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Localized and itinerant electrons in solids

The main topic of this book is the physics of solids containing transition elements: $3d$ – Ti, V, Cr, Mn, . . . ; $4d$ – Nb, Ru, . . . ; $5d$ – Ta, Ir, Pt, . . . These materials show extremely diverse properties. There are among them metals and insulators; some show metal–insulator transitions, sometimes with a jump of conductivity by many orders of magnitude. Many of these materials are magnetic: practically all strong magnets belong to this class (or contain rare earth ions, the physics of which is in many respects similar to that of transition metal compounds). And last but not least, superconductors with the highest critical temperature also belong to this group (high-T_c cuprates, with T_c reaching $\sim 150\,\mathrm{K}$, or the recently discovered iron-based (e.g., FeAs-type) superconductors with critical temperature reaching 50–60 K).

The main factor determining the diversity of behavior of these materials is the fact that their electrons may have two conceptually quite different states: they may be either localized at corresponding ions or delocalized, itinerant, similar to those in simple metals such as Na (and, of course, their state may be something in between). When dealing with localized electrons, we have to use all the notions of atomic physics, and for itinerant electrons the conventional band theory may be a good starting point.

This division in fact goes back to the first half of the 20th century. In the early stages of the development of quantum mechanics one used to treat in detail the electrons in atoms, with different aspects of atomic structure, shell model, atomic quantum numbers, etc. All these details are indeed important for transition metal compounds as well, and we will discuss these problems in the main body of the book. However at the beginning, in this introductory chapter, we will treat the simplest case, ignoring these complications and paying most attention to the competition between localized and itinerant states of electrons in solids.

1.1 Itinerant electrons, band theory

The “fate” of atomic electrons when individual atoms form a concentrated system – a solid – was treated in the first half of the last century, and it led to a very successful picture known as band theory; see, for example, Mott and Jones (1958), Ashcroft and Mermin (1976), Kittel (2004a), and many other textbooks on solid-state physics. In this theory

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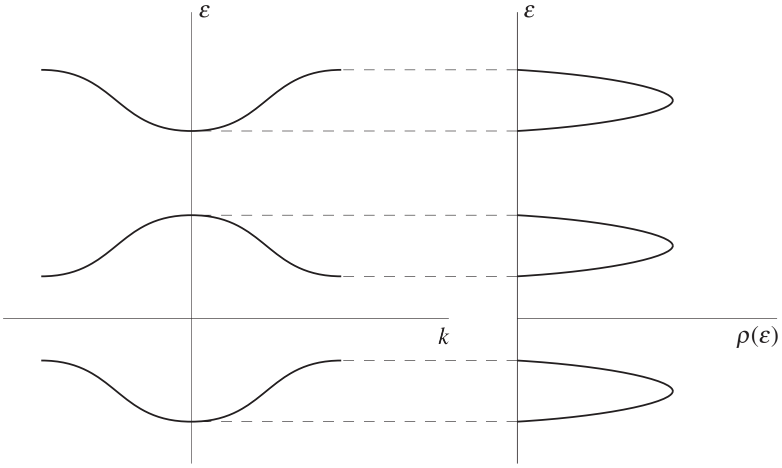

Figure 1.1 Schematic form of the energy spectrum $\varepsilon(k)$ and the density of states $\rho(\varepsilon)$ of free electrons in a crystal.

one considers the motion of noninteracting electrons on the background of a periodic lattice of ions. The spectrum of an electron in the periodic potential consists of allowed energy bands with forbidden states – energy gaps – between them; see the schematic picture of Fig. 1.1, where we show the energy bands $\varepsilon_i(k)$ and the corresponding density of states $\rho(\varepsilon)$.

If there are N atoms in a crystal, each band contains N k-points; for example in the one-dimensional case $k_n = 2\pi n/N$, $n = -\frac{1}{2}N, \ldots, +\frac{1}{2}N$, so that in the continuous limit $-\pi \leqslant k < \pi$ (here and below in most cases we will take the lattice constant $a = 1$). The values $-\pi \leqslant k \leqslant \pi$ form the (first) Brillouin zone. For a system with N sites each band contains N energy levels and, according to the Pauli principle, one can put two electrons with spins ↑ and ↓ on each level, so that each band has room for $2N$ electrons.

