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Determination of Electrostatic Potentials in Crystalline Compounds. The Application to Boric Acid

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Abstract

A formalism for deriving electrostatic potentials in crystals is presented, with emphasis on the choice of origin and the determination of the mean inner potential. Conditions for applying the conventional origin chosen for isolated molecules are specified. The formalism is applied to orthoboric acid, and maps of the electrostatic potentials are presented. Extinction appears to be a severe problem in mapping electrostatic potentials, and its effects are investigated with a multipole expansion of the electron density. The effects of thermal motion are seen to be small at points far from the atomic core regions.

Introduction

It has been shown that electrostatic potentials in crystals can be derived from X-ray diffraction data (Stewart, 1979). This paper will present our application of this formalism. Even though electrostatic potentials are of major importance in the investigation of chemical dynamics, only a few groups work, or have worked, with the mapping of potentials from diffraction data (Moss & Coppens, 1980; Moss & Feil, 1981; Feil & Moss, 1983; Stewart, 1982; Swaminathan, Craven & McMullan, 1985). Bertaut (1952, 1977) has worked with the mapping of potentials in ionic crystals.

The most frequently applied method for determining electrostatic potentials from crystallographic data

(e.g. Swaminathan, Craven & McMullan, 1985) is based on a multipole expansion of the electron density. So far, this method has been used to derive the potential of a single molecule from the multipole functions and the expansion coefficients.

In this paper we concentrate on the potential inside a crystal. The first section discusses the distinction between the electrostatic potential in a crystal, calculated either by a Fourier sum in reciprocal space or by a superposition in direct space of the potentials from the units which build up the crystal. The charge density of such a unit – the building block for the crystal – could be the charge density inside a single unit cell or it could be the charge density from the atoms or molecules in the unit cell.

The Fourier coefficient of the potential for the reciprocal-lattice vector of length zero is of special importance when discussing the two different ways of expressing the potential as this coefficient is the average value of the potential inside the crystal. It is known as the mean inner potential. Changing this Fourier coefficient corresponds to changing the origin for the potential inside the crystal. So in the first section we pay special attention to the question of how to determine the origin of the potential and how to calculate the mean inner potential. An important part of this section is found in Appendix A.

In the second chapter we discuss some of the potential maps and the chemical information which can be derived from X-ray diffraction data. Both maps of the potential in a crystal and the potential of a single molecule and their relations are discussed.

The actual calculations deal only with the potential in a crystal. We use the algorithm of Stewart (1982)

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where the total electrostatic potential in a crystal is determined from two summations: a Fourier summation of the deformation potential in reciprocal space, and the superposition of the potentials from neutral atoms in direct space. The contribution from the individual atoms to the direct-lattice sum can be based on self-consistent field wavefunctions calculated with Gaussian-type basis functions, see Appendix B (van Duineveldt, 1971). The structure factors used to determine the deformation potential are calculated using form factors derived from the same wavefunctions.

As far as we know the formulae applied in this formalism for deriving the electrostatic potential have not been described previously in the literature. Hence Appendices B, C, containing the mathematical details, have been included. The formalism has been used to study the electrostatic potential in boric acid crystals, where the electron density has already been investigated (Gajhede, Larsen & Rettrup, 1986).

Expression for the electrostatic potential in a crystal

When mapping the electrostatic potential, $\varphi(\mathbf{x})$, from a given charge distribution, $\rho(\mathbf{x})$, the zero of the potential can be chosen freely, since only differences in potential have physical meaning. On the other hand, it is normal to choose zero at infinity; consistent with the formula (Avery, Sommer-Larsen & Grodzicki, 1984):

$$\varphi(\mathbf{x}) = \int d^3x' \rho(\mathbf{x}')/|\mathbf{x} - \mathbf{x}'|. \quad (1)$$

For a crystal this choice of zero means that we can separate out the electrostatic part of the energy necessary to take an electron out of a crystal. This part is the mean inner potential.

Another convenient origin is the one imposed by the condition

$$\int_{V_c} d^3x \varphi(\mathbf{x}) = 0, \quad (2)$$

corresponding to choosing the average electrostatic potential over the unit cell with volume V_c as zero (Stewart, 1982).

The first origin will normally apply when the potential in the crystal is constructed by a superposition of the potentials from the building blocks of the crystal. The potential of the building block is then connected to its charge density through (1).

The second choice of origin naturally applies when the crystal potential is written as a Fourier series. It means that the Fourier coefficient for the reciprocal-lattice vector of length zero is set to zero. The connection between the two ways of writing the potential in the crystal and the two choices of origin are discussed in detail below. An exact mathematical derivation is given in Appendix A.

The charge density in an infinite crystal can be imagined to be constructed from units, with charge density $\rho_0(\mathbf{x})$, centered at the Bravais-lattice nodes:

$$\rho(\mathbf{x}) = \sum_{\mathbf{R}} \rho_0(\mathbf{x} - \mathbf{R}), \quad (3)$$

where $\mathbf{R} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$ is a direct-lattice vector, \mathbf{a} , \mathbf{b} , \mathbf{c} the direct-unit-cell vectors and n_1 , n_2 , n_3 integers. These units can be groups of atoms, molecules or unit cells.

In reciprocal space the charge density can be written as a Fourier series:

$$\rho(\mathbf{x}) = \sum_{\mathbf{H}} \rho_{\mathbf{H}} \exp(-2\pi i \mathbf{H} \cdot \mathbf{x}), \quad (4)$$

where $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ is a reciprocal-lattice vector, \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* the reciprocal-unit-cell vectors, and h , k , l the Miller indices. $\rho_{\mathbf{H}}$ is the Fourier coefficient of the charge density:

$$\rho_{\mathbf{H}} = (1/V_c) \int d^3x \exp(2\pi i \mathbf{H} \cdot \mathbf{x}) \rho_0(\mathbf{x}). \quad (5)$$

The unit from which the charge density in the crystal is built gives rise to an electrostatic potential $\varphi_0(\mathbf{x})$. This is connected to the charge density $\rho_0(\mathbf{x})$ through Poisson's equation:

$$\nabla^2 \varphi_0(\mathbf{x}) = -4\pi \rho_0(\mathbf{x}). \quad (6)$$

The Fourier transform of the potential for a general vector \mathbf{H} in reciprocal space can be written in the form

$$\varphi_{\mathbf{H}} = (1/V_c) \int d^3x \exp(2\pi i \mathbf{H} \cdot \mathbf{x}) \varphi_0(\mathbf{x}). \quad (7)$$

