

Electronic Properties of the Materials: Computational Approach
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Lecture: 22
Origin of Band Gaps Part 2

Hello friends we are going to continue our discussion on the origin of band gap in 1D lattice. So, far we have seen that a block electron with wave vector closer to the comma point which is the origin of the reciprocal lattice is very similar to free electrons. On the other hand, a block electron with a wave Vector equal to the first Brillouin zone boundary is reflected 100% by the periodic potential.

We have derived the wave functions in case of 100% reflection. In this lecture we are going to use the wave functions in case of 100% reflection and relate them to the origin of the band gap. **(Refer Slide Time: 01:00)**

Solution at Brillouin zone boundary

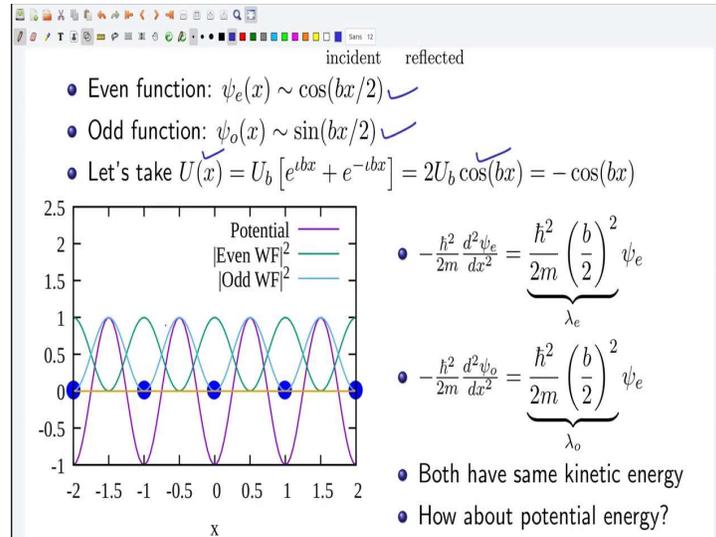
- At zone boundary: $\psi(x) = \underbrace{e^{ibx/2}}_{\text{incident}} \pm \underbrace{e^{-ibx/2}}_{\text{reflected}}$
- Even function: $\psi_e(x) \sim \cos(bx/2)$
- Odd function: $\psi_o(x) \sim \sin(bx/2)$
- Let's take $U(x) = U_b [e^{ibx} + e^{-ibx}] = 2U_b \cos(bx) = -\cos(bx)$

- $-\frac{\hbar^2}{2m} \frac{d^2 \psi_e}{dx^2} = \frac{\hbar^2}{2m} \left(\frac{b}{2}\right)^2 \psi_e$
- $-\frac{\hbar^2}{2m} \frac{d^2 \psi_o}{dx^2} = \frac{\hbar^2}{2m} \left(\frac{b}{2}\right)^2 \psi_o$

Let us focus on solution at Brillouin zone boundary that is the wave vector of the block electron is equals to $b/2$ where b is a reciprocal lattice point in that case the wave function ψ of x is $e^{ibx/2} + e^{-ibx/2}$ considering that positive sign we get an even wave function ψ of x is $\cos(bx/2)$ considering the negative sign we get an odd function that is ψ_{odd} is equal to ψ_{even} .

Keeping only one term in the Fourier series expansion of U of x we get U of x is equals to $2 U_b \cos$ of bx if you need any further explanation you are advised to refer to the lecture on Fourier series expansion of U of x .