In this scheme the electrons occupy the lowest energy levels, and if the number of electrons N_{el} is less than $2N$, that is the electron density $n = N_{\mathrm{el}}/N < 2$, the electrons would occupy the lowest energy band only partially, up to a certain maximal momentum k_{F} and energy ε_{F} (Fig. 1.2) and the system would be a metal. k_{F} and ε_{F} are correspondingly the Fermi momentum and Fermi energy.

In the one-dimensional (1d) case we would have two Fermi points $\pm k_{\mathrm{F}}$. In two-dimensional (2d) and three-dimensional (3d) systems the electrons occupy the states $\varepsilon(k) \leqslant \varepsilon_{\mathrm{F}}$, and the boundary of these occupied states forms the Fermi surface. There may exist several energy bands, which may intersect, and the corresponding Fermi surface of metals may in general be very complicated.

If, in the simplest case of one nondegenerate band of Fig. 1.1, we had $N_{\mathrm{el}} = 2N$, the electrons would fully occupy this first band and the system would be insulating, with an energy gap separating the completely full valence band and the empty conduction

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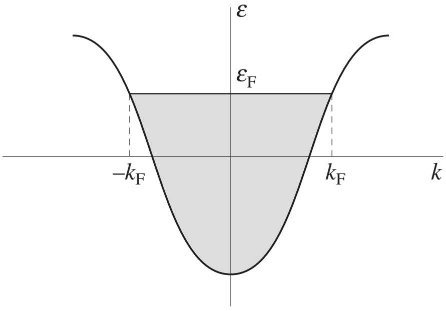

Figure 1.2 Energy spectrum of a metal: the occupied states are shaded. ε_F and k_F are the Fermi energy and Fermi momentum.

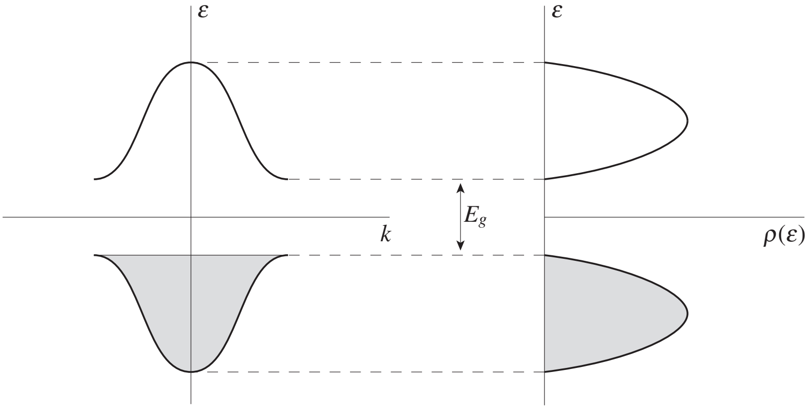

Figure 1.3 Typical energy spectrum of a semiconductor. The occupied states are shaded.

band (Fig. 1.3). This is the standard description of the ordinary band insulators or semiconductors such as Ge and Si.

There are two methods of describing band formation in solids, usually presented at the very beginning of textbooks on solid-state physics, see for example Ashcroft and Mermin (1976) and Kittel (2004a). The first method treats the motion of independent, noninteracting electrons in a periodic lattice potential (Fig. 1.4). One can start from free electrons with the spectrum $\varepsilon(k) = k^2/2m$ in a periodic potential. The corresponding Schrödinger equation for the electron is known in mathematics as the Mathieu equation, and its spectrum, shown in Fig. 1.5, has the form of energy bands separated by energy gaps at wave vectors equal to the Umklapp wave vectors of the given periodic lattice, $\mathcal{K} = 2\pi n/a$, where a is the corresponding lattice parameter. For a weak periodic potential we have the picture shown in Fig. 1.5 which, after we fold the spectrum to the first Brillouin zone, would give the spectrum shown schematically in Figs 1.1 and 1.3. This is the so-called *free electron approximation*. Of course, in contrast to the simple 1d case shown

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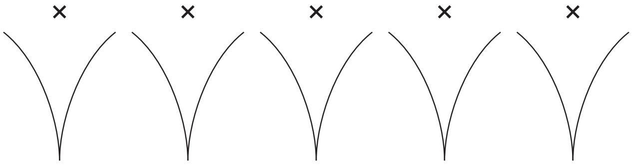

Figure 1.4 Periodic potential for treating the motion of electrons in the band theory.

