)-E)}\,dr$$

$E = V(a)$, $a = Ze^2/E$, $V(r) = Ze^2/r$

$$\gamma = \frac{1}{\hbar}\int_a^0 \sqrt{2m\left(\frac{Ze^2}{r}-E\right)}\,dr = \frac{\sqrt{2mE}}{\hbar}\int_{\frac{e^2Z}{E}}^0 \sqrt{\frac{Ze^2}{Er}-1}\,dr$$

put $x = \frac{Er}{Ze^2}$

$$\gamma = \frac{Ze^2}{\hbar}\sqrt{\frac{2m}{E}}\int_0^1 \sqrt{\frac{1}{x}-1}\,dx$$

$$= \frac{Ze^2\pi}{\hbar}\sqrt{\frac{m}{2E}}$$

$$\int_0^1 \sqrt{\frac{1}{x}-1}\,dx = \frac{\pi}{2}$$

Transmission coefficient is →

$$T = e^{-2\gamma}$$
$$= e^{-\frac{Ze^2\pi}{\hbar}\sqrt{\frac{2m}{E}}}$$

The value of this coefficient describes how difficult it is for a positively charged particle, such as a proton, to approach a nucleus.

Q17. Since the 2 particles have the same spin, the spin wave function of system $\chi_S(S_1, S_2)$ must be symmetric, so χ_S is any one of the triplet states

$$\chi_S = \begin{cases} |1,1\rangle = \left|\frac{1}{2},\frac{1}{2}\right\rangle_1 \left|\frac{1}{2},\frac{1}{2}\right\rangle_2, \\ |1,0\rangle = \frac{1}{\sqrt{2}}\left\{\left|\frac{1}{2},\frac{1}{2}\right\rangle_1 \left|\frac{1}{2},\frac{-1}{2}\right\rangle_2 + \left|\frac{1}{2},\frac{-1}{2}\right\rangle_1 \left|\frac{1}{2},\frac{1}{2}\right\rangle_2\right\} \\ |1,-1\rangle = \left|\frac{1}{2},\frac{-1}{2}\right\rangle_1 \left|\frac{1}{2},\frac{-1}{2}\right\rangle_2 \end{cases}$$

In addition, since this 2-particle system is a system of identical fermions, its wave function must be antisymmetric. Since the spin part is symmetric the spatial part of the wave funct^n has to be antisymmetric: $\psi(x_1, x_2) = \psi_A(x_1, x_2)\chi_S(S_1, S_2)$

$$\psi_A(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\phi_{n_1}(x_1)\phi_{n_2}(x_2) - \phi_{n_2}(x_1)\phi_{n_1}(x_2)\right]$$

$$= \frac{1}{L}\left[\sin\left(\frac{n_1\pi x_1}{L}\right)\sin\left(\frac{n_2\pi x_2}{L}\right) - \sin\left(\frac{n_2\pi x_1}{L}\right)\sin\left(\frac{n_1\pi x_2}{L}\right)\right]$$

The energy levels of this 2-particle system are

$$E = \frac{\pi^2\hbar^2}{2mL^2}(n_1^2 + n_2^2) = E_0(n_1^2 + n_2^2)$$

where $E_0 = \frac{\pi^2\hbar^2}{2mL^2}$

a) The ground state cannot correspond to $n_1 = n_2 = 1$ for the spatial wave function would be zero

$$E^{(0)} = E_0(1^2 + 2^2) = 5E_0 = \frac{5\pi^2\hbar^2}{2mL^2}$$

The 1st excited state corresponds to $n_1 = 1, n_2 = 3$

$$E^{(1)} = E_0(1^2 + 3^2) = 10E_0 = \frac{5\pi^2\hbar^2}{mL^2}$$

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The 2^{nd} excited state corresponds to $n_1 = 2, n_2 = 3$

$$E^{(2)} = 13E_0 = \frac{13\pi^2\hbar^2}{2mL^2}$$

b) $\hat{H}_P = -V_0 L^2 \delta\left(x_1 - \frac{L}{2}\right)\delta\left(x_2 - \frac{L}{2}\right)$

