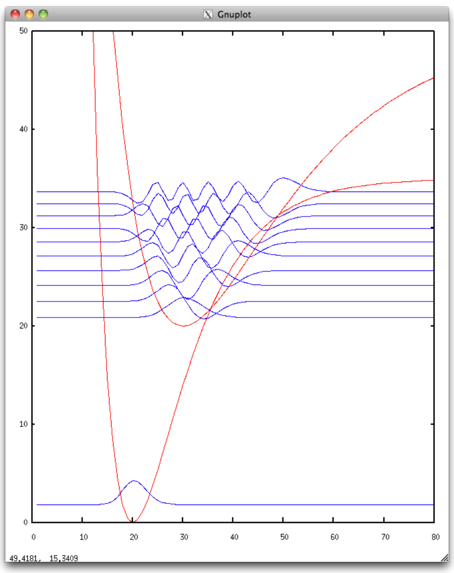
This material has been prepared and made freely available by the financial support of National Science Foundation (CAREER, CHE-0844448 and CHE-1118616) and Camille and Henry Dreyfus Foundation, Inc. Any opinions, findings, and conclusions or recommendations expressed in this materials are those of the author and do not necessarily reflect the views of the sponsoring agencies.

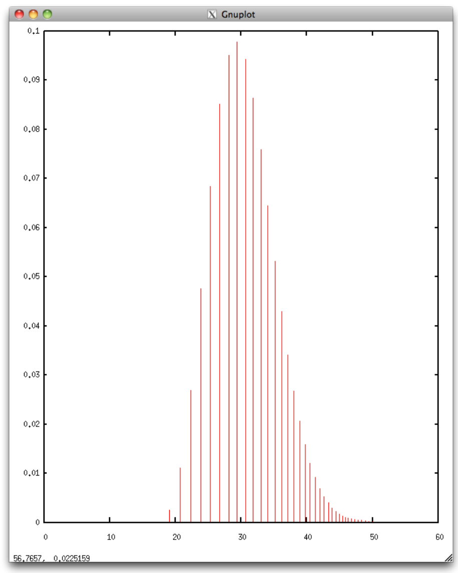
CHM 548 PROGRAMMING HOMEWORK 2

(1) Use the program from HW1 to compute the Franck–Condon factors, I_n, between two displaced Morse potentials:

$$I_n = \langle v_0 | v_n' \rangle \langle v_n' | v_0 \rangle,$$

where $|v_0\rangle$ denotes the zero-point vibrational wave function of the electronic ground state and $|v_n'\rangle$ is the *n*th vibrational wave function of the electronic excited state. Plot the Franck–Condon factors as a function of the transition energies, $\omega_n = E_n' - E_0$.



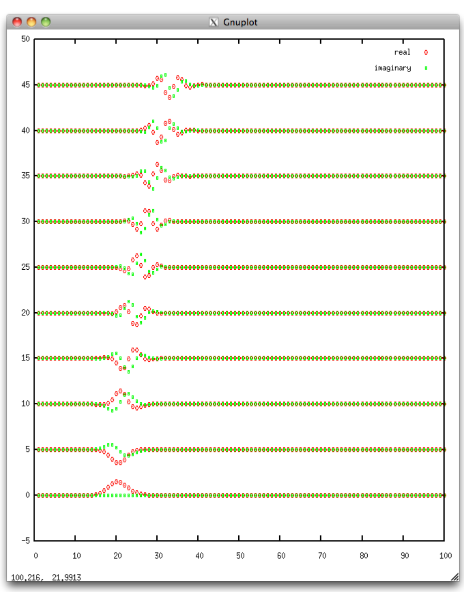


(2) Verify numerically that the wave packet, $|w(0)\rangle$, created on the electronic excited state's potential immediately after the transition is identical to $|v_0\rangle$, namely,

