A comprehensive, self-contained derivation of the one-body density matrices from single-reference excited-state calculation methods using the equation-of-motion formalism

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Abstract
In this contribution, we review in a rigorous, yet comprehensive fashion the assessment of the one-body reduced density matrices derived from the most used single-reference excited-state calculation methods in the framework of the equation-of-motion formalism. Those methods are separated into two types: those which involve the coupling of a deexcitation operator to a single-excitation transition operator, and those which do not involve such a coupling. The case of many-body auxiliary wave functions for excited states is also addressed. For each of these approaches we were interested in deriving the elements of the one-body transition and difference density matrices, and to highlight their particular structure. This has been accomplished by applying a decomposition of integrals involving one-determinant quantum electronic states on which two or three pairs of second quantization operators can act. Such a decomposition has been done according to a corollary to Wick’s theorem, which is brought in a comprehensive and detailed manner. A comment is also given about the consequences of using the equation-of-motion formulation in this context, and the two types of excited-state calculation methods (with and without coupling excitations to deexcitations) are finally compared from the point of view of the structure of their transition and difference density matrices.

KEYWORDS
equation-of-motion formalism, molecular excited states, reduced density matrix theory

1 | INTRODUCTION

Among the physical processes studied by theoreticians, light-induced molecular electronic transitions, due to their potential involvement in the development of new technologies, are now involving careful consideration from both experimental and theoretical (academic and industrial) research communities. Ubiquitous in biology and chemistry, they are under active study in the context of many crucial societal issues of our time. These issues include, among others, public health with optogenetics[1] and phototherapy,[2] or climate change with the design of efficient photovoltaic devices.[3] Quantum-molecular science, and in particular quantum-chemical excited-state calculation methods, are now established as a reliable mean to gain fundamental qualitative and quantitative insights into light-induced physical or chemical processes at the atomic level. Indeed, the theoretical characterization of electronic excited states is the aim of an increasing number of scientific contributions, and the tools used for such analysis involve generally the objects originating directly from the calculation of the excited states.[4–6] Depending on the method used for computing the electronic transitions, the objects derived from these calculations will not have the same structure and the same properties.[7] As the analysis of the nature of the excited states generally relies on the use of these objects (in particular the transition and difference density matrices, that will both be at the center of this contribution), either from a qualitative point of view using exciton analysis[4–35] or one-particle charge...
density functions and their corresponding density matrices,\(^{[4,5,20,36–40]}\) or under a quantitative perspective using descriptors,\(^{[6–8,26–33,39–49]}\) a proper knowledge of their structure is required for selecting the right post-processing strategy. Unfortunately, while the structure of the objects derived from the calculations are often known for the most common calculation methods, in most of the cases this structure is given without a demonstration. While the demonstration itself can sometimes be long and complicated, in this tutorial we show how we can use a simple formulation of the problem and find rapid routes for assessing the particular objects we target: the one-body reduced density matrices\(^{[50–57]}\) (1-RDM), about which a brief reminder is provided in the text. In this contribution, we start by revisiting a known and used tool for assessing integrals involving quantum electronic states on which pairs of second quantization operators have acted, that is, a variant of Wick’s theorem.\(^{[58–63]}\) As the application of this theorem can be somehow tedious, we provide here a graphical, yet rigorous, derivation of the integrals one can assess using this tool.

This theorem is then used in the context of the assessment of transition and difference density matrix elements for characterizing excited states originating from equation-of-motion\(^{[64–67]}\) (EOM) calculations performed using two types of methods.

The first class of methods involves a single-excitation transition operator, coupled to a deexcitation one. The basic principles of the EOM formalism are briefly recalled in first quantization, before the transition operator for the first class of methods mentioned above is introduced into this framework. The methods from this first class, that is, the random phase approximation\(^{[64–79]}\) (RPA), the time-dependent Hartree-Fock theory\(^{[4,64,67,70,80–85]}\) (TDHF), the time-dependent density functional theory\(^{[4,9,35,74–84]}\) (TDDFT), and the Bethe-Salpeter equation\(^{[102–107]}\) (BSE), have a central equation with the same structure, and the objects we will use in this contribution have the same physical interpretation within each method.

If the single excitations are not coupled to deexcitations, as in the configuration interaction singles\(^{[4,74,84,85,108]}\) (CIS) or the Tamm-Dancoff approximation\(^{[4,74,84,85,91,109]}\) (TDA), we have another class of methods, with objects having different structure and properties. These methods will be discussed in this paper. Note also that the algebraic diagrammatic construction\(^{[28,85,110–112]}\) (ADC) involves matrices with similar interpretation. They are constructed in the space of the so-called "intermediate states"\(^{[110,111]}\) and lead to density matrices in the intermediate states space with the same structure as the CIS and TDA ones in the space of singly-excited Slater determinants. Additionally, the linear response (LR) variant of the single-reference coupled cluster\(^{[74,85,113–121]}\) (CC) theory for excited states can be used for producing matrices that can be compared to those from CIS, TDA, and ADC, and classified among the second type of methods investigated in this contribution. Indeed, as for ADC and TD-DFRT\(^{[86]}\) (where “R” stands for “response”), in the LR-CC framework an auxiliary many-body wave function (AMBW) has also been proposed for the assignment of excited states ansätze.\(^{[85]}\) For ADC, this has been done in addition to the ansatz already introduced in the intermediate states basis. The three AMBWs are introduced as a linear combination of singly-excited Slater determinants so that, after a necessary renormalization,\(^{[103]}\) these ansätze can produce transition and difference density matrices that will belong to the second class of matrices we will derive in this tutorial, though the working equations for TD-DFRT (LR-CC) include (un)coupled excitations and deexcitations contributions to the transition energy. They are also mentioned in this report since, according to the results presented below, those ansätze for excited states can be formally considered, combined with the single-reference ground electronic state, as a compatible approximation to the EOM transition operator for producing the matrices of interest to characterize the electronic transition, in the same way the CIS and TDA ansätze do.

The two types of methods (including or not the deexcitation operator) mentioned above will finally be compared, based on the structure of their respective 1-RDMs, but also on the interpretation of the nature of their generating operator, and the consequence of its use in the EOM formalism.

## 2 | HYPOTHESES AND THEORETICAL BACKGROUND

Our \(N\)-electron reference ground state wave function \(\psi_0(s_1, ..., s_N)\) is a single Slater determinant wave function, written in the orthonormal, local basis of \(L\) one-particle wave functions called spinorbitals \(\{\psi_i\}_{i=1}^{L}\) (\(N\) of them being singly occupied, and \(L–N\) being unoccupied and called "virtual") where, since electrons are indiscernible, \(s\) represents the four spin-space coordinates of electron \(i\), with \(1 \leq i \leq N\).

For a given quantum electronic state \(|\psi_n\rangle (n \geq 0)\), we have \(\psi_n(s_1, ..., s_N) = \langle s_1, ..., s_N | \psi_n \rangle\). To any \(|\psi_n\rangle\) corresponds a 1-RDM written \(\gamma_n\) in the spinorbital. We therefore start by recalling the expression of the \(\gamma_n\) elements for any \(|\psi_n\rangle\), as well as the expression of the transition density matrix \(\langle \gamma^0 \rangle\) elements corresponding to the transition from the ground state \((n = 0)\) to any excited state \((n \neq 0)\). In second quantization (see Appendix A.1), those matrix elements write

\[
(\gamma_n)_{\alpha \beta} = \langle \psi_n | \hat{r}_\alpha \hat{s}_\beta | \psi_n \rangle; \quad (\gamma^0)_{\alpha \beta} = \langle \psi_0 | \hat{r}_\alpha \hat{s}_\beta | \psi_0 \rangle
\]

with \(r\) and \(s\) ranging from 1 to \(L\). Any \(\hat{q}\) operator (replace here \(q\) by \(r\) or \(s\) for instance) is the annihilation operator when it is acting on a ket placed on its right, and a creation operator when it is acting on a bra placed on its left. On the other hand, any \(\hat{q}^\dagger\) operator is the creation operator when it is acting on a ket placed on its right, and an annihilation operator when it is acting on a bra placed on its left.
Note that the formalism reported in this contribution is presented for spinorbitals, and could be generalized to single-particle orbitals which would be mixtures of spin-up and spin-down states. Such situations arise in noncollinear spin systems, and they are of interest in the so-called spin-flip approach to TDDFT or TDHF.

2.1 | Integrals of products of pairs of fermionic creation/annihilation operators

In this section, no restriction has been imposed regarding the attribution of the spinorbitals pointed by the second quantization operators to a given space (e.g., occupied or virtual canonical subspace).

In this contribution, we will mostly be dealing with integrals containing products of second quantization operators, such as

\[ \mathcal{J}_M = \langle \psi_0 | \hat{Q}_1 \hat{Q}_2 \ldots \hat{Q}_M | \psi_0 \rangle = \langle \psi_0 | \prod_{k=1}^{M} [c_1 \mid c_2] | \psi_0 \rangle \]  

(2)

with, in this example, \( |c_1] \) (\( |c_2]\)) being always a creation (annihilation) operator when acting on a given ket:

\[ |c_1] = \hat{c}_1 \hat{v}_1; \quad |c_2]\rangle = \hat{c}_2 \hat{v}_2; \quad |M]\rangle = \hat{c}_1 \hat{c}_2 = \hat{v}_1 \hat{v}_2, \]  

(3)

but first we would like to recall that the expectation value of a chain of \( M \) pairs of second quantization operators (i.e., a \( Q\)-operator, with \( Q = 2M \)) can be decomposed into a sum of products of two-operator integrals. As we are dealing with fermionic second quantization operators, a \((-1)^{m_h}\) sign is attributed to each product entering such a sum and the integral can be assessed as

\[ \langle \psi_0 | \prod_{k=1}^{2M} \hat{Q}_{p_k} | \psi_0 \rangle = \sum_{h=1}^{(2M-1)!} (-1)^{m_h} \prod_{k=1}^{M} \langle \psi_0 | \hat{Q}_{p_k} \hat{Q}_{p_{k+1}} | \psi_0 \rangle \]  

(4)

where the \( \hat{Q}_k \) and the \( \hat{Q}_{p_k} \) operators can be either creation or annihilation operators. This result is a corollary to Wick’s theorem, extensively discussed and demonstrated in Appendix A.2.

The number \( N_Q \) of possible products of integrals for a given \( Q\)-operator, is

\[ N_Q = (2M-1)! \frac{(2M)!}{M!2^M}. \]  

(5)

The details about the deduction of \( N_Q \) are given in Appendix A.3.

Note that these results are not restricted to integrals with products of pairs of creation/annihilation operators as in integral \( \mathcal{J}_M \) from Equation (2); they are relative to integrals with products of any second quantization operators, given that the total number \( Q \) of these operators is even.

In the particular case of integrals such as \( \mathcal{J}_M \) in Equation (2), that will be of interest to us in this paper, we see that due to the structure of its \( Q\)-operator the expectation value can be expanded into a sum of two-operator integrals as in Equation (4) and reduced to the sum of its \( M! \) non-vanishing terms

\[ \mathcal{J}_M = \sum_{\ell=1}^{M} (-1)^{\ell} \prod_{k=1}^{M} \langle \psi_0 | \hat{\ell}_{1,\ell} \hat{\ell}_{2,\ell} | \psi_0 \rangle \]  

(6)

where again, \( \hat{\ell}_{1,\ell} \) and \( \hat{\ell}_{2,\ell} \) are creation and annihilation operators, respectively. We will see later how the \( f_\ell \) value can be determined.

2.1.1 | Application to four- and six-operator integrals

In this section we will expose how the general formalism formulated above can be applied to the decomposition of integrals with two and three pairs of second quantization operators. These results will then be applied to the computation of matrix elements derived from excited-state calculation methods of different types.
Four-operator integrals

We start by writing any four-operator integral as

\[ \mathcal{F}_2 = \langle \psi_0 | \hat{u}^4 \hat{w}^3 \hat{x}^2 | \psi_0 \rangle \]  

(7)

The \( u, v, w, \) and \( x \) were randomly chosen and point any spinorbital (occupied or virtual) for the moment. We put labels on the second quantization operators:

\[ \hat{u}^i \rightarrow 1; \ \hat{v} \rightarrow 2; \ \hat{w}^j \rightarrow 3; \ \hat{x} \rightarrow 4 \]  

(8)

and we schematically write

\[ \langle \psi_0 | \hat{u}^4 \hat{w}^3 \hat{x}^2 | \psi_0 \rangle = (1 \ 2 \ 3 \ 4). \]  

(9)

The decomposition (4) is illustrated for this case in Figure 1, where we highlighted the pairing of operators with colored lines. From the left to the right, if a pairing line arises before another one is closed (as in \( P_2 \) for instance), it has to override the unterminated pairing line coming from its left. The sequence between square brackets is the new sequence of operators following the pairing chronological order from the left to the right. The number between parentheses is the number of times a colored line crosses other lines of different colors (\( m_n \) in Equation (4)). For instance, in \( P_2 \), the contraction in red crosses once the blue one, while in \( P_3 \) it crosses it twice (once when rising up, once when going down to 3). This number also corresponds to the number of times that numbers are superior to other(s) after themselves in the rearranged sequence. For example, in the sequence (not existing in the decomposition presented in Figure 1 since the pairing is done from the left to the right) (4312), 4 is superior to 3, 1, and 2, while 3 is superior to 1 and 2, so in total the number \( m_n \) of such an unexisting decomposition would be 5.

