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Author's Review

## The Electron Density of the Hydrogen Bond

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The general features of the electron density in hydrogen bonds, as derived from recent diffraction investigations and quantum mechanical calculations, are summarized.

In hydrogen bonds of weak and intermediate strengths, the electron distribution can be considered simply as a superposition of the densities of the undisturbed, constituent monomers. The modification actually taking place as the molecules interact with each other in the crystal, constitutes only a second-order effect, hardly detectable in the experimental maps. In very strong hydrogen bonds, however, a modification of the original monomer densities is quite noticeable. Special interest is concentrated on the electron distribution in the lone-pair region.

### INTRODUCTION

Since the electrons are ultimately responsible for the forces holding atoms together in a chemical system, it would seem desirable to discuss chemical bonding in terms of some experimentally observable quantity directly related to the behaviour of the electrons. From this point of view, many of the current concepts like  $\sigma$ - and  $\pi$ -bonding, covalency etc., are less satisfactory as they do not correspond to experimentally observable quantities and, furthermore, are intrinsically dependent on certain models utilized for their definition. The possibilities of interpreting the binding forces more directly in terms of the complete charge distribution (electrons + nuclei) is evidently of particular interest in this context (cf. the Hellman-Feynman theorem). Even if it is not clear at present whether such a description is useful in general for qualitative applications, it is obvious that systematic, accurate determinations of the electron density in closely related systems is most important for the further development of theories concerning the nature of the chemical bond.

During recent years considerable progress has been made in the experimental determination of electron density by diffraction methods. The precision is now such that significant effects in many cases can be observed in the electron density on chemical changes. However, these types of investigations require very high precision in the experimental data as well as in the mathematical analysis. In a similar way, relatively good precision can nowadays be achieved in quantum-mechanical calculations of the electron density of moderately large systems.

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Hydrogen-bonded systems have attracted considerable interest in this context. Such systems offer rather unique possibilities of making comparisons between the electron densities in closely related compounds with a large range of variations in bond strength.

In this paper a summary is given of the characteristic electron density features of simple hydrogen-bonded systems recently studied by diffraction and quantum-mechanical methods. The great majority of these studies have been performed on O—H...O hydrogen bonds. For a more extensive discussion of certain general aspects the reader is referred to Ref. 1.

#### ELECTRON DENSITY OF THE ISOLATED MOLECULES

Before analyzing the possible redistribution of the electrons as molecules interact with each other it is necessary to first study the electron density of the *isolated* molecules. This can only be obtained by theoretical calculations. The theoretical density is illustrated for *N*-methylacetamide in Figure 1. and for water in Figure 2. In these Figures is also illustrated the electron density

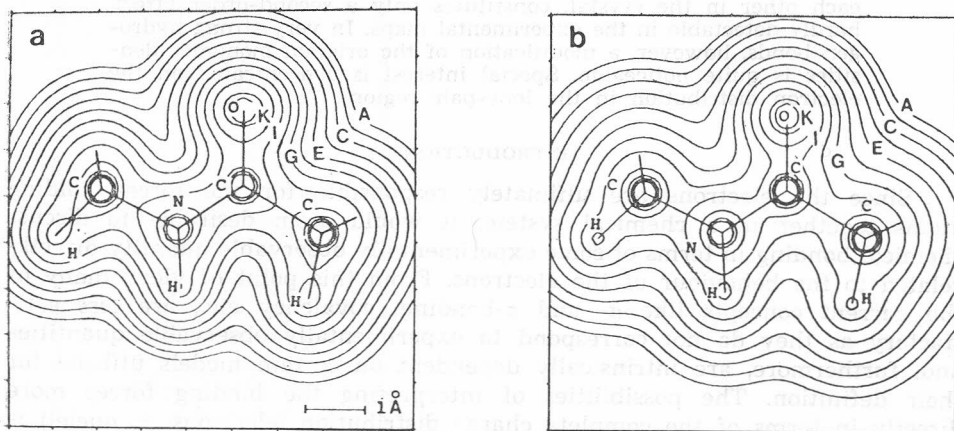


Figure 1. Contour maps of the electron density in the amide plane of *N*-methylacetamide as calculated with an extended 6-31 G basis set (Hagler and Lapicicella<sup>3</sup>).

(a): Total density from molecular wave function.

(b): Total density from superposition of spherical atoms. Contour lines: A = 0.0067, B = 0.0134, C = 0.0268 ... L = 13.4 e/Å<sup>3</sup>.

obtained by simply superposing the density of the constituent spherical atoms, placed in the same positions as in the actual molecule. This is done to demonstrate the relatively small changes in the overall electron density features that occurs when a molecule is formed from the constituent free atoms. Although the bond energy is relatively large, 200–400 kJ/mol, the effect on the electron density is evidently quite small and just barely noticeable at this level of observation. As might be expected, the electron density is slightly contracted as the molecule is formed, but the polarity of the N—H and O—H bonds, responsible for the specific hydrogen-bond interaction is

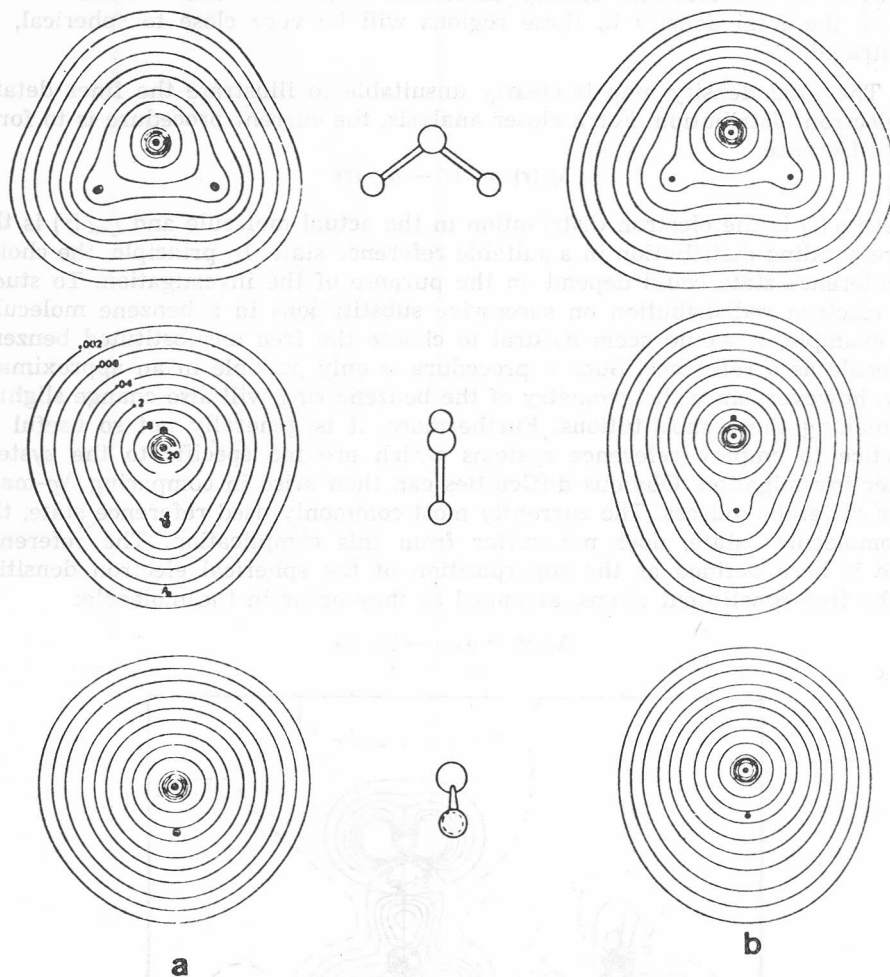


Figure 2. Contour maps of the electron density in three different planes of the free water molecule as calculated with a  $DZP^+$  basis (Smith<sup>3</sup>).

