
 FIP10601 – Text 3

Independent-electron approximation – Energy eigenstates –

The generic Hamiltonian of electrons and ions introduced in Text 1 may be simplified through various approximations. First of all, the motion of electrons and ions occur in very different time scales. This allows to study electronic states in a *rigid-lattice approximation*, keeping the ions fixed at their equilibrium positions in the crystal structure (the effects of ion motion can be included as a perturbation latter on). Then, the purely ionic part of the Hamiltonian becomes a constant, which can be dropped by a convenient choice of reference energy. Furthermore, the electron-ion interaction becomes a static potential acting on each electron independently. So, we are left with a purely electronic Hamiltonian.

The above simplifications do not change the many-body character of the problem, since interactions between electrons still exist. This is the main difficulty from a theoretical point of view, and will be dealt with in the second part of this course. For now we will resort to an additional simplification, not clearly justifiable at this moment, which is known as the *independent-electron approximation*. It consists in eliminating the explicit electron-electron interaction, implicitly assuming that its effect is (partially) incorporated into the “external” potential, which was initially considered to be due to ions only. This means that the effect of the remaining electrons on a given one is taken as averaged into a static potential. Hence, the motion of different electrons is **not correlated**, which is the meaning of *independent* in this context.

We can only judge how good or how bad this approximation might be after studying in some detail the interactions between electrons, which we will do later on. For the time being, this simplification is just assumed, but it will prove to be a useful step in the analysis of such a complex problem.

The *rigid-lattice* **and** *independent-electron* approximations reduce the Hamiltonian to a sum of single-particle terms associated to kinetic and potential energies,

$$\mathcal{H}_{\mathcal{N}} = \sum_{l=1}^{\mathcal{N}} \left[\frac{\mathbf{p}_l^2}{2m} + V(\mathbf{r}_l) \right], \quad (1)$$

where \mathcal{N} is the total number of electrons in the system.

Coordinates of different electrons are not mixed in the above Hamiltonian, implying that the corresponding eigenvalue equation is separable. Therefore, energy eigenvalues of the \mathcal{N} -electron system will be sums of \mathcal{N} individual energies, and the corresponding \mathcal{N} -electron eigenfunctions will involve products of \mathcal{N} one-electron wavefunctions, in appropriately anti-symmetric combinations with respect to pair exchanges to conform with the fact that

electrons are identical fermions. Since the electrons are indistinguishable, the “external” potential is the same for all of them, implying that the single-electron problem that we need to solve is unique. Here we see why the independent-electron approximation is appealing as it reduces the solution of a many-body problem to the solution of a single-particle problem.

Within this approximation, we need to find solutions to the eigenvalue equation

$$\mathcal{H}\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r}) , \quad (2)$$

where

$$\mathcal{H} = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) . \quad (3)$$

What characterizes the problem of an electron in a **crystalline solid** is that the potential $V(\mathbf{r})$ is **periodic in the lattice**, i.e.,

$$V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r}) , \quad (4)$$

for any lattice vector \mathbf{R} .

The explicit form of $V(\mathbf{r})$ is not *a priori* known. Nevertheless, much information about the solutions can be obtained by exploring its periodicity. In the following, we will look for general properties of the electronic spectrum that can be deduced from lattice symmetries.

Lattice-translation symmetry: Bloch’s theorem

Let us apply some principles of Group Theory, as reviewed in Text 2, beginning with the translation subgroup.

Equation (4) shows that $V(\mathbf{r})$ is explicitly invariant under all operations of the translation group. It is easy to see that the kinetic-energy term is also translation invariant, since in coordinate representation we have $\mathbf{p} = -i\hbar\nabla$. Thus, the one-electron Hamiltonian is invariant under translations.

It is convenient to consider a finite-size system of volume \mathcal{V} , containing N primitive cells of the lattice. In such a finite system, wave functions can be normalized, and the translation group is finite, composed of N distinct lattice translations. If N is sufficiently large, it is reasonable to suppose that the value of any quantity evaluated **per unit volume** inside this region is the same as would be obtained in any other equivalent region of the whole system. Then, an electron leaving this region at one of its boundaries finds itself in a situation completely equivalent to entering the same region from the opposite end. This allows us to use *periodic boundary conditions* in the volume \mathcal{V} to solve the eigenvalue equation.

