PHYSICAL REVIEW A VOLUME 32, NUMBER 2 AUGUST 1985

Interaction of chemical bonds. II. *Ab initio* theory for overlap, delocalization, and dispersion interactions

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(Received 28 January 1985)

A zeroth-order wave function is constructed as an antisymmetrized product of two-electron group wave functions (geminals) expanded in disjunct but overlapping subspaces of basis orbitals. The geminals are obtained as exact solutions of the two-electron Schrödinger equations within the corresponding local basis sets, and thus give a fully correlated description of the two-electron chemical bonds coupled by inductive (Coulomb and exchange) effects, the latter being taken into account by an appropriate effective core operator. A second-quantized formulation [P. R. Surján, Phys. Rev. A **30**, 43 (1984)] is applied where the wave functions of the individual bonds are represented by appropriate composite particle creation operators. Individual chemical bonds thus correspond to Bose quasiparticles composed of two electrons. Second-order perturbation theory is used for calculating interbond delocalization and dispersion effects. The treatment is based on a biorthogonal formulation [I. Mayer, Int. J. Quant. Chem. **23**, 341 (1983); Ph. W. Payne, J. Chem. Phys. **77**, 5630 (1982)] which makes the handling of interbond overlap very effective, and represents essentially a method of moments in the perturbation theory.

I. INTRODUCTION

A representative class of molecules is built up of more or less localized two-electron chemical bonds. This feature may significantly simplify the quantum-chemical treatment of molecules in their ground electronic state, and contribute to a better understanding of the electronic structure, as it was utilized in the early valence-bond-(VB) type approaches undergoing at present a considerable renaissance,[1] as well as in various geminal and localized molecular orbital (LMO) methods.[2] The most successful realizations of this theory were done at the semiempirical level of sophistication.[3] However, in spite of some considerable effort,[4] no widely accepted *ab initio* scheme has been proposed which would make use of the above concept in actual calculations. In the present paper we develop a theory according to the following lines.

(i) Basis orbitals are constructed so that each of them could be assigned to a particular two-electron chemical bond, lone pair, or inner-shell orbital. This is achieved by a hybridization procedure starting from a usual linear combination of atomic orbitals (LCAO) basis, and possibly by adding also off-centered bond functions to the basis subset assigned directly to bonds or lone pairs.

(ii) The second-quantized Born-Oppenheimer Hamiltonian of the molecule is written down in the above nonorthogonal basis, utilizing the biorthogonal formalism.[5,6] This operator is partitioned into one-bond, two-bond, etc., terms.[7]

(iii) A zeroth-order Hamiltonian $\hat{H}^0$ is defined as the sum of the effective intrabond Hamiltonians. This $\hat{H}^0$ is capable of describing interbond inductive (Coulomb and exchange) interactions which do not produce interbond charge transfer. Exact eigenfunctions of the effective intrabond Hamiltonians are determined within the corresponding limited basis set assigned to the chemical bond (lone pair, etc.) in question. These eigenfunctions are referred to as *strictly localized geminals* (SLG's).[7] The zeroth-order wave function is defined as the *antisymmetrized product* of these SLG's (AP-SLG). The biorthogonal geminals are defined over the biorthogonal basis functions and the zeroth-order energy is evaluated in the biorthogonal formalism according to the method of moments.[6,8,9] The creation operators for SLG's obey Bose-type commutation rules so at the zeroth-order the molecule is viewed as a system of Bose quasiparticles which are, of course, not elementary but are composed of two electrons. The internal structure of these Bose quasiparticles is affected by the inductive interbond interactions. Composite particles in electronic systems, although in another context, have been introduced previously by several authors.[10]

(iv) To improve the quasiboson approximation a many-body perturbation approach is developed. It has the special feature that it works with the biorthogonal orbitals and starts with a reference state which is an eigenfunction from the right of a formally non-Hermitian zeroth-order Hamiltonian. The *perturbation theory* (PT) is expected to show a very fine convergence behavior since we have a very accurate AP-SLG reference state: it is highly correlated giving essentially an exact account of the chemically most important ("left-right") electron correlation. So, the role of perturbation theory is merely to take into account indeed small interbond overlap, delocalization, and dispersion interactions.

II. THE PARTITION OF THE HAMILTONIAN

We define a set of reciprocal basis functions (spin orbitals)

$$\tilde{\varphi}_\mu = \sum_\nu S^{-1}_{\mu\nu} \chi_\nu \tag{1}$$

($S^{-1}_{\mu\nu}$ being a shorthand notation for the elements of the inverse of the overlap matrix $S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$), which are biorthogonal to the original basis spin orbitals χ_λ:

$$\langle \tilde{\varphi}_\mu | \chi_\lambda \rangle = \delta_{\mu\lambda} . \tag{2}$$

The creation and annihilation operators χ^+_μ and χ^-_μ, respectively, corresponding to the nonorthogonal basis $\{\chi\}$, obey the following commutation rules:[11]

$$\begin{aligned} &\chi^\pm_\mu \chi^\pm_\nu + \chi^\pm_\nu \chi^\pm_\mu = 0 , \\ &\chi^+_\mu \chi^-_\nu + \chi^-_\nu \chi^+_\mu = S_{\mu\nu} , \end{aligned} \tag{3}$$

and similarly for $\tilde{\varphi}^\pm_\mu$ with $S_{\mu\nu}$ replaced by $S^{-1}_{\mu\nu}$. Usual fermion commutation rules are formally recovered for pairs of operators of direct and reciprocal basis:[5,6]

$$\chi^+_\mu \tilde{\varphi}^-_\nu + \tilde{\varphi}^-_\nu \chi^+_\mu = \delta_{\mu\nu} . \tag{4}$$

That is, a mixed use of original and reciprocal fermion operators allows us to use the calculus (Wick's theorem,[12] etc.) valid for the orthogonal case.