- (a): Total density from molecular wave function.  
 (b): Total density from superposition of spherical atoms.

Top: In the H—O—H plane

Middle:  $\perp$  H—O—H plane, containing O—H

$\perp$  H—O—H plane, bisecting angle H—O—H

hardly noticeable in the maps, for instance. Particular attention should be paid to the density in the lone pair regions. The »lone-pair« density, sometimes imagined as rabbit ears sticking out from the oxygen atoms in  $C=O$  and  $H_2O$ , corresponds to only part of the contribution to the total electron

density in these regions (the electron density associated with the lone pair orbitals). If the electron density associated with the bond orbitals is also added, the total density in these regions will be very close to spherical, as illustrated.

The total density map is clearly unsuitable to illustrate the finer details of electron distribution. For a closer analysis, the current procedure is to form the difference

$$\Delta\rho(r) = \rho(r) - \rho_{\text{ref}}(r)$$

where  $\rho(r)$  is the electron distribution in the actual molecule and  $\rho_{\text{ref}}(r)$  is the corresponding distribution in a suitable reference state. In principle, the choice of reference state could depend on the purpose of the investigation. To study the electron redistribution on successive substitutions in a benzene molecule, for example, it would seem natural to choose the free unsubstituted benzene molecule as a reference. Such a procedure is only possible in an approximate way, however, since the geometry of the benzene ring will also change slightly on making these substitutions. Furthermore, it is generally not so useful in practice to employ reference systems which are too specific to the system under investigation. Obvious difficulties can then arise in comparing  $\Delta\rho$ -maps from different sources. The currently most commonly used reference state, the »promolecule« state, does not suffer from this complication. The reference state is here defined as the superposition of the spherical electron densities of the free constituent atoms, arranged as they occur in the molecule:

$$\Delta\rho(r) = \rho(r) - \sum_i \rho_i(r)$$

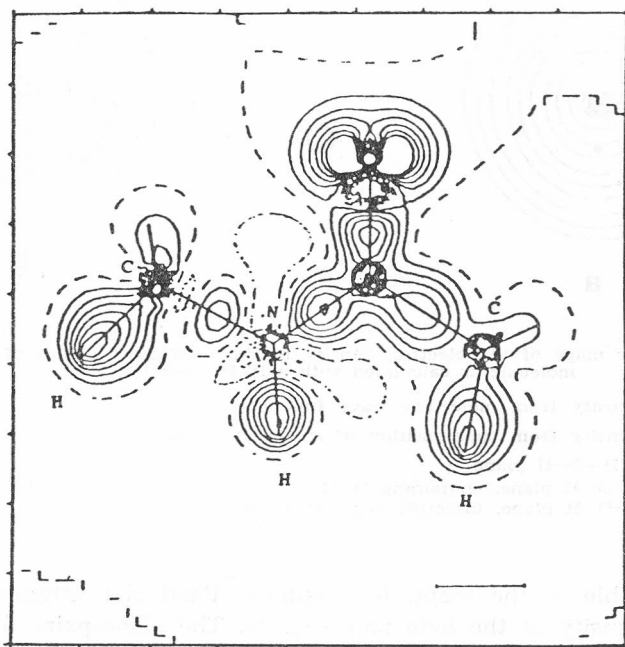


Figure 3. Deformation density maps of N-methylacetamide in the plane of the amide group, as calculated with an extended 6-31 G basis set (Hagler and Lapicciarella<sup>2</sup>) (cf. Figure 1)

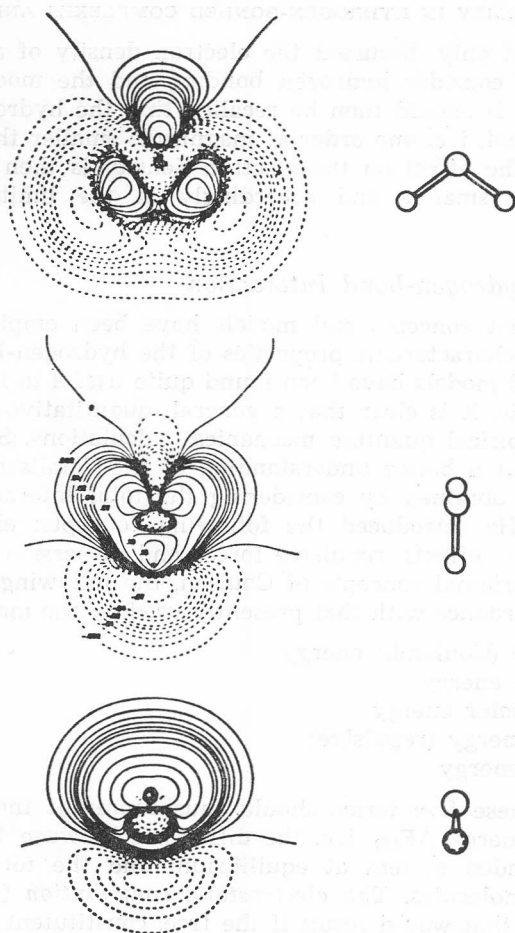


Figure 4. Deformation density maps of the free water molecule as calculated with a DZP<sup>+</sup> basis (Smith<sup>3</sup>) (cf. Figure 2).

We will refer to  $\Delta\rho(r)$  defined in this way as the deformation density. The deformation density of the *N*-acetamide, obtained by subtraction of Figure 1b from Figure 1a, is shown in Figure 3. The corresponding map for water is shown in Figure 4. The amount of charge actually migrating into the different bonding and lone-pair regions on molecular formation turns out to be quite small, about 0.05–0.25 electrons. In Figure 3 we notice that there is a certain electron concentration in the lone-pair directions of C=O, but the effect is indeed rather small. In the lone-pair region of the water oxygen in Figure 4 there is only one single maximum on the other hand. It should perhaps again be emphasized that the deformation density in this region does not represent the density of the lone pairs but only shows the excess with respect to the superposed spherical densities of the atoms. It is not possible to refer this excess to the contribution of any specific orbital.

## ELECTRON DENSITY IN HYDROGEN-BONDED COMPLEXES AND CRYSTALS

So far we have only discussed the electron density of an isolated molecule. We will now consider hydrogen bonding and the modifications caused by this interaction. It should then be recalled that the hydrogen-bond energy is only 20—40 kJ/mol, i. e. one order of magnitude smaller than the energy of a covalent bond. The effect on the electron density is then also expected to be correspondingly smaller and accordingly at the limit of the present accuracy.

*Partitioning of Hydrogen-bond Interaction*

Several different concepts and models have been employed in the past to account for the characteristic properties of the hydrogen-bond interactions. Although simplified models have been found quite useful in interpreting many experimental results, it is clear that a general, quantitative analysis requires the use of non-empirical quantum mechanical calculations. Several years ago, Coulson argued that a better understanding of the details of hydrogen-bond behaviour may be obtained by considering the total interaction in terms of four components. He introduced the following concepts: electrostatic interaction, delocalization effects, repulsive forces and dispersion forces. Deviating slightly from the original concepts of Coulson, the following partitioning will be adopted, in accordance with that presently used by the majority of authors:

- a) Electrostatic (Coulomb) energy
- b) Polarization energy
- c) Charge transfer energy
- d) Exchange energy (repulsive)
- e) Dispersion energy

The sum of these five terms should thus represent the total intermolecular interaction energy  $\Delta E_{\text{HB}}$ , i. e. the difference between the energy of the final hydrogen-bonded system at equilibrium and the total energy of the original, isolated molecules. The *electrostatic contribution* (a) corresponds to the energy change that would result if the free, constituent molecules, A and B, were somehow brought together into the relative positions in which they appear in the hydrogen-bonded complex, *without* deforming the original monomer charge distributions and without any electron exchange taking place. The *polarisation contribution* (b) corresponds to the additional energy-gain on deforming the monomer charge distributions from the previous hypothetical situation to a state more closely resembling the final hydrogen-bond situation, but *without* there occurring any transfer of electrons between the original constituents. The *charge transfer contribution* (c) represents the energy change on also allowing electron transfer between the systems.

