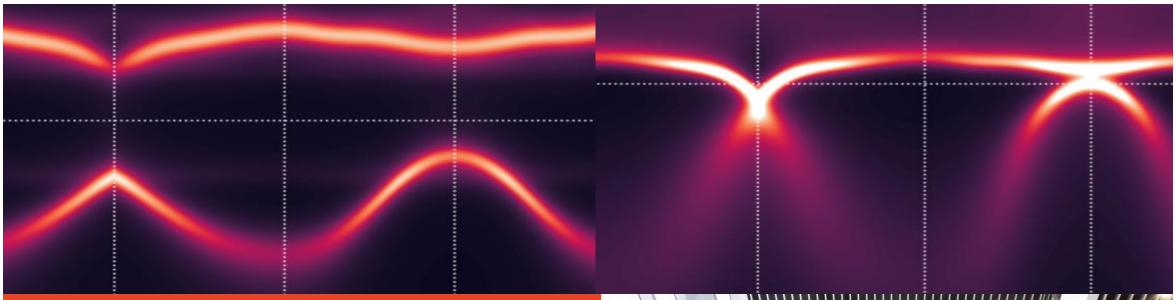
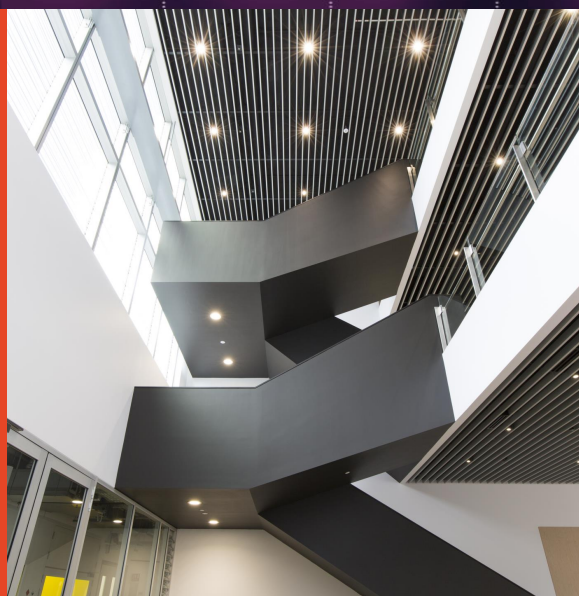


CMP Lecture 9

School of Physics
The University of Sydney

THE UNIVERSITY OF SYDNEY



Electrons in a periodic potential

Oxford Basics Ch. 15

We have seen that X-rays and neutrons scatter from solids by conserving crystal momentum.

Crystal momentum or "quasi-momentum" is a momentum-like vector **p** associated with electrons in a crystal lattice. It is related to the wavevectors, **k**, of the lattice: $\mathbf{p}=\hbar\mathbf{k}$.

Here we will consider the nature of electron waves in solids and will find **crystal momentum is conserved** and that the entire excitation spectrum can be described within a **single Brillouin zone** using a **reduced zone scheme**.

We are going to set up the formalism for dealing with a periodic potential, known as **Bloch's Theorem**.

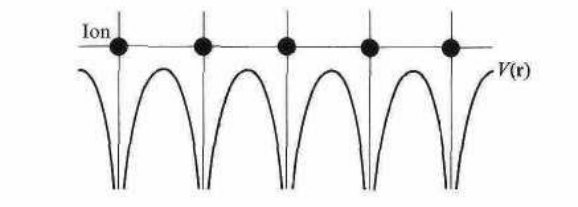
Electrons in a periodic potential

- The problem of electrons in a solid is in general a many-electron problem.
- The full Hamiltonian of the solid contains one-electron potentials describing the interactions of the electrons with the atomic nuclei but also pair potentials describing the electron-electron interactions.
- The many-electron problem is impossible to solve exactly and therefore we need simplified assumptions.

Electrons in a periodic potential

- The simplest approach we saw already, the free-electron model.
- The next step in building the complexity is to consider an independent electron approximation, assuming that all the interactions are described by an effective potential.
- One of the most important properties of the potential is that it is periodic on a lattice.

$V(\mathbf{r}) = V(\mathbf{r}+\mathbf{R})$ where $\mathbf{R}$ is a lattice vector.



The crystal potential seen by an electron

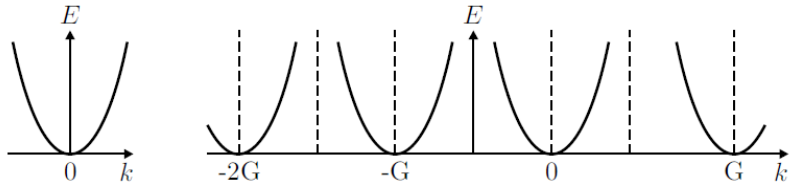
Electrons in a periodic potential

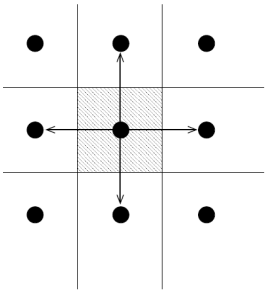
Recall the Hamiltonian of a completely free electron:

$$H_0 = \frac{\mathbf{p}^2}{2m} \qquad \epsilon_0(\mathbf{k}) = \frac{\hbar^2|\mathbf{k}|^2}{2m}$$

