

Nanoelectronics: Devices and Materials
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Lecture – 34
Energy bands in crystalline solids

Hello again, in the previous section of this class, we dealt with the Pauli exclusive principle and therefore we also got introduced to Fermions and Bosons.

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Then we want on to deal with the quantum tunneling as well as the problem of a particle in a box both of which are examples of the time independent Schrodinger equation and we learnt that the energy levels in the particle in a box are quantized.

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Outline

- Recap of previous session
- Interacting Potentials and the Formation of Energy Bands
- Dimensionality of Quantum Systems
- Density of States

So, what we will today is to deal with interacting potentials which leads for us to consider the formation of bands of energy and we deal with the dimensionality of quantum systems that is go from 3 to 2 to 1 to 0 dimensions and introduce ourselves to the concept of the density of states in quantum systems.

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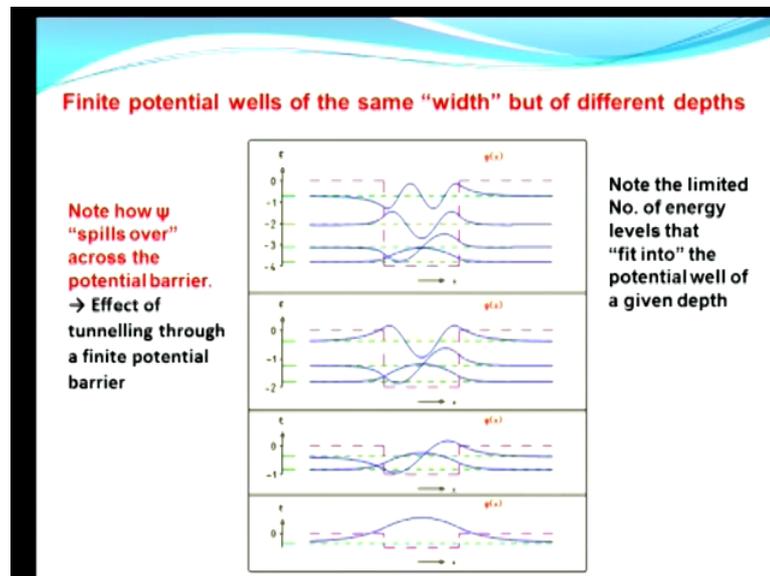
The wavefunction and its "square" for an infinitely deep potential well, or Quantum Well

This and the next few simulations are from: **A Picture Book of QM, Brandt and Dahmen**

Now, one of the things that we dealt with in the last class was the quantum well of finite depth but we started with a quantum well of infinite depth where the energy levels are quantize that we see here with wave functions that correspond to sinusoidal waves. Now

notice that the energy levels are quantized and the energy gap between the successive levels increases as the quantum number increases from 1 to 2 to 3 to 4; etcetera on to infinity.

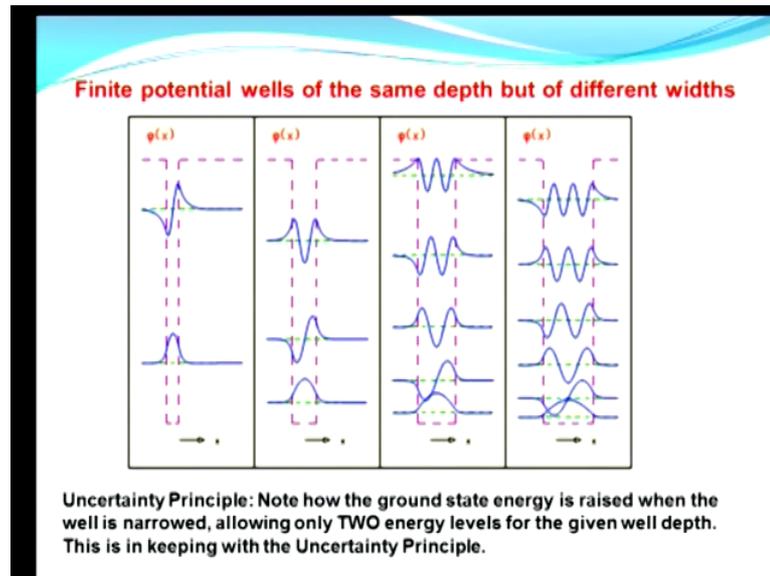
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What we also noticed is that if you had a potential well of finite depth as suppose be the infinitely the potential wells, then the concept of tunneling leads us to notice that the wave function no longer is confined to within the a well, but actually spills out into the outside the box within the box the potential is 0, outside the potential is v which is less than infinite in such case the tunneling phenomenon for quantum mechanics leads to the possibility a finite non zero possibility of the particles being outside the box even though the energy is less than that of the height of the well namely v .

And the shallower the depth of the well the greater the extent of leakage or spilling over the wave function beyond the walls of the well and the number of levels of energy quantized energy that a particle is such a shallow box or such a finite box can undertake the number of levels is greater as the depth of the well increases, the shallow of the wall the smaller the number of levels that it can accommodate for a given well width.

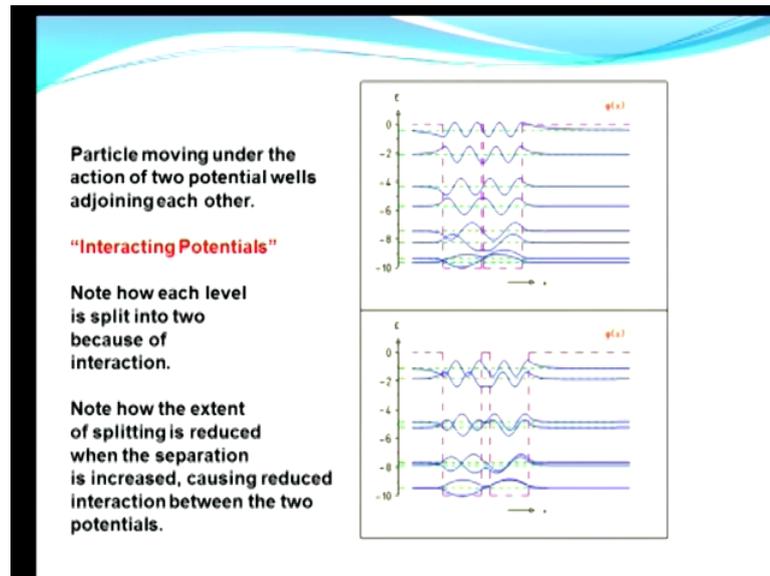
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We also learned that in a finite potential as you increase the width in a finite potential well as you increase the width of the well keeping the depth of the well constant, then the narrower the well the fewer the energy levels it can accommodate and this is a direct result of the Heisenberg uncertainty principle whereby, if Δx is smaller Δp_x is greater leading to higher energies in a more severely constrained system.

So, as the well width is increased the energy levels actually, gradually are reduced compare to this section a very narrow well and more and more number of levels are accommodated within the finite height of the well.

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So, far we have dealt with single potential wells that is a particle moving within a single potential well the under the influence where single potential well while that is a interested in itself because quantum wells are actually realized in practice as we shall see later in the session. While these single wells are interesting in themselves what is really interesting also is a particle that moves in under the influence of more than one such well insure them adjutant to the other.

So, let us consider the case of 2 potential wells adjoining each other. So, think about particle that is moving here in the first well on the left so to peak, but as we show earlier the wave function of any of these states which the particle can undertake over here wave function leaks into because of quantum tunneling into the adjoining cell as well adjoining well as well. Therefore, you can consider these as interacting potential wells, the particle that is moving in one of these boxes or one of these wells is also affected by the potential that is next door.

So, what I want to do see here is that I have shown here in this drawing 2 sets of adjoining potential wells, one in which they are close to each other and the other one in which they are slightly more separated from each other.

So, these are 2 identical wells adjoining each other very close to each other, these are 2 identical wells that are more separated from each other .What I want to see is that while we had a single earlier while we had a single energy level corresponding to each of these

wave functions over here. What we now have or split energies that now we have 2 energy levels closely spaced to each other for each of these states that used to be a single level in the single quantum well.

