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Multiple complete active space self-consistent field solutions

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It is proved that the CASSCF equations for the ground state of weakly interacting systems admit many non-equivalent solutions for a given type of active space. For instance, in the case of N weakly interacting hydrogen molecules, there are at least N different minima in the case of a CAS(2/2), involving one bonding and one antibonding orbital on the same molecule. A similar result still holds for many systems for which the interaction is far from small. As an example, the case of the ethylene molecule is discussed, where three CAS(2/2) and six CAS(4/4) non-equivalent minima are present. The use of localized orbitals permits one to choose the particular solution one wants to converge to. The implications of these results on CASSCF calculations are significant, since by choosing different minima one can focus the CASSCF description on a given characteristic (e.g., the spatial position) of the active orbitals. In this way, a significant reduction of the active-space size is possible, a fact particularly important in the case of large systems.

1. Introduction

The idea of the multiconfiguration self-consistent field (MCSCF) goes back to the beginning of quantum chemistry [1, 2] (see also [3]). MCSCF is useful to treat those situations where non-dynamical correlation plays a central role: chemical reactions (bond breaking), spectroscopy (excited states), magnetic systems, and many others. In more recent years, Björn Roos and co-workers developed a particular version of MCSCF, the 'complete active space self-consistent field' (CASSCF) formalism, which is remarkably simple and elegant [4]. Today, CASSCF is one of the most widely used computational methods in quantum chemistry [5, 6]. In the CASSCF formalism, the orbital space is divided into three classes: occupied, active and virtual orbitals (O, A and V, respectively). Occupied and virtual orbitals are doubly occupied and empty, respectively, in all the reference determinants of the CAS wave function, $|\Psi\rangle$. The remaining electrons are distributed in all the possible ways among the active orbitals [4]. The CASSCF solution $|\Psi_0\rangle$ is obtained by minimizing the mean value E of the Hamiltonian on $|\Psi\rangle$. The minimum of the

energy E is taken with respect to the molecular orbital (MO) coefficients *and* the configuration interaction (CI) coefficients.

With respect to the CI coefficients, the energy is a quadratic form, and if no degeneracy of the eigenvalues occurs, there exists only one minimum. However, with respect to orbital variation, the CASSCF conditions are nonlinear (like in the case of the SCF), and a whole set of solutions can occur. The energy E associated to $|\Psi\rangle$ is a functional of the MOs of the system. This functional is invariant for any unitary transformation that does not mix orbitals belonging to different classes. The energy surface structure is highly complicated, and several different minima, as well as other stationary points, can exist. The CAS-CI solution (the solution obtained by diagonalizing the Hamiltonian in the CI space, without orbital optimization) is an energy stationary point on the surface if the generalized Brillouin theorem (GBT) is satisfied [7, 8]. More restrictive conditions assure that a given stationary point is a minimum.

We have recently proposed a computational scheme to obtain CASSCF or quasi-CASSCF orbitals having a given physical nature [9–12]. It is a partial diagonalization procedure based on the iterative partial diagonalization of the one-body reduced density matrix. It takes

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advantage of the unitary invariance of the CAS wave function with respect to orbital rotations that are internal to each orbital class. In this way, the mixing between orbitals belonging to the same class is minimized at each iteration. As a result, the final orbitals maintain (as far as possible, since a rigorous CASSCF solution is obtained at convergence) the same nature of the guess orbitals. The formalism is particularly suited to obtaining local orbitals in a multireference context, a fact of particular interest for reducing the computational effort in the treatment of quasi-degenerate systems [13]. Two versions of the algorithm exist: a variational algorithm, based on single-excitation CI expansion on Slater determinants, that produces quasi-CASSCF orbitals [9, 10], and a perturbative version [11], based on an internally contracted multireference perturbative algorithm [14–16]. Since with the second algorithm the conditions of the GBT are satisfied, an *exact* CASSCF solution is obtained.

