CHAPTER 5
MOLECULAR VIBRATIONS AND
TIME-INDEPENDENT PERTURBATION THEORY
OUTLINE

Homework Questions Attached

PART A: The Harmonic Oscillator and Vibrations of Molecules.

SECT  TOPIC
1. The Classical Harmonic Oscillator
3. The Quantum Mechanical Harmonic Oscillator
4. Harmonic Oscillator Wavefunctions and Energies
5. Properties of the Quantum Mechanical Harmonic Oscillator
6. The Vibrations of Diatomic Molecules
7. Vibrational Spectroscopy
8. Vibrational Anharmonicity
9. The Two Dimensional Harmonic Oscillator
10. Vibrations of Polyatomic Molecules
### PART B: The Symmetry of Vibrations + Perturbation Theory + Statistical Thermodynamics

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Chapter 5 Homework

1. Consider the differential equation: \( \frac{d^2 y}{dx^2} = -4y \)
   
   Assume that the solution is of the form: \( y = \sum_{n=0}^{\infty} a_n x^n = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \ldots \)
   
   Develop “recursion relations” relating (1) \( a_2 \) to \( a_0 \), (2) \( a_3 \) to \( a_1 \), (3) \( a_4 \) to \( a_2 \).

2. One of the wavefunctions of the Harmonic Oscillator is:
   \[ \psi = A_n x e^{-\alpha x^2 / 2} \quad \alpha = \frac{\mu \omega}{\hbar} \quad \omega = \sqrt{\frac{k}{\mu}} \]
   
   (a) Calculate the normalization constant, \( A \) (in terms of \( \alpha \))
   (b) Determine \( \langle x \rangle \) (in terms of \( \alpha \))
   (c) Determine \( \langle x^2 \rangle \) (in terms of \( \alpha \))
   (d) Determine \( \langle p \rangle \) (in terms of \( \alpha \))
   (e) Determine \( \langle p^2 \rangle \) (in terms of \( \alpha \))
   (f) Determine \( \langle T \rangle \), average kinetic energy (in terms of \( \omega \))
   (g) Determine \( \langle V \rangle \), average potential energy (in terms of \( \omega \))

3. Consider a two dimensional Harmonic Oscillator for which \( k_y = 9 \cdot k_x \). Determine the energies (in terms of \( \omega_x \)) and degeneracies of the first 7 energy levels for this oscillator.

4. Consider the diatomic molecule, carbon monoxide, \(^{12}\text{C}\equiv^{16}\text{O}\), which has a fundamental vibrational frequency of 2170 cm\(^{-1}\).
   (a) Determine the CO vibrational force constant, in N/m.
   (b) Determine the vibrational Zero-Point Energy, \( E_0 \), and energy level spaces, \( \Delta E \), both in kJ/mol.

5. The \(^{35}\text{Cl}_2\) force constant is 320 N/m. Calculate the fundamental vibrational frequency of \(^{35}\text{Cl}_2\), in cm\(^{-1}\).

6. The 4 vibrational frequencies of \( \text{CO}_2 \) are: 2349 cm\(^{-1}\), 1334 cm\(^{-1}\), 667 cm\(^{-1}\), 667 cm\(^{-1}\).
   (a) Calculate the Zero-Point vibrational energy, i.e. \( E(0,0,0,0) \) in (1) cm\(^{-1}\) (i.e. \( E/\hbar c \)), (2) J, (3) kJ/mol.
   (b) Calculate the energy required to raise the vibrational state to \( (0, 2,1,0) \) in (1) cm\(^{-1}\) (i.e. \( E/\hbar c \)), (2) J, (3) kJ/mol.
7. The fundamental vibrational frequency of $^{127}$I$_2$ (observed by Raman spectroscopy) is 215 cm$^{-1}$.
   (a) Calculate the I$_2$ force constant, $k$, in N/m.
   (b) Calculate the ratio of intensities of the first “hot” band ($n=1 \rightarrow n=2$) to the fundamental band ($n=0 \rightarrow n=1$) at 300 °C.

8. The Thermodynamic Dissociation Energy of H$^{35}$Cl is $D_0 = 428$ kJ/mol, and the fundamental vibrational frequency is 2990 cm$^{-1}$. Calculate the Spectroscopic Dissociation Energy of H$^{35}$Cl, $D_e$.

9. A particle in a box of length $a$ has the following potential energy:
   
   $$
   V(x) \rightarrow \infty \quad x < 0 \\
   V(x) = B \quad 0 \leq x \leq a/2 \\
   V(x) = 2B \quad a/2 \leq x \leq a \\
   V(x) \rightarrow \infty \quad x > a
   $$

   Use first-order perturbation theory to determine the ground state energy of the particle in this box. Use $\psi_1 = A \sin(\pi x/a)$ where $A = (2/a)^{1/2}$ and $E_1 = h^2/8ma^2$ as the unperturbed ground state wavefunction and energy.

10. Use first-order perturbation theory to determine the ground state energy of the quartic oscillator, for which:

    $$
    H = -\frac{h^2}{2\mu} \frac{d^2}{dx^2} + \gamma x^4
    $$

    Use the Harmonic Oscillator Hamiltonian as the unperturbed Hamiltonian:

    $$
    \text{HO Hamiltonian: } H = -\frac{h^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2
    $$

    Use $\psi_0 = Ae^{-\alpha x^2/2}$ where $A = \left(\frac{\alpha}{\pi}\right)^{1/4}$, $\alpha^2 = \frac{k\mu}{h^2}$ and $E_0 = \frac{1}{2} \hbar \omega$ and

    as the unperturbed ground state wavefunction and energy

    Your answer should be in terms of $k$, $\mu$, $\hbar$, $\omega$, and $\gamma$

11. The Fundamental and First Overtone vibrational frequencies of HCl are 2885 cm$^{-1}$ and 5664 cm$^{-1}$. Calculate the harmonic frequency ($\tilde{\nu}$) and the anharmonicity constant ($x_0$).

12. The symmetric C-Br stretching vibration of CBr$_4$ has a frequency of 270 cm$^{-1}$. Calculate the contribution of this vibration to the enthalpy, heat capacity (constant pressure), entropy and Gibbs energy of two (2) moles of CBr$_4$ at 800 °C.
Three of the fundamental vibrational modes (CH bending) in methylenecyclopropene (C\textsubscript{2}V) are:

\[ \nu_1(a_2) = 860 \text{ cm}^{-1} \quad \nu_2(b_1) = 1270 \text{ cm}^{-1} \quad \nu_3(b_2) = 740 \text{ cm}^{-1} \]

(a) Determine whether each fundamental mode is active or inactive in the IR and Raman Spectra.

(b) Determine whether each combination mode below is active or inactive in the IR and Raman Spectra.

(i) \( \nu_1 + \nu_3 \)

(ii) \( \nu_2 - \nu_3 \)

\[
\begin{array}{cccccc}
\text{C}_2\text{V} & \text{E} & \text{C}_2 & \sigma_v(xz) & \sigma'_v(yz) \\
A_1 & 1 & 1 & 1 & 1 & z, x^2, y^2, z^2 \\
A_2 & 1 & 1 & -1 & -1 & R_z, xy \\
B_1 & 1 & -1 & 1 & -1 & x, R_y, xz \\
B_2 & 1 & -1 & -1 & 1 & y, R_x, yz \\
\end{array}
\]

**DATA**

\[ h = 6.63 \times 10^{-34} \text{ J} \cdot \text{s} \quad 1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2 \]
\[ h = h/2\pi = 1.05 \times 10^{-34} \text{ J} \cdot \text{s} \quad 1 \text{ Å} = 10^{-10} \text{ m} \]
\[ c = 3.00 \times 10^8 \text{ m/s} = 3.00 \times 10^{10} \text{ cm/s} \quad k \cdot N_A = R \]
\[ N_A = 6.02 \times 10^{23} \text{ mol}^{-1} \quad 1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg} \]
\[ k = 1.38 \times 10^{-23} \text{ J/K} \quad 1 \text{ atm.} = 1.013 \times 10^5 \text{ Pa} \]
\[ R = 8.31 \text{ J/mol-K} \quad 1 \text{ eV} = 1.60 \times 10^{-19} \text{ J} \]
\[ m_e = 9.11 \times 10^{-31} \text{ kg} \text{ (electron mass)} \]

\[
\begin{align*}
\int_0^\infty e^{-\beta x^2} \, dx &= \frac{1}{2} \sqrt{\frac{\pi}{\beta}} \\
\int_0^\infty x e^{-\beta x^2} \, dx &= \frac{1}{2\beta} \\
\int_0^\infty x^2 e^{-\beta x^2} \, dx &= \frac{1}{4\beta} \sqrt{\frac{\pi}{\beta}} \\
\int_0^\infty x^3 e^{-\beta x^2} \, dx &= \frac{1}{2\beta^2} \\
\int_0^\infty x^4 e^{-\beta x^2} \, dx &= \frac{3}{8\beta^3} \sqrt{\frac{\pi}{\beta}} \\
\int \sin^2(\alpha x) \, dx &= \frac{1}{2} x - \frac{1}{4\alpha} \sin(2\alpha x)
\end{align*}
\]
Some “Concept Question” Topics

Refer to the PowerPoint presentation for explanations on these topics.

- Asymptotic solution to HO Schrödinger equation
- The Recursion Relation for the HO solution and quantization of energy levels
- Vibrational Zero Point Energy
- Vibrational Anharmonicity
- Interpretation of the vibrational force constant, $k$ [curvature of $V(x)$]
- IR and Raman activity
- “Hot” bands
- Effect of vibrational anharmonicity on energy levels and vibrational frequencies
- Scaling of computed vibrational frequencies
- Equipartition of vibrational energy and heat capacity
Chapter 5

Molecular Vibrations and Time-Independent Perturbation Theory

Part A: The Harmonic Oscillator and Vibrations of Molecules

Part B: The Symmetry of Vibrations
+ Perturbation Theory
+ Statistical Thermodynamics

Part A: The Harmonic Oscillator and Vibrations of Molecules

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The Classical Harmonic Oscillator

The Potential Energy of a Diatomic Molecule

Harmonic Oscillator Approximation

\[ V(R) \approx \frac{1}{2}k(R-R_e)^2 \quad \text{k is the force constant} \]

or \[ V(x) \approx \frac{1}{2}kx^2 \quad x = R-R_e \]

Hooke’s Law and Newton’s Equation

Force:

\[ f = -\frac{dV}{dx} = -\frac{d}{dx}\left(\frac{1}{2}kx^2\right) = -kx \]

Newton’s Equation:

\[ f = \mu a = \mu \frac{d^2x}{dt^2} \quad \text{where} \quad \mu = \frac{m_1m_2}{m_1 + m_2} \]

Reduced Mass

Therefore:

\[ \mu \frac{d^2x}{dt^2} = -kx \]
Solution

\[ \mu \frac{d^2x}{dt^2} = -kx \quad \text{Assume:} \quad x(t) = A \sin(\omega t) + B \cos(\omega t) \]

\[ \frac{d^2x}{dt^2} = -k \mu x \]

\[ -\omega^2 x = -\frac{k}{\mu} x \]

\[ \omega = \sqrt{\frac{k}{\mu}} \]

or \[ \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \]

or \[ \tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \]

Initial Conditions (like BC's)

\[ x(t) = A \sin(\omega t) + B \cos(\omega t) \]

\[ \frac{dx}{dt} = \omega A \cos(\omega t) - \omega B \sin(\omega t) \]

\[ \left( \frac{dx}{dt} \right)_{t=0} = \omega A = 0 \]

\[ x(t) = B \cos(\omega t) \]

and \[ x(0) = x_0 = B \]

Let's assume that the HO starts out at rest stretched out to \( x = x_0 \).

\[ x(0) = x_0 \]

\[ \left( \frac{dx}{dt} \right)_{t=0} = 0 \]

\[ x(t) = x_0 \cos(\omega t) \]

\[ \nu = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \]
Conservation of Energy

\[ x(t) = x_0 \cos(\omega t) \quad \frac{dx}{dt} = -\omega x_0 \sin(\omega t) \quad \omega = \sqrt{\frac{k}{\mu}} \]

Potential Energy (V)  Kinetic Energy (T)  Total Energy (E)

\[ V = \frac{1}{2} k x^2 \]
\[ T = \frac{1}{2} \mu \left( \frac{dx}{dt} \right)^2 \]
\[ E = T + V \]
\[ T = \frac{1}{2} \mu \omega^2 x_0^2 \sin^2(\omega t) \]
\[ V = \frac{1}{2} k x_0^2 \cos^2(\omega t) \]
\[ T = \frac{1}{2} k x_0^2 \sin^2(\omega t) \]
\[ E = \frac{1}{2} k x_0^2 \]
\[ \omega t = 0, \pi, 2\pi, \ldots \quad \Rightarrow \quad x = \pm x_0 \]
\[ \omega t = \frac{\pi}{2}, \frac{3\pi}{2}, \ldots \quad \Rightarrow \quad x = 0 \]
\[ V = 0 \quad T = \frac{1}{2} k x_0^2 \]
\[ E = \frac{1}{2} k x_0^2 \]

Classical HO Properties

Energy:

\[ E = T + V = \frac{1}{2} k x_0^2 \quad \text{Any Value} \quad \text{i.e. no energy quantization} \]

If \( x_0 = 0 \), \( E = 0 \) \quad \text{i.e. no Zero Point Energy}

Probability:

\[ E = \frac{1}{2} k x_0^2 \]

Classical Turning Points
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Math Preliminary: Taylor Series Solution of Differential Equations

Taylor (McLaurin) Series

\[ f(x) = \sum_{n=0}^{\infty} \frac{1}{n!} f^{(n)}(0)x^n \]

Any "well-behaved" function can be expanded in a Taylor Series

Example: \[ f(x) = e^x = \sum_{n=0}^{\infty} \frac{1}{n!} x^n = 1 + x + \frac{1}{2} x^2 + \frac{1}{6} x^3 + \frac{1}{24} x^4 + \ldots \]
Example: \( f(x) = e^x = \sum_{n=0}^{\infty} \frac{1}{n!} x^n = 1 + x + \frac{1}{2} x^2 + \frac{1}{6} x^3 + \frac{1}{24} x^4 + \ldots \)

\[ f(x) = e^x \]
\[ f_1(x) = 1 + x + \frac{x^2}{2} \]
\[ f_2(x) = 1 + x + \frac{x^2}{2} + \frac{x^3}{6} \]

\[ f(x) = e^x \]
\[ f_1(x) = 1 + x + \frac{x^2}{2} + \frac{x^3}{6} \]
\[ f_2(x) = 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + \frac{x^4}{24} + \frac{x^5}{120} + \frac{x^6}{720} \]

**Taylor (McLaurin) Series**

\[ f(x) = \sum_{n=0}^{\infty} \frac{f^{(n)}(0)}{n!} x^n \] Any "well-behaved" function can be expanded in a Taylor Series

Example: \( f(x) = e^x = \sum_{n=0}^{\infty} \frac{1}{n!} x^n = 1 + x + \frac{1}{2} x^2 + \frac{1}{6} x^3 + \frac{1}{24} x^4 + \ldots \)

**A Differential Equation**

\[ \frac{df(x)}{dx} = f(x) \]

Solution: \( f(x) = Ae^x \)
Taylor Series Solution

\[ \frac{df(x)}{dx} = f(x) \]

\[ f(x) = a_0 + a_1x + a_2x^2 + a_3x^3 + \ldots = \sum_{n=0}^{\infty} a_n x^n \]

Our goal is to develop a "recursion formula" relating
\[ a_1 \text{ to } a_0, \ a_2 \text{ to } a_1 \ldots \ (\text{or, in general, } a_{n+1} \text{ to } a_n) \]

