completeness of data. To achieve high contrast in electron-density maps, for instance in studies of small-amplitude conformational changes, either additional structural information must be available or modified data collection strategies must be followed which involve Laue exposures at even more crystal orientations or a combination of Laue and monochromatic crystal rotation techniques.

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On the Mapping of Electrostatic Properties from the Multipole Description of the Charge Density

By Zhengwei Su and Philip Coppens

Chemistry Department, SUNY at Buffalo, Buffalo, NY 14214, USA

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Abstract

A method is presented to calculate the electrostatic potential, the electric field and the electric-field gradient in a crystal from the atomic multipole expansion of the experimental charge density, as described by the Hansen-Coppens formalism [Hansen & Coppens (1978), *Acta Cryst.* **A34**, 909-921]. The electrostatic properties are expressed in terms of the positions and the charge-density parameters of the individual atoms. Contributions due to the procrystal charge density and the deformation

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charge density are compared. The method is illustrated by the calculation of the electrostatic potential maps of fully deuterated benzene and of iron(II) tetraphenylporphyrin.

Introduction

The accessibility of charge densities from experimental measurements has drawn attention to the physical properties that can be derived from the charge density. Foremost among these are the electrostatic properties. The electrostatic potential Φ, the electric field $\mathbf{E}$ and the electric-field-gradient elements ∇E_{mn} at position $\mathbf{R}_p$ in a crystal are given by

$$\Phi(\mathbf{R}_p)=\int[\rho_t(\mathbf{r})/|\mathbf{R}_p-\mathbf{r}|] \qquad (1)$$

$$\mathbf{E}(\mathbf{R}_p)=\int[(\mathbf{R}_p-\mathbf{r})\rho_t(\mathbf{r})/|\mathbf{R}_p-\mathbf{r}|^3]\,\mathrm{d}\mathbf{r} \qquad (2)$$

$$\nabla E_{mn}(\mathbf{R}_p)=-\int\{[3x_mx_n-\delta_{mn}|\mathbf{R}_p-\mathbf{r}|^2]/|\mathbf{R}_p-\mathbf{r}|^5\}\times\rho_t(\mathbf{r})\,\mathrm{d}\mathbf{r} \qquad (3)$$

where $\rho_t(\mathbf{r})=\rho_n(\mathbf{r})-\rho_e(\mathbf{r})$ is the total charge density, the subscripts n and e denoting the nuclear and electronic densities, respectively. x_k is the kth component of $\mathbf{R}_p-\mathbf{r}$ in a Cartesian coordinate system and δ is the Kronecker delta.

The formalisms for the mapping of the electrostatic properties of the crystal directly from the experimental structure factors have been published (Bertaut, 1978; Stewart, 1979; Schwarzenbach & Thong, 1979). In general, the reciprocal-space summation is affected by series termination. This is true in particular for the electric field and the electric-field gradient, but less so for the electrostatic potential for which the Fourier coefficients are equal to $F(\mathbf{H})/|\mathbf{H}|^2$.

Alternatively, the electrostatic properties due to individual atomic or molecular densities may be calculated in direct space from the charge density as described by the multipole expansion, the coefficients of which can be obtained from the X-ray structure factors by least-squares methods (Stewart, 1976; Hirshfeld, 1977; Hansen & Coppens, 1978).

Formalisms for the direct-space evaluation of the electrostatic potential based on the Laplace expansion of $|\mathbf{R}_p-\mathbf{r}|^{-1}$ have been reported by Bentley (1981), and for diatomic molecules only by Fink & Bonham (1981). The Fourier convolution-theorem method has been used for the calculation of the electric-field gradient (EFG) at the atomic nuclei by Epstein & Swanton (1982). In the present paper, Epstein & Swanton's method is generalized to include the derivation of the electrostatic potential and the electric field as well as the electric-field gradient at any position in space. We note that several results for similar calculations have been published (*e.g.* Spackman & Stewart, 1981; Swaminathan & Craven, 1984; He, Swaminathan, Craven & McMullan, 1988; Destro, Bianchi & Morosi, 1989; Stewart, 1991). However, except in the case of the Epstein–Swanton expressions, we have not been able to compare the formalisms presented here with those used earlier as no record is available in the literature. A computer program for the calculation of electrostatic properties, *MOLPROP* (Su, 1991), is available for distribution.

Calculation of the electrostatic properties from the pseudoatom densities

In the following, we shall derive the relations corresponding to the Hansen–Coppens charge-density expansion formalism (Hansen & Coppens, 1978), in which the aspherical electron density of an atom is described by

$$\rho_e(\mathbf{r})=P_c\rho_c(r)+P_v\kappa'^3\rho_v(\kappa' r)\times\sum_{l=0}^{i_{\max}}\kappa''^3R_l(\kappa'' r)\sum_{m=0}^{l}\sum_{p}P_{lmp}d_{lmp}(\theta,\varphi) \qquad (4)$$

where $\rho_c(r)$ and $\rho_v(r)$ are core- and valence-electron densities constructed from the canonical Hartree–Fock atomic orbitals, $R_l(r)$ is a normalized Slater-type radial function (STF),

$$R_l(r)=[\zeta^{(n_l+3)}/(n_l+2)!]r^{n_l}e^{-\zeta r}, \qquad (5)$$

P_c, P_v and P_{lmp} are the population coefficients, p can be + or − for nonzero l. $d_{lmp}(\theta,\varphi)$ are real spherical harmonic functions satisfying the normalization condition

$$\int_0^{2\pi}\int_0^{\pi}|d_{lmp}(\theta,\varphi)|\sin(\theta)\,\mathrm{d}\theta\,\mathrm{d}\varphi=2-\delta_{0,l} \qquad (6)$$

which in (4) are referred to local symmetry-adapted Cartesian coordinate systems. The electron densities ρ_c and ρ_v, normalized to one electron, can be written in the form

$$N_c\rho(r)=\frac{1}{4\pi}\sum_{j=1}^{\mu_c}N_j\sum_{i=1}^{\nu_j}\sum_{k=1}^{\nu_j}C_{j,i}C_{j,k}\times\left[\frac{(2\zeta_{j,i})^{(2n_{j,i}+3}(2\zeta_{j,k})^{(2n_{j,k}+3)}}{(2n_{j,i}+2)!(2n_{j,k}+2)!}\right]^{1/2}\times r^{(n_{j,i}+n_{j,k})}\exp[-(\zeta_{j,i}+\zeta_{j,k})r] \qquad (7)$$

$$N_v\rho(r)=\frac{1}{4\pi}\sum_{j=1}^{\mu_v}N_j\sum_{i=1}^{\nu_j}\sum_{k=1}^{\nu_j}C_{j,i}C_{j,k}\times\left[\frac{(\zeta_{j,i})^{(2n_{j,i}+3)}(2\zeta_{j,k})^{(2n_{j,k}+3)}}{(2n_{j,i}+2)!(2n_{j,k}+2)!}\right]^{1/2}\times r^{(n_{j,i}+n_{j,k})}\exp[-(\zeta_{j,i}+\zeta_{j,k})r] \qquad (8)$$

where $\mu_{c,v}$ is the number of atomic orbitals in the core and valence shell, respectively, ν_j is the number of basis-set functions for orbital j, N_j is the occupancy of the jth orbital, $N_c=\sum_{j=1}^{\mu_c}N_j$, $N_v=\sum_{j=1}^{\mu_v}N_j$. The expansion coefficients $C_{j,i}$, $C_{j,k}$ and the exponents $\zeta_{j,i}$,

