

Performance of Shannon-entropy compacted N -electron wave functions for configuration interaction methods

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Abstract The coefficients of full configuration interaction wave functions (FCI) for N -electron systems expanded in N -electron Slater determinants depend on the orthonormal one-particle basis chosen although the total energy remains invariant. Some bases result in more compact wave functions, i.e. result in fewer determinants with significant expansion coefficients. In this work, the Shannon entropy, as a measure of information content, is evaluated for such wave functions to examine whether there is a relationship between the FCI Shannon entropy of a given basis and the performance of that basis in truncated CI approaches. The results obtained for a set of randomly picked bases are compared to those obtained using the traditional canonical molecular orbitals, natural orbitals, seniority minimising orbitals and a basis that derives from direct minimisation of the Shannon entropy. FCI calculations for selected atomic and molecular systems clearly reflect the influence of the chosen basis. However, it is found that there is no direct relationship between the entropy computed for each basis and truncated CI energies.

Keywords Entropy · Configuration interaction · Seniority · DOCI

1 Introduction

The full configuration interaction (FCI) wave function, usually expressed in terms of N -electron Slater determinants, corresponds to the exact solution of the Schrödinger equation of an N -electron system for a given one-electron basis set. However, its determination comes at a prohibitive computational cost, except for systems with few electrons and for small basis sets. This drawback is overcome by using approximate methods. The FCI wave function expansion includes all possible N -electron determinants that can be obtained from an orthonormal set of orbitals. Hence, the energy associated with the FCI wave function is independent of the actual chosen orthonormal basis. Truncated configuration interaction (CI) methods mitigate the prohibitive computational cost of FCI methods by restricting

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the number of N -electron determinants based on some predetermined criteria [1, 2]. The best-known CI methods include determinants up to a certain degree of excitation from a reference determinant. By usually strongly reducing the number of determinants the computational cost becomes much more affordable, although by no longer considering the complete space of determinants the energy depends on the number of Slater determinants retained and the orthonormal orbital basis used. Moreover, the coefficients of the N -electron determinants that express the wave functions are basis-set dependent, even in the FCI method. A wave function is considered more compact when fewer determinants have coefficients significantly different from zero. Hence, it is of interest to see whether expanding the CI wave functions in basis sets that render the FCI wave function more compact would result in lower energies in approximate truncated CI wave function. It has long been recognised that much of FCI space consists of deadwood, i.e. configurations that contribute almost nothing to the wave function [1]. This observation inspired work to examine ways to mask off small coefficients in the wave function against a predefined energy threshold, all in the quest of finding an optimally sparse wave function [3, 4]. In the present work, we establish a basis in which the FCI wave function becomes as sparse as possible, i.e. containing as many near-zero coefficients as possible but without altering the FCI energy. The hypothesis is that the basis that results in the most compact FCI wave function may be a good starting point for CI approaches by giving consistently low energies at the truncated levels. It has been commonly accepted that the natural orbitals (NO) [5], which diagonalise the first-order reduced density matrix [6–8], lead to faster expansions than those provided by the canonical Hartree–Fock molecular orbitals (CMO) [9–11]. However, there is no guarantee that the truncated CI energies arising from the FCI NO basis set are always lower than those obtained from the CMO basis ones. Other types of molecular orbitals have also been proposed, searching for CI expansions with faster convergence than those formulated in terms of natural orbitals. In the present paper we examine the performance of a new basis set that maximises the compactness using entropy considerations. This sets the proposed methods apart from using more localised basis sets [12–15].

We have previously reported results on the compactness of CI and FCI wave functions and their corresponding energies using seniority-number minimising orbitals [16–19]. The seniority number of an N -electron determinant is the number of singly occupied orbitals (or unpaired electrons) in that determinant [20, 21]. The extension of this concept to N -electron wave functions gives unpaired electron number averages for N -electron states [22, 23] as the expectation value of the seniority-number operator [16,

24]. Because these expectation values are dependent on the basis set utilised to express the wave functions, we have determined orbital sets minimising those expectation values; these resulting orbital sets have been denoted as M_{\min} sets [16]. Our studies have shown that the wave functions expressed in the M_{\min} orbitals are more compact than those based on the CMO and NO basis sets. This more compact nature has been confirmed using the Shannon entropy indices as compactness criterion for expansions of wave functions expressed in the CMO, NO, and M_{\min} basis sets [25]. However, to our knowledge no study has been made to establish whether there is any connection between the compactness of a FCI wave function and the performance of the underlying basis in truncated CI approaches. Our hypothesis is that a basis that results in a more compact FCI wave function is more biased towards a single determinant and that using this single determinant as a reference would result in lower energies at truncated CI levels. From there, any structure in this basis set could be examined to establish whether one could a priori design better orbital bases for truncated CI. In order to answer this, we describe a new method to specifically minimise the Shannon entropy index and compare the results obtained with those arising from using other basis sets. We also randomly generate a large number of orthonormal bases to examine any trend between truncated CI energies and compactness of the FCI wave function with those bases.