Specific Recursion Formulas:

\[ \frac{df(x)}{dx} = a_1 + 2a_2x + 3a_3x^2 + \ldots = \sum_{m=1}^{\infty} ma_m x^{m-1} \]

\[ \frac{df(x)}{dx} = a_1 + 2a_2x + 3a_3x^2 + \ldots = a_0 + a_1x + a_2x^2 + \ldots = f(x) \]

Coefficients of \( x^n \) must be equal for all \( n \)

\[ a_1 = a_0 \]
\[ 2a_2 = a_1 \quad \rightarrow \quad a_2 = \frac{a_1}{2} = \frac{a_0}{2} \]
\[ 3a_3 = a_2 \quad \rightarrow \quad a_3 = \frac{a_2}{3} = \frac{a_0}{6} \]

General Recursion Formula

\[ \frac{df(x)}{dx} = f(x) \]

\[ \sum_{m=1}^{\infty} ma_m x^{m-1} = \sum_{n=0}^{\infty} a_n x^n \]

\[ \sum_{n=0}^{\infty} (n+1)a_{n+1}x^n = \sum_{n=0}^{\infty} a_n x^n \]

\[ (n+1)a_{n+1} = a_n \quad \text{or} \quad a_{n+1} = \frac{a_n}{(n+1)} \]

Power Series Expansion for \( e^x \)

\[ f(x) = e^x = a_0 + a_1x + a_2x^2 + a_3x^3 + \ldots = a_0 \left(1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3 + \ldots \right) \]
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The Quantum Mechanical Harmonic Oscillator

Schrödinger Equation

Particle vibrating against wall

\[ -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2} kx^2 \psi = E\psi \]

Boundary Condition: \( \psi \rightarrow 0 \) as \( x \rightarrow \pm \infty \)

Two particles vibrating against each other

\[ -\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + \frac{1}{2} kx^2 \psi = E\psi \]

\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]

Boundary Condition: \( \psi \rightarrow 0 \) as \( x \rightarrow \pm \infty \)
Solution of the HO Schrödinger Equation

Rearrangement of the Equation

\[-\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + \frac{1}{2} kx^2 \psi = E\psi\]
\[-\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + \left( \frac{1}{2} kx^2 - E \right) \psi = 0\]

Define

\[\lambda = \frac{2\mu E}{\hbar^2}\]
\[\alpha^2 = \frac{k\mu}{\hbar^2} = \frac{\mu^2 \omega^2}{\hbar^2} \quad \omega = \sqrt[\hbar]{\mu}\]

\[\frac{d^2\psi}{dx^2} + \left( \lambda - \alpha^2 x^2 \right) \psi = 0\]

Should we try a Taylor series solution? \[\psi = \sum_{n=0}^{\infty} a_n x^n\]

No!! It would be difficult to satisfy the Boundary Conditions.

Instead, it’s better to use: \[\psi = \left( \sum_{n=0}^{\infty} a_n x^n \right) \psi_{\text{asymp}} = H(x)\psi_{\text{asymp}}\]

That is, we’ll assume that \(\psi\) is the product of a Taylor Series, \(H(x)\), and an asymptotic solution, \(\psi_{\text{asymp}}\), valid for large \(|x|\).
The Asymptotic Solution

\[ \frac{d^2\psi}{dx^2} + (\lambda - \alpha^2 x^2)\psi = 0 \]

We can show that the asymptotic solution is

\[ \psi_{\text{asympt}} = e^{-\alpha x^2/2} \]

For large |x|

\[ \frac{d\psi_{\text{asympt}}}{dx} = -\alpha x e^{-\alpha x^2/2} \]

\[ \frac{d^2\psi_{\text{asympt}}}{dx^2} = -\alpha^2 e^{-\alpha x^2/2} + \alpha^2 x^2 e^{-\alpha x^2/2} \]

\[ \frac{d^2\psi_{\text{asympt}}}{dx^2} \approx \alpha^2 x^2 e^{-\alpha x^2/2} \]

Plug in

\[ \frac{d^2\psi_{\text{asympt}}}{dx^2} - \alpha^2 x^2 \psi_{\text{asympt}} = 0 \]

\[ \alpha^2 x^2 e^{-\alpha x^2/2} - \alpha^2 x^2 e^{-\alpha x^2/2} = 0 \]

Note that \( \psi_{\text{asympt}} \) satisfied the BC’s; i.e. \( \psi_{\text{asympt}} \to 0 \) as \( x \to \pm \infty \)

A Recursion Relation for the General Solution

\[ \frac{d^2\psi}{dx^2} + (\lambda - \alpha^2 x^2)\psi = 0 \]

Assume the general solution is of the form

\[ \psi = \left( \sum_{n=0}^{\infty} a_n x^n \right) \psi_{\text{asympt}} = \left( \sum_{n=0}^{\infty} a_n x^n \right) e^{-\alpha x^2/2} = H(x)e^{-\alpha x^2/2} \]

If one: (a) computes \( d^2\psi/dx^2 \)

(b) Plugs \( d^2\psi/dx^2 \) and \( \psi \) into the Schrödinger Equation

(c) Equates the coefficients of \( x^n \)

Then the following recursion formula is obtained:

\[ a_{n+2} = \frac{\lambda}{(n+1)(n+2)} a_n \quad n = 0, 1, 2, 3, \ldots \]
Because \( a_{n+2} \) (rather than \( a_{n+1} \)) is related to \( a_n \), it is best to consider the Taylor Series in the solution to be the sum of an even and odd series

\[
\psi = \left( \sum_{n=0}^{\infty} a_n x^n \right) e^{-\alpha x^2/2} = \left( [a_0 + a_2 x^2 + a_4 x^4 + \ldots] + [a_1 x + a_3 x^3 + a_5 x^5 + \ldots] \right) e^{-\alpha x^2/2}
\]

**Even Series**

**Odd Series**

From the recursion formula:

- \( a_0 \rightarrow a_2 \rightarrow a_4 \rightarrow \ldots \) **Even Coefficients**
- \( a_1 \rightarrow a_3 \rightarrow a_5 \rightarrow \ldots \) **Odd Coefficients**

\( a_0 \) and \( a_1 \) are two arbitrary constants

So far:

(a) The Boundary Conditions have not been satisfied
(b) There is no quantization of energy

---

**Satisfying the Boundary Conditions: Quantization of Energy**

\[
\lambda = \frac{2\mu E}{\hbar^2} \quad \Rightarrow \quad E = \frac{\lambda \hbar^2}{2\mu}
\]

So far, there are no restrictions on \( \lambda \) and, therefore, none on \( E \)

Let’s look at the solution so far:

\[
\psi = \left( \sum_{n=0}^{\infty} a_n x^n \right) e^{-\alpha x^2/2} = \left( [a_0 + a_2 x^2 + a_4 x^4 + \ldots] + [a_1 x + a_3 x^3 + a_5 x^5 + \ldots] \right) e^{-\alpha x^2/2}
\]

**Even Series**

**Odd Series**

Does this solution satisfy the BC’s: i.e. \( \psi \rightarrow 0 \) as \( x \rightarrow \pm \infty \)?

It can be shown that:

\[
\lim_{x \to \pm \infty} \left( x^n e^{-\alpha x^2/2} \right) = 0 \quad \text{unless} \quad n \to \infty
\]

Therefore, the required BC’s will be satisfied if, and only if, both the even and odd Taylor series terminate at a finite power.
Even Series: $\psi = \left( \sum_{n=0}^{\infty} a_n x^n \right) e^{-\alpha x^2/2} = \left( a_0 + a_2 x^2 + a_4 x^4 + \ldots \right) + \left( a_1 x + a_3 x^3 + a_5 x^5 + \ldots \right) e^{-\alpha x^2/2}$

Odd Series: $a_{n+2} = \frac{\lambda - 2n - 1}{(n+1)(n+2)} a_n \quad n = 0, 1, 2, 3, \ldots$

We cannot let either Taylor series reach $x^\infty$.

We can achieve this for the even or odd series by setting $a_0 = 0$ (even series) or $a_1 = 0$ (odd series).

We can’t set both $a_0 = 0$ and $a_1 = 0$, in which case $\psi(x) = 0$ for all $x$.

So, how can we force the second series to terminate at a finite value of $n$?

By requiring that $a_{n+2} = 0 \cdot a_n$ for some value of $n$.

If $a_{n+2} = 0 \cdot a_n$ for some value of $n$, then the required BC will be satisfied.

$$a_{n+2} = \frac{\lambda - 2n - 1}{(n+1)(n+2)} a_n \quad n = 0, 1, 2, 3, \ldots$$

Therefore, it is necessary for some value of the integer, $n$, that:

$$\frac{\lambda - 2n - 1}{(n+1)(n+2)} = 0 \quad \rightarrow \quad \frac{\lambda - 2n - 1}{\alpha} = 0$$

This criterion puts restrictions on the allowed values of $\lambda$ and, therefore, the allowed values of the energy, $E$. 

---

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Allowed Values of the Energy

Earlier Definitions

\[ \lambda = \frac{2\mu E}{\hbar^2} \rightarrow E = \frac{\lambda \hbar^2}{2\mu} \]

Restriction on \( \lambda \):

\[ \frac{\lambda}{\alpha} = 2n - 1 = 0 \quad n = 0, 1, 2, 3, \ldots \]

\[ \lambda = \alpha (2n + 1) = \frac{\mu \omega}{\hbar} (2n + 1) \]

Quantized Energy Levels

\[ E = \frac{\lambda \hbar^2}{2\mu} = \frac{\hbar^2}{2\mu} \left[ \frac{\mu \omega}{\hbar} (2n + 1) \right] = \hbar \omega \frac{2n + 1}{2} \]

or

\[ E = \left( n + \frac{1}{2} \right) \hbar \omega \quad n = 0, 1, 2, 3, \ldots \]

\[ E = \left( n + \frac{1}{2} \right) \hbar \nu \quad \nu = \frac{\omega}{2\pi} \]

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**Harmonic Oscillator Wavefunctions and Energies**

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- Vibrational Anharmonicity
- The Two Dimensional Harmonic Oscillator
- Vibrations of Polyatomic Molecules
**HO Energies and Wavefunctions**

**Harmonic Oscillator Energies**

\[ E_n = \left(n + \frac{1}{2}\right) \hbar \omega = \left(n + \frac{1}{2}\right) \hbar \nu \quad n = 0, 1, 2, 3, \ldots \]

Angular Frequency: \[ \omega = \sqrt{\frac{k}{\mu}} \]

Circular Frequency: \[ \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \]

Wavenumbers: \[ \tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \]

where \[ \tilde{\nu} = \frac{1}{\lambda (cm)} = \frac{\nu}{c (cm/s)} \text{ cm}^{-1} \]

---

**Quantized Energies**

Only certain energy levels are allowed and the separation between levels is:

\[ \Delta E = \hbar \omega \]

The classical HO permits any value of \( E \).

**Zero Point Energy**

The minimum allowed value for the energy is:

\[ E_0 = \frac{1}{2} \hbar \omega \]

The classical HO can have \( E=0 \).

Note: All "bound" particles have a minimum ZPE. This is a consequence of the Uncertainty Principle.
The Correspondence Principle

The results of Quantum Mechanics must not contradict those of classical mechanics when applied to macroscopic systems.

The fundamental vibrational frequency of the \( \text{H}_2 \) molecule is 4200 \( \text{cm}^{-1} \). Calculate the energy level spacing and the ZPE, in J and in kJ/mol.

\[
\omega = 2\pi \nu = 2\pi c \tilde{v} = 2(3.14)(3.00 \times 10^8 \text{ cm/s})(4200 \text{ cm}^{-1}) = 7.92 \times 10^{14} \text{ s}^{-1}
\]

Spacing: \( \Delta E = \hbar \omega = (1.05 \times 10^{-34} \text{ J} \cdot \text{s})(7.92 \times 10^{14} \text{ s}^{-1}) = 8.3 \times 10^{-20} \text{ J} \)

\[
N_A \cdot \Delta E = (6.02 \times 10^{23} \text{ mol}^{-1})(8.3 \times 10^{-20} \text{ J}) = 5.00 \times 10^4 \text{ J/mol} = 50 \text{ kJ/mol}
\]

ZPE: \( E_0 = \frac{1}{2} \hbar \omega = \frac{1}{2}(1.05 \times 10^{-34} \text{ J} \cdot \text{s})(7.92 \times 10^{14} \text{ s}^{-1}) = 4.15 \times 10^{-20} \text{ J} \)

\[
N_A \cdot E_0 = (6.02 \times 10^{23} \text{ mol}^{-1})(4.15 \times 10^{-20} \text{ J}) = 2.5 \times 10^4 \text{ J/mol} = 25 \text{ kJ/mol}
\]

Macroscopic oscillators have much lower frequencies than molecular sized systems. Calculate the energy level spacing and the ZPE, in J and in kJ/mol, for a macroscopic oscillator with a frequency of 10,000 cycles/second.

\[
\omega = 2\pi \nu = 2(3.14)(1.00 \times 10^4 \text{ s}^{-1}) = 6.28 \times 10^4 \text{ s}^{-1}
\]

Spacing: \( \Delta E = \hbar \omega = (1.05 \times 10^{-34} \text{ J} \cdot \text{s})(6.28 \times 10^4 \text{ s}^{-1}) = 6.6 \times 10^{-30} \text{ J} \)

\[
N_A \cdot \Delta E = (6.02 \times 10^{23} \text{ mol}^{-1})(6.6 \times 10^{-30} \text{ J}) = 4.0 \times 10^{-6} \text{ J/mol} = 4.0 \times 10^{-9} \text{ kJ/mol}
\]

ZPE: \( E_0 = \frac{1}{2} \hbar \omega = \frac{1}{2}(1.05 \times 10^{-34} \text{ J} \cdot \text{s})(6.28 \times 10^4 \text{ s}^{-1}) = 3.3 \times 10^{-30} \text{ J} \)

\[
N_A \cdot E_0 = (6.02 \times 10^{23} \text{ mol}^{-1})(3.3 \times 10^{-30} \text{ J}) = 2.0 \times 10^{-6} \text{ J/mol} = 2.0 \times 10^{-9} \text{ kJ/mol}
\]
Harmonic Oscillator Wavefunctions

\[ \psi = \left( \sum_{n=0}^{\infty} a_n x^n \right) e^{-\alpha x^2/2} \]

Application of the recursion formula yields a different polynomial for each value of \( n \).

