This paper describes a method to do \textit{ab initio} molecular dynamics in electronically excited systems within the random phase approximation (RPA). Using a dynamical variational treatment of the RPA frequency, which corresponds to the electronic excitation energy of the system, we derive coupled equations of motion for the RPA amplitudes, the single particle orbitals, and the nuclear coordinates. These equations scale linearly with basis size and can be implemented with only a single holonomic constraint. Test calculations on a model two level system give exact agreement with analytical results. Furthermore, we examined the computational efficiency of the method by modeling the excited state dynamics of a one-dimensional polyene lattice. Our results indicate that the present method offers a considerable decrease in computational effort over a straight-forward configuration interaction (singles) plus gradient calculation performed at each nuclear configuration.

\textbf{Pacs}: 71.15-m, 71.15.Pd, 31.50.+w

\section{I. INTRODUCTION}

In recent years, there has been considerable advances towards fully \textit{ab initio} molecular dynamics simulations using inter- and intramolecular potentials derived from quantum many-body interactions. This activity has been largely spurred by the introduction of hybrid quantum/classical dynamics treatments, such as the density functional theory/molecular dynamics methods introduced by Car and Parrinello \cite{Car85, Parr85}. In this approach, the quantum electronic orbitals, \{\phi_i(1)\}, are coupled to the classical nuclear degrees of freedom, \{R_n\}, through a fictitious Lagrangian, which along with an appropriate set of Lagrange multipliers, \{\Lambda_{ij}\}, leads to a set of equations of motion

\begin{align}
\mu \ddot{\phi}_i(1) &= -\frac{\delta E[\{\phi_i\}, \{R_n\}]}{\delta \phi_i(1)} + \sum_k \Lambda_{ik} \phi_k(1), \\
M_n \ddot{R}_n &= -\nabla_{R}E[\{\phi\}, \{R\}],
\end{align}

where \(E[\{\phi_i\}, \{R_n\}]\) is the Hohenberg and Kohn energy functional. This approach has proven to be highly successful in simulating chemical dynamics in the condensed phase.

However, there are a number of distinct disadvantages to the method. First, the equations of motion involve both fast (the orbitals) and slow (the nuclei) degrees of freedom. Thus, the computational time-step must be rather small. Secondly, imposing the holonomic constraint of orbital orthogonality forces a single iteration of the approach to scale as \(\sim M \times N^2\) where \(N\) is the number of particles and \(M\) the size of the electronic basis. Finally, the method can only treat systems in the electronic ground state.

Several groups have attempted to overcome each of these difficulties. The time-step problem has been attacked via multiple time-scale methods \cite{Ehlers92, Cui95} and by using the electronic density instead of the Kohn-Sham orbitals as the dynamical variable \cite{Hohenberg64}. Several algorithms have been introduced to tackle the scaling problem \cite{Cohen96}. In these cases, scaling more favorable than \(\sim N^3\) is achieved only at the cost of several assumptions and approximations.

Recently, Alavi, Kohanoff, Parrinello, and Frenkel have developed a density functional based method for treating systems with finite temperature electrons \cite{Alavi98}. This approach has a number of attractive features, foremost being the inclusion of fractional occupation of the electronic orbitals. Dynamics in this scheme are isothermal rather than adiabatic, allowing for incoherent transitions between electronically excited states. While the approach works well for small bandgap systems (such as metals or dense hydrogen), this approach is not useful for systems with larger band gaps (\(\Delta E \gg kT\)) or photo-excited systems.

In this paper, we present an alternative formulation of the Car-Parrinello method for treating electronically excited systems. We begin by introducing the general computational algorithm for the dynamical optimization of excited electronic states in the presence of “classically propagating” ions. This general theoretical scheme is developed without
specific reference to the description of the electronic excited state. The principal results of this section are a set of dynamical equations of motion for the electronic amplitudes and nuclear coordinates in a generalized phase space. We then derive specific equations of motion for the electronic amplitudes and nuclear coordinates under the Random Phase Approximation (RPA) for the electrons. Finally, we demonstrate the salient features of the approach through a simplified SU(2) model of interacting electrons and via a realistic model of conjugated one-dimensional polymer lattices.

II. CLASSICAL EQUATIONS OF MOTION FOR THE DYNAMICAL OPTIMIZATION OF EXCITED QUANTUM STATES

We begin by developing a general dynamical theory for molecular dynamics in excited electronic states. We first define the \( N \)-electron Fock space as being parameterized by a set of dynamical variables \( \lambda(\tau) \) which include the nuclear positions and any other dynamical variables and ensemble constraints placed upon the system (e.g. pressure, temperature, volume etc...):

\[
\mathcal{F} = \left\{ n_1, n_2, \ldots (\lambda) \right\}, \quad \sum_i n_i = N
\]  

We describe the ground state wave function as an expansion on the basis in \( \mathcal{F} \):

\[
|\Psi_o(\lambda)\rangle = \sum_{1\ldots i\ldots} C_i(\lambda)|n_1\ldots n_i\ldots(\lambda)\rangle, \quad \langle \Psi_o(\lambda) | \Psi_o(\lambda) \rangle = 1
\]  

\( |\Psi_o(\lambda)\rangle \) is not a Slater determinant in general case.

We next define the mapping operators, \( P_\nu^\dagger \), which act on the ground state to produce a new state, \( |\nu(\lambda)\rangle \), which is orthogonal to \( |\Psi_o(\lambda)\rangle \) in the subspace \( \mathcal{F}_+ \) of the Fock space:

\[
|\nu(\lambda)\rangle = P_\nu^\dagger |\Psi_o(\lambda)\rangle, \quad P_\nu^\dagger |\Psi_o(\lambda)\rangle = 0
\]  

\[
\langle \nu(\lambda) | \Psi_o(\lambda) \rangle = \langle \Psi_o(\lambda) | P_\nu | \Psi_o(\lambda) \rangle = 0, \quad \langle \nu(\lambda) | \nu(\lambda) \rangle = 1
\]  

If the \( |\Psi_o(\lambda)\rangle \) is a true ground state of the \( N \)-particle system, the excited states should lie in the orthogonal subspace \( \mathcal{F}_+ \).

Variational determinations of the excited states are thus searches in the orthogonal subspace for the optimal mapping operator \( P_\nu^\dagger \) and for the optimal basis of the Fock space \( |n_1 n_2 \ldots n_i\ldots\rangle \) such that the energy functional

\[
\varepsilon_\nu = \langle \nu(\lambda) | H | \nu(\lambda) \rangle,
\]

\[
= \langle \Psi_o(\lambda) | H | \Psi_o(\lambda) \rangle
\]

\[
+ \left( \langle \nu(\lambda) | H | \nu(\lambda) \rangle - \langle \Psi_o(\lambda) | H | \Psi_o(\lambda) \rangle \right),
\]

\[
= \langle \Psi_o(\lambda) | H | \Psi_o(\lambda) \rangle + \langle \Psi_o(\lambda) | [P_\nu, [H, P_\nu^\dagger]] | \Psi_o(\lambda) \rangle,
\]

\[
= E_o + \omega_\nu,
\]  

is at a variational minimum. We write the excitation energy, \( \varepsilon_\nu \), as a functional of both the ground and excited state and introduce explicitly via the double commutator term the energy gap, \( \omega_\nu \), between the ground and the excited state.

