

Selected dissociation- and correlation-consistent configuration interaction by a perturbative criterion

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We propose a perturbative criterion to select the most important dissociation- or correlation-consistent type of contributions to perform generalized valence bond-configuration interaction (GVB-CI) calculations, dissociation-consistent configuration interaction (DCCI) or correlation-consistent configuration interaction (CCCI) approach, respectively. The procedure presented is computationally less demanding than the CCCI proposed by Goddard and co-workers. To ensure the distance consistency of the MOs used, the nonvalence virtual orbitals are obtained by a projection technique. The results obtained for a few test calculations show the ability of the suggested approach to get close results to full CI, DCCI, and CCCI values using a small CI expansion. It seems to be a promising way to treat correlation changes in large molecular systems which would be inaccessible by other methods.

I. INTRODUCTION

As a result of the recent advances in developing efficient quantum-mechanical algorithms and computer technology, full configuration interaction (FCI) calculations are becoming feasible to perform on small systems.¹ However, FCI solutions are not yet possible for molecular systems of moderate size which are usually involved in daily chemical applications. Thus, quantum chemists are forced to look into the many existing approaches to obtain an approximate solution to the FCI. This holds especially for molecules containing heavy atoms or transition metals.

In chemical applications, energy differences are more important than absolute energies, e.g., bond energy, excitation energy, etc. Consequently, if an "accurate" energy difference is desired, it is a critical step to truncate the whole space spanned by a many-electron basis set in such a way that the relevant differential part of the electron correlation is considered in the two different situations studied. Thus, in order to compare the energies, for instance, of A_2 and $2A$ systems, if the relevant terms in the two cases are treated in a balanced way, we can expect a binding energy close to the FCI result, but at a much lower cost.

Obtaining accurate bond dissociation energies has been the subject of previous attention. It is worthwhile mentioning the "optimized valence configurations" (OVC) method² of Das and Wahl, and the "dissociation-consistent configuration interaction" (DCCI) method³ of Goddard and co-workers. Both have a similar target: to take into account only those changes happening as the molecule forms. The two methods have their own intrinsic shortcomings from a computational point of view. In the OVC approach the choice of configurations to perform the independent multiconfiguration self-consistent field (MCSCF) calculations is quite specific to the particular molecule; the

number of the exploratory calculations may become large. However, the DCCI method and another related approach, namely the "correlation-consistent configuration interaction" (CCCI),^{3(g)-3(j)} present a more systematic scheme. For instance, the DCCI partition allows for a single bond full correlation of the two electrons involved in the bond to break and some additional correlation with the remaining electrons which are not involved in the breaking bond. This implies that the CIs to be performed may easily become quite large, depending on the system and basis set used. In fact, employing an effective core potential and a valence basis set of a moderate size, full DCCI calculations for RuH^+ were found excessively large to be carried out.^{3(e)} It is apparent that a criterion to choose the main configurations involved in the OVC approach or to reduce the dimension of the dissociation- and correlation-consistent CI might be welcome. An exploration of this possibility is presented here.

In this work, we propose a perturbative criterion to select the most important dissociation- and correlation-consistent type of contribution³ to the CI wave function, along with a systematic way to ensure the distance consistency behavior of the one-electron basis set used in the CI calculations. Valence MOs are obtained by means of the generalized valence bond-perfect pairing (GVB-PP) procedure, nonvalence ones by projection techniques. As it will be shown below, the "dissociation-consistent configuration interaction perturbatively selected" (DCCI-PS) and the "correlation-consistent configuration interaction perturbatively selected" (CCCI-PS) provide an inexpensive way to obtain a good estimation of dissociation energies and seem to be a promising way to treat the correlation changes in large molecular systems. Since the proposal has the framework of the DCCI (or CCCI) approach, the limitations of the algorithm presented here are at best the same as the DCCI (or CCCI) treatment. It is to point out

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that results obtained by these approaches are quite encouraging. Applications include dissociation energy calculations of diatomic and polyatomic molecules including transition-metal-ligand systems^{3(a)-3(f)} and has been also proved to be applicable to calculating excitation energies.^{3(g)-3(i)}

In the next section, we outline the scheme followed in the calculations. In order to assess the ability of the method proposed, our results for a few test molecules (H_2 , BH, N_2 , and C_2F_4) are presented in Sec. III; also, the adiabatic singlet-triplet splitting in methylene is calculated. Our results are compared with the full DCCI (or CC CI) and FCI values. The conclusions are summarized in Sec. IV.

