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THE POTENTIAL AND POTENTIAL ENERGY OF SPACE LATTICES

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Abstract

The electrostatic potential of a general space lattice is developed. The space lattice is characterized by a base cell containing a finite set of positive point charges arbitrary in strength and position, and a negative space charge of arbitrary density, subject to the condition that the total charge in the cell is zero.

Next the expression for the lattice energy is obtained in the form of a triply infinite series. It is shown that the coefficients in this series representing the distribution of the negative space charge can be identified with the structure factors of the lattice or crystal provided we replace the negative space charge by a corresponding electron distribution.

An application of this theory is made to the three halides NaCl, NaF, and LiF. The lattice energy of each crystal is calculated for different grating spaces. In all three cases it is shown that the lattice energy has a minimum in the neighborhood of the accepted grating space for the crystal under consideration. The agreement is better for NaCl than for NaF or LiF.

The Electrostatic Potential

THE electrostatic potential of an infinite space lattice with an arbitrary distribution of point charges in the base cell can be determined by a method due to Ewald.[1] This method consists in considering a continuous periodic distribution of charges the density of which can be represented by a triple Fourier series without a constant term.[2] The potential of such a system can be represented by a similar Fourier series whose coefficients can be determined by the use of Poisson's equation. Finally one arrives at the required result by taking the limiting case in which the continuous space charge shrinks into a discrete set of point charges. If, in this process, we allow the positive space charge to shrink into point charges but keep the negative charge as a continuous distribution of electricity, we obtain a space lattice with cells consisting of a set of positive point charges (nuclei) surrounded by an atmosphere of negative electricity which may be identified with the electron distribution under certain conditions. It is the potential and potential energy of such a space lattice which we wish to determine.

Let us consider the base cell of our lattice to be defined by the three vectors a^1, a^2, a^3. Our lattice can be built up by a simple translation of this base cell in three space directions defined by a^1, a^2, a^3. The lattice shall be referred to the rectangular axes x_1, x_2, x_3 whose origin shall be at a vertex

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[1] P. P. Ewald, Ann. d. Physik **64**, 253 (1921).

M. Born, Problems of Atomic Dynamics, 158–162 (1926).

[2] The lack of a constant term in the series means that the total charge in any cell of the lattice is zero.

of the base cell. The rectangular components of the three base vectors shall be designated by a_i^m; $m, i=1, 2, 3$. a_i^m is the x_ith component of the a^mth vector. The volume of the base cell shall be $\Delta = |a_i^m|$. We introduce the three vectors of the reciprocal lattice b^1, b^2, b^3 with their components b_j^n defined by the equations

$$\sum_{i=1}^{3} a_i^m b_i^n = \begin{Bmatrix} 0 \text{ if } n \neq m \\ 1 \text{ if } n = m \end{Bmatrix}; \; m, n = 1, 2, 3.$$

Let there be p positive point charges in the base cell, the kth charge having a strength e_k and coordinates x_i^k. The negative space charge shall have a density distribution of $\rho(x_1, x_2, x_3)$ in the base cell. We impose the condition that

$$\sum_{k=1}^{p} e_k + \iiint \rho dx_1 dx_2 dx_3 = 0$$

where the integral is taken throughout the entire base cell. This condition is equivalent to the statement that the total charge in the base cell, and therefore in any cell, is zero.

With this brief description of the lattice under consideration, we write down at once the potential of this lattice as given by Ewald's method.

$$V = \frac{1}{\pi\Delta} \sum_{l_1, l_2, l_3=-\infty}^{\infty}{}' \left\{ \frac{A_{l_1 l_2 l_3} + B_{l_1 l_2 l_3}}{\sum_{j=1}^{3} \left(\sum_{n=1}^{3} l_n b_j^n \right)^2} \right\} \exp\left(i2\pi \sum_{j,n=1}^{3} l_n b^n_j x_j \right) \tag{1}$$

where the coefficients $A_{l_1 l_2 l_3}$ and $B_{l_1 l_2 l_3}$ are given by the equations

$$\left\{ \begin{aligned} A_{l_1 l_2 l_3} &= \sum_{k=1}^{p} e_k \exp\left(- i2\pi \sum_{j,n=1}^{3} l_n b_j^n x_j^k \right) \\ B_{l_1 l_2 l_3} &= \iiint \rho(\xi_1, \xi_2, \xi_3) \exp\left(- i2\pi \sum_{j,n=1}^{3} l_n b_j^n \xi_j \right) d\xi_1 d\xi_2 d\xi_3 \end{aligned} \right\} \tag{2}$$