So, what we had now have therefore are 2 solutions to the Schrodinger equation. One is this so called symmetric wave function that you can see here sinusoidal mostly sinusoidal symmetric wave function and the other one that is the anti symmetric wave function you would have come across these things in your earlier classes.

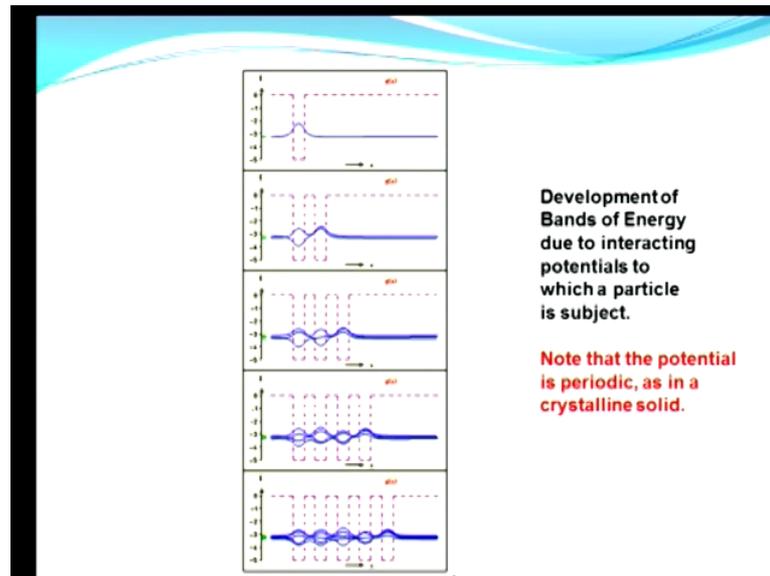
So, you have 2 solutions, one is symmetric and the other one is anti symmetric and the 2 have different energy levels. The anti symmetric wave function always has a higher energy level than the symmetric wave function so each of the levels that was a single one earlier in a single quantum well is now split into 2 and the separation between the symmetric and anti symmetric states the separation in energy becomes greater and greater as the quantum number increases from 1 to 2 to 3 to 4 etcetera.

Now notice that this separation between the levels of the symmetric and anti symmetric states, anti symmetric wave functions is greater in the case of the 2 wells that are close to each other than in the case of the well that is slightly separated from with a greater separation between each other that is the interaction between these 2 potentials that is the interaction that this particle in one well feels due to the potential next door.

This interaction is reduced when the 2 wells are slightly more separated, accordingly because in the reduced interaction you can see that the separation of these levels separation between the symmetric and anti symmetric states is now reduced. So, the point to take here is that when you have this interacting interaction between 2 adjacent potentials then you have splitting of the energy levels between the symmetric and anti symmetric states and the split between these symmetric and anti symmetric states is enhanced when the potentials are brought closer each other so that they interact more strongly.

Now, let us extend this and go to a number of potentials identical potentials that are in line which is the each other so to speak that is we subject our particle say an electron to the potential of a series of equally spaced potentials along the x axis these are in 1 dimensional potentials to make the problem easier.

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So, what we have here, here is a single potential well of a finite height 2 of them, 3 of them, 4 of them and 5 of them equally spaced. So, what you see here is that this single energy level corresponding to n equal to 1, only one n equal to 1 is shown for the sake of simplicity so that we avoid clutter.

So, this energy level split into 2, then when you have 3 adjacent levels, 3 interacting potentials then it is split into 3 and into 4 and into 5 and so on. So, this energy level which was unique in the case of a single potential is then split into as many levels as there are interacting potentials that are equally spaced along this x axis. So, we can think of this as a periodic potential you are all probably familiar from your early classes of the $f(x)$ of periodic potential in crystalline solids.

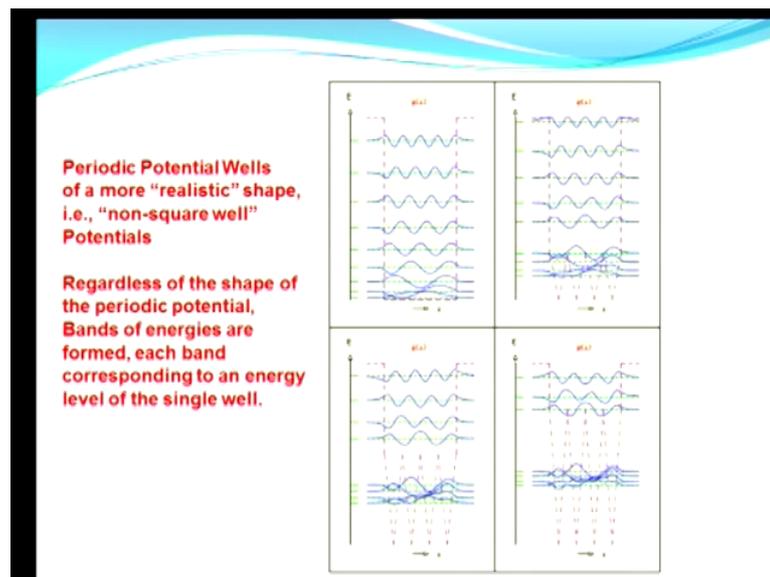
So, what we have here simulation of a simple case of a 1 dimension potential that is periodic and illustrating clearly that energy levels are split when you have a particle that is subject to the potentials of subject to the influence of interacting potentials especially in a periodic array so this is similar to periodic potential in crystalline solid. So, what this is illustrating is that bands of energy you can call these bands of energy so think of this as a potential due to an atom due to an ion in a solid so you have a another ion which is in a periodic array in that solid the crystalline solid.

So, what we can think of this as simplified illustration of a periodic potential in a crystalline solid, the periodic potential is simplified as a square well potential to make

the problem easier and what I want to do remember what I said last time I want to repeat that and that is that these are rigorous computer simulated solutions of the Schrodinger problem, Schrodinger equations for the 1 dimensional potentials by using appropriate boundary conditions as we have discussed before. So, this is showing for our understanding of the formation of bands this is showing that if you had a an electron in a crystalline solid for an example that is subject to the potentials of adjoining irons in a periodic array then it has energies that are in a band we can extend this further by noting the following.

So, what we have shown here in the previous case we had shown simply square well potentials so called square well potentials that as you can imagine is really an idealization real potentials have more complex form.

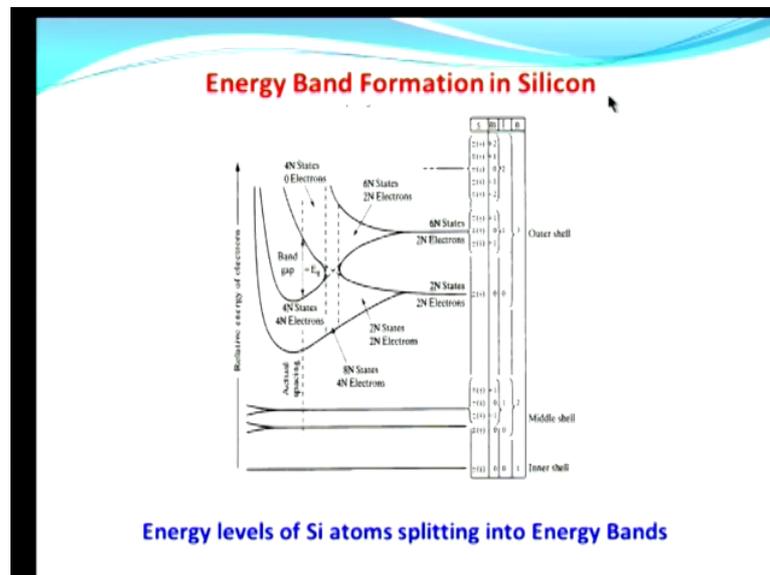
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To illustrate the complexity of the real potentials in a crystalline solid what is shown here are this so called Saw tooth wave potentials. So, we begin with a square well potential and then we modulate that as shown here with a saw tooth with increasing amplitude for the saw tooth that is we are going from a square well potential gradually from here to here to here to here we are replacing this square well potential with a saw tooth potential which is a bit more realistic than the square wave potential in representing the potentials in real solids.

