Direct Calculation Of Madelung Constant

M.Sc. THESIS

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Abstract

The calculation of Madelung constant for a crystal is actually a conditionally convergent series and thus tricky to evaluate. Here we have used fractional charge consideration to create a neutral atmosphere for the reference charge so that when we calculate Madelung constant the value does not fluctuate much. Using this method brings small fluctuations in error values for very large systems but its magnitude is very less on the other hand the sum converges very fast. We have also calculated Madelung constant values for slightly randomly distributed lattices and have shown that their energy increases with increasing disorder. Then lastly we have considered a few non-trivial systems like 3D lattice with 2D periodicity and calculated Madelung constant for them.

1 Introduction

1.1 Problem Statement and Prior work:

To calculate energy of electrostatic interaction in any ionic periodic structure we need to know its Madelung constant, which is a quantity that depends only on system structure, this constant was named after German physicist Erwin Madelung. This quantity, being a very slowly converging series, is problematic to find out (sec1.2). Through centuries many people have worked on this and have given many ways to find out, one very accurate method is to use mathematical substitution but that approach is limited in a way that we cannot use that method if the system is not ideal. Then for real crystals Ewald gave an very useful method (sec1.3)[5] but this method is mathematically complex and involve reciprocal space. Very recently many scientists have worked on using direct summation method to find out Madelung sum, W.A. Harrison[1], Michele Gaio[2], etc have stated very prominent ways to calculate this sum. We have used a way that has been spoken of in many published materials, that is to use fractional charges on ions. Our method has been explained elaborately in section 3, and the results are presented thereafter. We have used as many illustrations as we could.

1.2 Ionic Crystal:

When a solid is built of periodic structures of positive and negative ions it is called an ionic crystal, the bonding in this type of solids is of coulombic nature. The ionic crystal energy is mainly (i.e. more than 90 %) the electrostatic energy of the the constituting ions. This energy for 'N' no of ions is given by-

$$E = \frac{-N\alpha q^2}{4\pi\epsilon_0 a} \tag{1}$$

 ϵ_0 is the permeability of vacuum

'a' is the nearest neighbour distance between positive and negative ions

'q' is actually Ze, where e is the electronic charge and Z is the valency of the ions. Here α is the Madelung constant, considering the form of electrostatic potential, α is expressed as-

$$\alpha = \sum_{i=1}^{N} \frac{\pm Z_i}{r_i} \tag{2}$$

Where N is the number of ions in the system and r_i is the distance of i^{th} atom from the reference charge and $\pm Z_i$ comes from the positive and negative ions in the crystal.



Here we have assumed the crystal to be infinitely large $(N \rightarrow infinity)$ so that the sum (eq 2) gives same value for all the ions, that is how we can express the total energy as N multiplied by interaction energy for one ion in the crystal. Madelung constant values only depend on the crystal structures of the ionic solid more explicitly, how the ions are distributed in a crystal with respect to each other. The calculation of Madelung constant always had a numerical issue as stated below.

1.3 Madelung constant the conditionally convergent series:

The series- $\lim_{N\to\infty} \sum_{i=1}^{N} \frac{1}{r_i}$ is a divergent series called Harmonic Series, but in case of Madelung constant, we have a series with alternative plus-minus terms which is the alternating harmonic series. This series fortunately a conditionally convergent one, can be evaluated by direct summation of the terms but its convergence is very slow in reality. Also as the total charge in the system which is considered to calculate the sum, fluctuates more and more as we to larger and larger systems (fig. 2). For this reason the calculated Madelung constant values fluctuate too (fig. 3).



1.4 Ewald summation and direct calculation of Madelung constant:

To calculate Madelung constant and energy of the solid, the most used method is the Ewald summation method which replaces the $\sum_{i=1}^{N} \frac{\pm 1}{r_i}$ by two rapidly converging series [5] namely s_1 and s_2 where-

$$\frac{1}{r} = s_1 + s_2 \tag{3}$$

$$s_1 = \frac{erfc(pr)}{r} \tag{4a}$$

$$s_2 = \frac{erf(pr)}{r} \tag{4b}$$

erfc and erf are complementary error function and error function respectively p is a constant which determine convergence rate of the two sum values And we have

$$erfc(x) + erf(x) = 1 \tag{5}$$

Then the summation is evaluated in real space for s_1 and in fourier space for the s_2 series. This mathematically more complex and difficult to program method can be replaced by the direct summation method without compromising the sufficient accuracy of the result. In fact in direct summation we can achieve the result with less than 1% percentage error in conveniently small time using a modern day laptop and the program codes become very simple too.

