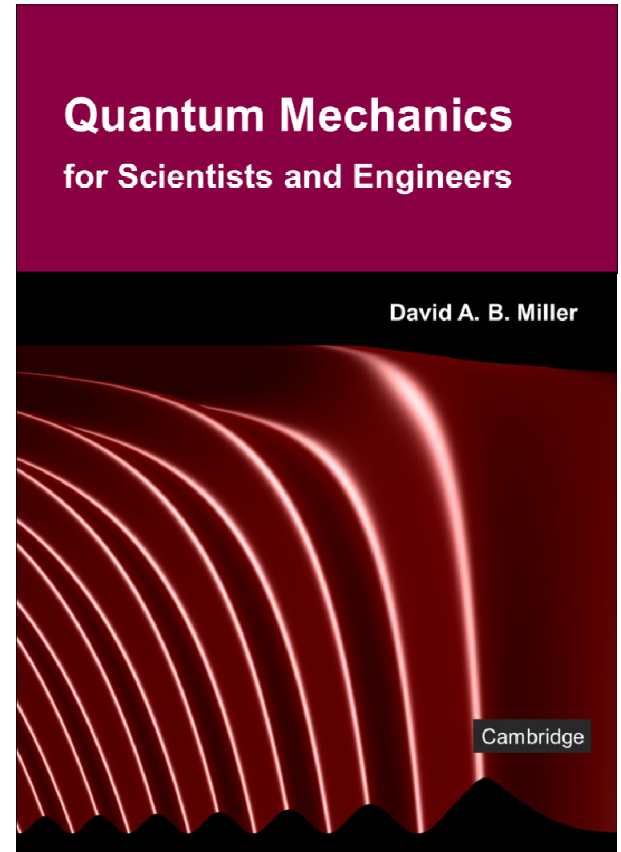


28 Bloch theorem

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

$$V_P(\mathbf{r} + \mathbf{R}_L) = V_P(\mathbf{r})$$

periodic with the crystal lattice periodicity

and therefore

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

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

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

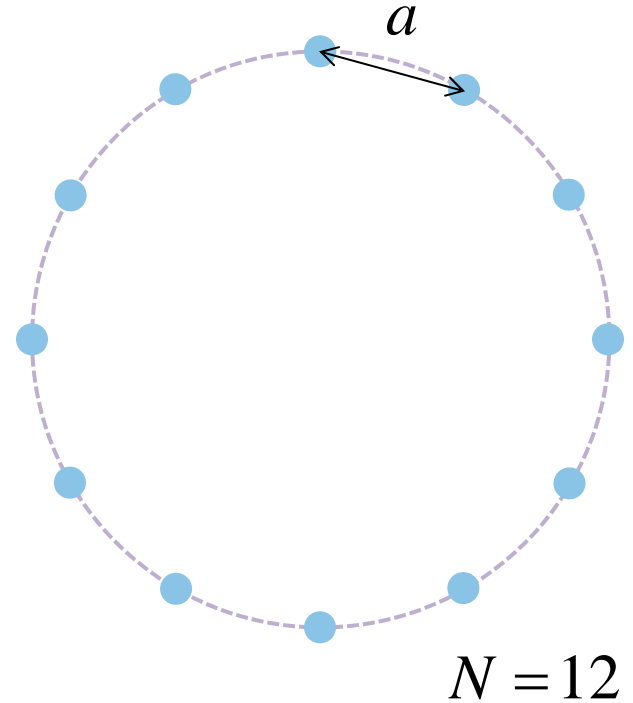
since it is not apparently an observable or measurable quantity

