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# Spin contamination-free $N$ -electron wave functions in the excitation-based configuration interaction treatment

Diego R. Alcoba,<sup>1</sup> Alicia Torre,<sup>2</sup> Luis Lain,<sup>2,a)</sup> Gustavo E. Massaccesi,<sup>3</sup> Ofelia B. Oña,<sup>4</sup> and Pablo Capuzzi<sup>1</sup>

<sup>1</sup>*Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires and Instituto de Física de Buenos Aires, Consejo Nacional de Investigaciones Científicas y Técnicas, Ciudad Universitaria, 1428 Buenos Aires, Argentina*

<sup>2</sup>*Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apdo. 644 E-48080 Bilbao, Spain*

<sup>3</sup>*Departamento de Ciencias Exactas, Ciclo Básico Común, Universidad de Buenos Aires, Ciudad Universitaria, 1428 Buenos Aires, Argentina*

<sup>4</sup>*Instituto de Investigaciones Físicoquímicas Teóricas y Aplicadas, Universidad Nacional de La Plata, CCT La Plata, Consejo Nacional de Investigaciones Científicas y Técnicas, Diag. 113 y 64 (S/N), Sucursal 4, CC 16, 1900 La Plata, Argentina*

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This work deals with the spin contamination in  $N$ -electron wave functions provided by the excitation-based configuration interaction methods. We propose a procedure to ensure a suitable selection of excited  $N$ -electron Slater determinants with respect to a given reference determinant, required in these schemes. The procedure guarantees the construction of  $N$ -electron wave functions which are eigenfunctions of the spin-squared operator  $\hat{S}^2$ , avoiding any spin contamination. Our treatment is based on the evaluation of the excitation level of the determinants by means of the expectation value of an excitation operator formulated in terms of spin-free replacement operators. We report numerical determinations of energies and  $\langle \hat{S}^2 \rangle$  expectation values, arising from our proposal as well as from traditional configuration interaction methods, in selected open-shell systems, in order to compare the behavior of these procedures and their computational costs. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4955159>]

## I. INTRODUCTION

The determination of electronic energies in  $N$ -electron systems requires to solve the corresponding Schrödinger equation. This task is usually performed representing the  $N$ -electron system Hamiltonian operator in the space constituted by the  $N$ -electron determinants of  $S_z$  spin quantum number that can be constructed with a chosen one-electron basis set. The diagonalization of the resulting  $N$ -electron matrix provides the calculation of the wave functions of the  $N$ -electron system, which are expanded on the  $N$ -electron Slater determinant basis set. These expansions are the exact solutions of the Schrödinger equation for the space in which the Hamiltonian operator has been represented. This procedure is denominated full configuration interaction (FCI) since the formulation of the wave functions involves all the  $N$ -electron determinants arising from the one-electron basis set used. As is well known, the determination of the FCI wave functions demands a high computational cost, due to the large number of determinants involved, and consequently it is necessary to search for approximations. One of the most popular approaches for approximating wave functions consists in truncating the corresponding expansions, limiting the number of  $N$ -electron determinants used to represent the

Hamiltonian; this type of treatment is known as configuration interaction (CI). There are several commonly admitted criteria to select the Slater determinants. One of them is based on the classification of the determinants in terms of their seniority number (the seniority number of a determinant is defined as the number of unpaired electrons in that determinant).<sup>1,2</sup> Alternatively, the more traditional CI procedure performs the selection of the determinants according to their excitation level with respect to a reference determinant.<sup>3–7</sup>

The seniority-number based CI treatment has proven to be a suitable approach to describe systems which present strong correlation.<sup>8–14</sup> Likewise, the extension of the seniority-number concept from Slater determinants to wave functions and  $N$ -electron spin-adapted spaces<sup>15</sup> has allowed us to tackle studies of other type of related properties, such as compactness of wave functions and scaling problems.<sup>16–22</sup> Our algorithms, arising from the commutation rules of the  $N$ -electron spin-squared operator  $\hat{S}^2$  and the  $N$ -electron seniority-number operator, provide spin contamination-free CI wave functions in both closed- and open-shell systems. Contrary to these results, in open-shell systems, the CI wave functions provided by the methods which select Slater determinants according to their excitation level with respect to a reference determinant can present spin contamination. The simple substitution of some spin-orbitals in the reference determinant by other spin-orbitals allows one to group Slater determinants in subsets constituted by determinants of identical excitation

