

Chapter 3 Band structure revisited

3.1 Band structure: atomistic view

Above, we started from wavefunctions that are infinite in space (plane waves) and treated the localised crystal potential as a perturbation. The *opposite* approach is also possible: treat highly localised atomic states as the starting basis and consider the long-range interaction between neighbours as a perturbation. As a starting point, consider two hydrogen atoms being brought closer together, Fig. 3.1.

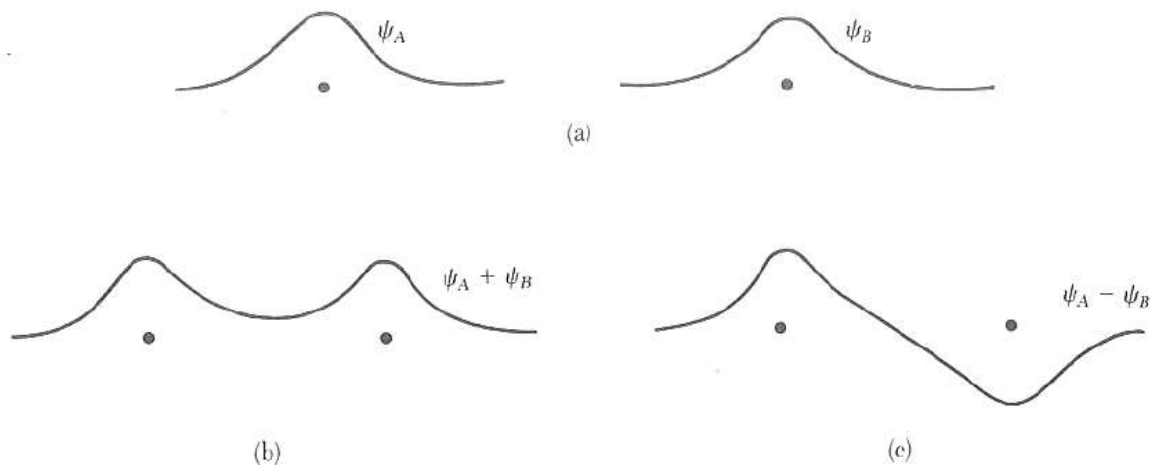


Figure 3.1: (a) Two isolated hydrogen atoms A and B are brought closer and their $1s$ orbitals $\psi_{A,B}$ hybridise into (b) bonding and (c) anti-bonding states. •

The wavefunctions for the two atoms together are $\psi_{bond} = 1/\sqrt{2}(\psi_A + \psi_B)$ and $\psi_{antibond} = 1/\sqrt{2}(\psi_A - \psi_B)$. A proper calculation of the wavefunctions and energies gives the following figure, Fig. 3.2:

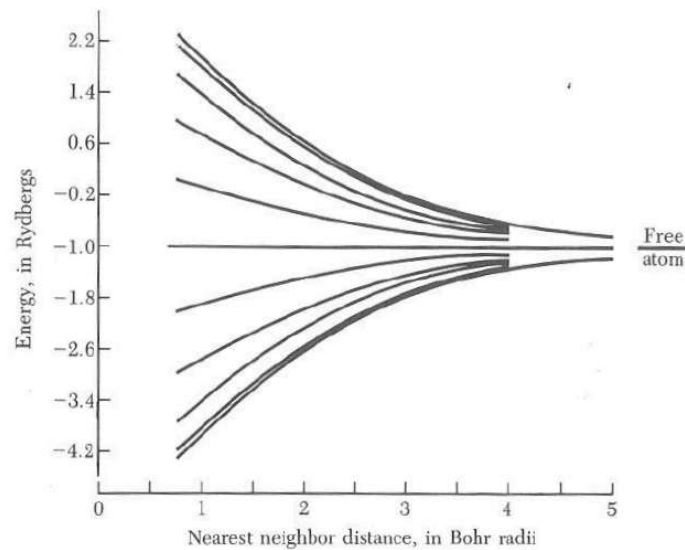


Figure 3.2: Energies of the bonding and anti-bonding states of two hydrogen atoms as a function of distance between them. This kind of figure appears often in textbooks but, unusually, this one is quantitatively correct. ●

Atomic orbitals of single atoms are modified by electron-electron interactions as atoms are brought together to form condensed matter. Discrete atomic energy levels become electronic energy bands in solids within which electrons are delocalised and interact with the lattice of ions.

