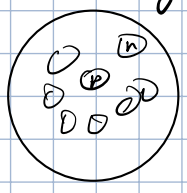
Pauli exclusion principle & atomic structure

atom:

nucleus

z protons



charge $+ze$

Mnucleus >> Melectron

↳ ignore C.O.M coords. reduced mass, ...

treat nucleus as ∞ heavy fixed

z electrons see a Coulomb potential $\frac{ze^2}{|\vec{r}|}$

Fermi statistics

$\psi(1,2,\dots i,\dots j,\dots z) = -\psi(1,2,\dots j,\dots i,\dots z)$

↑ includes spatial spin

$$H = \sum_{i=1}^{z} \frac{\vec{p}_i^{\,2}}{2m} - \sum_{i=1}^{z} \frac{ze^2}{|\vec{r}_i|^2} + \sum_{i=1}^{z} \sum_{\substack{j=1 \\ i<j}} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

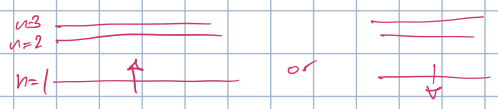
crude approx. drop this interaction between e^-

z=1 Hydrogen

energy eigenfn $\psi_{nlm}(\vec{r}_i) \otimes |\pm\rangle$

$E_n = -\frac{13.6\,eV}{n^2}$

picture



z=2 Helium

ground state - lowest energy

$\underbrace{\psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2)}_{\text{space symmetric}} \otimes \underbrace{|s=0, m=0\rangle}_{\text{spin antisym}}$

two ground state $n=3$, $n=2$, $n=1$ $\uparrow\downarrow$

1st excited states

$$\frac{1}{\sqrt{2}}\left(\psi_{100}(\vec{r}_1)\,\psi_{2\ell m}(\vec{r}_2) + \psi_{100}(\vec{r}_2)\,\psi_{2\ell m}(\vec{r}_1)\right) \otimes |s=0, m=0\rangle \quad \text{parahelium} \quad \ell=0 \text{ or } 1 \quad \ell=0,\ \ell=1 \quad 1+3 \text{ states}$$

$$\frac{1}{\sqrt{2}}\left(\psi_{100}(\vec{r}_1)\,\psi_{2\ell m}(\vec{r}_2) - \psi_{100}(\vec{r}_2)\,\psi_{2\ell m}(\vec{r}_1)\right) \otimes |s=1, m\rangle \quad \text{orthohelium} \quad \ell=0,\ \ell=1 \quad 1+3 \cdot 3_{\text{spin}} = 12 \text{ states}$$

energy of these states is $(-13.6\,\text{eV}) \cdot Z^2 \cdot \left(\frac{1}{n=1^2} + \frac{1}{n=2^2}\right) = E^{1\text{st}}$

$$E_{\text{grnd}} = -13.6 \cdot 4\left(\tfrac{1}{1^2} + \tfrac{1}{2^2}\right) = -108.9\,\text{eV}$$

$Z=3$ Lithium

Ground state $\psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2)\,\psi_{100}(\vec{r}_3)$ $\otimes$ (spin part) ?

no — symmetric under $\vec{r}_1 \leftrightarrow \vec{r}_2$ & $\vec{r}_2 \leftrightarrow \vec{r}_3$

3 fermions $|+\rangle \otimes |-\rangle \otimes |+\rangle$ or... has 2 entries same

$-$ (swap 1 & 3) $= 0$

Pauli - only 1 fermion in a 1-particle state $\psi_{nlm}|+\rangle$ or $\psi_{nlm}|-\rangle$

spatial part $\psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2)\,\psi_{100}(\vec{r}_3) \otimes$ spin part

picture $n=3$, $n=2$, $n=1$ $\uparrow\downarrow$ or

$n=1$ $\ell=0$ 1 or 2 state (incl. spin)

$n=2$ $\ell=0$ 1·2, $\ell=1$ 3·2 } 8 states

He $(1s)^2$ ← inert — spdf...

^1H ^2He

^3Li

$l = 0\ 1\ 2\ 3\cdots$

Li $(1s)^2(2s)$

Be $(1s)^2(2s)^2$

B $(1s)^2(2s)^2(2p)$

C $(1s)^2(2s)^2(2p)^2$

N

O

F

Ne $(1s)^2(2s)^2(2p)^6$ inert

closed shell: fill up all states at given n

$n=1$	2 sp'n	2
$n=2$	$l=1,0 \times 2$	$(3+1)\times 2 = 8$
$n=3$	$l=2,1,0 \times 2$	$(5+3+1)\times 2 = 18$
$n=4$	$l=3,2,1,0 \times 2$	$(7+5+3+1)\times 2 = 32$

$2+8 = 10$ ✓ Ne

$2+8+18 = 28$ ✗

Argon is $z = 18$