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



Periodic boundary conditions

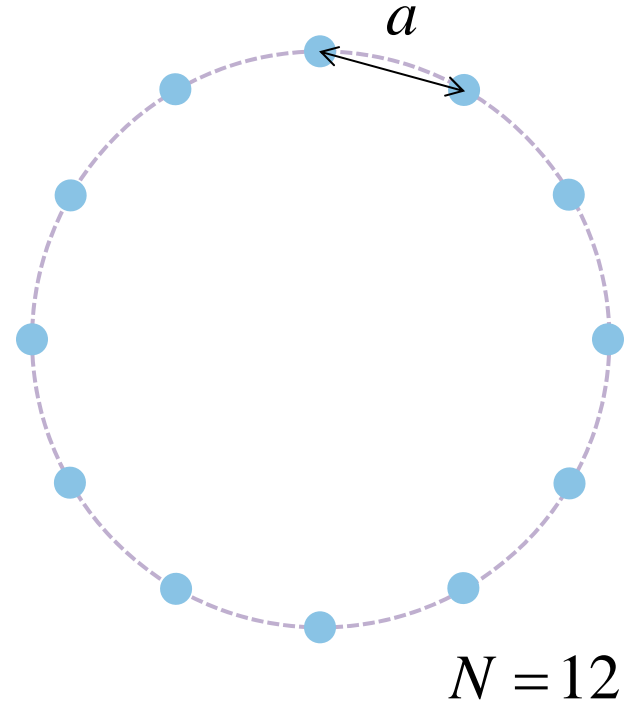
With x as the distance along this loop

then on this loop, the potential can be written

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

where m is any integer

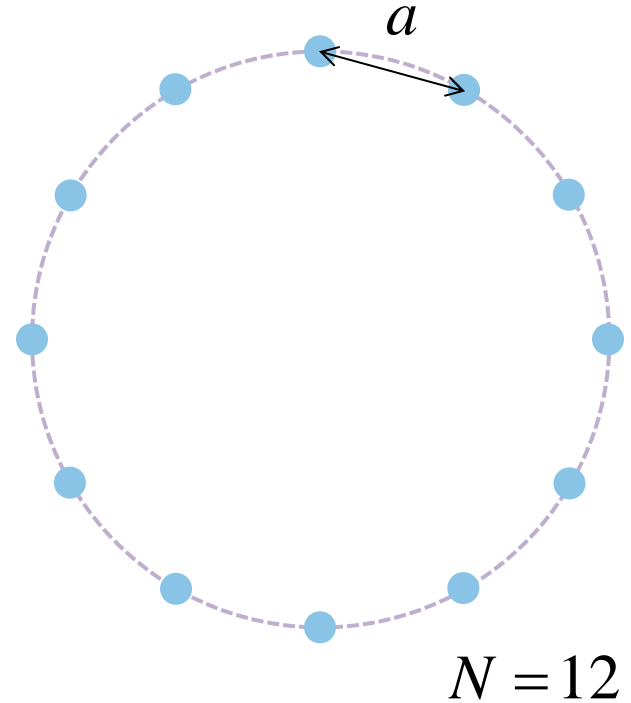
even possibly an integer much larger than N



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



Periodic boundary conditions

This loop gives a boundary condition

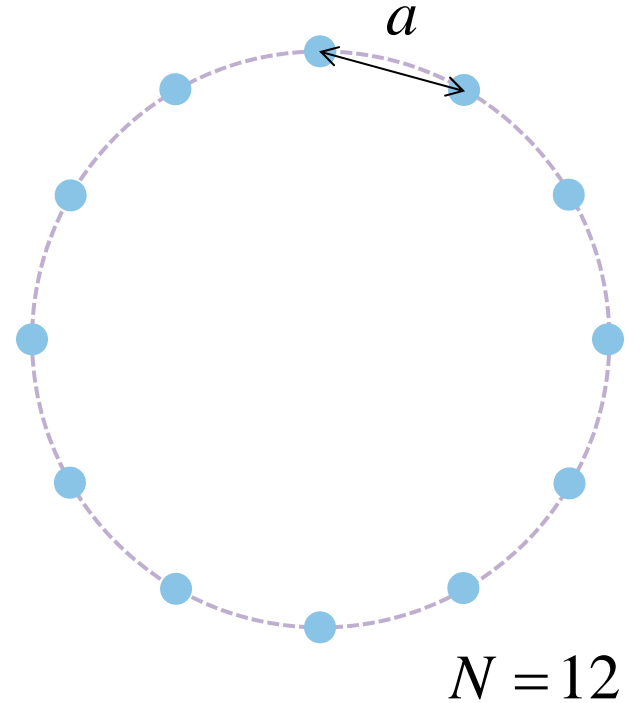
We do want the wavefunction to be single-valued

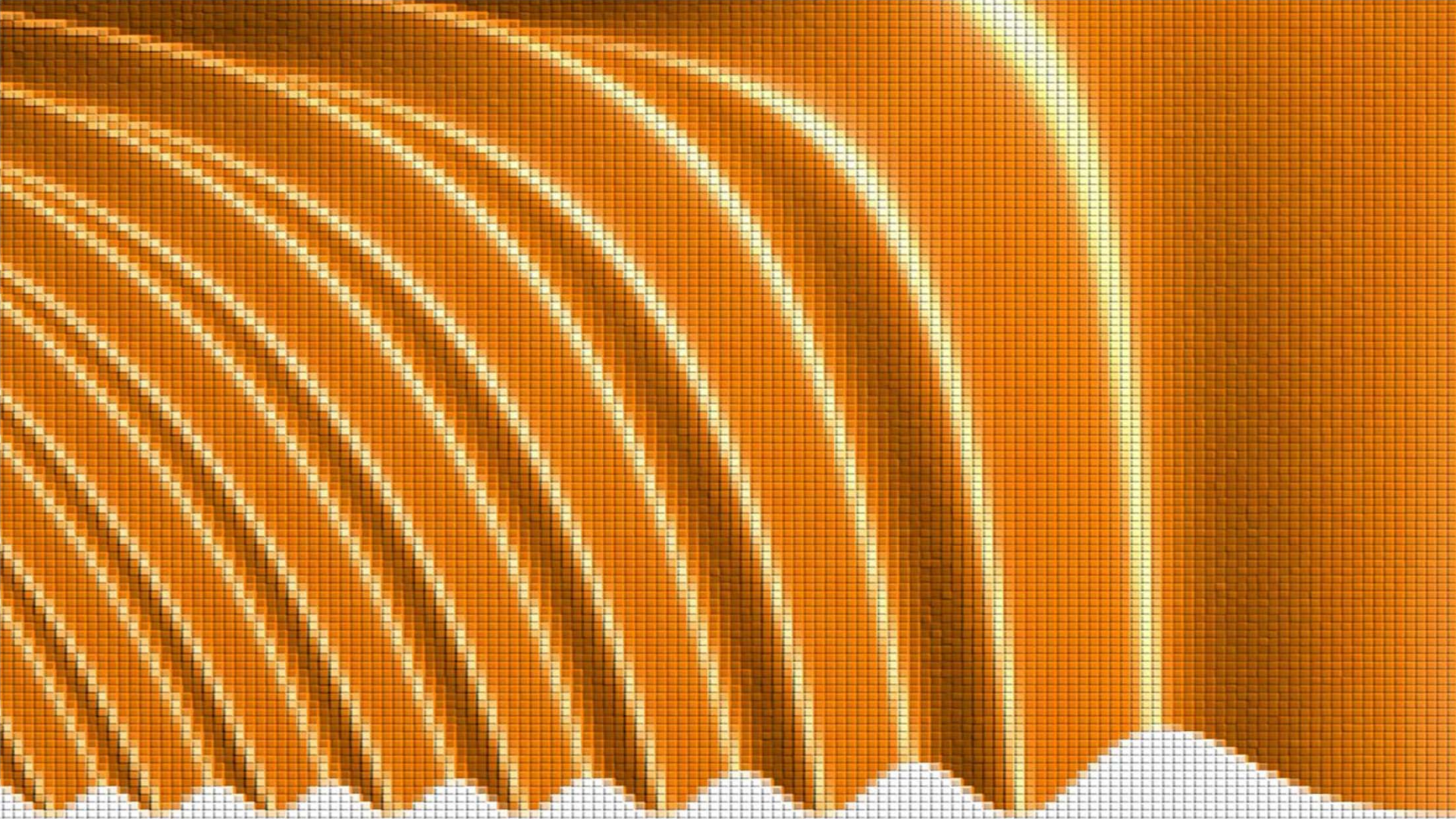
otherwise how could we differentiate it, evaluate its squared modulus, etc.

