## **10** - Electrons in Crystalline Solids

Aim of Section:

Analyze energy eigenstates of electrons in crystalline solids.

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## Introduction - I

- A solid can be thought of as a very large three-dimensional molecule.
- Solids are either crystalline or amorphous.
- Crystalline solids are regular periodic arrays of atoms, and possess long-range spatial order.
- Amorphous solids are aggregates of atoms having only short-range spatial order.
- Amorphous solids are much more difficult to analyze than crystalline solids (so we will not consider them).

## Introduction - II

- Can use many of techniques that we developed to analyze atoms and molecules to analyze crystalline solids.
- For instance, we can make use of Born-Oppenheimer approximation.
- As before, we argue that electron motion is much faster than nuclear motion, so electron motion can be analyzed assuming that nuclei are static.

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#### Introduction - III

- Suppose that there are N atomic nuclei, of charge Z<sub>I</sub>, located at position vectors X<sub>I</sub>, for I = 1, N.
- ► Suppose that there are N electrons, located at position vectors x<sub>i</sub>, for i = 1, N.
- Energy eigenvalue problem for electrons takes form

$$\sum_{i=1,\mathcal{N}} \left( -\frac{\hbar^2 \nabla_i^2}{2 m_e} - \sum_{I=1,\mathcal{N}} \frac{Z_I e^2}{4\pi \epsilon_0 |\mathbf{x}_i - \mathbf{X}_I|} + \frac{1}{2} \sum_{j=1,\mathcal{N}}^{j \neq i} \frac{e^2}{4\pi \epsilon_0 |\mathbf{x}_i - \mathbf{x}_j|} \right) \times \psi(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_{\mathcal{N}}) = E \,\psi(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_{\mathcal{N}}).$$

Let us write

$$\psi(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_{\mathcal{N}}) = \phi(\mathbf{x}_1) \phi(\mathbf{x}_2) \cdots \phi(\mathbf{x}_{\mathcal{N}}).$$
(1)

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#### Introduction - IV

As before, if we look for single-electron wavefunctions that minimize expectation value of Hamiltonian then we obtain

$$H_i(\mathbf{x}_i)\phi_i(\mathbf{x}_i) = \epsilon_i \phi_i(\mathbf{x}_i), \qquad (2)$$

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where

$$H_{i}(\mathbf{x}_{i}) = -\frac{\hbar^{2} \nabla_{i}^{2}}{2 m_{e}} - \sum_{I=1,N} \frac{Z_{I} e^{2}}{4\pi \epsilon_{0} |\mathbf{x}_{i} - \mathbf{X}_{I}|} + \sum_{j=1,N}^{j \neq i} \int \frac{e^{2} |\phi_{j}(\mathbf{x}_{j})|^{2}}{4\pi \epsilon_{0} |\mathbf{x}_{i} - \mathbf{x}_{j}|} d^{3}\mathbf{x}_{j},$$
(3)

and  $\epsilon_i$  is energy of *i*th electron.

## Introduction - V

- Wavefunction (1) is not properly anti-symmetric with respect to electron label interchange.
- However, we can incorporate symmetry requirement into our calculation by adopting Pauli exclusion principle that no two electrons can have same set of quantum numbers.
- In practice, this means we can put, at most, two electrons (i.e., spin-up and spin-down) into each spatial quantum state.

# Crystal Symmetry - I

- We have been able to formulate electron energy eigenvalue problem in crystalline solid in terms of single-electron Schrödinger equation (2).
- In practice, electron-electon interaction term in single-electron Hamiltonian (3) is far too complicated for us to evaluate.

- ► How do we proceed?
- Make use of symmetry properties of crystal.

# Crystal Symmetry - II

- Lattice translation vector defined as any vector in crystal such that translation of crystal by vector produces spatial distribution of matter identical to original one.
- If a, b, and c are three noncoplanar lattice translation vectors in crystal then general lattice translation vector written

$$\mathbf{T} = n_1 \,\mathbf{a} + n_2 \,\mathbf{b} + n_3 \,\mathbf{c},\tag{4}$$

where  $n_1$ ,  $n_2$ ,  $n_3$  are any integers.

- In crystal composed of identical atoms, a, b, and c are relative position vectors of neighboring atoms.
- Choice of a, b, and c is somewhat arbitrary.
- Let us demand that **a**, **b**, and **c** are set of primitive lattice translation vectors, which means that set of points  $\mathbf{x} + \mathbf{T}$ , where  $n_1$ ,  $n_2$ ,  $n_3$  take all possible values, contains all points equivalent to **x** by translation.

Crystal Symmetry - III



a, b and a', b' are sets of primitive lattice translation vectors;
 a", b" are not.

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# Crystal Symmetry - IV

Assume that average electron potential energy,

$$V(\mathbf{x}_i) = -\sum_{I=1,N} \frac{Z_I e^2}{4\pi \epsilon_0 |\mathbf{x}_i - \mathbf{X}_I|} + \sum_{j=1,N}^{j \neq i} \int \frac{e^2 |\phi_j(\mathbf{x}_j)|^2}{4\pi \epsilon_0 |\mathbf{x}_i - \mathbf{x}_j|} d^3 \mathbf{x}_j,$$

has same symmetry as crystal.

In other words,

$$V(\mathbf{x}_i + \mathbf{T}) = V(\mathbf{x}_i)$$

for any lattice translation vector.

 Given that kinetic energy operator is invariant under translation, we deduce that

$$H_i(\mathbf{x}_i + \mathbf{T}) = H_i(\mathbf{x}_i). \tag{5}$$

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 In other words, single-electron Hamiltonian is invariant under lattice translations.

#### Translation Operators - I

► Lattice translation operator, *T*<sub>op</sub>, has following definition:

$$T_{op} f(\mathbf{x}_i) = f(\mathbf{x}_i + \mathbf{T}).$$
(6)

 There is one translation operator for every lattice translation vector,

$$\mathbf{T} = n_1 \, \mathbf{a} + n_2 \, \mathbf{b} + n_3 \, \mathbf{c},$$

where  $n_1$ ,  $n_2$ ,  $n_3$  are unique set of integers.

► Given that T uniquely specified by n<sub>1</sub>, n<sub>2</sub>, n<sub>3</sub>, can specify corresponding translation operator as T<sub>op</sub>(n<sub>1</sub>, n<sub>2</sub>, n<sub>3</sub>).

#### Translation Operators - II

- Product of two translation operators,  $T'_{op}(n'_1, n'_2, n'_3)$  and  $T_{op}(n_1, n_2, n_3)$ , is third translation operator.
- Follows from (6) because

 $T'_{op} T_{op} f(\mathbf{x}_i) = T'_{op} f(\mathbf{x}_i + \mathbf{T}) = f(\mathbf{x}_i + \mathbf{T}' + \mathbf{T}) = T''_{op} f(\mathbf{x}_i).$ 

Given that

$$\mathbf{T}' = n'_1 \mathbf{a} + n'_2 \mathbf{b} + n'_3 \mathbf{c},$$
  
 $\mathbf{T} = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c},$ 

we have

 $\mathbf{T}'' = \mathbf{T} + \mathbf{T}' = (n_1' + n_1) \mathbf{a} + (n_2' + n_2) \mathbf{b} + (n_3' + n_3) \mathbf{c}.$ 

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### Translation Operators - III

Hence, we deduce that

 $T_{op}(n'_1, n'_2, n'_3) T_{op}(n_1, n_2, n_3) = T_{op}(n'_1 + n_1, n'_2 + n_2, n'_3 + n_3).$ (7)

It immediately follows that

 $[T_{op}, T'_{op}] = 0.$ 

In other words, any two lattice translation operators commute with one another.

## Translation Operators - IV

► Follows from (7) that

$$T_{op}^{-1}(n_1, n_2, n_3) = T_{op}(-n_1, -n_2, -n_3),$$

where  $T_{op}^{-1} T_{op} = 1$ .

Consider

$$\begin{split} \int [T_{op} \phi(\mathbf{x})]^* \ T_{op} \, \psi(\mathbf{x}) \, d^3 \mathbf{x} &= \int \phi^*(\mathbf{x} + \mathbf{T}) \, \psi(\mathbf{x} + \mathbf{T}) \, d^3 \mathbf{x} \\ &= \int \phi^*(\mathbf{x}) \, \psi(\mathbf{x}) \, d^3 \mathbf{x}, \end{split}$$

where we have made a simple change of variable.

It follows that

$$\int \phi^*(\mathbf{x}) \, T^\dagger_{op} \, T_{op} \, \psi(\mathbf{x}) \, d^3 \mathbf{x} = \int \phi^*(\mathbf{x}) \, \psi(\mathbf{x}) \, d^3 \mathbf{x},$$

which suggests that

$$T_{op}^{\dagger} = T_{op}^{-1}.$$
 (8)

In other words, lattice translation operator is unitary (but not Hermitian).

## Translation Operators - V

Invariance of Hamiltonian under lattice translation implies that

$$\int \phi_i^*(\mathbf{x}_i + \mathbf{T}) H_i(\mathbf{x}_i) \phi_i(\mathbf{x}_i + \mathbf{T}) d^3 \mathbf{x}_i = \int \phi_i^*(\mathbf{x}_i) H_i(\mathbf{x}_i) \phi_i(\mathbf{x}_i) d^3 \mathbf{x}_i.$$

Hence, we deduce that

$$\int \phi_i^*(\mathbf{x}_i) \ T_{op}^{\dagger} \ H_i(\mathbf{x}_i) \ T_{op} \ \phi_i(\mathbf{x}_i) \ d^3 \mathbf{x}_i = \int \phi_i^*(\mathbf{x}_i) \ H_i(\mathbf{x}_i) \ \phi_i(\mathbf{x}_i) \ d^3 \mathbf{x}_i,$$

or

$$T_{op}^{\dagger} H_i T_{op} = H_i.$$
<sup>(9)</sup>

(8) and (9) imply that

$$[T_{op}, H_i] = 0.$$

 In other words, as a consequence of crystal symmetry, single-electron Hamiltonian commutes with all lattice translation operators.