The »delocalization« effect of Coulson corresponds to the sum of the contributions (b) and (c). The concept of »covalency« in the hydrogen bond is also related to the charge transfer effect: an accumulation of charge density in the overlap region, where it is shared by the two original monomers, constitutes the traditional view of a covalency contribution.

The *dispersion contribution* (e) corresponds to the attraction between the systems due to the coordinated motion, or correlation, of the electrons in A and B (London dispersion forces). All contributions discussed so far are attract-

ive. The two interacting systems are prevented from collapse by the repulsion term (d), denoted as the *exchange energy* contribution. This represents the effect of electron exchange between A and B, and corresponds more physically to the repulsion of the two electron systems when too many electrons are located within the same volume, thus violating the Pauli exclusion principle. (Note that the classical Coulomb repulsion between equal charges (electron-electron, nucleus-nucleus) is already included as part of the electrostatic contribution.)

In the case of weak and moderately strong hydrogen bonds it is found in general that the polarization, exchange, charge transfer and dispersion contributions approximately cancel each other. Furthermore, the variation in electrostatic energy follows the same trend as the total hydrogen bond energy. Consequently, the electrostatic component of the total intermolecular interaction reflects by itself quite well the relative forces in the case of moderately strong interactions.

#### *Characteristics of Weak and Moderately Strong Hydrogen Bonds*

As the electrostatic approximation implies that there is no electron redistribution when the monomers interact with each other, we expect that the electron density in a hydrogen-bonded system may be approximately obtained by simply bringing together the unmodified electron densities of the isolated monomers. This is in good qualitative agreement with the electron density maps derived from experiments. The modification actually taking place, as the molecules interact with each other, only constitutes a second order effect. This will be illustrated for a carbonyl group and a water molecule forming a hydrogen bond: The characteristic deformation densities of a carbonyl group and a water molecule were illustrated in Figure 3 and 4, respectively. Bringing these groups together, without any redistribution of the electrons, should give a map with the qualitative features shown in Figure 5.

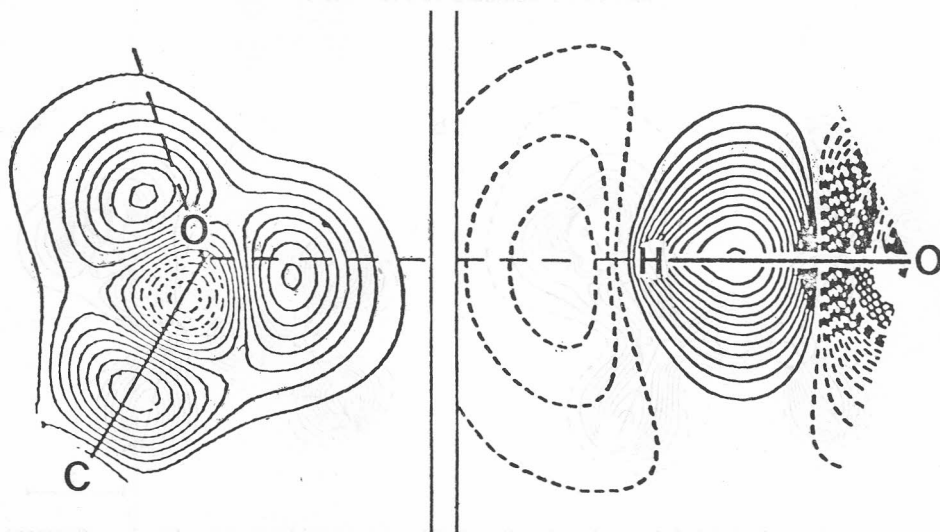


Figure 5. Characteristic deformation density expected for weak and intermediate hydrogen bonds within the electrostatic approximation: superposition of the electron densities of the isolated monomers.

The typical deformation density for a weak and moderately strong hydrogen bond  $X-H \dots Y$  thus consists of an electron excess in the  $X-H$  bond, a slight electron deficiency in the  $H \dots Y$  bond close to hydrogen, and an electron excess closer to the acceptor atom  $Y$ .

The experimental deformation density maps of weak and moderately strong hydrogen bonds are in quite good qualitative agreement with these expectations: in Figure 6 is illustrated the density in the same type of hydrogen bond as in Figure 5. In other words, within the electrostatic approximation, the experimental density of a molecule, weakly interacting with its crystal

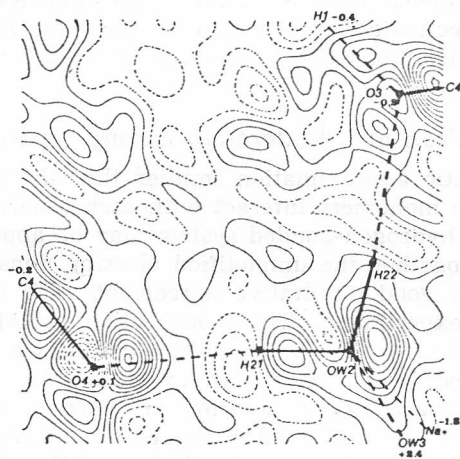


Figure 6. NaH Maleate  $\cdot 3H_2O$ .<sup>4</sup> X-N deformation density in the plane of one of the water molecules. Contours at  $0.10 e \cdot \text{\AA}^{-3}$ .

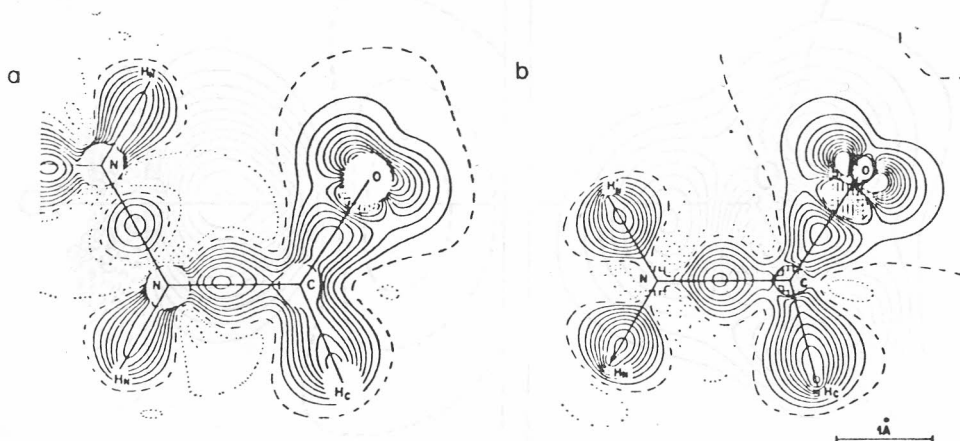


Figure 7. (a) Experimental deformation density of diformohydrazide from multipole refinement. (b) Theoretical deformation density of formamide from ab initio LCGO SCF calculations (EDZ). (Eisenstein<sup>5</sup>)



