

Madelung Constants for Ionic Crystals using the Ewald Sum

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ABSTRACT

Ionic crystal configuration energies have always been one of the bugbears of computational thermodynamics due to the inherent long-range interactions. Unlike the van der Waals forces associated with non-ionic compounds, it is not possible to utilize a long-range cutoff; ionic interactions require summation over an infinitely large crystal lattice. The situation is further complicated by the fact that the resulting infinite series for an ordered crystal lattice is non-convergent. This means that a direct summation over the charged particles is not feasible. This paper develops and analyzes a powerful yet underutilized method for calculating these lattice energies, the Ewald sum. Not only is this a powerful and accurate method of calculating the configuration energies of ionic crystals, it is also not dependent on the existence of crystal structure. Hence this method is useful in any application involving Coulombic interactions, including substances in the liquid phase. The general Ewald method is presented with some simplifying assumptions to produce a working equation amenable to computer evaluations and sample computations are made for NaCl and CsCl. Extensive discussion is presented on determining the optimum splitting parameter. A simple yet general FORTRAN program for calculating the Madelung constant for an ionic system of any phase is presented and a sensitivity analysis is performed.

Key words: *Ewald sum, Ionic crystals, Madelung constant, Long-range interactions, Molecular Simulation, Reciprocal space*

INTRODUCTION

Lattice energy calculations for ionic crystals are physically straightforward, yet in practice, quite difficult. The difficulty arises due to the long-range nature of Coulombic interactions. Unlike van der Waals type interactions which are often modeled using an r^{-6} decay rate (Smith et al. 1996 and Haile 1992), Coulombic interactions have a decay rate of r^{-1} . It can be shown (McQuarrie 1976) that decay rates of less than r^{-3} require special mathematical treatment. Various methods have been employed (Berry et al. 1980), but none as ingenious and powerful as the method proposed by Ewald (Ewald 1921).

The landmark paper of De Leeuw et al. 1980 developed a general method of using Ewald's method in the solution of problems involving charged particles. Their paper provides a terse derivation of the Ewald summations formula but unfortunately, their final results are not yet amenable to implementation on a computer. One of the goals of this paper is to present a simple, user-friendly and straightforward algorithm for employing the Ewald summation method. Also, a sensitivity analysis is made to discuss selection of the Ewald splitting parameter, correcting some common

misconceptions. Finally, the method is illustrated using a simple FORTRAN program applied to table salt and cesium chloride.

BACKGROUND

The difficulty in computing these ionic lattice sums is illustrated using an NaCl (table salt) crystal lattice which is shown in Figure 1. A simple and straightforward method to calculate the ionic configuration energy is to imagine an infinitely large crystal lattice, choose any arbitrary ion in the system as the center, and begin adding up charges, starting with the central ion's nearest neighbors. If we take the ionic spacing to be distance d and start from the center ion in Figure 1, we see that there are 6 nearest neighbors which are d units from the central ion. Moving outward, we then see that there are 12 second nearest neighbors at a distance $d\sqrt{2}$ units from the central ion. Continuing outward, there are 8 third nearest neighbors at a distance $d\sqrt{3}$ units from the center, 6 fourth nearest neighbors $2d$ units from the center, 24 fifth nearest neighbors $d\sqrt{5}$ units from the center, and so on. We are constructing an infinite series as follows:

$$E = \frac{e^2 q_1 q_2}{d} \left[6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}} - \dots \right] \quad (\text{Eq. 1})$$

where e is the electronic charge, q is the dimensionless ionic charge (± 1), and d is the ion spacing. This is usually written as

$$E = \frac{e^2 q_1 q_2}{d} M \quad (\text{Eq. 2})$$

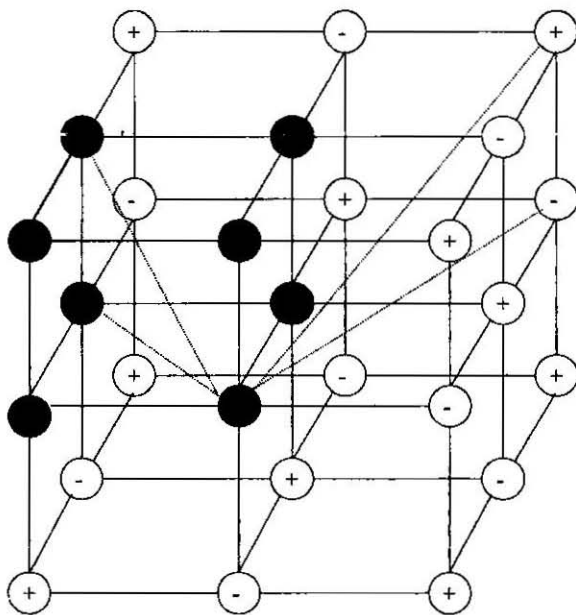


FIGURE 1. Spatial Arrangement of Ions in NaCl Crystal Lattice

where M is the Madelung constant. The reported value for table salt is $M = 1.747558$ (Berry et al. 1980). A direct evaluation of the series in (Eq. 1) is easily carried out by computer. Results are displayed in Figure 2, which show the occupancies out as far as 36 coordination shells. Figure 3 shows the cumulative value of the Madelung constant of (Eq. 2) out as far as 250 coordination shells, i.e. 250 terms in the series of (Eq. 1). We see from Figure 2 that the value of the series is not converging. It turns out that this series is conditionally convergent (De Leeuw et al. 1980) and no matter how many terms are included in the series of (Eq. 1), the series will not converge. More sophisticated methods are needed. A method of summing this series has been devised by H.M. Evjen (Berry et al. 1980), but this method works only when the particles are in their lattice positions. If the position of the

