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The Gram–Charlier and Multipole Expansions in Accurate X-ray Diffraction Studies: Can They Be Distinguished?

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Abstract

The Gram-Charlier temperature factor formalism has been applied to a set of accurate low-temperature data on bis(pyridine)(*meso*-tetraphenylporphinato)iron(II), and to a theoretical set of static structure factors on the hexaaquairon(II) ion. The refinements are compared with the multipole treatment for atomic asphericity due to chemical bonding. In a treatment of the experimental data in which only the iron atom asphericity is considered, the 'thermal motion' formalism is as efficient as the multipole formalism in accounting for the observations. It is slightly less efficient when applied to the static theoretical data, though model maps based on the two treatments are remarkably similar. A high-order Gram-Charlier refinement of the porphyrin data, followed by a multipole refinement of all data with the Gram-Charlier parameters initially fixed, and later varied, shows that simultaneous refinement of anharmonic and aspherical effects is possible, though the resulting separation may not be accurate. A combined Gram-Charlier multipole refinement on the static data, however, leads to non-significant thermal parameters. It is concluded that the statistical Gram-Charlier formalism is remarkably successful in representing bonding effects in the valence charge density if these are not specifically accounted for in the scattering formalism. Statistical anharmonic thermal motion formalisms should only be used for X-ray data analysis in combination with a formalism accounting for the effect of bonding on the atomic charge density.

Introduction

It is commonly assumed in crystallographic studies that thermal motion can be adequately described by a formalism based on a harmonic force field. The Fourier transform of the Gaussian probability distribution of harmonically vibrating atoms is the temperature factor component of the time-averaged atomic form factor first introduced by Cruickshank (1956). It has also been realized, however, that there exist not uncommon phenomena in which anharmonic motion might be a significant effect, for example pseudorotation (Cremer & Pople, 1975), ring oscillations in biphenyl-type compounds (Rietveld, Maslen & Clews, 1970), anharmonic vibrations in alloys (Kontio & Stevens, 1982) and semiconductors (McIntyre, Moss & Barnea, 1980) and many others. Internal vibrations of bonds in molecules have a less dominant effect in crystallographic work, but evidence for their anharmonicity is abundantly present in spectroscopic data. Indeed, inclusion of anharmonic covariant tensor coefficients has been reported to be essential in some structure determinations (*e.g.* Marsh & Abrahams, 1987; Zucker & Schulz, 1982; Johnson, 1969; Willis, 1969). Such anharmonicity leads to deviations from Gaussian shape, which may be represented by additional terms in the probability distribution function. Several algorithms for the anharmonic temperature factor have been proposed (see *International Tables for X-ray Crystallography*, 1974; *International Tables for Crystallography*, 1983). For a number of reasons (Kuhs, 1983; Scheringer, 1985) the preferred formalism is based on the three-dimensional Gram-Charlier (GC) expansion, in which the anharmonic terms are the zero and higher derivatives of a normal distribution (Kendal & Stuart, 1958; Johnson, 1969). Its Fourier transform $T(\mathbf{H})$ is a power-series expansion about the harmonic temperature factor $T_0(\mathbf{H})$, with even and odd terms

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Table 1. *Summary of refinements*

Bis(pyridine)(*meso*-tetraphenylporphinato)iron(II)

	Spherical, harmonic	Spherical, anharmonic Fe, H temperature factors fixed	Aspherical Fe, harmonic	All atoms aspherical, HO anharmonic, Fe fixed	All atoms aspherical, anharmonic Fe
N_0	8497	8497	8497	8497	8497
N_v	353	349	368	474	489
$wR(F)$ (%)	4·16	3·65	3·98	2·86	2·77

Hexaaquairon(II) ion

	Spherical, $U_{ij}=0$	Spherical, anharmonic Fe	Aspherical Fe, $U_{ij}=0$	Aspherical Fe, anharmonic Fe
N_0	1375	1375	1375	1375
N_v	3	6	6	9
$wR(F)$ (%)	4·35	4·17	4·01	3·98

respectively real and imaginary.

$$\begin{aligned} T(\mathbf{H}) = [1 &- \tfrac{4}{3}\pi^3 ic^{jkl}h_jh_kh_l + \tfrac{2}{3}\pi^4 c^{jklm}h_jh_kh_lh_m \\ &+ \tfrac{4}{15}\pi^5 ic^{jklm}h_jh_kh_lh_mh_n \\ &- \tfrac{4}{25}\pi^6 c^{jklmnp}h_jh_kh_lh_mh_nh_p + \ldots]T_0(\mathbf{H}). \end{aligned}$$

The statistical rather than physical basis of the GC formalism suggests that it might be capable of modeling properties other than thermal motion if enough terms are used, and in particular the deviations of the static atomic electron density from spherical symmetry, if the analysis is based on X-ray data. The GC treatment of anharmonic temperature factors was originally intended to be applied to neutron diffraction (Johnson & Levy, 1974), which is not affected by these deviations.

