



Project Report # 2

CHEM 548-Molecular Electronic Structure: Advanced Quantum
Chemistry & Numerical Methods – Spring 2017

Course Instructor

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1 Computational Project- 2 Programming Homework Questions

1. Computing the Frank-Condon factors between two displaced Morse potentials.
2. Verifying numerically that the wave packet, $|w_0\rangle$, created on the electronic excited states potential immediately after the transition is identical to $|v_0\rangle$.
3. Calculating and plotting the wave packet, $|v_0\rangle$, as a function of time t , using the given sum-over-state formula.
4. Calculating and plotting the correlation as a function of time.
5. Doing a Fourier transform on the correlation function and reproducing the Franck-Condon factors that was obtained in part 3.
6. Calculating and plotting the wave packet, $|w_0\rangle$, as a function of time t , by integrating the time-dependent Schrödinger equation using the finite difference method and plotting the correlation function, and the Franck-Condon factors by Fourier transforming the correlation function.

2 Franck-Condon Principal

The electronic level of a molecule can be thought of as having a subset of vibrational energy levels. The Franck-Condon principle says that the electronic excitation will be vertical in a diagram which shows the vibrational energy as a subset of the electronic levels because the nuclei respond to the change of electronic structure on a much longer timescale than the electronic transition itself.

The mass of a proton is 1836 times that of an electron and so the electron has a much smaller mass than even the H atom nucleus. This difference allows the functional form of the total wavefunction to be simplified by treating the electronic and vibrational states separately. This separation of the nuclear and electronic degrees of freedom is known as the Born-Oppenheimer approximation. This approximation can be represented as :

$$\Psi(r; R) = \Psi_e(r; R) \Psi_N(R; \Psi_e) \quad (1)$$

The semicolon is used to separate the coordinates which enter directly into the functional form of the wavefunction from other factors on which the wavefunction depends. Under the Born-Oppenheimer approximation:

$\Psi_e(r; R)$ – represents that the electronic part of the wavefunction is a function of the electronic coordinates only but these depend on a particular arrangement of the nuclei. The nuclei provide a potential in which the electrons move.

$\Psi_N(R; \Psi_e)$ – represents that the nuclear part of the wavefunction is a function of nuclear coordinates only but it does depend on the particular electronic state. On the timescale of the nuclear motion the electrons appear smeared out over a distribution defined by Ψ_e . They create forces acting on the nuclei which are effectively averaged over the electronic wavefunction and so the electronic coordinates do not explicitly appear. A change in electronic state will influence $\Psi_N(R; \Psi_e)$ through a change of these average effects.

Now consider an excitation represented as :

$$\Psi_{e0}(r; R) \Psi_{N0}(R; \Psi_e) \rightarrow \Psi_{e1}(r'; R) \Psi_{Nn}(R; \Psi_{e1}) \quad (2)$$

The molecule originally in the ground vibronic state absorbs a photon with the correct energy to move to the first electronic excited state with a shift in the electronic coordinates from r to r' . This also places the

molecule in the n th vibrational state of the electronically excited molecule. The Franck-Condon principle appears here since we assume that the nuclear coordinates R remain constant during the transition.

For the light to be absorbed, a change in dipole moment must occur so that the coupling matrix element between the two states is non-zero. So we must consider both the nuclear contributions μ_N and the electronic contributions μ_e to the transition dipole moment operator, so that the required matrix element is:

$$M_{1n:00} = \int \Psi_{e1}^*(r'; R) \Psi_{Nn}^*(R; \Psi_{e0}) (\mu_N + \mu_e) \Psi_{e0}(r; R) \Psi_{N0}(R; \Psi_{e0}) dr dr' dR \quad (3)$$

where the integration is over all space for all electron and nuclear coordinates. We keep the electron and nuclear contributions to the transition dipole moment operator separate since μ_N will only operate on the nuclear wavefunction, $\Psi_N(R; \Psi_e)$ and μ_e will only operate on electronic wavefunctions, $\Psi_e(r; R)$.

