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Seniority number in spin-adapted spaces and compactness of configuration interaction wave functions

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This work extends the concept of seniority number, which has been widely used for classifying N -electron Slater determinants, to wave functions of N electrons and spin S , as well as to N -electron spin-adapted Hilbert spaces. We propose a spin-free formulation of the seniority number operator and perform a study on the behavior of the expectation values of this operator under transformations of the molecular basis sets. This study leads to propose a quantitative evaluation for the convergence of the expansions of the wave functions in terms of Slater determinants. The non-invariant character of the seniority number operator expectation value of a wave function with respect to a unitary transformation of the molecular orbital basis set, allows us to search for a change of basis which minimizes that expectation value. The results found in the description of wave functions of selected atoms and molecules show that the expansions expressed in these bases exhibit a more rapid convergence than those formulated in the canonical molecular orbital bases and even in the natural orbital ones. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4818755>]

I. INTRODUCTION

Although the wave functions of N -electron systems arising from the full configuration interaction (FCI) treatment are the exact solutions of the Schrödinger equation for a given basis set, their determination requires a computational effort too high in most practical situations. As is well known, to reduce this computational cost one formulates expansions of configuration interaction (CI) in which only a limited number of N -electron Slater determinants is taken into account while the remainder of these determinants is neglected. The most popular criterion to select N -electron determinants is based on the particle-hole excitation level from a reference determinant, although other procedures as the seniority number of the determinants have also been used. The approximate character of the CI expansions has promoted attempts to achieve a rapid convergence of these expressions so that they yield results closer to those of the FCI method.¹ This task has predominantly been performed by means of the determination of molecular orbitals leading to more compact expansions. The conclusion commonly admitted is that the natural orbitals (NO) generate CI expansions that converge faster than their counterparts expressed in terms of the canonical molecular orbitals (CMO), the Hartree-Fock orbitals.²⁻⁵ However, other alternatives have also been studied.⁶

The concept of seniority number, which has been defined as the number of unpaired particles in a determinant,^{7,8} has proved to be a suitable tool in dealing with problems in several areas of physics. In quantum chemistry, this concept has been used, among others, within the pair-excited-multiconfigurational self-consistent field model⁹⁻¹¹ and in the even-replacement multiconfigurational self-consistent field method.¹² CI expansions based on the selection of N -electron determinants according to their seniority numbers have been proposed to evaluate electron correlation energies in atomic and molecular systems.¹³ In that reference, results obtained with this procedure have been compared with those arising from the more traditional particle-hole excitation CI expansions; a better behavior of the seniority number approach is observed in the case of systems where the strong correlation is important, that is, when the single-determinant reference is not a good zeroth order wave function. One of the objectives of this kind of studies is to find an appropriate measure to evaluate the closeness of the CI results to the FCI ones. In the present study, our aim is to utilize the seniority number concept to evaluate quantitatively the compactness of a given N -electron wave function of spin S and to generate more compact and rapidly convergent wave functions. In order to get these goals, we propose a spin-free formulation for the seniority number operator which allows one to calculate directly expectation values of this quantity with respect to an N -electron wave function and with respect to a spin-adapted space. We

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show that the expectation value of the seniority number operator with respect to a wave function depends on the basis in which that function has been expressed, while the sum of the seniority number values of all the eigenfunctions of spin S and a determined S_z projection of a N -electron Hamiltonian (the seniority number of a N -electron spin-adapted Hilbert space) is a constant. This framework also allows us to study the distribution of the Slater determinants which compose a wave function according to their seniority number values. The molecular orbital basis set dependence of the wave function seniority number enables us to propose a basis transformation in which this expectation value turns out to be minimum, providing a more compact expansion. To test this proposal, we report results arising from the minimized-seniority-number basis sets which are compared with those expressed in terms of CMO and NO.

This work has been organized as follows. The second section describes the spin-free formulation of the seniority number operator and the corresponding expectation values which can be obtained for a Slater determinant and for a wave function. In this section, we show the basis dependence of this property for a wave function and its invariance for the spin-adapted space. Likewise, we describe the procedure for minimizing the value of the wave function seniority number. Section III reports results obtained in different bases, in order to compare and to discuss the convergence of the ground state wave functions for selected atomic and molecular systems. We also describe results that show the distribution of the seniority number expectation values according to the seniority numbers of the Slater determinants which compose a wave function. Finally, in Sec. IV we summarize the main conclusions and perspectives of this work.

