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# A multiconfigurational time-dependent Hartree-Fock method for excited electronic states. I. General formalism and application to open-shell states

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The solution of the time-dependent Schrödinger equation for systems of interacting electrons is generally a prohibitive task, for which approximate methods are necessary. Popular approaches, such as the time-dependent Hartree-Fock (TDHF) approximation and time-dependent density functional theory (TDDFT), are essentially single-configurational schemes. TDHF is by construction incapable of fully accounting for the excited character of the electronic states involved in many physical processes of interest; TDDFT, although exact in principle, is limited by the currently available exchange-correlation functionals. On the other hand, multiconfigurational methods, such as the multiconfigurational time-dependent Hartree-Fock (MCTDHF) approach, provide an accurate description of the excited states and can be systematically improved. However, the computational cost becomes prohibitive as the number of degrees of freedom increases, and thus, at present, the MCTDHF method is only practical for few-electron systems. In this work, we propose an alternative approach which effectively establishes a compromise between efficiency and accuracy, by retaining the smallest possible number of configurations that catches the essential features of the electronic wavefunction. Based on a time-dependent variational principle, we derive the MCTDHF working equation for a multiconfigurational expansion with fixed coefficients and specialise to the case of general open-shell states, which are relevant for many physical processes of interest. © 2011 American Institute of Physics. [doi:10.1063/1.3600397]

## I. INTRODUCTION

Over the last couple of decades, substantial progress in the field of laser technology has provided powerful tools to probe the dynamics of excited electronic states in atoms and molecules. Indeed, new radiation sources combining high intensities with ultrashort pulse durations have been developed, allowing for the time-resolved investigation of dynamical processes which occur on subpicosecond time scales. Prominent examples include studies of photoexcitation dynamics<sup>1-4</sup> and ultrafast charge transfer processes<sup>5-7</sup> in complex molecular systems.

The theoretical interpretation of these experiments offers significant challenges, since it requires better approximations for solving the time-dependent Schrödinger equation for systems of many interacting electrons, taking into account the excited character of the electronic states without hampering computational performance. One of the most widely used methods is time-dependent density functional theory<sup>8,9</sup> (TDDFT), in which the electronic density is propagated in time. The popularity of TDDFT stems from the success of its time-independent counterpart in electronic structure calculations, as well as the possibility of including electron

correlation effects in a numerically tractable way. Although, in principle, TDDFT could yield the exact solution of the time-dependent Schrödinger equation, in practice its results need to be interpreted carefully, since it is nontrivial to build an exchange-correlation functional which can accurately describe localised excited states, e.g., polaron-excitons.<sup>10</sup> Further, since TDDFT only deals with the electronic density and not with the many-body wavefunction, it can be difficult to define several important physical observables in a rigorous way: one important exception is the single-particle excitation spectrum. The choice of a single Slater determinant representation for the charge density also makes it difficult to see how to construct a calculation starting from (for example) an excited singlet state that requires at least two determinants in a wavefunction calculation.

An alternative wavefunction-based approach, also with low computational cost, is the time-dependent Hartree-Fock<sup>11-13</sup> (TDHF) approximation. This method consists in restricting the electronic wavefunction to the form of a single Slater determinant, built using a number of single-particle orbitals, which are optimised according to a time-dependent variational principle. The single-configurational nature of TDHF is clearly insufficient to accurately describe the excited states involved in most physical processes of interest. This is especially true for the commonly used restricted

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version of TDHF, where the spatial parts of the single-particle orbitals are identical for both spin states. An improved description may be achieved by relaxing this constraint, but the resulting unrestricted formalism has only been employed with limited success.<sup>14</sup>

In recent years, considerable effort has been devoted to generalising the TDHF method, by expanding the electronic wavefunction into several Slater determinants,<sup>15–19</sup> rather than a single one. This multiconfigurational time-dependent Hartree-Fock (MCTDHF) approach exploits the idea of variationally optimising the expansion coefficients, as well as the single-particle orbitals used to build each configuration. This allows for a much more effective sampling of the many-body Hilbert space in comparison with expansions which use time-independent configurations. The MCTDHF method systematically improves the description of electron correlation effects towards the exact solution of the time-dependent Schrödinger equation, as more and more electrons are added to an increasingly large active space.

In its current formulation, MCTDHF is only practical for few-electron systems, since the wavefunction expansion quite rapidly becomes prohibitively large as the number of degrees of freedom increases (the computational time has an exponential dependence on the number of electrons). In this work, we take a complementary approach which aims at establishing a compromise between efficiency and accuracy, thus allowing for the study of much larger systems. The idea is to retain the smallest possible number of configurations that catches the essential features of the electronic wavefunction, notably its spin symmetry. This is important, as it allows us to distinguish between singlet and triplet excited states, which exhibit quite different properties. The single-particle orbitals used to construct the wavefunction expansion are then optimised according to a time-dependent variational principle. However, in contrast to the work of Refs. 15–19, the expansion coefficients are held fixed. In this way, we are implicitly assuming a minimal description of the electronic wavefunction, such that, for symmetry reasons, the expansion coefficients can be treated as time-independent. We are particularly interested in specialising to the case of general open-shell states,<sup>20–22</sup> which are relevant for many physical processes of interest, such as the dynamics of photoexcitations in molecules.

The remainder of this paper is organised as follows. In Sec. II, we derive the MCTDHF working equation for a multiconfigurational expansion with fixed coefficients, using the Dirac-Frenkel formulation of the time-dependent variational principle.<sup>12,23,24</sup> In Sec. III, the method is applied to the case of general open-shell states. The illustrative examples of closed-shell and open-shell singlet states are considered in detail. Finally, a comparison with related work is given in Sec. IV, and Sec. V is devoted to concluding remarks.

## II. GENERAL FORMALISM

### A. MCTDHF working equation

Consider a system of  $N$  interacting electrons, described by the Hamiltonian<sup>25</sup>

$$\hat{H} = \sum_{i,j} T_{ij} \hat{c}_i^\dagger \hat{c}_j + \frac{1}{2} \sum_{i,j,k,l} V_{ijkl} \hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_l \hat{c}_k, \quad (1)$$

where  $\hat{c}_i^\dagger$  ( $\hat{c}_i$ ) creates (annihilates) an electron in the molecular spin-orbital  $\phi_i$ , and

$$T_{ij} = \int \phi_i^*(\xi) \hat{T}(\xi) \phi_j(\xi) d\xi, \quad (2)$$

$$V_{ijkl} = \int \phi_i^*(\xi) \phi_j^*(\xi') \hat{V}(\xi, \xi') \phi_k(\xi) \phi_l(\xi') d\xi d\xi'.$$

The operators  $\hat{T}$  and  $\hat{V}$  gather all the one-electron and electron-electron interactions, respectively, and  $\xi = \{\mathbf{r}, \sigma\}$  denotes collectively the orbital and spin coordinates of an electron.

The task of finding an approximate solution to the time-dependent Schrödinger equation,

$$i\hbar|\dot{\Psi}\rangle = \hat{H}|\Psi\rangle, \quad (3)$$

requires that we specify an ansatz for the electronic wavefunction. We will assume that this has the form of a superposition of Slater determinants,

$$|\Psi\rangle = \sum_{\alpha} C_{\alpha} |\phi_{\alpha_1} \cdots \phi_{\alpha_N}\rangle \equiv \sum_{\alpha} C_{\alpha} |\Phi_{\alpha}\rangle, \quad (4)$$

with fixed expansion coefficients,  $C_{\alpha}$ . Although this multiconfigurational form is quite general, we have in mind a minimal description of the electronic wavefunction, which retains the smallest possible number of Slater determinants required to generate an eigenfunction of the spin operator. In this case, the expansion coefficients are uniquely defined (up to an overall phase factor) and can be regarded as time-independent. For instance, in a photoexcitation process, absorption of a photon creates an open-shell singlet state, which can be written as a sum of two Slater determinants, provided that electron correlation is not too important. The time evolution of such a state, under a spin-independent Hamiltonian, clearly does not introduce a phase difference between the two configurations, in order to preserve the proper spin symmetry. For this reason, in a minimal model to study the dynamics of such an excited state, the expansion coefficients can be considered time-independent.

