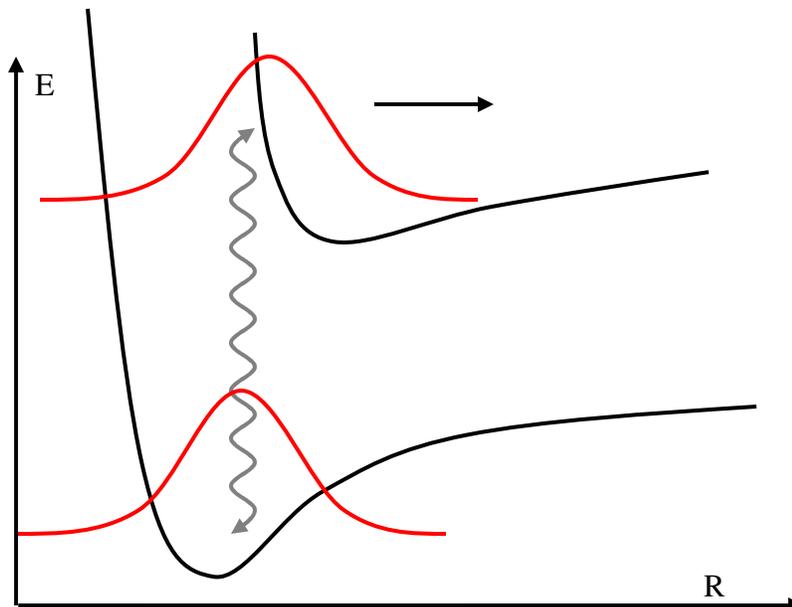


## XII. The Born-Oppenheimer Approximation

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 Born-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  $r_{\alpha\beta} \equiv |\mathbf{r}_\alpha - \mathbf{r}_\beta|$ , etc.) :

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

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:

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

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:

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

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  $\hat{H}_{el}$ :

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

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:

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

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 thought 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. The Coupled Channel Hamiltonian**

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.

To this end, 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

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

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:

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

Note that we have chosen a “mixed” representation: the nuclei are being described using wave mechanics, while the electrons use Dirac notation. This turns out to be the most convenient way to deal with mixed electron/nuclear systems. We can use this expansion to examine where the errors in the BO approximation come from. First, we represent the Hamiltonian as a matrix in the BO basis:

$$\begin{aligned} (\mathbf{H})_{i'J';iJ} &\equiv \int \langle \Omega_{i'}(\mathbf{R}) | \Phi_{J',i'}(\mathbf{R}) \left( -\sum_I \frac{1}{2M_I} \nabla_I^2 + \hat{H}_{el}(\mathbf{R}) \right) \Phi_{J,i}(\mathbf{R}) | \Omega_i(\mathbf{R}) \rangle d\mathbf{R} \\ &= \int \langle \Omega_{i'}(\mathbf{R}) | \Phi_{J',i'}(\mathbf{R}) \left( -\sum_I \frac{1}{2M_I} \nabla_I^2 + E_i(\mathbf{R}) \right) \Phi_{J,i}(\mathbf{R}) | \Omega_i(\mathbf{R}) \rangle d\mathbf{R} \\ &= \int \Phi_{J',i'}(\mathbf{R}) \left( -\sum_I \frac{1}{2M_I} \nabla_I^2 + E_i(\mathbf{R}) \right) \Phi_{J,i}(\mathbf{R}) \langle \Omega_{i'}(\mathbf{R}) | \Omega_i(\mathbf{R}) \rangle d\mathbf{R} \\ &\quad - \sum_I \frac{1}{M_I} \int \Phi_{J',i'}(\mathbf{R}) \nabla_I \Phi_{J,i}(\mathbf{R}) \cdot \langle \Omega_{i'}(\mathbf{R}) | \nabla_I \Omega_i(\mathbf{R}) \rangle d\mathbf{R} \\ &\quad - \sum_I \frac{1}{2M_I} \int \Phi_{J',i'}(\mathbf{R}) \Phi_{J,i}(\mathbf{R}) \langle \Omega_{i'}(\mathbf{R}) | \nabla_I^2 \Omega_i(\mathbf{R}) \rangle d\mathbf{R} \end{aligned}$$

