

**First-principles calculation of phonon-induced electron-hole
relaxation dynamics for finite systems within linear response
theory: Manual and Example**

Jonathan Trinastic - jptrinastic@gmail.com

*Department of Physics and Quantum Theory Project,
University of Florida, Gainesville, Florida, 32611, USA*

(Dated: June 21, 2016)

CONTENTS

I. Overview	3
II. Theory	3
A. Reduced density matrix and Redfield equations	3
B. Nonadiabatic system-reservoir coupling	4
C. Electronic nonadiabatic coupling within LR-TDDFT	5
D. Franck-Condon-weighted density of states	7
E. Phonon-induced relaxation dynamics	7
F. Further References	8
III. Example Calculation: Porphyrin	8
A. Electronic excitations with linear response theory	9
B. Electronic nonadiabatic coupling	12
1. Ab initio molecular dynamics	12
2. DFT and LR-TDDFT calculations	17
3. Kohn-Sham orbital overlap calculations	18
4. LR-TDDFT electronic coupling	20
C. Franck-Condon-weighted density of states	23
1. Phonons	24
2. Excited state geometry relaxation	25
3. Huang-Rhys factors	26
4. Franck-Condon-weighted density of states	29
D. Phonon-induced relaxation dynamics	31
References	34

I. OVERVIEW

This manual reviews the theory and computational methods to calculate phonon-induced relaxation dynamics of electron-hole pairs in finite systems within linear response theory. The method employs linear-response, time-dependent density functional theory (LR-TDDFT) to calculate excited states and the reduced density matrix formalism (RDM) to investigate the nonequilibrium relaxation dynamics of an initially excited electron-hole pair. Systems with hundreds of atoms can be explored using the steps described below.

Required software includes a C++ compiler, Fortran compiler, Matlab, Gaussian09, and VASP (optional for use in generating molecular dynamics trajectories). Input for the latter two DFT programs is only described briefly, and details about their use can be found at their respective websites.

The manual is organized as follows. Section II provides a brief introduction into the underlying theory, which is described in more detail in several references included in Section II F. Section III then provides a step-by-step example of how to use the code, applying the method to study phonon-induced relaxation of an excitation in the Soret state of the porphyrin molecule, which has been previously studied experimentally.

II. THEORY

A detailed overview of the theory and computational steps can be found in published work¹. Only primary equations and descriptions of major variables will be described here - please see references given for more details.

A. Reduced density matrix and Redfield equations

Within the RDM formalism,² dynamics of a system of interest are determined due to its interaction with a reservoir that contains many more degrees of freedom and cannot be described in detail. If a density matrix is constructed of the combined system and reservoir, then the reduced density matrix ($\sigma_{\alpha\beta}$) can be made by taking the trace of the density matrix with respect to the reservoir coordinates. The reduced density matrix then only depends on the system degrees of freedom. For the model described within, electronic ground and

excited states described by LR-TDDFT are the collective system interacting with a phonon reservoir that causes downward energy relaxation from an initial excited state.

If we construct the RDM with the electronic eigenstates of the system, then the Redfield equations describe both population transfer (diagonal elements) and coherence dephasing (offdiagonal) between eigenstates α and β :

1) Population relaxation:

$$\frac{d\sigma_{\alpha\alpha}^I(t)}{dt} = - \sum_{\mu} R_{\alpha\alpha,\mu\mu} \sigma_{\mu\mu}^I(t) \quad (1)$$

$$R_{\alpha\alpha,\mu\mu} = \delta_{\alpha\mu} \sum_{\kappa} k_{\alpha\kappa} - k_{\mu\alpha} \quad (2)$$

2) Coherence dephasing:

$$\frac{d\sigma_{\alpha\beta}^I(t)}{dt} = -R_{\alpha\beta,\alpha\beta} \sigma_{\alpha\beta}^I(t) \quad (3)$$

$$R_{\alpha\beta,\alpha\beta} = \sum_{\mu} \frac{1}{2} (k_{\alpha\mu} + k_{\beta\mu}) + \gamma_0, \quad (4)$$

Here, $R_{\alpha\beta,\mu\nu}$ is the Redfield relaxation tensor, $k_{\alpha\beta}$ is the relaxation rate due to the system-reservoir interaction, and γ_0 is a dephasing constant determined from experiment or other computational methods. Thus, determining energy relaxation rates of excited states requires the calculation of $k_{\alpha\beta}$, which has been shown to be:^{2,3}

$$k_{\alpha\beta} = \frac{2\pi}{\hbar} \left\langle \sum_j |\langle \phi_i \Psi_{\alpha} | V | \phi_j \Psi_{\beta} \rangle|^2 \delta(\hbar\omega_{\alpha\beta} - \hbar\omega_{ij}) \right\rangle, \quad (5)$$

where V is the system-reservoir interaction to be defined below, Ψ_{α} is an electronic excited or ground state, ϕ_i is a nuclear state, $\omega_{\alpha\beta}$ and ω_{ij} are electronic transition energies and phonon energies, respectively, and $\langle \dots \rangle = \sum_i f_i = e^{-\beta E_i} / (\sum_i e^{-\beta E_i})$, the thermal average over initial conditions. The sum over final reservoir states preserves conservation of energy. The principle of detailed balance ensures proper behavior as time goes to infinity and provides the following relationship between forward and backward transition rates $k_{\alpha\beta} = e^{\hbar\omega_{\alpha\beta}/k_B T} k_{\beta\alpha}$.

B. Nonadiabatic system-reservoir coupling

To model electron-phonon interactions, we follow previous literature that treats the nuclear kinetic energy operator as a perturbation to the adiabatically determined electronic

excited states: $\langle \phi_i \Psi_\alpha | V | \phi_j \Psi_\beta \rangle = V_{\alpha\beta,ij} = \langle \phi_i \Psi_\alpha | \sum_k -\frac{\hbar^2}{2M_k} \nabla_k^2 | \phi_j \Psi_\beta \rangle$, where M_k is the nuclear mass and k runs over the K nuclear degrees of freedom, $|\phi_i\rangle = |\phi_i^1\rangle |\phi_i^2\rangle \dots |\phi_i^K\rangle$.² If we only include terms to first order in the nuclear gradient operator, previous work has shown that the system-reservoir coupling can be rewritten to good approximation as⁴

$$V_{\alpha\beta,ij} \approx \sum_k -\frac{i\hbar}{M_k} \langle \Psi_\alpha | \nabla_k | \Psi_\beta \rangle \langle \hat{p} \rangle \prod_k \langle \phi_i^k | \phi_j^k \rangle, \quad (6)$$

where $\langle \hat{p} \rangle$ is the expectation value of the momentum operator and obeys classical equations of motion according to Ehrenfest's theorem. If we plug this expression for $V_{\alpha\beta}$ into Equation 5, then we express the relaxation rates as

$$k_{\alpha\beta} = \frac{2\pi}{\hbar} \langle |V_{\alpha\beta}|^2 \rangle F(\omega_{\alpha\beta}), \quad (7)$$

where $V_{\alpha\beta} = \sum_k -\frac{i\hbar}{M_k} \langle \Psi_\alpha | \nabla_k | \Psi_\beta \rangle \langle \hat{p} \rangle$ is the nonadiabatic electronic coupling and $F(\omega_{\alpha\beta}) = \sum_{i,j} f_i \prod_k |\langle \phi_i^k | \phi_j^k \rangle|^2 \delta(\hbar\omega_{\alpha\beta} - \hbar\omega_{ij})$ is the Franck-Condon-weighted density of states (FC-DOS). $V_{\alpha\beta}$ describes the coupling of states α and β due to atomic motion and $F(\omega_{\alpha\beta})$ describes the density of phonon states available to couple to the transition.

Equation 7 is the primary equation we will refer to during the example description in Section III. The calculation requires three major quantities: 1) the ground and excited electronic states used to construct the reduced density matrix, which we calculate within LR-TDDFT; 2) the nonadiabatic electronic coupling ($V_{\alpha\beta}$), which we calculate using *ab initio* molecular dynamics; and 3) the Franck-Condon-weighted density of states, which we calculate within the harmonic approximation using the minimum-energy configuration of each excited state and the ground state normal modes.

