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Electron Population Analysis of Accurate Diffraction Data. II. Application of One-Center Formalisms to Some Organic and Inorganic Molecules

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Abstract: A number of different one-center models have been applied in a charge-density refinement of accurate X-ray and neutron diffraction data on oxalic acid dihydrate, cyanuric acid, tetracyanoethylene, the tetracyanoethylene–perylene complex, and [*N*,*N*′-di(2-aminoethyl)malondiamidato]nickel(II) trihydrate. Self-consistent-field isolated-atom and molecule-optimized Slater-type minimal basis sets were used to obtain a description of the atomic charge densities. A parameter has been defined which measures the deformation of the atomic charge density from spherical symmetry. Where feasible, results have been compared with predictions made by INDO calculations. Reasonable agreement between theory and experiment is obtained for net atomic charges but not for the atomic deformations. The results for the nickel complex indicate a small positive charge (about ±0.5 electron) on the nickel atom. For the TCNE–perylene complex asymmetry of charge is observed in the perylene moiety which should be absent in the isolated molecule. Net atomic charges for the atoms of the water molecules in the two hydrates agree well with each other.

Though X-ray diffraction determines the electron distribution rather than the atomic positions in a crystal, relatively little attention has been given to a detailed study of the charge distribution because most experimental data have not been of sufficient quality for such a study. However, with the advance of automatic diffractometers and new data-processing techniques, both the quantity of data and their quality have improved. As a result electron-density studies have received renewed attention.[1–10]

In a preceding article we have discussed formalisms for the least-squares refinement of parameters describing the electron-density distribution.[11] In the present manuscript some of those formalisms are applied to diffraction data on small and medium-sized molecules. We shall first briefly review the different levels of treatment of the data and then give a number of applications, illustrating both the strength and the limitations of the methods.

Charge-Density Models

In conventional X-ray crystallography all atoms are assumed to have spherical symmetry and net charges equal to zero (or equal to a fixed integer number, in the case of a monatomic ion). It has been realized recently

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that this assumption introduces measurable errors into the thermal parameters which describe the atomic thermal motion and to a lesser extent also in the positional parameters.[1,4,12] Evidence has been obtained through difference density maps which show extra density in the bonding and lone-pair regions of the molecules studied.[1,2,4–10] These difference maps can be analyzed further by integration of the charge density over well-defined areas around the atoms or around the midpoints of the bonds, as described by Coppens and Hamilton.[13] Alternatively, one may use least-squares techniques with an appropriate model to obtain a description of the charge density. The models which improve on the fixed-charge–spherical-atom method range from a spherical valence shell with variable electron occupancy to a full description of the molecular charge density by the elements of the first-order density matrix. They are briefly discussed below in increasing order of complexity. More detailed accounts have been published.[3,11]

(a) Use of a Spherically Averaged Valence Shell with Variable Occupancy. Following Stewart,[12] it may be assumed that the core electrons are not significantly perturbed by bonding, at least not within the limits of the X-ray experiment. It should be pointed out that this assumption does not exclude charge migrations in the region immediately surrounding the nucleus, which are smeared out anyway by the thermal motion of the molecules in the crystal. The occupancies of the valence shell can be determined by least squares after the positional and thermal parameters have been obtained from a conventional least-squares refinement (the L-shell projection method[12]). However, one may argue that, as the incorrect assumptions of the conventional refinement affect the thermal parameters, the charge densities obtained will in turn be affected by the initial approximations. We have therefore extended the L-shell projection method (the extended L-shell projection method, ELS) by refining simultaneously on all structural and thermal parameters, as well as on the valence-shell occupancies and the scale factor relating calculated and observed structure factors. In addition, the total number of electrons is constrained to be constant, so that the crystal will remain neutral during the refinement.

(b) Refinement of the One-Center Terms of the First-Order Density Matrix. A full description of the electron density in a molecule can be provided by a density-matrix formalism.[3] For example, if the molecular orbitals ψ_i are mutually orthogonal linear combinations of atomic orbitals ϕ_μ, with coefficients $C_{i\mu}$, the one-electron density function ρ is described by a summation of orbital products $\phi_\mu\phi_\nu$ each multiplied by an appropriate population coefficient $P_{\mu\nu}$

$$\psi_i = \sum_\mu C_{i\mu}\phi_\mu \tag{1}$$

$$\rho = 2\sum_\mu\sum_\nu\sum_i^{\text{occ}} C_{i\mu}C_{i\nu}\phi_\mu\phi_\nu \equiv \sum_\mu\sum_\nu P_{\mu\nu}\phi_\mu\phi_\nu \tag{2}$$

