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A new method for the evaluation of lattice dynamical Coulomb sums

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Abstract. In modelling ionic crystals with the rigid-ion model under the adiabatic and harmonic approximations, the series involving the long-range Coulomb forces appear to be only conditionally convergent. The approach most commonly used to sum these series is the Ewald method, which separates them into two rapidly convergent parts in real and reciprocal space. Instead, the technique described here makes use of infinite sheets of charge to cancel effectively the long-range moments of these forces. The original series can then be rewritten in a form which rapidly converges, but still only in real space. The new method was tested by successfully duplicating Kellermann's model results, which made use of the Ewald method. The new technique is restricted to lattice dynamical problems as opposed to static problems but may be applied to any crystal lattice and incorporated into any lattice dynamical model which also makes use of the harmonic approximation.

1. Introduction

The long-range Coulomb forces in an ionic crystal give rise to sums which are apparently only conditionally convergent in the rigid-ion model [1] of lattice dynamics. The Ewald method [1–3] is the most commonly used to transform these sums into rapidly converging series in both real and reciprocal space. This is achieved by dividing each sum into one which approximates the ions by Gaussian charge distributions, and another which is the difference between this and the point charges of the model. A difficulty is that the terms of these new series are themselves not directly evaluable, as they include the error integral.

A technique is introduced here which allows the sums to be taken only over real space, where the individual terms of the new series can be exactly evaluated and the series is rapidly convergent. Other methods, such as that used in [4], exist, which allow the sums to be taken only in real space. These other methods have not, however, been widely used as they are difficult to work with.

Use is made in the new technique of the fact that, in a dynamical model under the harmonic approximation, only the double derivatives of the potential are involved. An infinite sheet of charge has a potential whose double derivatives are identically zero. It is therefore possible to introduce imaginary sheets of charge into a crystal without affecting the numerical results of a vibrational model calculation.

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Given a plane wave in a crystal, the ions can be naturally ordered into planes. Each plane is defined to consist of similar ions which share the same phase with respect to the wave. An infinite sheet of charge of opposite charge density can be superposed onto each plane of ions. Each ion is then at the centre of an associated section of charge sheets. Such entities have no total charge and no dipole moment. The sums now only involve quadrupole fields, which are short range. This allows the sums to converge and is the basis of the new method. If the associated sections of charge sheet for each ion are chosen to be parallelograms, the potential derivatives required for the dynamical matrix can be written in closed form.

Our approach is not restricted to cubic crystals. No special consideration is required to deal with the case of long waves; only the understanding that the results obtained are to be interpreted as finite limits as the wavelength approaches infinity. The method may only be applied to lattice dynamical problems where the harmonic approximation is used, but nevertheless most extensions to the rigid-ion model (such as the shell model for polarisable ions [3]) are suitable for its use.

2. Details

In the rigid-ion model [1] under the harmonic and adiabatic approximations, the equations of motion for a crystal are of the form

$$m_{\kappa} \ddot{u}_{\alpha} \left[\begin{matrix} l \\ \kappa \end{matrix} \right] = - \sum_{\kappa', \beta, l'} \varphi_{\alpha\beta} \left[\begin{matrix} l & l' \\ \kappa & \kappa' \end{matrix} \right] u_{\beta} \left[\begin{matrix} l' \\ \kappa' \end{matrix} \right]$$

where the displacement from equilibrium of ion κ in unit cell l is

$$\mathbf{u} \left[\begin{matrix} l \\ \kappa \end{matrix} \right], \text{ and the } \varphi_{\alpha\beta} \left[\begin{matrix} l & l' \\ \kappa & \kappa' \end{matrix} \right]$$

are the double derivatives of the inter-ionic potentials defined as

$$\varphi_{\alpha\beta} \left[\begin{matrix} l & l' \\ \kappa & \kappa' \end{matrix} \right] = \frac{\partial^2 \varphi}{\partial u_{\alpha} \left[\begin{matrix} l \\ \kappa \end{matrix} \right] \partial u_{\beta} \left[\begin{matrix} l' \\ \kappa' \end{matrix} \right]}.$$

