

# This Week's Citation Classic

Craig D P, Maccoll A, Nyholm R S, Orgel L E & Sutton L E. Chemical bonds involving d-orbitals. Parts I and II. *J. Chem. Soc.* 1954:332-57.  
[William Ramsay and Ralph Forster Lab., Univ. Coll. London, London, and Phys. Chem. Lab., Oxford, England]

The ideas of d-orbital participation in bonds in compounds like  $\text{PF}_5$ , and in complex ions like  $[\text{Ni}(\text{dipyridyl})_3]^{2+}$ , are given a basis by the calculation of overlap integrals between Slater orbitals. The concept of 'orbital contraction' is introduced to account for the preferential use of d-orbitals toward elements of higher electronegativity in compounds like  $\text{PF}_5$ . [The SCI<sup>®</sup> indicates that this paper has been cited in over 375 publications since 1961.]

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"Those were the days of what the late Charles Coulson called class A and class B theoretical chemists. In one class, theorists used rather simple models and calculations to get physical insight into problems of valence and spectroscopy. In the other, all stops were pulled out to give the full treatment of calculations as precise as any known at the time to get numerical agreements without being much concerned with the physical picture.

"This paper was firmly in the spirit of the first class. Linus Pauling<sup>1</sup> had said that phosphorus can form five bonds but nitrogen only three ( $\text{PCl}_5$  and  $\text{NCl}_3$ , for example) because P can promote an electron into a 3d-orbital and form five  $sp^3d$  hybrids, while N has to use  $sp^3$ . Others said that s and p orbitals were enough if the bonding was described in molecular orbital terms, including antibonding as well as bonding combinations. In addition, Ronald Nyholm, then studying stabilities of complexes of transition metals, had troublesome problems of a distinct type with d-orbital participation in  $\pi$ -bonding to the ligands ('back-bonding').

"Following Allan Maccoll's pioneering work<sup>2</sup> on overlap integrals as an index of bonding strength, we set about analyzing d-orbital bonding to try to get a unified viewpoint in these very different situations by studying overlaps for the d-orbital hybrids. Leslie Sutton and Leslie Orgel were in Oxford; Maccoll, Nyholm, and I in London. The ideas were teased out whenever we could talk together, usually in London, and in a variety of locations, such as the Chemical Society's rooms in Burlington House when there happened to be a meeting there. The heart of the work was the calculation of overlap integrals; they were not trivial. All were done before the end of 1952, too early for computers. We reckoned that each table of integrals took a man-week of effort. They were worked out independently in London and Oxford, and in London done twice, by Maccoll and myself. When the results of each group were sent to the other the pleasant experiences of finding we had the same answers were mixed with others less agreeable requiring a return to the Monroe and Marchant desk calculators to see whose results were correct. Nowadays the whole of the purely numerical work could be done, error free, in under a microsecond.

"An outstanding puzzle of the times was why the higher covalences of second row elements, as in  $\text{PF}_5$ , were displayed toward the more electronegative elements and not the less electronegative (no  $\text{PH}_5$ ). Our overlaps made good sense of the simple electrostatic idea that electronegative elements caused contraction of the diffuse d-orbitals, so making them better at bond formation. The concept of orbital contraction was widely taken up by others and further developed by us,<sup>3</sup> and remains part of the terminology of qualitative valence theory. That may be a reason for the frequent citation of the paper; another is that it was the first quantitative study of how the then mysterious valence problems in the second and later rows of the periodic table and in the transition series could be resolved by incorporation of d-atomic orbitals."

1. Pauling L. *The nature of the chemical bond and the structure of molecules and crystals: an introduction to modern structural chemistry*. Ithaca, NY: Cornell University Press, 1940. p. 109.
2. Maccoll A. The principle of maximum overlapping. *Trans. Faraday Soc.* 46:369-74, 1950.
3. Craig D P & Magnusson E A. d-Orbital contraction in chemical bonding. *J. Chem. Soc.* 1956:4895-909.