In this work we shall show that, given the number of occupied, active, and virtual orbitals, and the number of electrons, many different CASSCF minima can exist for the same system. Different minima correspond to different descriptions of the system ground state. By choosing a particular minimum, one can focus the CASSCF description on a given physical characteristic of the molecular orbitals (spatial localization, exact or approximate symmetry, etc.). The possibility of converging to a CASSCF solution that is higher in energy than the absolute minimum is something well known to those who perform this type of calculation [6]. In fact, it often happens that different calculations on the same system give different results, depending on the orbital guess, the method used to converge, and so on. The presence of such multiple solutions for the same system is often seen as a nuisance, since it introduces an element of 'randomness' in the result of the calculation. Moreover, it is difficult to understand the physical difference, if any, between two different solutions, and the convergence to one or another solution is essentially unpredictable (except in highly symmetric systems, where it is possible to converge to different minima by specifying for a given symmetry the number of orbitals belonging to each class). In particular, the existence of CASSCF solutions having active spaces of a different physical nature often occurs in the study of reaction paths [17], or, more generally, for different geometries of the system [18]. The possibility of choosing a particular reduced active space can be used in these cases to describe a particular state or process (see, for instance, [19]).

Our formalism permits great flexibility in the choice of the physical content of the active space, and therefore convergence to a specific solution among the multiple set. The key feature of the localization scheme discussed here is its ability to force the optimization process towards a given region in the orbital parameters, thus imposing the local minimum one wants it to converge to. In this way, the richness of CASSCF solutions, far from being a computational nuisance, becomes an extraordinary opportunity; it permits a description targeted on the particular physical aspect that is studied. It is possible in this way to obtain a significant reduction of the active-space size, by keeping only those orbitals that play a significant role in a multireference (MR) description. This point can be illustrated by considering a process of bond-breaking in a large molecule. In general, CASSCF is needed to correctly describe the breaking process, a CAS(2/2) being the minimum requirement in the case of a single bond. When the bond is broken, the active orbitals tend to localize spontaneously in the region of the bond, because of the large amount of non-dynamical correlation. On the other hand, for geometries close to the equilibrium geometry, the active orbitals tend to localize in those regions of the molecule that give the largest amount of dynamical correlation. As a result, the active spaces in the two cases can be of a completely different nature. If one takes the lowest CAS(2/2) solution for the two geometries, the energy barrier will generally be overestimated. Although in some cases this problem can be obviated by continuously following the active space from the broken-bond geometry to the equilibrium geometry, this is a very heavy procedure, since it requires in general a large amount of CASSCF calculations. Moreover, the continuity of the energy path is not guaranteed.

In the present article, the existence of different non-equivalent CASSCF minima is rigorously proved in the case of N weakly interacting hydrogen molecules. The argument can be straightforwardly generalized to any collection of weakly interacting systems. It is also shown that multiple CASSCF solutions exist even in situations where the interactions are rather strong, as in the case of molecular systems. Finally, it is shown that multiple solutions exist for quasi-CASSCF wave functions, obtained with the method of iterated single-excitation orbitals from a CAS (CAS-ISO) [9]. In all the cases we tested, the CASSCF and CAS-ISO orbitals gave almost identical results, whether at CAS-CI, CAS+S or CAS+SD levels.

2. The CASSCF wave function

Consider a set of orthogonal MOs, split into three classes (occupied, active and virtual orbitals). The CAS-CI wave function is obtained by diagonalizing the Hamiltonian operator expanded on the space $\mathcal{L}_0$ of the Slater determinants obtained by placing the active

electrons within the active orbitals, in all possible ways. Therefore, the CI coefficients are chosen is such a way as to minimize the mean energy

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \tag{1}$$

If the MOs are also optimized in the energy minimization, a CASSCF wave function $|\Psi_0\rangle$ and a corresponding energy E_0 are obtained.

