$(2d)$], it can be seen from $(A2)$ that the Bragg reflection condition for the vector $\mathbf{K}_{rs}^{-}(\mathbf{k}_B)$ reads

$$\theta_{00}^{+}(\mathbf{k}_B) = \theta_{rs}^{-}(\mathbf{k}_B) + 2\pi n. \qquad (A3)$$

2. η parameter

We have introduced η in (20):

$$\eta = \theta_{00}^{+}(\mathbf{k}) - \theta_{rs}^{-}(\mathbf{k}) - n2\pi. \qquad (A4)$$

Let $\mathbf{k}_B$ be a vector in the Bragg reflection position, *i.e.*

$$\mathbf{K}_{rs}^{-}(\mathbf{k}_B) = \mathbf{k}_B + r\mathbf{g}_1 + s\mathbf{g}_2 - n\mathbf{g}_3, \qquad (A5a)$$

$$\theta_{00}^{+}(\mathbf{k}_B) = \theta_{rs}^{-}(\mathbf{k}_B) + 2\pi n. \qquad (A5b)$$

Let $\mathbf{k}$ be a vector in the neighbourhood of the vector $\mathbf{k}_B$. Then using $(A4)$, $(A5b)$ and $(2e)$ we obtain

$$\begin{aligned}\eta &= \theta_{00}^{+}(\mathbf{k}) - \theta_{rs}^{-}(\mathbf{k}) - 2\pi n\\ &= \theta_{00}^{+}(\mathbf{k}) - \theta_{rs}^{-}(\mathbf{k}) - [\theta_{00}^{+}(\mathbf{k}_B) - \theta_{rs}^{-}(\mathbf{k}_B)]\\ &= \mathbf{a}_3\mathbf{k} - \mathbf{a}_3\mathbf{K}_{rs}^{-}(\mathbf{k}) - [\mathbf{a}_3\mathbf{k}_B - \mathbf{a}_3\mathbf{K}_{rs}^{-}(\mathbf{k}_B)]\\ &= a_{3z}[K_{rsz}(\mathbf{k}) - K_{rsz}(\mathbf{k}_B) + k_z - k_{Bz}], \qquad (A6)\end{aligned}$$

so that the η parameter is a function of the known vectors $\mathbf{k}_B$ and $\mathbf{k}$.

3. Correction of a misprint in equation (I.53)

There is a misprint in equation (I.53); the term

$$-\frac{1}{K_{pqz}}\,\Phi\left(\frac{iK_{pqz}}{2B}\right)$$

should be replaced by

$$-\frac{i}{K_{pqz}}\,\Phi\left(\frac{iK_{pqz}}{2B}\right).$$

4. P parameter appearing in equation (11*b*)

When comparing $(11b)$ and (I.53) we obtain

$$\begin{aligned}P &= ik\Phi(ik/2B) + (2/\pi^{1/2})B\exp(k^2/4B^2)\\ &\quad -\sum_{\substack{(n_1n_2)\\ \neq(00)}}{}' \frac{\exp[i\mathbf{k}^{\parallel}(n_1\mathbf{a}_1 + n_2\mathbf{a}_2)]}{2|n_1\mathbf{a}_1 + n_2\mathbf{a}_2|}\\ &\quad \times\{\exp(-ik|n_1\mathbf{a}_1 + n_2\mathbf{a}_2|)\\ &\quad \times[1 - \Phi(|n_1\mathbf{a}_1 + n_2\mathbf{a}_2|B - ik/2B)] + \text{c.c.}\}. \qquad (A7)\end{aligned}$$

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About the Coulomb Potential in Crystals

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Abstract

The Coulomb potential in a crystal is discussed. It is shown that its Fourier series expansion has a singularity for the $V(0, 0, 0)$ component, which is important when comparing different compounds, or when using the Coulomb potential as a probe for reactivity. Methods to calculate this term are discussed. Sum rules for multipolar moments of crystals in terms of structure factors are derived, which are of interest for

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the comparison of microscopic and macroscopic dielectric properties.

Introduction

Coulombic interactions play an important role in the understanding of the structure and reactivity of molecules and solids.

The electrostatic potential is extensively used to understand initial steps in some chemical reactions, and to study packing of molecules in solids (Politzer & Truhlar, 1981, and references therein). It is also a major part of the effective one-particle Hamiltonian used in Hartree–Fock or Kohn–Sham equations (Dahl & Avery, 1984; Erdahl & Smith, 1987).