<sup>a)</sup> Author to whom correspondence should be addressed. Electronic address: [qfplapel@ig.ehu.es](mailto:qfplapel@ig.ehu.es)

level. However, it is not always possible to construct spin-adapted configurations (eigenfunctions of the  $\hat{S}^2$  operator) in terms of combinations of Slater determinants belonging to one of these subsets.<sup>23–27</sup> The aim of this work is to propose an  $N$ -electron spin-free excitation operator to evaluate excitation levels in terms of orbitals for Slater determinants with respect to a given reference determinant. This operator commutes with the spin operator  $\hat{S}^2$  and provides a procedure for classifying Slater determinants that guarantees the construction of spin-adapted configurations with determinants of identical selected excitation level. This treatment can be applied to systems with even or odd number of electrons and any spin symmetry, and for open- or closed-shell reference Slater determinants.

We have organized this work as follows. In Sec. II we propose an  $N$ -electron spin-free excitation operator formulated by means of spin-free replacement operators. This operator allows one to calculate the excitation level, with respect to a reference determinant, for an  $N$ -electron determinant as well as for an  $N$ -electron wave function. We also describe in this section the commutation relations of this excitation operator with the  $N$ -electron one  $\hat{S}^2$ , and with the  $N$ -electron system Hamiltonian operator  $\hat{H}$ . We show the ability of our proposal to construct spin-adapted configurations with the Slater determinants possessing a determined excitation level evaluated by our method. Therefore, the diagonalization of the  $N$ -electron Hamiltonian matrix leads to spin contamination-free wave functions. Section III presents results of energies and expectation values  $\langle \hat{S}^2 \rangle$  for open-shell systems, in which the calculation of the excitation levels has been performed by the conventional spin-orbital excitation based CI procedure and by the expectation values of the proposed excitation operator. The computational details and the discussion of results are also included in this section. Finally, in Sec. IV we report the conclusions of this work.

## II. THE EXCITATION LEVEL OF CI WAVE FUNCTIONS

Let  $\{i, j, k, l, \dots\}$  be a set of  $K$  orthonormal spatial orbitals and let  $\hat{E}_j^i$  and  $\hat{E}_{jl}^{ik}$  be the spin-free first- and second-order replacement operators, respectively, which have been formulated as<sup>28–30</sup>

$$\hat{E}_j^i = \sum_{\sigma} a_{i\sigma}^{\dagger} a_{j\sigma}, \quad (1)$$

$$\hat{E}_{jl}^{ik} = \sum_{\sigma_1, \sigma_2} a_{i\sigma_1}^{\dagger} a_{k\sigma_2}^{\dagger} a_{l\sigma_2} a_{j\sigma_1}, \quad (2)$$

where  $a_{i\sigma}^{\dagger}$  is the fermion creation operator which acting on the vacuum state  $|0\rangle$  produces the state  $|i^{\sigma}\rangle$ , with one particle in the orbital  $i$  and spin  $\sigma$  ( $\alpha$  or  $\beta$ ), and  $a_{i\sigma}$  is its corresponding annihilation operator. The expectation values of the  $\hat{E}_j^i$  and  $\hat{E}_{jl}^{ik}$  operators with respect to an  $N$ -electron state generate the spin-free first- and second-order reduced density matrix elements,  ${}^1D_j^i$  and  ${}^2D_{jl}^{ik}$ , respectively, corresponding to that state, so that  ${}^1D_j^i = \langle \hat{E}_j^i \rangle$  and  ${}^2D_{jl}^{ik} = \frac{1}{2} \langle \hat{E}_{jl}^{ik} \rangle$ . In this last expression, the one half-fraction provides the normalization of the trace of the spin-free second-order reduced density matrix

to  $\binom{N}{2}$  electron pairs. The diagonal elements of these reduced density matrices evaluate the occupancies of the orbitals and pairs of orbitals, respectively, in the corresponding  $N$ -electron states.

### A. Evaluation of the excitation level

Using spin-free replacement operators, we formulate an  $N$ -electron excitation number operator  $\hat{X}_{exc}$  with respect to a reference Slater determinant as

$$\hat{X}_{exc} = \hat{N} - \sum_{i=1}^{rocc} \hat{E}_i^i + \frac{1}{2} \sum_{i=1}^{rsocc} \hat{E}_{ii}^{ii}, \quad (3)$$

where  $\hat{N}$  is the particle number operator and in the first sum  $\sum_{i=1}^{rocc}$  the index  $i$  runs over all the reference occupied (rocc) spatial orbitals (singly and doubly), while in the second sum  $\sum_{i=1}^{rsocc}$  that index only runs over the reference singly occupied (rsocc) spatial orbitals. The expectation value of this operator  $\langle \hat{X}_{exc} \rangle$  for an  $N$ -electron Slater determinant is an integer which expresses the excitation level of this determinant with respect to the reference Slater determinant.