Using the Born-Oppenheimer approximation we can rearrange the above equation to :

$$M_{1n:00} = \int \Psi_{e1}^*(r'; R) \Psi_{e0}(r; R) dr dr' \int \Psi_{Nn}^*(R; \Psi_{e1}) \mu_N \Psi_{N0}(R; \Psi_{e0}) dR \quad (4)$$

$$+ \int \Psi_{Nn}^*(R; \Psi_{e1}) \Psi_{N0}(R; \Psi_{e0}) dR \int \Psi_{e0}^*(r'; R) \mu_e \Psi_{e0}(r; R) dr dr' \quad (5)$$

The first term contains an integral over the ground and the excited states which are orthogonal and hence only the second term remains in the above equation:

$$M_{1n:00} = \int \Psi_{Nn}^*(R; \Psi_{e1}) \Psi_{N0}(R; \Psi_{e0}) dR \int \Psi_{e0}^*(r'; R) \mu_e \Psi_{e0}(r; R) dr dr' \quad (6)$$

This expression contains the transition dipole moment for the electronic states (the second integral) and symmetry rules will apply while evaluating this integral. This integral is over the n th vibrational state of the electronically excited molecule with the ground-state vibration.

2.1 The displaced Morse potential plots

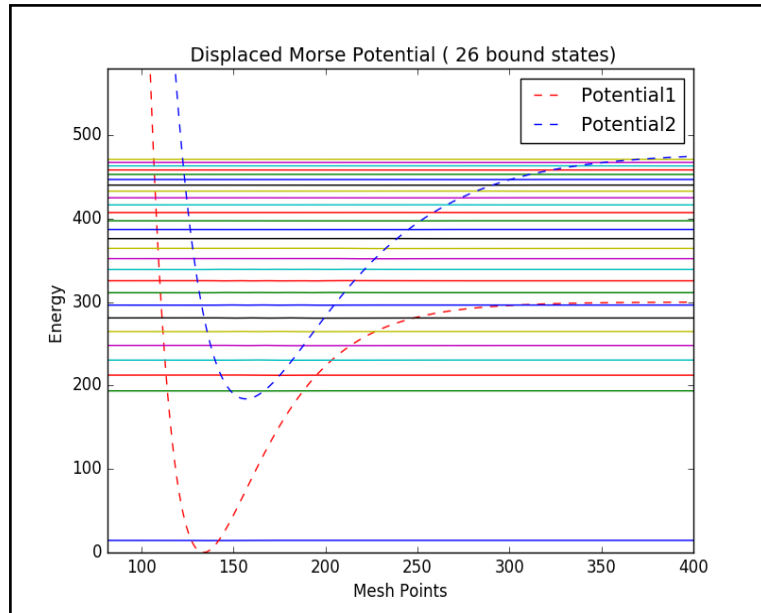


Figure 1: The ground and excited state Morse potentials obtained by using the finite difference method on a 1-dimensional grid of 400 points.

2.2 Franck-Condon Plots

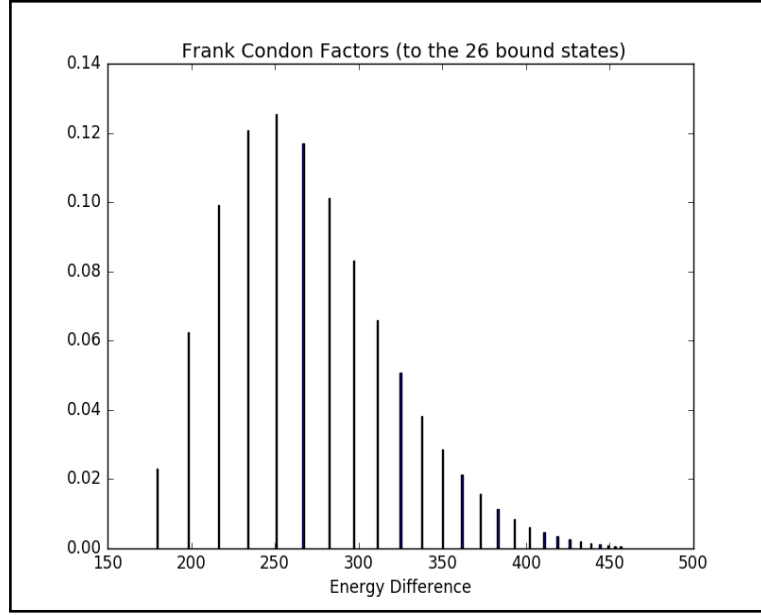


Figure 2: The plot of Franck-Condon factors. In the excited Morse potential obtained above we had 26 bound states. The Frank-Condon factors plot shows the intensity of transition to these states from the ground state of the lower Morse potential.

