Particles, atoms, and crystals
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Band structures in crystals

Modern physics for engineers

David Miller

Band structures in crystals

- A small lump of crystal material
  - could contain many more than 10^{20} atoms
- Directly calculating the properties of
  - such a large collection of atoms
    - would be impossible
- Crystals, however
  - are naturally very regular
    - which can simplify the problem

Band structures in crystals

Two particular approaches

taken together

the one-electron approximation

and the Bloch theorem

give some very useful models, including

band structures

and effective masses

One-electron approximation

One-electron approximation

As for many-electron atoms

in a crystal, we presume, as a first approximation

each electron sees an average potential from all the other electrons and nuclei

In a crystal, because it is periodic

we presume that average potential $V_P(\mathbf{r})$

is therefore periodic in the same way also

For example, for a one-dimensional periodic structure

we presume, for a period a

$$V_P(z+a)=V_P(z)$$

One-electron approximation

We can keep on extending this relation $V_P(z+a)=V_P(z)$

for subsequent periods

$$V_P(z+2a)=V_P(z+a)=V_P(a)$$

so we can write for our periodic potential

$$V_P(z+ma)=V_P(z)$$

where m is an integer

We could also generalize this for

two-dimensional or three-dimensional periodic structures

and corresponding periodic potentials

One-electron approximation

So we can write a Schrödinger equation

for just one electron

with a periodic potential $V_P(\mathbf{r})$

and hence an effective equation

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

This is certainly an approximation

and many phenomena are not covered by it

One-electron approximation

Example effects we are not covering completely include

- scattering of electrons off one another
  - or from the nuclei (or vibrations of them)
    - both of which cause electrical resistance

Often, though, we can model these

- starting with this one-electron model
  - and adding these other effects as "perturbations"

One-electron approximation

One important consequence of this one-electron approach

- is that it allows a simple way of looking at crystals
  - through what is called the “Bloch theorem”

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The Bloch theorem

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Periodic boundary conditions

We could generalize our “standing wave” solutions

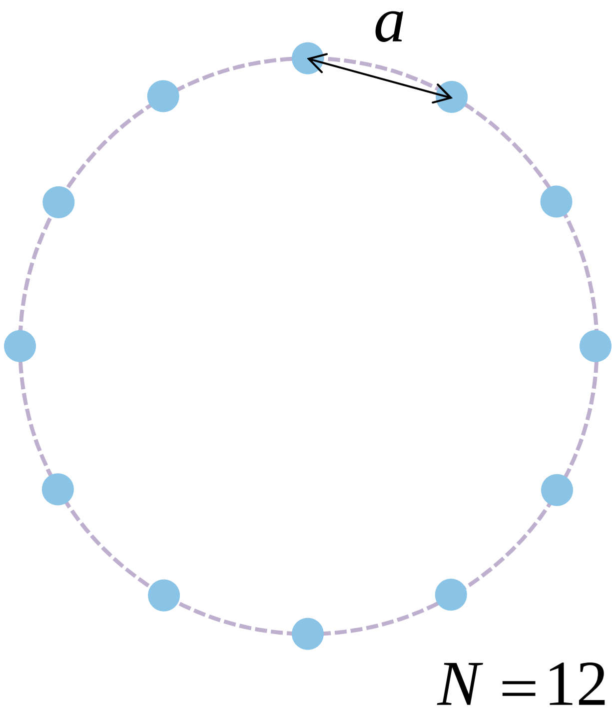
- to larger structures
  - choosing some simple approximation to handle
    - the “end effects” at the edge of finite structures

Periodic boundary conditions

An alternative approach
- which leads to particularly useful mathematics
  - is pretending we are solving for a chain of atoms
    - connected in a loop or ring
      - which is rigorously correct for, e.g.,
        - a benzene ring of 6 carbon atoms