$$\begin{aligned}
&= \int \Phi_{J,i}(\mathbf{R}) \left( - \sum_I \frac{1}{2M_I} \nabla_I^2 + E_i(\mathbf{R}) \right) \Phi_{J,i}(\mathbf{R}) d\mathbf{R} \delta_{i,i} \\
&\quad - \sum_I \frac{1}{M_I} \int \Phi_{J,i'}(\mathbf{R}) \nabla_I \Phi_{J,i}(\mathbf{R}) \cdot \langle \Omega_{i'}(\mathbf{R}) | \nabla_I \Omega_i(\mathbf{R}) \rangle d\mathbf{R} \\
&\quad - \sum_I \frac{1}{2M_I} \int \Phi_{J,i'}(\mathbf{R}) \Phi_{J,i}(\mathbf{R}) \langle \Omega_{i'}(\mathbf{R}) | \nabla_I^2 \Omega_i(\mathbf{R}) \rangle d\mathbf{R}
\end{aligned}$$

In the last equality, the first term is just the BO approximation; the product basis functions are eigenfunctions of the separate nuclear and electronic Hamiltonians. The terms on the second and third lines 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.

This representation of the Hamiltonian is called the coupled channel representation: each electronic state represents a different “channel” and the Hamiltonian governs the coupling between those channels. Before we move on to discuss when this happens, we note that the third term (involving  $\langle \Omega_{i'}(\mathbf{R}) | \nabla_I^2 \Omega_i(\mathbf{R}) \rangle$ , called the diagonal BO correction) is usually quite small, and we will not be concerned with it. The second term (involving  $\langle \Omega_{i'}(\mathbf{R}) | \nabla_I \Omega_i(\mathbf{R}) \rangle$ ), on the other hand, 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 Hamiltonian and take the first term (the BO result) as the zeroth order Hamiltonian and treat the second term as a perturbation (we neglect the small diagonal BO correction). Looking at the coupled channel equation, the matrix elements of the zeroth order Hamiltonian are:

$$(\mathbf{H}_0)_{iJ;iJ} = \int \Phi_{J,i}(\mathbf{R}) \left( -\sum_I \frac{1}{2M_I} \nabla_I^2 + E_i(\mathbf{R}) \right) \Phi_{J,i}(\mathbf{R}) d\mathbf{R} \delta_{i,i'}$$

In order to do perturbation theory, we need an operator that has these matrix elements. To get from a matrix to an operator, we use the fact that, in general, an operator is uniquely determined by its matrix elements:

$$\hat{H}_0 = \sum_{\alpha,\beta} |\Psi_\alpha\rangle \langle \Psi_\alpha | \hat{H}_0 | \Psi_\beta \rangle \langle \Psi_\beta | = \sum_{\alpha,\beta} |\Psi_\alpha\rangle (\mathbf{H}_0)_{\alpha,\beta} \langle \Psi_\beta |$$

In this case,  $\alpha$  and  $\beta$  are compound indices – they denote a particular choice of  $i, J$ . It turns out to be simplest to guess the operator  $\hat{H}_0$  and prove that it has the right matrix elements. Thus, assume that

$$\hat{H}_0 = \sum_i \left( \frac{1}{2} \sum_I \frac{\mathbf{P}_I^2}{M_I} + E_i(\mathbf{R}) \right) |\Omega_i(\mathbf{R})\rangle \langle \Omega_i(\mathbf{R})|$$

where, by definition, the nuclear momentum operator only acts on the nuclear wavefunction and does not effect the parametric dependence of the electronic wavefunction on  $\mathbf{R}$ . Then,

