(Some material in this lecture has been adapted from Cramer, C. J. *Essentials of Computational Chemistry*, Wiley, Chichester: 2002; pp. 6-10; 300-301; 490-492.)

The Potential Energy Surface Revisited

Chemists are typically used to drawing molecules as atoms connected by bonds. It takes some faith in quantum chemistry to give up one's reliance on those lines between the atoms. What we've learned in this course so far is that the physics of kinetic energy and electrostatic attraction and repulsion *determines* where the bonds are once the atomic positions in space are chosen. To avoid our prejudices, a good first step is to refrain from invoking particular structures initially, and instead to consider *all possible* structures for a given chemical formula. That is, we can use quantum chemistry to fully characterize the potential energy surface (PES) for any particular choice of chemical formula (as we will see below, this requires invocation of the Born-Oppenheimer approximation, which we've previously discussed in a very qualitative fashion). The PES is a "hypersurface" (meaning it may require more than 3 dimensions for its specification) that is defined by the potential energy of a collection of atoms over all possible atomic arrangements; the PES has $3N - 6$ internal coordinate dimensions, where N is the number of atoms ≥ 3. This dimensionality derives from the three-dimensional nature of Cartesian space. Thus each structure, which is a point on the PES, can be defined by a vector $\mathbf{X}$ where

$$\mathbf{X} \equiv \left(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N\right) \tag{34-1}$$

and x_i, y_i, and z_i are the Cartesian coordinates of atom i. However, this expression of $\mathbf{X}$ does not *uniquely* define the structure because it involves an arbitrary origin. We can reduce the dimensionality without affecting the structure by removing the three dimensions associated with translation of the structure in the x, y, and z directions (e.g., by insisting that the molecular center of mass be at the origin) and removing the three dimensions associated with rotation about the x, y, and z axes (e.g., by requiring that the principal moments of inertia align along those axes in increasing order, for instance).

A different way to appreciate this reduced dimensionality is to imagine constructing a structure vector atom by atom, in which case it is most convenient to imagine the dimensions of the PES being *internal* coordinates (i.e., bond lengths, valence angles, etc.) Thus, choice of the first atom involves no degrees of geometric freedom— the atom defines the origin. The position of the second atom is specified by its distance from the first. So, a 2-atom system has a single degree of freedom, the bond length; this corresponds to $3N - 5$ degrees of freedom (as should be the case for a *linear* molecule). The third atom must be specified either by its distances to each of the preceding atoms, or

by a distance to one and an angle between the two bonds thus far defined to a common atom. The three atom system, if collinearity is not enforced, has 3 total degrees of freedom, as it should ($3N$–6). Each additional atom requires three coordinates to describe its position. There are several ways to envision describing those coordinates. As in the below figure, they can either be a bond length, a valence angle, and a dihedral angle, or they can be a bond length and two valence angles. Or, one can imagine that the first three atoms have been used to create a fixed Cartesian reference frame, with atom 1 defining the origin, atom 2 defining the direction of the positive x axis, and atom 3 defining the first quadrant of the xy plane. The choice is simply a matter of convenience. Note, however, that the *shapes* of particular surfaces necessarily depend on the choice of their coordinate systems, although they will map to one another in a one-to-one fashion.
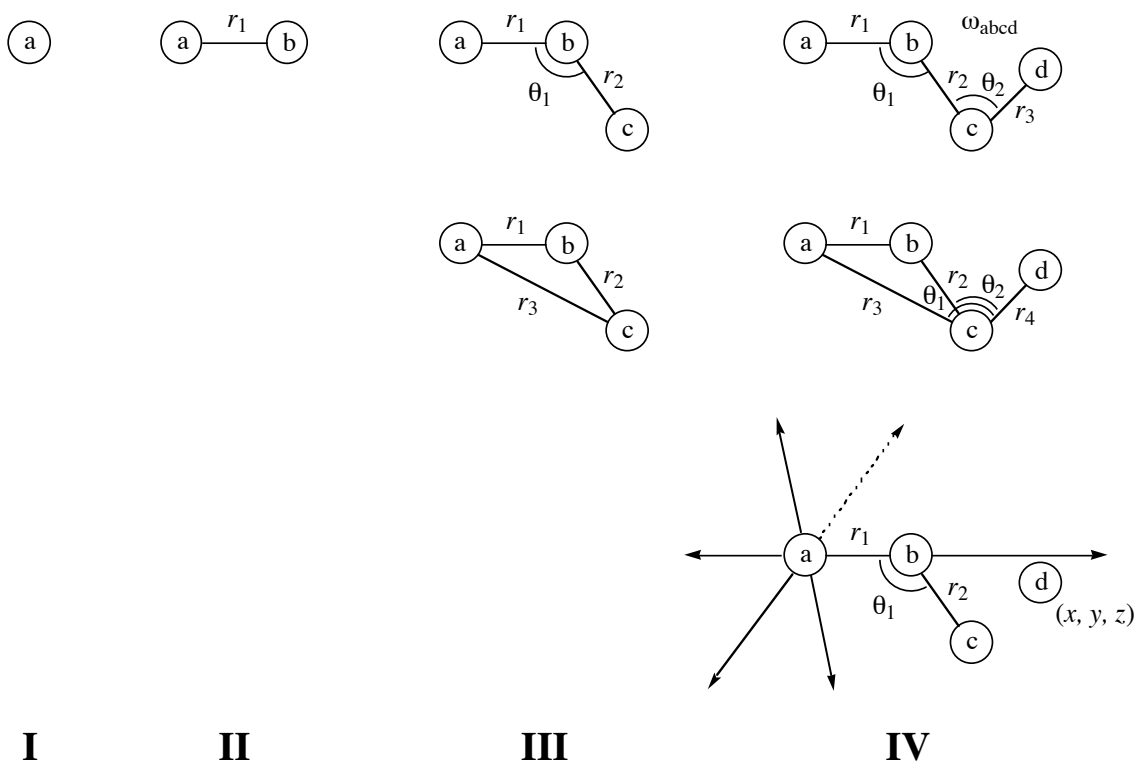

