The implementation of a self-consistent constricted variational density functional theory for the description of excited states

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We present here the implementation of a self-consistent approach to the calculation of excitation energies within regular Kohn-Sham density functional theory. The method is based on the n -order constricted variational density functional theory (CV(n)-DFT) [T. Ziegler, M. Seth, M. Krykunov, J. Autschbach, and F. Wang, *J. Chem. Phys.* **130**, 154102 (2009)] and its self-consistent formulation (SCF-CV(∞)-DFT) [J. Cullen, M. Krykunov, and T. Ziegler, *Chem. Phys.* **391**, 11 (2011)]. A full account is given of the way in which SCF-CV(∞)-DFT is implemented. The SCF-CV(∞)-DFT scheme is further applied to transitions from occupied π orbitals to virtual π^* orbitals. The same series of transitions has been studied previously by high-level *ab initio* methods. We compare here the performance of SCF-CV(∞)-DFT to that of time dependent density functional theory (TD-DFT), CV(n)-DFT and Δ SCF-DFT, with the *ab initio* results as a benchmark standard. It is finally demonstrated how adiabatic TD-DFT and Δ SCF-DFT are related through different approximations to SCF-CV(∞)-DFT. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3696967>]

I. INTRODUCTION

We have recently introduced a variational density functional theory (DFT) scheme for the description of excited states. The new method was based on an n -order constricted variation theory approach (CV(∞)-DFT).¹ Lately, the same method was given a self-consistent formulation and extended to all orders (SCF-CV(∞)-DFT).² The current account provides a full description of the way in which SCF-CV(∞)-DFT is implemented. We apply further SCF-CV(∞)-DFT to a series (T1) of transitions from occupied π orbitals to virtual π^* orbitals. This series has previously been studied³ by an iterative approximate coupled cluster singles, doubles, and triples model, CC3.⁴ We compare here the performance of SCF-CV(∞)-DFT for T1 with other DFT methods,⁵ employing *ab initio* results³ as the benchmark reference. It is finally discussed how popular DFT based methods applied in the study of excited states such as adiabatic time dependent density functional theory (TD-DFT (Refs. 6–8)) and $\Delta\Delta$ SCF-DFT (Refs. 9–16) are related through different approximations to SCF-CV(∞)-DFT.

II. COMPUTATIONAL DETAILS

All calculations were based on DFT as implemented in the Amsterdam Density Functional (ADF) version 2010.¹⁷ Our calculations employed a standard triple- ζ Slater type orbital (STO) basis with one set of polarization functions for all atoms.¹⁸ Use was made of the local density approximation (LDA) in the VWN parametrization¹⁹ as well as the B3LYP and B3LYP exchange hybrid functionals by Becke²⁰ with the correlation functional taken from Lee *et al.*²¹ All electrons were considered as valence. The accuracy integration

parameter (ACINT) for the precision of the numerical integration was set to 5.0. Use was made of a special auxiliary STO basis to fit the electron density in each cycle for an accurate representation of the exchange and Coulomb potentials. The Cartesian coordinates of the 20 ($\pi \rightarrow \pi^*$) benchmark transitions were taken from the supporting information of Ref. 3. The ground-state geometries of these molecules were optimized at the MP2/6-31G* level of theory.³

III. CONSTRICTED VARIATIONAL DFT

A. Generation of excited state orbitals

In the constricted variational density functional theory, CV(n)-DFT, we construct excited state KS-orbitals by performing a unitary transformation² among occupied²² $\{\psi_i; i = 1, occ\}$ and virtual $\{\psi_a; a = 1, vir\}$ ground state orbitals

$$Y \begin{pmatrix} \psi_{occ} \\ \psi_{vir} \end{pmatrix} = e^U \begin{pmatrix} \psi_{occ} \\ \psi_{vir} \end{pmatrix} = \left(\sum_{m=0}^{\infty} \frac{U^m}{m!} \right) \begin{pmatrix} \psi_{occ} \\ \psi_{vir} \end{pmatrix} = \begin{pmatrix} \psi'_{occ} \\ \psi'_{vir} \end{pmatrix}, \quad (1)$$

to $m = n$.

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 (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. The unitary transformation matrix Y is in Eq. (1) expressed in terms of a skew

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symmetric matrix U as

$$Y = e^U = I + U + \frac{U^2}{2} + \dots$$

$$= \sum_{m=0}^{\infty} \frac{U^m}{m!} = \sum_{n=0}^{\infty} \frac{(U^2)^n}{2n!} + U \sum_{n=0}^{\infty} \frac{(U^2)^n}{(2n+1)!}. \quad (2)$$

Here $U_{ij} = U_{ab} = 0$ where “ i,j ” refer to the occupied set $\{\psi_i; i = 1, occ\}$ whereas “ a,b ” refer to $\{\psi_a; a = 1, vir\}$. Further, U_{ai} are the variational mixing matrix elements that combine virtual and occupied ground state (reference) orbitals in the excited state with $U_{ai} = -U_{ia}$. Thus, the entire matrix U is made up of $occ \times vir$ independent elements U_{ai} . We shall on occasion also consider U as column vector where the index (ai) now runs over pairs of virtual and occupied orbitals. For a given U we can by the help of Eq. (2) generate a set of “occupied” excited state orbitals

$$\psi'_i = \sum_p^{occ+vir} Y_{pi} \psi_p = \sum_j^{occ} Y_{ji} \psi_j + \sum_a^{vir} Y_{ai} \psi_a, \quad (3)$$

that are orthonormal to order n in U_{ai} . To second order in U the excited state occupied orbitals are given by¹

$$\psi'_i = \psi_i + \sum_a^{vir} U_{ai} \psi_a - \frac{1}{2} \sum_j^{occ} \sum_a^{vir} U_{ai} U_{aj} \psi_j. \quad (4)$$

On the other hand, to infinite order in U the occupied excited state orbitals take on the form²

$$\psi'_j = \cos[\gamma_j] \varphi_j^o + \sin[\gamma_j] \varphi_j^v; \quad j = 1, occ. \quad (5)$$

Here γ_j is defined through the equations

$$(V_{vir}^+ U V_{occ})_{pq} = \gamma_p \delta_{pq}; \quad p = 1, \quad occ, q = 1, occ, \quad (6)$$

$$(V_{vir}^+ U V_{occ})_{pq} = 0; \quad p = occ + 1, \quad vir, q = 1, occ, \quad (7)$$

where V_{vir} and V_{occ} are two matrices that transforms U into the new matrix T according to $T = V_{vir}^+ U V_{occ}$ with $T_{pq} = 0$ for all non-diagonal elements whereas $T_{pp} = \gamma_{pp}$ for the $occ \times occ$ diagonal elements. V_{occ} is²³ the matrix that diagonalizes $D_{jk}^{occ} = (U^+ U)_{jk}$ whereas V_{vir} diagonalizes $D_{bc}^{vir} = (U U^+)_{bc}$. The pair φ_j^o, φ_j^v that defines ψ'_j in Eq. (5) are the set of *corresponding* orbitals introduced by Amos and Hall²³ and given by

$$\varphi_i^o = \sum_j (V_{occ})_{ji} \psi_j \quad i = 1, occ, \quad (8)$$

$$\varphi_i^v = \sum_a^{vir} (V_{vir})_{ai} \psi_a \quad i = 1, occ, \quad (9)$$

where $\sum_a \sum_j (V_{vir})_{ia}^+ U_{aj} (V_{occ})_{ji} = \gamma_i$ for $i = 1, occ$. Thus in the *corresponding* orbital representation²³ only one occupied ground state orbital φ_j^o mixes with one corresponding virtual ground state orbital φ_j^v for each occupied excited state orbital φ'_j . We shall now turn to a discussion of how to determine the variational parameters in U .

