THE AVERAGED COUPLED-PAIR FUNCTIONAL (ACPF): A SIZE-EXTENSIVE MODIFICATION OF MR CI(SD)

Robert J. GDANITZ and Reinhart AHLRICHS

Institut für Physikalische Chemie und Elektrochemie, Lehrstuhl für Theoretische Chemie, Universität Karlsruhe,
Kaiserstrasse 12, D-7500 Karlsruhe, Federal Republic of Germany

Received 5 December 1987

To account for unlinked-cluster effects at the multireference level, we propose a generalization (MR ACPF) of the "coupled-pair functional" (CPF). Comparison with full CI results for BeH_2, H_2O, CH_2, O_2 and the five lowest-lying $^2A_1$ states of CH_2^+, shows the superiority of MR ACPF over MR CI(SD) and MR LCCM. Large-scale calculations for F_2 (up to a [7s5p3d2f1g] CGTO basis set and 6 references) show better convergence to the experimental D_e values on basis set and reference space extension than does MR CI(SD).

1. Introduction

Single and multiple reference (MR) CI(SD) techniques have some important advantages which account for their widespread use. The method obeys the variation principle and it is the availability of efficient program systems [1–5], including those for gradient calculations [6–9], that allows applications to systems of chemical interest. The basic shortcoming of CI(SD) techniques is the lack of size extensivity [10–12]. This problem appears to be of less importance in MR CI(SD) if the number of electrons correlated is not too large. MR (CI) treatments of first-row diatomics, with around 10 references (and extended basis sets), apparently do not point to size-extensivity problems [13,14]. It may be expected, however, that size extensivity will be a problem with a larger number of electrons, e.g. in transition metal complexes, even at the MR CI(SD) level [15]. Various techniques to include multiple substitution corrections – to achieve size extensivity on the CI(SD) level – have proved useful at the single reference level [16–20]. The MR case appears to be less well explored [21,22], although this field is under intensive investigation at present [23,24].

In this article we propose a very simple modification of the MR CI(SD) method in order to achieve size extensivity. Our procedure is based on an energy functional – having a close analogy to the "coupled-pair functional" (CPF) method [19,20] – and is easily implemented into existing programs, thus taking advantage of the efficiency of these algorithms.

2. Theory

Let Ψ_0 denote the normalized zeroth-order wavefunction of single or MR type,

$$\Psi_0 = \sum_r c_r \phi_r \tag{1}$$

and Ψ_c the (extra) correlation function which arises from (a priori) all possible single and double substitutions of orbitals in the reference CSFs and which is required to be orthogonal to Ψ_0,

$$\langle \Psi_0 | \Psi_c \rangle = 0 . \tag{2}$$

We then consider the correlation energy functional $F_c[\Psi_c]$ (with respect to E_0)

$$F_c[\Psi_c] := \frac{\langle \Psi_0 + \Psi_c | H - E_0 | \Psi_0 + \Psi_c \rangle}{1 + g_a \langle \Psi_a | \Psi_a \rangle + g_e \langle \Psi_e | \Psi_e \rangle} , \tag{3}$$

$$E_0 := \langle \Psi_0 | H | \Psi_0 \rangle , \tag{4}$$

where Ψ_c is decomposed into two mutually orthogonal parts

$$\Psi_c = \Psi_a + \Psi_e . \tag{5}$$

Ψ_a includes all CSFs which have the same orbital occupation as the references, outside the active space (including references under the constraint of eq. (2)) and Ψ_e includes the remaining CSFs. F_c from eq. (3) is identical to the (extra) correlation energy functional of MR CI(SD) for the special choice $g_a = g_e = 1$. Since the effect of $\langle \Psi_c | \Psi_c \rangle$ in the denominator of F_c is cancelled to a large extent by energy contributions of higher excitations – the neglect of which causes non-size extensivity – it is tempting to rectify this shortcoming by a proper choice of g_a and g_e, i.e. $g_a, g_e \leqslant 1$.

