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Calculation of Correlation Energy by Many-Body Diagrammatic Perturbation Theory*

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The many-body diagrammatic perturbation theory is used for calculation of the correlation energy of closed-shell molecular systems. We apply Brueckner's concept of the two-particle renormalized interaction defined by a non-linear diagrammatic expression containing all possible (diagonal and/or non-diagonal) particle-particle, hole-hole and particle-hole intermediate elementary processes. Then, a "second-order" simple diagrammatic expression for the correlation energy can be formed, where the correlation energy is approximated by all the diagrams with biexcited intermediate states. An illustrative numerical application for the LiH molecule is presented.

Key words: Many-body diagrammatic perturbation theory – Correlation energy

1. Introduction

Much progress has recently been made in the calculation of the correlation energy of small molecular systems by the many-body diagrammatic perturbation theory [1–5]. It has, however, been pointed out that in order to obtain satisfactory agreement between the calculated and experimental correlation energy it is necessary to use (1) at least third order diagrammatic contributions, and (2) some class of diagrams should be summed up to all orders in the perturbation expansion [1]. The second item (2) is, up to now, usually realized *via* the summation of geometric series, which technique has been initially used by Kelly [1, 6]. He demonstrated that such summations produce the so-called *shifted denominators* containing not only the one-particle orbital energies but also some type of Coulomb and exchange two-particle matrix elements. In the framework of diagrammatic language this means that some

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*This article is dedicated to the memory of our friends and colleagues Dr. Jarka Surá and Dr. Marta Černayová, who tragically died in July 1976.

preselected higher-order *diagonal* ladder and ring diagrams are summed to infinite order. Nesbet [7] noted that in effect Kelly was employing the modified perturbation theory called in the current literature as the Epstein-Nesbet partitioning of the full Hamiltonian [8, 9]. Later, this general conclusion has been reconsidered and justified by many other authors [4, 5, 10, 11].

As was mentioned above, the technique of the shifted denominators affect only *diagonal* ladder and ring higher-order diagrams. An intermediate step, overcoming this restriction, represents the recent article of Mukhopadhyay *et al.* [10]. They have suggested a new partitioning of the Hamiltonian by which it is possible to eliminate the non-diagonal particle-hole ladders to all orders. In their approach it is necessary to solve iteratively a non-linear one-particle eigenproblem, the matrix elements of which are defined in the space of molecular orbitals. Therefore, in each iterative step the two-particle matrix elements should be recalculated for a new basis of molecular orbitals. The transformation process of the two-particle matrix elements from the basis of atomic orbitals to the basis of molecular orbitals is the most time-consuming step in numerical realization of any type of the many-body diagrammatic perturbation theory. For these reasons we turn our attention on another possibility to include the infinite summations of the *diagonal* as well as the *non-diagonal* ladder and ring diagrams. Especially, we attempt to use the Brueckner concept of the renormalized two-particle matrix elements [12–14], originally introduced in microscopic nuclear theory to surmount the difficulties associated with hard-core internuclear potential. In the original formulation [14] of the renormalized two-particle matrix elements only particle-particle elementary intermediate processes were included. We enlarge the original determination of the renormalized matrix elements in such a way that not only particle-particle but also hole-hole and particle-hole elementary processes are taken into account. Such possible generalization has been initially studied by Chisholm and Squires [15] for many-nucleon systems. In their formulation the renormalized two-particle matrix elements are determined by a non-linear diagrammatic expression containing the particle-particle and hole-hole elementary processes, the particle-hole processes are neglected. In the present communication we use the renormalized matrix elements for construction of a "second-order" diagrammatic expression which determines the correlation energy (cf. Eq. (4)). The correlation energy is then determined by an infinite summation of diagrams containing *only bi-excited* intermediate states. In order to affect other diagrams with mono-, three-, ... excited intermediate states it is necessary to introduce the renormalized two-particle vertices in some fourth- or higher-order diagrammatic terms. Of course, such manipulations should be made very carefully, since a straightforward realization of this approach may produce diagrammatic terms which are included more than once.

