

## Configuration interaction wave functions: A seniority number approach

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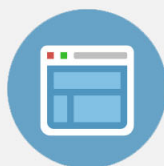
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## Configuration interaction wave functions: A seniority number approach

Diego R. Alcoba,<sup>1</sup> Alicia Torre,<sup>2</sup> Luis Lain,<sup>2,a)</sup> Gustavo E. Massaccesi,<sup>3</sup> and Ofelia B. Oña<sup>4</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 Fisicoquímicas 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 configuration interaction method when an  $N$ -electron Hamiltonian is projected on Slater determinants which are classified according to their seniority number values. We study the spin features of the wave functions and the size of the matrices required to formulate states of any spin symmetry within this treatment. Correlation energies associated with the wave functions arising from the seniority-based configuration interaction procedure are determined for three types of molecular orbital basis: canonical molecular orbitals, natural orbitals, and the orbitals resulting from minimizing the expectation value of the  $N$ -electron seniority number operator. The performance of these bases is analyzed by means of numerical results obtained from selected  $N$ -electron systems of several spin symmetries. The comparison of the results highlights the efficiency of the molecular orbital basis which minimizes the mean value of the seniority number for a state, yielding energy values closer to those provided by the full configuration interaction procedure. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4882881>]

### I. INTRODUCTION

The solutions of the Schrödinger equation corresponding to an  $N$ -electron system for a given basis set are those provided by the full configuration interaction (FCI) method. However, as is well known its practical application requires a high computational cost, especially when dealing with medium and large size systems and extended basis sets. Consequently, this treatment is usually approximated by means of configuration interaction (CI) procedures in which the  $N$ -electron Hamiltonian is projected on a limited number of Slater determinants, that involves truncations in the FCI wave function expansions.<sup>1–7</sup> Traditionally, these Slater determinants are selected according to the particle-hole excitation level from a determined reference; however in some situations that selection criterion yields spin contaminated wave functions.<sup>8,9</sup> Alternatively, the concept of seniority number of a determinant<sup>10,11</sup> is another feature which allows one to classify the Slater determinants involved in the Hamiltonian projection (the seniority number has been defined as the number of singly occupied functions or number of unpaired electrons in a determinant). Results arising from both excitation- and seniority-number-based CI expansions have been reported in Ref. 12 as well as a discussion on the conditions of applicability of each procedure. Likewise, the closed-shell wave functions in the double-occupied configuration interaction method

have been related to the seniority CI expansions.<sup>13,14</sup> One of the purposes of the present work is to enlarge the insights into the seniority-labeled CI method. We show that the wave functions arising from that procedure are eigenstates of the  $\hat{S}^2$  operator and hence it provides spin contamination-free wave functions. Furthermore, we describe the size of the matrices required to implement this procedure in any system (closed- or open-shell one) and for any spin symmetry.

In a recent work, the concept of seniority number of a determinant has been extended to  $N$ -electron wave functions and to  $N$ -electron spin-adapted spaces.<sup>15</sup> In this reference we have shown that the expectation value of the seniority number operator for an  $N$ -electron spin-adapted space is an invariant with respect to any unitary transformation of the basis set, while its expectation value for a determined wave function which describes a state is an orbital basis dependent magnitude. This dependence has allowed us to propose transformations of the orbital basis set in order to achieve a minimum value for the seniority number of the FCI  $N$ -electron wave function. The compactness of the FCI wave functions has been studied by means of an analysis of their expansions in the basis sets of the canonical molecular orbitals (CMO), in the natural orbitals (NO),<sup>16,17</sup> and in the molecular orbital sets in which the seniority number possesses a minimum value ( $M_{\min}$ ).<sup>15</sup> Since the energies and the convergence of the CI expansions depend upon the orbitals from which the configurations are formed, another purpose of the present work is to study the performance of these three types of molecular orbital basis in the seniority-number-based CI expansions, in order to

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

identify the basis which leads to the energy values closer to the FCI results.