II. THE SENIORITY NUMBER

Let $\{i, j, k, l, \dots\}$ be a set of K orthonormal orbitals and let $a_{i\sigma}^\dagger/a_{i\sigma}$ be the fermionic creation/annihilation operator corresponding to a spin-orbital i^σ , in which σ is the spin coordinate (α or β). The seniority number operator $\hat{\Omega}$ has been formulated in terms of these fermion operators as¹³

$$\hat{\Omega} = \sum_{i,\sigma} a_{i\sigma}^\dagger a_{i\sigma} - \sum_{i,\sigma_1,\sigma_2} a_{i\sigma_1}^\dagger a_{i\sigma_2}^\dagger a_{i\sigma_2} a_{i\sigma_1}. \quad (1)$$

According to this definition, the $\hat{\Omega}$ operator does not depend on the spin coordinates and consequently one can express this device by means of the spin-free formulation

$$\hat{\Omega} = \sum_i (\hat{E}_i^i - \hat{E}_{ii}^{ii}) \quad (2)$$

in which $\hat{E}_i^i = \sum_\sigma a_{i\sigma}^\dagger a_{i\sigma}$ and $\hat{E}_{ii}^{ii} = \sum_{\sigma_1,\sigma_2} a_{i\sigma_1}^\dagger a_{i\sigma_2}^\dagger a_{i\sigma_2} a_{i\sigma_1}$ are the first- and second-order spin-free replacement operators, respectively, corresponding to these orbital indices.¹⁴ In this notation, the one-electron creator operators $a_{i\sigma}^\dagger$ and the two-electron ones $a_{i\sigma_1}^\dagger a_{i\sigma_2}^\dagger$ are represented by the superscripts and their annihilation counterparts, $a_{i\sigma}$ and $a_{i\sigma_2} a_{i\sigma_1}$, by the subscripts.

Closing both sides of Eq. (2) by a N -electron Slater determinant, one obtains 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, that difference is the number of singly occupied orbitals or number of unpaired electrons in a determinant, which can be expressed by means of the expectation value of the $\hat{\Omega}$ operator with respect to that determinant.

A. The seniority number for a spin-adapted wave function

The seniority number concept can straightforwardly be extended to a spin-adapted wave function $\Psi(N, S)$, with a specified spin S and any S_z projection, which is an eigenfunction of a spin-free N -electron Hamiltonian projected onto the FCI space.¹⁵ As is well known, this kind of function as well as those approximated in the CI methods are expressed by means of linear combinations of Slater determinants.⁶ The expectation value of the seniority operator for this type of functions results from the weighted sum of the seniority numbers of all determinants in the expansion. However, according to Eq. (2) this expectation value can be directly formulated as

$$\begin{aligned} \langle \hat{\Omega} \rangle_{\Psi(N,S)} &= \langle \Psi(N, S) | \hat{\Omega} | \Psi(N, S) \rangle \\ &= \sum_i {}^1D_i^i - 2 \sum_i {}^2D_{ii}^{ii}, \end{aligned} \quad (3)$$

where ${}^1D_i^i = \langle \Psi(N, S) | \hat{E}_i^i | \Psi(N, S) \rangle$ and ${}^2D_{ii}^{ii} = \frac{1}{2} \langle \Psi(N, S) | \hat{E}_{ii}^{ii} | \Psi(N, S) \rangle$ are elements of the spin-free first- and second-order reduced density matrices, respectively, corresponding to the state $\Psi(N, S)$. As these matrix elements are independent of the spin projection, the S_z quantum number has been omitted in this formulation.

Efficient algorithms to perform studies of electron population analysis in N -electron wave functions have been described in Refs. 16 and 17 by means of formalisms related to the particle-hole reduced density matrix framework.^{18–24} In those references, it has also been suggested that the numerical value of the $\sum_i ({}^1D_i^i - 2 {}^2D_{ii}^{ii})$ quantity could constitute an alternative measure of the number of effectively unpaired electrons corresponding to the wave function $\Psi(N, S)$ and this result could be compared with those reported using other methods.^{25–33} According to Eq. (3), the number of unpaired electrons can also be evaluated in terms of the expectation value of the seniority operator.