C. Electronic nonadiabatic coupling within LR-TDDFT

We follow theory developed by Tavernelli et al.^{5,6} to calculate $V_{\alpha\beta}$ within LR-TDDFT. The theory is exact for first-order nonadiabatic coupling between ground and excited states and is a good approximation for coupling between excited states (exact within the Tamm-Dancoff approximation). Tavernelli showed that the nonadiabatic electronic coupling can be expressed as follows, replacing the nuclear gradient operator with a time derivative and using finite differences in the last expression:

$$V_{\alpha\beta} = -i\hbar \langle \Psi_\alpha | \frac{\partial}{\partial t} | \Psi_\beta \rangle \approx -\frac{i\hbar}{2\Delta t} [\langle \Psi_\alpha(t) | \Psi_\beta(t + \Delta t) \rangle - \langle \Psi_\alpha(t + \Delta t) | \Psi_\beta(t) \rangle], \quad (8)$$

where Δt is the time step. The next step is to define the wave function used to solve Equation 8. Within the Casida ansatz,⁷ an excited state within LR-TDDFT can be written as

$$|\Psi_\alpha\rangle = \sum_{ma} (X_\alpha^{ma} + Y_\alpha^{ma}) \hat{a}_a^\dagger \hat{a}_m |\Psi_0\rangle = \sum_{ma} (X_\alpha^{ma} + Y_\alpha^{ma}) |\Psi_{m \rightarrow a}\rangle, \quad (9)$$

where m and a index occupied and unoccupied Kohn-Sham orbitals, respectively, \hat{a}_a^\dagger and \hat{a}_m are creation and annihilation operators, X_α^{ma} and Y_α^{ma} are the normalized coefficients corresponding to an excitation from the m th to a th orbital and de-excitation from the a th to m th orbital, respectively, $|\Psi_0\rangle$ is the ground state Slater determinant, and $|\Psi_{m \rightarrow a}\rangle$ is a singly excited Slater determinant. Plugging this wave function definition into Equation 8, the wave function overlaps can be expressed by singly excited Slater determinant overlaps: $\langle \Psi_\alpha(t) | \Psi_\beta(t + \Delta t) \rangle = \sum_{ma} \sum_{nb} (X_\alpha^{ma}(t) + Y_\alpha^{ma}(t)) (X_\beta^{nb}(t + \Delta t) + Y_\beta^{nb}(t + \Delta t)) \langle \Psi_{m \rightarrow a}(t) | \Psi_{n \rightarrow b}(t + \Delta t) \rangle$. These Slater determinant overlaps can be further decomposed into single-particle Kohn-Sham orbital overlaps using Slater-Condon rules:

$$\begin{aligned} \langle \Psi_\alpha(t) | \Psi_\beta(t + \Delta t) \rangle = & \sum_{mab} (X_\alpha^{ma}(t) + Y_\alpha^{ma}(t))^\dagger (X_\beta^{mb}(t + \Delta t) + Y_\beta^{mb}(t + \Delta t)) v_{ab} \\ & - \sum_{amn} (X_\alpha^{ma}(t) + Y_\alpha^{ma}(t))^\dagger (X_\beta^{na}(t + \Delta t) + Y_\beta^{na}(t + \Delta t)) v_{mn}, \end{aligned} \quad (10)$$

where $v_{ab} = \langle \psi_a | \psi_b \rangle$, and a, b are unoccupied and m, n are occupied Kohn-Sham orbitals, respectively.

Thus, Equation 10 lays out all the required variables to calculate $V_{\alpha\beta}$. To do so, we perform an *ab initio* molecular dynamics simulation at 300K (or any relevant temperature) to generate a set of configurations - the time step of the simulation is Δt . Changes in the LR-TDDFT wave functions between time steps represent coupling of the electronic structure to phonon modes in the system. Thus, calculating $V_{\alpha\beta}$ at adjacent time steps and averaging across them will provide the thermally averaged, nonadiabatic electronic coupling we require. This requires knowledge of the LR-TDDFT coefficients and Kohn-Sham orbital wave functions at each step, which come from a self-consistent calculation for each configuration at each of the two time steps, and are entered into Equation 10. Results from this equation enter into Equation 8 to find $V_{\alpha\beta}$ for a given pair of adjacent time steps. The thermally averaged electronic nonadiabatic coupling that enters into Equation (7) is then calculated by averaging the value of $V_{\alpha\beta}$ across all time steps of the AIMD trajectory consisting of N time steps: $\langle |V_{\alpha\beta}|^2 \rangle = \frac{1}{N} \sum_{i=1}^N |V_{\alpha\beta}|^2$.

D. Franck-Condon-weighted density of states

The final term required to calculate relaxation rates is $F(\omega_{\alpha\beta})$, describing the density of phonon states that couple to a given $\alpha - \beta$ transition. Assuming a quantum harmonic oscillator phonon bath and that the ground state normal modes are an accurate approximation for all excited state modes, $F(\omega_{\alpha\beta})$ describes the density of phonon states coupled to a given nonadiabatic transition:²

$$F(\omega_{\alpha\beta}) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{i\omega_{\alpha\beta}t} e^{G(t)}, \quad (11)$$

where $G(t) = \sum_k S_{\alpha\beta}^k [(e^{-i\omega_k t} - 1)(n(\omega_k) + 1) + (e^{i\omega_k t} - 1)n(\omega_k)]$. $S_{\alpha\beta}^k$ is the Huang-Rhys factor, a dimensionless quantity representing the coupling strength of the k th normal mode to the transition, and $n(\omega_k)$ is the Bose-Einstein distribution for a phonon with energy $\hbar\omega_k$ at a given temperature. The function $F(\omega)$ peaks at energies corresponding to modes with nonzero $S_{\alpha\beta}$.

To calculate $S_{\alpha\beta}^k$, we relax the atomic positions for all excited states and project the change in atomic configuration between two states α and β onto the normal modes of the system. The Huang-Rhys factor is then calculated as

$$S_{\alpha\beta}^k = (\mu_k \omega_k d_{k\alpha\beta}^2) / \hbar, \quad (12)$$

where μ_k is the modal reduced mass and $d_{k\alpha\beta}$ is the configurational difference between excitations α and β projected onto the k th mode eigenvector. These values of $S_{\alpha\beta}^k$ enter Equation 11 along with phonon modes (ω_k) calculated within the harmonic approximation.

E. Phonon-induced relaxation dynamics

Once we have determined the LR-TDDFT excited states, $V_{\alpha\beta}$, and $F(\omega_{\alpha\beta})$, we can examine phonon-induced relaxation dynamics. We consider a system bathed in light with frequency ω at $t < 0$. After the light is switched off at $t = 0$, a nonequilibrium carrier distribution will relax due to interactions with phonons as described by Equations (1) and (7). The population change in $\sigma_{\alpha\beta}$ is then defined as $\Delta\eta(E, t) = \sum_{\alpha} \sigma_{\alpha\alpha}(t) \delta(E_{\alpha} - E) - \eta_{eq}$, where E_{α} is the energy of the α th excitation and η_{eq} is the equilibrium population.

F. Further References

Reduced density matrix and Redfield equations:

May, V and Kuhn, O. *Charge and energy transfer dynamics in molecular systems*. John Wiley and Sons, 2008.

Nonadiabatic system-reservoir coupling:

Prezhdo, O and Rossky, P. Evaluation of quantum transition rates from quantum-classical molecular dynamics simulations. *J. Chem. Phys.*, 107(15), 5863-5878, 1997.

Electronic nonadiabatic coupling within LR-TDDFT:

Tavernelli, I et al. Nonadiabatic coupling vectors for excited states within time-dependent density functional theory in the Tamm-Dancoff approximation and beyond. *J. Chem. Phys.*, 133(19), 194104, 2010.

Franck-Condon-weighted density of states:

May, V and Kuhn, O. *Charge and energy transfer dynamics in molecular systems*. John Wiley and Sons, 2008.

III. EXAMPLE CALCULATION: PORPHYRIN

Phonon-induced relaxation has been well studied in the porphyrin molecule, which demonstrates a strong absorption peak known as the Soret band between 350-400 nm depending the solvent (see Figure 1).⁸ Several experimental studies⁸⁻¹⁰ have measured relaxation times from the Soret band to lower states ranging from 50-200 fs. The availability of experimental data combined with the small size of the molecule makes this a nice system to demonstrate the steps for the present method with minimal computational resources.

All calculations and post-processing codes are developed to work with Gaussian09, version D.01, except for the *ab initio* molecular dynamics simulations, which can be done using either Gaussian09 or VASP. This manual will focus on describing the codes specific to calculating relaxation rates; see the Gaussian09 and VASP websites for detailed information about input. All files for submitting jobs are tailored to NERSC's Edison system - changes will need to be made as appropriate for the particular high-performance computing server being used.

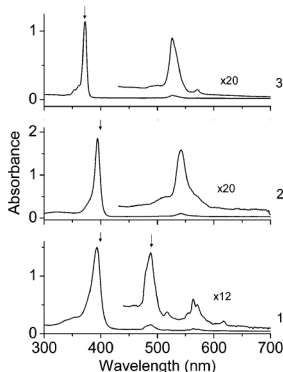


FIG. 1. Porphyrin absorption spectrum⁸ as a function of wavelength in the following solvents: 1) benzene/cyclohexane 1:10, 2) benzene/cyclohexane 1:10 added with CF_3COOH , and 3) concentrated HClO_4 . The Soret band is the large peak between 350-400 nm and the lowest excited state occurs between 500-600 nm.