From what we have learned about finite groups, we can make the following statements about the translation group (of N elements).

- All lattice translations **commute** (the group is *Abelian*). Therefore, each element is a class.
- The number of irreducible representations, which is equal to the number classes, is equal to the number of elements.
- Given the relationship $\sum_{\alpha} n_{\alpha}^2 = N$, we conclude that **all** the irreducible representations are **one-dimensional**.
- As the representation “matrices” of the group members are one-dimensional, and taking into account the conservation of the norm of state vectors (wave functions), in each irreducible representation the group members are represented by **complex numbers of absolute value equal to one**.
- On a lattice with N primitive cells, we have N classes, identified by N vectors \mathbf{R} . We use N wavevectors \mathbf{k} to identify the N irreducible representations.
- Given that the product rule is $T_{\mathbf{R}} T_{\mathbf{R}'} = T_{\mathbf{R}+\mathbf{R}'}$, it is easy to see that the set of numbers $\{e^{i\mathbf{k}\cdot\mathbf{R}}\}$ is isomorphic to the set of operators $T_{\mathbf{R}}$, with the same product rule, thus providing a faithful representation of the group. Note that the *identity representation* corresponds to $\mathbf{k} = \mathbf{0}$.
- The basis function of the \mathbf{k} -representation can be denoted by $\psi_{\mathbf{k}}(\mathbf{r})$, and satisfy the relationship

$$\langle \psi_{\mathbf{k}} | T_{\mathbf{R}} | \psi_{\mathbf{k}} \rangle = e^{i\mathbf{k}\cdot\mathbf{R}} . \quad (5)$$

- Therefore,

$$T_{\mathbf{R}} \psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{\mathbf{k}}(\mathbf{r}) . \quad (6)$$

Defining the action of the translation operator as $T_{\mathbf{R}} \phi(\mathbf{r}) = \phi(\mathbf{r} + \mathbf{R})$, we have

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{\mathbf{k}}(\mathbf{r}) , \quad (7)$$

which is the mathematical expression of **Bloch’s theorem**, since the functions $\{\psi_{\mathbf{k}}(\mathbf{r})\}$ may be chosen to be energy eigenfunctions (as seen in Text 2).

- Two useful relations can be derived from the orthogonality theorems that we saw in Text 2. Since $e^{i\mathbf{k}\cdot\mathbf{R}}$ is the character of class \mathbf{R} in the irreducible representation \mathbf{k} , we have

$$\sum_{\mathbf{R}} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}} = N \delta_{\mathbf{k},\mathbf{k}'} , \quad (8a)$$

$$\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}')} = N \delta_{\mathbf{R},\mathbf{R}'} . \quad (8b)$$

The choice of $\{\psi_{\mathbf{k}}(\mathbf{r})\}$ as energy eigenfunctions implies that energy eigenvalues must also be labeled by the wavevectors \mathbf{k} , and the time-independent Schrödinger's equation assumes the form

$$\mathcal{H} \psi_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r}) . \quad (9)$$

It is still possible to have multiple solutions of such an equation for a given value of \mathbf{k} without violating Bloch's theorem. This introduces a new quantum number, n , usually called *band index* (we will see why latter on).

In summary, we have seen that invariance of the Hamiltonian under lattice translations implies that energy eigenfunctions, which are solutions of the equation¹

$$\mathcal{H} \psi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_n(\mathbf{k}) \psi_{n\mathbf{k}}(\mathbf{r}) , \quad (10)$$

obey Bloch's theorem, i.e.,

$$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r}) . \quad (11)$$

For this reason, it is usual to refer to independent electrons in a periodic potential as *Bloch electrons*, and their energy eigenfunctions as *Bloch states*.

Reciprocal space and reciprocal lattice

We have not yet said anything about possible values of the wavevectors \mathbf{k} . In principle, they could be any real vectors in the *reciprocal space* (space of coordinates with dimension of inverse length). But there must be only N different \mathbf{k} 's. We can determine their values by enforcing periodic boundary conditions on the wavefunctions $\psi_{n\mathbf{k}}(\mathbf{r})$.

