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# On the relation between time-dependent and variational density functional theory approaches for the determination of excitation energies and transition moments.

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It is shown that it is possible to derive the basic eigenvalue equation of adiabatic time-dependent density functional theory within the Tamm–Dancoff approximation (TD-DFT/TD) from a variational principle. The variational principle is applied to the regular Kohn–Sham formulation of DFT energy expression for a single Slater determinant and leads to the same energy spectrum as TD-DFT/TD. It is further shown that this variational approach affords the same electric and magnetic transition moments as TD-DFT/TD. The variational scheme can also be applied without the Tamm–Dancoff approximation. Practical implementations of TD-DFT are limited to second order response theory which introduces errors in transition energies for charge transfer and Rydberg excitations. It is indicated that higher order terms can be incorporated into the variational approach. It is also discussed how the current variational method is related to traditional DFT schemes based on variational principles such as  $\Delta$ SCF-DFT, and how they can be combined. © 2009 American Institute of Physics. [DOI: [10.1063/1.3114988](https://doi.org/10.1063/1.3114988)]

## I. INTRODUCTION

Density functional theory is used extensively as the method of choice in the description of molecules with a closed shell ground state due to its favorable balance between accuracy and computational cost. This success can be attributed to the development of increasingly accurate energy density functionals  $\epsilon[\rho]$  and exchange correlation potentials  $V_{xc}[\rho]$ .<sup>1–21</sup>

There have been attempts to extend Kohn–Sham formulation of density functional theory (KS-DFT) to excited states.<sup>22</sup> Variational approaches include ensemble DFT,<sup>23,24</sup> variation of bifunctionals,<sup>25</sup> and  $\Delta$ DFT/ $\Delta$ SCF-DFT.<sup>26–30</sup> Whereas the two first approaches are difficult to realize computationally,  $\Delta$ DFT/ $\Delta$ SCF-DFT are straightforward to apply, at least for a few selected excitations. Essentially, one constructs<sup>26–28</sup> new “excited state determinants” or microstates<sup>29</sup> from the ground state wave function by replacing one (or more) of the “occupied” orbitals in the occupied set with one or more “virtual” orbitals. By now evaluating the energy of the new microstates<sup>29</sup> and subtracting the ground state energy, it becomes possible to calculate excitation energies corresponding to one-, two-, and multielectron excitations. Further, in the  $\Delta$ SCF-DFT method (but not  $\Delta$ DFT), the orbitals in the microstates are optimized variationally with orthogonality constraints applied so that the orbitals do not optimize to the originally occupied set.<sup>31</sup>

The  $\Delta$ DFT/ $\Delta$ SCF-DFT methods have been subject to

some criticism. For example, not all excited states can be represented by a single microstate as  $\Delta$ DFT/ $\Delta$ SCF-DFT seems to assume. Instead excited states are described by combinations of microstates, where the mixing is determined by configuration interaction.<sup>32</sup> Also, the variational treatment in  $\Delta$ SCF-DFT of the orbitals that makes up the excited state determinants introduces orthogonality requirements between the various optimized determinants for which there is no unique solution, especially when many state-to-state transitions are studied.<sup>31</sup> At an even more fundamental level, one might question<sup>23,30</sup> whether there exists a unique variational principle for excited states in DFT. Nevertheless, some of the first chemical applications of DFT successfully made use of schemes similar to  $\Delta$ SCF-DFT in calculations on excitation energies<sup>28–30</sup> for transition metal complexes, and  $\Delta$ SCF-DFT still has its proponents.<sup>33</sup>

Over the past decade time-dependent DFT (TD-DFT) (Ref. 34) has emerged as a new and promising approach in the study of excited state properties.<sup>35–38</sup> Much of the criticism leveled at  $\Delta$ SCF-DFT appears to have been met in the TD-DFT approach<sup>34</sup> to the calculation of excited state properties.<sup>35–38</sup> Thus, in TD-DFT,<sup>34</sup> excitation energies are conceptually evaluated from a perturbation calculation of a ground state property such as the time or frequency dependent polarizability, rather than an excited state variational treatment. Further, orthogonality problems are avoided as all excitation energies are found as eigenvalues to the same (Casida<sup>35</sup>) eigenfunction equation.

The eigenfunction equation due to Casida<sup>35</sup> is derived from linear TD-DFT response theory by invoking the adia-

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batic approximation. We shall now show that it is possible to derive a similar eigenfunction equation without recourse to time or frequency dependent DFT based solely on a variational principle. This variational equation can further be simplified to an expression that is identical to the Casida<sup>35</sup> equation based on TD-DFT within the adiabatic formulation and modified by the Tamm–Dancoff approximation.<sup>39</sup> We shall finally discuss how our variational approach is related to  $\Delta$ DFT/ $\Delta$ SCF-DFT methods and how our scheme might be combined with  $\Delta$ DFT/ $\Delta$ SCF-DFT and other variational DFT-techniques<sup>40</sup> applied in the calculation of excitation energies.

## II. DISCUSSION

### A. Ground state Kohn–Sham theory for closed shell molecules

A closed shell molecule is described in the KS-DFT (Ref. 1) by a single Slater determinant<sup>38</sup>

$$\Psi^0 = |\psi_1 \psi_2, \dots, \psi_i \psi_j, \dots, \psi_n|, \quad (1)$$

with the corresponding density matrix given by

$$\rho(1,1') = \sum_i^{\text{occ}} \psi_i^*(1') \psi_i(1). \quad (2)$$

The density matrix is optimized in such a way that it minimizes the energy expression

$$E_{\text{KS}} = E_{T+V_{\text{Ne}}} + E_H + E_{\text{XC,KS}}. \quad (3)$$

In Eq. (3)

$$E_{T+V_{\text{Ne}}} = \int [\hat{h}^0(1') \rho(1,1')]_{(1=1')} d\tau_1, \quad (4)$$

where  $\hat{h}^{(0)}$  contains the kinetic energy operator  $\hat{T}_e$  for a single electron as well as the electron potential  $V_{\text{Ne}}$  due to the attraction of all the nuclei. The term  $\hat{h}^{(0)}$  might also contain other electric or magnetic one-electron operators.

