CHEM 548: Advanced Electronic Structure

Project #2 Report

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by

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Contents

1 Abstract

This report presents a discussion on the time evolution of wavepackets after excitation. The wavepacket at time t is calculated using a sum over state formula and the finite difference or euler method. The correlation is also plotted to show the differences in the methods.

2 Questions

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

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 $|v_0\rangle$. $|v_0\rangle$ is the zero-point vibrational wavefunction.

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

4. Calculate and plot the correlation function.

5. Fourier transform the correlation function and reproduce the Franck–Condon factors.

6. Calculate and plot the wave packet, $|w(t)\rangle$, as a function of time t, by integrating the time-dependent Schrödinger equation, with finite-difference approximations in both time and space.

7. Calcuate the correlation function and fourier transform to reproduce the Frank Condon factors again.

3 1D Schrodinger Equation

The basic crux of quantum mechanics involves solving the schrodinger equation. The 1 Dimensional Schrodinger equation is given as follows:

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle \tag{1}$$

However, we can write the time independent schrodinger equation for stationery states:

$$\hat{H}|\Psi(x)\rangle = E|\Psi(x)\rangle \tag{2}$$

Where $\hat{H}$ is the hamiltonian, which is expressed as the sum of the kinetic energy and potential energy operators. Solving this equation gives us the stationery eigenstates of the system, along with their energies.

4 Frank Condon Principle

The frank condon principle states that the no nuclear motion occurs during an electronic transition, i.e electronic transitions occur near instantaneously[1]. The frank condon factors, which are the square of the overlap between the excited state and the ground state, are intensities of excitation, and are also the nuclear overlap. If the nuclear overlap is 0, no matter the magnitude of the electronic overlap, the transition will be forbidden.

Since during transition, the change in vibrational state is maintained, the transitions are termed as vertical transitions.

The frank condon principle operates under the born oppenheimer approximation where we can separate the electronic and nuclear coordinates.

5 Calculation Parameters and System Details

The assignment was done in python, with the numpy library being used for matrix calculations, and matplotlib library being used for plotting results.

A box of length **40** Angstrom was used, with **500** grid points.

Initial time was set to **0**, and final time was set to **10** seconds. **10000** grid points were used to discretise the time grid.

5.1 Morse Potential

The Morse Potential is given by the equation:

$$V(x) = D_e \left(1 - e^{-\sigma(x-x_e)}\right)^2 \tag{3}$$

2 morse wells were used for representing a ground electronic state and an excited electronic state.

The values used were as follows:

Parameter	Morse Potential 1	Morse Potential 2
Dissociation Energy D (eV)	20	20
Width Parameter σ (Å)	0.2	0.2
Equilibrium Position x_e (Å)	-15	-13

Table 1: Parameters for the two Morse potentials used in the simulation.

The excited potential well was shifted up by **8 eV**.

6 Code and Implementation

The code is available on Github

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7   Morse Potential Bound States

