

Lecture 19: Multielectron atoms

• Review: Basic Hydrogenic atom

Last semester we found the energy eigenstates and eigenvalues for ~~hydrogen~~ hydrogenic atoms consisting of bound states between two oppositely charged point particles interacting through an attractive Coulomb potential. For the case of a charge $+Ze$ nucleus and one electron $-e$, relative motion Hamiltonian is (ignoring spin)

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{Ze^2}{r} = \frac{\hat{p}_r^2}{2m} + \frac{\hbar^2 \hat{L}^2}{2mr^2} - \frac{Ze^2}{r}$$

This is a central potential. We found the common eigenfunctions of $\{\hat{H}, \hat{L}^2, \hat{L}_z\}$

denote $|n, l, m_l\rangle \doteq \underbrace{R_{n,l}(r)}_{\text{radial wave function}} \underbrace{Y_l^{m_l}(\theta, \phi)}_{\text{spherical harm.}}$

with eigenvalues of \hat{H}

$$E_n = -\frac{Z^2 R}{n^2}$$

$$R = \frac{e^2}{2a_0} = 13.6 \text{ eV}$$

= Rydberg energy

$$a_0 = 0.5 \text{ \AA} = \text{Bohr radius}$$

Recall: n = principal quantum #

Generally, for central potential

E depends on n_r (# radial nodes) and l .

For Coulomb $n = n_r + l \Rightarrow$ Degeneracy $n_r = 0, 1, \dots, n-1$

A complete description of the ^{electronic} state must include the spin of electron. If we ignore the small magnetic effects which couple the electron mag. moment, the energy spectrum is unchanged. The degeneracy of each state has now doubled (spin up and spin down)

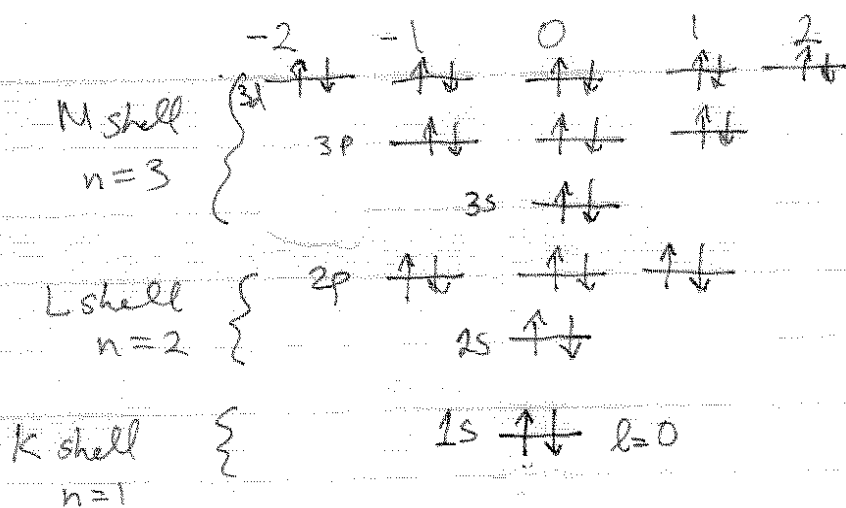
⇒ Total quantum state $|n, l, m_l, m_s\rangle$
 $\underbrace{}_{\leftarrow} |\uparrow\rangle \text{ or } |\downarrow\rangle$

Degeneracy: Given n , $l = 0, 1, \dots, n-1$
 $m_l = -l, -l+1, \dots, 0, 1, \dots, l-1, l$
 $m_s = +\frac{1}{2} \text{ or } -\frac{1}{2}$

$$\Rightarrow g_n = 2 \sum_{l=0}^{n-1} (2l+1) = 2n^2$$

Multi-electron atom: Shell Structure

Armed with the single electron orbitals and the Pauli exclusion principle we can build up the periodic table. To crudest (and very poor) approximation we neglect the interactions of the electrons with one another and treat each independently interacting with the nucleus. We then fill in the orbits one at a time, ~~with~~ with no more than one electron in a given state (including spin)



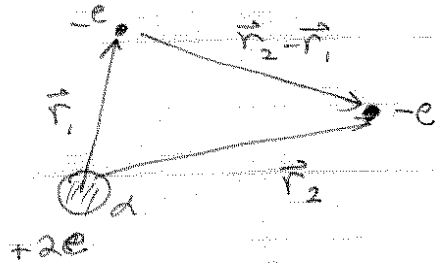
Note: For multielectron atoms the different l states are no longer degenerate. This is because the total field seen by one electron is not purely $\frac{1}{r}$, but a combination of $\frac{1}{r}$ due to nucleus and the screening potential of other electrons.

Low angular momentum states \rightarrow small impact parameter with nucleus
 \rightarrow stronger attraction
 \rightarrow lower energy.

Thus, one should fill shells with lowest angular momentum first.