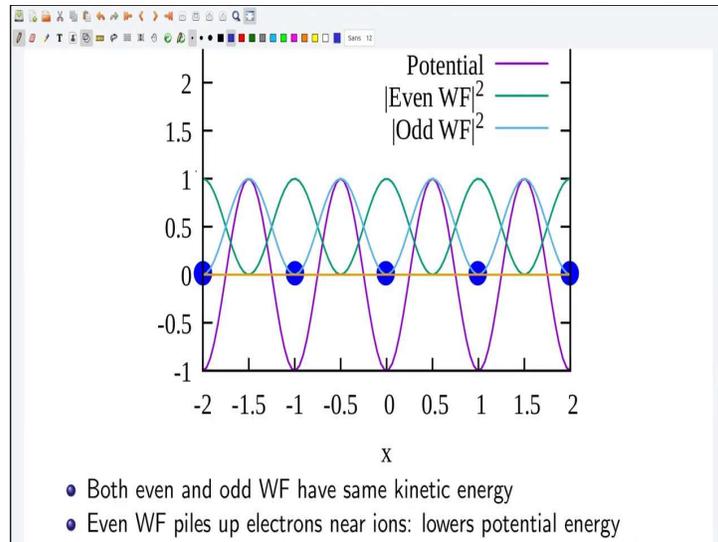
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Potential and probability densities of the even and odd wave function are shown in this diagram. For plotting the potential I have assumed U of b is equals to minus half the blue circles denote the location of the lattice points. Let us calculate the kinetic energy of the event and on wave function using the even wave function to be equal to $\cos bx$ by 2 the kinetic energy is \hbar^2 cross Square by $2m$ b by 2 whole square.

Similarly using odd is equals to $\psi_o(x) \sim \sin(bx/2)$ we get the kinetic energy of the odd wave function to be equal to \hbar^2 + Square by $2m$ b by 2 whole square thus we find that both the wave functions have same kinetic energy.

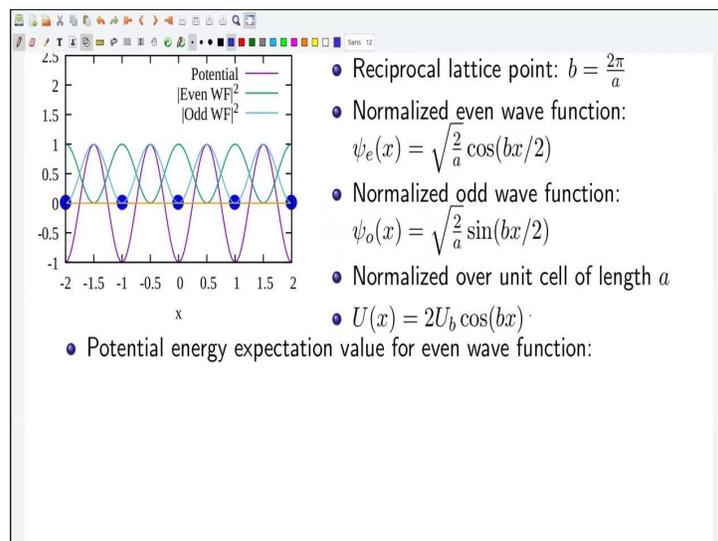
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Now let us find out the potential energy looking at the probability density plot of the even wave function clearly electron is going to be accumulated near the lattice points. Since a positively charged atomic core is located at each lattice point the negatively charged electron has less potential energy if the wave function is even. On the other hand probability density plot of the odd wave function shows that the electron is going to be accumulated in the middle of the two lattice points that is here.

Putting the negatively charged electrons away from the positively charged atomic force is going to raise the potential energy in case of on wave function. Let us calculate the potential energy difference between the even and odd wave function in one unit cell. Length of the unit cell is the distance between the two adjacent lattice points.

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We have to calculate the potential energy for the even and or wave function. Where we assume the potential to be equal to $U(x)$ is equals to $2U_b \cos(bx)$ where b is equal to $2\pi/a$. Note that wave functions are normalized considering the length of the unit cell to be equal to a .

