

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).

9.2 Spectroscopy (cont.)

- 12/1: • From last time, we have that

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

- The PES is $V(R) = \int \psi_{\text{elec}}^* \hat{H}_{\text{elec}} \psi_{\text{elec}} dx$.
- This begins to break down where we have **conical intersections**.
- **Conical intersection:** An intersection between potential energy surfaces, where electrons can jump from one to the other.
 - Allows for radiation-less transitions from one surface to another.
- Potential energy surface^[1] for the ground electronic wave function and its surface.
 - Think Figure 3.1b with its zero-point energy in the HO approximation.
 - The energies of the vibrational levels get closer and closer together until they're continuous forming a continuum at the level of the asymptote, reaching the classical limit.
- We have that

$$\begin{aligned} E_{\text{nucl}} &\approx E_{\text{HO}} + E_{\text{RR}} \\ &\approx \hbar\omega\left(n + \frac{1}{2}\right) + \frac{\hbar^2}{2I}l(l+1) \end{aligned}$$

- Since harmonic oscillator transitions are in the IR region and rigid rotor transitions are in the microwave region, vibrational transitions are of higher energy ($\hbar\omega > \hbar^2/2I$).
- Rotational levels.

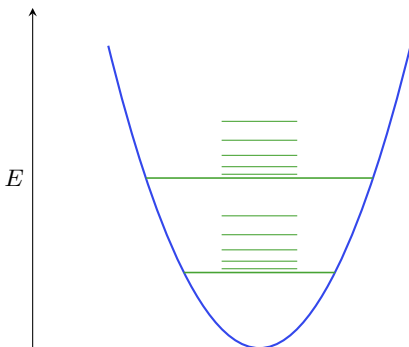


Figure 9.1: Rotational and vibrational energy levels.

- Each vibrational energy level has a number of smaller rotational states that are part of it.
- Changes in rotational levels often accompany changes in vibrational levels.
 - If we change the vibrational level by ± 1 , we have to change the rotational level (by ± 1) as well.

¹Note that we technically have a potential energy curve at this point; we will only have a surface in higher-dimensional systems.

- IR/vibrational spectroscopy.

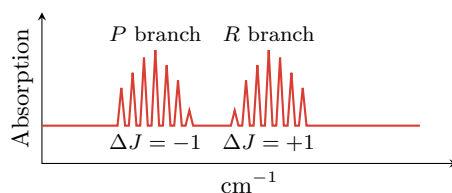


Figure 9.2: IR/vibrational spectrum.

- The whole spectrum represents a rovibrational transition.
- The *P* branch corresponds to when you go from a lower vibrational state to a higher vibrational state, *but* you go from a higher rotational state to a lower rotational state.
- The *R* branch corresponds to when you go from a lower vibrational state to a higher vibrational state, *and* you go from a lower rotational state to a higher rotational state.
- The number of peaks in the *R* and *P* branches reveals which rotational states are occupied (although we could theoretically go on forever, realistically, only lower energy rotational states are occupied).

- Electronic states.