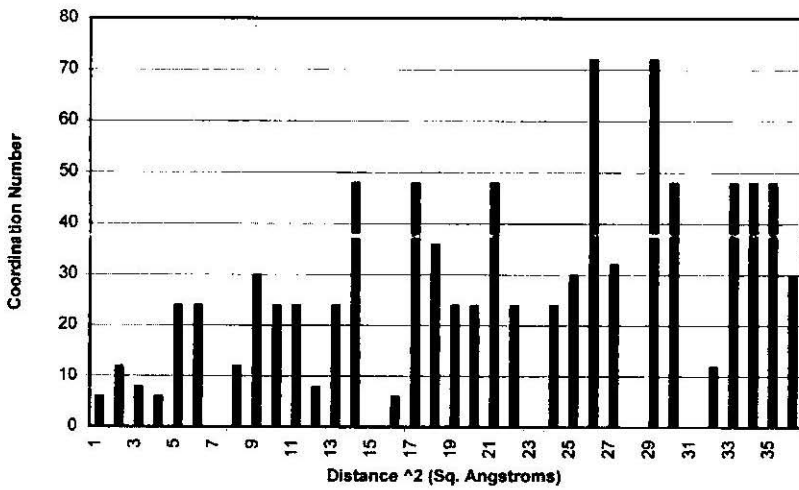


FIGURE 2. Coordination Number for First 36 Shells of NaCl Crystal

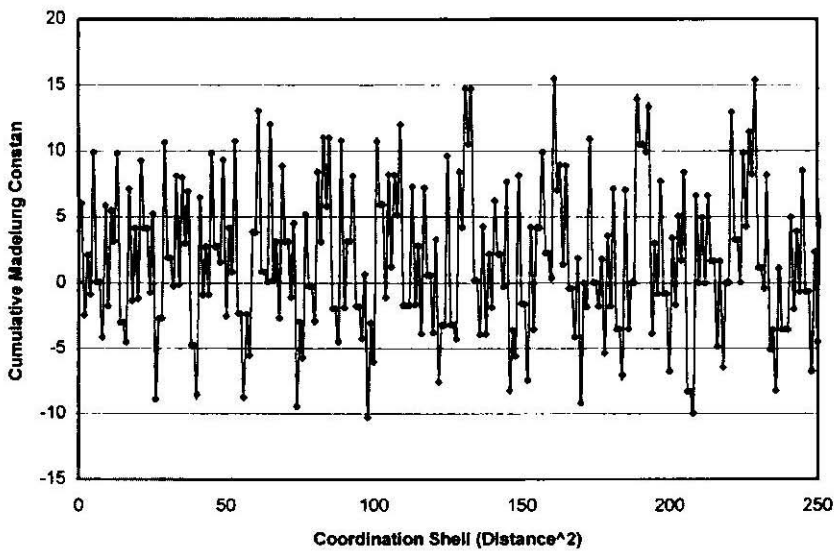


FIGURE 3. Direct Summation – Summation is not Converging

ions were perturbed (as in lattice vibration) or if they were to move freely about the system cell (as in a liquid) then this procedure would be unsuitable. These problems are overcome with the Ewald summation method which calculates the ionic energy for a system of ions in any spatial arrangement.

THE EWALD SUMMATION METHOD

Simply stated, the Ewald method carries out the summation in (Eq. 1) in two parts, a small region from zero to some convenient cutoff in real space, and the remainder in reciprocal wave space. The relative contributions of the two terms is governed by the splitting parameter, α . Essentially the method uses a Fourier transform to map real space to reciprocal space so that the summation of (Eq. 1) to infinity may be easily calculated. More specifically (Allen et al. 1987), the crystal is considered to be replicated infinitely in each of the three dimensions, as before. Each point charge in the system is surrounded by a Gaussian charge distribution of equal magnitude and opposite sign. This charge distribution screens the point charges making them short ranged and amenable to a small, real space cutoff. The set of point charges may be summed over all particles in the system and in the neighboring image systems. The summation is corrected by subtracting off the Gaussian distributions to retrieve the effect due to the original system of point charges. The canceling distribution is summed in reciprocal space.

Developing the Ewald summation formula is a difficult task involving imaginary numbers, and a complete and corrected derivation is available from the author. After considerable effort, we finally develop (see Appendix 1) the working equation:

$$E = \frac{2\pi}{V_0} \sum_{\vec{k}=0} \frac{\exp\left(-\frac{|\vec{k}|^2}{4\alpha^2}\right)}{|\vec{k}|^2} \left| \sum_{j=1}^N q_j \exp(i\vec{k} \cdot \vec{r}_j) \right|^2 + \sum_{1 \leq i < j \leq N} \left[\frac{q_i q_j}{|\vec{r}|} \operatorname{erfc}(\alpha|\vec{r}|) \right] - \frac{\alpha}{\sqrt{\pi}} \sum_{j=1}^N q_j^2 \quad (\text{Eq.3})$$

where $i = \sqrt{-1}$ and erfc is the complementary error function:

$$\operatorname{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$

and E is the total (dimensionless) Coulombic molar configuration energy. The vector \vec{k} represents a three dimensional vector in wave or reciprocal space, while the vector \vec{r} represents a vector in real space and indices i and j are over the number of particles (N) in the principal cell. It is assumed that the principal cell is a cube of Volume V_0 .

The dimensionless energy in (Eq. 3) for salt is found to be -6.99026 which corresponds to a Madelung constant (Appendix II) of 1.747565 over the range $5 < \alpha < 35$. This is shown in Figure 4. When splitting parameter, α , lies outside this range, then Madelung values are in error due to either over

