The Madelung Energy of an Ionic Crystal

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2D Lattice

Consider a 2D lattice from a rock-salt crystal (called bipartite lattice). Obtain the Madelung (electrostatic) energy and show how the calculation is sensitive to the way in which the infinite sum is truncated (squares or circles).

```
In[∘]:= (*i+j → interactions between positive or negative charges.*)
        (*Energy when 2 charges are at the same position → approaches to ∞.*)
```

```
In[∘]:= sqSum[n_] := Sum[If[i == j == 0, 0, N[(-1)^(i+j)/Sqrt[i^2 + j^2]]], {i, -n, n}, {j, -n, n}]
```

```
(*If i = j (particles are at the same position), the energy is 0.*)
```

(∨ is ESC or ESC)

```
In[∘]:= crSum[n_] := Sum[If[Sqrt[i^2 + j^2] > n ∨ i == j == 0, 0, N[(-1)^(i+j)/Sqrt[i^2 + j^2]]], {i, -n, n}, {j, -n, n}]
```

```
In[∘]:= (*The sum has to converge, since the energy of a ionic crystal is finite.*)
        (*This is the formula to compute the Coulombic energy of an arangement
         of charges distributed in a crystal (infinite in all directions).*)
```

Let’s understand what is doing sqSum[n]:

```
In[∘]:= sqSum[1]
Out[∘]= -1.17157
```

```
In[∘]:= Table[If[i == j, 0, f[i, j]], {i, -1, 1}, {j, -1, 1}] // Flatten
Out[∘]= {0, f[-1, 0], f[-1, 1], f[0, -1], 0, f[0, 1], f[1, -1], f[1, 0], 0}
```

```
In[∘]:= N[(-1)^(i+j)/Sqrt[i^2 + j^2]] /. {i → -1, j → -1}
Out[∘]= 0.707107
```

In[∘]:= $N\left[\frac{(-1)^{i+j}}{\sqrt{i^2+j^2}}\right]$ /. {i → -1, j → 0}

Out[∘]= -1.

In[∘]:= $N\left[\frac{(-1)^{i+j}}{\sqrt{i^2+j^2}}\right]$ /. {i → -1, j → 1}

Out[∘]= 0.707107

In[∘]:= $N\left[\frac{(-1)^{i+j}}{\sqrt{i^2+j^2}}\right]$ /. {i → 0, j → -1}

Out[∘]= -1.

In[∘]:= $N\left[\frac{(-1)^{i+j}}{\sqrt{i^2+j^2}}\right]$ /. {i → 0, j → 0} (*This case we made 0 with the if statement.*)

Power: Infinite expression $\frac{1}{\sqrt{0}}$ encountered.

Out[∘]= ComplexInfinity

In[∘]:= $N\left[\frac{(-1)^{i+j}}{\sqrt{i^2+j^2}}\right]$ /. {i → 0, j → 1}

Out[∘]= -1.

In[∘]:= $N\left[\frac{(-1)^{i+j}}{\sqrt{i^2+j^2}}\right]$ /. {i → 1, j → -1}

Out[∘]= 0.707107

In[∘]:= $N\left[\frac{(-1)^{i+j}}{\sqrt{i^2+j^2}}\right]$ /. {i → 1, j → 0}

Out[∘]= -1.

In[∘]:= $N\left[\frac{(-1)^{i+j}}{\sqrt{i^2+j^2}}\right]$ /. {i → 1, j → 1}

Out[∘]= 0.707107

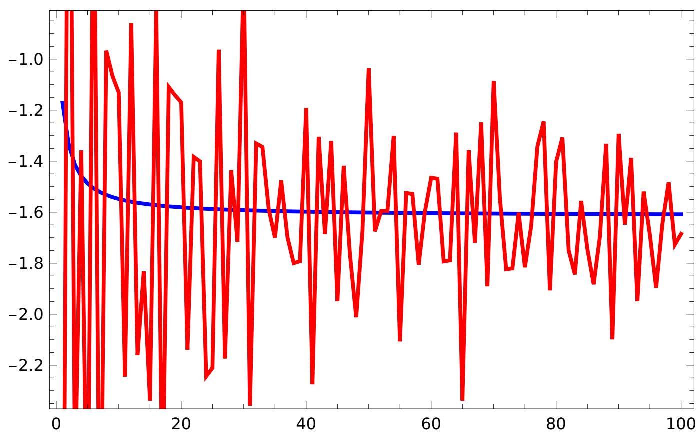
In[∘]:= (*What we did here is to debug what we want to do with the sqSUm[_n] function.*)