B. The seniority number for a spin-adapted space

The sum $\sum_i {}^1D_i^i$ is the well-known trace of the first-order reduced density matrix of the wave function $\Psi(N, S)$ and its value, N , is independent of the molecular orbital basis set used to describe that wave function. However, the quantity $\sum_i {}^2D_{ii}^{ii}$ is the sum of the elements of the spin-free second-order reduced density matrix trace related to doubly occupied orbitals and its value depends on the utilized basis set; a basis-set transformation changes its numerical value. Consequently, the expectation value of the seniority number operator for a wave function is also a basis-set dependent quantity.

In order to search for basis-set independent related quantities, we will consider an antisymmetric and spin-adapted Hilbert model space $H^A(N, K, S, S_z)$ (where A stands for antisymmetric). We will denote the expectation value of the seniority number operator for that space by

$$\begin{aligned} \langle \hat{\Omega} \rangle_{N,K,S} &= \sum_{\Psi(N,S)} \langle \Psi(N, S) | \hat{\Omega} | \Psi(N, S) \rangle \\ &= \sum_{\Psi(N,S)} \langle \hat{\Omega} \rangle_{\Psi(N,S)}, \end{aligned} \quad (4)$$

which is the sum of the seniority numbers corresponding to all N -electron Hamiltonian eigenstates of a spin S and any S_z projection, constructed with K orbitals.

Likewise, we will consider the external traces of the first- and second-order replacement operators over that space, defined as^{34–37}

$$\langle \hat{E}_j^i \rangle_{N,K,S} = \sum_{\Psi(N,S)} \langle \Psi(N, S) | \hat{E}_j^i | \Psi(N, S) \rangle \quad (5)$$

and

$$\langle \hat{E}_{jl}^{ik} \rangle_{N,K,S} = \sum_{\Psi(N,S)} \langle \Psi(N, S) | \hat{E}_{jl}^{ik} | \Psi(N, S) \rangle. \quad (6)$$

As has been shown in those references, the values of the traces $\langle \hat{E}_j^i \rangle_{N,K,S}$ and $\langle \hat{E}_{jl}^{ik} \rangle_{N,K,S}$ are always zero unless the creator index set in the replacement operator (the superscript set) is identical to the annihilation one (the subscript set), i.e., $i = j$ for the first-order replacement operator and $\{i, k\} = \{j, l\}$ for the second-order one. The presence or absence of repeated indices in the creation and annihilation sets, and the ordering of the annihilation indices with respect to the creation ones, determine the values of these external traces. These values are independent of the S_z parameter of the space $H^A(N, K, S, S_z)$; they only depend on the parameters N, K , and S , which have been indicated as subscripts in formulas (4), (5), and (6). The numerical determination of the quantity $\langle \hat{\Omega} \rangle_{N,K,S}$ requires, according to formulas (4) and (2), the calculation of the traces $\langle \hat{E}_i^i \rangle_{N,K,S}$ and $\langle \hat{E}_{ii}^{ii} \rangle_{N,K,S}$ whose values are independent of the nature of the orbital i , resulting^{34–37}

$$\langle \hat{E}_i^i \rangle_{N,K,S} = \frac{N}{K} D(N, K, S) \quad \forall i \quad (7)$$

and

$$\langle \hat{E}_{ii}^{ii} \rangle_{N,K,S} = 2 D[(N-2), (K-1), S] \quad \forall i, \quad (8)$$

where $D(N, K, S)$ is the dimension of the space $H^A(N, K, S, S_z)$, which can be calculated by means of the Weyl-Paldus formula³⁸

$$D(N, K, S) = \frac{2S+1}{K+1} \binom{K+1}{\frac{1}{2}N-S} \binom{K+1}{\frac{1}{2}N+S+1}. \quad (9)$$

Taking into account Eqs. (2), (4), (7), and (8) the seniority number expectation value for the $H^A(N, K, S, S_z)$ space turns out to be

$$\langle \hat{\Omega} \rangle_{N,K,S} = N D(N, K, S) - 2 K D[(N-2), (K-1), S], \quad (10)$$

which only depends on the parameters N, K , and S that define the space and consequently it is an invariant with respect to any unitary transformation of the basis set.