In a general four-operator integral decomposition, we have, according to Equation (4),

\[ \mathcal{F}_2 = (-1)^{m_1} P_1 + (-1)^{m_2} P_2 + (-1)^{m_3} P_3 \]  

(10)

with \( m_1 = 0, m_2 = 1, m_3 = 2 \). The case of Equation (7) for example, reads

\[ P_1 = \langle \psi_0 | \hat{u}^3 \hat{w}^2 \hat{x}^0 | \psi_0 \rangle; \quad P_2 = \langle \psi_0 | \hat{u}^2 \hat{w}^1 \hat{x}^0 | \psi_0 \rangle; \quad P_3 = \langle \psi_0 | \hat{u}^4 \hat{w}^0 \hat{x}^0 | \psi_0 \rangle \]  

(11)

where we have put the numbers above each operator for each product, as obtained in Figure 1. Since we know that, for all \( p, q, r, \) and \( s \),

\[ \langle \psi_0 | \hat{p} \hat{q} | \psi_0 \rangle = \langle \psi_0 | \hat{r} \hat{s} | \psi_0 \rangle = 0; \quad \langle \psi_0 | \hat{r} \hat{s} \hat{p} \hat{q} | \psi_0 \rangle = \delta_{pq} (1 - n_p) (1 - n_q); \quad \langle \psi_0 | \hat{r} \hat{s} \hat{p} \hat{q} | \psi_0 \rangle = \delta_{rs} n_r n_s, \]  

(12)

where \( n_r (n_s) \) is the occupation number (1 or 0) of \( \psi_r (\psi_s) \) in \( | \psi_0 \rangle \), it follows that \( \mathcal{F}_2 \) can be simplified:

\[ \mathcal{F}_2 = \langle \psi_0 | \hat{u}^4 \hat{w}^3 \hat{x}^2 | \psi_0 \rangle = \delta_{uv} \delta_{uw} n_u n_v n_w + \delta_{uw} \delta_{uw} n_u n_w (1 - n_v) (1 - n_w). \]  

(13)

that is,

\[ \mathcal{F}_2 = \langle \psi_0 | \hat{u}^4 \hat{w}^3 \hat{x}^2 | \psi_0 \rangle = \delta_{uv} \delta_{uw} n_u n_v n_w + \delta_{uw} \delta_{uw} n_u n_w (1 - n_v) (1 - n_w). \]  

(14)

In this example we have seen that from \( (4 - 1)!! = 3 \) products one reduces a four-operator integral such as (7) to 2!! = 2 products of Kronecker’s deltas.

\[ \langle 1 \ 2 \ 3 \ 4 \rangle \quad \langle 1 \ 2 \ 3 \ 4 \rangle \quad \langle 1 \ 2 \ 3 \ 4 \rangle \]

\[ P_1 \quad P_2 \quad P_3 \]

\[ \langle 1 \ 2 \ 3 \ 4 \rangle \quad \langle 1 \ 3 \ 2 \ 4 \rangle \quad \langle 1 \ 4 \ 2 \ 3 \rangle \]

\[ (0) \rightarrow \odot \quad (1) \rightarrow \odot \quad (2) \rightarrow \odot \]

**FIGURE 1** Possible decomposition of integrals with two ordered pairs of creation/annihilation second quantization operators into the sum of three products of integrals. The number between parentheses is the number \( m_n \) of times a pairing line crosses others (the number of times a line of a given color crosses lines with different colors) and the sign on the right of the arrow is the \( (-1)^{m_n} \) signature. The reordered labels of the operators are reported between square brackets.
### Six-operator integrals

For six-operator integrals, we start again by applying the decomposition from Equation (4), implying $(6 - 1)! = 15$ products of three two-operator integrals (See Appendix A.4) and, following the same considerations as for the four-operator integrals, we can reduce the sum of 15 terms in Equation (4) to the $3! = 6$ products of integrals in Equation (6). These six products are reported in Figure 2.

#### 2.2 General EOM derivation of transition properties

Let $\hat{T}$ be a transition operator corresponding to the transition between two quantum states:

$$\hat{T} = |\psi_n\rangle \langle \psi_0|,$$  

$$\hat{T}^\dagger = |\psi_0\rangle \langle \psi_n|$$  

(15)

with the constraint that the two states are normalized and orthogonal to each other (e.g., if they are eigenstates of the Hamiltonian operator)

$$\langle \psi_0 | \psi_n \rangle = \langle \psi_n | \psi_0 \rangle = 0; \quad \langle \psi_0 | \psi_0 \rangle = \langle \psi_n | \psi_n \rangle = 1.$$  

(16)

We have that

$$\hat{T} |\psi_0\rangle = |\psi_n\rangle \langle \psi_0| |\psi_0\rangle = |\psi_n\rangle; \quad \langle \psi_0 | \hat{T}^\dagger = \langle \psi_0| \langle \psi_0| |\psi_0\rangle = |\psi_n\rangle$$  

(17)

and

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

(18)

It comes that

$$\langle \psi_0 | \left[ \hat{T}^\dagger, \left[ \hat{O}, \hat{T} \right] \right] |\psi_0\rangle = \langle \psi_0 | \hat{T}^\dagger \hat{O} \hat{T} |\psi_0\rangle - \langle \psi_0 | \hat{T} \hat{O} \hat{T}^\dagger |\psi_0\rangle - \langle \psi_0 | \hat{O} \hat{T} \hat{O}^\dagger |\psi_0\rangle + \langle \psi_0 | \hat{O}^\dagger \hat{T}^\dagger |\psi_0\rangle$$  

(19)

can be simplified, according to Equations (16) and (17), as

$$\langle \psi_0 | \left[ \hat{T}^\dagger, \left[ \hat{O}, \hat{T} \right] \right] |\psi_0\rangle = \langle \psi_0 | \hat{O} |\psi_n\rangle - \langle \psi_0 | \hat{O} |\psi_0\rangle - \langle \psi_0 | \hat{O} |\psi_0\rangle + \langle \psi_0 | \hat{O} |\psi_n\rangle$$  

(20)

Indeed, we have
\[ \mathcal{D}_n^O = \langle \psi_n | \hat{O} | \psi_n \rangle : \mathcal{D}_n^V = \langle \psi_0 | \hat{O} | \psi_0 \rangle \]  

and

\[ \mathcal{D}_n^O = \langle \psi_0 | \hat{O} | \psi_n \rangle \langle \psi_n | \psi_0 \rangle = 0 = \langle \psi_0 | \psi_n | \hat{O} | \psi_0 \rangle \langle \psi_n | \psi_0 \rangle = \mathcal{D}_n^V. \]  

If, instead of the difference of expectation value between two states for a given operator, we are interested in transition properties, those can be deduced by using

\[ \langle \psi_0 | \hat{O} | \psi_0 \rangle = \langle \psi_0 | \hat{O}_\text{II} | \psi_0 \rangle \langle \psi_0 | \hat{O}_\text{III} | \psi_0 \rangle = \langle \langle \psi_0 | \hat{O}_\text{II} | \psi_0 \rangle \psi_n | \psi_0 - | \psi_0 | \psi_0 | \psi_0 | \hat{O}_\text{III} | \psi_0 \rangle \]  

which reduces to

\[ \langle \psi_0 | \hat{O} | \psi_0 \rangle = \langle \psi_0 | \hat{O} | \psi_n \rangle. \]  

### 3 | Evaluation of One-body Density Matrices Using Wick's Theorem

#### 3.1 | Hypotheses

As we have seen before, the canonical space \( C \) is divided into two sub-spaces: the occupied (O) and virtual (V) spaces

\[ O = \{ \psi_i | 1 \leq i \leq N \}; \quad V = \{ \psi_n | N < n < L \}. \]  

From now on, the second quantization operators with the letters \( i \) or \( j \) will point a spinorbital belonging to \( O \) while letters \( a \) and \( b \) will point those from \( V \), and \( p, q, r, \) and \( s \) will be pointing any spinorbital of the canonical space. In this section, the six-operator integrals (see Equation (2) with \( M = 3 \)) we will have to evaluate will involve two pairs of operators with each pair being the product of two operators belonging to two different subspaces (\( \hat{a}^\dagger \hat{j}^\dagger \) or \( \hat{j}^\dagger \hat{b}^\dagger \) for example) while the remaining pair of operators will be the \( \hat{r}^\dagger \hat{s}^\dagger \) pair with \( \psi_i \) and \( \psi_n \) simply belonging to \( C \) with no restriction. From this consideration we can write

\[ \forall (\hat{a}, \hat{R}), \quad \forall \psi_i \in V, \quad \langle \psi_i | \hat{R}^\dagger \hat{b}^\dagger \hat{c}_1 \hat{c}_2 | \psi_0 \rangle = 0 \]  

and

\[ \forall (\hat{R}^\dagger, \hat{R}), \quad \forall \psi_s \in V, \quad \langle \psi_s | \hat{R}^\dagger \hat{a}^\dagger \hat{c}_1 \hat{c}_2 | \psi_0 \rangle = 0. \]  

These rules can be deduced from a quick look at the structure of the products in Figures 2 and A2 where we see that every product starts by "(1)" and contains at least one integral ending by "(6)" or simply by considering the basic rules of second quantization recalled in Equations (A5) and (A10), and knowing that in the dual space a creation operator becomes an annihilation operator and vice versa.

As a direct consequence, the substantial number of combinations of chains of second quantization operators we could meet can be easily sorted without evaluating the decomposition (6) for each, so that only five of them will be useful in the following section. Those are identified in Table 1, where the only nonvanishing products \( \mathcal{P}_x \) from Figure 2 are reported and highlighted by a "✓" symbol.

From Table 1, we deduce that

\[ \lambda_n \rightarrow \langle \psi_0 | \hat{R}^\dagger \hat{S}^\dagger | \psi_0 \rangle \langle \psi_0 | \hat{a}^\dagger \hat{b}^\dagger | \psi_0 \rangle \langle \psi_0 | \hat{R}^\dagger \hat{J}^\dagger | \psi_0 \rangle = \delta_{n_1 n_2} \delta_{\alpha \beta} \delta_{\gamma \delta}. \]  

Similarly, we have
TABLE 1 The five typical six-operator integrals to evaluate in the determination of the one-body density matrices arising from single-excitation transition operators (coupled or not to deexcitation operators) in the single-reference equation-of-motion formalism we are using in this contribution.

<table>
<thead>
<tr>
<th>EV</th>
<th>Label</th>
<th>( P_5 (+) )</th>
<th>( P_7 (+) )</th>
<th>( P_8 (-) )</th>
<th>( P_{13} (+) )</th>
<th>( P_{15} (+) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \langle \psi_0</td>
<td>\hat{a}^\dagger \hat{s} \hat{b} \hat{s} b^\dagger</td>
<td>\psi_0 \rangle )</td>
<td>( \lambda )</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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<tr>
<td>( \langle \psi_0</td>
<td>\hat{a}^\dagger \hat{s} \hat{b} \hat{s} b^\dagger</td>
<td>\psi_0 \rangle )</td>
<td>( \delta )</td>
<td>✓</td>
<td>✓</td>
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<tr>
<td>( \langle \psi_0</td>
<td>\hat{a}^\dagger \hat{s} \hat{b} \hat{s} b^\dagger</td>
<td>\psi_0 \rangle )</td>
<td>( \beta )</td>
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<tr>
<td>( \langle \psi_0</td>
<td>\hat{a}^\dagger \hat{s} \hat{b} \hat{s} b^\dagger</td>
<td>\psi_0 \rangle )</td>
<td>( \xi )</td>
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<td>✓</td>
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<tr>
<td>( \langle \psi_0</td>
<td>\hat{a}^\dagger \hat{s} \hat{b} \hat{s} b^\dagger</td>
<td>\psi_0 \rangle )</td>
<td>( \chi )</td>
<td>✓</td>
<td>✓</td>
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</tr>
</tbody>
</table>

\[
\lambda_{13} \rightarrow \langle \psi_0 | \hat{\alpha}^\dagger \hat{\psi} \rangle \langle \hat{\psi} | \hat{a} \hat{s} \rangle \langle \hat{a} \hat{s} | \psi_0 \rangle \langle \psi_0 | \hat{a} \hat{s} \rangle = \delta_\lambda \delta_\mu (1-n_\mu) \delta_\sigma (1-n_\sigma) \tag{29}
\]

and

\[
\lambda_{15} \rightarrow \langle \psi_0 | \hat{\alpha}^\dagger \hat{\psi} \rangle \langle \hat{\psi} | \hat{a} \hat{s} \rangle \langle \hat{a} \hat{s} | \psi_0 \rangle \langle \psi_0 | \hat{a} \hat{s} \rangle = \delta_\lambda \delta_\mu \delta_\sigma n_\mu. \tag{30}
\]

Therefore, we see that

\[
\lambda_{15} \rightarrow \delta_\lambda \rightarrow \beta_\gamma, \tag{31}
\]

so actually only the knowledge of the value of three integrals will be required for evaluating the matrix elements in this section.

