SECOND PROOF OF BLOCH'S THEOREM

This second proof of Bloch's theorem illuminates its significance from a rather different point of view, which we shall exploit further in Chapter 9. We start with the observation that one can always expand any function obeying the Born–von Karman boundary condition (8.22) in the set of all plane waves that satisfy the boundary condition and therefore have wave vectors of the form (8.27):[9]

$$\psi(\mathbf{r}) = \sum_{\mathbf{q}} c_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}$$

Because the potential $U(\mathbf{r})$ is periodic in the lattice, its plane wave expansion will only contain plane waves with the periodicity of the lattice and therefore with wave vectors that are vectors of the reciprocal lattice:[10]

$$U(\mathbf{r}) = \sum_{\mathbf{K}} U_{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}}$$

$$U_{\mathbf{K}} = \frac{1}{v}\int_{\text{cell}} d\mathbf{r}\, e^{-i\mathbf{K}\cdot\mathbf{r}} U(\mathbf{r})$$

Since we are at liberty to change the potential energy by an additive constant, we fix this constant by requiring that the spatial average U_0 of the potential over a primitive cell vanish:

$$U_0 = \frac{1}{v}\int_{\text{cell}} d\mathbf{r}\, U(\mathbf{r}) = 0$$

Note that because the potential $U(\mathbf{r})$ is real, it follows from (8.32) that the Fourier coefficients satisfy

$$U_{\mathbf{K}}^* = \frac{1}{V}\int_{\text{cell}} d\mathbf{r} e^{i\mathbf{K}.\mathbf{r}} U^*(\mathbf{r}) = \frac{1}{V}\int_{\text{cell}} d\mathbf{r} e^{i\mathbf{K}.\mathbf{r}} U(\mathbf{r}) = U_{-\mathbf{K}}$$

If we assume that the crystal has inversion symmetry

$$U(-\mathbf{r}) = U(\mathbf{r})$$

$$U_{-\mathbf{K}} = \frac{1}{V}\int_{\text{cell}} d\mathbf{r} e^{i\mathbf{K}.\mathbf{r}} U(\mathbf{r}) = \frac{1}{V}\int_{\text{cell}} d\mathbf{r} e^{i\mathbf{K}.\mathbf{r}} U(-\mathbf{r}) = \frac{1}{V}\int_{\text{cell}} d\mathbf{r} e^{-i\mathbf{K}.\mathbf{r}} U(\mathbf{r}) = U_{\mathbf{K}}(\mathbf{r})$$

$$U_{-\mathbf{K}} = U_{\mathbf{K}} = U_{\mathbf{K}}^* \qquad \text{Thus } U_{\mathbf{K}} \text{ is also real}$$

The kinetic energy term gives

$$\frac{p^2}{2m}\psi = -\frac{\hbar^2}{2m}\nabla^2\psi = \sum_{\mathbf{q}} \frac{\hbar^2}{2m} q^2 c_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}$$

The term in the potential energy can be written

$$U\psi = \left(\sum_{\mathbf{K}} U_{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}}\right)\left(\sum_{\mathbf{q}} c_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}\right) = \sum_{\mathbf{K}\mathbf{q}} U_{\mathbf{K}} c_{\mathbf{q}} e^{i(\mathbf{K}+\mathbf{q})\cdot\mathbf{r}} = \sum_{\mathbf{K}\mathbf{q}'} U_{\mathbf{K}} c_{\mathbf{q}'-\mathbf{K}} e^{i\mathbf{q}'\cdot\mathbf{r}}$$

We change the names of the summation indices in (8.37)—from $\mathbf{K}$ and $\mathbf{q}'$, to $\mathbf{K}'$ and $\mathbf{q}$—so that the Schrödinger equation becomes

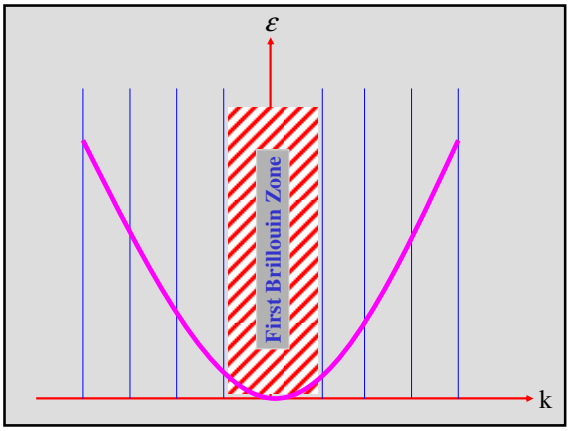
$$\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \left\{\left(\frac{\hbar^2}{2m} q^2 - \mathcal{E}\right) c_{\mathbf{q}} + \sum_{\mathbf{K}'} U_{\mathbf{K}}\, c_{\mathbf{q}-\mathbf{K}'}\right\} = 0$$

Since the plane waves satisfying the Born–von Karman boundary condition are an orthogonal set, the coefficient of each separate term in (8.38) must vanish,[14] and therefore for all allowed wave vectors $\mathbf{q}$,

$$\left(\frac{\hbar^2}{2m} q^2 - \varepsilon\right) c_{\mathbf{q}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'} c_{\mathbf{q}-\mathbf{K}'} = 0$$

It is convenient to write $\mathbf{q}$ in the form $\mathbf{q} = \mathbf{k} - \mathbf{K}$, where $\mathbf{K}$ is a reciprocal lattice vector chosen so that $\mathbf{k}$ lies in the first Brillouin zone. Equation (8.39) becomes

$$\left(\frac{\hbar^2}{2m}(\mathbf{k} - \mathbf{K})^2 - \varepsilon\right) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'} c_{\mathbf{k}-\mathbf{K}-\mathbf{K}'} = 0,$$



$$\left(\frac{\hbar^2}{2m} q^2 - \varepsilon\right) c_{\mathbf{q}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'} c_{\mathbf{q}-\mathbf{K}'} = 0$$

$$\left(\frac{\hbar^2}{2m}(\mathbf{k} - \mathbf{K})^2 - \varepsilon\right) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'} c_{\mathbf{k}-\mathbf{K}-\mathbf{K}'} = 0,$$

$$\mathbf{K}' \to \mathbf{K}' - \mathbf{K}$$

$$\left(\frac{\hbar^2}{2m}(\mathbf{k} - \mathbf{K})^2 - \varepsilon\right) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} c_{\mathbf{k}-\mathbf{K}'} = 0.$$

