

Problem Set PS06

ISSUED: 9/5/00 Due: 10/12/00

Prof. Darin J. Ulness

Name _____

Instructions. Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

Mathematical Exercises

1. Dig out your calc books and expand the following functions in a Taylor's series about zero (go to the quartic term).

(a) $f(x) = e^{-ax}$

(b) $f(x) = \sin x$

2. Find the minimum of the function $f(x) = (x - 4)^2$. First expand $f(x)$ in a Taylor's series about zero, then expand it about the minimum. Comment on the coefficients of the linear and quadratic term for each expansion.

Exercises

3. One important concept in spectroscopy is the *selection rules*. The selection rules determine which transitions are allowed and which are forbidden. The harmonic oscillator model is a very good model for describing low energy molecular vibrations. One can very quickly determine the selection rules for the harmonic oscillator using the raising and lowering operators, \hat{a}^\dagger and \hat{a} respectively. When discussing IR spectroscopy, one is interested in the so-called (electric) transition dipole. The electric dipole operator is $\hat{\mu} \equiv \epsilon \hat{x}$ (where ϵ is some electric charge). The transition dipole is calculated by

$$\mu_{nm} = \int \psi_n^* \hat{\mu} \psi_m dx. \quad (1)$$

How is this different from the average value theorem? If $\mu_{nm} \neq 0$ then the transition from state m to state n is allowed and one sees a line in the IR spectrum. If $\mu_{nm} = 0$ then the transition is forbidden and one does not see a line in the IR spectrum. Since all we need to do is determine if the integral is zero or not, we can ignore all constants and write the integral as

$$\mu_{nm} \propto \int \psi_n^* \hat{x} \psi_m dx \propto \int \psi_n^* (\hat{a} + \hat{a}^\dagger) \psi_m dx. \quad (2)$$

Determine the selection rules by finding the allowed transitions.

4. Expand the Morse potential in a Taylor's series about R_{eq} . Verify that the coefficient for the linear term is zero.

5. The Morse Oscillator allows for anharmonicity of the vibrational mode. This is parameterized by the anharmonicity constant $\tilde{\omega}_e x_e$ of the Morse oscillator (page 46 of the notes). What are the units of the anharmonicity constant (recall $\tilde{\omega}_e$ has units of wavenumbers). Sketch a graph of the anharmonicity constant versus the well depth assuming $\tilde{\omega}_e$ remains constant. Explain why your graph makes sense.
6. Derive an expression for the zero point energy of the Morse Oscillator.
7. Derive an expression for ΔE for the Morse oscillator and sketch the spectrum.
8. Starting with a Morse oscillator which has a vibrational constant ($\tilde{\omega}_e$) of 500cm^{-1} and taking the anharmonicity constant to be 1% of the vibrational constant, determine the bond dissociation energy in wavenumbers for this oscillator. (Note there is an error on the answer key for last year's problem set for a similar problem.)
9. The energy level dependence on vibrational quantum number for the Morse oscillator actually becomes nonsensical for high quantum numbers. Use ΔE from problem 7 to determine at what quantum number the Morse oscillator stops making sense. What is this quantum number if the anharmonicity is 1%.

Conceptual Problems

10. Use an analogy involving a wildebeest and several horseflies to explain the Born–Oppenheimer approximation.



A wildebeest

11. Explain in your own words exactly how the Born–Oppenheimer approximation is used to model vibrations of diatomic molecules.
12. How does the average bond length go as a function of energy for a diatomic molecule described by the Morse oscillator?
13. How would the hot bands in the IR spectrum of a perfect harmonic oscillator compare with a Morse oscillator.
14. Which of the symmetries discussed in section 3.3.1 of the notes are present in HF? in F_2 ?

