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

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

    - 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,

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

  ■ 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,

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

- 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:

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

  - 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

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

  - 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.

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

  - $V(R) = E_{\mathrm{elec}}(R) = \int \psi_{\mathrm{elec}}^* \hat{H}_{\mathrm{elec}} \psi_{\mathrm{elec}} \, \mathrm{d}x$ 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 $V(R) = \int \psi_{\text{elec}}^* \hat{H}_{\text{elec}}\psi_{\text{elec}}\,\mathrm{d}x$.
  - 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

$$E_{\text{nucl}} \approx E_{\text{HO}} + E_{\text{RR}}$$

$$\approx \hbar\omega(n + \tfrac{1}{2}) + \frac{\hbar^2}{2I}l(l+1)$$

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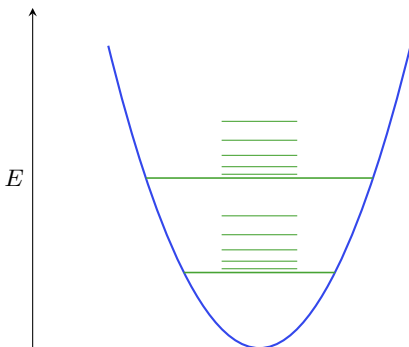
- Rotational levels.

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.

---

[1]Note that we technically have a potential energy curve at this point; we will only have a surface in higher-dimensional systems.
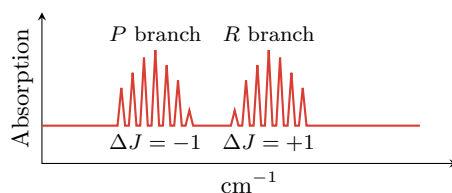
- IR/vibrational spectroscopy.

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).
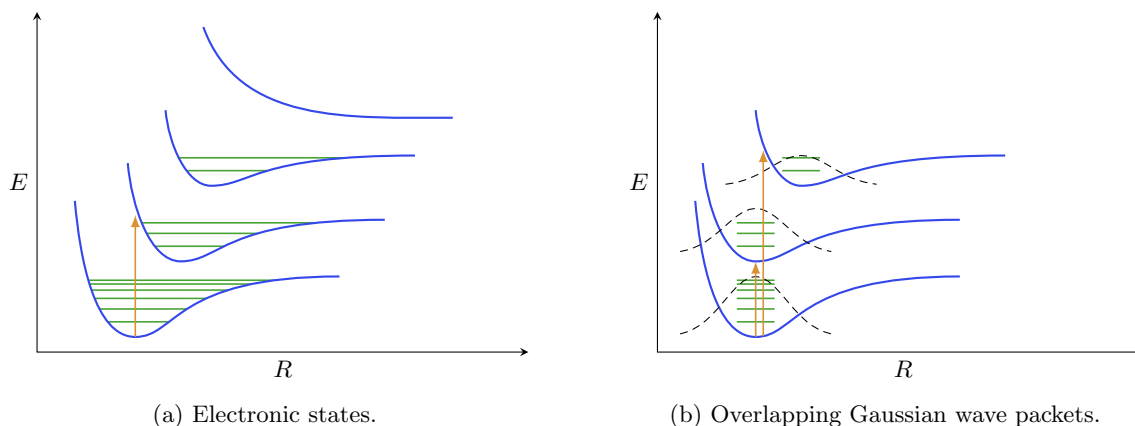
- Electronic states.

(a) Electronic states.

(b) Overlapping Gaussian wave packets.

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.

---

[2]Developed 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):

(a) Symmetric stretch.   (b) Asymmetric stretch.   (c) Bending mode.
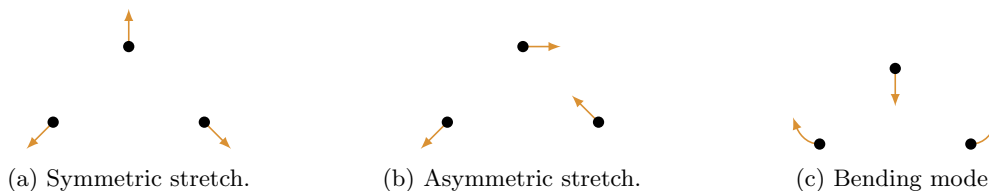
Figure 9.4: Normal modes of H_2O.

  - 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* $\boldsymbol{G(v)}$. *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 $g_J = 2J + 1$.

12/1:   • **Rotational term**: The rotational energy of a molecule. *Denoted by* $F(J)$. *Units* cm^{-1}. *Given by*

$$F(J) = \frac{E_J}{hc}$$

• Rotational selection rule: Transitions among rotational levels resulting from the absorption of radiation have $\Delta J = \pm 1$ and have a permanent dipole moment.

• The rotational and vibrational energy of a diatomic molecule within the rigid rotator-harmonic oscillator approximation is
$$\tilde{E}_{v,J} = G(v) + F(J) = (v + \tfrac{1}{2})\tilde{\nu} + \tilde{B}J(J+1)$$
where $\tilde{\nu} = \sqrt{k/\mu}/2\pi c$, $\tilde{B} = h/8\pi^2 cI$, and $v, J = 0, 1, 2, \ldots$.

  – Since $\tilde{\nu}$ and $\tilde{B}$ are on the order of $1 \times 10^3\,\text{cm}^{-1}$ and $1\,\text{cm}^{-1}$, respectively, vibrational energy levels are usually spaced about 100 to 1000 times farther apart than rotational energy levels.

• Rovibrational selection rule: $\Delta v = \pm 1$ and $\Delta J = \pm 1$.

• Observed frequencies for rovibrational transitions.

  – $\Delta J = +1$.
  $$\tilde{\nu}_{\text{obs}} = \tilde{E}_{v+1,J+1} - \tilde{E}_{v,J} = \tilde{\nu} + 2\tilde{B}(J+1)$$

  – $\Delta J = -1$.
  $$\tilde{\nu}_{\text{obs}} = \tilde{E}_{v+1,J-1} - \tilde{E}_{v,J} = \tilde{\nu} - 2\tilde{B}J$$

  – Note that J is the initial quantum number in both of the above equations.

• **R branch**: The series toward the high-frequency side of the rotational-vibrational spectrum, due to rotational transitions with $\Delta J = +1$.

• **P branch**: The series toward the low frequency side of the rotational-vibrational spectrum, due to rotational transitions with $\Delta J = -1$.

• **Vibration-rotation interaction**: The decrease in $\tilde{B}$ as v increases.

