

# Problem Set PS06

Issued: 10/3/02 Due: 10/10/02

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**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 book and expand the following functions in a Taylor's series about the point given (go to the quartic term). Check your answer with Mathematica using the Series command Also plot the functions
  - (a)  $f(x) = \frac{1}{x^{12}} - \frac{1}{x^6}$  about  $x = 1$ . By the way, this function is often used to model intermolecular potential energy. It is called the 6–12 potential or, more comonly, the Lennard–Jones potential.
  - (b)  $f(x) = \sin x$  about  $x = 0$ . Does it make sence that all the even order terms are zero?
2. Find the minimum of the function  $f(x) = \frac{1}{x^{12}} - \frac{1}{x^6}$ . First expand  $f(x)$  in a Taylor's series about the minimum. Compare this to problem 1(a) and comment on the coefficients of the linear and quadratic term for each expansion. Does this make sense?
3. The radius of curvature,  $\rho$ , of a function,  $f(x)$ , is a measure of how curvy a function is a a given point and is defined by

$$\rho = \frac{\left(1 + \left(\frac{df}{dx}\right)^2\right)^{3/2}}{\frac{d^2f}{dx^2}}.$$

The radius of curvature is interpreted as the radius a circle would have such that its curvature is equal to that at the point along the fuction. So, the smaller  $\rho$ , the more curvature the function has at that point. Evaluate the radius of curvature for the following functions at the point given. You might want to define a short function in Mathematica to assist you.

$$\text{RadofCurve}[f_, p_] := ((1 + D[f, x]^2)^(3/2))/(D[f, {x, 2}]) /. x -> p$$

- (a)  $f(x) = \frac{1}{x^{12}} - \frac{1}{x^6}$  at the minimum you found in the previous problem.
- (b)  $f(x) = \sin x$  at  $x = \frac{\pi}{2}$ .

## Exercises

4. Verify the discussion on page 50 of the notes that deals with Eqs. (3.14) and (3.15).
5. Evaluate the radius of curvature of the harmonic oscillator and the Morse oscillator potentials at their minima. If the best values of  $k$  for the H.O. and  $D_e$  and  $\beta$  for the M.O. are such that each curve has the same radius of curvature at the minimum, what is the relation of  $k$  to  $D_e$  and  $\beta$ ?
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 50 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  $\Delta E$  for the Morse oscillator and sketch the spectrum.
8. Derive an expression for  $\Delta\Delta E$  for the Morse oscillator
9. The energy level dependence on vibrational quantum number for the Morse oscillator actually becomes nonsensical for high quantum numbers. Use  $\Delta\Delta E$  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 1.5%.
10. Starting with a Morse oscillator which has a vibrational constant ( $\tilde{\omega}_e$ ) of  $1800\text{cm}^{-1}$  and taking the anharmonicity constant to be 1.75% 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 CO? in O<sub>2</sub>?
16. Draw the LCAO picture for
  - (a) a 2s/2s  $\sigma$ -antibond
  - (b) a 3s/3p<sub>z</sub>  $\sigma$ -bond
  - (c) a 2p<sub>x</sub>/2p<sub>x</sub>  $\pi$ -bond
  - (d) a 3d<sub>z<sup>2</sup>}/3d<sub>z<sup>2</sup>}</sub>  $\sigma$ -antibond</sub>
  - (e) a 3d<sub>xz</sub>/3d<sub>xz</sub>  $\pi$ -bond
  - (f) a 3d<sub>xy</sub>/3d<sub>xy</sub>  $\delta$ -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  $\beta$  from 1 to 2 (don't be fooled by how **Mathematica** displays the graphs for different values of  $\beta$ ). What physically does the Morse parameter represent?
18. Use **Mathematica** to expand the Morse potential of Eq. (3.15) of the notes in a Taylor series about  $R_e$ .

### Reflective Exercises

19. Should everyone's opinion be respected even if it is wrong?
20. 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?
21. Visit <http://www.usnews.com/usnews/edu/grad/rankings/phdsci/phdsciindex.htm> for U.S. News and World Report's ranking of graduate schools. What is the number one school in chemistry?

①  $R_{11} = 0 \quad \frac{df}{dx}|_{x=1} = -12x^{-13} + 6x^{-7} = -6$

$\frac{df}{dx}|_{x=1} = 156x^{-14} - 42x^{-8} = 114 \quad \frac{d^2f}{dx^2}|_{x=1} = -2184x + 336x = -1848$

So  $\frac{1}{x^{12}} - \frac{1}{x^6} = 0 \Rightarrow -6(x-1) + \frac{114}{2!}(x-1)^2 - \frac{1848}{3!}(x-1)^3 + O(x^4)$   
 $= -6(x-1) + 57(x-1)^2 - 308(x-1)^3 + O(x^4)$

②  $\sin 0 = 0 \quad \frac{df}{dx}|_{x=1} = 1 \quad \frac{d^2f}{dx^2}|_{x=1} = 0 \quad \frac{d^3f}{dx^3} = -1$

So  $\sin x = 0 + 1x + \frac{0}{2!}x^2 - \frac{1}{3!}x^3 + O(x^4)$   
 $= x - \frac{x^3}{3!} + O(x^4)$