II. THEORETICAL METHOD

A. A valence complete active space-configuration interaction (CAS-CI) wave function

As is well known, a very important step in molecular calculations is the adequate treatment of the electron correlation internal to the valence shell (nondynamical correlation energy) which allows a proper dissociation to the Hartree-Fock (HF) solution for the fragments. The best possible way to treat the nondynamical correlation is through MCSCF approaches using as configurations those belonging to the complete active space (CAS) of occupied and virtual valence MOs, i.e., the valence CASSCF solution.⁴ Unfortunately, the process can be quite expensive for a polyatomic molecule.⁵ However, taking into consideration previous experience,⁶ a good approximation to the valence CASSCF ideal can be obtained performing a CAS-CI calculation using optimized valence orbitals by some cheaper procedure; for instance, for the N_2 molecule, by using the valence orbitals obtained by MCSCF techniques taking only a few valence pairwise double excitations,⁷ the CAS-CI correlation energy is $-0.1312 E_h$ to be compared with the CASSCF value of $-0.1338 E_h$.

Since we are looking at a bond breaking process we choose a method to get good valence orbitals which shares as much as possible the advantages from both a physical and computational point of view. This can be accomplished by the generalized valence bond approach in its perfect-pairing approximation⁸⁻¹⁰ (GVB-PP). Using the GVB-PP natural orbitals, the nondynamical correlation energy can be estimated by the full CAS-CI or a restricted CAS-CI calculation.

B. Redefinition of the nonoccupied space

Excitations involving the valence and nonoccupied orbitals are required in order to account for the correlation out of the valence space. The occupied orbitals are already well defined (localized) at any molecular geometry by the GVB-PP procedure. We also need to define the nonoccupied MOs, in such a way that they keep the same character during the breaking bond process. In fact, identification by comparison of the nonoccupied MOs in two quite different molecular conformations is not straightforward. At the optimal bond distance, the nonoccupied MOs will be delocal-

ized as much as possible. Increasing r_{bond} , the MOs tend to localize on the separate atoms or subsystems. We have used localized MOs, a practical solution proposed elsewhere.⁶ This allows us to calculate a truncated dissociation- or correlation-consistent CI in a coherent way for two distinct molecular geometries since all the MOs (occupied and nonoccupied) are as similar as possible.

Localization of the nonoccupied MOs is performed by a projection of the virtual AOs (or MOs) of the atoms (or subsystems), i.e., the nonoccupied MOs at $r_{\text{bond}} = \infty$, into the nonoccupied space of the molecule at short r_{bond} distances. The nonoccupied space is defined by the projector W :

$$W = \sum_{j^*} |\Psi_{j^*}\rangle \langle \Psi_{j^*}|, \quad (1)$$

where j^* runs over all the nonoccupied MOs. The set of projected orbitals is orthogonalized to the occupied orbitals (doubly occupied orbitals and natural orbitals of the GVB-PP pairs) by the Schmidt procedure. Thus, we can find well-defined oscillating and polarization MOs, used to obtain in an effective way radial and angular correlation of the atom (in the atom itself and in the molecule), respectively. They are also useful in order to account for molecular distortion.

C. Beyond the dominant valence correlation

The most important dissociation- or correlation-consistent contributions are selected by perturbing the CAS-CI wave function. The multireference CAS-CI wave function is perturbed to second order according to the Epstein-Nesbet definition¹¹ of the unperturbed Hamiltonian using the Rayleigh-Schrödinger perturbative expansion. If $\{R\}$ represents the set of determinants D_k belonging to the CAS space, the CAS wave function Ψ_{CAS} can be expressed as

$$\Psi_{\text{CAS}} = \sum_k C_k D_k, \quad K \in \{R\}. \quad (2)$$

Then, all the single and double excitations of the configurations belonging to the reference space $\{R\}$ are built. Those correlation-consistent configurations having contributions to the first-order wave function larger than a certain threshold ϵ ,

