

1. Consider a diatomic molecule with two electronic states, $|1\rangle$ and $|2\rangle$ and a bond length R . The Hamiltonian for this system in the diabatic basis is given by:

$$\hat{H} = |1\rangle\left(-\frac{1}{2}\nabla_R^2 + V_{11}(\hat{R})\right)\langle 1| + |1\rangle V_{12}(\hat{R})\langle 2| \\ + |2\rangle V_{21}(\hat{R})\langle 1| + |2\rangle\left(-\frac{1}{2}\nabla_R^2 + V_{22}(\hat{R})\right)\langle 2|$$

where the relevant interactions are given by

$$V_{11}(\hat{R}) = 0$$

$$V_{22}(\hat{R}) = .05 - .1 e^{-.28 R^2}$$

$$V_{12}(\hat{R}) = V_{21}(\hat{R}) = .015 e^{-.06 R^2}$$

Plot the associated adiabatic potentials and non-adiabatic coupling. Describe what you see.

The adiabatic electronic states diagonalize the potential matrix:

$$V = \begin{pmatrix} 0 & V_{12} \\ V_{21} & V_{22} \end{pmatrix}$$

and the adiabatic energies are the eigenvalues of the adiabatic states. A little work with Mathematica gives the eigenvalues

$$E_{\pm} = \frac{V_{22}}{2} \pm \sqrt{\frac{V_{22}^2}{4} + V_{12}^2}$$

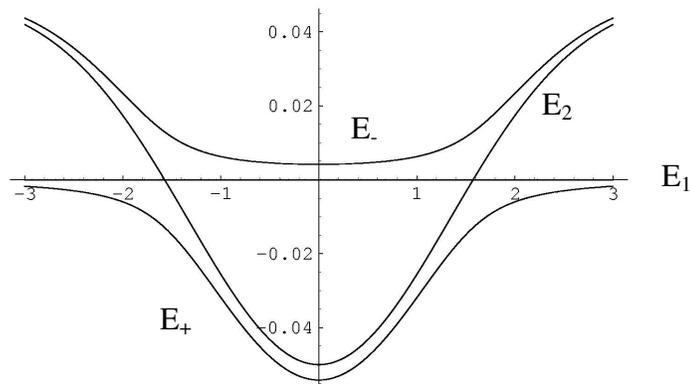
and eigenvectors ($\frac{V_{22}}{2} \equiv \Delta, \sqrt{\frac{V_{22}^2}{4} + V_{12}^2} \equiv \Gamma$):

$$\mathbf{c}_{\pm} = \frac{1}{\sqrt{(\Delta \mp \Gamma)^2 + V_{12}^2}} \begin{pmatrix} -\Delta \pm \Gamma \\ V_{12} \end{pmatrix}.$$

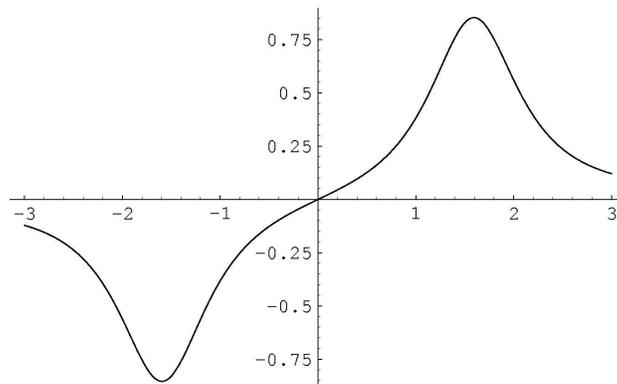
Thus, the non-adiabatic coupling between the two states is:

$$\mathbf{c}_+^T \cdot \frac{d}{dR} \mathbf{c}_- = \frac{1}{\sqrt{(\Delta + \Gamma)^2 + V_{12}^2}} \frac{1}{\sqrt{(\Delta - \Gamma)^2 + V_{12}^2}} (-\Delta + \Gamma \quad V_{12}) \begin{pmatrix} -\Delta' - \Gamma' \\ V_{12}' \end{pmatrix} \\ = \frac{(\Delta - \Gamma)(\Delta' + \Gamma') + V_{12}' V_{12}}{\sqrt{(\Delta^2 - \Gamma^2)^2 + V_{12}^4}}$$

If we plot the eigenenergies (along with the diabatic states), we find:



Thus, there are two crossings in the diabatic picture (around $R=\pm 1.5$) which turn into avoided crossings in the adiabatic picture. Meanwhile, the diabatic coupling looks like:



Clearly, the diabatic coupling is large near the two avoided crossings, indicating that the adiabatic states change rapidly around these points.

