JOURNAL OF COMPUTATIONAL PHYSICS **44**, 206–211 (1981)

# Note

# Lattice Sums for Long-Range Interactions Involving Charged Defects in Non-Cubic Ionic Crystals

Analytic expressions are derived for infinite lattice sums involved in the interaction energy of a charged defect with a surrounding non-cubic ionic lattice.

## 1. INTRODUCTION

In recent years the HADES[1] computational procedures devised by Norgett [1–4] have proved to be an invaluable asset in theoretical studies in ionic crystals (see, for example, Mackrodt [5]). The original formulation for cubic systems has now been extended to include lattices of arbitrary symmetry [6, 7] so that a wide variety of ionic and quasi-ionic materials are now amenable to detailed investigation. An important feature of this extension has been the treatment of anisotropic effects in the calculation of lattice relaxation [7]. Norgett's formulation of the problem [2–4] based on the Mott–Littleton method leads to an energy term, $E$, for the long-range interaction of a charge defect with the surrounding lattice of the form

$$E = Q \sum_i{}' q_i(\boldsymbol{\zeta}_i \cdot \mathbf{R}_i)/|\mathbf{R}_i|^3, \tag{1}$$

in which $Q$ is the effective charge of the defect and $q_i$, $\boldsymbol{\zeta}_i$ and $\mathbf{R}_i$ the charge, displacement (relaxation) and distance from the defect, respectively, of the $i$th ion. The restricted sum, $\sum_i'$, is over the outer part of the crystal away from the defect and is evaluated by calculating the complete lattice sum analytically and subtracting the explicit sum for the inner region (see, for example, Norgett [3]). For cubic materials it can be shown that Eq. (1) reduces to

$$E = \frac{1}{2} Q^2 \sum_i{}' K_i q_i/|\mathbf{R}_i|^4, \tag{2}$$

in which $K_i$ is the cubic Mott–Littleton factor. For non-cubic materials on the otherhand, Eq. (1) reduces to the more general form,

$$E = \frac{1}{2} Q^2 \sum_i{}' \sum_{\alpha,\beta} M_i^{\alpha\beta} R_i^{\alpha} R_i^{\beta}/|\mathbf{R}_i|^6, \tag{3}$$

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[1] *H*arwell *A*utomatic *D*efect *E*valuation *S*ystem.

0021-9991/81/110206-06$02.00/0

in which $M_i^{\alpha\beta}$ are the corresponding non-cubic Mott–Littleton constants which are characteristic of the material in question [7]. Expressions for complete lattice sums of the type given in Eq. (2) have been given previously based on extensions of the Ewald procedure (see, for example, Tosi [9]), but not those corresponding to Eq. (3), which arise from the interaction of charged point defects with a surrounding non-cubic lattice. The object of the present work, then, is to provide these expressions. They have been used extensively in recent calculations [6, 7, 10] without reference, and may find further use in alternative treatments of defective non-cubic lattices.

## 2. LATTICE SUMS

We begin by considering the complete lattice sum for cubic materials, viz., $\sum_i q_i/|\mathbf{R}_i|^4$, for the derivation of the analytic form contains the salient feature of the more general case. Following Epstein (see, for example, [9]), we consider the expression

$$S_4(\mathbf{r}) = \sum_{i}^{\substack{\text{all lattice}\\ \text{ions}}} 1/|\mathbf{r}-\mathbf{R}_i|^4 \qquad (\mathbf{r} \neq \mathbf{R}_i) \tag{4}$$

together with the identity

$$t^{-2} = \int_0^\infty a \exp(-ta)\, da, \tag{5}$$

from which we can write

$$S_4(\mathbf{r}) = \int_0^{\omega^2} a\, da \sum_i \exp(-|\mathbf{r}-\mathbf{R}_i|^2 a) + \sum_i \int_{\omega^2}^\infty a \exp(-|\mathbf{r}-\mathbf{R}_i|^2 a)\, da \tag{6}$$

