What variables do we need to characterize a molecule?

Nuclear and electronic configurations: What is the structure of the molecule? What are the bond lengths? How strong or stiff are the bonds? What is the symmetry? Where is the electron density?

Molecular Behavior: How much do the nuclei move (vibration/rotation)? How do the structural variables change with time?

**EXAMPLE: H–F**

What is your picture of the structure of this molecule? 2 nuclei + 10 e⁻? Molecular orbitals?

\[
\psi^{ab} = c_1 \psi_{1s}^{H} + c_2 \psi_{2p_z}^{F} \\
\psi^{ab} = c_2 \psi_{1s}^{H} - c_1 \psi_{2p_z}^{F}
\]

We quantitatively characterize the structure through the electronic energy as a function of nuclear configuration:

\[
E_{\text{elec}} = \text{electronic energy relative to isolated atoms}
\]
If we characterize this energy curve, we have learned much about our molecule:

1) \( r_e \): What is the equilibrium separation between atoms?
2) \( D_0 \): What is the strength of the bond? How stable is molecule?
3) Shape of \( \psi^b \) or \( \psi^{ab} \): Is \( r_e \) fixed? How stiff is bond? How does \( r_e \) change if you put energy into bond?
4) Splitting between surfaces: What is the nature and energy of the e\(^-\) orbitals involved in bonding?

How can you probe these energy surfaces with light?

- The light field will exert a force on the charged particles. Different frequencies of light will interact with the particles depending on: (1) if they are nuclei or electrons, and (2) the shape of the potential for the particle.
- The potential energy reflects the coulombic interactions between the charged nuclei and electrons.

Different frequencies of light will interact with different nuclear and electronic motions. To simplify problem, treat nuclear and electronic motion separately.

- 5.61: The basis for drawing these curves is the Born-Oppenheimer Approximation: Motion of electron is much faster than nuclei; doesn’t depend on nuclear kinetic energy.
- More generally, for any particle (nucleus or electron):

  Kinetic and potential energy associated with the motion of a particle

  Translation along \( x, y, z \rightarrow n \) particles \( \rightarrow 3n \) degrees of freedom (d.o.f).

  We usually think of this as the laboratory frame of reference.

- Energy involved in different motions varies.
- Separate different types of motion based on time-scale or energy of motion.

Change to a new set of internal coordinates

Electrons: the spatial extent motion is described by atomic or molecular orbitals.
**Nuclei:** Three types of motion for nuclei where the frame of reference originates at the center of mass.

\[ r_0 = \frac{1}{M} \sum m_i r_i \]

Consider a diatomic (with 6 d.o.f). Motion with respect to the (c.o.m.) of the molecule:

1) **Vibration:** along \( r \).
   - Displacement of atoms relative to one another / C.O.M. fixed

2) **Rotation**
   - Motion about C.O.M. / C.O.M. fixed

3) **Translation**
   - Move C.O.M.

For a polyatomic (n atoms) \( \rightarrow 3n \) degrees of freedom

<table>
<thead>
<tr>
<th></th>
<th><strong>Linear</strong></th>
<th><strong>Nonlinear</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>vibrational</td>
<td>3n–5</td>
<td>3n–6</td>
</tr>
<tr>
<td>rotational</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>translational</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

We would like to characterize the nature of these and how this reflects electronic potential. Different spectroscopies reflect different types of motion of particles.

What we will find is that different spectroscopies will tell us about different variables:

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Rotational spectroscopy: will tell us where $r_e$ is.

Vibrational spectroscopy: will tell us how stiff the bond is and about the curvature of potential.

Electronic spectroscopy: will tell us about where electronic states lie → potential energy curves.

A classical description allows you to say a lot about spectroscopy, but it doesn’t explain experiments very well! We need quantum mechanics!

- The energy that we can impart to a (molecular) system through the motion of one of these degrees of freedom is not continuous, but comes in discrete quantities.

- Energy levels are quantized—discrete, not continuous.