  – Cause: As v increases, R_e (the equilibrium bond length) increases (Figure 3.1a). Thus $\tilde{B} \propto 1/R_e$ decreases.

• Thus, for the $v = 0 \to 1$ transition, the frequencies of the R and P branches are truly given by

$$\tilde{\nu}_R = E_{1,J+1} - E_{0,J} = \tilde{\nu} + 2\tilde{B}_1 + (3\tilde{B}_1 - \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$
$$\tilde{\nu}_P = E_{1,J-1} - E_{0,J} = \tilde{\nu} - (\tilde{B}_1 + \tilde{B}_0)J + (\tilde{B}_1 - \tilde{B}_0)J^2$$

for $J = 0, 1, 2, \ldots$ and $J = 1, 2, 3, \ldots$, respectively.

  – $\tilde{B}_v$ denotes the value of $\tilde{B}$ at vibrational energy level v.
  – The above equations reduce to the original ones for $\tilde{B}_1 = \tilde{B}_0$.
  – Since $\tilde{B}_1 < \tilde{B}_0$, "the spacing between the lines in the R branch decreases and the spacing between the lines in the P branch increases with increasing J" (McQuarrie & Simon, 1997, p. 502).

• The dependence of $\tilde{B}$ on v is usually expressed as

$$\tilde{B}_v = \tilde{B}_e - \tilde{\alpha}_e(v + \tfrac{1}{2})$$

• Rotational lines are not exactly equally spaced since a chemical bond stretches due to the centrifugal force as a molecule rotates more and more energetically.

– This small deviation from the rigid rotator approximation can be treated by perturbation theory, resulting in

$$F(J) = \tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2$$

where $\tilde{D}$ is the **centrifugal distortion constant**.

– Modified frequencies of the absorption:

$$\tilde{\nu} = F(J+1) - F(J) = 2\tilde{B}(J+1) - 4\tilde{D}(J+1)^2$$

– Rotational energy levels of a nonrigid rotator are spaced closer together than those of a rigid rotator.

- The harmonic-oscillator approximation of a vibrating diatomic predicts only one line in its vibrational spectrum.

    – However, while there is an experimental **fundamental**, there are also **overtones**.

- **Fundamental**: The dominant line in the vibrational spectrum of a diatomic molecule.

- **Overtone**: A line in the vibrational spectrum of a diatomic molecules of weaker intensity than the fundamental, appearing at an almost integral multiple of the fundamental.

- Terms past the quadratic in the Taylor series expansion of the potential energy well $V(R)$ about the equilibrium bond length R_e can be accounted for by applying perturbation theory to the harmonic oscillator approximation.

    – Doing so gives rise to the vibrational term

    $$G(v) = \tilde{\nu}_e(v + \tfrac{1}{2}) - \tilde{x}_e\tilde{\nu}_e(v + \tfrac{1}{2})^2 + \cdots$$

    for $v = 0, 1, 2, \ldots$, where $\tilde{x}_e$ is the **anharmonicity constant**.

    – The separation between the energy levels of an anharmonic oscillator decreases with increasing v.

    – "The selection rule for an anharmonic oscillator is that Δv can have any integral value, although the intensities of the $\Delta v = \pm 2, \pm 3, \ldots$ transitions are much less than for the $\Delta v = \pm 1$ transitions" (McQuarrie & Simon, 1997, p. 506).

    – Since most diatomics are in the ground vibrational state at room temperature, the frequencies of the observed $0 \to v$ transitions will be

    $$\tilde{\nu}_{\mathrm{obs}} = G(v) - G(0) = \tilde{\nu}_e v - \tilde{x}_e\tilde{\nu}_e v(v+1)$$

    for $v = 1, 2, \ldots$.

- "Just as rotational transitions accompany vibrational transitions, both rotational and vibrational transitions accompany electronic transitions" (McQuarrie & Simon, 1997, p. 507).

- The BO approximation allows us to separate the electronic energy from the vibrational-rotational energy since vibration and rotation, overall, are nuclear-motion phenomena.

- **Vibronic transition**: A vibrational transition in an electronic spectrum.

- Vibronic selection rule: Δv may take on any integral value.

    – Rotational transitions in electronic spectra are not considered because they are so much smaller.

- Vibronic transitions usually originate from the $v = 0$ vibrational state, yielding predicted frequencies

$$\tilde{\nu}_{\mathrm{obs}} = \tilde{T}_e + (\tfrac{1}{2}\tilde{\nu}'_e - \tfrac{1}{4}\tilde{x}'_e\tilde{\nu}'_e) - (\tfrac{1}{2}\tilde{\nu}''_e - \tfrac{1}{4}\tilde{x}''_e\tilde{\nu}''_e) + \tilde{\nu}'_e v' - \tilde{x}'_e\tilde{\nu}'_e v'(v'+1)$$

where $\tilde{T}_e$ is the difference in energies of the minima of the two electronic potential energy curves in wave numbers, and the single and double primes indicate the upper and lower energy states, respectively.
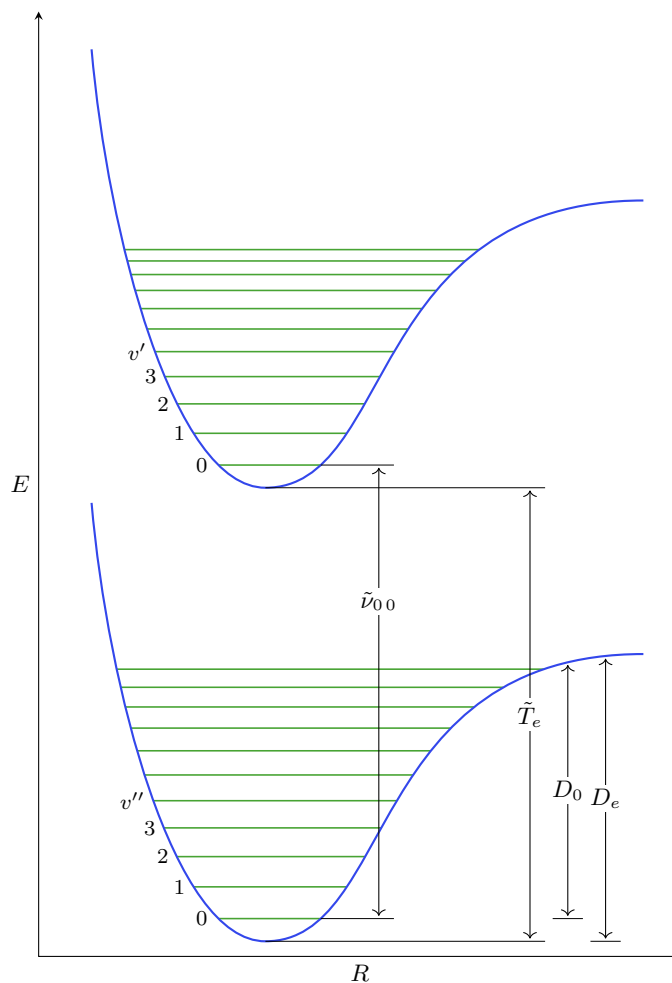
Figure 9.5: The quantities describing an electronic transition.