3 The wave-packet formed after excitation

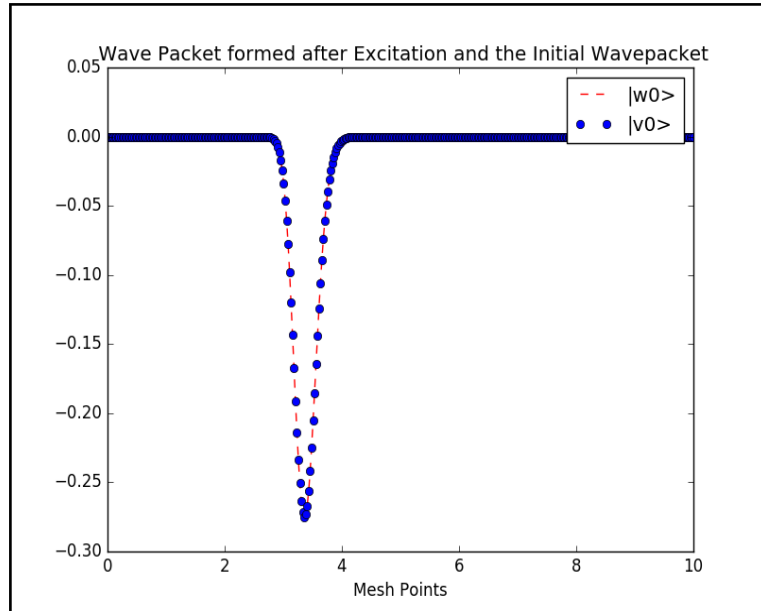


Figure 3: The plot shows the exact match between the ground state wavepacket and the wave packet formed immediately after excitation to the excited state.

4 The wave-packet propagated with time

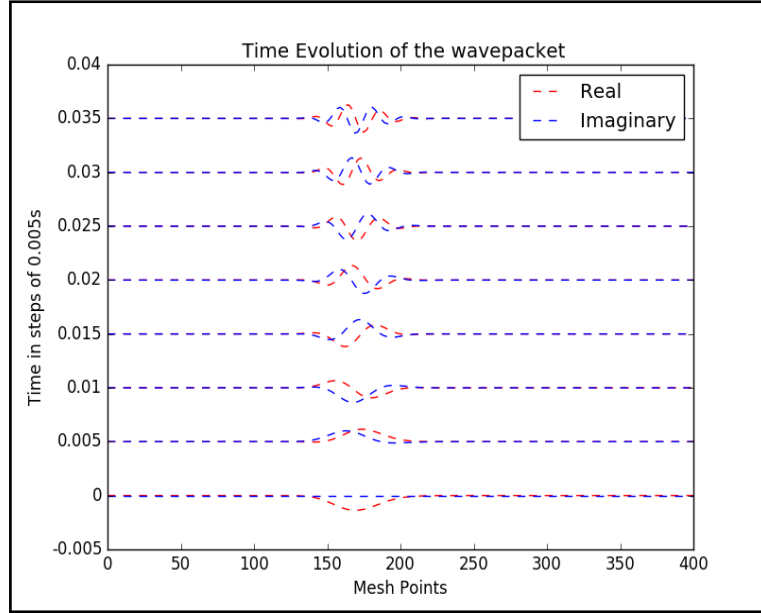


Figure 4: The wavepacket formed in the excited state is plotted as a function of time in the time steps of 0.005 seconds.

