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Chemistry 562 **Spring 2012**

Problem Set 6

Due beginning of class on Wednesday, March 7

(Make your reasoning clear. We need to understand your reasoning, not just see the final result.)

2 1. A fictional molecule HA (where H is hydrogen and A is a heavy atom) has a fundamental vibrational transition of 2000 cm^{-1}. Estimate the fundamental vibrational transition of DA (where D is deuterium (^{2}H)). Give your answer in units of cm^{-1} and nm.

4 2. For the Morse Potential,

$$V(x) = D_e(1 - e^{-ax})^2$$

where x is the displacement of the bond from its equilibrium position and D_e is the value of $V(x)$ at large separations. (Note that D_e in the above equation is in units of J.)

1 (a) Expand $V(x)$ in a Taylor Series about $x = 0$, through the x^2 term. (Taylor Series are discussed on page 462 in your book)

1 (b) Notice that the quadratic term looks like a harmonic oscillator. Write the force constant k as a function of D_e and a.

1 (c) Given that $D_e = 7.31 \times 10^{-19}$ J/molecule and $a = 1.82 \times 10^{10}\ \text{m}^{-1}$ for HCl, calculate the force constant of HCl.

1 (d) Using a graphing program, plot the Morse Potential (before the expansion) and plot the corresponding harmonic oscillator potential on the same graph. How do these two curves compare near the well minimum?

3 3. Using your notes from class, show that the classical expression for the energy of a hydrogenic atom can be written separably into one term that has the center-of-mass (X) kinetic energy and another term that has internal coordinates and the reduced mass (μ). Start from the equation

$$E = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(r)$$

2 4. *Atkins Problem 9.3.* Also predict the frequency (in Hz) and wavelength (in nm) of a photon that would excite the two longest-wavelength transitions of the Balmer series.

740 747 cm^{-1} 877 924 cm^{-1} 925 133 cm^{-1}

show $\frac{hcR}{n^2}$ find R

3 predict cm^{-1} of longest λ in Balmer

↓

$n_+ \to n = 2$

$$h_{bar} := \frac{6.626\cdot 10^{-34} J\cdot s}{2\cdot\pi} \qquad amu := \frac{kg}{6.022\cdot 10^{26}} = 1.661\times 10^{-27} kg$$

$$h := 6.626\cdot 10^{-34}\cdot J\cdot s \qquad A := 10^{-10} m \qquad aJ := 10^{-18} J$$

$$\mu_1 := 1 amu = 1.661\times 10^{-27} kg$$

$$E := h\cdot c\cdot 2000 cm^{-1} = 3.973\times 10^{-20} J$$

$$\omega := \frac{E}{h_{bar}} = 3.767\times 10^{14}\frac{1}{s}$$

$$k := \mu_1\cdot\omega^2 = 235.679\cdot\frac{N}{m}$$

$$E_D := \frac{h_{bar}\cdot\sqrt{\frac{k}{2amu}}}{h\cdot c} = 1414\cdot cm^{-1}$$

They are related by the square root of the masses of the ratio of the light atoms.

2) $D_e := 7.31\cdot 10^{-19} J \qquad \alpha := 1.82\cdot 10^{10} m^{-1}$

$$V(x) := D_e\cdot\left(1 - e^{-\alpha\cdot x}\right)^2$$

$$Taylor(x) := V(0) + \left(\frac{d}{dx}V(0)\right)\cdot x + \frac{1}{2}\cdot\frac{d^2}{dx^2}V(0)\cdot x^2$$

The first two terms are zero

Derivatives :

$$g(x) := 2\cdot D_e\cdot\left(1 - e^{-\alpha\cdot x}\right)\cdot\left(\alpha\cdot e^{-\alpha\cdot x}\right) \qquad g(0A) = 0 N$$

$$h(x) := 2\cdot D_e\cdot\left[\left(1 - e^{-\alpha\cdot x}\right)\cdot\left(-\alpha^2\cdot e^{-\alpha\cdot x}\right) + \alpha\cdot e^{-\alpha\cdot x}\cdot\left(\alpha\cdot e^{-\alpha\cdot x}\right)\right]$$

Evaluate this at x=0, and the first term in the sum goes to zero.