In this evaluation of the  $\langle \hat{X}_{exc} \rangle$  expectation value, the term  $\sum_{i=1}^{rocc} \langle \hat{E}_i^i \rangle$  is the summation of the occupation numbers of the spatial orbitals of the reference determinant which are also occupied in the Slater determinant being characterized, and consequently they do not contribute to the number of excitations. The  $\langle \hat{E}_i^i \rangle$  quantity can only get the values 2, 1, 0, according to which the spatial orbital  $i$  in the studied determinant is doubly occupied, singly occupied, or unoccupied, respectively; these values are discounted from the  $N = \langle \hat{N} \rangle$  quantity. The term  $\frac{1}{2} \sum_{i=1}^{rsocc} \langle \hat{E}_{ii}^{ii} \rangle$ , proposed in Eq. (3), is always zero, except for the spatial orbitals singly occupied in the reference determinant which are doubly occupied in the studied determinant; each of these orbitals contributes with one unit to the total amount of excitations, e.g., in the  $N = 3$  case, the determinant  $|12\bar{2}\rangle$  possesses a value  $\langle \hat{X}_{exc} \rangle = 1$  with respect to the determinant  $|12\bar{1}\rangle$  (the bar means a  $\beta$ -spin-orbital and  $\alpha$ -one otherwise) due to the contribution of the term  $\frac{1}{2} \langle \hat{E}_{22}^{22} \rangle = 1$ . Obviously, in the case of closed-shell reference Slater determinants, the term  $\sum_{i=1}^{rsocc} \langle \hat{E}_{ii}^{ii} \rangle$  has no contribution to the  $\langle \hat{X}_{exc} \rangle$  value.

In the case of an open-shell reference Slater determinant, one can find determinants which only differ from that reference determinant in pairs of spin-orbitals with a spin exchange, and consequently their excitation number vanishes,  $X_{exc} = \langle \hat{X}_{exc} \rangle = 0$ , e.g., for  $N = 4$  electrons, the determinant  $|13\bar{1}\bar{2}\rangle$  has a value  $\langle \hat{X}_{exc} \rangle = 0$  with respect to the  $|12\bar{1}\bar{3}\rangle$  reference determinant. This type of determinants of zeroth-order excitation level with respect to a reference one must also be taken into account to project the Hamiltonian in the CI treatments. This formulation of the excitation number operator in terms of spatial orbitals, instead of spin-orbitals arising from the particle-hole approach, can be applied to any system, with  $N$  (even or odd) number of electrons and any  $S_z$  quantum number in the determinants (closed- and open-shell situations), and coincides with other more conventional formulations<sup>10</sup> in the closed-shell case. The determination of expectation values for the operator  $\hat{X}_{exc}$  formulated in Eq. (3)

can be extended to  $N$ -electron wave functions expressed by means of linear combinations of Slater determinants. In such a case, the resulting expectation values are weighted sums of the excitations of the determinants which express the wave functions, and the quantities  $\langle \hat{X}_{exc} \rangle$  are no longer integers unless all the Slater determinants of the corresponding expansion possess an identical excitation level.

## B. Spin-adapted configurations

In order to analyze the spin features of wave functions expanded by Slater determinants, we will use the spin-free version of the  $N$ -electron spin-squared operator, which has also been formulated in terms of spin-free second-order replacement operators as<sup>31</sup>

$$\hat{S}^2 = \frac{1}{2} \sum_{i,j,k,l} \left[ \frac{4-N}{2(N-1)} \delta_{ij} \delta_{kl} - \delta_{il} \delta_{jk} \right] \hat{E}_{jl}^{ik} \quad (4)$$

in which the  $\delta$  symbols indicate the well-known Kronecker deltas. The formulation of Eqs. (3) and (4) by means of second-order replacement operators turns out to be especially suitable to evaluate the commutation relation between the operators  $\hat{X}_{exc}$  and  $\hat{S}^2$ , which requires to take the product of two second-order spin-free replacement operators. The general procedure to calculate products of spin-free replacement operators was reported in Refs. 32 and 33. According to that procedure, the product of two spin-free second-order replacement operators turns out to be

