

The Representation of the Chemical Bond in Quantum Chemical Calculations

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The mathematical representation of chemical bonds in molecules is discussed. The molecule is viewed as a system of weakly interacting chemical bonds. The intrabond problems and the averaged electrostatic interbond interactions are handled at the zeroth order, while the small interbond delocalization and dispersion effects are taken into account on the basis of the perturbation theory. A special diagrammatic technique is applied for obtaining delocalization corrections for strictly localized orbitals. A general second quantized theory is discussed in which the chemical bonds are identified with two-electron local bond structures characterized by composite-particle creation operators showing Bose-type commutation rules. This approach accounts for intrabond correlation already at the zeroth order.

I. INTRODUCTION

»Molecules consist of electrons and nuclei«. This view is that of a physicist who wants to calculate all molecular properties using only the first principles of quantum mechanics. It is, however, a very difficult job usually and does not agree with the standard practice in theoretical physics (cf. *e. g.* solid state theory), where specific models are introduced often.

»Molecules consist of (strongly interacting) atoms«. This is a more powerful view: one cannot systematize the chemistry without introducing the concept of the atom. Many attempts have been made to incorporate atomic properties into molecular calculations and to analyse atomic contributions (LCAO scheme, population analysis¹, energy partitioning^{2,3}, etc.). Despite its inevitable power, the LCAO model alone does not solve the problem of representing atoms in molecules. Some approaches which try to utilize atomic properties explicitly are worth mentioning. The »atoms in molecules«⁴ method constructs molecular wave functions in terms of atomic many-electron functions and takes interatomic interactions into account as perturbations. Mayer's recent »chemical Hamiltonian« formalism³ permits *a priori* identification of the effective intra- and interatomic energy operators. Interatomic interactions, however, can be very large (they are in fact responsible for the formation of the molecule), excluding the possibility of developing truly efficient perturbation theories.

»Molecules consist of (weakly interacting) chemical bonds.« This view represents the picture of molecules seen primarily from the chemical point of view. In this case, of course, the concept of the chemical bond has to be established. This concept is not free from some difficulties from the theoretical point

of view.⁵ The present paper is, in part, devoted to discussing the problem of representing the chemical bond in quantum chemical calculations. Once the mathematical description of the bonds has been established, molecular properties can be calculated in terms of bond contributions and interbond interactions. The latter are rather weak usually permitting to handle them as small perturbations.

We have to make some comments on the importance of bonds, atomic contributions and related concepts in molecular theory. During the early stages of quantum chemistry, more attention was paid to questions like these (cf. the life-work of Pauling, Coulson, etc.). At present, the so-called computational quantum chemistry is emerging. Without debating the extreme importance of large scale computations, we emphasize that qualitative considerations are also inevitable if one wants to understand the essence of different chemical effects.^{5c} It is a matter of scientific attitude whether or not one is interested in this kind of understanding. The present renaissance of valence bond type approaches⁶, mainly in the field of chemical interpretation, is possibly due to the feeling that something is missing from the (otherwise very fine) results of computational quantum chemistry. Moreover, many chemically relevant questions cannot be answered by state-of-art quantum chemistry. *Ab initio* calculations are available for molecules of (at most) medium size, while the results of semi-empirical and empirical calculations are often unreliable. The problem is even more pronounced if one takes electron correlation into account. That »brute force« calculations are unfavorable became evident, and effective schemes are always based on some very physical model of electron interaction (cf. e.g. IEPA⁷, CEPA⁸, etc.).

The aim of this paper is to summarize some previous results⁹⁻¹⁸ concerning the representation of chemical bonds and the theory of their interactions, and to present some recent results achieved in these spheres. Although, consistently in the spirit of the present Volume, computational aspects are not discussed, we always have to keep in mind that effective schemes can only be developed by constructing the appropriate model of the phenomenon in question. The corresponding mathematical formalism is not necessarily »simple«: a physical problem can only be understood or analysed in simple terms by a suitably effective formalism. We stress that we are not able to *derive* the concept of the chemical bond from quantum theory.¹⁹ We simply accept its existence as an empirical fact. Our aim is to find a *proper description* of the chemical bond within the framework of the Born-Oppenheimer model.

According to the general recipe followed in theoretical physics in studying the structure of matter, the primary task is to find the smallest possible building blocks which do not interact considerably with each other. They are usually composite in the sense that they contain many elementary particles. Then, the goal is reduced to describe the internal structure of these small building units, and the macroscopic properties are approximately deduced by perceiving these blocks independently.

In chemistry, molecules appear to be such natural building units of many macroscopic compounds*. Accordingly, one of the most typical aims of quantum chemistry is to calculate the internal structure of molecules. This can be done

* Although not free from some conceptual difficulties from the theoretical point of view^{20,21}, we are not discussing the reliability of the idea of molecules, rather we accept the common intuitive meaning.

perfectly if they are small, but the Schrödinger equation can never be solved for a very large molecule by present numerical techniques, due to the well-known catastrophic dependence of the computational work on the number of particles. This suggests that we *have not found the most appropriate (smallest) building blocks*, and that we have to analyse more extensively the structure of large molecules qualitatively.

In chemistry it is generally accepted that *bonds* are the weakly interacting subunits that comprise molecule. Thermodynamically extensive properties (energy, dipole moment, diamagnetic susceptibility, etc.) can be obtained as sums of bond increments.

The most typical kind of chemical bond is the two-electron one. Concerning the significance of localized two-electron subsystems in diverse chemical materials, we may divide different compounds into three categories:

(A) »*Well localizable*« systems consist of weakly interacting molecules; each molecule can be described by the classical Lewis-structure of two centre bonds, lone pairs, etc. These two-electronic units interact weakly.

(B) The »*locally delocalized*« systems contain molecules built up by two-electron bonds for the most part, but there are also (one or more) subunits for which the appropriate smallest weakly interacting blocks contain *a few* electrons⁵. The strong delocalization extends over a limited region. An example is benzene, in which the sigma bonds are two-electronic, while the pi system of 6 electrons is inherently delocalized.

(C) In »*completely delocalized systems*« the strong delocalization extends over the whole system. Typical examples are graphite, metals, metallic (equidistant) polyene, etc. Such kinds of electronic systems show collective phenomena in which the localization plays no role; rather the band-picture is appropriate.

In the subsequent text we focus on systems of type (A), which cover a wide range of chemical interest. Generalization of type (B) is possible (cf. *e. g.* the contribution by Náray-Szabó in the present issue and references therein), but the analysis of systems of category (C) requires a different formulation. The case of closed shell systems will be discussed; open shell molecules are usually delocalized and belong to category (B) (cf. the Koopmans theorem for ionized states valid for canonical orbitals).