C. Minimization of the seniority number

According to Eq. (3), it is possible to search for a basis set transformation which minimizes the expectation value of the seniority number operator $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$ for a given state $\Psi(N, S)$, what is equivalent to maximizing the sum $\sum_i {}^2D_{ii}^{ii}$ for that state. Within the expansion of the state $\Psi(N, S)$ by Slater determinants, the maximization of the $\sum_i {}^2D_{ii}^{ii}$ quantity implies an increase of the coefficients of the Slater determinants with doubly occupied orbitals, since these are the Slater determinants contributing to the matrix elements with repeated indices ${}^2D_{ii}^{ii}$. Consequently, the linear combination of Slater determinants which expresses the state $\Psi(N, S)$ resulting from such a treatment will be more compact in terms of determinants with high double orbital occupation (with low seniority number). Obviously, the minimization of a $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$ quantity for the state $\Psi(N, S)$ requires the increase of the seniority number expectation values of other states of the $H^A(N, K, S, S_z)$ space, so that the sum of all of them maintains the constant value formulated in Eq. (10). According to these considerations, a procedure leading to minimization of the seniority number of a determined $\Psi(N, S)$ state must be useful to obtain faster convergent CI expansions, particularly for the states with lowest energy values of each spin S in which generally the doubly occupied Slater determinants are dominant. This minimization implies an increase of the diffusion in the expansions of other states, such as those possessing low double orbital occupations which generally are excited states.

The maximization of the $\sum_i {}^2D_{ii}^{ii}$ quantity for a determined state $\Psi(N, S)$ can be performed by transforming an initial basis set $\{i, j, k, l, \dots\}$ to another $\{\mu, \nu, \lambda, \gamma, \dots\}$, through a matrix \underline{U} which relates the functions of both basis sets according to

$$|\mu\rangle = \sum_i U_{i\mu} |i\rangle. \quad (11)$$

In this work, we have computed the coefficients $U_{i\mu}$ by means of the iterative procedure reported in Ref. 39 in which, starting with the canonical molecular orbital basis set, the sum $\sum_{\mu} {}^2D_{\mu\mu}^{\mu\mu} = \sum_{\mu} \sum_{ijkl} U_{\mu i}^* U_{\mu j} U_{\mu k}^* U_{\mu l} {}^2D_{jl}^{ik}$ in the final transformed basis set is maximized. These mathematical frameworks for searching a basis set transformation maximizing/minimizing a determined quantity have been widely utilized in procedures of orbital localization, where other tensors different from the ${}^2D_{jl}^{ik}$ one have been manipulated.^{40–47} In Sec. III, we report results arising from this proposal to be compared with those provided by more conventional molecular orbital basis sets.

III. NUMERICAL RESULTS AND DISCUSSION

The performance of the above reported equations has been tested by means of numerical data on several atomic and molecular systems. For the sake of simplicity, we have chosen the Be atom and the molecules LiH, BeH⁺, Li₂, BH, BH₂⁺, and BeH₂, in which the calculations of the FCI wave functions can be implemented at an affordable computational cost and the STO-3G basis sets have been used for all these systems, for similar reasons. As mentioned in the Introduction,

TABLE I. Values of seniority numbers $\langle \hat{\Omega} \rangle_{N,K,S}$ for a N -electron spin-adapted space constructed with K functions and spin S . Values of seniority numbers $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$ for the ground states of the systems Be, LiH, BeH⁺, Li₂, BH, BH₂⁺, and BeH₂ described by FCI expansions expressed in the canonical molecular orbitals (CMO), in the orbitals which minimize the seniority number (M_{\min}) and in the natural orbitals (NO). Equilibrium distances (R_e) at experimental bond lengths and symmetrically stretched ones (R_{st}) at $R_{st} = 2.002R_e$ (for LiH), $R_{st} = 2.676R_e$ (for BeH⁺), $R_{st} = 1.599R_e$ (for Li₂), $R_{st} = 1.487R_e$ (for BH), $R_{st} = 1.826R_e$ (for BH₂⁺), $R_{st} = 2.066R_e$ (for BeH₂). Results correspond to standard STO-3G basis sets.

System	N	K	S	$\langle \hat{\Omega} \rangle_{N,K,S}$	CMO $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$	M_{\min} $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$	NO $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$
Be	4	5	0	100	0.0001	0.0000	0.0000
LiH(R_e)	4	6	0	240	0.0202	0.0001	0.0001
LiH(R_{st})	4	6	0	240	0.3575	0.0002	0.0002
BeH ⁺ (R_e)	4	6	0	240	0.0177	0.0001	0.0001
BeH ⁺ (R_{st})	4	6	0	240	0.4110	0.0001	0.0001
Li ₂ (R_e)	6	10	0	18900	0.0190	0.0007	0.0007
Li ₂ (R_{st})	6	10	0	18900	0.0765	0.0007	0.0007
BH(R_e)	6	6	0	450	0.0500	0.0016	0.0026
BH(R_{st})	6	6	0	450	0.0723	0.0051	0.0973
BH ₂ ⁺ (R_e)	6	7	0	1470	0.0329	0.0189	0.0324
BH ₂ ⁺ (R_{st})	6	7	0	1470	0.3141	0.1781	0.1804
BeH ₂ (R_e)	6	7	0	1470	0.0364	0.0109	0.0357
BeH ₂ (R_{st})	6	7	0	1470	0.5315	0.1480	0.1568

