

Multielectron Atoms

- The quantum mechanics approach for treating multielectron atoms is one of successive approximations
- The first approximation is to treat each electron as moving independently and assume it moves in a spherically symmetric Coulomb potential
 - This is called the Hartree approximation
 - The potential includes both the attractive Coulomb potential due to the nucleus and the repulsive Coulomb potential due to the $Z-1$ other electrons

Multielectron Atoms

- The potential energy term in the Hartree theory looks like

$$V(r) = -\frac{Z(r)e^2}{4\pi\epsilon_0 r} \text{ where}$$

$$Z(r) \rightarrow Z \text{ as } r \rightarrow 0$$

$$Z(r) \rightarrow 1 \text{ as } r \rightarrow \infty$$

- Hartree calculations show that

$$Z_1 \approx Z - 2$$

$$Z_n \approx n$$

Multielectron Atoms

➤ Results of Hartree theory for multielectron atoms

- Electrons in inner shells with small n have small radii (smaller than hydrogen e.g.) because of the large attractive Coulomb potential
- The energies of these inner shell electrons are correspondingly large and negative
- Electrons in outer shells with large n have radii roughly comparable to hydrogen ($\sim na_0$) because they are almost completely shielded
- The energies of these outer shell electrons are comparable to that of an electron in the ground state of hydrogen

Multielectron Atoms

➤ In the Hartree theory we approximated (or averaged) two weaker interactions

- Coulomb interaction between electrons

- ◆ This will couple the spins and orbital angular momenta of the electrons in unfilled subshells

- Spin-orbit interaction

- ◆ This will couple the total spin and total angular momenta of the electrons in unfilled subshells

➤ An additional interaction is present if we place the atom in an external magnetic field

- Zeeman effect

Multielectron Atoms

➤ Alkali group

- These atoms contain a filled p subshell plus an additional electron in the next s subshell
- The energy of the electrons in a filled p subshell is more negative than the energy of the electron in the next s subshell
- In describing excited states we only need consider the single electron in the s subshell
 - ◆ We are considering mainly low energy (few eV) excitations here
- The filled subshells can be considered a core whose energy does not change

Multielectron Atoms

➤ Alkali group

- The optical spectra of the alkali elements show a fine structure splitting where all energy levels are doublets except for those with $l=0$
- This is due to the spin-orbit interaction we studied earlier
- The states are

$$j = l \pm \frac{1}{2}$$

and the higher j state lies slightly higher

Multielectron Atoms

➤ Atoms with partially filled outer subshells

- Unlike the for the alkali atoms, we now must consider the effects of Coulomb repulsion between the electrons
- Because the subshell is only partially filled, the charge distribution will not be spherically symmetric
- The residual Coulomb interaction (not described by the Hartree theory) results in two effects
 - ◆ The spins of the outer subshell electrons couple
 - ◆ The orbital angular momentum of the outer subshell electrons couple
- There will be a spin-orbit interaction also

Multielectron Atoms

➤ Spin angular momentum

- Recall our discussion on the symmetry of the space-spin wavefunction
- The triplet state (spins parallel) lies lower in energy than the singlet state (spins antiparallel)

➤ Orbital angular momentum

- The space orientation of the charge distribution is related to the orbital angular momentum vector
- The state with the largest L will lie lowest in energy because the electrons will be rotating together and hence will be maximally separated

Multielectron Atoms

- There will also be a spin-orbit interaction that will couple L and S
- But it's weaker except for atoms of large Z because
 - Coulomb repulsion energy ~ 1 eV
 - Spin-orbit potential energy $\sim 10^{-5}$ eV
- We also know in the spin-orbit interaction the lowest energy state is the one with smallest J

Multielectron Atoms

➤ LS coupling or Russell-Saunders coupling

$$\vec{S} = \sum_i \vec{s}_i$$

$$\vec{L} = \sum_i \vec{l}_i$$

$$\vec{J} = \vec{L} + \vec{S}$$

- The rules for addition of angular momentum apply in each case
- Only J and m_j will be good quantum numbers

Multielectron Atoms

➤ jj coupling

- Important for heavy atoms where electrostatic repulsion energies are $\sim 10^3$ eV and spin-orbit energies are $\sim 10^4$ eV

$$\vec{j}_i = \vec{l}_i + \vec{s}_i$$

$$\vec{J} = \sum_i \vec{j}_i$$

- The rules for addition of angular momentum apply in each case
- Only J and m_j will be good quantum numbers