A. Electronic excitations with linear response theory

The first step requires the calculation of excited states within LR-TDDFT and confirmation that the results generally match experimental absorption spectra. This is a crucial check because a general match with experimental data is a good indication that the excited state wave functions are well described with the basis set and functional being used. If this is not the case, then the electronic nonadiabatic couplings ($V_{\alpha\beta}$) may be inaccurate and subsequent relaxation rates will not be correct.

- After untarring `Phonon_Induced_Relaxation_LRTDDFT.tar` attached with this manual, move into `Porphyrin_Example/Electronic_Excitations`.
- Within this folder, `porphyrin.xyz` provides the atomic coordinates for porphyrin in XYZ format. Look at the molecule using any visualization software (e.g., VESTA) to understand its general structure as shown in Figure 2.
- Next, open `porph_lrtddft.com`, which is the input file for Gaussian09 that will calculate the first six excitations (TD command). It is assumed that the geometry has already been optimized to the minimum-energy configuration. Several lines are of particular importance:

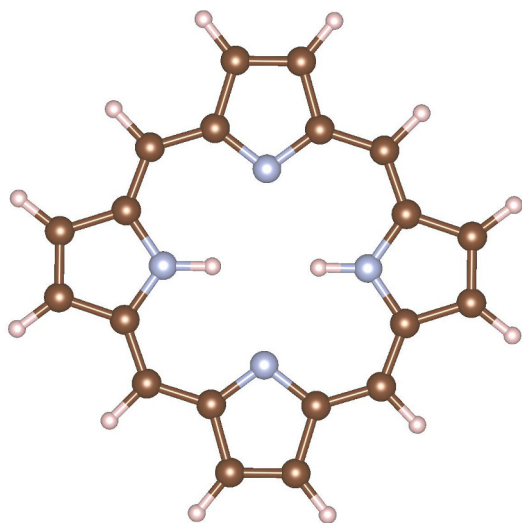


FIG. 2. Atomic structure of porphyrin. Brown spheres are carbon atoms, small pink spheres are hydrogen atoms, and gray spheres are nitrogen atoms.

- IOP(9/40=2) forces Gaussian to output the LR-TDDFT coefficients that are greater than 0.01 for each excitation, where IOP(9/40=X) corresponds to printing coefficients greater than 10^{-X} . This value should be at least 2 in order to accurately calculate $V_{\alpha\beta}$.
 - b3lyp/6-31g* denotes the functional and Gaussian basis set used in the calculation. Both the B3LYP functional and 6-31g* basis set reproduce excitations in porphyrin well, but **this should be tested for each new system**.
 - NOSYMMETRY prevents Gaussian from rotating the molecule during any calculation. **This command should be included in all calculations** as both $V_{\alpha\beta}$ and $F(\omega_{\alpha\beta})$ require comparisons between configurations with the same orientation.
 - SCRF initiates the Polarizable Continuum Model to represent the benzene solvent used in most experiments studying porphyrin, which is important to capture the correct excitation energies.
 - TD performs the LR-TDDFT calculation, where the included subcommands instruct the program to calculate 6 singlet states.
- After submitting and completing the calculation, `porph_lrtddft.out` will contain information about the excited state energies and LR-TDDFT coefficients. Within the

TABLE I. Excitation energies and oscillator strengths for first six excited states in porphyrin.

Excited State	Energy (eV)	Energy (nm)	Oscillator Strength (f)
1	2.28	544	0.0003
2	2.44	509	0.0000
3	3.22	385	0.8905
4	3.33	372	1.2500
5	3.42	362	0.0000
6	3.62	342	0.0000

file, look for the keyword **Excited State** to find energies listed for the first six states as listed in Table I. The Soret band corresponds to excited states 3 and 4, which show strong absorption between 350-400 nm as seen in experiment. This example will look at phonon-induced relaxation rates of an electron-hole pair initially excited to these states.

- Below each excited state, a list of Kohn-Sham electron-hole transitions are listed that make up each LR-TDDFT excitation along with their LR-TDDFT coefficient or weight. For example, under **Excited State 1**, '64 -> 83 -0.01058' indicates that the transition from the 64th to 83rd KS orbital has a coefficient of $-0.01058 \times \sqrt{2}$ (Gaussian normalizes the coefficients such that their sum of squares is 1 only if you multiply them by $\sqrt{2}$).

Having confirmed that the choice of functional and basis set provides an accurate description of excited states, the next step will be the calculation of the electronic nonadiabatic coupling ($V_{\alpha\beta}$) between these six states using AIMD and post-processing codes. The energies of the excitations will also be required as input for calculating $F(\omega_{\alpha\beta})$ in Section III C.

B. Electronic nonadiabatic coupling

1. Ab initio *molecular dynamics*

Calculating $V_{\alpha\beta}$ first requires an AIMD trajectory that provides the input configurations for subsequent LR-TDDFT and post-processing calculations. This can be done in two ways: 1) using Gaussian09 and the same functional used to calculate electronic structure or 2) using VASP and a more computationally efficient functional. The former is technically more accurate and consistent, however non-hybrid, GGA functionals often provide accurate structural information and describe phonon modes well. This makes them advantageous for calculating AIMD trajectories that can be computationally burdensome for large systems. Each option is outlined below:

GAUSSIAN AIMD

Performing molecular dynamics in Gaussian09 requires two sequential steps: 1) an initial density matrix propagation method (ADMP) in which the system is connected to a velocity-rescaling thermostat and nuclear velocities are obtained after reaching thermal equilibration, and 2) a second NVE run using Born-Oppenheimer dynamics (BOMD) with the ADMP velocities included as input. The configurations from the BOMD trajectory are then used to calculate $V_{\alpha\beta}$.

- Navigate to `Porphyrin_Example/Electronic_NAC/AIMD/Gaussian09`. In this folder, `porph_admp.com` contains all the input commands required to run the initial ADMP dynamics to obtain nuclear velocities:
 - The input configuration should be the optimized geometry of the system.
 - ADMP turns on the density matrix propagation method.
 - * `Maxpoints` is the maximum number of time steps in the simulation.
 - * `Stepsize` indicates the time step size N in units of $N * 0.0001$ femtoseconds (fs). Thus, 2500 is a 0.25 fs time step - a small enough time step must be used to find good temperature and energy behavior during the NVE run. Thus, the run will last $4000 * 0.25 = 1000$ fs - increase `Maxpoints` if the system requires longer time to reach equilibrium.

- * **NKE** indicates the initial nuclear kinetic energy in units of microHartree. The relevant formula is $NKE = (N_{atoms} - 1)(3/2)kT$, where N_{atoms} is the number of atoms, $k = 3.1668$ microHartree/K, and T is temperature in Kelvin. Thus, a 38-atom system (porphyrin) at 300K corresponds to $NKE = 52727$.
- The **I0ps** are described in the input file and provide controls over the velocity rescaling.
- Submit the job in this directory to perform the AIMD calculation, which will take at least several hours to complete.
- After the AIMD calculation complete, open the **porph_admp.out** file. This will contain information, such as energetics and nuclear velocities, about each time step of the trajectory (search for the **Summary information** keyword). Move to the last time step and copy the geometry and nuclear velocities into the input file for the BOMD NVE run (example found in the **BOMD** folder).
- In the **BOMD** folder, open **porph_bomd.com** to understand the input for the final NVE run:
 - BOMD initiates the BOMD NVE AIMD trajectory. Change **Maxpoints** to a smaller value, but large enough to have sufficient configurations to converge $V_{\alpha\beta}$ (at least 150 fs).
 - * **Readmvwel** tells the program to read in the nuclear velocities that will be included below.
 - * **Sample=Microcanonical** will perform the dynamics using the NVE ensemble.
 - * **Units=Bohr** tells the program to look for coordinates and nuclear velocities in units of bohr (make sure you do this!).
 - Below the 0 1, copy in the configuration from the last ADMP time step in units of bohr. Below the 0, copy in the nuclear velocities matrix from the ADMP output file. There are already numbers in these regions to show formatting, but these do not correspond to positions and velocities in equilibrium.

- Submit the job. Once finished, plot the temperature and energy as a function of time step to make sure the system was thermally equilibrated. If the energy is not roughly constant compared to the potential energy, or the temperature oscillations are too large, try running the ADMP calculation for a longer time to achieve equilibration, then rerun the BOMD calculation.
- After obtaining the BOMD trajectory, the last step is to extract each configuration from the `porph_bomd.out` output file into separate files that will be used as input for the next step. To do this, copy `porph_bomd.out` into the `Porphyrin_Example/Electronic_NAC/NAC` folder. In addition, from `Codes/Electronic_NAC/Config_Generator`, copy `Config_Generator_3Atoms_G09.f90` to the same folder.
- Rename the BOMD output file as `MD_G09` and look at the `input_cfg_gen` file to understand its contents (the code discusses its details). Compile and run this code with `MD_G09` and `input_cfg_gen` in the same directory, and a `posX` file should be created for each timestep of the trajectory. Each file should list atom labels and corresponding coordinates in the Gaussian09 input format (an example can be found in the `sample_output` folder). These files will be used as input for performing DFT and LR-TDDFT calculations at each step in the next section.

