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Electrostatic potentials, fields and field gradients from a general crystalline charge density

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Explicit expressions for the electrostatic potential, the electric field and the electric field gradient at the nuclear positions of a crystalline lattice are presented. They are derived for a charge density given as an expansion in terms of spherical harmonics around the nuclear sites and as a Fourier series in the interstitial. These expressions can be decomposed into contributions from the spherical region centered around the lattice site of interest, from spherical regions surrounding all the other lattice sites and a contribution from the interstitital region.

Key words: Electrostatic potential—electric field—electric field gradient—infinite crystal.

1. Introduction

The calculation of electrostatic potentials, electric fields and field gradients is a fundamental problem in solid state physics. An important application is the study of the interaction of a nuclear electric quadrupole with the electric field gradient created by the surrounding crystalline lattice [1, 2]. Since the electric field gradient depends on the electric charge density around the nuclear site, its evaluation provides valuable information on the chemical bonding.

The formalism given here can be applied in all cases where from a given charge density, expanded in spherical harmonics inside spherical regions around the lattice points and as a Fourier series in the interstitial, the electrostatic potential, the electric field and the field gradient have to be calculated.

Although various methods are available [3-6] to solve Poisson's equation for a general charge density thus obtaining the electric field and the field gradient by appropriately differentiating the potential with respect to x, y, and z, the proposed method based on the decomposition of the charge density according to Rudge [4] allows a corresponding decomposition of the electric field gradient and hence a better interpretation of the results. Moreover, the present approach is also applicable if a full potential is not available, and therefore no direct differentiation of the electrostatic potential is possible, without having to generate a full potential from the given charge density. Although reliable results for the electric field gradient can only be obtained from an accurate charge density (e.g. as computed by the full potential APW or LAPW method) or if corrections according to Sternheimer [7] are applied, ratios of electric field gradients of an atom in two non-equivalent positions can be calculated using much simpler computational methods.

2. Theory

The electric field at a lattice point is defined as the negative derivative of the electrostatic potential V with respect to the cartesian coordinates x_i, $i = 1, 2, 3$ taken at the nuclear site

$$E_i = -\left.\frac{\partial V}{\partial x_i}\right|_n . \tag{1}$$

Taking the second derivative of the electrostatic potential with respect to x_i, the components of the electric field gradient tensor are obtained

$$\Phi_{ij} = \left.\frac{\partial^2 V}{\partial x_i\, \partial x_j}\right|_n . \tag{2}$$

Since there is no interaction of a nuclear quadrupole with a potential caused by s electrons, the electric field gradient is defined more appropriately [8] as a traceless tensor

$$\Phi_{ij} = \left.\frac{\partial^2 V}{\partial x_i\, \partial x_j}\right|_n - \left.\frac{1}{3}\delta_{ij}\nabla^2 V\right|_n . \tag{3}$$

The definitions (1) and (2) are the standard definitions used by experimentalists.

From the theoretical point of view, however, it is more convenient to use the spherical tensor notation because electrostatic potentials (the negative of the potential energy of the electron) and charge (or, alternatively, electron) densities are usually given as expansions in terms of spherical harmonics. In this way one automatically deals with traceless tensors.

In order to obtain the electric field gradient as a spherical tensor, we start from the electrostatic potential centered at the i-th nuclear site

$$V(\mathbf{r}_i) = \int \frac{\rho(\mathbf{r}'_i)}{|\mathbf{r}_i - \mathbf{r}'_i|}\, d\mathbf{r}'_i . \tag{4}$$

Instead of using the ordinary spherical harmonics in the Condon-Shortley phase convention, we introduce modified spherical harmonics according to Brink and Satchler [9]

$$C_l^m = \sqrt{\frac{4\pi}{2l+1}}\, Y_l^m \tag{5}$$

thus writing the formulae in a simpler form. With the following expansion

$$\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}'_i|} = \sum_l \sum_m r_i^l C_l^m(\boldsymbol{r}_i)\, \frac{C_l^{m*}(\boldsymbol{r}'_i)}{r_i'^{l+1}} \tag{6}$$

an asymptotic expression for the electrostatic potential is obtained that is valid for $|\boldsymbol{r}_i| \rightarrow 0$ because of the condition on which Eq. (6) is based

$$V(\boldsymbol{r}_i \rightarrow \boldsymbol{0}) = \sum_l \sum_m r_i^l V_{l;i}^{m*} C_l^m(\boldsymbol{r}_i) \tag{7}$$

where

$$V_{l;i}^m = \int \rho(\boldsymbol{r}'_i)\, \frac{C_l^m(\boldsymbol{r}'_i)}{r_i'^{l+1}}\, d\boldsymbol{r}'_i. \tag{8}$$

