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Many-body perturbation theory of intermolecular interactions

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We suggest a general many-body perturbation theory for the ground state as well as for low-lying excited and charge-transfer intermolecular interactions. In this theory the interactions energies are expressed by the Rayleigh-Schrödinger perturbation formulas, where each individual contribution can be interpreted by a slightly modified Hugenholtz diagrammatic technique.

I. INTRODUCTION

The theory of intermolecular and/or interatomic interactions[1-3] is still one of the serious problems in the quantum theory of atoms and molecules. The correct treatment requires that the wave function of the bimolecular system "supersystem" be antisymmetric with respect to all the electrons. Then the wave function may be expressed in terms of an antisymmetrized product of exact isolated molecular wave functions, which allows one to write the total energy as the sum of the energies of the isolated molecules plus the perturbation corrections. The use of such unperturbed wave functions, however, renders the formulation of the problem in the framework of the Rayleigh-Schrödinger perturbation theory nontrivial, because such antisymmetrized unperturbed wave functions are not eigenfunctions of the unperturbed Hamiltonian describing the system of the two isolated molecules or atoms. Nevertheless, theoretical problems emerging in this approach are at present resolved[4-11] in several different ways. Unfortunately, these perturbation methods are based on the assumption that exact eigensystems for both isolated molecular systems are known, which severely limits actual applications. Therefore it seems that it might be of value to solve the problem of correlation effects of isolated systems simultaneously with that of intermolecular interactions. Sinanoğlu and Kestner[12-16] elaborated a very interesting many-body theory of interatomic interactions. Their approach is based on the simple application of the Sinanoğlu many-electron theory.[17] Then the interaction energy can be divided into contributions describing the intercorrelation and intracorrelation effects. Recently, another many-body theory of the intermolecular interactions has been suggested by Basilevsky and Berenfeld.[18] The relation between this and our approach will be discussed elsewhere.

In the present article we describe a quite general diagrammatic perturbation theory of intermolecular interactions, from which the particular cases, as for example, the Basilevsky and Berenfeld method[18] and the diagrammatic theory of long-range interactions (Sec. V), can be derived in a simple way. Furthermore, the suggested method is used for the construction of the diagrammatic perturbation theory of low-lying excited as well as charge-transfer intermolecular interactions (Sec. IV).

II. CONSTRUCTION OF THE HAMILTONIAN

We assume orthonormal sets of spin orbitals localized on the molecular systems A and B which form the column vectors

$$\Phi_A \equiv \{|\varphi_i\rangle ; i \in A\}, \tag{1a}$$

$$\Phi_B \equiv \{|\varphi_j\rangle ; j \in B\}. \tag{1b}$$

The matrix of the overlap integrals between the systems A and B (for the fixed distance R) is defined by

$$S_{AB} = \Phi_A^\dagger \Phi_B \equiv \{S_{ij} = \langle\varphi_i|\varphi_j\rangle ; i \in A, j \in B\}. \tag{2}$$

From the column vectors [(1a) and (1b)] we may construct a new column vector

$$\Phi = \begin{pmatrix} \Phi_A \\ \Phi_B \end{pmatrix}. \tag{3}$$

Let us assume that there exists such a nonsingular matrix A which (i) transforms Φ onto Ψ,

$$\Psi = A\Phi \equiv \{|\psi_i\rangle ; i \in A + B\}, \tag{4}$$

elements of which form an orthonormal system, and (ii) satisfies the asymptotic condition

$$\lim_{R\to\infty} A = 1. \tag{5}$$

Then, we have a one-to-one correspondence between the elements of the column vectors Ψ and Φ realized by the relation

$$\lim_{R\to\infty} |\psi_i\rangle = |\varphi_i\rangle, \tag{6}$$

for all $i \in A + B$.

One of the possible procedures for constructing the transformation (4) together with the asymptotic condition (5) is the Löwdin symmetric orthonormalization method[19]:

$$A=(1+S)^{-1/2}, \tag{7a}$$

$$S=\begin{pmatrix} 0 & S_{AB} \\ S_{AB}^{\dagger} & 0 \end{pmatrix}. \tag{7b}$$

Assuming that all the absolute values of eigenvalues of the matrix S are less than 1,[20] the right-hand side of (7a) can be expressed as a power series[19] of S:

$$A=\sum_{n=0}^{\infty}\binom{n}{-\frac{1}{2}}S^{n}=1-\tfrac{1}{2}S+\tfrac{3}{8}S^{2}-\dots . \tag{8}$$

From (4) we obtain for the individual components of the column vector Ψ an expression

$$|\psi_i\rangle=|\varphi_i\rangle-\frac{1}{2}\sum_{j\in B}S_{ij}|\varphi_j\rangle +\frac{3}{8}\sum_{k\in B}\sum_{l\in A}S_{ik}S_{kl}|\varphi_l\rangle-\dots, \tag{9}$$

where $i\in A$; for $i\in B$ one has to exchange $A\leftrightarrow B$ in the summations.

Now, after these introductory remarks, let us turn our attention to the construction of the Hamiltonian for the "supersystems" $A+B$. In the second-quantization formalism this Hamiltonian can be written in the form[21,22]

$$H=\sum_{ij\in A+B}h(i,j)X_i^{\dagger}X_j +\frac{1}{4}\sum_{ijkl\in A+B}g(ij,kl)X_i^{\dagger}X_j^{\dagger}X_lX_k, \tag{10}$$

where $X_i^{\dagger}(X_j)$ are creation (annihilation) operators defined on the orthonormal set of spin orbitals $\{|\psi_i\rangle; i\in A+B\}$ introduced by (4) [cf. also Eq. (8)]. One- and two-particle matrix elements from (10) are determined by

$$h(i,j)=\int\psi_i^{*}(1)h(1)\psi_j(1)\,d1, \tag{11a}$$

$$g(ij,kl)=\iint\psi_i^{*}(1)\psi_j^{*}(2)g(1,2)(1-P_{12})\times\psi_k(1)\psi_l(2)\,d1\,d2, \tag{11b}$$

where P_{12} is a transposition operator and $g(1,2)$ is the two-particle interaction operator. The one-particle operator $h(1)$ from (11a) can be expressed in the following identical ways:

$$\begin{aligned} h(1)&=t(1)+w_A(1)+w_B(1),\\ &=h_A(1)+w_B(1),\\ &=h_B(1)+w_A(1), \end{aligned} \tag{12}$$

where $t(1)$ is the kinetic-energy operator and $w_A(1)$ and $w_B(1)$ are the nuclear-attraction operators within the systems A and B, respectively. The matrix elements (11a) and (11b) can be written [cf. Eq. (9)] in the form

$$h(i,j)=h_0(i,j)+\Delta h(i,j), \tag{13a}$$

$$g(ij,kl)=g_0(ij,kl)+\Delta g(ij,kl), \tag{13b}$$

where $h_0(i,j)$ and $g_0(ij,kl)$, as in (11a) and (11b), are one- and two-particle matrix elements calculated in the initial nonorthogonal set $\{|\varphi_i\rangle; i\in A+B\}$,

$$h_0(i,j)=\int\varphi_i^{*}h(1)\varphi_j(1)\,d1, \tag{14a}$$

$$g_0(ij,kl)=\iint\varphi_i^{*}(1)\varphi_j^{*}(2)g(1,2)(1-P_{12})\times\varphi_k(1)\varphi_l(2)\,d1\,d2. \tag{14b}$$

Matrix elements $\Delta h(i,j)$ and $\Delta g(ij,kl)$, defined by (13a) and (13b), tend to zero for $R\to\infty$, which can be simply verified by (6).

For further considerations it is appropriate to introduce an unperturbed ground-state vector[22,23] $|\Phi_0\rangle$ of the "supersystem,"

$$|\Phi_0\rangle=\prod_{i\in A}^{\text{occ}}X_i^{\dagger}\prod_{j\in B}^{\text{occ}}X_j^{\dagger}|0\rangle, \tag{15}$$

where the product index i (j) runs over all occupied spin orbitals of the system A (B), and $|0\rangle$ is the normalized vacuum-state vector. Then, using Wick's theorem[21,22] and expressions (12) and (13), the Hamiltonian (10) can be rewritten in the form

$$H=\mathcal{E}_0+H_0+H_1. \tag{16}$$

Scalar quantity $\mathcal{E}_0$ from the right-hand side of (16) is defined by

$$\mathcal{E}_0=E_{\text{HF}}^{A}+E_{\text{HF}}^{B}+e_0, \tag{17}$$

where E_{HF}^{A} (E_{HF}^{B}) is the Hartree-Fock ground-state energy of the system A (B),

$$E_{\text{HF}}^{A}=\sum_{i\in A}^{\text{occ}}h_A(i,i)+\frac{1}{2}\sum_{ij\in A}^{\text{occ}}g_0(ij,ij), \tag{18a}$$

$$E_{\text{HF}}^{B}=\sum_{i\in B}^{\text{occ}}h_B(i,i)+\frac{1}{2}\sum_{ij\in B}^{\text{occ}}g_0(ij,ij), \tag{18b}$$

and for e_0 we have obtained the following expression:

$$e_0=\sum_{i\in A}^{\text{occ}}w_B(i,i)+\sum_{i\in B}^{\text{occ}}w_A(i,i)+\sum_{i\in A+B}^{\text{occ}}\Delta h(i,i)+\sum_{i\in A}^{\text{occ}}\sum_{j\in B}^{\text{occ}}[g_0(ij,ij)+\Delta g(ij,ij)]+\frac{1}{2}\sum_{ij\in A}^{\text{occ}}\Delta g(ij,ij)+\frac{1}{2}\sum_{ij\in B}^{\text{occ}}\Delta g(ij,ij). \tag{19}$$

The operator H_0 from the right-hand side of (16) is given by

$$H_0=\sum_{ij\in A} f_A(i,j)N[X_i^\dagger X_j]+\sum_{ij\in B} f_B(i,j)N[X_i^\dagger X_j], \tag{20}$$

where $N[\cdots]$ is the normal product[22] defined with respect to $|\Phi_0\rangle$ and $f_A(i,j)$ and $f_B(i,j)$ are the matrix elements of the Hartree-Fock operator of systems A and B:

$$f_A(i,j)=h_A(i,j)+\sum_{k\in A}^{\text{occ}} g_0(ik,jk), \tag{21a}$$

$$f_B(i,j)=h_B(i,j)+\sum_{k\in B}^{\text{occ}} g_0(ik,jk). \tag{21b}$$

We shall assume that sets of spin orbitals $\{|\varphi_i\rangle; i\in A\}$ and $\{|\varphi_j\rangle; j\in B\}$ are the eigenfunctions of the Hartree-Fock operator defined within the systems A and B, respectively, i.e.,

$$f_A(i,j)=\epsilon_i\delta_{ij} \text{ for } i,j\in A, \tag{22a}$$

$$f_B(i,j)=\epsilon_i\delta_{ij} \text{ for } i,j\in B, \tag{22b}$$

where ϵ_i are the Hartree-Fock one-particle energies. Then, the operator H_0 defined by (20) can be written in the diagonal form

$$H_0=\sum_{i\in A}\epsilon_i N[X_i^\dagger X_i]+\sum_{j\in B}\epsilon_j N[X_j^\dagger X_j], \tag{23}$$

which we shall call unperturbed Hamiltonian.

The operator H_1 from the right-hand side of (16) (called perturbation) has the form

$$H_1=\sum_{ij\in A+B} u(i,j)N[X_i^\dagger X_j] +\frac{1}{4}\sum_{ijkl\in A+B}[g_0(ij,kl)+\Delta g(ij,kl)] \times N[X_i^\dagger X_j^\dagger X_l X_k], \tag{24}$$

where one-particle matrix elements $u(i,j)$ are defined by

$$u(i,j)=\Delta h(i,j)+\sum_{k\in A+B}^{\text{occ}}\Delta g(ik,jk)+z(i,j), \tag{25a}$$

$$z(i,j)=\begin{cases} t_A(i,j)=w_B(i,j)+\displaystyle\sum_{k\in B}^{\text{occ}} g_0(ik,jk) \text{ for } i,j\in A, \\ h_0(i,j)+\displaystyle\sum_{k\in A+B}^{\text{occ}} g_0(ik,jk) \text{ for } i\in A, j\in B \text{ or } i\in B, j\in A, \\ t_B(i,j)=w_A(i,j)+\displaystyle\sum_{k\in A}^{\text{occ}} g_0(ik,jk) \text{ for } i,j\in B. \end{cases} \tag{25b}$$

