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Correlation Energies in Open Shell Systems. Comparison of CEPA, PNO-CI and Perturbation Treatments Based on the Restricted Roothaan–Hartree–Fock Formalism

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A set of simple molecules in closed and open-shell ground states is treated by the three techniques mentioned in the title, using the same geometries and basis sets ($DZ+P$). It is found that for nearly all molecules treated in this study (exceptions are H_2 and CH_3) consistently about 98% of the CEPA valence shell correlation energy is obtained by third-order many-body Rayleigh–Schrödinger perturbation theory (MB-RSPT). The CEPA and MB-RSPT results for reaction energies and barrier heights for some simple reactions differ by 0 to 30 kJ/mol, the CEPA results being in most cases closer to experiment than MB-RSPT, while CI results are much less reliable as long as CI is limited to singly and doubly substituted configurations only.

Key words: Correlation energy of radicals – Many-body perturbation theory – CEPA.

1. Introduction

The aim of this paper is to study the utility of the Many-Body Rayleigh–Schrödinger Perturbation Theory (MB-RSPT) in the restricted MO formalism, which was developed recently [1, 2] for the calculation of correlation energies in open-shell systems as a more economic alternative to the commonly used unrestricted Møller–Plesset approach [3]. The difference between the two perturbation approaches lies in the definition of the reference (unperturbed) wave function. In the former it is the SCF wave function given by the Roothaan restricted open shell method [4], whereas in the latter it is the unrestricted Hartree–Fock wave function. Hence, in contrast to the ordinary Møller–Plesset treatment, the perturbed Hamiltonian in the restricted MO approach is assumed to have the form

$$K = K_0 + W - U \tag{1}$$

which means that the perturbation, $W - U$ in Eq. (1), contains an additional one-electron operator U for the spin polarization. Accordingly, for systems with large spin polarization, the approach based on Eq. (1) may be expected to run into difficulties because of a too large perturbation. In such a case the unrestricted Møller–Plesset treatment should be preferred though preliminary calculations suggested that this is not necessary for a wide variety of radicals of many structural types.

Counterexamples could be radicals containing multiple bonds and hence large spin-polarization. In order to have a deeper insight into this problem we decided to perform CEPA and PNO-CI calculations for systems which were treated by MB-RSPT previously [1, 2] and to use CEPA and PNO-CI results as standards against which one may judge the MB-RSPT results.

2. Calculations

Three methods were used: MB-RSPT through third order based on the Hamiltonian partitioning (1), CEPA, and PNO-CI. The list of the systems treated and their geometries assumed in all three types of calculation are collected in Table

Table 1. Geometries assumed (bond lengths in a_0)

System	Geometry parameters	Source
H_2	$r_{HH} = 1.40$	experiment [5]
HF	$r_{HF} = 1.733$	experiment [5]
F_2	$r_{FF} = 2.677$	experiment [6]
H_3	$D_{\infty h}$, $r_{HH} = 1.757$	SCF-CI [7]
BH_2 ($^2A_1$)	C_{2v}, $r_{BH} = 2.2475$, $\measuredangle$HBH $= 129.48°$	SCF-CI [8]
NH_2 ($^2B_1$)	C_{2v}, $r_{NH} = 1.9443$, $\measuredangle$ HNH $= 103.08°$	SCF-CI [8]
NH_2 ($^2A_1$)	C_{2v}, $r_{NH} = 1.8892$, $\measuredangle$ HNH $= 143.35°$	SCF-CI [8]
HFH	$D_{\infty h}$, $r_{HF} = 2.16$	CEPA [9]
FHH	$C_{\infty v}$, $r_{FH} = 2.90$, $r_{HH} = 1.45$	SCF-CI [10]
HFF	$C_{\infty v}$, $r_{FH} = 3.175$, $r_{FF} = 2.842$	SCF-CI [11]
CH_3	D_{3h}, $r_{CH} = 2.039$	experiment [12]
CH_4	T_d, $r_{CH} = 2.0665$	experiment [13]
$H_3CH^1H^2$	C_{3v}, $r_{CH} = 2.0693$, $r_{CH^1} = 2.6003$, $r_{H^1H^2} = 1.7064$, $\measuredangle$ HCH $= 114.7°$	UHF-CI [14]

1. The basis set used was of double zeta plus polarization (*DZ*+*P*) quality: Dunning's [15] contraction [4*s*2*p*/2*s*] of Huzinaga's [16] (9*s*5*p*/4*s*) primitive Gaussian set, augmented with a set of six Gaussian *d*-type functions on the heavy atoms and a single set of *p*-type functions on the hydrogen atoms. The following exponents were selected to be consistent with the previous studies [1, 2]: 0.7 for B, 0.8 for C, 0.75 for N, 1.4 for F, 0.75 for H in the fluor-containing systems, and 1.0 for H in the other systems. Since our restricted MB-RSPT approach cannot accommodate degenerate electronic states, the fluorine atom was treated as having the configuration $(2p_x)^2(2p_y)^2(2p_z)$.

