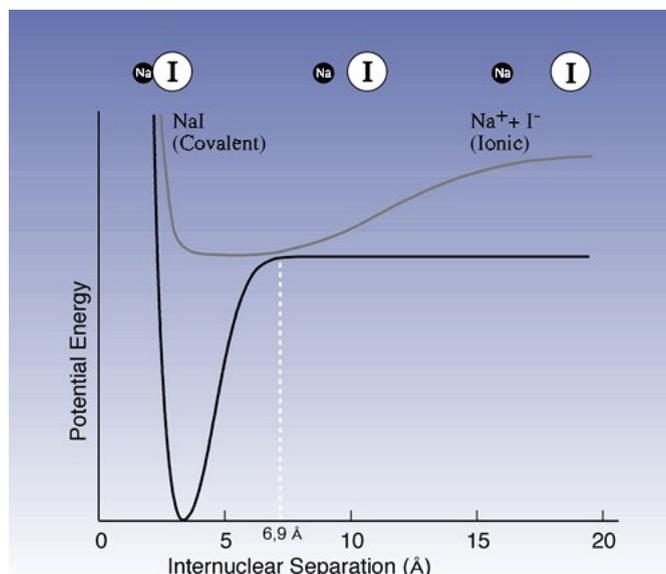


# Theoretical Photochemistry WiSe 2017/18 – Detailed discussion of Exercise 3



**Figure 1:** Adiabatic energies of the two lowest adiabatic states of the NaI molecule, as a function of the interatomic distance. The ground state (black line) has a ionic character at short distances and a covalent character at long distances. The opposite is true for the first excited adiabatic state (gray line).

The electronic wavefunctions  $\{|\psi_1(R)\rangle, |\psi_2(R)\rangle\}$  of the two lowest adiabatic states of the NaI molecule are expressed as linear combinations of diabatic wavefunctions  $\{|\varphi_1\rangle, |\varphi_2\rangle\}$ ,

$$\begin{aligned} |\psi_1(r_{\text{el}}; R)\rangle &= \cos \gamma(R) |\varphi_1(r_{\text{el}})\rangle + \sin \gamma(R) |\varphi_2(r_{\text{el}})\rangle \\ |\psi_2(r_{\text{el}}; R)\rangle &= \sin \gamma(R) |\varphi_1(r_{\text{el}})\rangle - \cos \gamma(R) |\varphi_2(r_{\text{el}})\rangle . \end{aligned} \quad (1)$$

The geometry-dependent adiabatic states are defined to be eigenstates of the electronic Schrödinger equation,

$$\hat{H}(r_{\text{el}}; R) |\psi_i(r_{\text{el}}; R)\rangle = V_i(R) |\psi_i(r_{\text{el}}; R)\rangle . \quad (2)$$

The electronic Hamiltonian  $\hat{H}(r_{\text{el}}; R)$  operates only on the electronic coordinates ( $r_{\text{el}}$ ) and is parametrized by the nuclear geometry ( $R$ ). As a consequence, the adiabatic wavefunctions are also geometry-dependent.

On the contrary, the diabatic wavefunctions  $\varphi_1(r_{\text{el}})$  and  $\varphi_2(r_{\text{el}})$  are defined to describe the same electronic configuration at all geometries, therefore they can be considered independent on  $R$ . In the case of NaI, we can define  $|\varphi_1\rangle$  as a ‘ionic’ wavefunction, in which the bonding electronic distributions is polarized in the direction of the I atom, and  $|\varphi_2\rangle$  as a ‘covalent’ distribution, in which the bonding electrons are equally shared between the two atoms.

Given the orthonormality relation between the diabatic states,  $\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$ , Equations (1) give generic linear combinations of diabatic states, which yield orthonormal adiabatic states. This can be verified explicitly (hereafter, the electronic coordinates  $r_{\text{el}}$  are not explicitly indicated):

$$\begin{aligned}
\langle \psi_1(R) | \psi_1(R) \rangle &= (\cos \gamma(R) \langle \varphi_1 | + \sin \gamma(R) \langle \varphi_2 |) (\cos \gamma(R) | \varphi_1 \rangle + \sin \gamma(R) | \varphi_2 \rangle) \\
&= \cos^2 \gamma(R) \underbrace{\langle \varphi_1 | \varphi_1 \rangle}_1 + \cos \gamma(R) \sin \gamma(R) \underbrace{\langle \varphi_1 | \varphi_2 \rangle}_0 \\
&\quad + \sin \gamma(R) \cos \gamma(R) \underbrace{\langle \varphi_2 | \varphi_1 \rangle}_0 + \sin^2 \gamma(R) \underbrace{\langle \varphi_2 | \varphi_2 \rangle}_1 \\
&= \cos^2 \gamma(R) + \sin^2 \gamma(R) = 1
\end{aligned} \tag{3}$$

