Interaction of chemical bonds: Strictly localized wave functions in orthogonal basis

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A second-quantized theory is presented with the aim to study the nature and interactions of well-localizable chemical bonds in molecules. The basis set is partitioned by assigning each basis function to a chemical bond possessing two electrons. The Schrödinger equation within each limited basis subset is solved exactly for each bond, leading to correlated, strictly localized, intrabond wave functions. The total many-electron wave function Ψ is defined as the antisymmetrized product of these strictly localized geminals. The second-quantized Hamiltonian $\hat{H}$ is partitioned as $\hat{H} = \hat{h}^0 + \hat{W}$, where the zeroth-order Hamiltonian $\hat{h}^0$ contains all terms which contribute to the energy of the strictly localized wave function Ψ, while the expectation value of $\hat{W}$, as calculated by Ψ, is zero. Since $\hat{h}^0$ is not simply the sum of intrabond Hamiltonians, the strictly localized wave function accounts for certain interbond interactions (inductive effects). The concept of bond creation and annihilation operators is introduced which formally shows Bose-type behavior since they refer to a two-electron composite system.

I. INTRODUCTION

The concept of two-electron binding is one of the most useful tools in theoretical chemistry. In valence-bond (VB) type methods one constructs the many-electron wave function of a molecule in terms of two-electron—two-orbital VB structures.[1,2] Within the molecular orbital (MO) scheme this feature is often lost when using canonical MO's, but the use of localized molecular orbitals (LMO's) offers the possibility to deal with two-electron bonds.[3,4] These LMO's can be determined *a posteriori* by a unitary transformation of the canonical self-consistent-field (SCF) Hartree-Fock (HF) MO's,[3—6] or they can be constructed directly, by avoiding the computation of the canonical SCF orbitals. Such *a priori* localized MO's can be obtained either by introducing a localization potential into the general form of the HF equations,[7—10] or by improving an initial approximate set of LMO's which can be written down easily from the chemical formula. A good initial guess to LMO's in well-localizable systems can be formed by the so-called strictly localized MO's (SLMO's)[11—14] representing the chemical bonds (inner shells and lone pairs) of the molecule. The SLMO's usually possess two (one) atomic hybrid orbitals if a minimal basis set is used. The Slater determinant of the occupied SLMO's represents an approximation to the many-electron HF wave function. The mutual interaction of the chemical bonds in a molecule at the HF level results in (i) a change in the polarities of the corresponding SLMO's[14,15] and (ii) a small electron delocalization between different SLMO's[16—19]. Interactions of type (i) are electrostatic in nature leading to a rearrangement of the electron distribution in the bonds without producing charge transfer between different bonds. Delocalization corrections of type (ii) account for the intrabond charge transfer effects. If the strictly localized character of the LMO's is maintained, one can consider only interbond interactions of type (i), also named inductive effects.

In going beyond the HF level, correlation effects can also be classified according to their intra- or interbond character. Simple physical arguments indicate that the former should be much larger than the latter, since in the intrabond case the two electrons are rather close to each other and their motion is expected to be strongly correlated (left-right correlation for the two-center case). In the PCILO method[18,19] (perturbative configuration interaction using localized orbitals) one constructs the configuration-interaction (CI) wave function in terms of SLMO's. Calculations performed by the PCILO method[20] showed that the interbond correlation corrections are usually less by an order of magnitude than intrabond ones. The perturbative treatment of large intrabond effects clearly can cause an unfavorably slow convergence of the perturbation series. Therefore, one expects that a much better starting point for further calculations arises if one takes into account all intrabond effects already at the zeroth order, also including intrabond correlation. Such formalisms are offered by the theory of separated electron pairs and various other geminal methods[21—25] which construct the many-electron wave function in terms of two-electron functions (geminals). As it was discussed by Hurley[26] and recently by Luken,[24] the geminals are localized in space to a high extent. This is quite natural because the localization of geminals maximizes the intrapair correlation energy which is energetically favorable. In this paper we utilize this fact by considering our approximate wave function as an *antisymmetrized product of strictly localized geminals*. That is, both SCF and correlation effects are accounted for as far as is possible in the strictly localized model. In other words, the basis set of the atomic (hybridized) orbitals is partitioned into several subsets. Each subset represents a chemical bond (inner shell or lone pair) of the molecule. The Schrödinger equation is exactly solved for each bond within the limited basis set of the corresponding subsystem, taking into account the inductive interactions between different bonds

which do not involve an electron transfer from one bond to another. The antisymmetrized product of strictly localized geminals approximation, as compared to the fully optimized geminal methods[21,22] is expected to work well to the same extent as the strictly localized MO model[16–19] does in the HF theory.

On the other hand, the development of the present formalism was motivated by realizing the fact that, although interatomic interactions in a molecule are large, interbond interactions are rather small.[17] The former lead to the formation of the molecule itself and should not be approximated when dealing with the intrabond problems, while the latter represent only minor effects which can be treated with less rigor.

The formalism is based on second quantization which was proven to be very useful to study many-body problems in a finite basis.[20,27–30] Since dealing with two-electron bonds as primary entities, the concept of "bond creation" (annihilation) operators is introduced which create (annihilate) a two-electron bond structure acting on vacuum state. The aim of this paper is to introduce the formalism and to present an analysis of the second-quantized Hamiltonian and the corresponding wave function. The results are illustrated by some sample calculations. The theory is formulated in the basis of orthogonalized (spin) orbitals. Extensions to the nonorthogonal case and the consideration of interbond delocalization and correlation effects, as well as more detailed numerical applications, will be reported in the forthcoming paper(s) of this series.[31]