The total Hamiltonian can be expressed by means of operators χ^+ and $\tilde{\varphi}^-$ as:[5,6]

$$\hat{H} = \sum_{\mu,\nu} h_{\tilde{\mu}\nu} \chi^+_\mu \tilde{\varphi}^-_\nu + \frac{1}{2} \sum_{\mu,\nu,\lambda,\sigma} [\tilde{\mu}\tilde{\nu} | \lambda\sigma] \chi^+_\mu \chi^+_\nu \tilde{\varphi}^-_\sigma \tilde{\varphi}^-_\lambda . \tag{5}$$

Here the indices refer to spin orbitals, $h_{\tilde{\mu}\nu} = \langle \tilde{\varphi}_\mu | \hat{h} | \chi_\mu \rangle$ is the matrix element of the core, while $[\tilde{\mu}\tilde{\nu} | \lambda\sigma]$ is the usual two-electron integral in the [12|12] convention. Here and further on the tilde refers to reciprocal orbitals. Now, the summation indices can be distinguished according to the bonds (lone pairs, etc.) that they belong to

$$\sum_\mu \equiv \sum_i \sum_\mu^{(i)} , \tag{6}$$

where i runs over all bonds and the symbol (i) indicates that the summation is to be performed over basis orbitals assigned to i. Equation (5) can thus be written in form of

$$\hat{H} = \sum_i \hat{H}_i + \sum_{i,j}{}' \hat{H}_{ij} + \sum_{i,j,k}{}' \hat{H}_{ijk} + \sum_{i,j,k,l}{}' \hat{H}_{ijkl} , \tag{7}$$

where the indices i, j, etc. do not coincide. For the one-bond and two-bond operators one obtains by simple algebraic manipulations

$$\hat{H}_i = \sum_{\mu,\nu}^{(i)} h_{\tilde{\mu}\nu} \chi^+_\mu \tilde{\varphi}^-_\nu + \frac{1}{2} \sum_{\mu,\nu,\lambda,\sigma}^{(i)} [\tilde{\mu}\tilde{\nu} | \lambda\sigma] \chi^+_\mu \chi^+_\nu \tilde{\varphi}^-_\sigma \tilde{\varphi}^-_\lambda , \tag{8}$$

$$\begin{aligned} \hat{H}_{ij} = &\sum_\mu^{(i)} \sum_\nu^{(j)} h_{\tilde{\mu}\nu} \chi^+_\mu \tilde{\varphi}^-_\nu \quad (\text{term } \hat{A}) \\ &+ \sum_{\eta,\epsilon,\kappa}^{(i)} \sum_\rho^{(j)} [\tilde{\eta}\epsilon | \kappa\rho] \chi^+_\eta \chi^+_\epsilon \tilde{\varphi}^-_\rho \tilde{\varphi}^-_\kappa \quad (\text{term } \hat{B}) \\ &+ \sum_{\eta,\kappa,\rho}^{(i)} \sum_\epsilon^{(j)} [\tilde{\eta}\tilde{\epsilon} | \kappa\rho] \chi^+_\eta \chi^+_\epsilon \tilde{\varphi}^-_\rho \tilde{\varphi}^-_\kappa \quad (\text{term } \hat{C}) \\ &+ \frac{1}{2} \sum_{\eta,\kappa}^{(i)} \sum_{\epsilon,\rho}^{(j)} ([\tilde{\eta}\tilde{\epsilon} | \kappa\rho] - [\tilde{\eta}\tilde{\epsilon} | \rho\kappa]) \chi^+_\eta \chi^+_\epsilon \tilde{\varphi}^-_\rho \tilde{\varphi}^-_\kappa \\ &+ \frac{1}{2} \sum_{\eta,\epsilon}^{(i)} \sum_{\kappa,\rho}^{(j)} [\tilde{\eta}\tilde{\epsilon} | \kappa\rho] \chi^+_\eta \chi^+_\epsilon \tilde{\varphi}^-_\rho \tilde{\varphi}^-_\kappa . \end{aligned} \tag{9}$$

The operators $\hat{H}_{ijk}$ and $\hat{H}_{ijkl}$ describe simultaneous three-bond and four-bond interactions which are of less importance, thus their expression is not reported here (see Ref. 7); this is expected both from qualitative reasoning as well as because they do not give contributions up to the second order of PT we are going to consider. A very simple Coulomb part of them will be, however, included in the effective core discussed below.

Various terms in Eq. (9) have simple physical meaning. The operator string in term $\hat{A}$, $\chi^+_\mu \tilde{\varphi}^-_\nu$, annihilates an electron on the bond j while it creates one on the bond i. Accordingly, it describes a $j \rightarrow i$ electron delocalization (transfer). The terms $\hat{B}$ and $\hat{C}$ have similar meaning. The operator string in the fourth sum of Eq. (9) conserves the particle number on both bonds i and j; this term describes the interbond Coulomb and exchange interaction and dispersion. Finally, the last term accounts for a two-electron charge transfer from j to i which is evidently of minor importance and will be neglected.