First, we notice that Bloch states can be written in the form

$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} , \quad (12)$$

provided that

$$u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r}) . \quad (13)$$

The functions $u_{n\mathbf{k}}(\mathbf{r})$ modulate a plane wave in the Bloch wavefunction.

We choose the N primitive cells of our system such that $N = N_1 N_2 N_3$, where N_i is the number of primitive cells along the direction defined by the primitive vector \mathbf{a}_i . So, when crossing the system along any one of these directions, the net displacement is $N_i \mathbf{a}_i$, which is a lattice vector. Consequently, the modulation function is unchanged, and the plane-wave part picks up a factor $\exp(iN_i \mathbf{k}\cdot\mathbf{a}_i)$ that must be equal to 1. Thus,

$$N_i \mathbf{k}\cdot\mathbf{a}_i = 2n_i \pi , \quad n_i = 0, \pm 1, \pm 2, \pm 3, \dots \quad (14)$$

This means that the possible vectors \mathbf{k} define a discrete grid in reciprocal space, with its points separated by distances $2\pi/L_i$, where $L_i = N_i |\mathbf{a}_i|$ is the system's length along the

¹When convenient, we use \mathbf{k} as an argument or as a subscript to the energies.

direction of \mathbf{a}_i . For $n_i > N_i$ the right-hand side of the first equality in Eq. (14) differs by $2N_i\pi$ from its value for $(n_i - N_i)$, thus being equivalent in the exponential $e^{i\mathbf{k}\cdot\mathbf{R}}$. Therefore, taking all directions into account, we have only N non-equivalent wavevectors, as expected for the number of irreducible representations of the translation group, which are labeled by \mathbf{k} .

We can rephrase the above observations in terms of the *reciprocal lattice*, which is defined as the set of vectors $\{\mathbf{K}\}$ of reciprocal space that satisfy the condition $\exp(i\mathbf{K}\cdot\mathbf{R}) = 1$ for all vectors \mathbf{R} of the Bravais lattice, yielding $\mathbf{K}\cdot\mathbf{R} = 2n\pi$ for any integer n . The reciprocal lattice is also a Bravais lattice (in reciprocal space), allowing to write a reciprocal-lattice vector \mathbf{K} in terms of primitive vectors as $\mathbf{K} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$, with integer m_i . We can now see that choosing $n_i = N_i$ in Eq. (14) implies that $\mathbf{k} = \mathbf{b}_i$, which means that the N non-equivalent \mathbf{k} vectors lie **within a primitive cell of the reciprocal lattice**. It is usual to choose this primitive cell as the *first Brillouin zone* (1st BZ), i.e., the Wigner-Seitz cell of the reciprocal lattice. We then can choose the N relevant \mathbf{k} vectors as those inside the 1st BZ.

We should keep in mind that the distance between neighboring points in the discrete \mathbf{k} -space (not the reciprocal lattice) is inversely proportional to the system's length along any direction. Since the volume V is arbitrarily chosen, we must suppose that it will be eventually taken to infinity, with the number of cells also growing to infinity so as to preserve the number of cells per unit volume, N/V , which is proportional to the mass density of the specific solid in question. When this *thermodynamic limit* is taken, the \mathbf{k} values tend to a continuum. This is the reason why the index n in the Bloch states is called *band* index, as the energies depend on this discrete quantum number but also on nearly continuous values of \mathbf{k} , so that instead of discrete energy states we have energy **bands** associated to each n .

The equivalence between wavevectors outside and inside the 1st BZ gives rise to a periodicity of the energy eigenvalues as functions of \mathbf{k} , which must obey the condition

$$\varepsilon_n(\mathbf{k} + \mathbf{K}) = \varepsilon_n(\mathbf{k}) . \quad (15)$$

This shows a translation symmetry of the energies in reciprocal space as a consequence of a translation symmetry of the potential in real space. As we should not expect infinite values or discontinuities in the energy spectrum within a band, this periodicity implies that bands have maxima and minima in \mathbf{k} -space, and finite widths.