It is a first approximation beyond the spherical valence-shell treatment to include in the refinement only those terms in (2) for which ϕ_μ and ϕ_ν are centered on the same atom. In the general case there are ten such one-center products for each atom, but further analysis has shown that it is not possible to refine simultaneously on the occupancies of $\phi(2s)$ and $\phi(p_x)$, $\phi(p_y)$, and $\phi(p_z)$, because the X-ray scattering of the sum of the last three terms is indistinguishable from the spherical $2s^2$ product.[11] Even when the population of $2s^2$ product is kept constant, further problems arise from the interaction between the population parameters and the parameters describing the thermal motion of the molecule in the crystal. In other words, it is difficult to distinguish, from the X-ray data alone, if an asymmetry is due to a preferential population of a certain orbital product or to anisotropy in the thermal vibrations. This difficulty can be eliminated, however, when the thermal parameters have been determined independently by neutron diffraction, because neutrons are scattered by the atomic nuclei, which are exactly spherical at X-ray resolution, rather than by the electrons. In applying nonspherical atomic scattering formalisms we have restricted ourselves to crystals for which both accurate X-ray and neutron data are available. The total electron density is again constrained for the crystal to remain neutral, while in contrast to earlier work[1b] the scale factor is varied together with the other parameters. It should be emphasized that use of one-center terms alone allows for asphericity of the atomic charge cloud,[11] but does not explicitly account for the overlap density between bonded atoms, which has frequently been observed in density difference maps.[1,2,4–10]

(c) Refinement of the One-Center Terms and the Two-Center Terms of Orbitals Centered on Adjacent Atoms. Since the available experimental evidence indicates that overlap density accumulates between adjacent atoms, it is a reasonable extension of the one-center model to add only those orbital products $\phi_\mu\phi_\nu$ to the scattering formalism for which ϕ_μ and ϕ_ν are centered on adjacent atoms. Even with this restriction an appreciable increase in the number of parameters occurs.[11]

A further complication arises from the thermal averaging in the crystal. It is not obvious how atomic thermal parameters obtained from neutron diffraction analysis are to be applied to an electron density concentrated between atoms. An approximation has been described[11] which has not yet been fully tested. At present we shall discuss models incorporating only one-center density terms in an attempt to assess their usefulness and limitations.

Use of Different Minimal Basis Sets

The experimental results, presented here, are only meaningful in terms of the atomic orbitals to which they refer. The situation is analogous to the charge integration over molecular regions; the number of electrons in a certain area may depend rather strongly on the integration boundaries. To investigate the dependence of the results on the choice of basis set, the refinements have been performed with more than one minimal basis set whenever possible.

The core was frozen at the self-consistent-field Hartree–Fock (HF) density, except for some test calculations with the one-center density-matrix formalism in which Slater-type orbitals (STO) with a single-ζ value were used[14] (ζ is defined by $\phi_{1s} = N_{1s}e^{-\zeta r}$, where N_{1s} is a

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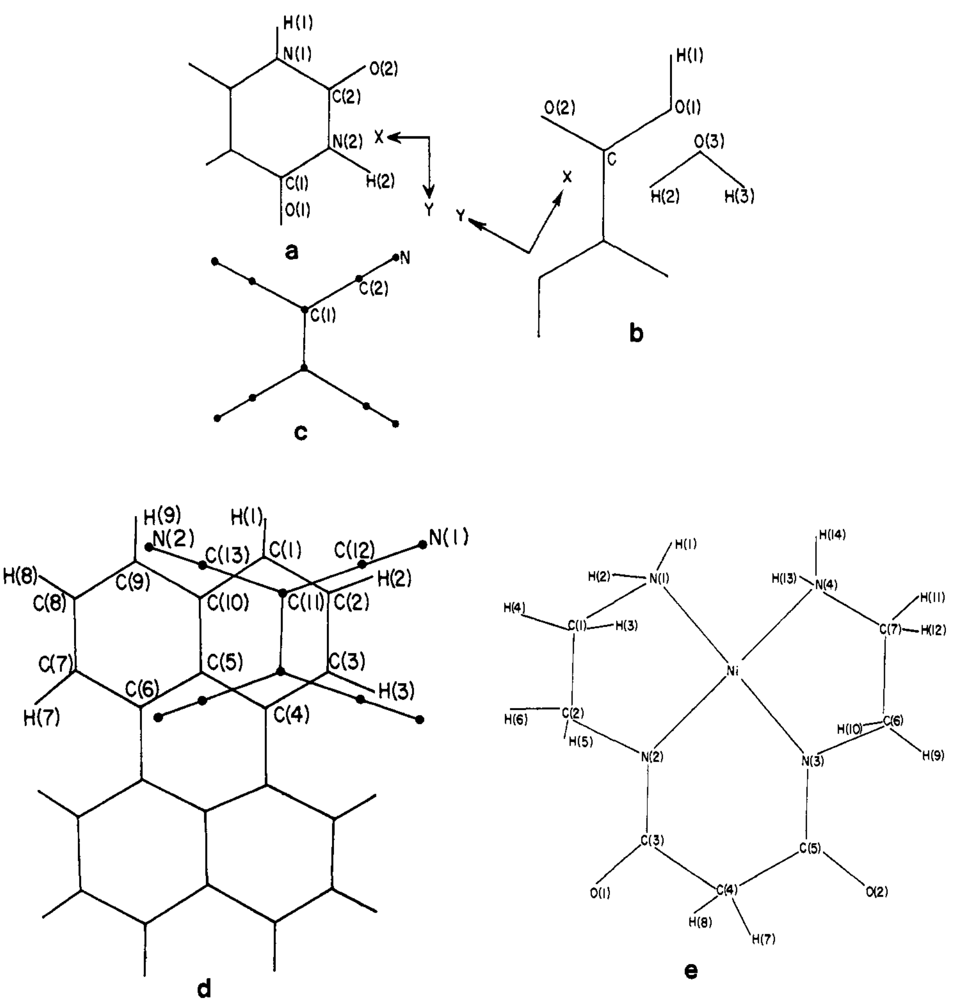

Figure 1. Numbering of the atoms: (a) cyanuric acid, (b) oxalic acid dihydrate, (c) tetracyanoethylene, (d) tetracyanoethylene–perylene, (e) [*N*,*N*′-di(2-aminoethyl)malondiamidato]nickel(II).

normalization factor, and similar expressions apply for ϕ_{2s} and ϕ_{2p}).