Also,

$$E_H = \frac{1}{2} \int \rho(1,1) \frac{1}{r_{12}} \rho(2,2) d\tau_1 d\tau_2 \quad (5)$$

is the Hartree term representing the interaction of the molecular electron density with itself whereas

$$E_{\text{XC,KS}} = E_{\text{XC,KS}}[\rho(1,1)] \quad (6)$$

is the exchange correlation energy expressed as a functional of  $\rho(1,1)$ .

The set of spin orbitals  $\{\psi_i(1); i=1, \text{occ}\}$  that optimize the ground state Slater determinant can be found as solutions to the one-electron KS equation

$$\hat{F}_{\text{KS}}(1) \psi_i(1) = \varepsilon_i \psi_i(1), \quad (7)$$

where

$$\hat{F}_{\text{KS}}(1) = \hat{h}^0 + \int \rho(2,2) \frac{1}{r_{12}} d\tau_2 + V_{\text{XC}}(1) \quad (8)$$

and the exchange correlation potential  $V_{\text{XC}}(1)$  is given as the functional derivative

$$V_{\text{XC}}[\rho] = \frac{\delta E_{\text{XC}}}{\delta \rho}. \quad (9)$$

Equation (8) has as solutions the optimized set of occupied spin orbitals  $\{\psi_i(1); i=1, \text{occ}\}$  as well as a set of “virtual spin orbitals  $\{\psi_a(1); a=1, \text{vir}\}$ . We can consider the combined set of spin orbitals  $\{\psi_p(1); p=1, \text{vir}+\text{occ}\}$  as being orthonormal. It further holds that

$$F_{rs}^{\text{KS}} = \int \psi_r^*(1) \hat{F}_{\text{KS}}(1) \psi_s(1) d\tau_1 = \delta_{rs} \varepsilon_r. \quad (10)$$

### B. The electronic ground state Hessian (Refs. 41 and 42)

As a first step toward a variational theory for the determination of excitation energies by KS-DFT we consider a variation of each of the occupied spin orbitals  $\{\Psi_i(1); i=1, \text{occ}\}$

$$\delta \psi_i = \sum_a^{\text{vir}} U_{ai} \psi_a, \quad (11)$$

such that a portion of  $U_{ai} \Psi_a(1)$  from each of the spin orbitals of the virtual set  $\{\Psi_a(1); i=1, \text{vir}\}$  has been added to each of the occupied orbitals  $\{\Psi_i(1); i=1, \text{occ}\}$ . The determinantal wave function  $\tilde{\Psi}$  constructed from  $\{\tilde{\psi}_i(1) = \psi_i(1) + \delta \psi_i(1); i=1, \text{occ}\}$  is not normalized, neither is the set  $\{\tilde{\psi}_i(1); i=1, \text{occ}\}$  orthonormal. Fortunately, it is possible<sup>43</sup> to generate a new determinantal wave function  $\Psi'$  with the same density as  $\tilde{\Psi}$  up to second order in  $\mathbf{U}$  by introducing the new set of orbitals  $\{\psi'_i(1); i=1, \text{occ}\}$  given by

$$\begin{aligned} \psi'_i(1) = \psi_i(1) + \sum_a^{\text{vir}} U_{ai} \psi_a(1) - \frac{1}{2} \sum_a^{\text{vir}} \sum_k^{\text{occ}} U_{ai} U_{ak}^* \psi_k(1) \\ + O^{(3)}[U]. \end{aligned} \quad (12)$$

Here  $\mathbf{U}$  is a vector with the general element  $U_{ai}$  and the length  $\text{occ} \times \text{vir}$ . Further on, the set  $\{\psi'_i(1); i=1, \text{occ}\}$  is orthonormal up to second order in  $\mathbf{U}$ . A substitution of Eq. (12) into Eq. (2) affords to second order in  $\mathbf{U}$  the density corresponding to  $\Psi'$  as

$$\begin{aligned}
\rho'(1,1') &= \rho^{(0)}(1,1') + \Delta\rho'(1,1') \\
&= \rho^{(0)}(1,1') + \sum_i \sum_a^{\text{occ vir}} U_{ai} \psi_i^*(1) \psi_a(1') \\
&\quad + \sum_i \sum_a^{\text{occ vir}} U_{ai}^* \psi_a^*(1) \psi_i(1) \\
&\quad + \sum_a \sum_b^{\text{vir vir}} \sum_i^{\text{occ}} U_{ai}^* U_{bi} \psi_a^*(1) \psi_b(1') \\
&\quad - \sum_i^{\text{occ}} \sum_k^{\text{vir}} \sum_a^{\text{vir}} U_{ak}^* U_{ai} \psi_i^*(1) \psi_k(1') + O^{(3)}[U].
\end{aligned} \tag{13}$$