We emphasize that Eqs. (8.39) and (8.41) are nothing but restatements of the original Schrödinger equation (8.2) in momentum space, simplified by the fact that because of the periodicity of the potential, $U_{\mathbf{k}}$ is nonvanishing only when $\mathbf{k}$ is a vector of the reciprocal lattice.

$$(\lambda_k - \epsilon)C(k) + \sum_G U_G C(k-G) = 0$$

$$U_g = U_{-g} = U \qquad U_{2g} = U_{-2g} = U_{3g} = U_{-3g} = \ldots = 0$$

$$\begin{cases} (\lambda_k - \varepsilon)C(k) + UC(k+g) + UC(k-g) = 0 \\ (\lambda_{k+g} - \varepsilon)C(k+g) + UC(k+2g) + UC(k) = 0 \\ (\lambda_{k-g} - \varepsilon)C(k-g) + UC(k) + UC(k-2g) = 0 \end{cases}$$

$$\begin{vmatrix} \lambda_{k+2g} - \epsilon & U & 0 & 0 & 0 \\ U & \lambda_{k-g} - \epsilon & U & 0 & 0 \\ 0 & U & \lambda_k - \epsilon & U & 0 \\ 0 & 0 & U & \lambda_{k+g} - \epsilon & U \\ 0 & 0 & 0 & U & \lambda_{k+2g} - \epsilon \end{vmatrix}$$

For fixed $\mathbf{k}$ in the first Brillouin zone, the set of equations (8.41) for all reciprocal lattice vectors $\mathbf{K}$ couples only those coefficients $c_{\mathbf{k}}$, $c_{\mathbf{k}-\mathbf{K}}$, $c_{\mathbf{k}-\mathbf{K}'}$, $c_{\mathbf{k}-\mathbf{K}''}$, . . . whose wave vectors differ from $\mathbf{k}$ by a reciprocal lattice vector. Thus the original problem has separated into N independent problems: one for each allowed value of $\mathbf{k}$ in the first Brillouin zone. Each such problem has solutions that are superpositions of plane waves containing only the wave vector $\mathbf{k}$ and wave vectors differing from $\mathbf{k}$ by a reciprocal lattice vector.

Putting this information back into the expansion (8.30) of the wave function ψ, we see that if the wave vector $\mathbf{q}$ only assumes the values $\mathbf{k}$, $\mathbf{k} - \mathbf{K}'$, $\mathbf{k} - \mathbf{K}''$, . . . , then the wave function will be of the form

$$\psi_{\mathbf{k}} = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{i(\mathbf{k}-\mathbf{K})\cdot\mathbf{r}}$$

u(r)

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \left(\sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{-i\mathbf{K}\cdot\mathbf{r}} \right)$$

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

☺

General Remarks about Bloch's Theorem

1. Bloch's theorem introduces a wave vector $\mathbf{k}$, which turns out to play the same fundamental role in the general problem of motion in a periodic potential that the free electron wave vector $\mathbf{k}$ plays in the Sommerfeld theory. Note, however, that although the free electron wave vector is simply $\mathbf{p}/\hbar$, where $\mathbf{p}$ is the momentum of the electron, in the Bloch case $\mathbf{k}$ is not proportional to the electronic momentum. This is clear on general grounds, since the Hamiltonian does not have complete translational invariance in the presence of a nonconstant potential, and therefore its eigenstates will not be simultaneous eigenstates of the momentum operator. This conclusion is confirmed by the fact that the momentum operator, $\mathbf{p} = (\hbar/i)\nabla$, when acting on ψ_{nk} gives

For free electrons we have: $\mathbf{p} = \hbar\mathbf{k}$

Which is no longer valid for Bloch electrons: $\mathbf{p} \neq \hbar\mathbf{k}$

The wave function of a free electron can be written as: $\psi_{\mathbf{k}} = e^{i\mathbf{k}.\mathbf{r}}$

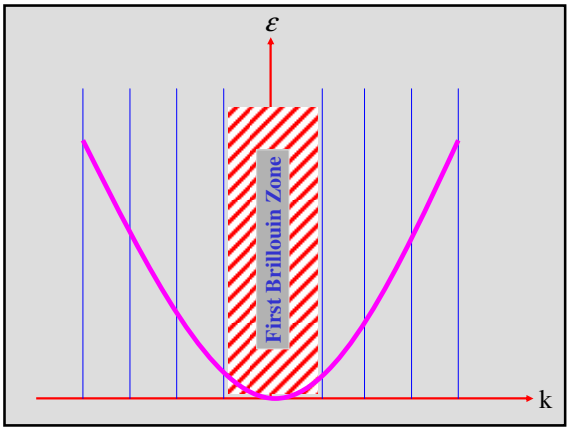
The momentum operator is: $\hat{\mathbf{p}} = -i\hbar\nabla$

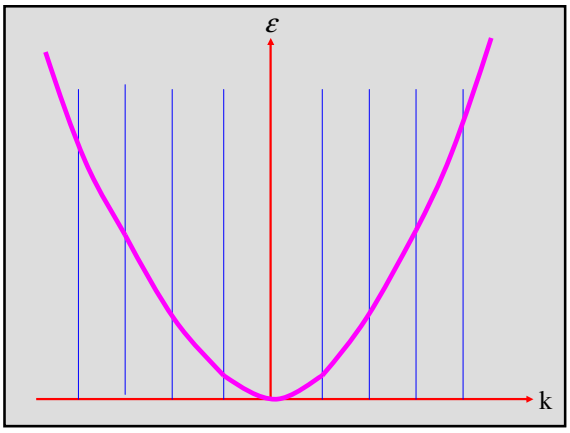
Free electron	Bloch electron
$\hat{\mathbf{p}}\psi_{\mathbf{k}} = -i\hbar\nabla e^{i\mathbf{k}.\mathbf{r}}$	$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$
$\hat{\mathbf{p}}\psi_{\mathbf{k}} = \hbar\mathbf{k}e^{i\mathbf{k}.\mathbf{r}}$	$\frac{\hbar}{i}\nabla\psi_{n\mathbf{k}} = \frac{\hbar}{i}\nabla(e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r}))$
$\hat{\mathbf{p}}\psi_{\mathbf{k}} = \mathbf{p}e^{i\mathbf{k}.\mathbf{r}}$	
$\hat{\mathbf{p}}\psi_{\mathbf{k}} = \mathbf{p}\psi_{\mathbf{k}}$ ☺	$= \hbar\mathbf{k}\psi_{n\mathbf{k}} + e^{i\mathbf{k}\cdot\mathbf{r}}\frac{\hbar}{i}\nabla u_{n\mathbf{k}}(\mathbf{r})$
$\mathbf{p} = \hbar\mathbf{k} = m\mathbf{v}$	$\neq \hbar\mathbf{k}\psi_{nk}$ ☹
$\mathbf{v} = \frac{\hbar\mathbf{k}}{m}$	If the periodic potential is not a function of r, then the Bloch wave function is also an eigenvector of the momentum operator (like free electron):