$$\left| \frac{\langle \Psi_{\text{CAS}} | H | D_l \rangle}{\Delta E} \right| > \epsilon \quad (3)$$

are the ones considered as the most important contributions in order to perform DCCI-PS or CC CI-PS calculations. In Eq. (3), the Epstein-Nesbet partition of the Hamiltonian is taken for the definition of H and ΔE . Since the ϵ value is *a priori* set up by the user, many different partitionings can be done. This ϵ threshold is the same as used in the configuration interaction by perturbation with multiconfigurational zeroth-order wavefunction selected by iterative process (CIPSI) algorithm¹² to increase iteratively the space treated variationally. In another context,

TABLE I. Total energies (in E_h) and calculated dissociation energies (kcal/mol) for H_2 at $r_{\text{bond}} = 1.4 a_0$.

Calculation level	Basis A ^a			Basis B ^b		
	NCF ^c	E_t	D_e^d	NCF ^c	E_t	D_e^d
HF	1	-1.129 262	82.0 ^f	1	-1.133 371	83.8 ^g
GVB(1/2)-PP	2	-1.147 492	93.5	2	-1.151 862	95.4
CAS-CI	2	-1.147 492	93.5	2	-1.151 862	95.4
CASSCF ^e						107.3
DCCI-PS						
Partition I	5	-1.159 177	100.8	5	-1.166 207	104.4
Partition II	10	-1.161 263	102.1	20	-1.169 671	106.5
FCI			103.0			107.3
Exptl. ^h						109.5

^aContracted (4s, 1p/2s, 1p). At $r_{\text{bond}} = 20.0 a_0$, the total energy is $-0.998\,555 E_h$.

^bContracted (7s, 3p/3s, 2p). At $r_{\text{bond}} = 20.0 a_0$, the total energy is $-0.999\,895 E_h$.

^cNCF, number of configurations.

^dConversion factors used in this paper $1 E_h = 627.5 \text{ kcal/mol} = 27.21 \text{ eV}$.

^eActive orbitals $1-4\sigma_g$, $1-4\sigma_u$, $1-2\pi_u$, $1-2\pi_g$; $r_{\text{bond}} = 1.4 a_0$ (Ref. 18)

^fReferred to the value given in (a).

^gReferred to the value given in (b).

^hReference 17.

for ground state MCSCF calculation purposes, second-order perturbation theory has been previously employed as a configuration, and also orbital generator.¹³

The DCCI-PS and CCCI-PS procedures are quite advantageous and systematic, due to the existence of a criterion for an *a priori* selection of the type of correlation excitations.¹⁴ The advantage lies in the fact that the binding energies can be estimated in a very inexpensive way. On the other hand, the correlation treatment can be improved if higher accuracy is needed and computer resources are available.

III. RESULTS AND DISCUSSION

A. Estimation of dissociation energies

1. H_2

In order to get some more insight in the DCCI-PS approach, let us start with a simple two-electron system such as the H_2 molecule. Two different basis sets were employed. In the double- ζ plus polarization quality (hereafter called basis set A), the hydrogen atoms were described with the Dunning double- ζ contraction¹⁵ of the Huzinaga (4s) basis set¹⁶, with one set of *p*-type polarization functions ($\zeta^p = 1.0$). Moreover, in order to come near to the D_e experimental value (4.75 eV),¹⁷ a much larger basis set¹⁸ of the general contraction type based on atomic natural orbitals (ANO)¹⁹ was also used (basis set B). At each theoretical level, the dissociation energy is calculated as the difference between the corresponding energy values at $r_{\text{bond}} 20.0$ and $1.4 a_0$, i.e., D_e is computed from a supermolecule calculation. Table I collects the results obtained for the different partitionings achieved.

