CORRELATION ENERGY IN TRIPLET ELECTRONIC STATES. APPLICATION OF THE MANY-BODY RAYLEIGH-SCHRÖDINGER PERTURBATION THEORY IN THE RESTRICTED ROOTHAAN-HARTREE-FOCK FORMALISM

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Explicit formulas over orbitals are given for the correlation energy in triplet electronic states of atoms and molecules. The formulas were obtained by means of the diagrammatic many-body Rayleigh-Schrödinger perturbation theory through third order assuming a single determinant restricted Roothaan-Hartree-Fock wave function as the reference function. A numerical example is presented for the NH molecule.

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 a more economic alternative to the commonly used Unrestricted Møller-Plesset (UMP) approach[2]. The calculations performed[1,3] and the formulas presented[3] referred, however, only to doublet electronic states. Since also triplet states are of considerable interest to chemists, we considered it expedient to extend a critical examination of our approach to systems in triplet electronic states. In this paper we present the explicit formulas for the evaluation of the correlation energy. A comparison of our MB-RSPT results with UMP, CI and CEPA calculations will be reported in a next paper.

THEORETICAL

In contrast to the common Møller-Plesset theory, the exact (perturbed) Hamiltonian, $\mathbf{K}$, assumed in our approach[1] as

$$\mathbf{K} = \mathbf{K}_0 + \mathbf{W} - \mathbf{U}\,, \tag{1}$$

contains an additional one-electron operator $\mathbf{U}$, which has the meaning of the difference

$$\mathbf{U} = \mathbf{f}_R - \mathbf{f}\,, \tag{2}$$

where $\mathbf{f}_R$ is the Hartree–Fock operator for SCF equations in the Roothaan restricted open shell method[4] and $\mathbf{f}$ is the common Hartree–Fock operator. Performing the MB-RSPT expansion for the Hamiltonian (*1*) according to a standard technique[5,6] gives us the diagrammatic representation of the correlation energy. Fig. 1 presents a set of the respective Hugenholtz diagrams, whereas Fig. 2 presents a set of the respective Goldstone diagrams. The formulas for the diagrams *I*–*XIII* given previously[1] in terms of spinorbitals are common to both doublet and triplet states. The formulas in terms of orbitals are presented in the Appendix of this paper.

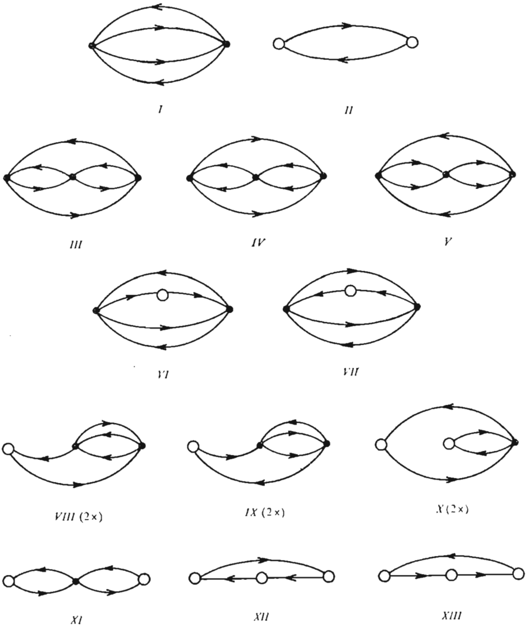
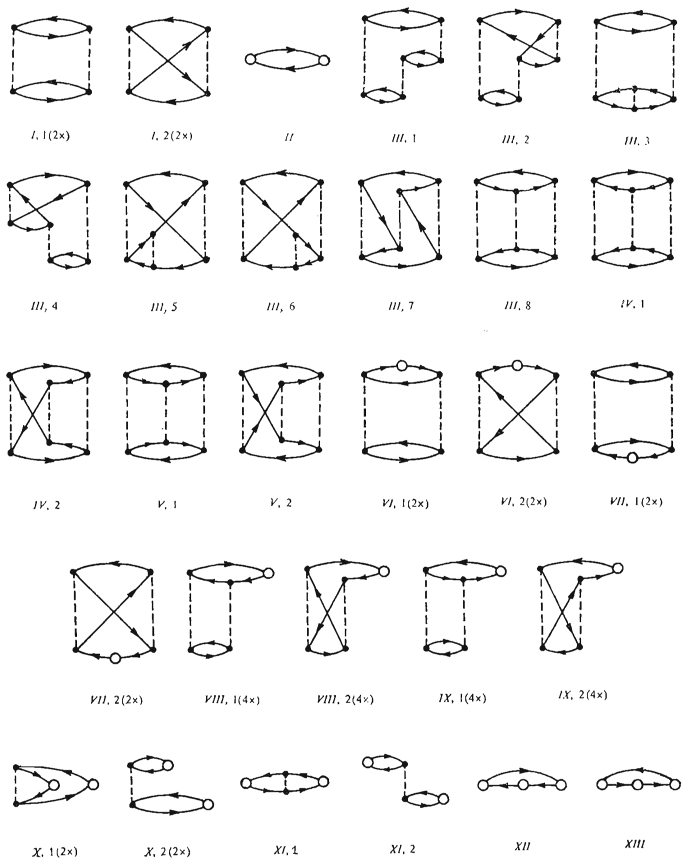