the integration to be taken throughout the base cell. The coefficients $A_{l_1 l_2 l_3}$ are functions of the positions and the strengths of the positive point charges, and the coefficients $B_{l_1 l_2 l_3}$ are functions of the distribution of the negative space charge. The total potential V is obviously the sum of the separate potentials of the positive and the negative charges, but the above series written with all of the $B_{l_1 l_2 l_3}$ coefficients omitted does not represent the potential of the positive charges alone. Rather it gives the potential of the positive charges imbedded in a negative space charge of uniform density such that the total charge in any cell is zero. It is seen by Eqs. (2) that for $\rho = \text{constant}$, $B_{l_1 l_2 l_3} = 0$ except for $l_1 = l_2 = l_3 = 0$, and this term is omitted in the series in Eq. (1) as indicated by the prime on the summation sign.

The Potential Energy

Having calculated the potential of the space lattice under consideration we turn to the problem of determining the potential energy of the lattice, or rather the potential energy of a single cell of the lattice. For this calculation we make use of Green's theorem which may be written in the form

$$\begin{aligned}&\iiint V\nabla^2 V dx_1 dx_2 dx_3\\&+\iiint [(\partial V/\partial x_1)^2+(\partial V/\partial x_2)^2+(\partial V/\partial x_3)^2]dx_1dx_2dx_3\\&+\sum\iint V(\partial V/\partial n)dS=0\end{aligned}$$

where the symbols have their customary significance.

The potential energy of the base cell will be given by the expression

$$(1/8\pi)\iiint [(\partial V/\partial x_1)^2+(\partial V/\partial x_2)^2+(\partial V/\partial x_3)^2]dx_1dx_2dx_3$$

where the integration is taken throughout the base cell. However this expression will give an infinite energy because of the presence of positive point charges in the cell of infinite self-energy. We can overcome this difficulty by deleting each of the positive charges with a small sphere of radius δ and subtracting off the self-energy of these positive charges. The resultant potential energy of the cell which we shall designate by Φ will then be given by the equation

$$\begin{aligned}\Phi=\lim_{\delta\to 0}\Big\{(1/8\pi)\iiint &[(\partial V/\partial x_1)^2+(\partial V/\partial x_2)^2\\&+(\partial V/\partial x_3)^2]dx_1dx_2dx_3-\sum_{k=1}^{p}(e_k)^2/2\delta\Big\}\end{aligned}\tag{3}$$

where the integration now extends through-out the base cell excluding the p small spheres of radii δ.

By the use of Green's theorem Φ can be written in the form

$$\begin{aligned}\Phi=\lim_{\delta\to 0}\Big\{&-(1/8\pi)\iiint V\nabla^2 V dx_1dx_2dx_3\\&-(1/8\pi)\sum\iint V(\partial V/\partial n)dS-\sum_{k=1}^{p}(e_k)^2/2\delta\Big\}.\end{aligned}\tag{4}$$

Now $\nabla^2 V=-4\pi\rho$ and $\iint V(\partial V/\partial n)dS$ vanishes over the external surface of the cell because of the periodicity of V and $\partial V/\partial n$.[3] Thus the surface integral of $V\partial V/\partial n$ reduces to that over the small spheres alone. Eq. (4) may now be written

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[3] If some of the point charges lie on the bounding surface of the cell, they may be deleted by small hemispherical indentations precisely as is done in the theory of elliptic functions.

$$\Phi = \lim_{\delta\to 0}\left\{(1/2)\iiint \rho V dx_1 dx_2 dx_3 - (1/8\pi)\sum_{k=1}^{p}\iint V(\partial V/\partial n)dS - \sum_{k=1}^{p}(e_k)^2/2\delta\right\}. \tag{5}$$

But $\lim_{\delta\to 0}(1/2)\iiint\rho V dx_1dx_2dx_3$ is equal to $(1/2)\iiint\rho V dx_1dx_2dx_3$, the integral being taken through-out the entire base cell, since the integral of ρV throughout any of the small spheres goes to zero as δ goes to zero. Also it is not difficult to show that

$$\lim_{\delta\to 0}\left\{-(1/8\pi)\sum_{k=1}^{p}\iint V(\partial V/\partial n)dS - \sum_{k=1}^{p}(e_k)^2/2\delta\right\} = (\tfrac{1}{2})\sum_{k=1}^{p}e_kV_k'$$

where V_k' is the potential at the point charge e_k with that charge removed. Making these substitutions in Eq. (5) we obtain

$$\Phi = (\tfrac{1}{2})\iiint \rho V dx_1dx_2dx_3 + (\tfrac{1}{2})\sum_{k=1}^{p}e_kV_k'. \tag{6}$$