II. THE PARTITIONING OF THE HAMILTONIAN

The Born-Oppenheimer Hamiltonian of a molecule in the second quantized notation is written as

$$\hat{H}=H^0+\sum_{\mu\nu}h_{\mu\nu}a_\mu^\dagger a_\nu+\tfrac{1}{2}\sum_{\mu\nu\lambda\sigma}(\mu\lambda\mid\nu\sigma)a_\mu^\dagger a_\nu^\dagger a_\sigma a_\lambda \qquad (1)$$

provided that the set of basis functions is orthogonalized. In Eq. (1) H^0 is a constant representing the nuclear repulsion, the μ, ν, λ, and σ indices refer to spin orbitals (AO's), while

$$h_{\mu\nu}=\left\langle\mu\left|-\tfrac{1}{2}\Delta-\sum_A\frac{Z_A}{\mid r-r_A\mid}\right|\nu\right\rangle \qquad (2)$$

and $(\mu\lambda\mid\nu\sigma)$ is the usual two-electron integral in the $(11\mid22)$ convention. All integrations, of course, also involve a summation over spins. The creation (annihilation)

operators $a_\mu^\dagger$ (a_μ) obey the usual anticommutation rules:

$$a_\mu^\dagger a_\nu^\dagger+a_\nu^\dagger a_\mu^\dagger=0 , \qquad (3)$$

$$a_\mu a_\nu+a_\nu a_\mu=0 , \qquad (4)$$

$$a_\mu^\dagger a_\nu+a_\nu a_\mu^\dagger=\delta_{\mu\nu} . \qquad (5)$$

The operator $a_\mu^\dagger$ (a_μ) creates (annihilates) an electron on the spin orbital μ. The anticommutation of the creation and annihilation operators is connected to the fermion nature of electrons.

Let us note that the zero differential overlap (ZDO) condition is not utilized in the general form of the Hamiltonian (1), which, therefore, is capable of describing the different neglect-of-differential overlap (NDO) schemes[32] as well as it being able to refer to an explicitly orthogonalized basis without any approximation in the integrals. We do not restrict the discussion to one of these quantum chemical models which can be defined by the list of one- and two-electron integrals appearing in the second-quantized form of $\hat{H}$.

Let us now suppose that the molecule under consideration consists of several chemical bonds, each containing two electrons (only closed-shell systems are considered for the sake of simplicity). Lone pairs and inner-shell orbitals are handled as "one-center bonds." Each basis orbital is assigned to one of the bonds (i) which may be denoted by the symbol $\mu\in i$. With this notation the Hamiltonian (1) can be written as

$$\hat{H}=H^0+\sum_{i,j}\sum_{\mu\in i\nu\in j}h_{\mu\nu}a_\mu^\dagger a_\nu$$

$$+\tfrac{1}{2}\sum_{i,j,k,l}\sum_{\mu\in i}\sum_{\nu\in j}\sum_{\lambda\in k}\sum_{\sigma\in l}(\mu\lambda\mid\nu\sigma)a_\mu^\dagger a_\nu^\dagger a_\sigma a_\lambda . \qquad (6)$$

Different terms in Eq. (6) can be classified whether the bond indices i, j, k, and l coincide or not. Accordingly, the Hamiltonian can be partitioned as

$$\hat{H}=H^0+\sum_i\hat{H}_i^1+\sum_{i,j}{}'\hat{H}_{ij}^2+\sum_{i,j,k}{}'\hat{H}_{ijk}^3+\sum_{i,j,k,l}{}'\hat{H}_{ijkl}^4 , \qquad (7)$$

where the primes indicate that the summations are to include all pairs, threesomes, and foursomes, of the bond indices, respectively (i.e., $i\neq j$, etc.). For the different operators in Eq. (7), by simple algebraic manipulations, one gets

$$\hat{H}_i^1=\sum_{\mu,\nu\in i}h_{\mu\nu}a_\mu^\dagger a_\nu+\tfrac{1}{2}\sum_{\mu,\nu,\lambda,\sigma\in i}(\mu\lambda\mid\nu\sigma)a_\mu^\dagger a_\nu^\dagger a_\sigma a_\lambda , \qquad (8)$$

$$\hat{H}_{ij}^2=\sum_{\mu\in i\nu\in j}h_{\mu\nu}a_\mu^\dagger a_\nu$$

$$+\sum_{\mu\in i\nu\in j}\left[\sum_{\lambda,\sigma\in j}(\mu\lambda\mid\nu\sigma)a_\mu^\dagger a_\nu^\dagger a_\sigma a_\lambda+\sum_{\lambda,\sigma\in i}(\mu\nu\mid\lambda\sigma)a_\mu^\dagger a_\lambda^\dagger a_\sigma a_\nu\right.$$

$$\left.+\tfrac{1}{2}\sum_{\sigma\in i\lambda\in j}\{(\mu\lambda\mid\nu\sigma)a_\mu^\dagger a_\sigma^\dagger a_\nu a_\lambda+[(\mu\sigma\mid\nu\lambda)-(\mu\lambda\mid\nu\sigma)]a_\mu^\dagger a_\nu^\dagger a_\lambda a_\sigma\}\right] , \qquad (9)$$

$$\hat{H}_{ijk}^3=\tfrac{1}{2}\sum_{\mu\in i\nu\in j\lambda\in k}\left[\sum_{\sigma\in i}\{[(\mu\lambda\mid\nu\sigma)-(\mu\sigma\mid\nu\lambda)]a_\mu^\dagger a_\nu^\dagger a_\sigma a_\lambda+(\mu\nu\mid\sigma\lambda)a_\mu^\dagger a_\sigma^\dagger a_\lambda a_\nu\}\right.$$

$$\left.+\sum_{\sigma\in j}[(\mu\sigma\mid\nu\lambda)-(\mu\lambda\mid\nu\sigma)]a_\mu^\dagger a_\nu^\dagger a_\lambda a_\sigma+\sum_{\sigma\in k}(\mu\lambda\mid\nu\sigma)a_\mu^\dagger a_\nu^\dagger a_\sigma a_\lambda\right] , \qquad (10)$$

and

$$\hat{H}^4_{ijkl}=\sum_{\mu\in i}\sum_{\nu\in j}\sum_{\lambda\in k}\sum_{\sigma\in j}(\mu\lambda\,|\,\nu\sigma)a^\dagger_\mu a^\dagger_\nu a_\sigma a_\lambda \ . \tag{11}$$

The matrix elements of the one-electron Hamiltonian $h_{\mu\nu}$, appear in $\hat{H}^1_i$ and $\hat{H}^2_{ij}$. As for the two-electron integrals, $\hat{H}^1_i$ contains only integrals centered on bond i, $\hat{H}^2_{ij}$ possesses integrals centered on two different bonds, etc. Integrals in $\hat{H}^1_i$ and $\hat{H}^2_{ij}$, of course, can be "three center" and "four center" referring to the center of basis orbitals, since i and j are generally two-center bonds.

