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 forcer 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 analyzas a powerful yet under utilized method for calculating these lattice energies, the Ewald sum. Not only is this a powerful and accurate of calculating the configuration energies of ionic crystals, it is also not dependent on existence of crystal structure. Hence this method is useful in any application involving Coulonbic 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. Extansive 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, Reviprocal space

INTRODUCTION

Lattice energy calculations for ionic crystals are physically straighforward, yet in practise, quite difficult. The difficulty arises due to the long-range nature of Colombic 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 Ewalds method in the solution of problems involving charged particles. Their paper provides a terse derivation of the Ewald summations formula but unfortunatly, 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 selecction of the Ewald splitting parameter, correcting some common

misconceptions. Finally, the method is illustrated using a simple FORTRAN program applied to table salt and cecium 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 straighforward 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 distanced 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. Moing 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 contructing an infinite series as follows:

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

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

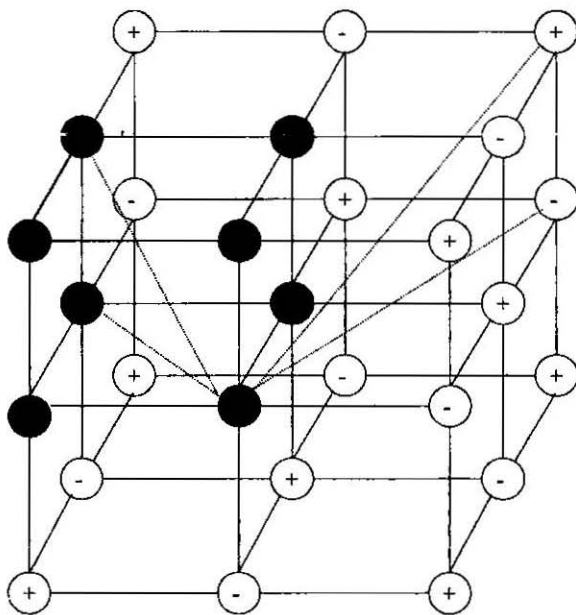$$E = \frac{e^2 q_1 q_2}{d} M \qquad \text{(Eq.2)}$$

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 lattive positions. If the position of the
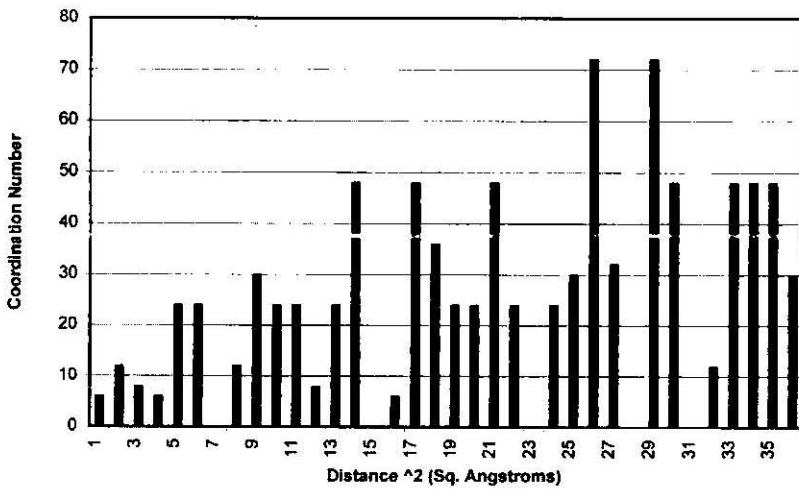