Classically, we think of no restriction on the energy needed to move a particle or the potential energy a particle may have. (If we put energy into a system to move a particle, we can add or remove this energy continuously.)

Quantum mechanics tells us that these energies are not continuous but discrete. Rather than continuing energy for a motion, we have quantized energy levels. → These “states” define the motion of a particle with a unit of energy, and no fractional amount is allowed.

- We represent the state of the system through quantum numbers—usually integers. The energy is related to these numbers.

The motion of any particle has 3 degrees of freedom associated with it—x, y, z—and we are going to talk about how energies associated with these motions are quantized.

“Ground State”: configuration of electrons, nuclei, … (a set of quantum numbers) that represent the lowest energy state of the system.

**Electronic States:**

We already started this lecture talking about atomic + molecular orbitals, which represent discrete energy states that electrons can occupy. You describe these through discrete quantum numbers, i.e. for atom: $n, l, m, m_s$

$n$: principle quantum number; $l$: orb. ang. mom.; $m$: degeneracy; $m_s$: spin

- These states have definite energy and electron density *distribution* (spatial dimension).
• There is no way for an electron to occupy an intermediate energy between quantized values.

• The energy to move an electron from the ground (lowest energy) state to another is a lot: Typically 20,000-100,000 cm\(^{-1}\) = 10-50 kJ/mol. This corresponds to UV and visible light, \(\lambda\sim 100-500\text{nm}\)

• For polyatomic molecules, we can use linear combinations of atomic orbitals.

**Quantization is also required for the energies corresponding to the nuclear degrees of freedom:**

There are 3 degrees of freedom for each nucleus, and in a molecule with \(n\) nuclei we partition the \(3n\) d.o.f. into vibration, rotation, and translation—each of these motions is quantized.

**Vibrations:**

**Classically** I can put any energy I want into vibrational motion \(\rightarrow\) moves energy levels to higher displacement. For a harmonic oscillator:

\[
E = V + T = \frac{1}{2}kQ^2 + \frac{p^2}{2m}
\]

\(Q(t) = A \sin \omega_0 t\)

**Quantum mechanics** says there are discrete vibrational energy levels corresponding to specific vibrational states (wave functions).

Each vibrational state has a probability distribution that tells me the probability of finding nuclei in particular position. (similar to electronic states)

**For a quantum mechanical H.O.,** (the simplest quantum
mechanical model for a vibration), the energies of these discrete vibrational energy levels is:

\[ E_v = E_{\text{vib}} = \hbar \omega_0 \left( v + \frac{1}{2} \right) \]

\[ \omega_0 = \sqrt{\frac{k}{m_R}} = 2\pi v_0 \]

\[ \frac{\omega_0}{2\pi c} \approx 3000 - 300 \text{ cm}^{-1} \]

typically 3-30 \( \mu \text{m} \) (Mid-IR)

- \( v \) is the vibrational quantum number, \( v = 0,1,2… \)
- Even in lowest state \( E_0 = h\nu_0 / 2 \).
- Spacing between vibrational levels uniform

\[ \Delta E = E_v - E_{v-1} = \hbar \omega_0 \]

- The proportionality constant between vibrational frequency and energy is Planck’s constant \( h = 6.626 \times 10^{-34} \text{ J s} \)
- So if we can measure \( E_v \) → determine \( \omega_0 \) → determine \( k \).

**Rotations:**

Classically, rotation is governed by angular momentum \( L=I\omega \) (equiv. to \( p=mv \) of linear motion)

\( \omega \) is the angular velocity \( (\omega=2\pi v) \)

Moment of Inertia \( I = m_r R_e^2 \) or \( I = \sum_i m_i r_i^2 \)

The energy of free rotational motion is all kinetic:

\[ E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \quad \text{linear motion} \]

\[ E = \frac{1}{2}I\omega^2 = \frac{\omega^2}{2I} \quad \text{angular motion} \]

- Classically, the more energy I put into a rigid rotor, the faster it rotates → higher angular momentum.
• **Quantum mechanically** rotational angular momentum is quantized.

