Solid State Physics
Lecture 17
Evaluation of the Madelung Constant

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So, we have calculated most of the things except the Madelung constant α. If we calculate that, our understanding of ionic crystals would be complete. So, let us now put some effort in calculating the Madelung constant. The first calculation of the Coulomb energy constant α that was made by Madelung, and a powerful general method for the lattice sum was developed by Ewald. So, we have already defined the Madelung constant α that is given as $\Sigma'_j \frac{(\pm)}{p_{ij}}$. And for a stable crystal, if you look at the expression for the total energy, then you will find that α must be positive; otherwise the crystal would have larger energy than the separate atoms isolated atoms and that crystal would never form. So, if we take the reference ion as negative charge negative charged one, then plus sign will apply for positive ions and minus sign will apply for negative ions. And with that we can write and so just an equivalent definition of this Madelung constant can be written as $\frac{\alpha}{R} = \Sigma'_j \frac{(\pm)}{p_{ij}}$ which is just the same where sorry it is not r_{ij}, it is r_j. Where r_j is the distance of the j^{th} atom from the reference ion, and capital R is the nearest neighbour distance. The value given for α will depend on whether it is defined in terms of the nearest neighbour distance or the lattice constant or some other relevant parameter. Now, let us consider a simple example for calculating the value of α the Madelung constant. So, we consider an infinite linear one-dimensional chain of ions where say this one is positive, the nearest neighbour is negative, the next one is positive, next one is negative and so on also this space so on it is infinite. And if it has a boundary we are not going to consider that boundary because the effect of boundary would be so tiny in case of very long chain that we can safely ignore that boundary effect. Now, if we pick up a negative ion as our reference ion, then capital R can be the adjacent can be the distance between adjacent ions so like this. And if we have that, then according to this definition this expression, we can write $\frac{\alpha}{R} = 2[\frac{1}{R} - \frac{1}{2R} + \frac{1}{3R} - \frac{1}{4R} + ...]$ and so on which means α can be expressed as $2[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + ...]$. How do we calculate this? So, the factor 2 outside that we have here, this comes because there are two neighbouring ions; one in this direction, one in this direction at equal distance. And this is not the case at the boundary; anyway we are ignoring the boundary. So, we do not mind about that. If we sum over this series now, how do we sum over this series? Let us refer to some similar series. The natural logarithm $\ln(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + ...$ If you put $x = 1$ here, then you will obtain exactly this series here, that means, we have $\alpha = 2\ln 2$, $2\log 2$; this is the value for α if we consider a 1D chain of alternating ions just like the one drawn here. But this cannot be extended to three dimension or two dimension because the things would become a lot more complicated. You will not find this kind of a reference series to sum it this way, and making the sum converge will also become very difficult. So, you will have a homework to write a computer program that estimates the Madelung constant in two dimension and three dimension of some in some simple structure not very difficult structure.