II. THE REPRESENTATION OF THE CHEMICAL BOND IN THE MO SCHEME

II.A. On Using Localized Orbitals

Usual MO schemes work with canonical orbitals which are delocalized over the whole molecule. Although the significance of canonical MOS is unquestionable in many respects, they are useless for the present purpose. However, one can localize the MOs by appropriate transformations.²²⁻²⁵ Localized molecular orbitals, LMOs, usually correspond to classical bonds, inner shell and lone pairs of molecules. It is often argued²⁶ that this representation has little value since the LMOs are not unique. We do not accept this criticism because of the following reasons:

- (i) Different localization procedures lead to very similar LMOs in general;
- (ii) The shape of LMOs can be related to the shape of Fermi holes^{27,28};

(iii) The HF orbitals can be made unique by demanding also the Hartree energy to be minimized; the resulting MOs are identical with the LMOs determined by the Edminston-Ruedenberg procedure^{29,30};

(iv) The physical significance of localization is supported by Daudel's loge theory³¹;

(v) A sophisticated generalization of the one-electron model is the theory of two-electron function geminals; the geminals are also localized in space usually, though they do not show the ambiguities of LMOs³².

The above points indicate that there is some physical reality in the LMO picture. We will show that LMOs permit the consideration of well localizable molecules as ensembles of weakly interacting chemical bonds.

II.B. *The Partitioning of the Basis Set*³³

The overall binding situation in the molecule is supposed to be known. Then, working in a finite basis, we assign each basis orbital (μ) to a definite chemical bond (i) which may be denoted as $\mu \in i$. This generally implies an appropriate hybridization procedure which is not discussed here in detail. Many attempts have been made to find proper atomic hybrids^{5,34-43}. For our purposes any set of hybrids can be used provided that the perturbation series expanding the wave function (*vide infra*) converge. We demand only that each hybrid be assigned to one of the bonds unequivocally.

The customary Roothaan formalism works within the LCAO scheme, where each basis function is assigned to an atom. This leads to the representation of atoms, rather than bonds, in the molecule. The bridge between the two formalisms can be the hybridization procedure. This is not the only possibility however: one can also deal with basis orbitals which are not centred on atoms (*e. g.* bond functions⁴⁴⁻⁴⁷ or floating functions⁴⁸⁻⁴⁹).

II.C. *The Zeroth Order: Strictly Localized Orbitals*^{5,9,50-52}

Let us assume that the basis orbitals are orthonormalized. Accordingly, the following treatment refers to a Löwdin- or a ZDO basis set. Note that in the former case the orthogonal hybrids assigned to the bond cannot be of pure atomic nature. The explicit treatment of non-orthogonality effects is given elsewhere¹³ (see also Sect. II.D).

An initial guess to the LMOs is constructed by expanding each LMO describing the bond i in the subspace of the basis orbitals assigned to this bond:

$$\varphi_i^0 = \sum_{\mu \in i} c_{\mu}^i \psi_{\mu} \quad (1)$$

That is, these initial orbitals φ_i^0 do not have any »tail« on other bonds:

$$c_{\nu}^i = 0 \quad \text{if} \quad \nu \notin i \quad (2)$$

Such orbitals will be referred to as strictly localized MOs (SLMOs). Note that the tails of LMOs are defined as delocalization correction to the SLMOs (see Section II.D). The occupied SLMOs are bonding, lone pair or inner shell orbitals. In the present formulation no distinction between these units is necessary since all the three subsystems possess two electrons and the corresponding SLMOs are expanded in their own subsets in the sense of Eq. (1)

in all three cases. Hereafter we will simply use the term »bond« for these subsystems.

Since the set of SLMOs is orthogonal, the usual density matrix is defined as

$$\mathbf{P}^0_{\mu\nu} = 2 \sum_i^{\text{occ}} c_{\mu}^i c_{\nu}^i \quad (3)$$

which, due to the restriction (2) expressing the strict localizability, clearly has a blockdiagonal form (Figure 1):

$$\mathbf{P}^0_{\mu\nu} = 0 \quad \text{if } i \neq k; \quad \mu \in i, \quad \nu \in k \quad (4)$$

The c_{μ}^i ($\mu \in i$) coefficients characterize the electronic structure of the bond i and they are determined variationally. Let us first introduce the following partition of the core Hamiltonian⁵:

$$h_{\mu\nu} = h^0_{\mu\nu} + h^1_{\mu\nu} \quad (5)$$

where \mathbf{h}^0 is a blockdiagonal matrix containing the *intra*bond matrix elements while \mathbf{h}^1 contains the interbond integrals (Figure 1). We have to investigate

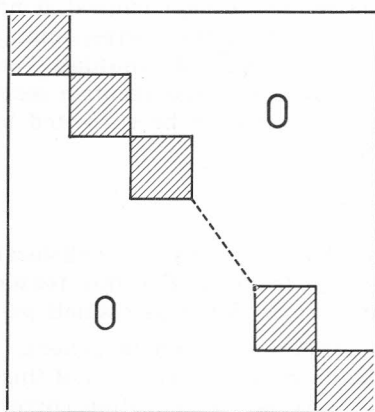


Figure 1. Blockdiagonal form of the zeroth order \mathbf{H} , \mathbf{F} and \mathbf{P} matrices. The diagonal blocks contain the large intra-bond matrix elements.

first of all *under what conditions* is the blockdiagonal character of the zeroth order density matrix \mathbf{P}^0 *self-consistent*. Let us write down the interbond matrix elements of the Fockian. Taking only the zeroth order matrix elements with \mathbf{h}^0 and \mathbf{P}^0 , we obtain:

$$F^0_{\mu\nu} = \sum_j \sum_{\lambda, \sigma \in j} P^0_{\lambda\sigma} [(\mu \nu | \lambda \sigma) - \frac{1}{2}(\mu \lambda | \nu \sigma)] \neq 0 \quad (6)$$

for $\mu \in i$ $\nu \in k$, $i \neq k$. One finds that the right-hand-side of Eq. (6) does not vanish automatically, thus the Fockian is not blockdiagonal. The SCF procedure now generates *tails* to the SLMOs. In other words, the blockdiagonality

of \mathbf{P} is not self-consistent. In order to ensure the blockdiagonal character of the Fockian, one should introduce a partition of the electron repulsion integrals, analogously to that of the core in Eq. (5). That is, at the zeroth order one assumes for $\mu \in i$, $\nu \in k$, $\lambda, \sigma \in j$:

$$(u \nu | \lambda \sigma) = \delta_{ik} (u \nu | \lambda \sigma) + \mathcal{O}(1) \quad (7a)$$

$$(u \lambda | \nu \sigma) = \delta_{ij} \delta_{kj} (u \lambda | \nu \sigma) + \mathcal{O}(1) \quad (7b)$$

Eqs. (7) express that the *interbond differential overlap is considered as a (first order) perturbation effect*. With this partition, Eq. (6) vanishes and \mathbf{F}^0 becomes blockdiagonal permitting the solving of intrabond SCF problems separately. The diagonal blocks of \mathbf{F}^0 become ($\mu, \nu \in i$):

$$F_{\mu\nu}^0 = h_{\mu\nu}^0 + \sum_{\lambda, \sigma \in i} P_{\lambda\sigma}^0 [(u \nu | \lambda \sigma) - \frac{1}{2}(u \lambda | \nu \sigma)] + \sum_{j(\neq i)} \sum_{\lambda, \sigma \in j} P_{\lambda\sigma}^0 (u \nu | \lambda \sigma) \quad (8)$$

where the last term describes the Coulomb interaction between different bonds responsible for inductive effects. Note that the (7) partition of the two-electronic integrals in Eq. (8) represents the fact that no interbond exchange interaction appears. That is, the interaction among different SLMOs is taken into account by a Hartree-like ansatz (see also Refs. 52, 53).