2. Theory

In the second-quantization representation, when the Hartree-Fock molecular orbitals are used, the full Hamiltonian H of a molecular system can be written as follows [16]:

$$H=\langle\Phi_0|H|\Phi_0\rangle+H_0+H_1, \tag{1a}$$

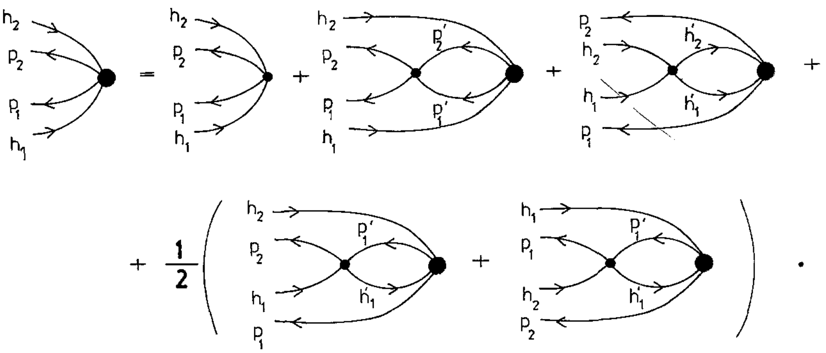
$$H_0=\sum_i \varepsilon_i N[X_i^+X_i], \tag{1b}$$

$$H_1=\tfrac{1}{4}\sum_{ijkl}\langle ij|v|kl\rangle_A N[X_i^+X_j^+X_lX_k], \tag{1c}$$

where the perturbation H_1 is built-up from the antisymmetrized two-particle matrix elements, $\langle ij|v|kl\rangle_A=\langle ij|v|kl\rangle-\langle ij|v|lk\rangle$. Applying the linked-cluster theorem [17, 18], the correlation energy of the molecular system described by H of Eqs. (1a–c) is

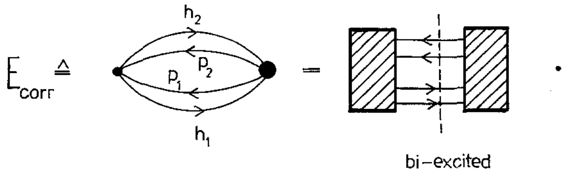
$$E_{\text{corr}}=\sum_{n=1}^{\infty}\langle\Phi_0|H_1\left(\frac{1}{-H_0}H_1\right)^n|\Phi_0\rangle_C, \tag{2}$$

where the subscript C means that only *connected* diagrams contribute. Now, we immediately introduce the generalized renormalized two-particle matrix elements. These matrix elements are the iterated interactions of two electrons in the many-electron medium. Diagrammatically, their defining equation can be presented as follows:



(3)

Here, the first diagram represents the original two-particle vertex, the second diagram represents the elementary particle-particle intermediate "scattering" process, and the third diagram represents a similar hole-hole process. Finally, the last two diagrams represent two distinct particle-hole elementary processes. They are symmetrized in order to ensure the same symmetric properties for the new renormalized two-particle matrix elements as have the original two-particle matrix elements from the perturbation (1c). Using the renormalized matrix elements (3), the correlation energy (2) can be approximated by the following simple diagrammatic expression:



(4)

Then, the correlation energy is approximated by *all* connected diagrams with *only* bi-excited intermediate states (this fact is schematically illustrated by the second diagram in (4)). Therefore, the diagrams with mono-, three, four-, ... excited intermediate states are neglected. From a detailed inspection of (2) it follows that such diagrams are emerging at fourth- and higher-order diagrammatic contributions. Up to the third order the formulae (4) and (2) give identical results for correlation energy.

Algebraic interpretation of (3) and (4) can be done by the use of the Hugeholtz graphology [18]. For simplicity, we shall assume that the given molecule forms the closed-shell many-electron system. The heavy-dot vertices from (3) correspond to antisymmetrized renormalized two-particle matrix elements, $\langle p_1p_2|g|h_1h_2\rangle_A = \langle p_1p_2|g|h_1h_2\rangle - \langle p_1p_2|g|h_2h_1\rangle$. We shall assume, without loss of generality, that $\langle p_1p_2|g|h_1h_2\rangle = \langle p_2p_1|g|h_2h_1\rangle$, and (2) the matrix elements $\langle p_1p_2|g|h_1h_2\rangle$ are spin independent. Using these two assumptions, the spin variables can be simply removed. Then, from (4) we obtain:

$$E_{\mathrm{corr}} \triangleq \sum_{p_1p_2} \sum_{h_1h_2} \frac{(2\langle h_1h_2|v|p_1p_2\rangle - \langle h_1h_2|v|p_2p_1\rangle)\langle p_1p_2|g|h_1h_2\rangle}{\varepsilon_{h_1}+\varepsilon_{h_2}-\varepsilon_{p_1}-\varepsilon_{p_2}}. \tag{5}$$