There have been several recent studies in which charge density analysis has been applied to series of compounds in order to extract pertinent chemical and physical information. Examples are studies on small compounds of biological relevance (Craven, Fox & Weber, 1982; Stevens, Pant & Klein, 1987), minerals (Downs, Hill, Newton, Tossell & Gibbs, 1982), metalloorganic compounds (Goddard & Kruger, 1982), and our studies on a series of iron porphyrins, which are hemoglobin model compounds (Lecomte, Blessing, Coppens & Tabard, 1986).

The present work is an attempt to analyze to what extent anharmonicity, if present, can be separated from atomic asphericity due to the chemical environment. We have carried out refinements using GC vibrational parameters with both accurate experimental and static-theoretical X-ray data, in order to estimate the extent to which static charge density asphericity can be modeled by the GC terms, and conversely the degree of modification of atomic multipole populations (Hansen & Coppens, 1978) when these are fitted to X-ray data in GC anharmonic refinements.

Two sets of refinements are described here. They use an accurate experimental data set on the porphyrin complex bis(pyridine) (*meso*-tetraphenylporphinato)iron(II) (Li, Coppens & Landrum, 1988), and a static-theoretical data set on the hexaaquairon(II) ion, based on a wave function by Newton and co-workers (Jafri, Logan & Newton, 1980; Logan, Newton & Noell, 1984). Both complexes are low spin, and have pronounced differences between the occupancies of the d-orbital levels, the d_{z^2} and $d_{x^2-y^2}$ orbitals being depleted relative to the t_{2g}-type orbitals. The refinements are summarized in Table 1.

Comparison of anharmonic and multipole models for iron(II)

(*a*) *Refinements of bis*(*pyridine*)(*meso-tetraphenylporphinato*)*iron*(II)

In a recently completed electron density study of this compound Li, Coppens & Landrum (1988) observed aspherical electron density accumulation around the Fe atom compatible with a low-spin electronic state, and found the harmonic vibrational amplitudes to be in good agreement with the rigid-bond postulate of Hirshfeld (1976). The asphericity conferred by the less-populated e_g orbitals, together with the probable lack of pronounced anharmonicity in the symmetric environment, make this compound a suitable test case. The refinements described in this section compare an anharmonic treatment of the iron atom only with a multipole description of the iron-atom valence density. A drawing of the molecule is given in Fig. 1(*a*).

The crystal data are $C_{54}H_{38}FeN_6$, $M_r = 826{\cdot}79$, triclinic, $P\bar{1}$, $a = 9{\cdot}423\,(1)$, $b = 10{\cdot}560\,(2)$, $c = 11{\cdot}998\,(2)$ Å, $\alpha = 101{\cdot}70\,(1)$, $\beta = 104{\cdot}96\,(2)$, $\gamma = 111{\cdot}95\,(2)°$, $V = 1008{\cdot}50\,(2)$ Å^3, $D_x = 1{\cdot}361$ g cm^{-3}, $T = 110\,(5)$ K.

Conventional refinement with harmonic temperature factors and neutral spherical atoms converged at $wR(F) = 4{\cdot}16\%$ for 8497 reflections with $(\sin\theta)/\lambda \le 1{\cdot}15$ Å^{-1}. The 353 variables included the coordinates of all atoms except Fe (which lies on a center of symmetry), anisotropic displacement parameters for Fe, N and C atoms, and isotropic displacement parameters for H atoms. In a second refinement, introduction of the GC fourth-order-tensor elements in the Fe-atom temperature factor gave convergence at $wR(F) = 3{\cdot}65\%$ for the same reflection data. Temperature factors of H atoms were fixed at the values obtained in conventional refinement, and harmonic parameters were varied for C and N atoms, giving 349 variables. In a third refinement, all temperature factors were harmonic, as in the conventional refinement, and multipole population coefficients up to hexadecapole level were varied for the Fe atom only, constrained to the crystallographic $\bar{1}$ symmetry. This gave 368 variables, all other atoms being kept spherical and neutral. The refinement converged at $wR(F) = 3{\cdot}98\%$ for the same reflection data as used in the two previous refinements. It was necessary in this multipole refinement to relax the electroneutrality constraint because of the electron transfer from the Fe atom. The residual electron densities around the Fe atom in the porphyrin plane obtained after the three refinements are compared in Fig. 2. It appears that the anharmonic model is at least as successful as the multipole model in describing the Fe-atom aspherical density.