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- Normalized odd wave function: $\psi_o(x) = \sqrt{\frac{2}{a}} \sin(bx/2)$ ✓
- Normalized over unit cell of length a
- $U(x) = 2U_b \cos(bx)$ ✓
- Potential energy expectation value for even wave function:

$$\int_0^a dx U(x) |\psi_e|^2 = \frac{2}{a} \int_0^a 2U_b \cos(bx) \cos^2\left(\frac{bx}{2}\right) dx$$

$$= \frac{2U_b}{a} \int_0^a \cos(bx) (\cos(bx) + 1) dx = \frac{U_b}{a} \int_0^a (2\cos^2(bx) + 2\cos(bx)) dx$$

$$= \frac{U_b}{a} \int_0^a (\cos(2bx) + 1 + 2\cos(bx)) dx = U_b$$
- Total energy of even wave function: $\lambda_e + U_b$

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Potential energy expectation value for the even wave function is given by

$$\int_0^a dx U(x) |\psi_e|^2 = \frac{2}{a} \int_0^a 2U_b \cos(bx) \cos^2\left(\frac{bx}{2}\right) dx$$

$$= \frac{2U_b}{a} \int_0^a \cos(bx) (\cos(bx) + 1) dx = \frac{U_b}{a} \int_0^a (2\cos^2(bx) + 2\cos(bx)) dx$$

$$= \frac{U_b}{a} \int_0^a (\cos(2bx) + 1 + 2\cos(bx)) dx = U_b$$

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• Normalized odd wave function:
 $\psi_o(x) = \sqrt{\frac{2}{a}} \sin(bx/2)$

• Normalized over unit cell of length a
 $U(x) = 2U_b \cos(bx)$

• Potential energy expectation value for odd wave function:

$$\int_0^a dx U(x) |\psi_o|^2 = \frac{2}{a} \int_0^a U_b \cos(bx) \sin^2 \frac{bx}{2} dx$$

$$= \frac{2U_b}{a} \int_0^a \cos(bx) (1 - \cos(bx)) dx = \frac{U_b}{a} \int_0^a (2\cos(bx) - 2\cos^2(bx)) dx$$

$$= \frac{U_b}{a} \int_0^a (2\cos(bx) - 1 - \cos(2bx)) dx = -U_b$$

• Total energy of odd wave function: $\lambda_o = -U_b$

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Now we already have found out the kinetic energy thus the total energy of the even wave function is λ_e which is the kinetic energy + the potential energy U of b . Similarly potential energy expectation value can be calculated for the odd wave function. This is given by integral

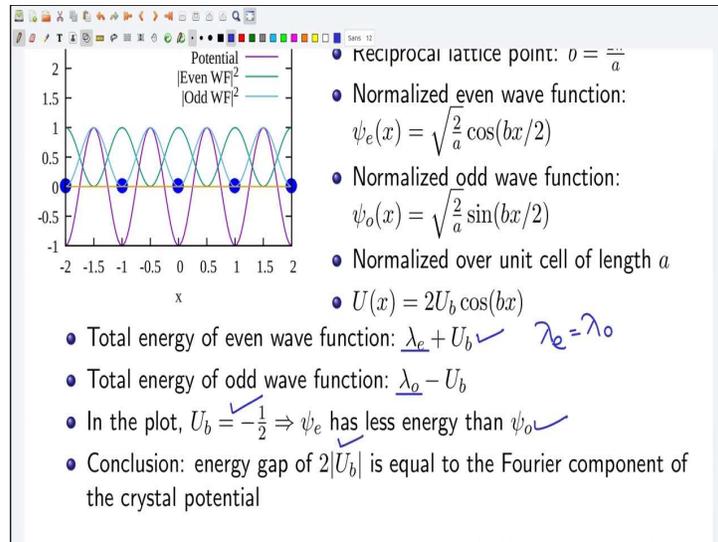
$$\int_0^a U(x) |\psi_o|^2 = \frac{2}{a} \int_0^a 2 U_b \cos(bx) \sin^2 \left(\frac{b}{2} \right) dx$$

$$= \frac{2U_b}{a} \int_0^a \cos(bx) (1 - \cos(bx)) dx = \frac{U_b}{a} \int_0^a (2\cos(bx) - 2\cos^2(bx)) dx$$

$$= \frac{U_b}{a} \int_0^a (2\cos(bx) - 1 - \cos(2bx)) dx = -U_b$$

We already have found the kinetic energy thus the total energy of the order function is kinetic energy plus the potential energy.