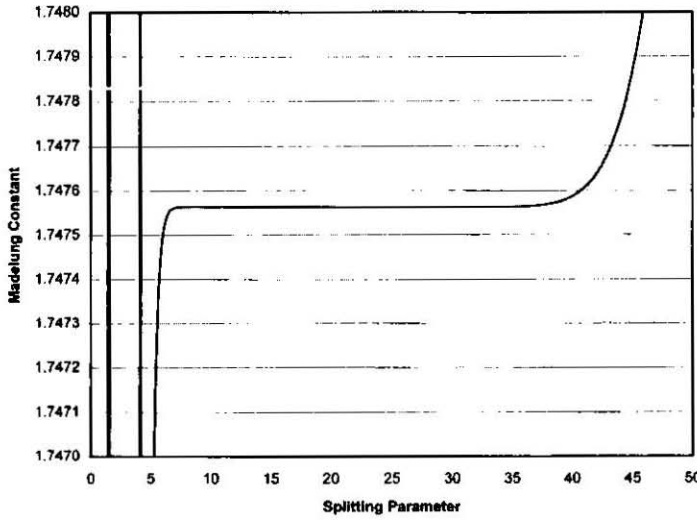


FIGURE 4. Madelung constant as a function of splitting parameter for rock salt. Four 'Molecules' in principal cell, 40 wave space vectors were used

or under weighting the wave space contribution at the expense of the real space contribution. Section IV discusses selection of this splitting parameter. The obtained value is in close agreement with the reported value of 1.747558 (Berry et al. 1980). The dimensionless energy, E , is readily converted to physical units, E_p , by multiplying by a conversion factor, F :

$$E_p = E \times F$$

where

$$F = \left(\frac{e^2}{4\pi\epsilon_0} \right) \left(\frac{2N_A}{N_m} \right) \left(\frac{\rho}{M_r} \right)^{\frac{1}{3}} \times 100 \text{ cm/m} \times 0.001 \text{ kJ/J} = 105.515 \text{ kJ/mol}$$

$$e = 1.60219 \times 10^{-19} \text{ C}$$

$$\epsilon_0 = 8.854188 \times 10^{-12} \text{ C}^2 \text{ s}^2/(\text{kg m}^3)$$

$$N_A = 6.02205 \times 10^{23} \text{ molecules/mol}$$

$$N_m = \text{Number of molecules in primary cell} = 4$$

$$\rho = 1.35 \text{ g/cm}^3$$

$$M_r = \text{Total mass of primary cell} = 232/N_A \text{ g}$$

yielding a value of $E_p = -737.58 \text{ kJ/mol}$, which agrees with the tabulated value $E_p = -737.37 \text{ kJ/mol}$ (Smith 1986). In addition, the same program was used to calculate the Madelung constant for CsCl, and yielded 2.03553 which agrees exactly with the recorded value (Born et al. 1998) of 2.0354 (Appendix II).

PARAMETER SELECTION AND SENSITIVITY

For discussion purpose, we consider (Eq. 3) to consist of three parts, i.e., three contribution to the total dimensionless Coulombic configuration energy,

E , of the salt lattice: Two real space contribution (E^S and E^E) and one reciprocal or wave space contribution (E^W):

the real space constant contribution (independent of particle configuration):

$$E^S = -\frac{\alpha}{\sqrt{\pi}} \sum_{j=1}^N q_j^2 \quad (\text{Eq. 4})$$

the complementary error term contribution:

$$E^E = \sum_{1 \leq i < j \leq N} \left[\frac{q_i q_j}{|\vec{r}|} \operatorname{erfc}(\alpha |\vec{r}|) \right] \quad (\text{Eq. 5})$$

and the reciprocal or wave space contribution:

$$E^W = \frac{2\pi}{V_0} \sum_{k=0} \frac{\exp\left(-\frac{|\vec{k}|^2}{4\alpha^2}\right)}{|\vec{k}|} \left| \sum_{j=1}^N i\vec{k} \cdot \vec{r}_j \right|^2 \quad (\text{Eq. 6})$$

Therefore,

$$E = E^S + E^E + E^W \quad (\text{Eq. 7})$$

where (dimensionless) $E = -6.9883$ corresponds to that reported by (Smith 1986) for rock salt.

A simple FORTRAN program for evaluation the Madelung constant and Coulombic configuration energy of a NaCl crystal is given and discussed in Appendix II. The most time consuming part of (Eq. 3) is evaluation of E^W which involves a complex sum over wave space vectors, \vec{k} , since this is effectively a triple-nested loop. It is therefore desirable to minimize the number of wave space vectors contained in the summation; this will be discussed consequently. The summation over i and j represent real space summations over particles in the principal cell. The key parameter is the splitting parameter, α . While there are no inherent restrictions on the value of the splitting parameter in the initial work of De Leeuw et al., we will soon see that the further assumptions proposed by Smith (1986) which have been incorporated into (Eq. 3) require judicious selection of this parameter. (See Appendix 1).

We have seen that the Ewald algorithm does indeed reproduce the correct value of the Madelung constant to five decimal places, 1.74756 and the value for cesium chloride, 2.03535. It is beneficial to observe the sensitivity of the calculation to three degrees of freedom in (Eq. 3).

1. The value of the splitting parameter, α ;
2. The number of wave vectors (KMAX in Appendix II) included in the reciprocal space calculation.
3. Number of ions contained in the unit cell, N ;

EFFECT OF CHANGING THE VALUE OF THE SPLITTING PARAMETER, (AND NUMBER OF WAVE VECTORS)

As mentioned above, the splitting parameter effectively determines the relative importance of the real and wave space contributions to the total energy. The larger the value of α , the larger the relative contribution of the reciprocal space term. This then requires more wave space vectors (KMAX in Appendix II) to be included in the summation in (Eq. 6). This is shown in Figures 4 and 5 which all employ four NaCl 'molecules' or eight ions ($N=8$ in Eq. 3) in the principal cell. Figure 4 shows the calculated Madelung constant as a function of splitting parameters, α , using 40 wave space vectors. We observe the correct value (1.74756) from along the plateau which extends from about $5 < \alpha < 35$. The large number of wave space vectors ($KMAX = 40$) enabled valid results over this wide range of the splitting parameter. This large number of wave space vectors also makes the program very slow to execute.

