

Maximum overlap approximation calculations on polyatomic molecules. III. Nature of the maximum overlap criterion

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The nature of the maximum overlap criterion for choice of optimum hybrid atomic orbitals (HAOs) was analyzed. Using the quantum-mechanical virial theorem the molecular binding energy on MO LCHAO level of approximation through kinetic integrals has been expressed. As the kinetic integrals for Slater-type AOs can be expressed in terms of overlap integrals, the maximization of the molecular binding energy corresponds to the maximization of a weighted sum of overlap integrals. Semiempirical weighted parameters K which secure the reproduction of the total molecular binding energy are transferable in a good approximation from one molecule to another. Binding energies for nine halomethanes using six different basis sets of AOs are perfectly reproduced.

Обсуждается природа критерия максимального перекрытия для выбора оптимальных гибридных атомных орбиталей (ГАО). Используя квантово-механическую вириальную теорему, была выражена молекулярная связывающая энергия на уровне МО ЛКАО приближения через кинетические интегралы. Поскольку кинетические интегралы для атомных орбиталей Слейтеровского типа могут быть выражены через интегралы перекрытия, достижению максимума молекулярной энергии связи соответствует максимум взвешенной суммы интегралов перекрытия. Семиэмпирические взвешенные параметры K , обеспечивающие воспроизводимость общей молекулярной энергии связи, можно с хорошим приближением применять от одной молекулы для другой. Энергии связи девяти галогенометанов с использованием шести различных наборов АО полностью воспроизводимы.

Hybrid atomic orbitals (HAOs) introduced by *Pauling* [1] form a suitable basis for developing “chemical concepts” in the theory of chemical bond. One of the very important applications of the use of HAOs is the construction of localized molecular orbitals. These localized orbitals enable the evaluation of collective molecular properties, such as binding energies, bond angles, force constants, dipole moments, molecular quadrupole moments, diamagnetic susceptibilities, charge distributions, nuclear magnetic coupling constants, quadrupole coupling constants, etc.

HAOs are defined by an orthogonal transformation applied to the basis of the atomic orbitals (AOs). The problem of selection of the “optimum” HAOs has been studied intensively [2–6], but an unambiguous criterion for choice of “optimum” HAOs does not exist.

A very important property of HAOs is their directional nature. The centre of electron density of HAO is situated outside of atomic nuclei, so that we can define the “direction” of HAO as a vector nucleus-centre of electron density of the HAO. HAOs are often chosen in order to be situated on “covalent bonds”, so that the directional vectors of pairs of HAOs are colinear.

It is well known that the resonance integrals are the major terms in the total molecular binding energy. The resonance integral is in a good approximation proportional to the overlap integral, so that the molecular binding energy can be approximated as a weighted sum of overlap integrals. Since HAOs situated on “covalent bonds” give a higher overlap than pure AOs, it is reasonable to assume that the hybridization procedure can be based on the criterion of maximum overlap [2–5]. Various methods based on the maximum overlap criterion have been successively generalized [7–12] and finally, an extended maximum overlap approximation (EMOA) method has been formulated [13]. This method enables the construction of maximum overlapping HAOs in arbitrary molecules. However, the maximum overlap criterion is widely used, its physical nature has not been yet properly demonstrated. In the present paper we shall try to demonstrate how the maximum overlap criterion is based on the quantum-mechanical virial theorem.

Theory

For a normalized electron ground-state wave function at the equilibrium geometry, in accordance with the quantum-mechanical virial theorem [14], the following equation

$$E_0 = \left\langle \Psi_0 \left| \frac{1}{2} \sum_p^N \nabla_p^2 \right| \Psi_0 \right\rangle \quad (1)$$

is valid. Here, E_0 is the ground-state total molecular energy in the Born—Oppenheimer approximation and N is the number of electrons in a molecule. The

electron wave function Ψ_0 in the MO LCAO approximation is expressed through an antisymmetrized product of occupied molecular spinorbitals, where molecular orbitals $\{\Phi_\mu\}$ are expanded into the basis of real one-centre functions $\{\psi_i\}$ — atomic orbitals (LCAO approximation) or hybrid atomic orbitals (LCHAO approximation)