In this context W.A. Harrison [1] and others [2][3] have made considerable improvements in direct calculation of Madelung constant for various types of lattices.

2 Processes Used to Calculate Madelung Constant :

2.1 The Fractional Charge Consideration:

The value of Madelung constant is evaluated here with direct summation method using a modification which can be named as Fractional Charge Consideration. The idea is to assign fractional charge values to the ions on the boundary to make the system electrically neutral. Also the system grows in cubic manner (square in 2D) i.e. sum is done on expanding cubes and the convergence of the sum value is investigated. An simple illustration is given here-

According to the picture the corner ions in a square lattice has $\frac{1}{4}$ charge and the ions on the edge has $\frac{1}{2}$ charge, but the ion inside the lattice charge is assigned to be one. For 3D lattice the ions on the boundary surface has 0.5 charge, and those on the edge has 0.25 charge and the eight corner ions has 0.125 charge.

This way of assigning fractional charges to ions also can be understood by finding out the actual co-ordination number of the ions in the system. The numbers are not same for all the ions. For example if we consider a simple cubic lattice(NaCl), the co-ordination number for all the ions is same, its 6. But this system is infinitely large unlike the systems used in our calculation. So for our finite systems the co-ordination numbers are like this-For corner ions it is 3

For the ions on the boundary surface it is 5

For the ions on the twelve edges it is 4

For the ions totally inside the crystal it is 6.

Now when we calculate Madelung constant with respect to a point in the lattice, we consider the unit cell (U_0) containing the point of reference to be at the origin of the



co-ordinate system and we number all the cells starting from U_0 which is numbered as (0,0,0). When we take a cell numbered (x,y,z), we define the distance between these two cells as \vec{R} . Also for each cell the eight ion positions (for NaCl) are all well defined, we take them as $\vec{r_1}, \vec{r_2}$ etc, they are measured from the origin of the co-ordinate system which is attached to that (x,y,z) cell. Then distance of reference ion from any ion in (x,y,z) cell is defined as-

$$\vec{d_i} = \vec{R} + \vec{r_i} \tag{6}$$

where i goes from 1 to 8 considering all the ion positions of the unit cell (fig.5). Now if we calculate Madelung constant using this method, considering all the unit cells of our finite system, its clear that every ion totally inside the crystal will be shared by 8 enclosing cells so considered 8 times, $8 * \frac{q_i}{d_i}$ but we know that one ion must be considered once only, so to balance the sum we assign 0.125 charge to every ion in the system. Due to this we can realize now that the ions on the boundary will have fractional charges. It will be like-Ions on the boundary surface will be shared by 4 unit cells so they will bear (4*0.125=)0.5 charge.

Ions on the edges will be shared by 2 unit cells so they will bear(2*0.125=) 0.25 charge. The eight ions in the corner will be shared by only one cell each so the charge value assigned for them is 0.125.

An illustration-

For the above figure two unit cells are taken to show how the distance is calculated in 3D simple cubic case. Here



- (7a)
- $\vec{d_i} = \vec{R} + \vec{r_i}$ $\vec{r_1} = 0$ (7b)
- $\vec{r}_2 = \vec{i}$ (7c)

$$\vec{r_3} = \vec{j} \tag{7d}$$

$$\vec{r_4} = k \tag{7e}$$

$$\vec{r_5} = i + j \tag{7f}$$

$$r_6 = i + k \tag{7g}$$

$$\vec{r}_7 = j + k \tag{7h}$$

$$\vec{r_8} = \vec{i} + \vec{j} + \vec{k} \tag{7i}$$

 r_1 is zero because P2 is the origin of co-ordinate system attached to U(x,y,z) All the distances from the reference charge to each atom is calculated in this way. We just did calculate the first quadrant terms and summed them as multiplied by eight, we could do that due to the symmetric nature of the crystal [1].

$$Madelung \quad constant = \sum_{i=1}^{N} S_i \quad where \tag{8a}$$

$$S_i = 8 \times s_1 \tag{8b}$$

$$s_1 = sum \quad evaluated \quad in \quad 1^{st}quadrant$$
 (8c)

That was the main idea of fractional charge consideration.

