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This Week's Citation Classic

McWeeny R. X-ray scattering by aggregates of bonded atoms. I. Analytical approximations in single-atom scattering. *Acta Crystallogr.* **4**:513-19, 1951. [Labs. Physical Chemistry and Coke Res., King's College, Univ. Durham, Newcastle upon Tyne, England]

In this paper analytical approximations to atomic wave functions are used in order to obtain closed expressions for the scattering factors of atoms hydrogen to neon. There are significant differences between the results of these calculations and those given many years earlier by James and Brindley.[1] [The ***SCI***® indicates that this paper has been cited over 355 times since 1961.]

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"This paper was the first in a series of four;[2,4] together they represent my only excursion into X-ray crystallography. The papers were written during my first years as a university lecturer, at King's College, Newcastle upon Tyne, in response to complaints from a crystallography research group that they had no reliable atomic scattering factors. The only factors available were those of James and Brindley, computed (with many interpolations) from numerical Hartree-Fock data. These were apparently inaccurate and particularly in-appropriate for atoms such as carbon, where the electron distribution is heavily distorted by chemical bonding. It was necessary to (1) use improved analytical approximations to the atomic orbitals, (2) admit the possibility of the atoms being in valence states (e.g., carbon with up to four singly occupied hybrid orbitals), and (3) investigate the effects of bonding in disturbing the spherical symmetry of the electron distribution. This appeared to be a straightforward, though computationally demanding, exercise in molecular quantum mechanics.

"The highly cited paper reported analytical expressions for scattering factors for atoms containing s and p electrons, in a variety of valence states, and gave numerical tables for first row atoms. The computations were per-formed, with the help of my wife, on a calculating machine with a handle —a small mechanical Brunsviga! The job was evidently worth doing and the scattering factors, which are still sufficiently accurate for most purposes, have been widely used for many years. The later papers, which investigate departures from spherical symmetry of the electron density caused by chemical bonding, were more specialized (much of the work was on carbon in graphite and diamond, where 'forbidden' reflections occur as a result of asphericity) and are thus of less general utility. Nevertheless, they were of seminal value in illustrating the use of Gaussian wave functions and in introducing the basic ideas of electron population analysis —developments which had a much wider impact in the general area of quantum chemistry. The time spent working in an unfamiliar field was —as is often the case —time well spent. A.J. Freeman reported further work in the field."[5,6]

1. **James R W & Brindley G W.** Some numerical calculations of atomic scattering factors. *Phil. Mag.* **12**:81-112, 1931.
2. **McWeeny R.** X-ray scattering by aggregates of bonded atoms. II. The effect of the bonds: with an application to H_2. *Acta Crystallogr.* **5**:463-8, 1952.
3. ....., X-ray scattering by aggregates of bonded atoms. III. The bond scattering factor: simple methods of approximation in the general case. *Acta Crystallogr.* **6**:63-7, 1953.
4. ....., X-ray scattering by aggregates of bonded atoms. IV. Applications to the carbon atom. *Acta Crystallogr.* 7:180-6, 1954.
5. **Freeman A J.** Atomic scattering factors for spherical and aspherical charge distributions. *Acta Crystallogr.* **12:**261-71, 1959.
6. ....., Compton scattering of x-rays from nonspherical charge distributions. *Phys. Rev.* **113**:169-75, 1959.