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On the Pairwise Nonorthogonality Problem in Quantum Chemistry

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It is shown that, starting from a set of local hybrid orbitals Φ_i $(i = 1, \ldots n)$ one can construct pairwise nonorthogonal set of functions χ_i $(i = 1, \ldots n)$ with the following feature

$$<\chi_i \mid \chi_j> = \begin{cases} R_{ij} & \text{if i and j are bonded orbitals} \\ \delta_{ij} & \text{otherwise} \end{cases}$$

where R_{ij} is the overlap integral. Pairwise overlapping functions are determined by the matrix equation

$$\chi = \mathbf{U}\,\mathbf{S}^{-1/2}\,\Phi$$

where χ and Φ are the column vectors of the functions χ_i $(i = 1, \ldots n)$ and Φ_i $(i = 1, \ldots n)$ respectively. **S** is the overlap matrix for the initial hybrid orbitals Φ_i. **U** is a positive matrix which possesses the property $\sum\limits_{i=1}^{n} U_{ij}^2 = \sum\limits_{j=1}^{n} U_{ij}^2 = 1$ $(i, j = 1, \ldots n)$. It can be calculated by employing maximum overlap criterion or by maximizing the average distance between the centroids of charge of the electronic pairs. The use of the pairwise nonorthogonal functions is advantageous in semiempirical methods since it minimizes the error introduced by the neglect of the many-center electron repulsion integrals.

INTRODUCTION

The quantum mechanical description of molecules and solids is based mainly on the independent particle model where one-electron wavefunctions are expressed as linear combinations of atomic orbitals. This is the most convenient form of wavefunctions, but sometimes considerable computational difficulties arise due to the nonorthogonality of atomic orbitals placed at different nuclei. The simplest way to circumvent this obstacle is in disregarding of overlap integrals. In that case the metric matrix, formed by the overlap integrals of the atomic orbitals, takes the form of a unit matrix. This approximation is hardly justified and sometimes represents serious oversimplification which leads to disastrous results. For example, the ionic crystals of alkali halides break down if the overlap integrals are neglected because the

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repulsive forces become zero[1]. One could orthogonalize the initial atomic orbitals by the Schmidt procedure but this method has a serious disadvantage because the final basis set depends on the choice of the first function and consequently the atomic orbitals are not treated on the same footing. The most convenient orthogonalization procedure for a set of linearly independent functions is that of Löwdin[2] which mixes all orbitals simultaneously. This is so called symetrical orthogonalization which possesses a very interesting and important property: the orthogonal functions resemble the initial ones as much as possible in a sense of the least square deviations[3]. The use of the symmetrically orthogonalized basis sets in quantum chemical calculations is advantageous since most of the polycenter two-electron integrals are then negligibly small[4]. In fact, the widely used zero-differential overlap approximation schemes are justified only if the suitable symmetrically orthogonalized hybrid orbitals basis sets are employed[5]. The orthogonalized atomic orbitals are, however, incompatible with the simple intuitive picture of the covalent bonding. Namely, it is well recognized by now that the formation of a covalent bond is accompanied by a build up of the electronic charge density in the region between the bonded nuclei. A good measure of the increased charge density is provided by the overlap integrals of the relevant hybrid orbitals[6–10]. Since the overlapping of the neighbouring atomic orbitals is energetically favourable* it is convenient to use the basis sets exhibiting pairwise nonorthogonality. The orbitals participating in a formation of the localized bond should overlap as much as possible being in the same time orthogonal to all other members of a basis set. This type of basis set was discussed first by Lennard-Jones *et al.*[11] in treating the correlation effect of the two electrons with coupled spins which occupy the same spatial orbital. The choice of the pairwise nonorthogonal basis set is not unambiguous and it is a purpose of this work to provide several simple recipes for its construction.

CONSTRUCTION OF THE PAIRWISE NONORTHOGONAL BASIS SET

We shall consider only the valence shell atomic orbitals for the sake of simplicity. The latter are assumed to be suitably hybridized in order to describe properly directional properties of covalent bonds. The use of the hybrid orbitals is of crucial importance for the following reasons. The hybrid orbitals provide the most natural choice of the atomic basis set functions because they conform the symmetry of the local potential exerted on an atom in a molecule**. Further, the hybrid orbitals are strongly polarized in a certain direction where they have considerable bonding power. Consequently, their (nonbonding) interactions in all other directions are minimized which makes them particularly suitable for a description of the localized electron pair bond. Let us denote a set of linearly independent and normalized hybrid orbitals as $\Phi_1 \ldots \Phi_n$. We shall suppose also that the hybrids placed on the same atom are mutually orthogonal. In order to form a basis set which is nonorthogonal only for pairs of bonding hybrids, we shall first symmetrically

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* The resonance integrals, which give the most important contribution to the molecular binding energy, are to a good accuracy proportional to the corresponding overlap integrals. This type of approximation is employed in most of the current semiempirical MO theories.

