Auxiliary many-body wavefunctions for TDDFRT electronic excited states
Consequences for the representation of molecular electronic transitions

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This contribution reports the study of a set of molecular electronic-structure reorganization representations related to light-induced electronic transitions, modeled in the framework of time-dependent density-functional response theory. More precisely, the work related in this paper deals with the consequences, for the electronic transitions natural-orbital characterization, that are inherent to the use of auxiliary many-body wavefunctions constructed a posteriori and assigned to excited states — since time-dependent density-functional response theory does not provide excited state ansätze in its native formulation. Three types of such auxiliary many-body wavefunctions are studied, and the structure and spectral properties of the relevant matrices (the one-electron reduced difference and transition density matrices) is discussed and compared with the native equation-of-motion time-dependent density functional response theory picture of an electronic transition — we see for instance that within this framework the detachment and attachment density matrices can be derived without diagonalizing the one-body reduced difference density matrix. The common “departure/arrival” wavefunction-based representation of the electronic transitions computed with this method is discussed, and two such common “departure/arrival” density-based pictures are also compared.

Keywords: Molecular electronic excited states; electronic-structure reorganization; one-body reduced density matrices.

I. Introduction

Time-dependent density-functional response theory (TDDFRT [1–5]) is probably the most used electronic excited-state calculation method. Such a method gives access to difference and transition properties — the first allows the comparison between the properties in the ground and in the excited state, while the second informs about the coupling between the states, and the response of the system to the light-induced perturbation of the system — but it does not come with an ansatz for the excited states that are computed, at least in its equation-of-motion (EOM) formulation. Knowledge of such an ansatz would however be very useful for analyzing the nature of excited states [6–8], but also in the context of non-adiabatic excited-state dynamics [5, 9, 10], for it allows the computation of quantities such as the non-adiabatic coupling between states [11, 12]. Therefore, multiple research groups have worked out expressions for approximate, auxiliary many-body wavefunctions (AMBW) that are constructed a posteriori, i.e., based on the data issued from the excited-state TDDFRT calculations. The “existence” of certain of these wavefunctions is sometimes conditioned by some constraints that will also be recalled in this paper.

The first of these AMBW’s [13] has been proposed by Casida in his famous paper where he exposes his transposition of the time-dependent Hartree-Fock (TDHF [4, 14]) excited-state calculation procedure to the realm of electron densities, introducing the TDDFRT method [1]. The construction of his AMBW — which has the same structure as a configuration interaction singles (CIS) wavefunction [4, 15–18] — is physically motivated, and related to the expression of the TDDFRT transition moments, but as we will see in this report, the excited states constructed with this procedure are not mutually orthogonal, and an orthogonalization procedure makes the nature of the considered states dependent on the number and nature of all the states that are initially computed. This ansatz has been extensively used in the context of excited-state dynamics simulations [19–25].

The second AMBW was brought by Luzanov and co-workers by solving an alternative TDDFRT response equation, yielding states that are normalized and mutually orthogonal [7]. The drawback of this procedure is that it produces coupled pairs of ansätze rather than a single electronic excited-state wavefunction.

The third AMBW analyzed in this paper comes from the work of Subotnik and co-authors [26]. It is based on Hellmann-Feynman theorem, includes Pulay terms associated with an atom-centered basis, as well as a correction ensuring translational invariance, and ensures a proper behavior near the crossing between two states and in the complete basis limit. However, as for the previous AMBW, these ansätze come in pairs.

The analysis and comparison of the EOM-TDDFRT picture of an electronic transition with the AMBW properties will be performed in terms of some relevant one-body reduced density matrices (1–RDM’s): the one-electron reduced unrelaxed difference density matrix (1–DDM) and the one-electron reduced transition density matrix (1–TDM) [3, 27–30], and their spectral decomposition yielding the so-called natural difference (NDO’s) and transition (NTO’s) orbitals [3, 15, 18, 27, 28, 31].

Since the principal AMBW dealt with in this report takes the form of a linear combination of Fock states that are singly-excited relatively to the Fermi vacuum, one section of this report will introduce a quick review of the basic properties of such ansätze: the CIS wave-
function itself will be introduced, and the properties of CIS electronic transitions will be given in terms of natural orbitals, before commenting the expression of the CIS transition dipole moments — those considerations are useful for deriving Casida’s AMBW in appendix VI B — and extending those considerations beyond CIS.

Casida’s AMBW will then be introduced and its properties studied. The structure and natural-orbital properties of this model will be compared with the EOM–TDDFRT picture, and the uniqueness of Casida’s AMBW will be discussed, among other things such as the consequences of this representation for the one-body reduced transition density kernel.

Finally, the AMBW introduced by Luzanov and co-workers, and the one introduced by Subotnik and co-workers, will be exposed and analyzed. The detachment/attachment density matrices [3, 32] will be derived for the AMBW of Luzanov and co-workers, while the AMBW of Subotnik and co-workers will be showed showed to elude the native TDDFRT de-excitation contributions when used for deriving the 1−TDM.

II. Hypotheses and notations

Ref. [28, 29] are two strong prerequisites papers for this contribution.

Bold Greek letters and bold, upper case letters from Latin alphabet will denote matrices with more than one column. For instance, while \((X)_{ia}\) will denote the \(ia\) component of vector \(x\) where \(ia\) is assimilated to an individual integer, \((X)_{i,a}\) will denote the \(i \times a\) element of matrix \(X\) and \((A)_{ia,jb}\) will denote the \((ia) \times (jb)\) element of matrix \(A\), where again \(ia\) and \(jb\) are assimilated to individual integers.

In this contribution we will consider \(N\)–electron systems. For any electronic quantum state considered below, the \(N\) electrons are distributed in \(L\) orthonormal real-valued spinorbitals \((L \geq N)\), each of them being denoted by an indexed \(\varphi\) symbol and defined on \(S_4 = \mathbb{R}^3 \times \{|\uparrow, \downarrow\}\).

Any molecular electronic ground-state wavefunction value considered in this manuscript is a single \(N\)–dimensional Slater determinant: When \(L\) spinorbitals are being produced when solving the Kohn-Sham equations for optimizing the ground state wavefunction, only \(N\) are “occupied” with occupation number equal to unity, while \((L – N)\) are “unoccupied” (or “virtual”) with their occupation number equal to zero in the ground state.

We define three integer intervals:

\[
I := [1, N], \\
C := [1, L]_L, \\
A := C \setminus I.
\]

The nomenclature is inspired from the traditional assignment of \(i\) and \(a\) indices for “occupied” \((\varphi_i\) with \(i \in I)\) and “virtual” \((\varphi_a\) with \(a \in A)\) spinorbitals respectively. The \(C\) integer interval is then seen as the set of indices covering the total canonical space (occupied plus virtual):

\[
\mathbf{C} := (\varphi_r)_{r \in C}.
\]

We will also assume that from any of the excited-state quantum chemical calculation method considered in this contribution we have produced a finite set of \(M\) molecular electronic excited states. We then set

\[
S := [1, M].
\]

For any electronic transition from the ground electronic state \(|\psi_0\rangle\) to an excited electronic state \(|\psi_m\rangle\) (with \(m \in S\)), when “0m” is used as a subscript or a superscript, it is intended to be representative of the \(|\psi_0\rangle \rightarrow |\psi_m\rangle\) transition — see the related comment in ref. [28] where it is explained that such an implicit convention is not universal at all. When there is no such “0m” subscript or superscript, the transition is implicitly supposed to be taking place from the ground electronic state to a higher-energy electronic state.

