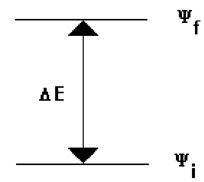
Physical Chemistry

Lecture 27
Spectroscopic Transitions

Nature of spectroscopic transition

- Change in the state of a system due to transfer of energy
- Wave function reflects this change
- Time-dependent process



$c_i = 1$, $c_f = 0$ ⇔ *before transition*

$c_i = 0$, $c_f = 1$ ⇔ *after transition*

$$\psi(t) = c_i(t)\psi_i + c_f(t)\psi_f$$

Time-dependent process

- Must use Schroedinger's time-dependent equation
- Hamiltonian consists of two parts
  - Stationary part that determines the energy levels
  - Time-dependent part that determines coupling that induces transition
- Gives the time-dependent coefficients, c_i and c_f

$$\frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar} H \Psi$$

$$H = H_0 + H_1(t)$$

Resonance

- For a coupling to have a strong effect on the time dependence of the coefficients, it must have the "proper" time dependence (given by its frequency)
- Resonant absorption

$$\omega = \frac{\Delta E}{\hbar}$$

Transfer rate

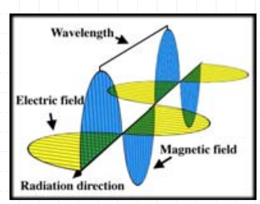
- Under resonant conditions, the rate of transfer is proportional to an integral
- Fermi's Golden Rule

$$Rate\ proportional\ to: \quad |<\psi_i | H_1 | \psi_f >|^2$$

- Basis for selection rules in spectroscopy

Light and radiation

- Light radiation is a time- and space-dependent energy field
- A system may couple to either the electric or magnetic field



Electric-dipole coupling

- An electric dipole couples to an electric field
- The energy of the dipole in the field depends on orientation

$$H_1(t) \quad = \quad \mathbf{d} \bullet \mathbf{E}(t)$$

- A mechanism of coupling between the spectroscopic system and the light

Selection rules

- Is the integral of the Golden Rule zero?
- Must know dipole form
  - A vector which can be shown to have components proportional to the cartesian co-ordinates
- Evaluation of integral becomes an evaluation of integral of x, y and z
- Can often evaluate integrals by knowing only certain properties of the wave functions

$$\int \psi_i^* x \psi_f d\tau$$

$$\int \psi_i^* y \psi_f d\tau$$

$$\int \psi_i^* z \psi_f d\tau$$

Summary

- Transitions are time-dependent processes
- Must use Schroedinger's time-dependent equation to explain
- Rate of transition determined by an integral over the states
  - Fermi's Golden Rule
- Evaluation of integrals can sometimes be done without knowledgeable of the total mathematical form of the wave functions