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

These polynomials are called Hermite polynomials, \( H_n \).

or

\[ \psi_n = N_n H_n(z)e^{-z^2/2} \text{ where } z = \sqrt{\alpha} x \]

Some specific solutions

\[ n = 0 \quad \psi_0 = N_0 e^{-\alpha x^2/2} = N_0 e^{-z^2/2} \quad \text{Even} \]

\[ n = 1 \quad \psi_1 = N_1 (2\sqrt{\alpha} x)e^{-\alpha x^2/2} = N_1 (2z)e^{-z^2/2} \quad \text{Odd} \]

\[ n = 2 \quad \psi_2 = N_2 (4\alpha x^2 - 2)e^{-\alpha x^2/2} = N_2 (4z^2 - 2)e^{-z^2/2} \quad \text{Even} \]

\[ n = 3 \quad \psi_3 = N_3 (8\alpha^3 x^3 - 12\sqrt{\alpha} x)e^{-\alpha x^2/2} = N_3 (8z^3 - 12z)e^{-z^2/2} \quad \text{Odd} \]
Quantum Mechanical vs. Classical Probability

Classical
- $P(x)$ minimum at $x=0$
- $P(x) = 0$ past $\pm x_0$

QM $(n=0)$
- $P(x)$ maximum at $x=0$
- $P(x) \neq 0$ past $\pm x_0$

Note that as $n$ increases, $P(x)$ approaches the classical limit.
For macroscopic oscillators $n > 10^6$
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Properties of the QM Harmonic Oscillator

Some Useful Integrals

\[ \int_{0}^{\infty} e^{-\beta x^2} \, dx = \frac{1}{2} \sqrt{\frac{\pi}{\beta}} \]

\[ \int_{0}^{\infty} x e^{-\beta x^2} \, dx = \frac{1}{2\beta} \]

\[ \int_{0}^{\infty} x^2 e^{-\beta x^2} \, dx = \frac{1}{4\beta^2} \sqrt{\frac{\pi}{\beta}} \]

\[ \int_{0}^{\infty} x^3 e^{-\beta x^2} \, dx = \frac{1}{2\beta^2} \]

\[ \int_{0}^{\infty} x^4 e^{-\beta x^2} \, dx = \frac{3}{8\beta^3} \sqrt{\frac{\pi}{\beta}} \]

Remember

\[ \int_{-\infty}^{\infty} f(x) \, dx = 2 \int_{0}^{\infty} f(x) \, dx \]

If \( f(-x) = f(x) \)

Even Integrand

\[ \int_{-\infty}^{\infty} f(x) \, dx = 0 \]

If \( f(-x) = -f(x) \)

Odd Integrand
Wavefunction Orthogonality

\[ \psi_0 = N_0 e^{-\alpha^2 x^2 / 2} \quad \infty < x < \infty \]
\[ \psi_1 = N_1 (2\sqrt{\alpha} x) e^{-\alpha^2 x^2 / 2} \quad \infty < x < \infty \]
\[ \psi_2 = N_2 (4\alpha x^2 - 2) e^{-\alpha^2 x^2 / 2} \quad \infty < x < \infty \]

\[ \langle \psi_0 | \psi_1 \rangle \]
\[ \langle \psi_0 | \psi_1 \rangle = \int_{-\infty}^{\infty} (N_0 e^{-\alpha^2 x^2 / 2})(N_1 2\sqrt{\alpha} x e^{-\alpha^2 x^2 / 2}) dx \]
\[ \langle \psi_0 | \psi_1 \rangle = N_0 N_1 2\sqrt{\alpha} \int_{-\infty}^{\infty} x e^{-\alpha^2 x^2} dx \]

Odd Integrand

\[ \langle \psi_0 | \psi_1 \rangle = 0 \]

Wavefunction Orthogonality

\[ \psi_0 = N_0 e^{-\alpha^2 x^2 / 2} \quad \infty < x < \infty \]
\[ \psi_1 = N_1 (2\sqrt{\alpha} x) e^{-\alpha^2 x^2 / 2} \quad \infty < x < \infty \]
\[ \psi_2 = N_2 (4\alpha x^2 - 2) e^{-\alpha^2 x^2 / 2} \quad \infty < x < \infty \]

\[ \langle \psi_0 | \psi_2 \rangle \]
\[ \langle \psi_0 | \psi_2 \rangle = \int_{-\infty}^{\infty} (N_0 e^{-\alpha^2 x^2 / 2})(N_2 [4\alpha x^2 - 2] e^{-\alpha^2 x^2 / 2}) dx \]
\[ \langle \psi_0 | \psi_2 \rangle = N_0 N_2 \left[ 4\alpha \int_{-\infty}^{\infty} x^2 e^{-\alpha^2 x^2} dx - 2\int_{-\infty}^{\infty} e^{-\alpha^2 x^2} dx \right] \]
\[ \langle \psi_0 | \psi_2 \rangle = N_0 N_2 \left[ 4\alpha \cdot 2 \cdot \frac{1}{4\alpha \sqrt{\alpha}} - 2 \cdot 2 \cdot \frac{1}{2 \sqrt{\alpha}} \right] \]
\[ \langle \psi_0 | \psi_2 \rangle = 0 \]
We performed many of the calculations below on $\psi_0$ of the HO in Chap. 2. Therefore, the calculations below will be on $\psi_1$.

$$\psi_1 = Ax e^{-\alpha x^2 / 2}, \quad \infty < x < \infty$$

**Normalization**

$$\langle \psi_1 | \psi_1 \rangle = \int_{-\infty}^{\infty} \left[ A x e^{-\alpha x^2 / 2} \right]^2 dx = 1$$

from HW Solns.

$$A = \sqrt{2\alpha} \cdot \left( \frac{\alpha}{\pi} \right)^{1/4}$$

---

**Positional Averages**

$$<x> = \langle \psi_1 | x | \psi_1 \rangle = \int_{-\infty}^{\infty} x \left[ A x e^{-\alpha x^2 / 2} \right]^2 dx$$

from HW Solns.

$$<x> = 0$$

$$<x^2> = \langle \psi_1 | x^2 | \psi_1 \rangle = \int_{-\infty}^{\infty} x^2 \left[ A x e^{-\alpha x^2 / 2} \right]^2 dx$$

from HW Solns.

$$<x^2> = \frac{3}{2\alpha}$$
Momentum Averages

\[
\langle p \rangle = \langle \psi_1 | \hat{p} | \psi_1 \rangle = \int_{-\infty}^{\infty} \left[ A_1 e^{-ax^2/2} \right] \frac{\hbar}{i} \frac{d}{dx} \left[ A_1 e^{-ax^2/2} \right] dx
\]

from HW Solns.

\[\langle p \rangle = 0\]

\[
\langle p^2 \rangle = \langle \psi_1 | \hat{p}^2 | \psi_1 \rangle = \int_{-\infty}^{\infty} \left[ A_1 e^{-ax^2/2} \right] \left[ -\hbar^2 \frac{d^2}{dx^2} \left[ A_1 e^{-ax^2/2} \right] \right] dx
\]

from HW Solns.

\[\langle p^2 \rangle = \frac{3}{2} \hbar^2 \alpha\]

Energy Averages

Kinetic Energy

\[
\langle T \rangle = \frac{\langle p^2 \rangle}{2\mu} = \frac{1}{2\mu} \langle p^2 \rangle
\]

\[\langle T \rangle = \frac{1}{2\mu} \left( \frac{3}{2} \hbar^2 \alpha \right)\]

from HW Solns.

\[\langle T \rangle = \frac{3}{4} \hbar \omega\]

Potential Energy

\[
\langle V \rangle = \langle \frac{1}{2} k x^2 \rangle = \frac{1}{2} k \langle x^2 \rangle
\]

\[\langle V \rangle = \frac{1}{2} k \left( \frac{3}{2\alpha} \right)\]

from HW Solns.

\[\langle V \rangle = \frac{3}{4} \hbar \omega\]

Total Energy

\[
E = \left( n + \frac{1}{2} \right) \hbar \omega = \frac{3}{2} \hbar \omega = \langle T \rangle + \langle V \rangle
\]

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The Vibrations of Diatomic Molecules

The Potential Energy

Define: \( x = R - R_{eq} \)

Expand \( V(x) \) in a Taylor series about \( x = 0 \) (\( R = R_{eq} \))

\[
V(x) = \sum_{n=0}^{\infty} \frac{1}{n!} \left( \frac{d^n V}{dx^n} \right)_{x=0} x^n
\]

\[
V(x) = \left( \frac{dV}{dx} \right)_{x=0} x + \frac{1}{2!} \left( \frac{d^2 V}{dx^2} \right)_{x=0} x^2 + \frac{1}{3!} \left( \frac{d^3 V}{dx^3} \right)_{x=0} x^3 + \frac{1}{4!} \left( \frac{d^4 V}{dx^4} \right)_{x=0} x^4 + \ldots
\]

\[
V(x) = \left( \frac{dV}{dx} \right)_{x=0} x + \frac{1}{2!} \left( \frac{d^2 V}{dx^2} \right)_{x=0} x^2 + \frac{1}{3!} \left( \frac{d^3 V}{dx^3} \right)_{x=0} x^3 + \frac{1}{4!} \left( \frac{d^4 V}{dx^4} \right)_{x=0} x^4 + \ldots
\]
By convention

By definition

\[
V(x) = \frac{1}{2} k x^2 + \gamma x^3 + \delta x^4 + \ldots
\]

\[
V(x) = \frac{1}{2} k x^2 + \gamma x^3 + \delta x^4 + \ldots
\]

The Harmonic Oscillator Approximation

Ignore \(x^3\) and higher order terms in \(V(x)\)

\[
V(x) = \frac{1}{2} k x^2 \quad \text{where} \quad k = \left( \frac{d^2 V}{dx^2} \right)_{x=0}
\]
The Force Constant (k)
The Interpretation of k

\[ k = \left( \frac{d^2 V}{dx^2} \right)_{x=0} = \frac{d}{dx} \left( \frac{dV}{dx} \right) = \frac{d}{dx} (\text{Slope}) \]

i.e. k is the "curvature" of the plot, and represents the "rapidity" with which the slope turns from negative to positive.

Another way of saying this is the k represents the "steepness" of the potential function at x=0 \((R=R_a)\).

Correlation Between k and Bond Strength

\( D_o \) is the Dissociation Energy of the molecule, and represents the chemical bond strength.

There is often a correlation between k and \( D_o \).
Note the approximately linear correlation between Force Constant (k) and Bond Strength (D_o).

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Vibrational Spectroscopy

Energy Levels and Transitions

\[ E_n = \left( n + \frac{1}{2} \right) \hbar \nu = \left( n + \frac{1}{2} \right) \hbar v \]

\[ v = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \]

Selection Rule

\[ \Delta n = \pm 1 \quad (+1 \text{ for absorption, } -1 \text{ for emission}) \]

IR Spectra: For a vibration to be IR active, the dipole moment must change during the course of the vibration.

Raman Spectra: For a vibration to be Raman active, the polarizability must change during the course of the vibration.

Transition Frequency

\[ n \rightarrow n+1 \]

\[ \Delta E = \left[ (n+1) + \frac{1}{2} \right] \hbar \nu - \left[ n + \frac{1}{2} \right] \hbar \nu = \hbar \nu \]

Wavenumbers:

\[ \tilde{\nu} = \frac{\Delta E}{\hbar c} = \frac{\nu}{c} \text{ cm}^{-1} \]

Note:

\[ \tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \]

The Boltzmann Distribution

\[ N_n \propto g_n e^{-E_n/kT} = e^{-E_n/kT} \]

The strongest transition corresponds to: \( n=0 \rightarrow n=1 \)
Calculation of the Force Constant

Units of \( k \)

\[
k = \left( \frac{d^2V}{dx^2} \right)_{x=0}
\]

\[
k = \frac{J}{m^2} = \frac{kg \cdot m^2}{s^2} = \frac{kg}{s^2} \cdot \frac{m}{s^2} = \frac{N}{m}
\]

Calculation of \( k \)

\[
\tilde{v} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}
\]

\[
k = \left( 2\pi c\tilde{v} \right)^2 \mu
\]

The IR spectrum of \(^{79}\text{Br}\text{19F}\) contains a single line at 380 cm\(^{-1}\)

Calculate the Br-F force constant, in N/m.

\[
\mu = \frac{m_{\text{Br}} \cdot m_{\text{F}}}{m_{\text{Br}} + m_{\text{F}}} = \frac{79 \text{ amu} \cdot 19 \text{ amu}}{79 \text{ amu} + 19 \text{ amu}}
\]

\[
\mu = 15.32 \text{ amu} \cdot 1.66 \times 10^{-27} \text{ kg/amu} = 2.54 \times 10^{-26} \text{ kg}
\]

\[
\tilde{v} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \rightarrow k = \left( 2\pi c\tilde{v} \right)^2 \mu = \left[ 2 (3.14) \left( 3 \times 10^{10} \text{ cm/s} \right) \left( 380 \text{ cm}^{-1} \right) \right]^2 \left( 2.54 \times 10^{-26} \text{ kg} \right)
\]

\[
k = 130 \text{ kg/s}^2 = 130 \left( \text{kg} \cdot \text{m/s}^2 \right) / m = 130 N/m
\]
Calculate the intensity ratio, \( R = \frac{I_{1 \rightarrow 2}}{I_{0 \rightarrow 1}} \), for the \(^{79}\text{Br}^{19}\text{F}\) vibration at 25 °C.

\[
\frac{I_{1 \rightarrow 2}}{I_{0 \rightarrow 1}} = \frac{N_1}{N_0} = \frac{e^{-\frac{E_1}{kT}}}{e^{-\frac{E_0}{kT}}} = e^{-\frac{(E_1 - E_0)}{kT}} = e^{-\frac{\nu}{kT}}
\]

\[
\frac{I_{1 \rightarrow 2}}{I_{0 \rightarrow 1}} = e^{-1.84} = 0.16
\]

\[
\frac{h\nu}{kT} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^{10} \text{ cm/s})(380 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J/K})(298 \text{K})} = 1.84
\]

The \( n=1 \rightarrow n=2 \) transition is called a **hot band**, because its intensity increases at higher temperature.

Dependence of hot band intensity on frequency and temperature

\[
R = \frac{I_{1 \rightarrow 2}}{I_{0 \rightarrow 1}} = \frac{N_1}{N_0} = \frac{e^{-\frac{E_1}{kT}}}{e^{-\frac{E_0}{kT}}} = e^{-\frac{\nu}{kT}}
\]

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<tr>
<th>Molecule</th>
<th>( \tilde{\nu} ) (cm(^{-1}))</th>
<th>T (°C)</th>
<th>R</th>
</tr>
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<td>25</td>
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Vibrational Anharmonicity

\[ V(x) = \frac{1}{2} kx^2 + \gamma x^3 + \delta x^4 + \ldots \]

Harmonic Oscillator
Approximation: \[ V(x) \approx \frac{1}{2} kx^2 \]

The effect of including vibrational anharmonicity in treating the vibrations of diatomic molecules is to lower the energy levels and decrease the transition frequencies between successive levels.
A treatment of the vibrations of diatomic molecules which includes vibrational anharmonicity [includes higher order terms in \( V(x) \)] leads to an improved expression for the energy:

\[
\frac{E_n}{\hbar c} = \left( n + \frac{1}{2} \right) \bar{\nu} - \left( n + \frac{1}{2} \right)^2 x_e \bar{\nu}
\]

\( \bar{\nu} \) is the harmonic frequency and \( x_e \) is the anharmonicity constant.