Each configuration in Eq. (4),  $|\Phi_{\alpha}\rangle$ , is built using  $N$  molecular spin-orbitals, indexed by  $\alpha_i$ , from the complete set  $\{\phi_j\}$ . Although some orbitals may not be included in the expansion, the existence of such a complete set can always be assumed.<sup>25</sup> Our goal is then to derive a set of optimal equations of motion for the (single-particle) molecular spin-orbitals. Stated in an equivalent way, we wish to find a single-particle, Hermitian operator,  $\hat{R}$ , that provides the best self-consistent approximation to the true evolution of the many-body wavefunction,  $|\Psi\rangle$ :

$$i\hbar|\dot{\Psi}\rangle \approx \hat{R}|\Psi\rangle = \sum_{i,j} R_{ij} \hat{c}_i^\dagger \hat{c}_j |\Psi\rangle, \quad (5)$$

where

$$R_{ij} = \int \phi_i^*(\xi) \hat{R}(\xi) \phi_j(\xi) d\xi = i\hbar \int \phi_i^*(\xi) \dot{\phi}_j(\xi) d\xi. \quad (6)$$

Note that  $\hat{R}|\Psi\rangle$  is equivalent to a sum over the time derivatives of the single-particle orbitals. It is clear that this can only provide an approximation to the true evolution of the many-body wavefunction, since  $\hat{R}$  is a single-particle operator, unlike the Hamiltonian [Eq. (1)]. This is a fundamental consequence of keeping the coefficients fixed in the wavefunction expansion, which is meant to be highlighted through the use of the approximation sign in Eq. (5).

The evolution operator  $\hat{R}$  (and, hence, the optimal equations of motion for the molecular spin-orbitals) may be found using the Dirac-Frenkel time-dependent variational principle.<sup>12,23,24</sup> In this formalism, one varies the action integral<sup>23</sup>

$$I[\Psi] = \int_{t_1}^{t_2} \langle \Psi | \hat{H} - i\hbar \frac{\partial}{\partial t} | \Psi \rangle dt, \quad (7)$$

with fixed end points. This procedure yields the variational equation

$$\left\langle \delta\Psi \left| \left( \hat{H} - i\hbar \frac{\partial}{\partial t} \right) \Psi \right. \right\rangle + \left\langle \left( \hat{H} - i\hbar \frac{\partial}{\partial t} \right) \Psi \right| \delta\Psi \rangle = 0, \quad (8)$$

which must be satisfied for arbitrary variations,  $\delta\Psi$ , of the approximate many-body wavefunction,  $\Psi$ . Although Eq. (8) is usually stated directly as the Dirac-Frenkel variational principle,<sup>12,24</sup> the underlying principle is always the integral formulation, which is necessary to justify the presence of the time derivative acting on the bra (in the second term) by partial integration.

To write the variation, let us consider the effect of a small rotation of the orthonormal set of molecular orbitals,

$$|\phi'_i\rangle = \sum_j e^{\Delta_{ji}} |\phi_j\rangle. \quad (9)$$

Notice that, since the new orbitals also form an orthonormal set, the matrix of orbital rotation (or mixing) parameters,  $\Delta$ , must be anti-Hermitian,

$$\Delta_{ij} = -\Delta_{ji}^*. \quad (10)$$

The transformed wavefunction can be written as

$$|\Psi'\rangle = \sum_{\alpha} C_{\alpha} \prod_i \hat{c}_i^{\dagger} \hat{c}_i |\Phi_{\alpha}\rangle, \quad (11)$$

where the symbol  $\prod'$  means that the product runs over the subset of spin-orbitals included in  $\Phi_{\alpha}$ , and  $\hat{c}_i^{\dagger}$  creates an electron in the rotated orbital  $\phi'_i$ . This operator can be expressed in the basis of the original orbitals as<sup>25</sup>

$$\hat{c}_i^{\dagger} = \sum_j \langle \phi_j | \phi'_i \rangle \hat{c}_j^{\dagger}, \quad (12)$$

or since we are considering small rotations,

$$\hat{c}_i^{\dagger} \approx \sum_j (\delta_{ji} + \Delta_{ji}) \hat{c}_j^{\dagger}. \quad (13)$$

Inserting Eq. (13) into Eq. (11), we obtain to first order in  $\Delta$ ,

$$\begin{aligned} |\Psi'\rangle &\approx \sum_{\alpha} C_{\alpha} \left[ \prod_i \hat{c}_i^{\dagger} \hat{c}_i |\Phi_{\alpha}\rangle + \sum_i \sum_j \Delta_{ji} \hat{c}_j^{\dagger} \hat{c}_i |\Phi_{\alpha}\rangle \right] \\ &= |\Psi\rangle + \sum_{i,j} \Delta_{ji} \hat{c}_j^{\dagger} \hat{c}_i |\Psi\rangle, \end{aligned} \quad (14)$$

from which we identify

$$|\delta\Psi\rangle = \sum_{i,j} \Delta_{ji} \hat{c}_j^{\dagger} \hat{c}_i |\Psi\rangle. \quad (15)$$

This methodology has the obvious advantage of incorporating the orthonormality constraints by construction. Furthermore, it provides physical insight into the structure of the variation, thus facilitating the elimination of redundant parameters, which is of key importance.

Combining Eqs. (5), (8), (10), and (15), the variational equation can be recast in the form

$$\sum_{i,j} \Delta_{ij} \langle \Psi | [\hat{H} - \hat{R}, \hat{c}_i^{\dagger} \hat{c}_j] | \Psi \rangle = 0, \quad (16)$$

or after inserting the Hamiltonian [Eq. (1)] and doing some operator algebra,

$$\begin{aligned} \sum_{i,j} \Delta_{ij} \left\{ \sum_k [(T_{ki} - R_{ki}) \rho_{kj}^{(1)} - (T_{jk} - R_{jk}) \rho_{ik}^{(1)}] \right. \\ \left. + \sum_{k,l,m} [V_{klim} \rho_{klmj}^{(2)} - V_{jklm} \rho_{iklm}^{(2)}] \right\} = 0, \end{aligned} \quad (17)$$

where

$$\begin{aligned} \rho_{ij}^{(1)} &= \langle \Psi | \hat{c}_i^{\dagger} \hat{c}_j | \Psi \rangle, \\ \rho_{ijkl}^{(2)} &= \langle \Psi | \hat{c}_i^{\dagger} \hat{c}_j^{\dagger} \hat{c}_k \hat{c}_l | \Psi \rangle \end{aligned} \quad (18)$$

denote the one- and two-body reduced density matrices,<sup>25,26</sup> respectively. Equation (17) constitutes the basic MCTDHF working equation. To carry on the derivation of the equations of motion for the single-particle orbitals, it is necessary to further specify the form of the one- and two-body reduced density matrices. In Sec. III, we will do so for general open-shell states, with the special cases of closed-shell and open-shell singlet states being treated explicitly.

## B. Conservation properties

In order to obtain proper dynamics, it is crucial that the equations of motion conserve energy (for time-independent Hamiltonians) and preserve the orthonormality of the molecular spin-orbitals. To establish energy conservation, we can resort to the Dirac-Frenkel variational principle directly. In general, we can write<sup>24</sup>

$$|\delta\Psi\rangle = |\dot{\Psi}\rangle \delta t. \quad (19)$$

Substitution into Eq. (8) yields

$$\langle \dot{\Psi} | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H} | \dot{\Psi} \rangle = 0, \quad (20)$$

which shows that energy is conserved throughout the dynamics if the Hamiltonian is time-independent. The conservation of orthonormality,

$$\frac{d}{dt} \langle \phi_i | \phi_j \rangle = \langle \dot{\phi}_i | \phi_j \rangle + \langle \phi_i | \dot{\phi}_j \rangle = 0, \quad (21)$$

follows trivially from the requirement that the effective single-particle operator  $\hat{R}$  is Hermitian, on view of Eq. (6).

