

Derivation of the RPA (Random Phase Approximation) Equation of ATDDFT (Adiabatic Time Dependent Density Functional Ground State Response Theory) from an Excited State Variational Approach Based on the Ground State Functional

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S Supporting Information

ABSTRACT: The random phase approximation (RPA) equation of adiabatic time dependent density functional ground state response theory (ATDDFT) has been used extensively in studies of excited states. It extracts information about excited states from frequency dependent ground state response properties and avoids, thus, in an elegant way, direct Kohn–Sham calculations on excited states in accordance with the status of DFT as a ground state theory. Thus, excitation energies can be found as resonance poles of frequency dependent ground state polarizability from the eigenvalues of the RPA equation. ATDDFT is approximate in that it makes use of a frequency independent energy kernel derived from the ground state functional. It is shown in this study that one can derive the RPA equation of ATDDFT from a purely variational approach in which stationary states above the ground state are located using our constricted variational DFT (CV-DFT) method and the ground state functional. Thus, locating stationary states above the ground state due to one-electron excitations with a ground state functional is completely equivalent to solving the RPA equation of TDDFT employing the same functional. The present study is an extension of a previous work in which we demonstrated the equivalence between ATDDFT and CV-DFT within the Tamm–Dancoff approximation.



I. INTRODUCTION

In wave function theory excited states have been studied by both ground state response methods and excited state variational theories.^{1,2} In general, both approaches are considered well founded, and in principle, they are able to afford estimates to any desired degree of accuracy. It is thus not surprising that the random phase approximation (RPA) equation in wave function theory has been derived from both a response and a variational point of view.^{1,2} In Kohn–Sham density functional theory the natural path to excited states would seem to be the ground state response approach given the status of KS-DFT as a ground state theory. Indeed, Runge and Gross³ have formulated a time dependent density functional ground state response theory (TDDFT)³ that, in principle, should be able to describe excited state properties without approximations. The exact TDDFT requires the knowledge of the “true” ground state functional as well as the frequency dependence of the energy response kernel related to this functional. In practice, one has to resort to approximate ground state functionals and neglect the frequency dependence of the kernel in what has now become known as the adiabatic

TDDFT approach (ATDDFT).^{4–9} Over the past 20 years, the ATDDFT approach has become the workhorse in DFT based studies of excited states and its strengths and weaknesses are well documented.^{10–33} On the other hand progress beyond the adiabatic approximation has been slow although work in this direction is ongoing.^{34–36} In DFT, all derivations of the RPA equation have been over the response route whereas no full variational derivation seems to have been given. We attribute this to the status of DFT as a ground state theory. A possible exception is the work of Furche, as discussed later.⁸

The variational DFT approach to excited states predates TDDFT with the work by Slater.³⁷ He introduced the Δ SCF procedure in which excited states are reached by promoting electrons from occupied to virtual ground state levels followed by a KS calculation on the new electron configuration. The procedure works well in practice for those lower excited states that can be represented by a single orbital replacement. However, it is riddled with SCF-convergence problems and

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deemed ad hoc and without any theoretical foundation as it applies a ground state functional in a variational excited state calculation. However, Van Voorhis et al.³⁸ have recently put forward some theoretical justification for Δ SCF.

The application of the ground state functional by Slater and others^{38–40} to variational excited state calculations seems intuitively appealing from the point of view that electron correlation should be quite similar in the ground and excited states, at least in the lower valence region. A step toward the formal justification of using ground state functionals in variational excited state calculations was taken in 2009 when we demonstrated²⁹ that the adiabatic TDDFT approach based on ground state response theory with the further use of the Tamm–Dancoff approximation (TDA)⁴¹ affords the same expression for the excitation energies as our second order Constraint Variational DFT method using the ground state functional and the TDA. Thus, ATDDFT/TDA can be derived from a variational principle using the ground state functional. In the present study, we take a further step by demonstrating that the complete random phase approximation (RPA) equation^{3–9} of adiabatic time dependent density functional ground state response theory without the Tamm–Dancoff approximation can be derived from an excited state time dependent variational approach using the ground state functional.

The ultimate goal and objective in this study is to pave the way for improvements of the DFT based RPA equation. This is, in our opinion, more easily done through a variational approach than by the construction of frequency dependent kernels. In fact, in our self-consistent all orders constricted variational DFT method with full orbital relaxation RSCF-CV(∞)-DFT, we have effectively taken steps in that direction.^{26,27,30}

2. RESULTS AND DISCUSSION

The DFT based constricted variational DFT method (CV-DFT)^{28,29} for excited states requires in the first place the construction of a variational excited state KS determinant Ψ' and the related variational Lagrangian L expressed in terms of a set of variational parameters $\{P_i; i = 1, M\}$ as $\Psi'[P]$ and $L[P]$, respectively. After that excited state, number I is located as an extremum points for which the Lagrangian $L[P^I + \delta P]$ generated from $\Psi'[P^I + \delta P] = \Psi'[P^I] + \delta\Psi'[P^I + \delta P]$ satisfy $\delta L = L[P^I + \delta P] = 0$ to first order in δP where δP is an arbitrary variation within the given parameter space. Further, the vector P^{I*} must satisfy $P^{I\dagger}P^K = 0$ with $K = 1, I - 1$ representing excited states of lower energy as well as $K = 0$ corresponding to the ground state.