Example: Helium

The simplest multielectron atom is $Z=2$, Helium



Ignoring
magnetic
effects

$$\hat{H} = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} + \frac{(-e)(2e)}{r_1} + \frac{(-e)(2e)}{r_2} + \frac{(-e)(-e)}{|\vec{r}_2 - \vec{r}_1|}$$

$$= \hat{H}_1 + \hat{H}_2 + \hat{H}_{12}$$

$$\hat{H}_i = \frac{\hat{p}_i^2}{2m} - \frac{2e^2}{r_i}$$

Interaction of each
electron w/ nucleus

$$\hat{H}_{12} = \frac{e^2}{|\vec{r}_2 - \vec{r}_1|}$$

Interaction of ~~with~~
electrons with each other

If neglect \hat{H}_{12} the Hamiltonian is separable
for the two electrons. Each Hamiltonian

\hat{H}_i is "hydrogenic" with orbitals $|n, l, m_l, m_s\rangle$

\Rightarrow Neglecting \hat{H}_{12} the energy eigenvalues are the
sum of two hydrogenic terms with $Z=2$

$$E_{n_1, n_2}^{(0)} = -\frac{2^2 R}{n_1^2} - \frac{2^2 R}{n_2^2} = -4R \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right)$$

In this crude approximation the ground state for "electron configuration" $(1s)^2$ $n_1=n_2=1$

$$\Rightarrow E_{1,1}^{(0)} = -8R = -108.8 \text{ eV}$$

This is about 30% larger in magnitude than measured ground state binding $E_{\text{ground}} = -78.8 \text{ eV}$

We have completely neglected the interaction of the electron with each other. This is a large effect!

Let us consider the expectation value of \hat{H}_{12} in the product state. First we must account for the fermion nature of the two electrons. Because the ground configuration has both electrons in the same $1s$ spatial orbital, the spin state must be antisymmetric \Rightarrow singlet

$$|\Psi_{\text{ground}}\rangle \cong (|1s\rangle \otimes |1s\rangle) \otimes |\chi_{\text{singlet}}\rangle$$

$$\parallel \begin{matrix} |n=1,0,0\rangle \otimes |n=1,0,0\rangle \\ \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \end{matrix}$$

$$\langle \Psi_{\text{ground}} | \hat{H}_{12} | \Psi_{\text{ground}} \rangle =$$

$$= \int r_1^2 dr_1 d\Omega_1 \int r_2^2 dr_2 d\Omega_2 \frac{e^2}{r_{12}} \frac{|R_{1s}(r_1)|^2 |R_{1s}(r_2)|^2}{4\pi}$$

lots of algebra

$$= \frac{5}{2} R = 34 \text{ eV}$$

If we add this to the zeroth order contribution

$$E_{1,1} \cong E_{1,1}^{(0)} + \langle 1s, 1s | \hat{H}_{12} | 1s, 1s \rangle$$

$$= -74.8 \text{ eV} \quad \text{not bad.}$$

We can in fact do better using more sophisticated approximation methods. An important one is the "variational approach" which we will not have time to cover in this course (see

What about excited states?

Consider the configuration $(1s)(nl)$ (one electron in ground orbital another in excited)

Two possibilities:

- Motional wave function even, spin odd (singlet)

$$|\Psi_{\text{sing}}\rangle = \left\{ \frac{|1s\rangle_1 |nl\rangle_2 + |nl\rangle_1 |1s\rangle_2}{\sqrt{2}} \right\} |\chi_{\text{singlet}}\rangle$$

- Motional wave function odd, spin even (triplet)

$$|\Psi_{\text{trip}}\rangle = \left\{ \frac{|1s\rangle_1 |nl\rangle_2 - |nl\rangle_1 |1s\rangle_2}{\sqrt{2}} \right\} |\chi_{\text{triplet}}\rangle$$

The interaction Hamiltonian has no explicit spin dependence. Nonetheless, the interaction strength depends on spin ~~via~~ implicitly through the "exchange density" discussed in lecture 18.

If we consider the probability density for these two states

$$|\Psi_{\pm}(\vec{r}_1, \vec{r}_2)|^2 = \frac{1}{2} (|\phi_{1s}(\vec{r}_1)|^2 |\phi_{ne}(\vec{r}_2)|^2 + |\phi_{ne}(\vec{r}_1)|^2 |\phi_{1s}(\vec{r}_2)|^2)$$

$$\begin{array}{c} \text{singlet} \\ \rightarrow \\ \left(\frac{+}{-} \right) \\ \rightarrow \\ \text{triplet} \end{array} \text{Re} \left\{ \underbrace{(\phi_{1s}(\vec{r}_1) \phi_{ne}^*(\vec{r}_1)) (\phi_{ne}(\vec{r}_2) \phi_{1s}^*(\vec{r}_2))}_{\text{positive \#}} \right\}$$

$$\langle \hat{H}_{12} \rangle_{\pm} = \int d^3r_1 d^3r_2 |\Psi_{\pm}(\vec{r}_1, \vec{r}_2)|^2 \frac{e^2}{|\vec{r}_2 - \vec{r}_1|}$$