It should be noticed that in the above equations $\rho(\boldsymbol{r}'_i)$ denotes the charge density and not the electron density.

Eq. (8) already defines the tensor components of the electric field (for $l = 1$) and of the electric field gradient ($l = 2$) but does not necessarily indicate the most suitable way of how these quantities can be obtained.

Before proceeding further it seems to be worthwhile to consider the electrostatic interaction energy between a nuclear charge distribution $\rho_n(\boldsymbol{r}_i)$ and the potential (7)

$$\mathscr{E}_i = \int \rho_n(\boldsymbol{r}_i)\, V(\boldsymbol{r}_i)\, d\boldsymbol{r}_i. \tag{9}$$

Inserting Eq. (7) into Eq. (9) one gets

$$\mathscr{E}_i = \sum_l \sum_m V_{l;i}^{m*} Q_{l;i}^m \tag{10}$$

where

$$Q_{l;i}^m = \int r_i^l \rho_n(\boldsymbol{r}_i) C_l^m(\boldsymbol{r}_i)\, d\boldsymbol{r}_i \tag{11}$$

is the nuclear multipole moment written as a spherical tensor. The definition of the multipole moments in the present paper is thus in agreement with Brink and Satchler [9] but is different from Ref. [10].

Eqs. (7) and (10) can be interpreted as scalar products of two tensors of rank l ($V^m_{l;i}$, $C^m_l(\boldsymbol{r}_i)$ and $V^m_{l;i}$, $Q^m_{l;i}$, respectively) which are tensors of zero rank (scalars), namely the electrostatic potential $V(\boldsymbol{r}_i)$ and the interaction energy $\mathscr{E}_i$.

The $l=0$ term in Eq. (10) describes the interaction between the spherically symmetric potential $V^0_{0;i}$ and the point charge $Q^0_{0;i}$, the $l=1$ term the interaction of an electric field $V^m_{1;i}$ with a dipole moment $Q^m_{1;i}$ and the $l=2$ term the interaction of an electric field gradient $V^m_{2;i}$ with a quadrupole moment $Q^m_{2;i}$.

The following derivation starts from a crystalline charge density which is expanded in terms of spherical harmonics inside spheres centered at the nuclear positions, the so-called atomic spheres, and which is given as a Fourier series elsewhere

$$\rho(\boldsymbol{r})=\begin{cases}\sum\limits_{l}\sum\limits_{m}\rho^{m*}_{l;i}(|\boldsymbol{r}-\boldsymbol{r}_i|)C^m_l(\boldsymbol{r}-\boldsymbol{r}_i)+Z_i\delta(\boldsymbol{r}-\boldsymbol{r}_i)\\ \sum\limits_{\boldsymbol{K}}\rho(\boldsymbol{K})\,e^{i\boldsymbol{K}\cdot\boldsymbol{r}}\end{cases}\tag{12}$$

where the expression in the first line of Eq. (12) refers to the i-th atomic sphere and the second line on the right hand side of (12) represents the charge density between the atomic spheres. Z_i is the i-th nuclear charge. The higher nuclear moments can easily be neglected since they are too small to have any influence on the results.

