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A Note on General Core-Valence Orthogonality

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A method of generating a set of basis functions, which satisfy the condition of "strong orthogonality", is developed.

Introduction

It is well-known that the results of an "orbital basis Hartree-Fock" calculation (SCFMO) are invariant against linear transformations of the basis orbitals which preserve normalization and linear independence [1] and that any method going beyond the independent particle model does not have this convenient invariance property [2]. Thus the choice of basis for a calculation of the CI/VB type is a non trivial factor to be considered [3]. The CI/VB analysis is considerably simplified by the use of an orthonormal basis [2] and for practical, computational, reasons most many electron calculations use such a basis set.

The most commonly used orthogonalization procedures, due to Schmidt [4] and Löwdin [5] do not produce an orbital basis which is entirely satisfactory for CI/VB calculations for different reasons. McWeeny and others [6] have shown that a VB type calculation is adversely affected by using an orthogonalization procedure in which the low-lying "core" orbitals contain admixture of "valence" orbitals after orthogonalization. Thus the Löwdin orthogonalization method (which has the physically appealing property of disturbing the orbital basis least consistent with orthogonality [7]) cannot be used directly. The well-known Schmidt orthogonalization method generates an orthonormal basis in which only one orbital is left unchanged and the whole process is highly unsymmetrical, producing an orthonormal set which is dependent on the ordering of the basis. The members of the Schmidt orthogonal basis do not have the symmetry properties of the original basis.

A compromise has been used in Ref. [6] in which a "local" Schmidt orthogonalization is performed on each "heavy" atom and the resulting set being symmetrically orthogonalized by the Löwdin procedure (with possibly a unitary transformation-hybridization). This compromise procedure works well for molecules containing one atom with core orbitals. For more complex molecules the interatomic core-valence overlap causes undesirable core-valence mixture. The interatomic core-valence overlap terms are typically about 0.1 for adjacent first row atoms.

In this note a method is presented for the generation of an orbital basis which leaves any number of core orbitals uncontaminated by valence orbitals on orthogonalization.

Method

We refer to a basis consisting of a set $\{\phi_{i_c}\}$ of n_c "core" orbitals and a set $\{\phi_{i_v}\}$ of n_v "valence" orbitals which are not orthogonal, i.e.

$$\left.\begin{array}{l} \langle\phi_{i_c}|\phi_{j_c}\rangle \neq 0 \\ \langle\phi_{i_c}|\phi_{j_v}\rangle \neq 0 \\ \langle\phi_{i_v}|\phi_{j_v}\rangle \neq 0 \end{array}\right\} \quad \begin{array}{l} i_c, j_c = 1, \dots, n_c \\ i_v, j_v = 1, \dots, n_v \end{array} \tag{1}$$

we require a linear transformation to produce a new set of valence orbitals $\{\bar{\phi}_{i_v}\}$ such that

$$\langle\phi_{i_c}|\bar{\phi}_{j_v}\rangle = 0 \left| \begin{array}{l} i_c = 1, \dots, n_c \\ j_v = 1, \dots, n_v \end{array}\right. \tag{2}$$

we write

$$\bar{\phi}_{j_v} = \phi_{j_v} + \sum_{i_c=1}^{n_c} W_{i_c j_v} \phi_{i_c} \tag{3}$$

and insist that (2) shall hold:

$$\text{i.e.} \quad 0 = \langle\phi_{k_c}|\bar{\phi}_{j_v}\rangle = \langle\phi_{k_c}|\phi_{j_v}\rangle + \sum_{i_c=1}^{n_c} \langle\phi_{k_c}|\phi_{i_c}\rangle\, W_{i_c j_v} \qquad (k_c = 1, \dots, n_c)$$

Collecting these equations we have

$$\boldsymbol{S}_c \boldsymbol{W} + \boldsymbol{S}_{cv} = \boldsymbol{0}$$

where

$$(\boldsymbol{S}_c)_{i_c j_c} = \langle\phi_{i_c}|\phi_{j_c}\rangle$$

$$(\boldsymbol{S}_{cv})_{i_c j_v} = \langle\phi_{i_c}|\phi_{j_v}\rangle$$

$$\text{i.e.} \quad \boldsymbol{W} = -\boldsymbol{S}_c^{-1} \boldsymbol{S}_{cv}$$

giving the matrix $\boldsymbol{W}$ which contains the required transformation coefficients since $\boldsymbol{S}_c$ is always non-singular. The remaining non-orthogonalities are now all core-core and valence-valence and can be treated by the Löwdin method still leaving the core orbitals unmixed with valence components.

General Applications

The argument has been developed within the physical idea of a multi-core/valence separation but the derivation is of general applicability to the strong orthogonality condition. Löwdin [8] has shown that the condition that the wave functions of two separate groups of electrons $\Phi_A(1, \dots, N)$ and $\Phi_B(1, \dots, N)$ are "strongly" orthogonal:

$$\int dV_i \Phi_A(1, \dots, i, \dots, N)\, \Phi_B(1, \dots, i, \dots, N) = 0 \qquad (i = 1, \dots, N)$$

if all the orbitals used in the construction of Φ_A are orthogonal to all those used in Φ_B. Clearly the matrix $\boldsymbol{W}$ achieves "strong" orthogonality between the set $\{\phi_{i_c}\}$ and $\{\phi_{i_v}\}$ without insisting on orthogonality *within* $\{\phi_{i_c}\}$ or $\{\phi_{i_v}\}$ which is the current general practice.

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References

1. Lennard-Jones, J. E.: Proc. Roy. Soc. (London) A **198**, 1 (1949).
2. Slater, J. C.: J. chem. Physics **19**, 220 (1951).
3. McWeeny, R.: Proc. Roy. Soc. (London) A **223**, 63 (1954).
4. See, for example, Hall, G. G.: Matrices and tensors, p. 51. Pergamon Press 1963.
5. Löwdin, P.-O.: J. chem. Physics **18**, 365 (1950).
6. McWeeny, R., Ohno, K.: Proc. Roy. Soc. (London) A **255**, 367 (1960).
   McWeeny, R., Klessinger, M.: J. chem. Physics **42**, 3343 (1965).
7. Carlson, B. C., Keller, J. M.: Physic. Rev. **105**, 102 (1950).
8. Löwdin, P.-O.: J. chem. Physics **35**, 78 (1961).

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