GEOMETRY OPTIMIZATIONS AND IR SPECTRA

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Our discussion so far has been to fix some nuclear coordinates and solve the corresponding electronic Hamiltonian to get our electronic wave functions and energies. Thus, our electronic energies depend parameterically on the nuclear coordinates.

$$\mathscr{E}\{\mathbf{R}\} \tag{1}$$

From the introduction of the Born-Oppenheimer approximation, it is understood though that the nuclei feel the potential generated by the electrons. That is, that $\mathscr{E}$ is the potential energy surface (PES) for the nuclei to move on. Our question is then, what are the stable nuclear configurations?

For this section, we won't worry about how to calculate the nuclear derivatives or Hessian, but just assume we can. We will revisit this point later.

1. Geometry Optimizations

To find the stable nuclear configurations, we must find the minimum of the PES. Lets take as an example a diatomic molecule such that there is only 1 nuclear degree of freedom, the internuclear distance R. We could scan the PES by computing the electronic energy at various R. If we did, we might find the PES looks something like Fig. 1. The stable nuclear configuration would be at the bottom of the well near $R = 1.15$, but how would we find that without constructing the entire PEC?

Just like we do for the optimization of our MO coefficients in HF theory, we first need some initial guess of the nuclear geometry, and then we will optimize the energy with respect to the nuclear coordinates. That is, we want to find the nuclear configurations where

$$\frac{\mathrm{d}\mathscr{E}}{\mathrm{d}\mathbf{R}} = 0 \tag{2}$$

This is our stationary condition. This alone, though, is not enough to guarantee that we are at a minimum! Recall from single variable calculus that maximum points also satisfy the stationary condition, and in multivariable calculus, saddle points also have zero derivatives. The only way we can guarantee that we are at a minimum, after finding the derivative is zero, is to look at the curvature of the PES at that point. For single variable, we must have that

$$\frac{\mathrm{d}^2\mathscr{E}}{\mathrm{d}R^2} > 0 \tag{3}$$

that is we are concave up. For multivariable (or when we have more than 2 atoms), we must look instead at the Hessian matrix which contains all second derivatives. Lets suppose that there were 3 geometrical coordinates, R_i for $i = 1, 2, 3$. Then the Hessian is given
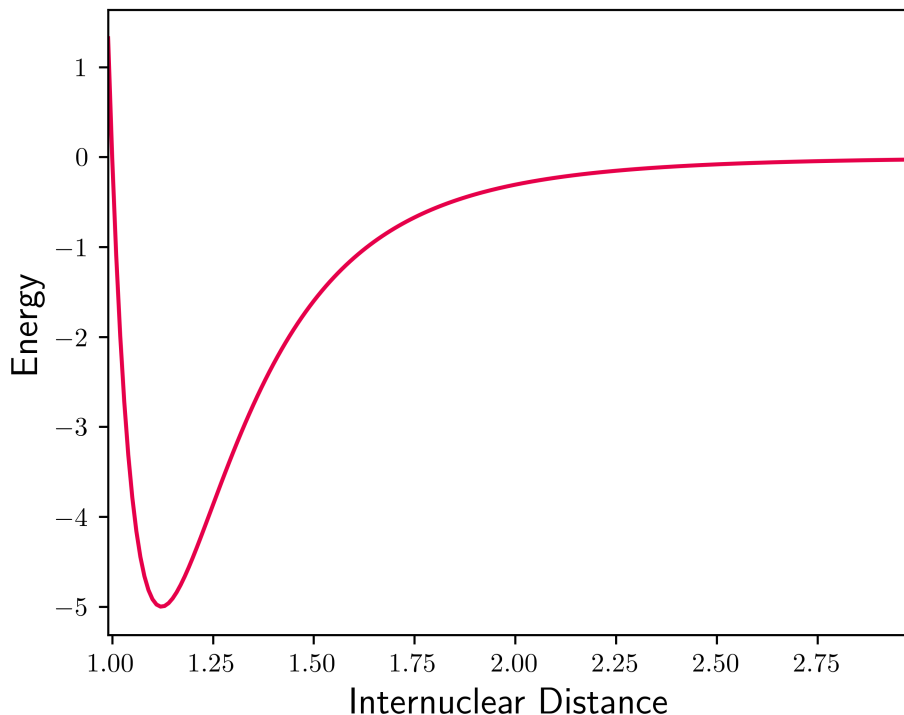

Figure 1.   Illustrative potential energy curve of a diatomic system. The potential energy curve in general takes the form of a Lennards-Jones potential.

by

$$\mathbf{H}_{\mathbf{R}}^{\mathscr{E}} = \begin{bmatrix} \frac{\partial^2 \mathscr{E}}{\partial R_1^2} & & \\ \frac{\partial^2 \mathscr{E}}{\partial R_1 \partial R_2} & \frac{\partial^2 \mathscr{E}}{\partial R_2^2} & \\ \frac{\partial^2 \mathscr{E}}{\partial R_1 \partial R_3} & \frac{\partial^2 \mathscr{E}}{\partial R_2 \partial R_3} & \frac{\partial^2 \mathscr{E}}{\partial R_3^2} \end{bmatrix} \tag{4}$$

This is a symmetric matrix, which means it is diagonalizable and its eigenvalues are real-valued. When we diagonalize it, we find that the eigenvalues tell us about the curvature of the surface at that point. If all eigenvalues are positive, then the surface is "concave up", which means we are at a local minimum. If they are all negative, then the surface is "concave down" and we are at a local maximum. If the sign of the eigenvalues are mixed, then you are at some saddle point where the number of negative eigenvalues determines the order of the saddle-point. That is, a first-order saddle point has one and only one negative eigenvalue. In chemistry, these are known as transition states and are the minimum energy structure that will be passed to go from one basin to the next. They are a minimum in all directions the eigenvalue is positive, and a maximum in the direction of the negative eigenvalue.