III. THE ZEROTH-ORDER WAVE FUNCTION: ANTISYMMETRIZED PRODUCT OF STRICTLY LOCALIZED GEMINALS

Let us assume an effective Hamiltonian $\hat{H}^{\text{eff}}_i$ to be known for the bond i. Its connection with the terms of Eq. (7) will be specified below. As will be seen, the operator $\hat{H}^{\text{eff}}_i$ is, in general, non-Hermitian due to the interbond overlap. The two-electron Schrödinger equation within the subspace of basis orbitals assigned to the bond i then reads

$$\hat{H}^{\text{eff}}_i \hat{\psi}^{+q}_i | \text{vac} \rangle = E^q_i \hat{\psi}^{+q}_i | \text{vac} \rangle \tag{10}$$

for the state q ($q = 0,1,2,\ldots$), where the two-electron creation operator $\hat{\psi}^{+q}_i$ has the general expansion

$$\hat{\psi}^{+q}_i = \sum_{\substack{\mu,\nu \\ \mu<\nu}}^{(i)} c^{iq}_{\mu\nu} \chi^+_\mu \chi^+_\nu . \tag{11}$$

The corresponding two-electron annihilation operator is defined over the reciprocal basis space as

$$\hat{\phi}^{-q}_i = \sum_{\substack{\mu,\nu \\ \mu<\nu}}^{(i)} c^{iq}_{\mu\nu} \tilde{\varphi}^-_\nu \tilde{\varphi}^-_\mu . \tag{12}$$

It can be shown easily that the operators $\hat{\psi}^+_i$, $\hat{\phi}^-_i$ obey the following commutation rules:

$$\hat{\psi}_i^+\hat{\psi}_k^+ - \hat{\psi}_k^+\hat{\psi}_i^+ = 0 , \quad (13)$$

$$\hat{\phi}_i^-\hat{\psi}_k^+ - \hat{\psi}_k^+\hat{\phi}_i^- = \hat{Q}_i\delta_{ik} . \quad (14)$$

Equations (13) and (14) correspond to Bose-type commutation which is a natural consequence of the fact that the operators $\hat{\psi}_i^+,\hat{\phi}_i^-$ defined by Eqs. (11) and (12) describe a system of integer spin. There is a deviation from the usual Bose-commutation rule, the appearance of operator $\hat{Q}_i$ for which one obtains, after some algebra,

$$\hat{Q}_i = 1 + \sum_{\mu,\nu,\lambda}^{(i)} c^i_{\nu\lambda} c^i_{\lambda\mu} \chi^+_\mu \tilde{\varphi}^-_\nu , \quad (15)$$

where the presence of the sum in the right-hand side (rhs) is the consequence of the composite nature of the Bose particles created by $\hat{\psi}_i^+$.

The operator $\hat{Q}_i$ has the important property that, acting on the vacuum state, it behaves in the same manner as the identity operator:

$$\hat{Q}_i \,|\,\mathrm{vac}\rangle = |\,\mathrm{vac}\rangle . \quad (16)$$

Therefore, from the commutation rule (14) one obtains

$$\hat{\phi}_i^-\hat{\psi}_i^+ \,|\,\mathrm{vac}\rangle = (\hat{\psi}_i^+\hat{\phi}_i^- + \hat{Q}_i)\,|\,\mathrm{vac}\rangle = |\,\mathrm{vac}\rangle . \quad (17)$$

That is, the biorthogonal operator $\hat{\phi}_i^-$ in fact annihilates the quasiparticle created by operator $\hat{\psi}_i^+$. The formalism of these Bose-type operators is based on Eq. (17), and the operator $\hat{Q}_i$ does not appear in any further formulas of ours.

For the sake of further development, the following quantities are defined.

(i) Generalized first-order density-matrix elements for the ground state of the bond $(\mu,\nu,\epsilon i)$:

$$P^i_{\mu\nu} = \langle \mathrm{vac}\,|\,\hat{\phi}_i^-\chi^+_\mu\tilde{\varphi}^-_\nu\hat{\psi}_i^+\,|\,\mathrm{vac}\rangle = \sum_\lambda^{(i)} c^i_{\mu\lambda} c^i_{\nu\lambda} . \quad (18)$$

(ii) Generalized first-order transition density-matrix elements corresponding to the local $0 \to q$ excitation within the bond i:

$$P^{iq}_{\mu\nu} = \langle \mathrm{vac}\,|\,\hat{\phi}_i^-\chi^+_\mu\tilde{\varphi}^-_\nu\hat{\psi}_i^{+q}\,|\,\mathrm{vac}\rangle = \sum_\lambda^{(i)} c^i_{\mu\lambda} c^{iq}_{\nu\lambda} \quad (q=1,2,3,\ldots) . \quad (19)$$

The validity of Eqs. (18) and (19) can easily be shown by inserting the expansion of the Bose operators (11) and (12), applying Wick's theorem and introducing the convention

$$c^i_{\nu\mu} = -c^i_{\mu\nu} \quad (20)$$

for $\mu < \nu$. (Note that only the upper triangle of matrix $c^i_{\mu\nu}$ enters the original definition Eq. (11) of ψ_i^+.)