VASP AIMD

Generating the AIMD trajectory using VASP requires three steps: 1) optimizing the geometry in VASP using the new, more computationally efficient functional; 2) annealing the structure to room temperature and reaching equilibrium within the NVT ensemble; and 3) obtaining a final NVE trajectory that will be used as input for calculating $V_{\alpha\beta}$ in the next section. This manual assumes that the new geometry optimization has already been performed and begins with the annealing steps using the NVT ensemble. Note that this method uses velocity rescaling, but VASP also has a thermostat that may be more accurate and can be used in a similar manner.

- Move to `Porphyrin_Example/Electronic_NAC/AIMD/VASP`. Several files should be found that will be used to obtain the AIMD trajectory:
 - `POTCAR` contains the pseudopotential for each atom in the system. For this example, the PBE-GGA pseudopotential is used.

- `KPOINTS` only includes Gamma point since the porphyrin molecule is a finite system.
 - `POSCAR_initial` is the molecule in the minimum-energy configuration using the PBE functional. Make sure the system is optimized using the PBE functional - don't just use the same geometry from the Gaussian09 calculation!
 - `INCAR` files contain the necessary control inputs to tell VASP what type of molecular dynamics simulations to perform, using a 0.25 fs time step for 1200 time steps.
- Copy `POSCAR_initial` to `POSCAR`, which VASP looks for as the input configuration file, and copy `INCAR_0_300_NVT` to `INCAR`. This first simulation will anneal the structure from 0K to 300K using velocity rescaling. Submit the job.
 - Once the job has completed, check the `vasp.out` file to make sure the system has heated up to roughly 300K as expected. If so, then copy the `CONTCAR` file, which contains the coordinates and nuclear velocities from the end of the run, as the new `INCAR` file. Copy `INCAR_300_300_NVT` as `INCAR` - this run will now equilibrate the system at 300K for another 1200 time steps. Submit the job.
 - Once that job is done, again check the `vasp.out` file and confirm that the system is staying roughly around 300K - if not, run another simulation within the NVT ensemble until equilibrium is reached.
 - Finally, again copy `CONTCAR` to `POSCAR` file and copy `INCAR_NVE` as `INCAR`. Submit this job, which will run an NVE ensemble with initial coordinates and nuclear velocities supplied from the end of the NVT simulation.
 - Once this job is complete, plot the temperature stored in `vasp.out` as well as the total energy and potential energy as a function of time (see example in Figure 3). Make sure temperature is oscillating reasonably (about 15-20% above and below the average) and that the total energy is conserved relative to the potential energy. If any of these are not true, rerun the NVT ensemble for a longer period of time to get closer to equilibrium, and then rerun the NVE simulation. In the `sample_output` folder, example `OUTCAR` and `vasp.out` files can be found from the final NVE simulation. The

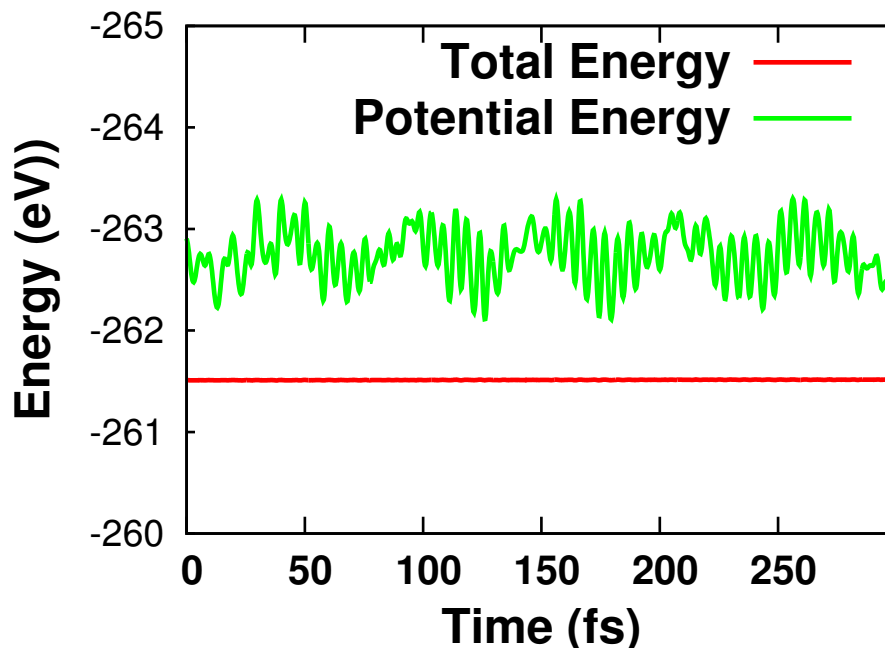


FIG. 3. Total energy and potential energy as a function of time over the course of AIMD trajectory using VASP.

temperature oscillates slightly more than desired, but the results work well enough for this manual.

- With the NVE trajectory in hand, copy the OUTCAR file to `Porphyrin_Example/Electronic_NAC/NAC`, where it will be used to generate the input configurations for the next section. Also, from `Codes/Electronic_NAC/Config_Generator`, copy `Config_Generator_3Atoms_VASP.f90` to the same folder.
- Look at the `input_cfg_gen` file to understand its contents (the code discusses more details). Compile and run the code with OUTCAR and `input_cfg_gen` in the same directory, and a `posX` file should be created for the X time steps of the trajectory. Each file should list atom labels and corresponding coordinates in the Gaussian09 input format (an example can be found in the `sample.output` folder). These files will be used as input for performing DFT and LR-TDDFT calculations at each step in the next section.

2. DFT and LR-TDDFT calculations

Using the `posX` files obtained in the previous section, DFT and LR-TDDFT calculations will be completed to obtain Kohn-Sham orbitals and LR-TDDFT coefficients at each time step. These orbitals and coefficients will be used as input into a post-processing code that calculates $V_{\alpha\beta}$ according to Equation 10.

- Copy the contents of `Codes/Electronic_NAC/DFT-TDDFT_Calc` to the NAC folder where the `posX` files were created. These files include several short bash scripts and header and footer files that will be used to create a folder and input files for each time step.
- Open `cycle_dft_script` to understand its contents. This will be the first script to run, as it will create a folder for each time step `X`, labeled `scfX`, in which the DFT and LR-TDDFT calculations are performed. Inside each folder, a Gaussian09 input file (`gauss_dft.com`) used to perform a standard DFT calculation will be created by combining the `head_dft`, `posX`, and `foot` files. The `foot` file lists the name of the `.wfx` file that will contain the orbital information for computing overlaps later in the section. Check the `head_dft` file to make sure all entries make sense - all commands should be identical to those used for the linear response calculation in Section III A, **except for two important changes**:
 - The TD command has been removed since only a ground state calculation is being performed.
 - `IOP(99/18=100)` has been added, which instructs Gaussian09 to calculate 100 empty orbitals. This number must be large enough to include all empty Kohn-Sham orbitals necessary to describe electron-hole transitions constituting each of the LR-TDDFT excited states as computed in Section III A. Look through all the excited states from the linear response calculation and make sure that enough empty orbitals are included, otherwise future steps will not work correctly. One hundred orbitals should be sufficient for porphyrin, but this must be tested on a case by case basis.
- Run the `cycle_dft_script` from the command line in the NAC folder, which will create 10 `scf` folders with a different configuration and Gaussian09 input file in each. It will also submit the job in each folder.

- While the DFT calculations are running, the next step will be to submit jobs to calculate the LR-TDDFT excitations for each time step. These calculations will provide the LR-TDDFT coefficients required to solve Equation 10.
- Open `cycle_lrtddft_script`. This bash script is very similar to `cycle_dft_script`, however now a `tddft` subfolder will be created and `head_lrtddft` will be combined with `posX` to create a Gaussian09 input file to calculate LR-TDDFT excitations for each configuration. Again, the `head_lrtddft` should contain identical commands as those used in the earlier linear response calculations. `POP=None` has been included to remove some orbital population analysis and save computational time.
- Submit `cycle_lrtddft_script` and 10 jobs should be submitted, one in each `scfX/tddft` folder.

It is important to note that more than 10 configurations will be necessary to converge $V_{\alpha\beta}$, however this small number will be enough to understand the basic steps. Convergence with respect to number of time steps must be checked rigorously for each system studied. Roughly 500-600 steps should be necessary in the porphyrin case.

3. Kohn-Sham orbital overlap calculations

Now that Kohn-Sham orbitals have been found for every time step, the overlaps (v_{ab}) can be calculated that appear in Equation 10.