The organization of this work is as follows. In Sec. II we describe the seniority number operator and the  $N$ -electron spin-squared operator in terms of spin-free replacement operators. This formulation allows one to study suitably the spin features of the seniority-number-based CI wave functions. We also show in that section the size of the matrices required to construct the seniority-number-based CI expansions for closed- and open-shell systems, in states of any spin  $S$ . Section III reports results of correlation energies in atomic systems and in linear molecular species at several internuclear distances. CI expansions composed of Slater determinants at a specified seniority number level are studied in the above mentioned molecular orbital bases, in order to investigate their convergence to the FCI values. Finally, Sec. IV discusses the main conclusions of this work.

## II. THEORETICAL ASPECTS

### A. Spin-adapted CI wave functions

Let  $\{i, j, k, l, \dots\}$  be a set of  $K$  orthonormal orbitals and let  $\hat{E}_j^i$  and  $\hat{E}_{jl}^{ik}$  be the first- and second-order spin-free replacement operators, respectively, which have been formulated as<sup>18</sup>

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

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

in which  $a_{i\sigma}^{\dagger}/a_{i\sigma}$  is the fermionic creation/annihilation operator corresponding to a spin-orbital  $i^{\sigma}$  ( $\sigma$  means the spin coordinate,  $\alpha$  or  $\beta$ ).

The  $N$ -electron seniority number operator  $\hat{\Omega}$  can be expressed by means of these spin-free replacement operators as<sup>15</sup>

$$\hat{\Omega} = \sum_{i=1}^K (\hat{E}_i^i - \hat{E}_{ii}^{ii}). \quad (3)$$

The expectation value of this operator  $\langle \hat{\Omega} \rangle$ , respect to an  $N$ -electron Slater determinant, expresses the difference between  $N$  (number of electrons), which is the expectation value of the  $\sum_i \hat{E}_i^i$  operator, and the number of electrons corresponding to doubly occupied orbitals in that determinant, which is the expectation value of the  $\sum_i \hat{E}_{ii}^{ii}$  operator. Consequently, the  $\Omega = \langle \hat{\Omega} \rangle$  quantity for a determinant is an integer which accounts for the number of singly occupied orbitals or number of unpaired electrons.<sup>19,20</sup>

The spin-free version of the  $N$ -electron spin-squared operator has also been formulated in terms of second-order replacement operators as<sup>21</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 relationship between the operators  $\hat{\Omega}$  and  $\hat{S}^2$ , which requires to take the product of two second-order spin-free replacement operators. The general procedure to calculate this type of products has been reported in Refs. 22 and 23 and according to that procedure, the product of two second-order replacement operators turns out to be

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

Consequently, one straightforwardly finds

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

Likewise, it can be shown that

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

These relationships show that the eigenfunctions of the operators  $\hat{S}^2$  and  $\hat{S}_z$  (the spin-adapted configurations) corresponding to an  $N$ -electron system may be expressed by means of linear combinations of Slater determinants having the same  $\Omega$  value. These eigenfunctions constitute an antisymmetric and spin-adapted finite-dimensional Hilbert space of  $N$  electrons constructed with  $K$  orbitals; that space will be denoted as  $H^A(N, K, S, S_z, \Omega)$ , where the superscript  $A$  stands for antisymmetric and obviously  $\Omega \geq 2S$ .