Let us now turn to the problem of defining the effective Hamiltonian for the bond i. First, it can be seen that the fourth term of Eq. (9), which describes interbond electrostatic interactions, does have an average value which can be incorporated into $\hat{H}_i^{\mathrm{eff}}$ as an effective core in the usual manner:

$$h^{\mathrm{eff}}_{\tilde{\mu}\nu} = h_{\tilde{\mu}\nu} + \sum_{k\,(\neq i)} \sum_{\lambda,\sigma}^{(k)} P^k_{\lambda\sigma}([\tilde{\mu}\tilde{\lambda}\,|\,\nu\sigma] - [\tilde{\mu}\tilde{\lambda}\,|\,\sigma\nu]) , \quad \mu,\nu \in i . \quad (21)$$

The Hamiltonian $\hat{H}_i^{\mathrm{eff}}$ using this effective core is capable of describing interbond inductive interactions. The next step is to symmetrize the integrals $h^{\mathrm{eff}}_{\tilde{\mu}\nu}$ and $[\tilde{\mu}\tilde{\nu}\,|\,\lambda\sigma]$ appearing in Eqs. (8) and (21), i.e., to introduce

$$\bar{h}^{\mathrm{eff}}_{\mu\nu} = (h^{\mathrm{eff}}_{\tilde{\mu}\nu} + h^{\mathrm{eff}}_{\tilde{\nu}\mu})/2 , \quad (22)$$

$$[\overline{\mu\nu\,|\,\lambda\sigma}] = \tfrac{1}{2}([\tilde{\mu}\tilde{\nu}\,|\,\lambda\sigma] + [\tilde{\lambda}\tilde{\sigma}\,|\,\mu\nu]) . \quad (23)$$

The antisymmetric counterparts, as, e.g., $(h^{\mathrm{eff}}_{\tilde{\mu}\nu} - h^{\mathrm{eff}}_{\tilde{\nu}\mu})/2$, will be considered as a perturbation. The reason for this symmetrization in Eqs. (22) and (23) is that it warrants that the states $\hat{\psi}_i^{+q}\,|\,\mathrm{vac}\rangle$ as obtained by the local Schrödinger equation (10) will be biorthonormal to each other for different states:

$$\langle \mathrm{vac}\,|\,\hat{\phi}_i^{-p}\hat{\psi}_i^{+q}\,|\,\mathrm{vac}\rangle = \delta_{pq} . \quad (24)$$

Accordingly, the final effective Hamiltonian for the bond i is defined as

$$\hat{H}_i^{\mathrm{eff}} = \sum_{\mu,\nu}^{(i)} \bar{h}^{\mathrm{eff}}_{\mu\nu}\chi^+_\mu\tilde{\varphi}^-_\nu + \tfrac{1}{2}\sum_{\mu,\nu,\lambda,\sigma}^{(i)} [\overline{\mu\nu\,|\,\lambda\sigma}]\chi^+_\mu\chi^+_\nu\tilde{\varphi}^-_\sigma\tilde{\varphi}^-_\lambda . \quad (25)$$

Note again that $\hat{H}_i^{\mathrm{eff}}$ is still not Hermitian since the fermion operators χ^+_μ and $\tilde{\varphi}^-_\mu$ are not the adjoints of each other.

The important point here is that this non-Hermiticity is somewhat formal; it accounts for basis overlap effects (in orthogonal metrics the direct and reciprocal basis orbitals would coincide and $\hat{H}_i^{\mathrm{eff}}$ would become Hermitian). The mixed use of operators $\chi^+,\hat{\psi}^+$, related to the direct orbital space, and of $\tilde{\varphi}^-$, $\hat{\phi}^-$ related to the reciprocal one permits us to apply formally the same calculus which would be valid in an orthogonal basis set. Once the list of integrals has been transformed to the biorthogonal basis (in the first two indices), and the intrabond integrals have been symmetrized, one need not take further care of basis overlap effects at the zeroth order—one has to solve, e.g., Hermitian matrix-eigenvalue problems for each bond.

The local Schrödinger Eq. (10) for the expansion coefficients $c^{iq}_{\mu\nu}$ and the bond energies E^i_q has the matrix representation

$$\sum_{\substack{\mu,\nu \\ \mu<\nu}} H^{i\,\mathrm{eff}}_{\lambda\sigma,\mu\nu} c^{iq}_{\mu\nu} = E^q_i c^{iq}_{\sigma\lambda} \quad (q=0,1,2,\ldots) . \quad (26)$$

It can also be rewritten in terms of spatial orbitals. After spin adaptation, the matrix elements of the effective Hamiltonian for singlets, e.g., become

$$H^{i\,\mathrm{eff}}_{lk,ij} = \bar{h}_{li}\delta_{kj} + \bar{h}_{kj}\delta_{li} + [\overline{lk\,|\,ij}] , \quad (27)$$

where the subscripts refer to spatial basis orbitals. The system of equations (26) for the different bonds i are coupled through the Coulomb and exchange interaction incorporated into the effective core, therefore it should be solved iteratively. However, according to our experience based on semiempirical schemes,[13] such iterations converge very fast.

