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QM 115B Lec. 15

Helium (2nd attempt)

$$H_0 = \sum_{i=1}^{2} \left(\frac{-\hbar^2 \vec{\nabla}_i^2}{2\mu} - \hbar c \frac{2\alpha}{r_i} \right), \quad H' = \frac{\hbar c \alpha}{|\vec{r}_1 - \vec{r}_2|}$$

recall: $\psi_{11}^0 = \psi_{100}(\vec{r}_1)\, \psi_{100}(\vec{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}$

$$E_{11}' = \left\langle \psi_{11}^0 \right| \frac{\hbar c \alpha}{|\vec{r}_1 - \vec{r}_2|} \left| \psi_{11}^0 \right\rangle$$

Prob 5.11 $\quad \left\langle \psi_{11}^0 \right| \frac{1}{|\vec{r}_1 - \vec{r}_2|} \left| \psi_{11}^0 \right\rangle = \frac{5}{4a}$

$$E_{11}' = \hbar c \alpha \frac{5}{4a} = \hbar c \alpha \frac{5}{4} \left(\frac{\alpha \mu c}{\hbar} \right)$$

$$= \frac{5}{4} \alpha^2 \mu c^2 = -\frac{5}{2} E_1 = \frac{-5}{2} (-13.6\, eV)$$

$$= 34\, eV$$

$$E_{11} \simeq E_{11}^0 + E_{11}' = -109\, eV + 34\, eV = -75\, eV$$

exp. : $\quad E_{11} = -79\, eV$

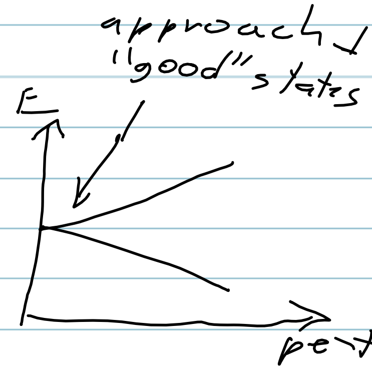
Degenerate Perturbation Theory

Two-fold degeneracy

$$H^0 \psi_a^0 = E^0 \psi_a^0$$
$$H^0 \psi_b^0 = E^0 \psi_b^0 \qquad \langle \psi_a | \psi_b \rangle = 0$$

general state: $\psi^0 = \alpha \psi_a^0 + \beta \psi_b^0$

$$H^0 \psi^0 = E^0 \psi^0$$



pert. H' breaks degeneracy

first order: $H^0 \psi' + H' \psi^0 = E^0 \psi' + E' \psi^0$

inner product with ψ_a^0

$$\langle \psi_a^0 | H^0 \psi' \rangle + \langle \psi_a^0 | H' \psi^0 \rangle = E^0 \langle \psi_a^0 | \psi' \rangle + E' \langle \psi_a^0 | \psi^0 \rangle$$

$$\langle \psi_a^0 | H' | \psi^0 \rangle = E' \langle \psi_a^0 | \psi^0 \rangle$$

$$\alpha \langle \psi_a^0 | H' | \psi_a^0 \rangle + \beta \langle \psi_a^0 | H' | \psi_b^0 \rangle = \alpha E'$$

$$W_{ij} \equiv \langle \psi_i^0 | H' | \psi_j^0 \rangle$$

$$\alpha W_{aa} + \beta W_{ab} = \alpha E' \qquad (*)$$

inner prod. with ψ_b^0

$$\alpha W_{ba} + \beta W_{bb} = \beta E'$$

$$\alpha W_{ab} W_{ba} + \beta W_{ab} W_{bb} = \beta W_{ab} E'$$

$$\alpha W_{ab} W_{ba} + \beta W_{ab} (W_{bb} - E') = 0$$

$$\beta W_{ab} = \alpha E' - \alpha W_{aa} \qquad \text{from } (*)$$

$$\cancel{\alpha} W_{ba} W_{ab} + (\cancel{\alpha} E' - \cancel{\alpha} W_{aa})(W_{bb} - E') = 0$$

$(\alpha \neq 0)$

$$E'^2 - (W_{bb} + W_{aa}) E' + W_{aa} W_{bb} - W_{ba} W_{ab} = 0$$

$$E'_\pm = \frac{1}{2}\left(W_{bb} + W_{aa} \pm \sqrt{(W_{aa} + W_{bb})^2 - 4(W_{aa} W_{bb} - |W_{ab}|^2)} \right)$$

$$= \frac{1}{2}\left(W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2} \right)$$

if $\alpha = 0$ then $\beta = 1$ $\quad W_{ab} = 0$ $\quad$ from $(*)$

$$E' = W_{bb}$$

cf $E'_\pm = \frac{1}{2}\left(W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2} \right)$

$$= \frac{1}{2}\left(W_{aa} + W_{bb} \pm (W_{aa} - W_{bb}) \right)$$

$$E'_+ = W_{aa} = \langle \psi_a^0 | H' | \psi_a^0 \rangle$$

$$E_- = W_{bb} = \langle \psi_b^0 | H' | \psi_b^0 \rangle$$

in this case ψ_a^0 and ψ_b^0 were already the "good" states "good" states are $\perp$

$$\langle \beta^* \psi_a^0 - \alpha^* \psi_b^0 | \alpha \psi_a^0 + \beta \psi_b^0 \rangle = \beta\alpha - \alpha\beta = 0$$

matrix elements

$$\langle \beta^* \psi_a^0 - \alpha^* \psi_b^0 | H' | \alpha \psi_a^0 + \beta \psi_b^0 \rangle$$

$$= \beta\alpha W_{aa} + \beta^2 W_{ab} - \alpha^2 W_{ba} - \alpha\beta W_{bb}$$

$$\left(\begin{array}{l} \alpha W_{aa} = \alpha E' - \beta W_{ab} \\ \beta W_{bb} = \beta E' - \alpha W_{ba} \end{array} \right|$$

$$= \beta(\alpha E' - \beta W_{ab}) + \beta^2 W_{ab} - \alpha^2 W_{ba} - \alpha(\beta E' - \alpha W_{ba})$$

$$= E'(\beta\alpha - \alpha\beta) + \beta^2(W_{ab} - W_{ab}) + \alpha^2(-W_{ba} + W_{\cdot})$$

$$= 0$$

"good" states diagonalize the perturbation Hamiltonian

Short-cut

find Hermitian operator $A = A^{+}$

such that $[A, H^{0}] = 0 \quad [A, H'] = 0$

if ψ_a^{0} and ψ_b^{0} have H^{0} eigenvalue E^{0}
and distinct A eigenvalues

$$A\psi_a^{0} = \mu \psi_a^{0} \,, \quad A\psi_b^{0} = \nu \psi_b^{0} \qquad \mu \neq \nu$$

then $W_{ab} = \langle \psi_a^{0} | H' | \psi_b^{0} \rangle = 0$

Proof: $0 = \langle \psi_a^{0} | [A, H'] | \psi_b^{0} \rangle$

$$= \langle \psi_a^{0} | AH' | \psi_b^{0} \rangle - \langle \psi_a^{0} | H'A | \psi_b^{0} \rangle$$

$$= \langle A\psi_a^{0} | H' | \psi_b^{0} \rangle - \langle \psi_a^{0} | H' | A\psi_b^{0} \rangle$$

$$= \mu \langle \psi_a^{0} | H' | \psi_b^{0} \rangle - \nu \langle \psi_a^{0} | H' | \psi_b^{0} \rangle$$

$$0 = (\mu - \nu) W_{ab}$$

$$W_{ab} = 0$$

find an observable A

then use non-degenerate perturbation theory