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Perturbation theory of effective interactions for many-electron systems in terms of nonorthogonal basis states

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Diagrammatic quasidegenerate Rayleigh-Schrödinger perturbation theory is used for the construction of an effective Hamiltonian, defined completely in a finite-dimensional model space. This effective Hamiltonian, containing one-, two-, three-, etc. particle terms, may serve as a useful tool for constructing an *ab initio* theory of quantum semiempirical effective Hamiltonians, widely used in quantum molecular and atomic physics, and also in some modified form in solid-state physics.

I. INTRODUCTION

The purpose of the present communication is to call attention to the interesting and fruitful possibility of introducing an effective Hamiltonian by the up-to-date diagrammatic (quasi-) degenerate Rayleigh-Schrödinger perturbation theory[1-8] (QD-RSPT). This theoretical many-body technique was *initially elaborated* in the framework of the "microscopic" theory of nuclei[9-12] as an adequate apparatus for introducing effective interactions of the many-nucleon system. Here, following Bloch and Horowitz,[13] an open-shell system (in principle also closed-shell systems) is divided into two subsystems: (i) an inert "core" which covers a closed-shell many-particle subsystem, and (ii) valence particles which determine the "open-shell nature" of the total system. Moreover, it is expected that the behavior of such a system is *mainly determined* by the properties of the valence particles, while the influence of the inert "core" emerges merely through higher-order perturbation effects. In other words, the method may be interpreted as a procedure reducing the number of particles explicitly treated. Generally, this idea has wide applicability also in other parts of many-body theory, namely, in quantum atomic, molecular, and solid-state physics.

A mathematical representation of this approach, in the framework of quantum many-body theory, is usually realized through the concept of one- and two-particle effective matrix elements (in quantum chemistry called the semiempirical parameters), actual numerical values of which are fitted to obtain agreement of some observables (e.g., energetic terms) with experiment.

A theoretical justification and foundation of these semiempirical parameters, which would enable their *complete a priori physical determination and understanding*, is a very interesting problem of the present quantum theory of many-electron systems.

Recently, the first introductory step toward solving this problem was made by Freed[14-17] using (i) an energy-dependent model Hamiltonian determined with the use of the Brillouin-Wigner perturbation theory[18] and (ii) the Sinanoğlu-type cluster functions.[19] In this theoretical approach the resulting effective matrix elements are dependent on energy as well as on the valence-bond configurations of the remaining electrons. On the basis of these two dependences Freed deduces some general properties of the semiempirical parameters, e.g., how these parameters change with the electronic state, or with the degree of ionicity of the state. In the present communication we shall use *another* approach for construction of the effective Hamiltonian, namely, the one based on the diagrammatic QD-RSPT,[8] where both dependences of the effective matrix elements are completely removed. Therefore, the above-mentioned conclusions of Freed may be premature; they seem to be only an artifact of his method which was used for the construction of the effective Hamiltonian.

Standard nondegenerate diagrammatic perturbation theory[20,21] has been used in order to obtain a simple approach for the introduction of effective interactions of atomic systems.[22,23] Although this theoretical construction of the effective interactions is very simple and straightforward for studying complex atomic systems, we are afraid that it is applicable only for monocentric atomic systems, where the atomic orbitals used are automatically identical to an orthonormal set of one-particle functions. Furthermore, such effective interactions are valid only for nondegenerate one-determinantal trial wave functions, wherewith the above-mentioned simple approach can be obtained as a limiting case of the presented more general method, where a trial wave function is taken as a linear combination of Slater determinants.

The outline of the present communication is as follows: In Sec. II the full original Hamiltonian in the second quantization formalism is constructed.

In Sec. III the effective Hamiltonian will be constructed by the diagrammatic QD-RSPT.

II. CONSTRUCTION OF THE ORIGINAL FULL HAMILTONIAN

In this section we introduce the notations and concepts that are necessary for the further development of the diagrammatic perturbation theory of the semiempirical effective Hamiltonians. First of all we shall introduce a nonorthogonal set of normalized atomic spin orbitals (ASOs). Following our recent communications[24,25] concerning the many-body theory of the intermolecular interactions, we construct an orthonormal set of the one-particle functions from the previous nonorthogonal one by the Löwdin symmetrization procedure.[26] Finally, the second-quantization formalism will be introduced, in which the creation and annihilation operators are defined with respect to this orthogonalized set of ASOs.

Let us have a set of ASOs (strictly localized on the individual nuclei of the given molecular system) which forms the column vector

$$\Phi \equiv \{ |\varphi_i\rangle ;\ i = 1, 2, \ldots \} . \tag{1}$$

Starting from intuitive quantum chemical assumptions, this set of ASOs can be divided into three disjoint subsets, namely, (i) the core orbitals $\{|\varphi_i\rangle ; i \in C\}$, (ii) the valence orbitals $\{|\varphi_i\rangle ;\ i \in V\}$, and finally, the excited orbitals $\{|\varphi_i\rangle ;\ i \in E\}$. Unifying these first two subsets, the *minimum basis set* of ASOs is obtained, which is the basic concept of all semiempirical theories.[27-30] The matrix of the overlap integrals between individual elements of (1) is defined as follows:

$$A = 1 + S \equiv \{ A_{ij} = \delta_{ij} + S_{ij} ;\ i, j = 1, 2, \ldots \} , \tag{2a}$$

$$S_{ij} = (1 - \delta_{ij}) \langle \varphi_i | \varphi_j \rangle . \tag{2b}$$

Let us now introduce the column vector[26]