Through all the text, the “\(\top\)” superscript will denote the transpose of a matrix, and should not be confused with the “\(\dagger\)” superscript, standing for “transition” — often used to denote the one-particle reduced transition density matrix.

III. A quick review of CIS(–like) many-body wavefunctions features

In this section we will start by introducing the CIS(–like) wavefunctions, i.e., wavefunctions being defined as or having the same properties as CIS wavefunctions. We will then review some basic properties related to those particular wavefunctions.

A. CIS(–like) wavefunctions

We now examine the case of any single-reference electronic excited state wavefunction value written as a linear combination of singly-excited Slater determinants

\[
\langle s_1, \ldots, s_N | \tilde{\psi}_m^* \rangle = \sum_{i=1}^{N} \sum_{a=N+1}^{L} (t_{ma})_{ia} \langle s_1, \ldots, s_N | \psi_i^0 \rangle
\]

with \((m \in S)\),

\[
\forall i \in I, \ s_i \in S_4, \\
t_m \in \mathbb{R}^{N(L-N) \times 1},
\]

and

\[
\forall (i, a) \in I \times A, \ |\psi_a^0\rangle := a^\dagger s_i |\psi_0\rangle.
\]

The \(t_m\) vector in (1) is released during the excited-state calculation. In (2), \(i\) is the second quantization operator annihilating an electron in spinorbital \(\varphi_i\) and \(a^\dagger\) is the second quantization operator creating an electron in spinorbital \(\varphi_a\).

Since every \(|\psi_a^0\rangle\) configuration in (2) is orthogonal to \(|\psi_0\rangle\) we find, using the definition of the general
1–TDM in [28, 29] for an orthonormal basis of real-valued spinorbitals, i.e.,

\[ \forall m \in S, \forall (r, s) \in C^2, \quad (\gamma^T_{0m})_{s,r} = \langle \psi_0 | \hat{r} \hat{s} | \psi_m \rangle, \]

that, for our trial wavefunction \( \tilde{\psi}_m \),

\[ \forall (i, a) \in I \times A, \quad (\tilde{\gamma}^T_{0m})_{i,a} = (\tilde{t}_m)_{ia}, \quad (3) \]
\[ \forall (r, i) \in C \times I, \quad (\tilde{\gamma}^T_{0m})_{r,i} = 0, \quad (4) \]
\[ \forall (a, b) \in A^2, \quad (\tilde{\gamma}^T_{0m})_{a,b} = 0. \quad (5) \]

If \( |\tilde{\psi}_m\rangle \) is not normalized, we can write the corresponding normalized ansatz as

\[ |\psi_m\rangle = z_{\zeta,m}^{-1/2} |\tilde{\psi}_m\rangle, \quad (6) \]

with

\[ z_{\zeta,m} := t^T_m t_m. \]

In what follows, any normalized ansatz that can be written as a linear combination of \( N \)-electron Fock states singly-excited relatively to the Fermi vacuum will be called a \( \zeta \)-ansatz (or \( \zeta \)-type ansatz).

**B. Properties of \( \zeta \)-type ansätze**

Let \( W^\zeta \) denote the set of all \( N \)-electron \( \zeta \)-type ansätze defined as in the previous subsection for any \( L \)-dimensional orthonormal spinorbital space. Any element of \( W^\zeta \) has the properties depicted in this subsection. For the sake of readability, we will consider “any” electronic transition — i.e., a generic transition among the \( M \) available — so we will drop the “0m” subscripts through all this subsection.

We define the 1–TDM corresponding to such a \( \zeta \)-ansatz as

\[ \gamma^T_{\zeta} := z_{\zeta}^{-1/2} \tilde{\gamma}^T_{\zeta} \in \mathbb{R}^{L \times L}. \]

Let \( 0_o \) be the \( N \times N \) zero matrix, \( 0_{ov} \) the \( N \times (L - N) \) zero matrix, and \( 0_v \) the \((L - N) \times (L - N) \) zero matrix. We see from (3), (4), and (5), that \( \gamma^T_{\zeta} \) is partitioned as

\[ \gamma^T_{\zeta} = \begin{pmatrix} 0_o & 0_{ov} \\ T^\top & 0_v \end{pmatrix} \]

with

\[ T \in \mathbb{R}^{N \times (L - N)}, \]

and

\[ \forall (i, a) \in I \times A, \quad z_{\zeta}^{-1/2} (t)_{ia} = (\gamma^T_{\zeta})_{a,i} = (T)_{i,a-N}. \]

We are now going to review few properties mostly related with the spectral decomposition of the CIS one-body reduced difference and transition density matrices.

**Proposition III.1** Any \( \zeta \)-type 1–TDM is nilpotent.
most compact representation of the electronic transition — the expansion is reduced from $N \times (L - N)$ terms to $\min(N, (L - N))$ — with the exact conservation of the $\zeta$—ansatz nature.

According to (8), we have that

$$O^T T^T O = \lambda^\top \lambda \in \mathbb{R}^{N \times N}, \quad (10)$$

$$V^T T^T V = \lambda \lambda^\top \in \mathbb{R}^{(L - N) \times (L - N)}. \quad (11)$$

Combining lemma VI.3 with time-independent Wick’s theorem we find

**Proposition III.2** $\zeta$—type 1—DDM is the direct sum of a negative semidefinite and a positive semidefinite matrix.

This was originally stated in ref. [32]. Complete proof is given in ref. [29] where the following structure for $\gamma_\zeta^\Delta$ was derived:

$$\gamma_\zeta^\Delta = (-TT^\top) \oplus T^\top T. \quad (12)$$

Using again lemma VI.3 we find

**Corollary III.1** $\zeta$—type detachment and attachment density matrices can be derived from the transition density matrix without matrix diagonalisation.

Due to the definition of the detachment and attachment density matrices in terms of the sign of the occupation numbers, i.e., eigenvalues of the one-body reduced difference density matrix, we find that

$$TT^\top \oplus \mathbf{0}_c = \gamma_\zeta^d,$$

$$\mathbf{0}_c \oplus T^\top T = \gamma_\zeta^e,$$

which was also originally stated in ref. [32].

**Proposition III.3** The non-zero natural difference and transition orbitals components are identical.

Due to the structure of $\gamma_\zeta^\Delta$ in (12), we have the following possible matrix of eigenvectors

$$U = O \oplus V \quad (13)$$

and, given (10) and (11), we find the following possible eigendecomposition:

$$U^\top \gamma_\zeta^\Delta U = (-\lambda^\top \lambda) \oplus \lambda \lambda^\top$$

which means that the CIS natural difference orbitals are paired just as the natural transition orbitals are.