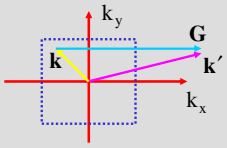
2. The wave vector $\mathbf{k}$ appearing in Bloch's theorem can always be confined to the first Brillouin zone (or to any other convenient primitive cell of the reciprocal lattice). This is because any $\mathbf{k}'$ not in the first Brillouin zone can be written as

$$\mathbf{k}' = \mathbf{k} + \mathbf{K}$$

where $\mathbf{K}$ is a reciprocal lattice vector and $\mathbf{k}$ does lie in the first zone. Since $e^{i\mathbf{K}\cdot\mathbf{R}} = 1$ for any reciprocal lattice vector, if the Bloch form (8.6) holds for $\mathbf{k}'$, it will also hold for $\mathbf{k}$.







$$\psi_{\mathbf{k}'}(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}'}(\mathbf{r}) e^{i\mathbf{G}.\mathbf{r}}$$

$$u_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = \underbrace{e^{i\mathbf{G}.\mathbf{R}}}_{1} e^{i\mathbf{G}.\mathbf{r}} \underbrace{u_{\mathbf{k}'}(\mathbf{r}+\mathbf{R})}_{u_{\mathbf{k}'}(\mathbf{r})}$$

$$\psi_{\mathbf{k}'}(\mathbf{r}) = e^{i\mathbf{k}'.\mathbf{r}} u_{\mathbf{k}'}(\mathbf{r})$$

$$\mathbf{k} \longrightarrow \mathbf{k}' - \mathbf{G}$$

$$u_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{G}.\mathbf{r}} u_{\mathbf{k}'}(\mathbf{r})$$

$$\psi_{\mathbf{k}'}(\mathbf{r}) = e^{i(\mathbf{k}+\mathbf{G}).\mathbf{r}} u_{\mathbf{k}'}(\mathbf{r})$$

$$u_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{\mathbf{k}}(\mathbf{r})$$

$$\psi_{\mathbf{k}'}(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}} \left\{ e^{i\mathbf{G}.\mathbf{r}} u_{\mathbf{k}'}(\mathbf{r}) \right\}$$

$$\psi_{\mathbf{k}'}(\mathbf{r}) = \psi_{\mathbf{k}}(\mathbf{r})$$

Therefore it is established that the wave function out side of the first Brillouin zone is equal to the wave function inside the Brillouin zone.

3. The index n appears in Bloch's theorem because for given $\mathbf{k}$ there are many solutions to the Schrödinger equation. We noted this in the second proof of Bloch's theorem, but it can also be seen from the following argument:

Let us look for all solutions to the Schrödinger equation (8.2) that have the Bloch form

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u(\mathbf{r}), \tag{8.47}$$

where $\mathbf{k}$ is fixed and u has the periodicity of the Bravais lattice. Substituting this into the Schrödinger equation, we find that u is determined by the eigenvalue problem

$$H_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r}) = \left(\frac{\hbar^2}{2m}\left(\frac{1}{i}\nabla + \mathbf{k}\right)^2 + U(\mathbf{r})\right) u_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}} u_{\mathbf{k}}(\mathbf{r}) \tag{8.48}$$

with boundary condition

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}). \tag{8.49}$$

Because of the periodic boundary condition we can regard (8.48) as a Hermitian eigenvalue problem restricted to a single primitive cell of the crystal. Because the eigenvalue problem is set in a fixed finite volume, we expect on general grounds to find an infinite family of solutions with *discretely* spaced eigenvalues,[16] which we label with the band index n.

Note that in terms of the eigenvalue problem specified by (8.48) and (8.49), the wave vector $\mathbf{k}$ appears only as a parameter in the Hamiltonian $H_{\mathbf{k}}$. We therefore expect each of the energy levels, for given $\mathbf{k}$, to vary continuously as $\mathbf{k}$ varies.[17] In this way we arrive at a description of the levels of an electron in a periodic potential in terms of a family of continuous[18] functions $\varepsilon_n(\mathbf{k})$.

Bloch's theorem transforms bands to first Brillouin zone

$$H_i \psi_i = \varepsilon_i \psi_i$$

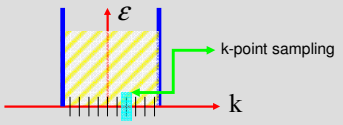
The index i refers to the number of electrons. The number of electrons is large. Bloch's theorem transform index i to two n,**k** indexes:

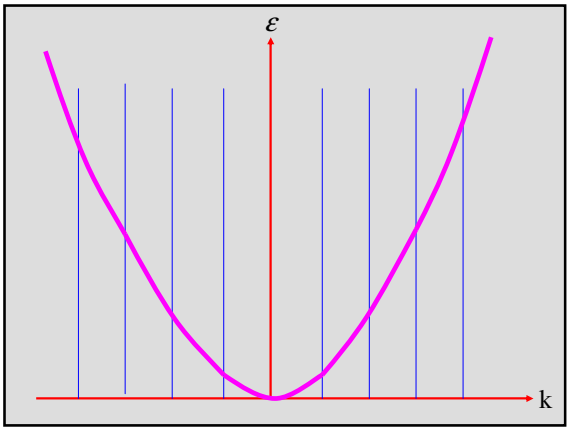
$$\psi_i \longrightarrow \psi_{n,\mathbf{k}} = \sum_{\mathbf{G}} C_{n,\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G}).\mathbf{r}}$$