$$\Psi = (1 + S)^{-1/2} \Phi \equiv \{ |\psi_i\rangle ;\ i = 1, 2, \ldots \} , \tag{3a}$$

elements of which form an orthonormal system, i.e., $\Psi^\dagger \Psi = 1$, or $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ for all possible $i, j = 1, 2, \ldots$. Assuming that all the absolute values of the eigenvalues of the matrix $A = 1 + S$ are less than one,[31] the rhs of (3a) can be expressed as a power series[25] in S,

$$\Psi = \Phi - \tfrac{1}{2} S \Phi + \tfrac{3}{8} S^2 \Phi - \cdots , \tag{3b}$$

or in component form,

$$|\psi_i\rangle = |\varphi_i\rangle - \tfrac{1}{2} \sum_j S_{ij} |\varphi_j\rangle + \tfrac{3}{8} \sum_{jk} S_{ij} S_{jk} |\varphi_k\rangle - \cdots . \tag{3c}$$

We then have a one-to-one correspondence between the elements of the column vectors Φ and Ψ realized by the equality $|\psi_i\rangle = |\varphi_i\rangle$, which is fulfilled merely when the overlap between different ASOs is neglected [an analog of the zero differential approximation (ZDOA)], i.e., $S_{ij} = 0$.

After these introductory remarks, let us now turn our attention to the construction of the *original full Hamiltonian* describing the given molecular system. In the second-quantization formalism this Hamiltonian can be written in the form[32,33]

$$H = \sum_{ij} h(i, j) X_i^\dagger X_j + \tfrac{1}{4} \sum_{ijkl} g(ij, kl) X_i^\dagger X_j^\dagger X_l X_k , \tag{4}$$

where the $X_i^\dagger$ (X_j) are creation (annihilation) operators defined on the orthonormal set of ASOs $\{|\psi_i\rangle\}$ introduced by (3). One- and two-particle matrix elements from (4) are determined by

$$h(i, j) = \int \psi_i^*(1) h(1) \psi_j(1)\, d1 , \tag{5a}$$

$$g(ij, kl) = \iint \psi_i^*(1) \psi_j^*(2) g(1, 2)(1 - P_{12}) \psi_k(1) \psi_l(2)\, d1\, d2 , \tag{5b}$$

where P_{12} is a transposition operator, $g(1, 2)$ is the two-particle operator for the interaction between electrons, and $h(1)$ is the one-particle operator (Hamiltonian) describing motion of an electron in the field of the fixed molecular skeleton (the Born-Oppenheimer approximation is used).

For further considerations it is appropriate to introduce an unperturbed ground-state vector of the "core" subsystem,[13]

$$|\Phi_0\rangle = \prod_{i \in C} X_i^\dagger |0\rangle , \tag{6}$$

where the product index runs over all core ASOs, and $|0\rangle$ is the normalized vacuum state vector. Then, using Wick's theorem,[32-34] the original full Hamiltonian (4) can be rewritten in the normal form

$$H = \mathcal{E}_0 + H_{(1)} + H_{(2)} . \tag{7}$$

The scalar quantity $\mathcal{E}_0$ is defined by

$$\mathcal{E}_0 = \sum_{i \in C} h(i, i) + \tfrac{1}{2} \sum_{i, j \in C} g(ij, ij) . \tag{8}$$

The one-particle part $H_{(1)}$ of (7) is given by

$$H_{(1)} = \sum_{i, j} f(i, j) N[X_i^\dagger X_j] ; \tag{9}$$

here $N[\cdots]$ is the normal product[34] defined with respect to $|\Phi_0\rangle$, and the $f(i, j)$ are determined as follows:

$$f(i, j) = h(i, j) + \sum_{k \in C} g(ik, jk) . \tag{10}$$

In this connection it is interesting to note that the matrix elements $f(i,j)$ may be formally interpreted as matrix elements of the Hartree-Fock operator constructed with respect to $|\Phi_0\rangle$. Finally, the two-particle part $H_{(2)}$ of (7) has the form

$$H_{(2)}=\tfrac{1}{4}\sum_{ijkl} g(ij,kl)N[X_i^\dagger X_j^\dagger X_l X_k]. \tag{11}$$

When (3c) is substituted into Eqs. (5), the power series for the one- and two-particle integrals can be easily obtained,

$$h(i,j)=\sum_{n=0}^{\infty} h^{(n)}(i,j), \tag{12a}$$

$$g(ij,kl)=\sum_{n=0}^{\infty} g^{(n)}(ij,kl), \tag{12b}$$

where $h^{(0)}(i,j)$ and $g^{(0)}(ij,kl)$ are determined by

$$h^{(0)}(i,j)=\int \varphi_i^*(1)h(1)\varphi_j(1)\,d1, \tag{13a}$$

$$g^{(0)}(ij,kl)=\iint \varphi_i^*(1)\varphi_j^*(2)g(1,2)(1-P_{12})\times\varphi_k(1)\varphi_l(2)\,d1\,d2, \tag{13b}$$

and for $n\geqslant 1$ the individual contributions to the rhs of Eqs. (12) are products of n overlap integrals S_{ij} and an original (nonorthogonalized) one-particle (13a) or two-particle (13b) integral. Then, these matrix elements (for $n\geqslant 1$) are identically equal to zero when $S_{ij}=0$, i.e., when the original basis $\{|\varphi_i\rangle\}$ of ASOs forms an orthonormal system, the following simple relations are true: $h(i,j)=h^{(0)}(i,j)$ and $g(ij,kl)=g^{(0)}(ij,kl)$. Similarly, the matrix elements $f(i,j)$ defined by (10) can then be expressed as follows:

$$f(i,j)=\sum_{n=0}^{\infty} f^{(n)}(i,j), \tag{14a}$$

$$f^{(n)}(i,j)=h^{(n)}(i,j)+\sum_{k\in C} g^{(n)}(ik,jk). \tag{14b}$$

Thus, the Hamiltonian (7) can be rewritten in the final form appropriate for an application of the diagrammatic perturbation theory:

$$H=\mathcal{E}_0+H_0+H_1, \tag{15}$$

where the scalar part $\mathcal{E}_0$ defined by (8) can be expressed, analogously to Eqs. (12), as an expansion

$$\mathcal{E}_0=\mathcal{E}_0^{(0)}+\sum_{n=1}^{\infty}\mathcal{E}_0^{(n)}\equiv\mathcal{E}_0^{(0)}+\epsilon_0. \tag{16}$$

Here $\mathcal{E}_0^{(0)}$ may be interpreted as an unperturbed (zero-order) ground-state energy of the "core" subsystem, when the overlap between core ASOs is neglected.

The operator H_0 from the rhs of (15) (called the *unperturbed Hamiltonian*) is given by

$$H_0=\sum_i \epsilon_i N[X_i^\dagger X_i], \tag{17a}$$

$$\epsilon_i=f^{(0)}(i,i), \tag{17b}$$

where the $\epsilon_i=f^{(0)}(i,i)$'s play the role of one-particle (Hartree-Fock) energies.

Finally, the operator H_1 (called the *perturbation*) from the rhs of (15) has the form

$$H_1=\sum_{ij}\sum_{n=0}^{\infty}(1-\delta_{n,0}\delta_{ij})f^{(n)}(i,j)N[X_i^\dagger X_j]+\tfrac{1}{4}\sum_{ijkl}\sum_{n=0}^{\infty} g^{(n)}(ij,kl)N[X_i^\dagger X_j^\dagger X_l X_k]. \tag{18}$$

The perturbation H_1 contains one-particle (first summation) as well as two-particle (second summation) terms, the diagrammatic interpretation of which in the framework of the Hugenholtz graphology[21,35] is presented in Fig. 1. Let us note that the perturbation H_1 describes two effects: (i) the correlation between electrons, and (ii) nonorthogonality effects. These last effects are canceled when the original basis set $\{|\varphi_i\rangle\}$ of ASOs forms an orthonormal system. From the property of the normal product, $\langle\Phi_0|N[\cdots]|\Phi_0\rangle=0$, it follows that matrix element of H_1 between two $|\Phi_0\rangle$ is zero, i.e., $\langle\Phi_0|H_1|\Phi_0\rangle=0$.

The one-particle core states contained in $|\Phi_0\rangle$ are called *hole states*, and either valence or excited one-particle states, *particle states* (cf. Fig. 2). The eigensystem of the unperturbed Hamiltonian H_0 can be generated from $|\Phi_0\rangle$ in the following way:

$$H_0|\Phi_0\rangle=0, \tag{19a}$$

$$H_0|\Phi_0'\rangle=E_0'|\Phi_0'\rangle, \tag{19b}$$

where $|\Phi_0'\rangle=X_{p_1}^\dagger X_{p_2}^\dagger\cdots X_{h_1}X_{h_2}\cdots|\Phi_0\rangle$, and E_0'

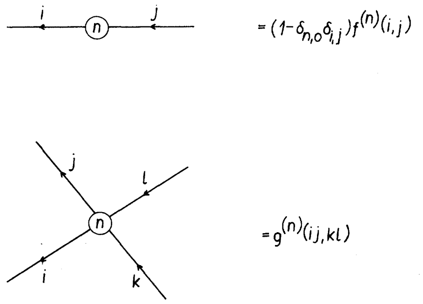

FIG. 1. Diagrammatic representation of the individual terms of the perturbation H_1 defined by Eq. (18).

$=\epsilon_{p_1}+\epsilon_{p_2}+\cdots-\epsilon_{h_1}-\epsilon_{h_2}-\cdots$ for $p_1, p_2, \ldots \in V+E$, and $h_1, h_2, \ldots \in C$.

Using the Goldstone-Hugenholtz linked-cluster theorem,[20,21] the diagrammatic expression for the exact ground-state energy of the "core" subsystem (described in the zero-order approximation by $|\Phi_0\rangle$) is obtained (see Fig. 3):

$$E_0^{\text{core}} = \mathcal{E}_0 + \langle\Phi_0| \left\{ H_1 \frac{1}{-H_0} H_1 + H_1 \frac{1}{-H_0} H_1 \frac{1}{-H_0} H_1 + \cdots \right\}_C |\Phi_0\rangle , \tag{20}$$

where the subscript C means that only connected ground-state diagrams contribute.

III. DIAGRAMMATIC PERTURBATION THEORY OF THE EFFECTIVE HAMILTONIAN

For the construction of the effective Hamiltonian, we use the diagrammatic quasidegenerate Rayleigh-Schrödinger perturbation theory (QD-RSPT).[8,36,37] Its main features have recently been given[8,36,37] (cf. also Refs. 38 and 39), and therefore they will be repeated here only in a rather sketchy form.