(*b*) *Refinements of* $[Fe(H_2O)_6]^{2+}$ *using static-theoretical structure factors*

As the results on the porphyrin compound described above seemed to imply that charge-density asphericity can be described quite well by the GC formalism, a set of static structure factors was generated for low-spin $[Fe(H_2O)_6]^{2+}$ from a wave function

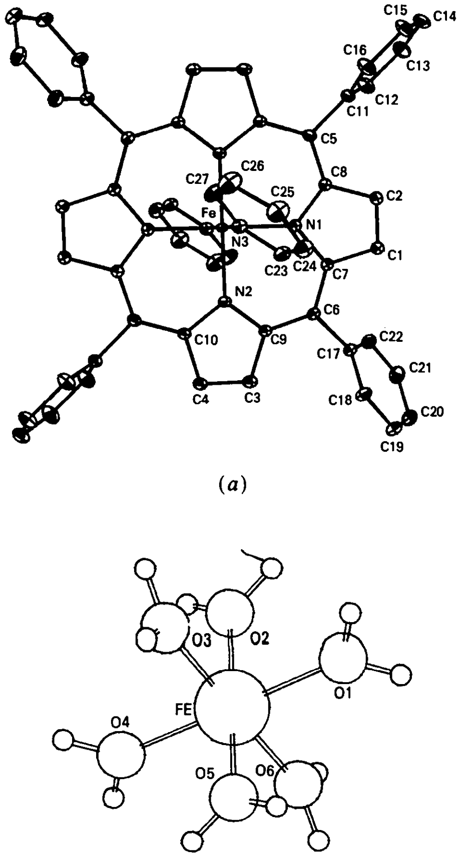

Fig. 1. (*a*) *ORTEP* drawing (Johnson, 1965) of bis(pyridine)-(*meso*-tetraphenylporphinato)iron(II). (*b*) Drawing of the hexaaquairon(II) ion.

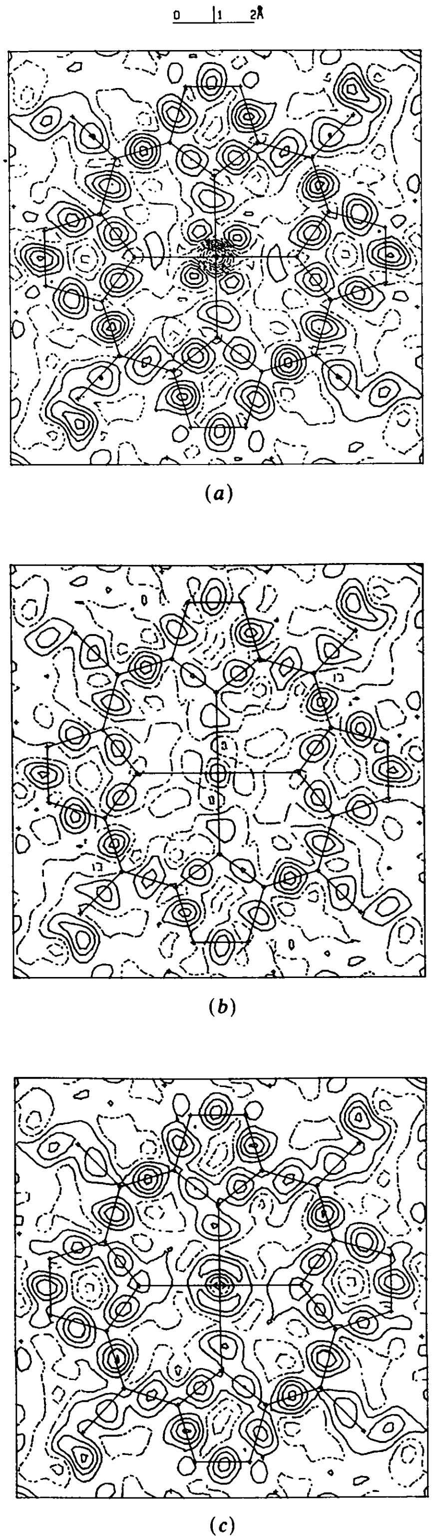

Fig. 2. Residual electron density in the porphyrin plane in bis(pyridine)(*meso*-tetraphenylporphinato)iron(II) after (*a*) conventional harmonic refinement; (*b*) refinement with GC anharmonic temperature factors for Fe atom; (*c*) multipole refinement of Fe atom. Contours at 0·10 e Å^{-3}. Negative contours broken. First positive contour at 0·05 e Å^{-3}.