For $\mathbf{H} \neq \mathbf{0}$ Poisson's equation gives the following identity:

$$\varphi_{\mathbf{H}} = (\rho_{\mathbf{H}} / \pi H^2) \quad (8)$$

and for $\mathbf{H} = \mathbf{0}$ we have

$$\varphi_{\mathbf{H}=\mathbf{0}} = (1/V_c) \int d^3x \varphi_0(\mathbf{x}). \quad (9)$$

This integral is only well defined if $\rho_0(\mathbf{x})$ fulfills the following three conditions:

$$(i) \quad \rho_0(\mathbf{x}) \text{ is totally neutral}; \quad (10)$$

$$(ii) \quad \rho_0(\mathbf{x}) \text{ has no dipole moment}; \quad (11)$$

$$(iii) \quad \rho_0(\mathbf{x}) \text{ has no quadrupole moment}. \quad (12)$$

In this case it is given by the expression

$$\begin{aligned} \int d^3x \varphi_0(\mathbf{x}) &= (-2\pi/3) \int d^3x r^2 \rho_0(\mathbf{x}) \\ &= (-2\pi/3) \langle r_0^2 \rangle. \end{aligned} \quad (13)$$

The derivation of these conditions is given in Appendix A.

If the electrostatic potential for an infinite crystal was written similar to (3) or (4), then the Fourier coefficient for the reciprocal-lattice vector $\mathbf{H} = \mathbf{0}$ had to be given in an unambiguous way by (9). The fact that $\varphi_{\mathbf{H}=\mathbf{0}}$ is not generally defined means that, in general, *one can only talk about the electrostatic potential in a finite crystal.*

For a real finite crystal the electrostatic potential includes two terms:

$$\varphi(\mathbf{x}) = \sum_{\mathbf{R} \in \text{crystal}} \varphi_0(\mathbf{x} - \mathbf{R}) + \varphi_{\text{surface}}(\mathbf{x}). \quad (14)$$

$\varphi_{\text{surface}}(\mathbf{x})$ is the potential from a surface charge distribution. This is due to effects like reconstructions in the surface and adsorption of molecules and charges.

If $\rho_0(\mathbf{x})$ has a total charge or a total dipole moment, then the first term in (14) will give a potential in the interior of the crystal, which does not have the lattice periodicity and which depends on the crystal size and shape. If $\rho_0(\mathbf{x})$ has a quadrupole moment only, then the potential in the interior will depend on the shape of the crystal, but not on the size (Redlack & Grindlay 1975). In Appendix A we derive the electrostatic potential for such a crystal. In the case of a vanishing quadrupole moment tensor, the potential is independent of the size and shape of the crystal, and the electrostatic potential in the interior of a finite crystal will be given by:

$$\varphi(\mathbf{x}) = \sum_{\mathbf{H} \neq 0} \varphi_{\mathbf{H}} \exp(-2\pi i \mathbf{H} \cdot \mathbf{x}) + (-2\pi/3 V_c) \int d^3 x' r'^2 \rho_0(\mathbf{x}'). \quad (15)$$

The constant term $\varphi_{\mathbf{H}=0}$ in (15) is evaluated in Appendix B, for the case where ρ_0 describes the charge density from a free atom and in Appendix C for the case where ρ_0 is the charge density of a unit cell.

The periodic charge density deep inside the crystal can be constructed from any one of an infinite number of different building blocks. Some of these correspond to different ways of choosing the unit cell from the same periodic charge density. Other choices like the charge density from the atoms or molecules in the unit cell have already been mentioned.

A change of building block for the crystal, e.g. the unit cell, will change the value of the constant term $\varphi_{\mathbf{H}=0}$. This is an effect of the long range of the Coulomb potential. When the charge density of a finite crystal is given by a sum as in (14), over the same direct-lattice vectors but with different building blocks, then the charge density at the surfaces of the crystals built this way will differ by a double layer of charge. Harris (1975) and Euwema & Surrat (1975) show that, deep inside the crystal, the potential from this double layer is given exactly by the difference of the constant terms for the two units.

As argued by Spackman & Stewart (1981) and Harris (1975), a building block from a periodic charge density can always be chosen, with all second-order moments equal to zero. In that case, the constant term in (15) is zero, so the choice of origin in (2) is equivalent to choosing a building block for the real crystal without any second order moments for the charge density. However, this kind of a building block does not give a very realistic description of the surface of a real crystal. On the other hand, the effect of the

surface charge is an undetermined parameter which makes the comparison between electrostatic potentials from X-ray diffraction data and other experimental techniques difficult. Another source of experimental information is the potential measured by electron diffraction, especially the mean inner potential (Tull, 1951). Here the effect of the exchange potential must also be taken into account. Another experimental observation is the work function for the crystal. In this case the electrostatic potential has to be combined with band-structure calculations in order to determine the Fermi energy (Sommer-Larsen & Avery, 1987). Still these observables depend strongly upon the surface effects, so again direct comparison is difficult.

Mapping electrostatic potentials

As suggested above, maps of the total electrostatic potential are mainly of interest in a solid-state physical context. Other potential maps which can be derived from X-ray diffraction data can give information about molecular bonding and reactivity, molecular response to a crystal field and structural influence on crystal binding.

The deformation potential, as the deformation electron density, gives information on the bonding. The potential from an isolated molecule, as found in a crystal with negligible sharing of electrons between molecules, can be calculated from a multipole expansion of the electron density (Stewart, 1982). In order to see differences in chemical reactivity due to effects of surrounding atoms of a molecular entity, one can compare the electrostatic potentials of the entities, calculated from a multipole expansion of the electron density, in two different crystal structures of which the entity is a part. These potentials give information concerning molecular reactivity.

The difference between the total electrostatic potential in the crystal and the potential from a single molecule, as determined from the multipole expansion gives the crystal field imposed on the molecule. The response of the molecule to this external field can be seen if the potential of an isolated molecule, e.g. from an *ab initio* calculation, is compared with the potential from the multipole expansion.

A problem is whether the errors in these difference maps can be reduced sufficiently to obtain reliable results. Hence in the following section, we present maps of total potentials and deformation potentials, with emphasis on the effects of extinction.