### 3.2 Coupled hole/particle and particle/hole (de)excitations

For this first class of single-reference excited-state calculation methods, that we will denote here by a "\( \eta \)" symbol, the transition operator is composed of a sum of single-excitation operators \( x_{ia} \hat{\alpha}^\dagger \hat{\psi} \) coupled to the corresponding deexcitations \( y_{ia} \hat{\alpha} \hat{\psi} \)

\[
\hat{T}_\eta = \sum_{i=1}^{N} \sum_{a=N+1}^{L} \left( x_{ia} \hat{\alpha}^\dagger \hat{\psi} - y_{ia} \hat{\alpha} \hat{\psi} \right) \tag{32}
\]

Since the sum is running over all the possible spinorbitals of each sub-space, that is, \( i \) runs over all the occupied space and \( a \) overall the virtual one, \( \hat{T}_\eta \) can be rewritten

\[
\hat{T}_\eta = \sum_{i=1}^{N} \sum_{a=N+1}^{L} x_{ia} \hat{\alpha}^\dagger \hat{\psi} - \sum_{i=1}^{N} \sum_{b=N+1}^{L} y_{ib} \hat{\alpha} \hat{\psi} \tag{33}
\]

The \( x \) and \( y \) coefficients entering into the composition of \( \hat{T}_\eta \) are the components of a transition vector satisfying

\[
x_{0a}^\dagger = x_{0i}^*, \quad y_{0b}^\dagger = y_{0j}^*, \tag{34}
\]

so that

\[
\hat{T}_\eta = \hat{T}_x^\dagger - \hat{T}_y = \sum_{i=1}^{N} \sum_{a=N+1}^{L} x_{ia} \hat{\alpha}^\dagger \hat{\psi} - \sum_{i=1}^{N} \sum_{b=N+1}^{L} y_{ib} \hat{\alpha} \hat{\psi}. \tag{35}
\]

While replacing \( \hat{\psi} \) in Equation (20) by the Hamiltonian leads naturally in the first quantization to the transition energy (see Appendix A.5), the transition operator \( \hat{T}_\eta \) is sometimes inserted in Equation (20) as a substitution to \( \hat{T} \) for computing matrix elements. Therefore, in this contribution
we will be interested in deriving the elements of the matrices (namely, the difference density matrix and transition density matrix) arising from the substitution of \( \hat{T} \) by \( \hat{T}_n \).

### 3.2.1 Derivation of the difference density matrix elements

The difference density matrix \( \gamma^A \) is simply defined as the difference between two state density matrices, so according to Equation (1), if the transition operator \( \hat{T} \) was known exactly, replacing \( \hat{T} \) in Equation (20) by \( \hat{T}_n \) would lead to the determination of the corresponding difference density matrix element

\[
\langle \psi_0 | \left[ \hat{T}_n^\dagger, \hat{T}_n \right] | \psi_0 \rangle = \langle \psi_0 | \hat{T}_n^\dagger | \hat{T}_n \psi_0 \rangle - \langle \psi_0 | \hat{T}_n \psi_0 \rangle = (\gamma^A)_n
\]

(36)

Here we will assess the approached value of these elements by inserting \( \hat{T}_n^\dagger \) and \( \hat{T}_n \) into Equation (20):

\[
(\gamma^A)_n = \langle \psi_0 | \left[ \hat{T}_n^\dagger, \hat{T}_n \right] | \psi_0 \rangle
\]

(37)

The \( (\gamma^A)_n \) can be decomposed into four contributions, as in Equation (19):

\[
\left( \gamma^A \right)_n = \gamma^A_{\text{I}} - \gamma^A_{\text{II}} - \gamma^A_{\text{III}} + \gamma^A_{\text{IV}}
\]

(38)

leading to four matrix contributions to \( \gamma^A \)

\[
\gamma^A_n = \gamma^A_{\text{I}} - \gamma^A_{\text{II}} - \gamma^A_{\text{III}} + \gamma^A_{\text{IV}}
\]

(39)

We will detail each of these four components by using the definition of \( \hat{T}_n \). For the first one, we have

\[
\gamma^A_{\text{I}} = \langle \psi_0 | \left( \hat{T}_n^\dagger - \hat{T}_n \right) \hat{T}_n^\dagger \hat{T}_n | \psi_0 \rangle = \gamma^A_{\text{I,III}} - \gamma^A_{\text{I,II}} - \gamma^A_{\text{I,IV}} + \gamma^A_{\text{I,IV}}
\]

(40)

with

\[
\gamma^A_{\text{I,III}} = \langle \psi_0 | \hat{T}_n^\dagger \hat{T}_n | \psi_0 \rangle = \sum_{i,j=1}^{N-1} \sum_{a,b=0}^{N+1} x_{ij}^a y_{ab} \langle \psi_0 | (\hat{a}^\dagger \hat{a}) (\hat{a}^\dagger \hat{a}) | \psi_0 \rangle,
\]

\[
\gamma^A_{\text{I,II}} = \langle \psi_0 | \hat{T}_n^\dagger \hat{T}_n | \psi_0 \rangle = \sum_{i,j=1}^{N-1} \sum_{a,b=0}^{N+1} y_{ij}^a \hat{a} \langle \psi_0 | \hat{a} \hat{a}^\dagger | \psi_0 \rangle,
\]

(41)

\[
\gamma^A_{\text{I,IV}} = \langle \psi_0 | \hat{T}_n^\dagger \hat{T}_n | \psi_0 \rangle = \sum_{i,j=1}^{N-1} \sum_{a,b=0}^{N+1} y_{ij}^a \hat{a} \langle \psi_0 | \hat{a} \hat{a}^\dagger | \psi_0 \rangle,
\]

\[
\gamma^A_{\text{I,IV}} = \langle \psi_0 | \hat{T}_n^\dagger \hat{T}_n | \psi_0 \rangle = \sum_{i,j=1}^{N-1} \sum_{a,b=0}^{N+1} y_{ij}^a \hat{a} \langle \psi_0 | \hat{a} \hat{a}^\dagger | \psi_0 \rangle.
\]

According to Equations (26) and (27), we see that only the first component of \( \gamma^A_{\text{I,III}} \) is not vanishing. Indeed, the second component starts by \( \hat{a}^\dagger \), and the two last components end by \( \hat{b} \). This consideration leads us to state that since we know that \( \hat{T}_x \) and \( \hat{T}_y \) both start with an \( \hat{a}^\dagger \) or \( \hat{b}^\dagger \) operator, with \( \varphi_0 \in V \) and \( \varphi_b \in V \), and that \( \hat{T}_y \) and \( \hat{T}_x \) are ending with an \( \hat{a} \) or a \( \hat{b} \) operator, we have that

\[
0 = \langle \psi_0 | \hat{T}_x \cdot \cdot | \psi_0 \rangle = \langle \psi_0 | \hat{T}_y \cdot \cdot | \psi_0 \rangle = \langle \psi_0 | \cdot \cdot \hat{T}_y | \psi_0 \rangle = \langle \psi_0 | \cdot \cdot \hat{T}_x | \psi_0 \rangle.
\]

(42)

This will be very helpful for considerably reducing the number of contributions to the difference density matrix to assess when evaluating \( D_{\text{II,III}}^{\hat{T}_n}, D_{\text{IV,III}}^{\hat{T}_n} \) and \( D_{\text{IV,III}}^{\hat{T}_n} \) later.
Before moving to the assessment of \( D_{\lambda}^{\alpha} \), and in order to develop \( D_{\lambda}^{\alpha} \), we recast the \( x \) and \( y \) vectors components into square matrices:

\[
x_{ij} = \left( x \right)_{ij}; \quad x_{ij} = \left( X \right)_{ij}; \quad X \in \mathbb{C}^{L \times L}.
\]

Similarly,

\[
y_{ij} = \left( y \right)_{ij}; \quad y_{ij} = \left( Y \right)_{ij}; \quad Y \in \mathbb{C}^{L \times L}.
\]

The \( X \) and \( Y \) matrices are in fact composed of four blocks (occupied x occupied \((oo)\), virtual x virtual \((vv)\), virtual x occupied \((ov)\) and occupied x virtual \((ov)\)). Since \( \psi_i \in O \) and \( \phi_v \in V \), the only nonzero elements from these matrices are in the \( ov \) block. The \( X \) and \( Y \) matrices have the following structure:

\[
X = \begin{pmatrix} 0 & X \\ 0 & 0 \end{pmatrix}; \quad X' = \begin{pmatrix} 0 & 0' \\ 0' & 0 \end{pmatrix} \Rightarrow XX' = XX' \oplus 0_N, X'X = 0_N \oplus XX'
\]

with

\[
XX' \in \mathbb{C}^{N \times N}; \quad X'X \in \mathbb{C}^{(L-N) \times (L-N)}
\]

and the zero matrices

\[
0_N (N \times N); \quad 0_{ov}(L-N \times N), \quad 0_{ov}(N \times (L-N)), \quad 0_{ov}((L-N) \times (L-N)).
\]

We also have

\[
y = \begin{pmatrix} 0 & Y \\ 0 & 0 \end{pmatrix}; \quad y' = \begin{pmatrix} 0 & 0' \\ 0' & 0 \end{pmatrix} \Rightarrow YY' = YY' \oplus 0_N, Y'Y = 0_N \oplus YY'
\]

with

\[
YY' \in \mathbb{C}^{N \times N}; \quad Y'Y \in \mathbb{C}^{(L-N) \times (L-N)}
\]

If we take the \( D_{\lambda}^{\alpha} \) integrals, we see that they have the structure of the \( \chi \) integral in Table 1, which means that \( D_{\lambda}^{\alpha} \) can be rewritten

\[
D_{\lambda}^{\alpha} = \sum_{1 \leq a, b \leq N+1} \sum_{j=1}^{N} x_{ij} x_{jb} \langle \psi_0 | \hat{\chi} \hat{\chi}^{\dagger} \hat{\chi} \hat{\chi}^{\dagger} | \psi_0 \rangle
\]

\[
= \sum_{1 \leq a, b \leq N+1} \left( X \right)_{ij} \left( X \right)_{ij} \left( \delta_{ab} \delta_{n_a \delta_{n_b}} - \delta_{\delta_{a} \delta_{b}} \left( 1 - n_a \right) \delta_{\delta_{b} \left( 1 - n_b \right)} + \delta_{\delta_{a} \delta_{b}} \right) n_a n_b
\]

If we consider the first term, we have

\[
- \sum_{1 \leq a, b \leq N+1} \left( X \right)_{ij} \left( X \right)_{ij} \delta_{ab} \delta_{n_a \delta_{n_b}} - \sum_{a, b = N+1} \left( X \right)_{ij} \left( X \right)_{ij} \delta_{ab} \delta_{n_a \delta_{n_b}} = - \sum_{a = N+1} \left( X \right)_{ij} \left( X \right)_{ij} \delta_{n_a \delta_{n_b}} - \sum_{a = N+1} \left( X \right)_{ij} \left( X \right)_{ij} n_a n_b
\]

Since any \( \left( \hat{\chi} \right)_{rq} \) and \( \left( \hat{\chi} \right)_{as} \) matrix element with \( q > N \) is zero, we can expand the sum over \( a \) to any value between 1 and \( L \) without affecting the result

\[
- \sum_{a = N+1} \left( X \right)_{ij} \left( X \right)_{ij} n_a n_b = - \sum_{q = 1} \left( X \right)_{rq} \left( X \right)_{qs} n_a n_b = - \left( XX' \right)_{rs} n_a n_b
\]

At this stage, we can drop the \( n_a \) and \( n_b \) factors since for any \( r \) or \( s \) superior to \( N \) the \( \left( XX' \right)_{rs} \) matrix element is zero.

For the second term of Equation (48), we have
\[
\sum_{l,j=1,a,b=N+1}^{L} \left( X^i \right)_a \left( X^{\dagger} \right)_b \delta_{l,p} \delta_{n_l} (1-n_s) \delta_{n_s} (1-n_t) = \sum_{l,j=1,a,b=N+1}^{L} \left( X^i \right)_a \left( X^{\dagger} \right)_b (1-n_l)(1-n_s) \tag{51}
\]

For the same reason as for the first term, we see that any \( \left( X^i \right)_{ps} \) and \( \left( X^{\dagger} \right)_{ip} \) matrix element with \( p > N \) is zero, so we can expand the sum over \( i \) to any value between 1 and \( L \) without affecting the result

\[
\sum_{p=1}^{L} \left( X^i \right)_{ip} (1-n_l)(1-n_s) = \left( \bar{X} \bar{X} \right)_{rs} (1-n_l)(1-n_s) \tag{52}
\]

and here the \((1 - n_l)(1 - n_s)\) factor can also be dropped since the \( \left( \bar{X} \bar{X} \right)_{rs} \) matrix elements are vanishing for any \( r \) or \( s \) inferior or equal to \( N \).

