MO Theoretical Studies of Electron Pair Decorrelation Processes. I. Pair Correlation Energy and Single Bond Dissociation

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The homolytic dissociation of a single bond involves the decorrelation of one electron pair. Thus, the contribution of electron correlation to dissociation energies is large. In the present paper a new procedure is presented which allows the computation of the (within the given basis) complete correlation energy of one optimized electron pair. The method which requires only modest computational effort has been applied to the calculation of dissociation energies of a number of bonds of different types. The results show that the correlation of the electron pair of the bond which is broken contributes about 50–80% to the change of the total correlation energy occuring during the dissociation process which amounts to 20–70 kcal/mol. The fraction of correlation contributed by the bond electron pair as well as the relative importance of the left-right correlation within the bond depend very much on the type of the bond. In the case of CC and CH single bonds our method yields dissociation energies which are low by only about 5 kcal/mol. Thus, the method seems to be well suited for the calculation of potential surfaces of non-concerted organic chemical reactions which involve diradicals as intermediates.

Key words: Dissociation energies – Hole NO expansion – Pair Correlation energies.

1. Introduction

When potential surfaces of reactions are investigated with MO theoretical methods it occurs frequently that the interesting part of the surface contains

regions where a bond has been broken and a diradicaloid [1] species is formed. In the computation of such a surface the problem arises of obtaining the energy in the different parts of the surface with approximately the same accuracy. As it is well known, the closed shell SCF method fails and configuration interaction has to be taken into account. This has been accomplished by

1) extensive CI calculations [2–4]
2) the MCSCF [5] or DCSCF [6] methods with OVC [7] as a special case
3) an MCSCF plus limited CI [8] and GVB–CI [9]
4) 3×3 CI or other small CI calculations with few selected non-optimized configurations [10]
5) comparison of the closed shell SCF energy of a ground state with the open shell SCF energy of the transition state (if well defined) [11]. (This procedure is equivalent to the application of the DCSF method to the transition state.)

Extensive CI calculations represent today the most accurate but also the most expensive solution of the problem. In the limited CI approaches of the types 2)–4) one is confronted with the problem of the selection of those configurations which contribute to the bond dissociation process. The 3×3 CI or other very small CI calculations ensure the correct dissociation behaviour, need little computer time and, thus, have been used for the calculation of potential surfaces of larger systems [10].

The purpose of the present work has been twofold:

1) We want to provide a method which needs much less computational effort than CI calculations of the types 1)–3) and which allows the proper description of processes involving the decorrelation of one electron pair (like single bond dissociations) with higher numerical accuracy than the methods 4) and 5). For this purpose a new procedure was developed which allows the calculation of the (within the given basis) complete correlation energy of one optimized electron pair.
2) The change in total correlation energy occurring in a single bond dissociation process can be partitioned into contributions of different electron pairs. We want to study the relative importance of the contribution of the external correlation of the bond electron pair as well as the fraction of left-right correlation in the bond.

The work discussed in this paper should be regarded as the starting point for a more detailed study of the correlation effects occuring in single bond dissociations and in other processes involving the decorrelation of one electron pair.

2. The Hydrogen Molecule

The simplest example of a two-electron bond, the H_2 molecule, allows the demonstration of some of the problems arising in the application of different methods to the bond dissociation process. Table 1 lists not only computed dissociation energies (complete basis assumed) but also the errors in total energy for the H_2 molecule at the equilibrium distance of 1.4 a.u. and at infinite distance.

Table 1. Dissociation energy of the H_2 molecule computed with different methods (values in kcal/mol)

Method	Error for H_2^a $R = 1.4$ a.u.	$R = \infty$	dissociation energy
Experimental	0		109
SCF (closed shell)	26	180	263
SCF/open shell SCF	26	0	83
3×3 CI	$\geq 14^b$	10	105
DCSCF	14	0	95
CI (double)^c	0.1	10	119
PNO	0	0	109
PNO $(5s, 2p)^d$	2.4	0.1	107
PNO $(5s, 2p)$, 5 NO's^e	4.0	0.1	105

^{a} Error with respect to the exact energy, complete basis assumed.
^{b} Error depends on the choice of the virtual MO.
^{c} CI with all double excitations with respect to the SCF determinant.
^{d} Basis of Huzinaga [15], augmented by two sets of p functions.
^{e} NO expansion restricted to 5 NO's.

