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On the Correlation Problem in Atomic and Molecular Systems. Calculation of Wavefunction Components in Ursell-Type Expansion Using Quantum-Field Theoretical Methods

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A method is suggested for the calculation of the matrix elements of the logarithm of an operator which gives the exact wavefunction when operating on the wavefunction in the one-electron approximation. The method is based on the use of the creation and annihilation operators, hole-particle formalism, Wick's theorem, and the technique of Feynman-like diagrams. The connection of this method with the configuration-interaction method as well as with the perturbation theory in the quantum-field theoretical form is discussed. The method is applied to the simple models of nitrogen and benzene molecules. The results are compared with those obtained with the configuration-interaction method considering all possible configurations within the chosen basis of one-electron functions.

I. FORMULATION OF THE PROBLEM

LET us consider a system consisting of fixed atomic nuclei and $2n$ electrons. Let us further exclude from our considerations systems having a degenerate ground state. Then, neglecting relativistic and magnetic effects, the Hamiltonian \hat{H} of our problem is given by the following equations:

$$\hat{H} = \hat{Z} + \hat{V}, \quad (1)$$

$$\hat{Z} = \sum_i \hat{z}_i, \quad \hat{V} = \sum_{i < j} \hat{v}_{i,j}, \quad (2)$$

where \hat{z}_i is a one-particle operator corresponding to the sum of the kinetic and nuclear field energy, and $\hat{v}_{i,j}$ is a two-particle operator of the interelectronic Coulombic repulsion.

Our problem is to find the ground-state eigenvector and the corresponding eigenvalue of the Hamiltonian (1)

$$\hat{H} |\Psi\rangle = E |\Psi\rangle. \quad (3)$$

In order to solve this problem the wavefunction $|\Psi\rangle$ is written in the following form

$$|\Psi\rangle = \exp(\hat{T}) |\Phi\rangle, \quad (4)$$

where $|\Phi\rangle$ is the ground-state wavefunction in the one-particle approximation. This form of the wavefunction¹⁻⁵ is connected with the so-called Ursell-type expansion. The use of an expansion of this type for the study of the electronic structure of atoms and molecules was suggested by Sinanoğlu.³

In this article, equations for the matrix elements of the operator \hat{T} are derived using quantum-field

theoretical concepts, namely, (1) the creation and annihilation operators, (2) the hole-particle formalism, (3) the time-independent Wick theorem and the diagram technique.

In addition, the connection of the proposed method with both the configuration-interaction method and the perturbation theory in the quantum-field theoretical form^{6,7} are shown. This comparison demonstrates the usefulness of the Ursell-type expansion of the exact wavefunction.

II. BASIC TERMS AND DEFINITIONS

Let us introduce a complete set of orthonormal spin-orbitals

$$|A\rangle = |a\rangle |\alpha\rangle, \quad (5)$$

where $|a\rangle$ and $|\alpha\rangle$ designate the space and the spin parts of the spin-orbital $|A\rangle$, respectively. Generally, capital letters are used to designate spin-orbitals, lower-case letters are associated with orbitals, while letters of the Greek alphabet are reserved for spin functions. In addition to this general system of spin-orbitals (5), we use spin-orbitals whose space parts are eigenfunctions of the operator

$$(\hat{z} + \hat{u}) |a\rangle = \omega_a |a\rangle, \quad (6)$$

where \hat{u} is an arbitrary spin-independent one-particle Hermitian operator. Let us note explicitly that Hartree-Fock spin-orbitals fall within this class.

The creation and annihilation operators defined on the system of spin-orbitals (5) are designated \hat{X}_A^+ and \hat{X}_A , respectively. These operators satisfy the following anticommutation relations:

$$\begin{aligned} \hat{X}_A^+ \hat{X}_B^+ + \hat{X}_B^+ \hat{X}_A^+ &= 0, \\ X_A \hat{X}_B + \hat{X}_B X_A &= 0, \\ \hat{X}_A^+ \hat{X}_B + \hat{X}_B \hat{X}_A^+ &= \langle A | B \rangle. \end{aligned} \quad (7)$$

⁶ J. Goldstone, Proc. Roy. Soc. (London) **239**, 267 (1957).

⁷ V. V. Tolmachev, "The field form of the perturbation theory applied to many electron problems of atoms and molecules," University of Tartu, 1963 (in Russian).

* Part of this study was carried out during the author's stay in the Centre de Mécanique Ondulatoire Appliquée, Paris, France.

¹ F. Coester and H. Kümmel, Nucl. Phys. **17**, 477 (1960).
² H. Kümmel, *Lectures on The Many-Body Problem*, E. R. Caioniello, Ed. (Academic Press Inc., New York, 1962), p. 265.

³ O. Sinanoğlu, J. Chem. Phys. **36**, 706 (1962); Advan. Chem. Phys. **6**, 315 (1964).

⁴ H. Primas, Lecture prepared for the Istanbul International Summer School of Quantum Chemistry, 1964 (preprint).

⁵ J. da Providencia, Nucl. Phys. **61**, 87 (1965).

The operators \hat{Z} and \hat{V} may then be expressed through the operators \hat{X}_A^+ and \hat{X}_A in the following form:

$$\hat{Z} = \sum_{C_1, B_1} \langle C_1 | \hat{z} | B_1 \rangle \hat{X}_{C_1}^+ \hat{X}_{B_1}, \quad (8)$$

$$\hat{V} = \frac{1}{2} \sum_{C_1, B_1; C_2, B_2} \langle C_1 C_2 | \hat{v} | B_1 B_2 \rangle \hat{X}_{C_1}^+ \hat{X}_{C_2}^+ \hat{X}_{B_2} \hat{X}_{B_1}. \quad (9)$$

The matrix elements in Formulas (8) and (9) satisfy the following relations:

$$\langle C_1 C_2 | \hat{v} | B_1 B_2 \rangle = \langle c_1 c_2 | \hat{v} | b_1 b_2 \rangle \langle \gamma_1 | \beta_1 \rangle \langle \gamma_2 | \beta_2 \rangle, \quad (10)$$

$$\langle C_1 | \hat{z} | B_1 \rangle = \langle c_1 | \hat{z} | b_1 \rangle \langle \gamma_1 | \beta_1 \rangle, \quad (11)$$

using the notation introduced in Eq. (5).

The symbol $|0\rangle$ is used to specify the "vacuum state."

Let us suppose that in the complete set of spin-orbitals introduced above there exist $2n$ spin-orbitals

$$|A_1'\rangle, |A_2'\rangle, \dots, |A_{2n}'\rangle, \quad (12)$$

such that the function

$$|\Phi\rangle = \hat{X}_{A_1'}^+ \hat{X}_{A_2'}^+ \dots \hat{X}_{A_{2n}'}^+ |0\rangle \quad (13)$$

is a reasonable approximation to the exact ground-state wavefunction $|\Psi\rangle$. Since we require the ground state to be nondegenerate, the spin-orbitals (12) may be formed as products of the following n orbitals:

$$|a_1'\rangle, |a_2'\rangle, \dots, |a_n'\rangle, \quad (14)$$

with spin functions corresponding to the positive and negative spin orientations, respectively. The spin-orbitals (12) which span the function $|\Phi\rangle$ are called nonexcited ones while all others, which do not enter the function $|\Phi\rangle$, are called excited spin-orbitals. The nonexcited and excited spin-orbitals are systematically designated by singly and doubly primed capitals, respectively.

