

Week 9

Quantum Dynamics and Control

9.1 Time-Dependent Schrödinger Equation and Spectroscopy

11/29:

- From last time:

- The probability of a two-level system being in state 2 at time τ is

$$|a_2(\tau)|^2 \equiv a_2^*(\tau)a_2(\tau) \propto \frac{\sin^2[(E_2 - E_1 - \hbar\omega)t/2\hbar]}{(E_2 - E_1 - \hbar\omega)^2}$$

- When $\hbar\omega = E_2 - E_1$, you'll have the maximum resonance/strongest absorption and the peak in the graph of the sinc function.
- Leads to selection rules: Only certain states directly couple with a weak perturbation.

- Now consider the transition dipole moment:

$$(\mu_z)_{12} = \int \phi_2^* \mu_z \phi_1 \, dx$$

- The integral will vanish in the rigid rotor approximation.

- Up to the approximation of the rigid rotor, l can only change by ± 1 and m stays the same.

- Taking the harmonic oscillator as the paradigm for vibrational motion, we find that the quantum number must be $\Delta n = \pm 1$.

- The harmonic oscillator wave functions are of the form

$$\psi_n(x) = N_n H_n(\sqrt{\alpha}x) e^{-\alpha x^2/2}$$

where $\alpha = \sqrt{k\mu}/\hbar$.

- Assume $\alpha = 1$. Then $\psi_n = N_n H_n(x) e^{-x^2/2}$.
- We want to evaluate

$$(\mu_z)_{12} = \int \psi_{n'}(q) \mu_z(q) \psi_n(q) \, dq$$

where

$$\mu_z(q) = \mu_0 + \left(\frac{d\mu}{dq} \right)_{q=0} q + \dots$$

- This means that the transition dipole moment changes as a function of the bond length.
- When $q = 0$ (at equilibrium), the transition dipole moment is the equilibrium one (μ_0).
- Then we Taylor series expand to correct the transition dipole moment away from equilibrium.

– Therefore,

$$(\mu_z)_{nn'} \equiv \mu_0 \int_{-\infty}^{\infty} H_{n'}(q) H_n(q) e^{-q^2} dq + \left(\frac{d\mu}{dq} \right)_{q=0} \int_{-\infty}^{\infty} H_{n'}(q) q H_n(q) e^{-q^2} dq + \dots$$

■ The first term goes to zero as long as $n \neq n'$ because the Hermite polynomials are orthonormal.

– Recall that we used a recurrence relation to define the Hermite polynomials.

– In addition to the one we used previously, we have the recurrence relation

$$qH_n(q) = nH_{n-1}(q) + \frac{1}{2}H_{n+1}(q)$$

for all n .

– Thus,

$$\int_{-\infty}^{\infty} H_{n'}(q) q H_n(q) e^{-q^2} dq = \int_{-\infty}^{\infty} H_{n'}(q) \left[nH_{n-1}(q) + \frac{1}{2}H_{n+1}(q) \right] e^{-q^2} dq$$

– Thus, unless $n' = n \pm 1$, the integral vanishes.

– This is the selection rule!

- Note that we're just tickling the molecule with a bit of radiation to get this to happen — if we hit it with too hard of a hammer, the selection rule will no longer hold.

- Spectroscopy.

– $\Delta E = E_n - E_l = h\nu$.

– Regions of EM:

Region	Microwave	Far IR	IR	Vis/UV
Wavenumber (cm ⁻¹)	0.033 – 3.3	3.3 – 330	330 – 14 500	14 500 – 500 000
Molecular property	Rotation of polyatomics	Rotation of small molecules	Vibration	Electron transitions

Table 9.1: Spectroscopy in various regions of the electromagnetic spectrum.

- The Schrödinger equation within the Born-Oppenheimer approximation:

$$\left[\sum_A \left(-\frac{\nabla_A^2}{2} \right) + \hat{H}_{\text{elec}} \right] \psi_{\text{elec}} \psi_{\text{nucl}} = (E_{\text{elec}} + E_{\text{nucl}}) \psi_{\text{elec}} \psi_{\text{nucl}}$$

– We invoke the Born-Oppenheimer approximation to split the wavefunction into electronic and nuclear components.

- We then split this equation into two parts. The first of which is the electronic Schrödinger equation

$$\hat{H}_{\text{elec}} \psi_{\text{elec}} = E_{\text{elec}} \psi_{\text{elec}}$$

– The BO approximation is what allows us to split the original Schrödinger equation in two.

- We now multiply by ψ_{elec} and integrate over all of the electrons.

$$\left[\sum_A \left(-\frac{\nabla_A^2}{2} \right) + V(R) \right] \psi_{\text{nucl}} = (E_{\text{elec}} + E_{\text{nucl}}) \psi_{\text{nucl}}$$

– $V(R) = E_{\text{elec}}(R) = \int \psi_{\text{elec}}^* \hat{H}_{\text{elec}} \psi_{\text{elec}} dx$ is the potential energy surface (PES).