

Lecture 36, April 28, 2006

(Some material in this lecture has been adapted from Cramer, C. J. *Essentials of Computational Chemistry*, Wiley, Chichester: 2002; pp. 319-331.)

**Solved Homework**

Since molecular hydrogen only has two electrons, there is only one Coulomb integral deriving from evaluation of the generic expression for interelectronic repulsion

$$\left\langle \Psi \left| \sum_{i < j} \frac{1}{r_{ij}} \right| \Psi \right\rangle_{i=1, j=2} = \iint \iint \frac{|\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 d\omega_1 d\omega_2$$

where recall that the integration over spin coordinates  $\omega_1$  and  $\omega_2$  will give 2 for the singlet spin function.

For closed-shell hydrogen we can call the above integral  $J_{\sigma\sigma}$ . For the closed-shell wave function of  $H_2$  in eq. 35-8,  $J_{\sigma\sigma}$  is

$$\begin{aligned} J_{\sigma\sigma} &= \iint \frac{|\sigma(1)|^2 |\sigma(2)|^2}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{1}{4} \iint \frac{[1s_a(1) + 1s_b(1)]^2 [1s_a(2) + 1s_b(2)]^2}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{1}{4} \left[ (aa|aa) + 2(aa|ab) + (aa|bb) + 2(ab|aa) + 4(ab|ab) \right. \\ &\quad \left. + 2(ab|bb) + (bb|aa) + 2(bb|ab) + (bb|bb) \right] \end{aligned}$$

where we've used the shorthand notation for Coulomb integrals and stopped writing 1s everywhere. Now, note that since both a and b are 1s orbitals, and since order of indices doesn't matter, there are really only 4 kinds of integrals: all 4 indices identical, 3 of one index and one of the other, 2 of each index in each case paired on the same side, and 2 of each index with both indices appearing once on each side. That is we can simplify to

$$J_{\sigma\sigma} = \frac{1}{2}(aa|aa) + 2(aa|ab) + \frac{1}{2}(aa|bb) + (ab|ab)$$

Now we'll do the same for the open-shell wave function of eq. 35-9. In that case we have

$$\begin{aligned} J_{\text{OSS}} &= \frac{1}{2} \iint \frac{[1s_a(1)1s_b(2) + 1s_b(1)1s_a(2)]^2}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{1}{2} [(aa|bb) + 2(ab|ba) + (bb|aa)] \\ &= (aa|bb) + (ab|ab) \end{aligned}$$

Notice that this is the expected result for the case of two electrons in two orbitals, namely,  $J_{ab} + K_{ab}$ .

Now, when the two atoms are very far apart, the only integral that won't be zero will be (aalaa). So, only the closed-shell wave function still has a Coulomb repulsion at long distance (this makes intuitive sense—in the open-shell wave function there is one electron on each atom, so if they are far apart, how can there be Coulomb repulsion?) This is another illustration of why RHF dissociates incorrectly, because of the contribution of the ionic term that places both electrons on one atom.

At short distance (i.e., bonding distance), both wave functions have one Coulomb contribution (ablab), so there's no distinction between them there. The open-shell case has a full (aalbb) and the closed-shell case only 1/2 (aalbb). However, the closed-shell case also has 1/2 (aalaa) and it is obvious that this must be bigger than 1/2 (aalbb) for every interatomic distance (until the two nuclei fuse into one!) So, even neglecting the extra repulsion from the 2(aalab) in the closed-shell wave function, it clearly has more Coulomb repulsion at bonding distance than the open-shell wave function.

So, why does  $\text{H}_2$  form a bonded closed-shell ground state? The answer must be that the attraction to the nuclei is much larger when both electrons are in the  $\sigma$  orbital than is the case when each is forced to separately occupy a single  $1s$  orbital. Just looking at the shapes of the orbitals this seems reasonable. The  $\sigma$  orbital has most of its amplitude "sandwiched" between the two nuclei, so it's close to both at the same time. The individual  $1s$  orbitals are each separately a bit too far from the other H nucleus to enjoy as much nuclear attraction.