I   II   III   IV

Figure. Different means for specifying molecular geometries. In frame **I**, there are no degrees of freedom as only the nature of atom "a" has been specified. In frame **II**, there is a single degree of freedom, namely the bond length. In frame **III**, atom "c" requires two additional degrees of freedom to locate, either two bond lengths or a bond length and a valence angle. Frame **IV** illustrates various ways to specify the location of atom "d"; note that in every case, three new degrees of freedom must be specified, either in internal or cartesian coordinates.

Particularly interesting points on PESs include local minima, which correspond to optimal molecular structures, and saddle points (i.e., points characterized by having no slope in any direction, downward curvature for a single coordinate, and upward curvature for all of the other coordinates). Simple calculus dictates that saddle points are lowest energy barriers to paths connecting minima, and thus they can be related to the chemical

concept of a transition state. So, a complete PES provides, for a given collection of atoms, complete information about all possible chemical structures and all isomerization pathways interconnecting them.

Unfortunately, complete PESs for polyatomic molecules are very hard to visualize, since they involve a large number of dimensions. Typically, we take slices through potential energy surfaces that involve only a single coordinate (e.g., a bond length) or perhaps two coordinates, and show the relevant reduced-dimensionality energy curves or surfaces. Note that some care must be taken to describe the nature of the slice with respect to the *other* coordinates. For instance, was the slice a hyperplane, implying that all of the non-visualized coordinates have fixed values, or was it a more general hypersurface? A typical example of the latter choice is one where the non-visualized coordinates take on values that minimize the potential energy given the value of the visualized coordinate(s). Thus, in the case of a single visualized dimension, the curve attempts to illustrate the minimum energy path associated with varying the visualized coordinate [We must say "attempts" here, because an actual continuous path connecting any two structures on a PES may involve any number of structures all of which have the same value for a single internal coordinate. When that path is projected onto the dimension defined by that single coordinate (or any reduced number of dimensions including it) the resulting curve is a non-single-valued function of the dimension.] See Figures on next two pages.

With the complete PES in hand (or, more typically, with the region of the PES that would be expected to be chemically accessible under the conditions of the experimental system being modeled), one can take advantage of standard precepts of statistical mechanics to estimate equilibrium populations for situations involving multiple stable molecular structures and compute ensemble averages for physical observables. We'll look at the stat. mech. issues associated with molecular ensembles a bit later. For now, simply recall the Boltzmann energy law which states that the fraction of molecules having a particular energy E_i may be computed as

$$\%\left(E_i\right) = \frac{e^{-E_i/k_B T}}{\sum_j e^{-E_j/k_B T}} \tag{34-2}$$

where the sum runs over all different possible energy levels, k_B is Boltzmann's constant, and T is temperature. Thus, we may compute the ratio of two structures having different energies (that ratio has the form of an equilibrium constant) as

$$K_{A/B} = \frac{[A]}{[B]} = \frac{\%(E_A)}{\%(E_B)} = \frac{e^{-E_A/k_B T}}{e^{-E_B/k_B T}} = e^{-(E_A - E_B)/k_B T} \tag{34-3}$$