Let us first consider the case where Ψ_a vanishes or is neglected. Size extensivity requires setting $g_e \propto 1/n$, where n denotes the number of electrons correlated. For a proof consider a single-reference description of a supersystem of m identical, non-interacting subsystems (at mutually infinite distances). Size extensivity on the zeroth-order level implies

$$\Psi_0 = \mathscr{A} \prod_{i=1}^{m} \Psi_0^{(i)} , \tag{6}$$

$$E_0 = \sum_{i=1}^{m} E_0^{(i)} , \tag{7}$$

where $i = 1, ..., m$ labels the identical subsystems and $\mathscr{A}$ denotes the antisymmetrizer in an otherwise obvious nomenclature. We consider a total correlation function which includes intrasystem correlation only,

$$\Psi_c = \sum_{i=1}^{m} \mathscr{A} \left(\Psi_c^{(i)} \prod_{j \neq i} \Psi_0^{(j)} \right) . \tag{8}$$

The functional F_c, eq. (3), is then size extensive in the sense

$$F_c[\Psi_c] = \sum_{i=1}^{m} F_c^{(i)}[\Psi_c^{(i)}] , \tag{9}$$

if and only if $g_e \propto 1/n \propto 1/m$, independent of the actual form of $\Psi_c^{(i)}$.

Since only singles and doubles are explicitly included in $\Psi_c^{(i)}$ and in Ψ_c, it is natural to require that two-electron systems and, by means of eqs. (6)–(9), supersystems of identical non-interacting pair systems are described correctly. This leads to our final choice

$$g_e = 2/n . \tag{10}$$

Consider now a more general case, where $\Psi_a \neq 0$ and the reference space is of the CAS type. Double (single) replacements from Ψ_0 which only involve active orbitals then never give rise to cluster corrections since a combination with any other double (single) replacement from Ψ_0 is already contained in the CI. This requires setting $g_a = 1$ since cluster corrections are not necessary. The situation is more complicated for non-CAS cases, where a proper choice for g_a may be difficult. However, in our experience one is usually close to the CAS case and we recommend always setting $g_a = 1$. With this choice one is on the safe side, i.e. the corresponding cluster corrections are slightly underestimated.

Size extensivity, eq. (9), does not hold in general since Ψ_c includes doubles involving singles of different subsystems, e.g. $\mathscr{A}\phi_s^{(1)}\phi_s^{(2)}$, which are not included in eq. (8). These terms may cause a violation of eq. (9) in fourth-order perturbation theory at most but vanish exactly in special cases, e.g. if the $\Psi_0^{(i)}$ are of closed-shell SCF type. Eq. (9) is also violated for non-identical subsystems. The discrepancies again occur in fourth order but cancel to a large extent.

It should be noted that F_c, eq. (3), has the same invariance properties with respect to unitary transformations of external and/or internal MOs as the corresponding CI functional.

3. Relations to other methods

If one evaluates F_c, eq. (3), for the MR CI(SD) wavefunction $^{CI}\Psi_c$, one gets

$$F_c[^{CI}\Psi_c] = {}^{CI}E_c[1 + (1 - 2/n)\langle {}^{CI}\Psi_e | {}^{CI}\Psi_e \rangle$$
$$+ \mathcal{O}(\|\Psi_c\|^4)] , \tag{11}$$

where $^{CI}E_c$ denotes the MR CI(SD) correlation energy. The rhs of eq. (11) is a Davidson-type [16,21,22] correction for $^{CI}E_c$ including Pople's factor $1 - 2/n$ [11].

A rigorous way to account for cluster corrections is provided by MR coupled-cluster (MR CC) theory [25]; however, this leads to rather complicated equations. An approximation which considerably simplifies matters is the linearized version (MR

LCCM) [26] of MR CC. MR LCCM corresponds in fact to the choice $g_a = g_e = 0$, together with the total neglect of Ψ_a. Linearized versions of CC methods usually tend to overestimate the effect of higher excitations [26], although contributions arising from Ψ_a are neglected.