- $\boldsymbol{D_e}$: The difference in energy between the minimum of the potential energy curve and the dissociated atoms.

- $\boldsymbol{D_0}$: The corresponding dissociation energy from the ground-vibrational level.

- We thus have that $D_e = D_0 + \frac{1}{2}h\nu$ in the harmonic oscillator approximation and $D_e = D_0 + \frac{1}{2}h(\nu_e - \frac{1}{2}x_e\nu_e)$ in the anharmonic oscillator approximation.

- Since the nuclei do not move appreciably during an electronic transition, such transitions can be depicted as vertical lines in the energy diagram, as we have done thus far.

- McQuarrie and Simon (1997) covers the Franck-Condon principle.

- Consider a rigid body, a polyatomic molecule modeled as a rigid network of N atoms.

- **Moments of inertia** (of a rigid body): Given a Cartesian coordinate system, the following values. *Denoted by $\boldsymbol{I_{xx}, I_{yy}, I_{zz}}$. Given by*

$$I_{xx} = \sum_{j=1}^{N} m_j[(y_j - y_{cm})^2 + (z_j - z_{cm})^2]$$

$$I_{yy} = \sum_{j=1}^{N} m_j [(x_j - x_{cm})^2 + (z_j - z_{cm})^2]$$

$$I_{zz} = \sum_{j=1}^{N} m_j [(x_j - x_{cm})^2 + (y_j - y_{cm})^2]$$

where m_j is the mass of the jth atom situated at the point (x_j, y_j, z_j) and (x_{cm}, y_{cm}, z_{cm}) are the coordinates of the center of mass of the rigid body.

- **Products of inertia** (of a rigid body): The quantities of the form

$$I_{xy} = - \sum_{j=1}^{N} m_j (x_j - x_{cm})(y_j - y_{cm})$$

- **Principal axes** (of a rigid body): The particular set of Cartesian coordinates X, Y, Z passing through the center of mass of a rigid body such that all of the products of inertia vanish.

- **Principal moments of inertia** (of a rigid body): The moments of inertia of a rigid body about the principal axes. *Denoted by $\boldsymbol{I_A}, \boldsymbol{I_B}, \boldsymbol{I_C}$ where $I_A \leq I_B \leq I_C$.*

  - Usually given in terms of rotational constants in units of reciprocal centimeters, e.g., $\tilde{A} = h/8\pi^2 c I_A$.

- **Spherical top**: A rigid body with all three principal moments of inertial equal.

  - For example, CH_4 and SF_6.

- **Symmetric top**: A rigid body with two principal moments of inertial equal.

  - For example, NH_3 and C_6H_6.

- **Asymmetric top**: A rigid body with all three principal moments of inertial unequal.

  - For example, H_2O.

- The quantum-mechanical problem of a spherical top can be solved exactly, yielding energy levels $F(J) = \tilde{B}J(J+1)$ for $J = 0, 1, 2, \ldots$ (the same as for a linear molecule) with respective degeneracies $g_J = (2J+1)^2$.

- Since spherical tops cannot have a permanent dipole moment, they do not have pure rotational spectra.

- The quantum-mechanical problem of a symmetric top can also be solved exactly.

- **Oblate symmetric top**: A symmetric top with unique moment of inertia larger than the two equal ones.

  - For example, C_6H_6 or an O-ring.
  - Energy levels $F(J, K) = \tilde{B}J(J+1) + (\tilde{C} - \tilde{B})K^2$ for $J = 0, 1, 2, \ldots$, $K = 0, \pm 1, \pm 2, \ldots, \pm J$, and degeneracy $g_{JK} = 2J + 1$.
    - J is a measure of the total rotational angular momentum of the molecule.
    - K is a measure of the component of the rotational angular momentum along the unique axis of the symmetric top.

- **Prolate symmetric top**: A symmetric top with unique moment of inertia smaller than the two equal ones.

  - For example, CH_3Cl or a cigar.

- Energy levels $F(J,K) = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2$ with the same quantum numbers and degeneracy as in the oblate case.

- Symmetric top molecule selection rule: The dipole moment must be directed along the axis of symmetry, and then we may have $\Delta J = 0, \pm 1$, $\Delta K = 0$ for $K \neq 0$ and $\Delta J = \pm 1$, $\Delta J = 0$ for $K = 0$.

- Centrifugal distortion effects are larger for larger molecules.

- To understand the vibrational spectra of polyatomic molecules in terms of the harmonic-oscillator approximation, we introduce normal coordinates.

- McQuarrie and Simon (1997) reviews degrees of freedom.

  - A complete specification of a molecule containing N nuclei in space requires $3N$ coordinates.
  - However, using some to specify the overall molecules position and orientation in space leaves the rest of the degrees of freedom available to describe vibration.

- "In the absence of external fields, the energy of a molecule does not depend upon the position of its center of mass or its orientation" (McQuarrie & Simon, 1997, p. 519).

- N_{vib}: The number of vibrational degrees of freedom.

- Thus, the potential energy is solely a function of the N_{vib} vibrational coordinates. Letting the displacements about the equilibrium values of these coordinates be $q_1, \ldots, q_{N_{\mathrm{vib}}}$, we have that

$$\Delta V = V(q_1, \ldots, q_{N_{\mathrm{vib}}}) - V(0, \ldots, 0) = \frac{1}{2} \sum_{i=1}^{N_{\mathrm{vib}}} \sum_{j=1}^{N_{\mathrm{vib}}} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right) q_i q_j + \cdots$$

where the $\cdots$ terms are anharmonic.

