

CHAPTER 5
MOLECULAR VIBRATIONS AND
TIME-INDEPENDENT PERTURBATION THEORY
OUTLINE

Homework Questions Attached

PART A: The Harmonic Oscillator and Vibrations of Molecules.

SECT	TOPIC
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|-----|---|
| 1. | The Classical Harmonic Oscillator |
| 2. | Math Preliminary: Taylor Series Solutions of Differential Equations |
| 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

SECT	TOPIC
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1. Symmetry and Vibrational Selection Rules
2. Spectroscopic Selection Rules
3. The Symmetry of Vibrational Normal Modes:
Application to the Stretching Vibrations in Ethylene
4. Time Independent Perturbation Theory
5. QM Calculations of Vibrational Frequencies and Molecular Dissociation Energies
6. Statistical Thermodynamics: Vibrational Contributions to the Thermodynamic
Properties of Gases
7. The Vibrational Partition Function
8. Internal Energy: ZPE and Thermal Contributions
9. Applications to $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$

Chapter 5 Homework

1. Consider the differential equation: $\frac{d^2 y}{dx^2} = -4y$

Assume that the solution is of the form: $y = \sum_{n=0}^{\infty} a_n x^n = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \dots$

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:

$$\psi = A_1 x e^{-\alpha x^2/2} \quad \alpha = \frac{\mu \omega}{\hbar} \quad \omega = \sqrt{\frac{k}{\mu}}$$

- (a) Calculate the normalization constant, A_1 (in terms of α)
 - (b) Determine $\langle x \rangle$ (in terms of α)
 - (c) Determine $\langle x^2 \rangle$ (in terms of α)
 - (d) Determine $\langle p \rangle$ (in terms of α)
 - (e) Determine $\langle p^2 \rangle$ (in terms of α)
 - (f) Determine $\langle T \rangle$, average kinetic energy (in terms of ω)
 - (g) Determine $\langle V \rangle$, average potential energy (in terms of ω)
3. Consider a two dimensional Harmonic Oscillator for which $k_y = 9 \cdot k_x$. Determine the energies (in terms of ω_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, ΔE , 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 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/hc), (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/hc), (2) J, (3) kJ/mol.

7. The fundamental vibrational frequency of $^{127}\text{I}_2$ (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 $300\text{ }^\circ\text{C}$.

8. The Thermodynamic Dissociation Energy of H^{35}Cl is $D_0 = 428\text{ kJ/mol}$, 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:

$$\begin{aligned} V(x) &\rightarrow \infty & x < 0 \\ V(x) &= B & 0 \leq x \leq a/2 \\ V(x) &= 2B & a/2 \leq x \leq a \\ V(x) &\rightarrow \infty & x > a \end{aligned}$$

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:

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

Use the Harmonic Oscillator Hamiltonian as the unperturbed Hamiltonian:

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

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

as the unperturbed ground state wavefunction and energy

Your answer should be in terms of k , μ , $\hbar$, ω , and γ

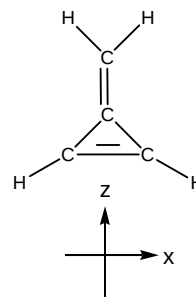
11. The Fundamental and First Overtone vibrational frequencies of HCl are 2885 cm^{-1} and 5664 cm^{-1} . Calculate the harmonic frequency ($\tilde{\nu}$) and the anharmonicity constant (x_e).
12. The symmetric C-Br stretching vibration of CBr_4 has a frequency of 270 cm^{-1} . Calculate the contribution of this vibration to the enthalpy, heat capacity (constant pressure), entropy and Gibbs energy of two (2) moles of CBr_4 at $800\text{ }^\circ\text{C}$.

13. Three of the fundamental vibrational modes (CH bending) in methylenecyclopropene (C_2v) 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) $\nu_2 - \nu_3$

C_{2v}	E	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



DATA

$$h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$\hbar = h/2\pi = 1.05 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$c = 3.00 \times 10^8 \text{ m/s} = 3.00 \times 10^{10} \text{ cm/s}$$

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$k = 1.38 \times 10^{-23} \text{ J/K}$$

$$R = 8.31 \text{ J/mol}\cdot\text{K}$$

$$R = 8.31 \text{ Pa}\cdot\text{m}^3/\text{mol}\cdot\text{K}$$

$$m_e = 9.11 \times 10^{-31} \text{ kg (electron mass)}$$

$$1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$$

$$1 \text{ \AA} = 10^{-10} \text{ m}$$

$$k \cdot N_A = R$$

$$1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$$

$$1 \text{ atm.} = 1.013 \times 10^5 \text{ Pa}$$

$$1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$$

$$\int_0^\infty e^{-\beta x^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{\beta}}$$

$$\int_0^\infty x e^{-\beta x^2} dx = \frac{1}{2\beta}$$

$$\int_0^\infty x^2 e^{-\beta x^2} dx = \frac{1}{4\beta} \sqrt{\frac{\pi}{\beta}}$$

$$\int_0^\infty x^3 e^{-\beta x^2} dx = \frac{1}{2\beta^2}$$

$$\int_0^\infty x^4 e^{-\beta x^2} dx = \frac{3}{8\beta^2} \sqrt{\frac{\pi}{\beta}}$$

$$\int \sin^2(\alpha x) dx = \frac{1}{2} x - \frac{1}{4\alpha} \sin(2\alpha x)$$

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**

Slide 1

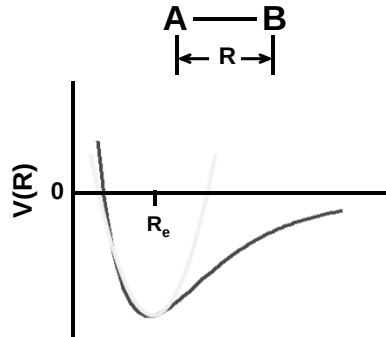
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Slide 2

The Classical Harmonic Oscillator

The Potential Energy of a Diatomic Molecule



Harmonic Oscillator Approximation

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

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

Slide 3

Hooke's Law and Newton's Equation



$$\text{Force: } f = -\frac{dV}{dx} = -\frac{d}{dx}\left(\frac{1}{2}kx^2\right) = -kx$$

$$\text{Newton's Equation: } f = \mu a = \mu \frac{d^2x}{dt^2} \quad \text{where} \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

Reduced Mass

$$\text{Therefore: } \mu \frac{d^2x}{dt^2} = -kx$$

Slide 4

Solution

$$\mu \frac{d^2 x}{dt^2} = -kx$$

Assume: $x(t) = A \sin(\omega t) + B \cos(\omega t)$

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

$$\begin{aligned} \frac{d^2 x}{dt^2} &= -\omega^2 A \sin(\omega t) - \omega^2 B \cos(\omega t) \\ &= -\omega^2 x \end{aligned}$$

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



$$\omega = \sqrt{\frac{k}{\mu}} \quad \text{2nd rev}$$

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

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

Slide 5

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 $x(0) = x_0 = B \longrightarrow$

$$x(t) = x_0 \cos(\omega t)$$

$$\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

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

$$x(0) = x_0$$

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

Slide 6

Conservation of Energy

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

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

$$V = \frac{1}{2} kx^2$$

$$T = \frac{1}{2} \mu \left(\frac{dx}{dt} \right)^2$$

$$E = T + V$$

$$T = \frac{1}{2} \mu \omega^2 x_0^2 \sin^2(\omega t)$$

$$V = \frac{1}{2} kx_0^2 \cos^2(\omega t)$$

$$T = \frac{1}{2} kx_0^2 \sin^2(\omega t)$$

$$E = \frac{1}{2} kx_0^2$$

$$\omega t = 0, \pi, 2\pi, \dots \longrightarrow x = \pm x_0$$

$$V = \frac{1}{2} kx_0^2$$

$$T = 0$$

$$E = \frac{1}{2} kx_0^2$$

$$\omega t = \pi/2, 3\pi/2, \dots \longrightarrow x = 0$$

$$V = 0$$

$$T = \frac{1}{2} kx_0^2$$

$$E = \frac{1}{2} kx_0^2$$

Slide 7

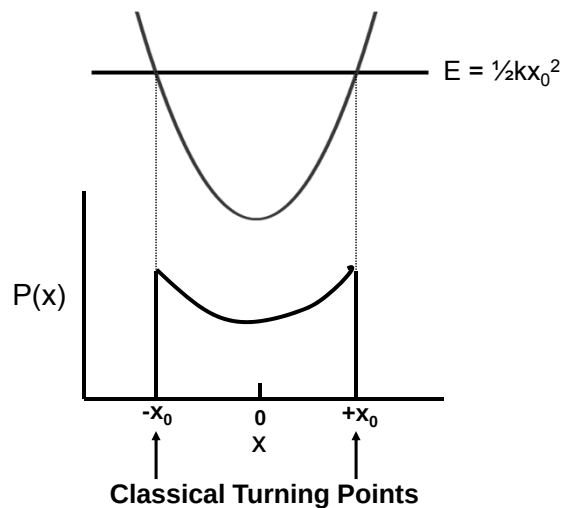
Classical HO Properties

Energy: $E = T + V = \frac{1}{2} kx_0^2 = \text{Any Value}$ i.e. no energy quantization

If $x_0 = 0$, $E = 0$

i.e. no Zero Point Energy

Probability:



Slide 8

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Slide 9

Math Preliminary: Taylor Series Solution of Differential Equations

Taylor (McLaurin) Series

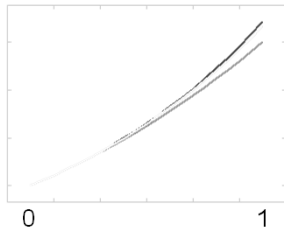
$$f(x) = \sum_{n=0}^{\infty} \left(\frac{1}{n!} \right) f^{(n)}(0) x^n$$

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

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

Slide 10

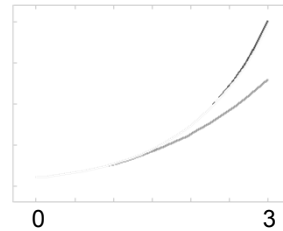
Example: $f(x) = e^x = \sum_{n=0}^{\infty} \left(\frac{1}{n!} \right) x^n = 1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3 + \frac{1}{24}x^4 + \dots$



(x ff f2 f3) $f(x) = e^x$

$$f_2(x) = 1 + x + \frac{x^2}{2}$$

$$f_3(x) = 1 + x + \frac{x^2}{2} + \frac{x^3}{6}$$



(x ff f3 f6) $f(x) = e^x$

$$f_3(x) = 1 + x + \frac{x^2}{2} + \frac{x^3}{6}$$

$$f_6(x) = 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + \frac{x^4}{24} + \frac{x^5}{120} + \frac{x^6}{720}$$

Slide 11

Taylor (McLaurin) Series

$$f(x) = \sum_{n=0}^{\infty} \left(\frac{1}{n!} \right) f^{(n)}(0) x^n$$

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

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

A Differential Equation

$$\frac{df(x)}{dx} = f(x)$$

Solution: $f(x) = Ae^x$

Slide 12

Taylor Series Solution

$$\frac{df(x)}{dx} = f(x)$$

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

Our goal is to develop a “recursion formula” relating a_1 to a_0 , a_2 to a_1 ... (or, in general, a_{n+1} to a_n)

Specific
Recursion
Formulas:

$$\frac{df(x)}{dx} = a_1 + 2a_2x + 3a_3x^2 + \dots = \sum_{m=1}^{\infty} m a_m x^{m-1}$$

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

Coefficients of x^n must be equal for all n

$$a_1 = a_0$$

$$2a_2 = a_1 \longrightarrow a_2 = a_1/2 = a_0/2$$

$$3a_3 = a_2 \longrightarrow a_3 = a_2/3 = a_0/6$$

Slide 13

$$a_1 = a_0$$

$$a_2 = a_0/2$$

$$a_3 = a_0/6$$

$$f(x) = a_0 + a_1x + a_2x^2 + a_3x^3 + \dots = a_0 \left(1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3 + \dots \right)$$

**Power Series
Expansion for e^x**

General Recursion Formula

$$\frac{df(x)}{dx} = f(x)$$

$$\sum_{m=1}^{\infty} m a_m x^{m-1} = \sum_{n=0}^{\infty} a_n x^n$$

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



$$(n+1)a_{n+1} = a_n \quad \text{or}$$

$$a_{n+1} = \frac{a_n}{(n+1)}$$

Coefficients of the two series may be equated only if the summation limits are the same.

Therefore, set $m = n+1 \rightarrow n=m-1$
and $m=1$ corresponds to $n = 0$

Slide 14

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Slide 15

The Quantum Mechanical Harmonic Oscillator

Schrödinger Equation

Particle vibrating against wall

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



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 $x \rightarrow \pm\infty$

Slide 16

Solution of the HO Schrödinger Equation

Rearrangement of the Equation

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

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

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

$$\frac{d^2\psi}{dx^2} + \left(\frac{2\mu E}{\hbar^2} - \frac{k\mu}{\hbar^2} x^2 \right) \psi = 0$$

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

Define

$$\lambda \equiv \frac{2\mu E}{\hbar^2}$$

$$\alpha^2 \equiv \frac{k\mu}{\hbar^2} = \frac{\mu^2 \omega^2}{\hbar^2} \quad \omega = \sqrt{\frac{k}{\mu}}$$

Slide 17

$$\frac{d^2\psi}{dx^2} + (\lambda - \alpha^2 x^2) \psi = 0 \quad \lambda \equiv \frac{2\mu E}{\hbar^2} \quad \alpha^2 \equiv \frac{k\mu}{\hbar^2}$$

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: $\psi = \left(\sum_{n=0}^{\infty} a_n x^n \right) \psi_{\text{asympt}} = H(x) \psi_{\text{asympt}}$

That is, we'll assume that ψ is the product of a Taylor Series, $H(x)$, and an asymptotic solution, ψ_{asympt} , valid for large $|x|$

Slide 18

The Asymptotic Solution

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

We can show that the asymptotic solution is

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

Plug in

For large $|x|$

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

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

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

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

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

Note that ψ_{asympt} satisfied the BC's;
i.e. $\psi_{\text{asympt}} \rightarrow 0$ as $x \rightarrow \pm\infty$

Slide 19

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 ψ into the Schrödinger Equation

(c) Equates the coefficients of x^n

Then the following recursion formula is obtained:

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

Slide 20

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

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

$$\psi = \left(\sum_{n=0}^{\infty} a_n x^n \right) e^{-\alpha x^2/2} = \left(\underbrace{[a_0 + a_2 x^2 + a_4 x^4 + \dots]}_{\text{Even Series}} + \underbrace{[a_1 x + a_3 x^3 + a_5 x^5 + \dots]}_{\text{Odd Series}} \right) e^{-\alpha x^2/2}$$

From the recursion formula: $a_0 \rightarrow a_2 \rightarrow a_4 \rightarrow \dots$ **Even Coefficients**

$a_1 \rightarrow a_3 \rightarrow a_5 \rightarrow \dots$ **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

Slide 21

Satisfying the Boundary Conditions: Quantization of Energy

$$\lambda = \frac{2\mu E}{\hbar^2} \longrightarrow E = \frac{\lambda \hbar^2}{2\mu}$$

So far, there are no restrictions on λ and, therefore, none on E

Let's look at the solution so far:

$$\psi = \left(\sum_{n=0}^{\infty} a_n x^n \right) e^{-\alpha x^2/2} = \left(\underbrace{[a_0 + a_2 x^2 + a_4 x^4 + \dots]}_{\text{Even Series}} + \underbrace{[a_1 x + a_3 x^3 + a_5 x^5 + \dots]}_{\text{Odd Series}} \right) e^{-\alpha x^2/2}$$

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

It can be shown that: $\lim_{x \rightarrow \infty} (x^n e^{-\alpha x^2/2}) = 0$ **unless** $n \rightarrow \infty$

Therefore, the required BC's will be satisfied if, and only if, both the even and odd Taylor series terminate at a finite power.