The stationery eigenstates were calculated by using the finite difference method. **31** bound states were found in the excited electronic state.
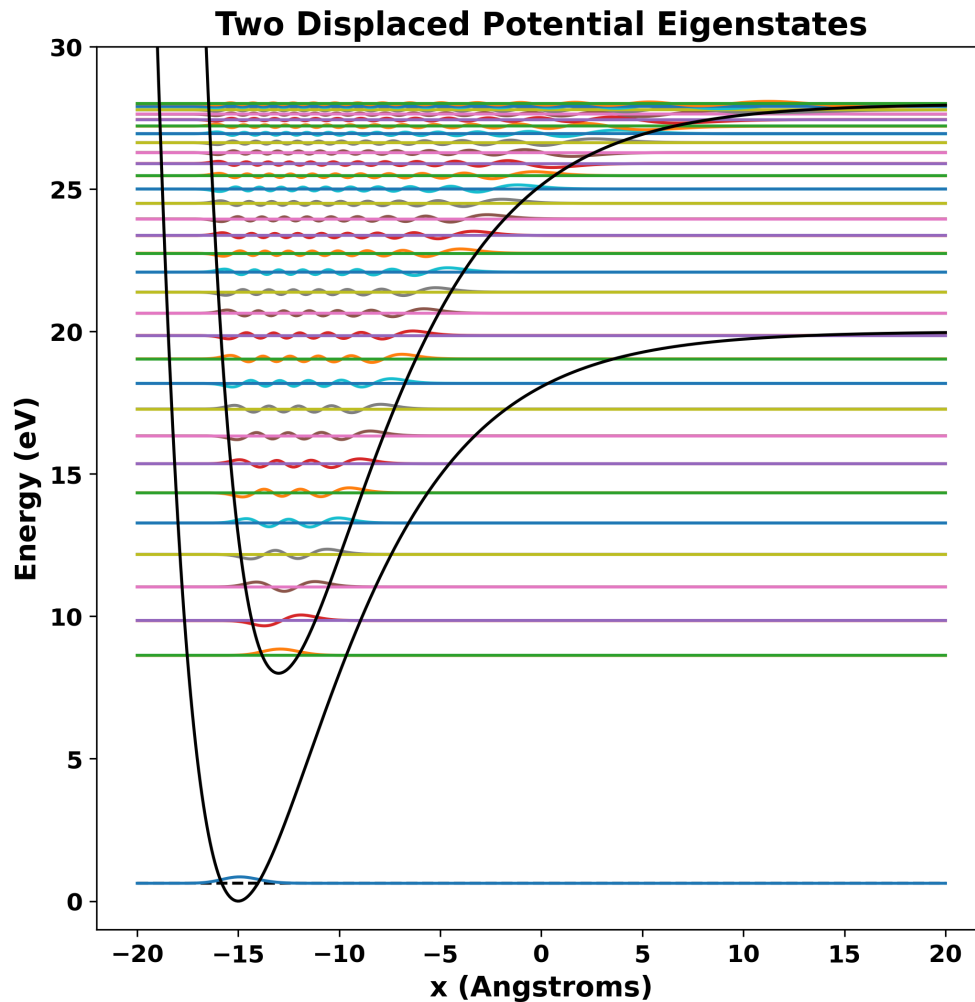

Figure 1: Ground State Eigenstate of the electronic ground state and bound eigenstates of the excite state.

8 Frank Condon Factors

Frank Condon Factors were calculated and a vibrational progression was simulated for excitation from the zero-point vibrational state to the bound vibrational states of the excited electronic state.
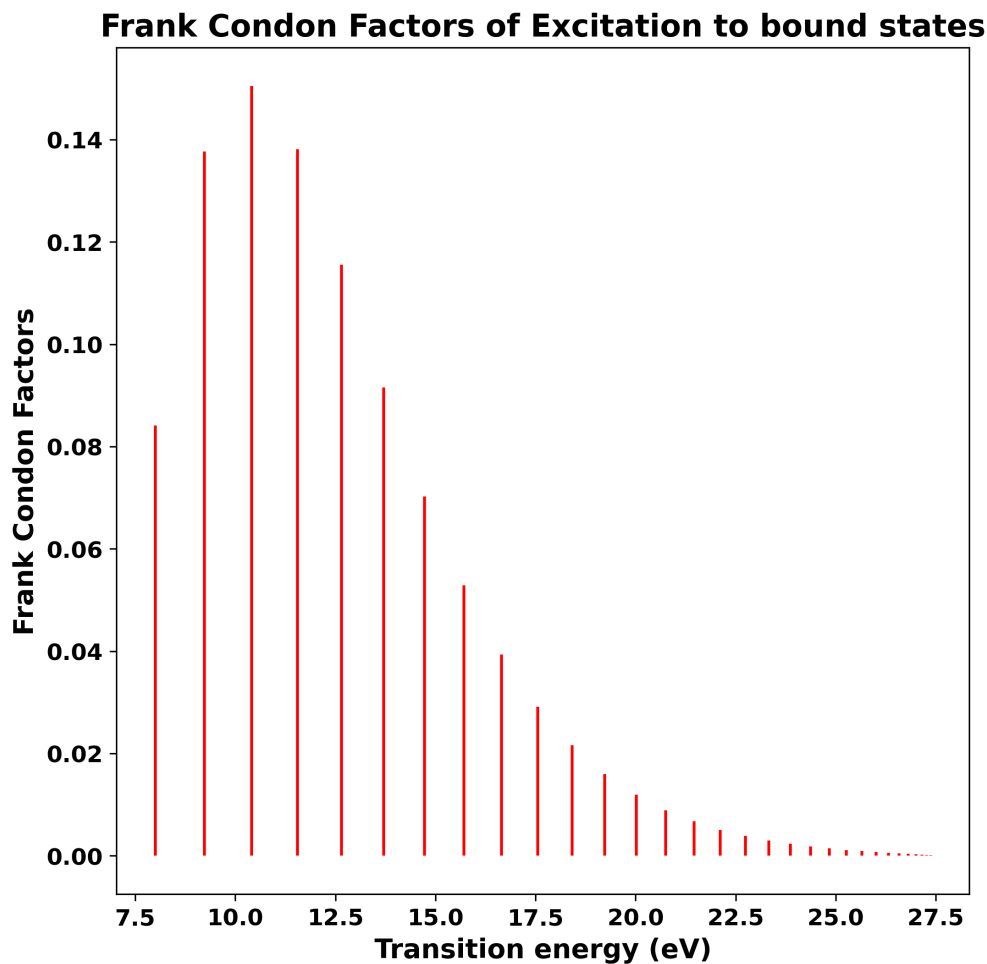