While the electrostatic potential in a crystal can be expanded in a Fourier series (Stewart, 1979), there is some ambiguity in the literature concerning the (0, 0, 0) Fourier component, which represents the average potential within the unit cell. If one studies a unique system, this constant would not be of great importance since it would correspond to an *ad hoc* zero for the potential. However, most studies are comparisons among various systems or correspond to finding preferential sites for a protonation or other reactions. In such cases, a unique convention for the zero of the potential is needed. Usually, this is defined as the potential at a position at infinite distance from any charge. Thus the (0, 0, 0) component of the Fourier series of the potential V must be carefully evaluated (Avery, 1987).

In this paper, we discuss practical methods for evaluating the Coulomb potential in a crystal. After a rigorous discussion of the Fourier expansion of the potential, $V(0, 0, 0)$ will be calculated by the use of a model multipole expansion firstly of the charge density and secondly of the structure factors.

Let $\rho_t(\mathbf{r})$ be the total charge density of a system composed of nuclei with charge Z_i at position $\mathbf{R}_i$ and electrons. $\rho_n(\mathbf{r})$, the nuclear charge density, is defined as

$$\rho_n(\mathbf{r})=\sum_j Z_j\delta(\mathbf{r}-\mathbf{R}_j). \tag{1}$$

Thus,

$$\rho_t(\mathbf{r})=\rho_n(\mathbf{r})-\rho(\mathbf{r}) \tag{2}$$

where $\rho(\mathbf{r})$ is the electron charge density.

The electroneutrality condition gives

$$\int \rho_t(\mathbf{r})\,\mathrm{d}\mathbf{r}=0. \tag{3a}$$

Or, for a crystal with unit cell volume Ω,

$$\int_\Omega \rho_t(\mathbf{r})\,\mathrm{d}\mathbf{r}=0. \tag{3b}$$

If $\rho_j^0(\mathbf{r})$ is the spherically symmetric electron density of isolated atom j, the 'pro-system' electron density may be defined as

$$\rho^0(\mathbf{r})=\sum_j \rho_j^0(|\mathbf{r}-\mathbf{R}_j|) \tag{4}$$

and the 'pro-system' total density as

$$\begin{aligned}\rho_t^0(\mathbf{r})&=\rho_n(\mathbf{r})-\rho^0(\mathbf{r})\\&=\sum_j \{Z_j\delta(\mathbf{r}-\mathbf{R}_j)-\rho_j^0(|\mathbf{r}-\mathbf{R}_j|)\}.\end{aligned} \tag{5}$$

The 'deformation' density $\Delta\rho(\mathbf{r})$ is defined as

$$\Delta\rho(\mathbf{r})=\rho(\mathbf{r})-\rho^0(\mathbf{r})=-\rho_t(\mathbf{r})+\rho_t^0(\mathbf{r}). \tag{6}$$

(See Coppens & Hall, 1982.)

Fourier representation of the Coulomb potential

The Coulomb potential $V(\mathbf{r})$ created by the total charge density $\rho_t(\mathbf{r})$ is (Jackson, 1975)

$$V(\mathbf{r})=\int \rho_t(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|\,\mathrm{d}\mathbf{r}'. \tag{7}$$

In this definition $V(\mathbf{r})\to 0$ at large distance from the distribution. V and ρ_t are related by the Poisson equation

$$\nabla^2 V(\mathbf{r})=-4\pi\rho_t(\mathbf{r})$$

or its reciprocal-space equivalent

$$k^2 V(\mathbf{k})=-4\pi A(\mathbf{k}), \tag{8}$$

where $A(\mathbf{k})$ and $V(\mathbf{k})$ are the Fourier transforms of ρ_t and V respectively:

$$\begin{aligned}A(\mathbf{k})&=\int \rho_t(\mathbf{r})\exp(2\pi i\mathbf{k}\,.\,\mathbf{r})\,\mathrm{d}\mathbf{r}\\V(\mathbf{k})&=\int V(\mathbf{r})\exp(2\pi i\mathbf{k}\,.\,\mathbf{r})\,\mathrm{d}\mathbf{r}.\end{aligned} \tag{9}$$

Insertion of (9) into (8) leads to the well known expression (Bertaut, 1952, 1978)

$$V(\mathbf{k})=A(\mathbf{k})/\pi k^2. \tag{10}$$

Since $A(0)=0$, due to the electroneutrality condition, $\lim_{k\to 0}[A(\mathbf{k})/\pi k^2]$ requires careful discussion.