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

$$\psi(x) = \psi(x + Na)$$

a “periodic boundary condition”



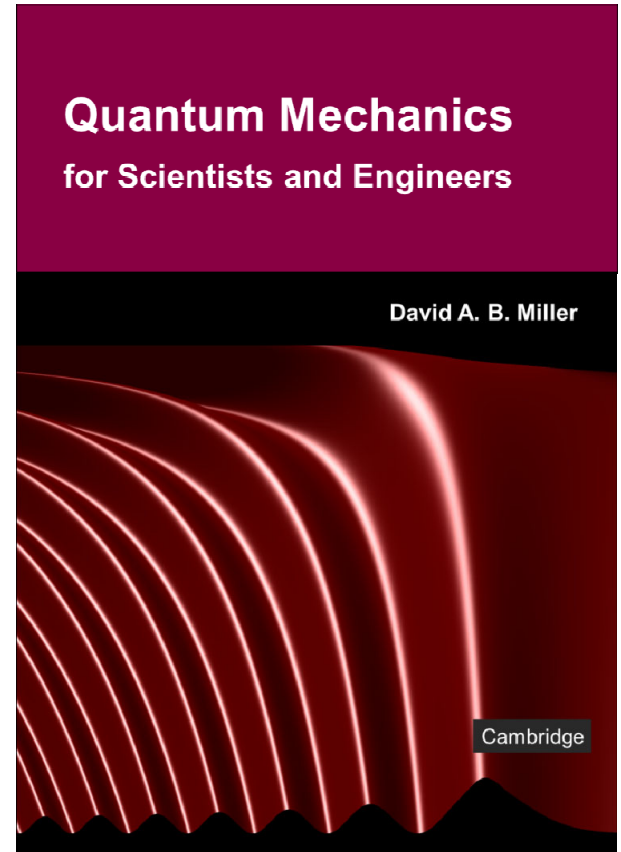


28 Bloch theorem

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

David Miller

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.,

$$C = \exp(2\pi i s / N); s = 0, 1, 2, \dots, N - 1$$

Bloch theorem derivation

Substituting C from

$$C = \exp(2\pi i s / N); s = 0, 1, 2, \dots, N-1$$

in

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

gives

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

where

$$k = \frac{2\pi s}{Na}; s = 0, 1, 2, \dots, N-1$$

Bloch theorem derivation

Though the form $C = \exp(2\pi i s / N)$; $s = 0, 1, 2, \dots, N-1$

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 $k = \frac{2\pi s}{Na}; s = 0, 1, 2, \dots, N-1$

we more conventionally use a symmetrical version

$$k = \frac{2\pi n}{Na} \quad \dots n = 0, \pm 1, \pm 2, \dots, \pm N/2$$

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 $k = \frac{2\pi n}{Na} \dots n = 0, \pm 1, \pm 2, \dots \pm N/2$

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

This point will have a specific significance later in "extended zone" schemes

Bloch theorem – one statement

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

$$k = \frac{2\pi n}{Na} \quad \dots n = 0, \pm 1, \pm 2, \dots \pm N/2$$

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

Bloch theorem – equivalent statement

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

$$k = \frac{2\pi n}{Na} \quad \dots n = 0, \pm 1, \pm 2, \dots \pm N/2$$

Bloch theorem –equivalence of statements

Note that the two forms

$$\psi(x) = u(x)\exp(ikx) \text{ and } \psi(x+a) = \exp(ika)\psi(x)$$

are entirely equivalent

We derived the “left” from the “right” one

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

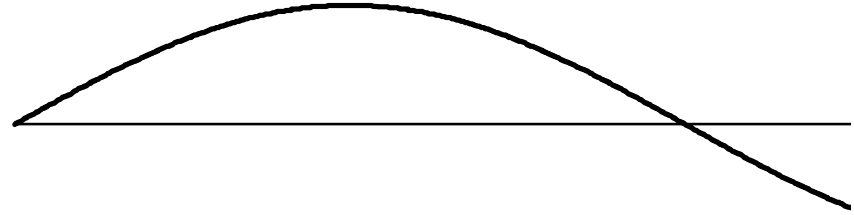
From the “left” form, we have

$$\begin{aligned}\psi(x+a) &= u(x+a)\exp[ik(x+a)] = u(x)\exp[ik(x+a)] \\ &= \exp(ika)u(x)\exp(ikx) = \exp(ika)\psi(x)\end{aligned}$$