## Thermochemistry

In the very recent past, it has become possible under certain circumstances to observe single molecules in the laboratory. Nevertheless, the vast majority of chemical research concerns itself not with individual molecules, but instead with macroscopic quantities of matter that are made up of unimaginably large numbers of molecules. The behavior of such ensembles of molecules is governed by the empirically determined laws of thermodynamics, and most chemical reactions and many chemical properties are

defined in terms of some of the fundamental variables of thermodynamics, like enthalpy, entropy, free energy, and others.

Until now, we have for the most part concerned ourselves only with the potential and kinetic energies of individual electrons and nuclei in *single* molecules, and one of our rare connections to thermodynamics has been in some sense a misleading one, namely that we have often converted atomic units into other units more typically associated with macroscopic quantities, e.g., kcal mol<sup>-1</sup> or kJ mol<sup>-1</sup>. This sometimes leads newcomers to the field to think of the atomic unit of energy, the hartree, as being enormously large, since 1  $E_h$  is equal to 627.51 kcal mol<sup>-1</sup>. In reality, however, the hartree is a tremendously *tiny* unit, since “kcal mol<sup>-1</sup>”, as its name makes clear, refers to the energy associated with *one mole* (i.e., 6.0221 × 10<sup>23</sup>) of molecules, not with the single molecule that is the typical subject of an electronic structure calculation. Moreover, when we make comparisons between two different calculations, say to determine the relative energies of two isomers, and we carry out such simple unit conversions, we tacitly (and often incorrectly) assume that the potential energy difference determined from the calculation is all that matters when comparing to a *measured* energy difference that is almost always in the form of some thermodynamic quantity, most typically enthalpy or free energy. Within the context of certain assumptions, however, a connection can be established in a rigorous way between single-molecule calculations and ensemble thermodynamic quantities.

The first step in moving from the microscopic regime to the macroscopic is to recognize that the Born-Oppenheimer potential energy surface is fundamentally a classical construct (although the energies of various points whose coordinates are defined by the fixed nuclear positions are determined from quantum mechanical calculations of the electronic energy). As we’ve discussed several times, when the motion of the nuclei on this surface is also accounted for in a quantum mechanical way, energy is “tied up” in the molecular vibrations. This is true even at a temperature arbitrarily close to absolute zero, since, although every vibrating molecule will be in its lowest energy vibrational state at so low a temperature, the lowest vibrational energy level for any bound vibration is *not zero*.

Instead, within the harmonic oscillator approximation, the energy of the lowest vibrational level for any individual vibration can be determined from eq. 35-1 as  $h\omega/2$  where  $h$  is Planck’s constant (6.6261 × 10<sup>-34</sup> J s) and  $\omega$  is the vibrational frequency given by eq. 35-2. The sum of all of these energies over all molecular vibrations defines the zero-point vibrational energy (ZPVE). We may then define the “internal energy”  $U$  at 0 K for a molecule as

$$U_0 = E_{\text{elec}} + \sum_i^{\text{modes}} \frac{1}{2} h\omega_i \quad (36-1)$$

where  $E_{\text{elec}}$  is the energy for the stationary point on the Born-Oppenheimer PES.

Statistical mechanics is, obviously, a course unto itself in the standard chemistry/physics curriculum (Chem 3501 here at Minnesota), and no attempt will be made here to introduce concepts in a formal and rigorous fashion. Instead, the fundamental equations describing the relationships between key thermodynamic variables are presented here without derivation. From a quantum chemistry standpoint, many simplifying assumptions make most of the details fairly easy to follow, so we will proceed with confidence.

In order to deal with collections of molecules in statistical mechanics, one typically requires that certain macroscopic conditions be held constant by external influence. The enumeration of these conditions defines an “ensemble”. We will confine ourselves in this chapter to the so-called “canonical ensemble”, where the constants are the total number of particles  $N$  (molecules, and, for our purposes, identical molecules), the volume  $V$ , and the temperature  $T$ . This ensemble is also sometimes referred to as the  $(N, V, T)$  ensemble.

Just as there is a fundamental function that characterizes the microscopic system in quantum mechanics, i.e., the wave function, so too in statistical mechanics there is a fundamental function having equivalent status, and this is called the “partition function”. For the canonical ensemble, it is written as

$$Q(N, V, T) = \sum_i e^{-E_i(N, V)/k_B T} \quad (36-2)$$

where  $i$  runs over all possible energy states of the system having energy  $E_i$  and  $k_B$  is Boltzmann’s constant ( $1.3806 \times 10^{-23} \text{ J K}^{-1}$ ).