$$|w(0)\rangle = \sum_n |v_n'\rangle \langle v_n' | v_0 \rangle = |v_0\rangle.$$

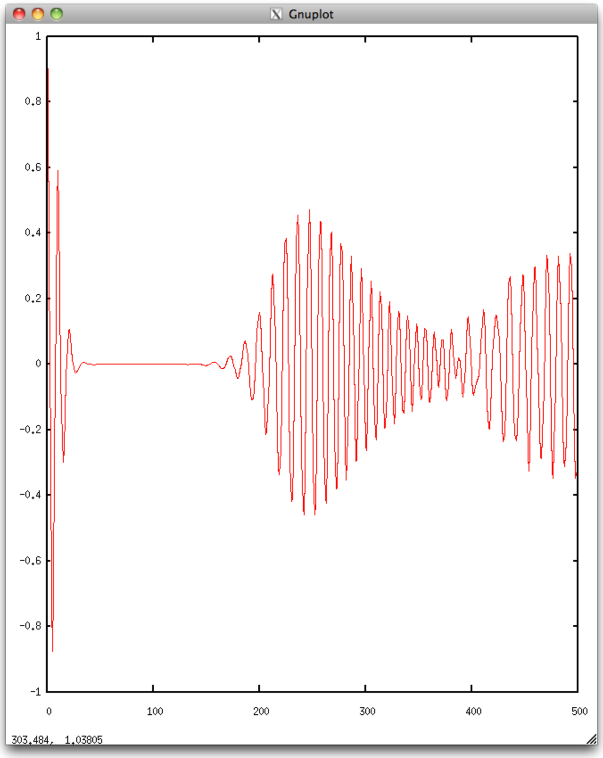
(3) Calculate and plot the wave packet, $|w(t)\rangle$, as a function of time *t*, using the following sum-over-state formula:

$$|w(t)\rangle = \sum_n |v_n'\rangle \langle v_n' | v_0 \rangle e^{-iE_n' t}.$$



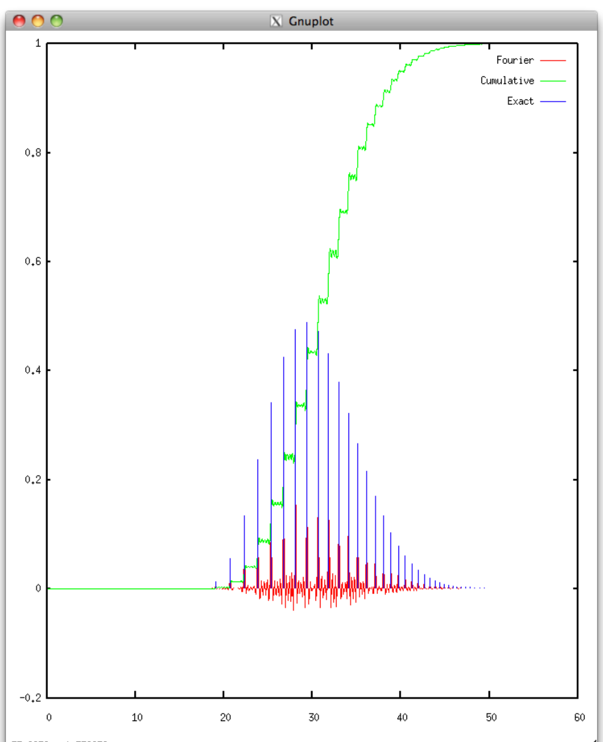
(4) Calculate and plot the correlation function,

$$C(t) = \langle w(0)|w(t)\rangle = \langle v_0| \sum_n |v_n'\rangle\langle v_n'|v_0\rangle e^{-iE_n' t} = \sum_n \langle v_0|v_n'\rangle\langle v_n'|v_0\rangle e^{-iE_n' t} = \sum_n I_n e^{-iE_n' t}.$$



(5) Fourier transform the correlation function and reproduce the Franck–Condon factors, as expected from

$$\frac{1}{2\pi}\int_{-\infty}^{+\infty} C(t)e^{i\omega t} dt = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \sum_n I_n e^{i(\omega - E_n')t}\, dt = \sum_n I_n \delta(\omega - E_n').$$