The ground-state wave function Ψ_0 of the molecule is now written at the zeroth order as

$$|\Psi_0\rangle=\hat{\psi}_1^+\hat{\psi}_2^+\cdots\hat{\psi}_n^+|\text{vac}\rangle\ . \tag{28}$$

Note that Ψ_0 is properly antisymmetric in the variables of electrons, while the two-electron bond creation operators obey the symmetric commutation rules (13). Accordingly, Ψ_0 can be referred to as the antisymmetrized product of strictly localized geminals. Its biorthogonal counterpart Φ_0 is defined as

$$\langle\Phi_0|=\langle\text{vac}|\hat{\phi}_1^-\hat{\phi}_2^-\cdots\hat{\phi}_n^-\ . \tag{28'}$$

The total electronic energy at the zeroth order is readily seen to be

$$\begin{aligned}E&=\langle\Phi_0|H|\Psi_0\rangle\\&=\sum_i E_i-\tfrac{1}{2}\sum_{\substack{k,i\\k\neq i}}\sum_{\mu,\nu}^{(i)}\sum_{\lambda,\sigma}^{(k)}P_{\mu\nu}^iP_{\lambda\sigma}^k([\widetilde{\mu}\widetilde{\nu}|\lambda\sigma]-[\widetilde{\mu}\widetilde{\nu}|\sigma\lambda])\ ,\end{aligned} \tag{29}$$

where the Coulomb and exchange correction appears because the sum of individual bond energies E_i accounts for the interbond electron-electron interaction twice.

IV. BIORTHOGONAL PERTURBATION THEORY

In this section the generalization of the nondegenerate Rayleigh-Schrödinger perturbation theory to the case of non-Hermitian zeroth-order Hamiltonians is considered. We apply essentially the method of moments,[8] the biorthogonal functions being chosen as weight functions.

Let H^0 be the non-Hermitian zeroth-order Hamiltonian and Ψ^0 be its eigenfunction from the right:

$$\hat{H}^0\Psi_K^0=E_K^0\Psi_K^0\ . \tag{30}$$

The exact wave function Ψ_K and the exact energy E_K fulfill the Schrödinger equation

$$(\hat{H}^0+\hat{W})\Psi_K=E_K\Psi_K\ . \tag{31}$$

Since the total Hamiltonian is Hermitian, but $\hat{H}^0$ is not, $\hat{W}$ is not Hermitian either. The Ψ_K can be expanded in terms of the zeroth-order solutions

$$\Psi_K=\sum_L C_{KL}\Psi_L^0\ . \tag{32}$$

The coefficients C_{KL} and the energies E_K are expanded in the usual manner

$$C_{KL}=\delta_{KL}+\sum_{\mu=1}^{\infty}C_{KL}^{\mu}\ , \tag{33}$$

$$E_K=E_K^0+E_K^1+E_K^2+\cdots\ . \tag{34}$$

These expansions can be substituted into Eqs. (31) and (32). In the usual PT the formulas so obtained are multiplied by the zeroth-order functions from the left, and then integrated, providing expressions for C_{KL}^{μ} and E_K^{μ}. In the present problem, however, the zeroth-order wave functions do not represent eigenfunctions from the left; neither form an orthogonal set, being obtained from a non-Hermitian eigenvalue problem. We have, however, another set of functions Φ_K^0 biorthogonal to the original ones:

$$\langle\Phi_K^0|\Psi_L^0\rangle=\delta_{KL}\ . \tag{35}$$

Then, multiplying with these biorthogonal functions from the left and integrating, one obtains the following straightforward generalization of the usual perturbation formulas:

$$E_K^1=\langle\Phi_K^0|\hat{W}|\Psi_K^0\rangle\ , \tag{36}$$

$$E_K^2=-\sum_{L\ (\neq K)}\frac{\langle\Phi_K^0|\hat{W}|\Psi_L^0\rangle\langle\Phi_L^0|\hat{W}|\Psi_K^0\rangle}{E_L^0-E_K^0}\ , \tag{37}$$

etc. Note that the matrix $W_{KL}=\langle\Phi_K^0|\hat{W}|\Psi_L^0\rangle$ is not symmetric. It will turn out that the evaluation of these matrix elements is extremely simple as compared to the difficulties which one would encounter without utilizing biorthogonality, i.e., using merely the overlapping direct space wave functions Ψ_K^0. Whenever the perturbation expansions (33) and (34) converge, one obtains the exact solutions E_K and Ψ_K for the given basis set.

As noted above, the present approach is similar to the method of moments.[6,8,9] One argument against the use of the method of moments in connection with configuration-interaction (Ref. 6) or VB (Ref. 9) approaches is that the resulting energies do not serve as upper bounds to the exact energy. This objection, however, is not relevant in connection with the PT which does not give upper bounds even in the traditional case. Moreover, it can be shown (cf. also Ref. 6) that our zeroth-order energy (29) does represent a strict upper bound.

At the expense of working with non-Hermitian operators, our formalism permits us to incorporate the most important overlap effects already at the zeroth order of PT. This offers the promise that quickly converging perturbation expansions will be obtained.

V. EXCITATIONS: ONE- AND THREE-ELECTRON STATES

The biorthogonal PT developed in Sec. IV is now applied for describing interbond interactions. We choose the AP-SLG wave function as the zeroth-order wave function and the sum of effective intrabond Hamiltonians

$$\hat{H}^0=\sum_i\hat{H}_i^{\text{eff}} \tag{38}$$

as the zeroth-order Hamiltonian. The perturbation operator $\hat{W}$ has the following terms:

$$\hat{W}=\sum_i\hat{S}_i+\sum_{i,j}\hat{H}_{ij}^{\text{eff}}\ , \tag{39}$$

where we consider only effective two-bond interaction terms since three- and four-bond interactions do not appear up to the second order of PT. In the first term on the rhs of Eq. (39), $\hat{S}_i$ is due to the antisymmetric component of the intrabond integral (hyper) matrices [note that only the symmetric component has been included at the zeroth order, cf. Eqs. (22) and (23)]:

$$\hat{S}_i = \sum_{\mu,\nu}^{(i)} \tfrac{1}{2}(h^{\text{eff}}_{\tilde{\mu}\nu} - h^{\text{eff}}_{\tilde{\nu}\mu})\chi^+_\mu \tilde{\varphi}^-_\nu + \tfrac{1}{4}\sum_{\mu,\nu,\lambda,\sigma}^{(i)} ([\tilde{\mu}\tilde{\nu}\,|\,\lambda\sigma] - [\tilde{\lambda}\tilde{\sigma}\,|\,\mu\nu])\chi^+_\mu\chi^+_\nu\tilde{\varphi}^-_\sigma\tilde{\varphi}^-_\lambda \; . \tag{40}$$

