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Density-optimized radial exponents for X-ray charge-density refinement from *ab initio* crystal calculations

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Structure factors based on periodic density-functional (DFT) calculations on 25 molecular crystals have been used to evaluate trends in refined values of the κ and κ' expansion–contraction parameters of the Hansen–Coppens multipole formalism. As found previously and expected physically, the spherical-valence-shell κ parameters are closely related to the net atomic charges, negative atoms being expanded and *vice versa*. κ' parameters, which scale the radial dependence of the non-spherical deformation functions, are remarkably consistent for particular bonding environments. Systematic trends are observed for both carbon and oxygen, but the values obtained for nitrogen show a larger variation. Average values for oxygen and carbon in different bonding environments are tabulated and can be used whenever refinement of experimental data is affected by lack of uniqueness of the charge-density parameter set. Values for nitrogen must be more finely tuned to the specific bonding environment. The relation between atomic charge and κ offers the possibility of introducing a constraint in the charge-density refinement of very large molecules, for which reduction of the size of the parameter set may be essential.

1. Introduction

The general multipole formalism describes the charge density in the crystal as a superposition of the aspherical pseudoatoms. In the original Stewart (1976) density model, the charge density of each pseudoatom $\rho_{\rm at}(\mathbf{r})$ is expanded as

$$\rho_{\rm at}(\mathbf{r}) = \rho_{\rm core}(\mathbf{r}) + \sum_{l=0}^{l_{\max}} \sum_{m=0}^{l} P_{lm\pm} R_l(r) d_{lm\pm}(\theta, \varphi). \quad (1)$$

The first term, $\rho_{\rm core}(\mathbf{r})$, represents the spherically averaged Hartree–Fock (HF) density of the core and the second term represents the aspherical deformation density. The refined coefficients $P_{lm\pm}$ are the population parameters and the angular functions $d_{lm\pm}$ are the real spherical harmonics. The radial functions $R_l(r)$ have the form

$$R_l(r) = N r^{n_l} \exp(-\zeta r), \quad (2)$$

where N is the normalization factor, r is the radial coordinate and ζ is the radial exponent. The standard molecular (SM) values (Hehre *et al.*, 1969, 1970) for radial exponents ζ are usually taken as starting values, which then can be adjusted in the least-squares refinement.

In the Hansen–Coppens multipole formalism (Hansen & Coppens, 1978; Coppens, 1997), the density at each pseudoatom is modeled using the following expansion:

$$\rho_{\rm at}(\mathbf{r}) = P_{\rm core}\rho_{\rm core}(r) + P_{\rm valence}\kappa^3\rho_{\rm valence}(\kappa r) + \sum_{l=0}^{l_{\max}} \kappa'^3 R_l(\kappa' r) \sum_{m=0}^{l} P_{lm\pm} d_{lm\pm}(\theta, \varphi). \quad (3)$$

The first and second terms are the spherically averaged HF core and valence densities. The population of the core $P_{\rm core}$ is always fixed, while the population of the spherical valence shell $P_{\rm valence}$ is allowed to refine together with the κ expansion–contraction parameter. As a result of electron–electron repulsion and correlation, the κ parameter strongly correlates with the transfer of the net atomic charge (Coppens *et al.*, 1979; Brown & Spackman, 1991), a negative charge being accompanied by an expansion of the valence shell, $\kappa < 1$, and *vice versa*, *i.e.* $\kappa > 1$ for positively charged atoms. In more recent applications, the Stewart model has been modified to include a variable κ-scaled HF valence shell, which significantly reduces the differences between the two algorithms.

The third term is the aspherical deformation density, similar to that in the original Stewart model, except that the adjustment of the radial extent of the aspherical deformation-density functions is performed *via* refinement of the dimensionless expansion–contraction coefficients κ', with $\kappa' = 1$ corresponding to single-ζ exponents as given by Clementi & Raimondi (1963). The refinement of the κ' parameter in the

Table 1
Experimental κ' parameters for oxygen atoms reported in the literature.

Compound	Functional group	κ'	Reference
L-Dopa	Average in $-\text{CO}_2$	0.54	[1]
DL-Histidine	$-\text{CO}_2$	0.84, 0.42	[7]
DL-Proline·H_2O	Average in $-\text{CO}_2$	0.71	[7]
2-Methyl-4-nitroaniline	Average in $-\text{NO}_2$	0.95	[3]
p-Amino-*p*′-nitrobiphenyl	Average in $-\text{NO}_2$	0.85	[8]
p-Nitroaniline	Average in $-\text{NO}_2$	0.94	[8]
m-Nitrophenol	Average in $-\text{NO}_2$	1.11	[2]
L-Dopa	$-\text{C}-\text{OH}$	0.80	[1]
m-Nitrophenol	$-\text{C}-\text{OH}$	1.02	[2]
N-Acetyl-L-tyrosine	$-\text{C}-\text{OH}$	0.91	[5]
α-Oxalic acid dihydrate	$-\text{C}-\text{OH}$	0.85	[6]
α-Oxalic acid dihydrate	$-\text{C}-\text{OH}$	1.19	[9]
N-Acetyl-L-tryptophan methylamide	$-\text{C}{=}\text{O}$	0.64	[4]
N-acetyl-L-tyrosine	$-\text{C}{=}\text{O}$	0.88	[5]
α-Oxalic acid dihydrate	$-\text{C}{=}\text{O}$	0.85	[6]
α-Oxalic acid dihydrate	$-\text{C}{=}\text{O}$	1.00	[9]
(*Z*)-*N*-Acetyl-α,β-dehydro-phenylalanine methylamide	$-\text{C}{=}\text{O}$	1.01, 0.90	[10]
DL-Proline·H_2O	H_2O	0.68	[7]
N-Acetyl-L-tyrosine	H_2O	0.76	[5]
α-Oxalic acid dihydrate	H_2O	0.89	[6]
α-Oxalic acid dihydrate	H_2O	1.01	[9]

References: [1] Howard *et al.* (1995); [2] Hamzaoui *et al.* (1996); [3] Howard *et al.* (1992); [4] Souhassou *et al.* (1991); [5] Dahaoui *et al.* (1999); [6] Zobel *et al.* (1992); [7] Abramov (2000), private communication; [8] Volkov (2000); [9] Stevens & Coppens (1980); [10] Souhassou *et al.* (1992).