which is the “right” form

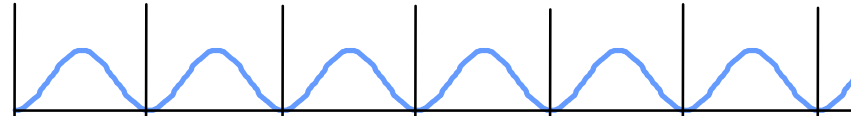
Bloch theorem visualization

envelope

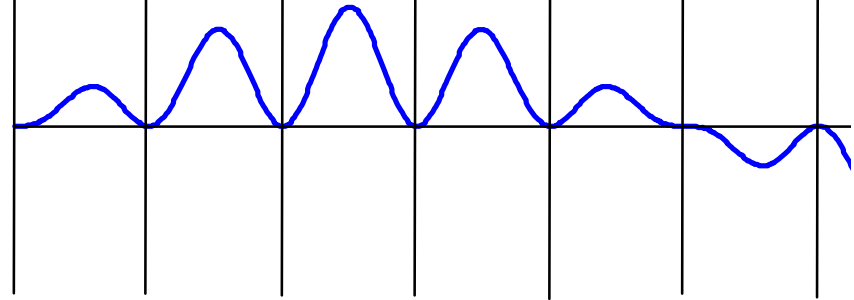


Visualization of
the real part of
the wavefunction

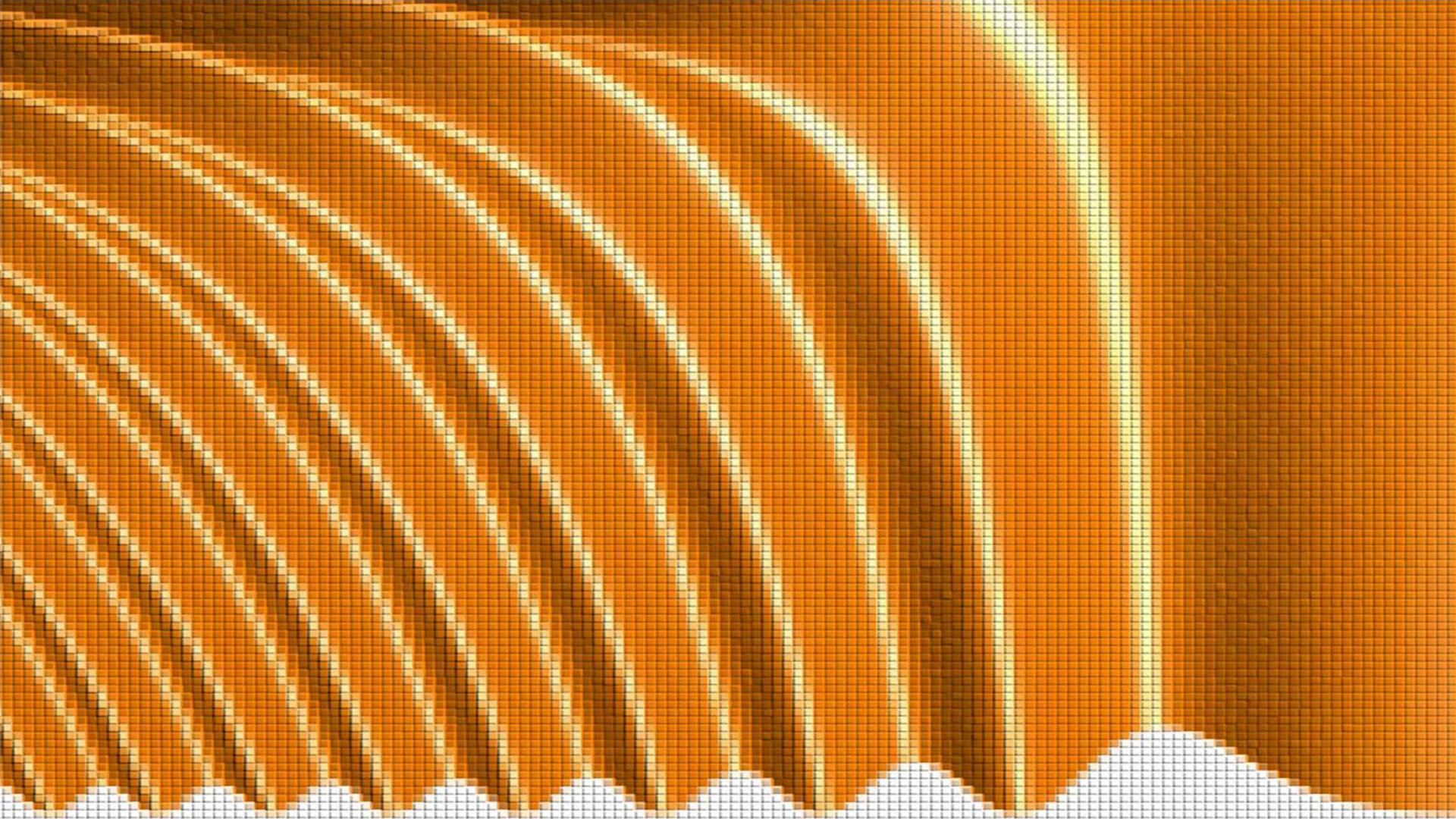
unit cell function



Bloch function



We can think of the $\exp(ikx)$ as an “envelope”
function multiplying the unit cell function $u(x)$

