PROFESSOR: Hi, I'm Sal. Today we will be doing problem number 4 of fall 2009, exam 1. Now before you attempt the problems there's certain background information that you should know before attempting it. One is knowledge in ionic bonding. Because the problem deals with ions. Two, how to draw an energy-level diagram. That's very important. And three, what Madelung's Constant is.

Now before attempting the problem, it's a good thing to read the whole problem in detail and make sure you don't skip anything out of it. So that you get all the information that's given to you. Because that's very important. So the problem reads as follows. For a given cation, c and anion a, show that the following four energy states on the same energy-level diagram. 1, Ions in infinite separation. 2, 9-pair c and a, c stands for cation, a stands anion. 3, An ion line, c a c a c a, just a repetitive line of anions and cations. And 4, crystalline solid of c a. So a three-dimensional crystal structure with t and a. And it says also that, assume that the comparison is based upon identical numbers of ions in all four states. The diagram need not to be drawn to scale, however you must convey relative values of different energy states.

So that's the problem reads. Now if you recall from lecture there's an important equation that actually describes the energy between two ions, between a cation and an anion. And this energy is directly proportional to the product of the two charges. And it's inversely proportional to the separation distance between them. And it's multiplied by some constants. So what does this mean? Well the fact that it's directly proportional to the product of your two charges means that your energy for any ion or anything that ionically bonds, it's going to be negative. Because your z minus will be negative and that's the whole value of your energy will be negative. And that's what dictates stability. How negative the energy is. So with that in mind, we can go ahead and start the problem.

So we have a cation a and anion c. Now I like to draw diagrams, or draw little pictures because that helps me when I'm solving the problem. So I'm just going to draw pictures of a cation and an anion. So I have a cation, c and then I have an anion, a. So c and a, and the value of r naught from our equation is pretty much the separation distance between the two. So project this up, this is r naught. And if you look from the picture, r naught is just simply the radius of your cation plus the radius of your anion. Now this is already describing the energy between just a cation and an anion with these magnitude of charges. So all that tells me is that, this is already answering number 2, pretty much from the problem that we're asked for, which is the ion pair.

So the problem asked you to draw an energy-level diagram. That's what I'm going to do over here. So I'm going to go ahead and start drawing the energy-level diagram. Now I'm going to go ahead and label my energy axis to be positive to be up. And I'm going to draw a baseline of 0 here. So I know that to be able to incorporate my ion pair-- like I said the energy is negative, so if the energy goes up to here and let's say the value of the energy here is 0, then that ion pair should lie somewhere below it. So I'm going to go ahead and draw this line. And I'll label this, s 2 for our energy level diagram. So this is the ion pair.

Now number 1 says ions at infinite separation. What is the energy of two charged species that are separated by infinity? Well if you look at your equation, your equation tells you that it's inversely proportional to the separation distance. So all that tells you is that if you divide by infinity, your energy should be essentially 0. Which makes physical sense because those two charged species can't feel each other when they're separated.

So this is actually already my number 1, which is 0. Separated away.

So now we need to find what the energy is of an ion pair. Which is the line of c a. So we want to draw a little picture. It's pretty much going to be a repetition of that. And if I draw a line-- that's not very straight-- I'm going to draw a bunch of cations and anions. Essentially I can just imagine that it extends to infinity in both ways. So with my energy between these two ions right here is given by my equation, then I should be able to figure out what the energy is of the whole system. Because we're talking about electrostatic interaction, which you can just add linearly.

So I can make one assumption. But look at my cation and anion pair, I can go ahead and simplify my life by letting z plus be 1. So I'll write that down. I'll let z plus equal to plus 1, which is the charge on our cation. And I'll let z minus equal minus 1, which is the charge on the anion. So that's to help with the math.

So if I come back over here and if I look at my equation line then I know that if I draw-- let's see-- a reference access here. Then the separation between the cation and anion is r naught. And between the cation and the other cation is going to be 2 r naught. And it's going to extend for that. So if I go ahead and relabel my energy equation for a line. I'll go ahead and call it e line of function of r naught. It's simply going to be the first one, which is going to be negative e squared over 4 pi epsilon naught, r naught, multiply the 1 over minus 1 over n. So that's the energy between these two ions.