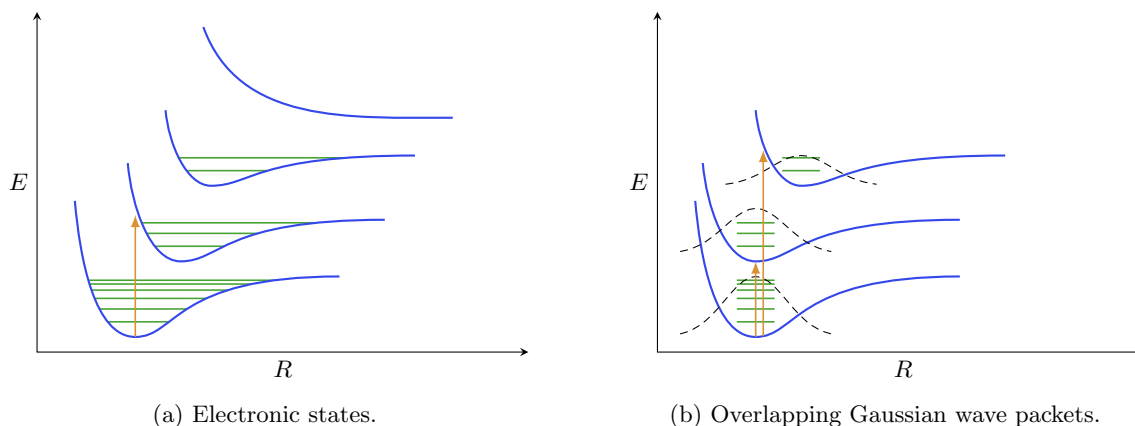
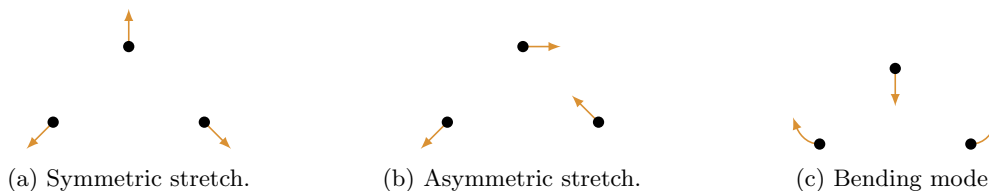


Figure 9.3: Exciting between electronic states.

- You can also do excitations from one potential energy surface to another.
- Recall that we have a Gaussian wave packet around the minimum energy on the PES.
- It's important that our Gaussian wave packets have some overlap for us to jump from one PES to the other.
- In Figure 9.3b, we'd expect a much higher probability of electronic transitions to the PES's with significant orbital overlap than from either to the third, where there is much less overlap.
- **Franck-Condon Principle**^[2]: The intensity of the transitions is proportional to the product of two harmonic oscillator wave functions — ψ_1 from the one vibrational state and ψ_2 from the other vibrational state.
- In a polyatomic molecule, any bond can be approximated as a spring, and any spring can be approximated as a harmonic oscillator.

²Developed at UChicago!

- Thus, any polyatomic molecule can be thought of as a bunch of harmonic oscillators linked together.
- Normal modes and normal coordinates:
 - Degrees of freedom: $3N$ (x, y, z coordinates).
 - There are translational, vibrational, and rotational DOFs.
 - We always have 3 translational DOFs, 2 or 3 rotational DOFs (depending on whether or not the molecule is linear), and $3N - 5$ or $3N - 6$ vibrational DOFs (depending on whether or not the molecule is linear once again).
 - Taking the right linear combinations of coupled oscillator stretches gives normal modes that are orthogonal to each other.
 - Diagonalizing gives normal modes that are decoupled from each other.
- Example (H_2O):

Figure 9.4: Normal modes of H_2O .

- 3 vibrational modes.
- Symmetric stretch, asymmetric stretch, and bending mode.
- Their respective frequencies are $\nu_1 = 3650 \text{ cm}^{-1}$, $\nu_2 = 3760 \text{ cm}^{-1}$, and $\nu_3 = 1600 \text{ cm}^{-1}$.

9.3 Chapter 13: Molecular Spectroscopy

From McQuarrie and Simon (1997).

- 11/30:
- **Spectroscopy:** The study of the interaction of electromagnetic radiation with atoms and molecules.
 - “Electromagnetic radiation is customarily divided into different energy regions reflecting the different types of molecular processes that can be caused by such radiation” (McQuarrie & Simon, 1997, pp. 495–96).
 - Vibrational selection rule: Transitions among vibrational levels resulting from the absorption of radiation have $\Delta v = \pm 1$ and have a dipole moment that varies during the vibration.
 - For a harmonic oscillator, the spectrum consists of one line in the infrared region at the frequency $\nu_{\text{obs}} = \sqrt{k/\mu}/2\pi$.
 - **Vibrational term:** The vibrational energy of a molecule. Denoted by $G(v)$. Units cm^{-1} . Given by

$$G(v) = \frac{E_v}{hc}$$

where $E_v = (v + 1/2)h\nu$ and $\nu = \sqrt{k/\mu}/2\pi$.

- Each energy $E_J = \hbar^2/(2I) \cdot J(J + 1)$ of the rigid rotator is associated with degeneracy $g_J = 2J + 1$.