$$E = \frac{5\pi^2\hbar^2}{2mL^2} + \langle \psi_0 | \hat{H}_P | \psi_0 \rangle$$

$$\langle \psi_0 | \hat{H}_P | \psi_0 \rangle = \int_0^L dx_1 \int_0^L dx_2\, \psi_0^*(x_1, x_2)\, \hat{H}_P(x_1, x_2)\, \psi_0(x_1, x_2)$$

$$\psi_0^*(x_1, x_2) = \psi_0(x_1, x_2)$$

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

$$\langle \psi_0 | \hat{H}_P | \psi_0 \rangle = \frac{-V_0 L^2}{L^2}\int_0^L dx_1\, \delta\left(x_1 - \frac{L}{2}\right)\int_0^L dx_2\, \delta\left(x_2 - \frac{L}{3}\right)\left[\sin\left(\frac{\pi x_1}{L}\right)\sin\left(\frac{2\pi x_2}{L}\right) - \sin\left(\frac{2\pi x_1}{L}\right)\sin\left(\frac{\pi x_2}{L}\right)\right]^2$$

$$= -V_0\left[\sin\left(\frac{\pi}{2}\right)\sin\left(\frac{2\pi}{3}\right) - \sin(\pi)\sin\left(\frac{\pi}{3}\right)\right]^2$$

$$= -\frac{3}{4}V_0$$

Hence, $E = \frac{5\pi^2\hbar^2}{2mL^2} - \frac{3}{4}V_0$

Q18. Neglecting the spin-orbit interaction, we can write the Hamiltonian of the 2 electron system as

$$\hat{H} = \hat{H}_0 + \hat{V}_{12} = \hat{H}_0 + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

$$\hat{H}_0 = -\frac{\hbar^2}{2\mu}\left(\nabla_1^2 + \nabla_2^2\right) - Ze^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

$$E_0 = -\frac{2Z^2e^2}{2a} = -27.2Z^2 eV$$

$$\Psi_0(\vec{r}_1, \vec{s}_1; \vec{r}_2, \vec{s}_2) = \Psi_0(\vec{r}_1, \vec{r}_2)\chi_{singlet}(\vec{s}_1, \vec{s}_2)$$

$$\chi_{singlet}(\vec{s}_1, \vec{s}_2) = \frac{1}{\sqrt{2}}\left(\left|\frac{1}{2}, \frac{1}{2}\right\rangle_1 \left|\frac{1}{2}, \frac{-1}{2}\right\rangle_2 - \left|\frac{1}{2}, \frac{-1}{2}\right\rangle_1 \left|\frac{1}{2}, \frac{1}{2}\right\rangle_2\right)$$

$$\phi_{100}(\vec{r}) = R_{10}(r)Y_{00}(\Omega) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2} e^{-Zr_1/a}$$

$$\Psi_0(\vec{r}_1, \vec{r}_2) = \frac{1}{\pi}\left(\frac{Z}{a}\right)^3 e^{-Z(r_1+r_2)/a}$$

a) A 1st order treatment yields →

$$E = E_0 + \langle\Psi_0|\hat{V}_{12}|\Psi_0\rangle$$

$$= -\frac{2Z^2e^2}{2a} + \langle\Psi_0|\hat{V}_{12}|\Psi_0\rangle$$

where $\langle\Psi_0|\hat{V}_{12}|\Psi_0\rangle = \int d^3r_1 \int d^3r_2\, \Psi_0^*(\vec{r}_1, \vec{r}_2)\hat{V}_{12}\Psi_0(\vec{r}_1, \vec{r}_2)$

$$= \int d^3r_1 \int d^3r_2\, |\phi_{100}(\vec{r}_1)|^2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}|\phi_{100}(\vec{r}_2)|^2$$

$$= \frac{5}{8}\frac{Ze^2}{a}$$

$$E = -\frac{Ze^2}{a}\left(2 - \frac{5}{8}\right)$$

For Helium, $Z=2 \rightarrow$

$$E = -108.8\,eV + 34\,eV = -74.8\,eV$$

This result disagrees with the experimental value, $E_{exp} = -78.975\,eV$ with a 5.3% relative error. In our calculations, we haven't taken into account the screening effect.