The *DZ*+*P* basis sets are certainly inadequate for a reliable calculation of correlation contributions to reaction energies and energy barriers. But we think that they are large enough to provide a model in which a comparison between MB-RSPT and CEPA will lead to correct conclusions.

There is a minor inconsistency between the MB-RSPT calculations on the one hand and the CEPA and PNO-CI calculations on the other hand. In the former Cartesian Gaussian basis sets were used, whereas the programs used for the latter are based on Gaussian lobe functions. The difference between the SCF energies calculated with these two types of basis sets was less than 0.0002 a.u. in all cases.

The computed correlation energies are valence shell correlation energies, i.e. the $1s^2$-cores are left uncorrelated. In order to maintain consistency with the previous MB-RSPT results [2] also the CEPA and PNO-CI calculations were performed with doubly substituted configurations only (denoted by PNO-CI(D) and CEPA(D) in the Tables 2–4 containing the results). In some cases we have also added the results of CEPA calculations including singles and doubles (CEPA(SD)) in order to check the influence of the singles on energy barriers and reaction energies.

The details of the MB-RSPT calculations can be found in previous papers [1, 2]. The CEPA and PNO-CI calculations were performed with the program described recently [17]. Consistently for all calculations, we used canonical SCF orbitals, a threshold of 10^{-6} a.u. for the truncation of the PNO expansion, and the CEPA-2 variant for the estimation of the contribution of unlinked clusters. For a recent comparison of different CEPA variants in closed-shell molecules compare Ref. [26].

3. Results and Discussion

The energies of the systems treated in this paper are given in Table 2. An overall observation from this Table is that MB-RSPT gives somewhat more correlation energy than PNO-CI but somewhat less correlation energy than CEPA. This is very similar to the situation found previously in closed-shell systems [18]. One further observes that in all but a few cases (H_2, CH_3) the ratio between MB-RSPT and CEPA correlation energies is nearly constant (98.5±1%); but the same

Table 2. Energies of the systems treated ($E^{(2)}$ and $E^{(3)}$ mean second and third order contributions, all entries are in a.u.)

System	SCF[a]	$E^{(2)}+E^{(3)}$	PNO-CI(D)	CEPA(D)	Percentage	
					$\frac{E^{(2)}+E^{(3)}}{\text{PNO-CI(D)}}$	$\frac{E^{(2)}+E^{(3)}}{\text{CEPA(D)}}$
H	−0.499277	0	0	0	—	—
F	−99.394521	−0.14698	−0.14346	−0.14751	102.4	99.6
H_2 ($\alpha_p = 1.0$)	−1.131197	−0.03247	−0.03429	−0.03429	94.7	94.7
H_2 ($\alpha_p = 0.75$)	−1.131066	−0.03354	−0.03543	−0.03543	94.7	94.7
HF	−100.047873	−0.19901	−0.19261	−0.20031	103.3	99.3
F_2	−198.730201	−0.38503	−0.35813	−0.39225	107.5	98.2
H_3	−1.589994	−0.05279	−0.05256	−0.05341	100.4	98.8
BH_2 ($^2A_1$)	−25.752516	−0.08293	−0.08013	−0.08281	103.5	100.1
NH_2 ($^2B_1$)	−55.573224	−0.16546	−0.15882	−0.16737	104.2	98.9
NH_2 ($^2A_1$)	−55.523338	−0.16133	−0.15524	−0.16314	103.9	98.9
HFH	−100.435460	−0.22955	−0.22035	−0.23362	104.2	98.3
FHH	−100.506711	−0.18767	−0.18260	−0.19071	102.8	98.4
HFF	−199.202451	−0.40159	−0.37029	−0.41187	108.5	97.5
CH_3	−39.567926	−0.15715	−0.14452	−0.15225	108.7	103.2
CH_4	−40.207389	−0.17877	−0.17251	−0.18321	103.6	97.6
CH_5	−40.655091	−0.19898	−0.18953	−0.20395	105.0	97.6

[a] Given by Cartesian Gaussian basis sets, see text.

does not hold for the ratio between MB-RSPT and PNO-CI. The size inconsistency of the CI approach (if this is limited to singles and doubles only) causes the PNO-CI correlation energies to become successively smaller if the size of the system is increased (compare F, HF, FHH, HFH versus F_2, HFF).

It has been shown earlier for closed shell systems [19–21] that the CI method and the several CEPA variants agree with each other and with MB-RSPT up to third order. Differences between these methods can be best understood by analyzing the fourth-order MB-RSPT contributions [19]. In particular, the CEPA variants differ in the way they approximate the so-called EPV (exclusion principle violating) contributions [19–21], which of course do not appear in third order MB-RSPT. Similarly, fourth and higher order contributions of doubles, which in general yield negative-energy contributions, are fully included both in CI and in CEPA. For the open-shell molecules studied here the previous analysis [19–21] is also valid since in all cases a single RHF determinant is a reasonable zeroth order reference which is used both in CEPA and MB-RSPT.