the seniority concept is important in systems having strong electronic correlation. Consequently, we have studied the influence of this feature on our results, describing molecules at equilibrium distances and at stretched ones; likewise, another reason to study the Be atom is its well-known strong correlation.¹³ Our calculations have been performed at the experimental geometries in the systems LiH, Li₂, BH, and BeH₂;⁴⁸ in the case of the molecular ion BeH⁺ we have used the internuclear distance reported in Refs. 49 and 50, while the geometry for the species BH₂⁺ has been that optimized with the GAUSSIAN code⁵¹ at the CI level with single and double excitations. 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.⁵² In subsequent steps, we have used our own codes to determine the ground state FCI wave functions $\Psi(N, S)$ for these systems, expressed in the basis sets of CMO, in those of NO and in those of orbitals minimizing (M_{\min}) the seniority number for a given wave function. We have also used our own programs to select the second-order reduced density matrix elements ${}^2D_{ii}^{ii}$, required for calculating the quantities $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$ according to Eq. (3). As it has been pointed out in Sec. II C, the determination of the orbitals which maximize the sum $\sum_i {}^2D_{ii}^{ii}$ has been performed following the iterative procedure described in Ref. 39, and the CMO sets have been used as initial bases of that iteration. However, we have seen that identical final orbital sets are obtained when other initial orthonormal basis sets, like the NO ones, are utilized.

Table I reports the value of the seniority number $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$ for the ground state as well as the total value of the seniority number $\langle \hat{\Omega} \rangle_{N,K,S}$ for the corresponding spin-adapted space $H^A(N, K, S, S_z)$, for each of the studied systems. As can be observed, the numerical values $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$ associated with the individual wave functions are very low in comparison with the total space values $\langle \hat{\Omega} \rangle_{N,K,S}$ in all situa-

tions; this behavior is fulfilled for the three basis sets utilized in this table. The basis sets in which the seniority numbers of the wave functions are minima present clearly lower values of this quantity than their counterparts CMO basis sets. The spin-free second-order reduced density matrix elements ${}^2D_{ii}^{ii}$ arise from the coefficients of the Slater determinants possessing repeated indices (doubly occupied orbitals) in the expansions of the wave functions. Hence, the basis set transformation which maximizes the sum $\sum_i {}^2D_{ii}^{ii}$ yields an increase in the weights of the repeated-index determinants (low seniority number) and decreases in the remainder of these determinants. Consequently, this basis transformation provides more compact expansions than those expressed in other basis sets. We have also included in Table I results for the $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$ quantities arising from the use of NO basis sets. As is well known, the NO have been considered as a benchmark to analyze the convergence of the wave function expansions in terms of Slater determinants.^{3,5,6} Our results show that the proposed M_{\min} basis sets lead to $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$ values close and even lower than those arising from the NO basis sets, indicating that more compact expansions are derived from our proposal in these cases. Another aspect which deserves to be highlighted in the results reported in Table I is the influence of the electron correlation on the numerical values of the $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$. All the reported molecular systems possess markedly higher values of these quantities in the stretched geometries than in the equilibrium ones in the CMO basis sets, and this tendency can also be observed for some of them in the NO and M_{\min} bases. This fact must be interpreted in terms of the increments of the contributions of excited Slater determinants, having higher seniority numbers, in the expansions of the wave functions for the stretched geometries. The results described in Table I, in agreement with Eq. (3), show that the quantities $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$ turn out to be suitable descriptors to measure the compactness of the wave function expansions.