If, for convenience, the crystal is assumed to be infinite (or Born-von Karman boundary conditions are used) its modes of vibration can be written as plane waves of wavevector \mathbf{q} and frequency ω :

$$u_{\alpha} \left[\begin{matrix} l \\ \kappa \end{matrix} \right] = m_{\kappa}^{-1/2} W_{\alpha}(\kappa) \exp[i\mathbf{q} \cdot \mathbf{R}(l) - i\omega t].$$

The equations of motion may now be written

$$\omega^2 W_{\alpha}(\kappa) = \sum_{\kappa', \beta} (m_{\kappa} m_{\kappa'})^{-1/2} W_{\beta}(\kappa') \left(\sum_{l'} \varphi_{\alpha\beta} \left[\begin{matrix} 0 & l' \\ \kappa & \kappa' \end{matrix} \right] \exp[i\mathbf{q} \cdot \mathbf{R}(l')] \right). \quad (1)$$

The sums of interest are those over the unit cell l' . These sums cover the entire volume of the crystal and therefore cause difficulties if the inter-ionic potentials do not fall away quickly enough with distance for the sum to be convergent.

Separating the crystal potential into short-range repulsive terms φ^R and long-range Coulomb terms φ^{ion} allows the Coulomb contribution to the lattice dynamics to be treated in isolation. In any standard model of an ionic crystal, the Coulomb force is the only significant long-range force.

To discuss the Coulomb contribution to the sum Σ_l in (1), we consider the component

$$S \equiv \sum_{l'} \varphi_{\alpha\beta}^{\text{ion}} \begin{bmatrix} 0 & l' \\ \kappa & \kappa' \end{bmatrix} \exp[i\mathbf{q} \cdot \mathbf{R}(l')]$$

and imagine its terms grouped according to the value of the phase $\mathbf{q} \cdot \mathbf{R}(l')$. Each $\mathbf{q} \cdot \mathbf{R}(l') = \text{constant} = \phi_P$, say, defines a lattice plane and this effectively divides the crystal into parallel planes, all perpendicular to the wavevector \mathbf{q} . We may then sum first over the l' within a plane P and then sum over all planes

$$S = \sum_P \exp(i\phi_P) \sum_{l' \in P} \varphi_{\alpha\beta}^{\text{ion}} \begin{bmatrix} 0 & l' \\ \kappa & \kappa' \end{bmatrix}.$$

(If the wavevector is null, all directions are equivalent; so the planes may be chosen to be perpendicular to any convenient direction.) Each plane contains a two-dimensional Bravais lattice of ions and we may use the primitive vectors \mathbf{a} , \mathbf{b} in the plane to define parallelograms of equal area, centred on each ion, as in figure 1.

Finally, in each infinite plane P , we superpose a fictitious uniform charge of density σ opposite to the ionic charge density:

$$\sigma = -Z(\kappa')e/|\mathbf{a} \times \mathbf{b}|$$

where $Z(\kappa')e$ is the charge on ion κ' . This is permissible as only the double derivatives of the potential are required for the dynamical matrix, and these double derivatives are all identically zero for an infinite sheet of charge. (For example, if q points along Oz , the potential of unit charge at z due to the density σ is $V = \pm(\sigma/2\epsilon)z$, and all its second derivatives vanish.) If

$$\varphi^{\text{par}} \begin{bmatrix} 0 & l' \\ \kappa & \kappa' \end{bmatrix}$$

refers to the potential of the parallelogram associated with the ion

$$\begin{bmatrix} l' \\ \kappa \end{bmatrix} \text{ and the ion } \begin{bmatrix} 0 \\ \kappa \end{bmatrix},$$

then

$$\sum_{l' \in P} \varphi_{\alpha\beta}^{\text{par}} \begin{bmatrix} 0 & l' \\ \kappa & l' \end{bmatrix} = 0$$

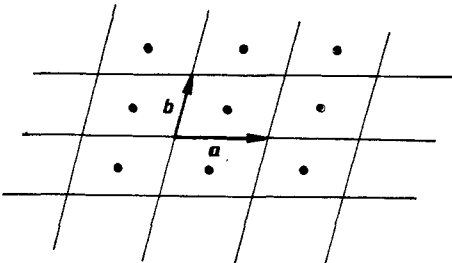


Figure 1. Plane of similar ions and constant phase $\mathbf{q} \cdot \mathbf{R}(l)$, divided into elementary parallelograms. Each parallelogram is uniformly charged, with a charge opposite to the central ion. This infinite sheet of charge makes no contribution to the dynamical matrix, but the field due to each parallelogram and its ion falls off rapidly with increasing distance.

