Solved Homework

From

$$K_{i/j} = \begin{bmatrix} A \\ B \end{bmatrix} = \frac{\% (E_A)}{\% (E_B)} = \frac{e^{-E_A/k_BT}}{e^{-E_B/k_BT}} = e^{-(E_A - E_B)/k_BT}$$

Let us assume $K = 1$, in which case $E_A - E_B$ is zero. An error of a factor of 10 means $K = 10$ (or 0.1, the only difference will be in the sign of $E_A - E_B$ and not its magnitude). So, we simply need solve

$$10 = e^{-(E_A - E_B)/k_BT}$$

for $\Delta E = E_A - E_B$, which is, at 25 °C (298 K)

$$\Delta E = -k_BT \ln 10$$

$$= -(1.3806 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})(2.3026)$$

$$= 9.4733 \times 10^{-21} \text{ J}$$

At 500 °C (773 K), we have

$$\Delta E = -k_BT \ln 10$$

$$= -(1.3806 \times 10^{-23} \text{ J K}^{-1})(773 \text{ K})(2.3026)$$

$$= 2.4573 \times 10^{-20} \text{ J}$$

The numbers above correspond to the errors in the predicted energy difference that would lead to an error of an order of magnitude in the equilibrium constant (the numbers are, of course, independent of what the equilibrium constant really is).

A quick glance at the form of the equation for the rate constant
should make clear that the energy errors will be the same for the rate constant as for the
equilibrium constant (prove this to yourself if you don’t see it! Note that the prefactor of
$k_B T$ makes no difference because an error that is a “factor” of ten implies that the ratio
of the wrong and right rate constants is 10, so the prefactor disappears as it is present in
both the numerator and denominator of the ratio).

These are, of course, tiny energy differences, but that is because we really in this
case need to think in terms of large collections of molecules, not single molecules (how
can there be an equilibrium constant for one molecule?) So, if we multiply by
Avogadro’s number $(6.02 \times 10^{23} \text{ mol}^{-1})$ and divide by 1,000 (so we have kJ instead of J),
we get the more typical molar quantities $5.7 \text{ kJ mol}^{-1}$ (298 K) and $14.8 \text{ kJ mol}^{-1}$ (773 K)
[or, $1.4 \text{ kcal mol}^{-1}$ (298 K) and $3.5 \text{ kcal mol}^{-1}$ (773 K)]. So, not much room for error,
particularly at low temperatures... (drat interesting chemical quantities always depending
exponentially on energy differences!)

The final question was what fraction is this energy difference at 298 K of the total
energy of HF/STO-3G water. Noting 1 a.u. of energy (1 $E_h$) is $4.36 \times 10^{-18}$ J, the total
energy of water, at $-74.9659012170$ a.u. is $3.27 \times 10^{-16}$ J. The energy error $9.47 \times 10^{-21}$
J is a mere 0.003% of that energy. So, an error of 0.003% in a calculation of water could
throw off an equilibrium constant or a rate constant by an order of magnitude. Imagine
how tight the requirements are for a really big molecule!

**Vibrational Spectroscopy Revisited**

Last lecture, we considered the solution of the 1-dimensional vibrational
Schrödinger equation for an arbitrary potential to compute accurate vibrational wave
functions and transition energies. While this approach is quite accurate for select
instances, it is too demanding for a molecule with many degrees of freedom. Given the
importance of vibrational (infrared) spectroscopy for identification of molecular
structure, it would be nice to have a quicker, approximate method to obtain all of the
vibrational frequencies for a molecule from quantum mechanics.

You will recall that, in the 1-dimensional case, a dramatic simplification occurs
when the potential is assumed to be harmonic. In that case, one has a Schrödinger
equation for which there are analytical solutions (the quantum mechanical harmonic
oscillator wave functions). These eigenfunctions are products of Hermite polynomials
and gaussian functions, and their eigenvalues are

$$E = \left( n + \frac{1}{2} \right) \hbar \omega$$

where $n$ is the vibrational quantum number beginning at 0 and
\[ \omega = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (35-2) \]

where \( \mu \) is the reduced mass and \( k \) is the bond force constant, i.e., the second derivative of the energy with respect to bond stretching evaluated at the equilibrium bond length (see eq. 9-3).