Finally, the third term in Equation (48) can be simplified into

\[
\sum_{l,j=1,a,b=N+1}^{L} \left( X^i \right)_a \left( X^{\dagger} \right)_b \delta_{l,p} \delta_{n_l} n_r = \sum_{l,j=1,a,b=N+1}^{L} \left( X^i \right)_a \left( X^{\dagger} \right)_b \delta_{n_l} n_r = \Delta \left( \bar{X} \bar{X} \right)_{rs} n_r \tag{53}
\]

Here the \( n_r \) factor cannot be dropped, as it is preceded by Kronecker’s delta multiplied by a scalar factor, so the \( n_r \) factor is here to ensure that this scalar factor will be multiplying the identity matrix \( I_0 \) covering the \textit{occupied} \( \times \textit{occupied} \) block in the difference density matrix.

We can therefore conclude from Equations (50), (52), and (53) that the first contribution to the difference density matrix reads

\[
\mathcal{D}^\omega = \delta_{l,p} n_r - \left( \bar{X} \bar{X} \right)_{rs} + \left( \bar{X} \bar{X} \right)_{rs} \tag{54}
\]

which gives the following matrix contribution to \( \gamma^\omega \):

\[
\mathcal{D}^\omega_{l0} = \left< \bar{\psi}_0 \right| \left( \bar{T}_x - \bar{T}_y \right) \left( \bar{T}_x - \bar{T}_y \right) \bar{I} \left| \psi_0 \right> \tag{55}
\]

with the identity matrix \( I_0 \) \((N \times N)\) spanning the occupied space. We now turn to the evaluation of \( \mathcal{D}^\omega_{l0} \), which, according to Equation (19) in which we shall use again \( \bar{r} \bar{s} \) as \( \bar{O} \) and substitute again \( \bar{T} \) by \( \bar{T}_q \), reads

\[
\mathcal{D}^\omega_{l0} = \left< \bar{\psi}_0 \right| \left( \bar{T}_x \bar{T}_y \right) \left( \bar{T}_x \bar{T}_y \right) \bar{I} \left| \psi_0 \right> \tag{56}
\]

This contribution, according to Equation (42), reduces to

\[
\mathcal{D}^\omega_{l0} = \left< \bar{\psi}_0 \right| \left( \bar{T}_x \bar{T}_y \right) \left( \bar{T}_x \bar{T}_y \right) \bar{I} \left| \psi_0 \right> \tag{57}
\]

so we only have to assess two six-operator integrals:

\[
\mathcal{D}^\omega_{l0} = \frac{\left< \psi_0 \right| \left( \bar{T}_x \bar{T}_y \bar{I} \right) \bar{I} \left| \psi_0 \right>} {r^2_{\text{av}}} - \frac{\left< \psi_0 \right| \left( \bar{T}_x \bar{T}_y \bar{I} \right) \bar{I} \left| \psi_0 \right>} {r^2_{\text{av}}} \tag{58}
\]

with, according to Table 1,

\[
\mathcal{D}^\omega_{l0} = \sum_{l,j=1,a,b=N+1}^{L} x^a_l x^b_j \left< \psi_0 \right| \left( \bar{a}^\dagger_{b} \bar{r}^\dagger \bar{s} \right) \left| \psi_0 \right> = \delta_{l,p} n_r \tag{59}
\]

and

\[
\mathcal{D}^\omega_{l0} = \sum_{l,j=1,a,b=N+1}^{L} x^a_l x^b_j \left< \psi_0 \right| \left( \bar{a}^\dagger_{b} \bar{r}^\dagger \bar{s} \right) \left| \psi_0 \right> = 0 \tag{60}
\]
so the second contribution to the difference density matrix is, according to Equations (31) and (53),

\[ \mathcal{D}^A_{li} = \delta_{li} \rho_0 \mathcal{D}_0. \]  

(61)

The matrix elements of the third contribution to \( \gamma^A \), \( \mathcal{D}^{3\gamma}_{li} \), reads

\[ \mathcal{D}^{3\gamma}_{li} = \left< \psi_0 \left| \rho^2 \hat{T}_x \hat{T}_y \right| \psi_0 \right> - \left< \psi_0 \left| \rho \hat{T}_x \hat{T}_y \right| \psi_0 \right> \]

(62)

From Equation (42), it reduces to

\[ \mathcal{D}^{3\gamma}_{li} = \left< \psi_0 \left| \rho^2 \hat{T}_x \hat{T}_y \right| \psi_0 \right> \]  

(63)

with, according to Table 1,

\[ \mathcal{D}^{Y}_{li} = \sum_{l,j=1}^{N} \sum_{a,b=1}^{2} Y_{ab} (\psi_0 | \rho | \hat{T}_a \hat{T}_b | \psi_0) = \text{tr} \left( \rho^2 \hat{Y} \right) \delta \delta_{lr} \]

(64)

and

\[ \mathcal{D}^{Y}_{is} = \sum_{l,j=1}^{N} \sum_{a,b=1}^{2} X_{ab} (\psi_0 | \rho \hat{T}_a \hat{T}_b | \psi_0) = 0 \]

(65)

so the third contribution to the difference density matrix is, according to Equations (31) and (53),

\[ \mathcal{D}^A_{li} = \delta_{li} \rho_0 \mathcal{D}_0. \]

(66)

Finally, the matrix elements of the fourth contribution to \( \gamma^A \), \( \mathcal{D}^{4\gamma}_{li} \), write

\[ \mathcal{D}^{4\gamma}_{li} = \left< \psi_0 \left| \hat{T}_x \hat{T}_y \right| \rho^2 \hat{T}_x \hat{T}_y \right| \psi_0 \right> \]  

(67)

From Equation (42), it reduces to

\[ \mathcal{D}^{4\gamma}_{li} = \left< \psi_0 \left| \hat{T}_x \hat{T}_y \right| \rho \hat{T}_x \hat{T}_y \right| \psi_0 \right> = \mathcal{D}^{Y}_{li} \]  

(68)

with, according to Table 1,

\[ \mathcal{D}^{Y}_{li} = \sum_{l,j=1}^{N} \sum_{a,b=1}^{2} X_{ab} (\psi_0 | \rho \hat{T}_a \hat{T}_b | \psi_0) = \text{tr} \left( \rho \hat{Y} \right) \delta \delta_{lr} \]

(69)

which leads to the following matrix contribution to \( \gamma^A \):

\[ \mathcal{D}^A_{li} = \left( \rho \left( -\mathcal{D}^{Y} \right) \right) \hat{Y}, \]

(70)

the last equalities being deduced by simply transferring the derivation of Equation (54) to \( \mathcal{D}^{Y}_{li} \).
We finally conclude from Equation (39), by combining the different results we just derived, that the difference density matrix \( \gamma^\Delta \) has the following structure:

\[
\gamma^\Delta = \frac{\left(\theta_0 \eta_0 - \mathbf{X} \mathbf{X}^\dagger\right) \otimes \mathbf{Y} \mathbf{Y} - \left(\theta_0 \eta_0 \otimes \mathbf{0}\right) + \left(\theta_0 \eta_0 - \mathbf{Y} \mathbf{Y}^\dagger\right) \otimes \mathbf{Y} \mathbf{Y}}{\rho_{\theta_0}}.
\]

(71)

that is,

\[
\gamma^\Delta = \left(-\mathbf{X} \mathbf{X}^\dagger - \mathbf{Y} \mathbf{Y}^\dagger\right) \otimes \left(\mathbf{X} \mathbf{X} + \mathbf{Y} \mathbf{Y}\right).
\]

(72)

### 3.2.2 Derivation of the transition density matrix elements

According to Equations (1) and (24), the transition density matrix elements write

\[
\left(\gamma^\Delta_{\alpha \beta}\right)_{rs} = \left\langle \psi_0 \left| \mathbf{T} \frac{\mathbf{s}}{\mathbf{r}} \mathbf{X} \mathbf{T}^\dagger \right| \psi_0 \right\rangle = \left(\psi_0 \left| \mathbf{T} \frac{\mathbf{s}}{\mathbf{r}} \mathbf{X} \right| \psi_0 \right) - \left(\psi_0 \left| \mathbf{T} \frac{\mathbf{s}}{\mathbf{r}} \mathbf{Y} \right| \psi_0 \right)
\]

(73)

with

\[
\mathbf{T} \frac{\mathbf{s}}{\mathbf{r}} = \left\langle \psi_0 \left| \mathbf{T} \frac{\mathbf{s}}{\mathbf{r}} \mathbf{X} \right| \psi_0 \right\rangle = \left(\psi_0 \left| \mathbf{T} \frac{\mathbf{s}}{\mathbf{r}} \mathbf{X} \right| \psi_0 \right)
\]

(74)

that we can rewrite

\[
\mathbf{T} \frac{\mathbf{s}}{\mathbf{r}} = \sum_{i=1}^{N} \sum_{a=N+1}^{L} x_{ia} \left\langle \psi_0 \left| \mathbf{T} \frac{\mathbf{s}}{\mathbf{r}} \mathbf{X} \right| \psi_0 \right\rangle = \sum_{i=1}^{N} \sum_{a=N+1}^{L} x_{ia} (\delta_{ia} + \delta_{ia}) = \sum_{i=1}^{N} \sum_{a=N+1}^{L} x_{ia} \delta_{ia} (1-n_i).
\]

(75)

Similarly, for \( \mathbf{T} \frac{\mathbf{\eta}}{\mathbf{r}} \), we find

\[
\mathbf{T} \frac{\mathbf{\eta}}{\mathbf{r}} = \left\langle \psi_0 \left| \mathbf{T} \frac{\mathbf{\eta}}{\mathbf{r}} \mathbf{Y} \right| \psi_0 \right\rangle = \left(\psi_0 \left| \mathbf{T} \frac{\mathbf{\eta}}{\mathbf{r}} \mathbf{Y} \right| \psi_0 \right)
\]

(76)

that is,

\[
\mathbf{T} \frac{\mathbf{\eta}}{\mathbf{r}} = -\sum_{i=1}^{N} \sum_{a=N+1}^{L} y_{ia} \left\langle \psi_0 \left| \mathbf{T} \frac{\mathbf{\eta}}{\mathbf{r}} \mathbf{Y} \right| \psi_0 \right\rangle = -\sum_{i=1}^{N} \sum_{a=N+1}^{L} y_{ia} (\delta_{ia} - \delta_{ia}) = -\sum_{i=1}^{N} \sum_{a=N+1}^{L} y_{ia} \delta_{ia} (1-n_i).
\]

(77)

The combination of \( \mathbf{T} \frac{\mathbf{s}}{\mathbf{r}} \) and \( \mathbf{T} \frac{\mathbf{\eta}}{\mathbf{r}} \) leads finally to the transition density matrix

\[
\begin{pmatrix}
0_r & \mathbf{X} \\
\mathbf{Y}^\dagger & 0_r
\end{pmatrix} \in \mathbb{C}^{L \times L}
\]

(78)

which is not Hermitian.

