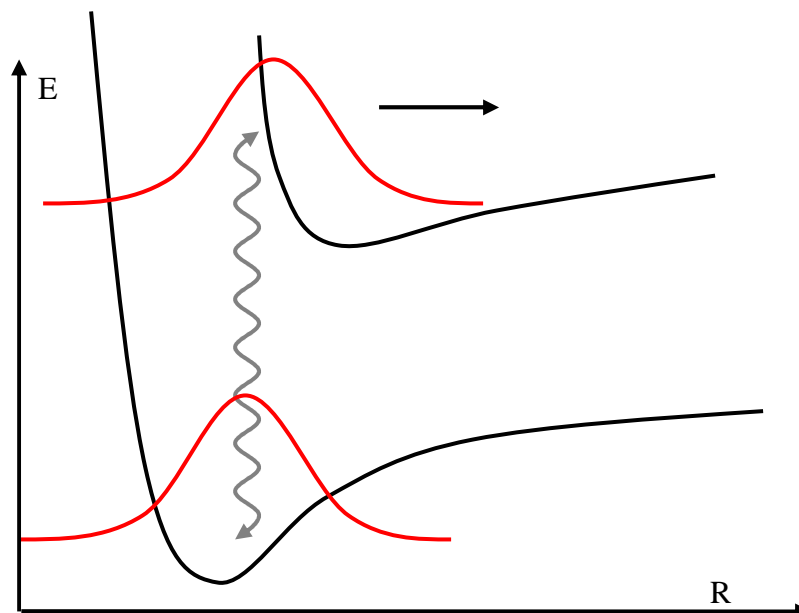# XII. The Born-Oppenheimer Approximation

The Born-Oppenheimer (BO) approximation is probably the most fundamental approximation in chemistry. From a practical point of view, it will allow us to treat the electronic structure of **molecules** very accurately without worrying too much

about the nuclei. However, in a more fundamental way, it underpins the way that most chemists think about molecules. Any time you see a chemist draw a picture like the one at right, you are implicitly making use of the framework suggested by the Bon-Oppenheimer approximation. So we are going to spend some time talking about this approximation and when we do and do not expect it to be valid.

a. The Adiabatic Approximation

For any molecule, we can write down the Hamiltonian in atomic units ($\hbar = m_e = e = 1$) as (defining $r_{\alpha\beta} \equiv |r_\alpha - r_\beta|$, etc.) :

$$\hat{H} = -\tfrac{1}{2}\sum_{I}^{nuclei}\frac{1}{M_I}\nabla_I^2 - \tfrac{1}{2}\sum_{i}^{electrons}\nabla_i^2 + \tfrac{1}{2}\sum_{IJ}^{nuclei}\frac{Z_I Z_J}{R_{IJ}} + \tfrac{1}{2}\sum_{ij}^{electrons}\frac{1}{r_{ij}} - \sum_{I,i}\frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}$$

| Nuclear Kinetic Energy | Electronic Kinetic Energy | Nuclear-Nuclear Repulsion | Electron-Electron Repulsion | Electron-Nuclear Attraction |

The physical motivation behind the Born-Oppenheimer Approximation is that the nuclei are much heavier than the electrons (e.g. a proton is 1800 times as heavy as an electron). At any given instant, the electrons will "feel" a Hamiltonian that depends on the position of the nuclei at that instant:

$$\hat{H}_{el}(\mathbf{R}) = -\tfrac{1}{2} \sum_{i}^{electrons} \nabla_i^2 + \tfrac{1}{2} \sum_{IJ}^{nuclei} \frac{Z_I Z_J}{R_{IJ}} + \tfrac{1}{2} \sum_{ij}^{electrons} \frac{1}{r_{ij}} - \sum_{I,i} \frac{Z_I}{\left| \mathbf{r}_i - \mathbf{R}_I \right|}.$$

Where $\mathbf{R}$ denotes the dependence of $\hat{H}_{el}$ on all of the nuclear positions $\{\mathbf{R}_I\}$ at once. In the limit that the nuclei are infinitely massive, they will never move and the positions $\mathbf{R}_I$ in the above expression will be fixed; i.e. the molecule will be frozen in some particular configuration. In this case, the $\mathbf{R}_I$'s can be considered as **parameters** (rather than operators) that define the effective Hamiltonian for the electrons.

