

# Many-Body Rayleigh–Schrödinger Perturbation Calculations of the Correlation Energy of Open Shell Molecules in the Restricted Roothaan–Hartree–Fock Formalism. Application to Heats of Reaction and Energies of Activation

Petr Čársky, Rudolf Zahradník

J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Máchova 7, 121 38 Prague 2, Czechoslovakia

Ivan Hubáč

Department of Biophysics, Faculty of Science, Comenius University, Mlynská dolina, 816 31 Bratislava, Czechoslovakia

Miroslav Urban, Vladimír Kellö

Department of Physical Chemistry, Faculty of Science, Comenius University, Mlynská dolina, 816 31 Bratislava, Czechoslovakia

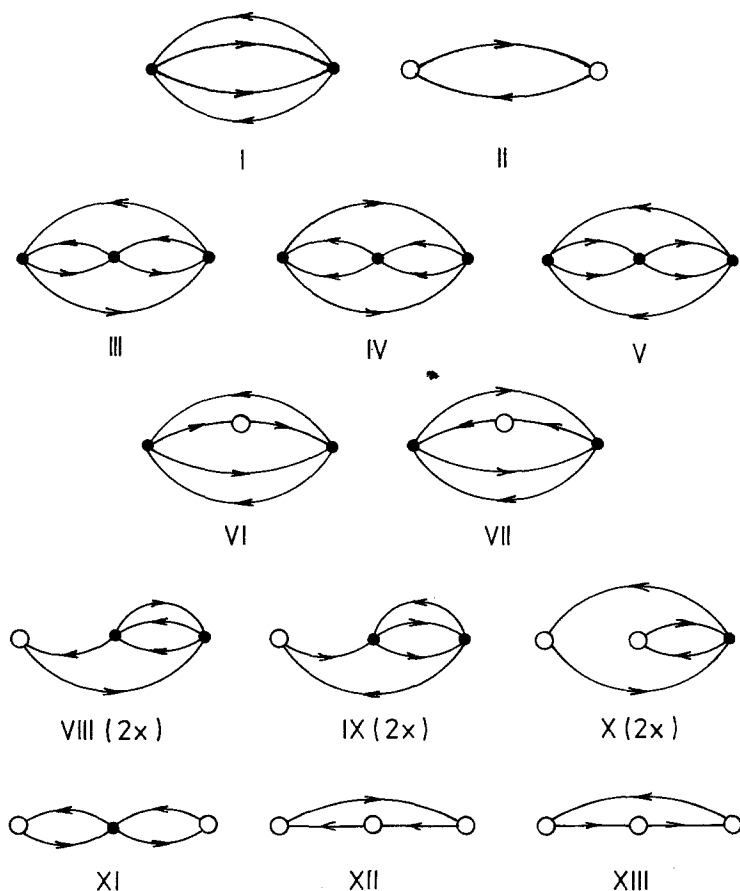
The title technique was applied to a series of elementary chemical reactions. Second and third order contributions to the correlation energy were computed for the basis sets of the double zeta and double zeta plus polarization quality. Calculated heats of reaction and energies of activation were compared with the experimental data and the results of the best *ab initio* calculations reported in the literature.

**Key words:** Correlation energy of radicals – Perturbation calculations of correlation energy of radicals.

## 1. Introduction

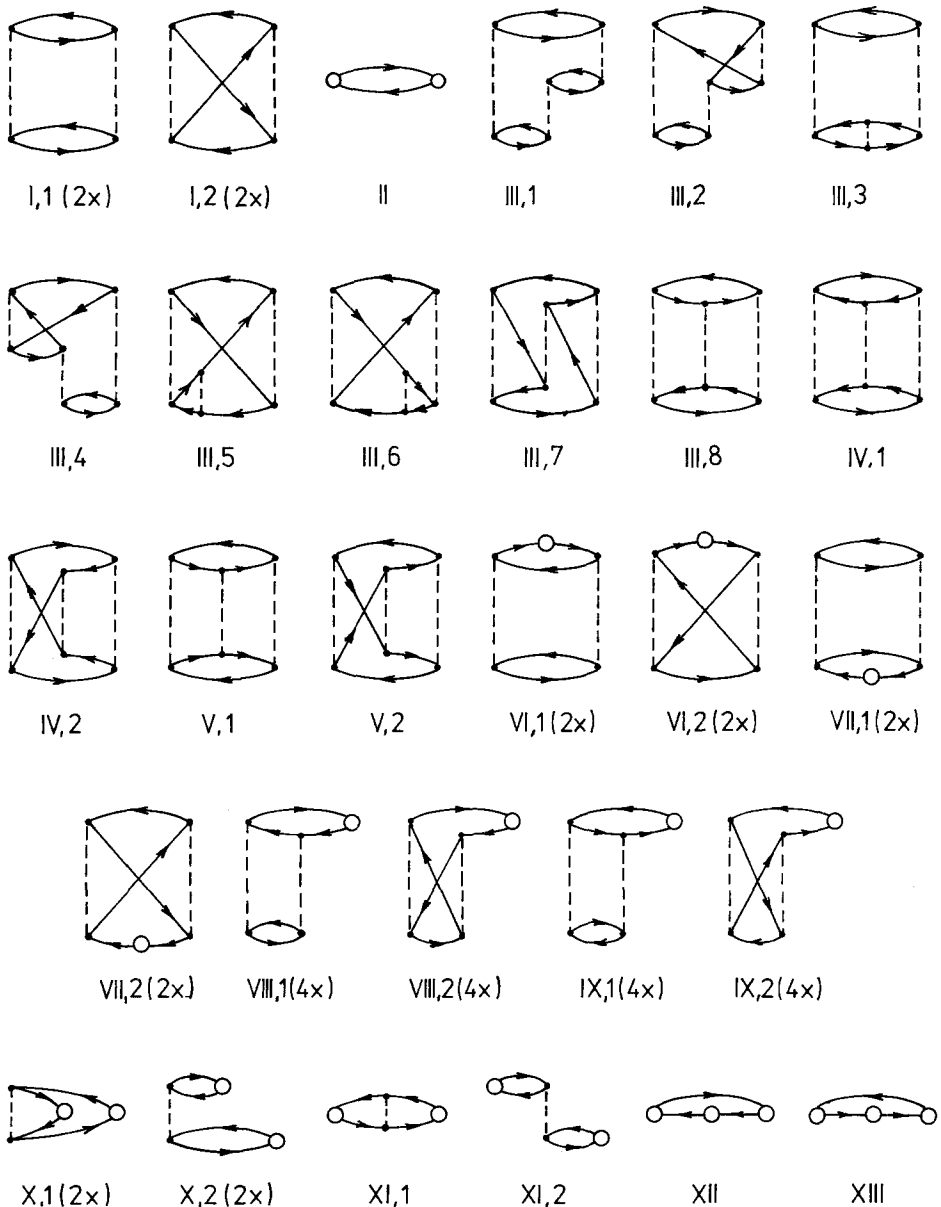
Recently we have proposed [1] the use of the Many-Body Rayleigh–Schrödinger Perturbation Theory (MB-RSPT) in the restricted MO formalism for the calculations of correlation energy in open shell systems as an alternative to the

