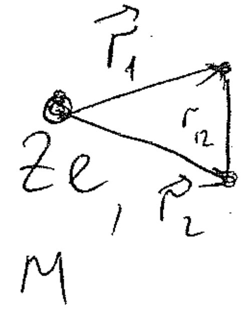
PH 585
AMO

Lecture # 15

Two-electron atoms

App. 8 (p. 1029 - 1031) of B&J



$\Leftarrow$ 3-body problem

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

$\mu = \frac{mM}{m+M}$, $r_{12} = |\vec{r}_1 - \vec{r}_2|$

mass polarization term ($= 0$ if $M \to \infty$ "very heavy nucleus")

$$H\Psi(\vec{r}_1, \vec{r}_2) = E\Psi(\vec{r}_1, \vec{r}_2)$$

(can't separate variables because of $\frac{1}{r_{12}}$ term $\Rightarrow$ entangled functions $\Rightarrow$ measurements can't be made on one particle without affecting the other

unchanged if $r_1 \Leftrightarrow r_2$

Introduce P_{12} $\leftarrow$ interchange operator $\Rightarrow$ $P_{12}\Psi(\vec{r}_1, \vec{r}_2) = \Psi(\vec{r}_2, \vec{r}_1) = \lambda\Psi(\vec{r}_1, \vec{r}_2)$

$$P_{12}^2(\Psi(\vec{r}_1, \vec{r}_2)) = P_{12}\Psi(\vec{r}_2, \vec{r}_1) = \lambda^2\Psi(\vec{r}_1, \vec{r}_2) \Rightarrow \lambda = \pm 1$$

ortho-states

$$\Psi_\pm(\vec{r}_1, \vec{r}_2) = \pm\Psi(\vec{r}_2, \vec{r}_1)$$

space antisymmetric

space-symmetric $\to$ para-states

So far: spin $\nearrow$ fine / $\rightarrow$ hyperfine structure (2)
(1-electron atoms)

2+ electron atoms: Pauli exclusion principle $\Rightarrow$ Spin affects spectra even when H doesn't explicitly contain spin interactions

need

$$\Psi(q_1, q_2) = \psi(\vec{r}_1, \vec{r}_2)\underbrace{\chi(1,2)}_{\text{spin wave function}}$$

generalized (spatial & spin) coordinates

$\alpha : \uparrow$, $\beta : \downarrow$

$S\,M_S$

$$\chi_{00}^{(1,2)} = \frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)$$

anti-symmetric $\rightarrow$ Singlet $S=0$

$$\vec{S}^2\chi = \hbar^2 S(S+1)\chi$$

$\vec{S}_1 + \vec{S}_2$ $\quad s_1 = s_2 = \frac{1}{2}$ $\Rightarrow$ $S = 0, 1$

$$\chi_{1,1} = \alpha(1)\alpha(2)$$
$$\chi_{1,0} = \frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2) + \beta(1)\alpha(2)\right)$$
$$\chi_{1,-1} = \beta(1)\beta(2)$$

symmetric $\Rightarrow$ triplet $S=1$

Pauli exclusion principle: total $\Psi(q_1, q_2, \ldots q_N)$ is anti-symmetric

N: # electrons

$$\Psi(q_1, q_2) = \psi_+(\vec{r}_1, \vec{r}_2)\frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)$$

S, A

or

$$\Psi(q_1, q_2) = \psi_-(\vec{r}_1, \vec{r}_2) \cdot \begin{cases} \alpha(1)\alpha(2) & ; \ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2) + \beta(1)\alpha(2)\right) \end{cases}$$

A, S

So, need to solve $H\Psi = E\Psi$ (3)

Simplest: $H = \underbrace{H_0}_{} + \underbrace{H'}_{= \frac{e^2}{r_{12}}}$ ← perturbation

$$H_0 = \underbrace{-\frac{\hbar^2}{2\mu}\nabla^2_{r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_1}}_{H_1} \underbrace{-\frac{\hbar^2}{2\mu}\nabla^2_{r_2} - \frac{Ze^2}{4\pi\varepsilon_0 r_2}}_{H_2}$$

$$E_1 = -\frac{Z^2 E_I}{n_1^2} \qquad E_2 = -\frac{Z^2 E_I}{n_2^2}$$

$$H_0 \Psi^{(0)}(\vec{r}_1, \vec{r}_2) = \underbrace{E^{(0)}}_{E_1 + E_2} \Psi^{(0)}(\vec{r}_1, \vec{r}_2);$$