So, what about the polyatomic case? In that case, we must carry out a multidimensional Taylor expansion analogous to the 1-dimensional eq. 9-2. This leads to the multidimensional analog

\[
\left[ -\sum_{i=1}^{3N} \frac{1}{2m_i} \frac{\partial^2}{\partial q_i^2} + \frac{1}{2} (\mathbf{q} - \mathbf{q}_{eq})^T \mathbf{H} (\mathbf{q} - \mathbf{q}_{eq}) \right] \Xi (\mathbf{q}) = E \Xi (\mathbf{q}) \quad (35-3)
\]

where \( \mathbf{q} \) is the vector of atomic cartesian coordinates, \( \mathbf{q}_{eq} \) defines the equilibrium structure, and \( \mathbf{H} \) is the Hessian matrix defined by eq. 32-6. (Remember, no gradient terms appear in this Taylor expansion because we’re expanding about a minimum, so all gradients are zero. Thus, to use this approach, one must have an optimized geometry from which \( \mathbf{q} \) is taken and for which \( \mathbf{H} \) is computed.)

While eq. 35-3 has a well defined potential energy function, it is quite difficult to solve in the indicated coordinates. However, by a clever transformation into a unique set of mass-dependent spatial coordinates \( \mathbf{q}' \), it is possible to separate the \( 3N \)-dimensional eq. 35-3 into \( 3N \) one-dimensional Schrödinger equations. These equations are identical to eq. 9-4 in form, that is they appear as

\[
\left[ -\frac{1}{2\mu} \frac{d^2}{dq'^2} + \frac{1}{2} kq'^2 \right] \xi (q') = E \xi (q') \quad (35-4)
\]

but they have force constants and reduced masses that are defined by the action of the transformation process on the original coordinates. Each component of \( \mathbf{q}' \) corresponding to a molecular vibration is referred to as a “normal mode” for the system, and with each component there is an associated set of harmonic oscillator wave functions and eigenvalues that can be written entirely in terms of square roots of the force constants found in the Hessian matrix and the atomic masses.

Note that because eq. 35-3 is over the full \( 3N \) coordinates, the transformed coordinate system \( \mathbf{q}' \) includes 3 translational and 3 rotational (2 for linear molecules) “modes”. The eigenvalues associated with these modes are typically very close to zero, and indeed, the degree to which they are close to zero can be regarded as a diagnostic of how well optimized the structure is in terms of being at the local minimum geometry.
A separate interesting point is that the form of eq. 35-3 is valid for all stationary points, not just minima on the PES. However, for non-minima there will be one or more normal mode force constants that will be negative, corresponding to motion along modes that lead to energy lowering. Insofar as the frequencies are computed from the square roots of the force constants, this leads to an imaginary frequency. Frequency calculations thus are diagnostic as to the nature of stationary points: All positive frequencies implies a (local) minimum, one imaginary frequency implies a transition state structure, and two or more imaginary frequencies refer to stationary points characterized by additional negative force constants. Such structures are sometimes useful in searching for TS structures by following the various energy-lowering modes, but they have no chemical significance. Thus, since there is no guarantee that a geometry minimization that leads to a structure with zero gradients will produce a minimum (or a transition-state, if that is what one is looking for), a frequency calculation is useful to verify what has happened.

So, how good is theory for IR spectral prediction? In the table below are listed experimental and computed vibrational frequencies (cm⁻¹) at the Hartree-Fock level using a basis set called 3-21G (it’s about twice the size of STO-3G, so more flexible) for s-trans 1,3-butadiene (s-trans means the two double bonds are trans about the single bond). There are 10 atoms, so there are 3N–6 = 24 degrees of freedom.

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<th>Experiment</th>
<th>Computed</th>
<th>Unsigned Error</th>
<th>Scaled Comput.</th>
<th>Unsigned Error</th>
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Mean error: 183.7 33.0
Notice that the performance of the raw HF level is not particularly impressive. There is a mean unsigned error of almost 184 cm\(^{-1}\), which is quite a bit in an IR spectrum. However, if we simply multiply each frequency by 0.9 (i.e., we apply a “scale factor”) we can improve the mean unsigned error to only 33 cm\(^{-1}\). This is really quite good! Indeed, the predictive quality is sufficient to be useful in identifying unknown molecules, as we will see in a moment. However, before doing that, it is instructive to consider, why do we need to apply a scale factor to get better accuracy?

