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Determination of Nuclear Positions from X-ray Data by a Double-Atom Refinement Method

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A double-atom (DA) refinement method is described in which the positions of the core and valence shells of first-row atoms are refined separately, together with valence-shell occupancies and scale, temperature, and extinction parameters. Since the core electrons are, to a good approximation, unperturbed by bonding effects, their centroid should correspond to the position of the atomic nucleus as determined by neutron diffraction. The method, as employed here, uses the spherical valence-shell approximation. Results obtained with data sets on three compounds suggest that the approximation is adequate for most room-temperature data. Thus, the neutron diffraction results of oxalic acid dihydrate are well reproduced, while the DA method gives a C≡N bond length for cubic tetracyanoethylene that agrees better with the electron diffraction value than the conventional X-ray results. Discrepancies between core positions and conventional atomic positions are about 0·01 Å or smaller. Results for cyanuric acid show the breakdown of the spherical valence-shell approximation. Discrepancies between X-ray and neutron data for this compound are small and would not have been detected in a room-temperature study. Temperature factors obtained with molecule-optimized Slater-type orbitals are in better agreement with the neutron-diffraction parameters than with those obtained with Hartree–Fock isolated-atom form factors. DA formalisms also show promise for the joint refinement of X-ray and neutron data.

Introduction

Combined use of X-ray and neutron diffraction data has shown that in conventional X-ray least-squares procedures, structural and thermal parameters are adjusted in such a way as to allow partly for the effects of bonding on the molecular charge density (Coppens, 1968; Coppens, Sabine, Delaplane & Ibers, 1969; Coppens, 1967; Matthews, Swanson & Stucky, 1970; Sakurai & Ito, 1969). With improved formalisms it is possible to obtain parameters that describe the molecular density distribution and explicitly allow for bonding effects (Coppens, Csonka & Willoughby, 1970; Coppens, Willoughby & Csonka, 1971). However, when these formalisms are applied to the X-ray data alone, serious problems arise because of the correlation between the asphericity of the atomic charge densities and the anisotropy of the thermal motion. It is, in general, very diffficult to deconvolute these two effects, though collection of accurate X-ray data at very low temperatures may open new possibilities.

A logical compromise between the conventional treatment and the full population refinement is to separate the core and valence shells of the atoms. Such a separation was proposed by Amoros & Canut-Amoros (1967), who determined an approximate (single Gaussian) shape of the radial distribution of the core electrons from high-order X-ray data, and used the result to obtain valence-electron density maps. However, experimental and theoretical evidence indicates that core electrons are unaffected by bonding within the limits of the X-ray experiment; this led Stewart (1970) to propose the use of a fixed calculated core scattering contribution. In Stewart's *L*-shell projection method, the occupancy of the valence shell is varied in a least-squares cycle after completion of the conventional refinement. This procedure leads to an experimental determination of the net atomic charges, as fitted to a spherical valence shell. But the thermal parameters obtained in the conventional refinement are affected by the total neglect of ionicity, and the errors in the thermal parameters may in turn affect the net atomic charges obtained with the *L*-shell projection method.

One may generalize the *L*-shell projection method by including as variables in the least-squares cycles all positional, thermal, and extinction parameters needed to describe the structure (Coppens, Pautler & Griffin, 1971).

In the extended *L*-shell (ELS) method, the core and valence shells of an atom are described by the same positional and thermal parameters. However, substantial evidence from combined X-ray and neutron analyses reveals that the centroid of the valence shell is slightly displaced when first-row atoms are in a highly asymmetric environment (Coppens *et al.*, 1969). Therefore, we may assign independent sets of positional parameters to the core and valence shell, in an attempt to reproduce, from the X-ray data alone, the observed discrepancies between X-ray and neutron atomic positions. Since, to a good approximation, the core is unperturbed by bonding, its centroid should correspond closely to the position of the atomic nucleus.

Extended *L*-shell method

The application of the ELS method has been described previously (Coppens, Pautler & Griffin, 1971). We may write:

$$A_{\mathbf{H}}=\left[\sum_n a_n(f_{n,c}+f'_n)\cos 2\pi(\mathbf{H}\,.\,\mathbf{r}_n) - \sum_n a_n f''_n \sin 2\pi(\mathbf{H}\,.\,\mathbf{r}_n) + \sum_n b_n f_{n,v} \cos 2\pi(\mathbf{H}\,.\,\mathbf{r}_n)\right] T_n,$$

and

$$B_{\mathbf{H}}=\left[\sum_n a_n(f_{n,c}+f'_n)\sin 2\pi(\mathbf{H}\,.\,\mathbf{r}_n) + \sum_n a_n f''_n \times \cos 2\pi(\mathbf{H}\,.\,\mathbf{r}_n) + \sum_n b_n f_{n,v} \sin 2\pi(\mathbf{H}\,.\,\mathbf{r}_n)\right] T_n \quad (1)$$

in which a_n and b_n are, respectively, the core and valence occupancy factors of the *nth* atom at a position defined by the vector $\mathbf{r}_n$; $f_{n,c}$ and $f_{n,v}$ are the spherically-symmetric core and valence scattering factors of the *n*th atom for the reflection $\mathbf{H}$. f' and f'' represent the real and imaginary part of the anomalous scattering factor of the atomic core, and T_n is an appropriate temperature factor.