Let us now suppose the system to be in the crystalline state. We define the total structure factor by

$$\begin{aligned}F_t(\mathbf{k})&=\int_\Omega \rho_t(\mathbf{r})\exp(2\pi i\mathbf{k}\,.\,\mathbf{r})\,\mathrm{d}r\\&=F_n(\mathbf{k})-F(\mathbf{k})\end{aligned} \tag{11a}$$

where

$$F_n(\mathbf{k})=\sum_j Z_j\exp(2\pi i\mathbf{k}\,.\,\mathbf{R}_j) \tag{11b}$$

is the nuclear structure factor, and $F(\mathbf{k})$ the usual X-ray electronic structure factor. Let

$$V_\Omega(\mathbf{k})=\int_\Omega V(\mathbf{r})\exp(2\pi i\mathbf{k}\,.\,\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{12}$$

and

$$\Phi(\mathbf{k})=\sum_{\mathbf{l}}\exp(2\pi i\mathbf{k}\,.\,\mathbf{l}) \tag{13}$$

be the interference function, where $\mathbf{l}$ is a lattice translation. One obtains

$$A(\mathbf{k}) = F_t(\mathbf{k})\Phi(\mathbf{k}) \qquad (14a)$$

$$V(\mathbf{k}) = V_\Omega(\mathbf{k})\Phi(\mathbf{k}). \qquad (14b)$$

When the crystal is infinite, one retrieves the well known diffraction conditions:

$$\Phi_\infty(\mathbf{k}) = (1/\Omega)\sum_{\mathbf{H}}\delta(\mathbf{k}-\mathbf{H}) \qquad (15)$$

where $\mathbf{H}$ is a reciprocal-lattice vector.

Suppose now we start from a finite crystal with N unit cells. When the size is increased to infinity, it is assumed that the crystal size increases in all directions.

As $\Phi(\mathbf{k})$ is periodic in reciprocal space, it can be written as

$$\Phi(\mathbf{k}) = (1/\Omega)\sum_{\mathbf{H}}\Delta(\mathbf{k}-\mathbf{H}). \qquad (16)$$

Δ is not uniquely defined. One can, for example, suppose that (Δ/Ω) is the restriction of Φ to the first Brillouin zone surrounding a given reciprocal-lattice point $\mathbf{H}$, so that the various terms in (16) do not overlap. Alternatively, Δ can be taken as the shape transform of the crystal.

$\Delta(\mathbf{k})$ must fulfil the conditions

$$\begin{aligned}&\int\Delta(\mathbf{k})\,\mathrm{d}\mathbf{k} = 1,\\ &\lim_{N\to\infty}\Delta(\mathbf{k}) = \delta(\mathbf{k}).\end{aligned} \qquad (17)$$

$\delta(\mathbf{k})$ has spherical symmetry when $N\to\infty$. In other words, an infinite crystal in every dimension is considered as the limit of a sphere of increasing radius.

Taking the Fourier inversion of (9),

$$V(\mathbf{r}) = \int V(\mathbf{k})\exp(-2\pi i\mathbf{k}\,.\,\mathbf{r})\,\mathrm{d}\mathbf{k}, \qquad (18)$$

and combining (10), (14) and (16), one gets

$$V(\mathbf{r}) = (1/\pi\Omega)\sum_{\mathbf{H}}\int[F_t(\mathbf{k})/k^2]\Delta(\mathbf{k}-\mathbf{H}) \times\exp(-2\pi i\mathbf{k}\,.\,\mathbf{r})\,\mathrm{d}\mathbf{k}. \qquad (19)$$

For $\mathbf{H}\neq\mathbf{0}$, we obtain

$$\lim_{N\to\infty}\int[F_t(\mathbf{k})/k^2]\exp(-2\pi i\mathbf{k}\,.\,\mathbf{r})\Delta(\mathbf{k}-\mathbf{H})\,\mathrm{d}\mathbf{k} = [F_t(\mathbf{H})/H^2]\exp(-2\pi i\mathbf{H}\,.\,\mathbf{r}). \qquad (20)$$

Let us now examine the term for $\mathbf{H}=\mathbf{0}$. Since $\Delta(\mathbf{k})\to\delta(\mathbf{k})$, the exponential $\exp(-2\pi i\mathbf{k}\,.\,\mathbf{r})$ may be replaced by 1 and

$$\lim_{N\to\infty}\int[F_t(\mathbf{k})/k^2]\exp(-2\pi i\mathbf{k}\,.\,\mathbf{r})\Delta(\mathbf{k})\,\mathrm{d}\mathbf{k} = \lim_{N\to\infty}\int F_t(\mathbf{k})\Delta(\mathbf{k})\,\mathrm{d}k\,\mathrm{d}\hat{k}, \qquad (21)$$

where $\mathrm{d}\mathbf{k}$ is written as $k^2\,\mathrm{d}k\,\mathrm{d}\hat{k}$, $\mathrm{d}\hat{k}$ being the variation of the solid angle.

