

Fractional charges in lattice sum calculations

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THE USE OF fractional charges in electrostatic lattice sum calculations is of importance in cases where a crystalline ionic compound contains a complex anion or cation (complex-ion). For example, materials such as $K(HF_2)$, KN_3 , K_2CO_3 can reasonably be described by a model in which the charge of K^+ interacts with fractional charges at the sites of the composing ions of the anion [1]. The bonding in the complex ion itself will generally contain important covalent contributions which invalidate a pure electrostatic description of the ion. This covalent bonding decreases the effective value of the charges of the ions in the complex-ion. Generally dipoles or multipoles with fractional charges are required to describe the interaction with other ions in a first approximation.

In performing calculations with fractional ion charges some problems occurred, which will be discussed subsequently.

(1) The physical description of the electrostatic energy of an ionic crystal relates this energy to the energy gained when the ions are brought from infinite distance to their crystalline lattice sites. Thus the situation of infinite distances between the ions is used as the zero level for the energy level diagram. When using fractional charges, the question is whether infinite large distances between the fractional charges must also be used to describe the zero level of the energy or if another reference level is more appropriate. This problem occurs when one tries to relate situations by the addition procedure to be described under Section (2).

The question of the different reference levels can be solved by considering the definition of the electrostatic energy of a set of point charges:

$$E = -\frac{1}{2} \sum_j \sum_i' \frac{q_j q_i}{r_{ij}} \quad (1)$$

in which q_i and q_j indicate different point charges of the set, r_{ij} their distance and \sum_j, \sum_i' summations over the set, \sum_i' excluding terms with $r_{ij} = 0$. Although actual calculations in a crystalline point lattice are, for example, performed by means of summation of two convergent series in the Ewald procedure [2, 3], this does not invalidate the use of Eqn. (1) in theoretical questions. When the charges q_i, q_j are replaced with charges having fractional values ($\alpha_i q_i, \alpha_j q_j, 0 \leq \alpha_i, \alpha_j < 1$), the electrostatic energy becomes less. It is just a matter of convenience whether one represents in an energy diagram the new situation by maintaining the zero level (Fig. 1b) or the end level (Fig. 1c). Using this freedom it is helpful to draw these diagrams in such a way that one and the same charge distribution is represented at one level, also when two different ways are used to get this distribution.

(2) In actual calculations the complex ion is sometimes described as a single point charge to which a multipole is added [4]. In this procedure lattice potentials are additive, but the electrostatic energy of the final situation is not the sum of the energies of the two composing lattices. The following derivation demonstrates the relationships.

When a charge distribution is obtained by adding two other charge distributions, we have

$$\begin{aligned} q_i &= q_i^{(1)} + q_i^{(2)} \\ q_j &= q_j^{(1)} + q_j^{(2)} \end{aligned} \quad (2a)$$

where $q_i^{(1)}, q_j^{(1)}$ represent, for example, an ionic lattice and $q_i^{(2)}, q_j^{(2)}$ an added quadrupole. Some of the $q^{(1)}(q^{(2)})$ values might be zero, although the corresponding q and $q^{(2)}(q^{(1)})$ values are not zero.

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2. P. P. Ewald, *Ann. Phys.* **64**, 253 (1921).
3. W. van Gool and A. Piken, *J. mat. Sci.* **4**, 95, 105 (1969).
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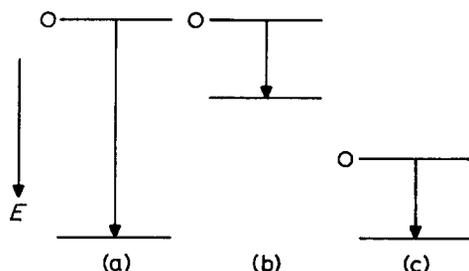


Fig. 1. (a) Energy levels corresponding to charges q_i, q_j ; (b) and (c) energy levels corresponding to charges $\alpha_i q_i, \alpha_j q_j$, two possibilities.

