Condensed Matter Physics
Prof. G. Rangarajan
Department of Physics
Indian Institute of Technology, Madras

Lecture - 8
Cohesion in Solids

We discussed symmetry in crystalline solids, which considered the atoms and molecules, which form a solid as purely entities in a geometrical arrangement apart from this geometrical consideration of symmetry. There is also another important aspect which really determines the nature of a given solid, this is because symmetry describes how the atoms and molecules are a arrange in different symmetric patterns in different crystalline solids, but it does not go into why this should be so. In order to attempt to answer this question it is necessary to go into the details detailed atomic or molecular structure.

And consider the electronic distributions and the interactions between the atoms and molecules, which brings about a certain which makes the solid a more stable configuration then that are the separated atoms and molecules, the situation here is somewhat similar to that have the formation of molecules from atoms. So, there are situations in which a separate atom is by itself tabor as in the case of for example, helium or neon. Whereas, in the case of hydrogen, we know it is a diatomic molecule, which consists of 2 atoms together, which are bonded together which is the stable configuration. So, the monocular stability is considered in quantum chemistry in solids the forces, which bring about the cohesion in a solid is also of fundamental importance this is what we will consider in this lecture.

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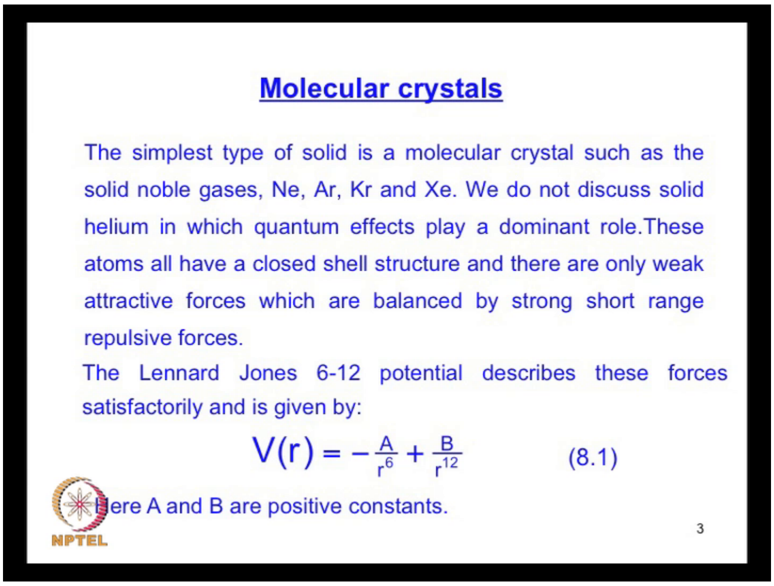

Molecular crystals

The simplest type of solid is a molecular crystal such as the solid noble gases, Ne, Ar, Kr and Xe. We do not discuss solid helium in which quantum effects play a dominant role.These atoms all have a closed shell structure and there are only weak attractive forces which are balanced by strong short range repulsive forces.

The Lennard Jones 6-12 potential describes these forces satisfactorily and is given by:

$$V(r) = -\frac{A}{r^6} + \frac{B}{r^{12}} \qquad (8.1)$$

Here A and B are positive constants.

At first we will consider the simplest type of solids which is a molecular crystal.

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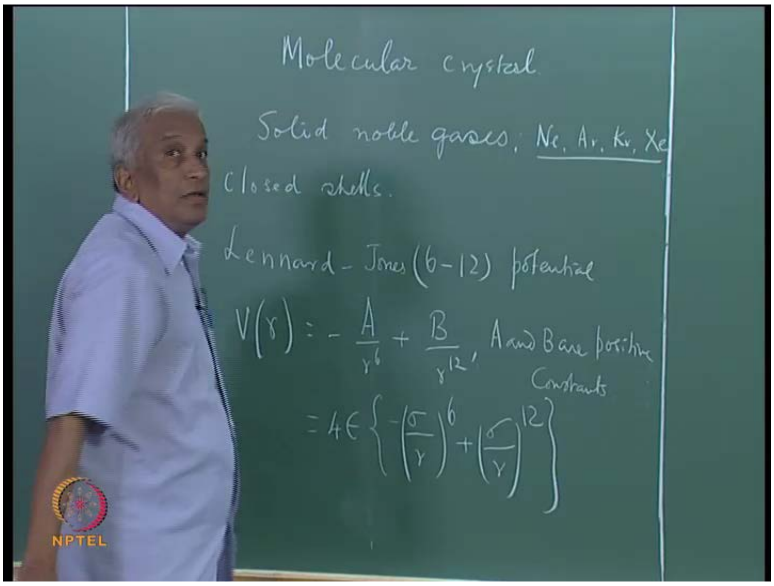

Molecular crystal

Solid noble gases, Ne, Ar, Kr, Xe

Closed shells.

Lennard-Jones (6-12) potential

$$V(r) = -\frac{A}{r^6} + \frac{B}{r^{12}}, \text{ A and B are positive Constants}$$

$$= 4\epsilon\left\{-\left(\frac{\sigma}{r}\right)^6 + \left(\frac{\sigma}{r}\right)^{12}\right\}$$

A typical example is that of the solid noble gas or inert gases such as neon argon krypton xenon helium is also in this family, but we do not discuss solid helium that is because, helium on account of its mall mass is a on atom in which quantum effects play a very dominant role. And because of this helium a does not solidify at any temperature above even at zero kelvin even it zero kelvin helium remains a liquid unless 1 applies an external pressure to squeeze the liquid.

And make it a freezen we have solid. So, we will not discuss solid helium which has somewhat special properties which have to be considered separately. If we leave out helium these other nobile gas solids have all got a closed shell configuration and because of the close shells the attractive forces between the atoms in the solid or rather weak and they are balanced by strong short-range repulsive forces.

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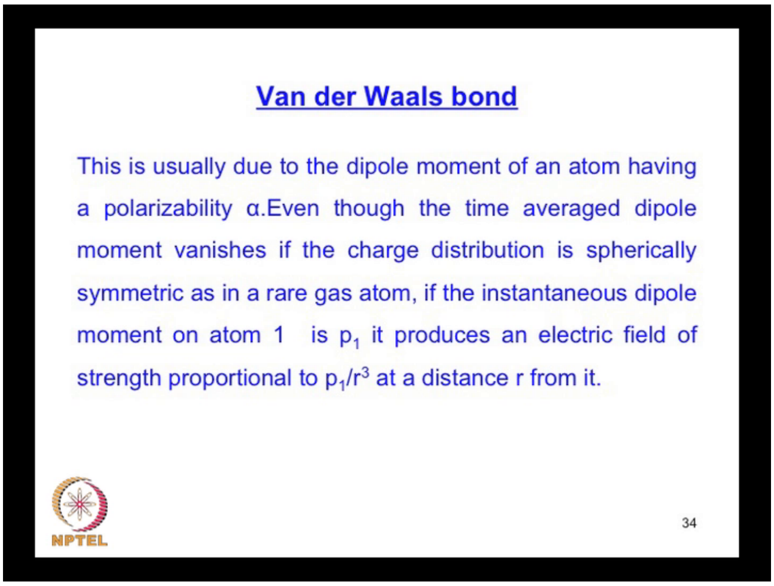

Van der Waals bond

This is usually due to the dipole moment of an atom having a polarizability α. Even though the time averaged dipole moment vanishes if the charge distribution is spherically symmetric as in a rare gas atom, if the instantaneous dipole moment on atom 1 is p_1 it produces an electric field of strength proportional to p_1/r^3 at a distance r from it.

The bonding mechanism known as the van der waal known the van der waal forces this usually occurs, because of the dipole moment for example, of a spherically symmetric inert gas atom, for example, if you take a dipole moment of such an atom of polarize ability alpha.

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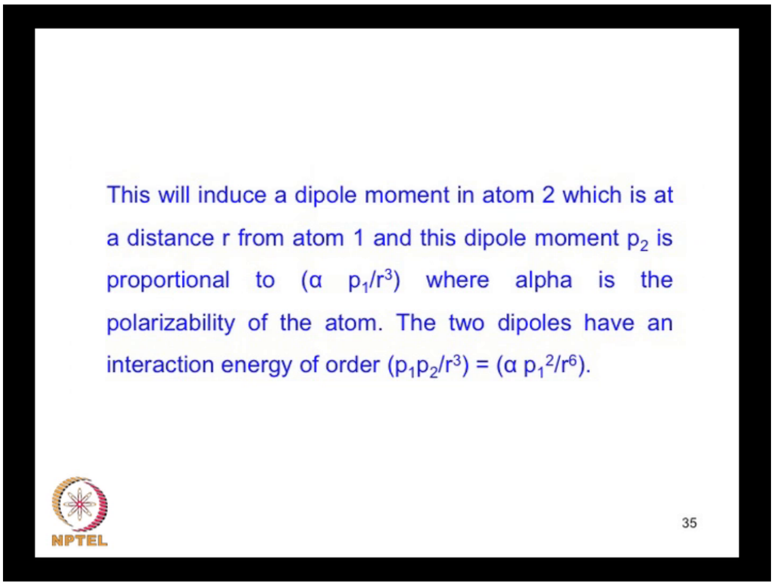

This will induce a dipole moment in atom 2 which is at a distance r from atom 1 and this dipole moment p_2 is proportional to (α p_1/r^3) where alpha is the polarizability of the atom. The two dipoles have an interaction energy of order (p_1p_2/r^3) = (α p_1^2/r^6).