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 several values of seniority number  $\Omega$  (distinct). These linear combination functions are also eigenfunctions of both spin operators but they are no longer eigenfunctions of the operator  $\hat{\Omega}$ , yielding an expectation value  $\langle \hat{\Omega} \rangle$ , which may be a non-integer number. They constitute the model space that will be denoted as  $H^A(N, K, S, S_z, \Omega, \Omega', \dots)$ ; obviously when all possible  $\Omega$  values are taken into account ( $\Omega = 2S, 2(S+1), \dots, N$ ) that space coincides with the spin-adapted full CI space  $H^A(N, K, S, S_z)$ . Let us now consider the model space  $H^A(N, K, S_z, \Omega, \Omega', \dots)$  constituted by the Slater determinants of  $S_z$  eigenvalue and  $\Omega, \Omega', \dots$  values. As is well known, the spin-free  $N$ -electron Hamiltonian operator  $\hat{H}$  commutes with the  $\hat{S}^2$  and  $\hat{S}_z$  spin operators, however the operators  $\hat{H}$  and  $\hat{\Omega}$  do not commute,<sup>12</sup> i.e.,  $[\hat{H}, \hat{\Omega}] \neq 0$ . Consequently, the diagonalization of the  $N$ -electron Hamiltonian matrix arising from a representation of the operator  $\hat{H}$  in the Hilbert space  $H^A(N, K, S_z, \Omega, \Omega', \dots)$  yields spin-adapted eigenstates with spin values  $S = S_z, (S_z + 1), \dots, \frac{N}{2}$  and identical  $S_z$  value; they are spin-adapted CI wave functions whose seniority numbers must be expressed by expectation values  $\langle \hat{\Omega} \rangle$ . These features ensure that the wave functions derived from the CI method based on the seniority number, which are linear combinations of all Slater determinants with selected  $\Omega$  values, are pure spin states. However, this result is not ensured in the case of the traditional CI method based on the construction of the  $N$ -electron Hamiltonian matrix over the Slater determinants arising from the excitations of a reference Slater determinant, where it is possible to find spin-contaminated states.<sup>8,9</sup> This feature ap-

pears mainly in open-shell systems, coming from the ambiguity in defining the excitations either in terms of orbitals or in terms of spin-orbitals.

## B. Dimension of the seniority-number-adapted spaces

The parameter  $\Omega$  for a Slater determinant is an integer number meaning the number of single occupied orbitals in the determinant. Consequently, that parameter may be formulated as  $\Omega = N - 2r$ , where  $r$  stands for the number of repeated indices (doubly occupied orbitals) in that determinant. For a quantum number  $S_z \geq 0$ , the number of  $\alpha$  and  $\beta$  orbitals occupied in a determinant is  $\frac{N}{2} + S_z$  and  $\frac{N}{2} - S_z$ , respectively. The number of ways of picking  $(\frac{N}{2} + S_z)$   $\alpha$ -spin orbitals from  $K$  basis orbitals is  $\binom{K}{\frac{N}{2} + S_z}$ . This partial result must be multiplied by the factor  $\binom{\frac{N}{2} + S_z}{r}$ , the number of possibilities for selecting  $r$  doubly occupied orbitals. Consequently, the number of possibilities to select the unpaired  $\beta$  orbitals is  $\binom{K - (\frac{N}{2} + S_z)}{\frac{N}{2} - S_z - r}$ . The product of these three binomial coefficients yields the dimension of the space  $H^A(N, K, S_z, \Omega)$ , that is the number of Slater determinants of  $N$  electrons having a  $S_z$  eigenvalue and a seniority number  $\Omega$  that can be constructed with  $K$  orbitals, so that

$$\begin{aligned} \dim H^A(N, K, S_z, \Omega)_{\Omega=N-2r} \\ = \binom{K}{\frac{N}{2} + S_z} \binom{\frac{N}{2} + S_z}{r} \binom{K - (\frac{N}{2} + S_z)}{\frac{N}{2} - S_z - r}. \end{aligned} \quad (8)$$

This result constitutes a generalization of that reported in Ref. 12, where only the particular case  $S_z = 0$  was considered. Formula (8) can be applied to any  $S_z$  value providing the description of both closed- and open-shell systems.

The sum of the right-hand side terms in Eq. (8) for all possible values of the index  $r$  ( $r = 0, \dots, (\frac{N}{2} - S_z)$ ) and the use of the Vandermonde relationship lead to

$$\begin{aligned} \binom{K}{\frac{N}{2} + S_z} \sum_{r=0}^{\frac{N}{2} - S_z} \binom{\frac{N}{2} + S_z}{r} \binom{K - (\frac{N}{2} + S_z)}{\frac{N}{2} - S_z - r} \\ = \binom{K}{\frac{N}{2} + S_z} \binom{K}{\frac{N}{2} - S_z} \end{aligned} \quad (9)$$

which is the dimension of the space  $H^A(N, K, S_z)$  that is the sum of the dimensions of the spaces  $H^A(N, K, S_z, \Omega) \forall \Omega$ .

