Handout 6

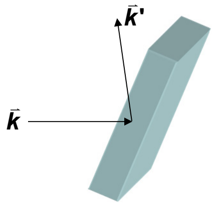
Electrons in Periodic Potentials

In this lecture you will learn:

- Bloch's theorem and Bloch functions
- Electron Bragg scattering and opening of bandgaps
- Free electron bands and zone folding
- Energy bands in 1D, 2D, and 3D lattices

The Reciprocal Lattice and X-Ray Diffraction

⇒ X-rays will scatter in only those directions for which:



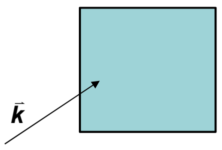
$$\vec{k}' = \vec{k} \pm \vec{G} \quad \text{and} \quad |\vec{k}'| = |\vec{k}|$$

$$\boxed{\pm \vec{k} \, . \, \vec{G} = \frac{|\vec{G}|^2}{2}}$$

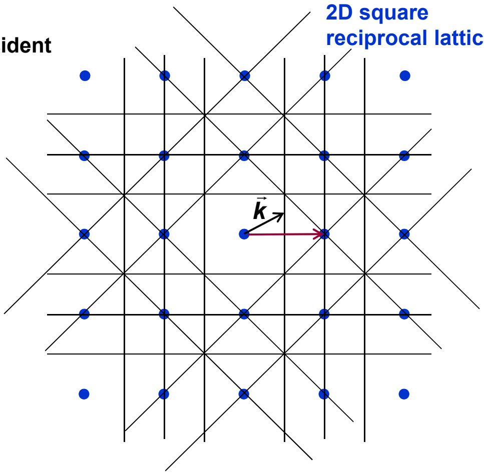
Bragg condition for X-ray scattering

X-Ray Diffraction and Bragg Planes

Consider x-rays with wavevector $\vec{k}$ incident on a crystal, as shown:



2D square reciprocal lattice



$$\vec{k}' = \vec{k} \pm \vec{G}$$

$$|\vec{k}'| = |\vec{k}|$$

What is $\vec{k}'$?

X-Ray Diffraction and Bragg Planes

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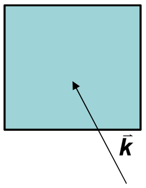

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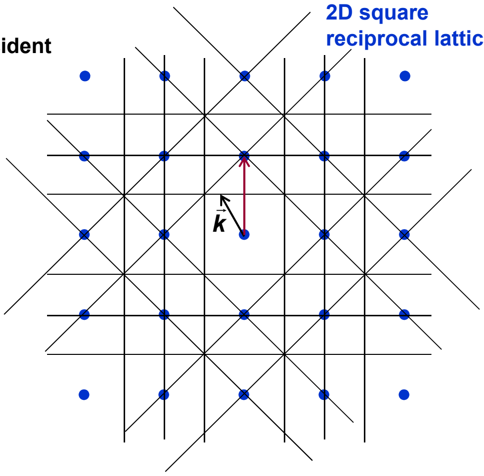

$$\vec{k}' = \vec{k} \pm \vec{G}$$

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X-Ray Diffraction and Bragg Planes

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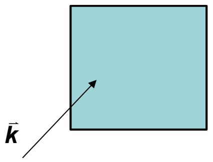
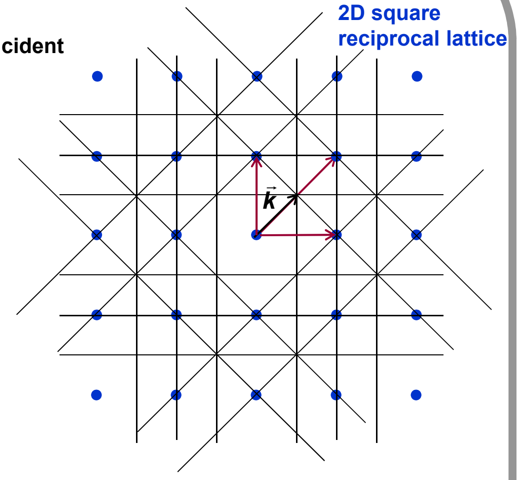




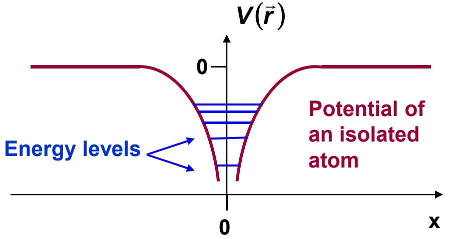
$$\vec{k}' = \vec{k} \pm \vec{G}$$

$$|\vec{k}'| = |\vec{k}|$$

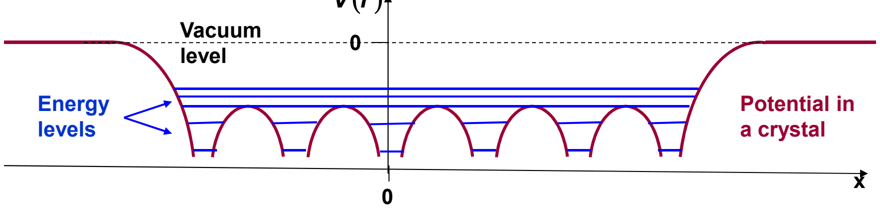
What is $\vec{k}'$?

Atomic Potentials in Crystals

The potential energy of an electron due to a single isolated atom looks like:



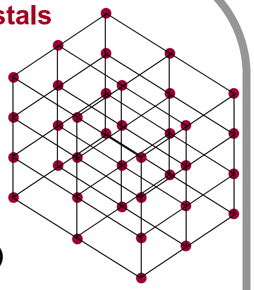
In a crystal, the potential energy due to all the atoms in the lattice looks like:



The lowest energy levels and wavefunctions of electrons remain unchanged when going from an isolated atom to a crystal

The higher energy levels (usually corresponding to the outermost atomic shell) get modified, and the corresponding wavefunctions are no longer localized at individual atoms but become spread over the entire crystal

Properties of Atomic Potentials in Crystals



- The atomic potential is lattice periodic (even for a lattice with a basis):

$$V(\vec{r}+\vec{R}) = V(\vec{r})$$

where $\vec{R}$ is any lattice vector

- Because the atomic potential is lattice periodic, it can be written as a convolution (assuming a lattice in "*d*" dimensions)

$$V(\vec{r}) = V_{\Omega}(\vec{r}) \otimes \sum_{j} \delta^{d}(\vec{r}-\vec{R}_j) \qquad \left\{ V_{\Omega}(\vec{r}) = \text{potential in one primitive cell} \right.$$

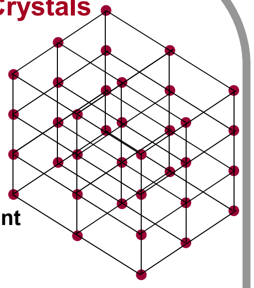
and expanded in a Fourier series of the type:

$$V(\vec{r}) = \sum_{j} \frac{V_{\Omega}(\vec{G}_j)}{\Omega_d} e^{i\,\vec{G}_j\,.\,\vec{r}} = \sum_{j} V(\vec{G}_j)\, e^{i\,\vec{G}_j\,.\,\vec{r}} \qquad \left\{ \text{Verify that: } V(\vec{r}+\vec{R}) = V(\vec{r}) \right.$$

where only the reciprocal lattice vectors appear in the exponential

⇒ The Fourier components of the periodic potential contain only the reciprocal lattice vectors