To describe properly the dissociation of the H_2 molecule to two neutral HF atoms, two configurations $1\sigma_g^2$ and $1\sigma_u^2$ are needed. The MCSCF wave function is designated GVB(1/2)-PP meaning that one electron pair is described by two natural orbitals (PP refers to the perfect singlet-

pairing restriction). In this case, the CAS-CI and GVB(1/2)-PP energies are the same. Once the localization of the nonoccupied space is achieved by projection techniques, the CAS wave function is perturbed to second order in energy. Different thresholds ϵ may be used to choose configurational spaces. By using this criterion, three configurations perturbing the CAS-CI wave function appear as the dominant ones: $2\sigma_g^2$ and $1\pi_{ux}^2(1\pi_{uy}^2)$, which form the partition I in Table I, and account for the in-out and angular correlation, respectively. If ϵ is decreased [and the number of configurations (NCF) increased], one will progressively approach to the basis set exact result (see partition II in Table I where nearly all the double excitations $1\sigma_g^2 \rightarrow \Psi_F^2$ are included). In this case, due to the simplicity of the model, the dissociation energy obtained by the DCCI method is equivalent to the FCI result, and a DCCI-PS value is a lower bound for it.

An interesting conclusion can be reached by inspection of Table I. Diagonalizing a low dimension matrix, a good estimation of D_e can be obtained compared with higher levels of calculation; in all cases, the difference is less than 3 kcal/mol referred to the FCI (partition I) or nearly equal to the FCI result (partition II). If this relatively small difference is maintained for larger molecular systems, the DCCI-PS or CCCI-PS procedures could be considered appropriate to deal with these systems. In any case, within the limitations of the basis set used, the reference values will be the FCI ones, rather than the experimental data, which include other effects not involved by the nonrelativistic Born-Oppenheimer standard molecular Hamiltonian.

2. BH

A basis set of valence double- ζ plus polarization quality was used in the BH calculations. It is the B(9s5p/3s2p) and H(4s/2s) Dunning contractions¹⁵ augmented by one set of $3d$ polarization functions (exponent 0.5) for boron

TABLE II. Total energies (in E_h) and dissociation energies (kcal/mol) for BH.

Calculation level	$r_{\text{bond}} (a_0)$			D_e
	NCF ^a	2.329	20.0	
HF	1	-25.119 837		59.2 ^b
GVB(1/2)-PP	2	-25.133 904	-25.025 525	68.0
CAS-Cl	4	-25.133 904	-25.025 525	68.0
CAS-Cl	9	-25.134 255	-25.025 525	68.2
DCCI-PS				
Partition I	15	-25.140 225	-25.027 636	70.6
Partition II	35	-25.150 803	-25.029 151	76.3
Partition III	109	-25.160 990	-25.036 470	78.1
Partition IV	175	-25.162 672	-25.036 717	79.0
FCI ^c				79.9
Exptl ^d				82.3

^aNCF, number of configurations.

^bReferred to $-25.025 525 E_h$ which is the sum of the total energy for B, $-24.526 248 E_h$ and H atom, $-0.499 277 E_h$, ground states at the open-shell restricted Hartree-Fock (OS-RHF) level.

^cReference 1(a)

^dReference 17.

(with the 3s combination excluded), and one set of 2p polarization functions (exponent 1.0) for hydrogen. This basis set is very similar to that used in the FCI^{1(a)} and CCCCI^{3(j)} studies. The bond length was settled up at the same value as in the previous studies, 2.329 a_0 (experimental geometry), so a meaningful comparison can be made. Table II shows the results obtained for the BH molecule.

Two configurations $1\sigma^2 2\sigma^2 3\sigma^2$ and $1\sigma^2 2\sigma^2 4\sigma^2$ are required to guarantee the dissociation of the molecule into the HF atoms. Optimization of the 3 σ and 4 σ orbitals by the MCSCF procedure cause a distortion of the 2 σ orbital out of the bonding region compared with the HF 2 σ orbital. That is, localization of the 2 σ orbital has been achieved at short r_{bond} distance: it resembles very much (except for a small delocalization tail) its asymptotic limit $2\sigma \rightarrow 2s$ (B) at $r_{\text{bond}} = 20.0 a_0$. The efficiency of the orbital optimization is reflected in the considerable improvement of the GVB(1/2)-PP D_e value compared with the HF one. In order to remove the restriction of singlet pairing imposed in the orbital optimization at the GVB-PP level, the CAS-Cl(4) wave function represents a configuration interaction expansion using the GVB-PP orbitals in which the two electrons of the pair are allowed to occupy the two natural orbitals of the pair in all three ways; this makes a total of four determinants. In order to allow the orbital shape changes, the CAS-Cl(9) wave function includes a complete CI in the valence space.