$$\begin{aligned} (\mathbf{H}_0)_{iJ;iJ} &= \sum_j \int \langle \Omega_{i'}(\mathbf{R}) | \Phi_{J,i}(\mathbf{R}) \left( \left( \sum_I \frac{\mathbf{P}_I^2}{2M_I} + E_j(\mathbf{R}) \right) |\Omega_j(\mathbf{R})\rangle \langle \Omega_j(\mathbf{R})| \right) \Phi_{J,i}(\mathbf{R}) |\Omega_i(\mathbf{R})\rangle d\mathbf{R} \\ &= \sum_j \int \Phi_{J,i}(\mathbf{R}) \left( \left( \sum_I \frac{\mathbf{P}_I^2}{2M_I} + E_j(\mathbf{R}) \right) \right) \Phi_{J,i}(\mathbf{R}) \langle \Omega_{i'}(\mathbf{R}) | \Omega_j(\mathbf{R}) \rangle \langle \Omega_j(\mathbf{R}) | \Omega_i(\mathbf{R}) \rangle d\mathbf{R} \\ &= \int \Phi_{J,i}(\mathbf{R}) \left( \left( \sum_I \frac{\mathbf{P}_I^2}{2M_I} + E_j(\mathbf{R}) \right) \right) \Phi_{J,i}(\mathbf{R}) d\mathbf{R} \delta_{i,i'} \end{aligned}$$

Which is identical to the original set of matrix elements.

It is a little more complicated to write the second term in operator form. The matrix elements of our perturbation are given by:

$$\begin{aligned} (\hat{V})_{i,J;i,J} &= -\sum_I \frac{1}{M_I} \int \Phi_{J,i'}(\mathbf{R}) \nabla_I \Phi_{J,i}(\mathbf{R}) \cdot \langle \Omega_{i'}(\mathbf{R}) | \nabla_I \Omega_i(\mathbf{R}) \rangle d\mathbf{R} \\ \Rightarrow (\hat{V})_{i,J;i,J} &= -\sum_I \frac{1}{M_I} \int \Phi_{J,i'}(\mathbf{R}) \nabla_I \Phi_{J,i}(\mathbf{R}) \cdot \mathbf{d}_{i',i}^I(\mathbf{R}) d\mathbf{R} \end{aligned}$$

Where, on the last line, we have defined the non-adiabatic coupling matrix by:

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

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  $I^{\text{th}}$  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  $\Omega_{j'}$ . This tells us, as we vary  $\mathbf{R}$ , how much the change in  $\Omega_j$  looks like a change from the current electronic state ( $\Omega_j$ ) to another ( $\Omega_{j'}$ ). Hence, there is a wealth of information here;  $\mathbf{d}_{i,j'}^I$  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  $\Omega_j$  with  $\Omega_{j'}$ ).

We are now able to guess the form of our perturbation operator:

$$\hat{V} = \sum_{j',j} |\Omega_{j'}(\mathbf{R})\rangle i \sum_I \frac{\mathbf{P}_I \cdot \mathbf{d}_{j',j}^I(\mathbf{R})}{M_I} \langle \Omega_j(\mathbf{R})|$$

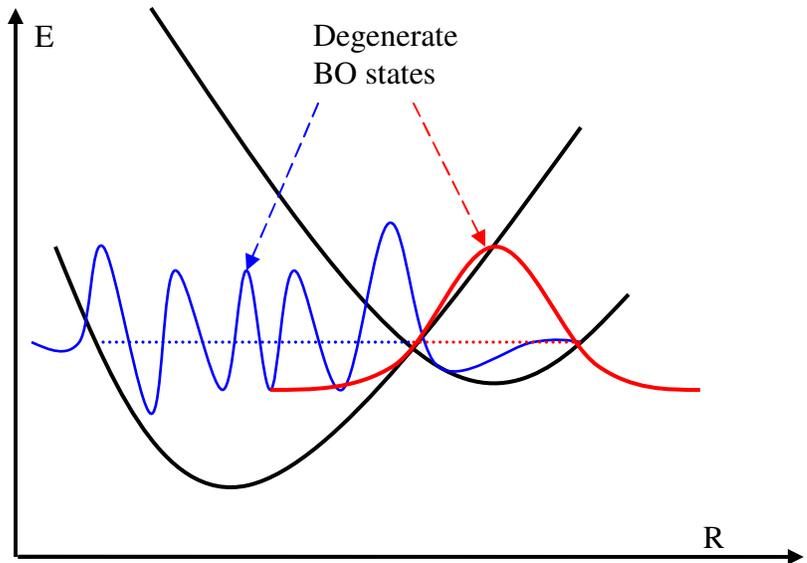
First, we verify that this gives the desired matrix elements:

$$\begin{aligned} (\hat{V})_{k',J';k,J} &= \sum_{I,j,j'} \int \langle \Omega_{k'}(\mathbf{R}) | \Phi_{J',k}(\mathbf{R}) \left( |\Omega_{j'}(\mathbf{R})\rangle i \sum_I \frac{\mathbf{P}_I \cdot \mathbf{d}_{j',j}^I(\mathbf{R})}{M_I} \langle \Omega_j(\mathbf{R})| \right) \Phi_{J,k}(\mathbf{R}) | \Omega_k(\mathbf{R}) \rangle d\mathbf{R} \\ &= \sum_{I,j,j'} \int \Phi_{J',k}(\mathbf{R}) i \sum_I \frac{\mathbf{P}_I \cdot \mathbf{d}_{j',j}^I(\mathbf{R})}{M_I} \Phi_{J,k}(\mathbf{R}) \langle \Omega_{k'}(\mathbf{R}) | \Omega_{j'}(\mathbf{R}) \rangle \langle \Omega_j(\mathbf{R}) | \Omega_k(\mathbf{R}) \rangle d\mathbf{R} \\ &= \sum_{I,j,j'} \int \Phi_{J',k}(\mathbf{R}) i \sum_I \frac{\mathbf{P}_I \cdot \mathbf{d}_{k',k}^I(\mathbf{R})}{M_I} \Phi_{J,k}(\mathbf{R}) d\mathbf{R} \end{aligned}$$

which is clearly the correct result, and so we conclude we have the right operator representation of  $\hat{V}$ . Now, this is a rather unusual perturbation, as it depends on the momentum of the nuclei. 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 “large”. What does this mean? Well, if we plot the adiabatic electronic energies as curves that are functions of  $R$ , then a degeneracy can occur if two of these curves

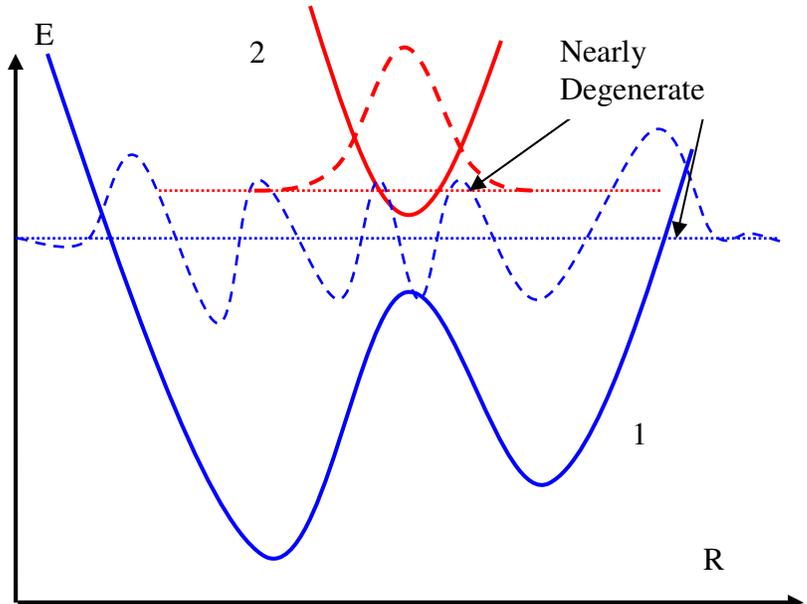


cross, as shown in the figure at right. In this case, our physical picture of the nuclear motion occurring on only one potential surface will fail and we need a linear combination of BO states on both surfaces to get a reasonable starting point

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

Note that we would have the same problem if the two states almost cross (a so-called “avoided crossing”), as illustrated in the figure at right. Thus we see that **the Born Oppenheimer approximation fails when two electronic states (almost) cross.**

Note that thermal fluctuations are unlikely to probe these crossings: the energy required to approach a crossing is typically the characteristic energy of an **electronic** excitation (1-2 eV), which is quite a lot of energy.



Hence, non-adiabatic transitions are only relevant in two situations: 1) if the molecule is photoexcited, either with a large amount of vibrational or electronic energy 2) if there are low-lying electronic excited states.