commonly used unrestricted Møller–Plesset approach [2]. The motivation for the use of the restricted MO formalism was that the latter permits to express all summations appearing in the formulae for the correlation energy over orbitals instead of spinorbitals. This change is profitable from the viewpoint of both the computer time saving and the reduction of the computer core requirements. Preliminary calculations on  $\text{BH}_2$  and  $\text{NH}_2$  radicals [1] showed much resemblance to ordinary closed shell MB-RSPT treatments. Particularly, the correlation energies given by MB-RSPT through third order were very close in absolute value to those given by CI treatments covering all singly and doubly excited configurations and using the same basis set. Drawing unequivocal conclusions about the utility of the restricted MO version of MB-RSPT requires, however, more



**Fig. 1.** Hugenholtz diagrams for the second order (I, II) and the third order (III–XIII) contributions to the correlation energy of half-closed shell systems. The diagrams VIII, IX and X can be obtained in two topologically different ways and their contributions must be therefore counted twice. The diagrams I and III–V are formally the same as those appearing in the closed shell and unrestricted open shell treatments [4], whereas the others (II, VI–XIII) are due to the additional term in the perturbation ( $\mathcal{U}$  operator in Eq. (1); in diagrams it is denoted by open circles)

numerical data. We decided therefore to perform a further testing in a more systematic way. Essentially, we follow two directions. In the first one, a detailed comparison is made for MB-RSPT and CEPA treatments using the same basis set and a theoretical analysis is attempted for clarifying the relative importance of



**Fig. 2.** Goldstone diagrams derived from the Hugenholtz diagrams in Fig. 1. Some diagrams can be obtained in two or four topologically different ways, so that their contributions to the correlation energy must be multiplied by the indicated factors

individual contributions to the total correlation energy. The results of this examination will be reported in a next paper. In this paper we adopt the other approach which is more practically oriented. We selected a few radical processes and we calculated for them heats of reaction and energies of activation. The former were compared with the experimental data, whereas the latter were judged against the best *ab initio* calculations reported in the literature.

## 2. Theoretical Approach and Computational Details

To avoid unnecessary repetition of our earlier paper [1], we note here only the essence of the theoretical approach used. Briefly, the exact (perturbed) Hamiltonian,  $\mathcal{H}$ , is assumed in the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{W} - \mathcal{U} \quad (1)$$

where the unperturbed Hamiltonian,  $\mathcal{H}_0$ , may be taken as the Hartree-Fock operator,  $f_R$ , for SCF equations in the Roothaan restricted open shell method [3]. Actually,  $\mathcal{H}$  and  $\mathcal{H}_0$ , respectively, differ from the commonly used Hamiltonian  $\mathcal{H}$  and the operator  $f_R$  by scalar quantities, so that the eigenvalue problem

$$\mathcal{H}\Psi = k\Psi \quad (2)$$

gives us directly [4] the correlation energy,  $k$ . In contrast to closed shell and unrestricted open shell MB-RSPT treatments, the perturbation,  $\mathcal{W} - \mathcal{U}$  in Eq. (1), contains an additional term  $\mathcal{U}$ . This is a one-electron operator, which has the meaning of the difference