In order to obtain the CASSCF conditions, a unitary transformation of the MOs is considered [20]; the new orbitals are given by

$$\phi'_i = \sum_j U_{j,i} \phi_j, \tag{2}$$

with the unitary matrix U that can be written as

$$U = \exp \Delta. \tag{3}$$

To maintain the orthonormality of the MOs, the coefficients $\Delta_{i,j}$ of the first-order variation must form an anti-hermitian matrix, $\Delta_{j,i} = -\Delta^*_{i,j}$. If the CI coefficients are held fixed while the orbitals are rotated, the new wave function (on the old set of MOs) is given by [20]

$$|\Psi'\rangle = \hat{U} |\Psi\rangle, \tag{4}$$

with

$$\hat{U} = \exp \hat{\Delta} \tag{5}$$

and

$$\hat{\Delta} = \sum_{i,j} \Delta_{i,j} a_i^+ a_j. \tag{6}$$

Therefore, the first-order variation (with respect to Δ) of the wave function under orbital rotation is

$$|\Psi\rangle = \left(1 + \sum_{i,j} \Delta_{i,j} a_j^+ a_i + \frac{1}{2} \sum_{i,j,k,l} \Delta_{i,j} \Delta_{k,l} a_j^+ a_i a_l^+ a_k\right) |\Psi_0\rangle, \tag{7}$$

while the corresponding energy expansion becomes

$$\begin{aligned} E &= \langle \Psi | H | \Psi \rangle \\ &= E_0 + \sum_{i,j} \Delta_{i,j} \langle a_j^+ a_i \Psi_0 | H | \Psi_0 \rangle \\ &\quad + \sum_{k,l} \Delta_{k,l} \langle \Psi_0 | H | a_l^+ a_k \Psi_0 \rangle. \end{aligned} \tag{8}$$

The requirement that the energy is stationary with respect to the coefficients $\Delta_{i,j}$ implies that the first-order variation must vanish. This gives

$$\langle a_j^+ a_i \Psi_0 | H | \Psi_0 \rangle - \langle \Psi_0 | H | a_i^+ a_j \Psi_0 \rangle = 0, \tag{9}$$

which is a condition equivalent to the GBT [7–16, 20, 21].

Equation (9) is trivially satisfied if $i, j \in O$ or $i, j \in V$, because of the structure of $|\Psi_0\rangle$. Therefore, E is invariant with respect to rotations within the internal and external orbital classes separately. If $i, j \in A$, $|a_i^+ a_j \Psi_0\rangle$ belongs to $\mathcal{L}_0$, and equation (9) is equivalent to $P_0 H | \Psi_0 \rangle = E_0 | \Psi_0 \rangle$, that is $|\Psi_0\rangle$ is a solution of the CAS-CI equations in $\mathcal{L}_0$. In order to improve the orbital basis set, one can diagonalize the Hamiltonian on the basis set $\{|\Psi_0\rangle, |a_i^+ a_j \Psi_0\rangle\}$ and compute the natural orbitals corresponding to the new wave function. If this process is repeated until convergence, a CASSCF solution is obtained [11, 21].

3. Weakly interacting hydrogen molecules

The case of N non-interacting systems admits an explicit CASSCF solution in terms of the CASSCF solutions of the individual systems. For simplicity, a collection of N non-interacting hydrogen molecules is considered (N H_2 molecules at infinite distance from each other). The argument can easily be extended to any collection of non-interacting molecules. In each hydrogen molecule I, the two atoms are separated by an internuclear distance d_I. At infinite intermolecular separation, each molecule can be treated separately from the other. The orbitals of each H_2 separate into orbitals of different *local* symmetries. In particular, there will be orbitals of g or u local symmetry with respect to the molecule inversion centre, even if this operation is not a symmetry operation for the whole system. The Hamiltonian of the system is the sum of the individual Hamiltonians:

$$H = \sum_I H(I). \tag{10}$$

The SCF solution for the Ith molecule is

$$|\Phi(I)\rangle = |\phi_I \bar{\phi}_I\rangle \equiv |\phi_I^2\rangle, \tag{11}$$