Measurement of the fundamental frequency (0 \( \rightarrow \) 1) and first overtone (0 \( \rightarrow \) 2) [or the "hot band" (1 \( \rightarrow \) 2)] permits determination of \( \bar{\nu} \) and \( x_e \). See HW Problem.
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The Two Dimensional Harmonic Oscillator

The Schrödinger Equation

\[ V(x, y) = \frac{1}{2} k_x x^2 + \frac{1}{2} k_y y^2 \]

\[ \left\{ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + \frac{1}{2} k_x x^2 \right\}\psi(x) + \left\{ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial y^2} + \frac{1}{2} k_y y^2 \right\}\psi(y) = E\psi(x, y) \]

The Solution: Separation of Variables

The Hamiltonian is of the form: \( H(x, y) = H_x(x) + H_y(y) \)

Therefore, assume that \( \psi \) is of the form: \( \psi(x, y) = \psi_x(x) \cdot \psi_y(y) \)

\[ \left\{ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + \frac{1}{2} k_x x^2 \right\}\psi_x(x) \cdot \psi_y(y) = E\psi_x(x) \cdot \psi_y(y) \]

\[ \psi_y \left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} k_x x^2 \right] + \psi_x \left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dy^2} + \frac{1}{2} k_y y^2 \right] = E\psi_x(x) \cdot \psi_y(y) \]

\[ \frac{1}{\psi_x} \left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} k_x x^2 \right] + \frac{1}{\psi_y} \left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dy^2} + \frac{1}{2} k_y y^2 \right] = E \]

\[ E_x = \frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} k_x x^2 \]

\[ E_y = \frac{\hbar^2}{2\mu} \frac{d^2}{dy^2} + \frac{1}{2} k_y y^2 \]

The above equation is of the form, \( f(x) + g(y) = \text{constant} \). Therefore, one can set each function equal to a constant.

\[ E = E_x + E_y \]
The above equations are just one dimensional HO Schrödinger equations. Therefore, one has:

\[
\psi_{nx} = N_n H_n (\sqrt{\alpha_x} x) e^{-\alpha_x x^2/2} \quad \psi_{ny} = N_n H_n (\sqrt{\alpha_y} y) e^{-\alpha_y y^2/2}
\]

\[
E_x = \left(n_x + \frac{1}{2}\right) \hbar \omega_x \quad E_y = \left(n_y + \frac{1}{2}\right) \hbar \omega_y
\]

\[
\omega_x = \sqrt{\frac{k_x}{\mu}} \quad \omega_y = \sqrt{\frac{k_y}{\mu}}
\]

\[
\alpha_x = \frac{\mu \omega_x}{\hbar} \quad \alpha_y = \frac{\mu \omega_y}{\hbar}
\]

Energies and Degeneracy

\[
E = E_x + E_y = \left(n_x + \frac{1}{2}\right) \hbar \omega_x + \left(n_y + \frac{1}{2}\right) \hbar \omega_y
\]

\[
\omega_y = 2 \omega_x
\]

\[
E = \left(n_x + \frac{1}{2}\right) \hbar \omega_x + (2n_y + 1) \hbar \omega_y
\]

\[
E = \left(n_x + 2n_y + \frac{3}{2}\right) \hbar \omega_x
\]

Depending upon the relative values of \(k_x\) and \(k_y\), one may have degenerate energy levels. For example, let’s assume that \(k_y = 4 \cdot k_x\).
Vibrations of Polyatomic Molecules

I’ll just outline the results.

If one has N atoms, then there are 3N coordinates. For the i’th. atom, the coordinates are $x_i, y_i, z_i$. Sometimes this is shortened to: $x_{i\alpha}$, where $\alpha = x, y, z$.

The Hamiltonian for the N atoms (with 3N coordinates), assuming that the potential energy, $V$, varies quadratically with the change in coordinate is:

$$H = \sum_{ia} -\frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial x_{i\alpha}^2} + \sum_{i} \sum_{j\beta} F_{i\alpha,j\beta} (x_{i\alpha} - x_{j\alpha}'^0)(x_{j\beta} - x_{j\beta}'^0)$$

$$F_{i\alpha,j\beta} = \left( \frac{\partial^2 V}{\partial x_{i\alpha} \partial x_{j\beta}'} \right)_{x_{i\alpha} = x_{j\beta} = x_{j\beta}'^0}$$
After some rather messy algebra, one can transform the Cartesian coordinates to a set of “mass weighted” Normal Coordinates.

\[ Q_i = \sum_{j,k} \sqrt{m_j L_{i,j,k}} (x_{i,j} - x_{i,k}) \]

There are 3N-6 Normal Coordinates.

Each normal coordinate corresponds to the set of vectors showing the relative displacements of the various atoms during a given vibration.

For example, for the 3 vibrations of water, the Normal Coordinates correspond to the 3 sets of vectors you’ve seen in other courses.

In the normal coordinate system, the Hamiltonian can be written as:

\[ H = \sum_{i=1}^{3N-6} \left[ -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \omega_i^2 Q_i^2 \right] \]

\[ H = \left[ -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_1^2} + \frac{1}{2} \omega_1^2 Q_1^2 \right] + \left[ -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_2^2} + \frac{1}{2} \omega_2^2 Q_2^2 \right] + \left[ -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_3^2} + \frac{1}{2} \omega_3^2 Q_3^2 \right] + \ldots \]

Note that the Hamiltonian is of the form:

\[ H = \sum_{i=1}^{3N-6} H_i(Q_i) = H_1(Q_1) + H_2(Q_2) + H_3(Q_3) + \ldots \]

Therefore, one can assume:

\[ \psi = \prod_{i=1}^{3N-6} \psi_i(Q_i) = \psi_1(Q_1) \bullet \psi_2(Q_2) \bullet \psi_3(Q_3) \ldots \]

and simplify the Schrödinger equation by separation of variables.
One gets 3N-6 equations of the form:

\[ -\frac{\hbar^2}{2} \frac{\partial^2 \psi_i}{\partial Q_i^2} + \frac{1}{2} \omega_i^2 Q_i^2 \psi_i = E_i \psi_i \]

The solutions to these 3N-6 equations are the familiar Harmonic Oscillator Wavefunctions and Energies.

As noted above, the total wavefunction is given by:

\[ \psi = \prod_{i=1}^{3N-6} \psi_i(Q_i) \]

The total vibrational energy is:

\[ E(n_1,n_2,n_3,\ldots) = \sum_{i=1}^{3N-6} \left( n_i + \frac{1}{2} \right) \hbar \omega_i = \left( n_1 + \frac{1}{2} \right) \hbar \omega_1 + \left( n_2 + \frac{1}{2} \right) \hbar \omega_2 + \left( n_3 + \frac{1}{2} \right) \hbar \omega_3 + \ldots \]

Or, equivalently:

\[ E(n_1,n_2,n_3,\ldots) = \sum_{i=1}^{3N-6} \left( n_i + \frac{1}{2} \right) \hbar \nu_i \]

In spectroscopy, we commonly refer to the “energy in wavenumbers”, which is actually \( \frac{E}{\hbar c} \):

\[ \frac{E(n_1,n_2,n_3,\ldots)}{\hbar c} = \sum_{i=1}^{3N-6} \left( n_i + \frac{1}{2} \right) \nu_i \]

The water molecule has three normal modes, with fundamental frequencies: \( \nu_1 = 3833 \text{ cm}^{-1}, \nu_2 = 1649 \text{ cm}^{-1}, \nu_3 = 3943 \text{ cm}^{-1} \).

What is the energy, in cm\(^{-1}\), of the (112) state (i.e. \( n_1=1, n_2=1, n_3=2 \))?

\[
\begin{align*}
E(112) &= \left(1 + \frac{1}{2}\right) \nu_1 + \left(1 + \frac{1}{2}\right) \nu_2 + \left(2 + \frac{1}{2}\right) \nu_3 \\
&= \frac{3}{2}(3833 \text{ cm}^{-1}) + \frac{3}{2}(1649 \text{ cm}^{-1}) + \frac{5}{2}(3943 \text{ cm}^{-1}) \\
&= 18,081 \text{ cm}^{-1}
\end{align*}
\]
The water molecule has three normal modes, with fundamental frequencies: $\tilde{\nu}_1 = 3833 \text{ cm}^{-1}$, $\tilde{\nu}_2 = 1649 \text{ cm}^{-1}$, $\tilde{\nu}_3 = 3943 \text{ cm}^{-1}$.

What is the energy difference, in cm$^{-1}$, between (112) and (100), i.e. $E(112)/\hbar c - E(100)/\hbar c$?

$$\frac{E(112)}{\hbar c} = 18,081 \text{ cm}^{-1}$$

$$\frac{E(100)}{\hbar c} = \left(1 + \frac{1}{2}\right)\tilde{\nu}_1 + \left(0 + \frac{1}{2}\right)\tilde{\nu}_2 + \left(0 + \frac{1}{2}\right)\tilde{\nu}_3$$

$$= \frac{3}{2} (3833 \text{ cm}^{-1}) + \frac{1}{2} (1649 \text{ cm}^{-1}) + \frac{1}{2} (3943 \text{ cm}^{-1}) = 8,546 \text{ cm}^{-1}$$

$$\frac{E(112)}{\hbar c} - \frac{E(100)}{\hbar c} = 18,081 \text{ cm}^{-1} - 8,546 \text{ cm}^{-1} = 9,535 \text{ cm}^{-1}$$

This corresponds to the frequency of the combination band in which the molecule’s vibrations are excited from $n_2=0 \rightarrow n_2=1$ and $n_3=0 \rightarrow n_3=2$. 

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Chapter 5

Molecular Vibrations and Time-Independent Perturbation Theory

Part B: The Symmetry of Vibrations + Perturbation Theory + Statistical Thermodynamics

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- The Symmetry of Vibrational Normal Modes: Application to the Stretching Vibrations in Ethylene
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Symmetry and Vibrational Selection Rules

By symmetry: \( f(-x) = -f(x) \)

\[
\int_{-\infty}^{\infty} xe^{-ax^2} \, dx = ??
\]

\[
\int_{-\infty}^{\infty} xe^{-ax^2} \, dx = 0
\]

By symmetry: \( f(-x) = -f(x) \)

Consider the 1s and 2p\(_x\) orbitals in a hydrogen atom.

\[
\iiint \psi_{1s} \psi_{2p_x} \, dV = ??
\]

\[
\iiint \psi_{1s} \psi_{2p_x} \, dV = 0
\]

By symmetry: Values of the integrand for \(-x\) are the negative of values for \(+x\); i.e. the portions of the integral to the left of the yz plane and right of the yz plane cancel.

If you understand this, then you know all (or almost all) there is to know about Group Theory.
The Direct Product

There is a theorem from Group Theory (which we won’t prove) that an integral is zero unless the integrand either:
(a) belongs to the totally symmetric \((A, A_1, A_{1g})\) representation
(b) contains the totally symmetric \((A, A_1, A_{1g})\) representation

\[ \int f \, d\tau = 0 \quad \text{unless} \quad \Gamma(f) = A \]

The question is: How do we know the representation of an integrand when it is the product of 2 or more functions?

\[ \int f \, d\tau = \int \varphi_a \varphi_b \, d\tau \quad \Gamma(\varphi_a \varphi_b) = ? \]

The product of two functions belongs to the representation corresponding to the Direct Product of their representations

\[ f = \varphi_a \cdot \varphi_b \]

\[ f[\Gamma_f] = \varphi_a[\Gamma_a] \cdot \varphi_b[\Gamma_b] \]

\[ \Gamma_f = \Gamma_a \times \Gamma_b \]

How do we determine the Direct Product of two representations?

Simple!! We just multiply their characters (traces) together.
<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>E</th>
<th>$C_2$</th>
<th>$\sigma_v(xz)$</th>
<th>$\sigma_v(yz)$</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
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<td>-1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

When will the Direct Product be $A_1$?

Only when the two representations are the same. (This is another theorem that we won’t prove)

What if the integrand is the product of three functions?
e.g. \[ \int f d\tau = \int \phi_a \phi_b \phi_c d\tau \quad \Gamma(\phi_a \phi_b \phi_c) = ? \]

The representation of the integrand is the Direct Product of the representations of the three functions.
i.e. $\Gamma_f = \Gamma_a \times \Gamma_b \times \Gamma_c$

What is $\Gamma_f$ if one of the 3 functions belongs to the totally symmetric representation (e.g. if $\Gamma(\phi_c) = A_1$) ?

\[ \Gamma_f = \Gamma_a \times \Gamma_b \times A_1 = \Gamma_a \times \Gamma_b \]

Therefore $\Gamma_f \neq A_1$ unless $\Gamma_a = \Gamma_b$
When will the Direct Product be $A_1$?

Only when the two representations are the same.
(This is another theorem that we won’t prove)

A minor addition.

When considering a point group with degenerate (E or T) representations, then it can be shown that the product of two functions will contain $A_1$ only if the two representations are the same.

e.g. $E \times E = A_1 + \text{other}$

\[ \int f d\tau = \int \phi_a \phi_b d\tau \quad \Gamma(\phi_a \phi_b) = ? \]

\[ \Gamma_f = \Gamma_a \times \Gamma_b \]

Based upon what we’ve just seen: $\Gamma_f \neq A_1$

unless $\Gamma_a = \Gamma_b$

Therefore, the integral of the product of two functions vanishes unless the two functions belong to the same representation.
What if the integrand is the product of three functions?

\[ \int f d\tau = \int \phi_a \phi_b \phi_c d\tau \quad \Gamma(\phi_a \phi_b \phi_c) = ? \]

The representation of the integrand is the Direct Product of the representations of the three functions.

i.e. \( \Gamma_f = \Gamma_a \times \Gamma_b \times \Gamma_c \)

What is \( \Gamma_f \) if one of the 3 functions belongs to the totally symmetric representation (e.g. if \( \Gamma(\phi_c) = A_1 \)?)

\[ \Gamma_f = \Gamma_a \times \Gamma_b \times A_1 = \Gamma_a \times \Gamma_b \]

Therefore \( \Gamma_f \neq A_1 \) unless \( \Gamma_a = \Gamma_b \)

---

Part B: The Symmetry of Vibrations + Perturbation Theory + Statistical Thermodynamics

- Symmetry and Vibrational Selection Rules
- **Spectroscopic Selection Rules**
  - The Symmetry of Vibrational Normal Modes:
    Application to the Stretching Vibrations in Ethylene
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Spectroscopic Selection Rules

When light (of frequency $\omega$) is shined on a sample, the light’s electric vector interacts with the molecule’s dipole moment, which adds a perturbation to the molecular Hamiltonian.

$$H = H^{(0)} + H^{(+)} = H^{(0)} - \hat{\mu} \cdot \vec{E} = H^{(0)} - \mu E \cos(\omega t)$$

The perturbation “mixes” the ground state wavefunction ($\Psi_0 = \Psi_{\text{init}}$) with various excited states ($\Psi_i = \Psi_{\text{fin}}$). A simpler way to say this is that the light causes transitions between the ground state and the excited states.

Consider a transition between the ground state ($\Psi_0 = \Psi_{\text{init}}$) and the i’th excited state ($\Psi_i = \Psi_{\text{fin}}$).

Time dependent perturbation theory can be used to show that the intensity of the absorption is proportional to the square of the “transition moment”, $M_{0i}$.

$$\text{Intensity} = C \cdot |M_{0i}|^2$$

The transition moment is: $M_{0i} = \langle \Psi_{\text{fin}} | \hat{\mu} | \Psi_{\text{init}} \rangle = \int \Psi_{\text{fin}}^* \hat{\mu} \Psi_{\text{init}} d\tau$

$\hat{\mu}$ is the dipole moment operator: $\hat{\mu} = \hat{\mu} = e \left( x\hat{i} + y\hat{j} + z\hat{k} \right)$

$$M_{0i} = \langle \Psi_{\text{fin}} | x | \Psi_{\text{init}} \rangle \hat{i} + \langle \Psi_{\text{fin}} | y | \Psi_{\text{init}} \rangle \hat{j} + \langle \Psi_{\text{fin}} | z | \Psi_{\text{init}} \rangle \hat{k}$$

Thus, the transition moment has x, y and z components.
The above equation leads to the Selection Rules in various areas of spectroscopy.

The intensity of a transition is nonzero only if at least one component of the transition moment is nonzero.

That’s where Group Theory comes in.

As we saw in the previous section, some integrals are zero due to symmetry.

Stated again, an integral is zero unless the integrand belongs to (or contains) the totally symmetry representation, A, A₁, A₂,...

---

**Selection Rules for Vibrational Spectra**

**Infrared Absorption Spectra**

The equation governing the intensity of a vibrational infrared absorption is allowed (i.e. the vibration is IR active) is:

\[
Intensity = C \cdot \left[ M_{0i} \right]^2
\]

\[
M_{0i} = M_{0i1} + M_{0i2} + M_{0i3}
\]

\[
M_{0i1} = e \langle \Psi_{in} | x \Psi_{init} \rangle
\]

\[
M_{0i2} = e \langle \Psi_{in} | y \Psi_{init} \rangle
\]

\[
M_{0i3} = e \langle \Psi_{in} | z \Psi_{init} \rangle
\]

\Psi_{init} and \Psi_{fin} represent vibrational wavefunctions of the initial state (often the ground vibrational state, n=0) and final state (often corresponding to n=1).
A vibration will be Infrared active if any of the three components of the transition moment are non-zero; i.e. if

\[ \Gamma(\Psi_{\text{in}}) \times \Gamma(\langle x \rangle) \times \Gamma(\Psi_{\text{out}}) = A_i \ (A_1, A_2, \ldots) \]

or \[ \Gamma(\Psi_{\text{in}}) \times \Gamma(\langle y \rangle) \times \Gamma(\Psi_{\text{out}}) = A_i \ (A_1, A_2, \ldots) \]

or \[ \Gamma(\Psi_{\text{in}}) \times \Gamma(\langle z \rangle) \times \Gamma(\Psi_{\text{out}}) = A_i \ (A_1, A_2, \ldots) \]

\[ \text{Slide 17} \]

Raman Scattering Spectra

When light passes through a sample, the electric vector creates an induced dipole moment, \( \mu^{\text{ind}} \), whose magnitude depends upon the polarizability, \( \alpha \). The intensity of Raman scattering depends on the size of the induced dipole moment.