## Translation Operators - VI

- Conclude that H<sub>i</sub>, and set of all translation operators, T<sub>op</sub>, constitute set of mutually commuting operators.
- Thus, should be possible to find simultaneous eigenstates of these operators.
- ► Let  $\psi_E(\mathbf{x})$  be spatial wavefunction of single-electron energy eigenstate corresponding to energy E (i.e.,  $H_i \psi_E = E \psi_E$ ).
- ▶ It follows that  $\psi_E(\mathbf{x})$  is also an eigenstate of  $T_{op}$ : that is,

$$T_{op}\,\psi_{E}(\mathbf{x}) = \gamma\,\psi_{E}(\mathbf{x}),\tag{10}$$

where  $\gamma$  is eigenvalue.

• Given that  $T_{op}$  depends on  $n_1$ ,  $n_2$ ,  $n_3$ , we deduce that  $\gamma = \gamma(n_1, n_2, n_3)$ .

#### Bloch's Theorem - I

► Require single-electron wavefunction,  $\psi_E(\mathbf{x})$ , to be properly normalized, so

$$\int |\psi_E(\mathbf{x})|^2 d^3 \mathbf{x} = 1.$$
 (11)

Function ψ<sub>E</sub>(x + T) = T<sub>op</sub> ψ<sub>E</sub>(x) = γ ψ<sub>E</sub>(x) must also be properly normalized, which, from (11), implies that

$$|\gamma|^2 = 1$$

Hence, we can write

$$\gamma = e^{i\beta}, \qquad (12)$$

where  $\beta$  is real.

• Given that  $\gamma = \gamma(n_1, n_2, n_3)$ , it follows that  $\beta = \beta(n_1, n_2, n_3)$ .

#### Bloch's Theorem - II

► Let us successively apply two different lattice translation operators to ψ<sub>E</sub>(x).

We get

 $T'_{op} T_{op} \psi_{\mathsf{E}}(\mathbf{x}) = T'_{op} \gamma \psi_{\mathsf{E}}(\mathbf{x}) = \gamma T'_{op} \psi_{\mathsf{E}}(\mathbf{x}) = \gamma \gamma' \psi_{\mathsf{E}}(\mathbf{x}).$ 

• But, we also know that  $T'_{op} T_{op} = T''_{op}$ .

So,

$$T'_{op} T_{op} \psi_{\mathsf{E}}(\mathbf{x}) = T''_{op} \psi_{\mathsf{E}}(\mathbf{x}) = \gamma'' \psi_{\mathsf{E}}(\mathbf{x}).$$

 Equating right-hand sides of previous two equations, we deduce that

$$\gamma'' = \gamma' \, \gamma, \tag{13}$$

where  $\gamma = \gamma(n_1, n_2, n_3)$ ,  $\gamma' = \gamma(n'_1, n'_2, n'_3)$ , and  $\gamma'' = \gamma(n_1 + n'_1, n_2 + n'_2, n_3 + n'_3)$ .

#### Bloch's Theorem - III

#### (12) and (13) imply that

 $\beta(n_1 + n'_1, n_2 + n'_2, n_3 + n'_3) = \beta(n_1, n_2, n_3) + \beta(n'_1, n'_2, n'_3).$ 

• Only way previous equation can hold for all  $n_1$ ,  $n_2$ ,  $n_3$  is if

 $\beta = x n_1 + y n_2 + z n_3,$ 

where x, y, z are independent of  $n_1$ ,  $n_2$ ,  $n_3$ .

Without loss of generality, can set x = a ⋅ k, y = b ⋅ k, z = c ⋅ k, because a, b, c are independent vectors.

Hence,

$$\beta = \mathbf{k} \cdot \mathbf{T},\tag{14}$$

where  $\mathbf{T} = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}$  is lattice translation vector associated with  $T_{op}(n_1, n_2, n_3)$ .

## Bloch's Theorem - IV

(12) and (14) imply that

$$\gamma = e^{i \mathbf{k} \cdot \mathbf{T}}, \tag{15}$$

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where **k** is constant vector that is independent of  $n_1$ ,  $n_2$ ,  $n_3$ . Follows from (10) and (15) that

$$T_{op} \psi_{E}(\mathbf{x}) = \psi_{E}(\mathbf{x} + \mathbf{T}) = e^{i \mathbf{k} \cdot \mathbf{T}} \psi_{E}(\mathbf{x}).$$
(16)

This result is known as Bloch's theorem.

- ► Bloch's theorem tells us that for every energy eigenfunction, ψ<sub>E</sub>(x), there exists a vector, k, known as wavevector, such that previous equation satisfied for general translation operator, T<sub>op</sub>.
- Hence, we can write

 $\psi_{\boldsymbol{E}}(\mathbf{x}) \equiv \psi_{\boldsymbol{E},\mathbf{k}}(\mathbf{x}).$ 

### Bloch's Theorem - V

- ► Note that (16) does not uniquely determine k. In other words, for given ψ<sub>E</sub>(x), there are many k vectors that satisfy (16).
- Let us define

$$u_{E,\mathbf{k}}(\mathbf{x}) = e^{-i\,\mathbf{k}\cdot\mathbf{x}}\,\psi_{E,\mathbf{k}}(\mathbf{x}). \tag{17}$$

We have

or

$$T_{op} u_{E,\mathbf{k}}(\mathbf{x}) = u_{E,\mathbf{k}}(\mathbf{x} + \mathbf{T}) = e^{-i \,\mathbf{k} \cdot (\mathbf{x} + \mathbf{T})} \psi_{E,\mathbf{k}}(\mathbf{x} + \mathbf{T}).$$

▶ Making use of Bloch's theorem, (16), we get

$$T_{op} u_{E,\mathbf{k}}(\mathbf{x}) = e^{-i\mathbf{k}\cdot(\mathbf{x}+\mathbf{T})} e^{i\mathbf{k}\cdot\mathbf{T}} \psi_{E,\mathbf{k}}(\mathbf{x}) = e^{-i\mathbf{k}\cdot\mathbf{x}} \psi_{E,\mathbf{k}}(\mathbf{x}),$$
, from (17),
$$T_{op} u_{E,\mathbf{k}}(\mathbf{x}) = u_{E,\mathbf{k}}(\mathbf{x}).$$

## Bloch's Theorem - VI

- We deduce that u<sub>E,k</sub>(x) is a periodic function that is invariant under translation by T.
- ► (17) yields

$$\psi_{\boldsymbol{E},\boldsymbol{k}}(\boldsymbol{x}) = e^{i\,\boldsymbol{k}\cdot\boldsymbol{x}}\,\boldsymbol{u}_{\boldsymbol{E},\boldsymbol{k}}(\boldsymbol{x}). \tag{18}$$

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► In other words, electronic wavefunction of energy eigenstate of crystal has form of periodic function, u<sub>E,k</sub>(x), modulated by plane-wave envelope, e<sup>ik·x</sup>.

#### Reciprocal Lattice - I

Let us search for a wavevector, G, that satisfies

$$e^{i \mathbf{G} \cdot \mathbf{T}} = 1, \tag{19}$$

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where  $\mathbf{T} = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}$  is a general lattice translation vector.

Given that

$$\mathrm{e}^{\mathrm{i}\,\theta} = \cos\theta + \mathrm{i}\,\sin\theta,$$

it is clear that (19) can only be satisfied if

 $\mathbf{G}\cdot\mathbf{T}=2\pi n,$ 

where *n* is an integer.

#### Reciprocal Lattice - II

Thus, we require

$$n_1 \mathbf{G} \cdot \mathbf{a} + n_2 \mathbf{G} \cdot \mathbf{b} + n_3 \mathbf{G} \cdot \mathbf{c} = 2\pi n.$$
 (20)

Suppose that  $n_2 = n_3 = 0$  and  $n_1$  is an arbitrary integer. (20) yields

 $n_1 \mathbf{G} \cdot \mathbf{a} = 2\pi n$ ,

which can only be satisfied if

$$\mathbf{G} \cdot \mathbf{a} = 2\pi \ n_a, \tag{21}$$

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where  $n_a$  is an integer.

#### Reciprocal Lattice - III

Similar reasoning reveals that

$$\mathbf{G} \cdot \mathbf{b} = 2\pi \, n_b, \tag{22}$$

$$\mathbf{G} \cdot \mathbf{c} = 2\pi \, n_c. \tag{23}$$

► Let us write

$$\mathbf{G} = n_a \,\mathbf{A} + n_b \,\mathbf{B} + n_c \,\mathbf{C}.\tag{24}$$

▶ (21)–(24) imply that

$\mathbf{A}\cdot\mathbf{a}=2\pi,$	$\mathbf{B} \cdot \mathbf{a} = 0,$	$\mathbf{C} \cdot \mathbf{a} = 0,$	(25)
$\mathbf{A} \cdot \mathbf{b} = 0,$	$\mathbf{B}\cdot\mathbf{b}=2\pi,$	$\mathbf{C} \cdot \mathbf{b} = 0,$	(26)
$\mathbf{A} \cdot \mathbf{c} = 0,$	$\mathbf{B} \cdot \mathbf{c} = 0,$	$\mathbf{C} \cdot \mathbf{c} = 2\pi.$	(27)

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#### Reciprocal Lattice - IV

▶ It can be seen, by inspection, that (25)–(27) are satisfied by

$$\mathbf{A} = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})},$$
(28)  
$$\mathbf{B} = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})},$$
(29)  
$$\mathbf{C} = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}.$$
(30)

Note that

$$\mathbf{G} \cdot \mathbf{T} = 2\pi (n_a n_1 + n_b n_2 + n_c n_3) = 2\pi n.$$

- (24) and (28)–(30) define what is known as a reciprocal lattice in k-space.
- **G** is known as a reciprocal lattice translation vector.
- A, B, and C are known as primitive reciprocal lattice translation vectors.