2.2The spherical Shell Consideration:

This idea is fairly simple, we take the system to be a sphere and we include ions on or inside the spherical surface (fig. 6).



Actually to use this type of system effectively we have to find out spheres where the total charge contained is zero, otherwise the Madelung constant values will fluctuate (fig.3). In W. A. Harrison's paper [1] he used compensating charges to make the system neutral but here we have separately found out those spacial spheres where naturally the sphere does not contain any total charge (i.e. no of negative ions and positive ions are the same) and then performed the sum to find out Madelung constant.

3 Madelung Constant in One Dimension:

3.1 Calculation on Regular Lattice:

Finding out Madelung constant in one dimension is trivial. The sum is given by-

$$MC = \sum_{i=1}^{N} \frac{\pm 1}{r_i} \quad where \tag{9a}$$

$$r_i = x_i \tag{9b}$$



here the sum was calculated up to system size L = 400, and the value converged at 1.3863

3.2 Calculation on Disordered Lattice:

To make calculations on disordered lattice we have introduced a small random deviation of the ions from their regular position in the lattice. The values for a maximum possible displacement 10% of the nearest neighbour distance were investigated and the mean of the 1000 Madelung constant values calculated was found to be **1.36077**. We have also presented a plot (fig.8) of values of Madelung constant with increasing disorder in the lattice to reveal the nature of the change.

$\frac{\delta a}{a}$	Madelung constant
0.05	1.3728
0.1	1.3609
0.15	1.3496
0.2	1.3392

The decreasing value of Madelung constant shows the increase in interaction energy (eq.1) in disordered lattice.



4 Madelung Constant in Two dimensions :

4.1 Calculation on Square Lattice :

In two dimensions the Madelung sum is given by-

$$MC = \sum_{i=1}^{N} \frac{\pm 1}{r_i} \quad where \tag{10a}$$

$$r_i = \sqrt{x_i^2 + y_i^2} \tag{10b}$$

We have calculated Madelung sum in both the ways, considering fractional charges in expanding square systems and in spherical (actually circular as it is in two dimensions) neutral systems and presented a comparison of these two. Firstly Madelung constant for square lattice- We can see from the figure.7 that the sum calculated using fractional charge contribution gives a better convergence. The value of the sum converges at **1.61554** where the reference value is 1.6155. Here is two tables containing the important results of the plots (fig.9 and fig.10)-

system size	MC* calculated	reference value	% error
10	1.61449	1.6155	0.0625
20	1.61541	1.6155	0.0055
50	1.61554	1.6155	0.0024
100	1.61554	1.6155	0.0024

For square system using fractional charge consideration:

For circular neutral systems:



fractional charge method shows better convergence

error in very small systems are excluded from figure

radius of system	MC calculated	reference value	% error
11.045	1.52066	1.6155	5.87
20.024	1.56956	1.6155	2.84
49.929	1.59617	1.6155	1.19
101.02	1.60532	1.6155	0.63

So we can say that if we calculate Madelung constant value in increasing square systems using fractional charge consideration, we get better convergence. The main problem of using direct calculation methods was the long time it takes to give fairly converged values, but the method we used needs a very small code and it takes very small time. Here is a table showing the time taken for running the program (in FORTRAN code) -

*MC is used for Madelung constant for short

size of system (L)	Time taken in sec
100	0.0312
200	0.2496
500	2.4024
1000	23.9305

Rectangular Central Lattice: 4.2

We have calculated the Madelung constant for rectangular central lattice type using fractional charge consideration. But one speciality of this lattice is that we must have the sides of of the rectangle such that the nearest neighbours bear opposite charge, any arbitrary value for the sides can not represent the lattice. We have done a simple calculation for that-

$$c = \frac{1}{2}\sqrt{a^2 + b^2} \quad where \tag{11a}$$

$$condition \quad c < a \tag{11b}$$

$$given \quad a < b \quad it \quad gives \tag{11c}$$

$$b < \sqrt{3} \times a \tag{11d}$$



Here 'c' is the nearest neighbour distance in this case. Here we have computed values of Madelung constants for $a < b < \sqrt{3} \times a$ taking a = 1.0. From the values (table) we have noticed that at the limit $b \rightarrow a$ the sum value almost converge to the sum value for square lattice.

a	b	Madelung constant
1.0	1.005	1.61463
1.0	1.1	1.55327
1.0	1.2	1.47029
1.0	1.3	1.37093
1.0	1.4	1.25409
1.0	1.5	1.12391
1.0	1.732	0.76544

At the limit $b \to \sqrt{3} \times a$ the Madelung constant becomes very low, that means the structure have a high energy (eq 1) thus it likely to be unstable and may be physically unrealizable.