In general, a_n is fixed in the refinement, while b_n, x_n, y_n, z_n (defined by $\mathbf{r}_n = x_n\,\mathbf{a} + y_n\,\mathbf{b} + z_n\mathbf{c}$) and the parameters of T_n are variables, together with the factors determining the experimental scale and the extinction in the crystal (Coppens & Hamilton, 1968).

Refinement is performed with least-squares program *ELSE* which is a modification of the standard least-squares program *LINUS*. As the input for the two programs is similar, it is relatively easy to apply the ELS method after completing the conventional least-squares refinement.

Double-atom method

If $\mathbf{r}_{n,c}$ and $\mathbf{r}_{n,v}$ represent the positions of the core and valence shells, expression (1) becomes:

$$A_{\mathbf{H}}=\left[\sum_n a_n(f_{n,c}+f'_n)\cos 2\pi(\mathbf{H}\,.\,\mathbf{r}_{n,c}) - \sum_n a_n f''_n \times \sin 2\pi(\mathbf{H}\,.\,\mathbf{r}_{n,c}) + \sum_n b_n f_{n,v} \cos 2\pi(\mathbf{H}\,.\,\mathbf{r}_{n,v})\right] T_n \quad (2)$$

with similar modifications for $B_{\mathbf{H}}$.

Compared with the ELS method, the additional parameters are the coordinates $x_{n,v}$, $y_{n,v}$, $z_{n,v}$ in $\mathbf{r}_{n,v} = x_{n,v}\,\mathbf{a} + y_{n,v}\,\mathbf{b} + z_{n,v}\,\mathbf{c}$. It is tempting to generalize the treatment further by assigning separate thermal parameters to the two shells. We decided against this extension for the following two reasons:

(1) Though the Coulombic attraction to the atomic nucleus is less for the valence shell than for the core electrons, it is very strong and any relative vibration of the valence electrons with respect to the nucleus is energetically unlikely. This argument is less convincing for those electrons located in the region around the midpoints of the bonds, which are centered on two nuclei rather than on one nucleus. However, it applies to a very large fraction of the electron density.

(2) A more pragmatic argument is that the scattering of the valence electrons is mainly restricted to the low-order region. Therefore, a separate valence–electron temperature factor would be poorly determined by the experimental information.

Following Stewart (1970), isolated-atom Hartree–Fock (HF) scattering factors are used for the core electrons in both the ELS and DA methods, while either

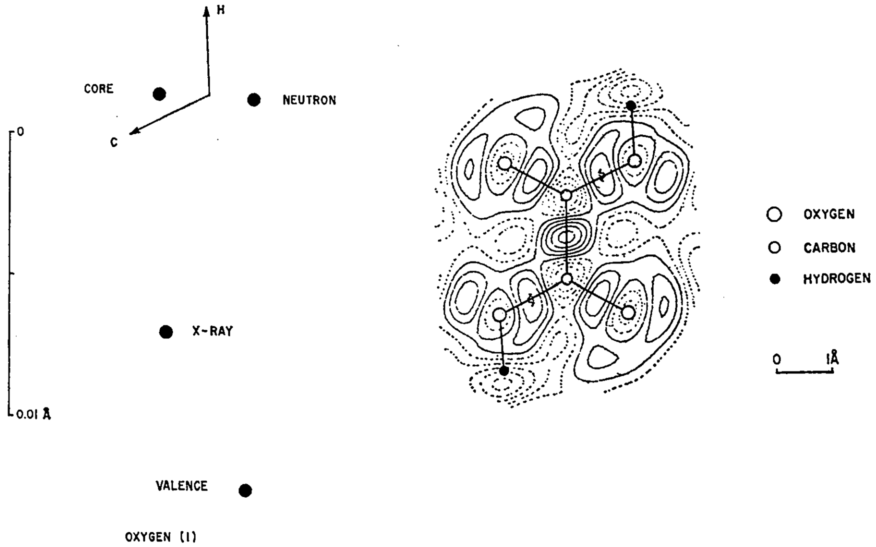

Fig. 1. X-ray and neutron positions for the hydroxyli coxygen atom in oxalic acid dihydrate compared with the results of double-atom refinement (left-hand side) and corresponding X-ray and neutron difference map (contours 0·05 e.Å^{-3}). Note the difference of scale in the two halves of the Figure.

HF or molecule-optimized Slater-type orbitals (STO) (Hehre, Stewart & Pople, 1969) may be used for the valence shell. A contracted hydrogen-molecule fitted curve is used for the HF hydrogen atom (Stewart, Davidson & Simpson, 1965).

Neutrality condition

In both methods the crystal is kept neutral by constraining the total number of electrons to be constant (see Hamilton (1963) for the expressions used). If this neutrality condition is not applied, the total number of electrons after refinement may be less than, or in excess of, the number of electrons in the neutral crystal (Table 1; similar results have been obtained in ELS refinements of a number of other compounds, including the TCNE-pyrene and TCNE-perylene complexes and Ni-diethylenediamine malonate.)

