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The Madelung Constant of the Sodium Chloride Crystal Lattice

An analysis of the Madelung constant of the sodium chloride crystal lattice has been made, in an effort to supplement information available in undergraduate textbooks. A method of approximation of the constant using the personal computer is presented.

Ionic lattice energy is defined as the energy released when isolated gaseous ions come together from infinite separation to form an ionic crystal. The model used for calculating this energy is the Born-Landé equation, the derivation of which is available in many undergraduate chemistry textbooks but what is not available is a thorough and correct treatment of the Madelung constant which forms an integral part of the equation. Here we take the sodium chloride (6:6) crystal and show how the infinite series giving the Madelung constant of the NaCl crystal lattice can be easily generated, relate it to the more familiar series, discuss convergence and the alternative rapidly converging expressions available for generating the constant. A method of approximation of the constant, based on simple three-dimensional geometry is also presented.

Relationship between the Madelung Constant and the Born-Landé Equation: Derivation of the Former

A large portion of the lattice energy (almost nine-tenth) is accounted for by electrostatic energy arising from electrostatic interactions between the ions in the formed crystal. The Born-Landé equation involves calculation of the electrostatic energy of a 'reference ion' resulting from electrostatic interactions with an infinite number of ions surrounding it in the crystal lattice and the Madelung constant plays a vital role in incorporating this infinite number of interactions into the equation. The assumptions made are: ions are point charges, the crystal is infinitely large, the distribution of ions is even and symmetric, so the environment around every ion in the crystal is the same.

Keywords

Madelung constant, 6:6 ionic crystal lattice, sodium chloride crystal, structural solid state chemistry, Born-Landé equation, computer aided learning.



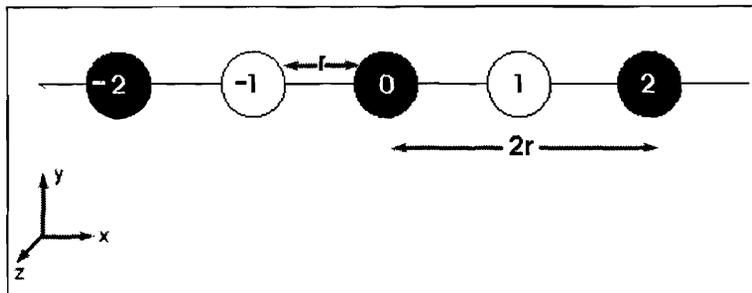


Figure 1. Linear arrangement of five point charges located on the positive and negative x axes.

Therefore once the energy for the reference ion is determined, it is multiplied by the Avogadro constant to obtain the electrostatic energy for one mole of ions. This forms the electrostatic component of the Born-Landé equation.

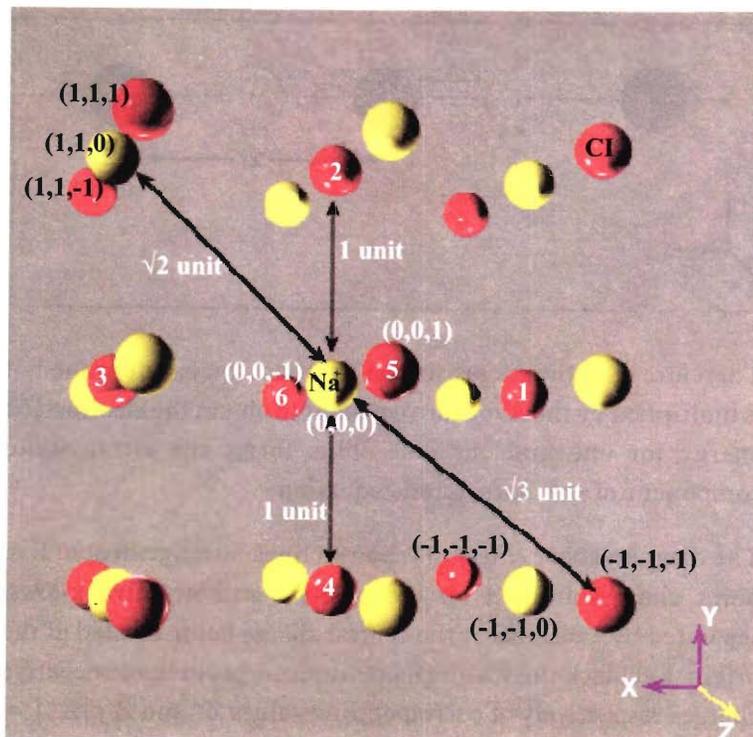
The diagram above (Figure 1) shows a linear arrangement of five point charges located on the positive and negative x-axes, separated by a distance r , the central charge being located at the origin. Let black and white spheres indicate positive and negative charges respectively of corresponding values Z^+ and Z^- , $|Z^+| = |Z^-|$. Taking r as unity, the electrostatic energy of the central charge in the presence of surrounding charges, is:

$$\begin{aligned}
 E &= Z^+Z^-/(4\pi\epsilon_0) + Z^+Z^+/(4\pi\epsilon_0 2) + Z^+Z^-/(4\pi\epsilon_0) + \\
 &\quad Z^+Z^+/(4\pi\epsilon_0 2) \\
 &= Z^+Z^-/(4\pi\epsilon_0)(1 - 1/2 + 1 - 1/2) \\
 &= \frac{Z^+Z^-}{4\pi\epsilon_0} \cdot \sum_{x=-2}^2 \frac{(-1)^{|x-1|}}{|x|}; \quad x \neq 0 \quad (1)
 \end{aligned}$$

The above expression can be extended to a system of linearly arranged infinite number of alternating charges on either side of the central reference charge by summing over x from $-\infty$ to $+\infty$ in (1). Note that $|x|$ in the denominator is nothing but the distance of respective charges along the x -axis from the origin. Assigning cartesian coordinates to the points, the expression becomes:

$$E = \frac{Z^+Z^-}{4\pi\epsilon_0} \cdot \sum_{i=-\infty}^{\infty} \sum_{j=0}^0 \sum_{k=0}^0 \frac{(-1)^{|i+j+k-1|}}{\sqrt{(i^2 + j^2 + k^2)}}; \quad i \neq 0 \quad (2)$$

Figure 2. Unit cell of sodium chloride with coordinates assigned. Like charges are represented by spheres of same colour.



Note that the above expression is a conditionally convergent alternating series. The NaCl crystal lattice can also be assigned Cartesian coordinates with the reference ion placed at the origin and the remaining placed at coordinates (x, y, z) where x, y, z are not all zeroes and x, y, z belong to the infinite set of integers ranging from $-\infty$ to $+\infty$. The justification is that all ions are orthogonal with respect to adjacent nearest neighbours and also equidistant from them (Figure 2); the NaCl crystals belong to $fm\bar{3}m$ space group that has all the symmetry elements of an octahedron.

The distribution of sodium and chloride ions is not random but is strictly alternating, so it is important to assign the individual interaction type for each lattice point with the origin. The type of interaction is given by $(-1)^{|x+y+z-1|}$ at point (x, y, z) , a positive term standing for a favourable interaction and a negative term for an unfavourable interaction.

Thus, for the three dimensional distribution of charge, the electrostatic energy of the ion at the origin is:

$$E = \frac{Z^+ Z^-}{4\pi\epsilon_0 r} \cdot \sum_{i=-\infty}^{\infty} \sum_{j=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \frac{(-1)^{|i+j+k-1|}}{\sqrt{(i^2 + j^2 + k^2)}}; (i, j, k) \neq (0,0,0) \quad (3)$$

For one mole of ions, the electrostatic energy is:

$$E = \frac{Z^+ Z^- N_A}{4\pi\epsilon_0 r} \cdot \sum_{i=-\infty}^{\infty} \sum_{j=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \frac{(-1)^{|i+j+k-1|}}{\sqrt{(i^2 + j^2 + k^2)}}; (i, j, k) \neq (0,0,0) \quad (4)$$

(since r was taken as the unit distance)

Comparing this with the electrostatic component of the Born-Landé equation for NaCl crystal, the Madelung constant equals:

$$M_c = \sum_{i=-\infty}^{\infty} \sum_{j=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \frac{(-1)^{|i+j+k-1|}}{\sqrt{(i^2 + j^2 + k^2)}}; (i, j, k) \neq (0,0,0) \quad (5)$$

or M_c = summation (interaction type/distance between a lattice point and the origin) which is an alternating conditionally convergent series in three dimensions [5].