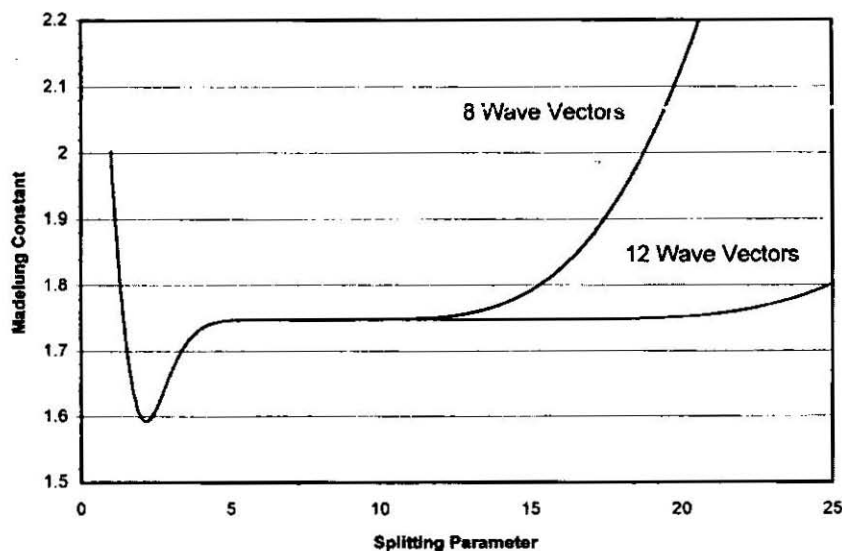


FIGURE 5. Madelung constant as a function of splitting parameter for NaCl crystal. Four 'molecules' in principal cell

In Figure 5 we see that when 12 wave vectors are used, the plateau extends from around $5 < \alpha < 17$, and when eight wave vectors are used the plateau extends from $5 < \alpha < 11$. Using less wave space vectors makes the program run much more quickly. We observe then that we can be less choosy about the splitting parameter (at the expense of a much slower computation) if we are willing to include additional wave vectors in the calculation. Figure 6 shows for eight wave vectors the relative contributions of E^s , E^E and E^w (in units of kJ/mol) to the total configuration energy, which should match the literature value of $E_p = -737.37$ kJ/mole (Smith 1986). We see that the range of validity for (is again $5 < \alpha < 11$ and that the principal contributions to the total energy are from the real space constant, E^s , and from the wave space term, E^w . This is because the small size of the principal

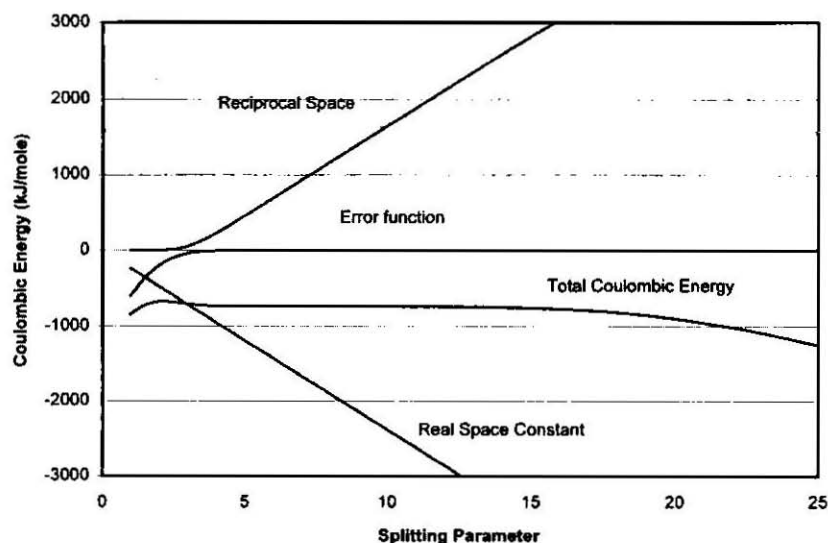


FIGURE 6. Energy contributions as a function of splitting parameter for NaCl crystal. Eight wave space vectors were used. Four 'molecules' in principal cell.

cell ($N=8$) precludes a significant real space contribution from the error function term.

Many applications, as in Monte Carlo or molecular dynamics simulation (Rapaport 1998), require repetitive calculations of Coulombic interaction energies. One would then want to use a minimum number of wave space vectors. This must be done very carefully and after much experimentation. An example is shown in Figure 7, where agains, we plot Madelung constant

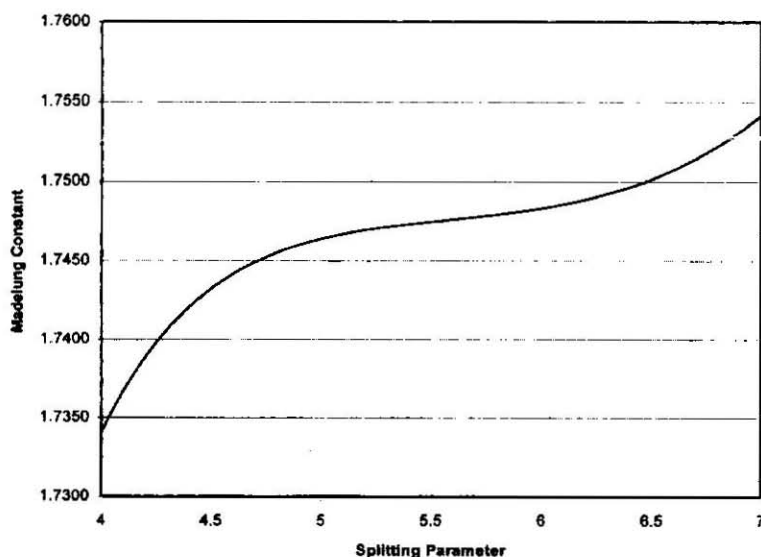


FIGURE 7. Madelung constant as a function of splitting parameter for NaCl crystal. Four 'molecules' in principal cell, three wave space vectors were used

as a function of splitting parameter. However, this time, we have only used three wave space vectors, i.e., $K_{MAX}=3$. This computation is extremely rapid and yields the Madelung constant to four decimal places accuracy (1.7476) but only when a splitting parameter value of 5.60 is used. A slightly different value from 5.60 (i.e., 5.59 or 6.01) will yield a less accurate value for the Madelung constant. It is quite risky doing these calculations when only a specific point value of the splitting parameter is able to yield correct results. De Leeuw et al., recommend an efficiency-optimized value of (of 5.714, which can be seen from Figure 7) would be somewhat less than optimal for this system. Also, we see from Figure 7 that selecting the splitting parameter on the basis of minimizing the potential energy will be fruitless, since in fact, the optimal value occurs at the inflection point, i.e.,

$$\frac{d^2M}{d\alpha^2} = 0 \quad (\text{Eq.8})$$

In short, these values must be determined very carefully for the specific system at hand since the plateau becomes an inflection point, not a local or global extrema efficiency is maximized.