The results labeled HF are obtained with isolated-atom Hartree–Fock valence-shell wave functions, while for those labeled STO valence shells with molecule-optimized molecular exponents[15] were employed. Hydrogen atom wave functions are contracted to give a best fit to the bonded hydrogen atom in the H_2 molecule, as proposed by Stewart, Davidson, and Simpson.[16]

A number of test calculations showed that charges obtained with the H_2-fitted hydrogen wave functions are almost equal to those obtained with an STO hydrogen atom with orbital exponent $\zeta = 1.24$ (au)$^{-1}$, the differences being a fraction of the experimental standard deviations.

INDO calculations with the molecule-optimized,[15] rather than standard Slater exponents showed that net atomic charges for C, N, and O are fairly independent of a variation of exponents (Table III).

Results

We have applied the models discussed above to a number of molecules for which accurate diffractometer data were available. The selection discussed here covers a fairly wide range of chemical interest and includes some small organic molecules (cyanuric acid, oxalic acid monohydrate, tetracyanoethylene), a charge-transfer complex (tetracyanoethylene–perylene), and an inorganic complex ([*N*,*N*′-di(2-aminoethyl)malondiamidato]nickel(II) trihydrate); details of the crystal structures of these compounds are discussed elsewhere (see references under the specific compound). The numbering of the atoms referred to in the text and the tables is defined in Figure 1.

Treatment of the Data. All the data used were corrected for absorption by numerical integration over the volume of the crystal, except the tetracyanoethylene Mo Kα data, for which test calculations showed absorption to vary by less than 0.5%.

In all cases allowance for extinction was made. In the case of cyanuric acid this was done by comparison of the intensities of a small and a large crystal,[7] while for the other compounds extinction was included as a variable in the least-squares program.[17] For the oxalic acid data, which were most affected, extinction was markedly anisotropic (see discussion in ref 4b and 17). For the other compounds studied, extinction was less severe and adequately described by a single isotropic parameter.

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Table I. Cyanuric Acid, Valence–Charge Correlation Coefficients[a]

	k	C(2)	C(1)	N(2)	N(1)	O(2)	O(1)	H(2)	H(1)
C(2)	−0.77								
C(1)	−0.68	0.75							
N(2)	−0.76	0.79	0.62						
N(1)	−0.69	0.62	0.68	0.66					
O(2)	−0.83	0.75	0.73	0.72	0.59				
O(1)	−0.80	0.77	0.72	0.79	0.66	0.77			
H(2)									
H(1)									

[a] Only coefficients larger than 0.5 have been entered in the table; k = scale factor relating observed and calculated structure factors ($F_o = kF_c$). Values obtained when neutrality constraint is not applied.

All data were diffractometer collected and for all crystals except those of the Ni complex at least two full symmetry-equivalent parts of reciprocal space were measured to reduce experimental errors. For the nickel complex full duplication was too time consuming, but a check on experimental accuracy was obtained by collecting 146 reflections a second time at symmetry-equivalent positions. The agreement may be described by an internal consistency factor R summed over all structure factors F measured more than once, and defined as $R = \Sigma|F^2 - \langle(F^2)\rangle|/\Sigma\langle(F^2)\rangle$. Typical values are 2.9% (nickel complex), 1.8% (tetracyanoethylene), and 1.6% (TCNE–perylene). Symmetry-equivalent reflections were averaged to obtain a unique data set for the least-squares refinements.

Table II. Net Atomic Charges in α-Oxalic Acid Dihydrate[a]

	Extended L-shell method		One-center model		
	HF	STO	HF	STO	INDO calcd
C(1)	+0.06 (3)	+0.16 (3)	+0.07 (7)	+0.23 (2)	+0.43
O(1)	−0.25 (3)	−0.29 (3)	−0.31 (6)	−0.36 (2)	−0.28
O(2)	−0.25 (6)	−0.30 (3)	−0.26 (3)	−0.32 (2)	−0.33
O(3)	−0.25 (4)	−0.23 (6)	−0.42 (4)	−0.43 (2)	−0.32
H(1)	+0.23 (6)	+0.29 (4)	+0.27 (3)	+0.29 (2)	+0.19
H(2)	+0.20 (4)	+0.08 (4)	+0.25 (3)	+0.22 (2)	+0.16
H(3)	+0.25 (5)	+0.28 (5)	+0.39 (3)	+0.37 (2)	+0.16
R, %[b]	2.1	2.0	3.3	2.3	
R_w, %	2.0	1.9	3.1	2.2	
No. of observations	548	548	548	548	
No. of variables	62	62	40	40	

[a] HF = Hartree–Fock basis set, STO = molecule-optimized Slater-type orbitals. [b] Here and in the other tables $R = \Sigma|F_o - |F_c||/\Sigma F_o$ and $R_w = \{(\Sigma w|F_o - |F_c||^2)/\Sigma wF_o^2\}^{1/2}$. Note that the agreement factors for the one-center model are higher because the positional and temperature parameters are kept fixed at the neutron values.