According to Rudge [4] the charge density (12) can be split up into three electrically neutral parts for which Poisson's equation

$$\nabla^2V(\boldsymbol{r})=-4\pi\rho(\boldsymbol{r})\tag{13}$$

can be solved separately

$$\rho(\boldsymbol{r})=\rho_1(\boldsymbol{r})+\sum_{lmi}\rho_{2lmi}(\boldsymbol{r})+\sum_{lmi}\rho_{3lmi}(\boldsymbol{r})\tag{14}$$

where

$$\rho_1(\boldsymbol{r})=\sum_{\boldsymbol{K}\neq\boldsymbol{0}}\rho(\boldsymbol{K})\,\mathrm{e}^{i\boldsymbol{K}\cdot\boldsymbol{r}}\quad\text{for all }\boldsymbol{r}\tag{15}$$

$$\rho_{2lmi}(\boldsymbol{r})=\begin{cases}\Big\{\rho^{m*}_{l;i}(|\boldsymbol{r}-\boldsymbol{r}_i|)-\dfrac{i^l}{2l+1}\sum\limits_{\boldsymbol{K}}j_l(K|\boldsymbol{r}-\boldsymbol{r}_i|)\rho(\boldsymbol{K})C^{m*}_l(\boldsymbol{K})\,\mathrm{e}^{i\boldsymbol{K}\cdot\boldsymbol{r}_i}\\ \qquad\qquad-\dfrac{(Q^{m*}_{l;i}-Z_i\delta_{l0})}{(2l+1)|\boldsymbol{r}-\boldsymbol{r}_i|^l}\,\delta(\boldsymbol{r}-\boldsymbol{r}_i)\Big\}C^m_l(\boldsymbol{r}-\boldsymbol{r}_i)\\ 0\end{cases}\tag{16}$$

$$\rho_{3lmi}(\boldsymbol{r})=\begin{cases}-\dfrac{Q^{m*}_{l;i}}{\Omega}\,\delta_{l0}+\dfrac{Q^{m*}_{l;i}}{(2l+1)|\boldsymbol{r}-\boldsymbol{r}_i|^l}\,\delta(\boldsymbol{r}-\boldsymbol{r}_i)C^m_l(\boldsymbol{r}-\boldsymbol{r}_i)\\ -\dfrac{Q^{m*}_{l;i}}{\Omega}\,\delta_{l0}\end{cases}\tag{17}$$

In Eqs. (16) and (17) Ω is the volume of the unit cell, $j_l(Kr)$ is a spherical Bessel function and $Q_{l;i}^m$ is the multipole moment defined by

$$Q_{l;i}^m = Z_i \delta_{l0} + \frac{4\pi}{2l+1} \int_0^{R_i} r^{l+2} \rho_{l;i}^m(r)\, dr$$
$$- 4\pi(-i)^l R_i^{l+2} \sum_{\boldsymbol{K}} \rho(\boldsymbol{K}) \frac{j_{l+1}(KR_i)}{K} C_l^m(\boldsymbol{K})\, e^{-\boldsymbol{K}\cdot \boldsymbol{r}_i} \tag{18}$$

where R_i is the radius of the i-th atomic sphere.

We now give the solutions of Poisson's Eq (13) for the three contributions to the total charge density (15–17). For the first two partial charge densities we closely follow Rudge [4].

2.1. *The Fourier series problem*

The solution for $\rho_1(\boldsymbol{r})$ is immediately obtained as

$$V_1(\boldsymbol{r}) = \sum_{\boldsymbol{K}\neq \boldsymbol{0}} \frac{4\pi \rho_1(\boldsymbol{K})}{K^2}\, e^{i\boldsymbol{K}\cdot \boldsymbol{r}}. \tag{19}$$

The term for $\boldsymbol{K} = \boldsymbol{0}$, which is excluded from the summation in Eq. (19), represents the average of $V_1(\boldsymbol{r})$ over the unit cell. It is therefore taken to be zero in Eq. (19).

In order to obtain an expansion of $V_1(\boldsymbol{r})$ around the i-th nuclear site we write

$$e^{i\boldsymbol{K}\cdot \boldsymbol{r}} = e^{i\boldsymbol{K}\cdot \boldsymbol{r}_i}\, e^{i\boldsymbol{K}\cdot(\boldsymbol{r}-\boldsymbol{r}_i)} \tag{20}$$

and use the well-known expansion

$$e^{i\boldsymbol{K}\cdot(\boldsymbol{r}-\boldsymbol{r}_i)} = \sum_l \sum_m (2l+1) i^l j_l(K|\boldsymbol{r}-\boldsymbol{r}_i|) C_l^{m*}(\boldsymbol{K}) C_l^m(\boldsymbol{r}-\boldsymbol{r}_i). \tag{21}$$

