

Theoretical Photochemistry WiSe 2017/18 – Exercise 8

Consider a molecular 2-state system described by a Hamiltonian \hat{H} which is prepared in the ground state $|\Psi(0)\rangle = |\psi_0\rangle \otimes |G\rangle$ (where a combined vibrational-electronic wavefunction is referred to, as indicated by the tensor product). When the system interacts with a time-dependent electric field $E(t)$, the induced polarisation of the system is defined as the time-dependent expectation value of the dipole operator:

$$P(t) = \langle \Psi(t) | \hat{\mu} | \Psi(t) \rangle \quad (1)$$

We aim to derive an expression for the first-order polarisation, *i.e.* the first term in a perturbative expansion of Eq. (1) with the electric field (see lesson “Interaction with light: Nonlinear optical spectroscopies”, p. 13). We will show that the first-order polarisation is related to the wavepacket autocorrelation function, and therefore also relates to the absorption spectrum.

In the perturbative expansion of the time-dependent wavefunction $|\Psi(t)\rangle$

$$|\Psi(t)\rangle = |\Psi^{(0)}(t)\rangle + |\Psi^{(1)}(t)\rangle + |\Psi^{(2)}(t)\rangle + \dots \quad (2)$$

the zero-th and first order terms of the expansion are given by

$$|\Psi^{(0)}(t)\rangle = \hat{U}_0(t - t_0) |\Psi(t_0)\rangle \quad (3)$$

$$|\Psi^{(1)}(t)\rangle = \left(-\frac{i}{\hbar}\right) \int_{-\infty}^t d\tau \hat{U}_0(t - \tau) (\hat{\mu} E(\tau)) \hat{U}_0(\tau - t_0) |\Psi(t_0)\rangle \quad (4)$$

where $\hat{U}_0(t - t_0) = \hat{U}_0(t, t_0)$ refers to the propagator in the absence of the interaction with the external field. The propagator can be written explicitly as the sum of two contributions for states $|G\rangle$ and $|X\rangle$, describing the evolution of the nuclear wavefunction on the ground and excited states respectively (assuming that non-adiabatic couplings can be neglected):

$$\hat{U}_0(t - t_0) = |G\rangle \hat{U}_0^G(t - t_0) \langle G| + |X\rangle \hat{U}_0^X(t - t_0) \langle X| \quad (5)$$

We further assume that the dipole moment operator induces transitions from the electronic ground state $|G\rangle$ to the excited state $|X\rangle$ and *vice versa*, and can thus be written as

$$\hat{\mu} = \mu_e (|G\rangle \langle X| + |X\rangle \langle G|) \quad (6)$$

where μ_e is the constant electric transition dipole moment.

1. Show that by a full specification of the electronic part of the various terms, the expressions of Eqs. (3) and (4) become $|\Psi^{(0)}(t)\rangle = |\psi^{(0)}(t)\rangle \otimes |G\rangle$ and $|\Psi^{(1)}(t)\rangle = |\psi^{(1)}(t)\rangle \otimes |X\rangle$ with the nuclear wavefunctions given by

$$|\psi^{(0)}(t)\rangle = \hat{U}_0^G(t - t_0)|\psi_0\rangle \quad (7)$$

$$|\psi^{(1)}(t)\rangle = \left(-\frac{i}{\hbar}\right) \int_{-\infty}^t d\tau \hat{U}_0^X(t - \tau) (\mu_e E(\tau)) \hat{U}_0^G(\tau - t_0)|\psi_0\rangle \quad (8)$$

Further show how the propagators $\hat{U}_0^G(\tau - t_0)$ and $\hat{U}_0^X(t - t_0)$ act on $|\psi_0\rangle$ if we choose $|\psi_0\rangle$ as an eigenfunction of the nuclear Hamiltonian in the ground adiabatic state:

$$\hat{H}^G|\psi_0\rangle = E_0|\psi_0\rangle \quad (9)$$

2. We now specify the first-order polarization by truncating the perturbative expansion of Eq. (1) at first order:

$$P^{(1)}(t) = \langle \Psi^{(0)}|\hat{\mu}|\Psi^{(1)}\rangle + \langle \Psi^{(1)}|\hat{\mu}|\Psi^{(0)}\rangle = 2 \text{Re}\langle \Psi^{(0)}|\hat{\mu}|\Psi^{(1)}\rangle \quad (10)$$

By using the explicit expressions for $|\Psi^{(0)}(t)\rangle$ and $|\Psi^{(1)}(t)\rangle$ obtained above, we will now obtain an explicit expression for $P^{(1)}(t)$.

3. Substitute $|\Psi^{(0)}(t)\rangle = |\psi^{(0)}(t)\rangle \otimes |G\rangle$ and $|\Psi^{(1)}(t)\rangle = |\psi^{(1)}(t)\rangle \otimes |X\rangle$, with $|\psi^{(0)}(t)\rangle$ and $|\psi^{(1)}(t)\rangle$ as specified in Eqs. (7)-(8), in the integral $\langle \Psi^{(0)}|\hat{\mu}|\Psi^{(1)}\rangle$ to show that

$$\langle \Psi^{(0)}|\hat{\mu}|\Psi^{(1)}\rangle = -\frac{i}{\hbar} \int_0^{+\infty} C(\tau) \exp\left(\frac{i}{\hbar} E_0 \tau\right) E(t - \tau) d\tau \quad (11)$$

where $C(\tau)$ is the autocorrelation function obtained by propagating the initial nuclear wavefunction on the potential energy surface of the excited state:

$$C(\tau) = \mu_e^2 \langle \psi_0|\hat{U}_0^X(\tau)|\psi_0\rangle \quad (12)$$

4. Show that $C(\tau)$ defined above coincides with

$$C(\tau) = \langle \Psi(0)|\hat{\mu} \hat{U}_0(\tau) \hat{\mu} |\Psi(0)\rangle \quad (13)$$

by performing the integration over the electronic coordinates in Eq. (13).

5. Finally, show using Eq. (10) that

$$P^{(1)}(t) = \frac{2}{\hbar} \text{Im} \int_0^{+\infty} C(\tau) \exp\left(\frac{i}{\hbar} E_0 \tau\right) E(t - \tau) d\tau \quad (14)$$