As we would expect from PH12002 (where interatomic Lennard-Jones potentials were considered), the bonding state does not become lower and lower in energy until the nuclei meet;

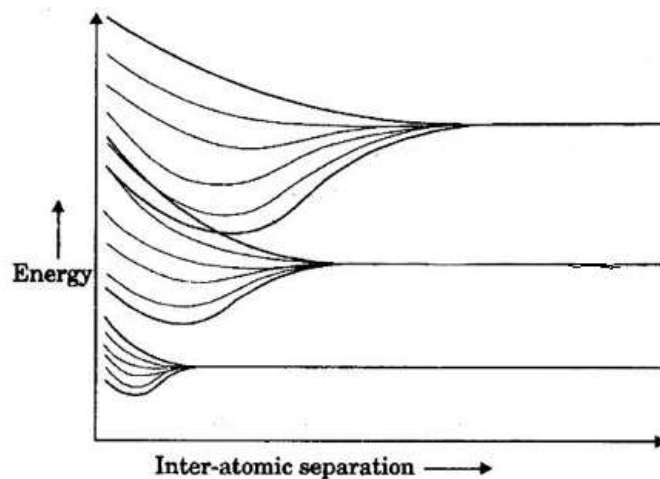


Figure 3.3: Schematic view of the atomic energy levels as several atoms are brought together; the crystal does not spontaneously collapse. ●

3.2 Introduction to tight-binding theory (or LCAO)

For one type of atom per unit cell, our unperturbed state is now the atomic orbital $\phi_n(r - R_n)$ of atom n with potential $U(r - R_n)$ located at position R_n (or, later, the set of orbitals belonging to atom n). For the atom in isolation,

$$H_0\phi_n(r - R_n) = -\frac{\hbar^2}{2m}\nabla^2\phi_n(r - R_n) + U(r - R_n)\phi_n(r - R_n) = E_0\phi_n(r - R_n) \quad (3.1)$$

We can construct a trial wavefunction $\psi_k(r)$ for the crystal by adding up these orbitals for all the atoms present, taking into account a possible phase shift between different atoms, $\exp(ik \cdot R_n)$; as usual, we include a normalisation factor:

$$\psi_k(r) = \frac{1}{\sqrt{N}} \sum_n e^{ik \cdot R_n} \phi_n(r - R_n). \quad (3.2)$$

We can check that this wavefunction satisfies the **Bloch condition** (which it must do: that requirement is general, and not specific to the nearly-free electron model): let $r \rightarrow r + l$ where l is some real space lattice vector. Then,

$$\begin{aligned} \psi_k(r + l) &= \frac{1}{\sqrt{N}} \sum_n e^{ik \cdot R_n} \phi_n(r + l - R_n) \\ &= \frac{1}{\sqrt{N}} e^{ik \cdot l} \sum_n e^{ik \cdot (R_n - l)} \phi_n(r - (R_n - l)) \\ &= \frac{1}{\sqrt{N}} e^{ik \cdot l} \sum_{n'} e^{ik \cdot (R_{n'})} \phi_n(r - (R_{n'})) \\ &= e^{ik \cdot l} \psi_k(r) \end{aligned} \quad (3.3)$$

Now consider the crystal Hamiltonian H_c : we can split the total potential $V(r)$ into a part that is the potential of one isolated atom n at R_n (the term in [...]) and the potential $\Delta V(r)$ due to all the other atoms (term in {...}):

$$\begin{aligned} H_c &= -\frac{\hbar^2}{2m}\nabla^2 + V(r) \\ &= \left[-\frac{\hbar^2}{2m}\nabla^2 + U(r - R_n) \right] + \{V(r) - U(r - R_n)\} \\ &= H_0 + \{V(r) - U(r - R_n)\} \\ &= H_0 + \Delta V(r) \end{aligned} \quad (3.4)$$