The difference between the dimensions of the spaces  $H^A[N, K, (S_z = S), \Omega]$  and  $H^A[N, K, (S_z = S + 1), \Omega]$  is the dimension of the spin-adapted space  $H^A(N, K, S, S_z, \Omega)$ , that is<sup>24</sup>

$$\begin{aligned} \dim H^A(N, K, S, S_z, \Omega)_{\Omega=N-2r} \\ = \binom{K}{\frac{N}{2} + S} \binom{\frac{N}{2} + S}{r} \binom{K - (\frac{N}{2} + S)}{\frac{N}{2} - S - r} \\ - \binom{K}{\frac{N}{2} + (S + 1)} \binom{\frac{N}{2} + (S + 1)}{r} \binom{K - (\frac{N}{2} + (S + 1))}{\frac{N}{2} - (S + 1) - r} \end{aligned} \quad (10)$$

which is identical  $\forall S_z$  quantum number corresponding to a spin  $S$ . Likewise, the sum of the right-hand side terms in Eq. (10) for all possible values of the  $\Omega$  parameter (all possible values of the index  $r$ ) reproduces the Weyl-Paldus formula,<sup>25,26</sup> which is the dimension of the space  $H^A(N, K, S)$ ,  $\forall S_z$

$$\dim H^A(N, K, S) = \frac{2S + 1}{K + 1} \binom{K + 1}{\frac{1}{2}N - S} \binom{K + 1}{\frac{1}{2}N + S + 1}. \quad (11)$$

The consistency of the dimensions of the  $\Omega$ -adapted subspaces confirms that the partitioning of  $S$ - and  $S_z$ -adapted spaces according to the values of the seniority number parameter  $\Omega$  guarantees the use of pure spin states.

## III. ENERGY DETERMINATION BY MEANS OF SENIORITY-NUMBER-BASED CI EXPANSIONS

We have calculated electronic energies of atomic and molecular systems in several spin symmetries using CI expansions expressed by means of Slater determinants which have been selected according to the values of the parameter  $\Omega$ . As mentioned in the Introduction, our purpose is to shed some light on which is the most suitable basis set to recover the largest amount of correlation energy (in absolute value) for a given sequence of values  $\Omega$  in those determinants. Three types of molecular orbital bases have been utilized in this study: (i) the canonical Hartree-Fock molecular orbitals (CMO), (ii) the natural orbitals (NO) in which the FCI spin-free first-order reduced density matrix is diagonal (generally considered as the one yielding the fastest CI convergence but whose behavior has been questioned,<sup>5,17</sup> and (iii) the orbitals ( $M_{\min}$ ) which minimize the expectation value  $\langle \Psi_{\text{FCI}} | \hat{\Omega} | \Psi_{\text{FCI}} \rangle$  for a given FCI wave function  $\Psi(N, S)$ .<sup>15</sup> The Hartree-Fock reference energies, the Hartree-Fock molecular orbital basis sets, and the one- and two-electron integrals have been obtained from a modified version of the PSI 3.3 package.<sup>27</sup> We have used our own codes to calculate the spin-free second-order reduced density matrix elements required to determine the orbitals of the basis set  $M_{\min}$ . These orbitals have been determined following a modified version of the iterative procedure described in Ref. 28 which uses the CMOs as initial basis. In subsequent steps we have also used our own codes to calculate the wave functions of the lowest energy states of each spin symmetry series at several CI levels and at FCI level for these systems; besides we constructed efficient codes to perform the corresponding basis set transformations. In the case of the atomic systems we have used the Huzinaga and Dunning double  $\zeta$  quality s-type GTO basis sets<sup>29,30</sup> while the energies of the molecular systems have been calculated in the STO-3G basis sets at several internuclear distances (close to the equilibrium distances and stretched ones). These computational conditions have allowed us to carry out our numerical determinations at an affordable computational cost.