For any fixed configuration of the molecule, then, one is interested in solving a Schrödinger equation that involves **only the electronic** degrees of freedom:

$$\hat{H}_{el}(\mathbf{R}) \left| \Psi_{el}(\mathbf{R}) \right\rangle = E_{el}(\mathbf{R}) \left| \Psi_{el}(\mathbf{R}) \right\rangle$$

where we have noted explicitly that the Hamiltonian, its eigenstates and eigenvalues depend on the particular nuclear configuration. This is the key element of the BO approximation; it allows one to compute the electronic structure of a molecule without saying anything about the quantum mechanics of the nuclei.

Once we have solved the electronic Schrödinger equation, we can write down the effective Hamiltonian for the nuclei by simply adding back in the terms that were left out of $\hat{H}_{el}$:

$$\hat{H}_N = -\tfrac{1}{2} \sum_{I}^{nuclei} \frac{1}{M_I} \nabla_I^2 + E_{el}(\mathbf{R})$$

Hence, the nuclei move on an effective potential surface that is defined by the electronic energy, and we can define wavefunctions for the nuclei alone that are eigenfunctions of this Hamiltonian:

$$\Rightarrow \hat{H}_N \left| \Psi_N \right\rangle = -\tfrac{1}{2} \sum_{I}^{nuclei} \frac{1}{M_I} \nabla_I^2 + E_{el}(\mathbf{R}) \left| \Psi_N \right\rangle = E \left| \Psi_N \right\rangle$$

Thus, another way to think about the BO approximation is that it is valid whenever the electronic and nuclear wavefunctions approximately decouple. Notice that the states we are using do **not** treat the nuclei and electrons as independent particles; the parametric dependence of the electronic eigenstates introduces a non-trivial coupling between the two, and so the decoupling need not be complete for the BO approximation to be valid.

Finally, we note that the electronic Schrödinger equation can also be derived by assuming that the high masses of the nuclei mean that they can be treated classically. Then the nuclei are completely described by a trajectory $\mathbf{R}(t)$. $\hat{H}_{el}$ can then be though of as depending either on $\mathbf{R}$ or on time. If we take the latter approach and assume the nuclei move infinitely slowly, we have a Hamiltonian $\hat{H}_{el}(t)$ that is changing very slowly with time and hence if the electrons start out in an eigenstate of $\hat{H}_{el}(0)$, they will **adiabatically follow** this eigenstate along the trajectory and end up in an eigenstate of $\hat{H}_{el}(t)$. Thus, if the nuclei are slow-moving classical particles, the electronic Schrödinger equation falls out naturally. For this reason the BO approximation is sometimes called the adiabatic approximation. Note however, that the BO approximation **does not** treat the nuclei classically. It describes nuclei that move quantum mechanically on an effective potential defined by the electrons.

b. <u>The Coupled Channel Representation</u>

By itself, the BO approximation is exceedingly accurate, which accounts for its widespread use throughout chemistry. Indeed, in most cases where it fails, one can usually explain the result by assuming that the system is adiabatic "almost all" the time, with only a few isolated regions where corrections need to be accounted for. Hence, it is extremely useful to consider the exact Schrödinger equation expressed in the **basis** defined by the BO approximation.

First we note that while it is usually convenient to consider the electronic wavefunction in Hilbert space (i.e. $\left|\Psi_{el}(\mathbf{R})\right\rangle\rangle$) it is usually convenient to specify the nuclear part in real space ($\Psi_N(\mathbf{R})$). This

notation is a bit unusual, but it is the most convenient for the problem at hand. There are two points that should be made. First, note that the dependence on $\mathbf{R}$ in $|\Psi_{el}(\mathbf{R})\rangle$ is fundamentally different than that in $\Psi_N(\mathbf{R})$. $\Psi_N(\mathbf{R})$ is properly thought of as the amplitude for finding the nuclei at in given configuration:

$$\Psi_N(\mathbf{R}) = \langle \mathbf{R} | \Psi_N \rangle$$

so that $|\Psi_N(\mathbf{R})|^2$ has the interpretation of a probability. On the other hand, there is no state $|\Psi_{el}\rangle$ that gives