It follows from the procedure above that any change in a stationary excited state KS determinant induced by a static (time independent) perturbation to first order leaves $L[P^I]$ unchanged. Further, such changes in Ψ' can in general be parametrized and represented by δP . We have in our CV-DFT method up to now restricted the variations δP to those cases that, in principle, are related to static perturbations. However, excited states are not only subject to static perturbations in terms of time independent magnetic and electric fields. They can be perturbed as well by a field that oscillates in time with a frequency ω . Thus, $L[P^I]$ should also be stationary with respect to variations δP that are induced by oscillating fields. In fact, it will be shown that introducing certain types of time oscillating variations $\delta P(\omega t)$ makes it possible to derive the full RPA equation of ATDDFT where we previously only were able to derive the RPA equation for ATDDFT/TDA with static

variations δP .^{28,29} We shall now first introduce the salient features of time dependent variation theory.^{42–45}

2.1. Time Dependent Variation Theory. It is possible to find approximate solutions to the time dependent Schrödinger equation given in atomic units as

$$\hat{H}(t, x)\Psi(t, x) = i\frac{\partial\Psi(t, x)}{\partial t} \quad (1)$$

where t indicates time and x all the particle coordinates. Such solutions $\Psi(t, x)$ must satisfy the Frenkel equation⁴²

$$\left\langle \delta\Psi(t, x) \left| \left(H(t, x) - i\hbar\frac{\partial}{\partial t} \right) \right| \Psi(t, x) \right\rangle = 0 \quad (2)$$

where $\delta\Psi(t, x)$ is an arbitrary variation perpendicular to $\Psi(t, x)$ and everything between the ket and the bra is integrated over x but not t . Equation 2 can be derived from an extremum condition

$$\delta\Gamma = \delta \int_{t_1}^{t_2} dt \int_x L dx = \int_{t_1}^{t_2} \delta L dt = 0 \quad (3)$$

using Hamilton's principle of least action⁴³ and the Lagrangian density^{43–45}

$$\mathcal{L} = \Psi^*(t, x)\hat{H}(t, x)\Psi(t, x) - i/2[\Psi^*(t, x)\dot{\Psi}(t, x) - \dot{\Psi}^*(t, x)\Psi(t, x)] \quad (4)$$

We shall in the following make use of eq 3 rather than the equivalent equation due to Frenkel as eq 3 actually clearly states⁴⁶ what we are optimizing in the variational procedure.

The variational wave function has in general the form^{43–46}

$$\Psi(t, x) = g(t) \frac{\Phi[P(t); x]}{\langle \Phi | \Phi \rangle^{1/2}} \quad (5)$$

where $\{P_i(t); i = 1, M\}$ is a set of variational parameters⁴⁴ that possibly might be time dependent. In our case, we shall employ a more limited form of $\Psi(t, x)$ in which $g(t) = 1$ and $P(t)$ is periodic with the period $\Delta t = 2\pi\omega^{-1}$. Further, in the general case,

$$\hat{H}(t, x) = \hat{H}^0(x) + \hat{H}'(t) \quad (6)$$

However, we shall adopt a time independent Hamilton given solely by $\hat{H}^0(x)$. Thus, the only reason for our time dependent treatment is that we shall assume that $P(t)$ is periodic or oscillatory in time.

Returning now to the extremum condition of eq 3, we have by the use of eqs 5 and 6

$$\Gamma = \int_{t_1}^{t_2} \delta t \left[\frac{\langle \Phi(P) | \hat{H}^0 | \Phi(P) \rangle}{\langle \Phi(P) | \Phi(P) \rangle} - \frac{i}{2} \frac{\langle \Phi(P) | \dot{\Phi}(P) \rangle - \langle \dot{\Phi}(P) | \Phi(P) \rangle}{\langle \Phi(P) | \Phi(P) \rangle} \right] = \int_{t_1}^{t_2} L \delta t \quad (7)$$

where $\dot{\Phi}(P(t)) = \delta\Phi(P(t))/\delta t$.

2.2. Variational Parametrization of the Excited State Kohn–Sham Determinants. In constricted variational density functional theory (CV(n)-DFT) we construct excited state KS-orbitals by performing a unitary transformation^{28,29} among occupied $\{\psi_i; i = 1, occ\}$ and virtual $\{\psi_a; a = 1, vir\}$ ground state orbitals

$$R \begin{pmatrix} \psi_{occ} \\ \psi_{vir} \end{pmatrix} = e^U \begin{pmatrix} \psi_{occ} \\ \psi_{vir} \end{pmatrix} = \left(\sum_{m=0}^{\infty} \frac{U^m}{m!} \right) \begin{pmatrix} \psi_{occ} \\ \psi_{vir} \end{pmatrix} = \begin{pmatrix} \psi'_{occ} \\ \psi'_{vir} \end{pmatrix} \quad (8a)$$

which can be truncated to order $m = n$.

