Hybrid Treatments Based on Determinant Seniority Numbers and Spatial Excitation Levels in the Configuration Interaction Framework

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Abstract

In this work we project the Hamiltonian of an N-electron system onto a set of N-electron determinants cataloged by their seniority numbers and their excitation levels with respect to a reference determinant. We show that, in open-shell systems, the diagonalization of the N-electron Hamiltonian matrix leads to eigenstates of the operator $\hat{S}^2$ when the excitation levels are counted in terms of spatial orbitals instead of spin-orbitals. Our proposal is based on the commutation relations between the N-electron operators seniority number and spatial excitation level, as well as between these operators and the spin operators $\hat{S}^2$ and $\hat{S}_z$. Energy and $< \hat{S}^2 >$ expectation values of molecular systems obtained from our procedure are compared with those arising from the standard hybrid configuration interaction methods based on seniority numbers and spin-orbital-excitation levels. We analyze the behavior of these methods, evaluating their computational costs and establishing their usefulness.

1. INTRODUCTION

The full configuration interaction (FCI) method provides the exact determination of electronic energies in N-electron systems but its practical use is limited to systems with few electrons and small basis sets, due to its high computational cost. To reduce this cost, configuration interaction (CI) methods have been proposed, in which only a limited number of N-electron Slater determinants is used to project the Hamiltonian onto the N-electron space [1–5]. This selection has been made following mainly two criteria. In the excitation-based scheme, the Hamiltonian is projected onto an N-electron determinant set constituted by the reference determinant and those possessing up to a given integer of different occupation numbers (counted in terms of spin-orbitals or spatial orbitals) with respect to that reference. Another criterion is to select N-electron Slater determinants using their seniority number, i.e. the number of unpaired electrons involved in each determinant [6–11]. The excitation-based methods have been qualified as more efficient to describe systems presenting essentially dynamic correlation while the seniority-based procedures are preferred [7] for systems exhibiting high static correlation. More recently, hybrid methods, combining both criteria, have been proposed to select the determinants [12–14]. This type of method has proven to be useful to describe systems which present both dynamic and static correlation [7, 13–17], as well as dissociation or bond-breaking processes, where the system can show mainly dynamic correlation near the equilibrium geometries and static correlation at stretched arrangements. However, to our knowledge, the reported results have been restricted to closed-shell systems and the spin-orbital excitation version.

The seniority-number based CI treatments provide spin-adapted wave-functions for all type of system, with any number of electrons (even or odd), and for any spin symmetry [8, 18]. However, in open-shell systems, the ordinary excitation-based CI procedures may lead to spin-contaminated wave-functions when the excitations are described in terms of spin-orbitals. In Ref. [19] we have recently proven that the spin contamination in the excitation-based CI treatments can be avoided counting the excitation levels in terms of spatial orbitals instead of spin-orbitals. We have proposed an N-electron spin-free excitation operator which suitably evaluates the spatial excitation number. In this work we point out that spin contamination is also detected in open-shell system wave-functions obtained from hybrid methods if the selection criterion is the spin-orbital one. Our aim is to extend the hybrid CI methodology to the study of open-shell systems, to ascertain the ability and applicability conditions of these procedures to describe a broader set of systems. Our proposal guarantees eigenstates without spin contamination for any N-electron Hamiltonian matrix generated by projection of the corresponding Hamiltonian operator onto a set of N-electron Slater determinants selected according to their seniority numbers and their spatial excitation numbers.

This work has been organized as follows. Section 2 describes the N-electron seniority number operator and the excitation number operators, that evaluate the excitation levels of an N-electron Slater determinant with respect to a reference determinant. We analyze the commutation relation between these operators, predicting the features of the linear combinations of Slater determinants, which depend on the nature of the determinant set used to project the Hamiltonian. We also describe in this section the commutation relations of these operators with the operators $\hat{S}^2$ and $\hat{S}_z$. Section 3 reports the computational details and numerical results in selected open-shell systems, confirming the predictions provided by the commutation relations and showing spin-contaminated wave-functions in the hybrid methods arising from the spin-orbital excitation version. We propose several procedures within the hybrid methodology, studying the quality of their results and their computational costs. Finally, in section 4 we point out the conclusions that can be drawn from this work.