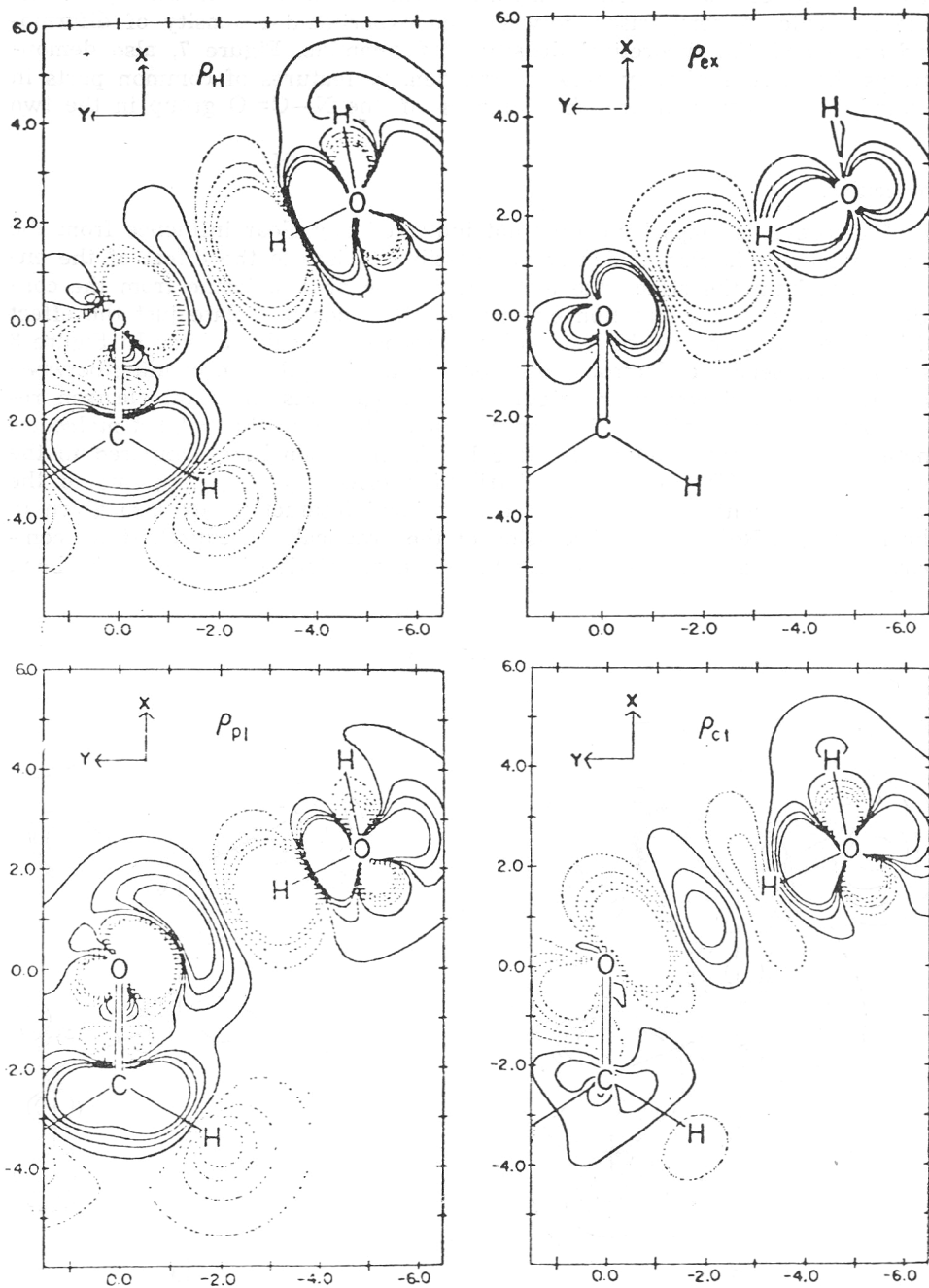


Figure 8. Theoretical deformation density and its components, relative to the isolated monomers for the system formaldehyde-water (Yamabe and Morokuma<sup>6</sup>)  
 A 4-31 G basis was used in the electron density decomposition analysis.

environment, can be directly compared with the theoretical density of the free molecule. A comparison between the experimental density of diformohydrazide and the theoretical density of formamide, Figure 7, also demonstrates the close similarity between the density features of common parts in related molecules: compare the features of the N—C=O group in the two



molecules.

The previous maps have thus not indicated any clear influence from the environment. It is also evidently not possible to isolate the effect of the environment from the effect due to the formation of a molecule from the constituent atoms in a diffraction experiment. In order to isolate just the effect of hydrogen bonding we have to refer to theoretical calculations. In Figure 8 is shown the separate electron redistribution due to hydrogen bonding between formaldehyde and water: the figure marked  $\rho_H$  gives the total electron redistribution in the hydrogen-bonded complex relative to the *isolated molecules* (note that a different reference state has been chosen here compared to the previous maps). The separate redistribution effects ( $\rho_{pl}$ ,  $\rho_{ex}$ ,  $\rho_{ct}$ ) due to the various components of the total hydrogen-bond interaction are also given in the figure (cf. Ref. 1 for a discussion of the practical procedure). If we compare  $\rho_H$  with Figure 5 we note just the same qualitative features in the bond

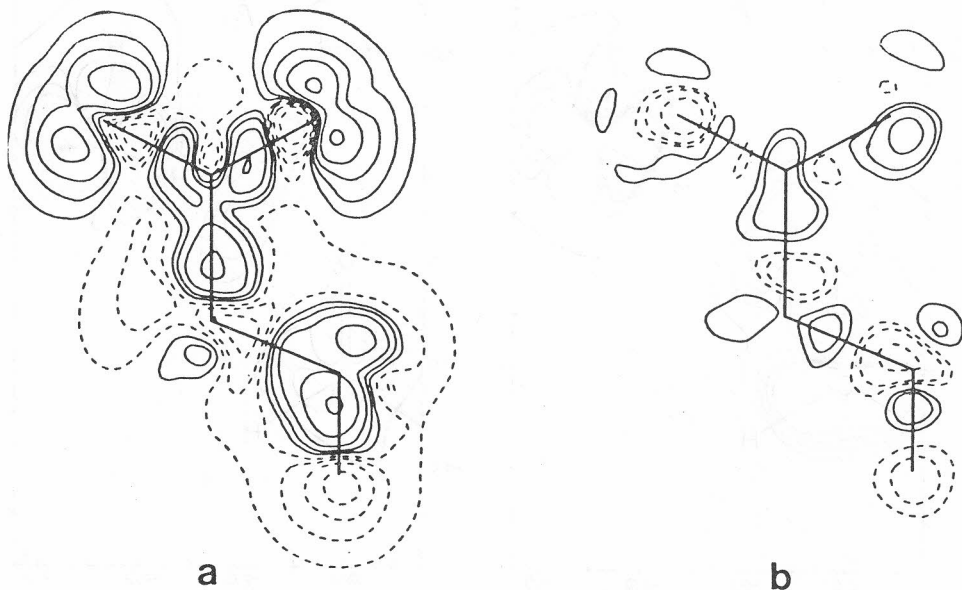
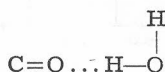


Figure 9. Theoretical deformation density of  $\alpha$ -glycine from ab initio-LCGO-SCF calculations (DZ) (Almlöf, Kvik, and Thomas<sup>7</sup>)

- (a): Free molecule  
 (b): Molecule in crystal field relative to free molecule

in both cases. This means that the net effect of hydrogen bonding ( $Q_H$ ) is to increase even further the polarity of the functional groups that already exists in the isolated molecules (Figure 5). Furthermore, the component due to polarization,  $Q_{pl}$  agrees quite closely with the total hydrogen-bond effect,  $Q_H$ , whereas the exchange and charge transfer effects,  $Q_{ex}$  and  $Q_{ct}$ , cancel each other to a large extent. We may accordingly conclude that, to a good approximation, the electron redistribution due to weak and moderately strong hydrogen bonding is mainly a polarization effect.