$$\mathcal{U} = f_R - f \quad (3)$$

**Table 1.** Geometries assumed (bond lengths in a.u.)

System	Geometry parameters	Source
H <sub>2</sub>	$r_{\text{HH}} = 1.40$	experiment [11]
HF	$r_{\text{HF}} = 1.733$	experiment [11]
F <sub>2</sub>	$r_{\text{FF}} = 2.677$	experiment [12]
H <sub>3</sub>	$D_{\infty h}, r_{\text{HH}} = 1.757$	SCF-CI [13]
HFH	$D_{\infty h}, r_{\text{HF}} = 2.16$	CEPA [14]
FHH (DZ) <sup>a</sup>	$C_{\infty v}, r_{\text{FH}} = 2.58, r_{\text{HH}} = 1.54$	DZ SCF-CI [15]
FHH (DZ+P) <sup>b</sup>	$C_{\infty v}, r_{\text{FH}} = 2.90, r_{\text{HH}} = 1.45$	DZ+P SCF-CI [16]
HFF (DZ) <sup>a</sup>	$C_{\infty v}, r_{\text{FH}} = 3.88, r_{\text{FF}} = 2.96$	DZ SCF-CI [17]
HFF (DZ+P) <sup>b</sup>	$C_{\infty v}, r_{\text{FH}} = 3.175, r_{\text{FF}} = 2.842$	DZ+P SCF-CI [18]
CH <sub>3</sub>	$D_{3h}, r_{\text{CH}} = 2.039$	experiment [11]
CH <sub>4</sub>	$T_d, r_{\text{CH}} = 2.0665$	experiment [19]
H <sub>3</sub> CH <sup>1</sup> H <sup>2</sup>	$C_{3v}, r_{\text{CH}} = 2.0693, r_{\text{CH}^1} = 2.6003,$ $r_{\text{H}^1\text{H}^2} = 1.7064, \angle\text{HCH} = 114.7^\circ$	UHF-CI [20]

<sup>a</sup> Used for DZ calculations.

<sup>b</sup> Used for DZ+P calculations.

where  $\mathcal{f}$  is the common Hartree–Fock operator. Performing now the MB-RSPT expansion through third order according to a standard technique [4, 5], one arrives at the diagrammatic representation of the correlation energy [1]. In Fig. 1 we present a set of the respective Hugenholtz diagrams, whereas in Fig. 2 we present a set of respective Goldstone diagrams. Explicit formulas for the diagrams I–XIII in terms of spinorbitals were given previously [1]. The formulas in terms of orbitals are presented in the Appendix of this paper.

Actual calculations were performed with two basis sets. The smaller of them, of double zeta quality (DZ), was the Dunning's [6] contraction [4s2p/2s] of the Huzinaga's [7] (9s5p/4s) primitive Gaussian set. The hydrogen *s*-type functions were scaled by the factor  $(1.2)^2 = 1.44$ . The larger basis set (DZ+P) was augmented with a set of six Gaussian *d*-type functions centered on the heavy atom and a single set of *p*-type functions on hydrogen atoms. The following exponents were selected: 0.8 for C, 1.4 for F, 0.75 for H in the fluor-containing systems and

**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	Basis set	SCF	Valence-shell $E_{\text{corr}}$		Total $E_{\text{corr}}$	
			$E^{(2)}$	$E^{(2)} + E^{(3)}$	$E^{(2)}$	$E^{(2)} + E^{(3)}$
H	DZ, DZ+P	-0.499277	0	0	0	0
F <sup>a</sup>	DZ	-99.394270	-0.07812	-0.07473	-0.09064	-0.08770
F <sup>a</sup>	DZ+P	-99.394521 <sup>b</sup>	-0.14914	-0.14698	-0.16309	-0.16132
H <sub>2</sub>	DZ	-1.126588	-0.01731	-0.02252	-0.01731	-0.02252
H <sub>2</sub>	DZ+P, $\alpha_p = 1.0$	-1.131197	-0.02680	-0.03247	-0.02680	-0.03247
H <sub>2</sub>	DZ+P, $\alpha_p = 0.75$	-1.131066	-0.02744	-0.03354	-0.02744	-0.03354
HF	DZ	-100.021971	-0.12158	-0.11934	-0.13420	-0.13239
HF	DZ+P	-100.047873	-0.19697	-0.19901	-0.21120	-0.21364
F <sub>2</sub>	DZ	-198.707581	-0.25053	-0.24311	-0.27571	-0.26914
F <sub>2</sub>	DZ+P	-198.730201	-0.38335	-0.38503	-0.41135	-0.41384
H <sub>3</sub>	DZ	-1.585262	-0.03895	-0.04053	-0.03895	-0.04053
H <sub>3</sub>	DZ+P	-1.589994	-0.05352	-0.05279	-0.05352	-0.05279
HFH	DZ	-100.422465	-0.15799	-0.14343	-0.17061	-0.15647
HFH	DZ+P	-100.435460	-0.24461	-0.22955	-0.25873	-0.24404
FHH <sup>c</sup>	DZ	-100.486364	-0.11529	-0.10848	-0.12786	-0.12149
FHH <sup>c</sup>	DZ+P	-100.506711	-0.18788	-0.18767	-0.20188	-0.20205
HFF <sup>c</sup>	DZ	-199.185840	-0.27498	-0.26267	-0.30016	-0.28869
HFF <sup>c</sup>	DZ+P	-199.202451	-0.41118	-0.40159	-0.43923	-0.43042
CH <sub>3</sub>	DZ	-39.549532	-0.08107	-0.08989	-0.09381	-0.10343
CH <sub>3</sub>	DZ+P	-39.567926	-0.14659	-0.15715	-0.16149	-0.17286
CH <sub>4</sub>	DZ	-40.185335	-0.09349	-0.10784	-0.10630	-0.12147
CH <sub>4</sub>	DZ+P	-40.207389	-0.15966	-0.17877	-0.17481	-0.19480
CH <sub>5</sub>	DZ	-40.631768	-0.12308	-0.12632	-0.13588	-0.13991
CH <sub>5</sub>	DZ+P	-40.655091	-0.19494	-0.19898	-0.20988	-0.21474

<sup>a</sup> The  $(2p_x)^2(2p_y)^2(2p_z)$  configuration assumed, see text.

<sup>b</sup> The difference between the DZ and DZ+P energies is due to the diffuse *s*-type function formed from the  $x^2 + y^2 + z^2$  combination of *d*-functions.

<sup>c</sup> Note in Table 1 that different geometries are assumed for DZ and DZ+P calculations.