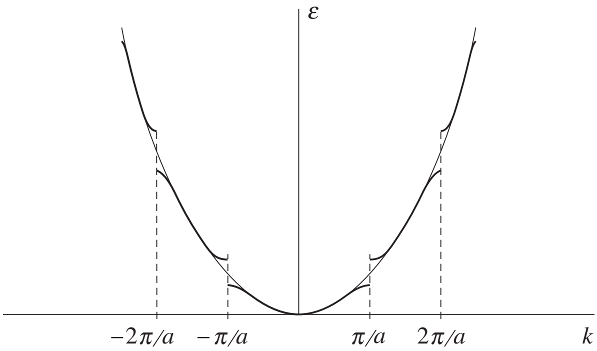

Figure 1.5 The origin of energy bands for free electrons in a periodic potential.

in Figs 1.4 and 1.5, in real crystals with complicated crystal structures the band structure may look much more complicated, with some bands possibly crossing in some directions, but the general rule remains the same: if we have an odd number of electrons per ion, or per unit cell, then in this approximation some bands will necessarily be partially filled and the system should be a metal; and if there is an even number of electrons per unit cell, we may have an insulator of the type shown in Fig. 1.3 (though in the case of overlapping bands we may still obtain a metal or semimetal).

Another approximation often used in band theory is the *tight-binding approximation*; this picture is usually closer to reality for d-electrons in transition metal compounds, and we will mostly use this approximation in what follows. This approach starts by considering isolated atoms with their localized atomic levels, and then treats the tunneling or hopping of electrons from one atom to another, that is from one potential well to the next in the crystal (Fig. 1.6). For two neighboring potential wells this leads to a splitting of energy levels (dashed lines in Fig. 1.6(a)) into bonding and antibonding configurations, $|b\rangle = \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle)$ and $|a\rangle = \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$, and in a periodic lattice composed of such centers each atomic level is broadened into a band, Fig. 1.6(b), with the states in the form of a plane wave with momentum $\boldsymbol{k}$,

$$|\boldsymbol{k}\rangle = \frac{1}{\sqrt{N}} \sum e^{i\boldsymbol{k}\cdot\boldsymbol{n}} |\boldsymbol{n}\rangle \ , \tag{1.1}$$

where $|\boldsymbol{k}\rangle$ is the plane wave wavefunction and $|\boldsymbol{n}\rangle$ is the atomic state at site $\boldsymbol{n}$. As a result we have again a band picture as shown in Fig. 1.1, with each band originating from the

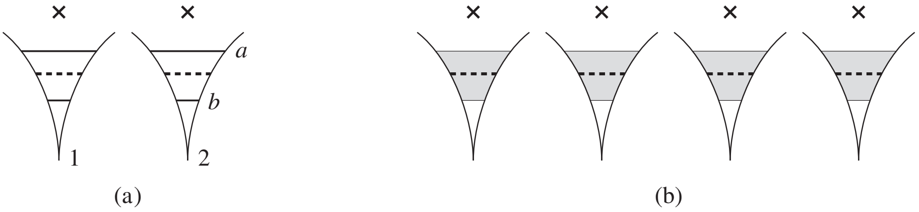

Figure 1.6 The origin of energy bands in the tight-binding approximation.

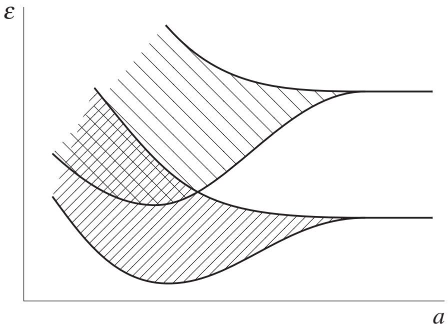

Figure 1.7 Typical dependence of the energy bands on interatomic distance a.

corresponding atomic level (again, these bands can in principle overlap; see the famous picture of Fig. 1.7, showing schematically the broadening of atomic levels into bands when the atoms are moved closer together, i.e. the interatomic distance a is reduced). For large interatomic distances, that is for small overlap of the corresponding wavefunctions of neighboring atoms and hence for small probability of tunneling between neighboring potential wells of Fig. 1.6, the bands will be narrow and one can treat each such band separately, ignoring the others. This is the approximation often used to describe the crossover from the band picture with itinerant electrons to the picture with localized electrons.