\[
E_{\text{rot}} = \frac{\Gamma^2}{2I} \quad \text{still holds, but } L \text{ is quantized}
\]

\[
|L| = \hbar \sqrt{J(J+1)} \quad J = 0,1,2,3 \ldots \quad (\text{rotational angular momentum quantum number})
\]

\[
E_{\text{rot}} = \frac{\hbar^2}{2I} J(J+1) = \frac{\hbar}{8\pi^2I} J(J+1) \equiv h\bar{B}J(J+1)
\]

\[
\bar{B} = \frac{\hbar}{8\pi^2cI} \quad \text{(in cm}^{-1}\text{)} \quad \text{typically 0.1-10 cm}^{-1} \quad \text{(FIR/µwave)}
\]

• Rotational levels are not equally spaced.
• Rotational levels have degeneracy. \(M_J = 0 \pm J; \quad g(J) = (2J+1)\)
• Rotational spectroscopy: measure \(E_{\text{rot}}\) → determine \(\bar{B}\) → \(I\) → \(r_e\)!

**TRANSLATION:** (motion of center of mass)

Quantum mechanically: Energy levels given by particle-in-a-box

One-dimension: \(E_{\text{trans}} = \frac{n^2\hbar^2}{8ma^2} \quad n = 1,2 \ldots \quad a: \text{length of box}\)

• This only matters for very small boxes.
• Free space: \(a \to \infty; \quad \text{energy levels are continuous.}\)

*Quantum mechanical energies are summed over all degrees of freedom:*
\[ E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{translational}} + E_{\text{nuclear}} + \ldots \]

\[ E = E_{\text{elec}} + \hbar \omega_0 \left( v + \frac{1}{2} \right) + \hbar c B J (J + 1) + \ldots \]

\[ \Delta E \approx 50,000 \text{ cm}^{-1} \quad \sim 1,000 \text{ cm}^{-1} \quad \sim 1-10 \text{ cm}^{-1} \]

- specify energy through a set of quantum numbers, and characteristic vib./rot./etc. constants

**Diagram:***

**Electronic**

- \( S_0 \)
  - \( v = 0 \)
  - \( v = 1 \)
  - \( v = 2 \)
  - \( v = 3 \)
- \( h\nu_0 \)

**Vibrational**

- \( S_1 \)
  - \( v = 0 \)
  - \( v = 1 \)
  - \( v = 2 \)
  - \( v = 3 \)
  - \( v = 0 \)

**Rotational**

- \( J = 0 \)
  - \( J = 1 \)
  - \( J = 2 \)
  - \( J = 3 \)
- \( 2\hbar c B \)
**LIGHT:**

Classically we talked about a light field driving a classical H.O. The external field allows us to drive the H.O. to higher displacement, the efficiency of displacing the oscillator depended on resonance: \( \omega = \omega_0 \)

How is this compatible with quantum energy levels?

To drive a quantum H.O. to higher amplitude \( \rightarrow \) higher energies \( \rightarrow \) higher V \( \rightarrow \) transitions are discrete!

- Light drives transitions between discrete states.
- Transition requires resonance.
- Light is also quantized: \( E = h\nu = \hbar \omega \)

Resonance \( \leftrightarrow \) Energy conservation

Energy of light = Energy difference between initial (i) and final (f) states

\[
E = E_f - E_i
\]

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

- **Absorption features related to energy level splittings!**

These transitions can be between different electronic, vibrational, rotational states:

\[
E_{\text{field}} = \Delta E_{\text{elec}} + \Delta E_{\text{vib}} + \Delta E_{\text{rot}} + \ldots
\]

<table>
<thead>
<tr>
<th>Spectroscopy</th>
<th>Light Freq.</th>
<th>Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rot-vib.: IR/Raman</td>
<td>UV/Vis 10^4-10^5 cm^{-1}</td>
<td>electronic (+ vib + rot)</td>
</tr>
<tr>
<td>pure rot.: FIR/µwave</td>
<td>10^2 – 10^3 cm^{-1}</td>
<td>vibrational (+ rot)</td>
</tr>
<tr>
<td></td>
<td>10^{-1} – 10 cm^{-1}</td>
<td>rotational</td>
</tr>
</tbody>
</table>

initial state: \( v'', J'' \) (double primed)

final state: \( v', J' \) (single primed)
In a quantum system . . . what does light do to energy levels?