For the better physical understanding of the Hamiltonian (16) and its individual terms (17), (20), and (24), it is suitable to rewrite (16) as

$$H=H_A+H_B+H_{AB}, \tag{26}$$

where

$$H_A=E_{\text{HF}}^A+\sum_{i\in A}\epsilon_i N[X_i^\dagger X_i] +\frac{1}{4}\sum_{ijkl\in A} g_0(ij,kl)N[X_i^\dagger X_j^\dagger X_l X_k] \tag{27}$$

is the Hamiltonian of the isolated system A. The operator H_B from (26) is the Hamiltonian of the isolated system B, and it is defined similarly as (27), with $A\rightarrow B$. The operator $H_{AB}=H-H_A-H_B$ satisfying the asymptotic condition

$$\lim_{R\rightarrow\infty} H_{AB}=0 \tag{28}$$

describes an interaction between the systems A and B. Then, the perturbation H_1 defined by (24) contains two effects: (i) the correlation between electrons inside the isolated systems A and B and (ii) a certain part of the interactions between A and B [the remainder is contained in the scalar quantity e_0 defined by Eq. (19)].

III. DIAGRAMMATIC PERTURBATION THEORY

In order to apply the diagrammatic nondegenerate perturbation theory[24-27] to the calculation of the interaction energy of two molecular systems, it is necessary to introduce the suitable diagrammatic interpretation of the individual terms of the perturbation H_1. We shall use the Hugenholtz diagrammatic technique and his classification of diagrams.[22,27] The diagrammatic representation of individual terms of H_1 is presented in Fig. 1. Using the Goldstone-Hugenholtz linked-cluster theorem,[24,25] the electronic ground-state energy of the "supersystem" can be expressed by

$$E_{AB}^{\text{ele}}=\mathcal{E}_0+\langle\Phi_0|\left\{H_1+H_1\frac{1}{-H_0}H_1+\cdots\right\}_C|\Phi_0\rangle, \tag{29}$$

where the subscript C means that only connected ground-state diagrams contribute. Using (17) we can rewrite (29) in the form

$$\Delta E_{AB}^{\text{ele}} = E_{AB}^{\text{ele}} - E_A^{\text{ele}} - E_B^{\text{ele}} = e_0 + \langle \Phi_0 | \left\{ H_1 + H_1 \frac{1}{-H_0} H_1 + \cdots \right\}_{C^*} | \Phi_0 \rangle , \tag{30}$$

where $\Delta E_{AB}^{\text{ele}}$ is the ground-state electronic interaction energy, $E_{A(B)}^{\text{ele}}$ is the perturbed electronic ground-state energy of the isolated system A (B), and, finally, the subscript C^* means that we omit the diagrams contributing to the correlation energy of isolated systems A and B. The interaction energy between the systems A and B is then (principal result of this section)

$$\Delta E_{AB} = W_{AB} + e_0 + \langle \Phi_0 | \left\{ H_1 + H_1 \frac{1}{-H_0} H_1 + \cdots \right\}_{C^*} | \Phi_0 \rangle , \tag{31}$$

where W_{AB} is the potential energy of the Coulomb repulsion of nuclei between A and B. The diagrammatic expression for the interaction energy up to the "second order"[28] is shown on Fig. 2. Using the rules of Hugenholtz's graphology,[25,27,29] the algebraic interpretation of this diagrammatic expression is

$$\begin{aligned}\Delta E_{AB} = {} & W_{AB} + e_0 + \sum_i^{\text{un}} \sum_j^{\text{occ}} \frac{u(i,j)u(j,i)}{\epsilon_j - \epsilon_i} + \frac{1}{4} \sum_{il}^{\text{occ}}{}' \sum_{jk}^{\text{un}}{}' \frac{g_0(il,jk) g_0(jk,il)}{\epsilon_i + \epsilon_l - \epsilon_j - \epsilon_k} \\ & + \frac{1}{4} \sum_{il}^{\text{occ}} \sum_{jk}^{\text{un}} \frac{1}{\epsilon_i + \epsilon_l - \epsilon_j - \epsilon_k} \{ g_0(il,jk) \Delta g_0(jk,il) + \Delta g(il,jk) g_0(jk,il) + \Delta g(il,jk) \Delta g(jk,il) \} .\end{aligned} \tag{32}$$

All the summations run over all indices of the "supersystem." The primes in the fourth term from the right-hand side of (32) mean that all the contributions which have the line indices only in A or B are excluded [see comment after Eq. (29)]. If we assume that the conditions for the existence of expansion (8) are satisfied, then it is possible to express the matrix elements $\Delta h(i,j)$ and $\Delta g(ij,kl)$ using the expansion (9) (cf. Ref. 18).

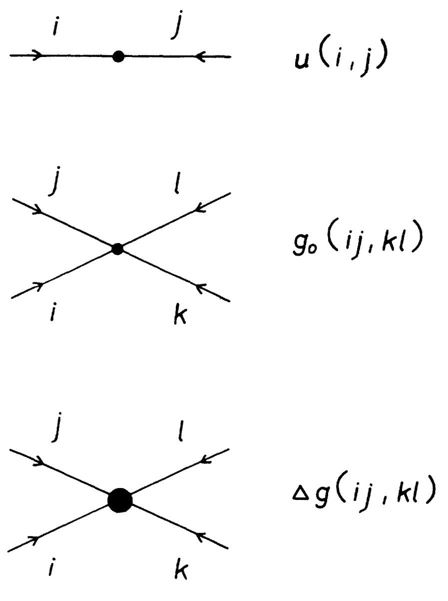

FIG. 1. Hugenholtz diagrammatic interpretation of individual terms of the perturbation H_1, defined by (24).

IV. EXCITED AND CHARGE-TRANSFER INTERACTION ENERGIES

Theoretical treatment of the excited[2,3] and charge-transfer intermolecular interactions represents a slightly more complicated problem than the treatment of the ground-state interaction energies, because a degenerate perturbation theory should be used. For simplicity we assume that the molecular systems A and B are different, i.e., additional degeneracy due to the resonant effects[2] is removed. Nevertheless, these effects (if the molecular systems A and B are identical) may be taken into account by straightforward generalization of the present theory.