We now realize that, without any assumption about the potential apart from its periodicity in the lattice, we deduced that the electronic energy spectrum forms a *band structure*, i.e., a sequence of finite-width energy bands. Depending on details of specific solids, these bands may be entirely separated by energy *gaps* or may overlap (not necessarily cross, since equal energies in two bands may correspond to different \mathbf{k} 's).

Velocity of a Bloch electron

Bloch's theorem has allowed us to obtain general properties of independent-electron states. In particular, it shows that Bloch-electron wavefunctions are identified by a wavevector. We tend to think that a definite wavevector associated to a particle is directly related to definite momentum eigenvalues. But it is not the case here. We have seen that Bloch states can be written as modulated plane waves, as given by Eq. (12), with modulation functions obeying Eq. (13). A pure plane wave is a momentum eigenfunction with eigenvalue $\hbar\mathbf{k}$, and describes a free particle with purely kinetic energy $\hbar k^2/2m$. But it is clear that the action of the momentum operator on a Bloch state generates an additional term proportional to $\nabla u_{n\mathbf{k}}(\mathbf{r})$. Therefore, $\hbar\mathbf{k}$ is **not** a momentum eigenvalue of a Bloch electron, although it is customary called "crystal momentum".

From the above discussion we conclude that we cannot simply associate a velocity $\hbar\mathbf{k}/m$ to a Bloch electron. It is still possible to attribute a velocity to a Bloch electron if we think of $\psi_{n\mathbf{k}}(r)$ as a wavepacket, centered at position \mathbf{r} in coordinate space, and at \mathbf{k} in wavevector space. Then, including the time-dependent part of the wavefunction, we identify $\varepsilon_n(\mathbf{k})/\hbar$ with the (\mathbf{k} -dependent) angular frequency, so that the *group velocity* of the packet is given by

$$\mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar} \nabla_{\mathbf{k}} \varepsilon_n(\mathbf{k}). \quad (16)$$

This is the natural choice for the Bloch electron's velocity.

The above equation shows that a flat band (ε_n independent of \mathbf{k}) yields zero velocity, and hence *localized states*. On the other hand, a dispersive band implies finite velocities, which are consistent with *extended states*, allowing the electron to visit the entire volume of the system. We should keep in mind that Bloch states are eigenstates of the electronic Hamiltonian, which contains a periodic potential that accounts for the presence of ions. Therefore, under the rigid-lattice assumption, an electron **cannot** change its state as a consequence of scattering by ions of the crystal structure. This will be an important point in a future discussion of transport processes.

Point-group symmetries

Up to now, the only symmetries considered were those of the translation subgroup, which led to Bloch's theorem and its consequences to the energy spectrum. We still have to investigate what new properties can be inferred from the point-group symmetries.

Let us consider a generic operation a of the point group, to which we associate the operator A . According to our discussion in Text 2, the action of this operator on an energy eigenfunction $\psi_{n\mathbf{k}}(\mathbf{r})$, corresponding to an eigenvalue $\varepsilon_n(\mathbf{k})$, is $A\psi_{n\mathbf{k}}(\mathbf{r}) = \psi_{n\mathbf{k}}(a^\dagger\mathbf{r})$, which is also an energy eigenfunction corresponding to the same eigenvalue. Applying Bloch's theorem to this latter function, we have

$$\psi_{n\mathbf{k}}(a^\dagger[\mathbf{r} + \mathbf{R}]) = \psi_{n\mathbf{k}}(a^\dagger\mathbf{r} + a^\dagger\mathbf{R}) = e^{i\mathbf{k}\cdot(a^\dagger\mathbf{R})} \psi_{n\mathbf{k}}(a^\dagger\mathbf{r}). \quad (17)$$

But,

$$\mathbf{k} \cdot (a^\dagger \mathbf{R}) = (a\mathbf{k}) \cdot \mathbf{R} , \quad (18)$$

so that we can write

$$A\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i(a\mathbf{k}) \cdot \mathbf{R}} A\psi_{n\mathbf{k}}(\mathbf{r}) . \quad (19)$$

Therefore,

$$A\psi_{n\mathbf{k}}(\mathbf{r}) = \psi_{n,a\mathbf{k}}(\mathbf{r}) . \quad (20)$$

Actually, the situation may be more complex if \mathbf{k} is a band-crossing point, i.e., a point at which two or more bands are degenerate, in which case the band index is not necessarily conserved. This will be discussed latter.