Hansen–Coppens multipole model is analogous to the refinement of the radial exponent ζ in the Stewart model.

The comparison of experimental and theoretical crystal charge densities reveals systematic discrepancies in topological properties, which are mainly attributed to the limited flexibility of the radial functions in experimental multipole formalism (Volkov, 2000; Volkov, Abramov *et al.*, 2000; Volkov, Gatti *et al.*, 2000). In addition, atomic and molecular properties derived from multipole refinement results are subject to errors resulting from the non-uniqueness of the definition of the basis set. The effect can be pronounced whenever density basis functions on adjacent molecules overlap significantly (Abramov *et al.*, 1999), as is the case when short interactions such as hydrogen bonds are present. Although the density fit achieved in the refinement may be satisfactory, the resulting atomic and molecular properties may be ambiguous. The absence of physical constraints in the multipole model provides a flexibility that may lead to electrostatic atomic and molecular properties that are not physically meaningful.

In the multipole refinement of *experimental* X-ray structure factors, the ambiguity is enhanced by (*a*) thermal smearing of electron density, (*b*) experimental noise and (*c*) correlation between atomic positional and thermal parameters and the variables of the multipole expansion (Kurki-Suonio, 1977).

The effect of the intermolecular basis-set overlap is evident from a survey of published κ' values for oxygen atoms in organic molecules (Table 1). The very large variation of κ' values is especially disturbing when found for the same functional group. For the carbonyl oxygen atom, for example, $0.64 \le \kappa' \le 1.01$. Low values of κ' produce very diffuse deformation functions; the resulting pseudoatom density no longer satisfies the requirement of locality (Kurki-Suonio, 1968).

The problem of the basis set overlap error (BSOE) is greatly reduced in the multipole refinement of *theoretical* structure factors, since the correlation of the multipole parameters with atomic positional and thermal parameters, thermal smearing and experimental noise effects are eliminated. As such, the use of the radial exponents ζ or κ' parameters derived from multipole refinements of theoretical structure factors (density-optimized radial exponents) has been suggested (Swaminathan *et al.*, 1984; Abramov *et al.*, 1999), when refining experimental X-ray data.

In the study by Swaminathan *et al.* (1984), the multipole refinement of *experimental* X-ray structure factors of urea employed the radial exponents derived from the multipole refinement of *theoretical* structure factors, which were generated from the superposition of isolated-molecule HF densities in the crystal lattice. One of the important conclusions of this study was that 'the standard α [radial exponent] values, which were derived from energy-minimization calculations for selected isolated small molecules, might not be optimal for the spatial fitting of the charge density deformations in urea' (Swaminathan *et al.*, 1984).

Similar conclusions were drawn by Spackman & Byrom (1996) based on the multipole refinements of *theoretical* (model) X-ray data sets for several organic compounds generated from superposition of HF molecular fragments in the corresponding crystal lattice (referred to as *molecules* values). Some significant differences have been found between SM and multipole refined radial function exponents. It was noticed that 'the optimal exponents for C atoms vary little, irrespective of the type of C atom . . . , while exponents for N atoms span a wide range' (Spackman & Byrom, 1996).

In a second study, Spackman *et al.* (1999) refined the radial exponents of the deformation functions from the model X-ray data obtained from *ab initio crystal* HF calculations. The values obtained were significantly different from SM and slightly different from *molecules* values, a difference that could be attributed to intermolecular interactions.

The use of density-optimized radial exponents from multipole refinements of *theoretical* crystal structure factors in *experimental* X-ray data refinement (the so-called κ'-restricted multipole model or KRMM) was introduced by Abramov *et al.* (1999). The application of the KRMM refinement to experimental data results in much better agreement with theoretical crystal charge densities compared to the standard (unrestricted) multipole refinement, especially after the theoretical densities had been projected onto the multipole density functions. Indeed, in a recent study of *p*-nitroaniline (Volkov, Gatti *et al.*, 2000), the largest discrepancy between Bader charges (Bader, 1990) from the KRMM-based experimental and multipole-refined theoretical density-functional densities were as small as 0.06 electrons. Unfortunately, only a small number of theoretical fully periodic crystal calculations have been reported up to date, and a variation of the κ' parameter (radial exponent) with atomic bonding environment has not yet been established.

In this paper, we report the results of the *ab initio* density-functional crystal calculations on a large number of organic compounds followed by a multipole refinement of the corresponding theoretical structure factors using Hansen–Coppens multipole formalism. This is arguably the largest number of periodic calculations made in a single study so far. The correlation of the κ parameter with charge transfer and the dependence of the κ' parameter on the atomic bonding environment are analyzed in this study.