In our recent paper[30] we have applied the degenerate many-body Rayleigh-Schrödinger perturbation theory (DMB-RSPT) to the calculation of low-lying singlet and triplet excitation energies for closed-shell molecular systems. This diagram-

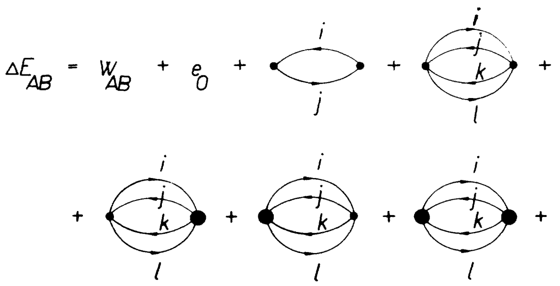

FIG. 2. Diagrammatic expression for the ground-state interaction energy up to the second order (see Ref. 28) in the framework of Hugenholtz graphology.

matic approach is also very convenient for the perturbation-theoretic treatment of the excited and charge-transfer interaction energies of two different closed-shell molecular systems. Therefore, in the following part of this section, we shall recapitulate the main features of DMB-RSPT from Ref. 30.

One of the basic concepts of this theory is the closed-shell nondegenerate "core" state vector, which is in our case identical with the nondegenerate state vector $|\Phi_0\rangle$ defined by (15). Using this core state vector we generate a certain finite d-dimensional model space

$$\Omega_0 \equiv \{\,|\Phi_\mu\rangle = \Xi_\mu^\dagger|\Phi_0\rangle\},$$

where $\Xi_\mu^\dagger$ are the ordered products of the creation and annihilation operators. We assume that the model space Ω_0 is an eigenspace of unperturbed Hamiltonian H_0 with an eigenenergy $E_\alpha^{(0)}$. Let P_0 be a projector onto Ω_0, then $\mathrm{Tr}(P_0)=d$ and $H_0P_0 = P_0H_0 = E_\alpha^{(0)}P_0$. If we assume that the perturbation H_1 is an "analytical perturbation,"[31] then there exist d perturbed eigenvalues

$$\{E_{\lambda_1}, E_{\lambda_2}, \ldots, E_{\lambda_d}\} \equiv \{E_\lambda;\lambda\in M\}$$

tending to the unperturbed energy $E_\alpha^{(0)}$ when the perturbation H_1 is "switched off," i.e., $H_1\to 0$. The excitation energies $\Delta E_\lambda = E_\lambda - E_0$, where $\lambda\in M$ and E_0 is perturbed energy of the core state, are then determined as eigenvalues of the following non-Hermitian d-dimensional eigenproblem:

$$H_{RS}^{LC}|\psi_\lambda\rangle = \Delta E_\lambda\,|\psi_\lambda\rangle\ , \tag{33a}$$

$$H_{RS}^{LC} = E_\alpha^{(0)}P_0 + G_{RS}^{LC}\ , \tag{33b}$$

where H_{RS}^{LC} is the model Hamiltonian defined in the model space Ω_0, and G_{RS}^{LC} is the model interaction defined in the framework of the diagrammatic technique as follows:

$$\begin{aligned} G_{RS}^{LC} &= \{P_0H_1P_0\}_{LC} + \sum_{n=1}^{\infty}\{P_0H_1G^{k_1}H_1G^{k_2}\cdots G^{k_n}H_1P_0\}_{LC} \\ &= \{P_0H_1P_0\}_{LC} + \left\{P_0H_1\frac{1-P_0}{E_\alpha^{(0)}-H_0}H_1P_0\right\}_{LC} + \left\{P_0H_1\frac{1-P_0}{E_\alpha^{(0)}-H_0}H_1\frac{1-P_0}{E_\alpha^{(0)}-H_0}H_1P_0\right\}_{LC} \\ &\quad - \left\{P_0H_1\frac{1-P_0}{(E_\alpha^{(0)}-H_0)^2}H_1P_0H_1P_0\right\}_{LC} + \cdots\ , \end{aligned} \tag{34}$$

where subscript LC means that only linked-connected diagrams are contributing, and non-negative summation indices $k_1, k_2, \ldots, k_n$ are determined by the two conditions

$$\sum_{i=1}^{n} k_i = n\ , \tag{35a}$$

$$\sum_{i=1}^{m} k_i \geq m \ \text{ for } m=1,2,\ldots,n-1\ . \tag{35b}$$

The powers of the unperturbed propagator G^k from (34) are defined by

$$G^k = \begin{cases} -P_0 & \text{for } k=0\ , \\ (1-P_0)/(E_\alpha^{(0)}-H_0)^k & \text{for } k\geq 1\ . \end{cases} \tag{36}$$

As has been shown in Ref. 32, a one-to-one correspondence exists between the presented diagrammatic technique of construction of model interaction G_{RS}^{LC} and Brandow's folded-diagram approach.[29]

After this short recapitulation of DMB-RSPT we turn our attention to the application of this theory to the calculation of excited interaction energies when the system A is in the ground closed-shell state and the system B is in the low-lying singlet or triplet excited state. The model space Ω_0 is then spanned by the two unperturbed state vectors

$$|\Phi_1\rangle = X_{k\alpha}^\dagger X_{i\alpha}|\Phi_0\rangle\ , \tag{37a}$$

$$|\Phi_2\rangle = X_{k\beta}^\dagger X_{i\beta}|\Phi_0\rangle\ , \tag{37b}$$

where the spin orbitals with the indices $k\alpha$, $k\beta$, $i\alpha$, and $i\beta$ are taken from B and unperturbed energy $E_\alpha^{(0)} = \epsilon_k - \epsilon_i$. The model space Ω_0 can be factorized on two orthogonal one-dimensional eigenspaces of the spin operator S^2,

$$|\Phi_S\rangle = (1/\sqrt{2}\,)(|\Phi_1\rangle + |\Phi_2\rangle)\ \ \text{(singlet)}, \tag{38a}$$

$$|\Phi_T\rangle = (1/\sqrt{2}\,)(|\Phi_1\rangle - |\Phi_2\rangle)\ \ \text{(triplet)}. \tag{38b}$$