- Copy the contents of `Codes/Electronic_NAC/KS_Orbital_Overlap` to the NAC folder where all the `scfX` folders have been created. These files consist of a parallelized or serialized version of the code to calculate Kohn-Sham overlaps between two wave functions (`ks_ovlap_gauss_mpi.cpp` and `ks_ovlap_serial.cpp`), the input file to run this code (`input_ovlap`), and a bash script to run this overlap code in each `scfX` folder (`cycle_ovlap`).
- This manual assumes the use of the parallelized code, but the same instructions follow for the serial version. Compile `ks_ovlap_gauss_mpi.cpp` using a C++ compiler and rename the executable `ovlap_code`. This code requires three inputs:

- `input_ovlap` should have two lines: the first line gives the minimum and maximum Kohn-Sham band index that will be included in the overlap matrix. So, `40 120` means that overlaps between Kohn-Sham orbitals indexed from 40 to 120 in the SCF calculations will be calculated. Again, make sure this encompasses all the electron-hole transitions making up each LR-TDDFT excitation of the system of interest. The second line is the time step from the molecular dynamics trajectory. This is included because the code calculates the single-particle coupling between Kohn-Sham states, even though the current method applies to LR-TDDFT state coupling.
 - The two wave functions used to calculate the overlap must be in the same folder and named `wfx1` and `wfx2`.
- Check that `input_ovlap` includes the correct quantities (it should for the porphyrin example - the 40-120 band range should be plenty). Next, open `cycle_ovlap` and understand its contents. Running this script from the command line will copy the compiled code and input file into each `scfX` folder, then copy the current time step's wave function file as `wfx1` and the adjacent time step's wave function file as `wfx2` into the same directory. For this reason, the bash script should only cycle up to $N - 1$ folders, where N is the total number of time steps, since the adjacent wave function file that is required will not exist for the final time step.
 - Make sure that the job file is suited for your server, and then run `cycle_ovlap` from the command line. Nine jobs should now be submitted, one for each of the first nine time steps, and each should only take a few minutes. The default number of processors to be used is four, but this can be changed.

The `ks_ovlap_gauss_mpi.cpp` file contains information about the different outputs (all written out with a `output` prefix), but the primary output required for the next step is `output_ovlap`. This file will contain the overlap matrix (v_{ab}) for the included bands as denoted in the `input_ovlap` file. Diagonal elements should be close to but less than one, as the nuclear motion creates nonzero offdiagonal overlaps. This file will be used as input for the next step that calculates $V_{\alpha\beta}$ between adjacent time steps.

4. LR-TDDFT electronic coupling

Now that Kohn-Sham orbital overlaps and LR-TDDFT excitation coefficients have been calculated for each time step, every quantity in Equation 10 is known and $V_{\alpha\beta}$ can be found. This step will use a post-processing code to calculate $V_{\alpha\beta}$ using the `output_ovlap` and `gauss_lrtdfft.out` files created in the previous sections.

- Copy the contents of `Codes/Electronic_NAC/LRTDDFT_Coupling` into the `NAC` folder, the directory that should contain all the `scf` folders. These files consist of a post-processing code (`lrtdfft_elec_coupling.cpp`) to calculate $V_{\alpha\beta}$ between adjacent time steps and the input file for the code to run properly (`input_nac`).
- First, open `lrtdfft_elec_coupling.cpp` and take time to understand the contents of the code. The code provides a description of each input and output. This code will take as input:
 - the `output_ovlap` file calculated in the previous section containing the v_{ab} matrix.
 - `input_nac`, which must list fifteen parameters for the code to run correctly:
 - * `dft_dir_name`: prefix of all folders containing DFT and overlap calculations from previous steps.
 - * `td_dir_name`: name of folder within `dft_dir_name` folders that contain Gaussian LR-TDDFT calculation.
 - * `overlap_file_name`: Name of output file within `dft_dir_name` folder for each time step containing the K-S overlap matrix.
 - * `tdfft_file_name`: name of output file in `td_dir_name` directory containing LR-TDDFT output information.
 - * `nsteps`: total number of MD time steps for which DFT, overlap, and LR-TDDFT calculations have been completed (number distinct `dft_dir_name` directories you have).
 - * `gaus_homo`: HOMO orbital index
 - * `gaus_emin`: lowest orbital index, must match lowest index in `output_ovlap` file.

- * **gaus_emax**: highest orbital index, must match highest index in **output_overlap** file.
 - * **num_exc**: number of LR-TDDFT excited states in **input_exc_gaussian** files. All files must have the same number of excitations and all must be included in coupling calculation.
 - * **time_step**: time step of MD trajectory in femtoseconds.
 - * **dft_ordering**: ('yes' or 'no') will enforce same ordering of K-S states across all time-steps by calculating K-S overlaps and switching the order of states in the overlap matrix to ensure the largest value is along the diagonal. This ensures that the same K-S states are being used to calculate the coupling even if their ordering changes throughout the MD trajectory.
 - * **td_ordering**: ('yes' or 'no') will enforce same ordering of LR-TDDFT states across all time-steps by calculating LR-TDDFT excitation overlaps and switching the order of states based on this overlap matrix such that the largest values are along the diagonal. This ensures that the same LR-TDDFT states are being used to calculate the coupling even if their ordering changes throughout the MD trajectory.
 - * **same_sign**: ('yes' or 'no') program will enforce the sign of all LR-TDDFT coefficients to not change between time steps. This is used in rare cases when all LR-TDDFT coefficients flip signs between adjacent time steps, which leads to unphysically large coupling values.
 - * **use_thresh**: ('yes' or 'no') program will output all LR-TDDFT excitation coefficients that change by more than the **thresh** value provided below. This can be helpful in determining whether nearly degenerate states are flipping positions between time steps, which leads to unphysically large coupling values.
 - * **thresh**: value of the threshold change in LR-TDDFT excitation coefficients between time steps above which it is reported in the **output_threshold** file.
- Compile **lrtdfft_elec_coupling.cpp** using a C++ compiler and run the code. In this case, we will only calculate the nonadiabatic coupling matrix using 10 time steps. More will be necessary in general to converge the matrix elements.

- As the code runs, it will calculate the thermally averaged, squared nonadiabatic coupling matrix by going into each `dft_dir_name` directory, using the DFT, LR-TDDFT, and overlap matrix information to calculate the coupling between adjacent time steps, and output information in a `coupling` folder created within `dft_dir_name`. It will do this for every `dft_dir_name`, and then calculate the thermally averaged nonadiabatic coupling matrix by averaging the square of each matrix output in each `coupling` folder.
- During the calculation, make sure that the correct number of `Excited_States` are printed to the screen for each step - in this case, six should be listed twice in a row, one for each time step. This indicates that the code has correctly read in all excitations to be included in the coupling matrix.
- Once the calculations have finished, the most important output will be `final_NAC_matrix_total`, which contains the squared, averaged nonadiabatic coupling matrix ($V_{\alpha\beta}$) to be used as input in the final step. There is also a `NAC_timeseries_total` file, which plots in rows the cumulative average of the nonadiabatic coupling value for each matrix element to check for convergence with respect to time steps.
- Next, move into a `coupling` folder to understand the various outputs specific to one time step:
 - `output_elec_details` and `output_hole_details`: For each excitation combination, these files list the electron and hole components (first and second terms in Equation10, respectively) contributing to $V_{\alpha\beta}$. These files are helpful to understand which Kohn-Sham orbitals are the dominant contributors to the coupling values.
 - `output_exc_gs_details`: provides the same information as the other `comp` files but applies to matrix elements between the ground and excited states.
 - `output_NAC_GS_X`: files contain the final $V_{\alpha\beta}$ matrix including the ground state for `X=total`, `X=elec`, and `X=hole`. By default in the cycling script, `output_nac_GS_total` is copied to the `lrtdfft_coupling` folder to be used to calculate the thermal average.

- `output_NAC_X`: include same matrix as `output_nac_GS_X` but does not include the ground state. Use this matrix if only concerned about excited state dynamics and not nonradiative recombination to ground state.
- `output_X_flip`: If `dft_ordering` or `td_ordering` are turned on, these output files will list which states have been flipped at this time step ($X = \text{KS or TD}$).
- `output_TD_overlap`: If `td_ordering` are turned on, will output the LR-TDDFT excitation overlap matrix before and after ordering of states.
- `output_coeff_exc1/2` and `output_coeff_de_exc_1/2` contain matrices of all LR-TDDFT excitation coefficients for the first (1) or second (2) time step.
- `output_threshold` lists each excitation combination that includes a change in LR-TDDFT excitation coefficients greater than the `thresh` value given as input.

As mentioned above, the squared thermal average of $V_{\alpha\beta}$ is in `output_NAC_matrix_total`, as this matrix has been calculated using both terms in Equation 10. `output_NAC_matrix_elec` or `output_NAC_matrix_hole` contain the coupling matrix calculated only using the electronic or hole component.