The reciprocal lattice has the consequence that instead of there being just one dispersion relationship $\epsilon(\mathbf{k})$, there are an infinite number:

$\epsilon(\mathbf{k})=\epsilon(\mathbf{k}+\mathbf{G})$ for all $\mathbf{G}$





Reciprocal lattice

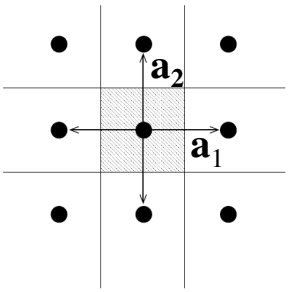
Electrons in a periodic potential

Now consider a weak periodic potential perturbation:

$$H = H_0 + V(\mathbf{r}) \qquad V(\mathbf{r}) = V(\mathbf{r}+\mathbf{R})$$

where $\mathbf{R}$ is a lattice vector:

$$\mathbf{R}_{[n_1\, n_2\, n_3]} = n_1\mathbf{a_1} + n_2\mathbf{a_2} + n_3\mathbf{a_3}$$



Real space lattice

Periodic nature of $V(\mathbf{r})$ implies we can express the potential as a Fourier series:

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}.\mathbf{r}},$$

where **G** are a set of reciprocal lattice vectors and the V_G are Fourier coefficients:

$$V_G = \frac{1}{Vc}\int_{cell} e^{-i\boldsymbol{G}.\boldsymbol{r}} V(\boldsymbol{r})\, dr$$

where Vc is the volume of the unit cell.

The Schrödinger equation in a periodic potential

The one-electron Schrödinger equation with a periodic potential:

$$H\psi = \{-\frac{\hbar^2\nabla^2}{2m} + V(\mathbf{r})\}\psi = E\psi. \qquad (1)$$

where ψ is a wavefunction for one electron.
Independent electrons that obey Eq. (1) are known as ***Bloch electrons***, in contrast to "free electrons", to which Bloch electrons reduce when the periodic potential is zero.

We represent the solution as an expansion over plane waves:
Fourier expansion

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k}.\mathbf{r}}.$$

and we had $$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}.\mathbf{r}},$$

The Schrödinger equation in a periodic potential

$$H\psi = \{-\frac{\hbar^2\nabla^2}{2m} + V(\mathbf{r})\}\psi = E\psi. \qquad (1)$$

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}.\mathbf{r}}, \qquad \psi(\mathbf{r}) = \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k}.\mathbf{r}}.$$

Substitute above into (1):

$$\sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} C_{\mathbf{k}} e^{i\mathbf{k}.\mathbf{r}} + \{\sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}.\mathbf{r}}\}\{\sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k}.\mathbf{r}}\} = E\sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k}.\mathbf{r}}.$$

Potential energy term $$V(\mathbf{r})\psi = \sum_{\mathbf{G},\mathbf{k}} V_{\mathbf{G}} C_{\mathbf{k}} e^{i(\mathbf{G}+\mathbf{k}).\mathbf{r}},$$

can rewrite as: $$V(\mathbf{r})\psi = \sum_{\mathbf{G},\mathbf{k}} V_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} e^{i\mathbf{k}.\mathbf{r}}.$$

The Schrödinger equation in a periodic potential

$$\sum_{\mathbf{k}} e^{i\mathbf{k}.\mathbf{r}}\{(\frac{\hbar^2 k^2}{2m} - E)C_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}}\} = 0.$$

$$\left(\frac{\hbar^2 k^2}{2m} - E\right) C_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} = 0.$$

Write $\mathbf{k} = (\mathbf{q} - \mathbf{G}')$ (where $\mathbf{q}$ is in the first BZ)

$$\left(\frac{\hbar^2 (\mathbf{q}-\mathbf{G}')^2}{2m} - E\right) C_{\mathbf{q}-\mathbf{G}'} + \sum_{\mathbf{G}} V_{\mathbf{G}} C_{\mathbf{q}-\mathbf{G}'-\mathbf{G}} = 0.$$

Finally write $\mathbf{G}'' \rightarrow \mathbf{G} + \mathbf{G}'$.

$$\left(\frac{\hbar^2 (\mathbf{q}-\mathbf{G}')^2}{2m} - E\right) C_{\mathbf{q}-\mathbf{G}'} + \sum_{\mathbf{G}''} V_{\mathbf{G}''-\mathbf{G}'} C_{\mathbf{q}-\mathbf{G}''} = 0.$$

This specifies the C_k that are used to express the wavefunction: $\psi(\mathbf{r}) = \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k}.\mathbf{r}}$.