So in practice, to optimize our nuclear geometries, we use the gradient to find our stationary points. We then confirm that our stationary point is indeed a minimum by computing the hessian and checking that all eigenvalues are positive.

2. Normal Modes

While we are discussing the Hessian of our PES, it is instructive to discuss normal modes. Lets assume that $\mathbf{R}_0$ represents some local minimum on the PES. That is that

$$\frac{\mathrm{d}\mathscr{E}}{\mathrm{d}\mathbf{R}}\bigg|_{\mathbf{R}_0} = 0 \tag{5}$$

Lets expand the PES, that is our electronic energy $\mathscr{E}$, in a Taylor series around this point, up to second order.

$$\mathscr{E}\{\mathbf{R}\} \approx \mathscr{E}\{\mathbf{R}_0\} + \frac{\mathrm{d}\mathscr{E}}{\mathrm{d}\mathbf{R}}\bigg|_{\mathbf{R}_0} \cdot (\mathbf{R} - \mathbf{R}_0) + \frac{1}{2}(\mathbf{R} - \mathbf{R}_0)^T \cdot \mathbf{H}_{\mathbf{R}}^{\mathscr{E}}\bigg| \cdot (\mathbf{R} - \mathbf{R}_0) \tag{6}$$

However, since the we are at a stationary point, the first derivative term vanishes. While we are simplifying, lets just set $\mathbf{R}_0$ to be our coordinate origin (just translate everything). Finally, lets just set $\mathscr{E}\{\mathbf{R}_0\} = 0$. This amounts to just scaling the PES up or down by some fixed amount. This simplifies our energy parameterization as

$$\mathscr{E}\{\mathbf{R}\} = \frac{1}{2}\sum_{i,j} \frac{\partial \mathscr{E}}{\partial R_i R_j} R_i R_j \tag{7}$$

What we have basically done, is approximated the nuclear coordinates to be just some simple harmonic oscillators! That is, near equilibrium, they will just vibrate around the minimum. The "spring constant" of this vibration is given by the Hessian. Lets now make our life even simpler. We can diagonalize the Hessian matrix and find the eigenvectors, call them q_i. Then, we could have written our energy in terms of these coordinates as

$$\mathscr{E}\{\mathbf{q}\} = \frac{1}{2}\sum_{i} \frac{\partial^2 \mathscr{E}}{\partial q_i^2} q_i^2 \tag{8}$$

All of this analysis means that we can write the nuclear Hamiltonian as just some sum of uncoupled simple harmonic oscillators

$$\hat{H}^{\mathrm{vib}} = \sum_{j=1}^{N_{\mathrm{vib}}} \hat{H}_{\mathrm{vib},j} \tag{9}$$

$$\hat{H}_{\mathrm{vib},j} = \frac{-\hbar^2}{2\mu_j}\frac{\mathrm{d}^2}{\mathrm{d}q_j^2} + \frac{1}{2}\frac{\mathrm{d}^2\mathscr{E}}{\mathrm{d}q_j^2} q_j^2 \tag{10}$$

This is because the electronic energy surface is the *potential* energy surface that our nuclei feel! As written it is separable, and we know how to solve the SHO analytically. Our final energy will just be then the sum of the individual modes

$$\mathscr{E}_{\mathrm{vib}} = \sum_{j=1}^{N_{\mathrm{vib}}} \hbar\omega_j\left(n_j + \frac{1}{2}\right) \tag{11}$$

where ω_j is the angular frequency for the jth mode. It is related to both the reduced mass and second derivative of the electronic PES as

$$\omega_j = \sqrt{\frac{1}{\mu_j}\frac{\partial^2\mathscr{E}}{\partial q_j^2}} \tag{12}$$

Lets try and understand this a bit more. Firstly, the number of normal modes has to be the number of internal coordinates. For a linear system, this is $3N - 5$ and for a general system it is $3N - 6$ where N is the number of nuclei. The reason we subtract off 5 or 6, is we are removing the translational and rotational degrees of freedom (these can be dealt with with the ideal gas and rigid rotor approximations). Secondly, the eigenvectors of the hessian matrix give us the normal modes of the molecule. That is, they are the various vibrations present within our system. The corresponding eigenvalue tells use about the "spring" constant of the vibration, or how fast it will vibrate. Recall also that $n_j = 0, 1, 2, \ldots.$ That is to say, that when we are zero temperature, and the molecules is in the absolute ground vibrational state, there is still some amount of vibration energy given by

$$\mathscr{E}_{\text{ZPE}} = \sum_{j=1}^{N_{\text{vib}}} \frac{\hbar \omega_j}{2} \tag{13}$$

This is known as the zero-point energy (ZPE) as it raises us off the electronic energy surface by some amount at absolute zero temperature.

3. IR Spectra and Raman Spectra

We now know how to calculate the normal modes (ie vibrations) of our molecule. What is more is that the infrared spectra of a molecule is directly related to the normal modes! When a molecule absorbs a photon in the IR region, there is not enough energy to cause it to go to a higher electronic energy, but the energy is instead absorbed into the vibrational modes. This can promote n_j to some higher state. It is known from the SHO that the allowed transitions are $n_j \pm 1$. Furthermore, there are more selection rules when it comes to which modes are IR or Raman active.

IR active modes are any vibration that causes a change in the molecule dipole moment. For Raman active modes, the vibration must result in a change in the molecular polarizability. So it is possible that we have some vibrations in our molecule that don't change the molecular dipole moment, in which case we won't see that peak in our IR spectrum. Similarly for the Raman spectrum.