Table I reports correlation energies for isoelectronic atomic series in singlet, doublet, triplet, and quartet spin symmetries arising from CI expansions constructed with several sequences of values of the parameter  $\Omega$ . These sequences start

TABLE I. Values of correlation energies (in millihartrees) for isoelectronic atomic systems in singlet, doublet, triplet, and quartet spin symmetries, described at CI (seniority  $\Omega$ ) and FCI levels, in the basis sets: molecular (CMO), natural (NO), and that minimizing the seniority number ( $M_{\min}$ ). Results correspond to Huzinaga and Dunning double  $\zeta$  quality s-type GTO basis sets.  $E_{\text{ref}}$  = energy(RHF/ROHF) (in  $E_h$ ).

| System           | Spin          | $E_{\text{ref}}$ | $\Omega = 0$ |         |            | $\Omega = 0, 2$ |         |            | $\Omega = 0, 2, 4$ |
|------------------|---------------|------------------|--------------|---------|------------|-----------------|---------|------------|--------------------|
|                  |               |                  | CMO          | NO      | $M_{\min}$ | CMO             | NO      | $M_{\min}$ | FCI                |
| B <sup>+</sup>   | 0             | -24.234344       | -12.114      | -10.240 | -12.403    | -14.740         | -14.269 | -14.769    | -14.964            |
| C <sup>++</sup>  | 0             | -36.403824       | -11.190      | -8.128  | -11.685    | -13.717         | -12.635 | -13.770    | -13.933            |
| N <sup>+++</sup> | 0             | -51.074229       | -10.649      | -6.795  | -11.506    | -13.169         | -11.359 | -13.241    | -13.374            |
|                  |               |                  | $\Omega = 1$ |         |            | $\Omega = 1, 3$ |         |            | $\Omega = 1, 3, 5$ |
|                  |               |                  | CMO          | NO      | $M_{\min}$ | CMO             | NO      | $M_{\min}$ | FCI                |
| B                | $\frac{1}{2}$ | -24.101537       | -11.446      | -12.564 | -12.755    | -12.769         | -12.769 | -12.769    | -12.769            |
| C <sup>+</sup>   | $\frac{1}{2}$ | -36.544050       | -10.952      | -12.352 | -12.466    | -12.503         | -12.503 | -12.503    | -12.503            |
| N <sup>++</sup>  | $\frac{1}{2}$ | -51.602375       | -10.679      | -12.246 | -12.251    | -12.365         | -12.365 | -12.365    | -12.365            |
|                  |               |                  |              |         |            | $\Omega = 2$    |         |            | $\Omega = 2, 4$    |
|                  |               |                  | CMO          | NO      | $M_{\min}$ | CMO             | NO      | $M_{\min}$ | FCI                |
| B <sup>+</sup>   | 1             | -23.592326       |              |         |            | -12.691         | -12.550 | -12.993    | -12.993            |
| C <sup>++</sup>  | 1             | -35.291522       |              |         |            | -12.454         | -12.318 | -12.787    | -12.993            |
| N <sup>+++</sup> | 1             | -49.350131       |              |         |            | -12.326         | -12.197 | -12.680    | -12.680            |
|                  |               |                  |              |         |            | $\Omega = 3$    |         |            | $\Omega = 3, 5$    |
|                  |               |                  | CMO          | NO      | $M_{\min}$ | CMO             | NO      | $M_{\min}$ | FCI                |
| B                | $\frac{3}{2}$ | -8.662608        |              |         |            | -1.419          | -1.419  | -1.419     | -1.419             |
| C <sup>+</sup>   | $\frac{3}{2}$ | -13.403273       |              |         |            | 0.000           | 0.000   | 0.000      | 0.000              |
| N <sup>++</sup>  | $\frac{3}{2}$ | -19.609185       |              |         |            | 0.000           | 0.000   | 0.000      | 0.000              |

with the lowest value  $\Omega = 2S$ , growing up to the highest one  $\Omega = N$  (the complete sequences become the FCI method). These numerical determinations have been performed in the three mentioned types of molecular orbitals, in order to analyze the performance of each of them and their closeness to the FCI values. Obviously the three molecular orbital sets lead to identical results in the FCI case. As can be observed in that table, the basis sets  $M_{\min}$  yield better results than the NO and CMO ones in all the cases studied. In the case of  $N = 4$  electrons for singlets and triplets the basis sets CMO also presents better results than those provided by the NO orbitals. We may

justify these results in terms of the high dominances found in the CI expansions of the Slater determinants possessing two doubly occupied orbitals ( $\Omega = 0$ ) for singlets and one doubly occupied orbital ( $\Omega = 2$ ) for triplets in the CMO basis sets. These features are not longer exhibited in the open-shell systems with  $N = 5$  electrons and  $\Omega = 1$  (doublets) in which the convergence in the NO basis sets is superior to the CMO ones. Tables II, III, and IV show results of the correlation energies in linear molecular systems of 4, 5, and 6 electrons, respectively, at several spin symmetries. The atoms of these species have been situated at distances shorter and longer than the