Closed shell SCF fails at infinite distance (energy high by 180 kcal/mol). Methods which allow only for double substitutions with respect to the SCF determinant yield an error of 10 kcal/mol [12] which can be identified as the error of the "half electron method" for the separate atoms [13]. For the H_2 molecule, on the other hand, the SCF energy is high by the correlation energy of the system which amounts to 25.6 kcal/mol [14]. Since only 11.5 kcal/mol are represented by left-right correlation, DCSCF and 3×3 CI which assure the correct dissociation behaviour miss 14 kcal/mol of the correlation energy of the molecule. The incompleteness of the basis in practical computations poses another problem. With the $5s$ basis of Huzinaga [15] contracted according [3, 1, 1] and augmented by two sets of p functions (thus representing a fairly large basis for molecular calculations) one cannot recover 2.4 kcal/mol of the correlation energy (by restriction to 5NO's [9] one would miss another 1.6 kcal/mol of the correlation energy). The surprisingly good value for the dissociation energy of H_2 obtained with the 3×3 CI is due to error compensation. The results of Table 1 show clearly that any method aimed at the reproduction of bond dissociation energies in molecules must at least include the (within the basis) full correlation energy of the electron pair of the respective bond.

3. Many-Electron Systems

3.1 NO *Expansion for One Occupied* MO

The straightforward procedure for obtaining the full external correlation energy of one electron pair is the NO expansion of Ahlrichs and Driessler [16]. In the computation of single bond dissociation energies in larger molecules with inclusion of the electron correlation of the bonding electron pair, one has to cope

Table 2. Total energy of the bicyclobutyl biradical **2** (values in a.u., minimal basis, angle between the three mentioned rings 112°)

| Method	total energy	CI coeff.[a]	relative energy[b]
closed shell SCF	151.8514	—	53.5
PNO for one pair	151.9095	−0.39	17.0
Triplet, open shell SCF	151.8965	—	25.2
3×3 CI[c]	151.9268	−0.46	6.2
PNO for one pair[c]	151.9290	−0.46	4.8
DCSCF[d]	151.9396	−0.43	0.0

[a] coefficient of the 2nd NO.
[b] Total energy relative to the DCSCF value in kcal/mol.
[c] Singlet energy, computed with the MO's of the triplet.
[d] computed by K. Wenzel [19].

with the ambiguity in the choice of the MO to be assigned to the bond under consideration. For bonded systems one may use the corresponding localized MO, while after bond-breaking one has to start from the singly occupied SCF MO's of the triplet in order to ensure the correct dissociation into open shell doublets. Which difficulties can arise in the intermediate range is best demonstrated with an example of a calculation on a diradicaloid species. Breaking of a bond in tetrahedrane **1** leads in the first step to the diradical **2** [17, 18]. In Table 2 we find

1   2
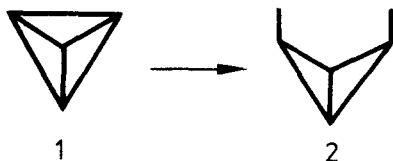
the values of the total energy of **2** as obtained from a PNO expansion starting from different types of SCF MO's. The DCSCF energy of the system computed by K. Wenzel [19] is still considerably lower than the PNO energy starting from the triplet SCF MO's (cf. Ref. 21). Thus, the SCF core MO's are far from being at the optimum for a pair correlated wave function. This optimization of the core MO's can be accomplished by a transformation of

a) the core MO's and the virtual MO's and
b) the core MO's and the two partially (in the triplet singly) occupied MO's.

In the present example the transformation of type a) gave an energy lowering of 0.1 kcal/mol, only. Thus, the internal transformation of type b) (main effect: increase of the exchange integral between the two partially filled MO's) is more important. An efficient procedure for performing this transformation is described below.

3.2 NO *Expansions for Electrons and for Holes*

The PNO expansion for one electron pair is depicted in Fig. 1. The corresponding wave function can be written as (N denotes the number of the highest occupied MO, n the number of basis orbitals):

$$\Phi_{PNO} = \sum_{i=N}^{n} c_i \Phi_{NN}^{ii}. \tag{1}$$

The energy expectation value is

$$E_{PNO} = 2 \sum_{i=N}^{n} c_i \langle i|h_{eff}|i \rangle + \sum_{i=N}^{n} \sum_{j=N}^{n} c_i c_j K_{ij} \tag{2}$$