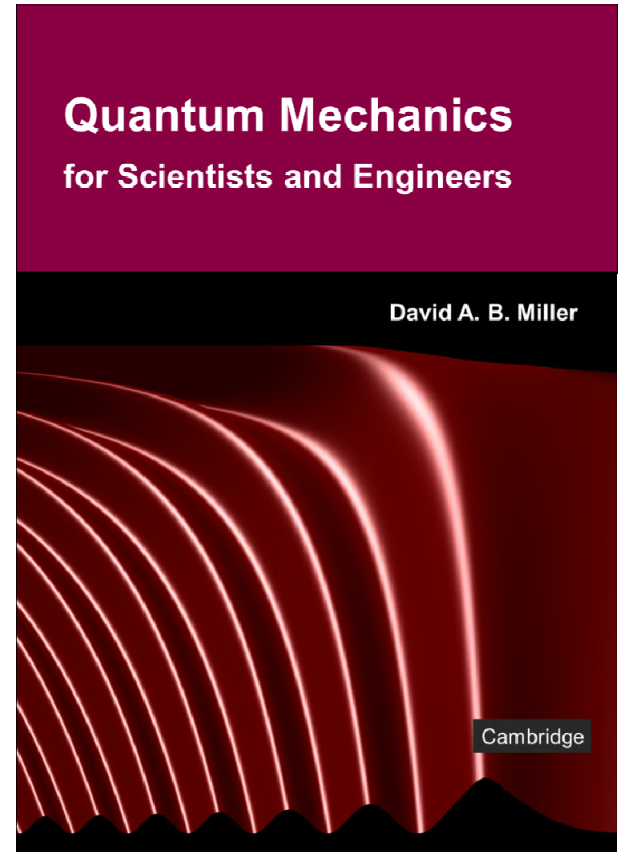


28 Bloch theorem

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

Quantum mechanics for scientists and engineers

David Miller

Bloch theorem in three dimensions

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

We have

$$\psi(\mathbf{r} + \mathbf{a}) = \exp(i\mathbf{k} \cdot \mathbf{a})\psi(\mathbf{r})$$

where \mathbf{a} is any crystal lattice vector

or equivalently

$$\psi(\mathbf{r}) = u(\mathbf{r})\exp(i\mathbf{k} \cdot \mathbf{r})$$

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

$$u(\mathbf{r} + \mathbf{a}) = u(\mathbf{r})$$

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

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

and similarly for the other two components of \mathbf{k} in
the other two crystal basis vector directions

Note that the number of possible values of \mathbf{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

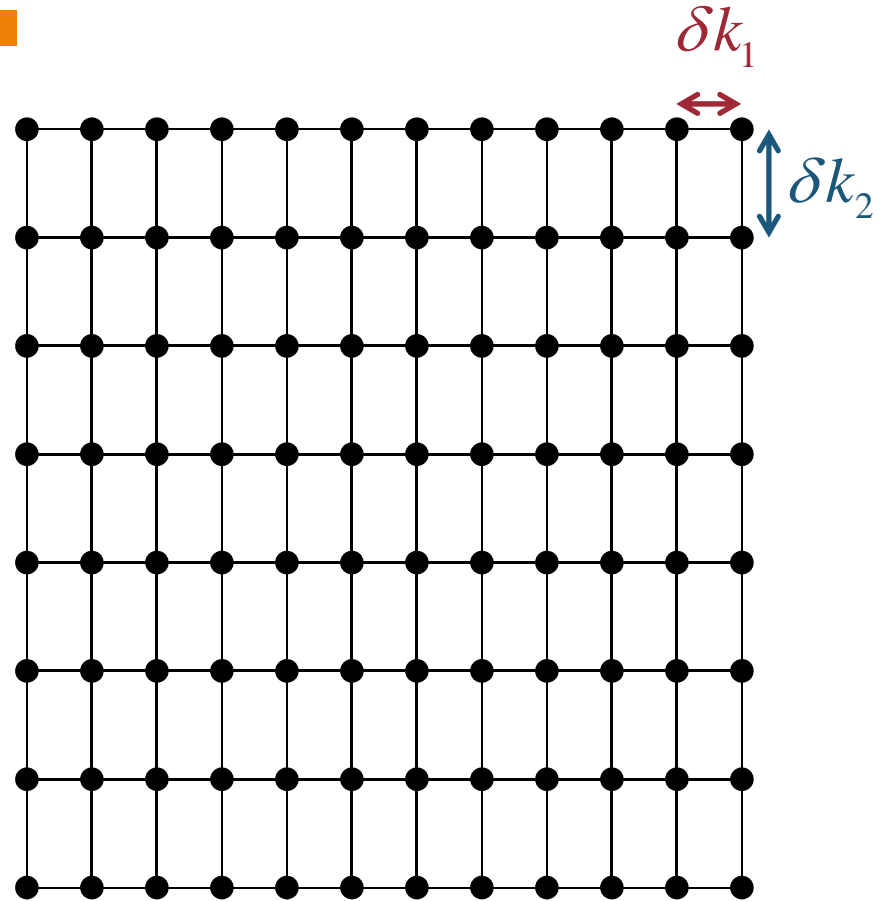
$$L_1 = N_1 a_1, \quad L_2 = N_2 a_2, \quad L_3 = N_3 a_3$$

Reciprocal lattice

We could draw a three-dimensional diagram with axes k_1 , k_2 , and k_3 and mark the allowed values of \mathbf{k}