According to the fact that the core state vector $|\Phi_0\rangle$ is the nondegenerate closed-shell state vector, the model interaction G_{RS}^{LC} defined by (34) is the spinless operator. The model eigenproblem (33a) can be factorized in two one-dimensional singlet and triplet subproblems. Then, for the singlet and triplet excited interaction energies we get

$$\Delta E_{AB^*}^{(S)} = \Delta E_{AB} + G_{11} + G_{12}\ \ \text{(singlet)}, \tag{39a}$$

$$\Delta E_{AB^*}^{(T)} = \Delta E_{AB} + G_{11} - G_{12}\ \ \text{(triplet)}. \tag{39b}$$

Here ΔE_{AB} is the interaction energy for the closed-shell supersystem studied in Sec. III by the nondegenerate diagrammatic perturbation theory [cf. Eq. (31)]. The matrix elements G_{11} and G_{12} from (39a) and (39b) are defined as follows:

$$G_{11} = \langle\Phi_0| X^\dagger_{i\alpha} X_{k\alpha} G^{LC}_{RS} X^\dagger_{k\alpha} X_{i\alpha} |\Phi_0\rangle, \tag{40a}$$

$$G_{12} = \langle\Phi_0| X^\dagger_{i\alpha} X_{k\alpha} G^{LC}_{RS} X^\dagger_{k\beta} X_{i\beta} |\Phi_0\rangle, \tag{40b}$$

where all the diagrams contributing to the excitation energy of the isolated system B are omitted.

As a second example we shall study so called charge-transfer intermolecular interactions in which one electron from the system B is shifted to the system A. The model space Ω_0 for this case is spanned by the following two unperturbed vectors:

$$|\Phi'_1\rangle = X^\dagger_{k\alpha} X_{i\alpha} |\Phi_0\rangle, \tag{41a}$$

$$|\Phi'_2\rangle = X^\dagger_{k\beta} X_{i\beta} |\Phi_0\rangle, \tag{41b}$$

which are formally similar to (37a) and (37b), but in this case the spin orbitals with the indexes $k\alpha$ and $k\beta$ are taken from A, and those with indexes $i\alpha$ and $i\beta$ from B. Similarly as in the first case, the model space Ω_0 can be factorized in two orthogonal one-dimensional subspaces

$$|\Phi'_S\rangle = (1/\sqrt{2})(|\Phi'_1\rangle + |\Phi'_2\rangle) \quad \text{(singlet)}, \tag{42a}$$

$$|\Phi'_T\rangle = (1/\sqrt{2})(|\Phi'_1\rangle - |\Phi'_2\rangle) \quad \text{(triplet)}. \tag{42b}$$

Then, the singlet and triplet charge-transfer interaction energy is determined by

$$\Delta E^{(S)}_{A^-B^+} = \Delta E_{AB} + G'_{11} + G'_{12} \quad \text{(singlet)}, \tag{43a}$$

$$\Delta E^{(T)}_{A^-B^+} = \Delta E_{AB} + G'_{11} - G'_{12} \quad \text{(triplet)}, \tag{43b}$$

where the matrix elements G'_{11} and G'_{12} are defined formally in a same way as (40a) and (40b). Here we have omitted diagrams contributing to the electron affinities of the system A and to the electron potentials of B as well.

To conclude this section we stress that these two simple examples presented here demonstrate the suitability and formal simplicity of DMB-RSPT for the treatment of "excited" interaction energies of various types.

V. LONG-RANGE INTERATOMIC INTERACTIONS

This section is concerned with the application of the present general theory to the problem of long-range[33,34,45] interatomic interactions. It is a well-known fact that the interatomic interaction energy can be expanded in a power series of R^{-n}. Our aim is to demonstrate how to calculate the expansion coefficients directly using the presented perturbation theory. Another possibility for calculating these coefficients is based on the results of Mavroyanis and Stephen[46] and Chan and Dalgarno.[47] In this approach the two-center problem is reduced to a one-center one, and only the polarizability functions of isolated atoms at imaginary frequencies should be calculated. In this way the Goldstone[24] and Hugenholtz[25] many-body perturbation theory has been adapted to the calculation of the frequency-dependent polarizabilities of imaginary arguments. The R^{-6} coefficient calculations[48,49] as well as the nonadditivity contributions calculations[50] are in excellent agreement with experiment.

In the first step we shall construct the Hamiltonian describing this simplest case of interaction between the many-electron systems, which are for simplicity specified as atomic systems. Assuming that the distance R between two atoms is sufficiently large, the important terms in the perturbation H_1 defined by (24) are those which are only of the Coulomb type. The remaining terms, similar to the exchange interactions or to other interactions depending approximately on the overlap, tend to zero. Then, from (16) we get the following Hamiltonian for long-range interactions:

$$H_{LR} = \mathscr{E}_{0,LR} + H_0 + H_{1,LR}. \tag{44}$$

The scalar part $\mathscr{E}_{0,LR}$ is defined similarly as (17),

$$\mathscr{E}_{0,LR} = E^A_{HF} + E^B_{HF} + e_{0,LR}, \tag{45}$$

but $e_{0,LR}$ has the following much more simple form than (19):

$$e_{0,LR} = \sum_{i\in A}^{\text{occ}} w_B(i,i) + \sum_{i\in B}^{\text{occ}} w_A(i,i) + \sum_{i\in A}^{\text{occ}} \sum_{j\in B}^{\text{occ}} g'_0(ij,ij), \tag{46}$$

where $g'_0(ij,kl)$ is the two-particle integral

$$g'_0(ij,kl) = \int\int \varphi^*_i(1)\,\varphi^*_j(2)\,g(1,2)\,\varphi_k(1)\,\varphi_l(2)\,d1\,d2. \tag{47}$$

The unperturbed Hamiltonian H_0 from (44) is defined in the same way as (23). For the perturbation $H_{1,LR}$ we get from (24), (25a) and (25b) this simple expression with clear physical interpretation of individual terms,

$$\begin{aligned} H_{1,LR} = {} & \frac{1}{4}\left(\sum_{ijkl\in A} + \sum_{ijkl\in B}\right) g_0(ij,kl)\,N[X^\dagger_i X^\dagger_j X_l X_k] \\ & + \sum_{ij\in A} t'_A(i,j)\,N[X^\dagger_i X_j] + \sum_{ij\in B} t'_B(i,j)\,N[X^\dagger_i X_j] \\ & + \sum_{ik\in A} \sum_{jl\in B} g'_0(ij,kl)\,N[X^\dagger_i X^\dagger_j X_l X_k]. \end{aligned} \tag{48}$$

