L59-Atoms

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* Hamiltonian for an atom with Z protons (and electrons)

$$\mathcal{H} = \sum_{j=1}^{Z}\left\{\underbrace{-\frac{\hbar^2}{2m}\nabla_j^2 - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_j}}_{\mathcal{H}_j \text{ (single electron)}}\right\} + \underbrace{\frac{1}{2}\frac{1}{4\pi\varepsilon_0}\sum_{j\neq k}^{Z}\frac{e^2}{|\vec{r}_j-\vec{r}_k|}}_{\text{electron repulsion.}}$$

- will use perturbation and variational methods to deal with the electron repulsion.
- the single-particle terms are separable:

  if $\mathcal{H}_j\psi_j = E_j\psi_j$ then $\mathcal{H}[\psi_1\psi_2\cdots\psi_Z] = (E_1+E_2+\cdots E_Z)[\psi_1\psi_2\cdots\psi_Z]$

- must still antisymmetrize whole wave function.

$$\Psi(\vec{r}_1,\vec{r}_2,\cdots\vec{r}_Z,\vec{s}_1,\vec{s}_2,\cdots\vec{s}_Z) = \psi(\vec{r}_1,\vec{r}_2,\cdots\vec{r}_Z)\,\chi(\vec{s}_1,\vec{s}_2\cdots\vec{s}_Z)$$

$\vec{r}_i$ = position, $\vec{s}_i$ = spin } of i^{th} electron

$$P_{ij}\Psi = P_{ij}\psi\cdot P_{ij}\chi = \pm\psi\cdot\mp\chi = -\psi \quad \text{for fermions}$$

- thus two valid combinations: $\psi_S\chi_A$ & $\psi_A\chi_S$ (other possibilities too!)

(different states, for example consider 2 electrons in states ψ_a, ψ_b, either with spin ↑ or ↓

$$\left.\begin{array}{l}\psi_a(\vec{r}_1)\chi_\uparrow(\xi_1)\cdot\psi_b(\vec{r}_2)\chi_\uparrow(\xi_2)\\ \psi_a(\vec{r}_1)\chi_\uparrow(\xi_1)\cdot\psi_b(\vec{r}_2)\chi_\downarrow(\xi_2)\\ \psi_a(\vec{r}_1)\chi_\downarrow(\xi_1)\cdot\psi_b(\vec{r}_2)\chi_\uparrow(\xi_2)\\ \psi_a(\vec{r}_1)\chi_\downarrow(\xi_1)\cdot\psi_b(\vec{r}_2)\chi_\downarrow(\xi_2)\end{array}\right\}\Rightarrow$$

$$\psi_A\left\{\begin{array}{l}[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2)-\psi_b(\vec{r}_1)\psi_a(\vec{r}_2)][\chi_\uparrow(\xi_1)\chi_\uparrow(\xi_2)]\\ [\psi_a(\vec{r}_1)\psi_b(\vec{r}_2)-\psi_b(\vec{r}_1)\psi_a(\vec{r}_2)][\chi_\uparrow(\xi_1)\chi_\downarrow(\xi_2)+\chi_\downarrow(\xi_1)\chi_\uparrow(\xi_2)]\\ [\psi_a(\vec{r}_1)\psi_b(\vec{r}_2)-\psi_b(\vec{r}_1)\psi_a(\vec{r}_2)][\chi_\downarrow(\xi_1)\chi_\downarrow(\xi_2)]\end{array}\right\}\begin{array}{l}S=1\\ \text{triplet}\end{array}\ \chi_S$$

$$\psi_S\left\{[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2)+\psi_b(\vec{r}_1)\psi_a(\vec{r}_2)][\chi_\uparrow(\xi_1)\chi_\downarrow(\xi_2)-\chi_\downarrow(\xi_1)\chi_\uparrow(\xi_2)]\right\}\begin{array}{l}S=0\\ \text{singlet}\end{array}\ \chi_A$$

- note that 4 states of the form $\psi(\vec{r}_1)\chi(\vec{s}_1)\psi(\vec{r}_2)\chi(\vec{s}_2)$ disappeared due to antisymmetry.
- there is only one state with $a=b$ since $\psi_a\psi_a$ symmetric:
  $\psi_a(\vec{r}_1)\psi_a(\vec{r}_2)(\uparrow\downarrow-\downarrow\uparrow)$

* Helium atom: $\psi(\vec{r}_1,\vec{r}_2) = \psi_{n\ell m}(\vec{r}_1)\,\psi_{n'\ell'm'}(\vec{r}_2)$ $\quad \chi(\vec{s}_1,\vec{s}_2) = \begin{cases} |1,m\rangle \text{ triplet} \\ |0,0\rangle \text{ singlet} \end{cases}$