Slide 22

$$\psi = \left(\sum_{n=0}^{\infty} a_n x^n \right) e^{-\alpha x^2/2} = \left(\underbrace{[a_0 + a_2 x^2 + a_4 x^4 + \dots]}_{\text{Even Series}} + \underbrace{[a_1 x + a_3 x^3 + a_5 x^5 + \dots]}_{\text{Odd Series}} \right) e^{-\alpha x^2/2}$$

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

We cannot let either Taylor series reach x^∞ .

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 .

Slide 23

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

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

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

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

This criterion puts restrictions on the allowed values of λ and, therefore, the allowed values of the energy, E .

Slide 24

Allowed Values of the Energy

Earlier Definitions

$$\lambda \equiv \frac{2\mu E}{\hbar^2} \rightarrow E = \frac{\lambda \hbar^2}{2\mu}$$

$$\alpha^2 \equiv \frac{k\mu}{\hbar^2} = \frac{\mu^2 \omega^2}{\hbar^2}$$

$$\downarrow$$

$$\alpha = \frac{\mu\omega}{\hbar}$$

Restriction on λ

$$\frac{\lambda}{\alpha} - 2n - 1 = 0 \quad n = 0, 1, 2, 3, \dots$$

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

Quantized Energy Levels

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

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

or

$$E = \left(n + \frac{1}{2} \right) h\nu \quad \nu = \frac{\omega}{2\pi}$$

Slide 25

Part A: The Harmonic Oscillator and Vibrations of Molecules

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Slide 26

HO Energies and Wavefunctions

Harmonic Oscillator Energies

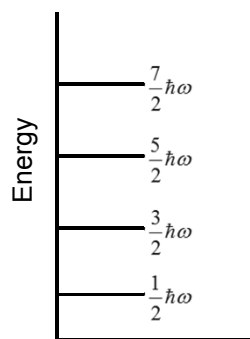
$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega = \left(n + \frac{1}{2}\right) h \nu \quad n = 0, 1, 2, 3, \dots$$

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



Slide 27

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.

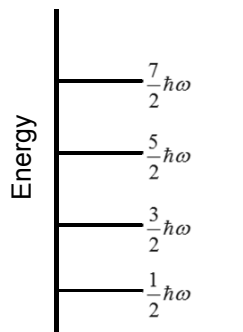
Zero Point Energy

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.



Slide 28

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 H_2 molecule is 4200 cm^{-1} . Calculate the energy level spacing and the ZPE, in J and in kJ/mol.

$\hbar = 1.05 \times 10^{-34}\text{ J}\cdot\text{s}$
 $c = 3.00 \times 10^8\text{ m/s}$
 $= 3.00 \times 10^{10}\text{ cm/s}$
 $N_A = 6.02 \times 10^{23}\text{ mol}^{-1}$

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

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

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

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

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

Slide 29

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.

$\hbar = 1.05 \times 10^{-34}\text{ J}\cdot\text{s}$
 $c = 3.00 \times 10^8\text{ m/s}$
 $= 3.00 \times 10^{10}\text{ cm/s}$
 $N_A = 6.02 \times 10^{23}\text{ mol}^{-1}$

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

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

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

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

$$N_A \cdot E_0 = (6.02 \times 10^{23}\text{ mol}^{-1})(3.3 \times 10^{-30}\text{ J}) = 2.0 \times 10^{-6}\text{ J/mol} = \boxed{2.0 \times 10^{-9}\text{ kJ/mol}}$$

Slide 30

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

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

Some specific solutions

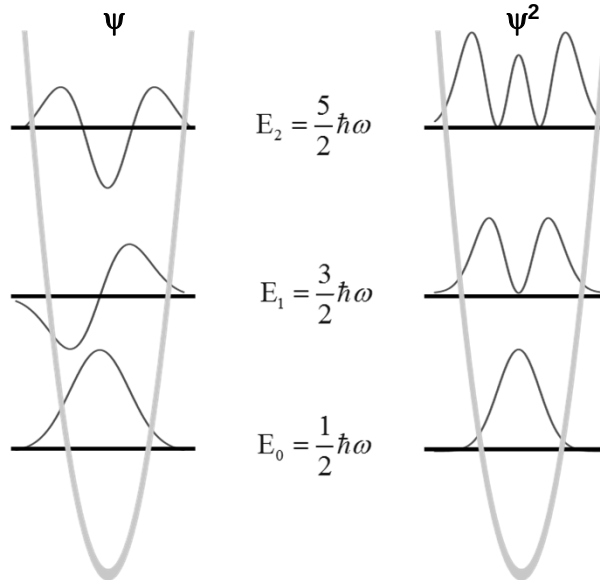
$$n = 0 \quad \psi_0 = N_0 e^{-\alpha x^2/2} = N_0 e^{-z^2/2} \quad \text{Even}$$

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

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

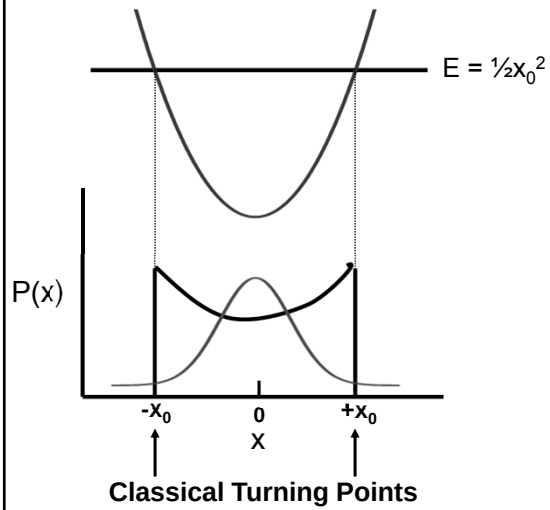
$$n = 3 \quad \psi_3 = N_3 (8\alpha^{3/2} x^3 - 12\sqrt{\alpha} x) e^{-\alpha x^2/2} = N_3 (8z^3 - 12z) e^{-z^2/2} \quad \text{Odd}$$

Slide 31



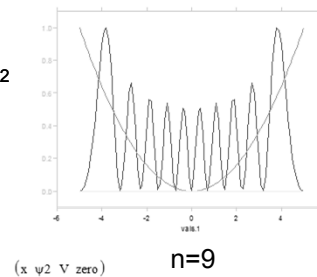
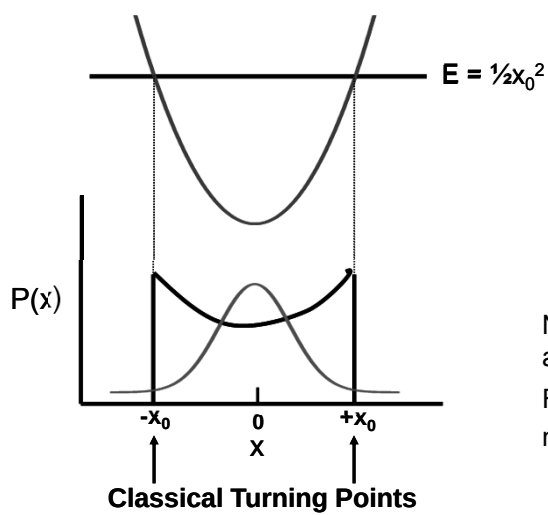
Slide 32

Quantum Mechanical vs. Classical Probability



Slide 33

Correspondence Principle



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

Slide 34

Part A: The Harmonic Oscillator and Vibrations of Molecules

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Slide 35

Properties of the QM Harmonic Oscillator

Some Useful Integrals

$$\int_0^{\infty} e^{-\beta x^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{\beta}}$$

$$\int_0^{\infty} x e^{-\beta x^2} dx = \frac{1}{2\beta}$$

$$\int_0^{\infty} x^2 e^{-\beta x^2} dx = \frac{1}{4\beta} \sqrt{\frac{\pi}{\beta}}$$

$$\int_0^{\infty} x^3 e^{-\beta x^2} dx = \frac{1}{2\beta^2}$$

$$\int_0^{\infty} x^4 e^{-\beta x^2} dx = \frac{3}{8\beta^2} \sqrt{\frac{\pi}{\beta}}$$

Remember

$$\int_{-\infty}^{\infty} f(x) dx = 2 \int_0^{\infty} f(x) dx$$

$$\text{If } f(-x) = f(x)$$

Even Integrand

$$\int_{-\infty}^{\infty} f(x) dx = 0$$

$$\text{If } f(-x) = -f(x)$$

Odd Integrand

Slide 36

Wavefunction Orthogonality

$$\psi_0 = N_0 e^{-\alpha x^2/2} \quad -\infty < x < \infty$$

$$\psi_1 = N_1 (2\sqrt{\alpha} x) e^{-\alpha x^2/2} \quad -\infty < x < \infty$$

$$\psi_2 = N_2 (4\alpha x^2 - 2) e^{-\alpha x^2/2} \quad -\infty < x < \infty$$

$$\langle \psi_0 | \psi_1 \rangle$$

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

$$\langle \psi_0 | \psi_1 \rangle = N_0 N_1 2\sqrt{\alpha} \int_{-\infty}^{\infty} x e^{-\alpha x^2} dx$$

Odd Integrand

$$\langle \psi_0 | \psi_1 \rangle = 0$$

Slide 37

Wavefunction Orthogonality

$$\psi_0 = N_0 e^{-\alpha x^2/2} \quad -\infty < x < \infty$$

$$\psi_1 = N_1 (2\sqrt{\alpha} x) e^{-\alpha x^2/2} \quad -\infty < x < \infty$$

$$\psi_2 = N_2 (4\alpha x^2 - 2) e^{-\alpha x^2/2} \quad -\infty < x < \infty$$

$$\langle \psi_0 | \psi_2 \rangle$$

$$\langle \psi_0 | \psi_2 \rangle = \int_{-\infty}^{\infty} \left(N_0 e^{-\alpha x^2/2} \right) \left(N_2 [4\alpha x^2 - 2] e^{-\alpha x^2/2} \right) dx$$

$$\langle \psi_0 | \psi_2 \rangle = N_0 N_2 \left\{ 4\alpha \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx - 2 \int_{-\infty}^{\infty} e^{-\alpha x^2} dx \right\} \quad \int_0^{\infty} e^{-\beta x^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{\beta}}$$

$$\langle \psi_0 | \psi_2 \rangle = N_0 N_2 \left\{ 4\alpha \cdot 2 \cdot \frac{1}{4\alpha} \sqrt{\frac{\pi}{\alpha}} - 2 \cdot 2 \cdot \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} \right\} \quad \int_0^{\infty} x^2 e^{-\beta x^2} dx = \frac{1}{4\beta} \sqrt{\frac{\pi}{\beta}}$$

$$\langle \psi_0 | \psi_2 \rangle = 0$$

Slide 38

We performed many of the calculations below on ψ_0 of the HO in Chap. 2. Therefore, the calculations below will be on ψ_1 .

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

Normalization

$$\langle \psi_1 | \psi_1 \rangle = \int_{-\infty}^{\infty} [A_1 x e^{-\alpha x^2/2}]^2 dx = 1$$

↓
from
HW Solns.

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

Slide 39

Positional Averages

$$\langle x \rangle$$

$$\langle x \rangle = \langle \psi_1 | x | \psi_1 \rangle = \int_{-\infty}^{\infty} x [A_1 x e^{-\alpha x^2/2}]^2 dx$$

↓
from
HW Solns.

$$\langle x \rangle = 0$$

$$\langle x^2 \rangle$$

$$\langle x^2 \rangle = \langle \psi_1 | x^2 | \psi_1 \rangle = \int_{-\infty}^{\infty} x^2 [A_1 x e^{-\alpha x^2/2}]^2 dx$$

↓
from
HW Solns.

$$\langle x^2 \rangle = \frac{3}{2\alpha}$$

Slide 40

Momentum Averages

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

↓
from
HW Solns.

$$\langle p \rangle = 0$$

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

↓
from
HW Solns.

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

Slide 41

Energy Averages

Kinetic Energy

$$\langle T \rangle = \left\langle \frac{p^2}{2\mu} \right\rangle = \frac{1}{2\mu} \langle p^2 \rangle$$

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

↓
from
HW Solns.

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

Potential Energy

$$\langle V \rangle = \left\langle \frac{1}{2} k x^2 \right\rangle = \frac{1}{2} k \langle x^2 \rangle$$

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

↓
from
HW Solns.