In mapping the potentials, we choose the origin according to (2) because more features show up in these maps. According to Stewart (1982) the potential can be written as a superposition of neutral atomic electrostatic potentials and the deformation potential. The mean inner potential from the neutral atoms is

subtracted:

$$\varphi(\mathbf{x}) = \sum_{\mathbf{R}, a} \varphi_a(\mathbf{x} - \mathbf{R} - \mathbf{x}_a) + (2\pi/3 V_c) \sum_a \langle r_a^2 \rangle + \sum_{\mathbf{H} \neq 0} (\Delta\rho_{\mathbf{H}}/\pi H^2) \exp(-2\pi i \mathbf{H} \cdot \mathbf{x}) \quad (16)$$

so the sum over a runs over all atoms in the unit cell, and $\langle r_a^2 \rangle$ is defined from the charge density of the neutral atom as in (13). $\Delta\rho_{\mathbf{H}}$ is the Fourier coefficient of the deformation charge density.

Formulae for evaluating the contribution to the electrostatic potential and the mean inner potential from a superposition of neutral atoms are given in Appendix B. Gaussian functions (van Duineveldt, 1971) have been chosen for the expansion of the wavefunctions. The choice of basis functions is arbitrary, since the free-atom contribution to the structure factors is first subtracted and then added for convergence reasons.

The calculated structure factors, used to derive the deformation potential were based on form factors from the same basis functions as those used in the calculation of the neutral-atom contribution to the electrostatic potential. Formulae for determining the form factor from a wavefunction based on a Gaussian expansion have been given by Stewart (1969).

The summation in reciprocal space is performed with a modified slant Fourier program (van de Waal, 1975).

Maps of the electrostatic potential of boric acid

The reciprocal-space contributions to all maps shown in Figs. 3-6 are all dynamic, *i.e.* are derived from observed structure factors from a thermally smeared electron density. Fig. 7 shows a static deformation potential calculated with structure factors from a multipole refinement. For Figs. 1, 2 and 4, the direct-space contribution is derived from a superposition of the potentials from static neutral atoms.

The details of the data collection, data reduction and the positional and thermal parameters have been published previously (Gajhede, Larsen & Rettrup, 1986). Seven reflections were then found to be severely affected by secondary extinction, and they were excluded from the Fourier transformation in the four electrostatic maps following. No averaging of non-crystallographic symmetry has been done, in order to see clearly the effects of experimental errors.

Fig. 1 shows a map of the electrostatic potential from superpositioning of free atoms. The electron density used was derived from atomic quantum-chemical calculations using a Gaussian-type basis set: (13s, 7p) for the oxygen and boron atoms and (10s) for the hydrogen atoms (van Duineveldt, 1971). Fig. 2 shows the same map but now with the mean inner potential (determined as described in Appendix B to be $0.52038 \text{ e}\text{\AA}^{-1}$) subtracted. This map is more infor-

mative since the range of contours around the molecule is much smaller than the range in Fig. 1.

Fig. 3 shows a map of the deformation electrostatic potential, derived from the experimental data. The non-crystallographic threefold symmetry is now not exact, but is still apparent. This map shows the expected negative regions in the parts of the molecule where

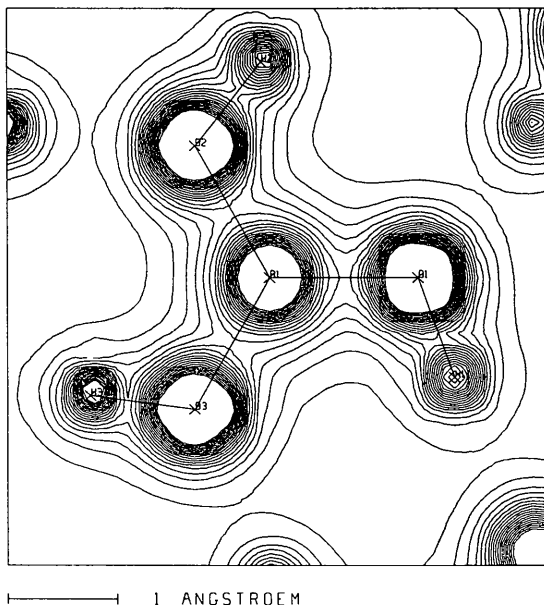


Fig. 1. Free-atom electrostatic potential derived from *ab initio* wavefunctions. Contour interval $0.05 \text{ e}\text{\AA}^{-1}$.

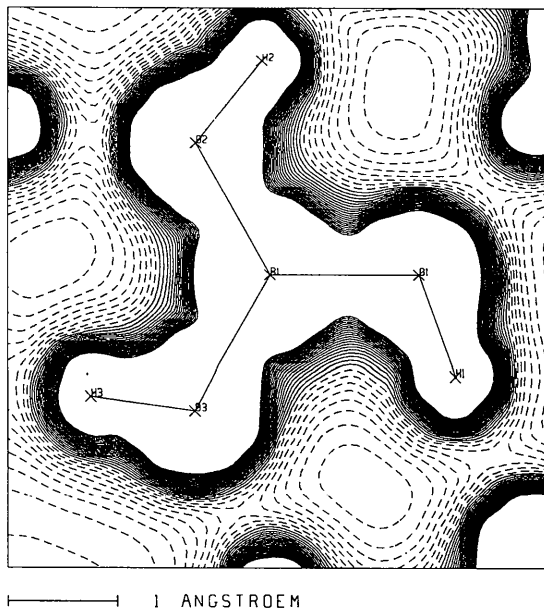


Fig. 2. Free-atom electrostatic potential with mean inner potential removed. Contour interval $0.05 \text{ e}\text{\AA}^{-1}$. Negative contours are represented by broken lines.

the deformation electron density is located, and positive regions in the hydrogen-bond regions. The electrostatic potential in the H1 hydrogen-bond region is significantly higher than in the other hydrogen-bond regions, which is most probably a consequence of the non-planarity of the boric acid molecule.