with energy $E_\Phi(I)$, where ϕ_I is the SCF bonding orbital of g local symmetry. The valence CASSCF solution for the same molecule requires a (2/2) active space. The corresponding wave function is given by

$$|\Psi(I)\rangle = \cos\theta_I |\gamma_I^2\rangle + \sin\theta_I |\upsilon_I^2\rangle, \tag{12}$$

with energy $E_\Psi(I)$, where γ_I and υ_I are the bonding and antibonding CASSCF orbitals of molecule I, and have

local symmetry g and u, respectively. Note that $\phi_I \neq \gamma_I$, since the CASSCF orbitals are different from the SCF orbitals. The SCF solution is a good approximation of the exact wave function at short distances, while its energy is much too high at long distances, because of the lack of non-dynamical correlation. This correlation is introduced at the CASSCF level, whose solution has essentially the same degree of accuracy at long and short distances. For this reason, the difference between the SCF and the CASSCF energies for molecule I ($E_\Phi(I)$ and $E_\Psi(I)$, respectively) increases as a function of the interatomic distance:

$$E_\Phi(I) - E_\Psi(I) \leq E_\Phi(J) - E_\Psi(J), \quad \text{if } d_I \leq d_J. \quad (13)$$

The solutions for the whole system are now considered. The global SCF solution is given by the Slater determinant

$$|\Phi\rangle = \prod_K |\Phi(K)\rangle = |\phi_1^2 \cdots \phi_N^2\rangle \quad (14)$$

with energy

$$\mathbf{E}_\Phi = \sum_K E_\Phi(K). \quad (15)$$

Let us consider a CASSCF(2/2) wave function for the total system. If the orbitals γ_I and υ_I are chosen as active orbitals, the CASSCF(2/2) total wave function is

$$|\Psi(I)\rangle = |\Psi(I)\rangle \otimes \prod_{K \neq I} |\Phi(K)\rangle \quad (16)$$

(here $\otimes$ indicates the antisymmetrized tensor product). This is because the different H_2 molecules do not interact, and therefore the global wave function is the product of the wave function of the individual H_2 molecules. The energy associated to this solution is

$$\mathbf{E}_\Psi(I) = E_\Psi(I) + \sum_{K \neq I} E_\Phi(K). \quad (17)$$

All these solutions have the form of a product of SCF or CASSCF functions on different molecules. This means that they are in effect CASSCF solutions, since the GBT conditions are trivially satisfied. Actually, single excitations involving orbitals belonging to the same molecule give vanishing interactions with $|\Psi(I)\rangle$, since the GBT conditions are satisfied on each molecule. On the other hand, single excitations involving two different molecules do not interact with $|\Psi(I)\rangle$, because of the local character of the Hamiltonian. Note that all these solutions correspond to a *minimum* of the energy with respect to orbital rotations.

Therefore, there exist at least N possibilities for the choice of a CASSCF(2/2) active space for the ground state of this system. They introduce the correlation on the bond of one molecule, and lead to N different CASSCF solutions, having in general different energies. Among these different CASSCF minima, the lowest one corresponds to the largest value of the interatomic distance. In fact, equation (17) implies that the energy difference between $\mathbf{E}_\Psi(I)$ and $\mathbf{E}_\Psi(J)$ is given by

$$\mathbf{E}_\Psi(I) - \mathbf{E}_\Psi(J) = E_\Psi(I) - E_\Phi(I) - E_\Psi(J) + E_\Phi(J). \quad (18)$$

Equation (13) implies that the sign of this difference is positive if $d_I \leq d_J$, and this shows that the absolute minimum (among the ones which are being considered) corresponds to the largest value of d.

The above results can be easily generalized to a CASSCF($2n/2n$) involving $2n$ active electrons into $2n$ active orbitals (n bonding and n antibonding). One gets a total of

$$\binom{N}{n}$$

possibilities. In general, for $n = 0$ (SCF) and $n = N$ (full valence CASSCF), a *unique* valence CASSCF solution exists, although multiple solutions cannot be ruled out even for these cases.