In view of Eq. (20) and the fact that the same energy eigenvalue should be associated with both eigenfunctions $\psi_{n\mathbf{k}}(\mathbf{r})$ and $A\psi_{n\mathbf{k}}(\mathbf{r})$, we conclude that

$$\varepsilon_n(a\mathbf{k}) = \varepsilon_n(\mathbf{k}) . \quad (21)$$

This last equality ensures that two wavevectors related by a point-group operation must belong to the same *constant-energy surface* in \mathbf{k} -space. In other words, the shapes of constant-energy surfaces in \mathbf{k} -space are invariant under point-group operations.

It is worth pointing out that the equality $\varepsilon_n(-\mathbf{k}) = \varepsilon_n(\mathbf{k})$ is **always** verified, even if space inversion is not a symmetry operation of a particular system. It is a consequence of time-reversal invariance, which is a property of any system (at the microscopic level).

Band crossing

In the preceding discussion, we obtained Eqs. (20) and (21), where it is assumed that the vectors \mathbf{k} and $a\mathbf{k}$ are not equivalent, but we found that the states associated with them have the same energy. Consider now the case where these vectors are **equivalent**, i.e., they are identical or differ by a reciprocal-lattice vector.

The **wavevector group**, $g_{\mathbf{k}}$, is a subgroup of the point group defined by the relation

$$g_{\mathbf{k}} \equiv \{ a \mid a\mathbf{k} = \mathbf{k} + \mathbf{K} \} . \quad (22)$$

We use the notation $G_{\mathbf{k}}$ for the corresponding group of operators ($A \leftrightarrow a$). Note that, in view of the reduction to the 1st BZ, only \mathbf{k} vectors at special points of this zone may have a nontrivial $g_{\mathbf{k}}$. Some points remain **fixed** under some symmetry operations, as the zone center and points of rotation axes or reflection planes. We may also have points at the BZ boundaries that are connected to each other by reciprocal-lattice vectors.

If the group $G_{\mathbf{k}}$ has only one-dimensional irreducible representations, there are no essential degeneracies. Therefore, the equivalence between the vectors connected by the group members is “trivial”, in the sense of just differing by a reciprocal-lattice vector. However, if $G_{\mathbf{k}}$ has an irreducible representation of dimension $p > 1$, there are p linearly independent

basis functions of this representation. These functions are also energy eigenfunctions, and should differ by the band index, since their wavevector label is the same. In other words, the eigenfunctions of the set $\{\psi_{n_1\mathbf{k}}, \psi_{n_2\mathbf{k}}, \dots, \psi_{n_p\mathbf{k}}\}$ correspond to a p -times degenerate energy eigenvalue, which means that p energy bands cross (or touch) at \mathbf{k} . Therefore, by studying the wavevector group of a degeneracy point found in a band-structure calculation we can check whether this degeneracy is essential or accidental.

Discrete Fourier transform

Given the importance of the reciprocal space for energy eigenvalues and eigenfunctions, it is often convenient to take the Fourier transform of functions of \mathbf{r} to obtain their Fourier components, which are functions of \mathbf{k} . In contrast to the standard Fourier transform, which involves an integral, here we have a sum over discrete \mathbf{k} values. A generic function $F(\mathbf{r})$ has a Fourier representation of the form

$$F(\mathbf{r}) = \sum_{\mathbf{k}} F_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} , \quad (23)$$

the inverse relation being

$$F_{\mathbf{k}} = \frac{1}{V} \int d^3r e^{-i\mathbf{k}\cdot\mathbf{r}} F(\mathbf{r}) , \quad (24)$$

where V is the system's volume. Consistency of these two relations is guaranteed by the identity

$$\frac{1}{V} \int d^3r e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} = \delta_{\mathbf{k},\mathbf{k}'} , \quad (25)$$

which is a consequence of the conditions (14) on possible wavevector values.