Strictly speaking, \( \alpha \) is a tensor (Yech!!)

\[
\mu^{\text{ind}} = \begin{bmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{bmatrix}
\begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}
\]

I have used the fact that the \( \alpha \) tensor is symmetric; i.e. \( \alpha_{ij} = \alpha_{ji} \)

There are 6 independent components of \( \alpha \): \( \alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}, \alpha_{xz}, \alpha_{yz} \)

\[ \text{Slide 18} \]
Therefore, a vibration will be active if any of the following six integrals are not zero.

\[ \left( \mu_0, \mu_1, \mu_2 \right) = \left( \alpha_{xx}, \alpha_{xy}, \alpha_{xz}, \alpha_{yy}, \alpha_{yz}, \alpha_{zz} \right) \left( E_x, E_y, E_z \right) \]

Therefore, a vibration will be active if any of the following six integrals are not zero.

\[ \langle \Psi_{f_{uv}} | \alpha_{uv} | \Psi_{init} \rangle \quad u = x, y, z \quad \text{and} \quad v = x, y, z \]

\( \alpha_{uv} \) has the same symmetry properties as the product \( uv \); i.e. \( \alpha_{xx} \) belongs to the same representation as \( xx \), \( \alpha_{yz} \) belongs to the same representation as \( yz \), etc.

Therefore, a vibration will be Raman active if the direct product:

\[ \Gamma(\Psi_{f_{uv}}) \times \Gamma(uv) = A_1(A_1, A_2, ...) \]

for any of the six uv combinations; \( xx, yy, zz, xy, xz, yz \)

---

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The Symmetry of Vibrational Normal Modes

We will concentrate on the four C-H stretching vibrations in ethylene, C\textsubscript{2}H\textsubscript{4}.

Ethylene has D\textsubscript{2h} symmetry. However, because all 4 C-H stretches are in the plane of the molecule, it is OK to use the subgroup, C\textsubscript{2h}.

<table>
<thead>
<tr>
<th></th>
<th>C\textsubscript{2h}</th>
<th>E</th>
<th>C\textsubscript{2}</th>
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<td>-1</td>
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<td>z</td>
</tr>
<tr>
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<td>-1</td>
<td>1</td>
<td>x, y</td>
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</table>

<table>
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<th></th>
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<th>x</th>
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<td>1</td>
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</table>

Symmetry of Vibrational Wavefunctions

One Dimensional Harmonic Oscillator

\[ n = 0 \quad \psi_0 = N_0 e^{-ax^2/2} \]
\[ n = 1 \quad \psi_1 = N_1 (2\sqrt{ax}) e^{-ax^2/2} \]
\[ n = 2 \quad \psi_2 = N_2 (4ax^2 - 2) e^{-ax^2/2} \]

Harmonic Oscillator Normal Mode: \( \nu_k \)
Normal Coordinate: \( Q_k \)

\[ n = 0 \quad \psi_0^h = N_0 e^{-\alpha Q_k^2/2} \quad \Gamma (\psi_0^h) = A_e \quad \text{(tot. symm. rep.)} \]
\[ n = 1 \quad \psi_1^h = N_1 (2\sqrt{ax}) e^{-\alpha Q_k^2/2} \quad \Gamma (\psi_1^h) = \Gamma (Q_k) \]
\[ n = 2 \quad \psi_2^h = N_2 (4ax^2 - 2) e^{-\alpha Q_k^2/2} \quad \Gamma (\psi_2^h) = A_e \quad \text{(tot. symm. rep.)} \]
Total Vibrational Wavefunction of Polyatomic Molecules

\[ \Psi_{n_1, n_2, n_3, \ldots}^{\text{vib}} = |n_1, n_2, n_3, \ldots \rangle = \psi_1^{n_1} \cdot \psi_2^{n_2} \cdot \psi_3^{n_3} \cdot \ldots \]

\[ \Gamma \left( \Psi_{n_1, n_2, n_3, \ldots}^{\text{vib}} \right) = \Gamma \left( \psi_1^{n_1} \right) \times \Gamma \left( \psi_2^{n_2} \right) \times \Gamma \left( \psi_3^{n_3} \right) \times \ldots \]

Ground State: \[ \Psi_{0,0,0,\ldots}^{\text{vib}} = |0,0,0,\ldots \rangle = \psi_0^{x_0} \cdot \psi_0^{y_0} \cdot \psi_0^{z_0} \cdot \ldots \]

\[ \Gamma \left( \Psi_{0,0,0,\ldots}^{\text{vib}} \right) = \Gamma \left( \psi_0^{x_0} \right) \times \Gamma \left( \psi_0^{y_0} \right) \times \Gamma \left( \psi_0^{z_0} \right) \times \ldots \]

\[ = a_3 \times a_3 \times a_3 \times \ldots = A_g \]

Singly Excited State: \[ \Psi_{0,1,0,\ldots}^{\text{vib}} = |0,1,0,\ldots \rangle = \psi_1^{x_1} \cdot \psi_0^{y_0} \cdot \psi_0^{z_0} \cdot \ldots \]

\[ \Gamma \left( \Psi_{0,1,0,\ldots}^{\text{vib}} \right) = \Gamma \left( \psi_1^{x_1} \right) \times \Gamma \left( \psi_0^{y_0} \right) \times \Gamma \left( \psi_0^{z_0} \right) \times \ldots \]

\[ = a_3 \times \Gamma \left( \psi_1^{x_1} \right) \times a_3 \times \ldots = \Gamma \left( \psi_1^{x_1} \right) \]

---

C-H Stretching Vibrations of Ethylene

IR Activity of Fundamental Modes

\[ A_g: \ |0,0,0,0 \rangle \rightarrow |1,0,0,0 \rangle \]

\[ \Gamma \left( \Psi_{1,0,0,0}^{\text{vib}} \right) = \Gamma \left( \psi_1^{x_1} \right) \times \Gamma \left( \psi_0^{y_0} \right) \times \Gamma \left( \psi_0^{z_0} \right) \times \Gamma \left( \psi_0^{x_1} \right) = A_g \]

\[ \Gamma \left( \Psi_{0,0,0,0}^{\text{vib}} \right) = \Gamma \left( \psi_0^{x_0} \right) \times \Gamma \left( \psi_0^{y_0} \right) \times \Gamma \left( \psi_0^{z_0} \right) \times \Gamma \left( \psi_0^{x_1} \right) = A_g \]

\[ M_{\alpha} = e \left\{ \Psi_{1,0,0,0}^{\text{vib}} \left| \cdot \right| \Psi_{0,0,0,0}^{\text{vib}} \right\} \quad \Gamma = A_x B_y A_y = B_y \]

\[ M_{\beta} = e \left\{ \Psi_{1,0,0,0}^{\text{vib}} \left| \cdot \right| \Psi_{0,0,0,0}^{\text{vib}} \right\} \quad \Gamma = A_x B_y A_y = B_y \]

\[ M_{\gamma} = e \left\{ \Psi_{1,0,0,0}^{\text{vib}} \left| \cdot \right| \Psi_{0,0,0,0}^{\text{vib}} \right\} \quad \Gamma = A_x A_y A_y = A_y \]

\[ A_g \text{ vibrations are IR Inactive} \]
IR Activity of Fundamental Modes

\[ \begin{align*}
B_u: & \quad |0,0,0,0 \rangle \rightarrow |0,0,1,0 \rangle \\
\Gamma(\psi_{0,0,1,0}^{vb}) &= \Gamma(\psi_0^{vi}) x \Gamma(\psi_0^{vi}) x \Gamma(\psi_0^{vi}) x \Gamma(\psi_0^{vi}) = B_e \\
\Gamma(\psi_{0,0,0,0}^{vb}) &= \Gamma(\psi_0^{vi}) x \Gamma(\psi_0^{vi}) x \Gamma(\psi_0^{vi}) x \Gamma(\psi_0^{vi}) = A_g
\end{align*} \]

\[ M_{g, xx} = e^{\langle \psi_{0,0,0,0}^{vb} | x | \Psi_{0,0,0,0}^{vb} \rangle} \Gamma = B_x B_y A_z = A_e \]

\[ M_{g, yy} = e^{\langle \psi_{0,0,1,0}^{vb} | y | \Psi_{0,0,0,0}^{vb} \rangle} \Gamma = B_x B_y A_z = A_e \]

\[ M_{g, zz} = e^{\langle \psi_{0,0,1,0}^{vb} | z | \Psi_{0,0,0,0}^{vb} \rangle} \Gamma = B_x A_y A_z = B_g \]

\( B_u \) vibrations are IR Active and polarized perpendicular to the axis.

---

Raman Activity of Fundamental Modes

\[ \begin{align*}
B_u: & \quad |0,0,0,0 \rangle \rightarrow |1,0,0,0 \rangle \\
\Gamma(\psi_{1,0,0,0}^{vb}) &= \Gamma(\psi_0^{vi}) x \Gamma(\psi_0^{vi}) x \Gamma(\psi_0^{vi}) x \Gamma(\psi_0^{vi}) = A_e \\
\Gamma(\psi_{0,0,0,0}^{vb}) &= \Gamma(\psi_0^{vi}) x \Gamma(\psi_0^{vi}) x \Gamma(\psi_0^{vi}) x \Gamma(\psi_0^{vi}) = A_g \\
\langle \Psi_v | \alpha_u | \Psi_0 \rangle & = x, y, z \quad \text{and} \quad v = x, y, z \quad \Gamma = \Gamma(\Psi_v) x \Gamma(\psi_0) \\
\langle \psi_{1,0,0,0}^{vb} | x | \Psi_{0,0,0,0}^{vb} \rangle &= A_z A_x A_z = A_e \\
\langle \psi_{1,0,0,0}^{vb} | y | \Psi_{0,0,0,0}^{vb} \rangle &= A_z A_y A_z = B_e \\
\langle \psi_{1,0,0,0}^{vb} | z | \Psi_{0,0,0,0}^{vb} \rangle &= A_z A_y A_z = B_g \\
\langle \psi_{1,0,0,0}^{vb} | xy | \Psi_{0,0,0,0}^{vb} \rangle &= A_z A_y A_z \\
\langle \psi_{1,0,0,0}^{vb} | yz | \Psi_{0,0,0,0}^{vb} \rangle &= A_z A_y A_z \\
\langle \psi_{1,0,0,0}^{vb} | zx | \Psi_{0,0,0,0}^{vb} \rangle &= A_z A_y A_z
\end{align*} \]

\( A_g \) vibrations are Raman Active

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Raman Activity of Fundamental Modes

\[ B_u: \quad |0,0,0,0\rangle \rightarrow |0,0,1,0\rangle \]

\[ \Gamma(\Psi_{0,0,1,0}^{vb}) = \Gamma(\Psi_0^{v_i}) x \Gamma(\Psi_0^{v_i}) x \Gamma(\Psi_0^{v_i}) = B_u \]

\[ \Gamma(\Psi_{0,0,0,0}^{vb}) = \Gamma(\Psi_0^{v_i}) x \Gamma(\Psi_0^{v_i}) x \Gamma(\Psi_0^{v_i}) = A_u \]

\[ \langle \Psi | \alpha_n | \Psi_0 \rangle \quad u = x, y, z \quad \text{and} \quad v = x, y, z \]

\[ \Gamma = \Gamma(\Psi_0^{v_i}) x \Gamma(\Psi_0^{v_i}) x \Gamma(\Psi_0^{v_i}) \]

\[ \langle \Psi_{0,0,0,0}^{vb} | x^2 \Psi_{0,0,0,0}^{vb} \rangle = B_u \]

\[ \langle \Psi_{0,0,0,0}^{vb} | y^2 \Psi_{0,0,0,0}^{vb} \rangle = B_u \]

\[ \langle \Psi_{0,0,0,0}^{vb} | z^2 \Psi_{0,0,0,0}^{vb} \rangle = B_u \]

\[ B_u \text{ vibrations are Raman Inactive} \]

---

The Shortcut

\[ C_{2v} \quad E \quad C_2 \quad i \quad \sigma_h \]

\[ A_g \quad 1 \quad 1 \quad 1 \quad 1 \quad x^2, y^2, z^2, xy \]

\[ B_g \quad 1 \quad -1 \quad 1 \quad -1 \quad xz, yz \]

\[ A_u \quad 1 \quad 1 \quad -1 \quad -1 \quad z \]

\[ B_u \quad 1 \quad -1 \quad -1 \quad 1 \quad x, y \]

Corky: Hey, Cousin Mookie. Wotcha doing all that work for? There’s a neat little shortcut.

Mookie: Would you please stop looking for shortcuts? They can get you in trouble.

Corky: But look!! If there’s an \( x, y \) or \( z \) attached to the representation, then the vibration’s IR active; \( B_u \) vibrations are IR Active.

\( A_g \) vibrations are IR Inactive.

If there’s an \( x^2, y^2 \), etc. attached to the representation, then the vibration’s Raman active; \( A_g \) vibrations are Raman Active.

\( B_u \) vibrations are Raman Inactive.

Mookie: How do you determine the activity of a combination mode?

