1

1) a) $V(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 + \frac{b}{24}x^4$ H.O.

$\hat{H}^{(0)} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$

$\hat{H}^{(1)} = \frac{1}{6}\gamma x^3 + \frac{b}{24}x^4$

$\psi^{(0)} = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$ $\alpha = \left(\frac{\mu k}{\hbar^2}\right)^{1/2}$

$E^{(0)} = (v+\frac{1}{2})\hbar\omega$, $v=0$

b) $V(x) = 0$ $0 \leq x < a/2$ P-1-B

$= b$ $\frac{a}{2} < x < a$

$\hat{H}^{(0)} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$

$\hat{H}^{(1)} = \begin{matrix} 0 & 0 \leq x < a/2 \\ b & a/2 \leq x < a \end{matrix}$

$\psi^{(0)} = \sqrt{\frac{2}{a}}\sin\frac{\pi x}{a}$, $E^{(0)} = \frac{h^2}{8ma^2}$

c) He atom (Born-Oppenheimer approx.)

$$\hat{H} = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

$$\hat{H}^{(1)} = \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$$\psi_s^{(0)} = \frac{Z^3}{\pi a_0^3} e^{-\frac{Zr_1}{a_0}} e^{-Zr_2/a_0}$$

$$E^{(0)} = -2 \cdot Z^2 \frac{m_e e^4}{8\varepsilon_0^2 h^2} = -8 \times (13 \cdot 6) = -108 \cdot 8 \text{ eV}$$

d) $$\hat{H}^{(0)} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

$$\hat{H}^{(1)} = eFr\cos\theta$$

$$\psi^{(0)} = \frac{1}{\pi^{1/2} a_0^{3/2}} e^{-r/a_0}$$

$$E^{(0)} = -13 \cdot 6 \text{ eV} = \left(\frac{m_e e^4}{8\varepsilon_0^2 h^2}\right)$$

e) $$\hat{H}^{(0)} = -\frac{\hbar^2}{2I}\nabla^2 \qquad \hat{H}^{(1)} = \mu F\cos\theta$$

$$\psi^{(0)} = 1/\sqrt{4\pi}$$

$$E^{(0)} = 0$$

2)

from 1 b) we know $\psi(x) = \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a}$ and

$$\hat{H}^{(1)} = \begin{cases} 0 & 0 \le x < a/2 \\ b & a/2 \le x < a \end{cases}$$

$$E^{(1)} = \int_0^a \psi(x)\, \hat{H}^{(1)}\, \psi(x)\, dx$$

$$= \int_0^{a/2} \frac{2}{a} \sin^2 \frac{\pi x}{a} (0)\, dx + \int_{a/2}^{a} \frac{2}{a} \sin^2 \frac{\pi x}{a} (b)\, dx$$

$$= 0 + \frac{b}{a} \int_{a/2}^{a} \left(1 - \cos \frac{2\pi x}{a}\right) dx$$

$$= 0 + \frac{b}{a} \left[x - \frac{\sin 2\pi x/a}{2\pi/a} \right]_{a/2}^{a}$$

$$= \frac{b}{a} \left[a - 0 - \frac{a}{2} + 0 \right] = \frac{b}{2}$$

3) for H.O. $V(x) = \frac{1}{2} kx^2$ and the G.S. wavefunction $\psi_0(x) = A e^{-\alpha x^2/2}$. Any other function would result in a higher energy. $\therefore$ $c = 0$ is necessary to ensure the functional form.

4) 3

④

$$\hat{H} = \frac{-\hbar^2}{2\mu r^2} \frac{d}{dr}\left(r^2 \frac{d}{dr}\right) + \frac{1}{2} k r^2$$

trial $\phi_1 = e^{-\alpha r^2}$ and $\phi_2 = e^{-\alpha r}$

Variational energy $\langle E \rangle = \dfrac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$

Integrate over $r^2 dr$ from 0 to ∞

Get $\langle E \rangle$ values and compare.

$e^{-\alpha r^2}$ is better ~~ea~~.

5) He atom (Born- Oppenheimer Approx.)