To summarize, in MO models each chemical bond is represented by an SLMO, which is an eigenfunction of the corresponding block of the Fockian. The molecule is viewed as a system of »mutually polarizing but otherwise independent«⁵⁴ bonds. This description represents a zeroth order approximation which, within the MO approach, has to be corrected by accounting for interbond delocalization effects.

II.D. Delocalization Interactions

The most important characteristics of well-localizable systems is the weakness of interbond charge transfer. For this reason, one expects that the electron delocalization can be considered as a small perturbation.

Exact LMOs are not strictly localized in general, but possess small tails on other bonds over the whole molecule. The aim of this section is to treat some methods for finding these tails as delocalization corrections to SLMOs. There exist several approaches dealing with this problem.^{10-15,17,52,54-61} At this point we discuss a general way proposed recently¹², in which we developed a special perturbational approach for finding the tails of non-orthogonal LMOs. The local Brillouin theorem

$$\langle \varphi_i | \hat{F} | \varphi_{k^*} \rangle = 0 \quad (9)$$

is used as the condition of self-consistency (\hat{F} is the Fockian). The exact bonding and antibonding LMOs are expanded in terms of SLMOs as

$$\varphi_i = \varphi_i^0 + \sum_{l^*}^{\text{virt}} \eta_{il^*} \varphi_{l^*}^0 \quad (10a)$$

$$\varphi_{k^*} = \varphi_{k^*}^0 - \sum_l^{\text{occ}} \eta_{lk^*} \varphi_l \quad (10b)$$

where the η -s are the tails to be determined by perturbation theory. Although the different occupied LMOs may overlap, this form of expansion keeps the occupied subspace orthogonal to the virtual one. It can be proven⁵⁵ that exact non-orthogonal LMOs, which have tails only on antibonding orbitals (cf Eq. 10a), can always be found; this condition determines the LMOs uniquely. If one assumes the effective one-electron Hamiltonian to be known, the following results are obtained¹²:

$$\eta^1_{ik^*} = -F^1_{ik^*} / \Delta E_{ik^*} \tag{11a}$$

$$\eta^2_{ik^*} = [\sum_l^{occ} \eta^1_{lk^*} F^1_{li} - \sum_{l^*}^{virt} \eta_{il^*} F^1_{k^*l^*}] / \Delta E_{ik^*} \tag{11b}$$

$$\eta^n_{ik^*} = \frac{\sum_l^{occ} \eta_{lk^*}^{n-1} F^1_{li} - \sum_l^{virt} \eta_{il^*}^{n-1} F^1_{k^*l^*} + \sum_{\mu=1}^{n-2} \sum_{j^*}^{virt} \sum_l^{occ} \eta_{ij^*}^\mu F^1_{lj^*} \eta_{lk^*}^{n-\mu-1}}{\Delta E_{ik^*}} \tag{11c}$$

($n \geq 3$)

where $F^1_{ik^*} = \langle \varphi_{i^0} | \hat{F} | \varphi_{k^*}^0 \rangle$, $i \neq k$, η^μ is the tail at order μ , and ΔE_{ik^*} is the energy of the $i \rightarrow k^*$ excitation. The above formulas are suitably represented by the diagrams of Figure 2. The graphs are to be understood as follows. Full

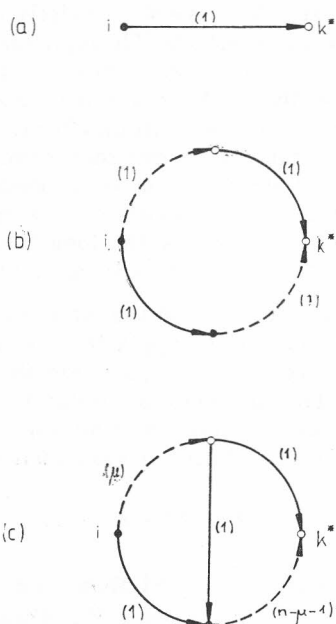


Figure 2. Diagrammatic representation of tail formulas (11) at the first (a), second (b), and n -th (c) orders of PT. A path from i ● to ○ k^* represents a term in the tail formula for η_{ik^*} . Solid line i ● ——— ○ k^* : $F^1_{ik^*}$ matrix element; dashed line i ● ———^(μ) ○ k^* : $\eta_{ik^*}^\mu$ tail coefficient determined by the previous orders.

dots ● represent occupied orbitals, empty dots ○ stand for virtual ones. A solid line bridging two vertices $i \bullet \longrightarrow \circ k^*$ means a direct interaction matrix element $F_{ik^*}^1$. A dashed line $i \bullet \text{---} \overset{\mu}{\circ} k^*$ corresponds to the tail coefficient $\eta_{ik^*}^1$ in the recursive formulas (11). Dashed lines can only bridge a full dot with an empty one, since only virtual SLMOs are mixed in Eq. (10a). Different paths from the initial vertex $i \bullet$ to the final one $\circ k^*$ describe the different terms in the corresponding tail formula; the sign of a term is given by the parity of the number of full vertices along the path. The intervening vertices involve a summation over all occupied or virtual orbitals. In the graph for the higher orders (Figure 3c), summation is to be performed over the previous orders μ .

It is apparent that at the first order the $i \rightarrow k^*$ delocalization described by the first order tail $\eta_{ik^*}^1$, results from a direct interaction between the two bonds in question (Figure 2a). Accordingly, we call it the *through space* delocalization, using the terminology by Hoffmann and Heilbronner^{62,63,64}. The second order graph (Figure 2b) describes two paths where the $i \rightarrow k^*$ delocalization is propagated by intervening bonds. This is called the *through bond* delocalization. The diagram in Figure 2c depicts *through-many-bond* effects appearing at the higher orders of perturbation theory.

Numerical realizations of the above results have been documented in our previous papers on some small sample molecules^{10,12,14,17} and also on larger systems of biological interest¹¹. Now we shall briefly discuss the physical significance of different delocalization effects. Through space tails are very sensitive to the relative orientation of bonds, and they are responsible for governing molecular conformations if the SLMOs are orthogonal to each other^{9-12,17,61}. The second order tails resulting from through bond delocalizations are rather independent of relative orientations^{12,17}, but they have some role in determining equilibrium bond lengths and angles¹², and are especially important in calculating spectroscopic properties such as oscillatory or rotational strengths¹⁴. The through-many-bond interactions describe the long-range charge transfer effects and determine the asymptotics of the density matrix^{15,65,66}.

