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Expansion of the Coulomb potential in crystals

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A method is presented by which the coefficients of a potential expansion into spherical harmonics are related to invariant components of multipole moments, centered at a representative point of crystallographically equivalent positions. The quantities which establish this relation (named K factors), are completely determined by the space group of the crystal and the unit-cell dimensions. They can be tabulated for any crystal structure, and tables are given for three important cubic space groups. On the basis of such tables, the determination of the expansion coefficients for the Coulomb potential in crystals is reduced to the evaluation of multipole moments of the charge density in spatial regions, partitioning the asymmetric unit. This method can be used in quantum-mechanical calculations as well as in classical treatments of the Coulomb potential. It permits large flexibility in potential calculations with differing electronic charge distribution and is therefore very convenient for self-consistent procedures. It also allows a systematic comparison of Coulomb interactions in different types of crystals and can therefore be an aid for the understanding of ionic structures.

I. INTRODUCTION

The study of electronic properties in crystals often requires a sufficiently accurate evaluation of the potential produced by the charge distribution within the crystal. It is mainly the long-range Coulombic part of the potential that makes this a rather difficult task, especially in ionic materials where the binding of valence electrons to the individual ions is too strong to allow for an effective screening of the ionic charges. In the literature two different methods have been used to treat crystalline potentials. The first is to replace the real charge distribution by a much simpler one, for example by point charges or Gaussian functions, which of course is only reasonable in ideally ionic materials. The resulting three-dimensional lattice sums are quite interesting from a mathematical point of view, and different methods have been used to evaluate them with high accuracy.[1-4] These methods have been established not only for the case where the lattice points are occupied by point charges, but also for the more general case of multipole moments of arbitrary order.[5,6] The results of such calculations have been used in a semiempirical way to get a better understanding of various physical properties, such as the crystal binding in ionic materials,[7] the lattice contribution to the electric field gradient at the nuclei,[8,9] and many others.

The second way is to replace the real crystalline Coulomb potential by a potential of a simpler form. In most band-structure calculations or in crystal-field theory, for example, only the interaction with a limited number of neighbors is taken into account. In most cluster calculations the effect of the crystalline potential is replaced by surrounding the cluster with a charged Watson sphere.

Recently, several approaches have been made using "embedded clusters."[10-12] Here the crystal potential is calculated in each cycle of a self-consistent procedure from the periodically arranged charge distribution obtained for the cluster. These calculations have shown that the potential from sources external to the cluster may have a rather significant effect on the cluster wave functions. The external potential effects not only the boundary conditions but also the periodicity of the potential within the cluster, neither of which can be obtained by the Watson sphere technique.[10]

The exact evaluation of the potential from a given charge distribution, however, requires the summation over a great number of lattice points with all the convergence problems well known from the evaluation of Madelung constants. These problems have led some authors to use only the point-charge contribution to the crystal potential for the stabilization of the clusters.[10] This approximation is reasonable for ionic materials where all ions are at high-symmetry positions, such as those of the NaCl or CsCl type. It will be rather poor for partly covalent compounds or for those ionic materials where the point symmetry of the ions allows the occurrence of low-order multipoles.

In the following, a method will be outlined which considerably simplifies the evaluation of the Coulomb potential for a given charge distribution. The basic point is the expansion of the potential into spherical harmonics and the relation of the expansion coefficients to certain invariant multipole components of the charge density centered around just one representative point of all crystallographically equivalent positions. It is a generalization of a method for the calculation of electric field gradients in multipole lattices, introduced by Hafner and Raymond,[8] who made use of the fact that multipole moments and potential derivatives are related by certain quantities (called K factors by these authors) which depend only on the structural geometry of the crystal and not on the magnitude of the multipole moments. Rudge has independently introduced similar factors for the evaluation of potentials in augmented-plane-wave (APW) band-structure calculations.[13,14] He has derived an expression for these factors from the Ewald series for the potential and called them "Ewald coefficients." From the present work it will become clear that the mathematical basis for the introduction of crystallographical factors which relate multipole moments of the charge density to expansion coefficients of the Coulomb potential (the term K factors will be kept for these) is independent of the Ewald method.

It will be outlined in the next sections how K factors can be calculated for any crystal structure. In the following section, basic relations among individual K factors are given, which considerably reduce these to a minimum set of independent factors. These are tabulated for some of the most important cubic space groups and provide the basis for potential calculations in a great number of different crystals. Finally, the relations of the present work to other approaches in this field and the applicability of the method to various problems dealing with Coulomb interactions in crystals, will be discussed.

II. POTENTIAL EXPANSION

The Coulomb potential, produced by the crystalline charge density $\rho(\vec{r})$, is obtained from the solution of Poisson's equation as

$$V(\vec{r}) = \int_{\Omega} \frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} d^3r' \,. \tag{1}$$

The crystalline space Ω is now partitioned into regions Ω_i and reference points $\vec{R}_i$ are chosen for each Ω_i according to the following rules:

1(a) $\bigcup_i \Omega_i = \Omega$,

1(b) $\Omega_i \bigcap \Omega_j = 0$ for all pairs i,j with $i \neq j$, and

1(c) $|\vec{r}-\vec{R}_i| < |\vec{R}_i - \vec{R}_j|$ for all $\vec{r} \in \Omega_i$ and all $j \neq i$.

The expansion of $1/|\vec{r}-\vec{r}\,'|$ into spherical harmonics Y_{lm} leads to the following expression for the potential in one of these regions, say i:

$$V^i(\vec{r}_i) = V_0^i(\vec{r}_i) + \sum_{l,m} V_{lm}^{i*} r_i^l Y_{lm}(\vec{r}_i) \tag{2}$$

$$|\vec{r}_i| \le \min\{\, |\vec{r}_i\,'| \,\}, \quad \vec{r}_i\,' \in \Omega_j, \quad j \neq i$$

with $\vec{r}_i = \vec{r} - \vec{R}_i$,

$$V_0^i(\vec{r}_i) = \int_{\Omega_i} \frac{\rho(\vec{r}_i\,')}{|\vec{r}_i - \vec{r}_i\,'|} d^3r' \,, \tag{3}$$

$$V_{lm}^i = \frac{4\pi}{2l+1} \sum_{j \neq i} \int_{\Omega_j} \rho(\vec{r}_i\,') r_i'^{\,-(l+1)} Y_{lm}(\vec{r}_i\,') d^3r' \,. \tag{4}$$

V_{lm}^i are the desired expansion coefficients for the potential in region Ω_i. They depend on the charge distribution in all regions Ω_j, disjunct from Ω_i.