Obviously, $\hat{H}^1_i$ is the Hamiltonian of bond i if this bond is independent of the other bonds. Operator $\hat{H}^2_{ij}$ describes direct pairwise interactions between bonds i and j, while $\hat{H}^3_{ijk}$ and $\hat{H}^4_{ijkl}$ account for the simultaneous interaction of three and four bonds, respectively. Different terms of the Hamiltonian will be analyzed below, whether or not they result in interbond electron delocalization (Sec. V). Before doing this, we discuss the form of the strictly localized many-electron wave function.

III. STRICTLY LOCALIZED WAVE FUNCTIONS

For the sake of simplicity, let us assume that a minimal atomic basis set is used, that is, each bond is constructed by at most two hybrid orbitals. The generalization to larger basis sets is straightforward provided that each basis function can be assigned to a given bond. The two hybrids represent four spin orbitals which can be denoted by the symbols $\chi^i_{1\alpha}$, $\chi^i_{1\beta}$, $\chi^i_{2\alpha}$, and $\chi^i_{2\beta}$ for the bond i. The general form of the two-electron singlet wave function (geminal) within the limited basis of the bond i reads

$$\psi_i(1,2)=\hat{A}\{A_i\chi^i_{1\alpha}(1)\chi^i_{1\beta}(2)+B_i\chi^i_{2\alpha}(1)\chi^i_{2\beta}(2)$$
$$+C_i[\chi^i_{2\alpha}(1)\chi^i_{1\beta}(2)+\chi^i_{1\alpha}(1)\chi^i_{2\beta}(2)]\} \ , \tag{12}$$

where the numbers in parentheses refer to electrons, $\hat{A}$ is the antisymmetrizer, and A_i, B_i, and C_i are appropriate coefficients obeying the normalization condition $A_i^2+B_i^2+2C_i^2=1$. As a consequence of the orthogonality of the basis orbitals and the strictly localized character of the geminals ψ_i, the strong orthogonality condition is automatically fulfilled. The first two terms in (12) describe the ionic configurations, while C_i is the coefficient of the covalent terms. If A_i, B_i, and C_i are determined fully variationally, the two-electron wave function $\psi_i(1,2)$ represents an "exact solution" of the Schrödinger equation within the subproblem of bond i. (For one-center "bonds," $B_i=C_i=0$ and $A_i=1$, naturally.) In the second-quantized notation, Eq. (12) can be rewritten as

$$\psi_i(1,2)=[A_ia^\dagger_{i1\alpha}a^\dagger_{i1\beta}+B_ia^\dagger_{i2\alpha}a^\dagger_{i2\beta}$$
$$+C_i(a^\dagger_{i2\alpha}a^\dagger_{i1\beta}+a^\dagger_{i1\alpha}a^\dagger_{i2\beta})]\,|\,\text{vac}\rangle \ , \tag{13}$$

where $|\,\text{vac}\rangle$ is the vacuum state. Let us now define the operator

$$\hat{\psi}^\dagger_i=A_ia^\dagger_{i1\alpha}a^\dagger_{i1\beta}+B_ia^\dagger_{i2\alpha}a^\dagger_{i2\beta}+C_i(a^\dagger_{i2\alpha}a^\dagger_{i1\beta}+a^\dagger_{i1\alpha}a^\dagger_{i2\beta}) \tag{14}$$

and its adjoint

$$\hat{\psi}_i=A_ia_{i1\beta}a_{i1\beta}+B_ia_{i2\beta}a_{i2\alpha}+C_i(a_{i1\beta}a_{i2\alpha}+a_{i2\beta}a_{i1\alpha}) \tag{15}$$

by means of which the wave function of the bond i, Eq. (13), can be written simply as

$$\psi_i(1,2)=\hat{\psi}^\dagger_i\,|\,\text{vac}\rangle \ . \tag{16}$$

One can say that operator $\hat{\psi}^\dagger_i$, acting on the vacuum state, "creates" a two-electron state for the bond i, as defined by the parameters A_i, B_i, and C_i. If these parameters were obtained by the Hartree-Fock-Roothaan procedure, $\hat{\psi}^\dagger_i\,|\,\text{vac}\rangle$ would correspond to a doubly filled (strictly localized) MO. In the general case, when the above coefficients are determined fully variationally, the geminal $\psi_i(1,2)$ also contains intrabond correlation effects (namely, the so-called left-right correlation for two-center bonds) and $\hat{\psi}^\dagger_i$ creates a state which is a linear combination of several configurations.

The total many-electron wave function of the molecule containing n two-electron bonds is clearly written as

$$\Psi=\hat{\psi}^\dagger_1\hat{\psi}^\dagger_2\cdots\hat{\psi}^\dagger_n\,|\,\text{vac}\rangle \ . \tag{17}$$

This wave function is properly antisymmetric since, through Eq. (14), it is constructed by the fermion operators $a^\dagger_\mu$ fulfilling the anticommutation rules of Eqs. (3)—(5). The Ψ of Eq. (17) can be called the *antisymmetrized product of strictly localized geminals*. It is nothing but a VB-type wave function where the ionic terms are optimized for each structure. Properties of operators $\hat{\psi}_i,\hat{\psi}^\dagger_i$ are analyzed in Sec. IV.