In deriving Eqs. (11) we assumed that the effective one-electron Hamiltonian F was known. In this contribution, we apply the above diagrammatic technique for the case when we also take into consideration the effect of the delocalization on the Fockian itself. This problem is similar to that of SCF perturbation theory^{54,67,68}, but in this case we have to find the tails of LMOs due to the perturbation of the Fockian. The latter is expanded as

$$\hat{F} = \hat{F}^0 + \hat{F}^1 + \hat{F}^2 + \dots$$

where \hat{F}^0 is the Fockian built up by SLMOs, and F^μ -s are μ -th order corrections due to the partitions of the core Hamiltonian (5), the list of two-electron integrals (7), and due to the delocalization of the orbitals which the Fockian is built from. The latter represent the true SCF effects. Expressions for \hat{F}^μ -s will be given elsewhere⁶⁹. The graphs describing the delocalization corrections $\eta_{ik^*}^\mu$ for this case are given in Figure 3. On the diagrams the solid lines

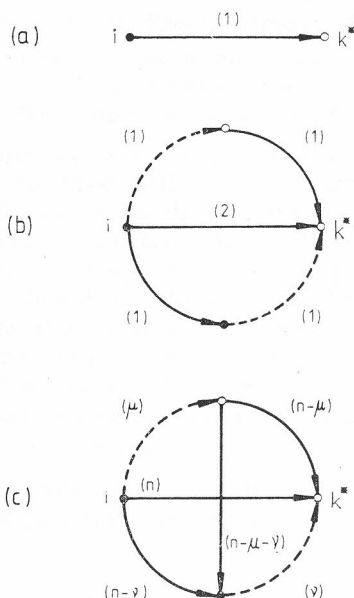


Figure 3. Generalization of the diagrams in Figure 2. to the case of SCF perturbation. Solid lines $i \overset{(\mu)}{\bullet} \longrightarrow \bullet k$ denote the matrix element of the μ -th order correction to the Fockian, F_{ik}^μ .

$i \overset{(\mu)}{\bullet} \longrightarrow \circ k^*$ represent the matrix element F_{ik}^μ . In Figure 3c describing the n -th order tail η_{ik}^n , the summation is extended over all μ and ν with the restriction that the sum of all orders along a path is equal n . These diagrams were constructed along the same rules as those working with the effective Hamiltonian (Figure 2). It is easy to put them into the corresponding tail formulae:

$$\eta_{ik}^1 = -F_{ik}^1 / \Delta E_{ik}^* \tag{12a}$$

$$\eta_{ik}^2 = \frac{-F_{ik}^2 + \sum_l^{occ} F_{il}^1 \eta_{lk}^1 - \sum_{l^*}^{virt} F_{l^*k}^1 \eta_{il}^1}{\Delta E_{ik}^*} \tag{12b}$$

$$\eta_{ik}^3 = \frac{-F_{ik}^3 - \sum_{l^*}^{virt} (\eta_{il}^1 F_{l^*k}^2 + \eta_{il}^2 F_{l^*k}^1)}$$

$$+ \frac{\sum_l^{occ} (F_{il}^1 \eta_{lk}^2 + F_{il}^2 \eta_{lk}^1) + \sum_{l^*}^{virt} \sum_j^{occ} \eta_{il}^1 F_{l^*j}^1 \eta_{jk}^1}{\Delta E_{ik}^*} \tag{12c}$$

These recursive expressions represent the formal solution of the present SCF perturbation problem. Note that the explicit solution at the first order has

formerly been given in the linearized SCF theory¹⁰. Since F_{ik}^n depends upon η_{ik}^n , explicit solutions at the order n can be obtained by solving the corresponding equation in (12) self-consistently. This, for the first order *e. g.*, requires the solution of a 2 by 2 algebraic equation¹⁰.

The set of SLMOs we have discussed so far was assumed to be orthogonalized. This means that either a ZDO basis set is used, or the orbitals are subjected to an explicit orthogonalization procedure. In the latter case, the local (transferable) character of the SLMOs is clearly lost. Therefore, Mayer and Surján have recently proposed a tail generation procedure¹³ in which the effect of the overlap of SLMOs is explicitly handled. The basic idea is the application of biorthogonal sets^{3,70,71}, which permits the use of formally same expressions as those valid in the orthogonal case. One can also introduce a partitioning of the overlap matrix written down in the basis of SLMOs, by taking into account intrabond overlaps precisely, but considering the relatively small interbond overlaps as perturbations¹³.

We have to cite here some other papers dealing also with non-orthogonal SLMOs^{16,17,72} and group functions^{33,73}. The works of Magnasco *et al.* are also worth mentioning⁷⁴.

III. CHEMICAL BOND AND CORRELATION

III.A. On the Strategy of Quantum Chemical Calculations

Let us decompose the »full CI« energy (E) of a well localizable molecule into Hartree-Fock (E_{HF}) and the correlation (E_{corr}) part, and let us represent these two components by the two axes of a coordinate system (Figure 4). This diagram visualizes the different »paths« by which one tries to approximate the value of the exact energy.

One usually follows path 1. That is, the HF energy is determined first, neglecting any correlation effect. Once the solution to the HF problem has been found, it is considered as the zeroth order description and the correlation is calculated with the HF reference state, by some variational or perturbational

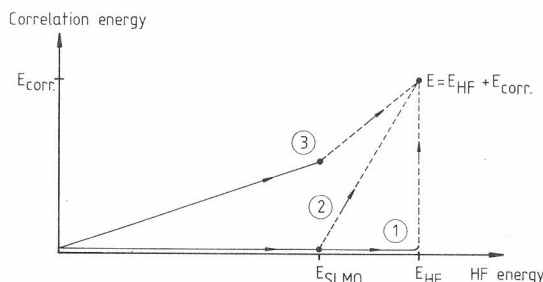


Figure 4. Different »paths« of approaching the full CI energy, line: corrections.

- 1 : »usual path« *via* solving the HF problem at the zeroth order
- 2 : »PCILO path«. The zeroth order is a simple fully localized determinant
- 3 : »proposed path«. The zeroth order is an easy-to-obtain reference state containing also trivial but large correlation effects

method. However, the electron correlation is generally accounted for only partly. This is indicated by the dashed vertical line on path 1 in Figure 4.

Quite a different approach is represented by the PCILO method⁷⁵ (path 2 in Figure 4). In this case a single determinant of SLMOs is used as the zeroth order reference state, which does not contain any correlation effect, and even the HF problem is only approximately solved. Perturbation theory is then used for improving this zeroth order description, up to the third (or fourth^{75b}) order. The zeroth order level is attained very easily (solid line), while the improvement is more laborious (dashed line on path 2).

Although the HF approximation represents a remarkable model, the distinction between E_{HF} and E_{corr} is somewhat arbitrary. Thus, there is not too much reason to compute E_{HF} exactly, while E_{corr} is only approximately calculated. In this sense the PCILO approach 2 is more realistic as compared to the usual path 1. Moreover, it is very easy to guess E_{HF} e.g. by a fully localized description, while the improvement, even towards the HF level, requires much work. The PCILO takes a simultaneous account of the two difficulties: the problems of electron delocalization and correlation.

However, there also exist some possibility of guessing the correlation energy already at the zeroth order. The corresponding path is denoted by 3 in Figure 4. In this »strategy« one considers both SCF and correlation effects as far as it is possible in a simple model. This may lead to a very good zeroth order description which can be further improved e.g. by perturbation theory.

The essential difference of the method following the »proposed path« 3 and the PCILO scheme is that in the latter the large intrabond electron correlation is also handled by perturbation theory, while in our procedure it is taken into account already at the zeroth order, leading to a more appropriate zeroth order description and furnishing much better convergence behavior of the perturbation series.