Within the canonical ensemble, and using established thermodynamic definitions, all of the following are true

$$U = k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{N, V} \quad (36-4)$$

$$H = U + PV \quad (36-5)$$

$$S = k_B \ln Q + k_B T \left( \frac{\partial \ln Q}{\partial T} \right)_{N, V} \quad (36-6)$$

$$G = H - TS \quad (36-7)$$

where the notation associated with the partial derivatives in eqs. 36-4 and 36-6 implies  $N$  and  $V$  held constant during differentiation with respect to  $T$ ,  $H$  is enthalpy,  $P$  is pressure,  $S$  is entropy, and  $G$  is (Gibbs) free energy.

Of course, the elegance of eqs. 36-4 to 36-7 is somewhat muted by the daunting prospect of finding an explicit representation of  $Q$  that permits the necessary partial differentiations of eqs. 36-4 and 36-6 to be carried out. For a true ensemble,  $Q$  must be some fantastically complex many-body function involving a staggeringly enormous number of energy levels. So, in order to make progress, we indulge in a number of simplifying assumptions.

We begin by assuming that our ensemble is an ideal gas. The first consequence of this assumption, since ideal gas molecules *by definition* do not interact with one another, is that we may rewrite the partition function as

$$\begin{aligned}
 Q(N, V, T) &= \frac{1}{N!} \sum_i e^{-[\varepsilon_1(V) + \varepsilon_2(V) + \dots + \varepsilon_N(V)] / k_B T} \\
 &= \frac{1}{N!} \left[ \sum_{j(1)} e^{-\varepsilon_{j(1)}(V) / k_B T} \right] \left[ \sum_{j(2)} e^{-\varepsilon_{j(2)}(V) / k_B T} \right] \dots \left[ \sum_{j(N)} e^{-\varepsilon_{j(N)}(V) / k_B T} \right] \\
 &= \frac{1}{N!} \left[ \sum_k^{\text{levels}} g_k e^{-\varepsilon_k(V) / k_B T} \right]^N \\
 &= \frac{[q(V, T)]^N}{N!}
 \end{aligned} \tag{36-8}$$

where the factor of  $1/N!$  derives from the quantum mechanical indistinguishability of the particles,  $\varepsilon$  is the total energy of an individual molecule, and the change on going from the first to second line derives from expressing the exponential of all possible sums of energies as a sum of all possible products of exponentials of individual energies. On going from the second to third line, the sum has been changed so that it goes over discrete energy levels, rather than individual states, and  $g_k$  is the degeneracy of level  $k$ . The quantity in brackets on the third line defines the *molecular* partition function  $q$ , which appears on the fourth line.

A second consequence of the ideal gas assumption is that  $PV$  in eq. 36-5 may be replaced by  $Nk_B T$ . In the special case where we are working with one mole of molecules, in which case  $N = N_A$  (Avogadro's number), we may replace  $PV$  with  $RT$ , where  $R$  is the universal gas constant ( $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ ).

Overall, then, we have reduced the problem from finding the ensemble partition function  $Q$  to finding the molecular partition function  $q$ . In order to make further progress, we assume that the molecular energy  $\varepsilon$  can be expressed as a separable sum of electronic, translational, rotational, and vibrational terms, i.e.,

$$\begin{aligned}
q(V,T) &= \sum_k^{\text{levels}} g_k e^{-\varepsilon_k(V)/k_B T} \\
&= \sum_k^{\text{levels}} g_k e^{-[\varepsilon_{\text{elec}} + \varepsilon_{\text{trans}}(V) + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}}]_k / k_B T} \\
&= \left[ \sum_i^{\text{elec}} g_i e^{-\varepsilon_i / k_B T} \right] \left[ \sum_j^{\text{trans}} g_j e^{-\varepsilon_j(V) / k_B T} \right] \left[ \sum_k^{\text{rot}} g_k e^{-\varepsilon_k / k_B T} \right] \left[ \sum_l^{\text{vib}} g_l e^{-\varepsilon_l / k_B T} \right] \\
&= q_{\text{elec}}(T) q_{\text{trans}}(V,T) q_{\text{rot}}(T) q_{\text{vib}}(T)
\end{aligned} \tag{36-9}$$

where again advantage is taken of the ability to express an exponential of sums as a sum of products of exponentials, and the separate lines make clear that the degeneracy of a total molecular energy level is simply the product of the degeneracies of each of its contributing components.