B. Determination of U for CV(2)-DFT

In the simple CV(2)-DFT theory¹ the unitary transformation (1) is carried out to second order in U . We thus obtain the occupied excited state orbitals to second order (4) from which we can generate the excited state Kohn-Sham density $\rho'(1, 1')$ and spin-density $s'(1, 1')$ matrices to second order.^{24,25}

The expressions^{24,25} for $\rho'(1, 1')$ and $s'(1, 1')$ make it next possible to write down the corresponding excited state Kohn-Sham energy to second order assuming at the moment real orbitals and U matrix elements. For spin conserving transitions²⁶ the density matrix is given by²⁵

$$\begin{aligned} \rho'(1, 1') &= \rho^{(0)}(1, 1') + \Delta\rho'(1, 1') \\ &= \rho^{(0)}(1, 1') + \sum_i^{occ} \sum_a^{vir} U_{ai} \psi_a(1') \psi_i(1) \\ &\quad + \sum_i^{occ} \sum_a^{vir} U_{ai} \psi_a(1) \psi_i(1') \\ &\quad + \sum_i^{occ} \sum_a^{vir} \sum_b^{vir} U_{ai} U_{bi} \psi_a(1') \psi_b(1) \\ &\quad - \sum_i^{occ} \sum_j^{occ} \sum_a^{vir} U_{ai} U_{aj} \psi_i(1') \psi_j(1), \end{aligned} \quad (10)$$

whereas the excited state energy takes on the form²⁵

$$\begin{aligned} E_{KS}[\rho'(1, 1')] &= E_{KS}[\rho^0] + \sum_{ai} \sum_{bj} U_{ai} U_{bj} A_{ai,bj} \\ &\quad + \sum_{ai} \sum_{bj} U_{ai} U_{bj} B_{ai,bj} + O[U^3], \end{aligned} \quad (11a)$$

where

$$A_{ai,bj} = \delta_{ab} \delta_{ij} (\epsilon_a - \epsilon_i) + K_{ai,bj}; \quad B_{ai,bj} = K_{ai,jb}. \quad (11b)$$

Here $E_{KS}[\rho^0]$ is the ground state energy and “ a,b ” run over virtual ground state canonical orbitals whereas “ i,j ” run over occupied ground state canonical orbitals, all of the same spin. Further $K_{ai,bj} = K_{ai,bj}^C + K_{ai,bj}^{XC}$ where

$$K_{ai,bj}^C = \iint \psi_a^*(1) \psi_i(1) \frac{1}{r_{12}} \psi_b(2) \psi_j^*(2) dv_1 dv_2, \quad (12)$$

whereas

$$K_{ai,bj}^{XC(HF)} = - \iint \psi_a^*(1) \psi_i^*(1) \frac{1}{r_{12}} \psi_b(2) \psi_j(2) dv_1 dv_2, \quad (13)$$

for Hartree Fock exchange correlation and

$$K_{ai,bj}^{XC(DFT)} = \int \psi_a^*(1) \psi_i(1) [f^{(+,+)}(\rho^0)] \psi_b(1) \psi_j^*(1) dv_1, \quad (14)$$

for spin conserving transitions ($i \rightarrow a; j \rightarrow b$) among orbitals of α spin and

$$K_{ai,bj}^{XC(\text{DFT})} = \int \psi_a^*(1) \psi_i(1) [f^{(-,-)}(\rho^0)] \psi_b(1) \psi_j^*(1) dv_1, \quad (15)$$

for spin conserving transitions ($i \rightarrow a; j \rightarrow b$) among orbitals of β spin.

Here the kernel $f^{\sigma,\tau}$ is defined as the second order functional derivative of E_{XC}

$$f^{\sigma,\tau}(\rho^+, \rho^-)_0 = \left(\frac{\delta^2 E_{XC}}{\delta \rho^\sigma \delta \rho^\tau} \right)_0 \sigma = +, -; \quad \tau = +, -, \quad (16)$$

where $\rho^+ = 1/2\rho + 1/2s$ and $\rho^- = 1/2\rho - 1/2s$. Further ρ is the density and s the corresponding spin-density.

For spin-flip excitations ($i \rightarrow a; j \rightarrow b$) where the occupied (i,j) and virtual (a,b) orbitals are of different spin, the energy expression for the excited state is similar²⁷ to that of (11) except that

$$K_{ai,bj}^{XC(\text{DFT})} = \frac{1}{2} \int \psi_a(1) \psi_i(1) [f_0^{+,+} + f_0^{-,-} - 2f_0^{+,-}] \psi_b(1) \psi_j(1) dv_1; \quad K_{ai,bj}^C = 0, \quad (17)$$

where the expressions in Eq. (17) have been derived from non-collinear exchange-correlation theory.^{28–30}

In CV(2)-DFT (Ref. 1) we seek points on the energy surface $E_{KS}[\rho']$ such that $\Delta E_{KS}[\Delta\rho'] = E_{KS}[\rho'] - E_{KS}[\rho^0]$ represents a transition energy. Obviously, a direct optimization of $\Delta E_{KS}[\Delta\rho']$ without constraints will result in $\Delta E_{KS}[\Delta\rho'] = 0$ and $U = 0$. We¹ now introduce the constraint that the electron excitation must represent a change in density $\Delta\rho'$ where one electron in Eq. (10) is transferred from the occupied space represented by $\Delta\rho_{occ} = -\sum_{ija} U_{ai} U_{aj}^* \psi_i(1') \psi_j^*(1)$ to the virtual space represented by $\Delta\rho_{vir} = \sum_{iab} U_{ai} U_{bi}^* \psi_a(1') \psi_b^*(1)$. An integration of $\Delta\rho_{occ}$ and $\Delta\rho_{vir}$ over all space affords $-\Delta q_{occ} = \Delta q_{vir} = \sum_{ai} U_{ai} U_{ai}^*$. We shall thus introduce the constraint $\sum_{ai} U_{ai} U_{ai}^* = 1$. Constructing next the Lagrangian $L = E_{KS}[\rho'] + \lambda(1 - \sum_{ai} U_{ai} U_{ai}^*)$ with λ being a Lagrange multiplier and demanding that L be stationary to any real variation in U results in the eigenvalue equation

$$(A^{KS} + B^{KS})U^{(I)} = \lambda_{(I)} U^{(I)}, \quad (18)$$

where $U^{(I)}$ is the eigenvector for excited state I . We can now from Eq. (18) determine the sets of mixing coefficients $\{U^{(I)}; I = 1, occ \times vir\}$ that make L stationary and represent excited states. The corresponding excitation energies are given by $\lambda_{(I)}$. This can be seen by multiplying on both sides of Eq. (18) with $U^{(I)+}$ and making use of the constraint and normalization condition $U^{(I)} + U^{(I)+} = 1$.

Within the Tamm-Dancoff approximation,³¹ Eq. (18) reduces to

$$A^{KS} U^{(I)} = \lambda_{(I)} U^{(I)}, \quad (19)$$

which is identical in form to the equation one obtains from TDDFT in its adiabatic formulation^{6–10} after applying the same Tamm-Dancoff³¹ approximation.

C. Excitation energies for SCF – CV(∞) – DFT

From the occupied excited state orbitals of Eq. (15) we can express the electron ($\rho^{(\infty)}$)³² and spin ($s^{(\infty)}$)³² density matrices as well as $\rho^{+(\infty)} = 1/2\rho^{(\infty)} + 1/2s^{(\infty)}$ and $\rho^{-(\infty)} = 1/2\rho^{(\infty)} - 1/2s^{(\infty)}$. Starting with a spin-conserving transition, we can without loss of generality assume that it takes place between orbitals of α -spin. Thus, for such a spin conserving transition the excited state orbitals^{32(a)} $\{\psi_i^\alpha \rightarrow \psi_{i\alpha}' = \cos[\eta^\alpha \gamma_j^\alpha] \phi_j^{o\alpha} + \sin[\eta^\alpha \gamma_j^\alpha] \phi_j^{v\alpha}; j = 1, occ/2\}$ are obtained by a unitary transformation to all orders involving the part of the U matrix ($U^{\alpha\alpha}$) that according to Eq. (1) mixes occupied ground state orbitals of α -spin with virtual ground state orbitals of α -spin. We can now write^{2,32(a)} the change in density within the α manifold due to the excitation as

$$\begin{aligned} \Delta\rho^{\alpha(\infty)}(1, 1') &= \sum_j^{occ/2} \sin^2[\eta^\alpha \gamma_j^\alpha] \\ &\times [\phi_j^{v\alpha}(1') \phi_j^{v\alpha}(1) - \phi_j^{o\alpha}(1') \phi_j^{o\alpha}(1)] \\ &+ \sum_j^{occ/2} \sin[\eta^\alpha \gamma_j^\alpha] \cos[\eta^\alpha \gamma_j^\alpha] \\ &\times [\phi_j^{v\alpha}(1) \phi_j^{o\alpha}(1') + \phi_j^{v\alpha}(1') \phi_j^{o\alpha}(1)]. \end{aligned} \quad (20a)$$

In Eq. (20a) the scaling factor η^α is introduced to ensure that $\Delta\rho^{\alpha(\infty)}(1, 1')$ represents the transfer of a single electron from the occupied orbital space density $-\sum_j^{occ/2} \sin^2[\eta^\alpha \gamma_j^\alpha] \phi_j^{o\alpha}(1') \phi_j^{o\alpha}(1)$ to the virtual orbital space density $\sum_j^{occ/2} \sin^2[\eta^\alpha \gamma_j^\alpha] \phi_j^{v\alpha}(1') \phi_j^{v\alpha}(1)$ or

$$\sum_{j(\alpha)}^{occ} \sin^2[\eta^\alpha \gamma_j^\alpha] = 1. \quad (20b)$$

Here the constraint of Eq. (20b) is a generalization of the corresponding second order constraint $\sum_{ai} U_{ai} U_{ai}^* = 1$ used to derive Eqs. (18) and (19).

