Variational determination of the two-electron reduced density matrix within the doubly occupied configuration interaction scheme: An extension to the study of open-shell systems

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ABSTRACT

This work proposes to describe open-shell molecules or radicals using the framework of the doubly occupied configuration interaction (DOCI) treatments, so far limited to closed-shell system studies. The proposal is based on considering molecular systems in singlet states generated by adding extra hydrogen atoms located at infinite distance from the target radical system. The energy of this radical is obtained by subtracting the energies of the dissociated hydrogen atoms from that provided by the two-electron reduced density matrix corresponding to the singlet state system in the DOCI space, which is variationally calculated by imposing a set of N-representability conditions. This method is numerically assessed by describing potential energy curves and reduced density matrices in selected ionic and neutral open-shell systems in the doublet spin symmetry ground state.

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I. INTRODUCTION

The exact solutions of the Schrödinger equation of an N-electron system within a subspace are the corresponding full configuration interaction (FCI) expansions. However, the practical application of this treatment is restricted to small systems, using small basis sets, due to its high computational cost. One of the most popular approximations of the FCI method is the configuration interaction (CI) technique, which consists in selecting, according to a determined criterion, some of the N-electron Slater determinants involved in the FCI expansion.[1] In the doubly occupied configuration interaction (DOCI) method, the N-electron wave functions are expanded in basis sets of N-electron Slater determinants in which all spatial orbitals are doubly occupied.[2,3] This method has aroused a considerable interest during the last decade, due to its mathematical simplicity and its ability to satisfactorily describe N-electron

systems possessing the so-called strong or static correlation.[4–12] As is well known, the strongly correlated N-electron systems require linear combinations of Slater determinants in order to achieve a suitable zeroth-order wave function description, which is a characteristic of the multi-reference methods. However, the applicability of the DOCI method is also limited by its high computational cost, since it scales factorially with the size of the one-electron basis set used.[6] Notwithstanding, this computational expense can be drastically reduced to a low polynomial scaling one if the elements of the two-electron reduced density matrix (2-RDM) corresponding to an N-electron DOCI wave function are variationally approximated imposing some N-representability conditions[13,14] to ensure its physical meaning. As is well known, all elemental physical quantities corresponding to one- and two-body operators, including the energy, can be determined from that matrix. This procedure has been called the v2RDM-DOCI method.[15,16] Another limitation of the DOCI methodology arises from the fact that the seniority number[17,18] (or number of unpaired electrons) of the determinants involved in the DOCI type wave function expansions is zero, and consequently, the standard treatments cannot describe open-shell N-electron systems.

On the other hand, many scientific areas such as atmospheric chemistry, chemical reactivity, medicine, and so forth are currently demanding the implementation of rigorous studies of N-electron systems having unpaired electrons. This is due to the importance, in those areas, of processes involving radicals, in which a very common feature is the presence of strong correlation. Consequently, strategies aimed at achieving suitable descriptions of open-shell N-electron systems by means of variational determinations of the 2-RDM elements or by geminal-based approaches have been reported by several authors.[19–22] Although this task has been undertaken by means of different procedures, one of the most successful approaches proposes the addition of some hydrogen atoms, which are situated at infinite distances from chemical species of interest, e.g., an open-shell molecule or radical (neutral or ionic), constituting a kind of aggregate in the singlet state. In a subsequent step, the 2-RDM elements of the whole system are variationally evaluated satisfying certain imposed N-representability conditions. Finally, the energy of the studied species is obtained by subtracting the energy of the extra hydrogen atoms that were added to generate a singlet state, and the open-shell 2-RDM is extracted from the composite 2-RDM.[19] The aim of this work is to incorporate this technique to the DOCI schemes, in order to assess the ability of the v2RDM-DOCI method for describing open-shell N-electron systems and to profit from its computational advantages. The quality of the results obtained with this treatment is analyzed, comparing energies, reduced density matrices, spin contamination, and computational expenses with their counterparts arising from conventional methods.

The article has been organized as follows: In Sec. II, we report all theoretical aspects involved in this work, including the N-representability constraints imposed in the 2-RDM variational determinations, the procedure followed in the open-shell system description, and the specific features of the DOCI methodology. The computational details, the results obtained in selected ionic and neutral open-shell systems, and their corresponding discussion are included in Sec. III. Finally, Sec. IV points out the conclusions of this work.

II. THEORETICAL BACKGROUND

A. Variational reduced density matrix method and N-representability conditions

Let us consider a nonrelativistic N-electron Hamiltonian $\hat{H}$, with clamped nuclei,

$$\hat{H} = \sum_{i,j} v_j^i \, a_i^\dagger a_j + \frac{1}{2} \sum_{i,j,k,l} w_{jl}^{ik} \, a_i^\dagger a_k^\dagger a_l a_j, \qquad (1)$$

in which the indices i, j, k, l, ..., denote the spin–orbitals of a finite orthonormal orbital basis set $\{\phi_i, \phi_j, \phi_k, \phi_l, ...\}$, $a_i^\dagger$, $a_k^\dagger$ ..., and a_j, a_l ..., are the usual creation and annihilation fermion operators, respectively, and v_j^i and w_{jl}^{ik} mean the standard one- and two-electron integrals (the last ones expressed in the $w_{j(1)l(2)}^{i(1)k(2)}$ convention).