TABLE II. Values of correlation energies (in millihartrees) for diatomic species of 4 electrons in singlet and triplet states at several internuclear distances (R), described at CI (seniority  $\Omega$ ) and FCI levels, in the basis sets: molecular (CMO), natural (NO), and that minimizing the seniority number ( $M_{\min}$ ). Results correspond to standard STO-3G basis sets.  $E_{\text{ref}}$  = energy(RHF/ROHF) (in  $E_h$ ).

| System                    | R (Å)  | $E_{\text{ref}}$ | $\Omega = 0$ |          |            | $\Omega = 0, 2$ |          |            | $\Omega = 0, 2, 4$ |
|---------------------------|--------|------------------|--------------|----------|------------|-----------------|----------|------------|--------------------|
|                           |        |                  | CMO          | NO       | $M_{\min}$ | CMO             | NO       | $M_{\min}$ | FCI                |
| LiH<br>(S=0)              | 0.9949 | -7.764767        | -14.150      | -17.010  | -17.010    | -16.959         | -17.044  | -17.044    | -17.121            |
|                           | 1.5949 | -7.862027        | -15.983      | -20.254  | -20.254    | -20.369         | -20.373  | -20.373    | -20.378            |
|                           | 2.5949 | -7.759038        | -33.790      | -58.464  | -58.464    | -58.613         | -58.663  | -58.663    | -58.670            |
|                           | 3.5949 | -7.653305        | -59.381      | -133.484 | -133.484   | -133.699        | -133.739 | -133.739   | -133.739           |
| BeH <sup>+</sup><br>(S=0) | 1.0926 | -14.637146       | -12.180      | -15.980  | -15.981    | -16.102         | -16.113  | -16.113    | -16.120            |
|                           | 1.3426 | -14.664616       | -15.336      | -21.004  | -21.004    | -21.151         | -21.189  | -21.189    | -21.192            |
|                           | 2.0926 | -14.565564       | -35.185      | -56.573  | -56.573    | -56.801         | -56.857  | -56.857    | -56.858            |
|                           | 3.0926 | -14.449637       | -88.887      | -120.741 | -120.741   | -121.031        | -121.031 | -121.031   | -121.031           |
|                           |        |                  |              |          |            | $\Omega = 2$    |          |            | $\Omega = 2, 4$    |
|                           |        |                  | CMO          | NO       | $M_{\min}$ | CMO             | NO       | $M_{\min}$ | FCI                |
| LiH<br>(S=1)              | 0.9949 | -7.656232        |              |          |            | -0.300          | -0.247   | -0.454     | -0.454             |
|                           | 1.3949 | -7.750976        |              |          |            | -0.235          | -0.232   | -0.280     | -0.280             |
|                           | 1.7949 | -7.773036        |              |          |            | -0.270          | -0.271   | -0.290     | -0.290             |
|                           | 2.1949 | -7.776973        |              |          |            | -0.288          | -0.289   | -0.303     | -0.303             |



TABLE III. Values of correlation energies (in millihartrees) for linear species of 5 electrons in doublet and quartet states at several internuclear distances ( $R$ ), described at CI (seniority  $\Omega$ ) and FCI levels, in the basis sets: molecular (CMO), natural (NO), and that minimizing the seniority number ( $M_{\min}$ ). In the  $\text{BeH}_2^+$  radical  $R$  stands for Be-H distance. Results correspond to standard STO-3G basis sets.  $E_{\text{ref}} = \text{energy(RHF/ROHF)}$  (in  $E_h$ ).