If the dipole moment of atom 1 is t 1.

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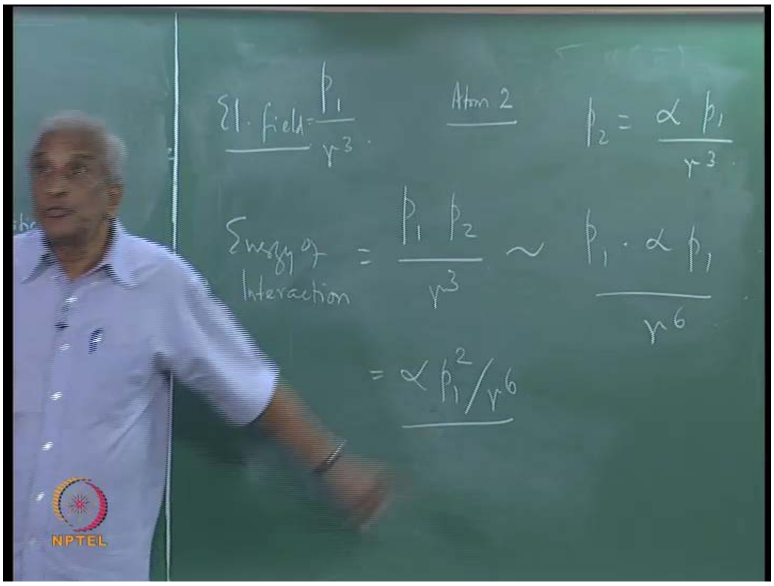

then the present are this dipole an electric field at a distance are from this atom which goes as p 1 by r cube is the electric field. And therefore if the polarisability is alpha if an atom 2 is situated at a distance are from the atom 1, then it experiences a dipole moment p 2 which is of the order of alpha p 1 r cube. So, we have now 2 dipole 1 at p 1 and another at p 2 equal to alpha p 1 by r cube where r at the distance from atom 1. So, you had the energy of interaction, which goes as humanoid p 2 by r cube which is p 1 times alpha p 1 by r to power 6. So, we have alpha p 1 square by r to power 6. So, even though in a spherically symmetric configuration the time average dipole moment is zero, but still this square term in p 1 which occurs in this energy of interaction between the 2 dipoles. It is a square of p 1, which occurs. And therefore, the square of p 1 does not vanish even though the time average p 1 manner ships.

So, this is the cause of the weak qualitative picture of the radar walls force mechanism since this as an r to power 6 dependent it is rather week. And therefore, that accounts for the low melting points and a boiling points, sub solid and liquid rare gas atoms there is a famous potential function known as the Leonard Jones potential it is also known as the 6 twelve potential is use to describe these atom week attractive. And strong shot range repulsive forces in terms of a potential function which as the form minus a by r power 6 plus b by r power twelve, these power 6 and twelve for the attractive and the repulsive forces is what gives this the main 6 twelve potential a and b are positive constants.

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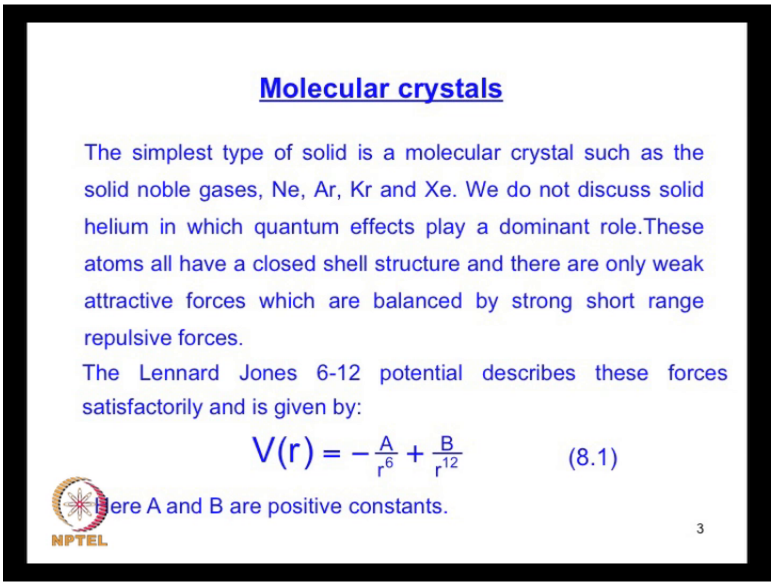

Molecular crystals

The simplest type of solid is a molecular crystal such as the solid noble gases, Ne, Ar, Kr and Xe. We do not discuss solid helium in which quantum effects play a dominant role.These atoms all have a closed shell structure and there are only weak attractive forces which are balanced by strong short range repulsive forces.

The Lennard Jones 6-12 potential describes these forces satisfactorily and is given by:

$$V(r) = -\frac{A}{r^6} + \frac{B}{r^{12}} \qquad (8.1)$$

Here A and B are positive constants.

And r is the inter atomic separation near neighbor separation this may be rewritten in a dimension less form as 4 epsilon times minus sigma by r to power 6 plus sigma by r to power twelve sigma and epsilon are known as the Lennard-Jones parameters and these are given for the 4 inert gas solids in table 1.

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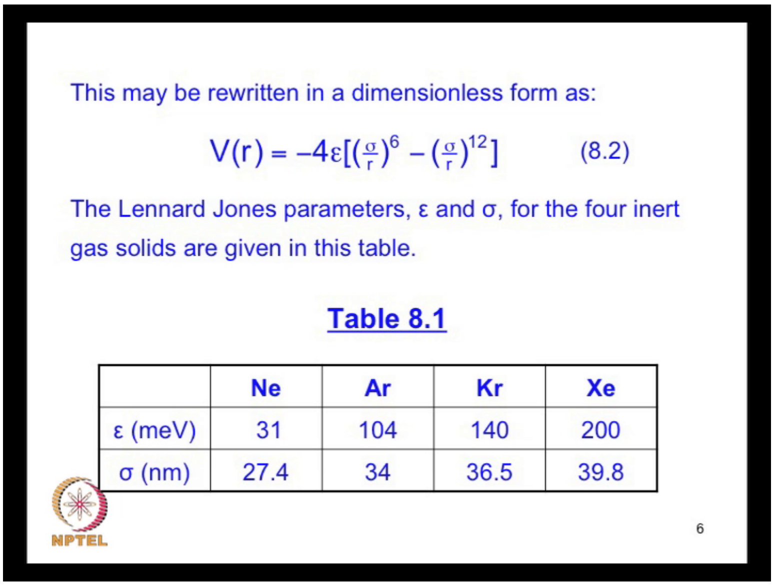

This may be rewritten in a dimensionless form as:

$$V(r) = -4\varepsilon[(\tfrac{\sigma}{r})^6 - (\tfrac{\sigma}{r})^{12}] \qquad (8.2)$$

The Lennard Jones parameters, ε and σ, for the four inert gas solids are given in this table.

Table 8.1

	Ne	**Ar**	**Kr**	**Xe**
ε (meV)	31	104	140	200
σ (nm)	27.4	34	36.5	39.8

So, you can see epsilon is given in milli electron olds and sigma is given in nano meters.

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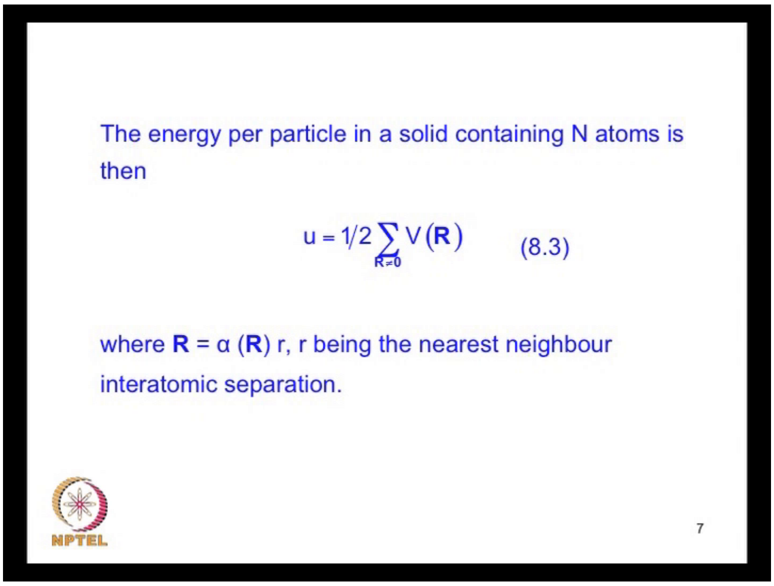

The energy per particle in a solid containing N atoms is then

$$u = 1/2 \sum_{\mathbf{R} \neq 0} V(\mathbf{R}) \qquad (8.3)$$

where **R** = α (**R**) r, r being the nearest neighbour interatomic separation.