for high-spin $[Fe(H_2O)_6]^{2+}$ by Newton and coworkers (Jafri, Logan & Newton, 1980; Logan, Newton & Noell, 1984) with a modified occupation of the orbitals. The octahedrally hydrated cation (see Fig. 1*b*) was placed in a cubic unit cell in space group *Pm*3 (No. 200), with $a = 10{\cdot}000$ Å. For the 1375 independent structure factors having $(\sin\theta)/\lambda \leq 1{\cdot}2\ \text{Å}^{-1}$, conventional (spherical) refinement gave $wR(F) = 4{\cdot}35\%$. The three variables were the x coordinate of the O atom [situated at position 6(*e*) with site symmetry *mm*] and the x and z coordinates of the H atom [at position 12(*j*) with symmetry *m*], the Fe atom being fixed at the origin with site symmetry *m*3. All temperature factors were fixed at zero. Introduction of the three allowed harmonic and anharmonic thermal parameters of the Fe atom (U_{11}, c^{1111} and c^{1122}, with constraints for U_{22}, U_{33}, c^{2222}, c^{3333}, c^{1133} and c^{2233}) as variables, together with the coordinates, reduced $wR(F)$ to 4·17% for the same reflection data. When multipole coefficients for the Fe atom were introduced instead of the thermal parameters, the refinement converged at $wR(F) = 4{\cdot}01\%$. In this last refinement the six variables were the coordinates, as before, together with, for the Fe atom only, the valence-shell expansion–contraction parameter κ'' and the two allowed population coefficients P_{00} and P_{40} with P_{44}, constrained to $0{\cdot}74048P_{40}$ in a Kubic harmonic basis set (Van der Lage & Bethe, 1947). All other atoms were treated as spherical and neutral and temperature factors for all atoms were fixed at zero.*

The residual electron densities around the Fe atom in the FeO_4 plane are compared for the three refinements in Fig. 3. The multipole model is seen to fit the static data rather better than the anharmonic model, as reflected in the *wR* values. Fig. 4 compares the models themselves, rather than the residual density not fitted by the models. The Fourier coefficients were obtained by subtracting the calculated structure factors after conventional refinement from, respectively, the calculated structure factors after anharmonic refinement in Fig. 4(*a*) and after multipole refinement in Fig. 4(*b*). The difference between the two models is shown in Fig. 4(*c*), in which the Fourier coefficients are $F_{c(\text{multipole})} - F_{c(\text{anharmonic})}$. The physical similarity between the multipole and anharmonic models is strikingly high, indicating the ability of the GC formalism to model the iron-atom asphericity, even in the case of static data.