For a determined N-electron wave function Ψ, the Hamiltonian $\hat{H}$ leads to an energy E_Ψ formulated as

$$E_\Psi = \mathrm{Tr}(v \, {}^1D) + \mathrm{Tr}(w \, {}^2D), \qquad (2)$$

where v and w are the matrices whose elements are v_j^i and w_{jl}^{ik}, respectively, and ${}^1D$ and ${}^2D$ are the one- and two-electron reduced density matrices (1-RDM and 2-RDM, respectively) corresponding to the wave function Ψ, whose elements are

$$\begin{aligned} {}^1D_j^i &= \langle \Psi | a_i^\dagger a_j | \Psi \rangle, \\ {}^2D_{jl}^{ik} &= \frac{1}{2} \langle \Psi | a_i^\dagger a_k^\dagger a_l a_j | \Psi \rangle. \end{aligned} \qquad (3)$$

For the ground state, the 1-RDM and 2-RDM elements can be variationally determined so that the corresponding energy reaches a minimum value E_{v2RDM}^g,

$$E_{\mathrm{v2RDM}}^g = \min_{\{{}^2D, {}^1D\}} \left\{ \mathrm{Tr}(v \, {}^1D) + \mathrm{Tr}(w \, {}^2D) \right\}. \qquad (4)$$

However, this direct procedure does not yield suitable results since the obtained matrices are not N-representable, that is, they do not arise from a true N-electron density matrix. To overcome this drawback, some constraint conditions, known as N-representability conditions,[13,14,23–35] have to be imposed in the variational determination of the reduced density matrix elements.

In relation to the 1-RDM and its linearly related one-electron hole reduced density matrix, whose elements are ${}^1Q_j^i = \langle \Psi | a_j a_i^\dagger | \Psi \rangle$, both matrices must be positive semidefinite. The 1-RDM must be normalized as $\mathrm{Tr}({}^1D) = N$, and its elements must satisfy the contraction rule of the 2-RDM, ${}^1D_j^i = \frac{2}{N-1} \sum_k {}^2D_{jk}^{ik}$. Regarding the 2-RDM, its trace must be $\mathrm{Tr}({}^2D) = \binom{N}{2}$, and its linearly related matrices,

$$\begin{aligned} {}^2P_{jl}^{ik} &= \langle \Psi | a_i^\dagger a_k^\dagger a_l a_j | \Psi \rangle \geq 0 \quad (P \text{ condition}), \end{aligned} \qquad (5)$$

$$\begin{aligned} {}^2Q_{jl}^{ik} &= \langle \Psi | a_j a_l a_k^\dagger a_i^\dagger | \Psi \rangle \geq 0 \quad (Q \text{ condition}), \end{aligned} \qquad (6)$$

$$\begin{aligned} {}^2G_{jl}^{ik} &= \langle \Psi | a_i^\dagger a_k a_l^\dagger a_j | \Psi \rangle \geq 0 \quad (G \text{ condition}), \end{aligned} \qquad (7)$$

must also be positive semidefinite. The ^2P and ^2Q matrices must be antisymmetric with respect to any permutation of creation/annihilation indices. The constraints (5)–(7) are usually known as two-positivity conditions.

N-representability conditions in terms of three- and four-electron reduced density matrices (3-RDM and 4-RDM) have also been proposed.[9,29–31,33–39] In this work, we will use

$$(T1)_{jln}^{ikm} = \langle\Psi|a_i^\dagger a_k^\dagger a_m^\dagger a_n a_l a_j + a_n a_l a_j a_i^\dagger a_k^\dagger a_m^\dagger|\Psi\rangle \geq 0 \quad (T1 \text{ condition}),$$
(8)

$$(T2)_{jln}^{ikm} = \langle\Psi|a_i^\dagger a_k^\dagger a_m a_n^\dagger a_l a_j + a_n^\dagger a_l a_j a_i^\dagger a_k^\dagger a_m|\Psi\rangle \geq 0 \quad (T2 \text{ condition}),$$
(9)

whose matrix elements can be linearly expressed by means of only 1-RDM and 2-RDM elements. $T1$ matrix must be antisymmetric with respect to any permutation of its trios, and $T2$ one must be antisymmetric with respect to any permutation of the first two indices of each trio. The $T1$ and $T2$ constraints have been called partial three-positivity conditions. Obviously, all these one-, two-, and three-electron matrices must be Hermitian.

The above mentioned conditions are necessary but not sufficient to guarantee the N-representability of the variationally obtained 2-RDM. However, the application of those conditions leads to results closer to the exact energy according to the sequence[9,29,30,40]

$$E_{PQG}^g \leq E_{PQGT1T2}^g \leq E_{exact}^g.$$
(10)

B. Description of open-shell systems

As has been mentioned in the Introduction, this work attempts to extend to the DOCI scheme the techniques reported in Refs. 19 and 20 for describing open-shell systems. Those techniques are based on the addition of a hydrogen atom H to an open-shell N-electron molecule or radical R, constituting a singlet state system R–H with wave function $\Psi(N+1)$, where the hydrogen atom is situated at infinite distance from the radical. The subsystems R [in a doublet state with wave function $\Psi_R(N)$] and H (with wave function ϕ_H) are described in the orbital basis sets $\{\phi_i, \phi_j, \phi_k, \phi_l, \ldots\}$ and $\{\phi_H\}$, respectively, with no spatial correlation between them. According to these depictions, these wave functions must satisfy the following equations:

$$\langle\Psi_R(N)|\hat{S}^2|\Psi_R(N)\rangle = S(S+1) = \frac{3}{4},$$
(11)

$$\langle\Psi_R(N)|\hat{S}_z|\Psi_R(N)\rangle = \pm\frac{1}{2},$$
(12)

$$\langle\phi_H|\hat{S}^2|\phi_H\rangle = S(S+1) = \frac{3}{4},$$
(13)

$$\langle\phi_H|\hat{S}_z|\phi_H\rangle = \pm\frac{1}{2},$$
(14)

and applying the well-known rules of angular momentum coupling, the wave function $\Psi(N+1)$ can be formulated as[20]

$$|\Psi(N+1)\rangle = \frac{1}{\sqrt{2}}\left\{|\Psi_R^\alpha(N)\rangle \wedge |\phi_H^\beta\rangle - |\Psi_R^\beta(N)\rangle \wedge |\phi_H^\alpha\rangle\right\},$$
(15)

satisfying the condition

$$\langle\Psi(N+1)|\hat{S}^2|\Psi(N+1)\rangle = 0,$$
(16)

where the symbol $\wedge$ stands for the Grassmann, wedge, or exterior product.