There are only two molecules for which we found a large discrepancy between the CEPA and MB-RSPT results: H_2 and CH_3. For H_2 the reason is obvious: CI and CEPA yield the exact correlation energy for a given orbital basis (at least as exact as the NO expansion is) while in MB-RSPT the higher orders of doubles are missing; quadruples etc. simply don't exist. For CH_3 we are inclined to attribute the too large MB-RSPT correlation energy to the large spin polarization. But the latter is of the same size as in F and even smaller than in H_3 and CH_5 (total CEPA contribution of the spin polarization terms: 0.01996 a.u. in H_3, 0.01916 a.u. in CH_5, 0.00897 a.u. in F, 0.00818 a.u. in CH_3). Both for H_2 and CH_3 the CEPA results seem to be more reliable (compare also Tables 3 and 4).

Tables 3 and 4 aim at more practical conclusions. These two tables were obtained from combinations of the entries of Table 2 and they present the heats of reaction and energy barriers for a series of simple reactions. The MB-RSPT data are seen to lie mostly between the PNO-CI and CEPA results which reflects the trends of Table 2. The best results are given by CEPA, as expected, but the difference between MB-RSPT and CEPA is much smaller than the difference between CEPA and experimental data or data given by the best reported ab

Table 3. Energies of reactions (all entries in kJ/mol)

Reaction	SCF	$E^{(2)}+E^{(3)}$	PNO-CI(D)	CEPA(D)	CEPA(SD)	Exptl[a]
$2H \rightarrow H_2$	−347.9	−436.0	−440.9	−440.9	−441.3	−458.4
$2F \rightarrow F_2$	+154.5	−84.6	−33.6	−101.9	−114.1	−159.2
$H+F \rightarrow HF$	−404.5	−541.1	−533.5	−543.1	−544.6	−590.0
$H_2+F_2 \rightarrow 2HF$	−615.6	−561.6	−593.3	−544.2	−534.7	−562.6
$F+H_2 \rightarrow FH+H$	−56.6	−105.1	−92.6	−102.2	−103.3	−131.7
$H+F_2 \rightarrow HF+F$	−559.0	−456.5	−500.3	−441.6	−431.0	−430.9
$H+CH_4 \rightarrow CH_3+H_2$	+19.8	−8.7	+3.3	+11.1	+11.3	+10.9

[a] From heats of formation corrected for zero-point energies [5].

Table 4. Barrier heights for some reactions (all entries in kJ/mol)

Reaction	SCF	$E^{(2)}+E^{(3)}$	PNO-CI (D)	CEPA (D)	CEPA (SD)	Reference Calculations
$H+H_2 \rightarrow H_2+H$	106.3	52.9	58.3	56.1	55.1	41.0[a]; 44.8[b]
$H+FH \rightarrow HF+H$	293.2	213.0	220.4	205.7	203.2	205.0[c]; 187.9[d]
$F+H_2 \rightarrow FH+H$	49.6	30.8	39.9	29.2	19.3	22.6[e]; 25.2[f]; 16.4[g]
$H+F_2 \rightarrow HF+F$	71.0	27.5	39.3	19.8		17.2[h]
$H+CH_4 \rightarrow CH_3+H_2$	135.4	82.3	90.7	80.9	78.5	74.0[i]; 67.4[j]; 64.5[k]

[a] CI calculations, STO ($4s3p2d$) basis set [7].
[b] CEPA, [$4s2p$] basis set [9].
[c] CI-SD calculations, [$5s3p1d/3s1p$] basis set [22].
[d] CEPA, [$9s6p3d1f/4s2p$] basis set [9].
[e] CEPA, [$9s7p3d/4s3p1d_{z^2}$] basis set [23].
[f] CI-SD with 1 reference function, *STO* ($6s4p3d1f/3s2p1d$) [24].
[g] CI-SD with 3 reference functions, *STO* ($6s4p3d1f/3s2p1d$) [24].
[h] CI-SD, $DZ+P$ basis set [11].
[i] UHF-CI, [$5s2p1d/2s1p$] basis set [14].
[j] CEPA, [$5s2p1d/2s1p$] basis set [14].
[k] POL-CI, extended basis [25].

initio calculations. From this it follows that when striving for more quantitative predictions by means of MB-RSPT, it is more important to extend the size of the basis set used than to try to include higher order terms from the perturbation expansion.

The entries in the columns CEPA (SD) show that single substitutions cannot be neglected completely though they occur only at fourth order of perturbation energy. In some cases they contribute to as much as 10 kJ/mol to the reaction energy and to the barrier height, in particular in F-atom containing reactions. But our results do not suffice for a systematic study of the influence of singles.

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