So, while there are details to be observed here regarding the preservation of symmetry and anti symmetry and so on as you go from a square well to this saw tooth configuration. The point to take away once again is that each of these levels notice that you have 4 periodic potentials here and therefore this level over here at the bottom is split into 4 levels in the band calling the incipient band as might say. Therefore, this is a more rigorous illustration of what happens in a periodic potential of a slightly more realistic potential function that approaches that of a solid a crystalline solid.

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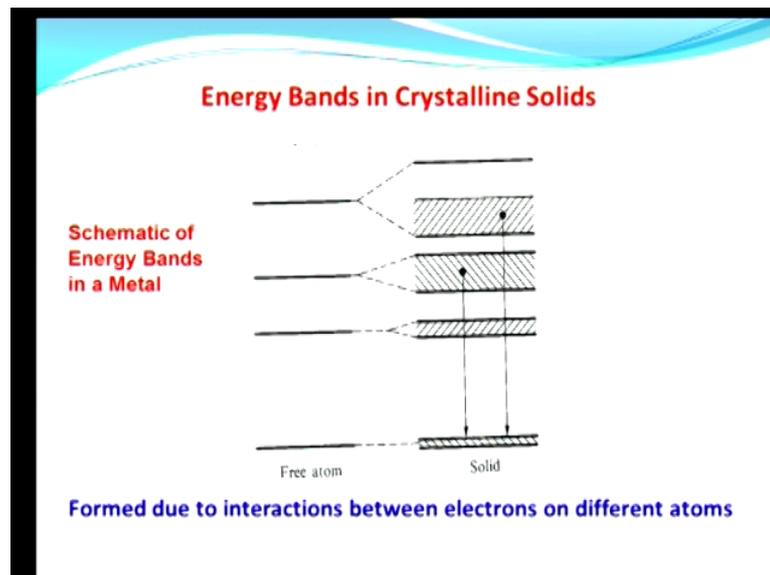
Now, you would have learnt earlier in the earlier part of the course you are dealt with band gaps and so on and certainly you are familiar with the energy bands in silicon and in the band gap and so on. So, what this is shows here is how the atomic states of silicon this represents the outer electrons, the valence electron shell of the silicon atom. How these levels split into bands as the silicon atoms condense into a crystalline solid. So, these levels represent energy state of silicon atom that is silicon atoms are far away from one another so that they do not influence one another.

So, these are atomic energy states, undisturbed atomic energy states as you bring these silicon atoms large numbers of them into a crystalline solid as it condenses in the crystalline solid because of the interaction between the potentials of the adjacent silicon atoms as we have seen in the simulation just shown because of that these atomic energy states which are distinct more like energy states these split into bands.

So, what we see here is the widening of these energy levels into band as shown here so here you have the upper electron energy levels, these are actually the anti symmetric states these are symmetric states so there is a lower energy over here for this band of silicon.

So, in the equilibrium configuration that is at the equilibrium distances so this x axis represents the separation between silicon atoms. At the equilibrium separation between silicon atoms then a band gap occurs between the upper band and the lower band, so the lower band is the valence band the upper band is the conduction band and there is a gap E_g which is 1.1 eV for silicon that develops as silicon atoms are condensed into a bulk crystal.

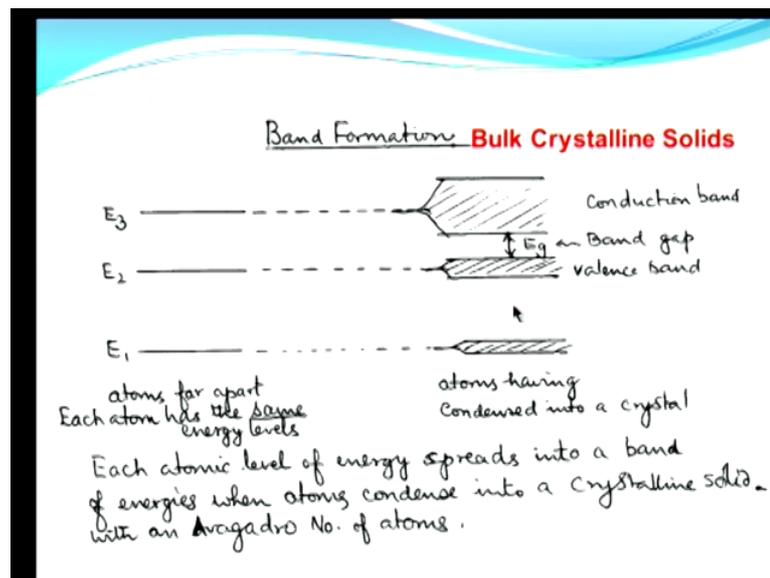
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So, here is a more schematic diagram of energy bands in a metal, silicon is a semiconductor so there is a band gap as we have just learned. Now in a metal something similar happens namely the free atom energy levels spread into bands these represents the inner core electrons and therefore they spread into narrower bands because the interaction between inner core electrons adjacent atoms is very minimal therefore, because of the reduced interaction then the spreading of these levels into a band is a narrow spread this is a narrow spread. So, as you go to outer and outer electrons these bands get wider and wider representing a greater degree of interaction between electrons in the outer orbits of an atom.

In the case of an metal as you know as you already learned in some earlier class the outer band the conduction band in this case is really not full unlike in the case of silicon where the valence band is full and the conduction band is empty here the conduction band is not full let us say it is half full therefore this is a representation of the energy bands of the crystalline metallic solid. Now what we have seen here is the formation of bands and what I want to do note is that atomic energy levels are spreading into bands of energy.

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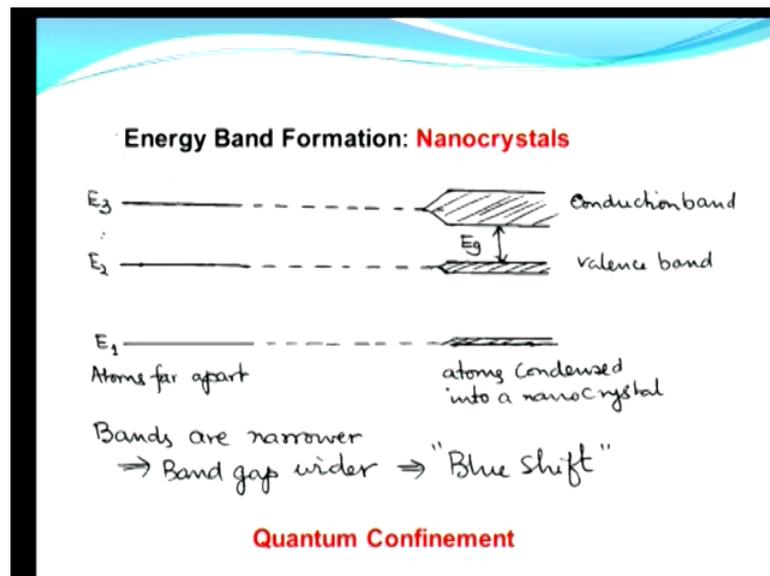


Now, consider a general case of band formation in a bulk crystalline solid let us forget about whether it is a metal or semiconductor atoms that are far apart from one another notionally at infinite separation. They have atomic levels E_1 , E_2 , E_3 etcetera. When you condense them condense large numbers of them into a crystalline solids then these levels spread into bands as we have learned. Now one thing that we must remember over here is that this spreading this splitting of these energy levels as they come together into a crystalline solid is influenced by the Pauli exclusion principle which if you recall says that 2 electrons cannot have the same wave function they cannot be in the same state. Therefore as they crowd into a solid crystalline solid these electrons have to spread into bands because of the Pauli Exclusion Principle being valid.

