Quantum Molecular Dynamics Homework 7 Spring, 2000

1. Consider a Gaussian pulse of the form:

$$E(t) = E_0 \exp[-\frac{t^2}{2\tau^2} - i\omega_0 t - ic\frac{t^2}{2}]. \tag{1.1}$$

Note that the Fourier transform of the pulse is:

$$\tilde{E}(\omega) = \tilde{E}_0 \exp[-\frac{(\omega-\omega_0)^2}{2\gamma^2}] \tag{1.2}$$

where $\gamma^2 = 1/\tau^2 + ic$.
a) Rewrite $\tilde{E}(\omega)$ as:

$$\tilde{E}(\omega) = \tilde{E}_0 \exp[-\frac{(\omega-\omega_0)^2}{2\Gamma^2} - ic'\frac{(\omega-\omega_0)^2}{2}] \tag{1.3}$$

where $1/\Gamma^2 = Re(1/\gamma^2)$ and $c' = Im(1/\gamma^2)$. Show the following relationships:
(i) $\Gamma^2 = 1/\tau^2 + c^2\tau^2$
(ii)$\tau^2 = 1/\Gamma^2 + (c'\Gamma)^2$
(iii) $c'\Gamma^2 = c\tau^2$. Γ is defined as the frequency bandwidth, τ is the pulse duration, c is the linear chirp rate in time, and c' is the linear chirp rate in frequency.
b) Show that the integrated intensity, P, is given by:

$$P \equiv \int_{-\infty}^{\infty} |E(t)|^2 dt = \pi^{1/2} E_0^2 \tau. \tag{1.4}$$

and therefore, for fixed P, the peak field amplitude E_0 decreases with pulse duration τ. Show that this implies that if P and Γ are both fixed, E_0 decreases with the frequency chirp rate c'.

2. Consider a three level system with frequency separation ω_1 and ω_2, respectively. Show that the population in level three is

$$\begin{aligned} N_2 &= |\int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{t_2} dt_1 e^{i\omega_2 t_2 + i\omega_1 t_1} E(t_2)E(t_1)|^2 & (2.1)\\ &= |C(\Delta)\int_{-\infty}^{\infty} dt E^2(t) e^{it(\omega_2+\omega_1)}|^2 & (2.2)\end{aligned}$$

where

$$C(\Delta) = \int_0^{\infty} ds \exp[-\frac{s^2}{4}(\frac{1}{\tau^2} + ic) + i\frac{\Delta s}{2}] \tag{2.3}$$

where $\Delta = \omega_2 - \omega_1$ is the detuning of the intermediate state.
(i) Show that for $\Delta >> \Gamma$, $N_2 \propto P^2/\tau\Gamma$.
(ii) Show that for $\Delta \approx \Gamma$ the optimal chirp is $c \propto \frac{\Delta}{\tau}$. Compare your results in (i) and (ii) with the numerical results from MATLAB (see J. Cao and K. R. Wilson, J. Phys. Chem. A 102, 4284 (1998) for this and subsequent exercises in this set).

3. Consider the following exact expression for N_2,

$$N_2 = \int dt_2' \int dt_2 < \psi_1(t_2')|e^{-iH_2(t_2'-t_2)/\hbar}|\psi_1(t_2) > E^*(t_2')E(t_2) \quad (3.1)$$

$$= \int dt \int ds < \psi_1(t)|e^{iH_1 s/2\hbar}e^{-iH_2 s/\hbar}e^{iH_1 s/2\hbar}|\psi_1(t) > E^*(t+s/2)E(t-s/2) \quad (3.2)$$

where $s = t_2' - t_2$ and $2t = t_2' + t_2$. Approximate

$$C_{11}(t) =< \psi_1(t)|e^{iH_1 s/2\hbar}e^{-iH_2 s/\hbar}e^{iH_1 s/2\hbar}|\psi_1(t) >\approx e^{i\omega_2(x(t))}. \quad (3.3)$$

where $x(t)$ is the center of the first order wavepacket ψ_1 at time t. Show that

$$N_2 \approx \int dt \int ds e^{-is\omega_2[x(t)]}E^*(t+s/2)E(t-s/2) = \int dt F(t, \omega_2[x(t)]) \quad (3.4)$$

where $F(t,\omega)$ is the Wigner transform of the pulse. The physical interpretation of this result is that the excited state population is the line integral of the Wigner function of the pulse along the trajectory of the frequency difference between potentials 1 and 2.

4. Show that the Wigner transform of a pulse with a continuing varying frequency,

$$E(t) = E_0 \exp[-\frac{(t-t_0)^2}{2\tau^2} - i\int_{t_0}^{t} \omega(t')dt'] \quad (4.1)$$

is given by

$$F(t,\omega) = E_0^2 \exp[-\frac{(t-t_0)^2}{\tau^2} - (\omega - \omega(t))^2\tau^2]. \quad (4.2)$$

Combine this result with the previous exercise to show that optimal pulse for maximizing N_2 is one which satifies chirp following, i.e. $\omega(t) = \omega_2[x(t)]$.

5. Return to exercise 3. and make the approximation:

$$C_{11}(t) =< \psi_1(t)|e^{iH_1 s/2\hbar}e^{-iH_2 s/\hbar}e^{iH_1 s/2\hbar}|\psi_1(t) >\approx \exp[i\omega_2(x_1)t_2 + i\omega_1(x_0)t_1] \quad (5.1)$$

(i) Show that if the second order transition is back to the ground state, this expression can be approximated by

$$C_{11}(t) \approx \exp[i\omega_1(x_0)t_2 + i\alpha s^2 t_2/2m\hbar + i\omega_1(x_0)t_1] \quad (5.2)$$

where $\alpha = (\nabla V_1)^2$.
(ii) Show that this implies that

$$N_0^{(2)} = \frac{P^2}{\Gamma\tau}|C(\Delta)|^2 \quad (5.3)$$

where

$$C(\Delta) = \int_0^\infty ds \exp[-\frac{s^2}{4\tau^2} - \frac{\tau^2 s^2}{4}(c+\alpha s)^2 - is\Delta + i\frac{\alpha}{2}s^3] \quad (5.4)$$

where $\Delta = \omega_1(x_0) - \omega_0$.
(iii) Optimizing N_0^2 requires minimizing the square term in the exponent of $C(\Delta)$. Show that this implies that if the second order transition is back to the ground state, the optimal chirp is always negative, since α is positive. Since the average value of s is on the order of the pulse duration τ, we obtain an estimate for the optimal linear chirp rate of $c \approx -\alpha\tau$. Check this estimate using MATLAB.

6. Chirped pulses can be used to prepare wavepackets that are either more focussed or more defocussed at a particular time than those prepared with transform limited pulses. Use the (first-order) MATLAB program for the I_2 system to show that a positively chirped pulse is favorable for producing focussing before the outer turning point is reached, while a negatively chirped pulse is favorable for producing focussing on time scales after the outer turning point is reached. (see J. Krause et al., J. Chem. Phys. 99, 6562 (1993); J. Cao and K. R. Wilson, J. Chem. Phys. 107, 1441 (1997).