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

Total Energy

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

Slide 42

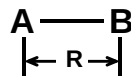
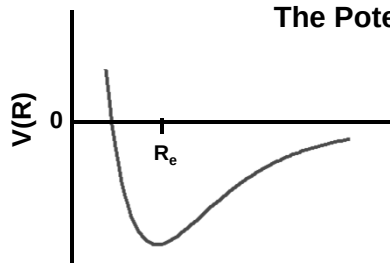
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- Math Preliminary: Taylor Series Solution of Differential Eqns.
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- Harmonic Oscillator Wavefunctions and Energies
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 - Vibrational Anharmonicity
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 - Vibrations of Polyatomic Molecules

Slide 43

The Vibrations of Diatomic Molecules

The Potential Energy



Define: $x = R - R_{eq}$

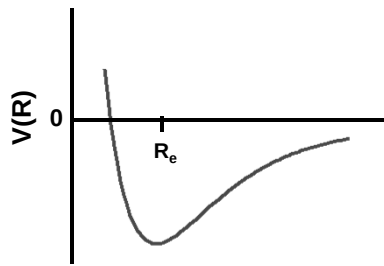
Expand $V(x)$ in a Taylor series about $x = 0$ ($R = R_{eq}$)

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

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

$$V(x) = (V)_{x=0} + \left(\frac{dV}{dx} \right)_{x=0} x + \frac{1}{2} \left(\frac{d^2 V}{dx^2} \right)_{x=0} x^2 + \frac{1}{6} \left(\frac{d^3 V}{dx^3} \right)_{x=0} x^3 + \frac{1}{24} \left(\frac{d^4 V}{dx^4} \right)_{x=0} x^4 + \dots$$

Slide 44



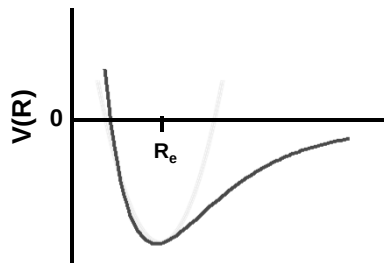
$$V(x) = \cancel{\left(\frac{d^0 V}{dx^0}\right)_{x=0}} + \cancel{\left(\frac{d^1 V}{dx^1}\right)_{x=0}} x + \frac{1}{2} \left(\frac{d^2 V}{dx^2}\right)_{x=0} x^2 + \frac{1}{6} \left(\frac{d^3 V}{dx^3}\right)_{x=0} x^3 + \frac{1}{24} \left(\frac{d^4 V}{dx^4}\right)_{x=0} x^4 + \dots$$

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

$$\left(\frac{dV}{dx}\right)_{x=0} = 0 \quad \text{By convention} \quad k = \left(\frac{d^2 V}{dx^2}\right)_{x=0} \quad \delta = \frac{1}{24} \left(\frac{d^4 V}{dx^4}\right)_{x=0}$$

$$\left(\frac{dV}{dx}\right)_{x=0} = 0 \quad \text{By definition of } R_e \text{ as minimum} \quad \gamma = \frac{1}{6} \left(\frac{d^3 V}{dx^3}\right)_{x=0}$$

Slide 45



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

The Harmonic Oscillator Approximation

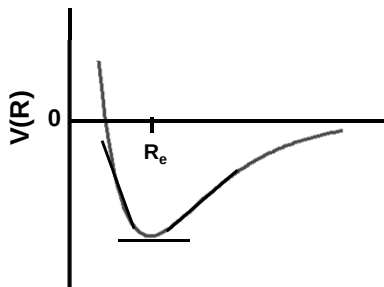
Ignore x^3 and higher order terms in $V(x)$

$$V(x) = \frac{1}{2} kx^2 \quad \text{where} \quad k = \left(\frac{d^2 V}{dx^2}\right)_{x=0}$$

Slide 46

The Force Constant (k)

The Interpretation of k



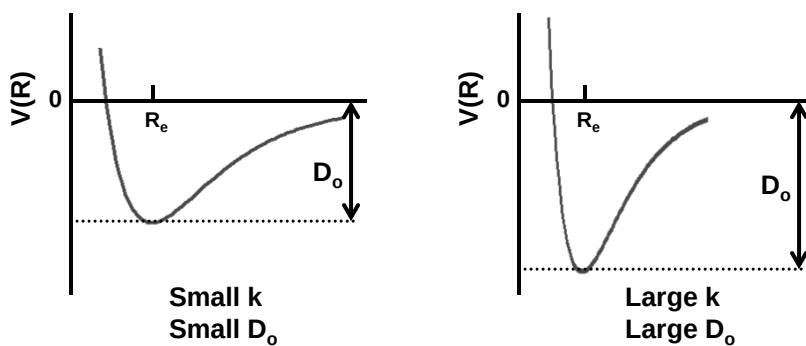
$$k = \left(\frac{d^2V}{dx^2} \right)_{x=0} = \frac{d}{dx} \left(\frac{dV}{dx} \right) = \frac{d}{dx} (\text{Slope})$$

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 $x=0$ ($R=R_e$).

Slide 47

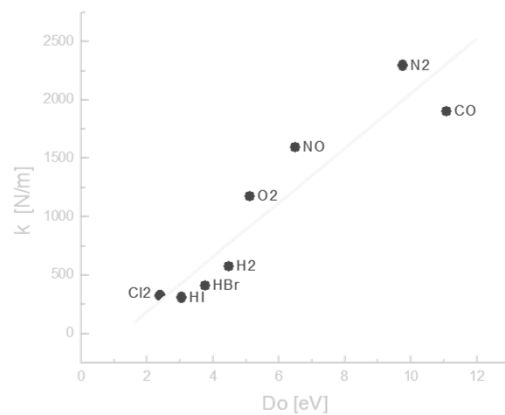
Correlation Between k and Bond Strength



D_0 is the Dissociation Energy of the molecule, and represents the chemical bond strength.

There is often a correlation between k and D_0 .

Slide 48



Note the approximately linear correlation between Force Constant (k) and Bond Strength (D_0).

Slide 49

Part A: The Harmonic Oscillator and Vibrations of Molecules

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- Harmonic Oscillator Wavefunctions and Energies
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Slide 50

Vibrational Spectroscopy

Energy Levels and Transitions

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega = \left(n + \frac{1}{2}\right) h\nu \quad \nu = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Selection Rule

$$\Delta n = \pm 1 \quad \begin{array}{l} (+1 \text{ for absorption,} \\ -1 \text{ for emission}) \end{array}$$

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.

Slide 51

Transition Frequency

$$n \rightarrow n+1$$

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

$$\text{Wavenumbers: } \tilde{\nu} = \frac{\Delta E}{hc} = \frac{\nu}{c} \text{ cm}^{-1}$$

$$\text{Note: } \tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

The Boltzmann Distribution

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

The strongest transition corresponds to: $n=0 \rightarrow n=1$

Slide 52

Calculation of the Force Constant

Units of k

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

$$k = \frac{J}{m^2} = \frac{kg \cdot m^2 / s^2}{m^2} = \frac{kg}{s^2} = \frac{kg \cdot m / s^2}{m} = \frac{N}{m}$$

Calculation of k

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

$$\downarrow$$

$$k = (2\pi c \tilde{\nu})^2 \mu$$

Slide 53

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

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

$$\mu = \frac{m_{\text{Br}} \cdot m_{\text{F}}}{m_{\text{Br}} + m_{\text{F}}} = \frac{(79 \text{ amu}) \cdot (19 \text{ amu})}{79 \text{ amu} + 19 \text{ amu}}$$

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

$$\begin{aligned} h &= 6.63 \times 10^{-34} \text{ J}\cdot\text{s} \\ c &= 3.00 \times 10^8 \text{ m/s} \\ c &= 3.00 \times 10^{10} \text{ cm/s} \\ k &= 1.38 \times 10^{-23} \text{ J/K} \\ 1 \text{ amu} &= 1.66 \times 10^{-27} \text{ kg} \\ 1 \text{ N} &= 1 \text{ kg}\cdot\text{m/s}^2 \end{aligned}$$

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

$$k = 130 \text{ kg / s}^2 = 130 (\text{kg} \cdot \text{m} / \text{s}^2) / \text{m} = 130 \text{ N / m}$$

Slide 54

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.

$$\frac{I_{1 \rightarrow 2}}{I_{0 \rightarrow 1}} = \frac{N_1}{N_0} = \frac{e^{-E_1/kT}}{e^{-E_0/kT}} = e^{-(E_1 - E_0)/kT} = e^{-hc\tilde{\nu}/kT}$$

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

$$\begin{aligned} h &= 6.63 \times 10^{-34} \text{ J}\cdot\text{s} \\ c &= 3.00 \times 10^8 \text{ m/s} \\ c &= 3.00 \times 10^{10} \text{ cm/s} \\ k &= 1.38 \times 10^{-23} \text{ J/K} \\ \tilde{\nu} &= 380 \text{ cm}^{-1} \end{aligned}$$

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

Slide 55

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

$$R = \frac{I_{1 \rightarrow 2}}{I_{0 \rightarrow 1}}$$

Molecule	$\tilde{\nu}$	T	R
$^{79}\text{Br}^{19}\text{F}$	380 cm^{-1}	25 °C	0.16
$^{79}\text{Br}^{19}\text{F}$	380	500	0.49
$^{79}\text{Br}^{19}\text{F}$	380	1000	0.65
H^{35}Cl	2880	25	9×10^{-7}
H^{35}Cl	2880	500	0.005
H^{35}Cl	2880	1000	0.04

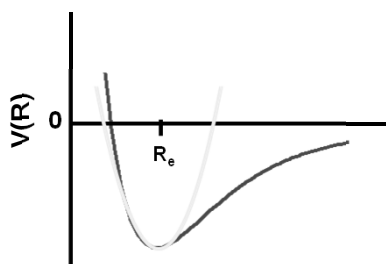
Slide 56

Part A: The Harmonic Oscillator and Vibrations of Molecules

- The Classical Harmonic Oscillator
- Math Preliminary: Taylor Series Solution of Differential Eqns.
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- Properties of the Quantum Mechanical Harmonic Oscillator
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- Vibrational Spectroscopy
- **Vibrational Anharmonicity**
- The Two Dimensional Harmonic Oscillator
- Vibrations of Polyatomic Molecules

Slide 57

Vibrational Anharmonicity



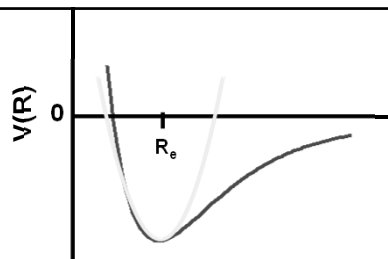
$$V(x) = \frac{1}{2}kx^2 + \gamma x^3 + \delta x^4 + \dots$$

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.

Slide 58



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

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:

$$\frac{E_n}{hc} = \left(n + \frac{1}{2}\right) \tilde{\nu} - \left(n + \frac{1}{2}\right)^2 x_e \tilde{\nu}$$

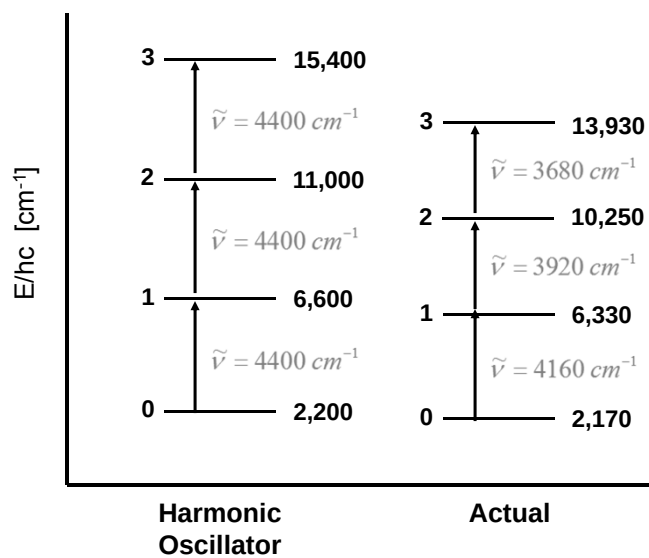
$\tilde{\nu}$ is the harmonic frequency and x_e is the anharmonicity constant.

Measurement of the fundamental frequency ($0 \rightarrow 1$) and first overtone ($0 \rightarrow 2$) [or the "hot band" ($1 \rightarrow 2$)] permits determination of $\tilde{\nu}$ and x_e .

See HW Problem

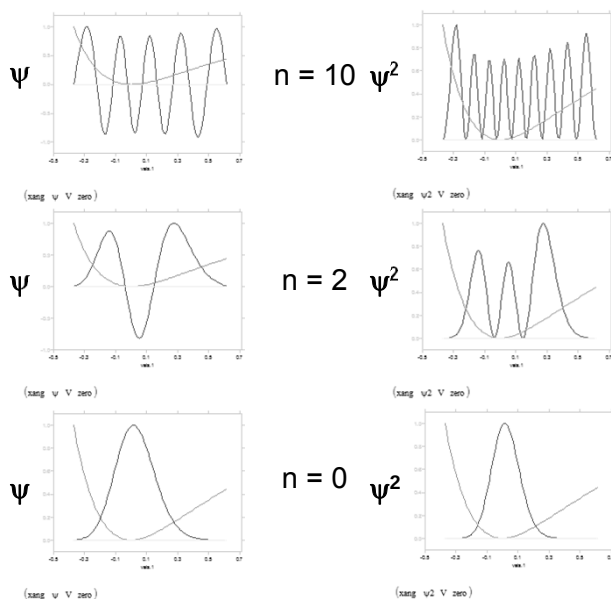
Slide 59

Energy Levels and Transition Frequencies in H_2



Slide 60

Anharmonic Oscillator Wavefunctions



Slide 61

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Slide 62

The Two Dimensional Harmonic Oscillator

The Schrödinger Equation

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

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

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

The Solution: Separation of Variables

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

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

Slide 63

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

↓

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

↓

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

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

$$E = E_x + E_y$$

Slide 64

$$\frac{1}{\psi_x} \left[-\frac{\hbar^2}{2\mu} \frac{d^2\psi_x}{dx^2} + \frac{1}{2} k_x x^2 \psi_x \right] = E_x$$

↓

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi_x}{dx^2} + \frac{1}{2} k_x x^2 \psi_x = E_x \psi_x$$

$$\frac{1}{\psi_y} \left[-\frac{\hbar^2}{2\mu} \frac{d^2\psi_y}{dy^2} + \frac{1}{2} k_y y^2 \psi_y \right] = E_y$$

↓

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi_y}{dy^2} + \frac{1}{2} k_y y^2 \psi_y = E_y \psi_y$$

The above equations are just one dimensional HO Schrödinger equations. Therefore, one has:

$$\psi_{nx} = N_{nx} H_{nx}(\sqrt{\alpha_x} x) e^{-\alpha_x x^2/2}$$

$$\psi_{ny} = N_{ny} H_{ny}(\sqrt{\alpha_y} y) e^{-\alpha_y y^2/2}$$

$$E_x = \left(n_x + \frac{1}{2} \right) \hbar \omega_x$$

$$E_y = \left(n_y + \frac{1}{2} \right) \hbar \omega_y$$

$$\omega_x = \sqrt{\frac{k_x}{\mu}}$$

$$\omega_y = \sqrt{\frac{k_y}{\mu}}$$

$$\alpha_x = \frac{\mu \omega_x}{\hbar}$$

$$\alpha_y = \frac{\mu \omega_y}{\hbar}$$

Slide 65

Energies and Degeneracy

$$E = E_x + E_y = \left(n_x + \frac{1}{2} \right) \hbar \omega_x + \left(n_y + \frac{1}{2} \right) \hbar \omega_y \quad \omega_x = \sqrt{\frac{k_x}{\mu}} \quad \omega_y = \sqrt{\frac{k_y}{\mu}}$$

Depending upon the relative values of k_x and k_y , one may have degenerate energy levels. For example, let's assume that $k_y = 4 \cdot k_x$.

$$\omega_y = 2 \omega_x$$

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

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

11/2	4 0	0 2	2 1	g = 3
9/2	3 0	1 1		g = 2
7/2	2 0	0 1		g = 2
5/2	1 0			g = 1
3/2	0 0			g = 1

Slide 66

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Slide 67

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: $x_{i\alpha}$. $\alpha = x, y$ or z .