If an interaction between the different H_2 molecules is introduced (assuming, for instance, that intermolecular distances are large but finite), the number of CASSCF stationary points can become even larger. The study of their nature would require the computation of the CASSCF Hessian, and this is beyond the scope of the present work. We can notice, however, that a small interaction cannot change qualitatively the topological properties of the energy surfaces as a function of the orbital rotations. In particular, in the neighbourhood of a minimum must be present a minimum. This means that each one of the N choices of the (2/2) active space leads, as in the non-interacting case, to a minimum for the interacting systems (for a sufficiently weak interaction). Their energies are close to the sum of the CASSCF energy of the molecule being correlated, plus the SCF energies of the remaining molecules.

It should be stressed that all these different solutions can by no means be seen as describing excited states of the system. Rather, they are all different possible descriptions of the ground state. Such solutions are in general strongly non-orthogonal, and have a very large overlap with the global SCF wave function. Since a CAS-CI wave function is invariant under a unitary transformation mixing orbitals within each of the three orbital classes, the form of the energy surface as a

function of the orbital parameters is unique, that is it is not related to the particular description (localized versus delocalized) that is adopted. This means that, in general, these CASSCF local minima can be described by using either a localized or a delocalized CASSCF approach. The fact that the normal (delocalized) CASSCF algorithms do not usually show such a wealth of solutions is simply due to the difficulty of convergence to a particular solution using delocalized orbitals. One should note, however, that there exist minima described by local orbitals that break the system symmetry; these minima cannot be described by delocalized symmetry orbitals.

4. Applications

The analysis of the previous sections is applied to two systems. The first is composed of two weakly interacting H_2 molecules. Following the analysis of section 3, there exist in this case two distinct CASSCF(2/2) minima, depending on the molecule where the active orbitals are located. The second system is given by the ethylene molecule. Three (2/2) and six (4/4) non-equivalent CASSCF solutions were found for this molecule.

For both molecules we applied two different formalisms, both based on local orbitals. The first is an internally contracted perturbative algorithm [11], and gives solutions that are rigorously equivalent to those obtained through the standard CASSCF approach (since the GBT is satisfied by the solution). The second approach, which is variational, is based on an uncontracted CI correction to the CAS-CI wave function, and is the CAS-ISO formalism [9]. The energies obtained with the two methods coincide within a fraction of a mhartree in all the considered cases.

4.1. *Two H_2 molecules*

Two weakly interacting hydrogen molecules have been considered, with a trapezoidal C_{2v} disposition, as shown in figure 1. The first one, molecule 1, has a bond length close to the equilibrium length, with an internuclear distance $d_1 = 1.40$ bohr. The second molecule, 2, has a slightly longer bond distance, $d_2 = 1.60$ bohr. The two molecular centres are relatively far apart, their distance being $R = 3.00$ bohr. Therefore, the two molecules are weakly interacting. An atomic natural orbital (ANO) basis set of 2s1p quality was used on each hydrogen atom [22].

The case $R = \infty$ was considered first. The system is composed of two non-interacting molecules, and there exists one valence CASSCF(2/2) solution for each molecule. The SCF wave functions of the two isolated molecules are $|\Phi(1)\rangle = |\phi_1^2\rangle$ and $|\Phi(2)\rangle = |\phi_2^2\rangle$, with energies $E_\Phi(1) = -1.132\,793\,18$ and $E_\Phi(2) = -1.126\,188\,28$. The corresponding CASSCF wave
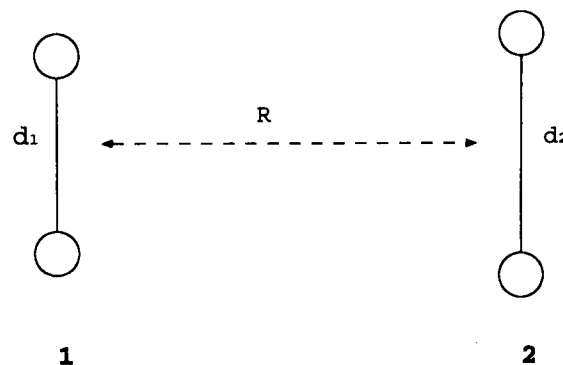

