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COMPUTATION OF MADELUNG SUMS AND CRYSTAL ENERGIES

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ABSTRACT

A strategy is outlined for the calculation of the Madelung constant according to Bertaut's method and the crystal energy with repulsion treated as a simple power dependence on distance. A program is described which permits these calculations to be done conveniently and rapidly with the IBM-704 computer.

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If one understands in sufficient detail the forces between atoms, then in principle one can calculate the thermodynamic properties of arbitrary structures, or, conversely, one can predict the structure which would be thermodynamically most stable. For the crystalline materials that we call salts, the force between a pair of atoms is well approximated by a term which is just the Coulomb force for a pair of point charges plus a second term which is strongly repulsive at short distances and ineffective at long distances. The potential energy of the crystal is calculated by adding the potential energies associated with these two terms for every pair of atoms in the crystal.

The Madelung sum, U_c, is:

$$U_c = - e^2 A/L = \sum_{i \neq j} e_i e_j / r_{ij} , \tag{1}$$

where e is the charge of the electron, L is a standard distance (often chosen as the nearest neighbor distance, r_o), A is the Madelung constant corresponding to this choice of L, e_i is the charge of an ion, and r_{ij} is the distance between two ions. In this sum, attention must be paid to the number of terms of each kind so that one gets the energy for a definite quantity of material, for example one mole. One wishes to have the limit of the sum as it extends to neighbors at very large distances. However, this sum is convergent only

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by cancellation of positive and negative contributions, each of which increases without limit, and therefore the series must be terminated properly. Except for this conditional convergence, this sum would be a relatively prosaic job for a fast electronic computer.

The short-range term includes the specific chemical effects, and its treatment depends on the nature of the problem. For salts consisting of monatomic ions which are isoelectronic with rare gases, interesting and useful results can be obtained with a simple repulsive potential proportional to some high negative power of the distance:

$$u_{ij} = B_{ij}/r_{ij}^{\,n} , \tag{2}$$

where B is characteristic of the kind of atoms involved. With a potential of this simplicity, the calculation of repulsion energy presents no special problems.

At Berkeley these calculations have been made by hand and with a variety of IBM computers, including the CPC (card programmed computer), the 650, and the 704. The strategy which has been developed will be discussed in terms of a 704 program which was completed early in 1960.

The Madelung Sum

We have been interested in problems involving various symmetries and with variable parameters. Enormous accuracy is not required, but it is essential to know the order of magnitude of the accuracy and especially to avoid convergence blunders. It is desirable to have a program which can be used for new problems without programming changes and with a minimum of new data. These considerations have controlled the choice of strategy for the Madelung sum.

We use the method of Bertaut,[1,2] as elatborated by Jones and Templeton[3,4] for spherical charge distributions whose densities are a linear function of the radial coordinate. The Madelung constant is:

$$A = \frac{(g-Q)L}{RZ} \sum_j (z_j)^2 - \frac{\pi R^2 L}{ZV} \sum_h |F|^2 \phi \tag{3}$$

g = 26/35

Q = a correction for termination of the h series

L = standard distance

R = an arbitrary distance less than half the nearest neighbor distance

Z = molecules per unit cell

z_j = charge number (with sign) of an atom

V = volume of unit cell

h = magnitude of reciprical vector $\underset{\sim}{h}$

$$F = \sum_j z_j \exp\left(2\pi i\, \underset{\sim}{h} \cdot \underset{\sim}{x}_j\right)$$

$$\phi = 288\,(\alpha \sin \alpha + 2 \cos \alpha - 2)^2\, \alpha^{-10}$$

$$\alpha = 2\pi h R$$

The sums over j include all atoms in the unit cell. The sum over h includes all reciprocal lattice vectors in a sphere of arbitrary radius. The series termination correction depends on the radius of this sphere as follows, according to a statistical theory:

Maximum α	Q
2π	0.00030
3π	0.000090
4π	0.000012
5π	0.0000057

Other values of Q are listed by Jones and Templeton.[4] Experience has shown that Q is reliable to 20 percent or better in most cases. Thus termination at 2π yields accuracy better than 0.1 percent with Q neglected and better than about 0.02 percent if the correction is made.

The 704 Program

The program for the 704 computer was written in Fortran language for a machine configuration of 32K core storage. Approximately 30 percent of this storage is used. No attention has been given to economy of storage, and such large storage capacity is not an intrinsic requirement of the strategy described here. One magnetic tape is used, for writing output. On-line printing is permitted by a sense switch, but is relatively time-consuming.

The program can be loaded as a deck of about 300 binary cards followed by a dozen or more cards which describe the data for the specific problem in alphabetic and decimal-numeric characters. The program loads the data, prints them as an identification of the problem, and then distinguishes between crystal systems. Triclinic problems are not provided for. Rhombohedral problems must be set up in hexagonal coordinate systems, and, like hexagonal problems, are considered by the machine as if they were monoclinic. One-fourth of reciprical space is considered in the h sum for monoclinic (and hexagonal) problems; otherwise only one-eighth is considered. Appropriate multiplicity factors are applied to give the result for the complete sphere.

The atomic positions have been loaded as coordinates of the atoms of the asymmetric unit, together with a code for the lists of equivalent positions. Coordinates are generated and printed for all atoms in the unit cell. A list of the shorter interatomic distances, up to a specified limit, is calculated and printed. The program chooses $R = 0.495\ D$, where D is the shortest distance in this list.

The Madelung constant is calculated according to equation (3), with series termination at a value of α specified by the input data. The charge structure factors F are calculated as if the structure were triclinic. A routine scans reciprocal space along rows, working outward in both directions from the point nearest the origin until vectors are found which lie outside the termination sphere. When F is zero, the program skips the calculation of ϕ. The calculation of the Madelung constant is the slowest step of the internal program.

The repulsive terms are calculated according to equation (2) with neglect of neighbors of a particular kind at distances greater than specified distance. The exponent in Eq. (2) need not be integral. The answers are printed.

If another set of data cards follows, the program proceeds to the new problem, saving the program-loading time.

Typical running times, with off-line printing and with series termination at $\alpha = 2\pi$, are 80 sec. to load the program, plus 10 sec. for rutile, 70 sec. for brookite, and 130 sec. for corundum. On-line printing adds about 70 sec. to each problem. The running time depends mainly on the number of atoms in the unit cell and the symmetry. Rutile is tetragonal with 6 atoms per unit cell. Brookite is orthorhombic with 24 atoms per unit cell. Corundum is rhombohedral, with 30 atoms in the hexagonal unit cell.

Applications

An application of these methods, described elsewhere,[5] is the determination of the positions of oxygen and fluorine in YOF, where they could not be distinguished with x-rays. These calculations were carried out with a more specialized program and the IBM-650 computer.

It is anticipated that the present 704 program may be modified to calculate first and second derivatives of the energy with respect to variation of parameters, but at the present writing this has not been done. Such modification would permit automatic refinement to the structure of minimum energy according to an arbitrary choice of interaction parameters.

More complicated functions could be used for the repulsive potential with little increase in running time.

It is hoped that further applications can be cited at Glasgow.

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