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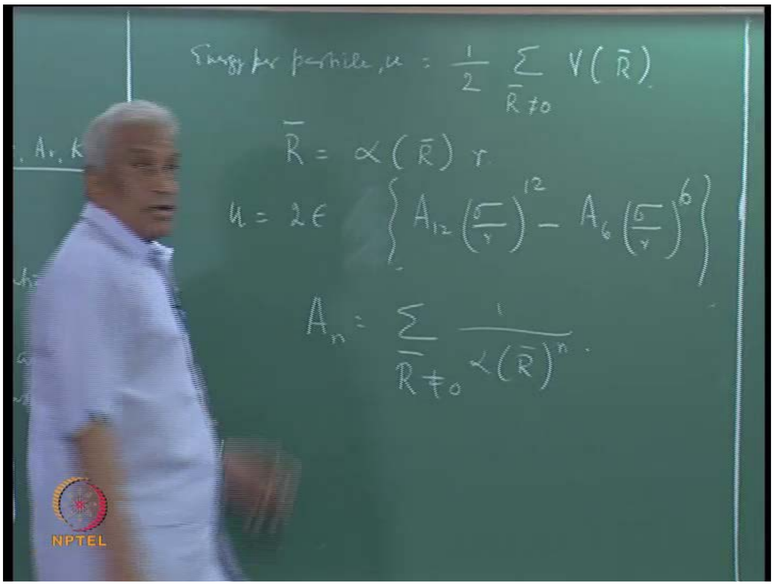

Energy per particle, $u = \frac{1}{2} \sum_{\bar{R} \neq 0} V(\bar{R})$

$$\bar{R} = \alpha(\bar{R})\, r$$

$$u = 2\epsilon \left\{ A_{12} \left(\frac{\sigma}{r}\right)^{12} - A_6 \left(\frac{\sigma}{r}\right)^6 \right\}$$

$$A_n = \sum_{\bar{R} \neq 0} \frac{1}{\alpha(\bar{R})^n}$$

Using this potential the energy per particle can be easily calculate at… Let us call it u and that will be just as simple some overall brave lattice vector r is a b r v e lattice vector, which can be written as a geometrical factor times the neighbor distance. So, expressing all these brave lattice vector in terms of the entire particle near neighbor distance.

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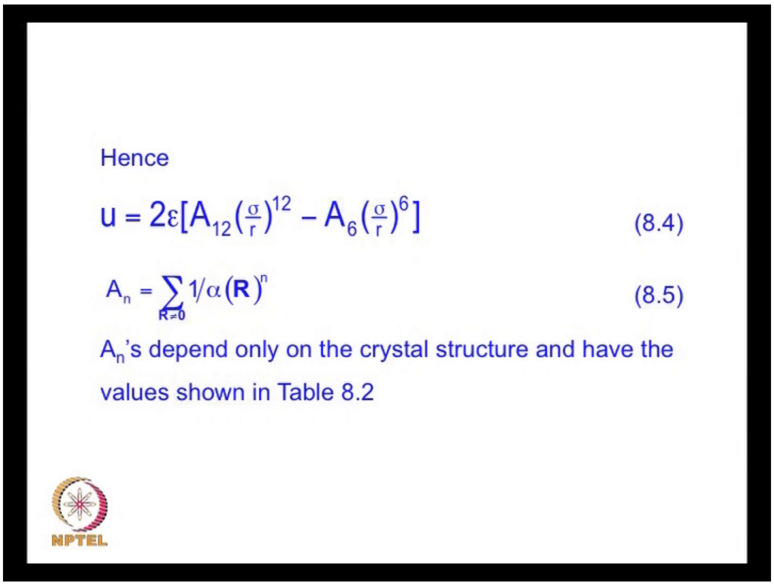

Hence

$$u = 2\varepsilon[A_{12}(\tfrac{\sigma}{r})^{12} - A_6(\tfrac{\sigma}{r})^6] \quad (8.4)$$

$$A_n = \sum_{\mathbf{R} \neq 0} 1/\alpha(\mathbf{R})^n \quad (8.5)$$

A_n's depend only on the crystal structure and have the values shown in Table 8.2

Then we can express u as 2 epsilon sigma r not equal to zero a twelve sigma by r to the power twelve minus a 6 sigma by r to the power 6 here the a hence. So, they can be calculated really and they are tabulated for the different crystal structures such as simple cubic body centered cubic. And then phase centered cubic they can be calculated because these constants depend 1 d and the crystal structure.

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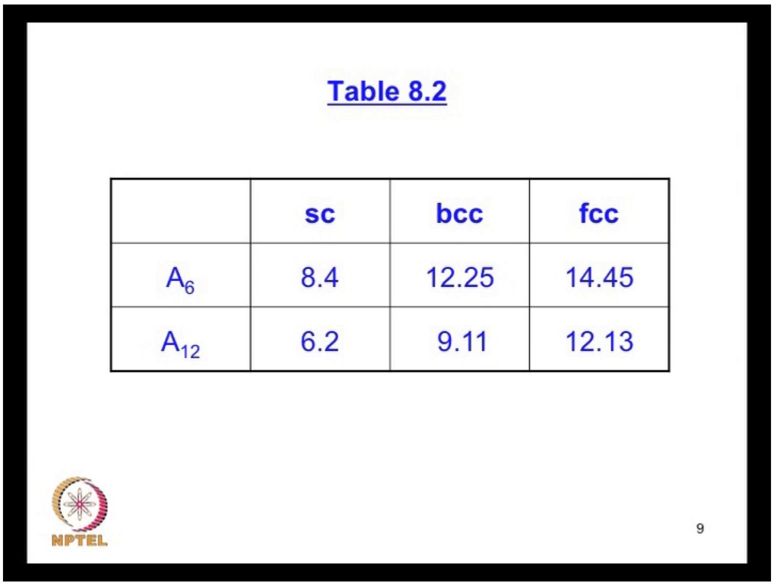

Table 8.2

	sc	bcc	fcc
A_6	8.4	12.25	14.45
A_{12}	6.2	9.11	12.13

Therefore they can be calculated these values are shown in table 2 for a three different cubic crystal structures in the case there r gas solids, we consider the phase centered cubic lattice in which they form. So, the constants A 6 and A 12appropriate to the phase centered cubic structure are phone in the last column of table 2.

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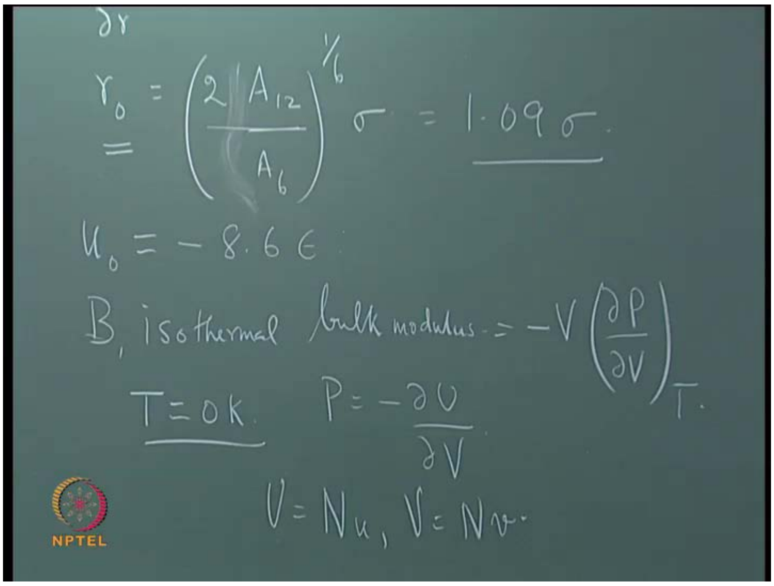

∂r

$$r_0 = \left(2\frac{A_{12}}{A_6}\right)^{1/6}\sigma = \underline{1.09\,\sigma}$$

$$U_0 = -8.6\,\epsilon$$

B, isothermal bulk modulus $= -V\left(\frac{\partial P}{\partial V}\right)_T$

$\underline{T = 0K}$ $\quad P = -\frac{\partial U}{\partial V}$

$U = Nu, \; V = Nv$

The equilibrium near neighbor separation is found readily by setting d u by d r equal to zero by minimizing the energy. So, this leads to the equilibrium inter atomics phasing as and a substituting for the A 12, and A 6. This readily becomes and using this equilibrium value we can calculate the minimum energy or the solid per particle as u 0, which is readily calculated to be minus 8.6 epsilon plugging in the appropriate values of a twelve and A 6.

So, this is something this inter atomic spacing is something that can be compared with actual measured values from say defection another quantity, which is of interest experimental quantity is the isothermal bulk modulus. This is defined as miners v and that absolute zero all our discussions are at t equal to zero k when it is considered as a static solid with no temperature effects p is minus d v, where u is n times u. And v is n times small v while n is the number of atoms will in the solid, so putting all these values together.