In the following considerations it is useful to regard the ground state $|\Phi\rangle$ as a "new vacuum state" as well as to interpret the excitation of a particle as creation of a hole in a nonexcited spin-orbital followed by the creation of a particle in an excited spin-orbital. For this purpose a new set of operators is introduced by the following relations:

$$\begin{aligned} \hat{Y}_{A'}^+ &= \hat{X}_{A'}^+, & \hat{Y}_{A''} &= \hat{X}_{A''}, \\ \hat{Y}_{A'} &= \hat{X}_{A'}^-, & \hat{Y}_{A''}^+ &= \hat{X}_{A''}^+. \end{aligned} \quad (15)$$

The operator $\hat{Y}_{A'}^+$ may now be interpreted as a hole-creating operator while the operator $\hat{Y}_{A'}$ as a hole-annihilating operator. Formal analogy of this approach with quantum electrodynamics is apparent: An electron corresponds to a particle in an excited spin-orbital while a positron corresponds to a hole in a nonexcited spin-orbital.

In the following considerations the terms creation and annihilation operators are associated with the

operators $\hat{Y}_{A'}^+$ and $\hat{Y}_{A'}$, respectively. These operators satisfy the same anticommutation relations as the operators $\hat{X}_{A'}^+$, $\hat{X}_{A'}$.

The operator \hat{T} introduced above may be expressed through the operators $\hat{Y}_{A'}^+$, $\hat{Y}_{A'}$ in the following form:

$$\hat{T} = \sum_{j=1}^{2n} \hat{T}_j, \quad (16)$$

where

$$\begin{aligned} \hat{T}_j = \frac{1}{j!} \sum_{\substack{A_j'', \dots, A_1'' \\ A_j', \dots, A_1'}} \langle A_j'' \dots A_1'' | \hat{t} | A_j' \dots A_1' \rangle \\ \times \prod_{i=1}^j \hat{Y}_{A_i''}^+ \hat{Y}_{A_i'} \end{aligned} \quad (17)$$

represents an operator of the j -times excited state.⁸

In the following section we have to evaluate the products of operators of the type

$$\hat{M}_1 \hat{M}_2 \dots \hat{M}_l, \quad (18)$$

where \hat{M}_i , $i=1, 2, \dots, l$ is either a creation or an annihilation operator. These products of operators are most easily treated with the aid of Wick's theorem. In order to state the theorem we introduce some necessary notions.⁹

The normal product $N[\hat{M}_1 \dots \hat{M}_l]$ of the operators $\hat{M}_1, \dots, \hat{M}_l$ is defined by the relation:

$$N[\hat{M}_1 \dots \hat{M}_l] = (-1)^p \hat{M}_{k_1} \hat{M}_{k_2} \dots \hat{M}_{k_l}, \quad (19)$$

where the permutation of indices

$$\begin{pmatrix} 1, 2, \dots, l \\ k_1, k_2, \dots, k_l \end{pmatrix} \quad (20)$$

is so chosen that in the product on the right-hand side of Eq. (19) all annihilation operators stand to the right of all the creation operators. The parity of the permutation (20) is designated by p .

Next we define the pairing $\hat{M}_1 \hat{M}_2$ of two operators \hat{M}_1 and \hat{M}_2 :

$$\hat{M}_1 \hat{M}_2 = \hat{M}_1 \hat{M}_2 - N[\hat{M}_1 \hat{M}_2]. \quad (21)$$

The notation $\hat{M}_1 \hat{M}_2 = \hat{M}_1 \hat{M}_2$ etc. is also used for pairing.¹⁰ Using the anticommutation relations (7) we immediately obtain explicit expressions for all possible pairings of two operators:

$$\begin{aligned} \hat{Y}_{A'}^+ \hat{Y}_{B'}^+ &= \hat{Y}_{A'}^+ \hat{Y}_{B'}^+ = \hat{Y}_{A'}^+ \hat{Y}_{B'}^+ = 0, \\ \hat{Y}_{A'} \hat{Y}_{B'}^+ &= \langle A | B \rangle. \end{aligned}$$

⁸ The following part of this chapter until Eq. (25) may be skipped by readers familiar with the mathematical methods of quantum-field theory.

⁹ S. S. Schweber, *An Introduction to Relativistic Quantum Field Theory* (Row, Peterson and Co., Evanston, Ill., 1961).

¹⁰ This notation is used for typographical reasons.

Further, we have to define the normal product with pairings

$$N[\hat{M}_1 \dots \hat{M}_{i_1} \dots \hat{M}_{i_2} \dots \hat{M}_{j_1} \dots \hat{M}_{j_2} \dots \hat{M}_{i_k} \dots \hat{M}_{j_k} \dots \hat{M}_l] \\ = (-1)^p (\hat{M}_{i_1} \hat{M}_{j_1}) (\hat{M}_{i_2} \hat{M}_{j_2}) \dots (\hat{M}_{i_k} \hat{M}_{j_k}) [NM_{m_1} \dots M_{m_r}]_1, \quad (22)$$

where k is the number of pairings, $r = l - 2k$, and p is the parity of the permutation

$$\begin{pmatrix} 1, 2, \dots, 2k, 2k+1, \dots, l \\ i_1, j_1, \dots, j_k, m_1, \dots, m_r \end{pmatrix}. \quad (23)$$

Now we are ready to state Wick's theorem:

The product of several creation and annihilation operators is equal to the sum of all normal products of these operators with all possible pairings (including no pairing):

$$M_1 \dots \hat{M}_l = N[\hat{M}_1 \dots \hat{M}_l] + N[\hat{M}_1 \hat{M}_2 \dots \hat{M}_l] + \dots + N[\hat{M}_1 \dots \hat{M}_l] + N[\hat{M}_1 \hat{M}_2 \dots \hat{M}_l] + \dots \quad (24)$$

Furthermore, we use the generalized form of Wick's theorem⁹ which states the following.

The product of normal products of operators

$$N[\hat{M}_1 \dots \hat{M}_{i_1}] N[\hat{M}_{i_1+1} \dots \hat{M}_{i_2}] \dots N[\dots \hat{M}_l] \quad (25)$$

may be expressed similarly as the ordinary product of operators (18) but with the omission of pairings between operators within each normal product of the expression (25).