We may define

$$\langle F_t(k)\rangle = \int\mathrm{d}\hat{k}\,F_t(\mathbf{k}) \qquad (22)$$

as the orientational average of the structure factor. Since $\langle F_t\rangle$ has small variations with k compared to Δ:

$$\lim_{N\to\infty}\int[F_t(\mathbf{k})/k^2]\exp(-2\pi i\mathbf{k}\,.\,\mathbf{r})\Delta(\mathbf{k})\,\mathrm{d}\mathbf{k} = \lim_{k\to 0}[\langle F_t(\mathbf{k})\rangle/k^2]. \qquad (23)$$

In summary, for an infinite crystal, the Coulomb potential can be represented by the Fourier series

$$V(\mathbf{r}) = (1/\Omega)\sum_{\mathbf{H}}V(\mathbf{H})\exp(-2\pi i\mathbf{H}\,.\,\mathbf{r}) \qquad (24)$$

with

$$\begin{aligned}V(\mathbf{H}) &= F_t(\mathbf{H})/\pi H^2 &&\text{for } \mathbf{H}\neq\mathbf{0},\\ V(\mathbf{0}) &= \lim_{k\to 0}[\langle F_t(\mathbf{k})\rangle/\pi k^2] &&\text{for } \mathbf{H}=\mathbf{0}.\end{aligned} \qquad (25)$$

$V(\mathbf{0})$ is also the average potential in the cell times the volume of the unit cell:

$$V(\mathbf{0}) = \int_\Omega V(\mathbf{r})\,\mathrm{d}\mathbf{r}. \qquad (26)$$

In order to calculate $V(\mathbf{0})$, let us expand $\exp(2\pi i\mathbf{k}\,.\,\mathbf{r})$ for small $\mathbf{k}$ and insert into (11)

$$F_t(\mathbf{k}) = 2\pi i\int_\Omega(\mathbf{k}\,.\,\mathbf{r})\rho_t(\mathbf{r})\,\mathrm{d}\mathbf{r} - 2\pi^2\int_\Omega(\mathbf{k}\,.\,\mathbf{r})^2\rho_t(\mathbf{r})\,\mathrm{d}\mathbf{r}+\ldots. \qquad (27)$$

The contribution of the first term to $\langle F_t(\mathbf{k})\rangle$ is zero. Thus,

$$\lim_{k\to 0}\langle F_t(\mathbf{k})\rangle/k^2 = -(2\pi^2/3)\int_\Omega r^2\rho_t(\mathbf{r})+\ldots \qquad (28)$$

and, finally,

$$V(\mathbf{0}) = -(2\pi/3)\int_\Omega r^2\rho_t(\mathbf{r})\,\mathrm{d}\mathbf{r}. \qquad (29)$$

Therefore, $V(\mathbf{0})$ is not a trivial quantity. It can only be calculated at the end of the structural analysis. This also holds true for the reciprocal-space evaluation of $V(\mathbf{0})$, discussed below, which requires knowledge of the phases of the structure factors.

Direct-space calculation of $V(\mathbf{0})$

$V(\mathbf{0})$ can be calculated from the results of the multipolar expansion of the electronic charge density (Hansen & Coppens, 1978; Coppens & Hall, 1982; Coppens, 1991; Becker & Coppens, 1991), ρ_t is written as the sum of pseudo-atom densities:

$$\rho_t(\mathbf{r}) = \sum_j\rho_{tj}(\mathbf{r}-\mathbf{R}_j) \qquad (30a)$$

$$\rho_{tj}(\mathbf{r}) = Z_j\delta(\mathbf{r})-\rho_j(\mathbf{r}). \qquad (30b)$$

We define

$$\begin{aligned}q_j &= \int\rho_{tj}(\mathbf{r})\,\mathrm{d}\mathbf{r}\\ \mathbf{D}_j &= \int\mathbf{r}\rho_{tj}(\mathbf{r})\,\mathrm{d}\mathbf{r}\\ \omega_j &= \int r^2\rho_{tj}(\mathbf{r})\,\mathrm{d}r\end{aligned} \qquad (31)$$

as the charge, dipole and second moment of each pseudo-atom. Substitution of (30*a*) and (31) into (29) leads to

$$V(\mathbf{0}) = -(2\pi/3) \sum_{j}^{\text{cell}} (R_j^2 q_j + 2\mathbf{R}_j \,.\, \mathbf{D}_j + \omega_j). \tag{32}$$

The values for q_j, $\mathbf{D}$ and ω_j can be extracted from a refinement based on the spherical-harmonic expansion (Hansen & Coppens, 1978; Coppens, 1991).