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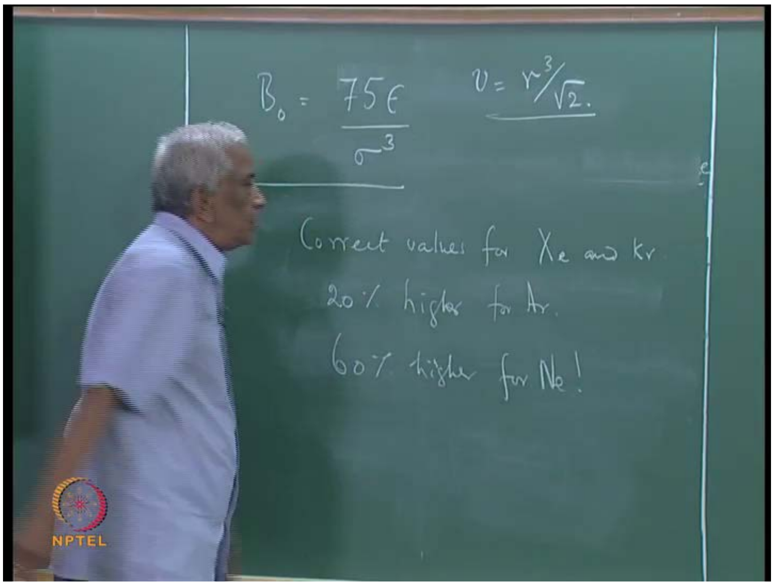

$$B_0 = \frac{75\epsilon}{\sigma^3} \qquad v = r^3/\sqrt{2}.$$

Correct values for Xe and Kr

20% higher for Ar.

60% higher for Ne!

We can find the equilibrium bulk modulus for the phase centered cubic lattice we can calculate the equilibrium bulk modulus using v. Equal to r cube by root 2 and a phase centered cubic solid. Therefore, this can be calculated as being equal to plugging in the appropriate values of a 6 a twelve et cetera and this is the equilibrium that. So, this is another thing which can be calculated, and compared with the experimental values. We find that this calculation gives correct values more or less in agreement between theory and experiment for xenon and krypton it gives a experimental values are 20 percent higher than calculated values for organ and 60 percent higher for neon indicating that these have zero-point contributions. So, that gives a brief idea of the forces which are responsible for formation of a molecular crystal such as a solid noble gas atom a very similar approach can also be adopted.

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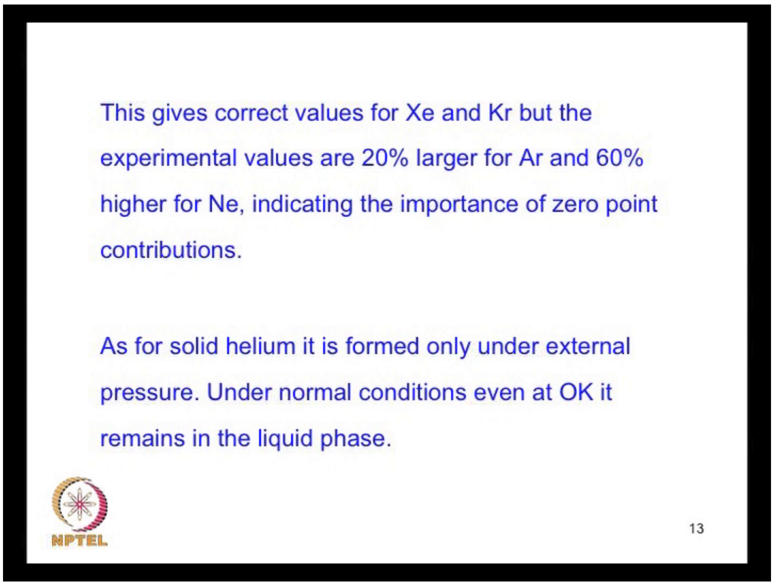

This gives correct values for Xe and Kr but the experimental values are 20% larger for Ar and 60% higher for Ne, indicating the importance of zero point contributions.

As for solid helium it is formed only under external pressure. Under normal conditions even at OK it remains in the liquid phase.

In the case of ionic solids ionic crystals are 1.

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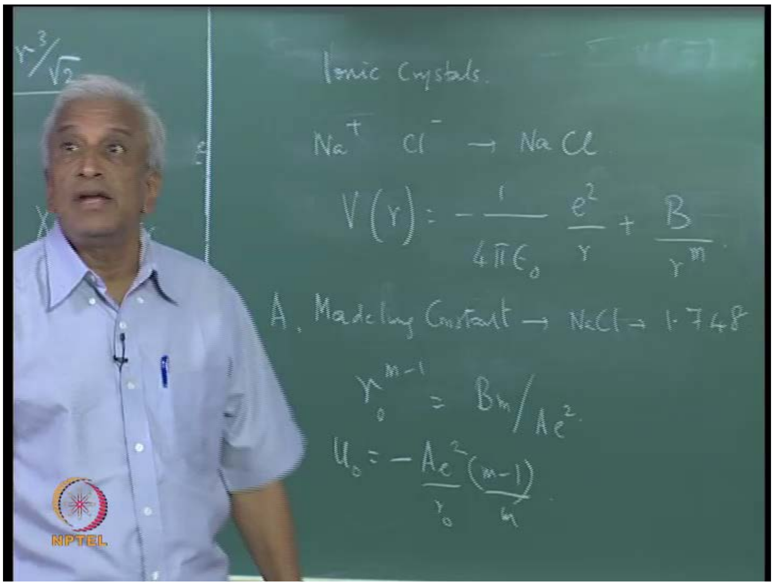

Ionic Crystals.

$Na^+ \quad Cl^- \rightarrow NaCl$

$$V(r) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r} + \frac{B}{r^m}$$

A. Madelung Constant → NaCl → 1.748

$$r_0^{m-1} = Bm/Ae^2$$

$$U_0 = -\frac{Ae^2}{r_0}\frac{(m-1)}{m}$$

In which there are ions such as sodium plus and chlorine minus farming sodium chloride. So, the sodium plus, and the chloride minus ions are arrange regularly in the crystal lattice of sodium chloride. And it is there mutual interaction electrostatic interaction which gives rise to the net stability this is the attractive electro static potential with r being the near neighbor separation, and the repulsive part of the potential we know that it is not as short-range as r to power twelve.

So, let it be some m where m is found comparison with experiment, and we can perform the energy per ion-pair can be calculated by summation overall the ion fail in the crystal lattice of n ions. And these lattice sums which give you the total contribution governed by this so-called madeleine constant which depends only on the structure of the crystal lattice and for n a c l it add value 1.748. So, using the madeleine constant and plugging in the this in this expression and forming over the n by 2 ion pair and minimizing the total energy for a phase centered lattice with a basis of 2.

Oppositely charged ion we can obtained the equilibrium inter near neighbor separation as are not to the power m minus 1 equal b m by a e square a is the madeleine constant. So, that is 1 experimental parameter that 1 can determine. And therefore, using this we can calculate the constant the equilibrium lattice energy corresponding to becomes u naught could go minus just like in the case of the molecular solids. We can also calculate equilibrium isothermal bulk modulus, which again is an experimentally accessible quantity.

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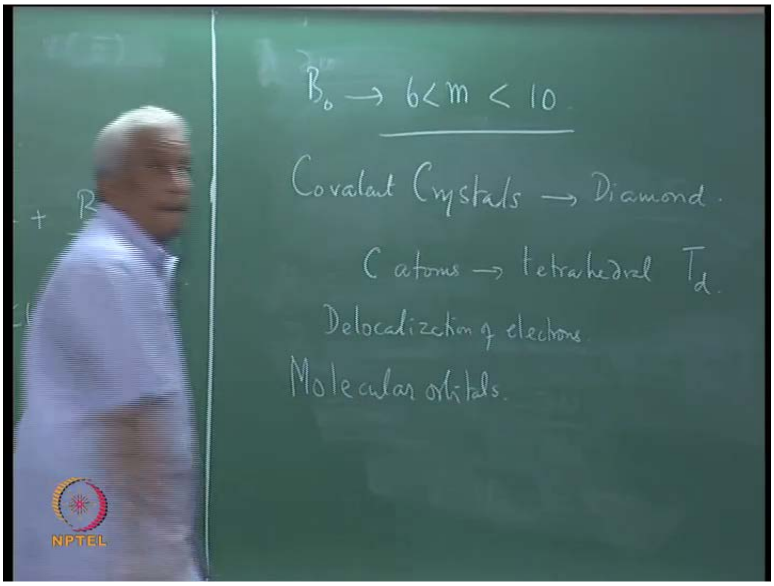

$B_0 \rightarrow 6 < m < 10$

Covalent Crystals → Diamond.

C atoms → tetrahedral T_d.

Delocalization of electrons

Molecular orbitals.

And the equilibrium bulk modulus can be calculated, and it can compared with the experimental value, and for the ionic solid comparison between the experimental theory set cell the limits for the values of m at between 6 and 10 with that is possible to find reasonable agreement between experiment. And theory in contrast with this situation for an ionic crystal. There are other types of solids which are known as covalent crystals diamond is a typical archetype of a covalent solid as we all know diamond consists of nothing but carbon atoms, which are bonded in a tetrahedral configuration inside a cube the point group symmetry appropriate to this is known to be T d.