2. THEORY

2.1. Commutation relations

Let $a^{\dagger}_{i^\sigma}$ and a_{i^σ} be the fermion creation and annihilation operators, respectively, corresponding to a spin-orbital i^σ; σ denotes the spin coordinate, α or β, and i is one of the K spatial orbitals of an orthonormal set $\{i, j, k, l, \dots\}$. The excitation level, in terms of spin-orbitals (so), of a given N-electron determinant with respect to a reference determinant (ref) is evaluated by means of the N-electron operator

$$\hat{X}^{so} = \hat{N} - \sum_{i^\alpha \in ref} a^{\dagger}_{i^\alpha} a_{i^\alpha} - \sum_{i^\beta \in ref} a^{\dagger}_{i^\beta} a_{i^\beta} \tag{1}$$

where $\hat{N}$ is the particle number operator. The expectation value of this operator $< \hat{X}^{so} >$ for a Slater determinant constitutes the excitation level of the analyzed determinant in terms of spin-orbitals. Alternatively, an N-electron spatial-orbital (sp) excitation-level operator can be defined by means of the spin-free first- and second-order replacement operators $\hat{E}^i_j = \sum_\sigma a^{\dagger}_{i^\sigma} a_{j^\sigma}$ and $\hat{E}^{ik}_{jl} = \sum_{\sigma_1,\sigma_2} a^{\dagger}_{i^{\sigma_1}} a^{\dagger}_{k^{\sigma_2}} a_{l^{\sigma_2}} a_{j^{\sigma_1}}$, respectively, [20, 21]; this N-electron excitation operator has been expressed as [19]

$$\hat{X}^{sp} = \hat{N} - \sum_{i \in ref} \hat{E}^i_i + \frac{1}{2} \sum_{i \in sref} \hat{E}^{ii}_{ii} \tag{2}$$

In this equation, the index i runs over all the reference singly or doubly occupied orbitals in the sum $\sum_{i \in ref}$, while that index only runs over the reference singly occupied ($sref$) spatial orbitals in the sum $\sum_{i \in sref}$. The expectation value $< \hat{X}^{sp} >$ for a given determinant evaluates its excitation level in the spatial-orbital procedure with respect to a given reference. Both operators $\hat{X}^{so}$ and $\hat{X}^{sp}$ coincide when the reference determinant is closed-shell. On the other hand, the N-electron seniority number operator has been formulated by means of spin-free replacement operators as [8, 12, 18]

$$\hat{\Omega} = \sum_i (\hat{E}^i_i - \hat{E}^{ii}_{ii}) \tag{3}$$

Its expectation value $< \hat{\Omega} >$ for an N-electron determinant evaluates the number of unpaired electrons involved.

The commutation relations between the spin operators $\hat{S}^2$ and $\hat{S}_z$ and the operators $\hat{\Omega}$ and $\hat{X}^{sp}$ have been previously reported [18, 19], concluding that $[\hat{S}^2, \hat{\Omega}] = 0$; $[\hat{S}^2, \hat{X}^{sp}] = 0$; $[\hat{S}_z, \hat{\Omega}] = 0$; and $[\hat{S}_z, \hat{X}^{sp}] = 0$. These relations have easily been shown by means of the spin-free replacement operator product rules [22, 23], expressing the spin-free $\hat{S}^2$ operator as [24, 25]

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

in which the δ symbol means the Kronecker delta. Using those operator product rules or the well-known commutation rules of the fermion operators, one also shows

$$[\hat{\Omega}, \hat{X}^{sp}] = 0 \tag{5}$$

and

$$[\hat{\Omega}, \hat{X}^{so}] = 0 \tag{6}$$

which allow us to decompose a space of determinants of a given seniority number into different subspaces characterized by their excitation levels, or vice versa. However, unlike the $\hat{X}^{sp}$ operator, for an open-shell reference one finds

$$[\hat{S}^2, \hat{X}^{so}] \neq 0 \tag{7}$$

This relation and the $[\hat{S}^2, \hat{X}^{sp}] = 0$ one [19] justify that the spin-orbital based and the spatial-orbital based determinant selection schemes lead to different spin features in the resulting CI wave functions.

2.2. Spin-adapted hybrid methods

Eqs. (2) and (3) mean that a given Slater determinant possesses integer eigenvalues $X^{sp} =< \hat{X}^{sp} >$ and $\Omega =< \hat{\Omega} >$ for the corresponding $\hat{X}^{sp}$ and $\hat{\Omega}$ operators respectively. Moreover, in agreement with Eq. (5) linear combinations of determinants of identical eigenvalue X^{sp} and those with identical Ω eigenvalue can also be eigenfunctions of the $\hat{S}^2$ and $\hat{S}_z$ operators. This feature is not maintained in the case of the $\hat{X}^{so}$ operator which, according to Eq. (7), does not commute with the $\hat{S}^2$ operator. These properties ensure the construction of spin-adapted configurations of Slater determinants with quantum numbers S, S_z, X^{sp}, and Ω. Likewise, these linear combinations of Slater determinants with different parameters X^{sp} and Ω but with identical quantum numbers S and S_z (spin degenerated functions) can be combined, yielding more general eigenfunctions of the $\hat{S}^2$ and $\hat{S}_z$ operators.