$$= S_4^R(\mathbf{r}) + S_4^D(\mathbf{r}). \tag{7}$$

Expanding the Gaussian function, $\sum_i \exp(-|\mathbf{r}-\mathbf{R}_i|^2 a)$, as a reciprocal lattice sum of the form

$$1/v_c(\pi/a)^{3/2} \sum_{\mathbf{g}} S(\mathbf{g}) \exp(-\pi^2 |\mathbf{g}|^2/a + 2\pi i \mathbf{g}\cdot\mathbf{r}),$$

in which the structure factor, $S(\mathbf{g})$, is given by

$$S(\mathbf{g}) = \sum_{\alpha}^{\substack{\text{ions in}\\ \text{unit cell}}} \exp(2\pi i \mathbf{g}\cdot\mathbf{R}_\alpha), \tag{8}$$

$S_4^R(\mathbf{r})$ reduces after some manipulation to

$$S_4^R(\mathbf{r}) = (2\omega\pi^{3/2}/v_c)\sum_{\mathbf{g}} S(\mathbf{g})\exp(2\pi i\mathbf{g}\cdot\mathbf{r}) \times \{\exp(-\pi^2|\mathbf{g}|^2/\omega^2) - (\pi^{3/2}|\mathbf{g}|/\omega)\operatorname{erfc}(\pi|\mathbf{g}|/\omega)\}. \tag{9}$$

$S_4^D(\mathbf{r})$, on the other hand, can be integrated directly to give

$$S_4^D(\mathbf{r}) = \sum_i \{1 + \omega^2|\mathbf{r}_i - \mathbf{R}_i|^2\}\exp(-|\mathbf{r} - \mathbf{R}_i|^2\omega^2)/|\mathbf{r} - \mathbf{R}_i|^4. \tag{10}$$

The term corresponding to $|\mathbf{g}| = 0$ in Eq. (9) reduces to $2\omega\pi^{3/2}/v_c$, in which $v_c$ is the unit cell volume. This expression for $S_4(\mathbf{r})$ is well known and has been discussed by Norgett [2], for example. A particular advantage of separating expressions such as $S_4(\mathbf{r})$ into a reciprocal lattice sum and a direct sum is that the former usually involves only a few lattice vectors which are easily calculated, while the latter is highly local, and for the most part need be carried out for only a small number of ions surrounding the point, $\mathbf{r}$.

Turning now to the more general expression of Eq. (3), we consider first the van der Waals interaction of an atom or ion at the point, $\mathbf{r}$, with the surrounding lattice. This is important both in its own right and as a useful starting point for lattice sums involving long-range interactions in non-cubic fields. From the general identity,

$$n!/t^{n+1} = \int_0^\infty a^n \exp(-ta)\, da, \tag{11}$$

we can write the appropriate lattice sum, $S_6(\mathbf{r})$, as

$$S_6(\mathbf{r}) = \sum_i 1/|\mathbf{r} - \mathbf{R}_i|^6 \tag{12}$$

$$= \frac{1}{2}\left\{\int_0^{\omega^2} da\, a^2 \sum_i \exp(-|\mathbf{r} - \mathbf{R}_i|^2 a) + \sum_i \int_{\omega^2}^\infty da\, a^2 \exp(-|\mathbf{r} - \mathbf{R}_i|^2 a)\right\} \tag{13}$$

$$= S_6^R(\mathbf{r}) + S_6^D\mathbf{r}). \tag{14}$$

As before, the direct sum, $S_6^D(\mathbf{r})$, can be integrated directly to give

$$S_6^D(\mathbf{r}) = \sum_i \left\{1 + \omega^2|\mathbf{r} - \mathbf{R}_i|^2 + \frac{1}{2}\omega^4|\mathbf{r} - \mathbf{R}_i|^4\right\} \times \exp(-|\mathbf{r} - \mathbf{R}_i|^2\omega^2)/|\mathbf{r} - \mathbf{R}_i|^6, \tag{15}$$