Fig. 4 shows the total electrostatic potential of crystalline boric acid in the plane of the molecules. No

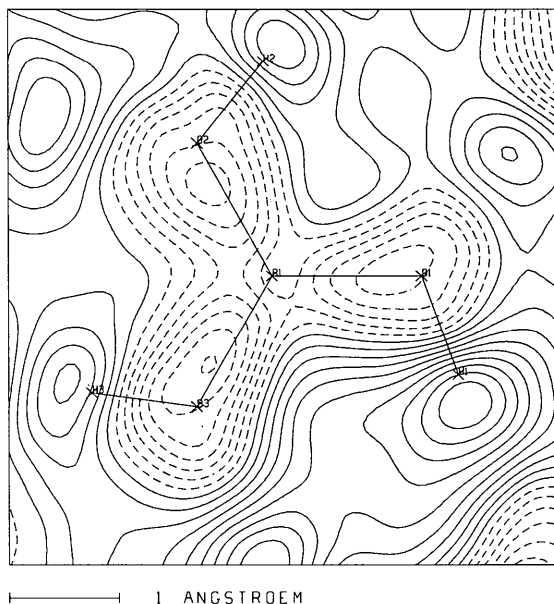


Fig. 3. Deformation electrostatic potential from observed data. Contours as in Fig. 2.

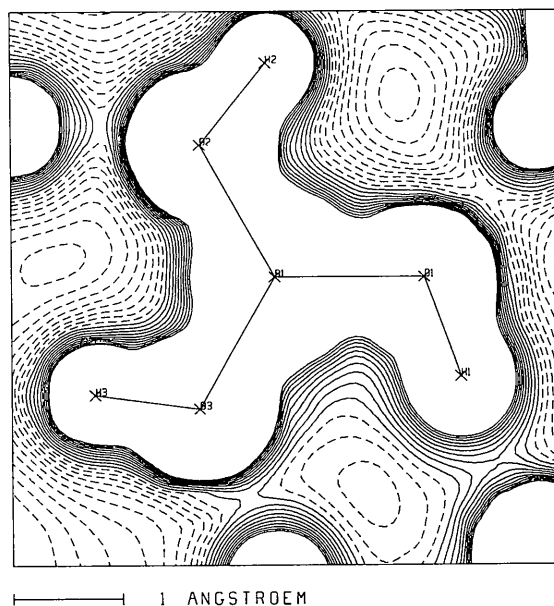


Fig. 4. Total electrostatic potential as a sum of a deformation electrostatic potentials, derived from observed data, and a free-atom contribution. Contours as in Fig. 2.

averaging has been performed, and the hydrogen bonds are not equivalent as expected. Two regions are negative and one is positive, again due to non-planarity.

In order to investigate the effects of the secondary extinction, a map was made which included the reflections previously found to be affected by extinction. This map is shown in Fig. 5. It shows that extinction is a severe problem in mapping electrostatic potentials, since all symmetry is lost. The effect is much more dramatic than in the deformation electron-density maps, where the extinction could hardly be seen (Kadziola, 1988). This is not surprising, since (8) gives high weights to the low-order reflections.

The 002 reflection is the observation by far the most affected by extinction. It is observed as 40 (1) but calculated to be 90.2 in the free-atom model. From the electron-density study (Gajhede, Larsen & Rettrup, 1986), structure factors calculated with the multipole refinement program *MOLLY* (Hansen & Coppens, 1978) are available. The 002 reflection is calculated to be 92.4 in the multipole description, giving an error comparable to the standard deviation of the observations by rejecting the reflection from the Fourier summation. Fig. 6 shows a deformation potential map, generated by the Fourier summation of $(F_{c,multipole} - F_{c,free\ atom})/\pi H^2$. This map is almost identical to the one shown in Fig. 3, indicating that the rejection of the seven reflections affected by extinction did not introduce significant errors.

The electron-density investigation showed that the static and dynamic electron densities are in qualitative agreement, but there was more electron density in the

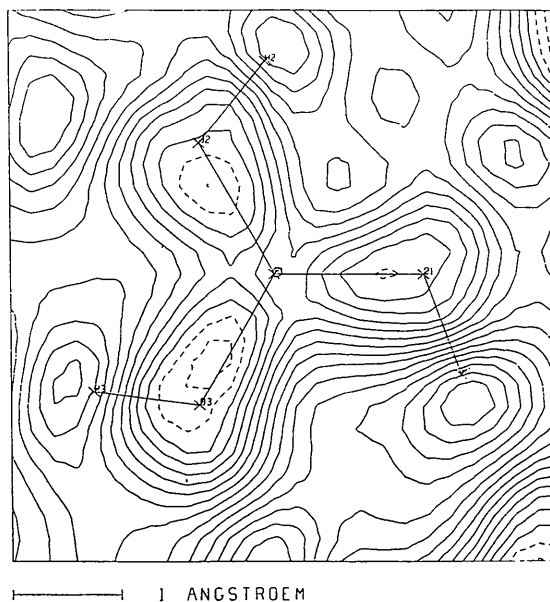


Fig. 5. Extinction-affected deformation electrostatic potential. Contours as in Fig. 2.

bonds of the static map than in the dynamic map. Hence similar results could be expected for the deformation electrostatic potential.

Fig. 7 shows a map of the static deformation potential generated by the Fourier summation of $(F_{c,multipole} - F_{c,free\ atom})/\pi H^2$ where the structure factors were calculated with displacement parameters set to zero. This map shows qualitative and quantitative features similar to the map in Fig. 3, except in

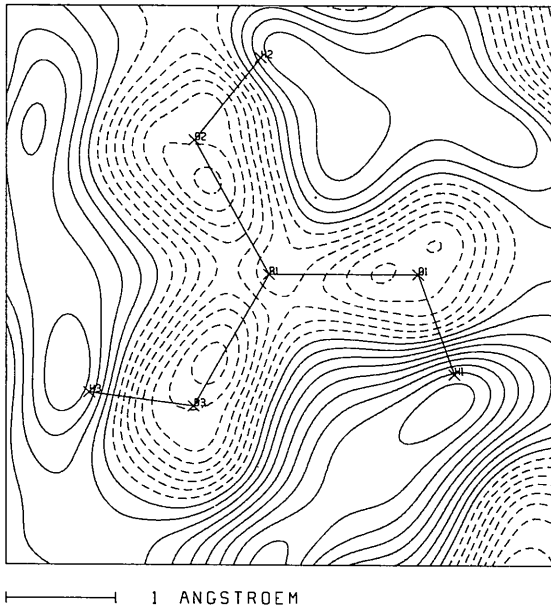


Fig. 6. Dynamic multipole-model deformation electrostatic potential. Contours as in Fig. 2.

