SOLUTIONS

PROBLEM SET 4

CHM 3411, Dr. Chatfield

1. The simplified equation $T \approx 16\varepsilon(1-\varepsilon)e^{-\kappa L}$ can be used if $\kappa L \gg 1$. In our case, we have $\kappa L = (7\,nm^{-1})(2\,nm) = 14$ or $\kappa L = (7\,nm^{-1})(1\,nm) = 7$. We will therefore use the simplified equation (although 7 is not obviously $\gg 1$, it is > 1).

$$\frac{T(1.0\,nm)}{T(2.0\,nm)} = \frac{e^{-2\cdot 7}}{e^{-2\cdot 14}} = e^{14} = 1.2\times 10^{6}$$

Decreasing the distance by half increases the transmission coefficient by 6 order of magnitudes!

2. I learned about a very strange phenomenon today: quantum mechanical tunneling. It is one of those phenomena that is peculiar to the world of the very small, and when you try to imagine it, it does not seem to "make sense." That is because we are not able to observe tunneling directly, and so we have no experience of it. This is the phenomenon: a small particle, say an electron, can enter regions of space it really shouldn't (thinking "classically"), because it has too little energy. An analogy would be, for example, a slow moving car turning off its engine, coasting toward a hill, and managing to get to the other side even though it doesn't really have enough speed to "go over the hill." In science-ese, we would say that the height of the hill corresponds to a particular potential energy barrier, and the car has less kinetic energy than that.

The reason this works for the electron, fundamentally, is that small particles like electrons are not small versions of, say, billiard balls. We know that small particles have some properties analogous to waves, which billiard balls do not (at least not to an observable extent). One way to rationalize tunneling is to think of a sound wave encountering a wall that is strong but transmits sound. The sound can be heard on the other side, often even sounds of modest intensity encountering quite strong walls. Because small particles possess a hybrid particle-wave nature, they can be transmitted through barriers that would forbid them classically (i.e., if they obeyed Newton's laws of motion).

Before you get too worried, I should tell you that according to the laws of quantum mechanics, the probability of tunneling gets small very quickly as mass increases, or as the difference between the potential energy barrier and the energy of the particle increases, or as the barrier gets wide. This provides consistency between what we observe at the macro scale (the laws of classical physics) and what very precise experiments show happens at the micro scale.

A few examples of quantum mechanical tunneling:

- Scanning tunneling microscope (useful for making images of the surfaces of tiny objects)
- Kinetic isotope effect (a way to learn about the mechanisms of chemical reactions, in particular whether the rate limiting step involves a hydrogen exchange)
- Radioactive decay
- Nuclear fusion in stars

3. Exercise 8B.1b $\quad N = kg\,m\,s^{-2}$

$$\omega = \sqrt{\frac{k}{m}} = \sqrt{\frac{285\,N\,m^{-1}}{5.16 \times 10^{-26}\,kg}} = 7.43 \times 10^{13}\,s^{-1}$$

$$ZPE = \frac{1}{2}\hbar\omega = \frac{1}{2} \cdot 1.055 \times 10^{-34}\,J\,s \cdot 7.43 \times 10^{13}\,s = 3.92 \times 10^{-21}\,J$$

4. Exercise 8B.2b

$\Delta E = E(v+1) - E(v) = (v+\frac{3}{2})\hbar\omega - (v+\frac{1}{2})\hbar\omega = \hbar\omega$

$\Delta E = 3.17 \text{ zJ} = 3.17 \times 10^{-21} \text{ J}$

$\omega = \frac{\Delta E}{\hbar} = 3.00 \times 10^{13} \text{ s}^{-1}$

$\omega = \sqrt{\frac{k}{m}} \Rightarrow k = \omega^2 m = (3.00 \times 10^{13} \text{ s}^{-1})^2 \cdot (2.88 \times 10^{-25} \text{ kg})$

$k = 260 \text{ kg s}^{-2} = 260 \text{ N m}^{-1}$

5. Exercise 8B.3b

$\Delta E = \hbar\omega \quad \omega = \sqrt{\frac{544\,N\,m^{-1}}{15.9949\,m_u}} = 1.43 \times 10^{12}\,s^{-1}$

$m_u = 1.6606 \times 10^{-27}\,kg$

$\Delta E = 1.51e^{-20}\,J$

$\Delta E = E_{photon} = h\nu \Rightarrow \nu = \frac{\Delta E}{h} = 2.28 \times 10^{13}\,s^{-1}$

$\lambda = \frac{c}{\nu} = \frac{2.99 \times 10^{8}\,m\,s^{-1}}{2.28 \times 10^{13}\,s^{-1}} = 1.31 \times 10^{-5}\,m$

6. (a) Determine force constant k from frequency ω:

$$\omega = \sqrt{\frac{k}{\mu}} \qquad k = \mu \omega^2$$

↑reduced mass in place of mass

Convert frequency in cm^{-1} (really wave number) to radians/s:

$^{35}Cl_2$: $\tilde{\nu} = 560\ cm^{-1}$ $\quad \tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \quad \nu = c\tilde{\nu}$

$$\omega = 2\pi\nu = 2\pi c\tilde{\nu}$$

$$k = \mu(2\pi c\tilde{\nu})^2 \qquad \mu = \frac{m_{Cl}\, m_{Cl}}{m_{Cl} + m_{Cl}} = \frac{35^2}{35+35}\ amu$$
$$= 17.5\ amu$$

$$k = 17.5\,(\underbrace{1.66\times 10^{-27}\ kg}_{1\ amu})(2\pi \cdot 2.99\times 10^{10}\ cm\ s^{-1} \cdot 560\ cm^{-1})^2$$

$$\boxed{k = 322\ kg\ s^{-2} = 322\ N\ m^{-1}} \quad (1\ N = 1\ kg\ m\ s^{-2})$$

(b) For $^{37}Cl_2$, $k = 322\ kg\ s^{-2}$ as for $^{35}Cl_2$

$$\mu = \frac{37\cdot 37}{37+37}\ amu = 18.5\ amu$$

$$\omega = \sqrt{\frac{k}{\mu}} = 1.02\times 10^{14}\ s^{-1}\ (\text{radians } s^{-1})$$
$$\nu = \frac{1}{2\pi}\omega = 1.62\times 10^{13}\ s^{-1}\ (\text{cycles } s^{-1})$$
$$\tilde{\nu} = \frac{\nu}{c} = 542\ cm^{-1}$$

(c) zero point energy $= \frac{1}{2}h\nu = 5.37 \times 10^{-21}\ J$ $(^{37}Cl_2)$

$$\left.\begin{aligned} E_0 &= \tfrac{1}{2}\underbrace{h\nu}_{\text{or } \hbar\omega} = 5.37 \times 10^{-21}\ J \\ E_1 &= \tfrac{3}{2}h\nu = 1.61 \times 10^{-20}\ J \\ E_2 &= \tfrac{5}{2}h\nu = 2.68 \times 10^{-20}\ J \end{aligned}\right\} \text{ from } E_v = (v+\tfrac{1}{2})\underbrace{h\nu}_{\text{or } \hbar\omega}$$

$v = 0, 1, 2, \ldots$

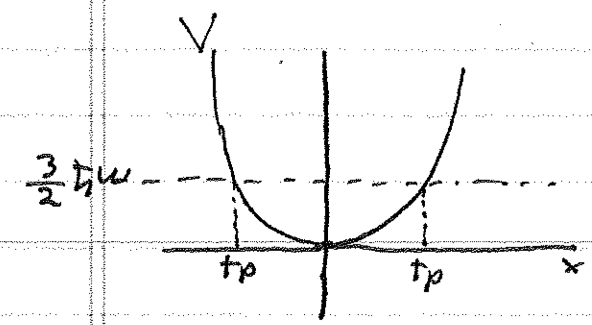
7. Calculations of the vibrational frequency and equilibrium bond length of Cl_2

	freq (cm^{-1})	error	r_e (Å)	error
Experiment	560		1.988	
HF/STO-3G	690	23.2%	2.063	3.8%
HF/6-31G*	595	6.3%	1.990	0.1%
B3LYP/6-31G*	506	-9.6%	2.042	2.7%
MP2/6-31G*	543	-3.0%	2.015	1.4%

There is quite a bit of variability among the methods. The best performer overall is MP2 in this case. In general, MP2 and B3LYP do similarly well and are better nhan HF; and the 6-31G* basis set does better than the STO-3G basis set, which is smaller. In any particular case, though, it is possible for a more approximate method to give a value closer to experiment; it may be an accident. Also note that for larger molecules, the higher levels of theory and bigger basis sets may take significantly more computer time. The method must be chosen with care. In this course, you will be told the appropriate method to use for each problem. Later, if you learn more about computational chemistry, you will be able to make informed choices.

8. (a) At classical turning point, total energy (E) equals potential energy (V)

$$E = (\overset{v=1}{v} + \tfrac{1}{2})\hbar\omega = V = \tfrac{1}{2} k x^2$$



tp = classical turning point

$$\tfrac{3}{2}\hbar\omega = \tfrac{1}{2} k x^2 \quad \text{at turning point}$$

$$x_{tp} = \pm\left(\frac{3\hbar\overset{\sqrt{k/m}}{\omega}}{k}\right)^{1/2} = \pm\sqrt{3}\left(\frac{\hbar^2}{mk}\right)^{1/4} = \boxed{\pm\sqrt{3}\,\alpha \quad \left(\alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4}\right)}$$

(b) $P(x > x_{tp}) = \int_{x_{tp}}^{\infty} |\psi_1|^2 dx$

$x_{tp} = \sqrt{3}\,\alpha \qquad \psi_1 = N_1 \cdot 2y e^{-y^2/2} \qquad N_1 = (\alpha \pi^{1/2} 2^1 1!)^{-\frac{1}{2}} = \frac{1}{\sqrt{2\alpha \pi^{1/2}}}$

$y = \frac{x}{\alpha} \qquad y_{tp} = \sqrt{3} \qquad dx = \alpha\, dy$

$$P = \underbrace{\frac{4\alpha}{2\alpha \pi^{1/2}}}_{\frac{2}{\sqrt{\pi}}} \underbrace{\int_{\sqrt{3}}^{\infty} y^2 e^{-y^2} dy}_{\frac{1}{2} z e^{-z^2} + \frac{\sqrt{\pi}}{4}(1 - \operatorname{erf}(z)) \text{ where } z = \sqrt{3}}$$

[given in problem]

$$P = \left(\frac{2}{\sqrt{\pi}}\right)\left(\frac{1}{2}\sqrt{3}\, e^{-3} + \frac{\sqrt{\pi}}{4}(1 - \operatorname{erf}(\sqrt{3}))\right)$$

$\boxed{P = 0.0557}$

Look up in Table in Text or online or in Excel.

$\operatorname{erf}(\sqrt{3}) = \operatorname{erf}(1.73) = 0.986$