The electron ($\rho^{(\infty)}$) (Refs. 32 and 33) and spin ($s^{(\infty)}$) (Ref. 32) density matrices as well as $\rho^{+(\infty)} = 1/2\rho^{(\infty)} + 1/2s^{(\infty)} = \rho^{+,0} + \Delta\rho^{+(\infty)}$ and $\rho^{-(\infty)} = 1/2\rho^{(\infty)} - 1/2s^{(\infty)} = \rho^{-,0} + \Delta\rho^{-(\infty)}$ allow us next to express the excitation energies^{32(b)} as

$$\begin{aligned} \Delta E^{(\infty)} &= E_{KS}[\rho^{+(\infty)}, \rho^{-(\infty)}] - E_{KS}[\rho^{+,0}, \rho^{-,0}] \\ &= \int F_{KS}^+ \left[\rho^{+,0} + \frac{1}{2} \Delta\rho^{+(\infty)}, \rho^{-,0} \right. \\ &\quad \left. + \frac{1}{2} \Delta\rho^{-(\infty)} \right] \Delta\rho^{+(\infty)} dv_1 \\ &\quad + \int F_{KS}^- \left[\rho^{+,0} + \frac{1}{2} \Delta\rho^{+(\infty)}, \rho^{-,0} \right. \\ &\quad \left. + \frac{1}{2} \Delta\rho^{-(\infty)} \right] \Delta\rho^{-(\infty)} dv_1 \\ &\quad + O^{[3]}(\Delta\rho^{+(\infty)}, \Delta\rho^{-(\infty)}), \end{aligned} \quad (21)$$

where for a closed shell ground state molecule with the density ρ^0 , we have $\rho^{+,0} = \rho^{-,0} = \rho^0/2$. Here Eq. (21) is derived by Taylor expanding³⁴ $E_{\text{KS}}[\rho^{+(\infty)}, \rho^{-(\infty)}]$ and $E_{\text{KS}}[\rho^{+,0}, \rho^{-,0}]$ from the intermediate point $(\rho^{+,T}, \rho^{-,T}) = (\rho^{+,0} + 1/2\Delta\rho^{+(\infty)}, \rho^{-,0} + 1/2\Delta\rho^{-(\infty)})$. Further $F_{\text{KS}}^\sigma[\rho^{+,0} + 1/2\Delta\rho^{+(\infty)}, \rho^{-,0} + 1/2\Delta\rho^{-(\infty)}]$ ($\sigma = +, -$) are the Kohn-Sham Fock operators defined with respect to the intermediate point. The expression in Eq. (21) is exact to third order in $\Delta\rho^{+(\infty)}, \Delta\rho^{-(\infty)}$, which is usually enough.³⁴ However, its accuracy can be extended to any desired order.³⁴

We get for a spin conserving transition the excitation energy^{32(b),35}

$$\begin{aligned} \Delta E^{(\infty)} &= E_{\text{KS}}^\infty[\rho^0 + \Delta\rho^{(\infty)}] - E_{\text{KS}}[\rho^0] \\ &= - \sum_j^{\text{occ}/2} \sin^2[\eta^\alpha \gamma_j^\alpha] F_{j^\alpha j^\alpha}^{\text{KS},T} \\ &\quad + \sum_j^{\text{occ}/2} \sin^2[\eta^\alpha \gamma_j^\alpha] F_{j^\alpha j^\alpha}^{\text{KS},T} \\ &\quad + \sum_j^{\text{occ}/2} \cos[\eta^\alpha \gamma_j^\alpha] \sin[\eta^\alpha \gamma_j^\alpha] F_{j^\alpha j^\alpha}^{\text{KS},T} \\ &\quad + \sum_j^{\text{occ}} \cos[\eta \gamma_j^\alpha] \sin[\eta \gamma_j^\alpha] F_{j^\alpha j^\alpha}^{\text{KS},T} + O^{[3]}(\Delta\rho^{(\infty)}). \end{aligned} \quad (22)$$

Here $\hat{F}^{\text{KS},T}$ is a Kohn-Sham operator defined with respect to the intermediate point $(\rho^{+,T}, \rho^{-,T})$ and $F_{pq}^{\text{KS},T}$ is a matrix element of this operator involving the two orbitals.

D. Energy gradient used in optimization of U for SCF – CV(∞) – DFT

We shall now find vectors $U_{(\infty)}^{(I)}$ that optimize $E_{\text{KS}}[\rho^{+(\infty)}, \rho^{-(\infty)}]$ subject to certain constraints. To that end we will need the energy gradient with respect to variations in U . Considering first a spin conserving transition^{37(a)} between orbitals of α -spin we take as a starting point for $U^{\alpha\alpha}$ that generates $\{\psi_i^\alpha \rightarrow \psi_i'^\alpha = \cos[\eta^\alpha \gamma_j^\alpha] \varphi_j^\alpha + \sin[\eta^\alpha \gamma_j^\alpha] \varphi_j^\alpha; j = 1, \text{occ}/2\}$ the elements in $U_{(2)}^{(I)} = U^{(I)}$ that has been found by solving Eq. (19) for a spin conserving transition. To the vector $U^{(I)}$ corresponds the matrix $\tilde{U}^{0,\alpha\alpha}$ and the set $\{\tilde{\gamma}_k^{\alpha,0}; k = 1, \text{occ}\}$. Scaling next $\tilde{U}^{0,\alpha\alpha}$ and $\{\tilde{\gamma}_k^{\alpha,0}; k = 1, \text{occ}\}$ by such that $\sum_j^{\text{occ}} \sin^2[\eta^\alpha \tilde{\gamma}_j^{\alpha,0}] = 1$ affords $U^{0,\alpha\alpha} = \eta^\alpha \tilde{U}^{0,\alpha\alpha}$ and $\{\gamma_k^{\alpha,0} = \eta^\alpha \tilde{\gamma}_k^{\alpha,0}; k = 1, \text{occ}\}$ where now $\sum_j^{\text{occ}} \sin^2[\gamma_j^{\alpha,0}] = 1$. The matrix $U^{\alpha\alpha}$ is obtained from a CV(2) calculation where $U^{\alpha\alpha}$ and $-U^{\alpha\alpha}$ afford the same energy according to Eq. (11a). However in CV(∞) with the energy expression given by Eq. (22), the sign matters through the terms containing $\cos[\eta^\alpha \gamma_j^\alpha] \sin[\eta^\alpha \gamma_j^\alpha]$. As we are dealing with a variational approach, we must pick the sign that affords the lowest energy.

Next, a Taylor expansion of $E^{(\infty)}(\rho^+(U^{\alpha\alpha}), \rho^-(U^{\alpha\alpha}))$ from $U^{0,\alpha\alpha}$ to $U^\alpha = U^{0,\alpha\alpha} + \Delta U^{\alpha\alpha}$ affords

$$\begin{aligned} E^{(\infty)}(U^{\alpha\alpha}) &= E^{(\infty)}(U^{0,\alpha\alpha}) + \sum_{ai} \left(\frac{dE^{(\infty)}}{dU_{ai}^{\alpha\alpha}} \right)_0 \Delta U_{ai}^{\alpha\alpha} \\ &\quad + \frac{1}{2} \sum_{ai} \sum_{bj} \left(\frac{d^2 E^{(\infty)}}{dU_{ai}^{\alpha\alpha} dU_{bj}^{\alpha\alpha}} \right)_0 \Delta U_{ai}^{\alpha\alpha} \Delta U_{bj}^{\alpha\alpha} \\ &= E^{(\infty)}(U^{0,\alpha\alpha}) + \sum_{ai} \mathbf{g}_{ai}^{\alpha,e} \Delta U_{ai}^{\alpha\alpha} \\ &\quad + \frac{1}{2} \sum_{ai} \sum_{bj} \mathbf{H}_{ai,bj}^{\alpha,\alpha} \Delta U_{ai}^{\alpha\alpha} \Delta U_{bj}^{\alpha\alpha} + O^{(3)}[\Delta U]. \end{aligned} \quad (23)$$