In[∘]:= 4 + 4 (*We got 4 times 0.71 and 4 times -1.*)

Out[∘]= -1.17157

In[∘]:=
```
DiscretePlot[
 {sqSum[n], crSum[n]}, {n, 1, 100},
 Filling → None,
 Frame → True,
 Joined → True,
 PlotStyle → {Blue, Red}
]
```

Out[∘]=



In[∘]:=
```
(*To get the data points, double click 3 times over the blue line and copy it.*)
(*Blue (circle sum) → clear convergence (we're gonna use it from now).*)
(*Why the red line is so irregular? It's an artifact;
we know that crystals have a finite energy,
but how we compute that energy is other hisotry (better ways than others). Each line
 here represents an algorithm. The red line repreents a very unstable algorithm.*)
(*Why the algorithm with circles converges faster than the algorithm with squares?*)
```

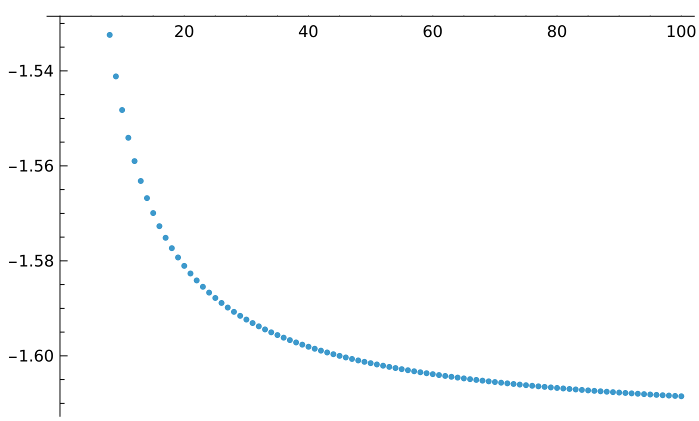
In[∘]:=
```
data =
```


Out[∘]=

In[∘]:=
```
line = data[[1, 4, 4, 1, 1]];
```

In[∘]:=
```
line // ListPlot
```

Out[∘]=



Model 1

In[∘]:=
```
model1 = c[1] + c[2] Exp[-c[3] x] + c[4] x^-c[5];
```

In[∘]:=
```
nlm1 = NonlinearModelFit[line, model1, Table[c[n], {n, 5}], x]
```

Out[∘]= FittedModel[$-1.62 - 0.798\, e^{-1.87\, x} + \frac{0.568}{x^{0.919}}$]

In[∘]:=
```
nlm1[x]
```

Out[∘]= $-1.61699 - 0.797536\, e^{-1.87376\, x} + \frac{0.567911}{x^{0.919467}}$

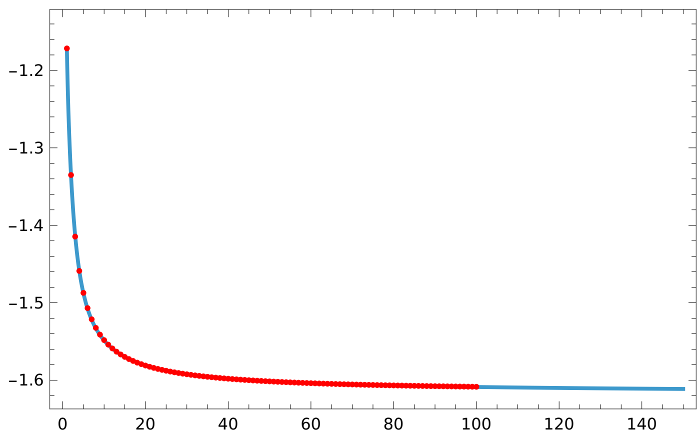
In[∘]:=
```
nlm1["RSquared"] // NumberForm[#, 16] &
```

Out[∘]//NumberForm=

0.999999970625266

In[∘]:=
```
Plot[nlm1[x], {x, 1, 150},
 Frame → True,
 Epilog → {Red, Point[line]},
 PlotRange → All
]
```

Out[∘]=



In[∘]:=
```
Limit[nlm1[x], x → ∞]
```

Out[∘]= -1.61699

Model 2

In[∘]:=
```
model2 = c[1] + c[2] Exp[-c[3]/x];
```

In[∘]:=
```
nlm2 = NonlinearModelFit[line, model2, Table[c[n], {n, 3}], x]
```

Out[∘]= FittedModel[$-0.925 - 0.691\, e^{-1.03/x}$]

