Theoret. chim. Acta (Berl.) 18, 389—390 (1970)

Justifiability of the ZDO Approximation in Terms of a Power Series Expansion

N. A. B. GRAY AND A. J. STONE
University Chemical Laboratory, Lensfield Road, Cambridge, England

Received July 3, 1970

The Zero Differential Overlap Approximation cannot be justified for all-valence-electron calculations in terms of a power series expansion of the overlap matrix, because the expansion diverges.

Several authors [1–3] have sought to justify the zero differential overlap (ZDO) approximation used in semi-empirical calculations by treating a ZDO method as an approximation to a calculation in a symmetrically orthogonalised basis. In these analyses the accuracy of the ZDO approximations is investigated in terms of a power series expansion. It is the purpose of this note to point out that this approach is unsatisfactory except for π-electron calculations.

The orthogonalized orbital basis φ is related to the normalized atomic orbital basis χ by

$$\varphi = \chi \Delta^{-1/2} \tag{1}$$

where

$$\Delta_{ij} = \delta_{ij} + S_{ij} = \langle \chi_i | \chi_j \rangle \tag{2}$$

If we assume that $\Delta^{-1/2}$ can be expressed as a convergent power series in $\boldsymbol{S}$:

$$\Delta^{-1/2} = (\mathbf{1} + S)^{-1/2} = \mathbf{1} - \tfrac{1}{2} S + \tfrac{3}{8} S^2 - \cdots, \tag{3}$$

then it is possible to relate integrals in the orthogonalized basis φ to those in the original basis χ, the relation involving a power series in $\boldsymbol{S}$ [1, 3].

However, if $\boldsymbol{T}$ is a matrix which diagonalizes S, so that $S = \boldsymbol{T} \Lambda \boldsymbol{T}^{-1}$ with Λ a diagonal matrix whose diagonal elements are the eigenvalues λ_i of S, then it is evident that $S^n = \boldsymbol{T} \Lambda^n \boldsymbol{T}^{-1}$ and that the expansion (3) can only converge if $\varrho < 1$, where ϱ is the spectral radius of S, given by $\varrho = \max \{ |\lambda_i| \}$.
The eigenvalues λ_i of a symmetric matrix A satisfy Gerschgorin's theorem [4]:

$$|\lambda_i - A_{ii}| \leqq \sum_{j \neq i} |A_{ij}| \,. \tag{4}$$

Since the diagonal elements of $\boldsymbol{S}$ are zero, we see that the spectral radius has an upper bound:

$$\varrho \leqq \max_i \sum_j |S_{ij}| \quad . \tag{5}$$

Now in the simple π electron model considered by Fischer-Hjalmars [1] only nearest neighbour orbitals overlap, so that in no row of $\boldsymbol{S}$ are there more than three non-zero elements, with values of order 0.25. Consequently the spectral

Table. *Overlap matrix **S** for valence orbitals of methane. (Slater type orbitals with exponents 1.625 for carbon and 1.16 for hydrogen, internuclear distance of 1.1 A)*

0.0	0.0	0.0	0.0	0.5239	0.5239	0.5239	0.5239
0.0	0.0	0.0	0.0	−0.2789	−0.2789	0.2789	0.2789
0.0	0.0	0.0	0.0	0.3944	−0.3944	0.0	0.0
0.0	0.0	0.0	0.0	0.0	0.0	−0.3944	0.3944
0.5239	−0.2789	0.3944	0.0	0.0	0.1970	0.1970	0.1970
0.5239	−0.2789	−0.3944	0.0	0.1970	0.0	0.1970	0.1970
0.5239	0.2789	0.0	−0.3944	0.1970	0.1970	0.0	0.1970
0.5239	0.2789	0.0	0.3944	0.1970	0.1970	0.1970	0.0

radius ϱ will be less than 1, and the power series will converge. Direct diagonalisation of the full π overlap matrices for benzene and naphthalene shows that the spectral radii are in fact 0.57 and 0.71 respectively. Thus Fischer-Hjalmar's use of (3) is fully justified.

In all-valence-electron calculations, however, there may be up to four nearest neighbour σ overlaps, with overlap integrals perhaps as large as 0.6. The upper-bound (5) on ϱ will therefore be much larger, and one may expect that ϱ itself will be larger. In the Table is shown the overlap matrix $\boldsymbol{S}$ for the valence orbitals of CH_4. No individual element exceeds 0.6, but we see from (5) that the upper bound on ϱ is 2.09, and direct diagonalisation shows that the largest eigenvalue is in fact 1.38. The corresponding values for ethane are 2.63 and 1.59. In these cases therefore the expansion (3) diverges and arguments based on it are fallacious. There is no reason to suppose that CH_4 and C_2H_6 are particularly unfavourable cases, and we may conclude that the ZDO approximation cannot be justified for all-valence-electron calculations by the argument used by Dahl [2] and Brown and Roby [3]. This is not to say that the approximation is unjustifiable, but a rigorous justification has yet to be found.

Acknowledgement. N.A.B.G. wishes to thank the SRC for a grant.

References

1. Fischer-Hjalmars, I.: Advances quant. Chem. **2**, 25 (1965).
2. Dahl, J. P.: Acta chem. scand. **21**, 1244 (1967).
3. Brown, R. D., Roby, K. R.: Theoret. chim. Acta (Berl.) **16**, 175 (1970).
4. Wilkinson, J. H.: The algebraic eigenvalue problem, p. 71. Oxford: Clarendon Press 1965.

Mr N. A. B. Gray
University Chemical Laboratory
Lensfield Road, Cambridge, England