The present approach is closely related to the single reference CPF method [19,20], which achieves size extensivity by means of individual partial normalization denominators. The CPF approach is difficult to generalize to the MR case since electron pairs are no longer unambiguously defined. The functional F_c, eq. (3), can be obtained from the CPF if the individual partial denominators are replaced by a single averaged partial denominator (eq. (3) has in fact been discussed in ref. [19] for the special case of identical non-interacting pair systems).

4. Variation of $F_c[\Psi_c]$

Variation of $F_c[\Psi_c]$, eq. (3), under the constraint of eq. (2) leads to the following equations for Ψ_c:

$$\sigma = Q(H - E_0 - E_c G)(\Psi_0 + \Psi_c) = 0 , \qquad (12)$$

$$Q = 1 - |\Psi_0\rangle\langle\Psi_0| , \qquad (13)$$

$$E_c = F_c[\Psi_c] , \qquad (14)$$

$$G = g_a P + g_e (1 - P) , \qquad (15)$$

where P is the projector onto the subspace on which Ψ_a is defined

$$P\Psi_c = \Psi_a . \qquad (16)$$

Although eq. (12) is very similar to the CI equations it is in general neither an eigenvalue problem, as for the CI case ($g_a = g_e = 1$), nor a linear system, as for CEPA(0) ($g_a = g_e = 0$).

We note in passing that the functional $F_c[\Psi_c]$, eq. (3), reduces to the well-known transition energy formula

$$E_c = F_c[\Psi_c] = \langle\Psi_0|H|\Psi_c\rangle \qquad (17)$$

provided eq. (12) is fulfilled. The n-particle reduced density matrix γ_{ACPF} within the ACPF formalism is given by [19]

$$\gamma_{ACPF} = (1 - a)\gamma[\Psi_0] + a\gamma[\Psi_0 + \Psi_c] , \qquad (18)$$

$$a = \frac{1 + \langle\Psi_c|\Psi_c\rangle}{1 + \langle\Psi_c|G|\Psi_c\rangle} , \qquad (19)$$

where $\gamma[\ ]$ is the density matrix evaluated with the wavefunction in brackets. F_c, eq. (3), is bounded from below by $^{CI}E_c/g_e$, where $^{CI}E_c$ is the lowest eigenvalue of the $H - E_0$ matrix (see ref. [19]).

5. Numerical details

Consider trial vectors $\Psi_c^{(\mu)}, \mu = 1, ..., k$, orthogonal to Ψ_0 as generated by some single vector iteration procedure, up to the kth iteration. We determine an improved solution, $\hat{\Psi}_c^{(k)}$, of eq. (12), by the linear variation method

$$\hat{\Psi}_c^{(k)} = \sum_{\mu=1}^{k} \alpha_\mu^{(k)} \Psi_c^{(k)} , \qquad (20)$$

which leads to (compare eqs. (3), (12) and (15))

$$(\mathbf{A} - E_c \mathbf{S})\boldsymbol{\alpha} = -\boldsymbol{b} , \qquad (21)$$

$$A_{\mu\nu} := \langle\Psi_c^{(\mu)}|H - E_0|\Psi_c^{(\nu)}\rangle , \qquad (22)$$

$$E_c := F_c[\hat{\Psi}_c] , \qquad (23)$$

$$S_{\mu\nu} := \langle\Psi_c^{(\mu)}|G|\Psi_c^{(\nu)}\rangle , \qquad (24)$$

$$b_\mu := \langle\Psi_0|H|\Psi_c^{(\mu)}\rangle . \qquad (25)$$

After each iteration we solve eq. (21) by a Newton–Raphson procedure to obtain E_c and the optimal $\alpha^{(k)}$. The set $\{\Psi_c^{(\mu)}\}$ is (in our program version) generated by a first-order update:

$$\Psi_c^{(k+1)} = \Psi_c^k - (H_0 - E_0 - E_c G)^{-1}\sigma^{(k)} , \qquad (26)$$

$$H_0 := \sum_{r,r' \in R} |\phi_r\rangle H_{rr'}\langle\phi_{r'}| + \sum_{i \notin R} |\phi_i\rangle H_{ii}\langle\phi_i| , \qquad (27)$$

$$H_{ij} := \langle\phi_i|H|\phi_j\rangle , \qquad (28)$$

where the first summation runs over the references and the second over the remaining CSFs. This partitioning of H can be considered as a generalization of the one introduced by Epstein and Nesbet [27,28] to the multireference case. The first trial function $\Psi_c^{(1)}$ is simply obtained by formally setting $\Psi_c^0 = 0$.

Note that the linear space spanned by the $\{\Psi_c^{(\mu)}\}$, eq. (26), is the same as that obtained if the $\Psi_c^{(k)}$ were generated by a straightforward extension of Davidson's [29] method for solving large eigenvalue problems. However, in Davidson's algorithm $\sigma^{(k)}$ is

the residual vector of the best linear combination of trial vectors and the $\Psi_c^{(\mu)}$ are forced to be mutually orthogonal, which requires additional operations, avoided in our method. If $\Psi_c^{(k)}$ converges too slowly to the solution of eq. (12) or even diverges, then the set $\{\Psi_c^{(\mu)}\}$ becomes approximately linearly dependent. In this case it is necessary to switch to the above-mentioned generalization of Davidson's method which is numerically much more stable.

6. Applications

For the sake of clarity we define the nomenclature used in this work to specify the various methods used:

(i) MR ACPF: Ψ_c, E_c obtained from optimization of the functional F_c, eq. (3),

(ii) MR CI(SD): as MR ACPF, but $g_a = g_e = 1$,

(iii) MR CEPA(0): as MR ACPF, but $g_a = g_c = 0$,

(iv) MR LCCM: as MR CEPA(0) with $\Psi_a = 0$.

The necessary modifications of an MR CI(SD) program system have been implemented in the Columbus system of programs [3,30]. The method to be used is specified by input parameters.

The first applications concern first-row diatomics treated at the single reference level. The sole purpose of these tests of the new method was to determine whether the use of a single "averaged" denominator has any appreciable influence. The ACPF results are

compared with the CPF results, since the individual denominators of CPF are certainly better justified. We computed R_e and D_e (computed as $\Delta D_e = 2 E_{\text{atom}} - E_{\text{mol}}$) of CO, O_2, N_2 and F_2 within the 2d1f basis sets described in ref. [31]. The energy differences $\Delta E = E_{\text{CPF}} - E_{\text{ACPF}}$, at R_e, were found to be in the range $\Delta E = 0.5$–1.0 mhartree for CO to N_2 (ascending in this order) but $\Delta E = 3.6$ mhartree in the case of F_2. The deviations between R_e and D_e, $\Delta R_e = R_e^{\text{ACPF}} - R_e^{\text{CPF}}$, $\Delta D_e = D_e^{\text{ACPF}} - D_e^{\text{CPF}}$ are insignificant for N_2, CO and O_2 ($\Delta R_e = 0.002$ a_0 and $\Delta D_e = 0.04$ eV at most). On the basis of the very close agreement between CPF and ACPF one would prefer ACPF since this method is technically much simpler. Deviations are more pronounced for F_2 ($\Delta R_e = 0.046$ a_0, $\Delta D_e = 0.11$ eV), which is in fact the only system showing near-degeneracy effects. The MC SCF-2 coefficient of the $3\sigma_g^2 \rightarrow 3\sigma_u^2$ excitation is $c = 0.261$ at $R = 2.672$ a_0. This example shows the limitations of ACPF: Ψ_0 should include all "near-degeneracy effects" such that the "electron pairs" correlated can be treated on an equal footing, i.e. by an averaged denominator.