An N-electron non-relativistic Hamiltonian, $\hat{H}$, of chemical interest possesses pairwise interactions satisfying the well-known commutation relations $[\hat{H}, \hat{S}^2] = 0$ and $[\hat{H}, \hat{S}_z] = 0$. Within the CI treatment methodology, this Hamiltonian is usually projected onto an N-electron Slater determinant set of $S_z \geq 0$ quantum number, leading to an N-electron Hamiltonian matrix. If the determinants of the set onto which the Hamiltonian is projected have been cataloged according to the parameters X^{sp} or Ω, diagonalizing this matrix one finds spin-adapted eigenstates corresponding to all possible spin quantum numbers $S = S_z, \ldots, S_{\max}$ ($S_{\max} = \min(\frac{N}{2}, K - \frac{N}{2})$). Contrary to this situation, one can obtain spin contaminated states, in systems described by open-shell reference determinants, if the excitation levels of the determinants arise from the expectation value of the operator in Eq. (1). The N-electron determinant set can be the union of sets corresponding to several values of X^{sp} and Ω, where the determinants common to both subsets are only taken into account once. A preliminary study of this procedure, limited to closed-shell systems, has been reported in Ref. [12] attempting to describe systems which present dynamic and static correlation. These union hybrid configuration interaction methods hereafter will be denoted by CI-$\bigcup_{X=0,\ldots,X_q^{sp}}^{\Omega=\Omega_1,\ldots,\Omega_p}$. In this notation, $\Omega_1, \ldots, \Omega_p$ is a sequence with extremes Ω_1 and Ω_p and some intermediate values meaning that all determinants of these seniority numbers have been selected, and similarly for the sequence of excitation levels $0, \ldots, X^{sp}_q$ which starts with $X^{sp} = 0$ and ends at a given X^{sp}_q value. Obviously, the case CI-$\bigcup^{\Omega=2S,\ldots,\Omega_{\max}}_{X=0,\ldots,X^{sp}_{\max}}$ corresponds to the FCI treatment, which requires the use of all Ω values, from the minimum $\Omega_{\min} = 2S$ to the maximum $\Omega_{\max} = \min(N, 2K - N)$ [12]; it contains the total number of possible determinants and, consequently, it also includes all possible excitations, from the zeroth level to the highest one, $X^{sp}_{\max} = \min(N, K - 2S, 2K - N)$ for the substates $S_z = S$. Alternatively, the selection of the determinants can be limited to the intersection of sets defined by the series of parameters X^{sp} and Ω, what will be denoted by CI-$\bigcap^{\Omega=\Omega_1,\ldots,\Omega_p}_{X=0,\ldots,X^{sp}_q}$; this kind of methods has been proposed for closed-shell systems in Ref. [14], trying to reduce the computational cost of the seniority-number CI methodology. Similarly to the CI-$\bigcup^{\Omega=2S,\ldots,\Omega_{\max}}_{X=0,\ldots,X^{sp}_{\max}}$ method, the CI-$\bigcap^{\Omega=2S,\ldots,\Omega_{\max}}_{X=0,\ldots,X^{sp}_{\max}}$ one coincides with the FCI treatment. These procedures offer a wide variety of possibilities whose behaviors and computational costs deserve to be analyzed in the case of open-shell systems. Moreover, the results for the energy and $< \hat{S}^2 >$ quantity arising from the proposed spatial selection procedure must be compared with those obtained when the excitation levels are selected according to the expectation values of the operator in Eq. (1).