5 Madelung constant for three dimensions:

5.1 Calculation in Regular Lattice :

In 3D Madelung sum is given by-

$$MC = \sum_{i=1}^{N} \frac{\pm 1}{r_i} \quad where \tag{12a}$$

$$r_i = \sqrt{x_i^2 + y_i^2 + z_i^2}$$
(12b)

We have calculated this sum in expanding cubic system by assigning fractional charges and compared it with the sum calculated in expanding spherical systems considering the neutral spheres only. Here are the plots of those results-



Here are the tables containing important data for simple cubic system using fractional charge consideration:

system size	MC calculated	reference value	% error
10	1.7475	1.747564	0.0036
20	1.7475	1.747564	0.0036
50	1.7479	1.747564	0.0192
100	1.7492	1.747564	0.0936

We have also calculated the sum for simple cubic in a slightly different manner and tested the convergence for very large systems also (up to system size $1000 \times 1000 \times 1000$). The data table is shown below-

n	MC calculated	reference value	% error
01	1.456029	1.747564	16.6823
02	1.751768	1.747564	0.2405
05	1.747498	1.747564	0.0037
10	1.747599	1.747564	0.0.0020
20	1.747593	1.747564	0.0016
50	1.748455	1.747564	0.0509
100	1.750908	1.747564	0.1913
200	1.747571	1.747564	0.0004
300	1.747252	1.747564	0.01785

Where system size, $L = 2 \times n$ (i.e. the system is $L \times L \times L$). As we can see from the result that the percentage error has a fluctuating trend but it is important to note that the error never exceeded 1% even when it was calculated for a system as large as $600 \times 600 \times 600$. From the papers of Michele Gaio et al [2] and W. A. Harrison [1] its clear that if the error in the value of Madelung constant is less than 1% then it is sufficient enough to use that value for energy calculation. The reason is the fact that energy of a ionic solid is not totally the coulomb interaction energy, the short range repulsive potential also contribute in the total energy of the solid.

The form of repulsive potential is given by-

$$V_{rep} = \frac{\beta}{r^n} \quad where \tag{13a}$$

$$\beta = repulsive \quad co - efficient \tag{13b}$$

'r' is the distance between two ions and 'n' is the Born exponent (value of n is in the order of 10). Due to this reason and other uncertainties W. A. Harrison in his paper [1] has suggested that it is enough if we limit our calculation of Madelung sum up to systems where $L = 300 \times a$. Below we have presented a comparison of the results obtained by our method and by M. Gaio and W.A. Harrison [2][1].

n*	Our values	% error	M. Gaio[2]	% error	Harrison[1]	% error	ref. value
10	1.747599	0.0.0020	1.7505	0.1680	1.6650	4.7245	1.747564
20	1.747593	0.0016	1.7483	0.0421	1.7826	2.0048	1.747564
50	1.748455	0.0509	1.7477	0.0077	1.7525	0.2824	1.747564
100	1.750908	0.1913	1.7476	0.0020	1.74	0.4328	1.747564
300	1.747252	0.01785	1.7476	0.0020	1.7457	0.1066	1.747564

Here this 'n' is a measure of system size, $n = \frac{L}{2}$. We have presented a plot of the three methods (fig 14). Though we have found our sum value to be fluctuating by small amount at very large systems, still at smaller systems our method provide with a very high rate of convergence (fig 15), in this aspect our method gave better results than the referred methods in [1] and [2].





The time taken to calculate Madelung sum in a 3D simple cubic lattice using fractional charge consideration by a laptop computer is given here.

size of system (L)	Time taken in sec
40	0.0312
100	0.0780
200	0.6552
300	2.2308
500	10.5300

We can surely say it is fairly fast.

5.2 Calculations on Disordered Lattice:

We have introduced a deviation of the ion's position from the regular simple cubic lattice by a maximum 10 % of the nearest neighbour distance and calculated Madelung constant more than 10,000 times and found the mean Madelung constant for disordered simple cubic lattice to be **1.74618**, which is less than the ordered lattice MC value. We have presented a table and its plot showing this change in MC values with increasing disorder.