*$\alpha$ -Glycine.* The effect of the environment may also be illustrated by  $\alpha$ -glycine which was the first case where the effect of the environment was taken into account in a theoretical calculation, Figure 9. Here, the total effect of the whole crystalline environment was taken into account. The figure clearly demonstrates that the polarization due to the environment is a second order effect compared to the redistribution when a molecule is formed from the constituent atoms.

### Characteristics of Strong Hydrogen Bonds

The lower limit on the length of an O...O hydrogen bond is around 2.40 Å, and the proton may be located at the centre of the shortest hydrogen bonds. It can be noted from the survey made by Olovsson & Jönsson<sup>8</sup> (Vol II, p. 426) that all crystallographically symmetric hydrogen bonds are found for

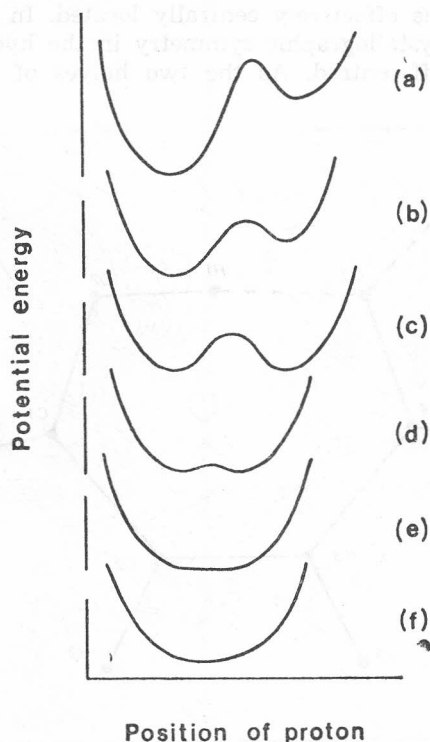


Figure 10. Schematic illustration of potential functions assumed to be characteristic of hydrogen bonds of different lengths.

O...O distances in the interval 2.40—2.50 Å, but also that asymmetric bonds are encountered equally frequently in this range. The feature common to all short hydrogen bonds is that the proton interacts with two chemically very similar acceptor groups X and Y, forming  $[X...H...Y]^-$  or  $[X...H...Y]^+$ . In the first case, X and Y are negatively charged (generally carboxylate ions), whereas the second case normally involves neutral molecules (water, etc.). The atoms in the groups X and Y which are directly bonded to the proton are, in all cases, identical (oxygen atoms) but the structural details further away from the hydrogen bond need not be identical. A slightly asymmetric hydrogen bond environment can thus arise due to chemical differences between the X and Y groups, such as in pyridine-2,3-dicarboxylic acid (Kvick et al.<sup>9</sup>). However, even if the two groups X and Y are chemically identical, slight asymmetry in the environment of the hydrogen bond may be present due to differences in the structural details. A distortion will be expected in the potential functions shown in Figure 10 c-e, if the arrangement with respect to the centre of the hydrogen bond is sufficiently asymmetric; Figure 10f illustrates such a slightly asymmetric situation. The mean position of the proton may then deviate significantly from the centre, the magnitude of the deviation depending on the degree of asymmetry of the environment. The influence of an asymmetry in the proton environment is demonstrated by the structure of potassium hydrogen maleate and sodium hydrogen maleate (Peterson & Levy<sup>10</sup>; Olovsson et al.<sup>4</sup>). In the first case, there is a crystallographic mirror symmetry in the hydrogen bond and the proton is effectively centrally located. In the second case (see below), there is no crystallographic symmetry in the hydrogen bond and the proton is markedly off-centred. As the two halves of the maleate ion are

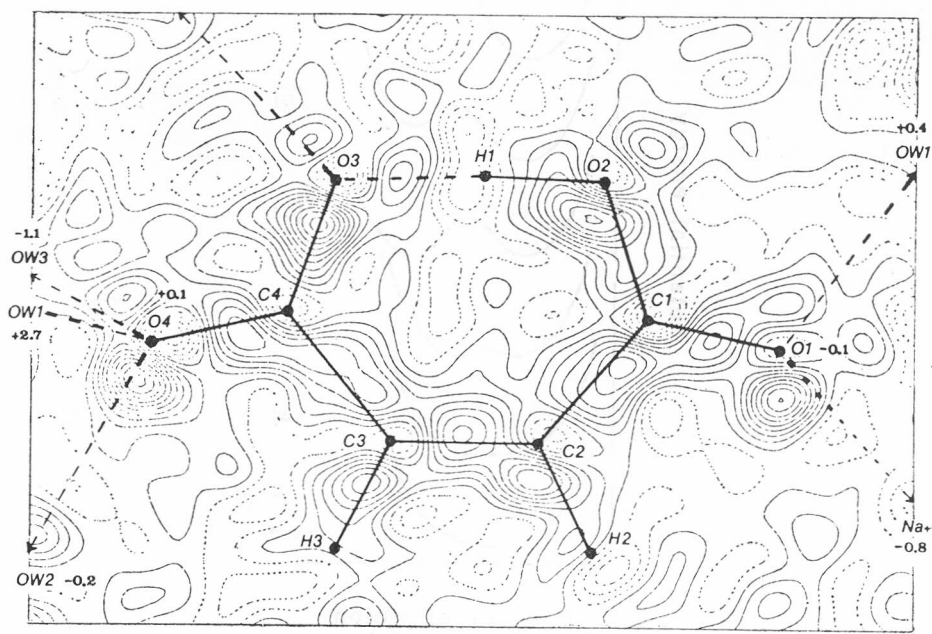


Figure 11. Experimental deformation density of NaH Maleate · 3H<sub>2</sub>O in the plane of the molecule (Olovsson, Kvick, Lehmann, and Olovsson<sup>4</sup>)

chemically identical, the asymmetry is clearly caused by the influence of more distant neighbours.

*NaH Maleate · 3H<sub>2</sub>O*. The data given below refer to X-ray and neutron diffraction results at 120 K (Olovsson et al.<sup>4</sup>). The two carboxyl groups of the maleate ion form a very short intramolecular hydrogen bond, O...O = 2.445 Å. The space group is centrosymmetric ( $P\bar{1}$ ) but there is no crystallographic symmetry in the short intramolecular hydrogen bond and the proton is clearly off-centered: O2—H = 1.079 Å and H...O3 = 1.367 Å. The end containing O2 may thus be considered approximately as a carboxylic group, and the other end as a carboxylate ion. The X—N deformation density map in the maleate ion is shown in Figure 11. We notice that the deformation density in the intramolecular hydrogen bond has a rather different appearance compared to previous maps: there is a much less pronounced charge build up in the donor O2—H bond as well as in the acceptor region H...O3. The electron density is also more symmetrically distributed around the midpoint.

#### THE LONE-PAIR DENSITY

##### *Characteristics of the C=O Group*

In the previous paragraphs several compounds containing C=O have been discussed. In all cases the deformation density shows a pronounced double maximum in the lone-pair region of oxygen, possibly somewhat distorted in the case of strong interaction with the environment. A few other cases will also be illustrated below.