1.0 for H in  $H_3$  and  $CH_n$  systems. Use of two different hydrogen  $p$ -sets was made for maintaining compatibility of the calculations with our previous studies [8, 9]. The geometries assumed are given in Table 1. The correlation energies were calculated either with no restriction of the number of occupied and virtual orbitals or the inner shell orbitals were kept doubly occupied. In the former case, the correlation energies will be hereafter referred to as the total correlation energies whereas in the latter case they will be referred to as the valence-shell correlation energies. Since our restricted MB-RSPT approach cannot accommodate degenerate ground states, the fluorine atom was treated as having the  $(2p_x)^2(2p_y)^2(2p_z)$  configuration. This restriction is irrelevant for the calculation of the correlation energy, though it has a minor effect on the SCF energy ( $-0.001$  a.u. with the DZ basis set), because the restricted Roothaan's method can generally give an energy that is not invariant under a unitary transformation of the orbitals [10].

### 3. Results and Discussion

The energies of the systems dealt with in this paper are summarized in Table 2. Combinations of the entries of Table 2 permit us to make a comparison with the observed heats of reaction for the processes listed in Table 3. For the energies of activation we make a comparison (in Table 4) with the results of the best *ab initio* calculations reported in the literature. This is preferable, since the Arrhenius energies obtained from experimental data are not compatible with the computed

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

Reaction	Basis set	SCF	Different levels of MB-RSPT				Exptl. <sup>a</sup>
			valence shell $E_{\text{corr}}$		total $E_{\text{corr}}$		
			$E^{(2)}$	$E^{(2)}+E^{(3)}$	$E^{(2)}$	$E^{(2)}+E^{(3)}$	
2H → H <sub>2</sub>	DZ	-336.2	-381.6	-395.3	-381.6	-395.3	-458.4
	DZ+P	-347.9	-419.9	-436.0	-419.9	-436.0	
2F → F <sub>2</sub>	DZ	+212.6	-35.0	-33.3	-35.3	-33.5	-159.2
	DZ+P	+154.5	-68.9	-84.6	-69.1	-84.9	
H+F → HF	DZ	337.2	-451.3	-454.3	-451.6	-454.5	-590.0
	DZ+P	-404.5	-530.1	-541.1	-530.8	-541.9	
H <sub>2</sub> +F <sub>2</sub> → 2HF	DZ	-550.8	-486.0	-480.0	-486.2	-480.2	-562.6
	DZ+P	-615.6	-571.4	-561.6	-572.6	-562.8	
F+H <sub>2</sub> → FH+H	DZ	-1.0	-69.7	-59.0	-69.9	-59.2	-131.7
	DZ+P	-56.6	-110.1	-105.1	-110.9	-105.9	
H+F <sub>2</sub> → HF+F	DZ	-549.7	-416.2	-420.9	-416.1	-420.9	-430.9
	DZ+P	-559.0	-461.2	-456.5	-461.7	-456.9	
H+CH <sub>4</sub> → CH <sub>3</sub> +H <sub>2</sub>	DZ	+22.3	+9.5	+10.3	+9.6	+10.5	+10.9
	DZ+P	+19.8	-16.2	-8.7	-15.6	-7.8	

<sup>a</sup> From heats of formation corrected for zero-point energies [11].

**Table 4.** Energies of activation (all entries in kJ/mol)

Reaction	Basis set	SCF	Different levels of MB-RSPT				Reference calculations
			valence shell $E_{\text{corr}}$		total $E_{\text{corr}}$		
			$E^{(2)}$	$E^{(2)}+E^{(3)}$	$E^{(2)}$	$E^{(2)}+E^{(3)}$	
H+H <sub>2</sub> → H <sub>2</sub> +H	DZ	106.6	49.8	59.3	49.8	59.3	41.0 <sup>a</sup> ; 44.8 <sup>b</sup>
	DZ+P	106.3	36.1	52.9	36.1	52.9	
H+FH → HF+H	DZ	259.4	163.8	196.2	163.8	196.2	205.0 <sup>c</sup> ; 187.9 <sup>d</sup>
	DZ+P	293.2	168.1	213.0	168.4	213.4	
F+H <sub>2</sub> → FH+H	DZ	90.6	38.5	61.1	38.3	61.0	6.9 <sup>e</sup> ; 22.6 <sup>f</sup>
	DZ+P	49.6	19.9	30.8	19.8	30.7	
H+F <sub>2</sub> → HF+F	DZ	55.2	-9.0	3.8	-9.0	3.9	17.2 <sup>g</sup>
	DZ+P	71.0	-2.1	27.5	-2.2	27.5	
H+CH <sub>4</sub> → CH <sub>3</sub> +H <sub>2</sub>	DZ	138.7	61.0	90.2	61.0	90.3	74.0 <sup>h</sup> ; 67.4 <sup>i</sup>
	DZ+P	135.4	42.8	82.3	43.3	83.0	

<sup>a</sup> CI calculations, STO (4s3p2d) basis set [13].

<sup>b</sup> CEPA, [4s2p] basis set [14].

<sup>c</sup> CI calculations, [5s3p1d/3s1p] basis set [21].

<sup>d</sup> CEPA, [9s6p3d1f/4s2p] basis set [14].

<sup>e</sup> CI, DZ+P basis set [16].

<sup>f</sup> CEPA, [6s3p1d] set for fluorine [22].

<sup>g</sup> CI, DZ+P basis set [18].

<sup>h</sup> UHF-CI, [5s2p1d/2s1p] basis set [20].

<sup>i</sup> CEPA, [5s2p1d/2s1p] basis set [20].

activation barriers and, moreover, the kinetic data for some processes are open to considerable uncertainties.