2. *Ab initio* crystal calculations and multipole refinements of theoretical structure factors

The compounds for which the crystal periodic calculations have been performed are summarized in Table 7 in Appendix *A*, together with the space groups and information on the diffraction studies from which the atomic positional coordinates were obtained. Crystal structures were selected using the Cambridge Structural Database system (Allen & Kennard, 1993). Preference was given to relatively small (under 100 atoms in the unit cell) molecular crystals with accurately determined structures (*R* factor generally under 5%) based on low-temperature X-ray or, preferably, neutron data. In the case of X-ray data, the hydrogen positions were modified by extending X—H distances (X = C, N, O) to their standard neutron diffraction values (*International Tables for Crystallography*, 1992). The presence of an inversion center was considered desirable, as it reduces the ambiguity of phase-angle determination in the refinement of structure factors to the sign of the phase angle.

Theoretical calculations were performed with the *CRYSTAL98* package (Saunders *et al.*, 1998) at the density-functional (DFT) level of theory. Within the approximation used in *CRYSTAL98*, the Bloch functions are defined in terms of local functions, which are, in turn, expanded as a linear combination of Gaussian-type functions. The DFT calculations employed Becke's gradient-corrected three-parameter hybrid exchange (Becke, 1993) combined with the gradient-corrected correlation functional of Lee *et al.* (1988), which includes both local and non-local terms (B3LYP functional). The calculations were performed using the standard molecular split-valence 6-31G** (Hariharan & Pople, 1973; Francl *et al.*, 1982) basis set.

Although in *ab initio* calculations the crystal density is obtained as a product of atomic Gaussian-type orbitals, in the multipole refinements scattering factors based on the Clementi–Roetti (1974) Slater-type expansion of HF wave functions are used. As shown by Stewart (1969), the difference in the radial scattering factors between Clementi orbital products and the corresponding expansion over five Gaussian-type orbitals (basically, the STO-5G basis set) is well under 1%. Much better agreement should be achieved for the 6-31G** basis used in this study.

To mimic the experimental refinements as much as possible, the calculation of theoretical structure factors was limited to the $\sin\theta/\lambda = 1.1$ Å^{-1} resolution. In the refinement of the static theoretical data, performed with the *XD* package (Koritsanszky *et al.*, 1997), temperature factors and atomic positions were not refined, thus eliminating an important source of correlation between parameters. The single-ζ exponents of the deformation functions as used in *XD* are unweighted averages over the *ns* and *np* exponents given by Clementi & Raimondi (1963). The values are 3.7795, 6.0021, 7.2579 and 8.4516 Å^{-1} for H, C, N, O, respectively. Values for n_l in the radial function [equation (2)] of 1, 2 for H and 2, 2, 3 for C, N, O (dipoles, quadrupoles, octupoles) were used. In each crystal structure, both κ and κ' parameters were refined independently for each atom, while only one κ and one κ' parameter were refined for all H atoms. The multipole expansion was truncated at the octupole level ($l_{\max} = 3$) for the non-hydrogen atoms and at the quadrupole level ($l_{\max} = 2$, only bond-directed quadrupole) for the H atoms, as justified in our previous studies on this type of molecule (Volkov, Abramov *et al.*, 2000; Volkov, Gatti *et al.*, 2000), in which no changes in topological properties of charge densities from multipole refinements of theoretical structure factors were observed when higher multipoles were included in the refinements. In order to reduce the number of refined parameters, local-symmetry constraints (not higher than *mm*2 symmetry) were applied to some atoms. A molecular electroneutrality constraint was applied when only one type of molecule was present. In case of hydrated complexes, only the total electronic charge of the complex was constrained to neutrality, thus allowing charge transfer between component molecules.

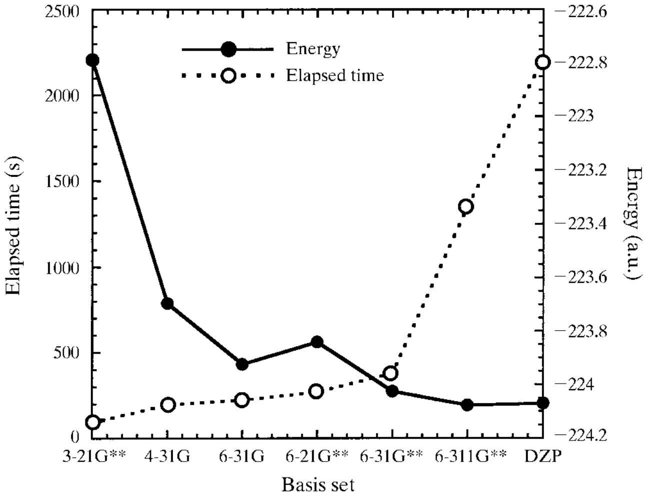
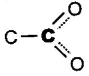
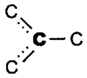
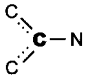
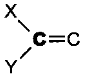
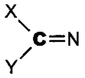
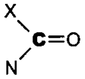
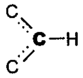
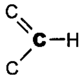
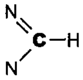
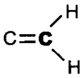
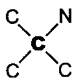
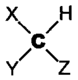
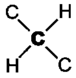
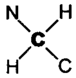
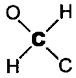
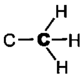
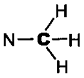
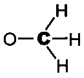


Figure 1
Effect of the molecular basis set on the molecular energy and elapsed time in crystal Hartree–Fock calculation of urea (Volkov, 1999). Calculations were performed on a Silicon Graphics Origin2000 supercomputer using 10 R10000 250 MHz processors.

Table 2
Averaged κ' parameters for sp^2 and sp C atoms.

Bold font marks the atoms for which κ' parameters are listed.