With only nine time steps included, $V_{\alpha\beta}$ in the primary output file will not be converged. After running the same steps above for 400 or more time steps, plot the row corresponding to the coupling between the 2nd and 3rd excited states from `final_NAC_matrix_total` to check convergence. Something similar to Figure 4 should be found, with $V_{32} \approx 35$ meV and convergence reached after about 100 fs, or 400 time steps.

Congratulations - the output matrix in `output_NAC_matrix_total` in this step will enter directly into the phonon-induced relaxation dynamics calculated in Section IIID! Now only the Franck-Condon-weighted density of states are required before we can determine relaxation rates!

C. Franck-Condon-weighted density of states

The second major component of the relaxation rates is $F(\omega_{\alpha\beta})$, the Franck-Condon-weighted density of states (FC-DOS, Section IID). To calculate this, three major steps are required: 1) phonon calculation within the harmonic approximation; 2) Huang-Rhys factors determined using the phonon modes and minimum-energy geometric configurations for each

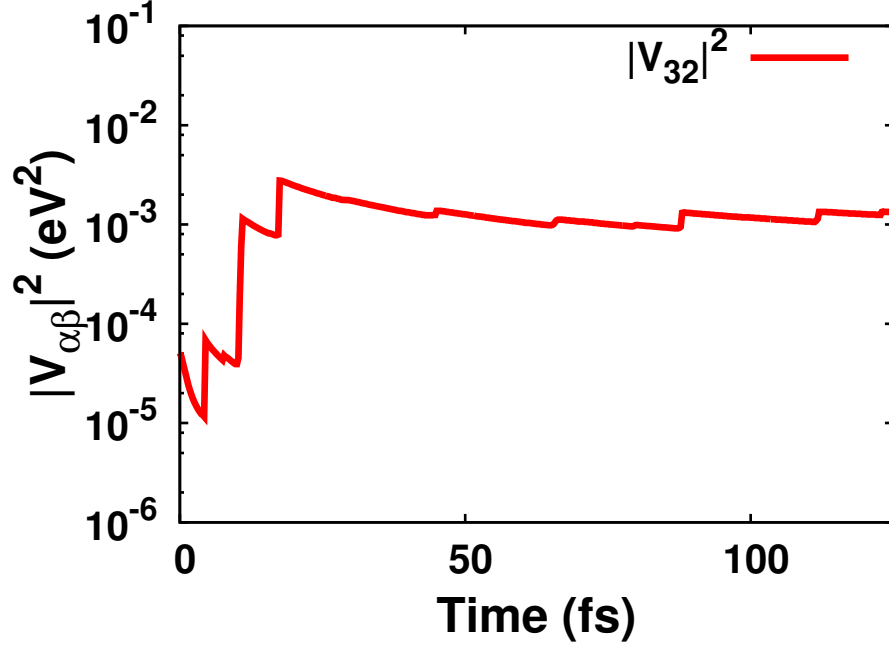


FIG. 4. Cumulative average of squared electronic nonadiabatic coupling between 2nd and 3rd excited state (V_{32}) in porphyrin as a function of time.

excited state; and 3) the calculation of $F(\omega_{\alpha\beta})$ using the Fourier transform as shown in Equation 11. Each step is outlined in detail below, again using porphyrin as an example.

1. Phonons

First, phonon modes will be calculated within the harmonic approximation using Gaussian09. This output, along with the excited state configurations, will be the input to calculate Huang-Rhys factors for each mode between each excitation.

- Move to `Porphyrin_Example/FC_DOS/Phonons`. The `porph_phonons.com` file acts as input for a Gaussian calculation that will calculate all harmonic modes of the system. Open the file to make sure all commands make sense - the addition of `FREQ` tells Gaussian to calculate phonon modes of the system. Note that the atomic positions have changed from the linear response calculations - this was just due to a symmetric rotation done during their initial optimization. As long as `NOSYMMETRY` is included in all calculations within this section, then this configuration is adequate.
- Submit the calculation using the job script, which should only take ten minutes or so

on two dozen or more processors. Once the job is finished, the `porph_phonons.out` file will include all frequencies of the system (search for the word **Frequencies** in the file).

- If any of the frequencies are negative (beyond a few tens of cm^{-1} , which could be within the margin of error for the calculation), then this indicates that the geometric configuration is not located at a stable minimum. Try nudging the atoms slightly along the directions of the negative mode and rerun an optimization to try to push the system to a stable ground state. Rerun the frequency calculation until all frequencies are positive.
- This output file will serve as one of the inputs to calculate Huang-Rhys factors. The second input will be the relaxed, excited state configurations.

2. *Excited state geometry relaxation*

In this step, six different calculations will be performed, a geometry relaxation for each of the six LR-TDDFT excitations included in this example calculation.

- Move to `Porphyrim_Example/FC_DOS/Excited_States`. In this folder, six folders labeled `s1` to `s6` exist. An optimization of the excited state configuration will be run in each folder. At the end, output of each final configuration will be concatenated together to serve as one input file for the Huang-Rhys factor calculations.
- Move into `s1`. Open the `porph_s1.com` input file to understand its contents. All input will be similar to the linear-response calculation except for two major differences:
 - `Root=1` has been included within the `TD` command - this tells Gaussian which excited state to use for geometry optimization (since each excitation will have a different charge density that will affect the nuclear configuration). This should be 1 for the first excited state, 2 for the second excited state, and so on.
 - `OPT` has been included in tandem with the `TD` command - this tells Gaussian to perform a geometry optimization using the excited state charge density determined from the LR-TDDFT calculation.

- Run this calculation to optimize the first excited state. These calculations can take several hours to complete, so while waiting for it to finish, copy the input file and job file into the other five folders, change the `Root=X` command to the relevant excited state, and run the optimization calculations for these as well.
- Note: Make sure `NOSYMMETRY` is included in all calculations! If not, the molecule could rotate during optimization, leading to unphysically large displacements in atoms and nonsensical Huang-Rhys factors!
- Once all jobs have finished, check each output file (`porph.sX.out`) to make sure the geometry has relaxed to a minimum-energy configuration meeting the force criteria set within Gaussian09. If any do not meet relaxation criteria, resubmit the job using the same `chk` file and included `GEOM=Check` as an input command. This will instruct Gaussian to read the last relaxed configuration from the `chk` file and continue optimization.

3. *Huang-Rhys factors*

With phonon modes and eigenvectors as well as all ground and excited state configurations, the next step will calculate the Huang-Rhys factors ($S_{\alpha\beta}^k$, Equation 12) between all combinations of ground and excited states.

- Copy the contents of `Codes/FC_DOS/Huang_Rhys_Factors` into `Porphyrin_Example/FC_DOS/Huang_Rhys_Factors`. These files include the code that calculates $S_{\alpha\beta}^k$ (`Huang_Rhys_Factors.cpp`), and two input files (`energy_pop` and `input_fcf`):
 - `energy_pop` lists the minimum and maximum indices of all states included (ground state starts as 1). The rest of the rows then include three columns: 1) state index; 2) state energy (in eV); and 3) occupancy (2 for occupied, 0 for unoccupied). Fill in this file using results from the linear response calculation.
 - `input_fcf` provides input to calculate $S_{\alpha\beta}^k$, mainly atom number and mass to calculate the reduced mass:
 - * `natoms` indicates the total number of atoms.
 - * `n_types` indicates the total number of atom types.

- * The first two lines must contain **natoms** and **n_types** (one on each line). There should then be a subsequent input line for each atom type. For each line, input the atomic symbol, atomic number, mass, and number of this atom type, in this order (see example input file for porphyrin example).
- In addition, three more input files must be created from the Gaussian calculations in the previous two steps:
 - First, copy the output file from the phonon calculation from **porph.phonons.out** to this directory and rename it **gauss.out_freq**.
 - Second, extract all phonon energies from the phonon output file and list them in a separate file called **modes_cm** in ascending order (the same order listed in the Gaussian output so they coincide with the correct eigenvectors). Use **grep** or **awk** to do this quickly.
 - Third, concatenate the final atomic configurations from each output file of the ground state calculation (taken from the phonon calculation) and each of the excited state geometry relaxation calculations. Do this by deleting all lines from each output file except for the final configuration, keeping the top four lines of the header that include the dashed lines and the text **Center Number, Atomic Number, Atomic Type, and Coordinates (Angstroms)**. See an example in the **sample_output** folder to better understand which part of the output to keep. Once each of these configurations have been concatenated, in order of ascending states, into one file, copy it to the **Huang_Rhys_Factors** folder and rename it **gauss.out_coord**.
- Compile and run the code with the above input files in the same directory. This will project atomic displacements between excited states onto mode eigenvectors and find reduced masses in order to calculate $S_{\alpha\beta}^k$ as in Equation 12. The following output files will be created:
 - **output_HRF_matrix** contains the $S_{\alpha\beta}^k$ matrix that will be used as input in the next section to calculate $F(\omega_{\alpha\beta})$.
 - **output_deltaR** provides the configurational difference between each ground and excited state configuration, both in sum and for each atom.