Multielectron Atoms

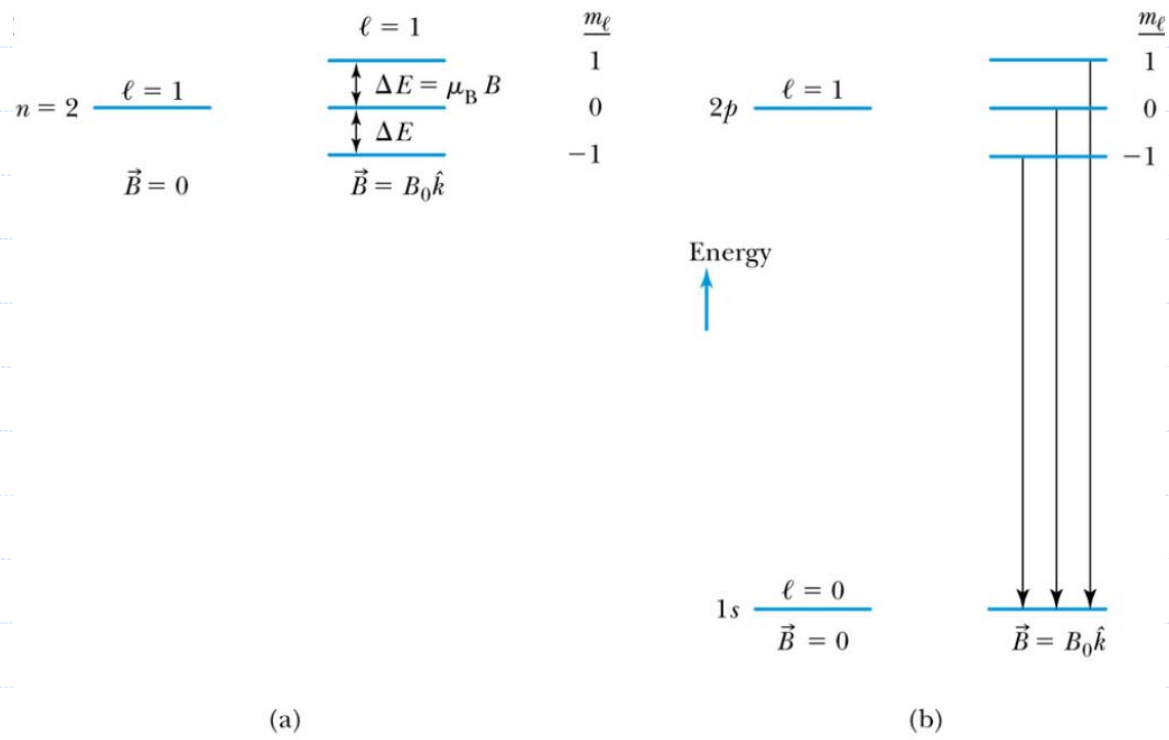
- The Pauli principle or the antisymmetry of fermion wave functions must be considered too
- Consider C ($1s^2 2s^2 2p^2$)
 - What are possible ground states?
 - Which of these states has the lowest energy?

Multielectron Atoms

- Once we know the allowed atomic states we would like to know the ordering in energy as well
- Hund's rules
 - The states with maximum S lie lowest in energy
 - ◆ Like spins repel and hence have lower repulsion energy
 - The states with maximum L lie lowest in energy
 - ◆ Large L can be pictured as arising from all the electrons orbiting in the same direction
 - The states with the minimum (maximum) J lie lowest in energy if the atomic configuration has a subshell less (more) than half filled

Zeeman Effect

➤ The normal Zeeman effect arises when an atom is placed in a magnetic field and we neglect spin



Zeeman Effect

➤ The degeneracy in l is broken by

$$\Delta E = -\vec{\mu}_l \cdot \vec{B} = \frac{g_l \mu_B \vec{L} \cdot \vec{B}}{\hbar} = \frac{\mu_B L_Z B_Z}{\hbar} \text{ where } g_l = 1$$

μ_B (Bohr magneton) is just a convenience of constants

$$\mu_B = \frac{e\hbar}{2m}$$

$$\Delta E = \mu_B B m_l$$

➤ This causes an energy shift depending on m_l

Zeeman Effect

➤ The anomalous Zeeman effect includes spin

$$\Delta E = -\vec{\mu} \cdot \vec{B} = -(\vec{\mu}_l + \vec{\mu}_s) \cdot \vec{B}$$

$$\Delta E = \left(\frac{1 \cdot \mu_B}{\hbar} \vec{L} + \frac{2 \cdot \mu_B}{\hbar} \vec{S} \right) \cdot \vec{B} \text{ where the 1,2 are } g_l, g_s$$

μ_B (Bohr magneton) is just a convenience of constants

$$\mu_B = \frac{e\hbar}{2m}$$

$$\Delta E = \left(\frac{e}{2m} \vec{L} + \frac{e}{m} \vec{S} \right) \cdot \vec{B} = \frac{e}{2m} (\vec{L} + 2\vec{S}) \cdot \vec{B}$$