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##### *Characteristics of the C—O Group*

*Formic acid*. The theoretical density, employing an EDZ basis set, is shown in Figure 12. In the lone-pair region of the double-bonded oxygen atom of the carbonyl group the same characteristics can be noticed as in the previous

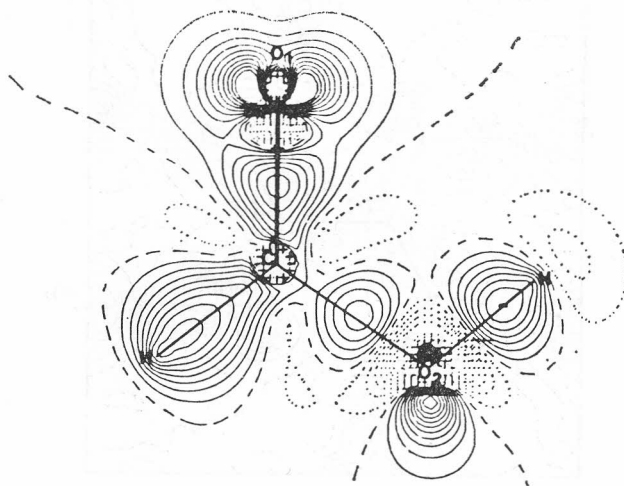


Figure 12. Theoretical deformation density of formic acid from ab initio-LCGO-SCF-calculation (DZP) (Eisenstein and Hirshfeld<sup>11</sup>)

cases. But now we will concentrate our attention to the corresponding region of the single-bonded oxygen atom  $O_2$  of the hydroxy group. In this case there is no double peak but only one single peak extending over a large part of the non-bonded region. The density in a plane perpendicular to the molecule is shown in Figure 13. One notices that there is no preferential electron concentration at all in the directions of the lone pairs.

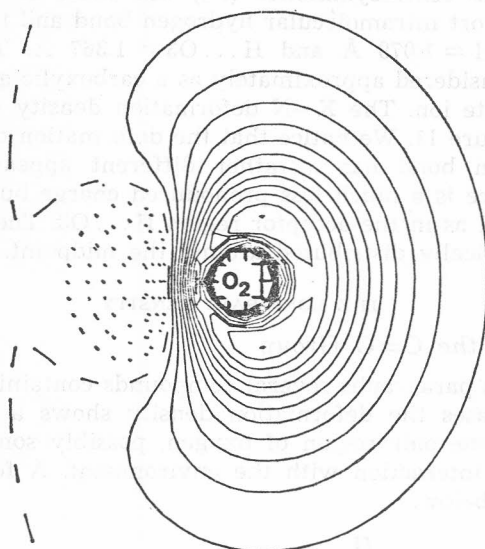


Figure 13. As in Figure 12, perpendicular to molecular plane. (Eisenstein and Hirshfeld<sup>11</sup>)

*Oxalic acid dihydrate.* The deformation density of the hydroxy group in the plane of the oxalic acid molecule is shown in Figure 14. The corresponding

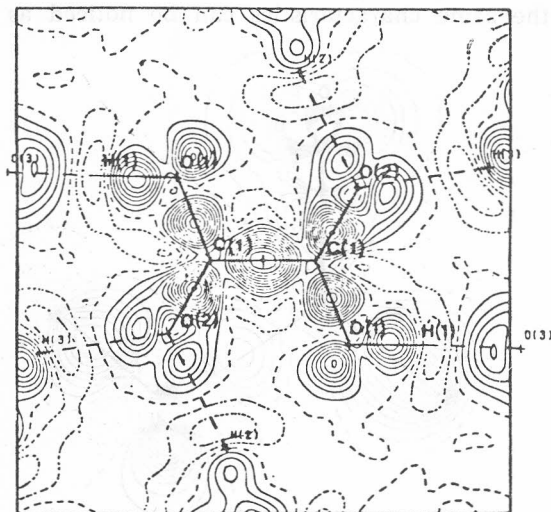


Figure 14. Experimental deformation density of  $H_2C_2O_4 \cdot 2H_2O$  from multipole refinement (Stevens and Coppens<sup>12</sup>)

density in a plane perpendicular to the molecular plane and bisecting the C—O angle is shown in Figure 15. This figure and the stereographic projection

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of the theoretical density in Figure 16 (left) demonstrate clearly that the electron density extends over the whole non-bonded region. Note the difference in the corresponding projection around the carbonyl oxygen (Figure 16, right).

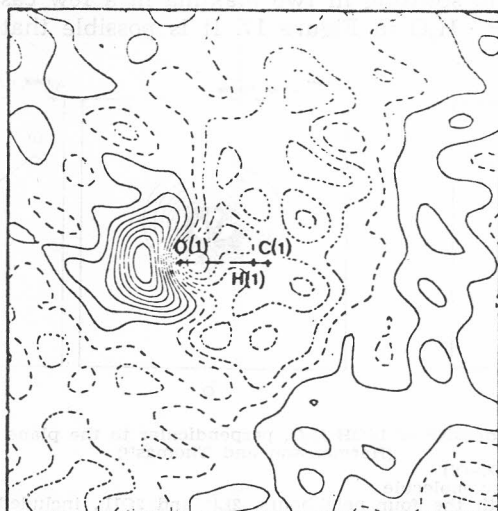
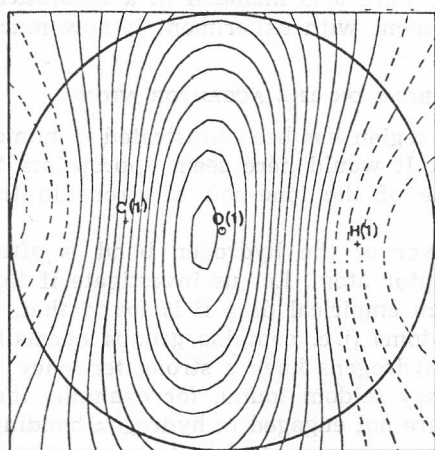
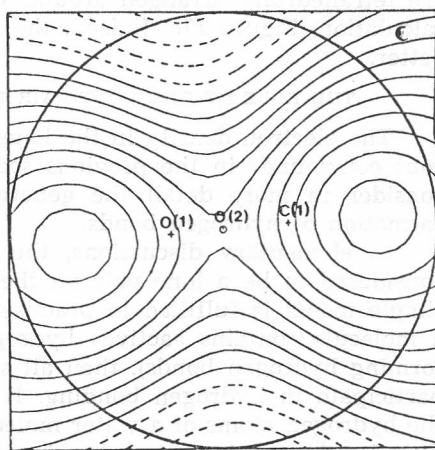


Figure 15. Experimental deformation density of  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , perpendicular to molecular plane, bisecting  $\angle\text{C-O-H}$  (Stevens and Coppens<sup>12</sup>)



Around O(1)



Around O(2)

Figure 16. Theoretical deformation density of  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (Stevens<sup>13</sup>): Stereographic projection on hemisphere around O(1) and O(2), respectively.