A relevant and interesting case is that of a function that is periodic in the lattice (as, for instance, the potential acting on Bloch electrons). If $F(\mathbf{r} + \mathbf{R}) = F(\mathbf{r})$, writing

$$F(\mathbf{r} + \mathbf{R}) = \sum_{\mathbf{k}} F_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r}+\mathbf{R})} , \quad (26)$$

and subtracting Eq. (23) from Eq. (26), we obtain

$$\sum_{\mathbf{k}} F_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} [e^{i\mathbf{k}\cdot\mathbf{R}} - 1] = 0 . \quad (27)$$

This shows that the only nonzero Fourier components of a function that is periodic in the lattice are those corresponding to **reciprocal-lattice vectors**. Therefore, its Fourier representation assumes the form

$$F(\mathbf{r}) = \sum_{\mathbf{K}} F_{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}} . \quad (28)$$

Density of states

Wavevector sums as those in the previous subsection often involve \mathbf{k} -dependent functions that are actually functions of energy, i.e., that depend on \mathbf{k} through $\varepsilon_{\mathbf{k}}$ (for simplicity of notation, we omit the band index here). In dealing with functions of $\varepsilon_{\mathbf{k}}$, it might be convenient to rewrite wavevector sums as integrals over energy values. As mentioned before, relevant quantities are evaluated per unit volume. So, a typical sum is written as

$$\frac{1}{V} \sum_{\mathbf{k}} F(\varepsilon_{\mathbf{k}}) = \int d\varepsilon D(\varepsilon) F(\varepsilon), \quad (29)$$

introducing the *density of states* (DOS), which can be seen to be given by

$$D(\varepsilon) = \frac{1}{V} \sum_{\mathbf{k}} \delta(\varepsilon - \varepsilon_{\mathbf{k}}). \quad (30)$$

By integrating this last equation over a finite energy interval, it is easy to check that the sum of delta functions just counts the number of Bloch states with energies in this interval. We see then that $D(\varepsilon) d\varepsilon$ gives the number of Bloch states with energies between ε and $\varepsilon + d\varepsilon$ per unit volume.

When we approach the thermodynamic limit, sums over \mathbf{k} can also be directly transformed into volume integrals in the reciprocal space. From our previous discussion about distances between neighboring points in the discrete \mathbf{k} -space we see that each \mathbf{k} point “occupies” a volume $(2\pi)^3/V$. Thus, the number of \mathbf{k} values per unit volume of the reciprocal space is $V/(2\pi)^3$. This yields the limit

$$\lim_{V \rightarrow \infty} \frac{1}{V} \sum_{\mathbf{k}} F(\mathbf{k}) = \int \frac{d^3k}{(2\pi)^3} F(\mathbf{k}). \quad (31)$$

Applying this to Eq. (30), we have

$$D(\varepsilon) = \int \frac{d^3k}{(2\pi)^3} \delta(\varepsilon - \varepsilon_{\mathbf{k}}) = \frac{1}{(2\pi)^3} \int_{S_\varepsilon} \frac{dS_{\mathbf{k}}}{|\nabla_{\mathbf{k}} \varepsilon(\mathbf{k})|}, \quad (32)$$

where the last equality involves integration over a constant-energy surface in \mathbf{k} -space, S_ε , defined by the condition $\varepsilon_{\mathbf{k}} = \varepsilon$. Note that the integrand contains a gradient in the denominator. This indicates that there may be singularities of the DOS near a minimum or maximum of $\varepsilon(\mathbf{k})$. They are known as *van Hove singularities*, and can be finite (change of derivative) or infinite (divergence).

Reinserting the band index on energy eigenvalues, Eqs. (30) or (32) give the contribution $D_n(\varepsilon)$ of a given band n to the total DOS $D(\varepsilon) = \sum_n D_n(\varepsilon)$.

Many-electron states

We have begun our discussion with a system of \mathcal{N} electrons. Noticing that we only needed to solve a **one-electron** problem in the independent-electron approximation, our subsequent analysis focused on properties of the energy eigenstates of a single electron in a periodic potential. We now come back to the \mathcal{N} -electron system.