The wave functions $\Psi(N+1)$ and $\Psi_R(N)$ are related by means of the creation/annihilation operators,[20]

$$|\Psi_R(N)\rangle = (a_H^\alpha + a_H^\beta)|\Psi(N+1)\rangle,$$
(17)

and consequently, the 1-RDM and 2-RDM elements corresponding to the spin–orbitals of the subsystem R are

$$\begin{aligned}^1D_j^i &= \langle\Psi_R(N)|a_i^\dagger a_j|\Psi_R(N)\rangle \\ &= \langle\Psi(N+1)|(a_H^{\dagger\alpha} + a_H^{\dagger\beta})a_i^\dagger a_j(a_H^\alpha + a_H^\beta)|\Psi(N+1)\rangle \\ &= \langle\Psi(N+1)|a_i^\dagger(a_H^{\dagger\alpha} + a_H^{\dagger\beta})(a_H^\alpha + a_H^\beta)a_j|\Psi(N+1)\rangle \\ &= \langle\Psi(N+1)|a_i^\dagger a_j|\Psi(N+1)\rangle\end{aligned}$$
(18)

and

$$\begin{aligned}^2D_{jl}^{ik} &= \frac{1}{2}\langle\Psi_R(N)|a_i^\dagger a_k^\dagger a_l a_j|\Psi_R(N)\rangle \\ &= \frac{1}{2}\langle\Psi(N+1)|a_i^\dagger a_k^\dagger a_l a_j|\Psi(N+1)\rangle,\end{aligned}$$
(19)

respectively. Equations (18) and (19) allow one to express the energy of the $R-H$ system $E_{\Psi(N+1)}$ as

$$E_{\Psi(N+1)} = v_{\phi_H}^{\phi_H} + \text{Tr}(v \, ^1D) + \text{Tr}(w \, ^2D),$$
(20)

where the first term, $v_{\phi_H}^{\phi_H}$, is the energy of the separated hydrogen atom, E_H, and the sum $\text{Tr}(v^1D) + \text{Tr}(w^2D)$ is the energy of the radical R, E_R.

This treatment has been reported here for a single hydrogen atom situated at infinite distance from a radical R, but it can be applied to several hydrogen atoms so that other spin symmetries than the doublet one can also be described.[19,20]

C. The DOCI methodology

The expectation value of the seniority number operator $\hat{\Omega}$ for an N-electron wave function Ψ has been formulated as[4,41–44]

$$\langle\hat{\Omega}\rangle_\Psi = N - 2\sum_\sigma\sum_{i^\sigma} {}^2D_{i^\sigma i^{\bar\sigma}}^{i^\sigma i^{\bar\sigma}}(\Psi),$$
(21)

where σ stands for the spin coordinate (α or β) of the spatial orbital ϕ_i and $\bar\sigma$ its spin conjugate. This quantity indicates the number of unpaired electrons of the wave function Ψ and, obviously, for a Slater determinant $\langle\hat{\Omega}\rangle = \Omega$, where Ω is an integer meaning the number of unpaired electrons in that determinant. Hence, $\langle\hat{\Omega}\rangle_{\text{DOCI}} = 0$ since only $\Omega = 0$ N-electron Slater determinants are involved in the expansion of the DOCI wave functions. Moreover, the 1-RDM and 2-RDM corresponding to a DOCI wave function, hereafter called as

$^1\tilde{D}$ and $^2\tilde{D}$, are considerably simpler than their counterparts ^1D and ^2D, satisfying[38]

$$^1\tilde{D}_i^i = {^1}D_i^i,$$
$$^2\tilde{D}_{ij}^{ij} = {^2}D_{ij}^{ij},$$
$$^2\tilde{D}_{ji}^{ij} = {^2}D_{ji}^{ij},$$
$$^2\tilde{D}_{j^\sigma j^{\bar\sigma}}^{i^\sigma i^{\bar\sigma}} = {^2}D_{j^\sigma j^{\bar\sigma}}^{i^\sigma i^{\bar\sigma}}. \tag{22}$$

The remainder of the $^1\tilde{D}$ and $^2\tilde{D}$ elements is zero.

The variational determination of the $^1\tilde{D}$ and $^2\tilde{D}$ elements, constrained by the selected N-representability conditions, leads to the evaluation of the corresponding ground state energy according to

$$E_{\text{v2RDM-DOCI}}^g = \min_{^1\tilde{D},{^2}\tilde{D},\langle\hat\Omega\rangle=0}\left\{\text{Tr}(v\,{^1}\tilde{D}) + \text{Tr}(w\,{^2}\tilde{D})\right\}, \tag{23}$$

which requires to satisfy the condition

$$\sum_\sigma\sum_{i^\sigma} {^2}\tilde{D}_{i^\sigma i^{\bar\sigma}}^{i^\sigma i^{\bar\sigma}} = \frac{N}{2}. \tag{24}$$