1.2 Hubbard model and Mott insulators

Consider the simplest idealized case of a lattice consisting of atoms with nondegenerate electron levels – for example, one can visualize it as a lattice of hydrogen atoms or protons separated by distance a (taken as 1) with one nondegenerate $1s$ level at each site (the dashed line in the potential wells of Fig. 1.6). The hopping of electrons from site to site,

$$\mathcal{H} = -t \sum_{\langle ij \rangle, \sigma} c^{\dagger}_{i\sigma} c_{j\sigma} \ , \tag{1.2}$$

where $c^{\dagger}_{i\sigma}$, $c_{i\sigma}$ are creation and annihilation operators of electrons at site i with spin σ, t is the hopping matrix element, and the summation $\langle ij \rangle$ goes over nearest neighbors,

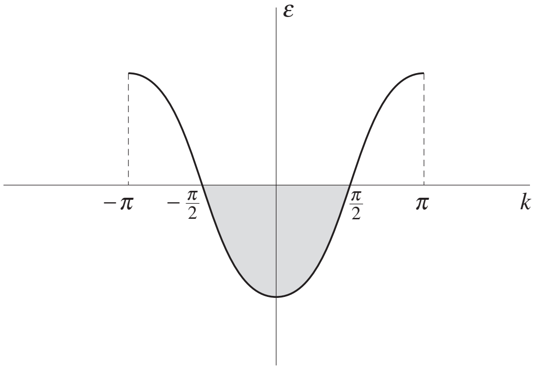

Figure 1.8 Nondegenerate band for noninteracting electrons in the tight-binding approximation for one electron per site, $n = N_{\mathrm{el}}/N = 1$.

leads to the formation of an energy band. (We use here and below the formalism and language of second quantization, which is widely used nowadays; a simple introduction to this technique is presented in Appendix B.) The Fourier transform of (1.2) gives for this band the Hamiltonian

$$\mathcal{H}_b = \sum_{\boldsymbol{k},\sigma} \varepsilon(\boldsymbol{k})\, c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} \tag{1.3}$$

with the spectrum (with one, two, or three terms for the simple chain, square, or cubic lattice)

$$\varepsilon(\boldsymbol{k}) = -2t(\cos k_x + \cos k_y + \cos k_z)\ , \tag{1.4}$$

see Fig. 1.8 (we again set the lattice constant $a = 1$). This is the standard tight-binding approximation. As discussed above, for a lattice of N sites there will be N energy levels in this band, which for N (or volume V) going to infinity gives the continuous spectrum (1.4). According to the Pauli principle there will be $2N$ places for electrons in this band. Thus, if there is one electron per site, with electron density $n = N_{\mathrm{el}}/N = 1$, the band will be half-filled, as shown in Fig. 1.8, and the system should be a metal.

Note that this conclusion does not depend on the distance between atoms in Fig. 1.6, that is on the value of the hopping matrix element t in (1.2), (1.4), which determines the total bandwidth $W = 2zt$ (where z is the number of nearest neighbors – e.g., $z = 2$ in 1d chain, $z = 4$ in square lattice, etc.). However this hopping t, which actually is proportional to the probability of electron tunneling from site to site, will be exponentially small when we increase the distance between sites. Nevertheless, according to (1.3), (1.4) and Fig. 1.8, such systems should still be metallic for any distance between sites and for arbitrarily small values of t. Thus, for example, we can put our “hydrogen atoms” one meter apart and still formally the system should be metallic!