Analogously, the algebraic interpretation of (3) has the following spin-free form:

$$\begin{aligned}\langle p_1p_2|g|h_1h_2\rangle = \langle p_1p_2|v|h_1h_2\rangle & \\ &+\sum_{p_1'p_2'} \frac{\langle p_1p_2|v|p_1'p_2'\rangle\langle p_1'p_2'|g|h_1h_2\rangle}{\varepsilon_{h_1}+\varepsilon_{h_2}-\varepsilon_{p_1'}-\varepsilon_{p_2'}} \\ &+\sum_{h_1'h_2'} \frac{\langle h_1'h_2'|v|h_1h_2\rangle\langle p_1p_2|g|h_1'h_2'\rangle}{\varepsilon_{h_1'}+\varepsilon_{h_2'}-\varepsilon_{p_1}-\varepsilon_{p_2}} \\ &+\tfrac{1}{2}[z(p_1p_2, h_1h_2)+z(p_2p_1, h_2h_1)],\end{aligned} \tag{6a}$$

$$\begin{aligned}z(p_1p_2, h_1h_2) = &-2\sum_{h_1'p_1'} \frac{\langle h_1'p_2|v|h_1p_1'\rangle\langle p_1p_1'|g|h_1'h_2\rangle}{\varepsilon_{h_1'}+\varepsilon_{h_2}-\varepsilon_{p_1}-\varepsilon_{p_1'}} \\ &-2\sum_{h_1'p_1'} \frac{\langle h_1'p_1|v|p_1'h_1\rangle\langle p_2p_1'|g|h_1'h_2\rangle}{\varepsilon_{h_1'}+\varepsilon_{h_2}-\varepsilon_{p_1'}-\varepsilon_{p_2}} \\ &+4\sum_{h_1'p_1'} \frac{\langle h_1'p_1|v|p_1'h_1\rangle\langle p_1'p_2|g|h_1'h_2\rangle}{\varepsilon_{h_1'}+\varepsilon_{h_2}-\varepsilon_{p_1'}-\varepsilon_{p_2}} \\ &-2\sum_{h_1'p_1'} \frac{\langle h_1'p_1|v|h_1p_1'\rangle\langle p_1'p_2|g|h_1'h_2\rangle}{\varepsilon_{h_1'}+\varepsilon_{h_2}-\varepsilon_{p_1'}-\varepsilon_{p_2}}.\end{aligned} \tag{6b}$$

In all expressions (5) and (6a–b) summation indices run over occupied (h_1', h_2') and unoccupied (p_1', p_2') spinless molecular orbitals, respectively. This system of nonlinear Eqs. (6a–b) can be solved by straightforward iterative scheme: $x_{k+1}=f(x_k)$, which means that the $(k+1)$'th iterative step for a quantity "x" (in our case the renormalized two-particle matrix elements) is calculated from the previous k'th step. The original matrix elements $\langle p_1p_2|v|h_1h_2\rangle$ are a good starting approximation to the renormalized matrix elements $\langle p_1p_2|g|h_1h_2\rangle$, i.e. in the zeroth ($k=0$) iterative step we put $\langle p_1p_2|g|h_1h_2\rangle = \langle p_1p_2|v|h_1h_2\rangle$. The resulting self-consistent renormalized matrix elements from this iterative procedure we shall use in (5) for calculation of the correlation energy.