Figure 2: Frank Condon Factors for excitation of ground electronic state to excited electronic state.

9 Excited Wavepacket Initial Shape

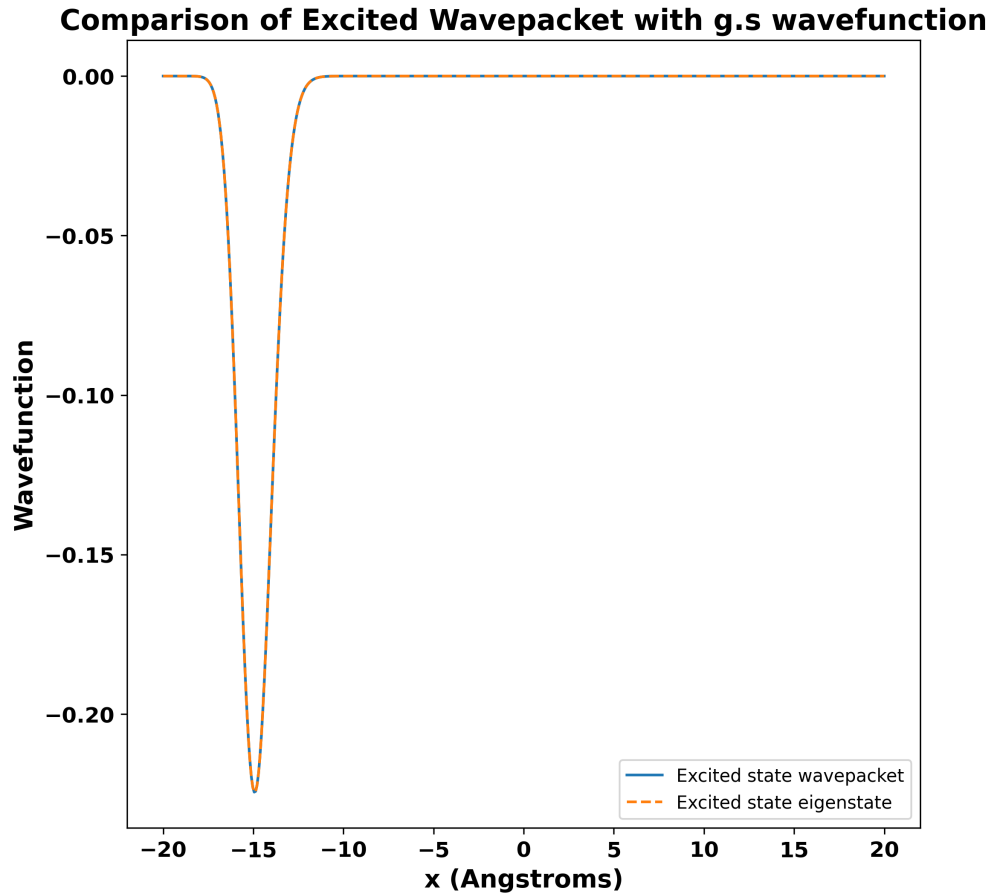As shown below, the form of the ground state wavefunction matches the excited wavepacket initially.