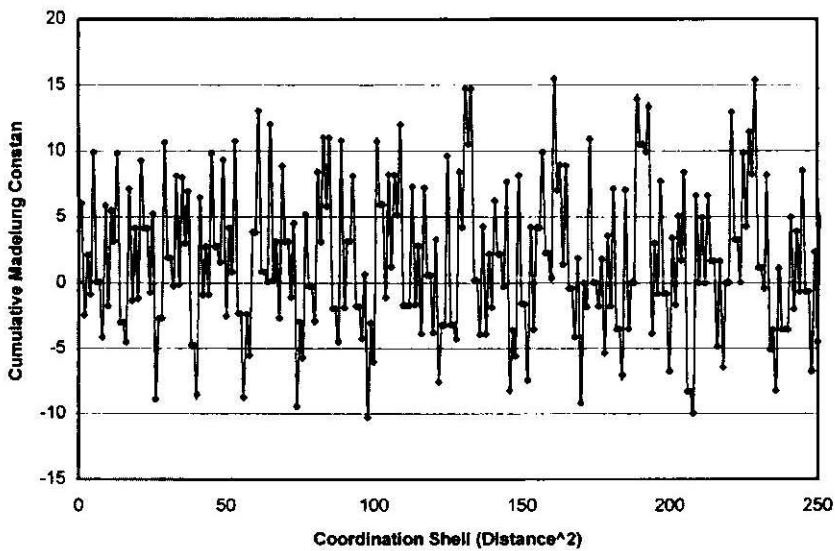FIGURE 2. Coordination Number for First 36 Shells of NaCl Crystal

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 form zero to some convenient cutoff in real space, and the reminder in reciprocalor wave space. The relative contributions of the two terms is goverened 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 Ewaki 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:

$$
E = \frac{2\pi}{V_0} \sum_{k=0} \frac{\exp\left(-\frac{|\bar{k}|^2}{4\alpha^2}\right)}{|\bar{k}|^2} \left| \sum_{j=1}^{N} q_j \exp(i\bar{k} \cdot \bar{r}_j) \right|^2
$$
$$
+ \sum_{1 \le i < j \le N} \left[\frac{q_i q_j}{|\bar{r}|} erfc(\alpha|\bar{r}|) \right] - \frac{\alpha}{\sqrt{\pi}} \sum_{j=1}^{N} q_j^2
$$

(Eq.3)

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

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

and E is the total (dimensionless) Coulombic molar configuration energy. The vector $\bar{k}$ represents a three dimensional vector in wave or reciprocal space, while the vector $\bar{r}$ 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
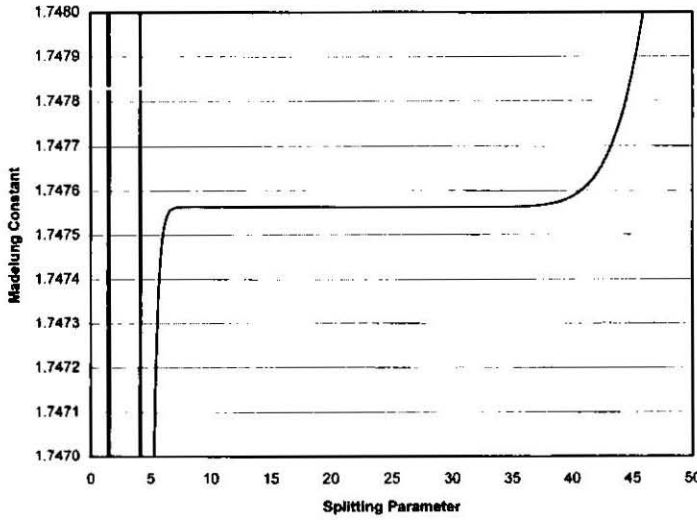
FIGURE 4. Madelung constant as a function of splitting parameter for rock salt. Four 'Molecules' in principal cell, 40 wave space vectors were used

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 withthe 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

$$F = \left(\frac{e^2}{4\pi\varepsilon_0} \right) \left(\frac{2N_A}{N_m} \right) \left(\frac{\rho}{M_r} \right)^{\frac{1}{3}} \times 100 \text{ cm/m} \times 0.001 \text{ kJ/J} = 105.515 \text{ kJ/mol}$$