The two-bond operator $\hat{H}^{\text{eff}}_{ij}$ is essentially the same as that given in Eq. (9), except that we neglect the two-electron charge-transfer term, but we use an effective two-bond core

$$h^{\text{eff}}_{\mu\nu} = h_{\mu\nu} + \sum_{k\,(\neq i,j)} \sum_{\lambda,\sigma}^{(k)} P^k_{\lambda\sigma}([\tilde{\mu}\tilde{\lambda}\,|\,\nu\sigma] - [\tilde{\mu}\tilde{\lambda}\,|\,\sigma\nu]) \tag{41}$$

which accounts for the electrostatic effect of the third bond k on the $i \rightarrow j$ delocalization, similarly to the corresponding electrostatic effect of all the nuclei, included in $h_{\mu\nu}$. We therefore know the explicit second-quantized expressions for the various terms of the perturbing operator and now we are faced with the problem of how to represent excited states.

In calculating the effects due to the overlap term Eq. (40), the particle-hole operators $\chi^+_\mu \tilde{\varphi}^-_\nu$, etc., describe merely intrabond excitations. This effect can be termed as "overlap polarization." This corresponds formally to a one-bond term originating from the overlap, which could not, however, be included in the zeroth order due to the reasons discussed above. Accordingly, such contributions can be evaluated in terms of zeroth-order excited states of individual bonds, i.e., by using the many-bond wave function

$$|\Psi^0_K\rangle = \hat{\psi}^{+q}_l \hat{\phi}^-_l \,|\,\Psi^0_0\rangle \; . \tag{42}$$

That is, the lth bond is excited to the state q.

Another type of terms appears in the two-bond part of the perturbing Hamiltonian describing electron delocalization. Here the particle-hole operators annihilate an electron on the bond i and put it on the bond j, or *vice versa.* The relevant many-electron excited states can be written as

$$|\Psi^{0\prime}_K\rangle = \hat{\psi}^{+(3)q}_j \hat{\psi}^{+(1)p}_i \hat{\phi}^-_j \hat{\phi}^-_i \,|\,\Psi^0_0\rangle \; , \tag{43}$$

where $\hat{\psi}^{+(1)p}_i$ and $\hat{\psi}^{+(3)q}_j$ are the creation operators for the one- and three-electron states on the corresponding bonds, respectively (see below).

Finally, in order to describe interbond dispersion effects generated by the fourth term of Eq. (9), one has to consider simultaneous local excitations on two different bonds:

$$|\Psi^{0\prime\prime}_K\rangle = \hat{\psi}^{+q}_j \hat{\psi}^{+p}_i \hat{\phi}^-_j \hat{\phi}^-_i \,|\,\Psi^0_0\rangle \; . \tag{44}$$

The biorthogonal counterparts of the last three equations, which are also needed in the biorthogonal perturbation theory [cf. Eq. (37)], are readily seen to be

$$\langle\Phi^0_K| = \langle\Phi^0_0|\,\hat{\psi}^+_l \hat{\phi}^{-q}_l \quad \text{(overlap polarization)} \; , \tag{42$'$}$$

$$\langle\Phi^{0\prime}_K| = \langle\Phi^0_0|\,\hat{\psi}^+_i \hat{\psi}^+_j \hat{\phi}^{-(1)p}_i \hat{\phi}^{-(3)q}_j \quad \text{(delocalization)} \; , \tag{43$'$}$$

$$\langle\Phi^{0\prime\prime}_K| = \langle\Phi^0_0|\,\hat{\psi}^+_i \hat{\psi}^+_j \hat{\phi}^{-p}_i \hat{\phi}^{-q}_j \quad \text{(dispersion)} \; . \tag{44$'$}$$

By means of the above expressions, using the actual form of operators $\hat{\psi}^{+q}_i$, $\hat{\psi}^{+(1)q}_i$, and $\hat{\psi}^{+(3)q}_i$, and applying Wick's theorem the perturbation energy corrections can be evaluated in a straightforward manner. The actual form of the matrix elements and that of energy corrections will be given in Sec. VI. Now we discuss the one- and three-electron states appearing in the perturbative treatment of electron delocalization in some detail.

As to the one-electron operators $\hat{\psi}^{+(1)q}_i$, they represent no special problem since they can be expanded simply as

$$\hat{\psi}^{+(1)q}_i = \sum_\mu^{(i)} c^{iq}_\mu \chi^+_\mu \tag{45}$$

and the coefficients c^{iq}_μ can easily be calculated by solving the local one-electron Schrödinger equation for the bond i, giving the various one-electron states q. Note that, for the sake of simplicity, we use the same effective core operator as a one-electron Hamiltonian which has been obtained by solving the coupled two-electron problems over the whole molecule iteratively.