Bloch's theorem

Oxford Basics, 15.2
Ashcroft Ch. 8, p.133

The coefficients C_k involve k's: $\mathbf{k} = \mathbf{q} - \mathbf{G}$,

For each $\mathbf{q}$, there is a wavefunction $\psi_{\mathbf{q}}(\mathbf{r})$

$$\psi_{\mathbf{q}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{q}-\mathbf{G}} e^{i(\mathbf{q}-\mathbf{G}).\mathbf{r}},$$

where we have put $\mathbf{k} = \mathbf{q} - \mathbf{G}$ in $\psi(\mathbf{r}) = \sum_{\mathbf{k}} C_{\mathbf{k}} e^{i\mathbf{k}.\mathbf{r}}$.

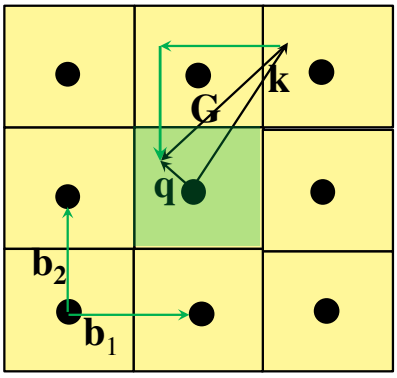
Bloch's Theorem: An electron in a periodic potential has eigenstates of the form

$$\psi_{\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q}.\mathbf{r}} \sum_{\mathbf{G}} C_{\mathbf{q}-\mathbf{G}} e^{-i\mathbf{G}.\mathbf{r}} = e^{i\mathbf{q}.\mathbf{r}} u_{\mathbf{q}},$$

where $u_{\mathbf{q}}$ has the periodicity of the lattice and $\mathbf{q}$ (the crystal momentum) can be chosen within the first Brillouin zone.

Bloch's theorem

In fact, the function u is periodic in the unit cell if and only if it can be written as a sum over reciprocal lattice vectors in this way.



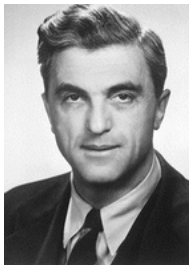
$\mathbf{G}=\mathbf{b}_1+\mathbf{b}_2$

$\mathbf{q}=\mathbf{k}-\mathbf{G}$

reciprocal lattice

Bloch's theorem

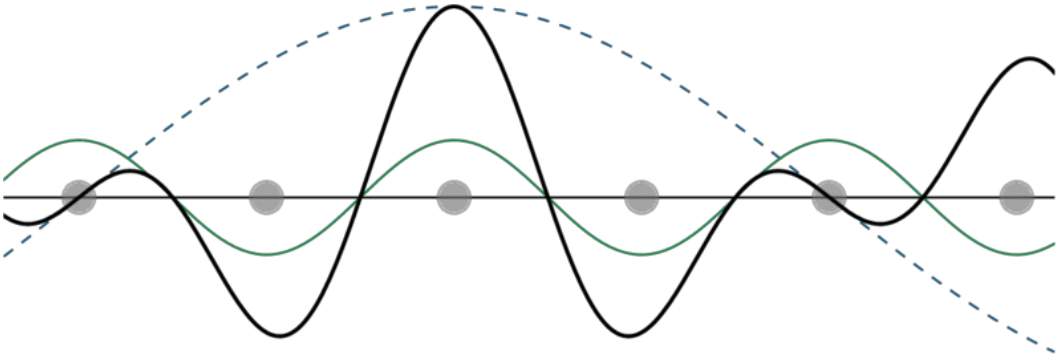
So the eigenstates ψ of the one-electron Hamiltonian of a periodic crystal can be written as a plane wave times a function with the periodicity of the Bravais lattice, u.



Felix Bloch later won a Nobel Prize in 1952 for inventing nuclear magnetic resonance. In medicine NMR was renamed MRI (magnetic resonance imaging) when people decided the word "nuclear" sounds too much like it must be related to some sort of bomb.

Bloch's theorem was actually discovered by a mathematician, Gaston Floquet in 1883, and rediscovered later by Bloch in the context of solids.
This is an example of what is known as Stigler's law of eponomy: "Most things are not named after the person who first discovers them". In fact, Stigler's law was discovered by Merton.