$\begin{aligned}
e &= 1.60219 \times 10^{-19} \text{ C} \\
\varepsilon_0 &= 8.854188 \times 10^{-12} \text{ C}^2 \text{ s}^2/(\text{kg m}^3) \\
N_A &= 6.02205 \times 10^{+23} \text{ molecules/mol} \\
N_m &= \text{Number of molecules in primary cell} = 4 \\
\rho &= 1.35 \text{ g/cm}^3 \\
M_r &= \text{Total mass of primary cell} = 232/N_A \text{ g}
\end{aligned}$

yielding a value of $E_p = -737.58$ kJ/mol, which agress with the tabulated value $E_p = -737.37$ kJ/mol (Smith 1986). In addition, the same program was used to calculate the Madelung constant for CsCl, and yielded 2.03553 which agress 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):

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

the complementary error term contribution:

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

and the reciprocal or wave space contribution:

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

Therefore,

$$E = E^S + E^E + E^W \tag{Eq. 7}$$

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, $\bar{k}$, since this is effectively a triple-nested loop. It is therefore desirable to minimize the number of wave space vectors contained inthe 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 spitting 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, a, 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 $5<a<17$, and when eight wave vectors are used the
plateau extends from $5<a<11$. 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 $5<a<11$ 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
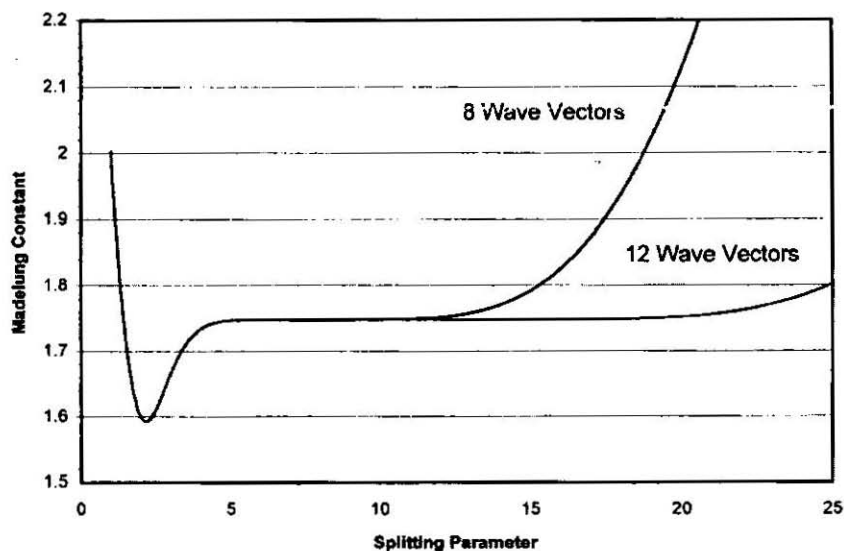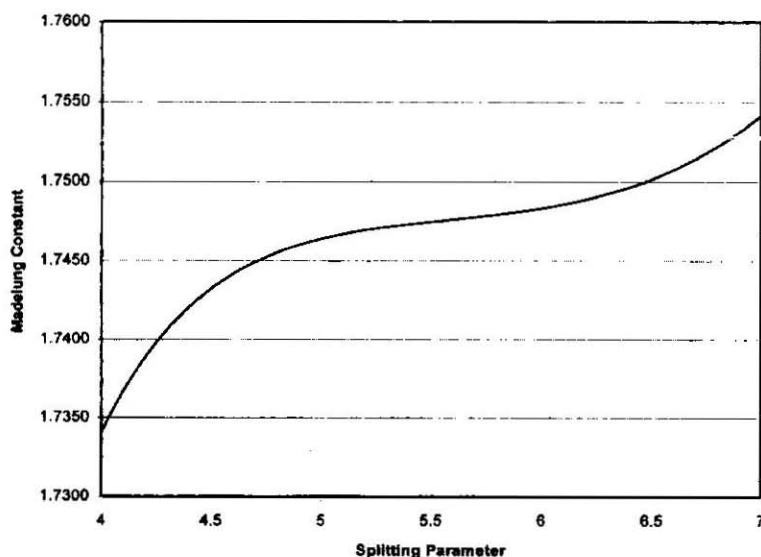