The above paths approaching the final solution, correspond to different partitions of the Hamiltonian. We feel that path 3 is the most useful, since it works with an easy-to-obtain and rather accurate zeroth order reference state, possessing a balanced account of SCF and correlation effects, while the remaining fine interactions can be considered by low-order perturbation theory. We can say that some VB type methods follow this path⁷⁶ in this sense. Further on we will introduce a special formalism to deal with such zeroth order wave functions representing chemical bonds in molecules. Numerical realizations of the proposed scheme are given elsewhere¹⁸.

III.B. Strictly Localized Geminals in Orthogonal Basis

In this section we develop a mathematical formulation of the zeroth order solution of the Schrödinger equation within a given finite basis set, in the sense of path 3 in Figure 4. The theory makes use of the second quantized formalism. The worth of using second quantization in the theory of interatomic interactions was recently explained by Mayer³. We shall see below that it also represents a suitable formalism for studying chemical bonds and interbond interactions.

We assume that the basis set is partitioned as described in Section II.B., by assigning each basis orbital to a given chemical bond. Each bond contains two electrons, thus the wave function of the bond i can be written as

$$\psi_i(1, 2) = \hat{A} \sum'_{\mu, \nu \in i} c_{\mu\nu}^i \psi_\mu(1) \psi_\nu(2) \quad (13)$$

where ψ_μ ($\mu \in i$) stands for a basis spinorbital belonging to the bond i , \hat{A} is the two-electronic antisymmetrizer, and the prime on the summation means the restriction $\mu < \nu$. The ψ_i is nothing but a VB type wave function, consisting of several ionic and covalent configurations. The coefficients obey the normalization condition

$$\sum_{\mu < \nu} (c_{\mu\nu}^i)^2 = 1 \quad (14)$$

The $\psi_i(1, 2)$ can be considered as a two-electronic wave function or *geminal*. The theory of separated electron pairs and geminal type wave functions is well elaborated^{27,32,77-83}, but it is rather rarely used in present-day quantum chemistry. Here we formulate a theory based on bond wave functions of type (13). Similar correlated electron pairs are used also in Goddard's generalized valence bond (GVB) method⁶ⁱ, in which the geminals are expressed over fully optimized orthogonal one-electron orbitals. (The non-orthogonal case has been treated by Chipman *et al.*^{6j}.)

The strictly localized nature of the two-electron bond wave functions (13) has similar advantages, as those of the strictly localized MOs in the SCF case. A better understanding of the chemical bond is expected, and, consequently, some possibilities for developing efficient computational schemes is also hoped for.

In the second quantized notation Eq. (13) can be rewritten as

$$\psi_i(1, 2) = \sum'_{\mu, \nu \in i} c_{\mu\nu}^i a_\mu^+ a_\nu^+ | \text{vac} \rangle$$

where $| \text{vac} \rangle$ is the vacuum state, while a_μ^+ , a_ν^+ are usual fermion creation operators obeying the anticommutation rules

$$a_\mu^+ a_\nu^+ + a_\nu^+ a_\mu^+ = 0$$

$$a_\mu^+ a_\nu + a_\nu a_\mu^+ = \delta_{\mu\nu}$$

Let us now introduce the following operator:

$$\psi_i^+ = \sum'_{\mu, \nu \in i} c_{\mu\nu}^i a_\mu^+ a_\nu^+ \quad (15a)$$

by which the wave function of the bond i is written as

$$\psi_i^+(1, 2) = \psi_i^+ | \text{vac} \rangle \quad (15b)$$

We can say that operator ψ_i^+ creates the wave function of the bond i . If there are n two-electronic bonds in the molecule, we approximate the total many-electron wave function as:

$$\Psi = \hat{A} \psi_1^+ \hat{A} \psi_2^+ \dots \hat{A} \psi_n^+ | \text{vac} \rangle \quad (16)$$

The wave function Ψ is properly antisymmetric in the variables of electrons, since the operators ψ_i^+ are built up by the operators a_{μ}^+ via Eq. (15a), obeying the fermion anticommutation rules. The Ψ is an antisymmetrized product of the bond wave functions, and it is multiconfigurational in general. Since each $\psi_i(1, 2)$ is strictly localized on the subspace of basis orbitals belonging to the bond i , the wave function Ψ of Eq. (16) can be called the antisymmetrized product of strictly localized geminals. The strict localizability in the space of orthogonalized basis orbitals also involves the strong orthogonality of the geminals.

The algebra of the operators $\hat{\psi}_i^+$ is defined by the relevant commutation rules. The corresponding annihilation operator is given by

$$\hat{\psi}_i = (\hat{\psi}_i^+)^{\dagger} = \sum_{\mu, \nu \in i} c_{\mu\nu}^i a_{\nu} a_{\mu} \quad (17)$$

By using Eqs. (15a) and (17), one finds that the creation and annihilation operators $\hat{\psi}_i^+$, $\hat{\psi}_k$ obey the following commutation rules:

$$\hat{\psi}_i^+ \hat{\psi}_k^+ - \hat{\psi}_k^+ \hat{\psi}_i^+ = 0 \quad (18a)$$

$$\hat{\psi}_i \hat{\psi}_k^+ - \hat{\psi}_k^+ \hat{\psi}_i = \delta_{ik} \hat{Q}_i \quad (18b)$$

where \hat{Q}_i is a one-particle operator defined as

$$\hat{Q}_i = \hat{I} + \sum_{\mu, \nu, \lambda \in i} c_{\nu\lambda}^i c_{\lambda\mu}^i a_{\mu}^+ a_{\nu} \quad (19)$$

In deriving Eqs. (18) we have utilized the normalization condition of Eq. (14). The \hat{I} is the unity operator. We have defined $c_{i\lambda}^i = -c_{i\nu}^i$ for $\lambda < \nu$, while $c_{i\nu}^i = 0$. It is apparent that the operators $\hat{\psi}_i$, $\hat{\psi}_k^+$ fulfil *Bose-type commutation rules*, in contrast to the anticommuting fermion operators a_{μ}^+ . This is quite natural since the former refer to a two-electronic composite system with an integer spin. The operator \hat{Q}_i has the property:

$$\hat{Q}_i | \text{vac} \rangle = | \text{vac} \rangle \quad (20)$$

This means that, in spite of the appearance of \hat{Q}_i in the commutation relation (18b), the adjoint operators $\hat{\psi}_k$ are true annihilation operators:

$$\hat{\psi}_k \hat{\psi}_k^+ | \text{vac} \rangle = [\hat{Q}_k - \hat{\psi}_k^+ \hat{\psi}_k] | \text{vac} \rangle = | \text{vac} \rangle \quad (21)$$

We have to find also the commutation relations between the bond creation operators and the original single-electronic operators a_{μ}^+ , a_{ν} . By evaluating the commutators, we obtain directly:

$$\hat{\psi}_i^+ a_{\mu}^+ - a_{\mu}^+ \hat{\psi}_i^+ = 0 \quad (22a)$$

$$\psi_i a_{i\mu}^+ - a_{i\mu}^+ \psi_i = \delta_{ik} \hat{R}_{i\mu} \quad (\mu \in k) \quad (22b)$$

where

$$\hat{R}_{i\mu} = \sum_{\lambda \in i} c_{i\mu\lambda}^i a_\lambda \quad (23)$$

Here again the conventions $c_{\lambda\mu}^i = -c_{\mu\lambda}^i$ ($\lambda > \mu$) and $c_{i\mu i}^i = 0$ have been used.