### 3.3 Comment on the nature of the transition operators

This section gives a comment related to the consequences of substituting \( \mathbf{T} \) by \( \mathbf{T}_\alpha \) in the Equations (20) and (24). While this substitution is sometimes introduced to approach the transition energy and to derive properties and objects related to the transition, one should be careful about the interpretation given to this substitution. Indeed, in the \( \mathbf{T}_\alpha \) operator, one could interpret the deexcitation part \( \mathbf{T}_\gamma \) as a correction to the full CI
truncation that constitutes \( \hat{T}_x \) for deriving the properties and objects related above. Due to the substitution of \( \hat{T} \) by \( \hat{T}_x \) for accomplishing such operations, one could also be tempted to interpret \( \hat{T}_x \) as being an approximation to \( \hat{T} \). Indeed, if we consider, in the first quantization, that, in the EOM theory,

\[
\langle \psi_0 | \psi_0 \rangle = 1 \Rightarrow \langle \psi_0 | \hat{T}_x | \psi_0 \rangle = (\psi_0 | \psi_n_0 \rangle | \psi_0 \rangle = 0 \text{ iif } (\psi_0 | \psi_n_0 \rangle = 0),
\]

and notice that, according to Equation (42),

\[
\langle \psi_0 | \hat{T}_n | \psi_0 \rangle = \langle \psi_0 | \hat{T}_x - \hat{T}_y | \psi_0 \rangle = \langle \psi_0 | \hat{T}_x | \psi_0 \rangle - \langle \psi_0 | \hat{T}_y | \psi_0 \rangle = 0;
\]

if we also consider that, given that the two states are orthogonal, in the EOM theory, we find

\[
\langle \psi_0 | [\hat{T}^\dagger, \hat{T}] | \psi_0 \rangle = \langle \psi_0 | \hat{T}^\dagger \hat{T} | \psi_0 \rangle - \langle \psi_0 | \hat{T} \hat{T}^\dagger | \psi_0 \rangle = 0 - 0 = 1,
\]

that is,

\[
\langle \psi_0 | [\hat{T}^\dagger, \hat{T}] | \psi_0 \rangle = 1 \Leftrightarrow \langle \psi_0 | \psi_n_0 \rangle = 1
\]

and notice that

\[
\langle \psi_0 | [\hat{T}^\dagger_1, \hat{T}^\dagger_2] | \psi_0 \rangle = \langle \psi_0 | (\hat{T}^\dagger_1 - \hat{T}^\dagger_2) (\hat{T}_2 - \hat{T}_y) | \psi_0 \rangle - \langle \psi_0 | (\hat{T}^\dagger_2 - \hat{T}^\dagger_1) (\hat{T}_2 - \hat{T}_y) | \psi_0 \rangle
\]

which reduces, due to Equation (42), to

\[
\langle \psi_0 | [\hat{T}^\dagger_2, \hat{T}^\dagger_1] | \psi_0 \rangle = \langle \psi_0 | \hat{T}^\dagger_2 \hat{T}_2 | \psi_0 \rangle - \langle \psi_0 | \hat{T}^\dagger_1 \hat{T}^\dagger_2 | \psi_0 \rangle
\]

with

\[
\langle \psi_0 | \hat{T}^\dagger_2 \hat{T}_2 | \psi_0 \rangle = \sum_{1, j = 1, b = N + 1}^{L} x_i^j x_j^a \langle \psi_0 | \hat{T}^\dagger_2 | \hat{T}_2 | \psi_0 \rangle = \sum_{1, j = 1, b = N + 1}^{L} (\hat{X}^\dagger)_{ai} (\hat{X})_{bj} (\delta_{ia} \delta_{jb} + \delta_{ib} \delta_{ja}) = \delta_x
\]

and

\[
\langle \psi_0 | \hat{T}^\dagger_1 \hat{T}^\dagger_2 | \psi_0 \rangle = \sum_{L, j = 1, b = N + 1}^{L} y_j^a y_j^b \langle \psi_0 | \hat{T}^\dagger_1 | \hat{T}^\dagger_2 | \psi_0 \rangle = \sum_{L, j = 1, b = N + 1}^{L} (\hat{Y}^\dagger)_{ai} (\hat{Y})_{bj} (\delta_{ia} \delta_{jb} + \delta_{ib} \delta_{ja}) = \delta_y
\]

so

\[
\langle \psi_0 | [\hat{T}^\dagger_2, \hat{T}^\dagger_1] | \psi_0 \rangle = \delta_x - \delta_y \equiv x^T \cdot y = 1
\]

where \( x^T \cdot x = y^T \cdot y \) is known to be equal to unity, due to the nonstandard normalization conditions of the \( x \) and \( y \) couple of vectors, we find quite good similarities between the first quantization EOM \( \hat{T} \) properties and the properties of \( \hat{T}_x \).

Indeed, putting in parallel results in Equation (79) with that of Equation (80), and the one in Equation (82) with the one from (87), one could be tempted to conclude that the quantum state \( |\psi_n_0 \rangle \) we could obtain by operating \( \hat{T}_2 \) on \( |\psi_0 \rangle \) is orthogonal to \( |\psi_0 \rangle \) and is normalized. However, one immediately sees that when acting on \( |\psi_0 \rangle \), \( \hat{T}_x \) is not nilpotent, unlike \( \hat{T} \); while

\[
\hat{T}_x = |\psi_n_0 \rangle \langle \psi_0 | \langle \psi_0 |
\]

is always zero, the ground state expectation value of \( \hat{T}_x \hat{T}_x \) reduces to the ground state expectation value of

\[
-\hat{T}_x \hat{T}_x = - \sum_{L, j = 1, b = N + 1}^{L} y_j^a y_j^b \hat{T}^\dagger_1 \hat{T}^\dagger_2 j
\]

which might differ from zero.
We also see that the result of the action of $\hat{T}_x$ on $|\psi_0\rangle$

$$\hat{T}_x |\psi_0\rangle = \left(\hat{T}_x - \hat{T}_y\right) |\psi_0\rangle = \sum_{i=1}^{N} \sum_{a=N+1}^{1} \left(\hat{X}_{ij}\right)_{\alpha} \hat{a}_i^\dagger |\psi_0\rangle \tag{90}$$

is not normalized since we have seen that

$$\langle \psi_0 | \hat{T}_x^\dagger \hat{T}_x |\psi_0\rangle = \langle \psi_0 | \hat{T}_x \hat{T}_x |\psi_0\rangle = \delta_x$$ \tag{91}

Note finally that such an application of $\hat{T}_x$ on $|\psi_0\rangle$ might not be number-conserving. Indeed, we see that if we could write a quantum excited-state ansatz $|\psi_{\alpha}\rangle$ from this application, the resulting density matrix, $\gamma_{\alpha\gamma}$, would have the following matrix elements

$$\langle \gamma_{\alpha\gamma}\rangle_{\alpha} = \sum_{i=1}^{N} \sum_{a=N+1}^{1} \left(\hat{X}_{ij}\right)_{\alpha} \left(\hat{X}_{ji}\right)_{\alpha} \langle \psi_0 | \hat{T}_x^\dagger \hat{T}_x |\psi_0\rangle \tag{92}$$

leading to

$$\gamma_{\alpha\gamma} = (\delta_{\alpha\beta} - \Delta X^2) \pm X^2 \Rightarrow \text{tr}(\gamma_{\alpha\gamma}) = N\delta.$$ \tag{93}

As a conclusion, if $\hat{T}_x$ had to be used as an approximation to the $T_x$ operator, it would not be nilpotent, nor norm-conserving and might not be number-conserving. It comes of course of such an approximation should not occur, and that, as mentioned before, the $\hat{T}_x$ operator should be seen as a corrected $\hat{T}_x$ (i.e., the full CI truncated to single excitations) in the computation of matrix elements and transition energy. Indeed, while there would be no action of the deexcitation operator $\hat{T}_x$ if $\hat{T}_x$ was directly applied on $|\psi_0\rangle$, the reality of its action in the superoperators from Equations (20) and (24) has been seen directly when computing the matrix elements in this section and transition energy in Appendix A.5.

### 3.4 | Switching off the particle/hole deexcitations

If we now switch off the deexcitations, we come to another class of methods (denoted here by a "\(\zeta\)" symbol) such as CIS or TDA. It has to be noted that while the following spinorbital-based derivation of the matrices structure is not directly applicable to the ADC method since the ADC ansatz consists in a linear combination of Intermediate States (ISs), the structure of the CIS/TDA density matrices in the space of singly-excited Slater determinants is transferrable to this method in the IS basis (see Appendix A.8). The following derivations also hold for the TD-DFRT, ADC, and LR-CC AMBW reported in Reference [85], but one has to keep in mind that these ansätze should be properly renormalized to yield the following matrices, and that in the LR-CC method, the Jacobian (J) is not Hermitian, so that there are left and right eigenvectors to it, on which the application of the following derivations might be performed for different purposes [85].

The direct consequence of switching off the deexcitations when going from TDHF or TDDFT to CIS or TDA for instance, is that

$$x_0^2 - x_1^2 = 1 \Leftrightarrow \delta_x = 1. \tag{94}$$

From this, we could postulate that there exists a nilpotent transition operator $\hat{T}_\zeta$ leading to an excited-state ansatz

$$\hat{T}_\zeta |\psi_0\rangle = \sum_{i=1}^{N} \sum_{a=N+1}^{1} \left(\hat{X}_{ij}\right)_{\alpha} \hat{a}_i^\dagger |\psi_0\rangle \tag{95}$$

with the excited state being orthogonal to $|\psi_0\rangle$, with $\hat{T}_\zeta$ being norm- and number-conserving (we simply replace $\hat{T}_x$ by $\hat{T}_\zeta$ and $\delta_x$ by one in Equations (91) and (93)). Unlike the $\eta$-methods, since we actually know the $\zeta$-ansatz from the methods themselves, we also know that the $\hat{T}_\zeta$ we would insert in the EOM formulation of the transition energy and the EOM derivation of the transition and difference density matrix elements, is the actual $|\psi_{\alpha}\rangle |\psi_0\rangle$ operator. Note that, in this particular case, we could also derive the difference density matrix directly from the excited-state wave function.
methods investigated in this contribution types of excited-state calculation density matrix (1-DDM) for the two density matrix (1-TDM) and difference equations and the one-particle transition density matrix (see Appendix A.6), it simply comes that

$$\gamma_{\alpha\zeta} = \langle \psi_0 | \bar{\delta}_{\alpha\beta} \bar{\delta}_{\zeta\eta} | \psi_0 \rangle = \langle \mathbf{X} | n_\alpha (1-n_\eta) \rangle$$

leading to

$$\gamma_{\alpha\zeta} = \left( I_0 - \mathbf{X} X_\zeta^T \right) \otimes \mathbf{X} \mathbf{X}_\zeta$$.

Knowing that a single-reference ground state has a block-diagonal \( \gamma_0 = I_0 \oplus 0, \) state density matrix (see Appendix A.6), it simply comes that

$$\gamma_{\alpha\zeta} = \left( -\mathbf{X} X_\zeta^T \right) \oplus (\mathbf{X}^T \mathbf{X}).$$

For the transition density matrix, we have

$$\langle \gamma_{\alpha\zeta} \rangle_n = \langle \psi_0 | \bar{\delta}_{\alpha\beta} \bar{\delta}_{\zeta\eta} | \psi_0 \rangle = \langle \mathbf{X} \rangle_n \langle 1-n_\eta \rangle$$

leading to the nilpotent matrix

$$\left( \begin{array}{cc} 0_X & \mathbf{X} \\ 0_{\alpha_0} & 0 \end{array} \right)^n = \gamma_{\alpha\zeta}^n \in \mathbb{C}^{L \times L}.$$
4 CONCLUSION

We reported a standalone derivation of the one-body density matrices of interest for the most common methods of single-reference electronic excited-state calculation methods. We have first revisited in a comprehensive way a variant of Wick's theorem, an important tool in the second quantization derivation of density matrices in quantum chemistry. Afterward, we have introduced the basic EOM formalism, before applying it to two cases of excited-state calculation methods: those implying a partial correction to the full CI truncated to single excitations, and those solely implying a linear combination of singly-excited Slater determinants. The structure of the difference and transition density matrices was derived, discussed, and compared for the two types of methods. Finally, we gave a comment on the substitution of the transition operator in the first quantization EOM formalism by transition operators from the two types of methods discussed in this contribution.

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REFERENCES

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APPENDIX

A.1 | BASICS OF FERMIONIC SECOND QUANTIZATION FOR THIS PAPER

In this Appendix, we recall the fundamentals of second quantization for fermions. For more details, see the introduction to second quantization in Reference [122].

Let us rewrite a one-determinant state...
We associate a creation operator \( \hat{r} \) to a spinorbital \( \phi_r \). When acting on a one-determinant state, it creates an electron in \( \phi_r \):

\[
\hat{r} \phi_r = \phi_r.
\]  

The second quantization operators sequence order matters:

\[
\hat{s}^\dagger \hat{r} \phi_u \phi_v = \phi_r \phi_u \phi_v - \phi_r \phi_u \phi_v = -\hat{s}^\dagger \hat{r} \phi_u \phi_v.
\]

We therefore see that

\[
\left[ \hat{r}, \hat{s}^\dagger \right] = 0.
\]  

where the "\( \lbrack \cdot, \cdot \rbrack \)" brackets denote the anticommutation superoperator:

\[
\left[ \hat{A}, \hat{B} \right] = -\hat{A} \hat{B} + \hat{B} \hat{A}.
\]

From Equation (A3) we find, setting \( r = s \), that \( \hat{r}^2 = 0 \). Since a determinant with two identical columns (or lines) vanishes, we have

\[
r \in \{ u, \ldots, v \} \Rightarrow \hat{r}^2 \phi_u \phi_v = 0
\]

which means that it is not possible to create an electron in \( \phi_r \) if that spinorbital is already occupied.

One can create a Slater determinant using the creation operators

\[
|\phi_1 \phi_2 \cdots \phi_N \rangle = \hat{C}_N^\dagger |
\]

with

\[
\hat{C}_N^\dagger = \prod_{m=1}^N \hat{m}^\dagger
\]

and \(| \rangle \) the normalized (i.e., \(| \rangle \langle | = 1 \)) physical vacuum state.