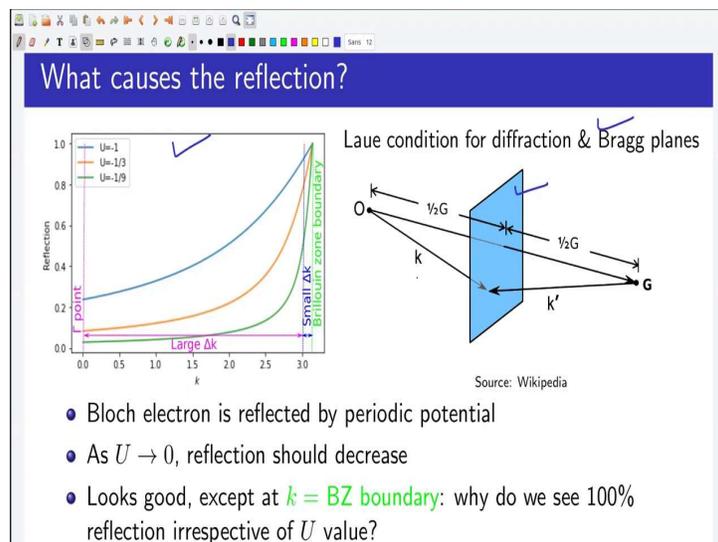
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Thus we have derived that the total energy of the even wave function is $\lambda_e + U_b$ where λ_e is the kinetic energy. Similarly total energy of the odd wave function is $\lambda_o - U_b$ where λ_o is the kinetic energy of the odd wave function remember that we already have seen that $\lambda_e = \lambda_o$ in the block I have used U_b is equal to minus half which implies that the even wave function has less energy than the odd wave function.

Subtracting the energy of the even and odd wave function we get the band gap to be equal to $2|U_b|$ thus band gap is equal to the Fourier component of the crystal potential.

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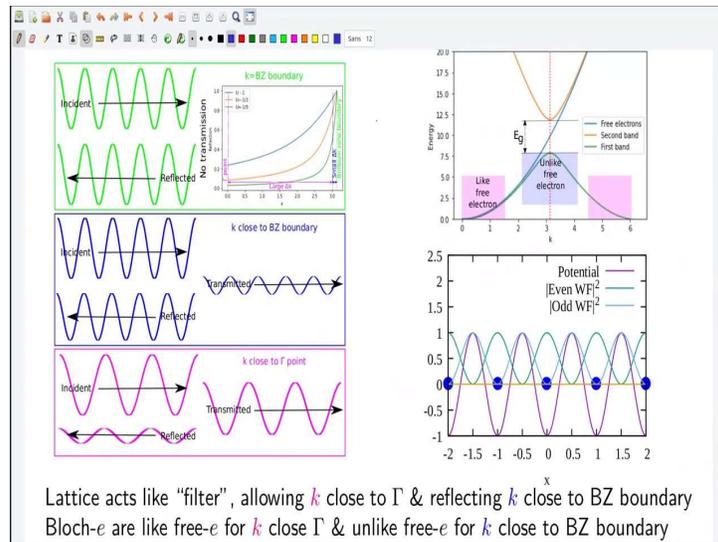


Let us try to understand what causes the reflection. In the left hand side I show the plot of reflection for different values of U . In the right hand side I show the Laue condition of diffraction and the blue shaded region is a black plane which is located at the Brillouin zone

boundary and a wave is reflected from the drag plane if allow a condition is satisfied. We know that block electron is reflected due to the periodic potential thus as U tends to zero reflection should decrease.

For example take some a point like k equal to 0.5 we see that reflection decreases with decreasing value of U . It is as expected except when K is equals to Brillouin zone boundary. Here we see 100% reflection irrespective of U value. Remember that black plane is located at the Brillouin zone boundary and allow a condition for diffraction is satisfied for electron with wave vector k which is equal to the Brillouin zone boundary. Thus the reflection that we observe is due to the reflection from the back plane.