Here, ψ_{occ} and ψ_{vir} are concatenated column vectors containing the sets of occupied $\{\psi_i; i = 1, occ\}$ and virtual $\{\psi_a; a = 1, vir\}$ ground state (or reference) KS-orbitals. The resulting ψ'_{occ} and ψ'_{vir} are concatenated column vectors which contain the sets $\{\psi'_i; i = 1, occ\}$ and $\{\psi'_a; a = 1, vir\}$ of occupied and virtual excited state orbitals, respectively, which we shall assume to be real. The unitary transformation matrix R is in eq 8a expressed in terms of a skew symmetric matrix U as

$$R = e^U = I + U + \frac{U^2}{2} + \dots = \sum_{m=0}^{\infty} \frac{U^m}{m!} \\ = \sum_{m=0}^{\infty} \frac{(U^2)^m}{2m!} + U \sum_{m=0}^{\infty} \frac{(U^2)^m}{(2m+1)!} \quad (8b)$$

Here, $U_{ij} = U_{ab} = 0$ where “ ij ” refer to the occupied set $\{\psi_i; i = 1, occ\}$ whereas “ ab ” refer to $\{\psi_a; a = 1, vir\}$. Further, U_{ai} is a variational mixing matrix element that combines virtual and occupied ground state (reference) orbitals in the excited state with $U_{ai} = -U_{ai}^*$. Thus, the entire matrix U is made up of $occ \times vir$ independent elements U_{ai} . We shall on occasion also consider U as a column vector where the index (ai) now runs over pairs of virtual and occupied orbitals of the same spin. For a given U we can by the help of 8a generate a set of “occupied” excited state orbitals

$$\psi'_i = \sum_p^{occ+vir} R_{pi} \psi_p = \sum_j^{occ} R_{ji} \psi_j + \sum_a^{vir} R_{ai} \psi_a \quad (9)$$

that are orthonormal to order n in U_{ai} . We shall assume that the orbitals in eq 9 are generated from a nonrelativistic ground state calculation and thus can be considered real. A generalization to complex relativistic ground state orbitals is straightforward but will not be considered here.

To second order in U the excited state occupied orbitals are given by²⁹

$$\psi_i^{\alpha'} = \psi_i^{\alpha} + \sum_a^{vir(\alpha)} U_{ai}^{\alpha\alpha} \psi_a^{\alpha} - \frac{1}{2} \sum_j^{occ(\alpha)} \sum_b^{vir(\alpha)} U_{bi}^{\alpha\alpha} U_{bj}^{\alpha\alpha*} \psi_j^{\alpha} \quad (10a)$$

$$\psi_i^{\beta'} = \psi_i^{\beta} + \sum_a^{vir(\beta)} U_{ai}^{\beta\beta} \psi_a^{\beta} - \frac{1}{2} \sum_j^{occ(\beta)} \sum_b^{vir(\beta)} U_{bi}^{\beta\beta} U_{bj}^{\beta\beta*} \psi_j^{\beta} \quad (10b)$$

from which we can construct the excited state KS-determinant

$$\Psi'[U, x] = |\psi_1^{\alpha'} \dots \psi_i^{\alpha'} \psi_j^{\alpha'} \dots \psi_{n(\alpha)}^{\alpha'} \psi_1^{\beta'} \dots \psi_i^{\beta'} \psi_j^{\beta'} \dots \psi_{n(\beta)}^{\beta'}| \quad (11)$$

as a variational wave function $\Psi'[U, x]$ similar to $\Phi[P(t); x]$ of eq 5. The orbitals in eq 10 correspond to spin conserving transitions as they are considered in regular TDDFT. It is also possible to treat spin-flip transitions by the same procedure outlined below with the help of noncolinear DFT;^{47–49} however, this will not be shown here.

As already mentioned, a parametrization of the KS determinant $\Psi'[P]$ where P is time independent led after an optimization of the associated KS energy with respect to static variations δP to the approximate RPA equation of ATDDFT in

which the TDA has been invoked.^{29,30} We shall now with $P(t) = U(t)$ introduce a periodic time dependence with the period $\Delta t = 2\pi\omega^{-1}$ and frequency $\omega [\sim 10^{-14} \text{ s}]$ in order to recover the full RPA equation. This will be done in two steps. We explore in the first a simple frequency dependent parametrization that still recovers the ATDDFT/TD equations but introduce the aspects of time dependent variation theory. In the second step, we introduce a frequency dependent variation that now leads to the full RPA equation.

2.3. Variational Derivation of RPA Equation within the Tamm–Dancoff Approximation. Starting with the simple frequency dependent parametrization we write⁴⁴

$$U_{ai} = X_{ai} e^{-i\omega t} \quad (12)$$

for all elements. The parameter ω is assumed to be a real constant that is to be determined in such a way that $\Psi'[U, x]$ represents a stationary state subject to certain constraints that will be specified shortly. In eq 12 X_{ai} has the same properties as stated for U_{ai} above aside from being time independent. Please note that $U = 0$ corresponds to the ground state. In the ground state, $\Psi(U, x)$ of eq 11 becomes equal to the time independent ground state KS-determinant $\Psi(0, x)$. This can be seen by substituting eqs 10 with $U = 0$ into eq 11.