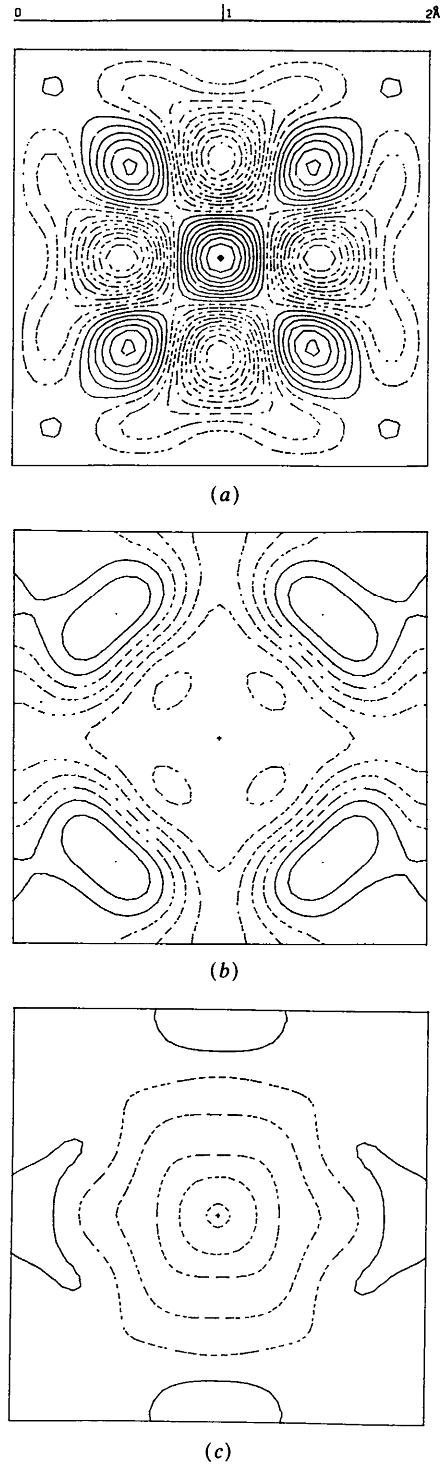

Fig. 3. Residual static electron density in the FeO_4 plane in low-spin $[Fe(H_2O)_6]^{2+}$. (*a*) After refinement of coordinates only. Contours at 0·20 e Å^{-3}. First positive contour at 0·1 e Å^{-3}. Negative contours broken. (*b*) Inclusion of GC anharmonic temperature factors for Fe atom in the refinement. Contours at 0·10 e Å^{-3}. (*c*) Multipole refinement of Fe atom. Contours at 0·10 e Å^{-3}. First positive contour at 0·05 e Å^{-3}. Oxygen atoms are at 2·131 Å from the iron atom in horizontal and vertical directions.

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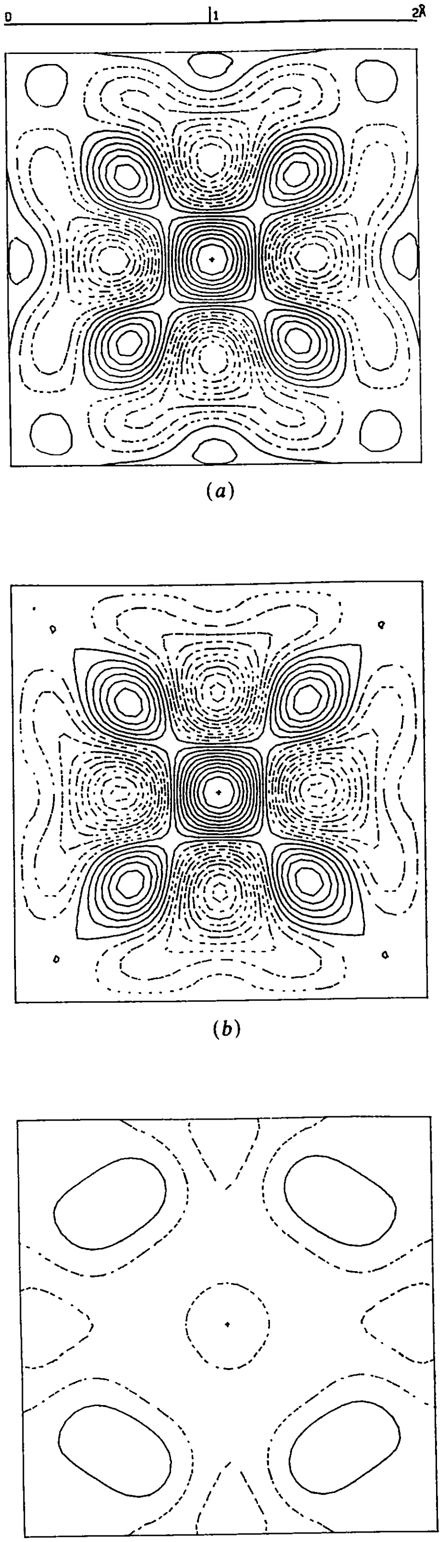
* Lists of theoretical and calculated structure factors for $[Fe(H_2O)_6]^{2+}$ and observed and calculated structure factors for bis(pyridine)(*meso*-tetraphenylporphinato)iron(II) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP44615 (61 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



(a)

(b)

(c)

Fig. 4. Static model maps in the FeO_4 plane in low-spin $[Fe(H_2O)_6]^{2+}$ for (*a*) anharmonic Fe atom; (*b*) aspherical Fe atom; (*c*) the difference between the aspherical and anharmonic models. Contours as in Fig. 3(*a*). Oxygen atoms are at 2·131 Å from the iron atom in horizontal and vertical directions.