IV. THE ALGEBRA OF OPERATORS $\hat{\psi}_i$ and $\hat{\psi}^\dagger_i$

The algebraic properties of operators $\hat{\psi}_i$ and $\hat{\psi}^\dagger_i$ are defined by their commutation relations. By evaluating the commutators and utilizing Eqs. (3)—(5) one obtains directly

$$\hat{\psi}_i\hat{\psi}_k-\hat{\psi}_k\hat{\psi}_i=0 \ , \tag{18}$$

$$\hat{\psi}^\dagger_i\hat{\psi}^\dagger_k-\hat{\psi}^\dagger_k\hat{\psi}^\dagger_i=0 \ , \tag{19}$$

$$\hat{\psi}^\dagger_i\hat{\psi}_k-\hat{\psi}_k\hat{\psi}^\dagger_i=\hat{Q}_i\delta_{ik} \ , \tag{20}$$

where the following notation is introduced:

$$\hat{Q}_i=A_i^2(\hat{n}_{i1\alpha}+\hat{n}_{i1\beta}-1)+B_i^2(\hat{n}_{i2\alpha}+\hat{n}_{i2\beta}-1)+(A_i+B_i)C_i(a^\dagger_{i1\alpha}a_{i2\alpha}+a^\dagger_{i1\beta}a_{i2\beta}+a^\dagger_{i2\alpha}a_{i1\alpha}+a^\dagger_{i2\beta}a_{i1\beta})+C_i^2(\hat{N}_i-2) \ . \tag{21}$$

Here the particle number operators $\hat{n}_\mu,\hat{N}_i$ are defined by

$$\hat{n}_\mu=a^\dagger_\mu a_\mu \ , \tag{22}$$

$$\hat{N}_i=\sum_{\mu\in i}\hat{n}_\mu \ . \tag{23}$$

Equation (18) and (19) show that the operators $\hat{\psi}_i$ and $\hat{\psi}^\dagger_i$, in contrast to a_μ and $a^\dagger_\mu$ in Eqs. (3) and (4), commuting instead of anticommuting among themselves, showing Bose-type behaviors. This is obvious since, though single

electrons are fermions, $\hat{\psi}_i^\dagger$ creates a bond structure of a pair of electrons with an integer spin. In this sense we can say that $\hat{\psi}_i^\dagger$ creates a quasi Bose particle i in a state defined by the parameters A_i, B_i, and C_i; this particle is not "elementary" but it is composed by the two electrons belonging to the bond i. It is to be emphasized however, that such quasi Bose particles in a usual molecule can be introduce only formally since the two electrons of a chemical bond do not form a bound state physically. We note that the well-known Cooper pairs, introduced phenomenologically in the theory of superconductivity, represent a completely different situation. We stress also that *no* approximation is used in our approach which would utilize the properties of these bosons; their formal introduction is to be considered as an appropriate notation. Anyway, it will turn out that the introduction of operators $\hat{\psi}_i, \hat{\psi}_i^\dagger$ offers a useful practical tool in studying the nature of the chemical bond in multiatomic molecules.

The appearance of operators $\hat{Q}_i$ in Eq. (20) is just a consequence of the composite nature of the quasi Bose particles describing the chemical bond i, since creation and annihilation operators $\hat{\phi}_i, \hat{\phi}_k^\dagger$ of true elementary bosons should obey the usual commutation rules

$$\hat{\phi}_k^\dagger \hat{\phi}_i - \hat{\phi}_i \hat{\phi}_k^\dagger = -\delta_{ik}$$

instead of Eq. (20). Thus the deviation of $\hat{Q}_i$ from the unity operator indicates the *composite nature of the quasiparticles*. It may be worthwhile to give the actual form of $\hat{Q}_i$ in some special cases.

(a) If the bond i is neutral, the two ionic terms in Eq. (12) have an equal weight: $A_i = B_i$. Then, using the definition (23) of the particle number operator, we have

$$\hat{Q}_i = (A_i^2 + C_i^2)(\hat{N}_i - 2)$$

$$+ 2A_i C_i (a_{i1\alpha}^\dagger a_{i2\alpha} + a_{i2\beta}^\dagger a_{i1\alpha}$$

$$+ a_{i1\beta}^\dagger a_{i2\beta} + a_{i2\beta}^\dagger a_{i1\beta}) \ . \tag{24}$$

Note that for a single-determinant HF wave function $A_i = C_i = \frac{1}{2}$ for the neutral ($A_i = B_i$) case.

(b) In the simple Heitler-London VB scheme one drops both ionic terms in Eq. (12), i.e., one has $A_i = B_i = 0$ and $C_i = 1/\sqrt{2}$. Then one finds simply

$$\hat{Q}_i = \tfrac{1}{2}\hat{N}_i - 1 \ . \tag{25}$$

Note that $\langle \Psi | \hat{Q}_i | \Psi \rangle = 0$ and $\langle \text{vac} | \hat{Q}_i | \text{vac} \rangle = -1$ for the Heitler-London wave function.