Figure 1. The two H_2 molecule geometry: $d_1 = 1.4$ bohr, $d_2 = 1.6$ bohr, $R = 3.0$ bohr.

functions are $|\Psi(1)\rangle$ and $|\Psi(2)\rangle$, with energies $E_\Psi(1) = -1.150\,596\,61$ and $E_\Psi(2) = -1.147\,325\,76$. The SCF total wave function is $|\Phi\rangle = |\Phi(1)\rangle \otimes |\Phi(2)\rangle$. There are two CAS(2/2) solutions: one with active space on molecule 1, $|\Psi(1)\rangle = |\Psi(1)\rangle \otimes |\Phi(2)\rangle$, and one with active space on molecule 2, $|\Psi(1)\rangle = |\Phi(1)\rangle \otimes |\Psi(2)\rangle$. Finally, there is one CAS(4/4) solution, $|\Psi(1,2)\rangle = |\Psi(1)\rangle \otimes |\Psi(2)\rangle$. Choosing the total SCF energy as zero, $E_\Phi = -0.0$ hartree, one obtains $E_\Psi(1) = -0.017\,803\,43$, $E_\Psi(2) = -0.021\,137\,48$, and $E_\Psi(1,2) = -0.038\,940\,91$ hartree, respectively.

The corresponding results for the weakly interacting case, $R = 3.0$ bohr, are reported in table 1. Notice that the localized-orbital approach is capable of finding both CAS(2/2) solutions (with $E_\Psi(1) = -0.018\,771\,01$ and $E_\Psi(2) = -0.022\,417\,74$ hartree, respectively), as well as the CAS(4/4) solution, ($E_\Psi(1,2) = -0.041\,844\,56$ hartree). On the other hand, only the lowest (2/2) solution can be found using the usual CASSCF approach.

The results obtained with the CAS-ISO orbitals are extremely close to those obtained with the CASSCF orbitals, the difference between the two formalisms being less than one mhartree at the three levels that were considered (CAS, CAS + S, CAS + SD). The difference between CASSCF and CAS-ISO becomes smaller as the excitation level is increased; about 1.0 mhartree for the CAS, 0.1 mhartree for CAS + S, and 0.01 mhartree for CAS + SD.

4.2. *Ethylene*

The ethylene molecule has been taken as a second, more realistic example. The geometry of the molecule is the experimental equilibrium one, that is $d_{C-C} = 1.339$ Å, $d_{C-H} = 0.85$ Å, $HCH = 124.8°$. An ANO basis set of 3s2p1d quality was used for each carbon atom, and 2s1p for each hydrogen atom [22]. Valence CASSCF(2/2) and CASSCF(4/4) solutions were computed, all involving an equal number of bonding and antibonding orbitals located on the same molecular

Table 1.   Two H_2 molecules.

(a) Usual CASSCF

	SCF	CASSCF(2/2)	CASSCF(4/4)
	−2.210 002 69	−2.232 420 43	−2.251 847 25

(b) Local orbitals (this work)

Active space	CASSCF	CASSCF + S	CASSCF + SD	CAS-ISO	CAS-ISO + S	CAS-ISO + SD
(σ_1)	−2.228 773 70	−2.230 108 98	−2.283 036 30	−2.228 002 37	−2.230 183 67	−2.283 023 28
(σ_2)	−2.232 420 43	−2.233 721 63	−2.283 148 39	−2.231 644 53	−2.233 792 88	−2.283 138 21
(σ_1, σ_2)	−2.251 847 25	−2.252 824 48	−2.283 492 70	−2.251 172 86	−2.252 815 52	−2.283 484 97

Figure 2.   The ethylene bond numbering.
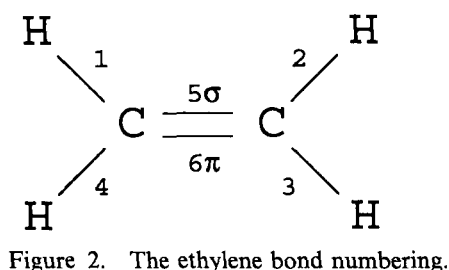
bond. The molecular structure and the bond numbering are shown in figure 2.