Then:

$$\begin{aligned}
 E &= -\frac{1}{2} \sum_j \sum_i' \frac{(q_j q_i)}{r_{ij}} = -\frac{1}{2} \sum_j \sum_i' \frac{(q_j^{(1)} + q_j^{(2)})(q_i^{(1)} + q_i^{(2)})}{r_{ij}} \\
 &= -\frac{1}{2} \sum_j \sum_i' \left\{ \frac{q_j^{(1)} q_i^{(1)}}{r_{ij}} + \frac{q_j^{(2)} q_i^{(2)}}{r_{ij}} + \frac{q_j^{(1)} q_i^{(2)}}{r_{ij}} + \frac{q_j^{(2)} q_i^{(1)}}{r_{ij}} \right\} \\
 &= E^{(1)} + E^{(2)} - \frac{1}{2} \sum_j \sum_i' \frac{q_j^{(1)} q_i^{(2)}}{r_{ij}} - \frac{1}{2} \sum_j \sum_i' \frac{q_j^{(2)} q_i^{(1)}}{r_{ij}}. \quad (3)
 \end{aligned}$$

$E, E^{(1)}, E^{(2)}$ represent the calculated energies of the three charge distributions. Equation (3) shows why the energy of the sum of two charge distributions is not equal to the sum of the energies of the separate distributions.

Actual calculations[3] make use of the potentials V_k at lattice sites (self-potentials). Here k indicates the symmetrically different lattice sites. When ν_k is the frequency of the site k in the unit cell and z the number of molecules per unit cell, the electrostatic energy of the system per mole compound is also given by

$$E = -\frac{1}{2z} N \sum_k \nu_k q_k V_k \quad (4)$$

in which V_k is given by ($i \neq k$)

$$V_k = \sum_i \frac{q_i}{r_{ik}}. \quad (5)$$

Thus the potential at some reference point is additive when two charge distributions are added and

$$\begin{aligned}
 E &= -\frac{1}{2z} N \sum_k \nu_k q_k V_k = -\frac{1}{2z} N \sum_k \nu_k (q_k^{(1)} + q_k^{(2)}) (V_k^{(1)} + V_k^{(2)}) \\
 &= E^{(1)} + E^{(2)} - \frac{1}{2z} N \sum_k \nu_k q_k^{(1)} V_k^{(2)} - \frac{1}{2z} N \sum_k \nu_k q_k^{(2)} V_k^{(1)}. \quad (6)
 \end{aligned}$$

This is the expression corresponding to Eqn. (3) when lattice self-potentials are used. In this form computer calculations of added charge distributions can be checked easily, or, given the calculations of the distributions ⁽¹⁾ and ⁽²⁾ the energy of the summed contribution can be obtained. (The summation \sum_k generally refers to a few points only and can be done without computers.)

(3) In the calculations described before, the interaction energy between the multipoles is required. In earlier calculations Waddington developed special formulas in which the particular symmetry of the lattice under discussion was used. Furthermore, approximations had to be made—see Section (4).

The question arose whether this interaction energy could be obtained by the normal application of the Ewald procedure to the multipole lattice. In an actual situation the electrostatic calculation gave 634.39 kcal/mole, whereas Waddington's formulas came to 9.2 kcal/mole. This big discrepancy is due to the fact that the total electrostatic energy includes the electrostatic energy of the quadrupoles themselves. This energy is easily calculated to be 627.47 kcal/mole, leading to a quadrupole-quadrupole

interaction energy of $634.39 - 627.47 = 6.92$ kcal/mole. The details of the calculations are discussed elsewhere[5]. The conclusion is that quadrupole–quadrupole interactions (and also ion–quadrupole interactions) can be calculated by general procedures.