** The local potential is a set all interactions between the particular atom and its nearest neighbours.

orthogonalize the orbitals $\Phi_1 \ldots \Phi_n$. As Löwdin has shown[2] the orthogonalized orbitals are given by

$$\psi_i = \sum_{j=1}^{n} (\mathbf{S}^{-1/2})_{ij} \, \Phi_j \tag{1}$$

where $\mathbf{S}$ is the overlap matrix with matrix elements $S_{ij} = < \Phi_i \mid \Phi_j >$. This is always possible since the functions $\Phi_1 \ldots \Phi_n$ are linearly independent and consequently $\mathbf{S}$ is a nonsingular matrix. It should be emphasized here that the orbitals ψ_i $(i = 1 \ldots n)$ are even better localized than the initial ones Φ_i $(i = 1 \ldots n)$. This is very important feature of the symmetrically orthogonalized functions because atomic orbitals remain localized around the their respective nuclei[2]. Namely, if the initial orbital Φ_i belongs to an atom A so does the corresponding function ψ_i given by the expression (1). Our next step is a deorthogonalization of the functions ψ_i and ψ_j which form the covalent bond i—j. This is achieved by a transformation:

$$\chi_i = (\psi_i + a \, \psi_j) \, / \, (1 + a^2)^{1/2}$$

and (2)

$$\chi_j = (\psi_j + a \, \psi_i) \, / \, (1 + a^2)^{1/2}$$

where a is a mixing parameter which is for the time being unspecified. It is easily checked that the overlap integral between the functions χ_i and χ_j is equal $2\,a/(1 + a^2)$:

$$< \chi_i \mid \chi_j > \; = 2\,a \, / \, (1 + a^2) \tag{3}$$

On the other hand, the pair of overlapping functions χ_i and χ_j are orthogonal to all remaining functions of the basis set obtained in the same fashion due to the orthogonality of ψ_i $(i = 1 \ldots n)$. Since the pairwise nonorthogonal basis functions are not unequivocally determined by relation (2), one can use this freedom to impose some simple and plausible conditions which the transformation (2) should satisfy. Firstly, the mixing parameter a should be small and positive in order to preserve the local properties of atomic orbitals and to ensure in the same time favourable overlap of the bonding functions (eqns. (2) and (3)). Simple analysis shows that it is possible to satisfy both requirements. For example, the mixing parameter $a = 1/3$ gives the overlap integral of 0.6, a value which is characteristic for overlapping of hybrid orbitals describing C—C bonds in hydrocarbons[9,10]. The content of χ_i function is 90% of ψ_i orbital and 10% of ψ_j orbital. In other words, the χ_i function is mainly composed of ψ_i orbital which is in turn predominantly composed of the initial Φ_i hybrid orbital. Hence, it is feasible to find $0 < a \ll 1$ which corresponds to localized χ_i and χ_j functions with significant overlap. Next, we shall suppose that the hybrid orbitals Φ_i $(i = 1 \ldots n)$ are optimized in a sense of the simple maximum overlap criterion[9,10]. Then, (condition (*a*)), the parameter a_{ij} could be calculated so that the overlap $< \Phi_i \mid \Phi_j >$ is maintained, *i. e.*:

$$< \chi_i \mid \chi_j > \; = \; < \Phi_i \mid \Phi_j > \; = S_{ij} \tag{4}$$

Simple algebra yields

$$a_{ij} = (1 - \sqrt{1 - S_{ij}^2}\,) \, / \, S_{ij} \tag{5}$$

where the sign of the square root is chosen according to the requirement

$0 < \alpha < 1$. The parameter α_{ij} (eqn. (5)) can be easily calculated if the overlap integral S_{ij} is known. However, we can get a rough idea about the shape of χ_i orbital if we develop α_{ij} in a Taylor series in terms of S_{ij}. Terminating the Taylor expansion of $\sqrt{1 - S_{ij}^2}$ after the second term one obtains $\alpha_{ij} = (S_{ij}/2) + O(S_{ij}^3)$. The nonorthogonal orbital χ_i takes the following form up to the order $O(S_{ij}^3)$:

$$\chi_i = (1 - S_{ij}^2/8)\,\Phi_i + (S_{ij}/2)\,\Phi_j \tag{6}$$

The corresponding orbital χ_j is easily obtained by a permutation of indices i and j. Taking again values $\alpha = 1/3$ and $S_{ij} = 0.6$ as an example and assuming equipartition of the mixed term $(\Phi_i\,\Phi_j/S_{ij})$ between the constituent atoms i and j, one obtains that Φ_i content of χ_i orbital is 84.3%.