| System                                  | $R$ (Å) | $E_{\text{ref}}$ | $\Omega = 1$ |          |            | $\Omega = 1, 3$ |          |            | $\Omega = 1, 3, 5$ |
|---|---------|------------------|--------------|----------|------------|-----------------|----------|------------|--------------------|
|   |         |                  | CMO          | NO       | $M_{\min}$ | CMO             | NO       | $M_{\min}$ | FCI                |
| $\text{BeH}_2^+$<br>( $S=\frac{1}{2}$ ) | 1.1987  | -15.154890       | -11.666      | -15.424  | -20.301    | -20.848         | -20.868  | -20.857    | -20.873            |
|   | 1.3700  | -15.169193       | -13.855      | -19.124  | -23.700    | -24.403         | -24.434  | -24.421    | -24.437            |
|   | 1.7250  | -15.122389       | -20.609      | -31.453  | -35.765    | -36.402         | -36.445  | -36.446    | -36.450            |
|   | 2.7400  | -14.947166       | -79.968      | -100.049 | -100.215   | -100.536        | -100.539 | -100.539   | -100.540           |
| $\text{BH}^+$<br>( $S=\frac{1}{2}$ )    | 0.8714  | -24.412268       | -18.884      | -18.928  | -19.687    | -19.776         | -19.776  | -19.776    | -19.776            |
|   | 1.2464  | -24.521517       | -28.494      | -28.068  | -31.558    | -31.684         | -31.684  | -31.684    | -31.684            |
|   | 1.7464  | -24.438312       | -47.027      | -41.218  | -69.980    | -70.022         | -70.022  | -70.022    | -70.022            |
|   | 2.2464  | -24.420022       | -59.389      | -59.345  | -62.020    | -62.022         | -62.022  | -62.022    | -62.022            |
|   |         |                  |              |          |            | $\Omega = 3$    |          |            | $\Omega = 3, 5$    |
|   |         |                  |              |          |            | CMO             | NO       | $M_{\min}$ | FCI                |
| $\text{BeH}_2^+$<br>( $S=\frac{3}{2}$ ) | 1.1987  | -14.950850       |              |          |            | -0.330          | -0.340   | -0.340     | -0.430             |
|   | 1.5412  | -14.982740       |              |          |            | -0.460          | -0.470   | -0.470     | -0.590             |
|   | 2.0550  | -14.939650       |              |          |            | -0.490          | -0.500   | -0.520     | -0.640             |
|   | 2.7400  | -14.896900       |              |          |            | -0.280          | -0.290   | -0.300     | -0.430             |

internuclear equilibrium ones, in order to analyze the possible influence of the internuclear distances on the results. A survey of the results in Table II shows a total coincidence of the obtained numerical values in the NO and  $M_{\min}$  basis sets for the singlet states (closed-shell systems), which are closer to the FCI values than those obtained in CMO basis sets; however for the triplet states (open-shell states) the best behavior is found in the  $M_{\min}$  basis sets. This performance is also found in Table III, where the closeness to the FCI values follows the sequence  $M_{\min} > \text{NO} > \text{CMO}$ , with notably higher correlation energy absolute values in the  $M_{\min}$  bases for the doublet systems. Similar comments apply to the results presented in Table IV where (except the  $\text{BeH}_2$  singlet system at the shortest internuclear distance) the  $M_{\min}$  basis sets markedly yield the best results.

#### IV. CONCLUDING REMARKS

In this work, we have studied spin properties of CI wave functions expanded in Slater determinants selected according to seniority number criteria. We have proved that the wave functions arising from this procedure are eigenfunctions of the  $\hat{S}^2$  operator with a defined spin quantum number  $S$  and consequently they have no spin contamination, making the seniority-number-based procedure an interesting option within the CI approaches. The dimensions of the matrices required for implementing this treatment at any seniority level have been reported for the general case of systems with a number of electrons  $N$ , any spin  $S$  and  $K$  orbitals in the basis set. The convergence of the CI results to the FCI ones have been tested in the very popular basis sets CMO and NO as