Standard Deviations. The standard deviations of the net atomic charges are those obtained from the least-squares variance–covariance matrix. To assess the significance of a difference Δ between the charges e_1 and e_2 on two atoms it is necessary to take into account correlation between parameters according to the following expression for the standard deviation σ

$$\sigma^2(e_1 - e_2) = \sigma^2(e_1) + \sigma^2(e_2) - 2r_{e_1e_2}\sigma(e_1)\sigma(e_2) \quad (3)$$

in which $r_{e_1e_2}$ is the correlation coefficient. *For the spherical charge refinements* many of the correlation coefficients between charges are large and positive when the neutrality constraint is not applied. As an example, the correlation coefficients for one of the cyanuric acid refinements are given in Table I. The correlation between the scale factor and the charges is negative. The magnitude of the correlation is a direct consequence of the simultaneous refinement on both charges and scale factor.

The implication of (3) is that *the difference between two charges is much more accurately known than their sum.* But when the variance–covariance matrix is modified to account for the constraint, the correlation coefficients between the net charges and between the scale factor and the charges are considerably reduced. For example, for cyanuric acid the only remaining correlation coefficient of this type with an absolute value larger than 0.5 (−0.52) is between the charges on O(1) and H(2).

Oxalic Acid Dihydrate.[4] Interpretation of the diffraction data[4b,c] on the α modification of oxalic acid dihydrate using Fourier-map techniques was discussed in a recent article.[4a] Results of one-center least-squares methods are summarized in Table II.

It is significant that all the experimental methods give positive net charges on the carbon and hydrogen atoms and negative charges on all oxygen atoms, in agreement with results from the semiempirical INDO method. Sign and magnitude of the charges obtained with the ELS method are rather closely confirmed by the aspherical one-center treatment. The standard deviations and correlations for the results of the latter treatment are smaller, because additional experimental information (from neutron diffraction) was used.

Differences between the basis functions used have a predictable effect. Thus, the STO carbon orbitals are considerably more contracted than the Hartree–Fock values, leading to less density on the carbon atoms. The oxygen orbitals in the two sets are almost identical. When an isolated-hydrogen-atom basis function was used with the HF set instead of the contracted function (results not included in the table), somewhat smaller positive charges were obtained for the hydrogen atom.[1b]

Cyanuric Acid. Results of the charge refinement of the liquid nitrogen temperature diffraction data on cyanuric acid[7,8] are listed in Table III. Also included are values obtained by Stewart, who applied the L-shell projection method (without the simultaneous refinement on structural parameters) to the same data set.[12] All

Table III. Net Atomic Charges in the Cyanuric Acid Molecule[a]

	Extended L-shell method		L-shell (Stewart)		One-center model		Calcd standard exponents	INDO optimized exponents
	HF	STO	HF	STO	HF	STO		
C(2)	+0.08 (4)	+0.27 (3)	+0.07 (7)	+0.41 (5)	+0.00 (7)	+0.21 (6)	+0.54	+0.49
C(1)	+0.15 (6)	+0.38 (5)	+0.18 (9)	+0.52 (7)	+0.09 (9)	+0.26 (8)	+0.54	+0.49
N(2)	−0.13 (4)	−0.31 (4)	−0.20 (6)	−0.38 (6)	−0.10 (6)	−0.34 (6)	−0.28	−0.25
N(1)	−0.16 (5)	−0.37 (5)	−0.12 (8)	−0.33 (7)	−0.04 (7)	−0.23 (7)	−0.28	−0.25
O(2)	−0.12 (3)	−0.07 (3)	−0.00 (4)	−0.21 (4)	−0.16 (4)	+0.02 (4)	−0.42	−0.39
O(1)	−0.24 (3)	−0.22 (3)	−0.10 (5)	−0.27 (5)	−0.07 (5)	−0.03 (5)	−0.42	−0.39
H(2)	+0.21 (4)	+0.15 (4)	+0.10 (4)	+0.15 (3)	+0.15 (3)	+0.06 (3)	+0.16	+0.15
H(1)	+0.16 (5)	+0.13 (5)	+0.08 (5)	+0.11 (4)	+0.21 (5)	+0.11 (5)	+0.16	+0.15
R, %	3.6	3.4			3.7	4.4		
R_w, %	3.2	3.0			3.5	4.0		
No. of observations	933	933			933	933		
No. of variables	57	57			45	45		

[a] HF = Hartree–Fock basis set, STO = molecule-optimized Slater-type orbitals.