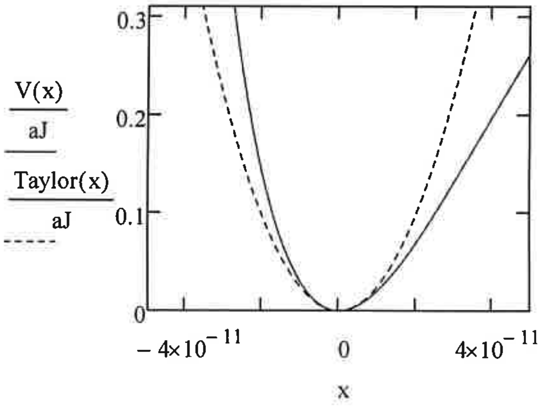
so h(0) = 2*De*alpha^2

$$\text{Taylor}(x) := \frac{1}{2}\cdot 2\cdot D_e\cdot \alpha^2\cdot x^2$$

and this looks like our regular harmonic oscillator problem with

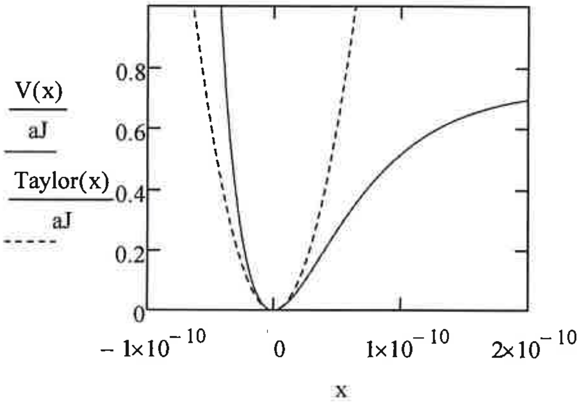
$$k := 2\cdot D_e\cdot \alpha^2 = 484.273\cdot \frac{N}{m}$$

Recall that we were given k=481 N/m on problem set 1.



Near the minimum, they are quite similar. Notice that the Morse potential (in red) is more repulsive when the bond is compressed, and softer when pulling the bond apart.

Here is an expanded view



$$E = \frac{p_1^2}{2m_1} + \frac{p_2^2}{m_2} + V(r)$$

C.o.m $\quad X = \frac{m_1}{m}x_1 + \frac{m_2}{m}x_2 \qquad m = m_1 + m_2$

↖ a weighted average

relative coord: $r = x_1 - x_2$

$x_2 = x_1 - r$

$=$ use in X

$$X = \frac{m_1}{m}x_1 + \frac{m_2}{m}(x_1 - r)$$

now use x_1 and x_2 to make fuctions of X and r

$$\frac{m_1}{m}x_1 = ~~[illegible]~~\ X - \frac{m_2}{m}(x_1 - r) \Rightarrow x_1 = \frac{m}{m_1}X_1 - \frac{\cancel{m}\,m_2}{m_1\cancel{m}}(x_1 - r)$$

$$x_1 = \frac{m}{m_1}X - \frac{m_2}{m_1}x_1 + \frac{m_2}{m_1}r \qquad \frac{m_1}{m_1}x_1 + \frac{m_2}{m_1}x_1 = \boxed{\frac{m}{m_1}X + \frac{m_2}{m_1}r}$$

$$\frac{m_1 + m_2}{\cancel{m_1}}x_1 = \frac{m}{\cancel{m_1}}X + \frac{m_2}{\cancel{m_1}}r \qquad \frac{1}{m} \Rightarrow x_1 = X + \frac{m_2}{m}r$$

$$x_2 = x_1 - r = X + \frac{m_2}{m}r - r = X + \frac{m_2}{m}r - \left(\frac{m_1 + m_2}{m}\right)r$$

$$= X + \frac{m_2}{m}r - \frac{m_1}{m}r - \frac{m_2}{m}r = \boxed{X - \frac{m_1}{m}r}$$