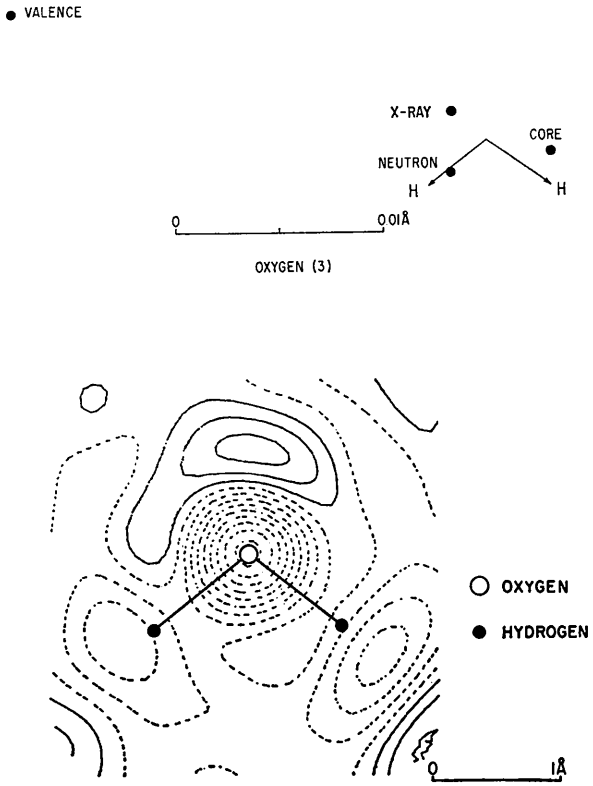

Fig. 2. Oxygen atom in the water molecule in oxalic acid dihydrate. Details as in Fig. 1.

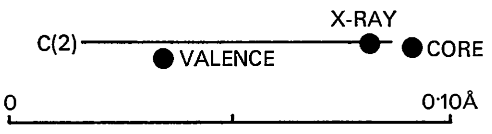

Fig. 3. X-ray, core, and valence-shell positions for the nitrogen atom in cubic tetracyanoethylene.

Table 1. *Changes in total number of electrons if constraint had not been applied*

	STO form factors		HF form factors	
	First cycle	Last cycle	First cycle	Last cycle
Cubic TCNE				
ELS	2·39	2·31	3·02	3·05
DA	2·15	2·01	3·07	3·03
Oxalic acid				
ELS	−4·11	−4·27	−7·18	−6·88
DA	−4·85	−5·05	−7·73	−7·50
Cyanuric acid				
ELS	−0·74	−1·62	2·42	1·91
DA	−2·39	−2·60	1·32	1·15

Because of the large correlation between the scale factor k and the valence-shell charges (Coppens, Pautler & Griffin, 1971), the apparent non-neutrality of the crystal can be compensated for by a change in the scale factor. It is a direct consequence of this correlation that the neutrality condition has to be applied, unless an accurate experimental measurement of the scale factor has been made. The correlation becomes very small when the constraint is applied.

Results

Results of the ELS refinement were discussed in an earlier article (Coppens, Pautler & Griffin, 1971). An essential test for an extension of the treatment, such as the splitting of the atoms into a core and a valence shell, is the significance of the improvement in the R values. The information summarized in Table 2 shows that the improvement of the DA method over the ELS one is considerable for the tetracyanoethylene STO results: the weighted R value drops from 4·0 to 3·5%. The change is much less pronounced with STO orbitals (which are considered since they give a better agreement for all three compounds) for oxalic acid

Table 2. *Survey of agreement factors* (%)

NO = number of observations, NV = number of variables.

$R=\sum|F_o-|F_c||/\sum F_o$ and $R_w=\left[\frac{\sum w|F_o-|F_c||^2}{\sum wF_o^2}\right]^{1/2}$

	Conventional least-squares	ELS		DA	
		STO	HF	STO	HF
Cubic TCNE					
R	5·9	4·9	5·5	4·8	5·5
R_w	4·8	4·0	4·0	3·5	4·0
NO	355	355		355	
NV	18	21		26	
Oxalic acid					
R	2·1	2·04	2·06	1·96	2·02
R_w	3·0	1·91	1·99	1·84	1·92
NO	548	548		548	
NV	55	62		74	
Cyanuric acid					
R	4·1	3·41	3·62	3·42	3·60
R_w	3·3	3·11	3·22	2·97	3·12
NO	967	933		933	
NV	49	57		69	

and cyanuric acid. Therefore, an *R* value significance test is required before the results can be discussed. Using Hamilton's (1965) tables, we find that for cyanuric acid a 2% improvement is significant at the conservative 0·005% confidence level (*i.e.*, $R_{12,876,0\cdot005} \sim 1\cdot02$), while for oxalic acid a 3% improvement is significant at this level. Since the *R*-value ratios obtained are actually 1·044 and 1·040, discussion of the DA results for these compounds is clearly justified.