#### Reciprocal Lattice - V

- Key property of vector **G** is  $e^{i \mathbf{G} \cdot \mathbf{T}} = 1$ .
- Because of this property, can use G to generate infinity of wavevectors, k', that are equivalent to any particular wavevector, k:

#### $\mathbf{k}' = \mathbf{k} + \mathbf{G}.$

- ► Recall, Bloch's theorem, which states that translation of ψ<sub>E,k</sub>(x) by vector T is equivalent to multiplication by phase factor e<sup>ik</sup>.T.
- But,

$$\mathrm{e}^{\,\mathrm{i}\,\boldsymbol{k}'\cdot\boldsymbol{\mathsf{T}}}=\mathrm{e}^{\,\mathrm{i}\,\boldsymbol{(k+G)}\cdot\boldsymbol{\mathsf{T}}}=\mathrm{e}^{\,\mathrm{i}\,\boldsymbol{k}\cdot\boldsymbol{\mathsf{T}}}\,\mathrm{e}^{\,\mathrm{i}\,\boldsymbol{G}\cdot\boldsymbol{\mathsf{T}}}=\mathrm{e}^{\,\mathrm{i}\,\boldsymbol{k}\cdot\boldsymbol{\mathsf{T}}}$$

► So, translation of \u03c6<sub>E,k'</sub>(x) by vector T also results in multiplication by factor e<sup>ik</sup>.T.

#### Reciprocal Lattice - VI

- ▶ By letting integers n<sub>a</sub>, n<sub>b</sub>, and n<sub>c</sub> in (24) take any values, we generate infinite set of wavevectors, k', each of which is equivalent to k.
- Let us denote set of equivalent wavevectors by {k'}.
- Any wavevector in {k'} is related to any other vector by some reciprocal lattice translation vector, G.

#### Reciprocal Lattice - VII

Consider cubic lattice in which inter-atomic spacing is *d*.
Follows that

 $\mathbf{a} = d \, \mathbf{e}_x, \qquad \mathbf{b} = d \, \mathbf{e}_y, \qquad \mathbf{c} = d \, \mathbf{e}_z.$ 

Easily seen from (28)–(30) that

$$\mathbf{A} = \frac{2\pi}{d} \mathbf{e}_{\mathsf{x}}, \qquad \mathbf{B} = \frac{2\pi}{d} \mathbf{e}_{\mathsf{y}}, \qquad \mathbf{C} = \frac{2\pi}{d} \mathbf{e}_{\mathsf{z}}.$$

- Thus, reciprocal lattice is also cubic.
- Lattice spacing in reciprocal space is inversely proportional to lattice spacing in real space.

#### Reciprocal Lattice - VIII

- Consider cuboid lattice.
- Follows that

$$\mathbf{a} = d_x \, \mathbf{e}_x, \qquad \mathbf{b} = d_y \, \mathbf{e}_y, \qquad \mathbf{c} = d_z \, \mathbf{e}_z.$$

Easily seen from (28)–(30) that

$$\mathbf{A} = \frac{2\pi}{d_x} \mathbf{e}_x, \qquad \mathbf{B} = \frac{2\pi}{d_y} \mathbf{e}_y, \qquad \mathbf{C} = \frac{2\pi}{d_z} \mathbf{e}_z.$$

- Thus, reciprocal lattice is also cuboid.
- Again, lattice spacing in reciprocal space is inversely proportional to lattice spacing in real space.

## Brillouin Zones - I

- ► Have seen that particular wavevector, **k**, is not unique.
- Can generate infinity of equivalent wavevectors, each corresponding to different point in reciprocal space, via
   k' = k + G.
- Choose to label each electronic wavefunction with smallest wavevector in set of wavevectors that characterize function.
- Is there particular region of reciprocal space that contains all of smallest wavevectors for particular crystal?

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#### Brillouin Zones - II

- ▶ Because k is smallest vector in set {k'}, we know that k'<sup>2</sup> ≥ k<sup>2</sup> for any k' in {k'}.
- ▶ So, if G is particular reciprocal translation vector then we need

 $(\mathbf{k}-\mathbf{G})^2 \ge k^2,$ 

which implies that

$$k_{\parallel} \leq \frac{1}{2} G, \tag{31}$$

where  $\mathbf{k}_{\parallel} = \mathbf{k} \cdot \mathbf{G}/G$  is projection of **k** along direction of **G**.

In other words, for k to be smallest vector in set {k'} its tip must lie on small-k side of perpendicular bisector of any possible reciprocal lattice translation vector, G.

## Brillouin Zones - III



- Procedure to find region of reciprocal space in which smallest k vectors reside:
  - 1. Connect origin to nearest neighbors in reciprocal space by smallest **G** vectors.
  - 2. Draw perpendicular bisectors of G vectors.
  - Region enclosed by perpendicular bisectors (including origin) is region in which smallest k vectors reside. This region known as first Brillouin zone. (Figure is for square lattice.)

## Brillouin Zones - IV

- Region of reciprocal space in which next smallest k vectors reside is known as second Brillouin zone.
- Can find second Brillouin zone by drawing next smallest G vectors and bisecting them. Region that lies within bisectors (excluding first Brillouin zone) is second Brillouin zone.



### Brillouin Zones - V

 Sections of second Brillouin zone can be mapped into equivalent sections of first Brillouin zone by means of displacement by appropriate G vectors.



#### Brillouin Zones - VI

Can continue process to find third Brillouin zone, and so on



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## Brillouin Zones - VII

- Higher and higher order Brillouin zones clearly become more and more fragmented.
- All Brillouin zones (in two dimensions) occupy same area in reciprocal space (because they all have to map into first Brillouin zone).

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# Brillouin Zones - VIII

- Of course, crystals are three dimensional, rather than two dimensional.
- This means that perpendicular bisectors of G vectors are planes, rather than lines.
- ▶ Planes enclose volumes, rather than areas, of reciprocal space.
- Easily appreciated that first Brillouin zone of cubic lattice is cubic in shape.

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 Moreover, each Brillouin zone occupies equal volume of reciprocal space.

## Brillouin Zones - IX

► Single-electron energy eigenstates have spatial wavefunctions, ψ<sub>E,k</sub>(x), that satisfy Bloch's theorem:

$$\psi_{\boldsymbol{E},\boldsymbol{k}}(\boldsymbol{x}+\boldsymbol{\mathsf{T}})=\mathrm{e}^{\mathrm{i}\,\boldsymbol{k}\cdot\boldsymbol{\mathsf{T}}}\,\psi_{\boldsymbol{E},\boldsymbol{k}}(\boldsymbol{x}).$$

- Each different k in first Brillouin zone corresponds to different spatial electronic state.
- How many distinct spatial electronic states are there in first Brillouin zone?
- If crystal is infinite in size then there are infinite number of states.

However, no real crystal is infinite in size.

### Brillouin Zones - X

- ► Consider one-dimensional crystal consisting of *N* unit cells.
- ► Let *d* be spacing between adjacent lattice points.
- Length of crystal is L = N d.
- Let us demand that

$$\psi_{E,k}(0) = \psi_{E,k}(L).$$
 (32)

Here, we are effectively taking finite size of crystal into account by treating it as infinite crystal that is periodic with periodicity length *L*.

#### Brillouin Zones - XI

According to Bloch's theorem,

$$\psi_{E,k}(L) = \psi_{E,k}(0+L) = e^{i \, k \, L} \, \psi_{E,k}(0). \tag{33}$$

- (32) and (33) imply that e<sup>ikL</sup> = 1. So, kL must be some multiple of 2π.
- ► Length of first Brillouin zone in k-space is 2π/d (i.e., distance between adjacent points in reciprocal lattice).
- Hence, allowed values of k in first Brillouin zone are

$$k = \frac{2\pi n}{L} = \frac{2\pi}{d} \frac{n}{N},$$
(34)

for  $-N/2 \le n \le +N/2$ .

# Brillouin Zones - XII

- ► Thus, there are *N* distinct spatial electronic states in first Brillouin zone.
- ► Argument can be extended to show that there are *N* distinct spatial electronic states in every Brillouin zone.
- Argument can be further extended to show that there are also N distinct spatial electronic states in every Brillouin zone for two-dimensional and three-dimensional crystals containing N unit cells.

# Free-Electron Approximation - I

- Potential energy of electron in crystal is periodic function of x that has singularities at nuclear sites.
- Predominant effect of potential energy is to keep electron confined within crystal.
- As very crude approximation, let us ignore periodicity of potential energy, and singularities, and regard crystal as three-dimensional square well.
- We replace potential energy function with constant value that is lower than potential energy outside crystal.

This approach known as free-electron approximation.

#### Free-Electron Approximation - II

- Let us take V = 0 inside crystal, and V > 0 outside.
- Schrödinger's equation inside crystal is that of free electron:

$$-\frac{\hbar^2}{2\,m_e}\,\nabla^2\psi_E(\mathbf{x})=E\,\psi_E(\mathbf{x}).$$

Solutions are

$$\psi_{\mathsf{E}}(\mathbf{x}) = A \,\mathrm{e}^{\mathrm{i}\,\mathbf{k}'\cdot\mathbf{x}},\tag{35}$$

where

$$E = \frac{\hbar^2}{2 m_e} k'^2.$$
 (36)

► Here, A is normalization constant, and wavevector k' is related to linear momentum of electron via p = ħ k'.