According to the calculus of variations, we can derive equations of motion which dynamically optimize the excited state system. We first define formally a set of “velocities” of the states in the Fock space

\[
|\dot{\nu}\rangle = \frac{d}{d\tau} |\nu\rangle, \quad |\dot{\Psi}_o\rangle = \frac{d}{d\tau} |\Psi_o\rangle,
\]  

where \( \tau \) is not the true physical time but rather a parameter which characterizes the evolution of the amplitudes through the Hilbert space subject to the orthogonalization constraints given above. The “classical” Lagrangian for our system is given by
\[ \mathcal{L} = \frac{1}{2} \mu |\dot{\Psi}_o\rangle \langle \dot{\Psi}_o| + \frac{1}{2} \mu' |\dot{\nu}\rangle \langle \dot{\nu}| + \frac{1}{2} m \dot{\lambda}^2(\tau) \\
- \varepsilon_{\nu} |0\rangle \langle \nu|, \lambda| \\
- \Lambda(|\Psi_o\rangle \langle \Psi_o| - 1) - \Gamma(|\nu\rangle \langle \nu| - 1), \]  
(9)

where \( \Lambda \) and \( \Gamma \) are Lagrange multipliers arising from the holonomic ortho-normalization constraint for the ground and excited states and which allow \(|\nu\rangle \) and \(|\Psi_o\rangle \) to be treated as independent variables. The masses \( \mu \) and \( \mu' \) are fictitious masses and have no true physical meaning. This Lagrangian leads to the classical Euler-Lagrange equations\(^{12} \) for the wave functions:

\[ \frac{d}{d\tau} \frac{\partial \mathcal{L}}{\partial |\dot{\Psi}_o\rangle} - \frac{\partial \mathcal{L}}{\partial |\Psi_o\rangle} = 0, \]  
(10)

\[ \frac{d}{d\tau} \frac{\partial \mathcal{L}}{\partial |\dot{\nu}\rangle} - \frac{\partial \mathcal{L}}{\partial |\nu\rangle} = 0. \]  
(11)

The Euler-Lagrange equation dictates the following equations of motion for quantum dynamical optimization in the Hilbert space:

\[ \mu |\ddot{\Psi}_o\rangle = - \frac{\delta \varepsilon_{\nu}}{\delta |\Psi_o\rangle} + \Lambda |\Psi_o\rangle, \]

\[ \mu' |\ddot{\nu}\rangle = - \frac{\delta \varepsilon_{\nu}}{\delta |\nu\rangle} + \Gamma |\nu\rangle, \]

\[ m \ddot{\lambda} = - \frac{\delta \varepsilon_{\nu}}{\delta \lambda}. \]  
(12)

This dynamical view is the starting point for the remainder of our calculations.

### III. RANDOM PHASE APPROXIMATION FOR ELECTRONIC MOTIONS

For a molecular system with \( N \) electrons and \( n \) nuclei, the full \( N \)-body Hamiltonian for a fixed set of nuclear positions \( \{R_\nu\} \), is given as (atomic units are used throughout)

\[ H = \frac{1}{2} \sum_i \nabla_i^2 - \sum_\nu \sum_i \frac{Z_\nu}{|R_\nu - r_i|} + \sum_{ij} \frac{1}{|r_i - r_j|}, \]  
(13)

\[ = \sum_i h^{(i)}_o + \sum_{ij} \frac{1}{|r_i - r_j|}, \]  
(14)

where \( h^{(i)}_o \) is the one-body electron operator which includes the electron kinetic energy and the interaction between the electron and the nuclear cores. We define the single-particle Hamiltonian \( H_1 \), through either the Hartree-Fock (HF) approximation\(^{13} \) or via the density functional theory of Kohn and Sham\(^{7} \). In either case, \( H_1 \) is a functional of the single particle density

\[ \rho(12) = \sum_{occ} \phi_i^*(1) \phi_i(2). \]  
(15)

The single particle states, \( \{\phi_i(1)\} \), are solutions of a nonlinear Schrödinger equation,

\[ H_1[\rho, \mathbf{R}]|\phi_i\rangle = E_i[\mathbf{R}]|\phi_i\rangle, \]  
(16)

which must be determined at the start of the calculation. Here \( E_i[\mathbf{R}] \) is the orbital energy. The HF spin-orbital wave functions and energies differ from the KS ones in the way the terms in the single-particle Hamiltonian are treated. We will denote the Slater determinant wave-function constructed from occupied single-particle HF (of KS) orbitals as \(|HF\rangle \) and note that this state represents either the Hartree-Fock ground state or the Kohn-Sham ground state.

Having obtained a basis of single-particle states, we can write the two-body Hamiltonian in second quantized form:
\[
H = E_{HF} + \sum_{i\sigma} E_i : a_{i\sigma}^\dagger a_{i\sigma} : \\
+ \frac{1}{2} \sum_{ijkl} (ij|v|kl) : a_{i\sigma}^\dagger a_{j\sigma}^\dagger a_{i\sigma'} a_{k\sigma'} :,
\]

where \( E_i \) is the HF single-particle eigenenergy, \( (ij|v|kl) \) is the matrix element of Coulomb electron-electron interactions, \( \cdots : \) denotes a normal ordered product and \( E_{HF} \) is the HF ground state energy. The operators \( a_{i\sigma}^\dagger \) (\( a_{i\sigma} \)) create (annihilate) single electrons in the \( \{i\sigma\} \) HF spin-orbital state, where \( \sigma = \pm \frac{1}{2} \) is the spin index of the electrons.

We can form a new set of exciton operators by taking bilinear combinations of the particle/hole operators with total angular momentum \( S \) and projection \( m_S \),

\[
A_{ph}(Sm_S) = \sum_{\sigma_1\sigma_2\sigma_3\sigma_4} \left\{ \frac{1}{2} \sigma_1 \frac{1}{2} \sigma_2 \right\} |Sm_s\rangle a_{\sigma_1}^\dagger a_{\sigma_2}^\dagger a_{\sigma_3} a_{\sigma_4} \\
A_{ph}(Sm_S) = \sum_{\sigma_1\sigma_2\sigma_3\sigma_4} \left\{ \frac{1}{2} \sigma_1 \frac{1}{2} \sigma_2 \right\} |Sm_s\rangle a_{\sigma_3} a_{\sigma_4} a_{\sigma_1} a_{\sigma_2},
\]

where \( \langle s_1s_1s_2s_2|Sm_s\rangle \) is a Clebsch-Gordon coefficient. Our notation is such that \( \overline{\sigma} \) denotes the action of time reversal operator on the hole state,
We apply the Wick theorem to the right hand side of Eq. 26 and then neglect the normal ordering contribution to is bosonic 

We then perform a canonical Bogolubov transformation

where $A_{ph}(S m_s) = (−)^{S+m} A_{ph}(S − m)$ is the time reversal exciton annihilation operator. This defines our “quasi-harmonic” exciton Hamiltonian.

The exact commutation relation between the exciton operators is

We apply the Wick theorem to the right hand side of Eq. 26 and then neglect the normal ordering contribution to this relation. This is the RPA and in this approximation the commutation relation between the exciton operators is bosonic

We then perform a canonical Bogolubov transformation for both singlet ($S = 0$) and triplet ($S = 1$) exciton bosons

where $X_{ph}^{i}$ and $Y_{ph}^{i}$ are the RPA amplitudes which are yet to be determined. These operators create and destroy harmonic excitations in the electronic degrees of freedom. Physically, the singlet RPA excitations correspond to “breathing” modes of the electron cloud and triple RPA excitations correspond to dipolar oscillations of the electronic system about the nuclear frame. In what follows, we will focus our attention upon the triplet excitations, as these are the states created upon photo-excitation of a singlet ground state. Equations of motion for singlet RPA excitations can be obtained as well.