Analysis of core and valence-shell positions

Positional parameters are listed in Table 3. Standard deviations in the valence-shell positions are large because they are derived from low-order intensities only. Also, a negative correlation exists between the core and valence-shell positions, which implies that a shift in one direction of the core can be compensated for, to some extent, by a shift in the opposite direction of the valence shell. (Correlation coefficients are about −0·8 in oxalic acid and between −0·5 and −0·6 or smaller in cyanuric acid and TCNE.) This correlation increases the standard deviation of the core-valence shell distance by about 10%. Because of the experimental uncertainty in the position of the valence shell, our analysis is concentrated mainly on the position of the core electrons relative to the atomic positions obtained with conventional X-ray diffraction and neutron diffraction.

Table 3. *Atomic coordinates* (Å)

For numbering of atoms see text and references indicated.

Oxalic acid dihydrate (Coppens, Sabine, Delaplane & Ibers, 1969)

		X-ray	Neutron	X-ray DA (STO)	
				Core	Valence
C	*x*	−0·278(1)	−0·275(1)	−0·277(1)	−0·273(10)
	y	0·197(1)	0·199(1)	0·195(2)	0·201(8)
	z	0·614(1)	0·616(2)	0·615(5)	0·603(7)
O(1)	*x*	0·526(1)	0·525(1)	0·521(2)	0·531(4)
	y	−0·220(1)	−0·220(1)	−0·221(3)	−0·221(4)
	z	1·788(1)	1·796(1)	1·794(3)	1·785(6)
O(2)	*x*	−1·344(1)	1·343(1)	−1·341(2)	−1·344(4)
	y	0·830(1)	0·829(1)	0·827(3)	0·830(3)
	z	1·788(1)	1·796(1)	1·794(2)	1·785(2)
O(3)	*x*	−2·765(1)	−2·767(1)	−2·767(4)	−2·755(6)
	y	−1·392(1)	−1·395(2)	−1·384(3)	−1·416(5)
	z	0·436(1)	0·436(1)	0·438(2)	0·435(5)
D(1)	*x*	2·85(1)	2·916(1)	2·89(1)	
	y	1·77(2)	1·835(1)	1·77(2)	
	z	3·56(2)	3·424(1)	3·53(2)	
D(2)	*x*	0·34(1)	0·438(1)	0·31(3)	
	y	0·57(2)	0·668(2)	0·58(1)	
	z	4·58(2)	4·658(1)	4·52(3)	
D(3)	*x*	−2·38(2)	−2·208 (1)	−2·24(3)	
	y	1·63(2)	1·609 (2)	1·64(3)	
	z	1·94(2)	1·842 (1)	1·87(2)	

Tetracyanoethylene (Little *et al.*, 1971)

Table 3 (*cont.*)

		X-ray	X-ray DA (STO)	
			Core	Valence
N	*x*	2·073(1)	2·077(1)	2·044(5)
	y	4·868	4·868	4·868
	z	7·025(1)	7·034(1)	6·989(5)
C(2)	*x*	1·438(1)	1·435(1)	1·438(6)
	y	4·868	4·868	4·868
	z	6·084(1)	6·081(1)	6·074(7)
C(1)	*x*	0·672(2)	0·679(2)	0·679(7)
	y	4·868	4·868	4·868
	z	4·868	4·868	4·868

Cyanuric acid (Verschoor & Keulen, 1970; Coppens & Vos, 1970)

		X-ray	Neutron	X-ray DA (STO)	
				Core	Valence
C(2)	*x*	1·900(1)	1·900(1)	1·900(1)	1·902(7)
	y	0·711(1)	0·713(1)	0·711(1)	0·734(8)
	z	1·741(1)	1·742(1)	1·742(1)	1·746(3)
C(1)	*y*	2·816(1)	2·815(1)	2·815(1)	2·832(12)
N(2)	*x*	1·895(1)	1·895(1)	1·895(1)	1·895(4)
	y	2·081(1)	2·081(1)	2·082(1)	2·067(4)
	z	1·791(1)	1·792(1)	1·789(1)	1·811(5)
N(1)	*y*	0·077(1)	0·074(1)	0·074(1)	0·106(6)
O(2)	*x*	1·882(1)	1·880(1)	1·883(1)	1·879(3)
	y	0·090(1)	0·093(1)	0·089(1)	0·094(2)
	z	0·675(1)	0·680(1)	0·676(1)	0·679(3)
O(1)	*y*	4·033(1)	4·029(1)	4·033(1)	4·027(3)
H(2)	*x*	1·87(1)	1·877(1)	1·88(1)	
	y	2·50(1)	2·590(1)	2·48(1)	
	z	1·01(1)	0·877(1)	1·02(2)	
H(1)	*y*	−0·74(2)	−0·950(1)	−0·75(2)	

It should be noted that the simultaneous refinement of two 'pseudoatoms' occupying almost identical positions is feasible, because the scattering factors of the core and valence shells differ considerably. Especialy the absence of valence-shell scattering in the high-order region leads to a reasonable separation of the two components. Thus, core positions obtained with the DA method are comparable to the atomic positions from a high-order refinement (Little, Pautler & Coppens, 1971), with the important difference that all, rather than part of, the data are utilized in the DA refinement.