$$|\Psi_{el}(\mathbf{R})\rangle \overset{?}{=} \langle \mathbf{R} | \Psi_{el} \rangle$$

and $\|\Psi_{el}(\mathbf{R})\rangle\|^2$ is not the probability of the outcome of any physical measurement. The dependence of $|\Psi_{el}(\mathbf{R})\rangle$ on $\mathbf{R}$ merely reflects the fact that the adiabatic states depend on where the nuclei are at that instant. The second point is that we will now begin talking about unusual objects like:

$$\Psi_N(\mathbf{R})|\Psi_{el}(\mathbf{R})\rangle$$

by which we mean that the nuclei are described by the (real space) wavefunction $\Psi_N(\mathbf{R})$ while the electrons are in the (Hilbert space) wavefunction $|\Psi_{el}(\mathbf{R})\rangle$. The rules of quantum mechanics proceed as before in this mixed representation.

Now, in order to represent the full Hamiltonian in the BO basis, we note that the electronic eigenstates for any fixed choice of the $\mathbf{R}$'s forms a complete basis. That is, the wavefunctions $|\Omega_i(\mathbf{R})\rangle$ that satisfy

$$\hat{H}_{el}(\mathbf{R})|\Omega_i(\mathbf{R})\rangle = E_i(\mathbf{R})|\Omega_i(\mathbf{R})\rangle$$

form a complete basis for the electrons. Likewise, once we have selected a particular electronic state, the vibrational eigenstates on this potential surface form a complete basis for the nuclei; thus, the wavefunctions $\Phi_{J,i}(\mathbf{R})$ that satisfy

$$\left(-\tfrac{1}{2} \sum_I^{nuclei} \frac{1}{M_I} \nabla_I^2 + E_i(\mathbf{R}) \right) \Phi_{J,i}(\mathbf{R}) = E_{J,i} \Phi_{J,i}(\mathbf{R})$$

for any fixed "i" form a complete basis for expanding any nuclear wavefunction. Therefore, applying our experience with many particles, we conclude immediately that the set of products

$\Phi_{J,i}(\mathbf{R})|\Omega_i(\mathbf{R})\rangle$ form a complete basis for any wavefunction that describes the electrons and the nuclei at once. Hence, we can write any wavefunction for the molecule as:

$$\left|\Psi(\mathbf{R})\right\rangle = \sum_{i,J} C_{i,J}\Phi_{J,i}(\mathbf{R})|\Omega_i(\mathbf{R})\rangle.$$

We can use this basis to examine where the errors in the BO approximation come from. We find

$$\left\langle \Omega_{i'}(\mathbf{R})|\Phi_{J',i'}(\mathbf{R})\hat{H}\Phi_{J,i}(\mathbf{R})|\Omega_i(\mathbf{R})\right\rangle$$

$$= \left\langle \Omega_{i'}(\mathbf{R})|\Phi_{J',i'}(\mathbf{R})\left(-\frac{1}{2}\sum_I \frac{1}{M_I}\nabla_I^2 + \hat{H}_{el}(\mathbf{R})\right)\Phi_{J,i}(\mathbf{R})|\Omega_i(\mathbf{R})\right\rangle$$

$$= \left\langle \Omega_{i'}(\mathbf{R})|\Phi_{J',i'}(\mathbf{R})\left(-\frac{1}{2}\sum_I \frac{1}{M_I}\nabla_I^2 + E_i(\mathbf{R})\right)\Phi_{J,i}(\mathbf{R})|\Omega_i(\mathbf{R})\right\rangle$$

$$= \left\langle \Omega_{i'}(\mathbf{R})|\Omega_i(\mathbf{R})\right\rangle\Phi_{J',i'}(\mathbf{R})\left(-\frac{1}{2}\sum_I \frac{1}{M_I}\nabla_I^2 + E_i(\mathbf{R})\right)\Phi_{J,i}(\mathbf{R}) -$$