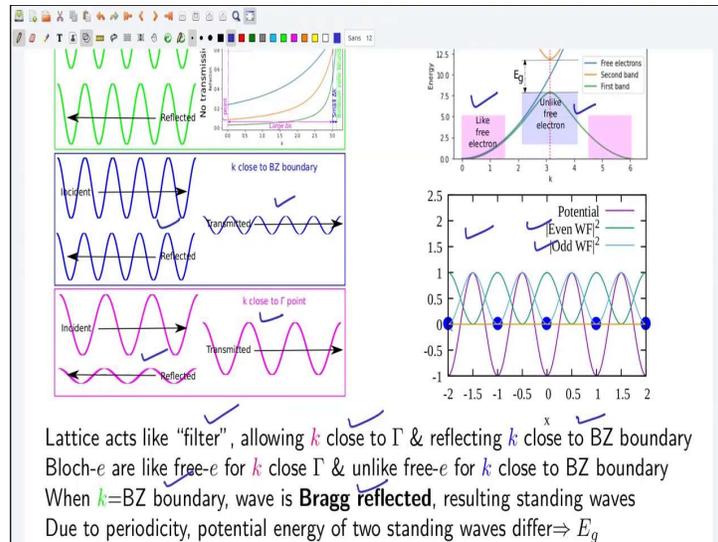
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Finally let me summarize our discussion on origin of band gap in a 1D lattice. We have seen that periodic potential reflects block electrons. How much of it is reflected depends on the wave vector. When the wave vector is closer to the Brillouin zone boundary more amount of wave is reflected and less amount is transmitted. On the other hand when the wave vector is closer to the gamma point more of it is transmitted and less of it is reflected.

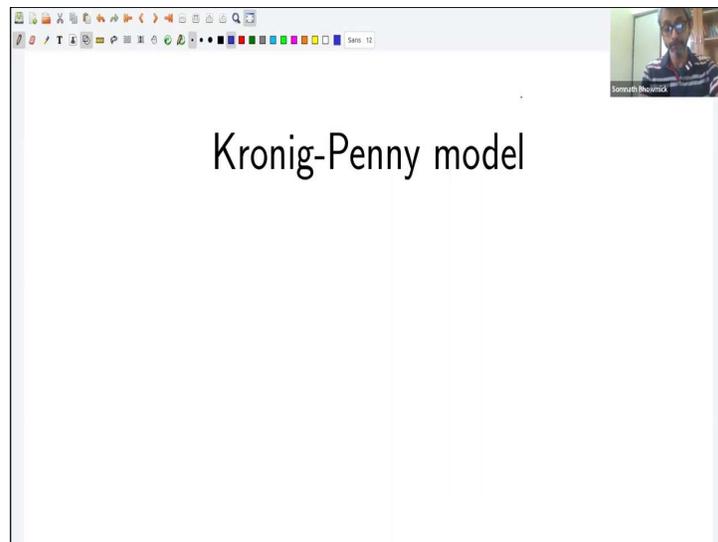
Thus the lattice acts like a filter allowing waves having K close to the gamma point to pass and reflecting waves with K close to the Brillouin zone boundary. Block electrons are like free electrons when K is close to the gamma point. Note that energy of the block electrons coincide with free electrons near the gamma point but differ significantly when K is near the Brillouin zone boundary.

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When k is exactly equal to the Brillouin zone boundary a condition for diffraction is satisfied and waves are Bragg reflected resulting two standing waves one given and another bond. As shown in the diagram probability density of the either and or wave function differ as a result potential energy of the two standing waves differ. This is what is manifested as a gap in the energy spectrum of the block electrons.