Then we can do k-point sampling around each selected k, where we assume that the wave functions around this k-point are nearly the same:

Number of bands is small

k still a large number

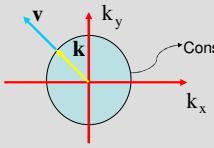




Electron velocity inside a crystal

$$\psi_{\mathbf{k}}(\mathbf{r}) \longrightarrow \mathbf{v}(\mathbf{k})$$

For Fermi electron: $\mathbf{p} = \hbar\mathbf{k} = m\mathbf{v} \Longrightarrow \mathbf{v} = \frac{\mathbf{p}}{m} = \frac{\hbar\mathbf{k}}{m}$



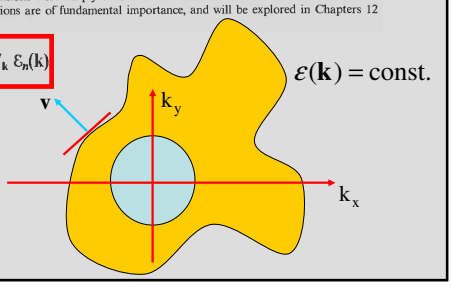
Constant energy surface: $\varepsilon = \frac{\hbar^2 \mathbf{k}^2}{2m} = \text{const.}$

$$\frac{1}{\hbar}\frac{\partial \varepsilon_{\mathbf{k}}}{\partial \mathbf{k}} = \frac{\hbar\mathbf{k}}{m} = \mathbf{v}$$

For the case of Bloch's electrons one can also derive the velocity of the Bloch electron (see appendix E): $\mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar}\nabla_{\mathbf{k}}\,\varepsilon_n(\mathbf{k})$

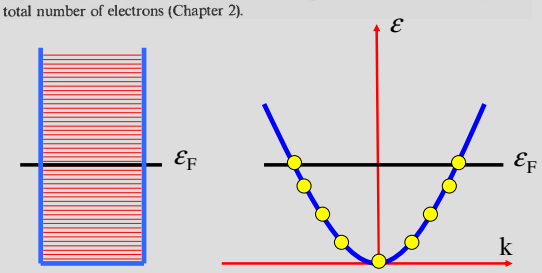
This is a most remarkable fact. It asserts that there are stationary (i.e., time-independent) levels for an electron in a periodic potential in which, in spite of the interaction of the electron with the fixed lattice of ions, it moves forever without any degradation of its mean velocity. This is in striking contrast to the idea of Drude that collisions were simply encounters between the electron and a static ion. Its implications are of fundamental importance, and will be explored in Chapters 12 and 13.

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

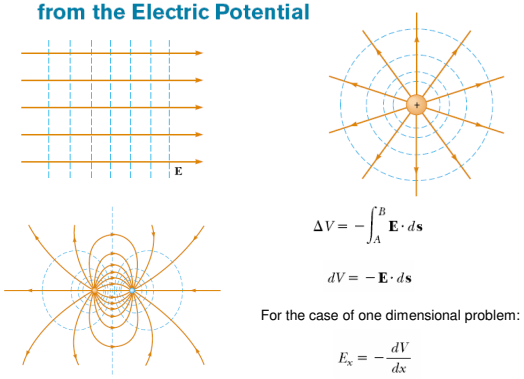


Ferrmi Surface

The ground state of N free electrons[19] is constructed by occupying all one-electron levels $\mathbf{k}$ with energies $\varepsilon(\mathbf{k}) = \hbar^2k^2/2m$ less than ε_F, where ε_F is determined by requiring the total number of one-electron levels with energies less than ε_F to be equal to the total number of electrons (Chapter 2).



Obtaining the Value of the Electric Field from the Electric Potential



$$\Delta V = -\int_A^B \mathbf{E}\cdot d\mathbf{s}$$

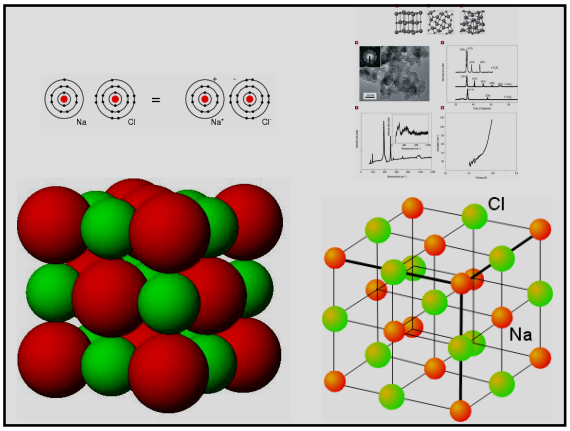
$$dV = -\mathbf{E}\cdot d\mathbf{s}$$

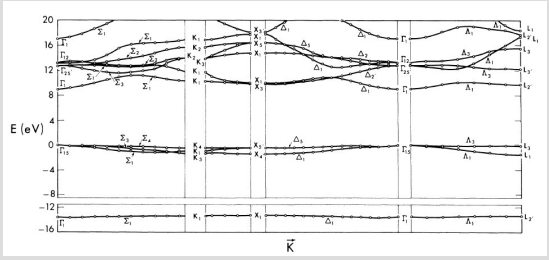
For the case of one dimensional problem:

$$E_x = -\frac{dV}{dx}$$

The ground state of N Bloch electrons is similarly constructed, except that the one-electron levels are now labeled by the quantum numbers n and $\mathbf{k}$, $\varepsilon_n(\mathbf{k})$ does not have the simple explicit free electron form, and $\mathbf{k}$ must be confined to a single primitive cell of the reciprocal lattice if each level is to be counted only once. When the lowest of these levels are filled by a specified number of electrons, two quite distinct types of configuration can result:

1. A certain number of bands may be completely filled, all others remaining empty. The difference in energy between the highest occupied level and the lowest unoccupied level (i.e., between the "top" of the highest occupied band and the "bottom" of the lowest empty band) is known as the *band gap*. We shall find that solids with a band gap greatly in excess of k_BT (T near room temperature) are insulators (Chapter 12). If the band gap is comparable to k_BT, the solid is known as an *intrinsic semiconductor* (Chapter 28). Because the number of levels in a band is equal to the number of primitive cells in the crystal (page 136) and because each level can accommodate two electrons (one of each spin), *a configuration with a band gap can arise (though it need not) only if the number of electrons per primitive cell is even.*





