NO.

DATE

the closure approximation

$$E_0^{(2)} \approx H_{00}^{(2)} - \frac{1}{\Delta E}\sum_{n\neq 0} H_{0n}^{(1)}H_{n0}^{(1)} = H_{00}^{(2)} - \frac{1}{\Delta E}\sum_n H_{0n}^{(1)}H_{n0}^{(1)} + \frac{1}{\Delta E}H_{00}^{(1)}H_{00}^{(1)}$$

$$\approx H_{00}^{(2)} - \frac{1}{\Delta E}\underbrace{(H^{(1)}H^{(1)})_{00}}_{\sum_n A_{rn}B_{nc} = (AB)_{rc}} + \frac{1}{\Delta E}H_{00}^{(1)}H_{00}^{(1)}$$

$$\approx H_{00}^{(2)} - \frac{\varepsilon^2}{\Delta E} \quad \varepsilon^2 = \langle 0|H^{(1)}H^{(1)}|0\rangle - \langle 0|H^{(1)}|0\rangle^2$$

Perturbation for degenerate states

suppose that the energy level of interest in the system is d-fold degenerate

the states corresponding to the energy $E_n^{(0)}$ are $|n,l\rangle$ $l = 1,2,\cdots;d = n$

$$H^{(0)}|n,l\rangle = E^{(0)}|n,l\rangle \qquad \phi_n^{(0)} = \sum_{i=1}^{r} c_i\psi_i^{(0)} \text{ are solutions}$$

$$\left.\begin{aligned} \psi_n &= \phi_n^{(0)} + \lambda\psi_n^{(1)} + \cdots \\ E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \cdots \end{aligned}\right\} \text{ substitution of these into } H\psi_i = E_i\psi_i \text{ and collect } \lambda$$

$$H^{(0)}\psi_{0,i}^{(0)} = E_0^{(0)}\psi_{0,i}^{(0)}$$

$$[H^{(0)} - E_d^{(0)}]\underline{\psi_n^{(1)}} = [E_n^{(1)} - H']\psi_n^{(0)} \quad \times\psi_m^{(0)}$$

$$= \sum_l c_l\psi_{0,l}^{(0)} + \sum_{n\neq 0} c_n\psi_n^{(0)}$$

$$\underline{\langle\psi_m^{(0)}|\hat{H}^{0}|\psi_n^{(1)}\rangle - E_d^{(0)}\langle\psi_m^{(0)}|\psi_n^{(1)}\rangle} = E_n^{(1)}\langle\psi_m^{(0)}|\phi_n^{(0)}\rangle - \langle\psi_m^{(0)}|\hat{H}'|\phi_n^{(0)}\rangle$$

$$= E_m^{(0)}\langle\psi_m^{(0)}|\psi_n^{(1)}\rangle = E_d^{(0)}\langle\psi_m^{(0)}|\psi_n^{(1)}\rangle$$

$$\Rightarrow \langle\psi_m^{(0)}|\hat{H}'|\phi_n^{(0)}\rangle - E_n^{(1)}\langle\psi_m^{(0)}|\phi_n^{(0)}\rangle = 0, \quad m = 1,2\ldots d$$

$$\sum_{i=1}^{d} c_i\langle\psi_m^{(0)}|\hat{H}'|\psi_i^{(0)}\rangle - E_n^{(1)}\langle\psi_m^{(0)}|\psi_i^{(0)}\rangle = 0$$

$$\sum_{i=1}^{d} c_i\langle\psi_m^{(0)}|\hat{H}'|\psi_i^{(0)}\rangle - E_n^{(1)}\sum_{i=1}^{d} c_i\langle\psi_m^{(0)}|\psi_i^{(0)}\rangle = 0, \quad \sum_{i=1}^{d}\left[\langle\psi_m^{(0)}|\hat{H}'|\psi_i^{(0)}\rangle - E_n^{(1)}\delta_{mi}\right]c_i = 0$$

$$\Rightarrow \left.\begin{aligned} &(H'_{11} - E_n^{(1)})c_1 + H'_{12}c_2 + \cdots + H'_{1d}c_d = 0 \\ &H'_{21}c_1 + (H'_{22} - E_n^{(1)})c_2 + \cdots + H'_{2d}c_d = 0 \\ &\qquad\vdots \\ &H'_{d1}c_1 + H'_{d2}c_2 + \cdots + (H'_{dd} - E_n^{(1)})c_d = 0 \end{aligned}\right\} \text{ d linear. homogeneous eq.}$$

$$\det\left[\langle\psi_m^{(0)}|\hat{H}'|\psi_i^{(0)}\rangle - E_n^{(1)}\delta_{mi}\right] = 0$$

