28 Bloch theorem

Slides: Lecture 28a Periodic boundary conditions

Text reference: Quantum Mechanics for Scientists and Engineers

Section 8.2 – 8.3 (through Eq. 8.6)
The Bloch theorem

Periodic boundary conditions

Quantum mechanics for scientists and engineers

David Miller
One electron approximation

In this approximation, we presume that we can write an effective periodic potential

$$V_p(r + R_L) = V_p(r)$$

periodic with the crystal lattice periodicity and therefore

an effective, approximate Schrödinger equation for the one electron in which we are interested

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

giving our one-electron approximation
Periodicity of $|\psi|^2$

In one dimension

the crystal is periodic with “repeat length” $a$ having the same potential at $x + sa$
as it has at $x$

Here

$s$ is an integer

Similarly, any observable quantity must also have the same periodicity

because the crystal must look the same in every unit cell
Consequences of periodicity of $|\psi|^2$

For example charge density $\rho \propto |\psi|^2$

must be periodic in the same way

Hence $|\psi(x)|^2 = |\psi(x + a)|^2$

which means

$\psi(x + a) = C\psi(x)$

where $C$ is a unit amplitude complex number

Note that there is no requirement that the wavefunction itself is periodic with the crystal periodicity

since it is not apparently an observable or measurable quantity
Periodic boundary conditions

In one dimension, we could argue as follows:

Suppose we have a long chain of $N$ equally spaced atoms and that we join the two ends of the chain together.

$N = 12$
Periodic boundary conditions

With $x$ as the distance along this loop, then on this loop, the potential can be written

$$V_P(x + ma) = V_P(x)$$

where $m$ is any integer, even possibly an integer much larger than $N$. 

$N = 12$
Periodic boundary conditions

This expression $V_P(x + ma) = V_P(x)$ is just like the one for the infinite crystal.

If this chain is very long, its internal properties will not be substantially different from an infinitely long chain. So this is a good model that gives us a finite system while keeping it periodic.

$N = 12$
Periodic boundary conditions

This loop gives a boundary condition

We do want the wavefunction to be single-valued

otherwise how could we differentiate it, evaluate its squared modulus, etc.

So, going round the loop, we must get back to where we started

\[ \psi(x) = \psi(x + Na) \]

a “periodic boundary condition”
28 Bloch theorem

Slides: Lecture 28b Bloch theorem derivation

Text reference: Quantum Mechanics for Scientists and Engineers

Section 8.3 (from Eq. 8.7)
The Bloch theorem

Bloch theorem derivation

Quantum mechanics for scientists and engineers

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Bloch theorem derivation

If we take this “single value” requirement $\psi(x) = \psi(x + Na)$ and combine it with the required periodicity of a measurable quantity like probability density

$$|\psi(x)|^2 = |\psi(x + a)|^2$$

which we deduced implied that $\psi(x + a) = C\psi(x)$

where $C$ is a unit complex number

then $\psi(x) = \psi(x + Na) = C^N \psi(x)$

so $C^N = 1$

Hence, $C$ is one of the $N$ “$N$th roots of unity”, e.g.,

$C = \exp\left(\frac{2\pi is}{N}\right); \ s = 0, 1, 2, \ldots N - 1$
Bloch theorem derivation

Substituting $C$ from

$$C = \exp \left( \frac{2\pi is}{N} \right); \; s = 0, 1, 2, \ldots N - 1$$

in

$$\psi(x) = \psi(x + Na) = C^N \psi(x)$$

gives

$$\psi(x + a) = \exp(ika) \psi(x)$$

where

$$k = \frac{2\pi s}{Na}; \; s = 0, 1, 2, \ldots N - 1$$
 bloch theorem derivation

though the form $C = \exp(2\pi is / N); s = 0, 1, 2, \ldots N - 1$ for $C$ is mathematically common, it is not unique

we can choose any consecutive set of $N$ values of the integer $s$

and end up with the same set of possible values for $C$, just in a different order

remember, for any integer $m$

$\exp(0) = \exp(2\pi i) = \exp(2m\pi i) = 1$

so the values for $C$ just keep cycling round as we keep increasing $s$
Bloch theorem derivation