Properties of Electron Wavefunctions in Crystals



Electrons in a crystal satisfy the Schrodinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\,\psi(\vec{r})$$

Where:

$$V(\vec{r}+\vec{R}) = V(\vec{r})$$

Since the potential is periodic, and one lattice site is no different than any other lattice site, the solutions must satisfy:

$$|\psi(\vec{r}+\vec{R})|^2 = |\psi(\vec{r})|^2$$

This implies that the wavefunction at positions separated by a lattice vector can only differ by a phase factor:

$$\psi(\vec{r}+\vec{R}) = e^{i\,\theta(\vec{R})}\,\psi(\vec{r})$$

It follows that both the following relations must hold:

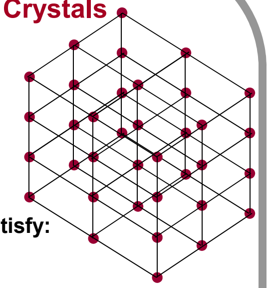
$$\psi(\vec{r}+\vec{R}+\vec{R}') = e^{i\,\theta(\vec{R})}\,\psi(\vec{r}+\vec{R}') = e^{i\,[\theta(\vec{R})+\theta(\vec{R}')]}\,\psi(\vec{r})$$

$$\psi(\vec{r}+\vec{R}+\vec{R}') = e^{i\,\theta(\vec{R}+\vec{R}')}\,\psi(\vec{r})$$

Which implies:

$$\theta(\vec{R}) + \theta(\vec{R}') = \theta(\vec{R}+\vec{R}')$$

Properties of Electron Wavefunctions in Crystals



The simplest, and the only way, that the relation:

$$\theta(\vec{R})+\theta(\vec{R}')=\theta(\vec{R}+\vec{R}')$$

can hold for all lattice vectors is if the phase is a linear scalar function of the vector $\vec{R}$:

$$\theta(\vec{R})=\vec{k}\,.\,\vec{R}$$

where $\vec{k}$ is some vector. It follows that our solutions must satisfy:

$$\psi(\vec{r}+\vec{R})=e^{i\,\vec{k}\,.\,\vec{R}}\,\psi(\vec{r})$$

Bloch's Theorem:

The above is one version of the so called **Bloch's theorem**, which says that associated with every solution of the Schrodinger equation in a periodic potential there is a wavevector $\vec{k}$ such that:

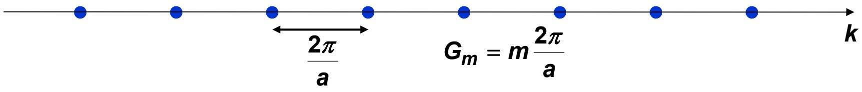
$$\psi(\vec{r}+\vec{R})=e^{i\,\vec{k}\,.\,\vec{R}}\,\psi(\vec{r})$$

Solutions of the Schrodinger equation for periodic potentials with the above property are called Bloch functions

Case Study: Electron in a 1D Periodic Potential

Consider the 1D Bravais lattice,

The position vector R_n of any lattice point is given by: $R_n = n\,a$
And the reciprocal lattice and reciprocal lattice vectors are:



$$G_m = m\frac{2\pi}{a}$$

Free Electron Approach:

We will suppose that the periodic atomic potential $V(x)$ is small, and that the electrons are essentially free, and we will treat the potential as a perturbation and see how it effects the free electrons. We have:

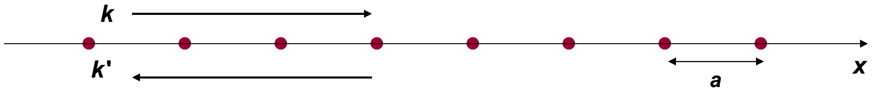
$$V(x+n\,a)=V(x)$$

Consequently, the Fourier series expansion of $V(x)$ will be:

$$V(x)=\sum_m V(G_m)\,e^{i\,G_m\,x} \qquad \text{where :}\;\; V(G_m)=\frac{V_\Omega(k=G_m)}{a}$$

Electron in a 1D Periodic Potential: Bragg Scattering

The key idea is that the electrons will Bragg scatter from the periodic atomic potentials just like X-rays:



For Bragg scattering, the difference between the final and initial wavevector must equal a reciprocal lattice vector:

$$\vec{k}'-\vec{k} = \pm\vec{G}_m$$

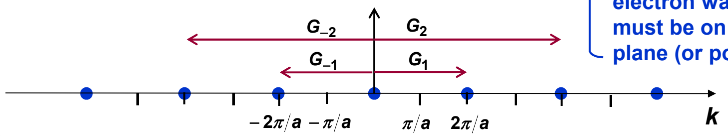
AND the final and initial electron energies must be equal:

$$\frac{\hbar^2|\vec{k}'|^2}{2m} = \frac{\hbar^2|\vec{k}|^2}{2m}$$

Both the above conditions are satisfied if:

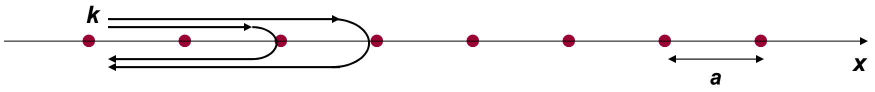
$$\vec{k}' = -\vec{k} \qquad \& \qquad \vec{k} = \pm\frac{\vec{G}_m}{2}$$

The initial electron wavevector must be one-half of a reciprocal lattice vector OR the initial electron wavevector must be on a Bragg plane (or point in 1D)



Electron in a 1D Periodic Potential: Bragg Scattering

The Bragg condition can also be thought in terms of interference of waves in scattering:



Consider an electron with wavevector $\vec{k}$. The electron will "Bragg scatter" from the atoms if the electron wave, with wavelength λ, reflecting off successive atoms adds in phase in the backward direction

This condition gives:

$$2\,a = m\,\lambda$$

$$\Rightarrow 2\frac{2\pi}{\lambda}a = 2\pi\,m$$

$$\Rightarrow 2\,|\vec{k}| = m\frac{2\pi}{a} = G_m$$

$$\Rightarrow |\vec{k}| = \frac{G_m}{2}$$

$$\Rightarrow \vec{k} = \pm\frac{\vec{G}_m}{2}$$

Perturbation Theory: A Review

Consider a Hamiltonian with eigenfunctions and energies given by:

$$\hat{H}_o|\phi_n\rangle = e_n|\phi_n\rangle$$

In the presence of a perturbing potential, the new eigenfunctions and energies are given by:

$$\left(\hat{H}_o + \hat{V}\right)|\psi_n\rangle = E_n|\psi_n\rangle$$

If the perturbation is small, then the new eigenfunctions are slightly perturbed from the original eigenfunctions and, to first order in the perturbation, can be written as:

$$|\psi_n\rangle \approx |\phi_n\rangle + \sum_{m\neq n} \frac{\langle\phi_m|\hat{V}|\phi_n\rangle}{e_n - e_m}|\phi_m\rangle + \text{higher order terms}$$

Thus, the perturbation "mixes" the eigenfunctions of the original Hamiltonian to generate the eigenfunction of the new Hamiltonian.