The DCCI configurational space used in the different partitions (Table II) has been built³ considering single and double excitations from the bond pair and those simultaneous with single excitations from the 2 σ nonbonding valence orbital. We have only chosen dissociation-consistent excitations which perturb more the CAS-Cl(4) wave function at short r_{bond} distances. In this case, the most important dissociation-consistent contributions are double excitations of the type $(3\sigma \rightarrow \Psi_{\sigma})^2$ and also $(3\sigma 3\sigma \rightarrow \Psi_{\sigma} \Psi_{\sigma})^2$ and $(2\sigma 3\sigma \rightarrow \Psi_{\sigma} \Psi_{\sigma})^2$. Since the occupied orbitals are well

TABLE III. Total energies (in E_h) and dissociation energies (kcal/mol) for the ground state of the N₂ molecule.

Calculation level	$r_{\text{bond}}(a_0)$			D_e
	NCF ^a	2.123	20.0	
HF	1	-108.953 140		103.5 ^b
GVB(3/6)-PP	8	-109.032 895		153.6 ^b
CAS-Cl ^c	32	-109.088 266	-108.788 136	188.3
CCCI-PS				
Partition I	48	-109.097 937	-108.788 143	194.4
Partition II	79	-109.100 770	-108.788 143	196.2
FCI ^d				201.8
Exptl. ^e				228.3

^aNCF, number of configurations.

^bReferred to the CAS-Cl energy calculated at $r_{\text{bond}} = 20.0 a_0$, $-108.788 136 E_h$, i.e., two ⁴S nitrogen atoms separated 20.0 a_0 singlet coupled. For comparison purposes, the HF total energy of the ⁴S N atom gives $-54.394 395 E_h$. It means that the total energy of two ⁴S N atoms infinitely separated is about 0.4 kcal/mol lower than the CAS-Cl energy at $r_{\text{bond}} = 20.0 a_0$.

^cValence CAS-Cl where only the 2p electrons are correlated; the σ , π_x , and π_y subsystems keep two electrons of opposite spins.

^dOnly the 2p electrons are correlated [Ref. 1(g)].

^eReference 17.

localized as well as the nonoccupied ones by the variational MCSCF procedure and projection techniques, respectively, the orbitals at short and large r_{bond} distances are one by one related. This fact allows to use the selected CI space at short r_{bond} distance to calculate the DCCI-PS energy at $r_{\text{bond}} = 20.0 a_0$. In this way, by using different threshold ϵ for the selection of the dissociation-consistent excitations, four estimations of increasing quality were performed (see Table II). It is to note that using more than 35 determinants the calculated dissociation energy has a difference less than 3 kcal/mol with respect to the FCI result^{1(a)} (79.9 kcal/mol). Including 175 dissociation-consistent determinants, a value close to the FCI one is obtained, 79.0 kcal/mol. The agreement with Goddard's CCCCI result^{3(j)} (79.2 kcal/mol) is also very good.

3. N₂

As representative of multiple bonded systems, the N₂ molecule was chosen since the FCI result has been reported^{1(g)} using a double- ζ plus polarization basis set. We have used that basis set, i.e., the N (9s5p/4s2p) Dunning contraction¹⁵ adding a set of polarization functions (exponent 0.8) with the 3s component eliminated. At $r_{\text{bond}} = 2.123 a_0$ using that basis set, the FCI value (correlating only the 2p electrons) for D_e was found to be 8.75 eV.^{1(g)} Our calculated D_e values at the same geometry are listed in Table III.