We can therefore end up with correspondingly different sets of values for $k$

all of which are physically equivalent

Instead of  \[ k = \frac{2\pi s}{Na}; \ s = 0, 1, 2, \ldots N - 1 \]

we more conventionally use a symmetrical version

\[ k = \frac{2\pi n}{Na} \quad \ldots n = 0, \pm 1, \pm 2, \ldots \pm N / 2 \]

which strictly has one too many values

We should omit one of the “end values” here
Bloch theorem derivation

Note also that it makes no difference in our expression
$$\psi(x + a) = \exp(ika)\psi(x)$$
if we add \(2\pi m / a\) (where \(m\) is any integer) to \(k\)

The set of allowed values of \(\exp(ika)\)
remains the same

So we can use
$$k = \frac{2\pi n}{Na} \quad \ldots n = 0, \pm 1, \pm 2, \ldots \pm N / 2$$

or
$$k = \frac{2\pi n}{Na} + \frac{2\pi m}{a} \quad \ldots n = 0, \pm 1, \pm 2, \ldots \pm N / 2$$

This point will have a specific significance later in "extended zone" schemes.
The wavefunction in a (one-dimensional) crystal with $N$ unit cells of length $a$ can be written in the form
\[ \psi(x + a) = \exp(ika)\psi(x) \]
subject to the condition
\[ k = \frac{2\pi n}{Na} \quad \text{...} n = 0, \pm 1, \pm 2, \ldots \pm N / 2 \]

Note the allowed $k$ values are evenly spaced by $2\pi / L$
where $L = Na$ is the length of the crystal (loop)
regardless of the detailed form of the periodic potential
Bloch theorem – alternative (equivalent) statement

Multiply $\psi(x + a) = \exp(ika)\psi(x)$ by $\exp(-ik(x + a))$

to obtain $\psi(x + a)\exp(-ik(x + a)) = \psi(x)\exp(-ikx)$

Hence if we define a function

$$u(x) = \psi(x)\exp(-ikx)$$

we have $u(x + a) = u(x)$

Hence $u(x)$ is periodic with the lattice periodicity

Equivalently, $u(x)$ is a function that is the same in every unit cell

Rearranging gives $\psi(x) = u(x)\exp(ikx)$
The wavefunction in a (one-dimensional) crystal with \( N \) unit cells of length \( a \) can be written in the form

\[
\psi(x) = u(x) \exp(ikx)
\]

where \( u(x) \) is the same in every unit cell subject to the condition

\[
k = \frac{2\pi n}{Na} \quad \text{...} n = 0, \pm 1, \pm 2, \ldots \pm N/2
\]
Bloch theorem – equivalence of statements

Note that the two forms
\[ \psi(x) = u(x) \exp(i k x) \quad \text{and} \quad \psi(x + a) = \exp(i k a) \psi(x) \]
are entirely equivalent

We derived the “left” from the “right” one
and we can derive the “right” one from the “left” one

From the “left” form, we have
\[ \psi(x + a) = u(x + a) \exp[i k (x + a)] = u(x) \exp[i k (x + a)] \]
\[ = \exp(i k a) u(x) \exp(i k x) = \exp(i k a) \psi(x) \]
which is the “right” form
We can think of the $\exp(ikx)$ as an “envelope” function multiplying the unit cell function $u(x)$.
28 Bloch theorem