2. A Jahn-Teller distortion occurs when a molecule that would have a degenerate electronic configuration if the nuclei were arranged symmetrically instead distorts so that the electronic degeneracy is lifted and the energy is lowered. This problem concerns a model of Jahn-Teller distortion. Consider a system with two low-lying diabatic electronic states, $|1\rangle$ and $|2\rangle$, and two vibrational modes, x and y . The Hamiltonian for this molecule is:

$$\hat{H} = |1\rangle \left(-\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} + V_{11}(x, y) \right) \langle 1| + |1\rangle V_{12}(x, y) \langle 2| \\ + |2\rangle V_{21}(x, y) \langle 1| + |2\rangle \left(-\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} + V_{22}(x, y) \right) \langle 2|$$

where the electronic matrix elements are

$$V_{11}(x, y) = V_{22}(x, y) = \frac{\omega}{2} (x^2 + y^2)$$

$$V_{12}(x, y) = V_{21}(x, y)^* = k(x + iy)$$

In this model, the origin ($x = y = 0$) corresponds to the symmetric configuration and the x and y modes correspond to vibrational motions that distort the molecule away from the symmetric geometry. Note that the first and second diabatic states are degenerate, as advertised.

a) Determine the adiabatic electronic energies of this potential. Express the result in terms of polar coordinates $x \rightarrow \rho \cos \theta$ and $y \rightarrow \rho \sin \theta$. Does this model properly describe a distorted molecule? If so what is the magnitude of the distortion (in terms of ω and k)? What is the energy lowering due to the distortion? What happens to the two surfaces at the symmetric geometry ($\rho = 0$)?

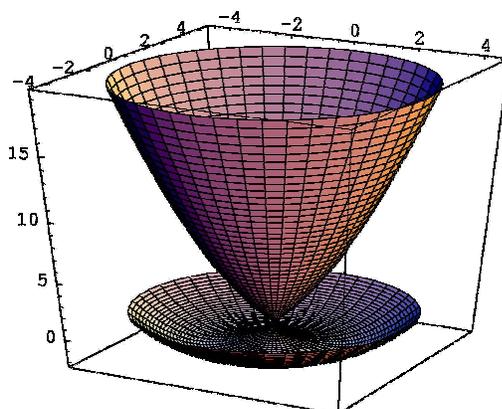
The adiabatic electronic states diagonalize the potential matrix:

$$V = \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix}$$

and the adiabatic energies are the eigenvalues of the adiabatic states. A little work with Mathematica gives the eigenvalues

$$V_{\pm} = \frac{\omega}{2} \rho^2 \pm k\rho = \frac{\omega}{2} \left(\rho \pm \frac{k}{\omega} \right)^2 - \frac{k^2}{2\omega}$$

Hence, the effect of the coupling is to take the two degenerate diabatic states and split them into two shifted harmonic oscillators. Pictorially, the two surfaces look like:



Note that the surfaces are rotationally symmetric (the potential just depends on ρ). Since $\rho=0$ is the symmetric geometry, the shifted oscillators do, indeed describe a distorted molecule, at least for the lower surface (which is what the Jahn-Teller theorem applies to). The magnitude of the distortion is the distance the oscillator minimum is from the symmetric geometry (k/ω) and the energetic stabilization is the energy at the minimum of the lower surface ($-k^2/2\omega$). At the symmetric geometry, the picture shows that there is a conical intersection, and the two surfaces cross (i.e. they are degenerate).

b) Determine the adiabatic electronic states. Use these states to compute the non-adiabatic coupling. Make sure to choose the relative phase of the two states so that the diagonal part is zero: $\langle \psi_{lower} | \nabla | \psi_{lower} \rangle = \langle \psi_{upper} | \nabla | \psi_{upper} \rangle = 0$.

c) What happens to the nonadiabatic coupling at the symmetric geometry? Note that the physical state of the molecule is the same at the polar points (ρ, θ) and $(\rho, \theta + 2\pi)$ since this just corresponds to a 360 degree

rotation. Show that the adiabatic wavefunctions at (ρ, θ) and $(\rho, \theta + 2\pi)$ **are not** the same. Could this have any experimental consequences?