That is, the ratio of A to B will be dictated by the energy difference between them.
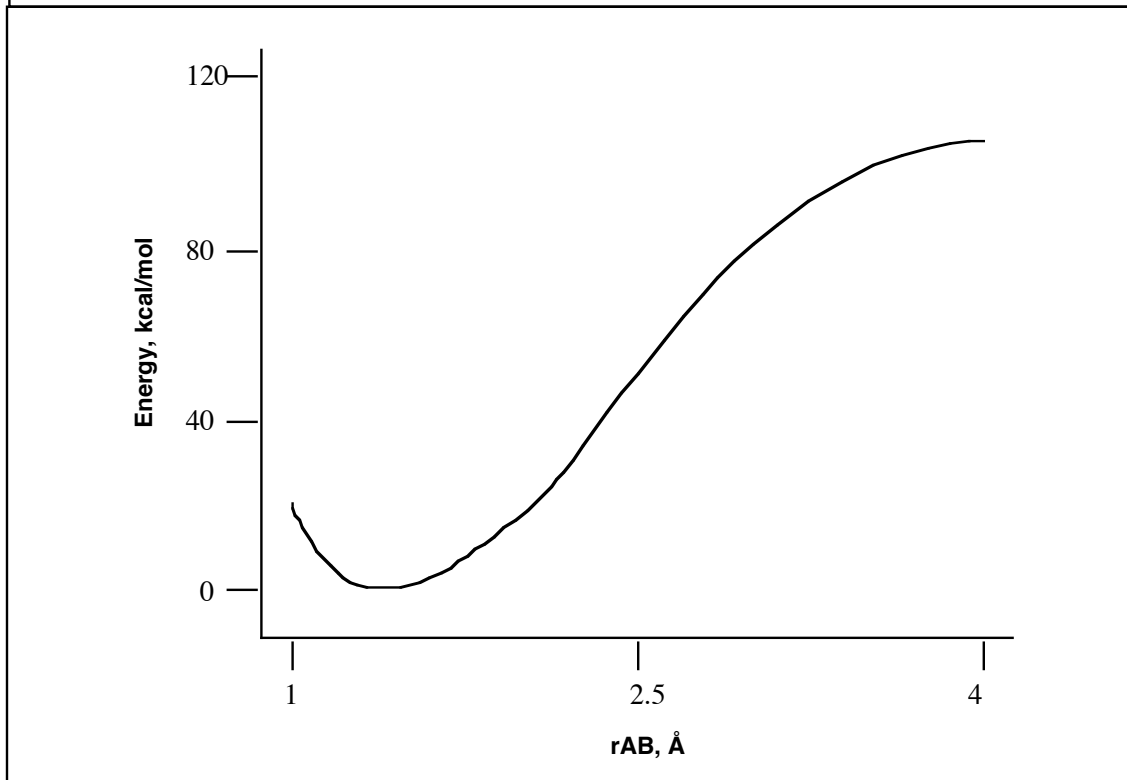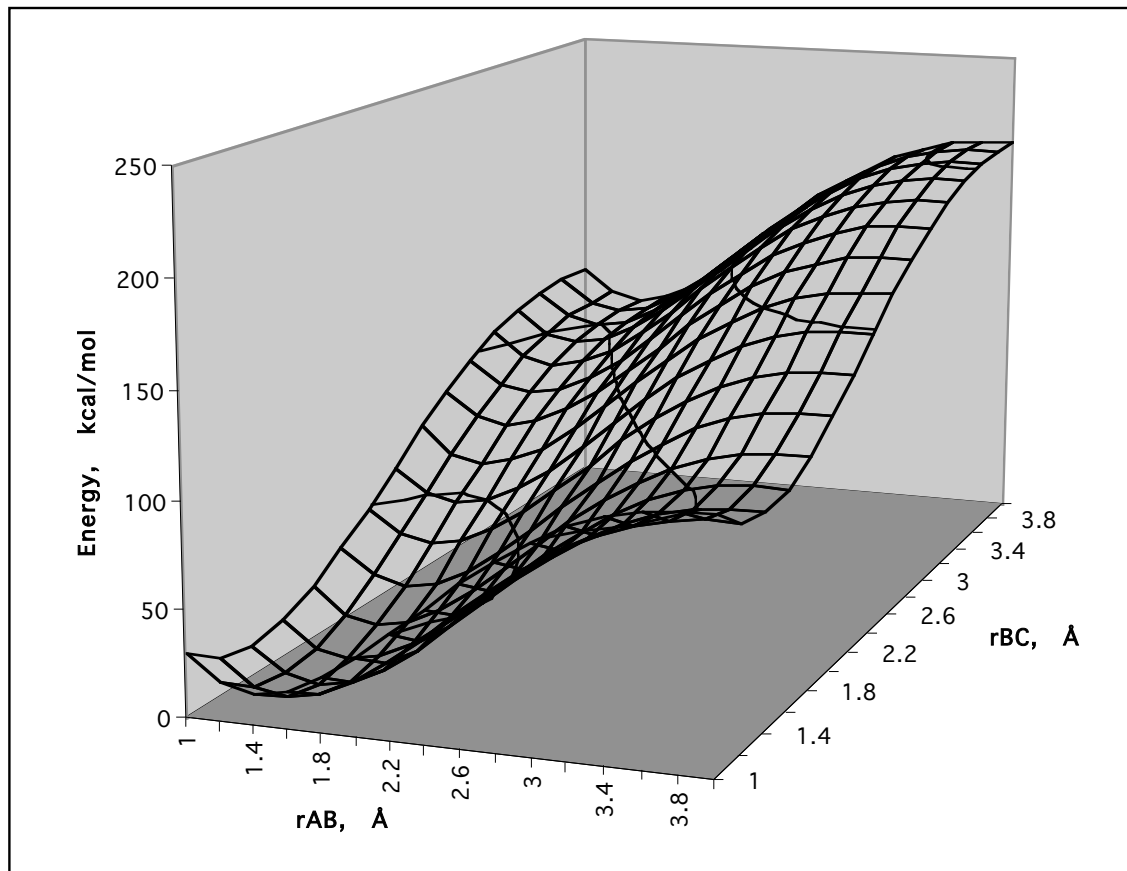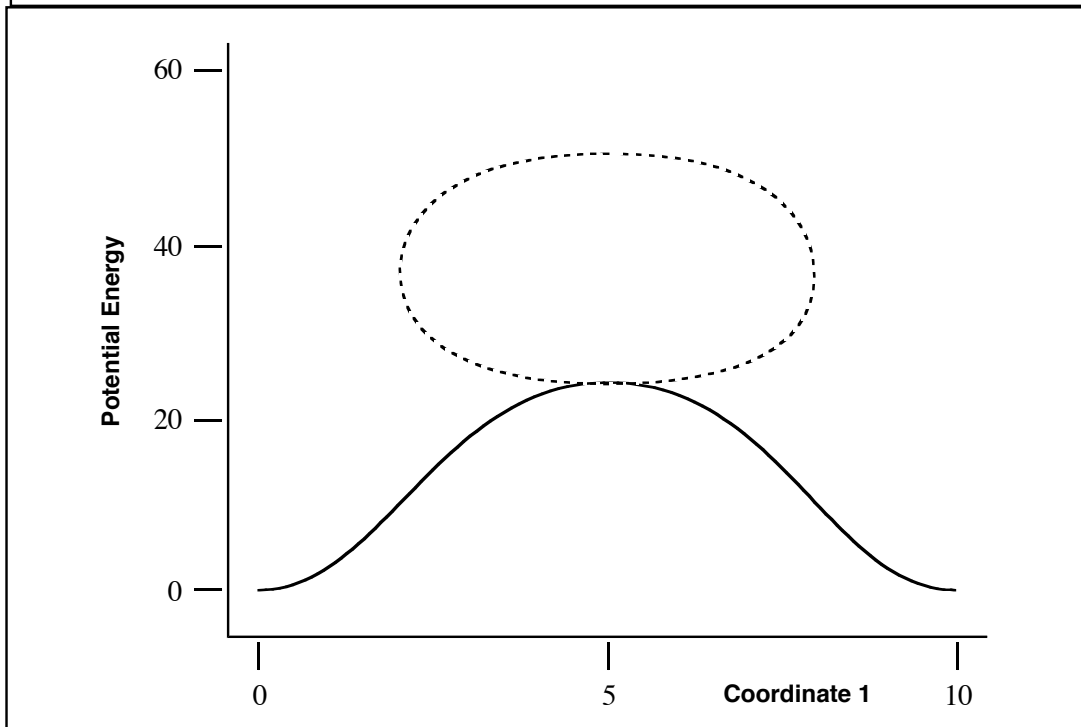