The matrix elements $t'_A(i,j)$ and $t'_B(i,j)$ are obtained from (25b), neglecting the exchange terms,

$$t'_A(i,j) = w_B(i,j) + \sum_{k\in B}^{\text{occ}} g'_0(ik,jk), \tag{49a}$$

$$t'_B(i,j) = w_A(i,j) + \sum_{k\in A}^{\text{occ}} g'_0(ik,jk). \tag{49b}$$

The first and second terms in (48) represent the electron correlation within the systems A and B, the third (fourth) term corresponds to the Coulomb interaction of an electron from A (B) with the whole atom B (A). The last term in (48) represents the Coulomb correlation between electrons of the systems A and B.

For the long-range interactions it is appropriate to apply the multipole expansions (mono- and bicentric) of the interaction potentials to simplify the last three terms in (48). Let us specify the matrix elements $w_A(i,j)$ and $w_B(i,j)$ appearing in (46), (49a) and (49b),

$$w_A(i,j)=\int \varphi_i^*(1)w_A(1)\varphi_j(1)\,d1, \tag{50a}$$

$$w_B(i,j)=\int \varphi_i^*(2)w_B(2)\varphi_j(2)\,d2, \tag{50b}$$

where $w_A(1)$ and $w_B(2)$ are the Coulomb nuclear-attraction potentials of nuclei A and B (cf. Fig. 3):

$$w_A(1)=-Z_A/r_1, \tag{51a}$$

$$w_B(2)=-Z_B/r_2, \tag{51b}$$

where $Z_{A(B)}$ is the nuclear charge of A (B). The two-particle operator $g(1,2)$ is the operator of the Coulomb mutual electronic repulsion,

$$g(1,2)=1/r_{12}. \tag{52}$$

Assuming that $R\rightarrow\infty$, these operators (51a), (51b), and (52) can be expressed by the following multipole expansions[1,33]:

$$w_A(1)=-Z_A\sum_{l_a=1}^{\infty}\frac{1}{R^{l_a+1}}\mathcal{Y}_{l_a,0}(1), \tag{53a}$$

$$w_B(2)=-Z_B\sum_{l_b=1}^{\infty}\frac{(-1)^{l_b}}{R^{l_b+1}}\mathcal{Y}_{l_b,0}(2), \tag{53b}$$

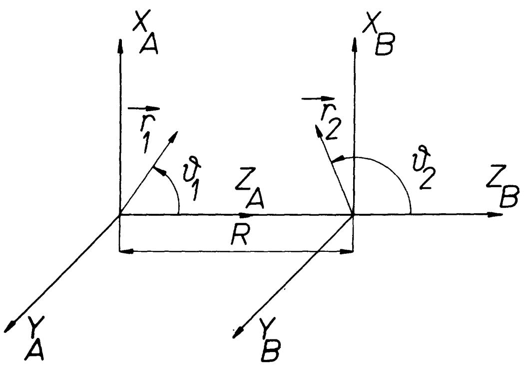

FIG. 3. Coordinate system for treating the long-range interatomic interactions.

$$g(1,2)=\sum_{l_a,l_b=0}^{\infty}\sum_{m=-l_<}^{l_<}\frac{A^m_{l_al_b}}{R^{l_a+l_b+1}}\mathcal{Y}_{l_am_a}(1)\mathcal{Y}^*_{l_bm_b}(2), \tag{53c}$$

where $l_<=\min(l_a,l_b)$. The functions $\mathcal{Y}_{lm}$ are defined by

$$\mathcal{Y}_{lm}(1)=[4\pi/(2l+1)]^{1/2}r_1^l\,Y_{lm}(\hat{r}_1), \tag{54}$$

and the coefficients $A^m_{l_al_b}$ are determined as follows[33]:

$$\begin{aligned}A^m_{l_al_b}&=(-1)^{l_b+m}(l_a+l_b)!\\&\quad\times[(l_a-m)!\,(l_a+m)!\,(l_b-m)!\,(l_b+m)!]^{-1/2}.\end{aligned} \tag{55}$$

Using these multipole expansions, the scalar quantity $e_{0,LR}$ can be written in the form

$$e_{0,LR}+W_{AB}=\sum_{k=0}^{\infty}\frac{1}{R^{k+1}}U^{(k)}, \tag{56a}$$

$$\begin{aligned}U^{(k)}=\sum_{l_a+l_b=k}\sum_{m=-l_<}^{l_<}A^m_{l_al_b}\{&\delta_{l_a,0}(N_A-Z_A)\\&+(1-\delta_{l_a,0})G^A_{l_am}\}\\\times\{\delta_{l_b,0}(N_B-Z_B)&+(1-\delta_{l_b,0})G^B_{l_bm}\},\end{aligned} \tag{56b}$$

$$\begin{aligned}G^A_{l_am}&=\sum_{i\in A}^{\text{occ}}\langle i|\mathcal{Y}_{l_am}|i\rangle,\\G^B_{l_bm}&=\sum_{i\in B}^{\text{occ}}\langle i|\mathcal{Y}_{l_bm}|i\rangle,\end{aligned} \tag{56c}$$

where $W_{AB}=Z_AZ_B/R$ is the internuclear Coulomb repulsion and $N_{A(B)}$ is the number of electrons in $A(B)$. The matrix elements $G^A_{l_am}$ and $G^B_{l_bm}$ represent the Hartree-Fock mean values of the atomic multipole moments. For atomic systems in the S state (zero total angular momentum) these matrix elements are equal to zero. Then, for the electroneutral atoms in S state these mean values are identically equal to zero.