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

$$H = \sum_{i\alpha} -\frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial x_{i\alpha}^2} + \frac{1}{2} \sum_{i\alpha} \sum_{j\beta} F_{i\alpha,j\beta} (x_{i\alpha} - x_{i\alpha}^{eq})(x_{j\beta} - x_{j\beta}^{eq})$$

$$F_{i\alpha,j\beta} = \left(\frac{\partial^2 V}{\partial x_{i\alpha} \partial x_{j\beta}} \right)_{x_{i\alpha}^{eq}, x_{j\beta}^{eq}}$$

Slide 68

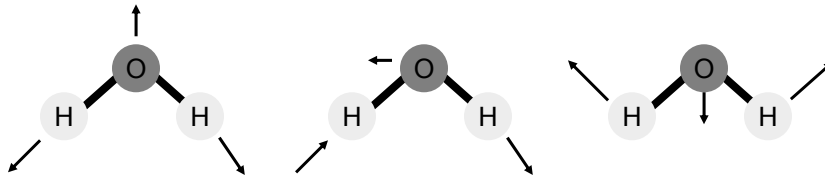
After some rather messy algebra, one can transform the Cartesian coordinates to a set of “mass weighted” **Normal Coordinates**.

$$Q_k = \sum_{i\alpha} \sqrt{m_i} L_{i\alpha,k} (x_{i\alpha} - x_{i\alpha}^{eq})$$

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.



Slide 69

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

$$H = \sum_{k=1}^{3N-6} \left[-\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_k^2} + \frac{1}{2} \omega_k^2 Q_k^2 \right]$$

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

Note that the Hamiltonian is of the form:

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

Therefore, one can assume:

$$\psi = \prod_{i=1}^{3N-6} \psi_i(Q_i) = \psi_1(Q_1) \cdot \psi_2(Q_2) \cdot \psi_3(Q_3) \cdot \dots$$

and simplify the Schrödinger equation by separation of variables.

Slide 70

One gets $3N-6$ equations of the form: $-\frac{\hbar^2}{2} \frac{\partial^2 \psi_i}{\partial Q_1^2} + \frac{1}{2} \omega_1^2 Q_1^2 \psi_i = E_i \psi_i$

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:

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

Or, equivalently: $E(n_1 n_2 n_3 \dots) = \sum_{i=1}^{3N-6} \left(n_i + \frac{1}{2} \right) \hbar \nu_i$

Slide 71

In spectroscopy, we commonly refer to the “energy in wavenumbers”, which is actually E/hc :

$$\frac{E(n_1 n_2 n_3 \dots)}{hc} = \sum_{i=1}^{3N-6} \left(n_i + \frac{1}{2} \right) \tilde{\nu}_i$$

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

$$\begin{aligned} \frac{E(112)}{hc} &= \left(1 + \frac{1}{2} \right) \tilde{\nu}_1 + \left(1 + \frac{1}{2} \right) \tilde{\nu}_2 + \left(2 + \frac{1}{2} \right) \tilde{\nu}_3 \\ &= \frac{3}{2} (3833 \text{ cm}^{-1}) + \frac{3}{2} (1649 \text{ cm}^{-1}) + \frac{5}{2} (3943 \text{ cm}^{-1}) \\ &= 18,081 \text{ cm}^{-1} \end{aligned}$$

Slide 72

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. $E(112)/hc - E(100)/hc$?

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

$$\begin{aligned} \frac{E(100)}{hc} &= \left(1 + \frac{1}{2}\right)\tilde{\nu}_1 + \left(0 + \frac{1}{2}\right)\tilde{\nu}_2 + \left(0 + \frac{1}{2}\right)\tilde{\nu}_3 \\ &= \frac{3}{2}(3833 \text{ cm}^{-1}) + \frac{1}{2}(1649 \text{ cm}^{-1}) + \frac{1}{2}(3943 \text{ cm}^{-1}) = 8,546 \text{ cm}^{-1} \end{aligned}$$

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

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 $n_3=0 \rightarrow n_3=2$.

Slide 73

Chapter 5

Molecular Vibrations and Time-Independent Perturbation Theory

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

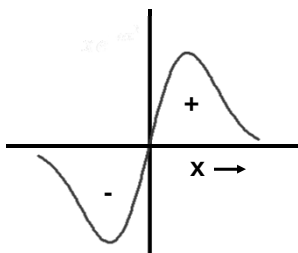
Slide 1

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
- Time Independent Perturbation Theory
- QM Calculations of Vibrational Frequencies and Dissoc. Energies
- Statistical Thermodynamics: Vibrational Contributions to
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- The Vibrational Partition Function
- Internal Energy: ZPE and Thermal Contributions
- Applications to $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$

Slide 2

Symmetry and Vibrational Selection Rules



$$\int_{-\infty}^{\infty} x e^{-ax^2} dx = ??$$

$$\int_{-\infty}^{\infty} x e^{-ax^2} dx = 0$$

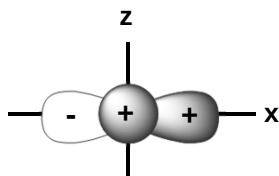
By symmetry: $f(-x) = -f(x)$

Slide 3

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.

Slide 4

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

$$\int f d\tau = 0 \quad \text{unless} \quad \Gamma(f) = A_1$$

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

$$\int f d\tau = \int \varphi_a \varphi_b d\tau \quad \Gamma(\varphi_a \varphi_b) = ?$$

Slide 5

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.

Slide 6

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
A_1	1	1	1	1	
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	
B_2	1	-1	-1	1	
$B_1 \times B_2$	1	1	-1	-1	A_2
$A_2 \times B_1$	1	-1	-1	1	B_2
$A_2 \times B_2$	1	-1	1	-1	B_1
$A_2 \times A_2$	1	1	1	1	A_1
$B_1 \times B_1$	1	1	1	1	A_1

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)

Slide 7

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 Γ_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 $\Gamma_a = \Gamma_b$

Slide 8

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

Slide 9

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

$$\Gamma_f = \Gamma_a \times \Gamma_b$$

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.

Slide 10

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 Γ_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 $\Gamma_a = \Gamma_b$

Slide 11

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

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Slide 12

Spectroscopic Selection Rules

When light (of frequency ω) 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.

$$H = H^{(0)} + H^{(1)} = H^{(0)} - \vec{\mu} \cdot \vec{E} = H^{(0)} - \mu E \cos(\omega t)$$

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} .

Slide 13

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

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: $\hat{\mu} = e\vec{r} = e(x\vec{i} + y\vec{j} + z\vec{k})$

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

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

$$M_{0i} = M_{0i}^x \vec{i} + M_{0i}^y \vec{j} + M_{0i}^z \vec{k}$$

$$\begin{aligned} M_{0i}^x &= e \langle \Psi_{\text{fin}} | x | \Psi_{\text{init}} \rangle \\ M_{0i}^y &= e \langle \Psi_{\text{fin}} | y | \Psi_{\text{init}} \rangle \\ M_{0i}^z &= e \langle \Psi_{\text{fin}} | z | \Psi_{\text{init}} \rangle \end{aligned}$$

Thus, the transition moment has x, y and z components.

Slide 14

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

$$M_{0i} = M_{0i}^x \vec{i} + M_{0i}^y \vec{j} + M_{0i}^z \vec{k}$$

$$M_{0i}^x = e \langle \Psi_{fvi} | x | \Psi_{init} \rangle$$

$$M_{0i}^y = e \langle \Psi_{fvi} | y | \Psi_{init} \rangle$$

$$M_{0i}^z = e \langle \Psi_{fvi} | z | \Psi_{init} \rangle$$

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, A_{1g}...

Slide 15

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:

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

$$M_{0i} = M_{0i}^x \vec{i} + M_{0i}^y \vec{j} + M_{0i}^z \vec{k}$$

$$M_{0i}^x = e \langle \Psi_{fvi} | x | \Psi_{init} \rangle$$

$$M_{0i}^y = e \langle \Psi_{fvi} | y | \Psi_{init} \rangle$$

$$M_{0i}^z = e \langle \Psi_{fvi} | z | \Psi_{init} \rangle$$

Ψ_{init} and Ψ_{fin} represent vibrational wavefunctions of the initial state (often the ground vibrational state, n=0) and final state (often corresponding to n=1).

Slide 16

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

$$M_{0i} = M_{0i}^x \vec{i} + M_{0i}^y \vec{j} + M_{0i}^z \vec{k} \quad \begin{aligned} M_{0i}^x &= e \langle \Psi_{fin} | x | \Psi_{init} \rangle \\ M_{0i}^y &= e \langle \Psi_{fin} | y | \Psi_{init} \rangle \\ M_{0i}^z &= e \langle \Psi_{fin} | z | \Psi_{init} \rangle \end{aligned}$$

A vibration will be Infrared active if any of the three components of the transition moment are non-zero; i.e. if

$$\Gamma(\Psi_{fin}) \times \Gamma(x) \times \Gamma(\Psi_{init}) = A_1 (A, A_g, \dots)$$

$$\text{or } \Gamma(\Psi_{fin}) \times \Gamma(y) \times \Gamma(\Psi_{init}) = A_1 (A, A_g, \dots)$$

$$\text{or } \Gamma(\Psi_{fin}) \times \Gamma(z) \times \Gamma(\Psi_{init}) = A_1 (A, A_g, \dots)$$

Slide 17

Raman Scattering Spectra

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

Strictly speaking, α is a tensor (Yecch!!)

$$\begin{pmatrix} \mu_x^{ind} \\ \mu_y^{ind} \\ \mu_z^{ind} \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{xy} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{xz} & \alpha_{yz} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

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

There are 6 independent components of α : α_{xx} , α_{yy} , α_{zz} , α_{xy} , α_{xz} , α_{yz}

Slide 18

$$\begin{pmatrix} \mu_x^{ind} \\ \mu_y^{ind} \\ \mu_z^{ind} \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{xy} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{xz} & \alpha_{yz} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

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

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

α_{uv} has the same symmetry properties as the product uv ;

i.e. α_{xx} belongs to the same representation as xx ,

α_{yz} belongs to the same representation as yz , etc.

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

$$\Gamma(\Psi_{fin}) \times \Gamma(uv) \times \Gamma(\Psi_{init}) = A_1(A, A_g, \dots)$$

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

Slide 19

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

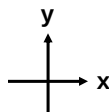
- Symmetry and Vibrational Selection Rules
- Spectroscopic Selection Rules
- **The Symmetry of Vibrational Normal Modes:
Application to the Stretching Vibrations in Ethylene**
- Time Independent Perturbation Theory
- QM Calculations of Vibrational Frequencies and Dissoc. Energies
- Statistical Thermodynamics: Vibrational Contributions to the Thermodynamic Properties of Gases
- The Vibrational Partition Function
- Internal Energy: ZPE and Thermal Contributions
- Applications to $O_2(g)$ and $H_2O(g)$

Slide 20

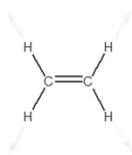
The Symmetry of Vibrational Normal Modes

We will concentrate on the four C-H stretching vibrations in ethylene, C_2H_4 .

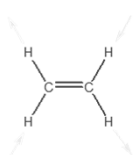
Ethylene has D_{2h} symmetry. However, because all 4 C-H stretches are in the plane of the molecule, it is OK to use the subgroup, C_{2h} .



