

HW3 Write-Up: Madelung Constant

Nina Martinez Diers*
Bryn Mawr College Department of Physics
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In this assignment, the madelung constants were calculated for a generic simple cubic lattice and body-centered cubic lattice crystal structures with atom types (charges and atomic radii) held constant.

1. INTRODUCTION

The Madelung constant for a simple-cubic lattice made of atoms with +1 and -1 charges can be calculated from two different formulas. Positively charged atoms make positive contributions, and negatively charged atoms make negative contributions to the constant. The first method uses a sum to calculate the contributions to the constant of all lattice sites with respect to a central reference point:

$$M = \sum_{j,k,l=-N}^N \frac{(-1)^{j+k+l}}{\sqrt{j^2 + k^2 + l^2}} \quad (1)$$

where N is the number of lattice sites along an edge of a cubic lattice. It takes into account the charge and the distance of each atom in the lattice from the central lattice point. The method is only considered exact when N approaches infinity.

The second method uses hyperbolic secant inside of an infinite sum instead of the more explicit lattice-site method:

$$M = 12\pi \sum_{m,n \geq 1, \text{ odd}} \operatorname{sech}^2 \left(\frac{\pi}{2} \sqrt{m^2 + n^2} \right) \quad (2)$$

In these methods, the distance between lattice sites was approximated to be equal to 1. Because the lattice is simple cubic, this means that the sum of the atomic radii = 1. To calculate the Madelung constant of the body-centered cubic lattice, a modification of Equation 1 was used, calculating the constant using a lattice of positively charged atoms superimposed on a lattice of negatively charged atoms that is shifted slightly. For each lattice site, the contribution of a positive and negative j, k, l atom was included, except that the lattice sites of the negatively charged atoms were translated from those of the positive ones by $a = \frac{2r}{\sqrt{3}}$ dependent on the sum r of the positive and negative atomic radii:

$$M = \frac{1}{a} \sum_{j,k,l=-N}^N \frac{1}{\sqrt{j^2 + k^2 + l^2}} - \frac{1}{\sqrt{(j+1/2)^2 + (k+1/2)^2 + (l+1/2)^2}} \quad (3)$$

2. EXPERIMENT

The pseudocode in Figure 1 outlines the method taken in building the algorithms to calculate the Madelung constant.

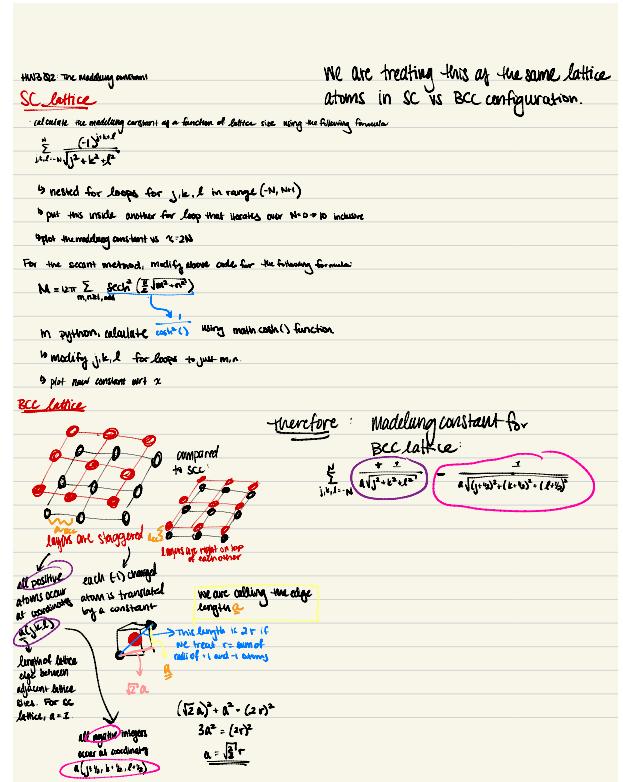


FIG. 1: [Pseudocode outlining SC algorithm and the derivation of a BCC lattice Madelung formula.]