In tables 1–5 we compare the present MR ACPF and some other MR methods with full-CI (FCI) for the BeH$_2$ [26], H$_2$O [32], CH$_2$ [33] and O$_2$ [34] ground states. The MR ACPF energies are closer to the FCI values than the variational MR CI(SD) with the exception of BeH$_2$ geometry 1, where both meth-

Table 1

C_{2v} insertion of Be into H$_2$. Energy differences in mhartree from the full-CI value in hartree. 10 CGTO basis set, geometries and reference CSFs as in ref. [26]

	Geometry		
	1	2	3
FCI [a]	−15.62288	−15.60292	−15.62496
MC SCF	53.31	64.35	66.68
MR CI(SD)	0.84	2.01	3.08
MR CI(SD) +Dav. [b]	−2.37	−3.22	−3.24
MR CEPA(0)	−3.28	4.30 [c]	−5.50
MR LCCM	−2.62	−2.40	−5.50
MR ACPF [d]	−0.90	−0.90	−0.53

[a] From ref. [26].

[b] MR CI(SD) with Davidson correction [16] as proposed by Bruna et al. [21].

[c] Saddle point with respect to variation of Ψ_c, due to near degeneracy of the 3a$_1$ and 1b$_2$ orbitals. Minimization of F_c leads to $E_c = -\infty$ and $\|\Psi_c\| = \infty$.

[d] $n = 4$, since the correlation energy of the orbital pair 1a$_1$–1a$_1$ had a value of only about -2 mhartree (in the given basis).

Table 2
H_2O with symmetrically stretched bonds. Energy differences in mhartree from the full-CI value in hartree. Geometries and DZP basis set as described in ref. [32]

	d(O–H)		
	R_e	$1.5R_e$	$2R_e$
FCI [a]	−76.25662	−76.07141	−75.95227
MC SCF-12 [b]	161.91	146.63	128.56
MR CI(SD)-12	4.98	4.53	3.71
MR CI(SD)+Dav. [c]	−1.36	−1.33	−0.70
MR LCCM-12	−1.27	−0.59	0.02
MR ACPF-12 [d]	−0.12	−0.22	0.18
MC SCF-55 [e]	126.75	118.27	112.36
MR CI(SD)-55	2.52	2.04	1.75
MR CI(SD)-55+Dav. [c]	−1.18	−1.54	−1.46
MR LCCM-55	−1.15	−1.43	−1.31
MR ACPF-55 [d]	−0.40	−0.79	−0.78

[a] From ref. [32].   [b] CAS with $3a_1$, $4a_1$, $1b_2$ and $2b_2$ orbitals active.   [c] See table 1, footnote b.
[d] $n=8$, since the $1a_1$ orbital was frozen in all correlation treatments.   [e] CAS as footnote b + $1b_1$ and $2b_1$ orbitals active.

Table 3
CH_2 ($X\ ^1A_1$), energy differences in mhartree from the full-CI value of $E_{FCI} = -39.027183$ hartree [33]. Geometry and DZP basis set as described in ref. [33]. The $1a_1$ orbital was obtained in the SCF calculation and not changed in subsequent MC SCF calculations. The $1a_1$ electrons were not correlated.

Number of references [a]	CAS SCF	MR CI(SD)	MR CI(SD) +Davidson [b]	CPF	MR ACPF [c]
1	140.886	8.899	−0.038	2.066	1.907
2	119.564	5.092	−0.492	−	1.187
56	81.713	1.493	−1.177	−	−0.395

[a] Reference CSFs as in ref. [33].   [b] See table 1, footnote b.   [c] $n=6$.