The commutation relations for the RPA excitation creation operators goes as follows:

By defining the RPA vacuum as

and the RPA excited state as
the orthogonality condition of Eq. 29 is fulfilled automatically for single RPA excitations
\[
\langle \text{RPA}| Q_{\mu i} Q^\dagger_{\mu' i'} \text{RPA} \rangle = \langle \text{RPA}| [Q_{\mu i}, Q^\dagger_{\mu' i'}]| \text{RPA} \rangle = \delta_{\mu\mu'} \delta_{ii'}.
\] (32)

The RPA excitations are true oscillations of electronic systems in the sense that the Heisenberg equations of motion for the excitation creation operators is precisely as we expect for a harmonic system,
\[
[H_2, Q^\dagger_{\mu i}] = Q^\dagger_{\mu i} \omega_i,
\] (33)
where \(\omega_i\) is the RPA frequency. From this we can derive the RPA amplitudes, \(X^i_{ph}\) and \(Y^i_{ph}\), and RPA frequencies \(\omega_i\). After a bit of algebra we arrive at the equations:
\[
E_{ph} X^i_{ph} + \sum_{p'h'} (pp'[v|h'|h]) Y^i_{p'h'} - \sum_{h'h'} (ph'[v|p'h]) X^i_{p'h'} = \omega_i X^i_{ph},
\] (34)
\[
E_{ph} Y^{i'}_{ph} + \sum_{p'h'} (pp'[v|h'|h]) X^{i'}_{p'h'} - \sum_{h'h'} (ph'[v|p'h]) Y^{i'}_{p'h'} = -\omega_i Y^{i'}_{ph}.
\] (35)

In matrix form:
\[
\begin{pmatrix}
A & B \\
B & A
\end{pmatrix}
\begin{pmatrix}
|X\rangle \\
|Y\rangle
\end{pmatrix} = \omega \begin{pmatrix}
|X\rangle \\
-|Y\rangle
\end{pmatrix}.
\] (36)

The diagonal blocks, \(A\), are determined by Coulombic interactions between single particle/hole excitations.
\[
A_{pp'h'} = E_{ph} \delta_{pp'} \delta_{hh'} - (ph'[v|p'h])
\] (37)

However, the off diagonal terms,
\[
B_{pp'h'} = (pp'[v|h'h]),
\] (38)
are related fluctuations about the HF vacuum and thus give rise to a net polarization of the HF vacuum. Thus, the RPA vacuum differs from the HF vacuum by the addition of these polarization fluctuations. Lastly, we note, that if we take \(Y \to 0\) or assume that \(B \approx 0\) and neglect the fluctuation terms, the RPA equations reduce to the Tamm-Dankoff or configuration interaction equations with single excitations.

The matrix RPA method can be also derived as the small amplitude limit of the time dependent HF equation. We emphasize that the time-dependent density functional theory is equivalent to matrix RPA if we also assume harmonic oscillation of the time-dependent density \(\rho(t)\) around equilibrium. The standard practical realization of the time-dependent density functional theory is the time-dependent local density approximation, where nonlocal exchange interaction is approximated by local density dependent interaction in adiabatic limit. In this respect the matrix RPA method we use is advantageous because this method can treat nonlocal Fock interactions in natural way.

We can transform this into an eigenvalue problem by multiplying the right hand side of this equation by the Pauli spin matrix, \(\sigma_z\),
\[
M|\Psi\rangle = \omega \sigma_z |\Psi\rangle,
\] (39)
where
\[
|\Psi\rangle = \begin{pmatrix}
|X\rangle \\
|Y\rangle
\end{pmatrix},
\] (40)
is a two component spinor state. The eigenvector solution to this equation can be obtained by transforming the RPA matrix equation
\[
\sigma^T_z M|\Psi\rangle = \omega |\Psi\rangle.
\] (41)
Thus, \(|\Psi\rangle\) is the right-handed eigenvector of the antisymmetric matrix.
\[ \sigma_z^T M = \begin{pmatrix} A & B \\ -B & -A \end{pmatrix}. \]  

(42)

The RPA eigenstates are subject to the orthogonality condition

\[ \sum_{ph} X_{ph}^i X_{ph}^j - Y_{ph}^i Y_{ph}^j = \delta_{ij}. \]  

(43)

Thus, we define \( \Psi^R \) as the right-handed eigenvector

\[ | \Psi^R_i \rangle = \begin{pmatrix} |X_i^i \rangle \\ |Y_i^i \rangle \end{pmatrix}, \]  

(44)

and \( \Psi^L \) as the left-handed eigenvector

\[ | \Psi^L_i \rangle = \begin{pmatrix} |X_i^i \rangle \\ -|Y_i^i \rangle \end{pmatrix} = \sigma_z | \Psi^R_i \rangle. \]  

(45)

The inner product relation between the left and right-handed eigenvectors produces the desired orthogonality relation for the RPA states.

\[ \langle \Psi^L_i | \Psi^R_j \rangle = \Psi^L_i \cdot \Psi^R_i = \delta_{ij}. \]  

(46)

These states are determined at the start of the calculation in a basis of single particle/hole states which spans the Fock space.

The RPA frequency, \( \omega_i \), is determined by taking the expectation value of \( M \) between the left and right-handed eigenvectors.

\[ \omega_i [X, Y, \phi, R] = \langle \Psi^L_i | M | \Psi^R_i \rangle \]  

(47)

A. Equations of motion for the excited states molecular dynamics in the RPA

The energy functional for the RPA equations is

\[ E_{ex}(i) = \langle \text{RPA}| Q_{\mu i} H Q_{\mu i}^\dagger |\text{RPA} \rangle, \]  

\[ = \langle \text{RPA}| H |\text{RPA} \rangle \]  

\[ + \langle \text{RPA}| \left[ Q_{\mu i}, \left[ H, Q_{\mu i}^\dagger \right] \right] |\text{RPA} \rangle, \]  

\[ = E_o + \omega_i, \]  

(48)

where \( E_o \) is the RPA ground state energy and

\[ \omega_i = \langle \text{RPA}| \left[ Q_{\mu i}, \left[ H, Q_{\mu i}^\dagger \right] \right] |\text{RPA} \rangle, \]  

(49)

is the RPA frequency. In the previous section the RPA equation is derived via the Heisenberg equation (Eq. 33) of motion for the excitation creation operators. The Heisenberg equation is physically the same as the requirement of a variational minimum for the RPA excited state. To demonstrate this, we multiply from the left with an arbitrary variation of the RPA excited state:

\[ \langle \text{RPA}| \delta Q_{\mu i} \left[ H, Q_{\mu i}^\dagger \right] |\text{RPA} \rangle = \omega_i \langle \text{RPA}| \delta Q_{\mu i} Q_{\mu i}^\dagger |\text{RPA} \rangle. \]  

(50)

We can rewrite this equation as a variational of the double commutator in Eq. 33, because \( \langle \text{RPA}| Q_{\mu i}^\dagger = 0 \).
\[
\frac{\delta}{\delta Q_{\mu i}} \left\{ (\text{RPA} | \left[ Q_{\mu i}, [H, Q_{\mu i}^\dagger] \right] | \text{RPA} ) - \omega_i ( (\text{RPA} | Q_{\mu i} Q_{\mu i}^\dagger | \text{RPA}) - 1) \right\} = 0
\] (51)

where \(\omega_i\) plays a role of the Lagrange multiplier and insures the normalization of the RPA excited states.