$$\Phi_\mu = \sum_i^M c_{\mu i} \psi_i \quad (2)$$

Then for an orthogonal set of molecular spinorbitals we obtain

$$E_0 = - \sum_{i,j}^M P_{ij} T_{ij} \quad (3)$$

where

$$T_{ij} \equiv \left\langle \psi_i \left| -\frac{1}{2} \nabla_p^2 \right| \psi_j \right\rangle \quad (4)$$

is the kinetic integral over one-centre basis function $\{\psi_i\}$ and

$$P_{ij} \equiv \sum_{\mu}^{\text{occ}} c_{\mu i} c_{\mu j} \quad (5)$$

is the charge density (bond order) matrix element (μ runs over all occupied spinorbitals). Eqn (3) may be used to test the MO LCAO wave function; but in the present work we exploit this equation as a criterion to determine the optimum hybrid atomic orbitals.

Let us define a unitary transformation between the orthogonal bases of one-centre functions $\{\psi_i^m\}$ and $\{\chi_k^m\}$ on the m -th centre

$$\psi_i^m = \sum_k^{M_m} a_{i,k}^m \chi_k^m \quad (6)$$

The total molecular energy is invariant by an arbitrary unitary transformation (including hybridization)

$$\begin{aligned} E_0 &= - \sum_{m,n}^G \sum_i^{M_m} \sum_j^{M_n} P_{ij} \left\langle \psi_i^m \left| -\frac{1}{2} \nabla_p^2 \right| \psi_j^n \right\rangle = \\ &= - \sum_{m,n}^G \sum_i^{M_m} \sum_j^{M_n} P_{kl} \left\langle \chi_k^m \left| -\frac{1}{2} \nabla_p^2 \right| \chi_l^n \right\rangle \end{aligned} \quad (7)$$

where G is the number of atoms in a molecule and

$$P_{kl} = \sum_i^{M_m} \sum_j^{M_n} P_{ij} a_{i,k}^m a_{j,l}^n \quad (8)$$

Analogously, for the total energy of individual m -th atom E_0^m the following expression is satisfied

$$E_0^m = - \sum_i^{M_m} P'_{ii} T_{ii} \quad (9)$$

where P'_{ii} is the atomic charge density matrix which has the trivial diagonal elements: 0, 1 or 2. Then, for the molecular binding energy ε we obtain

$$\varepsilon = \sum_m^G \sum_i^{M_m} \sum_j^{M_m} T_{ij} (P_{ij} - P'_{ii} \delta_{ij}) + \sum_{m \neq n}^G \sum_i^{M_m} \sum_j^{M_n} P_{ij} T_{ij} \quad (10)$$

Eqn (10) is valid on MO LCAO (or MO LCHAO) level of approximation and it is fulfilled at the self-consistency and at the equilibrium state. Therefore this equation cannot be used to derive a variational procedure for SCF variables, e.g. for charge density (bond order) matrix elements. These elements may be evaluated in given basis of one-centre functions by solving the *Roothaan* equations [15]. But eqn (10) permits the solution of a reverse problem: the explicit determination of basis set of one-centre functions $\{\psi_i^m\}$ in the form (6) if the elements P_{ij} are known. Introducing some assumptions into eqn (10) we obtain the criterion for choice of HAOs. Strictly speaking, the virial theorem is valid only at the Hartree—Fock limit. However, practical calculations showed that it is well satisfied even with small basis sets so that assuming a minimal basis set in eqn (10) does not mean any shortcoming of our theoretical approach. The other approximations involved are listed below.

Approximation 1

We assume the validity

$$\sum_m^G \sum_i^{M_m} \sum_j^{M_m} T_{ij} (P_{ij} - P'_{ii} \delta_{ij}) = 0 \quad (11)$$