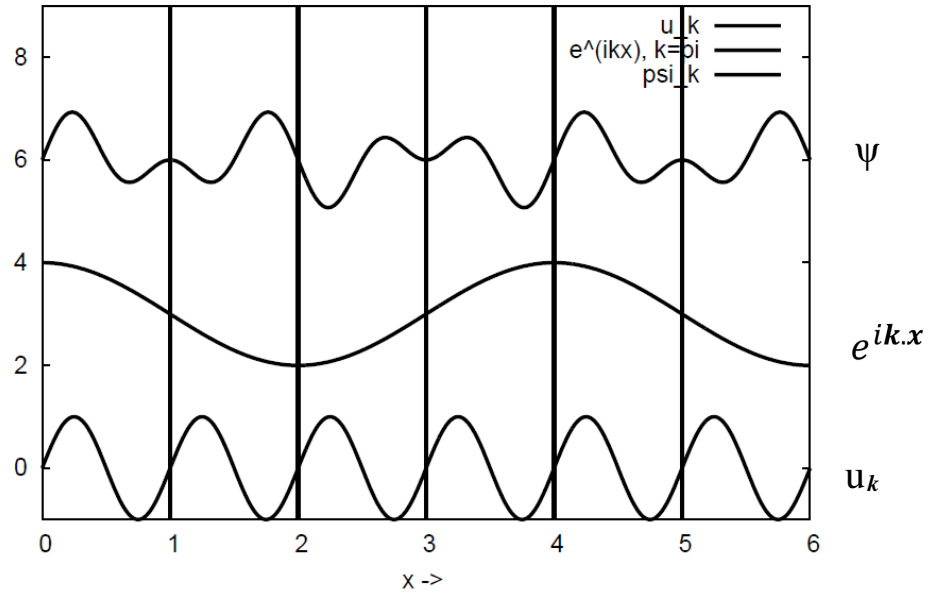
Example

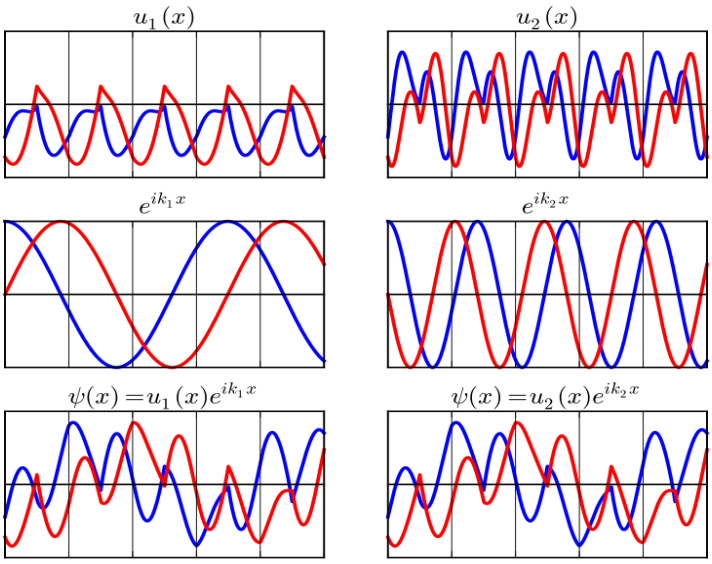


Representation of the real part of an eigenstate in 1D (black solid line), a periodic function u (green solid line) and plane wave (blue dashed line).

The wave differs from the plane wave of free electrons only by a periodic modulation.

Example





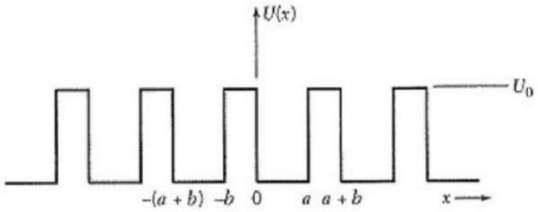
Another example

Blue, red = real and imaginary part

- A Bloch wave (bottom) can be broken up into the product of a periodic function (top) and a plane-wave (center).
- The left and right sides represent the same Bloch wave split in two different ways, one involving wave vector k_1 (left) the other k_2 (right). The difference $(k_1 - k_2)$ is a reciprocal lattice vector.

15

Kronig-Penney model



$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U(x)\psi = \varepsilon\psi$$

$$U = \begin{cases} 0 & n(a+b) < x < n(a+b)+a \\ U_0 & n(a+b)+a < x < (n+1)(a+b) \end{cases}$$

$0 < x < a \qquad U = 0 \qquad \psi = Ae^{iKx} + Be^{-iKx} \qquad \varepsilon = \frac{\hbar^2 K^2}{2m}$

$-b < x < 0 \qquad U = U_0 \qquad \psi = Ce^{Qx} + De^{-Qx} \qquad U_0 - \varepsilon = \frac{\hbar^2 Q^2}{2m}$

Bloch theorem: $\psi(a < x < a+b) = \psi(-b < x < 0)\, e^{ik(a+b)}$

$\psi(0)$ continuous: $A + B = C + D$

$\psi(a)$ continuous: $Ae^{iKa} + Be^{-iKa} = \psi(-b)e^{ik(a+b)} = \left(Ce^{-Qb} + De^{Qb}\right)e^{ik(a+b)}$

$\psi'(0)$ continuous: $iKA - iKB = QC - QD$

$\psi'(a)$ continuous: $iKAe^{iKa} - iKBe^{-iKa} = \psi'(-b)e^{ik(a+b)} = \left(QCe^{-Qb} - QDe^{Qb}\right)e^{ik(a+b)}$

16

Kronig-Penney model

$$\begin{pmatrix} 1 & 1 & -1 & -1 \\ e^{iKa} & e^{-iKa} & -e^{-Qb+ik(a+b)} & -e^{Qb+ik(a+b)} \\ iK & -iK & -Q & Q \\ iKe^{iKa} & -iKe^{-iKa} & -Qe^{-Qb+ik(a+b)} & Qe^{Qb+ik(a+b)} \end{pmatrix} \begin{pmatrix} A \\ B \\ C \\ D \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

$$\rightarrow \qquad \frac{Q^2 - K^2}{2QK} \sinh Qb \sin Ka + \cosh Qb \cos Ka = \cos k(a+b)$$

