Theoret. chim. Acta (Berl.) 6, 83—86 (1966)

Restriction on Approximations of Molecular Integrals

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Received July 1, 1966

The results of LCAO-MO-SCF calculations applied to molecules have to be invariant with respect to orthogonal transformations of the basis set of atomic orbitals. However, if the multicenter repulsion integrals needed for such a calculation are approximated, invariancy will in general not be retained. For two methods of approximation the behaviour of the multicenter integrals under such transformations has been investigated, along with the conditions which have to be fulfilled to ensure this invariancy.

Ergebnisse von LCAO-MO-SCF-Rechnungen an Molekülen werden nichtinvariant gegen orthogonale Basistransformationen, wenn für die Mehrzentrenintegrale Näherungsausdrücke verwendet werden. Für zwei Näherungsmethoden wird der Einfluß der Transformationen auf die Mehrzentrenintegrale untersucht; Bedingungen für bestimmte Invarianzeigenschaften werden angegeben.

Les résultats d'un calcul LCAO-MO-SCF doivent être invariants par rapport aux transformations orthogonales de la base des orbitales atomiques. Cette invariance n'est en général pas respectée si les intégrales de répulsion multicentriques nécessaires pour un tel calcul sont évaluées d'une manière approchée. Le comportement des intégrales multicentriques lors de telles transformations a été étudié par deux méthodes d'approximation; on a envisagé les conditions à remplir pour satisfaire à l'invariance.

1. Introduction

Recently Pople et al. [2] have shown that approximations to multicenter integrals in LCAO–MO–SCF calculations have to fulfill certain conditions in order to secure invariancy with respect to an orthogonal transformation of the basis set of atomic orbitals. They distinguished three types of orthogonal transformations:

1. Rotations of the local axes, for instance mixing of different $2p$-orbitals on the same atom.

2. Hybridisations, such as mixing of s- and p-orbitals on the same atom.

[1. and 2. together form the group of localized orthogonal transformations.]

3. General orthogonal transformations, resulting in a mixing of atomic orbitals on different atoms.

It is the purpose of this paper to sort out those transformations which are compatible with:

a) an approximation method introduced by Ruedenberg [3].

b) the well-known Mulliken approximation [1].

2. The Ruedenberg approximation

In a molecule any orbital on an atom A may be expanded in a complete *orthogonal* basis set of atomic orbitals on one of the other atoms of the molecule, say B (atomic orbitals on atom A are denoted by φ_i^A and φ_j^A, those on atom B by φ_r^B and φ_s^B):

$$\varphi_i^A = \sum_r^B c_{ir}\,\varphi_r^B \tag{1}$$

with

$$c_{ir} = \langle \varphi_i^A \mid \varphi_r^B \rangle = S_{ir}\,, \tag{2}$$

S_{ir} being an element of the overlapmatrix S_φ. Eq. (2) implies the orthogonality of all atomic orbitals on the same atom. An overlap density may now be written:

$$\begin{aligned}\langle \varphi_i^A\,\varphi_r^B \mid &= \sum_j^A S_{rj}\,\langle \varphi_i^A\,\varphi_j^A \mid = \sum_s^B S_{is}\,\langle \varphi_s^B\,\varphi_r^B \mid \\ &= \tfrac{1}{2}\left[\sum_j^A S_{rj}\,\langle \varphi_i^A\,\varphi_j^A \mid + \sum_s^B S_{is}\,\langle \varphi_s^B\,\varphi_r^B \mid\right].\end{aligned} \tag{3}$$

Using this expression formally exact expansions of three- and four-center integrals in terms of two-center integrals may be obtained. The expression is only workable, however, if the summations in (3) include only a limited number of terms. In most cases the LCAO calculation will be carried out with a restricted basis, containing only the $1s$, $2s$ and $2p$-orbitals of each atom. We will call this approach the Ruedenberg approximation.

For an investigation of the transformational properties of this method it is convenient to employ matrix notation. Each overlap density $\varphi_i^A\,\varphi_r^B$ is an element of the direct product matrix $\Phi = \varphi \times \varphi^\dagger$, in which φ is a column vector containing all atomic orbitals in the restricted basis set under consideration. Φ is symmetrical and has a block structure: the dimension of each block equals the number of atomic orbitals introduced in φ for the corresponding atom. In this notation the Ruedenberg approximation may be written as:

$$\Phi \cong \tfrac{1}{2}\,[S_\varphi \Phi^0 + \Phi^0 S_\varphi] = \Phi'\,. \tag{4}$$

Here Φ^0 is a block diagonal matrix, containing only one-center overlap densities $\varphi_i^A\,\varphi_j^A$. The Eqs. (3) and (4) are equivalent. Invariancy under an orthogonal transformation of the basis will only be obtained if (the approximate) Φ' transforms in the same manner as (the exact) Φ.