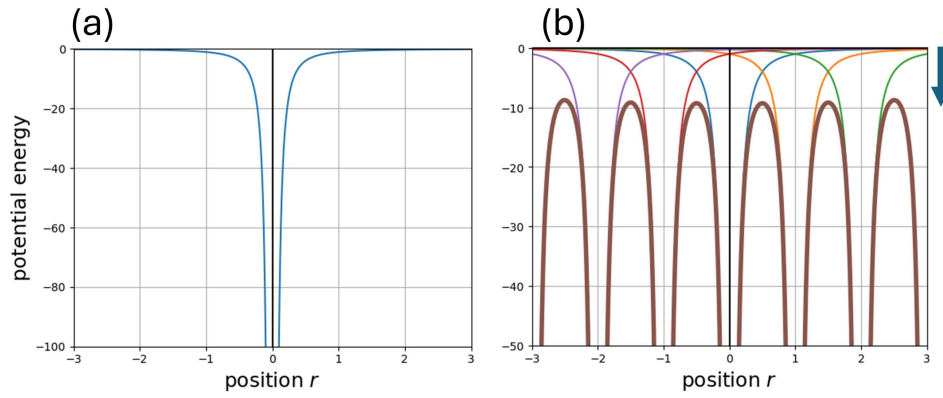


Figure 3.4: (a) potential due to a single atom; (b) thick line: total potential; thin lines: potentials due to individual atoms. Note the downward shift of the potential indicated by the arrow in (b). • Substitute the wavefunction from Eq. (3.2) into Eq. (3.4) to get an expression for E_k :

$$\begin{aligned}
 [H_0 + \Delta V(r)] \psi_k(r) &= E_k \psi_k(r) \\
 &= \frac{1}{\sqrt{N}} \sum_n e^{ik \cdot R_n} [H_0 + \Delta V(r)] \phi_n(r - R_n) \\
 &= E_0 \psi_k(r) + \frac{1}{\sqrt{N}} \sum_n e^{ik \cdot R_n} \Delta V(r) \phi_n(r - R_n) \quad (3.5)
 \end{aligned}$$

Multiply Eq.(3.5) from the left by $\psi_k^*(r)$ and integrate:

$$E_k = E_0 + \frac{1}{N} \sum_{n,n'} e^{ik \cdot (R_n - R_{n'})} \int \phi_n^*(r - R_{n'}) \Delta V(r) \phi_n(r - R_n) dr^3 \quad (3.6)$$

or, if you prefer bra-ket notation:

$$E_k = E_0 + \frac{1}{N} \sum_{n,n'} e^{ik \cdot (R_n - R_{n'})} \langle n' | \Delta V | n \rangle. \quad (3.7)$$

The term $e^{ik \cdot (R_n - R_{n'})}$ gives the dispersion of E_k and the term $\langle n' | \Delta V | n \rangle$ is a constant determined by the overlap between the separate atomic orbitals. It is not practical to evaluate this for all distant atoms, so we make the **tight-binding approximation** that only a few nearby atoms matter in determining $\langle n' | \Delta V | n \rangle$. If we think of the hydrogen $1s$ orbital, $\psi_{1s}(r) = \psi_0 \exp(-\alpha r)$, which decays exponentially with distance, this approximation seems reasonable.

We have not discussed in detail the normalisation constant N ; see textbooks on condensed matter theory to find out more about this point.