#### Free-Electron Approximation - III

▶ (35) has form of Bloch wavefunction,

$$\psi_{\boldsymbol{E},\boldsymbol{k}'}(\boldsymbol{x}) = \mathrm{e}^{\mathrm{i}\,\boldsymbol{k}'\cdot\boldsymbol{x}}\,\boldsymbol{u}_{\boldsymbol{E},\boldsymbol{k}'}(\boldsymbol{x}),$$

where  $u_{E,\mathbf{k}'}(\mathbf{x}) = A$ .

- ► No limit has been placed on the magnitude of k', which is known as extended-zone-scheme wavevector.
- However, we conventionally choose wavevector, k, appearing in Bloch's theorem, such that it lies in first Brillouin zone, in which case it is known as reduced-zone-scheme wavevector.

► Of course, k = k' - G, where G is appropriate reciprocal lattice translation vector.

### Free-Electron Approximation - IV

Follows that

$$\psi_{\boldsymbol{E},\boldsymbol{k}}(\boldsymbol{x}) = \boldsymbol{A} e^{\mathrm{i} \, \boldsymbol{G} \cdot \boldsymbol{x}} e^{\mathrm{i} \, \boldsymbol{k} \cdot \boldsymbol{x}},$$

so  $u_{E,\mathbf{k}}(\mathbf{x}) = A e^{i \mathbf{G} \cdot \mathbf{x}}$ .

Furthermore,

$$E = \frac{\hbar^2}{2 m_{\rm e}} \, |\mathbf{k} + \mathbf{G}|^2.$$

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# Free-Electron Approximation - V

- As example, consider one-dimensional crystal of lattice spacing *d* containing *N* unit cells.
- Allowed values of k in first Brillouin zone are

$$k=\frac{2\pi}{d}\frac{m}{N},$$

for  $-N/2 \le m \le N/2$ .

- ► There are N such values. In limit N ≫ 1 they are very closely spaced.
- To plot E versus k in reduced-zone scheme we plot

$$\mathsf{E} = \frac{\hbar^2}{2\,m_e}\,k^{\prime\,2},$$

where

$$k=k'\pm\frac{2\pi}{d}\,n',$$

and n' is chosen so as to ensure that  $-\pi/d \leq k \leq \pi/d$ .

### Free-Electron Approximation - VI

Helpful to write

$$k = \frac{2\pi}{d} \hat{k},$$
  

$$k' = \frac{2\pi}{d} \hat{k}',$$
  

$$E = \frac{\hbar^2 \pi^2}{2 m_e d^2} \hat{E}.$$

Follows that

 $\hat{E}=4\,\hat{k}^{\prime\,2}.$ 

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 We shall employ this normalization scheme extensively in following discussion.

### Free-Electron Approximation - VII



Dashed curve shows Ê(k̂'). Solid curve shows Ê(k̂). Red lines show boundaries of Brillouin zones.

#### Free-Electron Approximation - VIII

- In reduced-zone scheme there are infinite number of possible energies associated with each k value in first Brillouin zone.
- Let us denote these energies the E<sub>n</sub>(k) where E<sub>0</sub> < E<sub>1</sub> < E<sub>2</sub>, et cetera.
- Quantum number *n* is called band index.
- The  $E_n(k)$  constitutes *n*th band of allowed electron energies.
- Each band contains N distinct spatial electron states. Hence, according to Pauli exclusion principle, each band can accommodate 2 N electrons.

# Free-Electron Approximation - IX



### Density of States - I

- In one-dimensional crystal, density of states as function of wavevector denoted w(k).
- ► w(k) dk defined as number of unique electron states whose wavevectors lies between k and k + dk.
- According to (34), spatial states are evenly spaced in k-space with spacing Δk = 2π/(N d).
- There are two unique electron states per unique spatial state.
- So,

$$w(k)\,dk=\frac{2\,dk}{\Delta k}=\frac{N\,d\,dk}{\pi},$$

giving

$$w(k) = \frac{N d}{\pi} = \frac{L}{\pi},$$
(37)

where L is length of crystal.

### Density of States - II

- Density of states as function of energy denoted  $\mathcal{D}(E)$ .
- ▶  $\mathcal{D}(E) dE$  defined as number of unique electron states whose energies lies between *E* and *E* + *dE*.
- In free electron approximation,

$$E = \frac{\hbar^2 k^2}{2 m_e}.$$
 (38)

So,

$$\mathcal{D}(E) dE = 2 w(k) dk.$$
(39)

Factor of two arises because each value of *E* corresponds to two values of *k*; one positive, and one negative.

### Density of States - III

▶ (37)–(39) yield

$$\mathcal{D}(E) = \frac{L\sqrt{2m_e}}{\pi\hbar} E^{-1/2}.$$
 (40)

- Suppose that there are  $\eta$  electrons per unit cell, which implies that there are  $\eta N$  electrons in whole crystal.
- We need to put these electrons into lowest-energy available unique electron states.
- Given that  $E \propto k^2$  this implies putting electrons into states with lowest values of k.
- Let us fill all states for which  $k \leq k_F$ .
- Follows that

$$2\int_0^{k_F} w(k)\,dk = \eta\,N. \tag{41}$$

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### Density of States - IV

(37) and (41) yield

$$k_F = \frac{\pi}{2 \, d} \, \eta. \tag{42}$$

Here,  $k_F$  known as Fermi wavevector.

Corresponding energy, which is known as Fermi energy, is

$$E_F = \frac{\hbar^2 k_F^2}{2 m_e} = \frac{\hbar^2 \pi^2}{8 m_e d^2} \eta^2.$$
 (43)

- ► Thus, all electron states with E ≤ E<sub>F</sub> are filled, and those with E > E<sub>F</sub> are empty.
- In reality, probability of finding electron in state of energy E is

$$\rho(E)=\frac{1}{\mathrm{e}^{(E-E_F)/(k_B T)}+1}.$$

However, given that  $E_F \gg k_B T$  at room temperature, we deduce that  $p \simeq 1$  for  $E < E_F$ , and  $p \simeq 0$  for  $E > E_F$ .

### Density of States - V

In terms of previous normalization,

$$\hat{E}_{F} = \frac{\eta^{2}}{4}, \qquad (44)$$
$$\hat{\mathcal{D}}(\hat{E}) = \frac{N}{\hat{E}^{1/2}},$$

which ensures that

$$\int_0^{\hat{E}_F} \hat{\mathcal{D}}(\hat{E}) \, d\hat{E} = N \, \eta.$$

- Note that properties of crystal effectively determined by parameter η.
- Given that η is integer, conclude that Brillouin zones in 1-D crystal either empty, half-full, or completely full.

### Density of States - VI



### Density of States - VII



# Weak-Binding Approximation - I

- Let us now take into account electron potential energy, V(x).
- If potential energy sufficiently small then we can treat it as perturbation to system.
- This approach known as weak-binding approximation.

Let

$$\psi_{E,k}^{(0)}(x) = \frac{\mathrm{e}^{\mathrm{i}\,k\,x}}{\sqrt{L}},$$

be our zeroth-order energy eigenstate, corresponding to energy

$$E_0(k)=\frac{\hbar^2\,k^2}{2\,m_e}.$$

Note that

$$\int_{-L/2}^{L/2} \left| \psi_{E,k}^{(0)}(x) \right|^2 \, dx = 1,$$

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as required for proper normalization.

# Weak-Binding Approximation - II

Using standard perturbation theory, can write

$$\psi_{E,k}(x) = \psi_{E,k}^{(0)}(x) + V_{k,k} + \sum_{k' \neq k} \frac{V_{k',k} \,\psi_{E,k}^{(0)}(x)}{E_0(k) - E_0(k')}, \qquad (45)$$

where

$$V_{k',k} = \int_{-L/2}^{L/2} \psi_{E,k'}^{(0)*}(x) V(x) \psi_{E,k}^{(0)}(x) dx,$$

or

$$V_{k',k} = \frac{1}{L} \int_{-L/2}^{L/2} e^{i(k-k') \times} V(x) \, dx.$$
 (46)

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### Weak-Binding Approximation - III

► We know that V(x) is a periodic function of x with period d. Thus,

$$V(x+m\,d)=V(x),\tag{47}$$

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for any integer, *m*.

Making a change of variable, (46) becomes

$$V_{k',k} = \frac{1}{L} \int_{-L/2}^{L/2} e^{i(k-k')(x+md)} V(x+md) dx$$
  
=  $e^{i(k-k')md} \int_{-L/2}^{L/2} e^{i(k-k')x} V(x) dx$   
=  $e^{i(k-k')md} V_{k',k}$ .

Here, have assumed that  $m d \ll L$ .

# Weak-Binding Approximation - IV

Previous equation yields

$$\left[1-\mathrm{e}^{\mathrm{i}(k-k')\,m\,d}\right]V_{k',k}=0.$$

• Conclude that  $V_{k',k} = 0$  unless

$$e^{i(k-k')md} = 1.$$
 (48)

- However, (48) is definition of reciprocal lattice translation vector.
- Follows that only states that are coupled to ψ<sup>(0)</sup><sub>E,k</sub>, according to first-order perturbation theory, are states with wavevectors, k', that differ from k by reciprocal lattice translation vectors.
- Note that

$$V_{k,k} = \frac{1}{L} \int_{-L/2}^{L/2} V(x) \, dx = \frac{1}{d} \int_{-d/2}^{d/2} V(x) \, dx \equiv V_0,$$

is average (over unit cell) electron potential energy.

