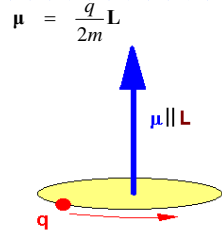


# Physical Chemistry

Lecture 21  
Atomic magnetism, photoelectron spectroscopy, and hyperfine coupling

## Orbital magnetic moments

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



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

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

## 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

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

$$g_L = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

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

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

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



## Magnetic susceptibilities

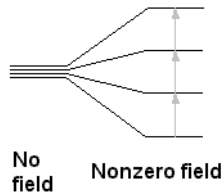
- ◆ Magnetic moments potentially give rise to magnetic susceptibility
  - Susceptibility is the ratio of the volume magnetic moment to the magnetic field
  - Caused by alignment of magnetic moments
- ◆ Measured by the magnetic force on a magnetizable sample
- ◆ Generally small (said to be **quenched**)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

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

$$\mathbf{M} = \frac{1}{V} \sum_j \boldsymbol{\mu}_j$$

## 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**



## 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

$$H_{HF} = \frac{4\pi^2 A_{HF}}{h} \mathbf{I} \cdot \mathbf{S} = \frac{2\pi^2 A_{HF}}{h} \{I^2 - I^2 - S^2\}$$

- ◆ States that arise from different values of T have different energies

## Hydrogen-atom hyperfine coupling

- ◆ Hydrogen atom has nuclear and electronic spin ( $I = \frac{1}{2}$  and  $S = \frac{1}{2}$ )
- ◆ 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

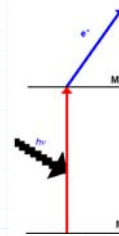
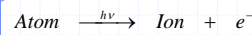
$$E_1 = \frac{hA_{HF}}{4}$$

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

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

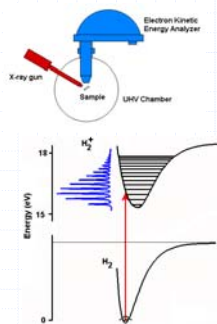
$$A = 1.4204057518 \text{ GHz}$$

## Photoelectron spectroscopy



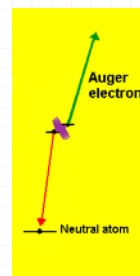
- ◆ Developed from Einstein's work
- ◆ Absorption of energy induces emission of electron
- ◆ Determine binding energy from kinetic energy of ejected electron
- ◆ Detects ionic state energies

## Photoelectron detection



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

## Auger electrons



- ◆ Ejection of electrons often leave the ion in an excited state
- ◆ Relaxation may produce ejection of further electrons
- ◆ Can measure the Auger electron energies to determine information on the atom

## 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