Table IV. Net Atomic Charges in TCNE and TCNE–Perylene

	TCNE			TCNE–perylene	
	HF	STO		HF	STO
C(1)	+0.19 (2)	+0.20 (2)	C(5)	−0.17 (4)	−0.07 (4)
C(2)	−0.34 (3)	−0.09 (3)	C(6)	−0.07 (4)	−0.01 (4)
N	+0.25 (2)	−0.01 (3)	C(7)	+0.10 (7)	+0.11 (7)
			C(8)	+0.53 (9)	+0.55 (8)
			C(9)	−0.24 (10)	−0.11 (9)
			C(10)	−0.19 (5)	−0.09 (5)
R, %	7.3	6.6	H(1)	−0.23 (8)	−0.32 (9)
R_w, %	4.9	4.5	H(2)	−0.09 (8)	−0.17 (8)
No. of observations	428	428	H(3)	−0.04 (7)	−0.13 (7)
			H(7)	+0.10 (6)	−0.11 (7)
No. of variables	21	21	H(8)	+0.02 (8)	−0.11 (8)
			H(9)	−0.26 (7)	−0.23 (8)
	TCNE–perylene				
C(11)	−0.00 (3)	+0.04 (3)	*R*, %	3.6	3.5
C(12)	−0.09 (5)	+0.04 (5)	R_w, %	3.2	3.1
C(13)	+0.07 (6)	+0.11 (5)	No. of observations	1181	1181
N(1)	+0.14 (5)	−0.04 (5)			
N(2)	+0.16 (5)	−0.02 (5)	No. of variables	183	183
C(1)	+0.38 (9)	+0.41 (8)			
C(2)	+0.13 (9)	+0.22 (8)			
C(3)	−0.08 (7)	−0.02 (7)			
C(4)	−0.16 (4)	−0.08 (4)			

methods agree that the carbon and hydrogen atoms bear positive charges, while the nitrogen and oxygen atoms tend to be negative, with some nonsignificant exceptions obtained with the HF basis set.

Qualitative agreement is found with the results of the INDO calculations, though the charges on the carbon and oxygen atoms are generally observed smaller than the calculated values.

In principle the observed and calculated charges may differ because the latter refer to the isolated molecule. However, uncertainties in both sets could easily be larger than the effect of intermolecular interactions in the cyanuric acid crystal.

Tetracyanoethylene and the Tetracyanoethylene–Perylene Complex. Crystallographic data on the cubic modification of tetracyanoethylene (TCNE) and the tetracyanoethylene–perylene complex were collected on an automatic diffractometer.[18,19] The results of the extended L-shell refinements on both data sets are given in Table IV. The signs of the charges in the TCNE molecule are very sensitive to the choice of basis set, which may reflect the shortness of the CN triple bond. For example, a small part of the carbon density could be included in the charge on the adjacent nitrogen atom as a result of change in the nitrogen-orbital wave functions. The charges in the perylene molecule are more consistent. It is interesting that they do not have the symmetry of the isolated molecule. Especially large differences are observed for the atoms C(1) and C(9). This asymmetry is not surprising as the TCNE molecule lies in a very asymmetric position above the perylene molecule (Figure 1). Thus, the perylene density may very well be disturbed by the interaction in the complex, but no sufficiently detailed calculation is available to allow comparison with theory. A further peculiarity of the results is that all the hydrogen atoms are negatively charged, in contrast to the results for all the other molecules investigated in this study. At present one can only speculate as to the meaning of this observation.

[*N*,*N*′-Di(2-aminoethyl)malondiamidato]nickel(II) Trihydrate. Diffraction data on this compound[20] were collected as part of a program to correlate structural and thermodynamic data on inorganic complexes. In the absence of reliable core and valence-shell scattering factors for the Ni atom we have used a core corresponding to the Ni^{2+} ion, the scattering factor of which is known,[21] and a valence-shell scattering factor equal to the difference between the scattering factors for neutral Ni and Ni^{2+}.[21] As the nickel scattering factors are for the isolated atom (ion), the Hartree–Fock set of scattering factors was used for C, N, and O.

The molecule of this nickel complex is relatively large. To economize on computer time the light-atom parameters were taken from the last cycle of the conventional refinement, while the nickel parameters were refined together with all valence charges and the scale factor. The results, together with those of the L-shell refinement with all parameters constant, are listed in Tables V and VI. Some interesting conclusions can be drawn.

First, the nickel atom does not seem to bear a dipositive charge, as would be implicit in an ionic formula. The experimental value of about +0.5 electron indicates a partial neutralization of the nickel atom.

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Table V. [*N*,*N*′-Di(2-aminoethyl)malondiaminato]nickel(II) Trihydrate Charges Obtained with HF Basis Set