Comparison of Excited Wavepacket with g.s wavefunction

Figure 3: Comparing ground state wavefucntion with excited wavepacket.

10 Excited Wavepacket Time evolution

The time evolution of the wavepacket was simulated using the following sum over state equation:

$$|w(t)\rangle = \sum_n |v'_n\rangle\langle v'_n|v_0\rangle e^{-iE'_n t} \qquad (4)$$

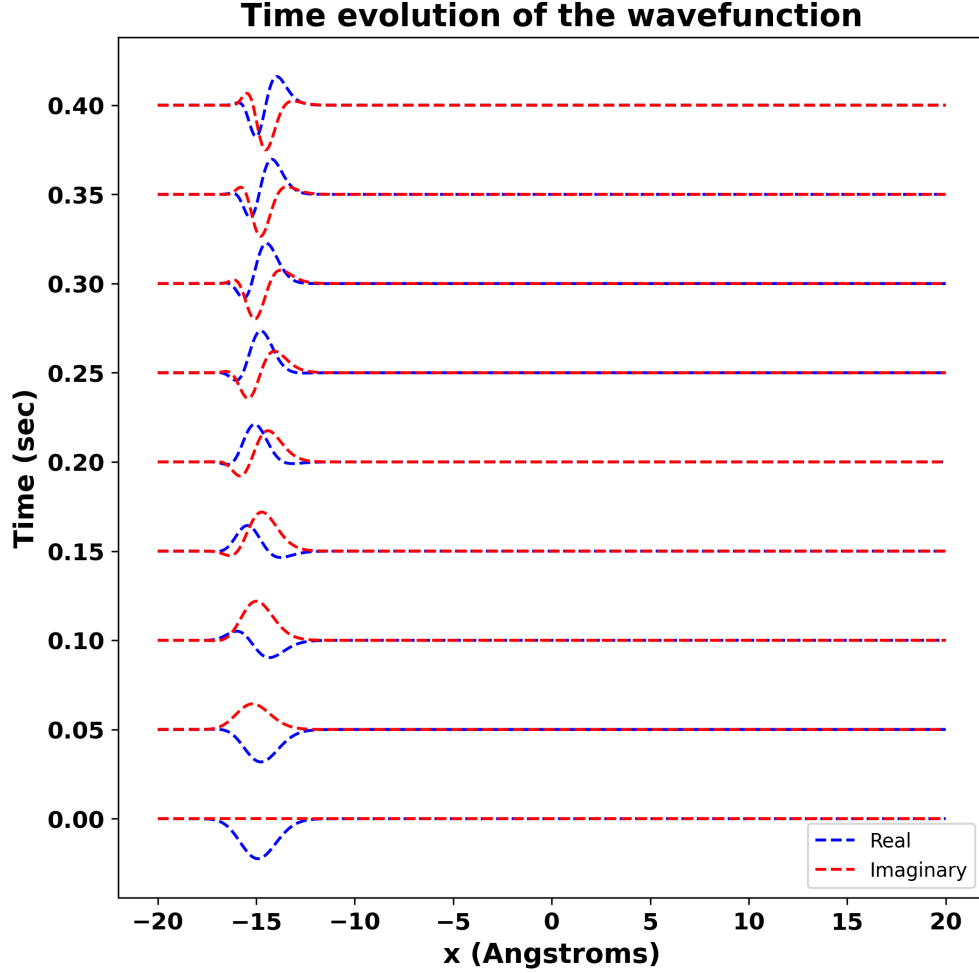The real and imaginary parts of the wavefunction were plotted in 0.05 second intervals. As

Figure 4: Time evolution of the excited wavepacket

shown in the previous figure, at t=0, the shape of the excited wavepacket matches the zero-point vibrational state wavefunction exactly, which is clear because of the zero imaginary part, and the wave being positioned at -15 Angstrom, which is exactly where the zero-point wavefunction is located. This is in agreement of vertical excitation of frank condon principle as well.