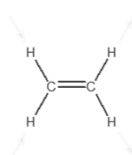
C _{2h}	E	C ₂	i	σ _h	
A _g	1	1	1	1	x ² ,y ² ,z ² ,xy
B _g	1	-1	1	-1	xz,yz
A _u	1	1	-1	-1	z
B _u	1	-1	-1	1	x,y
ν ₁	1	1	1	1	a _g
ν ₂	1	1	1	1	a _g
ν ₃	1	-1	-1	1	b _u
ν ₄	1	-1	-1	1	b _u



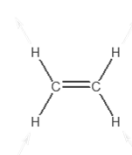
ν_1
(3030 cm^{-1})
 a_g



ν_2
(3100 cm^{-1})
 a_g



ν_3
(3110 cm^{-1})
 b_u



ν_4
(2990 cm^{-1})
 b_u

Slide 21

Symmetry of Vibrational Wavefunctions

One Dimensional Harmonic Oscillator

$$n = 0 \quad \psi_0 = N_0 e^{-\alpha x^2/2}$$

$$n = 1 \quad \psi_1 = N_1 (2\sqrt{\alpha} x) e^{-\alpha x^2/2}$$

$$n = 2 \quad \psi_2 = N_2 (4\alpha x^2 - 2) e^{-\alpha x^2/2}$$

Harmonic Oscillator Normal Mode: ν_k

Normal Coordinate: Q_k

$$n = 0 \quad \psi_0^{\nu_k} = N_0 e^{-\alpha_k Q_k^2/2} \quad \Gamma(\psi_0^{\nu_k}) = A_g \text{ (tot. symm. rep.)}$$

$$n = 1 \quad \psi_1^{\nu_k} = N_1 (2\sqrt{\alpha_k} Q_k) e^{-\alpha_k Q_k^2/2} \quad \Gamma(\psi_1^{\nu_k}) = \Gamma(Q_k)$$

$$n = 2 \quad \psi_2^{\nu_k} = N_2 (4\alpha_k Q_k^2 - 2) e^{-\alpha_k Q_k^2/2} \quad \Gamma(\psi_2^{\nu_k}) = A_g \text{ (tot. symm. rep.)}$$

Slide 22

Total Vibrational Wavefunction of Polyatomic Molecules

$$\Psi_{n_1, n_2, n_3, \dots}^{vib} = |n_1, n_2, n_3, \dots\rangle = \psi_{n_1}^{v_1} \cdot \psi_{n_2}^{v_2} \cdot \psi_{n_3}^{v_3} \cdot \dots$$

$$\Gamma(\Psi_{n_1, n_2, n_3, \dots}^{vib}) = \Gamma(\psi_{n_1}^{v_1}) \times \Gamma(\psi_{n_2}^{v_2}) \times \Gamma(\psi_{n_3}^{v_3}) \times \dots$$

Ground

State: $\Psi_{0,0,0,\dots}^{vib} = |0,0,0,\dots\rangle = \psi_0^{v_1} \cdot \psi_0^{v_2} \cdot \psi_0^{v_3} \cdot \dots$

$$\Gamma(\Psi_{0,0,0,\dots}^{vib}) = \Gamma(\psi_0^{v_1}) \times \Gamma(\psi_0^{v_2}) \times \Gamma(\psi_0^{v_3}) \times \dots$$

$$= a_g \times a_g \times a_g \times \dots = A_g$$

Singly

Excited State: $\Psi_{0,1,0,\dots}^{vib} = |0,1,0,\dots\rangle = \psi_0^{v_1} \cdot \psi_1^{v_2} \cdot \psi_0^{v_3} \cdot \dots$

$$\Gamma(\Psi_{0,1,0,\dots}^{vib}) = \Gamma(\psi_0^{v_1}) \times \Gamma(\psi_1^{v_2}) \times \Gamma(\psi_0^{v_3}) \times \dots$$

$$= a_g \times \Gamma(\psi_1^{v_2}) \times a_g \times \dots = \Gamma(\psi_1^{v_2})$$

Slide 23

C-H Stretching Vibrations of Ethylene

IR Activity of Fundamental Modes

$A_g: |0,0,0,0\rangle \rightarrow |1,0,0,0\rangle$

$$\Gamma(\Psi_{1,0,0,0}^{vib}) = \Gamma(\psi_1^{v_1}) \times \Gamma(\psi_0^{v_2}) \times \Gamma(\psi_0^{v_3}) \times \Gamma(\psi_0^{v_4}) = A_g$$

$$\Gamma(\Psi_{0,0,0,0}^{vib}) = \Gamma(\psi_0^{v_1}) \times \Gamma(\psi_0^{v_2}) \times \Gamma(\psi_0^{v_3}) \times \Gamma(\psi_0^{v_4}) = A_g$$

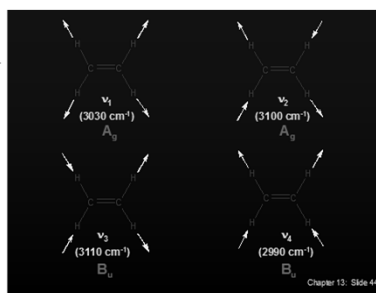
$$M_{0i}^x = e \langle \Psi_{1,0,0,0}^{vib} | x | \Psi_{0,0,0,0}^{vib} \rangle \quad \Gamma = A_g \times B_u \times A_g = B_u$$

$$M_{0i}^y = e \langle \Psi_{1,0,0,0}^{vib} | y | \Psi_{0,0,0,0}^{vib} \rangle \quad \Gamma = A_g \times B_u \times A_g = B_u$$

$$M_{0i}^z = e \langle \Psi_{1,0,0,0}^{vib} | z | \Psi_{0,0,0,0}^{vib} \rangle \quad \Gamma = A_g \times A_u \times A_g = A_u$$

A_g vibrations are IR Inactive

	C_{2h}	E	C_2	i	σ_h
A_g	1	1	1	1	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	xz, yz
A_u	1	1	-1	-1	z
B_u	1	-1	-1	1	x, y



Chapter 13: Slide 44

Slide 24

IR Activity of Fundamental Modes

$$B_u: |0,0,0,0\rangle \rightarrow |0,0,1,0\rangle$$

$$\Gamma(\Psi_{0,0,1,0}^{vib}) = \Gamma(\psi_0^{v_1}) \times \Gamma(\psi_0^{v_2}) \times \Gamma(\psi_1^{v_3}) \times \Gamma(\psi_0^{v_4}) = B_u$$

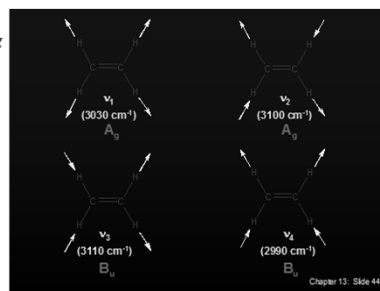
$$\Gamma(\Psi_{0,0,0,0}^{vib}) = \Gamma(\psi_0^{v_1}) \times \Gamma(\psi_0^{v_2}) \times \Gamma(\psi_0^{v_3}) \times \Gamma(\psi_0^{v_4}) = A_g$$

$$M_{0i}^x = e \langle \Psi_{0,0,1,0}^{vib} | x | \Psi_{0,0,0,0}^{vib} \rangle \quad \Gamma = B_u \times B_u \times A_g = A_g$$

$$M_{0i}^y = e \langle \Psi_{0,0,1,0}^{vib} | y | \Psi_{0,0,0,0}^{vib} \rangle \quad \Gamma = B_u \times B_u \times A_g = A_g$$

$$M_{0i}^z = e \langle \Psi_{0,0,1,0}^{vib} | z | \Psi_{0,0,0,0}^{vib} \rangle \quad \Gamma = B_u \times A_u \times A_g = B_g$$

C_{2h}	E	C_2	i	σ_h	
A_g	1	1	1	1	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	xz, yz
A_u	1	1	-1	-1	z
B_u	1	-1	-1	1	x, y



B_u vibrations are IR **Active** and polarized perpendicular to the axis.

Slide 25

Raman Activity of Fundamental Modes

$$A_g: |0,0,0,0\rangle \rightarrow |1,0,0,0\rangle$$

$$\Gamma(\Psi_{1,0,0,0}^{vib}) = \Gamma(\psi_1^{v_1}) \times \Gamma(\psi_0^{v_2}) \times \Gamma(\psi_0^{v_3}) \times \Gamma(\psi_0^{v_4}) = A_g$$

$$\Gamma(\Psi_{0,0,0,0}^{vib}) = \Gamma(\psi_0^{v_1}) \times \Gamma(\psi_0^{v_2}) \times \Gamma(\psi_0^{v_3}) \times \Gamma(\psi_0^{v_4}) = A_g$$

$$\langle \Psi_i | \alpha_{uv} | \Psi_0 \rangle \quad u = x, y, z \text{ and } v = x, y, z \quad \Gamma = \Gamma(\Psi_i) \times \Gamma(uv) \times \Gamma(\Psi_0)$$

$$\langle \Psi_{1,0,0,0}^{vib} | x^2 | \Psi_{0,0,0,0}^{vib} \rangle \quad \Gamma = A_g \times A_g \times A_g = A_g \quad \langle \Psi_{1,0,0,0}^{vib} | xz | \Psi_{0,0,0,0}^{vib} \rangle \quad \Gamma = A_g \times B_g \times A_g = B_g$$

$$\langle \Psi_{1,0,0,0}^{vib} | y^2 | \Psi_{0,0,0,0}^{vib} \rangle \quad \langle \Psi_{1,0,0,0}^{vib} | yz | \Psi_{0,0,0,0}^{vib} \rangle$$

$$\langle \Psi_{1,0,0,0}^{vib} | z^2 | \Psi_{0,0,0,0}^{vib} \rangle$$

$$\langle \Psi_{1,0,0,0}^{vib} | xy | \Psi_{0,0,0,0}^{vib} \rangle$$

A_g vibrations are Raman **Active**

Slide 26

Raman Activity of Fundamental Modes

	C_{2h}	E	C_2	i	σ_h	
B_u	1	1	1	1	1	x^2, y^2, z^2, xy
A_g	1	-1	1	-1	-1	xz, yz
A_u	1	1	-1	-1	-1	z
B_u	1	-1	-1	1	1	x, y

$$\Gamma(\Psi_{0,0,1,0}^{vib}) = \Gamma(\psi_0^{v_1}) \times \Gamma(\psi_0^{v_2}) \times \Gamma(\psi_1^{v_3}) \times \Gamma(\psi_0^{v_4}) = B_u$$

$$\Gamma(\Psi_{0,0,0,0}^{vib}) = \Gamma(\psi_0^{v_1}) \times \Gamma(\psi_0^{v_2}) \times \Gamma(\psi_0^{v_3}) \times \Gamma(\psi_0^{v_4}) = A_g$$

$$\langle \Psi_i | \alpha_{uv} | \Psi_0 \rangle \quad u = x, y, z \text{ and } v = x, y, z \quad \Gamma = \Gamma(\Psi_i) \times \Gamma(uv) \times \Gamma(\Psi_0)$$

$$\langle \Psi_{0,0,1,0}^{vib} | x^2 | \Psi_{0,0,0,0}^{vib} \rangle \quad \Gamma = B_u \times A_g \times A_g = B_u \quad \langle \Psi_{0,0,1,0}^{vib} | xz | \Psi_{0,0,0,0}^{vib} \rangle \quad \Gamma = B_u \times B_g \times A_g = A_u$$

$$\langle \Psi_{0,0,1,0}^{vib} | y^2 | \Psi_{0,0,0,0}^{vib} \rangle \quad \langle \Psi_{0,0,1,0}^{vib} | yz | \Psi_{0,0,0,0}^{vib} \rangle$$

$$\langle \Psi_{0,0,1,0}^{vib} | z^2 | \Psi_{0,0,0,0}^{vib} \rangle$$

$$\langle \Psi_{0,0,1,0}^{vib} | x^2 | \Psi_{0,0,0,0}^{vib} \rangle$$

B_u vibrations are Raman **Inactive**

Slide 27

The Shortcut

	C_{2h}	E	C_2	i	σ_h	
A_g	1	1	1	1	1	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	-1	xz, yz
A_u	1	1	-1	-1	-1	z
B_u	1	-1	-1	1	1	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?

Slide 28

IR Activity of Combination Modes

$$|0,0,0,0\rangle \rightarrow |0,1,0,1\rangle \quad \nu_2 + \nu_4$$

$$\Gamma(\Psi_{0,1,0,1}^{vib}) = \Gamma(\psi_0^{\nu_1}) \times \Gamma(\psi_1^{\nu_2}) \times \Gamma(\psi_0^{\nu_3}) \times \Gamma(\psi_1^{\nu_4})$$

$$= a_g \times a_g \times a_g \times b_u = B_u$$

$$\Gamma(\Psi_{0,0,0,0}^{vib}) = \Gamma(\psi_0^{\nu_1}) \times \Gamma(\psi_0^{\nu_2}) \times \Gamma(\psi_0^{\nu_3}) \times \Gamma(\psi_0^{\nu_4}) = A_g$$

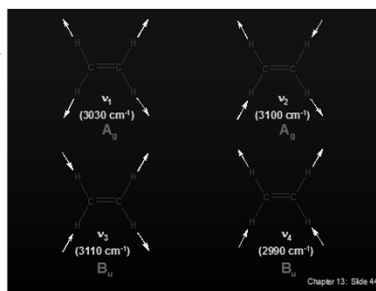
$$M_{0i}^x = e \langle \Psi_{0,1,0,1}^{vib} | x | \Psi_{0,0,0,0}^{vib} \rangle \quad \Gamma = B_u \times B_u \times A_g = A_g$$

$$M_{0i}^y = e \langle \Psi_{0,1,0,1}^{vib} | y | \Psi_{0,0,0,0}^{vib} \rangle \quad \Gamma = B_u \times B_u \times A_g = A_g$$

$$M_{0i}^z = e \langle \Psi_{0,1,0,1}^{vib} | z | \Psi_{0,0,0,0}^{vib} \rangle \quad \Gamma = B_u \times A_u \times A_g = B_g$$

$\nu_2 + \nu_4$ is IR **Active** and polarized perpendicular to the axis.

C_{2h}	E	C_2	i	σ_h	
A_g	1	1	1	1	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	xz, yz
A_u	1	1	-1	-1	z
B_u	1	-1	-1	1	x, y



Chapter 13: Slide 44

Slide 29

IR Activity of Combination Modes

$$|0,0,0,1\rangle \rightarrow |0,0,1,0\rangle \quad \nu_3 - \nu_4$$

$$\Gamma(\Psi_{0,0,1,0}^{vib}) = \Gamma(\psi_0^{\nu_1}) \times \Gamma(\psi_0^{\nu_2}) \times \Gamma(\psi_1^{\nu_3}) \times \Gamma(\psi_0^{\nu_4})$$

$$= a_g \times a_g \times b_u \times a_g = B_u$$

$$\Gamma(\Psi_{0,0,0,1}^{vib}) = \Gamma(\psi_0^{\nu_1}) \times \Gamma(\psi_0^{\nu_2}) \times \Gamma(\psi_0^{\nu_3}) \times \Gamma(\psi_1^{\nu_4})$$

$$= a_g \times a_g \times a_g \times b_u = B_u$$

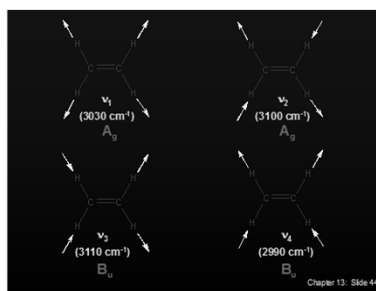
$$M_{0i}^x = e \langle \Psi_{0,0,1,0}^{vib} | x | \Psi_{0,0,0,1}^{vib} \rangle \quad \Gamma = B_u \times B_u \times B_u = B_u$$

$$M_{0i}^y = e \langle \Psi_{0,0,1,0}^{vib} | y | \Psi_{0,0,0,1}^{vib} \rangle \quad \Gamma = B_u \times B_u \times B_u = B_u$$

$$M_{0i}^z = e \langle \Psi_{0,0,1,0}^{vib} | z | \Psi_{0,0,0,1}^{vib} \rangle \quad \Gamma = B_u \times A_u \times B_u = A_u$$

$\nu_3 - \nu_4$ is IR **Inactive**.