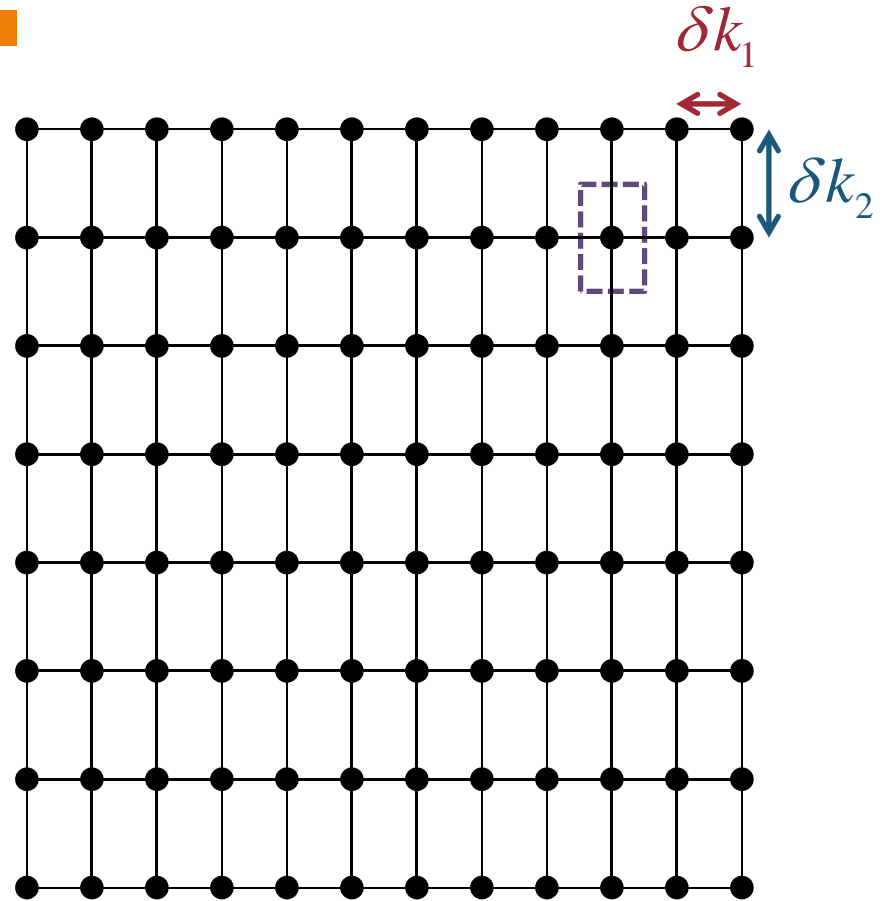
This set of dots themselves constitutes a mathematical lattice

This kind of lattice is one kind of "reciprocal lattice"



Density of states in k -space

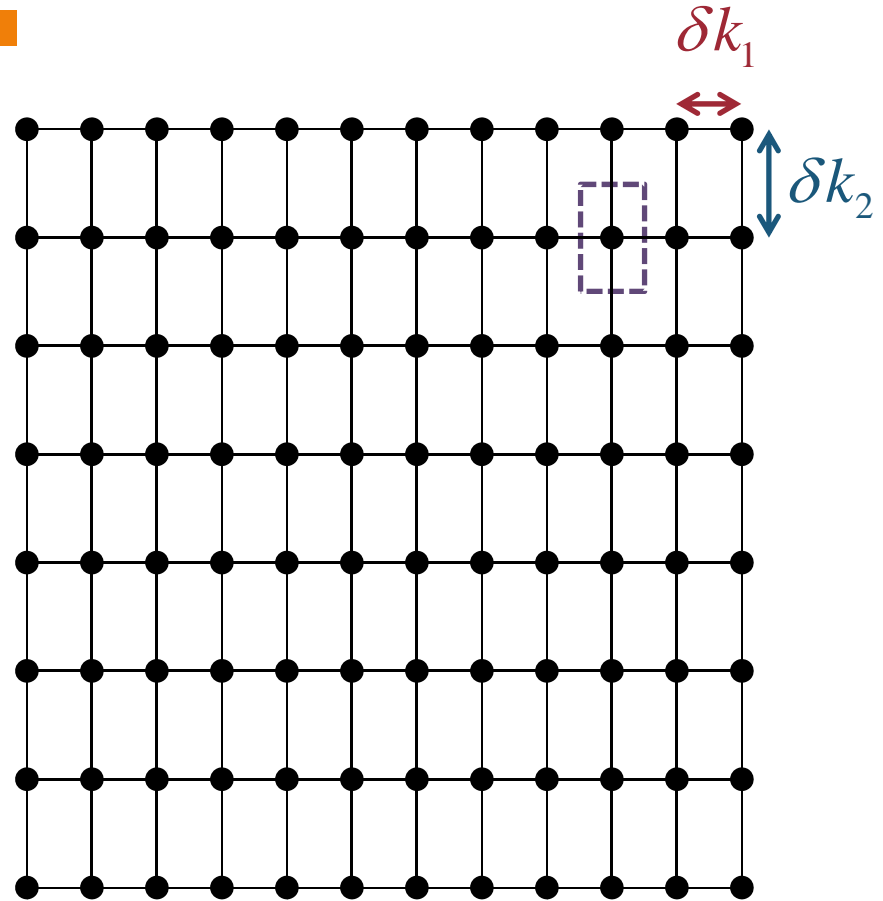
We imagine each point has a volume surrounding it
with these volumes touching
one another to completely
fill all the space



