

Electrostatic Properties of Ions in Crystals from X-Ray Diffraction Data *

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A procedure for calculating the electrostatic potential and the electrostatic energy of an ion in a crystal is presented. It is based on a mixed direct and reciprocal space approach, and it takes into account the detailed charge density distribution in the crystal which can be obtained from accurate X-ray diffraction measurements.

Key words: Electrostatic potential; X-ray diffraction; Charge density; Ionic crystals; Ionic conduction.

Introduction

The intensities of X-ray Bragg reflections from single crystals give a detailed information on the 3-dimensional distribution of the electron density, ρ^e , and on derived electrostatic properties. We will study the possibility of calculating the electrostatic potential within the crystal and the electrostatic potential energy of an ion. This may be especially interesting for materials showing large mobility of cations.

We may recall that within the Born-Oppenheimer approximation (adiabatic theory) the force on a nucleus equals the negative gradient vector of the total electronic plus nuclear-nuclear Coulomb energy: $\mathbf{K}_{\mathbf{R}_1} = -\nabla_{\mathbf{R}_1} E_{\text{tot}}(\mathbf{R}_1, \dots, \mathbf{R}_n; \rho^e)$, where $\mathbf{R}_1, \dots, \mathbf{R}_n$ are the position vectors of the atomic nuclei on which ρ^e depends parametrically. In this expression E_{tot} may be replaced by the electrostatic potential (the Hellmann-Feynman theorem [1]). It is trivial that in case \mathbf{R}_1 corresponds to a compact cation, i.e. its polarisability is low, $\mathbf{K}_{\mathbf{R}_1}$ is also the force on this ion. In the following we will limit the discussion to the calculation of the electrostatic potential and energies of ions, but let us speculate a bit more before entering this subject: If we were able to calculate all the second-order derivatives of the energy with respect to the coordinates of the ion positions, we could establish the equations which, within the harmonic approximation, determines the

lattice dynamics of the crystal. Let us write, in a kind of shorthand notation,

$$\frac{d^2 E_{\text{tot}}}{dR_1^2} = \frac{\partial^2 E_{\text{tot}}}{\partial(\rho^e)^2} \left(\frac{\partial \rho^e}{\partial R_1} \right)^2 + 2 \cdot \frac{\partial^2 E_{\text{tot}}}{\partial R_1 \partial \rho^e} \left(\frac{\partial \rho^e}{\partial R_1} \right) + \frac{\partial^2 E_{\text{tot}}}{\partial R_1^2} + \frac{\partial E_{\text{tot}}}{\partial \rho^e} \left(\frac{\partial^2 \rho^e}{\partial R_1^2} \right).$$

Since $(\partial E_{\text{tot}} / \partial \rho^e) = 0$ (the Hohenberg-Kohn theorem), the last term vanishes. The preceding term is purely electrostatic (nuclear-nuclear and nuclear-electronic coulomb interactions) and is easily calculated, whereas the two first terms are polarisability-like contributions to the energy derivatives $[(\partial \rho / \partial R_1)$ -polarisation of the electron density induced by a change in the nuclear coordinates], and we do not know of any straightforward way of calculating these.

A general description of the algorithms will be given. They follow quite closely the ideas developed by Stewart [2]. We illustrate their applications by two examples. The first with the aim of showing how to proceed in order to obtain reliable numerical results. To this end we study a hypothetical NaF crystal. The second example given is the potential felt by a potassium ion in KTiOPO_4 (KTP), for which the crystals show strong ionic conduction due to the mobility of the K^+ -ions.

Algorithms

An analytical description of the electron density in a crystal may be obtained by fitting a flexible model to the X-ray diffraction data. Presently the most commonly used approach is refining a so-called aspherical

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pseudoatom model using some kind of multipole expansion technique (see, e.g., Hansen and Coppens [3]), but for the following discussion the only important requirement is that the model must allow us to calculate a complete set of structure factors corresponding to the “at rest” electron density in the crystal. Accurate nuclear coordinates must also be known, either from such a model or from an independent neutron diffraction study.

