Review multiparticle states

$$\psi(1;2) = \psi(\vec{r}_1, m_{s_1}; \vec{r}_2, m_{s_2})$$

state of part. 1 to be at $\vec{r}_1$ position and m_{s_1} spin
and part. 2 —"— $\vec{r}_2$ —"— m_{s_2} —"—.

Simplest observable :

$$|\psi(\vec{r}_1, m_{s_1}; \vec{r}_2, m_{s_2})|^2 = |\psi(\vec{r}_2, m_{s_2}; \vec{r}_1, m_{s_1})|^2$$

cannot depend on labels if 1 & 2 are identical.

Only possible if $\hat{P}(1 \leftrightarrow 2)\, \psi(1,2) = e^{i\lambda}\, \psi(2,1)$
or $\hat{P}^2\, \psi(1,2) = \underbrace{e^{2i\lambda}}_{=1}\, \psi(1,2)$

$\Rightarrow e^{2i\lambda} = 1$ or
$e^{i\lambda} = \pm 1$

Fermions : choose -1 (half integer spin)
Bosons : choose $+1$ (integer spin)

Note : many part.

$$\hat{P}_{f_i \leftrightarrow f_j}\, \psi(\dots i \dots j \dots) = -\psi(\dots j \dots i \dots)$$

$$\hat{P}_{b_i \leftrightarrow b_j}\, \psi(\dots i \dots j \dots) = \psi(\dots j \dots i \dots)$$

He atom

2 identical fermions : antisym. state

$\psi(1,2) = \psi(1) \cdot \psi(2)$ is <u>not</u> good enough

single-particle : $\psi_a(i) = \underbrace{\psi_{n\ell m_\ell}(i)}_{\text{H-like}}\, \underbrace{\chi_\pm(i)}_{\text{spin}}$

i = electron 1 or 2

$$\psi(1,2;A) = \begin{pmatrix}\text{space}\\ \text{eigenfcn.}\end{pmatrix}_{\substack{\text{anti}\\ \text{sym}}} \times \begin{pmatrix}\text{spin}\\ \text{eigenfcn.}\end{pmatrix}_{\substack{\text{sym}\\ \text{anti}}}$$

Possibility 1 orthohelium

$$\psi(1,2) = \psi_{anti}(1,2) \times \chi_{sym}(1,2)$$

χ_{sym} : (z-proj.)

$$\left.\begin{array}{ll} |\uparrow\uparrow\rangle & , m_s = 1 \\ \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) & , m_s = 0 \\ |\downarrow\downarrow\rangle & , m_s = -1 \end{array}\right\} \quad \begin{array}{l} \hat{\vec{S}} = \hat{\vec{S}}_1 + \hat{\vec{S}}_2 \\ s = 1 \end{array}$$

"spin triplet"

Can He in ground state be orthohelium? NO

$$\psi_{anti} \propto \psi_{nlm_l}(1)\,\psi_{n'l'm_l'}(2) - \psi_{n'l'm_l'}(1)\,\psi_{nlm_l}(2)$$

$n = n' = 1$, $l = l' = 0$, $m_l = m_l' = 0$

$$\Rightarrow \psi_{100}(1)\psi_{100}(2) - \psi_{100}(1)\psi_{100}(2) = 0$$

Possibility 2 parahelium

$$\psi(1,2) = \psi_{sym}(1,2) \times \chi_{anti}(1,2)$$

$$\chi_{anti} : \quad \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) \qquad \begin{array}{l} s = 0 \\ m_s = 0 \end{array}$$

"spin singlet"

ground state

$$\psi_{gr} \propto \psi_{100}(1)\psi_{100}(2)\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$

Energy level : $E \simeq \underbrace{2E_1(z=2)}_{\text{H-like}} = -109\,eV$

True ground state : $-79\,eV$ (due to V_{int})

How to deal with $V_{int}(|\vec{r}_1 - \vec{r}_2|)$?

a) replace $Z \to Z_{eff} < Z$ to account for nucleus screening by other e^-

OK only if there is good distinction between outer & inner shells (e.g. alkalis)

b) Self-consistent fields: (Datta, Ch 3)

i^{th} $e^- \leftrightarrow \psi_i(\vec{r})$ single-part wavefcn.

charge density from other e^-'s:

$$\rho(\vec{r}) = \sum_{j \neq i} (-e) |\psi_j(\vec{r})|^2$$

$$V_{int,i}(\vec{r}) = \int d^3\vec{r}' \frac{(-e)\rho(\vec{r}')}{4\pi\varepsilon_0 |\vec{r} - \vec{r}'|}$$

update ψ_i

Periodic table

Minimum energy principle + Pauli exclusion

* $E_{n\ell}$ not degenerate with ℓ when $V(r) \neq -\frac{const}{r}$

smaller ℓ ← electron spends more time near nucleus ⇒ less shielding ⇒ lower energy

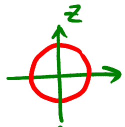
Energetically:

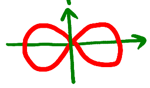
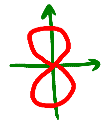
transition series

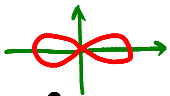
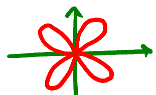
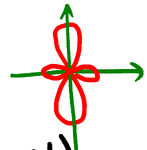
$$1s \ll 2s < 2p \ll 3s < 3p \ll 4s \lesssim 3d < 4p \ll 5s < 4d < 5p \ll 6s$$
$$< 4f \lesssim 5d < 6p \ll 7s < 6d \lesssim 5f$$

Max number of e^-'s in ℓ subshell: $2(2\ell+1)$

$\ell = 0$	s: 2	filled shells (if max #)
1	p: 6	
2	d: 10	
3	f: 14	

E.g. $|Y_0^0|^2$ 

$|Y_1^{\pm1}|^2$  $|Y_1^0|^2$ 

$|Y_2^{\pm2}|^2$  $|Y_2^{\pm1}|^2$  $|Y_2^0|^2$ 

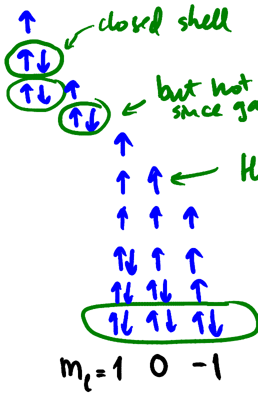
Filled shells: $\displaystyle\sum_{m_\ell=-\ell}^{\ell} |Y_\ell^{m_\ell}(\theta,\varphi)|^2 = \frac{2\ell+1}{4\pi}$ (spherical!)

total $\left.\begin{array}{l} L=0 \\ S=0 \\ J=0 \end{array}\right\}$ for filled shells

First few elements:

H	$1s^1$	
He	$1s^2$	
Li	$[He]2s^1$	
Be	$2s^2$	
B	$2s^2 2p^1$	
C	$2p^2$	
N	$2p^3$	
O	$2p^4$	
F	$2p^5$	
Ne	$2p^6$	

inert → He, large gap → Li



← closed shell

← but not inert since gap to 2p is small

← Hund's rule (higher multiplicity tends to have lower energy)

"bus seat rule"

← inert