$\zeta_{i,k}$ in the Slater-type basis functions are taken from the Roothaan-Hartree-Fock wave function for the ground-state atom (Clementi & Roetti, 1974). For a basis function with principal quantum number n, $n_i = n_k = n-1$. As an example, for a ground-state C atom the number of orbitals in the valence shell μ_v equals 4, with $N_v = 4$, $N_1 = 2$ and $N_2 = 2$; the subshells are expansions of six and four slater-type functions, respectively, *i.e.* $\nu_1 = 6$, $\nu_2 = 4$. Note that because of the spherical averaging of ρ_c and ρ_v the occupancies of orbitals with the same n and l values are the same, regardless of their m values. In other words, the electrons in a subshell are evenly distributed among the orbitals with different m quantum numbers.

The scattering factor for the atomic density in (4) is

$$\begin{aligned} f_e(\mathbf{S}) &= \int \rho_e(\mathbf{r}) \exp(2\pi i\mathbf{S}\cdot\mathbf{R})\,\mathrm{d}\mathbf{r} \\ &= P_c f_c(S) + P_v f_v(S/\kappa') \\ &\quad + 4\pi \sum_{l=0}^{l_{\max}} \sum_{m=0}^{l} \sum_{p} [i^l \langle j_l(S/\kappa'')\rangle P_{lmp} d_{lmp}(\mathbf{S}/S)] \end{aligned} \tag{9}$$

where $j_l(x)$ is the lth-order spherical Bessel function (Arfken, 1970) and $\langle j_l(S)\rangle$ is defined by the Fourier-Bessel transform

$$\langle j_l(S)\rangle = \int_0^\infty r^2 R_l(r) j_l(2\pi Sr)\,\mathrm{d}r \tag{10}$$

and

$$f_c(S) = \langle j_{0,c}(S)\rangle = 4\pi \int_0^\infty r^2 \rho_c(r) j_0(2\pi Sr)\,\mathrm{d}r \tag{11}$$

$$f_v(S) = \langle j_{0,v}(S)\rangle = 4\pi \int_0^\infty r^2 \rho_v(r) j_0(2\pi Sr)\,\mathrm{d}r. \tag{12}$$

Equations (1), (2) and (3) can be rewritten as

$$\Phi(\mathbf{R}_p) = \sum_{M\neq P} Z_m/|\mathbf{R}_{MP}| - \sum_M \int [\rho_{e,M}(\mathbf{r}_M)/|\mathbf{r}_P|]\,\mathrm{d}\boldsymbol{r}_M \tag{13}$$

$$\begin{aligned} \mathbf{E}(\mathbf{R}_P) &= \sum_{M\neq P} Z_M \mathbf{R}_{MP}/|\mathbf{R}_{MP}|^3 \\ &\quad + \sum_M \int [r_P \rho_{e,M}(\mathbf{r}_M)/|\mathbf{r}_P|^3]\,\mathrm{d}\mathbf{r}_M \end{aligned} \tag{14}$$

$$\begin{aligned} &\nabla \boldsymbol{E}_{mn}(\mathbf{R}_P) \\ &\quad = -\sum_{M\neq P} Z_M(3t_m t_n - \delta_{mn}|\mathbf{R}_{MP}|^2)/|\mathbf{R}_{MP}|^5 \\ &\qquad + \sum_M \int [\rho_{e,M}(\mathbf{r}_M)(3x_m x_n - \delta_{mn}|\mathbf{r}_P|^2)/|\mathbf{r}_P|^5]\,\mathrm{d}\mathbf{r}_M \end{aligned} \tag{15}$$

where Z_M and $\mathbf{R}_M$ are the nuclear charge and the position vector of atom M respectively. $\mathbf{r}_P$ and $\mathbf{r}_M$ are the vectors from P and from the nucleus M to a point $\mathbf{r}$ respectively (Fig. 1) such that $\mathbf{r}_P = \mathbf{r} - \mathbf{R}_P$ and $\mathbf{r}_M = \mathbf{r} - \mathbf{R}_M = \mathbf{r}_P + \mathbf{R}_P - \mathbf{R}_M = \mathbf{r}_P - \mathbf{R}_{MP}$. t_k is the kth component of $\mathbf{R}_{MP}$ and x_k is the kth component of $\mathbf{r}_P$ $(1 \le k \le 3)$.

The electrostatic properties at a nucleus can be split into contributions from the charge density centered at this nucleus and those of the densities associated with all other atoms. We refer to the former as *central* and the latter as *peripheral* (lattice) contributions respectively. If the point in question, P, is not at a nucleus, then only the peripheral contributions exist.

Peripheral contributions

The integrals involved are one-electron two-center integrals, which can be evaluated by the use of the Fourier convolution-theorem method (Prosser & Blanchard, 1962)

$$\int f(\mathbf{r}) g^*(\mathbf{r}-\mathbf{R})\,\mathrm{d}\mathbf{r} = \int F(\mathbf{S}) G^*(\mathbf{S}) \exp(-2\pi i\mathbf{S}\cdot\mathbf{R})\,\mathrm{d}\mathbf{S} \tag{16}$$

where $F(\mathbf{S})$ and $G(\mathbf{S})$ are the Fourier transforms of $f(\mathbf{r})$ and $g(\mathbf{r})$, respectively, and * indicates the complex conjugate,

$$F(\mathbf{S}) = \int f(\mathbf{r}) \exp(2\pi i\mathbf{S}\cdot\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{17}$$

$$G(\mathbf{S}) = \int g(\mathbf{r}) \exp(2\pi i\mathbf{S}\cdot\mathbf{r})\,\mathrm{d}\mathbf{r}. \tag{18}$$

The integrals in (13) through (15) can be rewritten as

$$\begin{aligned} &\int [\rho_{e,M}(\mathbf{r}_M)/|\mathbf{r}_P|]\,\mathrm{d}\mathbf{r}_M \\ &\quad = \pi^{-1} \int [f_{e,M}(\mathbf{S})/|\mathbf{S}|^2] \exp(2\pi i\mathbf{S}\cdot\mathbf{R}_{MP})\,\mathrm{d}\mathbf{S} \end{aligned} \tag{19}$$

$$\begin{aligned} &\int [\mathbf{r}_p \rho_{e,M}(\mathbf{r}_M)/|\mathbf{r}_p|^3]\,\mathrm{d}\mathbf{r}_M \\ &\quad = 2i \int [\mathbf{S} f_{e,M}(\mathbf{S})/|\mathbf{S}|^2] \exp(2\pi i\mathbf{S}\cdot\mathbf{R}_{MP})\,\mathrm{d}\mathbf{S} \end{aligned} \tag{20}$$

$$\begin{aligned} &\int [\rho_{e,M}(\mathbf{r}_M)(3x_{m,P}x_{n,P} - \delta_{mn}|\mathbf{r}_P|^2)/|\mathbf{r}_P|^5]\,\mathrm{d}\mathbf{r}_M \\ &\quad = -(4\pi/3) \int [(3S_m S_n - \delta_{mn}|\mathbf{S}|^2) f_{e,M}(\mathbf{S})/|\mathbf{S}|^2] \\ &\qquad \times \exp(2\pi i\mathbf{S}\cdot\mathbf{R}_{MP})\,\mathrm{d}\mathbf{S}. \end{aligned} \tag{21}$$

In the following, it is assumed that all the direct-space vectors are referred to the local Cartesian coordinate system of atom M.