The commutation relations (18) and (23) permit the calculation of expectation values and matrix elements of one- and two-particle operators expressed by $a_{i\mu}^+$, a_ν with respect to the wave function built up by ψ_i^+ . Before utilizing the effectivity of this formalism, we discuss the meaning of the bond-creation operators in some detail.

III.C. Are there Bose-Particles in Molecules?

The wave function Ψ of the molecule is the antisymmetrized product of two-electronic bond wave functions. We can say in this picture, that a molecule is nothing but a system of two-electronic quasi Bose-particles created by operators $\hat{\psi}_k^+$. These quasi-particles are the representatives of the chemical bonds. This section concerns the question of the reliability of this picture.

Bose particles, composed of two electrons, are well known in the theory of superconductivity as Cooper pairs⁸⁴. They are bound states of two electrons stabilized by the interaction with the phonons of the system. Such an interaction is not considered in the present formalism, and, in fact, there is no extra stabilization energy of the system of two electrons when the corresponding chemical bond is broken. In other words, when considering interbond interactions, the two electrons of a bond are considered individually in general and not as a single composite system.*

Accordingly, the reliability of the picture of molecular electronic structure as a system of weakly interacting quasi Bose-particles is restricted to the case when the strictly localized approximation is maintained. Mathematically this means that we express the wave function in terms of operators $\hat{\psi}_k^+$ without using the single-electronic operators $a_{i\mu}^+$. This is, of course, only an approximation, under which the following effects can be accounted for: intrabond SCF, intrabond (*e. g.* »left-right«) correlation, interbond polarization (inductive) interactions, and interbond dispersion. These are the interactions which do not involve any electron transfer from one bond to another⁸⁵. The role of interbond charge transfer can also be important, but in well-localizable systems its extent is small and can be taken into account by low-order perturbation theory.

In the subsequent treatment we elaborate the theory of localized molecular wave functions constructed by two-electronic Bose states by taking into account all interbond interactions appearing within this framework. It will turn out that the formal introduction of the Bose operators $\hat{\psi}_i^+$, $\hat{\psi}_k$ is a useful tool in analysing and constructing the wave function and corresponding energies.

* Connections between superconducting and molecular systems were established by Bratož and Durand⁹⁰ who proposed a wave function built up by geminals identical for each electron pair.

III.D. The Partitioning of the Hamiltonian: Inductive Interactions

The second quantized Born-Oppenheimer electronic Hamiltonian is written as

$$\hat{H} = \sum_{\mu,\nu} h_{\mu\nu} a_{\mu}^{\dagger} a_{\nu} + \frac{1}{2} \sum_{\mu,\nu,\lambda,\sigma} (\mu\lambda | \nu\sigma) a_{\mu}^{\dagger} a_{\nu}^{\dagger} a_{\sigma} a_{\lambda} \quad (24)$$

where $h_{\mu\nu}$ is the core Hamiltonian, and $(\mu\lambda | \nu\sigma)$ is a two-electron repulsion integral with the (11|22) convention. The Greek indices label the basis spin-orbitals. They can be partitioned according to the bonds what they belong to. Thus, the Hamiltonian can be rewritten as

$$\hat{H} = \sum_i \hat{H}_i^1 + \sum'_{i,j} \hat{H}_{ij}^2 + \sum'_{i,j,k} \hat{H}_{ijk}^3 + \sum'_{i,j,k,l} \hat{H}_{ijkl}^4 \quad (25)$$

where i, j, k and l label the bonds, \hat{H}_i^1 denotes those terms of H which contain matrix elements over basis functions centred only on bond i , \hat{H}_{ij}^2 contains two-bond matrix elements, etc. In (25) the primes on the summations indicate the restriction that the indices do not coincide. The explicit formulae for the different terms $\hat{H}_i^1 \dots \hat{H}_{ijkl}^4$ are given elsewhere¹⁸; here we need only the one- and two-bond terms

$$\hat{H}_i^1 = \sum_{\mu,\nu \in i} h_{\mu\nu} a_{\mu}^{\dagger} a_{\nu} + \frac{1}{2} \sum_{\mu,\nu,\lambda,\sigma \in i} (\mu\lambda | \nu\sigma) a_{\mu}^{\dagger} a_{\nu}^{\dagger} a_{\sigma} a_{\lambda} \quad (26)$$

$$\begin{aligned} \hat{H}_{ij}^2 = & \sum_{\mu \in i} \sum_{\nu \in j} h_{\mu\nu} a_{\mu}^{\dagger} a_{\nu} + \\ & + \frac{1}{2} \sum_{\mu \in i} \sum_{\nu \in j} \{ \sum_{\lambda, \sigma \in i} (\mu\lambda | \nu\sigma) a_{\mu}^{\dagger} a_{\nu}^{\dagger} a_{\sigma} a_{\lambda} + \\ & + \sum_{\lambda, \sigma \in i} [(\mu\nu | \lambda\sigma) a_{\mu}^{\dagger} a_{\nu}^{\dagger} a_{\sigma} a_{\lambda} + (\mu\lambda | \nu\sigma) a_{\mu}^{\dagger} (a_{\nu}^{\dagger} a_{\sigma} + a_{\sigma}^{\dagger} a_{\nu}) a_{\lambda}] + \\ & + \sum_{\sigma \in i} \sum_{\lambda \in j} [(\mu\lambda | \nu\sigma) a_{\mu}^{\dagger} a_{\sigma}^{\dagger} a_{\nu} a_{\lambda} + \\ & + [(\mu\sigma | \nu\lambda) - (\mu\lambda | \nu\sigma)] a_{\mu}^{\dagger} a_{\nu}^{\dagger} a_{\lambda} a_{\sigma}] \} \end{aligned} \quad (27)$$

Now, we introduce a partition of the Hamiltonian (25):

$$\hat{H} = \hat{H}^0 + \hat{W} \quad (28)$$

with the definition

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi | \hat{H}^0 | \Psi \rangle \quad (29)$$

That is

$$\langle \Psi | \hat{W} | \Psi \rangle = 0 \quad (30)$$

with the strictly localized wave function Ψ defined by Eq. (16). The zeroth order Hamiltonian, \hat{H}^0 , contains all terms of \hat{H} contributing to the expectation value by Ψ . The free parameters of Ψ can be determined variationally with

respect to \hat{H}^0 ; the energy of this wave function will be correct up to the second order since, due to Eq. (30), the first order perturbation correction vanishes.