15. Draw the LCAO picture for

- (a) a $2s/2s$ σ -antibond
- (b) a $2s/2p_z$ σ -bond
- (c) a $2p_y/2p_y$ π -bond
- (d) a $2p_z/2p_z$ σ -antibond

Computer Problems

16. Plot the Morse potential setting $D_e = 1$ and $R - R_{eq} = x$ for values of $\beta = 0.1, 0.2, 0.3, 0.4$ and 0.5 .

Reflective Exercises

17. Physical chemistry in the US has traditionally been dominated by men with the percentage of women physical chemists being far below 50%. Lately more women have been becoming physical chemists yet the percentage is still well below 50%.
- (a) Current hiring practices at US colleges and universities (and presumably industry) are such that women physical chemistry candidates are given special consideration. That is, a candidate's gender is one factor in the hiring decision (although most likely not the most important factor). Can you think of at least one advantage to this type of hiring practice? Can you think of at least one disadvantage?
 - (b) Do you think that it is important for the percentage of US women physical chemists to be at or very near 50%. If not, why not? If so, why? Also if so, how might this be accomplished?

① a) $f(x) = e^{-ax}$

$$f(x) = e^{-ax} \Big|_{x=0} + \frac{1}{1!} \frac{d}{dx} e^{-ax} \Big|_{x=0} x + \frac{1}{2!} \frac{d^2}{dx^2} e^{-ax} \Big|_{x=0} x^2 + \frac{1}{3!} \frac{d^3}{dx^3} e^{-ax} \Big|_{x=0} x^3 + \frac{1}{4!} \frac{d^4}{dx^4} e^{-ax} \Big|_{x=0} x^4 + \dots$$

$$f(x) = 1 + (-a)x + \frac{(-a)^2 x^2}{2!} + \frac{(-a)^3 x^3}{3!} + \frac{(-a)^4 x^4}{4!} + \dots$$

$$f(x) = 1 - ax + \frac{a^2 x^2}{2} - \frac{a^3 x^3}{6} + \frac{a^4 x^4}{24} - \dots$$

b) $f(x) = \sin x$

$$f(x) = \sin x \Big|_{x=0} + \frac{1}{1!} \frac{d}{dx} \sin x \Big|_{x=0} x + \frac{1}{2!} \frac{d^2}{dx^2} \sin x \Big|_{x=0} x^2 + \frac{1}{3!} \frac{d^3}{dx^3} \sin x \Big|_{x=0} x^3 + \frac{1}{4!} \frac{d^4}{dx^4} \sin x \Big|_{x=0} x^4 + \dots$$

$$f(x) = \sin 0 + \frac{\cos(0)}{1!} x + \frac{-\sin(0)}{2!} x^2 + \frac{-\cos(0)}{3!} x^3 + \frac{\sin(0)}{4!} x^4 + \dots$$

$$f(x) = x - \frac{x^3}{6} + \dots$$

② minimum at $x=4$

$$f(x) = (x-4)^2$$

$$f(x) = (x-4)^2 \Big|_{x=0} + \frac{1}{1!} \frac{d}{dx} (x-4)^2 \Big|_{x=0} x + \frac{1}{2!} \frac{d^2}{dx^2} (x-4)^2 \Big|_{x=0} x^2 + \dots$$

$$= (0-4)^2 + 2(0-4)x + \frac{2}{2!} x^2 + \dots$$

$$= 16 - 8x + x^2 + \dots \text{ expanded about } 0$$

When expanding about the minimum, the linear coefficient is always zero and the quadratic coefficient gives the curvature.

$$f(x) = (x-4)^2 \Big|_{x=4} + \frac{1}{1!} \frac{d}{dx} (x-4)^2 \Big|_{x=4} (x-4) + \frac{1}{2!} \frac{d^2}{dx^2} (x-4)^2 \Big|_{x=4} (x-4)^2 + \dots$$

$$= (4-4)^2 + 2(4-4)(x-4) + \frac{2}{2!} (x-4)^2 + \dots$$

$$= 0 + 0 + (x-4)^2 + \dots$$

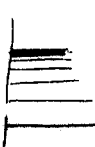
⑧ $\tilde{\omega}_e = 500 \text{ cm}^{-1}$ $\tilde{\omega}_e x_e = 5 \text{ cm}^{-1}$

From problem 6

$$D_0 = D_e - \frac{hc\tilde{\omega}_e^2}{2} + \frac{hc\tilde{\omega}_e x_e}{4}$$

$$\tilde{D}_0 = \tilde{D}_e - \frac{\tilde{\omega}_e^2}{2} + \frac{\tilde{\omega}_e x_e}{4} \quad \tilde{D}_e = \frac{\tilde{\omega}_e^2}{4\tilde{\omega}_e x_e} = \frac{(500)^2}{4(5)} = 12,500 \text{ cm}^{-1}$$

$$\tilde{D}_0 = 12,500 - \frac{500^2}{2} + \frac{5}{4} = 12,251.25 \text{ cm}^{-1}$$