TABLE II. Distribution of the norm of the ground state FCI wave functions according to the Slater determinants $\Lambda(0)$, $\Lambda(2)$, and $\Lambda(4)$ (with seniority numbers 0, 2, and 4, respectively) for the systems Be, LiH, BeH^+ , Li_2 , BH, BH_2^+ , and BeH_2 in the canonical molecular orbitals (CMO), in the orbitals which minimize the seniority number (M_{\min}) and in the natural orbitals (NO). Equilibrium distances (R_e) at experimental bond lengths and symmetrically stretched ones (R_{st}) at $R_{\text{st}} = 2.002R_e$ (for LiH), $R_{\text{st}} = 2.676R_e$ (for BeH^+), $R_{\text{st}} = 1.599R_e$ (for Li_2), $R_{\text{st}} = 1.487R_e$ (for BH), $R_{\text{st}} = 1.826R_e$ (for BH_2^+), $R_{\text{st}} = 2.066R_e$ (for BeH_2). Results correspond to standard STO-3G basis sets.

System	CMO			M_{\min}			NO		
	$\sum_{\Lambda(0)} c_{\Lambda} ^2$	$\sum_{\Lambda(2)} c_{\Lambda} ^2$	$\sum_{\Lambda(4)} c_{\Lambda} ^2$	$\sum_{\Lambda(0)} c_{\Lambda} ^2$	$\sum_{\Lambda(2)} c_{\Lambda} ^2$	$\sum_{\Lambda(4)} c_{\Lambda} ^2$	$\sum_{\Lambda(0)} c_{\Lambda} ^2$	$\sum_{\Lambda(2)} c_{\Lambda} ^2$	$\sum_{\Lambda(4)} c_{\Lambda} ^2$
Be	0.9999	$<10^{-4}$	0.0000	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000
LiH(R_e)	0.9899	0.0101	0.0000	0.9999	$<10^{-4}$	0.0000	0.9999	$<10^{-4}$	0.0000
LiH(R_{st})	0.8213	0.1787	$<10^{-4}$	0.9999	0.0001	0.0000	0.9999	0.0001	0.0000
BeH^+ (R_e)	0.9912	0.0088	0.0000	0.9999	$<10^{-4}$	0.0000	0.9999	$<10^{-4}$	0.0000
BeH^+ (R_{st})	0.7945	0.2055	0.0000	0.9999	$<10^{-4}$	0.0000	0.9999	$<10^{-4}$	0.0000
Li_2 (R_e)	0.9906	0.0092	0.0001	0.9998	0.0001	0.0001	0.9998	0.0001	0.0001
Li_2 (R_{st})	0.9619	0.0380	0.0001	0.9998	0.0001	0.0001	0.9998	0.0001	0.0001
BH(R_e)	0.9750	0.0250	0.0000	0.9992	0.0008	0.0000	0.9987	0.0013	0.0000
BH(R_{st})	0.9638	0.0361	0.0000	0.9975	0.0025	0.0000	0.9514	0.0486	0.0000
BH_2^+ (R_e)	0.9915	0.0006	0.0079	0.9911	0.0083	0.0005	0.9917	0.0003	0.0079
BH_2^+ (R_{st})	0.8930	0.0569	0.0501	0.9524	0.0060	0.0415	0.9516	0.0065	0.0418
BeH_2 (R_e)	0.9906	0.0006	0.0088	0.9947	0.0051	0.0001	0.9909	0.0003	0.0088
BeH_2 (R_{st})	0.8144	0.1053	0.0802	0.9591	0.0078	0.0331	0.9561	0.0094	0.0345

In Table II, we have shown the analysis of the ground state FCI wave function expansions (normalized to unity) for the mentioned systems, in order to complement the previous results. We describe the distributions of unity into contributions given by the weights of the Slater determinants Λ , grouped according to their seniority number. The amounts $\sum_{\Lambda(0)} |c_{\Lambda}|^2$, $\sum_{\Lambda(2)} |c_{\Lambda}|^2$, $\sum_{\Lambda(4)} |c_{\Lambda}|^2$, etc., are the sums of the square of the coefficients of the Slater determinants possessing zero, two, four, etc., unpaired orbital functions, respectively. In the systems with $N = 6$ electrons, we have omitted the quantities $\sum_{\Lambda(6)} |c_{\Lambda}|^2$ due to the low values found for these components. In Table III, we report the number of Slater determinants present in each seniority space for the studied systems. A survey of the results in Table II confirms once again that the CMO basis sets lead to more diffuse expansions than the basis sets proposed in this work, arising from the minimization of the $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$ quantities. Likewise, the contributions in the NO basis sets turn out to be slightly more diffuse than those obtained in the basis sets M_{\min} . The stretching of the molecular systems yields wave functions in which the reference Slater determinant is less dominant than in the equilibrium geometries, as is reflected by the increase of the values of the quantities $\langle \hat{\Omega} \rangle_{\Psi(N,S)}$ as well as in higher diffusions of the expansions of these functions.