3. Application and Discussion

In the first part of this section we present the model calculation of the correlation energy carried out for the LiH molecule. Our primary aim was to test the numerical behaviour of a simple iterative scheme suggested in the end of previous section. The LiH molecule Hartree-Fock calculation was performed at the internuclear separation 3.015 a.u. The basis set consists of the following contracted Gaussian atomic orbitals: Li atom – four s orbitals and two p_σ orbitals, H atom – two s orbitals and one p_σ orbital. The orbital exponents and contraction coefficients were taken from Refs. [19] and [20], the orbital exponent of hydrogen p_σ was 0.75. The Hartree-Fock energy for this basis is $E_{\mathrm{HF}} = -7.98250$ a.u. (Hartree-Fock energy limit $= -7.98731$ a.u. [21]). We present in Table 1 the individual perturbation contributions, $E^{(n)}_{\mathrm{corr}}$, for the correlation energy calculated in each iterative step. The first two rows correspond to exact (of course, in the given basis set of Gaussian AO's) second-order, $E^{(2)}_{\mathrm{corr}}$, and third-order, $E^{(3)}_{\mathrm{corr}}$, contributions, respectively. The next higher-order ($n \geqslant 4$) contributions are calculated by further iterative steps ($k \geqslant 2$). For instance, the second iterative step ($k=2$) determines fourth-order contribution, $E^{(4)}_{\mathrm{corr}}$, approximated by all fourth-order connected diagrams containing merely bi-excited intermediate states. The fourth-order diagrams with mono-, three-, and four-excited intermediate states are neglected. For the second-order contribution, $E^{(2)}_{\mathrm{corr}}$, the following breakdown onto individual pairs was obtained: $E^{(2)}_{\mathrm{corr}}(1\text{–}1) = -0.010939$ a.u., $E^{(2)}_{\mathrm{corr}}(1\text{–}2) = -0.000415$ a.u., and $E^{(2)}_{\mathrm{corr}}(2\text{–}2) = -0.013742$ a.u. Similarly, the third-order contribution, $E^{(3)}_{\mathrm{corr}}$, can be uniquely factorized onto quantities corresponding to single terms from (3), i.e. onto particle-particle, hole-hole, and particle-hole terms: $E^{(3)}_{\mathrm{corr}}(p\text{–}p) = 0.005459$ a.u., $E^{(3)}_{\mathrm{corr}}(h\text{–}h) = 0.004999$ a.u., and

Table 1. Individual perturbation contributions for correlation energy

k'th iterative step	n'th order	$E^{(n)}_{\mathrm{corr}}$ (a.u.)
0	2	−0.025096
1	3	−0.005765
2	4	−0.001692
3	5	−0.000601
4	6	−0.000240
5	7	−0.000102
6	8	−0.000045
7	9	−0.000020
8	10	−0.000009
9	11	−0.000004
10	12	−0.000002
11	13	−0.000001
	Total	−0.033577

$E_{\mathrm{corr}}^{(3)}(p\text{-}h) = -0.016223$ a.u. From this simple illustrative example follows that all non-linear terms from the r.h.s. of (3) have, probably, the same importance. Of course, the basis dependence of this conclusion must be further studied. The calculated correlation energy, $E_{\mathrm{corr}}^{\mathrm{cal}} = -0.033677$ a.u., represents about 40.5 % of the experimental correlation energy, $E_{\mathrm{corr}}^{\mathrm{exp}} = -0.083$ a.u. [3]. The basis set of AO's used here is not sufficient to obtain the full correlation energy of LiH molecule. The absence of functions which are able to affect an "angular" correlation energy, e.g. $p_\pi, p_{\bar{\pi}}, d_\pi, \ldots$, in the basis set is probably the source of this difference between the calculated and experimental correlation energy.

Finally, we give a few remarks about theoretical classification of the present method and also its efficiency with respect to other many-body diagrammatic techniques. The concept of the two-particle renormalized interaction can be theoretically established and justified by the technique of Coester and Kümmel [22, 23] (cf. also Refs. [24, 25, 16]). They have derived a coupled system of non-linear equations determining linked cluster amplitudes of the exact ground-state wave function. If we assume that this wave function is approximated only by biexcited unperturbed states, $|\Psi_0\rangle = (1+S_2)|\Phi_0\rangle$, then the matrix elements of the operator S_2 are determined by an equation very similar to our Eqs. (6a–b).