Here we assume that: (i) monocentric charge density matrix elements are equal in an individual atom and in that atom in a molecule (it is well valid in slightly polar molecules) and (ii) off-diagonal monocentric kinetic integrals vanish. Using this approximation the molecular binding energy can be rewritten in the form

$$\varepsilon = \frac{1}{2} \sum_{m \neq n}^G \sum_i^{M_m} \sum_j^{M_n} E_{i,j}^{m,n} \quad (12)$$

where

$$E_{i,j}^{m,n} \equiv 2P_{ij} T_{ij} \quad (13)$$

are the increments of the molecular binding energy which will be called the particular binding energies. Thus the maximum value of the following functional

$$\tilde{\gamma} = \varepsilon - \sum_m^G \sum_i^{M_m} \sum_r^{M_m} \lambda_{i,r}^m \langle \psi_i^m | \psi_r^m \rangle \quad (14)$$

may be regarded as a generalized criterion for determination of HAOs ($\lambda_{i,r}^m$ are Lagrangian multipliers). Eqn (14) represents the maximization of molecular binding energy under the constraint condition that the orbitals are kept orthonormal.

For normalized Slater-type AOs in real form

$$\chi_{n,l,m} = (2\xi)^{n+1/2} [(2n)!]^{-1/2} r^{n-1} e^{-\xi r} Z_{l,m}(\vartheta, \varphi) \quad (15)$$

($Z_{l,m}(\vartheta, \varphi)$ are the normalized spherical harmonics) the following equation is valid [16]

$$\begin{aligned} & \left\langle \chi_{n,l,m} \left| -\frac{1}{2} \nabla_p^2 \right| \chi_{n',l',m'} \right\rangle = -\frac{1}{2} \langle \nabla_p^2 \chi_{n,l,m} | \chi_{n',l',m'} \rangle = \\ & = -\frac{1}{2} \xi^2 \{ \langle \chi_{n,l,m} | \chi_{n',l',m'} \rangle - 2(2n)^{1/2} (2n-1)^{-1/2} \langle \chi_{n-1,l,m} | \chi_{n',l',m'} \rangle + \\ & + 4(n+l)(n-l-1) [2n(2n-1)(2n-2)(2n-3)]^{-1/2} \langle \chi_{n-2,l,m} | \chi_{n',l',m'} \rangle \} \end{aligned} \quad (16)$$

Combining eqns (4), (6), (12), (13), and (16) the condition

$$\delta \tilde{\gamma} = 0 \quad (17)$$

corresponds to the maximum of weighted sum of overlap integrals and thus the maximum overlap criterion for choice of HAOs is derived.

In a molecule any orbital on a given atom can be expanded in terms of the complete orthogonal set of one-centre functions of the other atom of the molecule

$$\langle \psi_i^m | = \sum_r^n \langle \psi_i^m | \psi_r^n \rangle \langle \psi_r^n | = \sum_r^n S_{i,r}^{m,n} \langle \psi_r^n | \quad (18)$$

Then

$$\begin{aligned} T_{i,j}^{m,n} &= \sum_s^m S_{s,j}^{m,n} T_{i,s}^{m,m} = \sum_r^n S_{i,r}^{m,n} T_{r,j}^{n,n} = \\ &= \frac{1}{2} \left(\sum_s^m S_{s,j}^{m,n} T_{i,s}^{m,m} + \sum_r^n S_{i,r}^{m,n} T_{r,j}^{n,n} \right) \end{aligned} \quad (19)$$

Approximation 2

Two-centre kinetic integrals in a minimum (or in the valence) basis set are approximated as follows

$$T_{ij} = \frac{1}{2} (T_{ii} + T_{jj}) S_{ij} \quad (20)$$

which is the well-known Mulliken approximation of two-centre one-electron integrals [17]. According to this approximation the molecular binding energy can be rewritten in the form

$$\varepsilon = \frac{1}{2} \sum_{m \neq n}^G \sum_i^{M_m} \sum_j^{M_n} K_{i,j}^{m,n} S_{i,j}^{m,n} \quad (21)$$

where

$$K_{i,j}^{m,n} = P_{ij} (T_{ii} + T_{jj}) \quad (22)$$

Expression (21) represents the weighted sum of overlap integrals between HAOs; particular binding energies $E_{i,j}^{m,n}$ are directly proportional to the overlap integrals of HAOs

$$E_{i,j}^{m,n} = K_{i,j}^{m,n} S_{i,j}^{m,n} \quad (23)$$

Approximation 3

Elements $K_{i,j}^{m,n}$ can be regarded as numerical parameters transferable from one molecule to another, which depend only on the quality of the bonded atomic pair. These parameters may be evaluated in a semiempirical way.