Quantum eigenstates are time-independent (stationary). There is no motion.

We shouldn’t think of absorption as taking molecules from one eigenstate and putting it in another—that’s not quite correct. Rather, the light couples these two states together.

What is the state of a vibration after turning on a light field?

\[ \psi(t) = c_0(t) \psi_0 + c_1(t) \psi_1 \]

\[ P_1 = |c_1(t)|^2 \propto \sin(E_1 - E_0) t / \hbar \]

\[ P_0 = 1 - |c_1(t)|^2 \propto \cos(E_1 - E_0) t / \hbar \]

The probability of finding the system in one state oscillates back and forth.

\[ P_{\text{tot}} = P_1 + P_0 \]
Intensity of absorption lines
What influences the strength of a line?

1) Population

Classically: Number of molecules — N → Beers Law

Quantum mechanically: What really matters is the population difference between the two quantum states!

\[ \Delta N = N_f - N_i \]

- The population of a quantum state – the fraction of molecules occupying that state – is dictated by the temperature.
- For many molecules, the particles distribute themselves through quantum states.
- Lowest E state is most probable. At T = 0 K all molecules are in the ground state—lowest electronic state, \( v = 0, J = 0 \).
- The equilibrium-thermal-energy that a collection of ensemble of molecules has is characterized by the temperature.

- The fraction of molecules occupying a quantum level of energy \( E_i \) at a temperature \( T \) is described by the

**Boltzmann distribution** (a probability function):

\[ N_i = \frac{1}{q} g_i \exp\left(-\frac{E_i}{k_B T}\right) \]

- \( N_i \) is the fraction of molecules in state \( i \).
- \( g_i \) is the degeneracy of the \( i^{th} \) state.
- \( q \), the partition function, is a sum over the population of all states

\[ q = \sum_i g_i \exp\left(-\frac{E_i}{k_B T}\right). \]

- \( k_B \) is the Boltzmann constant (1.38\( \times 10^{-23} \) J/K).
- \( \hbar c/k_B = 1.44 \text{ cm}^{-1} \text{ K} \)
At room temperature (300 K), $k_B T/\hbar c = 208 \text{ cm}^{-1}$. This means that energy states near or below 200 cm$^{-1}$ will have thermal population at room temperature. These are typically only rotational states in the ground vibrational and ground electronic state.

2) **What allows light to interact with molecules?**

The strength of the transition is dictated by the change in the dipole moment with coordinate.

\[
\text{dipole moment} \rightarrow \text{selection rules!}
\]

Selection rules tell you whether absorption or more generally a quantum transition is allowed.

**Classically:** Absorption requires change of dipole moment

\[a) \quad \frac{\partial \mu}{\partial Q} \rightarrow \text{vibration} \]

\[b) \quad \text{rotation requires polar molecule!} \]

**Quantum:** Transition dipole matrix element. The probability of transition (the transition amplitude is related to $\int \psi_\text{final}^* \hat{\mu} \psi_\text{initial} \, dr$

\[\hat{\mu} = \sum_i q_i \hat{r}_i \text{ is the dipole operator} \]

**Vibrations:** For a quantum H.O. : $\Delta v = \pm 1$ \((\frac{\partial \mu}{\partial Q} \text{ parallel to symmetry axis})\)

\[\text{H.O.} : \quad \int \psi_f^* q \hat{x} \psi_i \, dx \neq 0 \quad \text{if} \ f = i \pm 1 \]

Anharmonic oscillator $\Delta v$ relaxed.

**Rotations:** Photons also have angular momentum and to conserve A.M:

For a rigid rotor: $\Delta J = \pm 1$

For polyatomics $\partial \mu / \partial q \perp$ to symmetry axis $\Delta J = -1, 0, +1$. 

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