The adjoint of any \( \hat{r}^2 \) creation operator is the \( \hat{r} \) annihilation operator, and acts on a Slater determinant as

\[
\hat{r} \phi_1 \phi_u \phi_v \cdots \phi_N = |\phi_1 \cdots \phi_N \rangle.
\]  

The spinorbital sequence in the Slater determinant matters. Consider

\[
\hat{r} \phi_1 \phi_2 \cdots \phi_N.
\]

We first need to place the \( \phi_r \) spinorbital at the left of the Slater determinant before applying the second quantization operator \( \hat{r} \). For this, we permute \( \phi_u \) and \( \phi_v \) (without forgetting the minus sign arising from the permutation of two matrix columns in a determinant)

\[
\hat{r} \phi_1 \phi_2 \cdots \phi_N = -\hat{r} \phi_1 \phi_2 \cdots \phi_N
\]

where \( m(\sigma) \) is the number of inversions necessary for bringing back \( \phi_r \) in its original position (the left of the Slater determinant), to which we add the original \( \phi_r \) permutation with \( \phi_u \) performed prior to the application of the annihilation operator \( \hat{r} \) on the Slater determinant. In general, for the natural ordering \( \{ 1, 2, \ldots \} \) of the spinorbitals in the Slater determinant, we have

\[
\hat{r} \phi_1 \phi_2 \cdots \phi_N = (-1)^{m(\sigma)+1} \phi_1 \phi_2 \cdots \phi_N
\]

with one permutation to place \( \phi_r \) at the left of the Slater determinant, and \( r - 2 \) for replacing \( \phi_3 \) in its place after the annihilation of the electron in \( \phi_r \).

As for the creation operators, we also have

\[
\left[ \hat{r}, \hat{s} \right] = 0 \quad \text{and} \quad \tilde{r} = 0
\]  

\[
|\psi \rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} |\phi_1 (s_1) \rangle & |\phi_2 (s_1) \rangle & \cdots & |\phi_N (s_1) \rangle \\ |\phi_1 (s_2) \rangle & |\phi_2 (s_2) \rangle & \cdots & |\phi_N (s_2) \rangle \\ \vdots & \vdots & \ddots & \vdots \\ |\phi_1 (s_N) \rangle & |\phi_2 (s_N) \rangle & \cdots & |\phi_N (s_N) \rangle \end{vmatrix}
\]
and

\[ r \notin \{ u, \ldots, v \} \Rightarrow \hat{r} \mid \psi_u \cdots \psi_v \rangle = 0. \tag{A10} \]

One can also demonstrate the following property

\[ [\hat{r}, \hat{s}] = \delta_{rs} = [\hat{r}, \hat{s}]^\dagger. \tag{A11} \]

Indeed, we see that, independently from the occupation status of \( \phi_r \) and \( \phi_s \) in \( \mid \psi_u \cdots \psi_v \rangle \),

\[ [\hat{r}, \hat{s}] \mid \psi_u \cdots \psi_v \rangle = \mid \psi_u \cdots \psi_v \rangle \text{ if } r = s. \tag{A12} \]

and

\[ [\hat{r}, \hat{s}] \mid \psi_u \cdots \psi_v \rangle = 0 \text{ if } r \neq s. \tag{A13} \]

What is true for any \( [\hat{r}, \hat{s}] \) in these conditions will remain true for any \( [\hat{r}', \hat{s}'] \) in the same conditions, so we deduce Equation (A11).

Note also that, knowing that \( (\hat{r})^\dagger = \hat{r} \), we find that in the dual space, a creation operator becomes an annihilation operator and vice versa.

Considering the fact that for any two operators \( \hat{A} \) and \( \hat{B} \) we have

\[ (\hat{A} \hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger, \tag{A14} \]

we can deduce that, in the dual space,

\[ \langle \psi_u \cdots \psi_v | = \langle | \hat{C}_N \rangle \tag{A15} \]

Finally, if \( i \leq N \) and \( a > N \), a singly-excited Slater determinant reads, in second quantization,

\[ \mid \psi_a^\dagger \rangle = \hat{a}^\dagger \hat{C}_N \mid \psi_1 \cdots \psi_i \cdots \psi_N \rangle. \]

### A.2 | DECOMPOSITION OF CHAINS OF SECOND QUANTIZATION OPERATORS EXPECTATION VALUES

In this Appendix, we will see how one can use the time-independent Wick’s theorem to simplify the evaluation of the matrix elements of this contribution. For more details on the topic, we recommend References [62, 123, 124] and references therein.

### A.2.1 | “Augmented” second quantization operators

Similar to the behavior of second quantization operators relatively to the physical vacuum,

\[ \hat{r} | \psi_0 \rangle = 0 \text{ and } | \hat{r}^\dagger | \psi_0 \rangle = 0 \tag{A16} \]

we build two types of second quantization operators that will have the exact same behavior but relatively to a single-determinant (SD) reference state \( | \psi_0 \rangle \), namely

\[ \hat{p}_r | \psi_0 \rangle = 0 \text{ and } | \psi_0 | \hat{p}_r^\dagger = 0. \tag{A17} \]

For any spinorbital \( \phi_r \) in the canonical space, we can create two “augmented” second quantization operators:
A normal-ordered chain of creation/annihilation operators relatively to the physical vacuum reads

\[ \hat{p}_i = \hat{r} \times n_i + \hat{r}^2 \times (1 - n_i), \]

\[ \hat{r}_i = \hat{r} \times (1 - n_i) + \hat{r}^2 \times n_i. \]

where \( n_i \) is the occupation number of the \( \psi \) spinorbital in the SD reference state \( |\psi_0\rangle \). It takes the value 1 if the spinorbital is occupied, and 0 if it is unoccupied. This number is sometimes written \( n_\psi(\psi_0) \), but here we will use the shorter \( n_\psi \) since any occupation number in this Appendix will be given relatively to the SD reference state \( |\psi_0\rangle \).

As an illustration, we see that if \( n_\psi = 1 \) and \( n_\delta = 0 \),

\[ \hat{p}_i = \hat{r} \]
\[ = \hat{r} \times (1 - 1) + \hat{r}^2 \times 1, \]
\[ \hat{r}_i = \hat{r} \]
\[ = \hat{r} \times 1 + \hat{r}^2 \times (1 - 1), \]

and

\[ \hat{p}_\delta = \hat{\alpha} \]
\[ = \hat{\alpha} \times (1 - 0) + \hat{\alpha} \times 0, \]
\[ \hat{r}_\delta = \hat{\alpha} \]
\[ = \hat{\alpha} \times 0 + \hat{\alpha} \times (1 - 0). \]

### A.2.2 | Normal-ordered chain of operators

A normal-ordered chain of creation/annihilation operators relatively to the physical vacuum reads

\[ n \left[ \hat{Q}_1 \hat{Q}_2 \hat{Q}_3 \cdots \right] = (-1)^{m(\sigma)} \hat{c}_1 \hat{c}_2 \cdots \hat{c}_1, \]

where all the creation operators are at the left of all the annihilation operators. For example, for the \( \hat{u}^\dagger \hat{v} \hat{w}^\dagger \hat{x} \hat{y} \hat{z} \) chain, we have

\[ n \left[ \hat{u}^\dagger \hat{v} \hat{w}^\dagger \hat{x} \hat{y} \hat{z} \right] = (-1)^{m(\sigma)} \hat{u}^\dagger \hat{v} \hat{w}^\dagger \hat{x} \hat{y} \hat{z} \]

where \( m(\sigma) = 3 \) is the number of inversions in the \( \sigma \) permutation

\[ \sigma = \left( \begin{array}{c} \hat{u}^\dagger \hat{v} \hat{w}^\dagger \hat{x} \hat{y} \hat{z} \\ \hat{u} \hat{w}^\dagger \hat{x} \hat{y} \hat{z} \end{array} \right). \]

A normal-ordered chain of creation/annihilation operators with respect to the SD reference state \( |\psi_0\rangle \) reads

\[ N \left[ \hat{Q}_1 \hat{Q}_2 \hat{Q}_3 \cdots \right] = (-1)^{m(\sigma)} \hat{p}_1 \hat{p}_2 \cdots \hat{p}_1 \hat{p}_\psi \]

Note the lower-case \( n \) for the permutation relative to the physical vacuum, and upper-case \( N \) for the permutation relative to \( |\psi_0\rangle \). We see that the \( n \) permutation is performed solely based on the creation/annihilation character of the operators, while the \( N \) permutation takes into account both the creation/annihilation character of the operators and the occupation numbers in the SD reference state \( |\psi_0\rangle \). For illustrating the difference between the two permutations, we take the \( \hat{i}^\dagger \hat{a} \hat{b} \hat{c} \) chain, for which we give \( n_\psi(\psi_0) = n_\psi(\psi_0) = 1 \) and \( n_\delta(\psi_0) = n_\delta(\psi_0) = 0 \). Therefore,

\[ n \left[ \hat{i}^\dagger \hat{a} \hat{b} \hat{c} \right] = (-1)^4 \hat{i}^\dagger \hat{a} \hat{b} \hat{c}, \]
\[ N \left[ \hat{i}^\dagger \hat{a} \hat{b} \hat{c} \right] = (-1)^4 \hat{i}^\dagger \hat{a} \hat{b} \hat{c}. \]

Using the results in Equations (A16) and (A17), we have the following lemma:
Lemma A.1. The physical vacuum/SD reference state expectation value of a normal-ordered chain of second quantization operators is zero, which also reads

\[ \langle |n \{ \tilde{Q}_1 \tilde{Q}_2 \cdots | \rangle = 0, \quad \langle \psi_0 | N \{ \tilde{Q}_1 \tilde{Q}_2 \cdots | \psi_0 \rangle = 0. \]  

(A25)

A.2.3 | Contractions

We define the contractions of any two second quantization operators (\( Q_1 \) and \( Q_2 \)) as

\[ \tilde{Q}_1 \tilde{Q}_2 = \tilde{Q}_2 \tilde{Q}_1 - N \{ \tilde{Q}_1 \tilde{Q}_2 \}, \quad \tilde{\tilde{Q}}_1 \tilde{\tilde{Q}}_2 = \tilde{Q}_1 \tilde{Q}_2 - n \{ \tilde{Q}_1 \tilde{Q}_2 \} \]  

(A26)

where again \( n \) is the product in normal order relative to the physical vacuum, and \( N \) is the product in normal order relative to the SD reference state \( |\psi_0\rangle \). Note that this definition extends to the case where there is a product of second quantization operators between the contracted ones.

\[ \tilde{Q} \{ \tilde{Q}_1 \cdots \tilde{Q}_n \} \tilde{Q}' = (-1)^n \tilde{Q} \{ \tilde{Q}_1 \cdots \tilde{Q}_n \}, \quad \tilde{\tilde{Q}} \{ \tilde{Q}_1 \cdots \tilde{Q}_n \} \tilde{Q}' = (-1)^n \tilde{Q} \{ \tilde{Q}_1 \cdots \tilde{Q}_n \}. \]  

(A27)

Constructions relative to the physical vacuum

We have, according to Equations (A20) and (A26),

\[ \tilde{\tilde{s}} \tilde{t}^\dagger = 0, \quad \tilde{\tilde{s}}^\dagger \tilde{t}^\dagger = 0, \quad \tilde{\tilde{s}} \tilde{t}^\dagger = 0, \]  

(A28)

and, according to the anticommutation rule for fermionic second quantization operators in Equation (A11),

\[ \tilde{\tilde{s}} \tilde{s}^\dagger = \tilde{s} \tilde{t}^\dagger - n \tilde{s} \tilde{t}^\dagger - \tilde{s} \tilde{t}^\dagger + (\tilde{\tilde{s}} \tilde{t}^\dagger) = \delta_{ns}. \]  

(A29)

Constructions with respect to the SD reference state \( |\psi_0\rangle \)

In this case, we must not only care about the creation/annihilation nature of the operators, but distinguish the operators relative to spinorbitals that are occupied and unoccupied in \( |\psi_0\rangle \). Combining Equation (A26) to Lemma A.1, we find

Lemma A.2. The contraction (relative to a SD reference state \( |\psi_0\rangle \)) of a product of two second quantization operators is equal to the expectation value of this product, relative to that reference state.