The three-electron states are expanded as

$$\hat{\psi}^{+(3)q}_i = \sum_{\substack{\mu,\nu,\lambda \\ \mu<\nu<\lambda}} c^{iq}_{\mu\nu\lambda}\chi^+_\mu\chi^+_\nu\chi^+_\lambda \; . \tag{46}$$

The coefficients can be obtained by solving the local full configuration-interaction (CI) problems for three electrons, which read

$$\sum_{\substack{\mu,\nu,\lambda \\ \mu<\nu<\lambda}}^{(i)} \langle \text{vac}\,|\,\tilde{\varphi}^-_\alpha \tilde{\varphi}^-_\beta \tilde{\varphi}^-_\gamma \hat{H}^{\text{eff}}_i \chi^+_\mu\chi^+_\nu\chi^+_\lambda\,|\,\text{vac}\rangle c^{iq}_{\mu\nu\lambda} = E^q_i c^{iq}_{\alpha\beta\gamma} \; . \tag{47}$$

In larger basis sets, however, the solution of Eq. (47) can be rather expensive. So, it is desirable to solve it for doublets only since the quadruplets cannot be coupled with one-electron doublets to form a singlet excited state, the latter being of the only interest. Moreover, perhaps it will be sufficient to obtain an approximate solution of Eq. (47). The operator $\hat{H}^{\text{eff}}_i$ in Eq. (47) is built up by using the same effective core obtained by solving the two-electron problems, thus the evaluation of the matrix elements in Eq. (47) is straightforward. It is to be stressed that the exact full CI solution of Eq. (47) is manageable in most cases due to the limited number of basis orbitals assigned to the bond i. In a "double-zeta" (DZ) type basis set, e.g., one has four spatial, i.e., eight spin orbitals assigned to each bond; this means 10 two-electron singlets and 20 three-electron doublets only.

VI. MATRIX ELEMENTS: SECOND-ORDER ENERGY CORRECTIONS

Let us consider first the matrix elements of the overlap polarization terms of Eq. (40). We have pointed out that the polarization-type excitations (42) and (42′) are relevant in this case. For the $0 \rightarrow K$ matrix element we have

$$\left\langle \Phi_0^0 \left| \sum_i \hat{S}_i \right| \Psi_K^0 \right\rangle = \frac{1}{2} \sum_i \sum_l \sum_q \left\langle \Phi_0^0 \right| \left[\sum_{\mu\nu}^{(i)} (h_{\tilde{\mu}\nu}^{\text{eff}} - h_{\tilde{\nu}\mu}^{\text{eff}}) \chi_\mu^+ \tilde{\varphi}_\nu^- + \frac{1}{2} \sum_{\mu,\nu,\lambda,\sigma}^{(i)} ([\tilde{\mu}\tilde{\nu} \mid \lambda\sigma] - [\tilde{\lambda}\tilde{\sigma} \mid \mu\nu]) \chi_\mu^+ \chi_\nu^+ \tilde{\varphi}_\sigma^- \tilde{\varphi}_\lambda^- \right] \psi_l^{+q} \phi_l^- \left| \Psi_0^0 \right\rangle , \tag{48}$$

where i and l run over all bonds while q runs over the internal two-electron excited states of the bond l. By substituting the form of the AP-SLG wave function from Eqs. (28) and (28′), as well as the expansion of the direct and biorthogonal Bose operators of Eqs. (11) and (12), and applying Wick's theorem, Eq. (48) reduces to

$$\left\langle \Phi_0^0 \left| \sum_i \hat{S}_i \right| \Psi_K^0 \right\rangle = \frac{1}{2} \sum_{\mu,\nu}^{(l)} (h_{\tilde{\mu}\nu}^{\text{eff}} - h_{\tilde{\nu}\mu}^{\text{eff}}) P_{\mu\nu}^{lq} + \frac{1}{4} \sum_{\mu,\nu,\lambda,\sigma}^{(l)} ([\tilde{\mu}\tilde{\nu} \mid \lambda\sigma] - [\tilde{\lambda}\tilde{\sigma} \mid \mu\nu]) c_{\mu\nu}^{l0} c_{\lambda\sigma}^{lq} , \tag{49}$$

where the generalized first-order density-matrix elements $P_{\mu\nu}^{lq}$ have been defined in Eq. (19), and the particular excited state K considered is the $0 \rightarrow q$ excitation on the bond l.

It is easy to write down Eq. (49) in terms of spatial orbitals:

$$\left\langle \Phi_0^0 \left| \sum_i \hat{S}_i \right| \Psi_K^0 \right\rangle = \frac{1}{2} \sum_{m,n}^{(l)} (h_{\tilde{m}n}^{\text{eff}} - h_{\tilde{n}m}^{\text{eff}}) P_{mn}^{lq} + \frac{1}{4} \sum_{m,n,r,s}^{(l)} ([\tilde{m}\tilde{n} \mid rs] - [\tilde{r}\tilde{s} \mid mn]) c_{mn}^{l0} c_{rs}^{lq} , \tag{50}$$

where the generalized spatial transition density matrix P_{mn}^{lq} is defined as

$$P_{mn}^{lq} = \sum_\sigma P_{m\sigma,n\sigma}^{lq} , \tag{51}$$

the σ being the spin label (α or β). The spatial coefficients c_{mn}^{lq} correspond to a singlet (ground or excited) state.

