

Bloch's Theorem

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June 2025

Summary

- A single electron in a crystal obeys the Schrödinger equation with a potential $V(\mathbf{r})$ that comes from the electrostatic potential of the ions
- The periodicity of the crystal lattice is reflected in a periodicity of this potential

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

where \mathbf{a} is a primitive lattice translation vector

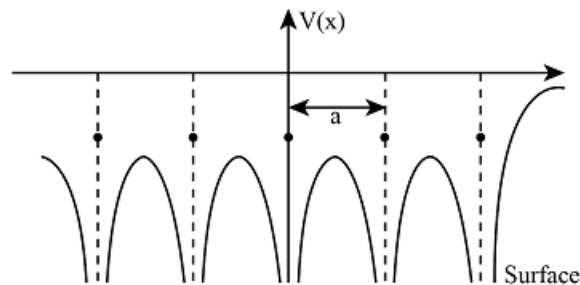
- Bloch's theorem is a general statement about the structure of eigenstates of the Schrödinger equation with potentials that exhibit this periodicity. The theorem says that eigenstates of the Schrödinger equation must be of the form

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{q}}(\mathbf{r})$$

for some crystal momentum \mathbf{q} in the first Brillouin zone, and a **Bloch wavefunction** $u_{\mathbf{q}}(\mathbf{r})$ that is periodic with the lattice $u_{\mathbf{q}}(\mathbf{r} + \mathbf{a}) = u_{\mathbf{q}}(\mathbf{r})$

Electrons in a crystal

In previous lectures, we discussed a simple model for the behaviour of electrons in a crystal. The crystal is made up of a lattice of ions, which produce an electrostatic potential $V(\mathbf{r})$ that is felt by the electrons.



If we ignore Coulomb interactions between the electrons (the *independent electron approximation*), then we can consider the motion of one electron at a time. The Schrödinger equation for a single electron in the potential $V(\mathbf{r})$ is

$$\left(\frac{-\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right) \psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (1)$$

We've seen several different problems of this kind before, including a particle in a box, the harmonic oscillator, and the hydrogen atom. The main difference here is that $V(\mathbf{r})$ will be a **periodic potential**, with the same periodicity as the lattice of ions. This means that the potential should be the same at different points that are related by translations of a primitive lattice vector \mathbf{a}

$$V(\mathbf{r} + \mathbf{a}) = V(\mathbf{r}) \quad \text{for any primitive lattice vector } \mathbf{a} \quad (2)$$

Solving the Schrödinger equation in one spatial dimension

Bloch's theorem is a statement that allows us to quickly infer properties of solutions to the Schrödinger equation (1) for *any* potential satisfying (2). We will begin by deriving it for the simple case where we work in **one spatial dimension**. The one-dimensional version of (1) will be familiar by now

$$(\hat{T} + \hat{V})\psi(x) = \left(\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + V(\hat{x}) \right) \psi(x) = E\psi(x) \quad (3)$$

and the period of $V(x)$ will be the lattice constant a , i.e.

$$V(x + a) = V(x) \quad (4)$$

Whenever we see a periodic function like this, we should think about its Fourier series

$$V(x) = \sum_{n=-\infty}^{\infty} V_n e^{inGx} \quad (5)$$

where we have used the solid-state physics convention of defining a **reciprocal lattice constant** $G = 2\pi/a$, which by construction satisfies $e^{iGa} = 1$. [*Exercise: Using this relation, show that the right hand side of (5) obeys (4).*] Because the potential is real-valued, we will have $V_{-n} = V_n^*$, but otherwise all the Fourier coefficients V_n can in principle take any values.

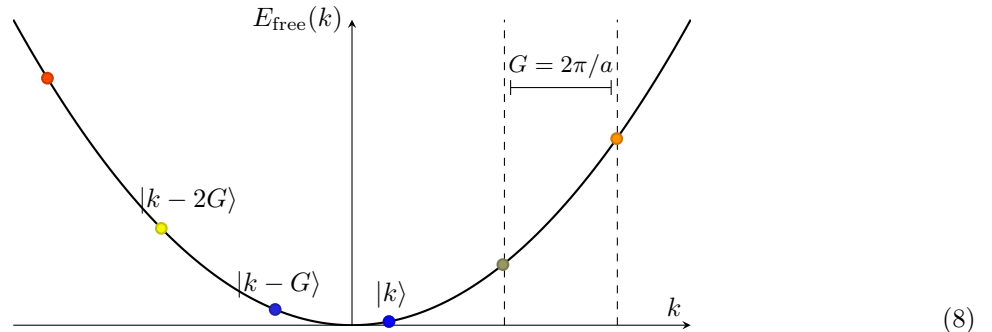
If the potential is flat $V(x) = V_0$, then (4) would be true for any translation a , not just translations by a lattice constant. In that case, we know that the solutions to the Schrödinger equation would be plane waves $|k\rangle$ with definite momentum k , whose wavefunctions are given by $\langle x|k\rangle = e^{ikx}$. The corresponding eigenenergies would then be $E = V_0 + \hbar^2 k^2/2m$. Therefore, it would seem like a good idea to work in the basis of plane wave states

