

CHM 3411, Dr. Chatfield, Spring 2018
Problem Set 4
Due Monday, Feb 12

Suggested “warmups” (not to turn in): For Tunneling: Discussion question 8A.3; Exercises 8A.13(b). For Harmonic Oscillator: Discussion questions 8B.1-3; Exercises [all (b)] 8B.1-5.

Problems 1 and 2 explore tunneling. Problems 3-8 explore the harmonic oscillator.

1. (P8A.5) Many biological electron transfer reactions, such as those associated with biological energy conversion, may be visualized as arising from electron tunneling between protein-bound cofactors, such as cytochromes, quinones, flavins, and chlorophylls. This tunneling occurs over distances that are often greater than 1.0 nm, with sections of protein separating electron donor from acceptor. For a specific combination of donor and acceptor, the rate of electron tunneling is proportional to the transmission probability, with $\kappa = 7 \text{ nm}^{-1}$ (eq 8A.23). **By what factor does the rate of electron tunneling between two cofactors increase as the distance between them changes from 2.0 nm to 1.0 nm?**
2. Pretend that you are talking with a non-scientist who has a natural interest in science. You might want to picture a parent, or someone else you know who fits this description. Describe the concept of tunneling. Include why it is surprising and why we can, nevertheless, believe that it occurs. Give a couple of examples of physical phenomena or technology that depend on tunneling.
3. Exercise 8B.1b
4. Exercise 8B.2b
5. Exercise 8B.3b
6. The vibration of a diatomic molecule is analogous to harmonic oscillator problem discussed in class. The only difference is that in place of the mass, m , we must use the reduced (or effective) mass, μ , which is defined as):

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

where m_A and m_B are the masses of the individual atoms. [We will demonstrate this later when we get to spectroscopy.] The vibrational frequency for $^{35}\text{Cl}_2$ is 560 cm^{-1} [frequencies are often given in units of cm^{-1} (wavenumber units: $\tilde{\nu} = 1/\lambda$) instead of s^{-1}]

- (a) Determine the force constant for the bond in $^{35}\text{Cl}_2$.
- (b) Determine the vibrational frequency for $^{37}\text{Cl}_2$, assuming that the force constant is the same as for $^{35}\text{Cl}_2$ (a good assumption: the force constant is nearly independent of isotope). Hint: be sure you use the masses of individual atoms, not the molar masses, in the equations.
- (c) Determine the zero-point energy and the energies of the first three vibrational levels for $^{37}\text{Cl}_2$ ($v=0,1,2$).

7. Use Spartan to calculate the equilibrium bond length and vibrational frequency for $^{35}\text{Cl}_2$ (Spartan will use the ^{35}Cl isotope by default) and compare your answer with the experimental values ($r_e = 1.988 \text{ \AA}$, $\tilde{\nu} = 560 \text{ cm}^{-1}$). Do so with the following levels of theory: HF/STO-3G, HF/6-31G, B3LYP/6-31G*, MP2/6-31G*. Make a table of the r_e and $\tilde{\nu}$ and the percent error in each by level of theory. What do you conclude about the theoretical calculations?

Note: when you set up the calculations in Spartan, be sure to choose Equilibrium Geometry, check Infrared Spectrum, and check Vibrational Modes. Note that the Total Charge is neutral, and there are no unpaired electrons. You will find the vibrational frequency in the output. You will need to check the interatomic distance by hand, in the usual way. If you click the IR spectrum icon (after the calculation has finished), click on the green plus sign that appears, choose IR Calculated, and play around a bit, you will be able to see the Cl_2 molecule vibrating.

8. This question concerns the classical turning points for the $v=1$ state of a harmonic oscillator. Classically, the turning points are the maximum extension and the maximum compression the oscillator can have. At a classical turning point, the total energy (E_v) equals the potential energy (V), and consequently the kinetic energy (E_k) is zero.
- (a) Calculate the values of the classical turning points for the $v = 1$ state of a harmonic oscillator.
- (b) Calculate the probability of finding the oscillator beyond its positive classical turning point (i.e. for a diatomic molecule, the probability of finding the molecule stretched beyond the classical turning point). You will need to use a table of $\text{erf}(z)$. See Atkins, Table 8B.2 or Google “error function.” You will also need to evaluate the integral below. This can be done with integration by parts, and the result is:

$$\int_z^\infty x^2 e^{-x^2} dx = \frac{1}{2} z e^{-z^2} + \frac{\sqrt{\pi}}{4} (1 - \text{erf}(z))$$

HINT: The units will cancel when you convert to y (see text). You will need to evaluate the normalization constant N_v for a harmonic oscillator, which is:

$$N_v = (\alpha \pi^{1/2} 2^v v!)^{-1/2}$$