$$\begin{aligned}
\langle \psi_1(R) | \psi_2(R) \rangle &= (\cos \gamma(R) \langle \varphi_1 | + \sin \gamma(R) \langle \varphi_2 |) (\sin \gamma(R) | \varphi_1 \rangle - \cos \gamma(R) | \varphi_2 \rangle) \\
&= \cos \gamma(R) \sin \gamma(R) \underbrace{\langle \varphi_1 | \varphi_1 \rangle}_1 - \cos^2 \gamma(R) \underbrace{\langle \varphi_1 | \varphi_2 \rangle}_0 \\
&\quad + \sin^2 \gamma(R) \underbrace{\langle \varphi_2 | \varphi_1 \rangle}_0 - \sin \gamma(R) \cos \gamma(R) \underbrace{\langle \varphi_2 | \varphi_2 \rangle}_1 \\
&= \cos \gamma(R) \sin \gamma(R) - \sin \gamma(R) \cos \gamma(R) = 0
\end{aligned} \tag{4}$$

$$\begin{aligned}
\langle \psi_2(R) | \psi_1(R) \rangle &= (\sin \gamma(R) \langle \varphi_1 | - \cos \gamma(R) \langle \varphi_2 |) (\cos \gamma(R) | \varphi_1 \rangle + \sin \gamma(R) | \varphi_2 \rangle) \\
&= \sin \gamma(R) \cos \gamma(R) \underbrace{\langle \varphi_1 | \varphi_1 \rangle}_1 - \sin^2 \gamma(R) \underbrace{\langle \varphi_1 | \varphi_2 \rangle}_0 \\
&\quad - \cos^2 \gamma(R) \underbrace{\langle \varphi_2 | \varphi_1 \rangle}_0 - \cos \gamma(R) \sin \gamma(R) \underbrace{\langle \varphi_2 | \varphi_2 \rangle}_1 \\
&= \sin \gamma(R) \cos \gamma(R) - \cos \gamma(R) \sin \gamma(R) = 0
\end{aligned} \tag{5}$$

$$\begin{aligned}
\langle \psi_2(R) | \psi_2(R) \rangle &= (\sin \gamma(R) \langle \varphi_1 | - \cos \gamma(R) \langle \varphi_2 |) (\sin \gamma(R) | \varphi_1 \rangle - \cos \gamma(R) | \varphi_2 \rangle) \\
&= \sin^2 \gamma(R) \underbrace{\langle \varphi_1 | \varphi_1 \rangle}_1 - \sin \gamma(R) \cos \gamma(R) \underbrace{\langle \varphi_1 | \varphi_2 \rangle}_0 \\
&\quad - \cos \gamma(R) \sin \gamma(R) \underbrace{\langle \varphi_2 | \varphi_1 \rangle}_0 + \cos^2 \gamma(R) \underbrace{\langle \varphi_2 | \varphi_2 \rangle}_1 \\
&= \cos^2 \gamma(R) + \sin^2 \gamma(R) = 1 .
\end{aligned} \tag{6}$$

In the adiabatic representation, the electronic Hamiltonian  $\hat{H}_{\text{el}}$  is diagonal,

$$\langle \psi_i(R) | \hat{H}_{\text{el}} | \psi_j(R) \rangle = V_i(R) \delta_{ij} \tag{7}$$

whereas the nuclear kinetic energy operator  $\hat{T}_R = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2}$  is non-diagonal (therefore the total Hamiltonian is non-diagonal),

$$\langle \psi_i(R) | \hat{H}_{\text{el}} | \psi_j(R) \rangle = \left( -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} \right) \delta_{ij} + \hat{\Lambda}_{ij} , \tag{8}$$

where the non-adiabatic couplings are given as

$$\hat{\Lambda}_{ij}(R) = -\frac{\hbar^2}{M} \left\langle \psi_i(R) \left| \frac{\partial \psi_j}{\partial R} \right\rangle \frac{\partial}{\partial R} - \frac{\hbar^2}{2M} \left\langle \psi_i(R) \left| \frac{\partial^2 \psi_j}{\partial R^2} \right\rangle \right. \quad (9)$$

and describe the non-radiative transitions between adiabatic electronic states.