Functional group	κ'	$N_{\rm obs}$
sp $-\mathbf{C}{\equiv}N$	0.80 (1)	6
sp^2 (NOT bonded to H atoms)		
	0.88 (2)	9
	0.87 (1)	5
	0.86 (1)	7
	0.87 (3)	8
	0.86 (2)	4
	0.86 (1)	13
sp^2 (bonded to one H atom)		
	0.92 (2)	27
	0.93 (1)	4
	0.90 (1)	5
sp^2 (bonded to two H atoms)		
	0.93 (2)	3
sp^3 (NOT bonded to H atoms)		
	0.85 (1)	2
sp^3 (bonded to one H atom)		
	0.92 (2)	12
sp^3 (bonded to two H atoms)		
	0.95 (2)	8
	0.98 (5)	5
	0.95 (3)	4
sp^3 (bonded to three H atoms)		
	0.97 (2)	6
	0.98	1
	1.00 (1)	2

3. Basis set and Hamiltonian dependence of theoretical charge densities

It is well known that a certain ambiguity is introduced in theoretical calculations by using an approximate form of the Hamiltonian [HF, DFT, MP (Møller-Plesset) *etc.*] and an approximate wave function. The theoretical charge densities to some extent depend on the introduced approximations. It has been shown that the use of Hamiltonians that include electron correlation effects (such as all DFT functionals) produces superior results compared to methods neglecting correlation, such as Hartree–Fock theory (Volkov, Gatti *et al.*, 2000). Furthermore, comparison of topological properties of charge densities from different density-functional calculations indicates the superiority of the gradient-corrected DFT functionals over those of local density approximations (Volkov, 2000).

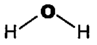
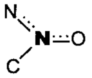
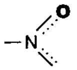
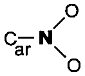
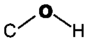
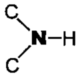
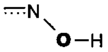
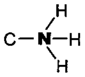
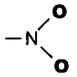
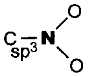
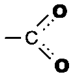
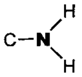
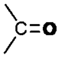
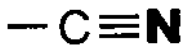
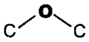
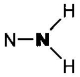
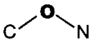
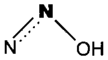
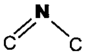
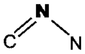
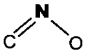
It was also shown that, in periodic calculations of molecular crystals, 6-31G** basis sets give charge densities that are physically more meaningful than those from less flexible basis sets such as 6-21G** (Volkov, 2000). The use of high-quality molecular basis sets, such as 'double ζ', 'triple ζ' and the larger basis sets of Huzinaga (Huzinaga *et al.*, 1984), Dunning (Dunning & Hay, 1977; Dunning, 1989), Ahlrichs (Schafer *et al.*, 1992) *etc.* is generally not recommended for two reasons (Saunders *et al.*, 1998). First, computation time increases dramatically with relatively little gain in energy when *s* and *p* functions are assigned different exponents (Fig. 1), compared

Table 3
κ' parameter of carbon atom as a function of hybridization and number of H atoms in the bonding environment.

	Number of H atoms in the bonding environment			
Hybridization	0	1	2	3
sp	0.80 (1)	–	–	–
sp^2	0.87 (1)	0.92 (2)	0.93 (2)	–
sp^3	0.85 (1)	0.92 (2)	0.96 (2)	0.98 (2)

Table 4
Averaged κ' parameters for O and N atoms in specific bonding environments from multipole refinements of crystal DFT structure factors.

Bold font marks the atoms for which κ' parameters are listed.

Oxygen			Nitrogen		
Functional group	κ'	$N_{\rm obs}$	Functional group	κ'	$N_{\rm obs}$
	1.00 (1)	4		0.75	1
	1.13	1		0.77 (1)	5
	1.16 (3)	10		0.81 (2)	2
	1.17	1		0.83 (2)	8
	1.17 (6)	14		0.95 (1)	2
	1.18 (4)	12		0.95 (4)	9
	1.18 (5)	16		0.99 (3)	6
	1.20 (1)	5		1.00 (1)	4
	1.20 (4)	3		1.00	1
				1.00 (3)	6
				1.03 (1)	2
				1.05 (1)	3

to the 6-31G** sp shells in which s and p functions share exponents (but have different contraction coefficients). Second, too diffuse outer functions will significantly overlap with each other in a periodic system, which may result in quasi-linear dependence.

Test calculations on single molecules indicate the 6-31G** basis set and B3LYP functional employed here to be fully adequate for evaluation of the charge density for the current purpose (Volkov, 2000).

4. Results and discussion

The results of the multipole refinements of DFT crystal structure factors are summarized in Tables 2–6, while Fig. 2 shows the correlation between κ and monopole-derived net atomic charge for C, N and O atoms. Tables 2–5 list the resulting κ' parameters for carbon, nitrogen and oxygen atoms as a function of the bonding environment, while in Table 6 the κ and κ' parameters of H atoms in all test compounds are reported.

4.1. κ parameters for C, N and O atoms

As expected from previous studies and illustrated in Fig. 2, the monopole-derived net atomic charge q correlates with the κ parameter from multipole refinements of the DFT crystal structure factors for the C, N and O atoms. Red, blue and green in Fig. 2 correspond to carbon, nitrogen and oxygen atoms, respectively. The correlation is close to being linear with $R = 0.87$ and a slope of about 6%. The fitted linear equation [$\kappa = 0.999\ (1) + 0.063\ (2)q$] predicts that for a neutral atom ($q = 0$) the κ parameter is 0.999, which suggests, within the validity of the model, the unchanged nature of the valence shell in the bonded neutral atom relative to that of the free atom. This result is in some disagreement with Slater's rules,