Note in equations 36-4 and 36-6,  $Q$  always appears as the argument of the natural logarithm function. Using eqs. 36-8 and 36-9, our assumptions to this point allow us to write

$$\begin{aligned}
\ln[Q(N,V,T)] &= \ln \left\{ \frac{[q_{\text{elec}}(T) q_{\text{trans}}(V,T) q_{\text{rot}}(T) q_{\text{vib}}(T)]^N}{N!} \right\} \\
&= N \{ \ln[q_{\text{elec}}(T)] + \ln[q_{\text{trans}}(V,T)] + \ln[q_{\text{rot}}(T)] + \ln[q_{\text{vib}}(T)] \} \\
&\quad - \ln(N!) \\
&\approx N \{ \ln[q_{\text{elec}}(T)] + \ln[q_{\text{trans}}(V,T)] + \ln[q_{\text{rot}}(T)] + \ln[q_{\text{vib}}(T)] \} \\
&\quad - N \ln N + N
\end{aligned} \tag{36-10}$$

where going from the second to third line makes use of Stirling's approximation for  $\ln(N!)$  when  $N$  is large. This separation of terms by the logarithm function makes evident that we may speak of individual components—electronic, translational, rotational, and vibrational—of thermodynamic functions within our approximate treatment. All that remains is to express the various components of the molecular partition function in some useful, preferably analytic, form.

*Electronic Partition Function.* For a typical, closed-shell singlet molecule, the degeneracy of the ground state is unity, and the various excited states are so high in energy that, at least at temperatures below thousands of degrees, they make no significant contribution to the partition function. Because  $U_0$  already includes  $E_{\text{elec}}$  (eq. 36-1), we can view the energy of the ground state as being the zero of energy in the exponential of the electronic partition function. In that case, the electronic partition function is simply  $q_{\text{elec}} = 1$  (we're assuming the higher energy contributions to be negligible, so only  $e^0$

survives). Inspection of eq. 36-6 then reveals that the electronic component of the entropy will be zero ( $\ln$  of 1 is zero, and the constant 1 obviously has no temperature dependence, so both terms in  $S$  involving  $q_{\text{elec}}$  are also zero). So, that one was easy.

*Molecular Translation Partition Function.* To evaluate  $q_{\text{trans}}$ , we assume that the molecule acts as a particle in a 3-dimensional cubic box of dimension  $a^3$  where  $a$  is the length of one side of the cube. The energy levels for this elementary quantum mechanical system are given by

$$\varepsilon_{\text{trans}}(n_x, n_y, n_z) = \frac{h^2}{8Ma^2} (n_x^2 + n_y^2 + n_z^2) \quad (36-11)$$

where  $M$  is the molecular mass, and each energy level has associated with it the three unique quantum numbers  $n_x$ ,  $n_y$ , and  $n_z$ . Because the energy levels for the particle in a box are very, very closely spaced (at least for a box of macroscopic dimensions), the sum appearing in the partition function may be replaced by an indefinite integral, and this integral can be evaluated analytically as

$$q_{\text{trans}}(V, T) = \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} V \quad (36-12)$$

where the volume of the box is now written  $V$  as opposed to  $a^3$ . Note that it is only the translational partition function that depends on volume, and it does so because particle-in-a-box wave functions cannot be normalized without choice of a specific, finite, non-zero volume (it can be shown that it is only the volume that matters, and not the shape of the box). It is this term, then, that dictates the necessity of choosing a “standard state” volume to ensure comparison of thermodynamic values in a consistent fashion. Because we have chosen to model our substance as an ideal gas, we may replace  $V$  by  $RT/P$  and specify a standard-state pressure instead. This is typically the language that is used in electronic structure calculations, and the usual choice for standard state is 1 atm pressure (corresponding to a standard-state molar volume of 24.45 L at 298 K). Typically, rather than list standard-state conditions in words again and again, the standard state is indicated by an accepted abbreviation, such as the superscript “o” appearing in eq. 36-14 below.