We finally establish that the trace of $\zeta$—type detachment and attachment 1—RDM’s, i.e., $\vartheta_\zeta$, is equal to

$$\vartheta_\zeta = \text{tr} (\lambda \lambda^\top) = \text{tr} (\lambda^\top \lambda) = \sum_{i=1}^q \lambda_i^2,$$

**C. Electronic transition dipole moment of CIS(—like) states and beyond**

For $\zeta$—type excited-state wavefunctions, the $w$ component ($w \in \{x, y, z\}$) of the electronic transition dipole moment between ground state $|\psi_0\rangle$ and excited state $|\psi_m\rangle$ reads

$$\langle \psi_0 | \hat{w} | \psi_m^\zeta \rangle = \sum_{r,s=1}^L \langle \varphi_r | \hat{w} | \varphi_s \rangle \langle \psi_0 | \hat{r}^\dagger \hat{s} | \psi_m^\zeta \rangle$$

$$= \sum_{r,s=1}^L \sum_{a=1}^N \sum_{i=a+1}^L (t_{ma})_{ia} \langle \varphi_r | \hat{w} | \varphi_s \rangle \langle \psi_0 | \hat{r}^\dagger \hat{s} \hat{a}^\dagger \hat{i} | \psi_m \rangle$$

where $(m \in S)$, and

$$\hat{w} = \sum_{i=1}^N w_i.$$

If we write $n_p$ the occupation number of spinorbital $\varphi_p$ (with $p \in C$), we deduce from

$$\langle \psi_0 | \hat{p}^\dagger \hat{a}^\dagger \hat{i} | \psi_0 \rangle = \delta_{r,i} \delta_{s,a} n_r n_s n_i$$

$$+ \delta_{r,i} \delta_{s,a} n_i (1 - n_s) (1 - n_a),$$

and

$$(I \cap A = \emptyset) \iff [\forall (i,a) \in I \times A, \delta_{i,a} = 0],$$

that the $w$ component of the electronic transition dipole moment becomes

$$\langle \psi_0 | \hat{w} | \psi_m^\zeta \rangle = \sum_{i=1}^N \sum_{a=N+1}^L \langle \varphi_i | \hat{w} | \varphi_a \rangle (t_{ma})_{ia} \quad \text{ (14)}$$

Setting

$$\forall (i,a) \in I \times A, \ (p_w)_{ia} := \langle \varphi_i | \hat{w} | \varphi_a \rangle,$$

we find

$$\langle \psi_0 | \hat{w} | \psi_m^\zeta \rangle = p_w^\top t_m.$$

Note finally that if the excited-state ansatz did include additional terms with higher level of excitation, as in

$$|\psi_m\rangle = \sum_{i=1}^N \hat{T}_m^{(i)} |\psi_0\rangle \quad \text{ (15)}$$

with, for the first two excitation operators,

$$\hat{T}_m^{(1)} = \sum_{i=1}^N \sum_{a=N+1}^L (t_{ma})_{ia} \hat{a}_i^\dagger,$$

$$\hat{T}_m^{(2)} = \sum_{i,j=1}^N \sum_{a,b=N+1}^L (t_{ma})_{ia} (t_{mb})_{ib} \hat{b}_j^\dagger \hat{a}_i^\dagger,$$

the structure of the 1—TDM would have remained unchanged and would solely include components from $t_m^{(1)}$, and the expression of $\langle \psi_0 | \hat{w} | \psi_m \rangle$ would solely include the single-excitation contributions and read $p_w^\top \hat{T}_m^{(1)}$.

**IV. Comparison of the EOM and auxiliary wavefunction pictures**

This section introduces and compares the two pictures (EOM [13, 33] and AMBW — with three variants) one meets when dealing with TDDFRT.
A. EOM representation of an electronic transition

Let $\hat{T}_m$ be a nilpotent, number- and norm-conserving transition operator corresponding to the transition between two quantum states $(m \in S)$:

$$\hat{T}_m = |\psi_m\rangle \langle \psi_0|, \quad \hat{T}_m^\dagger = |\psi_0\rangle \langle \psi_m|$$

with the constraint that the two states are normalized and orthogonal to each other:

$$\langle \psi_0|\psi_m\rangle = \delta_{0,m}.$$  

In these conditions, we can assess the equation-of-motion $1$–DDM elements $[(r, s) \in C^2]$

$$\langle \psi_0| [\hat{T}_m^\dagger \hat{r}^\dagger \hat{s}, \hat{T}_m] |\psi_0\rangle = \langle \psi_0| \hat{r}^\dagger \hat{s} |\psi_m\rangle - \langle \psi_0| \hat{r}^\dagger \hat{s} |\psi_0\rangle = (\gamma_{0m}^r)_{r,s},$$

and $1$–TDM elements

$$\langle \gamma_{0m}^T\rangle_{s,r} = \langle \psi_0| \hat{r}^\dagger \hat{s} |\hat{T}_m\rangle |\psi_0\rangle.$$

B. The case of EOM-TDDFRT

In an EOM formulation (denoted by a “$\eta$” symbol and sometimes called native in the following) of TDHF, the transition operator $\hat{T}$ in the derivation of the matrix elements is substituted by

$$\hat{T}_\eta := \sum_{i=1}^{N} \sum_{a=a'} \sum_{a''=a'''} \left( x_{ia} \hat{a}^\dagger_i - y_{ia} \hat{a}^\dagger_a \right),$$

i.e., a truncated CI excitation operator ($x$ – hole-particle, $y$ – particle-hole, $hp$), corrected by deexcitation contributions ($y$ – particle-hole, $ph$). Here again, for the sake of readability of the equations, we will consider a general electronic transition between the ground state and any excited state of a molecule. The components of the $x$ and $y$ vectors, solutions to the response equation

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \omega \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}, \quad (16)$$

with, for every $(i, j)$ in $I^2$ and every $(a, b)$ in $A^2$,

$$(A)_{ia,jb} := \langle \psi_0| \hat{a}^\dagger_i \hat{b}^\dagger_j |\psi_0\rangle, \quad (17)$$

$$(B)_{ia,jb} := \langle \psi_0| \hat{a}^\dagger_i \hat{b}^\dagger_j |\psi_0\rangle, \quad (18)$$

can be recast into square matrices:

$$X' = \begin{pmatrix} 0_x & X \\ 0_{x_0} & 0_v \end{pmatrix}, \quad (19)$$

$$Y' = \begin{pmatrix} 0_x & Y \\ 0_{x_0} & 0_v \end{pmatrix}, \quad (20)$$

and

$$\forall (i, a) \in I \times A, \quad x_{ia} = (X')_{ia} = (X)_{ia} - N, \quad (21)$$

$$y_{ia} = (Y')_{ia} = (Y)_{ia} - N. \quad (22)$$

Note that $x$ and $y$ satisfy

$$x^T x - y^T y = 1. \quad (23)$$

In $(16)$, $\omega$ is the transition energy between the ground state and the excited state of interest and $\hat{H}$ is the molecular Hamiltonian. $I$ and $0$ are the $[N \times (L - N)] \times [N \times (L - N)]$ identity and zero matrices, respectively. In equations $(17)$ and $(18)$, $ia$ and $jb$ are assimilated to individual integers (as it is done for the components of $x$ and $y$), for pointing the row (on the left of the comma) and column (on the right of the comma) indices of matrices $A$ and $B$ — see the introductory comments of this paper.

The native TDDFRT eigenproblem has the exact same structure as depicted above. So do the following matrices. This also stands for the Bethe-Salpeter excited-state calculation method [34]. Hence, the structure and properties of the objects discussed below are identical in the three methods.