An overall characterization, which may be given to the results presented in Tables 3 and 4, is that the level of accuracy achieved is comparable to that obtained with unrestricted MB-RSPT, CI-SD and CEPA treatments using a basis set of the same size. Agreement of the computed energies of reaction with the experimental data is far of being satisfactory. It should be recalled, however, that the processes assumed do not conform to the conditions for the "conservation" of the correlation energy [23] and that accounting for correlation effects in the processes of this type is difficult with any existing method. Actually, when striving for quantitative predictions by means of MB-RSPT, one should include some selected terms from higher orders of the perturbation expansion. Also a larger than DZ+P basis set should be used. In this respect our calculations may appear modest. We believe, however, that they still demonstrate the utility of the restricted MB-RSPT approach to the problems of chemical reactivity. This is perhaps more apparent from the entries of Table 4, where the activation energies given by third order DZ+P calculations are seen to be mostly within 10 kJ/mol, compared to results of considerably more elaborate calculations.

The last remark concerns a possible restriction imposed on the number of occupied and virtual MO's assumed in the perturbation expressions. The entries of Tables 3 and 4 suggest that it is sufficient to assume valence-shell correlation energies instead of total correlation energies for all reactions dealt with in this paper. The error introduced by that was at most 1 kJ/mol, but typically it was only 0.1–0.2 kJ/mol. We also performed calculations in which next to the inner shell orbitals also the counterparts of inner shells in the virtual MO space were disregarded (as it is commonly made in CI calculations). The additional error introduced in that way was less than 0.1 kJ/mol in all reactions dealt with.

## Appendix

### Explicit formulas for diagrams I–XIII

We present here the explicit formulas for Diagrams I–XIII in terms of orbitals generated by the RHF-SCF procedure for the nondegenerate doublet state. The electronic repulsion integrals are given in Parr's (11|22) notation. Singly and doubly primed indices, respectively, refer to occupied and virtual orbitals, the singly occupied orbital is denoted by  $m$ .  $D$ ,  $S$  and  $V$  mean spaces over doubly occupied, singly occupied and virtual orbitals, respectively.  $\varepsilon$ 's mean orbital energies. The formulas involve the multiplication factors given in Figs. 1 and 2.

#### Diagram I

$$\sum_{\substack{a''b'' \\ i'j'}} (a''i'|b''j'') \frac{1}{\varepsilon_{i'} + \varepsilon_{j'} - \varepsilon_{a''} - \varepsilon_{b''}} [2p(a''i'|b''j'') - q(a''j'|b''i'')]$$

where  $p$  and  $q$  become

$p$	$q$	Orbital occupation			
		$i'$	$j'$	$a''$	$b''$
1	1	$D$	$D$	$V$	$V$
1	1	$S$	$D$	$V$	$V$
1	1	$D$	$D$	$S$	$V$
$\frac{1}{2}$	0	$S$	$D$	$V$	$S$
0	0	all other cases			

#### Diagram II

$$\frac{1}{2} \sum_{\substack{a'' \in V \\ i' \in D}} (a''m|mi') \frac{1}{\varepsilon_{i'} - \varepsilon_{a''}} (i'm|ma'')$$



Diagram III (contributions from Goldstone diagrams 1, 2, 4 and 7)

$$2t \sum_{\substack{a''b''c'' \\ i'j'k'}} (a''i'|c''k') \frac{1}{(\varepsilon_{i'} + \varepsilon_{j'} - \varepsilon_{a''} - \varepsilon_{b''})(\varepsilon_{j'} + \varepsilon_{k'} - \varepsilon_{b''} - \varepsilon_{c''})}$$

$$\cdot \{ [2p(a''i'|b''j') - q(a''j'|b''i')] [2r(b''j'|c''k') - s(b''k'|c''j')] + u(a''i'|b''j')(b''j'|c''k') - v(a''j'|b''i')(b''k'|c''j') \}$$

where  $p, q, r, s, t, u$  and  $v$  become

$t$	$p$	$q$	$r$	$s$	$u$	$v$	Orbital occupation					
							$i'$	$j'$	$k'$	$a''$	$b''$	$c''$
1	1	1	1	1	0	0	$D$	$D$	$D$	$V$	$V$	$V$
1	1	1	1	1	0	0	$S$	$D$	$D$	$V$	$V$	$V$
$\frac{1}{2}$	1	1	1	1	0	0	$D$	$S$	$D$	$V$	$V$	$V$
1	1	1	1	1	0	0	$D$	$D$	$D$	$S$	$V$	$V$
$\frac{1}{2}$	1	1	1	1	0	0	$D$	$D$	$D$	$V$	$S$	$V$
$\frac{1}{2}$	$\frac{1}{2}$	1	$\frac{1}{2}$	1	1	0	$S$	$D$	$S$	$V$	$V$	$V$
$\frac{1}{2}$	$\frac{1}{2}$	1	$\frac{1}{2}$	1	1	0	$D$	$D$	$D$	$S$	$D$	$S$
1	$\frac{1}{2}$	0	1	1	0	0	$S$	$D$	$D$	$V$	$S$	$V$
1	$\frac{1}{2}$	0	1	1	0	0	$D$	$S$	$D$	$S$	$V$	$V$
1	$\frac{1}{2}$	1	$\frac{1}{2}$	1	1	1	$S$	$D$	$D$	$V$	$V$	$S$
$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	0	0	0	$S$	$D$	$S$	$V$	$S$	$V$
$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	0	0	0	$D$	$S$	$D$	$S$	$V$	$S$
0	0	0	0	0	0	0	all other cases					