The latter is true, for example, in a metal, which has a continuum of low-lying excited states.

#### **d. Diabatic States**

In the adiabatic (BO) representation, we found we could write the Hamiltonian as

$$\hat{H} = \sum_i \left( \frac{1}{2} \sum_I \frac{\mathbf{P}_I^2}{M_I} + E_i(\mathbf{R}) \right) |\Omega_i(\mathbf{R})\rangle \langle \Omega_i(\mathbf{R})| + \sum_{i,i'} \sum_I \frac{\mathbf{P}_I \cdot \mathbf{d}_{i,i'}^I(\mathbf{R})}{M_I} |\Omega_{i'}(\mathbf{R})\rangle \langle \Omega_i(\mathbf{R})|$$

where the first term was the BO Hamiltonian and the second was the nonadiabatic coupling, which generates transitions between the BO states. The nonadiabatic coupling is a bit difficult to deal with, and so we'd like to get rid of it. To this end, note that the nonadiabatic coupling only arises because the electronic wavefunctions change with  $\mathbf{R}$ , which arises because the electronic states are eigenstates of an  $\mathbf{R}$ -dependent Hamiltonian:

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

We can get rid of the  $\mathbf{R}$ -dependence by choosing a fixed, complete basis for the electrons. There are, of course, many possible choices in this case, but generically one calls any fixed basis of electronic states a **diabatic** basis. Thus, for example, one can expand the adiabatic states in terms of the diabatic states:

$$|\Omega_k(\mathbf{R})\rangle = \sum_{i=1} c_{ki}(\mathbf{R}) |\Omega_i^{dia}\rangle$$

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:

$$\hat{H} = \frac{1}{2} \sum_I \frac{\mathbf{P}_I^2}{M_I} + \sum_{ij} |\Omega_i^{dia}\rangle V_{ij}(\mathbf{R}) \langle \Omega_j^{dia}|$$

where the matrix elements of the electronic Hamiltonian are given by

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

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 crossing 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:

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

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

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

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.

## **e. Electron Transfer**

To illustrate some of the important points about when the Born-Oppenheimer approximation is (and is not) a good approximation, it is useful to work an example. Here, we will consider electron transfer between a donor (D) and an acceptor (A), coupled by some nuclear coordinate  $R$ . For simplicity, we will ignore all the other nuclear coordinates in this problem, so our nuclei will “live” in one dimension. Further, we will only be interested in two states, “electron on donor” (which we will denote  $|1\rangle$ ) and “electron on acceptor” (which we will denote  $|2\rangle$ ). These are clearly diabatic states because they do not change with  $R$ . We’ll be interested in finding out what the appropriate adiabatic states are for this situation and we will discuss when these states are useful.

In order to use these states, we need to be able to represent the electronic Hamiltonian in the diabatic basis. To this end, suppose the diabatic matrix elements are given by:

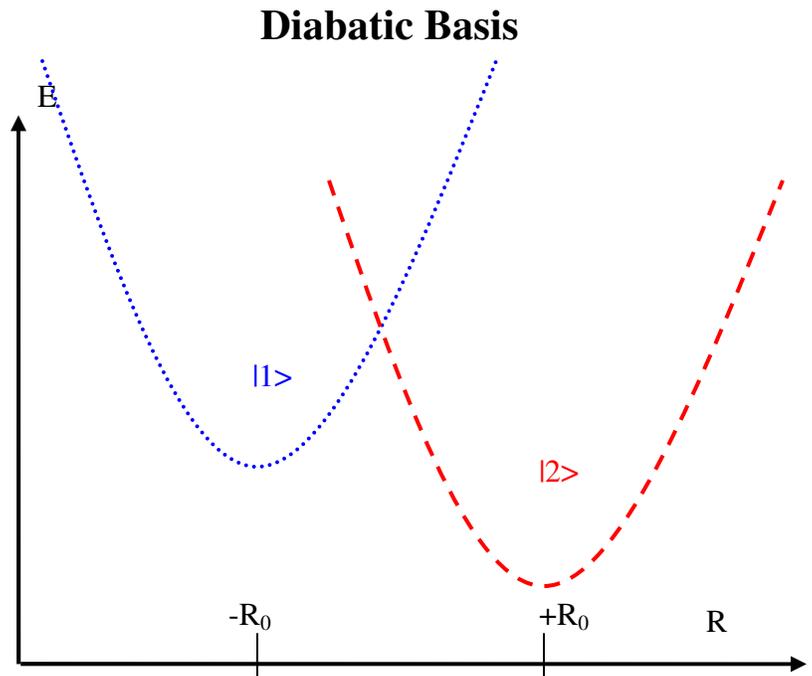
$$\hat{V}_{11}(R) \equiv E_1 + \frac{1}{2} m \omega^2 (\hat{R} + R_0)^2$$