A component of the gradient $\mathbf{g}_{ai}^{\alpha,e}$ evaluated at $U^{0,\alpha\alpha}$ reads

$$\begin{aligned} g_{ai}^{\alpha,e}(U^{0,\alpha\alpha}) &= \left(\frac{dE^{(\infty)}}{dU_{ai}^{\alpha\alpha}} \right)_0 = \sum_{\tau}^{\pm} \left(\frac{\partial E}{\partial \rho^\tau} \right)_0 \left(\frac{\partial \rho^\tau}{\partial U_{ai}^{\alpha\alpha}} \right)_0 \\ &= \sum_{\tau}^{\pm} \int \hat{F}_{\text{KS}}^\tau[\rho^+(U^0), \rho^-(U^0)] \left(\frac{\partial \rho^\tau}{\partial U_{ai}^{\alpha\alpha}} \right)_0 dv_1, \end{aligned} \quad (24)$$

where

$$\rho^+(U^0) = \frac{1}{2} \rho^0 + 1/2 \Delta\rho(U^{0,\alpha\alpha}) + 1/2 \Delta s(U^{0,\alpha\alpha}), \quad (25)$$

$$\rho^-(U^0) = \frac{1}{2} \rho^0 + 1/2 \Delta\rho(U^{0,\alpha\alpha}) - 1/2 \Delta s(U^{0,\alpha\alpha}). \quad (26)$$

Here $\Delta\rho(U^{0,\alpha\alpha})$ is the change in density in going from the ground state with $U^{0,\alpha\alpha} = 0$ to $U^{0,\alpha\alpha} \neq 0$. Further $\Delta s(U^{0,\alpha\alpha})$ is the corresponding change in the spin density matrix. The calculation of $\mathbf{g}$ and $\mathbf{H}(U^{0,\alpha\alpha})$ in Eq. (23) requires closed form expressions for $d\rho^\tau(U^{\alpha\alpha})/dU_{ai}^{\alpha\alpha}$ (Refs. 37(a) and 38) and $d^2\rho^\tau(U^{\alpha\alpha})/dU_{ai}^{\alpha\alpha} dU_{bj}^{\alpha\alpha}$ ($\tau = +, -$).³⁹

E. Optimization of U for SCF-CV(∞)-DFT

A differentiation of Eq. (23) by $\Delta U^{\alpha\alpha}$ affords

$$\mathbf{g}^{\alpha,e}(U^{0,\alpha\alpha}) + \mathbf{H}^{\alpha,\alpha}(U^{0,\alpha\alpha}) \Delta U^{\alpha\alpha} = 0, \quad (27)$$

from which we can find $\Delta U^{\sigma\sigma}$ iteratively. In the initial steps where $|\Delta U| \gg \delta_{\text{thresh}1}$ the Hessian is calculated approximately by assuming that $\mathbf{H}^{\alpha,\alpha}(U^{0,\alpha\alpha}) = \varepsilon^D$ with $(\varepsilon^D)_{ai,bj} = \delta_{ij} \delta_{ab} (\varepsilon_a - \varepsilon_i)$. Here $\varepsilon_i, \varepsilon_a$ are the orbital energies of the occupied and virtual ground state orbitals, respectively. We thus get for each new step

$$\Delta U^{\alpha\alpha} = (\varepsilon^D)^{-1} \mathbf{g}^{\alpha,e}(U^{0,\alpha\alpha}). \quad (28)$$

If $\tilde{U}^{0,\alpha\alpha} = U^{0,\alpha\alpha} + \Delta U^{0,\alpha\alpha}$ does not satisfy Eq. (20b) we introduce a scaling so that $\hat{U}^{0,\alpha\alpha} = \eta \tilde{U}^{0,\alpha\alpha}$ satisfy $\sum_{j(\alpha)}^{\text{occ}} \sin^2[\gamma_j^\alpha(\hat{U}^{0,\alpha\alpha})] = 1$. With $\hat{U}^{0,\alpha\alpha}$ satisfying Eq. (20b) we finally ensure that $\hat{U}^{0,\alpha\alpha}$ satisfy $\text{Tr}(U^{0,\alpha\alpha} + U^{K,\alpha\alpha}) = 0$ for the excited states $K = 1, I-1$ that are below the excited state I for which we are optimizing U . This is done by introducing

the projection

$$U^{0,\alpha\alpha} = \hat{U}^{0,\alpha\alpha} - \sum_{k=1}^{I-1} U^{K,\alpha\alpha} Tr(U^{K,\alpha\alpha} + \hat{U}^{0,\alpha\alpha}) / \\ \times Tr(U^{K,\alpha\alpha} + U^{K,\alpha\alpha}). \quad (29)$$

After that we go back to Eq. (28) for a new step with $U^{0,\alpha\alpha}$ defined in Eq. (29). When $\delta_{resh1} > |\Delta U| > \delta_{resh2}$ the iterative procedure is resumed by the help of the conjugated gradient technique described by Pople *et al.*⁴⁰ It is not required in this procedure explicitly to know the Hessian. Instead use is made of the fact that

$$\mathbf{H}^{\alpha\alpha}(U^{0,\alpha\alpha})\Delta U^{\alpha\alpha} = \mathbf{g}^{e,\alpha}(U^{0,\alpha\alpha} + \Delta U) \\ - \mathbf{g}^{e,\alpha}(U^{0,\alpha\alpha}) + O^{[3]}(\Delta U). \quad (30)$$

The value for δ_{resh1} is typically 10^{-2} whereas $\delta_{resh2} = 10^{-4}$. Convergence is obtained when the threshold δ_{resh2} is reached. Typically, 20–30 iterations are required to reach δ_{resh1} and 5–10 to reach δ_{resh2} . We have also attempted more advanced Hessians for the first part of the optimization such as the one suggested by Fletcher⁴¹ and implemented by Fischer and Almlöf.⁴² However, it was found to be less robust than the simple procedure in Eq. (28). The optimization procedure outlined here for spin-conserving transitions can readily be formulated for spin-flip transitions.

F. The resolution of singlet and triplet transitions from a closed shell molecule

The outcome of a spin-conserving transition is a state described by a Kohn-Sham determinant with two unpaired electrons of opposite spin. Such a determinant

$$\Psi_M'' = |\psi_1''\psi_2''\psi_3'' \dots \psi_i''\psi_j'' \dots \psi_n''| \quad (31)$$

has an energy¹³ that is half singlet and half triplet

$$E_M' = \frac{1}{2}[E_S' + E_T']. \quad (32)$$

On the other hand, the spin-flip transition results in a determinant

$$\Psi_T'' = |\psi_1''\psi_2''\psi_3'' \dots \psi_i''\psi_j'' \dots \psi_n''|, \quad (33)$$

with the energy of a triplet, E_T'' . We can thus get¹³ the triplet energy from Ψ_T'' as E_T'' and the singlet energy E_S' from Ψ_M' as¹³

$$E_S' \approx 2E_M' - E_T'' = E_S' + (E_T' - E_T''). \quad (34)$$

Strictly speaking E_S' can only be calculated from Eq. (34) if $E_T' = E_T''$. This will to a good approximation be the case¹³ if all the closed shell orbitals in Ψ_M' and Ψ_T'' are the same whereas the open shell orbitals have identical spatial parts. To ensure this we optimize $U^{\alpha\alpha}$ with respect to E_M' . The resulting orbitals describing Ψ_M' are subsequently used to construct Ψ_T'' and evaluate $E_T'' = E_T'$ after the required spin adjustment for the open shell orbitals. A slightly more accurate procedure would be to optimize $U^{\alpha\alpha}$ based on the energy $2E_M' - E_T''$.