Now what have shown here is a notional band gap between the valence band and the conduction band so as you condense this set of atoms into a solid crystalline solid a band gap develops. Now this is a bulk crystalline solid what I mean by that is that it is of a

microscopic size of the order of you know it contains of the order of 10 to the 23 have a Avogadro number of atoms. So, we were talking about a large number of atoms where there are large number of an electrons so the bands spreads into relatively wide bands the energy levels spread into relatively wide bands and therefore you have a gap between the valence band and conduction band as denoted here.

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Let us consider band formation in a Nanocrystal that is we go from a bulk crystal where, as I just said we have approximately a Avogadro number of atoms in to a Nanocrystal where you may have or may be 10000 atoms or a 100000 atoms something of that order. Now as you bring these atoms together this are the energy levels of the individual atoms non interacting atoms at infinite distance we bring them together. Now notice that we have a fewer number of atoms within this nanocrystal much fewer than what the case is in a bulk solid, crystalline solid.

So, as a result the spread of these atomic energy levels into the bands will now correspond to the relatively small number of electrons that are present relatively small number of atoms that are there in these nanocrystals. Let us say we have 10 to the 5 atoms in this nanocrystals or 10 to the 6 of that order, then the width of these bands each of these bands will be less than now what it would be for the same material in a bulk crystal that is we go back to this.

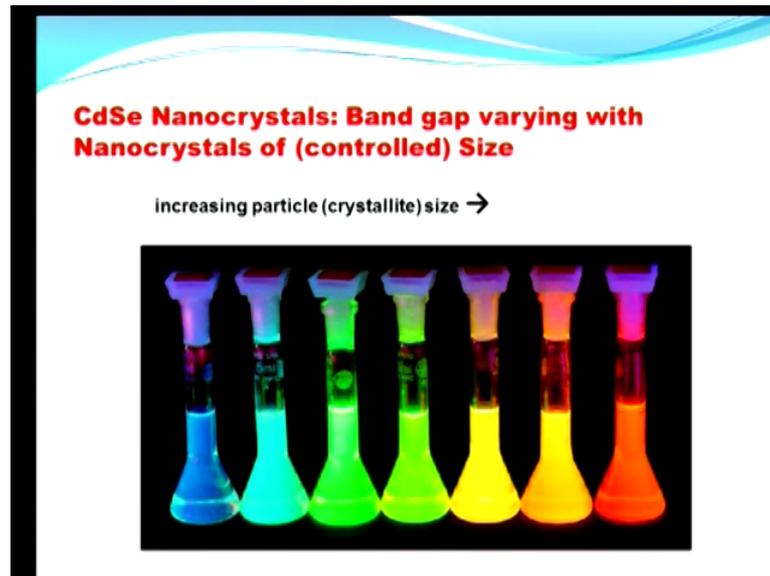
Let us say this material and this material of the same in one case you have the bulk crystal width about 10^8 to 10^{23} atoms and in the other case you have a nanocrystal width about 10^5 or 10^6 atoms. Correspondingly the width of the bands representing E_1, E_2, E_3 etcetera are now reduced so if there is a gap between conduction band and the valence band with each of them of a smaller width then before it means that the band gap between the top of the valence band and the bottom of the conduction band that band gap is now increased.

So, narrower bands in the case of smaller crystals, nanocrystals and therefore the band gap becomes wider, the band gap representing the frequency of the light that meant be emitted when there is a transition between the conduction band and the valence band E_g represents the band gap and therefore the frequency of light that would be emitted if there was a transition between the conduction band and the valence band if this becomes greater if the band gap becomes greater than the frequency of the light that is emitted is greater and because blue light has a higher frequency than red light.

Such a change in the wavelength of the light from a lower frequency to a higher frequency is called a blue shift and this phenomenon that leads to such an increase in band gap and therefore an increase in the frequency of light that might be emitted in a transition like this, this phenomena is the so called Quantum confinement phenomenon.

Actually quantum confinement take place in any solid, because the electrons cannot move out of the solid but here in any solid you would not notice difference between what happens in let us say a crystal of 1 millimeter versus a crystal of 1 centimeter in size whereas, when you come to the nanometric regime you begin to see the differences between what would be the case in the bulk material and the nano material and a nanocrystal the same material, so this is the blue shift.

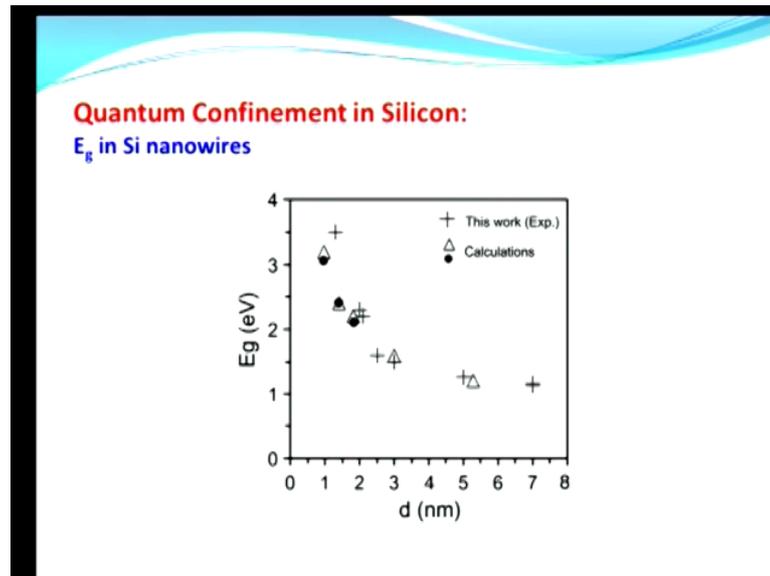
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This can be seen dramatically in the case of semiconductors like cadmium selenide so what is shown here is the famous picture of the light emission from under fluorescence from cadmium selenide nanocrystals with increase in particle size from left to right it turns out that it is possible to prepare cadmium selenide nanocrystals with the highly controlled diameter. All the wave from let us say about 8 nanometers on the right through about 2 nanometers on the left so in the size controlled crystals cadmium selenide one can observe the progressive change in the band gap as we reduced the size from about 8 nanometers to about 2 nanometers where the band gap is such that blue light is emitted.

So, this is a vivid illustration of how the band gap can be changed by controlling the size of crystalline semiconductors. Actually this phenomenon has very important practical applications which we shall probably return to later in the segment of the course.

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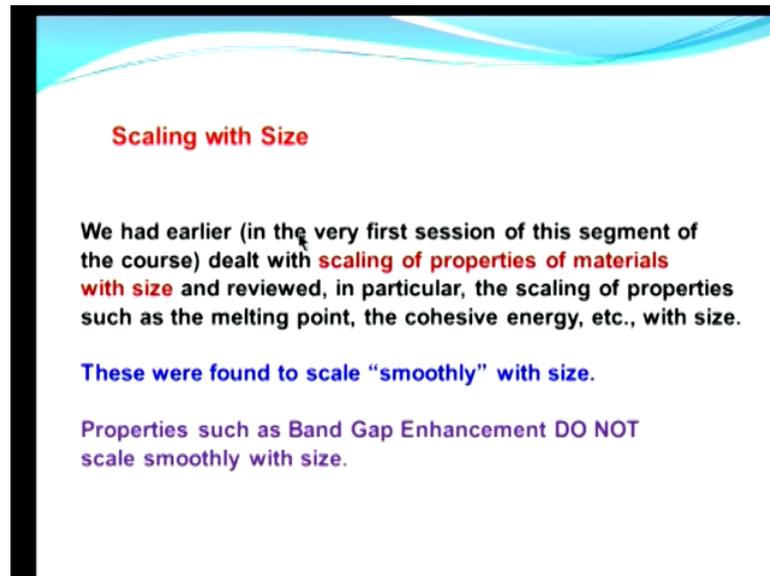


Now, such quantum confinement or the blue shift is not confined to cadmium selenide, cadmium selenide is a so called compound semiconductor. Silicon is the prototypical semiconductor which you are familiar with but silicon is an indirect band gap semiconductor which you know. Therefore, its light emission efficiency is very low because it is an indirect band gap semiconductor.

