Theoretical Photochemistry WiSe 2017/18 – Exercise 4

1. Consider the following diabatic potential matrix in one spatial dimension,

$$\mathbf{V}(x) = \begin{pmatrix} V_{11}(x) & V_{12} \\ V_{12} & V_{22}(x) \end{pmatrix} = V_0(x)\mathbf{1} + \begin{pmatrix} \kappa^{(1)}x & \lambda \\ \lambda & \kappa^{(2)}x \end{pmatrix} \tag{1}$$

with a harmonic zeroth-order potential term, $V_0(x) = (1/2)k_x x^2$, along with a diagonal "tuning" type[a] term, $V_i = \kappa^{(i)}x$, and an off-diagonal "coupling" type term, $V_{12} = \lambda$.

(a) Draw the diagonal potential functions $V_{11}(x)$ and $V_{22}(x)$ including the zeroth-order harmonic term. Show that the tuning terms give rise to shifts of the zeroth-order harmonic potential.

(b) Calculate the adiabatic potentials $\epsilon_1(x)$ and $\epsilon_2(x)$ by diagonalizing $\mathbf{V}(x)$. Next, calculate the eigenvectors, which correspond to adiabatic states expressed in a diabatic basis. Explain why (i) the adiabatic potentials describe a so-called avoided crossing, and (ii) the eigenvectors change character upon passage through the crossing region.

2. In two (and more) dimensions, we encounter a different type of topology denoted "conical intersection". An example of a diabatic potential in 3D exhibiting this topology is

$$\mathbf{V}_{\text{CoIn}}(x_1, x_2, y) = V_0(x_1, x_2, y) + \begin{pmatrix} \sum_{i=1}^{2} \kappa_i^{(1)} x_i & \lambda y \\ \lambda y & \sum_{i=1}^{2} \kappa_i^{(2)} x_i \end{pmatrix} \tag{2}$$

where the diabatic coupling now depends on the coordinate y, i.e., $V_{12}(y) = \lambda y$. The zeroth-order potential term is again taken to be harmonic,

$$V_0(x_1, x_2, y) = \Big(\sum_{i=1}^{2} \frac{1}{2} k_{x,i} x_i^2\Big) + \frac{1}{2} k_y y^2 \tag{3}$$

(a) Calculate the adiabatic potentials $\epsilon_1(x_1, x_2, y)$ and $\epsilon_2(x_1, x_2, y)$. What happens at $y = 0$? Draw the shape of the adiabatic potential surfaces as a function of x_1 and y, for $x_2 = \text{const}$. Explain why the observed topology corresponds to a double-cone shape. Where is the apex of the double cone located?

[a] These "tune" (or modulate) the diagonal energy gap – hence the name "tuning modes".

(b) Which conditions must be fulfilled at the crossing of the adiabatic potentials? What follows for the values of the tuning modes (x_1, x_2) and the coupling mode y at the crossing?

(c) From (b), deduce the dimension of the *intersection space*, i.e., the subspace where a crossing of the adiabatic potential surfaces occurs. Explain the notion of a conical intersection *seam*.

(d) The subspace complementary to the intersection space is the so-called *branching space* where the degeneracy is lifted. What is the dimension of the branching space?

(e) To make the notion of the branching space more precise, we consider a Taylor expansion of the potential about the point(s) of degeneracy, denoted $\boldsymbol{\xi}_X = (x_1^X, x_2^X, y^X)$. We therefore obtain in the neighborhood of the conical intersection, for $\boldsymbol{\xi} = \boldsymbol{\xi}_X + \boldsymbol{\Delta\xi}$:

$$\epsilon_{1/2} = V_0(\boldsymbol{\xi}_X) + \frac{1}{2}\boldsymbol{\kappa}_+ \cdot \boldsymbol{\Delta\xi} \pm \frac{1}{2}\sqrt{(\boldsymbol{\kappa}_- \cdot \boldsymbol{\Delta\xi})^2 + 4(\boldsymbol{\Lambda} \cdot \boldsymbol{\Delta\xi})^2} \qquad (4)$$

where we defined the following vectors:

$$\boldsymbol{\kappa}_+ = \begin{pmatrix} \kappa_1^{(1)} + \kappa_1^{(2)} \\ \kappa_2^{(1)} + \kappa_2^{(2)} \\ 0 \end{pmatrix} \quad \boldsymbol{\kappa}_- = \begin{pmatrix} \kappa_1^{(1)} - \kappa_1^{(2)} \\ \kappa_2^{(1)} - \kappa_2^{(2)} \\ 0 \end{pmatrix} \quad \boldsymbol{\Lambda} = \begin{pmatrix} 0 \\ 0 \\ \lambda \end{pmatrix} \qquad (5)$$

Explain why the degeneracy at the conical intersection is lifted by displacements in the direction of the vectors $\boldsymbol{\kappa}_-$ and $\boldsymbol{\Lambda}$. These are therefore referred to as *branching space vectors*. What is the role of the $\boldsymbol{\kappa}_+$ vector?