Table 4
O_2 comparison of differences of energies (in mhartree), equilibrium bond lengths (R_e) and dissociation energies (D_e) with respect to the full-CI values [34]. DZP basis set and reference CSFs as described in ref. [34]. The $1\sigma_g$, $1\sigma_u$, $2\sigma_g$ and $2\sigma_u$ orbitals were frozen in the correlation treatments

	R (a_0)				ΔR_e (a_0)	ΔD_e (eV)
	2.25	2.30	2.35	100.0		
CAS SCF	143.250	143.169	143.005	107.885	−0.004	−0.958
MR CI(SD)	4.073	4.105	4.132	3.219	0.000	−0.024
MR CI(SD)+Dav. [a]	−1.782	−1.811	−1.836	−0.361	0.001	0.040
MR LCCM	−0.586	−0.579	−0.570	−0.676	0.000	−0.003
MR ACPF [b]	−0.654	−0.676	−0.695	0.362	−0.001	0.031
FCI [c]	0.875147	0.876947	0.876694	0.706685	2.318	4.637

[a] See table 1, footnote b.   [b] $n=8$.   [c] From ref. [34]. Energies (hartree) are given as $-(E+149)$.

Table 5

F_2, comparison of total energy E (at R_e), equilibrium bond length R_e and dissociation energy D_e obtained with MR CI(SD) and MR ACPF. The $1\sigma_g$ and $1\sigma_u$ orbitals were frozen and interacting space restrictions [3] were imposed. Experimental values [35] are $R_e = 2.668$ a_0, $D_e = 1.66$ eV

	Basis [a]	Property	Number of references		
			1	2 [b]	6 [c]
MR CI(SD) [d]	A2d1f	$-(E+199)$ (hartree)	0.261582	0.281415	0.288334
		R_e (a_0)	2.594	2.691	2.681
		D_e (eV)	0.459/0.823 [e]	1.362	1.529
	B3d2f1g	$-(E+199)$ (hartree)	0.302303	0.322280	0.329826
		R_e (a_0)	2.581	2.677	2.668
		D_e (eV)	0.510/0.913 [e]	1.456	1.638
MR ACPF [f]	A2d1f	$-(E+199)$ (hartree)	0.308552	0.311223	0.312182
		R_e (a_0)	2.718	2.691	2.690
		D_e (eV)	1.417	1.492	1.512
	B3d2f1g	$-(E+199)$ (hartree)	0.352353	0.355393	0.356573
		R_e (a_0)	2.699	2.677	2.676
		D_e (eV)	1.515	1.600	1.624

[a] As specified in ref. [36].   [b] $3\sigma_g^2 1\pi_u^4 1\pi_g^4$ and $1\pi_u^4 1\pi_g^4 3\sigma_u^2$.

[c] As in footnote b $+3\sigma_g^1 1\pi_u^4 1\pi_g^3 3\sigma_u^1 2\pi_u^1$, all possible couplings.

[d] Ref. [36] and this work.

[e] First value computed as $2E_{atom} - E_{mol}$, second value through comparison of E_{mol} with the energy obtained for an F_2 supermolecule with a single reference $3\sigma_g^1 1\pi_u^4 1\pi_g^4 3\sigma_u^1$ $(^3\Sigma_u^+)$.

[f] $n = 14$.

ods are quite accurate (table 1). This is by no means a trivial result: cluster-corrected energies may easily show larger deviations from FCI than MR CI(SD), as demonstrated by MR LCCM for BeH_2 at all geometries considered (table 1). MR ACPF energies are generally closer to FCI than MR LCCM for BeH_2 (table 1) and H_2O (table 2). MR LCCM and MR ACPF are of comparable accuracy for O_2 (table 4), with MR LCCM slightly better. The accuracy of MR

LCCM is partly due to an error compensation, as mentioned above, which is very satisfactory for O_2, but cannot always be relied upon, as is shown by the results for BeH_2 and H_2O. The MR ACPF energies are typically closer to FCI than the corresponding Davidson-corrected MR CI(SD) energies, only $CH_2(X\,^1A_1)$ is an exception (table 3).

