

Week 3

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3.1 Lecture 5: Quantum Principles for Spectroscopy (Part 2)

- 1/19:
- Today: How *light* interacts with molecules.
 - Review of the classical vs. quantum resonance criterion (driven harmonic oscillator vs. matching energy difference between states).
 - Reminder of spectroscopic notation: E'' (ground state) vs. E' (excited state).
 - Different types of transitions (electronic, vibrational, rotational) can be observed using different parts of the EM spectrum (UV/Vis, IR/Raman, FIR/ μ wave) as probes.
 - What does light actually do?
 - Quantum mechanically, it's coupling to the eigenstates of the system.
 - Quantum eigenstates are stationary.
 - Light couples two states, dragging them together and mathematically creating a superposition.
 - Example.

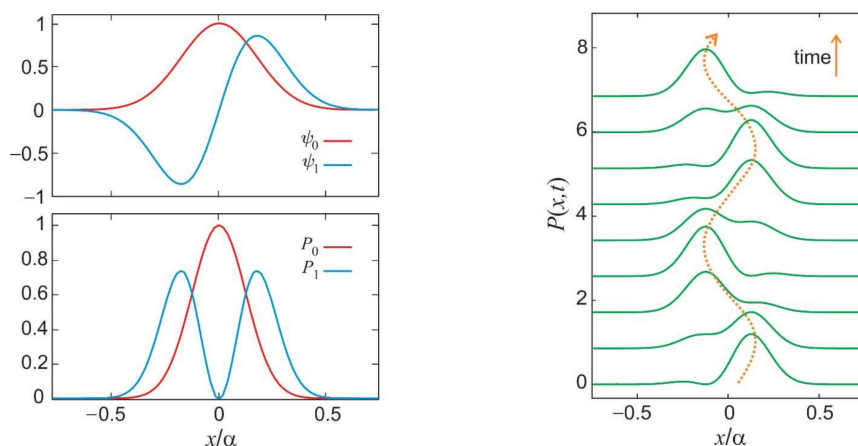


Figure 3.1: Light-induced coupling of quantum eigenstates.

- If we have two solutions to the particle in a box ψ_0, ψ_1 corresponding to the first and second energy levels, what light does is gives you a time-dependent wavefunction

$$\psi(t) = c_0(t)\psi_0 + c_1(t)\psi_1$$

- The probability that the particle is in one state or the other oscillates: Since $c_n(t) = c_n e^{-iE_n t/\hbar}$,

$$P_1 = |c_1(t)|^2 \approx \frac{\sin^2(E_1 - E_0)t}{\hbar} \qquad P_2 = |c_0(t)|^2 \approx \frac{\cos^2(E_1 - E_0)t}{\hbar}$$

- Electronic degrees of freedom can be discussed in the same way.
 - Light drives electrons back and forth (as per our classical molecule), but this time, we mathematically represent this change as a coupling of the s orbital and the more elongated p orbital.
- Factors governing absorption strength.
 - Beer's law.
 - Two important factors.
 1. Extinction coefficient.
 2. Concentration.
- Quantum mechanically, absorption strength depends on state population.
 - This is also a thermodynamic/statistical question.
 - Thermal energy is distributed via the Boltzmann distribution.
 - The probability of initially occupying an excited state increases with temperature.
- Thermal energy distributes molecules through states with different rotational and vibrational states.
- Worry if $E''_{\text{rot}}, E''_{\text{vib}} \leq 2k_B T$.
- Populations at higher states will give rise to additional features in the absorption spectrum.
- Final states don't matter for us because $E_{\text{final}} \gg k_B T$.
 - The only place where final energy matters is NMR because changes are so small; this is also why NMR is performed at cryogenic conditions.
- Transition dipole moment.
 - Classical (we need a change to grab onto) v. quantum (we take our transition dipole operator and square its expected value) again.
- Selection rules.
 - Light can drive a molecule to go up or down one vibrational quantum. This is not strictly true because most oscillators are *not* harmonic oscillators. Greater transitions are called **overtones**.
 - Rotations: Same type of thing with $\Delta J = \pm 1$.