The expression for  $\rho'(1,1')$  now makes it possible to calculate  $E'_{\text{KS}} = E'_{T+V_{\text{Ne}}} + E'_H + E'_{\text{XC,KS}}$ , where  $E_{T+V_{\text{Ne}}}$  is defined in Eq. (4),  $E_H$  in Eq. (5) and  $E'_{\text{XC,KS}}$  in Eq. (6). We get to second order in  $U$

$$\begin{aligned}
E_{\text{KS}}[\rho^0 + \Delta\rho'] - E_{\text{KS}}[\rho^0] &= \Delta E^{\text{KS}}[\Delta\rho'] + O^{(3)}[E_{\text{HF}}(U)] \\
&= \frac{1}{2} (U^* \ U) \begin{pmatrix} \mathbf{A}^{\text{KS}} & \mathbf{B}^{\text{KS}} \\ \mathbf{B}^{\text{KS}} & \mathbf{A}^{\text{KS}} \end{pmatrix} \begin{pmatrix} U \\ U^* \end{pmatrix} \\
&\quad + O^{(3)}[U].
\end{aligned} \tag{14}$$

In deriving Eq. (14) use has been made of Eq. (9) and the expansion in terms of functional derivatives

$$\begin{aligned}
E_{\text{XC}}[\rho^{(0)} + \Delta\rho] &= E_{\text{XC}}[\rho^{(0)}] + \int \left( \frac{\delta E_{\text{XC}}[\rho]}{\delta \rho} \right)_{(0)} \Delta\rho d\tau \\
&\quad + \frac{1}{2} \int \left( \frac{\delta^2 E_{\text{XC}}[\rho]}{\delta^2 \rho} \right)_{(0)} \Delta\rho^2 d\tau \\
&= E_{\text{XC}}[\rho^{(0)}] + \int V_{\text{XC}}[\rho^{(0)}] \Delta\rho d\tau \\
&\quad + \frac{1}{2} \int f_{\text{XC}}[\rho^{(0)}] \Delta\rho^2 d\tau + O^{(3)}[U],
\end{aligned} \tag{15}$$

where  $f_{\text{XC}}[\rho^{(0)}]$  is referred to as the exchange correlation kernel.

In Eq. (14)

$$A_{ai,bj}^{\text{KS}} = \delta_{ab} \delta_{ij} (\varepsilon_a - \varepsilon_i) + K_{ai,bj}^{\text{KS}}; \quad B_{ai,bj}^{\text{KS}} = K_{ai,jb}^{\text{KS}}, \tag{16}$$

with

$$\begin{aligned}
K_{rs,tq}^{\text{KS}} &= K_{rs,tq}^H + K_{rs,tq}^{\text{KS,XC}} \\
&= \int \psi_r^*(1) \psi_s(1) \frac{1}{r_{12}} \psi_t(2) \psi_q^*(2) d\tau_1 d\tau_2 \\
&\quad + \int \psi_r^*(1) \psi_s(1) f_{\text{XC}}(\rho^{(0)}) \psi_t(1) \psi_q^*(1) d\tau_1 d\tau_2.
\end{aligned} \tag{17}$$

The combined matrix in Eq. (14) with the elements  $A_{ai,bj}^{\text{KS}}$  and  $B_{ai,bj}^{\text{KS}}$  is often referred to as the electronic ground state Hessian.<sup>41,42</sup> It should hopefully not cause any confusion that the  $A$  and  $B$  matrices in some TD-DFT formulations<sup>35,44</sup> correspond to the negative of the two electronic Hessian matrices defined in Eq. (16).

The Hessian matrix makes it possible to relate the density  $\rho^0 + \Delta\rho'[U]$  to the energy  $E_{\text{KS}}[\rho^0] + \Delta E^{\text{KS}}[\Delta\rho'[U]]$ , up to second order in  $U$ . Thus for any variation of the density ( $\Delta\rho'[U] + O^{[3]}[U]$ ) relative to  $\rho^0$  there corresponds a change in energy ( $\Delta E^{\text{KS}}[\Delta\rho'[U]] + O^{[3]}[U]$ ) relative to  $E_{\text{KS}}[\rho^0]$ . We note that  $\Delta E^{\text{KS}}[\Delta\rho'[U]]$  only has quadratic contributions from  $U$  as  $\Psi^0$  is obtained variationally. Further,  $\Delta E^{\text{KS}}[\Delta\rho'[U]]$  is determined from the well-defined KS energy  $E_{\text{KS}}[\rho^0] + \Delta E^{\text{KS}}[\Delta\rho'[U] + O^{[3]}[U]]$  corresponding to the Slater determinant  $\Psi'[U]$ . We observe that  $\Psi'$  not in general will be orthogonal to  $\Psi^0$ . Thus, expanding<sup>32,41,42</sup>  $\Psi'$  as a linear combination of Slater determinants using the definition of the constituting orbitals given in Eq. (12) affords.

$$\begin{aligned}
\Psi' &= \left( 1 - \frac{1}{2} \sum_i \sum_a U_{ai}^* U_{ai} \right) \Psi^0 + \sum_i \sum_a U_{ai} \Psi_{i \rightarrow a} \\
&\quad + \sum_i \sum_j \sum_a \sum_b U_{ai} U_{bj} \Psi_{i,j \rightarrow a,b},
\end{aligned} \tag{18}$$

where  $\Psi_{i \rightarrow a}$  is generated from  $\Psi^0$  by a substitution of  $\psi_i$  with  $\psi_a$  whereas  $\Psi_{i,j \rightarrow a,b}$  is obtained from  $\Psi^0$  by replacing  $\psi_i$  and  $\psi_j$  with  $\psi_a$  and  $\psi_b$ , respectively. It follows from Eq. (18) that

$$\langle \Psi' | \Psi^0 \rangle = \left( 1 - \frac{1}{2} \sum_i \sum_a U_{ai}^* U_{ai} \right). \tag{19}$$

Thus  $\Psi^0$  and  $\Psi'$  will for most  $U$  be linear dependent. We shall return to this point after introducing our variational procedure.