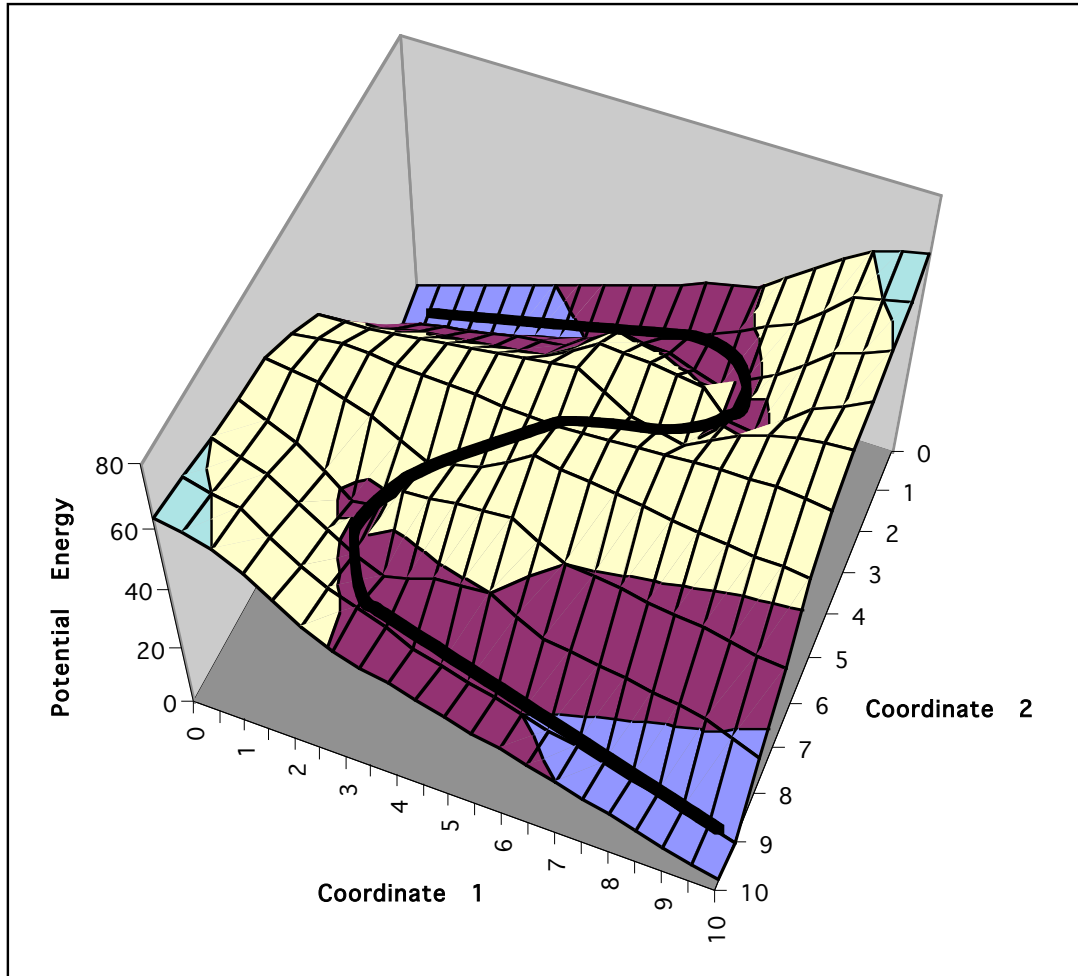
So, if we know the energies of different wells on our PES, we can predict the fraction of total mass that each structural well will contribute to a given equilibrium population.