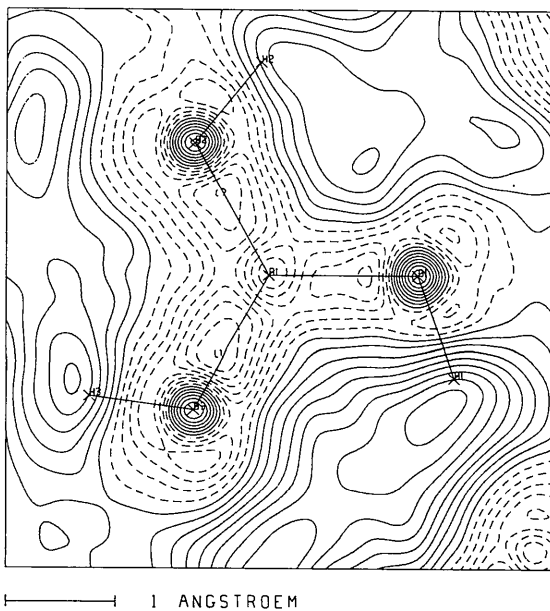


Fig. 7. Static multipole-model deformation electrostatic potential. Contours as in Fig. 2.

the atomic core regions (as expected), and it justifies the use of dynamic ΔF in the generation of Fig. 4. The peaks around the O-atom positions are due to series-termination effects which become important when the displacement parameters are set to zero.

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APPENDIX A

The electrostatic potential in a finite crystal

Following Guinier (1963), one can write the charge density in a real 'perfect' crystal as

$$\begin{aligned}\rho(\mathbf{x}) &= \rho_0(\mathbf{x}) * [\Omega(\mathbf{x})Z(\mathbf{x})] \\ &= \int d^3x' \rho_0(\mathbf{x} - \mathbf{x}') \Omega(\mathbf{x}') Z(\mathbf{x}').\end{aligned}\quad (\text{A.1})$$

In this equation $\rho_0(\mathbf{x})$ is the charge density of the building block for the crystal.

The shape of the crystal is determined by the form function $\Omega(\mathbf{x})$:

$$\Omega(\mathbf{x}) = \begin{cases} 1 & \text{if } \mathbf{x} \text{ is inside the crystal} \\ 0 & \text{if } \mathbf{x} \text{ is outside the crystal.} \end{cases}\quad (\text{A.2})$$

$\int d^3x \Omega(\mathbf{x}) = V$ is the volume of the crystal. $Z(\mathbf{x})$ defines the direct lattice

$$Z(\mathbf{x}) = \sum_{\mathbf{R}} \delta(\mathbf{x} - \mathbf{R}) = (1/V_c) \sum_{\mathbf{H}} \exp(-2\pi i \mathbf{H} \cdot \mathbf{x}).\quad (\text{A.3})$$

\mathbf{R} is a direct-lattice vector and \mathbf{H} is a reciprocal-lattice vector. With these two forms of $Z(\mathbf{x})$, the charge density is given by

$$\rho(\mathbf{x}) = \sum_{\mathbf{R}} \rho_0(\mathbf{x} - \mathbf{R}) \Omega(\mathbf{R}) = \sum_{\mathbf{R} \in \text{crystal}} \rho_0(\mathbf{x} - \mathbf{R})\quad (\text{A.4})$$

or

$$\begin{aligned}\rho(\mathbf{x}) &= (1/V_c) \sum_{\mathbf{H}} \exp(-2\pi i \mathbf{H} \cdot \mathbf{x}) \\ &\quad \times \int d^3x' \rho_0(\mathbf{x}') \exp(2\pi i \mathbf{H} \cdot \mathbf{x}') \Omega(\mathbf{x} - \mathbf{x}') \\ &= \Omega(\mathbf{x}) \sum_{\mathbf{H}} \exp(-2\pi i \mathbf{H} \cdot \mathbf{x}) \rho_{\mathbf{H}}\end{aligned}\quad (\text{A.5})$$

if \mathbf{x} is not too near the surface of the crystal. $\rho_{\mathbf{H}}$ is the Fourier transform of the charge density as in (5) of the main text.

Let $\varphi_0(\mathbf{x})$ denote the electrostatic potential from the building block for the crystal. The crystal's electrostatic potential can be written similar to (A.4) or (A.5):

$$\varphi(\mathbf{x}) = \sum_{\mathbf{R} \in \text{crystal}} \varphi_0(\mathbf{x} - \mathbf{R})\quad (\text{A.6})$$

or

$$\begin{aligned}\varphi(\mathbf{x}) &= (1/V_c) \sum_{\mathbf{H}} \exp(-2\pi i \mathbf{H} \cdot \mathbf{x}) \\ &\quad \times \int d^3x' \varphi_0(\mathbf{x}') \exp(2\pi i \mathbf{H} \cdot \mathbf{x}') \Omega(\mathbf{x} - \mathbf{x}').\end{aligned}\quad (\text{A.7})$$

The electrostatic potential, not too near the surface, can be transformed, if one writes $\exp(2\pi i \mathbf{H} \cdot \mathbf{x}')$ as $(-1/4\pi^2 H^2) \nabla^2 \exp(2\pi i \mathbf{H} \cdot \mathbf{x}')$, and combine this with Green's theorem and Poisson's equation to give

$$\varphi(\mathbf{x}) = \chi(\mathbf{x}) + \Omega(\mathbf{x}) \sum_{\mathbf{H} \neq 0} \exp(-2\pi i \mathbf{H} \cdot \mathbf{x}) (\rho_{\mathbf{H}} / \pi H^2) \quad (\text{A.8})$$

where

$$\begin{aligned} \chi(\mathbf{x}) = & (1/V_c) \int d^3 x' \varphi_0(\mathbf{x} - \mathbf{x}') \Omega(\mathbf{x}') \\ & + (1/V_c) \sum_{\mathbf{H} \neq 0} (-1/4\pi^2 H^2) \\ & \times \int d^3 x' \exp(-2\pi i \mathbf{H} \cdot \mathbf{x}') \\ & \times \{2\nabla \varphi_0(\mathbf{x} - \mathbf{x}') \cdot \nabla \Omega(\mathbf{x}') \\ & + \varphi_0(\mathbf{x} - \mathbf{x}') \nabla^2 \Omega(\mathbf{x}')\}. \end{aligned} \quad (\text{A.9})$$

$\chi(\mathbf{x})$ is the macroscopic potential in the crystal. It is the sum of the potential from a continuous distribution of charge density $(1/V_c)\rho_0(\mathbf{x})$ per volume element and the potential from a surface charge density. [$\nabla \Omega(\mathbf{x})$ is a δ function at the surface.]