- The cross terms in the above expression make the solution to the corresponding Schrödinger equation quite tedious, but a theorem of classical mechanics and a straightforward procedure using matrix algebra allows us to find a new set of coordinates $\{Q_j\}$ called **normal coordinates** or **normal modes** such that

$$\Delta V = \frac{1}{2} \sum_{j=1}^{N_{\mathrm{vib}}} F_j Q_j^2$$

- It follows that the vibrational Schrödinger equation $\hat{H}_{\mathrm{vib}} \psi_{\mathrm{vib}} = E_{\mathrm{vib}} \psi_{\mathrm{vib}}$ is separable and defined by

$$\hat{H}_{\mathrm{vib}} = \sum_{j=1}^{N_{\mathrm{vib}}} \left(-\frac{\hbar^2}{2\mu_j} \frac{\mathrm{d}^2}{\mathrm{d}Q_j^2} + \frac{1}{2} F_j Q_j^2 \right)$$

$$\psi_{\mathrm{vib}}(Q_1, \ldots, Q_{N_{\mathrm{vib}}}) = \psi_{\mathrm{vib},1}(Q_1) \cdots \psi_{\mathrm{vib},N_{\mathrm{vib}}}(Q_{N_{\mathrm{vib}}})$$

$$E_{\mathrm{vib}} = \sum_{j=1}^{N_{\mathrm{vib}}} h\nu_j (v_j + \tfrac{1}{2})$$

- Thus, the vibrational motion of a polyatomic molecule appears as N_{vib} independent harmonic oscillators, each with their own characteristic fundamental frequency ν_j.

- Vibrational absorption spectroscopy selection rule: The dipole moment of the molecule must vary during the normal mode.

- **Infrared active** (normal mode): A normal mode such that the dipole moment of the molecule does vary during the prescribed motion.

- **Infrared inactive** (normal mode): A normal mode such that the dipole moment of the molecule does not vary during the prescribed motion.

- McQuarrie and Simon (1997) analyzes the normal modes of CO_2, H_2CO, and CH_3Cl.

- **Parallel band**: An absorption band corresponding to a normal mode with dipole moment oscillating parallel to the molecular axis.

  - Governed by the selection rule $\Delta v = +1$, $\Delta J = \pm 1$, just like a diatomic molecules.
  - Generates a vibration-rotation spectrum consisting of a P branch and an R branch.

- The case of a dipole moment oscillating perpendicular to the molecular axis.

  - Governed by the selection rule $\Delta v = +1$, $\Delta J = 0, \pm 1$.
  - The band due to $\Delta J = 0$ is called the **Q branch**, and is centered between the P and R branches.

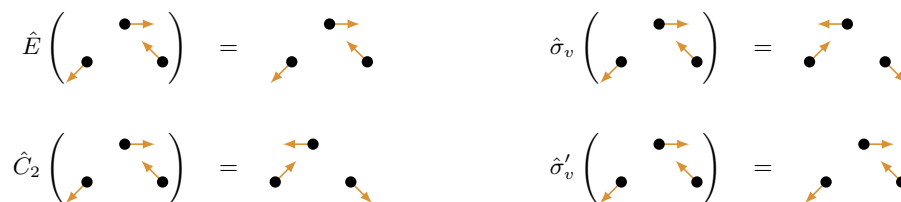- Identifying normal coordinates with irreducible representations.

Figure 9.6: The asymmetric stretch normal mode under the operations of the $\mathbf{C}_{2v}$ point group.

  - Consider, for example, H_2O, belonging to the $\mathbf{C}_{2v}$ point group.
  - Let the asymmetric stretch normal coordinate be Q_{as}.
  - Then by Figure 9.6, we have that

$$\hat{E}Q_{as} = Q_{as} \qquad \hat{C}_2 Q_{as} = -Q_{as} \qquad \hat{\sigma}_v Q_{as} = -Q_{as} \qquad \hat{\sigma}'_v Q_{as} = Q_{as}$$

  so Q_{as} belongs to B_2.

- McQuarrie and Simon (1997) also derives the relevant irreducible representations as in Labalme (2021, p. 40).

- We now begin the derivation of selection rules.

- Since we are considering *transitions*, we will need the time-dependent Schrödinger equation.

  - Stationary states, such as those wave functions we have considered thus far, only pertain to isolated systems with Hamiltonians that do not depend on time.
  - As such, to consider transitions between states, we will be working not just with the time-dependent Schrödinger equation but also with a time-dependent Hamiltonian.

- In particular, let the molecule interact with electromagnetic field

$$\mathbf{E} = \mathbf{E}_0 \cos 2\pi\nu t$$

  where ν is the frequency of the radiation incident on the molecule and $\mathbf{E}_0$ is the electric field vector.

- It follows by Problem 13-49 that the Hamiltonian operator for the interaction of the electric field with the molecule is

$$\hat{H}^{(1)} = -\boldsymbol{\mu} \cdot \mathbf{E} = -\boldsymbol{\mu} \cdot \mathbf{E}_0 \cos 2\pi\nu t$$

- Thus, the overall problem is to solve

$$\hat{H}\Psi = i\hbar\frac{d\Psi}{dt}$$

where $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} = \hat{H}^{(0)} - \boldsymbol{\mu}\cdot\mathbf{E}_0\cos 2\pi\nu t$ and $\hat{H}^{(0)}$ is the Hamiltonian of the isolated molecule.

- Treating $\hat{H}^{(1)}$ as a small perturbation, we can solve the above with **time-dependent perturbation theory**, an extension of time-independent perturbation theory worked through as follows.

    - For simplicity, we consider only a two-state system (in spite of the fact that an isolated molecule generally has an infinite number of stationary states).

- In such a system, the solutions to

$$\hat{H}^{(0)}\Psi = i\hbar\frac{d\Psi}{dt}$$

are

$$\Psi_1(t) = \psi_1 e^{-iE_1 t/\hbar} \qquad\qquad \Psi_2(t) = \psi_2 e^{-iE_2 t/\hbar}$$

where ψ_1, ψ_2 are the two stationary states.

- Let the system initially be in state 1, and assume that the overall solution $\Psi(t)$ is a linear combination of $\Psi_1(t), \Psi_2(t)$ that evolves over time. In particular, assume

$$\Psi(t) = a_1(t)\Psi_1(t) + a_2(t)\Psi_2(t)$$

and let our initial conditions be $a_1(t) = 1$ and $a_2(t) = 0$.

    - Recall that $a_i^* a_i$ gives the probability that the molecule is in state i.

- Substituting our wave function into the full time-dependent Schrödinger equation gives

$$(\hat{H}^{(0)} + \hat{H}^{(1)})\Psi(t) = i\hbar\frac{d\Psi}{dt}$$

$$a_1(t)\hat{H}^{(0)}\Psi_1 + a_2(t)\hat{H}^{(0)}\Psi_2 + a_1(t)\hat{H}^{(1)}\Psi_1 + a_2(t)\hat{H}^{(1)}\Psi_2 = a_1(t)i\hbar\frac{d\Psi_1}{dt} + i\hbar\Psi_1\frac{da_1}{dt} + a_2(t)i\hbar\frac{d\Psi_2}{dt} + i\hbar\Psi_2\frac{da_2}{dt}$$

$$a_1(t)\hat{H}^{(1)}\Psi_1 + a_2(t)\hat{H}^{(1)}\Psi_2 = i\hbar\Psi_1\frac{da_1}{dt} + i\hbar\Psi_2\frac{da_2}{dt}$$

where we cancel terms that are equal by the TD SE in going from the second to the third equality.