In the conditions detailed above, the transition density matrix reads

$$\begin{pmatrix} 0_x & Y \\ X^T & 0_v \end{pmatrix} = \gamma_{\eta}^T \in \mathbb{R}^{L \times L}. \quad (24)$$

Its transpose is often seen in the literature to denote the same transition — here, “$T$” denotes an electronic transition with electronic energy promotion, as stated at the beginning of this paper. However we have showed and discussed in refs. [28, 29] that the transpose of the matrix given above corresponds to the transition between the two same states but with the departure/arrival states being permuted.

Proposition IV.1. The EOM $1$–DDM is the direct sum of a negative semidefinite matrix and a positive semidefinite matrix.

In the conditions detailed above, the difference density matrix is [29]

$$-XX^T - YY^T \oplus (X^T X + Y^T Y) = \gamma_{\eta}^\Delta \in \mathbb{R}^{L \times L} \quad (25)$$

Hence, we see that the $1$–DDM and $1$–TDM in TDDFRT and in the Bethe-Salpeter method have identical structures to those in equations (25) and (24) [29]. According to lemma VI.4 given in the appendix,

$$-XX^T - YY^T \geq 0,$$

$$X^T X + Y^T Y \geq 0,$$

which confirms the proposition.

Corollary IV.1. The native TDDFRT detachment and attachment density matrices can be derived without matrix diagonalization.

According to what precedes, and according to the definition of the detachment and attachment, we can now
give the expression of the EOM detachment and attachment one-body reduced density matrices:

\[
\begin{aligned}
\left(XX^T + YY^T\right) \oplus 0_a &= \gamma^d_a, \\
0_a \oplus \left(X^TX + Y^TY\right) &= \gamma^s_a \\
\end{aligned}
\]

We deduce from the expression of the detachment and attachment density matrices that

**Proposition IV.2** The native TDDFRT natural difference orbitals are not paired in general.

Indeed, unlike the CIS method for which the negative semidefinite and positive semidefinite blocks share eigenvalues, the negative semidefinite and positive semidefinite blocks in CIS, which means here that the \(\eta\)-type detachment/attachment 1-RDM’s might not share eigenvalues — so the natural difference orbitals are not necessarily paired. We also find that the integral of the detachment/attachment density satisfies

\[
\vartheta_\eta \geq 1.
\]

The square, non-hermitian 1–TDM has non-zero entries covering the whole canonical space. Hence, it is not meaningful — unless the \(y\) components are all close to zero — to speak in terms of “occupied” and “virtual” NTOs when performing its singular value decomposition. Its left and right singular vectors have components in both the occupied and virtual spaces, so in the general case picturing a TDDFRT electronic transition as a composition of right-to-left NTOs single-electron promotions as in CIS — the right-singular vectors correspond to the “electron” of the hole/electron model while the left-singular vectors correspond to the “hole” of the hole/electron model while the left-singular vectors correspond to the “electron” of the hole/electron simplified representation [28]. Such an approximate picture is often met in the literature: The elements of the one-body reduced transition density matrix are seen as the singles coefficients in the single-electron-replacement truncation of a complete expansion of the type encountered in (15), and the NTOs used to present this expansion in second quantization as

\[
|\psi^\eta_{nm}\rangle \simeq \sum_{r=1}^L \lambda^\eta_r \hat{f}_r \hat{u}_r |\psi_0\rangle + \cdots
\]

where the \(\lambda^\eta_r\) coefficients are the singular values corresponding to the \(i^{th}\) couple of left (\(\hat{f}\)) and right (\(\hat{r}\)) singular vectors of \(\gamma^T_\eta\). In the expression above, we have used the \(\hat{f}_r\) and \(\hat{r}_r\) operators to signify that they have components in both the occupied and virtual spaces. Therefore, the 1–TDM obtained with this pseudo-ansatz will differ from the 1–TDM that was used for producing it, which is in contradiction with what was stated about any such ansatz [see the discussion after (15)]. This means that, in the general case, picturing an electronic transition as a linear combination single-NTO population transfers — or using the 1–TDM elements as CIS-like coefficients — can be problematic. Since such an ansatz in TDDFRT leads to losing the de-excitation contributions, there has been a quest for proposing meaningful ansätze — this is the so-called TDDFRT “assignment problem”, that will be discussed in the next section.

When the approximate picture of the transition is given in terms of one-body reduced density functions rather than one-body wavefunctions, the transition-hole density \(\to\) transition-electron density representation can appear. Since the native TDDFRT transition-hole \((h)\) and the transition-electron \((e)\) one-body reduced density matrices have the following structure

\[
\begin{aligned}
\gamma^h_\eta &:= XX^T \oplus YY^T, \\
\gamma^e_\eta &:= YY^T \oplus XX^T,
\end{aligned}
\]

we see that, though the trace of \(\gamma^d_\eta, \gamma^s_\eta, \gamma^h_\eta,\) and \(\gamma^e_\eta\) are equal — and superior or equal to unity —, the detachment (respectively, attachment) density matrix solely involves the orbitals that are occupied (respectively, unoccupied) in the ground state, while both the transition-hole and the transition-electron density matrices involve orbitals from the full canonical space. There would be a true interpretative ambiguity when comparing the hypothetical hole/electron and the detachment/attachment pictures if some disambiguation had not been proposed relatively to that representation matter [28], which suggested that the hole/electron density matrices and the NTOs are simply not meant to bear the same physical information as the detachment/attachment density matrices and the NDOs, concluding that, since NDOs are, in general, unpaired, there is no exact “departure/arrival” picture that can be drawn from natural transition
or difference orbitals in the general case, and that among the objects discussed here only the detachment/attachment densities should be seen as being part of a “departure/arrival” simplified picture.

In the absence of de-excitations, $Y$ vanishes, the Frobenius norm of $X$ becomes equal to unity, and the resulting representation of the electronic transition is exactly consistent with the one of a $\zeta$–ansatz. We call this the Tamm-Dancoff Approximation (TDA).

Note finally that $\tilde{T}_{\gamma}$ is not used as a direct approximation to an EOM transition operator $|\psi_0\rangle\langle\psi_0|$ to write an excited state ansatz. Indeed, $\tilde{T}_{\gamma}$ is not nilpotent, not number-conserving, and not norm-conserving — this comment is in line with our remark concerning the use of the 1–TDM elements directly for producing a CIS-like ansatz.

C. Auxiliary many-body wavefunctions

In this section we will discuss three alternative pictures to the original equation-of-motion TDDFRT, using auxiliary many-body wavefunctions for the electronic excited states.

1. Casida’s assignment problem

We will introduce here the TDDFRT AMBW originally proposed by Casida [1] and extensively used in the context of non-adiabatic dynamics. After a necessary normalization, we will inspect the properties of the 1–TDM and 1–DDM one can derive from inspecting such an ansatz and the structure of the related objects. The AMBW proposed by Casida has the following expression:

$$|\tilde{\psi}\rangle := \sum_{i=1}^{N} \sum_{a=N+1}^{L} (x_{ia} + y_{ia}) |\psi_a\rangle$$

obtained by recasting (16) into a Hermitian eigenproblem

$$R_+ f_+ = \omega^2 f_+$$

with

$$R_+ := (A - B)^{1/2}(A + B)(A - B)^{-1/2},$$

$$f_+ := (A - B)^{-1/2}(x + y).$$

All the details for reaching the Hermitian eigenproblem and for deriving (26) from it are given in Appendix VII.B.