Note: The effect of the perturbation is not small, and the perturbation theory breaks down, if for:

$$\langle\phi_m|\hat{V}|\phi_n\rangle \neq 0$$

we have:

$$e_n - e_m \approx 0$$

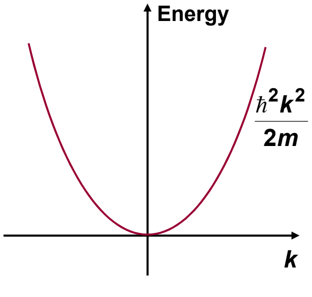
Electron in a 1D Periodic Potential: Perturbation Theory

The goal here is to treat the periodic potential as a perturbation to the free electron Hamiltonian. So in the absence of the perturbation we have the free electron case:

$$\hat{H}_o = \frac{\hat{P}^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \quad \Rightarrow \quad \phi_k(x) = \sqrt{\frac{1}{L}}\, e^{i\,k\,x} \qquad e(k) = \frac{\hbar^2 k^2}{2m}$$

$$\hat{H}_o|\phi_k\rangle = e(k)\,|\phi_k\rangle$$

The energy dispersion relation of free electrons is parabolic, as shown in the figure



Now assume that the perturbation is the periodic potential of the atoms:

$$V(x)$$

which can also be expressed in a Fourier series as:

$$V(x) = \sum_m V(G_m)\; e^{i\,G_m\,x} \qquad \text{where: } V(G_m) = \frac{V_\Omega(k = G_m)}{a}$$

Electron in a 1D Periodic Potential: Perturbation Theory

So we try perturbation theory and write:

$$\left(\hat{H}_o + \hat{V}(x)\right)|\psi_k\rangle = E(k)|\psi_k\rangle$$

And write the new eigenfunction as:

$$|\psi_k\rangle \approx |\phi_k\rangle + \sum_{k'} \frac{\langle\phi_{k'}|\hat{V}|\phi_k\rangle}{e(k)-e(k')}|\phi_{k'}\rangle + \text{higher order terms}$$

First evaluate the potential matrix element (*L* is the size of the entire 1D crystal):

$$\begin{aligned}\langle\phi_{k'}|\hat{V}|\phi_k\rangle &= \int_{-L/2}^{L/2} dx \sqrt{\frac{1}{L}}\, e^{-i k' x}\, V(x)\, \sqrt{\frac{1}{L}}\, e^{i k x} \\ &= \frac{1}{L}\sum_m V(G_m) \int_{-L/2}^{L/2} dx\, e^{-i k' x}\, e^{i G_m x}\, e^{i k x} \\ &= \sum_m V(G_m)\, \delta_{k'-k,\,G_m} = 0 \quad \text{unless} \quad k' = k + G_m\end{aligned}$$

Electron in a 1D Periodic Potential: Perturbation Theory

The new eigenfunction is:

$$\begin{aligned}|\psi_k\rangle &\approx |\phi_k\rangle + \sum_{k'} \frac{\langle\phi_{k'}|\hat{V}|\phi_k\rangle}{e(k)-e(k')}|\phi_{k'}\rangle + \text{higher order terms} \\ &= |\phi_k\rangle + \sum_m \frac{V(G_m)}{e(k)-e(k+G_m)}|\phi_{k+G_m}\rangle + \text{higher order terms}\end{aligned}$$

$$\left\{ \begin{aligned}&\langle\phi_{k'}|\hat{V}|\phi_k\rangle \\ &= \sum_m V(G_m)\,\delta_{k'-k,\,G_m}\end{aligned} \right.$$

⇒ The new eigenfunction corresponding to the wavevector *k* consists of a superposition of only those plane waves whose wavevectors differ from *k* by reciprocal lattice vectors

The effects of the periodic perturbation will be large for those electron states for which the denominator is zero or is close to zero:

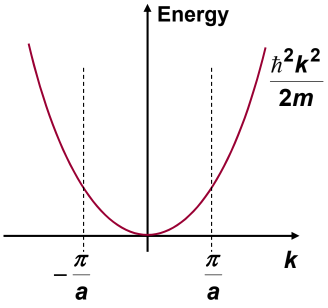
$$e(k) - e(k+G_m) \approx 0 \longrightarrow \left\{ \text{and} \quad V(G_m) \neq 0 \right.$$

$$\Rightarrow -\frac{\hbar^2}{2m}\left(G_m^2 + 2kG_m\right) \approx 0$$

$$\Rightarrow k \approx -\frac{G_m}{2} = -m\frac{\pi}{a} \longrightarrow \left\{ \text{Bragg condition} \right.$$

⇒ Perturbation theory breaks down for those electron states that Bragg scatter from the periodic potential!

Electron in a 1D Periodic Potential: Variational Solution



We consider a periodic atomic potential of the form:

$$V(x) = V(G_1)\, e^{i G_1 x} + V(G_{-1})\, e^{i G_{-1} x}$$

$$G_1 = \frac{2\pi}{a} \qquad G_{-1} = -\frac{2\pi}{a} = -G_1$$

Since the potential is always real: $V(G_{-1}) = V^*(G_1)$

The potential will strongly couple plane wave eigenstates with wavevectors that differ by $\pm G_1$ and the strongest coupling will be between states with wavevectors,

$$\frac{\pi}{a}, -\frac{\pi}{a} = \frac{G_1}{2}, \frac{G_{-1}}{2}$$

because they have equal energy

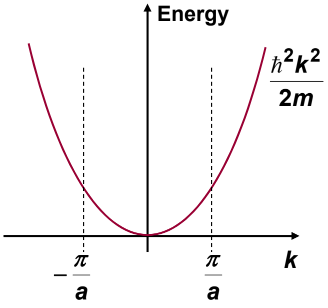
Variational Solution (Finite Basis Expansion):

For states with wavevectors k near $+\pi/a$, we assume a variational solution for the perturbed state:

$$|\psi_k\rangle \approx c(k)\,|\phi_k\rangle + c(k+G_{-1})\,|\phi_{k+G_{-1}}\rangle$$

Or: $$\psi_k(x) \approx c(k)\sqrt{\frac{1}{L}}\, e^{i k x} + c(k+G_{-1})\sqrt{\frac{1}{L}}\, e^{i (k+G_{-1}) x}$$

Electron in a 1D Periodic Potential: Variational Solution



$$|\psi_k\rangle \approx c(k)\,|\phi_k\rangle + c(k+G_{-1})\,|\phi_{k+G_{-1}}\rangle$$

Plug it into the Schrodinger equation:

$$\left(\hat{H}_o + V(x)\right)|\psi_k\rangle = E(k)|\psi_k\rangle$$

And then take the bra with $\langle\phi_k|$ and then with $\langle\phi_{k+G_{-1}}|$ to get the matrix eigenvalue equation:

$$\begin{bmatrix} e(k) & V(G_1) \\ V(G_{-1}) & e(k+G_{-1}) \end{bmatrix}\begin{bmatrix} c(k) \\ c(k+G_{-1}) \end{bmatrix} = E(k)\begin{bmatrix} c(k) \\ c(k+G_{-1}) \end{bmatrix}$$