It is well known that multiple bonds involve large correlation effects. The HF approximation is specially unsuited in these cases due to the overweight of the highly ionic terms (in the VB sense) imposed by the single determinant constraints. The HF configuration is

$$|1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4| \quad (4)$$

for the ground state of the N_2 molecule $^1\Sigma_g^+$. As can be seen from Table III, the dissociation energy at the HF level gives a poor result. Optimization of the valence bonding orbitals is carried out by the GVB(3/6)-PP approach. Owing to the MCSCF procedure, the localization of the lone pair of the same symmetry as the bonding orbital has been achieved in relation to the HF description, where the lone pair appear completely mixed. It implies that a good estimation of the nondynamical correlation energy can be obtained by performing a CAS-CI calculation in which the three bond electron pairs in the six valence orbitals (σ , σ^* , $\pi_{x,y}$, $\pi_{x,y}^*$) are active, freezing the lone pair MOs ($2\sigma_g$, $2\sigma_u$). The GVB (3/6)-PP wave function does not dissociate correctly to the HF products when the molecule splits in two separated atoms. However, the GVB (3/6)-PP orbitals serve as a good basis set to do the CI required for spin optimization. The virtual orbitals obtained by the MCSCF procedure at $r_{\text{bond}} = 20.0 a_0$ are the ones used as reference orbitals for the localization of the nonoccupied space at short r_{bond} distances. We had certain problems in order to get the correct convergence of the GVB (3/6)-PP wave function at $r_{\text{bond}} = 20.0 a_0$. However, using as trial the MOs obtained from the HF calculation of the upper valence multiplet $^7\Sigma_u^+$, $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^1 3\sigma_u^1 1\pi_u^2 1\pi_g^2$ configuration, the convergence was nicely achieved.

The spin coupling required to ensure the correct molecular dissociation is obtained with the valence $2p$ CAS-CI wave function by using the natural orbitals of the three GVB pairs. The valence CAS-CI wave function includes 32 determinants where the σ , π_x , and π_y subsystems are restricted to keep two electrons of opposite spins, as in the GVB-RCI wave function.³ Thus, CAS-CI involves all configurations arising from different occupations of each pair of natural orbitals for each GVB bond pair. The decreasing of energy by spin coupling is more significant at long r_{bond} distances (≈ 66 kcal/mol) than at short ones (≈ 35 kcal/mol).

In our approximation to the CCCI approach, the configurations chosen which perturb the CAS-CI wave function belong to the following classes²⁰: single and double excitations from the restricted CAS-CI(4) space relative to the N-N σ bond pair, simultaneous with the restricted CAS-CI(4) space for the N-N π_x (or π_y) bond pairs. Similar possibilities for the π_x and π_y bond pairs are also considered. Table III shows the results obtained for the different partitionings performed. Of course, determinants belonging to the valence CAS-CI wave function are also included in each case, i.e., partition I in Table III includes only (48–32) selected correlation-consistent determinants, etc. The most important correlation-consistent type of contributions selected by a perturbative criterion are those involving double excitations from the valence bonding MOs (PP natural orbitals) to the nonoccupied space. From the D_e results collected in Table III, it is clear that in this type of multiple-bonded system, a satisfying approximation to the FCI result is feasible by means of the CCCI-PS procedure.

TABLE IV. Results for C_2F_4 . Total energies (in E_h) and diabatic dissociation energies (kcal/mol), $D_e^{\text{diab}}(C_2F_4) = 2 \times E(^3B_1)CF_2 - E(C_2F_4)$. The CCCI-PS contributions considered dissociate at the HF level. The HF total energy of 3B_1 CF_2 is $-236.647\ 343 E_h$.

Calculation level	NCF ^a	E_t^b	D_e^{diab}
HF	1	-473.492 738	124.3
GVB(2/4)-PP	4	-473.532 554	149.3
CAS-CI	16	-473.549 085	159.6
CCCI-PS			
Partition I	29	-473.552 338	161.7
Partition II	57	-473.564 400	169.2
Partition III	132	-473.567 085	170.9
CCCI ^c			178.4

^aNCF, number of configurations.

^bExperimental geometry taken from Ref. 21.

^cSee Ref. 3(j).

4. C_2F_4

The original aim in developing the CCCI approach^{3(j)} was to treat large systems, impossible to deal with standard methods. A more realistic test case can be C_2F_4 , the test case that Carter and Goddard^{3(j)} used to show the value of CCCI, since a FCI calculation on this molecule is impossible. Thus, let us now apply the CCCI-PS approach to describe the double bond rupture of C_2F_4 , in order to analyze its accuracy and efficacy on a larger system, comparing the CCCI result.