3. RESULTS AND DISCUSSION

We have selected several N-electron Slater determinant sets cataloged by the parameters $\Omega =< \hat{\Omega} >$ and $X =< \hat{X}^{sp} >$ (in the spatial-orbital treatment) as well as by $\Omega =< \hat{\Omega} >$ and $X =< \hat{X}^{so} >$ (in the spin-orbital one), to construct the projected N-electron Hamiltonian matrices for open-shell systems in ground states. These N-electron matrices have been expressed in the canonical Hartree-Fock molecular orbitals and the molecular orbitals minimizing the energy of all the CI-expansions (as is well known, the CI methods are not invariant to arbitrary orbital rotations [7] except in the FCI limit case). The excitation levels of the determinants have been calculated with respect to those restricted open-shell Hartree-Fock (ROHF) Slater ones when the canonical molecular orbitals have been used; otherwise, the references have been built from the optimized orbital basis sets. To obtain an affordable computational cost we have used the one-electron minimal STO-3G atomic basis sets. Calculations have been carried out with all electrons and all orbitals correlated. The lowest energies of each spin symmetry and the expectation values $< \hat{S}^2 >$ have been described at optimized FCI/STO-3G geometries and at stretched ones (in one of the systems). The standard one- and two-electron integrals required to formulate the N-electron Hamiltonians of these species have been obtained from a modified version of the PSI 3.3 package [26]. The determination of energy and $< \hat{S}^2 >$ values of all CI methods described comes from our own codes, based on Refs. [27].

In Tables 1 and 2 we report results corresponding to doublet (CO^+ molecule-ion) and triplet (CH_2 diradical) states, respectively; these results arise from optimized geometries and canonical Hartree-Fock molecular orbital basis sets. In these calculations we have assumed the largest Abelian subgroup of the point group describing the full symmetry of each compound, which is selected by the PSI 3.3 package ($C_{2v} \subset C_{\infty v}$ or $D_{2h} \subset D_{\infty h}$). In both Tables we specify FCI results on the first line which, as mentioned in previous section, arise from the projection of the Hamiltonians onto sets of all possible determinants of $S_z = S$ value constructed with the used one-electron basis set; these sets can be described either in terms of the seniority-number parameter $\Omega = \Omega_{\text{min}}, \ldots, \Omega_{\text{max}}$ or in terms of the excitation one $X = 0, \ldots, X_{\text{max}}$. Both sets are identical and consequently their intersection set is again the same. The results reported in lines 2, 3, and 4 of these Tables correspond to the configuration interaction at single excitations (CIS), at single and double excitations (CISD), and at single, double, and triple ones (CISDT), respectively. The subsets of determinants described by these excitations, $X = 0, 1$, $X = 0 - 2$, and $X = 0 - 3$ are included in the whole set $\Omega = \Omega_{\text{min}}, \ldots, \Omega_{\text{max}}$; consequently, in our formalism, they can be represented by the corresponding intersection set. Similarly, the results in lines 5 and 6 arise from a pure seniority-number CI approach and correspond to the lower values of the Ω parameter. All these values have been included in those Tables to be compared with those obtained from hybrid CI methods of intersection and union types reported in the rest of the lines.

The results shown in Table 1 (a doublet system) present a spin contamination in most of the states described within the spin-orbital scheme reaching a value $<\hat{S}^2>= 0.78604$ in the CIS method while the spatial-orbital treatments always yield values $<\hat{S}^2>= 0.75000$. The energy values of the pure spin states are lower than the spin-contaminated counterparts, what shows the approximated methods yielding spin-adapted wave-functions are more suitable, without a significant increase of computational cost. These features can also be observed in Table 2, in which we describe the methylene radical in its triplet ground state reaching up $<\hat{S}^2>= 2.00852$ values for spin contamination in the spin-orbitals treatments and with $<\hat{S}^2>= 2.00000$ values for the spatial-orbital methods. The number of Slater determinants contained in the intersection sets defined by the parameters Ω and X is markedly lower than in their counterpart pure or union set CI methods. Consequently, the energies obtained from the intersection methods are higher, since they arise from shorter determinant expansions. The CI-$\bigcap_{X=0,1}^{\Omega=1}$, CI-$\bigcap_{X=0,1}^{\Omega=2}$, and CI-$\bigcap_{X=0,1}^{\Omega=3}$ methods for doublet and triplet respectively, require the addition of very few Slater determinants to the reference one; they do not alter the restricted open-shell Hartree-Fock energies ($\mathrm{E_{ROHF}}$) and do not yield spin-contaminated wave functions, meaning such configurations do not contribute to the approximate wave function expansion. All these results also indicate that the counterpart union methods CI-$\bigcup_{X=0,1}^{\Omega=1}$, CI-$\bigcup_{X=0,1}^{\Omega=2}$, and CI-$\bigcup_{X=0,1}^{\Omega=3}$ lower the energy with respect to the ROHF one. As shown in Table 1, the CI-$\bigcap_{X=0-3}^{\Omega=1,3}$ method yields energies close to those of the pure seniority-number CI-$\bigcap_{X=0-X_{\max}}^{\Omega=1,3}(\Omega = 1,3)$ method, at a drastically lower computational cost. In Table 2 we show the results for the triplet system obtained from the methods CI-$\bigcap_{X=0-3}^{\Omega=2,4}$. These results are also close to those obtained from the pure seniority-number CI-$\bigcap_{X=0-X_{\max}}^{\Omega=2,4}(\Omega = 2,4)$ one. All these results point out the practical usefulness of the intersection methods; they approach their pure seniority-number CI counterparts (including static correlation) at a considerable reduced computational cost. We must highlight the results arising from the methods CI-$\bigcup_{X=0-2}^{\Omega=\Omega_{\min}}$ and CI-$\bigcup_{X=0-3}^{\Omega=\Omega_{\min}}$ in relation to the FCI ones. In the case of doublet system