We propose the application of the variational DOCI scheme to the study of doublet N-electron systems R, performing the following steps: (a) addition of a hydrogen atom which is situated at infinite distance from R, constituting a singlet $(N+1)$-electron system with $\langle\hat\Omega\rangle_{\Psi(N+1)} = 0$, and computation of the electron integrals of the radical and addition of the hydrogen integrals which, due to that infinite distance, do not couple with those of the radical, (b) determination of the 2-RDM and the energy corresponding to this composite system according to the v2RDM-DOCI treatment, and (c) subtraction of the hydrogen atom energy from the singlet entity energy and extraction of the open-shell system 2-RDM. In Sec. III, we report results arising from this method, hereafter called as
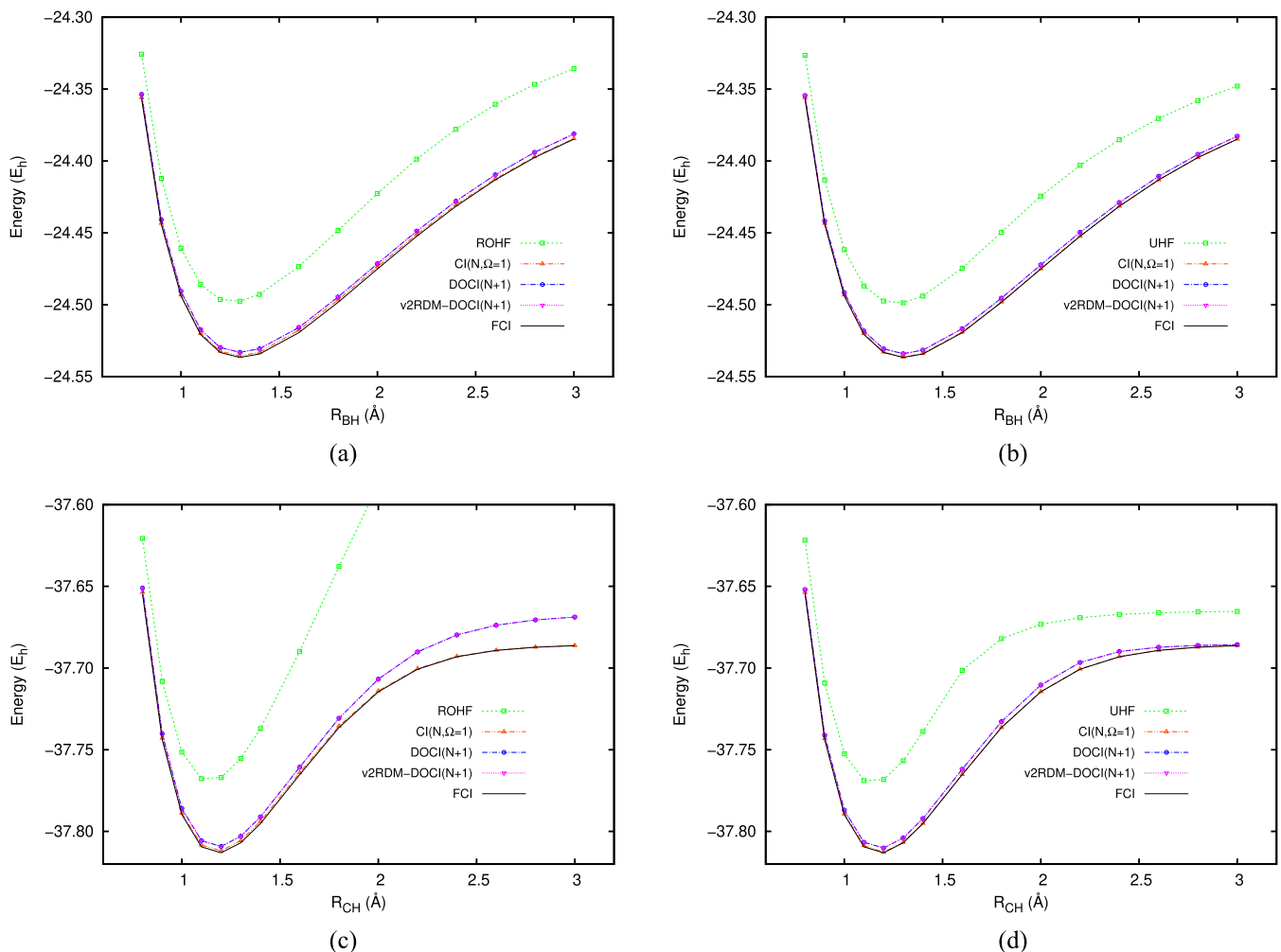

FIG. 1. Ground state PECs for the diatomic systems of seven electrons BH^- [(a) and (b)] and CH [(c) and (d)] arising from different methods (see the text). Results correspond to STO-3G basis sets transformed into the orbital sets that minimize the energy (OPTE) with ROPTE [(a) and (c)] and UOPTE [(b) and (d)] treatments.

v2RDM-DOCI(N + 1). These results will be compared with those obtained from the counterpart wave function-based DOCI method DOCI(N + 1), that is, with the energies obtained for the (N + 1)-electron system from the CI wave function constructed with seniority-zero Slater determinants, followed by the subtraction of E_H energy. Both series of results will also be compared with those obtained directly in system R [with N (odd) electrons] using the CI method with seniority number $\langle \hat{\Omega} \rangle_{\Psi(N)} = 1$, i.e., with the R wave function expressed by means of all N-electron Slater determinants of seniority number $\Omega = 1$ that can be constructed with the used radical basis set, which will be denoted as CI(N, $\Omega = 1$).

III. COMPUTATIONAL ASPECTS, RESULTS, AND DISCUSSION

In this work, we have chosen the diatomic radicals and ion-radicals BH$^-$, CH, OH, and FH$^+$, as well as the triatomic systems

