

## Overlap Integrals and Chemical Binding

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Citation: *J. Chem. Phys.* **17**, 510 (1949); doi: 10.1063/1.1747311

View online: <http://dx.doi.org/10.1063/1.1747311>

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brated with water using the viscosity data obtained with the Bingham instrument. Values for the absolute viscosity of water and deuterium oxide shown in Table I are estimated to be accurate within 0.1 percent in relation to the value 1.005 centipoise which was used as the absolute viscosity of water at 20°.

Incidental to the viscosity measurements with the Ostwald type instrument it was necessary to determine the density of the deuterium oxide sample in the range 90° to 125°. Values for the density of 100 percent deuterium oxide obtained by extrapolation of the observed data are given in Table II.

TABLE II. Density of deuterium oxide.\*

Temperature °C	A* g/cm <sup>3</sup>	Deuterium oxide B* g/cm <sup>3</sup>
90	1.0716	1.0708
100	1.0638	1.0630
110	1.0554	1.0547
120	1.0466	1.0459
125	1.0421	1.0414

\* Density values obtained by linear extrapolation of measurements on material of 99.5-mol percent purity with respect to D content. This material contained 0.9-mol percent of O<sup>18</sup>. Values in Column A have not been corrected for abnormal concentration of O<sup>18</sup>. Column B contains values for D<sub>2</sub>O with normal (0.2-mol percent) concentration of O<sup>18</sup>.

The work is described more fully in a paper soon to be published in the Journal of Research of the National Bureau of Standards.

\* This work was supported by the AEC.

<sup>1</sup> G. N. Lewis and R. T. McDonald, J. Am. Chem. Soc. **55**, 4730 (1933); H. S. Taylor and P. W. Selwood, J. Am. Chem. Soc. **56**, 998 (1934); W. N. Baker and V. K. LaMer, J. Chem. Phys. **3**, 406 (1935); G. Jones and H. J. Fornwalt, J. Chem. Phys. **4**, 30 (1936).

### Overlap Integrals and Chemical Binding\*

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March 28, 1949

THE overlap integral  $S$  ( $S = \int \chi_a^* \chi_b d\tau$ ) for the AO's (atomic orbitals)  $\chi_a$  and  $\chi_b$  of two atoms which form a bond is a quantity of recognized importance in the theory of chemical binding. Although the literature contains formulas and numerical values for several cases, a more systematic and comprehensive study seemed desirable. Accordingly, we have made computations for detailed numerical tables on all the most important AO pairs involving  $ns$ ,  $np\sigma$ , and  $np\pi$  AO's, using simple AO's of the Zener-Slater type. The  $S$  values are recorded in 20 master tables against two parameters  $p$  and  $t$ , where  $p = \frac{1}{2}(\mu_a + \mu_b)R/a_0$ ,  $R$  being the interatomic distance, and

$t = (\mu_a - \mu_b)/(\mu_a + \mu_b)$ ;  $\mu$  is  $Z/n^*$ , where  $Z$  and  $n^*$  are Slater's effective nuclear charge and principal quantum number for the atom and AO in question. The tables cover wide ranges of  $p$  and  $t$  values, at fairly small intervals to permit interpolation. Five similar tables and two graphs are also given for  $1s$ ,  $2s$  and  $2p$ ,  $2s$  overlap integrals for various  $s-p\sigma$  hybrid AO's. Although the master tables are for Slater AO's, simple linear combinations of the tabulated integrals can be used to obtain  $S$  values for AO-pairs including any desired types of  $ns$ ,  $np\sigma$ , or  $np\pi$  AO's (orthogonalized AO's, hybrid AO's of all kinds, self-consistent-field AO's); also for molecular group orbitals.

$S$  values for selected atom pairs have also been tabulated with interesting results. The integral  $S$  seems to be the most natural quantitative measure of overlap in applying the well-known "criterion of maximum overlapping," proposed by Slater and by Pauling in 1931 as an index of bond strength. However, Pauling has used a different index, namely a number proportional to the magnitude of the bond orbital in the direction of the bond.<sup>1</sup> In agreement with Pauling's index, the present computations give much larger  $S$  values for  $s$ ,  $p\sigma$  hybrid bonds than for pure  $s$  or pure  $p\sigma$  bonds. In sharp contrast to Pauling's index, however,  $S$  is larger for  $s$  than for  $p\sigma$  bonds, except at large  $R$  values as in  $F_2$ .<sup>2</sup> Also,  $S$  is somewhat less for tetrahedral AO's than for AO's with more  $s$  character, contrary to the results with Pauling's index. In partial disagreement with Pauling,  $p\pi$  AO's give larger overlap than  $p\sigma$  AO's at triple-bond distances, although the order is reversed at larger  $R$  values. The foregoing results are illustrated for two-quantum homopolar bonds by the following computed  $S$  values.<sup>3</sup> (Similar results are obtained for  $\sigma$ -bonds in diatomic hydrides.)

$S$ for:	$2s$	$2d_i$	$2t_r$	$2t_e$	$2p\sigma$	$2p\pi$
$C_2H_2$ (1.20Å)	0.51	<b>0.87</b>	0.81	0.76	0.29	<b>0.34</b>
$C_2H_4$ (1.34Å)	0.44	0.82	<b>0.78</b>	0.73	0.32	<b>0.27</b>
$C_2H_6$ (1.54Å)	0.34	0.70	0.68	<b>0.65</b>	0.33	0.19
$F_2$ (1.44Å)	0.12	0.29	0.29	0.29	<b>0.18</b>	0.04

Notes: (a)  $d_i$ =digonal,  $t_r$ =trigonal,  $t_e$ =tetrahedral. (b) Bold-face is used for  $S$  values believed to correspond most closely to actual bond AO's.

The computed  $S$  values are interesting and suggestive also in other ways which space forbids enumerating here. The master formulas and tables will be submitted for publication shortly, with discussion in a second paper somewhat later. In conclusion, our thanks are due Mr. Tracy J. Kinyon for his indispensable work on the numerical computations.

\* This work was assisted by the ONR under Task Order IX of Contract N6ori-20 with the University of Chicago.

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<sup>1</sup> Computations in support of this criterion are given by Pauling and Sherman, J. Am. Chem. Soc. **59**, 1450 (1937).

<sup>2</sup> A. McColl of University College, London, England (private communication, 1948) has independently noted this same point, in connection with computations on  $S$  values for  $p\pi$ ,  $s$ ,  $p\sigma$ , and  $s$ ,  $p\sigma$ -hybrid bonds.

<sup>3</sup> The results for the hydrocarbons were presented at a symposium some time ago, but only an abstract has hitherto been published: R. S. Mulliken and C. A. Rieke, Rev. Mod. Phys. **14**, 259 (1942).