### III. APPLICATIONS

#### A. Closed-shell singlet state

We now specialise the variational approach of Sec. II A to the case of a closed-shell singlet state and a spin-independent Hamiltonian. The wavefunction takes the form of a single Slater determinant,

$$|\Psi\rangle = |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\cdots\phi_n\bar{\phi}_n\rangle. \quad (22)$$

In the above expression,  $\phi_i$  ( $\bar{\phi}_i$ ) denotes a spin-up (spin-down) state and  $n = N/2$ . Spin symmetry suggests the use of a restricted formalism, for which the spin-up and spin-down states possess the same orbital part. It also suggests that we set

$$\Delta_{i\sigma_i,j\sigma_j} = \tilde{\Delta}_{ij}\delta_{\sigma_i\sigma_j}, \quad (23)$$

thus considering only the mixing between the spatial parts of the molecular spin-orbitals. The relevant operators are all spin-independent, with matrix elements satisfying

$$\begin{aligned} T_{i\sigma_i,j\sigma_j} &= \tilde{T}_{ij}\delta_{\sigma_i\sigma_j}, \\ V_{i\sigma_i,j\sigma_j,k\sigma_k,l\sigma_l} &= \tilde{V}_{ijkl}\delta_{\sigma_i\sigma_k}\delta_{\sigma_j\sigma_l}, \\ R_{i\sigma_i,j\sigma_j} &= \tilde{R}_{ij}\delta_{\sigma_i\sigma_j}, \end{aligned} \quad (24)$$

where

$$\begin{aligned} \tilde{T}_{ij} &= \int \phi_i^*(\mathbf{r})\hat{T}(\mathbf{r})\phi_j(\mathbf{r})\,d\mathbf{r}, \\ \tilde{V}_{ijkl} &= \int \phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\hat{V}(\mathbf{r},\mathbf{r}')\phi_k(\mathbf{r})\phi_l(\mathbf{r}')\,d\mathbf{r}d\mathbf{r}', \\ \tilde{R}_{ij} &= \int \phi_i^*(\mathbf{r})\hat{R}(\mathbf{r})\phi_j(\mathbf{r})\,d\mathbf{r} = i\hbar \int \phi_i^*(\mathbf{r})\dot{\phi}_j(\mathbf{r})\,d\mathbf{r}, \end{aligned} \quad (25)$$

and  $\phi_i$  now denotes the spatial part of the molecular spin-orbitals alone.

Using the standard rules for the behaviour of creation and annihilation operators,<sup>25</sup> the elements of the one- and two-body reduced density matrices can be easily computed. The result is

$$\begin{aligned} \rho_{i\sigma_i,j\sigma_j}^{(1)} &= \delta_{ij}\delta_{\sigma_i\sigma_j}, \\ \rho_{i\sigma_i,j\sigma_j,k\sigma_k,l\sigma_l}^{(2)} &= \delta_{il}\delta_{jk}\delta_{\sigma_i\sigma_l}\delta_{\sigma_j\sigma_k} - \delta_{ik}\delta_{jl}\delta_{\sigma_i\sigma_k}\delta_{\sigma_j\sigma_l}, \end{aligned} \quad (26)$$

when all the indices refer to occupied orbitals, and zero otherwise. Inserting Eq. (26) into Eq. (17), we can write the variational condition as

$$\begin{aligned} &\sum_{i,\sigma_i}\sum_{j,\sigma_j}'\Delta_{i\sigma_i,j\sigma_j}\left[(T_{j\sigma_j,i\sigma_i} - R_{j\sigma_j,i\sigma_i})\right. \\ &\quad \left. + \sum_{k,\sigma_k}'(V_{j\sigma_jk\sigma_k,i\sigma_ik\sigma_k} - V_{j\sigma_jk\sigma_k,k\sigma_ki\sigma_i})\right] \\ &\quad - \sum_{i,\sigma_i}\sum_{j,\sigma_j}'\Delta_{i\sigma_i,j\sigma_j}\left[(T_{j\sigma_j,i\sigma_i} - R_{j\sigma_j,i\sigma_i})\right. \\ &\quad \left. + \sum_{k,\sigma_k}'(V_{j\sigma_jk\sigma_k,i\sigma_ik\sigma_k} - V_{j\sigma_jk\sigma_k,k\sigma_ki\sigma_i})\right] = 0, \end{aligned} \quad (27)$$

where the symbol  $\sum'$  means that the sum extends only over occupied molecular orbitals. Performing the summations over spin, with the help of Eqs. (23) and (24), yields

$$\begin{aligned} &\sum_i\sum_j'2\tilde{\Delta}_{ij}\left[(\tilde{T}_{ji} - \tilde{R}_{ji}) + \sum_k'(2\tilde{V}_{jkik} - \tilde{V}_{jkki})\right] \\ &\quad - \sum_i\sum_j'2\tilde{\Delta}_{ij}\left[(\tilde{T}_{ji} - \tilde{R}_{ji}) + \sum_k'(2\tilde{V}_{jkik} - \tilde{V}_{jkki})\right] = 0. \end{aligned} \quad (28)$$

Let us now introduce the (closed-shell) Fock operator,<sup>12,24</sup>

$$\hat{F} = \hat{T} + \sum_k'(2\hat{J}_k - \hat{K}_k), \quad (29)$$

where  $\hat{J}_k$  and  $\hat{K}_k$  are Coulomb and exchange operators,<sup>12,24</sup> defined by

$$\begin{aligned} \hat{J}_k(\mathbf{r})\phi_i(\mathbf{r}) &= \left[\int \phi_k^*(\mathbf{r}')\hat{V}(\mathbf{r},\mathbf{r}')\phi_k(\mathbf{r}')\,d\mathbf{r}'\right]\phi_i(\mathbf{r}), \\ \hat{K}_k(\mathbf{r})\phi_i(\mathbf{r}) &= \left[\int \phi_k^*(\mathbf{r}')\hat{V}(\mathbf{r},\mathbf{r}')\phi_i(\mathbf{r}')\,d\mathbf{r}'\right]\phi_k(\mathbf{r}). \end{aligned} \quad (30)$$

Clearly, we have

$$\tilde{F}_{ji} = \langle\phi_j|\hat{F}|\phi_i\rangle = \tilde{T}_{ji} + \sum_k'(2\tilde{V}_{jkik} - \tilde{V}_{jkki}), \quad (31)$$

and thus the variational equation can be rewritten as

$$\sum_i\sum_j'2\tilde{\Delta}_{ij}(\tilde{F}_{ji} - \tilde{R}_{ji}) - \sum_i\sum_j'2\tilde{\Delta}_{ij}(\tilde{F}_{ji} - \tilde{R}_{ji}) = 0. \quad (32)$$

Introducing the occupation numbers,

$$n_i = \begin{cases} 2, & \text{if } \phi_i \text{ is doubly occupied} \\ 0, & \text{otherwise,} \end{cases} \quad (33)$$

it is possible to gather the two terms in Eq. (32),

$$\sum_{i,j}\tilde{\Delta}_{ij}(n_j - n_i)\langle\phi_j|\hat{F} - \hat{R}|\phi_i\rangle = 0. \quad (34)$$

Hence, the choice  $\hat{R} = \hat{F}$  satisfies the Dirac-Frenkel variational principle, and the optimal equations of motion for the spatial part of the single-particle orbitals read

$$i\hbar|\dot{\phi}_i\rangle = \hat{F}|\phi_i\rangle, \quad (35)$$

as expected (this is the usual TDHF result<sup>11-13</sup>). Notice that there is a certain degree of arbitrariness in this choice of the effective single-particle operator  $\hat{R}$ , since Eq. (34) is automatically satisfied when  $n_i = n_j$ . Thus, the relevant matrix elements are those connecting the occupied and virtual subspaces, for which the choice of  $\hat{R}$  is unique.