Neglecting vacuum polarization effects, i.e. approximating \(\langle \text{RPA} | \rangle\) by the HF Slater determinant \(|0_{HF}\rangle\) in Eq. 51 we obtain the so-called equation of motion method which was originally proposed by D.J. Rowe\(^{14}\) and widely used in the studies of molecular excited states in quantum chemistry\(^{20-22}\). The same matrix RPA equation can be derived by several methods, e.g. by Green function methods\(^{13,23}\), linear response function method\(^{24,25}\). Each of these methods has the strong points in specific aspects but is deficient in other respects. As we demonstrated by Eq. 51 our method is equivalent to the Rayleigh - Ritz variational principle for the RPA excitation amplitudes and the use of the variational approach is pivotal to formulation classical equations of motion for the dynamical optimization of the excited states.

Finally, we assume that polarization of the ground state vacuum due to particle-hole interaction is weak, then the RPA vacuum is approximately the same as the HF or KS vacuum and we can write the RPA ground state energy as 
\[E_0 \approx E_{HF} .\]

Following these considerations, we can write the Lagrangian
\[
\mathcal{L} = \frac{1}{2} \sum_i \nu \int d1 |\dot{\phi}(1)|^2 + \frac{1}{2} \sum_{k} \mu \sum_{ph} |\dot{X}_{ph}^{k}|^2 \\
+ \frac{1}{2} \sum_{k} \mu \sum_{ph} |\dot{Y}_{ph}^{k}|^2 + \frac{1}{2} \sum_{n} m_n \dot{R}_n^2 \\
- E_{HF}[\phi, R] - \omega_i [\phi, X, Y, R] \\
+ \sum_{ij} \Lambda_{ij} (\int d1 \phi^*_i(1) \phi_j(1) - \delta_{ij}) \\
+ \sum_{kl} \Gamma_{kl} (\langle \Psi_k | \Psi_l \rangle - \delta_{kl})
\] (52)

where the constraint
\[
\sum_{kl} \Gamma_{kl} (\langle \Psi_k | \Psi_l \rangle - \delta_{kl})
\]
insures the orthogonality of the RPA excited states. Solving the Euler-Lagrange equations for the single particle amplitudes, \(\phi_k(1)\),
\[
\nu \ddot{\phi}_k(1) = - \frac{\delta E_{HF}[\phi, R]}{\delta \phi^*_k(1)} - \frac{\delta \omega_i [\phi, X, Y, R]}{\delta \phi^*_k(1)} \\
+ \sum_{j} \Lambda_{ij} \phi_j(1)
\] (54)

The equations for the single particle orbitals are similar to the CP equations written above (Eq. 3) and include a term due to the electronic excitations. In the case of a collective excitation, in which the RPA excitation is delocalized over a number of single particle states (or in other worlds, the oscillator strength of the RPA excitations is distributed more or less uniformly over a number of particle-hole excitations) the variation of the energy of collective excitation \(\omega\) with an infinitesimal change in one of the single particle orbitals will be very small. Because of this, the RPA excitation variables will evolve on a slower time-scale than the single particle variables and we can invoke an adiabatic separation between the RPA variables and the single particle states. That is to say
\[
\frac{\delta \omega_k}{\delta \phi_j} \ll \frac{\delta E_{HF}}{\delta \phi_j},
\] (55)
so that if one deals with collective electron motions, Eq. 54 can be approximated with very high degree of accuracy by the CP equations.
\[ \nu \dot{\phi}_i (1) = - \delta E_{HF} [\phi, R] \frac{\delta \phi_i (1)}{\delta \phi_j (1)} + \sum_j \Lambda_{ij} \phi_j (1). \] 

This should be a reasonable approximation for many real molecular systems where one has delocalized valence electrons and relatively strong residual Coulomb interaction between them. We emphasize that our computational scheme is not restricted by the case of collective electronic excitation, i.e. by the approximation (Eq. 55). Taking into account the explicit expression for the functional derivatives of \( \omega_k \) in respect to the molecular orbitals \( \phi_i \), our dynamical equations can be straightforwardly used to do molecular dynamics on “non-collective” excited state surfaces.

The dynamical equations for the RPA amplitudes are determined to be (assuming only a single RPA excitation in the system),

\[ \mu \ddot{X}_{ph}^k = - \frac{\delta \omega_k [\phi, X, Y, R]}{\delta X_{ph}^k} + \Gamma_{kk} X_{ph}^k 
= E_{ph} X_{ph}^k + \sum_{p'h'} ((pp'|v|h'h) Y_{ph}^k - (p'h'|v|p'h) X_{ph}^k) 
+ \Gamma_{kk} X_{ph}^k, \] 

\[ \mu \ddot{Y}_{ph}^k = - \frac{\delta \omega_k [\phi, X, Y, R]}{\delta Y_{ph}^k} - \Gamma_{kk} Y_{ph}^k 
= E_{ph} Y_{ph}^k + \sum_{p'h'} ((pp'|v|h'h) X_{ph}^k - (p'h'|v|p'h) Y_{ph}^k) 
- \Gamma_{kk} Y_{ph}^k, \]

or in matrix form

\[ \mu \begin{pmatrix} \ddot{X} \\ \ddot{Y} \end{pmatrix} = \begin{pmatrix} A + \Gamma & B \\ B & A - \Gamma \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} \]

One important point to consider is that the functional derivatives of \( E_{HF} \) with respect to the particle states (i.e. single particle states above the Fermi energy) vanish since the HF density matrix does not include these states. As we seen below, we need these states and their energies to compute the Coulomb matrix elements in the RPA dynamical equations. However, all is not lost since we have at hand the states below the Fermi energy and hence the ground state density. We can thus reconstruct and simply diagonalize \( H_1 [\rho] \) to obtain the single particle excited states.

Finally for the nuclear positions we have classical equations of motion on the excited state potential energy surface,

\[ \mu \ddot{R}_n = \frac{\delta E_{ex} [\phi, X, Y, R]}{\delta R_n} 
= \frac{\delta E_{HF} [\phi, R_n]}{\delta R_n} - \frac{\delta \omega_k [\phi, X, Y, R_n]}{\delta R_n} \]

The details of the derivation of each of the functional derivatives above are provided in the Appendix A. The derivation of the molecular dynamics equations of motion in the RPA compose the central result of this paper.