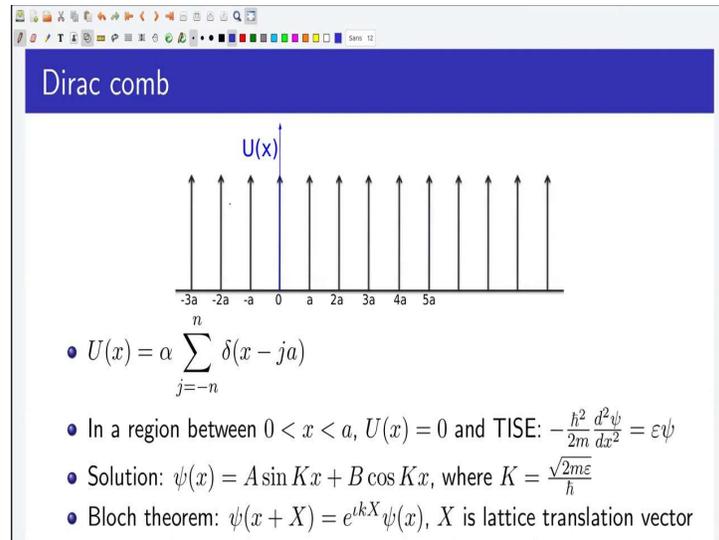
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Now let me discuss Kronig-Penny model this is an alternate way of proving that a periodic potential leads to band gaps in the energy spectrum. Mathematically Kronig-Penny model is very simple and it avoids many details like Fourier series expansion of the periodic potential Fourier series expansion of the wave function and converting time independent Schrodinger equation to a system of linear equations.

Despite its simplicity the model manages to capture the physics of the electrons in a periodic potential in an elegant manner.

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Let us approximate the periodic potential via Dirac comb. As shown in the figure Dirac comb is a Delta function potential at every lattice point. Mathematically it can be expressed in this form in a region between x equal to 0 and x equal to a potential is equals to 0 and the time independent Schrodinger equation is given by this which can be written as $d^2 \psi/dx^2 = -K^2 \psi$ where K^2 is equals to $2m\epsilon/h^2$.

Solution of time independent Schrodinger equation is $\psi(x)$ is equals to $A \sin Kx + B \cos Kx$ where K is given by this. Since we have a periodic potential we can apply Bloch theorem that is $\psi(x + X) = e^{ikX} \psi(x)$ where X is a lattice translation vector. In general X is equals to na where n is some integer. For example a lattice transition vector can be $-2a$ or $-a$ or a or $2a$ etcetera.

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- $U(x) = \alpha \sum_{j=-n}^n \delta(x - ja)$
- In a region between $0 < x < a$, $U(x) = 0$ and TISE: $-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} = \epsilon \psi$
- Solution: $\psi(x) = A \sin Kx + B \cos Kx$, where $K = \frac{\sqrt{2m\epsilon}}{\hbar}$
- Bloch theorem: $\psi(x + X) = e^{ikX} \psi(x)$, X is lattice translation vector
- Example: take $X = -a$, such that $\psi(x - a) = e^{-ika} \psi(x)$
- Substituting $x \rightarrow x + a$, we get: $\psi(x) = e^{-ika} \psi(x + a)$
- $\psi(x) = A \sin Kx + B \cos Kx$, when $0 < x < a$
- $\psi(x) = e^{-ika} [A \sin K(x + a) + B \cos K(x + a)]$, when $-a < x < 0$

Now take x is equals to $-a$ that is the lattice translation Vector is equals to $-a$. So, from Bloch theorem we get $\psi(x - a)$ is equals to e^{-ika} times $\psi(x)$. In this equation if we substitute x is equals to $x + a$ then we can write as $\psi(x)$ is equals to e^{-ika} times $\psi(x + a)$. Now when x is between 0 and a the wave function is $\psi(x)$ is equals to $A \sin Kx + B \cos Kx$. Similarly when x is between 0 and $-a$ the wave function $\psi(x)$ is given by this.

Note that small k in this equation is the wave vector of the block electron whereas capital K is related to the energy as shown here. We know that the wave function has to be continuous at x equal to 0 . How about the first derivative of the wave function we need to learn one small thing before we can answer this question.