The term $V_0^i(\vec{r}_i)$, i.e., the contribution from the charge density in the region where the potential is evaluated, is of no further interest here (cf. Ref. 15). For the evaluation of the integral over Ω_j the origin is shifted from $\vec{R}_i$ to $\vec{R}_j$:

$$\int_{\Omega_j} \rho(\vec{r}_i\,') r_i'^{\,-(l+1)} Y_{lm}(\vec{r}_i\,') d^3r' = \int_{\Omega_j} \rho^j(\vec{r}_j) \, |\vec{r}_j + \vec{R}_{ij}|^{-(l+1)} Y_{lm}(\vec{r}_j + \vec{R}_{ij}) d^3r_j \,, \tag{5}$$

where $\rho^j(\vec{r}_j)$ has been used instead of $\rho(\vec{r}_j + \vec{R}_{ij})$ and $\vec{R}_{ij} = \vec{R}_j - \vec{R}_i$. Now the poly-polar expansion of the "irregular solid spherical harmonic" in the integrand is performed[16]:

$$|\vec{r}_< + \vec{r}_>|^{-(l+1)} Y_{lm}(\vec{r}_< + \vec{r}_>) = \sum_{l'=0}^{\infty} \sum_{m'=-l'}^{l'} (-1)^{l'+m'} a_{lm;l'm'} r_<^{l'} Y_{l'm'}(\vec{r}_<) r_>^{-(l+l'+1)} Y_{l+l',m-m'}(\vec{r}_>) , \tag{6}$$

$$a_{lm;l'm'} = \left[4\pi \frac{2l+1}{(2l+2l'+1)(2l'+1)} \frac{(l+l'+m-m')!(l+l'-m+m')!}{(l'+m')!(l'-m')!(l+m)!(l-m)!} \right]^{1/2} , \tag{7}$$

and $|\vec{r}_<| < |\vec{r}_>|$.

As $|\vec{r}_j| < |\vec{R}_{ij}|$ is always valid because of rule 1(c) above, this leads to

$$V_{lm}^{i} = \sum_{j \neq i} \sum_{l',m'} (-1)^{l'+m'} Q_{l'm'}^{j} a_{l'm';lm} |\vec{R}_{ij}|^{-(l+l'+1)} \times Y_{l+l',m-m'}(\vec{R}_{ij}) . \tag{8}$$

Q_{lm}^{j} is the multipole moment of the charge distribution in region Ω_j relative to the reference point $\vec{R}_j$ and defined as

$$Q_{lm}^{j} = \frac{4\pi}{2l+1} \int_{\Omega_j} \rho^{j}(\vec{r}_j) r_j^{l} Y_{lm}(\vec{r}_j) d^3 r_j . \tag{9}$$

Thus, the determination of the expansion coefficients V_{lm}^{i} is reduced to the calculation of multipole moments for the different spatial regions[15] and the evaluation of a lattice sum (8).

III. SPACE-GROUP SYMMETRY AND *K* FACTORS

The evaluation of the lattice sum (8) can be considerably simplified if the full space-group symmetry of the crystal is taken into account. In order to apply symmetry considerations, it is essential to impose another constraint on the choice of regions Ω_i:

1(d) The shape of the surfaces of regions Ω_i must be invariant under the space-group operations.

For the identification of a point $\vec{R}_i$, the following notations are used:

2(a) Subscripts μ,ν refer to the point position.

2(b) M_μ is the multiplicity of μ.

2(c) Subscripts i,j number all equivalent points belonging to a given position ($i_\mu = 1, \ldots, M_\mu$).

2(d) $\vec{T}_\lambda$ gives the position of some reference point in the unit cell λ.

2(e) $\vec{\tau}$ is a vector relative to this reference point. point.

Following these rules, any vector of a fixed position is given by $\vec{T}_\lambda + \vec{\tau}_{i_\mu}$ and (8) is now written as

$$V_{lm}^{i_\mu} = \sum_{\nu} \sum_{j_\nu=1}^{M_\nu} \sum_{l'} \sum_{m'=-l'}^{l'} Q_{l'm'}^{j_\nu} (-1)^{l'+m'} a_{l'm';lm} \times S_{l+l',m-m'}(\vec{\tau}_{i_\mu,j_\nu}) \tag{10}$$

($\vec{\tau}_{i_\mu,j_\nu} = \vec{\tau}_{j_\nu} - \vec{\tau}_{i_\mu}$). Here, a notation is used which is similar to that of Nijboer and De Wette[17] for lattice sums of the type

$$S_{lm}(\vec{\tau}) = \sum_{\lambda}{}' |\vec{T}_\lambda + \vec{\tau}|^{-(l+1)} Y_{lm}(\vec{T}_\lambda + \vec{\tau}) \tag{11}$$

where $\sum'$ indicates that in the case $\vec{\tau} = 0$ the term with $\vec{T}_\lambda = 0$ is excluded. If the lattice is not primitive, (11) includes also a sum over the face-centered or body-centered points.

As the potential is invariant under the operations of the space group G of the crystal, it is suitable to use invariant combinations of spherical harmonics in the potential expansion instead of ordinary spherical harmonics. Their determination is described in Appendix B. For position μ, these invariant combinations are given by

$$\mathcal{Y}_{l,n}^{\mu}(\vec{r}) = \sum_{i_\mu=1}^{M_\mu} \sum_{m=-l}^{l} d_{n,m}^{l}(i_\mu) Y_{lm}(\vec{r}_{i_\mu}) \tag{12}$$

$$(n = 1, \ldots, N_\mu^l ;\ N_\mu^l \leq 2l+1) .$$

n distinguishes between the N_μ^l different invariant combinations for the same value of l. The functions

$$\mathcal{Y}_{l,n}^{i_\mu}(\vec{r}_{i_\mu}) = \sum_{m=-l}^{l} d_{n,m}^{l}(i_\mu) Y_{lm}(\vec{r}_{i\mu}) \tag{13}$$

with the same coefficients $d_{n,m}^{l}(i_\mu)$ as in (12) are now invariant under the operations of the point group G_μ of position μ.

When expanded in invariant combinations of spherical harmonics, the potential $V^{i_\mu}(\vec{r}_{i_\mu})$ has the form

$$V^{i_\mu}(\vec{r}_{i_\mu}) = V_0^{i_\mu}(\vec{r}_{i_\mu}) + \sum_l \sum_{n=1}^{N_\mu^l} \mathscr{V}_{l,n}^{\mu *} r_{i_\mu}^l \mathscr{Y}_{l,n}^{i_\mu}(\vec{r}_{i_\mu}) \tag{14}$$

where the coefficients $\mathscr{V}_{l,n}^{\mu}$ are now independent of a particular choice of an equivalent point i_μ. Comparison with (2) gives

$$V_{l,m}^{i_\mu} = \sum_{n=1}^{N_\mu^l} \mathscr{V}_{l,n}^{\mu} d_{n,m}^{l*}(i_\mu) \,. \tag{15}$$

Using the orthogonality condition (B12), one obtains

$$\mathscr{V}_{l,n}^{\mu} = \sum_{m=-l}^{l} d_{n,m}^{l}(i_\mu) V_{l,m}^{i_\mu} \tag{16}$$

which is valid for all i_μ. Therefore, it is sufficient to calculate $V_{lm}^{i_\mu}$ just for one of the equivalent points, say 1_μ (see also Appendix C).