This lemma also reads

\[ \tilde{Q}_1 \tilde{Q}_2 = \langle \psi_0 ^{\{ \tilde{Q}_1 \tilde{Q}_2 \} | \psi_0 \rangle. \]  

(A30)

The four possibilities are

\[ \tilde{\tilde{s}} \tilde{t}^\dagger = \langle \psi_0 ^{\{ \tilde{Q}_1 \tilde{Q}_2 \} | \psi_0 \rangle = \delta_{ns} n_s, \]  

(A31)

\[ \tilde{\tilde{s}}^\dagger \tilde{t}^\dagger = \langle \psi_0 ^{\{ \tilde{Q}_1 \tilde{Q}_2 \} | \psi_0 \rangle = \delta_{ns} (1 - n_s) (1 - n_s), \]  

(A32)

\[ \tilde{\tilde{s}} \tilde{t}^\dagger = \langle \psi_0 ^{\{ \tilde{Q}_1 \tilde{Q}_2 \} | \psi_0 \rangle = \delta_{ns} n_s (1 - n_s) = 0 \]  

(A33)

\[ \tilde{\tilde{s}} = \langle \psi_0 ^{\{ \tilde{Q}_1 \tilde{Q}_2 \} | \psi_0 \rangle = \delta_{ns} (1 - n_s) n_s = 0 \]  

(A34)

A.2.4 | Normal-ordered chains with contractions

We can define contracted normal-ordered chains of second quantization operators as
relatively to the physical vacuum and

\[ N[\hat{Q}_1 \hat{Q}_2 \hat{Q}_3 \cdots \hat{Q}_4 \hat{Q}_5 \hat{Q}_6 \cdots \hat{Q}_{7} \cdots ] = (-1)^{m(\sigma)}(\hat{Q}_4 \hat{Q}_5 \hat{Q}_6 \cdots \hat{Q}_{7} \cdots N[\hat{Q}_1 \hat{Q}_2 \hat{Q}_3 \cdots] \]

(A35)

relatively to the SD reference state. In both cases, \( m(\sigma) \) is the number of inversions in the permutation

\[ \sigma = \left( \begin{array}{c} \hat{Q}_1 \hat{Q}_2 \hat{Q}_3 \cdots \hat{Q}_4 \hat{Q}_5 \hat{Q}_6 \cdots \hat{Q}_{7} \cdots \\ \hat{Q}_4 \hat{Q}_5 \hat{Q}_6 \hat{Q}_7 \cdots \hat{Q}_1 \hat{Q}_2 \hat{Q}_3 \cdots \end{array} \right) \]

(A37)

From Lemma A.1 and definitions (A35) and (A36), we find.

**Lemma A.3** The single-reference expectation value of a contracted normal-ordered chain of second quantization operators is equal to zero unless the product is fully contracted.

The number of possible full contractions of a product of \( 2n \) operators is \((2n)! = \frac{(2n)!}{n!} = \), as derived in Appendix 5.3.

### A.2.5 Wick's theorem

We will bring here a tool extensively used in quantum field theory: the time-independent Wick's theorem. In particular, its adaptation to normal-ordered products relative to a SD reference state, and the corollary to it will be of great interest to us in this contribution. The theorem itself reads

**Theorem A.4** Any chain of second quantization operators can be rewritten as the corresponding normal-ordered product plus the sum of all of the possible contracted normal-ordered products.

This theorem also reads

\[ \hat{Q}_1 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \cdots = n[\hat{Q}_1 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \cdots] + \sum_{\text{all contractions}} n[\hat{Q}_1 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \cdots] \]

(A38)

Due to the construction of the "augmented" second quantization operators and the identical structure of the tools elaborated relatively to the physical vacuum or the SD reference state |\( \psi_0 \)\>, the theorem is fully transferrable to normal-ordered chains of second quantization operators relative to the SD reference state |\( \psi_0 \)\>,

\[ \hat{Q}_1 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \cdots = N[\hat{Q}_1 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \cdots] + \sum_{\text{all contractions}} N[\hat{Q}_1 \hat{Q}_2 \hat{Q}_3 \hat{Q}_4 \cdots] \]

(A39)

Note that in the two formulations of the theorem, the sum holds for all the singly-, doubly-(...)-contracted normal-ordered products.

According to what precedes, the demonstration of the theorem is identical using any of the two references (physical vacuum or SD reference state). Here we will use the SD reference state |\( \psi_0 \)\> for demonstrating time-independent Wick's theorem.

**Proof by induction**

We need to prove that if the theorem is valid for any product of \( n \) operators (induction hypothesis, with \( n \geq 1 \)), it holds for \( n + 1 \) operators (step case). If the last statement is true, and if the theorem holds for the case where \( n = 1 \) (base case), then we have that the theorem holds for any \( n \).

**Induction hypothesis**: Equation (A39) is assumed to hold for any chain \( \hat{Q}_1 \hat{Q}_2 \cdots \hat{Q}_n \) of second quantization operators. The sum in the right-hand side of Equation (A39) will be written \( S[\hat{Q}] \) in what follows.

**Step case**: we need to show that Equation (A39) holds for any chain \( \hat{P} = \hat{Q}\hat{Q}_{n+1} \), with \( \hat{Q}_{n+1} \) being any (creation or annihilation) operator. The theorem for \( \hat{P} \) reads...
\[ \hat{P} = N[\hat{P}] + S[\hat{P}] \]  

If the theorem is true,

\[ \hat{P} = \hat{Q} \hat{Q}_{n+1} = N[\hat{Q}] \hat{Q}_{n+1} + S[\hat{Q}] \hat{Q}_{n+1} \]  

(A41)

Case 1 — \( \hat{Q}_{n+1} \) is an annihilation operator. Then,

\[ N[\hat{Q}] \hat{Q}_{n+1} = N[\hat{P}], \quad S[\hat{Q}] \hat{Q}_{n+1} = S[\hat{P}] \]  

(A42)

the last equality being true due to the fact that any contraction with \( \hat{Q}_{n+1} \) vanishes if \( \hat{Q}_{n+1} \) is placed at the right of \( \hat{Q} \). In these conditions, we find Equation (A40), so the theorem holds in this case.

Case 2 — \( \hat{Q}_{n+1} \) is a creation operator. Then, using Equations (A26) and (A27), we have that

\[ \hat{P} = \hat{Q}_1 \hat{Q}_2 \cdots \hat{Q}_{n+1} \hat{Q}_n = - \hat{Q}_1 \hat{Q}_2 \cdots \hat{Q}_{n+1} \hat{Q}_n + \hat{Q}_1 \hat{Q}_2 \cdots \hat{Q}_{n-1} \hat{Q}_n \hat{Q}_{n+1}, \]  

(A43)

with

\[ x = - \hat{Q}_1 \hat{Q}_2 \cdots \hat{Q}_{n+1} \hat{Q}_n \]  

(A44)

that is, using (A27),

\[ x = - \hat{Q}_1 \hat{Q}_2 \cdots \hat{Q}_{n+1} \hat{Q}_n + (-1)^x \hat{Q}_1 \hat{Q}_2 \cdots \hat{Q}_{n-1} \hat{Q}_n \hat{Q}_{n+1}, \]  

(A45)

so that

\[ \hat{P} = \hat{Q}_1 \hat{Q}_2 \cdots \hat{Q}_{n+1} \hat{Q}_n - \hat{Q}_1 \hat{Q}_2 \cdots \hat{Q}_{n-1} \hat{Q}_n \hat{Q}_{n+1}. \]  

(A46)

The following step consists in developing \( y \) as we developed \( x \). We then proceed likewise until \( \hat{Q}_{n+1} \) is at the left of \( \hat{Q} \), and find

\[ \hat{P} = (-1)^{n-1} \hat{Q}_n \hat{Q} + \sum_{1 \leq i \leq n} \hat{Q}_1 \hat{Q}_2 \cdots \hat{Q}_i \hat{Q}_{i-1} \hat{Q}_n \hat{Q}_{i+1} \]  

(A47)

In the special case \( \hat{Q} = N[\hat{Q}] \), we have

\[ N[\hat{Q}] \hat{Q}_{n+1} = (-1)^n \hat{Q}_{n+1} N[\hat{Q}] + N[\hat{Q}] \hat{Q}_{n+1} \]  

(A48)

Since

\[ \hat{Q}_{n+1} N[\hat{Q}] = N[\hat{Q}_{n+1} \hat{Q}] = (-1)^n N[\hat{Q} \hat{Q}_{n+1}]. \]  

(A49)

we have

\[ N[\hat{Q}] \hat{Q}_{n+1} = N[\hat{Q} \hat{Q}_{n+1}] + N[\hat{Q}] \hat{Q}_{n+1} \]  

(A50)

We can apply this procedure again to find

\[ S[\hat{Q}] \hat{Q}_{n+1} = N[S[\hat{Q}] \hat{Q}_{n+1}] + S[\hat{Q}] \hat{Q}_{n+1}. \]  

(A51)
Adding Equations (A50) to (A51), and injecting the result in Equation (A41), we find that

$$\mathcal{P} = N\left[\bar{Q}_{n+1}\right] + N\left[\bar{Q}_{n+1}\right] + N\left[\bar{Q}_{n+1}\right] + N\left[\bar{Q}_{n+1}\right],$$

that is, we find Equation (A40), so the theorem holds for \(n+1\) operators. Since it naturally holds for \(n=1\), we conclude that it holds for any \(n\).

Combining Lemma A.1 and Lemma A.2 with Theorem A.4, we find

**Corollary A.4.1** The single-reference expectation value of a chain of \(2M\) fermionic second quantization operators can be decomposed into a sum of products of \(M\) two-operator expectation values, each product being affected by a sign.

Corollary A.4.1 also reads

$$\langle \psi_0 | \prod_{k=1}^{2M} \bar{Q}_k | \psi_0 \rangle = \sum_{h=1}^{(2M-1)!} (-1)^h \prod_{k=1}^{M} \langle \psi_0 | \hat{Q}_{1h} \hat{Q}_{2h} | \psi_0 \rangle$$

where the \(\bar{Q}_k\) and the \(\hat{Q}_{1h}\) operators can be either creation or annihilation operators, and \(m_h\) is the resulting signature of the \(h\)th full contraction.

*Why are we using the "augmented" second quantization operators?*

This choice is motivated by the fact that, according to Equations (A6), (A7), and (A15), we have, for any product \(\bar{Q}\) of \(2M\) operators (in the text we deal with even numbers of operators) relatively to an \(N\)-electron one-determinant reference state |\(\psi_0\rangle\),

$$\langle \psi_0 | \bar{Q} | \psi_0 \rangle = \langle \psi_0 | \bar{Q} \hat{Q}^{-1} | \psi_0 \rangle,$$

with \(2(M+N)\) operators in \(\bar{Q}\hat{Q}^{-1}\), hence leading to

$$(2M+2N-1)!! = \frac{(2M+2N)!}{(M+N)! 2^M 2^N}$$

possible full contractions relative to the physical vacuum rather than \(2(2M-1)!!\) if we use the SD reference state |\(\psi_0\rangle\). Note finally that in the case of an integral as \(\mathcal{J}_M\) in Equation (2), there are only \(M\) non-vanishing contractions that are possible for a fully-contracted product, leading to \(M!\) possible full contractions, hence solely \(M!\) terms in the expectation value decomposition.

### A.3 DETERMINATION OF \(N_Q\)

When pairing one of the \(Q\) (= \(2M\)) operators with another one from the \(Q\)-chain, one can choose among the \(Q-1\) (1 being itself) remaining operators. When constituting a second pair of operators, the choice is reduced to \(Q-2\), where 2 is pointing the first pair already constituted, and 1 is pointing the operator we want to pair with another one. For a third pairing we have the choice among the \(Q\) operators reduced by the number of already paired operators (4, ie, 2 pairs), and the operator we want to pair, so the number of possibilities is reduced to \(Q-1-2\times2\). For a given \(k\)th pairing operation, the number of possibilities is reduced to \(Q-1-k\times2\). The number of possibilities for pairing operators are reported in Figure A1, according to the number of pairs already constituted (so for the first pair, none has been already constituted before):

The number \(N_Q\) of possible products of integrals for a given \(Q\)-operator is therefore

$$1^{st} \leftrightarrow Q - 1$$
$$2^{nd} \leftrightarrow Q - 1 - 2 = Q - 3$$
$$3^{rd} \leftrightarrow Q - 1 - 2 - 2 = Q - 5$$
$$\vdots$$
$$k^{th} \leftrightarrow Q - 1 - 2(k-1) = Q - 2k + 1$$
$$\vdots$$
$$(M-1)^{th} \leftrightarrow Q - 1 - 2(M-1) = 3$$
$$M^{th} \leftrightarrow Q - 1 - 2(M-1) = 1$$

**FIGURE A1** Assessment of the number of possibilities one has when pairing two operators, according to the number of operators that have already been paired, that is, the position of the pairing operation (left side of the figure) in the pairing sequence.
\[ N_Q = \prod_{k=1}^{M} (Q-k) : \; k = 2k-1. \]  

(A56)

Since \( 2k-1 = Q - 2(M-k + 1) + 1 \), \( N_Q \) can be rewritten as

\[ N_Q = \prod_{k=1}^{M} (2k-1) = (Q-1)!! \]  

(A57)

where "!!" denotes a double factorial. This last result has been deduced by considering the fact that the \( k \)th factor in Equation (A57) is the \( (M-k+1) \)th factor in Equation (A56).

