

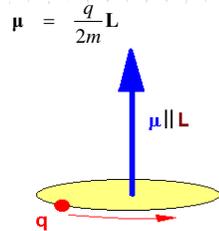
Physical Chemistry

Lecture 21

Atomic magnetism, photoelectron spectroscopy, and hyperfine coupling

Orbital magnetic moments

- ◆ Circulating charge couples to a magnetic field
- ◆ Coupling described by magnetic moment, μ
- ◆ Proportional to the orbital angular momentum
- ◆ Quantum mechanical operator proportional to angular momentum operator
 - Bohr magneton, μ_B



$$\mu_L = \frac{\mu_B}{h} \mathbf{L}$$

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

Spin magnetic moments

- ◆ Similar to orbital magnetic moments
 - Proportional to spin angular momentum
 - Proportionality constant includes the **g factor**
- ◆ Magnitude of magnetic moment found by usual operation to find the magnitude of a vector

$$\mu_S = g\mu_B \mathbf{S}$$

$$|\mu_S| = \sqrt{\mu_S \cdot \mu_S} = g\mu_B \sqrt{S(S+1)}$$

Total magnetic moment

- ◆ When total angular momentum is important, there is a total magnetic moment
- ◆ Proportional to \mathbf{J}
- ◆ Relation to orbital and spin components more complicated

$$\mu_J = g_J \mu_B \mathbf{J}$$

$$g_J \cong 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

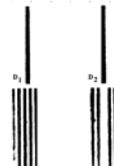
determined by J, L and S

Zeeman effect

- ◆ Coupling of magnetic moments to an applied magnetic field, \mathbf{B}
- ◆ Energy depends on the orientation of the magnetic moment in the field
- ◆ Zeeman energies depend on the quantum number, m
- ◆ Small effect
- ◆ Selection rules for spectroscopic transitions
 - $\Delta m_j = 0, \pm 1$

$$H_Z = -\mu \cdot \mathbf{B}$$

$$E_Z = -g_J \mu_B |\mathbf{B}| m_j$$



Magnetic susceptibilities

- ◆ Magnetic moments potentially give rise to magnetic susceptibility
 - Susceptibility is the ratio of the volume magnetic moment to the magnetic field
 - Caused by alignment of magnetic moments
- ◆ Measured by the magnetic force on a magnetizable sample
- ◆ Generally small (said to be **quenched**) when atoms are coupled to other atoms, as in solvation
 - Spin magnetization remains

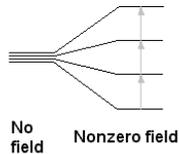
$$\mathbf{M} = \chi \cdot \mathbf{B}$$

$$\mathbf{M} = \frac{1}{V} \sum_j \mu_j$$

Magnetic resonance

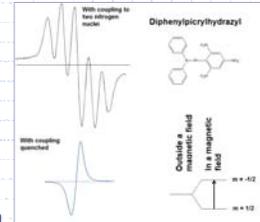
- ◆ Transitions among the magnetic states of a material occur
 - Very low energy compared to electronic-state separations
- ◆ Transitions between magnetic states of electron – **electron spin resonance**
- ◆ Transitions between magnetic states of a nucleus – **nuclear magnetic resonance**

$$\hat{H}_Z = -g\mu_B \hat{S} \cdot \mathbf{B} = -g\mu_B B_0 \hat{S}_z$$



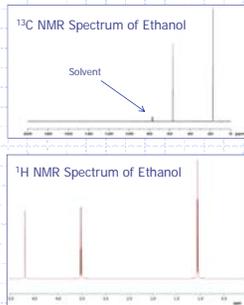
Electron spin resonance

- ◆ Transitions between electron spin states in a magnetic field
- ◆ Unpaired electrons
 - Example: DPPH, a stable radical
- ◆ Transition energy affected by coupling to nuclei (^{14}N) under certain conditions
 - Five (5) lines indicates coupling to two (2) nitrogen nuclei