We next performed calculations for F_2 with Ψ_0 of single, double and sextuple reference type. The re-

Table 6

$CH_2^+ (1-5\,^2A_1)$. Energy differences in mhartree from the full-CI value in hartree. Basis set, geometry and reference space as specified in ref. [37]

State	CAS SCF [a]	MR CI(SD) [a]	MR ACPF [b]	FCI [c]	$\|\Psi_c\|$ [d]
1	53.629	0.474	−0.236	−38.650312	0.153
2	63.705	0.722	−0.650	−38.213539	0.201
3	69.798	1.250	−1.138	−38.170071	0.429
4	70.529	0.918	−0.751	−38.143006	0.323
5	82.859	2.581	−10.492	−38.040317	1.106

[a] Ref. [37] and this work.   [b] $n = 5$.   [c] Ref. [37].   [d] For MR ACPF.

sults, collected in table 5, show a gratifying convergence for the computed D_e and R_e values on basis set and reference space extension and converge smoothly towards the experimental values. The MR ACPF results for D_e display a much better convergence than MR CI(SD) on reference expansion, and two references – which allow for proper dissociation – appear to be sufficient. The situation is similar to that for H_2O (table 2) where 12 references are sufficient.

The considerations presented so far are not restricted to ground states but also apply to excited states, see e.g. ref. [25]. Since FCI calculations are available for the five lowest-lying $^2A_1$ states of CH_2^+ [37] we have applied the MR ACPF to these cases for comparison. In our treatment we solve eq. (12) with Ψ_0 as obtained from the MC SCF for the corresponding state. The results, table 6, show best agreement (FCI versus MR ACPF) for the ground state, $1\,^2A_1$, but MR ACPF is still slightly closer to FCI than MR CI(SD) for $N\,^2A_1$, $N=2$, 3, 4. MR ACPF breaks down for the highest state $5\,^2A_1$. However, for this state one gets $\|\Psi_c\| = 1.106$ which implies that Ψ_0 is a poor zeroth-order approximation and MR ACPF should not be applied. For $N=2$, 3, 4 we also find quite appreciable magnitudes for $\|\Psi_c\|$ (as given in table 6; values from 0.201 to 0.429) and it is encouraging that the new method is stable under these circumstances. There is, in fact, a close correlation between $\|\Psi_c\|$ and the accuracy of MR CI(SD) and MR ACPF, as expected.

7. Conclusion

Our approach to remedy the size-extensivity problems of MR CI(SD) treatments is quite pragmatic and lacks the rigour of multiple-reference coupled-cluster theories. It has the advantage of great simplicity and is easily implemented in existing MR CI(SD) and corresponding gradient programs. This means that one can draw on the accumulated experience and efficiency of MR CI(SD) programs, which at present supercede those of coupled-cluster methods. The results of an initial series of applications, presented in this article, indicate that unlinked-cluster effects are reliably taken into account.

References

[1] B.O. Roos and P.E.M. Siegbahn, in: Methods of electronic structure theory, ed. H.F. Schaefer III (Plenum Press, New York, 1977) p. 189.

[2] P.E.M. Siegbahn, Intern. J. Quantum Chem. 18 (1980) 1229.

[3] H. Lischka, R. Shepard, F.B. Brown and I. Shavitt, Intern. J. Quantum Chem. Symp. 15 (1981) 91.

[4] H.-J. Werner and E.-A. Reinsch, J. Chem. Phys. 76 (1982) 3144.

[5] R.A. Phillips, R.J. Buenker, P.J. Bruna and S.D. Peyerimhoff, Chem. Phys. 84 (1984) 11.

[6] B.R. Brooks, W.D. Laidig, P. Saxe, J.D. Goddard, Y. Yamaguchi and H.F. Schaefer III, J. Chem. Phys. 72 (1980) 4652.

[7] R. Krishnan, H.B. Schlegel and J.A. Pople, J. Chem. Phys. 72 (1980) 4654.

[8] J.E. Rice and R.D. Amos, Chem. Phys. Letters 122 (1985) 585.