(4) In the addition procedures one quadrupole is placed in an ionic lattice. The interaction energy $E_{\text{quad-ion}}$ was calculated by approximate procedures. The exact value can be obtained by the procedure outlined under Section (3). The interesting question is whether the symmetrically different ions when placed in an infinite quadrupole lattice yield the same energy ($E_{\text{ion-quad}}$). The equivalence of both methods can be demonstrated as follows.

Let $q_i^{(1)}$, $q_u^{(1)}$ and $q_k^{(1)}$ be charges in the ion-lattice and $q_j^{(2)}$, $q_v^{(2)}$ and $q_l^{(2)}$ in the quadrupole-lattice. Let i , u , j and v be running numbers for the infinite sets, where i and u refer to the same ionic set, and j and v to the quadrupole set. Let k and l refer to the (few) symmetrically different sites in set $^{(1)}$ and set $^{(2)}$. The electrostatic energy E_{sum} of the joined sets can be calculated.

In a somewhat extended version Eqn. (1) is as follows

$$E_{\text{sum}} = -\frac{1}{2} \sum_i \sum_u' \frac{q_i^{(1)} q_u^{(1)}}{r_{ui}} - \frac{1}{2} \sum_j \sum_v' \frac{q_j^{(2)} q_v^{(2)}}{r_{vj}} - \sum_i \sum_j \frac{q_i^{(1)} q_j^{(2)}}{r_{ji}} \quad (7)$$

The last summation refers to two different sets of point charges and thus no double counting of interactions or zero distances occurs. Instead of performing this last summation over two infinite sets, we can follow the normal procedure of using potentials for symmetrically different points only. However, there are now two different sets of such points which leads to

$$\sum_i \sum_j \frac{q_i^{(1)} q_j^{(2)}}{r_{ji}} = -\frac{N}{z^{(1)}} \sum_k \nu_k q_k^{(1)} \sum_j \frac{q_j^{(2)}}{r_{jk}} = -\frac{N}{z^{(1)}} \sum_k \nu_k q_k^{(1)} V_k^{(2)} \quad (8)$$

$$\sum_i \sum_j \frac{q_i^{(1)} q_j^{(2)}}{r_{ji}} = -\frac{N}{z^{(2)}} \sum_l \nu_l q_l^{(2)} \sum_i \frac{q_i^{(1)}}{r_{il}} = \frac{N}{z^{(2)}} \sum_l \nu_l q_l^{(2)} V_l^{(1)} \quad (9)$$

Here $V_k^{(2)}$ is the potential in reference point k (of set $^{(1)}$) due to the charges of set $^{(2)}$. Thus Eqn. (8) represents the ion–quadrupole interaction. Correspondingly, Eqn. (9) describes the same energy but now as quadrupole–ion interaction. The equivalence of both procedures is a useful check on the accuracy of computer calculations[5]. This discussion shows that the approach followed earlier is justified [4]. In this approach only one interaction (quadrupole–ion) was approximated and the other interaction was not even mentioned. Including the ion–quadrupole interaction should have required another set of approximative formulas with the same outcome. Dividing by two should have been necessary since then the interactions between the two sets should also have been counted twice. Besides the justification of the earlier procedure, the present description indicates how the quadrupole–ion interaction can be obtained from accurate standard potential calculations without requiring special formulas for each new situation.

(5) An interesting aspect of the summation procedure used in the earlier calculations is that the intermediate situation, consisting of the quadrupole-lattice and the ionic-lattice, contains much more electrostatic energy than the final situation. This is obvious, since the intermediate situation has a larger electrostatic charge than the final situation. The problem, however, occurs in the summation step, in which electrostatic charges simply disappear. This summation is not done in a pure electrostatic way, since infinite large energies should have occurred in adding the charges. The disappearing energy is exactly equivalent to the disappearance of N quadrupoles and can be obtained as before. A complete agreement between the different descriptions of the final situation can be obtained with this approach. The major aspect to be stressed here is the annihilation of electrostatic charges used implicitly in the summation procedure and the calculation of the required correction.

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