and therefore

$$\sum_{l'} \varphi_{\alpha\beta}^{\text{par}} \begin{bmatrix} 0 & l' \\ \kappa & \kappa' \end{bmatrix} \exp[i\mathbf{q} \cdot \mathbf{R}(l')] = \sum_P \exp(i\phi_P) \sum_{l' \in P} \varphi_{\alpha\beta}^{\text{par}} \begin{bmatrix} 0 & l' \\ \kappa & \kappa' \end{bmatrix} = 0$$

may be added to S without affecting its value.

The ion-parallelgrams so constructed have no net charge and no dipole moment. Together they contribute to the double derivatives of potential as the inverse fifth power of distance and thereby ensure rapid unconditional convergence of the sums. Further, as shown in the Appendix, closed-form expressions may be obtained for the potential derivatives due to a parallelogram.

The equations of motion can now be written

$$\begin{aligned} \omega^2 W_\alpha(\kappa) = & \sum_{\kappa', \beta} (m_\kappa m_{\kappa'})^{-1/2} W_\beta(\kappa') \left\{ \sum_{l'} \varphi_{\alpha\beta}^R \begin{bmatrix} 0 & l' \\ \kappa & \kappa' \end{bmatrix} \exp[i\mathbf{q} \cdot \mathbf{R}(l')] \right. \\ & \left. + \sum_{l'} \left(\varphi_{\alpha\beta}^{\text{ion}} \begin{bmatrix} 0 & l' \\ \kappa & \kappa' \end{bmatrix} + \varphi_{\alpha\beta}^{\text{par}} \begin{bmatrix} 0 & l' \\ \kappa & \kappa' \end{bmatrix} \right) \exp[i\mathbf{q} \cdot \mathbf{R}(l')] \right\}. \end{aligned}$$

3. Duplication of Kellermann's results for NaCl

To test the new method of evaluating lattice Coulomb sums, it was decided to attempt to duplicate the results of a well known model of a simple ionic crystal. Kellermann's model of NaCl [2] was chosen. Mode frequencies were calculated in the [001], [110] and [111] directions.

To evaluate the Coulomb sums, planes perpendicular to each direction of the wavevector needed to be identified. As these planes are defined to contain only corresponding ions within the crystal's basis, and NaCl is composed of interpenetrating FCC lattices, the planes were chosen from the FCC lattice. They are illustrated in figure 2, where the parallelograms surrounding each ion are also shown. For each of the three directions, the primitive vectors used to define the parallelograms were as follows: in the [001] direction, $(r_0, r_0, 0)$ and $(-r_0, r_0, 0)$; in the [110] direction, $(0, 0, 2r_0)$ and $(-r_0, r_0, 0)$; in the [111] direction, $(r_0, -r_0, 0)$ and $(0, -r_0, r_0)$; r_0 is the nearest-neighbour separation. These vectors are not uniquely determined for any given crystal and wavevector but must be real lattice vectors perpendicular to the wavevector \mathbf{q} . The number of ion-parallelgram combinations included in the summing was left as a variable. The ion-parallelgram combinations to be included would be found within a cube centred on the ion that they were influencing. The size of the cube was used to control the extent of the summing.

At a rough estimate, the error caused by restricting the sums to a volume of the crystal bounded by a sphere of radius R should be proportional to

$$\int_R^\infty \frac{1}{r^5} 4\pi r^2 dr \approx \frac{1}{R^2}.$$

So, doubling the radius of the sphere of included ions reduces the error fourfold.