CH$_2^-$, NH$_2$, and H$_2$O$^+$, as suitable examples for assessing the v2RDM-DOCI(N + 1) method. The one- and two-electron integrals of these systems, and those of the hydrogen atom added to them in the calculation procedure, have been drawn out from the PSI4 codes.[45] These codes were also used to evaluate the results corresponding to the FCI, restricted open-shell Hartree–Fock (ROHF), and unrestricted Hartree–Fock (UHF) methods that have been obtained as reference values to be compared with those arising from our method. Modified versions of the packages described in Refs. 46 and 47 have been used to calculate 1- and 2-RDMs and energies corresponding to the CI(N, $\Omega = 1$) and DOCI(N + 1) methods. The results arising from the v2RDM-DOCI(N + 1) procedure have been obtained from our own codes imposing all the above mentioned N-representability conditions in the energy minimization, which is carried out by means of semidefinite programming algorithms.[48,49] STO-3G atomic basis sets have been used in all performed calculations, in order to be able to compare our results with
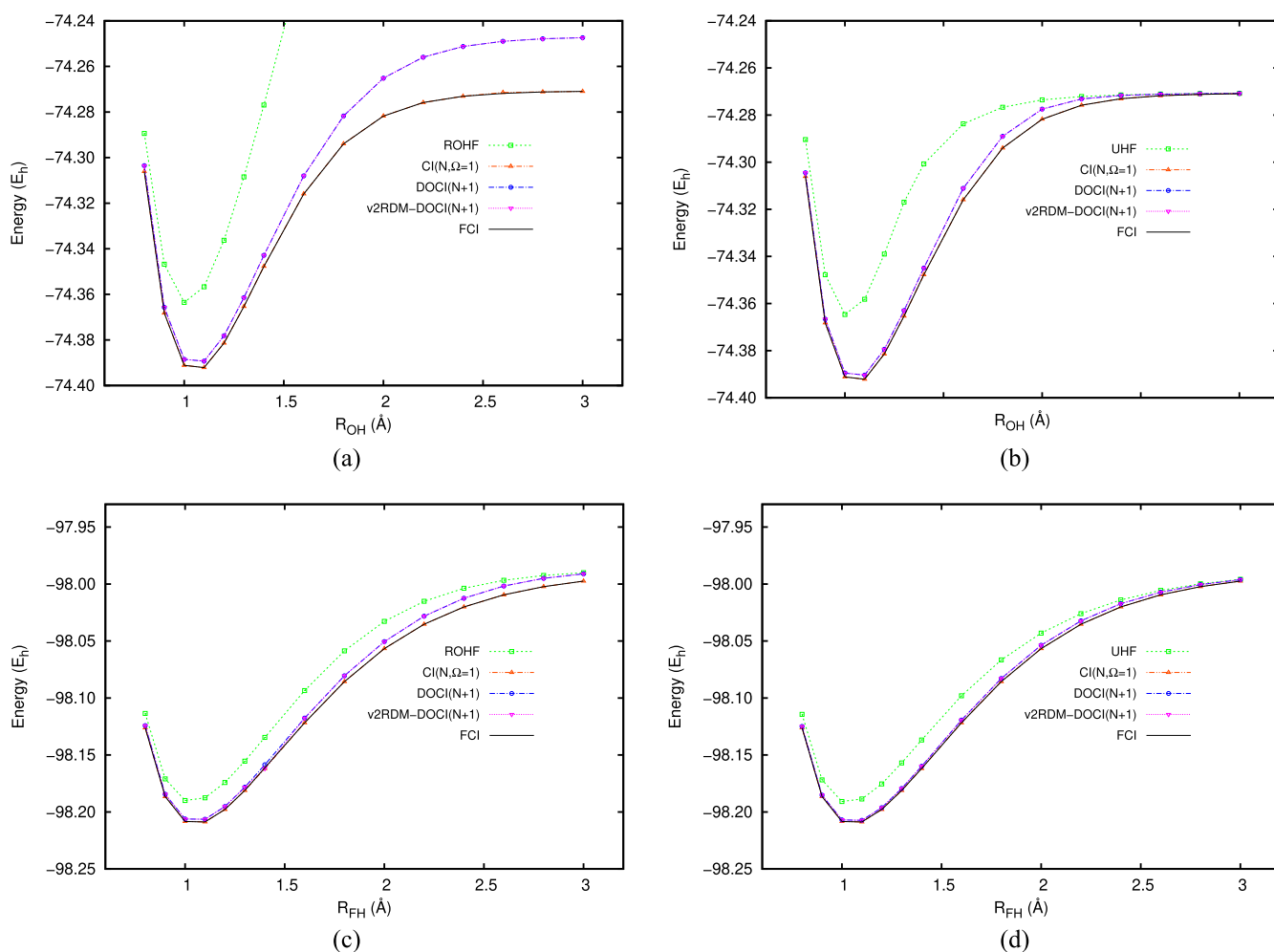

FIG. 2. Ground state PECs for the diatomic systems of nine electrons OH [(a) and (b)] and FH$^+$ [(c) and (d)] arising from different methods (see the text). Results correspond to STO-3G basis sets transformed into the orbital sets that minimize the energy (OPTE) with ROPTE [(a) and (c)] and UOPTE [(b) and (d)] treatments.
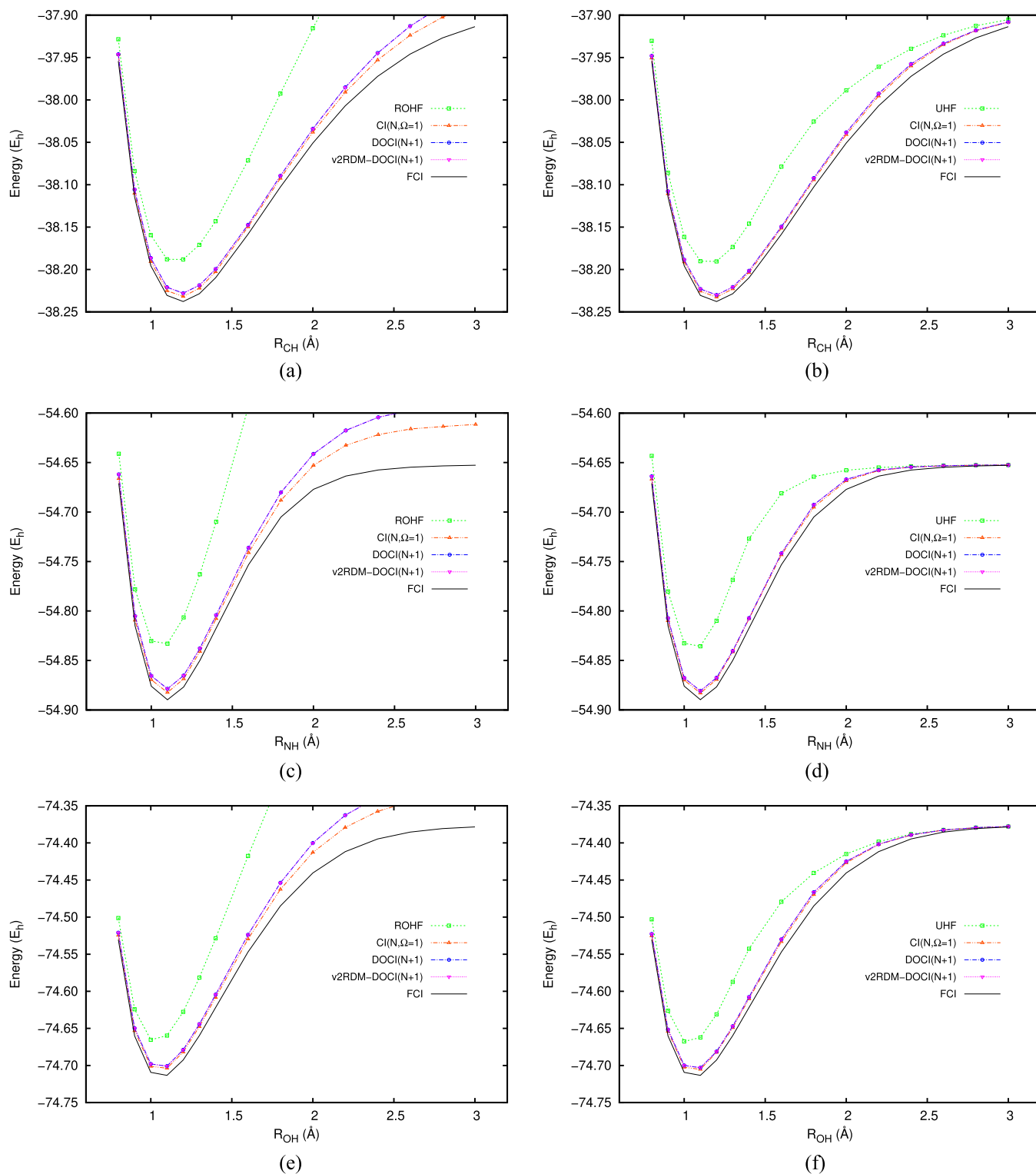
FIG. 3. Ground state PECs (symmetric stretching) for the triatomic systems of nine electrons CH_2^- [(a) and (b)], NH_2 [(c) and (d)], and H_2O^+ [(e) and (f)] arising from different methods (see the text). Results correspond to STO-3G basis sets transformed into the orbital sets that minimize the energy (OPTE) with ROPTE [(a), (c), and (e)] and UOPTE [(b), (d), and (f)] treatments.