2 Theoretical aspects

We express the electronic wave function of an N -electron system according to

$$|\Psi(N, S, S_z)\rangle = \sum_{\Lambda(N, S_z)} C_{\Lambda}^S |\Lambda(N, S_z)\rangle \quad (1)$$

in which S and S_z are the spin quantum numbers of an N -electron spin-adapted wave function $|\Psi(N, S, S_z)\rangle$. $|\Lambda(N, S_z)\rangle$ stands for an N -electron Slater determinant, and C_{Λ}^S is its expansion coefficient. If the summation in Eq. (1) contains all the Slater determinants $|\Lambda(N, S_z)\rangle$ that can be constructed with the chosen molecular spin-orbital basis set, expansion (1) corresponds to the FCI wave function. As stated above, limited configuration interaction methods arise from approximating expansion (1), in which some N -electron Slater determinants are neglected according to predetermined criteria, such as the excitation degree of the determinants with respect to a reference determinant [2] or their seniority-number values [16, 24]. An example of the latter criterion is the double-occupied configuration interaction (DOCI) method, in which the $|\Psi(N, S, S_z)\rangle$ wave function is expanded in terms of all seniority-zero determinants [26].

The spin-free version of the N -electron seniority-number operator, $\hat{\Omega}$, is given as [16]

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

where i represents the orbitals of a finite orthonormal basis set, \hat{N} is the electron number operator, and $\hat{E}_{ii}^{ii} = \sum_{\sigma_1, \sigma_2} a_{i\sigma_1}^\dagger a_{i\sigma_2}^\dagger a_{i\sigma_2} a_{i\sigma_1}$ is the second-order replacement operator [27–30] corresponding to the double occupation of the orbital i . $a_{i\sigma_1}^\dagger$ and $a_{i\sigma_1}$ are the usual creation and annihilation operators of the spin-orbital i^{σ_1} , respectively, and σ_1 and σ_2 the spin functions. The expectation value of the seniority-number operator $\langle \hat{\Omega} \rangle_\Psi = \langle \Psi(N, S, S_z) | \hat{\Omega} | \Psi(N, S, S_z) \rangle$ is then a weighted sum of the seniority numbers of all determinants involved in expansion (1) [16]. In previous work, we have performed unitary transformations of the molecular orbital set to minimise $\langle \hat{\Omega} \rangle_\Psi$ [16–18, 31], giving rise to the so-called M_{\min} basis set. This has been done using a specific adaptation of the procedure reported by Subotnik et al. [32].

The invariance of the FCI energy with respect to the orthonormal basis is no longer maintained in the case of limited CI methods. The C_A^S expansion coefficients in Eq. (1) depend on the basis set used in both limited CI and FCI procedures. Hence, it is useful to search for molecular basis sets in which the expansion (1) turns out to be more compact also making limited CI series converge more rapidly to the FCI wave functions. This obviously hinges on the presence of an underlying (yet hidden) structure as truncated CI schemes rely on connected one-electron excitations.

One of the quantitative procedures to measure the compactness of a given N -electron wave function expressed by Eq. (1) is the informational content (I_C) index, defined as

$$I_C = - \sum_{\Lambda(S_z)} |C_A^S|^2 \log_2 |C_A^S|^2, \quad |C_A^S| \geq 0 \quad (3)$$

This and other related indices, which arise from the Shannon information entropy theory [33, 34], have been previously satisfactorily used as a measure of the compactness of a given wave function expressed in several molecular basis sets. These indices have been used both in the traditional excitation-based CI scheme [35] and in the seniority-number-based one [25]. As mentioned in the Introduction, one of the basis sets sought is that which minimises the I_C value for a given N -electron wave function. This scheme associates minimal entropy values with maximal compactness of wave functions. Since it is assumed that the wave function $|\Psi(N, S, S_z)\rangle$ is normalised to unity and the coefficients lie in the range $0 \leq |C_A^S| \leq 1$, the entropic index satisfies $I_C \geq 0$. Consequently, compact wave functions, which require as few as possible but consequently high $|C_A^S|$ values, provide low values for I_C . The idea behind the use of entropic indices is based on the supposed link between

correlation energy and entropy [36–40]. This idea underlies several recent studies, including that by Delle Site that also uses Shannon entropic indices albeit directly on the electron density [41–43].

For minimising the I_C index, we have used the simulated annealing (SA) technique [44, 45]. This has proven to be a very efficient method to find the global minimum of a function possessing many local minima [31]. The SA method consists in emulating a physical process in which a solid system is gradually cooled and frozen in a minimum energy configuration. In the present work, sequences of elementary Jacobi rotations [46] between pairs of orbitals are performed over a randomly chosen angle. The rotation angles are drawn from the normal distribution around zero and limited to a determined interval. Each rotation provides a new I_C value. The actual rotation is effectively retained when this value is lower than the previous one; otherwise, a uniform random intermediate parameter is calculated and according to its magnitude the proposed rotation is accepted or rejected. This procedure allows one to escape from local minima. Full technical details of the method can be found in Ref. [31]. In the I_C minimisation set-up, we have both used a scheme where only rotations among orbitals of the same symmetry are considered $I_C(\text{sym})$ and one where the symmetry may be broken $I_C(\text{nonsym})$.

In practice, obtaining a I_C value from FCI is not an efficient approach. However, the present paper first establishes whether a good correlation exists between limited CI energies and I_C . In case a meaningful correlation is found, new approaches will be sought to obtain low entropy bases, e.g. by using I_C optimised bases from limited CI calculations.