The expansion of $\exp(i\mathbf{S}\cdot\mathbf{R})$ (Cohen-Tannoudji, Diu & Laloë, 1977; Arfken, 1970)

$$\exp(i\mathbf{S}\cdot\mathbf{r}) = \sum_{l=0}^{\infty} i^l (2l+1) j_l(Sr) P_l(\cos\gamma) \tag{22}$$

[where $P_l(x)$ is the lth-order Legendre polynomial and γ is the angle between $\mathbf{S}$ and $\mathbf{r}$] can then be used to separate the integration into a radial and an angular

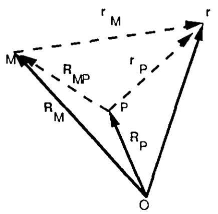

Fig. 1. Definition of the vectors used in the electrostatic functions.

part. The results are as follows:[†]

$$\begin{aligned}
&\Phi^{\mathrm{per}}(\mathbf{R}_p)\\
&\quad=\sum_{M\neq P} Z_M/|\mathbf{R}_{MP}|\\
&\qquad-\sum_{M\neq P}\Big\{(2/\pi)(P_{M,c}/N_c)\sum_{j=1}^{\mu_c}N_j\sum_{i=1}^{\nu_j}\sum_{k=1}^{\nu_j}C_{j,i}C_{j,k}\\
&\qquad\times\left[\frac{(2\zeta_{j,i})^{(2n_{j,i}+3)}(2\zeta_{j,k})^{(2n_{j,k}+3)}}{(2n_{j,i}+2)!(2n_{j,k}+2)!}\right]^{1/2}\\
&\qquad\times A_{n_i+n_k,0,0,0}(\zeta_{j,i}+\zeta_{j,k},\,|\mathbf{R}_{MP}|)\\
&\qquad+(2/\pi)(P_{M,v}/N_v)\sum_{j=1}^{\mu_v}N_j\sum_{i=1}^{\nu_j}\sum_{k=1}^{\nu_j}C_{j,i}C_{j,k}\\
&\qquad\times\left[\frac{(2\kappa'\zeta_{j,i})^{(2n_{j,i}+3)}(2\kappa'\zeta_{j,k})^{(2n_{j,k}+3)}}{(2n_{j,i}+2)!(2n_{j,k}+2)!}\right]^{1/2}\\
&\qquad\times A_{n_{j,i}+n_{j,k},0,0,0}[\kappa'(\zeta_{j,i}+\zeta_{j,k}),\,|\mathbf{R}_{MP}|]\\
&\qquad+8\sum_{l_1=0}^{l_{1,\max}}\sum_{m_1=0}^{l_1}\sum_{p_1}(-1)^{l_1}[\zeta_{l_1}^{(n_{l_1}+3)}/(n_{l_1}+2)!]\\
&\qquad\times A_{n_{l_1},l_1,l_1,0}(\kappa''\zeta_{l_1},\,|\mathbf{R}_{MP}|)\\
&\qquad\times P_{l_1m_1p_1}d_{l_1m_1p_1}(\theta_{\mathbf{R}_{MP}},\varphi_{\mathbf{R}_{MP}})\Big\}. \qquad (23)
\end{aligned}$$

In (23) and the equations to follow, the electronic density parameters inside the curly brackets are for the atom M and the polar coordinate system has the z axis of the local Cartesian coordinate system as its polar axis and the vector $\mathbf{R}_{MP}$ is referred to this local Cartesian coordinate system.

$$\begin{aligned}
&E^{\mathrm{per}}_{1u\pm}(\mathbf{R}_P)\\
&\quad=\sum_{M\neq P}{}''\,(Z_M/|\mathbf{R}_{MP}|^2)P_1^u[\cos(\theta_{R_{MP}})]\\
&\qquad\times\begin{Bmatrix}\cos(u\varphi_{R_{MP}})\\ \sin(u\varphi_{R_{MP}})\end{Bmatrix}\\
&\qquad-\sum_{M\neq P}{}''\Big\{(2/\pi)(P_{M,c}/N_c)\sum_{j=1}^{\mu_c}N_j\sum_{i=1}^{\nu_j}\sum_{k=1}^{\nu_j}C_{j,i}C_{j,k}\\
&\qquad\times\left[\frac{(2\zeta_{j,i})^{(2n_{j,i}+3)}(2\zeta_{j,k})^{(2n_{j,k}+3)}}{(2n_{j,i}+2)!(2n_{j,k}+2)!}\right]^{1/2}\\
&\qquad\times A_{n_i+n_k,\,0,1,1}(\zeta_{j,i}+\zeta_{j,k},\,|\mathbf{R}_{MP}|)\\
&\qquad\times P_1^u[\cos(\theta_{\mathbf{R}_{MP}})]\begin{Bmatrix}\cos(u\varphi_{\mathbf{R}_{MP}})\\ \sin(u\varphi_{\mathbf{R}_{MP}})\end{Bmatrix}\\
&\qquad+(2/\pi)(P_{M,v}/N_v)\sum_{j=1}^{\mu_v}N_j\sum_{i=1}^{\nu_j}\sum_{k=1}^{\nu_j{}'}C_{j,i}C_{j,k}\\
&\qquad\times\left[\frac{(2\kappa'\zeta_{j,i})^{(2n_{j,i}+3)}(2\kappa'\zeta_{j,k})^{(2n_{j,k}+3)}}{(2n_{j,i}+2)!(2n_{j,k}+2)!}\right]^{1/2}\\
&\qquad\times A_{n_i+n_k,0,1,1}[\kappa'(\zeta_{j,i}+\zeta_{j,k}),\,|\mathbf{R}_{MP}|]\\
&\qquad\times P_1^u[\cos(\theta_{\mathbf{R}_{MP}})]\begin{Bmatrix}\cos(u\varphi_{\mathbf{R}_{MP}})\\ \sin(u\varphi_{\mathbf{R}_{MP}})\end{Bmatrix}\\
&\qquad-16\,(\pi/3)^{1/2}\sum_{l_1=0}^{l_{1,\max}}\sum_{m_1=0}^{l_1}\sum_{p_1}\sum_{l}\sum_{m}i^{(l_1+l+1)}\\
&\qquad\times[\zeta_{l_1}^{(n_{l_1}+3)}/(n_{l_1}+2)!]\,A_{n_{l_1},l_1,l,1}(\kappa''\zeta_{l_1},\,\mathbf{R}_{MP})\\
&\qquad\times C'\begin{pmatrix} m & m_1 & u\\ l & l_1 & 1\\ \pm p_1 & p_1 & \pm\end{pmatrix}\\
&\qquad\times P_{l_1m_1p_1}[d_{l_1m_1p_1}(\theta,\varphi)/y_{l_1m_1p_1}(\theta,\varphi)]\\
&\qquad\times y_{lm\pm p_1}(\theta_{\mathbf{R}_{MP}},\varphi_{\mathbf{R}_{MP}})\Big\}. \qquad (24)
\end{aligned}$$