Simultaneous refinements of anharmonic and multipole parameters

First attempts at simultaneous refinement of multipole populations and iron GC coefficients for the iron–porphyrin complex resulted in divergence. Initially, therefore, neutral spherical atoms including GC anharmonic parameters for the Fe atom were fitted to 3105 high-angle reflections [$(\sin\theta)/\lambda \geq 0{\cdot}8$ Å^{-1}]. The information in this subset of data represents dynamic effects to a greater degree than it describes static atomic asphericity, since scattering from the valence electrons is concentrated at relatively low angles. It should be noted, however, that comparison of the two available low-temperature data sets on $Fe(tpp)(py)_2$ (Li, Coppens & Landrum, 1988) confirms earlier evidence indicating that the effects of *d*-orbital scattering persist well into the high-order region, so that the deconvolution can only be approximate.

The GC parameters were fixed at the high-order values in subsequent refinement of multipole parameters for all atoms, constrained to have site symmetry D_{4h} for Fe, C_{2v} for N, C_{2v} or C_s for C, and C_s for H atoms (Li, Coppens & Landrum, 1988). The 474 variables included all atomic coordinates (except for Fe atom), anisotropic displacement parameters for Fe, N and C atoms, isotropic displacement parameters for H, κ' for C and N, κ'' for C and Fe atoms. Convergence was obtained at $wR(F) = 2{\cdot}86\%$ for 8497 reflections with $(\sin\theta)/\lambda \leq 1{\cdot}15$ Å^{-1}, essentially identical to the earlier harmonic aspherical-atom *R* factor of 2·85% (Li, Coppens & Landrum, 1988).

Subsequently the GC parameters were allowed to refine simultaneously with the multipole parameters, giving 489 variables, using all 8497 reflections. This was successful, convergence being obtained at $wR(F) = 2{\cdot}77\%$ after a slight divergence in the first cycle.

The largest correlation coefficients were found among harmonic and anharmonic parameters: $\gamma[U(11), C(1111)] = 0{\cdot}90$; $\gamma[U(22), U(23)] = 0{\cdot}95$; $\gamma[U(22), C(2222)] = 0{\cdot}97$; $\gamma[U(22), C(2223)] = 0{\cdot}92$; $\gamma[U(23), C(2222)] = 0{\cdot}91$; $\gamma[U(23), C(2223)] = 0{\cdot}94$; $\gamma[C(2222), C(2223)] = 0{\cdot}93$; $\gamma[C(2223), C(2233)] = 0{\cdot}91$. The only large correlation between the population and thermal parameters occurred for $U(22)$ and $U(23)$ of iron and the P_{20} population parameter on this atom, for which the correlation coefficients were $-0{\cdot}90$ and $-0{\cdot}93$ respectively.

Table 2 shows the displacement parameters for the Fe atom from the anharmonic spherical refinement, together with those from the harmonic and anharmonic multipole refinements. The U_{ij} values in the last case are about 50% higher than in the second, but smaller than those in the anharmonic spherical refinement, which are about twice as large as the

Table 2. *Anisotropic displacement parameters for the iron atom in the iron–porphyrin complex*

	Harmonic multiple*	Anharmonic spherical†	Anharmonic multiple†
U_{11}(Å^2)	0·00501 (10)	0·01155 (27)	0·00752 (42)
U_{22}	0·00772 (10)	0·01658 (31)	0·01203 (76)
U_{33}	0·00774 (10)	0·01644 (31)	0·01197 (32)
U_{12}	0·00244 (8)	0·00572 (22)	0·00359 (17)
U_{13}	0·00287 (8)	0·00609 (22)	0·00427 (18)
U_{23}	0·00293 (10)	0·00582 (23)	0·00418 (48)
C_{1111}($\times10^2$ Å^4)‡		0·070 (5)	0·018 (4)
C_{2222}		0·116 (7)	0·048 (9)
C_{3333}		0·121 (7)	0·049 (5)
C_{1112}		0·032 (3)	0·008 (2)
C_{1222}		0·048 (4)	0·014 (3)
C_{1113}		0·047 (3)	0·014 (2)
C_{1333}		0·045 (4)	0·018 (2)
C_{2223}		0·032 (4)	0·013 (5)
C_{2333}		0·045 (4)	0·016 (3)
C_{1122}		0·044 (3)	0·013 (2)
C_{1133}		0·053 (3)	0·019 (2)
C_{2233}		0·050 (3)	0·020 (3)
C_{1123}		0·027 (2)	0·008 (1)
C_{1223}		0·027 (2)	0·009 (2)
C_{1233}		0·033 (2)	0·010 (1)

* Li, Coppens & Landrum (1988)

† This work.