Corky: What’s a combination mode?
IR Activity of Combination Modes

\[ |0,0,0,0\rangle \rightarrow |0,1,0,1\rangle \quad \nu_2 + \nu_4 \]
\[
\Gamma (\psi_{0,1,0,1}^{\nu_2}) = \Gamma (\psi_{0,0,0,1}^{\nu_3}) \chi \Gamma (\psi_{0,0,1,0}^{\nu_4}) \chi \Gamma (\psi_{0,1,0,1}^{\nu_2})
= a_x x a_z x b_x = B_x
\]
\[
\Gamma (\psi_{0,0,0,0}^{\nu_2}) = \Gamma (\psi_{0,0,0,1}^{\nu_3}) \chi \Gamma (\psi_{0,0,0,0}^{\nu_4}) \chi \Gamma (\psi_{0,0,0,1}^{\nu_2}) = A_y
\]
\[
M^{z}_{\nu_2} = e^{\langle \psi_{0,0,0,0}^{\nu_2} | x | \psi_{0,0,0,0}^{\nu_2} \rangle} \Gamma = B_x x A_x = B_x
\]
\[
M^{z}_{\nu_3} = e^{\langle \psi_{0,0,0,0}^{\nu_3} | x | \psi_{0,0,0,0}^{\nu_3} \rangle} \Gamma = B_x x A_y = B_y
\]
\[
\nu_2 + \nu_4 \text{ is IR Active and polarized perpendicular to the axis.}
\]

IR Activity of Combination Modes

\[ |0,0,0,1\rangle \rightarrow |0,0,1,0\rangle \quad \nu_3 - \nu_4 \]
\[
\Gamma (\psi_{0,0,1,0}^{\nu_3}) = \Gamma (\psi_{0,0,0,0}^{\nu_3}) \chi \Gamma (\psi_{0,0,0,1}^{\nu_4}) \chi \Gamma (\psi_{0,0,1,0}^{\nu_3})
= a_x x a_z x b_x = B_x
\]
\[
\Gamma (\psi_{0,0,0,1}^{\nu_3}) = \Gamma (\psi_{0,0,0,0}^{\nu_3}) \chi \Gamma (\psi_{0,0,0,1}^{\nu_4}) \chi \Gamma (\psi_{0,0,0,1}^{\nu_3})
= a_y x a_y x b_x = B_y
\]
\[
M^{z}_{\nu_3} = e^{\langle \psi_{0,0,0,1}^{\nu_3} | x | \psi_{0,0,0,1}^{\nu_3} \rangle} \Gamma = B_x x A_x = B_x
\]
\[
M^{z}_{\nu_4} = e^{\langle \psi_{0,0,0,1}^{\nu_4} | x | \psi_{0,0,0,1}^{\nu_4} \rangle} \Gamma = B_x x A_y = B_y
\]
\[
\nu_3 - \nu_4 \text{ is IR Inactive.}
\]
Raman Activity of Combination Modes

\[ |0,0,0,0\rangle \rightarrow |0,1,0,1\rangle \quad v_2 + v_4 \]

\[ \Gamma (\psi_{0,0,0}^{vb}) = \Gamma (\psi_0^e) x\Gamma (\psi_0^o) x\Gamma (\psi_0^e) x\Gamma (\psi_1^i) \]

\[ = a_y x a_x b_y a_y b_x = B_u \]

\[ \Gamma (\psi_{0,0,0}^{vb}) = \Gamma (\psi_0^e) x\Gamma (\psi_0^o) x\Gamma (\psi_0^e) x\Gamma (\psi_0^o) = A_v \]

\[ \langle \psi_i | x | \psi_o \rangle \quad u = x, y, z \quad \text{and} \quad v = x, y, z \quad \Gamma = \Gamma (\psi_i) x(\psi) x\Gamma (\psi_o) \]

\[ \langle \psi_{0,0,0}^{vb} | x^2 | \psi_{0,0,0}^{vb} \rangle \]

\[ \Gamma = B_x A_x x A_x = A_u \quad \langle \psi_{0,0,0}^{vb} | x^2 | \psi_{0,0,0}^{vb} \rangle \]

\[ \langle \psi_{0,0,0}^{vb} | z^2 | \psi_{0,0,0}^{vb} \rangle \]

\[ \langle \psi_{0,0,0}^{vb} | x^2 | \psi_{0,0,0}^{vb} \rangle \]

\[ \nu_2 + \nu_4 \text{ is Raman Inactive.} \]

---

Raman Activity of Combination Modes

\[ |0,0,0,1\rangle \rightarrow |0,1,1,0\rangle \quad v_3 - v_4 \]

\[ \Gamma (\psi_{0,0,1}^{vb}) = \Gamma (\psi_0^e) x\Gamma (\psi_0^o) x\Gamma (\psi_0^e) x\Gamma (\psi_0^o) \]

\[ = a_y x a_x b_y a_y b_x = B_u \]

\[ \Gamma (\psi_{0,0,1}^{vb}) = \Gamma (\psi_0^e) x\Gamma (\psi_0^o) x\Gamma (\psi_0^e) x\Gamma (\psi_0^o) = A_v \]

\[ \langle \psi_i | x | \psi_o \rangle \quad u = x, y, z \quad \text{and} \quad v = x, y, z \quad \Gamma = \Gamma (\psi_i) x(\psi) x\Gamma (\psi_o) \]

\[ \langle \psi_{0,0,1}^{vb} | x^2 | \psi_{0,0,1}^{vb} \rangle \]

\[ \Gamma = B_x A_x x A_x = A_u \quad \langle \psi_{0,0,1}^{vb} | x^2 | \psi_{0,0,1}^{vb} \rangle \]

\[ \langle \psi_{0,0,1}^{vb} | z^2 | \psi_{0,0,1}^{vb} \rangle \]

\[ \langle \psi_{0,0,1}^{vb} | x^2 | \psi_{0,0,1}^{vb} \rangle \]

\[ \nu_3 - \nu_4 \text{ is Raman Active.} \]
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**Time Independent Perturbation Theory**

**Introduction**

One often finds in QM that the Hamiltonian for a particular problem can be written as:

$$H = H^{(0)} + H^{(1)}$$

$H^{(0)}$ is an exactly solvable Hamiltonian; i.e. $H^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$

$H^{(1)}$ is a smaller term which keeps the Schrödinger Equation from being solvable exactly.

One example is the Anharmonic Oscillator:

$$H = \frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} k x^2 + \gamma x^3 + \delta x^4 + \ldots$$

$H^{(0)}$ Exactly Solvable

$H^{(1)}$ Correction Term
In this case, one may use a method called “Perturbation Theory” to perform one or more of a series of increasingly higher order corrections to both the Energies and Wavefunctions.

\[ E = E^{(0)} + E^{(1)} + E^{(2)} + \cdots + E^{(n)} \]

\[ \psi = \psi^{(0)} + \psi^{(1)} + \psi^{(2)} + \cdots + \psi^{(n)} \]

Some textbooks outline the method for higher order corrections. However, we will restrict the treatment here to first order perturbation corrections.

We will use the notation: \( E = E^{(0)} + \Delta E \) and \( \psi = \psi^{(0)} + \Delta \psi \)

**Note:** Quantum Chemistry (5th. Ed.), by I. N. Levine, Chap. 9

---

**First Order Perturbation Theory**

\[ H = H^{(0)} + H^{(1)} \quad \text{where} \quad H^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)} \]

Assume: \( E = E^{(0)} + \Delta E \) and \( \psi = \psi^{(0)} + \Delta \psi \)

\[ H\psi = E\psi \]

\[ (H^{(0)} + H^{(1)})(\psi^{(0)} + \Delta \psi) = (E^{(0)} + \Delta E)(\psi^{(0)} + \Delta \psi) \]

\[ H^{(0)}\psi^{(0)} + H^{(1)}\psi^{(0)} + H^{(0)}\Delta \psi + H^{(1)}\Delta \psi = E^{(0)}\psi^{(0)} + \Delta E\psi^{(0)} + E^{(0)}\Delta \psi + \Delta E\Delta \psi \]

One can eliminate the two terms involving the product of two small corrections. One can eliminate two additional terms because: \( H^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)} \)
Multiply all terms by $\psi_0^*$ and integrate:

$$\int \psi_0^* H(0) \psi_0^* d\tau + \int \psi_0^* H(0) \Delta \psi d\tau = \int \psi_0^* \Delta E \psi_0^* d\tau + \int \psi_0^* E(0) \Delta \psi d\tau$$

$H(0)$ is Hermitian. Therefore:

$$\int \psi_0^* H(0) \Delta \psi d\tau = \int \Delta \psi \left( H(0) \psi_0^* \right)^* d\tau = \int \Delta \psi \left( E(0) \psi_0^* \right)^* d\tau = E(0) \int \psi_0^* \Delta \psi d\tau$$

Plug in to get:

$$\int \psi_0^* H(0) \psi_0^* d\tau + E(0) \int \psi_0^* \Delta \psi d\tau = \int \psi_0^* \Delta E \psi_0^* d\tau + \int \psi_0^* E(0) \Delta \psi d\tau$$

Therefore:

$$\int \psi_0^* H(0) \psi_0^* d\tau = \Delta E \int \psi_0^* \psi_0^* d\tau = \Delta E$$

$\Delta E = \int \psi_0^* H(0) \psi_0^* d\tau$ is the first order perturbation theory correction to the energy.

---

**Applications of First Order Perturbation Theory**

**PIB with slanted floor**

Consider a particle in a box with the potential:

$$V(x) \rightarrow \infty \quad x < 0, x > a$$

$$V(x) = \frac{V_0}{a} x \quad 0 \leq x \leq a$$

For this problem:

$$H^{(0)} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + 0$$

$$E_n^{(0)} = \frac{n^2 \hbar^2}{8ma^2}$$

$$\psi_n^{(0)} = \frac{2}{\sqrt{a}} \sin \left( \frac{n\pi x}{a} \right)$$

The perturbing potential is:

$$H^{(1)} = \frac{V_0}{a} x$$
We will calculate the first order correction to the \( n \)th energy level. In this particular case, the correction to all energy levels is the same.

\[
\Delta E = \int \psi_0^{(0)} \ast H^{(1)} \psi_0^{(0)} \, dx = \int_0^a \frac{2V_0}{a} x \cdot \sin \left( \frac{n \pi x}{a} \right) dx = \frac{2V_0}{a^2} \int_0^a x \cdot \sin \left( \frac{n \pi x}{a} \right) dx = \frac{2V_0}{a^2} \left[ \left( \frac{a^2}{4} - \frac{a \sin(2a) - \cos(2a)}{8a^2} \right) - \left( 0 - \frac{\cos(0)}{8a^2} \right) \right]
\]

\[
\Delta E = \frac{V_0}{2} \quad \text{Independent of } n
\]

---

Anharmonic Oscillator

Consider an anharmonic oscillator with the potential energy of the form:

\[ V(x) = \frac{1}{2} kx^2 + \gamma x^3 + \delta x^4 \]

We’ll calculate the first order perturbation theory correction to the ground state energy.

For this problem:

\[ H^{(0)} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \]

\[ E_0^{(0)} = \frac{1}{2} \hbar \omega \]

\[ \psi_0^{(0)} = \frac{e^{-\alpha x^2/2}}{\sqrt{\alpha \pi}} \]

\[ \omega = \sqrt{\frac{k}{\mu}}, \quad \alpha = \frac{\sqrt{k \mu}}{\hbar} \]

The perturbing potential is:

\[ H^{(1)} = \gamma x^3 + \delta x^4 \]

\[
\Delta E = \int \psi_0^{(0)} \ast H^{(1)} \psi_0^{(0)} \, dx = \int_{-\infty}^{\infty} \left( \frac{\alpha}{\pi} \right)^{3/4} e^{-\alpha x^2/2} \cdot (\gamma x^3 + \delta x^4) \cdot \left( \frac{\alpha}{\pi} \right)^{3/4} e^{-\alpha x^2/2} \, dx
\]

\[
= \left( \frac{\alpha}{\pi} \right)^{\sqrt{2}} \int_{-\infty}^{\infty} (\gamma x^3 + \delta x^4) e^{-\alpha x^2} \, dx
\]

\[
= \left( \frac{\alpha}{\pi} \right)^{\sqrt{2}} \int_{-\infty}^{\infty} (\gamma x^3 + \delta x^4) e^{-\alpha x^2} \, dx
\]

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\[ \Delta E = \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} \left( \gamma x^3 + \delta x^4 \right) e^{-\alpha x^2} \, dx = \gamma \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} x^3 e^{-\alpha x^2} \, dx + \delta \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} \, dx \]

\[ = 0 + 2\delta \left( \frac{\alpha}{\pi} \right)^{1/2} \int_{0}^{\infty} x^4 e^{-\alpha x^2} \, dx = 2\delta \left( \frac{\alpha}{\pi} \right)^{1/2} \left( \frac{3}{8\alpha^2} \right) \left( \frac{\pi}{\alpha} \right)^{1/2} \int_{0}^{\infty} x^4 e^{-\alpha x^2} \, dx = \frac{3\delta}{8\beta^2} \left( \frac{\pi}{\beta} \right) \]

\[ \Delta E = \frac{3\delta}{4\alpha^2} = \frac{3\delta}{4 \left( \frac{k \mu}{\hbar} \right)^2} = \frac{3\hbar^2 \delta}{4k \mu} \]

**Note:** There is no First order Perturbation Theory correction due to the cubic term in the Hamiltonian.

However, there IS a correction due to the cubic term when Second order Perturbation Theory is applied.

---

**Brief Introduction to Second Order Perturbation Theory**

As noted above, one also can obtain additional corrections to the energy using higher orders of Perturbation Theory; i.e.

\[ E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \cdots \]

\( E_n^{(0)} \) is the energy of the \( n \)th level for the unperturbed Hamiltonian

\( E_n^{(1)} \) is the first order correction to the energy, which we have called \( \Delta E \)

\( E_n^{(2)} \) is the second order correction to the energy, etc.

The second order correction to the energy of the \( n \)th level is given by:

\[ E_n^{(2)} = \sum_{k=1}^{\infty} \frac{\left| \langle \psi_k^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle \right|^2}{E_n^{(0)} - E_k^{(0)}} \quad \text{for} \ k \neq n \]

where

\[ \langle \psi_k^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle = \int \psi_k^{(0)} \ast H^{(1)} \psi_n^{(0)} \, d\tau \]

---

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If the correction is to the ground state (for which we'll assume n=1), then:

\[ E_1^{(2)} = \sum_{k=2}^{\infty} \frac{\langle \psi_k^{(0)} | H^{(1)} | \psi_1^{(0)} \rangle^2}{E_1^{(0)} - E_k^{(0)}} \]

\[ E_2^{(2)} = \frac{\langle \psi_2^{(0)} | H^{(0)} | \psi_1^{(0)} \rangle^2}{E_1^{(0)} - E_2^{(0)}} + \frac{\langle \psi_2^{(0)} | H^{(1)} | \psi_1^{(0)} \rangle^2}{E_1^{(0)} - E_2^{(0)}} + \frac{\langle \psi_2^{(0)} | H^{(2)} | \psi_1^{(0)} \rangle^2}{E_1^{(0)} - E_2^{(0)}} + \ldots \]

Note that the second order Perturbation Theory correction is actually an infinite sum of terms.

However, the successive terms contribute less and less to the overall correction as the energy, \( E_k^{(0)} \), increases.

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The Potential Energy Curve of H₂

Calculation at QCISD(T)/6-311++G(3df,3pd) level

Re(cal) = 0.742 Å
Re(exp) = 0.742 Å

Eₘᵦ(cal) = 2(-0.49982) hartrees = -0.99964 hartrees (au)

Eₘᵦ(cal) = -1.17253 hartrees (au)

Rₑ(cal) = 0.742 Å
Rₑ(exp) = 0.742 Å

The Dissociation Energy

Dₑ: Spectroscopic Dissociation Energy
Dₑ: Thermodynamic Dissociation Energy

Dₑ(cal) = Eₑ(cal) − Eₘᵦ(cal) = 0.17289 au • 2625.5 kJ/mol / au
Dₑ(cal) = 453.9 kJ/mol
D₀(exp) = 432 kJ/mol
Relating $D_e$ to $D_0$

$D_e = D_0 + E_{vib} = D_0 + (1/2)\hbar\nu$

$H_2^+$: $\nu(\text{cal}) = 4403 \text{ cm}^{-1}$ [QCISD(T)/6-311++G(3df,3pd)]

versus $\nu(\text{exp}) = 4395 \text{ cm}^{-1}$

The experimental frequency is the “harmonic” value, corrected from the observed anharmonic frequency.

$D_e(\text{cal}) = 453.9 \text{ kJ/mol}$

$D_0(\text{cal}) = D_e(\text{cal}) - E_{vib}$

$= 453.9 - 26.4$

$= 427.5 \text{ kJ/mol}$

$D_0(\text{exp}) = 432 \text{ kJ/mol}$

$E_{vib} = \frac{1}{2} \hbar\nu = \frac{1}{2} \hbar c \nu$

$= \frac{1}{2} \left( 6.63 \times 10^{-34} \text{ J} \cdot \text{s} \right) \left( 3.00 \times 10^8 \text{ cm/s} \right) \left( 4403 \text{ cm}^{-1} \right)$

$= 4.379 \times 10^{-20} \text{ J} \cdot \text{mol}^{-1} \cdot 6.02 \times 10^{23} \text{ mol}^{-1}$

$E_{vib} = 26.4 \text{ kJ/mol}$
### Calculated Versus Experimental Vibrational Frequencies

<table>
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<tr>
<th></th>
<th>$\nu$(Harm)$^a$</th>
<th>$\nu$(cal)$^b$</th>
<th>$\nu$(cal)$^c$</th>
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<tr>
<td></td>
<td>3943 cm$^{-1}$</td>
<td>3956 cm$^{-1}$</td>
<td>4188 cm$^{-1}$</td>
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<tr>
<td></td>
<td>1649</td>
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</table>

(a) Corrected Experimental Harmonic Frequencies  
(b) QCISD(T)/6-311+G(3df,2p)  
(c) HF/6-31G(d)  
Lack of including electron correlation raises computed frequencies.

