

Problem Set PS06

ISSUED: 10/4/01 Due: 10/11/01

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). Check your answer with MATHEMATICA using the `Series` command
 - (a) $f(x) = e^{-ax}$
 - (b) $f(x) = \cos x$. Does it make sense that all the odd order terms are zero?
2. Find the minimum of the function $f(x) = (x - 3)^2$. 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. Show that the energy convention for the Morse potential given by Eq. (3.14) of the notes is such that the bottom of the potential well corresponds to the zero of energy. Also show that with a change of the energy convention such that the zero of energy corresponds to the dissociated state, the Morse potential can be written as

$$D_e \left(e^{-2\beta(R-R_{eq})} - 2e^{-\beta(R-R_{eq})} \right).$$

4. 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

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

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.

5. In more elaborate analysis than the one described in the previous problem, the transition operator, \hat{M} , can be written as a power series in x as

$$\hat{M} = \sum_{n=0}^{\infty} c_n \hat{x}^n.$$

The $n = 0$ term represents the interaction of the light field with a permanent dipole, the $n = 1$ term is the transition dipole described in the previous problem and the $n > 1$ terms are higher order effects which are progressively weaker. Use the same technique as in the previous problem to show that all transitions are at least very weakly allowed even if they are dipole forbidden.

6. 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.
7. Derive an expression for the zero point energy of the Morse Oscillator.
8. Derive an expression for ΔE for the Morse oscillator and sketch the spectrum.
9. The energy level dependence on vibrational quantum number for the Morse oscillator actually becomes nonsensical for high quantum numbers. Use ΔE from the previous problem to determine at what quantum number the Morse oscillator stops making sense. What is this quantum number if the anharmonicity is 1%.
10. Starting with a Morse oscillator which has a vibrational constant ($\tilde{\omega}_e$) of 1500cm^{-1} and taking the anharmonicity constant to be 2% of the vibrational constant, determine the bond dissociation energy in wavenumbers for this oscillator.

Conceptual Problems

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



A wildebeest

12. Explain in your own words exactly how the Born–Oppenheimer approximation is used to model vibrations of diatomic molecules.
13. How does the average bond length go as a function of energy for a diatomic molecule described by the Morse oscillator
14. How would the hot bands in the IR spectrum of a perfect harmonic oscillator compare with a Morse oscillator.
15. Which of the symmetries discussed in section 3.3.1 of the notes are present in HF? in F₂?
16. Draw the LCAO picture for
 - (a) a 2s/1s σ -antibond
 - (b) a 2s/3p_z σ -bond
 - (c) a 2p_y/2p_y π -bond
 - (d) a 2p_z/2p_z σ -antibond
 - (e) a 3d_{xy}/3d_{xy} δ -bond (difficult to draw—do the best you can)

and label the positive and negative regions of the molecular wavefunctions.

Computer Problems

17. Download the MATHEMATICA program Morse.nb. Work through the example for $D_e = 20$, $\beta = 1$ and $m = 1$.
 - (a) Explain the plot of $\langle \hat{x} \rangle$.
 - (b) Explain the plot of variance.
 - (c) Make a series of graphs in which you change the Morse parameter β from 1 to 2 (don't be fooled by how MATHEMATICA displays the graphs for different values of β). What physically does the Morse parameter represent?

Reflective Exercises

18. 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?
19. Visit <http://www.usnews.com/usnews/edu/beyond/bcphd.htm> for U.S. News and World Report's ranking of graduate schools. What is the number one school of chemistry?

- ① Taylor series about $x=0$: $f(x) = f(0) + \frac{df}{dx}|_{x=0} x + \frac{d^2f}{dx^2}|_{x=0} \frac{x^2}{2} + \dots$
- ② $f(x) = e^{-ax} = 1 - ax + \frac{a^2 x^2}{2} - \frac{a^3 x^3}{6} + \frac{a^4 x^4}{24} + \dots$
- ③ $f(x) = \cos x = 1 + 0 - \frac{x^2}{2} + 0 + \frac{x^4}{24} + \dots$

④ $\frac{df}{dx} = 2(x-3) = 0 \Rightarrow x=3$

about 0: $f(x) = (x-3)^2 = 9 - 6x + x^2 + 0 + 0 + \dots = 9 - 6x + x^2$
 about 3: $f(x) = 0 + 0 + (x-3)^2 + 0 + \dots = (x-3)^2$

Whenever one expands a function about a critical point (min, max, inflection) the linear term is zero, all the quadratic coefficient is >0 for a max, <0 for min and equal to 0 for an inflection.