3 Computational details

We have chosen several two-electron systems as well as the beryllium atom, the lithium dimer, and neutral and ionic hydrides of the second-row elements as prototype of systems with four, six, eight and ten electrons, for which the FCI calculations are computationally affordable. In all cases, we have considered the singlet ground state wave functions of these systems, which have been expressed in all the above-mentioned orthonormal orbital bases obtained from the STO-3G atomic basis set, except for the two-electron systems where larger basis sets have been used. The use of a minimal basis set allows FCI calculations, including the optimisation of I_C . Although larger basis sets are required to account more thoroughly for dynamic correlation, in this proof of principle test failure to find a good correlation between limited CI energies and I_C values would indicate that no good correlation can be expected for larger basis sets. The molecular systems have been studied at both equilibrium (R_e) and symmetrically stretched (R_{st})

Table 1 Calculated I_C values for the FCI ground state wave functions of selected two-electron systems expressed in several orthonormal bases using different atomic basis sets

System	Basis	CMO	NO	M_{\min}	$I_C(\text{sym})$	$I_C(\text{nonsym})$
He	6-31G	0.040	0.040	0.040	0.040	0.040
	6-311G	0.045	0.040	0.040	0.040	0.040
	6-311G(d,p)	0.084	0.079	0.079	0.079	0.079
$\text{H}_2(R_e)$	6-31G	0.141	0.119	0.119	0.119	0.119
	6-311G	0.158	0.124	0.124	0.124	0.124
	6-311G(d,p)	0.185	0.150	0.150	0.150	0.150
$\text{H}_2(R_{\text{st}})$	6-31G	0.710	0.622	0.622	0.622	0.622
	6-311G	0.820	0.621	0.621	0.621	0.621
	6-311G(d,p)	0.810	0.608	0.608	0.608	0.608
$\text{HeH}^+(R_e)$	6-31G	0.087	0.067	0.067	0.067	0.067
	6-311G	0.088	0.063	0.063	0.063	0.063
	6-311G(d,p)	0.122	0.092	0.092	0.092	0.092
$\text{HeH}^+(R_{\text{st}})$	6-31G	0.097	0.071	0.071	0.071	0.071
	6-311G	0.097	0.068	0.068	0.068	0.068
	6-311G(d,p)	0.137	0.102	0.102	0.102	0.102

Equilibrium distances (R_e) at experimental or optimised bond lengths and symmetrically stretched ones (R_{st}) at $R_{\text{st}}=2.349R_e$ (for H_2), $R_{\text{st}}=1.324R_e$ (for HeH^+)

geometries. The equilibrium distances for the molecules H_2 , HeH^+ , LiH , Li_2 , BH , BeH_2 , BH_3 , CH_4 , NH_3 , H_2O and FH are those reported in Ref. [47]. For BeH^+ we have used the internuclear distance from Refs. [48, 49], while in BeH_2^+ the geometry was optimised at CI single and double excitation level using the CMO basis set, with the GAUSSIAN code [50]. The one- and two-electron integrals to build the FCI N -electron Hamiltonian matrix, as well as the CMO sets, have been obtained from a modified version of the PSI 4 package [51]. Our own codes have been used to calculate the NO, M_{\min} , $I_C(\text{sym})$ and $I_C(\text{nonsym})$ minimising orbital sets as well as a large number of randomly chosen sets, and to perform the required basis-set transformations. The random basis sets were generated by applying unitary matrix transformations on the molecular orbital basis sets. These matrices were built from the eigenvectors of Hermitian matrices. As it was observed that completely random Hermitian matrices resulted systematically in larger values for I_C , we included also matrices that are expected to lead to lower I_C values. This was done by stepwise building matrices with an increasing number of orbitals participating in the Jacobi rotations while keeping other orbitals fixed.

4 Results and discussion

To allow proper comparison among the different orthonormal basis sets, we first report the I_C values obtained for CMO, NO, M_{\min} and I_C minimising sets in both the symmetry and nonsymmetry conserving approaches. Table 1 gathers the I_C values for the two-electron atomic and molecular systems. Table 2 reports the results corresponding to that

index for the four- and six-electron systems, while Table 3 collects those values for the eight- and ten-electron ones.

Tables 1, 2 and 3 clearly illustrate the fact that indeed the I_C index value depends on the orthonormal basis chosen for the expansion (1). In case of two-electron systems, Table 1 shows that the values obtained using the NO and M_{\min} bases coincide. This is because a FCI wave function for this type of systems must be expanded in terms of Slater determinants of seniority numbers $\Omega = 0$ (with only doubly occupied orbitals) and $\Omega = 2$ (with nonrepeated orbitals). However, a unitary transformation allows one to formulate these wave functions as [24, 52, 53]

$$|\Psi(N=2, S=0)\rangle = \sum_i C_i |i^\alpha i^\beta\rangle \quad (4)$$

in which all the Slater determinants possess seniority number $\Omega = 0$. Hence, the value of the $\langle \hat{\Omega} \rangle_\Psi$ quantity for wave functions of that type is zero, which is the minimum expectation value of the seniority number operator. On the other hand, the spin-free first-order reduced density matrix corresponding to a wave function satisfying Eq. (4) is diagonal and consequently the orbitals i are the natural ones. This argument shows that for two-electron systems in singlet states the NO and M_{\min} basis sets must coincide. The direct minimisation of the I_C index through the simulated annealing technique (in both symmetry and nonsymmetry conserving approaches) also yields that same basis, in accordance with the results reported in Ref. [52].