those of the FCI method. As is well known, the energies resulting from the seniority-based CI procedures are not invariant with respect to a rotation of the basis set, and consequently, the optimization of the energy (OPTE) is necessary by performing basis set rotations so that the final energy reaches a minimum value. This task can be accomplished following two procedures: (a) rotation of all spatial orbitals (including those of core-1s electrons), which will be called restricted optimization of the energy (ROPTE),[6] and (b) rotation of the α- and β-spin–orbital subsets independently, which is called unrestricted optimization of energy (UOPTE); the use of unrestricted orbitals in wave function expansions within the DOCI framework has been described in Ref. 38. As a consequence of these basis set optimizations, it is not possible to identify the wave functions and RDMs of the subsystems R and H. Hence, once the wave functions and RDMs have been evaluated in the OPTE basis sets, we must back-transform them to the original basis sets in order to identify both fragments. We have checked that the values of the traces of the 1-RDMs corresponding to the radical R and the separated hydrogen atom are N and 1, respectively, which assures that the dissociation process of the composite system does not yield hydrogen ions.[19]

In Figs. 1 and 2, we have gathered the potential energy curves (PECs) of the diatomic chemical species of seven (BH$^-$ and CH) and nine (OH and FH$^+$) electrons, respectively, arising from the above mentioned methods using both ROPTE and UOPTE treatments. In Fig. 3, we show those corresponding to the triatomic systems CH$_2^-$, NH$_2$, and H$_2$O$^+$. A survey of these figures shows the similarity between the results produced by the v2RDM-DOCI(N + 1) and DOCI(N + 1) methods, which turn out to be indistinguishable and very close to those arising from the CI(N, Ω = 1) procedure. This closeness is higher in the UOPTE treatments, but their use entails the appearance of spin contamination, which has not been found in the results arising from the ROPTE technique. This is an interesting information because spin contamination is a common shortcoming of all unrestricted treatments. We have measured

the spin contamination in terms of the expectation value of the N-electron spin-squared operator, $\langle \hat{S}^2 \rangle$.[50] For all the studied systems, we have found values $\langle \hat{S}^2 \rangle_R$ = 0.75 in the ROPTE treatments and $\langle \hat{S}^2 \rangle_R \neq$ 0.75 in the UOPTE ones, while $\langle \hat{S}^2 \rangle_H$ = 0.75 in both cases; the highest $\langle \hat{S}^2 \rangle_R$ values have been found in the region close to the dissociation limit. In the diatomic species, the spin contamination appears in the UOPTE version of the v2RDM-DOCI(N + 1) and DOCI(N + 1) methods, although its values are lower than those arising from the UHF one. The triatomic systems present higher spin contamination than the diatomic ones, and it can also be detected in the results arising from the CI(N, Ω = 1) method. These observations can be explained in terms of the higher number of unpaired electrons[51] near the dissociation limit in the triatomic species (two bonds breaking). In Fig. 4, we show the $\langle \hat{S}^2 \rangle_R$ values for the OH and NH$_2$ radicals; the remainder systems present lower spin contamination. In Table I, we report values of nonparallelity errors (NPEs) and maximum absolute errors (MAEs) of the PECs corresponding to the CI(N, Ω = 1) method (with respect to the FCI one) and for the DOCI(N + 1) and v2RDM-DOCI(N + 1) methods [both with respect to the CI(N, Ω = 1) one] for the diatomic and triatomic systems studied, in order to provide a quantitative assessment. As can be seen, these values confirm again the closeness of the results arising from the DOCI(N + 1) and v2RDM-DOCI(N + 1) methods, highlighting the low values obtained for NPE and MAE quantities in the UOPTE procedures.