Therefore, such dramatic effects as we see here in the case of cadmium selenide due to size variation cannot be seen in the case of silicon. Nevertheless, measurements have been made of the band gap of silicon in silicon nanowires that is by controlling the diameters of nanowires of silicon which can be grown through a method known as the VLS method we shall return to later.

As a function of the diameter of nanowires as you go from about 7 or 8 nanometers for the diameter nanowires and that is steadily reduced to about 1 nanometer you can see that the familiar 1.1 eV band gap for silicon present at about 7 or 8 nanometers of diameter of the nanowire that increases steadily to go beyond 3 electron volts from 1.1 to 3 electron volts when the wire diameter is reduced wire is actually single crystal wires. So, when the wire diameter is reduced to about 1 nanometer the energy band gap shoots up all the way to about 3 electron volts. This is borne out by this actual data points from calculations but it is borne out by experimental work that there is indeed a blue shift in the silicon semiconductor as well.

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Scaling with Size

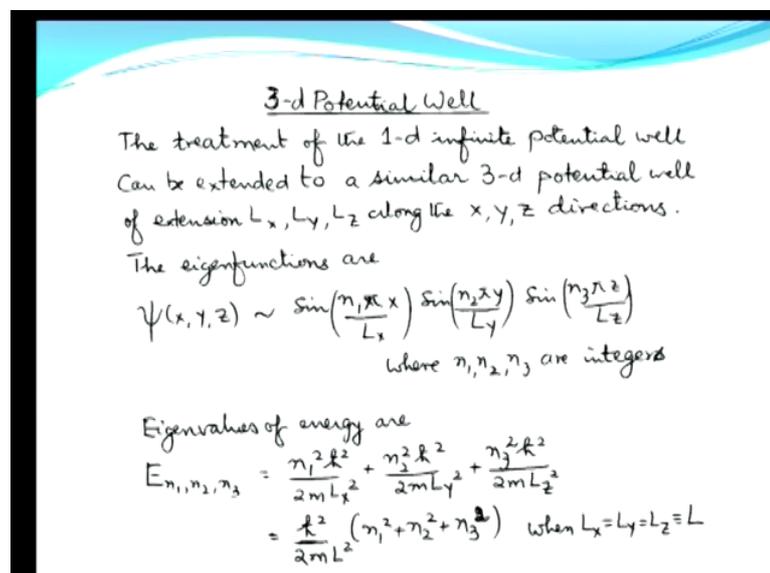
We had earlier (in the very first session of this segment of the course) dealt with **scaling of properties of materials with size** and reviewed, in particular, the scaling of properties such as the melting point, the cohesive energy, etc., with size.

These were found to scale “smoothly” with size.

Properties such as Band Gap Enhancement **DO NOT** scale smoothly with size.

Now, in the very first class of the segment we learned about how properties of materials scale with size and we talked about the smooth scaling with size that is as a size reduced there is a smooth scaling of the melting point cohesive energy and so forth. Now it turns out that set of properties where there is a smooth scaling is different from such a variation in the band gap of a semiconductors. So the variation in the band gap of the enhancement of band gap in the same reduced is not one of those that scales smoothly with size as a size reduced or enhanced. So, this is a this part of a second set of properties where scaling with size is not smooth

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3-d Potential Well

The treatment of the 1-d infinite potential well can be extended to a similar 3-d potential well of extension L_x, L_y, L_z along the x, y, z directions.

The eigenfunctions are

$$\psi(x, y, z) \sim \sin\left(\frac{n_1 \pi x}{L_x}\right) \sin\left(\frac{n_2 \pi y}{L_y}\right) \sin\left(\frac{n_3 \pi z}{L_z}\right)$$

where n_1, n_2, n_3 are integers

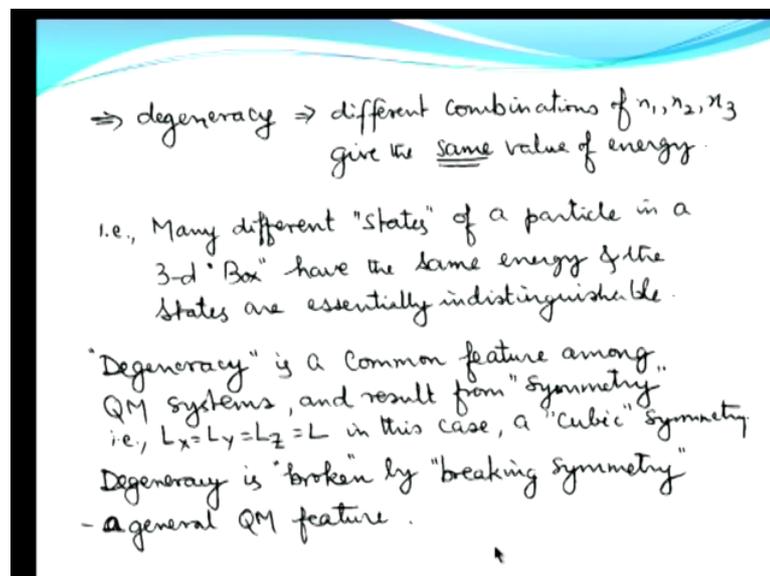
Eigenvalues of energy are

$$E_{n_1, n_2, n_3} = \frac{n_1^2 \hbar^2}{2mL_x^2} + \frac{n_2^2 \hbar^2}{2mL_y^2} + \frac{n_3^2 \hbar^2}{2mL_z^2}$$
$$= \frac{\hbar^2}{2mL^2} (n_1^2 + n_2^2 + n_3^2) \text{ when } L_x = L_y = L_z = L$$

Let us return to the potential well or the particle in a box earlier we dealt with the infinite 1 dimensional potential well that it is easy to extend this to to 3 dimensions that is a potential well that extends along the x y and z axis. So, if you recall the treatment there we had an extension of L for along the x axis for the potential well so, you can have L_x , L_y and L_z in a 3 dimensional potential well in which case the energy Eigen functions in analogy with the 1 dimensional case would then be the product of 3 sinusoidal functions each with the quantum number n_1 , n_2 and n_3 which all integers that n_1 , n_2 and n_3 will correspond to the length L_x , L_y and L_z for the boxes along the respective directions.

The Eigen values of energy for such a case of a 3 dimensional potential well would have 3 quantum numbers E_{n_1, n_2, n_3} with the expression for the energy being $\frac{\hbar^2}{2m} \left(\frac{\pi^2}{L_x^2} n_1^2 + \frac{\pi^2}{L_y^2} n_2^2 + \frac{\pi^2}{L_z^2} n_3^2 \right)$ where each of them is an integer and we have simplified this case by making this into $L_x = L_y = L_z = L$. So, the algebra of this is simplified when all the L's are equal so the energy Eigen values then would be $\frac{\hbar^2 \pi^2}{2m L^2} (n_1^2 + n_2^2 + n_3^2)$.

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Now, there are 3 quantum numbers and you can observe from the formation of these from the nature of the expression that you can have different solutions that yield same

value of energy. You can have n_1, n_2, n_3 with certain numbers you can have n_2, n_3, n_1 with same certain numbers but distributed separately and so forth.

So, you can have multiple solutions for which the energy is the same that is the case of degeneracy. Different combinations of $n_1, n_2,$ and n_3 are giving the same value of energy that is many different states of a particle in a certain 3 dimensions box would have the same energy and the states are essentially indistinguishable.

So, such degeneracy which I suppose you are come across earlier is a common feature among quantum mechanical systems and it is a result of the symmetry namely, L_x, L_y and L_z being the same so in this case it provides cubic symmetry so because of this symmetry then the degeneracy is enhanced and this is a general phenomenon in quantum mechanics that this degeneracy is broken by breaking the symmetry that is if you had L_x, L_y and L_z different from one another then the symmetry is broken and that then you would have a smaller extent of degeneracy.