Slides: Lecture 28c Density of states in k-space

Text reference: Quantum Mechanics for Scientists and Engineers

Section 8.4
The Bloch theorem

Density of states in k-space
Bloch theorem in three dimensions

To construct the Bloch theorem in three dimensions we propose a straightforward extension from 1-D. We have

\[ \psi(r + a) = \exp(ik \cdot a) \psi(r) \]

where \( a \) is any crystal lattice vector, or equivalently

\[ \psi(r) = u(r) \exp(ik \cdot r) \]

and \( u(r) \) is the same in every unit cell, i.e.,

\[ u(r + a) = u(r) \]
Bloch theorem in three dimensions

With the three crystal basis vector directions 1, 2, and 3 with lattice constants (repeat distances) $a_1$, $a_2$, and $a_3$ and numbers of atoms $N_1$, $N_2$, and $N_3$

$$k_1 = \frac{2\pi n_1}{N_1 a_1} \quad \ldots \quad n_1 = 0, \pm 1, \pm 2, \ldots \pm N_1 / 2$$

and similarly for the other two components of $k$ in the other two crystal basis vector directions

Note that the number of possible values of $k$ is the same as the number of unit cells in the crystal (formally dropping the $k$ values at one end or the other)
Reciprocal lattice

We see that the allowed values of $k_1$, $k_2$, and $k_3$ are each equally spaced, with separations

$$\delta k_1 = \frac{2\pi}{N_1 a_1} = \frac{2\pi}{L_1}, \quad \delta k_2 = \frac{2\pi}{N_2 a_2} = \frac{2\pi}{L_2}, \quad \text{and} \quad \delta k_3 = \frac{2\pi}{N_3 a_3} = \frac{2\pi}{L_3}$$

respectively along the three axes

where the lengths of the crystal along the three axes are respectively

$$L_1 = N_1 a_1, \quad L_2 = N_2 a_2, \quad L_3 = N_3 a_3$$
Reciprocal lattice

We could draw a three-dimensional diagram with axes $k_1$, $k_2$, and $k_3$ and mark the allowed values of $k$.

This set of dots themselves constitutes a mathematical lattice.

This kind of lattice is one kind of “reciprocal lattice”.
Density of states in $k$-space

We imagine each point has a volume surrounding it, with these volumes touching one another to completely fill all the space.
Density of states in $k$-space

We imagine each point has a volume surrounding it with these volumes touching one another to completely fill all the space.

For our cubic lattices, we can define

\[ \delta k_1 \]

\[ \delta k_2 \]
Density of states in $k$-space

We imagine each point has a volume surrounding it with these volumes touching one another to completely fill all the space.

For our cubic lattices, we can define

$$\delta k_1 = \frac{2\pi}{L_1}$$
Density of states in $k$-space

We imagine each point has a volume surrounding it with these volumes touching one another to completely fill all the space.

For our cubic lattices, we can define

$$\delta k_1 = \frac{2\pi}{L_1} \quad \delta k_2 = \frac{2\pi}{L_2} \quad \delta k_3 = \frac{2\pi}{L_3}$$
Density of states in $k$-space

For our cuboidal lattices, these volumes in $k$-space will be of size

$$\delta V_k = \delta k_1 \delta k_2 \delta k_3$$

i.e.,

$$\delta V_k = \frac{2\pi}{L_1} \frac{2\pi}{L_2} \frac{2\pi}{L_3}$$

Since the crystal is $V = L_1 L_2 L_3$, the $k$-space "volume" round each point is

$$\delta V_k = \frac{(2\pi)^3}{V}$$
Density of states in $k$-space

With this specific $k$-space "volume" $\delta V_k = \frac{(2\pi)^3}{V}$ round each point in $k$-space, we could define a "density of states in $k$-space"

$$\frac{1}{\delta V_k} = \frac{V}{(2\pi)^3}$$
Density of states in $k$-space

This density of states in $k$-space

$$\frac{1}{\delta V_k} = \frac{V}{(2\pi)^3}$$

is $\propto$ crystal volume $V$

So, more commonly, we define

a “density of states in $k$-space per unit (real space) volume”

$$g(k) = \frac{1}{(2\pi)^3}$$

for quantum mechanical calculations in crystals