FIGURE 7. Madelung constant as a function of splitting parameter for NaCl crystal. Four 'molecules' in principal cell, three wave space vectors were used

as a function fo splitting parameter. However, this time, we have only used three wave space vectors, i.e., KMAX=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 calculation 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 see 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.,

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

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.
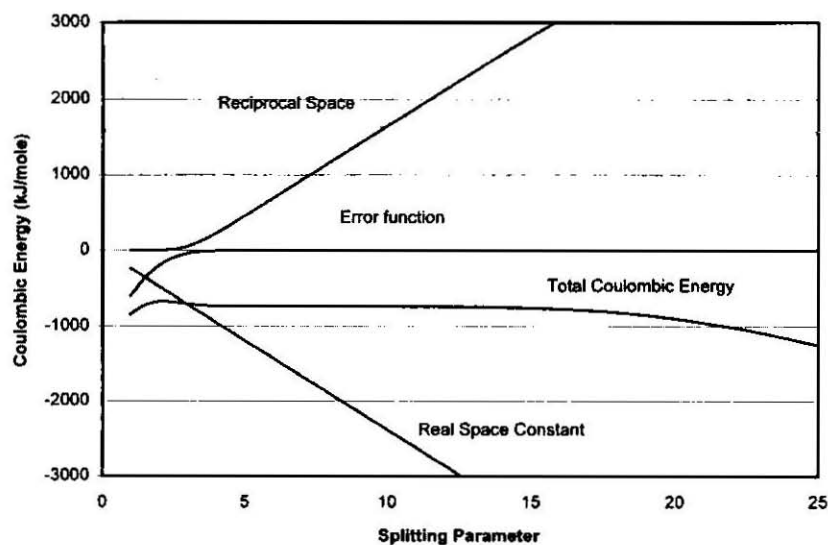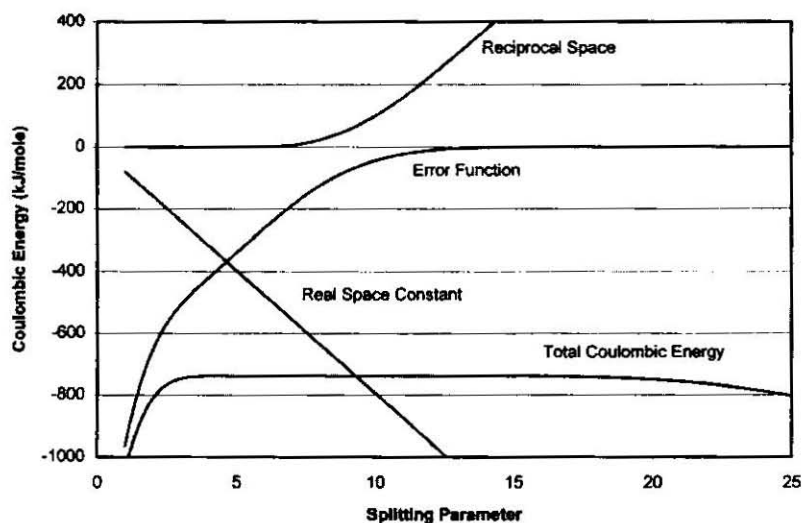

FIGURE 8. Energy contribution as a function of splitting parameter for NaCl crystal. Eight wave space vectors were used. 108 'molecules' in principal cell