11 Correlation Function

The correlation function was evaluated by taking the dot product of the wavefunction at each time step with the initial excited wavepacket.

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

(5)

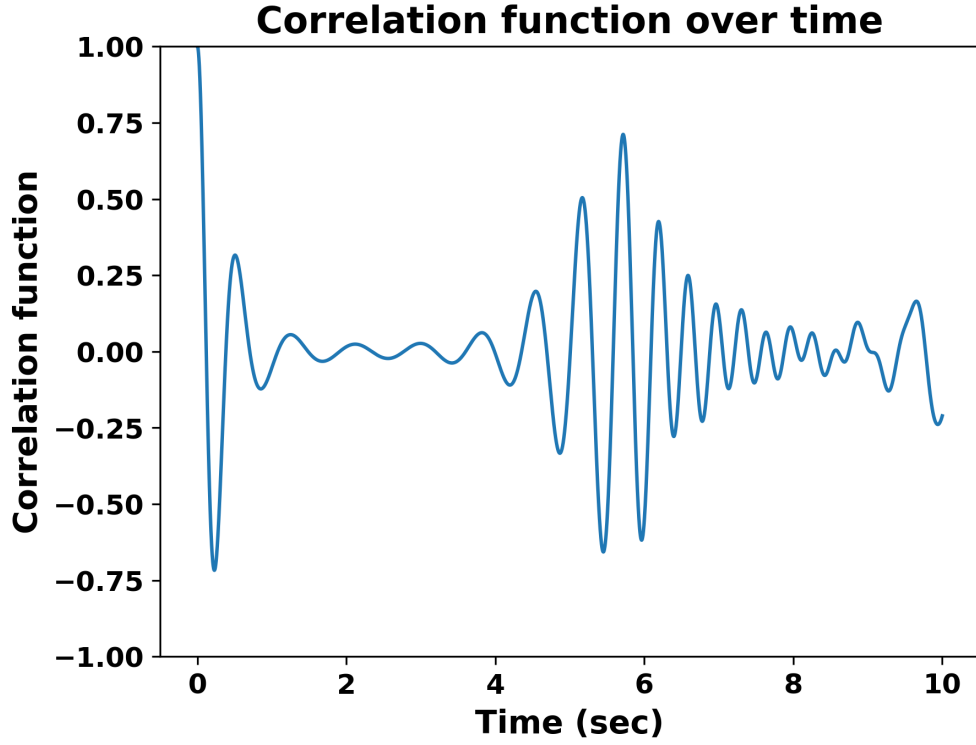Figure 5: Correlation Function C(t)

12 Fourier Transform to get Frank Condon Factors

A Fourier transform was done of the correlation function to recover the frank condon factors.