$\frac{\delta a}{a}$	Madelung constant
0.03	1.74757
0.05	1.74711
0.1	1.74618
0.2	1.74128

We can see (fig.16) that with increasing disorder in the lattice the MC values are decreasing and from the energy expression (eq.1) it is evident that the energy of the disordered systems are greater than the regular systems. This result also support the fact that liquids (like molten NaCl : disordered system) contain more energy than solid (crystallized NaCl), that is why we need to provide energy to change a solid into liquid (i.e. to bring disorder into the system).



5.3 BCC Lattice:

The BCC lattice gives two different Madelung constant values if we consider two types of ions as reference point in calculation. We get the actual value if we take average of these two values . This happens because two types of ions in BCC (say CsCl, Cs^+ and Cl^-) sense different environments around them[3]. Table shows values we got in increasing cubic systems and the respective percentage errors.

system size	MC calculated	reference value	% error
10	1.756813	1.7627	0.3339
20	1.758072	1.7627	0.2625
50	1.758353	1.7627	0.2466
100	1.758847	1.7627	0.2185

Graphical representation of the above results are given in (fig.17 and fig.18). All the calculations are done considering the fractional charges on ions. The results are within 1% error so we can conclude that the fractional charge consideration can be applied to lattices other than the simple cubic.



5.4 Calculation on a 3D body with 2D periodicity:

Plate Like Structure: The idea is to span the lattice in X (L_x) and Y (L_y) direction only restricting the Z (L_z) direction growth. The MC values was noticed to converge to usual 3D simple cubic lattice values with increasing L_z values. $L_x = 100, L_y = 100$.

L_z	Madelung constant
1	0.841162
2	1.682328
4	1.748332
6	1.747568
8	1.747570
10	1.747579
20	1.747584

Stick Like Structure: Here we increase L_x and L_y from small values and see the effect on Madelung constant values. $L_z = 100$.

L_x, L_y	Madelung constant
2	1.595352
4	1.748923
6	1.747542
8	1.747565
10	1.747556

Plot of the values gives us (fig.19) and (fig.20).

As we expected the Madelung constant values for two systems converged to simple cubic MC value 1.7475 as their size increased. But at low values of L_z and L_x , L_y both the systems gave very different sum values, which indicate the probable change in their physical properties when we take plate or stick like systems of bulk materials.



We also checked that for plate like system keeping L_z low, increasing L_x and L_y does not have any significant effect on the sum value. This shows consistency with our understanding of Madelung Constant, validate our results too.

6 Summery and Conclusion:

We have used a method, the fractional charge consideration to calculate Madelung constant of various lattice systems in all three dimensions and compared our findings with standard results and recent publications and our values were within sufficient error limit. We have observed that the advantage of using our method is the fast convergence rate of it and the disadvantage is the oscillation of error values with very small amplitude at very large systems. We could not investigate it fully and properly but from judging the nature of this error in many systems we can point out a probable reason for this peculiarity that is the local imbalance of charges due to fractional charge consideration in larger systems. Some modification of the method can be done in large systems to stabilize this charge imbalance.

Secondly we have calculated Madelung sum values for slightly disordered lattice and our findings were supported by the fact that this disorder increases energy of the system. Actually the system energy was found to increase with increasing disorder ,however we restricted the disorder up to maximum 20% of the nearest neighbour distance, to preserve the co-ordination number of ions and other details of the regular lattice. Then we have investigated some non-trivial cases where the system is in 3D but the periodicity is only restricted to one and two dimensions. We observed interesting results in plate-like and stick-like structures, the Madelung constant values found was not like 1D nor like 2D. We also justified our codes and methods by observing that if we increase the system size in the previously restricted directions, the Madelung constant values converge to the trivial 3D lattice values. Same kind of results were noted for a 2D system with 1D periodicity also.

we firmly believe that using fractional charge distribution, a lot more things can be accomplished. A few promising ideas that we could not verify properly due to circumstances are listed here. We can calculate energy change in ionic solid due to point defects in the lattice, the disordered lattice calculation was the first step towards that. Similarly change in Madelung constant value due to substitution with ions with same valency but different size (like Na^+ with K^+) can be calculated. With help of self avoiding random walk we can also calculate the Coulombic interaction energy in a gel where the constituent molecules are long chain organic molecules with ionic parts attached.