Substituting in Eq. (6) the value of V as given in Eq. (1) we get

$$\Phi = (1/2\pi\Delta)\sum_{l_1,l_2,l_3=-\infty}^{\infty}{}' \frac{(A_{l_1l_2l_3}+B_{l_1l_2l_3})B_{-l_1-l_2-l_3}}{\sum_{j=1}^{3}\left(\sum_{n=1}^{3}l_nb_j^{\,n}\right)^2} + (\tfrac{1}{2})\sum_{k=1}^{p}e_kV_k'. \tag{7}$$

Let us consider the quantity $(1/2)\sum_{k=1}^{p}e_kV_k'$ appearing in Eq. (7). V_k' is the potential at the k th positive charge with that charge removed. It is made up of two parts, that due to all the other positive charges, and that due to the negative space charge. Calling the former $V_k'{}_+$ and the latter $V_k'{}_-$ we see by the use of Eq. (1) that

$$\begin{aligned}(\tfrac{1}{2})\sum_{k=1}^{p}e_kV_k' &= (\tfrac{1}{2})\sum_{k=1}^{p}e_k(V_k'{}_+ + V_k'{}_-)\\ &= (\tfrac{1}{2})\sum_{k=1}^{p}e_kV_k'{}_+ + (1/2\pi\Delta)\sum_{l_1,l_2,l_3=-\infty}^{\infty}{}'\frac{B_{l_1l_2l_3}A_{-l_1-l_2-l_3}}{\sum_{j=1}^{3}\left(\sum_{n=1}^{3}l_nb_j^{\,n}\right)^2}.\end{aligned} \tag{8}$$

Substituting in Eq. (7) the results expressed in Eq. (8) and collecting terms we obtain Φ in its final form

$$\Phi = (1/2\pi\Delta)\sum_{l_1,l_2,l_3=-\infty}^{\infty}{}'\frac{B_{l_1l_2l_3}B_{-l_1-l_2-l_3}+2A_{l_1l_2l_3}B_{-l_1-l_2-l_3}}{\sum_{j=1}^{3}\left(\sum_{n=1}^{3}l_nb_j^{\,n}\right)^2} + (\tfrac{1}{2})\sum_{k=1}^{p}e_kV'_{k+}. \tag{9}$$

Eq. (9) gives in compact form the potential energy of the base cell of the lattice under consideration. Given the quantities $a_j^{\,n}$, e_k, $x_i^{\,k}$, and the function $\rho(x_1, x_2, x_3)$, the value of Φ may be calculated by Eq. (9). A method devised by Ewald enables us to calculate the quantity $(1/2)\sum_{k=1}^{p} e_k V_k'{}_{+}$ without too much difficulty.[4]

An examination of Eq. (9) shows that the potential energy of the cell consists of three parts. The first part is the energy of the negative space charge and involves the coefficients $B_{l_1l_2l_3}$ $B_{-l_1-l_2-l_3}$. The second part is the mutual energy of the negative space charge and the positive point charges. It involves the coefficients $A_{l_1l_2l_3}$ $B_{-l_1-l_2-l_3}$. The third part as given by $(1/2)\sum_{k=1}^{p} e_k V_k'{}_{+}$ is the energy of the positive point charges. The first and third parts are essentially positive while the second part is negative.

The expression for Φ as given in Eq. (9) has some advantages over the expressions usually given for the potential energy of a lattice cell. It is usually assumed that the ions making up an ionic crystal can be treated as point charges. No attempt is made to take into account the actual distribution of electrons around the nuclei. As a result it is necessary, for the sake of achieving equilibrium, to introduce an additive term in the energy expression representing the effect of certain repulsive forces existing between the sions. In the expression here developed we have taken into consideration the distribution of the electrons in the crystal in so far as it is possible to replace a negative space charge by a corresponding electron atmosphere. This obviates the necessity of introducing extra terms representing repulsion since the sheath of electrons around each nuclei will automtically bring into play repulsive forces of considerable magnitude when the ions are close together.