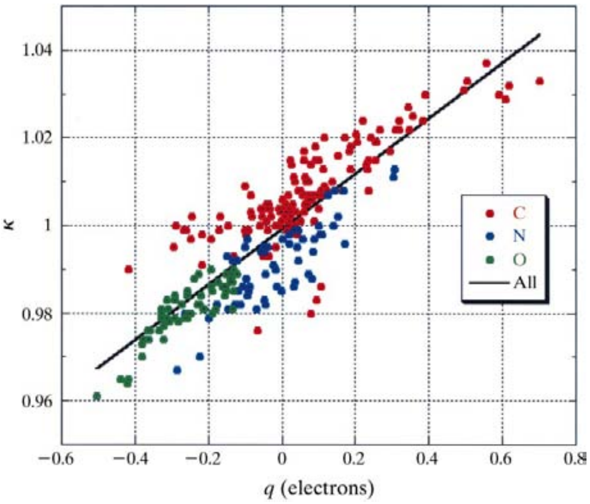


Figure 2
The relation between expansion–contraction of the valence shell (κ) and net atomic charge (q) derived from monopole population for carbon, nitrogen and oxygen atoms from multipole refinements of *crystal* B3LYP/6-31G** structure factors.

Table 5
Variations in κ' parameter of the nitrogen atom.

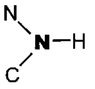
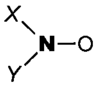
Compound	κ'
	
α-Cyanoacetohydrazide	0.98 (1)
1,3-Diaminourea	1.02 (1)
1,3-Diaminourea	1.02 (1)
p-Nitrophenylhydrazonomalononitrile	0.85 (1)
1,2,4-Triazole	0.80 (1)
	
Creatine monohydrate ($X\rightarrow$C, $Y\rightarrow$C)	1.06 (1)
2-Amino-2-hydro-6-hydroxypyridazin-3-one ($X\rightarrow$N, $Y\rightarrow$N)	0.83 (1)
Adenosine ($X\rightarrow$C, $Y\rightarrow$C)	0.80 (1)

Table 6
κ and κ' parameters for hydrogen atom from multipole refinement of crystal DFT structure factors.

Compound	κ	κ'
Adenosine	1.125 (2)	1.31 (1)
4-Amino-2-(cyanomethoxy)-2-(hydroxymethyl) oxazolidine	1.126 (2)	1.27 (1)
2-Amino-2-hydro-6-hydroxypyridazin-3-one	1.146 (4)	1.36 (1)
1,2,4-Triazole	1.158 (5)	1.29 (1)
Creatine monohydrate	1.107 (2)	1.29 (1)
2-Methyl-4-nitroaniline	1.116 (3)	1.29 (1)
4-Nitrobenzamide	1.134 (3)	1.28 (1)
p-Nitroanisole	1.116 (2)	1.21 (1)
p-Nitrophenylhydrazonomalononitrile	1.125 (3)	1.21 (1)
4-Nitrobenzoic acid	1.139 (3)	1.29 (1)
α-Cyanoacetohydrazide	1.139 (3)	1.34 (1)
Methyl carbamate	1.109 (4)	1.24 (1)
1,3-Diaminourea	1.155 (3)	1.38 (1)
L-Dopa	1.148 (3)	1.34 (1)
L-Asparagine monohydrate	1.119 (3)	1.32 (1)
DL-Aspartic acid	1.143 (3)	1.35 (1)
γ-Aminobutyric acid	1.091 (2)	1.23 (1)
4-Cyanoimidazolium-5-olate	1.166 (6)	1.33 (1)
L-Alanosine	1.166(4)	1.40(1)
Benzamide	1.126 (2)	1.22 (1)
Methylenecyclopropane-2-carboxamide	1.130 (2)	1.21 (1)
2,3-Dimethyl-2,3-dinitrobutane	1.090 (3)	1.17 (1)
α-Cyanoacrylic acid	1.142 (5)	1.34 (2)
(4S,5R)-4-Amino-5-methyl-3-isoxazolidinone hemihydrate	1.110 (3)	1.29 (1)
5-Ammoniomethyl-3-isoxazolonide hemihydrate	1.119 (2)	1.31 (1)
Average	1.13 (2)	1.29 (6)

according to which the neutral bonded atom would be slightly contracted (Coppens *et al.*, 1979). Furthermore, the slope of the curve obtained in this study (6%) is slightly smaller than that predicted by Slater's recipe (8–11% for C, N, O atoms). Nevertheless, the overall correlation between κ and net charge q is quite pronounced. We note that this correlation may have practical use through introduction of a κ/charge constraint in the charge-density refinement of large molecules.

4.2. κ' parameter for C, N and O atoms

As the κ' parameter characterizes the angular deformation functions, it is expected to be sensitive to the geometry of the bonding environment and to the origin of the angular deformations, which can be due to accumulation of overlap density in the covalent bonds, or to more compact lone-pair densities.

The multipole refinements of DFT crystal structure factors indicate remarkably consistent deviations from unity of the κ' parameter. While the small experimental κ' parameters have been attributed to the expansion of the deformation functions owing to the presence of strong hydrogen bonds (Howard *et al.*, 1995), they are not reproduced by our multipole refinements of theoretical *crystal* structure factors. This indicates that the correct interpretation originates in the effect of the BSOE in multipole refinements of experimental X-ray data.

