# Theoretical Photochemistry WiSe 2017/18 – Exercise 3
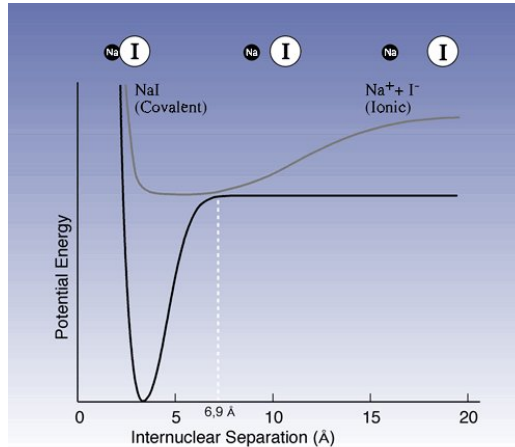


Figure 1: Potential energy curves for NaI

Consider the first two *adiabatic* states of the NaI system as a function of the interatomic distance $R$ (Figure 1). At large distance the ground state has a *covalent character*, whereas the excited state is *ionic* and lies higher in energy, with an energy difference that equals the ionization potential of $Na$ minus the electron affinity of $I$ (496-295 kJ/mol). At closer $R$, the Coulomb interaction makes the ionic configuration more stable: the nature of the states is then reversed, with the ground state having an ionic character and the excited state being covalent.

These considerations imply the existence of a transition in proximity to an intermediate distance $R_0$, *i.e.* the *avoided crossing* between the adiabatic curves, where the two states are close in energy and there is a sudden change of electronic character. As a consequence, close to the avoided crossing the adiabatic states show large derivatives with respect to the interatomic distance, which means strong *non-adiabatic couplings*.

In this condition, it is convenient to express the electronic *adiabatic* states $\{\psi_n(r_{el}|R), n = 1, 2\}$ as a $R$-dependent linear combination of the two ionic and covalent wavefunctions, $\{\varphi_1(r_{el}), \varphi_2(r_{el})\}$, that define the *diabatic* electronic basis of our system:

$$\psi_1(r_{el}|R) = \varphi_1(r_{el})\cos\left(\gamma(R)\right) + \varphi_2(r_{el})\sin\left(\gamma(R)\right) \tag{1}$$

$$\psi_2(r_{el}|R) = \varphi_1(r_{el})\sin\left(\gamma(R)\right) - \varphi_2(r_{el})\cos\left(\gamma(R)\right) \tag{2}$$

We assume that these wave functions $\varphi_i(r_{el})$ are an orthonormal set and have no dependence on $R$, or at least neglibible, so that their derivative couplings are zero.

Recall that in the *adiabatic basis* the *non-adiabatic couplings* $\hat{\Lambda}_{mn}$ are computed with the formula

$$\hat{\Lambda}_{mn} = -\frac{\hbar^2}{M}\langle\psi_m|\frac{\partial}{\partial R}|\psi_n\rangle\frac{\partial}{\partial R} - \frac{\hbar^2}{2M}\langle\psi_m|\frac{\partial^2}{\partial R^2}|\psi_n\rangle \qquad (3)$$

(see lesson 2: "Born-Oppenheimer Approximation & beyond").

1. Express the first derivative coupling matrix elements as a function of the mixing angle $\gamma(R)$ (and its derivative)

$$F_{mn} = \langle\psi_m|\frac{\partial}{\partial R}|\psi_n\rangle = \int dr_{el}\,\psi_m(r_{el}|R)\frac{\partial}{\partial R}\psi_n(r_{el}|R) \qquad (4)$$

2. Express the second derivative coupling matrix elements as a function of the mixing angle $\gamma(R)$ (and its derivative)

$$G_{mn} = \langle\psi_m|\frac{\partial^2}{\partial R^2}|\psi_n\rangle = \int dr_{el}\,\psi_m(r_{el}|R)\frac{\partial^2}{\partial R^2}\psi_n(r_{el}|R) \qquad (5)$$

Assuming that the R-dependent matrix elements of the electronic Hamiltonian $\hat{H}$, in the diabatic basis,

$$H_{ij}(R) = \langle\varphi_i(r_{el})|\hat{H}(r_{el}, R)|\varphi_j(r_{el})\rangle \qquad (6)$$

are given by

$$H_{11} = \alpha_1(R - R_0) \qquad (7)$$
$$H_{22} = \alpha_2(R - R_0) \qquad (8)$$
$$H_{12} = H_{21} = \beta \qquad (9)$$

We are now looking closely at the point where there is the inversion between the ionic and covalent states, and we are assuming that they cross linearly (*N.B.* unlike the adiabatic states, the energies of the diabatic states may cross in a one-dimensional system).

3. Compute the mixing angle $\gamma(R)$ as a function of the slopes of the diabatic potentials, $\alpha_1$ and $\alpha_2$, and the R-independent coupling $\beta$ (*hint*: recall that the adiabatic states $\psi_n(r_{el}|R)$ are eigenfunctions of the Hamiltonian).

4. For which interatomic distance are the nonadiabatic transitions between the two electronic states most likely to occur?