Similarly, the one- and two-particle matrix elements from the last terms in (48) can be written in the following form: For $i,j\in A$

$$t'_A(i,j)=\sum_{k=0}^{\infty}\frac{1}{R^{k+1}}U^{(k)}_{ij}, \tag{57a}$$

$$\begin{aligned}U^{(k)}_{ij}=\sum_{l_a+l_b=k}\sum_{m=-l_<}^{l_<}&A^m_{l_al_b}\langle i|\mathcal{Y}_{l_am}|j\rangle\\&\times\{\delta_{l_b,0}(N_B-Z_B)+(1-\delta_{l_b,0})G^B_{l_b0}\},\end{aligned} \tag{57b}$$

for $i,j\in B$

$$t'_B(i,j)=\sum_{k=0}^{\infty}\frac{1}{R^{k+1}}U^{(k)}_{ij}, \tag{57c}$$

$$U_{ij}^{(k)}=\sum_{l_a+l_b=k}\sum_{m=-l_<}^{l_<}A_{l_al_b}^{m}\langle i|\mathcal{Y}_{l_bm}|j\rangle\times\{\delta_{l_a,0}(N_A-Z_A)+(1-\delta_{l_a,0})G_{l_a0}^{A}\},\tag{57d}$$

and finally

$$g_0'(ij,kl)=\sum_{k'=0}^{\infty}\frac{1}{R^{k'+1}}U_{ij,kl}^{(k')},\tag{57e}$$

$$U_{ij,kl}^{(k')}=\sum_{l_a+l_b=k'}\sum_{m=-l_<}^{l_<}A_{l_al_b}^{m}\{\delta_{l_a,0}\delta_{i,k}+(1-\delta_{l_a,0})\langle i|\mathcal{Y}_{l_am}|k\rangle\}\times\{\delta_{l_b,0}\delta_{j,l}+(1-\delta_{l_b,0})\langle i|\mathcal{Y}_{l_bm}^{*}|l\rangle\}.\tag{57f}$$

Substituting (57a), (57c), and (57e) into (48) gives the final form for the perturbation,

$$H_{1,LR}=\frac{1}{4}\Big(\sum_{ijkl\in A}+\sum_{ijkl\in B}\Big)g_0(ij,kl)N[X_i^{\dagger}X_j^{\dagger}X_lX_k]+\Big(\sum_{ij\in A}+\sum_{ij\in B}\Big)\sum_{k=0}^{\infty}\frac{1}{R^{k+1}}U_{ij}^{(k)}N[X_i^{\dagger}X_j]+\sum_{ik\in A}\sum_{jl\in B}\sum_{k'=0}^{\infty}\frac{1}{R^{k'+1}}U_{ij,kl}^{(k')}N[X_i^{\dagger}X_j^{\dagger}X_lX_k].\tag{58}$$

Now, let us turn our attention to the interpretation[1,3,33] of the individual terms of (44) describing the long-range interactions. The scalar term $e_{0,LR}+W_{AB}$ expressed by (56a)–(56c) represents the interaction of the permanent multipoles of the systems A and B. The third (fourth) term of (58) expresses the interaction of the permanent multipoles of the system B (A) with the induced multipoles of system A (B). The last term expresses the mutual interaction of the induced multipoles of the system A and B.

To formulate the many-body perturbation theory for the calculation of the long-range interatomic interactions it is necessary, similarly as in Sec. III, to introduce the diagrammatic interpretation of all terms from the perturbation $H_{1,LR}$ (see Fig. 4). According to Basilevsky and Berenfeld,[18] the horizontal border line is used. Then, the line indices above (below) the border line are taken from B (A). Now we are ready to apply the general formula (31) to the calculation of the long-range interaction energy. Using (56a) we get

$$\Delta E_{AB,LR}=\sum_{k=0}^{\infty}\frac{1}{R^{k+1}}U^{(k)}+\langle\Phi_0|\Big\{H_{1,LR}+H_{1,LR}\frac{1}{-H_0}\times H_{1,LR}+\cdots\Big\}_{C^*}|\Phi_0\rangle,\tag{59}$$

where the subscript C^* means, similarly as in (31), that we take into account only the connected ground-state diagrams and we omit the diagrams contributing merely to the correlation energy of the isolated atomic systems. These diagrams are, in our diagrammatic technique, completely either above or below the border line. The diagrammatic expression up to the second order, i.e., containing only two vertices, is presented in Fig. 5. Using the rules of the Hugenholtz graphology,[25,27] the corresponding algebraic expression is

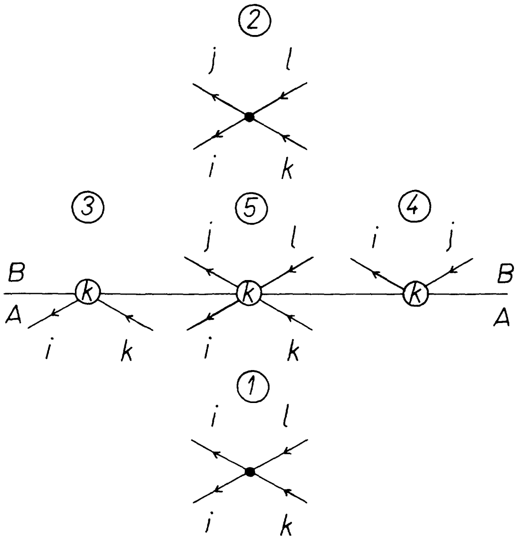

FIG. 4. Diagrammatic interpretation of individual terms of the long-range-interaction perturbation operator $H_{1,LR}$ defined by (58). The numbering of the vertices is the same as in (58).