Let us deal now with directional properties of HAOs. It is well known that HAOs may be chosen in such a way that their directional vectors with directions of "covalent bonds" are parallel. For example, in the methane molecule using group theory we obtain HAOs on carbon atom the directional vectors of which are situated on C—H bonds. However, many examples are known in which real HAOs oriented in the bond directions do not exist (e.g. in the cyclopropane molecule), and it is necessary to introduce some deviation from the bond direction [18, 19]. The directional nature of HAOs enables us to construct strictly localized molecular orbitals which describe two-centre "covalent bonds". Therefore we define the "optimum" hybrid atomic orbitals as those:

- (i) which maximize the total molecular binding energy according to eqn (21) under the condition of orthonormality of HAOs on each centre;
- (ii) which have the minimum deviation from bond directions.

In order to secure the second condition we must define some “bonding situation” in a molecule, e.g. we must describe “covalent bonds” in terms of HAOs’ pairs. Let us have independent numbering of:

- (i) atoms (index $m \in \langle 1, G \rangle$);
- (ii) HAOs on the given atom (index $i \in \langle 1, M_m \rangle$);
- (iii) “covalent bonds” (1, 2, ...).

We define a discrete topological function $f(m, i)$ on the set of indices $\{m, i\}$, the value of which is equal to the bond number. The topological function $f(m, i)$ fully describes the molecular bonding model: the nonzero topological factor $(1 - \delta_{m,n}) \delta_{f(m,i), f(n,j)}$ selects from all indices $\{m, i\}$ and $\{n, j\}$ only pairs of HAOs ψ_i^m and ψ_j^n which are oriented in the direction of the same bond (Fig. 1). Lone lobes (“nonbonding HAO”) may be considered as “nonconnected bonds” which do not give a contribution to the molecular binding energy. For lone lobe ψ_i^m we have

$$\sum_n^G \sum_j^{M_n} (1 - \delta_{m,n}) \delta_{f(m,i), f(n,j)} = 0 \quad (24)$$

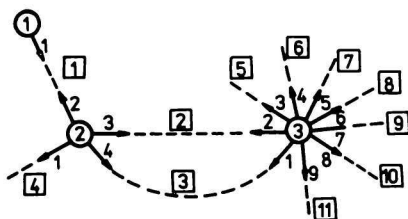


Fig. 1. Numbering system for description of molecular bonding model.

With respect to both conditions mentioned for optimum HAOs, these may be chosen so as to maximize the following expression

$$\varepsilon = \frac{1}{2} \sum_{m,n}^G \sum_{i,k}^{M_m} \sum_{j,l}^{M_n} K_{i,j}^{m,n} a_{i,k}^m a_{j,l}^n \langle \chi_k^m | \chi_l^n \rangle (1 - \delta_{m,n}) \delta_{f(m,i), f(n,j)} \quad (25)$$

Eqn (25) corresponds to the weighted sum of overlap integrals between “bonding” HAOs and was used as a criterion for selection of HAOs in the EMOA method. A simple matrix formula for simultaneous optimization of “bonding” HAOs on all centres of the molecule has been derived in [13]. “Nonbonding” HAOs may be obtained as a complement to the orthonormal set of HAOs on each centre.

It is possible to show [20] that the molecular binding energy expressed by eqn (25) can be regarded as a scalar invariant of a second-rank tensor which is constructed through the Kronecker products of all vector spaces W_m where HAOs = $\psi_i^m \in W_m$. However, a scalar invariant of any tensor does not depend on the use of basic functions. Thus the molecular binding energy should be invariant using various basis sets of atomic orbitals. Strictly speaking, it is true only in complete Hilbert space. The validity of this assumption must be verified by numerical calculations for various valence basis sets.

Results and discussion

In this paper the maximum overlap criterion for the choice of optimum hybrid atomic orbitals has been theoretically studied. Using the quantum-mechanical virial theorem the molecular binding energy has been expressed as a function of kinetic integrals in the HAOs' basis. As the kinetic integrals for Slater-type AOs through overlap integrals can be expressed, the generalized criterion of the maximum overlap can be obtained by maximization of total binding energy. Due to some approximations the molecular binding energy has been expressed as a weighted sum of overlap integrals. Weighted parameters $K_{i,j}^{m,n}$ which secure the reproduction of molecular binding energy depend only on monocentric kinetic integrals and bond-order matrix elements $P_{i,j}^{m,n}$.