The results in Table 2 show that all the orbital basis sets considered, except the CMO one, yield identical I_C values in the four-electron systems (Be , $\text{LiH}(R_e)$, $\text{LiH}(R_{\text{st}})$, $\text{BeH}^+(R_e)$ and $\text{BeH}^+(R_{\text{st}})$). The higher values exhibited by

Table 2 Calculated I_C values for the FCI ground state wave functions of selected four- and six-electron systems expressed in several orthonormal bases using STO-3G basis sets

	Be	LiH(R_e)	LiH(R_{st})	BeH ⁺ (R_e)	BeH ⁺ (R_{st})	Li ₂ (R_e)	Li ₂ (R_{st})	BH(R_e)	BH(R_{st})	BH ₂ ⁺ (R_e)	BH ₂ ⁺ (R_{st})	BeH ₂ (R_e)	BeH ₂ (R_{st})
CMO	0.649	0.231	1.709	0.222	1.767	0.664	1.103	0.681	0.979	0.301	2.041	0.282	2.695
NO	0.648	0.167	0.864	0.164	0.990	0.598	0.854	0.556	1.005	0.298	1.684	0.278	1.892
M_{\min}	0.648	0.167	0.864	0.164	0.990	0.598	0.854	0.552	0.802	0.299	1.682	0.265	1.883
I_C (sym)	0.648	0.167	0.864	0.164	0.990	0.597	0.853	0.552	0.802	0.298	1.679	0.278	1.876
I_C (nonsym)	0.648	0.167	0.864	0.164	0.990	0.597	0.853	0.552	0.802	0.298	1.679	0.265	1.876

Equilibrium distances (R_e) at experimental or optimised 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)

the CMO set indicate, as expected, a less compact wave function in that basis. The stretched configurations of the systems LiH(R_{st}) and BeH⁺(R_{st}) also show systematically higher values with respect to their equilibrium counterparts LiH(R_e) and BeH⁺(R_e). These results are coherent with the higher static correlation [24] in the stretched geometries, where the FCI expansion requires a higher number of Slater determinants with significant weight. Table 2 also shows I_C values for the six-electron systems (Li₂(R_{st}), BH(R_e), BH(R_{st}), BH₂⁺(R_e), BH₂⁺(R_{st}), BeH₂(R_e), and BeH₂(R_{st})). As can be observed, the highest values of the entropic index are again found with the CMO basis. Only small differences appear between the results with the other bases. The NO and M_{\min} basis sets lead to very similar values, although in the BH(R_{st}) system the M_{\min} basis set provides a markedly more compact wave function than the NO one. The results from the I_C (sym) and I_C (nonsym) optimisations reflect the highest compactness, particularly in the latter case, although the values remain similar to those obtained with the M_{\min} basis. The stretched configurations of these systems also entail very high I_C values with respect to the equilibrium geometries, again coherent with their higher static correlation.

