Ph 585
AMO

Lecture # 16

The ground & excited states of two-electron atoms

$$H = -\frac{\hbar^2}{2m}\vec{\nabla}^2_{r_1} - \frac{\hbar^2}{2m}\vec{\nabla}^2_{r_2} - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

1) Independent particle approx. $H = H_1 + H_2 + \underbrace{H_{12}}_{\text{perturbation}}$

$$\underset{\text{ground state}}{E_0} = \underbrace{E_0^{(0)}}_{E_1+E_2} + E_0^{(1)} = -Z^2 + \frac{5}{8}Z \ \text{a.u.}$$

$E_{He^+} = -2\,\text{a.u.}$ $\quad 1\,\text{a.u.} = \frac{e^2}{4\pi\varepsilon_0 a_0}$

$\Leftarrow E_{H} = -\frac{Z^2 E_I}{n^2} = -\frac{1}{2}Z^2\,\text{a.u.}$

For He $\Rightarrow E_0^{(0)} = -4\,\text{a.u.}$

exact: $-2.904\,\text{a.u.}$

$$E_0^{(0)} + E_0^{(1)} = -2.75\,\text{a.u.}$$

2) Variational principle (method) $\Rightarrow$ choose $\varphi_{(\alpha,\beta,\dots)} \leftarrow$ trial function (the best guess you can make)

with variational parameters

$$E[\varphi] = \frac{\langle \varphi | H | \varphi \rangle}{\langle \varphi | \varphi \rangle} \Rightarrow \delta E = 0 \Rightarrow \underline{\underline{E[\varphi(\alpha_0,\beta_0)]}}$$

$\frac{\partial E}{\partial \alpha}\Big|_{\alpha_0}, \frac{\partial E}{\partial \beta}, \dots = 0$

derivatives with respect to variational parameters

$\Downarrow$

get an estimate for ground-state energy

For He $\Rightarrow$

$$\varphi = \frac{1}{\pi a_0^3} Z_e^3\, e^{-\frac{Z_e}{a_0}(r_1+r_2)}$$

Z_e: variational parameter $\Leftarrow$ effective charge

$E[\Psi] = Z_e^2 - 2ZZ_e + \frac{5}{8}Z_e$ (in a.u.) $\Rightarrow$ ②

work through p. 330 of BsJ; from kinetic energies; from $\frac{1}{r_{12}}$ term

$$\frac{\partial E}{\partial Z_e} = 2Z_e - 2Z + \frac{5}{8} = 0 \Rightarrow Z_e = Z - \frac{5}{16} \Rightarrow$$

$$E\left(Z_e = Z - \frac{5}{16}\right) = -\left(Z - \frac{5}{16}\right)^2 \text{ a.u.} \leftarrow -2.848 \text{ a.u.}$$

much closer to exact!

Note; If $Z_e = Z \Rightarrow$ get the same E as with 1st-order perturbation theory $E = E_0^{(0)} + E_0^{(1)}$

What about excited states? $\Rightarrow$

Consider "genuinely discrete" states $\Rightarrow \overbrace{1s}^{\text{electron 1}} + \overbrace{nlm}^{2}$

$H = \underbrace{H_1 + H_2}_{H_0} + H_{12}$

$H_{12} = \frac{e^2}{(4\pi\varepsilon_0)r_{12}} \leftarrow$ treat as perturbation

$H_0 \Psi_\pm^{(0)} = E_0^{(0)} \Psi_\pm^{(0)}$

unperturbed states

$E_{1s} + E_n$

In principle, $\Psi_\pm^{(0)} \leftarrow$ exchange degeneracy; also $\overbrace{E_0^{(0)}}$ is l- & m-degenerate

So, would need degenerate perturbation theory $\Rightarrow$

$\langle \Psi^{(0)} | H_{12} | \Psi^{(0)} \rangle$ - find matrix elements

$$\frac{1}{\sqrt{2}}\left(\Psi_{1s}(\vec{r}_1)\Psi_{nlm}(\vec{r}_2) \pm \Psi_{1s}(\vec{r}_2)\Psi_{nlm}(\vec{r}_1)\right) \cdot \chi_{A/S}$$

But $\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{r_<^{l}}{r_>^{l+1}} P_l(\cos\theta) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \cdot$

larger of r_1 & r_2 App. 4

$$\cdot \frac{r_<^{l}}{r_>^{l+1}} Y_{lm}^{*}(\theta_1, \varphi_1) Y_{lm}(\theta_2, \varphi_2)$$