TABLE III. Number of Slater determinants Λ , with seniority numbers 0, 2, 4, and 6 for the studied systems in the STO-3G basis sets.

System	$\Lambda(0)$	$\Lambda(2)$	$\Lambda(4)$	$\Lambda(6)$
Be	10	60	30	...
LiH	15	120	90	...
BeH^+	15	120	90	...
Li_2	120	2520	7560	4200
BH	20	180	180	20
BH_2^+	35	420	630	140
BeH_2	35	420	630	140

IV. CONCLUDING REMARKS

In this work, we have described a spin-free formulation of the seniority number operator. This formulation allows us to extend the seniority number concept to states described by N -electron wave functions of spin S as well as to spin-adapted antisymmetric Hilbert spaces constructed with K one-electron functions, N electrons, and spin S , providing the direct evaluation of the corresponding expectation values. Taking into account the behavior of these expectation values under transformations of the molecular orbital basis sets, we have proposed an orbital basis set in which the expansion of the wave function in terms of Slater determinants turns out to be more compact than in the CMO basis sets and even in the NO ones. Such a basis set is obtained through the maximization of the sum of the spin-free second-order reduced density matrix diagonal elements with repeated indices of the corresponding state function (minimization of its seniority number expectation value). The results arising from the test of our proposal on several simple systems indicate that this basis set can be efficient for the formulation of more convergent CI expansions and that the expectation value of the seniority number operator with respect to a given wave function can be useful as a quantitative measure of the diffusion/compactness of the expansion of that function in terms of Slater determinants. Work along these lines is being pursued in our laboratories.