EFFECT OF CHANGING THE SIZE OF THE PRINCIPAL CELL

Figure 8 shows the relative contributions to the total Coulombic energy for a system comprised of 216 ions ($N=216$) which employs eight wave space vectors. We see now, that over the acceptable range of α , that all three energy contributions in turn make a significant contribution to the total. Note that the valid range of α is not significantly enlarged by incorporating more particles in the principal cell. Neither is there any improvement in the accuracy of the calculated value of the Madelung constant.

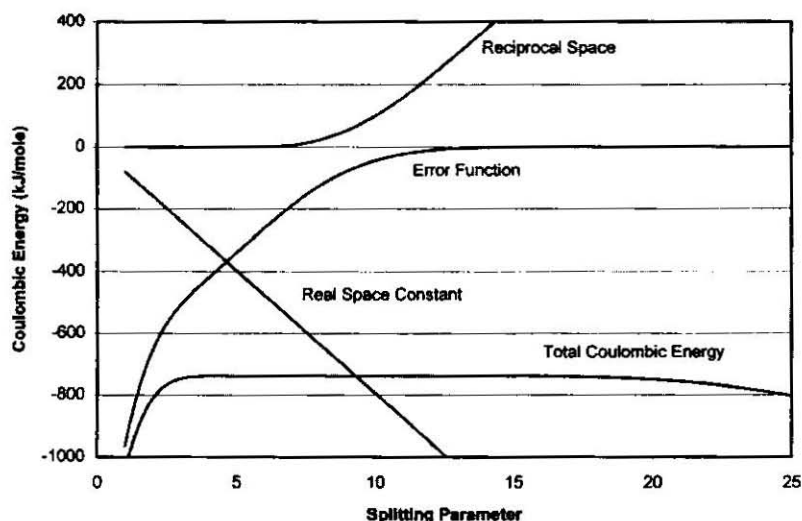


FIGURE 8. Energy contribution as a function of splitting parameter for NaCl crystal. Eight wave space vectors were used. 108 'molecules' in principal cell

From Figure 9, we observe how the three contributions to the Coulombic energy vary as a function of size of the principal cell. The wave space contribution becomes negligible for $N > \approx 500$ ions in the principal cell. This would then offer a considerable savings in computation time, and it may be possible in some application to neglect this computationally expensive term. Again, this must be done very carefully.

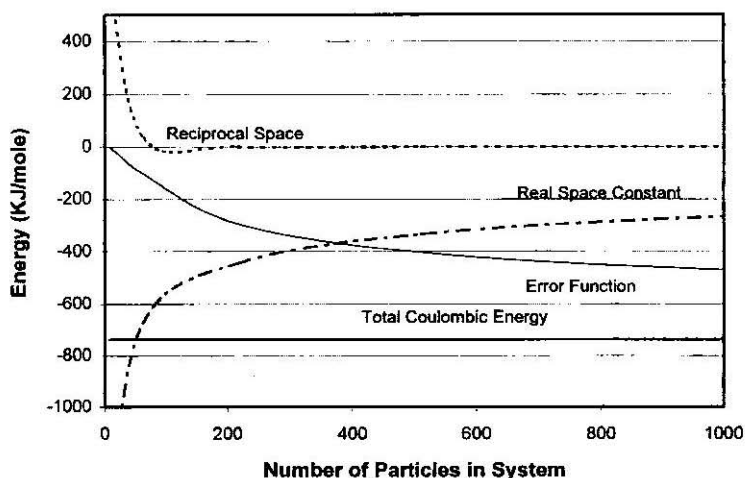


FIGURE 9. Energy contributions as a function of principal cell size, (N). Eight wave Space vectors were used

CONCLUSIONS

In this study we have presented a development of the Ewald equation, subsequent simplifications making the equation suitable for computer evaluation, and a brief sensitivity analysis along with a simple and complete computer program. The Madelung constant for rock salt has been reproduced with five decimal places accuracy or about 0.0004% error and the Madelung constant for cesium chloride matches all decimal places of reported values. Much of the application of the Ewald summation method is in the area of molecular simulation and molecular mechanics where systems characteristically involve hundreds or thousands of particles, and the calculation must be repeated hundreds of thousands of times for ever changing configurations. In these situations, program efficiency is absolutely essential.

From the discussion above, we can see that one would want to choose the minimum number of necessary wave space vectors (since this is triple nested loop) and then very judiciously choose the splitting parameter, α , to yield an acceptable value of the Madelung constant (or configurational energy). For large systems, it may be possible to neglect the reciprocal space term entirely. Again, the power of the Ewald method is that there is no dependence on any particular crystal symmetry, indeed, there is no dependence on symmetry at all, making the calculation suitable for liquid simulations. Further considerations on efficiency are not considered here, but the reader is referred to the excellent discourse of Smith (1986) for

discussion of using De Moivre's theorem with recursion and wave space symmetry considerations. The reader is also recommended to peruse the CCP5 website for downloadable molecular simulation programs, many of which incorporate the Ewald sum.