### Weak-Binding Approximation - V

▶ (45) becomes

$$\psi_{E,k}(x) = \psi_{E,k}^{(0)}(x) + \sum_{G \neq 0} \frac{V_G \, \psi_{E,k-G}^{(0)}(x)}{E_0(k) - E_0(k-G)}.$$

where  $G = n(2\pi/d)$ , and

$$V_{G} = \frac{1}{L} \int_{-L/2}^{L/2} e^{i G \times} V(x) \, dx.$$

► Given that V(x) and e<sup>iGx</sup> are both periodic functions of x with period d, can write

$$V_G = \frac{1}{d} \int_{-d/2}^{d/2} e^{i G \times} V(x) dx.$$

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# Weak-Binding Approximation - VI

Finally, to second-order in perturbation expansion,

or

$$E(k) = E_0(k) + V_0 + \sum_{G \neq 0} \frac{|V_G|^2}{E_0(k) - E_0(k - G)}.$$
 (49)

 In order for perturbation theory not to break down, last term on right-hand side of previous equation must be small compared to first. In other words,

$$|V_G| \ll \left[1 - \frac{E_0(k-G)}{E_0(k)}\right]^{1/2} = \left[1 - \frac{(k-G)^2}{k^2}\right]^{1/2},$$
$$|V_G| \ll \frac{\sqrt{G(2k-G)}}{|k|}.$$

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# Weak-Binding Approximation - VII

- ▶ Deduce that, assuming V<sub>G</sub> sufficiently small, perturbation theory can be safely used for electronic states for which k is not close to G/2.
- Relative energies of such states only modified to second-order in perturbation expansion, so they are essentially same as in free-electron approximation.

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- ► On other hand, perturbation theory fails for states with k ≃ G/2, because e<sup>i(k-G)×</sup> mixes strongly with e<sup>ikx</sup>.
- Must treat such strongly-mixed states differently.

### Weak-Binding Approximation - VIII

- Strongly-mixed states such that k = G/2 = nπ/d, where n is non-zero integer.
- Thus, strongly-mixed states correspond to  $\hat{k} = n/2$ .
- Clear from figure that strongly-mixed states lie at boundaries of Brillouin zones.



### Weak-Binding Approximation - IX

- ► Consider strongly-mixed state with wavevectors k ≃ G/2 and k ≃ k − G.
- Schrödinger's equation is

 $(H-E)\psi_E(x)=0,$ 

where

$$H=-\frac{\hbar^2}{2\,m_e}\frac{d^2}{dx^2}+V(x),$$

and

$$\psi_E(x) \simeq \frac{a}{\sqrt{L}} \mathrm{e}^{\mathrm{i}\,k\,x} + \frac{b}{\sqrt{L}} \mathrm{e}^{\mathrm{i}\,k'\,x}.$$

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Note that strongly-mixed states are almost degenerate.

# Weak-Binding Approximation - X

Previous three equations yield

$$\frac{a}{\sqrt{L}} \left( \frac{\hbar^2 k^2}{2 m_e} + V - E \right) e^{i k x} + \frac{b}{\sqrt{L}} \left( \frac{\hbar^2 k'^2}{2 m_e} + V - E \right) e^{i k' x} = 0.$$

 Operating on previous equation with  $(1/L) \int_{-L/2}^{L/2} e^{-ikx} (\cdots) dx$  and  $(1/L) \int_{-L/2}^{L/2} e^{-ik'x} (\cdots) dx$ , we get  $\begin{pmatrix} H_{k,k} - E, & H_{k,k'} \\ H_{k',k}, & H_{k',k'} - F \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix}$ 

$$\begin{pmatrix} H_{k,k} - E, & H_{k,k'} \\ H_{k',k}, & H_{k',k'} - E \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = 0.$$
 (50)

Here.

$$H_{k,k} = \frac{\hbar^2 k^2}{2 m_e} + V_0, \qquad H_{k,k'} = V_{-G} = V_G^*,$$
$$H_{k',k} = V_G, \qquad H_{k',k'} = \frac{\hbar^2 k'^2}{2 m_e} + V_0.$$

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### Weak-Binding Approximation - XI

Setting determinant of matrix in (50) to zero, we get

$$E = \frac{1}{2} \left[ \frac{\hbar^2 k^2}{2 m_e} + \frac{\hbar^2 k'^2}{2 m_e} \right] + V_0 \pm \frac{1}{2} \sqrt{\left[ \frac{\hbar^2 k^2}{2 m_e} - \frac{\hbar^2 k'^2}{2 m_e} \right]^2} + 4 |V_G|^2$$

• At Brillouin zone boundary, we have |k| = |k'| = G/2, and

$$E = \frac{\hbar^2 k^2}{2 m_e} + V_0 \pm |V_G|.$$

- ▶ Thus, energies of two strongly-mixed states at zone boundary are split about average value,  $\hbar^2 k^2/2 m_e + V_0$ , by energy separation  $2|V_G|$ .
- Energy separation is known as band-gap, because it separates two free-electron bands,

## Weak-Binding Approximation - XII

 Figure shows band-gap induced between first and second bands.



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# Weak-Binding Approximation - XIII

- ► Consider one-dimensional crystal with one electron per unit cell; that is, η = 1.
- ► According to (44), normalized Fermi energy is  $\hat{E}_F = 0.25$ . Hence, first band is half-full.
- Consequently, exist empty states infinitesimally close in energy to highest occupied state.
- Infinitesimal increment of energy (e.g., via application of small electric field) can excite electron to one of these empty states.
- Crystal that exhibits such behavior is said to exhibit metallic behavior, and is, in fact, an electrical conductor.

# Weak-Binding Approximation - XIV

- Consider one-dimensional crystal with two electrons per unit cell; that is, η = 2.
- According to (44), normalized Fermi energy is  $\hat{E}_F = 1$ . Hence, first band is completely filled.
- Consequently, because of presence of band-gap, there are no empty states infinitesimally close in energy to highest occupied state.
- Crystal that exhibits such behavior is said to exhibit nonmetallic behavior, and is, in fact, an electrical insulator.
## Weak-Binding Approximation - XV

According to (39),

$$D(E)=\frac{2\,w(k)}{dE/dk}.$$

- ► However, clear from previous figure that dE/dk → 0 as edges of band-gap approached.
- ► Suggests that density of states, D(E), becomes infinite as edges of band-gap approached. (Obviously, D(E) = 0 inside band-gap.)

## Kronig-Penny Model - I

- As specific example, consider one-dimensional crystal in which V(x) takes form of infinite series of square wells.
- This example is known as Kronig-Penny model.
- Each square well of width d s and depth U.
- Length of primitive cell (i.e., periodicity distance) is *d*.



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### Kronig-Penny Model - II

► Only need to solve Schrödinger's equation in interval 0 ≤ x ≤ d, because if we have wavefunction, ψ<sub>E,k</sub>(x), in this interval then Block's theorem, (16), yields

$$\psi_{E,k}(x+n\,d) = \mathrm{e}^{\mathrm{i}\,k\,n\,d}\,\psi_{E,k}(x). \tag{51}$$

In interval 0 ≤ x ≤ d − s, in which V = 0, Schrödinger's equation yields

$$\frac{\hbar^2}{2m_e}\,\frac{d^2\psi_{E,k}}{dx^2}+E\,\psi_{E,k}=0.$$

Solution is

$$\psi_{E,k}(0 \le x \le d-s) = A e^{i \alpha x} + B e^{-i \alpha x}, \qquad (52)$$

where

$$\alpha = \sqrt{\frac{2 m_e E}{\hbar^2}}.$$

### Kronig-Penny Model - III

According to (51),

$$\psi_{E,k}(d \le x \le 2d - s) = \left[A e^{i\alpha(x-d)} + B e^{-i\alpha(x-d)}\right] e^{ikd},$$
(53)

In interval d − s ≤ x ≤ d, in which V = U, Schrödinger's equation yields

$$\frac{\hbar^2}{2 m_e} \frac{d^2 \psi_{E,k}}{dx^2} + (E - U) \psi_{E,k} = 0.$$

Solution is

$$\psi_{E,k}(d-s \le x \le d) = C e^{i\beta x} + D e^{-i\beta x}, \qquad (54)$$

where

$$\beta = \sqrt{\frac{2\,m_e\,(E-U)}{\hbar^2}}.$$

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#### Kronig-Penny Model - IV

Need to match ψ<sub>E,k</sub>(x), and its first derivative, at x = d − s.
 According to (52) and (54),

$$A e^{i\alpha (d-s)} + B e^{-i\alpha (d-s)} = C e^{i\beta (d-s)} + D e^{-i\beta (d-s)},$$
(55)
$$A \alpha e^{i\alpha (d-s)} - B \alpha e^{-i\alpha (d-s)} = C \beta e^{i\beta (d-s)} - D \beta e^{-i\beta (d-s)}.$$
(56)

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### Kronig-Penny Model - V

- ▶ Need to match  $\psi_{E,k}(x)$ , and its first derivative, at x = d.
- According to (53) and (54),

$$A e^{i k d} + B e^{i k d} = C e^{i \beta d} + D e^{i \beta d}, \qquad (57)$$

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$$A \alpha e^{i k d} - B \alpha e^{i k d} = C \beta e^{i \beta d} - D \beta e^{-i \beta d}.$$
 (58)

#### Kronig-Penny Model - VI

▶ Eliminating *A* and *B* between (55)–(58), we obtain

$$C(\alpha + \beta) e^{i\beta d} \left\{ e^{i[k d - \alpha (d - s) - \beta s]} - 1 \right\}$$
  