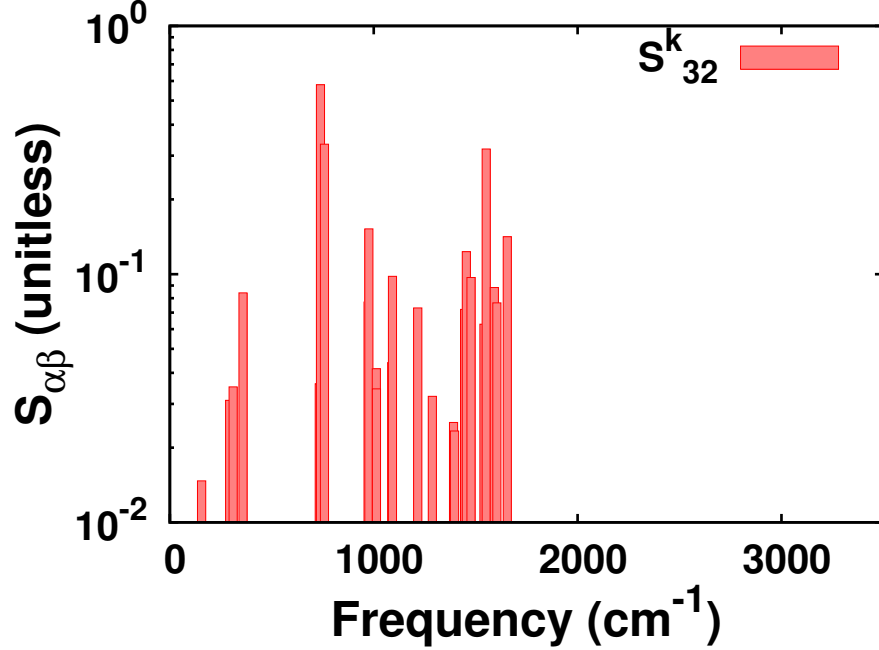


FIG. 5. Huang-Rhys factors ($S_{\alpha\beta}^k$) as a function of phonon mode energy coupling the 2nd and 3rd excited states in porphyrin.

- `output_HRF_info` contains a list of phonon mode index, energy, absolute displacement along this mode, $S_{\alpha\beta}^k$, and reorganization energy for each state combination. This can be helpful for plotting Huang-Rhys factors and finding dominant modes coupled to a given transition. For example, Figure 5 plots the Huang-Rhys factors S_{23}^k (corresponding to Bands 3 and 4 in the output, since the ground state is indexed as 1).
- `output_dos_unweighted` provides a phonon density of states with 25 meV smearing.
- `output_phonon` lists phonon mode energies and reduced masses.

The key output file here is `output_HR_matlab`, as it contains all $S_{\alpha\beta}^k$ elements necessary to construct $G(t)$ in Equation 11 and calculate $F(\omega_{\alpha\beta})$ for each possible transition. This will be done in the next section, after which the phonon-induced relaxation rates can be calculated.

4. Franck-Condon-weighted density of states

The `output_HR_matlab`, `modes_cm`, and `energy_pop` files will be used as input to calculate the matrix elements of $F(\omega_{\alpha\beta})$ elements for each transition using a Matlab code (see Section IID).

- Copy `output_HR_matlab`, `modes_cm`, and `energy_pop` from `Porphyrin_Example/FC_DOS/Huang_Rhys_Factors` to `Porphyrin_Example/FC_DOS/FC_DOS_Calc`.
- Copy the Matlab code in `Codes/FC_DOS/FC_DOS_Calc` to the same folder. The code, `FC_DOS_Calculation.m`, will perform three major functions: 1) construct $G(t)$ in Equation 11 using $S_{\alpha\beta}^k$ and phonon modes ω_k provided as input from `output_HR_matlab` and `modes_cm`; 2) perform the inverse Fourier transform to construct the $F(\omega)$ function for each transition; and 3) fit a cubic spline to each $F(\omega)$ and pick out the value of the function at the corresponding transition energy $\omega_{\alpha\beta}$, $F(\omega_{\alpha\beta})$. A matrix of the same size as $V_{\alpha\beta}$ will be created with the values of $F(\omega_{\alpha\beta})$ to be used as input in the final section to calculate phonon-induced relaxation dynamics.
- Open the file to understand the input section (and rest of code if desired):
 - `e_min` and `e_max` indicate the first and last excited state indices. Remove the row containing these values in `energy_pop`.
 - `energy_pop` loads in the system's energy levels from file.
 - `HR_factors` loads in the system's Huang-Rhys factors from the file created in the previous section.
 - `modes_cm` loads in the system's phonon modes from the file created for the previous section. These modes are then converted to units of eV and angular frequency.
 - **IMPORTANT:** The Fourier transform in this code should result in a lineshape whose real part is always positive. In Matlab, this only occurs if enough timesteps and a short enough unit time step is used to exactly capture the period of all normal mode frequencies. Unfortunately, this can be prohibitively costly if using the modes with their default floating point representation. Thus, the code converts the modes to units of inverse femtosecond, and then rounds to three significant

digits by default. This usually works well for the default 10,000 timesteps in the code, however a user can test and change these parameters. Just make sure to always check that the real part of the Fourier transform is positive!

- **IMPORTANT:** `num_ts` indicates the number of time steps used to construct $G(t)$, and `f_s` indicates the sampling frequency used for the Fourier transform to calculate $F(\omega_{\alpha\beta})$. Again, make sure these choice of values gives only positive values for the real part of the Fourier transform performed later in the code. Values of 10,000 and 10 Hz (default) should suffice for most cases.
 - Outputs: 1) `x_axis_ev` provides the x-axis in units of eV for plotting $F(\omega)$ for each transition; 2) `x_axis_cm` provides the same in units of cm^{-1} ; 3) `lineshapes` plots $F(\omega)$ in columns corresponding to each transition in the same order they appear in `output_disp_norm` from the Huang-Rhys factor calculations. Use either of the previous axis files to plot against; and 4)
 - `temp_smearing` provides the temperature used in calculating the Bose-Einstein distribution.
 - `l_smearing` and `g_smearing` provide broadening parameters in eV for optional Lorentzian and Gaussian smearing, respectively. Traditionally, the spectrum should be broadened at least using Lorentzian lineshapes to account for dephasing times. Gaussian smearing can also be used to account for thermal effects.
 - `fcf_weighted_dos_values.txt` contains the $F(\omega_{\alpha\beta})$ matrix used as input for the next section.
- After understanding the input and code, run the Matlab code using `num_ts=10000` and `f_s=10`. The 12th column of the `lineshapes` output contains $F(\omega)$ for the S_3 - S_2 transition. Rerun the code after turning on Lorentzian smearing (`smearing_l = 1`). Plot $F(\omega)$ with and without smearing using the `x_axis_ev` file as the x-axis input. Compare results to those shown in Figure 6. Applying smearing makes the end result more realistic when considering homogeneous broadening from electronic dephasing.
 - Note that the transition energy for the S_3 - S_2 transition is about 0.78 eV - the code then uses the cubic spline fitting to evaluate $F(\omega)$ at this energy value, which ends up

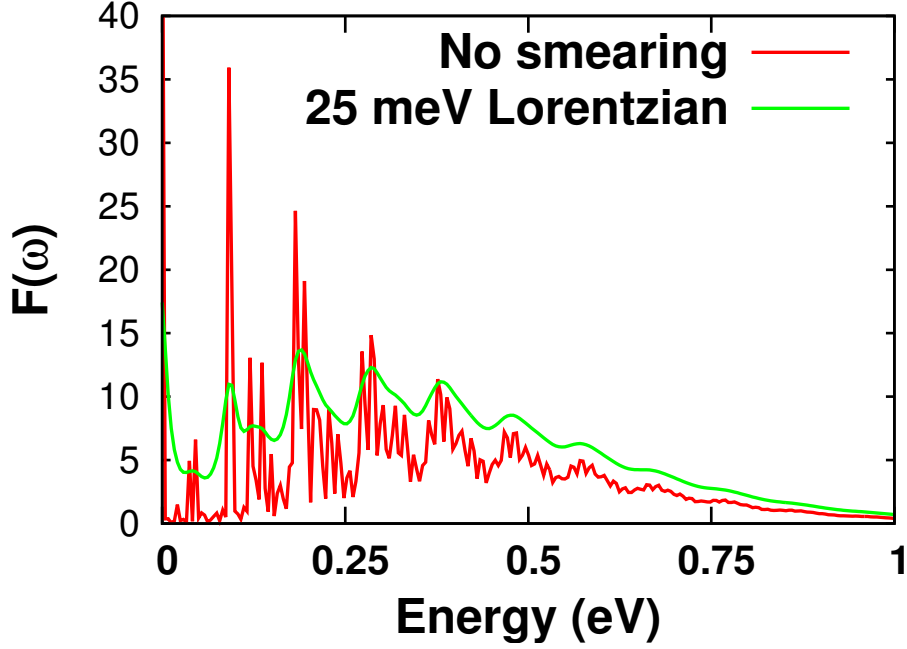


FIG. 6. The $F(\omega)$ function for the S_3 - S_2 transition with and without 25 meV Lorentzian smearing. $F(\omega_{\alpha\beta})$ is evaluated at the transition energy, which is around 0.78 eV.

being $F(\omega_{32}) \approx 2.5$ (remember, S_0 is the ground state, so $F(\omega_{32})$ corresponds to the 4th row and 3rd column of the matrix in `fcf_weighted_dos_values`).