Diagram III (contributions from Goldstone diagrams 3, 5, 6 and 8)

$$-t \sum_{\substack{a''b''c'' \\ i'j'k'}} (a''c''|k'i') \frac{1}{(\varepsilon_{i'} + \varepsilon_{j'} - \varepsilon_{a''} - \varepsilon_{b''})(\varepsilon_{j'} + \varepsilon_{k'} - \varepsilon_{b''} - \varepsilon_{c''})}$$

$$\cdot \{ [2p(a''i'|b''j') - q(a''j'|b''i')] [2r(b''j'|c''k') - s(b''k'|c''j')] + 3u(a''j'|b''i')(b''k'|c''j') \}$$

where  $p, q, r, s, t$  and  $u$  become

$t$	$p$	$q$	$r$	$s$	$u$	Orbital occupation					
						$i'$	$j'$	$k'$	$a''$	$b''$	$c''$
1	1	1	1	1	1	<i>D</i>	<i>D</i>	<i>D</i>	<i>V</i>	<i>V</i>	<i>V</i>
$\frac{1}{2}$	1	1	1	1	1	<i>D</i>	<i>S</i>	<i>D</i>	<i>V</i>	<i>V</i>	<i>V</i>
$\frac{1}{2}$	1	1	1	1	1	<i>D</i>	<i>D</i>	<i>D</i>	<i>V</i>	<i>S</i>	<i>V</i>
1	0	0	0	0	$\frac{1}{3}$	<i>D</i>	<i>S</i>	<i>D</i>	<i>V</i>	<i>S</i>	<i>V</i>
1	1	1	1	1	1	<i>S</i>	<i>D</i>	<i>D</i>	<i>V</i>	<i>V</i>	<i>V</i>
2	$\frac{1}{2}$	0	$\frac{1}{2}$	0	0	<i>S</i>	<i>D</i>	<i>D</i>	<i>V</i>	<i>S</i>	<i>V</i>
$\frac{1}{2}$	1	1	1	1	1	<i>S</i>	<i>D</i>	<i>S</i>	<i>V</i>	<i>V</i>	<i>V</i>
1	$\frac{1}{2}$	0	$\frac{1}{2}$	0	0	<i>S</i>	<i>D</i>	<i>S</i>	<i>V</i>	<i>S</i>	<i>V</i>
1	1	1	1	1	1	<i>D</i>	<i>D</i>	<i>D</i>	<i>S</i>	<i>V</i>	<i>V</i>
2	$\frac{1}{2}$	0	$\frac{1}{2}$	0	0	<i>D</i>	<i>S</i>	<i>D</i>	<i>S</i>	<i>V</i>	<i>V</i>
$\frac{1}{2}$	1	1	1	1	1	<i>D</i>	<i>D</i>	<i>D</i>	<i>S</i>	<i>V</i>	<i>S</i>
1	$\frac{1}{2}$	0	$\frac{1}{2}$	0	0	<i>D</i>	<i>S</i>	<i>D</i>	<i>S</i>	<i>V</i>	<i>S</i>
2	0	0	0	0	$\frac{1}{3}$	<i>S</i>	<i>D</i>	<i>S</i>	<i>S</i>	<i>V</i>	<i>V</i>
2	0	0	0	0	$\frac{1}{3}$	<i>S</i>	<i>D</i>	<i>D</i>	<i>S</i>	<i>V</i>	<i>V</i>
2	0	0	0	0	$\frac{1}{3}$	<i>S</i>	<i>D</i>	<i>D</i>	<i>V</i>	<i>V</i>	<i>S</i>
2	0	0	0	0	$\frac{1}{3}$	<i>S</i>	<i>D</i>	<i>D</i>	<i>S</i>	<i>V</i>	<i>S</i>
1	0	0	0	0	$\frac{1}{3}$	<i>S</i>	<i>D</i>	<i>S</i>	<i>S</i>	<i>V</i>	<i>S</i>
0	0	0	0	0	0	all other cases					

Diagram IV

$$\sum_{\substack{a''b''c''d'' \\ i'j'}} (a''i'|b''j') \frac{1}{\varepsilon_{i'} + \varepsilon_{j'} - \varepsilon_{a''} - \varepsilon_{b''}} (a''c''|b''d'')$$

$$\cdot \frac{1}{\varepsilon_{i'} + \varepsilon_{j'} - \varepsilon_{c''} - \varepsilon_{d''}} [2p(c''i'|d''j') - q(c''j'|d''i')]$$

where  $p$  and  $q$  become

$p$	$q$	Orbital occupation					
		$i'$	$j'$	$a''$	$b''$	$c''$	$d''$
1	1	<i>D</i>	<i>D</i>	<i>V</i>	<i>V</i>	<i>V</i>	<i>V</i>
1	1	<i>S</i>	<i>D</i>	<i>V</i>	<i>V</i>	<i>V</i>	<i>V</i>
1	1	<i>D</i>	<i>D</i>	<i>S</i>	<i>V</i>	<i>V</i>	<i>V</i>
1	1	<i>D</i>	<i>D</i>	<i>V</i>	<i>V</i>	<i>S</i>	<i>V</i>
1	0	<i>S</i>	<i>D</i>	<i>V</i>	<i>S</i>	<i>V</i>	<i>V</i>
1	1	<i>D</i>	<i>D</i>	<i>S</i>	<i>V</i>	<i>S</i>	<i>V</i>
$\frac{1}{2}$	1	<i>D</i>	<i>D</i>	<i>S</i>	<i>V</i>	<i>V</i>	<i>S</i>
$\frac{1}{2}$	0	<i>S</i>	<i>D</i>	<i>V</i>	<i>S</i>	<i>V</i>	<i>S</i>
0	0	all other cases					