The short-range repulsive forces were treated exactly as in Kellermann's paper, using the same numerical values for the appropriate constants. As the purpose here is to try

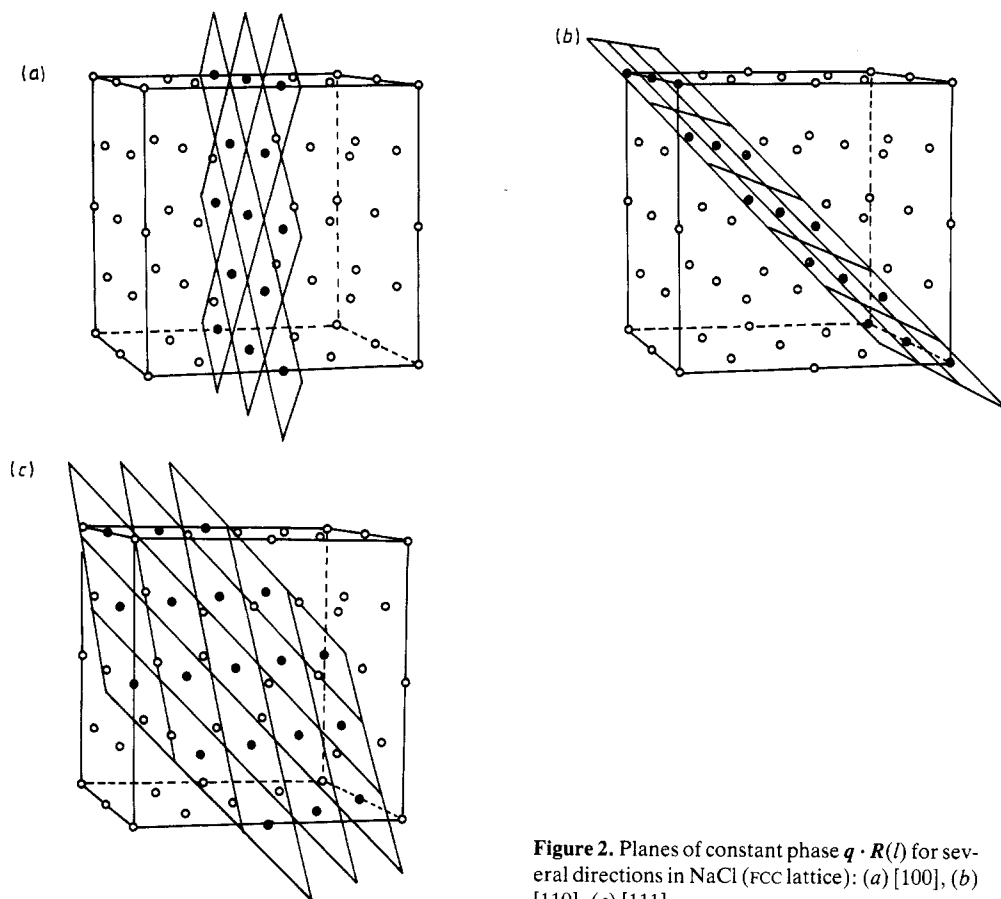


Figure 2. Planes of constant phase $\mathbf{q} \cdot \mathbf{R}(l)$ for several directions in NaCl (FCC lattice): (a) [100], (b) [110], (c) [111].

the Coulomb summing technique, it is necessary to agree in every other detail with Kellermann's model.

The dynamical matrix was constructed and its eigenvalues found for wavevectors in the three directions considered. The dispersion curves are shown in figure 3. The frequencies agree with Kellermann's to within the accuracy that he was working to (1%). Table 1 gives sample frequencies for the various wavevectors for comparison.

Figure 4 shows the results of calculations where Coulomb sums were only extended to first- and second-nearest neighbours. The general form of the dispersion curves is correct, and the numerical values are close to Kellermann's results. Some of the degeneracies which should occur are not, however, present. This is because the truncation errors in the Coulomb summing reflect the symmetry of the cube of summed sites and the shape of the individual parallelograms rather than that of the wavevector and the crystal. Incomplete summing would therefore be expected to break the symmetry properties of the solutions in general.