If you ask Mathematica to give you the eigenvectors of the potential matrix (and are careful to make sure they are normalized), you get the two states:

$$|\psi_+\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{i\theta} \\ 1 \end{pmatrix} \quad |\psi_-\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} -e^{i\theta} \\ 1 \end{pmatrix}$$

Unfortunately, an equivalent set of eigenvectors is obtained if you multiply the above vectors by $e^{-i\theta/2}$:

$$|\psi_+\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{i\theta/2} \\ e^{-i\theta/2} \end{pmatrix} \quad |\psi_-\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} -e^{i\theta/2} \\ e^{-i\theta/2} \end{pmatrix}$$

Both expressions are correct. However, the second set of states is the traditional choice because it makes the diagonal elements of the non-adiabatic coupling zero:

$$\langle \psi_+ | \nabla | \psi_+ \rangle \propto \begin{pmatrix} e^{-i\theta/2} & e^{i\theta/2} \end{pmatrix} \frac{\partial}{\partial \theta} \begin{pmatrix} e^{i\theta/2} \\ e^{-i\theta/2} \end{pmatrix} = \begin{pmatrix} e^{-i\theta/2} & e^{i\theta/2} \end{pmatrix} \begin{pmatrix} ie^{i\theta/2} \\ -ie^{-i\theta/2} \end{pmatrix} = i - i = 0$$

$$\langle \psi_- | \nabla | \psi_- \rangle \propto \begin{pmatrix} -e^{-i\theta/2} & e^{i\theta/2} \end{pmatrix} \frac{\partial}{\partial \theta} \begin{pmatrix} -e^{i\theta/2} \\ e^{-i\theta/2} \end{pmatrix} = i - i = 0$$

The first states are single-valued for all θ while the second set acquires a “-“ sign on going from θ to $\theta+2\pi$. This minus sign problem occurs anytime there is a conical intersection. In order to have a single valued wavefunction overall, the extra phase in the adiabatic electronic wavefunction is exactly cancelled by an extra phase (of the opposite sign) in the nuclear part – the so-called “Berry’s phase”. The extra phase required is different on the two different surfaces, and so for non-adiabatic processes the phase shows up as an experimentally observable interference pattern.

To calculate the non-adiabatic coupling, we need $\langle \psi_- | \nabla | \psi_+ \rangle$. This can be computed in one of two ways; we can either re-write the eigenvectors in terms of x and y and then compute

the gradient in those coordinates, or we can use the expression for ∇ in polar coordinates (which can be found in the back of CTDL):

$$\nabla = \mathbf{e}_\rho \frac{\partial}{\partial \rho} + \mathbf{e}_\theta \frac{1}{\rho} \frac{\partial}{\partial \theta}.$$

Taking the second route and remembering to take the conjugate transpose of the bra vector,

$$\begin{aligned} \langle \psi_- | \nabla | \psi_+ \rangle &= \frac{1}{2} \mathbf{e}_\rho \begin{pmatrix} -e^{-i\theta} & 1 \end{pmatrix} \frac{\partial}{\partial \rho} \begin{pmatrix} e^{i\theta} \\ 1 \end{pmatrix} + \frac{1}{2} \mathbf{e}_\theta \begin{pmatrix} -e^{-i\theta} & 1 \end{pmatrix} \frac{1}{\rho} \frac{\partial}{\partial \theta} \begin{pmatrix} e^{i\theta} \\ 1 \end{pmatrix} \\ &= \mathbf{e}_\theta \frac{-i}{2\rho} \end{aligned}$$

where it is important to note that this is still a vector, even though the ρ component is zero. The direction of the non-adiabatic coupling tells us the direction along which the adiabatic wavefunction has its maximum rate of change. In this case, the change is always in the θ direction, so the wavefunction changes as we circle around the origin. At the origin $\rho=0$, and the non-adiabatic coupling is infinite. This reflects the fact that, for small ρ , the adiabatic wavefunctions change rapidly as one makes a tiny circuit around the origin. For example, for $\theta=0$

$$|\psi_+\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{i0} \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

while for $\theta=\pi$

$$|\psi_+\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{i\pi} \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 \\ 1 \end{pmatrix}.$$

Hence near the origin the adiabatic wavefunctions change infinitely rapidly and the non-adiabatic coupling blows up. This signals the catastrophic breakdown of the Born-Oppenheimer approximation in this region.