⑤ $E_2(3,14)$: $V(x) = D_e [1 - e^{-B(R-R_e)}]^2$ min at R_e
 so $V'(R_e) = D_e [-2e^{-B(R-R_e)}] = 0$

change zero of energy convention \leftarrow this puts the zero of energy at the bottom of the well
 $V'(R_e) = D_e [1 - e^{-B(R-R_e)}]^2 - D_e$
 $= D_e (1 - 2e^{-B(R-R_e)} + e^{-2B(R-R_e)}) - D_e$
 $= e^{-2B(R-R_e)} - 2e^{-B(R-R_e)}$

⑥ $n_{nm} \propto \int \psi_n^* (a+a^\dagger) \psi_m dx = \int \psi_n^* a \psi_m dx + \int \psi_n^* a^\dagger \psi_m dx$
 $= \sqrt{m} \int \psi_n^* \psi_{m-1} dx + \sqrt{m+1} \int \psi_n^* \psi_{m+1} dx$
 $= 1$ if $n=m-1$ $= 1$ if $n=m+1$
 so selection rules are $\Delta n = \pm 1$

SO 4

above certain quantum numbers ΔE becomes negative \rightarrow Nonsense!
 so for problem 8 $\Delta E = 0 = hc\tilde{\omega}_e - 2hc\tilde{\omega}_e x_e (n+1)$
 $n = \frac{hc\tilde{\omega}_e}{2hc\tilde{\omega}_e x_e} - 1 \Rightarrow$ above $n = \frac{1}{2x_e} - 1$

for 1% anharmonicity $x_e = 0.01$
 $n = \frac{1}{2 \cdot 0.01} - 1 = 49$

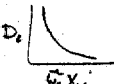
⑩ $\tilde{\omega}_e = 1500 \text{ cm}^{-1}$ $\tilde{\omega}_e x_e = 30 \text{ cm}^{-1}$
 from problem 7 $\tilde{D}_0 = \tilde{D}_e - \frac{\tilde{\omega}_e^2}{4} + \frac{\tilde{\omega}_e x_e}{4}$ but $\tilde{D}_e = \frac{hc^2}{4hc x_e} = \frac{(1500 \text{ cm}^{-1})^2}{4(30 \text{ cm}^{-1})} = 18,750$
 $\tilde{D}_0 = 18,750 \text{ cm}^{-1} - \frac{1500^2}{4} + \frac{30}{4} =$

⑪ wildebeest \rightarrow nuclei
 horseflies \rightarrow electrons
 as the wildebeest grazes the horseflies adjust "instantaneously" to the movement of the wildebeest.

⑫ your words

⑥ Consider the n th term $c_n x^n = c_n (a+a^\dagger)^n$
 $= a a \dots a + a a \dots a^\dagger + a a \dots a^\dagger a^\dagger + \dots + a^\dagger a^\dagger \dots a^\dagger$
 by using the same analysis as the previous problem the selection rules for the n th term will be $\Delta n = \pm n, \pm n-1, \pm n-2, \dots, \pm 1, 0$ if n is even
 same in \hat{M} $n \rightarrow n$ all transitions are allowed

⑦ $\tilde{\omega}_e x_e = \frac{hc\tilde{\omega}_e^2}{4D_e} \Rightarrow D_e = \frac{hc\tilde{\omega}_e^2}{4\tilde{\omega}_e x_e}$



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

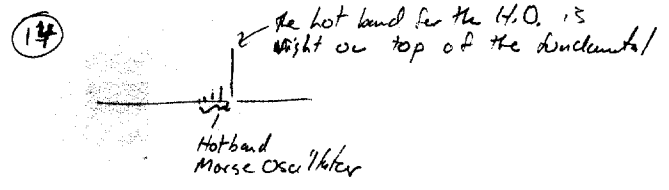
⑧ $D_0 = -E_0 = + D_e - hc\tilde{\omega}_e (n+\frac{1}{2}) + hc\tilde{\omega}_e x_e (n+\frac{1}{2})^2$
 $= D_e - \frac{hc\tilde{\omega}_e}{2} + \frac{hc\tilde{\omega}_e x_e}{4}$

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

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

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⑫ $n \uparrow$ bond length \uparrow



⑭ HF : cylindrical
 F_2 : inversion, cylindrical, mirror