We can thus extract the lm-contribution to $V_1(\boldsymbol{r})$ around the i-th nuclear site

$$V_{1lmi}(\boldsymbol{r}_{0i}) = 4\pi(2l+1) \sum_{\boldsymbol{K}\neq \boldsymbol{0}} \frac{\rho(\boldsymbol{K})}{K^2} j_l(K|\boldsymbol{r}-\boldsymbol{r}_i|) C_l^{m*}(\boldsymbol{K})\, e^{i\boldsymbol{K}\cdot \boldsymbol{r}_i} C_l^m(\boldsymbol{r}-\boldsymbol{r}_i) \tag{22}$$

where $\boldsymbol{r}_{0i} = \boldsymbol{r} - \boldsymbol{r}_i$.

2.2. *The zero multipole moment problem*

For the charge density $\rho_{2lmi}(\boldsymbol{r})$ the multipole moments $Q_{l;i}^m$ are chosen in such a way that all atomic spheres are electrically neutral and all higher multipole moments disappear. This means that the charge in each atomic sphere only gives rise to a potential within the same sphere but not outside of it. We can therefore write

$$V_{2lmi}(\boldsymbol{r}_{0i}) = \int \frac{\rho_{2lmi}(\boldsymbol{r}'_{0i})}{|\boldsymbol{r}_{0i} - \boldsymbol{r}'_{0i}|}\, d\boldsymbol{r}'_{0i}. \tag{23}$$

Inserting (16) into (23) and expanding according to Eq. (6), the result for the i-th atomic sphere reads [4]

$$
\begin{aligned}
V_{2lmi}(\boldsymbol{r}_{0i}) = \Bigg\{ & \frac{1}{|\boldsymbol{r}-\boldsymbol{r}_i|^{l+1}} \int_0^{|\boldsymbol{r}-\boldsymbol{r}_i|} x^{l+2} \left[\frac{4\pi}{2l+1}\, \rho_{l;i}^{m*}(x) \right. \\
& \left. -4\pi i^l \sum_{\boldsymbol{K}} j_l(Kx)\rho(\boldsymbol{K}) C_l^{m*}(\boldsymbol{K})\, \mathrm{e}^{i\boldsymbol{K}\cdot\boldsymbol{r}_i} \right] dx \\
& +|\boldsymbol{r}-\boldsymbol{r}_i|^l \int_{|\boldsymbol{r}-\boldsymbol{r}_i|}^{R_i} x^{1-l} \left[\frac{4\pi}{2l+1}\, \rho_{l;i}^{m*}(x) \right. \\
& \left. -4\pi i^l \sum_{\boldsymbol{K}} j_l(Kx)\rho(\boldsymbol{K}) C_l^{m*}(\boldsymbol{K})\, \mathrm{e}^{i\boldsymbol{K}\cdot\boldsymbol{r}_i} \right] dx \\
& + \frac{(Z_i\delta_{l0} - Q_{l;i}^{m*})}{|\boldsymbol{r}-\boldsymbol{r}_i|^{l+1}} \Bigg\} C_l^m(\boldsymbol{r}-\boldsymbol{r}_i). \qquad (24)
\end{aligned}
$$

This equation can be simplified by carrying out the integration over the two Fourier series using [11]

$$
\int_0^{|\boldsymbol{r}-\boldsymbol{r}_i|} x^{l+2} j_l(Kx)\, dx = \frac{|\boldsymbol{r}-\boldsymbol{r}_i|^{l+2}}{K}\, j_{l+1}(K|\boldsymbol{r}-\boldsymbol{r}_i|) \qquad (25)
$$

and

$$
\int_{|\boldsymbol{r}-\boldsymbol{r}_i|}^{R_i} x^{1-l} j_l(Kx)\, dx = \frac{j_{l-1}(K|\boldsymbol{r}-\boldsymbol{r}_i|)}{K|\boldsymbol{r}-\boldsymbol{r}_i|^{l-1}} - \frac{j_{l-1}(KR_i)}{KR_i^{l-1}} \qquad (26)
$$

and the recurrence relation [11]