We can next obtain $E'_{KS}[U]$ from $\Psi'[U, x]$ by first using the occupied KS-orbitals $\{\psi'_i, i = 1, n\}$ of eq 10 to construct the KS density to second order in U as

$$\rho^{(2)}(1, 1') = \sum_{\sigma}^{\alpha, \beta} \rho_{\sigma}^0 + \Delta \rho_{\sigma}^{(2)}(1, 1') \quad (13)$$

Here,

$$\Delta \rho_{\sigma}^{(2)}(1, 1') = \sum_i^{occ(\sigma)} \sum_a^{vir(\sigma)} U_{ai}^{\sigma\sigma} [\psi_i^{\sigma}(1) \psi_a^{\sigma}(1')] \\ + \psi_i^{\sigma}(1') \psi_a^{\sigma}(1) + \sum_i^{occ(\sigma)} \sum_a^{vir(\sigma)} U_{ai}^{\sigma\sigma*} [\psi_i^{\sigma}(1) \psi_a^{\sigma}(1') \\ + \psi_i^{\sigma}(1') \psi_a^{\sigma}(1)] - \sum_{i,j}^{occ(\sigma)} \sum_a^{vir(\sigma)} U_{ai}^{\sigma\sigma} U_{aj}^{\sigma\sigma*} \psi_i^{\sigma}(1') \psi_j^{\sigma}(1) \\ + \sum_i^{occ(\sigma)} \sum_{a,b}^{vir(\sigma)} U_{ai}^{\sigma\sigma} U_{bi}^{\sigma\sigma*} \psi_a^{\sigma}(1') \psi_b^{\sigma}(1) \quad (14)$$

$E'_{KS}[U]$ can now be obtained from the regular KS procedure as

$$E'_{KS}[U] = E_{KS}[\rho_{\alpha}^0 + \Delta \rho_{\alpha}^{(2)}(1, 1'); \rho_{\beta}^0 + \Delta \rho_{\beta}^{(2)}(1, 1')] \quad (15a)$$

We can further Taylor expand $E'_{KS}[U]$ out from the ground state energy $E_{KS}^0 = E_{KS}[\rho_{\alpha}^0; \rho_{\beta}^0]$ to afford to second order in $\Delta \rho_{\sigma}^{(2)}(1, 1')$

$$E'_{KS}[U] = E_{KS}^0 + \Delta E'_{KS}[U] \quad (15b)$$

where

$$\begin{aligned}\Delta E'_{KS}[U] = & \sum_{\sigma}^{\alpha,\beta} \int F_{KS}^{\sigma}[\rho_{\alpha}^0(1,1') + \Delta\rho_{\alpha}^{(2)}(1,1'); \rho_{\beta}^0(1,1') \\ & + \Delta\rho_{\beta}^{(2)}(1,1')] \Delta\rho_{\sigma}^{(2)}(1,1') dv_1 \\ & + \frac{1}{2} \sum_{\sigma}^{\alpha,\beta} \sum_{\tau}^{\alpha,\beta} \int \int \frac{\Delta\rho_{\sigma}^{(2)}(1) \Delta\rho_{\tau}^{(2)}(2)}{r_{12}} dv_1 dv_2 \\ & + \frac{1}{2} \sum_{\sigma}^{\alpha,\beta} \sum_{\tau}^{\alpha,\beta} \int \left(\frac{\delta^2 E_{XC}(1)}{\delta\rho_{\sigma} \delta\rho_{\tau}} \right)_0 \Delta\rho_{\sigma}^{(2)}(1) \Delta\rho_{\tau}^{(2)}(1) dv_1 \\ & + O^{[3]}(\Delta\rho_{\sigma}^{(2)})\end{aligned}\quad (16)$$

Expanding now $\Delta\rho_{\sigma}^{(2)}(1)$ in powers of U and keeping terms in the expression for $\Delta E'_{KS}[U]$ up to second order in U gives

$$\begin{aligned}\Delta E'_{KS}[U] = & \sum_{\sigma}^{\alpha,\beta} \sum_a^{vir(\sigma)} \sum_i^{occ(\sigma)} U_{ai}^{\sigma\sigma*} U_{ai}^{\sigma\sigma} [\varepsilon_a^{\sigma}(\rho^0) - \varepsilon_i^{\sigma}(\rho^0)] \\ & + \sum_a^{vir(\sigma)} \sum_b^{vir(\tau)} \sum_i^{occ(\sigma)} \sum_j^{occ(\tau)} U_{ai}^{\sigma\sigma*} U_{bj}^{\tau\tau} K_{aibj} \\ & + \frac{1}{2} \sum_a^{vir(\sigma)} \sum_b^{vir(\tau)} \sum_i^{occ(\sigma)} \sum_j^{occ(\tau)} U_{ai}^{\sigma\sigma*} U_{bj}^{\tau\tau} K_{aijb} \\ & + \frac{1}{2} \sum_a^{vir(\sigma)} \sum_b^{vir(\tau)} \sum_i^{occ(\sigma)} \sum_j^{occ(\tau)} U_{ai}^{\sigma\sigma} U_{bj}^{\tau\tau} K_{aijb}\end{aligned}\quad (17)$$