$$= \int d^3r_1 d^3r_2 (|\phi_{1s}(\vec{r}_1)|^2 |\phi_{ne}(\vec{r}_2)|^2) \frac{e^2}{|\vec{r}_2 - \vec{r}_1|}$$

$$\pm \int d^3r_1 d^3r_2 \left\{ \text{Re} \left\{ \phi_{1s}(\vec{r}_1) \phi_{ne}^*(\vec{r}_1) \phi_{ne}(\vec{r}_2) \phi_{1s}^*(\vec{r}_2) \right\} \right\} \frac{e^2}{|\vec{r}_2 - \vec{r}_1|}$$

$$= A \pm B$$

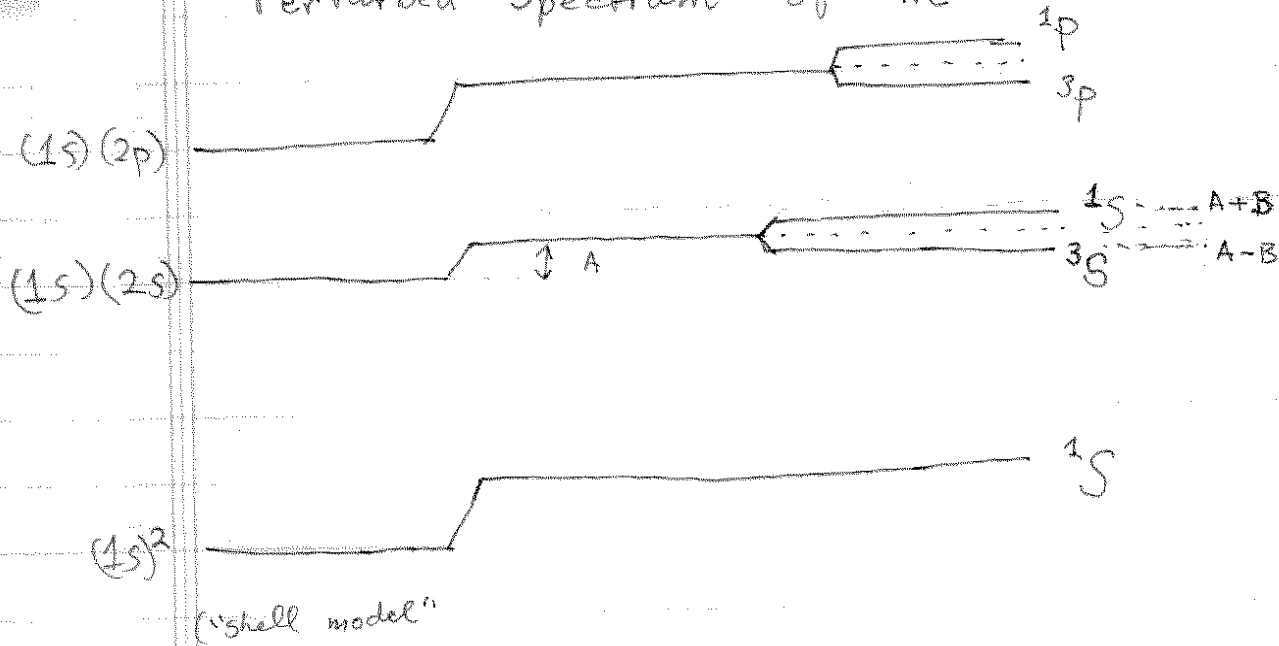
↑
direct
term

↑
exchange (quantum interference
term due to symmetrization)

Note: Both A and B are positive #'s with

$$A > B$$

"Perturbed Spectrum" of He



Here we have introduced "term notation" for the energy levels of the multielectron state

$gpm \rightarrow 2s+1 \begin{matrix} \text{L} \\ \text{J} \end{matrix}$
 multiplicity \leftarrow total orbital angular momentum

Careful: "S" is used two different ways

- Orbital state $L=0 \Rightarrow$ "S-state"
- Spin quantum # $S = 0 \leftarrow$ singlet
 $1 \leftarrow$ triplet

More generally, we write term:

$2S+1 \begin{matrix} \text{L} \\ \text{J} \end{matrix} \leftarrow$ total spin + orbital ang. mom.

L-S coupling.

At this point, we have represented the two electron state in terms of total orbital and total spin angular momentum, the common eigenstates of $\{\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z\}$. Orbital and spin angular momentum are not coupled.

$$|L, M_L\rangle \otimes |S, M_S\rangle$$

We can also consider the coupled representation of orbital and spin $\{\hat{J}^2, \hat{J}_z, \hat{L}^2, \hat{S}^2\}$

$$|J, M_J, L, S\rangle = \sum_{M_L, M_S} C_{M_L, M_S} |L, M_L\rangle |S, M_S\rangle$$

For a given L and S the possible values of J must satisfy the "triangle inequality"

$$|L-S| \leq J \leq L+S$$

Thus, for example, the $3p$ state of He has three possible "terms"

$$\text{Here } L=1, S=1 \Rightarrow J=0, 1, 2$$

$$\Rightarrow {}^3P_0, {}^3P_1, {}^3P_2$$