### C. The determination of stationary points in the energy region described by the ground state Hessian

We shall now in our variational treatment require that  $E_{\text{KS}}[\rho^0 + \Delta\rho']$  be stationary with respect to a variation of each of the parameters contained in the vector  $\mathbf{U}$  under certain constraints. To derive these constraints we note that the term

$$\Delta\rho'^+(1,1') = \sum_a \sum_b^{\text{vir}} \sum_i^{\text{occ}} U_{ai}^* U_{bi} \psi_a^*(1) \psi_b(1') \tag{20}$$

in the expression for  $\Delta\rho'(1,1')$  of Eq. (13) represents the part of the change in density that is spanned by products of virtual orbitals. We obtain the total charge  $q'^+$  associated with  $\Delta\rho'^+(1,1')$  as

$$\begin{aligned}
q'^+ &= \sum_a \sum_b^{\text{vir}} \sum_i^{\text{occ}} U_{ai}^* U_{bi} \int [\psi_a^*(1) \psi_b(1')]_{(1=1')} dv_1 \\
&= \sum_a \sum_i^{\text{vir occ}} U_{ai}^* U_{ai}.
\end{aligned} \tag{21}$$

We find on the other hand that

$$\Delta\rho'^-(1,1') = - \sum_i^{\text{occ}} \sum_k^{\text{vir}} \sum_a^{\text{vir}} U_{ak}^* U_{ai} \psi_i^*(1) \psi_k(1') \quad (22)$$

from the last term in Eq. (13) represents the part of the change in density that is spanned by products of occupied orbitals. The corresponding associated charge is given by

$$\begin{aligned} q'^- &= - \sum_i^{\text{occ}} \sum_k^{\text{vir}} \sum_a^{\text{vir}} U_{ak}^* U_{ai} \int [\psi_i^*(1) \psi_k(1')]_{(1=1')} dv_1 \\ &= - \sum_a^{\text{vir}} \sum_i^{\text{occ}} U_{ai}^* U_{ai}. \end{aligned} \quad (23)$$

Thus  $q'^+$  and  $q'^-$  have the same absolute values but are opposite in sign, with  $q'^-$  being negative. Further,  $|q'^-|$  represents the charge removed from the density matrix spanned by the occupied orbitals and  $q'^+$  corresponds to the charge added to the density matrix spanned by the virtual orbitals. We shall now require for an electron transition that  $q'^+=1$  or

$$\sum_a^{\text{vir}} \sum_i^{\text{occ}} U_{ai}^* U_{ai} = 1. \quad (24)$$

There is an analogy here to the simple  $\Delta$ DFT scheme where we move one electron from an occupied orbital  $\psi_i$  to a virtual orbital  $\psi_a$ . In that case we reduce a diagonal element of the density matrix spanned by the occupied orbitals ( $P_{ii} = -U_{ai}^* U_{ai} = -1$ ) by one and increase the diagonal element of the density matrix spanned by the virtual orbitals ( $P_{aa} = U_{ai}^* U_{ai} = 1$ ). Obviously in order to enforce transitions, constraints such as that of Eq. (24) are required. Otherwise, a search for stationary points would give us back the ground state with  $U=0$ .

In wave mechanics the required constraints for the  $U$ 's representing excited states are found by considering the energy  $E(U)$  of  $\Psi'(U)$  from Eq. (18):

$$\begin{aligned} \langle \Psi'(U) | \hat{H} | \Psi'(U) \rangle &= \langle \Psi' | \Psi^0 \rangle \langle \Psi^0 | \Psi' \rangle \langle \Psi^0 | \hat{H} | \Psi^0 \rangle \\ &+ \sum_i \sum_a \sum_j \sum_b U_{ai} U_{bj}^* \langle \Psi_{i \rightarrow a} | \hat{H} | \Psi_{j \rightarrow b} \rangle \\ &+ \sum_i \sum_a \sum_j \sum_b U_{ai} U_{bj} \langle \Psi_{ij \rightarrow ab} | \hat{H} | \Psi^0 \rangle \\ &+ \sum_i \sum_a \sum_j \sum_b U_{ai}^* U_{bj}^* \langle \Psi^0 | \hat{H} | \Psi_{ij \rightarrow ab} \rangle, \end{aligned} \quad (25)$$

and require that there is no contribution to  $\langle \Psi'(U) | \hat{H} | \Psi'(U) \rangle$  from  $\langle \Psi^0 | \hat{H} | \Psi^0 \rangle$  for  $U \neq 0$ . This requirement is usually equivalent to the orthonormality condition  $\langle \Psi' | \Psi^0 \rangle = \langle \Psi^0 | \Psi' \rangle = 0$ . However, when dealing with terms up to second order only, the requirement becomes more precisely

$$\begin{aligned} \langle \Psi' | \Psi^0 \rangle \langle \Psi^0 | \Psi' \rangle &= \left( 1 - \frac{1}{2} \sum_i \sum_a U_{ai}^* U_{ai} \right) \left( 1 - \frac{1}{2} \sum_i \sum_a U_{ai} U_{ai}^* \right) \\ &= \left( 1 - \sum_i \sum_a U_{ai}^* U_{ai} \right) + \mathcal{O}^{[3]}[U] \\ &= 0. \end{aligned} \quad (26)$$

To second order, this is exactly the same constraint for  $U$  as the one introduced in Eq. (24). Please note that we in order to derive Eq. (25) made use of substituting Eq. (19) into Eq. (18).