The last term in (A.9) gives a contribution to the potential deep inside the crystal if $\rho_0(\mathbf{x})$ does not fulfil (10) and (11) of the main text. If $\rho_0(\mathbf{x})$ has a net dipole moment but is totally neutral the contribution is just a constant.

Thus for a crystal built from a unit without net charge or net dipole moment, the electrostatic potential not too near the surface of the crystal can be written as

$$\begin{aligned} \varphi(\mathbf{x}) = & (1/V_c) \int d^3 x' \varphi_0(\mathbf{x} - \mathbf{x}') \Omega(\mathbf{x}') \\ & + \Omega(\mathbf{x}) \sum_{\mathbf{H} \neq 0} (\rho_{\mathbf{H}} / \pi H^2) \exp(-2\pi i \mathbf{H} \cdot \mathbf{x}). \end{aligned} \quad (\text{A.10})$$

If one considers the electric field, rather than the potential, ρ_0 may even have a dipole moment, and (A.10) marks the connection between the microscopic and macroscopic theories of dielectrics.

The conditions (10)–(12) for the integral (9) in the main text to be uniquely defined can be shown by analyzing the combination of Green's theorem and Poisson's equation:

$$\begin{aligned} \int_V d^3 x \varphi_0(\mathbf{x}) = & -(2\pi/3) \int_V d^3 x r^2 \rho_0(\mathbf{x}) \\ & + (1/3) \int_{\Omega} d\mathbf{A} \mathbf{n} \cdot \mathbf{x} \varphi_0(\mathbf{x}) \\ & + (1/6) \int_{\Omega} d\mathbf{A} r^2 \mathbf{n} \cdot \nabla \varphi_0(\mathbf{x}). \end{aligned} \quad (\text{A.11})$$

The integral is over a volume V enclosed by the surface Ω . $d\mathbf{A}$ is an area element on Ω and \mathbf{n} is a unit vector normal to $d\mathbf{A}$. The integral (9) in the main text is understood to be the limit of (A.11) when the volume V tends to infinity. The integral (A.11) is only independent of the size and shape of the volume if the conditions (10)–(12) are fulfilled.

Similarly, by analyzing the function $(1/V_c) \int d^3 x' (\mathbf{x} - \mathbf{x}')^2 \rho_0(\mathbf{x} - \mathbf{x}') \Omega(\mathbf{x}')$, one can show that deep inside the crystal the first term in (A.10) gives the constant

$$\begin{aligned} \varphi_{\mathbf{H}=0} = & (1/V_c) \int d^3 x' \frac{1}{2} \sum_{i,j} Q_{ij} (x'_i x'_j / r'^5) \Omega(\mathbf{x}') \\ & - (2\pi/3 V_c) \int d^3 x' r'^2 \rho_0(\mathbf{x}') \end{aligned} \quad (\text{A.12})$$

if ρ_0 fulfils (10) and (11). Q_{ij} are the elements of the quadrupole tensor:

$$Q_{ij} = \int d^3 x (3x_i x_j - r^2 \delta_{ij}) \rho_0(\mathbf{x}). \quad (\text{A.13})$$

As written in (14) we must add the contribution from a surface charge density to (A.8) or (A.10).

Deep inside the crystal such a contribution can always be written as a constant plus the potential corresponding to a constant electric field. This can be shown by a Taylor expansion of the potential.

In general one can write the potential inside the crystal as

$$\begin{aligned} \varphi(\mathbf{x}) = & \varphi_{\text{surface}}(\mathbf{x}) + (1/V_c) \int d^3 x' \varphi_0(\mathbf{x} - \mathbf{x}') \Omega(\mathbf{x}') \\ & + \Omega(\mathbf{x}) \sum_{\mathbf{H} \neq 0} (\rho_{\mathbf{H}} / \pi H^2) \exp(-2\pi i \mathbf{H} \cdot \mathbf{x}) \end{aligned} \quad (\text{A.14})$$

where $\varphi_{\text{surface}}(\mathbf{x})$ contains all surface effects including the second term in (A.9) if $\rho_0(\mathbf{x})$ has a total charge or a total dipole moment.

APPENDIX B

Free-atom contribution to the electrostatic potential

The electrostatic potential from static free atoms in a crystal (procrystal) is written as

$$\varphi_{\text{pro}}(\mathbf{x}) = \sum_{\mathbf{R}, a} \varphi_a(\mathbf{x} - \mathbf{R} - \mathbf{x}_a), \quad |\mathbf{x} - \mathbf{R} - \mathbf{x}_a| < r_{\text{max}}, \quad (\text{B.1})$$

where

$$\varphi_a(\mathbf{x}) = \int d^3 x' \rho_a(\mathbf{x}') / |\mathbf{x} - \mathbf{x}'|, \quad (\text{B.2})$$

and ρ_a is the free atomic spherical charge density. Only contributions from atoms within a specified distance r_{max} are taken into account.

The charge density ρ_a is written as

$$\rho_a(\mathbf{x}) = Z_a e \delta(\mathbf{x}) - e \rho_{a,e}(\mathbf{x}), \quad (\text{B.3})$$

where Z_a is the atom number, e is the charge of the proton, and $\rho_{a,e}$ is the electron density from atom a . The atomic electron density $\rho_{a,e}$ is described as a sum of contributions from different shells:

$$\rho_{a,e}(\mathbf{x}) = \sum_{\nu}^{\text{shells}} \text{occ}_{\nu} \rho_{\nu}(\mathbf{x}), \quad (\text{B.4})$$

where occ_{ν} is the number of electrons occupying shell ν . The electron density of shell ν is described by the radial wavefunctions ψ_{ν} , which are expanded in

spherical normalized Gaussian-type functions (GTF's):

$$\psi_\nu(\mathbf{x}) = \sum_{i=1}^{N_\nu} c_{i\nu} A(l_\nu, \alpha_{i\nu}) \rho_{l_\nu, \alpha_{i\nu}}^{\text{GTF}}(\mathbf{x}), \quad (\text{B.5})$$

where

$$\rho_{l,\alpha}^{\text{GTF}}(\mathbf{x}) = r^l \exp(-\alpha r^2), \quad (\text{B.6})$$

