

# Band Structures and the Meaning of the Wave Vector $k$

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## 1 Introduction

Band structures are a representation of the allowed electronic energy levels of solid materials and are used to better inform their electrical properties. A band structure is a 2D representation of the energies of the crystal orbitals in a crystalline material. Sometimes referred to as “spaghetti diagrams,” a band structure plot can quickly reveal whether a material is metallic, semi-metallic, or insulating, and for those materials with band gaps whether they are direct or indirect as well as the magnitude of the gap. Additionally, the curvature of the bands can reflect the carrier mobility through those bands. A sample band structure for silicon is shown in Figure 1. As no bands cross from the valence band (bottom set of bands) to the conduction band (top set of bands), Si is a semiconductor with a band gap of about 0.62 eV (based off of this calculation). As the conduction band minimum (orange dot) and the valence band maximum (blue dots) are not vertically aligned, the band gap is indirect.

While one is able to quickly determine many materials properties by examining a band structure diagram, an intuitive understanding of how the band structures arise and why they are presented in such ways requires deeper study. The energies of the bands are calculated in “ $k$ -space” or sometimes called “momentum space”. This is an abstract space intimately related to real, or position space. As will be explained in this document,

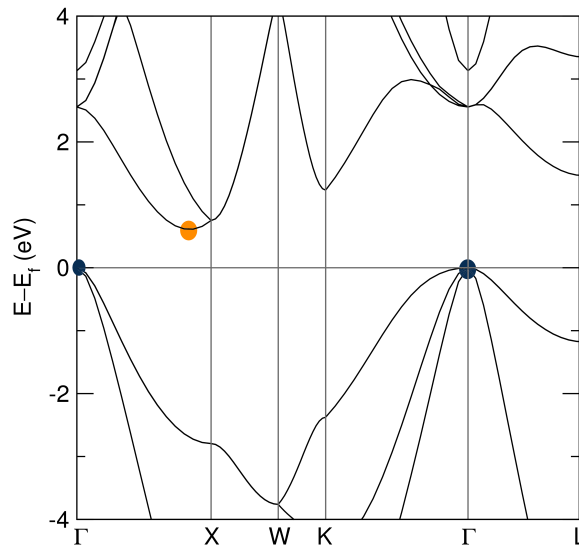


Figure 1: Band structure of elemental Si ( $Fd\bar{3}m$ ) calculated using density functional theory (DFT). The blue circles represent the valence band maximum and the orange circle is the conduction band minimum. The band gap of approximately 0.62 eV can be seen through the difference in energy (y-axis) at these two points. As the valence band maximum and conduction band minimum are not vertically aligned, the band gap is indirect.

utilizing the  $k$  wavevector is a convenient way to calculate and present the energies of the extended orbital interactions in solids.

To begin, we first want to develop a relation between the energies of the wavefunction of a system with the idea of a wavenumber  $k$ . We start by solving the Schrödinger equation for a free particle moving in 1 dimension with no potential.

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} = E\Psi(x) \quad (1)$$

Where  $\hbar$  is the reduced Planck's constant,  $m$  is the particle mass,  $\Psi(x)$  is the particle wave function and  $E$  the energy of the system. We can guess a possible solution of  $\Psi(x) = Ce^{ikx}$ , where  $C$  is a constant,  $i$  is  $\sqrt{-1}$  and  $k$  will be called the wavenumber. Then

$$\frac{d\Psi(x)}{dx} = -ikCe^{ikx} \quad (2)$$

$$\frac{d^2\Psi(x)}{dx^2} = i^2k^2Ce^{ikx} = -k^2Ce^{ikx} \quad (3)$$

We can then multiply both the left and right sides of Equation 3 by  $\frac{\hbar^2}{2m}$  to get

$$\frac{-\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} = \frac{\hbar^2}{2m} k^2 C e^{ikx} \quad (4)$$