IV. NUMERICAL AND ANALYTICAL EXAMPLES

A. The dynamical optimization of the excited state on a two level model

In order to get an indication of how our approach works, we apply our scheme to a model two-level system consisting of \( N \) distinguishable electrons labeled by \( p = 1, 2, \ldots, N \). Each of these can occupy one of two orbitals, a lower and upper, having energies \( \frac{1}{2} \varepsilon (R) \) and \( -\frac{1}{2} \varepsilon (R) \) and distinguished by \( g = 1 \) and \( g = 2 \) respectively. The coupling constant \( V(R) \) does not depend on any quantum number. The gap between orbital \( \varepsilon (R) \) and the strength of interaction \( V(R) \) depends on a classical variable \( R \). The HF approximation is obtained by setting \( V = 0 \), such that the lower level is fully occupied and the upper is empty, i.e. \( \bar{N} = \Omega \) where \( \Omega \) is the degeneracy of the levels. This model encapsulates
the salient effects one expects to see in physically realistic systems. The model Hamiltonian possesses the SU(2) symmetry and can be written in terms of quantum quasi-spin operators and the classical variable $R$:

$$H = \varepsilon(R)\hat{J}_z - \frac{1}{2}V(R)\left(\hat{J}_+\hat{J}_+ + \hat{J}_-\hat{J}_-\right)$$

$$+ \frac{M\dot{R}^2}{2} + \frac{1}{2}K(R - R_0)^2$$

(60)

where the operators $\hat{J}_+ , \hat{J}_-$ are defined as follows:

$$\hat{J}_z = \frac{1}{2} \sum_{p=1}^{\Omega} \left(a_{g2p}^{\dagger}a_{g2p} - a_{g1p}^{\dagger}a_{g1p}\right),$$

$$\hat{J}_+ = \sum_{p=1}^{\Omega} a_{g2p}^{\dagger}a_{g1p}$$

$$\hat{J}_- = \left(\hat{J}_+\right)^{\dagger}.$$ 

(61)

Above $a_{gp}^{\dagger}, a_{gp}$ are particle creation and annihilation operators on the lower ($g = 1$) or the upper ($g = 2$) level. $K$ is the spring constant which does not allow to classical system to move far from the equilibrium.

Place the classical variable at the position

$$R = R_0 + q,$$ 

(62)

which is the sum of the equilibrium position $R_0$ and the displacement $q$. Assuming the displacement from equilibrium is small, we can expand the Hamiltonian in $q$.

$$\varepsilon(R) = \varepsilon(R_0) + \frac{d\varepsilon}{dR}\bigg|_{R_0} q + O(q^2)$$

(63)

$$V(R) = V(R_0) + \frac{dV}{dR}\bigg|_{R_0} q + O(q^2).$$

(64)

Truncating this at first order gives a linear interaction between classical and quantum systems. Neglecting the terms of $O(q^2)$ we get the following quantum many-body Hamiltonian which depends parametrically on the displacement $q$ of the classical variable:

$$H(q) = \left(\varepsilon(R_0) + \frac{d\varepsilon}{dR}\bigg|_{R_0} q\right)\hat{J}_z$$

$$- \frac{1}{2} \left(V(R_0) + \frac{dV}{dR}\bigg|_{R_0} q\right)\left(\hat{J}_+\hat{J}_+ + \hat{J}_-\hat{J}_-\right)$$

$$+ \frac{Mq^2}{2} + \frac{1}{2}Kq^2$$

(65)

In the RPA, the operators $\hat{J}_+ , \hat{J}_-$ behave like pure bosonic operators

$$\left[\sqrt{\frac{\hat{J}_-}{\sqrt{N}}, \sqrt{\frac{\hat{J}_+}{\sqrt{N}}}\right] = 1$$

(66)

Using these bosons, we construct the RPA excitation creation operator (in the two-level model there is only one possible RPA excitation)

$$Q^\dagger = \frac{1}{\sqrt{N}}(X\hat{J}_+ - Y\hat{J}_-)$$

(67)

The orthogonality of the RPA excited state imposes the following normalization condition on the RPA amplitudes:
\[ X^2 - Y^2 = 1 \]  

The RPA frequency is given by the matrix element

\[
\omega[X,Y,q] = \langle \text{RPA} | \left[ Q, [H(q),Q^\dagger] \right] | \text{RPA} \rangle 
= \left( \varepsilon(R_0) + \left| \frac{d\varepsilon}{dR} \right|_{R_0} q \right) (X^2 + Y^2) 
- 2 \left( V(R_0) + \left| \frac{dV}{dR} \right|_{R_0} q \right) NXY 
\]  

We can rewrite the \( \omega[X,Y,q] \) as a functional of only the \( Y \) amplitudes and classical \( q \) variable:

\[
\omega[Y,q] = \left( \varepsilon(R_0) + \left| \frac{d\varepsilon}{dR} \right|_{R_0} q \right) (1 + 2Y^2) 
- 2 \left( V(R_0) + \left| \frac{dV}{dR} \right|_{R_0} q \right) N\sqrt{1 + Y^2}Y 
\]  

The variational minimum of the RPA frequency can be determined analytically and is given as a the function of \( q \):

\[
\omega(q) = \sqrt{\left( \varepsilon(R_0) + \left| \frac{d\varepsilon}{dR} \right|_{R_0} q \right)^2 - \left( V(R_0) + \left| \frac{dV}{dR} \right|_{R_0} q \right)^2} N^2. 
\]  

The classical Lagrangian for the annealing of the electronic excited state is given by

\[
L[q,Y] = \frac{1}{2} \mu \dot{Y}^2 - E_{HF}[q] - \omega[Y,q] + \frac{1}{2} m\dot{q}^2 - \frac{1}{2} Kq^2, 
\]  

where the \( E_{HF}[q] \) is the HF ground state energy.

The Lagrangian produces the equations of motion for the RPA amplitudes

\[
\mu \ddot{Y} = -4 \left( \varepsilon(R_0) + \left| \frac{d\varepsilon}{dR} \right|_{R_0} q \right) Y 
+ 2 \left( V(R_0) + \left| \frac{dV}{dR} \right|_{R_0} q \right) N\frac{1 + 2Y^2}{\sqrt{1 + Y^2}} 
\]  

\[
m\ddot{q} = \left( 1 + 2Y^2 + \frac{N}{2} \right) \left( \varepsilon(R_0 + q_0) + \omega(q_0) \right) 
- 2 \left| \frac{dV}{dR} \right|_{R_0} N\sqrt{1 + Y^2}Y - Kq 
\]  

The solution of these differential equations starting from an arbitrary value of \( Y(\tau = 0) \) and \( q(\tau = 0) \) is shown in Fig.1. The solutions oscillate about the minimum so that in order to get converged solution we introduced a velocity damping term to suppress oscillation around the equilibrium configuration. The final value of the amplitudes \( Y \) and \( X = \sqrt{1 + Y^2} \) are in excellent agreement with the analytical RPA results for a given equilibrium value of the classical displacement \( q_0 = q(\tau \rightarrow \infty) \):
The simplified form of the usual CPMD equation of motion can be derived within our model if we set the residual interaction $V(R) = 0$ and consider HF gap $\varepsilon(R)$ as a fixed parameter. In this case only the classical degree of freedom evolve in time. One can see from the lower part of the Fig.1 that there is a profound difference between excited and ground state dynamics for a classical system. This difference is due to the Hellmann-Feynman force from the RPA excited state (App. A.1).