- $E \propto \frac{Z}{r} \propto Z^2$ since $r \propto \frac{1}{Z}$ so $E = 4(E_n + E_{n'})$

$\psi_0 = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}$ $\quad \chi_0 = |0,0\rangle = (\uparrow\downarrow - \downarrow\uparrow)$

ψ_0 symmetric $\rightarrow$ χ_0 antisymmetric (singlet) : PARAHELIUM

$E_0 = -8 \cdot 13.6\,eV = -109\,eV$ singlet vs. $-79\,eV$ singlet observed.
(interaction energy $= 30\,eV$)

- excited states may be either be:

$$\left[\psi_{n\ell m}(\vec{r}_1)\,\psi_{100}(\vec{r}_2) + \psi_{100}(\vec{r}_1)\,\psi_{n\ell m}(\vec{r}_2)\right] |0,0\rangle \quad \text{PARAHELIUM}$$

$$\left[\psi_{n\ell m}(\vec{r}_1)\,\psi_{100}(\vec{r}_2) - \psi_{100}(\vec{r}_1)\,\psi_{n\ell m}(\vec{r}_2)\right] \left|1, \begin{matrix}+1\\0\\-1\end{matrix}\right\rangle \quad \text{ORTHOHELIUM}$$

parahelium: 1S, 2S, 3S, 4S, ...
2P, 3P, 4P, ...
3D, 4D, ...
4F, ...

orthohelium: ~~1S~~, 2S, 3S, 4S, ...
2P, 3P, 4P ...
3D 4D ...
4F ...

- capital letters: TOTAL N, L, M
- same as single excited electron $n\ell m$

* Atoms

		ℓ= 1 (sharp)	2 (principle)	3 (diffuse)	4 (fundamental)
K	n=1	S			
L	2	S	P		
M	3	S	P	D	
N	4	S	P	D	F
O	5	S	P	D	F, g, h, i, k, l...
P	6	S	P	D	
Q	7	S	P		

spectroscopic term

$^{2S+1}L_J$

* capitol letters for multiparticle state

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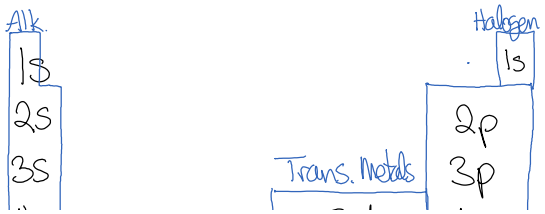

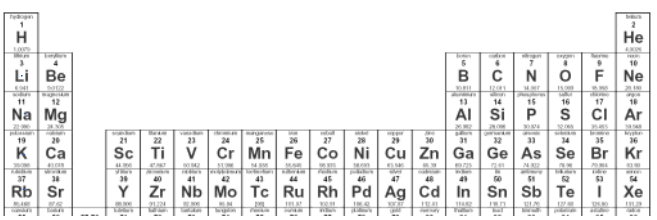

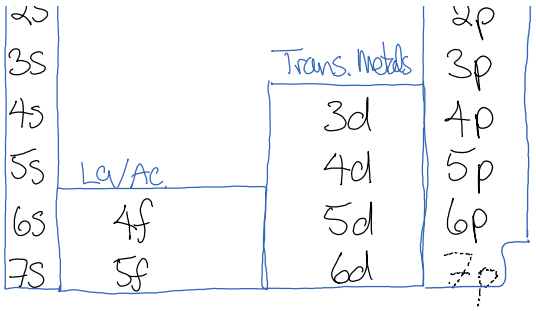

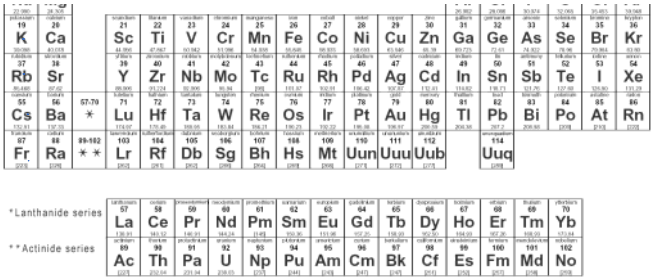

* Hund's Rules: (remember antisymmetrization always)

1) the state with largest S comes first. (lowest energy)

2) for given spin, the highest L comes first

3) if a subshell is less than half full then $J = |L-S|$ comes first
otherwise $J = |L+S|$ comes first

see Problem 5.13 for examples.