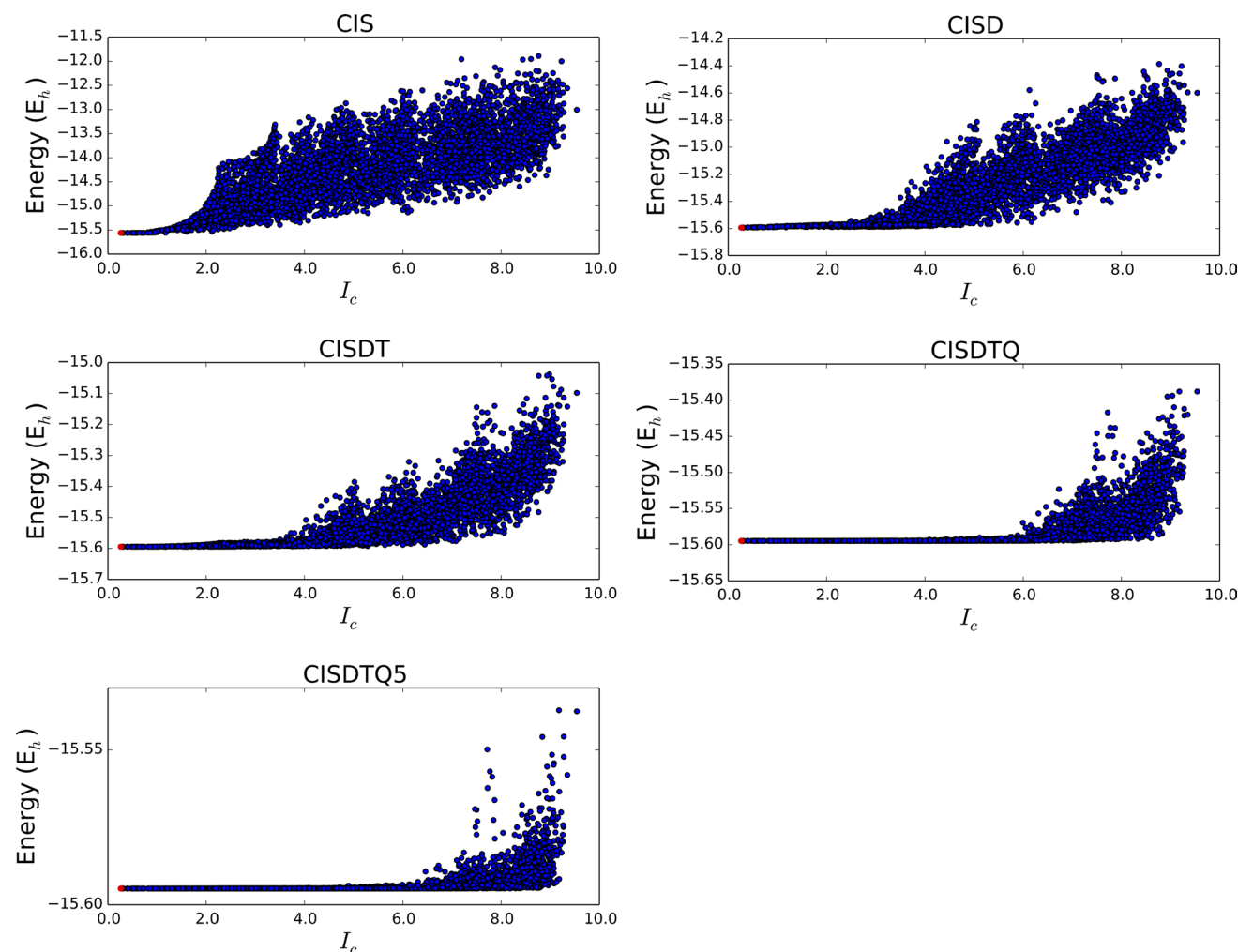
Table 3 describes the results for the eight-electron systems, BH₃(R_e) and BH₃(R_{st}), in which the lowest value of the I_C index is obtained with the I_C (nonsym) optimisation although the M_{\min} basis leads to very similar results. For the ten-electron systems, again the basis sets obtained from the I_C (nonsym) and M_{\min} procedures yield similar results. We do notice that in several cases, releasing the constraints of the I_C (sym) procedure to give the I_C (nonsym) results significantly increases the compaction of the wave function. The similarity of the I_C values for the I_C (nonsym) and M_{\min} bases can be explained as follows. According to Eq. (2), the minimisation of the $\langle \hat{\Omega} \rangle_\psi$ quantity requires the maximisation of the $\sum_i \langle E_{ii}^i \rangle_\psi$ one, which implies reaching wave function expansions with larger coefficients for the Slater determinants containing doubly occupied orbitals i , which is equivalent to getting more ordered configurations. The numerical values of the I_C index arising from these last two methods are markedly lower than those provided by the NO basis sets and consequently they must be preferred in the task of compacting wave functions.

In truncated single-reference CI methods, one starts with a single determinant wave function and adds excitations of a given order by replacing occupied orbitals by virtual orbitals. This requires a rationale to distinguish between occupied and virtual orbitals or at least some meaningful order among the orbitals. In case of CMOs, the ordering is based on the expectation values of the Fock operator. The reference determinant is built from the

Table 3 Calculated I_C values for the FCI ground state wave functions of selected eight- and ten-electron systems expressed in several orthonormal bases using STO-3G basis sets

	BH ₃ (R_e)	BH ₃ (R_{st})	CH ₄ (R_e)	CH ₄ (R_{st})	NH ₃ (R_e)	NH ₃ (R_{st})	H ₂ O(R_e)	H ₂ O(R_{st})	HF(R_e)	HF(R_{st})
CMO	0.358	2.803	0.495	3.850	0.462	4.788	0.281	2.442	0.132	0.860
NO	0.357	2.792	0.515	3.822	0.443	4.142	0.261	2.362	0.117	0.829
M_{min}	0.312	2.599	0.417	3.239	0.383	3.660	0.234	2.031	0.117	0.829
I_C (sym)	0.331	2.619	0.495	3.812	0.408	3.889	0.260	2.362	0.117	0.829
I_C (nonsym)	0.312	2.598	0.417	3.239	0.383	3.659	0.234	2.030	0.117	0.829

Equilibrium distances (R_e) at experimental or optimised bond lengths and symmetrically stretched ones (R_{st}) at $R_{st} = 1.750R_e$ (for BH₃), $R_{st} = 1.750R_e$ (for CH₄), $R_{st} = 1.894R_e$ (for NH₃), $R_{st} = 1.995R_e$ (for H₂O), $R_{st} = 2.00R_e$ (for HF)

**Fig. 1** STO-3G Truncated CI energies for different orthonormal bases versus FCI I_C for BeH₂ at equilibrium geometry. The red dot locates the CMO, NO and seniority minimising basis sets (indistinguishable on the I_C axis)

lowest energy orbitals. In NOs, one uses the occupation numbers of the natural orbitals and constructs a reference determinant that includes only the most populated natural orbitals. In case of the seniority and I_C minimising orbitals, there appears no simple ordering between the different orbitals in the orthonormal basis. In that case, the most

obvious choice is to use as a reference the Slater determinant with the largest absolute coefficient of the FCI wave function.