#### B. Open-shell singlet state

Let us now consider the case of an open-shell singlet state and a spin-independent Hamiltonian. The spin symmetry arguments of the single-configurational case can

still be invoked, and thus Eqs. (23)–(25) remain valid. In this case, the wavefunction is the sum of two Slater determinants,

$$\begin{aligned} |\Psi\rangle &= \frac{1}{\sqrt{2}}|\phi_1\bar{\phi}_1 \cdots \phi_{n-1}\bar{\phi}_{n-1} \phi_v\bar{\phi}_c\rangle \\ &+ \frac{1}{\sqrt{2}}|\phi_1\bar{\phi}_1 \cdots \phi_{n-1}\bar{\phi}_{n-1} \phi_c\bar{\phi}_v\rangle \\ &\equiv \frac{1}{\sqrt{2}}(|\Phi_1\rangle + |\Phi_2\rangle), \end{aligned} \quad (36)$$

corresponding to a singlet arrangement of a set of  $n - 1$  doubly occupied orbitals and two singly occupied orbitals, labelled “ $v$ ” and “ $c$ ” (motivated by the physical picture of an excitation from the valence band to the conduction band in periodic systems, e.g., conjugated polymers). As before, the elements of the one-body reduced density matrix are trivial,

$$\rho_{i\sigma_i, j\sigma_j}^{(1)} = \frac{n_i}{2}\delta_{ij}\delta_{\sigma_i\sigma_j}, \quad (37)$$

with the populations

$$n_i = \begin{cases} 2, & \text{if } \phi_i \text{ is doubly occupied} \\ 1, & \text{if } \phi_i \text{ is singly occupied} \\ 0, & \text{otherwise.} \end{cases} \quad (38)$$

However, the two-body reduced density matrix possesses a more involved structure, which we will describe briefly. When all the indices refer to occupied orbitals, its elements can be written as the sum of two terms (we recall that they are zero otherwise),

$$\rho_{i\sigma_i, j\sigma_j, k\sigma_k, l\sigma_l}^{(2)} = \frac{1}{2}(\gamma_{i\sigma_i, j\sigma_j, k\sigma_k, l\sigma_l} + \zeta_{i\sigma_i, j\sigma_j, k\sigma_k, l\sigma_l}). \quad (39)$$

The first one, given by

$$\begin{aligned} \gamma_{i\sigma_i, j\sigma_j, k\sigma_k, l\sigma_l} &= (\delta_{il}\delta_{jk}\delta_{\sigma_i\sigma_l}\delta_{\sigma_j\sigma_k} - \delta_{ik}\delta_{jl}\delta_{\sigma_i\sigma_k}\delta_{\sigma_j\sigma_l}) \\ &\times [(1 - \delta_{iv}\delta_{\sigma_i\downarrow} - \delta_{jv}\delta_{\sigma_j\downarrow}) \\ &\times (1 - \delta_{ic}\delta_{\sigma_i\uparrow} - \delta_{jc}\delta_{\sigma_j\uparrow}) \\ &+ (1 - \delta_{iv}\delta_{\sigma_i\uparrow} - \delta_{jv}\delta_{\sigma_j\uparrow}) \\ &\times (1 - \delta_{ic}\delta_{\sigma_i\downarrow} - \delta_{jc}\delta_{\sigma_j\downarrow})], \end{aligned} \quad (40)$$

arises from contributions, such as  $\langle\Phi_1|\hat{c}_{i\sigma_i}^\dagger\hat{c}_{j\sigma_j}^\dagger\hat{c}_{k\sigma_k}\hat{c}_{l\sigma_l}|\Phi_1\rangle$ , which are only nonzero when we annihilate and create the same pair of orbitals. Since each configuration is “missing” two states ( $\bar{\phi}_v, \phi_c$  are not included in  $\Phi_1$ , and  $\phi_v, \bar{\phi}_c$  are not included in  $\Phi_2$ ), some combinations of indices referring to occupied orbitals only give a partial contribution to the total matrix element, via  $\langle\Phi_1|\hat{c}_{i\sigma_i}^\dagger\hat{c}_{j\sigma_j}^\dagger\hat{c}_{k\sigma_k}\hat{c}_{l\sigma_l}|\Phi_1\rangle$  or  $\langle\Phi_2|\hat{c}_{i\sigma_i}^\dagger\hat{c}_{j\sigma_j}^\dagger\hat{c}_{k\sigma_k}\hat{c}_{l\sigma_l}|\Phi_2\rangle$  (but not both). In Eq. (40), this is accounted for by the term in square brackets. The second contribution is given by

$$\begin{aligned} \zeta_{i\sigma_i, j\sigma_j, k\sigma_k, l\sigma_l} &= \delta_{iv}\delta_{jc}\delta_{\sigma_i\uparrow}\delta_{\sigma_j\downarrow}(\delta_{kv}\delta_{lc}\delta_{\sigma_k\downarrow}\delta_{\sigma_l\uparrow} - \delta_{kc}\delta_{lv}\delta_{\sigma_k\uparrow}\delta_{\sigma_l\downarrow}) \\ &+ \delta_{ic}\delta_{jv}\delta_{\sigma_i\downarrow}\delta_{\sigma_j\uparrow}(\delta_{kv}\delta_{lc}\delta_{\sigma_k\downarrow}\delta_{\sigma_l\uparrow} - \delta_{kc}\delta_{lv}\delta_{\sigma_k\uparrow}\delta_{\sigma_l\downarrow}) \\ &+ \delta_{ic}\delta_{jv}\delta_{\sigma_i\uparrow}\delta_{\sigma_j\downarrow}(\delta_{kv}\delta_{lc}\delta_{\sigma_k\downarrow}\delta_{\sigma_l\uparrow} - \delta_{kc}\delta_{lv}\delta_{\sigma_k\uparrow}\delta_{\sigma_l\downarrow}) \\ &+ \delta_{iv}\delta_{jc}\delta_{\sigma_i\downarrow}\delta_{\sigma_j\uparrow}(\delta_{kv}\delta_{lc}\delta_{\sigma_k\downarrow}\delta_{\sigma_l\uparrow} - \delta_{kc}\delta_{lv}\delta_{\sigma_k\uparrow}\delta_{\sigma_l\downarrow}), \end{aligned} \quad (41)$$

and arises from the cross terms  $\langle\Phi_1|\hat{c}_{i\sigma_i}^\dagger\hat{c}_{j\sigma_j}^\dagger\hat{c}_{k\sigma_k}\hat{c}_{l\sigma_l}|\Phi_2\rangle$  and  $\langle\Phi_2|\hat{c}_{i\sigma_i}^\dagger\hat{c}_{j\sigma_j}^\dagger\hat{c}_{k\sigma_k}\hat{c}_{l\sigma_l}|\Phi_1\rangle$ . Since the configurations included in the wavefunction differ in two orbitals, namely the singly occupied ones, these terms are only nonzero when we annihilate the singly occupied states that appear in one configuration and create the respective states included in the other. Equation (41) expresses all the allowed ways in which we can accomplish this.

