Chapter 1:

From Quantum Mechanics to Classical Mechanics

Chapter 1 - Exercises:

1) Derive formulae (1.6) and (1.7) (p.4) following the recipe given in the script: insertion of Ansatz (1.5) into the time-dependent electronic-nuclear Schrodinger equation, multiplication from the left with ϕ_k^* and integration over all electronic coordinates r.

2) Derive formulae (1.13) and (1.14) (p.7) by inserting Ansatz (1.12) into Eq. (1.11) and separating real and imaginary parts.

3) Show that the diagonal elements of the first-order nonadiabatic coupling vectors $\vec{d}_{kl}^{\,I}$ zero for real electronic wavefunctions ϕ_k and ϕ_l .

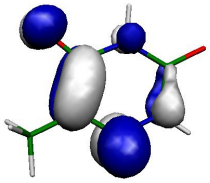
$$\boxed{\vec{d}_{kl}^{\,I}(R) = \int \phi_k^* \nabla_I \phi_l \, dr}$$

4) Derive the formula

$$\boxed{\vec{d}_{kl}^{\,I}(R) = \frac{\int \phi_k^* \nabla_I \hat{H} \phi_l \, dr}{E_l - E_k}}$$

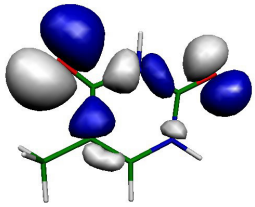
Recipe: start with the time-independent Schrodinger equation for ϕ_l , multiply from the left by ϕ_k^* and do the derivative with respect to ∇_I.

Nonadiabatic Coupling Vectors



LUMO

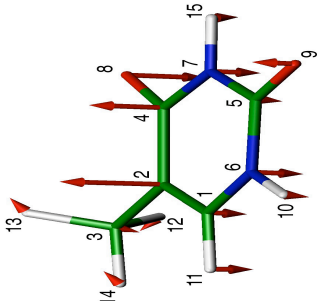
First excited state S_1



HOMO

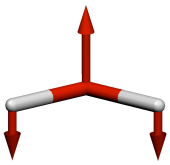
ground state S_0

Thymine



Nonadiabatic coupling vectors Between S_0 and S_1.

Water



Polar Representation of the Nuclear Wavefunction

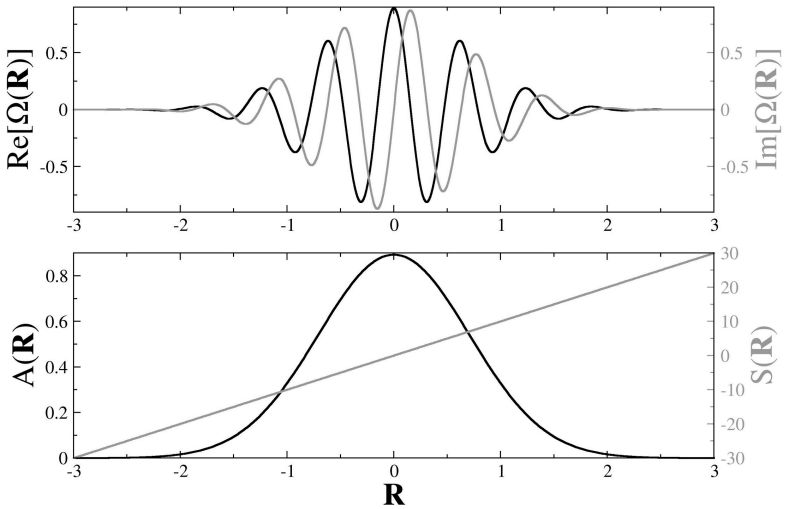
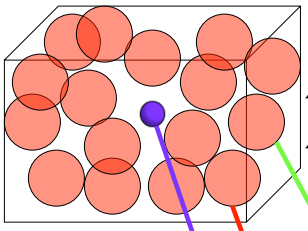


Illustration of a complex nuclear wavefunction χ(R), represented in terms of real and imaginary part (χ(R) = Re[χ(R)] + i Im[χ(R)]; upper panel) and in terms of the two real functions A(R) and S(R) (χ(R) = A(R)exp[iS(R)/ $\hbar$]; lower panel).

Illustration for Dephasing/Decoherence of Nuclear Wavepacket



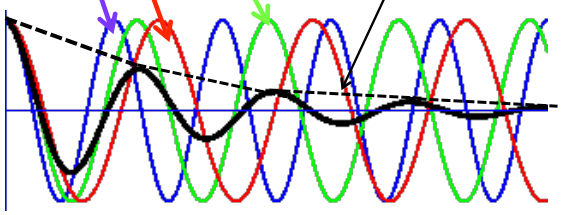
$$\chi_1(t) = A_1 \sin\left(\omega_1 t + \delta_1\right) = \sin(\varphi_1(t))$$

$$\chi_1(t) = A_1 e^{i\varphi_1(t)}$$

$$I(t) = Ae^{-t/\tau_2}$$

Particle in a bath

τ_2: dephasing time
Measurable by time-resolved Spectroscopy
(Fourrier-Transform -> frequency spectrum)



Adapted from:

http://homepages.physik.uni-muenchen.de/~Florian.Marquardt/dephasing/dephasing.html