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APPENDIX I. DERIVATION OF THE EWALD SUM EQUATION

A partial derivation is found in De Leeuw, et al., 1980, and a complete and corrected derivation is available from the author. The total energy of a simulation cell can be written as

$$E = \frac{1}{2} \sum_{\vec{n}} \left(\sum_{i=1}^N \sum_{j=1}^N \frac{q_i q_j}{|\vec{r}_{ij} + \vec{n}|} \right) \quad (\text{A1})$$

where there are N charged particles in the primary or principal cell and indices i and j represent sums over all charged particles in a particular cell. The primary cell is taken to be replicated infinitely in three dimensions, with the summation over \vec{n} summing over this infinite number of replicas. The prime (') indicates that when $\vec{n} = 0$ (i.e., the principal cell) the $i=j$ terms are not included. Charge neutrality is also required,

$$\sum_{i=1}^N q_i = 0 \quad (\text{A2})$$

The lattice sum in (A1) is conditionally convergent, i.e., it yields results as shown in Figure 2. The sum may be made absolutely convergent by insertion of the convergence factor, $e^{-s|\vec{n}|}$, and then taking the limit as $s \rightarrow 0$.

$$E(s) = \frac{1}{2} \sum_{\vec{n}} \left(e^{-s|\vec{n}|} \sum_{i=1}^N \sum_{j=1}^N \frac{q_i q_j}{|\vec{r}_{ij} + \vec{n}|} \right) \quad (\text{A3})$$

which finally yields the De Leeuw, et al., 1980 result:

$$\begin{aligned} E = & \sum_{1 \leq i < j \leq N} q_i q_j \left[\sum_{\vec{n}} \frac{\text{erfc}[\alpha|\vec{n} + \vec{r}|]}{|\vec{n} + \vec{r}|} + \frac{1}{\pi} \sum_{\vec{n} \neq 0} |\vec{n}|^{-2} \exp \left(2\pi i(\vec{r} \cdot \vec{n}) - \frac{\pi^2 |\vec{n}|^2}{\alpha^2} \right) \right] \\ & + \frac{1}{2} \sum_{i=1}^N q_i^2 \left[\sum_{\vec{n} \neq 0} \left(\frac{\text{erfc}(|\vec{n}|\alpha)}{|\vec{n}|} + \frac{e^{-\pi^2 |\vec{n}|^2 / \alpha^2}}{\pi |\vec{n}|^2} \right) - \frac{2\alpha}{\sqrt{\pi}} \right] + \frac{2\pi}{3} \left[\sum_{i=1}^N q_i \vec{r}_i \right]^2 \end{aligned} \quad (\text{A4})$$

This expression can be put into a more convenient form by making some additional assumptions. Due to charge neutrality and the fact that charges and spatial positions are independent, we can assume:

1. The $\frac{2\pi}{3} \left[\sum_{i=1}^N q_i \vec{r}_i \right]^2$ term is negligible;

By judicious selection of the splitting parameter, α , we can assume:

2. Truncate the erfc contributions at $\bar{n}=0$.
This greatly simplifies (A4):

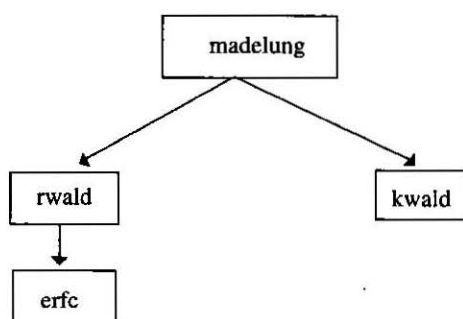
$$E = \frac{2\pi}{V_0} \sum_{\bar{k} \neq 0} \frac{\exp\left(-\frac{|\bar{k}|^2}{4\alpha^2}\right)}{|\bar{k}|^2} \left| \sum_{i=1}^N q_i \exp(i\bar{k} \cdot \bar{r}_i) \right|^2 + \sum_{1 \leq i < j \leq N} \left[\frac{q_i q_j}{|\bar{r}|} \operatorname{erfc}(\alpha|\bar{r}|) \right] - \frac{\alpha}{\sqrt{\pi}} \sum_{i=1}^N q_i^2 \quad (\text{Eq. 3})$$

This final expression is used in the computer program of Appendix II to calculate the Coulombic configuration energy and Madelung constant of NaCl and CsCl.

APPENDIX II. A SIMPLE FORTRAN PROGRAM TO CALCULATE THE MADELUNG CONSTANT

The program given below calculates the Madelung constant and Coulombic configuration energy based on infinite replication of a principal cell consisting of four salt "molecules", i.e., four sodium ions and four chloride ions in the cubic spatial arrangement shown in Figure 1. Programming emphasis is on clarity, not efficiency, and the reader is referred to the CCP-5 publication of Smith, 1986 for discussion and an example code segment of an efficient algorithm used in a molecular dynamics application. Program input and output for both NaCl and CsCl is given below.

Coordinates for ions in the principal cell and their ionic charges ((1) are read in from the external file 'nacl.dat' (or 'cscl.dat') which is listed below. These are the only external data read into the program. Program output, the Madelung constant and Coulombic configurational energy are written out to the file 'nacl.out' ('cscl.out'), also given below. Representations of the ions in the data file 'nacl.dat' are shown by the shaded spheres of Figure 1. The main program, 'madelung', calls three subroutines as shown below:



The main program, 'madelung', specifies various parameter values required in the calculation and handles all input and output. The splitting parameter, α , is set in line 33. The real space contribution to (Eq. 3) is calculated in subroutine 'rwald'. Lines 13-17 in 'rwald' calculate the constant term, 'SPE':

$$\text{SPE} = -\frac{\alpha}{\sqrt{\pi}} \sum_{i=1}^N q_i^2$$

while line 33 in 'rwald' calculates the complementary error function term, 'QPE':

$$\text{QPE} = \sum_{1 \leq i < j \leq N} \left[\frac{q_i q_j}{|\vec{r}|} \text{erfc}(\alpha |\vec{r}|) \right]$$

and uses the 'erfc' function also provided below (Abramowitz, et al. 1970).