$$|\psi\rangle = \sum_k c_k |k\rangle \quad (6)$$

for a set of coefficients c_k . As before, the plane wave states $|k\rangle$ are eigenstates of the kinetic energy operator $\hat{T}|k\rangle = \frac{\hbar^2 k^2}{2m}|k\rangle =: E_{\text{free}}(k)|k\rangle$. Separately, using the Fourier expansion (5) we can compute how the potential operator \hat{V} acts on plane wave states

$$\hat{V}|k\rangle = \hat{V}e^{ikx} = \sum_{n=-\infty}^{\infty} V_n e^{inGx} e^{ikx} = \sum_{n=-\infty}^{\infty} V_n |nG + k\rangle \quad (7)$$

Observe that by applying \hat{V} to $|k\rangle$, we have generated superpositions of other plane wave states that are all related to one another by a multiple of G .



The above plot shows the free electron energy $E_{\text{free}}(k) = \hbar^2 k^2/2m$ as a function of momentum k , along with values of k that are each related by a reciprocal lattice constant $G = 2\pi/a$. If we had a potential that was not periodic, we would generate superpositions of plane waves of all different wavevectors. So the periodicity makes the action of the potential a great deal simpler in the plane wave basis.

Combining the expression (7) with the expansion (6), we can rewrite the Schrödinger equation as

$$(\hat{T} + \hat{V} - E)|\psi\rangle = \sum_k c_k (E_{\text{free}}(k) - E)|k\rangle + \sum_n \sum_k c_k V_n |nG + k\rangle = 0 \quad (9)$$

In the second sum, it is helpful to relabel $k \rightarrow k - nG$ which gives

$$\sum_k \left((E_{\text{free}}(k) - E) c_k + \sum_n V_n c_{k-nG} \right) |k\rangle = 0 \quad (10)$$

The advantage of this expression over Eq. (9) is that each term in the sum over k is proportional to the same plane wave state $|k\rangle$. Since plane wave states are mutually orthogonal, for (10) to hold we must have the coefficient of each plane wave state $|k\rangle$ being equal to zero, i.e.

$$(E_{\text{free}}(k) - E) c_k + \sum_n V_n c_{k-nG} = 0 \quad \text{for each } k \quad (11)$$

As in the diagram (8), this equation only relates different plane wave states k that are related by multiples of G . So, we can obtain solutions by fixing a reference wavevector q and considering all wavevectors that are connected to q by multiples of G

$$|\psi_q\rangle = \sum_{n=-\infty}^{\infty} b_n |q + nG\rangle \quad (12)$$

where $b_n = c_{q+nG}$ is the coefficient of the plane wave that is n reciprocal lattice constants away from q . In the coordinate representation,

$$\psi_q(x) = \sum_{n=-\infty}^{\infty} b_n e^{i(q+nG)x}. \quad (13)$$

The eigenstates of electrons in a periodic potential can always be written in this form. If we know the Fourier components of the potential V_n , we can in principle determine b_n by solving (11). Explicitly in terms of b_n , we get

$$(E_{\text{free}}(q + nG) - E) b_n + \sum_{n'} V_{n'} b_{n-n'} = 0 \quad \text{for all } n \quad (14)$$

which is an (infinite) set of simultaneous linear equations, and thus finding the coefficients b_n becomes a linear algebra problem. Rather than solving the above equation for specific values of V_n , we will instead be interested in the structure of eigenstates (13) in general.

The structure of eigenstates

Let us examine the expression (13) in more detail. The first thing to notice is that we can shift q by multiples of the reciprocal lattice constant G without changing the form of the wavefunction: If we replace $q \mapsto q + mG$ for an integer m , we can just reassign the coefficients $b_n \mapsto b_{n-m}$ and there will be no change. So without loss of generality, we can assume that **q belongs to the first Brillouin zone**, i.e. $q \in [-\pi/a, \pi/a]$.