Periodic boundary conditions

- In one dimension, we could argue as follows
  - Suppose we have a long chain of N equally spaced atoms
    - spaced by some distance a
      - and that we join the two ends of the chain together



Periodic boundary conditions

With z as the distance along this loop

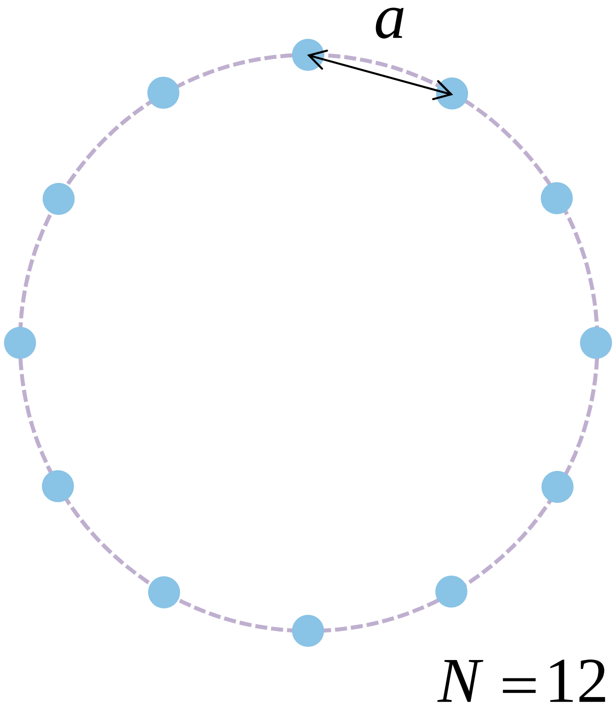
then on this loop

the potential can be written

$$V_P(z+ma)=V_P(z)$$

where m is any integer

even possibly an integer much larger than N



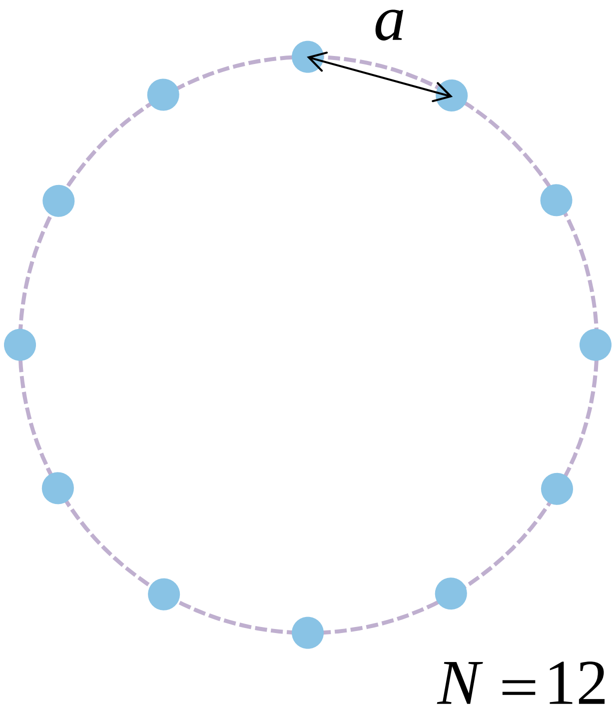
Periodic boundary conditions

This expression $V_P\left(z+ma\right)=V_P\left(z\right)$

- 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

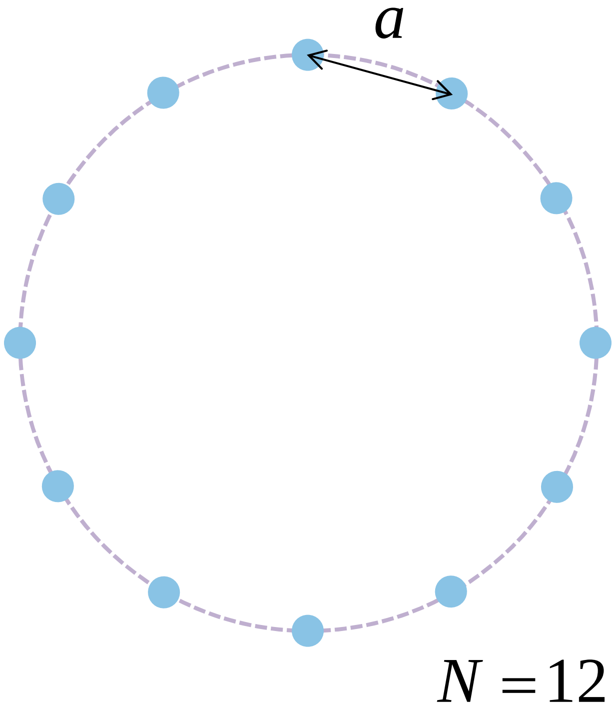
This loop gives a boundary condition

- 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

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

a "periodic boundary condition"

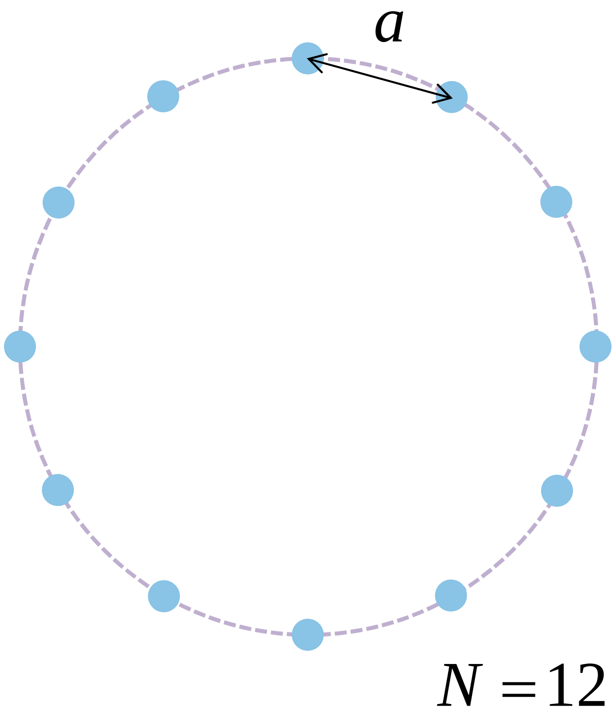


Periodic boundary conditions

In quantum mechanics

- we also want any measurable quantity
  - such as electron density
    - to be the same in every unit cell of the crystal
      - so we also require

$$\left|\psi(z+a)\right|^2 = \left|\psi(z)\right|^2$$



The Bloch theorem

We can satisfy both of these conditions

$$\psi(z) = \psi(z + Na) \qquad \left|\psi(z+a)\right|^2 = \left|\psi(z)\right|^2$$

if we require $\psi(z) = u(z)\exp(ikz)$

where the “unit cell function” $u(z)$

is the same in every unit cell, i.e., $u(z+a) = u(z)$

and k takes on any of a set of N values that are

spaced by an amount $2\pi / Na$

conventionally written as

$$k = \frac{2n\pi}{Na} \quad \text{with} \quad n = 0, \pm 1, \pm 2, \ldots \pm \frac{N}{2}$$

Allowed values of *k*

Technically, the list

$$k = \frac{2n\pi}{Na} \quad \text{with} \quad n = 0, \pm 1, \pm 2, \ldots \pm \frac{N}{2}$$

has one too many elements (i.e., $N + 1$)

- and is written this way just for symmetry
  - We can take one element off one end if we like
- Also, this list presumes N is even
  - which is not a necessary restriction
    - Neither of these would matter for large N