For carbon and fluorine atoms, the Dunning valence double- ξ contraction¹⁵ of the Huzinaga (9s5p) basis set¹⁶ was employed. For the carbon atom, it was augmented by one set of Cartesian $3d$ polarization functions (exponent 0.64) with the $3s$ combination excluded. The experimental geometry for the ground state of the C_2F_4 molecule was taken from Ref. 21. The GVB(2/4)-PP orbitals calculated at $r_{C-C} = 20.0 a_0$, using an optimal geometry²² for the $CF_2(^3B_1)$ units, was employed in the projection step.

The scheme followed is parallel as described for N_2 . At the CAS-CI level, the rupture of the double bond of C_2F_4 produces two $CF_2(^3B_1)$ fragments singlet coupled. Let us focus our attention to the diabatic dissociation energy. As suggested by Carter and Goddard,^{3(j)} a subsequent CCCI deexcitation of each $CF_2(^3B_1)$ unit to the ground state of $CF_2(^1A_1)$ would result in the adiabatic bond dissociation energy. Analysis of the CCCI-PS approach to describe the electronic state splittings will be discussed below to calculate the singlet-triplet gap in methylene, which has been subject of many theoretical studies, including FCI³⁽ⁱ⁾ and CCCI^{1(c)} calculations, and also experimental determination.

Table IV shows the results for the diabatic dissociation energy D_e^{diab} of $C_2F_4(^1A_1)$. At the HF and GVB(2/4)-PP level, D_e^{diab} are calculated taking as reference twice the total energy of the $CF_2(^3B_1)$ fragment. Of course, at the CAS-CI level, the same reference was used. Even with the largest number of determinants considered, the most important CCCI-type contributions selected by a perturbative criterion vanishes at the infinite separated CF_2 units (it was also the case for N_2). Enlarging the number of determinants from partition I to III, the CCCI-PS results

TABLE V. Total energies (in E_h) and the calculated singlet–triplet splittings, ΔE_{ST} (kcal/mol), for the 1A_1 and 3B_1 states of methylene.

Calculation level	NCF _S ^a	1A_1	NCF _T ^b	3B_1	ΔE_{ST}
HF	1	− 38.885 956	1	− 38.927 619	26.1
GVB($M/2M$)-PP ^c	8	− 38.939 146	4	− 38.953 416	9.0
CAS-CI ^d	32	− 38.941 603	16	− 38.957 404	9.9
CCCI-PS	50	− 38.956 033	30	− 38.973 068	10.7
CCCI ^e					9.0
FCI ^f					11.97
Exptl. ^g					9.1

^aNCF_S, number of configurations for the singlet state.

^bNCF_T, number of configurations for the triplet state.

^c $M/2M$, number of GVB pairs/number of orbitals. For the singlet $M = 3$. For the triplet $M = 2$.

^dA restricted valence CAS-CI (see the text). For the sake of comparison, a CAS-CI with no restrictions has been carried out: NCF_S = 200, NCF_T = 125, being the total energies − 38.944 482 E_h and − 38.963 736 E_h for the singlet and triplet, respectively; $\Delta E_{ST} = 12.1$ kcal/mol, to be compared with the CASSCF value [Ref. 1(e)] of 12.82 kcal/mol.

^eReference 1(e).

^fReference 3(i).

^gReference 23.

smoothly tend to the CCCI value reported by Carter and Goddard.³⁽ⁱ⁾ Even more, with only 29 determinants, the calculated D_e^{diab} 161.7 kcal/mol already represents a considerable improvement in relation with the singly and doubly excited configuration interaction (SDCI) value^{3(j)} 135.9 kcal/mol.

From the tests studied in this work on the estimation of dissociation energies, it seems to be clear that only a few percent of determinants belonging to the DCCI or CCCI configurational space make a relevant contribution to the differential correlation and to the total energies. This suggests that the remaining contributions which are not considered in the variational truncation could be taken into account perturbatively. Indeed, a variational–perturbational approximation to DCCI has been recently proposed²⁴ and applied to characterize the HF and F₂ single bonds. Of course, enlarging the variational spaces considered here (the largest one 175 determinants) dissociation energies should converge to the DCCI or CCCI value.