It is of interest to note that the first term of Eq. (50), for instance, containing the core integrals h_{mn}^{eff}, can be rewritten by substituting the form of the biorthogonal orbitals from Eq. (1) as

$$\frac{1}{2} \sum_{m,n}^{(l)} [\underline{\mathbf{S}}^{-1}, \underline{\mathbf{h}}^{\text{eff}}]_{mn} P_{mn}^{lq} \tag{50′}$$

which shows that, as far as $\underline{\mathbf{h}}^{\text{eff}}$ were proportional to the overlap matrix $\underline{\mathbf{S}}$, the overlap polarization effect would disappear. This condition, of course, is not fulfilled exactly but some correlation between $\underline{\mathbf{h}}$ and $\underline{\mathbf{S}}$ matrix elements certainly exists.

Matrix elements of the delocalization and dispersion operators can be evaluated in a similar manner. Let us denote the charge-transfer terms of the two-electron Hamiltonian, Eq. (9), by $\hat{A}$, $\hat{B}$, and $\hat{C}$ [the first three terms of Eq. (9), respectively]. For their matrix elements one obtains, in terms of spatial orbitals,

$$\langle \Phi_0^0 \mid \hat{A} \mid \Psi_K^0 \rangle = 2 \sum_{m,n}^{(l)} \sum_{r,t,s}^{(j)} h_{\tilde{m}r}^{\text{eff}} c_n^{lp} c_{rts}^{jq} c_{mn}^{l} c_{ts}^{j} , \tag{52}$$

$$\langle \Phi_0^0 \mid \hat{B} \mid \Psi_K^0 \rangle = -2 \sum_{h,e,k}^{(l)} \sum_{r,t,s}^{(j)} [\tilde{h}\tilde{e} \mid kr] c_k^{lp} c_{he}^{l} c_{rts}^{jq} c_{ts}^{j} , \tag{53}$$

$$\langle \Phi_0^0 \mid \hat{C} \mid \Psi_K^0 \rangle = 2 \sum_{h,k,r,s}^{(j)} \sum_{e,f}^{(l)} [\tilde{h}\tilde{e} \mid kr] c_f^{lp} c_{ef}^{l} c_{hs}^{j} (c_{krs}^{jq} - c_{rsk}^{jq}) , \tag{54}$$

where the particular excitation considered is the electron transfer from the bond l to the bond j, with the one-electron state p on the bond l and with the three-electron state q on the bond j. A quite similar set of expressions holds for the matrix elements of type $\langle \Phi_K^0 \mid \hat{W} \mid \Psi_0^0 \rangle$. The relevant perturbation corrections can be obtained by substituting the above matrix elements into the general second-order formula Eq. (37). We have for the overlap polarization

$$\Delta E(S) = -\sum_l \sum_q^{(\text{singlets})} \frac{\left\langle \Phi_0^0 \left| \sum_i \hat{S}_i \right| \Psi_K^0 \right\rangle \left\langle \Phi_K^0 \left| \sum_i \hat{S}_i \right| \Psi_0^0 \right\rangle}{E_l^q - E_l^0} , \tag{55}$$

for the delocalization terms

$$\Delta E(\text{deloc}) = -\sum_{l,j} \sum_{p,q}^{(\text{doublets})} \frac{\langle \Phi_0^0 \mid \hat{A} + \hat{B} + \hat{C} \mid \Psi_K^0 \rangle \langle \Phi_K^0 \mid \hat{A} + \hat{B} + \hat{C} \mid \Psi_0^0 \rangle}{E_l^p + E_j^q - E_l^0 - E_j^0} , \tag{56}$$

while for the interbond dispersion we get

$$\Delta E(\mathrm{disp}) = -\sum_{\substack{j,l\\ j<l}} \sum_{p,q}^{(M_S=0)} \frac{\left| \sum_{h,k}^{(j)} \sum_{e,r}^{(l)} ([\widetilde{h}\widetilde{e} \,|\, kr] - \tfrac{1}{2}[\widetilde{h}\widetilde{e} \,|\, rk]) P_{hk}^{jp} P_{er}^{lq} \right|^2}{E_l^q + E_j^p - E_l^0 - E_j^0} - \tfrac{1}{4} \sum_{\substack{j,l\\ j<l}} \sum_{p,q}^{(M_S^{p,q}=\pm 1;\, M_S^p + M_S^q = 0)} \frac{\left| \sum_{h,k}^{(j)} \sum_{e,r}^{(l)} [\widetilde{h}\widetilde{e} \,|\, rk] P_{hk}^{jp} P_{er}^{lq} \right|^2}{E_l^q + E_j^p - E_l^0 - E_j^0} \tag{57}$$

with obvious notations for the S_z quantum numbers M_S.

Equations (50)—(57) are the working formulas for the perturbation calculation of interbond interactions in the present scheme. Although they may appear to be complicated, they are computable with a rather small effort. The working integral list is obtained by a two-index transformation to the biorthogonal basis set. Only one- and two-bond integrals are needed except the two-bond effective core in which certain types of three-bond integrals appear [cf. Eq. (41)]. Anyway, only a very small portion of the whole integral list should be transformed into the biorthogonal basis. Since it is expected that some 90% of the (self-consistent-field *and* correlation) energy is accounted for already at the zeroth order, the perturbation theory up to the second order should give very accurate results. The proposed method is not a variational one, partly due to the application of the perturbation theory and partly due to the biorthogonal formalism. The method is, however, size consistent and accounts for dissociation properties properly. Therefore it is adequate in studying potential energy hypersurfaces. Preliminary zeroth-order results,[7] as obtained by semiempirical model Hamiltonians, are encouraging; the computer realization of the present *ab initio* theory is now in progress.

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