Let us assume that the perturbed and unperturbed eigenproblems have the form

$$HP_\lambda = E_\lambda P_\lambda , \tag{21a}$$

$$H_0 P_0(K) = E_K^{(0)} P_0(K) , \tag{21b}$$

where H and H_0 are the original full (perturbed) and unperturbed Hamiltonians determined by (15) and (17a); P_λ, $P_0(K)$ and E_λ, $E_K^{(0)}$ are perturbed and unperturbed eigenprojectors and eigenenergies, respectively. We shall assume that the perturbed eigenenergies E_λ's (in contrast to $E_K^{(0)}$'s) are nondegenerate, i.e., $\text{Tr}(P_\lambda)=1$ and $\text{Tr}[P_0(K)] = d_K \geq 1$. Let us introduce a d-dimensional *model space* Ω_0 defined by the projection operator

$$P_0 = \sum_{K \in \mathcal{K}_0} P_0(K) , \tag{22a}$$

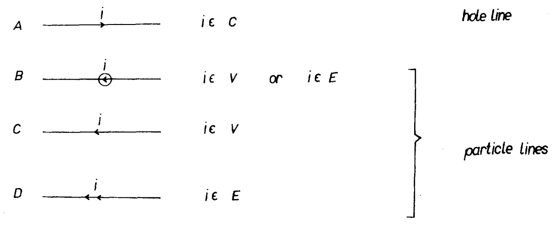

FIG. 2. Diagrammatic convention for the hole and particle lines, where (*A*) is the hole line, (*B*) is the particle line either for valence or excited one-particle state, (*C*) is the particle line for the valence state, and (*D*) is the particle line for the excited state.

$$\text{Tr}(P_0) = \sum_{K \in \mathcal{K}_0} d_K = d , \tag{22b}$$

$$\bar{H}_0 = P_0 H_0 P_0 = H_0 P_0 = P_0 H_0 = \sum_{K \in \mathcal{K}_0} E_K^{(0)} P_0(K) , \tag{22c}$$

where the summations run over all unperturbed states K taken from the fixed finite set $\mathcal{K}_0$. If we assume that H_1 is an "analytical perturbation,"[40] then there exist d perturbed eigenenergies $\{E_{\lambda_1}, E_{\lambda_2}, \ldots, E_{\lambda_d}\} \equiv \{E_\lambda, \lambda \in \mathcal{K}\}$ tending to some unperturbed eigenenergy $E_K^{(0)}$ from $\{E_K^{(0)}; K \in \mathcal{K}_0\}$ when the perturbation H_1 is "switched off," i.e., when $H_1 \to 0$.

After these introductory remarks concerning a one-to-one correspondence between the perturbed and unperturbed eigenenergies, let us focus our attention on the actual construction of the model space Ω_0 in the case when the unperturbed Hamiltonian is defined by (17) and its eigensystem can be generated according to expressions (19a) and (19b). We introduce this model space as a subspace spanned by *all possible* p-particle (where p is the number of the occupied particle-valence states) unperturbed state vectors, i.e.,

$$\Omega_0 \equiv \{ |\Phi_K\rangle ; \text{ for all possible } K \in \mathcal{K}_0 \} , \tag{23}$$

where the "configuration" index K is taken from the finite set $\mathcal{K}_0$ of *all possible* p-particle configurations

$$|\Phi_K\rangle = X_{k_1}^\dagger X_{k_2}^\dagger \cdots X_{k_p}^\dagger |\Phi_0\rangle . \tag{24}$$

Here, $|\Phi_0\rangle$ is the "core" unperturbed state vector defined by (6), and the "configuration" index K is determined as follows:

$$K \equiv \{ k_1 < k_2 < \cdots < k_p \} , \tag{25a}$$

$$k_1, k_2, \ldots, k_p \in V . \tag{25b}$$

In other words, the model space Ω_0 is spanned by *all possible* N-electron Slater determinants ($|\Phi_K\rangle$ in the x representation) with fixed "core" (q-particle subsystem), and the remaining p electrons ($N=p+q$) occupy merely the valence ASOs. In the Freed terminology,[16] this model space Ω_0 is equivalent to his "chemical sea." The unperturbed state vectors $|\Phi_K\rangle$'s, introduced by (22), form an eigensystem of the unperturbed Hamiltonian (17a),

$$H_0 |\Phi_K\rangle = E_K^{(0)} |\Phi_K\rangle , \tag{26a}$$

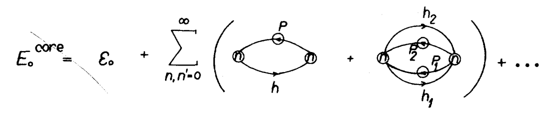

FIG. 3. Diagrammatic expression "up to the second order" (cf. Ref. 41) for the exact ground-state energy of the "core" subsystem.

$$E_K^{(0)} = \epsilon_{k_1} + \epsilon_{k_2} + \cdots + \epsilon_{k_p} . \tag{26b}$$