However, to most students the more familiar form of the Madelung constant is:

$$M_c = 6 - 12/\sqrt{2} + 8\sqrt{3} - 6/\sqrt{4} + 24/\sqrt{5} - 24/\sqrt{6} - 12/\sqrt{8} + 30\sqrt{9} - \dots \quad (6)$$

Unfortunately this infinite series does not converge to anything and the above representation is wrong [6]. In equation (6), the terms have the form: (type of interaction \times number of equivalent lattice points)/(distance of the points from the origin). By 'equivalent lattice points' we mean all equidistant lattice points having the same type of interaction with the reference ion. The multiplicity arises from the fact that the distances of points $(\pm l, \pm m, \pm n)$, $(\pm m, \pm n, \pm l)$, $(\pm n, \pm l, \pm m)$, $(\pm n, \pm m, \pm l)$, $(\pm l, \pm n, \pm m)$, $(\pm m, \pm l, \pm n)$ from the origin are the same. Thus $(0,0,1)$,

$(0,0,-1)$, $(0,1,0)$, $(0,-1,0)$, $(1,0,0)$, $(-1,0,0)$ corresponding to the six Cl^- ions surrounding the central reference sodium ion, are all at a distance of one unit from the center and have the same interaction type (positive) (*Figure 2*). This forms the first term in (6). Similarly the points $(0, \pm 1, \pm 1)$; $(\pm 1, \pm 1, 0)$ and $(\pm 1, 0, \pm 1)$ (12 in all) occupied by sodium ions (given that sodium and chloride ions alternate each other) are equidistant with negative interaction, forming term 2 of (6) and points $(\pm 1, \pm 1, \pm 1)$ (8 in all) are equidistant with positive interaction being occupied by chloride ions, forming term 3 of (6).

There is one more instance which can yield multiplicity, as in the term $30/\sqrt{9}$ in (ii). Since the distance $\sqrt{9}$ arises from the application of Pythagoras theorem to the three-dimensional lattice, the number 9 is a sum of three integers, which must themselves be squares of integers. But $9=9+0+0$ and $9=4+4+1$, so the points $(\pm 3, 0, 0)$, $(0, \pm 3, 0)$, $(0, 0, \pm 3)$ (6 in all) and $(\pm 2, \pm 2, \pm 1)$, $(\pm 2, \pm 1, \pm 2)$, $(\pm 1, \pm 2, \pm 2)$ (24 in all) are all at an equal distance from the origin with the same type of interaction ($3+1=\text{even}$, $2+2+1+1=\text{even}$). This gives us the term $(6+24)/\sqrt{9}$ or $30/\sqrt{9}$.

Thus the procedure for generating the multiplicity in a term in (6) is:

1. Uniquely decompose the square of distance of a particular lattice point from the origin into sum of three squares of integers (e.g. 9 to $4+4+1$ and $9+0+0$).
2. For a particular group of three squares, the multiplicity is given by:

$$m = \frac{3! \times 2^3}{x! \times 2^3} \quad (7)$$

where x is the number of coordinates having the same magnitude and y is the number of coordinates with magnitude 0. For example, for $9+9+0$ or $(3,3,0)$, $x=2, y=1$ and $m=12$. The formula follows from the fact that for non-zero coordinates', two values



(positive and negative) are possible unlike a coordinate with magnitude zero where only 1 value is possible. Any three coordinates can be arranged in $3!$ ways, where repetition in counting in case of existence of recurring values (the recurring value of 3 for instance in the above example) can be eliminated by dividing $3!$ by $x!$.