And thus,

$$E = \frac{\hbar^2}{2m} k^2 \quad (5)$$

We see for this solution that the energy of the system in which there is no potential on the particle has a quadratic dependence on the wavenumber  $k$ . To get an intuitive sense of what this wavenumber is, we can look at the de Broglie relation and see how the wavelength of a particle can be directly related to the energy expression given in Equation 5. The de Broglie relation elucidates the wave-like nature of matter and is given by

$$\lambda = \frac{h}{mv} = \frac{h}{p} \quad (6)$$

Where  $\lambda$  is the wavelength of a particle,  $h$  the Planck constant,  $m$  the particle mass,  $v$  the particle velocity, and  $p$  is the momentum of the particle. Instead of thinking of the wavelength of a particle, we can think in terms of its wavenumber  $k = 2\pi/\lambda$  which simply expresses the wave in terms of wavelengths per unit distance, rather than the wavelength which is distance per period. Then

$$p = \hbar k \quad (7)$$

Assuming the particle has no potential energy, only kinetic energy, then

$$E = \frac{1}{2} m v^2 = \frac{p^2}{2m} \quad (8)$$

$$E = \frac{\hbar^2}{2m} k^2 \quad (9)$$

which is exactly the same as the energy of a free particle from Schrodinger's equation (Equation 5).

From these two results, we can begin to understand the relation of the momentum, wavenumber, and energy of a system. While  $k$  has units of 1/length, it is related to a real space wavelength and a momentum and can be used to calculate the energy of the system. In order to relate this  $k$  to the calculation of band structures we must move from a single particle in 1 dimension to more complicated systems.

## 2 Band Structure of a 1 Dimensional Chain of Atoms

In this section, we will see how periodic conditions on a crystal result in quantum states which can be expressed conveniently in discrete wavenumbers which are related to the wavelengths of the crystal orbitals. The energies of the states characterized by these wavenumbers can be calculated and plotted giving rise to an orbital band, forming the basis for electronic structures of more complicated crystals.\*

We assume a 1 dimensional chain of  $N$  atoms separated by a lattice spacing  $a$  each with just one valence  $s$  orbital. A periodic boundary condition is imposed so that the  $N^{\text{th}}$  atom interacts with the  $1^{\text{st}}$  atom of an adjacent chain. Thus,

$$\Psi(x) = \Psi(x + Na) \quad (10)$$

Since the electron density must be unchanged with each lattice spacing as the chain is uniform, we have  $\rho(x+a) = \rho(x)$  and knowing  $\rho(x) = \Psi^*(x)\Psi(x)$  which must be real, it must be that  $\Psi(x+a) = \mu\Psi(x)$  where  $\mu$  is a complex number such that  $\mu^*\mu = 1$  Thus,

$$\Psi(x + na) = \mu^n\Psi(x) \quad (11)$$

with  $\mu^N = 1$  to satisfy Equation 10, so

$$\mu = e^{2\pi ip/N} = \cos(2\pi p/N) + i\sin(2\pi p/N) \quad (12)$$

Here  $p$  is a quantum number that must span the integers from  $-N$  to  $N$ . We can define  $k$  such that  $k = \frac{2\pi p}{Na}$ .  $k$  is now a quantum number with units of inverse length that is dependent on the number of atoms in the crystal. For any reasonably large  $N$ ,  $k$  is functionally continuous. We can now write that

$$\Psi(x + a) = e^{(ika)}\Psi(x) \quad (13)$$

and see a solution to the wavefunction as

$$\Psi(x) = e^{ikx} \quad (14)$$

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\*The derivations here closely follow Chapter 4 of P.A Cox's "The Electronic Structure and Chemistry of Solids" Oxford University Press (2005)

By taking into Equation 13 we can further generalize the wave function assuming a periodic function  $u(x) = u(x + a)$  as

$$\Psi(x) = e^{ikx}u(x) \quad (15)$$

This is the familiar Bloch function. Thus, we see that the wavefunction is a combination of the periodic potential  $u(x)$  on each atom with an exponential term that varies with the wavenumber  $k$ .