Evaluating equations 36-4 and 36-6 for a molar quantity of particles using eq. 36-12 for the translational partition function gives

$$U_{\text{trans}} = \frac{3}{2} RT \quad (36-13)$$

$$S_{\text{trans}}^{\circ} = R \left\{ \ln \left[ \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{V}{N_A} \right] + \frac{5}{2} \right\} \quad (36-14)$$

where the last two terms in the final line of eq. 36-10, i.e., those deriving from Stirling’s approximation, are typically assigned to the translational partition function as well. As

they have no temperature dependence, this has no impact on  $U_{\text{trans}}$ , however,  $N_A$  appears in the entropy of translation because of them. Note that to compute  $U_{\text{trans}}$  and  $S_{\text{trans}}$  does not require *any* quantum chemistry. All one needs to know is the molecular mass; everything else is just constants and choice of standard state. Quantum chemistry only entered in providing the solution of the particle-in-a-box energy levels.

*Molecular Rotational Partition Function.* We previously derived in detail the approach that is taken to solving the rigid-rotor nuclear Schrödinger equation in order to compute rotational wave functions and energy levels, and discussed the particular cases of diatomic molecules and polyatomic prolate tops (see Lecture 13). The completely general rigid-rotor Schrödinger equation for a molecule characterized by 3 unique axes and associated moments of inertia does not lend itself to easy solution. However, by pursuing a generalization of the *classical* mechanical rigid rotor problem, one can derive a quantum mechanical approximation that is typically quite good. Within that approximation, the rotational partition function becomes

$$q_{\text{rot}}(T) = \frac{\sqrt{\pi I_A I_B I_C}}{\sigma} \left( \frac{8\pi^2 k_B T}{h^2} \right)^{3/2} \quad (36-15)$$

where  $I_A$ ,  $I_B$ , and  $I_C$  are the principal moments of inertia, and  $\sigma$  is a symmetry number. In this case,  $\sigma$  is the number of pure rotations that carry the molecule into itself (e.g., 2 for water).

Evaluation of the rotational components of the internal energy and entropy using this partition function for non-linear molecules gives

$$U_{\text{rot}} = \frac{3}{2} RT \quad (36-16)$$

$$S_{\text{rot}} = R \left\{ \ln \left[ \frac{\sqrt{\pi I_A I_B I_C}}{\sigma} \left( \frac{8\pi^2 k_B T}{h^2} \right)^{3/2} \right] + \frac{3}{2} \right\} \quad (36-17)$$

Again, it should be noted that evaluating the rotational components of  $U$  and  $S$  requires relatively little in the way of molecular information. Only the principal moments of inertia are required, which derive entirely from the molecular structure. Note that the units for quantities appearing in the partition function must be chosen consistently so as to render  $q$  dimensionless.

*Molecular Vibrational Partition Function.* In a polyatomic molecule with many vibrations, we simplify the vibrational partition function much as the original molecular partition function was simplified: we assume that the total vibrational energy can be expressed as a sum of individual energies associated with each mode, in which case, for a non-linear molecule, we have

$$\begin{aligned}
 q_{\text{vib}}(T) &= \sum_i g_i e^{-[\varepsilon_1 + \varepsilon_2 + \dots + \varepsilon_{3N-6}]_i / k_B T} \\
 &= \left[ \sum_{j(1)} e^{-\varepsilon_{j(1)} / k_B T} \right] \left[ \sum_{j(2)} e^{-\varepsilon_{j(2)} / k_B T} \right] \dots \left[ \sum_{j(3N-6)} e^{-\varepsilon_{j(3N-6)} / k_B T} \right]
 \end{aligned} \tag{36-18}$$

where the energies  $\varepsilon_k$  are the vibrational energy levels associated with each mode  $k$ , and there are  $3N-6$  such modes in a non-linear molecule ( $3N-5$  in a linear molecule) where  $N$  is the number of atoms.

To evaluate the sums associated with each mode, we assume that the modes can be approximated as quantum mechanical harmonic oscillators, in which case the energy levels are known from analytic solution of that Schrödinger equation, and the partition function for any individual mode is

$$q_{\text{vib}}^{\text{QMHO}}(T) = \sum_{k=0}^{\infty} e^{-kh\omega / k_B T} \tag{36-19}$$

(note that  $k$ , and not  $k + (1/2)$ , appears in the energies because the zero-point vibrational energy  $(1/2)h\omega$  has already been included in the zero of energy by eq. 36-1).