If the new basis set t is related to the original basis φ by $t = O\varphi$, then:

$$\langle t_i \mid t_r \rangle = \sum_j \sum_s O_{ij}\,O_{rs}\,\langle \varphi_j \mid \varphi_s \rangle\,,$$

or in matrix notation:

$$S_t = O S_\varphi\, O^\dagger\,,$$

and:

$$T = t \times t^\dagger = O\varphi \times \varphi^\dagger\, O^\dagger = O\,(\varphi \times \varphi^\dagger)\, O^\dagger = O\,\Phi\, O^\dagger\,. \tag{5}$$

In analogy to (4), T may be approximated by T':

$$T \cong T' \equiv \tfrac{1}{2}\,[S_t\, T^0 + T^0\, S_t] = \tfrac{1}{2}\,[O S_\varphi\, O^\dagger\, T^0 + T^0\, O S_\varphi\, O^\dagger]\,.$$

The desired result that Φ and Φ' transform in the same way is obtained if:

$$T^0 = O\,\Phi^0\, O^\dagger\,, \tag{6}$$

for then

$$T' = \tfrac{1}{2}\,[O S_\varphi\, O^\dagger\, O\,\Phi^0\, O^\dagger + O\,\Phi^0\, O^\dagger\, O S_\varphi\, O^\dagger] = O\,\Phi'\, O^\dagger\,.$$

However, (6) holds only if O and Φ^0 possess an *identical* (diagonal) block structure. Then, since different blocks in Φ^0 are not mixed by the orthogonal transformation, T^0 also has the same block diagonal structure, and we have for each block K on the diagonal:

$$T_K^0 = t_K \times t_K^\dagger = O_K \varphi_K \times \varphi_K^\dagger O_K^\dagger = O_K \Phi_K^0 O_K^\dagger .$$

Consequently (6) requires that atomic orbitals on the *same* atom only may be mixed, i.e. the Ruedenberg approximation to multicenter integrals gives results which are invariant under rotations of the local axes and which are independent of the choice of hybrids.

3. The Mulliken approximation

If the Ruedenberg approximation is simplified by neglecting a number of terms in the summations in (3), the Mulliken approximation [1] may be obtained:

$$\begin{aligned} \langle\varphi_i^A \varphi_r^B | &\cong \tfrac{1}{2} [\sum_j^A S_{rj} \cdot \langle\varphi_i^A \varphi_j^A | \cdot \delta_{ij} + \sum_s^B S_{is} \cdot \langle\varphi_s^B \varphi_r^B | \cdot \delta_{rs}] \\ &= \tfrac{1}{2} S_{ir} [\langle\varphi_i^A \varphi_i^A | + \langle\varphi_r^B \varphi_r^B |] . \end{aligned} \tag{7}$$

Eq. (7) reads in matrix notation:

$$\Phi \cong \tfrac{1}{2} [S_\varphi \Phi_M^0 + \Phi_M^0 S_\varphi] = \Phi'_M \tag{8}$$

where now *all* off-diagonal elements in Φ_M^0 are zero. For a four-center repulsion integral this leads to:

$$\langle\varphi_i^A \varphi_j^C \left| \frac{1}{r_{12}} \right| \varphi_r^B \varphi_s^D\rangle = \tfrac{1}{4} S_{ij} S_{rs} [\gamma_{ir} + \gamma_{is} + \gamma_{jr} + \gamma_{js}] . \tag{9}$$

The γ_{ir} etc. are two-center Coulomb integrals, defined by

$$\gamma_{ir} \equiv \langle\varphi_i^A \varphi_i^A \left| \frac{1}{r_{12}} \right| \varphi_r^B \varphi_r^B\rangle . \tag{10}$$

However, the Mulliken approximation, as defined by (8) and (9), does not give results which are invariant to orthogonal transformations of the basis. Condition (6) is fulfilled only if all diagonal elements which are mixed by the orthogonal transformation are made equal, otherwise T^0 would not be diagonal.

Two types of orthogonal transformations will now be considered:

1. *Localized orthogonal transformations.* If all diagonal elements in Φ_M^0 pertaining to the same atom are made equal, the approximation of a four-center integral becomes:

$$\langle\varphi_i^A \varphi_j^C \left| \frac{1}{r_{12}} \right| \varphi_r^B \varphi_s^D\rangle = \tfrac{1}{4} S_{ij} S_{rs} [\gamma_{AB} + \gamma_{AD} + \gamma_{BC} + \gamma_{CD}] ,$$

where the values of γ_{AB} etc. are invariant to changes in the corresponding orbitals caused by a localized orthogonal transformation (conf. [2], pag. S 132). A simple way to obtain the desired invariancy is to take averages of the two-center Coulomb integrals (10) for the γ_{AB}-integrals:

$$\gamma_{AB} = \frac{1}{n_A n_B} \sum_i^{n_A} \sum_r^{n_B} \gamma_{ir} . \tag{11}$$

A result independent of the hybrids chosen is obtained only if the two-center Coulomb integrals which are used to approximate the multicenter integrals are independent of the type of the orbitals appearing in the corresponding multicenter integral. So in contrast to the Ruedenberg approximation the Mulliken approximation has to be used with some care, as the original Eq. (9) gives results which are not independent of the choice of hybrids or even of the choice of local axes.

2. *Rotations of local axes.* If the results of a molecular calculation are to be invariant only under rotations of the local axes it is sufficient to restrict the averaging process to those integrals which involve $2p$-orbitals, for then no mixing takes place between s- and p-orbitals or between $1s$- and $2s$-orbitals. In this case the deviations of the mean values [in contrast to the more general case (11)] of the two-center Coulomb integrals from the values of the original integrals (10) will be reasonably small, since in general the orientation of a $2p$-orbital does not have much effect on the value of a two-center Coulomb integral involving this orbital.

Acknowledgement. The author is greatly indebted to Prof. DEN BOER for his help and encouragement.

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