As in the previous section,  $k$  is inversely related to a wavelength. Whereas before it was the wavelength of a free particle, now  $k = 2\pi/\lambda$  where  $\lambda$  is the crystal orbital wavelength. As shown in Figure 2, at  $k = 0$  the orbitals are all in phase with each other leading to no nodes between them and an infinite crystal orbital wavelength. As  $k$  moves from 0, nodes are introduced into the chain when some orbitals switch phases until  $k = \pm\pi/a$  at which every orbital is out of phase with its neighbors. This leads to a minimum crystal orbital wavelength of  $2a$ . Now seeing how  $k$  arises in a crystal due to a periodic potential, we can use a linear combination of atomic orbitals approach to calculate the energy of the chain with varying  $k$  to see how a band develops.

The wave function of the chain can be written as

$$\Psi(x) = \sum_n c_n \chi_n(x) \quad (16)$$

where  $c_n = e^{ikna}$  and  $\chi_n(x)$  is the wavefunction of the atomic orbital on atomic  $n$ . The energy of the system is

$$E_k = \frac{\int \Psi_k^* H \Psi_k}{\int \Psi_k^* \Psi_k} \quad (17)$$

expressing these as sums over the chain

$$\int \Psi_k^* H \Psi_k = \sum_{n=1}^N \left\{ \sum_{m=1}^N e^{ika(n-m)} \int \chi_m^* H \chi_n \right\} \quad (18)$$

$$\int \Psi_k^* \Psi_k = \sum_{n=1}^N \left\{ \sum_{m=1}^N e^{ika(n-m)} \int \chi_m^* \chi_n \right\} \quad (19)$$

For simplicity, we approximate the overlap of the atomic orbitals to be negligible such that  $\int \chi_m^* \chi_n = 1$  if  $m = n$  and 0 if  $m \neq n$ . Then Equation 19 is simply equal to  $N$ . Further, we assume that each atom only interacts with its direct 2 neighbors such that

$$\int \chi_m^* H \chi_n = \alpha \quad (20)$$

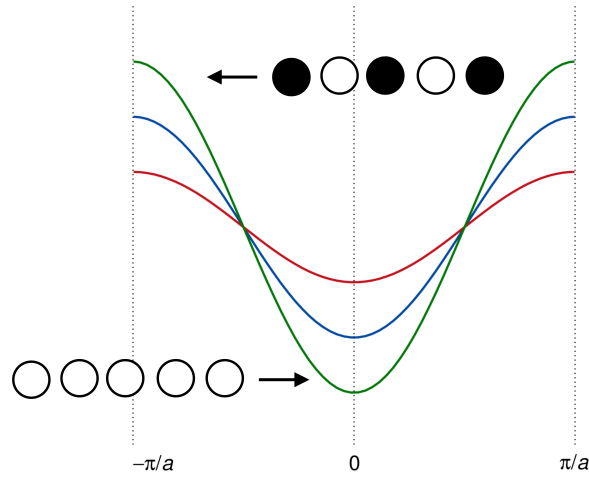


Figure 2: Band structure of a 1 dimensional chain of atoms with varying orbital interactions energies.  $k = 0$  corresponds to an infinite crystal orbital wavelength with all the orbitals in phase. As  $k$  deviates from 0, the wavelength gets smaller as nodes are introduced until it reaches a minimum at  $k = \pm\pi/a$  corresponding to each orbital completely out of phase with its neighbors. Strong orbital interactions lead to a more dispersive band (green curve) which becomes successively flatter with weaker interactions (blue and red curves).

when  $m = n$  where  $\alpha$  is simply the energy of an electron in one atomic orbital and

$$\int \chi_m^* H \chi_n = \beta \quad (21)$$

when  $m = (n \pm 1)$  where  $\beta$  is the interaction energy. Now we can evaluate the total energy as a function of  $k$

$$\int \Psi_k^* H \Psi_k = N \{ \alpha + \beta [e^{-ika} + e^{ika}] \} \quad (22)$$

$$= N \{ \alpha + \beta [\cos(-ka) + i \sin(-ka) + \cos(ka) + i \sin(ka)] \} \quad (23)$$

$$= N \{ \alpha + 2\beta \cos(ka) \} \quad (24)$$

and thus

$$E_k = \alpha + 2\beta \cos(ka) \quad (25)$$

A plot of the energy with varying  $\beta$  is given in Figure 2. For stronger orbital interactions, corresponding to a large magnitude of  $\beta$  we see that the band becomes more dispersive in energy (green curve). Successively weaker orbital interactions correspond to flatter bands (blue and red curves). This simple model informs

the fact that disperse bands lead to higher carrier mobility (stronger interaction between adjacent orbitals), while flat bands indicate more localized carriers (weaker interactions between adjacent orbitals).