To answer that question, first notice the sense of the error in the unscaled predictions. Every single frequency is predicted to be too large compared to experiment. Since the frequency depends only on the force constant and the reduced mass, and since there is no quantum chemistry in the reduced mass (it just comes from coordinate transformation), it must be that HF theory predicts the force constants all to be too large. Put differently, HF bonds are too strong. So, why might HF bonds be too strong?

In this case, it is helpful to think about a very simple molecule, H\(_2\). If we were to do an HF calculation on molecular hydrogen, taking as our basis set a 1s function on each H (label the two H atoms “a” and “b”), we would find that our two MOs (one occupied with 2 electrons, one empty) would be an in-phase combination of equally weighted 1s basis functions (the occupied MO) and an out-of-phase such combination (the empty one). These are the classic \(\sigma\) bonding and \(\sigma^*\) antibonding orbitals of H\(_2\). So, the many electron determinant is just

\[
\Psi = \left| \phi^2 \right>
\]

But, let’s actually write this simple Slater determinant out in more detail, noting that

\[
\phi = \frac{1}{\sqrt{2}} (1s_a + 1s_b)
\]

Then we have
which is the usual result for the closed-shell singlet. Let’s consider only the spatial part of the wave function. If we expand that using eq. 35-6 we have

\[
\Psi = \frac{1}{\sqrt{2}} \sigma(1)\sigma(2) \\
= \frac{1}{\sqrt{2}} \sigma(1)\sigma(2) \left[ \sigma(1)\sigma(2) - \sigma(2)\sigma(1) \right] \\
= \frac{1}{\sqrt{2}} \sigma(1)\sigma(2) \left[ \alpha(1)\beta(2) - \alpha(2)\beta(1) \right]
\]

(35-7)

which is the usual result for the closed-shell singlet. Let’s consider only the spatial part of the wave function. If we expand that using eq. 35-6 we have

\[
\Psi = \frac{1}{\sqrt{2}} \sigma(1)\sigma(2) \\
= \frac{1}{\sqrt{2}} \left[ \frac{1}{\sqrt{2}} \left( l_s^a(1) + l_s^b(1) \right) \right] \left[ \frac{1}{\sqrt{2}} \left( l_s^a(2) + l_s^b(2) \right) \right] \\
= \frac{1}{2\sqrt{2}} \left[ l_s^a(1)l_s^a(2) + l_s^a(1)l_s^b(2) + l_s^b(1)l_s^a(2) + l_s^b(1)l_s^b(2) \right]
\]

(35-8)
Qualitatively, what does eq. 35-8 mean? It says that we should think of the spatial part of the wave function as being one part both electrons around $H_a$ (the first term in brackets), two parts one electron around $H_a$ while the other is around $H_b$ (the next two terms), and one part where both electrons are around $H_b$. This is evidently perfectly fine when the two H atoms are separated by their equilibrium bond length (about 0.7 Å).

But, what happens if we pull the two hydrogen atoms far away from one another? In that case, the parts of the wave functions with one electron around each H atom seem quite reasonable—that’s how $H_2$ separates. But, the two components where both electrons are around a single H atom correspond to the situation where one H is $H^+$ and the other $H^-$. This is a very high energy situation since the ionization potential of H (to make $H^+$) is 13.6 eV (remember that we know this from exact one-electron quantum mechanics), and the electron affinity of H (to make $H^-$) is very, very small.

So, those so-called ionic terms make the energy very high. We know that the reasonable long-distance wave function should include only the one-electron-on-each-H terms, i.e.,

$$\Phi = \frac{1}{2} [l_s_a(1)l_s_b(2) + l_s_b(1)l_s_a(2)] [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

(35-9)

where we’ve put the singlet spin function back in explicitly. But, notice that this is our old friend the open-shell singlet (cf. eq. 22-5), which we know is not a single determinant but is instead a linear combination of two determinants. Since restricted Hartree-Fock theory requires a single determinant, it can’t ever “make” this better wave function, so when bonds stretch the energy goes too high too fast.

