

5.73 Problem Set 7

Due: Friday, Dec. 9 2004

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.

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 ($\rho = 0$)?

b) Determine the adiabatic (Born-Oppenheimer) 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 of the coupling 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?

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?