Further, making use of eq 12 affords

$$\begin{aligned}\Delta E'_{KS}[U] = & \sum_{\sigma}^{\alpha,\beta} \sum_a^{vir(\sigma)} \sum_i^{occ(\sigma)} X_{ai}^{\sigma\sigma*} X_{ai}^{\sigma\sigma} [\varepsilon_a^{\sigma}(\rho^0) - \varepsilon_i^{\sigma}(\rho^0)] \\ & + \sum_a^{vir(\sigma)} \sum_b^{vir(\tau)} \sum_i^{occ(\sigma)} \sum_j^{occ(\tau)} X_{ai}^{\sigma\sigma*} X_{bj}^{\tau\tau} K_{aibj} \\ & + \frac{1}{2} e^{2i\omega t} \sum_a^{vir(\sigma)} \sum_b^{vir(\tau)} \sum_i^{occ(\sigma)} \sum_j^{occ(\tau)} X_{ai}^{\sigma\sigma*} X_{bj}^{\tau\tau*} K_{aijb} \\ & + \frac{1}{2} e^{-2i\omega t} \sum_a^{vir(\sigma)} \sum_b^{vir(\tau)} \sum_i^{occ(\sigma)} \sum_j^{occ(\tau)} X_{ai}^{\sigma\sigma} X_{bj}^{\tau\tau} K_{aijb}\end{aligned}\quad (18)$$

Here, $\Delta E'_{KS}[U]$ is real as shown in section 1.4 of Supporting Information (SI) and the last two terms are further periodic in time.

In the equations above, $\varepsilon_a^{\sigma}(\rho^0)$ and $\varepsilon_i^{\sigma}(\rho^0)$ are the ground state orbital energies for ψ_a^{σ} and ψ_i^{σ} , respectively. Further

$$K_{pq,st} = K_{pq,st}^C + K_{pq,st}^{XC}\quad (19)$$

$$K_{pq,st}^C = \int \int \psi_p(1) \psi_q(1) \frac{1}{r_{12}} \psi_s(2) \psi_t(2) dv_1 dv_2\quad (20)$$

In addition, $K_{pq,st}^{XC}$ is given by

$$K_{pq,st}^{XC(HF)} = - \int \int \psi_p(1) \psi_q(1) \frac{1}{r_{12}} \psi_s(2) \psi_t(2) dv_1 dv_2\quad (21)$$

for Hartree–Fock exchange-correlation and by

$$K_{pq,st}^{XC(KS)} = \int \psi_p^{\mu}(\vec{r}_1) \psi_q^{\mu}(\vec{r}_1) f^{\mu\nu}(\vec{r}_1) \psi_s^{\nu}(\vec{r}_1) \psi_t^{\nu}(\vec{r}_1) d\vec{r}_1\quad (22)$$

for local KS exchange-correlation. The integration in eqs 20 and 21 is over space and spin whereas it is over space only in eq 22. The factor $f^{\mu\nu}(\vec{r}_1)$ in eq 22 represents the regular energy kernel

$$f^{\mu\nu} = \left(\frac{\partial^2 E_{XC}}{\partial\rho^{\mu} \partial\rho^{\nu}} \right)_0\quad (23)$$

given by the functional derivative of E_{XC} with respect to the density of electrons of μ, ν spin taken at the ground state reference.

We can also write eq 18 in a compact form as

$$\begin{aligned}\Delta E'_{KS}[U] = & U^{\dagger} A U + \frac{1}{2} U^{\dagger} B U^{*} + \frac{1}{2} U^{*\dagger} B U = X^{\dagger} A \\ & X + e^{2i\omega t} \frac{1}{2} X^{\dagger} B X^{*} + e^{-2i\omega t} \frac{1}{2} X^{*\dagger} B X\end{aligned}\quad (24a)$$

where

$$X^{\dagger} X = \sum_{\sigma}^{\alpha,\beta} \sum_a^{vir(\sigma)} \sum_i^{occ(\sigma)} X_{ai}^{\sigma\sigma*} X_{ai}^{\sigma\sigma}\quad (24b)$$

.Thus, X is a column vector with the element $X_{ai}^{\sigma\sigma}$ and X^{\dagger} is the corresponding row vector with the general element $X_{ai}^{\sigma\sigma*}$.

In eq 24a, A is the well-known Hermetian matrix

$$A_{a_i^{\sigma}, b_j^{\tau}} = [\varepsilon_a^{\sigma}(\rho^0) - \varepsilon_i^{\sigma}(\rho^0)] \delta_{a_i^{\sigma} b_j^{\tau}} + K_{a_i^{\sigma}, b_j^{\tau}}\quad (25)$$

that makes up the first part of the ground state Hessian.^{1,2} It is in our case real, since we shall be dealing with real ground state orbitals obtained from a nonrelativistic calculation. In eq 25, the two matrix indices (i^{σ}, a^{σ}) and (j^{τ}, b^{τ}) run over pairs of occupied and virtual ground state orbitals of the same spin starting with orbitals of α -spin. The real and hermetian matrix B in eq 24a is given by

$$B_{a_i^{\sigma}, b_j^{\tau}} = K_{a_i^{\sigma}, b_j^{\tau}}\quad (26)$$

It makes up the second part of the ground state Hessian.^{1,2} Returning now to the extremum condition of eq 6, we can make the transition from wave function to KS theory by the substitutions

$$\frac{\langle \Phi(P) | H^0 | \Phi(P) \rangle}{\langle \Phi(P) | \Phi(P) \rangle} \rightarrow E'_{KS}[\Psi'(U), H^0] = E_{KS}^0 + \Delta E'_{KS}[U]\quad (27)$$

and $\Phi(P) \rightarrow \Psi'(U)$, where $\Psi'(U)$ is the KS determinant and E_{KS}^0 the ground state energy. We thus get