On testing the effects of different extents of summing on the frequencies, it was found that the cube side lengths of $7r_0$ were adequate to allow an accuracy of better than 1% for the [110] and [111] directions. This corresponds to the inclusion of 342 ion-parallelogram pairs. In the [110] direction, the results were more sensitive to truncation errors. A cube side length of $11r_0$ was required to achieve an error well below 1%. This

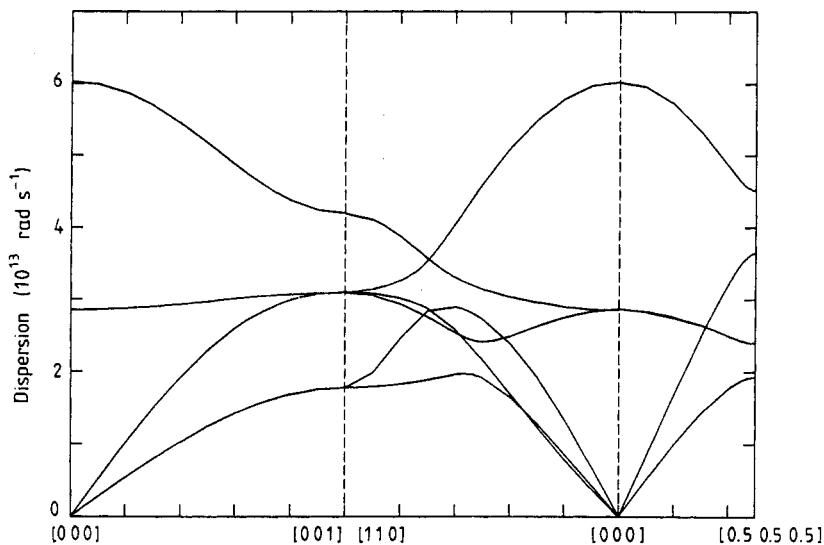


Figure 3. Dispersion curve for Kellermann's model of NaCl, calculated using the new summing technique.

corresponds to 1330 ion-parallelgram pairs. This greater sensitivity was perhaps due to the relative lack of symmetry in that direction.

Table 2 compares the convergence of the Ewald method and the new method for the particular point $[1, 1, 0]0.4$. The parameter ϵ in Kellermann's paper (his equation (5.10)) was given the value 0.1 (a choice that yields good results for the Ewald method) and the following notation is used:

$$c \begin{bmatrix} \kappa & \kappa' \\ \alpha & \beta \end{bmatrix} = - \sum_{l'} \varphi_{\alpha\beta}^{\text{ion}} \begin{bmatrix} 0 & l' \\ \kappa & \kappa' \end{bmatrix} \exp[iq \cdot \mathbf{R}(l')].$$

The point $[0.4, 0.4, 0]$ was selected because it is a direction in which the new method has 'trouble' getting the symmetry correct and because it is a value tabulated by Kellermann.

Table 1. Comparison of mode frequencies at some representative wavevectors in important symmetry directions. For each wavevector the new method's results are shown first, followed on the next row by Kellermann's results. All mode frequencies are in units of $10^{13} \text{ rad s}^{-1}$.

[000]	0.00	0.00	0.00	2.86	2.86	6.02
	0.00	0.00	0.00	2.86	2.86	6.01
[004]	1.02	1.02	1.91	2.92	2.92	5.45
	1.03	1.03	1.90	2.94	2.94	5.44
[001]	1.77	1.77	3.10	3.09	3.09	4.20
	1.77	1.77	3.10	3.09	3.09	4.20
[0.4 0.4 0.0]	1.65	2.39	1.69	2.48	3.03	5.09
	1.65	2.39	1.69	2.49	3.03	5.09
[110]	1.77	1.77	3.10	3.09	4.20	3.09
	1.77	1.77	3.10	3.09	4.20	3.09
[0.5 0.5 0.5]	1.93	1.93	3.64	2.39	2.39	4.52
	1.93	1.93	3.64	2.40	2.40	4.52