Clearly, $\frac{1}{r_{12}}$ won't affect exchange $\Rightarrow \langle \Psi_{\mp}^{(0)} | \frac{1}{r_{12}} | \Psi_{\pm}^{(0)} \rangle = 0$

What about $\langle \Psi^{(0)}_{1s,nl'm'} | \frac{1}{r_{12}} | \Psi^{(0)}_{1s,nlm} \rangle$? $\Rightarrow$

get terms like $\int \psi^{*}_{nl'm'}(\vec{r}_2) \underbrace{\psi^{*}_{1s}(\vec{r}_1)}_{\Rightarrow Y_{00}(\theta_1,\varphi_1)} Y^{*}_{l''m''}(\theta_1, \varphi_1) \cdot$

$$\cdot Y_{l''m''}(\theta_2, \varphi_2) \underbrace{\psi_{1s}(\vec{r}_2)}_{\Rightarrow Y_{00}(\theta_2,\varphi_2)} \psi_{nlm}(\vec{r}_1)\, d\Omega_1\, d\Omega_2 \sim$$

$$\sim \int Y^{*}_{l'm'}(\theta_2, \varphi_2) Y_{l''m''}(\theta_2, \varphi_2)\, d\Omega_2 \int Y^{*}_{l''m''}(\theta_1, \varphi_1) \cdot$$

$$\cdot Y_{lm}(\theta_1, \varphi_1)\, d\Omega_1 = \delta_{l'l''} \delta_{m'm''} \delta_{l''l} \delta_{m''m} \Rightarrow$$

So, all cross terms cancel $\Rightarrow$

use non-degenerate perturbation theory $\Rightarrow$ $m = m' = m''$, $l = l' = l''$

$$E_{\pm}^{(1)} = \left\langle \Psi_{\pm}^{(0)} \right| \frac{e^2}{4\pi\varepsilon_0 r_{12}} \left| \Psi_{\pm}^{(0)} \right\rangle \Rightarrow$$ in both cases ($+$ & $-$) have two types of terms

$$J_{ne} = \int |\Psi_{1s}(\vec{r}_1)|^2 \frac{e^2}{4\pi\varepsilon_0 r_{12}} |\Psi_{nem}(\vec{r}_2)|^2 \, d\vec{r}_1 \, d\vec{r}_2 \quad \text{or } r_1 \leftrightarrow r_2$$

Coulomb (direct) integral $\Rightarrow$ Coulomb interaction between charge distributions of two electrons

and

$$K_{ne} = \int \Psi_{1s}^{*}(\vec{r}_1) \Psi_{nem}^{*}(\vec{r}_2) \frac{e^2}{4\pi\varepsilon_0 r_{12}} \Psi_{1s}(\vec{r}_2) \Psi_{nem}(\vec{r}_1) \, d\vec{r}_1 \, d\vec{r}_2$$

exchange integral $\leftarrow$ no classical analog

$$E_{ne,\pm}^{(1)} = J_{ne} \pm K_{ne}$$

$\leftarrow$ Note: J, K do not depend on m

$$\Updownarrow$$

$$\left[L_z, \frac{1}{r_{12}} \right] = 0$$

So, $E_{ne,\pm} = \underbrace{E_{1,n}^{(0)}}_{= E_{1s} + E_n} + J_{ne} \pm K_{ne}$

Spatial Spin

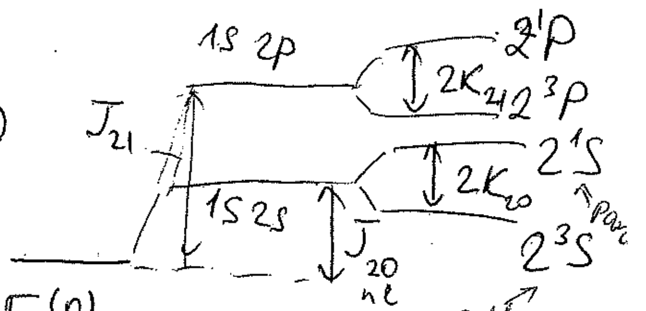
S A

A S

Para ortho

$J_{ne} > 0$ (always) $\quad K > 0$

$\Rightarrow$



$\underbrace{E_{1,2}^{(0)}}_{= E_1 + E_2}$

Splitting due to exchange!

much stronger than $\vec{L} \cdot \vec{S}$ interactions

responsible for ferromagnetism!

^{2S+1}L

total S $\quad$ total L