As mentioned before, \mathcal{N} -electron states are antisymmetric combinations of products of \mathcal{N} single-electron wavefunctions (Bloch states). Here it is important to include an additional quantum number σ to account for the two possible projections of the electron *spin* along a given quantization axis. These spin eigenvalues are $\pm\hbar/2$, so that we can choose $\sigma = \pm$, or $\sigma = \uparrow, \downarrow$, which are the most common notations. So, the **individual states** are now characterized by the **band index**, the **wavevector**, and the **spin state**. They can be formally represented as vectors in the Hilbert space denoted by $|n\mathbf{k}\sigma\rangle$. A simple way to construct possible states of the whole system is to build up $\mathcal{N} \times \mathcal{N}$ *Slater determinants*, associating \mathcal{N} vectors of type $|n\mathbf{k}\sigma\rangle$, one to each of the \mathcal{N} electrons, in all possible combinations.

At present, our Hamiltonian does not have spin-dependent terms, which means that individual energy eigenvalues are doubly degenerate with respect to spin. We usually say that each Bloch state can be “occupied” at most by two electrons with opposite spins, in view of Pauli’s *exclusion principle*. The energy of a given \mathcal{N} -electron state is the sum of their individual energies.

From the above comments, we infer that the ground state of \mathcal{N} electrons can be thought as being built up by distributing these electrons in the $\mathcal{N}/2$ Bloch states of lowest energy, in pairs of opposite spins. It is worth noticing that the general symmetry $\varepsilon_n(-\mathbf{k}) = \varepsilon_n(\mathbf{k})$ implies that an equal number of states of opposite wavevectors are occupied in the ground-state. So, from our discussion of electron velocity in Bloch states we conclude that there is no net charge flow, even though the electrons occupy extended states.

Depending on the number of electrons, we can have two qualitatively different results for the ground state:

1. A certain number of energy bands is completely filled, and there is an energy gap separating the upper bands, which are empty. So, the solid is either an **insulator** or a **semiconductor**. The difference between them is only quantitative, associated with the width of the energy gap, which is large in insulators, but sufficiently small to allow electrons to be thermally promoted to the next band in semiconductors.
2. The highest occupied energy band(s) is(are) not completely filled. Then, an imbalance in the occupation of states with opposite wavevectors can be induced by an external field, resulting in a net charge current, which characterizes a **conductor** or **metal**.

In a metal, the highest energy of occupied Bloch states in non-filled bands is called *Fermi energy*, here denoted by ε_F . The equality

$$\varepsilon_n(\mathbf{k}) = \varepsilon_F \tag{33}$$

defines a special constant-energy surface in \mathbf{k} -space called the *Fermi surface*. It separates the region of occupied states (inside) from that of empty states (outside) in the ground-state of the whole system. Note that this definition is only applicable to metals, for which the distribution of states in energy is essentially continuous. For an insulator or a semiconductor such surface could be anywhere inside the gap, with a shape not uniquely defined. We will come back to this point when briefly discussing temperature effects on semiconductors. For now we suppose that we are dealing with a metal.

The Fermi surface may be entirely contained in a single band, or may have branches in more than one band, depending on possible overlaps in the specific band structure. Being constant-energy surfaces, all branches of the Fermi surface have shapes that are invariant under all operations of the point group.

It is worth noticing that the general symmetry $\varepsilon_n(-\mathbf{k}) = \varepsilon_n(\mathbf{k})$ implies that an equal number of states of opposite wavevectors are occupied in the ground-state. So, in view of Eq. (16), one concludes that there is no **net** flow of electrons, even though they occupy extended states.

Finally, we should keep in mind that the Fermi surface is a ground-state concept, while real solids are not in the ground state. So, the nature of excitations and their role in thermodynamic equilibrium must be addressed in order to judge the relevance of the Fermi surface to observed properties of solids. This includes a comparison between thermal energy and the natural energy scale set by ε_F . Quantitative estimations of the latter can only be made by choosing specific models. This will be done in our next Text.