=  $D(\alpha - \beta) e^{-i\beta d} \left\{ 1 - e^{i[k d - \alpha (d - s) + \beta s]} \right\},$   
 $C(\alpha - \beta) e^{i\beta d} \left\{ e^{i[k d + \alpha (d - s) - \beta s]} - 1 \right\}$   
=  $D(\alpha + \beta) e^{-i\beta d} \left\{ 1 - e^{i[k d + \alpha (d - s) + \beta s]} \right\}.$ 

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#### Kronig-Penny Model - VII

 Eliminating C and D between previous two equations, and rearranging, we obtain dispersion relation

$$\cos(k d) = \cos[\alpha (d - s)] \cos(\beta s) - \left(\frac{\alpha^2 + \beta^2}{2 \alpha \beta}\right) \sin[\alpha (d - s)] \sin(\beta s).$$
(59)

- Dispersion relation specifies wavevector, k, as function of energy, E (because α and β are functions of E).
- If E < U then β is imaginary. In this case, more convenient to write dispersion relation in form

$$\cos(k d) = \cos[\alpha (d - s)] \cosh(|\beta| s) - \left(\frac{\alpha^2 - |\beta|^2}{2\alpha |\beta|}\right) \sin[\alpha (d - s)] \sinh(|\beta| s).$$
(60)

### Kronig-Penny Model - VIII

Adopting usual normalizations, dispersion relation becomes

$$\cos(2\pi\,\hat{k}) = F(\hat{E}),\tag{61}$$

where  $-1/2 \leq \hat{k} \leq 1/2$ , and

$$F(\hat{E}) = \cos[\hat{\alpha} (1-\hat{s})] \cos(\hat{\beta} \,\hat{s}) - \left(\frac{\hat{\alpha}^2 + \hat{\beta}^2}{2 \,\hat{\alpha} \,\hat{\beta}}\right) \sin[\hat{\alpha} (1-\hat{s})] \sin(\hat{\beta} \,\hat{s})$$
for  $\hat{E} > \hat{U}$ , and

$$F(\hat{E}) = \cos[\hat{\alpha} (1-\hat{s})] \cosh(\hat{\beta} s) - \left(\frac{\hat{\alpha}^2 - \hat{\beta}^2}{2 \,\hat{\alpha} \,\hat{\beta}}\right) \sin[\hat{\alpha} (1-\hat{s})] \sinh(\hat{\beta} \,\hat{s})$$

for  $\hat{E} < \hat{U}$ , where

$$\hat{\alpha} = \pi \hat{E}^{1/2},$$

$$\hat{\beta} = \pi |\hat{E} - \hat{U}|^{1/2},$$

$$\hat{s} = \frac{s}{d}.$$

#### Kronig-Penny Model - IX

Figure shows F(Ê) for Û = 2 and ŝ = 0.2. Given that | cos θ| ≤ 1, it is clear from (61) that some ranges of energies are disallowed. These are band-gaps.



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## Kronig-Penny Model - X

Figure shows band structure deduced from previous figure.
 Band-gaps are clearly visible.



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## Kronig-Penny Model - XI

 Can estimate band-gap sizes from previous weak-binding theory, according to which extents of band-gaps are 2 |V<sub>G</sub>|, where

$$V_G = \frac{1}{d} \int_{-d/2}^{d/2} e^{i G \times} V(x) dx,$$

and  $G = n 2\pi/d$ .

Easily seen that for Kronig-Penney model,

$$|V_G| = U \frac{|\sin(n\pi\,\hat{s})|}{n\pi}.$$

Thus, our estimate for width of *n*th band-gap (first gap separates Band 1 from Band 2, et cetera) is

$$\Delta E_n = 2 U \frac{|\sin(n\pi\,\hat{s})|}{n\pi}.$$
 (62)

## Kronig-Penny Model - XII

- ▶ Note that, in general,  $\Delta E_n$  decreases with increasing *n*.
- In other words, high-order band-gaps tend to be smaller in extent than low-order band-gaps.

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## Kronig-Penny Model - XIII

- Note that each band still contains 2 N electron states (because this property is determined by the extent of band in k-space, which has not changed).
- If there are η electron per unit cell then normalized Fermi wavevector is k̂<sub>F</sub> = η/4.

Defining

$$\int_0^{\hat{E}_F} \hat{\mathcal{D}}(\hat{E}) \, d\hat{E} = \eta \, N,$$

where  $\hat{D}(\hat{E})$  is normalized density of states, and  $\hat{E}_F$  is normalized Fermi energy, it follows that

$$\hat{D}(\hat{E}) = rac{4 N}{d\hat{E}/d\hat{k}}.$$

## Kronig-Penny Model - XIV

Figure shows density of states deduced from previous figure. Can be seen that density of states approximates that predicted by free-electron theory in middle of bands, goes to infinity at edges of band-gaps, and is zero within band-gaps.



## Two-Dimensional Crystals - I

- Let us consider two-dimensional crystals.
- ► For sake of definiteness, and simplicity, we restrict our attention to a two-dimensional crystal with a square lattice of interatomic spacing *d*.
- Reciprocal lattice is also square, with grid spacing  $2\pi/d$ .
- Suppose that crystal lies in x-y plane with its symmetry axes aligned with coordinate axes.

#### Two-Dimensional Crystals - II

 Figure shows first four Brillouin zones of square lattice in extended-zone scheme. (Red: Zone 1; Blue: Zone 2; Green: Zone 3; Magenta: Zone 4.)



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## Two-Dimensional Crystals - III

- Note that, in previous figure, there are lines along which two zones touch. As before, in weak-binding approximation, would expect strong mixing of two states along such lines, giving rise to band-gaps.
- There are also corners along which four zones touch. By analogy, in weak-binding approximation, would expect strong mixing of four states at such points.

## Two-Dimensional Crystals - IV

- Let us commence our analysis by adopting free-electron approximation.
- Wavevector of electron is written

$$\mathbf{k}=k_{x}\,\mathbf{e}_{x}+k_{y}\,\mathbf{e}_{y}.$$

Energy of electron is

$$E = \frac{\hbar^2 k^2}{2 m_e}.$$
 (63)

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In terms of standard normalizations,

$$\hat{E} = 4\,\hat{k}^2 = 4\,(\hat{k}_x^2 + \hat{k}_y^2).$$

#### Two-Dimensional Crystals - V

In extended-zone scheme, constant energy contours are circles in reciprocal space.



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## Two-Dimensional Crystals - VI

 In restricted-zone scheme, need to map sections of higher Brillouin zones into first Brillouin zone. Each section transports its constant energy contours.



## Two-Dimensional Crystals - VII

 Constant energy contours in first Brillouin zone are, unsurprisingly, circles. Lowest energy state lies at center of zone.



### Two-Dimensional Crystals - VIII

 Constant energy contours in second Brillouin zone are arcs of circles. Highest energy state lies at center of zone.



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### Two-Dimensional Crystals - IX

Constant energy contours in third Brillouin zone are more convoluted. Highest energy state lies at center of zone.



### Two-Dimensional Crystals - X

Constant energy contours in fourth Brillouin zone are really convoluted. Highest energy state lies at center of zone.



# Two-Dimensional Crystals - XI

An alternative way of visualizing energies of Brillouin zones is to plot energies along a path in reciprocal space. Conventional path is shown below. It starts from center of first Brillouin zone, goes to edge of zone, runs along edge until it get to corner, and goes back to center.



#### Two-Dimensional Crystals - XII

Figure shows band energies as function of path length along path show in previous slide. Red, blue, yellow vertical lines indicate points  $(\hat{k}_x, \hat{k}_y) = (0, 0), (1/2, 0), (1/2, 1/2)$ , respectively.



#### Two-Dimensional Crystals - XIII

- Let N denote number of primitive unit cells in crystal.
- ► Let w(k) dk<sub>x</sub> dk<sub>y</sub> be number of states whose wavevectors lie between k<sub>x</sub> and k<sub>x</sub> + dk<sub>x</sub> and k<sub>y</sub> and k<sub>y</sub> + dk<sub>y</sub>.
- Area of first Brillouin zone is  $(2\pi/d)^2$ .
- Know that there are N distinct spatial states—and, hence, 2 N, distinct electron states—in first Brillouin zone.
- Hence,

$$w(\mathbf{k}) = \frac{2N}{(2\pi/d)^2} = \frac{2Nd^2}{(2\pi)^2}.$$
 (64)

## Two-Dimensional Crystals - XIV

- ► Let  $\mathcal{D}(E) dE$  be number of distinct electron states whose energies lie between E and E + dE.
- In two dimensions, there is annular area in k-space, 2π k dk, corresponding to energy interval dE.
- Thus,

 $\mathcal{D}(E) dE = w(\mathbf{k}) 2\pi k dk,$ 

or

$$\mathcal{D}(E) = w(\mathbf{k}) 2\pi k \frac{dk}{dE}.$$

Making use of (63) and (64), we obtain

$$\mathcal{D}(E) = \frac{N \, m_e \, d^2}{\pi \, \hbar^2}.\tag{65}$$

## Two-Dimensional Crystals - XV

- Note that, unlike one-dimensional case, in which D(E) ∝ E<sup>-1/2</sup>, two-dimensional density of states is independent of energy.
- ▶ (65) includes contributions from all bands.
- Let  $D^{(n)}(E)$  be density of states in *n*th band.
- ► Given that density of states is uniform in k-space, D<sup>(n)</sup>(E) dE is proportional to area of annular region of radius k(E) and thickness dk = (dk/dE) dE that lies in nth Brillouin zone. Area of part of annular region proportional to product of its infinitesimal thickness and its arc length.
- Hence,

$$\mathcal{D}^{(n)}(E) = f_n(E) \mathcal{D}(E).$$
(66)

where  $f_n(E)$  is fraction of circumference of circle of radius  $k(E) = \sqrt{2 m_e E/\hbar^2}$  that lies in *n*th Brillouin zone.