$$\frac{1}{2}\left\langle \Omega_{i'}(\mathbf{R})|\Phi_{J',i'}(\mathbf{R})\sum_I \frac{1}{M_I}\left(2\nabla_I\Phi_{J,i}(\mathbf{R})\cdot|\nabla_I\Omega_i(\mathbf{R})\rangle + \Phi_{J,i}(\mathbf{R})|\nabla_I^2\Omega_i(\mathbf{R})\rangle\right)\right.$$

$$= \delta_{i',i}\Phi_{J',i}(\mathbf{R})\left(-\frac{1}{2}\sum_I \frac{1}{M_I}\nabla_I^2 + E_i(\mathbf{R})\right)\Phi_{J,i}(\mathbf{R})$$

$$- \Phi_{J',i'}(\mathbf{R})\sum_I \frac{1}{M_I}\left\langle \Omega_{i'}(\mathbf{R})|\nabla_I\Omega_i(\mathbf{R})\right\rangle\cdot\nabla_I\Phi_{J,i}(\mathbf{R})$$

$$- \frac{1}{2}\Phi_{J',i'}(\mathbf{R})\Phi_{J,i}(\mathbf{R})\sum_I \frac{1}{M_I}\left\langle \Omega_{i'}(\mathbf{R})|\nabla_I^2\Omega_i(\mathbf{R})\right\rangle$$

Now, we note that we can use the matrix elements as an *effective* Hamiltonian for the nuclei alone:

$$\left\langle \Omega_{i'}(\mathbf{R})|\Phi_{J',i'}(\mathbf{R})\hat{H}\Phi_{J,i}(\mathbf{R})|\Omega_i(\mathbf{R})\right\rangle = \Phi_{J',i'}(\mathbf{R})\hat{H}_{eff}^{i',i}\Phi_{J,i}(\mathbf{R})$$

if we make the definitions

$$\hat{H}_{eff}^{i,i} = \left(\frac{1}{2}\sum_I \frac{\mathbf{P}_I^2}{M_I} + E_i(\mathbf{R})\right)\delta_{i,i'} \qquad i = i'$$

$$\hat{H}_{eff}^{i',i} = i\sum_I \frac{1}{M_I}\left(\left\langle \Omega_{i'}(\mathbf{R})|\nabla_I\Omega_i(\mathbf{R})\right\rangle\cdot\mathbf{P}_I - \tfrac{1}{2}\left\langle \Omega_{i'}(\mathbf{R})|\nabla_I^2\Omega_i(\mathbf{R})\right\rangle\right) \qquad i \neq i'.$$

This is termed the "coupled channel" Schrödinger equation, because it describes the dynamics of the molecule in terms of several possible adiabatic states, or "channels". The diagonal ($i = i'$) term is just the

BO Hamiltonian; the product basis functions we have chosen are eigenfunctions of the BO Hamiltonian by construction. The off-diagonal ($i \neq i'$) terms on the second line are the *corrections* to the BO approximation; they arise because the electronic wavefunction depends (parametrically) on the nuclear coordinates and the magnitude of the corrections will depend on the rate of change (gradient) of the electronic wavefunction as we change our nuclear configuration. If the electronic state changes rapidly over a small distance, we expect these terms to be large.

Before we move on to discuss when this happens, we note that $\langle \Omega_i(\mathbf{R}) | \nabla_I^2 \Omega_i(\mathbf{R}) \rangle$ is usually quite small, and we will not be concerned with it in what follows. Hence, we will use the approximation

$$\hat{H}_{eff}^{i',i} \approx i \sum_I \frac{1}{M_I} \langle \Omega_{i'}(\mathbf{R}) | \nabla_I \Omega_i(\mathbf{R}) \rangle \cdot \mathbf{P}_I \qquad i \neq i'$$

The remaining term couples the nuclei and electrons and can be quite large. It is usually called the non-adiabatic coupling.

c. **Non-Adiabatic Effects**

When does the BO approximation fail? This is a tricky question. One might be tempted to conclude that it will fail whenever the nuclei are light but this turns out not to be the major problem.