- We now multiply through by ψ_2^*, integrate over all space, and simplify.

$$\psi_2^* a_1(t)\hat{H}^{(1)}\Psi_1 + \psi_2^* a_2(t)\hat{H}^{(1)}\Psi_2 = \psi_2^* i\hbar\Psi_1\frac{da_1}{dt} + \psi_2^* i\hbar\Psi_2\frac{da_2}{dt}$$

$$a_1(t)\int\psi_2^*\hat{H}^{(1)}\Psi_1\,d\tau + a_2(t)\int\psi_2^*\hat{H}^{(1)}\Psi_2\,d\tau = i\hbar\frac{da_1}{dt}\int\psi_2^*\psi_1 e^{-iE_1 t/\hbar}\,d\tau + i\hbar\frac{da_2}{dt}\int\psi_2^*\psi_2 e^{-iE_2 t/\hbar}\,d\tau$$

$$a_1(t)\int\psi_2^*\hat{H}^{(1)}\Psi_1\,d\tau + a_2(t)\int\psi_2^*\hat{H}^{(1)}\Psi_2\,d\tau = i\hbar e^{-iE_1 t/\hbar}\frac{da_1}{dt}\int\psi_2^*\psi_1\,d\tau + i\hbar e^{-iE_2 t/\hbar}\frac{da_2}{dt}\int\psi_2^*\psi_2\,d\tau$$

$$a_1(t)\int\psi_2^*\hat{H}^{(1)}\Psi_1\,d\tau + a_2(t)\int\psi_2^*\hat{H}^{(1)}\Psi_2\,d\tau = i\hbar e^{-iE_2 t/\hbar}\frac{da_2}{dt}$$

- Solve for $i\hbar\,da_2/dt$ and simplify.

$$i\hbar\frac{da_2}{dt} = a_1(t)e^{iE_2 t/\hbar}\int\psi_2^*\hat{H}^{(1)}\psi_1 e^{-iE_1 t/\hbar}\,d\tau + a_2(t)e^{iE_2 t/\hbar}\int\psi_2^*\hat{H}^{(1)}\psi_2 e^{-iE_2 t/\hbar}\,d\tau$$

$$= a_1(t)e^{-i(E_1 - E_2)t/\hbar}\int\psi_2^*\hat{H}^{(1)}\psi_1\,d\tau + a_2(t)\int\psi_2^*\hat{H}^{(1)}\psi_2\,d\tau$$

- Since $\hat{H}^{(1)}$ is a small perturbation, the initial values corresponding to the TD SE may be approximated as identical to those corresponding to the TI SE. As such, substitute $a_1(0) = 1$ and $a_2(0) = 0$ into the above to obtain

$$i\hbar\frac{da_2}{dt} = e^{-i(E_1 - E_2)t/\hbar} \int \psi_2^* \hat{H}^{(1)} \psi_1 \, d\tau$$

- Take the electric field to be in the z-direction. Then

$$\hat{H}^{(1)} = -\mu_z E_{0z} \cos 2\pi\nu t$$
$$= -\frac{\mu_z E_{0z}}{2}(e^{i2\pi\nu t} + e^{-i2\pi\nu t})$$

- Substituting this into the above then yields

$$i\hbar\frac{da_2}{dt} = e^{-i(E_1 - E_2)t/\hbar} \int \psi_2^* \cdot -\frac{\mu_z E_{0z}}{2}(e^{i2\pi\nu t} + e^{-i2\pi\nu t})\psi_1 \, d\tau$$
$$= -\frac{E_{0z}}{2}e^{i(E_2 - E_1)t/\hbar}(e^{ih\nu t 2\pi/h} + e^{-ih\nu t 2\pi/h}) \int \psi_2^* \mu_z \psi_1 \, d\tau$$
$$\frac{da_2}{dt} = -\frac{1}{2i\hbar}\int \psi_2^* \mu_z \psi_1 \, d\tau\, E_{0z}(e^{i(E_2 - E_1 + h\nu)t/\hbar} + e^{i(E_2 - E_1 - h\nu)t/\hbar})$$
$$\propto (\mu_z)_{12} E_{0z}(e^{i(E_2 - E_1 + h\nu)t/\hbar} + e^{i(E_2 - E_1 - h\nu)t/\hbar})$$

where we define

$$(\mu_z)_{12} = \int \psi_2^* \mu_z \psi_1 \, d\tau$$

to be the z-component of the **transition dipole moment** between states 1 and 2.

   - Note that if $(\mu_z)_{12} = 0$, then $da_2/d0 = 0$ and there will be no transition out of state 1 and into state 2.

   - In other words, the dipole must change during the transition, and we have derived the first part of the selection rule!

- Before finishing our derivation of explicit selection rules, integrate the above.

$$a_2(t) \propto \int_0^t (\mu_z)_{12} E_{0z}(e^{i(E_2 - E_1 + h\nu)t/\hbar} + e^{i(E_2 - E_1 - h\nu)t/\hbar}) \, dt$$
$$\propto (\mu_z)_{12} E_{0z}\left(\frac{1 - e^{i(E_2 - E_1 + h\nu)t/\hbar}}{E_2 - E_1 + h\nu} + \frac{1 - e^{i(E_2 - E_1 - h\nu)t/\hbar}}{E_2 - E_1 - h\nu}\right)$$

   - Note that since $E_2 > E_1$, when $E_2 - E_1 \approx h\nu$, the **resonance denominators** cause the second term above to be of major importance in determining $a_2(t)$.

   - Thus, the Bohr frequency condition arises naturally from the quantum mechanics!

- **Resonance denominators**: The two denominators in the above equation for $a_2(t)$.

- Given the above function, we can now determine the probability of observing the molecule in state 2.

   - This quantity is proportional to both the probability of absorption and the intensity of absorption.

   - It is given by $a_2^* a_2$. In calculating this quantity, though, we need only take into account the second term in the definition of a_2 as per the above discussion of resonance denominators.

   - This gives us (see Problem 13-40)

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

which has its largest peak (largest probability of a transition) at $\hbar\omega = E_2 - E_1$ (see Figure 8.1).