Now, symmetrized multipole moments $\mathscr{Q}_{l,n}^{\mu}$ can be introduced instead of $Q_{lm}^{i_\mu}$:

$$\mathscr{Q}_{l,n}^{\mu} = \frac{4\pi}{2l+1} \int_{\Omega_{1_\mu}} \rho^{1_\mu}(\vec{r}_{1_\mu}) r_{1_\mu}^l \mathscr{Y}_{l,n}^{1_\mu}(\vec{r}_{1_\mu}) d^3 r \,. \tag{17}$$

As the charge density $\rho(\vec{r})$ and the shape of regions Ω_{i_μ} are invariant under the space-group operations [rule 1(d)], these are the only independent quantitites which completely determine all individual multipole moments $Q_{lm}^{i_\mu}$:

$$Q_{lm}^{i_\mu} = \sum_{n=1}^{N_\mu^l} \mathscr{Q}_{l,n}^{\mu} d_{n,m}^{l*}(i_\mu) \,. \tag{18}$$

Equations (16), (10), and (18) lead to a very convenient expression for the expansion coefficients:

$$\mathscr{V}_{l,n}^{\mu} = \sum_{\nu} \sum_{l'} \sum_{n'} K_{\mu,l,n;\nu,l',n'} \mathscr{Q}_{l',n'}^{\nu} \,, \tag{19}$$

$$K_{\mu,l,n;\nu,l',n'} = \sum_{m=-l}^{l} d_{n,m}^{l}(1_\mu) \sum_{j_\nu=1}^{M_\nu} \sum_{m'=-l'}^{l'} d_{n',m'}^{e'*}(j_\nu)(-1)^{l'+m'} a_{l'm';lm} S_{l+l',m-m'}(\vec{\tau}_{1_\mu,j_\nu}) \,. \tag{20}$$

The K factors $K_{\mu,l,n;\nu,l',n'}$ relate the n'th independent component of the multipole of order $2^{l'}$ at all equivalent points of position ν, to the nth independent expansion coefficient of order l for the potential in any of the equivalent regions Ω_{i_μ} of position μ. The great advantage of expression (19) is that the K factors are fully determined by the crystal structure and do not depend on the charge distribution. They can be tabulated for any particular structure and allow for an analytic expression for the potential in different spatial regions if only the multipole moments are known up to sufficiently high order.

IV. CALCULATION OF *K* FACTORS

The main problem in the calculation of the K factors is the evaluation of the lattice sums (11):

$$S_{l,m}(\vec{\tau}) = \sum_{\lambda}{}' |\vec{T}_\lambda + \vec{\tau}|^{-(l+1)} Y_{lm}(\vec{T}_\lambda + \vec{\tau}) \,. \tag{11}$$

For a detailed mathematical discussion of this problem the reader is referred to Tosi.[7]

It is well known that the sum (11) is absolutely convergent only for $l > 2$, whereas it is conditionally convergent in the case $l = 2$ and divergent for $l < 2$. Therefore, the insertion of the sum (11) into the expression for the K factors (20) is meaningless in the cases $l + l' < 2$. In these cases, however, an absolutely convergent expression for $S_{l,m}$ can be obtained if one starts from the Ewald series[7] for the potential of a set of point charges $q^\nu = Q_{0,0}^{\nu}/\sqrt{4\pi}$ at the equivalent positions j_ν of point position ν which fulfill the neutrality requirement $\sum_\nu M_\nu q^\nu = 0$:

$$
{}^{p}V^{i_\mu}(\vec{\mathrm{r}}_{i_\mu})=\sum_{\nu} q^{\nu}\sum_{j_\nu=1}^{M_\nu}\sum_{\lambda}{}'\frac{\Gamma(\frac{1}{2},\pi\,|\vec{\mathrm{T}}_\lambda+\vec{\tau}_{j_\nu}-\vec{\tau}_{i_\mu}|^{2}/a_0^{2})}{\Gamma(\frac{1}{2},0)}\,|\vec{\mathrm{T}}_\lambda+\vec{\tau}_{j_\nu}-\vec{\tau}_{i_\mu}|^{-1}-2q^{\mu}/a_0
$$

$$
+\frac{1}{\pi\Omega_0}\sum_{\lambda}{}'G(\vec{\mathrm{K}}_\lambda)\,|\vec{\mathrm{K}}_\lambda|^{-2}\exp(-\pi a_0^{2}\,|\vec{\mathrm{K}}_\lambda|^{2}+2\pi i\vec{\mathrm{K}}_\lambda\cdot\vec{\mathrm{r}}_{i_\mu}) \tag{21}
$$

Here, the superscript p indicates that only the point charge contribution to the potential is considered. Ω_0 is the volume of the unit cell, $\vec{\mathrm{K}}_\lambda$ are vectors in the reciprocal lattice, Γ is the incomplete gamma function

$$
\Gamma(n,x)=\int_x^{\infty} e^{-t}t^{n-1}dt\ , \tag{22}
$$

and $G(\vec{\mathrm{K}})$ is the structure factor of the unit cell

$$
G(\vec{\mathrm{K}})=\sum_{\nu} q^{\nu}\sum_{j_\nu=1}^{M_\nu}\exp[-2\pi i\vec{\mathrm{K}}\cdot(\vec{\tau}_{j_\nu}-\vec{\tau}_{i_\mu})]\ . \tag{23}
$$

a_0 is the length unit chosen for the sums (21). To achieve approximately the same rate of convergence for the sums both over the real and reciprocal lattice, a_0 has to be chosen such that $a_0=\Omega_0^{1/3}$. In the sum over the reciprocal lattice, the term with $\vec{\mathrm{K}}_\lambda=0$ is absent because of the charge neutrality of the unit cell.

Now, ${}^{p}V_{0,0}^{i_\mu}=\sqrt{4\pi}\,{}^{p}V^{i_\mu}(0)$ and the ${}^{p}V_{1,m}^{i_\mu}$ are related to $\vec{\nabla}\,{}^{p}V^{i_\mu}(\vec{\mathrm{r}}_{i_\mu})\,|_{r_{i_\mu}=0}$. Forming the gradient of (21) and rearranging the order of summations as in (19) and (20), one finally arrives at the following expression for S_{lm} with $l<2$:

$$
S_{lm}(\vec{\tau})=[\Gamma(l+\tfrac{1}{2},0)]^{-1}\Bigg[\sum_{\lambda}{}'\Gamma(l+\tfrac{1}{2},\pi\,|\vec{\mathrm{T}}_\lambda+\vec{\tau}|^{2}/a_0^{2})\,|\vec{\mathrm{T}}_\lambda+\vec{\tau}|^{-(l+1)}Y_{lm}(\vec{\mathrm{T}}_\lambda+\vec{\tau})-\delta_{l,0}\delta_{|\tau|,0}2/a_0
$$

$$
+i^{l}\pi^{l-1/2}\Omega_0^{-1}\sum_{\lambda}{}'\,|\vec{\mathrm{K}}_\lambda|^{l-2}\exp(-2\pi i\vec{\mathrm{K}}_\lambda\cdot\vec{\tau}-\pi a_0^{2}\,|\vec{\mathrm{K}}_\lambda|^{2})Y_{lm}(\vec{\mathrm{K}}_\lambda)\Bigg]\ . \tag{24}
$$

The justification to use this expression for S_{lm} in (20) not only for the case $l'=0,l<2$ but also for the case $l=0,l'<2$, results from a reciprocality relation for the K factors which will be discussed in the next section.