Transition-state Structures and Chemical Kinetics

We've already defined what a transition-state (TS) structure is. TS structures are chemically important insofar as they represent transition points between different stable wells on a PES. One of the greatest powers of quantum chemistry is its ability to well define a TS structure—experimentally it is almost impossible to "see" one since their lifetimes are on the order of one molecular vibrational period, this being in the sub-picosecond regime.

Since TS structures are the bottlenecks in chemical reactions, it probably will come as no surprise that speeds of chemical reactions depend on the relative energies of TS structures compared to minima. Indeed, this would seem to follow immediately from thinking about the equilibrium constant defined above. If a TS is very high in energy, only a tiny fraction of molecules will be that TS structure, and hence it will be hard to get from one minimum to the other connected by that TS structure.

We will not derive the result, but from transition-state theory (TST), one finds that a unimolecular chemical reaction (i.e., one involving only a single molecule, as a rearrangement, for example), generically A → B, proceeds according to

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = k[A] \tag{34-4}$$

where t is time. Eq. 34-4 states that the rate of disappearance of A is equal to the rate of appearance of B (simply from mass balance) and depends on how much A there is (obviously) and the "rate constant" k. The rate constant, from TST, is

$$k = \frac{k_B T}{h} e^{-(G_{TS} - G_A)/RT} \tag{34-5}$$

where h is Planck's constant and R is the universal gas constant. The difference between the free energy (G) of the TS structure and the reactant is called the free energy of activation. We have not yet learned how to convert from potential energy for a molecule to free energy for a collection of molecules, but if we temporarily assume that there is no difference, we can immediately see the analogy between eqs. 34-3 and 34-5, where using a molar ensemble causes k_B to be replaced by R (which is k_B times Avogadro's number) in the denominator of the exponential in eq. 34-5.

So, if we can use quantum mechanics to compute an accurate PES, we can predict all of the forms of all stable molecules at any temperature, and how quickly reactions to convert one to another will take place!

The One-dimensional Schrödinger Equation for Molecular Vibration

Within the context of the Born-Oppenheimer approximation, the potential energy surface may be regarded as a "property" of an empirical formula. With a defined PES, it is possible to formulate and solve Schrödinger equations for *nuclear* motion (as opposed to electronic motion)

$$\left[-\sum_i^N \frac{1}{2m_i} \nabla_i^2 + V(\mathbf{q}) \right] \Xi(\mathbf{q}) = E\Xi(\mathbf{q}) \tag{34-6}$$

where N is the number of atoms, m is the atomic mass, V is the potential energy from the PES as a functions of the $3N$ nuclear coordinates $\mathbf{q}$, and Ξ is the nuclear wave function that is expressed in those coordinates. Solution of eq. 34-6 provides entry into the realms of rotational and vibrational spectroscopy, some aspects of which we've already visited.

When thinking about chemical thermodynamics and kinetics, it is a convenient formalism to picture a molecule as being like a ball rolling on a PES. In this simple model, the exact position of the ball determines the molecular geometry and the potential energy, and its speed as it rolls in a frictionless way determines its kinetic energy. Of course, quantum mechanical particles are different than classical ones in many ways. One of the more important differences is that they are subject to the Heisenberg uncertainty principle, one consequence of which is that, even at absolute zero, polyatomic molecules *must vibrate*—within the simple ball and surface picture, the ball must always be moving, with a sum of potential and kinetic energy that exceeds the energy of the nearest minimum by some non-zero amount. This energy is contained in molecular vibrations.

In the simplest possible case, a diatomic, eq. 34-6 when restricted to the vibrational motion alone is clearly a function of only a single variable, the interatomic distance r. We have now solved several one-dimensional Schrödinger equations. Our only challenge here is that we do not know exactly what the potential energy function V looks like as a function of r. Given a level of theory, however, we can compute V point by point to an arbitrary level of fineness (i.e., simply compute the electronic energy of the system for various fixed values of r). Those points may then be fit to any convenient analytic function—polynomial, Morse, etc.—and the one-dimensional Schrödinger equation solved using standard numerical recipes to yield eigenfunctions and eigenvalues. Note that the harmonic oscillator equation would be recovered if we fit V to a parabolic form. However, if we are willing to generate more complicated wave functions (typically involving power series expansions times gaussians) we can do better than the harmonic oscillator. An example is shown graphically on the next page.