Localized "covalent bonds" can be described with strictly localized molecular orbitals (SLMOs) which are defined as follows

$$\Phi_\mu = b_i \psi_i^m + b_j \psi_j^n \quad (26)$$

where coefficients b_i and b_j expand the μ -th SLMO into pair of HAOs with maximum overlap. Expanding coefficients are constrained by the following normalization condition

$$b_i^2 + b_j^2 + 2b_i b_j S_{i,j}^{m,n} = 1 \quad (27)$$

In this case the bond-order matrix elements are

$$P_{i,j}^{m,n} = w_\mu b_i b_j \quad (28)$$

(w_μ is the SLMO's occupation number). It is interesting to examine the functional dependence of $(b_i b_j)$ vs. b_i for fixed overlap integrals $S_{i,j}^{m,n}$. In Fig. 2 we can see that a change in bond polarity does not affect the bond orders significantly. Therefore, it is reasonable to assume that parameters $K_{i,j}^{m,n}$ for a given atomic pair are transferable from one molecule to another.

The ideas presented in the previous part of this article have been numerically tested on the series of halomethanes. During the calculation we have used the experimental geometries of the molecules. The invariance of the molecular binding

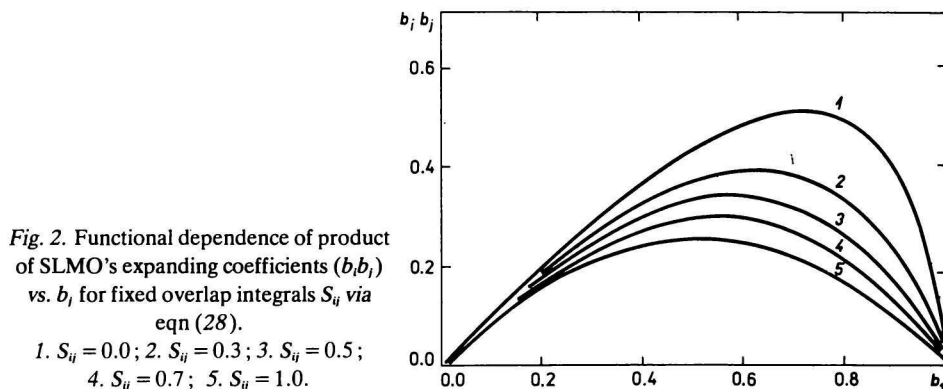


Fig. 2. Functional dependence of product of SLMO's expanding coefficients ($b_i b_j$) vs. b_j for fixed overlap integrals S_{ij} via eqn (28).

1. $S_{ij} = 0.0$; 2. $S_{ij} = 0.3$; 3. $S_{ij} = 0.5$;
4. $S_{ij} = 0.7$; 5. $S_{ij} = 1.0$.

energy was tested using six different basis sets of AOs. Parameters $K_{i,j}^{m,n}$ for bonds C—X (X = H, F, Cl, Br) were determined in order to reproduce the molecular binding energies of CX_4 molecules (Table 1). These parameters were used in the EMOA method for calculations of optimum HAOs, particular binding energies and total binding energy of CH_3X , CH_2X_2 , CHX_3 (X = F, Cl, Br) types of molecules. The results are presented in Tables 2 and 3.

Particular binding energies (Table 2) are in a good agreement with empirical values [21]: $E_{\sigma}^{C,H} = 414-439$, $E_{\sigma}^{C,F} = 443-485$, $E_{\sigma}^{C,Cl} = 310-326$, and $E_{\sigma}^{C,Br} = 259-268$ (in kJ mol^{-1}). In the series of the molecules CH_3X , CH_2X_2 , and CHX_3 the particular binding energies for C—H as well as for C—X bonds increase. This is in a good harmony with the established thermal stability of tri-halomethanes relative to mono-halomethanes. Total molecular binding energies (Table 3) for all six bases are in a good agreement with experiments: deviations from experimental data are less than 2%.