Using Wick's theorem the operator $\hat{H} = \hat{Z} + \hat{V}$ may be written in the form

$$\hat{H} - \langle \Phi | \hat{H} | \Phi \rangle = \sum_{C_1, B_1} \langle C_1 | \hat{f} | B_1 \rangle N[\hat{X}_{C_1} + \hat{X}_{B_1}] + \frac{1}{2} \sum_{C_1, B_1; C_2, B_2} \langle C_1 C_2 | \hat{v} | B_1 B_2 \rangle N[\hat{X}_{C_1} + \hat{X}_{C_2} + \hat{X}_{B_2} + \hat{X}_{B_1}], \quad (26)$$

where

$$\langle C_1 | \hat{f} | B_1 \rangle = \langle C_1 | \hat{z} | B_1 \rangle + \sum_{A'} (\langle C_1 A' | \hat{v} | B_1 A' \rangle - \langle C_1 A' | \hat{v} | A' B_1 \rangle). \quad (27)$$

The matrix element (27) satisfies the relation

$$\langle C_1 | \hat{f} | B_1 \rangle = \langle c_1 | \hat{f} | b_1 \rangle \langle \gamma_1 | \beta_1 \rangle, \quad (28)$$

where

$$\langle c_1 | \hat{f} | b_1 \rangle = \langle c_1 | \hat{z} | b_1 \rangle + \sum_{a'} (2 \langle c_1 a' | \hat{v} | b_1 a' \rangle - \langle c_1 a' | \hat{v} | a' b_1 \rangle). \quad (29)$$

III. SYSTEM OF EQUATIONS FOR MATRIX ELEMENTS OF THE OPERATOR \hat{T}

Considerations of a topological character are used extensively in this section. Before proceeding it is necessary to introduce a few definitions. A topological formation consisting of dashed nonoriented lines, full lines both oriented and nonoriented, and vertices are called a skeleton.

Two skeletons are said to be equivalent if they can be mutually transformed into each other through topological deformations.

The topological deformation converting a given skeleton into itself is called an automorphism. The weight of a skeleton is the reciprocal value of the number of all different automorphisms (including the identical one) of a given skeleton.

Furthermore, the two oriented full lines of a skeleton are considered to be equivalent if there exists an automorphism transferring these lines one into the other.

In the following considerations we define four different types of skeletons, namely the H , T , M , and R skeletons. Nonequivalent skeletons of a given type are

distinguished by their arguments

$$S_H(h), S_T(t), S_M(m), S_R(r).$$

Therefore, equivalent skeletons are denoted by identical symbols. The respective weights are designated by

$$w_H(h), w_T(t), w_M(m), w_R(r).$$

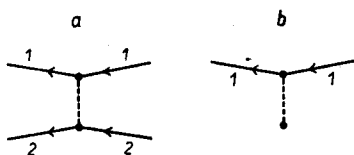
Further, let a positive integer be associated with any full oriented line in such a way that the following rules are respected:

(a) Equivalent lines carry different integers.

(b) Let us have two equivalent skeletons. Then a topological deformation exists, which transfers the skeletons into each other in such a way that the mutually corresponding full oriented lines in both skeletons carry the same integers.

Therefore, the possibility that different lines are labeled by the same integer is not excluded.

The H skeletons are those shown in Fig. 1. The left skeleton in Fig. 1 is designated $S_H(1)$, the right one $S_H(2)$. The assumed numbering of lines is shown as

FIG. 1. (a) $S_H(1)$ skeleton, (b) $S_H(2)$ skeleton.

well. The weights associated with the skeletons of Fig. 1 are

$$w_H(1) = \frac{1}{2}, \quad w_H(2) = 1. \quad (30)$$

On labeling the oriented lines of an H skeleton with spin-orbital indices we obtain a so-called H diagram. These diagrams are shown in Fig. 2.

To the left diagram of Fig. 2 we assign the following scalar quantity:

$$d_H(1, \chi) = \langle C_1 C_2 | \hat{v} | B_1 B_2 \rangle, \quad (31)$$

as well as the following operator:

$$\hat{D}_H(1, \chi) = d_H(1, \chi) N[\hat{X}_{C_1} + \hat{X}_{C_2} + \hat{X}_{B_1} + \hat{X}_{B_2}], \quad (32)$$

where χ represents the sequence of numbers C_1, C_2, B_1, B_2 .

Similarly, to the right diagram of Fig. 2 the scalar quantity

$$d_H(2, \chi) = \langle C_1 | \hat{f} | B_1 \rangle \quad (33)$$

and the operator

$$\hat{D}_H(2, \chi) = d_H(2, \chi) N[\hat{X}_{C_1} + \hat{X}_{B_1}] \quad (34)$$

are assigned. Here χ represents the numbers C_1 and B_1 .

Further, to the oriented line labeled $B_i(C_i)$ and entering (leaving) the vertex of the H diagram the operator $\hat{X}_{B_i}(\hat{X}_{C_i}^+)$ is assigned ($i=1, 2$).

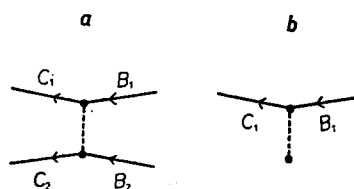
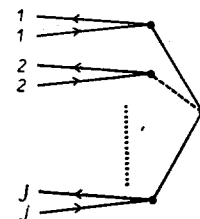
Consequently, Eq. (26) may be written in the following form:

$$\hat{H} - \langle \Phi | \hat{H} | \Phi \rangle = \sum_{h=1}^2 w_H(h) \sum_{\chi} \hat{D}_H(h, \chi). \quad (35)$$

A general T -type skeleton as well as the labeling of its oriented lines are shown in Fig. 3. These skeletons differ in the number of pairs of oriented lines, so that the index j may be any positive integer. The skeletons are generally designated $S_T(j)$. The weight of the $S_T(j)$ skeleton is given by the relation

$$w_T(j) = 1/j!. \quad (36)$$

On labeling the oriented lines entering (leaving) the vertices of the T skeleton by the indices of nonexcited

FIG. 2. (a) Diagram formed from the $S_H(1)$ skeleton, (b) diagram formed from the $S_H(2)$ skeleton.FIG. 3. A general $S_T(j)$ skeleton,

(excited) spin-orbitals we obtain the T diagram shown in Fig. 4.

We assign to the T diagram the following scalar quantity

$$d_T(j, \tau) = \langle A_1'' \dots A_j'' | \hat{t} | A_1' \dots A_j' \rangle \quad (37)$$

and the operator

$$\hat{D}_T(j, \tau) = d_T(j, \tau) \prod_{i=1}^j \hat{Y}_{A_i', +} \hat{Y}_{A_i'', +}, \quad (38)$$

where τ represents the sequence of numbers

$$A_1'', A_1', A_2'', A_2', \dots, A_j'', A_j'. \quad (39)$$

Furthermore, we attach the operator $\hat{Y}_{A_i', +}(\hat{Y}_{A_i'', +})$ to every oriented line labeled $A_i'(A_i'')$ and entering (leaving) some vertex of the T diagram.

Using the notation specified above, the operator \hat{T} may be expressed in the form

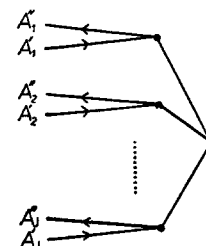
$$\hat{T} = \sum_{t=1}^{2n} w_T(t) \sum_{\tau} \hat{D}_T(t, \tau). \quad (40)$$

A set of T skeletons are called an M skeleton. Generally, an M skeleton is composed of n_1 skeletons $S_T(t_1)$, n_2 skeletons $S_T(t_2)$, etc. The M skeletons are designated $S_M(m)$, where m represents a sequence of indices t_i of the T skeletons involved, the order of the individual indices being immaterial. Among the M skeletons we also include the so-called empty M skeleton consisting of any empty set of T skeletons.

The weight of an M skeleton is given by the formula¹¹

$$w_M(m) = \left(\prod_{i=1}^k n_i! \right)^{-1} \prod_{i=1}^k [w_T(t_i)]^{n_i}. \quad (41)$$

The weight of the empty M skeleton is equal to a unit by definition.

