

3 Chapter 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:

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

- Calculate the normalization constant, A_1 (in terms of α)
- Determine $\langle x \rangle$ (in terms of α)
- Determine $\langle x^2 \rangle$ (in terms of α)
- Determine $\langle p \rangle$ (in terms of α)
- Determine $\langle p^2 \rangle$ (in terms of α)
- Determine $\langle T \rangle$, average kinetic energy (in terms of ω)
- 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} .

- Determine the CO vibrational force constant, in N/m.
- 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} .

- 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.
- 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°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:

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

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Use the Harmonic Oscillator Hamiltonian as the unperturbed Hamiltonian:

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

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

as the unperturbed ground state wavefunction and energy

Your answer should be in terms of k , 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°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.

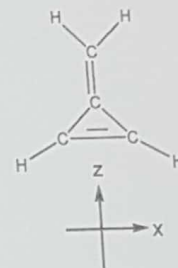
(b) Determine whether each combination mode below is active or inactive in the IR and Raman Spectra.

(i) $\nu_1 + \nu_3$

(ii) $\nu_2 - \nu_3$

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Symmetry

| 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

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

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

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

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

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

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

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

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

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

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

$$k \cdot N_A = R$$

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

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

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

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

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

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

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

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

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