That’s why RHF force constants are too large, because the single determinant formalism of RHF forces dissociation to be unrealistically high in energy by inclusion of ionic terms in the wave function. What is fascinating is that the same scale factor that improved our computed frequencies for 1,3-butadiene works equally well for just about any HF/3-21G frequency calculation. That is, the scale factor is universal, not molecule-specific. So, the HF method, after scaling, is still an excellent way to predict IR spectra.

Matrix Isolation Spectroscopy (A Case Study)

The class of antitumor-antibiotics known as enediyynes undergo in vivo Bergman cyclization of the enediyne functionality to generate $p$-benzyne reactive intermediates that damage genetic material (see figure below). Because the damage results in double-stranded DNA cleavage, they are extraordinarily cytotoxic, and this has sparked interest in better understanding $p$-benzyynes in general. One issue associated with the parent $p$-benzyne is that it is thermochemically unstable relative to its enediyne precursor, making its isolation quite challenging. In work reported in Wenk, H. H.; Balster, A.; Sander, W.; Hrovat, D. A.; Borden, W. T. “Matrix Isolation of Perfluorinated $p$-Benzyne”
Angew. Chem., Int. Ed. Engl. **2001**, *40*, 2295, Wenk et al. sought to identify a precursor not suffering from this problem, and determined from computational quantum chemistry that perfluorinated \( p \)-benzyne was roughly 8 kcal mol\(^{-1} \) more stable than the enediyne that would be produced from retro-Bergman ring opening, and moreover that the barrier to that ring opening was nearly 38 kcal mol\(^{-1} \), this being nearly double the barrier in the unfluorinated case. Girded with this thermochemical armor, they set out to synthesize the diradical by UV photolysis of 1,4-diiodo-2,3,5,6-tetrafluorobenzene.

When this precursor is photolyzed at 3 K (brrr) in a neon matrix, IR spectroscopy indicates rapid formation of a new species **A** (at 3 K in a matrix made of frozen neon, individual molecules can’t bump into other molecules, and it is too cold to do any reaction chemistry unless a photon brings in new energy). Prolonged photolysis (i.e., more photons) creates a second product **B** whose IR bands are distinct from the first. And, if the matrix containing the second product is irradiated with UV light of somewhat longer wavelength, IR analysis indicates that a third product **C** is generated. All of the IR bands observed for **A**, **B**, and **C** are listed in the below table. These bands are compared to frequencies computed by quantum chemistry (to be perfectly honest, it’s a level of quantum theory better than HF theory, but the point of this case study is to show how predictive IR spectroscopy is useful, not to show off HF theory).

The generally excellent agreement between the experimental and computed spectra permits the secure assignment of the bands for **A** to the ITFP, the bands for **B** to PFPB, and the bands for **C** to PFHED as would be suggested by the synthetic scheme in the figure above. The “missing” bands in the experimental IR spectra are all predicted to be very low in intensity in the computed spectra (we haven’t talked about how to compute intensity, but as always it depends on the transition dipole moment since it is a measure of “allowedness”). In the absence of IR spectroscopy and theoretical confirmation, it is difficult to imagine what experiments one would do in a 3 K neon
Table. Experimental and computed IR spectra (cm\(^{-1}\)) for A, B, and C, and ITFP, PFPB, and PFHED, respectively.

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<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>PFPB</th>
<th>C</th>
<th>PFHED</th>
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</table>

matrix to prove that the various reactive intermediates had been created. This represents, then, an excellent example of how theory can aid experiment in the identification of short-lived reactive species.

Homework

To be solved in class:

What is the Coulomb integral for the interelectronic repulsion for the closed-shell wave function of \( \text{H}_2 \) in eq. 35-8? (Don’t try to come up with a number, just express it in some useful shorthand notation, like Dirac notation.) Now, compute the same thing for the open-shell wave function of eq. 35-9. Which wave function has the greater Coulomb repulsion, and how might that depend on interatomic distance? Why do you think \( \text{H}_2 \) forms a stable, closed-shell singlet bond?

To be turned in for possible grading Apr. 28:

Use the virial theorem (described in the solved homework of Lecture 16) to prove that since \( \text{H}_2 \) is bound (i.e., is lower in energy than two separated \( \text{H} \) atoms) then the kinetic energy of the electrons in \( \text{H}_2 \) must be greater than it is in two separated \( \text{H} \) atoms.