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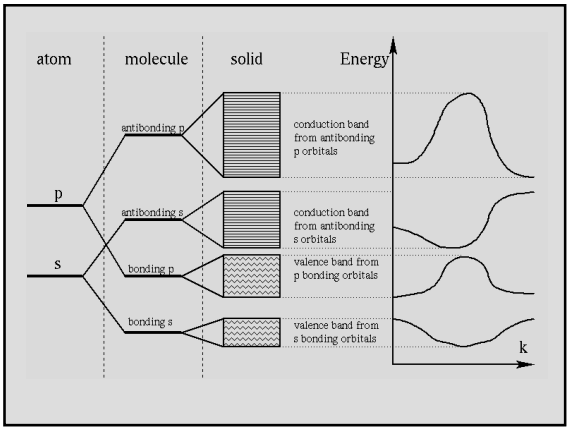
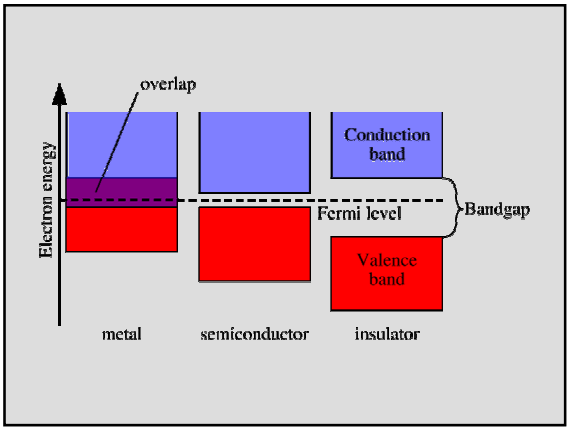
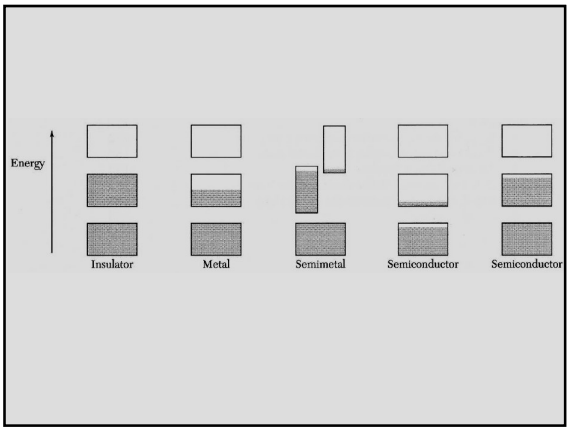






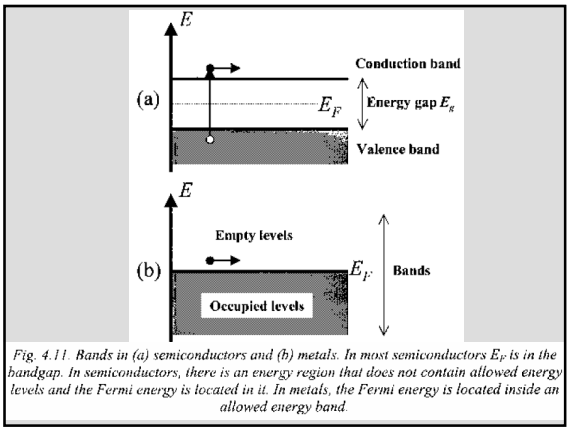


Fig. 4.11 Bands in (a) semiconductors and (b) metals. In most semiconductors E_F is in the bandgap. In semiconductors, there is an energy region that does not contain allowed energy levels and the Fermi energy is located in it. In metals, the Fermi energy is located inside an allowed energy band.

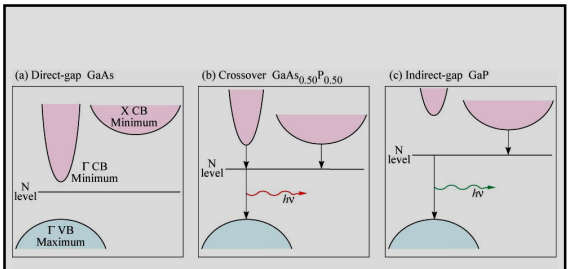
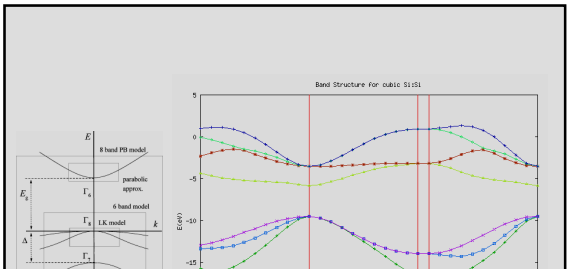
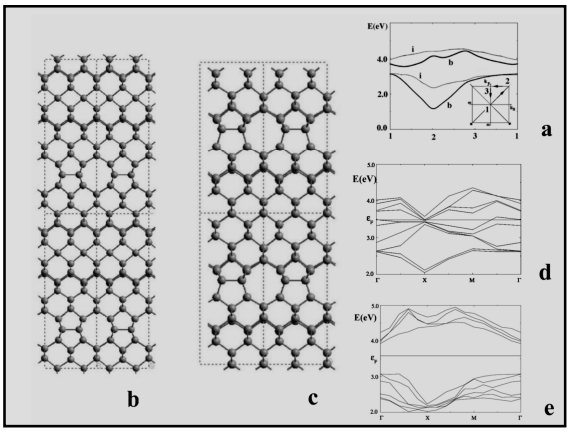


Fig. 12.1. Schematic band structure of GaAs, GaAsP, and GaP. Also shown is the nitrogen level. At a P mole fraction of about 45–50 %, the direct–indirect crossover

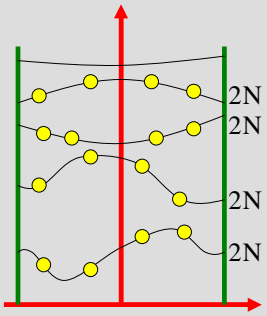




NaCl

Let N be total number of lattice points of NaCl. Total number of valence electrons in each unit cell is: 1+7=8

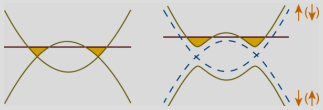
Therefore total number oif valence electrons is 8N.