(*a*) *Deutero-oxalic acid dihydrate*. Comparison of the X-ray and neutron positional parameters showed a difference of 0·008 Å just outside the experimental errors for the hydroxylic oxygen atom of the oxalic acid molecule (Coppens, Sabine, Delaplane & Ibers, 1969). This shift was confirmed in the protonated compound, for which neutron data had been collected by Sabine, Cox & Craven (1969).

The X-N difference map (Fig. 1) shows that both the carbon and oxygen atoms of the carbonyl group are surrounded by a trigonal arrangement of bond and lone-pair density features. But this arrangement

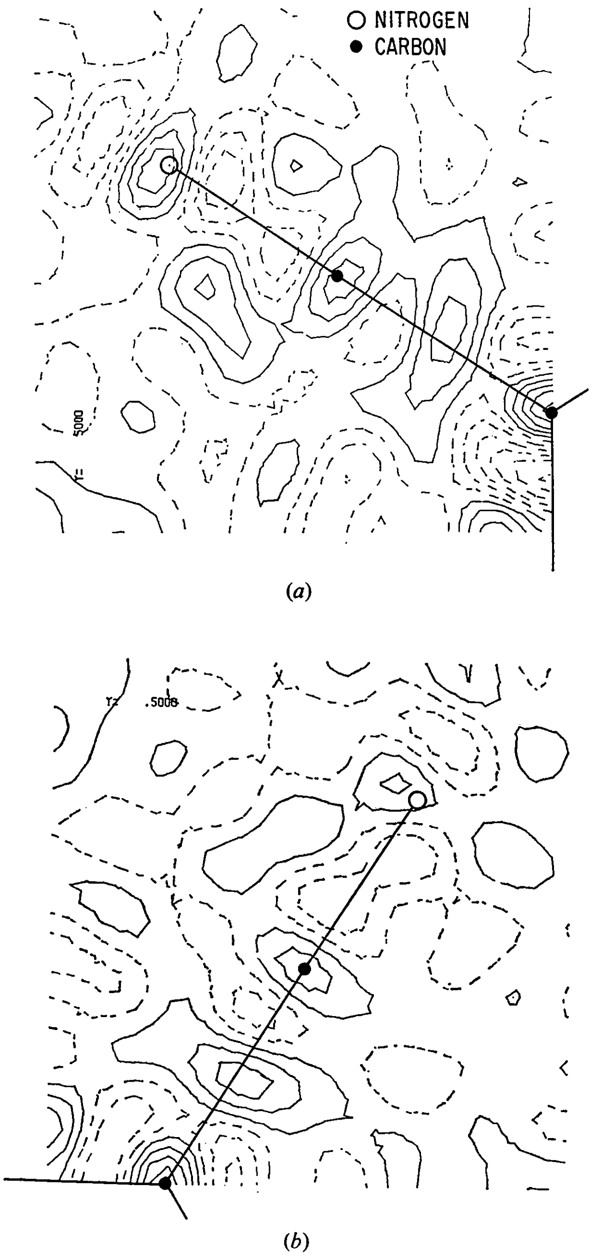

Fig. 4. X-ray difference density in the plane of the tetracyanoethylene molecule: (*a*) after conventional X-ray refinement, (*b*) after double-atom refinement. Contours at 0·1 e.Å^{-3}.

is disturbed for the hydroxylic-oxygen atom, because there is very little density in the O–D bond. As a result, the centroid of the O(1) atomic density is shifted in a direction away from the O–D bond, as is confirmed by comparing X-ray and neutron diffraction positions. Coordinates are given in Table 1. Relative positions for O(1), obtained in the various refinements, are given in the first half of Fig. 1. It is seen that the core and neutron positions agree well, while the X-ray position is in between the core and valence locations. The position from the conventional X-ray refinement should correspond to a weighted average between core and valence-shell positions, the weighting being a function of the data cutoff and, to some extent, of the weighting of the observations in the least-squares refinement. Since $(\sin \theta/\lambda)_{\max}$ is 0·55 Å^{-1} for the oxalic acid data, a relatively large effect of the valence shell on the conventional X-ray position can be expected, which is confirmed in Fig. 1.

Other atoms in the oxalic acid molecule do not show a discrepancy between X-ray and neutron results, and no differences between core and valence-shell positions are found with the DA method. The absence of an X-ray and neutron discrepancy for the oxygen atom in the water molecule was somewhat surprising, because an asymmetric density feature attributed to the lone-pair electrons was found at the back of this oxygen atom (Fig. 2). The DA method shows the core close to the expected position, but the valence shell displaced not along the bisectrix of the H–O–H angle, but in a way that seems to allow for the lack of symmetry in the lone-pair peak (Fig. 2).

(*b*) *Tetracyanoethylene*. The application of the DA refinement method to cubic tetracyanoethylene is described in an earlier publication (Little *et al.*, 1971). As the molecular center occupies a site of *mmm* symmetry, only $\frac{1}{4}$ of the molecule is measured, the other parts being equivalent by symmetry. A large shift of the valence-shell position of the terminal nitrogen atom towards the center of the triple C≡N bond was found (Fig. 3). The compensating small shift of the core away from the bond center led to a bond length of 1·166(2) Å, which is in better agreement with the electron diffraction value [1·162 (2) Å, Hope, 1968] than the result of the conventional X-ray refinement [1·153 (2) Å].