The system has D_{2h} symmetry. Because of the nonlinear nature of CASSCF and CAS-ISO methods, broken symmetry solutions can exist. For this reason, working with different symmetry subgroups of the full molecular group can give different results. In table 2, the results using the usual CASSCF algorithm are reported. Using the C_s symmetry subgroup, two (2/2) solutions are found, one with a (σ, σ^*) and the other one with a (π, π^*) active space. (Other 'unphysical' solutions are also possible, having an active space with both σ and π orbitals.) The second solution has an active space located on the π C=C bond, while the first solution is of a broken-symmetry nature and corresponds to an active space located on one of the C–H bonds (table 2, part (a)). Of course, there exist four equivalent solutions on the four equivalent bonds, with strictly degenerated energies. The lowest (4/4) solution is found to involve mainly the central double bond, with localized σ and a π pair as active orbitals.

If the calculation is performed using the full group of the molecule, the previously found lowest σ (2/2) solution no longer exists (see table 2, part (b)). Instead, in this case, the lowest solution corresponds to an active space involving two σ orbitals of the central C=C bond. The two active orbitals are in this case of a_g and b_{1u} symmetries. Many other solutions involving different symmetries are possible, as shown in the table.

Table 2.   Ethylene molecule. Canonical orbitals: the SCF energy for this molecule is −78.051 434 63 hartree.

(a) C_s symmetry

CASSCF(2/2)	orbital symmetry	
	(σ, σ^*)	−78.066 678 26
	(π, π^*)	−78.079 055 73
CASSCF(4/4)	$(\sigma, \sigma^*, \pi, \pi^*)$	−78.105 123 15

(b) D_{2h} symmetry

CASSCF(2/2)	orbital symmetry	
	(a_g, a_g)	−78.053 822 80
	(a_g, b_{3u})	−78.055 748 96
	(a_g, b_{1u})	−78.061 846 93
	(a_g, b_{2g})	−78.051 734 57
	(b_{3u}, b_{3u})	−78.054 094 63
	(b_{3u}, b_{1u})	−78.052 202 01
	(b_{3u}, b_{2g})	−78.052 734 98
	(b_{1u}, b_{2g})	−78.051 780 97
	(b_{2g}, b_{2g})	−78.053 630 92

Their energies are much higher and close to the SCF energy of −78.051 434 63 hartree.

The previous results show that by using the usual CASSCF algorithm, either localized or delocalized MOs can be obtained, in an essentially unpredictable way. Moreover, although many different solutions can be obtained, it is extremely difficult to associate a physical interpretation to these multiple minima, which are usually discarded. The situation is different if local orbitals are used. Table 3 reports the CASSCF and CAS-ISO results using orbitals that are localized on molecular bonds. The (2/2) CASSCF solutions are found. There are six in total: two on the central double bond, and one for each of the four C–H bonds. This makes a total of three non-equivalent solutions. It is also possible to find six non-equivalent (4/4) solutions, corresponding to an active space that correlates two bonds of the molecule. The lowest energy corresponds

Table 3. Ethylene molecule. Localized orbitals: the SCF energy for this molecule is $-78.051\,434\,63$ hartree.