Solution for the energy eigenvalue is:

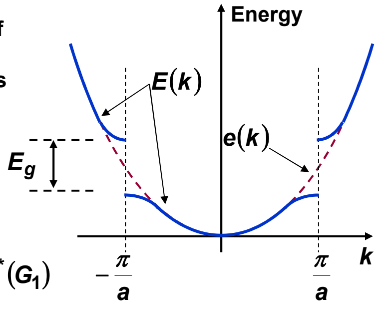
$$E(k) = \frac{e(k)+e(k+G_{-1})}{2} \pm \sqrt{\left(\frac{e(k)-e(k+G_{-1})}{2}\right)^2 + |V(G_{-1})|^2} \quad \Big\{ \text{ for } k \text{ near } +\pi/a$$

Now, in a similar way, had we started off by trying to find a solution for k near –π/a we would have obtained:

$$E(k) = \frac{e(k)+e(k+G_1)}{2} \pm \sqrt{\left(\frac{e(k)-e(k+G_1)}{2}\right)^2 + |V(G_1)|^2} \quad \Big\{ \text{ for } k \text{ near } -\pi/a$$

Electron in a 1D Periodic Potential: Variational Solution

The obtained solutions *E*(*k*) are plotted on top of the free electron energy dispersion *e*(*k*) so that you can see the difference. An energy gap opens up!



$$\boxed{E_g = 2|V(G_1)| = 2|V(G_{-1})|}$$

$$V(x) = V(G_1)\,e^{i\,G_1\,x} + V(G_{-1})\,e^{i\,G_{-1}\,x}$$

$$G_1 = \frac{2\pi}{a} \qquad G_{-1} = -\frac{2\pi}{a} = -G_1 \qquad V(G_{-1}) = V^*(G_1)$$

$$E(k) = \frac{e(k)+e(k+G_{-1})}{2} \pm \sqrt{\left(\frac{e(k)-e(k+G_{-1})}{2}\right)^2 + |V(G_{-1})|^2} \quad \Big\{ \text{ for } k \text{ near } +\pi/a$$

$$E(k) = \frac{e(k)+e(k+G_1)}{2} \pm \sqrt{\left(\frac{e(k)-e(k+G_1)}{2}\right)^2 + |V(G_1)|^2} \quad \Big\{ \text{ for } k \text{ near } -\pi/a$$

Electron in a 1D Periodic Potential: Variational Solution

Lets find the wavefunctions for k=π/a

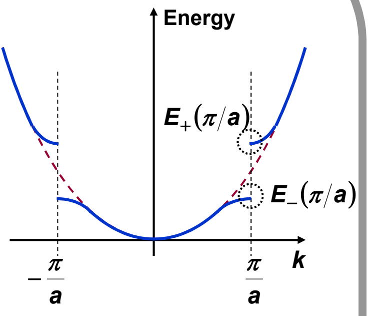
The matrix equation becomes:

$$\begin{bmatrix} e(\pi/a) & V(G_1) \\ V(G_{-1}) & e(-\pi/a) \end{bmatrix} \begin{bmatrix} c(\pi/a) \\ c(-\pi/a) \end{bmatrix} = E(\pi/a) \begin{bmatrix} c(\pi/a) \\ c(-\pi/a) \end{bmatrix}$$

The two solutions for *V*(*G*$_1$) real are:

$$E_\pm(\pi/a) = e(\pi/a) \pm V(G_1)$$

$$\begin{bmatrix} c(\pi/a) \\ c(-\pi/a) \end{bmatrix}_+ = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 1 \end{bmatrix} \qquad \begin{bmatrix} c(\pi/a) \\ c(-\pi/a) \end{bmatrix}_- = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix}$$



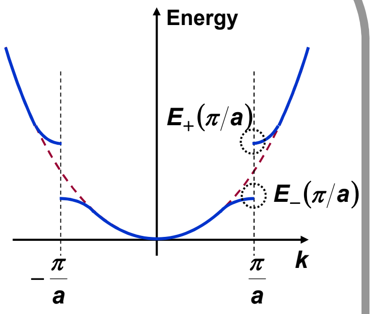
$$\Rightarrow |\psi_{\pi/a}\rangle \approx c(\pi/a)\,|\phi_{\pi/a}\rangle + c(-\pi/a)\,|\phi_{-\pi/a}\rangle$$

$$\Rightarrow \psi_{\pi/a}(x) \approx \sqrt{\frac{1}{2L}}\left(e^{i\frac{\pi}{a}x} \pm e^{-i\frac{\pi}{a}x}\right) = \begin{cases} \sqrt{\frac{2}{L}}\cos\left(\frac{\pi}{a}x\right) \\ i\sqrt{\frac{2}{L}}\sin\left(\frac{\pi}{a}x\right) \end{cases}$$

Electron in a 1D Periodic Potential: Origin of the Bandgaps

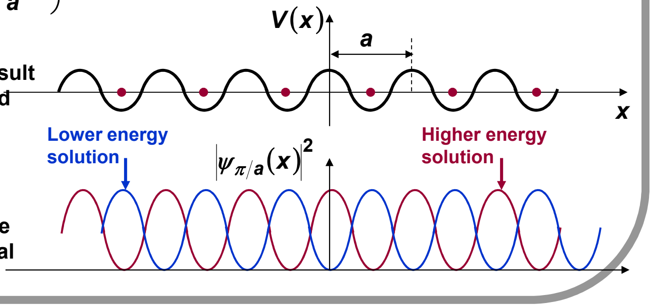
We have: $E_{\pm}(\pi/a) = e(\pi/a) \pm V(G_1)$

$$\psi_{\pi/a}(x) \approx \sqrt{\frac{1}{2L}}\left(e^{i\frac{\pi}{a}x} \pm e^{-i\frac{\pi}{a}x}\right) = \begin{cases} \sqrt{\frac{2}{L}}\cos\left(\frac{\pi}{a}x\right) \\ i\sqrt{\frac{2}{L}}\sin\left(\frac{\pi}{a}x\right) \end{cases}$$



Note that (for $V(G_1)$ real):

$$V(x) = V(G_1)\,e^{i\,G_1\,x} + V(G_{-1})\,e^{i\,G_{-1}\,x}$$
$$= 2\,V(G_1)\cos\left(\frac{2\pi}{a}x\right)$$



- The solutions are standing waves (as a result of forward and backward Bragg scattering)
- The higher energy solution has larger probability density in the region of higher potential

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Electron in a 1D Periodic Potential: Summary

Summary of Findings:

- For a perturbative periodic potential with the following Fourier Series representation,

$$V(x) = V(G_1)\,e^{i\,G_1\,x} + V(G_{-1})\,e^{i\,G_{-1}\,x}$$

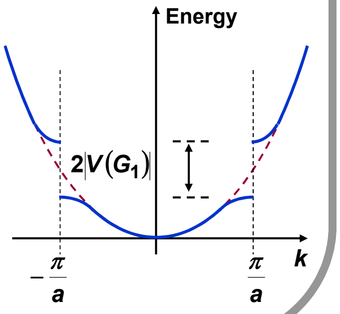
the plane wave eigenfunctions of the free electron with wavevector k get coupled with the wavevectors $(k+G_1)$ and $(k+G_{-1})$ as a result of the fact that the potential had wavevectors G_1 and G_{-1} in its Fourier series.

$$G_1 = \frac{2\pi}{a}$$
$$G_{-1} = -\frac{2\pi}{a} = -G_1$$

- If the electron wavevector k is such that $e(k)$ and $e(k+G_1)$ have the same energy, or if $e(k)$ and $e(k+G_{-1})$ have the same energy, then a bandgap of magnitude $2|V(G_1)|$ will open up in the free electron dispersion for the wavevector value k

$$e(k) = e(k+G_1) \qquad e(k) = e(k+G_{-1})$$
$$\Rightarrow k = -\frac{G_1}{2} \qquad \Rightarrow k = -\frac{G_{-1}}{2}$$

Bandgap will open for these values of k



Electron in a 1D Periodic Potential: More General Case

Now suppose the potential looks like:

$$V(x) = V(G_1)\,e^{i G_1 x} + V(G_{-1})\,e^{i G_{-1} x} + V(G_2)\,e^{i G_2 x} + V(G_{-2})\,e^{i G_{-2} x}$$

Bandgaps will open at these k-points:

(1) $e(k) = e(k + G_{-1})$

$$\Rightarrow k = -\frac{G_{-1}}{2} = \frac{\pi}{a}$$

(2) $e(k) = e(k + G_1)$

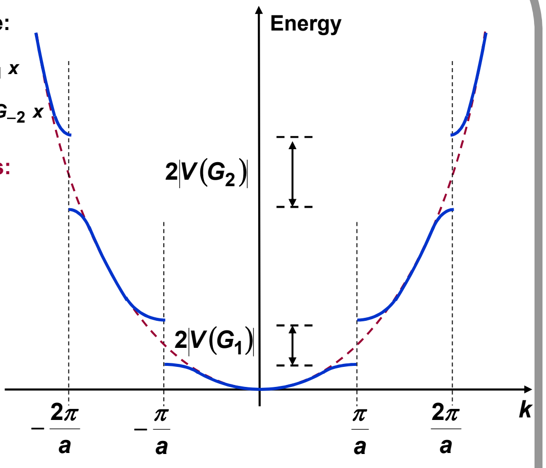
$$\Rightarrow k = -\frac{G_1}{2} = -\frac{\pi}{a}$$

(3) $e(k) = e(k + G_{-2})$

$$\Rightarrow k = -\frac{G_{-2}}{2} = \frac{2\pi}{a}$$

(4) $e(k) = e(k + G_2)$

$$\Rightarrow k = -\frac{G_2}{2} = -\frac{2\pi}{a}$$



$$G_1 = \frac{2\pi}{a} \qquad G_{-1} = -\frac{2\pi}{a} = -G_1$$

$$G_2 = \frac{4\pi}{a} \qquad G_{-2} = -\frac{4\pi}{a} = -G_2$$

Bandgaps and Bragg Planes

Bandgaps will open at these k-points:

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$$\Rightarrow k = -\frac{G_{-1}}{2} = \frac{\pi}{a}$$

(2) $e(k) = e(k + G_1)$

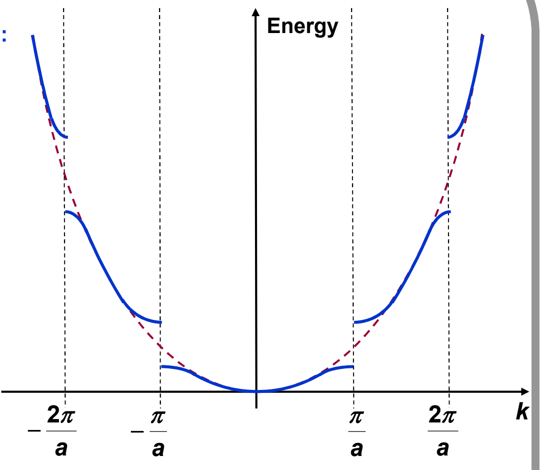
$$\Rightarrow k = -\frac{G_1}{2} = -\frac{\pi}{a}$$

(3) $e(k) = e(k + G_{-2})$

$$\Rightarrow k = -\frac{G_{-2}}{2} = \frac{2\pi}{a}$$

(4) $e(k) = e(k + G_2)$

$$\Rightarrow k = -\frac{G_2}{2} = -\frac{2\pi}{a}$$



Bandgaps open at Bragg points (1D), lines (2D), planes (3D) in the reciprocal space. Recall that a wavevector is on a Bragg point (1D), line (2D), plane (3D) if the following condition holds:

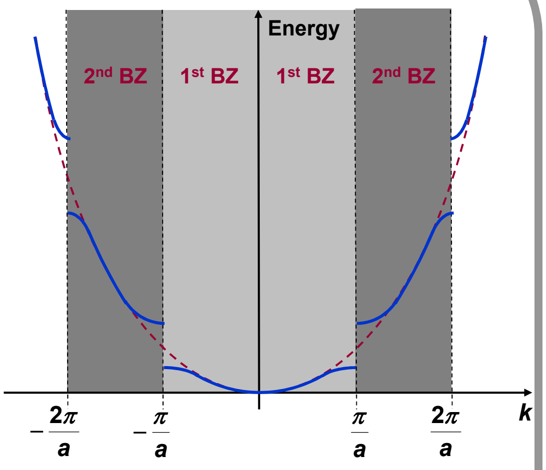
$$\vec{k}\,.\,\vec{G} = \pm\frac{|\vec{G}|^2}{2} \qquad \text{and for 1D it becomes:} \qquad k = \pm\frac{G_m}{2}$$

Bandgaps and Brillouin Zone Boundaries

Some very important observations:

- Bandgaps open at Bragg points (1D), lines (2D), planes (3D) in the reciprocal space.
- The Bragg points (1D), lines (2D), planes (3D) define the boundary between Brillouin zones

⇒ Bandgaps open at the Brillouin zone boundaries



The Restricted k-Space Convention and Energy Bands

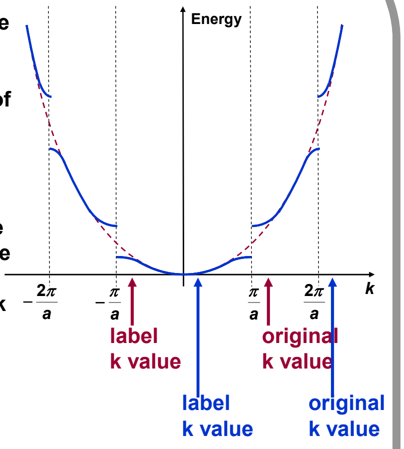
Consider any value of the wavevector outside the FBZ, as shown