Let us now study the commutational properties between the operators $\hat{\psi}_i^\dagger (\hat{\psi}_i)$ and the original single-electron creation (annihilation) operators. The explicit evaluation of the commutators yields

$$\hat{\psi}_i a_\mu - a_\mu \hat{\psi}_i = 0 \ , \tag{26}$$

$$\hat{\psi}_i^\dagger a_\mu^\dagger - a_\mu^\dagger \hat{\psi}_i^\dagger = 0 \ , \tag{27}$$

$$\hat{\psi}_i a_\mu^\dagger - a_\mu^\dagger \hat{\psi}_i = \hat{R}_{i\mu} \delta_{ik} \quad (\mu \in k) \tag{28}$$

where $\hat{R}_{i\mu}$ is given by

$$\hat{R}_{i\mu} = A_i (\delta_{\mu,1\alpha} a_{i1\beta} - \delta_{\mu,1\beta} a_{i1\beta}) + B_i (\delta_{\mu,2\alpha} a_{i2\beta} - \delta_{\mu,2\beta} a_{i2\alpha})$$

$$+ C_i (\delta_{\mu,2\alpha} a_{i1\beta} - \delta_{\mu,1\beta} a_{i2\alpha} + \delta_{\mu,1\alpha} a_{i2\beta} - \delta_{\mu,2\beta} a_{i1\alpha}) \ . \tag{29}$$

Again, the bond creation (annihilation) operators $\hat{\psi}_i^\dagger (\hat{\psi}_i)$ commute the creation (annihilation) operators $a_\mu^\dagger (a_\mu)$ of atomic orbitals. This is also quite natural since $\hat{\psi}_i^\dagger$ and $\hat{\psi}_i$ are linear combinations, each term containing a product of two operators, $a_\mu^\dagger a_\nu^\dagger$ and $a_\mu a_\nu$, respectively.

It should be noted at this point that the second-quantized theory of composite particles was outlined by several authors in another context.[33-38] The recent papers by Girardeau[39] and Kvasnička[40] are also worth mentioning. In the latter, e.g., a system of hydrogen atoms, free protons, and electrons was studied *via* second quantization.

The above commutation properties of the bond creation and annihilation operators allow calculation of any expectation value or matrix element by the multideterminant molecular wave function of Eq. (17) in a straightforward manner. We are therefore in a position to undertake further analyses on the Hamiltonian (7).

V. THE INDUCTIVE INTERACTION

Let us introduce the following partition of the total Hamiltonian $\hat{H}$ of Eq. (1):

$$\hat{H} = \hat{h}^0 + \hat{W} \ , \tag{30}$$

where the terms $\hat{h}^0$ and $\hat{W}$ are defined by requiring that the expectation value of $\hat{W}$ as calculated by strictly localized geminal wave function (17) be zero:

$$\langle \Psi | \hat{W} | \Psi \rangle = 0 \ . \tag{31}$$

That is, we define a model Hamiltonian $\hat{h}^0$ whose expectation value is just the energy of the approximate wave function Ψ:

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi | \hat{h}^0 | \Psi \rangle \ . \tag{32}$$

The operator $\hat{h}^0$ can be called the strictly localized Hamiltonian. It will be constructed as follows.

Expectation values of operators expressed by $a_\mu^\dagger, a_\nu$ can easily be calculated by the commutation properties (18)—(20) and (26)—(28). For example, simple algebraic manipulations lead to the following result:

$$\langle \Psi | \hat{H}_{ijkl}^4 | \Psi \rangle = \sum_{\substack{\mu \in i, \\ \nu \in j, \\ \lambda \in k, \\ \sigma \in l}} (\mu\lambda | \nu\sigma) \langle \text{vac} | \hat{\psi}_1 \hat{\psi}_2 \cdots a_\mu^\dagger a_\nu^\dagger a_\sigma a_\lambda \hat{\psi}_1^\dagger \hat{\psi}_2^\dagger \cdots \hat{\psi}_n^\dagger | \text{vac} \rangle = 0 \ . \tag{33}$$

And, similarly,

$$\langle \Psi \mid \hat{H}^3_{ijk} \mid \Psi \rangle = 0 \ . \tag{34}$$

In the above equations the operators $\hat{H}^3_{ijk}$ and $\hat{H}^4_{ijkl}$ were defined in Eqs. (10) and (11). These results show that operators $\hat{H}^3_{ijk}$ and $\hat{H}^4_{ijkl}$ are to be included into $\hat{W}$, since they *do not contribute to the energy* as far as the "antisymmetrized product of strictly localized geminals" wave function is used. The same does not hold for the operator $\hat{H}^2_{ij}$ representing the pairwise interbond interaction, for which we obtain

$$\langle \Psi \mid \hat{H}^2_{ij} \mid \Psi \rangle = \langle \text{vac} \mid \psi_1 \psi_2 \cdots \psi_n \hat{H}^2_{ij} \hat{\psi}^\dagger_1 \hat{\psi}^\dagger_2 \cdots \hat{\psi}^\dagger_n \mid \text{vac} \rangle$$
$$= \tfrac{1}{2} \sum_{\mu,\sigma \in i} \sum_{\nu,\lambda \in j} P^i_{\mu\sigma} P^j_{\nu\lambda} [(\mu\sigma \mid \nu\lambda) - (\mu\lambda \mid \nu\sigma)] \ , \tag{35}$$

where $P^i_{\mu\sigma}$ is defined by

$$P^i_{\mu\sigma} = \langle \text{vac} \mid \hat{\psi}_i a^\dagger_\mu a_\sigma \hat{\psi}^\dagger_i \mid \text{vac} \rangle \ , \tag{36}$$

i.e., $P^i_{\mu\sigma}$ is the representation of the first-order density matrix for the bond i. Note that $P^i_{\mu\sigma}$ is not idempotent in general since it corresponds to a multiconfiguration wave function $\hat{\psi}^\dagger_i \mid \text{vac} \rangle$. The total molecular density matrix corresponding to the wave function Ψ is given by the direct product of the $\underline{P}^i$ matrices:

$$\underline{P} = \underline{P}^1 \otimes \underline{P}^2 \otimes \cdots \otimes \underline{P}^n \ . \tag{37}$$

That is, no interbond density elements occur, which is a consequence of the strict localization. The trace of the matrix $\underline{P}$, as usual, gives the total number of electrons in the molecule:

$$\text{Tr}\underline{P} = \sum_i \text{Tr}\underline{P}^i = \sum_i \sum_{\mu \in i} \langle a^\dagger_\mu a_\mu \rangle = \sum_i \langle \hat{N}_i \rangle = 2n \ ,$$

where n is the total number of bonds.