When inspecting (26), we see that multiplication of $|\tilde{\psi}\rangle$ by the inverse of

$$z_{\zeta}^{1/2} := \sqrt{(x + y)^\dagger(x + y)}$$

is required to yield a normalized ansatz $|\psi\rangle$ belonging to $W^{\zeta}$, with the corresponding $\gamma_{\zeta}^A$ 1–DDM having a zero trace, depicting a number-conserving electronic transition. Indeed, without the normalization, the norm of the excited-state wavefunction would be the square root of $z_{\zeta}$ from (27), and the trace of the 1–DDM would be

$$\text{tr} (\gamma_{\zeta}^A) = N(z_{\zeta} - 1)$$

which might differ from zero.

The construction of $|\tilde{\phi}\rangle$ as in (26), hence of $|\psi\rangle$, relies on the existence of the $R_+$ matrix and the $f_+$ vector, so the existence criterion for $|\psi\rangle$ as in (26) relies on the positive definiteness of $(A - B)$. Note that such a condition is ensured for pure–DFT xc–functionals for which $(A - B)$ is always diagonal and positive definite. The abovementioned criterion is often forgotten when using hybrid functionals, and the AMBW is constructed directly by taking the $x$ and $y$ vectors from (16) to write an ansatz, as if $(A - B)$ was a priori positive definite. Using the same manipulations as in equations (19) to (22), the TDDFRT renormalized ansatz $|\psi\rangle$ produces a traceless 1–DDM

$$W_d \oplus W_a = z_{\zeta} \gamma_{\zeta}^A \in \mathbb{R}^{L \times L}$$

with

$$W_d := (X + Y)(X + Y)^\dagger,$$

$$W_a := (X + Y)(X + Y).$$

The transition density matrix is the nilpotent

$$\begin{pmatrix}
0 & X + Y \\
0 & 0
\end{pmatrix} = z_{\zeta}^{1/2} (\gamma_{\zeta}^A)^\dagger \in \mathbb{R}^{L \times L}.$$ 

According to lemma VI.3 (see Appendix),

$$-(X + Y)(X + Y)^\dagger \preceq 0,$$

$$(X + Y)^\dagger(X + Y) \succeq 0.$$ 

Therefore,

$$(X + Y)(X + Y)^\dagger \oplus 0 = z_{\zeta} \gamma_{\zeta}^d,$$

$$0 \oplus (X + Y)^\dagger(X + Y) = z_{\zeta} \gamma_{\zeta}^\gamma$$

and the $\zeta$–type detachment and attachment 1–RDM’s share eigenvalues [see lemma VI.2 and equations (10) and (11)] and can be derived without requiring the diagonalization of the $\zeta$–type 1–DDM. We also have that $\delta_{\zeta} = 1$.

The transition density matrix is nilpotent, and its non-zero elements can be collected into a rectangular $T_{\zeta}^d$ matrix:

$$z_{\zeta}^{-1/2} \begin{pmatrix}
X^\dagger + Y^\dagger
\end{pmatrix} = T_{\zeta}^d \in \mathbb{R}^{(L-N)\times N}.$$ 

This matrix can be diagonalized by an SVD to produce its left and right singular vectors, i.e., the left and right aNTOs (auxiliary Natural Transition Orbitals), eigenvectors of $\gamma_{\zeta}^A$ and $\gamma_{\zeta}^d$ paired by their eigenvalue.
The one-body reduced transition density kernel \([28]\) for the TDDFT \(\zeta\)-ansatz reads

\[
\gamma^T(m; n) = \sum_{i=1}^{N} \sum_{a=N+1}^{L} \langle \psi_m | \phi_i \rangle \langle \phi_i | \psi_n \rangle
\]

For the EOM approach, it reads

\[
\gamma^T_\lambda(m; n) = \sum_{i=1}^{N} \sum_{a=N+1}^{L} \langle \psi_m | \phi_i \rangle \langle \phi_i | \psi_n \rangle
\]

Though the two kernels are different, the corresponding one-body transition densities are identical, up to a scaling factor:

\[
z^{-1/2}_m \gamma^T_\lambda(m; n) = n_\lambda(m; n)
\]

3. Orthogonalization of Casida’s AMBW’s

In practice there are usually more than one excited state computed at the same time during a calculation. Hence, a set of data and matrices is produced as the outcome of such a calculation, and the AMBW’s one can construct based on the proposed scheme are not orthogonal to each other. After orthogonalizing the set of TDDFT AMBW’s, we verify that the conclusions from the previous paragraph are transferable when orthogonalization of the excited states is done \textit{a posteriori}.

We consider the \(M\) normalized but non-orthogonal ansätze constructed using the procedure depicted in the previous paragraph. Any of these ansätze reads

\[
|\psi_m\rangle = \sum_{i=1}^{N} \sum_{a=N+1}^{L} (c_m)_{ia} |\psi_i\rangle
\]

with \(m \in S\), and

\[
z^{-1/2}_m (c_m)_{ia} = (x_m)_{ia} + (y_m)_{ia}
\]

where we have explicitly identified the number of the excited state, \(m\), using subscripts.

The overlap between two of these states is

\[
\langle \psi_m | \psi_n \rangle = c_m^\dagger c_n.
\]

One can orthonormalize the set of primitive AMBW’s by considering a linear combination of them \((k \in S)\)

\[
|\psi_k^\perp\rangle = \sum_{p=1}^{M} \left( S^{-1/2} \right)_{k,p} |\psi_p^\parallel\rangle
\]

which is equivalent to writing

\[
|\psi_k^\perp\rangle = \sum_{i=1}^{M} \sum_{a=N+1}^{L} (c_k^\perp)_{ia} |\psi_i^\parallel\rangle.
\]

Let \(W^\perp\) be the set of these \(M\) orthonormal states:

\[
W^\perp = \{ |\psi_m^\parallel\rangle : |\psi_m^\parallel\rangle = 1, (m \neq n) \implies \langle \psi_m^\parallel | \psi_n^\parallel \rangle = 0, [(m, n) \in S^2] \}
\]

Obviously,

\[
W^\perp \subset W^\parallel.
\]

According to (28) showing a normalized linear combination of singly-excited configurations, we see that the same rules for constructing the \(\gamma^T_\lambda\) and \(\gamma^T_\mu\) corresponding to elements of \(W^\parallel\) also apply to elements of \(W^\perp\), so a \(\gamma^T_\lambda\) matrix can be constructed and its non-zero elements can be encoded into an \((L - N) \times N\) matrix leading to the derivation of projected-auxiliary NTOs. One can also obtain \(\gamma^T_\mu\) and detachment/attachment 1-RDM’s from this picture. Note however that the representation of the electronic transitions will rely on the size and nature of the set of excited states ansätze used for constructing the abovementioned objects. In that case, we also have that \(\theta_\perp = 1\).