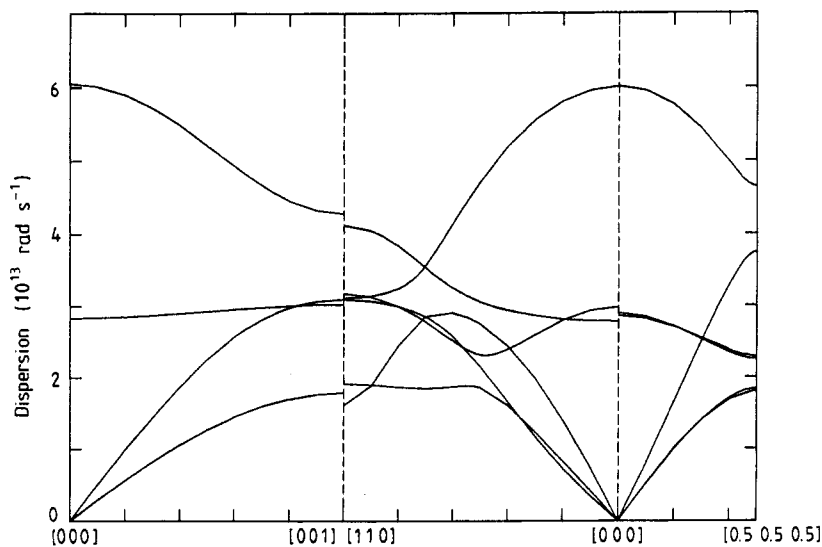


Figure 4. Dispersion curve calculated to second-nearest neighbours only.

The number of sites N involved is related to the index n by $N = (2n + 1)^3$, the last value $n = 10$ therefore corresponding to 9261 sites. On the basis of these results, the method appears to have significantly improved convergence properties over the Ewald method.

Table 2. Comparing the convergence of Coulomb sums by Ewald's and by the present method at the point $[1, 1, 0]$ 0.4: v_a , volume of unit cell.

n	$c \begin{bmatrix} 1 & 1 \\ x & x \end{bmatrix} \frac{v_a}{e^2}$	$c \begin{bmatrix} 1 & 1 \\ x & y \end{bmatrix} \frac{v_a}{e^2}$	$c \begin{bmatrix} 1 & 1 \\ z & z \end{bmatrix} \frac{v_a}{e^2}$	$c \begin{bmatrix} 1 & 2 \\ x & x \end{bmatrix} \frac{v_a}{e^2}$	$c \begin{bmatrix} 1 & 2 \\ x & y \end{bmatrix} \frac{v_a}{e^2}$	$c \begin{bmatrix} 1 & 2 \\ z & z \end{bmatrix} \frac{v_a}{e^2}$
Ewald's method ($\epsilon = 0.1$)						
1	-0.2963	-3.8374	0.6095	2.7580	2.7850	-5.5338
2	-1.1348	-5.8624	2.2725	3.3062	4.4591	-6.6096
3	-1.1717	-5.2966	2.3740	3.3502	3.9240	-6.7313
4	-1.2036	-5.1186	2.4233	3.3824	3.7309	-6.7787
5	-1.2167	-5.1237	2.4424	3.3941	3.7391	-6.7989
6	-1.2023	-5.0874	2.4356	3.3804	3.7001	-6.7915
7	-1.2237	-5.1173	2.4471	3.4013	3.7315	-6.8036
8	-1.2138	-5.0914	2.4449	3.3918	3.7052	-6.8010
9	-1.2197	-5.0930	2.4466	3.3976	3.7073	-6.8028
10	-1.2225	-5.0933	2.4474	3.4006	3.7074	-6.8035
Present method						
1	-1.3769	-4.6742	2.7538	3.5074	3.3708	-7.0147
2	-1.2619	-5.5259	2.5239	3.4545	4.1408	-6.9090
3	-1.2314	-5.1876	2.4628	3.4081	3.8079	-6.8161
4	-1.2248	-5.1002	2.4495	3.4029	3.7134	-6.8058
5	-1.2240	-5.1067	2.4480	3.4021	3.7216	-6.8041
6	-1.2238	-5.0877	2.4475	3.4018	3.7009	-6.8036
7	-1.2238	-5.1067	2.4476	3.4019	3.7209	-6.8037
8	-1.2238	-5.0895	2.4475	3.4018	3.7033	-6.8036
9	-1.2238	-5.0935	2.4476	3.4018	3.7077	-6.8037
10	-1.2238	-5.0940	2.4476	3.4018	3.7080	-6.8037

The method introduced here clearly allows the Coulomb contribution to the dynamical matrix to be calculated accurately without the sums extending very far into the crystal. The farthest summing used in the calculation for figure 3 involved a cube of side length 11 times the nearest-neighbour distance. The fact that the sums converge so quickly (as was anticipated) is an indication that the Coulomb sums are in fact convergent. It would appear that cancellations of various sorts effectively reduce the range of the Coulomb force where lattice dynamics is concerned. A similar conclusion was reached in [4] at the end of their §II: 'Hence, the effect of the other blocks is, for all practical purposes, negligible.'