③  $\frac{df}{dx} = -12x^{-13} + 6x^{-7} = 0 \Rightarrow 2x^{-13} = x^{-7} \Rightarrow 2 = x^6$

This has 6 roots but only one "physical" one  
 $x = 2^{1/6}$

$\frac{1}{x^{12}} - \frac{1}{x^6} = -\frac{1}{4} + \frac{9(x-2^{1/6})^2}{2^5} + (-\frac{9}{10} + 14\sqrt{6})(x-2^{1/6})^3 + O(x^4)$

- ④ (a)  $\frac{1}{96^{1/3}}$   
 (b)  $-1$  } from mathematics

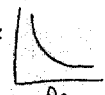
⑤  $D_e(1 - e^{-\beta(R-R_e)})^2 = D_e(1 - 2e^{-\beta(R-R_e)} + e^{-2\beta(R-R_e)})$   
 $= D_e + D_e[e^{-2\beta(R-R_e)} - 2e^{-\beta(R-R_e)}]$   
 Shift energy by  $-D_e \Rightarrow D_e[e^{-2\beta(R-R_e)} - 2e^{-\beta(R-R_e)}]$

⑥  $\rho_{0,0} = \frac{1}{L} \quad \rho_{0,1} = \frac{1}{2\beta^2 D_e}$

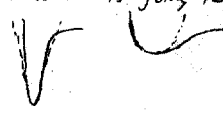
$\frac{1}{L} = \frac{1}{2\beta^2 D_e} \Rightarrow L = 2\beta^2 D_e$

⑦  $\tilde{\omega}_e x_e$  has units of wavenumbers

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



A deeper well is going to exhibit more harmonic behavior



⑧  $\Delta E = -D_e + k\omega(n+1/2) - k\omega^2((n+1/2)^2) + D_e - k\omega(n+1/2) + k\omega^2(n+1/2)^2$   
 $= k\omega n + \frac{1}{2}k\omega - k\omega n - k\omega^2 n - k\omega^2 n - k\omega^2 \frac{1}{4} - k\omega n - \frac{1}{2}k\omega + k\omega^2 n + k\omega^2 \frac{1}{4}$   
 $= k\omega - 2n k\omega - 2k\omega^2$   
 $= k\omega + 2k\omega^2(n+1)$

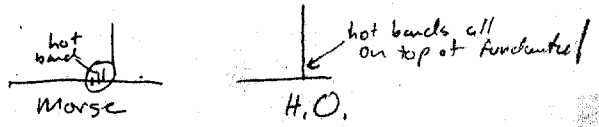
⑨  $\Delta E = k\omega - 2k\omega^2(n+1) - k\omega + 2k\omega^2(n+1)$   
 $\Delta E = -2k\omega^2$

⑩  $\Delta E = 0 = k\omega - 2k\omega^2(n+1) \Rightarrow 0 = 1 - 2\alpha n + 2\alpha$   
 $n = \frac{2\alpha + 1}{2\alpha} = \frac{2(0.015) + 1}{2(0.015)} = 34.33$   
 So max  $n = 34$

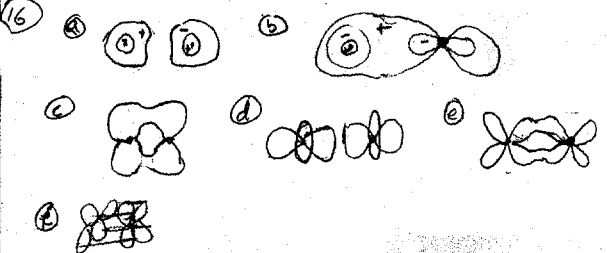
⑪ Working in wavenumbers  $x = \frac{\tilde{\omega}_e}{4D_e} \Rightarrow \tilde{\omega}_e = \frac{4x D_e}{1}$   
 $\tilde{\omega}_e = 25,715 \text{ cm}^{-1}$   
 $\tilde{\omega}_0 = \tilde{\omega}_e - 2x \tilde{\omega}_e$   
 $\tilde{\omega}_0 = 25,715 - 892$   
 $\tilde{\omega}_0 = 24,822 \text{ cm}^{-1}$

⑫ Wildbeest  $\rightarrow$  heavy slow  $\rightarrow$  nuclei  
 horseflies  $\rightarrow$  light fast  $\rightarrow$  electrons  
 The horseflies adjust instantaneously to the motion of the wildbeest.

- ⑬ your words  
 ⑭  $\langle R \rangle \uparrow \quad n \uparrow$



⑮  $O_2$ : All  $CO_2$ : only cylindrical



⑰ The average bond length increases with increasing energy level. This is consistent with the wavefunctions they spread to higher values of  $x$  because the potential energy curve is not symmetric.

The variance also increases which again makes sense from the wavefunctions

there is no linear term because minimum

⑱  $\ln(31) = \text{Series}[D_e(\text{Exp}[-2b(R-R_e)] - 2\text{Exp}[-b(R-R_e)]), (R, R_e, 3)]$   
 $\text{Out}[31] = -D_e + b^2 D_e (R-R_e)^2 - b^3 D_e (R-R_e)^3 + O[(R-R_e)^4]$

Notice this is the form problem 5. The quadratic term gives the harmonic part of the potential energy curve  
 zeroth order term gives energy offset

- ⑲, ⑳ ㉑ your words