We could alternatively in wave mechanics express  $\langle \Psi'(U) | \hat{H} | \Psi'(U) \rangle$  in terms of the density matrix given in Eq. (13) as

$$\begin{aligned} \langle \Psi'(U) | \hat{H} | \Psi'(U) \rangle &= \int [\hat{h}^0(1') \rho'(1,1')]_{(1=1')} d\tau_1 \\ &+ \frac{1}{2} \int \left[ \rho'(1,1) \frac{1}{r_{12}} \rho'(2,2) \right] dv_1 dv_2 \\ &+ \frac{1}{2} \int \left[ \rho'(1,2) \frac{1}{r_{12}} \rho'(1,2) \right] dv_1 dv_2. \end{aligned} \quad (27)$$

It is readily shown that enforcing the condition that  $\Delta\rho'^+(1,1)$  of Eq. (20) integrates to 1 or  $\Delta\rho'^-(1,1)$  to  $-1$ , which is equal to the constraint of Eq. (24), ensures that  $\langle \Psi'(U) | \hat{H} | \Psi'(U) \rangle$  has no contribution from  $\langle \Psi^0 | \hat{H} | \Psi^0 \rangle$  for  $U \neq 0$ .

In KS theory we can express  $E_{\text{KS}}[\rho^0 + \Delta\rho']$  in terms of  $\rho'(1,1')$  by the help of Eq. (3), just as we can express  $\langle \Psi'(U) | \hat{H} | \Psi'(U) \rangle$  in terms of  $\rho'(1,1')$  according to Eq. (27). On the other hand, KS theory does not allow us to express  $E_{\text{KS}}[\rho^0 + \Delta\rho']$  in a form similar to Eq. (25). It is thus natural that we in KS theory justify the constraint for excited states given in Eq. (24) based on considerations of  $\Delta\rho'^+(1,1)$  and  $\Delta\rho'^-(1,1)$  as it was done above, rather than  $\langle \Psi' | \Psi^0 \rangle$  and Eq. (25).

We now have that the stationary points for  $E_{\text{KS}}[\rho^0 + \Delta\rho']$  that fulfills the condition of Eq. (24) satisfy the equation  $\delta L / \delta U_{ai} = 0$ , where

$$L = E_{\text{KS}}[\rho^0 + \Delta\rho'] - E_{\text{KS}}[\rho^0] + \lambda \left( 1 - \sum_a \sum_i U_{ai} U_{ai}^* \right) \quad (28)$$

and  $\lambda$  is a Lagrange multiplier. Thus the requirement that  $\delta L / \delta U_{ai} = 0$  leads to

$$\begin{aligned} &\frac{1}{2} \left[ (\delta U^* \quad \delta U) \begin{pmatrix} \mathbf{A}^{\text{KS}} & \mathbf{B}^{\text{KS}} \\ \mathbf{B}^{\text{KS}*} & \mathbf{A}^{\text{KS}*} \end{pmatrix} \begin{pmatrix} U \\ U^* \end{pmatrix} - \lambda (\delta U^* \quad \delta U) \begin{pmatrix} U \\ U^* \end{pmatrix} \right] \\ &+ \frac{1}{2} \left[ (U^* \quad U) \begin{pmatrix} \mathbf{A}^{\text{KS}} & \mathbf{B}^{\text{KS}} \\ \mathbf{B}^{\text{KS}*} & \mathbf{A}^{\text{KS}*} \end{pmatrix} \begin{pmatrix} \delta U \\ \delta U^* \end{pmatrix} - \lambda (U^* \quad U) \begin{pmatrix} \delta U \\ \delta U^* \end{pmatrix} \right] \\ &= 0. \end{aligned} \quad (29)$$

We must thus have<sup>42</sup>



$$\begin{pmatrix} \mathbf{A}^{\text{KS}} - \lambda & \mathbf{B}^{\text{KS}} \\ \mathbf{B}^{\text{KS}*} & \mathbf{A}^{\text{KS}*} - \lambda \end{pmatrix} \begin{pmatrix} U \\ U^* \end{pmatrix} = 0 \quad (30)$$

in order for Eq. (29) to hold for any variation  $\delta U$  and  $\delta U^*$ . We note that the trivial solution to Eq. (30) with  $U=U^*=0$ , corresponds to the ground state.

The eigenfunction equation above allows us to determine the energies  $\{\lambda_I; I=1, 2 \times \text{occ} \times \text{vir}\}$  relative to  $E_{\text{KS}}[\rho^0]$  for the stationary points along with the associated eigenvectors  $(U^{(I)} \ U^{(I)*})$ . The set of eigenvectors  $(U^{(I)} \ U^{(I)*})$  makes it further possible to construct the associated determinants  $\Psi'_I$  from

$$\begin{aligned} \psi'_I(1) = & \psi_I(1) + \sum_a^{\text{vir}} U_{ai}^{(I)} \psi_a(1) - \frac{1}{2} \sum_a^{\text{vir}} \sum_k^{\text{occ}} U_{ai}^{(I)} U_{ak}^{(I)*} \psi_k(1) \\ & + O^{(3)}[U]. \end{aligned} \quad (31)$$

Here to second order in  $\mathbf{U}$  the determinant  $\Psi'_I$  has the energy  $\lambda_I$  relative to the ground state. The determinant  $\Psi'_I$  is not the wave function that represents the excited state  $I$ . In fact, it is not even orthogonal to  $\Psi^0$  as it follows from Eq. (18). However, the energy  $E_{\text{KS}}[\rho^0 + \Delta\rho']$  of the determinant  $\Psi'_I$  represents a stationary points for  $E_{\text{KS}}[\rho^0 + \Delta\rho'] - E_{\text{KS}}[\rho^0]$  of Eq. (14) with respect to any variation  $\delta\mathbf{U}$  under the constraint that  $\mathbf{U}^\dagger \mathbf{U} = 1$  without any contribution from  $E_{\text{KS}}[\rho^0]$ .