In[∘]:=
```
nlm2[x]
```

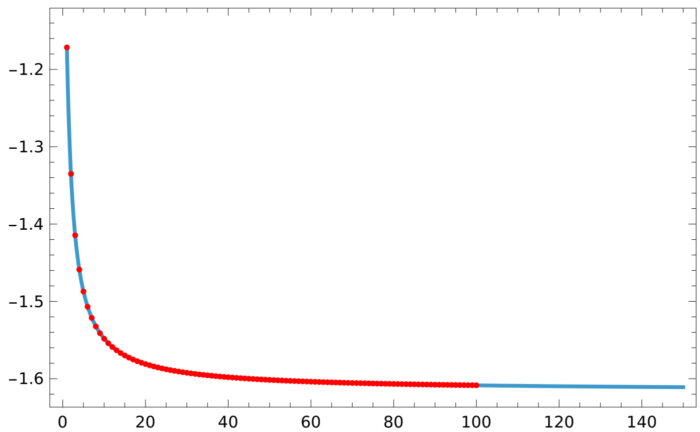
Out[∘]= $-0.924787 - 0.690899\, e^{-1.03194/x}$

In[∘]:=
```
nlm2["RSquared"] // NumberForm[#, 16] &
```

Out[∘]//NumberForm=
```
0.999999974427625
```

In[∘]:=
```
Plot[nlm2[x], {x, 1, 150},
 Frame → True,
 Epilog → {Red, Point[line]},
 PlotRange → All
]
```

Out[∘]=



In[∘]:=
```
Limit[nlm2[x], x → ∞]
```

Out[∘]= -1.61569

In[∘]:=
```
(*This model is better, since we have almost the same R value,
but we have only 3 variables.*)
```

3D Lattice: The NaCl Crystal

Now let's evaluate the Madelung energy for the NaCl crystal, considering that r0 = 2.81 Å (from experiments). The experimental value of the cohesion energy is -7.9 eV/atom.

In[∘]:=

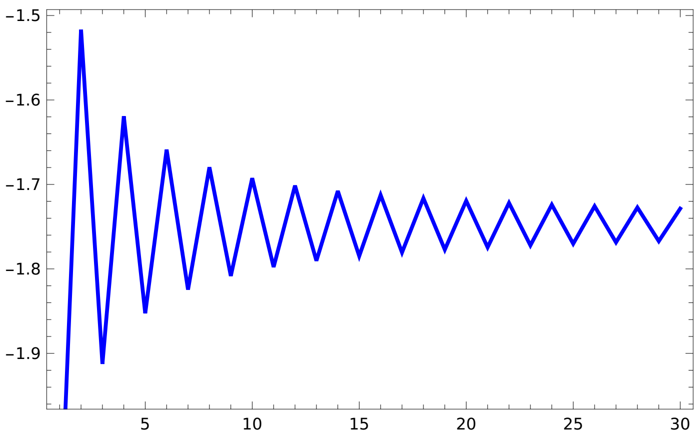
$$\text{sqSum[n\_] := Sum}\left[\text{If}\left[i == j == k == 0, 0, N\left[\frac{(-1)^{i+j+k}}{\sqrt{i^2+j^2+k^2}}\right]\right], \{i, -n, n\}, \{j, -n, n\}, \{k, -n, n\}\right]$$

In[∘]:=

$$\text{crSum[n\_] :=}$$
$$\text{Sum}\left[\text{If}\left[\sqrt{i^2+j^2+k^2} > n \lor i == j == k == 0, 0, N\left[\frac{(-1)^{i+j+k}}{\sqrt{i^2+j^2+k^2}}\right]\right], \{i, -n, n\}, \{j, -n, n\}, \{k, -n, n\}\right]$$

In[•]:=
```
DiscretePlot[
 {sqSum[n]}, {n, 1, 30},
 Filling → None,
 Frame → True,
 Joined → True,
 PlotStyle → Blue
]
```

