**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

\[ \psi_i \rightarrow \psi_f \]

\[ \Delta E = E_f - E_i \]

**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 \( c_f \)

\[ \frac{\partial \psi}{\partial t} = -\frac{i}{\hbar} \hat{H} \psi \]

\[ \hat{H} = \hat{H}_0 + \hat{H}_1(t) \]

**Resonance**

- For a coupling, such as a coupling of the dipole moment to a time-dependent electric field, to have a strong effect on the coefficients, it must have the "proper" time dependence (given by its frequency, \( \omega \))
- Resonant absorption occurs if matching occurs

\[ \omega = \frac{\Delta E}{\hbar} = \frac{E_f - E_i}{\hbar} \]

**Transfer rate**

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

\[ \text{Rate proportional to } | \langle \psi_i | \hat{H}_1 | \psi_f \rangle |^2 \]

- 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
  - Mostly consider coupling to the electric field of light

\[ \text{Wavelength} \]

\[ \text{Electric field} \]

\[ \text{Magnetic field} \]

\[ \text{Radiation direction} \]
Electric-dipole coupling

- An electric dipole couples to an electric field
- The energy of the dipole in the field depends on orientation
- A mechanism for coupling between the spectroscopic system and the light
- Rate \( \propto |\langle \psi_f | \hat{d} \cdot \mathbf{E}(t) | \psi_i \rangle|^2 \)
- \( \hat{H}_i(t) = \hat{d} \cdot \mathbf{E}(t) \)

Selection rules

- Is the integral of the Golden Rule zero?
- Must know dipole form
  - A vector (the dipole moment) 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

Summary

- Transitions are time-dependent processes
- Must use Schrödinger’s time-dependent equation
- Rate of transition determined by an integral over the states
  - Fermi’s Golden Rule
  - Electric dipole and magnetic dipole transitions
- Evaluation of whether integrals are zero can sometimes be without knowledgeable of the total mathematical form of the wave functions
- Selection rules