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

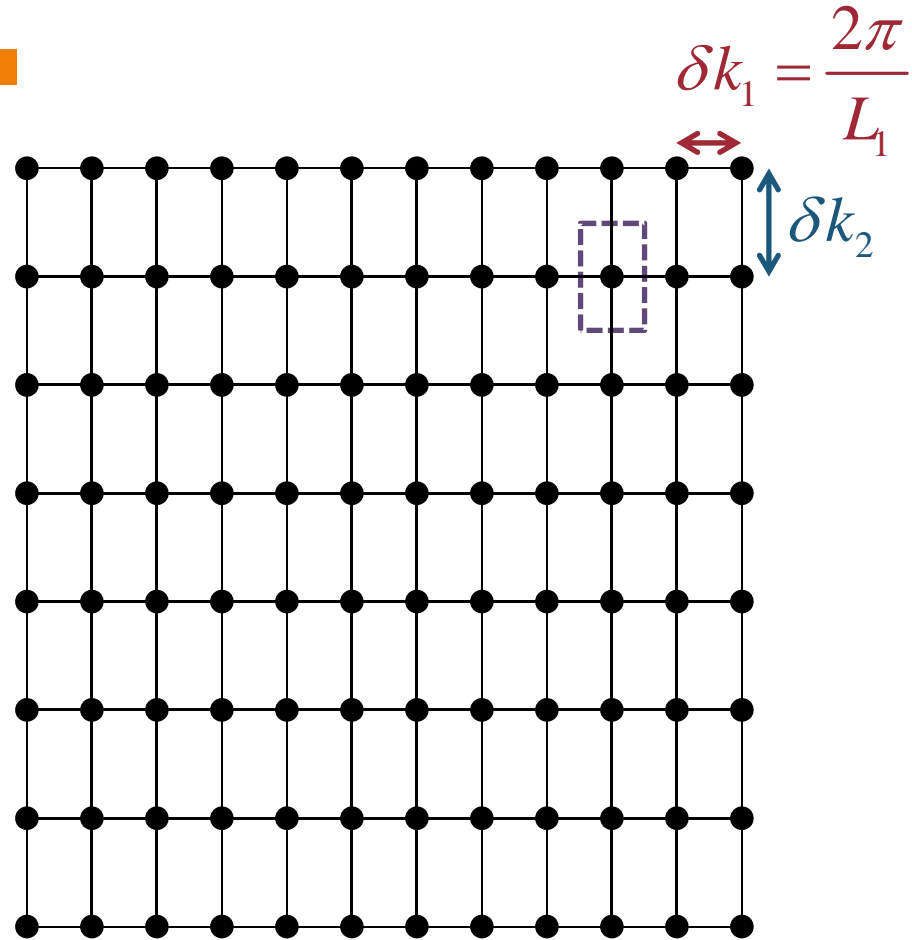


Density of states in k -space

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

$$\delta k_1 = \frac{2\pi}{L_1}$$

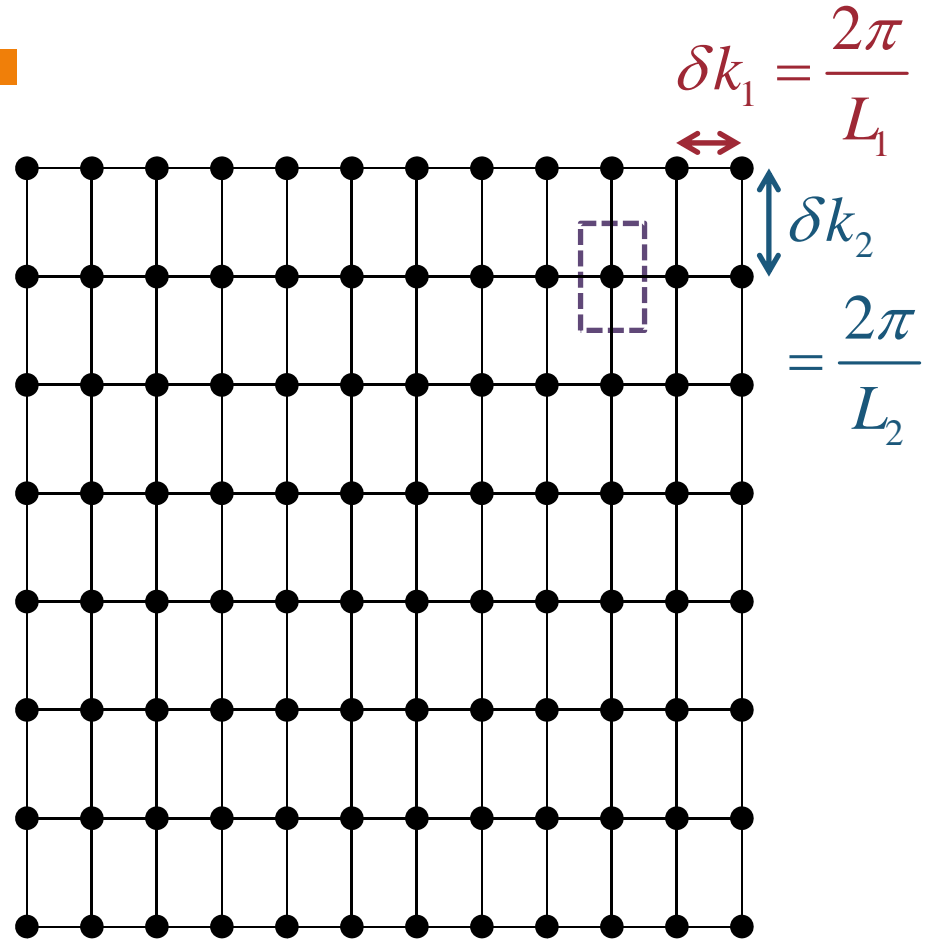


Density of states in k -space

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

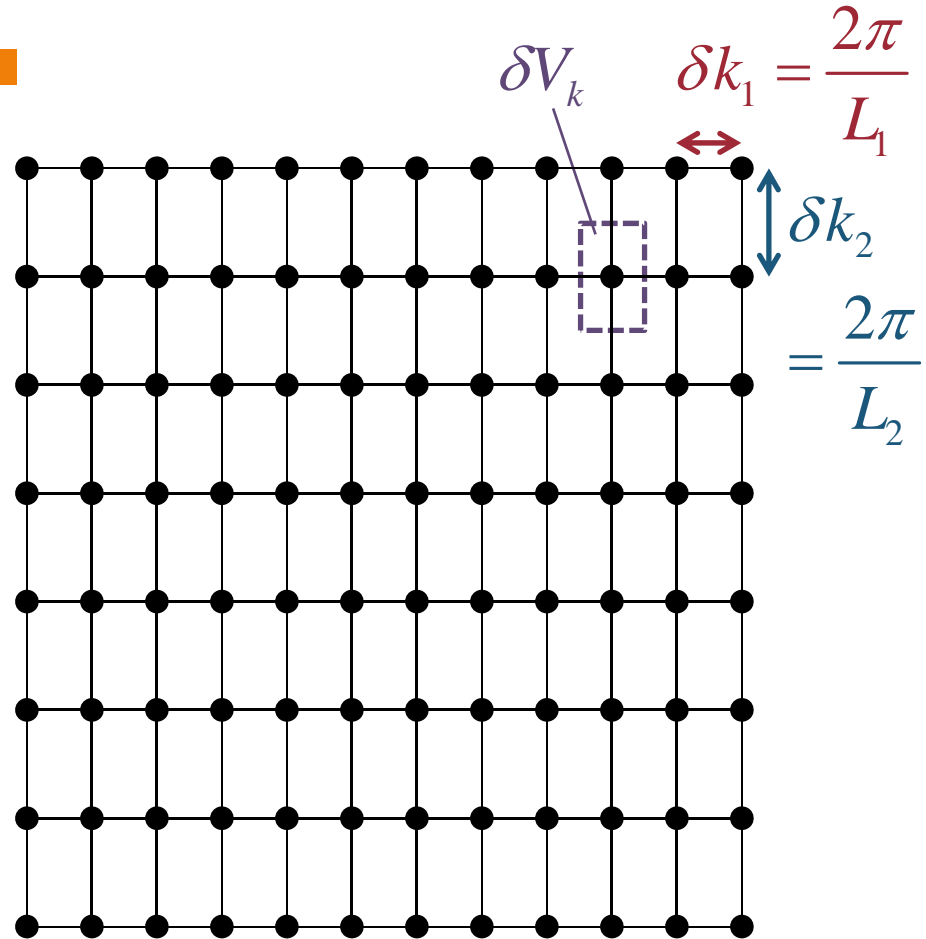
For our cuboidal lattices

these volumes in k -space will
be of size $\delta V_k = \delta k_1 \delta k_2 \delta k_3$

$$\text{i.e., } \delta V_k = \frac{2\pi}{L_1} \frac{2\pi}{L_2} \frac{2\pi}{L_3}$$