Ex: double degenerate pair of orthonormal states, first order

$$\begin{vmatrix} H_{11}^{(1)} - E_0^{(1)} & H_{12}^{(1)} \\ H_{21}^{(1)} & H_{22}^{(1)} - E_0^{(1)} \end{vmatrix} = 0, \quad E_0^{(1)2} - (H_{11}^{(1)} + H_{22}^{(1)})E_0^{(1)} + (H_{11}^{(1)}H_{22}^{(1)} - H_{12}^{(1)}H_{21}^{(1)}) = 0$$

$$E_0^{(1)} = \frac{1}{2}(H_{11}^{(1)} + H_{22}^{(1)}) \pm \frac{1}{2}\sqrt{(H_{11}^{(1)} + H_{22}^{(1)})^2 - 4(H_{11}^{(1)}H_{22}^{(1)} - H_{12}^{(1)}H_{21}^{(1)})}$$

Ex: Stark effect for H atom

without pertub. $n=2$, $E_2^{(0)} = -\frac{13.6}{2^2}\,eV = -3.4\,eV$

$d=4$. $|200\rangle$ $|211\rangle$ $|210\rangle$ $|21,-1\rangle$, $|n\ell m\rangle = \psi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r)\,Y_\ell^m(\theta,\varphi)$

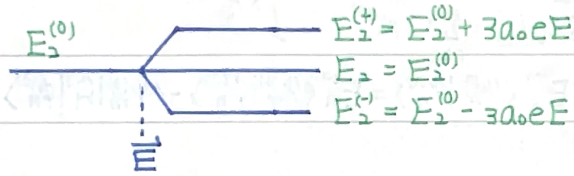
$\lambda \hat{H}' = eEr\cos\theta$

$$0 = \begin{vmatrix} \langle 200|\lambda\hat{H}'|200\rangle - \lambda E_2^{(1)} & \langle 200|\lambda\hat{H}'|211\rangle & \langle 200|\lambda\hat{H}'|210\rangle & \langle 200|\lambda\hat{H}'|21,-1\rangle \\ \langle 211|\lambda\hat{H}'|200\rangle & \langle 211|\lambda\hat{H}'|211\rangle - \lambda E_2^{(1)} & \langle 211|\lambda\hat{H}'|210\rangle & \langle 211|\lambda\hat{H}'\cdots\rangle \\ \langle 210|\lambda\hat{H}'|200\rangle & \langle 210|\lambda\hat{H}'|211\rangle & \langle 210|\lambda\hat{H}'|210\rangle - \lambda E_2^{(1)} & \langle 210|\lambda\hat{H}'\cdots\rangle \\ \langle 21,-1|\lambda\hat{H}'|200\rangle & \langle 21,-1|\lambda\hat{H}'|211\rangle & \langle 21,-1|\lambda\hat{H}'|210\rangle & \langle 21,-1|\lambda\hat{H}'|21,-1\rangle - \end{vmatrix}$$

$$\cos\theta\, Y_\ell^m = \sqrt{\frac{(\ell+1)^2-m^2}{(2\ell+1)(2\ell+3)}}\,Y_{\ell+1}^m + \sqrt{\frac{\ell^2-m^2}{(2\ell-1)(2\ell+1)}}\,Y_{\ell-1}^m$$

$$\Rightarrow \begin{vmatrix} -\lambda E_2^{(1)} & 0 & -3a_0eE & 0 \\ 0 & -\lambda E_2^{(1)} & 0 & 0 \\ -3a_0eE & 0 & -\lambda E_2^{(1)} & 0 \\ 0 & 0 & 0 & -\lambda E_2^{(1)} \end{vmatrix} = 0$$