with

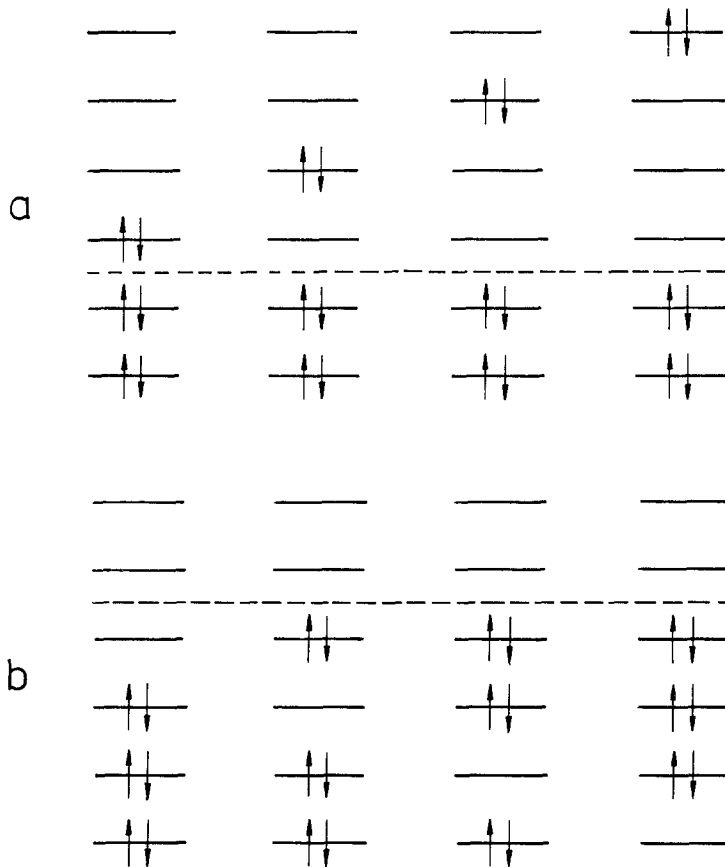$$h_{eff} = h + \sum_{i=1}^{N-1} (2J_i - K_i). \tag{3}$$

Fig. 1. Graphical representation of diagonal NO expansions for **a** two electrons and **b** for two holes

As it is shown in Fig. 1, one can as well give an NO expansion for two holes in the space of the occupied MO's and one virtual MO (e.g. the 2nd important NO of the PNO expansion above):

$$\Phi_{HNO} = \sum_{i=1}^{N+1} c_i \Phi_{ii}^{N+1,N+1}. \tag{4}$$

The energy expectation value reads:

$$E_{HNO} = 2 \sum_{i=1}^{N+1} c_i \langle i|h_{eff}|i \rangle + \sum_{i=1}^{N+1} \sum_{j=1}^{N+1} c_i c_j K_{ij} \tag{5}$$

with

$$h_{eff} = -h - \sum_{i=1}^{N+1} (2J_i - K_i). \tag{6}$$

Thus, h_{eff} of the hole expansion is the Fock operator of the dianion with reversed sign. With the hole expansion one can essentially optimize the MO's of a DCSCF function by transformation of the strongly occupied MO's among each other. The example of the C_4H_4 diradical has shown, that this kind of transformation is the most important step towards a DCSCF wave function. Since the energy expressions (2) and (5) are of the same form, the PNO and the HNO expansions can be performed with the same program.

One can obtain a wave function which is essentially an MCSCF function for one electron pair (PMCSCF) by performing the following steps successively:

1) PNO expansion for the highest occupied MO (or, alternatively, for a localized MO which can be assigned to the bond under consideration)
2) HNO expansion for the lowest hole pair
3) Improvement of the core MO's by a CI with single excitations into the virtual space. This step can be performed by a SCF like procedure for the DCSCF part of the wave function. The Fock operator can be written as

$$f = h + \sum_{i=1}^{N-1} (2J_i - K_i) + c_1^2(2J_N - K_N) + c_2^2(2J_{N+1} - K_{N+1}).$$

The variation is then performed in the space which is complementary to the two MO's N and $N+1$.
4) step 1).

The individual steps need the computational time of a few SCF iteration cycles. The resulting energy contains the full correlation energy of one optimized electron pair and, in addition, the contributions of all internal double excitations (into the 2nd NO of the PNO expansion). The procedure converges rapidly, as it is shown in Table 3 for the example of the preceeding section. In practical computations one can stop with step 4). The convergence behaviour does not worsen with increasing weight of the second configuration. We reported recently the

Table 3. Convergence behaviour of the PMCSCF method; Calculation on the bicyclobutyl diradical **2** (values in a.u.)