## Two-Dimensional Crystals - XVI

 Perusal of Brillouin zone diagram leads to schematic density of states diagram shown below.



## Two-Dimensional Crystals - XVII

- In one dimension, various bands do not overlap in energy (even in free-electron approximation).
- In two dimensions, bands overlap in energy.
- Expect all electron states whose energy is less than Fermi energy, *E<sub>F</sub>*, to be occupied.
- ► All of these states lie within Fermi surface in reciprocal space.

In free-electron approximation, Fermi surface is a circle of radius k<sub>F</sub>, where k<sub>F</sub> is Fermi wavevector.

## Two-Dimensional Crystals - XVIII

- Suppose that there are  $\eta$  electrons per unit cell.
- Region within Fermi surface must contain  $\eta N$  electron states.
- ► So,

$$\pi k_F^2 w(\mathbf{k}) = \eta N,$$

where we have made use of fact that  $w(\mathbf{k})$  is uniform.

Using (64), we obtain

$$k_F = \sqrt{rac{\eta}{2\pi}} rac{2\pi}{d}$$

Fermi energy is

$$E_F = \frac{\hbar^2 k_F^2}{2 m_e} = \frac{\eta}{2\pi} \frac{\hbar^2}{2 m_e} \left(\frac{2\pi}{d}\right)^2.$$

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## Two-Dimensional Crystals - XIX

In terms of usual normalizations,

$$\hat{k}_F = \sqrt{rac{\eta}{2\pi}},$$
  
 $\hat{E}_F = rac{2\eta}{\pi}.$ 

#### Two-Dimensional Crystals - XX

Figure shows Fermi surfaces (in free-electron approximation) for η = 1, 2, 3, 4, 5, and 6.



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#### Two-Dimensional Crystals - XXI

Figure shows Fermi surfaces (in free-electron approximation) in first Brillouin zone. Black, red, green surfaces correspond to η = 1, 2, 3. Occupied states lie inside surfaces and boundary.



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## Two-Dimensional Crystals - XXII

Figure shows Fermi surfaces (in free-electron approximation) in second Brillouin zone. Red, green, blue, yellow, cyan surfaces correspond to η = 2, 3, 4, 5, 6. Occupied states lie between surfaces and boundary.



## Two-Dimensional Crystals - XXIII

Figure shows Fermi surfaces (in free-electron approximation) in third Brillouin zone. Blue, yellow, cyan surfaces correspond to η = 4, 5, 6. Occupied states lie between surfaces and boundary.



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## Two-Dimensional Crystals - XXIV

Figure shows Fermi surfaces (in free-electron approximation) in fourth Brillouin zone. Blue, yellow, cyan surfaces correspond to η = 4, 5, 6. Occupied states lie between surfaces and boundary.



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## Two-Dimensional Crystals - XXV

- First Brillouin zone is partially occupied for η < 4, and fully occupied for η ≥ 4.</p>
- Second Brillouin zone is empty for η = 1, and partially occupied for 2 ≤ η ≤ 6.
- ► Third and fourth Brillouin zones are empty for η < 4 and partially occupied for 4 ≤ η ≤ 6.</p>

## Two-Dimensional Crystals - XXVI

 In weak-binding approximation, properly normalized zeroth-order states are

$$\psi_{E,\mathbf{k}}^{(0)}(\mathbf{x}) = \frac{\mathrm{e}^{\mathrm{i}\,\mathbf{k}\cdot\mathbf{x}}}{\sqrt{A}},$$

corresponding to energy

$$E_0(\mathbf{k}) = \frac{\hbar^2 \, |\mathbf{k}|^2}{2 \, m_e}$$

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where  $A = N d^2$  is area of crystal.

### Two-Dimensional Crystals - XXVII

Matrix elements of perturbing potential are

$$V_{\mathbf{k}',\mathbf{k}} = \left\langle \frac{\mathrm{e}^{-\mathrm{i}\,\mathbf{k}'\cdot\mathbf{x}}}{\sqrt{A}} \right| V(\mathbf{x}) \left| \frac{\mathrm{e}^{\mathrm{i}\,\mathbf{k}\cdot\mathbf{x}}}{\sqrt{A}} \right\rangle.$$

Matrix elements only nonzero if

 $\mathbf{k} - \mathbf{k}' = \mathbf{G}.$ 

Denote nonzero matrix elements as

$$V_{\mathbf{G}} = \frac{1}{d^2} \int_{-d/2}^{d/2} \int_{-d/2}^{d/2} e^{i(G_x \, x + G_y \, y)} \, V(x, y) \, dx \, dy.$$

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## Two-Dimensional Crystals - XXVIII

- Strongly-mixed states are those with wavevectors close to Brillouin zone boundaries.
- ► All other states can be dealt with using perturbation theory.
- At boundary between two Brillouin zones there are two strongly-mixed states. Calculation of induced band-gap is analogous to that in one-dimensional crystal.
- At boundary between four Brillouin zones there are four strongly-mixed states.

Let us examine this case.

## Two-Dimensional Crystals - XXIX

- Consider corner of first Brillouin zone,  $\hat{\mathbf{k}} = (1/2, 1/2)$ .
- At this point, four Brillouin zones touch, so four free-electron states are strongly mixed.
- These states have normalized wavevectors

 $\hat{\mathbf{k}} = (1/2, 1/2), (1/2, -1/2), (-1/2, 1/2), (-1/2, -1/2).$ 

 Normalized reciprocal lattice translation vectors connecting these values of k are

$$\hat{\mathbf{G}} = (1,0), (0,1), (1,1), (-1,1),$$

and their negatives.

### Two-Dimensional Crystals - XXX

► If we denote normalized reciprocal lattice translation vectors as Ĝ = (m, n) then associated normalized matrix elements are

$$\hat{V}_{m,n} = \int_{-1/2}^{1/2} \int_{-1/2}^{1/2} e^{i 2\pi (m \hat{x} + n \hat{y})} \hat{V}(\hat{x}, \hat{y}) d\hat{x} d\hat{y}.$$

Let us write normalized wavefunction as normalized linear combination of four strongly-coupled states:

$$\hat{\psi}_{E}(\hat{\mathbf{x}}) = \sum_{i=1,4} a_i \, \hat{\psi}_{E,i}^{(0)}(\hat{\mathbf{x}}).$$

Here, i = 1, 2, 3, 4 corresponds to  $\hat{\mathbf{k}} = (1/2, 1/2), (1/2, -1/2), (-1/2, 1/2), (-1/2, -1/2).$ 

## Two-Dimensional Crystals - XXXI

Normalized Hamiltonian is

$$\hat{H} = -\frac{\hat{\nabla}^2}{\pi^2} + \hat{V}(\hat{x}, \hat{y}).$$
(67)

Energy eigenvalue problem yields

$$\sum_{j=1,4} \hat{H}_{ij} \, a_j = \hat{E} \, a_i, \tag{68}$$

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where

$$\hat{H}_{ij} = \left\langle \hat{\psi}_{E,i}^{(0)}(\hat{\mathbf{x}}) \middle| \hat{H} \middle| \hat{\psi}_{E,j}^{(0)}(\hat{\mathbf{x}}) \right\rangle.$$
(69)

### Two-Dimensional Crystals - XXXII

▶ (67)–(69) lead to determinant equation

$$|\hat{H}_{ij}-\hat{E}\,\delta_{ij}|=0,$$

where

$$\begin{vmatrix} 4\hat{k}^{2} - \hat{E}', & \hat{V}_{0,-1}, & \hat{V}_{-1,0}, & \hat{V}_{-1,-1} \\ \hat{V}_{0,1}, & 4\hat{k}^{2} - \hat{E}', & \hat{V}_{-1,1}, & \hat{V}_{-1,0} \\ \hat{V}_{1,0}, & \hat{V}_{1,-1}, & 4\hat{k}^{2} - \hat{E}', & \hat{V}_{0,-1} \\ \hat{V}_{1,1}, & \hat{V}_{1,0}, & \hat{V}_{0,1}, & 4\hat{k}^{2} - \hat{E}' \end{vmatrix} = 0,$$
(70)

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and  $\hat{E}' = \hat{E} - \hat{V}_{0,0}$ .