4. Conclusion

The new technique for Coulomb summing was applied successfully to the NaCl lattice. The method most commonly used for Coulomb summing is that devised by Ewald. It can be said that the new method has at least the following advantages over the Ewald (or ' θ -function') technique.

- (i) It does not require summing in reciprocal space as well as real space.
- (ii) The integrals involved can all be exactly evaluated (the Ewald method makes use of the error function).
- (iii) The case of infinitely long waves may be treated as a finite limit of dynamical matrix elements rather than requiring a separate form of the equations.

Further work is required to determine more clearly the relative merits of each approach. Of particular importance would be the relative efficiency of the methods as measured in truncation error per unit of computer time required by the program.

The new method is restricted to lattice dynamical problems under the harmonic approximation but can be applied to regular lattices of any symmetry. The harmonic approximation is still widely used in models of lattice dynamics, such as the shell model for polarisable ions; so it should be noted that the new method is not tied to the rigid-ion model alone.

Appendix

With r denoting the relative displacement from ion

$$\begin{bmatrix} l' \\ \kappa' \end{bmatrix} \text{ to } \begin{bmatrix} l \\ \kappa \end{bmatrix}$$

and $Z(\kappa)e$ the charge on ion κ , the first and second derivatives of the Coulomb potential between the two point charges at equilibrium, are

$$\varphi_{\alpha}^{\text{ion}} \begin{bmatrix} l & l' \\ \kappa & \kappa' \end{bmatrix} = \frac{Z(\kappa)Z(\kappa')e^2 r_{\alpha}}{4\pi\epsilon_0 r^3}$$

and

$$\varphi_{\alpha\beta}^{\text{ion}} \begin{bmatrix} l & l' \\ \kappa & \kappa' \end{bmatrix} = \frac{Z(\kappa)Z(\kappa')e^2}{4\pi\epsilon_0 r^3} \left(\delta_{\alpha\beta} - \frac{3r_{\alpha}r_{\beta}}{r^2} \right).$$

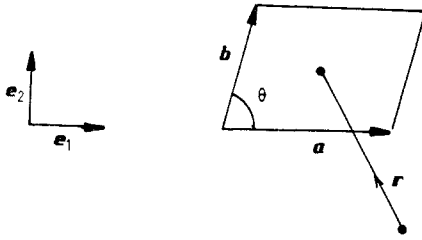


Figure 5. Unit vectors defining the coordinate system used to evaluate the derivatives of the potential due to a parallelogram. The unit vector e_3 is parallel to $\mathbf{a} \times \mathbf{b}$.

A given ion in a two-dimensional Bravais lattice with basis vectors \mathbf{a} and \mathbf{b} (figure 1) will have an associated parallelogram defined such that it is centred on the ion, has sides \mathbf{a} and \mathbf{b} and has a uniform charge opposite to the ion. The double derivatives of the interaction potential are

$$\varphi_{\alpha\beta}^{\text{par}} = \frac{-1}{|\mathbf{a} \times \mathbf{b}|} \iint_{\text{par}} \varphi_{\alpha\beta}^{\text{ion}} ds_1 ds_2$$

where the integral is over the area of the parallelogram. To evaluate this integral, it is convenient to work in a coordinate system based on the parallelogram (figure 5), choosing unit vectors $\mathbf{e}_1 \parallel \mathbf{a}$, $\mathbf{e}_3 \parallel \mathbf{a} \times \mathbf{b}$ and $\mathbf{e}_2 = \mathbf{e}_3 \times \mathbf{e}_1$. The double derivatives of the potential in this system (indexed by ξ and η) may be related back to those in the usual coordinate system (indexed by α and β) by the orthogonal transformation

$$\varphi_{\alpha\beta}^{\text{par}} = \sum_{\xi, \eta} (\mathbf{e}_\xi)_\alpha \varphi_{\xi\eta}^{\text{par}} (\mathbf{e}_\eta)_\beta$$