To examine the possible relationship between the I_C value and truncated CI energies, CIS, CISD, CISDT, CISDTQ, and CISDTQ5 energies were computed starting from

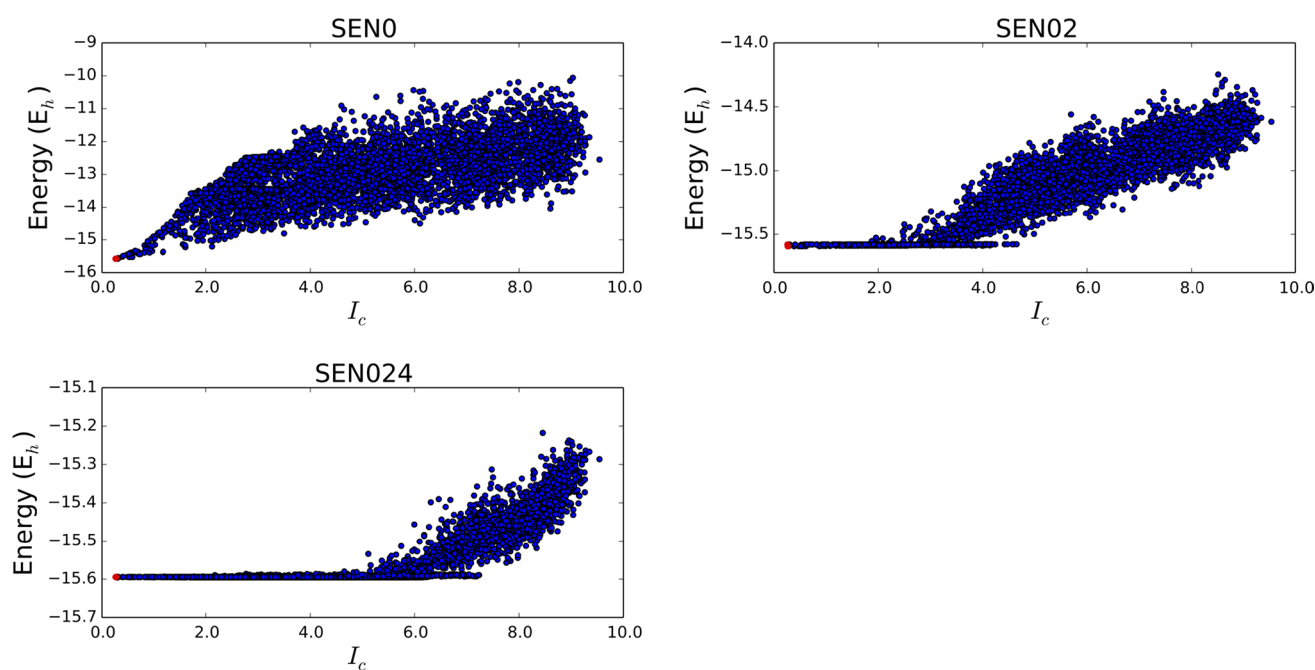


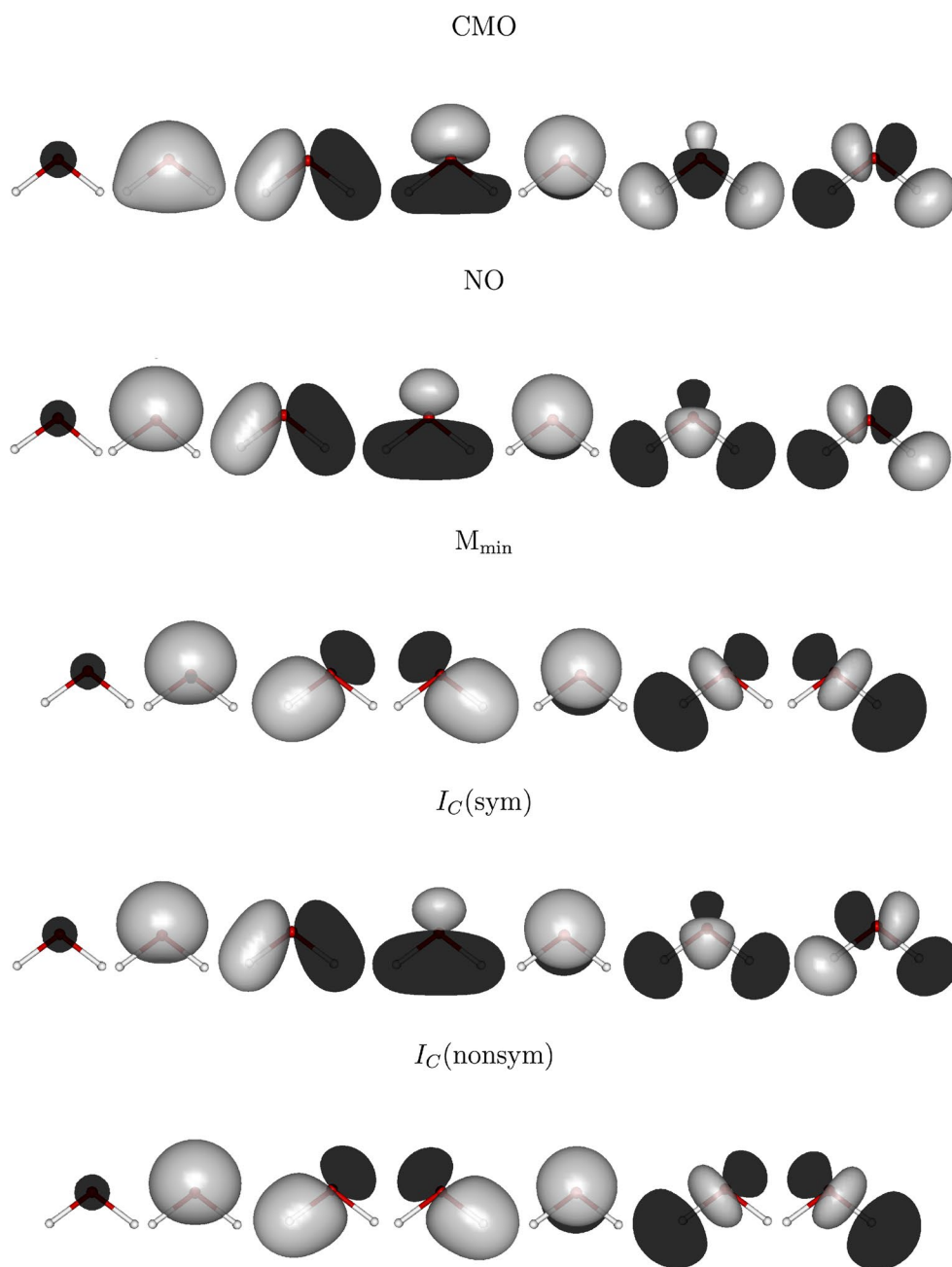
Fig. 2 STO-3G Seniority-based CI energies for different orthonormal bases versus FCI I_C for BeH_2 at equilibrium geometry. The red dot locates the CMO, NO and seniority minimising basis sets (indistinguishable on the I_C axis)