b) $\psi_0(r_1, r_2) = A e^{-\alpha(r_1+r_2)/a}$

A → normalization constant

using $\int_0^\infty x^n e^{-bx} dx = \frac{n!}{b^{n+1}}$

We show that → $A = \left(\frac{\alpha}{a}\right)^{3}/\pi$

$$\therefore,\quad \psi_\alpha(r_1, r_2) = \frac{1}{\pi}\left(\frac{\alpha}{a}\right)^3 e^{-\alpha(r_1+r_2)/a}$$

$$E(\alpha) = \langle\psi_\alpha|\hat{H}_0|\psi_\alpha\rangle + \langle\psi_\alpha|\hat{V}_{12}|\psi_\alpha\rangle$$

$$= \langle\psi_\alpha|\hat{H}_0|\psi_\alpha\rangle + \frac{5}{8}\frac{\alpha e^2}{a}$$

$$\langle\psi_\alpha|\hat{H}_0|\psi_\alpha\rangle = \frac{-\hbar^2}{2\mu}\langle\psi_\alpha|\nabla_1^2 + \nabla_2^2|\psi_\alpha\rangle$$

$$-Ze^2\langle\psi_a|\frac{1}{r_1} + \frac{1}{r_2}|\psi_a\rangle$$

$$= \frac{-\hbar^2}{2\mu}\langle\psi_a|\nabla_1^2 + \nabla_2^2|\psi_a\rangle - \alpha e^2\langle\psi_a|\frac{1}{r_1} + \frac{1}{r_2}|\psi_a\rangle$$

$$-(Z-\alpha)e^2\langle\psi_a|\frac{1}{r_1} + \frac{1}{r_2}|\psi_a\rangle$$

This form is quite suggestive; since ~~$-\hbar^2\langle\psi_0|\vec{\nabla}|\psi_0\rangle$~~

$$\frac{-\hbar^2\langle\psi_0|\vec{\nabla}|\psi_0\rangle}{2\mu} - Ze^2\langle\psi_0|\frac{1}{r}|\psi_0\rangle = \frac{-Z^2e^2}{2a}$$

Since → $\langle\psi_\alpha|\frac{1}{r_1}|\psi_\alpha\rangle = \langle\psi_\alpha|\frac{1}{r_2}|\psi_\alpha\rangle$

$$= 4\left(\frac{\alpha}{a}\right)^3\int_0^\infty r e^{-2\alpha r/a} dr = \frac{\alpha}{a}$$

$$E(\alpha) = -\frac{2\alpha^2 e^2}{2a} - 2(Z-\alpha)e^2\frac{\alpha}{a} + \frac{5}{8}\frac{\alpha e^2}{a}$$

$$= \left[\alpha^2 - 2\left(Z - \frac{5}{16}\right)\alpha\right]\frac{e^2}{a}$$

$$\frac{dE(\alpha)}{d\alpha} = 0 \Rightarrow \alpha_0 = Z - \frac{5}{16}$$

$\therefore$, the ground state energy is $\rightarrow$

$$E(\alpha_0) = -\left[1 - \frac{5}{8Z} + \left(\frac{5}{16Z}\right)^2\right]\frac{Z^2 e^2}{a}$$

$$\& \ \psi(r_1, r_2) = \frac{1}{\pi}\left(\frac{Z}{a} - \frac{5}{16a}\right)^3 e^{-\left(\frac{Z}{a} - \frac{5}{16a}\right)(r_1 + r_2)}$$

By variational method, it overestimates the correct result by a mere 1.9%. It is significantly more accurate than 1st order perturbation theory because variational method takes into account the screening effect.