while the reciprocal lattice term, $S_6^R(\mathbf{r})$, takes the form

$$S_6^R(\mathbf{r}) = (\pi^{3/2}/2v_c) \sum_{\mathbf{g}} S(\mathbf{g}) \exp(2\pi i \mathbf{g} \cdot r) \int_0^{\omega^2} da\, a^{1/2} \exp(-\pi^2 |\mathbf{g}|^2/a), \tag{16}$$

which reduces to

$$S_6^R(\mathbf{r}) = (\omega \pi^{3/2}/3v_c) \sum_{\mathbf{g}} S(\mathbf{g}) \exp(2\pi i g \cdot \mathbf{r}) \{(\omega^2 - 2\pi^2 |\mathbf{g}|^2) \times \exp(-\pi^2 |\mathbf{g}|^2/\omega^2) - (\pi^{3/2} |\mathbf{g}|/\omega) \operatorname{erfc}(\pi |\mathbf{g}|/\omega)\}. \tag{17}$$

Combining Eqs. (15) and (17), therefore, we have an analytic expression for the energy of a van der Waals lattice.

Now the general expression of Eq. (3) contains two distinct types of sum, viz., $\sum_i z_i^2/|\mathbf{R}_i|^6$ (with $x_i^2$ and $y_i^2$) and $\sum_i x_i z_i/|\mathbf{R}_i|^6$ (with $y_i z_i$, etc.). Once again we consider the general expression for the first type of sum,

$$S_{zz;6}(\mathbf{r}) = \sum_i (z - z_i)^2/|\mathbf{r} - \mathbf{R}_i|^6, \tag{18}$$

which we write as

$$S_{zz;6}(\mathbf{r}) = \frac{1}{2} \left\{ \int_0^{\omega^2} da\, a^2 \sum_i (z - z_i)^2 \exp(-|\mathbf{r} - \mathbf{R}_i|^2 a) + \sum_i (z - z_i)^2 \int_{\omega^2}^{\infty} da\, a^2 \exp(-|\mathbf{r} - \mathbf{R}_i|^2 a) \right\} \tag{19}$$

$$= S_{zz;6}^R(\mathbf{r}) + S_{zz;6}^S(\mathbf{r}). \tag{20}$$

$S_{zz;6}^D(\mathbf{r})$ can be integrated by parts to give

$$S_{zz;6}^D(\mathbf{r}) = \sum_i (z - z_i)^2 \left\{ 1 + \omega^2 |\mathbf{r} - \mathbf{R}_i|^2 + \frac{1}{2} \omega^4 |\mathbf{r} - \mathbf{R}_i|^4 \right\} \times \exp(-|\mathbf{r} - \mathbf{R}_i|^2 \omega^2)/|\mathbf{r} - \mathbf{R}_i|^6, \tag{21}$$

in which the lattice sum, as before, includes only a small number of ions around the point, **r**.

The reciprocal lattice term, $S_{zz;6}^R(\mathbf{r})$ is somewhat more troublesome. We begin by considering the Fourier expansion for the expression

$$F_{zz}(\mathbf{r}) = \sum_i^{\substack{\text{all lattice} \\ \text{ions}}} (z - z_i)^2 \exp(-|\mathbf{r} - \mathbf{R}_i|^2 \omega^2). \tag{22}$$

In the usual way we write

$$F_{zz}(\mathbf{r}) = 1/v_c \sum_{\mathbf{g}} f_{zz}(\mathbf{g}) \exp(2\pi i \mathbf{g} \cdot r) \tag{23}$$

and

$$\begin{aligned} f_{zz}(\mathbf{g}) &= \int_{\text{unit cell}} d^3\mathbf{r}\, F_{zz}(\mathbf{r}) \exp(-2\pi i \mathbf{g} \cdot r) \\ &= S(\mathbf{g}) \int_{\text{all space}} d^3\mathbf{r}\, z^2 \exp(-\omega^2 r^2 - 2\pi i \mathbf{g} \cdot r) && (25) \\ &= S(\mathbf{g}) f'_{zz}(\mathbf{g}). && (26) \end{aligned}$$