TABLE IV. Values of correlation energies (in millihartrees) for linear species of 6 electrons in singlet and triplet states at several internuclear distances ( $R$ ), described at CI (seniority  $\Omega$ ) and FCI levels, in the basis sets: molecular (CMO), natural (NO), and that minimizing the seniority number ( $M_{\min}$ ). In the  $\text{BeH}_2$  molecule  $R$  stands for Be-H distance. Results correspond to standard STO-3G basis sets.  $E_{\text{ref}} = \text{energy(RHF/ROHF)}$  (in  $E_h$ ).

| System                      | $R$ (Å) | $E_{\text{ref}}$ | $\Omega = 0$ |         |            | $\Omega = 0, 2$ |          |            | $\Omega = 0, 2, 4$ |          |            | $\Omega = 0, 2, 4, 6$ |
|-----------------------------|---------|------------------|--------------|---------|------------|-----------------|----------|------------|--------------------|----------|------------|-----------------------|
|                             |         |                  | CMO          | NO      | $M_{\min}$ | CMO             | NO       | $M_{\min}$ | CMO                | NO       | $M_{\min}$ | FCI                   |
| $\text{BeH}_2$<br>( $S=0$ ) | 1.0225  | -15.474345       | -16.139      | -16.561 | -15.069    | -16.827         | -16.839  | -26.262    | -26.330            | -26.330  | -26.330    | -26.330               |
|                             | 1.3400  | -15.559404       | -18.598      | -19.014 | -30.733    | -19.410         | -19.440  | -35.197    | -35.455            | -35.455  | -35.455    | -35.455               |
|                             | 1.6575  | -15.485359       | -25.364      | -26.055 | -47.798    | -26.775         | -26.882  | -54.319    | -54.961            | -54.961  | -54.961    | -54.961               |
|                             | 2.1338  | -15.300586       | -46.579      | -50.883 | -89.471    | -53.895         | -56.054  | -108.127   | -111.861           | -111.861 | -111.861   | -111.861              |
| $\text{BH}$<br>( $S=0$ )    | 1.0324  | -24.730362       | -39.085      | -50.979 | -51.121    | -52.011         | -52.009  | -52.008    | -52.014            | -52.014  | -52.014    | -52.014               |
|                             | 1.2324  | -24.752780       | -37.992      | -55.514 | -56.026    | -57.159         | -57.158  | -57.156    | -57.163            | -57.163  | -57.163    | -57.163               |
|                             | 1.6324  | -24.695182       | -44.023      | -65.248 | -75.027    | -76.919         | -76.918  | -76.912    | -76.919            | -76.919  | -76.919    | -76.919               |
|                             | 2.0324  | -24.604717       | -90.621      | -98.269 | -108.498   | -110.257        | -110.257 | -110.257   | -110.264           | -110.264 | -110.264   | -110.264              |
|                             |         |                  |              |         |            | $\Omega = 2$    |          |            | $\Omega = 2, 4$    |          |            | $\Omega = 2, 4, 6$    |
|                             |         |                  |              |         |            | CMO             | NO       | $M_{\min}$ | CMO                | NO       | $M_{\min}$ | FCI                   |
| $\text{BH}$<br>( $S=1$ )    | 1.0324  | -24.739304       |              |         |            | -15.161         | -15.149  | -15.319    | -17.612            | -17.612  | -17.612    | -17.612               |
|                             | 1.2324  | -24.747861       |              |         |            | -20.180         | -20.111  | -20.785    | -23.488            | -23.488  | -23.488    | -23.488               |
|                             | 1.4324  | -24.716764       |              |         |            | -27.310         | -26.910  | -29.359    | -32.451            | -32.451  | -32.451    | -32.451               |
|                             | 1.8324  | -24.620833       |              |         |            | -42.675         | -30.184  | -62.242    | -65.154            | -65.154  | -65.154    | -65.154               |

well as in the recently proposed bases in which the FCI wave functions reach a minimum seniority number value. The results found in atomic and molecular systems indicate that, for restricted CI spaces according to the seniority number, the  $M_{\min}$  bases more often lead to energy values closer to the FCI ones than those provided by the more traditional bases. These results also suggest that the rate of convergence towards FCI value can be optimized by working in the orbital basis in which the corresponding CI wave function reaches its minimum seniority number value.

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