3.3 Nearest-neighbour TB approximation

Assume that only atoms $n' = n + 1, n, n - 1$ matter; this is the *nearest-neighbour* approximation. Then $R_{n'} - R_n = 0, \pm a$ where a is a real space lattice vector l . Rewrite the sum as a sum over the positions of the atom and its nearest-neighbours $l = 0, \pm a$:

$$E_k = E_0 + \frac{1}{N} \sum_{l=0,\pm a} e^{-ik \cdot l} \int \phi^*(r-l) \Delta V(r) \phi(r) dr^3. \quad (3.8)$$

There are two values of the integral; for convenience, give them symbols:

$$\begin{aligned} \frac{1}{N} \int \phi^*(r) \Delta V(r) \phi(r) dr^3 &= -\alpha; \\ \frac{1}{N} \int \phi^*(r-a) \Delta V(r) \phi(r) dr^3 &= -\gamma. \end{aligned} \quad (3.9)$$

α represents the downward shift in potential at site n due to the neighbours, shown in Fig.3.4; γ is the *overlap* or *transfer* integral and determines the width of the band $E(k)$ (see below). Our final result for the dispersion of the band makes this clear:

$$E(k) = E_0 - \alpha - \gamma \sum_{\text{neighb.}} e^{-ik \cdot l}. \quad (3.10)$$

We can now apply this result to some simple situations.

3.4 Simple cubic lattice

An atom in the 3D simple cubic structure (let's place it at the origin, $(0, 0, 0)$) has six nearest neighbours:

$$l = (\pm a, 0, 0), (0, \pm a, 0), (0, 0, \pm a).$$

Substitute these coordinates into the sum in Eq.(3.10):

$$\begin{aligned} E(k) &= E_0 - \alpha - \gamma(e^{\pm i k_x a} + e^{\pm i k_y a} + e^{\pm i k_z a}) \\ &= E_0 - \alpha - 2\gamma [\cos(k_x a) + \cos(k_y a) + \cos(k_z a)] \end{aligned} \quad (3.11)$$

3.4.1 Predictions for the simple cubic bands

The width W of a band is defined simply as the difference between the highest and lowest energies of the band. From Eq.(3.11), by inspection, the **band width** is $W = 12\gamma$.

Near the Γ point, $k \sim 0$, we can approximate $\cos(ka) \sim 1 - (ka)^2/2$ so that we can obtain the **effective mass** easily from Eq.(2.1):

$$\begin{aligned} E(k) &= E_0 - \alpha - 6\gamma + \gamma(k_x^2 + k_y^2 + k_z^2)a^2 \\ &= E_0 - \alpha - 6\gamma + \gamma k^2 a^2 \\ m^* &= \frac{\hbar^2}{2\gamma a^2} = \frac{6\hbar^2}{W a^2}. \end{aligned} \quad (3.12)$$

We can plot the shape of the predicted band from $k = 0$ to the Brillouin zone boundary, as in Fig.3.5 (right). Also shown is a cross-section through the constant energy surfaces in reciprocal space, showing a set of contours increasing in energy outwards from the centre. These contours indicate possible shapes for the Fermi surface.

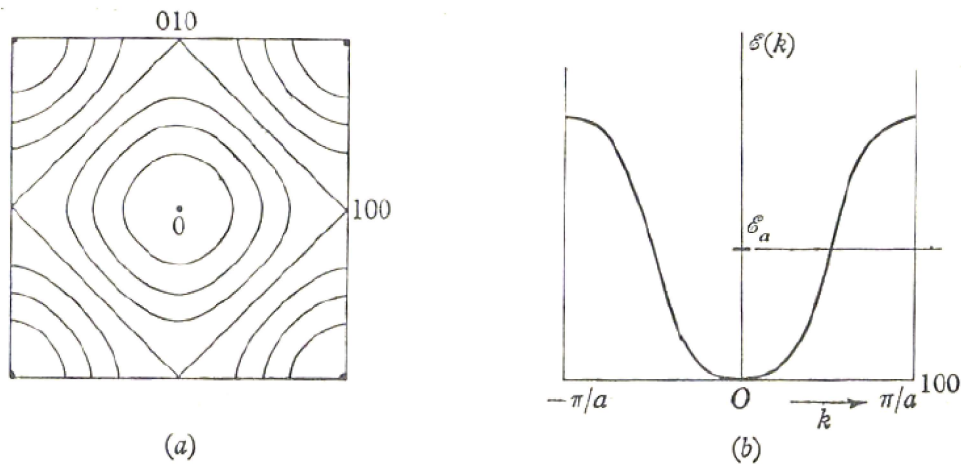


Figure 3.5: Left: constant energy surfaces (horizontal and vertical axes are k_x, k_y respectively). Right: lowest energy TBA band for the simple cubic lattice. •