4.2.1. Carbon. The most consistent behavior of the κ' parameter is observed for carbon (Tables 2–3). The $\kappa'_{\rm C}$ values in general are <1, corresponding to an expansion of the deformation functions. However, $\kappa'_{\rm C}$ clearly depends on the nature of the hybridization of the C atom and on the number of H atoms in the bonding environment. The smallest $\kappa'_{\rm C}$ value (0.80) is observed for *sp* carbon, which forms a triple bond with one of its neighbors. The largest $\kappa'_{\rm C}$ parameter corresponds to carbon in the sp^3 hybridization state, bonded to three H atoms (average value 0.98). In general, $\kappa'_{\rm C}$ increases with increasing number of H atoms bonded to the carbon (Table 3). Similarly, low $\kappa'_{\rm C}$ values (0.80, 0.87 and 0.85) are observed for carbon atoms in *sp*, sp^2 and sp^3 hybridization states, respectively, without C—H bonds. For sp^2 or sp^3 C atoms, the replacement of one carbon or nitrogen atom in the bonding environment by an H atom significantly increases the value of the $\kappa'_{\rm C}$ parameter from 0.87 to 0.92 and from 0.85 to 0.92, respectively. Replacement of additional C and N atoms by H atoms further increases the value of $\kappa'_{\rm C}$ up to 0.98, as for sp^3 carbon in the C—**C**H$_3$ group.

4.2.2. Oxygen. In general, the deformation functions on the oxygen atom are significantly contracted (Table 4), except in the water molecule, for which the radial dependence of the oxygen deformation functions is close to that of the isolated atom ($\kappa'_{\rm O} = 1.00$). Excluding the water molecule, the average $\kappa'_{\rm O}$ value is 1.17 (2), and almost independent of the bonding environment and presence of short intermolecular hydrogen bonds. Thus, in DL-aspartic acid one of the carboxyl oxygen atoms participating in a very strong H bond ($d_{\rm O\cdots H} = 1.54$ Å) has a κ' parameter of 1.19 (1). Even for L-dopa, for which the reported experimental κ' value for the carboxyl oxygen atoms is 0.54 (Howard *et al.*, 1995), the multipole refinement of *crystal* DFT structure factors predicts $\kappa'_{\rm O} = 1.18$ (1). It is interesting that our value is smaller than $\kappa'_{\rm O} = 1.27$ for carboxyl O atoms in L-dopa, obtained from the multipole refinement of the theoretical restricted Hartree–Fock/double-ζ structure factors generated from the *superposition of molecules* in the L-dopa crystal lattice (Howard *et al.*, 1995).

The only trend for the $\kappa'_{\rm O}$ parameter is observed in the series H—**O**—H, C—**O**—H, C—**O**—C, N—**O**—H, C—**O**—N.

Table 7
Crystal structures used in theoretical periodic calculations.

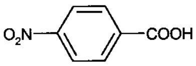
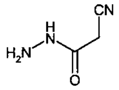
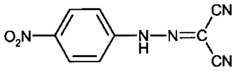
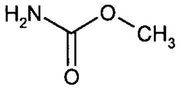
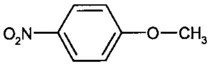
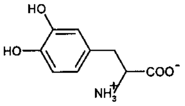
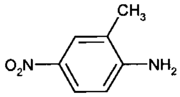
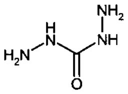
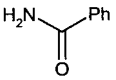
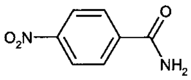
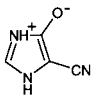
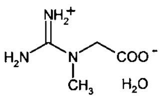
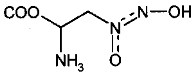
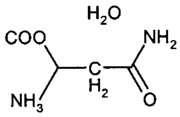
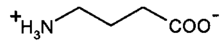
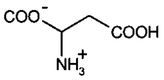
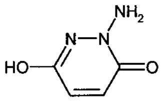
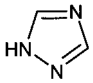
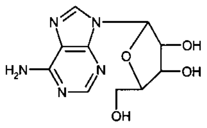
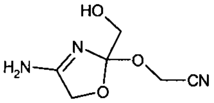
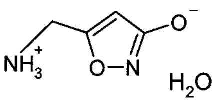
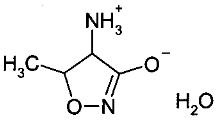
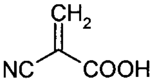
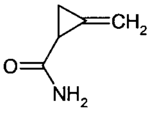
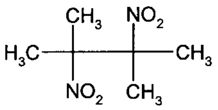
Chemical diagram	Name; formula	Space group	Data type	*R* factor (%)	Reference
	4-Nitrobenzoic acid; $C_7H_5NO_4$	$A2/a$	X-ray data at 120 K; high-order refinement	2.8	Tonogaki *et al.* (1993)
	α-Cyanoacetohydrazide; $C_3H_5N_3O$	$P2_1/c$	Neutron study at 15 K	3.0	Nanni *et al.* (1986)
	*p*-Nitrophenylhydrazonomalononitrile; $C_9H_5N_5O_2$	$P2_1/c$	Room-temperature X-ray data	5.1	Mitsuhashi *et al.* (1992)
	Methyl carbamate; $C_2H_5NO_2$	$P\bar{1}$	X-ray data at 123 K	7.1	Sepehrnia *et al.* (1987)
	*p*-Nitroanisole; $C_7H_7NO_3$	$P2_1/c$	X-ray data at 108 K	4.2	Talberg (1978)
	(2*S*)-3-(3′,4′-Dihydroxyphenyl)alanine (L-dopa); $C_9H_{11}NO_4$	$P2_1$	X-ray data at 173 K	1.7	Howard *et al.* (1995)
	2-Methyl-4-nitroaniline; $C_7H_8N_2O_2$	Ia	Multipole refinement of X-ray data at 125 K	3.54	Howard *et al.* (1992)
	1,3-Diaminourea (carbohydrazide); CH_6N_4O	$P2_1/c$	Neutron study at 15 K	3.1	Jeffrey *et al.* (1985)
	Benzamide; C_7H_7NO	$P2_1/c$	Neutron study at 15 K	4.4	Gao *et al.* (1991)
	4-Nitrobenzamide; $C_7H_6N_2O_3$	$P2_1/c$	X-ray study at 120 K	3.3	Tonogaki *et al.* (1993)
	4-Cyanoimidazolium-5-olate; $C_4H_3N_3O$	$Pna2_1$	Multipole refinement of X-ray data at 120 K	3.7	Bianchi *et al.* (1998)
	*N*-(Aminoiminomethyl)-*N*-methylglycine monohydrate (creatine monohydrate); $C_4H_9N_3O_2H_2 \cdot H_2O$	$P2_1/c$	Neutron study at 15 K	4.6	Frampton *et al.* (1997)
	L-Alanosine; $C_3H_7N_3O_4$	$P2_12_12_1$	X-ray study at 138 K	3.2	Jalal *et al.* (1986)
	L-Asparagine monohydrate; $C_4H_8N_2O_3 \cdot H_2O$	$P2_12_12_1$	Multipole refinement of X-ray data at 20 K	2.0	Arnold *et al.* (2000)

