Theoretical Photochemistry WiSe 2017/18 – Exercise 1

1. **Wavepackets.** Construct a coherent superposition (i.e., wavepacket) $\psi(x, t = 0)$ for a harmonic oscillator, $\hat{H} = -(\hbar^2/2m)\partial^2/\partial x^2 + 1/2\, kx^2$, using the basis of eigenstates $\phi_n(x)$ (with the $\phi_n(x)$ given as $\phi_n(x) = N_n H_n(y)\exp(-y^2/2)$, where $y = (m\omega/\hbar)^{1/2}x$, $\omega = (k/m)^{1/2}$, and the H_n are the Hermite polynomials). The construction of the time-evolving wavepacket $\psi(x, t)$ involves phase factors relating to the harmonic-oscillator eigenvalues E_n.

   (a) The classical period is $T = 2\pi/\omega$. Show that for times $t = nT$, $n = 1, 2, \ldots$, the wavepacket returns to its initial condition, i.e., we have $|\psi(x, t = nT)|^2 = |\psi(x, t = 0)|^2$. Note, however, that $\psi(x, t = nT) = \psi(x, t = 0)$ is not necessarily fulfilled, i.e., there could be a change of sign. Verify whether this is the case.

   (b) The iodine molecule I_2 has a frequency of 87 cm^{-1} in one of its excited electronic states, where a wavepacket is created by a femtosecond laser pulse. What is the vibrational period T of the wavepacket (assuming that the potential is harmonic)? Use the conversion factor 1 cm^{-1} = $1.986\ 10^{-23}$ J and $\hbar = 1.055\ 10^{-34}$ J s.

2. **Born-Oppenheimer Approximation.** In the framework of the Born-Oppenheimer approximation, the wavefunction for electrons and nuclei is represented as a product, $\Psi(\mathbf{r}, \mathbf{R}) = \psi^{\text{el}}(\mathbf{r}|\mathbf{R})\chi^{\text{nuc}}(\mathbf{R})$, where the electronic wavefunction $\psi^{\text{el}}(\mathbf{r}|\mathbf{R})$ depends parametrically upon the nuclear coordinates $\mathbf{R}$.

   Using the above *ansatz*, the molecular Schrödinger equation separates into two effective Schrödinger equations,

   $$\hat{H}_{\text{el}}\psi_n^{\text{el}}(\mathbf{r}|\mathbf{R}) = \epsilon_n(\mathbf{R})\psi_n^{\text{el}}(\mathbf{r}|\mathbf{R}) \tag{1}$$

   and

   $$(\hat{T}_{\text{nuc}} + \epsilon_n(\mathbf{R}))\chi_n^{\text{nuc}}(\mathbf{R}) = E\chi_n^{\text{nuc}}(\mathbf{R}) \tag{2}$$

   From the second equation, one recognizes that the eigenvalues $\epsilon_n(\mathbf{R})$ of the electronic Schrödinger equation appear as potential functions in the

Schrödinger equation for the nuclear motion. This is why the functions $\epsilon_n(\mathbf{R})$ are often denoted "Born-Oppenheimer potentials".

(a) Draw a typical Born-Oppenheimer potential for the electronic ground state of a diatomic molecule as a function of the internuclear distance coordinate R.

(b) Explain with reference to Eq. (1) why there's not one, but many Born-Oppenheimer potentials.

(c) Discuss with reference to Eq. (2) whether the nuclear motion can lead to transitions between two potentials $\epsilon_n(\mathbf{R})$ and $\epsilon_{n'}(\mathbf{R})$, within the Born-Oppenheimer approximation.

(d) What is meant by "non-Born-Oppenheimer effects" (or "non-adiabatic effects")? Why are these of central importance in photochemistry?