3. Use simple molecular orbital theory to obtain energy expressions for the lowest two singlet states of H_2 in terms of the basic quantities:

$$\varepsilon_1 \equiv \langle \sigma | h | \sigma \rangle \quad J_{11} \equiv \langle \sigma \sigma | \frac{1}{r_{12}} | \sigma \sigma \rangle \quad J_{12} \equiv \langle \sigma \sigma^* | \frac{1}{r_{12}} | \sigma \sigma^* \rangle$$

$$\varepsilon_2 \equiv \langle \sigma^* | h | \sigma^* \rangle \quad K_{12} \equiv \langle \sigma^* \sigma | \frac{1}{r_{12}} | \sigma \sigma^* \rangle \quad J_{22} \equiv \langle \sigma^* \sigma^* | \frac{1}{r_{12}} | \sigma^* \sigma^* \rangle$$

Use the attached table to evaluate several values of the H-H bond length (R). Does MO theory obey the non-crossing rule? How can you justify your results?

First, we write down the two lowest singlet states, in the convenient space-times-spin form:

$$|\Psi_0\rangle = |\sigma\rangle|\sigma\rangle \frac{1}{\sqrt{2}} (|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle)$$

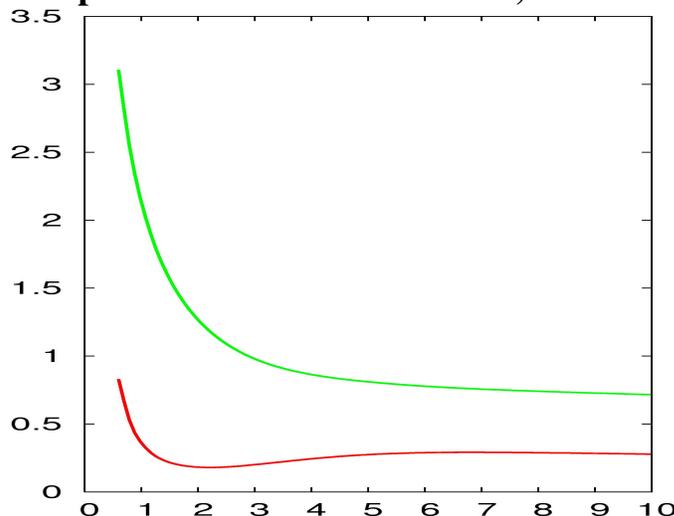
$$|\Psi_1\rangle = \frac{1}{\sqrt{2}} (|\sigma\rangle|\sigma^*\rangle + |\sigma^*\rangle|\sigma\rangle) \frac{1}{\sqrt{2}} (|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle)$$

Next, we determine the energy expressions in terms of the integrals we've been given (omitting some algebra here):

$$\langle \Psi_0 | \hat{H}_{el} | \Psi_0 \rangle = 2\varepsilon_1 + J_{11} + \frac{1}{R}$$

$$\langle \Psi_1 | \hat{H}_{el} | \Psi_1 \rangle = \varepsilon_1 + \varepsilon_2 + J_{12} + K_{12} + \frac{1}{R}$$

If we plot these as a function of R , we find:



At this point I have to apologize; I gave you the wrong integrals here. The numbers I've labeled are actually

$$\varepsilon_1 \equiv \langle \sigma | h | \sigma \rangle + \langle \sigma \sigma | \frac{1}{r_{12}} | \sigma \sigma \rangle$$

$$\varepsilon_2 \equiv \langle \sigma^* | h | \sigma^* \rangle + \langle \sigma^* \sigma^* | \frac{1}{r_{12}} | \sigma^* \sigma^* \rangle$$

That is, they include some average piece of the electron-electron repulsion. As a result, all the energies above are too high. However, the no crossing rule is still obeyed (as would have been if we used the correct integrals, as well) and we see that the excited state dissociates to excited H-atom fragments. We can see this from the wavefunction, because

$$|\Psi_1\rangle = \frac{1}{\sqrt{2}} (|\sigma\rangle|\sigma^*\rangle + |\sigma^*\rangle|\sigma\rangle) \frac{1}{\sqrt{2}} (|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle)$$

$$= \frac{1}{\sqrt{2}} (|1s_A\rangle|1s_A\rangle + |1s_B\rangle|1s_B\rangle) \frac{1}{\sqrt{2}} (|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle)$$

So, the first excited singlet contains only ionic terms and dissociates exactly to H+ ... H-. You would have been able to tell this from the picture if I had given you the correct integrals.