Table 7 (continued)

Chemical diagram	Name; formula	Space group	Data type	*R* factor (%)	Reference
	γ-Aminobutyric acid; $C_4H_9NO_2$	$P2_1/a$	Neutron study at 122 K	4.4	Weber *et al.* (1983)
	DL-Aspartic acid; $C_4H_7NO_4$	$C2/c$	Multipole refinement of X-ray data at 20 K	3.1	Flaig *et al.* (1998)
	2-Amino-2-hydro-6-hydroxypyridazin-3-one; $C_4H_5N_3O_2$	$P2_1/c$	X-ray data at 233 K	5.5	Dreiding, Bieri, Prewo, Linden & Hilpert, unpublished results
	1,2,4-Triazole; $C_2H_3N_3$	$Pbca$	X-ray data at 15 K	4.0	Fuhrmann *et al.* (1997)
	Adenosine; $C_{10}H_{13}N_5O_4$	$P2_1$	Neutron diffraction at 123 K	4.4	Klooster *et al.* (1991)
	4-Amino-2-(cyanomethoxy)-2-(hydroxymethyl) oxazolidine; $C_6H_9N_3O_3$	$P2_1/n$	X-ray study at 169 K	4.5	Arrhenius *et al.* (1997)
	5-Ammoniomethyl-3-isoxazolonide hemihydrate; $C_4H_6N_2O_2{\cdot}(H_2O)_{0.5}$	$P\bar{1}$	X-ray at 122 K	3.2	Brehm *et al.* (1997)
	(4*S*,5*R*)-4-Amino-5-methyl-3-isoxazolidinone hemihydrate (*cis*-cyclothreonine hemihydrate); $C_4H_8N_2O_2{\cdot}(H_2O)_{0.5}$	$C2$	X-ray study at 122 K	2.5	Anthoni *et al.* (1998)
	α-Cyanoacrylic acid; $C_4H_3NO_2$	$P2_1/n$	X-ray study at 150 K	5.5	Shklover *et al.* (1991)
	Methylenecyclopropane-2-carboxamide; C_5H_7NO	$P2_1/c$	Neutron study at 20 K	6.4	Schultz *et al.* (1990)
	2,3-Dimethyl-2,3-dinitrobutane; $C_6H_{12}N_2O_4$	$P\bar{1}$	X-ray study at 95 K	3.5	Kai *et al.* (1982)

When the oxygen atom is bonded to two H atoms, as in the water molecule, the κ'_{O} parameter is 1.00, while the replacement of one of the H atoms by carbon or nitrogen dramatically increases the value of κ'_{O} up to 1.16 and 1.17, respectively. The replacement of the second H atom by an additional C or N atom, again, increases the κ'_{O} value (up to 1.20), but not as significantly as in the first step. There is no obvious difference in κ'_{O}, however, between C—**O**—C and C—**O**—N groups. Interestingly, this trend is opposite to that described above for the carbon atom.

Thus, the averaged value $\kappa'_{\mathrm{O}} = 1.17$ is recommended for use in all bonding environments of the oxygen atom, except in the water molecule, where $\kappa'_{\mathrm{O}} = 1.00$ should be used.

4.2.3. Nitrogen. The largest overall spread of κ' values ($0.77 \le \kappa' \le 1.05$) is observed for the nitrogen atom (Table 4), which confirms the previously reported observation

(Spackman & Byrom, 1996). The deformation functions of the N atom can be significantly expanded, as in the case of the $C_{ar}—\mathbf{N}O_2$ group ($\kappa'_N = 0.77$), or slightly contracted as in the $C{=}\mathbf{N}—O$ ($\kappa'_N = 1.05$) group. The smallest κ' value of 0.75 was found for the N atom in the $N—\mathbf{N}(C)—O$ group but, since there is only one observation, this value should be treated with caution. In the majority of cases, however, the deformation functions of the nitrogen atom are slightly expanded.

Some noticeable differences are observed for κ' parameters of nitrogen atoms. The κ'_N parameter in the $C—\mathbf{N}H_3^+$ group (0.83) is significantly smaller than that in the $C—\mathbf{N}H_2$ group (0.95). The replacement of the carbon atom in the $C—\mathbf{N}H_2$ group by another N atom ($N—\mathbf{N}H_2$) increases the κ' value of the central N atom to 1.00. A unique feature is the sensitivity of the κ' parameter of the central N atom in the $C—\mathbf{N}O_2$ group to the type of the carbon atom. Thus, when the $—\mathbf{N}O_2$ group is bonded to aromatic carbon ($C_{ar}—\mathbf{N}O_2$), $\kappa'_N = 0.77$ is much smaller, compared to $\kappa'_N = 0.95$ when the $—\mathbf{N}O_2$ group is bonded to an sp^3 carbon atom ($C_{sp^3}—\mathbf{N}O_2$). Another noticeable trend occurs in the $C{=}\mathbf{N}—C$ group, where replacement of the single-bonded C atom by a nitrogen ($C{=}\mathbf{N}—N$) or oxygen ($C{=}\mathbf{N}—O$) atom increases the κ' parameter of the central nitrogen from 1.00 to 1.03 and 1.05, respectively.