N_ν is the number of GTF's in the basis set, l_ν is the angular momentum quantum number and $A(l, \alpha)$ is a normalization constant given by

$$A(l, \alpha) = \left(\frac{2^l}{1 \times 3 \times 5 \dots (2l+1)} \right)^{1/2} \left(\frac{(2\alpha)^{2l+3}}{\pi^3} \right)^{1/4}. \quad (\text{B.7})$$

That is to say

$$\begin{aligned} 1/A(l, \alpha)^2 &= \int d^3x r^{2l} \exp(-2\alpha r^2) \\ &= \int d^3x \rho_{2l, 2\alpha}^{\text{GTF}}(\mathbf{x}). \end{aligned} \quad (\text{B.8})$$

From (B.5), the electron-density contribution from shell ν can be written as

$$\begin{aligned} \rho_\nu(\mathbf{x}) &= \sum_{i=1}^{N_\nu} \sum_{j=1}^{N_\nu} c_{i\nu} c_{j\nu} A(l_\nu, \alpha_{i\nu}) \\ &\quad \times A(l_\nu, \alpha_{j\nu}) \rho_{2l_\nu, (\alpha_{i\nu} + \alpha_{j\nu})}^{\text{GTF}}(\mathbf{x}). \end{aligned} \quad (\text{B.9})$$

Similar to the expressions (B.3), (B.4) and (B.9), the potential can be written:

$$\varphi_a(\mathbf{x}) = Z_a e / r + \varphi_{a,e}(\mathbf{x}), \quad (\text{B.10})$$

$$\varphi_{a,e}(\mathbf{x}) = \sum_{\nu}^{\text{shells}} \text{occ}_\nu \varphi_\nu(\mathbf{x}), \quad (\text{B.11})$$

$$\begin{aligned} \varphi_\nu(\mathbf{x}) &= \sum_{i=1}^{N_\nu} \sum_{j=1}^{N_\nu} c_{i\nu} c_{j\nu} A(l_\nu, \alpha_{i\nu}) A(l_\nu, \alpha_{j\nu}) \\ &\quad \times \varphi_{2l_\nu, (\alpha_{i\nu} + \alpha_{j\nu})}^{\text{GTF}}(\mathbf{x}) \end{aligned} \quad (\text{B.12})$$

where

$$\varphi_{2l,\alpha}^{\text{GTF}}(\mathbf{x}) = (-e) \int d^3x' \frac{(r')^{2l} \exp[-\alpha(r')^2]}{|\mathbf{x} - \mathbf{x}'|}. \quad (\text{B.13})$$

Integrals in the form (B.13) are evaluated as

$$\begin{aligned} &\int d^3x' \frac{(r')^{2l} \exp[-\alpha(r')^2]}{|\mathbf{x} - \mathbf{x}'|} \\ &= 4\pi \left\{ (1/r) \int_0^r dr' (r')^{(2l+2)} \exp[-\alpha(r')^2] \right. \\ &\quad \left. + \int_r^\infty dr' (r')^{(2l+1)} \exp[-\alpha(r')^2] \right\} \end{aligned} \quad (\text{B.14})$$

by the recursion formulae:

$$\begin{aligned} (1/r) \int_0^r dr' (r')^{(2l+2)} \exp[-\alpha(r')^2] \\ = (-1/2\alpha) r^{2l} \exp(-\alpha r^2) \\ + [(2l+1)/2\alpha r] \int_0^r dr' (r')^{2l} \exp[-\alpha(r')^2] \end{aligned} \quad (\text{B.15})$$

valid for $l \geq 0$ and

$$\begin{aligned} &\int_r^\infty dr' (r')^{(2l+1)} \exp[-\alpha(r')^2] \\ &= (1/2\alpha) r^{2l} \exp(-\alpha r^2) \\ &\quad + (l/\alpha) \int_r^\infty dr' (r')^{(2l-1)} \exp[-\alpha(r')^2] \end{aligned} \quad (\text{B.16})$$

valid for $l \geq 1$. The recursions are initiated by

$$(1/r) \int_0^r dr' \exp[-\alpha(r')^2] = (\sqrt{\pi}/2r\sqrt{\alpha}) \text{erf}(\sqrt{\alpha}r), \quad (\text{B.17})$$

where

$$\text{erf}(r) = (2/\sqrt{\pi}) \int_0^r dr' \exp[-(r')^2] \quad (\text{B.18})$$

and

$$\int_r^\infty dr' r' \exp[-\alpha(r')^2] = (1/2\alpha) \exp[-\alpha r^2]. \quad (\text{B.19})$$

In the given definition the error function erf is available as a Fortran routine in NAG for example.

If the boundary conditions are chosen according to (2), one needs to calculate the terms $\langle r_a^2 \rangle$ in (18). Similar to (B.3), (B.4) and (B.9) one obtains

$$\begin{aligned} \langle r_a^2 \rangle &= \int d^3x r^2 \rho_a(\mathbf{x}) \\ &= \int d^3x r^2 [Z_a e \delta(\mathbf{x}) - e \rho_{a,e}(\mathbf{x})] \\ &= (-e) \int d^3x r^2 \rho_{a,e}(\mathbf{x}), \end{aligned} \quad (\text{B.20})$$

$$\int d^3x r^2 \rho_{a,e}(\mathbf{x}) = \sum_{\nu}^{\text{shells}} \text{occ}_\nu \int d^3x r^2 \rho_\nu(\mathbf{x}), \quad (\text{B.21})$$

$$\begin{aligned} \int d^3x r^2 \rho_\nu(\mathbf{x}) &= \sum_{i=1}^{N_\nu} \sum_{j=1}^{N_\nu} c_{i\nu} c_{j\nu} A(l_\nu, \alpha_{i\nu}) A(l_\nu, \alpha_{j\nu}) \\ &\quad \times \int d^3x r^2 \rho_{2l_\nu, (\alpha_{i\nu} + \alpha_{j\nu})}^{\text{GTF}}(\mathbf{x}). \end{aligned} \quad (\text{B.22})$$