Since the potential $V(x)$ that we are considering is periodic, we might ask whether the resulting eigenstate $\psi_q(x)$ is also periodic. Let us evaluate

$$\psi_q(x + a) = \sum_{n=-\infty}^{\infty} b_n e^{i(q+nG)(x+a)} = \sum_{n=-\infty}^{\infty} b_n e^{i(q+nG)x} e^{iqa} e^{inGa} = e^{iqa} \sum_{n=-\infty}^{\infty} b_n e^{i(q+nG)x} = e^{iqa} \psi_q(x) \quad (15)$$

So, even though the eigenstate is not exactly periodic, it is **periodic up to a phase e^{iqa}** . This is consistent with our intuition that the eigenstates of a periodic potential should display some kind of periodicity. For instance, if we looked at the density of electrons $n_q(x) = |\psi_q(x)|^2$, this would have the same period as the lattice.

These two observations can be brought together to obtain Bloch's theorem.

Bloch's Theorem (1D)

Eigenstates of the Schrödinger equation with a periodic potential $V(x+a) = V(x)$ can be written in the form

$$\psi_q(x) = e^{iqx} u_q(x) \quad (16)$$

where q is a wavevector in the first Brillouin zone $[-\pi, \pi]$, and $u_q(x)$ is a periodic function of x , satisfying $u_q(x+a) = u_q(x)$.

The periodic part of the wavefunction $u_q(x)$ is known as the **Bloch state** or Bloch wavefunction, and is given by factoring out the factor of e^{iqx} in Eq. (13), i.e. $u_q(x) = \sum_n b_n e^{inGx}$, which is evidently periodic.

Three dimensions

All of the steps we have made can be generalized to three spatial dimensions. In this case, we have three primitive lattice vectors $\mathbf{a}_{1,2,3}$, with $V(\mathbf{r})$ being periodic with respect to all three [Eq. (2)]. The potential then has a three-dimensional Fourier series representation, which is the analogue of (5)

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}} \quad (17)$$

The sum here is over all reciprocal lattice vectors \mathbf{G} , which we recall are vectors that satisfy $e^{i\mathbf{a} \cdot \mathbf{G}} = 1$ for all primitive lattice vectors \mathbf{a} . We can go through the same steps as in the previous section to arrive at a general form for eigenstates, which is analogous to (13) [*Exercise: Try deriving this yourself*]

$$\psi_{\mathbf{q}}(\mathbf{r}) = \sum_{\mathbf{G}} b_{\mathbf{G}} e^{i\mathbf{r} \cdot (\mathbf{q} + \mathbf{G})} \equiv e^{i\mathbf{r} \cdot \mathbf{q}} u_{\mathbf{q}}(\mathbf{r}) \quad (18)$$

where $u_{\mathbf{q}}(\mathbf{r}) = \sum_{\mathbf{G}} b_{\mathbf{G}} e^{i\mathbf{r} \cdot \mathbf{G}}$ is the Bloch state, which is periodic in the same way as the lattice potential $V(\mathbf{r})$.

Band structures

For any q in the first Brillouin zone, we will find many different solutions to Eq. (14) (in fact, an infinite number), just as we find many eigenstates of the hydrogen atom. As in the case of the atom, we can use an integer $m = 1, 2, \dots$ to distinguish the different solutions, which is referred to as the **band index**. Thus, we will have many pairs of eigenvalues $E_{\mathbf{q},m}$ and corresponding Bloch states $u_{\mathbf{q},m}(\mathbf{r})$, which make up the **band structure** of a given lattice potential.

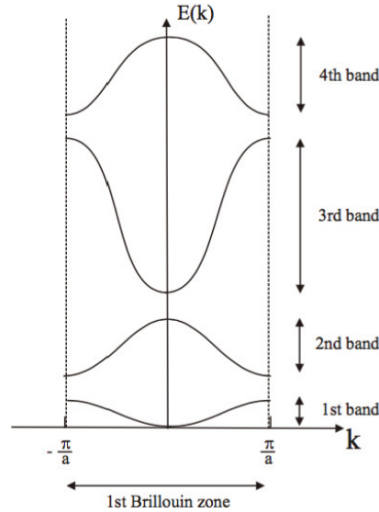


Image credit: David Tong. The above shows the eigenenergies $E_{q,m}$ as a function of the wavevector q for a particular one-dimensional lattice potential, showing the first four bands.

Further Reading

- See Section 7 in Kittel's book 'Introduction to Solid State Physics' for a discussion of electron bands, Bloch's theorem, and some simple examples where band structures can be computed.
- For those more mathematically minded, page 134 of Ashcroft and Mermin's book 'Solid state physics' gives an alternative, highly general derivation of Bloch's theorem based on the properties of symmetry operators and group theory