With these results, Eq. (17) reads

$$\begin{aligned} &\sum_{i, j, \sigma_i, \sigma_j} \Delta_{i\sigma_i, j\sigma_j} \left[ \frac{n_j}{2}(T_{j\sigma_j, i\sigma_i} - R_{j\sigma_j, i\sigma_i}) - \frac{n_i}{2}(T_{j\sigma_j, i\sigma_i} - R_{j\sigma_j, i\sigma_i}) \right] \\ &+ \sum_{i, \sigma_i} \sum_{j, \sigma_j}''' \Delta_{i\sigma_i, j\sigma_j} \left[ \sum_{k, \sigma_k} \frac{n_k}{2}(V_{j\sigma_j k\sigma_k, i\sigma_i k\sigma_k} - V_{j\sigma_j k\sigma_k, k\sigma_k i\sigma_i}) \right] \\ &- \sum_{i, \sigma_i} \sum_{j, \sigma_j}''' \Delta_{i\sigma_i, j\sigma_j} \left[ \sum_{k, \sigma_k} \frac{n_k}{2}(V_{j\sigma_j k\sigma_k, i\sigma_i k\sigma_k} - V_{j\sigma_j k\sigma_k, k\sigma_k i\sigma_i}) \right] \\ &- \frac{1}{2} \sum_{i, \sigma_i} \sum_{j, \sigma_j}' \Delta_{i\sigma_i, j\sigma_j} \left[ \sum_{k, \sigma_k}''' (V_{j\sigma_j k\sigma_k, i\sigma_i k\sigma_k} - V_{j\sigma_j k\sigma_k, k\sigma_k i\sigma_i}) \right] \\ &+ \frac{1}{2} \sum_{i, \sigma_i} \sum_{j, \sigma_j}' \Delta_{i\sigma_i, j\sigma_j} \left[ \sum_{k, \sigma_k}''' (V_{j\sigma_j k\sigma_k, i\sigma_i k\sigma_k} - V_{j\sigma_j k\sigma_k, k\sigma_k i\sigma_i}) \right] \\ &+ \frac{1}{2} \sum_{i, \sigma_i} [\Delta_{i\sigma_i, v\uparrow}(V_{v\uparrow c\downarrow, i\sigma_i c\downarrow} - V_{c\downarrow v\uparrow, i\sigma_i c\downarrow} + V_{c\uparrow v\downarrow, i\sigma_i c\downarrow} - V_{v\downarrow c\uparrow, i\sigma_i c\downarrow}) \\ &+ \Delta_{i\sigma_i, v\downarrow}(V_{v\downarrow c\uparrow, i\sigma_i c\uparrow} - V_{c\uparrow v\downarrow, i\sigma_i c\uparrow} + V_{c\downarrow v\uparrow, i\sigma_i c\uparrow} - V_{v\uparrow c\downarrow, i\sigma_i c\uparrow}) \end{aligned}$$

$$\begin{aligned}
& + \Delta_{i\sigma_i, c\uparrow} (V_{c\uparrow v\downarrow, i\sigma_i v\downarrow} - V_{v\downarrow c\uparrow, i\sigma_i v\downarrow} + V_{v\uparrow c\downarrow, i\sigma_i v\downarrow} - V_{c\downarrow v\uparrow, i\sigma_i v\downarrow}) \\
& + \Delta_{i\sigma_i, c\downarrow} (V_{c\downarrow v\uparrow, i\sigma_i v\uparrow} - V_{v\uparrow c\downarrow, i\sigma_i v\uparrow} + V_{v\downarrow c\uparrow, i\sigma_i v\uparrow} - V_{c\uparrow v\downarrow, i\sigma_i v\uparrow}) \\
& - \frac{1}{2} \sum_{j, \sigma_j} [\Delta_{v\uparrow, j\sigma_j} (V_{j\sigma_j c\downarrow, v\uparrow c\downarrow} - V_{j\sigma_j c\downarrow, c\downarrow v\uparrow} + V_{j\sigma_j c\downarrow, c\uparrow v\downarrow} - V_{j\sigma_j c\downarrow, v\downarrow c\uparrow}) \\
& + \Delta_{v\downarrow, j\sigma_j} (V_{j\sigma_j c\uparrow, v\downarrow c\uparrow} - V_{j\sigma_j c\uparrow, c\uparrow v\downarrow} + V_{j\sigma_j c\uparrow, c\downarrow v\uparrow} - V_{j\sigma_j c\uparrow, v\uparrow c\downarrow}) \\
& + \Delta_{c\uparrow, j\sigma_j} (V_{j\sigma_j v\downarrow, c\uparrow v\downarrow} - V_{j\sigma_j v\downarrow, v\downarrow c\uparrow} + V_{j\sigma_j v\downarrow, v\uparrow c\downarrow} - V_{j\sigma_j v\downarrow, c\downarrow v\uparrow}) \\
& + \Delta_{c\downarrow, j\sigma_j} (V_{j\sigma_j v\uparrow, c\downarrow v\uparrow} - V_{j\sigma_j v\uparrow, v\uparrow c\downarrow} + V_{j\sigma_j v\uparrow, v\downarrow c\uparrow} - V_{j\sigma_j v\uparrow, c\uparrow v\downarrow})] = 0, \quad (42)
\end{aligned}$$

where the symbol  $\sum''$  means that the sum runs over both doubly and singly occupied molecular orbitals (but not empty ones), and  $\sum'$  is used for sums which extend only over singly occupied orbitals. Using Eqs. (23) and (24) to perform the summations over spin, yields

$$\begin{aligned}
& \sum_{i,j} \tilde{\Delta}_{ij} [n_j (\tilde{T}_{ji} - \tilde{R}_{ji}) - n_i (\tilde{T}_{ji} - \tilde{R}_{ji})] + \sum_i \sum_j'' \tilde{\Delta}_{ij} \sum_k n_k (2\tilde{V}_{jkik} - \tilde{V}_{jkki}) - \sum_i'' \sum_j \tilde{\Delta}_{ij} \sum_k n_k (2\tilde{V}_{jkik} - \tilde{V}_{jkki}) \\
& - \sum_i \sum_j' \tilde{\Delta}_{ij} \sum_k'' (2\tilde{V}_{jkik} - \tilde{V}_{jkki}) + \sum_i' \sum_j \tilde{\Delta}_{ij} \sum_k'' (2\tilde{V}_{jkik} - \tilde{V}_{jkki}) + \sum_i [\tilde{\Delta}_{iv} (\tilde{V}_{vcic} + \tilde{V}_{vcci}) + \tilde{\Delta}_{ic} (\tilde{V}_{cviv} + \tilde{V}_{cvvi})] \\
& - \sum_j [\tilde{\Delta}_{vj} (\tilde{V}_{jvcv} + \tilde{V}_{jccv}) + \tilde{\Delta}_{cj} (\tilde{V}_{jvcv} + \tilde{V}_{jvcc})] = 0. \quad (43)
\end{aligned}$$

Explicitly separating the sums that run over all occupied states into contributions from orbitals with double and single occupancies, and collecting similar terms, we obtain

$$\begin{aligned}
& \sum_{i,j} \tilde{\Delta}_{ij} [n_j (\tilde{T}_{ji} - \tilde{R}_{ji}) - n_i (\tilde{T}_{ji} - \tilde{R}_{ji})] \\
& + \sum_i \left\{ \sum_j'' \tilde{\Delta}_{ij} n_j \left[ \frac{1}{2} \sum_k n_k (2\tilde{V}_{jkik} - \tilde{V}_{jkki}) \right] \right. \\
& + \sum_j' \tilde{\Delta}_{ij} n_j \left[ \frac{1}{2} \sum_k'' n_k (2\tilde{V}_{jkik} - \tilde{V}_{jkki}) \right. \\
& \left. \left. + \frac{1}{2} \sum_k' n_k (2\tilde{V}_{jkik} + 2\tilde{V}_{jkki})(1 - \delta_{jk}) \right] \right\} \\
& - \sum_j \left\{ \sum_i'' \tilde{\Delta}_{ij} n_i \left[ \frac{1}{2} \sum_k n_k (2\tilde{V}_{jkik} - \tilde{V}_{jkki}) \right] \right. \\
& + \sum_i' \tilde{\Delta}_{ij} n_i \left[ \frac{1}{2} \sum_k'' n_k (2\tilde{V}_{jkik} - \tilde{V}_{jkki}) \right. \\
& \left. \left. + \frac{1}{2} \sum_k' n_k (2\tilde{V}_{jkik} + 2\tilde{V}_{jkki})(1 - \delta_{ik}) \right] \right\} = 0, \quad (44)
\end{aligned}$$

where the symbol  $\sum''$  means that the sum extends only over doubly occupied molecular orbitals, and we have conveniently introduced some occupation numbers.

