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Relatio

Overlap Integrals of Clementi Orbitals for Bonds Involving Some First Row Atoms

L. KLASINC* and D. SCHULTE-FROHLINDE

Kernforschungszentrum Karlsruhe, Institut für Strahlenchemie, Karlsruhe, Deutschland

M. RANDIĆ

Institute "Ruđer Bosković", Zagreb, Yugoslavia

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The interest in overlap integrals originates from an intuitive feeling that overlap integrals may indicate bond strengths. This idea was formulated by PAULING and SLATER as a principle, or more correctly as a criterion, of maximum overlap [1, 2] and ever since the pioneer work of MULLIKEN [3, 4] it has been recognized that the numerical value of the overlap integral gives considerable information about the strength of the bond. However, it became evident that Slater orbitals show some deficiency. For example the computed values of overlap integrals for medium and large distances are considerably smaller than those based on SCF Hartree-Fock functions. The Slater orbitals not only give reduced absolute values of the relevant atomic overlap integrals at larger separations, but affects also their relatives magnitude.

Therefore it would be better to use self-consistent-field atomic orbitals than Slater orbitals. We selected for the basic orbitals, a set of functions recently given and recommended for molecular calculations by CLEMENTI [5] (Table). They are not quite so accurate as truly SCF orbitals, but they are nearly so. These orbitals are of the so-called "double zeta" type [6]. Each orbital is a linear combination of Slater-type functions. They form an orthogonal set and may be considered as an extension of orthogonalized Slater orbitals, since for each Slater function there are *two* such exponentials, but their parameters are obtained by minimization of atomic energy.

We computed values of Clementi orbital overlap integrals for single and multiple homopolar bonds of first row atoms from boron to fluorine. Also considered are single and multiple heteropolar bonds and finally hybrides of these atoms. Here a comparison with similar results for Slater orbitals, given by MULLIKEN is made. Details of the calculation of overlap integrals for Slater functions, of which Clementi functions are linear combinations, are summarized in Ref. [3].

Homopolar bonds. The most significant difference between the results for Slater and Clementi orbitals are in the relative values of $(p, p)_\sigma$ and $(p, p)_\pi$ inte-

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* On leave from Institute "Ruđer Bošković", Zagreb.

Table. *Clementi orbitals for several first row atoms.* ϕ_{1s}, ϕ_{2s} *and* ϕ_{2p} *are normalized Slater type functions the exponents of wich ave given in brackets.*

$$\begin{aligned}
\text{Boron:}\quad \psi_{2s} &= -0.25123\,\phi_{1s}(4.30481) + 0.00989\,\phi_{1s}(6.84691) + \\
&\quad +0.18097\,\phi_{2s}(0.88143) + 0.87265\,\phi_{2s}(1.40704) \\
\psi_{2p} &= 0.83837\,\phi_{2p}(1.00366) + 0.21763\,\phi_{2p}(2.20855)
\end{aligned}$$

$$\begin{aligned}
\text{Carbon:}\quad \psi_{2s} &= -0.27176\,\phi_{1s}(5.23090) + 0.01555\,\phi_{1s}(7.96897) + \\
&\quad +0.27368\,\phi_{2s}(1.16782) + 0.78907\,\phi_{2s}(1.82031) \\
\psi_{2p} &= 0.80168\,\phi_{2p}(1.25572) + 0.26048\,\phi_{2p}(2.72625)
\end{aligned}$$

$$\begin{aligned}
\text{Nitrogen:}\quad \psi_{2s} &= -0.28596\,\phi_{1s}(6.11863) + 0.01913\,\phi_{1s}(8.93843) + \\
&\quad +0.30811\,\phi_{2s}(1.39327) + 0.76300\,\phi_{2s}(2.22157) \\
\psi_{2p} &= 0.78256\,\phi_{2p}(1.50585) + 0.28321\,\phi_{2p}(3.26741)
\end{aligned}$$

$$\begin{aligned}
\text{Oxygen:}\quad \psi_{2s} &= -0.30084\,\phi_{1s}(7.06227) + 0.02533\,\phi_{1s}(10.10850) + \\
&\quad +0.32340\,\phi_{2s}(1.62705) + 0.75263\,\phi_{2s}(2.62158) \\
\psi_{2p} &= 0.74190\,\phi_{2p}(1.65372) + 0.33549\,\phi_{2p}(3.68127)
\end{aligned}$$

$$\begin{aligned}
\text{Fluorine:}\quad \psi_{2s} &= -0.31340\,\phi_{1s}(7.91788) + 0.02923\,\phi_{1s}(11.01100) + \\
&\quad +0.40163\,\phi_{2s}(1.94665) + 0.68011\,\phi_{2s}(3.09603) \\
\psi_{2p} &= 0.72531\,\phi_{2p}(1.84539) + 0.35754\,\phi_{2p}(4.17099)
\end{aligned}$$

grals. For actual distances of normal double bonds a π-type overlap is considerably larger than a σ-overlap in $C=C$, it is of equal magnitude for $N=N$, and it is somewhat smaller for the $O=O$ bond. With Slater orbitals the corresponding π-overlaps are always smaller than the σ-overlaps.

In this respect, the Clementi orbitals resemble SCF orbitals [3]. The different behaviour of σ- and π-type overlaps of Clementi and Slater orbitals is more pronounced for $C\equiv C$ and $N\equiv N$ triple bonds. The decrease in $(p, p)_\sigma$ overlap is due to penetration of the positive and negative lobes of the two relatively diffuse p orbitals.

Heteropolar bonds. In the heteropolar bonds of small and moderate polarity, the magnitudes of various atomic overlap integrals will be related and similar to those of the corresponding homopolar bonds. This expectation was confirmed for Slater orbitals, and is also true for Clementi orbitals. Comparison with the results based on Slater orbitals shows that Slater $2s$ orbitals are remarkably good approximations for first row atoms. However, the overlaps involving p-orbitals differ in both cases disclosing a deficiency of the Slater $2p$ orbitals. The major change is, as mentioned before, the considerable increase in the $(p, p)_\pi$ overlap which is now similar in magnitude to the $(p, p)_\sigma$ overlap, and in the cases of multiple bonds, considerably higher. Another change is the somewhat reduced difference between (s, p) and (p, s) overlaps for a pair of heteroatoms.

Hydrides. An important special case of heteropolar bonds are bonds involving hydrogen. Since Clementi orbitals are more extended than the corresponding Slater orbitals, one could expect large overlaps for hydride bonds. But this is not the case. The very diffuse $1s$-orbital of hydrogens extends into the negative region of the $2s$-orbital of carbon (which was introduced by orthogonality), and the partial contribution to overlap of the negative region is not negligible.

Tables. Extensive tables of overlap integrals for bonds between atoms of the first row for the range of interatomic distances which occur in their various compounds are published in "Croatica Chemica Acta" **39**, 125 (1967).

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Professor Dr. M. Randić
Institute "Ruđer Bosković"
Zagreb, Yugoslavia

Erratum

The Inclusion of Non-nearest Neighbor β Terms in Pariser-Parr-Pople Type S.C.M.O. Calculations. II

R. L. Flurry, Jr., E. W. Stout, and J. J. Bell

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All of the numbers in Tab. 1, page 204 should be multiplied by 2.