Active space	Bonds	CASSCF	CASSCF + S	CASSCF + SD	CAS-ISO	CAS-ISO + S	CAS-ISO + SD
(σ_{CH})	(1)	$-78.066\,678\,26$	$-78.081\,027\,72$	$-78.331\,789\,25$	$-78.066\,567\,03$	$-78.080\,628\,78$	$-78.331\,761\,00$
(σ_{CC})	(5)	$-78.061\,846\,87$	$-78.095\,848\,85$	$-78.331\,578\,77$	$-78.061\,546\,69$	$-78.095\,268\,21$	$-78.331\,640\,91$
(π_{CC})	(6)	$-78.079\,055\,73$	$-78.117\,778\,64$	$-78.337\,769\,22$	$-78.078\,577\,04$	$-78.118\,074\,32$	$-78.337\,728\,65$
$(\sigma_{CH}, \sigma_{CH})$	(1,2)	$-78.082\,131\,40$	$-78.110\,849\,66$	$-78.335\,457\,23$	$-78.081\,862\,29$	$-78.110\,181\,99$	$-78.335\,387\,27$
$(\sigma_{CH}, \sigma_{CH})$	(1,3)	$-78.081\,994\,79$	$-78.111\,561\,88$	$-78.335\,479\,31$	$-78.081\,673\,73$	$-78.110\,943\,01$	$-78.335\,405\,43$
$(\sigma_{CH}, \sigma_{CH})$	(1,4)	$-78.084\,495\,25$	$-78.111\,759\,27$	$-78.335\,861\,77$	$-78.084\,015\,02$	$-78.111\,805\,37$	$-78.335\,855\,59$
$(\sigma_{CH}, \sigma_{CC})$	(1,5)	$-78.079\,235\,31$	$-78.125\,864\,97$	$-78.335\,754\,74$	$-78.078\,571\,07$	$-78.126\,229\,92$	$-78.335\,833\,80$
(σ_{CH}, π_{CC})	(1,6)	$-78.097\,054\,53$	$-78.148\,712\,96$	$-78.341\,823\,49$	$-78.094\,952\,02$	$-78.149\,185\,72$	$-78.341\,706\,28$
(σ_{CC}, π_{CC})	(5,6)	$-78.105\,123\,15$	$-78.148\,894\,66$	$-78.342\,937\,25$	$-78.104\,431\,82$	$-78.148\,603\,98$	$-78.342\,908\,40$

to the calculation where central C=C double bond is correlated. The (4/4) results are coherent with the importance of the correlation contribution that is deduced from the (2/2) results. Electron correlation has a non-additive behaviour, as shown by the CASSCF and CAS-ISO results involving two C–H bonds: the lowest energy is obtained in the case of two bonds involving the same C atom, (1,4); then, with very similar energies, (1,2) and (1,3). The (1,2) pair has lower energy than the (1,3) pair, according to the fact that correlation is larger if the active orbitals are closer. This effect is very strong in the case of the double bond, which has the lowest (4/4) energy, although a single C–H bond is more correlated than the C–C σ bond. Note, however, that the energy ordering of the different solutions may change when single or single + double excitations are added.

5. Conclusion

It has been shown that the CASSCF equations admit in general a very large number of different solutions. By using the usual CASSCF formalisms, which search for the global energy minimum, it is difficult to have a control on the nature of the solution obtained at the end of the iterative process, and the interpretation of the resulting active orbitals is often problematic. On the other hand, recently proposed formalisms can be successfully used to choose the particular solution to which one wants to converge. The methods are based on the partial diagonalization of the density matrix, and, in the case of a contracted expansion of the wave-function correction, give results identical to the usual CASSCF formalism, although expressed on a different (but equivalent) basis set.

These facts have important consequences on actual CASSCF calculations. It is well known that CASSCF is not a black-box method, but that the definition of the active space requires a careful analysis of the problem. In some cases, getting a solution involving the desired active orbitals may be extremely problematic, or even impossible. It is also known that different calculations on the same system may produce different results, the method being extremely sensitive to the initial orbital guess, and to other convergence features. We believe that the partial diagonalization methods provide a highly flexible tool that can be used for a fine definition of the active orbitals in CASSCF calculations. This fact could permit the application of CASSCF to the study of large systems, while keeping the size of the active space within reasonable limits.

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