Since \( Q = 2M \) is necessarily even, we can finally write

\[ N_Q = (2M-1)!! = \frac{(2M)!}{M! 2^M} \]  

(A58)

### A.4 | SIX-OPERATOR INTEGRAL DECOMPOSITION INTO A SUM OF 15 TWO-OPERATOR INTEGRALS

In Figure A2, we report the different products of integrals that can be constructed for decomposing a six-operator integral according to Equation (4).

![Figure A2](image_url)

**FIGURE A2** Decomposition of a six-operator integral into the sum of 15 integrals products \( P_h \). The number between parentheses is the number \( m_h \) of times a pairing line crosses others (the number of times a line of a given color crosses lines with different colors) and the sign on the right of the arrow is the \((-1)^{m_h}\) signature. The reordered labels of the operators are reported between square brackets.
A.5 | APPLICATION OF THE EOM FORMALISM TO THE CALCULATION OF THE TRANSITION ENERGIES

We start by applying the $[\hat{H}, \hat{T}]$ superoperator to $|\psi_0\rangle$

$$
[\hat{H}, \hat{T}] |\psi_0\rangle = \hat{H} \hat{T} |\psi_0\rangle - \hat{T} \hat{H} |\psi_0\rangle = \hat{H} |\psi_n\rangle - \hat{H} |\psi_0\rangle = (\hat{H} - \hat{H}) |\psi_0\rangle = \omega \hat{T} |\psi_0\rangle.
$$

(A59)

This result, together with $\langle \psi_0 | \psi_n \rangle = \langle \psi_n | \psi_0 \rangle = 0$, can simplify the assessment of the transition energy when replacing $\hat{O}$ by $\hat{H}$ in Equation (20):

$$
\langle \psi_0 | [\hat{T}^2, [\hat{H}, \hat{T}]] |\psi_0\rangle = \langle \psi_0 | [\hat{T}^2, \omega \hat{T}] |\psi_0\rangle = \omega \langle \psi_0 | \hat{T}^2 |\psi_0\rangle - \langle \psi_0 | \hat{T}^2 |\psi_0\rangle = \omega
$$

(A60)

If instead we used the full development following Equation (20), we would obtain

$$
\hat{D}^N_\psi = \langle \psi_n | \hat{H} |\psi_0\rangle = \hat{\mathcal{E}}_n ; \quad \hat{D}^N_n = \langle \psi_0 | \hat{H} |\psi_0\rangle = \hat{\mathcal{E}}_0
$$

(A61)

and

$$
\hat{D}^N_\psi = \langle \psi_0 | \hat{H} |\psi_n\rangle |\psi_n\rangle = 0 = \langle \psi_0 | \hat{H} |\psi_n\rangle \langle \psi_n | \psi_0 \rangle = \hat{D}^N_n
$$

(A62)

which finally gives

$$
\langle \psi_0 | [\hat{T}^2, [\hat{H}, \hat{T}]] |\psi_0\rangle = \hat{\mathcal{E}}_n - \hat{\mathcal{E}}_0 = \omega.
$$

(A63)

A.6 | 1-RDM OF SINGLE-DETERMINANT WAVE FUNCTIONS

An N-electron single Slater determinant wave function

$$
\psi(s_1, ..., s_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\psi_1(s_1) & \psi_2(s_1) & ... & \psi_N(s_1) \\
\psi_1(s_2) & \psi_2(s_2) & ... & \psi_N(s_2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_1(s_N) & \psi_2(s_N) & ... & \psi_N(s_N)
\end{vmatrix}
$$

can be developed along the first line: We have

$$
\psi(s_1, ..., s_N) = \frac{1}{\sqrt{N!}} \sum_{i=1}^{N} (-1)^{i+1} \det(p^2) \psi_i(s_i)
$$

(A65)

where, if $\psi$ is the matrix from which $\sqrt{N!} \psi(s_1, ..., s_N)$ is obtained by taking its determinant, $\psi^k$ is the matrix obtained by suppressing the $k$th line and the $r$th column of $\psi$.

The 1-RDM kernel is a function written as

$$
\gamma(s_1, s_1') = N \int ds_2 ... ds_N \psi(r_1, s_1, ..., s_N) \psi^r(r_1', s_1, ..., s_N)
$$

(A66)

so that
where \( n \) is the one-electron charge density function. It is assumed that, in an \( L \)-spinorbital basis \( (L \geq N) \), there exists a 1-RDM, \( \gamma \), so that the kernel is written as a linear combination of products between spinorbital functions and 1-RDM elements

\[
\gamma(s_1; s'_1) = n(r_1)
\]  

(A67)

Since it is imposed that, given \( T = \{1, \ldots, L\} \)

\[
\forall (r,s) \in T^2, \quad \langle \phi_r | \phi_s \rangle = \delta_{rs},
\]  

(A69)

we have

\[
\langle \gamma \rangle_{rs} = \int ds_1 \int ds'_1 \varphi_r(s_1) \varphi_s(s'_1) \gamma(s_1; s'_1).
\]  

(A70)

According to the development of the Slater determinant along the first line given in Equation (A65), we can write the product of the two \( N \)-electron one-determinant wave functions in the 1-RDM kernel as

\[
\psi(r_1, \sigma_1, \ldots, s_N) \psi^*(r'_1, \sigma_1, \ldots, s'_N) = (N!)^{-1} \left\{ \sum_{i=1}^{N} (-1)^{i+1} \det(\psi^{i\dagger}) \phi_i(s_1) \right\} \left\{ \sum_{j=1}^{N} (-1)^{j+1} \det(\psi^{j\dagger}) \phi_j(s'_1) \right\}
\]  

(A71)

with \( s_1 = \{r_1, \sigma_1\} \) and \( s'_1 = \{r'_1, \sigma_1\} \). This can be rewritten

\[
\psi(s_1, \ldots, s_N) \psi^*(s'_1, \ldots, s'_N) = (N!)^{-1} \left\{ \sum_{i=1}^{N} (-1)^{i+1} \det(\psi^{i\dagger}) \det(\psi^{1\dagger}) \phi_i(s_1) \phi_j(s'_1) \right\}
\]  

(A72)

where \( \det(\psi^{i\dagger}) \) and \( \det(\psi^{1\dagger}) \) correspond to the determinants that can be used for writing two arbitrary \( (N-1) \)-electron wave functions

\[
\psi^{i\dagger}(s_2, \ldots, s_N) = \frac{1}{\sqrt{(N-1)!}} \det(\psi^{i\dagger})
\]  

(A73)

and

\[
\psi^{1\dagger}(s_2, \ldots, s_N) = \frac{1}{\sqrt{(N-1)!}} \det(\psi^{1\dagger}).
\]  

(A74)

According to the fact that the integral over all the space of the product between one wave function and its complex conjugate is equal to one, and that two one-determinant wave functions differing by one spinorbital have a zero spatial overlap (see Appendix 5.7),

\[
\int ds_2 \ldots \int ds_N \psi^{i\dagger}(s_2, \ldots, s_N) \psi^{1\dagger}(s_2, \ldots, s_N) = \delta_i \Leftrightarrow \prod_{m=2}^{N} \int ds_m \det(\psi^{i\dagger}) \det(\psi^{1\dagger}) = \delta_i (N-1)!
\]  

(A75)

Therefore, integrating over the \( N-1 \) spin-spatial coordinates the product of \( \psi \) by \( \psi^* \) gives

\[
\int ds_2 \ldots \int ds_N \psi(s_1, \ldots, s_N) \psi^*(s'_1, \ldots, s'_N) = (N!)^{-1} \left\{ \sum_{i=1}^{N} (-1)^{i+1} \psi_i(s_1) \psi^*_j(s_1) \right\} \delta_i (N-1)!
\]  

(A76)

which can be simplified:

\[
N \int ds_2 \ldots \int ds_N \psi(s_1, \ldots, s_N) \psi^*(s'_1, \ldots, s'_N) = \sum_{i=1}^{N} \psi_i(s_1) \psi^*_i(s'_1).
\]  

(A77)
where the left hand-side is nothing but the 1-RDM kernel $\gamma(s_1; s_1')$ written as in Equation (A66). Multiplying now by $\psi_i(s_1)$ and $\psi_i(s_1')$ and integrating as in Equation (A68) returns

$$
(\gamma)_{ij} = \int ds_1 \int ds_1' \phi_i^*(s_1) \phi_i(s_1') \sum_{i=1}^{N} \phi_i(s_1) \phi_i(s_1') = \sum_{i=1}^{N} \delta_{ij} \delta_{ii} = \delta_{ij} n_i n_j = \delta_{ij} \langle \psi | \hat{\gamma}^2 | \psi \rangle,
$$

that is,

$$
\gamma = I_o \equiv 0_v.
$$

### A.7 | OVERLAP BETWEEN TWO SLATER DETERMINANTS DIFFERING BY ONE SPINORBITAL

We explicitly define the $\psi$ matrix elements as

$$
(\psi)_{ij} = \psi_i(s_j)
$$

such that

$$
\psi(s_1, ..., s_N) = \frac{1}{\sqrt{N!}} \psi
$$

and the $\psi^\dagger$ matrix such that, for every $i \in \{1, ..., N\}$, $\psi(s_i)$ in $\psi$ has been substituted by $\psi_a(s_i)$, with $1 \leq j \leq N$ and $N < a \leq L$. Then, according to

$$
\det(\psi) \det(\psi^\dagger) = \det(\psi^\dagger \psi),
$$

we have

$$
\psi(s_1, ..., s_N)\psi^\dagger(s_1, ..., s_N) = (N!)^{-1} \det(\psi) \det(\psi^\dagger).
$$

We therefore have

$$
(\psi \psi^\dagger)_i = \sum_{k=1}^{N} (\psi)_ik (\psi^\dagger)_k = \sum_{k=1}^{N} \psi_k(s_i) \psi_a^*(s_k),
$$

which leads to

$$
\det(\psi \psi^\dagger) = \sum_{i=1}^{N} (-1)^{i+j} (\psi \psi^\dagger)_i D(i|j) = \sum_{i=1}^{N} \sum_{k=1}^{N} (-1)^{i+j} \psi_k(s_i) \psi_a^*(s_k) D(i|j).
$$

where the sub-determinant $D(i|j)$ is obtained by subtracting the $i$th line and the $j$th column from $\psi \psi^\dagger$. Integrating the wave function product reads

$$
S^a_i = \int ds_1 \ldots \int ds_N \psi(s_1) \psi^\dagger(s_N) = (N!)^{-1} \int ds_1 \ldots \int ds_N \sum_{i=1}^{N} (-1)^{i+j} \psi_k(s_i) \psi_a^*(s_k) D(i|j).
$$

For every occurrence of $i = k$, we have

$$
(N!)^{-1} (-1)^{i+j} \int ds_1 \ldots \int ds_N D(i|j) \psi(s_i) \psi_a^*(s_k) \propto \int ds_1 \psi(s_i) \psi_a^*(s_k) = \delta_{a0} = 0.
$$
For other occurrences \((i \neq k)\), we must develop \(D(i|j)\). Since \(\psi_0^*\) will always be multiplied by an occupied spinorbital before integration, each term of the overlap integral \(S_{ij}^0\) will be vanishing.

### A.8 | THE CASE OF ADC EXCITED STATES

Using the intermediate state representation in ADC leads to the following excited-state ansatz:

\[
|\psi_n^{\text{ADC}}\rangle = \sum_j \left( \chi^{\text{ADC}}_j \right)_n |\bar{\psi}_j\rangle
\]  

where \(|\bar{\psi}_j\rangle\) being the so-called “intermediate states,” forming the space of states within which the ADC ansatz is defined, with the property that

\[
\langle \bar{\psi}_i | \bar{\psi}_j \rangle = \delta_{ij}, \quad \langle \bar{\psi}_j | \psi_0 \rangle = \langle \psi_0 | \bar{\psi}_j \rangle = 0.
\]  

where \(|\psi_0\rangle\) is the correlated ground state reference used in ADC. On the other hand, Equation (95) could be rewritten to form another space with the same properties as those reported for the intermediate states in Equation (A84), that is,

\[
|\psi_n^\ast\rangle = \sum_{i=1}^{N} \sum_{a=N+1}^{L} \left( X_i \right)_{a} |\psi_i^\ast\rangle
\]  

with the singly-excited Slater determinants \(|\psi_i^\ast\rangle\) forming another space with the same properties as those reported for the intermediate states in Equation (A84), that is,

\[
\langle \psi_i^\ast | \psi_j^\ast \rangle = \delta_{ij} \delta_{ab}, \quad \langle \psi_i^\ast | \psi_0 \rangle = \langle \psi_0 | \psi_i^\ast \rangle = 0.
\]  

Since the structure of both ansätze is identical, and the two related spaces have the same vectorial properties, we can conclude that an electronic transition within the ADC framework will have a matrix representation (transition and difference density matrix) in the space of intermediate states with a structure identical to the matrix representation of an electronic transition corresponding to the \(|\psi_n^{\text{ADC}}\rangle\) ansatz in the space of singly-excited Slater determinants.