Then, the unperturbed eigenprojector $P_0(K)$ appearing in (21b) and (22a)–(22c) may be expressed as

$$P_0(K) = |\Phi_K\rangle\langle\Phi_K| . \tag{27}$$

Now, we are ready to introduce the *model eigenproblem* completely defined in the model space (23), which is the basic concept of the diagrammatic QD-RSPT,

$$H_{LC}|\varphi_\lambda\rangle = \Delta E_\lambda |\varphi_\lambda\rangle , \tag{28}$$

where $|\varphi_\lambda\rangle \in \Omega_0$ for all possible $\lambda \in \mathcal{K}$. The perturbed eigenenergy E_λ is defined by

$$E_\lambda = \Delta E_\lambda + E_0^{\text{core}} . \tag{29}$$

Here, E_0^{core} is the perturbed (exact) energy of the "core" subsystem which in the framework of the diagrammatic nondegenerate perturbation is determined by (20). Following our recent studies, the *model Hamiltonian* H_{LC} from the lhs of (28) can be exactly determined by an expression which has (i) a proper counterpart in the formal QD-RSPT, and (ii) a simple diagrammatic interpretation compatible with the Brandow[2] folded-diagram approach. Unfortunately, this simple possibility has one serious drawback; namely, the resulting model Hamiltonian is a non-Hermitian operator. This is a very unpleasant feature for its further applications. Therefore, in the following theoretical considerations, concerning the construction of the effective Hamiltonian, we shall use an approximate straightforward possibility[36] to obtain a Hermitian model Hamiltonian H_{LC} by a simple symmetrization of the non-Hermitian model Hamiltonian of the above-mentioned theory. Thus

$$H_{LC} \cong \tfrac{1}{2}(\hat{H}_{LC} + \hat{H}_{LC}^\dagger) . \tag{30}$$

Here, $\hat{H}_{LC}$ is the non-Hermitian model Hamiltonian determined, up to the third order, as follows:

$$\begin{aligned}\hat{H}_{LC} = {} & P_0 H_0 P_0 + \{P_0 H_1 P_0\}_{LC} + \sum_{K\in\mathcal{K}_0} \left\{ P_0 H_1 \frac{1-P_0}{E_K^{(0)} - H_0} H_1 P_0(K) \right\}_{LC} + \sum_{K\in\mathcal{K}_0} \left\{ P_0 H_1 \frac{1-P_0}{E_K^{(0)} - H_0} H_1 \frac{1-P_0}{E_K^{(0)} - H_0} H_1 P_0(K) \right\}_{LC} \\ & - \sum_{K,K'\in\mathcal{K}_0} \left\{ P_0 H_1 \frac{1-P_0}{(E_K^{(0)} - H_0)(E_{K'}^{(0)} - H_0)} H_1 P_0(K') H_1 P_0(K) \right\}_{LC} + \cdots .\end{aligned} \tag{31}$$

The subscript LC means that only those terms contribute which are in the Hugenholtz graphology[21,35] denoted as linked and connected. The higher-order terms appearing in the rhs of (31) can be constructed by a simple recurrence formula.[36] Let us note that the terms from the rhs of (31) which have an intermediate state between two perturbations (vertices) from the model space [see for example the last term in (31)] can be properly interpreted by Brandow's folded diagrams.

Since the model eigenproblem (28) is completely defined in the model space, the eigenfunctions $|\varphi_\lambda\rangle$ should be determined as a linear combination of the unperturbed state vectors $|\Phi_K\rangle$, i.e.,

$$|\varphi_\lambda\rangle = \sum_{K\in\mathcal{K}_0} c_{K\lambda} |\Phi_K\rangle . \tag{32}$$

The model eigenproblem (28) can be rewritten in the matrix form

$$\underline{H}_{LC}\underline{c}_\lambda = \Delta E_\lambda \underline{c}_\lambda , \tag{33}$$

where H_{LC} is a Hermitian matrix ($d\times d$ type) built-up from the matrix elements $\langle\Phi_K|H_{LC}|\Phi_L\rangle$, and $\underline{c}_\lambda$ is a column vector of $c_{K\lambda}$ coefficients. Because the model Hamiltonian contains *only* linked-connected contributions, it is possible to introduce an effective Hamiltonian $\mathcal{H}_{\text{eff}}$ by the following defining identity:

$$\langle\Phi_K|H_{LC}|\Phi_L\rangle \equiv \langle\Phi_K|\mathcal{H}_{\text{eff}}|\Phi_L\rangle . \tag{34}$$

In the second-quantization formalism $\mathcal{H}_{\text{eff}}$ can be expressed in the following form (the principal result of this section):

$$\mathcal{H}_{\text{eff}} = \sum_{t=1}^{p} \mathcal{H}_{\text{eff}}^{(t)} , \tag{35a}$$

$$\mathcal{H}_{\text{eff}}^{(t)} = \frac{1}{t!} \sum_{i_1\ldots i_t\in V} \sum_{j_1\ldots j_t\in V} h_{\text{eff}}^{(t)}(i_1\ldots i_t, j_1\ldots j_t) \times N[X_{i_1}^\dagger \cdots X_{i_t}^\dagger X_{j_t} \cdots X_{j_1}] . \tag{35b}$$

Here, the matrix elements $h_{\text{eff}}^{(t)}(i_1\ldots i_t, j_1\ldots j_t)$ from the t-particle operator $\mathcal{H}_{\text{eff}}^{(t)}$ are defined [in accordance with (30)] as follows:

$$\begin{aligned} h_{\text{eff}}^{(t)}(i_1\ldots i_t, j_1\ldots j_t) = {} & \epsilon_{i_1}\delta_{t,1}\delta_{i_1,j_1} \\ & + \tfrac{1}{2}[v_{\text{eff}}^{(t)}(i_1\ldots i_t, j_1\ldots j_t) \\ & + v_{\text{eff}}^{(t)*}(j_1\ldots j_t, i_1\ldots i_t)] ,\end{aligned} \tag{36}$$