CO^+ (Table 1) the methods CI-$\bigcup_{X=0-2}^{\Omega=1}$ and CI-$\bigcup_{X=0-3}^{\Omega=1}$ yield energy values (spatial-orbital version) -110.950882 E_h and -110.955263 E_h while the FCI gives -110.961561 E_h, with computational costs 1722, 5950 and 25200 determinants, respectively. The numerical determinations shown in Table 2 for triplet state yield similar behaviors if we compare the results arising from the CI-$\bigcup_{X=0-2}^{\Omega=2}$, CI-$\bigcup_{X=0-3}^{\Omega=2}$, and FCI methods. These results show the improvement of the numerical values obtained from the pure minimum-seniority-number CI methods when the set of determinants projecting the Hamiltonian is extended with the set of lower excitation levels.

To complement this type of study we have gathered, in Table 2, other results corresponding to the methylene radical at optimized geometry. These results have been obtained performing a minimization of the energy for each CI expansion by means of orbital rotations. A comparison of these results with their counterparts also reported in Table 2 shows that greatest energy differences are shown mainly by the pure and hybrid seniority-based methods. This behavior has also been observed for the other molecular systems studied. All these results confirm the strong dependence of these seniority-based methods on the used basis set, which has been pointed out in other works for closed-shell systems [7, 9, 12, 14], as well as the possibility of improving this type of results if optimized orbitals are used instead of those Hartree-Fock ones.

In closed-shell systems, the hybrid treatments have proven to be specially useful to describe dissociation or bond-breaking processes presenting both dynamic and static correlation, depending on their geometrical arrangements [12]. To explore the behavior of the proposed spin-contamination-free methods along dissociation paths, in the open-shell case, we have chosen the linear hydrogen chain H_7 in its ground state, which is a benchmark system for testing new methods and represents a very challenging case of breaking many bonds. We report, in Table 3, results arising from optimized orbital basis sets for that system at several internuclear distances R_{H-H}. We have calculated the non-parallelity error (NPE) for each method (the difference between the maximum and minimum deviation from the FCI energy values in the interval of bond distances R_{H-H} studied). The H_7 chain presents predominantly static correlation in its symmetrically stretched geometries and, consequently, the seniority-number CI methods provide a more suitable description. This behavior is confirmed by the results shown in Table 3 in which the values of the NPE quantity arising from the pure seniority-number CI methods ($\bigcap_{X=0-X_{\max}}^{\Omega=1}(\Omega = 1)$ and $\bigcap_{X=0-X_{\max}}^{\Omega=1,3}(\Omega = 1,3)$) are much lower than those obtained from the pure excitation CI ones ($\bigcap_{X=0,1}^{\Omega=1-\Omega_{\max}}$(CIS), $\bigcap_{X=0-2}^{\Omega=1-\Omega_{\max}}$(CISD), and $\bigcap_{X=0-3}^{\Omega=1-\Omega_{\max}}$(CISDT)). In the intersection methods the low excitation levels restrict the number of determinants involved in a determined Ω value, yielding higher values of the NPE quantity than the corresponding pure seniority-number CI methods although they require a considerable lower computational cost, due to their polynomial scaling with orbital basis set size. It must be noted that determinant subspaces corresponding to quadruple excitations must be included in these CI expansions to properly describe the many-bond-breaking process involved in the symmetric stretching of this molecular system. Figure 1 shows that at near-equilibrium bond distances the intersection method proposed (CI-$\bigcap_{X=0-4}^{\Omega=1}$) yields results very close to those obtained from the seniority-based procedure CI-$\bigcap_{X=0-X_{\max}}^{\Omega=1}(\Omega = 1)$, at lower computational cost; however at stretched configurations, the accuracy of the results begins to deteriorate due to the increasing static correlation. The union hybrid methods provide very low NPE values, e.g. the CI-$\bigcup_{X=0-2}^{\Omega=1}$ method gives NPE=0.0183 with 365 determinants, which is a quarter of those required in the FCI method (1225). Figure 1 also allows one to show that the union method (CI-$\bigcup_{X=0-2}^{\Omega=1}$) incorporates the dynamic correlation missing in the results of the pure seniority-based method (CI-$\bigcap_{X=0-X_{\max}}^{\Omega=1}(\Omega = 1)$) providing better results at near-equilibrium bond distances, while at the same time it leads to close results to that method at stretched distances, where the strong correlation dominates.