Delta function potential: $b = 0,\ U_0 = \infty$ such that $\frac{1}{2} Q^2 ba = P = finite$

Thus $Q \gg K,\ Qb \ll 1$ so that

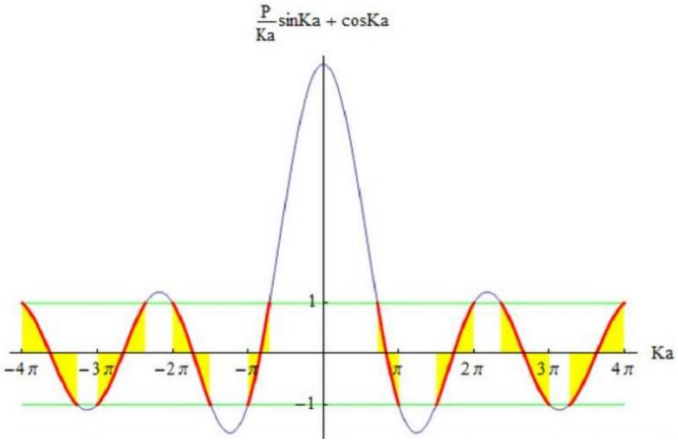
$$\frac{P}{Ka} \sin Ka + \cos Ka = \cos ka$$

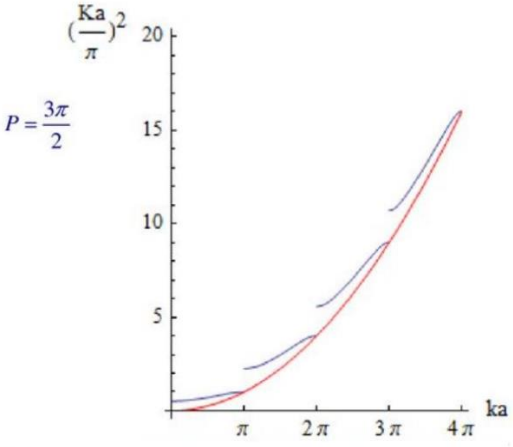
Kronig-Penney model

$$\frac{P}{Ka} \sin Ka + \cos Ka = \cos ka$$

$$\left(\varepsilon = \frac{\hbar^2 K^2}{2m} \text{ in units of } \frac{\hbar^2 \pi^2}{2ma^2} \right) = \left(\frac{Ka}{\pi} \right)^2$$

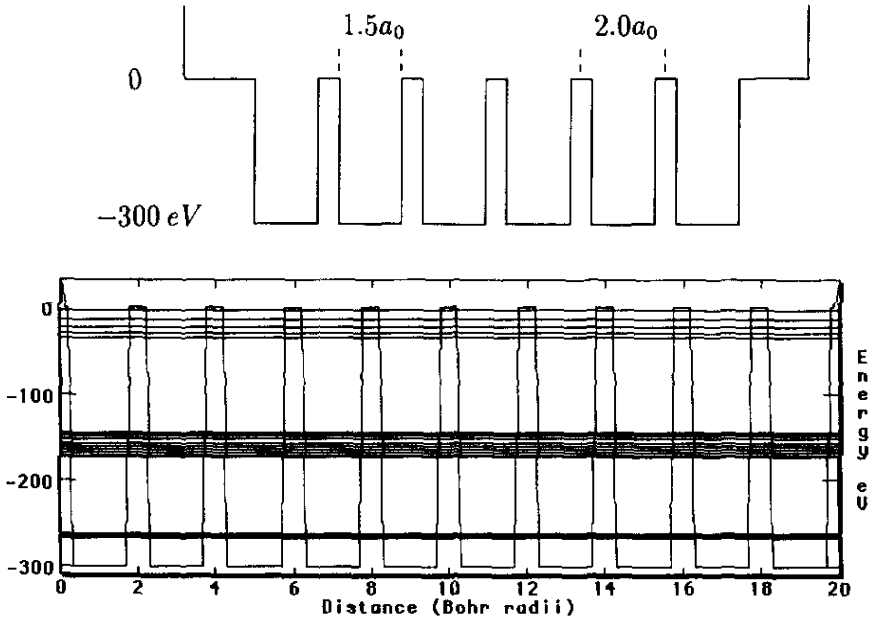
RHS can only be between –1 and 1, for values exceeding this limit there is no wavelike solution of the S.E. This gives rise to band gaps in energy.