IV. RESULTS AND DISCUSSION

We present here as a first demonstration of our scheme calculations on $20 \pi \rightarrow \pi^*$ excitation in a series of unsaturated hydrocarbons. The calculations were based on the LDA (Ref. 19) (VWN), B3LYP (Refs. 20 and 21) and BHLYP (Refs. 20 and 21) functionals. For each functional results are given for adiabatic TDDFT,^{6–10} adiabatic TDDFT with the Tamm-Dankoff approximation (TDDFT-TD) and second order constricted variation DFT (CV(2)-TD) within the Tamm-Dankoff approximation according to Eq. (29). The latter two methods should in theory give identical results. We have in addition for each functional results for all order constricted variational DFT (CV(∞) – DFT) (Ref. 2) based on a U matrix obtained with CV(2)-DFT as well as SCF-CV(∞) – DFT in which U is optimized. We compare further the DFT-based results with the “best estimate” by Schreiber *et al.*³ obtained from high-level *ab initio* wave function methods. Also discussed is

$$\lambda_{\max} = \eta^\alpha \gamma_{\max}^\alpha, \quad (35)$$

where $\gamma_{\max}^\alpha$ is the largest eigenvalue in Eq. (16) with respect to $U^{\alpha\alpha}$ and the scaling factor η^α is introduced to satisfy Eq. (20b). If $U^{\alpha\alpha}$ is obtained from CV(2)-TD this is indicated by using $\lambda'_{\max}$. On the other hand the use of an optimized $U^{\alpha\alpha}$ matrix corresponds to $\lambda''_{\max}$.

We deal in the current test set with two groups of excitations. Group A (1,2,5,7,8,9,11,14,17) of Table I is associated with $\pi \rightarrow \pi^*$ transitions of the type HOMO – $n \rightarrow$ LUMO + n ($n = 0,1,2$) where $n = 1,2$ applies exclusively to naphthalene. At the simple level of Hückel theory the group A excitations do not have any other $\pi \rightarrow \pi^*$ transition of comparable energy to interact with. Thus, Group A has the potential to be represented by a single orbital transition. Group B (3,4,6,10,12,13,15,16,18,19,20) on the other hand are associated with a pair of $\pi \rightarrow \pi^*$ transitions of the type HOMO $\rightarrow$ LUMO + n and HOMO – $n \rightarrow$ LUMO ($n = 1,3$) that in the case of the simple Hückel theory are degenerate in energy. Thus group B excitations are likely to have contributions from at least two $\pi \rightarrow \pi^*$ transitions.

A. LDA results for $\pi \rightarrow \pi^*$ excitations in unsaturated hydrocarbons

Table I displays the LDA results. We find that the three second order methods TDDFT, TDDFT-TD, and CV(2)-TD have large root-mean-square deviation (RMSD) values of 0.62 eV, 0.50 eV, and 0.50 eV, respectively. On the average the calculated energies tend to be too small relative to the best estimate³ (BE). We note further that TDDFT-TD and CV(2)-TD as expected give nearly identical results. Any difference of 0.03 eV or smaller stems from the fact that the TDDFT-TD energies are expressed in terms of K integrals according to Eq. (11a) whereas excitation energies for CV(2)-TD are derived using Taylor expansions as in Eq. (32). We find that RMSD is 0.59 eV for group A and 0.39 eV for group B in the case of CV(2)/LDA. The corresponding numbers are 0.77 eV and 0.43 eV for TDDFT.

TABLE I. Vertical singlet excitation^a energies for a series of $\pi \rightarrow \pi^*$ excitations in unsaturated hydrocarbons based on LDA (VWN).

Molecule	No ^b Group	State	Type	Best ^c	TDDFT ^d	CV(2) ^e	CV(2) ^f	CV(∞) ^g	$\lambda_{\max}$ ^h	SCF-CV(∞) ⁱ	$\lambda_{\max}$ ^j
Ethene	1 A ^k	B _{1u}	$\pi \rightarrow \pi^*$	7.80	7.78	8.48	8.46	8.45	1.181	6.57	1.571
Butadiene	2 A	B _u	$\pi \rightarrow \pi^*$	6.18	5.59	6.16	6.17	6.12	1.169	4.45	1.571
	3 B ^l	A _g	$\pi \rightarrow \pi^*$	6.55	6.23	6.24	6.23	6.66	0.841	6.56	0.860
Hexatriene	4 B	A _g	$\pi \rightarrow \pi^*$	5.09	5.02	5.03	5.03	5.35	0.787	5.22	1.099
	5 A	B _u	$\pi \rightarrow \pi^*$	5.10	4.50	5.05	5.06	4.94	1.197	3.40	1.571
Octatetraene	6 B	A _g	$\pi \rightarrow \pi^*$	4.47	4.16	4.17	4.17	4.41	0.799	4.30	1.130
	7 A	B _u	$\pi \rightarrow \pi^*$	4.66	3.81	4.34	4.34	4.16	1.212	2.78	1.571
Cyclopropene	8 A	B ₂	$\pi \rightarrow \pi^*$	7.06	5.99	6.30	6.33	7.55	1.249	5.73	1.571
Cyclopentadiene	9 A	B ₂	$\pi \rightarrow \pi^*$	5.55	4.97	5.39	5.39	5.88	1.254	4.39	1.571
	10 B	A ₁	$\pi \rightarrow \pi^*$	6.31	6.03	6.05	6.05	6.45	0.810	6.24	1.040
Norbornadiene	11 A	A ₂	$\pi \rightarrow \pi^*$	5.34	4.39	4.52	4.52	5.10	1.158	4.32	1.571
	12 B	B ₂	$\pi \rightarrow \pi^*$	6.11	4.93	4.95	4.95	5.37	0.942	5.01	1.569
Naphthalene	13 B	B _{3u}	$\pi \rightarrow \pi^*$	4.24	4.19	4.20	4.20	4.38	0.788	4.39	0.792
	14 A	B _{2u}	$\pi \rightarrow \pi^*$	4.77	4.05	4.25	4.25	4.71	1.104	3.67	1.571
	15 B	B _{1g}	$\pi \rightarrow \pi^*$	5.99	4.97	4.97	4.97	5.24	0.850	5.23	0.847
	16 B	A _g	$\pi \rightarrow \pi^*$	5.87	5.78	5.80	5.80	5.98	0.854	5.83	1.028
	17 A	B _{2u}	$\pi \rightarrow \pi^*$	6.33	5.86	6.12	6.12	6.09	1.043	5.21	1.570
	18 B	A _g	$\pi \rightarrow \pi^*$	6.67	6.16	6.21	6.20	6.41	0.904	6.35	0.786
	19 B	B _{3u}	$\pi \rightarrow \pi^*$	6.06	5.71	6.22	6.22	6.15	0.730	6.23	0.775
	20 B	B _{1g}	$\pi \rightarrow \pi^*$	6.47	6.14	6.47	6.48	6.37	0.791	6.45	0.829
RMSD A					0.77	0.59	0.59	0.41	...	1.37	...
RMSD B					0.43	0.39	0.39	0.28	...	0.28	...
RMSD ^m A+B				—	0.62	0.50	0.50	0.35	...	0.99	...

^aExcitation energies in eV.^bRoot mean square deviation.^cReference 2.^dTD-DFT without Tamm-Dankoff approximation defined in Eq. (31).^eCV(2)-DFT without Tamm-Dankoff approximation, Eq. (28).^fCV(2)-DFT with Tamm-Dankoff approximation, Eq. (29) which is equivalent to TDDFT with the Tamm-Dankoff approximation.^gSinglet excitation energies for CV(∞) with U taken as solution to Eq. (29).^hBased on U taken as solution to Eq. (29) this is the largest eigenvalue from Eq. (16) for this particular excitation.ⁱExcitation energy for CV(∞) with U optimized.^jBased on optimized an optimized U matrix this is the largest eigenvalue from Eq. (16) for this particular excitation.^kSingle orbital transition.^lDouble orbital transition.^mNumber used for excitation in text.

For the CV(∞) scheme, RMSD is reduced to 0.36 eV as the calculated energies on average are slightly higher. In this scheme we add energy terms to all orders in U, with U determined by CV(2) through Eq. (29). Further, RMSD is 0.41 for A and 0.28 for B. Also shown are the maximal scaled eigenvalues $\lambda'_{\max}$ from Eq. (35) based on U^α with $\gamma_{\max}^\alpha$ determined from Eq. (16). Here $\lambda_{\max}$ cannot exceed $\pi/2$ as a consequence of Eq. (20b). The maximum value of $\lambda'_{\max} = \pi/2$ (1.571) radians corresponds to a single orbital transition.

It follows from Table I that the members of group B all have $\lambda'_{\max} < 0.9$. This indicates as expected that these excitations have contributions from more than one $\pi \rightarrow \pi^*$ orbital transition at the CV(2) theory level and thus also for CV(∞). For group A each member only has a significant contribution from one $\pi \rightarrow \pi^*$ orbital transition at the CV(2) level, as expected. Nevertheless, we find $\lambda'_{\max} \approx 1.2$ rather than $\lambda'_{\max} = \pi/2$ (1.571). The reason for this is that other types of transitions than $\pi \rightarrow \pi^*$ contribute, notably $\sigma \rightarrow \pi^*$, $n \rightarrow \pi^*$ and Rydberg transitions. In terms of groups, RMSD is 0.41 eV for A and 0.28 eV for B in the case of CV(∞).