### 3 Generalizing to Higher Dimensions

While the energies of a 1 dimensional chain of atoms can be calculated easily with some approximations, the band structure is rather simple. A real band structure consists of many bands corresponding to all of the orbitals on all of the atoms in the unit cell. In order to inform the more complicated band structures of real materials, it can help to extend our images of crystal wavelengths to higher dimensions and with orbitals other than  $s$ . Quantitatively calculating the energy is infeasible and requires computational programs, though a qualitative understanding can be further developed.

Figure 3 shows a hypothetical 2 dimensional lattice consisting of a  $p$  orbital on each atom. In 2 dimensions we move from a wavenumber to a wavevector. When  $k = (0, 0)$  the crystal orbital wavelength is infinite in both directions as the orbitals do not switch phase throughout the crystal. For the chain of  $s$  orbitals this was the most stable energy. However in this case, the orbitals are most stabilized in the  $y$  direction (adjacent orbital overlap is in phase in the  $y$  direction) and destabilized in the  $x$  (adjacent orbital overlap out of phase in the  $x$  direction). This model highlights the intricacies of band structure calculations as both the orbital phases and the relative orbital overlap in each direction must be considered in order to calculate an energy for a discrete  $k$  vector. In this case, the  $\sigma$  bonding of the  $p$  orbitals in the  $x$  direction is stronger than the  $\pi$  bonding in the  $y$ , and thus it is not the most stable configuration. We see that for  $k = (\pi/a, 0)$ , the orbitals have the most favorable interactions in both directions as adjacent orbitals have overlap that is completely in phase, leading to the lowest energy configuration. At  $k = (\pi/a, \pi/a)$  the orbitals have favorable overlap in the  $x$  direction, and at  $k = (0, \pi/a)$  the orbitals are most antibonding (adjacent orbitals out of phase) leading to the highest energy  $k$  vector. This crystal would be further complicated if we did not have a square lattice, but a rectangular lattice with two different lattice vectors.

From this hypothetical lattice, it becomes easier to appreciate the features of real band structures. One must consider orbital interactions in 3 dimensions arising from  $s$ ,  $p$ ,  $d$ , and potentially  $f$  orbitals on each atom. This leads to complex energy landscapes with many bands. Moving into 3 dimensions, the set of all unique  $k$  vectors comprises the Brillouin Zone of the crystal. The Brillouin Zone exists in reciprocal space and is directly related to the real space lattice. Due to the periodicity of the lattice and Bloch functions, every  $k$  vector is equivalent to a  $k$  vector inside this Brillouin Zone and the electronic band structure can be determined solely by calculating energies within the Brillouin Zone. In the case of our 1 dimensional chain

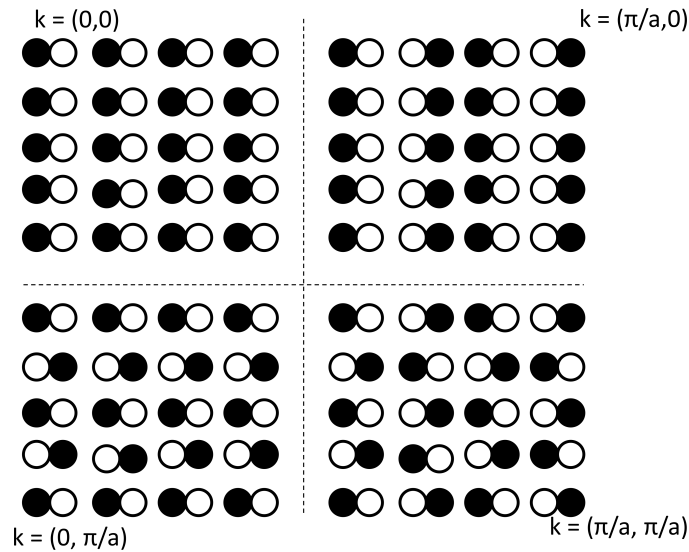


Figure 3: A hypothetical 2 dimensional lattice consisting of 1  $p$  orbital per atom. The crystal orbital arrangements for 4  $k$  vectors are shown. The lowest energy  $k$  vector,  $k = (\pi/a, 0)$  has the orbitals in the most bonding arrangement in the  $x$  and  $y$  directions.  $k = (0, \pi/a)$  is the most antibonding arrangement and the highest energy.