Out[•]=



In[•]:= data =

Out[•]= 

In[•]:=
```
line = data⟦1, 4, 4, 1, 1⟧
```

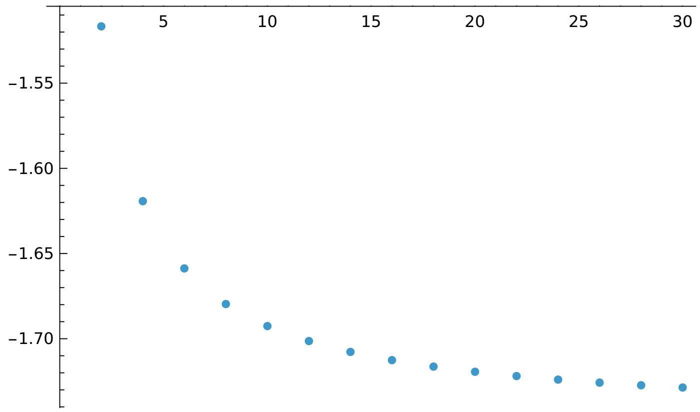
Out[•]=
```
{{1., -2.13352}, {2., -1.51665}, {3., -1.9125}, {4., -1.61927}, {5., -1.85254},
 {6., -1.65874}, {7., -1.82454}, {8., -1.67964}, {9., -1.80834}, {10., -1.69258},
 {11., -1.79777}, {12., -1.70138}, {13., -1.79033}, {14., -1.70775}, {15., -1.78481},
 {16., -1.71257}, {17., -1.78056}, {18., -1.71636}, {19., -1.77717}, {20., -1.7194},
 {21., -1.77442}, {22., -1.7219}, {23., -1.77213}, {24., -1.724}, {25., -1.77021},
 {26., -1.72578}, {27., -1.76856}, {28., -1.72731}, {29., -1.76714}, {30., -1.72864}}
```

In[•]:=
```
linea = data⟦1, 4, 4, 1, 1⟧⟦2 ;; 30 ;; 2⟧
```

Out[•]=
```
{{2., -1.51665}, {4., -1.61927}, {6., -1.65874}, {8., -1.67964}, {10., -1.69258},
 {12., -1.70138}, {14., -1.70775}, {16., -1.71257}, {18., -1.71636}, {20., -1.7194},
 {22., -1.7219}, {24., -1.724}, {26., -1.72578}, {28., -1.72731}, {30., -1.72864}}
```

In[∘]:=
```
linea // ListPlot
```

Out[∘]=

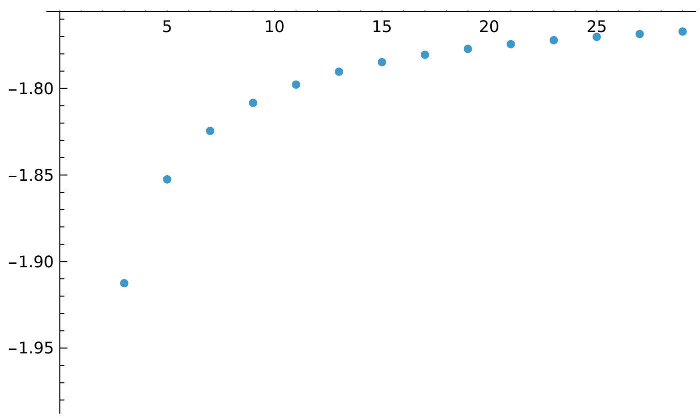


In[∘]:=
```
lineb = data[[1, 4, 4, 1, 1]][[1 ;; 30 ;; 2]]
```

Out[∘]=
```
{{1., -2.13352}, {3., -1.9125}, {5., -1.85254}, {7., -1.82454}, {9., -1.80834},
 {11., -1.79777}, {13., -1.79033}, {15., -1.78481}, {17., -1.78056}, {19., -1.77717},
 {21., -1.77442}, {23., -1.77213}, {25., -1.77021}, {27., -1.76856}, {29., -1.76714}}
```

In[∘]:=
```
lineb // ListPlot
```

Out[∘]=



Model 1

In[∘]:=
```
model1 = c[1] + c[2] Cos[c[3] x^c[4]] Exp[-c[5] x];
```

In[∘]:=
```
nlm1 = NonlinearModelFit[line, model1, Table[c[n], {n, 5}], x]
```

Out[∘]= FittedModel[$-1.75 + 0.439\, e^{-\ll 20 \gg x} \operatorname{Cos}[2.7\, x^{1.05}]$]

In[∘]:=
```
nlm1[x]
```

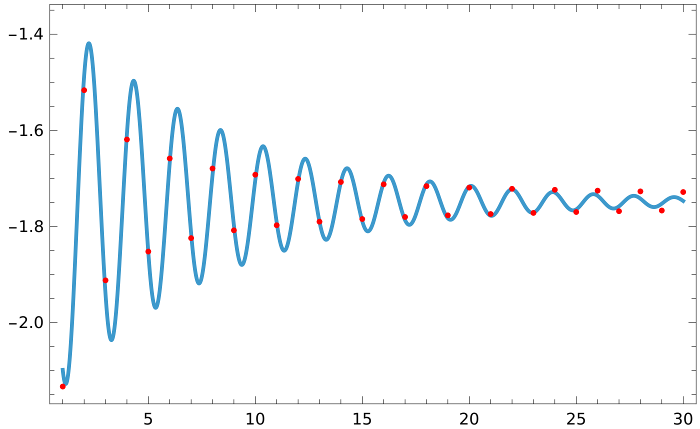
Out[∘]= $-1.74892 + 0.439448\, e^{-0.128775\, x} \operatorname{Cos}[2.704\, x^{1.04839}]$