We have implemented an analysis of the reduced density matrices obtained in each of the mentioned methods by studying the distribution of the occupation numbers of the resulting natural orbitals. This task has required the calculation of the eigenvalues of their corresponding spin-free 1-RDMs. In Table II, we have collected the values of these occupation numbers for the CH radical, as a prototype system possessing seven electrons, at the equilibrium and stretched configurations, while in Table III, we have grouped the values of these quantities for the OH radical (a diatomic system
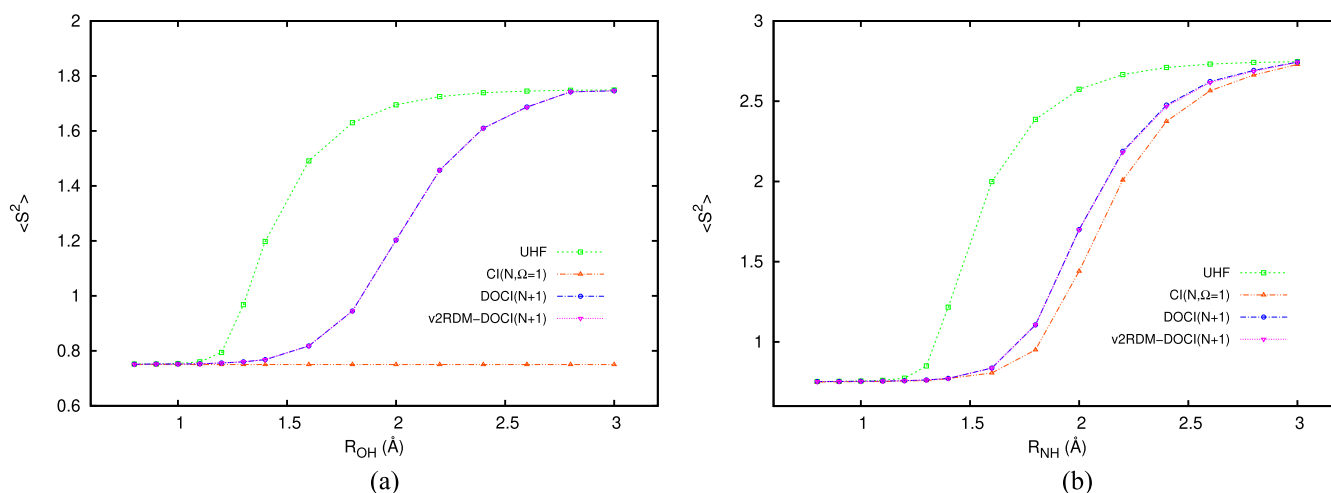

FIG. 4. Spin contamination found in the OH radical (a) and the NH$_2$ one (b). Results correspond to STO-3G basis sets transformed into the orbital sets that minimize the energy (OPTE) within the UOPTE treatment.

TABLE I. Nonparallelity errors (NPEs) and Maximum Absolute errors (MAEs) (in square brackets), in mE_h, for the ground state of BH$^-$, CH, OH, FH$^+$, CH$_2^-$, NH$_2$, and H$_2$O$^+$ systems. The CI(N, $\Omega = 1$) results have been calculated with respect to the FCI ones and those of the DOCI($N + 1$) and v2RDM-DOCI($N + 1$) methods with respect to the CI(N, $\Omega = 1$) ones. The $PQGT1T2$ conditions have been imposed in the v2RDM-DOCI($N + 1$) calculations. Results correspond to STO-3G atomic basis sets transformed into the orbital sets which minimize the energy (OPTE) (ROPTE and UOPTE treatments).

System	ROPTE			UOPTE		
	CI(N, $\Omega = 1$)	DOCI($N + 1$)	v2RDM-DOCI($N + 1$)	CI(N, $\Omega = 1$)	DOCI($N + 1$)	v2RDM-DOCI($N + 1$)
BH$^-$	1.452	1.402	1.401	0.827	1.311	1.309
	[1.809]	[3.232]	[3.228]	[0.850]	[2.757]	[2.753]
CH	1.299	14.80	14.80	0.805	3.473	3.471
	[1.330]	[17.42]	[17.42]	[0.821]	[4.003]	[3.999]
OH	0.382	21.05	21.05	0.044	4.829	4.829
	[0.373]	[23.56]	[23.56]	[0.044]	[4.962]	[4.962]
FH$^+$	0.027	5.707	5.709	0.001	1.757	1.758
	[0.028]	[7.712]	[7.712]	[0.002]	[3.032]	[3.032]
CH$_2^-$	21.818	16.907	16.820	8.717	2.707	2.657
	[26.180]	[17.241]	[17.150]	[12.250]	[2.925]	[2.860]
NH$_2$	36.434	17.912	17.916	9.584	2.883	2.881
	[41.220]	[21.188]	[21.188]	[9.903]	[2.892]	[2.888]
H$_2$O$^+$	39.953	20.181	20.192	14.765	3.157	3.120
	[45.730]	[22.963]	[22.959]	[15.286]	[3.224]	[3.187]

possessing nine electrons). The results corresponding to the BH$^-$ and FH$^+$ systems are shown in the supplementary material. As can be observed in these tables, at the equilibrium geometry, all those systems present some doubly or near doubly occupied orbitals and a singly occupied orbital (with 1.0000 or near 1.0000 occupation number), while the remainder of the orbitals possesses a very low occupation number, which shows the radical character of these systems. In the stretched configurations, we can observe a decrease in the electronic population in some of the orbitals that were doubly or near doubly occupied at the equilibrium, as well as an increase in

TABLE II. Natural-orbital occupation numbers of the spin-free 1-RDM corresponding to the ground state of the CH radical calculated by DOCI($N + 1$), v2RDM-DOCI($N + 1$), CI(N, $\Omega = 1$), and FCI methods. $PQGT1T2$ conditions have been imposed in the variational method. Results correspond to STO-3G atomic basis sets (internuclear distances at equilibrium and stretched geometries are Req = 1.2 Å and Rst = 3.0 Å, respectively).