Nijboer and De Wette[17,18] have shown that (24) holds also for the case $l\geq 2$ for the sums (11) if the term with $\vec{\mathrm{K}}_\lambda=0$ is included in the second sum in (24). This term vanishes for $l>2$. For $l=2$ it gives a contribution which depends on how $\vec{\mathrm{K}}_\lambda$ is approaching zero in the reciprocal lattice, or, in the real lattice it depends on the shape of the crystal.[19] For a spherical shape this term vanishes also for $l=2$ and (24) can be used for all values of l.

For $l+l'>2$ it is also possible to obtain the lattice sums by direct summation in the real lattice, since the sums are then absolutely convergent and do not depend on the order of summation. This procedure is often much faster than the use of (24), especially for large values of $l+l'$ or if the unit cell contains many atoms. A detailed discussion of the direct summation has been given by Mathies.[5,6]

Here, a different derivation of the relevant expressions is given and applied to the evaluation of K factors. Comparison of (20) with (10) shows that for fixed ν,l',n' the sums over equivalent points j_ν in (20) correspond to those in (10), but with multipoles of strength $d_{n',m'}^{l'*}(j_\nu)$ at the points j_ν. The idea is now to treat the unit cell as a whole, evaluate its multipole moments $Q_{lm}^{uc}(\nu,l',n';i_\mu)$ as produced by the individual multipole moments $d_{n',m'}^{l'*}(j_\nu)$, with respect to the point $\vec{\tau}_{i_\mu}$, and then sum over all unit cells.

If the sum over the unit cells would start just from the first neighboring shell of unit cells, Q_{lm}^{uc} would have to be calculated to rather high order to achieve convergence. Instead, the expression for the K factors is split into two parts:

$$
K_{\mu,l,n;\nu,l',n'}=K_{\mu,l,n;\nu,l',n'}^{(\lambda_0)}+K_{\mu,l,n;\nu,l',n'}^{[\lambda_0]}\ , \tag{25}
$$

where the first part is obtained by explicit summation over the first λ_0 shells of neighboring unit cells

$$K^{(\lambda_0)}_{\mu,l,n;\nu,l',n'} = \sum_{m=-l}^{l} d^{l}_{n,m}(1_\mu) \sum_{j_\nu=1}^{M_\nu} \sum_{m'=-l'}^{l'} d^{l'*}_{n',m'}(j_\nu)(-1)^{l'+m'} a_{l'm';lm} \sum_{\lambda}^{(\lambda_0)} |\vec{\mathrm{T}}_\lambda + \vec{\tau}_{i_\mu,j_\nu}| \, Y_{lm}(\vec{\mathrm{T}}_\lambda + \vec{\tau}_{i_\mu,j_\nu}) \; . \tag{26}$$

$\sum_\lambda^{(\lambda_0)}$ means that only the first λ_0 neighboring shells of unit cells are included in the sum.

In the second part, the contributions from the multipole moments of the whole unit cell are summed

$$K^{[\lambda_0]}_{\mu,l,n;\nu,l',n'} = \sum_{m=-l}^{l} d^{l}_{n,m}(1_\mu) \sum_{l''=l'}^{\infty} \sum_{m''=-l''}^{l''} Q^{uc}_{l''m''}(\nu,l',n';1_\mu)(-1)^{l''+m''} a_{l''m'';lm} S^{[\lambda_0]}_{l''+l,m-m''}(0) \; . \tag{27}$$

$S^{[\lambda_0]}_{l,m}(0)$ is equivalent to (11) but with the contributions from the first λ_0 shells of neighboring unit cells excluded from the sum

$$S^{[\lambda_0]}_{l,m}(0) = \sum_{\lambda}^{[\lambda_0]} |\vec{\mathrm{T}}_\lambda|^{-(l+1)} Y_{lm}(\vec{\mathrm{T}}_\lambda) \; . \tag{28}$$

These sums run over all points of the periodic lattice and need to be calculated only once for a given lattice type. Furthermore, the symmetry of the lattice reduces the number of independent sums (28) considerably. The multipole moments of the unit cell are given by

$$Q^{uc}_{lm}(\nu,l',n';i_\mu) = \sum_{j_\nu=1}^{M_\nu} \sum_{m'} d^{l'*}_{n',m'}(j_\nu) c_{lm;l'm'} \, |\vec{\tau}_{i_\mu,j_\nu}|^{l-l'} Y_{l-l',m-m'}(\vec{\tau}_{i_\mu,j_\nu}) \tag{29}$$

with

$$c_{lm;l'm'} = \left[4\pi \frac{2l'+1}{(2l+1)(2l-2l'+1)} \frac{(l+m)!(l-m)!}{(l'+m')!(l'-m')!(l-l'+m-m')!(l-l'-m+m')!} \right]^{1/2} ,$$

a relation which can be easily derived from the general expression (9) for the multipole moments and the poly-polar expansion of

$$|\vec{\mathrm{r}}_{j_\nu} + \vec{\tau}_{i_\mu,j_\nu}|^{l} Y_{lm}(\vec{\mathrm{r}}_{j_\nu} + \vec{\tau}_{i_\mu,j_\nu})$$

as given by Steinhorn.[16]

V. RELATIONS BETWEEN *K* FACTORS

The number of *K* factors that have to be determined for a complete description of the potential is considerably reduced because of interrelations among different *K* factors which will be derived in the following. Three different kinds of such relations can be distinguished:

(a) relations between *K* factors for the same structure,

(b) relations between *K* factors for different structures, and

(c) relations between *K* factors that refer to different sets of invariant spherical harmonics.

Relations (a) and (b) can be derived from the following expression for the *K* factors:

$$K_{\mu,l,n;\nu,l',n'} = \frac{1}{M_\mu} \sum_{i_\mu=1}^{M_\mu} \sum_{m=-l}^{l} d^{l}_{n,m}(i_\mu) \sum_{j_\nu=1}^{M_\nu} \sum_{m'=-l'}^{l'} d^{l'*}_{n',m'}(j_\nu)(-1)^{l'+m'} a_{l'm';lm} S_{l+l',m-m'}(\vec{\tau}_{i_\mu,j_\nu}) \tag{30}$$

which is equivalent to (20) as the summand does not depend on i_μ and the properties of the lattice sums $S_{l,m}$:

$$\begin{aligned} S_{l,m}(-\vec{\tau}) &= (-1)^l S_{l,m}(\vec{\tau}) \; , \\ S_{l,-m}(\vec{\tau}) &= (-1)^m S^{*}_{l,m}(\vec{\tau}) \; . \end{aligned} \tag{31}$$

(a) For all K factors related to the same structure, a general relation of reciprocity is valid,

$$\text{(I)}\quad M_\mu(2l+1)K_{\mu,l,n;\nu,l',n'} = M_\nu(2l'+1)K^*_{\nu,l',n';\mu,l,n}\ . \tag{32}$$

If the point groups of both μ and ν are the point groups isogonal with the space group, then $M_\mu = M_\nu = 1$ and

$$\text{(II)}\quad K_{\mu,l,n;\nu,l',n'} = (-1)^{l+l'} K_{\nu,l,n;\mu,l',n'} \quad (\mu \neq \nu) \tag{33}$$

$$\text{(III)}\quad K_{\mu,l,n;\mu,l',n'} = 0,\quad l+l' \text{ odd}\ . \tag{34}$$

Besides (I)—(III) there are additional relations for special cases which are not quoted here.