It is of interest to compare the difference maps obtained after the conventional and the DA refine-

Table 4. *Comparison of net atomic charges (electrons) in oxalic acid dihydrate*

	Slater-type orbitals		Hartree–Fock orbitals		Calculated
	ELS	DA	ELS	DA	
C	+0·16 (3)	+0·20 (4)	+0·06 (3)	+0·07 (4)	+0·43
O(1)	−0·29 (3)	−0·23 (5)	−0·25 (3)	−0·20 (4)	−0·28
O(2)	−0·30 (3)	−0·30 (4)	−0·25 (3)	−0·24 (3)	−0·33
O(3)	−0·23 (6)	−0·19 (7)	−0·25 (5)	−0·11 (6)	−0·32
H(1)	+0·29 (4)	+0·21 (6)	+0·23 (4)	+0·20 (6)	+0·19
H(2)	+0·08 (4)	−0·10 (9)	+0·20 (4)	−0·08 (9)	+0·16
H(3)	+0·28 (5)	+0·44 (6)	+0·25 (5)	+0·36 (6)	+0·16

ments. The conventional map [Fig. 4(*a*)] shows density in, or near, the centers of the C–C and C=C bonds. No density is found near the midpoint of the C≡N bond, probably because two spherical atoms at the short distance of 1·135 Å apart are subtracted out. But the map, and a parallel section at 0·5 Å above the molecular plane, indicate a ring of residual density around the bond at a distance of about 0·4 Å from its midpoint; this may be attributed to the triple-bond π-density. Also, a small amount of residual positive density exists at the atomic positions. The main differences in the parameters obtained with the DA method are in the region of the cyano group, and the difference map [Fig. 4(*b*), STO scattering factors] shows that, especially in this region, residual features are reduced appreciably but not completely.

(*c*) *Cyanuric acid* (100°K). Small but significant discrepancies between the X-ray and neutron results were found for the positional parameters of the oxygen atoms in cyanuric acid [$(\sin\theta/\lambda)_{\max}=0{\cdot}8$ Å^{-1}] (Verschoor & Keulen, 1971; Coppens & Vos, 1971); the X-ray positions for the two atoms were displaced by 0·006 (1) and 0·003 (1) Å respectively. It was noticed, however, that with the lower data cutoff of 0·5 Å^{-1}, a much closer correspondence between the X-ray and neutron positions could be obtained. Thus, discrepancies would not have been detected in a room-temperature study. This effect was explained in terms of the scattering-factor curves for the bond density and the lone-pair density. In the low-order refinement, the lone-pair electrons and the overlap density in the C=O bond almost balance each other (as they do for the C=O group in the room-temperature oxalic acid study), while at higher angles the lone-pair electrons dominate. This is because the lone-pair electrons, which correspond to a concentration of the valence density in a particular region, scatter to much higher angles than the overlap density (Coppens, 1969).

Positional parameters resulting from the DA refinement are given in Table 2. Since the valence-shell scattering factor of the DA refinement is practically zero beyond 0·5 Å^{-1}, it is in accordance with the explanation given before that the valence-shell positions for the oxygen atoms correspond fairly closely to the neutron positions. For both atoms, however, core positions are closer to the X-ray results than to the neutron results. This suggests that the DA core positions are affected by the high-order scattering of the lone-pair electrons, and it points to a fundamental deficiency in both the ELS and DA methods in which the valence shell is approximated by an isolated-atom spherical density distribution.

That this shortcoming becomes apparent in cyanuric acid is not surprising, because the data set contains 967 reflections, 724 of which have a $\sin\theta/\lambda$ value $>0{\cdot}5$.

For the two nitrogen atoms core locations are very close to both the X-ray and neutron positions, while the valence shell is displaced by about 0·026 (6) Å (in both cases) in a direction away from the N–H bond. This effect is similar to the shift observed for O(1) in oxalic acid.

Table 5. *Temperature factors* ($\beta\times10^4$, B *in* Å^2)

