3.4. Accelerated convergence treatment of R^{-n} lattice sums

By D. E. Williams†

3.4.1. Introduction

The electrostatic energy of an ionic crystal is often represented by taking a pairwise sum between charge sites interacting *via* Coulomb's law (the $n = 1$ sum). The individual terms may be positive or negative, depending on whether the pair of sites have charges of the same or different signs. The Coulombic energy is very long-range, and it is well known that convergence of the Coulombic lattice-energy sum is extremely slow. For simple structure types Madelung constants have been calculated which represent the Coulombic energy in terms of the cubic lattice constant or a nearest-neighbour distance. Glasser & Zucker (1980) give tables of Madelung constants and review the subject giving references dating back to 1884. If the ionic crystal structure is not of a simple type usually no Madelung constant will be available and the Coulombic energy must be obtained for the specific crystal structure being considered. In carrying out this calculation, accelerated-convergence treatment of the Coulombic lattice sum is indispensable to achieve accuracy with a reasonable amount of computational effort. A model of a molecular crystal may include partial net atomic charges or other charge sites such as lone-pair electrons. The ($n = 1$) sum also applies between these site charges.

The dispersion energy of ionic or molecular crystals may be represented by an ($n = 6$) sum over atomic sites, with possible inclusion of ($n = 8, 10, \ldots$) terms for higher accuracy. The dispersion-energy sum has somewhat better convergence properties than the Coulombic sum. Nevertheless, accelerated-convergence treatment of the dispersion sum is strongly recommended since its use can yield at least an order of magnitude improvement in accuracy for a given calculation effort. The repulsion energy between nonbonded atoms in a crystal may be represented by an exponential function of short range, or possibly by an ($n = 12$) function of short range. The convergence of the repulsion energy is fast and no accelerated-convergence treatment is normally required.

3.4.2. Definition and behaviour of the direct-space sum

This pairwise sum is taken between atoms (or sites) in the reference unit cell and all other atoms (or sites) in the crystal, excluding the self terms. Thus, the second atom (or site) is taken to range over the entire crystal, with elimination of self-energy terms. If V_n represents an energy, each atom is assigned one half of the pair energy. Therefore, the energy per unit cell is

$$V_n = (1/2) \sum_{j}^{\text{one cell}} \sum_{k}^{\text{all cells}} {}' Q_{jk} R_{jk}^{-n},$$

where Q_{jk} is a given coefficient, R_{jk} is an interatomic distance, and the prime on the second sum indicates that self terms are omitted. In the case of the Coulombic sum, $n = 1$ and $Q_{jk} = q_j q_k$ is the product of the site charges.

Table 3.4.2.1 gives an example of the convergence behaviour of the untreated ($n = 1$) Coulombic sum for sodium chloride. Even

at the rather large summation limit of 20 Å the Coulombic lattice sum has not converged and is incorrect by about 8%. The 20 Å sum included 832 molecules and 2494 individual distances. At various smaller summation limits the truncation error fluctuates wildly and can be either positive or negative. Note that the results shown in the table always refer to summation over whole molecules, that is, over neutral charge units.

If the Coulombic summation is not carried out over neutral charge units the truncation error is even larger. These considerations support the conclusion that accelerated-convergence treatment of the Coulombic lattice sum should be regarded as mandatory. Table 3.4.2.2 gives an example of the convergence behaviour of the untreated ($n = 6$) dispersion sum for benzene. In obtaining this sum it is not necessary to consider whole molecules as in the Coulombic case. The exclusion of atoms (or sites) in the portions of molecules outside the summation limit greatly reduces the number of terms to be considered. At the summation limit of 20 Å, 439 benzene molecules and 22 049 individual distances are considered; the dispersion-sum truncation error is 0.4%. Thus, if sufficient computer time is available it may be possible to obtain a moderately accurate dispersion sum without the use of accelerated convergence. However, as shown below, the use of accelerated convergence will greatly speed up the calculation, and is in practice necessary if higher accuracy is required.

3.4.3. Preliminary description of the method

Ewald (1921) developed a method which modified the mathematical representation of the Coulombic lattice sum to improve the rate of convergence. This method was based on partially transforming the lattice sum into reciprocal space. Bertaut (1952) presented another method for derivation of the Ewald result which used the concept of the crystallographic structure factor. His formula extended the Ewald treatment to a composite lattice with more than one atom per lattice point. Nijboer & DeWette (1957) developed a general Fourier transform method for the evaluation of R^{-n} sums in simple lattices. Williams (1971) extended this treatment to a composite lattice and gave general formulae for the R^{-n} sums for any crystal. A review article, on which this chapter is based, appeared later (Williams, 1989*a*,*b*).

Consider a function, $W(R)$, which is unity at $R = 0$ and smoothly declines to zero as R approaches infinity. If each term of the lattice sum is multiplied by $W(R)$, the rate of convergence is increased. However, the rate of convergence of the remainder of

Table 3.4.2.1. *Untreated lattice-sum results for the Coulombic energy (n = 1) of sodium chloride (kJ mol⁻¹, Å); the lattice constant is taken as 5.628 Å*

Truncation limit	Number of molecules	Number of terms	Calculated energy
6.0	23	67	−696.933
8.0	59	175	−597.371
10.0	108	322	−915.152
12.0	201	601	−773.475
14.0	277	829	−796.248
16.0	426	1276	−826.502
18.0	587	1759	−658.995
20.0	832	2494	−794.619
Converged value			−862.825

references