where the t-particle matrix elements $v_{\text{eff}}^{(t)}(i_1\ldots i_t, j_1\ldots j_t)$ express a *summation of all possible linked-connected diagrams* with outgoing (incoming) valence particle lines indexed by $i_1, \ldots, i_t$ $(j_1, \ldots, j_t)$; cf. Fig. 4. The diagrammatic expression up to the second order[41] for the matrix elements $v_{\text{eff}}^{(1)}(i,j)$ and $v_{\text{eff}}^{(2)}(i_1i_2, j_1j_2)$ are presented in Figs. 5 and 6, where, for the sake of simplicity, for the last two-particle matrix elements only the basic diagrammatic skeletons are presented. Using the rules of the Hugenholtz graphology,[21,35] we get for the matrix elements $v_{\text{eff}}^{(1)}(i,j)$,

$$
\begin{aligned}
v_{\text{eff}}^{(1)}(i,j) = {} & \sum_{n=0}^{\infty} (1-\delta_{n,0}\delta_{i,j}) f^{(n)}(i,j) \\
& + \sum_{n,n'=0}^{\infty} \Bigg\{ \sum_{p\in E} \frac{f^{(n)}(i,p) f^{(n')}(p,j)}{\epsilon_j - \epsilon_p} - \sum_{h\in C} \frac{f^{(n)}(h,j) f^{(n')}(i,h)}{\epsilon_h - \epsilon_i} + \tfrac{1}{2} \sum_{p_1,p_2\in V+E} \sum_{h_1\in C} \frac{g^{(n)}(h_1 i, p_1p_2) g^{(n')}(p_1p_2, h_1 j)}{\epsilon_{h_1} + \epsilon_j - \epsilon_{p_1} - \epsilon_{p_2}} \\
& \quad - \tfrac{1}{2} \sum_{h_1,h_2\in C} \sum_{p_1\in V+E} \frac{g^{(n)}(h_1h_2, p_1 j) g^{(n')}(p_1 i, h_1h_2)}{\epsilon_{h_1} + \epsilon_{h_2} - \epsilon_{p_1} - \epsilon_i} - \sum_{h_1\in C} \sum_{p_1\in V+E} \frac{f^{(n)}(h_1, p_1) g^{(n')}(i p_1, h_1 j)}{\epsilon_{h_1} - \epsilon_{p_1} - \epsilon_{p_2} + \epsilon_j} \\
& \quad - \sum_{h_1\in C} \sum_{p_1\in V+E} \frac{g^{(n)}(i h_1, p_1 j) f^{(n')}(p_1, h_1)}{\epsilon_{h_1} - \epsilon_{p_1}} + \cdots \Bigg\} .
\end{aligned}
\tag{37}
$$

A similar expression may also be obtained for the matrix elements $v_{\text{eff}}^{(2)}(i_1i_2, j_1j_2)$. Unfortunately, these expressions are slightly more complicated than (37). They can be obtained directly from Fig. 6 by prescribing to outgoing and incoming valence lines all the possible combinations of indices i_1, i_2 and j_1, j_2, respectively. This procedure can be easily extended for the construction of the three-, four-, ..., p-particle matrix elements $v_{\text{eff}}^{(t)}(i_1 \ldots i_t, j_1 \ldots j_t)$ by taking into account all possible proper diagrammatic contributions. From the detailed inspection of these perturbation expressions for the matrix elements $v_{\text{eff}}^{(t)}(i_1i_2, j_1j_2)$, one may conclude that these contributions can be divided into two main classes: (i) The zero-order contribution with $n=0$, i.e., the nonorthogonality effects not considered, and (ii) the mixture of the correlation and nonorthogonality effects. This last class of the diagrammatic contributions contains the zero-order (with $n \geq 1$) as well as the higher-order diagrams. Thus,

$$v_{\text{eff}}^{(1)}(i,j) = (1-\delta_{ij}) f^{(0)}(i,j) + \Delta^{(1)}(i,j), \tag{38a}$$

$$v_{\text{eff}}^{(2)}(i_1i_2, j_1j_2) = g^{(0)}(i_1i_2, j_1j_2) + \Delta^{(2)}(i_1i_2, j_1j_2), \tag{38b}$$

and for $t \geq 3$,

$$v_{\text{eff}}^{(t)}(i_1 \ldots i_t, j_1 \ldots j_t) = \Delta^{(t)}(i_1 \ldots i_t, j_1 \ldots j_t), \tag{38c}$$

where Δ's denote the mixture of the correlation and nonorthogonality effects. In the "zero-order" approximation, the matrix elements $h_{\text{eff}}^{(t)}(\ldots, \ldots)$

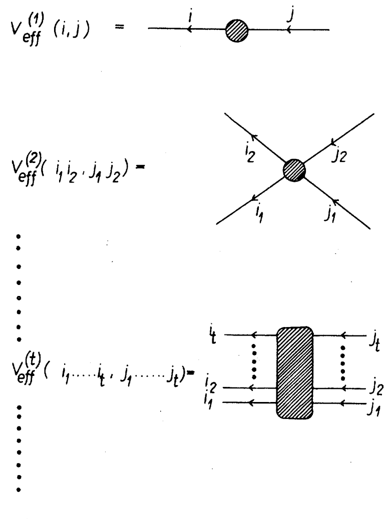

FIG. 4. Schematic diagrammatic interpretation of the individual matrix elements of the effective Hamiltonian defined by Eq. (35). The blocks represent the summation of all possible proper linked-connected diagrams.