FIG. 1

Hugenholtz Diagrams for the Second (*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. Open circles in diagrams *II* and *VI*—*XIII* refer to the **U** operator.



I, 1(2×) *I*, 2(2×) *II* *III*, 1 *III*, 2 *III*, 3

III, 4 *III*, 5 *III*, 6 *III*, 7 *III*, 8 *IV*, 1

IV, 2 *V*, 1 *V*, 2 *VI*, 1(2×) *VI*, 2(2×) *VII*, 1(2×)

VII, 2(2×) *VIII*, 1(4×) *VIII*, 2(4×) *IX*, 1(4×) *IX*, 2(4×)

X, 1(2×) *X*, 2(2×) *XI*, 1 *XI*, 2 *XII* *XIII*

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.

Application to the NH *Molecule*

As an illustrative example of the application of our approach we selected the NH molecule for which the UMP calculation through third order has already been reported[2]. Assuming the same bond length and the same basis set as in the cited paper[2] permits us to make a direct comparison of the two approaches. The comparison presented in Table I shows that the restricted MO approach overestimates the second order contribution. At the third order, the energy difference between the two approaches is small, as it of course has to be if the convergence of the MB-RSPT expansion for the partitioning of the Hamiltonian (*1*) is fast enough.

TABLE I

Comparison of Restricted MO and Unrestricted MO MB-RSPT Treatments for the Molecule NH Using the $(8s4p1d/4s1p)$ Basis Set[a]

Approach	SCF energy	Second order	Second + third order
RHF reference wave function and the use of Eq. (*1*)	—54·95748	—55·14019	—55·13498
Unrestricted Møller-Plesset[b]	—54·96450	—55·11562	—55·13248
Difference	+ 0·00702	— 0·02457	— 0·00250

[a] All entries are in dimensionless quantities E/e_0, where $e_0 = 2625{\cdot}5\ \text{kJ mol}^{-1}$; [b] Data taken from ref.[2].

APPENDIX

Explicit Formulas for Diagrams *I—XIII*

To avoid unnecessary repetition, we make extensive use of the formulas derived previously[3] for doublet states. Actually, one can obtain the formulas for triplet states by supplementing the formulas for the doublet states for some additional terms, which in the case of doublet states are vanishing. We present here therefore only the additional terms, whereas for the others we refer the reader to ref.[3]. In the formulas the lower-case characters a, b, c, d, i, j, k, l, m denote molecular orbitals given by the RHF-SCF procedure[4] for the half-closed shell triplet state. The symbol m is reserved to denote the two singly occupied orbitals. Singly and doubly primed indices, respectively, refer to occupied and virtual orbitals. D, S and V mean manifolds of doubly occupied, singly occupied and virtual orbitals, respectively. ε's mean orbital energies. The electronic repulsion integrals are given in Parr's $(11 \mid 22)$ notation. The formulas involve the multiplication factors given in Figs 1 and 2.

DIAGRAM *I*

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

where p and q in additional nonvanishing terms become

p	q	Orbital occupation			
		i'	j'	a''	b''
$\frac{1}{4}$	$\frac{1}{2}$	D	D	S	S
$\frac{1}{4}$	$\frac{1}{2}$	S	S	D	D