With a complete PES for a polyatomic, this process can be too tedious, and the harmonic approximation becomes useful again, as we will see next time.
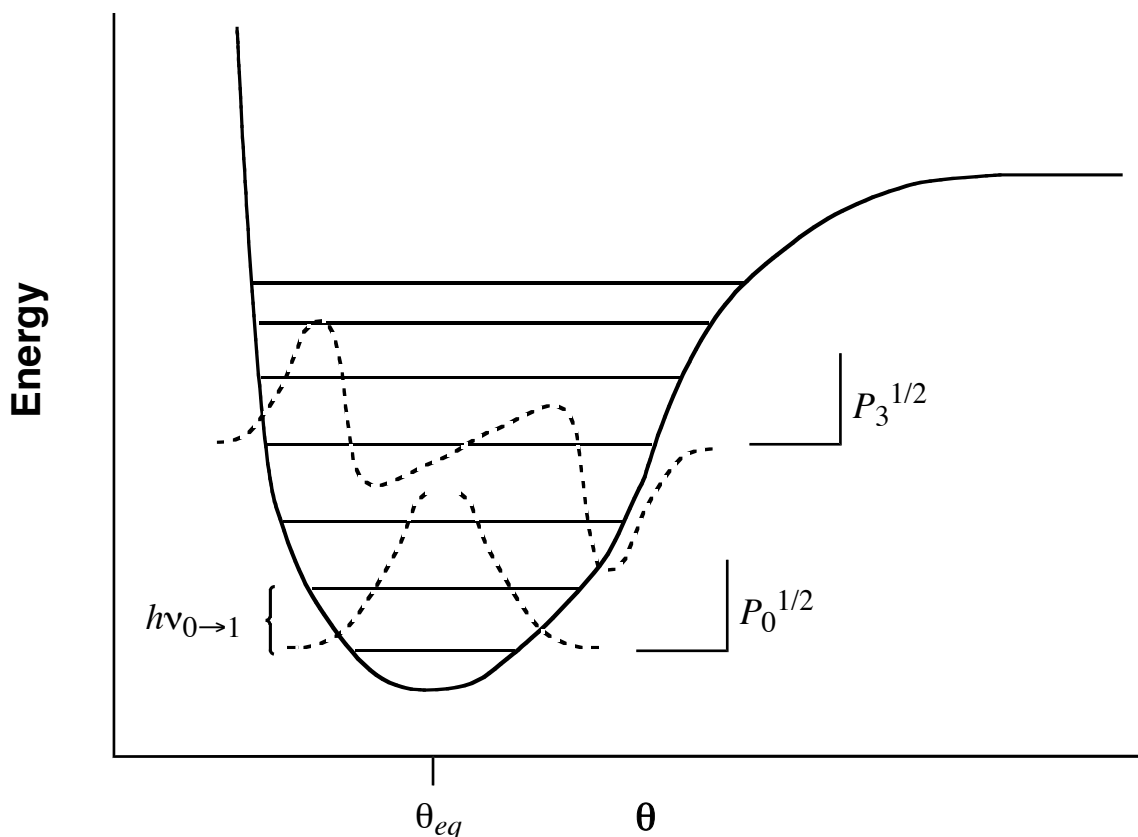
Figure. Vibrational energy levels determined from solution of the one-dimensional Schrödinger equation for some arbitrary variable θ (some higher levels not shown). In addition to the energy levels (horizontal lines across the potential curve), the vibrational wave functions are shown for levels 0 and 3. Conventionally, the wave functions are plotted in units of (probability)$^{1/2}$ with the same abscissa as the potential curve and an individual ordinate having its zero at the same height as the location of the vibrational level on the energy ordinate—those coordinate systems are explicitly represented here. Note that the absorption frequency typically measured by infrared spectroscopy is associated with the 0→1 transition, as indicated on the plot. For the harmonic oscillator potential, *all* energy levels are separated by the same amount, but this is not necessarily the case for a more general potential—here the levels become more closely spaced near the dissociation limit.

The Born-Oppenheimer Approximation Revisited (Optional, Non-testable Material)

How might we construct a wave function that *does* depend on nuclear coordinates in a more complete way than as fixed positions in the electronic wave function? The simplest introduction of complexity might be to take a complete wave function as

$$\Psi(\mathbf{Q},\mathbf{q}) = c_1(\mathbf{Q})\psi_1(\mathbf{q};\mathbf{Q}) + c_2(\mathbf{Q})\psi_2(\mathbf{q};\mathbf{Q}) \tag{34-7}$$

where ψ_1 and ψ_2 are two *different electronic* wave functions that depend on the electronic coordinates **q** and the nuclear coordinates **Q** and the coefficients c also depend on the nuclear coordinates because the mixing of the states will vary with different geometries. Note that since the coefficients c_1 and c_2 depend only on nuclear coordinates, each is formally a nuclear wave function (e.g., a harmonic oscillator wave function).