Let us consider the coupled channel equation and take the first term (the BO result) as the zeroth order Hamiltonian and treat the second term as a perturbation. The zeroth order Hamiltonian for the nuclei can easily be written in operator form:

$$\left(\hat{H}_0 \right)_{i,i'} = \left(\frac{1}{2} \sum_I \frac{\mathbf{P}_I^2}{M_I} + E_i(\mathbf{R}) \right) \delta_{i,i'}$$

where we stress that the nuclear momentum operator (by convention) does not act on the parametric dependence of the electronic wavefunction on $\mathbf{R}$. Our perturbation is given by:

$$\hat{V}_{i,i'} = i \sum_I \frac{\mathbf{d}_{i,i'}^I(\mathbf{R}) \cdot \mathbf{P}_I}{M_I} \qquad i \neq i'$$

Where we have defined the non-adiabatic coupling matrix by:

$$\mathbf{d}_{i,i'}^I(\mathbf{R}) \equiv \langle \Omega_{i'}(\mathbf{R}) | \nabla_I \Omega_i(\mathbf{R}) \rangle$$

This is a rather unusual matrix in that each of its elements is a **vector**. What does this vector tell us? Well, first, we note that it comes from the gradient of the electronic wavefunction with respect to the Ith nuclear coordinate. The direction of this gradient tells us the direction in which the electronic wavefunction is changing the *fastest,* while its magnitude tells us how large this change is in an absolute sense. One then takes the overlap of this gradient with the electronic function $\Omega_{i'}$. This tells us, as we vary $\mathbf{R}_I$, how much the change in Ω_i looks like a change from the current electronic state (Ω_i) to another ($\Omega_{i'}$). Hence, there is a wealth of information here; $\mathbf{d}_{i,i'}^I$ tells us how likely non-adiabatic events are (through its magnitude) what physical motions it can be associated with (through its direction) and which electronic states are involved (because of the overlap of the gradient of Ω_i with $\Omega_{i'}$).

This is a rather unusual perturbation, as it depends on the momentum of the nuclei in addition to the dependence on $\mathbf{d}_{i,i'}^I$. This means that the probability of a non-adiabatic event will depend on **how fast** the nuclei are going. If they are moving rapidly, the perturbation is larger and non-adiabatic effects are expected to be larger.

What does this tell us about when the BO approximation is expected to break down? Well, our BO states are eigenstates of $\hat{H}_0$ and this will cease to be a good approximation to the eigenstates of $\hat{H}$ when $\hat{V}$ is "large". We have already encountered the most common cause for this: if two eigenstates of $\hat{H}_0$ are degenerate then $\hat{V}$ is always


E

Degenerate
BO states

R
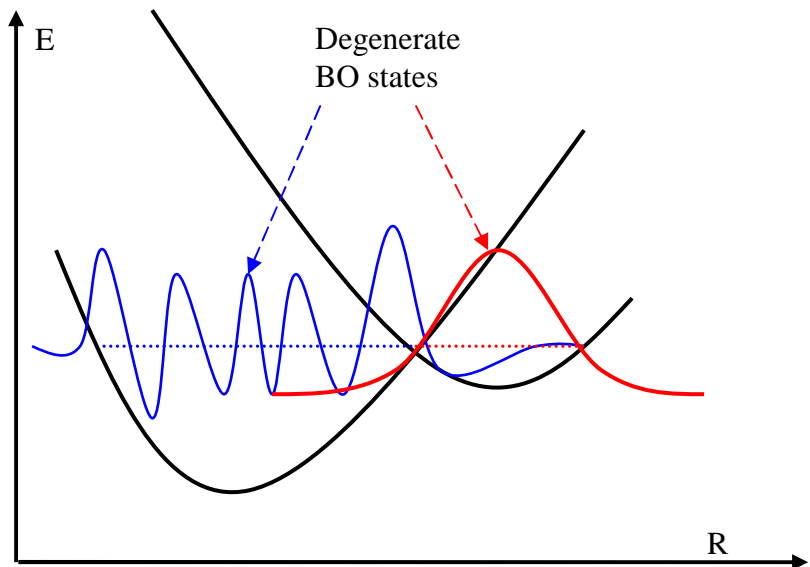
"large". What does this mean? Well, if we plot the adiabatic electronic energies as curves that are functions of R, then a degeneracy can easily occur if the curves cross, as shown in the figure above. In this case, our physical picture of the nuclear motion occurring on only one potential surface will fail and we need a linear combination of BO states on both surfaces to get a reasonable starting point

$$\Psi(\mathbf{r},\mathbf{R}) \approx c_1 \Phi_{J;1}(\mathbf{R})|\Omega_1(\mathbf{R})\rangle + c_2 \Phi_{J';2}(\mathbf{R})|\Omega_2(\mathbf{R})\rangle$$