4. Uniqueness of Casida’s AMBW’s

In many references the TDDFT AMBW in (26) reads

\[
|\tilde{\psi}_\zeta\rangle := \sum_{i=1}^{N} \sum_{a=N+1}^{L} \sqrt{\epsilon_a - \epsilon_i} (z_+)^{ia} |\psi_i^\parallel\rangle
\]

with \(z_+\) being the normalized \(f_i\) vector

\[
z_+ = \sqrt{\omega} (A - B)^{-1/2} (x + y) = \sqrt{\omega} f_+,
\]

and \(\epsilon_p\) the energy of the \(p\)th canonical spinorbital \((p \in C)\). For pure-DFT xc-functionals, the expression of \(|\tilde{\psi}_\zeta\rangle\) in (29) is identical to the one of (26) since in that case,

\[
\forall (i,j) \in I^2, \forall (a,b) \in A^2, (A - B)_{ia,jb} = (\epsilon_a - \epsilon_i) \delta_{i,j} \delta_{a,b}.
\]

From equations (41) and (42) we have that

\[
(A - B)(x - y) = \omega^2 (A + B)^{-1/2} (x - y).
\]

Multiplying to the left by \((A + B)^{1/2}\) and inserting the \((A + B)^{1/2}(A + B)^{-1/2}\) matrix between \((A - B)\) and \((x - y)\) in the left-hand side gives

\[
\mathbf{R}_- f_- = \omega^2 f_-
\]
The AMBW’s of Luzanov and co-workers

The formulation of any component of the dynamic polar-
response of the density matrix into the sum-over-state
expression of the real part of the TDDFR T linear
results here that the proposed ansätze in (16) lead the authors to state that the CIS–
possibility of writing two ansätze from the
central (31) lead the authors to state that the CIS–
Due to the non-uniqueness of the electronic-transition
properties in the eigenvalue problem: (31) has both the exact same
properties in the (ϕ, r) ∈ C basis as ζ-ansätze [see (6)].

5. The AMBW’s of Luzanov and co-workers

Due to the non-uniqueness of the electronic-transition
representation involving z+ or z− as nilpotent transition
operator, Luzanov and Zhikol have proposed an
alternative scheme for reducing (16) into an Hermitian eigenvalue problem: (16), that we can rewrite as

\[ \mathbf{A} \mid u \rangle = \omega \mathbf{J} \mid u \rangle, \]  

(31)

with

\[ \mid u \rangle := \begin{pmatrix} x \\ y \end{pmatrix}, \]

is, upon certain conditions that are detailed below and in appendix VI C, isospectral to

\[ \Omega \mid u_\ast \rangle = \omega \mid u_\ast \rangle, \]  

(32)

with

\[ \Omega := \mathbf{A}^{1/2} \mathbf{J} \mathbf{A}^{-1/2}, \]

\[ \mid u_\ast \rangle := (\omega^{-1} \mathbf{A})^{1/2} \mid u \rangle = \begin{pmatrix} x_\ast \\ y_\ast \end{pmatrix}. \]

The detailed derivation of (32) from (31) is given in Appendix VI C. We see that it involves the \( \mathbf{A}^{1/2} \) matrix, which reads

\[ 2\mathbf{A}^{1/2} = \begin{pmatrix} \mathbf{Q}_+ & \mathbf{Q}_- \\ \mathbf{Q}_- & \mathbf{Q}_+ \end{pmatrix}, \]

with

\[ \mathbf{Q}_+ = (\mathbf{A} + \mathbf{B})^{1/2} + (\mathbf{A} - \mathbf{B})^{1/2}, \]

\[ \mathbf{Q}_- = (\mathbf{A} + \mathbf{B})^{-1/2} - (\mathbf{A} - \mathbf{B})^{-1/2}, \]

which implies that \( \mathbf{A} + \mathbf{B} \) and \( \mathbf{A} - \mathbf{B} \) must be positive semidefinite in order to reduce (31) to (32).

We note here few interesting properties of any \( \mid u_\ast \rangle \) vector:

\[ \langle u_\ast \mid u_\ast \rangle = \omega^{-1} \langle u \mid \mathbf{A} \mid u \rangle = \langle u \mid \mathbf{J} \mid u \rangle = x^\ast x - y^\ast y = 1, \]

i.e.,

\[ x^\ast x + y^\ast y = 1, \]  

(33)

and

\[ x^\ast x = z_\ast + z_+ = \omega^{-1/2} \left[ (\mathbf{A} + \mathbf{B})^{1/2} (x + y) + (\mathbf{A} - \mathbf{B})^{1/2} (x - y) \right], \]

\[ y^\ast y = z_\ast - z_+ = \omega^{-1/2} \left[ (\mathbf{A} + \mathbf{B})^{1/2} (x + y) + (\mathbf{A} - \mathbf{B})^{1/2} (y - x) \right]. \]

From these results, Luzanov and Zhikol have suggested to build two normalized ansätze, namely

\[ \mid \psi^x_\ast \rangle = \left( x^\ast x, x_\ast \right)^{-1/2} \sum_{i=1}^{N} \sum_{a=N+1}^{L} (x_\ast)_ia \mid \psi^a_\ast \rangle, \]

\[ \mid \psi^y_\ast \rangle = \left( y^\ast y, y_\ast \right)^{-1/2} \sum_{i=1}^{N} \sum_{a=N+1}^{L} (y_\ast)_ia \mid \psi^a_\ast \rangle. \]

These two ansätze are of ζ type, with two state 1–RDM which read, using the same manipulations as in equations (19) to (22),

\[ \gamma^x_\ast = \gamma_0 + \left( x^\ast x \right)_n - \left[ (-X^\ast X_n) \oplus (X^\ast X_n) \right], \]

\[ \gamma^y_\ast = \gamma_0 + \left( y^\ast y \right)_n - \left[ (-Y^\ast Y_n) \oplus (Y^\ast Y_n) \right], \]

where \( \gamma_0 \) is the ground-state 1–RDM. They then use a statistical mixture of the corresponding 1–RDM to build the total excited-state 1–RDM:

\[ \gamma_\ast = \left( x^\ast x_\ast \right)_n \gamma^x_\ast + \left( y^\ast y_\ast \right)_n \gamma^y_\ast \]

which we can show leads to the 1–DDM

\[ \gamma_\ast = \left(-X^\ast X_n - Y^\ast Y_n \right) \oplus \left( X^\ast X_n + Y^\ast Y_n \right) \]

and to the detachment/attachment density matrices

\[ \gamma^d_\ast = \left(X^\ast X_n + Y^\ast Y_n \right) \oplus 0_v, \]

\[ \gamma^z_\ast = 0_v \oplus \left( X^\ast X_n + Y^\ast Y_n \right), \]

which share the same algebraic properties as the matrices in the EOM picture, though they are derived from AMBW’s. The difference with the EOM picture is that there are restrictions (positive semidefiniteness of the \( \mathbf{A} + \mathbf{B} \) and \( \mathbf{A} - \mathbf{B} \) matrices) to the existence of this picture, and, according to (33), the fact that \( \phi_\ast \) is 1.
Recently [26], an alternative ansatz was introduced by Subotnik and co-workers for computing TDHF and TDDFT derivative couplings. It comes with pairs of ansätze (denoted hereafter by the Greek letter \( \Lambda \)):

\[
\forall (m, n) \in S^2, \quad \langle \psi_{m,n}^\Lambda | \hat{p}^\dagger \hat{\mathbf{s}} | \psi_{m,n}^\Lambda \rangle := \left( \tilde{X}_m + \tilde{X}_n \tilde{Y}_n \hat{Y}_m \right) | \psi \rangle,
\]

\[
\langle \psi_{m,n}^\Lambda | \hat{p}^\dagger \hat{\mathbf{s}} | \psi_{m,n}^\Lambda \rangle := \left( \tilde{X}_n + \tilde{X}_m \tilde{X}_n \tilde{Y}_m \right) | \psi \rangle,
\]

where “m:n” reads “m given n”, and

\[
\forall m \in S, \quad \tilde{X}_m = \sum_{i=1}^N \sum_{a=N+1}^L (x_m)_{ia} a_i^\dagger,
\]

\[
\tilde{Y}_m = \sum_{i=1}^N \sum_{a=N+1}^L (y_m)_{ia} a_i^\dagger,
\]

i.e., \( \tilde{X} \) and \( \tilde{Y} \) are both excitation operators, but with coefficients taken from the components of \( \mathbf{x} \) and \( \mathbf{y} \).