$$\begin{aligned} \hat{E}_{jl}^{ik} \hat{E}_{qs}^{pr} = & \hat{E}_{jlqs}^{ikpr} + \delta_{pj} \hat{E}_{qls}^{ikr} + \delta_{rj} \hat{E}_{slq}^{ikp} + \delta_{pl} \hat{E}_{jq}^{ikr} \\ & + \delta_{rl} \hat{E}_{jsq}^{ikp} + \delta_{pj} \delta_{rl} \hat{E}_{qs}^{ik} + \delta_{pl} \delta_{rj} \hat{E}_{sq}^{ik} \end{aligned} \quad (5)$$

in which third- and fourth-order spin-free replacement operators appear,<sup>29,30</sup> which can be defined similarly to the lower order ones according to Eqs. (1) and (2). Taking into account Eq. (5), one straightforwardly finds

$$[\hat{S}^2, \hat{X}_{exc}] = 0. \quad (6)$$

Likewise, it can be shown that

$$[\hat{S}_z, \hat{X}_{exc}] = 0. \quad (7)$$

These commutation relations show that the spin-adapted configurations (the eigenfunctions of the operators  $\hat{S}^2$  and  $\hat{S}_z$  corresponding to an  $N$ -electron system) may be expressed by means of linear combinations of Slater determinants having the same  $X_{exc}$  value. As is well known, an open-shell Slater determinant is not always an eigenfunction of the  $\hat{S}^2$  operator; however, linear combinations of those determinants possessing a zero excitation level lead to the construction of spin-adapted configurations with  $X_{exc} = 0$ . Likewise, it is possible to construct linear combinations of degenerate eigenfunctions of the  $\hat{S}^2$  and  $\hat{S}_z$  operators with  $S$  and  $S_z$  spin quantum numbers, corresponding to different values of excitation number  $X_{exc}$ . These linear combination functions are also eigenfunctions of both spin operators but they are no longer eigenfunctions of the operator  $\hat{X}_{exc}$ , yielding an expectation value  $\langle \hat{X}_{exc} \rangle$  which may be a non-integer number.

In this work, we describe  $N$ -electron systems by means of nonrelativistic, clamped nuclei, and spin-independent Hamiltonians formulated as<sup>32</sup>

$$\hat{H} = \frac{1}{2} \sum_{i,j,k,l} H_{jl}^{ik} \hat{E}_{jl}^{ik}, \quad (8)$$

where

$$H_{jl}^{ik} = (ik|jl) + \frac{1}{N-1} (\delta_{kl} \epsilon_{ij} + \delta_{ij} \epsilon_{kl}) \quad (9)$$

in which  $(ik|jl)$  are the standard two-electron integrals in the (12|12) notation and  $\epsilon_{ij}$  the one-electron integrals.

The spin-free  $N$ -electron Hamiltonian operator  $\hat{H}$  expressed in Eq. (8) commutes with the  $\hat{S}^2$  and  $\hat{S}_z$  spin operators. However the operators  $\hat{H}$  and  $\hat{X}_{exc}$  do not commute, i.e.,  $[\hat{H}, \hat{X}_{exc}] \neq 0$ . On the other hand, as is well known, the CI methods carry out a representation of the operator  $\hat{H}$  in a set of  $N$ -electron Slater determinants with a given  $S_z$  quantum number, constructed with  $K$  orbitals.<sup>34</sup> Consequently, the diagonalization of the  $N$ -electron Hamiltonian matrix arising from that representation of the operator  $\hat{H}$  yields spin-adapted eigenstates with spin values  $S = |S_z|, (|S_z| + 1), \dots, \frac{N}{2}$  (in the case of  $K \geq N$ ) or  $S = |S_z|, (|S_z| + 1), \dots, (K - \frac{N}{2})$  (in the case of  $K < N$ ). All these eigenstates have an identical  $S_z$  value. If the set of Slater determinants has been chosen according to the excitation level provided by Eq. (3), this procedure leads to eigenstates of the  $N$ -electron matrix which are linear combinations of degenerate eigenfunctions of the  $\hat{S}^2$  and  $\hat{S}_z$  operators corresponding to the selected  $X_{exc}, X'_{exc}, \dots$  values. However, this result is not ensured in the case of CI methods based on the construction of the  $N$ -electron Hamiltonian matrix over the Slater determinants selected according to the other criteria, i.e., sets of Slater determinants arising from the spin-orbital excitations of a reference Slater determinant, where it is possible to find spin-contaminated states.<sup>23,26</sup> This feature appears in open-shell systems, coming from the ambiguity in defining the excitations either in terms of orbitals or in terms of spin-orbitals.