Turning next to SCF – CV(∞)/LDA in which $U^{\alpha\alpha}$ is optimized so as to minimize Eq. (32), we note a substantial change in Table I. Thus, all group A members now have a $\lambda''_{\max}$ value of $\pi/2$, indicating that they have become single orbital in character. A closer look reveals that the group A members all are represented by pure $\pi \rightarrow \pi^*$ transitions with no significant contribution from $\sigma \rightarrow \pi^*$, $n \rightarrow \pi^*$ and Rydberg transitions. On the SCF-CV(∞)/LDA level, the group B retains a multi-orbital composition although $\lambda''_{\max}$ has increased slightly on average. The only two exceptions are transitions 10 and 12 for which $\lambda''_{\max}$ are 1.3–1.5. Thus, these two transition prefer to be single configurational although a second configuration is available for interaction.

For group A the SCF-CV(∞)/LDA transition energies have dropped as much as 2 eV compared to the CV(∞)/LDA results whereas the energies for the remaining group B transitions hardly have changed. As a result of the substantial change in the predicted group A excitation energies, the RMSD value increases to 0.99 eV for SCF-CV(∞)/LDA. This is exclusively due to group A for which the RMSD is 1.37 eV whereas RMSD is 0.28 eV for B.

TABLE II. Vertical singlet excitation^a energies for a series of $\pi \rightarrow \pi^*$ excitations in unsaturated hydrocarbons based on B3LYP.

Molecule	No ^b Group	State	Type	Best ^c	TDDFT ^d	CV(2) ^e	CV(∞) ^f	$\lambda_{\max}$ ^g	SCF-CV(∞) ^h	$\lambda_{\max}$ ⁱ
Ethene	1 A ^j	B _{1u}	$\pi \rightarrow \pi^*$	7.80	7.73	8.37	8.42	1.209	7.23	1.541
Butadiene	2 A	B _u	$\pi \rightarrow \pi^*$	6.18	5.73	6.26	6.33	1.237	5.08	1.563
	3 B ^k	A _g	$\pi \rightarrow \pi^*$	6.55	6.76	6.78	6.72	0.879	6.52	0.865
Hexatriene	4 B	A _g	$\pi \rightarrow \pi^*$	5.09	5.67	5.68	5.25	0.791	5.17	0.789
	5 A	B _u	$\pi \rightarrow \pi^*$	5.10	4.69	5.18	5.20	1.273	4.02	1.567
Octatetraene	6 B	A _g	$\pi \rightarrow \pi^*$	4.47	4.82	4.84	4.30	0.800	4.23	0.802
	7 A	B _u	$\pi \rightarrow \pi^*$	4.66	4.02	4.47	4.45	1.301	3.38	1.569
Cyclopropene	8 A	B ₂	$\pi \rightarrow \pi^*$	7.06	6.34	6.70	7.29	1.201	6.43	1.500
Cyclopentadiene	9 A	B ₂	$\pi \rightarrow \pi^*$	5.55	5.04	5.43	5.99	1.291	4.86	1.571
	10 B	A ₁	$\pi \rightarrow \pi^*$	6.31	6.48	6.50	6.34	0.809	6.20	0.879
Norbornadiene	11 A	A ₂	$\pi \rightarrow \pi^*$	5.34	4.77	4.93	5.51	1.248	4.81	1.534
Naphthalene	12 B	B ₂	$\pi \rightarrow \pi^*$	6.11	5.49	5.52	5.63	0.956	5.53	0.970
	13 B	B _{3u}	$\pi \rightarrow \pi^*$	4.24	4.41	4.43	4.42	0.784	4.41	0.784
	14 A	B _{2u}	$\pi \rightarrow \pi^*$	4.77	4.35	4.56	4.92	1.130	4.23	1.570
	15 B	B _{1g}	$\pi \rightarrow \pi^*$	5.99	5.54	5.55	5.64	0.903	5.61	0.947
	16 B	A _g	$\pi \rightarrow \pi^*$	5.87	6.13	6.16	5.86	0.831	5.76	0.841
	17 A	B _{2u}	$\pi \rightarrow \pi^*$	6.33	6.12	6.42	6.22	1.049	5.78	1.570
	18 B	A _g	$\pi \rightarrow \pi^*$	6.67	6.82	6.90	6.61	0.861	6.65	0.632
	19 B	B _{3u}	$\pi \rightarrow \pi^*$	6.06	5.91	6.43	6.20	0.747	6.35	0.772
	20 B	B _{1g}	$\pi \rightarrow \pi^*$	6.47	6.32	6.65	6.07	0.859	6.15	0.925
RMSD ^l A				—	0.50	0.33	0.32	—	0.80	—
RMSD ^l B				—	0.30	0.33	0.20	—	0.21	—
RMSD ^l A+B				—	0.41	0.33	0.27	—	0.59	—

^aExcitation energies in eV.^bNumber used for excitation in text.^cReference 2.^dTD-DFT without Tamm-Dankoff approximation defined in Eq. (31).^eCV(2)-DFT with Tamm-Dankoff approximation, Eq. (29) which is equivalent to TDDFT with the Tamm-Dankoff approximation.^fSinglet excitation energies for CV(∞) with U taken as solution to Eq. (29).^gBased on U taken as solution to Eq. (29) this is the largest eigenvalue from Eq. (16) for this particular excitation.^hExcitation energy for CV(∞) with U optimized.ⁱBased on an optimized U matrix this is the largest eigen-value from Eq. (16) for this particular excitation.^jSingle orbital transition.^kDouble orbital transition.^lRoot mean square deviation.

To understand the large drop in energy for A we note that the singlet excitation energy for a single orbital pair transition ($\varphi_i^o \rightarrow \varphi_i^v$) in CV(2)/TD is given by

$$\Delta E_S^{(2)} = \varepsilon_{iv} - \varepsilon_{io} + 2K_{ioiv,ioiv} - K_{ioiv,ioiv}, \quad (36)$$

whereas the singlet excitation energy after summing to all orders takes on the form

$$\Delta E_S^{(\infty)} = \varepsilon_{iv} - \varepsilon_{io} + 1/2K_{ioiv,ioiv} + 1/2K_{iviv,iviv} - 2K_{iviv,ioiv} + K_{iviv,ioiv}, \quad (37)$$

The expression for $\Delta E_S^{(2)}$ of Eq. (36) appears to be quite different from $\Delta E_S^{(\infty)}$ of Eq. (37). However, we note that if use is made of pure Hartree-Fock exchange then $K_{ioiv,ioiv}^{\text{HF}} = K_{iviv,iviv}^{\text{HF}} = 0$ whereas $K_{ioiv,iviv}^{\text{HF}} = -K_{iviv,ioiv}^{\text{HF}}$ and $K_{ioiv,ioiv}^{\text{HF}} = -K_{iviv,iviv}^{\text{HF}}$, where $K_{ru,tq}^{\text{HF}} = K_{ru,tq}^C + K_{ru,tq}^{X(\text{HF})}$ with reference to Eqs. (22) and (23). Thus, in this case $\Delta E_S^{(2)\text{HF}} = \Delta E_S^{(\infty)\text{HF}}$. As a consequence, for Hartree-Fock the excitation energy of a single-orbital transition is fully determined

by $\Delta E_S^{(2)\text{HF}}$ and higher order terms are zero.^{2,5,43} However, this is not so for LDA since $K_{ioiv,ioiv}^{\text{LDA}} \neq K_{iviv,iviv}^{\text{LDA}} \neq 0$ and $K_{ioiv,iviv}^{\text{LDA}} \neq -K_{iviv,ioiv}^{\text{LDA}}$ whereas $K_{ioiv,ioiv}^{\text{LDA}} \neq -K_{iviv,iviv}^{\text{LDA}}$, where $K_{ru,tq}^{\text{LDA}} = K_{ru,tq}^C + K_{ru,tq}^{X(\text{LDA})}$ with reference to Eqs. (22), (24), and (25). Thus, for LDA the calculated excitation energies are quite different depending on whether $\Delta E_S^{(2)}$ or $\Delta E_S^{(\infty)}$ is used. The same is true for functionals based on the generalized gradient approximation (GGA). In general HF satisfy the symmetry relation $K_{ru,tq}^{\text{HF}} = K_{ru,tq}^C + K_{ru,tq}^{X(\text{HF})} = -K_{rt,uq}^C - K_{rt,uq}^{X(\text{HF})} = -K_{rt,uq}^{\text{HF}}$ since $K_{ru,tq}^{X(\text{HF})} = -K_{rt,uq}^C$ and $K_{rt,uq}^{X(\text{HF})} = -K_{ru,tq}^C$. In LDA and GGA no such relationship exists. Instead we find for $\pi \rightarrow \pi^*$ transitions that $|K_{rt,uq}^{X(\text{LDA})}| \ll |K_{ru,tq}^C|$.