B. Estimation of the singlet–triplet splitting in methylene

In order to test how well the CCC-PS behaves in the correlation of electronic state splittings, the calculation of the singlet–triplet splitting in methylene has been carried out.

A basis set of double- ζ plus polarization quality was used for carbon and hydrogen atoms. The carbon basis set is the Dunning double- ζ contraction¹⁵ with hydrogen exponents scaled by 1.2, augmented by one set of 3d polarization functions (3s combination removed) on carbon (exponent 0.6), and one set of 2p polarization functions on hydrogen (exponent 1.0). The geometries used for 1A_1 and 3B_1 states of methylene³ⁱ are $r_{C-H} = 1.113$ Å and HCH = 101.8° for the 1A_1 state, and $r_{C-H} = 1.084$ Å and

HCH = 133.2° for the 3B_1 state. Basis set and geometries are very similar to those used in previous studies.^{1(e),3(g)–3(i)}

Our results following Carter and Goddard's description of this system³ⁱ are listed in Table V. The GVB($M/2M$)-PP wave function allows optimization of the same number of orbitals for both states, i.e., $M = 3$ for the 1A_1 state and $M = 2$ for the 3B_1 state. In this way, six valence electrons are allowed to occupy six orbitals in both states. The restriction of singlet pairing within the GVB pair is eliminated by allowing the two electrons in each GVB pair to occupy the two natural orbitals of the pair in all three ways (36 determinants for the 1A_1 state and 16 determinants for the 3B_1 state). This restricted CAS-CI wave function includes the same degree of flexibility for both states.

In order to localize the nonoccupied orbitals the virtual orbitals of the upper valence quintuplet calculated at $r_{C-H} = 20.0 a_0$ were used as reference MOs for the projection step. That is, localization of nonoccupied orbitals for 1A_1 and 3B_1 CH₂ is performed using the same point of reference, the virtuals MOs of the C(³P) and H(²S) ground states. This brings the possibility to relate the corresponding nonoccupied orbitals in both states of methylene, sharing as much as possible the same basic character.

In addition to the CAS-CI configurations, all single and double excitations (from each configuration of a pair) of the carbon electrons in the nonbonding σ and π orbitals to all virtual MOs are relevant. Thus, in the CCCI-PS approach, we should choose the most important contribution of that type in a balanced way for both states. Although the nonoccupied MOs have the same basic features, it is not an easy task. A careful comparison of the perturbed wave function for the 1A_1 and 3B_1 states allows us to include the same few types of the most important correlation-consistent contributions for both states, involving radial and angular correlation for the σ nonbonding

orbital, and also contributions involving those single excitations simultaneous with single excitations from bonding MOs of C–Hs to their antibonding counterparts at the CAS-CI level. Working in this way, a value of 10.7 kcal/mol was found as an estimation for the singlet–triplet gap of methylene which is midway between the FCI value^{1(e)} 12.0 kcal/mol and the CCCI result³ⁱ 9.0 kcal/mol. Thus, the CCCI-PS procedure (using a few determinants) may serve to obtain good results for splittings of electronic states, although it is certainly a more involved choice than the CCCI-PS treatment of bond breaking/making processes.

Of course, the improvement of the results presented in this section would imply enlarging, in an adequate way, the variational spaces considered here. It could be achieved in an effective way using the criterion that the remaining CCCI contributions, which are not taken into account in the CCCI-PS approach at a given partition, make a negligible perturbative contribution, e. g., less than $10^{-4} E_h$ to the total energy of each state. It actually means converging to the CCCI ΔE_{ST} value. Although this possibility has not been explored yet, there is strong evidence to support it based on the convergence characteristics of the CCCI perturbative expansion.

IV. CONCLUSIONS

The results indicate that the DCCI-PS and CCCI-PS procedures, using small CI expansions, can be considered of valuable help to obtain good estimated dissociation energies, i.e., close to FCI quality, in a very inexpensive way. The CCCI-PS approach has been also found adequate, at least in a first step, to describe electronic state splittings. Thus, the DCCI-PS and CCCI-PS approaches appear as a systematic, inexpensive, and easy way to treat correlation changes in molecular systems with a large number of electrons, where other more involved techniques are either impossible to use or very expensive.

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