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

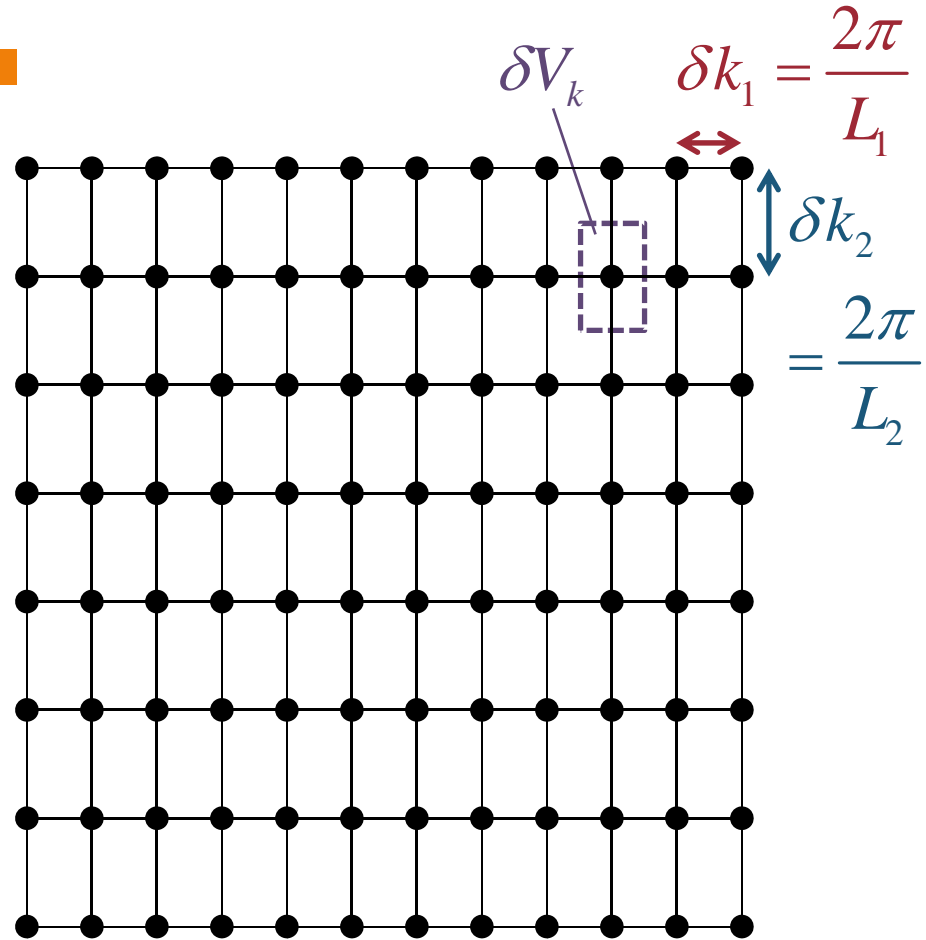
$$\delta V_k = \frac{(2\pi)^3}{V}$$



Density of states in k -space

With this specific k -space
"volume" $\delta V_k = (2\pi)^3 / V$
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

$$1 / \delta V_k = V / (2\pi)^3$$

is \propto crystal volume V

So, more commonly, we define

a "density of states in k -space per unit (real space) volume"

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

for quantum mechanical calculations in crystals