3. Add the value obtained from step 2 for all groups obtained from step 1 to generate the total multiplicity.

A simple physical interpretation of multiplicity can be given as the number of lattice points coinciding with the surface of a hypothetical spherical shell of radius equal to the distance of the lattice points from the reference ion, with its centre at the origin. The sum of the first three terms corresponds to summing up (5) from -1 to 1 for i, j, k . However the basic difference between the two is that while summing up (5) leads to summation of corresponding values of lattice points contained within and located on the surface of an expanding cube, summing up (6) leads to summation of the same in and on an expanding sphere [1]. The former approach converges whereas the latter does not [6]. However, in [1], the authors have imposed the condition of charge neutrality for the convergence of (5). Though this approach speeds up convergence to some extent, the condition is not a prerequisite for the convergence of (5).

The value of the Madelung constant correct up to 15 decimal digits is 1.747564594633182. The problem with summing up of the series represented by (5), even by using computers, is its very slow convergence making its use impractical. How slow is the convergence can be realized from the following estimation: Summing up (5) from -11 to $+11$ for i, j, k (or 23^3-1 steps), convergence is achieved at 1 place after the decimal point, at 2 places after the decimal point after a whopping $(475^3 - 1)$ steps and if we approximate 475 to square of 23, the computation time increase becomes exponential with respect to increase in degree of accuracy.



However, analytic series that generate the constant but do so by converging much more rapidly have been propounded, notable among them being the Benson-Mackenzie formula and the Hautot formula. With just 100 steps the latter is accurate to 14 decimal places, whereas the former gives the same result with just 36 steps.

Benson-Mackenzie formula:

$$M_c = 12\pi \sum_{m=1, n=1}^6 \sec h^2 \{[\pi\sqrt{((2m-1)^2 + (2n-1)^2)}/2]\} \cdot$$

$$= 1.7475645946 3318 \quad (8)$$

Hautot formula :

$$M_c = -\frac{\pi}{2} + \frac{9\ln 2}{2} - 12 \sum_{m=1, n=1}^6 \frac{(-1)^m \operatorname{cosec} h[\pi\sqrt{(m^2 + n^2)}]}{\sqrt{(m^2 + n^2)}} =$$

$$1.7475645946 3318 \quad (9)$$

A Considerably Fast and Simple Algorithm to Approximate the Constant on a PC

From (7), the following facts stand true:

For

1. $(N, 0, 0)$, there are at least six equivalent lattice points,
 2. $(N, n, 0)$, $n < N$, $N > 1$, there are at least 24 equivalent lattice points,
 3. $(N, N, 0)$, there are at least 12 equivalent lattice points (all with negative interaction for the NaCl crystal),
 4. (N, n, m) , $m < n < N$, $N > 2$, there are at least 48 equivalent lattice points,
 5. (N, n, n) , $n < N$, $N > 1$ there are at least 24 equivalent lattice points,
 6. (N, N, n) , $n < N$, $N > 1$, there are at least 24 equivalent lattice points,
 7. (N, N, N) , there are at least 8 equivalent lattice points,
- where N, n, m are natural numbers.



For any natural number N such that $n = 1$ to $N - 1$ and m is always less than n , if we calculate the inverse of the distance from the origin, multiply it with the interaction type and the number of equivalent points mentioned above for all coordinates falling under 1-7 and sum them up (see (6)), we get a fast summation of corresponding values for lattice points on the surface of a cube of side $2N + 1$ units. Summing up all values obtained for $N = 1$ corresponds to summing up (5) from -1 to 1 for i, j, k . Adding this to the value obtained for $N = 2$, corresponds to summing up (5) from -2 to 2 for i, j, k . Thus the sequence of partial sums of series (5) can be generated easily. A characteristic of this sequence is that its term S_n oscillates about the limit (the Madelung constant), with steadily decreasing amplitude for $n = 1, 2, 3, \dots, N$ (See *Figure 3*, the value of S_n corresponds to the value of $X1/Y1$, for the n th cycle. The value can be resident in either memory space $X1$ or $Y1$, depending on the initial allocation, see below), (sequence of partial sums of an alternating conditionally convergent series in dimension one).