It is clear from the form of Eq. (44) the emergence of Fock-like operators which depend on the orbital occupation, in contrast with the case of a single Slater determinant. Specifically, all the doubly occupied orbitals possess the same Fock operator, whereas each singly occupied orbital has its own. Gathering groups of orbitals with the same Fock operator in a

shell, labelled by  $\mu, \nu, \dots$ , we can rewrite Eq. (44) as

$$\sum_{\mu, \nu} \sum_{i_\mu, j_\nu} \tilde{\Delta}_{i_\mu j_\nu} \langle \phi_{j_\nu} | n^\nu \hat{F}^\nu - n^\mu \hat{F}^\mu - (n^\nu - n^\mu) \hat{R} | \phi_{i_\mu} \rangle = 0, \quad (45)$$

where  $i_\mu$  runs over orbitals of shell  $\mu$ ,  $n^\mu = 0, 1, 2$  denotes the occupation number of an orbital in shell  $\mu$ , and the Fock operator for shell  $\mu$  ( $\mu \neq 0$ ) is given by

$$\hat{F}^\mu = \hat{T} + \frac{1}{2} \sum_\nu \sum_{j_\nu} n^\nu (2\hat{J}_{j_\nu} - b^{\mu\nu} \hat{K}_{j_\nu}), \quad (46)$$

with

$$\mathbf{b} = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 2 & -2 \\ 1 & -2 & 2 \end{pmatrix}, \quad (47)$$

where we adopted the conventional ordering,<sup>20-22</sup> in which  $\mu = 1$  labels the doubly occupied shell, and  $\mu = 2, 3$  refer to the singly occupied ones. Notice that we also consider the subspace of unoccupied orbitals as a proper shell (labelled by  $\mu = 0$ ), even though its Fock operator is undefined (this is, however, irrelevant since it is always premultiplied by zero), and therefore this shell is not included in the definition of  $\mathbf{b}$  given above.

From Eq. (45), we can see that mixing orbitals that belong to the same shell does not lead to any change in the variational quantity, and thus the terms with  $\mu = \nu$  can be safely disregarded. Equivalently, as already encountered in the single-configurational case, there is a gauge freedom to choose the matrix elements of  $\hat{R}$  within the subspaces spanned by each shell. For simplicity, these will be set to zero. Additionally, the contributions which arise from mixing orbitals of different shells, but with the same occupation number, in general differ from zero regardless of the choice of

the operator  $\hat{R}$ . Hence, the corresponding orbital rotation parameters must be set to zero in order to satisfy the variational principle. This is consistent with neglecting two-electron processes which change the shell structure and can only be described using a formalism with time-dependent expansion coefficients.

With the above considerations, the variational equation reduces to

$$\sum_{\substack{\mu, \nu \\ (n^\mu \neq n^\nu)}} \sum_{i_\mu, j_\nu} \tilde{\Delta}_{i_\mu j_\nu} \langle \phi_{j_\nu} | n^\nu \hat{F}^\nu - n^\mu \hat{F}^\mu - (n^\nu - n^\mu) \hat{R} | \phi_{i_\mu} \rangle = 0, \quad (48)$$

which suggests that we set

$$\hat{R} = \sum_{\substack{\mu, \nu \\ (n^\mu \neq n^\nu)}} \hat{P}^\nu \frac{n^\nu \hat{F}^\nu - n^\mu \hat{F}^\mu}{n^\nu - n^\mu} \hat{P}^\mu, \quad (49)$$

where  $\hat{P}^\mu$  is a projector onto the subspace spanned by shell  $\mu$ ,

$$\hat{P}^\mu = \sum_{i_\mu} |\phi_{i_\mu}\rangle \langle \phi_{i_\mu}|. \quad (50)$$

Clearly, this choice satisfies the Dirac-Frenkel variational principle. The optimal equations of motion for the spatial part of the single-particle orbitals thus read

$$i\hbar |\dot{\phi}_{i_\mu}\rangle = \sum_{\substack{\nu, \lambda \\ (n^\nu \neq n^\lambda)}} \hat{P}^\lambda \frac{n^\lambda \hat{F}^\lambda - n^\nu \hat{F}^\nu}{n^\lambda - n^\nu} \hat{P}^\nu |\phi_{i_\mu}\rangle. \quad (51)$$

### C. General open-shell states

We now turn to general open-shell states, within a spin-restricted formalism. These are characterised by the one- and two-body reduced density matrices

$$\begin{aligned} \rho_{i_\mu \sigma_{i_\mu} j_\nu \sigma_{j_\nu}}^{(1)} &= \frac{n^\mu}{2} \delta_{i_\mu j_\nu} \delta_{\sigma_{i_\mu} \sigma_{j_\nu}}, \\ \rho_{i_\mu \sigma_{i_\mu} j_\nu \sigma_{j_\nu} k_\lambda \sigma_{k_\lambda} l_\kappa \sigma_{l_\kappa}}^{(2)} &= \frac{n^\mu n^\nu}{12} [(4a^{\mu\nu} - b^{\mu\nu})(\delta_{i_\mu l_\kappa} \delta_{j_\nu k_\lambda} \delta_{\sigma_{i_\mu} \sigma_{l_\kappa}} \delta_{\sigma_{j_\nu} \sigma_{k_\lambda}} \\ &\quad - \delta_{i_\mu k_\lambda} \delta_{j_\nu l_\kappa} \delta_{\sigma_{i_\mu} \sigma_{k_\lambda}} \delta_{\sigma_{j_\nu} \sigma_{l_\kappa}}) \\ &\quad + 2(a^{\mu\nu} - b^{\mu\nu})(\delta_{i_\mu k_\lambda} \delta_{j_\nu l_\kappa} \delta_{\sigma_{i_\mu} \sigma_{l_\kappa}} \delta_{\sigma_{j_\nu} \sigma_{k_\lambda}} \\ &\quad - \delta_{i_\mu l_\kappa} \delta_{j_\nu k_\lambda} \delta_{\sigma_{i_\mu} \sigma_{k_\lambda}} \delta_{\sigma_{j_\nu} \sigma_{l_\kappa}})], \end{aligned} \quad (52)$$

where

$$\begin{aligned} a^{\mu\nu} &= a^{v\mu}, \\ b^{\mu\nu} &= b^{v\mu} \end{aligned} \quad (53)$$

are numerical coefficients (or state parameters) specific to the particular form of the wavefunction,<sup>20–22</sup> which in general is a sum of many Slater determinants. Equation (52) leads to the energy expression

$$E = \sum_{\mu} \sum_{i_\mu} n^\mu \tilde{T}_{i_\mu i_\mu} + \frac{1}{4} \sum_{\mu, \nu} \sum_{i_\mu, j_\nu} n^\mu n^\nu (2a^{\mu\nu} \tilde{J}_{i_\mu j_\nu} - b^{\mu\nu} \tilde{K}_{i_\mu j_\nu}), \quad (54)$$

which is the more familiar way to define a general open-shell state.<sup>20–22</sup> Notice that the closed-shell and open-shell singlet states of Secs. III A and III B are special cases of this broad definition. For a closed-shell singlet state, there is only one occupied shell, and the state parameters read  $a = b = 1$ . As we have already seen, in the case of an open-shell singlet state, there are three shells,  $\mathbf{b}$  is given by Eq. (47), and

$$\mathbf{a} = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}. \quad (55)$$

Many other important electronic states of atoms and molecules fall into this category. Most notably, it includes all possible spin-adapted states that can be generated from a given electronic configuration.<sup>20–22</sup>