5 The Correlation Function

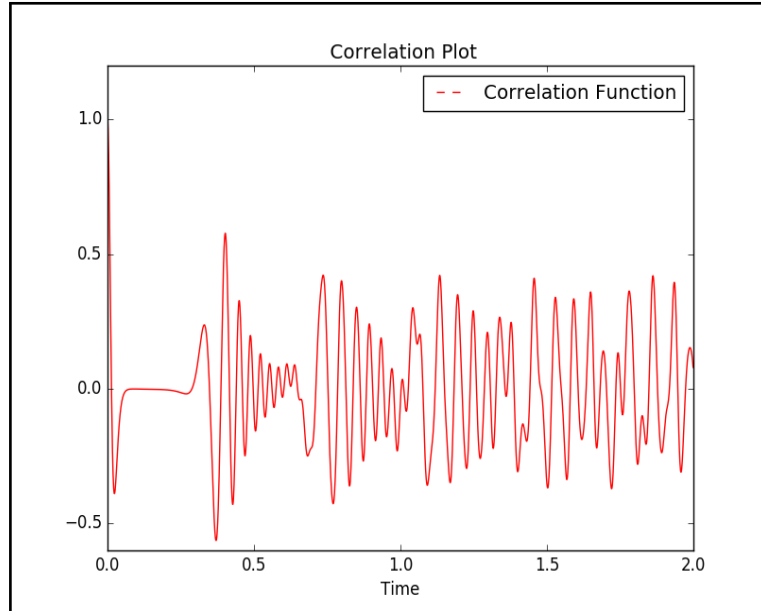


Figure 5: The plot of the correlation function between the initial wavepacket and the wavepacket propagated over time using the sum over states formula.

5.1 The FT of the Correlation Function

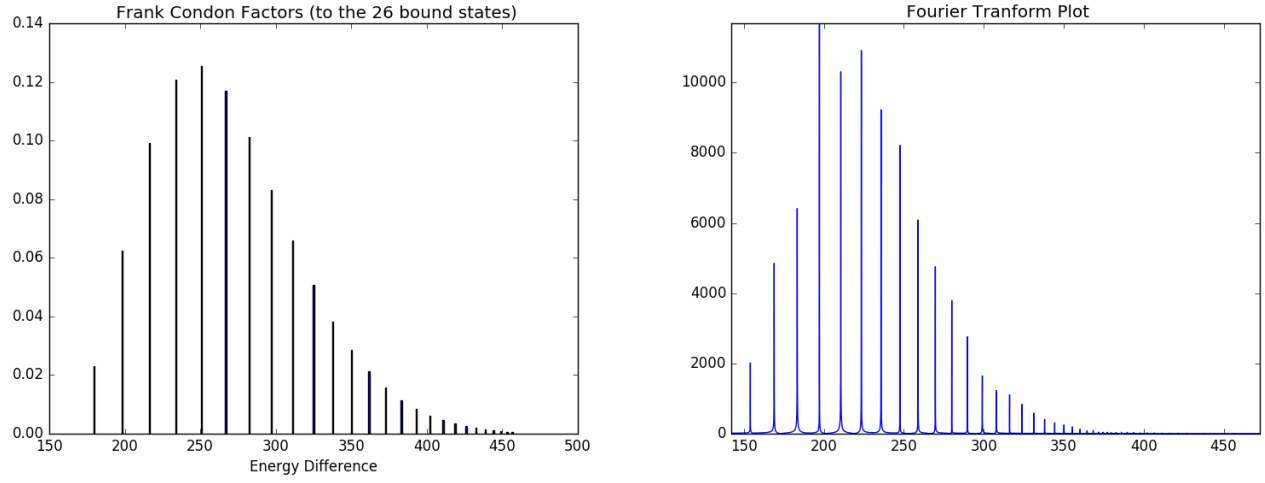


Figure 6: The plot on the left is the plot of Franck-Condon factor obtained in question 1 and on the right is that of the Franck-Condon factors obtained by the Fourier transform of the correlation function.