So now because the energy is electrostatic, this cation also feels the repulsion of this other cation. So therefore with that you have got to add what that interaction is. So the product of the two charges is plus 1, which gives it a plus in front of your equation. And I end up getting e squared over 4 pi epsilon naught. Now here's something that you should pay particular attention. The separation between these two cation is not r naught. It's actually 2 r naught. Because of where exactly where it sits on the line.

So my separation distance now becomes 2 r naught and it's multiplied by the same 1 minus 1 over n factor. Then if you repeat it again, you're analyzing the interaction energy between the cation and the other anion that's next on the line. So as you can see you end up getting this nice-- 4 pi epsilon naught, 3 r naught, 1 minus 1 over n. And essentially it repeats until it ends.

Now I'm just analyzing on the right side. Because it extends, it's an infinite line, because it extends from negative infinity to infinity, then you can also assume that there's an anion to the left. So all you really have to do is, you take your overall energy for the right side and you multiply it by 2. Because it's additive. So this whole thing gets multiplied by 2. And that's essentially what the energy is of a line.

Now in order to be able to know where it lies on the energy-level diagram, it's important to try to get it into the same basic form as the energy of an ion pair, just something simple like over there. So just by looking at the equation I know there's a lot of factors here that are common. Like that e squared, 4 pi epsilon naught, even r naught and this factor can all come out of the equation. You can take it out. So if I do that, my equation of my line then simply becomes negative e squared over 4 pi epsilon naught. Now I'm going to go ahead and take out the r naught as well. And I'm going to multiply it by the factor. And essentially what stays from here is just your 1 over 1. From this one it's your 1/2 and then your 1/3 and then we're happy. And because I also took out the negative, I want to make sure that I take out the negative from all the other ones too. So this product then gets multiplied by 1 minus 1 over 2, plus 1/3 minus 1/4 plus... and it goes on forever.

Now it so happens that this is actually a series that we have an answer or an answer to. And this product that's being multiplied by your fundamental base of your equation is just simply-- oh sorry I forgot the times 2, don't forget that, that's very important because you're summing from both sides-- this essentially right here it's simply arised because of your geometry. You're analyzing your systems. And this value happens to be greater than 1, which is a good thing. And the value of this is actually 1.386. So the fact that the whole equation is still negative, because we're talking about coulombic interaction between a negative charged species and a positive charged species. And we're multiplying that by a value that is greater than 1 this means that if this is 1 right here, then our energy level diagram should lie somewhere below it, like right here. So this is 3. And that's your ion line.

Now in real life we know that crystals don't exist in lines really. Or they're not just an ion pair. it's literally something that is three-dimensional and has an ordered structure. Sometimes could be different geometries, but normally it's a cubic structure. So because that forms in nature, then that tells me that the energy of a three-dimensional crystal, which is the fourth one that we need to put on the energy-level diagram, the value should be greater than 1.386. And this value of 1.386 is actually Madelung's Constant, which you should know. It was a required preliminary to the problem.

So I know that below this value of 1.386 I have my three-dimensional crystal. Now an energy-level diagram is pretty much quantized by different steps. Now what is quantizing our problem here? Well this is 0 because our energy is 0. So we can almost assume that we're multiplying-- or that the Madelung's Constant for ion pair with infinite separation is 0. And this is 1, so we can assume that the Madelung Constant is 1 or we know that it's 1 for the ion pair. So if I start writing this out on the side here-- give me some space-- I know that's one. I'm going to go ahead and label this by Madelung's Constant, which is 1.386. So I come over here. Relabel this. This value here's is 1.386. And this value here has to be greater than 1.386 for a three-dimensional crystal.

And this little diagram here is the answer to your question from the exam. So when you take the exam you don't really have to go through all this math to answer the problem. If you know the material from lecture, then the solution should be very straight-forward very easily. And also if you keep in mind that there's a lot of material that you need to know before you take the exam, and knowing how to absorb that material and apply it will help you in solving these type of problems, which can be pretty difficult.