Table 1

Parameters K by different valence bases [kJ mol^{-1}]

Bond	Valence set					
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>
C—H	604.617	592.266	547.861	569.928	575.559	575.329
C—F	852.913	825.712	718.589	762.325	791.747	796.634
C—Cl	549.229	566.430	465.922	530.594	536.887	540.443
C—Br	—	496.310	438.533	451.705	—	470.838

a) Slater [24]; *b*) single zeta SCF [25]; *c*) Burns [26]; *d*) Froese [27, 28]; *e*) double zetas SCF [29]; *f*) poly zetas SCF [29].

Table 2

Particular binding energies [kJ mol⁻¹]

Molecule	Bond	Used geometry		Valence set*					
		Distance [10 ⁻¹⁰ m]	Angle [degree]	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>
CH ₃ F	C—H	1.097	FCH 108.9	418.8	418.8	417.6	418.0	417.1	418.0
	C—F	1.3852		443.9	446.4	457.7	453.1	457.7	453.1
CH ₂ F ₂	C—H	1.093	HCH 109.46	424.3	423.8	420.9	422.2	420.1	422.2
	C—F	1.360	FCF 108.5	461.5	463.2	470.3	467.4	470.3	467.4
CHF ₃	C—H	1.098	FCH 110.14	428.0	427.2	423.0	424.7	421.3	424.7
	C—F	1.332		480.7	481.2	483.3	482.4	483.3	482.4
CH ₃ Cl	C—H	1.0959	ClCH 108.4	419.2	419.7	423.0	424.7	421.3	424.7
	C—Cl	1.78123		311.7	312.1	315.9	313.4	314.6	313.4
CH ₂ Cl ₂	C—H	1.082	HCH 109.5	427.2	427.2	423.4	425.5	424.3	425.5
	C—Cl	1.772	ClCCl 112.0	317.6	318.0	320.5	318.8	319.7	318.8
CHCl ₃	C—H	1.073	ClCH 108.2	434.3	434.7	427.6	431.8	429.3	431.8
	C—Cl	1.762		323.8	323.8	324.3	324.3	324.3	323.8
CH ₃ Br	C—H	1.0954	BrCH 107.23	—	420.5	419.2	419.7	—	419.7
	C—Br	1.9388		—	261.1	262.8	261.9	—	261.9
CH ₂ Br ₂	C—H	1.093	BrCBr 112.0	—	425.1	422.6	423.8	—	423.8
	C—Br	1.93	HCH 109.5	—	266.9	267.8	267.4	—	267.4
CHBr ₃	C—H	1.068	BrCH 108.11	—	438.9	432.6	435.6	—	435.6
	C—Br	1.93		—	269.4	269.4	269.4	—	269.4

* References see in Table 1.

Table 3

Molecular binding energies [kJ mol⁻¹]

Molecule	Exptl.*	Valence set**					
		<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>
CH ₃ F	1719.6	1700.8	1702.5	1710.4	1707.1	1710.4	1708.7
CH ₂ F ₂	1761.9	1771.9	1773.6	1782.4	1778.6	1780.7	1780.3
CHF ₃	1867.7	1870.2	1870.7	1873.2	1871.9	1871.5	1871.5
CH ₃ Cl	1576.1	1569.8	1570.3	1570.3	1570.3	1569.8	1569.4
CH ₂ Cl ₂	1488.2	1489.9	1490.3	1487.0	1489.1	1487.4	1487.0
CHCl ₃	1397.0	1405.8	1406.2	1401.2	1404.2	1402.1	1401.6
CH ₃ Br	1518.4	—	1522.1	1520.5	1521.3	—	1518.8
CH ₂ Br ₂	1378.6	—	1384.5	1380.7	1382.4	—	1378.6
CHBr ₃	1243.1	—	1247.3	1241.4	1244.3	—	1240.1

* Ref. [30].

** References see in Table 1.

The obtained results demonstrate that the EMOA method is useful for construction of the optimum HAOs in polar molecules. From this point of view we doubt the statement of *Randič* and *Maksič* [22, 23] that the maximum overlap criterion should be used only for nonpolar hydrocarbons. This method has been applied on the large number of molecules (of the various types) which are built from H to Br atoms, including first transition metal row atoms.

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