- We now derive the selection rule in the rigid-rotator approximation.

- We require that

$$0 \neq (\mu_z)_{J,M;J',M'} = \int_0^{2\pi} \int_0^{\pi} Y_{J'}^{M'}(\theta, \phi)^* \mu_z Y_J^M(\theta, \phi) \sin \theta \, d\theta \, d\phi$$

- Invoke $\mu_z = \mu \cos \theta$.

$$(\mu_z)_{J,M;J',M'} = \mu \int_0^{2\pi} \int_0^{\pi} Y_{J'}^{M'}(\theta, \phi)^* Y_J^M(\theta, \phi) \cos \theta \sin \theta \, d\theta \, d\phi$$

  – Thus, $\mu \neq 0$ for a nonzero transition dipole moment.
  – In other words, the molecule must have a permanent dipole moment for it to have a pure rotational spectrum, as asserted earlier!

- As to the rest of the selection rule, substitute the spherical harmonics into the above equation and simplify. Also substitute $x = \cos \theta$.

$$(\mu_z)_{J,M;J',M'} = \mu \int_0^{2\pi} \int_0^{\pi} (N_{J'M'} P_{J'}^{|M'|}(\cos \theta) e^{-iM'\phi})(N_{JM} P_J^{|M|}(\cos \theta) e^{iM\phi}) \cos \theta \sin \theta \, d\theta \, d\phi$$

$$= \mu N_{JM} N_{J'M'} \int_0^{2\pi} d\phi \, e^{i(M-M')\phi} \int_0^{\pi} d\theta \, P_{J'}^{|M'|}(\cos \theta) P_J^{|M|}(\cos \theta) \cos \theta \sin \theta$$

$$= \mu N_{JM} N_{J'M'} \int_0^{2\pi} d\phi \, e^{i(M-M')\phi} \int_{-1}^{1} dx \, x P_{J'}^{|M'|}(x) P_J^{|M|}(x)$$

  – For the leftmost integral above to be nonzero, we must have $M = M'$.
  – This is the $\Delta M = 0$ selection rule!

- Evaluating the leftmost integral yields

$$(\mu_z)_{J,M;J',M'} = 2\pi \mu N_{JM} N_{J'M'} \int_{-1}^{1} dx \, x P_{J'}^{|M'|}(x) P_J^{|M|}(x)$$

- Given the recursion rule

$$(2J+1)x P_J^{|M|}(x) = (J - |M| + 1) P_{J+1}^{|M|}(x) + (J + |M|) P_{J-1}^{|M|}(x)$$

pertaining to the associated Legendre functions, we have

$$(\mu_z)_{J,M;J',M} = 2\pi \mu N_{JM} N_{J'M} \int_{-1}^{1} dx \, P_{J'}^{|M|}(x) \left[\frac{J - |M| + 1}{2J + 1} P_{J+1}^{|M|}(x) + \frac{J + |M|}{2J + 1} P_{J-1}^{|M|}(x) \right]$$

  – Thus, by the orthogonality of the associated Legendre functions, we must have $J' = J + 1$ or $J' = J - 1$ for the above integral not to vanish.
  – This is the $\Delta J = \pm 1$ selection rule!

- We now derive the selection rule in the harmonic-oscillator approximation.

- As before, let

$$(\mu_z)_{v,v'} = \int_{-\infty}^{\infty} [N_{v'} H_{v'}(\sqrt{\alpha} q) e^{-\alpha q^2/2}] \mu_z(q) [N_v H_v(\sqrt{\alpha} q) e^{-\alpha q^2/2}] \, dq$$

- Expand $\mu_z(q)$ about the equilibrium nuclear separation to two terms

$$\mu_z(q) = \mu_0 + \left(\frac{\mathrm{d}\mu}{\mathrm{d}q}\right)_0 q$$

where μ_0 is the dipole moment at the equilibrium bond length and q is the displacement from that equilibrium value.

- Substituting this expansion into the original equation yields

$$(\mu_z)_{v,v'} = \int_{-\infty}^{\infty} [N_{v'}H_{v'}(\sqrt{\alpha}q)\mathrm{e}^{-\alpha q^2/2}]\left[\mu_0 + \left(\frac{\mathrm{d}\mu}{\mathrm{d}q}\right)_0 q\right][N_v H_v(\sqrt{\alpha}q)\mathrm{e}^{-\alpha q^2/2}]\,\mathrm{d}q$$

$$= N_v N_{v'}\mu_0 \int_{-\infty}^{\infty} H_{v'}(\sqrt{\alpha}q)H_v(\sqrt{\alpha}q)\mathrm{e}^{-\alpha q^2}\,\mathrm{d}q + N_v N_{v'}\left(\frac{\mathrm{d}\mu}{\mathrm{d}q}\right)_0 \int_{-\infty}^{\infty} H_{v'}(\sqrt{\alpha}q)qH_v(\sqrt{\alpha}q)\mathrm{e}^{-\alpha q^2}\,\mathrm{d}q$$

- The first integral above vanishes if $v \neq v'$ by the orthogonality of the Hermite polynomials with respect to a Gaussian weighting function.

- As to the second integral, invoke the Hermite polynomial recursion formula

$$\xi H_v(\xi) = vH_{v-1}(\xi) + \tfrac{1}{2}H_{v+1}(\xi)$$

from Problem 5-24 to get

$$(\mu_z)_{v,v'} = \frac{N_v N_{v'}}{\alpha}\left(\frac{\mathrm{d}\mu}{\mathrm{d}q}\right)_0 \int_{-\infty}^{\infty} H_{v'}(\xi)[vH_{v-1}(\xi) + \tfrac{1}{2}H_{v+1}(\xi)]\mathrm{e}^{-\xi^2}\,\mathrm{d}\xi$$

  - Note that we substitute $\xi = \sqrt{\alpha}q$.
  - Thus, by the orthogonality of the Hermite polynomials, we must have $v' = v \pm 1$ for the above integral not to vanish.
  - This is the $\Delta v = \pm 1$ selection rule!
  - Additionally, the $(\mathrm{d}\mu/\mathrm{d}q)_0$ term indicates that the dipole moment must vary during the vibration.

- A normal mode will have a nonzero transition only if it belongs to the same irreducible representation as one of the $\mu_{x,y,z}$[3].