### B. Excited state dynamics in conjugated polymer lattices

In this example we take a more challenging case in which the ground state can be determined exactly, but the excited states cannot. The $\pi$-electrons in linear polyene systems, such as trans-poly-acetylene, can to a fair approximation be treated as a quasi-one dimensional electron gas within the tight-binding approximation. Accordingly, we start our consideration from the following model electronic Hamiltonian for the polymer chain

$$H = H_o + H_{int}$$

Where $H_o$ is based upon the so called Su-Schrieffer-Heeger (SSH) model for the band-structure of trans-polyacetylene. The first term in the $H_o$ gives the energy for an electron with spin $\sigma$ to hop between neighboring $p$-orbitals. The strength of this term is modulated by linear coupling to distortions in the polymer lattice away from evenly spaced lattice positions. Finally, the last terms in $H_o$ gives the harmonic interactions between lattice-sites arising from the $\sigma$-bonds between neighboring lattice atoms. The $H_{int}$ is the normal ordered, i.e. irreducible to one body operators, interaction between valence electrons from the $p_z$-orbitals.

The Hamiltonian $H_o$ is quadratic form in fermion creation/annihilation operators. This quadratic form can be exactly diagonalized by the canonical transformation:

$$c_{n\sigma} = \frac{1}{\sqrt{N}} \sum_k (\beta_k^\dagger i(-)^na_k a_{k\sigma} + (\alpha_k^* - i(-)^n\beta_k^*)a_{k\sigma}^*)$$

$$c_{n\sigma}^\dagger = \frac{1}{\sqrt{N}} \sum_k (\beta_k^\dagger i(-)^na_k^* a_{k\sigma}^* + (\alpha_k^* + i(-)^n\beta_k^*)a_{k\sigma}^*)$$

This canonical transformations is equivalent to a Hartree-Fock diagonalization of the electronic Hamiltonian and produces the uncorrelated mean field Hamiltonian:

$$H_o = \sum_k E_k (a_{k\sigma}^\dagger a_{k\sigma} + a_{k\sigma}^\dagger (a_{k\sigma} a_{k\sigma}^*) + 2NKu^2$$

where $E_k$ is the HF energy of a quasi-particle, $a_{k\sigma\pm}$, with wavevector $k$ in the first reduced Brillouin zone of the system, $-\pi/2a < k < \pi/2a$. We also define + to correspond to states above the Fermi-energy (particles) and – to those below (holes). The single-particle energy, $E_k = \sqrt{E_k^2 + \Delta_k^2}$, is a function of the unperturbed band energy, $\epsilon_k = 2t_0 \cos(k a)$, and the phonon-induced energy gap, $\Delta_k(u) = 2\omega u \sin(ka)$. A plot of the Hartree-Fock ground state energy surface in shown in Fig 2c.

In this paper we are primarily interested in the details of computational algorithm and method. In order to make our consideration as model independent as possible we take the following general form of the residual interaction:

$$H_{int} = \sum_{kk'} \sum_{q\sigma\sigma'} V(q) a_{k\sigma\pm}^\dagger a_{k'\sigma\pm} a_{k-q\sigma\pm} a_{k'+q\sigma\pm}$$

where the interaction $V(q)$ is just a Fourier transformation of the physically meaningful interaction in coordinate representation (with $U = 0.01$ eV and $r_o = a$):
Using the 2-body interaction of this form (with $U = 0.01 \text{ eV}$ and $r_o = a$) and the description of the ground state given above, we integrated the RPA equations (Eq. 57 and Eq. 58) in $k$-space over the first reduced Brillouin zone using the Verlet algorithm for both the RPA amplitudes and classical coordinate. In all of our runs, we monitored the orthogonality of the amplitudes and re-orthogonalized whenever the orthogonality strayed from unity by 1 part in $10^6$. In the first example, we chose our initial excited state such that $X_{ph}$ corresponded to the first CI(singles) triplet state and $Y_{ph} = 0$. In all of these calculations, the fictitious electronic mass was chosen to be $\mu = 400 \text{ a.u.}$ and the classical mass to be that of a -CH- monomer ($m = 26000\text{a.u.}$).

In the first example, shown in Fig. 2a, we started from purely random distribution of initial amplitudes for $X$ and $Y$ again with $u(0) = 0.1\text{Å}$. As before, we dampened the RPA velocities to attempt to cool the system down to the excited state Born-Oppenheimer energy. Notice, that the system rapidly finds the lowest energy configuration of the excited state surface and begins to oscillate on the BO surface after only a few periods. This demonstrates the utility of our method in determining very rapidly minimal energy configurations on the excited state energy surface.

In the next example, our initial excited state was taken to be an eigenstate of the $A$ matrix (equivalent to the CI singles matrix) with orbital angular momentum 1 (triplet state). Starting from a lattice distortion of $u=0.1\text{Å}$, we solved the full RPA equations of motion with the inclusion of a term to dampen the RPA amplitude velocities. This helped to keep the electronic velocities in sufficient check and prevented significant excursions from the excited state Born-Oppenheimer energy surface. The results of this calculation are shown in Fig. 2b. Here we have plotted the excitation energy, $\omega$ as a function of $u$ as the RPA amplitudes are quenched to their minimal values. Notice, however, that even though we kept the electronic velocities fairly ”cool”, there is some ”fuzziness” to our energy surface. This is partially due to the fact that our initial state was not an exact solution to the RPA equations and to the fact that there is some dynamical coupling between the motions of the amplitudes and the classical degrees of freedom. Thus, the RPA amplitudes acquire a small amount of velocity as they are quenched to the final solutions.

A final comment regarding the computational efficiency of our approach is in due order. First of all, in the calculations presented herein, we made use of an analytic representation of the ground state orbitals and energies. In general, one will need to determine these for each new molecular configuration either by using integrating the ground state CP equations or by converging the KS or HF equations. Assuming we were handed a set of single particle orbitals, we can compare the computational cost associated with each molecular dynamics step in the RPA with the cost required to setup and diagonalize the CI singles (CIS) matrix. In Fig. 4, we show the ratio of CPU times required to perform a CIS calculation versus the effort required to perform a similar sized single MD time-step using the RPA/MD method developed here as run on an SGI Origin2000 (on a single 195 MHz R10000 processor). In each case, the RPA/MD results were between 2 to 10 times as fast per time-step as diagonalizing the CI matrix with performance degrading with the size of the number of particle/hole states used. The CIS results reported are the CPU times required for the construction and diagonalization of the CIS matrix (converging only the lowest eigenstate) and does not include the additional effort need to compute analytical gradients which are needed in order to perform any sort of molecular dynamics on the excited state surface. Finally, we note that the each RPA/MD step requires the construct of both the $A$ and $B$ matrices whereas CIS requires only the $A$ matrix.

We also point out that the majority of the CPU effort per time-step went into the construction of the two-body interaction matrix elements. These matrix elements, along with the single particle orbitals, must be in hand at every time step and are a necessary component of any many-body treatment of the excited states. This effort scales as $\approx N_p^2$ due to the transformation between the quasi-particle basis and the lattice representation. For larger calculations involving the combination of many particle/hole state, this part of the calculation dominates the effort. Furthermore, in a full implementation of this scheme, one is required to diagonalize the HF or KS matrix to obtain the orbitals above the Fermi-energy. This too, adds to the net effort as it scales as $\approx N_s^2$. In a general plane-wave implementation of this methods, we can utilize efficient and scalable multi-dimensional fast Fourier transformation algorithms and matrix-diagonalization methods to facilitate these two phases of the calculation.

V. DISCUSSION

In this paper, we have presented a theoretical scheme for doing molecular dynamics simulations of electronically excited systems within the HF(KS)+random phase approximation. In the spirit of Car and Parrinello, we treat the
RPA amplitudes, the single particle orbitals, and the nuclear coordinates as dynamical variables subject to a set of holonomic constraints which enforce the orthogonality relations of the RPA amplitudes and orbitals.