Transforming to cylindrical co-ordinates, $z$, $\rho$ and $\Phi$, it can be shown after some manipulation that the Fourier coefficients, $f'_{zz}(\mathbf{g})$, are given by

$$f'_{zz}(\mathbf{g}) = \tfrac{1}{2}\pi^{3/2}\omega^{-7}(\omega^2 - 2\pi^2 |\mathbf{g}|^2 \cos^2 \alpha) \exp(-\pi^2 |\mathbf{g}|^2/\omega^2), \tag{27}$$

in which $\alpha$ is the polar angle of the reciprocal lattice vector $\mathbf{g}$, i.e.,

$$\cos \alpha = g_z/\mathbf{g}. \tag{28}$$

Thus, $S^R_{zz;6}(\mathbf{r})$ is given by

$$S^R_{zz;6}(\mathbf{r}) = (\pi^{3/2}/4v_c) \sum_{\mathbf{g}} S(\mathbf{g}) \int_0^{\omega^2} da\, a^{-3/2}(a - 2\pi^2 |\mathbf{g}|^2 \cos^2 \alpha) \exp(-\pi^2 |\mathbf{g}|^2/a), \tag{29}$$

which after further manipulation can be shown to reduce to the form

$$\begin{aligned} S^R_{zz;6}(\mathbf{r}) = (\omega\pi^{3/2}/2v_c) \sum_{\mathbf{g}} S(\mathbf{g}) \{&\exp(-\pi^2 |\mathbf{g}|^2/\omega^2) \\ &- [\pi^{3/2} |\mathbf{g}|\, (1 + \cos^2 \alpha)/\omega] \operatorname{erfc}(\pi |\mathbf{g}|/\omega)\}. \end{aligned} \tag{30}$$

The term corresponding to $|\mathbf{g}| = 0$ reduces to $\omega\pi^{3/2}/2v_c$. Similiar expressions hold for $S^R_{xx;6}(\mathbf{r})$ and $S^R_{yy;6}(\mathbf{r})$ with

$$\cos \beta = g_\nu/\mathbf{g}, \qquad \nu = x, y, \tag{31}$$

in place of $\cos \alpha$ in Eqs. (29) and (30).

Cross terms such as $\sum_i x_i z_i/|\mathbf{R}_i|^6$ can be treated in much the same way. Thus, the direct lattice terms, $S^D_{xz;6}(\mathbf{r})$, etc., are given immediately by

$$\begin{aligned} S^D_{xz;6}(\mathbf{r}) = \sum_i (x - x_i)(z - z_i) &\left\{1 + \omega^2 |\mathbf{r} - \mathbf{R}_i|^2 + \frac{1}{2}\omega^4 |\mathbf{r} - \mathbf{R}_i|^4\right\} \\ &\cdot \exp(-|\mathbf{r} - \mathbf{R}_i|^2 \omega^2)/|\mathbf{r} - \mathbf{R}_i|^6, \qquad \text{etc.} \end{aligned} \tag{32}$$

The Fourier coefficients $f'_{xz}(\mathbf{g})$, etc., can be shown to take the form

$$f'_{xz}(\mathbf{g}) = -(\pi^{1/2}/\omega)^7 \, |\mathbf{g}|^2 \sin\alpha \cos\alpha \exp(-\pi^2 |\mathbf{g}|^2/\omega^2), \tag{33}$$

from which the reciprocal lattice term is finally given by

$$S^R_{xz;6}(\mathbf{r}) = -(\omega\pi^{3/2}/2v_c) \sum_{\mathbf{g}} S(\mathbf{g})(\pi^{3/2} |\mathbf{g}|/\omega) \sin\alpha \cos\alpha \operatorname{erfc}(\pi |\mathbf{g}|/\omega), \tag{34}$$

and likewise for $S^R_{yz;6}(\mathbf{r})$, etc. All cross terms corresponding to $|\mathbf{g}| = 0$ are identically zero.

These expressions have been implemented in HADES and other computational procedures for the calculation of defect energies in non-cubic ionic materials [6, 7, 10].

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RECEIVED: April 27, 1981

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