The number of excited  $N$ -electron Slater determinants with respect to a given reference determinant that can be constructed with  $K$  orbitals is constrained by the value of the  $S_z$  spin projection. It is possible to derive simple expressions which calculate the number of determinants corresponding to excitation levels  $X_{exc}$  according to Eq. (3). In the Appendix, we formulate the dimensions,  $\dim(X_{exc})$ , corresponding to the subspaces with lowest excitation values  $X_{exc}$ . These expressions show that the number of determinants of each of the subspaces scales polynomially with the  $K$  parameter. For example, in the simplest cases  $\text{CI}(X_{exc} = 0)$ ,  $\text{CI}(X_{exc} = 0, 1)$ ,  $\text{CI}(X_{exc} = 0, 2)$ , and  $\text{CI}(X_{exc} = 0-2)$ , one finds that the computational cost of diagonalizing the corresponding  $N$ -electron matrices is  $O(1)$ ,  $O(K^3)$ ,  $O(K^6)$ , and  $O(K^6)$ , respectively. This computational cost is identical to that found for the traditional spin-orbital excitation-based CI methods. However, the proposed procedure has the advantage of assuring that the eigenvectors of the counterpart  $\text{CI}(X_{exc})$   $N$ -electron matrices are eigenfunctions of the  $\hat{S}^2$  operator. This behavior has been numerically tested in Sec. III.

### III. COMPUTATIONAL DETAILS, RESULTS, AND DISCUSSION

We have determined energies and expectation values  $\langle \hat{S}^2 \rangle$  arising from CI wave functions expanded on  $N$ -electron Slater determinants whose excitation levels with respect to restricted open-shell Hartree-Fock (ROHF) Slater determinants have been cataloged according to their corresponding  $\langle \hat{X}_{exc} \rangle$  values in Eq. (3). These results have been compared with those provided by the traditional spin-orbital excitation-based determinant-selection procedure, at the corresponding excitation levels with respect to the identical reference determinants. We have chosen some open-shell diatomic molecules and radicals constituted by second-row elements from 11 up to 16 electrons, as prototype systems of several spin symmetries. The STO-3G atomic basis sets have been utilized in order to be able to implement the calculations at an affordable computational cost. In all cases, we describe the lowest energy states of each spin symmetry at experimental equilibrium bond lengths,<sup>35</sup> using the molecular orbital bases. The one- and two-electron integrals, which define the  $N$ -electron Hamiltonians according to Eq. (8), and the ROHF energies have been evaluated by a modified version of the PSI 3.3 package.<sup>36</sup> We have elaborated our own codes for determining spatial-orbital-excitation based CI, spin-orbital-excitation based CI, and FCI energies, as well as expectation values  $\langle \hat{S}^2 \rangle$ .

Table I reports energy and  $\langle \hat{S}^2 \rangle$  expectation values corresponding to the 11, 12, and 13 electron diatomic species BC, C<sub>2</sub>, and CN in the lowest quartet, triplet, and doublet spin states, respectively. The excitation level in both treatments is indicated by means of the parameter value  $X_{exc}$  and by

the traditional nomenclature (i.e., configuration interaction at single excitations (CIS), at double ones (CID), and at single and double ones (CISD)), respectively. The number of Slater determinants involved in each case has also been included in this table, in order to show the computational cost required for each system. Likewise, in Table II we have gathered results from the diatomic molecules CO, NO, and O<sub>2</sub>, which correspond to systems with 14, 15, and 16 electrons, in their lowest triplet, doublet, and triplet energy states, respectively. As can be observed in both tables, the zeroth-order excitation determinants ( $X_{exc} = 0$ ) are the simple ROHF ones for these spin symmetries; these determinants are eigenfunctions of the  $\hat{S}^2$  and  $\hat{S}_z$  operators (we are referring to the highest quantum number  $S_z$  substate  $S_z = S$ ). However, adding to that CI wave functions the determinant sets corresponding, respectively, to spatial-orbital excitations and spin-orbital excitations at single level  $X_{exc} = 1$  and CIS, at double level  $X_{exc} = 2$  and CID, at single and double levels  $X_{exc} = 1, 2$  and CISD, or at higher levels yields, in all cases, different  $\langle \hat{S}^2 \rangle$  results according to the nature of the procedure are used to count the excitations. As expected, in the case of spatial excitations, the resulting CI wave functions are again spin-adapted configurations, while this feature is no longer maintained in the spin-orbital excitation based procedure which leads to spin contaminated wave functions. In fact, a Slater determinant such as  $|\cdots 13\bar{2} \cdots\rangle$  is doubly excited with respect to the reference determinant  $|\cdots 1\bar{2}\bar{1} \cdots\rangle$  within the spin-orbital excitation approach. However, according to Eq. (3) that determinant turns out to be singly excited in the spatial excitation based procedure and consequently the determinant  $|\cdots 13\bar{2} \cdots\rangle$  is necessary to construct a spin-adapted space with the determinants having  $X_{exc} = 1$