3.4.2 Form of the wavefunctions

It's instructive to compare the wavefunctions at the Brillouin zone centre and at the BZ edge, where $k \cdot R_n = n\pi/a$:

$$\begin{aligned}
 k = 0 : \quad \psi_k(r) &\propto \sum_n \phi_n(r - R_n) \\
 k = g/2 : \quad \psi_k(r) &\propto \sum_n e^{in\pi} \phi_n(r - R_n) = \sum_n (-1)^n \phi_n(r - R_n)
 \end{aligned} \tag{3.13}$$

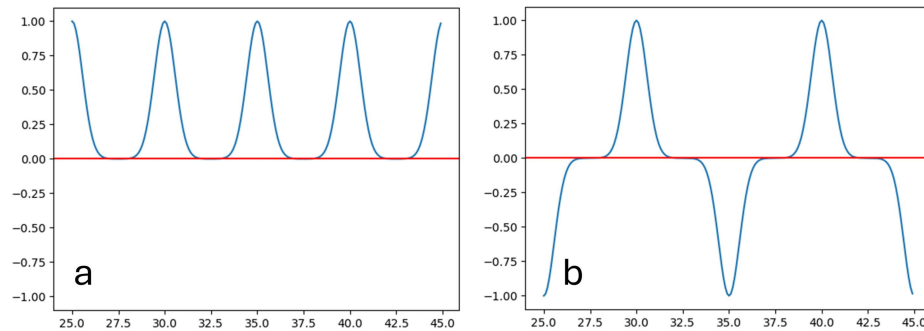


Figure 3.6: (a): wavefunction at $k = 0$; (b): wavefunction at $k = g/2$. •

3.5 Beyond simple structures and one-electron atoms

The tight-binding approach is widely applied and models real materials well. particularly when the transfer integrals γ can be evaluated from fundamental quantum mechanical treatments, rather than being treated as arbitrary adjustable parameters. A schematic view of the complexity of the problem is given by Fig.3.7:

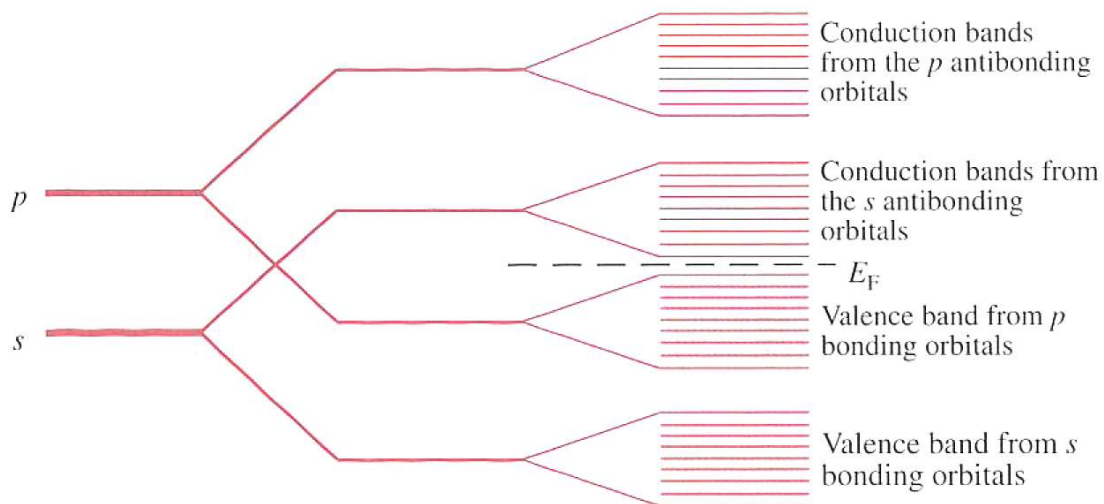


Figure 3.7: Evolution of the bands of a typical compound semiconductor (such as GaP) as atoms are brought together. •

An important recent application is to model the band structure of graphene and other 2D materials, which will be discussed further in later courses.