C_{2h}	E	C_2	i	σ_h	
A_g	1	1	1	1	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	xz, yz
A_u	1	1	-1	-1	z
B_u	1	-1	-1	1	x, y



Chapter 13: Slide 44

Slide 30

Raman Activity of Combination Modes

$$|0,0,0,0\rangle \rightarrow |0,1,0,1\rangle \quad \nu_2 + \nu_4$$

$$\Gamma(\Psi_{0,1,0,1}^{vib}) = \Gamma(\psi_0^{\nu_1}) \times \Gamma(\psi_1^{\nu_2}) \times \Gamma(\psi_0^{\nu_3}) \times \Gamma(\psi_1^{\nu_4})$$

$$= a_g \times a_g \times a_g \times b_u = B_u$$

$$\Gamma(\Psi_{0,0,0,0}^{vib}) = \Gamma(\psi_0^{\nu_1}) \times \Gamma(\psi_0^{\nu_2}) \times \Gamma(\psi_0^{\nu_3}) \times \Gamma(\psi_0^{\nu_4}) = A_g$$

$$\langle \Psi_i | \alpha_{uv} | \Psi_0 \rangle \quad u = x, y, z \text{ and } v = x, y, z \quad \Gamma = \Gamma(\Psi_i) \times \Gamma(uv) \times \Gamma(\Psi_0)$$

$$\langle \Psi_{0,1,0,1}^{vib} | x^2 | \Psi_{0,0,0,0}^{vib} \rangle \quad \Gamma = B_u \times A_g \times A_g = B_u \quad \langle \Psi_{0,1,0,1}^{vib} | xz | \Psi_{0,0,0,0}^{vib} \rangle \quad \Gamma = B_u \times B_g \times A_g = A_u$$

$$\langle \Psi_{0,1,0,1}^{vib} | y^2 | \Psi_{0,0,0,0}^{vib} \rangle \quad \langle \Psi_{0,1,0,1}^{vib} | yz | \Psi_{0,0,0,0}^{vib} \rangle$$

$$\langle \Psi_{0,1,0,1}^{vib} | z^2 | \Psi_{0,0,0,0}^{vib} \rangle$$

$$\langle \Psi_{0,1,0,1}^{vib} | xy | \Psi_{0,0,0,0}^{vib} \rangle$$

$\nu_2 + \nu_4$ is Raman **Inactive**.

Slide 31

Raman Activity of Combination Modes

$$|0,0,0,1\rangle \rightarrow |0,0,1,0\rangle \quad \nu_3 - \nu_4$$

$$\Gamma(\Psi_{0,0,1,0}^{vib}) = \Gamma(\psi_0^{\nu_1}) \times \Gamma(\psi_0^{\nu_2}) \times \Gamma(\psi_1^{\nu_3}) \times \Gamma(\psi_0^{\nu_4})$$

$$= a_g \times a_g \times b_u \times a_g = B_u$$

$$\Gamma(\Psi_{0,0,0,1}^{vib}) = \Gamma(\psi_0^{\nu_1}) \times \Gamma(\psi_0^{\nu_2}) \times \Gamma(\psi_0^{\nu_3}) \times \Gamma(\psi_1^{\nu_4})$$

$$= a_g \times a_g \times a_g \times b_u = B_u$$

$$\langle \Psi_i | \alpha_{uv} | \Psi_0 \rangle \quad u = x, y, z \text{ and } v = x, y, z \quad \Gamma = \Gamma(\Psi_i) \times \Gamma(uv) \times \Gamma(\Psi_0)$$

$$\langle \Psi_{0,0,1,0}^{vib} | x^2 | \Psi_{0,0,0,1}^{vib} \rangle \quad \Gamma = B_u \times A_g \times B_u = A_g \quad \langle \Psi_{0,0,1,0}^{vib} | xz | \Psi_{0,0,0,1}^{vib} \rangle \quad \Gamma = B_u \times B_g \times B_u = B_g$$

$$\langle \Psi_{0,0,1,0}^{vib} | y^2 | \Psi_{0,0,0,1}^{vib} \rangle \quad \langle \Psi_{0,0,1,0}^{vib} | yz | \Psi_{0,0,0,1}^{vib} \rangle$$

$$\langle \Psi_{0,0,1,0}^{vib} | z^2 | \Psi_{0,0,0,1}^{vib} \rangle$$

$$\langle \Psi_{0,0,1,0}^{vib} | xy | \Psi_{0,0,0,1}^{vib} \rangle$$

$\nu_3 - \nu_4$ is Raman **Active**.

Slide 32

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Slide 33

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:

$$H = \underbrace{-\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2}_{H^{(0)} \text{ Exactly Solvable}} + \underbrace{\gamma x^3 + \delta x^4 + \dots}_{H^{(1)} \text{ Correction Term}}$$

Slide 34

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

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.

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \dots + E^{(n)}$$

$$\psi = \psi^{(0)} + \psi^{(1)} + \psi^{(2)} + \dots + \psi^{(n)}$$

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

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

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

Slide 35

First Order Perturbation Theory

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

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

$$H\psi = E\psi$$

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

$$\begin{aligned} H^{(0)}\psi^{(0)} + H^{(1)}\psi^{(0)} + H^{(0)}\Delta\psi + H^{(1)}\Delta\psi \\ = E^{(0)}\psi^{(0)} + \Delta E\psi^{(0)} + E^{(0)}\Delta\psi + \Delta E\Delta\psi \end{aligned}$$

$$\cancel{H^{(0)}\psi^{(0)}} + H^{(1)}\psi^{(0)} + H^{(0)}\Delta\psi + \cancel{H^{(1)}\Delta\psi} = \cancel{E^{(0)}\psi^{(0)}} + \Delta E\psi^{(0)} + E^{(0)}\Delta\psi + \cancel{\Delta E\Delta\psi}$$

One can eliminate the two terms involving the product of two small corrections.

One can eliminate two additional terms because: $H^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)}$

Slide 36

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

Multiply all terms by $\psi^{(0)*}$ and integrate:

$$\int \psi^{(0)*} H^{(1)} \psi^{(0)} d\tau + \int \psi^{(0)*} H^{(0)} \Delta\psi d\tau = \int \psi^{(0)*} \Delta E \psi^{(0)} d\tau + \int \psi^{(0)*} E^{(0)} \Delta\psi d\tau$$

$H^{(0)}$ is Hermitian. Therefore:

$$\int \psi^{(0)*} H^{(0)} \Delta\psi d\tau = \int \Delta\psi (H^{(0)} \psi^{(0)})^* d\tau = \int \Delta\psi (E^{(0)} \psi^{(0)})^* d\tau = E^{(0)} \int \psi^{(0)*} \Delta\psi d\tau$$

Plug in to get:

$$\int \psi^{(0)*} H^{(1)} \psi^{(0)} d\tau + \cancel{E^{(0)} \int \psi^{(0)*} \Delta\psi d\tau} = \int \psi^{(0)*} \Delta E \psi^{(0)} d\tau + \cancel{\int \psi^{(0)*} E^{(0)} \Delta\psi d\tau}$$

$$\text{Therefore: } \int \psi^{(0)*} H^{(1)} \psi^{(0)} d\tau = \Delta E \int \psi^{(0)*} \psi^{(0)} d\tau = \Delta E$$

$$\boxed{\Delta E = \int \psi^{(0)*} H^{(1)} \psi^{(0)} d\tau} \text{ is the first order perturbation theory correction to the energy.}$$

Slide 37

Applications of First Order Perturbation Theory

PIB with slanted floor

Consider a particle in a box with the potential:

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

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

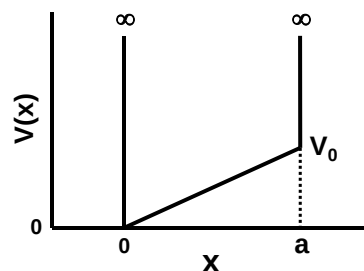
For this problem:

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

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

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

$$\text{The perturbing potential is: } H^{(1)} = \frac{V_0}{a}x$$



Slide 38

Integral Info

$$\int x \sin^2(\alpha x) dx = \frac{x^2}{4} - \frac{x \sin(2\alpha x)}{4\alpha} - \frac{\cos(2\alpha x)}{8\alpha^2}$$

$$\begin{aligned} \sin(2\alpha a) &= \sin\left(2\frac{n\pi}{a}a\right) = 0 \\ \cos(2\alpha a) &= \cos\left(2\frac{n\pi}{a}a\right) = 1 \end{aligned}$$

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.

$$\begin{aligned} \Delta E &= \int \psi^{(0)*} H^{(1)} \psi^{(0)} d\tau = \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \cdot \left(\frac{V_0}{a} x\right) \cdot \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) dx \\ &= \frac{2}{a} \frac{V_0}{a} \int_0^a x \cdot \sin^2\left(\frac{n\pi x}{a}\right) dx = \frac{2V_0}{a^2} \int_0^a x \cdot \sin^2(\alpha x) dx \quad \alpha = \frac{n\pi}{a} \\ &= \frac{2V_0}{a^2} \left[\left(\frac{a^2}{4} - \frac{a \sin(2\alpha a)}{4\alpha} - \frac{\cos(2\alpha a)}{8\alpha^2} \right) - \left(0 - 0 - \frac{\cos(0)}{8\alpha^2} \right) \right] \\ &= \frac{2V_0}{a^2} \left[\left(\frac{a^2}{4} - \frac{1}{8\alpha^2} \right) - \left(-\frac{1}{8\alpha^2} \right) \right] \longrightarrow \boxed{\Delta E = \frac{V_0}{2}} \quad \text{Independent of } n \end{aligned}$$

Slide 39

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:

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

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

$$\psi_0^{(0)} = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

$$\omega = \sqrt{\frac{k}{\mu}} \quad \alpha = \frac{\sqrt{k\mu}}{\hbar}$$

The perturbing potential is:

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

$$\begin{aligned} \Delta E &= \int \psi_0^{(0)*} H^{(1)} \psi_0^{(0)} d\tau \\ &= \int_{-\infty}^{\infty} \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \cdot (\gamma x^3 + \delta x^4) \cdot \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} dx \\ &= \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} (\gamma x^3 + \delta x^4) e^{-\alpha x^2} dx \end{aligned}$$

Slide 40

$$\begin{aligned}
\Delta E &= \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} (\gamma x^3 + \delta x^4) e^{-\alpha x^2} dx = \gamma \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^3 e^{-\alpha x^2} dx + \delta \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} dx \\
&= 0 + 2\delta \left(\frac{\alpha}{\pi}\right)^{1/2} \int_0^{\infty} x^4 e^{-\alpha x^2} dx = 2\delta \left(\frac{\alpha}{\pi}\right)^{1/2} \left(\frac{3}{8\alpha^2}\right) \left(\frac{\pi}{\alpha}\right)^{1/2} \int_0^{\infty} x^4 e^{-\beta x^2} dx = \frac{3}{8\beta^2} \sqrt{\frac{\pi}{\beta}} \\
\Delta E &= \frac{3\delta}{4\alpha^2} = \frac{3\delta}{4\left(\frac{\sqrt{k\mu}}{\hbar}\right)^2} = \frac{3\hbar^2\delta}{4k\mu}
\end{aligned}$$

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.

Slide 41

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.

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \dots$$

$E_n^{(0)}$ 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 ΔE

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

The second order correction to the energy of the n^{th} level is given by:

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

$$\text{where } \langle \psi_k^{(0)} | H^{(1)} | \psi_n^{(0)} \rangle = \int \psi_k^{(0)*} H^{(1)} \psi_n^{(0)} d\tau$$

Slide 42

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

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

$$E_1^{(2)} = \frac{\left| \langle \psi_2^{(0)} | H^{(1)} | \psi_1^{(0)} \rangle \right|^2}{E_1^{(0)} - E_2^{(0)}} + \frac{\left| \langle \psi_3^{(0)} | H^{(1)} | \psi_1^{(0)} \rangle \right|^2}{E_1^{(0)} - E_3^{(0)}} + \frac{\left| \langle \psi_4^{(0)} | H^{(1)} | \psi_1^{(0)} \rangle \right|^2}{E_1^{(0)} - E_4^{(0)}} + \dots$$

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.

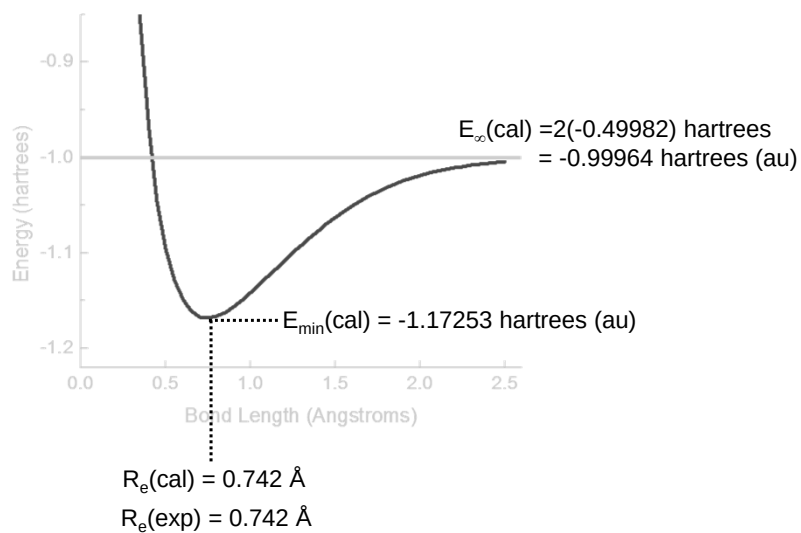
Slide 43

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Slide 44

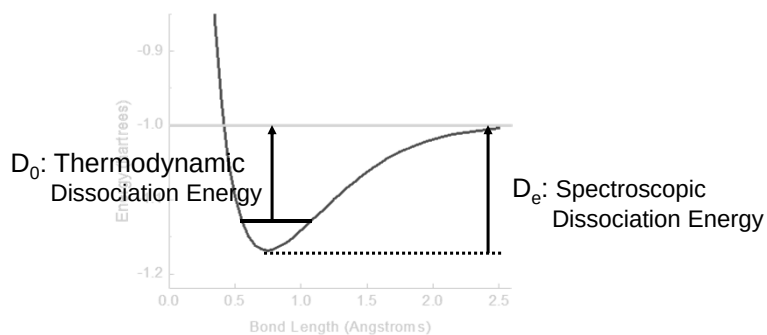
The Potential Energy Curve of H₂



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

Slide 45

The Dissociation Energy



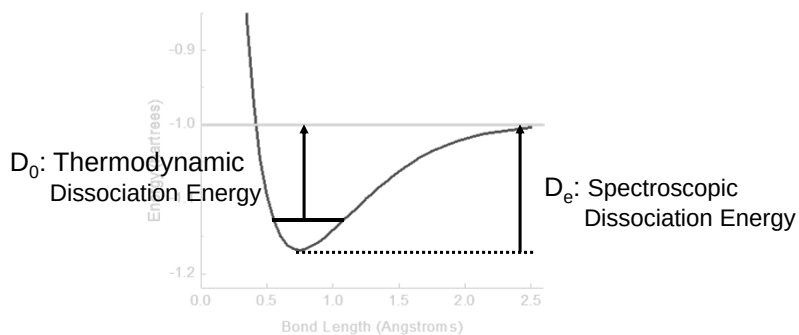
$$D_e(\text{cal}) = E_{\infty}(\text{cal}) - E_{\min}(\text{cal}) = 0.17289 \text{ au} \cdot 2625.5 \text{ kJ/mol / au}$$