Of course that is a very unphysical result. Intuitively it is evident that in this case the system would consist of neutral hydrogen atoms, with exactly one electron localized at each site, and it would be insulating. What is wrong then, what is missing in the treatment

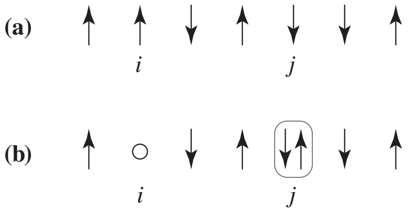

Figure 1.9 Creation of charge-carrying excitations (holes and extra electrons, or doublons) from the state with electrons localized one per site.

which led to the conclusion of Fig. 1.8 that such systems would be metallic for arbitrarily small hopping t and bandwidth $W \sim t$? At least one very important physical effect was missing in this treatment and in the corresponding one-electron Hamiltonian (1.2): it completely ignored the interaction, the Coulomb repulsion between the electrons. Physically we expect that if the distance between atoms is large enough, there will be exactly one electron localized at each site, and because of the repulsion with the first electron, the second electron would not go to the already occupied site.

Let us start from such a state, with one electron per site – see Fig. 1.9(a). To create charge-carrying excitations we should take one electron from a certain site, say site i, and transfer it to another site j – see Fig. 1.9(b). Then the hole left at site i and the extra electron at site j (a doubly occupied site or "doublon") can start to move across the crystal, contributing to the electric current (nobody has told us that the hole should remain at site i; an electron from a neighboring site $i+1$ can hop to site i, i.e. the hole would move to site $i+1$, without any energy cost; the same is true for an extra electron or doublon).

However, to create such charge-carrying excitations, a hole and a doublon, we first had to move electrons and put an extra electron at site j, which already had an electron! And this would cost us at least the energy of Coulomb repulsion of two electrons at site j. This energy is traditionally denoted U, and the corresponding term in the Hamiltonian describing this interaction has the form

$$\mathcal{H}_{\text{int}} = U \sum_i n_{i\uparrow} n_{i\downarrow} \tag{1.5}$$

(for the nondegenerate case, such as our "1s" level, one can put only two electrons with opposite spins at each site, and that is why the interaction (1.5) contains the electron densities at each site i, $n_{i\sigma} = c^{\dagger}_{i\sigma} c_{i\sigma}$, with opposite spins). The resulting full model would then be (combining (1.2) and (1.5))

$$\mathcal{H} = -t \sum_{\langle ij \rangle, \sigma} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \; ; \tag{1.6}$$

this is known as the *Hubbard model* (Hubbard, 1963).

It is clear that when we include this physical effect, the on-site electron repulsion (1.5) to create such an electron–hole (or doublon–hole) pair would cost us energy U. What we can

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gain here is the kinetic energy of both electron and hole: when they start to move through the crystal, they would form energy bands (1.3), (1.4) and both would occupy the lowest states in these bands, with energy $-\frac{1}{2}W = -zt$. That is, the total energy gain obtained by creating such excitations would be $W = 2zt$, but the energy loss would be U – the on-site electron repulsion. Qualitatively, we expect that if $U > W$ then the electrons would remain at their sites and the system would remain insulating. To create electron and hole excitations which would then be able to carry currents, we need to overcome the energy gap

$$E_g \sim U - W = U - 2zt \ , \tag{1.7}$$

which plays the same role as the energy gap between the filled valence band and the empty conduction band in ordinary insulators or semiconductors such as Ge or Si (see Fig. 1.3).

Thus for one electron per site, $n = 1$, and for small electron hopping t (or for a narrow band W) the inclusion of the on-site Coulomb repulsion $Un_{i\uparrow}n_{i\downarrow}$ (1.5) can make the system insulating if $U \gtrsim W = 2zt$, despite the fact that this system would have been metallic in the conventional band picture, which is a one-electron picture and ignores electron–electron interactions. Such insulators are called *Mott* or *Mott–Hubbard insulators* (see, e.g., Mott, 1990).[1] The nature of this insulating state is quite different from that of ordinary band insulators; it is caused not by the periodic potential of the lattice, as is the case for band insulators, but is due completely to electron–electron interaction or, as this is frequently called, *strong electron correlations*. Correspondingly, most of the properties of Mott insulators are also very different from those of ordinary insulators, although some of the notions from ordinary insulators (such as energy gaps) can also be used in the description of Mott insulators. Often this analogy is helpful, but one has to be careful in using it and in transferring the notions of band insulators to Mott insulators. We will see many examples of differences between these two types of insulators later on.