The unperturbed solution would be plane wave of wavevector ***k***:

$$\phi_k(x) = \sqrt{\frac{1}{L}}\, e^{i\,k\,x}$$

The periodic potential perturbation would couple this plane wave state with all other states that are separated from it in k-space by reciprocal lattice vectors. Therefore the actual solution would look something like:

$$\psi_k(x) = \sum_m c(k+G_m)\sqrt{\frac{1}{L}}\, e^{i\,(k+G_m)\,x}$$



The above is a superposition of plane waves with wavevectors that differ from the unperturbed wavevector by reciprocal lattice vectors

The convention is to label the actual solutions $\psi_k(x)$ not by the k-value of the unperturbed wavefunction but by that wavevector in the superposition solution that falls in the FBZ, as shown

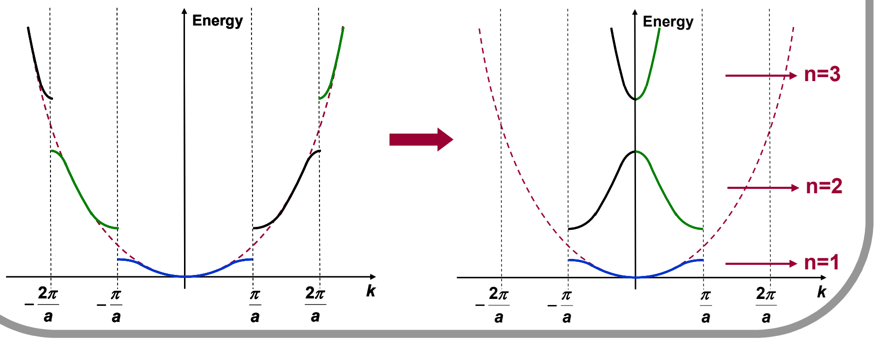
The Restricted k-Space Convention and Energy Bands

In the actual solution: $\psi_k(x) = \sum_m c(k+G_m)\sqrt{\frac{1}{L}}\, e^{i(k+G_m)x}$

The k-value used for labeling is always understood to be in the first BZ

Consequently, the energy-vs-k dispersion relation is always drawn only for the first BZ by translating the energy-vs-k curves lying in higher BZs to the the first BZ by appropriate reciprocal lattice vectors, as shown below:

The resulting different "bands" of energy in the first BZ are called "energy bands" and are labeled as *n*=1,2,3,….



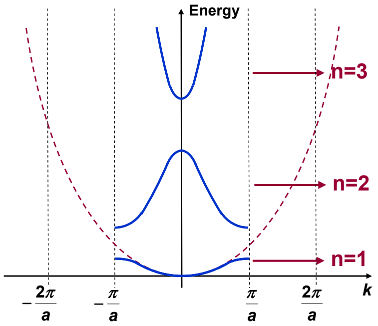
The Restricted k-Space Convention and Energy Bands

Since now we have multiple energy values for the same k-label, we use an additional label "*n*" to indicate the energy band. The final solutions and energy values are then written as follows:

$$\psi_{n,k}(x) \quad \text{and} \quad E_n(k)$$

where k-value is understood to be in the first BZ. And the solution can be expanded as:

$$\psi_{n,k}(x) = \sum_m c_n(k+G_m)\sqrt{\frac{1}{L}}\, e^{i(k+G_m)x}$$



Bloch's theorem check:

We know that solutions of the Schrodinger equation in periodic potentials (Bloch functions) need to satisfy the Bloch's theorem:

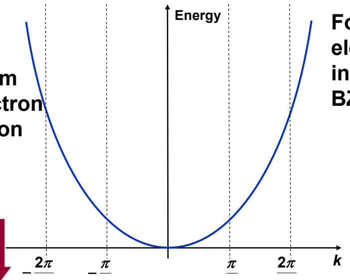
$$\psi(\vec{r}+\vec{R}) = e^{i\,\vec{k}\,.\,\vec{R}}\,\psi(\vec{r})$$

$$\psi_{n,k}(x+R) = \sum_m c_n(k+G_m)\sqrt{\frac{1}{L}}\, e^{i(k+G_m)(x+R)} = e^{i\,k\,R}\sum_m c_n(k+G_m)\sqrt{\frac{1}{L}}\, e^{i(k+G_m)x}$$
$$= e^{i\,k\,R}\psi_{n,k}(x)$$

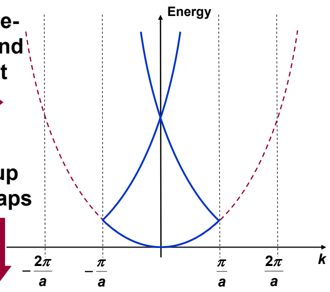
From Free Electron Dispersion to Energy Bands – 1D

One can always get an approximate idea of how the bands will look:

Start from free electron dispersion

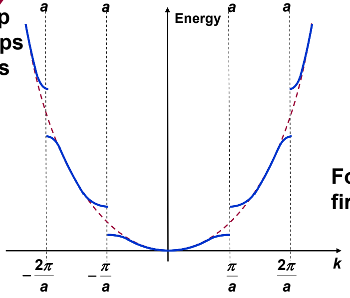


Fold the free-electron band into the first BZ

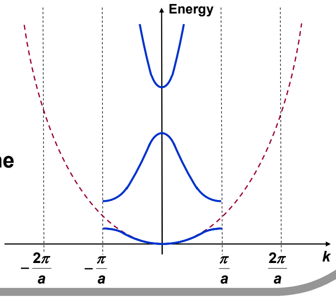


Open up bandgaps

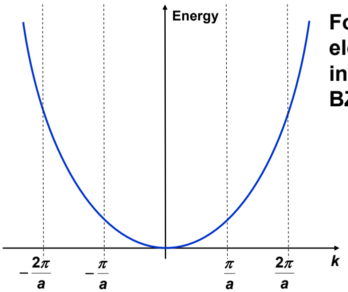
Open up bandgaps at edges of BZs



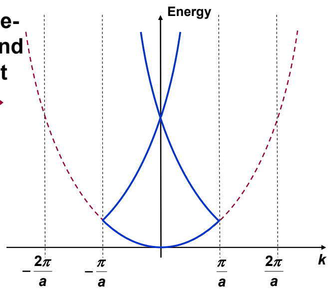
Fold into the first BZ

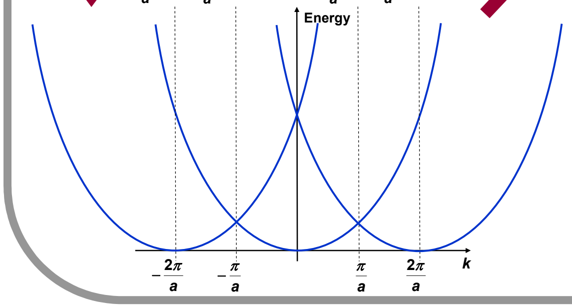


From Free Electron Dispersion to Energy Bands: Zone Folding



Fold the free-electron band into the first BZ





An easy trick to construct the free electron bands folded into the first BZ is to assume that a replica of the free electron band is sitting at each reciprocal lattice point

