# Theoretical Photochemistry WiSe 2017/18 – Solution Exercise 2

1. (a) We need to evaluate the action of the operator $\hat{T}_{nuc} = -\frac{\hbar^2}{2\,M}\frac{\partial^2}{\partial R^2}$ on the wavefunction $\Psi(r,R) = \sum_n \psi_n^{el}(r|R)\chi_n^{nuc}(R)$. We start by computing the first derivative of $\Psi(r,R)$ with respect to $R$:

$$\frac{\partial}{\partial R}\Psi(r,R) = \sum_n \frac{\partial \psi_n^{el}}{\partial R}\chi_n^{nuc} + \psi_n^{el}\frac{\partial \chi_n^{nuc}}{\partial R} \tag{1}$$

Note that we have used the derivative product rule since both the nuclear wavefunctions $\chi_n^{nuc}$ and the the adiabatic electronic states $\psi_n^{el}(r|R)$ depends on $R$ (the dependence of $\psi_n^{el}(r|R)$ is parametric, since we assume that $R$ is a parameter in the electronic hamiltonian). We then derive the first derivative to get the second derivative:

$$\frac{\partial}{\partial R}\Psi(r,R) = \sum_n \frac{\partial^2 \psi_n^{el}}{\partial R^2}\chi_n^{nuc} + 2\frac{\partial \psi_n^{el}}{\partial R}\frac{\partial \chi_n^{nuc}}{\partial R} + \psi_n^{el}\frac{\partial^2 \chi_n^{nuc}}{\partial R^2} \tag{2}$$

We conclude that:

$$\hat{T}_{nuc}\Psi = -\frac{\hbar^2}{2\,M}\left(\sum_n \frac{\partial^2 \psi_n^{el}}{\partial R^2}\chi_n^{nuc} + 2\frac{\partial \psi_n^{el}}{\partial R}\frac{\partial \chi_n^{nuc}}{\partial R} + \psi_n^{el}\frac{\partial^2 \chi_n^{nuc}}{\partial R^2}\right) \tag{3}$$

(b) The summation of Eq. 3 contains three addends. We multiply and integrate separately each term. The first gives:

$$\int dr\ \psi_m^{el\star}(r|R)\ \frac{\partial^2 \psi_n^{el}}{\partial R^2}(r|R)\chi_n^{nuc}(R) = \\ \chi_n^{nuc}(R)\int dr\ \psi_m^{el\star}(r|R)\frac{\partial^2 \psi_n^{el}}{\partial R^2}(r|R) = G_{mn}(R)\chi_n^{nuc}(R) \tag{4}$$

where we have moved the nuclear wavefunction $\chi_n^{nuc}(R)$ outside the integral (because it is not dependent on $r$) and we have renamed the integral $G_{mn}(R)$. The integrand depends on both the electron and nuclear coordinates and on the indices of the adiabatic electronic states $m$ and $n$. After carrying out the integration on $r$, the resulting integral $G_{mn}(R)$ does not depend on the electron coordinate. Likewise,

$$\int dr\ \psi_m^{el\star}(r|R)\, 2\frac{\partial\psi_n^{el}}{\partial R}(r|R)\frac{\partial\chi_n^{nuc}}{\partial R}(R) =$$
$$2\frac{\partial\chi_n^{nuc}}{\partial R}(R)\int dr\ \psi_m^{el\star}(r|R)\frac{\partial\psi_n^{el}}{\partial R}(r|R) = 2\,F_{mn}(R)\frac{\partial}{\partial R}\chi_n^{nuc}(R) \quad (5)$$

For the third term, we have

$$\int dr\ \psi_m^{el\star}(r|R)\ \psi_n^{el}(r|R)\frac{\partial^2\chi_n^{nuc}}{\partial R^2}(R) =$$
$$\frac{\partial^2\chi_n^{nuc}}{\partial R^2}(R)\int dr\ \psi_m^{el\star}(r|R)\ \psi_n^{el}(r|R) = \delta_{mn}\frac{\partial^2\chi_n^{nuc}}{\partial R^2}(R) \quad (6)$$

where we have carried out the integration by making use of the the orthogonality of the electronic wavefunctions. Summing all the terms, we obtain