$$\begin{aligned}\Gamma = & \int_{t_1}^{t_2} \delta t \left[E_{KS}^0 + \Delta E'_{KS}[U] \right. \\ & \left. - \frac{i}{2} \frac{\langle \Psi'(U) | \dot{\Psi}'(U) \rangle - \langle \dot{\Psi}'(U) | \Psi'(U) \rangle}{\langle \Psi'(U) | \Psi'(U) \rangle} \right] \\ = & \int_{t_1}^{t_2} L \delta t\end{aligned}\quad (28)$$

where $\Delta E'_{KS}[U]$ has been expressed in final form in eq 18. Turning next to the second term in eq 28, we obtain readily

$$-\frac{i}{2} \frac{\langle \Psi'(U) | \dot{\Psi}'(U) \rangle - \langle \dot{\Psi}'(U) | \Psi'(U) \rangle}{\langle \Psi'(U) | \Psi'(U) \rangle} = -\omega \sum_{ai} X_{ai}^{*} X_{ai}\quad (29)$$

as shown in sections 1.2 and 1.3 of SI, where it also is demonstrated that $\langle \Psi'(U) | \Psi'(U) \rangle = 1$ in sections 1.0 and 1.1. We have in eq 29 that $i\langle \Psi'(U) | \Psi'(U) \rangle / 2 = -i\langle \Psi'(U) | \Psi'(U) \rangle / 2$ since the frequency operator $-i\delta/\delta t$ is a hermitian operator for “normal” boundary conditions of $\Psi'(U)$. For a general oscillatory wave function written as a linear combination of stationary states

$$\Psi_{os} = \sum_k C_k \Psi_k e^{-i\omega_k t} \quad (30)$$

we have

$$\langle \omega \rangle = -i \int \langle \Psi_{os} | \dot{\Psi}_{os} \rangle dt = \sum_k \omega_k C_k^* C_k \quad (31)$$

where ω_k is the energy of the stationary state k relative to the ground state. In the case at hand with $U_{ai} = X_{ai} e^{-i\omega t}$ we see that $\langle \omega \rangle$ in eq 29 only has a contribution from the frequency used to define U_{ai} as one might have expected.⁴⁶

In order to satisfy the extremum condition

$$\delta \Gamma = \int_{t_1}^{t_2} \delta L dt = 0 \quad (32)$$

where

$$L = \Delta E'_{KS}[U, U^*] - \omega X^\dagger X \quad (33)$$

one might now continue with the general procedure outlined in the literature^{43–45}

However, here a different route will be adopted that makes use of the fact that eq 29 on the right-hand side is time independent in our special case.

Let now $\delta L = 0$ be satisfied for every time t by $U^I(t)$. This means that $\delta L = 0$ for the same set of parameters (X^I, X^{*I}, ω_I) throughout the interval (t_1, t_2) since our ansatz is $U^I = X^I e^{-i\omega t}$ rather than $U^I = X(t)^I e^{-i\omega(t)t}$. Further, $\delta L = 0$ should be satisfied by (X^I, ω_I) for any interval. We can thus integrate over the periodic interval $(t_1 = -\pi\omega^{-1}, t_2 = \pi\omega^{-1})$ in order to eliminate the time dependence and obtain an expression for $\Gamma(X, X^*, \omega)$ of eq 32 from which we can determine the set (X^I, ω_I) that satisfies the extremum condition.

We get from eq 26 and 29 after division by the length of the time interval $2\pi\omega^{-1}$

$$\frac{\omega}{2\pi} \int_{t_1}^{t_2} L dt \equiv \Gamma(X, X^*, \omega) = X^\dagger A X - \omega X^\dagger X \quad (34)$$

Substituting next $X = X^I + \delta X$ into eq 34 affords the following stability condition

$$X^{I\dagger} A \delta X + \delta X^{I\dagger} A X = -\omega_I \delta X^{I\dagger} X^I - \omega_I X^{I\dagger} \delta X = 0 \quad (35)$$

after collecting terms to first order in the variations $(\delta X, \delta X^*)$. Equation 35 is satisfied provided that X^I is a solution to

$$A X^I = \omega_I X^I \quad (36)$$

Here, we have used that A and ω_I both are real so that X^I will be real aside from an arbitrary phase factor. Equation 36 is identical to the RPA equation of adiabatic time dependent density functional ground state response theory within the Tamm–Dancoff approximation⁴¹ (ATDDFT/TD) in which B is neglected. However, we have derived eq 36 from the variational condition of eq 32 using a ground state functional to construct $\Delta E'_{KS}[U]$. A multiplication of eq 36 from the left with $X^{I\dagger}$ under the normalization condition $X^{*I} X^I = 1$ finally affords

$$X^{I\dagger} A X^I \equiv \Delta E'_{KS}/TD[X^I] = \omega_I \quad (37)$$

Thus, I is a stationary state under the constraint $X^{*I} X^I = 1$ provided that ω_I satisfies eq 37. We note that ω_I is positive and thus bound from below if the ground state corresponding to the Hessian A is stable. The stationary state I has a frequency expectation value $\langle \omega \rangle$ of ω_I . It is thus natural to refer to $[\Delta E'_{KS}/TD[X^I] = \omega_I]$ as the excitation energy for this state.

