

This Week's Citation Classic

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Richardson J W, Nieuwpoort W C, Powell R R & Edgell W F. Approximate radial functions for first-row transition-metal atoms and ions. I. Inner-shell, 3d and 4s atomic orbitals. *J. Chem. Phys.* **36**:1057-61, 1962. [Dept. Chemistry, Purdue Univ., Lafayette, IN]

Approximate wavefunctions are constructed for first-row transitionmetal atoms and ions from Watson's recent self-consistent-field (SCF) results. The especially important 3d orbitals occur as combinations of two Slater-type orbitals. These simplified functions are judged sufficiently accurate for calculations of chemical bonding to these ions. [The *SCF*[®] indicates that this paper has been cited over 420 times since 1962.]

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"By 1960, the highly empirical ligand-crystal field (LF) theory approach based upon the molecular orbital (MO) model was recognized as a useful means to rationalize and correlate magnetic, spectral, and chemical properties of compounds of transition metals. R.E. Watson at MIT had just compiled a set of 'Hartree-Fock' orbitals in his monumental study of the energetics of these iron-group elements.^{1,2} His functions, however, were far too cumbersome (given the computational facilities at that time) for use in quantitative tests of LF theory by SCF MO methods, which we were then contemplating.

"We reduced Watson's functions to forms which were (a) simple enough so that evaluating some of the elementary chemical bonding parameters could be done even *by hand*, but (b) accurate enough to permit meaningful comparisons to be drawn from more elaborate calculations on molecular-type complex ions of these elements, in which these atomic orbitals are basic ingredients. In this respect our biggest concern involved the 3d orbitals, which exhibit something of a dual personality. They have characteristics both of inner-shell orbitals like 3s and 3p (which largely determine their energetics) and of the outer valence-shell orbitals (which commingle

chemically with other atoms). Furthermore, despite the electroneutrality postulate of Pauling, these metals' ions do retain a high and variable net charge in their compounds. We were able to encompass these factors by using a 'doublezeta' basis (two independent functions contributing in the two different regions of space) which I'd investigated earlier in connection with a study of the N₂ molecule.³

"While the referee was 'not overly enthusiastic about what the authors have chosen to do,' we and evidently numerous other workers have discovered considerable utility in these functions. Among my own associates, Nieuwpoort immediately extended this initial foray in machine computation to a theoretical study of bonding in Ni(CO)₄; Soules, Powell, Vaught, Kalman, and Kelly investigated a variety of oxide, fluoride, and ammine complexes of these metal ions.^{4,7}

"Initially, we expected to obtain only semiquantitative comparisons to known experimental data using these functions. As time went on, however, we were pleasantly surprised to learn that quite accurate bonding parameters and excitation energies can be calculated, once proper SCF procedures are used and effects of electron correlation, spin-orbit interaction, and crystalline environment are included.⁸

"Researchers continue to be interested in bonding, structure, spectroscopy, magnetism, electrical conductivity, and reactivity of transitionmetal compounds; they require atomic wavefunctions for these elements in order to test quantitatively various theoretical models proposed. Although other representations of these orbitals (e.g., Gaussians) and computational methods (e.g., Hartree-Fock-Slater or X_a) have subsequently been developed, these relatively ancient functions retain considerable value, since they combine flexibility and simplicity with reasonable accuracy."

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2. Iron series Hartree-Fock calculations. II. *Phys. Rev.* **119**:1934-9, 1960.
3. **Richardson J W.** Double-4 SCF MO calculation of the ground and some excited states of N₂. *J. Chem. Phys.* **35**:1829-39, 1961.
4. **Richardson J W, Vaught D M, Soules T F & Powell R R.** Electron delocalization and spectra of transitionmetal fluorides. *J. Chem. Phys.* **50**:3633-4, 1969.
5. **Soules T F, Richardson J W & Vaught D M.** Electronic structure and spectrum of the NiF₆⁴⁻ cluster. *Phys. Rev. B* **3**:2186-204, 1971.
6. **Kalman B L & Richardson J W.** Calculation of the electronic structure and spectrum of comparisons with isoelectronic CoF₃⁻. *J. Chem. Phys.* **55**:4443-56, 1971.
7. **Soules T F, Kelly E J, Vaught D M & Richardson J W.** Energy-band structure of SrTiO₃ from a self-consistent-fieldtight-binding calculation. *Phys. Rev. B* **6**:1519-32, 1972.
8. **Pueyo L A Richardson J W.** Optical spectrum of Cr³⁺ in octahedral fluoride lattices. *J. Chem. Phys.* **67**:3583-91, 1977.