$$
j_{l+1}(x) + j_{l-1}(x) = \frac{2l+1}{x}\, j_l(x) \qquad (27)
$$

Eq. (24) can therefore be written as

$$
\begin{aligned}
V_{2lmi}(\boldsymbol{r}_{0i}) = \Bigg\{ & \frac{4\pi}{2l+1} \left[\frac{1}{|\boldsymbol{r}-\boldsymbol{r}_i|^{l+1}} \int_0^{|\boldsymbol{r}-\boldsymbol{r}_i|} x^{l+2} \rho_{l;i}^{m*}(x)\, dx \right. \\
& \left. +|\boldsymbol{r}-\boldsymbol{r}_i|^l \int_{|\boldsymbol{r}-\boldsymbol{r}_i|}^{R_i} x^{1-l} \rho_{l;i}^{m*}(x)\, dx \right] \\
& +4\pi i^l \sum_{\boldsymbol{K}\neq\boldsymbol{0}} \frac{\rho(\boldsymbol{K})}{K^2} \left[\frac{K|\boldsymbol{r}-\boldsymbol{r}_i|^l}{R_i^{l-1}}\, j_{l-1}(KR_i) \right. \\
& \left. -(2l+1) j_l(K|\boldsymbol{r}-\boldsymbol{r}_i|) \right] C_l^{m*}(\boldsymbol{K})\, e^{i\boldsymbol{K}\cdot\boldsymbol{r}_i} \\
& +2\pi\rho(\boldsymbol{0}) \left(\frac{|\boldsymbol{r}-\boldsymbol{r}_i|^2}{3} - R_i^2 \right) \delta_{l0} + \frac{(Z_i\delta_{l0} - Q_{l;i}^{m*})}{|\boldsymbol{r}-\boldsymbol{r}_i|^{l+1}} \Bigg\} C_l^m(\boldsymbol{r}-\boldsymbol{r}_i) \qquad (28)
\end{aligned}
$$

where the $\boldsymbol{K}=\boldsymbol{0}$ term of the Fourier series, which is given separately, is chosen in such a way that this partial potential is zero outside the atomic spheres.

2.3. *The point multipole problem*

The problem now is to solve Poisson's equation for an array of point multipoles. In the special case of point charges a constant charge density over the whole crystal lattice is required to maintain electroneutrality. This problem was solved originally by Rudge [3]. Here we use a different approach which is more convenient for the present purpose. To some extent we follow the work by Herzig and Neckel [10] where an expression for the electrostatic interaction energy has been derived along similar lines. The formalism is also similar to the approaches of Nagel [12] and Hama [6].

We first consider the potential around the i-th lattice site caused by a charge distribution centered at the i'-th nucleus

$$V_i^{i'}(\boldsymbol{r}_{0i}) = \int \frac{\rho_{i'}(\boldsymbol{r}_{0i'})}{|\boldsymbol{r}_{ii'} - \boldsymbol{r}_{0i'} + \boldsymbol{r}_{0i}|}\, d\boldsymbol{r}_{0i'} \tag{29}$$

where the vector $\boldsymbol{r}_{ii'}$ points from the i'-th to the i-th nuclear site.

We now expand $|\boldsymbol{r}_{ii'} - \boldsymbol{r}_{0i'} + \boldsymbol{r}_{0i}|^{-1}$ according to Steinborn [13] and obtain

$$V_i^{i'}(\boldsymbol{r}_{0i}) = \sum_{lm} \sum_{l'm'} \mathscr{C}(l'm', lm) Q_{l';i'}^{m'} \frac{Y_{l+l'}^{m+m'}(\boldsymbol{r}_{ii'})}{r_{ii'}^{l+l+1}} r_{0i}^{l} C_l^m(\boldsymbol{r}_{0i}) \tag{30}$$

where

$$\mathscr{C}(l'm', lm) = (-1)^{l} \left(\frac{4\pi}{(2l+2l'+1)} \frac{(l+l'+m+m')!(l+l'-m-m')!}{(l+m)!(l-m)!(l'+m')!(l'-m')!} \right)^{1/2}. \tag{31}$$

In order to generalize this result for a crystal lattice one has to sum over all multipoles i' and perform the lattice summation

$$\Psi_{l+l'}^{m+m'}(\boldsymbol{r}) = \sum_j \frac{Y_{l+l'}^{m+m'}(\boldsymbol{R}_j - \boldsymbol{r})}{|\boldsymbol{R}_j - \boldsymbol{r}|^{l+l+1}} \tag{32}$$

which can be done following Nijboer and de Wette [14]. It should be noted that in Eq. (32) the ordinary spherical harmonics and not the modified ones as defined in Eq. (5) are used in order to keep the compatibility with Refs. [10, 14].