The Bloch theorem

The Bloch theorem (in one dimension)

can be viewed as the statement that

solutions for the quantum mechanical wavefunctions in a periodic potential of period a

can be written in the (Bloch) form

$$\psi(z) = u(z)\exp(ikz)$$

where the unit cell function is the same in every unit cell, i.e., $u(z+a) = u(z)$

and $k = \dfrac{2n\pi}{Na}$ with $n = 0, \pm 1, \pm 2, \ldots \pm \dfrac{N}{2}$

Difference between standing and “Bloch” waves

(i) the Bloch form corresponds to traveling wave “envelope functions” $\exp(ikz)$, not standing wave envelopes

(ii) standing wave “envelopes” correspond to fitting integer numbers of half-waves between the ends

whereas these Bloch form solutions fit integer numbers of whole waves round the ring

Propagating waves in opposite directions count as different solutions

giving the same number of different solutions overall

(iii) solutions in the Bloch form will in general be complex

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Solving with periodic boundary conditions

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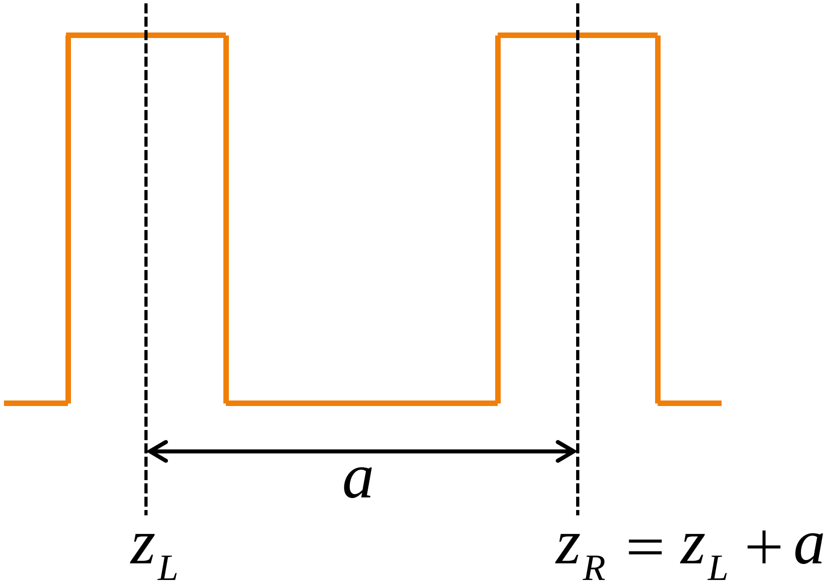
Solving with periodic boundary conditions

For our potential wells

we can take

- the left of the "unit cell" at position z_L
  - for example, in the middle of the barrier on the left
- and the right of the "unit cell" at position $z_R = z_L + a$
  - so, in the middle of the barrier on the right