Generalization to Higher Dimensions - I

Consider a 2D or a 3D crystal with the periodic potential given as:

$$V(\vec{r}) = \sum_j V(\vec{G}_j)\, e^{i\,\vec{G}_j\,.\,\vec{r}}$$

- The potential will couple the free-electron state with wavevector $\vec{k}$ to all other states with wavevectors $\vec{k}+\vec{G}_j$
- The strongest coupling will be with states whose energy $\frac{\hbar^2|\vec{k}+\vec{G}_j|^2}{2m}$ equals $\frac{\hbar^2|\vec{k}|^2}{2m}$
- Therefore, strong coupling will occur if the wavevector $\vec{k}$ satisfies:

$$\frac{\hbar^2|\vec{k}+\vec{G}_j|^2}{2m} = \frac{\hbar^2|\vec{k}|^2}{2m}$$

$$\Rightarrow 2\vec{G}_j.\vec{k} + |\vec{G}_j|^2 = 0$$

$$\Rightarrow \vec{k}.\vec{G}_j = -\frac{|\vec{G}_j|^2}{2}$$

- Since, the reciprocal lattice vector $\vec{G}_j$ is arbitrary, one can also write the above condition as:

$$\vec{k}\,.\,\vec{G} = \pm\frac{|\vec{G}|^2}{2} \longrightarrow \Big\{$$

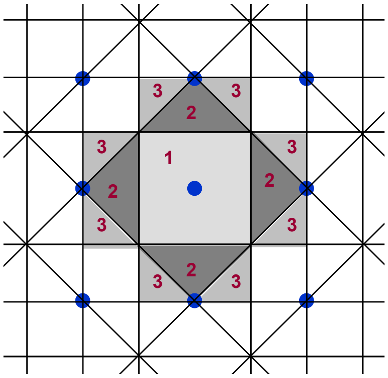
Bragg condition

Generalization to Higher Dimensions - II

In a 1D lattice, bandgaps opened up at k-values at the Bragg points (edges of BZs):

1D reciprocal lattice

2D square reciprocal lattice



Same thing happens in higher dimensions: bandgaps open up for wavevectors that lie on the Bragg lines (2D), planes (3D).

- Recall that a wavevector will like on a Bragg line/plane if it satisfies:

$$\vec{k}\,.\,\vec{G} = \pm\frac{|\vec{G}|^2}{2}$$

for some reciprocal lattice vector $\vec{G}$

- Bragg lines/planes in k-space are perpendicular bisectors of some reciprocal lattice vector

Generalization to Higher Dimensions - III

- Bandgaps will open up at the edges of the Brillouin zones

- Wavevector is restricted to the first BZ, and electron energy-vs-k dispersion curves in higher BZs can be translated by appropriate reciprocal lattice vectors to be in the first BZ to obtain energy bands

- Electron energies and solutions are written as:

$$\psi_{n,\vec{k}}(\vec{r}) \qquad \text{and} \qquad E_n(\vec{k})$$

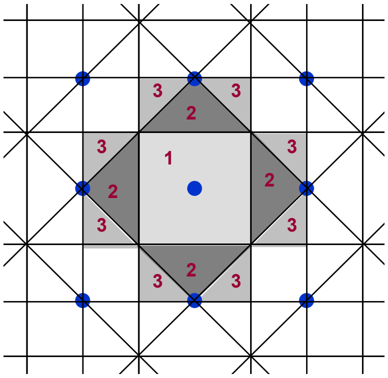
- The solutions satisfy the Bloch's theorem:

$$\psi(\vec{r}+\vec{R}) = e^{i\,\vec{k}\,.\,\vec{R}}\,\psi(\vec{r})$$

and can be written as a superposition of plane waves, as shown below for 3D:

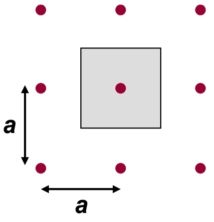
$$\psi_{n,\vec{k}}(\vec{r}) = \sum_j c_n(\vec{k}+\vec{G}_j)\sqrt{\frac{1}{V}}\,e^{i(\vec{k}+\vec{G}_j).\vec{r}}$$

2D square reciprocal lattice



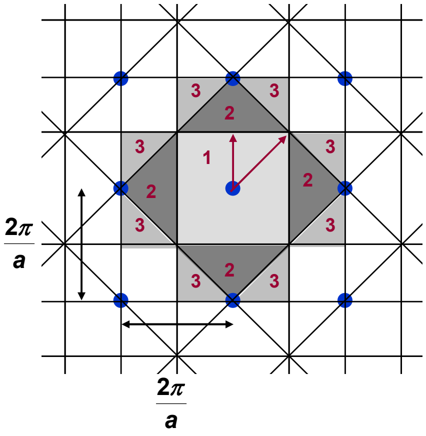
Energy Bands of a 2D Square Lattice - I

2D square direct lattice



Question: How to draw the free electron bands?

Answer: Assume a free electron band sitting at each reciprocal lattice point and then consider its contribution to the bands in the first BZ

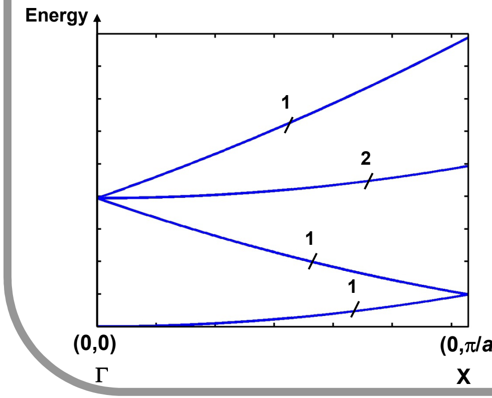


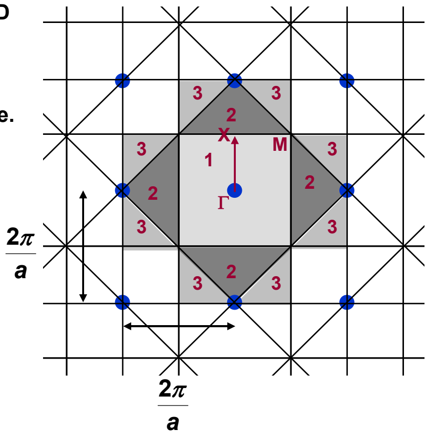
Reciprocal lattice

$$\vec{G} = m\frac{2\pi}{a}\hat{x} + n\frac{2\pi}{a}\hat{y}$$

Energy Bands of a 2D Square Lattice - II

- It is obviously difficult to draw bands for 2D or 3D lattices
- The bands are usually drawn along some specific high-symmetry directions in k-space. The figure below shows the bands from Γ to the X point (the numbers indicate the degeneracy of each energy band)