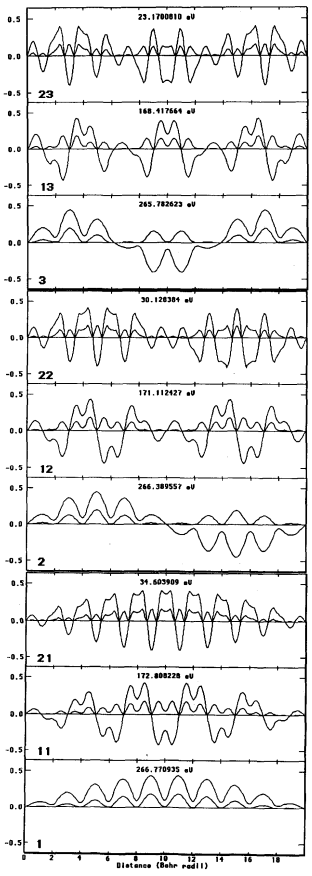




Numerical solution of a finite array of square well potentials is easy (Kronig-Penney model)

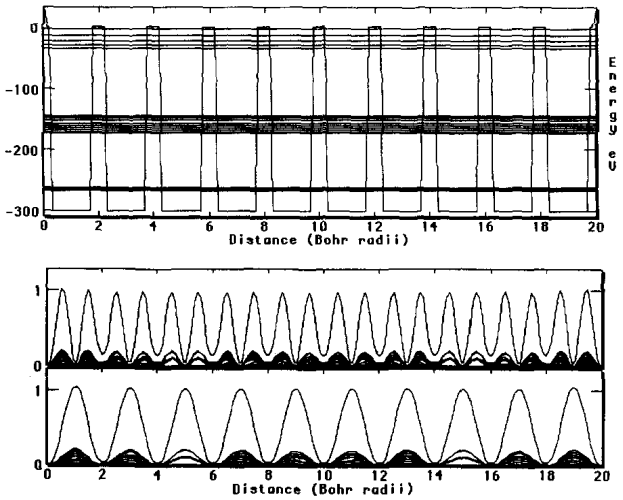
From: Johnston and Segal, Am. J. Phys 60 (7), 1992





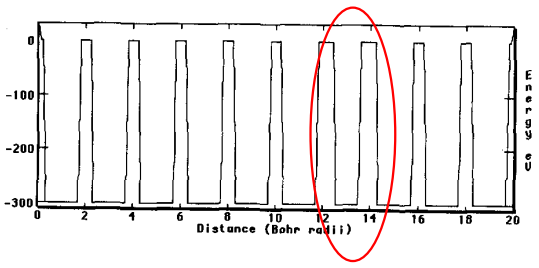
What do the wavefunctions look like?

They have standing waves that form an envelope just like the standing waves on a violin string.
The standing wave multiplies a function that has the period of the potential.

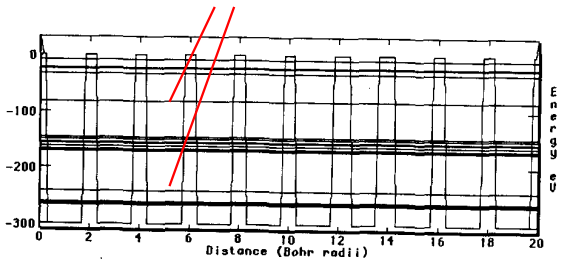


Introduce a “defect/dopant”

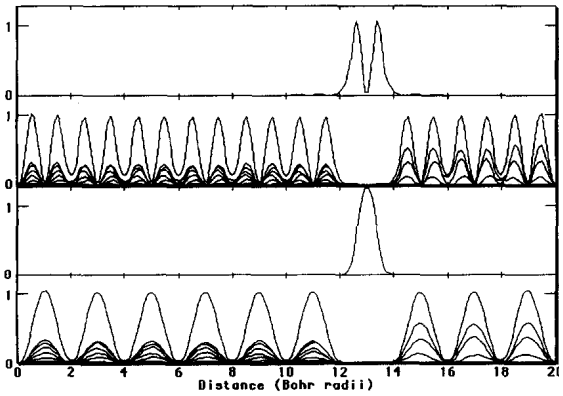
“defect/dopant” level separated from main bands

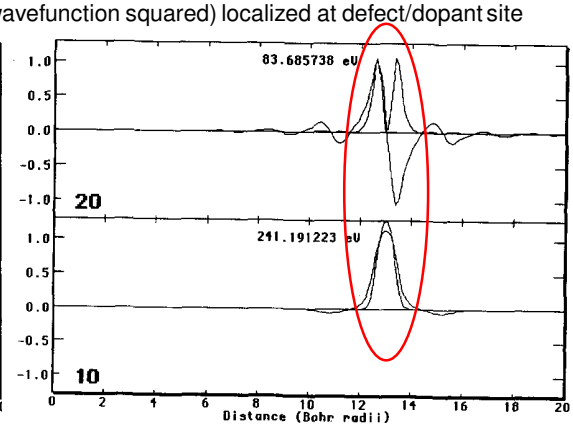


narrower well



“defect/dopant” wavefunction and electron density (wavefunction squared) localized at defect/dopant site