FIG. 4. The diagram formed from the skeleton $S_T(j)$ of Fig. 3.

¹¹ J. Hubbard, Proc. Roy. Soc. (London) **240**, 539 (1957).

On labeling the oriented lines of an M skeleton with spin-orbital indices in the same way as specified for a T skeleton we obtain the so-called M diagram. Therefore, an M diagram is composed of a certain number of T diagrams.

A scalar quantity $d_M(m, \mu)$ and an operator $\hat{D}_M(m, \mu)$ associated with an M diagram are given by the products of the corresponding quantities assigned to the T diagram constituting a given M diagram (unity and the unit operator are assigned to an empty M diagram by definition). Further, μ specifies the sequence of spin-orbital indices assigned to the oriented lines of an M diagram.

We can write now⁹

$$e^{\hat{T}} = \sum_m w_M(m) \sum_{\mu} \hat{D}_M(m, \mu). \quad (42)$$

Next we have to evaluate the following vector

$$(\hat{H} - \langle \Phi | \hat{H} | \Phi \rangle) e^{\hat{T}} | \Phi \rangle = \sum_h \sum_m w_H(h) w_M(m) \times \sum_{\chi} \sum_{\mu} \hat{D}_H(h, \chi) \hat{D}_M(m, \mu) | \Phi \rangle. \quad (43)$$

This is most easily done using an auxiliary theorem, the proof of which, based on the generalized Wick theorem, is given in the Appendix. In order to state the theorem we introduce the notion of R skeletons and R diagrams.

An R skeleton is formed from one H and one M skeleton by connecting some lines (none, one, or two) entering the vertices of the H skeleton with lines issuing from the vertices of the M skeleton and, further, by connecting some lines (none, one, or two) issuing from the vertices of the H skeleton with lines entering the vertices of the M skeleton. The lines connecting the vertices of the H and M skeletons are called internal lines. All other lines are called external. The internal hole lines of the R skeleton are those which start from a vertex of the H skeleton and enter a vertex of the M skeleton. The internal lines having opposite directions, that is, starting at a vertex of the M skeleton and entering a vertex of the H skeleton, are called internal particle lines.

Furthermore, the external hole (particle) lines are those external lines which enter (leave) a vertex of the M or H skeletons. A sequence of oriented lines are generally referred to as the path. A closed path is called the loop. We number the lines of an R skeleton independently of the numberings of the corresponding M and H skeletons in the following manner.

Let the R skeleton considered contain j open paths, h internal hole lines, and k internal particle lines. We number the external hole lines $1, 2, \dots, j$ and the internal hole lines $j+1, \dots, j+h$. Similarly, the external particle lines will be numbered $1, \dots, j$ and the internal particle lines $j+1, \dots, j+k$. The numbering of the external lines is carried out in such a way that the external particle and hole lines associated with the same path have the same number.

By labeling the i th particle (hole) line of the R skeleton with the index of an excited (nonexcited) spin-orbital $D_i''(D_i')$ we obtain the R diagram.

On dissecting the internal lines of the R diagram we obtain the H and M diagrams. Let the $d_H(h, \chi)$ and $d_M(m, \mu)$ be scalar quantities associated with these H and M diagrams. Then the scalar quantity $d_R(r, \rho)$ assigned to this diagram is given by the expression

$$d_R(r, \rho) = (-1)^{l+h} d_H(h, \chi) d_M(m, \mu), \quad (44)$$

where l is the number of loops, h is the number of internal hole lines, and ρ represents the following two sequences ρ_1, ρ_2 :

$$\begin{aligned} \rho_1 &\equiv D_1'', D_1', D_2'', D_2' \dots D_j'', D_j', \\ \rho_2 &\equiv D_{j+1}'' \dots D_{j+k}'', D_{j+1}' \dots D_{j+k}'. \end{aligned} \quad (45)$$

For diagrams lacking external lines we write

$$d_R(r, \rho) = d_R(r, \rho_2). \quad (46)$$

The operator associated with an R diagram is given by the following equation:

$$\hat{D}_R(r, \rho) = d_R(r, \rho) \prod_{i=1}^j \hat{Y}_{D_i''} + \hat{Y}_{D_i'} +. \quad (47)$$

Again, for diagrams having only internal lines we write

$$\hat{D}(r, \rho) = d(r, \rho_2). \quad (48)$$

We are now ready to state the above-mentioned auxiliary theorem:

$$\begin{aligned} w_H(h) w_M(m) \sum_{\chi} \sum_{\mu} \hat{D}_H(h, \chi) \hat{D}_M(m, \mu) | \Phi \rangle \\ = \sum_r {}'w_R(r) \sum_{\rho} \hat{D}_R(r, \rho) | \Phi \rangle, \end{aligned} \quad (49)$$

where $\sum_r {}'$ designates the summation over all topologically distinct R skeletons which may be formed from $H(h)$ and $M(m)$ skeletons.

The Schrödinger equation may now be given the following form:

$$\sum_r w_R(r) \sum_{\rho} \hat{D}_R(r, \rho) | \Phi \rangle = (E - \langle \Phi | \hat{H} | \Phi \rangle) e^{\hat{T}} | \Phi \rangle, \quad (50)$$

where the summation extends over all topologically distinct R skeletons formed from arbitrary H and M skeletons.

We distinguish connected and disconnected R skeletons. In a connected R skeleton any two vertices are connected by at least one sequence of lines consisting of full oriented and nonoriented and dashed lines. A disconnected R skeleton is composed of a connected R skeleton and an M skeleton. The weight of the disconnected skeleton is given by the product of the weights of the connected R skeleton and the M skeleton which constitute the given R skeleton. The scalar quantities and operators assigned to disconnected R

diagram in an analogous manner are obtained. On the basis of the above considerations, the Schrödinger equation may be rewritten in the form

$$e^{\hat{T}} \left[\sum_{r \in \Delta} w_R(r) \sum_{\rho} \hat{D}_R(r, \rho) - (E - \langle \Phi | \hat{H} | \Phi \rangle) \right] | \Phi \rangle = 0, \quad (51)$$

where Δ is a set of connected R skeletons.

Equation (51) will be satisfied if the following equations hold:

$$\sum_{r \in \Delta_0} w_R(r) \sum_{\rho_2} d_R(r, \rho_2) = E - \langle \Phi | \hat{H} | \Phi \rangle, \quad (52)$$

$$\sum_{r \in \Delta_j} w_R(r) \sum_{\rho_1 \in \theta} \sum_{\rho_2} d_R(r, \rho_1, \rho_2) = 0, \quad (53)$$

where Δ_j is a set of R skeletons having j open paths. The sets θ are formed in accordance with the following rule: If the sequence

$$D_1'', D_1' \dots D_j'', D_j'$$

belongs to θ , then also the sequence

$$D_{k_1}'', D_{k_1}' \dots D_{k_j}'', D_{k_j}'$$

where

$$\begin{pmatrix} 1, \dots, j \\ k_1, \dots, k_j \end{pmatrix}$$

is an arbitrary permutation of indices $1 \dots j$.