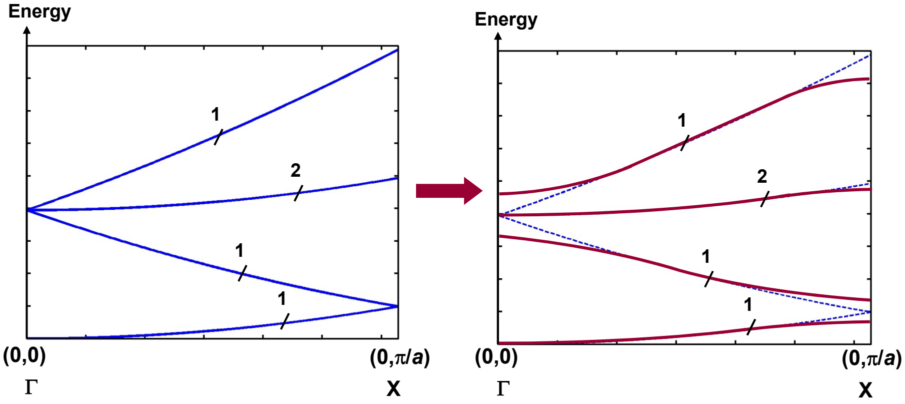




Reciprocal lattice

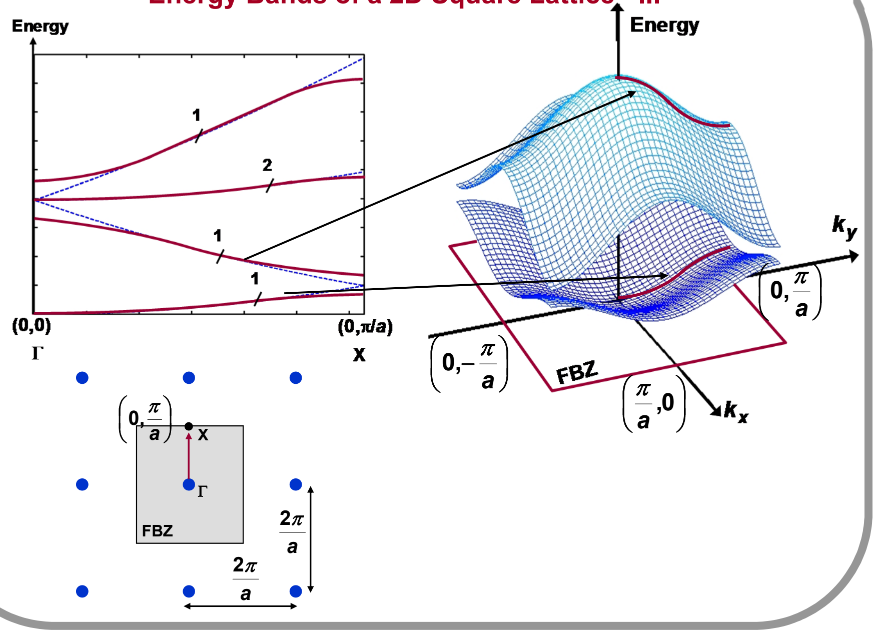
$$\vec{G} = m\frac{2\pi}{a}\hat{x} + n\frac{2\pi}{a}\hat{y}$$

Energy Bands of a 2D Square Lattice - II



- Once the free electron energy bands have been drawn in the first BZ then the locations where bandgaps are likely to be opened are identified
- A rough sketch of the actual bands can then be made, as shown above

Energy Bands of a 2D Square Lattice - III



Appendix: Obtaining the 2x2 Matrix Equation (On Slide 14)

Remember the matrix element of the periodic potential between the plane wave states:

$$\langle \phi_{k'} | \hat{V} | \phi_k \rangle = \sum_m V(G_m)\ \delta_{k'-k\,,\,G_m}$$

Trial solution for values of *k* near G_1:

$$|\psi_k\rangle \approx c(k)\,|\phi_k\rangle + c(k+G_{-1})\,|\phi_{k+G_{-1}}\rangle$$

Plug it into the Schrodinger equation:

$$\left(\hat{H}_o + V(x)\right)|\psi_k\rangle = E(k)|\psi_k\rangle$$

And then take the bra with $\langle\phi_k|$ to get:

$$\langle\phi_k|\left(\hat{H}_o + \hat{V}(x)\right)|\psi_k\rangle = E(k)\langle\phi_k|\psi_k\rangle$$

$$\Rightarrow \langle\phi_k|\left(\hat{H}_o + \hat{V}(x)\right)\left[c(k)|\phi_k\rangle + c(k+G_{-1})|\phi_{k+G_{-1}}\rangle\right]$$

$$= E(k)\langle\phi_k|\left[c(k)|\phi_k\rangle + c(k+G_{-1})|\phi_{k+G_{-1}}\rangle\right]$$

$$\Rightarrow e(k)\,c(k) + \langle\phi_k|\hat{V}(x)|\phi_{k+G_{-1}}\rangle\, c(k+G_{-1}) = E(k)\,c(k)$$

$$\Rightarrow e(k)\,c(k) + V(G_1)\,c(k+G_{-1}) = E(k)\,c(k)$$ ← **First result**

Appendix: Obtaining the 2x2 Matrix Equation

$$\left|\psi_k\right\rangle \approx c(k)\left|\phi_k\right\rangle + c(k+G_{-1})\left|\phi_{k+G_{-1}}\right\rangle$$

Plug it into the Schrodinger equation:

$$\left(\hat{H}_o + V(x)\right)\left|\psi_k\right\rangle = E(k)\left|\psi_k\right\rangle$$

And then take the bra with $\left\langle\phi_{k+G_{-1}}\right|$ to get:

$$\left\langle\phi_{k+G_{-1}}\right|\left(\hat{H}_o + \hat{V}(x)\right)\left|\psi_k\right\rangle = E(k)\left\langle\phi_{k+G_{-1}}\middle|\psi_k\right\rangle$$

$$\Rightarrow \left\langle\phi_{k+G_{-1}}\right|\left(\hat{H}_o + \hat{V}(x)\right)\left[c(k)\left|\phi_k\right\rangle + c(k+G_{-1})\left|\phi_{k+G_{-1}}\right\rangle\right]$$

$$= E(k)\left\langle\phi_{k+G_{-1}}\right|\left[c(k)\left|\phi_k\right\rangle + c(k+G_{-1})\left|\phi_{k+G_{-1}}\right\rangle\right]$$

$$\Rightarrow e(k+G_{-1})\,c(k+G_{-1}) + \left\langle\phi_{k+G_{-1}}\right|\hat{V}(x)\left|\phi_k\right\rangle c(k) = E(k)\,c(k+G_{-1})$$

$$\Rightarrow e(k+G_{-1})\,c(k+G_{-1}) + V(G_{-1})\,c(k) = E(k)\,c(k+G_{-1}) \longleftarrow$$

Second result

Appendix: Obtaining the 2x2 Matrix Equation

We have the two equations:

(1) $$e(k)\,c(k) + V(G_1)\,c(k+G_{-1}) = E(k)\,c(k)$$

(2) $$e(k+G_{-1})\,c(k+G_{-1}) + V(G_{-1})\,c(k) = E(k)\,c(k+G_{-1})$$

which can be written in the matrix form:

$$\begin{bmatrix} e(k) & V(G_1) \\ V(G_{-1}) & e(k+G_{-1}) \end{bmatrix}\begin{bmatrix} c(k) \\ c(k+G_{-1}) \end{bmatrix} = E(k)\begin{bmatrix} c(k) \\ c(k+G_{-1}) \end{bmatrix}$$