Recently, after completing this work, a similar method as the presented one was published by Bartlett and Silver [26]. We thank the referee for turning our attention to this reference. The final formulae of Bartlett and Silver are constructed from detailed analysis of the third- and higher-order perturbation contributions with 2-particle-2-hole (biexcited) intermediate states. Our approach including the infinite summations of diagrammatic perturbation terms to correlation energy is elaborated from an apparently different standpoint than that of Bartlett and Silver. We started from Brueckner's concept of two-particle renormalized interactions simply defined by a non-linear diagrammatic expression. Such an approach can then be straightforwardly generalized also to other types of higher-order diagrammatic terms than those containing merely biexcited intermediate states.

Infinite summation of diagonal ladders, which is automatically included in the Epstein-Nesbet partitioning of the Hamiltonian, can be criticized for a loss of the invariance to unitary transformations within degenerate sets of one-particle functions [27]. This shortcoming cannot appear in our approach, since both the diagonal and non-diagonal ladders are consequently used. Therefore we still remain in the framework of the Møller-Plesset Hamiltonian.

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References

1. Kelly, H. P.: Advan. Chem. Phys. **14**, 129 (1969)
2. Kaldor, U.: J. Chem. Phys. **62**, 4634 (1975)
3. Bartlett, R. J., Silver, D. M.: Phys. Rev. A **10**, 1927 (1974); **13**, 912 (1976); J. Chem. Phys. **62**, 3258 (1975); **64**, 1260 (1976); **64**, 4578 (1976); Chem. Phys. Letters **29**, 199 (1974); **37**, 198 (1976)

4. Silver, D. M., Bartlett, R. J.: Phys. Rev. A **13**, 1 (1976)
5. Freeman, D. L., Karplus, M.: J. Chem. Phys. **64**, 2641 (1976)
6. Kelly, H. P.: Phys. Rev. **131**, 384 (1963)
7. Nesbet, R. K.: Advan. Chem. Phys. **9**, 321 (1965)
8. Diner, S., Malrieu, J., Claverie, P.: Theoret. Chim. Acta (Berl.) **8**, 390 (1967)
9. Freed, K. F.: Phys. Rev. **173**, 1 (1968); Chem. Phys. Letters **4**, 416 (1970)
10. Mukhopadhyay, A., Moitra, R. K., Mukerjee, D.: Intern. J. Quantum Chem. **9**, 545 (1975)
11. Kvasnička, V.: Chem. Phys. Letters **43**, 377 (1976)
12. Brueckner, K. A., Levinson, C. A.: Phys. Rev. **97**, 1344 (1955)
13. Bethe, H. A.: Phys. Rev. **103**, 1353 (1956)
14. Day, B. D.: Rev. Mod. Phys. **39**, 719 (1967)
15. Chisholm, J. S. R., Squires, E. J.: Nucl. Phys. **13**, 156 (1959)
16. Čížek, J.: J. Chem. Phys. **45**, 4256 (1966); Advan. Chem. Phys. **14**, 35 (1969); Paldus, J., Čížek, J.: Advan. Quantum Chem. **9**, 106 (1975)
17. Goldstone, J.: Proc. Roy. Soc. London **A239**, 267 (1957)
18. Hugenholtz, N. M.: Physica **23**, 481 (1957)
19. Pearson, P. K., Hunt, W. J., Bender, C. F., Schaefer III, H. F.: J. Chem. Phys. **58**, 5358 (1973)
20. Dunning, T. H.: J. Chem. Phys. **53**, 2823 (1970)
21. Cade, P. E., Huo, W. M.: J. Chem. Phys. **47**, 614 (1967)
22. Coester, F., Kümmel, H.: Nucl. Phys. **17**, 477 (1960)
23. Coester, F.: Nucl. Phys. **7**, 421 (1958)
24. Da Providencia, J.: Nucl. Phys. **61**, 87 (1965)
25. Kümmel, H.: Nucl. Phys. **A176**, 205 (1971)
26. Bartlett, R. J., Silver, D. M., in: Quantum science, Calais, J. L., Goscinski, O., Linderberg, J., Öhrn, Y. Eds. New York: Plenum Press 1976
27. Ostlund, N. S., Bowen, M. F.: Theoret. Chim. Acta (Berl.) **40**, 175 (1976)

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