[9] R. Shepard, in: Geometrical derivatives of energy surfaces and molecular properties, eds. P. Jørgensen and J. Simons (Reidel, Dordrecht, 1986) p. 193.

[10] J.A. Pople, J.S. Binkley and R. Seeger, Intern. J. Quantum Chem. Quantum Chem. Symp. 10 (1976) 1.

[11] J.A. Pople, R. Seeger and R. Krishnan, Intern. J. Quantum Chem. Quantum Chem. Symp. 11 (1977) 149.

[12] R.J. Bartlett and G.D. Purvis, Intern. J. Quantum Chem. 14 (1978) 561.

[13] S.R. Langhoff, C.W. Bauschlicher Jr. and P.R. Taylor, Chem. Phys. Letters 135 (1987) 543.

[14] R. Ahlrichs, K. Jankowski and J. Wasilewski, Chem. Phys. 111 (1987) 263.

[15] P.E.M. Siegbahn, talk delivered at the 23. Symposium für Theoretische Chemie, Waldfischbach (1987).

[16] S.R. Langhoff and E.R. Davidson, Intern. J. Quantum Chem. 8 (1974) 61.

[17] R. Ahlrichs, Computer Phys. Commun. 17 (1979) 31.

[18] R.J. Bartlett, C.E. Dykstra and J. Paldus, in: Advanced theories and computational approaches to the electronic structure of molecules, ed. C.E. Dykstra (Reidel, Dordrecht, 1984) p. 127.

[19] R. Ahlrichs, P. Scharf and C. Ehrhardt, J. Chem. Phys. 82 (1985) 890.

[20] R. Ahlrichs and P. Scharf, in: Ab initio methods in quantum chemistry – part I, ed. K.P. Lawley (Wiley, New York, 1987) p. 501.

[21] P. Bruna, S.D. Peyerimhoff and R.J. Buenker, Chem. Phys. Letters 72 (1980) 278.

[22] K. Jankowski, L. Meissner and J. Wasilewski, Intern. J. Quantum Chem. 28 (1985) 525.

[23] W. Laidig, P. Saxe and R.J. Bartlett, J. Chem. Phys. 86 (1987) 887.

[24] L. Meissner, Ph. D. Thesis, University of Thorun (1987).

[25] B. Jeziorski and H.J. Monkhorst, Phys. Rev. A24 (1981) 1668.

[26] W.D. Laidig and R.J. Bartlett, Chem. Phys. Letters 104 (1984) 424.

[27] P.S. Epstein, Phys. Rev. 28 (1926) 695.

[28] R.K. Nesbet, Proc. Roy. Soc. A230 (1955) 312.

[29] E.R. Davidson, J. Comput. Phys. 17 (1975) 87.

[30] R. Ahlrichs, H.-J. Böhm, C. Ehrhardt, P. Scharf, H. Schiffer, H. Lischka and M. Schindler J. Comput. Chem. 6 (1985) 200.

[31] R. Ahlrichs, P. Scharf and K. Jankowski, Chem. Phys. 98 (1985) 381.

[32] C.W. Bauschlicher Jr. and P.R. Taylor, J. Chem. Phys. 85 (1986) 2779.

[33] C.W. Bauschlicher Jr. and P.R. Taylor, J. Chem. Phys. 85 (1986) 6510.

[34] C.W. Bauschlicher Jr. and S.R. Langhoff, J. Chem. Phys. 86 (1987) 5595.

[35] E.A. Colborn, M. Dagenais, E.A. Douglas and J.W. Raymonda, Can. J. Phys. 54 (1976) 1343.

[36] K. Jankowski, R. Becherer, P. Scharf, H. Schiffer and R. Ahlrichs, J. Chem. Phys. 82 (1985) 1413.

[36] C.W. Bauschlicher Jr. and P.R. Taylor, J. Chem. Phys. 86 (1987) 2844.