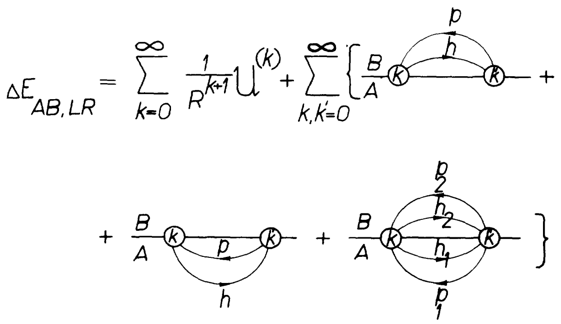

FIG. 5. Diagrammatic expression for the long-range interaction energy corresponding to Eq. (60).

$$\Delta E_{AB,LR} = \sum_{k=0}^{\infty} \frac{1}{R^{k+1}} U^{(k)} + \sum_{kk'=0}^{\infty} \frac{1}{R^{k+k'+2}} \times \left(\sum_{h\in B}^{\text{occ}} \sum_{p\in B}^{\text{un}} \frac{U_{hp}^{(k)} U_{ph}^{(k)}}{\epsilon_h - \epsilon_p} + \sum_{h\in A}^{\text{occ}} \sum_{p\in A}^{\text{un}} \frac{U_{hp}^{(k)} U_{ph}^{(k)}}{\epsilon_h - \epsilon_p} + \sum_{h_1\in A}^{\text{occ}} \sum_{p_1\in A}^{\text{un}} \sum_{h_2\in B}^{\text{occ}} \sum_{p_2\in B}^{\text{un}} \frac{U_{h_1h_2,p_1p_2}^{(k)} U_{p_1p_2,h_1h_2}^{(k')}}{\epsilon_{h_1} + \epsilon_{h_2} - \epsilon_{p_1} - \epsilon_{p_2}} \right). \tag{60}$$

For the electroneutral closed-shell atomic systems this expression is reduced to a simple one, since the matrix elements $U^{(k)}$ and $U_{ij}^{(k)}$ are identically equal to zero. Then, the long-range interaction energy corresponds only to an interaction of the induced multipoles [last term in Eq. (58)–dispersion forces].

The matrix elements $U^{(k)}$, $U_{ij}^{(k)}$, and $U_{ij,kl}^{(k')}$ can be simplified in the case where the Hartree-Fock atomic orbitals are expressed as a product of radial and angular parts. After integrating the angular parts to the Gaunt coefficients,[35] we find that the above matrix elements depend only on the radial integrals of the type

$$\int_0^{\infty} R_{nl}(r) r^k R_{n'l'}(r) r^2 \, dr, \tag{61}$$

where $R_{nl}(r)$ is the radial part of the Hartree-Fock atomic orbitals.

The correlation effects inside the systems A or B appear in the interaction energy $\Delta E_{AB,LR}$ only through the diagrammatic contributions having at least one two-particle vertex corresponding to the first or second term in Eq. (58). The present method is applicable not only in the case of two atomic (monocentric) systems, but also in the case of molecular (polycentric) systems. Unfortunately, the mathematical form of the multipole expansions [as in Eqs. (53a)–(53c)] will be much more complex than in the atom-atom cases.

VI. SUMMARY AND DISCUSSION

In Secs. II and III a general many-body perturbation theory for the calculation of the ground-state interaction energies has been formulated. The applicability of this approach strongly depends on whether the operator of perturbation (24) is "sufficiently small." This operator contains terms of two types: (i) terms describing the electron correlation within the isolated molecular systems and (ii) terms describing the intermolecular interaction. Since it follows from the numerical results for the correlation energy of small atoms or molecules, the diagrammatic perturbation method gives results which agree very well with experimental correlation energies.[36] Therefore it seems that part (i) will not bring any difficulties with the convergency of the perturbation expansions. A more complicated situation exists for part (ii), describing the intermolecular interaction. In the case of short-range interactions this part may be "so large" that the perturbation expansions will be diverging. Moreover, the assumption about the fixed geometries of the considered molecular systems will be a very rough approximation. A much more favorable situation is the case of the intermediate-range intermolecular interactions. Here, as certain numerical results indicate,[37] the perturbation approach gives quite satisfactory values for the interaction energies. These results indicate that the presented diagrammatic method might be of value mainly in the framework of the *ab initio* calculations. Already, for the intermediate-range interactions, the conditions for existence of the expansion (8) [cf. comment below Eq. (7b)] may be fulfilled, which allows us to express the matrix elements $\Delta h(i,j)$ and $\Delta g(ij,kl)$ through the products of the original matrix elements $h_0(i,j)$ and $g_0(ij,kl)$ and the overlap integrals S_{ij}. In this case our general theory is reduced to the diagrammatic method of Basilevsky and Berenfeld.[18] Their approach takes explicitly into account the overlap integrals, which produce very complicated rules for the construction of the diagrams.

The applications of the present theory to the study of the intermolecular interactions in the framework of semiempirical Hamiltonians[38] frequently used in quantum chemistry are very interesting. In the extended Hückel theory[39] the corresponding effective Hamiltonian contains only one-particle terms, repulsion between electrons (two-particle terms) being neglected. In this case the Hamiltonian (16) is built up only from the matrix elements $h_0(i,j)$ and $\Delta h(i,j)$. Using the expansion (9) and the general formula (31) for the interaction energy, we have obtained a result[40] which is identical with Imamura's expression.[41] The semiempirical CNDO (complete-neglect-of-differential-overlap) of INDO (intermediate-neglect-of-differential-overlap) methods[42] contain the electron repulsion in a some approximate way, i.e., the CNDO or INDO Hamiltonian contains the one-particle as well as two-particle terms. Assuming the validity of the zero-differential-overlap (ZDO) approximation[42] between interacting systems also, the spin orbitals of the "supersystem" will form an orthonormal set automatically. Therefore we do not need to perform the orthogonalization procedure (4). A similar situation also exists in the case of construction of the long-range Hamiltonian H_{LR} in Sec. V, where it is justified by assumption that overlap tends to zero when $R\to\infty$. Then, the Hamiltonian of the "supersystem" in the CNDO or INDO method is formally identical with the long-range Hamiltonian (44), where the perturbation should be modified by the additional one-particle terms

$$\sum_{i\in A}\sum_{j\in B} h_0(i,j)(N[X_i^\dagger X_j]+N[X_j^\dagger X_i]), \qquad (62)$$

which, in the case of long-range interactions, are equal to zero. For the individual terms of the perturbation constructed in this way, it is possible to introduce the diagrammatic interpretation and then to use the general formula (31) for the calculation of the interaction energy. This approach has been applied to the study of interactions between small organic molecules.[43]

The diagrammatic perturbation theory for the long-range interatomic interactions elaborated in Sec. V allows us the possibility of using the classical interpretation with the help of permanent and induced multipoles. An application of this method to the calculation of the long-range interaction for He-He is in progress.[44]

In conclusion, we wish to stress that the present general diagrammatic perturbation theory of the intermolecular interactions covers many types of the many-body approaches for studying this problem and may serve as a common procedure for handling them.

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