Now, let us modify the operators $\hat{H}^1_i$ and $\hat{H}^2_{ij}$ introduced in Eqs. (7)—(9) in the following manner:

$$\hat{H}^1_i \to \hat{H}^{1\,\text{eff}}_i = \sum_{\mu \in i} \sum_{\nu \in i} h^{\text{eff}}_{\mu\nu} a^\dagger_\mu a_\nu$$
$$+ \tfrac{1}{2} \sum_{\mu,\nu \in i} \sum_{\lambda,\sigma \in i} (\mu\lambda \mid \nu\sigma) a^\dagger_\mu a^\dagger_\nu a_\sigma a_\lambda \ , \tag{38}$$

where

$$h^{\text{eff}}_{\mu\nu} = h_{\mu\nu} + \tfrac{1}{2} \sum_{j\,(\neq i)} \sum_{\lambda,\sigma \in j} P^j_{\sigma\lambda} [(\mu\nu \mid \sigma\lambda) - (\mu\lambda \mid \nu\sigma)] \ . \tag{39}$$

Furthermore,

$$\hat{H}^2_{ij} \to \hat{H}^{\prime\,2}_{ij}$$
$$= \hat{H}^2_{ij} - \tfrac{1}{2} \sum_{\mu,\nu \in i} \sum_{\sigma,\lambda \in j} P^j_{\sigma\lambda} [(\mu\nu \mid \sigma\lambda) - (\mu\lambda \mid \nu\sigma)] a^\dagger_\mu a_\nu \ . \tag{40}$$

As is easy to see, this repartitioning of the Hamiltonian leads to the result that

$$\langle \Psi \mid \hat{H}^{\prime\,2}_{ij} \mid \Psi \rangle = 0 \ . \tag{41}$$

That is, utilizing Eqs. (33) and (34), we have

$$\langle \Psi \mid \hat{H} \mid \Psi \rangle = \left\langle \Psi \left| \sum_i \hat{H}^{1\,\text{eff}}_i \right| \Psi \right\rangle \ . \tag{42}$$

Accordingly, the operator $\hat{h}^0$ can be identified with $\sum_i \hat{H}^{1\,\text{eff}}_i$.

The operator $\hat{H}^{1\,\text{eff}}_i$ can be considered as the effective Hamiltonian for the bond i. It no longer describes an independent bond but takes into account the electrostatic influence of all other bonds through the effective core $h^{\text{eff}}_{\mu\nu}$. This inductive interaction describes the polarization of the bonds, but it does not affect the strict localization, i.e., it does not produce any charge transfer between different bonds. Since each bond is in the electrostatic field of other bonds, the wave-function coefficients A_i, B_i, and C_i ($i = 1,2,\ldots,n$) can be obtained by an iterative procedure. Such procedures are often used for calculating the optimal bond polarities at the Hartree-Fock level.[14,15,19,41,42] Another possibility to solve such a nonlinear problem is the application of special perturbation theories developed for nonlinear Schrödinger equations,[43] where the system under consideration (here a chemical bond) is perturbed by an operator which depends on the wave function itself.

The energy of the strictly localized geminal wave function is expressed as [cf. Eq. (42)]

$$E = E_{\text{nucl}} + \sum_i \left[\sum_{\mu,\nu \in i} h^{\text{eff}}_{\mu\nu} P^i_{\mu\nu} + \tfrac{1}{2} \sum_{\mu,\nu,\lambda,\sigma \in i} (\mu\lambda \mid \nu\sigma) \Gamma^i_{\mu\nu\lambda\sigma} \right] \ , \tag{43}$$

where E_{nucl} is the nuclear repulsion and

$$\Gamma^i_{\mu\nu\lambda\sigma} = \langle \text{vac} \mid \hat{\Psi}_i a^\dagger_\mu a^\dagger_\nu a_\sigma a_\lambda \hat{\Psi}^\dagger_i \mid \text{vac} \rangle \tag{44}$$

is the element of the second-order density matrix of the bond i. The first- and second-order density matrix elements can easily be expressed by the coefficients A_i, B_i, and C_i, using the commutation rules of Eqs. (18)—(20) and (26)—(28). For example, in order to illustrate the worth of using operators $\hat{\psi}_i, \hat{\psi}^\dagger_i$ we give here the explicit formula for $P^i_{\mu\nu}$ ($\mu,\nu \in i$):

$$P^i_{\mu\nu} = \langle \text{vac} \mid \hat{\psi}_i a^\dagger_\mu a_\nu \hat{\psi}^\dagger_i \mid \text{vac} \rangle$$
$$= \langle \text{vac} \mid \hat{R}_{i\mu} \hat{R}^\dagger_{i\nu} \mid \text{vac} \rangle \ , \tag{45}$$

where use was made of Eqs. (26)—(29) and the operator $\hat{R}^\dagger_{i\nu}$ is defined as the adjoint of $\hat{R}_{i\nu}$ in Eq. (29). The substitution of $\hat{R}_{i\mu}$ and $\hat{R}^\dagger_{i\nu}$ into (45) immediately gives

$$P^i_{1\alpha,1\alpha} = P^i_{1\beta,1\beta} = A^2_i + C^2_i \ , \tag{46}$$

$$P^i_{2\alpha,2\alpha} = P^i_{2\beta,2\beta} = B^2_i + C^2_i \ , \tag{47}$$

$$P^i_{1\alpha,2\alpha} = P^i_{1\beta,2\beta} = P^i_{2\alpha,1\alpha} = P^i_{2\beta,1\beta}$$
$$= (A_i + B_i)C_i \ , \tag{48}$$

while other $P^i_{\mu\nu}$ elements are zero. That is, the spinless density matrix $\underline{D}^i = \underline{P}^i(\alpha) + \underline{P}^i(\beta)$ reads

$$\underline{D}^i = 2 \begin{bmatrix} A^2_i + C^2_i & (A_i + B_i)C_i \\ (A_i + B_i)C_i & B^2_i + C^2_i \end{bmatrix} \ . \tag{49}$$

Similarly, the second-order density matrix can be expressed by using Eq. (28) as

$$\Gamma_{\mu\nu\lambda\sigma}^{i} = \langle \text{vac} \mid R_{\mu}a_{\nu}^{\dagger}a_{\sigma}R_{\lambda}^{\dagger} \mid \text{vac} \rangle \qquad (50)$$

which can easily be evaluated for every given foursome of the indices μ, ν, λ, and σ.