$\Rightarrow$ 4 solutions: $\lambda E_2^{(1)} = 0, 0, 3a_0eE, -3a_0eE$



$|\psi_2^{(0)}\rangle = a\,|200\rangle + b\,|211\rangle + c\,|210\rangle + d\,|21,-1\rangle$

$$\begin{bmatrix} -\lambda E_2^{(1)} & 0 & -3a_0eE & 0 \\ 0 & -\lambda E_2^{(1)} & 0 & 0 \\ -3a_0eE & 0 & -\lambda E_2^{(1)} & 0 \\ 0 & 0 & 0 & -\lambda E_2^{(1)} \end{bmatrix} \begin{bmatrix} a \\ b \\ c \\ d \end{bmatrix} = 0$$

when $\lambda E_2^{(1)} = 3a_0eE$, $a+c=0$, $b=d=0$ $\quad |\psi_2^{(0)}\rangle = \frac{1}{\sqrt{2}}(|200\rangle - |21,-1\rangle)$

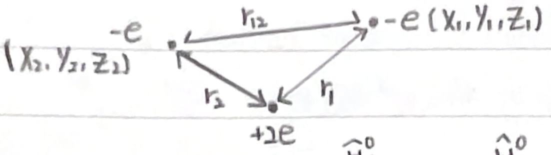
$\lambda E_2^{(1)} = -3a_0eE$ $\quad a-c=0$, $b=d=0$ $\quad |\psi_2^{(0)}\rangle = \frac{1}{\sqrt{2}}(|200\rangle + |21,-1\rangle)$

$\lambda E_2^{(1)} = 0$ $\quad a=c=0$, $b=d=\mathbb{R}$ $\quad |\psi_2^{(0)}\rangle = |211\rangle$ or $|21,-1\rangle$

NO.

DATE

Perturbation treatment of He ground state



$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2}}_{\hat{H}^0} + \underbrace{\frac{e^2}{4\pi\varepsilon_0 r_{12}}}_{\hat{H}'}$$

$\hat{H}_1^0$ $\hat{H}_2^0$

$$\psi^0(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) = F_1(r_1, \theta_1, \phi_1) F_2(r_2, \theta_2, \phi_2)$$

unperturbed $E^{(0)} = E_1 + E_2$ $\qquad E_1 = -\frac{Z^2}{n_1^2}\frac{e^2}{8\pi\varepsilon_0 a_0}$

$\boxed{\hat{H}_1^0} F_1 = E_1 F_1$ $\qquad E_2 = -\frac{Z^2}{n_2^2}\frac{e^2}{8\pi\varepsilon_0 a_0}$

$\boxed{\hat{H}_2^0} F_2 = E_2 F_2$ hydrogenlike Hamiltonians $\qquad E^{(0)} = -Z^2\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)\frac{e^2}{8\pi\varepsilon_0 a_0}$

$$\psi^{(0)}_{1s^2} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Z\frac{r_1}{a_0}} \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Z\frac{r_2}{a_0}}$$

$$= 1s(1)1s(2)$$

$E^{(0)}_{1s^2} = -Z^2\, 2\, \frac{e^2}{8\pi\varepsilon_0 a_0} = -108.83\text{ eV}$ error 38% (experiment -79.00eV)

$$E^{(1)} = \langle \psi^{(0)} | \hat{H}' | \psi^{(0)} \rangle = \frac{Z^6 e^2}{4\pi\varepsilon_0 \pi^2 a_0^6} \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}\int_0^{\infty}\int_0^{\infty} e^{-\frac{2Zr_1}{a_0}} e^{-\frac{2Zr_2}{a_0}} \frac{1}{r_{12}} r_1^2 \sin\theta_1\, r_2^2 \sin\theta_2\, dr_1 dr_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2$$

$$= \frac{5Z}{8}\frac{e^2}{4\pi\varepsilon_0 a_0} = 34.01\text{ eV}$$

$\Rightarrow E^{(0)} + E^{(1)} = -108.83 + 34.01 = -74.82$ error 5.3%

$E \approx -108.83 + 34.01 - 4.29 + 0.12 = -78.99\text{eV}$

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DATE / /

Variation treatment of the ground state of He

if we use the zeroth-order perturbation ground state wave function $\psi_g^{(0)}$

$$\langle\phi|\hat{H}|\phi\rangle = \langle\psi_g^{(0)}|\hat{H}^0+\hat{H}'|\psi_g^{(0)}\rangle = \langle\psi_g^{(0)}|\hat{H}^0\psi_g^{(0)}+\hat{H}'\psi_g^{(0)}\rangle = \langle\psi_g^{(0)}|E_g^{(0)}\psi_g^{(0)}\rangle+\langle\psi_g^{(0)}|\hat{H}'\psi_g^{(0)}\rangle$$