$$\hat{V}_{22}(R) = E_2 + \frac{1}{2} m \omega^2 (\hat{R} - R_0)^2$$

$$\hat{V}_{12} = \text{constant}$$

The two diabatic surfaces are shown at right; clearly, there is a crossing between the two at some value of  $R$  between  $-R_0$

(the optimal distance for the donor) and  $+R_0$  (the optimal distance for the acceptor). The assumption that the coupling ( $V_{12}$ ) between the two states is constant is merely the simplest; more complicated forms could also be imagined.



Now, the adiabatic state energies are the eigenvalues of the electronic Hamiltonian for a given  $R$ . In the diabatic basis,

$$\hat{H}_{el}(R) \equiv \begin{pmatrix} V_{11}(R) & V_{12}(R) \\ V_{12}(R) & V_{22}(R) \end{pmatrix}$$

Hence, the adiabatic energies are:

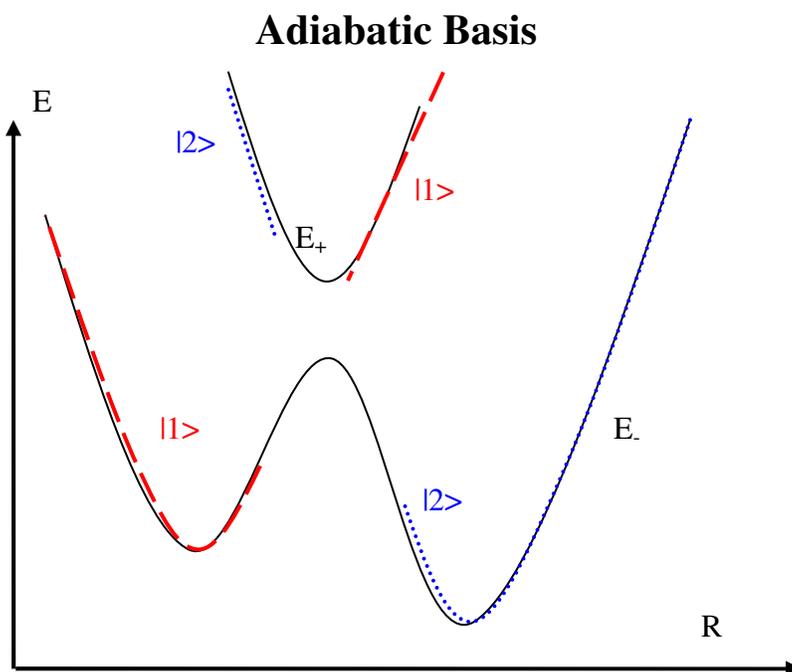
$$E_{\pm}(R) = \frac{V_{11}(R) + V_{22}(R)}{2} \pm \sqrt{\frac{(V_{11}(R) - V_{22}(R))^2}{4} + V_{12}^2}$$

If we plot these two energies as a function of  $R$ , we obtain the picture below. Note that these two surfaces **almost** intersect, but not quite. This is usually referred to as an “avoided” crossing. It can be shown that these intersections never (or at least almost never) occur if there is only one nuclear dimension. The argument proceeds as follows: in order for  $E_+$  to equal  $E_-$ , the term under the square root above would need to be zero. In order for this to be true we need to satisfy two equations:

$$V_{11}(R) = V_{22}(R) \text{ and } V_{12}(R) = 0$$

If we only have one degree of freedom ( $R$ ) it is, generally, not possible to satisfy two independent equations. Though this is not a particularly rigorous proof (there are many exceptions based on symmetry and just blind luck) this observation holds quite generally and is known as the “no crossing rule”: adiabatic states cannot cross in 1D.