The quantities that we want to compute from the charge density distribution of the crystal are the potential

$$V(\mathbf{r}) = V[\varrho^{\text{tot}}](\mathbf{r}) = \int \frac{\varrho^{\text{tot}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \quad (1)$$

and the energy of an ion centred at the position \mathbf{R} ,

$$E(\mathbf{R}) = \int V(\mathbf{r}) \varrho_{\text{ion}}^{\text{tot}}(\mathbf{r} - \mathbf{R}) d^3\mathbf{r}, \quad (2)$$

where ϱ^{tot} denotes the total charge density, i.e. electronic as well as nuclear, V and E are linear functionals of the charge density distribution. We can therefore take advantage of a decomposition of the total charge density

$$\varrho^{\text{tot}}(\mathbf{r}) = \sum_i^{\text{atoms}} Z_i \delta(\mathbf{r} - \mathbf{R}_i) - \varrho^e(\mathbf{r}), \quad (3)$$

which is simply the division into the nuclear and electronic parts. Next we rewrite the electron density

$$\varrho^e(\mathbf{r}) = \sum_i \varrho_i^e(\mathbf{r} - \mathbf{R}_i) + \Delta\varrho(\mathbf{r}), \quad (4)$$

where ϱ_i^e is some convenient (see below) spherical atomic density function centred at \mathbf{R}_i (the nuclear position) and integrating to Z_i electrons; $\Delta\varrho$ is the corresponding deformation density correcting for the deficiencies of the atomic functions.

When defining the total atomic charge density by

$$\varrho_i^{\text{tot}}(\mathbf{r}) = Z_i \delta(\mathbf{r}) - \varrho_i^e(\mathbf{r}), \quad (5)$$

we obtain for the potential

$$V[\varrho^{\text{tot}}](\mathbf{r}) = \sum_i V[\varrho_i^{\text{tot}}](\mathbf{r} - \mathbf{R}_i) - V[\Delta\varrho](\mathbf{r}). \quad (6)$$

In this expression, $V[\varrho_i^{\text{tot}}]$ is short-range; thus only a small cluster of atoms surrounding the point \mathbf{r} may be included in the summation. By choosing ϱ_i^e properly, $\Delta\varrho$ is slowly varying, and consequently its Fourier series

$$\begin{aligned} V[\Delta\varrho](\mathbf{r}) &= V[\Delta F](\mathbf{r}) \\ &= \frac{1}{\pi V} \sum_{\mathbf{H} \neq 0} \frac{\Delta F(\mathbf{H})}{H^2} \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}) \end{aligned} \quad (7)$$

will converge rapidly. It may be stressed that the nuclear contributions are taken care of in the cluster summation, and that the Fourier series only accounts for the contribution of the electron density. By this procedure we obtain the potential due to the entire crystal. If we want to get the potential at the site of an ion from the surrounding crystal, we simply subtract the contribution of this single ion,

$$\begin{aligned} V_{\text{x-ion}}(\mathbf{r}) &= \sum_i V[\varrho_i^{\text{tot}}](\mathbf{r} - \mathbf{R}_i) - V[\Delta\varrho](\mathbf{r}) \\ &\quad - V[\varrho_{\text{ion}}^{\text{tot}}](\mathbf{r} - \mathbf{R}_{\text{ion}}) \\ &= \sum_i^{\text{surround}} V[\varrho_i^{\text{tot}}](\mathbf{r} - \mathbf{R}_i) - V[\Delta\varrho](\mathbf{r}) \\ &\quad + V[\varrho_{\text{ion}}^e - \varrho_{\text{atom}}^e](\mathbf{r} - \mathbf{R}_{\text{ion}}), \end{aligned} \quad (8)$$

where in the first term we only need to sum over close surroundings of the ion. The last term is the potential due to the deformation density of the ion itself, correcting the fact that the Fourier sum necessarily accounts for the full crystal, including this ion.