1. In order to express the so-called derivative couplings,  $F_{ij}(R) = \left\langle \psi_i(R) \left| \frac{\partial \psi_j}{\partial R} \right\rangle$  in terms of the mixing angle  $\gamma(R)$ , we evaluate the derivative of the adiabatic wavefunctions, given as in Eq. (1),

$$\begin{aligned} \left| \frac{\partial \psi_1}{\partial R} \right\rangle &= -\gamma'(R) \sin \gamma(R) |\varphi_1\rangle + \gamma'(R) \cos \gamma(R) |\varphi_2\rangle \\ \left| \frac{\partial \psi_2}{\partial R} \right\rangle &= \gamma'(R) \cos \gamma(R) |\varphi_1\rangle + \gamma'(R) \sin \gamma(R) |\varphi_2\rangle . \end{aligned} \quad (10)$$

Using the orthonormality condition  $\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$ , we get

$$\begin{aligned} F_{11}(R) &= \left\langle \psi_1(R) \left| \frac{\partial \psi_1}{\partial R} \right\rangle \\ &= -\gamma'(R) \cos \gamma(R) \sin \gamma(R) + \gamma'(R) \sin \gamma(R) \cos \gamma(R) = 0 \end{aligned} \quad (11)$$

$$\begin{aligned} F_{12}(R) &= \left\langle \psi_1(R) \left| \frac{\partial \psi_2}{\partial R} \right\rangle \\ &= \gamma'(R) \cos^2 \gamma(R) + \gamma'(R) \sin^2 \gamma(R) = \gamma'(R) \end{aligned} \quad (12)$$

$$\begin{aligned} F_{21}(R) &= \left\langle \psi_2(R) \left| \frac{\partial \psi_1}{\partial R} \right\rangle \\ &= -\gamma'(R) \sin^2 \gamma(R) - \gamma'(R) \cos^2 \gamma(R) = -\gamma'(R) \end{aligned} \quad (13)$$

$$\begin{aligned} F_{22}(R) &= \left\langle \psi_2(R) \left| \frac{\partial \psi_2}{\partial R} \right\rangle \\ &= \gamma'(R) \sin \gamma(R) \cos \gamma(R) - \gamma'(R) \cos \gamma(R) \sin \gamma(R) = 0 \end{aligned} \quad (14)$$

Note the following general property of derivative couplings:

$$F_{ij}(R) + F_{ji}(R) = 0 . \quad (15)$$

2. The scalar couplings,  $G_{ij}(R) = \left\langle \psi_i(R) \left| \frac{\partial^2 \psi_j}{\partial R^2} \right. \right\rangle$ , can be expressed in terms of  $\gamma(R)$  by taking the second derivative of the adiabatic wavefunctions. From Eqs. (17) we get

$$\begin{aligned} \left\langle \frac{\partial^2 \psi_1}{\partial R^2} \right\rangle &= [-\gamma''(R) \sin \gamma(R) - \gamma'(R)^2 \cos \gamma(R)] |\varphi_1\rangle \\ &\quad + [\gamma''(R) \cos \gamma(R) - \gamma'(R)^2 \sin \gamma(R)] |\varphi_2\rangle \\ \left\langle \frac{\partial^2 \psi_2}{\partial R^2} \right\rangle &= [\gamma''(R) \cos \gamma(R) - \gamma'(R)^2 \sin \gamma(R)] |\varphi_1\rangle \\ &\quad + [\gamma''(R) \sin \gamma(R) + \gamma'(R)^2 \cos \gamma(R)] |\varphi_2\rangle . \end{aligned} \tag{16}$$

The overlaps with  $\langle \psi_i(R) |$  give

$$\begin{aligned} G_{11}(R) &= \left\langle \psi_1(R) \left| \frac{\partial^2 \psi_1}{\partial R^2} \right. \right\rangle = -\gamma'(R)^2 \\ G_{12}(R) &= \left\langle \psi_1(R) \left| \frac{\partial^2 \psi_2}{\partial R^2} \right. \right\rangle = \gamma''(R) \\ G_{21}(R) &= \left\langle \psi_2(R) \left| \frac{\partial^2 \psi_1}{\partial R^2} \right. \right\rangle = -\gamma''(R) \\ G_{22}(R) &= \left\langle \psi_2(R) \left| \frac{\partial^2 \psi_2}{\partial R^2} \right. \right\rangle = -\gamma'(R)^2 . \end{aligned}$$