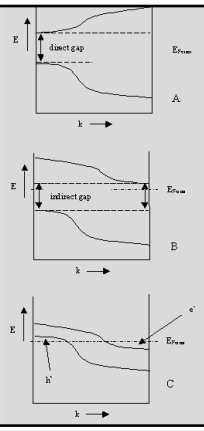


The total 8N electrons should be distributed over the valence bands.

A **semimetal** is a material with a small overlap in the energy of the conduction band and valence bands.

A) a semiconductor with a direct gap (like e.g. CuInSe2),
B) a semiconductor with an indirect gap (like Si) and
C) a semimetal (like Sn or graphite).





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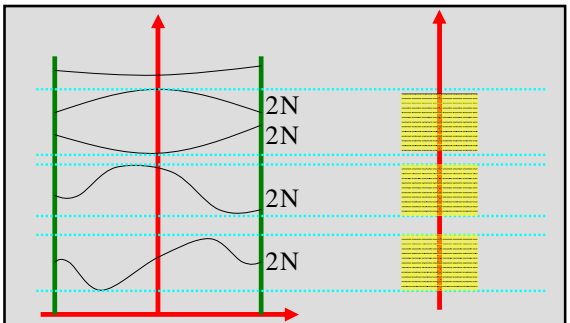
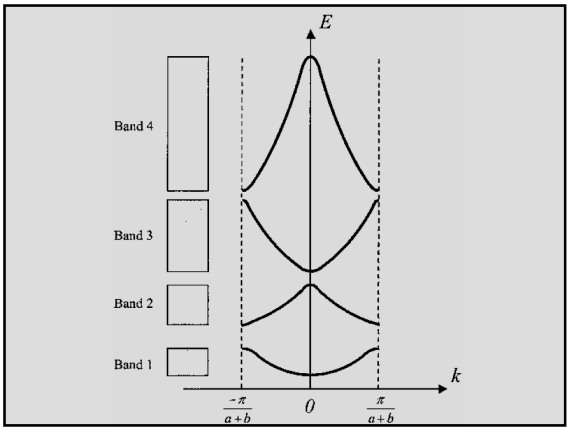
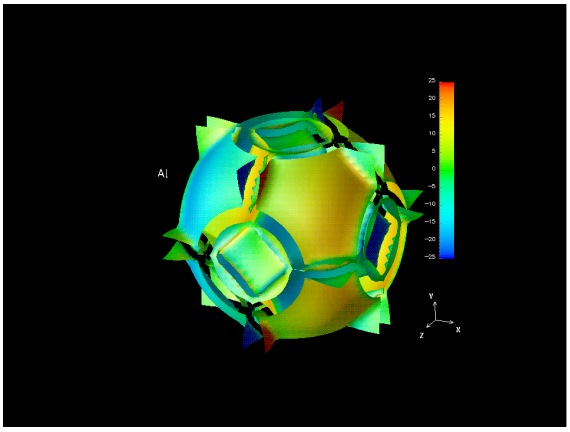
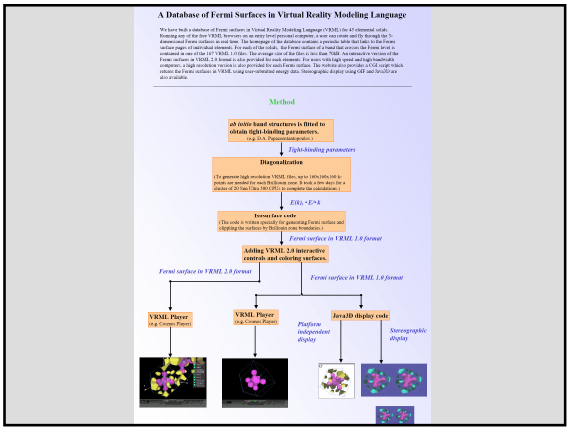
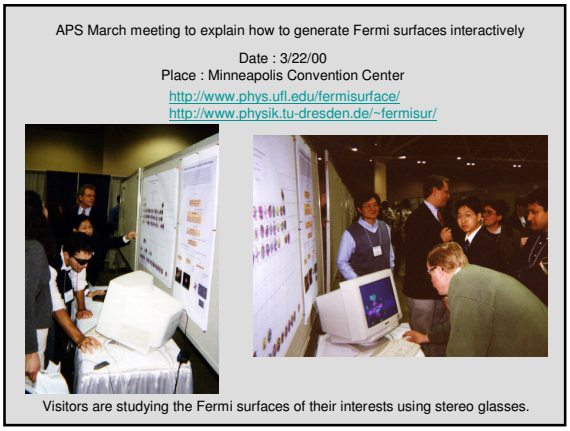
Structure of energy spectrum in a semimetal (left) and in an excitonic insulator (right).

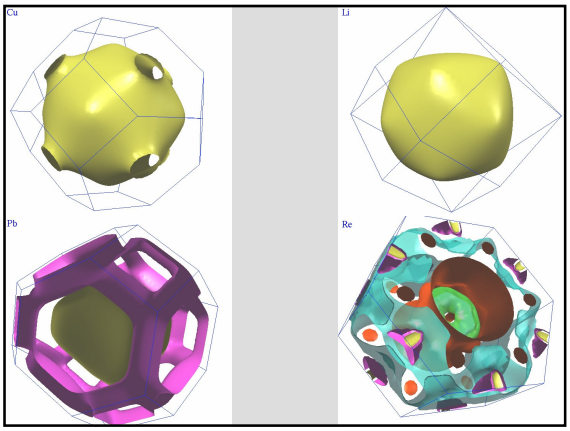


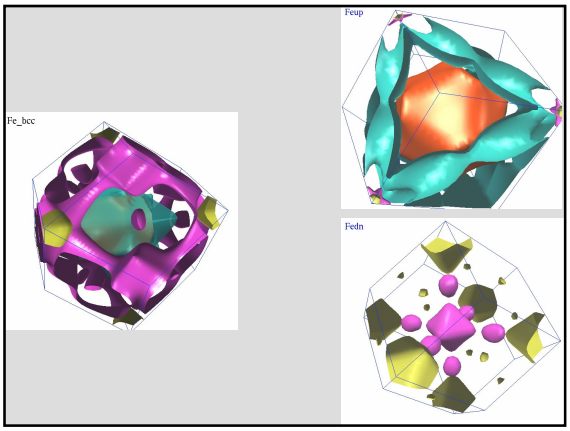












Density of States (DOS)