Having obtained the potential, we can express the electrostatic energy of the ion as a function of displacement around its mean position \mathbf{R}_0 ,

$$\begin{aligned} E_{\text{ion}}(\mathbf{R} - \mathbf{R}_0) &= \sum_i \int V_{\text{x-ion}}[\varrho_i^{\text{tot}}](\mathbf{r} - \mathbf{R}_i) \varrho_{\text{ion}}^{\text{tot}}(\mathbf{r} - \mathbf{R}) d^3\mathbf{r} \\ &\quad - E[\Delta F](\mathbf{R}) + \int V[\varrho_{\text{ion}}^e - \varrho_{\text{atom}}^e](\mathbf{r} - \mathbf{R}_i) \\ &\quad \cdot \varrho_{\text{ion}}^{\text{tot}}(\mathbf{R} - \mathbf{R}_0) d^3\mathbf{r}. \end{aligned} \quad (9)$$

The terms in the cluster summation may be rewritten according to

$$\begin{aligned} &\int V[\varrho_1](\mathbf{r}) \varrho_2(\mathbf{r} - \mathbf{R}_2) d^3\mathbf{r} \\ &= \int \frac{\varrho_1(\mathbf{r}_1 - \mathbf{R}_1) \varrho_2(\mathbf{r}_2 - \mathbf{R}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2, \end{aligned} \quad (10)$$

which will contain nucleus–nucleus, nucleus–electron and electron–electron Coulomb interactions. The last term in (9) may be expressed in a similar manner and can be considered as a kind of self-deformation energy

$$\int \frac{\Delta\varrho_{\text{ion}}^e(\mathbf{r}_1 - \mathbf{R}_0) \varrho_{\text{ion}}^{\text{tot}}(\mathbf{r}_2 - \mathbf{R})}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2. \quad (11)$$

The Fourier contribution (a “crystal deformation energy”) equals

$$\begin{aligned} E[\Delta F](\mathbf{R}) &= \frac{1}{\pi V} \sum_{\mathbf{H} \neq 0} \frac{\Delta F(\mathbf{H})}{H^2} (Z_{\text{ion}} - f_{\text{ion}}(\mathbf{H})) \\ &\quad \cdot \exp(-2\pi i \mathbf{H} \cdot \mathbf{R}). \end{aligned} \quad (12)$$

Practical Aspects

The total electron density of the crystal is explicitly accounted for by the structure factors $\Delta F = F - F_A$, where F_A is calculated from atom-like density functions. These may be chosen freely, but it is preferable to choose them such that ΔF becomes small for large values of $\sin \theta / \lambda$. The important point is that we must use the same density functions in the calculation of F_A as for the cluster contributions to the potential and energy. Special care must be taken when computing the electrostatic energy; here a good-quality density must be used for describing the “mobile” ion, $\varrho_{\text{ion}}^{\text{tot}}$ and f_{ion} , respectively. Actually, we calculate densities and form factors from atomic orbitals compiled by Clementi and Roetti [4]. An original computer code was written for the potentials and nucleus–electron interaction energies, whereas standard electron–electron Coulomb repulsion routines were taken from quantum chemistry programs [5].

Since there may be a build-up of round-off and series termination errors close to the centre of the ion in question, $\mathbf{R} \approx \mathbf{R}_0$, primarily owing to an imperfect convergence of the Fourier synthesis, special care must be taken in this region. We minimise this by using a simplified description of the ion deformation density, $\Delta \varrho_{\text{ion}}^e$, putting it equal to a valence-shell deformation described by a single Slater-type orbital (STO). For the self-deformation energy this should not change the result when added to $E[\Delta F]$, but the interaction of the ion with neighbouring, symmetry related ions may be modified. Nevertheless these ions will be at rather long distances, and details in their charge density description will not play an important rôle for the potential in the region of interest.

We shall illustrate these points by a simple hypothetical test: NaF composed of spherical free ions Na^+ and F^- [4]. This example has the advantage of enabling us to calculate the energy by the procedure outlined above, but also to do it directly from a cluster calculation summing over the free ions. The second procedure does converge rapidly (3 shells of neighbours) when considering the variation of the energy, $E(\mathbf{R}) - E(\mathbf{R}_0)$; inclusion of further shells only adds or subtracts a, for practical purposes, constant contribution in the region of interest, $|\mathbf{R} - \mathbf{R}_0| \leq 0.2 \text{ \AA}$.