The complete potential V_{3mli} is obtained by adding the contributions from the multipole moment of the i-th sphere as well as a quadratic term originating from the constant charge density

$$\begin{aligned} V_{3lmi}(\boldsymbol{r}_{0i}) = {} & \frac{Q_{l;i}^{m*}}{|\boldsymbol{r} - \boldsymbol{r}_i|^{l+1}} C_l^m(\boldsymbol{r} - \boldsymbol{r}_i) - \frac{2\pi}{3\Omega} \rho(\mathbf{0}) |\boldsymbol{r} - \boldsymbol{r}_i|^2 \delta_{l0} \\ & + \sum_{l'm'i'} \mathscr{C}(l'm', lm) Q_{l';i'}^{m'} \Psi_{l+l'}^{m+m'*}(\boldsymbol{r}_i - \boldsymbol{r}_{i'}) |\boldsymbol{r} - \boldsymbol{r}_i|^{l} C_l^m(\boldsymbol{r} - \boldsymbol{r}_i) \end{aligned} \tag{33}$$

where $\boldsymbol{r}_{ii'} = \boldsymbol{r}_i - \boldsymbol{r}_{i'}$.

The average value over the unit cell of the partial potential (33) is zero.

Adding the partial potentials (22), (28) and (33) several terms cancel each other and the result is

$$\begin{aligned} V_i(\boldsymbol{r}_{0i}) = \Bigg\{ & \frac{4\pi}{2l+1} \left[\frac{1}{|\boldsymbol{r}-\boldsymbol{r}_i|^{l+1}} \int_0^{|\boldsymbol{r}-\boldsymbol{r}_i|} x^{l+2} \rho_{l;i}^{m*}(x)\, dx \right. \\ & \left. + |\boldsymbol{r}-\boldsymbol{r}_i|^l \int_{|\boldsymbol{r}-\boldsymbol{r}_i|}^{R_i} x^{1-l} \rho_{l;i}^{m*}(x)\, dx \right] \\ & + 4\pi i^l |\boldsymbol{r}-\boldsymbol{r}_i|^l \sum_{\boldsymbol{K}\neq\boldsymbol{0}} \frac{\rho(\boldsymbol{K})}{K} \frac{j_{l-1}(KR_i)}{R_i^{l-1}} C_l^{m*}(\boldsymbol{K})\, e^{i\boldsymbol{K}\cdot\boldsymbol{r}_i} \\ & + \frac{Z_i \delta_{l0}}{|\boldsymbol{r}-\boldsymbol{r}_i|^{l+1}} - 2\pi R_i^2 \rho(\boldsymbol{0}) \delta_{l0} \\ & + \sum_{l'm'i'} \mathscr{C}(l'm', lm) Q_{l';i'}^{m'} \Psi_{l+l'}^{m+m'*}(\boldsymbol{r}_i - \boldsymbol{r}_{i'}) |\boldsymbol{r}-\boldsymbol{r}_i|^l \Bigg\} C_l^m(\boldsymbol{r}-\boldsymbol{r}_i). \end{aligned} \tag{34}$$

The asymptotic expansion for $\boldsymbol{r}_{0i} \to \boldsymbol{0}$ of the potential (34) is obtained by collecting the terms which represent the solutions of Laplace's equation regular in the origin