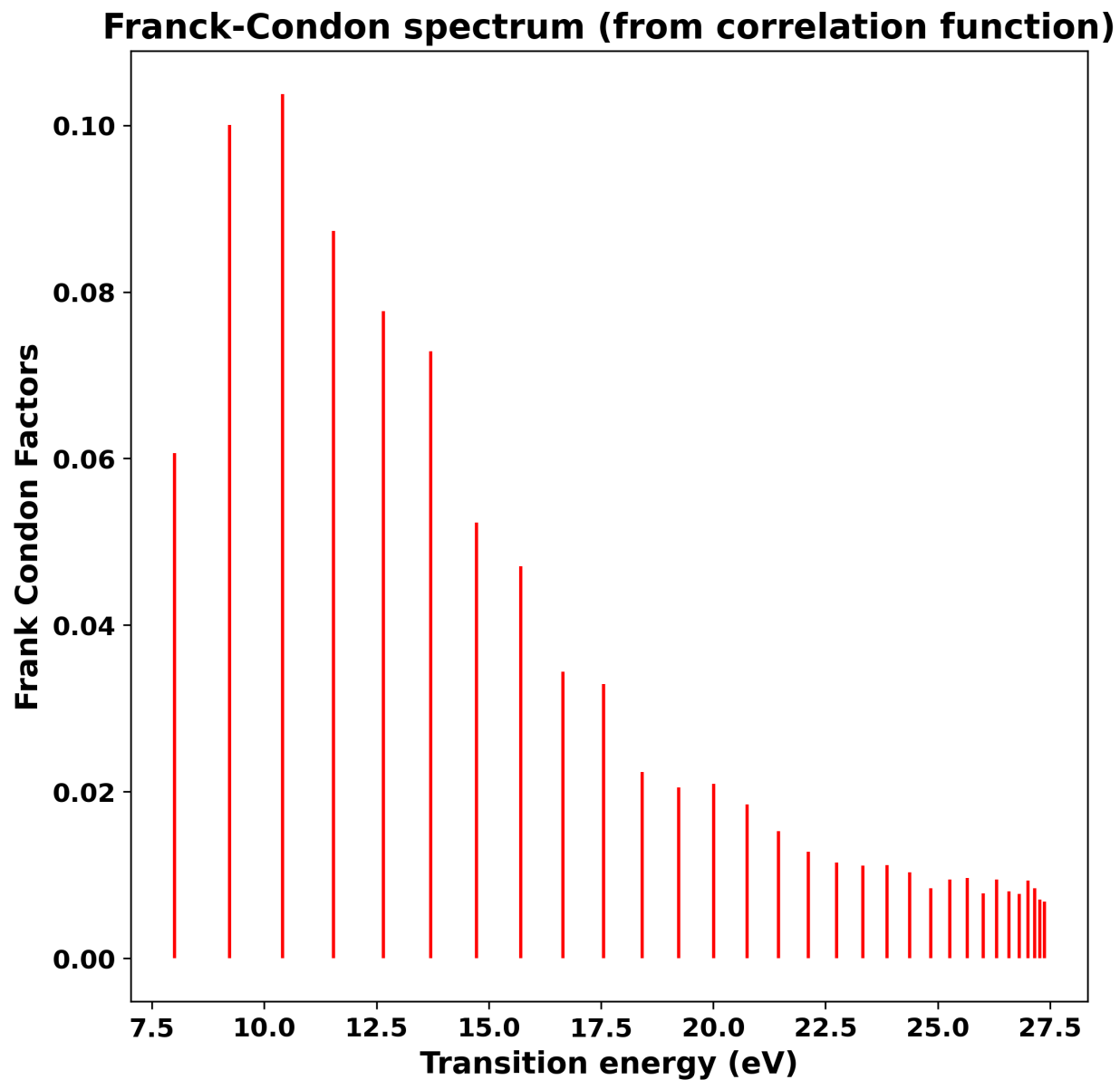

Figure 6: Frank Condon Factors recovered from FT of the