

136

QM 115B Lec. 15

Helium (2nd attempt)

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

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

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

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

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

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

$$= 34 \text{ eV}$$

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

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

(57)

Degenerate Perturbation Theory

Two-fold degeneracy

$$H^0 \psi_a^0 = E^0 \psi_a^0$$

$$H^0 \psi_b^0 = E^0 \psi_b^0$$

$$\langle \psi_a | \psi_b \rangle = 0$$

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: $H^0 \psi' + H' \psi^0 = E^0 \psi' + E^1 \psi^0$
inner product with ψ_a^0

$$\langle \psi_a^0 | H^0 \psi' \rangle + \langle \psi_a^0 | H' \psi^0 \rangle = E^0 \langle \psi_a^0 | \psi' \rangle + E^1 \langle \psi_a^0 | \psi^0 \rangle$$

$$\langle \psi_a^0 | H' | \psi^0 \rangle = E^1 \langle \psi_a^0 | \psi^0 \rangle$$
$$\alpha \langle \psi_a^0 | H' | \psi_a^0 \rangle + \beta \langle \psi_a^0 | H' | \psi_b^0 \rangle = \alpha E^1$$

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

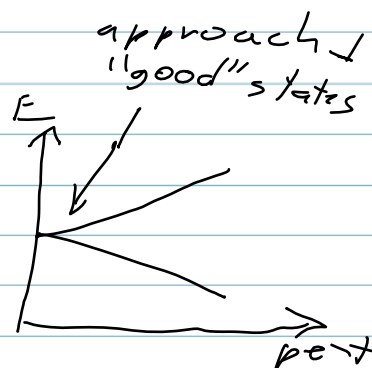
$$\alpha W_{aa} + \beta W_{ab} = \alpha E^1 \quad (*)$$

inner prod. with ψ_b^0

$$\alpha W_{ba} + \beta W_{bb} = \beta E^1$$

$$\alpha W_{ab} W_{ba} + \beta W_{ab} W_{bb} = \beta W_{ab} E^1$$

$$\alpha W_{ab} W_{ba} + \beta W_{ab} (W_{bb} - E^1) = 0$$



(58)

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

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

($\alpha \neq 0$)

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

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

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

$$E' = W_{bb}$$

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

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

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

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

in this case ψ_a^0 and ψ_b^0 were already the "good" states

(59)

"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

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

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

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

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

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

$$= 0$$

"good" states diagonalize the
perturbation Hamiltonian

(60)

Short-cut
find Hermitian operator $A = A^\dagger$

such that $[A, H^0] = 0$ $[A, H'] = 0$

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

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

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

$$\begin{aligned} \text{Proof: } 0 &= \langle \psi_a^0 | [A, H'] | \psi_b^0 \rangle \\ &= \langle \psi_a^0 | AH' | \psi_b^0 \rangle - \langle \psi_a^0 | H'A | \psi_b^0 \rangle \\ &= \langle A\psi_a^0 | H' | \psi_b^0 \rangle - \langle \psi_a^0 | H' | A\psi_b^0 \rangle \\ &= \mu \langle \psi_a^0 | H' | \psi_b^0 \rangle - \nu \langle \psi_a^0 | H' | \psi_b^0 \rangle \end{aligned}$$

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

$$W_{ab} = 0$$

find an observable A

then use non-degenerate perturbation theory