7 Main FORTRAN codes used in project:

7.1 Code for calculation of Madelung constant for 3D simple cubic lattice:

```
c PROGRAM TO CALCULATE MADELUNG SUM OF A SIMPLE CUBIC LATTICE
```

```
c USING FRACTIONAL CHARGE CONSIDERATION :
```

```
c TIME MEASUREMENT
real etime
real elapsed(2)
real total
real a,b,d,sum,charge,r1(1:3),r2(1:3),factor
real centreQ
integer i,j,k,n,cell,x,y,z,count,sign1
open(unit=31,file='nacl.txt')
```

```
NORMALISATION W.R.T. NEAREST NEIGHBOUR DISTANCE
с
      factor=1
      write(*,*)factor
      DEFINITING SYSTEM SIZE L=2*n
С
      n=250
      MAIN CALCULATION PART
С
      sum=0.0
      count=0
      centreQ=1.0
      cell=(2*n)**3
      do 10 x=0,n-1
      do 11 y=0,n-1
      do 12 z=0,n-1
      count=count+8
       r1(1)=1.0*x
       r1(2)=1.0*y
       r1(3)=1.0*z
      FRACTIONAL CHARGE CONSIDERATION LOGIC
С
       do j=1,8
        if(j.eq.1) then
        r2(1)=0.0
        r2(2)=0.0
        r2(3)=0.0
        sign1=(-1)**(x+y+z)
        charge=sign1*0.125
        endif
        if(j.eq.2) then
        r2(1)=1.0
        r2(2)=0.0
        r2(3)=0.0
        charge=(-sign1)*0.125
        endif
        if(j.eq.3) then
        r2(1)=0.0
        r2(2)=0.0
        r2(3)=1.0
        charge=(-sign1)*0.125
        endif
        if(j.eq.4) then
        r2(1)=0.0
        r2(2)=1.0
        r2(3)=0.0
        charge=(-sign1)*0.125
        endif
        if(j.eq.5) then
```

```
r2(1)=1.0
        r2(2)=1.0
        r2(3)=0.0
        charge=sign1*0.125
        endif
        if(j.eq.6) then
        r2(1)=1.0
        r2(2)=0.0
        r2(3)=1.0
        charge=sign1*0.125
        endif
        if(j.eq.7) then
        r2(1)=0.0
        r2(2)=1.0
        r2(3)=1.0
        charge=sign1*0.125
        endif
        if(j.eq.8) then
        r2(1)=1.0
        r2(2)=1.0
        r2(3)=1.0
        charge=(-sign1)*0.125
        endif
        d=sqrt((r1(1)+r2(1))**2+(r1(2)+r2(2))**2+(r1(3)+r2(3))**2)
        if(d.NE.0) then
         sum=sum+(8.0*centreQ*charge*(1/d))*factor
        endif
        end do
12
      continue
11
      continue
10
      continue
      OUTPUT OF RESULT:
С
      write(*,*)n, sum
      total = etime(elapsed)
      print *, 'End: total=', total, ' user=', elapsed(1)
      stop
      end
7.2
    Code for calculation of Madelung constant for 2D square lattice:
      CODE FOR CALCULATION OF MADELUNG CONSTANT FOR
```

2D SQUARE LATTICE : с

с

ELAPSED TIME CALCULATION С

```
real etime
      real elapsed(2)
      real total
      real d, sum, qT,n,charge,sign
      integer i, j, k, r, Q
      Q=1
      OPEN OUTPUT FILE
с
      open(unit=21,file='fractional_charge.txt')
      sum=0
      CHANGING SYSTEM SIZE L=2*k
с
      do 6 k=1,250
      MAIN CALCULATION
с
      do i=-k,k
       do j=-k,k
       r= i*i +j*j
       d=sqrt(1.0*r)
       sign=(-1.0)**(i+j)
       charge=1.0*sign
с
      FRACTIONAL CHARGE CONSIDERATION LOGIC
       if(d.GT.0) then
         if(abs(i).EQ.k) then
           charge=0.5*sign
           endif
         if(abs(j).EQ.k) then
           charge=0.5*sign
           endif
         if((abs(i).EQ.k).AND.(abs(j).EQ.k)) then
           charge=0.25*sign
           endif
         sum=sum+1.0*charge*Q*(1/d)
       endif
      end do
      end do
      WRITING OUTPUT FILE
С
      write(21,*)2*k,sum
      sum=0
6
      continue
      total = etime(elapsed)
      print *, 'End: total=', total, ' user=', elapsed(1)
```