Now have x_1, x_2 in $\overset{\text{c.o.m}}{X}$, $\overset{\text{internal}}{r}$

$$p_1 = m_1\dot{x}_1 = m_1\frac{d}{dt}\left(X + \frac{m_2}{m}r\right) = m_1\dot{X} + \underbrace{\frac{m_1 m_2}{m}}_{\mu}\dot{r}$$

$$\underline{p_1 = m_1\dot{X} + \mu\dot{r}}$$

$$p_2 = m_2\dot{x}_2 = m_2\frac{d}{dt}\left(X - \frac{m_1}{m}\dot{r}\right) = m_2\dot{X} - \frac{m_1 m_2}{m}\dot{r}$$

$$p_2 = m_2\dot{X} - \mu\dot{r}$$

$$E = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \underset{\text{already internal coordinates}}{V(r)} = \cancel{\frac{\left(m_2 X - \frac{m_1 m_2}{m}\dot{r}\right)}{2m_1} +}$$

$$E = \frac{1}{2m_1}(m_1\dot{X} + \mu\dot{r})^2 + \frac{1}{2m_2}(m_2\dot{X} - \mu\dot{r})^2 + V(r)$$

$$= \frac{1}{2m_1}\left(m_1^2\dot{X}^2 + \mu^2\dot{r}^2 + \cancel{2m_1\mu\dot{X}\dot{r}}\right)$$

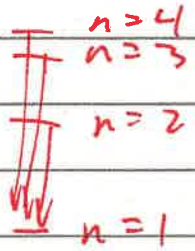
$$+ \frac{1}{2m_2}\left(m_2^2\dot{X}^2 + \mu^2\dot{r}^2 - \cancel{2m_2\dot{X}\mu\dot{r}}\right)$$

$$+ V(r)$$

$$E = \frac{1}{2}m_1\dot{X}^2 + \frac{1}{2}m_2\dot{X}^2 + \frac{1}{2}\left(\frac{\mu^2}{m_1} + \frac{\mu^2}{m_2}\right)\dot{r}^2 + V(r)$$

E27

Lyman ends @ $n = 1$



$$\Delta E = E_f - E_i = \frac{-hcR}{n^2} - \frac{-hcR}{1^2}$$

$$= +hcR\left(\frac{-1}{n^2} + \frac{1}{1^2}\right)$$

$$740747 \text{ cm}^{-1} \cdot \frac{4}{3} = 987669 \text{ cm}^{-1} = hcR$$

$$987669 \cdot \frac{8}{9} = 877921 \text{ cm}^{-1} \checkmark$$

$$987669 \cdot \frac{15}{16} = 925933 \text{ cm}^{-1} \checkmark$$

$R_H = 109691 \text{ cm}^{-1}$

$$\frac{R}{R_H} = 9 \qquad Z = 3 \quad \checkmark$$

Balmer $n_f = 2$

$$\Delta E_1 = 987669\left(\frac{-1}{3^2} + \frac{1}{2^2}\right) = 137176 \text{ cm}^{-1} = 72.9 \text{ nm}$$

$(4.11 \times 10^{15} \text{ Hz}$

$$\Delta E_2 = 987669\left(\frac{-1}{4^2} + \frac{1}{2^2}\right) = 185188 \text{ cm}^{-1} = 53.99 \text{ nm}$$

$(5.55 \times 10^{15} \text{ Hz})$

#5)

l	radial node/a_0	radial node/Å	# of angular nodes	l
0 (s)	1.89, 7.08	0.98, 3.68	0	0
1 (p)	~~1.97~~ 6.06	~~1.02~~ 3.15	1	$\sqrt{2}\hbar$
2 (d)	–	–	2	$\sqrt{6}\hbar$

b) i) Highest prob. near nucleus for 3s

ii) As Z increases, the maximum of the w.f. moves closer to r=0, but the size of the maximum also increases.

The e^- is concentrated to the nucleus as Z increases