## Two-Dimensional Crystals - XXXIII

► Now,

$$\hat{V}_{m,n} = \int_{-1/2}^{1/2} \int_{-1/2}^{1/2} e^{i 2\pi (m \hat{x} + n \hat{y})} \hat{V}(\hat{x}, \hat{y}) d\hat{x} d\hat{y}.$$

However, because of square symmetry of crystal,

$$egin{aligned} \hat{V}(-\hat{x},\hat{y}) &= \hat{V}(\hat{x},\hat{y}), \ \hat{V}(\hat{x},-\hat{y}) &= \hat{V}(\hat{x},\hat{y}), \ \hat{V}(\hat{y},\hat{x}) &= \hat{V}(\hat{x},\hat{y}). \end{aligned}$$

Follows that

$$\hat{V}_{m,n} = \int_{-1/2}^{1/2} \int_{-1/2}^{1/2} \cos(2\pi \ m \ \hat{x}) \ \cos(2\pi \ n \ \hat{y}) \ \hat{V}(\hat{x}, \hat{y}) \ d\hat{x} \ d\hat{y}.$$

Two-Dimensional Crystals - XXXIV

► Hence,

$$\hat{V}_{1,0} = \hat{V}_{0,-1} = \hat{V}_{-1,0} = \hat{V}_{0,1} \equiv \hat{V}_1,$$
  
 $\hat{V}_{1,1} = \hat{V}_{1,-1} = \hat{V}_{-1,-1} = \hat{V}_{-1,1} \equiv \hat{V}_2.$ 

Thus, (70) reduces to

$$\begin{vmatrix} -\mathcal{E}, & \hat{V}_{1}, & \hat{V}_{1}, & \hat{V}_{2} \\ \hat{V}_{1}, & -\mathcal{E}, & \hat{V}_{2}, & \hat{V}_{1} \\ \hat{V}_{1}, & \hat{V}_{2}, & -\mathcal{E}, & \hat{V}_{1} \\ \hat{V}_{2}, & \hat{V}_{1}, & \hat{V}_{1}, & -\mathcal{E} \end{vmatrix} = 0,$$
(71)

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where  $\mathcal{E} = \hat{E} - \hat{V}_{0,0} - 4 \,\hat{k}^2$ .

### Two-Dimensional Crystals - XXXV

Multiplying out determinant equation (71), we obtain

 $\mathcal{E}^{4} - 2\left(2\,\hat{V}_{1}^{2} + \hat{V}_{2}^{2}\right)\mathcal{E}^{2} - 8\,\hat{V}_{1}^{2}\,\hat{V}_{2}\,\mathcal{E} + \hat{V}_{2}^{2}\left(-4\,\hat{V}_{1}^{2} + \hat{V}_{2}^{2}\right) = 0.$ 

Previous equation factorizes to give

 $(\mathcal{E} + \hat{V}_2)^2 (\mathcal{E} - \hat{V}_2 + 2 \hat{V}_1) (\mathcal{E} - \hat{V}_2 - 2 \hat{V}_1) = 0.$ 

Thus, energy eigenvalues are

$$\hat{E}_1 = 4 \,\hat{k}^2 + \hat{V}_{0,0} + \hat{V}_2 + 2 \,\hat{V}_1,$$
 (72)

$$\hat{E}_2 = 4\,\hat{k}^2 + \hat{V}_{0,0} - \hat{V}_2,\tag{73}$$

$$\hat{E}_3 = 4 \hat{k}^2 + \hat{V}_{0,0} - \hat{V}_2,$$
 (74)

$$\hat{E}_4 = 4\,\hat{k}^2 + \hat{V}_{0,0} + \hat{V}_2 - 2\,\hat{V}_1. \tag{75}$$

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### Two-Dimensional Crystals - XXXVI

- ▶ Generally speaking, we expect |V<sub>2</sub>| < |V<sub>1</sub>|. In other words, we expect matrix elements corresponding to longer G vectors to be smaller.
- ▶ Hence, (72)–(75) indicate that, in weak-binding approximation, degeneracy of energies of four Brillouin zones that meet at  $\hat{\mathbf{k}} = (1/2, 1/2)$  is lifted such that  $\hat{\mathcal{E}}_1$  and  $\hat{\mathcal{E}}_4$ straddle two remaining degenerate energies,  $\hat{\mathcal{E}}_2$  and  $\hat{\mathcal{E}}_3$ .

## Two-Dimensional Crystals - XXXVII

- Let us now try to solve general energy eigenvalue problem.
- Normalized wavefunction takes form

$$\hat{\psi}(\hat{x},\hat{y}) = \sum_{n_x,n_y} a_{n_x,n_y} e^{i 2\pi (n_x + \hat{k}_x) \hat{x}} e^{i 2\pi (n_y + \hat{k}_y) \hat{y}}$$

where  $n_{\chi}$ ,  $n_{\gamma}$  are integers.

Previous expression can also be written

$$\hat{\psi}(\hat{x}, \hat{y}) = e^{i(\hat{k}_x \, \hat{x} + \hat{k}_y \, \hat{y})} \, u(\hat{x}, \hat{y}), \tag{76}$$

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where

$$u(\hat{x},\hat{y}) = \sum_{n_x,n_y} a_{n_x,n_y} e^{i 2\pi (n_x \hat{x} + n_y \hat{y})}$$

### Two-Dimensional Crystals - XXXVIII

► (76) accords with Block theorem, because u(x̂, ŷ) is periodic function with same period of crystal: i.e., u(x̂ + 1, ŷ) = u(x̂, ŷ + 1) = u(x̂, ŷ).

Normalized Hamiltonian is

$$\hat{H}=rac{\hat{
abla}^2}{\pi^2}+\hat{V}(\hat{x},\hat{y}).$$

So, energy eigenvalue problem becomes

$$\sum_{n'_{x},n'_{y}} \hat{H}_{n_{x},n_{y};n'_{x},n'_{y}} a_{n'_{x},n'_{y}} = \hat{E} a_{n_{x},n_{y}}.$$
 (77)

Here,

$$\hat{H}_{n_x,n_y;n'_x,n'_y} = \int_{-1/2}^{1/2} \int_{-1/2}^{1/2} e^{-i 2\pi \left[ (n_x + \hat{k}_x) \,\hat{x} + (n_y + \hat{k}_y) \,\hat{y} \right]} \hat{H}$$
$$\times e^{i 2\pi \left[ (n'_x + \hat{k}_x) \,\hat{x} + (n'_y + \hat{k}_y) \,\hat{y} \right]} \, d\hat{x} \, d\hat{y}.$$

## Two-Dimensional Crystals - XXXIX

### Easily seen that

$$\hat{H}_{n_{x},n_{y};n'_{x},n'_{y}} = \hat{E}^{(0)}_{n_{y},n_{y}} \,\delta_{n_{x},n'_{x}} \,\delta_{n_{y},n'_{y}} + \hat{V}_{n_{x},n_{y};n'_{x},n'_{y}}, \tag{78}$$

#### where

$$\hat{E}_{n_y,n_y}^{(0)} = 4 \left[ (n_x + \hat{k}_x)^2 + (n_y + \hat{k}_y)^2 \right],$$
(79)

and

$$\hat{V}_{n_x,n_y;n'_x,n'_y} = \int_{-1/2}^{1/2} \int_{-1/2}^{1/2} e^{i 2\pi \left[ (n'_x - n_x) \hat{x} + (n'_y - n_y) \hat{y} \right]} \hat{V}(\hat{x}, \hat{y}) \, d\hat{x} \, d\hat{y}.$$
(80)

# Two-Dimensional Crystals - XL

 Let us implement two-dimensional Kronig-Penney model in which

$$\hat{V}(\hat{x},\hat{y}) = \begin{cases} 0 & |\hat{x}| < (1/2)(1-\hat{s}), |\hat{y}| < (1/2)(1-\hat{s}) \\ \hat{U} & \text{otherwise} \end{cases}$$
(81)

- ► Thus, each unit cell occupied by square potential well, of depth Û that occupies area fraction (1 ŝ)<sup>2</sup> of cell.
- (80) and (81) yield

# Two-Dimensional Crystals - XLI

- ► (77), (78), (79), and (82) constitute matrix eigenvalue problem that can easily be solved numerically.
- ▶ In following, show results for  $\hat{U} = 1$ ,  $\hat{s} = 0.2$ ,  $-7 \le n_x \le +7$ , and  $-7 \le n_y \le +7$ .
- Start by calculating energy eigenvalues along path in reciprocal space specified below.



## Two-Dimensional Crystals - XLII

Figure shows band energies as function of path length along path show in previous slide. Red, blue, yellow vertical lines indicate points  $(\hat{k}_x, \hat{k}_y) = (0, 0), (1/2, 0), (1/2, 1/2)$ , respectively.



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## Two-Dimensional Crystals - XLIII

- Previous figure shows induced band-gaps [e.g., between first and second band along path (1/2, 0) to (1/2, 1/2)].
- ► At point (1/2, 1/2), where four Brillouin zones touch, there are indeed two bands that straddle two degenerate bands, as predicted by our analysis.
- ► Note that, unlike in one-dimensional case, there are no values of Ê (above V̂<sub>0,0;0,0</sub>) for which no electronic states exist.

## Two-Dimensional Crystals - XLIV

 Constant energy contours in first Brillouin zone are similar to those in free-electron approximation, except that contours modified to meet zone boundaries at right-angles.



## Two-Dimensional Crystals - XLV

Likewise for second Brillouin zone.



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## Two-Dimensional Crystals - XLVI

Likewise for third Brillouin zone.



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## Two-Dimensional Crystals - XLVII

Likewise for fouth Brillouin zone.



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## Two-Dimensional Crystals - XLVIII

Figure shows Fermi surfaces in first Brillouin zone. Black, red, surfaces correspond to η = 1, 2. Occupied states lie inside surfaces and boundary.



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## Two-Dimensional Crystals - XLIX

Figure shows Fermi surfaces in second Brillouin zone. Red, green, blue, yellow, cyan surfaces correspond to η = 2, 3, 4, 5, 6. Occupied states lie between surfaces and boundary.



## Two-Dimensional Crystals - L

Figure shows Fermi surfaces in third Brillouin zone. Blue, yellow, cyan surfaces correspond to η = 4, 5, 6. Occupied states lie between surfaces and boundary.



## Two-Dimensional Crystals - LI

Figure shows Fermi surfaces in fourth Brillouin zone. Blue, yellow, cyan surfaces correspond to η = 4, 5, 6. Occupied states lie between surfaces and boundary.



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## Two-Dimensional Crystals - LII

 Figure illustrates how density of states of first four bands is modified from free-electron prediction in weak-binding approximation.