The form of the effective one-electron Hamiltonian h^{eff}, as given in Eq. (39), is the same as that usual at the Hartree-Fock level,[42,44−46] but it is calculated by the exact intrabond density matrix elements $P_{\mu\nu}^{i}$ taking into account some correlation effects as well. By means of Eq. (39) the total ground-state energy, E of Eq. (43), can be rewritten as

$$E = \sum_{i}E_{i}^{0} + \tfrac{1}{2}\sum_{i,j}{}'E_{ij} + E_{\text{nucl}} , \qquad (51)$$

where E_{i}^{0} is the energy of the ith bond, and

$$E_{ij} = \sum_{\mu,\nu\in i}\sum_{\lambda,\sigma\in j} P_{\mu\nu}^{i}P_{\lambda\sigma}^{j}[(\mu\nu\mid\lambda\sigma)-(\mu\lambda\mid\nu\sigma)] \qquad (52)$$

is the interaction energy of bonds i and j. Note that even E_{i}^{0} depends on the other bonds implicitly, through the parameters A_{i}, B_{i}, and C_{i} if they are optimized with the strictly localized effective Hamiltonian $\hat{h}^{0}$.

VI. CONCLUSIONS

In this paper a formalism is developed for analyzing the second-quantized form of the Hamiltonian and to discuss the form of approximate wave functions in an orthogonalized basis. Correspondence is established between the chemical bonds of a molecule and formally bounded electron pairs which can be handled as quasiparticles showing Bose-type behaviors. Accordingly, the bond creation and annihilation Bose operators are introduced for which commutation rules are derived reflecting also the composite nature of the formal Bose quasiparticles.

The physical reality of these formal bosons is the same as those of two-electron chemical bonds; the latter is certainly approximate but it represents obviously one of the most fruitful interpretative tools in chemistry.

In the present approach it is possible to solve the relevant Schrödinger equation exactly for each bond, in the subset of basis functions assigned to the bond in question. The wave function is constructed in terms of the strictly localized geminals. This wave function corresponds to a strictly localized Hamiltonian $\hat{h}^{0}$ possessing only integrals centered on one and two bonds. The strictly localized Hamiltonian can be written as a sum of the effective intrabond Hamiltonians $\hat{H}_{i}^{\text{eff}}$.

The antisymmetrized product of strictly localized geminals wave function is expected to give a rather satisfactory approximation for a wide class of molecules since (a) it accounts for the inductive interactions of the chemical bonds and (b) it is highly correlated since it describes properly the left-right correlation effect within each chemical bond. Feature (a) ensures a proper electrostatics of the bonds, while feature (b) results in obtaining correct dissociation properties of the molecule (which is not the case, e.g., in the Hartree-Fock method). We note also that the discussed wave function is size extensive and size consistent.[47]

The density matrix of the present wave function is block diagonal as a consequence of the strict localization. That is, we have taken into account all types of interbond interactions which maintain the block diagonality of the density matrix. Such interactions do not produce electron transfer between different bonds. The weakness of the interbond charge transfer is the condition for the applicability of the strictly localized geminal wave function. This condition is fulfilled for the majority of saturated molecules, for which all the effects neglected in this work are expected to be sufficiently small to be handled by means of a fast convergent perturbational treatment.[31]

APPENDIX: NUMERICAL ILLUSTRATIONS

In this appendix some test calculations are presented using Pople's CNDO/2 Hamiltonian,[48] with the aim to illustrate the effectivity of the present scheme. Though the CNDO/2 was introduced as an all-valence-electron SCF method working at the HF level, the popular PCILO method[18,19] accounts for some correlation effects as well, within the CNDO/2 scheme and using the original semi-empirical parameter set. In the present (preliminary) applications we follow the same approach. Since the CNDO makes use of the ZDO condition, the underlying basis set is orthonormal so the present scheme can be applied. (For a closely related approach, using the HF spinorbitals as a basis set, see Ref. 49.)

1. Chain of hydrogen atoms

Table I presents total energies of a few short H_n chains ($n = 2$, 4, 6, 8, and 10) in the approximation using (i) strictly localized molecular orbitals, (ii) standard CNDO/2 wave functions at the closed-shell restricted HF level (SCF), and (iii) the present strictly localized geminals (SLG's), respectively. For the positions of the hydrogen atoms, a linear alternating geometry is assumed with $r_< = 0.74$ Å and $r_> = 1.0$ Å.

In the case of the hydrogen molecule ($n = 2$), one has only a single two-center bond, thus there is no interbond delocalization effect. Consequently, $E_{\text{SLMO}} = E_{\text{SCF}}$ in this case. A significant improvement of energy is obtained, however, when the SLG approximation is used which

TABLE I. Total energies (a.u.) of alternating chains of n hydrogen atoms for several n in different approximations (see text).

Chain	SLMO	SCF	SLG
H_2	−1.4746	−1.4746	−1.4846
H_4	−2.8864	−2.9212	−2.9063
H_6	−4.2980	−4.3682	−4.3279
H_8	−5.7097	−5.8152	−5.7495
H_{10}	−7.1213	−7.2621	−7.1711

INTERACTION OF CHEMICAL BONDS: STRICTLY . . .
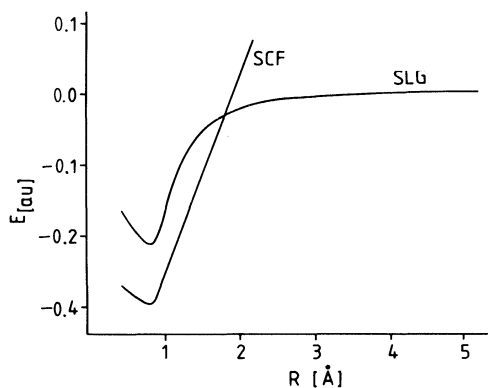
FIG. 1. Potential curve of the $H_{10} \rightarrow H_9 + H$ dissociation.

represents now the exact solution ("full CI") in this minimal basis. The correlation energy obtained (0.001 a.u.=0.27 eV) is in agreement with the analytical result[50] serving as a test of the procedure.