We further specify the form of the equations (53) for the case, that the spin orbitals are eigenfunctions of the operator $(\hat{z} + \hat{u})$. In this case the system of Eqs. (53) has the following form:

$$\sum_{i=1}^j (\omega_{D_i''} - \omega_{D_i'}) \langle D_1'' \dots D_j'' | \hat{t} | D_1' \dots D_j' \rangle + \sum_{r \in \Delta_j} w_R(r) \sum_{\rho_1 \in \theta} \sum_{\rho_2} \tilde{d}_R(r, \rho_1, \rho_2) = 0, \quad (54)$$

where the indices $D_1'', D_1' \dots D_j'', D_j'$ form one of the sequences belonging to θ . Further, the tilde above \tilde{d}_R indicates that the following scalar quantity is associated with the right diagram of Fig. 2:

$$\begin{aligned} \langle C_1 | \hat{q} | B_1 \rangle &= \langle C_1 | \hat{f} | B_1 \rangle - \langle C_1 | \hat{z} + \hat{u} | B_1 \rangle \\ &= \sum_{A'} (\langle C_1 A' | \hat{v} | B_1 A' \rangle \\ &\quad - \langle C_1 A' | \hat{v} | A' B_1 \rangle - \langle C_1 | \hat{u} | B_1 \rangle) \end{aligned} \quad (55)$$

instead of the scalar quantity (33).

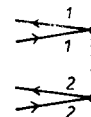
The matrix elements $\langle B_1 | \hat{q} | C_1 \rangle$ are identically equal to zero for Hartree-Fock spin orbitals, as follows immediately from Eq. (55).

In the following considerations the summation over

FIG. 5. R skeletons lacking external lines formed from the $S_H(1)$ and $S_T(2)$ skeletons.



FIG. 6. The R skeleton having two open paths formed from the $S_H(1)$ skeleton and the empty M skeleton.



the spin parts is carried out. It immediately follows from Eqs. (10) and (11) that a nonzero scalar quantity is assigned only to such H diagrams having the same spin along each path. Thus, the relation

$$\langle D_1'' \dots D_j'' | \hat{t} | D_1' \dots D_j' \rangle = \langle d_1'' \dots d_j'' | \hat{t} | d_1' \dots d_j' \rangle \times \prod_{i=1}^j \langle \delta_i'' | \delta_i' \rangle \quad (56)$$

for the matrix elements over spin-orbitals is obtained, so that the equations (53) may be easily transformed into equations for the matrix elements over the orbitals $\langle d_1'' \dots d_j'' | \hat{t} | d_1' \dots d_j' \rangle$.

The equations for the matrix elements over orbitals are then obtained in a similar way as Eq. (53) except that: (a) spin-orbital indices are replaced by orbital indices and (b) the multiplicative factor 2 is assigned to each loop.

The requirement (b) expressed the fact that both spin orientations are allowed along any loop. In order to illustrate the general formalism presented above we write down explicitly the system of equations (53) for the case where all components of the operator T except T_2 are disregarded. This approximation is discussed from the physical point of view in the following section.

In this special case, the M skeletons consist of a set of T skeleton (the empty set being included) each of which has two open paths. The possible R skeletons, having none or two open paths, which can be obtained from these M skeletons are shown in Figs. 5-8. The skeletons shown in Fig. 5 do not have any external lines while those in Figs. 6-8 have always two open paths. Figure 6 shows the R skeleton resulting from the empty M skeleton. Figures 7 and 8 present the R skeletons constructed from the M skeletons consisting of one and two T skeletons, respectively.

The energy difference $E - \langle \Phi | \hat{H} | \Phi \rangle$ may now be expressed through the matrix elements over the spin orbitals or the orbitals as follows:

$$\begin{aligned} E - \langle \Phi | \hat{H} | \Phi \rangle &= \frac{1}{2} \sum_{D_1', D_2'; D_1'', D_2''} \langle D_1' D_2' | \hat{v} | D_1'' D_2'' \rangle \\ &\times (\langle D_1'' D_2'' | \hat{t} | D_1' D_2' \rangle - \langle D_1'' D_2'' | \hat{t} | D_2' D_1' \rangle), \end{aligned} \quad (57)$$

$$\begin{aligned} E - \langle \Phi | \hat{H} | \Phi \rangle &= \sum_{d_1', d_2'; d_1'', d_2''} \langle d_1' d_2' | \hat{v} | d_1'' d_2'' \rangle \\ &\times (2 \langle d_1'' d_2'' | \hat{t} | d_1' d_2' \rangle - \langle d_1'' d_2'' | \hat{t} | d_2' d_1' \rangle). \end{aligned} \quad (58)$$

We now present the corresponding algebraic equations for the matrix elements over the orbitals only.

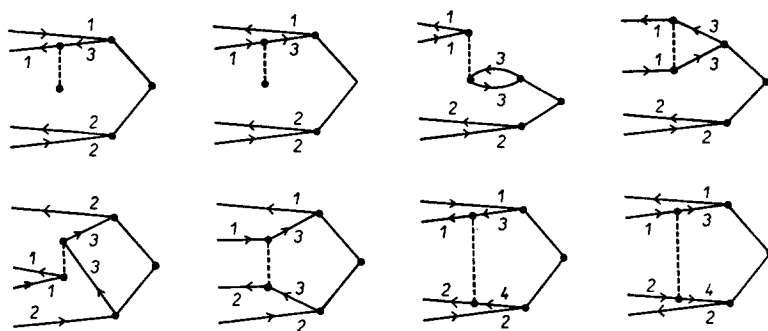


FIG. 7. All possible R skeletons having two open paths formed from the $S_H(1)$ or $S_H(2)$ skeleton and from the M skeleton consisting of one $S_T(2)$ skeleton.

Let us define a new quantity $\lambda(d_1'', d_1'; d_2'', d_2')$ by the following equation:

$$\begin{aligned} \lambda(d_1'', d_1'; d_2'', d_2') = & \frac{1}{2} \langle d_1'' d_2'' | \hat{v} | d_1' d_2' \rangle + \sum_{d_3''} \langle d_1'' | \hat{f} | d_3'' \rangle \langle d_3'' d_2'' | \hat{t} | d_1' d_2' \rangle \\ & - \sum_{d_3'} \langle d_1' | \hat{f} | d_3' \rangle \langle d_1'' d_2'' | \hat{t} | d_3' d_2' \rangle + \sum_{d_3', d_3''} [2 \langle d_1'' d_3' | \hat{v} | d_1' d_3'' \rangle - \langle d_1'' d_3' | \hat{v} | d_3'' d_1' \rangle] \langle d_3'' d_2'' | \hat{t} | d_3' d_2' \rangle \\ & - \langle d_1'' d_3' | \hat{v} | d_1' d_3'' \rangle \langle d_2'' d_3'' | \hat{t} | d_3' d_2' \rangle - \langle d_2'' d_3' | \hat{v} | d_3'' d_1' \rangle \langle d_1'' d_3'' | \hat{t} | d_3' d_2' \rangle \\ & + \frac{1}{2} \sum_{d_3'', d_4''} \langle d_1'' d_2'' | \hat{v} | d_3'' d_4'' \rangle \langle d_3'' d_4'' | \hat{t} | d_1' d_2' \rangle + \frac{1}{2} \sum_{d_3', d_4'} \langle d_1' d_2' | \hat{v} | d_3' d_4' \rangle \langle d_1'' d_2'' | \hat{t} | d_3' d_4' \rangle \\ & + \sum_{d_3', d_4'; d_3'', d_4''} \{ [2 \langle d_3' d_4' | \hat{v} | d_3'' d_4'' \rangle - \langle d_3' d_4' | \hat{v} | d_4'' d_3'' \rangle] [\langle d_1'' d_3'' | \hat{t} | d_1' d_3' \rangle \langle d_2'' d_4'' | \hat{t} | d_2' d_4' \rangle \\ & - \langle d_1'' d_3'' | \hat{t} | d_3' d_1' \rangle \langle d_2'' d_4'' | \hat{t} | d_2' d_4' \rangle - \langle d_3'' d_4'' | \hat{t} | d_3' d_1' \rangle \langle d_1'' d_2'' | \hat{t} | d_4' d_2' \rangle \\ & - \langle d_1'' d_3'' | \hat{t} | d_4' d_3' \rangle \langle d_2'' d_4'' | \hat{t} | d_2' d_1' \rangle] + \frac{1}{2} \langle d_3' d_4' | \hat{v} | d_3'' d_4'' \rangle [\langle d_1'' d_3'' | \hat{t} | d_3' d_1' \rangle \langle d_2'' d_4'' | \hat{t} | d_4' d_2' \rangle \\ & + \langle d_2'' d_3'' | \hat{t} | d_4' d_1' \rangle \langle d_1'' d_4'' | \hat{t} | d_3' d_2' \rangle + \langle d_1'' d_2'' | \hat{t} | d_3' d_4' \rangle \langle d_3'' d_4'' | \hat{t} | d_1' d_2' \rangle] \}. \quad (59) \end{aligned}$$

Then, Eqs. (53) have the form

$$\lambda(d_1'', d_1'; d_2'', d_2') + \lambda(d_2'', d_2'; d_1'', d_1') = 0. \quad (60)$$

For orbitals which are eigenfunctions of the operator $(\hat{z} + \hat{d})$, the second and third terms on the rhs of Eq. (59) have the form

$$\begin{aligned} \sum_{d_3''} \langle d_1'' | \hat{f} | d_3'' \rangle \langle d_3'' d_2'' | \hat{t} | d_1' d_2' \rangle - \sum_{d_3'} \langle d_1' | \hat{f} | d_3' \rangle \langle d_1'' d_2'' | \hat{t} | d_3' d_2' \rangle \\ = (\omega_{d_1''} - \omega_{d_1'}) \langle d_1'' d_2'' | \hat{t} | d_1' d_2' \rangle + \sum_{d_3''} \langle d_1'' | \hat{q} | d_3'' \rangle \langle d_3'' d_2'' | \hat{t} | d_1' d_2' \rangle \\ - \sum_{d_3'} \langle d_1' | \hat{q} | d_3' \rangle \langle d_1'' d_2'' | \hat{t} | d_3' d_2' \rangle. \quad (61) \end{aligned}$$

In this case, therefore, the following term appears in the expression (60):

$$(\omega_{d_1''} + \omega_{d_2''} - \omega_{d_1'} - \omega_{d_2'}) \langle d_1'' d_2'' | \hat{t} | d_1' d_2' \rangle.$$

IV. DISCUSSION

The method which is most commonly used in investigations of the correlation effects in atoms and molecules is the configuration-interaction method. In this procedure the wavefunction may be written in the following form:

$$|\Psi\rangle = |\Phi\rangle + \sum_{i=1}^{2n} \hat{C}_i |\Phi_i\rangle, \quad (62)$$

where the term $\hat{C}_i |\Phi_i\rangle$ represents a linear combination of i -times excited configurations.

By defining the operators \hat{C}_i as

$$\begin{aligned} \hat{C}_1 &= \hat{T}_1, \\ \hat{C}_2 &= \hat{T}_2 + \hat{T}_1 \hat{T}_1 / 2!, \\ \hat{C}_3 &= \hat{T}_3 + \hat{T}_1 \hat{T}_2 + \hat{T}_1 \hat{T}_1 \hat{T}_1 / 3!, \\ &\dots \end{aligned} \quad (63)$$

both Expansions (62) and (4) of the exact wavefunction become identical.

The spin-orbitals which are usually used to set up the Slater determinant of the ground state $|\Phi\rangle$ are either HF spin-orbitals or localized orbitals obtained from these by an appropriate unitary transformation. In both cases the Brillouin theorem is valid [i.e., the matrix elements of the Hamiltonian (1) between the

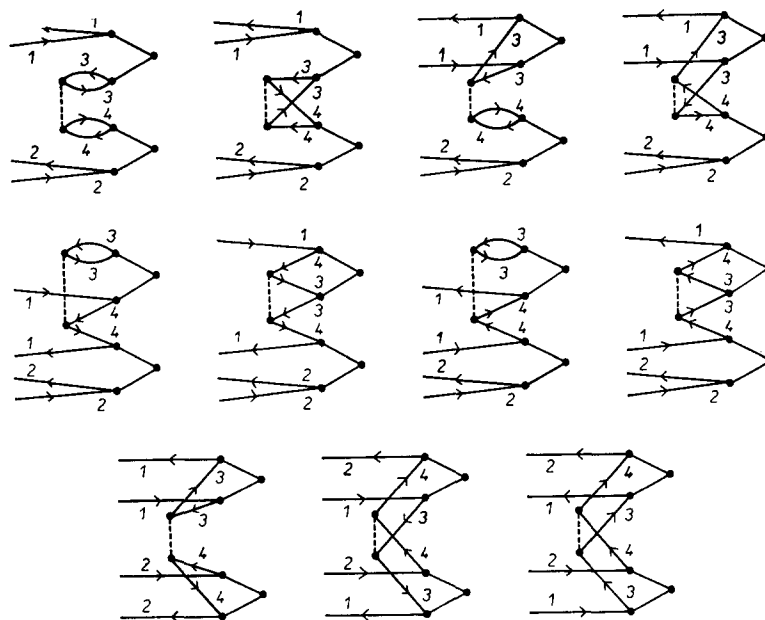


FIG. 8. All possible R skeletons having two open paths formed from the $S_H(1)$ skeleton and the M skeleton consisting of two $S_T(2)$ skeletons.

ground-state function $|\Phi\rangle$ and any singly excited state are equal to zero].

Therefore, one can expect the singly excited states to have negligible coefficients in the expansion (62). Actual computations corroborate this assumption.

In most calculations the triply and higher excited configurations are disregarded in order to make the computation manageable. The effect of triply and quadruply excited configurations was investigated for the simplest possible systems only, as for example in Refs. 12–14. These studies indicate that quadruply excited configurations are more significant than triply excited configurations.

It should now be pointed out that the neglect of all components of the operator \hat{T} except \hat{T}_2 yields a wavefunction $|\Psi\rangle$ containing in part quadruply excited configurations given by the term³

$$(1/2!) \hat{T}_2 \hat{T}_2 |\Phi\rangle. \quad (64)$$

The calculations for beryllium³ (a case of localized electrons) as well as for benzene and butadiene¹⁵ (a case of delocalized electrons) clearly demonstrate that the term (64) is a good approximation of the general term

$$\hat{C}_4 |\Phi\rangle. \quad (65)$$

This may be justified using perturbation theory.¹⁶

For the sake of completeness let us note that the system of equations (54), in which only R skeletons shown in Figs. 6 and 7 are included, is equivalent to the

¹² R. A. Watson, Phys. Rev. **119**, 170 (1960).