Figure 1 here

FIG. 1. Potential energy curve representing the symmetric dissociation of the H_7 linear chain for the ground state arising from the intersection hybrid method CI-$\bigcap_{X=0-4}^{\Omega=1}$ and union hybrid method CI-$\bigcup_{X=0-2}^{\Omega=1}$ and comparison with those obtained from the ROHF, CI-pure-excitacion-based CISD, CI-pure-seniority-based $\Omega = 1$, and FCI methods. Results correspond to molecular orbitals arising from standard STO-3G atomic basis sets. For all CI-expansions the energy is minimized by performing orbital rotations (using all orbitals of the basis set).

4. CONCLUDING REMARKS

We have proposed to project an N-electron Hamiltonian by means of sets of N-electron Slater determinants selected by hybrid procedures, based on seniority-number and excitation-number schemes, within the CI methodology framework. We show that the selection of determinants with excitation number defined in terms of spatial orbitals ensures spin contamination-free wave functions in open- and closed-shell systems, while the spin-orbital criterion can lead to spin contamination. Our proposal is based on the commutation relation between the N-electron seniority number operator and the recently reported spatial excitation one. We have tested this theoretical achievement performing numerical determinations in doublet and triplet systems, proving that the energies obtained from our determinant-union-set hybrid methods improve on those arising from the individual seniority-number and spin-orbital-excitation based treatments. An analysis of closeness to the exact energies (the FCI ones) shows that the pure seniority-level methods can be improved at a reasonable increase of computational cost, if the set of N-electron determinants which projects the Hamiltonian is extended to those possessing low excitation levels or vice versa, although in this latest case its cost is higher. Moreover, we have found energy results close to the pure seniority-number CI treatments, with an important reduction of the computational cost, when one uses hybrid methods whose N-electron Slater determinants belong to the intersection sets between the excitation-levels and the seniority-number ones. Other possibilities of using union and intersection hybrid methods are currently being explored in our laboratories.

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TABLE 1. No. determinants and energies (in E_h) arising from CI methods for the doublet system $CO^+(^2\Sigma^+)$ at FCI/STO-3G optimized geometry. Results correspond to Hartree-Fock molecular orbitals arising from standard STO-3G atomic basis sets. Molecular orbital occupation numbers in the reference-ROHF determinant: $\sigma^2\sigma^2\sigma^2\sigma^2\pi^2\pi^2\sigma^1\pi^0\pi^0\sigma^0$. $E_{\mathrm{ROHF}} = -110.797197$ E_h. $\Omega_{\max} = 7$. $X_{\max} = 7$.

	spatial-orbital treatment		spin-orbital treatment	
CI method	No. determ.	Energy	No. determ.	Energy
$\bigcap_{X=0-X_{\max}}^{\Omega=1-\Omega_{\max}}$(FCI)	25200	-110.961561	25200	-110.961561
$\bigcap_{X=0,1}^{\Omega=1-\Omega_{\max}}$(CIS)	64	-110.808622	46	-110.802231
$\bigcap_{X=0-2}^{\Omega=1-\Omega_{\max}}$(CISD)	946	-110.946612	703	-110.946384
$\bigcap_{X=0-3}^{\Omega=1-\Omega_{\max}}$(CISDT)	5300	-110.952460	4220	-110.951380
$\bigcap_{X=0-X_{\max}}^{\Omega=1}(\Omega = 1)$	840	-110.871825	840	-110.871825
$\bigcap_{X=0-X_{\max}}^{\Omega=1,3}(\Omega = 1, 3)$	8400	-110.910133	8400	-110.910133
$\bigcap_{X=0,1}^{\Omega=1}$	10	-110.797197	10	-110.797197
$\bigcap_{X=0-2}^{\Omega=1}$	64	-110.869018	64	-110.869018
$\bigcap_{X=0-3}^{\Omega=1}$	190	-110.869482	190	-110.869482
$\bigcap_{X=0,1}^{\Omega=1,3}$	64	-110.808622	46	-110.802231
$\bigcap_{X=0-2}^{\Omega=1,3}$	496	-110.901978	433	-110.901975
$\bigcap_{X=0-3}^{\Omega=1,3}$	1900	-110.905897	1790	-110.905009
$\bigcup_{X=0,1}^{\Omega=1}$	894	-110.885796	876	-110.878489
$\bigcup_{X=0-2}^{\Omega=1}$	1722	-110.950882	1479	-110.950662
$\bigcup_{X=0-3}^{\Omega=1}$	5950	-110.955263	4870	-110.954101
$\bigcup_{X=0,1}^{\Omega=1,3}$	8400	-110.910133	8400	-110.910133
$\bigcup_{X=0-2}^{\Omega=1,3}$	8850	-110.956276	8670	-110.956093
$\bigcup_{X=0-3}^{\Omega=1,3}$	11800	-110.957628	10900	-110.957203