the reference determinant obtained from CMOs, NOs, seniority minimising, I_C minimising orbitals and 5000 randomly chosen basis sets obtained as described above. For each basis, the FCI coefficients were computed and from there the I_C values. Figure 1 shows the scatterplot for the truncated CI energies of BeH_2 versus the I_C value computed using the STO-3G basis at the equilibrium geometry. The fact that the CIS energies differ from the Hartree–Fock energy is due to the fact that single excitations generally interact with the reference determinant. Only in case of the Hartree–Fock single determinant, Brillouin’s theorem renders these interactions zero. The random basis sets cover the entire range of I_C values from the lowest values obtained with the entropy minimising basis sets to the theoretical upper bound corresponding to equal coefficients for all determinants. As Fig. 1 clearly shows, a qualitative trend may be discerned. However, the main observation is that low truncated CI energies are not exclusively connected to the lowest values of I_C . The lowest values of I_C are derived from the CMO, NO and seniority and entropy minimising basis sets, but several other random basis sets result in low energies as well although with higher I_C values. This means there is no fundamental quantitative relationship between the I_C values and truncated CI energies.

The seniority minimising basis results in low entropies (similar to those obtained from the $I_C(\text{nonsym})$ and

slightly better than the $I_C(\text{sym})$ basis) and so more compact wave functions and tends to result in low energies for the closed shell systems tested. Besides one-electron excitations, we also explored seniority-based CI expansions such as DOCI (seniority-zero sector), wave functions including the (0+2) sectors (combining DOCI and two unpaired electron determinants), (0+2+4) sector wave functions, and FCI (here equal to (0+2+4+6) wave functions). Figure 2 shows the results, again indicating that there is no obvious relationship. As in Fig. 1, virtually indistinguishable energies are obtained once below a cut-off value in I_C . Any fundamental and quantitative relationship between I_C and the truncated CI energies should apply over the entire range of I_C values, including the large number of random basis sets with high I_C in Figs. 1 and 2 and as discussed such a good correlation is absent. As higher excitations are included, more basis sets of quite different I_C values converge to a lower energy plateau as eventually FCI is independent of the basis chosen. That some high I_C basis sets result often in the highest energies is not surprising as one could also imagine maximising the entropy and using one of the many determinants with all (virtually) the same absolute coefficient in the FCI expansion. Still, the main observation is that high entropy does not automatically mean high energy despite an apparent but not quantitative tendency.