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

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

Slide 46

Relating D_e to D_0



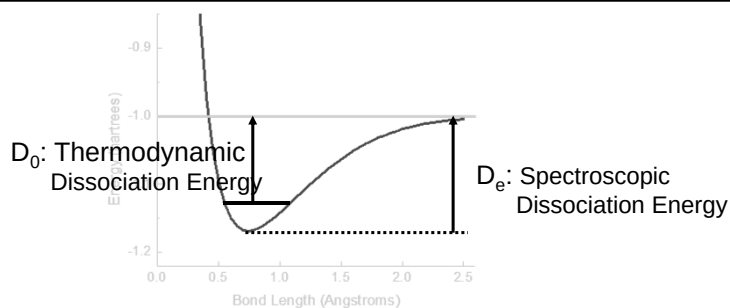
$$D_e = D_0 + E_{vib} = D_0 + (1/2)h\nu$$

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

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

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

Slide 47



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

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

$$E_{vib} = \frac{1}{2}h\nu = \frac{1}{2}hc\tilde{\nu}$$

$$\begin{aligned} D_0(\text{cal}) &= D_e(\text{cal}) - E_{vib} \\ &= 453.9 - 26.4 \\ &= 427.5 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} &= \frac{1}{2} \cdot (6.63 \times 10^{-34} \text{ J} \cdot \text{s}) \cdot (3.00 \times 10^{10} \text{ cm/s}) \cdot (4403 \text{ cm}^{-1}) \\ &= 4.379 \times 10^{-20} \text{ J} \cdot \frac{1 \text{ kJ}}{10^3 \text{ J}} \cdot 6.02 \times 10^{23} \text{ mol}^{-1} \end{aligned}$$

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

$$E_{vib} = 26.4 \text{ kJ/mol}$$

Slide 48

Calculated Versus Experimental Vibrational Frequencies

H ₂ O		
$\nu(\text{Harm})^a$	$\nu(\text{cal})^b$	$\nu(\text{cal})^c$
3943 cm ⁻¹	3956 cm ⁻¹	4188 cm ⁻¹
3833	3845	4070
1649	1640	1827

(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.

Slide 49

Harmonic versus Anharmonic Vibrational Frequencies

H ₂ O			
$\nu(\text{exp})^z$	$\nu(\text{Harm})^a$	$\nu(\text{cal})^b$	$\nu(\text{cal})^c$
3756 cm ⁻¹	3943 cm ⁻¹	3956 cm ⁻¹	4188 cm ⁻¹
3657	3833	3845	4070
1595	1649	1640	1827

(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.

Slide 50

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.

Slide 51

An Example: CHBr_3

$\nu(\text{exp})^a$	$\nu(\text{cal})^b$	$\nu(\text{scaled})^c$
3050 cm^{-1}	3222 cm^{-1}	3061 cm^{-1}
1149 (E)	1208 (E)	1148 (E)
669 (E)	691 (E)	656 (E)
543	546	519
223	228	217
155 (E)	158 (E)	150 (E)

(a) Measured "anharmonic" vibrational frequencies.

(b) Computed at QCISD/6-311G(d,p) level

(c) Computed frequencies scaled by 0.95

Slide 52

Another Example: $\text{CBr}_3\bullet$

$\nu(\text{exp})^{\text{a}}$	$\nu(\text{cal})^{\text{b}}$	$\nu(\text{scaled})^{\text{c}}$
773 (E) cm^{-1}	799 (E) cm^{-1}	759 (E) cm^{-1}
???	324	308
???	235	223
???	164 (E)	156 (E)

(a) Measured "anharmonic" vibrational frequencies.

(b) Computed at QCISD/6-311G(d,p) level

(c) Computed frequencies scaled by 0.95

Slide 53

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.

- (3) Structure determination.

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.

Slide 54

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Slide 55

Statistical Thermodynamics: Vibrational Contributions to Thermodynamic Properties of Gases

Remember these?

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

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N}$$

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

$$C_P = \left(\frac{\partial H}{\partial T} \right)_{P,N}$$

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

$$A = U - TS = -kT \ln Q$$

$$G = H - TS = -kT \ln Q + kT \left(\frac{\partial \ln Q}{\partial \ln V} \right)_{T,N}$$

Slide 56

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Slide 57

The Vibrational Partition Function

$$\text{HO Energy Levels: } E_n = \left(n + \frac{1}{2}\right)h\nu, \quad n = 0, 1, 2, \dots \quad \nu = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

The Partition Function

$$q^{vib} = \sum_{n=0}^{\infty} e^{-\frac{E_n}{kT}} = \sum_{n=0}^{\infty} e^{-\frac{(n+1/2)h\nu}{kT}} = \sum_{n=0}^{\infty} e^{-\frac{n h\nu}{kT}} \cdot e^{-\frac{(1/2)h\nu}{kT}} = e^{-\frac{(1/2)h\nu}{kT}} \cdot \sum_{n=0}^{\infty} e^{-\frac{n h\nu}{kT}}$$

$$q^{vib} = e^{-\frac{\Theta_v}{2T}} \cdot \sum_{n=0}^{\infty} e^{-\frac{n\Theta_v}{T}} \quad \text{where} \quad \Theta_v = \frac{h\nu}{k} = \frac{hc\bar{\nu}}{k}$$

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

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

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

$$\frac{\Theta_v}{T} = \frac{2277 \text{ K}}{298 \text{ K}} = 7.64 \quad \text{Sorry Charlie!! No luck!!}$$

Slide 58

Simplification of q^{vib}

$$q^{vib} = e^{-\frac{\Theta_v}{2T}} \cdot \sum_{n=0}^{\infty} e^{-\frac{n\Theta_v}{T}} \quad \Theta_v = \frac{h\nu}{k} = \frac{hc\bar{\nu}}{k}$$

Let's consider: $\sum_{n=0}^{\infty} e^{-\frac{n\Theta_v}{T}} = \sum_{n=0}^{\infty} x^n$ where $x = e^{-\frac{\Theta_v}{T}}$

We learned earlier in the chapter that any function can be expanded in a Taylor series: $f(x) = \sum_{n=0}^{\infty} \left(\frac{1}{n!} \right) f^{(n)}(0) x^n$

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

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

$$\text{Therefore: } \sum_{n=0}^{\infty} e^{-\frac{n\Theta_v}{T}} = \sum_{n=0}^{\infty} x^n = \frac{1}{1-x} = \frac{1}{1 - e^{-\frac{\Theta_v}{T}}}$$

Slide 59

$$q^{vib} = e^{-\frac{\Theta_v}{2T}} \cdot \sum_{n=0}^{\infty} e^{-\frac{n\Theta_v}{T}} \quad \text{and} \quad \sum_{n=0}^{\infty} e^{-\frac{n\Theta_v}{T}} = \frac{1}{1 - e^{-\frac{\Theta_v}{T}}} \quad \Theta_v = \frac{h\nu}{k} = \frac{hc\bar{\nu}}{k}$$



$$q^{vib} = \frac{e^{-\frac{\Theta_v}{2T}}}{1 - e^{-\frac{\Theta_v}{T}}}$$

For N molecules, the total vibrational partition function, Q^{vib} , is:

$$Q^{vib} = (q^{vib})^N = \left(\frac{e^{-\frac{\Theta_v}{2T}}}{1 - e^{-\frac{\Theta_v}{T}}} \right)^N$$

Slide 60

Some comments on the Vibrational Partition Function

$$Q^{vib} = (q^{vib})^N = \left(\frac{e^{-\frac{\Theta_v}{2T}}}{1 - e^{-\frac{\Theta_v}{T}}} \right)^N \quad \Theta_v = \frac{h\nu}{k} = \frac{hc\bar{\nu}}{k}$$

If we look back at the development leading to q^{vib} and Q^{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^{vib} because all terms above $n=0$ are zero at low temperatures

In some books, the ZPE is not included in q^{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

$$\ln Q^{vib} = N \ln \left(e^{-\frac{\Theta_v}{2T}} \right) - N \ln \left(1 - e^{-\frac{\Theta_v}{T}} \right) = \underbrace{-N \frac{\Theta_v}{2T}}_{\text{ZPE Term}} - \underbrace{N \ln \left(1 - e^{-\frac{\Theta_v}{T}} \right)}_{\text{Thermal Term}}$$

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

Slide 61

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
- Time Independent Perturbation Theory
- QM Calculations of Vibrational Frequencies and Dissoc. Energies
- Statistical Thermodynamics: Vibrational Contributions to the Thermodynamic Properties of Gases
- The Vibrational Partition Function
- **Internal Energy: ZPE and Thermal Contributions**
- Applications to $O_2(g)$ and $H_2O(g)$

Slide 62

Internal Energy

$$U^{vib} = kT^2 \left(\frac{\partial \ln Q^{vib}}{\partial T} \right)_{V,N} \quad \ln Q^{vib} = -N \frac{\Theta_v}{2T} - N \ln \left(1 - e^{-\frac{\Theta_v}{T}} \right)$$

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

ZPE Contribution

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

$$U_{ZPE}^{vib} = \frac{Nk}{2} \frac{hc\bar{\nu}}{k} = n \frac{N_A hc\bar{\nu}}{2}$$

$$\text{or } \bar{U}_{ZPE}^{vib} = \frac{N_A hc\bar{\nu}}{2}$$

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

Slide 63

Thermal Contribution

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

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

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

$$= Nk\Theta_v \frac{e^{-\frac{\Theta_v}{T}}}{1 - e^{-\frac{\Theta_v}{T}}} = nN_A k\Theta_v \frac{e^{-\frac{\Theta_v}{T}}}{1 - e^{-\frac{\Theta_v}{T}}} = nR\Theta_v \frac{e^{-\frac{\Theta_v}{T}}}{1 - e^{-\frac{\Theta_v}{T}}}$$

Slide 64

$$U_{therm}^{vib} = nR\Theta_v \frac{e^{-\frac{\Theta_v}{T}}}{1 - e^{-\frac{\Theta_v}{T}}}$$

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

$$U_{therm}^{vib} = nR\Theta_v \frac{e^{-\frac{\Theta_v}{T}}}{1 - e^{-\frac{\Theta_v}{T}}} \cdot \frac{e^{\frac{\Theta_v}{T}}}{e^{\frac{\Theta_v}{T}}}$$

$$U_{therm}^{vib} = \frac{nR\Theta_v}{e^{\frac{\Theta_v}{T}} - 1}$$

or

$$\bar{U}_{therm}^{vib} = \frac{R\Theta_v}{e^{\frac{\Theta_v}{T}} - 1}$$

Slide 65

Limiting Cases

$$\bar{U}_{therm}^{vib} = \frac{R\Theta_v}{e^{\frac{\Theta_v}{T}} - 1}$$

Low Temperature: $\bar{U}_{therm}^{vib} = R \frac{\Theta_v}{e^{\frac{\Theta_v}{T}} - 1} \rightarrow 0$
($T \rightarrow 0$)

Because the denominator approaches infinity

High Temperature: $\bar{U}_{therm}^{vib} = \frac{R\Theta_v}{1 + \left(\frac{\Theta_v}{T}\right) + \dots - 1} \rightarrow RT$
($\Theta_v \ll T$)

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.

Slide 66

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

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

Slide 67

$$\bar{U}_{ZPE}^{vib} = \frac{N_A h c \bar{\nu}}{2}$$

Numerical Example

$$\bar{U}_{therm}^{vib} = \frac{R\Theta_v}{e^{\frac{\Theta_v}{T}} - 1}$$

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

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

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

**Independent of
Temperature**

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

vs. $RT = 2.48 \text{ kJ/mol}$

Thus, the thermal contribution to the vibrational internal energy of O₂ at room temperature is negligible.

Slide 68

A comparison between O₂ and I₂

$$\text{I}_2: \tilde{\nu} = 214 \text{ cm}^{-1} \rightarrow \Theta_v = 309 \text{ K}$$

T (K)	$\bar{U}_{\text{therm}}^{\text{vib}}$ O ₂ (kJ/mol)	$\bar{U}_{\text{therm}}^{\text{vib}}$ I ₂ (kJ/mol)	RT (kJ/mol)
298	0.009	1.41	2.48
500	0.20	3.00	4.16
1000	2.16	7.10	8.31
2000	8.92	15.4	16.6
3000	16.7	23.7	24.9

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.