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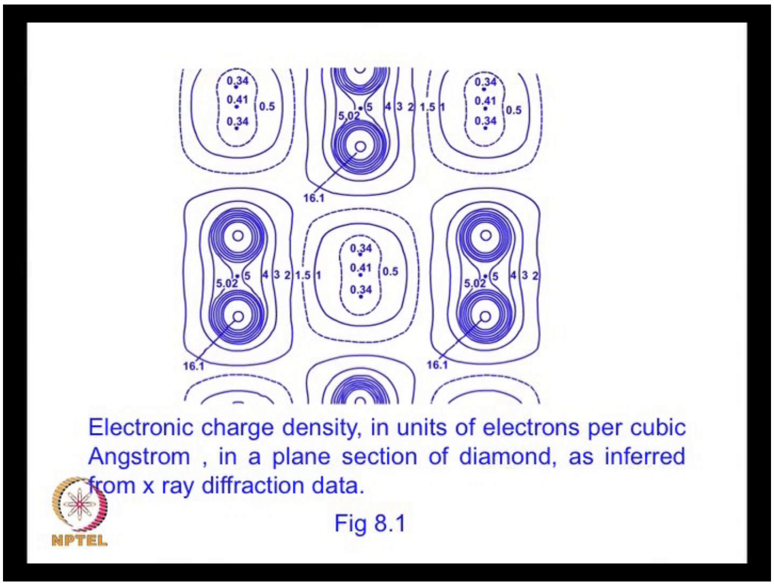

Electronic charge density, in units of electrons per cubic Angstrom , in a plane section of diamond, as inferred from x ray diffraction data.

Fig 8.1

This covalent crystal is characterized by an appreciable delocalization of electrons c inferred compares the x ray diffract a gram of an ionic solid with that of on a covalent solid 1 mean find that the electronic density peaks are exactly situated at the sites the ion with their a little electron density in between the ions, there as in the case of a covalent solid like diamond. The electron density between the carbon atoms is found to be appreciable to indicating the considerable degree of delocalization the electronic charge. So, such a situation is most conveniently described by the theory of molecular arbiters.

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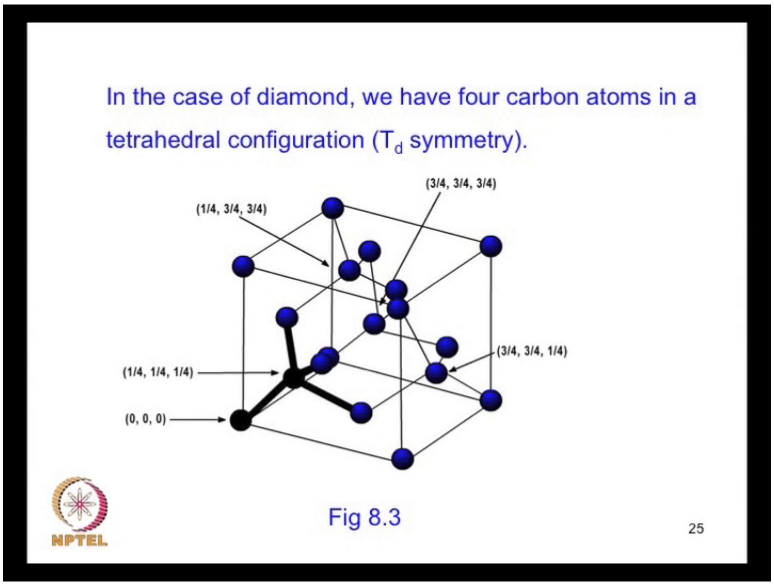

In the case of diamond, we have four carbon atoms in a tetrahedral configuration (T_d symmetry).

Fig 8.3

For example the simplest prototype molecular orbital theory which explains the formulation of a covalent bond, which which binds atoms together to form molecules.

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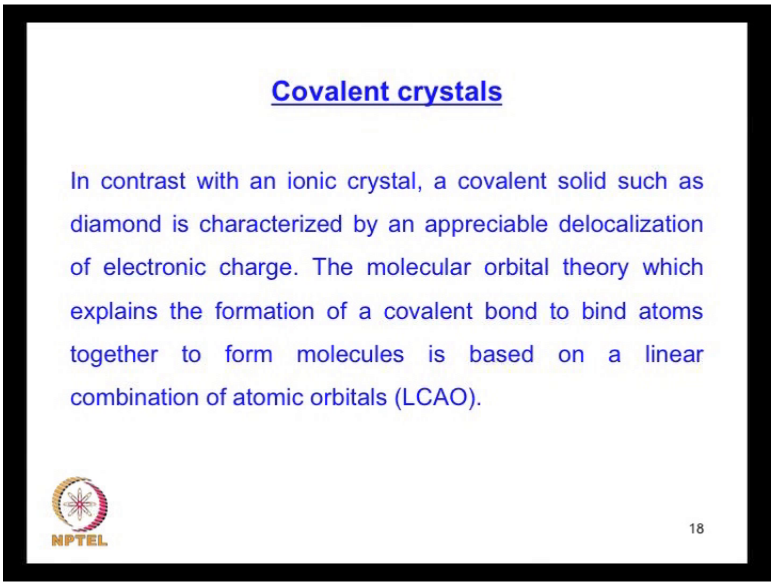

Covalent crystals

In contrast with an ionic crystal, a covalent solid such as diamond is characterized by an appreciable delocalization of electronic charge. The molecular orbital theory which explains the formation of a covalent bond to bind atoms together to form molecules is based on a linear combination of atomic orbitals (LCAO).

Is based on an approximation known as a LCAO approximation.

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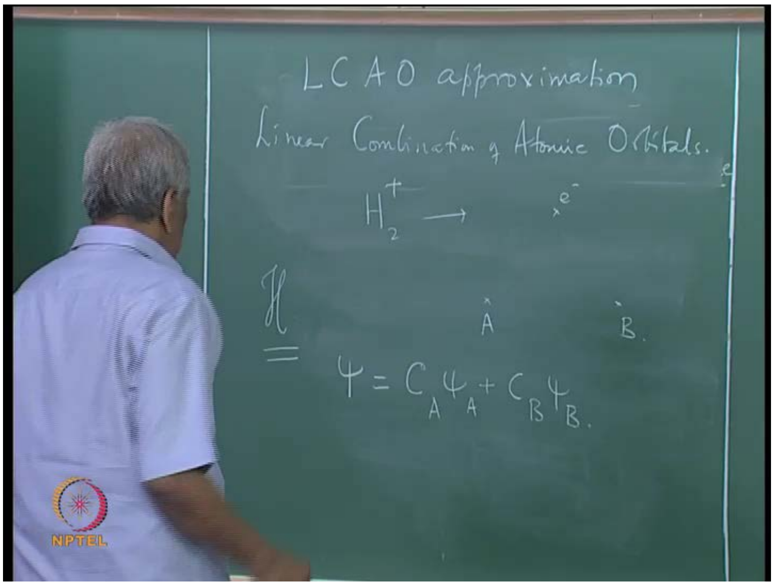

LCAO a short form linear combination of atomic orbiters for example, if you consider the hydrogen molecular ion h 2 plus. So, that we have a single electron in this potential of the 2 nuclei due to the 2 atoms the 2 protons which have designated as a and b. So, you have various terms the Hamiltonian consists of the potential of the electron in the fields of these 2 nuclear nuclear. So, the electro static potential can be readily written to form the Hamiltonian of the system’ and we write the wave function the monocular orbital as a linear combination c a psi a plus c b psi b plus c a and c b are constant to be chosen to minimize the energy.

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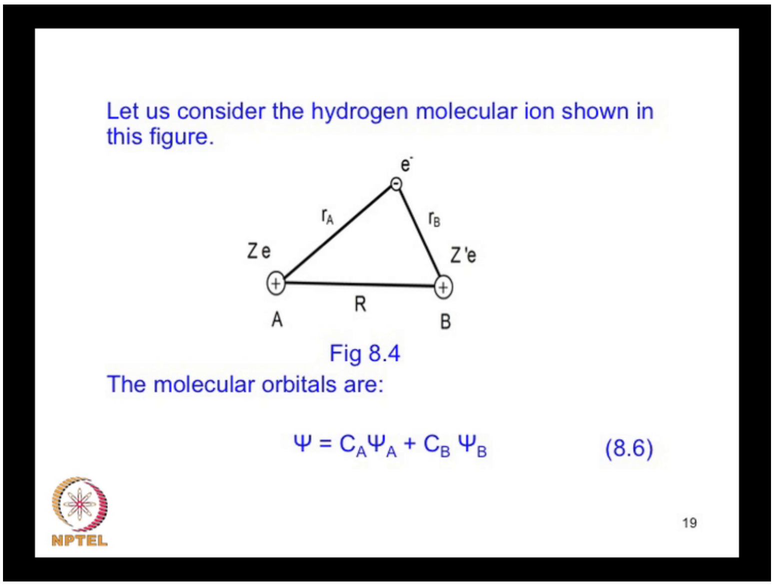

Let us consider the hydrogen molecular ion shown in this figure.