Solving with periodic boundary conditions

Now, we have, with simple algebra

$$\psi(z+a) = u(z+a)\exp[ik(z+a)]$$

$$= u(z)\exp(ikz)\exp(ika)$$

$$= \exp(ika)\psi(z)$$

This result $\psi(z+a) = \exp(ika)\psi(z)$

is an equivalent way of stating the Bloch theorem

It is saying that the wavefunction in one unit cell

is the same as in the adjacent unit cell

just “phase shifted” by $\exp(ika)$

Solving with periodic boundary conditions

With this result $\psi(z+a)=\exp(ika)\psi(z)$

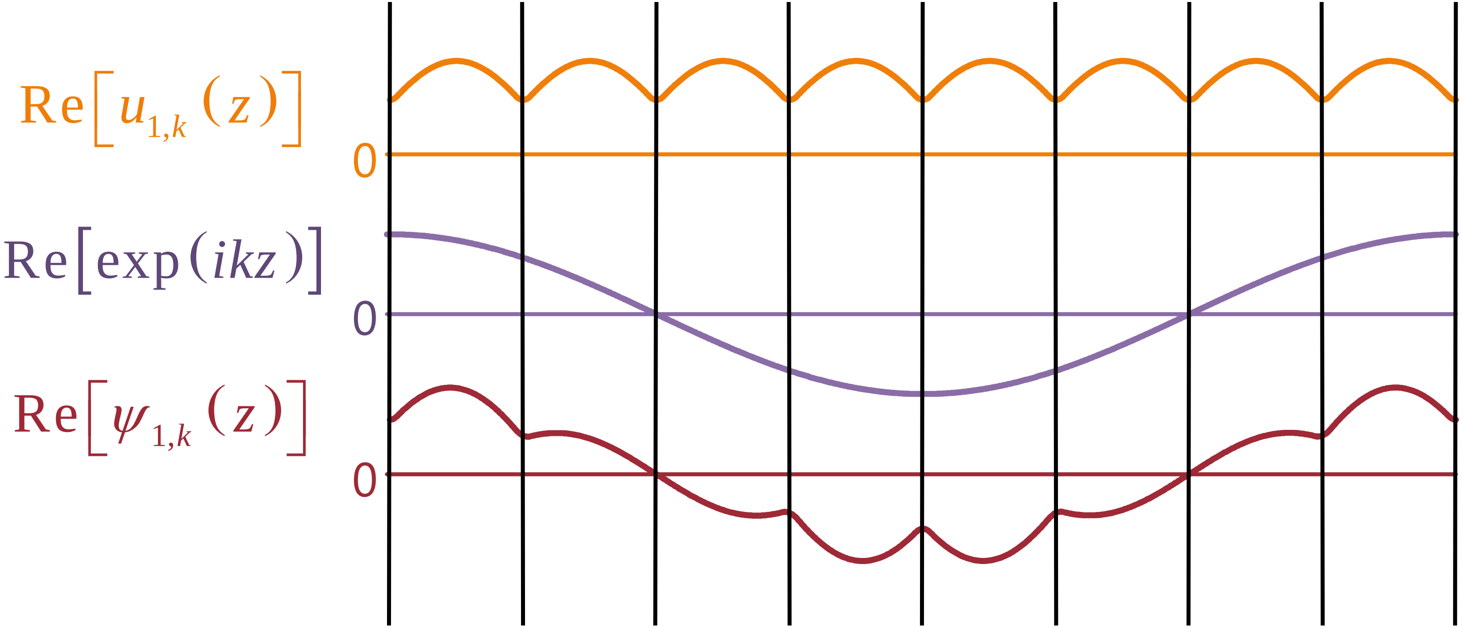
our boundary conditions for solving the Schrödinger equation can be rewritten as

$$\psi_{q,k}(z_R)=\exp(ika)\psi_{q,k}(z_L)$$

where our notation for the wavefunction $\psi_{q,k}(z_R)$ indicates explicitly a specific “band” q and a specific one of the allowed values of k which will give solutions in the form

$$\psi_{q,k}(z)=u_{q,k}(z)\exp(ikz)$$

Example solution in Bloch form



"unit cell"

"propagating wave envelope"

"overall wave in Bloch form"

well width 1.2 nm, barrier width 0.15 nm (so a = 1.35 nm) barrier height 1 eV, for the "second" level in band 1 and using a k value of $0.25\pi / a \simeq 0.582 \text{ nm}^{-1}$

Bloch solutions

Effectively, for each k

- we are solving for the unit cell function $u_{q,k}(z)$
  - and a set of associated eigenenergies $E_{q,k}$

The Bloch theorem has transformed a difficult problem of

- solving for all the states of a system of many atoms
  - into solving for the states of
    - just one "unit cell"

Bloch solutions

This is more complicated than the hydrogen atom because

(i) we have to guess what the potential energy is

possibly iterating to get a form that gives results that agree with experiments

(ii) we have to solve the problem again for each k

though we can use the same potential

Such “band structure” calculations are a major branch of solid-state physics