Diagram V

$$\sum_{\substack{a''b'' \\ i'j'k'l'}} (a''i'|b''j') \frac{1}{\varepsilon_{i'} + \varepsilon_{j'} - \varepsilon_{a''} - \varepsilon_{b''}} (i'k'|j'l')$$

$$\cdot \frac{1}{\varepsilon_{k'} + \varepsilon_{l'} - \varepsilon_{a''} - \varepsilon_{b''}} [2p(a''k'|b''l') - q(a''l'|b''k')]$$

where  $p$  and  $q$  become

$p$	$q$	Orbital occupation					
		$i'$	$j'$	$k'$	$l'$	$a''$	$b''$
1	1	<i>D</i>	<i>D</i>	<i>D</i>	<i>D</i>	<i>V</i>	<i>V</i>
1	1	<i>D</i>	<i>D</i>	<i>D</i>	<i>D</i>	<i>S</i>	<i>V</i>
1	1	<i>S</i>	<i>D</i>	<i>D</i>	<i>D</i>	<i>V</i>	<i>V</i>
1	1	<i>D</i>	<i>D</i>	<i>S</i>	<i>D</i>	<i>V</i>	<i>V</i>
1	0	<i>S</i>	<i>D</i>	<i>D</i>	<i>D</i>	<i>V</i>	<i>S</i>
1	1	<i>S</i>	<i>D</i>	<i>S</i>	<i>D</i>	<i>V</i>	<i>V</i>
$\frac{1}{2}$	1	<i>S</i>	<i>D</i>	<i>D</i>	<i>S</i>	<i>V</i>	<i>V</i>
$\frac{1}{2}$	0	<i>S</i>	<i>D</i>	<i>S</i>	<i>D</i>	<i>V</i>	<i>S</i>
0	0	all other cases					

Diagram VI

$$\sum_{\substack{a''b'' \\ i'j'k'}} (a''i'|b''j') \frac{1}{\varepsilon_{i'} + \varepsilon_{j'} - \varepsilon_{a''} - \varepsilon_{b''}} (k'm|mi')$$

$$\cdot \frac{1}{\varepsilon_{j'} + \varepsilon_{k'} - \varepsilon_{a''} - \varepsilon_{b''}} [2p(a''k'|b''j') - q(a''j'|b''k')]$$

where  $p$  and  $q$  become

$p$	$q$	Orbital occupation				
		$i'$	$j'$	$k'$	$a''$	$b''$
2	2	<i>D</i>	<i>D</i>	<i>D</i>	<i>V</i>	<i>V</i>
1	1	<i>S</i>	<i>D</i>	<i>D</i>	<i>V</i>	<i>V</i>
1	$\frac{3}{2}$	<i>D</i>	<i>S</i>	<i>D</i>	<i>V</i>	<i>V</i>
1	1	<i>D</i>	<i>D</i>	<i>S</i>	<i>V</i>	<i>V</i>
$\frac{1}{2}$	$\frac{1}{2}$	<i>D</i>	<i>D</i>	<i>D</i>	<i>S</i>	<i>V</i>
1	$\frac{1}{2}$	<i>D</i>	<i>D</i>	<i>D</i>	<i>V</i>	<i>S</i>
$\frac{1}{2}$	0	<i>S</i>	<i>D</i>	<i>D</i>	<i>V</i>	<i>S</i>
$\frac{1}{2}$	$\frac{1}{2}$	<i>S</i>	<i>D</i>	<i>S</i>	<i>V</i>	<i>V</i>
$\frac{1}{2}$	0	<i>D</i>	<i>D</i>	<i>S</i>	<i>V</i>	<i>S</i>
$\frac{1}{4}$	0	<i>S</i>	<i>D</i>	<i>S</i>	<i>V</i>	<i>S</i>
$\frac{1}{4}$	0	<i>D</i>	<i>S</i>	<i>D</i>	<i>S</i>	<i>V</i>
0	0	all other cases				

## Diagram VII

$$\sum_{\substack{a''b''c'' \\ i'j'}} (a''i'|b''j') \frac{1}{\varepsilon_{i'} + \varepsilon_{j'} - \varepsilon_{a''} - \varepsilon_{b''}} (b''m|mc'') \\ \cdot \frac{1}{\varepsilon_{1'} + \varepsilon_{j'} - \varepsilon_{a''} - \varepsilon_{c''}} [2p(a''i'|c''j') - q(a''j'|c''i')]$$

where  $p$  and  $q$  become

$p$	$q$	Orbital occupation				
		$i'$	$j'$	$a''$	$b''$	$c''$
2	2	$D$	$D$	$V$	$V$	$V$
1	$\frac{1}{2}$	$S$	$D$	$V$	$V$	$V$
$\frac{1}{2}$	$\frac{1}{2}$	$D$	$S$	$V$	$V$	$V$
1	$\frac{3}{2}$	$D$	$D$	$S$	$V$	$V$
1	1	$D$	$D$	$V$	$S$	$V$
1	1	$D$	$D$	$V$	$V$	$S$
$\frac{1}{2}$	$\frac{1}{2}$	$D$	$D$	$V$	$S$	$S$
$\frac{1}{2}$	0	$S$	$D$	$V$	$S$	$V$
$\frac{1}{2}$	0	$S$	$D$	$V$	$V$	$S$
$\frac{1}{4}$	0	$D$	$S$	$S$	$V$	$V$
$\frac{1}{4}$	0	$S$	$D$	$V$	$S$	$S$
0	0	all other cases				

## Diagram VIII

$$\sum_{\substack{a''b''c'' \\ i'j'}} (a''i'|b''j') \frac{1}{\varepsilon_{i'} + \varepsilon_{j'} - \varepsilon_{a''} - \varepsilon_{b''}} (c''m|mi'') \frac{1}{\varepsilon_{i'} - \varepsilon_{c''}} \\ \cdot [2p(a''c''|b''j') - q(a''j''|b''c'')]$$

where  $p$  and  $q$  become

$p$	$q$	Orbital occupation				
		$i'$	$j'$	$a''$	$b''$	$c''$
1	1	$D$	$D$	$S$	$V$	$V$
0	1	$D$	$D$	$V$	$S$	$V$
0	-1	$D$	$S$	$V$	$V$	$V$
$\frac{1}{2}$	0	$D$	$S$	$S$	$V$	$V$
0	0	all other cases				