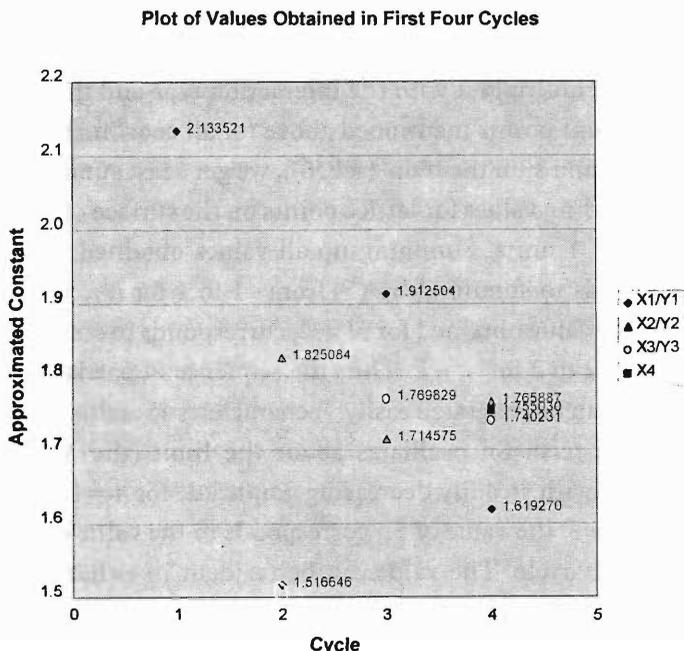
This characteristic is exploited by a recursive algorithm which employs a method of successive means to accelerate convergence and reach as close to the limit as the computer permits.

1. In the first cycle all interactions for $N = 1$ are calculated and stored in memory space, say $X1$.
2. In the second cycle all interactions for $N = 2$ are calculated, added to the value obtained for $N = 1$ and stored in memory space, say $Y1$.
3. Next the mean of $X1$ and $Y1$ is taken and stored in memory space, say $X2$.
4. In the third cycle all interactions for $N = 3$ are calculated and added to the value obtained for $N = 1 + N = 2$ and stored in memory space $X1$, replacing the old value of $X1$.
5. Next the mean of $X1$ and $Y1$ is taken and stored in $Y2$.
6. The mean of $X2$ and $Y2$ is taken and stored in memory space $X3$.

The process is continued until the computer finds that values of



Figure 3. Plot of approximated values in various memory spaces against the cycle number.



Suggested Reading

- [1] P Grosso and others, *J. Chem. Educ.*, Vol. 78 pp. 1198, 2001.
- [2] J E Huheey, E A Keiter and R L Keiter, *Inorganic Chemistry, Principles of Structure and Reactivity*, Fourth Edition; Addison Wesley Longman, Delhi, pp .74-80, 2001.
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- [5] D Borwein and J M Borwein, A note on alternating series in several dimensions, *Amer. Math. Monthly*, Vol.93, pp.531-539, 1986.
- [6] D Borwein and J M Borwein, Convergence of lattice sums and Madelung's constant, *J. Math. Phys.*, Vol.26, pp.2999-3009, 1985.

two memory spaces say X_a and Y_a , where a is any natural number less than N , are the same. This is the condition for assumption that convergence has been achieved. The accuracy and the number of cycles made depend on the limit of precision of the computer used and/or that set by the programmer. For the standard IBM compatible personal computer this is the first 16 decimal digits with double precision arithmetic [4]. A program written in MS Visual Basic which uses the above algorithm, takes less than a second on a puny 500 MHz Celeron processor based PC, for just 50 cycles (50 generated terms of the sequence) with memory allocation for 15 successive means to assume convergence at 1.74756459463317 (accurate up to first 14 decimal digits). Though the number of computation steps is considerably larger than for either (8) or (9), the process is easier to understand, does not require prior input of the value of pi or computation of logarithmic/hyperbolic functions and accuracy can be improved simply by switching to a higher precision compiler with increased number of cycles and memory space.