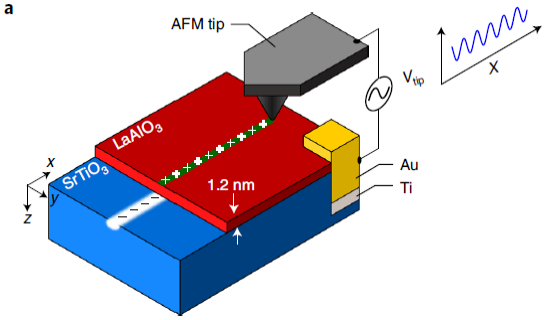


LETTERS
https://doi.org/10.1038/s41567-021-01217-z
nature physics
(2021)
Check for updates

One-dimensional Kronig–Penney superlattices at the $LaAlO_3/SrTiO_3$ interface

Megan Briggeman[1,2], Hyungwoo Lee[3], Jung-Woo Lee[3], Kitae Eom[3], François Damanet[2,4,5], Elliott Mansfield[2,4], Jianan Li[1,2], Mengchen Huang[1,2], Andrew J. Daley[2,4], Chang-Beom Eom[3], Patrick Irvin[1,2] and Jeremy Levy[1,2]

Semiconductor heterostructures[1] and ultracold neutral atomic lattices[2] capture many of the essential properties of one-dimensional electronic systems. However, fully one-dimensional superlattices are highly challenging to fabricate in the solid state due to the inherently small length scales involved. Conductive atomic force microscope lithography applied to an oxide interface can create ballistic few-mode electron waveguides with highly quantized conductance and strongly attractive electron–electron interactions[3]. Here we show that artificial Kronig–Penney-like superlattice potentials can be imposed on such waveguides, introducing a new superlattice spacing that can be made comparable to the mean separation between electrons. The imposed superlattice potential fractures the electronic subbands into a manifold of new subbands with magnetically tunable fractional conductance. The lowest plateau, associated with ballistic transport of spin-singlet electron pairs[3], shows enhanced electron pairing, in some cases up to the highest magnetic fields explored. A one-dimensional model of the system suggests that an engineered spin-orbit interaction in the superlattice contributes to the enhanced pairing observed in the devices. These findings are an advance in the ability to design new families of quantum materials with emergent properties and the development of solid-state one-dimensional quantum simulation platforms.



Conclusions that follow from Bloch's theorem

- Bloch's theorem introduces a wave vector **k** which plays the same fundamental role in the general problem of motion in a periodic potential that the free electron wave vector **k** plays in free-electron theory.
- In the Bloch case, **k** is known as the *crystal momentum* or *quasi-momentum* of the electron.
- The wave vector **k** can always be confined to the first Brillouin zone, since any **k**' not in the first Brillouin zone can be written as **k**'=**k**+**G** where **G** is a reciprocal lattice vector and **k** is in the first zone (sometimes we use **q**).
- Even though the potential that the electrons feel from each atom is very strong, the electrons still behave almost like they do not see the atoms. Still almost form plane wave eigenstates, modulated by the periodic Bloch functions.

Conclusions that follow from Bloch's theorem

$u_{\mathbf{k}}(\mathbf{r})$ is determined by the eigenvalue problem:

$$H(\mathbf{k})u_{\mathbf{k}}(\mathbf{r}) = \left[-\frac{\hbar^2}{2m}\left(i\mathbf{k}+\nabla\right)^2 + U(\mathbf{r})\right]u_{\mathbf{k}}(\mathbf{r}) = E(\mathbf{k})u_{\mathbf{k}}(\mathbf{r})$$

where $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}+\mathbf{R})$

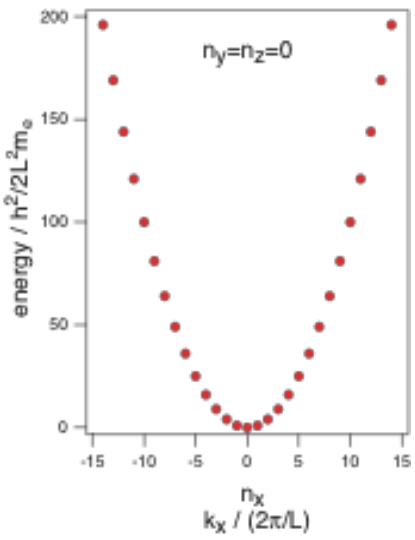
- We can regard this equation as an eigenvalue problem restricted to a single primitive cell of the crystal.
- Since the eigenvalue problem is set in a fixed finite volume, on general grounds we expect an infinite family of solutions with discretely spaced eigenvalues, n (just as in the case of a free electron in a box)
- The wave functions are therefore denoted as $\psi_{n\mathbf{k}}(\mathbf{r})$ indicating that the value of the band index n and the vector $\mathbf{k}$ specifies an electron state.