(b) K factors that refer to different structures, say A and B, can be related to each other if A and B have the same Bravais lattice with identical dimensions. In this case, the lattice sums $S_{l,m}(\vec{\tau})$ have the same value in both structures:

$$S^A_{l,m}(\tau) = S^B_{l,m}(\vec{\tau})\ .$$

Now let positions μ_A, ν_A of structure A have the same coordinates as positions μ_B, ν_B of structure B. Then, for all values l, l' which have the same invariant combinations of spherical harmonics in both structures ($\mathscr{Y}^{\mu_A}_{l,n} = \mathscr{Y}^{\mu_B}_{l,n}; \mathscr{Y}^{\nu_A}_{l',n'} = \mathscr{Y}^{\nu_B}_{l',n'}$), the K factors are the same in both structures:

$$\text{(IV)}\quad K^A_{\mu_A,l,n;\nu_A,l',n'} = K^B_{\mu_B,l,n;\nu_B,l',n'}\ . \tag{35}$$

(c) The third set of relations concerns transformations in the set of invariant combinations of spherical harmonics. Let such a transformation be

$$\mathscr{Y}^\mu_{l,n} = \sum_{\bar{n}} a^l_{n,\bar{n}}(\mu)\hat{\mathscr{Y}}^\mu_{l,\bar{n}}\ . \tag{36}$$

The new functions $\hat{\mathscr{Y}}^\mu_{l,n}$ are orthonormal in the sense of (B4) if the transformation matrices $\underline{A}$ with elements $A_{n,\bar{n}} = a^l_{n,\bar{n}}(\mu)$ are unitary, $\underline{A}^{-1} = \underline{A}^+$.

Transformation (36) transforms also the invariant multipole components

$$\mathscr{Q}^\mu_{l,n} = \sum_{\bar{n}} a^l_{n,\bar{n}}(\mu)\hat{\mathscr{Q}}^\mu_{l,\bar{n}}\ . \tag{37}$$

Then $K_{\mu,l,n;\nu,l',n'}$, which refer to the sets $\mathscr{Y}^\mu_{l,n}$ and $\mathscr{Q}^\mu_{l,n}$, are transformed to $\hat{K}_{\mu,l,n;\nu,l',n'}$, which refer to the sets $\hat{\mathscr{Y}}^\mu_{l,n}$ and $\hat{\mathscr{Q}}^\mu_{l,n}$, by

$$\hat{K}_{\mu,l,n;\nu,l',n'} = \sum_{\bar{n}}\sum_{\bar{n}'} a^{l*}_{\bar{n},n}(\mu) K_{\mu,l,\bar{n};\nu,l',\bar{n}'} a^{l'}_{\bar{n}',n'}(\nu)\ . \tag{38}$$

An example for such a transformation is that from complex to real spherical harmonics and vice versa, the transformation matrices of which can be easily derived from relations (A1)—(A4).

TABLE I. Representative points for different positions for which coefficients of invariant functions are given in Table II.

Space group \ Point group	$Pm3m$	$Fm3m$	$F\bar{4}3m$
$m3m$	$1a\,(0,0,0)$ $1b\,(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	$4a\,(0,0,0)$ $4b\,(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	
$\bar{4}3m$		$8c\,(\frac{1}{4},\frac{1}{4},\frac{1}{4})$	$4a\,(0,0,0)$ $4c\,(\frac{1}{4},\frac{1}{4},\frac{1}{4})$
$4/mmm$	$3c\,(\frac{1}{2},\frac{1}{2},0)$		

TABLE II. Coefficients $\bar{d}^{\,l}_{n,m}(i_\mu)$ of real spherical harmonics $\bar{Y}_{lm}(\vec{r}_{i_\mu})$ in invariant combinations $\bar{\mathscr{Y}}^\mu_{l,n}$. Coefficients are only given for the representative points of Table I.

$m3m$		
l \ m	0	4
0	1	
4	$\sqrt{7/12}$	$\sqrt{5/12}$
6	$-\sqrt{1/8}$	$\sqrt{7/8}$

$\bar{4}3m$			
l \ m	-2	0	4
0		1	
3	1		
4		$\sqrt{7/12}$	$\sqrt{5/12}$
6		$-\sqrt{1/8}$	$\sqrt{7/8}$

$4/mmm$			
l	n \ m	0	4
0		1	
2		1	
4	1	$\sqrt{9/44}$	$\sqrt{35/44}$
4	2	$-\sqrt{35/44}$	$\sqrt{9/44}$
6	1	$-\sqrt{25/88}$	$-\sqrt{63/88}$
6	2	$-\sqrt{63/88}$	$\sqrt{25/88}$

TABLE III. Independent K factors, $\bar{K}_{\mu,l,n;\nu,l',n'} \times a_0^{l+l'+1}$, for space group $Pm3m$. The numbers in brackets give the power of ten.

		μ:1a;ν:1a/μ:1b;ν:1b	
	l' 0	4	6
l			
0	−1.837 297(0)	1.220 887(1)	−5.846 834(0)
4		2.607 434(2)	−3.773 148(2)
6			1.091 675(3)

		μ:1a;ν:1b	
	l' 0	4	6
l			
0	1.980 640(−1)	−2.441 081(1)	−4.969 736(1)
4		3.511 278(2)	3.890 408(3)
6			1.567 999(4)

				ν:3c			
	l'	0	2	4	4	6	6
	n'			1	2	1	2
l	n						
				μ:1a			
0		1.252 435(0)	−2.907 245(1)	−1.018 142(2)	−1.336 294(2)	−1.127 820(2)	2.625 726(2)
4		−4.641 022(0)	−1.730 983(2)	7.215 516(3)	1.059 147(3)	1.392 969(4)	1.171 726(4)
6		2.134 391(1)	−1.768 711(3)	−1.528 077(4)	−3.784 559(4)	−1.693 074(5)	3.877 591(5)
				μ:1b			
0		2.712 203(0)	1.008 982(2)	2.708 592(2)	−5.013 696(2)	−1.496 224(3)	−2.347 401(3)
4		4.940 612(1)	6.605 869(3)	7.604 583(4)	−1.454 243(5)	−1.317 021(6)	−1.969 847(6)
6		−7.464 007(1)	−1.888 895(4)	−2.857 158(5)	7.061 800(5)	5.991 456(6)	1.520 299(7)
				μ:3c			
0		−1.002 341(0)	9.690 818(0)	6.709 101(0)	5.604 949(1)	−1.262 013(2)	1.291 566(2)
2			1.799 656(2)	2.648 139(1)	−2.041 521(2)	9.764 758(2)	2.659 716(3)
4	1			3.487 573(3)	−9.376 738(2)	−1.128 750(4)	1.348 516(3)
4	2				5.182 975(3)	−1.389 953(4)	1.205 728(4)
6	1					2.893 882(5)	−2.232 725(4)
6	2						2.336 076(5)