DIAGRAM *III*

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

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

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

$$+ u(a''i' \mid b''j')(b''j' \mid c''k') - v(a''j' \mid b''i')(b''k' \mid c''j')\},$$

where p, q, r, s, t, u and v in additional nonvanishing terms become

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

DIAGRAM *III*

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

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

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

$$+ 3u(a''j' \mid b''i')(b''k' \mid c''j')\},$$

where *p*, *q*, *r*, *s*, *t* and *u* in additional nonvanishing terms become

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

DIAGRAM *IV*

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

$$\cdot [2p(c''i' \mid d''j') - q(c''j' \mid d''i')],$$

where *p* and *q* in additional nonvanishing terms become

p	*q*	Orbital occupation					
		i'	*j'*	*a''*	*b''*	*c''*	*d''*
$\frac{1}{4}$	$\frac{1}{2}$	D	D	S	S	V	V
$\frac{1}{4}$	$\frac{1}{2}$	D	D	V	V	S	S
$\frac{1}{4}$	$\frac{1}{2}$	D	D	S	S	S	V
$\frac{1}{4}$	$\frac{1}{2}$	D	D	S	S	V	S
$\frac{1}{4}$	$\frac{1}{2}$	D	D	S	V	S	S
$\frac{1}{4}$	$\frac{1}{2}$	D	D	V	S	S	S
$\frac{1}{4}$	$\frac{1}{2}$	D	D	S	S	S	S

DIAGRAM *V*

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

$$. \left[2p(a''k' \mid b''l') - q(a''l' \mid b''k')\right],$$

where p and q in additional nonvanishing terms become

p	q	Orbital occupation					
		i'	j'	k'	l'	a''	b''
$\frac{1}{4}$	$\frac{1}{2}$	S	S	D	D	V	V
$\frac{1}{4}$	$\frac{1}{2}$	D	D	S	S	V	V
$\frac{1}{4}$	$\frac{1}{2}$	D	D	D	D	S	S
$\frac{1}{2}$	1	S	S	S	D	V	V
$\frac{1}{2}$	1	S	D	S	S	V	V
$\frac{1}{4}$	$\frac{1}{2}$	S	S	S	S	V	V

DIAGRAM *VI*

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

$$. \left[2\mathrm{p}(a''k' \mid b''j') - q(a''j' \mid b''k')\right],$$

where p and q in additional nonvanishing terms become

p	q	Orbital occupation				
		i'	j'	k'	a''	b''
$\frac{1}{2}$	1	S	S	D	V	V
$\frac{1}{2}$	1	D	S	S	V	V
$\frac{1}{4}$	$\frac{1}{2}$	D	D	D	S	S
$\frac{1}{4}$	$\frac{1}{2}$	S	S	S	D	D

DIAGRAM *VII*

$$\sum_{\substack{a''b''c''\\ i'j'}} (a''i' \mid b''j') \frac{1}{\varepsilon_{i'} + \varepsilon_{j'} - \varepsilon_{a''} - \varepsilon_{b''}} (b''m \mid mc'') \frac{1}{\varepsilon_{i'} + \varepsilon_{j'} - \varepsilon_{a''} - \varepsilon_{c''}} \,.$$

$$. \left[2p(a''i' \mid c''j') - q(a''j' \mid c''i')\right]$$

where p and q in additional nonvanishing terms become

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

DIAGRAM *VIII*

$$\sum_{\substack{a''b''c''\\ i'j'}} (a''i' \mid b''j') \frac{1}{\varepsilon_{i'} + \varepsilon_{j'} - \varepsilon_{a''} - \varepsilon_{b''}} (c''m \mid mi') \frac{1}{\varepsilon_{i'} - \varepsilon_{c''}} \,.$$

$$\cdot \left[2p(a''c'' \mid b''j') - q(a''j' \mid b''c'')\right]$$

where $p = \frac{1}{2}$ and $q = 1$ for the additional term with $i' \in \mathrm{D}$, $j' \in \mathrm{D}$, $a'' \in \mathrm{S}$, $b'' \in \mathrm{S}$ and $c'' \in V$

DIAGRAM *IX*

$$\sum_{\substack{a''b''\\ i'j'k'}} (a''i' \mid b''j') \frac{1}{\varepsilon_{i'} + \varepsilon_{j'} - \varepsilon_{a''} - \varepsilon_{b''}} (b''m \mid mk') \frac{1}{\varepsilon_{k'} - \varepsilon_{b''}} \,.$$

$$. \left[2p(a''i' \mid k'j') - q(a''j' \mid k'i')\right]$$

where $p = \frac{1}{2}$ and $q = 1$ for additional nonvanishing term with $i' \in \mathrm{S}$, $j' \in \mathrm{S}$, $k' \in D$, $a'' \in V$ and $b'' \in V$.

For diagrams *II* and *X—XIII* the respective formulas from ref.[3] may be applied without any additional term.

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