As mentioned in the introduction, the two primary computational cost incurred in applying the CPMD scheme are enforcing the orthogonality constraints between the single particle states and the small time-step required to integrate the CP equations. As mentioned above, the constraint part of each iteration scales as \( \sim M \times N^2 \). In the present scheme, we have and additional set of constraints for the orthogonality of the RPA states. Likewise, the evaluation of the RPA constraint should scale as \( \sim M_{\text{rpa}} \times N_{\text{RPA}}^2 \) where \( M_{\text{rpa}} \) is the number of particle-hole basis states used to construct the RPA excitation and \( N_{\text{RPA}} \) the number of RPA excitations in the system. Since we are primarily interested in systems with one RPA excitations and we can restrict the excitation to a limited number of particle-hole states, the added constraint does not pose a substantial increase in the computational effort. Furthermore, the orthogonality between the RPA state and the ground state is implicit in the construction of the RPA state and, hence, imposes no additional difficulties. Note, that this would not be the case had we chosen a perturbative construction of the excited state.

A sample calculation on an albeit simple model system produces exact agreement with analytical results. While this model avoids a number of computational difficulties in using this approach, it does give an indication of how the equations of motion can be applied. The more realistic simulations of the excited state dynamics of one-dimension polymer chains demonstrate that our proposed approach is much more computationally advantageous since it considerably decreases the computational efforts over the direct solution of the RPA eigen-problem. We are currently developing a much more realistic and generalizable application of our excited states molecular dynamics for simulating the photo-excitation dynamics in \( \pi \)-conjugated systems such as conducting polymers, as well as the inclusion of transitions between RPA states, such as non-radiative triplet-singlet transitions.

ACKNOWLEDGMENTS

This work was supported in part by the R. A. Welch Foundation (E-1337) and by the National Science Foundation (CHE-9713681).

APPENDIX A: EVALUATION OF FUNCTIONAL DERIVATIVES

In this Appendix we compute the various functional derivatives of the RPA energy functional needed to solve the dynamical RPA equations presented above.

1. Hellmann-Feynman forces for excited states

We first invoke the Hellmann-Feynman theorem to provide the forces for the evolution of the nuclei on the Born-Oppenheimer energy surface of the RPA excitations.

\[
\frac{\delta E_{\text{ex}}[\phi, X, Y, \mathbf{R}]}{\delta \mathbf{R}} = \frac{\delta \langle \text{RPA}|Q_{\mu i} \hat{H} Q_{\mu i}^\dagger| \text{RPA} \rangle}{\delta \mathbf{R}}
\]  

(A1)

The Hellmann-Feynman theorem is indeed valid for the RPA excited states, since

\[
\frac{\delta \langle \text{RPA}|Q_{\mu i} Q_{\mu i}^\dagger| \text{RPA} \rangle}{\delta \mathbf{R}} = \frac{\delta \langle \text{RPA}| \left[ Q_{\mu i}, Q_{\mu i}^\dagger \right] | \text{RPA} \rangle}{\delta \mathbf{R}} = 0
\]  

(A2)

Thus,

\[
\frac{\delta E_{\text{ex}}[\phi, X, Y, \mathbf{R}]}{\delta \mathbf{R}} = \langle \text{RPA}|Q_{\mu i} \frac{\partial H}{\partial \mathbf{R}} Q_{\mu i}^\dagger| \text{RPA} \rangle
\]  

(A3)

To calculate this matrix element we first rewrite the gradient of \( H_2 \) with respect to the nuclear coordinates in a second quantized form in the basis of electron creation and annihilation operators:

\[
\frac{\partial H}{\partial \mathbf{R}} = \sum_{ij} \langle i | \frac{\partial H}{\partial \mathbf{R}} | j \rangle \sum_{\sigma} a_{i\sigma}^\dagger a_{j\sigma}.
\]  

(A4)
Here the matrix element

\[ (i | \frac{\partial H}{\partial \mathbf{R}} | j) = \int dr \phi_i^*(r) \frac{\partial H}{\partial \mathbf{R}} \phi_j(r) \]  

(A5)

Using this, one can easily show

\[ \langle \text{RPA} | Q_\mu \frac{\partial H}{\partial \mathbf{R}} Q_\mu^\dagger | \text{RPA} \rangle = \langle \text{RPA} \frac{\partial H}{\partial \mathbf{R}} | \text{RPA} \rangle + \langle \text{RPA} \left[ Q_{\mu i}, \left[ \frac{\partial H}{\partial \mathbf{R}}, Q_{\mu i}^\dagger \right] \right] | \text{RPA} \rangle \]  

(A6)

Neglecting the polarization fluctuation in HF vacuum, we arrive at the following expression for the classical forces:

\[ \langle \text{RPA} | Q_\mu \frac{\partial H}{\partial \mathbf{R}} Q_\mu^\dagger | \text{RPA} \rangle = 2 \sum_{hh} (h | \frac{\partial H}{\partial \mathbf{R}} | h) + \sum_{p p' h h'} (h | \frac{\partial H}{\partial \mathbf{R}} | h') \left( X_{p h}^i X_{p h'}^i \phi_i | \phi_i \right) \]  

\[ + \sum_{p p' h h'} (h | \frac{\partial H}{\partial \mathbf{R}} | h') \left( Y_{p h}^i Y_{p h'}^i \phi_i | \phi_i \right) \]  

(A7)

where the first term is simply the ground state Hellmann-Feynman force and the remaining terms are due to the electronic excitations.

2. Functional derivatives for the amplitude motions.

The functional derivatives for the evolution of the RPA state and HF vacuum are straightforward to compute and are presented below.

a. The functional derivative of the HF energy with respect to the single particle/hole states.

\[ \frac{\delta E_{HF}[\phi, \mathbf{R}]}{\delta \phi_i(1)} = \frac{\delta}{\delta \phi_i(1)} \sum_{j} \text{occ} \int d2d3\phi_j^*(2)\phi_j(3) H(23; \rho) \]  

\[ = \int d2\phi_i^*(2) H(21; \rho) + \left( \int d4\phi_i^*(4) \right) \sum_{j} \text{occ} \langle \phi_j | \frac{\delta H[\rho]}{\delta \rho} | \phi_j \rangle \]  

(A8)

b. Functional derivatives for the RPA amplitudes

First, in vector form

\[ \frac{\delta \omega_k}{\delta (X_k)} = A | X_k \rangle + B | Y_k \rangle \]  

(A9)

and

\[ \frac{\delta \omega_k}{\delta (Y_k)} = B | X_k \rangle + A | Y_k \rangle . \]  

(A10)

Written in terms of the components:
\[
\frac{\delta \omega_k[\phi, X, Y, R]}{\delta X_{ph}^k} = \sum_{p'h'} (A_{p'h'} X_{p'h'}^k + B_{p'h'} Y_{p'h'}^k) \tag{A11}
\]

\[
\frac{\delta \omega_k[\phi, X, Y, R]}{\delta Y_{ph}^k} = \sum_{p'h'} (A_{p'h'} Y_{p'h'}^k + B_{p'h'} X_{p'h'}^k) \tag{A12}
\]

**APPENDIX B: DYNAMICAL CALCULATION OF THE LAGRANGE MULTIPLIERS FOR THE RPA EXCITED STATES**

The evolution of excited states is subject to holonomic constraints which enforce the orthogonality of the RPA amplitudes, (Eq. 29). Because of this, we have constraint forces \(-\Gamma_{kk} X_{ph}^k\) and \(\Gamma_{kk} Y_{ph}^k\) in the dynamical equations (Eq. 57 and Eq. 58) which keep the RPA amplitudes on the constrained surface. However, the Lagrange multiplier \(\Gamma\) is unknown.