$$\int dr\ \psi_m^{el\star}(r|R)\ \hat{T}_{nuc}\Psi(r,R) =$$
$$-\frac{\hbar^2}{2\,M}\sum_n\left(G_{mn}(R)\chi_n^{nuc}(R) + 2\,F_{mn}(R)\frac{\partial\chi_n^{nuc}(R)}{\partial R} + \delta_{mn}\frac{\partial^2\chi_n^{nuc}}{\partial R^2}(R)\right) =$$
$$-\frac{\hbar^2}{2\,M}\left[\frac{\partial^2\chi_m^{nuc}}{\partial R^2}(R) + \sum_n\left(G_{mn}(R) + 2\,F_{mn}(R)\frac{\partial}{\partial R}\right)\chi_n^{nuc}(R)\right] \quad (7)$$

where we have used the definition of Kronecker delta

$$\delta_{mn} = \begin{cases} 0 & m \neq n \\ 1 & m = n \end{cases} \quad (8)$$

By setting $\hat{\Lambda}_{mn}(R) = -\frac{\hbar^2}{2\,M}\left(G_{mn}(R) + 2\,F_{mn}(R)\frac{\partial}{\partial R}\right)$ we obtain Eq. (2) from the text of the exercise:

$$\int dr\ \psi_m^{el\star}(r|R)\ \hat{T}_{nuc}\Psi(r,R) =$$
$$-\frac{\hbar^2}{2\,M}\frac{\partial^2\chi_m^{nuc}}{\partial R^2}(R) + \sum_n\hat{\Lambda}_{mn}(R)\chi_n^{nuc}(R) \quad (9)$$

(c) We start from the complete Hamiltonian for the system and the associated eigenvalue–eigenvector problem:

$$\left(-\frac{\hbar^2}{2\,M}\frac{\partial^2}{\partial R^2}+\mathcal{H}_{el}\right)\Psi(r,R)=E\Psi(r,R) \tag{10}$$

As we have done in the second part of the exercise, we have to substitute the group Born-Oppenheimer wavefunction, then multiply by $\psi_m^{el\star}(r|R)$ and finally integrate. We proceed one term at a time.

We start from the term $\mathcal{H}_{el}\Psi(r,R)$. We first exploit the fact that $\Psi(r,R)$ is a superposition of adiabatic electronic wavefunctions, which are eigenvectors of the electronic hamiltonian $\mathcal{H}_{el}\psi_n^{el}(r|R)=\varepsilon_n(R)\psi_n^{el}(r|R)$. In detail

$$\begin{aligned}\mathcal{H}_{el}\Psi(r,R)=\mathcal{H}_{el}\sum_n\psi_n^{el}(r|R)\chi_n^{nuc}(R)=\\ \sum_n\left(\mathcal{H}_{el}\psi_n^{el}(r|R)\right)\chi_n^{nuc}(R)=\sum_n\varepsilon_n(R)\psi_n^{el}(r|R)\chi_n^{nuc}(R)\end{aligned} \tag{11}$$

By multiplying last formula by $\psi_m^{el\star}(r|R)$ and integrating over $r$ we get

$$\int dr\;\psi_m^{el\star}(r|R)\mathcal{H}_{el}\Psi(r,R)=\varepsilon_m(R)\chi_m^{nuc}(R) \tag{12}$$

where we have used again the orthogonality of the adiabatic electronic wavefunctions. Using again this orthogonality property, we can obtain

$$\int dr\;\psi_m^{el\star}(r|R)E\Psi(r,R)=E\chi_m^{nuc}(R) \tag{13}$$

Now, if we take Eq. 10 and we multiply and integrate, we can substitute the results of Eq.s 9, 12 and 13 to obtain Eq. (3) of the text of the exercise:

$$\left(-\frac{\hbar^2}{2\,M}\frac{\partial^2}{\partial R^2}+\varepsilon_m(R)\right)\chi_m^{nuc}(R)+\sum_n\hat{\Lambda}_{mn}(R)\chi_n^{nuc}(R)=E\chi_m^{nuc}(R) \tag{14}$$

We then realize that $\varepsilon_m(R)$ is the $m$-th eigenvalue of the electronic hamiltonian (the $m$-th "potential energy surface") whereas $E$ stands for the eigenvalue of the full Hamiltonian.