of atoms, the Brillouin Zone would be  $(-\pi/a, \pi/a)$ . In 3 dimensions, the Brillouin Zone is a primitive unit cell in  $k$ -space directly related to the unit cell of the real crystal.

An example Brillouin Zone of a face-centered cubic lattice is given in Figure 4.<sup>†</sup> The basis vectors in  $k$ -space are given by  $b_1$ ,  $b_2$ , and  $b_3$ . The marked points labeled  $\Gamma$ , L, K, etc. correspond to high symmetry points in the Brillouin Zone. In order to calculate the band structure, a path through the Brillouin Zone must be chosen to best capture the energy landscape in 3 dimensions. Typically, this is done by following the high symmetry points in the Brillouin Zone. The labels given on the x-axis in typical band structure plots correspond to these high symmetry points and the path chosen. Lower symmetry crystals require more extensive paths to accurately capture the electronic structure.

## 4 Conclusions

The electronic structure of a material represents the allowed electronic energy levels according to band theory and informs many of its physical properties. It is convenient when discussing the energy of bands to work in  $k$ -space, in which the energy of the crystal orbitals is calculated in relation to a wavevector,  $k$ . The periodic nature of a crystal lattice results in discrete energy values that are easily expressed in terms of  $k$ .

<sup>†</sup>Taken from Setyawan, W. and Curtarolo, S. *Comp. Mater. Sci.* **49** (2010) pp. 299–312



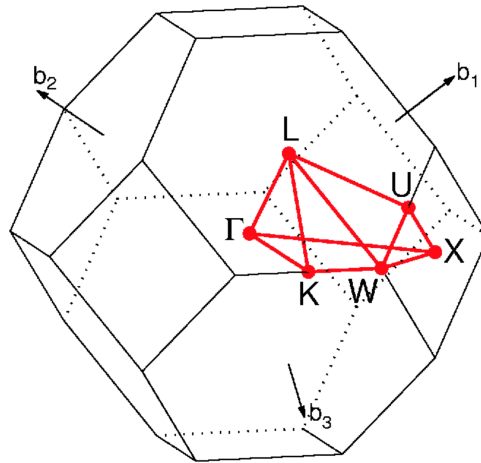


Figure 4: Brillouin Zone of a face-centered cubic crystal. The basis vectors are given by  $b_1$ ,  $b_2$ , and  $b_3$ , and labeled red points correspond to points of high symmetry in the Brillouin Zone. Paths through  $k$ -space dictated by these points accurately capture the whole energy landscape.

This wavevector is inversely related to the crystal orbital wavelength which is determined by the phases of the atomic orbitals throughout the crystal. In a 1 dimensional chain of atoms with only  $s$  orbitals,  $k$  takes on a range from  $(-\pi/a, \pi/a)$  where  $k = 0$  corresponds to the  $s$  orbitals all in phase with each other, and thus the lowest energy configuration. At  $k = \pm\pi/a$  (and thus the shortest possible crystal orbital wavelength  $2a$ ) each orbital is out of phase with its neighbors leading to a higher energy state. The picture gets more complicated when accounting for 2 and 3 dimensions with multiple orbitals and atoms, but the premise remains the same. In 3 dimensions, the unique  $k$  vectors are presented in the Brillouin Zone. In order to accurately capture the energy landscape in 3 dimensions, the energy is calculated with respect to a path of high symmetry points in the Brillouin Zone. While calculating band structures requires advanced computational programs, an understanding of band structures and  $k$ -space from simple hypothetical crystals can help develop intuition regarding more complicated, real systems.