In (24) and in the following equation, sums over l and m are limited to nonzero values of C', which is defined by (29), and y_{lmp} are the real spherical harmonic functions with normalization defined by (28).

$$\begin{aligned}
&\nabla E^{\mathrm{per}}_{2u\pm}(R_P)\\
&\quad=-\sum_{M\neq P}{}''\,(Z_M/|\mathbf{R}_{MP}|^3)\,P_2^u[\cos(\theta_{\mathbf{R}_{MP}})]\\
&\qquad\times\begin{Bmatrix}\cos(u\varphi_{\mathbf{R}_{MP}})\\ \sin(u\varphi_{\mathbf{R}_{MP}})\end{Bmatrix}\\
&\qquad+(2/3\pi)(P_{M,c}/N_c)\sum_{j=1}^{\mu_c}N_j\sum_{i=1}^{v_j}\sum_{k=1}^{v_j}C_{j,i}C_{j,k}\\
&\qquad\times\left[\frac{(2\zeta_{j,i})^{(2n_{j,i}+3)}(2\zeta_{j,k})^{(2n_{j,k}+3)}}{(2n_{j,i}+2)!(2n_{j,k}+2)!}\right]^{1/2}\\
&\qquad\times A_{n_{j,i}+n_{j,k},0,2,2}[(\zeta_{k,i}+\zeta_{j,k}),\,|\mathbf{R}_{MP}|]\\
&\qquad\times P_2^u[\cos(\theta_{\mathbf{R}_{MP}})]\begin{Bmatrix}\cos(u\varphi_{\mathbf{R}_{MP}})\\ \sin(u\varphi_{\mathbf{R}_{MP}})\end{Bmatrix}\\
&\qquad+(2/3\pi)\,(P_{M,v}/N_v)\sum_{j=1}^{\mu_v}N_j\sum_{i=1}^{y_j}\sum_{k=1}^{\nu_j}C_{j,i}C_{j,k}\\
&\qquad\times\left[\frac{(2\kappa'\zeta_{j,i})^{(2n_{j,i}+3)}(2\kappa'\zeta_{j,k})^{(2n_{j,k}+3)}}{(2n_{j,i}+2)!(2n_{j,k}+2)!}\right]^{1/2}\\
&\qquad\times A_{n_{j,i}+n_{j,k},0,2,2}[\kappa'(\zeta_{j,i}+\zeta_{j,k}),\,|\mathbf{R}_{MP}|]\\
&\qquad\times P_2^u[\cos(\theta_{\mathbf{R}_{MP}})]\begin{Bmatrix}\cos(u\varphi_{\mathbf{R}_{MP}})\\ \sin(u\varphi_{\mathbf{R}_{MP}})\end{Bmatrix}\\
&\qquad-(8/3)\left[\frac{5(2-u)!}{2\pi(1+\delta_{u,0})(2+u)!}\right]^{-1/2}\\
&\qquad\times\sum_{l_1=0}^{l_{1\max}}\sum_{m_1=0}^{l_1}\sum_{p_1}\sum_{l}\sum_{m}i^{(l_1+l)}\\
&\qquad\times[\zeta_{l_1}^{(n_{l_1}+3)}/(n_{l_1}+3)!]\,A_{n_{l_1},l_1,l,2}(\kappa''\zeta_{l_1},\,|\mathbf{R}_{MP}|)
\end{aligned}$$

[†] The symbol $\sum''$ indicates that the contributions of the individual atoms must be referred to the same coordinate system.

$$\times C'\begin{pmatrix} m & m_1 & u \\ l & l_1 & 2 \\ \pm p_1 & p_1 & \pm \end{pmatrix}$$
$$\times P_{l_1 m_1 p_1}[d_{l_1 m_1 p_1}(\theta, \varphi)/y_{l_1 m_1 p_1}(\theta, \varphi)]$$
$$\times y_{lm\pm p_1}(\theta_{\mathbf{R}_{MP}}, \varphi_{\mathbf{R}_{MP}}) \tag{25}$$

where

$$A_{N,l_1,l_2,k}(Z, R) = \int_0^\infty G_{N+2,l_1}(Z, S) j_{l_2}(SR) S^k \,\mathrm{d}S \tag{26}$$

$$G_{N,l}(Z, S) = \int_0^\infty r^N \exp(-Zr) j_l(Sr) \,\mathrm{d}r. \tag{27}$$

The expressions for $G_{N,l}(Z, S)$ have been tabulated (see Avery & Watson, 1977; Su & Coppens, 1990), and the evaluation of $A_{N,l_1,l_2,k}(Z, R)$ is included in Appendix *A*.

In (24) and (25), $y_{lmp}(\theta, \varphi)$ are the real surface spherical-harmonic functions that are normalized according to

$$\int_0^{2\pi}\int_0^{\pi} [y_{lmp}(\theta, \varphi)]^2 \sin(\theta) \,\mathrm{d}\theta \,\mathrm{d}\varphi = 1 \tag{28}$$

and

$$C'\begin{pmatrix} m_1 & m_2 & m_3 \\ l_1 & l_2 & l_3 \\ p_1 & p_2 & p_3 \end{pmatrix}$$
$$= \int_0^{2\pi}\int_0^{\pi} y_{l_1 m_1 p_1}(\theta, \varphi) y_{l_2 m_2 p_2}(\theta, \varphi)$$
$$\times y_{l_3 m_3 p_3}(\theta, \varphi) \sin(\theta) \,\mathrm{d}\theta \,\mathrm{d}\varphi \tag{29}$$

has a non-vanishing value when $|l_2 - l_3| \leq l_1 \leq l_2 + l_3$, $l_1 + l_2 + l_3 = \text{even}$, $p_1 = p_2 p_3$, $m_1 = |m_2 - m_3|$ or $m_1 = m_2 + m_3$. The numerical values of

$$C'\begin{pmatrix} m_1 & m_2 & m_3 \\ l_1 & l_2 & l_3 \\ p_1 & p_2 & p_3 \end{pmatrix}$$

for $0 \leq l_1 \leq 2$ are tabulated elsewhere (Coppens, 1992). A general formula is given in Appendix *B*.