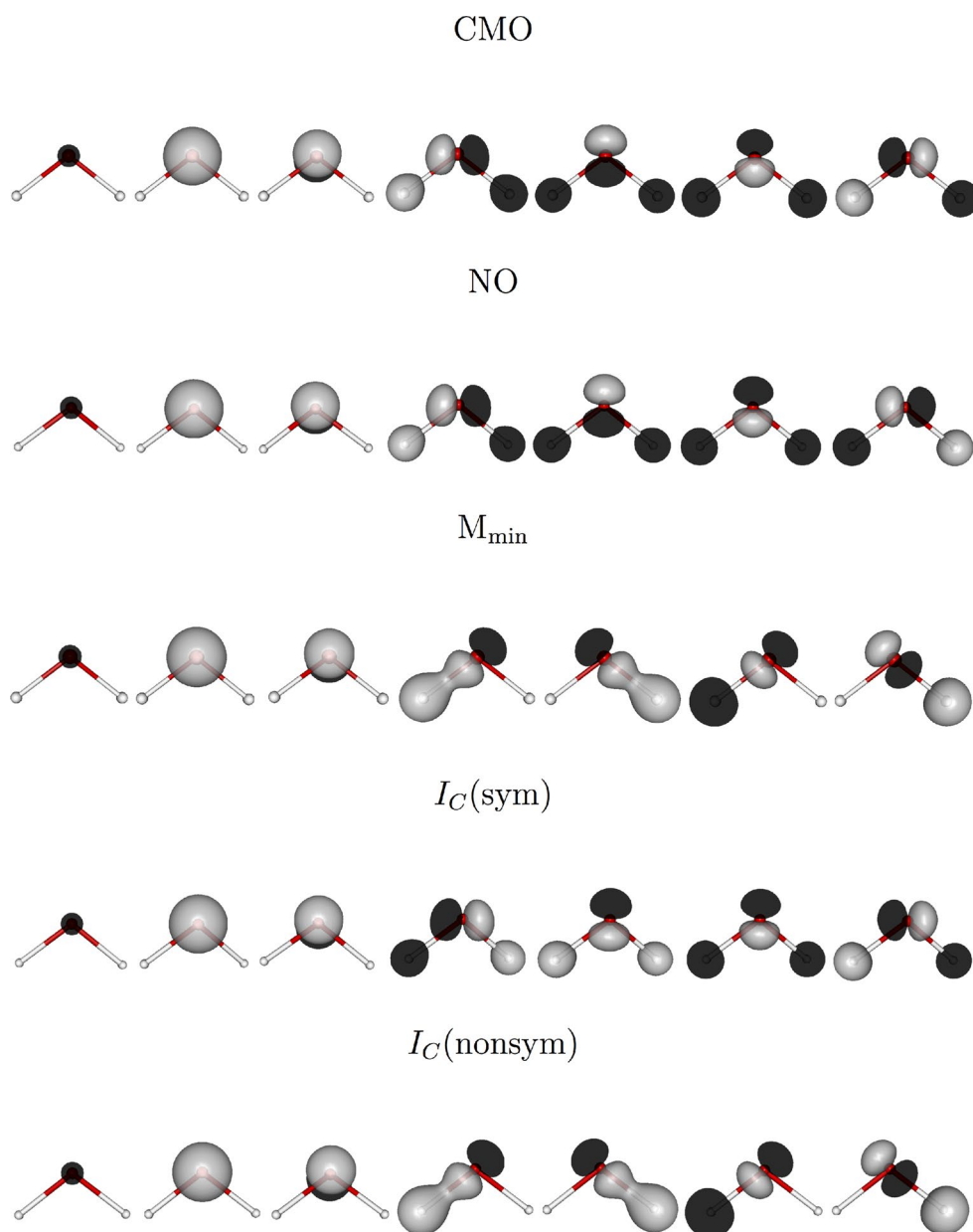
Fig. 3 Symmetry of the orbitals used in this work for the H₂O at equilibrium geometry. ± 0.11 a.u. isosurfaces in all plots



Another aspect mentioned in the Introduction, which deserves to be remarked, is the localisation properties of the orbitals that compose the basis sets used in this work. As is well known, the split-localised natural orbitals are among the best sets in terms of CI series convergence. However, this localisation entails symmetry breaking [14]. We have checked this property plotting in Figs. 3 and 4 the orbitals arising from all reported methods for the H₂O molecule at the equilibrium and stretched geometries. As can be observed, the CMO, NO and $I_C(\text{sym})$

orbitals maintain the symmetry, while it is broken in the cases of the M_{\min} and $I_C(\text{nonsym})$ methods; the unconstrained minimisation of seniority number or entropy causes orbital localisation on atoms and bonding directions, which agrees with genuine chemical behaviour. This agrees with what was previously pointed out in Ref. [14] for natural orbitals (symmetry adapted) and split-localised ones where the symmetry adaptation is sacrificed to obtain a better localisation and a faster convergence for CI expansions.

Fig. 4 Symmetry of the orbitals used in this work for the H₂O at stretched geometry, ± 0.11 a.u. isosurfaces in all plots



5 Conclusions

The compactness of FCI N -electron wave functions expressed in different molecular basis sets has been scrutinised, including a basis designed to minimise the Shannon entropy as a benchmark. For the latter, both symmetry conserving and nonsymmetry conserving simulated annealing procedures have been used. Numerical determinations of Shannon entropy indices on several systems using FCI wave functions have revealed that the compactness of the wave functions may depend significantly on the molecular basis.

The seniority-number minimising basis performs nearly as well as the nonsymmetry conserving entropy minimising

basis set, and both of them lead to more compact wave functions than the natural orbital and canonical molecular orbital basis sets. In case of two-electron systems, all the studied basis sets, except the canonical molecular orbital one, give rise to the same entropy value due to their special features.

The hypothesis that a more compact FCI wave function would allow us to extract a better single-reference determinant to initiate one-electron excitation-based truncated CI or seniority-based truncated CI calculations that give lower energies is shown to be false. Some basis sets with higher I_C values may still result in low truncated CI energies although there appears to be a cut-off above which

there is a tendency towards higher energies. Choosing an orbital basis that makes FCI more compact does not seem to automatically lead to more rapidly convergent truncated CI expansions using either the excitation hierarchy or the seniority hierarchy. Choosing the right configurations seems to be more important than choosing the right orbitals.

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