Slide 69

Enthalpy

Q^{vib} independent of V

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

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

$$\text{and: } H_{\text{ZPE}}^{\text{vib}} = U_{\text{ZPE}}^{\text{vib}}$$

$$H_{\text{therm}}^{\text{vib}} = U_{\text{therm}}^{\text{vib}}$$

$$\text{Similarly: } C_P^{\text{vib}} = \left(\frac{\partial H^{\text{vib}}}{\partial T} \right)_{P,N} = \left(\frac{\partial U^{\text{vib}}}{\partial T} \right)_{V,N} = C_V^{\text{vib}}$$

Slide 70

$$U_{ZPE}^{vib} = \frac{nN_A h c \bar{\nu}}{2}$$

Heat Capacity (C_V^{vib} and C_P^{vib})

$$U_{therm}^{vib} = \frac{nR\Theta_v}{e^{\frac{\Theta_v}{T}} - 1}$$

Independent of T

$$C_V^{vib} = \left(\frac{\partial U^{vib}}{\partial T} \right)_{V,N} = \cancel{\left(\frac{\partial U_{ZPE}^{vib}}{\partial T} \right)_{V,N}} + \left(\frac{\partial U_{therm}^{vib}}{\partial T} \right)_{V,N}$$

$$\begin{aligned} C_V^{vib} &= \frac{d}{dT} \left[\frac{nR\Theta_v}{e^{\frac{\Theta_v}{T}} - 1} \right] = nR\Theta_v \frac{d}{dT} \left[\left(e^{\frac{\Theta_v}{T}} - 1 \right)^{-1} \right] = nR\Theta_v (-1) \left(e^{\frac{\Theta_v}{T}} - 1 \right)^{-2} \frac{d}{dT} \left[e^{\frac{\Theta_v}{T}} - 1 \right] \\ &= - \frac{nR\Theta_v}{\left(e^{\frac{\Theta_v}{T}} - 1 \right)^2} \cdot e^{\frac{\Theta_v}{T}} \cdot \left(-\frac{\Theta_v}{T^2} \right) = nR \left(\frac{\Theta_v}{T} \right)^2 \frac{e^{\frac{\Theta_v}{T}}}{\left(e^{\frac{\Theta_v}{T}} - 1 \right)^2} \end{aligned}$$

It can be shown that in the limit, $\Theta_v \ll T$, $C_V^{vib} \rightarrow R$

Slide 71

Numerical Example

$$C_V^{vib} = C_P^{vib} = nR \left(\frac{\Theta_v}{T} \right)^2 \frac{e^{\frac{\Theta_v}{T}}}{\left(e^{\frac{\Theta_v}{T}} - 1 \right)^2}$$

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

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

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

$$C_V^{vib} = C_P^{vib} = 8.314 (7.64)^2 \frac{e^{7.64}}{(e^{7.64} - 1)^2} = 0.23 \text{ J/mol} \cdot \text{K}$$

vs. $R = 8.314 \text{ J/mol} \cdot \text{K}$

Slide 72

A comparison between O₂ and I₂

$$\text{I}_2: \tilde{\nu} = 214 \text{ cm}^{-1} \rightarrow \Theta_v = 309 \text{ K}$$

Vibrational Heat Capacities ($C_p^{\text{vib}} = C_v^{\text{vib}}$)

T (K)	O ₂ (J/mol-K)	I ₂ (J/mol-K)
298	0.23	7.61
500	1.85	8.05
1000	5.49	8.25
2000	7.47	8.30
3000	7.93	8.31

Vibrational contribution to heat capacity of I₂ 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.

Slide 73

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

Entropy

$$S^{\text{vib}} = k \ln Q^{\text{vib}} + \frac{U^{\text{vib}}}{T}$$

$$U_{\text{ZPE}}^{\text{vib}} = \frac{Nk\Theta_v}{2} = \frac{nR\Theta_v}{2}$$

$$U_{\text{therm}}^{\text{vib}} = \frac{nR\Theta_v}{e^{\frac{\Theta_v}{T}} - 1}$$

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

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

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

$Nk = nN_A k = nR$

Slide 74

Numerical Example

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

Let's try O₂ ($\tilde{\nu} = 1580 \text{ cm}^{-1}$) at 298 K (one mole).

$$\Theta_v = \frac{hc\tilde{\nu}}{k} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^{10} \text{ cm/s})(1580 \text{ cm}^{-1})}{1.38 \times 10^{-23} \text{ J/K}} = 2277 \text{ K} \quad \frac{\Theta_v}{T} = \frac{2277}{298} = 7.64$$

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

"Total" Entropy

$$\bar{S}^{trans} + \bar{S}^{rot} + \bar{S}^{vib} = 151.9 + 43.8 + 0.035 = 195.7 \text{ J/mol} \cdot \text{K}$$

Chap. 3 Chap. 4

O₂: S_{mol}(exp) = 205.1 J/mol-K at 298.15 K

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

Slide 75

The vibrational contribution to the entropy of O₂ is very low at 298 K. It increases significantly at higher temperatures.

T	S ^{vib}
298 K	0.035 J/mol-K
500	0.49
1000	3.07
2000	7.86
3000	10.82

Slide 76

Output from G-98 geom. opt. and frequency calculation on O₂ (at 298 K)

QCISD/6-311G(d)

	E (Thermal)	CV	S
	KCAL/MOL	CAL/MOL-K	CAL/MOL-K
TOTAL	3.750	5.023	48.972
ELECTRONIC	0.000	0.000	2.183
TRANSLATIONAL	0.889	2.981	36.321
ROTATIONAL	0.592	1.987	10.459
VIBRATIONAL	2.269	0.055	0.008
	Q	LOG10(Q)	LN(Q)
TOTAL BOT	0.330741D+08	7.519488	17.314260
TOTAL V=0	0.151654D+10	9.180853	21.139696
VIB (BOT)	0.218193D-01	-1.661159	-3.824960
VIB (V=0)	0.100048D+01	0.000207	0.000476
ELECTRONIC	0.300000D+01	0.477121	1.098612
TRANSLATIONAL	0.711178D+07	6.851978	15.777263
ROTATIONAL	0.710472D+02	1.851547	4.263345

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

$$\bar{U}^{vib} = U_{ZPE}^{vib} + \bar{U}_{therm}^{vib} = 2.269 \text{ kcal/mol} = 9.49 \text{ kJ/mol}$$

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

$$\bar{C}_v^{vib} = 0.055 \text{ cal/mol} \cdot K = 0.23 \text{ J/mol} \cdot K \text{ (same as our result)}$$

$$\bar{S}^{vib} = 0.008 \text{ cal/mol} \cdot K = 0.033 \text{ J/mol} \cdot K$$

We got $0.035 \text{ J/mol} \cdot K$ (sig. fig. difference)

Slide 77

Helmholtz and Gibbs Energy

$$A^{vib} = -kT \ln Q^{vib} \quad G^{vib} = -kT \ln Q^{vib} + kT \left(\frac{\partial \ln Q^{vib}}{\partial \ln V} \right) = A^{vib}$$

~~Q^{vib} independent of V~~

$$Q^{vib} = (q^{vib})^N = \left(\frac{e^{-\frac{\Theta_v}{2T}}}{1 - e^{-\frac{\Theta_v}{T}}} \right)^N$$

$$G^{vib} = A^{vib} = -kT \ln (q^{vib})^N = -NkT \ln q^{vib} = -nRT \ln q^{vib} = -nRT \ln \left(\frac{e^{-\frac{\Theta_v}{2T}}}{1 - e^{-\frac{\Theta_v}{T}}} \right)$$

O₂ ($\tilde{\nu} = 1580 \text{ cm}^{-1}$) at 298 K (one mole).

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

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

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

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

Slide 78

Polyatomic Molecules

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

Energy: $\varepsilon^{vib} = \varepsilon_1^{vib} + \varepsilon_2^{vib} + \dots = (n_1 + 1/2)hc\bar{\nu}_1 + (n_2 + 1/2)hc\bar{\nu}_2 + \dots$

Partition Function

$$Q^{vib} = \left(\sum e^{-\frac{\varepsilon_{1,j} + \varepsilon_{2,j} + \dots}{kT}} \right)^N = \left(\sum e^{-\frac{\varepsilon_{1,j}}{kT}} \cdot \sum e^{-\frac{\varepsilon_{2,j}}{kT}} \dots \right)^N = \left(\sum e^{-\frac{\varepsilon_{1,j}}{kT}} \right)^N \cdot \left(\sum e^{-\frac{\varepsilon_{2,j}}{kT}} \right)^N \dots$$

Therefore: $Q^{vib} = Q_1^{vib} \cdot Q_2^{vib} \dots$

Slide 79

$$Q^{vib} = Q_1^{vib} \cdot Q_2^{vib} \dots$$

Thermodynamic Properties

$$\ln Q^{vib} = \ln Q_1^{vib} + \ln Q_2^{vib} + \dots$$

$$\left(\frac{\partial \ln Q^{vib}}{\partial T} \right)_{V,N} = \left(\frac{\partial \ln Q_1^{vib}}{\partial T} \right)_{V,N} + \left(\frac{\partial \ln Q_2^{vib}}{\partial T} \right)_{V,N} + \dots$$

Therefore: $U^{vib} = U_1^{vib} + U_2^{vib} + \dots$

$$S^{vib} = S_1^{vib} + S_2^{vib} + \dots$$

etc.

Thus, you simply calculate the property for each vibration separately, and add the contributions together.

Slide 80

Comparison Between Theory and Experiment: $\text{H}_2\text{O}(\text{g})$

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:

$$H^{\text{tran}} = (3/2)RT + RT \quad C_p^{\text{tran}} = (3/2)R + R = (5/2)R$$

$$H^{\text{rot}} = (3/2)RT \quad C_p^{\text{rot}} = (3/2)R$$

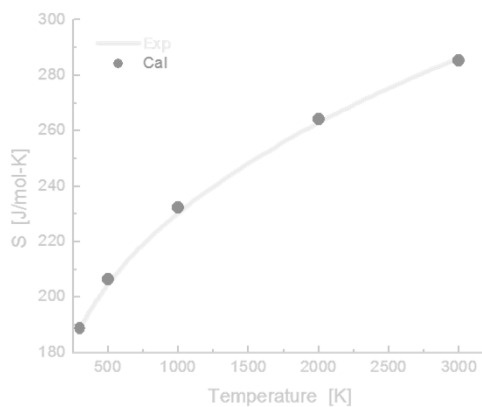
$$H^{\text{vib}} = 3RT \quad C_p^{\text{vib}} = 3R$$

$$\text{Low T Limit: } H^{\text{tran}} + H^{\text{rot}} = 4RT \quad C_p^{\text{tran}} + C_p^{\text{rot}} = 4R$$

$$\text{High T Limit: } H^{\text{tran}} + H^{\text{rot}} + H^{\text{vib}} = 7RT \quad C_p^{\text{tran}} + C_p^{\text{rot}} + C_p^{\text{vib}} = 7R$$

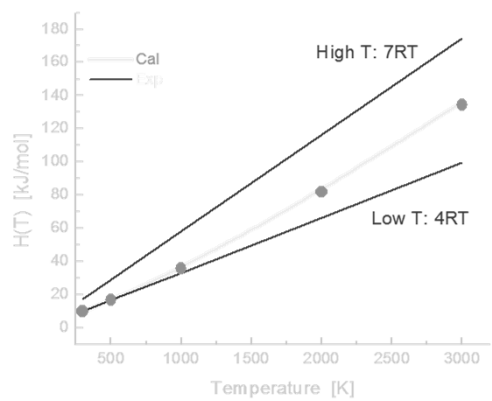
Slide 81

Calculated and Experimental Entropy of $\text{H}_2\text{O}(\text{g})$



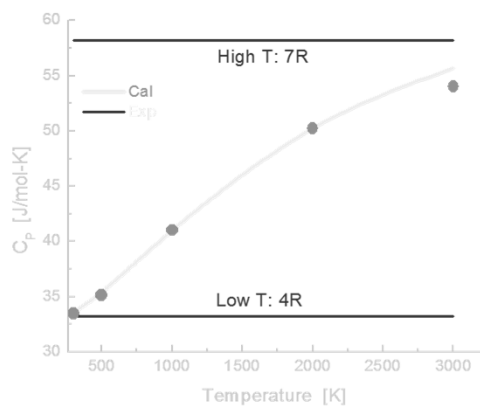
Slide 82

Calculated and Experimental Enthalpy of $\text{H}_2\text{O}(\text{g})$



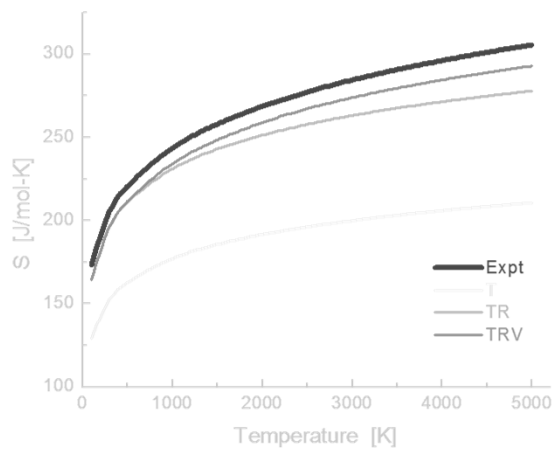
Slide 83

Calculated and Experimental Heat Capacity (C_p) of $\text{H}_2\text{O}(\text{g})$



Slide 84

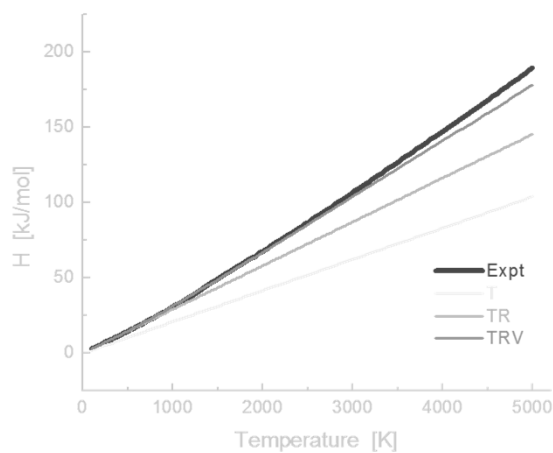
Translational + Rotational + Vibrational Contributions to O₂ Entropy



Unlike in H₂O, the remaining contribution (electronic) to the entropy of O₂ is significant. We'll discuss this in Chapter 10.

Slide 85

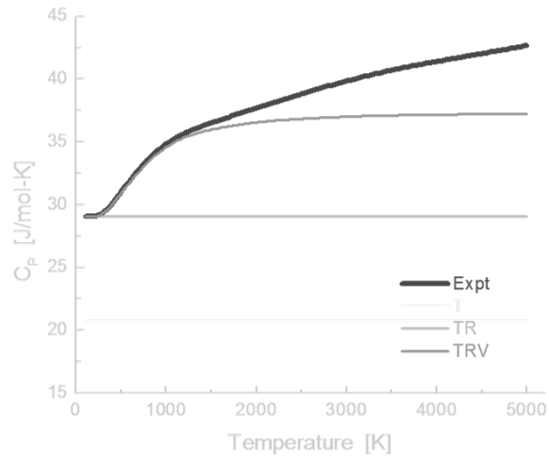
Translational + Rotational + Vibrational Contributions to O₂ Enthalpy



There are also significant additional contributions to the Enthalpy.

Slide 86

Translational + Rotational + Vibrational Contributions to O_2 Heat Capacity



- 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.

Slide 87