The components of the electric field and the elements of the electric-field gradient due to the peripheral contributions can be readily calculated from $E_{1u\pm}$ $(u = 0, 1)$ and $\nabla E_{2u\pm}$ $(u = 0, 1, 2)$.

$$\begin{aligned} E_x^{\mathrm{per}}(\mathbf{R}_P) &= E_{11+}^{\mathrm{per}}(\mathbf{R}_P) \\ E_y^{\mathrm{per}}(\mathbf{R}_P) &= E_{11-}^{\mathrm{per}}(\mathbf{R}_P) \\ E_z^{\mathrm{per}}(\mathbf{R}_P) &= E_{10}^{\mathrm{per}}(\mathbf{R}_P) \end{aligned} \tag{30}$$

$$\begin{aligned} \nabla E_{xx}^{\mathrm{per}}(\mathbf{R}_P) &= \tfrac{1}{2}\nabla E_{22+}^{\mathrm{per}}(\mathbf{R}_P) - \nabla E_{20}^{\mathrm{per}}(\mathbf{R}_P) \\ \nabla E_{yy}^{\mathrm{per}}(\mathbf{R}_P) &= \tfrac{1}{2}\nabla E_{22+}^{\mathrm{per}}(\mathbf{R}_P) - \nabla E_{20}^{\mathrm{per}}(\mathbf{R}_P) \\ \nabla E_{zz}^{\mathrm{per}}(\mathbf{R}_P) &= 2\nabla E_{20}^{\mathrm{per}}(\mathbf{R}_P) \\ \nabla E_{xy}^{\mathrm{per}}(\mathbf{R}_P) &= \nabla E_{yx}^{\mathrm{per}}(\mathbf{R}_P) = \tfrac{1}{2}\nabla E_{22-}^{\mathrm{per}}(\mathbf{R}_P) \\ \nabla E_{xz}^{\mathrm{per}}(\mathbf{R}_P) &= \nabla E_{zx}^{\mathrm{per}}(\mathbf{R}_P) = \nabla E_{21+}^{\mathrm{per}}(\mathbf{R}_P) \\ \nabla E_{yz}^{\mathrm{per}}(\mathbf{R}_P) &= \nabla E_{zy}^{\mathrm{per}}(\mathbf{R}_P) = \nabla E_{21-}^{\mathrm{per}}(\mathbf{R}_P). \end{aligned} \tag{31}$$

Central contributions

If $P = M$, *i.e.* in the case where the point $\mathbf{R}_P$ happens to be at the nucleus of atom M, the electron density of M makes the central contribution to each of these electrostatic properties. In the multipole expansion model, only the spherical density (monopoles) makes a central contribution to the electrostatic potential, only the dipoles make central contributions to the electric field, and only quadrupoles to the electric-field gradient. These electronic contributions are given by

$$\Phi^{\mathrm{central}}(\mathbf{R}_M) = -(P_{M,c}/N_c) \sum_{j=1}^{\mu_c} N_j \sum_{i=1}^{\nu_j} \sum_{k=1}^{\nu_j} C_{j,i} C_{j,k}$$
$$\times \left[\frac{(2\zeta_{j,i})^{(2n_{j,i}+3)}(2\zeta_{j,k})^{(2n_{j,k}+3)}}{(2n_{j,i}+2)!(2n_{j,k}+2)!}\right]^{1/2}$$
$$\times \frac{(n_{j,i}+1)!}{(\zeta_{j,i}+\zeta_{j,k})^{(n_{j,i}+n_{j,k}+2)}}$$
$$-\frac{P_{M,v}}{N_v} N_j \sum_{i=1}^{\nu_j} \sum_{k=1}^{\nu_j} C_{j,i} C_{j,k}$$
$$\times \left[\frac{(2\kappa'\zeta_{j,i})^{(2n_{j,i}+3)}(2\kappa'\zeta_{j,k})^{(2n_{j,k}+3)}}{(2n_{j,i}+2)!(2n_{j,k}+2)!}\right]^{1/2}$$
$$\times \frac{(n_{j,i}+n_{j,k}+1)!}{[\kappa'(\zeta_{j,i}+\zeta_{j,k})]^{(n_{j,i}+n_{j,k}+2)}}$$
$$-P_{M,00}\,\kappa''\zeta_0/(n_0+2) \tag{32}$$

$$\begin{aligned} E_x^{\mathrm{central}}(\mathbf{R}_M) &= \tfrac{4}{3}P_{M,11+}(\kappa''\zeta_1)^2/(n_1+1)(n_1+2) \\ E_y^{\mathrm{central}}(\mathbf{R}_M) &= \tfrac{4}{3}P_{M,11-}(\kappa''\zeta_1)^2/(n_1+1)(n_1+2) \\ E_z^{\mathrm{central}}(\mathbf{R}_M) &= \tfrac{4}{3}P_{M,10}(\kappa''\zeta_1)^2/(n_1+1)(n_1+2) \end{aligned} \tag{33}$$

$$\nabla E_{xx}^{\mathrm{central}}(\mathbf{R}_M) = \frac{3}{5}\frac{(\kappa''\zeta_2)^3}{n_2(n_2+1)(n_2+2)}$$
$$\times(\pi P_{M,22+} - 3^{1/2} P_{M,20})$$

$$\nabla E_{yy}^{\mathrm{central}}(\mathbf{R}_M) = -\frac{3}{5}\frac{(\kappa''\zeta_2)^3}{n_2(n_2+1)(n_2+2)}$$
$$\times(\pi P_{M,22+} + 3^{1/2} P_{M,20})$$

$$\nabla E_{zz}^{\text{central}}(\mathbf{R}_M)=\frac{6}{5}\frac{(\kappa''\zeta_2)^3}{n_2(n_2+1)(n_2+2)}3^{1/2}P_{M,20} \qquad (34)\dagger$$

$$\begin{aligned}\nabla E_{xy}^{\text{central}}(\mathbf{R}_M)&=\nabla E_{yx}^{\text{central}}(\mathbf{R}_M)\\&=\frac{3}{5}\frac{(\kappa''\zeta_2)^3}{n_2(n_2+1)(n_2+2)}\pi P_{M,22-}\\ \nabla E_{xz}^{\text{central}}(\mathbf{R}_M)&=\nabla E_{zx}^{\text{central}}(\mathbf{R}_M)\\&=\frac{3}{5}\frac{(\kappa''\zeta_2)^3}{n_2(n_2+1)(n_2+2)}\pi P_{M,21+}\\ \nabla E_{yz}^{\text{central}}(\mathbf{R}_M)&=\nabla E_{zy}^{\text{central}}(\mathbf{R}_M)\\&=\frac{3}{5}\frac{(\kappa''\zeta_2)^3}{n_2(n_2+1)(n_2+2)}\pi P_{M,21-}.\end{aligned}$$

It should be noted that in (24), (25), (30)-(34) the contributions to the electrostatic properties from atom M are referred to the same Cartesian coordinates as the density functions centered on M. Therefore, the summations over M are understood as being made after transformation to a common Cartesian coordinate system. The $''$ sign in (24) and (25) implies such summations; when the peripheral contributions and the central contributions are summed, the same consideration must be taken into account. There is no $''$ sign in (23) because the scalar electrostatic potential remains unchanged when referred to a second Cartesian coordinate system.

Application of the formalisms

(*a*) *Procrystal model*

The free-atom model is a special case of the Hansen–Coppens density model for which the deformation density is zero, $P_c = N_c$ = number of core electrons, $P_v = N_v$ = number of valence electrons and $\kappa' = 1$. Thus the relations given above can be simplified to give a method for evaluating the procrystal contributions, which is an alternative to the methods described by Schwarzenbach & Thong (1979). Test calculations show good agreement between the two methods. For example, for the procrystal contribution to ∇E_{zz} at the Fe nucleus in the iron(II) tetraphenylporphyrin molecule, Schwarzenbach & Thong's method gives a value of 0.73 e Å^{-3}, whereas our method leads to a value of 0.74 e Å^{-3}.

