Work Summary of Excited States and Nonadiabatic Dynamics CyberTraining Workshop 2021

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Abstract

I enrolled in the Cybertraining workshop with two goals, one more pedagogical and other more focused on my dissertation research. I intended to: (1) gain exposure/experience with several electronic structure/molecular dynamics packages outside my technical field of quantum dynamics and (2) to write a code to leverage Libra's gaussian wavepacket module to obtain numerical calculations of coherence dynamics to compare with a theory developed in my current graduate research. Because the latter has more concrete results, I focus on that.

1 Summary

a. One contribution I made was to add a Morse potential

$$V_j(q) = D_j^e \left(e^{-2a_j(q-Q_j^e)} - 2e^{-a_j(q-Q_j^e)} + E_j + D_e^j \right)$$

module in Libra's `model` library (where D_j^e, Q_j^e, a_j, and E_j are the dissociation energy, equilibrium position, curvature constant, and energy datum for state j respectively). A relatively simple alteration of Akimov's `Holstein model 2` for coupled harmonic oscillators (changing the input, function, and derivatives) allowed me to make a model for coupled Morse oscillators. Morse potentials are fairly exact representations of the interatomic potential in chemical bonds and therefore are quite relevant to vibronic spectroscopy.

b. I modified Akimov's tutorial script on wavepackets to perform simulations of a two-level vibronic system for the new Morse potential wherein I varied the dissociation energy of the excited state. In each simulation I obtained a time-series of the populations of the two levels and the coherence between them with the original goal of computing absorption spectra to compare with my research. Unfortunately, I was not able to get the Fourier transforms required for the spectrum calculation to work due to what I believe to be a numerical or aliasing issue of the signal.

c. In place of the spectra, I decide to focus on analyzing the effect of anharmonicity introduced through the Morse potential. I did this by harmonically approximating the Morse potential

$$\begin{aligned} V_j(q) &\approx \sum_{n=0}^{2} \frac{1}{n!} \frac{d^n}{dq} V_j(q) \Big|_{Q_j^e} (q - Q_j^e)^n = V_j(Q_j^e) + V_j'(Q_j^e)(q - Q_j^e) + \frac{1}{2} V_j''(Q_j^e)(q - Q_j^e) \\ &\approx a_j^2 D_j^e \left(q - Q_j^e \right)^2 + E_j \end{aligned}$$

and by comparison with a harmonic potential of the form

$$U_j(q) = \frac{1}{2} m \Omega_j^2 (q - Q_j^e)^2 + E_j$$

we have the condition relating the two,

$$\frac{1}{2} m \Omega_j^2 = a_j^2 D_j^e$$

Then running identical simulations using of the potential derived of the form above and examining the time series (aka correlation functions) for the populations and coherences. The results are illustrated below in Figures 1-3.

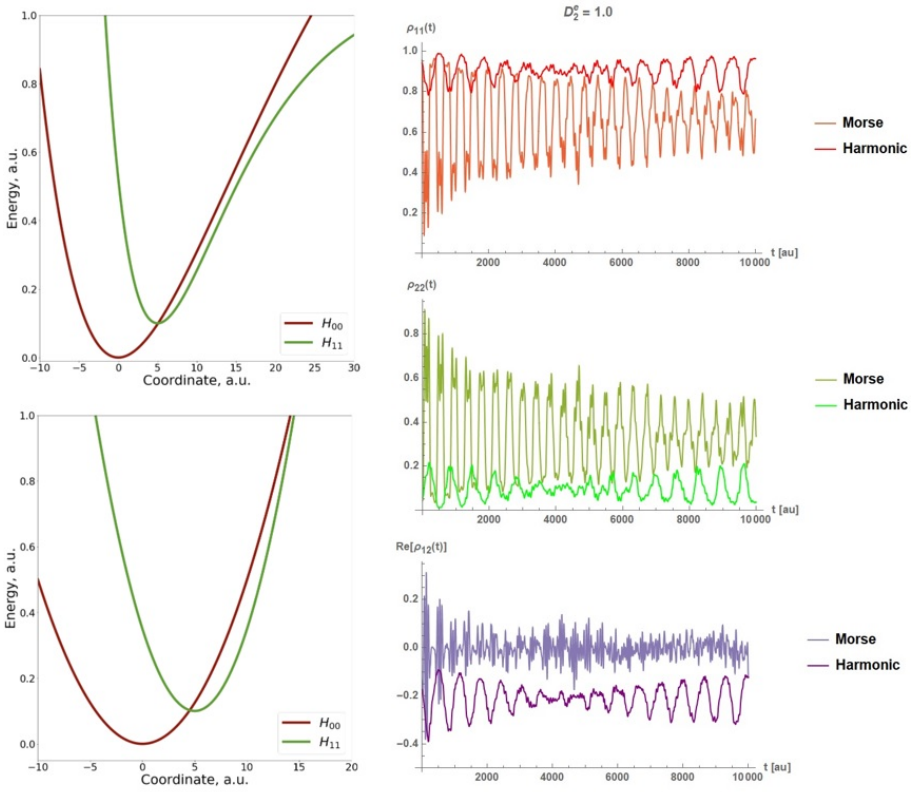

Figure 1: Simulation for $D_2^e = \frac{m\omega_2^2}{2a_2^2} = 1.0$

2 Future Work

I intend to resolve the numerical issues encounters in my Fourier transforms so that I can obtain exact spectra to compare with analogous phase space wavepacket calculations derived in my dissertation research. Martens and I have shown wavepacket Wigner functions can solve the phase space dynamics of two-level vibronic systems. Their method is exact harmonic potentials and accurate for slightly anharmonic systems (ex. Morse potentials). This method provides a quantum phase space description of coherence dynamics which has applications to correcting spectroscopic calculations and trajectory based rate theories such as surface hopping. Once numerical agreement is obtained with Libra for anharmonic spectra, the method can be integrated into packages with surface hopping methods (`Libra`, `NEX-MD`, `NewtonX`).