¹³ J. Koutecký, J. Čížek, J. Dubský, and K. Hlavatý, Theoret. Chim. Acta **2**, 462 (1964).

¹⁴ J. Koutecký, K. Hlavatý, and P. Hochmann, Theoret. Chim. Acta **3**, 341 (1965).

¹⁵ J. Čížek and J. Paldus (to be published).

¹⁶ H. P. Kelly, Phys. Rev. **134**, A1450 (1964).

system of equations (11) of Kelly and Sessler¹⁷ in which the right-hand side is neglected.¹⁶ This system of equations is also identical with the system given in the paper by da Providencia.⁵ In the papers just mentioned the diagram technique is not used systematically.

The connection of our method with the Goldstone perturbation theory^{6,7} is now discussed.

According to Eqs. (54) the following correspondence is valid: The scalar quantity associated with an R diagram is equal to the sum of the scalar quantities assigned to all possible connected diagrams of Goldstone having the same number of open paths, the external lines of which are labeled with the same spin-orbitals as in the R diagram given. Furthermore, it must be required that the indices of external lines of the given path are identical in both Goldstone and R diagrams.

In order to prove this correspondence the following algebraic identity and its generalizations have to be used:

$$[1/a(a+b)] + [1/b(a+b)] = 1/ab. \quad (66)$$

A standard procedure in applying the Goldstone perturbation theory⁶ is to find out the type of the second- and third-order diagrams which gives the largest contributions to the energy. For example, in the theory of nuclear matter the so-called ladder diagrams are most important,^{6,18} while in the electron-gas problem the so-called ring diagrams are essential.^{11,19} The contributions of these most important diagrams are then summed to all orders.

¹⁷ H. P. Kelly and A. M. Sessler, Phys. Rev. **132**, 2091 (1963).

¹⁸ K. A. Brueckner and J. L. Gammel, Phys. Rev. **109**, 1023 (1958).

¹⁹ M. Gell-Mann and K. Brueckner, Phys. Rev. **106**, 364 (1957).

This summation is equivalent to the solution of Eqs. (54) in which appropriate approximations are introduced.

For example, let us suppose that in Eqs. (54) all contributions are neglected except those corresponding to the diagrams formed from the skeleton of Fig. 6 and from the seventh skeleton of Fig. 7. Then the solution of these equations is equivalent to the summation of all ladder diagrams. Therefore, the system of equations obtained in this way is closely connected with the Bethe–Goldstone equation.

On the other hand, if in Eqs. (54) only contributions of diagrams formed from the skeleton of Fig. 6, from the third one of Fig. 7, and from the first one of Fig. 8 are considered, the solution of these equations is equivalent to the summation of all ring diagrams.

The first attempts to determine the most important type of diagrams for the electronic structure of atoms were made by Kelly.²⁰ In any case the situation here is more complicated than in both the electron-gas and the nuclear-matter problems and further studies will have to be carried out.

V. EXAMPLES

In this section the results concerning two models studied are presented. These models were chosen to be simple enough to allow a complete configuration-interaction treatment within an accepted system of one-electron functions. The results obtained in this way are used as a standard for a comparison with the results of approximate methods.

The quantities compared are first of all the correlation energies

$$\varepsilon_{\text{cor}} = \langle \Phi | \hat{H} | \Phi \rangle - E \quad (67)$$

for different approximations used and, further, the effects of correlation on the wavefunction. Due to the high symmetry of the models studied the first-order density matrix is diagonal when expressed in the representation of Hartree–Fock spin-orbitals. Therefore, the following quantity q may be chosen as a characteristic of the correlation effect on the wavefunction

$$q = \sum_{A''} \langle A'' | \hat{\gamma} | A'' \rangle = 2n - \sum_{A'} \langle A' | \hat{\gamma} | A' \rangle, \quad (68)$$

where $\hat{\gamma}$ is the first-order density matrix:

$$\langle A | \hat{\gamma} | A \rangle = \langle \Psi | \hat{X}_A + \hat{X}_A^\dagger | \Psi \rangle / \langle \Psi | \Psi \rangle. \quad (69)$$

Apparently, the quantity q is equal to zero in the one-particle approximation.

The first example concerns the nitrogen molecule. The Slater determinant describing the ground state of the nitrogen molecule in the Hartree–Fock approximation is built up from six spin-orbitals σ_g , four spin-orbitals σ_u , and four spin-orbitals π_u . From

virtual orbitals we consider only the four lowest-lying spin-orbitals π_g . The required molecular integrals were taken from Grimaldi's²¹ SCF MO LCAO study of the nitrogen molecule. In this study the following basis of Slater-type orbitals localized on atomic nuclei was used for every nitrogen atom [the corresponding exponential coefficients are given in parentheses: two $1s$ orbitals (7, 1.9), two $2s$ orbitals (7, 19), two $3s$ orbitals (7, 1.9), nine $2p$ orbitals (1.4, 2.44, 5.85), and five $3d$ orbitals (2.5). The internuclear distance between the nitrogen nuclei was 2.0675 a.u.

In our study only excitations of the type $\pi_u \rightarrow \pi_g$ were considered, so that "complete configuration interaction" may easily be carried out. The singly and triply excited configurations do not interact with the ground state since they belong to different symmetry species. The consideration of doubly and quadruply excited configurations yields the secular equation of the fifth order.

This model was further studied by means of the method suggested in this paper. Two different approximations were applied. In both of these only the component \hat{T}_2 of the operator \hat{T} was considered. That means that the exact wavefunction was written in the form $|\Psi\rangle = \exp(\hat{T}_2) |\Phi\rangle$.

In the first approximation only skeletons given in Figs. 6 and 7 were considered. In this case the system of equations (54) is linear. In the second approximation the skeletons given in Fig. 8 were taken into account in addition to those considered in the first approximation. Consequently, a nonlinear system of equations (54) is obtained.

In both cases there are three unknown variables in Eqs. (54). The solution of the nonlinear system of equations was obtained using a general program for the Elliott 803 computer written by Paldus.²² This program uses the Newton–Raphson method for the solution of nonlinear systems of equations. The errors in the correlation energy and the quantity q in different approximations are given in Table I.

TABLE I. The error^a in correlation energy and in the quantity q for different approximations used in the study of the model of nitrogen molecule.

%	B^b	L^c	N^a
ε_{cor}	−3.4	1.9	−0.9
q	−10.6	2.6	−3.6

^a The percentage error is calculated with respect to the results of the "complete" configuration-interaction treatment, taken as a standard. By "complete" configuration interaction is meant a treatment in which all possible configurations, arising from the limited basis set selected, are considered.

^b B designates the configuration-interaction treatment limited to doubly excited configurations only.

^c $L(N)$ designates the first (second) approximation described in the main text, which yields a linear (nonlinear) system of equations for components (matrix elements) of the operator \hat{T}_1 .

²¹ F. Grimaldi, J. Chem. Phys. **43**, S59 (1965).

²² J. Paldus (private communication).

²⁰ H. P. Kelly, Phys. Rev. **131**, 684 (1963).