VI. *K* FACTORS FOR CUBIC SPACE GROUPS

In cubic structures there is only one lattice constant, a_0. Thus, if the K factors are given in units of a_0, they can be used for any crystal structures of the same space group. As an example, tables of K factors (Tables I–V) are presented for space groups $Pm3m$, $Fm3m$, and $F\bar{4}3m$, including the point positions $1a,1b,3c$ of $Pm3m$, $4a,4b,8c$ of $Fm3m$, and $4a$,$4c$ of $F\bar{4}3m$. These cases comprise all crystal structures of, e.g., CsCl-type, perovskite ($CaTiO_3$)-type, NaCl-type, fluorite (CaF_2)-type, and zinc-blende (ZnS)-type compounds. All tables are based on real spherical harmonics. For complex spherical harmonics they can be simply transformed using Eqs. (36)–(38) with (A3) and (A4).

Only independent K factors are listed. All others can be obtained from the relations (32)–(34) and an additional relation

$$\bar{K}_{4a,l,n;8c,l',n'} = (-1)^{l+l'} \bar{K}_{4b,l,n;8c,l',n'}$$

valid for the K factors that refer to space group $Fm3m$. For the zinc-blende structure (space group $F\bar{4}3m$) the K factors may be compared with similar factors, recently calculated by Szmulowicz[20] for use in APW calculations on the basis of Rudge's

TABLE IV. Independent K factors, $\bar{K}_{\mu,l,n;\nu,l',n'}\times a_0^{l+l'+1}$, for space group $Fm3m$.

l \ l'	μ:4a ; ν:4a / μ:4b ; ν:4b 0	4	6
0	−5.848 621(−1)	−2.956 033(1)	2.716 237(2)
4		6.494 916(3)	5.699 014(2)
6			4.125 126(5)

l \ l'	μ:4a ; ν:4b 0	4	6
0	2.910 267(0)	4.202 442(2)	−1.020 018(3)
4		1.270 057(5)	−7.733 107(5)
6			8.530 487(6)

l \ l'	0	ν:8c 3	4	6
		μ:4a		
0	6.396 128(0)	−4.197 781(2)	−7.811 458(2)	−6.361 262(3)
4	−8.679 398(1)	8.561 073(4)	1.797 774(5)	7.967 556(6)
6	−4.893 278(2)	9.115 007(5)	5.516 000(6)	1.284 504(8)
		μ:8c		
0	2.325 405(0)	0.0	3.906 839(2)	−7.483 948(2)
3		6.079 485(3)	0.0	0.0
4			1.335 006(5)	−7.727 408(5)
6				8.943 000(6)

method.[13] The factors $A_{ln\nu}^{l'n'\nu'}$ of Ref. 20 for $l,l'\neq 0$ can be related to the K factors $K_{\nu,l,n;\nu' l' n'}$ by

$$K_{\nu,l,n;\nu',l',n'}=2^{l+l'+1}(2l'+1)A_{ln\nu}^{l'n'\nu'} .$$

Considering this relation and the slightly different definition of invariant spherical harmonics used by Szmulowicz, complete agreement is found between the two different approaches for the factors with

TABLE V. Independent K factors, $\bar{K}_{\mu,l,n;\nu,l',n'}\times a_0^{l+l'+1}$, for space group $F\bar{4}3m$.

l \ l'	0	μ:4a ; ν:4a / μ:4c ; ν:4c 3	4	6
0	−5.848 621(−1)	0.0	−2.956 033(1)	2.716 237(2)
3		1.278 475(3)	0.0	0.0
4			6.494 916(3)	5.699 014(2)
6				4.125 126(5)

l \ l'	0	μ:4a ; ν:4c 3	4	6
0	3.198 064(0)	−2.098 890(2)	−3.905 729(2)	−3.180 631(3)
3		−1.497 055(4)	−5.503 547(4)	−8.463 935(5)
4			8.988 872(4)	3.983 778(6)
6				6.422 522(7)

TABLE VI. Potential expansion coefficients $\overline{\mathscr{V}}_{l,n}^{\mu}$ for different crystal classes with cubic Bravais lattice. The entries give $\overline{\mathscr{V}}_{l,n}^{\mu}\times a_0^{l+1}$ where a_0 is the lattice constant and μ the position given in the second column. The respective invariant spherical harmonics are given in Table II. The numbers in brackets give the power of ten.

			l	0	2	3	4	4	6	6
			n				1	2	1	2
Type		Position	q/e							
$Pm3m$	CsCl	$1a$(Cs)	+1	−7.215 169(0)			1.442 371(1)		1.195 739(1)	
		$1b$(Cl)	−1	7.215 169(0)			−1.442 371(1)		−1.195 739(1)	
	CaTiO$_3$	$1a$(Ca)	+2	−1.909 716(1)			4.062 040(0)		−2.087 198(2)	
		$1b$(Ti)	+4	−4.387 698(1)			−3.502 748(2)		4.957 036(2)	
		$3c$(O)	−2	2.288 560(1)	6.789 753(1)		1.102 274(2)	−3.425 476(2)	−4.956 736(2)	−8.761 736(2)
$Fm3m$	NaCl	$4a$(Na)	+1	−1.238 991(1)			−1.771 684(2)		3.522 117(2)	
		$4b$(Cl)	−1	1.238 991(1)			1.771 684(2)		−3.522 117(2)	
	CaF$_2$	$4a$(Ca)	+2	−2.682 025(1)			2.843 903(2)		1.882 758(3)	
		$8c$(F)	−1	1.443 034(1)		−2.125 821(2)	−4.615 587(2)		−1.530 546(3)	
$F\bar{4}3m$	ZnS	$4a$(Zn)	+2	−2.682 025(1)		−2.125 821(2)	2.843 903(2)		1.882 758(3)	
		$4c$(S)	−2	2.682 025(1)		−2.125 821(2)	−2.843 903(2)		−1.882 758(3)	

$l,l'\neq 0$. For the cases $l=0$ or $l'=0$ Rudge's method[13] uses different expressions resulting from the decomposition of the charge density used in APW calculations and a special normalization of the potential.[14,21] It should be noted that the convergence problems of Rudge's method for $l=l'$ (Ref. 20) do not occur in the method presented here as the lattice sums are obtained by direct summation over the real lattice.