‡ C_{ijkl} are related to c^{ijkl} of the expression given in the text by $C_{ijkl}\, a_i^* a_j^* a_k^* a_l^* = c^{ijkl}$.

Table 3. *Iron d-orbital populations (electrons) and percentages of the total population obtained from the two multipole refinements*

	Harmonic		Anharmonic	
P_{z^2}	1·05	14·4%	0·75	11·8%
P_{xz}, P_{yz}	3·86	53·0%	3·38	53·3%
$P_{x^2-y^2}$	0·35	4·8%	0·39	6·1%
P_{xy}	2·02	27·7%	1·82	28·8%

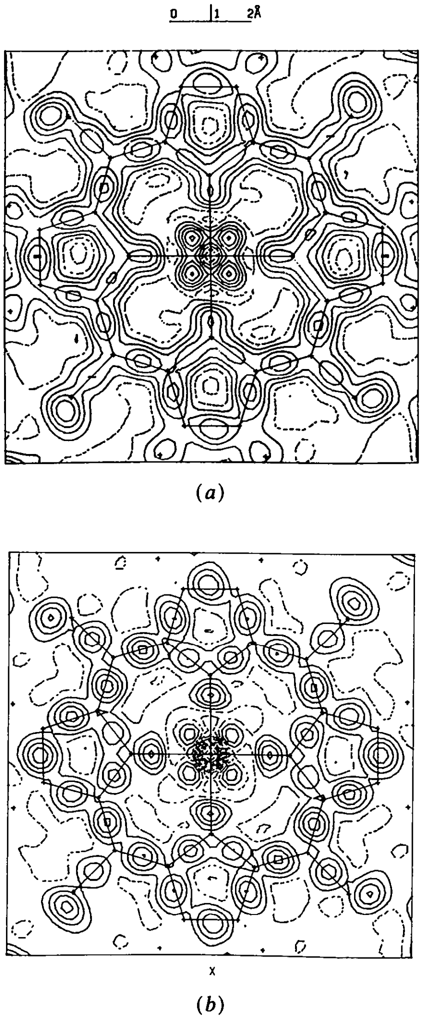
harmonic multipole refinement values. This factor of two seems unrealistic and not in agreement with the experience of the GC formalism as applied to neutron data. In each of the anharmonic refinements, the GC coefficients have a high level of significance, and there are highly significant differences between corresponding spherical and multipole values. These observations indicate that consideration of the atomic asphericity is essential in obtaining meaningful anharmonic displacement parameters.

Table 3 compares the iron *d*-orbital populations derived from the multipole coefficients (Holladay, Leung & Coppens, 1983). Although the relative populations of the orbitals are not much affected by the introduction of anharmonicity, there is a reduction in the total population of about one electron. A graphical representation of this appears in Fig. 5, where the decrease in electron population of the iron atom is clearly evident.

Finally, the static data on the hexaaquairon(II) complex were refined with the multipole model and an anharmonic temperature factor for the Fe atom. The refinement led to a small decrease in *R* factor from 4·01 to 3·98% (Table 1). Though this improvement is significant at the 0·5% confidence level according to the Hamilton (1965) test, all values of the temperature parameters are smaller than three times their estimated standard deviations. For the static data at least, the refinement properly attributes the asphericity to the multipole functions.

Concluding remarks

It is clear that in a conventional X-ray refinement the GC formalism does not solely represent thermal motion and that sometimes the high-order GC terms might not represent thermal motion at all. Since some degree of anharmonicity may always be present, the metal-atom asphericity from a harmonic multipole refinement of X-ray data on a coordination complex may be an upper limit. Combined multipole-anharmonicity refinements may be desirable in many



(*a*)

(*b*)

Fig. 5. Multipole deformation density maps in the porphyrin plane in bis(pyridine)(*meso*-tetraphenylporphinato)iron(II) with (*a*) harmonic temperature parameters for all atoms; (*b*) anharmonic temperature parameters for Fe atom. Contours as in Fig. 2.

studies. In cases where overlap density in the bonds rather than the density in preferentially occupied atomic orbitals is dominant, as for example in silicon (Aldred & Hart, 1973; Yang & Coppens, 1974), third-order anharmonic terms may represent additional vibration away from the bonds, in which case neglect of anharmonic effects *reduces* charge asphericity. It is well known that the 'forbidden' 222 reflection of Si decreases in intensity with increasing temperature, goes through zero where asphericity and anharmonicity balance, and then increases again when the temperature is raised further (Roberto & Batterman, 1970; Roberto, Batterman & Keating, 1974).