Fig 8.4

The molecular orbitals are:

$$\Psi = C_A\Psi_A + C_B\,\Psi_B \qquad (8.6)$$

So, with such a wave function the expectation value the energy can be calculated.

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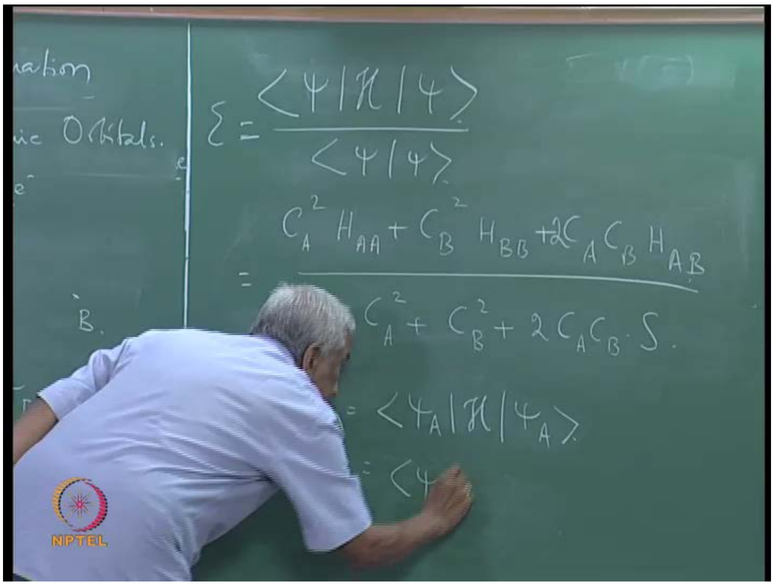

$$\mathcal{E} = \frac{\langle \psi | \mathcal{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{C_A^2 H_{AA} + C_B^2 H_{BB} + 2C_A C_B H_{AB}}{C_A^2 + C_B^2 + 2C_A C_B S}.$$

$$= \langle \psi_A | \mathcal{H} | \psi_A \rangle$$

$$= \langle \psi$$

So, if we plug in the expression for psi. We get something like c a square h a a plus c be square h b b plus c a c b h a b divided by c a square plus c b square plus 2 c a c b time s where h a a. For example' this is the metrics element of the Hamiltonian h between the wave function psi a and psi a similarly h b b is psi b h psi b.

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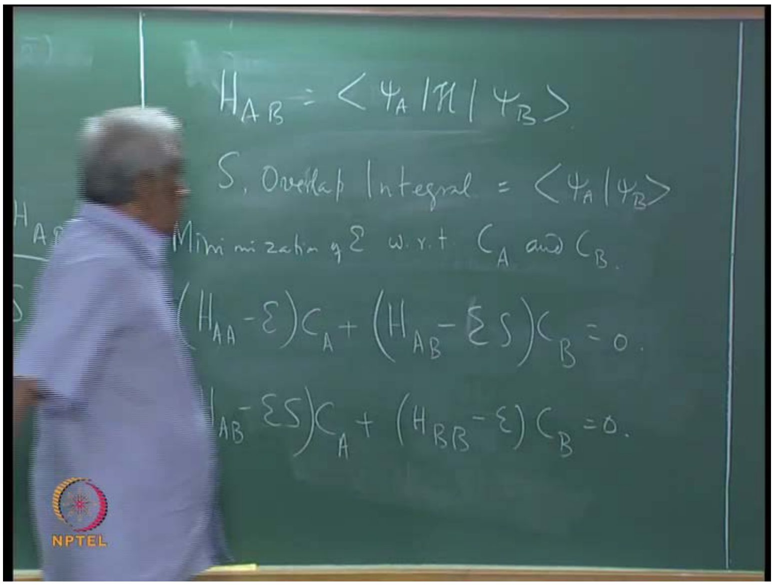

$H_{AB} = \langle \psi_A | \mathcal{H} | \psi_B \rangle$

S, Overlap Integral $= \langle \psi_A | \psi_B \rangle$

Minimization of ε w.r.t C_A and C_B.

$(H_{AA} - \varepsilon)C_A + (H_{AB} - \varepsilon S)C_B = 0.$

$H_{AB} - \varepsilon S)C_A + (H_{BB} - \varepsilon)C_B = 0.$

Whereas h a b is psi a h psi b and f is known as the overlap integral between psi a and psi b and this defined as psi a psi b the product. So, minimizing this energy with respect to minimization of e with respect to variations in the variationly constant c a and c b leads to equations a couple of equations which have the form and solving these 2 simultaneously means that.

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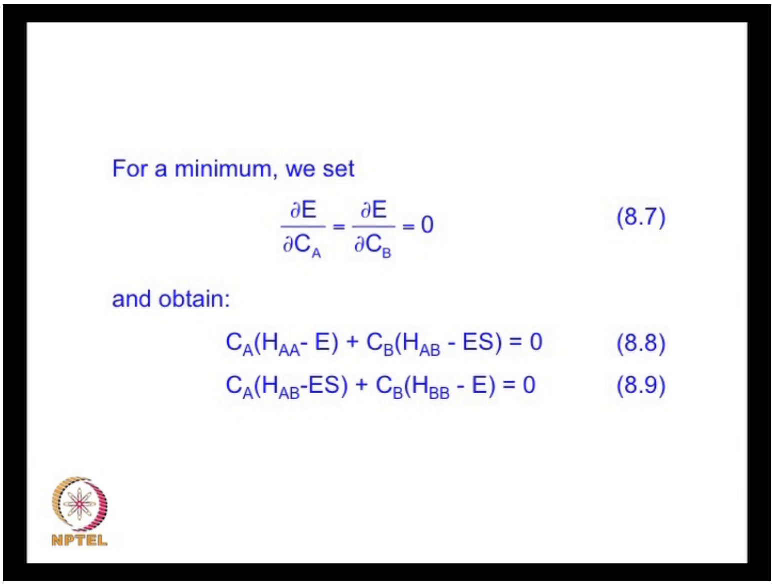

For a minimum, we set

$$\frac{\partial E}{\partial C_A} = \frac{\partial E}{\partial C_B} = 0 \qquad (8.7)$$

and obtain:

$$C_A(H_{AA} - E) + C_B(H_{AB} - ES) = 0 \qquad (8.8)$$

$$C_A(H_{AB} - ES) + C_B(H_{BB} - E) = 0 \qquad (8.9)$$

They determine entire the coefficient should vanish and that gives us a quadratic equation in the simpler case of a 4 more.

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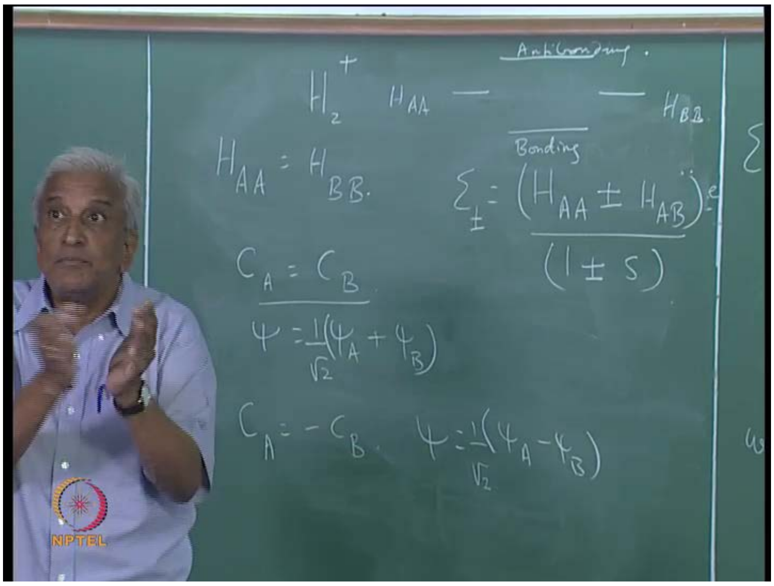

Nuclear diatomic molecular ion such as h 2 plus we can set h a a equal to h b b and get e as the minimum energy this needs to a quadratic equation. So, it will have 2 roads 1 with a positive and another with a negative science. So, I have e plus minus. So, this will be h a a plus h a b by 1 plus or minus s if this the plus sign corresponds to c a equal to c b. So, that we can choose psi s psi a plus psi b with a 1 hour the normalization where have the minus root the other route as this solution.

So, that this is an anti symmetric linear combination it turns out that the original energy which are the same which are degenerate in the case of the separate at atoms atoms now in depression for the interaction there are 2 energy. Now the degeneracy is lifted the energy is lowered in 1 case and the energy becomes higher in the other this is known as a bonding orbital this is the anti bonding. So, this corresponds to this symmetric linear combination the bonding orbital and. So, it piles up the charge between the 2 atoms and the anti bonding which is same excited state corresponds to the anti symmetrically will have accomplished.