In this case, the Schrödinger equation becomes

$$H\Psi(\mathbf{Q},\mathbf{q}) = E_{\text{full}}\big[c_1(\mathbf{Q})\psi_1(\mathbf{q};\mathbf{Q}) + c_2(\mathbf{Q})\psi_2(\mathbf{q};\mathbf{Q})\big] \qquad (34\text{-}8)$$

where the Hamiltonian operator now includes nuclear kinetic energy as well as the nuclear repulsion and electronic energy, i.e.,

$$H = \sum_k^{\text{nuclei}} -\frac{1}{2m_k}\nabla_k^2 + H_{\text{el}} + V_N \qquad (34\text{-}9)$$

where m_k is the mass of nucleus k in atomic units and H_{el} and V_N are the usual electronic Hamiltonian and nuclear repulsion. To determine a given c as a function of nuclear coordinates **Q**, we can multiply both sides of eq. 34-8 on the left by the electronic wave function corresponding to that c and integrate over the electronic coordinates, giving

$$\big\langle\psi_1(\mathbf{q};\mathbf{Q})\big|H\big|c_1(\mathbf{Q})\psi_1(\mathbf{q};\mathbf{Q}) + c_2(\mathbf{Q})\psi_2(\mathbf{q};\mathbf{Q})\big\rangle =$$
$$E_{\text{full}}\big\langle\psi_1(\mathbf{q};\mathbf{Q})\big|c_1(\mathbf{Q})\psi_1(\mathbf{q};\mathbf{Q}) + c_2(\mathbf{Q})\psi_2(\mathbf{q};\mathbf{Q})\big\rangle \qquad (34\text{-}10)$$

The r.h.s. is simple to evaluate since the electronic wave functions are orthonormal; thus, the expectation value on the r.h.s. is just $E_{\text{full}}c_1(\mathbf{Q})$. Expanding the l.h.s. is a bit more demanding. Since both the nuclear and electronic wave functions depend on **Q**, the coordinates of the nuclei, the application of the del-squared operator must be carried out using the chain rule of differentiation. Some quick calculus shows that

$$\nabla_k^2(fg) = \left(\nabla_k^2 f\right)g + 2\left(\nabla_k f\right)\bullet\left(\nabla_k g\right) + f\left(\nabla_k^2 g\right) \qquad (34\text{-}11)$$

where the vector operator del is defined as

$$\nabla_k = \left(\frac{\partial}{\partial x_k}, \frac{\partial}{\partial y_k}, \frac{\partial}{\partial z_k}\right) \qquad (34\text{-}12)$$

So, the l.h.s. of eq. 34-10 is

$$\left\langle \psi_1(\mathbf{q};\mathbf{Q}) \left| \sum_k^{\text{nuclei}} -\frac{1}{2m_k}\nabla_k^2 + H_{\text{el}} + V_N \right| c_1(\mathbf{Q})\psi_1(\mathbf{q};\mathbf{Q}) + c_2(\mathbf{Q})\psi_2(\mathbf{q};\mathbf{Q}) \right\rangle =$$

$$\left\langle \psi_1(\mathbf{q};\mathbf{Q}) \left| \sum_k^{\text{nuclei}} -\frac{1}{2m_k}\nabla_k^2 \right| c_1(\mathbf{Q})\psi_1(\mathbf{q};\mathbf{Q}) \right\rangle + \left\langle \psi_1(\mathbf{q};\mathbf{Q}) \left| \sum_k^{\text{nuclei}} -\frac{1}{2m_k}\nabla_k^2 \right| c_2(\mathbf{Q})\psi_2(\mathbf{q};\mathbf{Q}) \right\rangle$$

$$+ \left\langle \psi_1(\mathbf{q};\mathbf{Q}) | H_{\text{el}} | c_1(\mathbf{Q})\psi_1(\mathbf{q};\mathbf{Q}) \right\rangle + \left\langle \psi_1(\mathbf{q};\mathbf{Q}) | H_{\text{el}} | c_2(\mathbf{Q})\psi_2(\mathbf{q};\mathbf{Q}) \right\rangle$$

$$+ \left\langle \psi_1(\mathbf{q};\mathbf{Q}) | V_N | c_1(\mathbf{Q})\psi_1(\mathbf{q};\mathbf{Q}) \right\rangle + \left\langle \psi_1(\mathbf{q};\mathbf{Q}) | V_N | c_2(\mathbf{Q})\psi_2(\mathbf{q};\mathbf{Q}) \right\rangle =$$

$$\sum_k^{\text{nuclei}} -\frac{1}{2m_k} \left\{ \begin{array}{l} \left\langle \psi_1(\mathbf{q};\mathbf{Q}) | \psi_1(\mathbf{q};\mathbf{Q}) \right\rangle \left[\nabla_k^2 c_1(\mathbf{Q}) \right] + 2\left\langle \psi_1(\mathbf{q};\mathbf{Q}) | \nabla_k | \psi_1(\mathbf{q};\mathbf{Q}) \right\rangle \bullet \left[\nabla_k c_1(\mathbf{Q}) \right] \\ + \left\langle \psi_1(\mathbf{q};\mathbf{Q}) | \nabla_k^2 | \psi_1(\mathbf{q};\mathbf{Q}) \right\rangle c_1(\mathbf{Q}) + \left\langle \psi_1(\mathbf{q};\mathbf{Q}) | \psi_2(\mathbf{q};\mathbf{Q}) \right\rangle \left[\nabla_k^2 c_2(\mathbf{Q}) \right] \\ + 2\left\langle \psi_1(\mathbf{q};\mathbf{Q}) | \nabla_k | \psi_2(\mathbf{q};\mathbf{Q}) \right\rangle \bullet \left[\nabla_k c_2(\mathbf{Q}) \right] + \left\langle \psi_1(\mathbf{q};\mathbf{Q}) | \nabla_k^2 | \psi_2(\mathbf{q};\mathbf{Q}) \right\rangle c_2(\mathbf{Q}) \end{array} \right\}$$