6 Wavepacket propagation using the finite-difference Hamiltonian

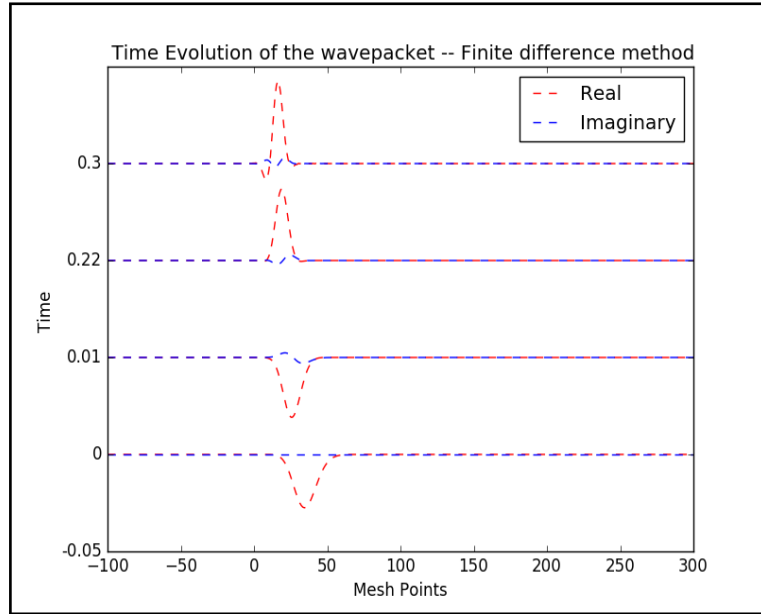


Figure 7: The propagation of the wavepacket in the excited state Morse potential using the finite difference Hamiltonian obtained in Project - 1

6.1 The correlation function obtained using the finite-difference Hamiltonian

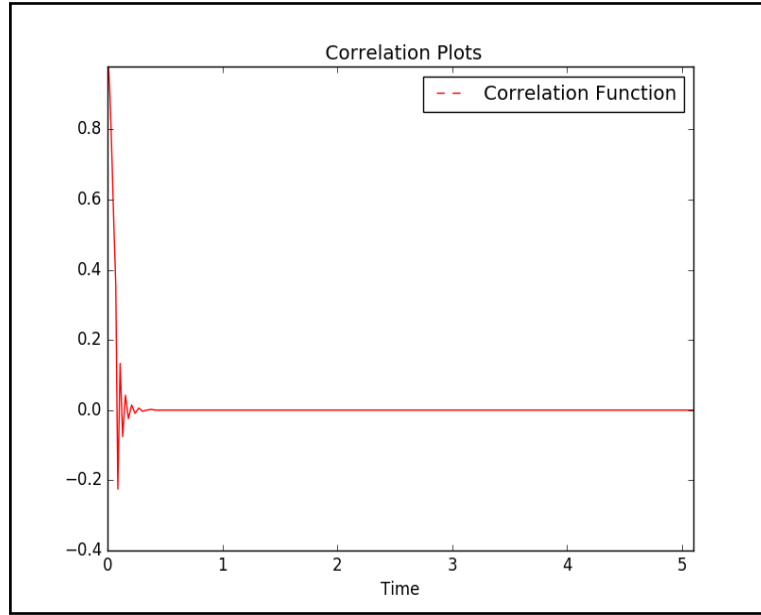


Figure 8: The plot of the correlation function obtained by using the finite difference grid method in both the time and space dimensions. Due to the accumulation of numerical errors the long time correlation is completely missing.

7 Conclusions

The dynamics of the wavepacket in the excited Morse potential was analyzed in this project. The plots for which are shown in the respective sections. Due to the accumulation of numerical errors the Fourier transform of the correlation function of question no.6 did not reproduce the expected Franck-Condon spectra. The codes written in FROTRAN using the LAPACK subroutine for the first project were rewritten in C++ using the Armadillo library. So programming skills in C++ were acquired. The plots were created using the Python programming language.

8 References

- [1] Molecular Symmetry, David J. Willock, John Wiley & Sons, Ltd.
- [2] Chemistry-2 Lecture 11 Electronic spectroscopy of polyatomic molecules on slideplayer.com
- [3] [https : //en.wikipedia.org/wiki/FranckCondon_principle](https://en.wikipedia.org/wiki/FranckCondon_principle) accessed on 8th February
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