Thus (except in the case of “accidental” solutions) one thus needs at least two degrees of freedom to get an intersection, 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. Further, even in more than two dimensions, an intersection between two adiabatic surfaces is called a “conical intersection”.



Now, the adiabatic states can be written in terms of the eigenvectors of the electronic Hamiltonian as:

$$|+\rangle = c_1^+(R)|1\rangle + c_2^+(R)|2\rangle \quad \text{and} \quad |-\rangle = c_1^-(R)|1\rangle + c_2^-(R)|2\rangle$$

The actual forms of the coefficients are rather complicated and will not be reproduced here. We will satisfy ourselves with the qualitative observation that, for large, negative  $R$  we have  $|+\rangle \approx |1\rangle$  while for large positive  $R$  we have  $|+\rangle \approx |2\rangle$ . Thus, between  $-R_0$  and  $+R_0$  the lower adiabatic state changes character – it goes from looking mostly like “electron on donor” to looking mostly like “electron on acceptor”. Thus, while the adiabatic states do not cross, they do change rapidly between  $-R_0$  and  $+R_0$  to “avoid” each other.

What are the consequences of this? Well, the adiabatic states factor in to the nonadiabatic coupling as follows:

$$\mathbf{d}_{i,i}(R) = \left\langle \Omega_i(R) \left| \frac{\partial}{\partial R} \Omega_i(R) \right. \right\rangle$$

In principle, there are four couplings ( $d_{++}$ ,  $d_{+-}$ ,  $d_{-+}$  and  $d_{--}$ ). However, we note that if we replace each of the adiabatic states by the same state multiplied by a phase, then  $d_{++}$  becomes:

$$\begin{aligned} \mathbf{d}_{++}(R) &= \left\langle \Omega_+(R) \left| e^{-i\phi_+(R)} \left( \frac{\partial}{\partial R} e^{i\phi_+(R)} \right) \Omega_+(R) \right. \right\rangle \\ &= i \frac{\partial}{\partial R} \phi_+(R) + \left\langle \Omega_+(R) \left| \frac{\partial}{\partial R} \Omega_+(R) \right. \right\rangle \end{aligned}$$

And similarly for  $d_{--}$ . Now, multiplying an eigenstate by a constant gives a state that is indistinguishable from the original state. It is therefore conventional to **choose the phase of each eigenstate so that the diagonal nonadiabatic couplings vanish**. Then, we only need to worry about the off-diagonal term:

$$\mathbf{d}_{-+}(R) = \left\langle \Omega_-(R) \left| \frac{\partial}{\partial R} \Omega_+(R) \right. \right\rangle$$

This term will be large when the “+” state changes rapidly with  $R$ . We have already seen that this occurs between  $-R_0$  and  $+R_0$ . Thus, **the nonadiabatic coupling is large in the vicinity of an avoided crossing**.

Thus, the picture of electron transfer is as follows: if the nuclei move very, very slowly the adiabatic picture is appropriate. Then, as the nuclei move from  $-R_0$  to  $+R_0$  the electron moves from donor (state 1) to acceptor (state 2) without any difficulty. Nonadiabatic effects are small because the nuclear momentum is small, making the perturbation  $\hat{V} = \mathbf{P} \cdot \mathbf{d}_{-+}(R)$  negligible. However, if the nuclei move quickly, then the adiabatic approximation begins to break down – the electron does not have enough time to transfer from donor to acceptor. This shows up as an increase in the size of the perturbation  $\hat{V} = \mathbf{P} \cdot \mathbf{d}_{-+}(R)$ , which causes **transitions** between the adiabatic states. This non-adiabatic transition is easily described in the **diabatic** basis, because the movement from the lower adiabatic surface to the upper one corresponds 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. On the other hand, slow-moving nuclei are difficult to describe in the diabatic basis (the dynamics involves many transitions between the diabatic states) and are more easily dealt with in the adiabatic basis.