The second example concerns the benzene molecule in the π -electron approximation. The resonance integrals were considered only between nearest neighbors. Further, the approximation of zero differential overlap was used in evaluation of two-electron repulsion integrals. The calculation were carried out for two different sets of parameters^{23,24} given in Table II. The calculations for Pariser and Parr parametrization are not presented here since the correlation effects in this approximation due to the higher-than-doubly-excited states are negligibly small (cf. Refs. 13, 14).

Using the approximations just indicated the complete configuration-interaction treatment was carried out.¹⁵ The resulting secular equation was of the 22nd order. The correctness of our calculations was checked by comparison with results published in a paper from this laboratory.¹⁴ Further, the configuration-interaction treatment of the benzene molecule considering only doubly excited states was carried out.¹¹

The method suggested in this paper was applied²⁵ to this case using the same two approximations as in the first example. The system of nonlinear equations, having now eight unknown variables, was solved in the same way as above. The results obtained are shown in Table III.

It is apparent from Tables I and III that the configuration-interaction method limited to doubly excited states underestimates both ϵ_{cor} and q (in the case of ϵ_{cor} this is the consequence of the variational principle).

On the other hand, in the above-presented examples, our approximation which yields a linear system of equations for the matrix elements of the operator T_2 overestimates both quantities ϵ_{cor} and q .

Finally, intermediate results are obtained with the approximation leading to a nonlinear system of equations (54).

TABLE II. The values of integrals used in the study of the benzene molecule in π -electron approximation (all quantities are in electron volts).

(eV)	β^a	γ_{00}^d	γ_{01}^d	γ_{02}^d	γ_{03}^d
M^a	-2.388	10.840	5.298	3.855	3.505
T^b	-2.734	17.618	8.924	5.574	4.876

^a The parameters according to Mataga and Nishimoto.²¹

^b The parameters obtained by transformation to the orthonormal Löwdin orbitals.²²

^c The resonance integrals between nearest neighbors.

$$^d \gamma_{\mu,\nu} = \iint r_{12}^{-1} [a_{\mu}(1)]^2 [a_{\nu}(2)]^2 dV_1 dV_2,$$

where $a_{\mu}(i)$ is an orbital localized on the μ th carbon atom.

²³ M. Mataga and K. Nishimoto, Z. Physik. Chem. (Frankfurt) **13**, 140 (1957).

²⁴ R. McWeeny, Proc. Roy. Soc. (London) **A227**, 288 (1959).

²⁵ J. Čížek and L. Šroubková (to be published).

TABLE III. The error^a in correlation energy and in the quantity q for different approximations used in the study of the benzene molecule in π -electron approximation.

	%	B^d	L^d	N^d
M^b	ϵ_{cor}	-7.5	5.0	-0.3
	q	-19.8	12.5	0.6
T^c	ϵ_{cor}	-12.9	12.9	0.7
	q	-29.7	37.3	7.0

^a See Table I.

^b The parameters according to Mataga and Nishimoto²¹ have been used.

^c "Theoretical parameters" used.²²

^d B , L , and N have the same meaning as in Table I.

Both examples presented above should only illustrate the applicability of the proposed method. Further applications of this method are currently being undertaken.

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APPENDIX

In order to prove the auxilliary theorem essential for our derivation of the method suggested in this paper, the generalized Wick theorem is used.

With the creation and annihilation operators defined in the main section the following four types of pairings are possible:

$$\hat{X}_B \hat{Y}_{A''}^+ = \langle B | A'' \rangle, \quad (A1)$$

$$\hat{X}_C^+ \hat{Y}_A^+ = \langle C | A' \rangle, \quad (A2)$$

$$\hat{X}_B \hat{Y}_A^+ = 0, \quad (A3)$$

$$\hat{X}_C^+ \hat{Y}_{A''}^+ = 0. \quad (A4)$$

Therefore, only those normal products which contain the pairings of the types (A1) and (A2) will be different from zero.

Any normal product with pairings of the types (A1)

and (A2) may be depicted by an R diagram, which is formed from the corresponding H and M diagrams by connecting lines carrying indices of contracted operators.

Since only contractions of the types (A1) and (A2) give nonzero contributions, we have to join the lines starting at some vertex with the lines entering some other or even the same vertex.

On the basis of Relations (A1) and (A2) it is immediately apparent why the lines starting at the vertex of the M skeleton (H skeleton) and entering the vertex of the H skeleton (M skeleton) are called particle (hole) lines and why these lines carry an index of the

excited (nonexcited) spin-orbital in the corresponding R diagram.

Noncontracted operators are then associated with the external lines of the R diagram. Provided at least one of these operators is an annihilation operator a zero vector results on applying this normal product to the vector $|\Phi\rangle$. Therefore, only such R diagram have to be considered in which indices of the excited (nonexcited) states are assigned to the external lines leaving (entering) the vertexes of the H diagram.

The rule which determines the sign of the resulting expressions is illustrated by the following three typical examples:

$$\begin{aligned} l=0, \quad h=0: N[\hat{X}_{C_1}^+ \hat{X}_{B_1} \hat{Y}_{A_1'}^{++} \hat{Y}_{A_1'}^+] &= (\hat{X}_{B_1} \hat{Y}_{A_1'}^{++}) N[\hat{X}_{C_1}^+ \hat{Y}_{A_1'}^+], \\ l=0, \quad h=1: N[\hat{X}_{C_1}^+ \hat{X}_{B_1} \hat{Y}_{A_1'}^{++} \hat{Y}_{A_1'}^+] &= -(\hat{X}_{C_1}^+ \hat{Y}_{A_1'}^+) N[\hat{Y}_{A_1'}^{++} \hat{X}_{B_1}], \\ l=1, \quad h=1: N[\hat{X}_{C_1}^+ \hat{X}_{B_1} \hat{Y}_{A_1'}^{++} \hat{Y}_{A_1'}^+] &= (\hat{X}_{C_1}^+ \hat{Y}_{A_1'}^+) (\hat{X}_{B_1} \hat{Y}_{A_1'}^{++}). \end{aligned} \quad (\text{A5})$$

Among the R skeletons corresponding to all possible normal products with pairings one can generally find topologically equivalent skeletons.

It can be proved generally, that g equivalent skeletons $R(r)$ with the given structure r will result among all possible R skeletons formed from the $H(h)$ and

$M(m)$ skeletons, where

$$g = w_R(r) / w_H(h) w_M(m). \quad (\text{A6})$$

We demonstrate this statement on a typical example. Let us consider the $S_H(1)$ skeleton (Fig. 1) and the M skeleton consisting of a single $S_T(2)$ skeleton (Fig. 3, $j=2$). Both of these skeletons have the weight equal to $\frac{1}{2}$. The examples of skeletons which one can form from the skeletons just mentioned are shown in Fig. 9. It is immediately apparent that the skeletons shown in Fig. 9 are mutually equivalent, both having the weight $\frac{1}{2}$, so that we indeed obtain $g=2$.

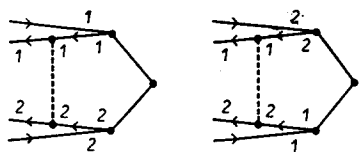


FIG. 9. Examples of R skeletons formed from an $S_H(1)$ skeleton and an M skeleton consisting of a single $S_T(2)$ skeleton.