We may write

$$\rho_j = \rho_j^s + \delta\rho_j, \tag{33}$$

where the spherical part ρ_j^s is

$$\rho_j^s = N_{jc}\rho_{jc}(r) + P_{jv}\lambda_j^3\rho_{jv}(\lambda_j r). \tag{34}$$

N_{jc} is the number of core electrons, ρ_{jc} is the normalized core electron density, ρ_{jv} is the normalized valence electron density, λ_j a screening coefficient and P_{jv} the effective valence population for pseudo-atom *j*. Notice that the free-atom electron density ρ_j^0 is

$$\rho_j^0(r) = N_{jc}\rho_{jc}(r) + N_{jv}\rho_{jv}(r) \tag{35a}$$

where N_{jv} is the number of valence electrons of the *j*th free atom, with

$$Z_j = N_{jc} + N_{jv}. \tag{35b}$$

The second term in (33) is given by

$$\delta\rho_j(\mathbf{r}) = \sum_{l,m,p} P^j_{lmp} R_{jl}(r) y_{lmp}(\hat{r}), \tag{36}$$

where $y_{lmp}(\mathbf{r})$ are real spherical harmonics, P^j_{lmp} the population coefficients and $p = \pm$. The radial functions $R_{jl}(r)$ are generally approximated by Slater-type functions:

$$R_{jl}(r) = [\zeta_{jl}^{(n_{jl}+3)}/(n_{jl}+2)!]r^{n_{jl}} \exp(-\zeta_{jl} r). \tag{37}$$

Let *x*, *y*, *z* be an orthonormal local coordinate system for a given pseudo-atom. The three terms in (32) are given by

$$\begin{aligned} q_j &= N_{jv} - P_{jv} - P^j_{00} \\ D_{jx} &= -P^j_{11+}[4(n_{j1}+3)/3\zeta_{j1}] \\ D_{jy} &= -P^j_{11-}[4(n_{j1}+3)/3\zeta_{j1}] \\ D_{jz} &= -P^j_{10-}[4(n_{j1}+3)/3\zeta_{j1}] \\ \omega_j &= -[N_{jc}\langle r_{jc}^2\rangle + P_{jv}\langle r_{jc}^2\rangle/\lambda_j^2] \\ &\quad -[(n_{j0}+4)(n_{j0}+3)/\zeta_{j0}^2]P^j_{00}, \end{aligned} \tag{38}$$

where the mean square radii $\langle r_{jc}^2\rangle$ and $\langle r_{jv}^2\rangle$ are

$$\begin{aligned} \langle r_{jc}^2\rangle &= \int r^2\rho_{jc}(r)\,\mathrm{d}\mathbf{r} = (1/4\pi^2)\nabla^2 f_{jc}(k)|_{k=0} \\ \langle r_{jv}^2\rangle &= \int r^2\rho_{jv}(r)\,\mathrm{d}\mathbf{r} = -(1/4\pi^2)\nabla^2 f_{jv}(k)|_{k=0}. \end{aligned} \tag{39}$$

It should be remarked that the pro-crystal density $\rho_t^0(\mathbf{r})$ gives a contribution to $V(\mathbf{0})$:

$$V^0(\mathbf{0}) = (2\pi/3) \sum_{j}^{\text{cell}} Z_j\langle r_j^2\rangle$$

with

$$Z_j\langle r_j^2\rangle = \int r^2\rho_j^0(r)\,\mathrm{d}\mathbf{r}. \tag{40}$$

Finally, we notice that the expressions that have been derived correspond to a system at rest.

Reciprocal-space expansion of $V(\mathbf{0})$; sum rules for multipolar moments

It is also possible to express $V(\mathbf{0})$ in terms of the structure factors. This can be done by using either calculated or 'observed' structure factors. The latter correspond to the thermally averaged charge density, and thus lead to the potential of the thermally averaged density.