For the H_n ($n > 2$) chains the calculated delocalization energy $|E_{SCF} - E_{SLMO}|$ is higher than the correlation energy contribution which can be obtained by the SLG wave function ($|E_{SLG} - E_{SLMO}|$, see Table I). This is not surprising because this hydrogenic chain is far from being well localizable.[17,51] However, the superiority of the SLG wave function becomes evident if one studies the dissociation process of the H_{10} chain

$$H_{10} \rightarrow H_9 + H .$$
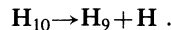
The corresponding potential curves are depicted in Fig. 1. At the SLG level the H_{10} supermolecule dissociates properly, while the SCF method possesses the well known "dissociation catastrophe."

2. Methane

For the next example methane (CH_4) is chosen, which is a typically well-localizable system. The calculated energies are presented in Table II. The standard geometry was assumed. The PCILO values, given for comparison, are obtained by using the perturbation energy corrections given in Ref. 55. As it is seen, the SLG model in CH_4 represents a really good approximation: E_{SLG} is better than E_{SCF}. This is connected to the good localizability of

TABLE II. Total energy of methane (a.u.) in different approximations. MP and EN refer to the Moller-Plesset (Ref. 52) and Epstein-Nesbet (Ref. 53 and 54) partitions of the Hamiltonian, respectively.

SLMO	-10.1122
SCF	-10.1136
SLG	-10.1493
PCILO-MP	
Second order	-10.1372
Third order	-10.1456
PCILO-EN	
Second order	-10.1518
Third order	-10.1510
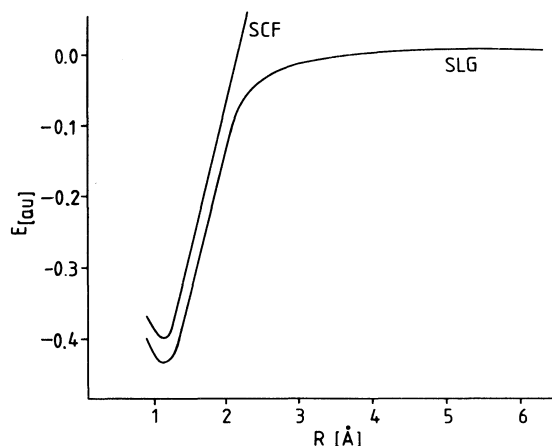
FIG. 2. Potential curve of the $CH_4 \rightarrow CH_3 \cdot + \cdot H$ dissociation.

this molecule, since $E_{deloc} = |E_{SCF} - E_{SLMO}| = 0.038$ eV, while $E_{corr} = |E_{SLG} - E_{SLMO}| = 1.009$ eV. The second- and third-order PCILO results in the Moller-Plesset partitioning, though they contain also some delocalization contributions, are worse than E_{SLG}, which does not. The PCILO values corresponding to the Epstein-Nesbet partition of the Hamiltonian are seemingly deeper, but it is to be realized that the PCILO being a perturbative method, its energy predictions do not serve as upper bounds to the exact (full CI) energy, while E_{SLG} is obtained as an expectation value, thus it is a strict upper bound. Moreover, we note that the third-order PCILO computations are much more expensive than the calculation of SLG's and their energies.

To illustrate the attributes of the SLG approximation, we have studied also the dissociation of methane to a methyl radical and a H atom:

$$CH_4 \rightarrow CH_3 \cdot + \cdot H .$$

Figure 2 shows that, again, a proper dissociation is obtained by the SLG wave function, while the SCF method is unable to give, even qualitatively, a correct potential curve.

3. Rotation around double bonds: The ethylene barrier

The examples given in Figs. 1 and 2 show that the SLG approximation is capable of describing molecular process-

TABLE III. Contributions to the ethylene barrier (kcal/mol).

	ΔE
Change in E_{SLMO}	261.1
Change in E_{deloc}	-118.9
Change in E_{corr}	-60.3
Sum of contributions	81.8
Ab initio SCF + CI barrier (Ref. 57)	83.0
Experimental barrier (Ref. 56)	65.0

es when a two-electron chemical bond is broken. A related important application concerns the treatment of barriers to internal rotations around *double* bonds. The SCF theories at the closed-shell restricted Hartree-Fock level cannot give reliable estimations to such barriers, since the change in the correlation energy in the process is significant. For instance, the barrier of ethylene, $H_2C=CH_2$, by the standard CNDO/2 SCF method was found to be 142 kcal/mol at standard bond lengths and angles. This is extremely large as compared to the experimental value of 65 kcal/mol,[56] though the CNDO/2 method predicts rather correct barriers to rotations around single bonds.[57] *Ab initio* SCF calculations predict similarly incorrect barriers for ethylene.[57]

The correlation energy change during the ethylene rotation from the planar to the perpendicular conformer, as calculated by the difference of the SLG and SLMO energies, is 60.3 kcal/mol. If we correct the SCF barrier of 142 kcal/mol by this change, we obtain 81.8 kcal/mol which is a more reliable estimation. *Ab initio* SCF + CI results[57] predict, e.g., 83 kcal/mol. Accordingly, we can say that the SLG wave function accounts for the dominant part of the correlation energy change in calculating barriers to rotations around double bonds. We note, however, that delocalization effects are never negligible when calculating barriers within orthogonal basis sets.[16,17,58] Our conclusions are summarized in Table III.

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