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{2e^2}{4\pi\varepsilon_0 r_2}$$

$$\hat{H}^{(1)} = \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$$\hat{H}^{(0)} = \hat{H}_1^{(0)} + \hat{H}_2^{(0)}$$ (sum of two hydrogenlike Hamiltonians)

∴ unperturbed system is a He atom

$$\phi^{(0)}(r_1\,\theta_1\,\phi_1\,r_2\,\theta_2\,\phi_2) = F(r_1\,\theta_1\,\phi_1)\,F(r_2\,\theta_2\,\phi_2)$$

$$E^{(0)} = E_1 + E_2$$ unperturbed energies.

$$\hat{H}_i^{0} F_i = E_i F_i \qquad i = 1, 2.$$

$$E^{(0)} = -Z^2\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)\frac{e^2}{8\pi\varepsilon_0 a_0}$$

for G.S. $E^{(0)} = -4 \times 2 \times 13.6 = -108.83$ eV

and

$$\phi_{1s^2}^{(0)} = \frac{1}{\sqrt{\pi}}\left(\frac{2}{a_0}\right)^{3/2} e^{-Zr_1/a_0} \cdot \frac{1}{\sqrt{\pi}}\left(\frac{2}{a_0}\right)^{3/2} e^{-Zr_2/a_0}$$

$$= 1s(1)\;1s(2)$$

$$E^{(1)} = \langle \psi^{(0)} | \hat{H}^{(1)} | \psi^{(0)} \rangle$$

$$= \frac{Z^6 e^2}{4\pi^3 \varepsilon_0 a_0^6} \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}\int_0^{\infty}\int_0^{\infty} e^{-2Zr_1/a_0}\, e^{-2Zr_2/a_0} \cdot \frac{1}{r_{12}} \cdot$$

$$r_1^2 \sin\theta_1\, r_2^2 \sin\theta_2\, dr_1\, dr_2\, d\theta_1\, d\theta_2\, d\phi_1\, d\phi_2$$

$$E^{(1)} = \frac{5Z}{8}\left(\frac{e'^2}{a_0}\right) \qquad e'^2 = \frac{e^2}{4\pi\varepsilon_0}$$

$$\frac{1}{2} e'^2/a_0 = 13.604 \text{ eV}$$

Using $Z = 2$, $E^{(1)} = \frac{10}{4}(13.604) = 34.01$ eV

$$E^{(0)} + E^{(1)} = -108.83 + 34.01 = -\cancel{78}\,74.82 \text{ e}$$

Experiment -79.01 eV

Pertubation -74.82 eV

Variation -77.48 eV

6) $$V(x) = D\left(1 - e^{-\beta x}\right)^2$$

$$e^{-\beta x} = 1 - \beta x + \frac{(\beta x)^2}{2!} - \frac{(\beta x)^3}{3!} + \cdots$$

$$\therefore V(x) = D\left(\beta x - \frac{\beta^2 x^2}{2} + \cdots\right)^2$$ dropping higher order terms $\because x$ i[s] small

$$= D\left(\beta^2 x^2 + \frac{\beta^4 x^4}{4} - \beta^3 x^3 + \cdots\right)$$

Anharmonic Oscillator

$$V(x) = \frac{1}{2} k x^2 + \frac{1}{6} \gamma x^3 + \frac{b}{24} x^4 + \cdots$$

$$\frac{1}{2} k = D\beta^2 \qquad \frac{1}{6}\gamma = D\beta^3 \qquad \frac{b}{24} = \frac{D\beta^4}{4} + \text{higher terms.}$$

7)

$$\phi = \sum_{n=1}^{2} C_n x^n (a-x)^n$$

$$= C_1 x (a-x) + C_2 (a-x)^2 x^2$$

$\hat{H} = -\hbar^2/2m \frac{d^2}{dx^2}$

Well behaved?

1) continuous

2) 1^{st} derivative is continuous

3) single valued

4) $=0$ at $x=0$, $x=a$

5) square integrable.

So, $\phi = C_1 f_1 + C_2 f_2$ where $f_1 = x(a-x)$; $f_2 = x^2(a-x)^2$

Use $a=1$ for convenience.

Secular determinant

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

Calculate the matrix elements $H_{ij} = \int_0^1 f_i \hat{H} f_j \, dx$; $S_{ij} = \int_0^1 f_i f_j \, dx$

$H_{11} = \frac{\hbar^2}{6m}$ $\quad H_{12} = H_{21} = \frac{\hbar^2}{30m}$ $\quad H_{22} = \frac{\hbar^2}{105m}$

$S_{11} = \frac{1}{30}$ $\quad S_{12} = S_{21} = \frac{1}{140}$ $\quad S_{22} = 1/630$

$$\begin{vmatrix} \frac{1}{6} - \frac{E'}{30} & \frac{1}{30} - \frac{E'}{140} \\ \frac{1}{30} - E'/140 & 1/105 - E'/630 \end{vmatrix} = 0, \quad E' = Em/\hbar^2$$

$\Rightarrow E'^2 - 56E' + 252 = 0$

$$E' = \frac{56 \pm \sqrt{2128}}{2} = 51.065 \text{ and } 4.93487$$

$$E_{min} = 4.93487 \frac{\hbar^2}{m} = 0.125002 \frac{h^2}{m}$$

compared with $E_{exact} = \frac{h^2}{8m} = 0.125000 \frac{h^2}{m}$

$(a=1)$

Excellent agreement.