Furthermore the coefficients $B_{l_1l_2l_3}$ which play an important part in this theory can, with only a few minor assumptions, be identified with the structure factors of the crystal in question.[5] The structure factors for some crystals have been determined experimentally. For these crystals Φ may be calculated not only for the accepted crystal parameters but also for arbitrary parameters. This enables us to determine parameter values which give minimum values of Φ and therefore states of stable equilibrium. In the following section we give the results of some determinations of Φ for the halides NaCl, NaF, and LiF.

APPLICATIONS

The halides NaCl, NaF, and LiF are simple cubic crystals. The expression for Φ as given in Eq. (9) becomes considerably simpler for this type of a crystal. We carry through the computation of Φ for NaCl as illustrating the general method. In order to use the experimentally determined values of the structure factors it is necessary to take the origin at the heaviest ion in the crystal.[6] This is at the Cl ion for NaCl.

There are two kinds of ions in the NaCl crystal so that

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[4] e. g. M. Born, 159–162.

[5] A. H. Compton, X-Rays and Electrons, Chap. 5 (1926).

[6] R. J. Havighurst, Phys. Rev. **29**, 4 (1927).

$$e_1 = e_3 = e_5 = e_7 = 17e, \quad \text{and} \quad e_2 = e_4 = e_6 = e_8 = 11e$$

where e is numerically equal to the charge on the electron. Since NaCl is a cubic crystal we have

$$a_j{}^n = \begin{Bmatrix} 0 & \text{if} & n \neq j \\ a & \text{if} & n = j \end{Bmatrix}, \quad \text{and} \quad b_j{}^n = \begin{Bmatrix} 0 & \text{if} & n \neq j \\ b & \text{if} & n = j \end{Bmatrix}.$$

Evidently $a=1/b$ and $\Delta=a^3$. There are eight ions in each cell so that k runs from 1 to 8. The coordinates of the nuclei of these ions are

$$x_1{}^1 = x_2{}^1 = x_3{}^1 = x_2{}^2 = x_3{}^2 = x_2{}^3 = x_1{}^4 = x_3{}^4 = x_1{}^5 = x_1{}^6 = x_2{}^6 = x_3{}^7 = 0,$$

and

$$x_1{}^2 = x_1{}^3 = x_3{}^3 = x_2{}^4 = x_2{}^5 = x_3{}^5 = x_3{}^6 = x_1{}^7 = x_2{}^7 = x_1{}^8 = x_2{}^8 = x_3{}^8 = a/2.$$

We consider $\rho(\xi_1, \xi_2, \xi_3)$ as an even function of its arguments so that

$$B_{l_1l_2l_3} = \iiint \rho \exp\left[-\, i2\pi b(l_1\xi_1 + l_2\xi_2 + l_3\xi_3)\right]d\xi_1 d\xi_2 d\xi_3$$

$$= \iiint \rho \cos\left[2\pi b(l_1\xi_1 + l_2\xi_2 + l_3\xi_3)\right]d\xi_1 d\xi_2 d\xi_3 = B_{\pm l_1 \pm l_2 \pm l_3}.$$

So far we have considered ρ to be the negative space charge density in the crystal. We assume that it may be set equal to $-e\sigma$ where σ is the electron density in the crystal. But

$$\iiint \sigma \cos\left[2\pi b(l_1\xi_1 + l_2\xi_2 + l_3\xi_3)\right]d\xi_1 d\xi_2 d\xi_3 = 4F_{l_1l_2l_3}$$

where $F_{l_1 l_2 l_3}$ is the l_1, l_2, l_3 structure factor for the NaCl molecule in the crystal.[7] The factor 4 enters because there are four molecules in each cell of the crystal. Thus we have

$$B_{\pm l_1 \pm l_2 \pm l_3} = -\, 4eF_{l_1l_2l_3}.$$

The expression for Φ with the above modifications now takes the form

$$\Phi = (\tfrac{1}{2}) \sum_{k=1}^{8} e_k V'_{k+} + (1/2\pi a) \sum_{l_1, l_2, l_3=0}^{\infty}{}' \delta_{l_1l_2l_3}\left(\frac{-8e\alpha_{l_1l_2l_3}F_{l_1l_2l_3} + 16e^2(F_{l_1l_2l_3})^2}{l_1{}^2 + l_2{}^2 + l_3{}^2}\right) \tag{10}$$

where

$$\delta_{l_1l_2l_3} = \begin{Bmatrix} 8 \text{ if none of the subscripts are zero,} \\ 4 \text{ if only one of the subscripts is zero,} \\ 2 \text{ if only two of the subscripts are zero} \end{Bmatrix},$$

and where

$$\alpha_{l_1l_2l_3} = \begin{Bmatrix} 112e & \text{for the subscripts all even} \\ 24e & \text{for the subscripts all odd} \\ 0 & \text{otherwise} \end{Bmatrix}.$$

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[7] A. H. Compton, p. 160.