(*b*) *The electrostatic potential for deuterated benzene*

As a test of the procedure the electrostatic potential due to the benzene molecule was evaluated using 123 K X-ray diffraction data of fully deuterated benzene, kindly supplied by Dr Ruble (Jeffrey, Ruble, Yeon & Lehmann, 1991).

An aspherical-atom refinement was done using the program *LSMOL90* (1990), which is an upgraded version of *MOLLY* (Hansen & Coppens, 1978). Positional and thermal parameters of the C and D atoms were fixed at the 123 K neutron values (Jeffrey, Ruble, McMullan & Pople, 1987). The multipole populations were constrained to be the same on each of the atom types, and the 'index picking rules' (Kurki-Suonio, 1977) were applied to the multipoles with respect to the properly defined local Cartesian coordinate systems. The multipole expansion was truncated at the octapolar level for the C atoms and at the quadrupolar level for the D atoms. The κ' and κ'' of the C atoms were refined, while κ' and κ'' for the D atoms were fixed at a value of 1.4. This gave 28 variables in the least-squares refinement, minimizing the function $\sum w(F_o - k|F_c|)^2$ where $w = 1/\sigma^2(F_o)$. Of the 2335 unique reflections, 934 reflections with $I \geq 3\sigma(I)$ were used in the refinement to yield $R(F) = 0.0381$, $R_w(F) = 0.0346$ and a goodness of fit of 2.03.

Fig. 2 shows the experimental electrostatic potential due to a single C_6D_6 molecule, plotted in a plane parallel to, but 1 Å, above the C_6D_6 molecular plane. Figs. 2(*a*), (*b*) and (*c*) represent, respectively, the potential due to the total charge density, the promolecule and the deformation density. The map may be compared with the results obtained by Stewart (1991) with the same data set but a different least-squares refinement. The two maps are qualitatively the same, but differ in the value of the potential directly above the C atoms, which is less positive according to the present results.

(*c*) *Electrostatic potential in the plane of the iron*(II) *tetraphenylporphyrin molecule*

Figs. 3(*a*), (*b*) and (*c*) show the electrostatic potential due to the total charge density, the promolecule and the deformation density in the least-squares plane of the iron(II) tetraphenylporphyrin molecule. The multipole expansion coefficients and geometry are based on results obtained earlier (Li, Su, Coppens & Landrum, 1990).

(*d*) *Electric-field gradient at the nuclear position*

Comparison of X-ray field gradients with results of Mössbauer measurements for a number of iron compounds have been reported elsewhere (Coppens 1991), and will be discussed more fully in a subsequent publication.

Discussion

The calculations indicate that the dominant components in the peripheral contributions are due to the point nuclear charges and the electronic monopoles, while at the nuclear positions the central contribution from the atom dominates.

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† See also Stevens, DeLucia & Coppens (1980); Pant & Stevens (1988); Coppens & Becker (1992).

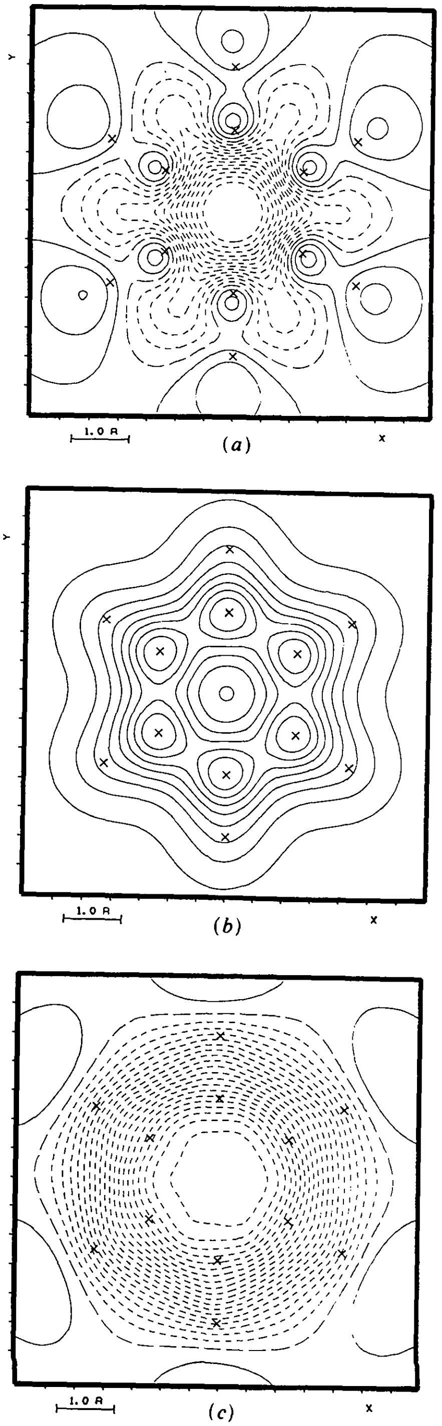

Fig. 2. Electrostatic potential contour plot for C_6D_6 from a single extracted molecule. Sections shown are at 1 Å above the C_6D_6 least-squares plane, and are 7 × 7 Å. Negative contours are short dashed lines, zero contours are long dashed lines and positive contours are solid lines. (*a*) Potential due to the total charge density. Minimum contour $-0.24\,e\,Å^{-1}$; maximum contour $0.06\,e\,Å^{-1}$. Contour intervals at $0.02\,e\,Å^{-1}$. (*b*) Potential due to the promolecule. Minimum contour $0.02\,e\,Å^{-1}$; maximum contour $0.30\,e\,Å^{-1}$. Contour intervals at $0.04\,e\,Å^{-1}$. (*c*) Deformation density potential. Minimum contour $-0.38\,e\,Å^{-1}$; maximum contour $0.02\,e\,Å^{-1}$. Contour intervals at $0.02\,e\,Å^{-1}$.