	Total energy	2×2 CI[a]	$-c_2$[b]	Energy gain[c]
SCF	151.85146			
PNO	151.90995	151.90800	0.386	
HNO	151.93651	151.93603	0.417	
single excitations[c]				1.4
PNO	151.93683	151.93653	0.422	
HNO	151.93703	151.93655	0.422	
single excitations				0.0
PNO	151.93684	151.93655	0.422	
HNO	151.93704	151.93655	0.422	
single excitations				0.0
PNO	151.93684	151.93655	0.422	

[a] 1st and 2nd NO of the PNO expansion, only.
[b] Coefficient of the 2nd NO.
[c] Energy gain in 10^{-4} a.u. by external single excitations for the remaining SCF MO's.

application of our method to the calculation of the reaction path connecting tetrahedrane and cyclobutadiene involving three conformers of the diradical **2** [18].

4. Computational Results

Single bond dissociation energies were calculated with our method for a number of molecules containing different types of bonds (Table 4). The dissociation energies obtained from the DCSCF part of the wave function as well as the differences between the closed shell SCF energies of the molecules and the open shell SCF doublet energies of the corresponding components are also given in Table 4.

The calculations were performed for experimental structures (With PMCSCF and with DCSCF smooth potential curves for the dissociation process can be obtained). Mostly, the $9s, 5p$ basis sets of Huzinaga [15] in the contraction [5, 1, 1, 1, 1, .3, 1, 1] were used. For hydrocarbons, also the $7s, 3p$ basis in the contraction [4, 1, 1.2, 1] and a $5s, 2p$ minimal basis [20] were applied. Augmentations by polarization functions are indicated in the table. In the cases of Li_2 and LiH diffuse s and p functions were added to the basis.

For two-valence-electron systems our method reduces to a simple PNO expansion. The reported values for the bond dissociation energies of H_2, LiH and Li_2 do not indicate the virtues of our method but rather are included, in order to demonstrate the basis set requirements. For recovering the external correlation energy of a bond pair within a few kcal/mol one needs fairly large basis sets which must certainly include polarization functions.

Table 4. Single bond dissociation energies (values in kcal/mol)

Bond	Molecule	Exper.[a]	Basis	SCF[b]	DCSCF	PMCSCF [c]	
H–H	H_2	109.4	$5s$	80.4	92.9	96.4	—
			$5s, 1p$	83.1	94.6	105.7	—
			$5s, 2p$	83.7	95.1	107.4	
Li–H	LiH	58.0	$10s, 3p/6s, 3p$	33.4	43.4	55.1	
			$10s, 3p, 1d/7s, 4p, 1d$	33.5	43.5	56.2	
C–H	CH_4	112	$5s, 2p/2s$ (MB)	107.1	116.0	116.6	0.3
			$7s, 3p/3s$	86.3	96.0	98.8	0.2
			$7s, 3p, 1d/3s, 1p$	89.9	99.3	108.9	0.1
			$9s, 5p, 1d/5s, 1p$	88.3	98.0	107.6	0.1
			$9s, 5p, 2d/5s, 2p$	88.9	98.6	109.0	0.1
N–H	NH_3	111	$9s, 5p, 1d/5s, 1p$	84.7	96.0	104.1	0.2
O–H	H_2O	126	$9s, 5p, 1d/5s, 1p$	88.2	101.1	107.9	0.4
F–H	FH	141	$9s, 5p, 1d/5s, 1p$	96.5	111.1	117.1	0.5
			$9s, 5p, 2d/5s, 2p$	98.2	112.7	119.7	0.4
Li–Li	Li_2	24.6	$10s, 3p$	3.5	—	20.8	—
			$10s, 3p, 1d$	3.6	—	23.2	—
C–C	C_2H_6	97	$5s, 2p/2s$ (MB)	91.8	100.3	101.4	0.5
			$7s, 3p/3s^d$	67.2	76.7	78.8	0.4
			$7s, 3p, 1d/3s^d$	76.2	85.6	92.2	0.3
	$C_3H_6{}^e$	64[f]	$5s, 2p/2s$ (MB)	—	55.7	57.5	1.3
			$7s, 3p/3s^d$	—	44.2	47.1	1.1
			$7s, 3p, 1d/3s^d$	—	54.9	60.5	1.0
N–N	N_2H_4	63	$9s, 5p, 1d/5s$	40.0	54.0	60.1	0.7
O–O	O_2H_2	56	$9s, 5p, 1d/5s$	3.6	31.3	36.9	1.9
F–F	F_2	38	$9s, 5p, 1d$	−35.7	12.4	17.6	2.7
			$9s, 5p, 2d$	−33.4	13.9	19.6	2.7
			$9s, 5p, 2d, 1f$	−32.3	15.1	21.5	3.0