We are now in a position to calculate Φ for NaCl by the use of Eq. (10). The calculation of the term $(1/2)\sum_{k=1}^{8} e_k V_k{}^1{}_+$ is a rather long and laborious process. The standard method due to Ewald[8] is used for this calculation and need not be repeated here. The result for NaCl is $355e^2/a$. This amounts to less than three percent of the total value of Φ and thus contributes little to the energy of the cell.

The values of the structure factors for NaCl, and also for NaF and LiF, have been taken from a table of structure factors given by R. J. Havighurst.[6] These values as given by Havighurst include the Debye temperature factor. Using forty of these values and substituting in Eq. 10 we obtain for Φ of NaCl the value

$$\Phi\ (NaCl) \equiv -\ 13590\ e^2/a_0$$

where $a_0 = 5.628 \times 10^{-8}$ cm. This value of Φ cannot be compared with Born's value of the potential energy of a NaCl cell since this value includes the energy of the ions and takes into account the electron distribution in the crystal.

It is possible to compute Φ (NaCl) for various arbitrary values of the grating space since the structure factors for various values of a can be determined. The same can be done for NaF and LiF. The results are shown in tabulated form. a_0 represents the accepted grating space for the crystals under consideration and has the values $a_0(\text{NaCl}) = 5.628 \times 10^{-8}$ cm., $a_0(\text{NaF}) = 4.620 \times 10^{-8}$ cm, and $a_0(\text{LiF}) = 4.014 \times 10^{-8}$ cm. Values of $w = (a_0/e^2)\Phi$ are shown for the grating spaces $0.75a_0$, a_0, $1.25a_0$, $1.50a_0$, and $2.00a_0$.

TABLE I

	$0.75a_0$	a_0	$1.25a_0$	$1.50a_0$	$2.00a_0$
w(NaCl)	−11860	−13590	−12850	—	—
w(NaF)	− 4350	− 5360	− 5470	−4850	
w(LiF)[9]	− 1710	− 1950	—	−1980	−1800

An examination of Table I yields the interesting fact that a minimum value of w, and therefore of Φ, occurs for each of the three crystals in the neighborhood of the accepted grating space for that crystal. For NaCl a minimum occurs in the interval defined by $0.75a_0 < a < 1.25a_0$. It is quite likely that $w = -13590$ at $a = a_0$ is an actual minimum for NaCl, as it should be from theoretical considerations.

For NaF a minimum value of w lies in the interval $0.75a_0 < a < 1.50a_0$ but it appears to be closer to $a = 1.25a_0$ than to $a = a_0$. For LiF a minimum lies in the interval $0.75a_0 < a < 2a_0$ but it appears to be closer to $1.5a_0$ than to a_0. The reason for this shifting of the minimum value of w toward values of a greater than a_0 in the case of NaF and LiF is not clear. It may be that

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[8] M. Born, 158–162 (1926).

[9] The term $1/2\sum_{k=1}^{8} e_\kappa V_{\kappa+}{}^1$ has been omitted for LiF.

w has not been determined accurately enough to make the difference between the values of w at a_0 and at $1.25a_0$ or $1.5a_0$ significant. Or it may be that we are not justified in assuming that a negative space charge can be replaced by an electron distribution in the case of NaF and LiF, since the total number of electrons per cell diminishes rapidly as we go from NaCl to LiF. NaCl has 112 electrons per cell, NaF has 80, and LiF has only 48.

Although we have determined approximately the position of a single minimum value of Φ for each of the three crystals, there remains the question as to whether or not this is the only minimum value of Φ. From the form of Eq. 10 and from the general relation between the structure factors and the grating space we hazard the guess that it is, although this conjecture has not been proved.

By the general method outlined in this paper one ought to be able to determine other crystal parameters besides grating spaces. Also it may be possible to relate Φ, the lattice energy which is not a directly measurable quantity, to other quantities which are measurable by some kind of a cyclical process as has been done by Born and others.