	L-shell	Extended L-shell[a]		L-shell	Extended L-shell
Ni	+0.69 (17)	+0.46 (17)	H(3)-C(1)	+0.06 (5)	+0.03 (5)
N(1)	−0.32 (7)	−0.24 (7)	H(4)-C(1)	+0.06 (5)	+0.08 (5)
N(2)	−0.31 (6)	−0.30 (6)	H(5)-C(2)	+0.08 (5)	+0.06 (5)
N(3)	−0.37 (6)	−0.32 (6)	H(6)-C(2)	+0.05 (5)	+0.05 (5)
N(4)	−0.16 (6)	−0.11 (6)	H(7)-C(4)	+0.13 (6)	+0.13 (6)
C(1)	−0.15 (9)	−0.10 (8)	H(8)-C(4)	+0.11 (5)	+0.09 (5)
C(2)	−0.18 (9)	−0.12 (8)	H(9)-C(6)	+0.05 (5)	+0.06 (5)
C(3)	+0.17 (8)	+0.14 (8)	H(10)-C(6)	+0.01 (5)	+0.01 (5)
C(4)	−0.29 (9)	−0.26 (9)	H(11)-C(7)	+0.08 (5)	+0.08 (5)
C(5)	+0.26 (8)	+0.18 (8)	H(12)-C(7)	+0.13 (5)	+0.10 (5)
C(6)	−0.05 (8)	−0.09 (8)	H(13)-N(4)	+0.16 (5)	+0.15 (5)
C(7)	−0.10 (8)	−0.09 (8)	H(14)-N(4)	+0.24 (6)	+0.19 (6)
O(1)	−0.37 (5)	−0.31 (5)	H(15)-O(3)	+0.20 (6)	+0.17 (6)
O(2)	−0.51 (5)	−0.43 (5)	H(16)-O(3)	+0.14 (6)	+0.13 (6)
O(3)	−0.31 (6)	−0.22 (5)	H(17)-O(4)	+0.20 (6)	+0.18 (6)
O(4)	−0.33 (5)	−0.26 (5)	H(18)-O(4)	+0.18 (6)	+0.15 (6)
O(5)	−0.28 (6)	−0.19 (6)	H(19)-O(5)	+0.24 (7)	+0.19 (6)
H(1)-N(1)[b]	+0.11 (5)	+0.11 (5)	H(20)-O(5)	+0.20 (6)	+0.19 (6)
H(2)-N(1)	+0.16 (6)	+0.11 (6)			
R, %	4.5	4.4	4.6[c]		
R_w, %	4.2	4.0	4.5		
No. of observations	3325	3323			
No. of variables	39	48			

[a] Only the positional and thermal parameters of the nickel atom were refined. [b] The second atom indicates the atom to which hydrogen is bonded. Oxygen atoms 3, 4, and 5 belong to water molecules. [c] Before charge refinement.

Table VI. Change in Nickel Parameters on Charge Refinement[a]

Parameter[b]	A	B
x	0.28223 (4)	0.28223 (3)
y	0.08195 (3)	0.08195 (3)
z	0.10805 (1)	0.10805 (1)
β_{11}	0.00895 (5)	0.00922 (5)
β_{22}	0.00401 (3)	0.00418 (3)
β_{33}	0.000950 (8)	0.000992 (7)
β_{12}	0.00005 (3)	0.00004 (3)
β_{13}	0.00080 (1)	0.00083 (1)
β_{23}	−0.00013 (1)	−0.00013 (1)

[a] Column A gives results of conventional refinement; column B gives results of charge-density refinement. [b] x, y, and z are in fractional coordinates. The β_{ij}'s are the coefficients in the following expression for the temperature factor: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

In the extended L-shell refinement the nickel temperature factors increase by about 3.5% while positional parameters remain constant (Table VI). There is a corresponding decrease in the positive charge on the nickel. Thus, a slightly larger number of electrons are more smeared out by thermal motion, a typical example of the interaction between thermal parameters and experimental charges, which demonstrates the necessity of the simultaneous refinement on both sets of parameters whenever feasible.

The oxygen atoms and nitrogen atoms are again negative, while the carbon and hydrogen atoms bear larger positive charges when bonded to the electronegative oxygen and nitrogen atoms. The carbon atoms are slightly negative except for C(5) and C(7), which belong to the carbonyl group of the malonate moiety.

Definition of an Atomic Deformation Parameter. In addition to net atomic charges the one-center population parameter model provides a description of the deformation of the atomic charge density from spherical symmetry. To obtain a measure of this deformation for comparison with theory, one may define an atomic deformation parameter

$$\eta = \left(\int_{\text{atom}} (\langle\rho_{\text{sph}}\rangle - \rho_{\text{obsd}})^2 \mathrm{d}\tau\right)^{1/2} \tag{4}$$

in which $\langle\rho_{\text{sph}}\rangle$ is the spherically averaged atomic density, including the net atomic charge if present, while ρ_{obsd} is the density that corresponds to the experimental population parameters $P_{\mu\nu}$. If

$$\Delta P_{\mathrm{p}_i\mathrm{p}_i} = \frac{P_{\mathrm{p}_x\mathrm{p}_x} + P_{\mathrm{p}_y\mathrm{p}_y} + P_{\mathrm{p}_z\mathrm{p}_z}}{3} - P_{\mathrm{p}_i\mathrm{p}}$$