Condition (*b*): The mixing parameter α can be chosen so that the functions χ_i and χ_j have the best overlap with Φ_i and Φ_j respectively. Then the following requirement has to be satisfied:

$$\frac{\partial}{\partial \alpha_{ij}}\left[\langle \chi_i | \Phi_i \rangle + \langle \chi_j | \Phi_j \rangle \right] = 0 \tag{7}$$

Simple calculation shows that α'_{ij}

$$\alpha'_{ij} = \left[\langle \psi_i | \Phi_j \rangle + \langle \psi_j | \Phi_i \rangle \right] / \left[\langle \psi_i | \Phi_i \rangle + \langle \psi_j | \Phi_j \rangle \right] \tag{8}$$

meets the condition (7). Here prime indicates that α' is determined according to the maximum overlap criterion. If we employ electrostatic hamiltonian, than it is equal to its complex conjugate value *i. e.* it is a real operator. The best hybrid orbitals are then also real functions[12]. Taking into account this fact and the relationship (1), we obtain $\langle \psi_i | \Phi_i \rangle = (S^{1/2})_{ii}$ and $\langle \psi_i | \Phi_j \rangle = \langle \psi_j | \Phi_i \rangle = (S^{1/2})_{ij}$. Hence, the relation (8) reads as follows:

$$\alpha'_{ij} = 2\,(S^{1/2})_{ij} / \left[(S^{1/2})_{ii} + (S^{1/2})_{jj} \right] \tag{9}$$

Substitution of α'_{ij} into eqns. (2) gives a pair of nonorthogonal functions χ_i and χ_j which have the optimum overlap with the initial hybrid orbitals Φ_i and Φ_j. It is interesting to mention that in this case χ_i and χ_i resemble the hybrids Φ_i and Φ_j as much as possible in a sense of the least square deviations. Requirement that the sum of squared deviations is a minimum reads:

$$\| \chi_i - \Phi_i \|^2 + \| \chi_j - \Phi_j \|^2 = \text{min.} \tag{10}$$

where $\| \chi_i - \Phi_i \|$ is a norm of the vector $\chi_i - \Phi_i$. It follows immediately that (10) takes the form:

$$4 - 2\left[\langle \chi_i | \Phi_i \rangle + \langle \chi_j | \Phi_j \rangle \right] = \text{min.} \tag{11}$$

which is equivalent to the condition (7).

Although it seems at first sight that conditions (*a*) and (*b*) give widely different results it can be shown that α_{ij} and α'_{ij} have practically the same values. Namely, if we neglect all overlap integrals S_{ij} between hybrids Φ_i and Φ_j which are not directly bonded, it follows that $\chi_i = \Phi_i$ and $\chi_j = \Phi_j$. In that case α is exactly equal to α' $(\alpha = \alpha')$ because both conditions (*a*) and (*b*) are satisfied in the same time *i. e.* $< \chi_i | \Phi_i > = < \chi_j | \Phi_j > = 1$ and $< \chi_i | \chi_j > = < \Phi_i | \Phi_j >$. Since the overlap integrals between the nonbonded hybrids are an order of magnitude smaller than the overlaps between the bonded ones, it is plausible that the approximate relation $\alpha \cong \alpha'$ holds. The use of maximum overlap hybrids is of crucial importance here because the polarization of the hybrid in one direction diminishes its overlapping power in all other directions. Therefore, the application of the simple maximum overlap criterion enables the construction of a pairwise nonorthogonal basis set in a consistent way.

CONCLUSION

We have shown that, starting from a set of local hybrid orbitals Φ_i (i = 1 ... n), it is possible to construct a basis set χ_i (i = 1 ... n) exhibiting pairwise nonorthogonality:

$$< \chi_i | \chi_j > = \begin{cases} R_{ij} & \text{if i and j are nearest neighbours} \\ \delta_{ij} & \text{otherwise} \end{cases}$$

where R_{ij} is the overlap integral. If we denote the column vectors of the final and initial basis functions as χ and Φ then

$$\chi = \mathbf{U}\,\mathbf{S}^{-1/2}\,\Phi \tag{12}$$

where $\mathbf{S}$ is overlap matrix of the initial hybrids Φ_i and $\mathbf{U}$ is a positive matrix* which is in turn a product of $\mathbf{V}$ (ij) matrices:

$$\mathbf{U} = \prod_{(ij)} \mathbf{V}\,(ij) \tag{13}$$

where indices ij correspond to neighbouring orbitals forming a covalent bond ij. Matrices $\mathbf{V}$ (ij) are defined by the equation (2) and explicitly read as follows:

$$\underline{V}(ij) = \begin{array}{cc} & \begin{array}{ccccc} \quad & \quad i & \quad & \quad\quad j & \quad \end{array} \\ \begin{array}{c} \\ i \\ \\ j \\ \\ \end{array} & \left(\begin{array}{ccccc} 1 \ddots 1 \quad 0 & \vdots & 0 & \vdots & 0 \\ 0 \cdots & \frac{1}{1+\alpha_{ij}^2} & \cdots & \frac{\alpha_{ij}}{1+\alpha_{ij}^2} & \cdots \\ 0 & \vdots & 1 \ddots 1 \quad 0 & \vdots & 0 \\ \cdots & \frac{\alpha_{ij}}{1+\alpha_{ij}^2} & \cdots & \frac{1}{1+\alpha_{ij}^2} & \cdots \\ 0 & \vdots & 0 & \vdots & 1 \ddots 1 \quad 0 \end{array} \right) \end{array}$$

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* A matrix $\mathbf{U}$ is called positive if its elements satisfy the condition $U_{ij} \geqslant 0$ (i, j = 1, ... n).

where the off diagonal elements apart to ij ones are equal zero. It is easily checked that the elements of **V** (ij) matrix satisfy the relation

$$\sum_{l=1}^{n} V_{kl}^2 = \sum_{k=1}^{n} V_{kl}^2 = 1 \tag{15}$$

and that the same holds for the matrix **U**, *i. e.* rows and columns of the matrices **V** and **U** are normalized. The parameter α_{ij} in the matrix **V** (ij), formula (13), is given either by the equation (5) or by equation (9). The use of the χ_i $(i = 1 \dots n)$ basis set functions in semiempirical methods should be advantageous. Namely, the basis sets related by a unitary transformations are equivalent in *ab initio* approach, where all matrix elements of the Hartree-Fock matrix are rigorously calculated. Hovewer, if some integrals are neglected and the others are estimated from the experimental data, the requirement of the unitary invariance is too severe a restriction. For a particular semiempirical scheme some basis sets are more suitable than the others. Intuitively, it is obvious that the use of pairwise nonorthogonal functions will minimize the errors introduced by the neglect of the many-centre electron repulsion integrals. On the other hand, the overlap between the neighbouring functions χ_i and χ_j ensures the adequate estimate of the resonance integrals. Thus the basis set has the properties which are compatible with common approximations employed in current samiempirical methods. The use of the pairwise nonorthogonal localized orbitals may be helpful in order to circumvent convergency difficulties in *ab initio* SCF calculations which occur if the guessed starting wave functions are far from the minimum energy solutions. It is well documented that the problems of this kind are overcomed by the use of localized orbitals[13]. Finally, this type of basis set might be useful in simulated *ab initio* molecular orbital technique where the Hartree-Fock matrix elements in a large molecule are transferred from the calculations on similar small molecules known as »pattern molecules«. The source of this transferability is the use of hybrid orbitals[14].

In this paper we discussed in some detail the construction of the pairwise overlapping functions employing simple maximum overlap criterion. However, the mixing parameter α_{ij} (eqn. (2)) can be determined in such a manner that the pairs of nonorthogonal functions give the best description of a system or a property under consideration. For example, one can maximize the average distance of the centroids of charge for lone pairs and bonding pairs. It is possible to combine the above mentioned criteria in order to find the best recipe, which of course can be found only in practice. Such an endavour is in progress.

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SAŽETAK

O problemu neortogonalnosti parova (valnih funkcija) u kvantnoj kemiji

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Pokazano je da se korištenjem osnovnog skupa lokalnih hibridnih orbitala Φ_i (i = 1, . . . n) može konstruirati skup parno neortogonalnih funkcija χ_i (i = 1, . . . n) koje imaju slijedeće svojstvo: $< \chi_i | \chi_j > = R_{ij}$, gdje se oznake i, j odnose na susjedne vezne orbitale dok je $< \chi_i | \chi_j > = \delta_{ij}$ kada χ_i i χ_j nisu susjedne vezne orbitale. R_{ij} je integral prekrivanja. Ovakav skup funkcija je pogodan za razne semiempirijske sheme, jer približne formule (posebno u ZDO aproksimaciji) za jedno- i dvo-elektronske integrale postaju njegovom uporabom mnogo opravdanije i točnije.

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