Zeeman Effect

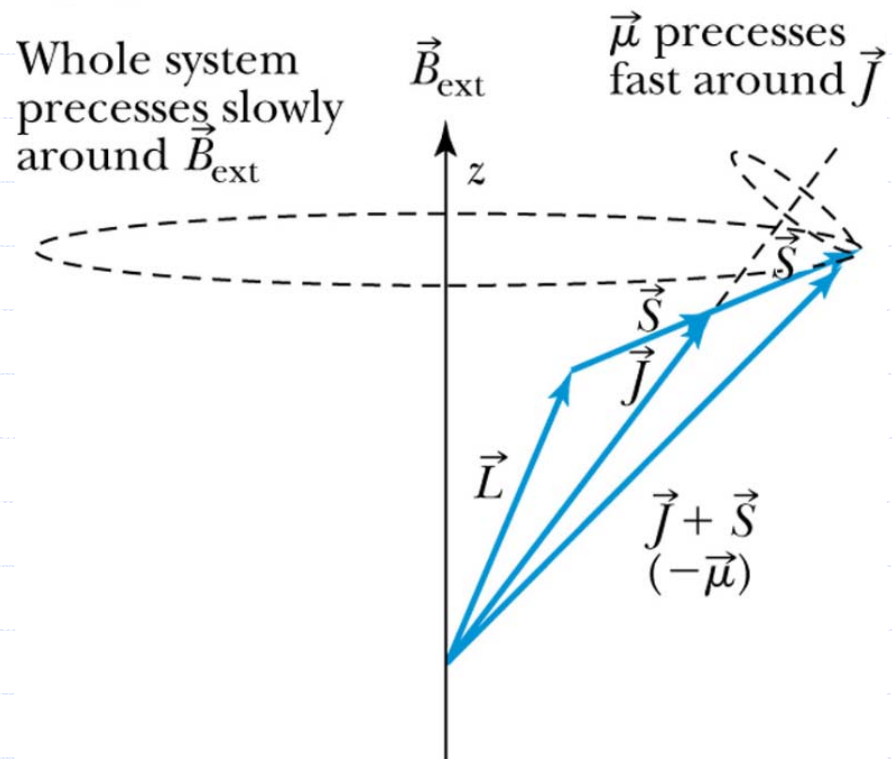
- The nature of this new splitting depends on the strength of B_{ext} in comparison to B_{int}
- Let's only look at the case where $B_{\text{ext}} < B_{\text{int}}$
 - Thus the fine structure (spin-orbit coupling) dominates the Zeeman effect
 - Then we can write

$$\Delta E = \frac{e}{2m} (\vec{L} + 2\vec{S}) \cdot \vec{B} = \frac{e}{2m} (\vec{J} + \vec{S}) \cdot \vec{B}$$

Zeeman Effect

- We know the expectation value of J but not of S
- However the time averaged value of S is just its projection along J

$$\vec{S}_{ave} = \frac{\vec{S} \cdot \vec{J}}{J^2} \vec{J}$$



Zeeman Effect

➤ To calculate $S \cdot J$ we re-use a trick

$$\vec{L} = \vec{J} - \vec{S}$$

$$L^2 = J^2 + S^2 - 2\vec{J} \cdot \vec{S}$$

$$\vec{S} \cdot \vec{J} = \frac{1}{2}(J^2 + S^2 - L^2)$$

$$\vec{S} \cdot \vec{J} = \frac{\hbar^2}{2}[j(j+1) + s(s+1) - l(l+1)]$$

Zeeman Effect

➤ Then

$$\Delta E = \frac{e}{2m} (\vec{L} + 2\vec{S}) \cdot \vec{B} = \frac{e}{2m} (\vec{J} + \vec{S}) \cdot \vec{B}$$

$$\Delta E = \frac{e}{2m} \left(1 + \frac{\vec{S} \cdot \vec{J}}{J^2} \right) \vec{J} \cdot \vec{B}$$

$$\Delta E = \mu_B \left(1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \right) m_J B_{ext}$$

➤ Thus in the case of a weak external B field, each J state gets split into $2J+1$ equally spaced levels with separation ΔE

Zeeman Effect

➤ Reviewing the selection rules for allowed transitions we have

$$\Delta n = \text{anything}$$

$$\Delta l = \pm 1$$

$$\Delta s = 0$$

$$\Delta j = \pm 1, 0 \text{ but not } j_{\text{initial}} = 0 \rightarrow j_{\text{final}} = 0$$

$$\Delta m_j = \pm 1, 0$$

Zeeman Effect

➤ Anomalous splittings for Na