Correlation Function

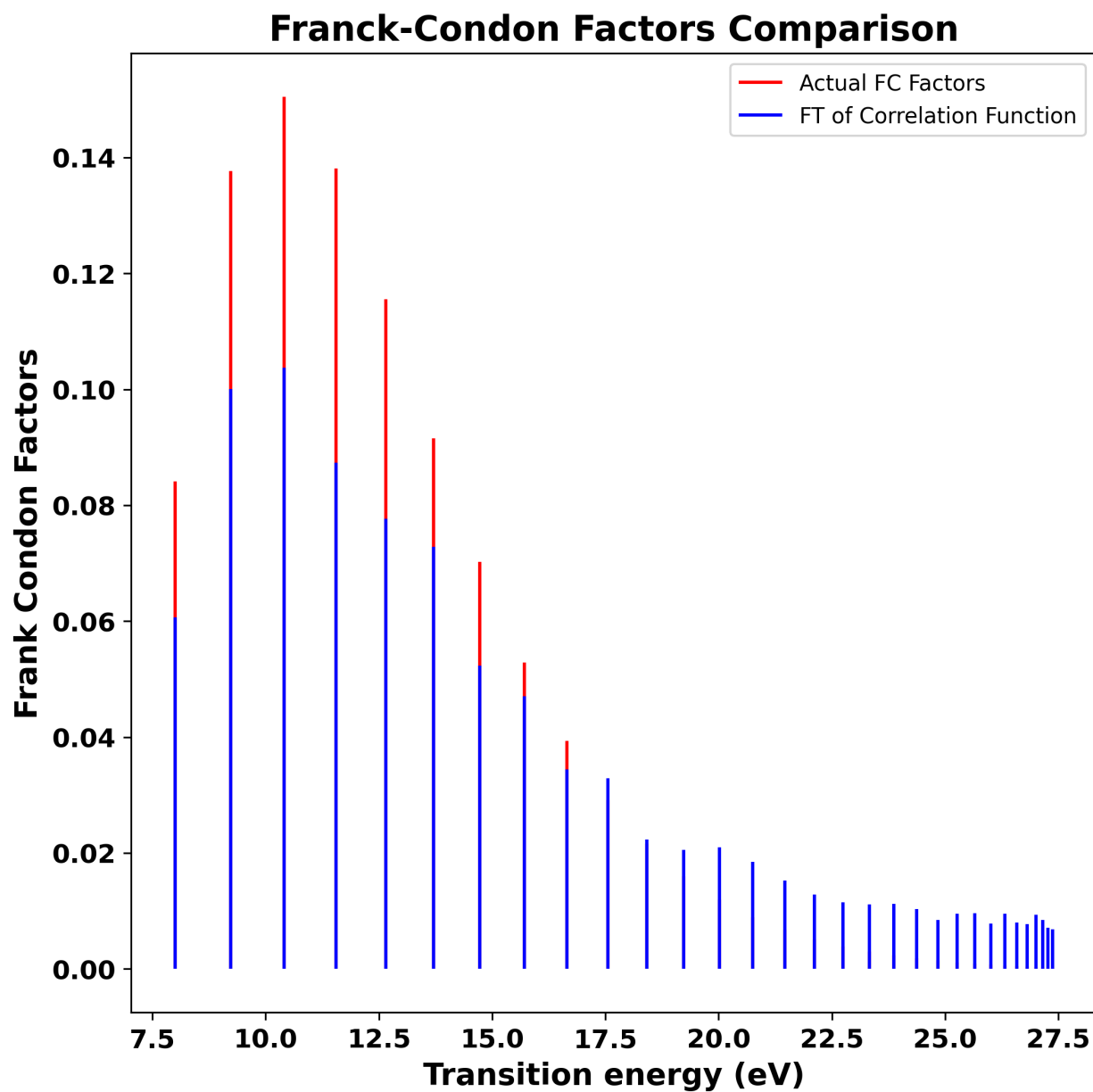Comparing fourier transformed vs exact:

Figure 7: Comparison with Exact

13 Finite-Difference Time propagation

The time evolution of the wavefunction was simulated by using the finite difference method to solve the time dependent schrodingers equation:
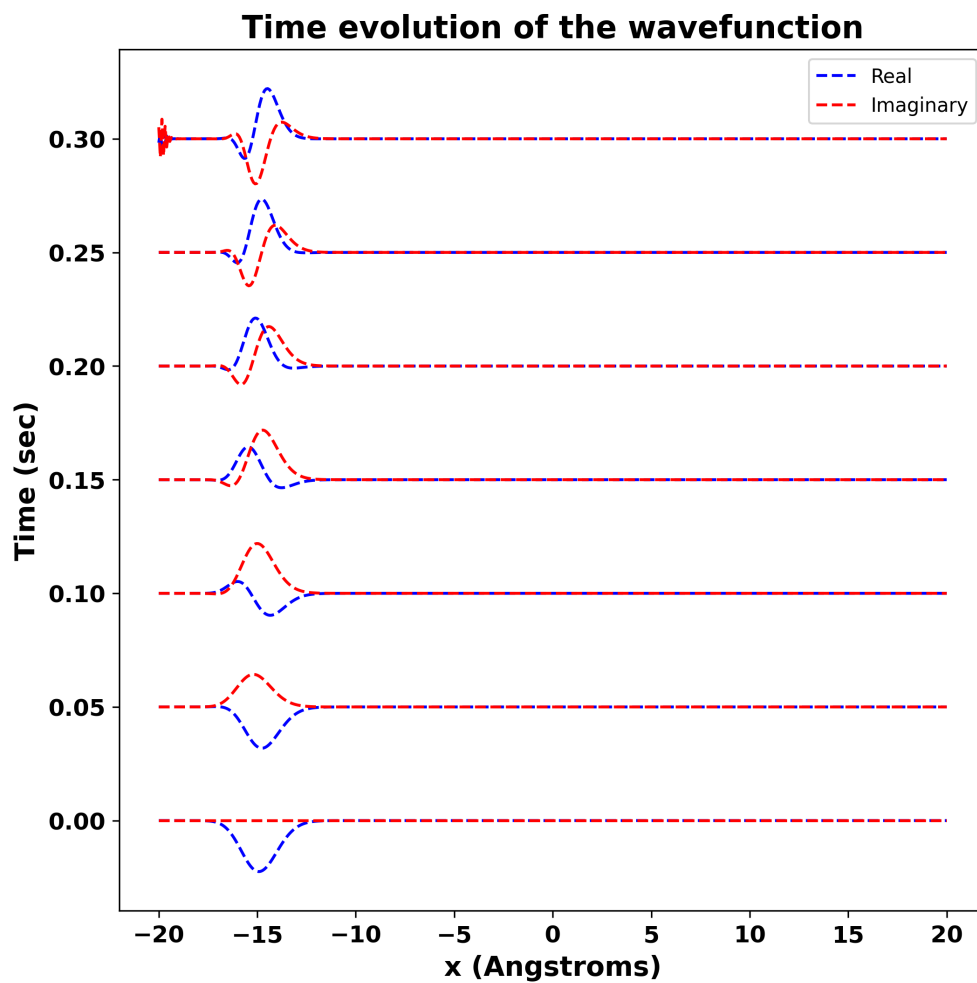

Figure 8: Time evolution of wavepacket using Finite Difference Method

14 Finite Difference Correlation Function

The correlation function was calculated again and it is clear that the correlation drops very quickly due to the accumulation of numerical errors.

If we use this correlation function and Fourier Transform it, we recover the frank condon factors but they follow the original shape very roughly:
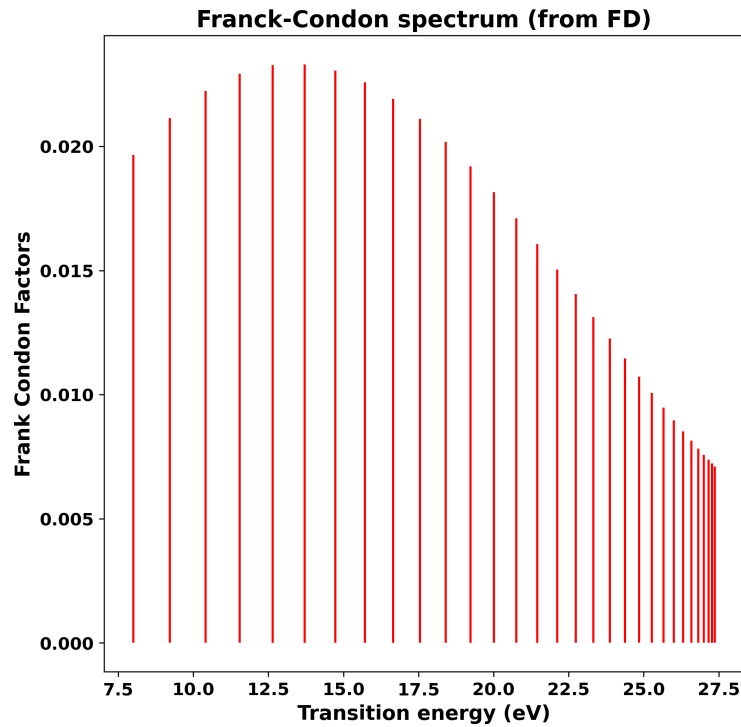

Figure 9: Frank Condon Factors recovered from Finite Difference Correlation function

References

[1] S. F. Matthew Ziering, 13.7: The Franck-Condon Principle — chem.libretexts.org, `https://chem.libretexts.org/Courses/Pacific_Union_College/Quantum_Chemistry/13%3A_Molecular_Spectroscopy/13.07%3A_The_Franck-Condon_Principle`, [Accessed 31-03-2025].