With (B.6) and (B.8) the integrals in (B.22) can be rewritten as

$$\begin{aligned} \int d^3x r^2 \rho_{2l_\nu, (\alpha_{i\nu} + \alpha_{j\nu})}^{\text{GTF}}(\mathbf{x}) &= \int d^3x \rho_{2l_\nu + 2, (\alpha_{i\nu} + \alpha_{j\nu})}^{\text{GTF}}(\mathbf{x}) \\ &= \{1/A^2[l_\nu + 1, (\alpha_{i\nu} + \alpha_{j\nu})/2]\}. \end{aligned} \quad (\text{B.23})$$

APPENDIX C

$\varphi_{\mathbf{H}=0}$ expressed by Fourier coefficients $\rho_{\mathbf{H}}$ in the case where ρ_0 is the charge density in the unit cell

From (9) and (13), $\varphi_{\mathbf{H}=0}$ can be evaluated as

$$\varphi_{\mathbf{H}=0} = (-2\pi/3V_c) \int d^3x r^2 \rho_0(\mathbf{x}). \quad (\text{C.1})$$

In the case where the unit ρ_0 is given by the charge density in the unit cell, *i.e.* the restriction of the periodic charge density ρ to the unit cell, (C.1) can be written

$$\varphi_{\mathbf{H}=0} = (-2\pi/3V_c) \int_{V_c} d^3x r^2 \rho(\mathbf{x}). \quad (\text{C.2})$$

By inserting the Fourier expansion of ρ given by (4), transforming to fractional coordinates and assuming that the unit cell is electrically neutral, one obtains

$$\begin{aligned} & (-2\pi/3V_c) \int_{V_c} d^3x r^2 \rho(\mathbf{x}) \\ &= (-2\pi/3) \sum_{\mathbf{H} \neq 0} \rho_{hkl} \int_0^1 \int_0^1 \int_0^1 (\mathbf{x}\mathbf{a} + \mathbf{y}\mathbf{b} + \mathbf{z}\mathbf{c})^2 \\ & \quad \times \exp[-2\pi i(hx + ky + lz)] dx dy dz, \quad (C.3) \end{aligned}$$

where $\rho_{hkl} = \rho_{\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*}$. Evaluation and introduction of the unit-cell parameters gives the formula:

$$\begin{aligned} & (-2\pi/3V_c) \int_{V_c} d^3x r^2 \rho(\mathbf{x}) \\ &= \frac{a^2}{3} \sum_{h \neq 0} \rho_{h00} \left[\frac{1}{ih} - \frac{1}{\pi h^2} \right] + \frac{b^2}{3} \sum_{k \neq 0} \rho_{0k0} \left[\frac{1}{ik} - \frac{1}{\pi k^2} \right] \\ & \quad + \frac{c^2}{3} \sum_{l \neq 0} \rho_{00l} \left[\frac{1}{il} - \frac{1}{\pi l^2} \right] \\ & \quad + \frac{ab \cos \gamma}{3} \left\{ \sum_{h \neq 0} \sum_{k \neq 0} \rho_{hko} \frac{1}{\pi hk} \right. \\ & \quad \left. + \sum_{h \neq 0} \rho_{h00} \frac{1}{ih} + \sum_{k \neq 0} \rho_{0k0} \frac{1}{ik} \right\} \\ & \quad + \frac{bc \cos \alpha}{3} \left\{ \sum_{k \neq 0} \sum_{l \neq 0} \rho_{0kl} \frac{1}{\pi kl} \right. \\ & \quad \left. + \sum_{k \neq 0} \rho_{0k0} \frac{1}{ik} + \sum_{l \neq 0} \rho_{00l} \frac{1}{il} \right\} \\ & \quad + \frac{ca \cos \beta}{3} \left\{ \sum_{l \neq 0} \sum_{h \neq 0} \rho_{hol} \frac{1}{\pi lh} \right. \\ & \quad \left. + \sum_{l \neq 0} \rho_{00l} \frac{1}{il} + \sum_{h \neq 0} \rho_{h00} \frac{1}{ih} \right\}. \quad (C.4) \end{aligned}$$

When the unit cell is chosen with a vanishing dipole moment according to (11), the formula reduces to

$$\begin{aligned} & (-2\pi/3V_c) \int_{V_c} d^3x r^2 \rho(\mathbf{x}) \\ &= -\frac{a^2}{3} \sum_{h \neq 0} \rho_{h00} \frac{1}{\pi h^2} - \frac{b^2}{3} \sum_{k \neq 0} \rho_{0k0} \frac{1}{\pi k^2} \\ & \quad - \frac{c^2}{3} \sum_{l \neq 0} \rho_{00l} \frac{1}{\pi l^2} \\ & \quad + \frac{ab \cos \gamma}{3} \sum_{h \neq 0} \sum_{k \neq 0} \rho_{hko} \frac{1}{\pi hk} \\ & \quad + \frac{bc \cos \alpha}{3} \sum_{k \neq 0} \sum_{l \neq 0} \rho_{0kl} \frac{1}{\pi kl} \\ & \quad + \frac{ca \cos \beta}{3} \sum_{l \neq 0} \sum_{h \neq 0} \rho_{hol} \frac{1}{\pi lh}. \quad (C.5) \end{aligned}$$

The condition (12) for the components of the quadrupole tensor to be zero can be expressed in fractional coordinates as

$$\begin{aligned} & (\mathbf{a}^* \cdot \mathbf{a}^*)(-2\pi/3V_c) \int_{V_c} d^3x r^2 \rho(\mathbf{x}) \\ &= -2\pi \int_0^1 \int_0^1 \int_0^1 x^2 \rho(\mathbf{x}) dx dy dz \\ & (\mathbf{a}^* \cdot \mathbf{b}^*)(-2\pi/3V_c) \int_{V_c} d^3x r^2 \rho(\mathbf{x}) \\ &= -2\pi \int_0^1 \int_0^1 \int_0^1 x y \rho(\mathbf{x}) dx dy dz \end{aligned} \quad (C.6)$$

with equivalent expressions for the remaining tensor components.

This finally reduces (C.5) and gives the equation for $\varphi_{\mathbf{H}=0}$ as

$$\varphi_{\mathbf{H}=0} = - \sum_{h \neq 0} \varphi_{h00} \quad (C.7)$$

where $\varphi_{h00} = \varphi_{\mathbf{H} = h\mathbf{a}^*}$. Although (C.7) is equivalent to the expression for a crystal with cubic symmetry, the condition (12) that the charge density has a vanishing quadrupole-moment tensor is a weaker condition than requiring the charge density to have cubic symmetry.

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