Solid State Physics
Lecture 59
Rare Earth Atoms, Hund's Rule

Hello, we have earlier discussed about diamagnetism and paramagnetism. Now, we shall discuss about Rare Earth Elements, their contribution to magnetism. We shall also discuss Hund's rule and Crystal Field's Contribution to Magnetism. So, let us start with Rare Earth Elements. (Refer Slide Time: 00:50)

What are rare earth elements? (Refer Slide Time: 01:04)

If we look at the periodic table, here we can see starting from cerium, lanthanum is does not have any 4f electron, but starting from lanthanum already we can see that these are rare and it is found on earth. So, these are the rare earth elements. Starting from cerium 4f orbitals are occupied, and steadily it gets occupied up to ytterbium. So, the chemical properties of these trivalent ions are similar because the outermost electron shells are identical for all these, 4f is somewhere inside; 4f is not the outermost shell, but 4f electron the count of 4f electrons differ in these atoms. In lanthanum that is just before the rare earth group begins that is its 4f shell is empty. And the subsequent elements have increasingly more 4f electrons in here. So, we are considering only this one only the lanthanides not the actinides yet. And the radii of these trivalent ions, they contract somewhat smoothly. If we consider the first one that is cerium, that has an ionic radius of 1.11 Armstrong. And if we consider ytterbium the ionic radius is 0.94 armstrong. And the ionic radius contracts this is the famous lanthanide contraction, the contraction is pretty smooth. With that we earlier considered the discussion of paramagnetism, it applies on these atoms as well. But then we have 2(J + 1) fold degenerate ground states, and the degeneracy is lifted by a magnetic field. The influence of all higher energy states of the system is neglected. And these assumptions appear to be satisfied by a number of rare earth ions. We can obtain the Bohr magneto number and lambda g value this way. There is a discrepancy between this consideration and experiments in the magnetron number Bohr magnetron number. And those, so it is mostly found in europium and samarium these two are the wicked atoms. So, after discussing this, let us go on to discuss the Hund's rule. There are multiple rules of Hund. So, the Hund's rules are applied to electrons in a given shell of an atom that makes sure that the electrons will occupy orbitals in such a way that the ground state obeys certain properties. What are the properties? The first property is that the maximum value of the total spin allowed by the exclusion principle that would be realized, the maximum value of the orbital angular momentum consistent with the value of spin that would be realized. And the value of the total angular momentum J = —L - S— when the shell is less than half filled. And it would be —L + S— when the shell is more than half filled. And when the shell is exactly half filled the orbital angular momentum will go to 0, therefore, J = S. So, let us write down these rules. The ground state electronic arrangement would be such that the maximum value of the total spin that is S allowed by the Pauli Exclusion Principle. Number 2 is the maximum value of the orbital angular momentum that is consistent with the value of S. And number 3 is the value of the total angular momentum J that would be equals —L - S— absolute value for less than half filling, and it would be equal to L + S for more than half filling. The first rule that comes from the exclusion principle Pauli Exclusion Principle and Coulomb repulsion between electrons. The exclusion principle prevents two electrons of the same spin from having in the same quantum number. Therefore, electrons of the same spin are kept apart. Further apart than electrons of opposite spin they can come a bit closer. And because of Coulomb interaction, the energy of the electrons of the same spin is lower. The average potential energy is less positive for parallel spins than antiparallel spins that is because exclusion principle keeps the same spin further apart than the opposite spins, that justifies the first Hund's rule. The second Hund's rule can be approached can be understood by model calculations that Pauling and Wilson calculated the spectral terms that arise from a p_2 configuration and that was justified. The third rule is a consequence of the sign of spin orbit interaction. For a single electron, the energy is lowest when the spin is anti parallel to orbital angular momentum, hence the third rule can be justified.