The using of the Bose operators $\hat{\psi}_i$, together with the corresponding commutation rules (18) and (22), makes it very easy to calculate expectation values. One finds for example

$$\langle \Psi | \hat{H}_{ijkl}^4 | \Psi \rangle = \langle \text{vac} | \hat{\psi}_1 \hat{\psi}_2 \dots \hat{\psi}_n \hat{H}_{ijkl}^4 \hat{\psi}_1^+ \hat{\psi}_2^+ \dots \hat{\psi}_n^+ | \text{vac} \rangle = 0 \quad (31a)$$

$$\langle \Psi | \hat{H}_{ijk}^3 | \Psi \rangle = 0, \text{ while} \quad (31b)$$

$$\langle \Psi | \hat{H}_{ij}^2 | \Psi \rangle = \frac{1}{2} \sum_{\mu, \sigma \in i} \sum_{\nu, \lambda \in j} P_{\mu\sigma}^i P_{\nu\lambda}^j [(\mu \sigma | \nu \lambda) - (\mu \lambda | \nu \sigma)] \quad (32)$$

$$\langle \Psi | \hat{H}_i^1 | \Psi \rangle = \sum_{\mu, \nu \in i} h_{\mu\nu} P_{\mu\nu}^i + \frac{1}{2} \sum_{\mu, \nu, \lambda, \sigma \in i} (\mu \lambda | \nu \sigma) \Gamma_{\mu\nu\lambda\sigma}^i \quad (33)$$

where the first- and second order density matrices are defined as

$$P_{\mu\nu}^i = \langle \text{vac} | \hat{\psi}_i a_{\mu}^+ a_{\nu} \hat{\psi}_i^+ | \text{vac} \rangle \quad (\mu, \nu \in i) \quad (34)$$

$$\Gamma_{\mu\nu\lambda\sigma}^i = \langle \text{vac} | \hat{\psi}_i a_{\mu}^+ a_{\nu}^+ a_{\sigma} a_{\lambda} \hat{\psi}_i^+ | \text{vac} \rangle \quad (35)$$

$\mu, \nu, \lambda, \sigma \in i$

The elements of the density matrices can be expressed over the geminal coefficients $c_{\mu\nu}^i$. For the first order density matrix, using (22) and (23) we obtain:

$$P_{\mu\nu}^i = \langle \text{vac} | \hat{R}_{i\mu} \hat{R}_{i\nu}^+ | \text{vac} \rangle = \sum_{\lambda \in i} c_{\mu\lambda}^i c_{\nu\lambda}^i \quad (36)$$

For the second order density matrix one simply gets

$$\Gamma_{\mu\nu\lambda\sigma}^i = \langle \text{vac} | \hat{R}_{i\mu} a_{\nu}^+ a_{\sigma} \hat{R}_{i\lambda}^+ | \text{vac} \rangle = c_{\mu\nu}^i c_{\lambda\sigma}^i \quad (37)$$

Let us return now to the definition of \hat{H}^0 . We define the following effective core matrix elements ($\mu, \nu \in i$):

$$h_{\mu\nu}^{\text{eff}} = h_{\mu\nu} + \frac{1}{2} \sum_{j(\neq i)} \sum_{\lambda, \sigma \in j} P_{\lambda\sigma}^j [(\mu \nu | \sigma \lambda) - (\mu \lambda | \nu \sigma)] \quad (38)$$

A repartitioning of the Hamiltonian can be defined by using \mathbf{h}^{eff} instead of \mathbf{h} , and reducing accordingly the two-bond term as

$$\hat{H}_{ij}^{2 \text{ red}} = \hat{H}_{ij}^2 - \frac{1}{2} \sum_{\mu, \nu \in i} \sum_{\lambda, \sigma \in j} P_{\lambda\sigma}^j [(\mu \nu | \sigma \lambda) - (\mu \lambda | \nu \sigma)] a_{\mu}^+ a_{\nu} \quad (39)$$

Then, since $\langle \Psi | \hat{H}_{ij}^{2 \text{ red}} | \Psi \rangle = 0$, for the zeroth order Hamiltonian we obtain

$$\hat{H}^0 = \sum_i H_i^{1 \text{ eff}} \quad (40)$$

where H_i^{eff} is defined in the same way as H_i^1 , but using \mathbf{h}^{eff} instead of \mathbf{h} . We have arrived thus to the result that the strictly localized Hamiltonian in nothing but the sum of the effective intrabond Hamiltonians, which contain the averaged electrostatic interbond interactions through \mathbf{h}^{eff} . The energy of the strictly localized geminal wave function is easily expressed as

$$E = \sum_i [\sum_{\mu, \nu \in i} h_{\mu\nu}^{\text{eff}} P_{\mu\nu}^i + \frac{1}{2} \sum_{\mu, \nu, \lambda, \sigma \in i} (\mu \lambda | \nu \sigma) I_{\mu\nu\lambda\sigma}^i] \quad (41)$$

which can be written in the form

$$E = \sum_i E_i^0 + \frac{1}{2} \sum_{\mu, \nu \in i} \sum_{\substack{\lambda, \sigma \in j \\ (j \neq i)}} P_{\mu\nu}^i P_{\lambda\sigma}^j [(\mu \nu | \lambda \sigma) - (\mu \lambda | \nu \sigma)] \quad (42)$$

Here E_i^0 stands for the energy of the independent bonds, while the second sum gives the interaction energy. This interaction is that of a system of mutually polarizing bonds, called also the inductive effect.

Inductive interactions can also be considered at the SCF HF level (cf. Eq. (8)). Since in Eq. (42) the matrices \mathbf{P}^i refer to a multiconfiguration wave function describing intrabond correlation, the above formulas also contain the correlation contribution to the inductive interaction.

III.E. Interbond Dispersion

The strictly localized geminal wave function Ψ accounts for the intrabond (*e. g.*, left-right) correlation. There is another important correlation effect which can be considered within the present framework, *i. e.* by using a wave function constructed merely of two-electronic Bose type creation operators: namely, the dispersion interaction. This corresponds to the correlation in the motion of electrons belonging to different bonds. It is expected to be quite important for »geminal« bonds, where the electrons are rather close to each other, and also for far-lying bonds where it represents the dominant long range correlation effect.

Dispersion interactions, though important, are usually very weak, and thus we can obtain them at the second order of perturbation theory with excellent accuracy.

In the present formalism we can pick up those terms of the second quantized Hamiltonian which are directly responsible for interbond dispersion. A characteristic feature of dispersion is that it does not involve an interbond electron transfer. Therefore, as can be easily seen, the three- and four bond terms of the Hamiltonian cannot contribute to dispersion. We have to, therefore, investigate the reduced two-bond Hamiltonian $H_{ij}^{2,\text{red}}$ of Eq. (39). The only noncharge transfer term in H_{ij}^2 is the last one in Eq. (27) containing the operator product $a_{\mu}^+ a_{\nu}^+ a_{\lambda} a_{\sigma}$ ($\mu, \sigma \in i, \nu, \lambda \in j$). It is apparent that this term describes the $\sigma \rightarrow \mu$, and $\lambda \rightarrow \nu$ transitions on the bond i and j , respectively, thus preserving the distribution of electrons among the bonds. The second term in $H_{ij}^{2,\text{red}}$ of Eq. (39) is also a non-charge transfer one, corresponding to the transition $\nu \rightarrow \mu$ on the bond i . The operator of interbond dispersion is the sum of these relevant terms, and it can be written as:

$$\hat{H}_{\text{disp}} = \frac{1}{2} \sum_{ij} \sum_{\mu, \nu \in i} \sum_{\lambda, \sigma \in j} [(\mu \nu | \sigma \lambda) - (\mu \lambda | \nu \sigma)] a_{\mu}^+ a_{\sigma}^+ a_{\lambda} a_{\nu} - P_{\sigma\lambda}^j a_{\mu}^+ a_{\nu} \quad (43)$$

The interbond dispersion energy at the second order of perturbation theory is calculated as

$$E_{\text{disp}} = - \sum_J \frac{|\langle \Psi_0 | \hat{H}_{\text{disp}} | \Psi_J \rangle|^2}{E_J - E_0} \quad (44)$$

where E_0 and E_J are the energies of the unperturbed ground and J -th excited states, while Ψ_0 and Ψ_J are the corresponding wave functions. Now, we are faced with the problem of how to represent excited states.