3. Considering a potential energy diagram as in Fig. 1, in the close proximity of the avoided crossing,  $R \approx R_0$ , the diabatic potentials, i. e. the matrix elements of the electronic Hamiltonian, can be approximated at the lowest order as

$$\begin{aligned} H_{11}(R) &= \left\langle \varphi_1 \left| \hat{H}_{\text{el}}(R) \right| \varphi_1 \right\rangle = \alpha_1(R - R_0) \\ H_{22}(R) &= \left\langle \varphi_2 \left| \hat{H}_{\text{el}}(R) \right| \varphi_2 \right\rangle = \alpha_2(R - R_0) \\ H_{12}(R) &= \left\langle \varphi_1 \left| \hat{H}_{\text{el}}(R) \right| \varphi_2 \right\rangle = \beta = H_{21}(R) . \end{aligned} \tag{17}$$

This is the key difference between adiabatic states: The adiabatic states are the eigenstates of the electronic Hamiltonian, but the full molecular Hamiltonian has off-diagonal kinematic couplings [see Eqs. (7) and (8)]; in the diabatic representation the kinematic couplings are negligible, but potential couplings arise.

The mixing angle  $\gamma(R)$ , which defines the transformation between diabatic and adiabatic states, depends on the diabatic matrix elements  $\{H_{ij}\}$ . It can be found by imposing that the electronic Hamiltonian has no off-diagonal term in the adiabatic basis,

$$\left\langle \psi_1(R) \left| \hat{H}_{\text{el}} \right| \psi_2(R) \right\rangle = 0 . \tag{18}$$

Replacing Eqs. (1) and (17) into Eq. (18),

$$\begin{aligned}
0 &= [\cos \gamma(R)\langle\varphi_1| + \sin \gamma(R)\langle\varphi_2|] \hat{H}_{\text{el}} [\sin \gamma(R)|\varphi_1\rangle - \cos \gamma(R)|\varphi_2\rangle] \\
&= \cos \gamma(R) \sin \gamma(R) H_{11}(R) - \cos^2 \gamma(R) H_{12}(R) \\
&\quad + \sin^2 \gamma(R) H_{21}(R) - \sin \gamma(R) \cos \gamma(R) H_{22}(R) \\
&= \sin \gamma(R) \cos \gamma(R) [H_{11}(R) - H_{22}(R)] - [\cos^2 \gamma(R) - \sin^2 \gamma(R)] H_{12}(R) \\
&= \frac{1}{2} \sin(2\gamma(R)) [H_{11}(R) - H_{22}(R)] - \cos(2\gamma(R)) H_{12}(R) .
\end{aligned} \tag{19}$$

Dividing both sides by  $\cos(2\gamma(R))$ , we finally obtain

$$\tan(2\gamma(R)) = \frac{2H_{12}(R)}{H_{11}(R) - H_{22}(R)} \tag{20}$$

$$= \frac{2\beta}{(\alpha_1 - \alpha_2)(R - R_0)} . \tag{21}$$

Eq. (20) has a general validity for any system of two electronic states and any form of the diabatic potentials. Eq (21) is specified for the model of Eq. (17).

4. Transitions between electronic states are likely to occur when the non-adiabatic couplings, in particular derivative couplings, are large. The magnitude of  $F_{12}(R)$  is given by the derivative of the mixing angle  $\gamma(R)$ . In order to calculate  $\gamma'(R)$ , we differentiate both sides of Eq. (21),<sup>1</sup>

$$\begin{aligned}
(1 + \tan^2(2\gamma(R))) 2\gamma'(R) &= -\frac{2\beta}{(\alpha_1 - \alpha_2)(R - R_0)^2} \\
\frac{(\alpha_1 - \alpha_2)^2(R - R_0)^2 + 4\beta^2}{(\alpha_1 - \alpha_2)^2(R - R_0)^2} \gamma'(R) &= -\frac{\beta}{(\alpha_1 - \alpha_2)(R - R_0)^2} \\
\frac{(\alpha_1 - \alpha_2)^2(R - R_0)^2 + 4\beta^2}{(\alpha_1 - \alpha_2)} \gamma'(R) &= -\beta .
\end{aligned} \tag{22}$$

The final expression for magnitude of the derivative coupling is

$$|F_{12}(R)| = |\gamma'(R)| = \frac{|\beta(\alpha_1 - \alpha_2)|}{(\alpha_1 - \alpha_2)^2(R - R_0)^2 + 4\beta^2} . \tag{23}$$

As a function of  $R$ ,  $\gamma'(R)$  is a Lorentzian with center at  $R = R_0$  and full width at half maximum of  $|2\beta/(\alpha_1 - \alpha_2)|$ . The range of Na—I distances in which the internal conversion is likely is directly proportional to the diabatic coupling  $\beta$  and inversely proportional to the difference between the slopes of the diabatic potentials.

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<sup>1</sup>Remember that  $\frac{d}{dx} \tan x = 1 + \tan^2 x$ .