**Diagram IX**

$$\sum_{\substack{a''b'' \\ i'j'k'}} (a''i'|b''j') \frac{1}{\varepsilon_{i'} + \varepsilon_{j'} - \varepsilon_{a''} - \varepsilon_{b''}} (b''m|mk') \frac{1}{\varepsilon_{k'} - \varepsilon_{b''}} \\ \cdot [2p(a''i'|k'j') - q(a''j'|k'i')]$$

where  $p$  and  $q$  become

$p$	$q$	Orbital occupation				
		$i'$	$j'$	$k'$	$a''$	$b''$
1	1	$D$	$S$	$D$	$V$	$V$
0	1	$S$	$D$	$D$	$V$	$V$
0	-1	$D$	$D$	$D$	$S$	$V$
$\frac{1}{2}$	0	$D$	$S$	$D$	$S$	$V$
0	0	all other cases				

**Diagram X**

Of the two respective Goldstone diagrams, only X,1 gives a nonvanishing contribution:

$$- \sum_{\substack{a'',b'' \in V \\ i',j' \in D}} (a''i'|b''j') \frac{1}{\varepsilon_{i'} + \varepsilon_{j'} - \varepsilon_{a''} - \varepsilon_{b''}} (b''m|mi') \frac{1}{\varepsilon_{j'} - \varepsilon_{a''}} (a''m|mj').$$

**Diagram XI**

Of the two respective Goldstone diagrams, only XI,1 gives a nonvanishing contribution:

$$-\frac{1}{2} \sum_{\substack{a'',b'' \in V \\ i',j' \in D}} (a''m|mi') \frac{1}{\varepsilon_{i'} - \varepsilon_{a''}} (a''b''|i'j') \frac{1}{\varepsilon_{j'} - \varepsilon_{b''}} (b''m|mj').$$

**Diagram XII**

$$\frac{1}{2} \sum_{\substack{a'',b'' \in V \\ i' \in D}} (i'm|ma'') \frac{1}{\varepsilon_{i'} - \varepsilon_{a''}} (a''m|mb'') \frac{1}{\varepsilon_{i'} - \varepsilon_{b''}} (b''m|mi').$$

**Diagram XIII**

$$\frac{1}{2} \sum_{\substack{a'' \in V \\ i',j' \in D}} (a''m|mi') \frac{1}{\varepsilon_{i'} - \varepsilon_{a''}} (i'm|mj') \frac{1}{\varepsilon_{j'} - \varepsilon_{a''}} (j'm|ma'').$$

## References

1. Hubač, I., Čársky, P.: *Phys. Rev. A*, in press, (1980)
2. Pople, J. A., Binkley, J. S., Seeger, R.: *Intern. J. Quantum Chem., Symp.* **10**, 1 (1976)
3. Roothaan, C. C. J.: *Rev. Mod. Phys.* **32**, 179 (1960)
4. Paldus, J., Čížek, J.: *Advan. Quantum Chem.* **9**, 105 (1975)
5. Hubač, I., Čársky, P.: *Topics Curr. Chem.* **75**, 97 (1978)
6. Dunning, Jr., T. H.: *J. Chem. Phys.* **53**, 2823 (1970)
7. Huzinaga, S.: *J. Chem. Phys.* **42**, 1293 (1965)
8. Urban, M., Kellö, V., Čársky, P.: *Theoret. Chim. Acta (Berl.)* **45**, 205 (1977)
9. Urban, M., Hubač, I., Kellö, V., Noga, J.: *J. Chem. Phys.*, in press
10. Walker, T. E. H.: *Chem. Phys. Letters* **9**, 174 (1971)
11. JANAF thermochemical tables, Second Edn. Washington: National Bureau of Standards 1971
12. Classen, H. H., Selig, H., Shamir, J.: *Appl. Spectrosc.* **23**, 8 (1969)
13. Liu, B.: *J. Chem. Phys.* **58**, 1925 (1973)
14. Botschwina, P., Meyer, W.: *Chem. Phys.* **20**, 43 (1977)
15. Bender, C. F., Pearson, P. K., O'Neil, S. V., Schaefer III, H. F.: *J. Chem. Phys.* **56**, 4626 (1972)
16. Bender, C. F., O'Neil, S. V., Pearson, P. K., Schaefer III, H. F.: *Science* **176**, 1412 (1972)
17. O'Neil, S. V., Pearson, P. K., Schaefer III, H. F., Bender, C. F.: *J. Chem. Phys.* **58**, 1126 (1973)
18. Bender, C. F., Bauschlicher, Jr., C. W., Schaefer III, H. F.: *J. Chem. Phys.* **60**, 3707 (1974)
19. Tables of interatomic distances and configuration in molecules and ions, ed. by Sutton, L. E.. London: The Chemical Society 1958
20. Niblaeus, K., Roos, B. O., Siegbahn, P. E. M.: *Chem. Phys.* **26**, 59 (1977)
21. Bender, C. F., Garrison, B. J., Schaefer III, H. F.: *J. Chem. Phys.* **62**, 1188 (1975)
22. Botschwina, P.: Presented at the Microsymposium on Quantum Chemistry, Bechyně (Czechoslovakia), 1979
23. Kutzelnigg, W.: *Topics Curr. Chem.* **41**, 31 (1973)

Received April 10, 1980