One must often calculate quantities that are weighted sums over the electronic levels of various one-electron properties. Such quantities are of the form[23]

$$Q = 2\sum_{n,\mathbf{k}} Q_n(\mathbf{k}),$$

where for each n the sum is over all allowed $\mathbf{k}$ giving physically distinct levels, i.e., all $\mathbf{k}$ of the form (8.27) lying in a single primitive cell.[24]

In the limit of a large crystal the allowed values (8.27) of $\mathbf{k}$ get very close together, and the sum may be replaced with an integral. Since the volume of k-space per allowed $\mathbf{k}$ (Eq. (8.29)) has the same value as in the free electron case, the prescription derived in the free electron case (Eq. (2.29)) remains valid, and we find that[25]

$$q = \lim_{V\to\infty}\frac{Q}{V} = 2\sum_n \int \frac{d\mathbf{k}}{(2\pi)^3} Q_n(\mathbf{k}),$$

where the integral is over a primitive cell.

If, as is often the case,[26] $Q_n(\mathbf{k})$ depends on n and $\mathbf{k}$ only through the energy $\varepsilon_n(\mathbf{k})$, then in further analogy to the free electron case one can define a density of levels per unit volume (or "density of levels" for short) $g(\varepsilon)$ so that q has the form (cf. (2.60)):

$$q = \int d\varepsilon\, g(\varepsilon) Q(\varepsilon).$$

[26] For example, if q is the electronic number density n, then $Q(\varepsilon) = f(\varepsilon)$, where f is the Fermi function; if q is the electronic energy density u, then $Q(\varepsilon) = \varepsilon f(\varepsilon)$.

Comparing (8.54) and (8.55) we find that

$$g(\varepsilon) = \sum_n g_n(\varepsilon),$$

where $g_n(\varepsilon)$, the density of levels in the nth band, is given by

$$g_n(\varepsilon) = \int \frac{d\mathbf{k}}{4\pi^3}\,\delta(\varepsilon - \varepsilon_n(\mathbf{k})),$$

where the integral is over any primitive cell.

An alternative representation of the density of levels can be constructed by noting that, as in the free electron case (Eq. (2.62)):

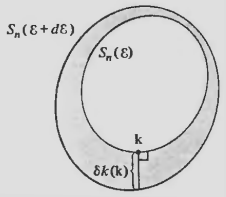
$$g_n(\varepsilon)\,d\varepsilon = (2/V) \times \begin{pmatrix}\text{(the number of allowed wave vectors}\\ \text{in the } n\text{th band in the energy range}\\ \text{from } \varepsilon \text{ to } \varepsilon + d\varepsilon\text{).}\end{pmatrix}$$

The number of allowed wave vectors in the nth band in this energy range is just the volume of a k-space primitive cell, with $\varepsilon \leqslant \varepsilon_n(\mathbf{k}) \leqslant \varepsilon + d\varepsilon$, divided by the volume per allowed wave vector, $\Delta\mathbf{k} = (2\pi)^3/V$. Thus

$$g_n(\varepsilon)\,d\varepsilon = \int \frac{d\mathbf{k}}{4\pi^3} \times \begin{Bmatrix} 1, & \varepsilon \leqslant \varepsilon_n(\mathbf{k}) \leqslant \varepsilon + d\varepsilon, \\ 0, & \text{otherwise} \end{Bmatrix}.$$

Since $d\varepsilon$ is infinitesimal, this can also be expressed as a surface integral. Let $S_n(\varepsilon)$ be the portion of the surface $\varepsilon_n(\mathbf{k}) = \varepsilon$ lying within the primitive cell, and let $\delta k(\mathbf{k})$ be the perpendicular distance between the surfaces $S_n(\varepsilon)$ and $S_n(\varepsilon + d\varepsilon)$ at the point $\mathbf{k}$. Then (Figure 8.2):

$$g_n(\varepsilon)\,d\varepsilon = \int_{S_n(\varepsilon)} \frac{dS}{4\pi^3}\,\delta k(\mathbf{k}).$$



An illustration in two dimensions of the construction expressed in Eq. (8.60). The closed curves are the two constant-energy surfaces, the required area is that lying between them (shaded), and the distance $\delta k(\mathbf{k})$ is indicated for a particular $\mathbf{k}$.

To find an explicit expression for $\delta k(\mathbf{k})$ note that, since $S_n(\varepsilon)$ is a surface of constant energy, the k-gradient of $\varepsilon_n(\mathbf{k})$, $\nabla\varepsilon_n(\mathbf{k})$, is a vector normal to that surface whose magnitude is equal to the rate of change of $\varepsilon_n(\mathbf{k})$ in the normal direction; i.e.,

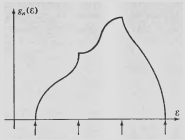
$$\varepsilon + d\varepsilon = \varepsilon + \left|\nabla\varepsilon_n(\mathbf{k})\right| \delta k(\mathbf{k}),$$

$$\delta k(\mathbf{k}) = \frac{d\varepsilon}{\left|\nabla\varepsilon_n(\mathbf{k})\right|}. \qquad g_n(\varepsilon) = \int_{S_n(\varepsilon)} \frac{dS}{4\pi^3} \frac{1}{\left|\nabla\varepsilon_n(\mathbf{k})\right|}$$

which gives an explicit relation between the density of levels and the band structure.