TABLE I. CI energies (in  $E_h$ ),  $\langle \hat{S}^2 \rangle$  values, No. of determinants, and excitation levels for quartet, triplet, and doublet systems with 11, 12, and 13 electrons, respectively. Results correspond to standard STO-3G basis sets.

| System         | $E_{\text{ROHF}}$ | $E_{\text{FCI}}$ | Spatial excitations |                     |             |                             | Spin-orbital excitations |                     |             |                             |
|----------------|-------------------|------------------|---------------------|---------------------|-------------|-----------------------------|--------------------------|---------------------|-------------|-----------------------------|
|                |                   |                  | $X_{exc}$           | No. of determinants | Energy      | $\langle \hat{S}^2 \rangle$ | $exc$ level              | No. of determinants | Energy      | $\langle \hat{S}^2 \rangle$ |
| BC             | -61.477 359       | -61.582 949      | 0                   | 1                   | -61.477 359 | 3.750 00                    |                          | 1                   | -61.477 359 | 3.750 00                    |
|                |                   |                  | 0,1                 | 82                  | -61.484 641 | 3.750 00                    | CIS                      | 46                  | -61.478 162 | 3.751 86                    |
|                |                   |                  | 0,2                 | 1 162               | -61.546 556 | 3.750 00                    | CID                      | 658                 | -61.550 156 | 3.751 49                    |
|                |                   |                  | 0-2                 | 1 243               | -61.571 284 | 3.750 00                    | CISD                     | 703                 | -61.570 268 | 3.751 16                    |
|                |                   |                  | 0-3                 | 6 564               | -61.578 780 | 3.750 00                    | CISDT                    | 4 220               | -61.577 108 | 3.750 96                    |
|                |                   |                  | 0-5                 | 23 064              | -61.582 949 | 3.750 00                    | CISDTQQ                  | 20 930              | -61.582 949 | 3.750 00                    |
| C <sub>2</sub> | -74.489 374       | -74.640 478      | 0                   | 1                   | -74.489 374 | 2.000 00                    |                          | 1                   | -74.489 374 | 2.000 00                    |
|                |                   |                  | 0,1                 | 77                  | -74.501 563 | 2.000 00                    | CIS                      | 47                  | -74.492 946 | 2.006 67                    |
|                |                   |                  | 0,2                 | 1 109               | -74.620 129 | 2.000 00                    | CID                      | 689                 | -74.623 323 | 2.001 98                    |
|                |                   |                  | 0-2                 | 1 185               | -74.626 318 | 2.000 00                    | CISD                     | 735                 | -74.625 765 | 2.001 10                    |
|                |                   |                  | 0-3                 | 6 605               | -74.631 921 | 2.000 00                    | CISDT                    | 4 545               | -74.629 654 | 2.001 18                    |
|                |                   |                  | 0-6                 | 29 830              | -74.640 478 | 2.000 00                    | CISDTQQ                  | 29 267              | -74.640 478 | 2.000 00                    |
| CN             | -90.997 412       | -91.173 247      | 0                   | 1                   | -90.997 412 | 0.750 00                    |                          | 1                   | -90.997 412 | 0.750 00                    |
|                |                   |                  | 0,1                 | 64                  | -91.009 344 | 0.750 00                    | CIS                      | 46                  | -91.002 723 | 0.786 84                    |
|                |                   |                  | 0,2                 | 883                 | -91.142 724 | 0.750 00                    | CID                      | 658                 | -91.148 368 | 0.763 27                    |
|                |                   |                  | 0-2                 | 946                 | -91.155 128 | 0.750 00                    | CISD                     | 703                 | -91.154 996 | 0.750 10                    |
|                |                   |                  | 0-3                 | 5 300               | -91.159 735 | 0.750 00                    | CISDT                    | 4 220               | -91.158 027 | 0.751 62                    |
|                |                   |                  | 0-6                 | 24 900              | -91.173 242 | 0.750 00                    | CISDTQQS                 | 24 675              | -91.173 239 | 0.750 00                    |