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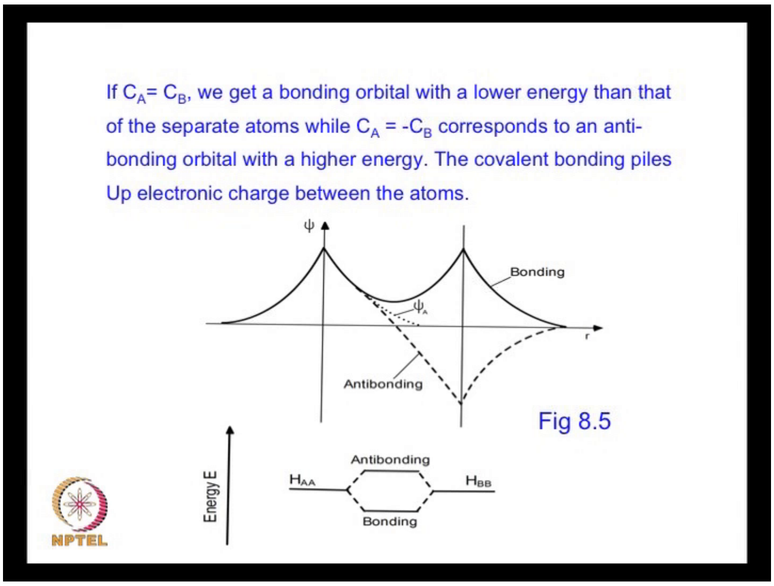

If $C_A = C_B$, we get a bonding orbital with a lower energy than that of the separate atoms while $C_A = -C_B$ corresponds to an anti-bonding orbital with a higher energy. The covalent bonding piles Up electronic charge between the atoms.

Fig 8.5

So, the covalent bonding piles up the electronic charge between the atoms. And therefore maximizes this overlap integral the essence of covalent bond formation is that it corresponds to a configuration if the overlap between the atomic orbitals is maximum.

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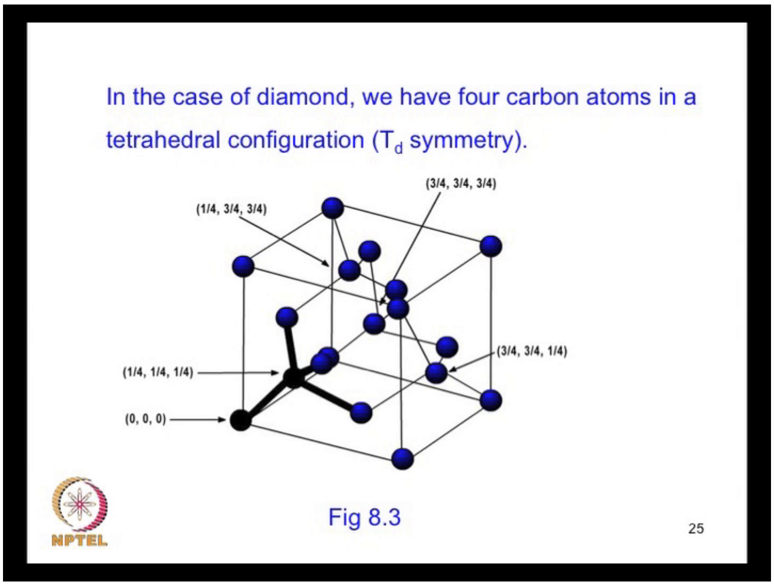

In the case of diamond, we have four carbon atoms in a tetrahedral configuration (T_d symmetry).

Fig 8.3

Now, when we come diamond to discuss the case of diamond we find that’ it has a tetrahedral, configuration.

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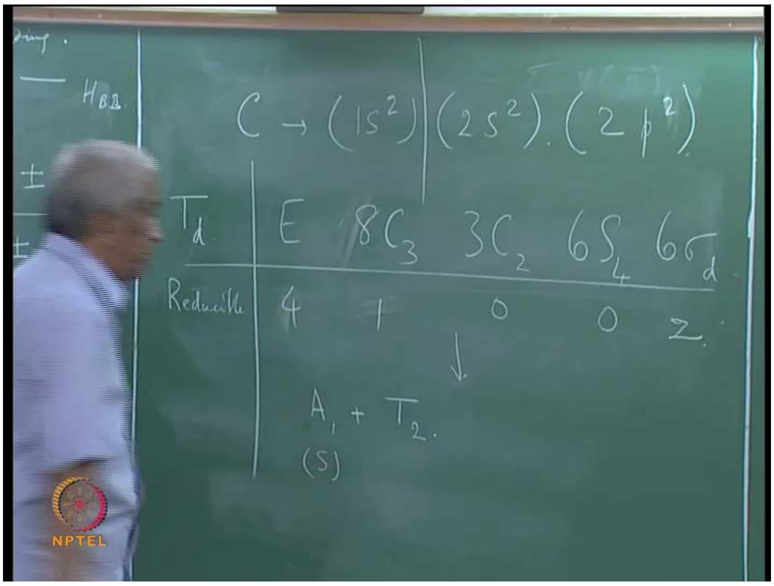

$C \rightarrow (1s^2)(2s^2).(2p^2)$

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Reducible	4	1	0	0	2.

$\downarrow$

$A_1 + T_2.$

(S)

So, the overlap to find with linear combination up the atomic orbitals of the carbon atoms involved be carbon half the electronic configuration 1 s 2 2 s 2 and 2 p 1 s 2 of course, is a close shell. So, it is a 2 s 2 and 2 p 2 2 electrons in the s shell and 2 electrons in the p shell at the carbon atom these are the 1s, which are these are the atomic orbitals, which are involved in the covalent bonding in order to maximize overlap between them. It is necessary to consider this symmetry of the special arrangement of the carbon atom which as we know corresponds to a tetrahedral t d symmetry.

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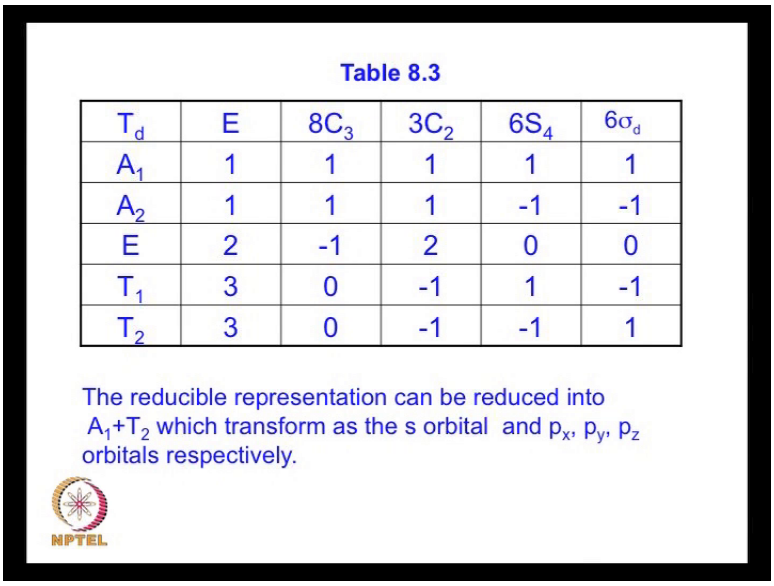

Table 8.3

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

The reducible representation can be reduced into A_1+T_2 which transform as the s orbital and p_x, p_y, p_z orbitals respectively.

So’ the red usable representation of the point group this point group t d for the 4 orbital is given can be readily found is are the various symmetry elements and the reducible representation for this for the 4’ orbital can be easily found. So, this reducible representation can be broken up into a reducible representations which corresponds to the symmetry therefore, these irreducible representations can readily shown to be a and t a 1 plus t 2. So, that mean that a 1 is a 1 is a dimensional irreducible representation for which the basis is that of an s orbital and t 2 is a three-dimensional representation which has the basis p x p y p z.

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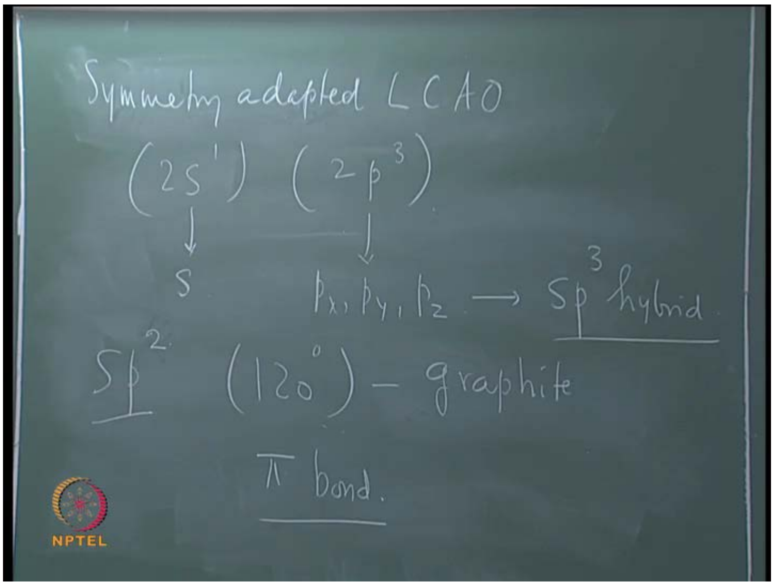

So, the symmetry adopted l c a o linear combination of the atomic orbitals should conform to this situation of an s orbital and three p orbital instead of 2 s orbital and 2 p orbital. So, the symmetry adopted l c a o linear combination of the atomic orbital corresponds to a situation in which say’ 1 of the s electron indeed 2 s shell is excited into the p orbital. So, that we have 1-electron left here and three electron in the 2 p shell. So, they is occupy this corresponds to an s orbital and these have now three orbitals with p x p y p z that. So, you can farm linear combination for these since there is an s orbital and three p orbital it is known as the s p p high hybrid is phenomenon is known as hybridization and this hybridization has the consequence.