[a] Thermochemical data and vibrational energies (corrections for zero point vibrations) were taken from Ref. 26 and 27.
[b] Closed shell SCF energy for the molecules and open shell doublet energies for the fragments.
[c] Contribution of internal double excitations (included in the PMCSCF values).
[d] The hydrogen s lobes were contracted to one basis function with the contraction coefficients taken from a SCF calculation of H_2.
[e] Cyclopropane; dissociation to trimethylene (0, 0) [28].
[f] Ref. 28; value does not include correction for zero point vibration.

In all cases considered so far, the PMCSCF procedure yields dissociation energies which are smaller than the experimental values (The large values obtained with the minimal basis are due to the unsaturation of the basis). While the computed dissociation energies of C–C and C–H bonds are low by only about 5 kcal/mol, the errors are much larger for bonds involving atoms with lone pairs.

The total contribution of electron correlation to bond dissociation energies (defined as the differences between the closed shell/open shell and the experimental dissociation energy) varies from about 20 kcal/mol (Li–Li, C–C and C–H bonds) to 70 kcal/mol (F_2). Of these correlation contributions, our method recovers more than 70% in most cases, though the fraction is smaller (~50%) for the O–H and the F–H bonds.

Table 5. Pair correlation energies (values in a.u.)

Bond	Molecule	Basis	Pair correlation energy total	left-right	(%)
H–H	H_2	$5s, 2p$	0.0379	0.0182	48
		$8s, 3p, 1d$	0.0396	0.0183	46
Li–H	LiH	$10s, 3p, 1d/7s, 4p, 1d$	0.0362	0.0159	44
C–H	CH_4	$5s, 2p/2s\ (MB)$	0.0147	0.0142	97
		$7s, 3p/3s$	0.0200	0.0159	80
		$7s, 3p, 1d/3s$	0.0238	0.0160	67
		$7s, 3p, 1d/3s, 1p$	0.0304	0.0155	51
		$9s, 5p, 1d/5s, 1p$	0.0308	0.0157	51
		$9s, 5p, 2d/5s, 2p$	0.0321	0.0157	49
N–H	NH_3	$9s, 5p, 1d/5s, 1p$	0.0305	0.0181	59
O–H	OH_2	$9s, 5p, 1d/5s, 15$	0.0309	0.0207	67
F–H	FH	$9s, 5p, 1d/5s, 1p$	0.0320	0.0232	73
		$9s, 5p, 2d, 1f/5s, 2p$	0.0351	0.0232	66
Li–Li	Li_2	$10s, 3s, 1d$	0.0313	0.0052	17
C–C	C_2H_6	$7s, 3p/3s$	0.0174	0.0146	84
		$7s, 3p, 1d/3k$	0.0242	0.0146	60
π–C–C	C_2H_4	$7s, 3p/3s$	0.0330	0.0305	92
		$7s, 3p, 1d/3s$	0.0336	0.0283	84
N–N	N_2H_4	$9s, 5p, 1d/5s$	0.0320	0.0238	74
O–O	O_2H_2	$9s, 5p, 1d/5s$	0.0500	0.0441	88
F–F	F_2	$9s, 5p, 1d$	0.0807	0.0766	95
		$9s, 5p, 2d, 1f$	0.0810	0.0755	93

More insight into the nature of the different bond types is provided by an alalysis of the corresponding correlation energies of the optimized pairs (Table 5). While the total correlation energies of X–H bonds vary over a small range (0.03 to 0.04 a.u.), the fraction of left-right correlation increases considerably in the series (LiH . . . FH). This increase in left-right correlation is even more pronounced in the series (Li_2, C_2H_6, N_2H_4, 0_2H_2, F_2). In the latter series also the total pair correlation energy increases considerably. The angular correlation is most important in bonds with high s character, while hybridization with p orbitals favours left-right correlation. The repulsion of the lone pairs in O_2H_2 and in F_2 is so strong that only comparatively weak p_σ–p_σ bonds with high correlation energy contributions can be formed. As a general rule, our method seems to yield the least satisfactory results (Table 4) in those cases where the left-right correlation in the bond is most important.