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Density of States

Consider the 3-d infinitely deep potential well.

$$E_n = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

For an electron "boxed" in a cube of edge $L = 1\text{cm} (10^{-2}\text{m})$

$$E_n \approx (3.7 \times 10^{-5}) (n_x^2 + n_y^2 + n_z^2) \text{ eV.}$$

The difference between neighbouring levels increases at higher energies

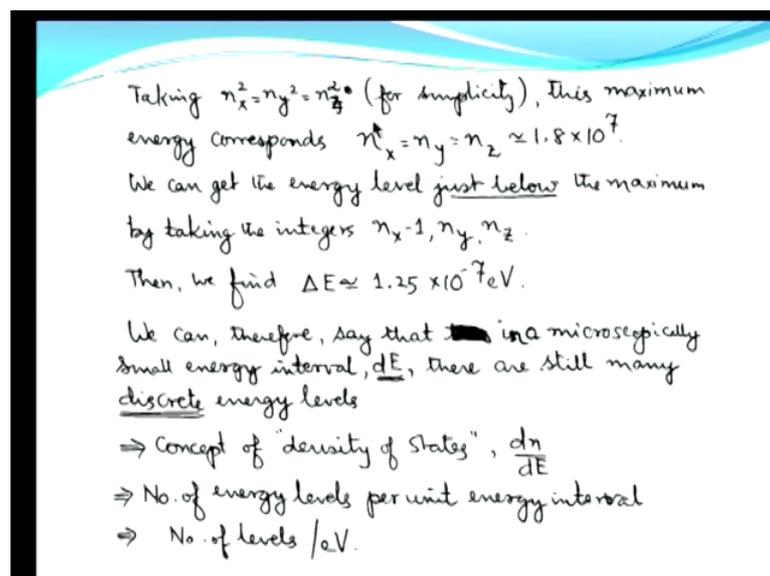
Let us assume a metallic sample, in which case, experiments show that the maximum value of E_n is of the order of 5 eV.

In a previous section I introduce you to the density of states, the concept of the density of states that is how many states of energy that a particle can assume in a given energy interval in a quantum mechanical system. Consider the 3 dimensional infinitely deep potential well as we have just did. So, then you have E_n equal to \hbar^2 square there is another here I am sorry it is not 8, it is $2\hbar^2$ square over $2mL^2$ into n_x^2 square plus n_y^2 square plus n_z^2 square.

Now if you consider l to be equal to 1 centimeter that is we consider a microscopic box not a quantum box in the usual sense, but a microscopic box of extension 1 centimeter, so, we substitute L equal to 1 centimeter when we do that and we consider the value of the Planck's constant E_n , E_n then becomes $3.7 \times 10^{-15} (n_x^2 + n_y^2 + n_z^2)$ so many electron volts.

So, by plugging in the values of different quantum numbers one can calculate the energy of corresponding states. As you said earlier, the difference between successive levels or neighboring levels increases as the quantum number increase so for higher quantum numbers succeeding levels are separated by a greater interval of energy. Now let us assume a metallic sample which is a crystalline sample with a periodic potential as we have said earlier let us assume metallic sample in which case experiments show that the maximum value of E_n is of the order of 5 eV is so called Fermi energy.

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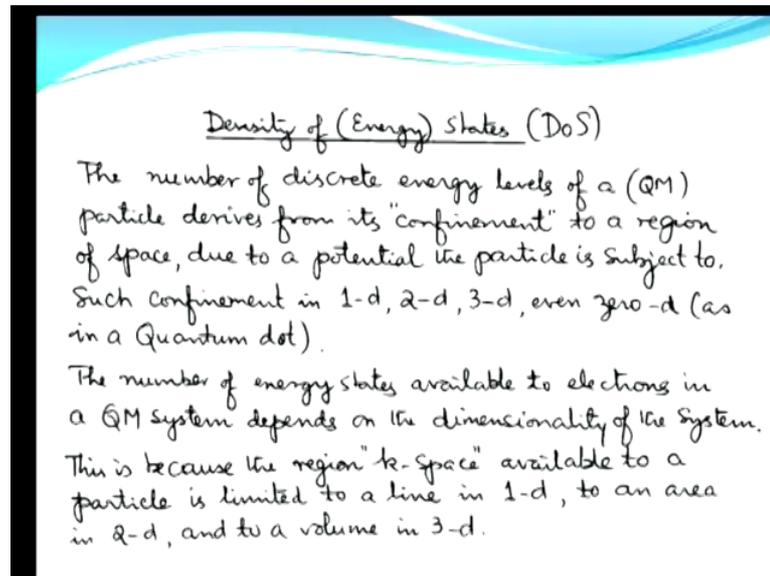
So the experiments show that the maximum value of E_n is about 5 eV, now if you put that 5 eV in into this expression and we take n_x equal to n_y equal to n_z for simplicity, the quantum number corresponding to the highest energy level namely 5 electron volts is about 1.8×10^7 so you can imagine that these numbers you know for bulk materials quantum numbers are very large. Now this is the top most level we can get the energy level just below the maximum level, just below the top most level by the

substituting for one of the quantum numbers instead of n_x you would have $n_x - 1$ that is 10 to the power of $7 - 1$.

If we do that arithmetic will tell us that the energy difference between the top most level and the one just below that is of the order of 1.25 times 10 to the power of -7 e V which is indeed a small energy interval. So, what this is telling us is that in a microscopic sample levels of energy that an electron can assume are very closely spaced that is interval of energy dE between successive levels which are all discrete by the way you know this is important to remember that all these energies are discrete because these numbers are discrete. The energy interval between successive levels is very small 10 to the power -7 e V; therefore, it makes sense to talk about by the way these are called Quasi continuous states, they are actually not continuous they are discrete, but they are quasi continuous because there are such large number of levels in an interval of let us say 1 electron volt.

The separation between them being 10 to the power of -7 in a one electron energy one electron volt interval there would be a large number of energy levels possible. Therefore, one can speak of the concept of the density of state this is where the concept of density of states comes in defined as dn divided by dE or the number of energy levels per unit energy interval that interval being electron volts let us remember 10 to the power of 1 electron volt is about 10 to the power of -19 joules. So, the density of levels then talks about the number energy levels that a quantum system has per electron volt energy interval.

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The number of discrete energy levels of the quantum mechanical particle derives from its confinement to a region of space. Even if that confinement is not necessarily even if the confined region is not very small there is a confinement and confinement in variably results in quantization of energy levels. Now such confinement can take place not only in the familiar 3 dimensional objects that we can have, but such confinement can be in 1 dimension, in 2 dimensions, in 3 dimensions and even in 0 dimensions.

So, in the world of nano materials, nano technology not only do you have confinement on all along all 3 dimensions which is referred to as a quantum dot, so the quantum dot in principle as no extension so in all dimensions it is a very small object all 3 dimensions. So, there is a quantum dot or a 0 dimension object or you can have a 1 dimensional object such as for example, the carbon nano tube you can think of that as 1 dimensional object nano object or a 2 dimensional quantum object the prototypical example of that is the grapheme sheet which I think we shall return to later.

So, you can have confinement in 1 dimensions, 2 dimensions, 3 dimensions and even in 0 dimensions. Now, the number of energy states available to electrons in a quantum mechanical system must therefore really depend on the dimensionality of the system this is sort of intuitively obvious that this number of energy states should be dependent on this because the number of atoms and the number of electrons present would be dictated

by the fact whether it is a 1 dimensional, 2 dimensional, 3 dimensional, or 0 dimensional object.

Now if you recall the solution to the time independent Schrodinger equation for the infinite potential well we had the reciprocal vector k so we can think of the so called k space when your confinement the region of k space available to a particle is limited for example, to a line in 1 dimension, to an area in 2 dimensions, and to a volume in 3 dimensions. Therefore, we can see that this density of states should really behave differently should have different kinds of functional dependence on the number of dimensions in the object.