Regarding dispersion, we should consider only localized excitations, where there is no electron transfer from one bond to another, but the bonds may be in »locally excited« states. These states arise as solutions of the eigenvalue problems of the effective intrabond Hamiltonians :

$$\hat{H}_i^{\text{eff}} \psi_i^p(1, 2) = E_i^p \psi_i^p(1, 2) \quad (45)$$

where p labels the locally excited states of the bond i with $p = 0$ referring to the ground state. Accordingly, we introduce the superscript p on the bond creation operators as well:

$$\psi_i^p(1, 2) = \hat{\psi}_i^{+p} | \text{vac} \rangle \quad (46)$$

For the total molecule we should distinguish between singly and doubly excited states (higher excitations need not be considered at the second order). The singly excited states of the molecule can be written as

$$\hat{\Psi}_J^s = \hat{\psi}_k^{+p} \hat{\psi}_k \hat{\psi}_1^+ \hat{\psi}_2^+ \dots \hat{\psi}_n^+ | \text{vac} \rangle \quad (47)$$

where the particular excitation is the $0 \rightarrow p$ transition on the bond k . Similarly, the doubly excited states are written as

$$\hat{\Psi}_J^s = \hat{\psi}_k^{+p} \hat{\psi}_l^{+q} \hat{\psi}_k \hat{\psi}_l \hat{\psi}_1^+ \hat{\psi}_2^+ \dots \hat{\psi}_n^+ | \text{vac} \rangle \quad (48)$$

for the $0 \rightarrow p$ and $0 \rightarrow q$ transitions on bonds k and l , respectively. As for the single excitations, they do not interact with the ground state:

$$\langle \Psi_0 | \hat{W} | \Psi_J^s \rangle = 0 \quad (49)$$

This statement is analogous to the Brillouin theorem for HF wave functions, but valid also for the present geminal-type wave function, provided that the coefficients $c_{\mu\nu}^i$ are optimized variationally. The proof is not reported here, but it can be done easily *e.g.* by using Mayer's proof^{86,87} of the usual Brillouin theorem *mutatis mutandis*. Accordingly, we should deal only with the double excitations and evaluate the following matrix elements entering into Eq. (44):

$$\langle \Psi_0 | \hat{H}_{\text{disp}} | \Psi_J^d \rangle = \langle \text{vac} | \psi_1 \dots \psi_n \hat{H}_{\text{disp}} \psi^{+p} \psi^{+q} \psi_k \psi_l \psi_1^+ \dots \psi_n^+ | \text{vac} \rangle \quad (50)$$

This expression can be calculated in a straightforward manner by substituting the dispersion operator, Eq. (43), and utilizing the commutation rules. By putting the result into Eq. (44) we find:

$$E_{\text{disp}} = - \sum_{k < l} \sum_{p, q (\neq 0)} \frac{|\sum_{\mu, \nu \in k} \sum_{\lambda, \sigma \in l} P_{\mu\nu}^k(0 \rightarrow p) P_{\lambda\sigma}^l(0 \rightarrow q) [(\mu \nu | \sigma \lambda) - (\mu \lambda | \nu \sigma)]|^2}{E_k^p + E_l^q - E_k^0 - E_l^0} \quad (51)$$

where the intrabond transition density matrices are defined by ($\mu, \nu \in k$):

$$P_{\mu\nu}^k(0 \rightarrow p) = \langle \text{vac} | \hat{\psi}_k a_{\mu}^{\dagger} a_{\nu} \hat{\psi}_k^{\dagger} | \text{vac} \rangle \quad (52)$$

which is readily seen to be

$$P_{\mu\nu}^k(0 \rightarrow p) = \sum_{\lambda \in k} c_{\lambda\mu}^{k(p)} c_{\lambda\nu}^{k(p)} \quad (53)$$

where $c_{\lambda\nu}^{k(p)}$ -s are the expansion coefficients of the geminal ψ_k^p with a straightforward generalization of Eq. (10) for the p -th excited state.

The formula (51) for the dispersion energy formally agrees with those obtained by other methods (c. f. e. g. Ref. 88). It is evident that the present second quantized theory provides a powerful tool for deriving such formulae.

IV. CONCLUSIONS

In this paper the representation of the chemical bond in different schemes has been discussed. At the HF level, strictly localized MOs were found to represent the chemical bonds appropriately. The consistent treatment of SLMOs requires a partition of the basis set, and the corresponding partitions of the core Hamiltonian and the list of two-electron integrals. The SLMOs appear as solutions of the zeroth order SCF problem. The Coulomb type interbond integrals, however, are not cut at the zeroth order. This feature permits us to account for interbond inductive effects. The exact solution of the molecular HF problem within the given basis set can be constructed by adding tails to the SLMOs describing delocalization corrections, for which recursive tail formulae were derived and represented by a special diagrammatic technique.

In going beyond the HF model, the theory of separated electron pairs seems to be an appropriate initial guess as to the exact wave function permitting the representation of chemical bonds in a molecule. We introduced a second quantized formalism where the bonds are considered as composite two-electronic quasi-particles showing Bose-type behaviours. The significance of these formal Bose particles is the same as that of the concept of two-electronic chemical bonds. A zeroth order Hamiltonian can be defined and it accounts for all intrabond plus inductive interbond effects. The zeroth order wave function is an antisymmetrized product of strictly localized geminals. Each geminal describes the internal structure of the corresponding quasi Boson, which is affected by the inductive interactions. This description can be improved by perturbation theory; we have presented here the second order interbond dispersion corrections. The proposed scheme can be considered as a new, equivalent path towards the exact solution of the Schrödinger equation within a given basis set. The zeroth order localized reference state can be obtained easily at very low cost, while the remaining fine SCF and correlation effects are well suited for perturbational treatment. The final wave function and the corresponding energies are easy to interpret in terms of bond contributions and interbond interactions.

The theory is formulated in the space of an orthogonalized set of basis orbitals. The explicit consideration of non-orthogonality effects is also in progress and will be presented elsewhere^{13,89}.

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SAŽETAK

Opis kemijske veze u kvantno-kemijskim računima

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Razmotren je problem kvantno-teorijskog opisa kemijskih veza. Pri tome se polazi od stajališta da je molekula sastavljena od kemijskih veza čije su međusobne interakcije malene. Intravezne i prosječne elektrostatske interakcije između različitih veza tretirane su računom smetnje nultog reda. Efekti disperzije i slabije izražene delokalizacije veza uzeti su u obzir perturbacijama višega reda. Primijenjena je posebna dijagramska tehnika da bi se dobila delokalizacija striktno lokaliziranih orbitala. Razmatrana je također teorija druge kvantizacije, u kojoj se kemijske veze mogu karakterizirati s pomoću posebnih operatora stvaranja čestica koji zadovoljavaju komutacijska pravila Boseova tipa. U tom pristupu intravezna korelacija uključena je već u računu nultoga reda.