$$\begin{aligned} V_{lmi}(\boldsymbol{r}_{0i} \to \boldsymbol{0}) = \Bigg\{ & \frac{4\pi}{2l+1} \int_0^{R_i} x^{1-l} \rho_{l;i}^{m*}(x)\, dx \\ & + 4\pi i^l \sum_{\boldsymbol{K}\neq 0} \frac{\rho(\boldsymbol{K})}{K} \frac{j_{l-1}(KR_i)}{R_i^{l-1}} C_l^{m*}(\boldsymbol{K})\, e^{i\boldsymbol{K}\cdot\boldsymbol{r}_i} - 2\pi R_i^2 \rho(\boldsymbol{0}) \delta_{l0} \\ & + \sum_{l'm'i'} \mathscr{C}(l'm', lm) Q_{l';i'}^{m'} \Psi_{l+l'}^{m+m'*}(\boldsymbol{r}_i - \boldsymbol{r}_{i'}) \Bigg\} |\boldsymbol{r}-\boldsymbol{r}_i|^l C_l^m(\boldsymbol{r}-\boldsymbol{r}_i). \end{aligned} \tag{35}$$

From a comparison of Eq. (7) with Eq. (35) the expansion coefficients $V_{l;i}^m$ are obtained

$$\begin{aligned} V_{l;i}^m = & \frac{4\pi}{2l+1} \int_0^{R_i} x^{1-l} \rho_{l;i}^m(x)\, dx - 2\pi R_i^2 \rho(\boldsymbol{0}) \delta_{l0} \\ & + 4\pi(-i)^l \sum_{\boldsymbol{K}\neq\boldsymbol{0}} \rho(\boldsymbol{K}) \frac{j_{l-1}(KR_i)}{KR_i^{l-1}} C_l^m(\boldsymbol{K})\, e^{-i\boldsymbol{K}\cdot\boldsymbol{r}_i} \\ & + \sum_{l'm'i'} \mathscr{C}(l'm', lm) Q_{l';i'}^{m'*} \Psi_{l+l'}^{m+m'}(\boldsymbol{r}_i - \boldsymbol{r}_{i'}). \end{aligned} \tag{36}$$

Taking $l = 0, 1, 2,$ in Eq. (36) one arrives at the respective expressions for the electrostatic potential, the electric field and the electric field gradient at the nuclear site i

$$\begin{aligned} V_{0;i}^0 = & 4\pi \int_0^{R_i} x \rho_{0;i}^0(x)\, dx + 4\pi \sum_{\boldsymbol{K}\neq\boldsymbol{0}} \rho(\boldsymbol{K}) \frac{\cos KR_i}{K^2} e^{-i\boldsymbol{K}\cdot\boldsymbol{r}_i} \\ & + \sum_{l'm'i'} \sqrt{\frac{4\pi}{2l'+1}} Q_{l';i'}^{m'*} \Psi_{l'}^{m'}(\boldsymbol{r}_i - \boldsymbol{r}_{i'}) - 2\pi R_i^2 \rho(\boldsymbol{0}), \end{aligned} \tag{37}$$

$$V_{1;i}^{m} = \frac{4\pi}{3} \int_{0}^{R_i} \rho_{1;i}^{m}(x)\, dx + 4\pi i \sum_{\boldsymbol{K} \neq \boldsymbol{0}} \rho(\boldsymbol{K}) \frac{j_0(KR)}{K} C_1^m(\boldsymbol{K})\, e^{-i\boldsymbol{K}\cdot\boldsymbol{r}_i}$$

$$+ \sum_{l'm'i'} \mathscr{C}(l'm', 1m) Q_{l';i'}^{m'*} \Psi_{1+l'}^{m+m'}(\boldsymbol{r}_i - \boldsymbol{r}_{i'}), \tag{38}$$

$$V_{2;i}^{m} = \frac{4\pi}{5} \int_{0}^{R_i} \frac{\rho_{2;i}^{m}(x)}{x}\, dx - 4\pi \sum_{\boldsymbol{K} \neq \boldsymbol{0}} \rho(\boldsymbol{K}) \frac{j_1(KR_i)}{KR_i} C_2^m(\boldsymbol{K})\, e^{-i\boldsymbol{K}\cdot\boldsymbol{r}_i}$$

$$+ \sum_{l'm'i'} \mathscr{C}(l'm', 2m) Q_{l';i'}^{m'*} \Psi_{2+l'}^{m+m'}(\boldsymbol{r}_i - \boldsymbol{r}_{i'}). \tag{39}$$