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Therefore, the DOS has different functional forms for 1-d, 2-d, 3-d, and zero-d.
Simple analysis shows that the DOS has the following dependence on the No. of dimensions:

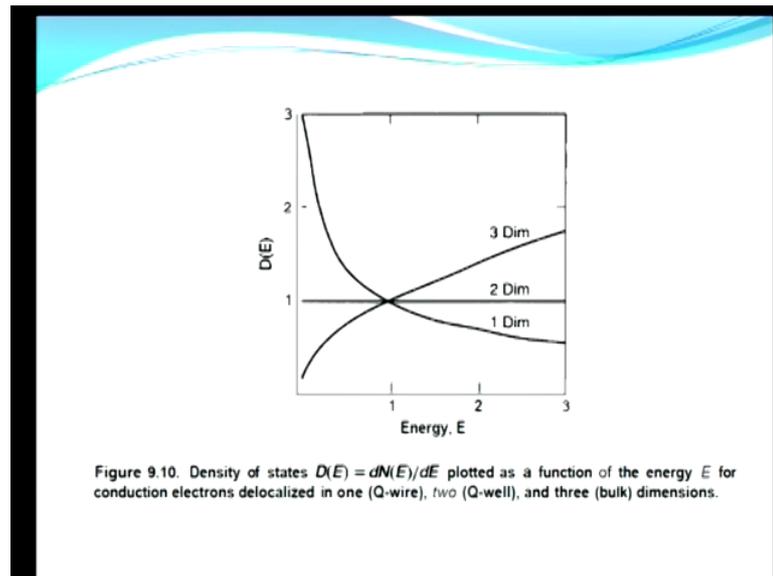
Structure	degree of Confinement	DOS $\equiv \frac{dn}{dE}$
Bulk material	0	$\sim E^{3/2}$
Quantum well	1	Constant
Quantum wire	2	$\sim E^{-1/2}$
Quantum dot	3	$\delta(E)$ Dirac Delta fun.

Simple analysis which we shall not go through here shows that the density of states has the following dependence on the number of dimensions in a crystal. If it is bulk material 3 dimensional bulk material there is really no confinement if you take a 1 centimeter object as I was saying a moment ago in such case for all instance and purposes there is no confinement of the electron, 1 centimeter is very much larger than the mean free path of an electron and therefore is really not confined.

In such a case the functional dependence of the density of states that is dn/dE number of states per unit energy interval this varies as E to the power of half, if you have a quantum well where there is a 1 degree of confinement, then the density of states is independent of an energy dn/dE is equal to constant.

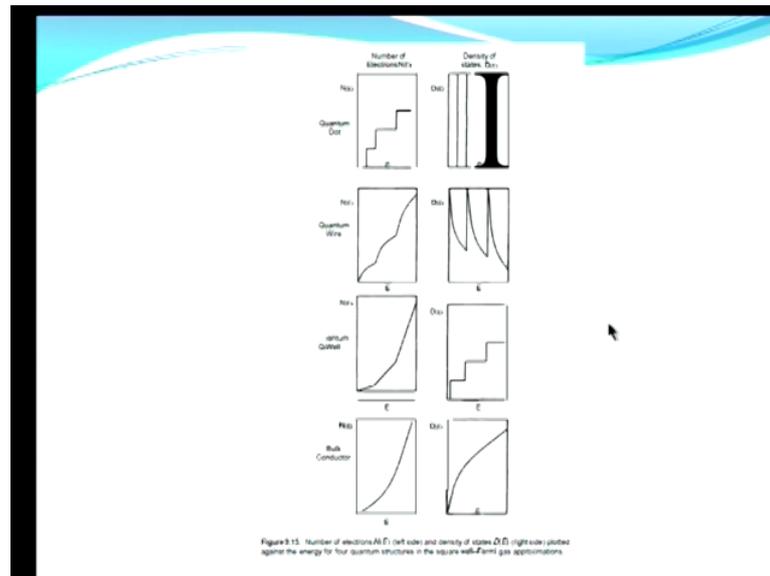
If you have a quantum wire so that an electron for example, is confined to move along a line. So, there are 2 degree degrees of confinement then the density of states varies as $E^{-1/2}$ if it is a quantum dot where an electron for example is confined in all dimensions then the density of states is a Dirac delta function that is it spikes at specific values of energy, but it is 0 on either side of such a value of energy.

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So, graphically what this shows is the density of states dN/dE as a function of energy E . So, what I just said earlier about the functional dependence of the density of states on energy is shown here graphically. In 3 dimensions there is a parabolic dependence of the density of states on energy E and then you have a $1/E$ dependence in 1 dimension and in 2 dimensions the density of states is independent of energy.

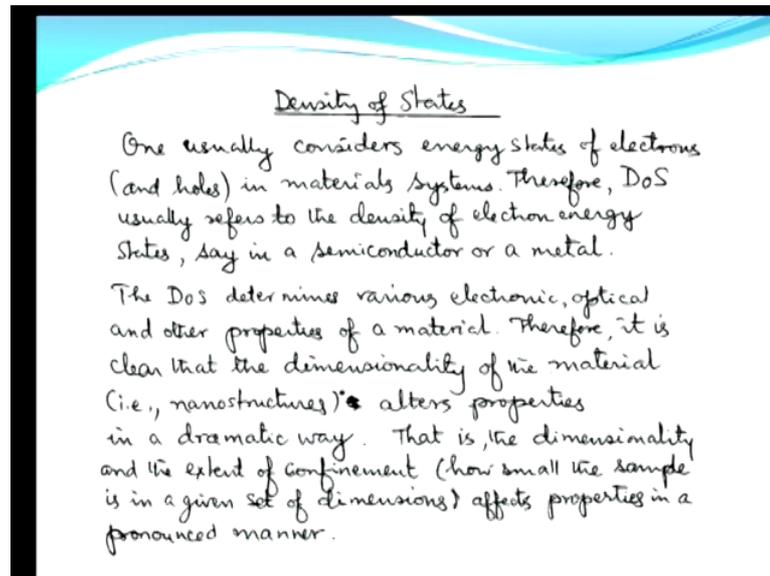
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In a slightly different representation what I have shown here on the right hand is the density of states as a function of energy in 3 dimensions over here so you have this parabolic dependence, we are thinking of an nano system here and in a quantum well you have a shorter a stair case over here and in the case of a quantum wire you have this spikely dependences where there is a sharp fall often either side of a certain value of energy whereas, in the case of a quantum dot you have the density of states 0 except that is specific values of energy as shown here.

So, you have spikes of density of states in the case of a quantum dot which is the reason why in the illustration of cadmium selenide what do you saw was sharply blue, and sharply green, in other words emission of light monochromatic light from particles of a fixed wavelength, fixed size so that is an illustration of the density of states being very sharply defined in the case of a quantum dot system.

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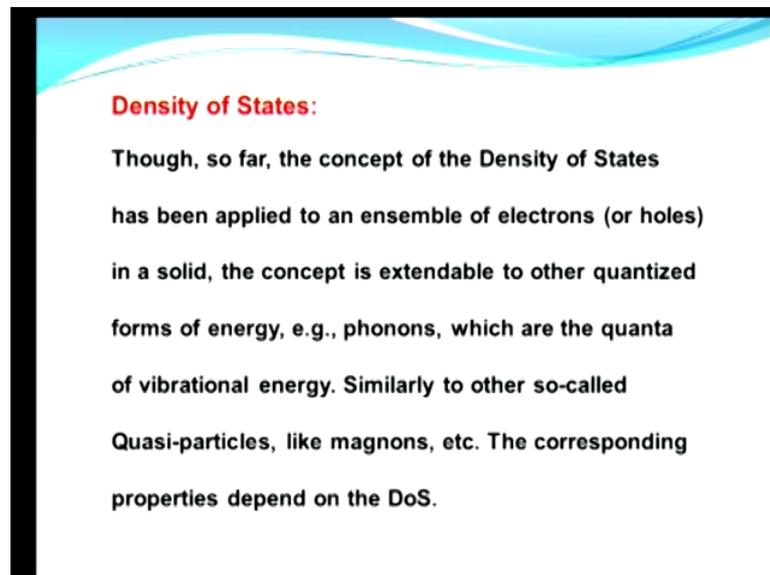
Now, continuing with the concept of the density of states one usually considers energy states of electrons or holes in materials systems to understand its behavior. Therefore, the density of states usually refers to the density of electron energy states say in a semiconductor or a metal, as you might expect although we have not really gone through the treatment, the density of states determines the various electronic optical and other properties of the material because the density of states determines the actual energy configuration of a system.