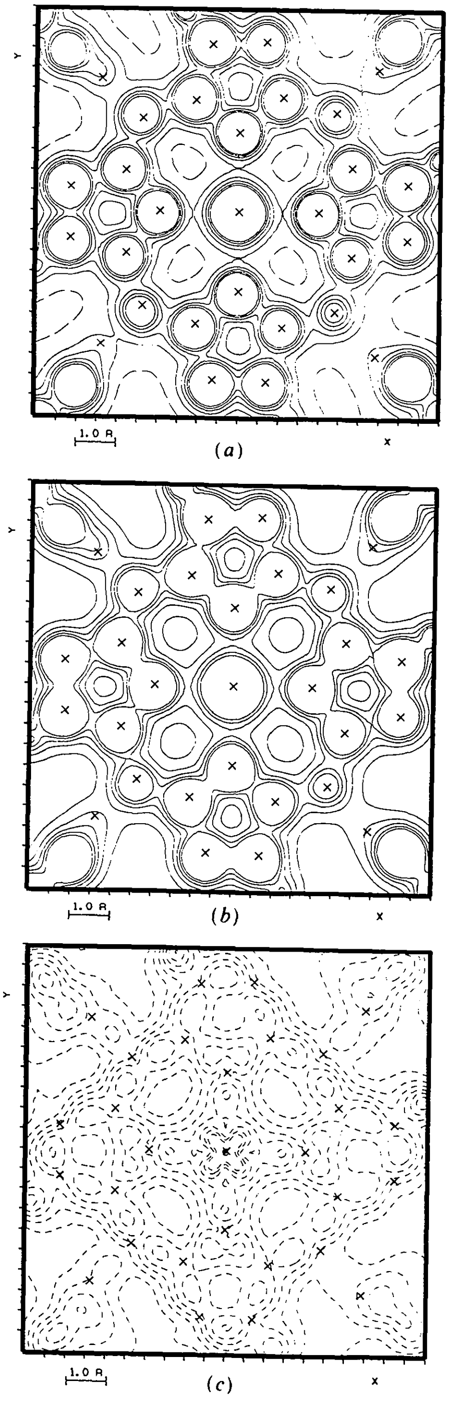

Fig. 3. Electrostatic potential contour plot for iron(II) tetraphenylporphyrin from a single extracted molecule. Sections are in the least-squares plane through the molecule and are 10 × 10 Å. Negative contours are short dashed lines, zero contours are long dashed lines and positive contours are solid lines. (*a*) Potential due to the total charge density. Minimum contour $0.0\,e\,Å^{-1}$; maximum contour $2.0\,e\,Å^{-1}$. Contour interval at $0.4\,e\,Å^{-1}$. (*b*) Potential due to the promolecule. Minimum contour $0.40\,e\,Å^{-1}$; maximum contour $2.0\,e\,Å^{-1}$. Contour interval at $0.4\,e\,Å^{-1}$. (*c*) Deformation density potential. Minimum contour $-1.0\,e\,Å^{-1}$; maximum contour $0.0\,e\,Å^{-1}$. Contour interval at $0.1\,e\,Å^{-1}$.

It is worth noting that the promolecule electrostatic potential is positive everywhere and the deformation potential, which is the difference between the total potential and the promolecule potential, is negative almost everywhere in the regions plotted. It can be shown by using Gauss's law in electrostatics (Jackson, 1975) that for nuclear point charges and spherical free-atom-model charge distributions, the promolecule potential is positive everywhere. In the promolecule the nuclear charges are incompletely shielded; the closer a point is to a nucleus, the less shielded the nuclear charge and the larger the potential.

This point can also be illustrated by considering the peripheral contribution to the potential due to a one-electron atom located at *M*. The charge-density distribution is given by

$$\rho(\mathbf{r}) = \delta(\mathbf{r}-\mathbf{r}_M) - (1/4\pi)(\zeta^3/2)\exp(-\zeta|\mathbf{r}-\mathbf{r}_M|). \tag{35}$$

From (23) and (*A*5), we obtain for the peripheral contribution due to the H atom

$$\begin{aligned}\Phi^{\rm per}(\mathbf{R}_p) &= |\mathbf{R}_{MP}|^{-1} - |\mathbf{R}_{MP}|^{-1} \\ &\quad + [\exp(-\zeta|\mathbf{R}_{MP}|)/2|\mathbf{R}_{MP}|](\zeta|\mathbf{R}_{MP}|+2) \\ &= +[\exp(-\zeta|\mathbf{R}_{MP}|)/2|\mathbf{R}_{MP}|](\zeta|\mathbf{R}_{MP}|+2). \end{aligned} \tag{36}$$

In other words, the total contribution, after a partial cancellation of the nuclear charge and electronic charge contributions, can be considered as being due to the part of the nuclear charge that is not shielded by the electrons. It falls off rapidly with $\zeta|\mathbf{R}_{MP}|$ and becomes negligible for large values of $|\mathbf{R}_{MP}|$.

In regions where the deformation of the electronic density is such that on average the nuclear charges are better shielded, negative deformation potentials can be expected. That is the case for many parts of the regions plotted in Figs. 2(*c*) and 3(*c*).

The contribution to the electrostatic properties due to the higher multipoles falls off rapidly with $\zeta|\mathbf{R}_{MP}|$. Calculations show that when $|\mathbf{R}_{MP}|$ is greater than 5 Å the electronic density can be treated as a point charge centered at *M*. Therefore the point-charge approximation may be used to account for charge-density fragments far from the point being considered.

The application of the formalism does not have to be limited to single molecules, and may be used to examine the electrostatic properties of selected groups of atoms, such as functional groups of organic compounds, ligands and metals in coordination compounds and dimers. Electrostatic properties from the X-ray charge density can be used to improve our understanding of chemical interactions and other related properties of molecules.

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APPENDIX *A*

The integrals

$$A_{N,l_1,l_2,k}(Z,R) = \int_0^\infty G_{N+2,l_1}(Z,S)\, j_{l_2}(SR) S^k\, {\rm d}S \tag{A1}$$

can be evaluated by the substitution of the expressions for $G_{N+2,l_1}(Z,S)$ and $j_{l_2}(x)$ given in the literature (Avery & Watson, 1977; Su & Coppens, 1990; Arfken, 1970) and subsequent use of the following integrals (Gradshteyn & Ryzhik, 1965).

$$\int_0^\infty \frac{\sin(ax)\,{\rm d}x}{x(x^2+\beta^2)^{(n+1)}} = \frac{\pi}{2\beta^{(2n+2)}}\left[1-\frac{\exp(-a\beta)}{2^n n!}F_n(a\beta)\right] \tag{A2}$$

[$a>0$, ${\rm Re}\,\beta>0$, $F_0(z)=1$, $F_1(z)=z+2,\ldots, F_n(z)=(z+2n)F_{n-1}(z)-zF'_{n-1}(z)$].

$$\int_0^\infty \frac{x^{(2m+1)}\sin(ax)\,{\rm d}x}{(x^2+z)^{(n+1)}} = \frac{(-1)^{(m+n)}}{n!}\frac{\pi}{2}\frac{{\rm d}^n}{{\rm d}z^n}[z^m\exp(-az^{1/2})] \tag{A3}$$

[$a>0$, $0\le m\le n$, $|\arg z|<\pi$].

$$\int_0^\infty \frac{x^{(2m)}\cos(ax)\,{\rm d}x}{(x^2+z)^{(n+1)}} = \frac{(-1)^{(m+n)}}{n!}\frac{\pi}{2}\frac{{\rm d}^n}{{\rm d}z^n}[z^{m-1/2}\exp(-az^{1/2})] \tag{A4}$$

[$a>0$, $0\le m<n+1$, $|\arg z|<\pi$].

