Theoretical Photochemistry WiSe 2017/18 – Exercise 2

1. **Beyond the Born-Oppenheimer Approximation.** Within the group Born-Oppenheimer (BO) representation, the electronic-nuclear wavefunction is described as a superposition of BO wavefunctions:

$$\Psi(r,R) \;=\; \sum_n \psi_n^{\mathrm{el}}(r|R)\chi_n^{\mathrm{nuc}}(R) \tag{1}$$

For simplicity, we refer to a single electronic (r) and nuclear (R) coordinate.

(a) Using the above generalized *ansatz*, show how the operator of the nuclear kinetic energy, $\hat{T}_{\mathrm{nuc}} = -(\hbar^2/2M)(\partial^2/\partial R^2)$, acts on the total wavefunction.

(b) Now multiply from the left by $\psi_m^{\mathrm{el}*}(r)$ and integrate over the electronic coordinates (making use of the orthogonality of the electronic wavefunctions, i.e., $\int dr\, \psi_m^{\mathrm{el}*}(r)\psi_n^{\mathrm{el}}(r) = \delta_{mn}$):

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

Formulate the so-called non-adiabatic couplings $\hat{\Lambda}_{mn}$ explicitly. Rewrite $\hat{\Lambda}_{mn}$ in terms of the so-called non-adiabatic derivative couplings F_{mn} and the non-adiabatic scalar couplings G_{mn}.

(c) Show that the following coupled set of equations for the nuclear wavefunctions $\{\chi_n^{\mathrm{nuc}}(R)\}$ is obtained:

$$\Big(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2} + \epsilon_m(R)\Big)\chi_m^{\mathrm{nuc}}(R) + \sum_n \hat{\Lambda}_{mn}\chi_n^{\mathrm{nuc}}(R) = E\chi_m^{\mathrm{nuc}}(R) \tag{3}$$

How are $\epsilon_m(R)$ and E defined?

(d) What is the complementary time-dependent form of Eq. (3)?

(e) What do the coupled equations for the nuclear wavefunctions describe physically? Compare with the standard form of the Born-Oppenheimer approximation.

2. Re-write Eq. (3) in matrix form, for two electronic states.

3. Re-write Eqs. (1)-(3) in bra-ket notation.