The most time-consuming part of the calculation is subroutine 'kwald' which calculates the reciprocal (Fourier) or wave space contribution to the energy. This is the subroutine where the computer spends 99+% of its time. This is due to the triple loop over wave space vectors (KMAX) between lines

32-58 (inside of which is a single loop over ions) in subroutine 'kwald'. The value of KMAX is set in line 4. The program makes use of FORTRAN's built-in complex arithmetic functions. The exponential factors are first calculated in lines 26-28 to be used later. Lines 44 and 55 explicitly calculate the wave space contribution, 'EPE':

$$\text{EPE} = \frac{2\pi}{V_0} \sum_{\vec{k} \neq 0} \frac{\exp\left(-\frac{|\vec{k}|^2}{4\alpha^2}\right)}{|\vec{k}|^2} \left| \sum_{i=1}^N q_i \exp(i\vec{k} \cdot \vec{r}_i) \right|^2$$

These three dimensionless contributions summed and may be converted to real units as outlined above. The Madelung constant is calculated from the dimensionless energy in line 47 of the main program (for salt, this means divide by -4).

1. FORTRAN program

```

C ..... 1
C This program uses the Ewald sum method to calculate the 2
C Coulombic potential energy and Madelung constant for 3
C salt (NaCl). Coordinate data for 4 NaCl molecules in a 4
C crystal lattice are read in from the file 'nacl.dat'. 5
C ..... 6
PROGRAM MADELUNG 7
implicit double precision (a-h,o-z) 8
implicit integer*4 (i-n) 9
PARAMETER(NATOMS=8) 10
COMMON/CMCNST/ PI 11
COMMON/CMQANT/ CHGE(NATOMS) 12
COMMON/CMPPARM/ RCUTSD,ALPHAD,FACPE 13
COMMON/CMNUMS/ NOM,NSPEC,NION(2),NOP,H,RCUT,ALPHAL 14
COMMON/CMCRDS/ X(NATOMS),Y(NATOMS),Z(NATOMS) 15
open(8,file='nacl.out') 16
open(9,file='nacl.dat') 17
C PHYSICAL CONSTANTS 18
PI = 4.*ATAN(1.) 19
C NO. OF MOLECULES(4), SPECIES/MOLECULE(2), IONS(4 Na,4 Cl,8 TOTAL) 20
NOM=4 21
NSPEC=2 22
NION(1)=NOM 23
NION(2)=NOM 24
NOP=2*NOM 25
C READ IN ION X,Y,Z COORDINATES AND IONIC CHARGES 26
DO I=1,NOP 27
READ(9,*) X(I),Y(I),Z(I),CHGE(I) 28
ENDDO 29
C CUT-OFF RADIUS IS HALF BOX LENGTH 30
RCUT=1.0 31
C CHARGE DISTRIBUTION PARAMETER FOR EWALD SPLITTING 32
ALPHAL=8.0 33
C FLOAT NUMBER OF MOLECULES 34
FNOM=FLOAT(NOM) 35
C SQUARE OF DIMENSIONLESS CUT-OFF 36
RCUTS=RCUT**2 37
C DIMENSIONLESS VALUE OF ALPHA 38
ALPHAD=ALPHAL/2.0 39
C CALCULATE REAL SPACE CONTRIBUTIONS, QPE AND SPE 40
CALL RWALD(QPE,SPE) 41
C CALCULATE RECIPROCAL SPACE CONTRIBUTION, EPE 42
CALL KWALD(EPE) 43
C CONVERT INTO J/MOL 44
TPF = QPF+FPF+SPF 45