(d) According to the time–dependent Schrödinger equation:

$$\frac{\partial}{\partial t}\Psi(r,R,t) = \frac{1}{\imath\hbar}\mathcal{H}_{\text{full}}\Psi(r,R,t) \tag{15}$$

where we have now generalized the group Born-Oppenheimer representation by considering time–dependent nuclear wavefunctions (we still assume to expand our full wavefunction on the time–independent electronic adiabatic wavefunction)

$$\Psi(r,R,t) = \sum_n \psi_n^{el}(r|R)\chi_n^{nuc}(R,t) \tag{16}$$

If we now start from Eq. 15 and repeat the procedure outlined in the previous parts of the exercise (substitution of the wavefunction *ansatz*, multiplication by an arbitrary electronic adiabatic wavefunction, integration along the electronic coordinates), we obtain

$$\begin{aligned}\frac{\partial}{\partial t}\chi_n^{nuc}(R,t) = \frac{1}{\imath\hbar}\left(-\frac{\hbar^2}{2\,M}\frac{\partial^2}{\partial R^2} + \varepsilon_m(R)\right)\chi_m^{nuc}(R,t)\\ + \sum_n \hat{\Lambda}_{mn}(R)\chi_n^{nuc}(R,t)\end{aligned} \tag{17}$$

(e) Within the group Born-Oppenheimer representation, we consider the global wavefunction of the system as a superposition of different electronic states and the nuclear wavefunctions as the R–dependent expansion coefficients on the adiabatic electronic states. Each nuclear wavefunction describe then the probability of finding the system in that electronic states. In this picture, the coupling terms determine the interaction between the components of the whole wavefunction in the different electronic states. In the time–dependent Schrödinger equation, Eq. 17, the coupling terms determine the possibility of moving the wavepacket from one electronic state to the other, i.e. the possibility of a non–adiabatic electronic transition. In the standard form of the Born-Oppenheimer approximation, the nuclear Hamiltonian does not contain the coupling terms $\sum_n \hat{\Lambda}_{mn}(R)\chi_n^{nuc}(R,t)$ and then there is no interaction between the different electronic states. Accordingly, in the time evolution described by the time–dependent Schrödinger equation, transitions between different electronic states are not possible.

2. Eq. (3) in matrix form is

$$\mathbf{H}\chi^{nuc} = E\chi^{nuc} \tag{18}$$

where $\mathbf{H}$ is the matrix

$$\mathbf{H} = \begin{bmatrix} -\frac{\hbar^2}{2\,M}\frac{\partial^2}{\partial R^2} + \varepsilon_1(R) + \hat{\Lambda}_{11}(R) & \hat{\Lambda}_{12}(R) \\ \hat{\Lambda}_{21}(R) & -\frac{\hbar^2}{2\,M}\frac{\partial^2}{\partial R^2} + \varepsilon_2(R) + \hat{\Lambda}_{22}(R) \end{bmatrix} \tag{19}$$

and $\chi^{nuc}$ is the vector

$$\chi^{nuc} = \begin{bmatrix} \chi_1^{nuc}(R,t) \\ \chi_2^{nuc}(R,t) \end{bmatrix} \tag{20}$$

(to verify this equivalence, simply compute the matrix-vector product $\mathbf{H}\chi^{nuc}$ and then confront the two vector elements obtained with the corresponding element of the vector on the r.h.s)

3. In the common “mixed” notation that is used for non–adiabatic problems, we use to indicate the electronic states as bra/ket and keep the nuclear states as wavefunctions. For the sake of brevity, we also omit the dependence on $R$, Eq. (1) of the text of the exercise is:

$$|\Psi\rangle = \sum_n |\psi_n^{el}\rangle \chi_n^{nuc} \tag{21}$$

Eq. (2) is:

$$\langle\psi_m^{el}|\,\hat{T}_{nuc}|\Psi\rangle = \,-\,\frac{\hbar^2}{2\,M}\frac{\partial^2\chi_m^{nuc}}{\partial R^2} + \sum_n \hat{\Lambda}_{mn}\chi_n^{nuc} \tag{22}$$

In this braket notation, Eq. (3) is left unchanged, since it does not contain electronic wavefunctions:

$$\left(\hat{T}_{nuc} + \varepsilon_m\right)\chi_m^{nuc} + \sum_n \hat{\Lambda}_{mn}\chi_n^{nuc} = E\chi_m^{nuc} \tag{23}$$