The connection with the theory of chemical bonding in molecules should be mentioned here. The simplest description of the formation of a chemical bond, for example in the H_2 molecule, uses the so-called molecular orbital (MO) description: the wavefunction of an electron moving between sites (protons) a and b is written as

$$|\Psi_\pm\rangle = \frac{1}{\sqrt{2}}(\Psi_a \pm \Psi_b), \tag{1.8}$$

where the $+$ and $-$ signs refer to bonding and antibonding orbitals. The ground state of the H_2 molecule with two electrons on bonding orbitals (with antiparallel spins) will then be described by the state

$$|\Psi_{\text{MO}}\rangle = \frac{1}{2}\big(\Psi_a(r_1) + \Psi_b(r_1)\big)\big(\Psi_a(r_2) + \Psi_b(r_2)\big) \cdot \frac{1}{\sqrt{2}}(1\uparrow 2\downarrow - 1\downarrow 2\uparrow) \tag{1.9}$$

(a singlet state, symmetric in coordinates and antisymmetric in spins). This state is called an MO state, often also an MO LCAO state (molecular orbital – linear combination of atomic orbitals), or Hund–Mulliken state. One sees that in expression (1.9) there are terms corresponding to electrons located at different sites ($\Psi_a(r_1)\Psi_b(r_2)$) – these are nonpolar

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[1] Some interesting historical notes connected with the origin of the notion of Mott insulators are presented in Appendix A.

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or homopolar states. However the MO state also contains, with equal probability, the ionic states of type $\Psi_a(r_1)\Psi_a(r_2)$ in which both electrons reside on the same atom a. When extended to a large periodic crystal, such MO states give rise to the standard band picture of noninteracting electrons (1.3), (1.4).

It is, however, clear that the ionic states such as $\Psi_a(r_1)\Psi_a(r_2)$ cost a large Coulomb on-site energy of electron–electron repulsion. To avoid this cost, one often describes the chemical bond using another state, known as the Heitler–London state:

$$|\Psi_{\rm HL}\rangle = \frac{1}{\sqrt{2}}\Big(\Psi_a(r_1)\!\uparrow \Psi_b(r_2)\!\downarrow - \Psi_a(r_1)\!\downarrow \Psi_b(r_2)\!\uparrow\Big)\,. \tag{1.10}$$

In this state all ionic configurations with two electrons at the same site are excluded, and the corresponding energy loss is avoided.[2] On the energy diagram the MO state corresponds to two electrons occupying a bonding orbital with energy $-t$, see Fig. 1.10(a). The Heitler–London state can also be shown on a similar diagram, see Fig. 1.10(b), but one has to remember that the basic states in this case are not the single-electron states of noninteracting electrons but rather many-electron (here two-electron) states, with the electron–electron interaction taken into account. As a result, the energy of such a Heitler–London bonding state is not $-t$ as was the case for the MO state, but rather $\sim -t^2/U$, see below, where U is the on-site Hubbard repulsion (1.5). Once again, these are many-electron states, the lower one corresponding to a singlet state and the upper one to a triplet state of our two sites–two electrons problem. In fact, these two approaches are the main ones used in the

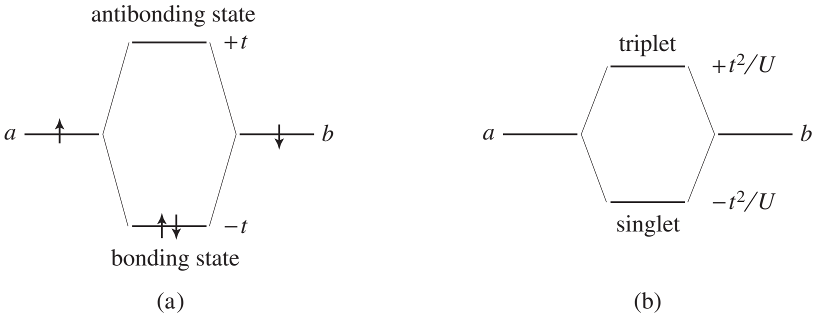

Figure 1.10 (a) Creation of bonding and antibonding states for two centers in the MO LCAO approximation. (b) Creation of singlet bonding and triplet antibonding states in the Heitler–London approximation.