2.4. Variational Derivation of the Full RPA Equation.

We shall now introduce a new and more involved oscillatory ansatz⁴⁴

$$U_{ai} = X_{ai} e^{-i\omega t} + Y_{ai}^* e^{i\omega t} \quad (38)$$

that will afford the full RPA equation containing both the A and B matrix. The form of U is chosen in such a way that Γ after the time interval integration of L will have a contribution from B . Again ω is assumed to be a real constant that is to be determined in such a way that $\Psi'[U, x]$ represents a stationary state subject to certain constraints

With U defined according to eq 38 the last term in eq 13 representing $\langle \omega \rangle$ becomes

$$\begin{aligned} & -\frac{i}{2} \frac{\langle \Psi'(U) | \dot{\Psi}'(U) \rangle - \langle \dot{\Psi}'(U) | \Psi'(U) \rangle}{\langle \Psi'(U) | \Psi'(U) \rangle} \\ & = -\omega [X^\dagger X - Y^\dagger Y] \end{aligned} \quad (39)$$

as shown in section 1.6 of SI. Further, a time integration of $L[U, U^*]$ over the interval $(t_1 = -\pi\omega^{-1}, t_2 = \pi\omega^{-1})$ affords according to section 1.5 of SI

$$\begin{aligned} \Gamma & \equiv \frac{\omega}{2\pi} \int_{t_1}^{t_2} L[U, U^*] dt = X^\dagger A X + Y^\dagger A Y + X^\dagger B Y \\ & + Y^\dagger B X - \omega [X^\dagger X - Y^\dagger Y] \end{aligned} \quad (40)$$

Γ can alternatively be expressed as

$$\Gamma = (X^\dagger \ Y^\dagger) \begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} - \omega (X^\dagger \ Y^\dagger) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} \quad (41)$$

Next, we substitute $X = X^I + \delta X$ and $Y = Y^I + \delta Y$ as well as $X^\dagger = X^{I\dagger} + \delta X^\dagger$ and $Y^\dagger = Y^{I\dagger} + \delta Y^\dagger$ into eq 41 and expand in powers of the variations $(\delta X, \delta Y, \delta X^\dagger, \delta Y^\dagger)$. Collecting terms to first order in $(\delta X^\dagger, \delta Y^\dagger)$ allow us to write down the following stability condition for Γ

$$\delta \Gamma = \begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} X^I \\ Y^I \end{pmatrix} - \omega_I \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X^I \\ Y^I \end{pmatrix} = 0 \quad (42)$$

with an identical expression coming from δX and δY . Thus, Γ has an extremum for the vector (X^I, Y^I) that is a solution to the full RPA equation derived above. It can be solved by well-established methods as indicated in SI.^{4–9}

We note further that the multiplication of eq 42 from the left by $(X^{I\dagger}, Y^{I\dagger})$ affords the following expression

$$\omega_I = (Y^{I\dagger} \ X^{I\dagger}) \begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} X^I \\ Y^I \end{pmatrix} \quad (43)$$

provided that

$$X^{I\dagger} X^I - Y^{I\dagger} Y^I = 1 \quad (44)$$

which is the standard normalization condition for the solution set (X, Y) .

Thus, I is again stationary under the constraint of eq 44 provided that ω_I satisfy eq 43. We note further that ω_I is positive and thus bound from below if the ground state Hessian in eq 43 made up of A and B is positive definite, which is the case for a stable ground state. We shall refer to ω_I as the excitation energy for the stationary state I since the frequency expectation value $\langle \omega \rangle$ for I is ω_I subject to the normalization convention of eq 44.

Furche⁸ has previously noted that the Lagrangian of eq 41 after the variation of $(\delta Y^I, \delta X^I)$ leads to the RPA equation of eq 42. However, Furche did not actually derive Γ from a variational KS determinant using excited state variational DFT theory and the ground state functional. Nevertheless, noting^{8,9} the variational connection between Γ and the RPA equation has considerably simplified the calculation of excited state properties such as geometries.⁹

2.5. Transition Moments. We shall as a last point briefly outline how one would derive expressions for the transition moments in our variational RPA approach similar to those derived from frequency dependent response theory. To achieve this, we shall consider the static electronic polarizability and magnetic susceptibility tensors α and κ , respectively. A component of α is in Raleigh–Schrödinger perturbation theory given in terms of the sum over state (SOS) expression as

$$\alpha_{rs} = 2 \sum_{I \neq 0} \frac{\text{Re} \langle \Psi_0 | \hat{D}_r | \Psi_I \rangle \langle \Psi_I | \hat{D}_s | \Psi_0 \rangle}{\tilde{E}_0 - \tilde{E}_I} \quad (45)$$

Here, the energy and wave function of the ground and excited state are labeled 0 and I , respectively. Here, $\hat{D}_r = -\sum_{i=1}^n \hat{\mu}_r(i)$ is the r th Cartesian component of the electric dipole moment operator in atomic units for electron i . The integral $\langle \Psi_0 | \hat{D}_r | \Psi_I \rangle$ is further the electronic electric transition dipole moment with respect to component r for the transition $0 \rightarrow I$. We shall introduce the shorthand notation μ_{0I}^r for $\langle \Psi_0 | \hat{D}_r | \Psi_I \rangle$ and μ_{I0}^s for $\langle \Psi_I | \hat{D}_s | \Psi_0 \rangle$.