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- TISE: $-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + U(x) \psi(x) = \epsilon \psi(x)$
- $-\frac{\hbar^2}{2m} \int_{-\epsilon}^{+\epsilon} \frac{d^2 \psi}{dx^2} dx + \int_{-\epsilon}^{+\epsilon} U(x) \psi(x) dx = \epsilon \int_{-\epsilon}^{+\epsilon} \psi(x) dx$
- $-\frac{\hbar^2}{2m} \left[\frac{d\psi}{dx} \Big|_{-\epsilon}^{+\epsilon} \right] + \alpha \int_{-\epsilon}^{+\epsilon} \delta(x) \psi(x) dx = \epsilon \int_{-\epsilon}^{+\epsilon} \psi(x) dx$
- $\lim_{\epsilon \rightarrow 0}, -\frac{\hbar^2}{2m} \Delta \left(\frac{d\psi}{dx} \right) = -\alpha \psi(0)$
- First derivative not continuous at $x = 0$: $\Delta \left(\frac{d\psi}{dx} \right) = \frac{2m\alpha}{\hbar^2} \psi(0)$

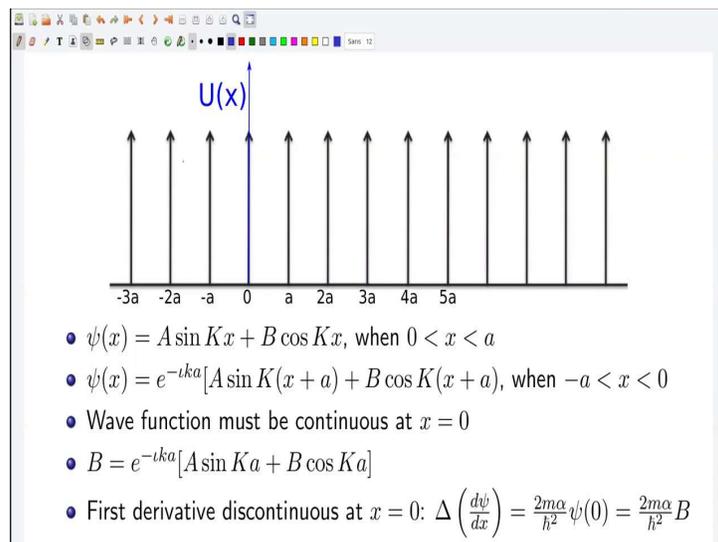
Let us consider a single Dirac Delta potential given by $U(x)$ is equal to α times Delta of x this is a single spike at x equal to 0 that is the potential has a spike of height α at x equal to 0 and the potential is 0 everywhere else. The independent Schrodinger equation is given by this. Now let us integrate the time independent Schrodinger equation $-\hbar^2 \frac{d^2 \psi}{dx^2} + U(x) \psi(x) = E \psi(x)$.

Now we said the upper and lower limit of the integral to $+\epsilon$ and $-\epsilon$, ϵ is some small number chosen arbitrarily. For example we can choose this as $-\epsilon$ and this as $+\epsilon$. Now let us calculate the integral $-\hbar^2 \frac{d^2 \psi}{dx^2}$ at x equal to $+\epsilon - \frac{d \psi}{dx}$ at x equal to $-\epsilon + \int_{-\epsilon}^{+\epsilon} U(x) \psi(x) dx$ and α is a constant.

So, we have $\alpha \int_{-\epsilon}^{+\epsilon} \delta(x) \psi(x) dx$ which is equal to energy times integral $-\epsilon$ to $+\epsilon$ $\psi(x) dx$. Now this integral involves some Delta function and this is equal to α times $\psi(0)$. Now we get limit ϵ going to 0 in that case the right hand side of the integral is equal to 0 and we get $-\hbar^2$ cross square by $2m$ and then this is the difference of the first derivative and this is equal to $-\alpha$ times $\psi(0)$.

Thus in the presence of a Dirac Delta potential the first derivative of the wave function is not continuous and the discontinuity is given by this.

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Now let us try to solve the actual Dirac comb problem. We have defined the wave function between x equal to 0 and x equal to a . Similarly we have defined the wave function between x equal to $-a$ and x equal to 0. We know that the wave function must be continuous at x equal to 0. So, putting x equal to 0 in the first equation we get b similarly putting x equal to 0 in the second equation we get this term.