Nitrogen is also the only element of those examined here for which variations in the κ' parameter within similar bonding environments are found (Table 5). However, it is quite possible that, for the first case listed in Table 5, the type of neighboring C and N atoms significantly affects the κ' parameter of the central N atom. Indeed, in both α-cyanoacetohydrazide and 1,3-diaminourea, the neighboring N and C atoms are the same (belonging to NH_2 and $C{=}O$ groups), while in *p*-nitrophenylhydrazonomalononitrile and 1,2,4-triazole the neighboring N and C atoms are quite different. This effect is somewhat similar to that observed for $C_{sp^3}—\mathbf{N}O_2$ and $C_{ar}—\mathbf{N}O_2$ groups.

Thus, no general recipe can be provided for the κ' parameter of an N atom, in contrast to C and O atoms. However, the optimal κ'_N values listed in Tables 4 and 5 may be used in each specific case.

4.3. κ and κ' parameters for H atoms

The determination of κ and κ' parameters for the H atom from the multipole refinement of experimental X-ray data is only possible when the neutron positional and thermal parameters for hydrogen atoms are available (Coppens *et al.*, 1979). Usually, κ and κ' parameters of the hydrogen atom are not refined,[1] but fixed at recommended values (Coppens, 1997). The multipole refinements of theoretical structure factors provide a unique opportunity to reliably determine the extent of the contraction of the valence and deformation functions of hydrogen atoms (Table 6). In the multipole refinement for each test compound, only one κ_H and one κ'_H parameter were refined for all H atoms in the structure, while monopole populations $P_{valence}$ [equation (3)] were allowed to refine separately for each hydrogen atom.

The average $\kappa_H = 1.13$ (2) is quite different from κ_H values determined from the refinement of experimental data with a monopole-only formalism, *i.e.* $\kappa_H =$ 1.35–1.4 (Coppens *et al.*, 1979; Coppens, 1997) and $\kappa_H = 0.995$ (Madsen *et al.*, 2000), but in very good agreement with previously reported κ_H values of 1.166 (Stewart *et al.*, 1965) and 1.126 (Chandler *et al.*, 1980), obtained from monopole fits to H_2 electron densities beyond the Hartree–Fock limit. The result is also in agreement with the values of 1.16_5 and 1.16 derived from theoretical densities by, respectively, Spackman & Byrom (1996) and Spackman *et al.* (1999).

In contrast to the valence shell, the deformation functions of the H atom are indeed more contracted, the average κ' value being 1.29 (6), which is between the recommended values (1.2–1.4) obtained from refinement of experimental data (Coppens, 1997). It is worth noting that the current result is in excellent agreement with the κ'_H value of 1.353 (5) determined from $X + N$ multipole refinement of experimental phosphangulene data (Madsen *et al.*, 2000) and the results of Spackman & Byrom (1996) (1.33) and Spackman *et al.* (1999) (1.31), based on theoretical structure factors. As expected, the overall variation of the κ' parameter (1.17–1.40) among test compounds is somewhat larger than for the κ parameter (1.09–1.17).

A large spread in the values of κ and κ' for hydrogen is reflected in the uncertainties given above. Not unexpectedly, the spread is due to chemical differences among the molecules included in the analysis. Further test refinements show that κ values for H(C) cluster around 1.10, while those for H(N) and H(O) atoms are between 1.12 and 1.18, with an average of about 1.15. κ' values for H(C) are close to 1.18, for H(N) about 1.40, while for H(O) a large range from about 1.4 to 1.6 is observed. These differences merit further analysis.

5. Conclusions

The multipole refinements of DFT crystal structure factors confirm the previously determined correlation of the valence expansion—contraction coefficient κ and the monopole-derived net atomic charge. The resulting dependence is linear with $R = 0.87$ and a slope of ~6%. Our results also imply an unchanged nature of the radial dependence of the valence shell of the bonded neutral atom.

The multipole refinements of theoretical crystal structure factors provide a reliable estimate of the expansion–contraction κ' parameters of the deformation functions as determined from the excellent overall consistency of the atomic κ' parameter in a specific functional group among all test compounds. The $\kappa_H = 1.13$ and $\kappa'_H = 1.29$ values for hydrogen (Table 6) and κ' for C, N and O atoms in purely organic molecular crystals, listed in Tables 2–4, are recommended for use in multipole refinements of experimental X-ray data whenever the refinement is hampered by lack of uniqueness of the parameter set.

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[1] In the recent paper by Madsen *et al.* (2000), both κ and κ' parameters of hydrogen atoms in phosphangulene were refined using a combination of accurate 11 K X-ray and 11 K neutron power diffraction data. However, such a complete very low temperature set of experimental data is not yet common.

The correlation between κ and q and density-optimized values of κ' should be useful in multipole refinements of experimental X-ray data for large crystal structures such as polypeptides and proteins, for which a reduction of the number of variables may be essential.

The interpretation of the trends in the κ' parameters described above in terms of topological features of the charge-density distribution requires further attention.

APPENDIX *A*

The compounds for which the crystal periodic calculations have been performed are summarized in Table 7, together with the space groups and information on the diffraction studies from which the atomic positional coordinates were obtained.

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