VII. POSSIBLE APPLICATIONS AND DISCUSSION

Expression (14) for the potential together with (19) and tables of K factors considerably simplify the treatment of the Coulomb part of the lattice potential, and can be applied to different problems in solid-state physics. The method is most satisfactory in cases where the multipole decomposition of the charge density is rapidly converging, which is generally the case in ionic crystals. It can, however, also be applied in other cases as the influence of distant charge distributions is mainly determined by its low-order multipoles. In these cases the nearest neighbors should be treated separately.

The most important contribution to the potential in ionic crystals arises from the ionic charges. In Table VI the expansion coefficients for the point-charge contribution to the potential are given for different cubic arrangements, using in each case the formal ionic charges q^{ν}. It should be noted that the definition of the multipole moments Q_{lm}^{ν} is such that $Q_{00}^{\nu}=\sqrt{4\pi}q^{\nu}$. For the NaCl structure the expansion coefficients were previously calculated by De Wette and Nijboer[18] and with higher accuracy by Matthies.[6] The values given in Table VI for NaCl are in full agreement with those obtained by Matthies.

The expression for the lattice potential can be used, for example, in the study of local effects as is done in crystal-field theory where the influence of the lattice potential on the d levels of implanted transition metal ions is investigated. Here, only the terms with $l=0,2,4$ in the series (14) are important, which are the only ones giving nonvanishing matrix elements with d functions. These coefficients describe the influence of the total lattice potential and not only that of next-nearest neighbors to which the considerations of crystal-field theory are usually restricted. Comparison with the corresponding coefficients that include only the potential of next-nearest neighbors, gives an idea of the error inherent in this approximation. For the position $4a$ in the NaCl arrangement, for example, the correct values for the coefficients $\mathscr{V}_0^{\mathrm{Na}}$ and $\mathscr{V}_4^{\mathrm{Na}}$ are $-12.39/a_0$ and $-177.17/a_0^5$, respectively, whereas the restriction to next-nearest neighbors would lead to $-42.54/a_0$ and $-173.28/a_0^5$, respectively.

Let us consider now the calculation of the Coulomb part of the lattice energy. The energy per unit cell is

$$W=\int_{\Omega_0}\rho(\vec{r})V(\vec{r})d^3r \ . \tag{39}$$

With the use of (14), (19), and (17) one obtains

$$W=\sum_{\nu,l,n}\sum_{\nu',l',n'}\frac{M_\nu}{2}\frac{2l+1}{4\pi}\mathscr{Q}_{l,n}^{\nu}K_{\nu,l,n;\nu',l',n'}\mathscr{Q}_{l',n'}^{\nu'} \ . \tag{40}$$

Each summand gives the contribution to the energy from the interaction of multipoles $\mathscr{Q}_{l,n}^{\nu}$ at position ν with $\mathscr{Q}_{l',n'}^{\nu'}$ at position ν'. As this interaction must be the same when the indices are exchanged, the validity of the reciprocality relation (32) can be seen immediately.

For the case when only point charges are considered ($l=l'=0$), the terms $\frac{1}{2}M_\nu K_{\nu,0,1;\nu',0,1}$ are just the Jenkins-Hartman coefficients.[22,23] Inclusion of multipoles of order $l>0$ requires explicit knowledge about the multipoles centered at the different positions. These can be obtained either from electronic wave functions of the crystal or a cluster, or in a semi-empirical way starting from atomic or ionic polarizabilities.[8,9] If the polarizabilities α_l^ν of the ion at position ν and order 2^l are defined through the relation

$$\mathscr{Q}_{l,n}^{\nu}=-\alpha_l^\nu\mathscr{V}_{l,n}^{\nu} \ , \tag{41}$$

one obtains from (19)

$$\sum_{\nu}\sum_{l'}\sum_{n'}(\delta_{\mu,\nu}\delta_{l,l'}\delta_{n,n'}+\alpha_{l'}^{\nu}K_{\mu,l,n;\nu,l',n'})\mathscr{V}_{l',n'}^{\nu} =\sum_{\nu}\mathscr{Q}_{0,1}^{\nu}K_{\mu,l,n;\nu,0,1} \ , \tag{42}$$

which is a system of inhomogeneous linear equations for $\mathscr{V}_{l,n}^{\nu}$ with $l>0$. As the polarizabilities of ions are in many cases strongly dependent on their environment,[24] the α_l^ν can be used as parameters for the reproduction of experimentally known quantities such as electric field gradients (EFG).

The relation between EFG tensors and the expansion coefficients is given by

$$V_{r,s}(0)=\left[\frac{15}{4\pi}\right]^{1/2}\begin{bmatrix} V_{2,2}-V_{2,0}/\sqrt{3} & V_{2,-2} & V_{2,1} \\ V_{2,-2} & -V_{2,2}-V_{2,0}/\sqrt{3} & V_{2,-1} \\ V_{2,1} & V_{2,-1} & 2V_{2,0}/\sqrt{3} \end{bmatrix}, \quad r,s=x,y,z \ .$$

These examples show that the concept of K factors may be helpful in quite different kinds of problems dealing with Coulomb interactions in crystals.[25]

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APPENDIX A: DEFINITIONS OF SPHERICAL HARMONICS

Complex spherical harmonics are defined with Condon-Shortley phase convention[26] as

$$Y_{lm}(\vec{r})=(-1)^{1/2(m+|m|)}\left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} \times P_l^{|m|}(\cos\theta)e^{im\varphi} \ , \tag{A1}$$

where $P_l^m(z)$ is the associated Legendre function. Real spherical harmonics are defined as

$$\bar{Y}_{lm}(\vec{r})=\left[\epsilon_m\frac{2l+1}{4\pi}\frac{(l+|m|)!}{(l-|m|)!}\right]^{1/2} \times P_l^{|m|}(\cos\theta)\cos(m\varphi+\delta_m) \ , \tag{A2}$$

where

$$\epsilon_m=\begin{cases}2, & m\neq 0\\ 1, & m=0\end{cases}$$

$$\delta_m=\begin{cases}0, & m\geq 0\\ \pi/2, & m<0 \ .\end{cases}$$

Real and complex spherical harmonics are related to each other by

$$\bar{Y}_{lm}(\vec{r})=\tfrac{1}{2}\sqrt{\epsilon_m}(-1)^{1/2(m+|m|)} \times[e^{i\delta_m}Y_{lm}(\vec{r})+e^{-i\delta_m}Y_{lm}^*(\vec{r})] \ , \tag{A3}$$

$$Y_{lm}(\vec{\mathrm{r}})=\tfrac{1}{2}\sqrt{\epsilon_m}(-1)^{1/2(m+|m|)}\times[e^{-i\delta_m}\bar{Y}_{lm}(\vec{\mathrm{r}})+e^{i\delta_{-m}}\bar{Y}_{l-m}(\vec{\mathrm{r}})]\ . \tag{A4}$$