Denote by

\[
\sigma_k = \sum_{ph} X_{ph}^k X_{ph}^k - Y_{ph}^k Y_{ph}^k - 1. \tag{B1}
\]

Since \(\sigma_k\) is the integral of motion for the differential equations (Eq.57 and Eq. 58), the first and second time derivatives of \(\sigma_k\) should be zero.

\[
\dot{\sigma}_k = \left(2 \sum_{ph} \dot{X}_{ph}^k X_{ph}^k - \dot{Y}_{ph}^k Y_{ph}^k\right) + \sum_{ph} \left(\ddot{X}_{ph}^k Y_{ph}^k + X_{ph}^k \ddot{X}_{ph}^k - \ddot{Y}_{ph}^k Y_{ph}^k - Y_{ph}^k \ddot{Y}_{ph}^k\right) \tag{B2}
\]

We can then eliminate the “amplitudes accelerations” \(\ddot{X}_{ph}^k, \ddot{Y}_{ph}^k, \dddot{X}_{ph}^k, \dddot{Y}_{ph}^k\) by the use of the RPA equation of motion. From these considerations, we obtain the expression for the Lagrange multiplier \(\Gamma_{kk}\):

\[
\Gamma_{kk} = -\frac{1}{2 \sum_{ph} X_{ph}^k X_{ph}^k + Y_{ph}^k Y_{ph}^k} \times \sum_{ph} \left(2 \mu(X_{ph}^k \dot{X}_{ph}^k - \dot{Y}_{ph}^k Y_{ph}^k)\right) - \frac{\delta \omega}{\delta X_{ph}^k} X_{ph}^k - \frac{\delta \omega}{\delta Y_{ph}^k} Y_{ph}^k + \frac{\delta \omega}{\delta X_{ph}^k} X_{ph}^k + \frac{\delta \omega}{\delta Y_{ph}^k} Y_{ph}^k \right] \tag{B3}
\]

1. R. Car and M. Parrinello, Phys. Rev. Lett. 55, 2471 (1985).
2. R. Car and M. Parrinello, *Simple Molecular Systems at Very High Density*, Plenum, New York, 1981.
3. G. Galli and M. Parrinello, *Computer Simulations in Material Science*, Kluwer, Dordrecht, 1991.
4. P. Hohenberg and W. Kohn, Phys. Rev. 136, 864 (B) (1964).
5. M. E. Tuckerman and M. Parrinello, J. Chem. Phys. 101, 1302 (1994).
6. M. E. Tuckerman and M. Parrinello, J. Chem. Phys. 101, 1316 (1994).
7. W. Kohn and L. J. Sham, Phys. Rev. 140, 1133 (A) (1965).
8. M. Pearson, E. Smatgiasi, and P. Madden, J. Phys. Condens. Matter 5, 3221 (1993).
9. A. Alavi, J. Kohanoff, M. Parrinello, and D. Frenkel, Phys. Rev. Lett. 73, 2599 (1994).
10. P. L. Silvestrelli, A. Alavi, M. Parrinello, and D. Frenkel, Phys. Rev. Lett. 77, 3149 (1996).
11. A. Messiah, Quantum Mechanics (J.Wiley&Sons, Inc., New York, 1968).
12. H. Goldstein, Classical Mechanics (Addison-Wesley, Reading, MA, 1980).
13. J. W. Negele and H. Orland, Quantum Many Particle Systems (Addison-Wesley, Redwood City, CA, 1988).
14. D. J. Rowe, Nuclear Collective Motion (Methuen,London, 1970).
15. J. Blaizot and G. Ripka, Quantum theory of finite systems (MIT Press, Cambridge, MA, 1988).
16. A. K. Kerman and S. E. Koonin, Ann. Phys. 100, 332 (1976).
17. M. Petersilka, U.L. Grossmann, E.K.U. Gross, Phys.Rev.Lett. 76, 1212 (1996).
18. R. Bauernschmitt, R.Ahlrichs, Chem.Phys.Lett. 256, 454 (1996).
19. K. Yabana and G.F. Bertsch, Preprint LANL physics/9808013.
20. D. L. Yeager and V. McKoy, J. Chem. Phys. 63, 4881 (1975).
21. A. C. Lasaga and M. Karplus, J. Chem. Phys. 71, 1218 (1979).
22. H. Ito, H. Kameshima and T.-i. Shibuya, J. Chem. Phys. 104, 1309 (1996).
23. M. Baldo and R. Pucci, J. Chem. Phys. 67, 4747 (1977).
24. J. Olsen and P. Jørgensen, J. Chem. Phys. 82, 3235 (1985).
25. P. Ring and P. Schuck, The nuclear many-body problem, (New York : Springer-Verlag, 1979).
26. J. V. Ortiz J. Chem. Phys. 101, 6743 (1994).
27. H. J. Lipkin, N. Meshkov, and A. J. Glick, Nucl. Phys. 62, 188 (1965).
28. D. S. Kosov and E. R. Bittner, (1998), in prepartation.
29. A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W.-P. Su, Rev. Mod. Phys. 60, 781 (1988).
30. L. Verlet, Phys. Rev. 159, 98 (1967); Phys. Rev. 165, 201 (1968).
31. H. Hellmann, Einführung in die Quantenchemie (Deuticke, Leipzig, 1937).
32. R. P. Feynman, Phys. Rev 56, 340 (1939).
FIG. 1. The evolution of the RPA amplitude $Y$ (a.) and the displacement $q$ (b.) in the classically-extended-SU(2) model. The dashed line is for simplified ground state CPMD; the result of our approach is shown by solid line. The following set of parameters is used in this calculation: $\mu = M = 1, \epsilon = 1, V = 0.06, N = 10, (d\epsilon/dr)_{R_0} = 0.1, (dV/dR)_{R_0} = 0.06, K = 10$.

FIG. 2. Energy surfaces for ground and excited states for linear polyene model. (a.) Excited state molecular dynamics starting from a random RPA vector converging to the excited state Born-Oppenheimer energy surface. The excited state energy surface is the sum of the excitation energy and the ground state surface plotted in c. Here, only the energy difference is plotted. (b.) Excited state molecular dynamics starting from the lowest triplet CI(S) eigenstate. As in a., only the energy difference between the triplet and ground state is shown. (c.) Ground state Born-Oppenheimer surface. Note the change in energy scale between the ground and excited state plots. See text for details.

FIG. 3. Comparison of CPU effort for RPA/MD vs CI(S) per molecular dynamics time step as a function of the number of particle/hole states. In both cases, the effort to construct the two body interactions is included; however, the CI(S) does not include the effort required to compute energy gradients. As the number of particle/hole states increases, this becomes the dominant part of the effort.
(a.) RPA Amplitude

(b.) Classical Coordinate

Y

q

RPA/MD

Ground State
# p/h states

RPA/MD

CI (Singles)