Since we are dealing with delta function potentials first derivative is discontinuous at x equal to 0. and the discontinuity is equal to $2m\alpha$ by \hbar cross square times b . Let us calculate the discontinuity of the first derivative at x equal to 0.

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\bullet 1st derivative discontinuous at $x = 0$: $\Delta \left(\frac{d\psi}{dx} \right) = \frac{2m\alpha}{\hbar^2} B$

$\psi(x) = A \cos kx - B \sin kx$ — (1)

$\psi(x) = e^{-ika} [A \cos k(x+a) - B \sin k(x+a)]$ — (2)

$A \cos ka - e^{-ika} [A \cos ka - B \sin ka] = \frac{2m\alpha}{\hbar^2} B$

$\rightarrow k - e^{-ika} k \cos ka + \frac{B}{A} (e^{-ika} k \sin ka - \frac{2m\alpha}{\hbar^2}) = 0$ — (3)

$\frac{B}{A} = \frac{e^{-ika} \sin ka}{1 - e^{-ika} \cos ka} = \frac{\sin ka}{e^{ika} - \cos ka}$ — (4)

$k e^{ika} - k \cos ka - k \cos ka + e^{-ika} k \cos ka + e^{-ika} k \sin ka - \frac{2m\alpha}{\hbar^2} \sin ka = 0$

$k \frac{(e^{ika} + e^{-ika})}{2 \cos ka} = 2k \cos ka + \frac{2m\alpha \sin ka}{\hbar^2} \Rightarrow \cos ka = \cos ka + \frac{m\alpha \sin ka}{\hbar^2 k}$

So, this is the wave function when x is between 0 and a and this is the wave function when x is between 0 and $-a$ and we know that these two wave functions must be continuous at x equal to 0 and that gives us this equation. Now we want to calculate the discontinuity of the first derivative at x equal to 0 the first derivative is discontinuous because we are dealing with a delta function potential.

So, from the first equation we write the is equals to $A K \cos$ of $Kx - B K \sin$ of x from the second equation we write the first derivative to be equal to $e^{-ika} AK \cos$ of $Kx + a - BK \sin$ of $Kx + a$ at x equal to 0 the first equation is just A times k and the second equation is e^{-ika} times $AK \cos ka - BK \sin ka$. Now we have to subtract the first derivatives and they are equal to distance $2m\alpha$ divided by \hbar cross square times B .

Now if we divide it by A then we can just rewrite the equation as $K - e^{-ika} \cos ka + B e^{-ika} \sin ka - \frac{2m\alpha a}{\hbar^2} K = 0$. Now from this equation we can get the ratio of B by A which is equal to $e^{-ika} \sin ka$ divided by $1 - e^{-ika} \cos ka$ which can be written in a simpler form as $\sin ka$ divided by $e^{ika} - \cos ka$.

Now substituting the value of B by A in equation 3 from equation 4 we can write $K e^{-ika} \cos ka - k \cos ka + e^{-ika} k \cos^2 ka + e^{-ika} k \sin^2 ka - \frac{2m\alpha a}{\hbar^2} K = 0$. Now we can combine these three terms and write as $K e^{-ika} + e^{-ika} k$ and bring the rest of the terms to the right hand side such that $2k \cos ka = \frac{2m\alpha a}{\hbar^2} K + k$.

Now this term is equals to $2 \cos ka$ we bring k to the right hand side such that we can rewrite this equation as $\cos ka = \frac{m\alpha a}{\hbar^2 K} + \frac{k}{2}$. This is an important equation and I call it the governing equation for rest of our discussion. Note that there are two k's in the equation one small k in the left hand side and capital K in the right hand side.

Keep in mind that small k is the wave vector of block electrons allowed value of small k is given by the periodic boundary condition on the other hand capital K is related to the kinetic energy. In the next lecture I am going to plot this equation and show the existence of gap in energy Spectra of electrons in a periodic potential.