06.7-01 ELECTRIC FIELD GRADIENTS IN IMIDAZOLE AT 103K FROM X-RAY DIFFRACTION. By Joel Epstein and David J. Swanton, Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, A.C.T. 2600, Australia.

NQR experiments have revealed marked differences in the ^{14}N coupling constants and asymmetry parameters for the two nitrogen sites of imidazole at 77K (M.J. Hunt, A.L. Mackay and D.T. Edmonds, Chem. Phys. Lett. (1975) 34, 473).

The electric field gradients at the two nitrogen nuclei of imidazole at 103K have been calculated from the charge density derived from Bragg diffraction data. The resulting coupling constants and asymmetry parameters were

N1: $e^2qQ/h = -2.6(0.3)$MHz : $\eta = 0.3(0.2)$
N3: $e^2qQ/h = -2.2(0.3)$MHz : $\eta = 0.4(0.2)$

These calculations could therefore not distinguish between the two nitrogen sites. At each site, the parameters were approximately equal to the mean of the NQR values for N1 and N3.

Model calculations for the diatomic molecules N_2 and BF suggest that the accuracy with which field gradients are obtained directly from the Bragg structure factors depends critically on the description of quadrupole components induced by vibrational averaging.

Estimates of the coupling constants and asymmetry parameters for imidazole obtained directly from the Bragg structure factors were

N1: $e^2qQ/h = -1.4(0.3)$MHz : $\eta = 0.2(0.3)$
N3: $e^2qQ/h = -0.9(0.3)$MHz : $\eta = 0.7(0.5)$

Detailed analysis shows that the magnitudes of the coupling constants estimated in this way are too small due to residual vibrationally-induced quadrupoles.

06.7-02 STUDIES OF THE ELECTRON DENSITY AND POTENTIAL DISTRIBUTION AS WELL AS OTHER PROPERTIES OF CRYSTALS FROM DIFFRACTION DATA. By R.P.Ozerov, V.G.Tsirelson, A.A.Varnek, M.V. Krasheninnikov, E.V.Parini and L.A.Pozdnjakov, Mendeleev Institute of Chemical Technology, Moscow 125820, USSR.

The main aim of this research is to obtain the electron density and electrostatic potential distribution for the futher calculation of the important physico-chemical properties of molecules and crystals. Particular attention has been paid to the development of methods of accurate diffraction data processing.

1. Method of the quantitative description of the electron charge distribution based on MO LKAO approximation has been developed. Matrix Y=2P-I (P - matrix of charge-bond orders) can be obtained by iteration procedure from diffraction data with an additional condition $Y^2 = I$. It provides the N-representability of the experimental electron density. This method has been used for the investigation of the lithium formate deuterate $LiCOOH.D_2O$ and effective atomic net charges and bond orders have been obtained.Dipole moments of water molecule, non-linear optical coefficients and lattice energy of this compound have been computed (Krystallogr. (1979) 24,1156; (1980) 25,735; (1981) in press).

2. The comparison of experimental and theoretical results has to be carried out with the same basis set. For that the method of X-ray form factors computation has been developed with orthogonalized Slater basis set(Dokl. Ac. Nauk USSR, (1980) 254, 370). Atomic and partial scattering amplitudes for H to Kr atoms have been computed. The use of the partial amplitudes makes the least-squeres refinement more fiexible.

3. The method of the electrostatic potential $\varphi(r)$ determination from X-ray diffraction data has been developed. To determine the energy characteristics E of crystals the semi-empirical variant of density functional method, which used the experimental potential $\varphi(r)$, has been worked out. This method was applied to $\varphi(r)$ and E calculation in diamond, Si,Ge, and some molecular crystals.

4. The scheme of assessment of errors in experimental electron (deformation, valence) density has been built up. For non-centrosymmetrical structures errors in phases were taken into account. The other sources of errors have been discussed in detail.

5. The set of programms "XRED - 81" has been created. The set allows: to calculate full and/or partial scattering amplitudes, to determine charge-bond orders matrix, to compute molecular dipole and quadrupole moments, to compute energy characteristics, to draw maps and surfaces of scalar and diagrams of vector functions etc.

6. The methods developed applied to α- DOX as well as to other crystals. The results will be presented at the Congress.

06.7-03 MOLECULAR INTERACTIONS FROM PARTITIONED ELECTRON DENSITIES. By Grant Moss, Medical Foundation of Buffalo, Inc., Buffalo, NY 14203, U.S.A.

The medium and long range interaction of molecules having permanent multipoles can often be described by the electrostatic term alone [Scrocco, E. & Tomasi, J., Adv. Quant. Chem. (1978) 11, 116]. The electrostatic potential is determined by the electron charge distribution, which is accessible through X-ray diffraction experiments. Molecular dipole moments determined from X-ray data are in reasonably good agreement with theoretical values suggesting that these properties are relatively insensitive to the effect of neighboring molecules. Thus, X-ray diffraction data offers an alternative to theoretical calculations of the electrostatic potential, particularly in large systems where computational limitations arise. At large distances the classical electrostatic potential can be calculated as a multipole series, the convergence of which improves with an increase in the number of centers used. A common approach particularly suited to current methods of electron density analysis, is to use atomic centers. Such an approach requires a careful consideration of the partitioning of the molecular density into atomic fragments. One particularly useful method is the stockholder partitioning proposed by Hirshfeld [Hirshfeld, F. L., Theoret. Chim. Acta (1977) 44, 129]. This scheme, and some modifications thereof, have been applied to theoretical densities of several small molecules as a preliminary to the use of experimental diffraction data. The resultant atomic charges are consistent with other methods, and inclusion of higher order atomic moments reproduces the molecular moments to better than 0.5%. The atomic moments have been used to calculate the electrostatic component of the H_2O-CO_2 interaction. The results are in qualitative agreement with quantum chemical calculations. Supported by NIGMS GM-26195.