It can be shown that these intersections never (or at least almost never) occur if there is only one nuclear dimension; one needs at least two degrees of freedom, and even then the intersection only occurs at a point. This point is called a "conical intersection" because this is the characteristic shape of two surfaces that touch at a point.

A more common occurrence is for two surfaces to **almost** intersect, but not quite.   This is shown at right and is usually referred to as an "avoided" crossing. Now if one examines the character of the electronic wavefunction near the avoided crossing, one often finds that the lower state on the left hand side is more similar to the excited

Adiabatic Basis
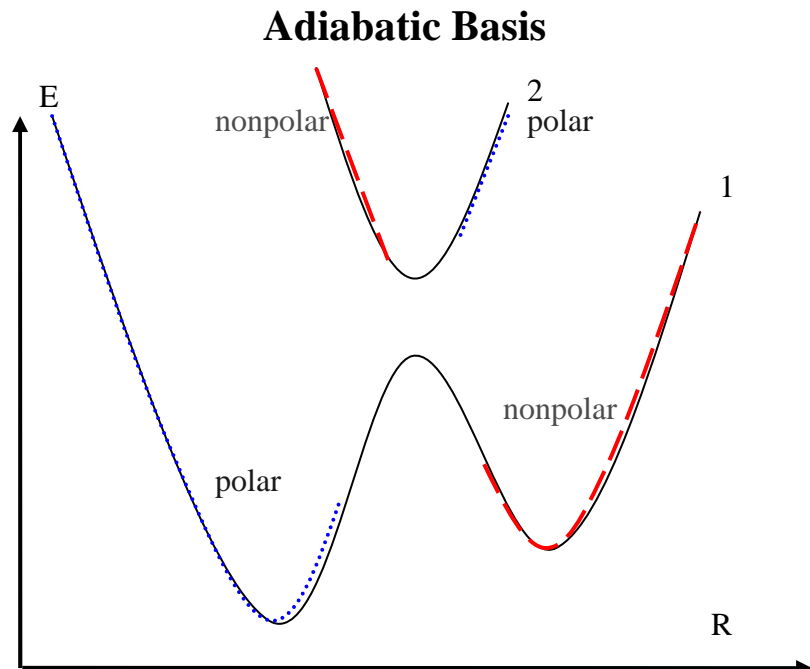
state on the right than to the ground state. For example, the molecule might be polar on the left hand side of the lower state and non-polar on the right and the excited state might have the reverse: polar on the right and non-polar on the left. This means that the adiabatic electronic wavefunctions are changing rapidly in the vicinity of the avoided crossing, which means the non-adiabatic coupling is large. Looking at this from a dynamical point of view, unless the nuclei move through the avoided crossing region **very slowly**, the

electrons will not have time to rearrange (e.g. from polar to non-polar) and we will get significant probability transfer from one surface to the other. This is often called a non-adiabatic transition between the two adiabatic surfaces.

It is disconcerting that the adiabatic electronic wavefunctions change so rapidly in the vicinity of an avoided crossing; it makes the chemistry look unnecessarily complicated. For this reason, one often invokes the concept of a **diabatic** basis. In this basis, it is the **electrons** that are held fixed and the nuclei are allowed to move freely; thus, in the above case, one would have two diabatic surfaces. One would remain polar through the crossing region, while the other would remain non-polar. The adiabatic electronic states will be linear combinations of the diabats. The non-adiabatic transition would be easily described in the diabatic basis, because the movement from the lower adiabatic surface to the upper one will correspond to staying on the **same** diabatic surface. Thus, if the nuclei move quickly through the avoided crossing region, the electronic wavefunction will not have time to react and a diabatic picture is appropriate.