	ROPTE			UOPTE			
	DOCI($N + 1$)	v2RDM-DOCI($N + 1$)	CI(N, $\Omega = 1$)	DOCI($N + 1$)	v2RDM-DOCI($N + 1$)	CI(N, $\Omega = 1$)	FCI
Req	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000
	1.9709	1.9709	1.9689	1.9702	1.9702	1.9684	1.9696
	1.9488	1.9488	1.9475	1.9483	1.9483	1.9407	1.9359
	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	0.0506	0.0506	0.0508	0.0505	0.0505	0.0565	0.0597
	0.0297	0.0297	0.0328	0.0309	0.0310	0.0343	0.0349
Rst	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000
	1.9534	1.9534	1.9534	1.9534	1.9534	1.9534	1.9533
	1.1447	1.1447	1.1064	1.0739	1.0739	1.1066	1.1066
	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	0.8554	0.8553	0.8936	0.9261	0.9262	0.8935	0.8935
	0.0465	0.0465	0.0465	0.0466	0.0466	0.0465	0.0466

TABLE III. Natural-orbital occupation numbers of the spin-free 1-RDM corresponding to the ground state of the OH radical calculated by DOCI($N + 1$), v2RDM-DOCI($N + 1$), CI(N, $\Omega = 1$), and FCI methods. *PQGT1T2* conditions have been imposed in the variational method. Results correspond to STO-3G atomic basis sets (internuclear distances at equilibrium and stretched geometries are Req = 1.1 Å and Rst = 3.0 Å, respectively).

	ROPTE			UOPTE			
	DOCI($N + 1$)	v2RDM-DOCI($N + 1$)	CI(N, $\Omega = 1$)	DOCI($N + 1$)	v2RDM-DOCI($N + 1$)	CI(N, $\Omega = 1$)	FCI
Req	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000
	1.9992	1.9992	1.9992	1.9992	1.9992	1.9992	1.9992
	1.9992	1.9992	1.9986	1.9990	1.9990	1.9986	1.9986
	1.9536	1.9536	1.9501	1.9522	1.9522	1.9501	1.9501
	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	0.0479	0.0479	0.0521	0.0496	0.0496	0.0521	0.0521
Rst	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000
	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000
	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000
	1.0616	1.0617	1.0447	1.0295	1.0295	1.0447	1.0447
	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	0.9384	0.9383	0.9553	0.9705	0.9705	0.9553	0.9553

some of the low occupied ones; the radical character is also maintained in the stretched geometries. Table IV shows the results corresponding to the triatomic species H_2O^+ (the results of the CH_2^- and NH_2 systems have been included in the supplementary material). Again, the stretched geometries present more orbitals with the occupation number close to 1 and less orbitals with the occupation number close to 2, indicating the dissociation process. These results guarantee the reliability of the treatment based on placing hydrogen atoms at infinite distance from a radical R to describe systems

with unpaired electrons. This effectiveness occurs with the conventional DOCI procedure applied to the composite system with $N + 1$ electrons, DOCI($N + 1$), and with its variational version v2RDM-DOCI($N + 1$).

The above reported numerical determinations have proved the closeness of the results arising from the DOCI($N + 1$) and v2RDM-DOCI($N + 1$) methods in the description of radical systems. However, the computational expense required in the use of the v2RDM-DOCI($N + 1$) method is of polynomial type $O(K^4)$

TABLE IV. Natural-orbital occupation numbers of the spin-free 1-RDM corresponding to the ground state of the H_2O^+ cation calculated by DOCI($N + 1$), v2RDM-DOCI($N + 1$), CI(N, $\Omega = 1$), and FCI methods. *PQGT1T2* conditions have been imposed in the variational method. Results correspond to STO-3G atomic basis sets (internuclear distances at equilibrium and symmetric stretched geometries are Req = 1.1 Å and Rst = 3.0 Å, respectively, $\widehat{HOH} = 109.3°$).

	ROPTE			UOPTE			
	DOCI($N + 1$)	v2RDM-DOCI($N + 1$)	CI(N, $\Omega = 1$)	DOCI($N + 1$)	v2RDM-DOCI($N + 1$)	CI(N, $\Omega) = 1$)	FCI
Req	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000
	1.9995	1.9995	1.9989	1.9990	1.9990	1.9988	1.9981
	1.9737	1.9737	1.9738	1.9725	1.9725	1.9734	1.9721
	1.9737	1.9737	1.9708	1.9722	1.9722	1.9696	1.9644
	1.0000	1.0000	1.0000	1.0000	1.0000	1.0001	1.0000
	0.0266	0.0266	0.0300	0.0283	0.0283	0.0292	0.0338
	0.0266	0.0266	0.0265	0.0281	0.0281	0.0289	0.0316
Rst	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000
	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000
	1.2590	1.2591	1.2752	1.1036	1.1036	1.1058	1.1407
	1.2381	1.2382	1.1487	1.0657	1.0657	1.0744	1.1003
	1.0000	1.0000	1.0000	1.0002	1.0002	1.0000	1.0000
	0.7619	0.7618	0.8513	0.9344	0.9344	0.9256	0.8997
	0.7410	0.7409	0.7248	0.8965	0.8965	0.8942	0.8593

(K is the number of the spatial orbitals of the basis set),[9] while the DOCI($N + 1$), CI(N, $\Omega = 1$), and FCI methods present a factorial behavior.[6] Consequently, the use of the v2RDM-DOCI($N + 1$) method is strongly recommended, as it provides suitable results at a lower computational cost.

IV. CONCLUDING REMARKS

In this work, we have proposed the description of N-electron systems in doublet spin symmetry by means of the DOCI methodology. We have managed singlet systems composed of $N + 1$ electrons, resulting from the addition of a hydrogen atom that is placed at infinite distance from the radical atoms. Then, we have obtained the radical ground state energy by subtracting the contribution corresponding to the hydrogen atom energy and extracted its RDMs from the composite system. Our results, which have been compared with those arising from standard methods, prove the reliability of this technique for the two reported versions of the DOCI procedure, the conventional DOCI($N + 1$) version, and the variational v2RDM-DOCI($N + 1$) one. The closeness of the results provided by these two procedures and the lower computational cost required in the use of the v2RDM-DOCI($N + 1$) method point to this last procedure as the most suitable one to describe doublet radicals within the DOCI framework.

SUPPLEMENTARY MATERIAL

See the supplementary material for additional results not included in this work: natural-orbital occupation numbers of the spin-free 1-RDM corresponding to the ground state of the systems BH^-, FH^+, CH_2^-, and NH_2.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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