- Try testing `ts_int` in the same way - increasing this variable will decrease the maximum energy for which $F(\omega)$ is calculated.

Save the `fcf_weighted_dos_values.txt` output file from the Lorentzian smearing calculation. This will be used as input in the final section to calculate relaxation rates.

D. Phonon-induced relaxation dynamics

The final step will gather excitation energy information (`energy_pop`, the nonadiabatic electronic coupling matrix ($V_{\alpha\beta}$, `final_mat`), and the Franck-Condon-weighted density of states matrix ($F(\omega_{\alpha\beta}$, `fcf_weighted_dos_values`) in the same directory and run a final Matlab code to calculate phonon-induced relaxation rates over time.

- Copy `energy_pop` and `fcf_weighted_dos_values` from the FC-DOS calculations into `Porphyrin_Example/Relaxation_Dynamics`. Also, copy the final output ma-

trix containing $V_{\alpha\beta}$ from Section ?? into the same directory (here it is referred to as `final_mat`). Finally, copy `Phonon_Induced_Dynamics_LRTDDFT_RDM.m` from `Codes/Relaxation_Dynamics` into this directory as well.

- This final code solves the Redfield equations given in Equation 1 using relaxation rates defined in 7. For each transition, $k_{\alpha\beta}$ is calculated using the $V_{\alpha\beta}$ and $F(\omega_{\alpha\beta})$ matrix elements, and the resulting phonon-induced relaxation rates are determined. If this Matlab code is run with visualization enabled, then the output will be a graph of the an excited population's energy as a function of time as described in Section II E. The population of a given state can then be fit to an exponential decay to determine excited state lifetimes.
- Open the code to understand the input:
 - `energy_pop` loads in the ground and excited state energies.
 - `Vab2` loads in the thermally averaged, squared nonadiabatic electronic coupling matrix ($V_{\alpha\beta}$).
 - `field` loads in the Franck-Condon-weighted density of states matrix ($F(\omega_{\alpha\beta})$).
 - `forME` calculates the relaxation rates ($k_{\alpha\beta}$) and converts them to units of ps^{-1} .
 - `Omin` and `Omax` are the minimum and maximum state index (ground state is 1).
 - `inib` indicates the initial excitation - phonon-induced relaxation dynamics will initiate with the entire excitation in this state.
 - `time` indicates the time (x-axis) grid along which to calculate energies of the excited state as a function of time. Over time, electron-phonon interactions will reduce the energy of the initially excited state until it reaches the ground state. Each of the possible choices for `time` provides a different range, from 200 ps up to 100 ns. The choice of range depends on the system being studied. Here, choose the first range that goes up to 200 ps.
 - `Egrid` provides the energy range to visualize state dynamics - make sure this range encompasses all excited state energies included in `energy_pop`.
- Since the Soret band corresponds to excited states 3 and 4, this corresponds to states 4 and 5 in `energy_pop`. We will begin with a photoexcited electron in the higher of

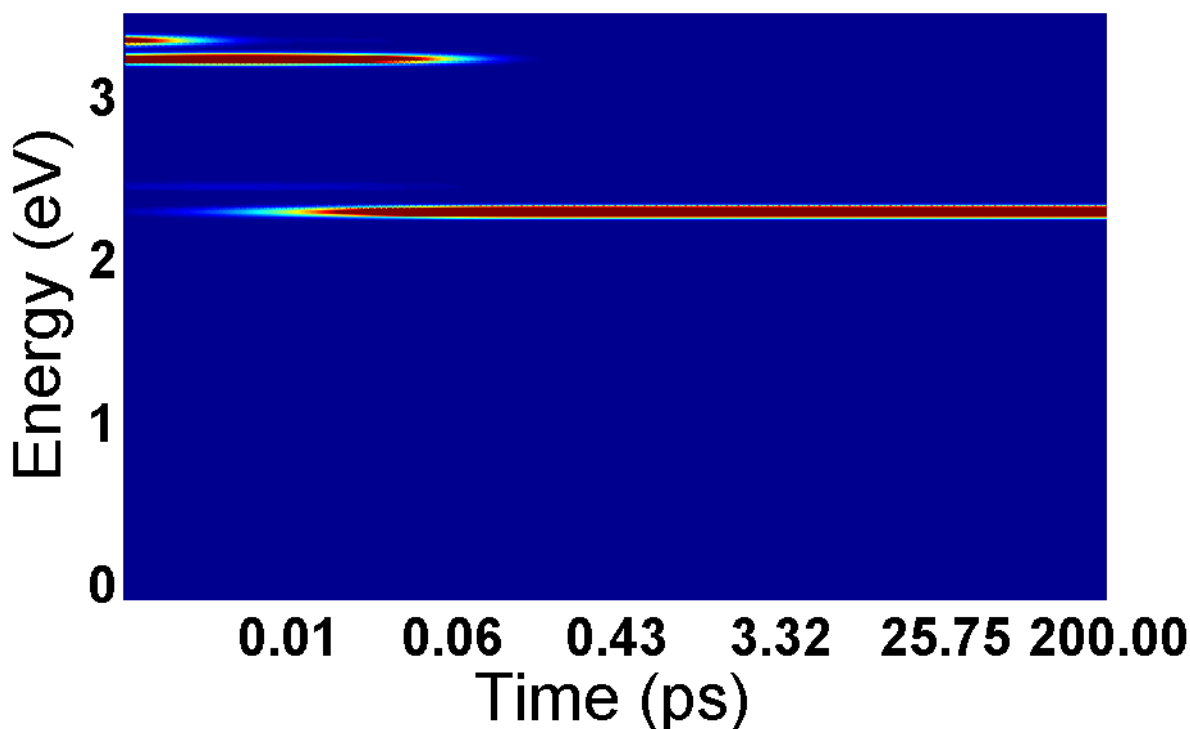


FIG. 7. Excited state energy as a function of time for porphyrin molecule with initial excitation to Soret band (3.33 eV).

the two states, so set `inib=5`.

- Make sure the names of all input files match what the Matlab code will look for, and then run the code. If visualization is enabled, the output should look like Figure 7, where darker red colors indicate more population at that energy at a given time. This graph just visualizes the PPe output file, which can be visualized using any other software as well.

From these results, one can see that an initial excitation to the top Soret band (3.33 eV), leads to fast relaxation to the lower Soret band (3.22 eV) in under 10 fs. From there, it takes about 30 fs to relax to the lowest excited state at 2.28 eV. This 30 fs Soret lifetime agrees extremely well with experimental results that predict the relaxation rate to be under 50 fs⁸, supporting the accuracy of the present method. The excitation stays in this state for over 200 ps - if the time range were extended, nonradiative relaxation to the ground state would be seen in around 10 ns.

Congratulations! This example illustrates all the major tools included in this method - although porphyrin only contains 38 atoms, this method can be applied to systems with hundreds of atoms and is still computationally feasible.

Good luck and please provide feedback about the method and manual at jptrinastic@gmail.com.

-
- ¹ J. Trinastic, I.-H. Chu, and H.-P. Cheng, J Phys Chem C , under review (2015).
- ² V. May and O. Kühn, *Charge and energy transfer dynamics in molecular systems* (John Wiley & Sons, 2008).
- ³ M. Khalil, N. Demirdven, and A. Tokmakoff, J. Chem. Phys. **121**, 362 (2004).
- ⁴ O. V. Prezhdo and P. J. Rossky, J. Chem. Phys. **107**, 5863 (1997).
- ⁵ I. Tavernelli, B. F. E. Curchod, A. Laktionov, and U. Rothlisberger, J. Chem. Phys. **133**, 194104 (2010).
- ⁶ I. Tavernelli, E. Tapavicza, and U. Rothlisberger, J. Chem. Phys. **130**, 124107 (2009).
- ⁷ M. E. Casida, Journal of Molecular Structure: THEOCHEM **914**, 3 (2009).
- ⁸ A. Marcelli, P. Foggi, L. Moroni, C. Gellini, and P. R. Salvi, The Journal of Physical Chemistry A **112**, 1864 (2008).
- ⁹ K. Y. Yeon, D. Jeong, and S. K. Kim, Chemical Communications **46**, 5572 (2010).
- ¹⁰ Y. He, Y. Xiong, Q. Zhu, and F. Kong, Acta Physico-Chimica Sinica **15**, 636 (1999).