One of the things I want to point out is that the density of states is really the density of states available for electrons to occupy, the actual occupation of these levels depends on the statistics of the system for example, the Fermi Dirac statistics for electrons. The Fermi Dirac statistics determine the probability of occupation of a given energy level, so the actual energy configuration that is the energy levels actually occupied by a population of a electrons in let us say semiconductor is given by the product of the density of energy states and the probability of occupancy of a given energy state which is derived from the statistics. Therefore, the density of states is not these density of electron occupation.

The density of states is density of states available for occupation and that has been multiplied the probability of occupancy of a given state to get the actual configuration of occupation of different of levels of energy.

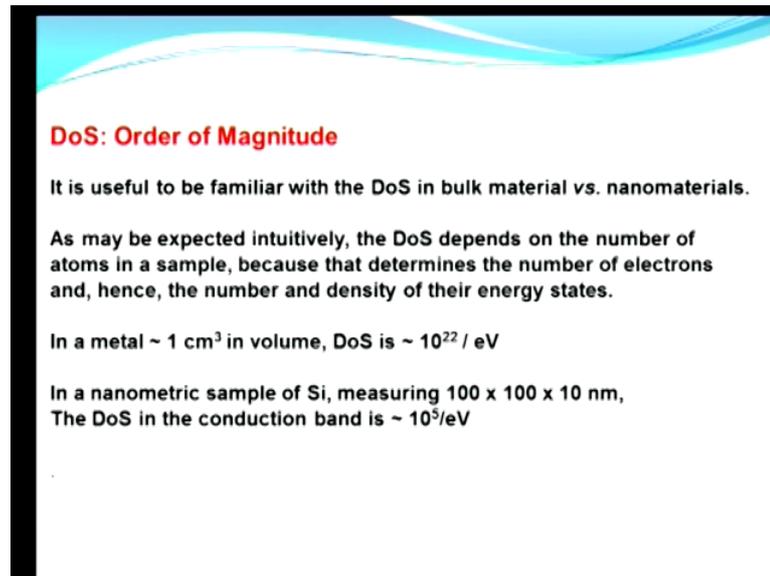
Now because of the way this is defined it is clear that the dimensionality of the material namely, the nanostructures that we are dealing with alters the properties in a dramatic way because the density of states would be different in these objects have different dimensionality that is the dimensionality and the extent of confinement affect the properties in a pronounced fashion. So, this is one of the fundamental aspects of nanomaterials, nanocrystals where the behavior is determined by the fact that they may have fewer dimensions than in a typical bulk sample.

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Now, one more thing to extend this concept of the density of states though it has been applied to an ensemble of electrons or holes we have basically refer to that so far. The concept is extendable to other quantized forms of energy for example phonons which are the quanta of vibrational energy. So, this density of states is extendable through all so called Quasi particles, phonons, magnons polonons and so on and the corresponding properties that is the phonon density of states then determines for example the mechanical properties of a solid material.

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DoS: Order of Magnitude

It is useful to be familiar with the DoS in bulk material vs. nanomaterials.

As may be expected intuitively, the DoS depends on the number of atoms in a sample, because that determines the number of electrons and, hence, the number and density of their energy states.

In a metal $\sim 1 \text{ cm}^3$ in volume, DoS is $\sim 10^{22} / \text{eV}$

In a nanometric sample of Si, measuring $100 \times 100 \times 10 \text{ nm}$, The DoS in the conduction band is $\sim 10^5 / \text{eV}$

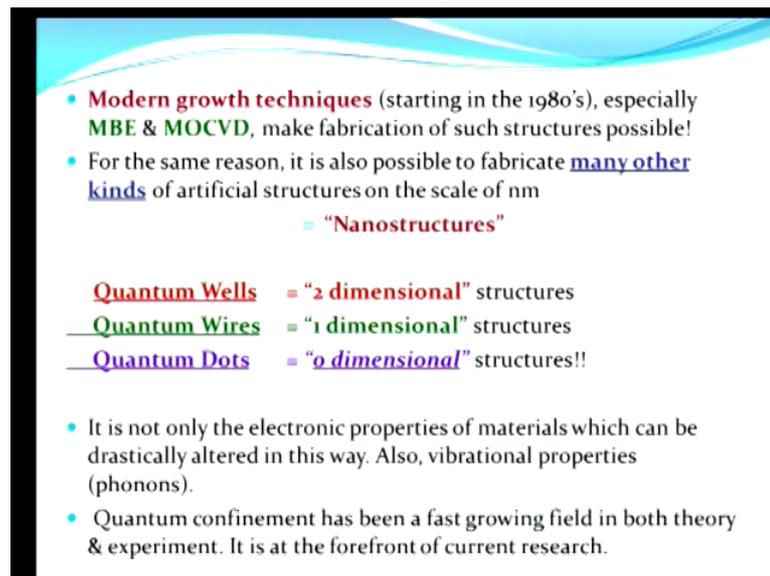
It is useful to be familiar with the density of states in a bulk material versus a nanometric sample. As you may expect intuitively the density of states depends on the number of atoms in a sample because this number determines the number of electrons in that sample if you are dealing with electronic properties in a material. And this therefore the density of states depends on the number of atoms in the sample the size is sample and therefore the number in the density of the energy states is determined by the size of the sample.

In a metal one can show that in a metal of let us say 1 centimeter cube volume, 1 centimeter by 1 centimeter by 1 centimeter which is a sample we considered a while ago one can show that the density of states is of the order of 10^{22} per electron volt that is essentially we have an Avogadro number of energy states possible in a bulk metal sample of 1 centimeter in extension. By contrast if you consider a nanometric sample of silicon measuring let us say 100 nanometers by 100 nanometers by 10 nanometers. Then one can show that the density of states in the conduction band you remember this silicon sample has a band gap and you have the valence band that is full and the conduction that is empty at 0, temperature.

The density of states in conduction band is of the order of 10^5 per electron volt that is you can see the enormous difference in the density of states between difference between the density of states and in a bulk sample versus the same quantity in a

nanometric sample. Therefore, you can appreciate that quite apart from the dimensionality of the sample namely, 0 d, 1 d, 2 d, and 3 d the density of states is also dictated by the small number of atoms relatively small number of atoms present such a structure and therefore the density of states which affects the properties such ensembles is significantly smaller than in a bulk sample.

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- **Modern growth techniques** (starting in the 1980's), especially **MBE & MOCVD**, make fabrication of such structures possible!
- For the same reason, it is also possible to fabricate many other kinds of artificial structures on the scale of nm
 - = "Nanostructures"

Quantum Wells = "2 dimensional" structures
Quantum Wires = "1 dimensional" structures
Quantum Dots = "0 dimensional" structures!!

- It is not only the electronic properties of materials which can be drastically altered in this way. Also, vibrational properties (phonons).
- Quantum confinement has been a fast growing field in both theory & experiment. It is at the forefront of current research.

I think we will conclude there this section we will come back in the next section to deal with real quantum wells. So, what we have done today is to work with quantum wells and arrays of quantum wells to lead to the concept of bands of energy and how these bands of energy formed in bulk material of microscopic extension versus and nanomaterials, where the bands are narrower than corresponding bands of energy in bulk material.

Leading to the concept of enhancement of band gap when the size of a sample is size of a given material is greatly reduced to nanometric dimensions so that is the so called blue shift and then we have considered the concept of the density of states, density of quantum energy states in a confined material and we have shown that at least we have reviewed not really a established that the density of states depends differently an energy in objects of 0, 1, 2, and 3 dimensions and we have said that the density of states is a very important quantity that determines the electronic and other properties of material.

So, we will continue with the realization or illustrations of the realization of actual quantum wells and the devices that come out of that in the next section.

Thank you.