```

C CALCULATE MADEUNG CONSTANT FROM MOLAR COULOMBIC ENERGY	46
CMDLNG = TPE/FNOM/CHGE(1)/CHGE(NOM+1)	47
C DISPLAY RESULTS	48
write(*,*) 'Dimensionless energies:'	49
write(8,*) 'Dimensionless energies:'	50
write(*,10) QPE	51
write(8,10) QPE	52
10 format('ERF : ',t20,f10.4)	53
write(*,11) EPE	54
write(8,11) EPE	55
11 format('Fourier : ',t20,f10.4)	56
write(*,12) SPE	57
write(8,12) SPE	58
12 format('Self Interaction : ',t20,f10.4)	59
write(*,13) TPE	60
write(8,13) TPE	61
13 format('Total energy: ',t20,f10.4)	62
write(8,20) CMDLNG	63
write(*,20) CMDLNG	64
20 format('Madelung Constant [NaCl] = ',t30,f8.6)	65
END	66
 SUBROUTINE RWALD(QPE,SPE)	1
implicit double precision (a-h,o-z)	2
implicit integer*4 (i-n)	3
PARAMETER(NATOMS=8)	4
COMMON/CMCNST/ PI	5
COMMON/CMNUMS/ NOM,NSPEC,NION(2),NOP,H,RCUT,ALPHAL	6
COMMON/CMQANT/ CHGE(NATOMS)	7
COMMON/CMPARM/ RCUTS,ALPHAD,FACPE	8
COMMON/CMCRDS/ X(NATOMS), Y(NATOMS), Z(NATOMS)	9
C	10
C CONSTANT TERM IN SELF INTERACTION CONTRIBUTION TO POT ENGY	11
C	12
SUM=0.0	13
DO I=1,NOP	14
SUM=SUM+CHGE(I)**2	15
ENDDO	16
SPE=-ALPHAD/SQRT(PI) * SUM	17
C	18
C ERROR FUNCTION TERM	19
C	20
QPE=0.0	21
DO 2 I=1,NOP-1	22
DO 3 J=I+1,NOP	23
C SEPARATION OF PARTICLES	24
RX=X(I)-X(J)	25
RY=Y(I)-Y(J)	26
RZ=Z(I)-Z(J)	27
C CUT-OFF CRITERION	28
RSQ=RX*RX+RY*RY+RZ*RZ	29
IF(RSQ.GT.RCUTS) GO TO 3	30
R=SQRT(RSQ)	31
C ERROR FUNCTION TERMS	32
QPE=QPE+CHGE(I)*CHGE(J)*ERFC(R*ALPHAD)/R	33
3 CONTINUE	34
2 CONTINUE	35
RETURN	36
END	37
 SUBROUTINE KWALD(EPE)	1
implicit double precision (a-h,o-z)	2
implicit integer*4 (i-n)	3
PARAMETER(NATOMS=8,KMAX=26)	4
DOUBLE PRECISION KSQ	5
COMMON/CMNUMS/ NOM,NSPEC,NION(2),NOP,H,RCUT,ALPHAL	6
COMMON/CMQANT/ CHGE(NATOMS)	7
COMMON/CMPARM/ RCUTS,ALPHAD,FACPE	8
COMMON/CMCRDS/ X(NATOMS), Y(NATOMS), Z(NATOMS)	9


```

COMPLEX EXPIKR(NATOMS),SUM          10
COMPLEX EL(NATOMS,-KMAX:KMAX)        11
COMPLEX EM(NATOMS,-KMAX:KMAX)        12
COMPLEX EN(NATOMS,-KMAX:KMAX)        13
C .....                               14
C RECIPROCAL SPACE (K-SPACE) CONTRIBUTION TO POTENTIAL ENERGY 15
C .....                               16
  DATA ZERO/1.0E-10/                 17
  TWOPI=8.0*ATAN(1.0)                 18
C SIZE OF BOX                          19
  DATA CL,CM,CN/2.0,2.0,2.0/         20
  V=CL*CM*CN                          21
  EPE=0.0                              22
C STORE EXPONENTIAL FACTORS            23
  DO I=1,NOP                           24
    DO K=-KMAX,KMAX                    25
      EL(I,K)=CMPLX(COS(K*TWOPI*X(I)/CL),SIN(K*TWOPI*X(I)/CL)) 26
      EM(I,K)=CMPLX(COS(K*TWOPI*Y(I)/CM),SIN(K*TWOPI*Y(I)/CM)) 27
      EN(I,K)=CMPLX(COS(K*TWOPI*Z(I)/CN),SIN(K*TWOPI*Z(I)/CN)) 28
    ENDDO                              29
  ENDDO                                30
C START LOOPS OVER WAVE VECTORS (L,M,N) AND NUMBER OF ATOMS (I) 31
  DO 10 L=-KMAX,KMAX                  32
    RL=TWOPI*FLOAT(L)/CL              33
    DO 20 M=-KMAX,KMAX                34
      RM=TWOPI*FLOAT(M)/CM            35
      DO 30 N=-KMAX,KMAX              36
        RN=TWOPI*FLOAT(N)/CN          37
C TESTS ON MAGNITUDE OF K VECTOR        38
  KK=L*L+M*M+N*N                     39
C SKIP WHEN K VECTOR = ZERO (EQ 3)      40
  IF(KK.LT.ZERO) GO TO 30             41
C COEFFICIENT A(K)                     42
  KSQ=RL*RL+RM*RM+RN*RN              43
  AK=TWOPI/V * EXP(-KSQ/(4.*ALPHAD**2))/KSQ 44
C FORM EXP(IKR) FOR EACH PARTICLE       45
  DO I=1,NOP                           46
    EXPIKR(I)=EL(I,L)*EM(I,M)*EN(I,N) 47
  ENDDO                                48
C FORM SUMS FOR EACH SPECIES            49
  SUM=(0.,0.)                          50
  DO I=1,NOP                           51
    SUM=SUM+CHGE(I)*EXPIKR(I)         52
  ENDDO                                53
C ACCUMULATE K-SPACE POTENTIAL ENERGY 54
  EPE=EPE+AK*REAL(CONJG(SUM)*SUM)      55
30 CONTINUE                           56
20 CONTINUE                           57
10 CONTINUE                           58
  RETURN                              59
  END                                  60

  DOUBLE PRECISION FUNCTION ERFC(X)    1
C ERROR FUNCTION USING 7.1.26 OF ABRAMOWITZ AND STEGUN 2
  IMPLICIT DOUBLE PRECISION (A-H,O-Z) 3
  DATA P/0.3275911/                   4
  DATA A1,A2,A3/0.254829592,-0.284496736,1.421413741/ 5
  DATA A4,A5/-1.453152027,1.061405429/ 6
  T=1./((1.+P*X))                      7
  EXPAR2=EXP(-X**2)                    8
  ERFC=(((A5*T+A4)*T+A3)*T+A2)*T+A1)*T*EXPAR2 9
  RETURN                               10
  END                                  11

```

2. Input data file, 'nacl.dat'

0.00	0.00	0.00	-1.0
1.00	1.00	0.00	-1.0
1.00	0.00	1.00	-1.0
0.00	1.00	1.00	-1.0
1.00	0.00	0.00	1.0
0.00	1.00	0.00	1.0
0.00	0.00	1.00	1.0
1.00	1.00	1.00	1.0

3. Program output, 'nacl.out'

Dimensionless energies:
 ERF : 0.0000
 Fourier : 11.0638
 Self Interaction : -18.0541
 Total energy: -6.9903
 Madelung Constant [NaCl] = 1.747565

4. Input data file, 'cscl.dat'

0.50	0.50	0.50	1.0
1.50	0.50	0.50	1.0
0.50	1.50	0.50	1.0
1.50	1.50	0.50	1.0
0.50	0.50	1.50	1.0
1.50	0.50	1.50	1.0
0.50	1.50	1.50	1.0
1.50	1.50	1.50	1.0
0.00	0.00	0.00	-1.0
1.00	0.00	0.00	-1.0
0.00	1.00	0.00	-1.0
1.00	1.00	0.00	-1.0
0.00	0.00	1.00	-1.0
1.00	0.00	1.00	-1.0
0.00	1.00	1.00	-1.0
1.00	1.00	1.00	-1.0

5. Program output, 'cscl.out'

Dimensionless energies:
 ERF : 0.0000
 Fourier : 19.8253
 Self Interaction : -36.1081
 Total energy: -16.2828
 Madelung Constant [CsCl] = 2.035353

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