$E_{min} > E_{exact}$ (variational theorem)

8) a) Hermitian $\int \psi^* \hat{A} \psi \, d\tau = \int \psi \hat{A}^* \psi^* \, d\tau$

$\hat{S}_+$

LHS $= \int \psi^* (\hat{S}_x + i\hat{S}_y) \psi \, d\tau = \int \psi^* \hat{S}_x \psi \, d\tau + i \int \psi^* \hat{S}_y \psi \, d\tau$

RHS $= \int \psi (\hat{S}_x + i\hat{S}_y)^* \psi^* \, d\tau = \int \psi (\hat{S}_x - i\hat{S}_y) \psi^* \, d\tau$

$= \int \psi \hat{S}_x \psi^* \, d\tau - i \int \psi \hat{S}_y \psi^* \, d\tau$

LHS $\neq$ RHS $\therefore$ non-Hermitian.

Likewise for $\hat{S}_-$

b) $[\hat{S}_z, \hat{S}_+] f = [\hat{S}_z \hat{S}_+ - \hat{S}_+ \hat{S}_z] f$

$= \hat{S}_z (\hat{S}_x + i\hat{S}_y) f - (\hat{S}_x + i\hat{S}_y) \hat{S}_z f$

$= \hat{S}_z \hat{S}_x f + i \hat{S}_z \hat{S}_y f - \hat{S}_x \hat{S}_z f - i \hat{S}_y \hat{S}_z f$

$= [\hat{S}_z, \hat{S}_x] f + i [\hat{S}_z, \hat{S}_y] f$

$= (i\hbar \hat{S}_y + \hbar \hat{S}_x) f = \hbar (\hat{S}_x + i\hat{S}_y) = \hbar \hat{S}_+$

Similarly prove for $\hat{S}_-$

c) $\hat{S}_+ \hat{S}_- = (\hat{S}_x + i\hat{S}_y)(\hat{S}_x - i\hat{S}_y) = \hat{S}_x^2 - i \hat{S}_x \hat{S}_y + i \hat{S}_y \hat{S}_x + \hat{S}_y^2$

$= \hat{S}_x^2 + \hat{S}_y^2 - i (i\hbar \hat{S}_z) = \hat{S}^2 - \hat{S}_z^2 + \hbar \hat{S}_z$

Similarly for $\hat{S}_- \hat{S}_+$

8) d) $\hat{S}_+$ raises the spin

$\hat{S}_-$ lowers the spin

$\alpha \equiv +1/2 \qquad \beta \equiv -1/2$ - only two values for

$\hat{S}_+ |\beta\rangle = \hbar |\alpha\rangle$ from $-1/2$ to $+1/2$

$\hat{S}_- |\alpha\rangle = \hbar |\beta\rangle$ from $+1/2$ to $-1/2$

other operations yield 0.

9) $$\hat{S}_{z,\text{total}} = \sum_{j=1}^{3} \hat{S}_{z,j} = \hat{S}_{z,1} + \hat{S}_{z,2} + \hat{S}_{z,3}$$

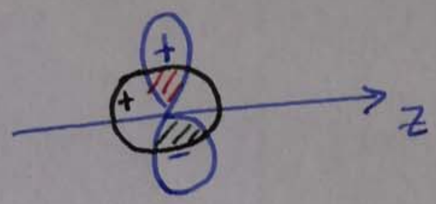
operate on ψ ; $\hat{S}_{z,\text{total}}\psi = \hat{S}_{z,1}\psi + \hat{S}_{z,2}\psi + \hat{S}_{z,3}\psi$

$$\hat{S}_{z,1}\psi = \frac{1}{\sqrt{3!}} \begin{vmatrix} \frac{\hbar}{2}\, 1s\alpha(1) & -\frac{\hbar}{2}\, 1s\beta(1) & 2s\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\alpha(3) \end{vmatrix}$$

$$= \frac{\hbar}{2} \cdot \frac{1}{\sqrt{6}} \begin{vmatrix} 1s\alpha(1) & -1s\beta(1) & 2s\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\alpha(3) \end{vmatrix}$$

Likewise get for $\hat{S}_{z,2}\psi$ and $\hat{S}_{z,3}\psi$ and sum up to get $\frac{\hbar}{2} \cdot \cancel{\frac{2}{\sqrt{6}}}\, \psi$ which is $\hat{S}_{z,\text{total}}\psi$

$\therefore$ ψ is an eigenfunction of $\hat{S}_{z,\text{total}}$

10) 

the +ve and negative overlaps cancel.

Net overlap = 0.