$$= E_g^{(0)}+\underline{E_g^{(1)}} \quad ⑤$$

use $\psi_g^{(0)}$ as trial function, get the first order perturbation result -74.82 eV

to improve on this result, we try the normalized function

$$\phi = \frac{1}{\pi}\left(\frac{\alpha}{a_0}\right)^3 e^{-\alpha\frac{r_1}{a_0}} e^{-\alpha\frac{r_2}{a_0}}$$

$$\hat{H} = \underbrace{\left[-\frac{\hbar^2}{2m_e}\nabla_1^2-\frac{\alpha e^2}{4\pi\varepsilon_0 r_1}-\frac{\hbar^2}{2m_e}\nabla_2^2-\frac{\alpha e^2}{4\pi\varepsilon_0 r_2}\right]}_{\text{sum of two hydrogenlike Hamiltonians for nuclear charge } \alpha}+(\alpha-Z)\frac{e^2}{4\pi\varepsilon_0 r_1}+(\alpha-Z)\frac{e^2}{4\pi\varepsilon_0 r_2}+\frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$$\left(-\frac{\hbar^2}{2m_e}\nabla_1^2-\frac{\alpha e^2}{4\pi\varepsilon_0 r_1}-\frac{\hbar^2}{2m_e}\nabla_2^2-\frac{\alpha e^2}{4\pi\varepsilon_0 r_2}\right)\phi = -\alpha^2 2\frac{e^2}{8\pi\varepsilon_0 a_0}\phi \ ?$$

$$\int\phi^*\hat{H}\phi\,d\tau = -\frac{\alpha^2e^2}{4\pi\varepsilon_0 a_0}\int\phi^*\phi\,d\tau+\frac{(\alpha-Z)e^2}{4\pi\varepsilon_0}\int\frac{\phi^*\phi}{r_1}d\tau-\frac{(\alpha-Z)e^2}{4\pi\varepsilon_0}\int\frac{\phi^*\phi}{r_2}d\tau+\frac{e^2}{4\pi\varepsilon_0}\int\frac{\phi^*\phi}{r_{12}}d\tau$$

let $\phi = f_1f_2$ $\quad f_1=\frac{1}{\sqrt{\pi}}\left(\frac{\alpha}{a_0}\right)^{\frac{3}{2}}e^{-\alpha\frac{r_1}{a_0}}$ $\quad f_2=\frac{1}{\sqrt{\pi}}\left(\frac{\alpha}{a_0}\right)^{\frac{3}{2}}e^{-\alpha\frac{r_2}{a_0}}$

$$\int\phi^*\phi\,d\tau=\iint f_1^*f_2^*f_1f_2\,d\tau_1d\tau_2=\int f_1^*f_1d\tau_1\int f_2^*f_2d\tau_2=1$$

$$\int\frac{\phi^*\phi}{r_1}d\tau=\int\frac{f_1^*f_1}{r_1}d\tau_1\int f_2^*f_2d\tau_2=\int\frac{f_1^*f_1}{r_1}d\tau_1$$

$$=\frac{1}{\pi}\frac{\alpha^3}{a_0^3}\int_0^\infty e^{-2\alpha\frac{r_1}{a_0}}\frac{r_1^2}{r_1}dr_1\int_0^\pi\sin\theta_1\,d\theta_1\int_0^{2\pi}d\phi_1=\frac{\alpha}{a_0}$$

$$\int\frac{\phi^*\phi}{r_2}d\tau=\frac{\alpha}{a_0}$$

$$\frac{e^2}{4\pi\varepsilon_0}\int\frac{\phi^*\phi}{r_{12}}d\tau=\frac{5\alpha e^2}{32\pi\varepsilon_0 a_0}$$

$$\Rightarrow\int\phi^*\hat{H}\phi\,d\tau=\left(\alpha^2-2Z\alpha+\frac{5}{8}\alpha\right)\frac{e^2}{4\pi\varepsilon_0 a_0}=-\left(Z-\frac{5}{16}\right)^2\frac{e^2}{4\pi\varepsilon_0 a_0}=-77.48\text{ eV} \quad \text{error } 1.9\%$$

$$\frac{\partial}{\partial\alpha}\int\phi^*\hat{H}\phi\,d\tau=0\Rightarrow\alpha=Z-\frac{5}{16}$$

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