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- ¹C. D. Sherrill and H. F. Schaefer III, *Adv. Quantum Chem.* **34**, 143 (1999).
- ²P. O. Löwdin, *Adv. Phys.* **5**, 1 (1956).
- ³E. R. Davidson, *Rev. Mod. Phys.* **44**, 451 (1972).
- ⁴I. Shavitt, B. J. Rosenberg, and S. Palakit, *Int. J. Quantum Chem.* **10**, 33 (1976).
- ⁵I. Shavitt, *Mol. Phys.* **94**, 3 (1998).
- ⁶L. Bytautas, J. Ivanic, and K. Ruedenberg, *J. Chem. Phys.* **119**, 8217 (2003).
- ⁷P. Ring and P. Schuck, *The Nuclear Many-Body Problem* (Springer-Verlag, New York, 1980).
- ⁸D. S. Koltun and J. M. Eisenberg, *Quantum Mechanics of Many Degrees of Freedom* (Wiley, New York, 1988).
- ⁹D. B. Cook, *Mol. Phys.* **30**, 733 (1975).
- ¹⁰D. D. Shilady, S. Cutler, L. F. Jones, and L. B. Kier, *Int. J. Quantum Chem.* **38**, 153 (1990).
- ¹¹M. Couty and M. B. Hall, *J. Phys. Chem. A* **101**, 6936 (1997).
- ¹²C. C. J. Roothaan, J. Detrich, and D. G. Hopper, *Int. J. Quantum Chem.* **16**, 93 (1979).
- ¹³L. Bytautas, T. M. Henderson, C. A. Jiménez-Hoyos, J. K. Ellis, and G. E. Scuseria, *J. Chem. Phys.* **135**, 044119 (2011) and references therein.
- ¹⁴J. Paldus and B. Jeziorski, *Theor. Chim. Acta* **73**, 81 (1988).
- ¹⁵J. Paldus, in *Theoretical Chemistry: Advances and Perspectives*, edited by H. Eyring and D. Henderson (Academic, New York, 1976).
- ¹⁶P. Karafiloglou, *J. Chem. Phys.* **130**, 164103 (2009).
- ¹⁷P. Karafiloglou and K. Kyriakidou, *Int. J. Quantum Chem.* **113**, 1775 (2013).
- ¹⁸C. Garrod and J. K. Perkus, *J. Math. Phys.* **5**, 1756 (1964).
- ¹⁹F. Wienhold and E. B. Wilson, *J. Chem. Phys.* **47**, 2298 (1967).
- ²⁰M. Nakata, H. Nakatsuji, M. Ehara, M. Fukuda, K. Nakata, and K. Fujisawa, *J. Chem. Phys.* **114**, 8282 (2001).
- ²¹M. Nakata, M. Ehara, and H. Nakatsuji, *J. Chem. Phys.* **116**, 5432 (2002).
- ²²D. R. Alcoba, *Int. J. Quantum Chem.* **97**, 776 (2004).
- ²³D. A. Mazziotti, *Phys. Rev. A* **72**, 032510 (2005).
- ²⁴G. Gidofalvi and D. A. Mazziotti, *Phys. Rev. A* **72**, 052505 (2005).
- ²⁵K. Takatsuka, T. Fueno, and K. Yamaguchi, *Theor. Chim. Acta* **48**, 175 (1978).
- ²⁶V. N. Staroverov and E. R. Davidson, *Chem. Phys. Lett.* **330**, 161 (2000).
- ²⁷L. Lain, A. Torre, R. C. Bochicchio, and R. Ponec, *Chem. Phys. Lett.* **346**, 283 (2001).
- ²⁸M. Head-Gordon, *Chem. Phys. Lett.* **372**, 508 (2003).
- ²⁹D. R. Alcoba, R. C. Bochicchio, L. Lain, and A. Torre, *Chem. Phys. Lett.* **429**, 286 (2006).
- ³⁰L. Lain, A. Torre, D. R. Alcoba, and R. C. Bochicchio, *Chem. Phys. Lett.* **476**, 101 (2009).
- ³¹D. R. Alcoba, R. C. Bochicchio, L. Lain, and A. Torre, *J. Chem. Phys.* **133**, 144104 (2010).
- ³²L. Lain, A. Torre, D. R. Alcoba, and R. C. Bochicchio, *Theor. Chem. Acc.* **128**, 405 (2011).
- ³³A. V. Luzanov and O. V. Prezhdo, *J. Chem. Phys.* **135**, 094107 (2011).
- ³⁴J. Planelles, C. Valdemoro, and J. Karwowski, *Phys. Rev. A* **41**, 2391 (1990).
- ³⁵C. Valdemoro, A. Torre, and L. Lain, in *Structure, Interactions and Reactivity*, edited by S. Fraga (Elsevier, Amsterdam, 1992).
- ³⁶A. Torre, L. Lain, and J. Millan, *Phys. Rev. A* **47**, 923 (1993).
- ³⁷L. Lain and A. Torre, *Phys. Rev. A* **52**, 2446 (1995).
- ³⁸J. Paldus, *J. Chem. Phys.* **61**, 5321 (1974).
- ³⁹J. E. Subotnik, Y. Shao, W. Liang, and M. Head-Gordon, *J. Chem. Phys.* **121**, 9220 (2004).
- ⁴⁰C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.* **35**, 457 (1963).
- ⁴¹J. M. Foster and S. F. Boys, *Rev. Mod. Phys.* **32**, 300 (1960).
- ⁴²V. Magnasco and A. Perico, *J. Chem. Phys.* **47**, 971 (1967).
- ⁴³W. von Niessen, *J. Chem. Phys.* **56**, 4290 (1972).
- ⁴⁴J. Pipek and P. G. Mezey, *J. Chem. Phys.* **90**, 4916 (1989).
- ⁴⁵J. Cioslowski, *Int. J. Quantum Chem.* **S24**, 15 (1990).
- ⁴⁶D. R. Alcoba, L. Lain, A. Torre, and R. C. Bochicchio, *J. Comput. Chem.* **27**, 596 (2006).
- ⁴⁷O. B. Oña, D. R. Alcoba, W. Tiznado, A. Torre, and L. Lain, *Int. J. Quantum Chem.* **113**, 1401 (2013).
- ⁴⁸*NIST Computational Chemistry Comparison and Benchmark Database*, NIST Standard Reference Database No. 101, edited by R. D. Johnson III (National Institute of Standard and Technology, 2006). Available at <http://www.srdata.nist.gov/cccbdb>.
- ⁴⁹J. B. Roos, M. Larson, A. Larson, and A. E. Orel, *Phys. Rev. A* **80**, 112501 (2009).
- ⁵⁰K. Chakrabarti and J. Tennyson, *Eur. Phys. J. D* **66**, 31 (2012).
- ⁵¹M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.* GAUSSIAN 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.
- ⁵²T. D. Crawford, C. D. Sherrill, E. F. Valeev, J. T. Fermann, R. A. King, M. L. Leininger, S. T. Brown, C. L. Janssen, E. T. Seidl, J. P. Kenny, and W. D. Allen, *J. Comput. Chem.* **28**, 1610 (2007).