Two important points have to be noticed in an application of the formalism given above. First, it might be necessary to shift the potential calculated from Eqs. (37) or (34) to adjust it to the appropriate zero. This problem is discussed in the papers of Rudge [3, 4]. Secondly, there is the problem of convergence of the series involved. For the electric field gradient the lattice sums are absolutely convergent if a neutral basis is assumed. The electric field is well-defined if the unit cell is electrically neutral and does not have a permanent multipole moment. In the former case the electric field is infinite, in the latter case it depends on the shape of the crystal [15]. For the electrostatic potential the series diverge if the unit cell is not electrically neutral or carries a dipole moment and is conditionally convergent for a unit cell having a permanent quadrupole moment. It can be shown to depend on the quadrupole moment of the unit cell if the Ewald method is used [16]. In the present formalism electroneutrality is always guaranteed by the presence of a constant charge density.

Before we come to a discussion of the present formalism a recipe shall be given for the conversion of the spherical components of the electric field and field gradient tensors, as defined by Eq. (8), into the components of the corresponding traceless cartesian tensors. For an investigation of the general case see the work by Normand and Raynal [17].

With the conventions of the present paper one finds for the electric field

$$E_x = -\frac{1}{\sqrt{2}} (V_1^1 - V_1^{-1}) \tag{40a}$$

$$E_y = \frac{i}{\sqrt{2}} (V_1^1 + V_1^{-1}) \tag{40b}$$

$$E_z = -V_1^0 \tag{40c}$$

and for the electric field gradient

$$\Phi_{xx} = \frac{\sqrt{3}}{\sqrt{2}} V_2^2 - V_2^0 + \frac{\sqrt{3}}{\sqrt{2}} V_2^{-2} \tag{41a}$$

$$\Phi_{yy} = -\frac{\sqrt{3}}{\sqrt{2}} V_2^2 - V_2^0 - \frac{\sqrt{3}}{\sqrt{2}} V_2^{-2} \tag{41b}$$

$$\Phi_{zz} = 2V_2^0 \tag{41c}$$

$$\Phi_{xy} = -i\frac{\sqrt{3}}{\sqrt{2}} V_2^2 + i\frac{\sqrt{3}}{\sqrt{2}} V_2^{-2} \tag{41d}$$

$$\Phi_{yz} = i\frac{\sqrt{3}}{\sqrt{2}} V_2^1 + i\frac{\sqrt{3}}{\sqrt{2}} V_2^{-1} \tag{41e}$$

$$\Phi_{xz} = -\frac{\sqrt{3}}{\sqrt{2}} V_2^1 + \frac{\sqrt{3}}{\sqrt{2}} V_2^{-1}. \tag{41f}$$

3. Discussion

Eqs. (37)-(39) represent expressions for the electrostatic potential, the electric field and the electric field gradient at the lattice sites of an infinite crystal as obtained from a general charge density. Special cases, mainly restricted to point multipole lattices, have been attracting interest for a long time. A few papers shall be mentioned here, namely the calculation of the internal electric field in dipole lattices by Nijboer and de Wette [15], the calculation of electric field gradients in point ion and uniform background lattices by de Wette [18] and the calculation of electrostatic potentials and fields [19, 20] and field gradients [19] in point charge lattices.

For a physical interpretation of the terms in Eqs. (37)-(39) a little manipulation is necessary because the Fourier series in these equations extend over the whole crystalline lattice although they have a definite meaning only in the interstitial region. To overcome this difficulty the multipole moments defined in Eq. (18) have to be split up into two parts. The first one contains the first two terms of Eq. (18) and is nothing else than the multipole moment of the atomic sphere around the lattice site *i*. The last term of Eq. (18) represents the correction for extending the Fourier series into the atomic spheres. If the last terms of Eqs. (37)-(39) are split up correspondingly the following interpretation is possible: The first term in Eqs. (37)-(39) describes the contribution of the atomic sphere around the lattice point of interest, the second term plus the corresponding part of the third term represents the contribution of the interstitial region and the remainder of the third term the contribution of the other atomic spheres.

The formalism given in Sect. 2 can be applied to all practically occurring cases. If point multipole lattices have to be considered only the lattice summation part of the approach needs to be used.

The practical application of the present formalism will be demonstrated in a forthcoming paper [21] where an *ab initio* calculation of the electric field gradients in Li_3N from a full potential LAPW charge density is presented.

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