TABLE 2. No. determinants and energies (in E_h) arising from CI methods for the triplet system $CH_2(^3B_1)$ at FCI/STO-3G optimized geometry. Results correspond to (A) Hartree-Fock molecular orbitals arising from standard STO-3G atomic basis sets; (B) orbitals which minimize the energy of all CI-expansions by means of orbital rotations (using all orbitals of the basis set). Molecular orbital occupation numbers in the reference-ROHF determinant: $a_1^2 a_1^2 b_2^2 b_1^1 a_1^1 b_2^0 a_1^0$. $E_{\text{ROHF}} = -38.430850\ E_h$. $\Omega_{\max} = 6$. $X_{\max} = 5$.

	spatial-orbital treatment			spin-orbital treatment		
CI method	No. determ.	Energy (A)	Energy (B)	No. determ.	Energy (A)	Energy (B)
$\bigcap_{X=0-X_{\max}}^{\Omega=2-\Omega_{\max}}$(FCI)	735	-38.474746	-38.474746	735	-38.474746	-38.474746
$\bigcap_{X=0,1}^{\Omega=2-\Omega_{\max}}$(CIS)	35	-38.438238	-38.455016	23	-38.434237	-38.451219
$\bigcap_{X=0-2}^{\Omega=2-\Omega_{\max}}$(CISD)	234	-38.474020	-38.474281	171	-38.473982	-38.474005
$\bigcap_{X=0-3}^{\Omega=2-\Omega_{\max}}$(CISDT)	558	-38.474433	-38.474745	475	-38.474292	-38.474704
$\bigcap_{X=0-X_{\max}}^{\Omega=2}(\Omega = 2)$	210	-38.449096	-38.468084	210	-38.449096	-38.468084
$\bigcap_{X=0-X_{\max}}^{\Omega=2,4}(\Omega = 2, 4)$	630	-38.461601	-38.474726	630	-38.461601	-38.474726
$\bigcap_{X=0,1}^{\Omega=2}$	11	-38.430850	-38.434888	11	-38.430850	-38.434888
$\bigcap_{X=0-2}^{\Omega=2}$	57	-38.448995	-38.465874	57	-38.448995	-38.465874
$\bigcap_{X=0-3}^{\Omega=2}$	129	-38.449019	-38.467744	129	-38.449019	-38.467744
$\bigcap_{X=0,1}^{\Omega=2,4}$	35	-38.438238	-38.455016	23	-38.434237	-38.451219
$\bigcap_{X=0-2}^{\Omega=2,4}$	189	-38.461134	-38.473913	153	-38.461121	-38.473779
$\bigcap_{X=0-3}^{\Omega=2,4}$	453	-38.461486	-38.474668	401	-38.461381	-38.474644
$\bigcup_{X=0,1}^{\Omega=2}$	234	-38.457048	-38.470934	222	-38.452784	-38.469557
$\bigcup_{X=0-2}^{\Omega=2}$	387	-38.474382	-38.474532	324	-38.474344	-38.474412
$\bigcup_{X=0-3}^{\Omega=2}$	639	-38.474746	-38.474746	556	-38.474595	-38.474739
$\bigcup_{X=0,1}^{\Omega=2,4}$	630	-38.461601	-38.474726	630	-38.461601	-38.474726
$\bigcup_{X=0-2}^{\Omega=2,4}$	675	-38.474745	-38.474746	648	-38.474716	-38.474745
$\bigcup_{X=0-3}^{\Omega=2,4}$	735	-38.474746	-38.474746	704	-38.474737	-38.474746