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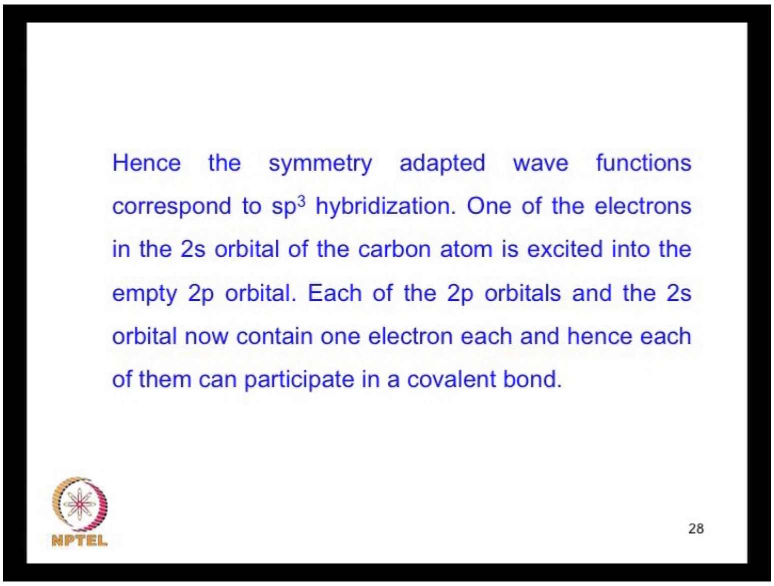

Hence the symmetry adapted wave functions correspond to sp^3 hybridization. One of the electrons in the 2s orbital of the carbon atom is excited into the empty 2p orbital. Each of the 2p orbitals and the 2s orbital now contain one electron each and hence each of them can participate in a covalent bond.

That the overlap between these wave functions are maximum making for single covalent bonds for all the 4 orbitals concern in which is the low pointing along the tetrahedral directions. So, that is how we have the s p three hybridization in the covalent solid of diamond. So, this gives the diamond its stability, because of the sharing at the electron charge in a covalent mark just like the carbon there are other solids in which there are s p to hybrid an s orbital, and 2 p orbital can form in a plain at the angles 120 degrees.

And this is what happens in for example, graphite bed s p 2 hybrid performed and there are layers with covalent bonds in the plane and then there are weak render wall forces between the layers in addition, you have a p z orbital which is with 1 electron perpendicular to the plane containing the s p 2 hybrids. So, the overlap between the neighboring p z orbital is a pi bond.

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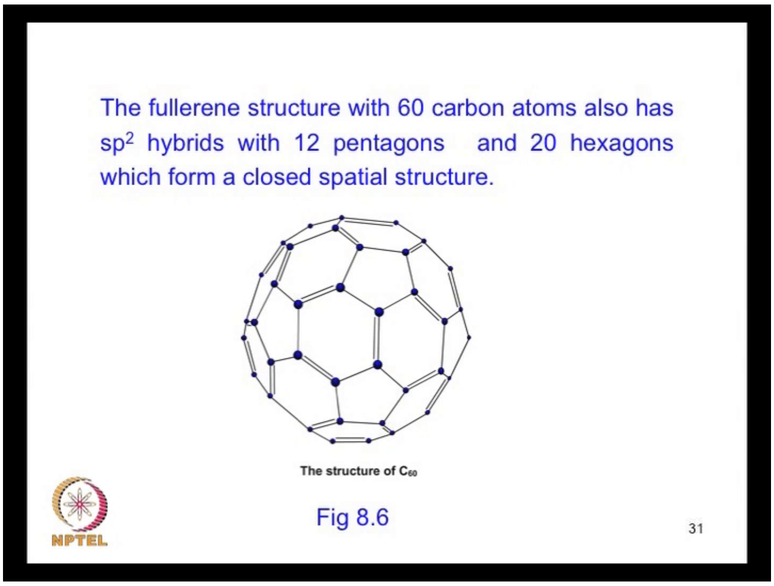

The fullerene structure with 60 carbon atoms also has sp^2 hybrids with 12 pentagons and 20 hexagons which form a closed spatial structure.

The structure of C_{60}

Fig 8.6

So, this contributes to an additional stability of materials like graphite a s p 2 hybrid can also form a close this special network such as in the fullerene, which has as 6ty carbon atoms in a kind of buckeye ball configuration containing twelve pentagons and twenty hexagon which form a closed spatial structure. So, these are the various interesting solids in which covalent bonding plays a major role with a appreciably delocalization of the electron density and extreme case of this delocalization occurs in the case of metals.

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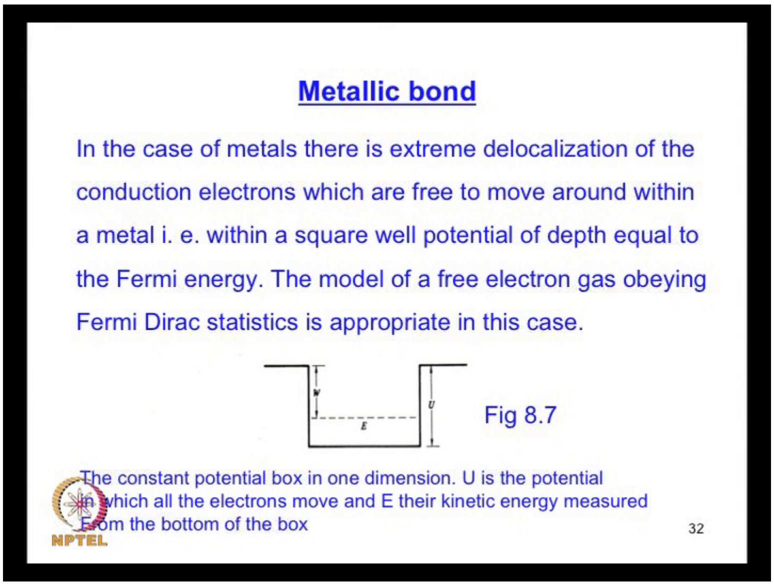

Metallic bond

In the case of metals there is extreme delocalization of the conduction electrons which are free to move around within a metal i. e. within a square well potential of depth equal to the Fermi energy. The model of a free electron gas obeying Fermi Dirac statistics is appropriate in this case.

Fig 8.7

The constant potential box in one dimension. U is the potential in which all the electrons move and E their kinetic energy measured From the bottom of the box

The metallic bond is corresponds to extreme delocalization that the electrons balance electrons you have a metallic bond.

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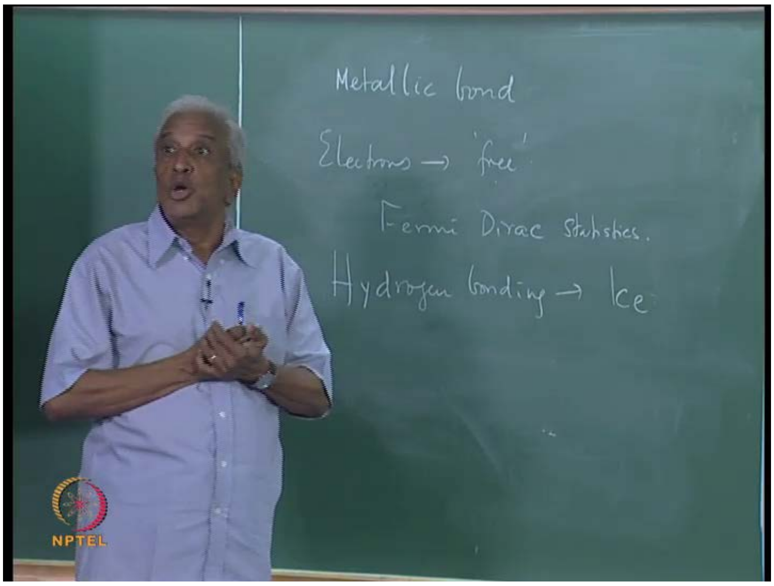

In which the balanced electron or conduction electron or free to wonder, so will prove all the crystal lattice within a say a square well potential. So, the free-electron approximation satisfies the behavior he is satisfactorily able to describe the behavior of electrons in metals provided big take into consideration the fermi direct statistics, which is obeyed by electrons apart from all the solid. There are other interesting classes the solid such are the hydrogen-bonded, which is the principal source in for example, solid ice the water molecule as 2 hydrogen atoms, and each hydrogen atom is covalently bonded to the oxygen atom and then it farms also a bridge to a neighboring oxygen atom belonging to another atom molecule. So, there is an extensive hydrogen bonded network. So, that is we have covered the entire gamut of different types of bonding mechanisms which bring about the cohesion in solids and this is a very topic of great importance to bare in main when discussing solids of different kinds.