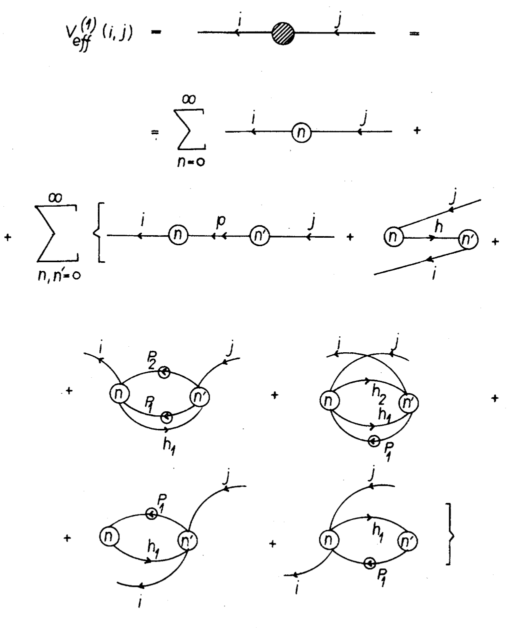

FIG. 5. Diagrammatic expression "up to the second order" (cf. Ref. 41) for the matrix elements $v_{\text{eff}}^{(1)}(i,j)$.

defined by (36) may be written as follows:

$$h_{\text{eff}}^{(1)}(i,j) \cong f^{(0)}(i,j)$$

$$= h^{(0)}(i,j) + \sum_{k\in C} g^{(0)}(ik,jk)\,, \tag{39a}$$

$$h_{\text{eff}}^{(2)}(i_1 i_2, j_1 j_2) \cong g^{(0)}(i_1 i_2, j_1 j_2)\,, \tag{39b}$$

$$h_{\text{eff}}^{(t)}(i_1 \ldots i_t, j_1 \ldots j_t) \cong 0\,, \tag{39c}$$

for $3 \leqslant t \leqslant p$. This means, that in the "zero-order" approximation the effective Hamiltonian $\mathcal{H}_{\text{eff}}$ is equal to the full original Hamiltonian (15) when its nonorthogonality terms are neglected. Accepting the above-mentioned approximations (39), the solution of the model eigenproblem (28) is then equivalent to a solution of the original Schrödinger equation in the model space Ω_0 defined by (23)–(25), where the perturbed energy of the "core" subsystem is equal to $\mathcal{E}_0^{(0)}$ from (16), and the orthonormality of the original set of ASOs is assumed.

IV. SUMMARY AND DISCUSSION

First, a few remarks about some general features of the diagrammatic QD-RSPT, which is taken as a theoretical background in our approach for constructing the effective Hamiltonian: The diagrammatic (quasi-) degenerate RSPT has been initially developed and widely used in the "microscopic" theory of nuclei[9-12] as a powerful "machinery" for a theoretical treatment of "open-shell" nuclei as well as for an introduction of effective interactions. This last problem is closely related with attempts to support and establish firmly the shell model of nuclei. Unfortunately, applications of the diagrammatic QD-RSPT are limited, up to now, by the fact that, in this method, an exact theory of the model Hamiltonian exists only for its non-Hermitian form. As has been mentioned in our recent work,[37] the formulation of a diagrammatic QD-RSPT with Hermitian as well as non-Hermitian model Hamiltonians should be realized hand in hand with the formulation of its formal (without diagrammatic interpretation) theoretical counterpart with *simple recurrence rules* for the construction of the individual perturbation contributions. Some progress in this direction has been made,[37] but unfortunately, its further generalization to a diagrammatic version will be a rather complex problem, probably. Therefore, let us turn our attention to the possibility of constructing the approximate diagrammatic Hermitian model Hamiltonian resulting from the surprising observation[36,37] that, up to third order, the formal Hermitian model Hamiltonian can be obtained by a simple symmetrization of the non-Hermitian model Hamiltonian. This observation can be generalized to fourth order in the case of the degenerate RSPT.[42,43] A similar approximate possibility was discussed by Brandow[11] and Sandars[6] as a proper and probably accurate resolution of the above-mentioned difficulty. Generally speaking, the diagrammatic Hermitian model Hamiltonian may be taken as a well established method of the many-body theory, and some additional difficulties of its construction are of more computational than theoretical significance. To conclude these remarks we note that the present approximate procedure for the construction of the Hermitian diagrammatic model Hamiltonian has been successfully used for the direct calculation of low-lying ionization potentials[38] and excitation energies,[39] respectively, and also for construction of a one-particle pseudoeigenvalue problem determining the Brueckner and/or generalized natural orbitals.[44]

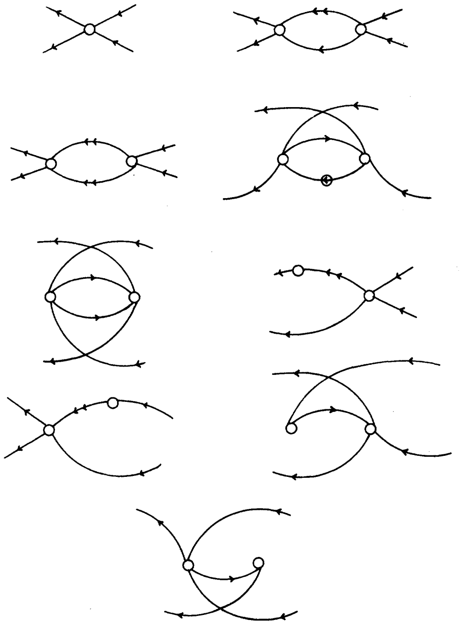

FIG. 6. All possible "first" and "second" order skeletons of the diagrams contributing to the matrix elements $v_{\text{eff}}^{(2)}(i_1 i_2, j_1 j_2)$.