where $(\mathbf{e}_\xi)_\alpha$ indicates the component α of the vector \mathbf{e}_ξ . Further, since $\varphi_{\xi\eta}^{\text{par}}$ is symmetric in ξ and η , and φ^{par} obeys Laplace's equation ($\sum_\eta \varphi_{\eta\eta}^{\text{par}} = 0$), it suffices to calculate only the derivatives corresponding to $\xi, \eta = 11, 12, 13, 22$ and 23 . The five corresponding integrals are calculated by making use of the two-dimensional Green theorem. Setting

$$f(\mathbf{r}) = Z(\kappa)Z(\kappa')e^2 r_\eta / 4\pi\epsilon_0 |\mathbf{a} \times \mathbf{b}| r^3$$

we have

$$\begin{aligned} \varphi_{1\eta}^{\text{par}} &= \frac{-1}{|\mathbf{a} \times \mathbf{b}|} \iint_{\text{par}} \frac{\partial \varphi_\eta^{\text{ion}}}{\partial s_1} ds_1 ds_2 = \frac{-1}{|\mathbf{a} \times \mathbf{b}|} \int_{\text{par}} \varphi_\eta^{\text{ion}} ds_2 \\ &= |\mathbf{b}| \sin \theta \int_0^1 [f(\mathbf{r} - \frac{1}{2}\mathbf{a} - \frac{1}{2}\mathbf{b} + l\mathbf{b}) - f(\mathbf{r} + \frac{1}{2}\mathbf{a} - \frac{1}{2}\mathbf{b} + l\mathbf{b})] dl, \end{aligned}$$

and

$$\begin{aligned} \varphi_{2\eta}^{\text{par}} &= \frac{-1}{|\mathbf{a} \times \mathbf{b}|} \iint_{\text{par}} \frac{\partial \varphi_\eta^{\text{ion}}}{\partial s_2} ds_1 ds_2 \\ &= \int_0^1 [|\mathbf{a}| f(\mathbf{r} - \frac{1}{2}\mathbf{a} - \frac{1}{2}\mathbf{b} + l\mathbf{a}) - |\mathbf{a}| f(\mathbf{r} - \frac{1}{2}\mathbf{a} + \frac{1}{2}\mathbf{b} + l\mathbf{a}) \\ &\quad + |\mathbf{b}| \cos \theta f(\mathbf{r} + \frac{1}{2}\mathbf{a} - \frac{1}{2}\mathbf{b} + l\mathbf{b}) - |\mathbf{b}| \cos \theta f(\mathbf{r} - \frac{1}{2}\mathbf{a} - \frac{1}{2}\mathbf{b} + l\mathbf{b})] dl. \end{aligned}$$

The integrals to be calculated are all of the form

$$\int_0^1 \frac{u_\eta + lv_\eta}{|\mathbf{u} + l\mathbf{v}|^3} dl = \frac{1}{u^2v^2 - |\mathbf{u} \cdot \mathbf{v}|^2} \left(\frac{u_\eta(v^2 + \mathbf{u} \cdot \mathbf{v} - v_\eta(u^2 + \mathbf{u} \cdot \mathbf{v}))}{|\mathbf{u} + \mathbf{v}|} + \frac{u^2v_\eta - (\mathbf{u} \cdot \mathbf{v})u_\eta}{u} \right).$$

If $u^2v^2 = (\mathbf{u} \cdot \mathbf{v})^2$, then the above form is inappropriate. In this case, \mathbf{u} and \mathbf{v} are parallel, say $\mathbf{v} = K\mathbf{u}$, and

$$\int_0^1 \frac{u_\eta + lv_\eta}{|\mathbf{u} + l\mathbf{v}|^3} dl = \frac{u_\eta}{u^3(1+K)}.$$

All the remaining cases where the denominators vanish correspond to the integration beginning or ending at the origin. In such cases the 'origin' must be at the centre of four ions. If the four separate parallelograms (which all belong to the one infinite sheet) are fused back into one larger one, then the integrals can be evaluated since the origin will no longer be at a corner. This fusing together of sections of charge sheet is in any case of use in avoiding unnecessary integrals along common edges. This last fact would be exploited by any efficient implementation of the Coulomb summing method described here.

Inspection of the original integrals shows other special cases where they appear divergent. In particular, it is not obvious how these integrals could be performed if a parallelogram includes the origin. The assignment of values to the integrals in all these cases must then be understood in the sense of finite limits as these special cases are approached.

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