As an example, for the first $1A_g \rightarrow 1B_u$ transition of butadiene the terms $K_{\pi\pi,\pi\pi}$ and $K_{\pi\pi^*,\pi\pi^*}$ that both should be zero have a value of ≈ 8 eV due to the lack of cancellation of the “self-interaction” Coulomb term by the exchange part. In this case the exchange part is “too small” in absolute terms by one order of magnitude. Further, $K_{\pi\pi,\pi\pi^*}^{\text{LDA}}$ and $-K_{\pi\pi^*,\pi\pi^*}^{\text{LDA}}$ are quite different with $K_{\pi\pi,\pi\pi^*}^{\text{LDA}} \approx 8$ eV and

$-K_{\pi\pi^*,\pi\pi^*}^{\text{LDA}} \approx -2$ eV. Likewise $K_{\pi\pi,\pi^*\pi^*}^{\text{LDA}}$ and $-K_{\pi\pi^*,\pi\pi^*}^{\text{LDA}}$ differ since $K_{\pi\pi,\pi^*\pi^*}^{\text{LDA}} \approx 8$ eV whereas $-K_{\pi\pi^*,\pi\pi^*}^{\text{LDA}} \approx -2$ eV. For the last two cases the exchange is “too small” by one order of magnitude for $|K_{rt,uq}^{XC(\text{LDA})}|$ to be equal to $|K_{ru,tq}^C|$.

With the Coulomb terms dominating and $K_{\pi\pi,\pi\pi}^C \approx K_{\pi^*\pi^*,\pi^*\pi^*}^C \approx K_{\pi^*\pi^*,\pi\pi}^C \approx K_{\pi\pi^*,\pi^*\pi^*}^C$, we get almost cancellation of all K-terms in Eq. (37) with $\Delta E_S^{(\infty)} = 4.5$ eV compared to $\varepsilon_{\pi^*} - \varepsilon_{\pi} = 3.9$ eV. For $\Delta E_S^{(2)}$ of Eq. (36) we have again the Coulomb parts dominating and $K_{\pi\pi,\pi^*\pi^*}^C \approx K_{\pi\pi,\pi^*\pi^*}^C$. However, with more positive than negative K contributions we get after cancellation that $\Delta E_S^{(2)} \cong \varepsilon_{\pi^*} - \varepsilon_{\pi} + K_{\pi\pi^*,\pi\pi^*} = 6.0$ eV. Thus, we have rationalized why a transition described by a single $\pi \rightarrow \pi^*$ excitation in both CV(2)/LDA and SCF-CV(∞)/LDA affords a larger $\Delta E_S^{(n)}$ for $n = 2$ than for $n = \infty$.

The result obtained here where $\Delta E_S^{(2)} > \Delta E_S^{(\infty)}$ for $\pi \rightarrow \pi^*$ excitations is typical for transitions ($\varphi_i^o \rightarrow \varphi_i^v$) where φ_i^o and φ_i^v occupy the same spatial extent such that the densities $\varphi_i^o\varphi_i^{o*}$ and $\varphi_i^v\varphi_i^{v*}$ have a large overlap. On the other hand for transitions $\varphi_i^o \rightarrow \varphi_i^v$ where φ_i^o and φ_i^v oc-

cupy quite different spatial extents such that the densities $\varphi_i^o\varphi_i^{o*}$ and $\varphi_i^v\varphi_i^{v*}$ have little or no overlap, we find a reversal to $\Delta E_S^{(2)} < \Delta E_S^{(\infty)}$. Examples are charge transfer, $\sigma \rightarrow \pi^*$, $n \rightarrow \pi^*$, and Rydberg transitions. As already discussed previously,^{5,10,43,44} the reversal comes from the fact that for these types of transitions $1/2K_{i^o i^o, i^o i^o} + 1/2K_{i^v i^v, i^v i^v}$ in Eq. (37) is far from canceled by $-2K_{i^v i^v, i^o i^o} + K_{i^v i^v, i^o i^o}$ such that $\Delta E_S^{(\infty)}$ becomes large compared to $\varepsilon_{i^v} - \varepsilon_{i^o}$. On the other hand, in Eq. (36) $2K_{i^o i^v, i^o i^v} - K_{i^o i^v, i^o i^v} \approx 0$, so that $\Delta E_S^{(2)}$ approach $\varepsilon_{i^v} - \varepsilon_{i^o}$. The reversal is responsible for that TD-DFT and CV(2) affords too low excitation energies for charge transfer, $\sigma \rightarrow \pi^*$, $n \rightarrow \pi^*$, and Rydberg transitions at the LDA and GGA level of theory. In the present case the reversal explains why $\sigma \rightarrow \pi^*$, $n \rightarrow \pi^*$, and Rydberg transitions contribute to the group A excitation at the CV(2) level of theory but is absent at the SCF-CV(∞)/LDA level of theory where $\lambda''_{\text{max}} \approx \pi/2(1.571)$.

It is worth to mention that for the 10 excitations of group A in Table I where $\lambda''_{\text{max}} = 1.57$, supplementary $\Delta\text{SCF/LDA}$ calculations were carried out. The $\Delta\text{SCF/LDA}$ calculations resulted within 0.05 eV in excitation energies similar to those

TABLE III. Vertical singlet excitation^a energies for a series of $\pi \rightarrow \pi^*$ excitations in unsaturated hydrocarbons based on BHLYP.

Molecule	No ^b Group	State	Type	Best ^c	TDDFT ^d	CV(2) ^e	CV(∞) ^f	λ_{max}^g	SCF-CV(∞) ^h	λ_{max}^i
Ethene	1 A ^j	B _{1u}	$\pi \rightarrow \pi^*$	7.80	7.68	8.22	8.45	1.229	8.02	1.571
Butadiene	2 A	B _u	$\pi \rightarrow \pi^*$	6.18	5.91	6.36	6.64	1.292	5.98	1.571
	3 B ^k	A _g	$\pi \rightarrow \pi^*$	6.55	7.54	7.58	6.96	1.002	6.39	0.869
Hexatriene	4 B	A _g	$\pi \rightarrow \pi^*$	5.09	6.63	6.65	5.08	0.817	4.87	0.802
	5 A	B _u	$\pi \rightarrow \pi^*$	5.10	4.93	5.32	5.54	1.311	4.92	1.571
Octatetraene	6 B	A _g	$\pi \rightarrow \pi^*$	4.47	6.28	5.84	4.01	0.799	3.85	0.805
	7 A	B _u	$\pi \rightarrow \pi^*$	4.66	4.28	4.63	4.77	1.319	4.25	1.570
Cyclopropene	8 A	B ₂	$\pi \rightarrow \pi^*$	7.06	6.49	6.83	7.15	1.191	7.16	1.570
Cyclopentadiene	9 A	B ₂	$\pi \rightarrow \pi^*$	5.55	5.15	5.50	6.09	1.311	5.45	1.571
	10 B	A ₁	$\pi \rightarrow \pi^*$	6.31	7.16	7.19	6.07	0.813	5.85	0.828
Norbornadiene	11 A	A ₂	$\pi \rightarrow \pi^*$	5.34	5.11	5.31	5.88	1.369	5.35	1.567
	12 B	B ₂	$\pi \rightarrow \pi^*$	6.11	6.15	6.21	5.93	1.019	5.83	1.021
Naphthalene	13 B	B _{3u}	$\pi \rightarrow \pi^*$	4.24	4.66	4.73	4.26	0.781	4.22	0.774
	14 A	B _{2u}	$\pi \rightarrow \pi^*$	4.77	4.64	4.87	4.81	1.110	4.33	1.111
	15 B	B _{1g}	$\pi \rightarrow \pi^*$	5.99	6.23	6.32	6.48	1.169	6.33	1.318
	16 B	A _g	$\pi \rightarrow \pi^*$	5.87	6.55	6.59	5.46	0.822	5.30	0.820
	17 A	B _{2u}	$\pi \rightarrow \pi^*$	6.33	6.38	6.76	6.29	1.012	6.48	1.120
	18 B	A _g	$\pi \rightarrow \pi^*$	6.67	7.67	7.83	6.85	0.659	6.49	0.810
	19 B	B _{3u}	$\pi \rightarrow \pi^*$	6.06	6.18	6.68	6.23	0.757	6.43	0.771
	20 B	B _{1g}	$\pi \rightarrow \pi^*$	6.47	6.63	6.85	6.24	1.126	6.41	1.255
RMSD ^l A				—	0.95	0.94	0.38	—	0.25	—
RMSD ^l B				—	0.29	0.23	0.31	—	0.36	—
RMSD ^l A+B				—	0.70	0.69	0.35	—	0.31	—

^aExcitation energies in eV.