we obtain

$$\begin{aligned}\eta^2 = {} & (\Delta P_{\mathrm{p}_x\mathrm{p}_x}{}^2 + \Delta P_{\mathrm{p}_y\mathrm{p}_y}{}^2 + \Delta P_{\mathrm{p}_z\mathrm{p}_z}{}^2)\int \phi^4(\mathrm{p}_x)\mathrm{d}\tau + \\ & (P_{\mathrm{p}_x\mathrm{p}_y}{}^2 + P_{\mathrm{p}_x\mathrm{p}_z}{}^2 + P_{\mathrm{p}_y\mathrm{p}_z}{}^2 + 2\Delta P_{\mathrm{p}_x\mathrm{p}_x}P_{\mathrm{p}_y\mathrm{p}_y} + \\ & 2\Delta P_{\mathrm{p}_x\mathrm{p}_x}P_{\mathrm{p}_z\mathrm{p}_z} + 2P_{\mathrm{p}_y\mathrm{p}_y}P_{\mathrm{p}_z\mathrm{p}_z})\int \phi^2(\mathrm{p}_x)\phi^2(\mathrm{p}_y)\mathrm{d}\tau + \\ & (P_{\mathrm{sp}_x}{}^2 + P_{\mathrm{sp}_y}{}^2 + P_{\mathrm{sp}_z}{}^2)\int \phi^2(\mathrm{s})\phi^2(\mathrm{p}_x)\mathrm{d}\tau \end{aligned} \tag{5}$$

The definition of η is convenient, as the integrals can be easily evaluated for Slater-type orbitals. For Hartree–Fock SCF orbitals one may obtain approximate values for η by using the best single-ζ values given by Clementi and Raimondi.[14] In principle the deformation parameter defined in (4) provides a measure of the validity of the spherical valence-shell models. But it should be kept in mind that in the ELS method deviations from spherical symmetry can be partially allowed for by an adjustment of the anisotropic temperature parameters.

Deformation parameters obtained in the one-center refinements of oxalic acid and cyanuric acid and in corresponding INDO calculations are listed in Table VII. Experimentally, much less variation in the deformation is found than predicted. Thus, the calculations predict the carbon atoms in these compounds to be close to spherically symmetric and the oxygen atoms to be highly

Table VII. Deformation Parameters (electrons) $\eta = (\int_{\text{atom}} (\langle\rho_{\text{sph}}\rangle - \rho_{\text{obsd}})^2 d\tau)^{1/2}$ for Oxalic Acid Dihydrate and Cyanuric Acid

	Exptl		Calcd INDO (exptl geometry)	
	HF	STO		
		Oxalic Acid		
C	0.08	0.06	0.03[a]	
O(1)	0.07	0.07	0.37	
O(2)	0.10	0.09	0.37	
O(3)	0.13	0.16	0.16	
		Cyanuric Acid		
C(2)	0.07	0.07	0.02[a]	0.02[b]
C(1)	0.07	0.07	0.02	0.02
N(2)	0.06	0.04	0.09	0.10
N(1)	0.06	0.04	0.09	0.10
O(2)	0.13	0.10	0.38	0.37
O(1)	0.07	0.06	0.36	0.35

[a] Values in this column refer to standard exponents. [b] Values in this column refer to optimized exponents.

aspherical, while the experimental difference between the two types of atoms is rather small. It is interesting that good agreement with theory is obtained for the oxygen atom of the water molecule in oxalic acid dihydrate, but not for the other oxygen atoms.

The comparison is complicated by the neglect of the bond density in both the calculations and the experimental model. Thus, the experimental one-center parameter will, to some extent, reflect the presence of density in the bonds. Since for a carbonyl oxygen atom such bond density occurs opposite the lone-pair region, its effect can be an apparent reduction in atomic sphericity. The increase in experimental distortion of the carbon atoms in cyanuric acid can be traced to a smaller population of the p_π^2 orbital products for the carbon atoms, which is also observed for the nitrogen atoms (Table VIII). (For the nitrogen the calculation predicts an excess π population. The reduction of this excess population decreases the atomic deformation.) This effect, which is not compensated by an increase in the π density (in terms of the basis sets used) on the oxygen atoms, indicates that the electron density in cyanuric acid is more concentrated in the molecular plane than predicted by the approximate calculation on the isolated molecule.

The Effect of Systematic Errors on the Accuracy of the Experimental Charges. One of the most difficult tasks in evaluating the results of the one-center charge refinements is the assessment of the effect of systematic errors in the data on these results.

Major sources of error would be incomplete allowance for absorption and secondary extinction. Fortunately, the numerical evaluation of the absorption correction is very accurate for weakly absorbing crystals,[22] while the Zachariasen extension of the kinematic theory of diffraction, which forms the basis of the extinction correction applied,[17] is accurate, at least when extinction is not excessive. Since, except for oxalic acid monohydrate, extinction is small in the data sets used here, extinction and absorption are not likely to be major sources of errors in the present results.

To some extent a check on systematic errors is also provided by the collection of symmetry-equivalent data sets (see above). However, certain errors may be the same for symmetry-equivalent reflections, like errors that are dependent on the Bragg angle θ.