Oxalic acid

				ELS		DA	
		X-ray	Neutron	STO	HF	STO	HF
C(1)	11	183(3)	163(3)	153 (4)	168(4)	150(5)	169(5)
	22	588(11)	501(9)	505(11)	549(11)	500(11)	546(11)
	33	44(1)	36(1)	38(1)	43(1)	38(1)	43(1)
	12	−6(5)	44(4)	15(5)	16(5)	17(6)	16(6)
	13	23(1)	23(1)	19(1)	21(1)	18(2)	21(2)
	23	−3(2)	−2(2)	1(2)	2(2)	1(2)	1(2)
O(1)	11	257(3)	223(4)	218(2)	245(2)	217(3)	244(3)
	22	1041(11)	915(15)	945(10)	1019(10)	947(10)	1021(10)
	33	38(1)	34(1)	31(1)	38(1)	30(1)	38(1)
	12	149(4)	143(5)	146(3)	144(3)	146(4)	145(3)
	13	28(1)	21(1)	22(1)	27(1)	25(2)	28(1)
	23	11(2)	8(2)	12(2)	10(2)	10(2)	10(2)
O(2)	11	234(3)	217(4)	211(3)	240(3)	211(4)	239(4)
	22	994(10)	894(15)	918(10)	991(10)	918(10)	992(10)
	33	50(1)	43(1)	41(1)	48(1)	41(1)	48(1)
	12	162(4)	169(5)	159(4)	153(4)	157(5)	153(5)
	13	40(1)	35(1)	36(1)	39(1)	36(1)	39(1)
	23	13(2)	6(2)	11(2)	10(2)	11(2)	11(2)
O(3)	11	238(4)	222(4)	201(3)	230(3)	197(4)	223(4)
	22	1025(16)	889(15)	991(12)	1066(12)	999(12)	1079(12)
	33	49(1)	42(1)	39(1)	46(1)	37(1)	43(1)
	12	102(5)	88(6)	110(4)	109(4)	109(4)	110(4)
	13	37(1)	35(2)	34(1)	38(1)	30(2)	32(2)
	23	21(3)	20(3)	20(2)	20(2)	25(2)	25(2)
H(1)	*B*			2·4(6)	3·5(6)	2·4(5)	3·2(5)
H(2)	*B*			4·0(5)	3·4(5)	4·1(5)	4·1(4)
H(3)	*B*			3·3(6)	4·7(6)	2·8(7)	4·3(7)

Table 5 (*cont.*)

Cyanuric acid

			ELS		DA	
		X-ray	STO	HF	STO	HF
C(2)	11	45(2)	36(2)	43(2)	37(2)	44(2)
	22	30(1)	22(1)	28(1)	24(1)	29(1)
	33	18(1)	14(1)	17(1)	14(1)	17(1)
	12	−2(1)	−2(1)	−2(1)	−2(1)	−2(1)
	13	18(1)	15(1)	18(1)	15(1)	18(1)
	23	2(1)	1(1)	2(1)	2(1)	2(1)
C(1)	11	58(3)	48(3)	55(3)	49(2)	56(3)
	22	28(2)	19(2)	26(2)	21(2)	27(2)
	33	23(1)	19(1)	22(1)	20(1)	22(1)
	13	25(1)	21(1)	24(1)	22(1)	25(1)
N(2)	11	81(2)	68(2)	79(2)	70(2)	80(2)
	22	25(1)	15(1)	22(1)	16(1)	23(1)
	33	23(1)	18(1)	22(1)	18(1)	22(1)
	12	−3(11)	−2(10)	−2(10)	−0(1)	−3(10)
	13	35(1)	29(1)	34(1)	30(1)	34(1)
	23	3(1)	3(1)	3(1)	3(1)	3(1)
N(1)	11	78(2)	65(2)	75(2)	67(2)	77(2)
	22	18(2)	11(2)	18(2)	10(2)	16(2)
	33	20(1)	15(1)	19(1)	16(1)	20(1)
	13	31(1)	26(1)	30(1)	26(1)	31(1)
O(2)	11	85(1)	70(2)	83(2)	71(1)	84(2)
	22	35(1)	24(1)	34(1)	25(1)	35(1)
	33	24(1)	17(1)	23(1)	18(1)	23(1)
	12	−3(1)	−3(1)	−3(1)	−3(1)	−3(1)
	13	36(1)	30(1)	35(1)	30(1)	36(1)
	23	4(1)	−4(1)	−4(1)	−4(1)	−4(1)
O(1)	11	111(2)	99(2)	112(2)	100(2)	113(2)
	22	23(1)	11(2)	22(2)	12(2)	23(2)
	33	41(1)	35(1)	41(1)	36(1)	42(1)
	13	50(1)	45(1)	50(1)	46(1)	51(1)
H(2)	*B*	1·2(2)	0·2(4)	−0·2(3)	1·0(4)	0·6(4)
H(1)	*B*	1·8(4)	0·2(5)	0·3(5)	1·4(5)	1·6(5)

Comparison of net atomic charges obtained with ELS *and* DA *methods*

The charges obtained for the carbon, nitrogen, and oxygen atoms with the ELS and DA methods are quite similar, as shown for oxalic acid dihydrate in Table 4. But when a considerable discrepancy is found between core and valence-shell positions, adjacent hydrogen-atom charges may be affected substantially. In the water molecule, for example, the shift of the valence shell of the oxygen atom (Fig. 2) is towards H(3). As a result, the apparent charge on this hydrogen atom decreases, while that on H(2) increases. The splitting of core and valence shell makes the 'atomic charge' a less well-defined quantity in the DA method: it is no longer the sum of the electron density centered at the atomic position. It follows that the ELS method should be selected when the molecular charge density is to be subdivided into atomic charges.