### Characteristics of the Water Molecule

The theoretical deformation density of the free water molecule was shown in Figure 4. As in the C—O groups just discussed, one here finds only one



peak extending over a major part of the lone-pair region of oxygen. This is commonly also the case in crystalline hydrates although there appears to be a certain tendency to splitting in two maxima in a few cases studied. This is illustrated for  $\text{LiOH} \cdot \text{H}_2\text{O}$  in Figure 17. It is possible that the splitting is a

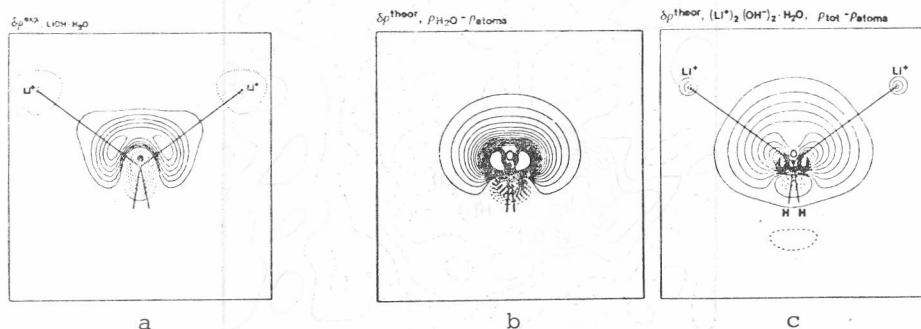


Figure 17. Deformation density of  $\text{LiOH} \cdot \text{H}_2\text{O}$ , perpendicular to the plane of the water molecule (Hermansson and Thomas<sup>14</sup>)

- (a) Experimental (X—N)
- (b) Theoretical, free molecule
- (c) Theoretical, with the four neighbours,  $2\text{Li}^+$  and  $2\text{OH}^-$ , included.

significant distortion effect caused by the tetrahedral environment around the water molecule. In order to investigate if this splitting may be caused by the environment, the four closest neighbours, two  $\text{Li}^+$  and two  $\text{OH}^-$  ions, which are tetrahedrally arranged around water, were also included in a theoretical calculation, Figure 17c. Indeed, the agreement with experiment is now much better.

#### THE ROLE OF THE LONE-PAIR ELECTRONS ON THE ACCEPTOR ATOM

The electron density in the lone-pair region has been illustrated in numerous compounds in the previous sections. It would here seem appropriate to consider in more detail the general role of the lone-pair electrons in the formation of hydrogen bonds.

In elementary discussions, the receiver of the hydrogen bond is often considered to be a lone pair on the acceptor atom. Let us investigate if this simple model is fulfilled in practise. From empirical data it is found that, if a molecule contains »active« hydrogen atoms (i. e. contains groups normally forming hydrogen bonds), then all such hydrogens have a strong tendency to participate in hydrogen bonding. It is very seldom found, for example, that the hydrogen atoms of a water molecule are not engaged in hydrogen bonding. This fact has an important bearing on the arrangement of hydrogen bonds, as will be illustrated for the case of a molecule  $\text{AH}_n$ , containing  $n$  active hydrogen atoms. Suppose that we wish to build up a three-dimensional structure containing only  $\text{AH}_n$  molecules, and assume that all these molecules have equi-



valent surroundings. Thus, if each molecule acts as a donor for  $n$  hydrogen bonds, Figure 18a, each molecule must also act as an acceptor of the same number of hydrogen bonds, Figure 18b. We will thus need  $n$  lone-pairs on each  $AH_n$  molecule. However, one seldom finds molecules with the same number

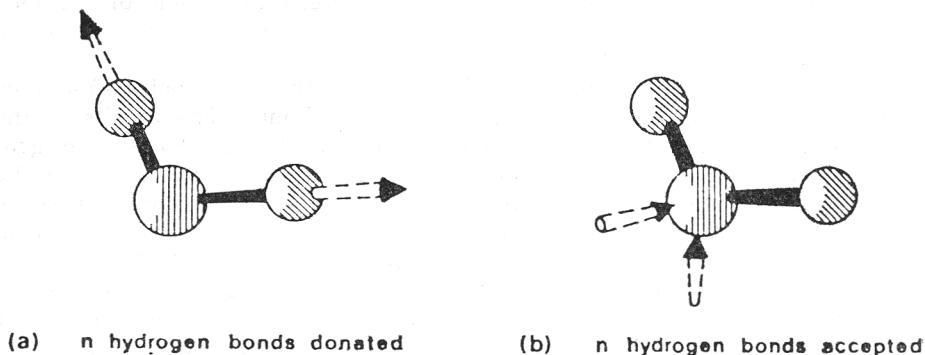


Figure 18. Geometrical requirements in hydrogen bond formation

of hydrogen atoms as lone-pairs. Water is thus a rather unique molecule in this respect. The ideal situation is not found in most other compounds; ammonia is a typical example. Here, there is only one lone-pair available and it might therefore be concluded that only one of the three hydrogen atoms can be engaged in hydrogen bonding. The structure of solid ammonia is illustrated in Figure 19 (Olovsson and Templeton<sup>15</sup>). We notice that all three hydrogen atoms do, in fact, participate in hydrogen bonding, which means that the single lone pair has to accept no less than three hydrogen bonds. The simple model of one lone pair per hydrogen bond is clearly not particularly relevant. The

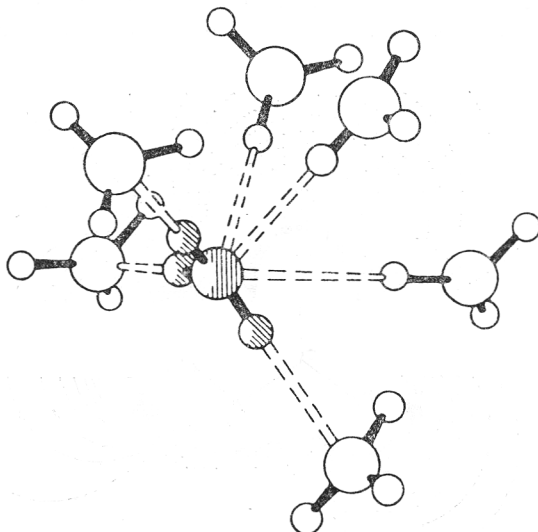


Figure 19. Structure of solid ammonia<sup>15</sup>.

above discussion may be extended to include cases with more than one type of molecule in the structure. If the number of lone pairs available is less than the number of active hydrogens, we may encounter situations like those described above. In many other cases there is an excess of available lone pairs as, for example, in many organic compounds. Here, either some of the lone pairs are not involved in hydrogen bonding, or the donor hydrogen atom is directed towards some point between several lone pairs.

From the above discussion, it is doubtful whether lone pairs should be regarded as the immediate receivers of hydrogen bonds. The details of the hydrogen-bond arrangement are often mainly determined by simple geometrical requirements. An inspection of the electron density features in the lonepair regions further supports this point of view. Many examples may be taken to illustrate that it is important to take into account the whole electron *and* nuclear distribution in discussing the relative arrangement of interacting molecules. As long as the electrostatic component plays the dominant role in the intermolecular interaction, the total influence of the electron and nuclear distribution may be directly illustrated by the electrostatic potential energy surface. This represents the electrostatic energy of interaction between a molecule and a positive unit charge at different positions. Such diagrams have been used, for example, to discuss preferred protonation sites in molecules. In studying these maps, it should then be noted that the molecular charge distribution is assumed not to be modified by the presence of the positive test charge. This is precisely the same assumption which underlies our electrostatic model for the hydrogen-bond interaction.