In DFT variational perturbation theory affords the following expression for a component of the electronic polarizability tensor

$$\alpha_{rs} = 2D^{(r)}[A + B]^{-1}D^{(s)\dagger} \quad (46)$$

Here, $D_{ai}^{(r)} = \langle \psi_a | \hat{\mu}_r | \psi_i \rangle$ whereas $D_{ai}^{(s)} = \langle \psi_i | \hat{\mu}_s | \psi_a \rangle = \langle \psi_a | \hat{\mu}_s | \psi_i \rangle$ and ψ_i is an occupied and ψ_a a virtual ground state orbital. Next, making use of the spectral resolution of $[A + B]^{-1}$ in terms of $(X^I + Y^I)$ allow us to write⁸

$$[A + B]^{-1} = \sum_I \frac{(X^I + Y^I)(X^I + Y^I)^\dagger}{\omega_I} \quad (47)$$

where the sum is over the solutions $(X^I + Y^I)$ to eq 43 with the eigenvalues ω_I . Combining eqs 46 and 47 finally affords

$$\alpha_{rs} = \sum_I \frac{D^{(r)}(X^I + Y^I)(D^{(s)}(X^I + Y^I)^\dagger)}{\omega_I} \quad (48)$$

Thus, a comparison of eqs 48 and 45 leads to the conclusion that the KS electronic electric transition dipole moment is given by

$$\mu_{I0}^{(r),KS} = D^{(r)}(X^I + Y^I) \quad (49)$$

As shown in section 1.7 of SI, $(X^I + Y^I)$ can alternatively be written⁸ as $(X^I + Y^I) = [A - B]^{1/2}F^I$ where F^I is an eigenfunction to

$$[A - B]^{1/2} [A + B] [A - B]^{1/2} F^I = \omega_I^2 F^I \quad (50)$$

so that $\hat{\mu}_{I0}^{(r),KS}$ takes on the familiar form from RPA theory

$$\mu_{I0}^{(r),KS} = D^{(r)}[A - B]^{1/2} F^I \quad (51)$$

Raleigh–Schrödinger perturbation theory affords the following SOS expression for the rs component of the magnetic susceptibility tensor

$$\kappa_{rs} = 2 \sum_{I \neq 0} \frac{\text{Re} \langle \Psi_0 | \hat{M}_r | \Psi_I \rangle \langle \Psi_I | \hat{M}_s | \Psi_0 \rangle}{\tilde{E}_0 - \tilde{E}_I} \quad (52)$$

where in atomic units

$$\hat{M} = -\frac{1}{c} \sum_{i=1}^n \vec{r}_i \vec{p}_i = \sum_{i=1}^n \hat{m}_i \quad (53)$$

and c is the speed of light. Further, $m_{OI}^r = \langle \Psi_0 | \hat{M}_r | \Psi_I \rangle$ is the electronic magnetic transition dipole moment with respect to Cartesian component r for the transition $0 \rightarrow I$. In DFT we have from variational perturbation theory

$$\kappa_{rs} = -2M^{(r)}[A - B]^{-1}M^{(s)\dagger} \quad (54)$$

Thus, using the spectral resolution of $[A - B]^{-1}$ in terms of $(Y^I - X^I)$

$$[A - B]^{-1} = \sum_I \frac{(X^I - Y^I)(X^I - Y^I)^\dagger}{\omega_I} \quad (55)$$

affords^{8,49–51}

$$\kappa_{rs} = -2 \sum_I \frac{\sqrt{\omega_I} M^{(r)}(X^I - Y^I)(\sqrt{\omega_I} M^{(s)}(X^I - Y^I)^\dagger)}{\omega_I} \quad (56)$$

from which we must conclude that

$$m_{OI}^{r,KS} = -M^{(r)}(Y^I - X^I) = \sqrt{\omega_I} M^{(r)}[A - B]^{-1/2} F^I \quad (57)$$

where we have used section 1.7 of SI.

3. CONCLUDING REMARKS

We have in the present study demonstrated that the RPA equation of adiabatic time dependent density functional ground state response theory equally well can be derived from a variational excited state treatment based on the ground state functional. As such, our work lend further credence to the direct use of variational KS calculations on excited states using ground state functionals initiated by Slater and others.^{37–40} In fact, we have previously shown^{28,29} that both ATDDFT/TD and Slater's Δ SCF scheme are related through different approximations to the more general CV-DFT(n) method.²⁸ Thus, ATDDFT/TD is CV-DFT(n) to second order ($n = 2$) in U within the Tamm–Dancoff approximation⁴¹ whereas Slater's Δ SCF scheme is RSCF-CV-DFT(∞)²⁶ with full optimization of U to all orders²⁷ and relaxation of the excited state orbitals to second order²⁶ under the restriction that the excitation can be represented by a single orbital replacement. The present work demonstrates that the full RPA theory also is a CV-DFT(2) scheme in which U is allowed to be oscillatory.

■ ASSOCIATED CONTENT

■ Supporting Information

Detailed derivations of some of the key equations. This material is available free of charge via the Internet at <http://pubs.acs.org>

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Notes

The authors declare no competing financial interest.

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