### Harmonic versus Anharmonic Vibrational Frequencies

<table>
<thead>
<tr>
<th></th>
<th>$\nu$(exp)$^z$</th>
<th>$\nu$(Harm)$^a$</th>
<th>$\nu$(cal)$^b$</th>
<th>$\nu$(cal)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3756 cm$^{-1}$</td>
<td>3943 cm$^{-1}$</td>
<td>3956 cm$^{-1}$</td>
<td>4188 cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>3657</td>
<td>3833</td>
<td>3845</td>
<td>4070</td>
</tr>
<tr>
<td></td>
<td>1595</td>
<td>1649</td>
<td>1640</td>
<td>1827</td>
</tr>
</tbody>
</table>

(z) Actual measured Experimental Frequencies  
(a) Corrected Experimental Harmonic Frequencies  
(b) QCISD(T)/6-311+G(3df,2p)  
(c) HF/6-31G(d)  
Lack of including electron correlation raises computed frequencies.
Differences between Calculated and Measured Vibrational Frequencies

There are two sources of error in QM calculated vibrational frequencies.

(1) QM calculations of vibrational frequencies assume that the vibrations are “Harmonic”, whereas actual vibrations are anharmonic.

Typically, this causes calculated frequencies to be approximately 5% higher than experiment.

(2) If one uses “Hartree-Fock (HF)” rather than “correlated electron” calculations, this produces an additional ~5% increase in the calculated frequencies.

To correct for these sources of error, multiplicative “scale factors” have been developed for various levels of calculation.

An Example: CHBr$_3$

<table>
<thead>
<tr>
<th></th>
<th>$\nu^{(exp)}$</th>
<th>$\nu^{(cal)}$</th>
<th>$\nu^{(scaled)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3050</td>
<td>3050 cm$^{-1}$</td>
<td>3222 cm$^{-1}$</td>
<td>3061 cm$^{-1}$</td>
</tr>
<tr>
<td>1149 (E)</td>
<td>1149 (E)</td>
<td>1208 (E)</td>
<td>1148 (E)</td>
</tr>
<tr>
<td>669 (E)</td>
<td>669 (E)</td>
<td>691 (E)</td>
<td>656 (E)</td>
</tr>
<tr>
<td>543</td>
<td>543</td>
<td>546</td>
<td>519</td>
</tr>
<tr>
<td>223</td>
<td>223</td>
<td>228</td>
<td>217</td>
</tr>
<tr>
<td>155 (E)</td>
<td>155 (E)</td>
<td>158 (E)</td>
<td>150 (E)</td>
</tr>
</tbody>
</table>

(a) Measured "anharmonic" vibrational frequencies.
(b) Computed at QCISD/6-311G(d,p) level
(c) Computed frequencies scaled by 0.95
### Another Example: CBr₃⁺

<table>
<thead>
<tr>
<th></th>
<th>v(exp)ᵃ</th>
<th>v(cal)ᵇ</th>
<th>v(scaled)ᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>773 (E) cm⁻¹</td>
<td>799 (E) cm⁻¹</td>
<td>759 (E) cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>???</td>
<td>324</td>
<td>308</td>
<td></td>
</tr>
<tr>
<td>???</td>
<td>235</td>
<td>223</td>
<td></td>
</tr>
<tr>
<td>???</td>
<td>164 (E)</td>
<td>156 (E)</td>
<td></td>
</tr>
</tbody>
</table>

(a) Measured “anharmonic” vibrational frequencies.
(b) Computed at QCISD/6-311G(d,p) level
(c) Computed frequencies scaled by 0.95

---

### Some Applications of QM Vibrational Frequencies

1. Aid to assigning experimental vibrational spectra
   One can visualize the motions involved in the calculated vibrations

2. Vibrational spectra of transient species
   It is usually difficult to impossible to experimentally measure the vibrational spectra in short-lived intermediates.

   If you have synthesized a new compound and measured the vibrational spectra, you can simulate the spectra of possible proposed structures to determine which pattern best matches experiment.
Part B: The Symmetry of Vibrations + Perturbation Theory + Statistical Thermodynamics

• Symmetry and Vibrational Selection Rules
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• The Symmetry of Vibrational Normal Modes: Application to the Stretching Vibrations in Ethylene
• Time Independent Perturbation Theory
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• The Vibrational Partition Function Function
• Internal Energy: ZPE and Thermal Contributions
• Applications to O₂(g) and H₂O(g)

Statistical Thermodynamics: Vibrational Contributions to Thermodynamic Properties of Gases

Remember these?

\[
U = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{T,N}
\]

\[
C_P = \left( \frac{\partial U}{\partial T} \right)_{P,N}
\]

\[
H = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{P,N} + kT \left( \frac{\partial \ln Q}{\partial V} \right)_{T,N}
\]

\[
C_V = \left( \frac{\partial H}{\partial T} \right)_{P,N}
\]

\[
S = k \ln Q + \frac{U}{T}
\]

\[
A = U - TS = -kT \ln Q
\]

\[
G = H - TS = -kT \ln Q + kT \left( \frac{\partial \ln Q}{\partial V} \right)_{T,N}
\]
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**The Vibrational Partition Function Function**

- Internal Energy: ZPE and Thermal Contributions
- Applications to O₂(g) and H₂O(g)

---

The Vibrational Partition Function

HO Energy Levels: \( E_n = \left( n + \frac{1}{2} \right) \hbar \nu \), \( n = 0, 1, 2, \cdots \)

\[
\nu = \frac{\Theta_v}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}
\]

Partition Function

\[
q^{vb} = \sum_{n=0}^{\infty} e^{-\frac{\Delta E_n}{kT}} = \sum_{n=0}^{\infty} e^{-\frac{(n+1/2)\hbar \nu}{kT}} = \sum_{n=0}^{\infty} e^{-\frac{n\hbar \nu}{2kT}} \cdot e^{-\frac{(1/2)\hbar \nu}{2kT}} = e^{-\frac{(1/2)\hbar \nu}{2kT}} \cdot \sum_{n=0}^{\infty} e^{-\frac{n\hbar \nu}{2kT}}
\]

\[
q^{vb} = e^{-\frac{\Theta_v}{2T}} \cdot \sum_{n=0}^{\infty} e^{-\frac{n\hbar \nu}{kT}}
\]

where \( \Theta_v = \frac{\hbar \nu}{k} = \frac{hc\nu}{k} \)

If \( \Theta_v/T << 1 \) (i.e., if \( \Delta \epsilon/kT << 1 \)), we can convert the sum to an integral.

Let’s try O₂ (\( \nu = 1580 \text{ cm}^{-1} \)) at 298 K.

\[
\Theta_v = \frac{h \nu}{k} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^{10} \text{ cm/s})(1580 \text{ cm}^{-1})}{1.38 \times 10^{-23} \text{ J/K}} = 2277 \text{ K}
\]

\[
\frac{\Theta_v}{T} = \frac{2277 \text{ K}}{298 \text{ K}} = 7.64 \quad \text{Sorry Charlie!! No luck!!}
\]
Let's consider:

\[ \sum_{n=0}^{\infty} e^{-\frac{\Theta_n}{T}} = \sum_{n=0}^{\infty} x^n \quad \text{where} \quad x = e^{-\frac{\Theta_n}{T}} \]

We learned earlier in the chapter that any function can be expanded in a Taylor series:

\[ f(x) = \sum_{n=0}^{\infty} \frac{1}{n!} f^{(n)}(0)x^n \]

It can be shown that the Taylor series for \( 1/(1-x) \) is:

\[ \frac{1}{1-x} = \sum_{n=0}^{\infty} x^n \]

Therefore:

\[ \sum_{n=0}^{\infty} e^{-\frac{\Theta_n}{T}} = \sum_{n=0}^{\infty} x^n = \frac{1}{1-x} = \frac{1}{1 - e^{-\frac{\Theta_n}{T}}} \]

\[ q_{\text{vib}} = e^{-\frac{\Theta_v}{2T}} \sum_{n=0}^{\infty} e^{-\frac{\Theta_n}{T}} \quad \text{and} \quad \sum_{n=0}^{\infty} e^{-\frac{\Theta_n}{T}} = \frac{1}{1 - e^{-\frac{\Theta_v}{T}}} \]

\[ \Theta_v = \frac{\hbar \nu}{k} = \frac{\hbar c v}{k} \]

For \( N \) molecules, the total vibrational partition function, \( Q_{\text{vib}} \), is:

\[ Q_{\text{vib}} = (q_{\text{vib}})^N = \left( e^{-\frac{\Theta_v}{2T}} \right)^N \left( \frac{1}{1 - e^{-\frac{\Theta_v}{T}}} \right)^N \]
Some comments on the Vibrational Partition Function

\[ Q^{\text{vib}} = \left( q^{\text{vib}} \right)^N = \left( \frac{\Theta_v}{1 - e^{-\Theta_v}} \right)^N \]

\[ \Theta_v = \frac{h\nu}{k} = \frac{hc\nu}{k} \]

If we look back at the development leading to \( q^{\text{vib}} \) and \( Q^{\text{vib}} \), we see that:

(a) the numerator arises from the vibrational Zero-Point Energy \( (1/2h\nu) \)

(b) the denominator comes from the sum over \( \exp(-nh\nu/kT) \)

The latter is the "thermal" contribution to \( q^{\text{vib}} \) because all terms above \( n=0 \) are zero at low temperatures

In some books, the ZPE is not included in \( q^{\text{vib}} \); i.e. they use \( \epsilon_n = nh\nu \).

In that case, the numerator is 1 and they then must add in ZPE contributions separately

\[ \ln Q^{\text{vib}} = N \ln \left( \frac{\Theta_v}{e^{\Theta_v/kT}} \right) - N \ln \left( 1 - e^{-\Theta_v/kT} \right) = -N \frac{\Theta_v}{2T} - N \ln \left( 1 - e^{-\Theta_v/kT} \right) \]

\[ \text{ZPE Term} \quad \text{Thermal Term} \]

In further developments, we'll keep track of the two terms individually.

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Internal Energy

\[ U_{\text{vib}} = kT^2 \left( \frac{\partial}{\partial T} \ln Q_{\text{vib}}^{\text{ib}} \right)_{r, N} \]

\[ \ln Q^{\text{vib}} = -N \frac{\Theta_v}{2T} - N \ln \left( 1 - e^{-\frac{\Theta_v}{T}} \right) \]

\[ U_{\text{ZPE vib}} = kT^2 \left( \frac{\partial}{\partial T} \left[ -N \frac{\Theta_v}{2T} \right] \right)_{r, N} + kT^2 \left( \frac{\partial}{\partial T} \left[ -N \ln \left( 1 - e^{-\frac{\Theta_v}{T}} \right) \right] \right)_r = U_{\text{ZPE vib}}^{\text{ib}} + U_{\text{therm vib}}^{\text{ib}} \]

ZPE Contribution

\[ U_{\text{ZPE vib}} = kT^2 \left( \frac{\partial}{\partial T} \left[ -N \frac{\Theta_v}{2T} \right] \right)_{r, N} = -\frac{N\Theta_v kT^2}{2} \left( \frac{1}{T} \right) \frac{d}{dT} = -\frac{NT\Theta_v kT^2}{2T^2} \frac{1}{T} = \frac{Nk\Theta_v}{2} \]

This is just the vibrational Zero-Point energy for n moles of molecules

or

\[ U_{\text{ZPE vib}} = \frac{Nk\hbar c \nu}{2} = \frac{n N \frac{\hbar c \nu}{2}}{2} \]

Thermal Contribution

\[ U_{\text{therm vib}} = kT^2 \left( \frac{\partial}{\partial T} \left[ -N \ln \left( 1 - e^{-\frac{\Theta_v}{T}} \right) \right] \right)_{r, N} = -NkT^2 \frac{d}{dT} \ln \left( 1 - e^{-\frac{\Theta_v}{T}} \right) \]

\[ = -NkT^2 \frac{d}{dT} \left( 1 - e^{-\frac{\Theta_v}{T}} \right) = -NkT^2 \frac{1}{1 - e^{-\frac{\Theta_v}{T}}} \left( -1 \right) \frac{d}{dT} \left( e^{-\frac{\Theta_v}{T}} \right) \]

\[ = NkT^2 \frac{\Theta_v}{1 - e^{-\frac{\Theta_v}{T}}} \frac{d}{dT} \left( \frac{\Theta_v}{T} \right) = NkT^2 \frac{e^{-\frac{\Theta_v}{T}}}{1 - e^{-\frac{\Theta_v}{T}}} \left( \frac{\Theta_v}{T} + \frac{\Theta_v}{T^2} \right) \]

\[ = Nk\Theta_v \frac{e^{-\frac{\Theta_v}{T}}}{1 - e^{-\frac{\Theta_v}{T}}} = nN\frac{k\Theta_v}{1 - e^{-\frac{\Theta_v}{T}}} = nR\Theta_v \frac{e^{-\frac{\Theta_v}{T}}}{1 - e^{-\frac{\Theta_v}{T}}} \]

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Although this expression is fine, it's commonly rearranged, as follows:

\[ U_{\text{vib}}^{\text{shrm}} = nR\Theta_v \frac{e^{\frac{\Theta_v}{T}}}{1 - e^{\frac{\Theta_v}{T}}} \]

Limiting Cases

Low Temperature: \( (T \to 0) \)

\[ \frac{U_{\text{vib}}}{\text{shrm}} = R \frac{\Theta_v}{e^{\frac{\Theta_v}{T}} - 1} \to 0 \]

Because the denominator approaches infinity.

High Temperature: \( (\Theta_v \ll T) \)

\[ \frac{U_{\text{vib}}}{\text{shrm}} = \frac{R\Theta_v}{1 + \left(\frac{\Theta_v}{T}\right)^{-1} + \cdots - 1} \to RT \]

The latter result demonstrates the principal of equipartition of vibrational internal energy: each vibration contributes RT of internal energy.

However, unlike translations or rotations, we almost never reach the high temperature vibrational limit.

At room temperature, the thermal contribution to the vibrational internal energy is often close to 0.
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Numerical Example

\[
\begin{align*}
\bar{U}_{\text{vib, ZPE}} &= \frac{N_a h c \bar{v}}{2} \\
\bar{U}_{\text{vib, therm}} &= \frac{R \Theta_v}{e^{\frac{\Theta_v}{RT}} - 1}
\end{align*}
\]

Let’s try \( \text{O}_2 \) (\( \bar{v} = 1580 \text{ cm}^{-1} \)) at 298 K.

\[
\Theta_v = \frac{h c \bar{v}}{k} = \frac{(6.63 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm/s})(1580 \text{ cm}^{-1})}{1.38 \times 10^{-23} \text{ J/K}} = 2277 \text{ K}
\]

\[
\bar{U}_{\text{vib, ZPE}} = \frac{(6.02 \times 10^{23} \text{ mol}^{-1})(6.63 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm/s})(1580 \text{ cm}^{-1})}{2} = 9459 \text{ J/mol} = 9.46 \text{ kJ/mol}
\]

\[
\bar{U}_{\text{vib, therm}} = \frac{R \Theta_v}{e^{\frac{\Theta_v}{RT}} - 1} = \frac{8.314 \text{ J/mol K} \cdot 2277 \text{ K}}{e^{(\frac{2277 \text{ K}}{298 \text{ K}})} - 1} = 9.1 \text{ J/mol} = 0.009 \text{ kJ/mol}
\]

Thus, the thermal contribution to the vibrational internal energy of \( \text{O}_2 \) at room temperature is negligible.
A comparison between O₂ and I₂

I₂: \( \tilde{\nu} = 214 \text{ cm}^{-1} \rightarrow \Theta_\nu = 309 \text{ K} \)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>O₂ (kJ/mol)</th>
<th>I₂ (kJ/mol)</th>
<th>RT (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.009</td>
<td>1.41</td>
<td>2.48</td>
</tr>
<tr>
<td>500</td>
<td>0.20</td>
<td>3.00</td>
<td>4.16</td>
</tr>
<tr>
<td>1000</td>
<td>2.16</td>
<td>7.10</td>
<td>8.31</td>
</tr>
<tr>
<td>2000</td>
<td>8.92</td>
<td>15.4</td>
<td>16.6</td>
</tr>
<tr>
<td>3000</td>
<td>16.7</td>
<td>23.7</td>
<td>24.9</td>
</tr>
</tbody>
</table>

Because of its lower frequency (and, therefore, more closely spaced energy levels), thermal contributions to the vibrational internal energy of I₂ are much more significant than for O₂ at all temperatures.

