Theoretical Photochemistry WiSe 2017/18 – Exercise 6

The wavepacket autocorrelation function $C(t) = \langle\psi(0)|\psi(t)\rangle$ (i.e., overlap of the time-evolving wavepacket with the initial condition) is an important quantity in the calculation, e.g., of absorption spectra.

Here, we will use the eigenstate representation of the time-evolving excited-state wavepacket,

$\psi(x,t) = \sum_{n=0}^{\infty} c_n \phi_n(x) \exp(-iE_n t/\hbar)$

to obtain an explicit expression for $C(t)$.

(a) Define the coefficients c_n in terms of the initial condition $\psi(x, t = 0)$.

(b) Write the Fourier transform of the autocorrelation function $C(t)$ based upon the above eigenstate representation, using the relation

$$\mathcal{F}\left[e^{-i\omega_n t}\right] = 2\pi\,\delta(\omega - \omega_n)$$

(c) Obtain an explicit expression for the absorption spectrum

$$\sigma(\omega) = \frac{2\pi\omega}{3\hbar c} \int_{-\infty}^{\infty} dt\, C(t) e^{i\omega t}$$

(d) Interpret the above result by comparing with the conventional expression for the absorption spectrum, using Fermi's Golden Rule.

(e) Now consider a Gaussian wavepacket moving in a harmonic potential. The initial condition is given as $\psi(x, t = 0) = N \exp(-\alpha_0 x^2)$, with the normalization factor $N = (2\alpha_0/\pi)^{1/4}$. In a harmonic potential, the Gaussian wavepacket keeps its Gaussian shape at all times. What is the value of $C(t)$ at times $t = nT$, $n = 0, 1, 2, \ldots$, where T is the classical period $T = 2\pi/\omega_0$?

(f) For the case of the Gaussian wavepacket, show how the time-domain recurrence structure translates to the vibrational progression of the absorption spectrum.