Diabatic Basis

E

polar

nonpolar

R

By definition, the diabatic electronic states do not depend on $\mathbf{R}$ and so $\mathbf{d}_{i,i'}^I(\mathbf{R}) = 0$. Hence, the terms involving the nuclear kinetic energy are exceedingly simple in the diabatic representation. The electronic Hamiltonian is more complicated, however, because the diabatic states do not diagonalize $\hat{H}_{el}$. Thus, the full Hamiltonian in the diabatic basis is given by:
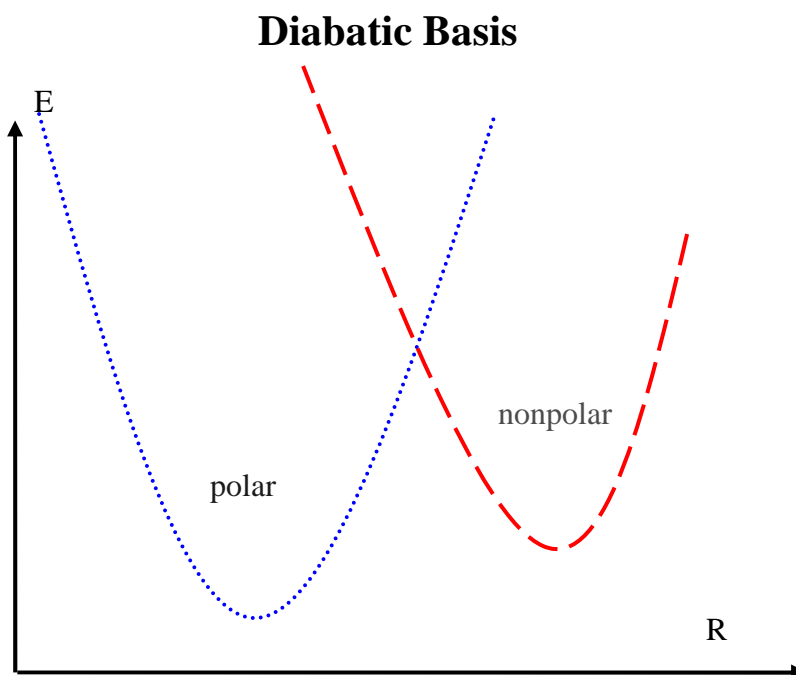
$$\hat{H} = \frac{1}{2}\sum_I \frac{\mathbf{P}_I^2}{M_I} + \sum_{ij}\left|\Omega_i^{dia}\right\rangle V_{ij}(\mathbf{R})\left\langle\Omega_j^{dia}\right|$$

where the matrix elements of the electronic Hamiltonian are given by

$$V_{ij}(\mathbf{R}) = \left\langle\Omega_i^{dia}\left|\hat{H}_{el}(\mathbf{R})\right|\Omega_j^{dia}\right\rangle.$$

In the adiabatic basis, this matrix would be diagonal, but in the diabatic basis, it is the source of transitions between the surfaces. In practice, the diabatic basis is most useful very near a conical intersection or avoided crossing.

In practice, it is usually not possible to find strictly diabatic electronic states for which $\mathbf{d}_{i,i'}^I(\mathbf{R})$ vanishes everywhere, and indeed such states are not terribly useful since a large number of strictly diabatic states would be required to describe the electronic structure. In practice, one instead wishes to find the linear combination of a small set of adiabatic states that is *maximally* diabatic:

$$\left|\tilde{\Omega}_k^{dia}(R)\right\rangle = \sum_{i=1}^{N} c_{ki}(R)\left|\Omega_i^{adia}(R)\right\rangle$$

where N is the number of adiabatic states (often 2) that we are interested in. If there is one nuclear degree of freedom, we can do this by choosing our maximal diabatic states so that $\mathbf{d}_{i,i'}(\mathbf{R})$ is diagonal; that is so that

$$\left\langle\tilde{\Omega}_j^{dia}(R)\left|\frac{\partial}{\partial R}\right|\tilde{\Omega}_k^{dia}(R)\right\rangle \propto \delta_{jk}$$

Thus, in this case, the diabatic basis becomes the set of electronic states that diagonalize the nuclear kinetic energy operator, whereas the adiabatic basis diagonalizes the electronic Hamiltonian.