TABLE II. CI energies (in  $E_h$ ),  $\langle \hat{S}^2 \rangle$  values, No. of determinants, and excitation levels for triplet, doublet, and triplet systems with 14, 15, and 16 electrons, respectively. Results correspond to standard STO-3G basis sets.

| System         | $E_{\text{ROHF}}$ | $E_{\text{FCI}}$ | $X_{\text{exc}}$ | Spatial excitations |             |                             | Spin-orbital excitations |                     |             |                             |
|----------------|-------------------|------------------|------------------|---------------------|-------------|-----------------------------|--------------------------|---------------------|-------------|-----------------------------|
|                |                   |                  |                  | No. of determinants | Energy      | $\langle \hat{S}^2 \rangle$ | $\text{exc level}$       | No. of determinants | Energy      | $\langle \hat{S}^2 \rangle$ |
| CO             | -111.016441       | -111.127053      | 0                | 1                   | -111.016441 | 2.00000                     |                          | 1                   | -111.016441 | 2.00000                     |
|                |                   |                  | 0,1              | 65                  | -111.024002 | 2.00000                     | CIS                      | 41                  | -111.019531 | 2.02333                     |
|                |                   |                  | 0,2              | 758                 | -111.109730 | 2.00000                     | CID                      | 503                 | -111.114716 | 2.01742                     |
|                |                   |                  | 0-2              | 822                 | -111.120907 | 2.00000                     | CISD                     | 543                 | -111.120728 | 2.00007                     |
|                |                   |                  | 0-3              | 3630                | -111.124104 | 2.00000                     | CISDT                    | 2735                | -111.123758 | 2.00015                     |
|                |                   |                  | 0-5              | 9225                | -111.127053 | 2.00000                     | CISDTQQ                  | 9030                | -111.127050 | 2.00000                     |
| NO             | -127.526064       | -127.659338      | 0                | 1                   | -127.526064 | 0.75000                     |                          | 1                   | -127.526064 | 0.75000                     |
|                |                   |                  | 0,1              | 52                  | -127.527768 | 0.75000                     | CIS                      | 38                  | -127.526708 | 0.75194                     |
|                |                   |                  | 0,2              | 547                 | -127.645811 | 0.75000                     | CID                      | 428                 | -127.646934 | 0.75159                     |
|                |                   |                  | 0-2              | 598                 | -127.650611 | 0.75000                     | CISD                     | 465                 | -127.650520 | 0.75005                     |
|                |                   |                  | 0-3              | 2460                | -127.654061 | 0.75000                     | CISDT                    | 2046                | -127.653980 | 0.75004                     |
|                |                   |                  | 0-4              | 4665                | -127.659113 | 0.75000                     | CIDSTQ                   | 4420                | -127.659084 | 0.75000                     |
| O <sub>2</sub> | -147.632161       | -147.744030      | 0                | 1                   | -147.632161 | 2.00000                     |                          | 1                   | -147.632161 | 2.00000                     |
|                |                   |                  | 0,1              | 45                  | -147.635123 | 2.00000                     | CIS                      | 31                  | -147.633825 | 2.00298                     |
|                |                   |                  | 0,2              | 323                 | -147.736236 | 2.00000                     | CID                      | 253                 | -147.737632 | 2.00269                     |
|                |                   |                  | 0-2              | 367                 | -147.739518 | 2.00000                     | CISD                     | 283                 | -147.739349 | 2.00009                     |
|                |                   |                  | 0-3              | 955                 | -147.740315 | 2.00000                     | CISDT                    | 885                 | -147.740297 | 2.00001                     |
|                |                   |                  | 0-4              | 1200                | -147.744030 | 2.00000                     | CISDTQ                   | 1200                | -147.744030 | 2.00000                     |