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[2] In the second quantization formalism, the wavefunctions (1.9) and (1.10), written using the electron creation and annihilation operators $c^\dagger$, c used for example in eq. (1.6) have the form

$$|\Psi_{\rm MO}\rangle = \tfrac{1}{2}(c^\dagger_{1\uparrow} + c^\dagger_{2\uparrow})(c^\dagger_{1\downarrow} + c^\dagger_{2\downarrow})|0\rangle\,,$$
$$|\Psi_{\rm HL}\rangle = \frac{1}{\sqrt{2}}(c^\dagger_{1\uparrow}c^\dagger_{2\downarrow} - c^\dagger_{1\downarrow}c^\dagger_{2\uparrow})|0\rangle\,,$$

where $|0\rangle$ is the vacuum state without any electrons. The required antisymmetry of the total wavefunction is guaranteed by the anticommutativity of the fermion operators c_i, c_j on different sites i, j: $c^\dagger_{i\sigma}c^\dagger_{j\sigma'} = -c^\dagger_{j\sigma'}c^\dagger_{i\sigma}$.

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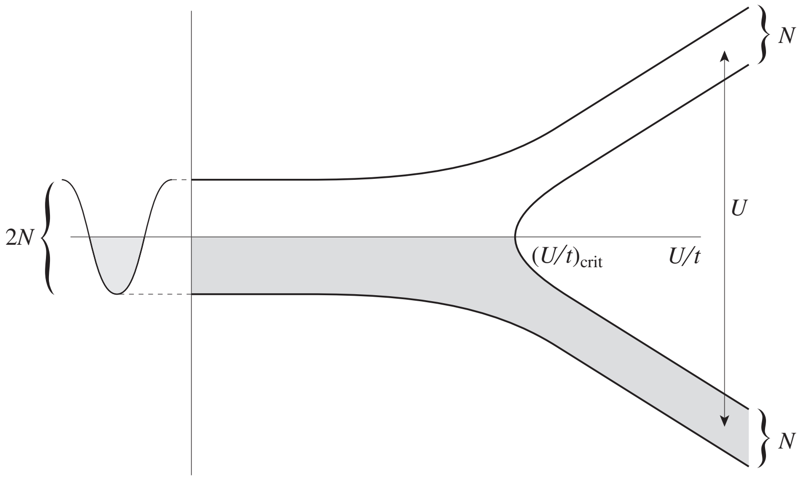

Figure 1.11 Schematic form of the energy band in the Hubbard model as a function of the strength of electron–electron (Hubbard) repulsion. The two bands on the right are the lower (shaded) and the upper (unshaded) Hubbard (sub)bands.

description of chemical bonds in molecules, for example in the hydrogen molecule H_2 (see, e.g., Slater, 1963).

We see that the MO or MO LCAO description of the chemical bond corresponds to the band picture of concentrated solids, while the Heitler–London description corresponds to Mott or Mott–Hubbard insulators, where the electrons avoid each other and are localized at different sites, one per site.

The picture often used to describe Mott insulators, constructed by analogy with band insulators, is that of Hubbard subbands (Fig. 1.11). We can say that the energy band, which for noninteracting electrons ($U = 0$) would be half-filled, for large enough U, $(U/t) > (U/t)_{\text{crit}}$ (or $U > U_{\text{crit}} \sim W = 2zt$), would split into two subbands, with the energy gap between them being $E_g \sim U$ (or, more accurately, $E_g \sim U - W = U - 2zt$). For one electron per site, $n = N_{\text{el}}/N = 1$, each of these subbands will then have "space" for N electrons. The lower band will then be occupied, and the upper one empty. These bands are called *lower and upper Hubbard (sub)bands*. This picture resembles that of ordinary semiconductors, see Fig. 1.3.

However, there is an important difference here. If for band insulators or semiconductors the energy gap was determined by the periodic potential of the crystal lattice, here it is entirely due to electron–electron interactions. Also, each band in Fig. 1.3 contained $2N$ places. In Mott insulators, however, the band for $U = 0$ contains $2N$ places, but when the band is split into two Hubbard subbands for large U (Fig. 1.11), each of these subbands (for one electron per site) would contain only N places; it is precisely because of this that the system with one electron per site, $n = N_{\text{el}}/N = 1$, would completely occupy the lower Hubbard band, leaving the upper one empty.