In Fig. 1 three curves of the electrostatic energy are shown. One is obtained from an ionic-cluster calculation and may be considered as the exact result. The other two graphs are computed by our procedure, one

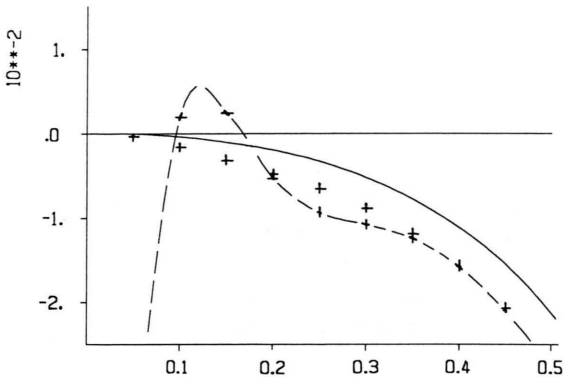


Fig. 1. Variation of the electrostatic potential energy of a sodium ion in NaF. Vertical axis in $e^2/\text{\AA}$ ($1 e^2/\text{\AA} = 14.4 \text{ eV}$). Abscissa: displacement in \AA of the ion from its equilibrium position, parallel to $[100]$. Continuous curve: ionic cluster calculation; broken curve: using accurate atomic orbitals for the deformation energy calculation; and crosses: using an STO representation of the deformation energy.

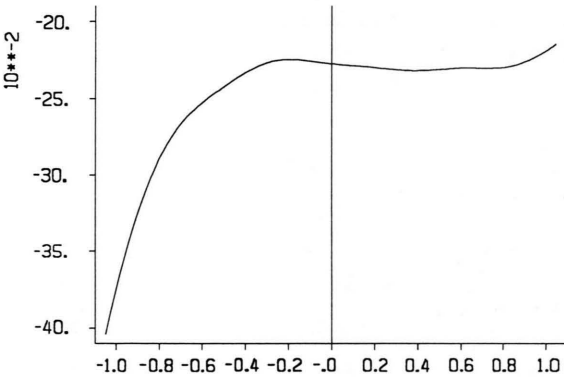


Fig. 2. Variation of the electrostatic potential energy of a potassium ion (K1) in KTiOPO_4 . Same units as in Figure 1.

is based on good quality wavefunctions [4], and the other one using the STO representation of the deformation term: $\Delta \varrho_{\text{Na}^+}^e = -\varrho(\text{STO-3s})$. In the Fourier synthesis of $E[\Delta F]$ all terms out to $\sin \theta / \lambda = 1.8 \text{ \AA}^{-1}$ were included. Actually, when using the “STO representation”, satisfactory convergence was already obtained at the level of $(\sin \theta / \lambda)_{\text{max}} = 1.0 \text{ \AA}^{-1}$.

The second example is KTP using the density model obtained from an X-ray diffraction study [6]. In the crystal structure of KTP the potassium ions occupy large cavities, and among all the atoms it is the K^+ -ion which undergoes the largest-amplitude thermal vibrations. In Fig. 2 we show the electrostatic potential energy as a function of the ion displacement parallel to the crystallographic c -axis (spacegroup

$\text{Pna}2_1$), which is also the direction of very large ionic conductivity.

Discussion

As already remarked, we are only interested in the variation of the electrostatic potential energy, since forces and force constants are related to the derivatives of this function. We will therefore not go into the discussion about the contribution of the Fourier coefficient corresponding to $\mathbf{H}=\mathbf{0}$ in (7) and (12) [7, 8].

The derivative of the electrostatic potential at an ion site (the spherical contribution of the ion itself may be subtracted out, see (8)) gives the Feynman force [1]. It should be equal to zero, if the extrapolation to the at-rest structure and density also corresponds to the equilibrium structure.

It is more difficult to interpret the electrostatic potential energy. This function will only be useful for cations having a compact electron density distribution with low polarisability. In the two calculations presented in the present work, the result is a negative force constant; there is a negative curvature in an

extended region around \mathbf{R}_0 of radius $\approx 1 \text{ \AA}$. It should be recalled that the effective forces determining the independent-atom vibrational tensors are thermal averages and, as already mentioned in the introduction, other than electrostatic forces between rigid ions come into play.

Conclusion

We have presented a practical procedure for calculating electrostatic properties in a crystal. Nevertheless, the present work raises the question: Is the electrostatic potential energy of a cation in a crystal a useful function? May it be correlated with effective one-particle potentials and with mobility of the ion, or will we have to look at thermal averages, and to take into account the polarisation of the surrounding crystal lattice or the electron exchange repulsion when displacing the ion away from its equilibrium position? In that case the calculations will become much more cumbersome, and we shall need complementary information to the structure and electron density as obtained from an X-ray diffraction measurement.

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