⑨  above certain quantum numbers ΔE becomes negative \Rightarrow nonsense!
so for problem 7 $\Delta E = 0 = hc\tilde{\omega}_e - 2hc\tilde{\omega}_e x_e (n+1)$

$$n = \frac{hc\tilde{\omega}_e}{2hc\tilde{\omega}_e x_e} - 1 \Rightarrow \text{above } n = \frac{1}{x_e} - 1$$

Set 1% anharmonicity $x_e = 0.01$

$$n = \frac{1}{0.01} - 1 = 99$$

⑩ wildebeest \rightarrow nuclei
horseflies \rightarrow electrons

as the wildebeest grazes the horseflies adjust "instantaneously" to the moment of the wildebeest.

⑪ your words

③ $\int \psi_n(\hat{a} + \hat{a}^\dagger) \psi_m dx = \int \psi_n^\dagger \hat{a} \psi_m + \int \psi_n^\dagger \hat{a}^\dagger \psi_m$

$$= \sqrt{n} \int \psi_n^\dagger \psi_{m-1} = \sqrt{n+1} \int \psi_n^\dagger \psi_{m+1}$$

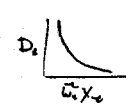
In order for $\int \psi_n(\hat{a} + \hat{a}^\dagger) \psi_m dx \neq 0$

ψ_n $m = n+1$ or $m = n-1$

Selection rule: Δ quantum # = ± 1

④ $D_e [1 - e^{-\beta(x-R_{eq})}]^2 = \beta^2 D_e (R - R_{eq})^2 - \beta^2 D_e (R - R_{eq})^3 + \dots$

⑤ $\tilde{\omega}_e x_e = \frac{hc\tilde{\omega}_e^2}{4D_e} \Rightarrow D_e = \frac{hc\tilde{\omega}_e^2}{4\tilde{\omega}_e x_e}$



The more anharmonic the system the less deep the well is, the less like a harmonic oscillator.

⑥ $D_0 = -E_0 = D_e - hc\tilde{\omega}_e(n+\frac{1}{2}) + hc\tilde{\omega}_e x_e(n+\frac{1}{2})^2$

$$= D_e - \frac{hc\tilde{\omega}_e^2}{2} + \frac{hc\tilde{\omega}_e x_e}{4}$$

Zero point = $D_e - D_0 = D_e - (D_e - \frac{hc\tilde{\omega}_e^2}{2} + \frac{hc\tilde{\omega}_e x_e}{4})$

$$\text{Zero point} = \frac{hc\tilde{\omega}_e^2}{2} - \frac{hc\tilde{\omega}_e x_e}{4}$$

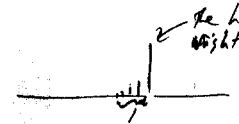
⑦ $\Delta E = -D_e + hc\tilde{\omega}_e(n+1+\frac{1}{2}) - hc\tilde{\omega}_e x_e(n+1+\frac{1}{2})^2 - (D_e + hc\tilde{\omega}_e(n+\frac{1}{2}) - hc\tilde{\omega}_e x_e(n+\frac{1}{2})^2)$

$$= hc\tilde{\omega}_e [(n+\frac{3}{2}) - (n+\frac{1}{2})] - hc\tilde{\omega}_e x_e [(n+\frac{3}{2})^2 - (n+\frac{1}{2})^2]$$

$$= hc\tilde{\omega}_e - hc\tilde{\omega}_e x_e [n^2 + 3n + \frac{9}{4} - n^2 - n - \frac{1}{4}] = hc\tilde{\omega}_e - 2hc\tilde{\omega}_e x_e (n+1)$$

$$\frac{11111}{\Delta E}$$

⑫ $n \uparrow$ bond length \uparrow

⑬  The hot band for the H₂O is right on top of the fundamentals!
Hot band Morse oscillator

⑭ HF: cylindrical
F⁻: inversion, cylindrical, mirror