APPENDIX B: CONSTRUCTION OF INVARIANT COMBINATIONS OF SPHERICAL HARMONICS

For the construction of invariant combinations $\mathcal{Y}_{l,n}^{\mu}(\vec{\mathrm{r}})$ of spherical harmonics $Y_{lm}(\vec{\mathrm{r}}-\vec{\tau}_{i_\mu})$ centered at the equivalent points i_μ of point position μ, the projection operator ρ^{Γ_1} for the identity representation Γ_1 of space group G is applied to the functions $Y_{lm}(\vec{\mathrm{r}}-\vec{\tau}_{1_\mu})$ centered at one of the equivalent points i_μ, say 1_μ:

$$\rho^{\Gamma_1}Y_{lm}(\vec{\mathrm{r}}-\vec{\tau}_{1_\mu})=\sum_R RY_{lm}(\vec{\mathrm{r}}-\vec{\tau}_{1_\mu})\ , \tag{B1}$$

where the sum is over all operations R of space group G. Thus, one obtains $2l+1$ “vectors”

$$\tilde{\mathcal{Y}}_{l,n}^{\mu}(\vec{\mathrm{r}})=\sum_{i_\mu}\sum_m \tilde{d}^{l}_{n,m}(i_\mu)Y_{lm}(\vec{\mathrm{r}}_{i_\mu})\quad (n=1,\ldots,2l+1)\ . \tag{B2}$$

Now all linearly dependent vectors are eliminated and one is left with N_μ^l linearly independent vectors, which are invariant under all space group operations.

The functions

$$\tilde{\mathcal{Y}}_{l,n}^{i_\mu}(\vec{\mathrm{r}}_{i_\mu})=\sum_m \tilde{d}^{l}_{n,m}(i_\mu)Y_{lm}(\vec{\mathrm{r}}_{i_\mu}) \tag{B3}$$

are now invariant under the operations of the point group of position μ. In addition, as any linear combination of the N_μ^l functions (B2) and (B3) is invariant under the space-group or point-group operations, respectively, such combinations $\mathcal{Y}_{l,n}^{\mu}$ can be chosen that are orthonormal in the sense

$$\int\int \mathcal{Y}_{l,n}^{i_\mu}(\vec{\mathrm{r}}_{i_\mu})\mathcal{Y}_{l',n'}^{i_\mu *}(\vec{\mathrm{r}}_{i_\mu})d\cos\theta_{i_\mu}d\varphi_{i_\mu}=\delta_{n,n'}\ . \tag{B4}$$

If the intended orthonormal functions $\mathcal{Y}_{l,n}^{i_\mu}$ are written as

$$\mathcal{Y}_{l,n}^{i_\mu}=\sum_{n'=1}^{N_\mu^l} b^{l}_{n,n'}(\mu)\tilde{\mathcal{Y}}_{l,n'}^{i_\mu}\ , \tag{B5}$$

(B4) leads to

$$\underline{B}\,\underline{S}\,\underline{B}^{\dagger}=\underline{I}\ . \tag{B6}$$

$\underline{B}$ is the matrix of the coefficients $b^{l}_{n,n'}(\mu)$ which have to be determined, and $\underline{B}^{\dagger}$ is the Hermitian conjugate of $\underline{B}$. $\underline{I}$ is the unit matrix and $\underline{S}$ is the overlap matrix of functions $\tilde{\mathcal{Y}}_{l,n}^{i_\mu}$:

$$S_{n,n'}=\sum_m \tilde{d}^{l}_{n,m}(i_\mu)\tilde{d}^{l*}_{n',m}(i_\mu)\ . \tag{B7}$$

(B6) can be transformed to

$$\underline{B}^{-1}(\underline{B}^{\dagger})^{-1}=\underline{S}\ . \tag{B8}$$

As $\underline{S}$ is Hermitian, a Cholesky decomposition can be performed

$$\underline{S}=\underline{\tilde{S}}\,\underline{\tilde{S}}^{\dagger}\ , \tag{B9}$$

where $\underline{\tilde{S}}$ is a lower triangular matrix ($\tilde{S}_{n,n'}=0$ for $n>n'$). Thus, the matrix $\underline{B}$ is identical to $\underline{\tilde{S}}^{-1}$. Then, if one writes

$$\mathcal{Y}_{l,n}^{\mu}(\vec{\mathrm{r}})=\sum_{i_\mu}\sum_m d^{l}_{n,m}(i_\mu)Y_{lm}(\vec{\mathrm{r}}_{i_\mu})\quad (n=1,\ldots,N_\mu^l)\ , \tag{B10}$$

the coefficients $d^{l}_{n,m}(i_\mu)$ are given by

$$d^{l}_{n,m}(i_\mu)=\sum_{n'=1}^{n}(\tilde{S}^{-1})_{n,n'}\tilde{d}^{l}_{n',m}(i_\mu)\ . \tag{B11}$$

They obey the relation

$$\sum_m d^{l}_{n,m}(i_\mu)d^{l*}_{n',m}(i_\mu)=\delta_{n,n'}\ . \tag{B12}$$

APPENDIX C: CALCULATION OF INDEPENDENT MULTIPOLE COMPONENTS

Equations (16) and (17) were concerned with the problem of calculating independent multipole components $\mathcal{Q}_{l,n}^{\mu}$ and independent expansion coefficients $\mathcal{V}_{l,n}^{\mu}$ from the multipole moments $Q_{lm}^{i_\mu}$ and expansion coefficients $V_{lm}^{i_\mu}$. The orthonormality of the invariant functions $\mathcal{Y}_{l,n}^{\mu}$ led to

$$Q_{lm}^{i_\mu}=\sum_{n=1}^{N_\mu^l}\mathcal{Q}_{l,n}^{\mu}d^{l*}_{n,m}(i_\mu)\ , \tag{C1}$$

$$\mathcal{Q}_{l,n}^{\mu}=\sum_{m=-l}^{l}d^{l}_{n,m}(i_\mu)Q_{lm}^{i_\mu}\ , \tag{C2}$$

and similarly for V_{lm}, where the value of the sum does not depend on the point i_μ chosen. Equation (C2) is, however, not efficient for calculations as the point symmetry of position μ may force various relations between different $Q_{lm}^{i_\mu}$. These show up in linear dependences between different columns of the $N_\mu^l \times (2l+1)$ matrix $\underline{D}$ of coefficients $d_{n,m}^{l*}(i_\mu)$. Only N_μ^l of its columns can be linearly independent.

If one now chooses N_μ^l independent columns $d_{n,m_s}^{l*}(i_\mu)$ $(s=1,\ldots,N_\mu^l)$ and forms from these the $N_\mu^l \times N_\mu^l$ matrix $\hat{\underline{D}}$, the independent components are obtained from

$$\mathscr{D}_{l,n}^{\mu} = \sum_{s=1}^{N_\mu^l} (\hat{D}^{-1})_{n,m_s} Q_{l,m_s}^{i_\mu} \tag{C3}$$

and similarly for $\mathscr{V}_{l,n}^{\mu}$. This expression, in general, requires the evaluation of fewer values of $Q_{lm}^{i_\mu}$ or $V_{lm}^{i_\mu}$ than would be the case in Eq. (C2).

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[25] For readers who want to do their own calculations on this subject, a program is available from the author, which manages all necessary symmetry calculations for any space-group symmetry and evaluates the lattice sums by the method outlined in Sec. IV.

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