parahelium

$$\Psi^{(0)}_{\pm}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left(\Psi_{n_1 l_1 m_1}(\vec{r}_1)\Psi_{n_2 l_2 m_2}(\vec{r}_2) \pm \Psi_{n_2 l_2 m_2}(\vec{r}_1)\Psi_{n_1 l_1 m_1}(\vec{r}_2)\right)$$

orthohelium

Both have same energy ⇒ exchange degeneracy ⇒ it's removed by $H' = \frac{e^2}{r_{12}}$ perturbation

Note: in ground state $n l m = 100$ for both electrons ⇒ need $m_{s_1} = \frac{1}{2}$, $m_{s_2} = -\frac{1}{2}$

↑↓ ⇒ spin function (A)

$S = 0$ ⇒ Ψ_+, i.e. (S), only ← para

Ground state: $\Psi^{(0)}(\vec{r}_1,\vec{r}_2) = \Psi_{1s}(\vec{r}_1)\Psi_{1s}(\vec{r}_2)$

$1\,a.u. = \frac{e^2}{4\pi\varepsilon_0 a_0}$ $\longleftrightarrow$ $E_0^{(0)} = -2Z^2 E_I = -108.8\,eV$

$E_0^{(0)} = -Z^2\,a.u. = -4\,a.u.$

$Z=2$ experiment: $-79\,eV$

Note: $E_{0He^+} = -Z^2 E_I = 54.4\,eV$

$$E^{(0)}_{He} = -Z^2 E_I\left(\frac{1}{n_1^2}+\frac{1}{n_2^2}\right) \Rightarrow$$

$n_1\ n_2$

$1\ 2 \Rightarrow -\frac{5}{4}Z^2E_I$ $-2.9\,a.u.$

$1\ 3 \Rightarrow -\frac{10}{9}Z^2E_I$

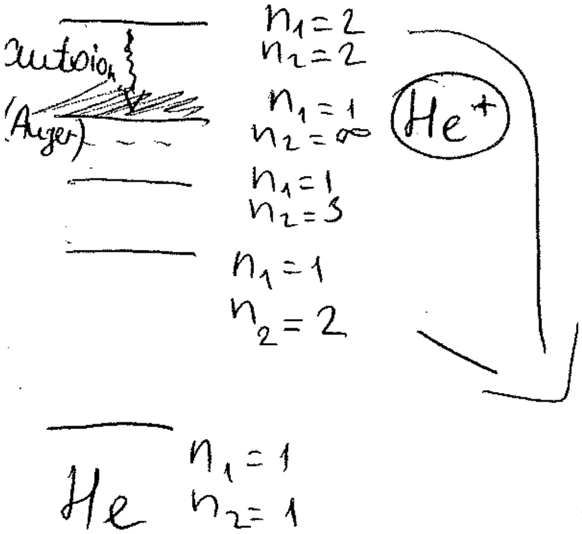
...

$1\ \infty \Rightarrow -Z^2E_I$

But

$2\ 2 \Rightarrow -\frac{Z^2}{2}E_I$

...



doubly-excited states $(n_1\geq 2, n_2\geq 2)$ lie in the continuum $\Rightarrow$ only $n_1=1,\ n_2\geq 1$ states are genuinely discrete

$$E^{(0)}_{1,n} = -Z^2E_I\left(1+\frac{1}{n^2}\right)$$ ← degenerate in l and m

Next: energy correction $E_0^{(1)}$ to ground state $\Rightarrow$

$$E_0^{(1)} = \langle\Psi_0^{(0)}|H'|\Psi_0^{(0)}\rangle = \int|\Psi_{1s}(\vec{r}_1)|^2\frac{e^2}{4\pi\varepsilon_0 r_{12}}|\Psi_{1s}(\vec{r}_2)|^2\,d\vec{r}_1^{\,3}\,d\vec{r}_2^{\,3}$$

$$= \frac{5}{8}Z\frac{e^2}{4\pi\varepsilon_0 a_0} = \frac{5}{8}Z\,(a.u.) \Rightarrow E_0 = \underbrace{-Z^2+\frac{5}{8}Z}_{-2.75\,a.u.}$$ ← in a.u.

work through pp. 326-327 of B&J