^bNumber used for excitation in text.

^cReference 2.

^dTD-DFT without Tamm-Dankoff approximation defined in Eq. (31).

^eCV(2)-DFT with Tamm-Dankoff approximation, Eq. (29) which is equivalent to TDDFT with the Tamm-Dankoff approximation.

^fSinglet excitation energies for CV(∞) with U taken as solution to Eq. (29).

^gBased on U taken as solution to Eq. (29) this is the largest eigenvalue from Eq. (16) for this particular excitation.

^hExcitation energy for CV(∞) with U optimized.

ⁱBased on an optimized U matrix this is the largest eigenvalue from Eq. (16) for this particular excitation.

^jSingle orbital transition.

^kDouble orbital transition.

^lRoot mean square deviation.

obtained by RSCF-CV(∞)/LDA and the two methods produced quite similar KS orbitals.

B. B3LYP and BHLYP results for $\pi \rightarrow \pi^*$ excitations in unsaturated hydrocarbons

Both of the second order methods TDDFT and CV(2)-TD are seen to perform well for B3LYP with RMSD's of 0.41 eV and 0.33 eV, respectively. The two second order schemes fare much worse for BHLYP where the RMSD's are 0.70 eV (TDDFT) and 0.69 eV (CV(2)-TD), respectively. Similar poor results were obtained in the last section for LDA with RMSD's of 0.62 eV (TDDFT) and 0.50 eV (CV(2)-TD), respectively. Thus, RMSD's for the simple second order methods exhibit a strong dependency on the fraction of exact HF-exchange α with a minimum at B3LYP for $\alpha = 20\%$. Most of the error in the second order methods for LDA and BHLYP comes from the group A transitions.

The perturbative all order approach CV(∞) exhibits a weak dependence on the fraction of HF-exchange with RMSD's of 0.35 eV (LDA), 0.27 eV (B3LYP), and 0.31 eV (BHLYP). Thus, although the scheme performs best for B3LYP, CV(∞) is seen to be rather robust with a better performance than the second order theories for all three functionals.

We note for group A that a significant increase in the calculated excitation energies for SCF-CV(∞) as we move to the hybrid functionals and raise the fraction α of HF-exchange in going from LDA (0%) over B3LYP (20%) to BHLYP (50%), Tables I–III. The increase in the calculated excitation energies is associated with the fact that only a fraction $(1-\alpha)$ of the excitation energy now is given by the LDA (or GGA) expression $\Delta E_S^{(\infty)}$ of Eq. (37) whereas the remaining part takes on the form of the HF-equivalent expression $\Delta E_S^{\text{HF}(\infty)} = \varepsilon_{i^v}^{\text{HF}} - \varepsilon_{i^o}^{\text{HF}} - 2K_{i^v i^v, i^o i^o}^{\text{HF}} + K_{i^v i^v, i^o i^o}^{\text{HF}}$ since $K_{i^o i^o, i^o i^o}$ and $K_{i^v i^v, i^v i^v}$ both are zero for HF. Numerically $\Delta E_S^{\text{HF}(\infty)} > \Delta E_S^{(\infty)}$ which accounts for the gradual increase. In terms of RMSD the values for group A decreases gradually from 1.37 eV (LDA) to 0.80 eV (B3LYP) and 0.25 eV (BHLYP). For group B we simply note that RMSD remains relatively constant at the SCF-CV(∞) level of theory with RMSD of 0.28 eV (LDA), 0.21 eV (B3LYP), and 0.27 eV (BHLYP). Thus for the two groups combined we find the RMSD trend 0.99 eV (LDA), 0.59 eV (B3LYP), and 0.26 eV (BHLYP).

V. CONCLUDING REMARKS

We have here introduced the implementation of the self-consistent constricted variational density functional theory for the description of excited states. The n order constricted variational density functional theory CV(n)-DFT is a generalization of CV(2)-DFT presented in Eq. (29). Combined with the Tamm-Dancoff approximation³¹ CV(2)-DFT affords Eq. (28). Here Eq. (28) is equivalent to the basic equation in TDDFT after the Tamm-Dancoff approximation is applied. In CV(n) we start with the U_I matrix obtained from CV(2)-DFT/TD via Eq. (28). Based on U_I for the I th excited state we perform in CV(n) a unitary transformation $\exp[U_I]$ to order n in U_I on the set of occupied and virtual ground state

orbitals under the constraint of Eq. (20b). The result is a new set of occupied and virtual orbitals representing excited state I . This transformation can be carried out to infinite order in n , CV(∞)-DFT. In the self-consistent formulation of CV(∞)-DFT we optimize U_I under the constraints of Eqs. (20b) and (41), thus preventing a variational collapse onto the ground state and lower lying excited states. The SCF-CV(∞)-DFT scheme requires on top of a TD-DFT treatment one SCF calculation for each excited state.

We have applied LDA, B3LYP, and BHLYP to a test set (T1) of 20 $\pi \rightarrow \pi^*$ transitions in unsaturated hydrocarbons and compared the calculated excitation energies for TDDFT, CV(2)-TD, CV(∞), and SCF-CV(∞)-DFT to estimates based on high level *ab initio* calculations.³ The test set T1 was comprised of two groups where all excitations in A could be represented by a single orbital excitation whereas the excitations in B consisted of two or more orbital transitions.

We find that the performance of the second order methods TDDFT and CV(2) is strongly dependent on the fraction α of exact exchange included in the functional. Acceptable results are only obtained with B3LYP where the RMSD's are 0.41 eV (TDDFT) and 0.33 eV (CV(2)-TD), respectively. The poor performance of TDDFT and CV(2) for LDA and BHLYP is primarily to be found among the group A transitions. The CV(∞) scheme where terms to all orders in U are included perturbatively have RMSD's of 0.35 eV (LDA), 0.27 eV (B3LYP), and 0.31 eV (BHLYP). Thus, this scheme is rather insensitive to the fraction α of exact exchange although the best results are obtained for B3LYP. The CV(∞) schemes performs somewhat better for group B than group A. In the case of SCF-CV(∞) we find that the scheme performs well for group B irrespectively of the fraction of HF-exchange with RMSD's of 0.28 eV (LDA), 0.21 eV (B3LYP), and 0.27 eV (BHLYP). On the other hand the performance of SCF-CV(∞) exhibits a strong dependence on α for group A with RMSD's of 1.37 eV (LDA) to 0.80 eV (B3LYP) and 0.25 eV (BHLYP).

Traditionally DFT based studies on excited states have been carried out with either the TD-DFT (Refs. 6 and 10) method or the Δ SCF (Refs. 11 and 15) scheme. The Δ SCF method³⁶ is as SCF-CV(∞)-DFT variational and can thus describe orbital relaxation due to excitations. However, for a single electron transition it is by design restricted to cases that can be described by a single orbital excitation ($i \rightarrow a$). Nevertheless, when applicable, Δ SCF performs well and has been used recently by Van Voorhis *et al.*⁴⁵ to describe $\pi \rightarrow \pi^*$ transition in conjugated systems using BHLYP or MO6-2 $\times$ (Ref. 46) that contain a high percentage of HF-exchange. The SCF-CV(∞)-DFT method is a natural generalization of the Δ SCF scheme as it can deal with both group A and B excitations. Moreover, it is seen to give good results for BHLYP for both A and B with a RMSD of 0.26 eV. In contrast to the Δ SCF method our scheme ensures that there will be no variational collapse into the ground state. The problem of variational collapse has been discussed in the case of $\pi \rightarrow \pi^*$ transitions for the Hartree method by Davidson and Nitzsche.^{36e}

Work is now under way to apply SCF-CV(∞)-DFT to charge transfer, $\sigma \rightarrow \pi^*$, $n \rightarrow \pi^*$ and Rydberg transitions as well as transition metal complexes.

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