To derive the optimal equations of motion for the single-particle orbitals, we now proceed as in Secs. III A and III B. Inserting Eq. (52) into Eq. (17), and summing over spin, after using the Kronecker deltas to eliminate several sums, we obtain

$$\begin{aligned} \sum_{\mu, \nu} \sum_{i_\mu, j_\nu} \tilde{\Delta}_{i_\mu j_\nu} \left\{ n^\nu (\tilde{T}_{j_\nu i_\mu} - \tilde{R}_{j_\nu i_\mu}) - n^\mu (\tilde{T}_{j_\nu i_\mu} - \tilde{R}_{j_\nu i_\mu}) \right. \\ \left. + n^\nu \left[ \frac{1}{2} \sum_{\lambda} \sum_{k_\lambda} n^\lambda (2a^{\nu\lambda} \tilde{V}_{j_\nu k_\lambda i_\mu k_\lambda} - b^{\nu\lambda} \tilde{V}_{j_\nu k_\lambda k_\lambda i_\mu}) \right] \right. \\ \left. - n^\mu \left[ \frac{1}{2} \sum_{\lambda} \sum_{k_\lambda} n^\lambda (2a^{\mu\lambda} \tilde{V}_{j_\nu k_\lambda i_\mu k_\lambda} - b^{\mu\lambda} \tilde{V}_{j_\nu k_\lambda k_\lambda i_\mu}) \right] \right\} = 0, \end{aligned} \quad (56)$$

i.e.,

$$\sum_{\mu, \nu} \sum_{i_\mu, j_\nu} \tilde{\Delta}_{i_\mu j_\nu} \langle \phi_{j_\nu} | n^\nu \hat{F}^\nu - n^\mu \hat{F}^\mu - (n^\nu - n^\mu) \hat{R} | \phi_{i_\mu} \rangle = 0, \quad (57)$$

where the Fock operator for shell  $\mu$  ( $\mu \neq 0$ ) takes the generalised form

$$\hat{F}^\mu = \hat{T} + \frac{1}{2} \sum_{\nu} \sum_{j_\nu} n^\nu (2a^{\mu\nu} \hat{J}_{j_\nu} - b^{\mu\nu} \hat{K}_{j_\nu}). \quad (58)$$

As before, in order to satisfy the Dirac-Frenkel variational principle it is necessary to zero the mixing parameters between orbitals of different shells, but with the same occupation number. Also, the terms with  $\mu = \nu$  may be ignored, as they do not change the variational quantity (again, we will use this gauge freedom to set the matrix elements of  $\hat{R}$  within each shell subspace to zero). We are, thus, lead to the choice

$$\hat{R} = \sum_{\substack{\mu, \nu \\ (n^\mu \neq n^\nu)}} \hat{P}^\nu \frac{n^\nu \hat{F}^\nu - n^\mu \hat{F}^\mu}{n^\nu - n^\mu} \hat{P}^\mu, \quad (59)$$

and the optimal equations of motion for the spatial part of the single-particle orbitals have the form of Eq. (51), with the Fock operators given by Eq. (58).

We conclude this section with a discussion of the cost of the numerical implementation of the proposed scheme. In all the applications we envisage, the number of occupied

shells,  $N_{\text{shells}}$ , will be fixed by the spin symmetry, independent of system size, and in addition will be much lower than the size of the basis set,  $N_{\text{basis}}$ . This is typically the case when only a few configurations are included in the wavefunction expansion, e.g., for an open-shell singlet state. In such a case, the computational bottleneck lies in the calculation of the two-electron Coulomb and exchange terms required to build the matrix form of the Fock operators, exactly as in the TDHF method. The formal scaling is  $N_{\text{shells}}N_{\text{basis}}^4$ , since the total number of two-electron integrals increases as  $N_{\text{basis}}^4$  and  $N_{\text{shells}}$  different Fock operators must be constructed. If semiempirical parameters are used instead, the numerical effort can be more favourable, of the order of  $N_{\text{basis}}^3$ . In the limit of  $N_{\text{shells}} \ll N_{\text{basis}}$ , the proposed method requires only a few more matrix multiplications than the TDHF method, and thus exhibits a comparable computational cost.

#### IV. COMPARISON WITH RELATED WORK

Let us now consider the case of a multiconfigurational expansion [Eq. (4)] with time-dependent coefficients,  $C_{\alpha}(t)$ . The time evolution of the approximate many-body wavefunction reads

$$i\hbar|\dot{\Psi}\rangle = i\hbar\sum_{\alpha}\dot{C}_{\alpha}|\Phi_{\alpha}\rangle + \hat{R}|\Psi\rangle, \quad (60)$$

where the first term on the right-hand side arises from the time dependence of the expansion coefficients, and the second one emerges from the time dependence of the molecular spin-orbitals. As we have seen in Sec. II A, this latter contribution is conveniently expressed in terms of a single-particle, Hermitian operator,  $\hat{R}$ , which is to be found through a variational procedure. In the case under consideration, the expansion coefficients need to be variationally optimised as well.

Since the expansion coefficients and the single-particle orbitals used to build each configuration are independent variables, the many-body wavefunction can be varied separately with respect to each of them. The variation with respect to the expansion coefficients can be written as

$$|\delta_C\Psi\rangle = \sum_{\alpha}\delta C_{\alpha}|\Phi_{\alpha}\rangle. \quad (61)$$

Application of the Dirac-Frenkel time-dependent variational principle [Eq. (8)], with the variation given by Eq. (61), yields

$$i\hbar\dot{C}_{\alpha} = \sum_{\beta}\langle\Phi_{\alpha}|\hat{H} - \hat{R}|\Phi_{\beta}\rangle C_{\beta}. \quad (62)$$

As shown in Sec. II A, the variation with respect to the orbitals can be expressed as

$$|\delta_{\phi}\Psi\rangle = \sum_{i,j}\Delta_{ij}\hat{c}_i^{\dagger}\hat{c}_j|\Psi\rangle. \quad (63)$$

Combining Eqs. (8), (60), and (63), we obtain

$$\sum_{i,j}\Delta_{ij}\left[\langle\Psi|[\hat{H} - \hat{R}, \hat{c}_i^{\dagger}\hat{c}_j]|\Psi\rangle + i\hbar\sum_{\alpha,\beta}(C_{\alpha}^*\dot{C}_{\beta} + C_{\alpha}^*\dot{C}_{\beta})\langle\Phi_{\alpha}|\hat{c}_i^{\dagger}\hat{c}_j|\Phi_{\beta}\rangle\right] = 0. \quad (64)$$

Notice that, if the time evolution of the expansion coefficients only changes the wavefunction by an overall phase factor, Eq. (64) reduces to Eq. (16). In this case, the derivation of the optimal equations of motion for the single-particle orbitals follows that of Sec. III C, for general open-shell states and a spin-independent Hamiltonian. Also, in such a case, Eq. (62) may be disregarded, since an overall phase factor is unimportant for the calculation of physical observables.