One element of the 1–TDM for the \( | \psi \rangle \rightarrow | \psi_{m,n}^\Lambda \rangle \) transition reads

\[
\langle \psi_{m,n}^\Lambda | \hat{p}^\dagger \hat{\mathbf{s}} | \psi_{m,n}^\Lambda \rangle = \langle \psi_{m,n}^\Lambda | \hat{p}^\dagger \hat{\mathbf{s}} \tilde{X}_m | \psi \rangle,
\]

\[
+ \langle \psi_{m,n}^\Lambda | \hat{p}^\dagger \hat{\mathbf{s}} \tilde{X}_m \tilde{Y}_n | \psi \rangle.
\]

(34)

The second term in (34) vanishes, and the 1–TDM element reduces to

\[
\langle \psi_{m,n}^\Lambda | \hat{p}^\dagger \hat{\mathbf{s}} | \psi_{m,n}^\Lambda \rangle = \sum_{i=1}^N \sum_{a=N+1}^L x_{ia} \left( \langle \psi | \hat{p}^\dagger \hat{\mathbf{s}} a_i^\dagger | \psi \rangle \right)
\]

\[
= \sum_{i=1}^N \sum_{a=N+1}^L x_{ia} \delta_{r,i} \delta_{s,a} n_{r}(1 - n_{s})
\]

leading to

\[
\begin{pmatrix}
0_r & 0_{ov} \\
X_m^T & 0_r
\end{pmatrix} = \gamma_{\Lambda}^{m,n} \in \mathbb{R}^{L \times L},
\]

with

\[
\forall (i, a) \in I \times A, \quad (x_m)_{ia} = (X_m)_{i,a-N}
\]

which has the exact same structure as the \( \zeta \)–type 1–TDM. This eludes the de-excitation coefficients.

On the other hand, one element of the 1–DDM for the \( | \psi \rangle \rightarrow | \psi_{m,n}^\Lambda \rangle \) transition reads

\[
\langle \psi_{m,n}^\Lambda | \hat{p}^\dagger \hat{\mathbf{s}} | \psi_{m,n}^\Lambda \rangle = \delta_{r,s} n_{r}, n_{s},
\]

but the first term

\[
\langle \psi_{m,n}^\Lambda | \hat{p}^\dagger \hat{\mathbf{s}} | \psi_{m,n}^\Lambda \rangle = \langle \psi | \left( \hat{\mathbf{1}}_{m}^\dagger \hat{X}_n^\dagger \hat{X}_m^\dagger + \hat{X}_n^\dagger \right) \hat{p}^\dagger \hat{\mathbf{s}}
\]

\[
\times \left( \hat{X}_m + \hat{X}_n \hat{X}_n \hat{Y}_n \right) | \psi \rangle
\]

has to be developed into four parts:

\[
\langle \psi_{m,n}^\Lambda | \hat{p}^\dagger \hat{\mathbf{s}} | \psi_{m,n}^\Lambda \rangle = \left( L_{m,n}^{\Lambda} \right)_{r,s} + \left( L_{m,n}^{\Lambda} \right)_{r,s},
\]

\[
+ \left( L_{3}^{\Lambda} \right)_{r,s} + \left( L_{4}^{\Lambda} \right)_{r,s},
\]

with

\[
\left( L_{1}^{\Lambda} \right)_{r,s} = \langle \psi | \hat{X}_m^\dagger \hat{X}_n^\dagger \hat{\mathbf{s}} \hat{X}_m | \psi \rangle,
\]

\[
\left( L_{2}^{\Lambda} \right)_{r,s} = \langle \psi | \hat{Y}_n^\dagger \hat{X}_n^\dagger \hat{\mathbf{s}} \hat{X}_m | \psi \rangle,
\]

\[
\left( L_{3}^{\Lambda} \right)_{r,s} = \langle \psi | \hat{X}_m^\dagger \hat{\mathbf{s}} \hat{X}_m \hat{Y}_n | \psi \rangle,
\]

\[
\left( L_{4}^{\Lambda} \right)_{r,s} = \langle \psi | \hat{Y}_n^\dagger \hat{\mathbf{s}} \hat{X}_m \hat{X}_n \hat{Y}_n | \psi \rangle.
\]

After developing the \( \tilde{X} \) and \( \tilde{Y} \) operators, we see that \( L_{2}^{\Lambda} \) and \( L_{3}^{\Lambda} \) are two \( L \times L \) zero matrices, and that

\[
\left( L_{4}^{\Lambda} \right)_{r,s} = (-X_m X_m^T + Y_m X_m^T).
\]

which is a \( \zeta \)–like 1–DDM. However, there is still the \( L_{4}^{\Lambda} \) matrix to add to \( L_{1}^{\Lambda} \) for getting the full \( \gamma_{\Lambda}^{m,n} \).

One matrix element of \( \gamma_{\Lambda}^{m,n} \) is a sum of expectation values of chains of fourteen second quantization operators with respect to the one-determinant reference state, each expectation value being decomposed into a minimum of 252 products of Kronecker’s deltas.

V. Conclusion

We have unveiled and discussed properties of molecular electronic transitions representations issued by TDDFT calculations and their post-processing into auxiliary many-body wavefunctions for the electronic excited states. The native EOM formulation of TDDFT was extensively discussed in terms of natural-orbital representation of the transitions — with the important result that the related detachment/attachment density matrices can be derived without requiring the diagonalization of the 1–DDM —, and such a representation was compared with the CIS-like picture derived by Casida’s ansatz. The NTO population-transfer approximate picture for a transition has also been discussed in the EOM–TDDFT framework, as well as the detachment/attachment and transition-hole/transition-electron pictures, for which a disambiguation has been previously proposed in another publication.

Two alternative types of ansätze were reported: the one introduced by Luzanov and co-workers, and the one introduced by Subotnik and co-workers. The structure and properties of the relevant matrices (the 1–DDM and the 1–TDM) were resolved for these two types of ansätze. The detachment/attachment density matrices corresponding to the AMBW by Luzanov and co-workers, though being issued from a couple of CIS-like expansions, have their structure identical to the one from the EOM picture. On the other hand, the 1–TDM in the frame proposed by Subotnik and co-authors eludes the TDDFT “de-excitations” contributions, and the 1–DDM in that model contains multi-excitation contributions.

We would like to conclude this contribution by mentioning that without the disambiguation
in [28] relatively to the interpretation of the detachment/attachment and transition-hole/transition-electron models, the TDDFRT picture of an electronic transition would have remained either equivocal (EOM-TDDFRT), either incomplete or arbitrary (AMBW’s).