$$+ \left\langle \psi_1(\mathbf{q};\mathbf{Q}) | H_{\text{el}} | \psi_1(\mathbf{q};\mathbf{Q}) \right\rangle c_1(\mathbf{Q}) + \left\langle \psi_1(\mathbf{q};\mathbf{Q}) | H_{\text{el}} | \psi_2(\mathbf{q};\mathbf{Q}) \right\rangle c_2(\mathbf{Q})$$

$$+ \left\langle \psi_1(\mathbf{q};\mathbf{Q}) | V_N | \psi_1(\mathbf{q};\mathbf{Q}) \right\rangle c_1(\mathbf{Q}) + \left\langle \psi_1(\mathbf{q};\mathbf{Q}) | V_N | \psi_2(\mathbf{q};\mathbf{Q}) \right\rangle c_2(\mathbf{Q}) =$$

$$\sum_k^{\text{nuclei}} -\frac{1}{2m_k} \left\{ \begin{array}{l} \left[\nabla_k^2 c_1(\mathbf{Q}) \right] + 2\left\langle \psi_1(\mathbf{q};\mathbf{Q}) | \nabla_k | \psi_1(\mathbf{q};\mathbf{Q}) \right\rangle \bullet \left[\nabla_k c_1(\mathbf{Q}) \right] \\ + \left\langle \psi_1(\mathbf{q};\mathbf{Q}) | \nabla_k^2 | \psi_1(\mathbf{q};\mathbf{Q}) \right\rangle c_1(\mathbf{Q}) + 0 \\ + 2\left\langle \psi_1(\mathbf{q};\mathbf{Q}) | \nabla_k | \psi_2(\mathbf{q};\mathbf{Q}) \right\rangle \bullet \left[\nabla_k c_2(\mathbf{Q}) \right] + \left\langle \psi_1(\mathbf{q};\mathbf{Q}) | \nabla_k^2 | \psi_2(\mathbf{q};\mathbf{Q}) \right\rangle c_2(\mathbf{Q}) \end{array} \right\}$$

$$+ E_1 c_1(\mathbf{Q})$$

$$(34\text{-}13)$$

where E_1 is the usual electronic energy including nuclear repulsion (note that terms involving $\langle\psi_1|\psi_2\rangle$ or $\langle\psi_1|H_{\text{el}}|\psi_2\rangle$ were set to zero based on the orthonormality of the electronic eigenfunctions). An imposing equation, admittedly. But, let's just consider the situation. We have a whole bunch of nasty terms preceded by -1 over twice the nuclear mass, and the electronic energy of state 1 and the nuclear repulsion energy. If we assume that the nuclear masses are so large that the del and del squared terms involving electronic wave functions are negligible compared to the del squared terms already present in the electronic part of the Hamiltonian, we lose all of the terms in curly braces except for the first. Noting from our discussion of eq. 34-10 that eq. 34-13 must equal $E_{\text{full}}c_1(\mathbf{Q})$ we would then have a "normal" Schrödinger equation of the nuclear wave function

$$\left(\sum_k^{\text{nuclei}} -\frac{1}{2m_k}\nabla_k^2 + E_1 \right) c_1(\mathbf{Q}) = E_{\text{full}}c_1(\mathbf{Q}) \qquad (34\text{-}14)$$

i.e., the nuclei for state 1 move subject only to the potential from state 1 (which is E_1), and the problem is separable. That is the *real* Born-Oppenheimer approximation, if you like. It says, however, that there can be no transition from state 1 to state 2 that does not involve a photon (normalization of eq. 34-14 means that $|c_2(\mathbf{Q})|^2$ must be zero in eq. 34-7). Experiment indicates, however, that such radationless transitions *do* occur, so sometimes one must work with the full eq. 34-13 and abandon the Born-Oppenheimer approximation.

Models that do not invoke the Born-Oppenheimer approximation are called "non-adiabatic". A model that considers only a single potential energy surface from which transitions can occur only via absorption or emission of radiation is called "adiabatic".

Homework

To be solved in class:

What error in a computed energy difference is enough to make a predicted equilibrium constant be off by a factor of 10 at 25 °C? What about 500 °C? What error in a computed energy difference is enough to make a predicted rate constant be off by a factor of 10 at 25 °C? What about 500 °C? Take the value you determined for the case of an equilibrium constant at 25 °C: what fraction of the total energy of our HF/STO-3G optimized water molecule is your answer?

To be turned in for possible grading Apr. 28:

What is the rate constant at 298 K for a unimolecular reaction that has a free-energy of activation of 21 kcal mol^{-1}? Now, rearrange eq. 34-4 so that all terms involving the variables t and [A] are on opposite sides of the equation. Integrate both sides from the starting point $t = 0$, $[A] = [A]_0$ to $t = t'$, $[A] = [A]_{t'}$ to obtain an expression for the concentration $[A]_{t'}$ relative to the starting concentration $[A]_0$ at any time t'. Using this equation, what is the half-life (the time required for $[A]_{t'}$ to equal $\frac{1}{2}[A]_0$) for a unimolecular reaction as a function of the rate constant k? What is the half-life for the specific case of the unimolecular reaction having a free energy of activation of 21 kcal mol^{-1} (which is about right for rotation about the C–N bond in an amide, for instance)?