  - We have
  $$\psi_0(Q_1, \ldots, Q_{N_{\mathrm{vib}}}) = c\mathrm{e}^{-\alpha_1 Q_1^2 - \cdots - \alpha_{N_{\mathrm{vib}}} Q_{N_{\mathrm{vib}}}^2}$$
  where c is a normalization constant and $\alpha_j = \sqrt{\mu_j k_j}/2\hbar$.
    - Since the normal modes belong to the irreducible representations of the relevant molecular point group, the effect of an arbitrary symmetry operation $\hat{R}$ on Q_j gives $\pm Q_j$.
    - Thus, ψ_0 as a function of quadratic terms of Q_j is wholly invariant under any $\hat{R}$.
  - We also have
  $$\psi_1(Q_1, \ldots, Q_{N_{\mathrm{vib}}}) = c'Q_j\mathrm{e}^{-\alpha_1 Q_1^2 - \cdots - \alpha_{N_{\mathrm{vib}}} Q_{N_{\mathrm{vib}}}^2}$$
  since an excited state necessitates exciting one and only one normal mode.
    - Thus, ψ_1 transforms as Q_j under the symmetry operations of the group.
  - Since $I_{0 \to 1}$ is invariant under all operations of the group,

  $$I_{0 \to 1} = \hat{R}I_{0 \to 1} = \int (\hat{R}\psi_0)(\hat{R}\mu_x)(\hat{R}\psi_1)\,\mathrm{d}Q_1 \cdots \mathrm{d}Q_{N_{\mathrm{vib}}} = \chi_{A_1}(\hat{R})\chi_{\mu_x}(\hat{R})\chi_{Q_j}(\hat{R})I_{0,1}$$

  - Thus, the product of the characters equals 1. More specifically, since $\chi_{A_1}(\hat{R})$ always equals 1, the excited state and dipole must transform together, i.e., must belong to the same irreducible representation for the transition to be nonzero.

---

[3]Related to Module 12 on Labalme (2021, pp. 49–50).

Problems

13-40. Derive Equation 13.57 from Equation 13.55 in McQuarrie and Simon (1997).

Answer. Since we are considering proportionality and ignoring the first term, we will work with the following version of Equation 13.55.

$$a_2(t) \propto \frac{1 - e^{i(E_2 - E_1 - h\nu)t/\hbar}}{E_2 - E_1 - h\nu}$$
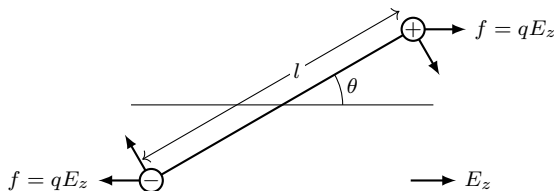
Let

$$x = E_2 - E_1 - h\nu = E_2 - E_1 - \frac{h}{2\pi} \cdot 2\pi\nu = E_2 - E_1 - \hbar\omega$$

Then

$$\begin{aligned}
a_2^*(t)a_2(t) &= \frac{1 - e^{-ixt/\hbar}}{x} \cdot \frac{1 - e^{ixt/\hbar}}{x} \\
&= \frac{1 - e^{ixt/\hbar} - e^{-ixt/\hbar} + e^0}{x^2} \\
&= \frac{2 - (e^{ixt/\hbar} + e^{-ixt/\hbar})}{x^2} \\
&= \frac{2 - 2\cos(xt/\hbar)}{x^2} \\
&= \frac{4}{x^2} \cdot \frac{1 - \cos(2(xt/2\hbar))}{2} \\
&= \frac{4}{x^2} \cdot \sin^2(xt/2\hbar) \\
&\propto \frac{\sin^2(xt/2\hbar)}{x^2}
\end{aligned}$$

Returning the substitution yields the desired result. □

13-49. Consider a molecule with a dipole moment $\boldsymbol{\mu}$ in an electric field $\boldsymbol{E}$. We picture the dipole moment as a positive charge and a negative charge of magnitude q separated by a vector $\mathbf{l}$.

The field $\boldsymbol{E}$ causes the dipole to rotate into a direction parallel to $\boldsymbol{E}$. Therefore, work is required to rotate the dipole to an angle θ to $\boldsymbol{E}$. The force causing the molecule to rotate is actually a torque (torque is the angular analog of force) and is given by $l/2$ times the force perpendicular to $\mathbf{l}$ at each end of the vector $\mathbf{l}$. Show that this torque is equal to $\mu E \sin\theta$ and that the energy required to rotate the dipole from some initial angle θ_0 to some arbitrary angle θ is

$$V = \int_{\theta_0}^{\theta} \mu E \sin\theta' \, d\theta'$$

Given that θ_0 is customarily taken to be $\pi/2$, show that

$$V = -\mu E \cos\theta = -\boldsymbol{\mu} \cdot \boldsymbol{E}$$

The magnetic analog of this result will be given in Chapter 14.

9.4   Chapter 15: Lasers, Laser Spectroscopy, and Photochemistry

From McQuarrie and Simon (1997).

12/2:
- "Laser is an acronym for light amplification by stimulated emission of radiation" (McQuarrie & Simon, 1997, p. 591).

- **Photochemistry**: The study of light-initiated reactions.

- **Photodissociation**: Light-induced dissociation.

- **Radiative transition**: A transition between energy levels that involves either the absorption or the emission of radiation.

- **Nonradiative transition**: A transition between energy levels that occurs without the absorption or the emission of radiation.

- **Vibrational relaxation**: A collision between an excited molecule and another molecule in the sample resulting in an exchange of energy that removes some of the excess vibrational energy.
    - Causes an excited molecule to quickly relax to the lowest vibrational state of the electronic excited state.

- **Fluorescence**: The radiative decay process involving a transition between states of the same spin multiplicity.

- **Internal conversion**: The nonradiative decay process involving a transition between states of the same spin multiplicity.

- **Intersystem crossing**: A nonradiative transition between states of the same spin multiplicity enabled by overlap between vibrational and rotational states.
    - Requires a change in the spin of the electron.

- **Phosphorescence**: The radiative decay process involving a transition between states of differing spin multiplicities.

- Einstein's approach to the dynamics of atomic spectroscopic transitions.
    - Einstein makes several assumptions that can be justified via time-dependent quantum mechanics.
    - No quantum mechanics is required for Einstein's approach except that the energy levels of the atom are assumed to be quantized.