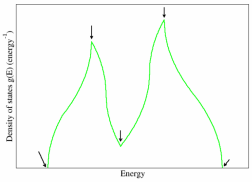
Because $\varepsilon_n(\mathbf{k})$ is periodic in the reciprocal lattice, bounded above and below for each n, and, in general, everywhere differentiable, there must be values of $\mathbf{k}$ in each primitive cell at which $|\nabla\varepsilon| = 0$. For example, the gradient of a differentiable function vanishes at local maxima and minima, but the boundedness and periodicity of each $\varepsilon_n(\mathbf{k})$ insure that for each n there will be at least one maximum and minimum in each primitive cell.[28]

When the gradient of ε_n vanishes, the integrand in the density of levels (8.63) diverges. It can be shown that in three dimensions[29] such singularities are integrable, yielding finite values for g_n. However, they do result in divergences of the slope, $dg_n/d\varepsilon$. These are known as *van Hove singularities*.[30] They occur at values of ε for which the constant energy surface $S_n(\varepsilon)$ contains points at which $\nabla\varepsilon_n(\mathbf{k})$ vanishes. Since derivatives of the density of levels at the Fermi energy enter into all terms but the first in the Sommerfeld expansion,[31] one must be on guard for anomalies in low-temperature behavior if there are points of vanishing $\nabla\varepsilon_n(\mathbf{k})$ on the Fermi surface.



$$g(E) = \frac{a^3}{(2\pi)^3} \int\int \frac{dk'_x\,dk'_y}{|\vec{\nabla}E|}$$

$$|\vec{\nabla}E| = \hbar^2 k/m = \hbar\sqrt{\frac{2E}{m}}$$



The density of states g(E) for a typical three-dimensional solid showing van Hove singularities indicated by black arrows. The function g(E) tends to have square-root singularities since $g(E) \approx \int \frac{dE}{\vec{\nabla}E}$ and since for a spherical Fermi surface $E = \hbar^2k^2/2m$ so that $\vec{\nabla}E = \hbar^2k/m = \hbar\sqrt{\frac{2E}{m}}$.

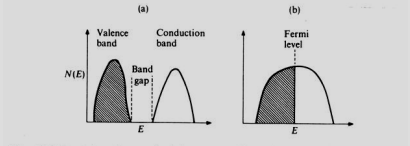
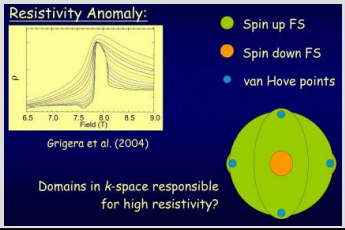
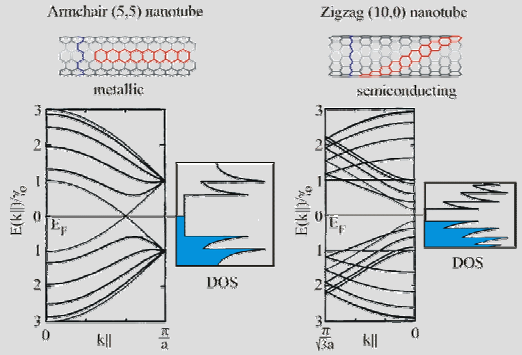
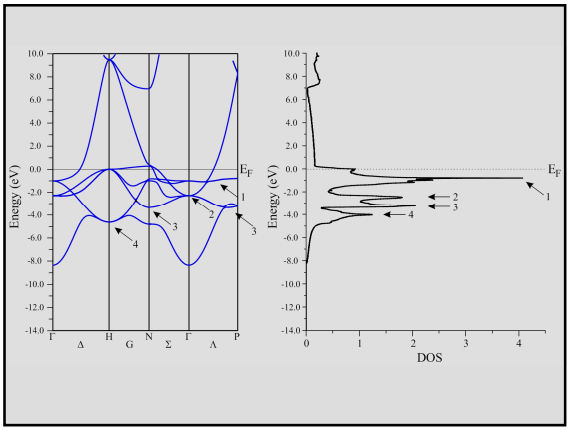
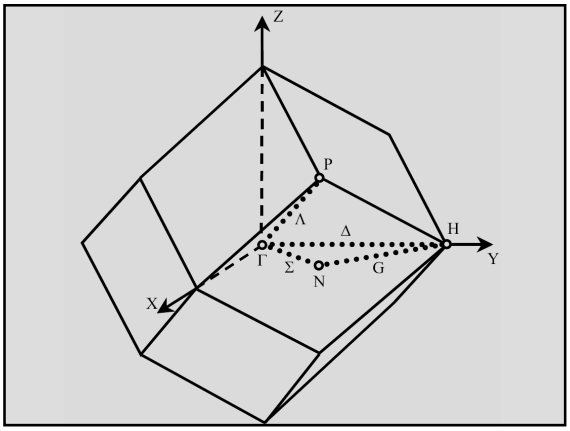


Fig. 1.8 Densities of states in (a) non-metallic solid, and (b) metal. Shading represents occupied levels.









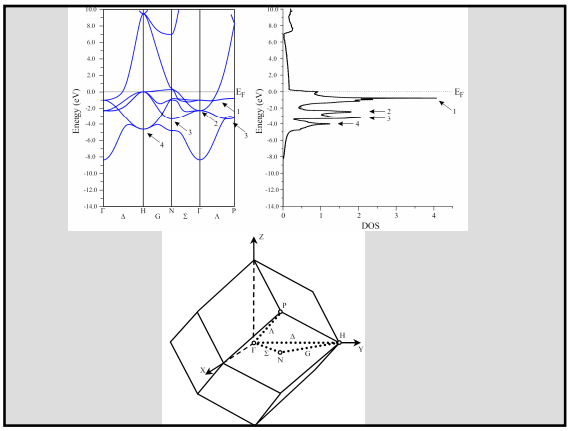


Figure B.5: *Bottom: The first Brillouin zone of a bcc lattice, with 4 high symmetry points indicated: Γ, H, N and P. These points are connected by lines, labeled Δ, G, Σ and Λ. These 4 lines define a path through the Brillouin zone. Top left: the eigenvalues of all the k-vectors along the path are plotted, for some bcc compound (bcc-Fe, spin up). This so-called* band structure plot *contains less information than the full eigenvalues-versus-$\vec{k}$ plot, but the latter would require 5 dimensions. The fact that for every $\vec{k}$ multiple eigenvalues are possible, is due to different n. Top right: the DOS for the same material, plotted in such a way that the energy scale matches with the energy scale of the band structure plot. The DOS too contains less information than the full eigenvalues-versus-$\vec{k}$ plot, but compared to the band structure other information is omitted or included: the DOS is an integral over the full Brillouin zone (and not limited to a onedimensional path only), but on the other hand does not give information for a specific $\vec{k}$. Peaks in the DOS mean that many $\vec{k}$-vectors have the same eigenvalue. If the path goes through the region of the Brillouin zone that is responsible for this, we see relatively flat (horizontal) lines in the left picture, at the same energies where a peak is in the DOS. Four peaks are labeled 1-4 in the DOS, and are related to features of the band structure plot.*