The dipole moment $\mathbf{D}$ of the unit cell is

$$\mathbf{D} = \int_{\Omega} \mathbf{r}\rho_t(\mathbf{r})\,\mathrm{d}\mathbf{r} = D_x\mathbf{a} + D_y\mathbf{b} + D_z\mathbf{c}, \tag{41}$$

where **a**, **b**, **c** define the unit cell.

Notice that $\mathbf{D}$ is related to the bulk polarization $\mathbf{P}$ by the simple relation

$$\mathbf{P} = \mathbf{D}/\Omega. \tag{42}$$

Let us write the structure factor $F_t(\mathbf{H})$ as

$$F_t(\mathbf{H}) = A_t(\mathbf{H}) + iB_t(\mathbf{H}). \tag{43}$$

Using the Fourier-series expansion of $\rho_t(\mathbf{r})$ in (41), one finds

$$\begin{aligned} D_x &= -(1/\pi) \sum_{h=1}^{\infty} B_t(h,0,0)/h \\ D_y &= -(1/\pi) \sum_{k=1}^{\infty} B_t(0,k,0)/k \\ D_z &= (-1/\pi) \sum_{l=1}^{\infty} B_t(0,0,l)/l. \end{aligned} \tag{44}$$

Equation (44) is a sum rule that has to be satisfied by the structure factors. It relates microscopic quantities (the structure factors) with macroscopic quantities (D_x, D_y, D_z).

We now turn our attention to the quadrupolar contributions, and we define

$$\omega = \int_{\Omega} r^2\rho_t(\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{45}$$

such that [from (29)]

$$V(\mathbf{0}) = -(2\pi/3)\omega.$$

Let $Q_{\alpha\beta}$ be the quadrupolar tensor:

$$Q_{\alpha\beta} = \int_{\Omega} x_\alpha x_\beta \rho_t(\mathbf{r})\,\mathrm{d}\mathbf{r}, \tag{46}$$

where α, β stand for the **a**, **b**, **c** directions. If $g_{\alpha\beta}$ is the direct-space metric tensor,

$$\omega = \sum_{\alpha\beta} g_{\alpha\beta} Q_{\alpha\beta} \tag{47}$$

and $Q_{\alpha\beta}$ can be written as

$$\begin{aligned}
Q_{xx} &= D_x - (1/\pi^2) \sum_{h=1}^{\infty} [A_t(h,0,0)/h^2] \\
Q_{yy} &= D_y - (1/\pi^2) \sum_{k=1}^{\infty} [A_t(0,k,0)/k^2] \\
Q_{zz} &= D_z - (1/\pi^2) \sum_{l=1}^{\infty} [A_t(0,0,l)/l^2] \\
Q_{xy} &= (1/2)(D_x + D_y) \\
&\quad - (1/4\pi^2) \sum_{h,k\neq 0} [F_t(h,k,0)/hk] \\
Q_{yz} &= (1/2)(D_y + D_z) \\
&\quad - (1/4\pi^2) \sum_{k,l\neq 0} [F_t(0,k,l)/kl] \\
Q_{zx} &= (1/2)(D_z + D_x) \\
&\quad - (1/4\pi^2) \sum_{l,h\neq 0} [F_t(h,0,l)/hl].
\end{aligned} \tag{48}$$

Equation (48) is the sum rule relating the microscopic information to bulk quadrupolar tensor.

Concluding remarks

A careful discussion of the Coulomb potential has shown the necessity to consider the $V(\mathbf{0})$ term in its Fourier expansion. This term is important when comparative studies are to be done. It can be calculated either in direct space, using a multipolar expansion of the density, or in reciprocal space, from total structure factors. The reciprocal-space expansion leads to sum rules which must be fulfilled by the structure factors, and which connect the microscopic charge density with bulk multipolar moments that can be measured by different techniques.

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Crystal Structure Determination from Low-Resolution X-ray Powder Diffraction Data

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Abstract

The previously known structures of the modified nucleic acid bases 3-deazauracil (4-hydroxy-2-pyridone) and 6-azauracil (2*H*,4*H*-1,2,4-triazine-3,5-dione) have been shown to be determined by model-based reciprocal-space Patterson methods from low-resolution X-ray powder diffraction data. The data sets used in structural solution consisted of 26 and 23 reflections respectively, with $|F_{\mathbf{h}}|$ values extracted by a simple fitting procedure. The structural parameters found are of limited accuracy and only severely constrained refinements (on F) are possible from these data. However, these determinations indicate the strength of model-based Patterson methods to reveal structural information even from poor data.

Introduction

The solution of crystal structures from laboratory X-ray powder data using Patterson methods has

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