The electrostatic potential of formic acid is shown in Figure 20. There is a minimum which extends over a major part of the non-bonded region around each oxygen and in particular also around the carbonyl oxygen, in contrast with the deformation density. This means that the major part of the lone-pair region around the carbonyl oxygen should be approximately equally favourable to an approaching proton, as long as the latter does not cause a significant

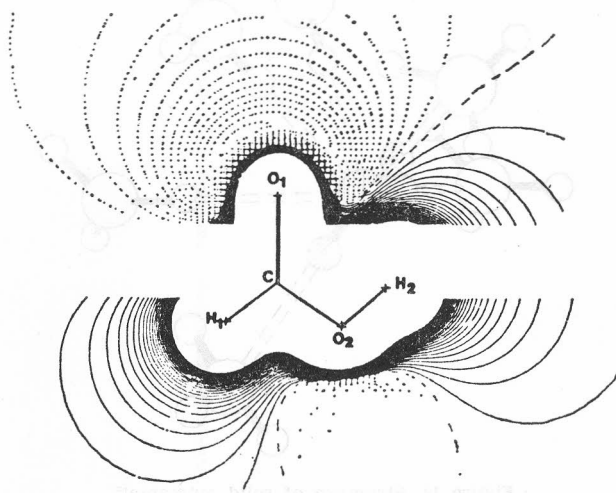


Figure 20. Electrostatic potential of formic acid (cf. Fig. 12) (Eisenstein and Hirshfeld<sup>14</sup>)

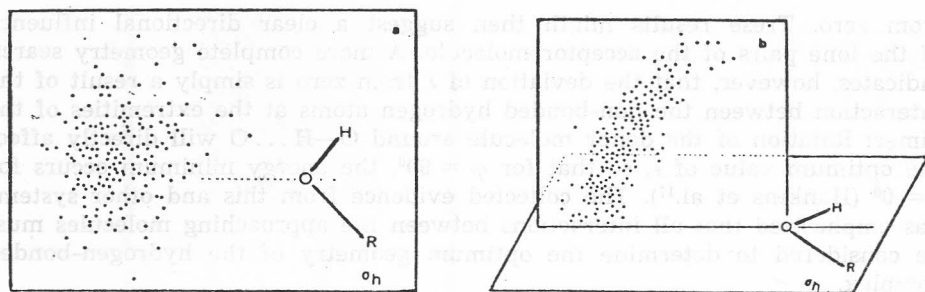


Figure 21. Observed hydrogen positions in donors to ROH<sup>16</sup>.

perturbation of the charge distribution in the molecule. Consideration of the Coulomb interaction with only the local electronic charges in the lone-pair regions can often be very misleading.

Several attempts have previously been made to study the directional influence of the lone-pair electrons on a carbonyl group when acting as a hydrogen-bond acceptor. A statistical study of the angle  $H \dots O = C$  in compounds accurately studied by neutron diffraction shows a certain accumulation around  $120^\circ$ , but there are many large deviations from this value (cf. Olovsson and Jönsson<sup>8</sup>, Vol. II p. 417). Naturally, it is impossible to decide from structural data alone whether this effect is caused by a genuine directional influence of the lone-pair electrons or by other geometrical factors, e. g. the most favourable direction of approach considering the form of the molecule.

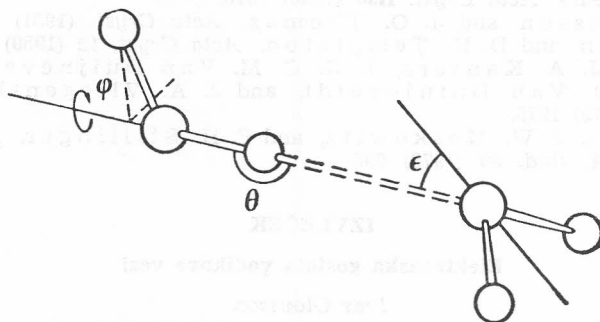


Figure 22. Structure of the water dimer.  $\Phi$  is the dihedral angle between the HOH plane of the donor molecule and the bisector plane of the acceptor molecule. For the geometry illustrated  $\Phi = 0^\circ$ .

From a statistical analysis of 196 hydrogen bonds from 45 crystal structures of polyalcohols, saccarides and related ROH compounds studied by X-ray diffraction, there appears to be no distinct preference for acceptance along the lone-pair directions (Kroon et al.<sup>16</sup>), Figure 21. The entire non-bonded region seems to be equally accessible for hydrogen bonding. The same conclusions were drawn from their extensive search of the optimum geometry for the water dimer from minimal basis *ab initio* calculations.

Theoretical calculations on water dimers are also illustrative in this context. In several accurate *ab initio* calculations, the energy minimum for the water dimer shown in Figure 22. is found for an angle  $\epsilon$  which is different

from zero. These results might then suggest a clear directional influence of the lone pairs of the acceptor molecule. A more complete geometry search indicates, however, that the deviation of  $\epsilon$  from zero is simply a result of the interaction between the non-bonded hydrogen atoms at the extremities of the dimer: Rotation of the donor molecule around O—H...O will directly affect the optimum value of  $\epsilon$ , so that for  $\varphi = 90^\circ$ , the energy minimum occurs for  $\epsilon = 0^\circ$  (Hankins et al.<sup>17</sup>). The collected evidence from this and other systems has emphasized that all interactions between the approaching molecules must be considered to determine the optimum geometry of the hydrogen-bonded complex.

## REFERENCES

1. I. Olovsson, (1980) in *Electron and Magnetization Densities in Molecules and Crystals* (Ed: P. Becker, Plenum Press).
2. A. T. Hagler and A. Lapicciarella, *Biopolymers* **15** (1975) 1167.
3. V. H. Smith, (1978) Private communication.
4. G. Olovsson, Å. Kvik, M. Lehmann, and I. Olovsson, (1981) To be published.
5. M. Eisenstein, *Acta Cryst.* **B35** (1979) 2614
6. S. Yamabe and K. Morokuma, *Int. J. Quantum Chem.* **10** (1976) 325.
7. J. Almlöf, Å. Kvik, and J. O. Thomas, *J. Chem. Phys.* **59** (1973) 3901.
8. I. Olovsson and P. G. Jönsson, (1976) in *The Hydrogen Bond. Recent Developments in Theory and Experiments*, Vol. I—III. (Eds.: P. Schuster, G. Zundel, and C. Sandorfy.) North Holland Publ. Co., Amsterdam.
9. Å. Kvik, T. F. Koetzle, R. Thomas, and R. Takusagawa, *J. Chem. Phys.* **60** (1974) 3866
10. S. W. Peterson and H. A. Levy, *J. Chem. Phys.* **29** (1958) 948.
11. M. Eisenstein, and F. L. Hirshfeld, *Chem. Phys.* **38** (1979) 1.
12. E. D. Stevens and P. Coppens, *Acta Cryst.* **B36** (1980) 1864.
13. E. D. Stevens *Acta Cryst.* **B36** (1980) 1876.
14. K. Hermansson and J. O. Thomas, *Acta Cryst.* (1981) (in press).
15. I. Olovsson and D. H. Templeton, *Acta Cryst.* **12** (1959) 832.
16. J. Kroon, J. A. Kanters, J. G. C. M. Van Duijneveldt-van de Rijdt, F. B. Van Duinjeveldt, and J. A. Vliegenthart, *J. Mol. Struct.* **24** (1975) 1975.
17. D. Hankins, J. W. Moskowitz, and F. H. Stillinger, *J. Chem. Phys.* **53** (1970) 4544. *Ibid.* **59** (1973) 995

## IZVLEČEK

## Elektronska gostota vodikove vezi

Ivar Olovsson

Raziskave natančno določenih elektronskih gostot za posamezne podobne sisteme so izredno pomembne za nadaljni razvoj teorij o kemijski vezi, med katere uvrščamo tudi vodikovo vez.

V članku je podan pregled difrakcijskih raziskav in kvantno-mehanskih izračunov elektronskih gostot vodikove vezi. Porazdelitev elektronske gostote v šibkih in srednje močnih vodikovih vezeh lahko obravnavamo preprosto kot seštevek elektronskih gostot posameznih ločenih delov molekule. Majhne spremembe, ki se pojavijo zaradi interakcije teh molekul med seboj v kristalu, so komaj opazne. V spojinah z močnimi vodikovimi vezmi pa opazimo izrazite spremembe v mapah elektronske gostote. V članku je posebej obdelana tudi elektronska gostota v območju samskega elektronskega para.