- The approach (absorption only).
    - Consider a sample of N_{total} identical atoms having only two nondegenerate electronic energy levels $E_1 < E_2$.
    - Let number of atoms in stated i be denoted by N_i.
    - Let the sample of atoms have insufficient thermal energy to occupy state 2, i.e., $k_{\text{B}}T << E_2 - E_1$.
    - Expose the sample to EM radiation of frequency ν_{12} where $h\nu_{12} = E_2 - E_1$.
    - The energy density of said EM radiation is described by the **radiant energy density** and the **spectral radiant energy density**.
    - Einstein proposes that the rate $-\,\mathrm{d}N_1/\mathrm{d}t\,=\,\mathrm{d}N_2/\mathrm{d}t$ of excitation from the ground electronic state to the excited electronic state is proportional to $\rho_v(\nu_{12})$ and $N_1(t)$. In particular,

$$-\frac{\mathrm{d}N_1}{\mathrm{d}t} = B_{12}\rho_v(\nu_{12})N_1(t)$$

where B_{12} is a proportionality constant called an **Einstein coefficient**.

- **Radiant energy density**: The radiant energy per unit volume. *Denoted by $\boldsymbol{\rho}$. Units* $\mathrm{J\,m^{-3}}$.

  - The intensity I of light is of the form $I = \rho c$.

- **Spectral radiant energy density**: The radiant energy density per unit frequency. *Denoted by $\boldsymbol{\rho_v}$. Units* $\mathrm{J\,m^{-3}\,s}$. *Given by*

$$\rho_v = \frac{\mathrm{d}\rho}{\mathrm{d}v}$$

- The approach (relaxation).

  - Einstein proposes **spontaneous emission** and **stimulated emission** as two pathways by which atoms atoms relax back into the ground state.

- **Spontaneous emission**: The process by which atoms spontaneously emit a photon of energy $h\nu_{12} = E_2 - E_1$ at some time after the excitation.

  - The rate can be described by $-\,\mathrm{d}N_2/\mathrm{d}t$, which we assume is simply proportional to the number of atoms $N_2(t)$ in the excited state at time t. In particular,

$$-\frac{\mathrm{d}N_2}{\mathrm{d}t} = A_{21}N_2(t)$$

  where A_{21} is another Einstein coefficient.

- **Stimulated emission**: The process by which exposure of an atom in an excited electronic state to electromagnetic radiation of energy $h\nu_{12} = E_2 - E_1$ could stimulate the emission of a photon and thereby regenerate the ground state.

  - The rate, we assume, is proportional to $N_2(t)$ and $\rho_v(\nu_{12})$. In particular,

$$-\frac{\mathrm{d}N_2}{\mathrm{d}t} = B_{21}\rho_v(\nu_{12})N_2(t)$$

  where B_{21} is a third Einstein coefficient.

  - In this process, one photon at frequency ν_{12} stimulates an atom to emit another. These two photons can then go on to cause more excited atoms to release photons, and on and on resulting in a substantial amplification of an incident light beam at frequency ν_{12}.

    ■ Lasers (light amplification by stimulated emission of radiation devices) exploit this phenomenon.

- Since a sample of atoms exposed to light undergoes absorption, spontaneous emission, and stimulated emission, the true rate of change in the population is

$$-\frac{\mathrm{d}N_1}{\mathrm{d}t} = \frac{\mathrm{d}N_2}{\mathrm{d}t} = B_{12}\rho_v(\nu_{12})N_1(t) - A_{21}N_2(t) - B_{21}\rho_v(\nu_{12})N_2(t)$$

- Deriving a relation between the three Einstein coefficients.

  - Consider the limit at which the two energy states are in thermal equilibrium, i.e., $-\,\mathrm{d}N_1/\mathrm{d}t = \mathrm{d}N_2/\mathrm{d}t = 0$. Also let $\rho_v(\nu_{12})$ be the equilibrium spectral radiant energy density, which we assume comes from a thermal blackbody radiation source.

  - Solving the above overall population rate of change equation for $\rho_v(\nu_{12})$ yields

$$\rho_v(\nu_{12}) = \frac{A_{21}}{(N_1/N_2)B_{12} - B_{21}}$$

  - Applying the fact (see Chapter 17) that for a system in equilibrium at temperature T, the number of atoms or molecules in the state j with energy E_j is $N_j = ce^{-E_j/k_\mathrm{B}T}$, we have that

$$\frac{N_2}{N_1} = e^{-(E_2-E_1)/k_\mathrm{B}T} = e^{-h\nu_{12}/k_\mathrm{B}T}$$

– Plug this into the above equation and set it equal to Planck's blackbody distribution law.

$$\frac{8\pi h}{c^3}\frac{\nu_{12}^3}{e^{h\nu_{12}/k_B T}-1} = \frac{A_{21}}{B_{12}e^{h\nu_{12}/k_B T}-B_{21}}$$

– From the above equation it is clear that

$$B_{12} = B_{21}$$

and

$$A_{21} = \frac{8h\pi\nu_{12}^3}{c^3}B_{21}$$

– This allows us to write the rate equation for a nondegenerate two-level system as

$$-\frac{dN_1}{dt} = \frac{dN_2}{dt} = B\rho_v(\nu_{12})[N_1(t) - N_2(t)] - AN_2(t)$$

• For a laser to amplify light, a photon that passes through the sample must have a greater probability of stimulating emission from an excited atom then of being absorbed by an atom in its ground state.

– Symbolically, we must have

$$\text{rate stimulated emission} > \text{rate absorption}$$
$$B_{21}\rho_v(\nu_{12})N_2 > B_{12}\rho_v(\nu_{12})N_1$$
$$N_2 > N_1$$

• **Population inversion**: A situation where the population of the excited state is greater than that of the lower state.

– By the above equation for N_2/N_1, we must have $N_2/N_1 < 1$ when the system is at equilibrium since $h\nu_{12}/k_B T$ is a strictly positive quantity.

– Thus, population inversions constitute nonequilibrium situations.

• A population inversion cannot occur in a nondegenerate two-level system.

– Integrating the rate equation for a such a system yields

$$N_2(t) = \frac{B\rho_v(\nu_{12})N_{\text{total}}}{A + 2B\rho_v(\nu_{12})}\{1 - e^{-[A+2B\rho_v(\nu_{12})]t}\}$$

– This equation's behavior as $t \to \infty$ converges to

$$\frac{N_2}{N_{\text{total}}} = \frac{B\rho_v(\nu_{12})}{A + 2B\rho_v(\nu_{12})}$$

which, since $A > 0$, will always be strictly less than $1/2$.

– Therefore, no such population inversion can be achieved.

• Relaxing back to equilibrium after an incident light source is turned off.

– The rate equation simplifies to just spontaneous emission, i.e.,

$$\frac{dN_2}{dt} = -AN_2$$
$$N_2(t) = N_2(0)e^{-At}$$

• **Fluorescence lifetime**: The reciprocal of A. *Also known as* **radiative lifetime**. *Denoted by* τ_R.