## D. Relation between adiabatic TD-DFT/TD and the current variational approach

We shall in a later study return to Eq. (30). For now let us introduce a number of simplifications in order to relate our variational approach to the calculation of excitation energies by TD-DFT in its adiabatic formulation.<sup>34,35</sup> We shall in the first place assume that we are dealing with the nonrelativistic case where  $\hat{h}^{(0)}$  is real and only contains the kinetic energy operator  $\hat{T}_e$  for a single electron as well as the attractive potential  $V_{\text{Ne}}$  between an electron and all the nuclei. In addition only Coulombic  $1/r_{12}$  interactions are considered between the electrons. With these assumptions the sets  $\{\psi_i(1); i=1, \text{occ}\}$  and  $\{\psi_a(1); a=1, \text{vir}\}$  as well as  $\mathbf{A}^{\text{KS}}$  and  $\mathbf{B}^{\text{KS}}$  can be considered to be real without loss of generality. With  $\mathbf{A}^{\text{KS}}$ ,  $\mathbf{B}^{\text{KS}}$ , and  $\lambda$  all real, it is readily shown that Eq. (28) only is stationary with respect to a general variations, Eq. (29), if  $U^{(I)}$  is either completely imaginary with  $U^{(I)} = U_{\text{im}}^{(I)}$  or completely real with  $U^{(I)} = U_R^{(I)}$ .

In the first case the requirement of Eq. (29) reduces to the equation

$$(\mathbf{A}^{\text{KS}} - \mathbf{B}^{\text{KS}})U_{\text{im}}^{(I)} = \lambda_I U_{\text{im}}^{(I)}. \quad (32)$$

For pure density functionals  $(\mathbf{A}^{\text{KS}} - \mathbf{B}^{\text{KS}})$  is a diagonal matrix with  $(\mathbf{A}^{\text{KS}} - \mathbf{B}^{\text{KS}})_{ai, ai} = \varepsilon_a - \varepsilon_i$ . Thus, for pure functionals Eq. (32) would afford  $\lambda_I = \varepsilon_a - \varepsilon_i$  with the corresponding eigenvector  $U^{(I)}$  containing the single element  $U_{ai} = 1$ . We shall reject this set of solutions.

For  $U^{(I)} = U_R^{(I)}$  we obtain the equation

$$(\mathbf{A}^{\text{KS}} + \mathbf{B}^{\text{KS}})U^{(I)} = \lambda_I U^{(I)}, \quad (33)$$

where we for the sake of economy has omitted the subscript  $R$  in  $U_R^{(I)}$  with the understanding that all elements of  $U^{(I)}$  are

assumed to be real. This is the equation we shall adopt rather than Eq. (32). The eigenvalue equation above can be solved readily as  $\mathbf{A}^{\text{KS}}$  and  $\mathbf{B}^{\text{KS}}$  both are real and Hermitian operators.

The eigenvalue equation above differ somewhat from the Casida eigenvalue equation of adiabatic TD-DFT where the eigenvectors  $\hat{U}^{(I)}$  and eigenvalues  $\hat{\lambda}_I$  are solutions to

$$\Omega \hat{U}^{(I)} = \hat{\lambda}_I^2 \hat{U}^{(I)}, \quad (34)$$

with  $\Omega = S^{-1/2}(A+B)S^{-1/2}$  and  $S^{-1} = A-B$ . We shall compare the solutions to Eqs. (33) and (34) in a later study.

It is, however, possible to make a connection between our variational scheme and TD-DFT by introducing one additional simplification in terms of the Tamm–Dancoff approximation where the  $\mathbf{B}^{\text{KS}}$  part of the Hessian is neglected in Eq. (33). We obtain in this way the simplified equation:

$$\mathbf{A}^{\text{KS}} \tilde{U}^{(I)} = \tilde{\lambda}_I \tilde{U}^{(I)}. \quad (35)$$

This expression is identical to the Casida equation of TD-DFT where the same Tamm–Dancoff approximation<sup>39</sup> has been applied (TD-DFT/TD). Thus, we have from Eq. (34) with  $B=0$  that  $\Omega = A^2$ . As a consequence  $A^2 \tilde{U}^{(I)} = A \tilde{\lambda}_I \tilde{U}^{(I)} = \tilde{\lambda}_I^2 \tilde{U}^{(I)}$ . Clearly, within the TD approximation Eq. (34) has the same eigenfunctions and eigenvalues as Eq. (34).

We have thus shown that it is possible from variational consideration to derive an equation for the determination of excitation energies that is identical to TD-DFT/TD in its adiabatic approximation. It is finally worth to note that Eq. (32) also conforms to TD-DFT/TD within the Tamm–Dancoff approximation.<sup>39</sup>

## E. Derivation of transition moments

We shall now turn to a derivation of magnetic and electric transition dipole moments that is consistent with our current static variational approach. It is to this end useful to consider the static electronic polarizability and magnetic susceptibility tensors  $\alpha$  and  $\kappa$ , respectively. It follows from Raleigh–Schrodinger perturbation theory that a component of the electronic polarization tensor can be written in terms of a sum over state (SOS) expression as<sup>45</sup>

$$\alpha_{rs} = 2 \sum_{I \neq 0} \frac{\text{Re} \langle \Psi_0 | \hat{D}_r | \Psi_I \rangle \langle \Psi_I | \hat{D}_s | \Psi_0 \rangle}{\tilde{E}_0 - \tilde{E}_I}. \quad (36)$$

Here  $\Psi_0$  and  $\Psi_I$  are the exact many-electron wave functions representing, respectively, the ground state with the energy  $\tilde{E}_0$  and an excited state labeled  $I$  with the energy  $\tilde{E}_I$ . The summation is over all excited states  $I$  and  $\hat{D}_r = -\sum_{i=1}^n \chi_r = \sum_{i=1}^n \hat{\mu}_r$  is the  $r$ th Cartesian component of the electric dipole moment operator in atomic units. 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  $\mu_{0I}^{(r)}$  for  $\langle \Psi_0 | \hat{D}_r | \Psi_I \rangle$  whereas  $\langle \Psi_I | \hat{D}_r | \Psi_0 \rangle$  will be termed  $\mu_{I0}^{(s)}$ .

