17.I- 1 GENERALIZED X-RAY SCATTERING FACTORS FOR PSEUDOATOMS IN MOLECULES AND CRYSTALS, R. F. Stewart, Chem. Dept., Carnegie-Mellon Univ., Pgh., Pa. 15213 USA.

The intensity for coherently scattered X-rays for a molecule or crystal is a canonical ensemble average over the nuclear motion,[1]

$$I_{obs} \propto \langle F^*(\underset{\sim}{S},\underset{\sim}{Q})F(\underset{\sim}{S},\underset{\sim}{Q})\rangle_{can.\ av.} \qquad (1)$$

where

$$F(\underset{\sim}{S},\underset{\sim}{Q}) = \int \rho(\underset{\sim}{r},\underset{\sim}{Q}) \exp(i\underset{\sim}{S}\cdot\underset{\sim}{r})d\underset{\sim}{r}) \qquad (2)$$

$\underset{\sim}{Q}$ are nuclear coordinates, $\underset{\sim}{S}$ is the scattering vector (Bragg vector) and $\rho(\underset{\sim}{r},\underset{\sim}{Q})$ is the one-electron density function for the molecule or unit cell for a particular $\underset{\sim}{Q}$. The central problem is to decompose (1) into a model that is useful for extracting charge density information from X-ray diffraction data. Debye suggested that $\rho(\underset{\sim}{r},\underset{\sim}{Q}_e)$ (where $\underset{\sim}{Q}_e$ is the equilibrium nuclear configuration) be represented by a superposition of isolated atoms[2] that rigidly follow the nuclei on which they are centered. With Debye's model and the assumption of harmonic nuclear motion, (1) can be reduced to the conventional X-ray structure factor model that is used in structure analysis. (A thermal diffuse scattering contribution in (1) is usually neglected.) An extension of Debye's suggestion is to partition the molecular charge density into pseudoatom charge densities. Each pseudoatom density is defined by a finite surface harmonic (multipole) expansion about its nucleus and the coefficient radial functions are determined by a least squares fit to the given molecular density. All molecular one-center averages of the form

$\langle g(\underset{\sim}{r}_a)P_\ell^m(\cos\theta_a)\cos m\varphi_a\rangle$ and $\langle g(\underset{\sim}{r}_a)P_\ell^m(\cos\theta_a)\sin m\varphi_a\rangle$

are correctly given by the pseudoatom superposition whenever $\ell \leq L$ where L is the highest order multipole included in the a pseudoatom, regardless of the highest multipole orders for the other centers. $g(\underset{\sim}{r}_a)$ is an arbitrary function of $\underset{\sim}{r}_a$ (scalar) for which the molecular average exists and $P_\ell^m(\cos\theta_a)$ is an associated Legendre polynomial. In Fourier space the procedure is equivalent to approximating the molecular form factor in terms of generalized X-ray scattering factors for the pseudoatoms. A number of generalized X-ray scattering factors have been extracted from diatomic molecules. The static charge properties of these pseudoatoms will be reported. Vibrational force constants have been calculated in the rigid pseudoatom approximation. Results are generally excellent except for polar diatomic hydrides.

To date, X-ray diffraction data have been analyzed for static charge density information with generalized X-ray scattering factors that are constructed from restricted radial functions. Even in the rigid pseudoatom approximation, the restricted radial pseudoatoms do not rigorously satisfy molecular average static charge properties. Thus the results can serve only as estimates to static charge properties in the unit cell. Studies of restricted radial functions in the charge density analysis of diatomic molecules will be reported. Some results on the estimates of physical properties from single crystal X-ray diffraction data will be reported.

1. M. Born, Rep.Progr.Phys. 9, 294 (1942-1943)
2. P. Debye, Phys.Z. 31, 419 (1930)

17.I- 2 A SURVEY OF METHODS AND RESULTS IN THE FIELD OF DETERMINATION OF ELECTRON DENSITIES BY DIFFRACTION METHODS, P. Coppens*, Institut Laue-Langevin, B.P. 156, et Laboratoire des Rayons X, CNRS, B.P. 166, 38042-Grenoble, France.

Methods for analysis of accurate diffraction data can be broadly divided into Fourier and least-squares techniques. In the former either deformation or valence densities are analysed. The most informative maps are obtained by combining X-ray and neutron data, but qualitative information of chemical significance can often be obtained with accurate low-temperature X-ray data alone. A number of examples (e.g. ethylene imine quinone, Ito & Sakurai, Acta Cryst. B29 1594 (1966) ; acetylene $(Ni\ cpd)_2$, Wang & Coppens ; p-nitropyridine N-oxide, Wang, Blessing, Rees & Coppens ; Lehmann, Yelon & Coppens) supports this statement in the bonding, but not in the lone-pair regions. Aspherical least-squares methods (e.g. Stewart, Hirshfeld et al, these abstracts) offer an attractive alternative. Analysis of positional parameters and calculated deformation densities from such refinements indicates some residual effects of model limitations (i.e. tetracyanoethylene, Becker, Coppens & Ross, JACS 95, 7604 (1973) ; tetracyanocyclobutane, Harel & Hirshfeld, Acta Cryst. B31, 162 (1975);p-nitropyridine N-oxide loc. cit.).

Electron density maps on a number of bond types have recently become available. They include CC (Helmholdt & Vos), NN (Stevens & Hope), SS (Yang, Blessing, Larsen & Coppens), Si Si (Yang & Coppens, Solid State Comm. 15, 1555 (1974)) and Ni Ni (Wang & Coppens). Differences between bond types are readily apparent and will be discussed. Studies on hydrogen bonded systems support the electrostatic nature of this interaction (i.e. glycylglycine, Griffin & Coppens : α glycine, Almlöf, Kvick & Thomas, J. Chem. Phys. 59, 3901 (1973)). Molecular density maps can be further exploited for the calculation of derived quantities such as net molecular or ionic charges, dipole and quadrupole moments. A procedure using numerical integration will be described, which has given a value of 0.55±0.15 electrons for the charge transfer in the TTF-TCNQ organic salt at 100°K and is being applied to other sets of diffraction data.

The accuracy in the X-N maps is affected by experimental errors in both X-ray and neutron measurements. Standard deviations are, at present, typically 0.05 $e\text{Å}^{-3}$, but larger in the vicinity of heavier atoms and near nuclei. The neutron diffraction errors are replaced in methods based on X-ray data alone by model assumptions of the high-order or aspherical atom refinements. In general higher experimental accuracy is required, the stronger the scattering of the core electrons. A suitability criterion is defined as $V/\sqrt{(\Sigma\, n^2(\text{core}))}$ where V is the volume of the unit cell and n is the number of core electrons for each atom. Values are typically 20-30 for first-row atom molecules, 10-15 for 3d organometallics and 1-2 for solids such as Si and Al.

* On leave of absence from the Chemistry Department, State University of New York at Buffalo, Buffalo N.Y. 14214, USA. Research supported in part by the National Science Foundation.