*Electronic address: nmartinezd@brynmawr.edu

3. RESULTS

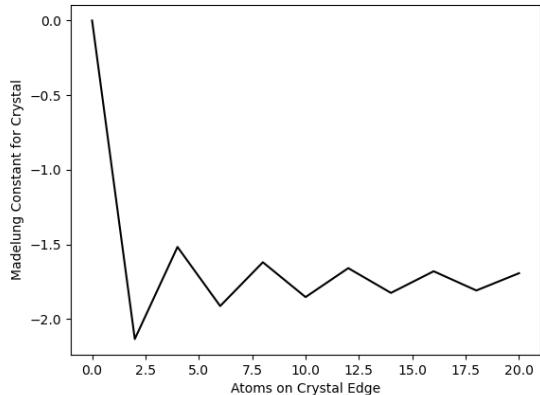


FIG. 2: [Madelung constant for a simple cubic lattice as a function of lattice size calculated using the summation method (Eq. 1). Atoms were assigned +1 or -1 charge.]

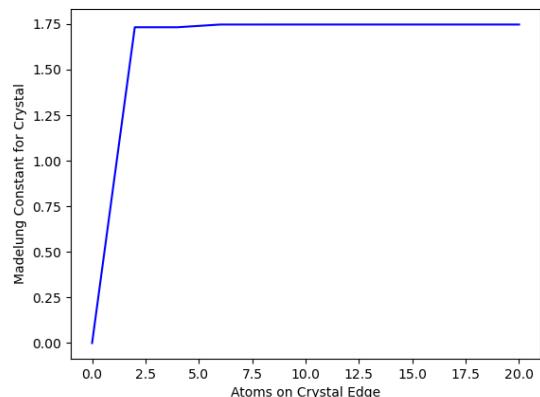


FIG. 3: [Madelung constant for a simple cubic lattice as a function of lattice size calculated using the secant method (Eq. 2). Atoms were assigned +1 or -1 charge.]

The Madelung constants for both simple (secant method) and body-centered cubic converged when the lattice size reached about 125 atoms. It took longer for the lattice-site method to converge than the secant method for simple-cubic because its nature is alternating additions of positive and negative shells of atoms around a reference atom. The simple cubic Madelung constants each converged at around 1.75, except one was negative and one was positive. This difference is due to the Madelung sum starting from the reference point of a positive atom, so the largest contributions to the constant are from a shell of negatively charged atoms. The body-centered cubic Madelung constant converged at approximately -0.40.

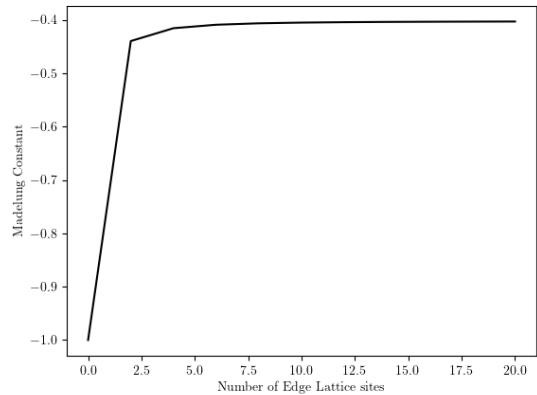


FIG. 4: [Madelung constant for a body-centered cubic lattice as a function of lattice size calculated using the a modified summation method (Eq. 3). Atoms were assigned +1 or -1 charge. Positively and negatively charged atoms were approximated to have the same radius.]

4. CONCLUSIONS

The Madelung constants for both simple cubic lattice was calculated to be 1.75, while the constant for the body-centered cubic lattice converged at approximately -0.40.

Appendix A: Statement of Collaborators

I did not collaborate on this assignment.

Appendix B: Survey Question

I spent about 10 hours on pseudocode. 9 of these were figuring out how to approach the bcc lattice madelung

constant problem. Coding took about 3 hours, and the write-up took about 1. I really enjoyed puzzling through the bcc lattice problem, and something I learned was that there are multiple different ways to calculate the madelung constant. I had only seen one way of doing it before, and it was really nice to be allowed to calculate it computationally (in the previous class we had to calculate it by hand which was a pain and very prone to mistakes.)