The sum in eq. 36-19 is well known as a convergent geometric series, so that we may write

$$q_{\text{vib}}^{\text{QMHO}}(T) = \frac{1}{1 - e^{-h\omega / k_B T}} \tag{36-20}$$

This is a serendipitous result, insofar as the energy level spacing for most molecular vibrations is sufficiently large that significant errors would be introduced by replacing the sum with the corresponding indefinite integral as we did successfully for translation and rotation (such a replacement actually would amount to assuming a *classical* harmonic oscillator, for which  $q_{\text{vib}} = k_B T / h\omega$ ; by expanding the exponential in eq. 36-20 as its corresponding power series, one can see that the classical and quantum partition functions agree only when  $k_B T \gg h\omega$ ).

Using eq. 36-20 for each mode, the full vibrational partition function of eq. 36-18 can be expressed as

$$q_{\text{vib}}(T) = \prod_{i=1}^{3N-6} \left( \frac{1}{1 - e^{-h\omega_i / k_B T}} \right) \tag{36-21}$$

where  $\Pi$  implies a product series (the multiplicative analogy of a sum), and the upper limit would be  $3N-5$  for a linear molecule. Evaluation of the vibrational components of the internal energy and entropy using the partition function of eq 36-21 provides

$$U_{\text{vib}} = R \sum_{i=1}^{3N-6} \frac{h\omega_i}{k_{\text{B}}(e^{h\omega_i/k_{\text{B}}T} - 1)} \quad (36-22)$$

$$S_{\text{vib}} = R \sum_{i=1}^{3N-6} \left[ \frac{h\omega_i}{k_{\text{B}}T(e^{h\omega_i/k_{\text{B}}T} - 1)} - \ln(1 - e^{-h\omega_i/k_{\text{B}}T}) \right] \quad (36-23)$$

Note that eqs. 36-22 and 36-23 take the vibrational frequencies as independent variables, and as such cannot be calculated *ab initio* without first optimizing a structure at some level of quantum theory and then computing the second derivatives in order to obtain the frequencies within the harmonic oscillator approximation as we discussed last lecture.

In practice, then, it is fairly straightforward to convert the potential energy determined from an electronic structure calculation into a wealth of thermodynamic data—all that is required is an *optimized structure* with its associated *vibrational frequencies*. The agreement between theory and experiment can be extraordinarily good. For example, more than 20 years ago Hout et al. computed absolute entropies  $S^\circ$  at 300 K for a large number of small molecules at the HF/3-21G level and obtained agreement with experiment within  $0.1 \text{ cal mol}^{-1} \text{ K}^{-1}$  for many cases (Hout, R. F., Jr.; Levi, B. A.; Hehre, W. J. *J. Comput. Chem.* **1982**, 3, 234). For our old friend water, the predicted entropy is 45.11 e.u. at the HF/3-21G level, and 45.10 e.u. experimentally.

Absolute heat capacities at constant volume can also be computed using the thermodynamic definition

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V \quad (36-24)$$

and the various equations for components of  $U$  above.

So, to summarize, within the context of the ideal gas assumption, *we can compute any thermochemical quantity of interest for a given molecule simply by computing, for its optimized geometry, its electronic energy (including nuclear repulsion) and its vibrational frequencies from the harmonic oscillator approximation.* Thus, we can compare theoretical quantities directly to measured experimental quantities, which are nearly always in the form of  $\Delta H^\circ$  or  $\Delta G^\circ$ .

**Homework**

To be solved in class:

To what value does the free energy associated with a vibrational mode tend as the frequency of the vibration tends to zero? (Hint: Use a power series expansion for the exponential function.) Does this result seem physically meaningful?

To be turned in for possible grading May 5:

Write a haiku about quantum mechanics. Recall that haiku refers to a Japanese form of poetry that involves three lines having five, seven, and five syllables, respectively (see <http://www.toyomasu.com/haiku/> for more history and examples). Poetry forms other than haiku will *not* earn any points, although you are welcome to turn them in as supplemental art if you are feeling inspired. A proper haiku will earn a full grade of 5 points (we will not attempt to grade on the subjective measure of quality...)