A further aspect of the different degree of importance of left-right correlation for different bond types should be noted. Small basis sets (minimal or double zeta without polarization functions) describe essentially the left-right correlation only. When systems with different bond types are compared in calculations which include electron correlation, spurious results might be obtained, if small basis sets are used. As an illuminating example, Table 6 gives the relative SCF and CEPA [22, 23] (including–within the basis–the full valence electron correlation) energies

Basis set	SCF	CEPA
$5s, 2p/2s$ MB	45.4	59.6
$7s, 3p/3s$	63.9	74.3
$7s, 3p, 1d/3s$	27.3	25.5

Table 6. SCF and CEPA of tetrahedrane relative to two acetylene molecules (values in kcal/mol)

for tetrahedrane and for two acetylene molecules. The system with π bonds (acetylene) is artificially favoured over the σ bonded system (tetrahedrane) if correlation is computed with small basis sets (cf. Ref. 24). This is the consequence of the higher fraction of left-right correlation in π as compared to σ bond orbitals (Table 5).

A large coefficient of the PNO which describes the left-right correlation in a bond pair means a large change in the two-electron density in the hybrid AO's forming the bond when going from the SCF to the pair correlated wave function. In such cases large contributions to bond dissociation energies are expected from the correlation between the bond pair and the remaining electrons. In order to support this statement, the equilibrium bond distances in ethane and in fluorine were calculated using the following methods (Table 7):

1) SCF; due to the (within SCF neglected) large bond orbital correlation energy in F_2, the SCF bond distance in F_2 is much too short. For C_2H_6 almost the experimental CC bond length is obtained.
2) DCSCF; when only left-right correlation is included in the calculation too long bond lengths result.
3) PMCSCF; inclusion of the full correlation of the bonding pair yields too long bonds, which are, however, somewhat shorter than those calculated with DCSCF. The error for the F–F bond is much larger than for the C–C bond.
4) PMCSCF + inter-orbital pair CI; these calculations which take into account the external correlation of the optimized bond electron pair plus all double excitations describing the correlation between the bond electron pair and the remaining electrons were performed with a PNO–CI program [23]. The intra-orbital pair of the optimized bond MO and all respective semi-joint inter-orbital pairs [23] were included. The bond lengths obtained from these calculations are in good agreement with experiment and with values obtained

Method	Ethane[a] C–C	F_2[b]
SCF	1.532	1.336
DCSCF	1.558	1.501
PMCSCF	1.545	1.475
PMCSCF + CI	1.530	1.414
CEPA (no singles)	1.530	1.411[c]
Experiment	1.531[d]	1.418[c]

Table 7. Bond lengths of ethane and of fluorine computed with different methods (values in Å)

[a] Basis: $7s, 3p, 1d/3s$.
[b] Basis: $9s, 5p, 1d$.
[c] Ref. [25].
[d] Ref. [29].

from computations which include the correlation of all valence electrons using the
5) CEPA method [22, 23].

The result that method 4) yields reasonable bond lengths seems to be at variance with the CEPA analysis [25] which showed that the inter-orbital pair contributions between the vicinal CH bonds in ethane have a considerable influence on the computed CC bond length (their neglect would lead to a 0.014 Å longer bond). However, the CEPA analysis was based on localized MO's while our PNO–CI calculation started from PMCSCF orbitals.

5. Conclusions

We have presented a method which needs little computational effort and which allows the description of dissociation processes of single bonds. The results obtained for hydrocarbons are encouraging. The computed values for dissociation energies of bonds connecting atoms which bear lone pairs are not satisfactory. The method is not aimed at competing with extensive CI calculations but rather at the application to problems for which so far only 3×3 or other small CI methods could be applied like the computation of reaction surfaces of larger systems involving diradicaloid species as possible intermediates.

The method can be extended in two directions:

1) Application of the formalism to more than one doubly occupied MO in a molecule augmented by a CI in the resultant small space of the MO's of the different DCSCF components. This would lead to a GVB–CI [9] like procedure, including, however, an IEPA estimate of the external intra-pair orbital correlation.
2) Taking the PMCSCF wave function (or rather the DCSCF part of it) as a reference function for a modest CI which includes the important coupling terms between the corresponding bond orbital pair and the remaining electrons in the molecule. The physical nature of these coupling contributions and a procedure which allows their inclusion with modest computational effort will be discussed in a future paper.

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