We conclude that the statistical Gram-Charlier formalism is remarkably successful in representing bonding effects in the valence charge density. It cannot be used as a thermal motion formalism for X-ray data if such effects are significant, unless atomic asphericity is specifically included in the scattering formalism. The results suggest that an approximate separation between aspherical charge-density effects and anharmonic motion is feasible.

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Negative Volumes and Central Moments of Anharmonic Probability Density Functions

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Abstract

The suitability of different functions used for anharmonic temperature factors in describing anharmonicity in structures is studied from the point of view of whether the respective probability density functions (p.d.f.'s) (isolated-atom-potential expansions, Gram-Charlier series, p.d.f. of the cumulant expansion of the temperature factor) are non-negative for the final values of the parameters. Certain central moments of the p.d.f. should also not become negative. Analytical formulae have been derived for the central moments of several (different) p.d.f.'s. 20 p.d.f.'s of atoms in published structures have been examined, their negative volumes determined by numerical integration and their central moments calculated. For Al(4) in the structure of $VAl_{10\cdot42}$ at 293 K (strong anharmonicity) the negative volume was $-0\cdot238$ and several moments were negative. Here the temperature factor and p.d.f. used are not acceptable. For the remaining structures (weak anharmonicity) the negative volumes found were $<|-0\cdot03|$ and the respective central moments were positive. Temperature factors and p.d.f.'s proved to be acceptable except for the cumulant expansion. In some cases its p.d.f. is not accessible, and, if it is, its negative volumes were found to be relatively large. A p.d.f. is proposed which is non-negative for all values of the parameters and whose Fourier transform can be derived in analytical form. An explicit formula is given for the cubic site symmetries.

1. Introduction

The commonly used functions for anharmonic probability density functions (abbreviated p.d.f.'s), *i.e.* the isolated-atom-potential expansions of the Boltzmann function (Willis, 1969; Willis & Pryor, 1975; Tanaka & Marumo, 1983; Scheringer, 1985*a*), the Fourier-invariant expansions of the Boltzmannn function (Merisalo & Larsen, 1977; Kurki-Suonio, Merisalo & Peltonen, 1979; Rossmanith, 1984) and the Gram-Charlier series (*International Tables for X-ray Crystallography*, 1974, p. 316; Zucker & Schulz, 1982; Kuhs, 1983) do not exclude that they may become negative for certain values of the parameters. By definition, a p.d.f. should be non-negative everywhere. If the negative volume is large, the function used with the set of given parameters cannot be accepted on physical grounds and should be eliminated. For the cumulant expansion (Johnson, 1969, 1970) of the temperature factor (abbreviated t.f.), the p.d.f. is not known but we have shown earlier (Marcinkiewicz, 1938; Scheringer, 1985*b*) that it always has some negative volume, although of unknown size. For the isolated-atom-potential p.d.f. (abbreviated IAP p.d.f.), Mackenzie & Mair (1985) arrive at a similar conclusion: the IAP p.d.f. (moment expansion) '... always [*i.e.* for any set of parameters] goes negative for some value of [the argument] x... and so is not a proper p.d.f.'. It will be shown that this statement is not valid to this degree of generality. Apart from this, Mackenzie & Mair (1985) have shown by means of one-dimensional model calculations that the negative volumes of the p.d.f.'s are small in the case of weak anharmonicity.

In this paper several structures are selected from the literature where anharmonic refinements were reported, and the negative volumes of the p.d.f.'s are determined by means of numerical integration. In this way we could examine the usability of a p.d.f. for the given values of the parameters in a structure. Another approach to obtain insight into the quality of a p.d.f. is given by the evaluation of its central moments. Certain moments should be non-negative if the p.d.f. is non-negative everywhere. Calculation of the moments of the p.d.f. renders the numerical integration of the negative volumes superfluous to some extent. We have derived analytical expressions for the central moments of several (different) p.d.f.'s. In this way the control of the quality of a p.d.f. is simplified. The examination of the cumulant expansion of the t.f. (Johnson, 1969, 1970) poses some special problems which we shall discuss. Finally, we shall show that it is possible to construct p.d.f.'s which are non-negative everywhere for every set of parameters.

2. Calculation of the negative volumes and central moments of a p.d.f.

Negative volumes

For a p.d.f. $f(\mathbf{u})$, the normalization condition $\int f(\mathbf{u})\,d\mathbf{u}=1$, $\mathbf{u}=$ vibrational coordinates of the

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