Working

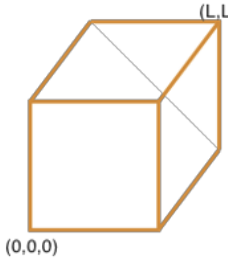
Reminder: free electron model

Schrödinger equation

$$-\frac{\hbar^2\nabla^2}{2m_e}\psi(\mathbf{r}) = E\psi(\mathbf{r})$$



plot in 1D (x-direction)



Solutions

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}}e^{i\mathbf{kr}}$$

Energy levels

$$E(\mathbf{k}) = \frac{\hbar^2k^2}{2m_e} = \frac{\hbar^2}{2m_e}(k_x^2 + k_y^2 + k_z^2)$$

Boundary conditions give

$$\psi(\mathbf{r}) = \psi(x,y,z) = \psi(x+L,y,z)$$

$$\mathbf{k} = (k_x, k_y, k_z) = (\frac{n_x 2\pi}{L}, \frac{n_y 2\pi}{L}\frac{n_z 2\pi}{L})$$

n_x, n_y, n_z integers

Conclusions that follow from Bloch's theorem

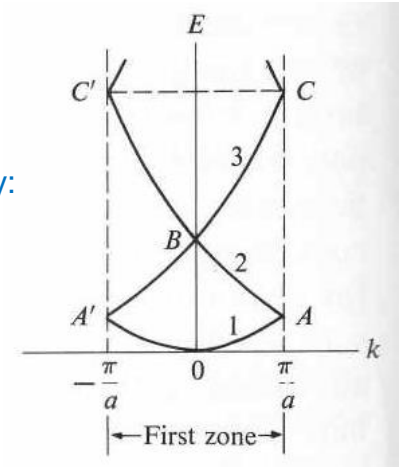
Each energy level for a given **k** varies as **k** varies – obtain a description of the energy levels of an electron in a periodic potential in terms of a family of continuous functions $E_n(\mathbf{k})$.

The information contained in these functions for different n and $\mathbf{k}$ is called the **band structure of a solid**.

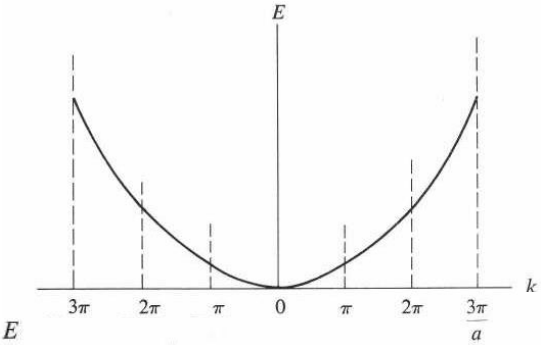
An electron in a level specified by band index n and wave vector $\mathbf{k}$ has a mean velocity given by:

$$\mathbf{v}_n(\mathbf{k}) = \frac{dE_n(\mathbf{k})}{\hbar d\mathbf{k}}$$

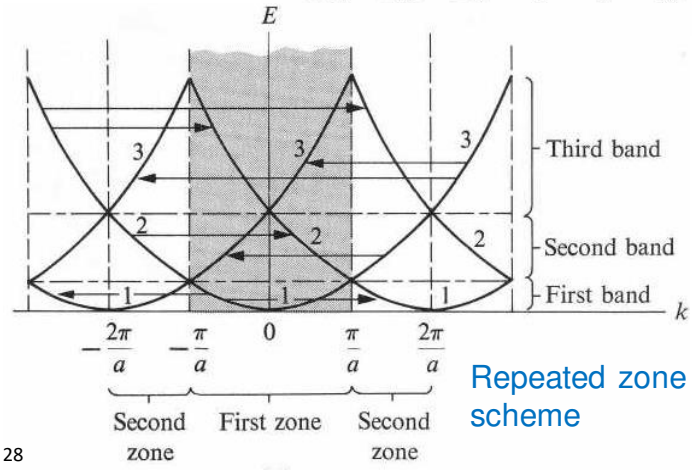
group velocity



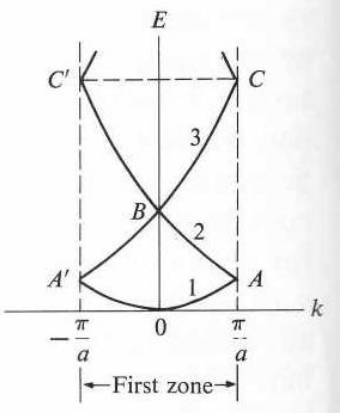
Conclusions that follow from Bloch's theorem



Extended zone scheme



Repeated zone scheme



Reduced zone scheme

Nearly free electron model

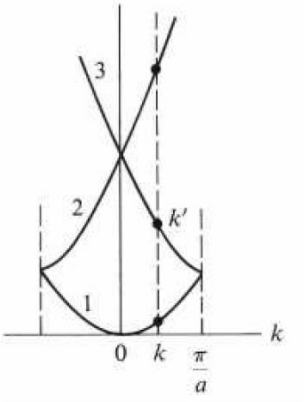
- Going to consider two limits, very weak periodic potential (treated by perturbation theory) and a very strong periodic potential (treated by tight-binding theory).

- Both extreme limits give rise to bands, with band gaps between them. In both extremes the bands are qualitatively very similar, so real potentials must lie somewhere between.

Firstly, recall, for the free electron

$$\epsilon_0(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$$

and the solutions to the SE are plane waves



Each band (1,2,3 ..) corresponds to a different value of **G** in the extended scheme

End