3.6 Density of states

We start by revising the discussion in Foundations of Physics II. The density of states in energy is written $g(E)$, defined so that the number of electronic states with energies between E and $E + dE$ is given by $g(E)dE$. This form of definition is necessary in order to count a finite number of states in a finite energy range.

In the 3D nearly-free electron model with an equally-spaced grid of states in k -space, for example, it was shown that:

$$g(E)dE = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} dE. \quad (3.14)$$

It's beyond the scope of this course to calculate how the density of states in quantum structures in detail (this may have been discussed in PH22006 and will be part of future courses) but we can at least show a picture of the results, Fig. 3.8. A “quantum well” here implies a crystal where one dimension L has been reduced to the order of tens of atomic spacings or less, and so on for q-wire and q-dot.

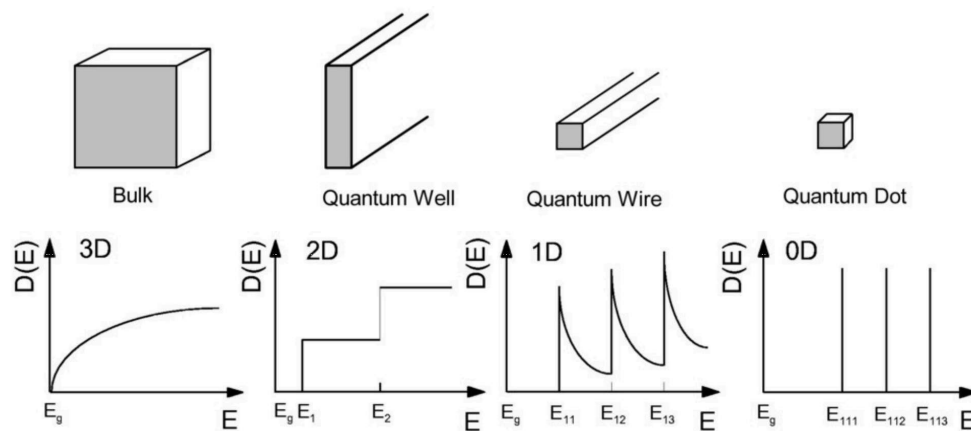


Figure 3.8: Shape of the density of states in energy for nearly-free electron bands in 3D, 2D and 1D. For 0D, there are no bands, of course: the wavefunctions are not plane waves, so k has no meaning, but a density of states in energy can still be plotted. •

Note the divergences in the 1D density of states at the bottom of each band (E_{11} , etc). This can be compared to our tight-binding predictions for the bands of monatomic crystals, Fig. 3.8. For example, if we consider a one-dimensional chain, so that Eq. (3.10) gives

$$E(k) = E_0 - \alpha - 2\gamma \cos(k_x a), \quad (3.15)$$

then

$$g(E) = \frac{1}{\pi \gamma a \sqrt{1 - \left(\frac{E - E_0}{2\gamma}\right)^2}}. \quad (3.16)$$

These are plotted in Fig.3.9:

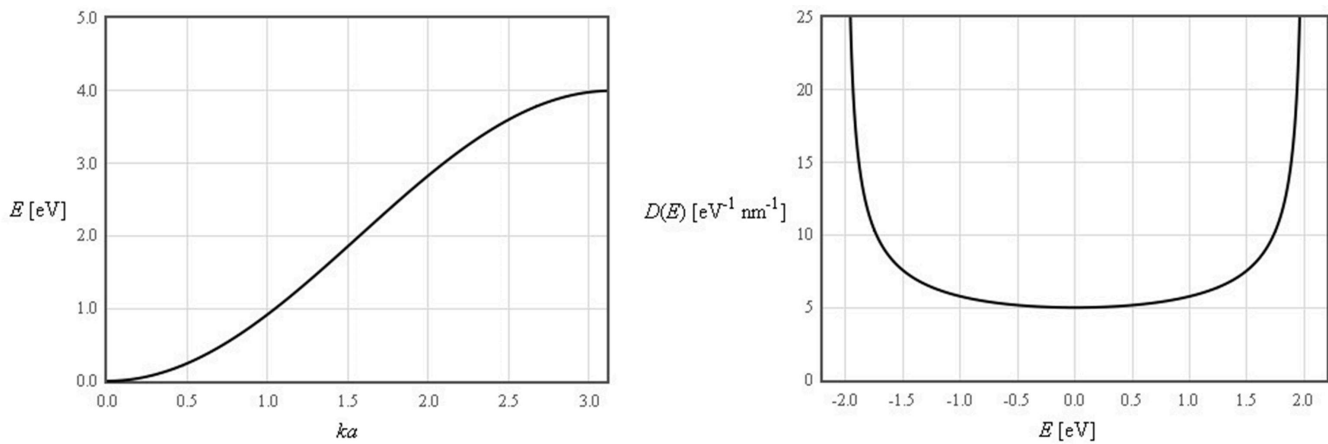


Figure 3.9: Shape of the density of states in energy for the one-dimensional single band tight-binding model. Note, $D(E)$ is another common symbol for $g(E)$. •

Again, there is a divergence at the band edges. Finally, for completeness, Fig.3.10 shows the bands and density of state in energy for the 3D simple cubic s-band in the tight-binding approximation.

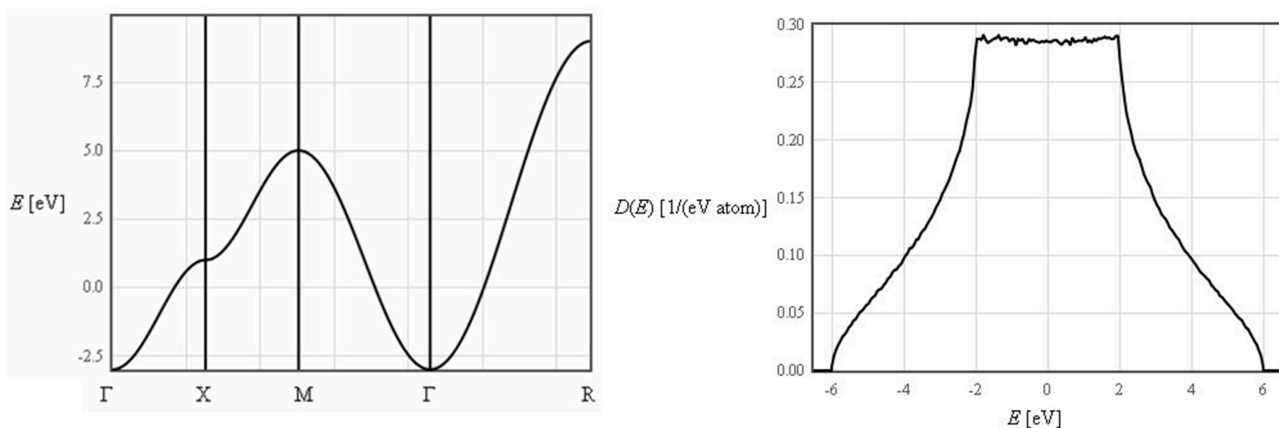


Figure 3.10: Shape of the density of states in energy for the three-dimensional single band tight-binding model. ●

For more examples, see <https://lampz.tugraz.at/~hadley/ss1/bands/tbtable/tbtable.html> (where I obtained the figures above).