In[∘]:=
```
nlm1["RSquared"] // NumberForm[#, 16] &
```

Out[∘]//NumberForm=
```
0.999946772807275
```

In[•]:=
```
Plot[nlm1[x], {x, 1, 30},
 Frame → True,
 Epilog → {Red, Point[line]},
 PlotRange → All
]
```

Out[•]=



In[•]:=
```
Limit[nlm1[x], x → ∞]
```

Out[•]= -1.74892

Model 2

In[•]:= nlma = NonlinearModelFit[linea, $c[1] + c[2]\,\mathrm{Exp}\left[-\frac{c[3]}{x}\right]$, Table[c[i], {i, 3}], x]

Out[•]= FittedModel[$-1.11 - 0.639\, e^{-0.896/x}$]

In[•]:= nlmb = NonlinearModelFit[lineb, $c[1] + c[2]\,\mathrm{Exp}\left[-\frac{c[3]}{x}\right]$, Table[c[i], {i, 3}], x]

Out[•]= FittedModel[$-2.44 + 0.687\, e^{-0.823/x}$]

In[•]:=
```
nlma["RSquared"] // NumberForm[#, 16] &
```

Out[•]//NumberForm=

0.999999999401422

In[•]:=
```
nlma[x]
```

Out[•]= $-1.1085 - 0.638893\, e^{-0.896129/x}$

In[•]:=
```
nlmb["RSquared"] // NumberForm[#, 16] &
```

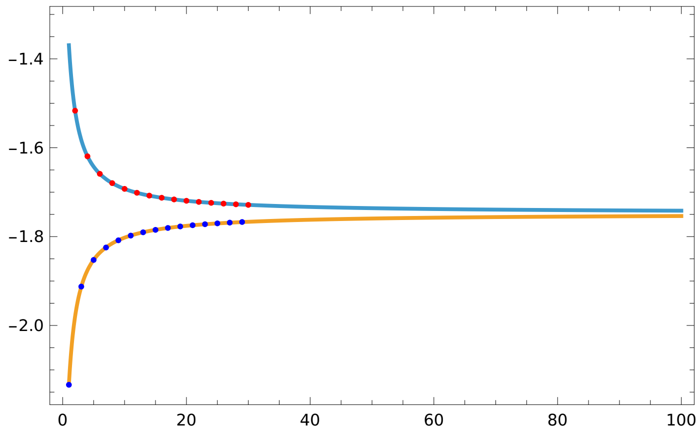
Out[•]//NumberForm=

0.9999999911306

In[•]:=
```
nlmb[x]
```

Out[•]= $-2.43539 + 0.687311\, e^{-0.822665/x}$

In[∘]:=
```
Plot[{nlma[x], nlmb[x]}, {x, 1, 100},
 Frame → True,
 Epilog → {{Red, Point[linea]}, {Blue, Point[lineb]}},
 PlotRange → All
]
```

Out[∘]=


In[∘]:= `limita = Limit[nlma[x], x → ∞]`

Out[∘]= -1.74739

In[∘]:= `limitb = Limit[nlmb[x], x → ∞]`

Out[∘]= -1.74808

In[∘]:= $\text{limit} = \frac{\text{limita} + \text{limitb}}{2}$

Out[∘]= -1.74774

In[∘]:=

Vacuum permitivity

In[∘]:= $\text{um} = \frac{q^2}{4\,\pi\,\epsilon 0\,r0}\,\text{limit}\,\frac{1}{1.6\times 10^{-19}}\ /.\ \left\{q \to 1.6\times 10^{-19},\ \epsilon 0 \to 8.8541\times 10^{-12},\ r0 \to 2.81\times 10^{-10}\right\}$

(*Madelung energy approximation in eV.*)

Out[∘]= -8.94407

In[∘]:= $\frac{\text{expv} - \text{um}}{\text{expv}}\,100\ /.\ \text{expv} \to -7.9$ (*Error in percentage.*)

Out[∘]= -13.2161

In[∘]:=
```
(*Discuss why do we get this error
 (we need QM to explain it, but here we used only CM).*)
(*Upload the NB until today's midnight.*)
```