In DFT the static polarizability tensor component  $\alpha_{rs}$  is given by<sup>45,46</sup>

$$\alpha_{rs} = 2D^{(r)}[A^{\text{KS}} + B^{\text{KS}}]^{-1}D^{(s)T}. \quad (37)$$

Here  $D_{ai}^{(r)} = \langle \psi_a | \hat{\mu}_r | \psi_i \rangle$  whereas the transposed matrix  $D^{(s)T}$  has elements  $D_{ai}^{(s)T} = \langle \psi_i | \hat{\mu}_s | \psi_a \rangle = \langle \psi_a | \hat{\mu}_s | \psi_i \rangle$ . Writing next the real matrix  $[A^{\text{KS}} + B^{\text{KS}}]^{-1}$  in its spectral resolution<sup>45</sup> as

$$[A^{\text{KS}} + B^{\text{KS}}]^{-1} = \sum_I \frac{U^{(I)}U^{(I)T}}{\lambda_I}, \quad (38)$$

where  $U^{(I)T}$  is a row vector containing the  $I$ 's eigenvector of  $A^{\text{KS}} + B^{\text{KS}}$  corresponding to eigenvalue  $\lambda_I$  affords after substitution into Eq. (37)

$$\alpha_{rs} = 2 \frac{\sum_I D^{(r)}U^{(I)}(U^{(s)}U^{(I)})^T}{\lambda_I}. \quad (39)$$

A comparison between Eqs. (36) and (39) allows us to identify the electric transition dipole moment for the Cartesian component  $U_{I0}^{(r),\text{KS}}$  as

$$U_{I0}^{(r),\text{KS}} = D^{(r)}U^{(I)} \quad (40)$$

in our KS-based variational theory since all components in Eq. (39) are real. We note that in the adiabatic TD-DFT theory<sup>35</sup> based on Eq. (34), we obtain for the electric transition moment  $\hat{\mu}_{I0}^{(r),\text{KS}}$  the expression<sup>46</sup>

$$\hat{\mu}_{I0}^{(r),\text{KS}} = D^{(r)}S^{-1/2}\hat{U}^{(I)}. \quad (41)$$

The expression for  $\hat{\mu}_{I0}^{(r),\text{KS}}$  in Eq. (41) appears different from that for  $\mu_{I0}^{(r),\text{KS}}$  in Eq. (40) just as the eigenvalues  $\lambda_I$  of Eq. (33) are different from the eigenvalues  $\hat{\lambda}_I$  of Eq. (34). Nevertheless, just as the SOS expression in Eq. (39) affords  $\alpha_{rs}$  of Eq. (39), a similar SOS expression involving  $\hat{\mu}_{I0}^{(r),\text{KS}}$  and  $\hat{\lambda}_I$  would likewise<sup>45,46</sup> afford  $\alpha_{rs}$  of Eq. (39).

Within the Tamm–Dancoff approximation,<sup>39</sup> it is readily seen<sup>45,46</sup> that the electric transition dipole moment  $\mu_{I0}^{(r),\text{KS/TD}}$  becomes

$$\mu_{I0}^{(r),\text{KS/TD}} = D^{(r)}\tilde{U}^{(I)}, \quad (42)$$

where  $\tilde{U}^{(I)}$  is an eigenfunction to Eq. (34). This is the same expression<sup>46</sup> one would obtain from TD-DFT/TD.<sup>46</sup>

For a component  $\kappa_{rs}$  of the electronic magnetic susceptibility tensor, Raleigh–Schrödinger perturbation theory affords the following SOS expression

$$\kappa_{rs} = 2 \sum_{I \neq 0} \frac{\text{Re}(\langle \Psi_0 | \hat{M}_r | \Psi_I \rangle \langle \Psi_I | \hat{M}_s | \Psi_0 \rangle)}{\tilde{E}_0 - \tilde{E}_I}, \quad (43)$$

where in atomic units

$$\hat{M} = -\frac{1}{2c} \sum_{i=1}^n \vec{r}_i \times \vec{p}_i = \sum_{i=1}^n \hat{m}_i \quad (44)$$

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

$$\kappa_{rs} = M^{(r)}S^{1/2}S^{1/2}M^{(s)T}, \quad (45)$$

where  $M_{ai}^{(r)} = \langle \psi_a | \hat{m}_r | \psi_i \rangle$  whereas the transposed matrix  $M^{(s)T}$  has elements  $M_{ai}^{(s)T} = \langle \psi_i | \hat{m}_s | \psi_a \rangle = -\langle \psi_a | \hat{m}_s | \psi_i \rangle$ . Again,  $S$  is here defined as  $S = [A^{\text{KS}} - B^{\text{KS}}]^{-1}$ .

Making use of the fact that  $\sum_I U^{(I)}U^{(I)T} = I$  where  $I$  is a unit vector, allows us also to write

$$\frac{\sum_I \sqrt{\lambda_I} U^{(I)} \sqrt{\lambda_I} U^{(I)T}}{\lambda_I} = I. \quad (46)$$