Nuclear magnetic resonance

- ◆ Transitions among nuclear spin states in a magnetic field
- ◆ Shows
 - Types of nuclear centers
 - Connectivity of nuclear framework through nuclear-nuclear couplings
- ◆ Many different nuclei show this sort of spectrum
 - ^1H , ^{13}C , ^{23}Na , ^{31}P , ..., ^{207}Pb



Hyperfine coupling

- ◆ Like spin-orbit coupling
 - Two angular momenta coupled
 - Electronic and nuclear spins, S and I
- ◆ Energy depends on relative orientation of the nuclear and electronic spin angular momenta

$$H_{HF} = \frac{4\pi^2 A_{HF}}{h} \mathbf{I} \cdot \mathbf{S} = \frac{2\pi^2 A_{HF}}{h} \{T^2 - I^2 - S^2\}$$
- ◆ States that arise from different values of T have different energies

Hydrogen-atom hyperfine coupling

- ◆ Hydrogen atom has nuclear and electronic spin ($I = 1/2$ and $S = 1/2$)
- ◆ Total angular momentum, T , may be 1 or 0
- ◆ Transitions between states ($T=0 \leftrightarrow T=1$) occur
- ◆ Most accurately known fundamental constant
- ◆ Used in radio-astronomy to detect hydrogen

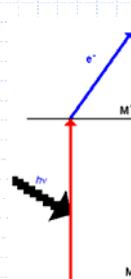
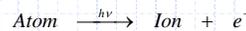
$$E_1 = \frac{hA_{HF}}{4}$$

$$E_0 = -\frac{3hA_{HF}}{4}$$

$$\Delta E_{HF} = hA$$

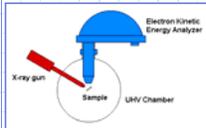
$$A = 1.4204057518 \text{ GHz}$$

Photoelectron spectroscopy

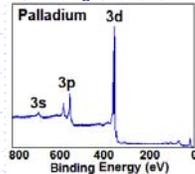
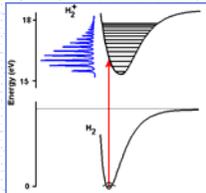


- ◆ Developed from Einstein's work
- ◆ Absorption of energy induces emission of electron
- ◆ Determine binding energy from kinetic energy of ejected electron
- ◆ Detects ionic state energies

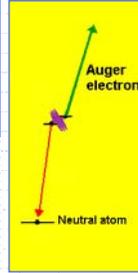
Photoelectron detection



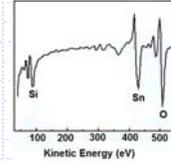
- ◆ Source: X-radiation
- ◆ Electron's kinetic energy determination
- ◆ Must be in high vacuum
- ◆ Determines the electronic state energies of the ion



Auger electrons

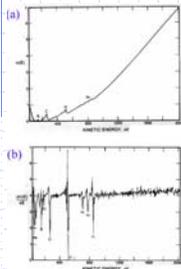


- ◆ Ejection of core electrons leaves the ion in an excited energetic state
- ◆ Relaxation by electrons dropping to replace the ejected electron sometimes causes ejection of further electrons with excess kinetic energy
- ◆ Measure the Auger electrons' energies to determine information on the atom
- ◆ Discovered by Lise Meitner (1923); rediscovered by Pierre Auger (1925)



Lise Meitner Pierre Auger

Auger spectroscopy



- ◆ Measure number of electrons escaping with a specific energy
- ◆ Usually plot the derivative rather than the signal
- ◆ Shown is the Auger spectrum of a contaminated nickel surface

From Hudson, J. B. *Surface Science*; Butterworth-Heinemann: Stoneham, MA; 1992.

Summary

- ◆ Angular momentum of charged particles is associated with a magnetic moment
 - Name depends on the angular momentum
- ◆ Coupling to a field causes energy differences among states
 - Labeled by m
- ◆ Spectroscopic transitions determine energy differences
 - Generally much lower energy
 - ◆ ESR
 - ◆ NMR
 - ◆ Hyperfine spectroscopy