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 $N > \cong 500$ 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.
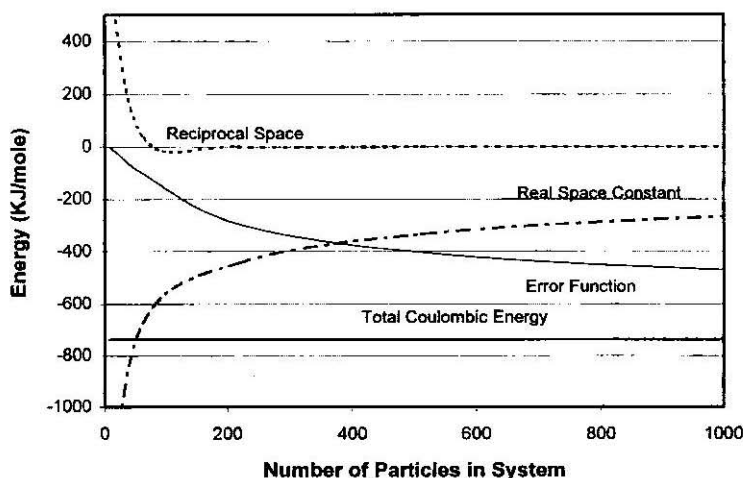
FIGURE 9. Energy contributions as a function of principal cell size, (N). Eight wave Space vectors were used

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 syammetry, 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 as also recommended to peruse the CCP5 website for dowaloadable molecular simulation programs, many of which incorporate the Ewald sum.

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

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

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 $\bar{n}$ summing over this infinite number of replicas. The prime (') indicates that when $\bar{n} = 0$ (i.e., the principal cell) the $i=j$ terms are not included. Charge neutrality is also required,

$$\sum_{i=1}^{N}q_i=0 \tag{A2}$$

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, $e^{-s|\bar{n}|^2}$, and then taking the limit as $s \to 0$.

$$E(s)=\frac{1}{2}\sum_{\bar{n}}{}'\left(e^{-s|\bar{n}|}\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{q_i q_j}{|\bar{r}+\bar{n}|}\right) \tag{A3}$$

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

$$E=\sum_{1\le i<j\le N}q_i q_j\left[\sum_{\bar{n}}\frac{erfc[\alpha|\bar{n}+\bar{r}|]}{|\bar{n}+\bar{r}|}+\frac{1}{\pi}\sum_{\bar{n}\ne 0}|\bar{n}|^{-2}\exp\left(2\pi i(\bar{r}\cdot\bar{n})-\frac{\pi^2|\bar{n}|^2}{\alpha^2}\right)\right]$$

$$+\frac{1}{2}\sum_{i=1}^{N}q_i^2\left[\sum_{\bar{n}\ne 0}\left(\frac{erfc(|\bar{n}|\alpha)}{|\bar{n}|}+\frac{e^{-\pi^{2|\bar{n}|^2}/\alpha^2}}{\pi|\bar{n}|^2}\right)-\frac{2\alpha}{\sqrt{\pi}}\right]+\frac{2\pi}{3}\left[\sum_{i=1}^{N}q_i\bar{r}_i\right]^2 \tag{A4}$$

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 $\frac{2\pi}{3}\left|\sum_{i=1}^{N}q_i\bar{r}_i\right|^2$ 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):

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

$$
- \frac{\alpha}{\sqrt{\pi}} \sum_{i=1}^{N} q_i^2 \qquad\qquad\qquad\qquad\qquad\qquad (\text{Eq. 3})
$$

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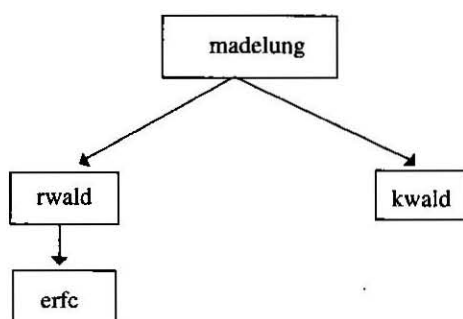
The main program, 'madelung', specifies various parameter values required in the calculation and handles all input and output. The splitting parameter, α, is set in line 33. The real space contribution to (Eq. 3) is calculated in subroutine 'rwald'. Lines 13-17 in 'rwald' calculate the constant term,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

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

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

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

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/CMPARM/ 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
      TPE = QPE+EPE+SPE                                          45
```

```
C CALCULATE MADELUNG 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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