We now proceed assuming that the wavefunction expansion is built from all  $\binom{M}{N}$  possible configurations obtained by distributing  $N$  electrons over  $M$  spin-orbitals. In principle, Eq. (64) should uniquely determine the single-particle operator  $\hat{R}$ , which in turn could be used in Eq. (62), that governs the time evolution of the expansion coefficients. Let us examine Eq. (64) more closely to see whether this statement holds for such a complete active space expansion. First, we note that the terms which involve mixing unoccupied orbitals are equal to zero, since, in this case,  $\hat{c}_i^{\dagger}\hat{c}_j|\Phi_{\alpha}\rangle = 0$  for all configurations included in the wavefunction expansion. The contributions which arise from mixing occupied orbitals are also equal to zero. This is most clearly seen by combining Eqs. (62) and (64),

$$\sum_{i,j}\Delta_{ij}[\langle\Psi|(\hat{H} - \hat{R})(1 - \hat{P})\hat{c}_i^{\dagger}\hat{c}_j|\Psi\rangle - \langle\Psi|\hat{c}_i^{\dagger}\hat{c}_j(1 - \hat{P})(\hat{H} - \hat{R})|\Psi\rangle] = 0, \quad (65)$$

with

$$\hat{P} = \sum_{\alpha}|\Phi_{\alpha}\rangle\langle\Phi_{\alpha}|. \quad (66)$$

When the indices  $i, j$  both refer to occupied states,  $\hat{c}_i^{\dagger}\hat{c}_j|\Psi\rangle$  generally yields a superposition of Slater determinants, all of which are included in the expansion. However, this is eliminated by the action of the projector onto the virtual subspace,  $1 - \hat{P}$ . Finally, we note that the matrix elements  $\langle\Phi_{\alpha}|\hat{c}_i^{\dagger}\hat{c}_j|\Phi_{\beta}\rangle$  are only nonzero when the indices  $i, j$  both correspond to occupied orbitals. With these considerations, Eq. (64) can be recast in the form

$$\sum_i'\sum_j''\Delta_{ji}^*\left[\sum_k'(T_{jk} - R_{jk})\rho_{ik}^{(1)} + \sum_{k,l,m}'V_{jkml}\rho_{iklm}^{(2)}\right] + \sum_i''\sum_j'\Delta_{ij}\left[\sum_k'(T_{ki} - R_{ki})\rho_{kj}^{(1)} + \sum_{k,l,m}'V_{klim}\rho_{klmj}^{(2)}\right] = 0, \quad (67)$$

where the symbol  $\sum'$  means that the sum extends only over occupied molecular orbitals, and  $\sum''$  is used for sums which run over empty states. It is clear that Eq. (67) can only determine the matrix elements of  $\hat{R}$  between occupied and unoccupied orbitals (and vice versa), but not within the occupied subspace. On the other hand, these latter terms are precisely the ones required in Eq. (62). They remain, however, undetermined and it is necessary to introduce further constraints. This is in striking contrast with the case of a multiconfigurational expansion with fixed coefficients, for which the necessary matrix elements are determined from the Dirac-Frenkel variational principle alone, as we have seen in Sec. III.

This problem can be overcome by exploiting the invariance of a complete active space wavefunction with respect to unitary transformations of the single-particle orbitals, compensated by reverse transformations of the coefficients.<sup>17,19</sup> Such property guarantees that the single-particle operator  $\hat{R}$  can be chosen arbitrarily within the occupied subspace, in analogy with the (more restricted) gauge freedom observed for general open-shell states. The simplest possible choice reads<sup>15-19</sup>

$$R_{ij} = i\hbar \langle \phi_i | \dot{\phi}_j \rangle = 0, \quad (68)$$

for all pairs  $i, j$  of occupied states. With this choice, Eq. (62) reduces to

$$i\hbar \dot{C}_\alpha = \sum_\beta \langle \Phi_\alpha | \hat{H} | \Phi_\beta \rangle C_\beta, \quad (69)$$

and the optimal equations of motion for the occupied orbitals follow from Eq. (67). Since the real and imaginary parts of the orbital rotation parameters can be regarded as independent variables, the two terms on the left-hand side of Eq. (67) can be equated to zero separately. Taking only the first term into consideration, we find

$$\sum_k' \left[ (T_{jk} - R_{jk}) \rho_{ik}^{(1)} + \sum_{l,m}' V_{jkml} \rho_{iklm}^{(2)} \right] = 0, \quad (70)$$

where the indices  $i, j$  refer to occupied and unoccupied states, respectively. Multiplying Eq. (70) by the inverse of the one-body reduced density matrix,  $\bar{\rho}^{(1)}$ , whose existence can always be assumed,<sup>26</sup> yields

$$\langle \phi_j | \hat{R} | \phi_i \rangle = \langle \phi_j | \left( \hat{T} | \phi_i \rangle + \sum_{k,l,m,n}' \bar{\rho}_{ik}^{(1)} \rho_{klmn}^{(2)} \hat{V}_{lm} | \phi_n \rangle \right), \quad (71)$$

where

$$\hat{V}_{lm}(\xi) = \int \phi_l^*(\xi') \hat{V}(\xi, \xi') \phi_m(\xi') d\xi'. \quad (72)$$

Since  $j$  labels an empty state, we can introduce the projector onto the subspace spanned by the unoccupied orbitals,

$$\hat{Q} = 1 - \sum_i' | \phi_i \rangle \langle \phi_i | = \sum_j'' | \phi_j \rangle \langle \phi_j |, \quad (73)$$

and rewrite Eq. (71) in the equivalent form

$$\langle \phi_j | \hat{R} | \phi_i \rangle = \langle \phi_j | \hat{Q} \left( \hat{T} | \phi_i \rangle + \sum_{k,l,m,n}' \bar{\rho}_{ik}^{(1)} \rho_{klmn}^{(2)} \hat{V}_{lm} | \phi_n \rangle \right). \quad (74)$$

Thus, the optimal equations of motion for the occupied molecular spin-orbitals read

$$i\hbar | \dot{\phi}_i \rangle = \hat{Q} \left( \hat{T} | \phi_i \rangle + \sum_{k,l,m,n}' \bar{\rho}_{ik}^{(1)} \rho_{klmn}^{(2)} \hat{V}_{lm} | \phi_n \rangle \right). \quad (75)$$

The presence of the projector in the above expression guarantees that the conditions specified by Eq. (68) are met at all times throughout the propagation of the orbitals. Also, it is easy to show that equating the second term on the left-hand side of Eq. (67) to zero, provides no further information, as it yields the complex conjugate of Eq. (75).

The coupled set of Eqs. (69) and (75) has been previously derived in Refs. 15–19. It is clear that the numerical implementation of these expressions incurs a much higher cost than for the equations of motion derived in Sec. III C for general open-shell states. Indeed, the computational cost is exponential in the number of electrons, and thus quite rapidly becomes prohibitive as the number of degrees of freedom increases. For this reason, the application of this method is currently limited to few-electron systems.<sup>15-19</sup>

In many processes of interest, the description of electron correlation effects does not require the level of accuracy inherent to the MCTDHF method for a large wavefunction expansion with time-dependent coefficients, and the essential physics is well described in terms of simple spin-adapted states, for which the expansion coefficients can be regarded as time-independent. In such cases, the method devised in Sec. III C for general open-shell states offers an attractive alternative. Strictly speaking, the description of several important two-electron processes, such as those governing exciton transfer between molecules,<sup>27</sup> requires a formalism with time-dependent coefficients (although not necessarily a large number of configurations). Within the proposed scheme, this is only accounted for in a mean-field way. The advantage is, of course, that it is designed to treat the dynamics of excited electronic states at a computational cost comparable to that of the TDHF method, thus allowing for the study of large systems of interacting electrons.

## V. SUMMARY AND OUTLOOK

We have developed a multiconfigurational method for the approximate solution of the time-dependent Schrödinger equation for systems of interacting electrons, which effectively establishes a compromise between efficiency and accuracy in the description of excited electronic states. Based on a time-dependent variational principle, we have derived the MCTDHF working equation for a multiconfigurational expansion with fixed coefficients, and specialised to the case of general open-shell states, which are relevant for many physical processes of interest.

The proposed scheme offers an attractive alternative to the MCTDHF method based on a complete active space expansion with time-dependent coefficients, when an accurate description of electron correlation effects is impractical, or not required. With a computational cost comparable to that of the TDHF method, the study of large systems of interacting electrons can be readily performed.

As we shall see in forthcoming articles in this series,<sup>28,29</sup> when combined with a classical description of the ionic degrees of freedom (mean-field approximation), this method provides a powerful tool to study the effects of Coulomb interactions and interchain coupling on the dynamics of photoexcitations in conjugated polymers.

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