Temperature factors

Since it has been observed many times that X-ray temperature factors are affected by bonding (see references in the Introduction), the ELS and DA temperature factors are worth examining. The following trends are evident in all three compounds discussed here (Table 5 and Little *et al.*, 1971):

(1) The effect of the separate refinement of the valence shell position is minimal; ELS and DA temperature factors are very similar provided the same basic sets were used.

(2) HF temperature factors are sometimes smaller or sometimes larger than the conventional X-ray temperature factors.* But there is no clear correlation between atomic charge and the sign of the difference. This suggests that the neglect of ionicity has only a small effect, if any, on temperature factors, since the HF form factors are comparable to the curves used in conventional refinements.

(3) STO temperature factors are always smaller than those from the conventional X-ray refinement and closer to the neutron values. They are also smaller than the corresponding values obtained with HF form factors,

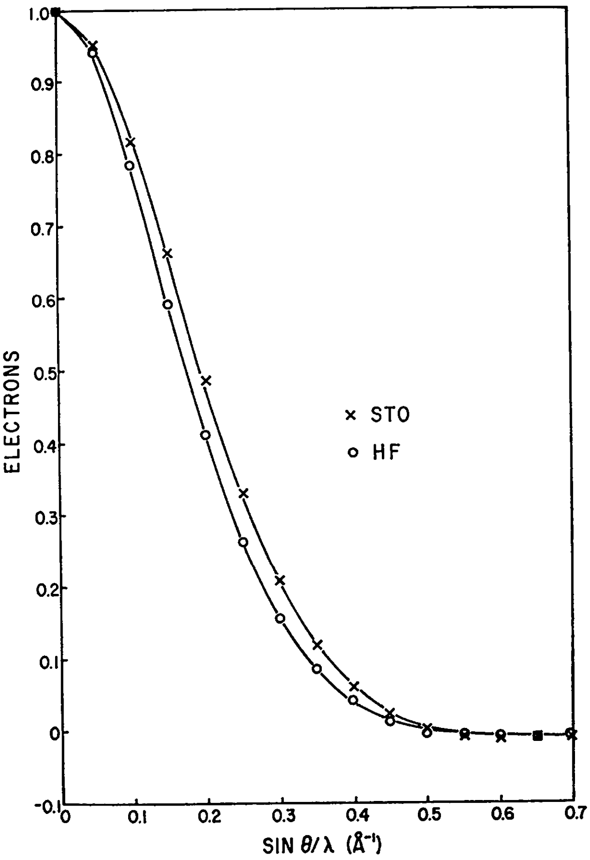

Fig. 5. Normalized valence-shell form factors for the carbon atom. HF: isolated-atom Hartree–Fock wave function. STO: molecule optimized Slater-type orbitals (Hehre, Stewart & Pople, 1969).

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* Form factors used in the conventional refinements were as follows: in cyanuric acid and tetracyanoethylene, C (ground state) and N as given in *International Tables for X-ray Crystallography* (1962); in oxalic acid, C and O as given by Cromer & Waber (1965); hydrogen form factors according to Stewart, Davidson & Simpson (1965) were used for oxalic acid and cyanuric acid.

which is curious because the optimized STO's generally correspond to *more compact* valence shells than the HF orbitals (as illustrated by the scattering factors for carbon, given in Fig. 5). A possible explanation lies in the observation that the scale factors from the STO refinements are consistently lower than those from the HF treatments (cyanuric acid: STO 9·49, HF 9·85; oxalic acid: STO 0·774, HF 0·842; TCNE:STO 2·16, HF 2·31; k defined by $F_o = kF_c$). This correlation between scale factors and temperature factors allows form-factor errors to be compensated for by adjusting the apparent thermal motion. The STO form factors give better agreement factors, so the lower values of the thermal parameters are more likely to be correct. This view is supported by the improved comparison with the neutron temperature factors.

Joint refinement of X-ray and neutron data

It was suggested by Duckworth, Willis & Pawley (1969) that X-ray and neutron data should be subjected to a joint refinement in which one set of temperature parameters, but two sets (X-ray and neutron) of positional parameters, are refined. The DA refinement offers an extension of such a treatment, because the core and neutron positions can be taken as identical, while the valence-shell position is defined from the X-ray data alone. Also, allowance for net charges, and selection of molecule-optimized atomic orbitals (*e.g.*, STO's of Hehre *et al.*, 1969) justifies use of a single set of temperature factors, as evidenced by the better agreement between STO and neutron diffraction temperature factors obtained in this study.

Conclusion

We conclude that the DA refinement can lead to a determination of the nuclear positions of first-row atoms from the X-ray data alone. Deficiencies in the spherical valence-shell approximation that is used become apparent when a large fraction of the data is from the high-order region. Discrepancies between the conventional X-ray and DA core positions are about 0·01 Å or smaller. In discussions of molecular geometry, they can be ignored unless great accuracy is required. As described here, the method does not give nuclear positions of the hydrogen atoms, which have only valence-electron density. A conceivable extension would be the use of a polarized hydrogen atom as proposed by Hirshfeld & Rabinovich (1967).

The better agreement with the neutron temperature parameters, obtained when molecule-optimized STO's are used in calculating valence scattering, supports the use of these form factors as a way to reduce the effect of bonding on temperature parameters.

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