TABLE 3. No. determinants, energies (in E_h) and non-parallelity errors (NPE) arising from CI methods for the symmetric dissociation of the ground state linear chain $\mathrm{H}_7(^2\Sigma_u^+)$ in the spatial-orbital treatment. Results correspond to molecular orbitals arising from standard STO-3G atomic basis sets. For all CI-expansions the energy is minimized by performing orbital rotations (using all orbitals of the basis set). $\mathrm{E}_{\mathrm{ROHF}} = -2.332387\ E_h$ ($\mathrm{R}_{\mathrm{H-H}} = 0.5$Å), $\mathrm{E}_{\mathrm{ROHF}} = -3.619286\ E_h$ ($\mathrm{R}_{\mathrm{H-H}} = 1.0$Å), $\mathrm{E}_{\mathrm{ROHF}} = -3.208888\ E_h$ ($\mathrm{R}_{\mathrm{H-H}} = 1.5$Å), $\mathrm{E}_{\mathrm{ROHF}} = -2.790254\ E_h$ ($\mathrm{R}_{\mathrm{H-H}} = 2.0$Å). $\Omega_{\max} = 7$. $X_{\max} = 6$.

		Energy				
CI method	No. determ.	0.5Å	1.0Å	1.5Å	2.0Å	NPE
$\bigcap_{X=0-X_{\max}}^{\Omega=1-\Omega_{\max}}$(FCI)	1225	-2.377684	-3.735490	-3.484820	-3.319563	-
$\bigcap_{X=0,1}^{\Omega=1-\Omega_{\max}}$(CIS)	34	-2.359550	-3.673101	-3.311253	-2.982748	0.3187
$\bigcap_{X=0-2}^{\Omega=1-\Omega_{\max}}$(CISD)	259	-2.377345	-3.728787	-3.430805	-3.165486	0.1537
$\bigcap_{X=0-3}^{\Omega=1-\Omega_{\max}}$(CISDT)	744	-2.377660	-3.734540	-3.483909	-3.267026	0.0525
$\bigcap_{X=0-4}^{\Omega=1-\Omega_{\max}}$(CISDTQ)	1119	-2.377684	-3.735485	-3.484810	-3.319559	<0.0001
$\bigcap_{X=0-X_{\max}}^{\Omega=1}(\Omega = 1)$	140	-2.358448	-3.696174	-3.448042	-3.304486	0.0242
$\bigcap_{X=0-X_{\max}}^{\Omega=1,3}(\Omega = 1,3)$	770	-2.377000	-3.734178	-3.483144	-3.318770	0.0010
$\bigcap_{X=0,1}^{\Omega=1}$	7	-2.342917	-3.619286	-3.237604	-2.840664	0.4441
$\bigcap_{X=0-2}^{\Omega=1}$	34	-2.357674	-3.684688	-3.394301	-3.156930	0.1426
$\bigcap_{X=0-3}^{\Omega=1}$	70	-2.358425	-3.693982	-3.417059	-3.167314	0.1330
$\bigcap_{X=0-4}^{\Omega=1}$	115	-2.358448	-3.695781	-3.440819	-3.276667	0.0248
$\bigcap_{X=0,1}^{\Omega=1,3}$	34	-2.359550	-3.673101	-3.311253	-2.982748	0.3187
$\bigcap_{X=0-2}^{\Omega=1,3}$	169	-2.375968	-3.724878	-3.425913	-3.161032	0.1568
$\bigcap_{X=0-3}^{\Omega=1,3}$	439	-2.376920	-3.732269	-3.453935	-3.241648	0.0772
$\bigcap_{X=0-4}^{\Omega=1,3}$	664	-2.377002	-3.733937	-3.478972	-3.298642	0.0202
$\bigcup_{X=0,1}^{\Omega=1}$	167	-2.369921	-3.714751	-3.452424	-3.306457	0.0246
$\bigcup_{X=0-2}^{\Omega=1}$	365	-2.377412	-3.731666	-3.466279	-3.308474	0.0183
$\bigcup_{X=0-3}^{\Omega=1}$	814	-2.377675	-3.735126	-3.484022	-3.310441	0.0091
$\bigcup_{X=0-4}^{\Omega=1}$	1144	-2.377684	-3.735482	-3.484816	-3.316080	0.0035
$\bigcup_{X=0,1}^{\Omega=1,3}$	770	-2.377000	-3.734178	-3.483144	-3.318770	0.0010
$\bigcup_{X=0-2}^{\Omega=1,3}$	860	-2.377640	-3.735104	-3.484242	-3.318876	0.0006
$\bigcup_{X=0-3}^{\Omega=1,3}$	1075	-2.377683	-3.735472	-3.484660	-3.319092	0.0005
$\bigcup_{X=0-4}^{\Omega=1,3}$	1225	-2.377684	-3.735490	-3.484820	-3.319563	0.0000