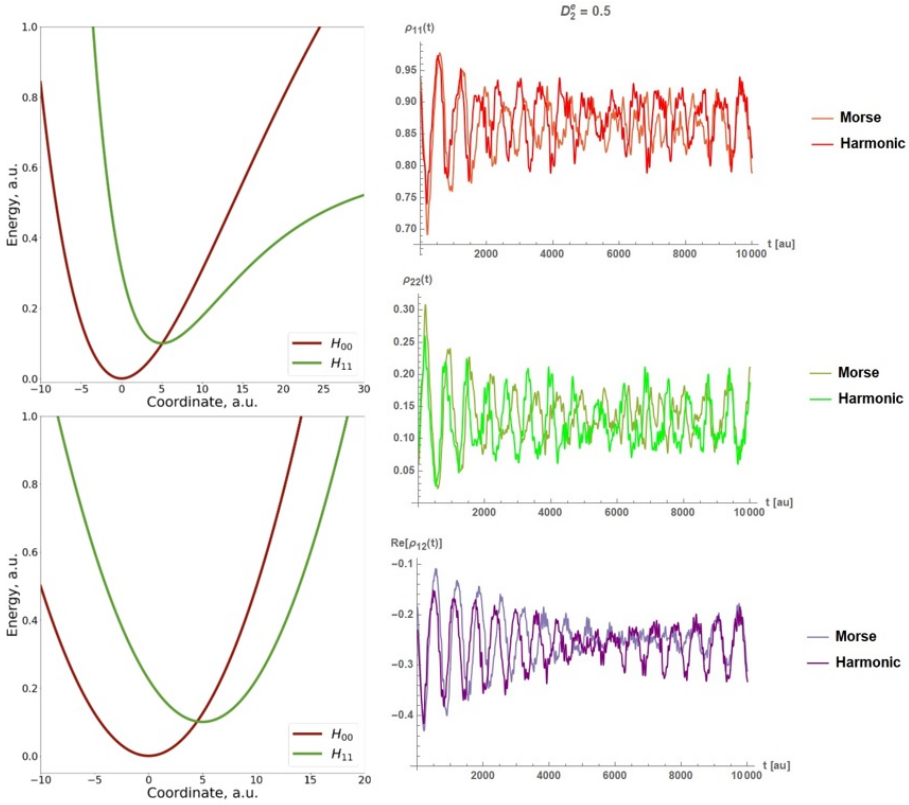

Figure 2: Simulation for $D_2^e = \frac{m\omega_2^2}{2a_2^2} = 0.5$

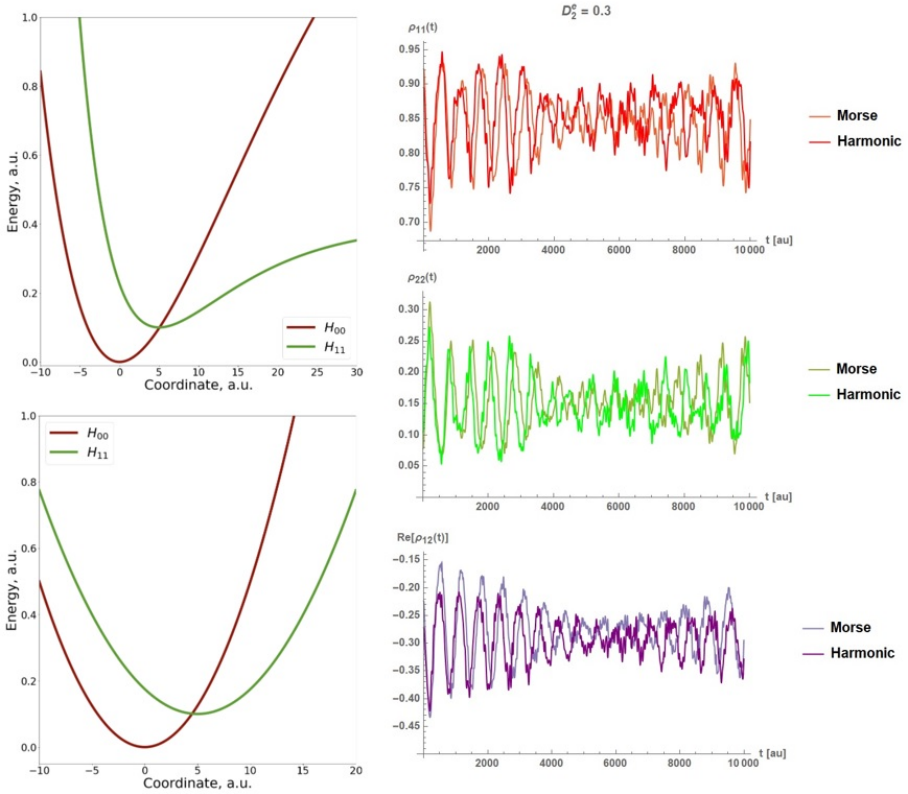

Figure 3: Simulation for $D_2^e = \frac{m\omega_2^2}{2a_2^2} = 0.3$