At higher temperatures, thermal contributions to the vibrational internal energy of O₂ become very significant.

Enthalpy

\( Q_{\text{vib}} \) independent of V

\[
H^{\text{vib}} = kT^2 \left( \frac{\partial \ln Q^{\text{vib}}}{\partial T} \right)_{V,N} + kT \left( \frac{\partial \ln \Theta_\nu}{\partial T} \right)_{V,N}
\]

Therefore:

\[
H^{\text{vib}} = kT^2 \left( \frac{\partial \ln Q^{\text{vib}}}{\partial T} \right)_{V,N} = U^{\text{vib}}
\]

and:

\[
H^{\text{vib}}_{ZPE} = U^{\text{vib}}_{ZPE}
\]

\[
H^{\text{vib}}_{\text{therm}} = U^{\text{vib}}_{\text{therm}}
\]

Similarly:

\[
C^{\text{vib}} = \left( \frac{\partial H^{\text{vib}}}{\partial T} \right)_{P,N} = \left( \frac{\partial U^{\text{vib}}}{\partial T} \right)_{V,N} = C^{\text{vib}}_{V}
\]
Heat Capacity ($C^\text{vib}_V$ and $C^\text{vib}_P$)

Independent of $T$

$$U^\text{vib}_\text{ZPE} = \frac{nN_e h c v}{2}$$

$$U^\text{vib}_\text{therm} = \frac{nR T^2}{e^{\frac{\Theta}{T}} - 1}$$

$$C^\text{vib}_V = \left( \frac{\partial U^\text{vib}}{\partial T} \right)_{P,N} = \frac{nR \Theta}{e^{\frac{\Theta}{T}} - 1} + \left( \frac{\partial U^\text{vib}_\text{therm}}{\partial T} \right)_{P,N}$$

$$C^\text{vib}_P = \frac{d}{dT} \left[ \frac{nR \Theta}{e^{\frac{\Theta}{T}} - 1} \right] = nR \Theta \frac{d}{dT} \left[ \frac{\Theta}{e^{\frac{\Theta}{T}} - 1} \right] = nR \Theta \left( -1 \right) \left( \frac{\Theta}{e^{\frac{\Theta}{T}} - 1} \right)^2 \frac{d}{dT} \left[ \frac{\Theta}{e^{\frac{\Theta}{T}} - 1} \right]$$

$$= - nR \Theta \left( \frac{\Theta}{e^{\frac{\Theta}{T}} - 1} \right)^2 \left( \frac{- \Theta}{T^2} \right) = nR \left( \frac{\Theta}{T} \right)^2 \frac{\Theta}{e^{\frac{\Theta}{T}} - 1}$$

It can be shown that in the limit, $\Theta_V \ll T$, $C^\text{vib}_V \to R$

**Numerical Example**

Let's try $O_2$ ($\tilde{\nu} = 1580$ cm$^{-1}$) at 298 K (one mole).

$$\Theta_V = \frac{\hbar \tilde{\nu}}{k} = \frac{\left( 6.63 \times 10^{-34} \text{ J s} \right) \left( 3.00 \times 10^{10} \text{ cm s}^{-1} \right) \left( 1580 \text{ cm}^{-1} \right)}{1.38 \times 10^{-23} \text{ J K}^{-1}} = 2277 \text{ K}$$

$$\frac{\Theta_V}{T} = \frac{2277}{298} = 7.64$$

$$C^\text{vib}_V = C^\text{vib}_P = 8.314 \left( 7.64 \right)^2 \frac{\Theta}{e^{\frac{\Theta}{T}} - 1} = 0.23 \text{ J mol}^{-1} \text{ K}^{-1}$$

vs. $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
A comparison between $O_2$ and $I_2$

$\nu_i = 214 \text{ cm}^{-1} \rightarrow \Theta_v = 309 \text{ K}$

Vibrational Heat Capacities ($C_{p,vib} = C_{v,vib}$)

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$O_2$ (J/mol-K)</th>
<th>$I_2$ (J/mol-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.23</td>
<td>7.61</td>
</tr>
<tr>
<td>500</td>
<td>1.85</td>
<td>8.05</td>
</tr>
<tr>
<td>1000</td>
<td>5.49</td>
<td>8.25</td>
</tr>
<tr>
<td>2000</td>
<td>7.47</td>
<td>8.30</td>
</tr>
<tr>
<td>3000</td>
<td>7.93</td>
<td>8.31</td>
</tr>
</tbody>
</table>

Vibrational contribution to heat capacity of $I_2$ is greater because of its lower frequency (i.e. closer energy spacing).

The heat capacities approach $R$ (8.31 J/mol-K) at high temperature.

**Entropy**

\[
S^{vib} = k \ln Q_v^{vib} + \frac{U^{vib}}{T}
\]

\[
U^{vib} = \frac{Nk\Theta_v}{2} = \frac{nR\Theta_v}{2}
\]

\[
U_{vib}^{vib} = \frac{nR\Theta_v}{\Theta_v - 1}
\]

\[
k \ln Q_v^{vib} = k \ln \left( \frac{\Theta_v}{e^{\frac{\Theta_v}{T}}} \right)^N = Nk \ln \left( \frac{\Theta_v}{e^{\frac{\Theta_v}{T}}} \right) - Nk \ln \left( 1 - e^{-\frac{\Theta_v}{T}} \right)
\]

\[
S^{vib} = -\frac{nNk}{2T} - Nk \ln \left( 1 - e^{-\frac{\Theta_v}{T}} \right) + \frac{nR}{T} \Theta_v + \frac{1}{T} \left( \frac{nR\Theta_v}{\Theta_v - 1} \right)
\]

\[
S^{vib} = -nR \ln \left( 1 - e^{-\frac{\Theta_v}{T}} \right) + \frac{nR(\Theta_v/T)}{\Theta_v - 1}
\]

$Nk = nN \gamma k = nR$
Numerical Example

\[ S^{\text{vib}} = -nR \ln \left[ 1 - e^{-\frac{\Theta_v}{T}} \right] + \frac{nR(\Theta_v/T)}{e^{\Theta_v/T} - 1} \]

Let's try O\(_2\) (\( \nu = 1580 \text{ cm}^{-1} \)) at 298 K (one mole).

\[ \Theta_v = \frac{\hbar \nu}{k} = \frac{(6.63 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm/s})(1580 \text{ cm}^{-1})}{1.38 \times 10^{-23} \text{ J/K}} = 2277 \text{ K} \]

\[ \frac{\Theta_v}{T} = \frac{2277}{298} = 7.64 \]

\[ S^{\text{vib}} = -8.314 \ln \left[ 1 - e^{-7.64} \right] + \frac{8.314 \cdot 7.64}{e^{7.64} - 1} = +0.004 + 0.031 = 0.035 \text{ J/mol K} \]

"Total" Entropy

\[ S^{\text{tot}} = S^{\text{rot}} + S^{\text{vib}} = 151.9 + 43.8 + 0.035 = 195.7 \text{ J/mol K} \]

O\(_2\): \( S_{\text{mol(exp)}} = 205.1 \text{ J/mol-K at 298.15 K} \)

We're still about 5% lower than experiment, for now.

The vibrational contribution to the entropy of O\(_2\) is very low at 298 K. It increases significantly at higher temperatures.

<table>
<thead>
<tr>
<th>T</th>
<th>( S^{\text{vib}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298 K</td>
<td>0.035 J/mol-K</td>
</tr>
<tr>
<td>500</td>
<td>0.49</td>
</tr>
<tr>
<td>1000</td>
<td>3.07</td>
</tr>
<tr>
<td>2000</td>
<td>7.86</td>
</tr>
<tr>
<td>3000</td>
<td>10.82</td>
</tr>
</tbody>
</table>
### Output from G-98 geom. opt. and frequency calculation on O₂ (at 298 K)

<table>
<thead>
<tr>
<th>Component</th>
<th>CV</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOTAL</td>
<td>3.750</td>
<td>48.972</td>
</tr>
<tr>
<td>ELECTRONIC</td>
<td>0.000</td>
<td>2.183</td>
</tr>
<tr>
<td>TRANSLATIONAL</td>
<td>0.889</td>
<td>26.321</td>
</tr>
<tr>
<td>ROTATIONAL</td>
<td>0.592</td>
<td>10.459</td>
</tr>
<tr>
<td>VIBRATIONAL</td>
<td>0.592</td>
<td>10.459</td>
</tr>
</tbody>
</table>

QCISD/6-311G(d)

G-98 tabulates the sum of $U_{ZPE}^{\text{ vib}} + U_{\text{therm}}^{\text{ vib}}$ even though they call it $E(\text{Therm.})$.

\[ E_{\text{Therm.}} = U_{ZPE}^{\text{ vib}} + U_{\text{therm}}^{\text{ vib}} = 2.269 \text{ kcal} / \text{ mol} = 9.49 \text{ kJ} / \text{ mol} \]

We got 9.46 + 0.009 = 9.47 \text{ kJ/mol} (sig. fig. difference)

\[ C_{V}^{\text{ vib}} = 0.055 \text{ cal} / \text{ mol} \cdot \text{K} = 0.23 \text{ J} / \text{ mol} \cdot \text{K} \] (same as our result)

\[ S_{\text{ vib}} = 0.008 \text{ cal} / \text{ mol} \cdot \text{K} = 0.033 \text{ J} / \text{ mol} \cdot \text{K} \]

We got 0.035 J/mol-K (sig. fig. difference)

---

### Helmholtz and Gibbs Energy

\[ A^{\text{ vib}} = -kT \ln Q^{\text{ vib}} \]

\[ G^{\text{ vib}} = A^{\text{ vib}} - kT \ln (Q^{\text{ vib}}) \]

\[ G^{\text{ vib}} = A^{\text{ vib}} = -kT \ln \left( \frac{e^{\frac{\Theta}{T}}}{1 - e^{\frac{\Theta}{T}}} \right) \]

$Q^{\text{ vib}}$ independent of $V$

O₂ (ν = 1580 cm⁻¹) at 298 K (one mole).

\[ \Theta_v = \frac{h c v}{k} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s}) (3.00 \times 10^{10} \text{ cm/s}) (1580 \text{ cm}^{-1})}{1.38 \times 10^{-23} \text{ J/K}} = 2277 \text{ K} \]

\[ \Theta_v = 2277 \text{ K} \]

\[ \frac{\Theta_v}{T} = \frac{2277}{298} = 7.64 \]

\[ q^{\text{ vib}} = \frac{e^{\frac{\Theta_v}{T}}}{1 - e^{\frac{\Theta_v}{T}}} = e^{-7.64/2} = 0.0219 \]

\[ G^{\text{ vib}} = A^{\text{ vib}} = (-8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})\ln(0.0219) = 9460 \text{ J/mol} = 9.46 \text{ kJ/mol} \]
Polyatomic Molecules

It is straightforward to handle polyatomic molecules, which have 3N-6 (non-linear) or 3N-5 (linear) vibrations.

Energy: \( e^{\text{ vib}} = e_1^{\text{ vib}} + e_2^{\text{ vib}} + \cdots = (n_1 + 1/2)\hbar \nu_1 + (n_2 + 1/2)\hbar \nu_2 + \cdots \)

Partition Function

\[
Q^{\text{ vib}} = \left( \sum e^{-\frac{\delta_{ij} + s_{ji} - \eta_{N}}{kT}} \right)^N = \left( \sum e^{-\frac{\delta_{ij}}{kT}} \right)^N \left( \sum e^{-\frac{\delta_{ji}}{kT}} \right)^N \cdots
\]

Therefore: \( Q^{\text{ vib}} = Q_1^{\text{ vib}} \cdot Q_2^{\text{ vib}} \cdots \)

Thermodynamic Properties

\[
\ln Q^{\text{ vib}} = \ln Q_1^{\text{ vib}} + \ln Q_2^{\text{ vib}} + \cdots
\]

\[
\left( \frac{\partial \ln Q^{\text{ vib}}}{\partial T} \right)_{V,N} = \left( \frac{\partial \ln Q_1^{\text{ vib}}}{\partial T} \right)_{V,N} + \left( \frac{\partial \ln Q_2^{\text{ vib}}}{\partial T} \right)_{V,N} + \cdots
\]

Therefore: \( U^{\text{ vib}} = U_1^{\text{ vib}} + U_2^{\text{ vib}} + \cdots \)

\( S^{\text{ vib}} = S_1^{\text{ vib}} + S_2^{\text{ vib}} + \cdots \)

etc.

Thus, you simply calculate the property for each vibration separately, and add the contributions together.
Comparison Between Theory and Experiment: H$_2$O(g)

For molecules with a singlet electronic ground state and no low-lying excited electronic levels, translations, rotations and vibrations are the only contributions to the thermodynamic properties.

We'll consider water, which has 3 translations, 3 rotations and 3 vibrations.

Using Equipartition of Energy, one predicts:

\[
\begin{align*}
\mathcal{H}_{\text{tran}} &= \frac{3}{2}RT + RT \quad \mathcal{C}_p^{\text{tran}} = \frac{3}{2}R + R = \frac{5}{2}R \\
\mathcal{H}_{\text{rot}} &= \frac{3}{2}RT \quad \mathcal{C}_p^{\text{rot}} = \frac{3}{2}R \\
\mathcal{H}_{\text{vib}} &= 3RT \quad \mathcal{C}_p^{\text{vib}} = 3R
\end{align*}
\]

Low T Limit: \( \mathcal{H}_{\text{tran}} + \mathcal{H}_{\text{rot}} = 4RT \quad \mathcal{C}_p^{\text{tran}} + \mathcal{C}_p^{\text{rot}} = 4R \)

High T Limit: \( \mathcal{H}_{\text{tran}} + \mathcal{H}_{\text{rot}} + \mathcal{H}_{\text{vib}} = 7RT \quad \mathcal{C}_p^{\text{tran}} + \mathcal{C}_p^{\text{rot}} + \mathcal{C}_p^{\text{vib}} = 7R \)
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Calculated and Experimental Enthalpy of \( \text{H}_2\text{O}(g) \)

Slide 84

Calculated and Experimental Heat Capacity (\(C_P\)) of \( \text{H}_2\text{O}(g) \)
Unlike in $\text{H}_2\text{O}$, the remaining contribution (electronic) to the entropy of $\text{O}_2$ is significant. We'll discuss this in Chapter 10.

There are also significant additional contributions to the Enthalpy.
Notes:  
(A) The calculated heat capacity levels off above ~2000 K. This represents the high temperature limit in which the vibration contributes R to $C_p$.

(B) There is a significant electronic contribution to $C_p$ at high temperature.