Acknowledgements

Drs Pierre-François Loos, Anthony Scemama, Emmanuel Fromager, Benjamin Lasorne, Matthieu Saubanère, Nicolas Saby, Mario Barbatti, Miquel Huix-Rotllant, Christophe Raynaud and Evgeny Posenitskiy are gratefully acknowledged for very fruitful discussions on the topic.

VI. Appendix

A. Basic results from linear algebra

From the existence of a singular value decomposition for any matrix, we get

**Lemma VI.1** Let \( A \) be an \( m \times n \) complex matrix and \( A^\dagger \) its adjoint. Let \( p \) be any strictly positive integer lower or equal to \( \min(m, n) \). Then, the \( p \)th left-singular vector \( w_p \in \mathbb{C}^{m \times 1} \) of \( A \) corresponds to the same singular value \( \sigma_p \) as the \( p \)th right-singular vector \( v_p \in \mathbb{C}^{n \times 1} \) of \( A \).

Lemma VI.1 also reads

\[
\forall p \in [1, \min(m, n)], \quad A v_p = \sigma_p w_p, \quad (35) \\
A^\dagger w_p = \sigma_p v_p. \quad (36)
\]

**Lemma VI.2** Let \( A \) be an \( m \times n \) complex matrix and \( A^\dagger \) its adjoint. Let \( q \) be the strictly positive integer equal to \( \min(m, n) \). Then, \( A A^\dagger \) and \( A^\dagger A \) share \( q \) eigenvalues. Those eigenvalues are the squared singular values of \( A \).

Proof: Let \( p \) be any strictly positive integer lower or equal to \( g = \min(m, n) \). Then, multiplying (35) to the left by \( A^\dagger \) leads, according to (36), to

\[
A^\dagger A v_p = \sigma_p^2 v_p, \quad (37)
\]

while multiplying (36) to the left by \( A \) leads, according to (35), to

\[
A A^\dagger w_p = \sigma_p^2 w_p. \quad (38)
\]

From what precedes we also conclude to the following lemmas:

**Lemma VI.3** Let \( A \) be an \( m \times n \) complex matrix and \( A^\dagger \) its adjoint. Then,

\[
A A^\dagger \succeq 0, \\
A^\dagger A \succeq 0,
\]

i.e., the product of a matrix by its adjoint is a positive semi-definite matrix.

**Lemma VI.4** Let \( A \) and \( B \) be two \( n \times n \) complex matrices. Then,

\[
(A \succeq 0 \text{ and } B \succeq 0) \implies (A + B \succeq 0),
\]

i.e., the sum of two positive semi-definite matrices is a positive semi-definite matrix.

B. Derivation of Casida’s TDDFRT AMBW

Our starting point here will be (16). In a first step we will derive the working equations for a general, electronic transition between the ground state and one excited state, so the target excited state will not have a particular label (we omit the indices for a while). We get, for real \( A \) and \( B \) matrices,

\[
A x + B y = \omega x, \quad (39) \\
B x + A y = -\omega y. \quad (40)
\]

Subtracting (39) to (40) gives

\[
(A - B)(x - y) = \omega(x + y) \iff (x - y) = (A - B)^{-1}(x + y), \quad (41)
\]

while adding them and using (41) gives

\[
(A + B)(x + y) = \omega(x - y) = \omega^2(A - B)^{-1}(x + y). \quad (42)
\]

Multiplication to the left by \( (A - B)^{1/2} \)

\[
(A - B)^{1/2}(A + B)(x + y) = \omega^2(A - B)^{-1/2}(x + y)
\]

and insertion of \( (A - B)^{1/2}(A - B)^{-1/2} \) between \( (A + B) \) and \( (x + y) \) finally leads to

\[
R_+ f_+ = \omega^2 f_+
\]

with

\[
R_+ := (A - B)^{1/2}(A + B)(A - B)^{-1/2}
\]

and

\[
f_+ := (A - B)^{-1/2}(x + y) \quad (43)
\]

For pure–DFT exchange–correlation (xc) functionals, the \( f_+ \) vectors are then used to write the components of the electronic transition dipole moment. In TDDFRT, these components read, for a given excited state \( |\psi_m\rangle \),

\[
\langle \psi_0 | \hat{w} | \psi_m \rangle = p_{w}^\dagger (\alpha_m a_m), \quad (m \in S)
\]

with \( p_{w} \) from (14),

\[
\alpha_m = \left( \omega_m \tilde{f}_{+,m} f_{+,m} \right)^{-1/2},
\]

and

\[
a_m = (A - B)^{1/2} f_{+,m}.
\]

Dropping again the \( m \) subscripts for readability, we have that, if the excited state could be written as a
linear combination of Slater determinants, its single-excitation part would be, according to what precedes,
\[ \langle s_1, \ldots, s_N | \tilde{\psi}_\xi \rangle := \alpha \sum_{i=1}^{N} \sum_{a=N+1}^{L} a_{ia} \langle s_1, \ldots, s_N | \psi_{ia}^\xi \rangle. \] (44)

The linear combination of singly-excited Slater determinants in (44) has then been used in the context of non-adiabatic dynamics as an auxiliary many-body wavefunction assigned to the excited state reached by the linear response treatment of the Kohn-Sham DFT system: From equations (41) and (43), we deduce
\[ (x+y) = (A-B)^{1/2} f_\xi, \]
\[ (x-y) = \omega (A-B)^{-1/2} f_\xi. \]

Using (23), and considering that the AMBW was originally derived for pure–DFT xc-functionals, for which \((A-B)\) is diagonal, hence \((A-B)^{1/2}\) is self-adjoint,
\[ 1 = (x+y)^t (x-y) = f_\xi^t (A-B)^{1/2} (A-B)^{-1/2} f_\xi, \]
i.e.,
\[ f_\xi^t f_\xi = \omega^{-1} \implies \alpha = 1, \] (45)
so that \(R_\xi\) and \(f_\xi\) satisfy
\[ f_\xi^t R_\xi f_\xi = \omega. \]

From (45), we have that (44) transforms into
\[ |\tilde{\psi}_\xi := \sum_{i=1}^{N} \sum_{a=N+1}^{L} (x_{ia} + y_{ia}) |\psi_{ia}^\xi \rangle. \]

C. Derivation of the alternative TDDFT response equation of Luzanov and co-workers

We start by multiplying (31) by \(\omega^{-1/2}\), and by rewriting \(\Lambda\) as \(\Lambda^{1/2} \Lambda^{1/2}\) — the existence criterion for this matrix product is that \((A+B)\) and \((A-B)\) are positive semi-definite —, which gives
\[ \Lambda^{1/2} \left( \omega^{-1/2} \Lambda \right)^{1/2} |u\rangle = \sqrt{\omega} \Omega |u\rangle. \]

Given that \(J\) is involutory \((J = J^{-1})\), we multiply the previous to the left by \(\Lambda^{1/2} J\)
\[ \Lambda^{1/2} J \left( \omega^{-1} \Lambda \right)^{1/2} |u_\ast\rangle = \omega \left( \omega^{-1} \Lambda \right)^{1/2} |u_\ast\rangle, \]
i.e.,
\[ \Omega |u_\ast\rangle = \omega |u_\ast\rangle. \]

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