Following the up-to-date results obtained in the "microscopic" theory of nuclear effective interactions,[9-11] we believe that in quantum chemistry also (or generally, in the quantum theory of many-electron systems) a complete and tractable theory of the effective Hamiltonian, starting from first principles, should be founded *only* on the diagrammatic QD-RSPT with a Hermitian model Hamiltonian. Recently, this approach for the construction of the effective Hamiltonian has been criticized by Freed[16] on the following two points: (i) A dependence of the model Hamiltonian on some reference energy E_0, and (ii) the necessity for the selective summation of certain classes of terms to all orders of perturbation theory. The first of Freed's objection is in our case irrelevant, because we have used such quasidegenerate RSPT, where the appearance of the reference energy E_0 is completely removed. The origin of this reference energy can be explained as a result of some straightforward approach for constructing the quasidegenerate RSPT. Here, the unperturbed eigenenergies $\{E_K^{(0)};\, K\in\mathcal{K}_0\}$ are suppressed[45] to some reference energy E_0; then, of course, some additional terms depending on E_0 in the perturbation appear. The second critical objection mentioned by Freed is of a very serious nature. We accept that the necessity of taking into consideration the infinite summations of some preselected (presumably dominant) diagrams may cause some theoretical as well as computational difficulties. Nevertheless, following the recent results obtained in connection with the direct many-body calculation of the ionization potentials,[46,47] it seems that the infinite summations of the diagrams is a problem which can be resolved, at least in an approximate way. The main *advantages* of the present approach (the diagrammatic QD-RSPT with Hermitian approximate model Hamiltonian) for the construction of the effective Hamiltonian are the following: (i) The matrix elements (36) of the effective Hamiltonian $\mathcal{H}_{\text{eff}}$ are *independent* of the energy, and (ii) this approach allows a *direct construction* (without an intermediate calculation) of the effective 1-, 2-, 3-, . . . , p-particle matrix elements (36) in the terms of the one- and two-particle integrals (13a) and (13b), and overlap integrals S_{ij}.

In Sec. II the original full Hamiltonian of a given molecular system was constructed in the second-quantization formalism. We emphasize in this connection that because the set (1) of ASOs is a nonorthogonal one, some formal difficulties should be surmounted. A direct introduction of the second quantization formalism[48,49] with respect to this nonorthogonal set of ASOs leads to many formal complications, because the corresponding creation and annihilation operators do not obey the well-known anticommutation relations. Bazilevsky and Berenfeld[50] and others[24,25] in their studies of the general many-body theory of intermolecular interactions have circumvented this difficulty by the formal assumption that an original one-particle basis forms an orthonormal system, and by adding to the Hamiltonian some new terms describing the "overlap effects." A similar idea has also been used in the construction of our original full Hamiltonian (15).

In Sec. III the effective Hamiltonian $\mathcal{H}_{\text{eff}}$ was constructed by the diagrammatic QD-RSPT with the approximate Hermitian model Hamiltonian. One of the basic concepts of this powerful many-body theoretical approach is the d-dimensional model space Ω_0. In our special case of interest, this model space is spanned by *all possible* unperturbed state vectors $|\Phi_K\rangle$ generated by prescriptions (24), (25a), and (25b). Thus, these vectors are built-up from a "frozen core" identical for all $|\Phi_K\rangle$'s from Ω_0, and the valence one-particle states $\{k_1<\cdots<k_p\}\equiv K$. Then, the model eigenproblem (28) and (33) may be understood as a *complete configuration interaction* realized in the d-dimensional model space with either model Hamiltonian H_{LC} or effective Hamiltonian $\mathcal{H}_{\text{eff}}$ [cf. identity (34)], because in the present method the "core" subsystem contained in each vector $|\Phi_K\rangle\in\Omega_0$ should not be explicitly treated.

Our approach of the construction of the effective Hamiltonian $\mathcal{H}_{\text{eff}}$ can be very profitable for an *ab initio* physical establishment of semiempirical effective Hamiltonians.[27-30] *We shall not repeat the main reasons for it here, since they have recently been presented in an exhaustive form in the excellent papers of Freed.*[14-17] We only note that the well-known three semiempirical parameters α_i, β_{ij}, and γ_{ij}, appearing in almost all semiempirical methods, may be determined as follows:

$$\alpha_i = h_{\text{eff}}^{(1)}(i,i)\,, \tag{40a}$$

$$\beta_{ij} = h_{\text{eff}}^{(1)}(i,j)\,, \quad \text{for } i\neq j \tag{40b}$$

$$\gamma_{ij} = h_{\text{eff}}^{(2)}(ij,ij)\,, \tag{40c}$$

where $i,j\in V$. This means that in the semiempirical methods the remaining two-particle and all three- to p-particle effective matrix elements are neglected. Consequently, if we have selected some actual basis (1) of ASOs, then we may by using (37) calculate (up to the "second order") values for the Coulomb α_i as well as resonance β_{ij} integrals.

To conclude this section, we stress that the presented diagrammatic theory of the effective Hamiltonian might be of value in an alternate attempt to solve the *ab initio* calculation (or generally, *ab initio* theory) of the semiempirical parameters, which is a basic problem of present quantum chemistry. While some theoretical and computational problems and questions remain, we believe that the present approach represents a very serious introductory step in this field.

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