excitations. We have included in these tables excitations up to the level required so that the spin-orbital based selection procedure starts to yield spin contamination-free wave functions, e.g.,  $X_{\text{exc}} = 0-5$  (CISDTQQ) in the BC molecule and  $X_{\text{exc}} = 0-6$  (CISDTQQS) in the C<sub>2</sub> one. As shown in both tables, the number of Slater determinants involved in the construction of each CI wave function at the reported excitation levels turns out to be higher in the spatial excitation case. This is because a given spatial excitation level may include determinants belonging to upper levels in terms of spin-orbital excitations. However, as mentioned in Section III, both methods scale with identical power of the parameter  $K$ , the number of orbital functions constituting the basis set, and consequently both of them have the same order of computational cost. We must also point out that the energies arising from the spatial excitation based CI procedure are closer to the FCI values than those obtained from the spin-orbital excitation based CI method, except for the  $X_{\text{exc}} = 0,2$  and CID levels. In this case, some CID level determinants belong to the  $X_{\text{exc}} = 1$  one and they are not included in the  $X_{\text{exc}} = 0,2$  determinant set; similarly, some  $X_{\text{exc}} = 2$  level Slater determinants correspond to higher levels than the CID ones in the spin-orbital treatment. Hence, the variational principle cannot be applied in this case.

#### IV. CONCLUDING REMARKS

In this work, we have proposed a spin-free  $N$ -electron excitation operator  $\hat{X}_{\text{exc}}$  which allows to classify the  $N$ -electron determinants that can be constructed with a given

one-electron basis set, in terms of their excitation level with respect to a reference determinant. The operator  $\hat{X}_{\text{exc}}$  commutes with the  $N$ -electron spin operators  $\hat{S}^2$  and  $\hat{S}_z$ , and consequently each of its expectation values with respect to those Slater determinants defines a subset of  $N$ -electron determinants which can be used to formulate spin-adapted configurations. This feature guarantees the construction of spin contamination-free CI wave functions expanded on  $N$ -electron determinants selected by this criterion. Our procedure can be applied to any open- or closed-shell system, with even or odd number of electrons. Our proposal provides, in most cases, energies closer to the FCI values than those arising from conventional CI methods based on spin-orbital excitation criteria, at similar computational cost. We are currently working on hybrid methods which combine the seniority- and excitation-based treatments.<sup>19</sup> These methods also lead to spin-adapted CI wave functions if the excitation-based component is constructed according to Eq. (3), following the spatial-orbital-based selection criterion. Likewise, the efficiency and the computational cost are being compared to the multi-reference methods in which the excited configurations are generated as spin eigenfunctions.

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## APPENDIX: NUMBER OF EXCITED SLATER DETERMINANTS WITHIN THE SPATIAL-ORBITAL APPROACH

The evaluation of the number of Slater determinants of  $S_z$  spin quantum number and excitation level  $X_{exc}$  according to formula (3) with respect to a reference determinant is a straightforward calculation. Here, we report the simplest cases corresponding to the excitation values  $X_{exc} = 0$ ,  $X_{exc} = 1$ , and  $X_{exc} = 2$ ,

$$\dim(X_{exc} = 0) = \binom{A}{\frac{A}{2} + S_z} \quad (A1)$$

$$\dim(X_{exc} = 1) = OV \binom{A+2}{\frac{A+2}{2} + S_z} + A(O+V) \binom{A}{\frac{A}{2} + S_z} + \frac{A(A-1)}{2} \binom{A-2}{\frac{A-2}{2} + S_z} \quad (A2)$$

$$\begin{aligned} \dim(X_{exc} = 2) = & \left[ \frac{O(O-1)V(V-1)}{2} \right] \binom{A+4}{\frac{A+4}{2} + S_z} + \left[ \frac{O(O-1)V}{2} + O \frac{V(V-1)}{2} \right. \\ & + \left. \frac{O(O-1)AV + OA \frac{V(V-1)}{2}}{2} \right] \binom{A+2}{\frac{A+2}{2} + S_z} + \left[ \frac{O(O-1)A(A-1)}{2} \right. \\ & + \left. \frac{A(A-1)V(V-1)}{2} + OV + 2OAV + OA(A-1)V \right] \binom{A}{\frac{A}{2} + S_z} \\ & + \left[ O \frac{A(A-1)}{2} + \frac{A(A-1)V}{2} + O \frac{A(A-1)(A-2)}{2} \right. \\ & + \left. \frac{A(A-1)(A-2)V}{2} \right] \binom{A-2}{\frac{A-2}{2} + S_z} + \left[ \frac{A(A-1)(A-2)(A-3)}{4} \right] \binom{A-4}{\frac{A-4}{2} + S_z}, \quad (A3) \end{aligned}$$

where  $A = N - 2O$  is the number of singly occupied orbitals in the reference determinant,  $O$  stands for the number of repeated orbitals in the reference determinant (counted once),  $V = K - (N - O)$  means the number of unoccupied orbitals in the reference determinant, and  $K$  is the number of orbitals of the basis set used.

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