Substituting Eq. (46) between the two factors  $S^{1/2}$  in Eq. (45) finally affords the SOS expression

$$\kappa_{rs} = 2 \sum_I \frac{(\sqrt{\lambda_I} M^{(r)} S^{1/2} U^{(I)}) (\sqrt{\lambda_I} M^{(s)} S^{1/2} U^{(I)})^T}{\lambda_I} \quad (47)$$

from which we conclude after comparison with Eq. (37) that

$$m_{I0}^{(r),\text{KS}} = \sqrt{\lambda_I} M^{(r)} S^{1/2} U^{(I)} \quad (48)$$

since the expression for  $\kappa_{rs}$  is real. The expression for the magnetic transition moment in adiabatic TD-DFT ( $\hat{m}_{I0}^{(r),\text{KS}}$ ) has the same form<sup>45</sup> as in Eq. (48) with  $U^{(I)}$  and  $\lambda_I$  replaced by  $\tilde{U}^{(I)}$  and  $\hat{\lambda}_I$ , respectively. Thus, numerically  $\hat{m}_{I0}^{(r),\text{KS}}$  and  $m_{I0}^{(r),\text{KS}}$  will differ. Nevertheless a SOS expression for  $\kappa_{rs}$  similar to that of Eq. (41) where  $m_{I0}^{(r),\text{KS}}$  and  $\lambda_I$  are replaced with  $\hat{m}_{I0}^{(r),\text{KS}}$  and  $\hat{\lambda}_I$  leads to the same expression given in Eq. (39) as Eq. (47).

Within the Tamm–Dancoff approximation,<sup>39</sup> it is readily seen that the magnetic transition dipole moment  $\mu_{I0}^{(r),\text{KS/TD}}$  becomes<sup>45,46</sup>

$$m_{I0}^{(r),\text{KS/TD}} = M^{(r)}\tilde{U}^{(I)}, \quad (49)$$

where  $\tilde{U}^{(I)}$  is an eigenfunction to Eq. (35). This is the same expression<sup>45,46</sup> one would obtain from TD-DFT/TD.

### III. CONCLUDING REMARKS

It is customary to make a distinction between, on the one hand, DFT methods that evaluate excitation energies directly by variational approaches and on the other hand TD-DFT where excitation energies are determined indirectly from a perturbation calculation on a ground state property such as frequency dependent polarizability. We have shown here that not only  $\Delta\text{SCF-DFT}$  (Refs. 26–30) but also the basic equation in TD-DFT/TD can be derived from a variational principle. Our variation theory is closely related to Kohn–Sham coupled perturbed variation theory where one introduces a static perturbation and calculate the change in the KS determinant  $\Psi'(U)$  and associated energy  $E_{\text{KS}}[\rho^0 + \Delta\rho'[U]]$ . In our case the perturbation is represented by a constraint such as that given for second order theory in Eq. (24) and the change  $E_{\text{KS}}[\rho^0 + \Delta\rho'[U]] - E_{\text{KS}}[\rho^0]$  represents an excitation energy. We shall in the following refer to the variational metal as constrained variational density functional theory or CV( $n$ )-DFT, where  $n$  indicates the order in  $U$  to which we evaluate the excitation energies. When use is made of the TD approximation our method will be referred to as CV( $n$ )-DFT/TD.

Both  $\Delta$ SCF-DFT (Refs. 26–30) and CV(*n*)-DFT are based on associating each excited state with the energy of a single determinant which is a well-defined entity in DFT. In  $\Delta$ SCF-DFT, the energy of each determinant representing an excited state is minimized by optimizing the constituting KS orbitals in a self-consistent procedure. In practice such a requirement is difficult to satisfy for more than a few states as the determinants must be orthogonal.

In TD-DFT and our variational approach CV(2)-DFT, one introduces a more limited variational space that allows for the determination of stationary states based on the mixing of virtual and occupied ground state orbitals to second order in the energy through *U*. The advantage of this approach is that it ensures to second order in *U* a set of determinantal functions that are orthogonal to each other. In  $\Delta$ SCF-DFT the occupied orbitals  $\{\psi_i(1)|i=1,\text{occ}\}$  are optimized through variations  $\delta\psi_i(1)$  in which  $\psi_i(1)$  and  $\delta\psi_i(1)$  belong to the same symmetry representation. In CV(2)-DFT,  $\delta\psi_i = U_{ai}(1)\psi_a$  and  $\psi_i(1)$  need not belong to the same representation as long as there is another occ/vir pair (*b*,*j*) such that  $(A^{\text{KS}} + B^{\text{KS}})_{ai,bj} \neq 0$ . Thus CV(*n*)-DFT is a more general variational procedure than  $\Delta$ SCF-DFT. Nevertheless,  $\Delta$ SCF-DFT is a more expedient procedure that within its limits incorporates higher order terms more efficiently.

One can readily imagine procedures where one minimizes the energy of a single determinant by optimizing simultaneously the orbital sets  $\{\psi_i(1); i=1,\text{occ}\}$  and  $\{\psi_a(1); a=1,\text{vir}\}$  as well as *U*, in what would amount to a SCF-CV(*n*)-DFT method that effectively combines  $\Delta$ SCF-DFT (Refs. 26–30) and TD-DFT/CV(*n*) within the proper DFT constraint of being based on the energy expression for a single Slater determinant. We plan to explore this prospect further.

It is true that space and spin degenerate excited states at a minimum need the symmetry determined linear combination of a few Slater determinants for a proper description. However, it has been demonstrated in several studies that the energy of such degenerate states can be written as a sum of well-defined energy expressions of symmetry related determinants.<sup>29</sup> In fact, such relations have already been used implicitly in TD-DFT to symmetry block the *A* and *B* matrices. Similar procedures can be applied to a CV(*n*) and a SCF-CV(*n*)-DFT treatment.

Practical implementations of TD-DFT are limited to single excitations and second order in *U*, as are CV(2) in the form presented here. It is however quite possible to extend the variational procedures outlined here to double and multiexcitations as well as higher orders in *U* [CV(*n*)]. In fact, contributions from terms that are higher than second order in *U* seem to be important for charge transfer and Rydberg excitations.<sup>47</sup> We intend to explore these possibilities in future studies. Charge transfer transitions are typically described better by D-SCF than TD-DFT.

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