Table VIII. σ and π Charges Obtained with Different Basis Sets

Atom	Method	s[a]	σ	π
		Cyanuric Acid		
C(2)	HF	1.00	2.36	0.64
	STO	1.00	2.18	0.61
	INDO	1.00	1.65	0.80
C(1)	HF	1.00	2.27	0.64
	STO	1.00	2.14	0.60
	INDO	1.00	1.66	0.80
N(2)	HF	1.21	2.73	1.12
	STO	1.21	2.90	1.23
	INDO	1.21	2.33	1.76
N(1)	HF	1.21	2.73	1.10
	STO	1.21	2.80	1.22
	INDO	1.21	2.35	1.74
O(2)	HF	1.78	3.05	1.33
	STO	1.78	2.89	1.31
	INDO	1.78	3.18	1.46
O(1)	HF	1.78	2.95	1.34
	STO	1.78	2.92	1.33
	INDO	1.78	3.18	1.46
		Oxalic Acid		
C	HF	1.00	2.22	0.71
	STO	1.00	1.96	0.82
	INDO	1.00	1.74	0.83
O(1)	HF	1.68	3.13	1.51
	STO	1.68	3.03	1.65
	INDO	1.68	2.75	1.85
O(2)	HF	1.77	3.12	1.37
	STO	1.77	3.00	1.55
	INDO	1.77	3.23	1.33

[a] The experimental population of the 2s orbitals has been adjusted to the theoretical values. Compensating changes have been made in the spherical average of the coefficients of the p_π^2 and p_σ^2 orbital products.

Here it is pertinent to point out that Stewart[12] has investigated the errors in the population parameters P that result from a bias in the thermal parameters B (such a bias is similar to θ-dependent errors). He has found the values of $\partial P/\partial B$ to be typically about 0.1 e Å^{-2}, which means that the effect of θ-dependent errors on the population parameters is weak.

An alternative approach is a passive check on experimental errors through an analysis of the internal consistency of the results, for example, by comparison of chemically, but not crystallographically, equivalent groups, or by comparing similar molecular fragments in different structures. This is possible because systematic errors in the data would generally not affect crystallographically nonequivalent parameters in the same way.

As summarized below and in Tables III, V, and VIII, charges on chemically comparable atoms generally agree well (within $3\sigma(\Delta e)$, σ's based on random errors only), indicating again that the effect of systematic errors is not predominant.

The one exception to this agreement is the charge asymmetry in perylene–TCNE, which could conceivably result from systematic errors rather than from the asymmetry of the complex.

Conclusions

The results presented show a certain consistency, which indicates that meaningful information on net charges can be obtained from accurate diffraction data. Thus, the water molecules in the [N,N'-di(2-amino-

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Table IX. Average Net Atomic Charges from Extended L-Shell Refinement

Water Molecule (HF Basis Set)

	Oxalic acid	Nickel complex			Av
O	−0.25	−0.22	−0.26	−0.19	−0.22
H	+0.20	+0.20	+0.20	+0.24	+0.20
H	+0.25	+0.14	+0.18	+0.20	

Carbonyl Oxygen Atom

Cyanuric acid		Oxalic acid	Nickel complex	
HF	STO			
−0.12	−0.07	−0.25	−0.31	−0.43
−0.24	−0.22	−0.30		

ethyl)malondiamidato]nickel(II) and oxalic acid crystals show very similar atomic charges (Table IX). A similar comparison can be made between carbonyl oxygens in oxalic acid, the nickel complex, and cyanuric acid (Table IX). Since the carbonyl groups are attached to different molecules, less close agreement is expected.

It is clear that a large amount of chemical information can be obtained from experimental atomic charges. Perhaps the most challenging results are the small positive charge on the nickel atom and the asymmetric charge distribution in the perylene moiety of the perylene–TCNE complex.

The deformation parameters from the one-center model provide a less obvious picture and it is quite likely that different results will be obtained when the two-center overlap terms are included in both the theoretical and experimental treatments.

The correlations between parameters observed in the extended L-shell refinement when the scale factor is included as a parameter indicate the desirability of a sufficiently accurate experimental determination of the scale factor.

We conclude that with further improvements in experimental and computational techniques (such as collection of accurate data at liquid helium temperatures and the inclusion of two-center terms in the model), a whole new area is becoming accessible to X-ray crystallographic methods.

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Application of Simple Theoretical Methods to the Solution of Chemical Problems. IV.[1] Hydrogen, Carbon-13, and Oxygen-17 Hyperfine Splitting Constants in Rigid Bicyclic Semidiones

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Abstract: An examination is made of the usefulness of the INDO–SCF molecular orbital method as a means of calculating long-range epr coupling constants and factoring them into the components due to various spin delocalization mechanisms. The rigid bicyclic semidione radical anions are employed as models. Satisfactory agreement is obtained between the experimental and calculated hfsc's for hydrogen and carbon atoms, although no attempts were made to optimize the geometry of the radicals. Several possible spin delocalization mechanisms are discussed and it is concluded that opposing mechanisms are operative, particularly for the γ protons, and that further application of this approximate theory should be of value.

The fine details of electron spin interactions in paramagnetic molecules or radicals and diradicals are of considerable interest in many aspects of radical reactions and reactivity, photochemistry, nmr and esr, etc. The nature of these interactions can be deduced to a certain extent from the dependence of the magnitude of the epr hyperfine splitting constant (hfsc) on the geometry of the radical or radical ion under investigation.[1,2] Experimentally, changes in geometry can be effected by substitution or, more satisfactorily, by forcing the radical to assume a rigid structure as a result of bridging within the molecule, the latter having recently been achieved for bicyclic and polycyclic radicals.[3–6] There are, however, some limitations inherent in trying to use these methods to predetermine the geometry of a radical. Upon substitution in flexible radicals, the exact conformer population is not known, possibly resulting in ambiguous or misleading interpretations.[7] Also, the substitution of a hydrogen by an alkyl group may have consequences

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