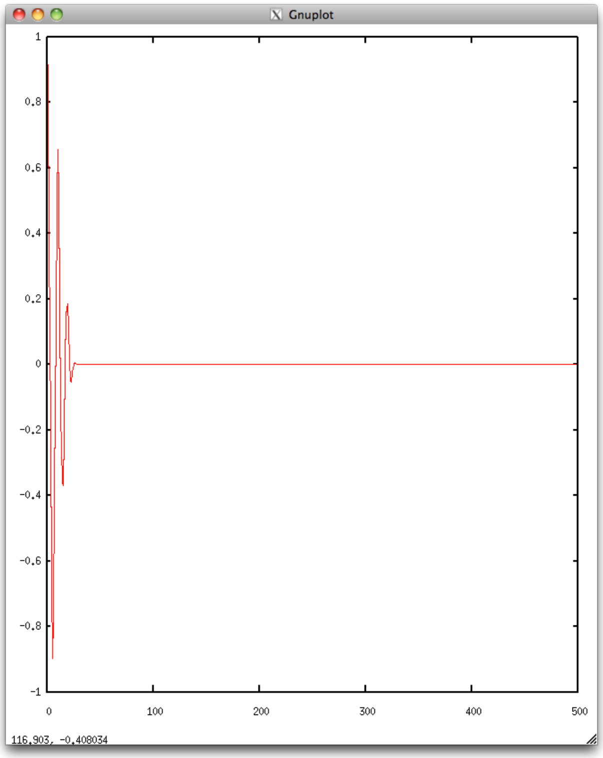
(6) Calculate and plot the wave packet, $|w(t)\rangle$, as a function of time t, by integrating the time-dependent Schrödinger equation,

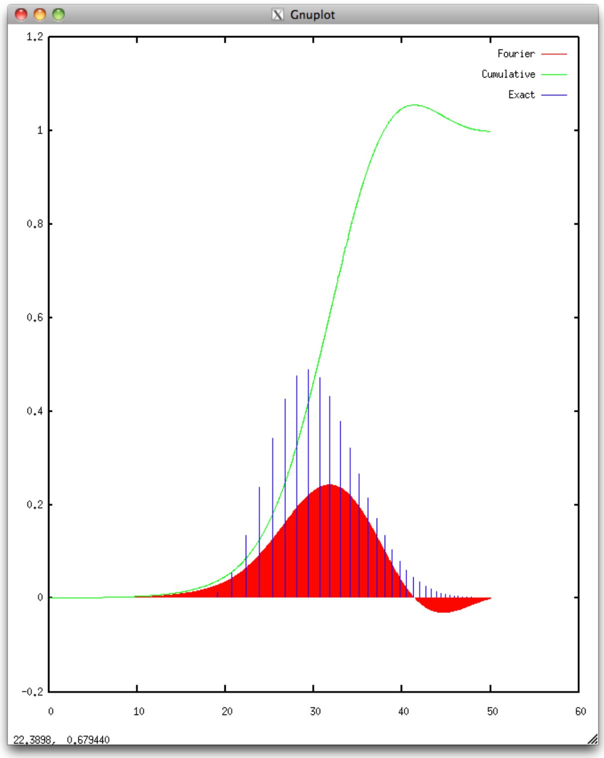
$$\hat{H}|w(t)\rangle = i\frac{\partial}{\partial t}|w(t)\rangle,$$

with finite-difference approximations in both time and space, leading to

$$|w(t+\Delta t)\rangle = |w(t)\rangle + \frac{\hat{H}}{i}|w(t)\rangle\Delta t,$$

where the action of the Hamiltonian on a wave function on a grid can be obtained by multiplying the Hamiltonian matrix defined in HW1 with the vector representing the wave function. Repeat steps (4) and (5) for this propagated wave packet.





Note that the above shown correlation function is almost completely missing long-time correlation owing to the accumulation of numerical errors and, as a result, the Franck–Condon factors obtained from it have no fine structure and are negative in some energy domains, which is nonphysical. It, however, recovers an overall envelope of the exact spectrum to some degree. Try to obtain a better result.

A sample 200-line program used to generate above figures is available upon request. However, a student is strongly encouraged to write a program from scratch by taking advantage of the instructor's office hours for assistance.