L59-Atoms

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

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

- 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 $\mathcal{H}[\psi_1\psi_2\cdots\psi_Z] = (E_1+E_2+\dots E_Z)[\psi_1\psi_2\cdots\psi_Z]$

- must still antisymmetrize whole wave function.

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

$\left.\begin{array}{l}\vec{r}_i = \text{position}\\ \vec{s}_i = \text{spin}\end{array}\right\}$ 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 $\uparrow$ or $\downarrow$

$$\left.\begin{array}{l}
\psi_a(\vec{r}_1)\,\chi_\uparrow(\vec{s}_1)\cdot\psi_b(\vec{r}_2)\,\chi_\uparrow(\vec{s}_2)\\
\psi_a(\vec{r}_1)\,\chi_\uparrow(\vec{s}_1)\cdot\psi_b(\vec{r}_2)\,\chi_\downarrow(\vec{s}_2)\\
\psi_a(\vec{r}_1)\,\chi_\downarrow(\vec{s}_1)\cdot\psi_b(\vec{r}_2)\,\chi_\uparrow(\vec{s}_2)\\
\psi_a(\vec{r}_1)\,\chi_\downarrow(\vec{s}_1)\cdot\psi_b(\vec{r}_2)\,\chi_\downarrow(\vec{s}_2)
\end{array}\right\} \Rightarrow
\begin{array}{l}
\psi_A\left\{\begin{array}{l}
\left.\begin{array}{l}
[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2)-\psi_b(\vec{r}_1)\psi_a(\vec{r}_2)][\chi_\uparrow(\vec{s}_1)\chi_\uparrow(\vec{s}_2)]\\
[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2)-\psi_b(\vec{r}_1)\psi_a(\vec{r}_2)][\chi_\uparrow(\vec{s}_1)\chi_\downarrow(\vec{s}_2)+\chi_\downarrow(\vec{s}_1)\chi_\uparrow(\vec{s}_2)]\\
[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2)-\psi_b(\vec{r}_1)\psi_a(\vec{r}_2)][\chi_\downarrow(\vec{s}_1)\chi_\downarrow(\vec{s}_2)]
\end{array}\right\}\ \begin{array}{l}S=1\\ \text{triplet}\end{array}\ \chi_S
\end{array}\right.\\
\psi_S\left\{[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2)+\psi_b(\vec{r}_1)\psi_a(\vec{r}_2)][\chi_\uparrow(\vec{s}_1)\chi_\downarrow(\vec{s}_2)-\chi_\downarrow(\vec{s}_1)\chi_\uparrow(\vec{s}_2)]\right\}\ \begin{array}{l}S=0\\ \text{singlet}\end{array}\ \chi_A
\end{array}$$

- note that 4 states of the form $\psi_b(\vec{r}_1)\,\chi(\vec{s}_1)\,\psi_a(\vec{r}_2)\,\chi(\vec{s}_2)$ 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: $\psi(\vec{r}_1, \vec{r}_2) = \psi_{n\ell m}(\vec{r}_1)\, \psi_{n'\ell' m'}(\vec{r}_2)$ $\qquad \chi(\vec{s}_1, \vec{s}_2) = \begin{cases} |1, m\rangle & \text{triplet} \\ |0,0\rangle & \text{singlet} \end{cases}$

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

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

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

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

- excited states may be either be:

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

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

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

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

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

* Atoms

	$\ell =$ sharp	principle	diffuse	fundamental		
$n = 1$	s					
2	s	p				
3	s	p	d			
4	s	p	d	f		
5	s	p	d	f	g	
6	s	p	d	f	g	h

spectroscopic term

$$\boxed{{}^{2S+1}L_J}$$