stop end

7.3 Codes for sum on non-trivial systems:

```
CODE FOR CALCULATING MADELUNG CONSTANT IN PLATE-LIKE OR
С
С
      STICK-LIKE SYSTEMS:
      real a,b,c,d,charge,sum
      integer i,j,k,k1,sign,n
      open(unit=21,file='fractional_surface.txt')
      SYSTEM SIZE ALONG Z DIRECTION 2*n
с
      n=1
      SYSTEM SIZE IN OTHER DIRECTIONS 2*k1
с
      k1=200
      sum=0.0
      do 10 i=-k1,k1
      do 11 j=-k1,k1
      do 12 k=-n,n
      sign=(-1)**(i+j+k)
      d=1.0*sqrt(1.0*(i**2+j**2+k**2))
      charge=1.0
       if(d.NE.0) then
      FRACTIONAL CHARGE LOGIC
С
       if((abs(i).EQ.k1).OR.(abs(j).EQ.k1).OR.(abs(k).EQ.n)) then
       charge=0.5
       endif
       if((abs(i).EQ.k1).AND.(abs(j).EQ.k1)) then
       charge=0.25
       endif
       if((abs(j).EQ.k1).AND.(abs(k).EQ.n)) then
       charge=0.25
       endif
       if((abs(i).EQ.k1).AND.(abs(k).EQ.n)) then
       charge=0.25
       endif
       if((abs(i).EQ.k1).AND.(abs(j).EQ.k1).AND.(abs(k).EQ.n)) then
       charge=0.125
       endif
       sum=sum+1.0*charge*sign*(1/d)
       endif
```

```
12 continue
11 continue
10 continue
c OUTPUT
write(*,*)k1,sum
```

stop end

7.4 Code for calculating Madelung sum in disordered lattice: 1D

```
CODE TO CALCULATE MADELUNG SUM IN DISORDERED LATTICE:
с
      INITIALISATION OF RANDOM NUMBER GENERATOR
С
      real a,b,c,d(-100:100),sign,charge,sum,x,del
      integer i,j,k,l,sign1
      integer*4 timeArray(3)
      call itime(timeArray)
      i=rand(timeArray(3))
      del=0.6
      open(unit=22,file='random_1D.txt')
      NO OF RUN 20000. AVERAGED OVER THIS NO OF MC VALUES
с
      do 10 k=1,20000
      SYSTEM SIZE
С
      do 12 l=-100,100
      RANDOM NO GENERATED
С
       x=del*rand()
       sign1=abs(3*rand())-1
       d(l)=abs(l)+sign1*x
 12
      continue
      sum=0.0
      do 11 j=-100,100
      if(j.NE.0) then
      sign=(-1.0)**j
      charge=1.0
      if(abs(j).EQ.100) then
      charge=0.5
      endif
      sum=sum+1.0*sign*charge/d(j)
      endif
```

11 c	continue OUTPUT write(22,*)-sum
10	continue
	stop end

8 Appendix:

8.1 Random number generator

We have used a library function defined random number generator, using 'time array' outputs as feeds. Here we have shown the uniformity of the used generator.



8.2 Frenkel defect in 2D square lattice:

We have presented a few values from the Frenkel defect code we developed, the pairwise point defect. n is no of defects in the crystal n=1% of total ions

n	Madelung constant
118	1.504043
116	1.333160
111	1.411336

 $n{=}2\%$ of total ions

n	Madelung constant
208	1.751187
210	2.439424
188	1.109287

9 References

- 1. Simple calculation of Madelung constants. Walter A. Harrison. PHYSICAL RE-VIEW B 73, 212103 ,(2006)
- 2. Efficient calculation of Madelung constants for cubic crystals. Michele Gaio and Pier Luigi Silvestrelli PHYSICAL REVIEW B 79, 012102 (2009)
- 3. Rapid calculation of individual ion Madelung constants and their convergence to bulk values. A. D. Baker and M. D. Baker. Am. J. Phys. 78 (1), January 2010.
- 4. book: Solids:an introduction by A. Hart Davis .
- 5. Ewald summation techniques in perspective: a survey. Abdulnour Y. Toukmaji, John A. Board Jr. . Computer Physics Communications 95 (1996) 73-92.
- 6. book: Introduction to solid state physics by Charles Kittel.