06.2–4   THE ELECTRONDENSITY DISTRIBUTION IN THE HY-
DROGEN BOND: QUANTUMCHEMICAL CALCULATIONS; COMPARISON
WITH DIFFRACTION RESULTS ON OXALIC ACID. By M. Krijn
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sity of Technology, Enschede, The Netherlands

Quantumchemical calculations of the electrondensity dis-
tribution in hydrogen bonded dimers abound but their re-
levance is severely restricted by two important factors:
the basissets used are too small and the assumed gasphase
geometry differs considerably from the geometry found in
short hydrogen bonds in condensed matter. The present
calculations are based on the Hartree-Fock-LCAO method,
using the local density approximation to account for ex-
change effects. (Baerends & Ros, Int. J. Quant. Chem.
S12, 169 (1978)). The basisset effect is shown by carry-
ing out calculations on the water dimer, using two dif-
ferent sets of Slater-type orbitals as basis functions
and the frozen core approximation for the oxygen atoms.
The basissets are:
I)   O: s,s,p,p,d   H: s,s,s,p,p,d
II) O: s,s,s,p,p,p,f   H: s,s,s,p,p,d
The smaller one is slightly more extensive than the much
used 6-31G** set of Gaussian orbitals.
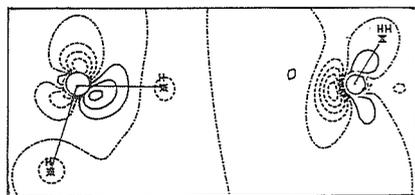
Figure 1. The dif-
ference in elec-
tron density be-
tween dimer and
monomers. O–O dis-
tance 2.98 Å as in
gasphase. Basisset
I.

$$\Delta\rho_h = \rho(H_2O)_2 - \rho_A(H_2O) - \rho_B(H_2O)$$

Figures 1 and 2 show the effect of hydrogen bonding on
the density of the molecules.
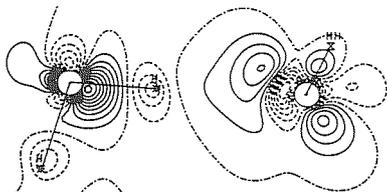
Figure 2. $\Delta\rho_h$
O–O distance 2.49 Å
as in oxalic acid
dihydrate. Basisset
II.

The difference between the two figures is shown to be due
to the extension of the basisset and to the shortening of
the O–O distance. The distribution in the hydrogen bond
region is similar to the corresponding distribution in
oxalic acid·2H$_2$O, as shown in Figure 3.
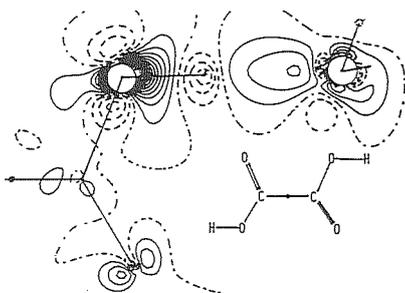
Figure 3.
ρ(oxalic·acid·2H$_2$O)
$-\rho$(oxalic acid)–
ρ(H$_2$O); basisset
II.

The various effects are of such a magnitude that compari-
son with the results of accurate X-ray diffraction expe-
riments becomes meaningful. The most important features
of the hydrogen bond are confirmed by the diffraction re-
sults on oxalic acid·2H$_2$O and oxalic acid·urea.

06.2–5   EXPERIMENTAL ELECTRON DEFORMATION DENSITY OF
7,7,8,8-TETRACYANOQUINODIMETHANE (TCNQ) AT 110K*. By
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Since the discovery of high electrical conductivity
in the organic charge transfer complex TTF-TCNQ, interest
in the physics and chemistry of the organic solid state
has undergone an explosive growth. Although TCNQ itself
is not highly conducting, its ability to form the radical
anions TCNQ$^-$ and (TCNQ)$_2^-$ as well as forming partially
charged species make it a frequent component of charge
transfer salts. We have begun low temperature studies of
the electron density distributions in some of these salts
to obtain a direct measure of the charge transfer.

The electron distribution of TCNQ has been
determined from high resolution x-ray measurements at
110K. Cell dimensions (110K): a=8.865(2), b=6.883(1),
c=16.387(1)Å, β=98.21(3)$^\circ$, C2/c, Z=4. Experimental
X-X$_{H_2O}$ deformation maps have been calculated using
atomic parameters from a refinement of data with
sin$\theta/\lambda > 0.65$Å^{-1}. As expected, density accumulation is
observed in all covalent bonds, and in the lone pair
regions of the nitrogen atoms. The triple bond is
clearly distinguished by a large density peak extending
perpendicular to the bond axis. The quinoid character of
the aromatic ring is also clearly evident in the
deformation density. Model dynamic and static
deformation densities based on a least-squares fit to the
x-ray data using multipole deformation functions will be
presented.

06.2–6   ELECTRON DENSITY MAPPING IN HEMOGLOBIN
MODEL SYSTEMS: COMPARISON OF CHARGE DENSITIES IN
SEVERAL IRON PORPHYRINS AND PHTHALOCYANINES By P. Cop-
pens, C. Lecomte, K. Tanaka and Liang Li, Department of
Chemistry, SUNY/Buffalo, Buffalo, NY 14214, USA.

Accurate crystallographic methods are being applied to
the mapping of the three-dimensional electron distribu-
tion in iron porphyrins and phthalocyanines with differ-
ent spin states, metal oxidation number and coordination
geometry. Studies on Fe(III) methoxytetraphenylporphy-
rin (=TPP)(Lecomte, Chadwick, Coppens and Stevens, In-
org. Chem (1983) 22, 2982) and Fe(II) phthalocyanine
(=Pc)(Coppens, Li and Zhu, J. Am. Chem. Soc. (1983) 105,
6173) have been completed, while studies on Fe(II) bis-
tetrahydrofurane tetraphenylporphyrin, FeTPP and Fe(III)
bis 2-imidazole octaethylporphyrin are in progress. In
all but the Fe(III) high spin complexes a marked aspher-
icity of the iron valence density is observed, which can
be quantitatively expressed in terms of the occupancies
of the Fe d-orbitals (Holladay, Leung and Coppens. Acta
Cryst. (1983) A39, 377), thus leading to an assignment
of the ground state electronic configuration. In parti-
cular in the case of the intermediate spin complexes Fe-
Pc and FeTPP the assignment resolves an existing contro-
versy caused by conflicting results from theoretical
calculations. The electric field gradient calculated
from the X-ray data is within its large error limits in
agreement with values from Mössbauer spectroscopy and
serves to interpret the Mössbauer results. The electron
density in the porphyrin macrocycle is remarkably simi-
lar in the different complexes, except at the nitrogen
pyrrole atoms where the effect of the iron configuration
is discernable.