For example,

$$A_{0,0,0,0}(Z,R) = \pi[2-\exp(-RZ)(RZ+2)]/2RZ^3 \tag{A5}$$

$$A_{0,0,1,1}(Z,R) = \pi\{2-\exp(-RZ) \times[(RZ)^2+2RZ+2]\}/2R^2Z^3 \tag{A6}$$

$$A_{0,0,2,2}(Z,R) = \pi\{6-\exp(-RZ)[(RZ)^3 +3(RZ)^2+6RZ+6]\}/2R^3Z^3. \tag{A7}$$

Alternatively, the integrals in (*A*1) can be reduced to integrals of the following form (Gradshteyn &

Ryzhik, 1965)

$$\int_0^\infty \frac{x^{\rho-1}J_\nu(ax)}{(x^2+k^2)^{\mu+1}}\,\mathrm{d}x$$

$$= \frac{a^\nu k^{\rho+\nu-2\mu-2}\Gamma(\tfrac{1}{2}\rho+\tfrac{1}{2}\nu)\Gamma(\mu+1-\tfrac{1}{2}\rho-\tfrac{1}{2}\nu)}{2^{\nu+1}\Gamma(\mu+1)\Gamma(\nu+1)}$$

$$\times {}_1F_2(\tfrac{1}{2}\rho+\tfrac{1}{2}\nu;\ \tfrac{1}{2}\rho+\tfrac{1}{2}\nu-\mu,\ \nu+1;\ a^2k^2/4)$$

$$+\frac{a^{2\mu+2-\rho}\Gamma(\tfrac{1}{2}\rho+\tfrac{1}{2}\nu-\mu-1)}{2^{2\mu+3-\rho}\Gamma[\mu+2+\tfrac{1}{2}(\nu-\rho)]}$$

$$\times {}_1F_2(\mu+1;\ \mu+2+\tfrac{1}{2}(\nu-\rho),\ \mu+2$$

$$-\tfrac{1}{2}(\nu+\rho);\ a^2k^2/4) \qquad (A8)$$

$[a>0, -\mathrm{Re}\,\nu<\mathrm{Re}\,\rho<2\mathrm{Re}\,\mu+\tfrac{7}{2}]$, where the hypergeometric function ${}_1F_2(a;\,b,\,c;\,x)$ is defined as

$${}_1F_2(a;\,b,\,c;\,x)=\sum_{n=0}^{\infty}[(a)_n/(b)_n(c)_n n!]x^n \qquad (A9)$$

and $(a)_n=a(a+1)\dots(a+n-1), (a)_0=1$.

APPENDIX *B*

Integral of the product of three real spherical-harmonic functions

$$C'\begin{pmatrix} m_1 & m_2 & m_3 \\ l_1 & l_2 & l_3 \\ p_1 & p_2 & p_3 \end{pmatrix} = \int_0^{2\pi}\int_0^{\pi} y_{l_1m_1p_1}(\theta,\varphi)y_{l_2m_2p_2}(\theta,\varphi)$$

$$\times y_{l_3m_3p_3}(\theta,\varphi)\sin(\theta)\,\mathrm{d}\theta\,\mathrm{d}\varphi \qquad (B1)$$

The above integral will be 0 unless $|l_2-l_3|\le l_1\le l_2+l_3$, $l_1+l_2+l_3=$ even, $p_1=p_2p_3$, $m_1=|m_2-m_3|$ or $m_1=m_2+m_3$. If these conditions are fulfilled, we can rewrite C' in the form

$$C'\begin{pmatrix} m & m' & m+m' \\ l & l' & l'' \\ p & p' & pp' \end{pmatrix} \qquad (B2)$$

and $(B2)$ can be expressed in terms of the integral of the product of three complex spherical-harmonic functions

$$C\begin{pmatrix} m & m' & m+m' \\ l & l' & l'' \end{pmatrix}.$$

We have

$$C'\begin{pmatrix} m & m' & m+m' \\ l & l' & l'' \\ p & p' & pp' \end{pmatrix}$$

$$=(-1)^{(\delta_{p,-}-\delta_{p',-})}[2^{1/2}/2(1-\delta_{m_1m_2m_30})$$

$$+\max(\delta_{m_1,0},\delta_{m_2,0},\delta_{m_3,0})]C\begin{pmatrix} m & m' & m+m' \\ l & l' & l'' \end{pmatrix} \qquad (B3)$$

where the integral of the product of three complex spherical-harmonic functions is (Edmonds, 1960)

$$C\begin{pmatrix} m & m' & m+m' \\ l & l' & l'' \end{pmatrix}$$

$$=(-1)^{(m+m')}[(2l+1)(2l'+1)/4\pi]^{1/2}\begin{pmatrix} l & l' & l'' \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times(l\,ml'm'|l''m+m') \qquad (B4)$$

where $(l\,ml'm'|l''m'')$ is the Clebsch–Gordon coefficient (Edmonds, 1960) and

$$\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} = \begin{cases} 0 & \text{if } J=l_1+l_2+l_3=\text{odd} \\ [(J-2l_1)!(J-2l_2)!(J-2l_3)!/(J+1)]^{1/2} & \\ \quad\times[(J/2)!/(J/2-l_1)!(J/2-l_2)!(J/2-l_3)!] & \\ & \text{if } J=l_1+l_2+l_3=\text{even}. \end{cases} \qquad (B5)$$

For example,

$$C'\begin{pmatrix} 0 & 1 & 1 \\ 1 & 1 & 2 \\ + & - & - \end{pmatrix} = \frac{1}{10}(15/\pi)^{1/2}$$

$$=0.218509686118416\dots.$$

Note that by definition $y_{l0}=y_{l0+}$.

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Minimizing Free Energy as a Direct Method for Phase Determination

By Ian R. Castleden

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

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Abstract

A general joint probability distribution between structure factors is derived and is expressed as an exponential of the free energy for a system of interacting atoms. The free energy is an explicit function of the atomic densities and the interatomic potentials. In the limit of infinite temperature, energy effects are unimportant and the probability distribution becomes identical to those derived by Hauptman & Karle [*The Solution of the Phase Problem.* I. *The Centrosymmetric Crystal.* (1953). ACA Monogr. Wilmington: The Letter Shop; *Acta Cryst.* (1959), **12**, 93-97] and Bricogne [*Acta Cryst.* (1984), A**40**, 410-445].

1. Introduction

The principle of maximum entropy (PME) has been applied to crystallographic problems from a statistical inference viewpoint by Bricogne (1984) and Gull, Livesey & Sivia (1987). Navaza (1985, 1986) has shown that the type of constraint used with the PME determines the final form of the maximum-entropy functional. Recently, Bryan (1988) has also incorporated correlations into the entropy expression. However, no one has attempted to incorporate stereochemistry in a general way, although Wilson (1981) has considered the possibility. This paper shows that if chemical information can be represented as potential functions, then it can be applied with the PME to yield the Helmholtz free energy as a function of the structure factors. Moreover, the free energy is shown to be, within a normalization factor, the log of a structure-factor joint probability distribution (j.p.d.). Phase determination can therefore be considered as a constrained free-energy minimization.

In calculating structure-factor j.p.d.s the crystal is usually modelled as a sample from an ensemble of structures in which all possible atomic configurations are equally represented. This assumption is free from stereochemical bias and is routinely used to solve small-molecule crystal structures. For larger structures, however, current procedures do not work well. From a theoretical point of view, one possible alternative for improving the success rate is to eliminate from the ensemble those configurations that are stereochemically impossible.

Energetic constraints yield preferred bond lengths and angles which alter the number of 'reasonably probable' configurations. Since the information theoretic entropy is a measure of reasonably probable configurations* and is equivalent to the entropy defined in statistical mechanics [up to a multiplicative Boltzmann constant k_B (Jaynes 1957)], it is clear that a physical approach offers an opportunity for extending the principle of maximum entropy within crystallography.

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* And this measure is dependent only on a reasonable definition for 'reasonably probable' (Jaynes, 1965).

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