

# Metal-Insulator Transitions

Second Edition

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where the  $C_k^n$  are complex variables, and the sum is over all  $\mathbf{k}$  for a given value of  $|\mathbf{k}|$ . We then have

$$\langle \phi_1 | q | \phi_2 \rangle = \sum \sum C_k^1 C_k^2 \langle \psi_k | q | \psi_k \rangle.$$

Here  $\langle \phi_1 | q | \phi_2 \rangle$  etc. is written for  $\langle \phi_1^* | e^{iq \cdot r} | \phi_2 \rangle$ . If  $|\mathbf{k} - \mathbf{k}'| \gg 1/l$  then the matrix element  $\langle \psi_k | q | \psi_{k'} \rangle$  becomes negligible, so we restrict ourselves to  $q < 1/l$ . It is thus a reasonable approximation to write  $k = k'$ , and

$$\langle \phi_1 | q | \phi_2 \rangle = \sum_k C_k^{1*} C_k^2 \langle \psi_k | q | \psi_k \rangle.$$

Taking the square, we find

$$|\langle \phi_1 | q | \phi_2 \rangle|^2 = \sum \sum C_k^{1*} C_k^2 C_k^1 C_k^{2*} |\langle \psi_k | q | \psi_k \rangle|^2.$$

We argue that all the quantities  $|C_k|$  must be identical, but that the  $C_k$  have random phases, so, on averaging, the summation reduces to

$$\sum |C_k|^2 \sum |C_k|^2,$$

which is unity by the normalization condition. Thus we find when  $q \neq 0$ ,

$$|\langle \psi_k | q | \psi_k \rangle|^2 = [\pi \hbar D q^2 N_0(E_F)]^{-1}. \quad (70)$$

From this, we can deduce  $|a(q)|$ , noting that  $\langle k | q | k \rangle = 0$ , and we find

$$2a(q) = \langle \psi_k | q | \psi_k \rangle,$$

so that

$$|a(q)|^2 = [\pi \hbar D q^2 N(E_F)]^{-1} \quad (71)$$

To obtain the current, we make two assertions (cf. Kaveh 1985d). Neither the term in  $\sum a(q) |\mathbf{k} + \mathbf{q}\rangle$  nor its product with  $|\mathbf{k}\rangle$  make a contribution to the current in the Kubo-Greenwood formula. Thus the effect of this term on the conductivity arises from the normalization of the plane waves, written as

$$a_0 \left[ |\mathbf{k}_F\rangle + \sum a(\mathbf{q}) |\mathbf{k}_F + \mathbf{q}\rangle \right]. \quad (72)$$

We see that

$$|a_0|^2 = \left[ 1 + \sum |a(q)|^2 \right]^{-1} \\ \approx 1 - \sum |a(q)|^2.$$

The sum can be replaced by an integral, and is

$$\left( \frac{L}{2\pi} \right)^d \int_{1/L}^{1/l} d^d q |a(q)|^2, \quad (73)$$

where  $d$  is again the dimensionality of the system and  $L$  is the size of the specimen, or the inelastic diffusion length, or the cyclotron radius  $(ch/eH)^2$ , whichever is the smaller. The upper and lower limits are somewhat arbitrary; thus Berggren takes  $\pi/l$ ,  $\pi/L$ , but we use  $1/l$ ,  $1/L$ .

To evaluate  $|a_0|^2$ , we write, in three dimensions,

$$D = \frac{1}{3} \frac{\hbar k_F}{m} l, \quad N(E) = \frac{L^3 m k_F}{4\pi \hbar^2},$$

and find

$$\sum |a(q)|^2 = \frac{1}{\pi(k_F l)^2} \left( 1 - \frac{l}{L} \right).$$

Thus for  $|a_0|^2$  we obtain

$$|a_0|^2 = 1 - \frac{1}{2(k_F l)^2} \left( 1 - \frac{l}{L} \right) \quad (74 a)$$

for the three-dimensional case, and

$$|a_0|^2 = 1 - \frac{1}{\pi k_F l} \ln \left( \frac{L}{l} \right) \quad (74 b)$$

for the two-dimensional case.

As regards the conductivity, in the Kubo-Greenwood formalism this will depend on  $|a_0|^4$ , so

$$\sigma = \sigma_B \left[ 1 - \frac{1}{(k_F l)^2} \left( 1 - \frac{l}{L} \right) \right] \quad (75)$$

in three dimensions, and

$$\sigma = \sigma_B \left[ 1 - \frac{2}{\pi k_F l} \ln \left( \frac{L}{l} \right) \right] \quad (76)$$

in two dimensions. Here the constants 1 and 2 are rather uncertain, but both should be universal.

In the three-dimensional problem, it will be noticed from (71) that in  $\sum |a_n|^2$  the density of states and the diffusion coefficient occur in the denominator, as they do also in the expression given by Kawabata (1981). If the disorder broadens the band, as will occur in the Anderson model if  $V_0 > B$ , then (75) should be modified to

$$\sigma = \sigma_B g^2 \left[ 1 - \frac{C}{(k_F l)^2 g^2} \left( 1 - \frac{l}{L} \right) \right], \quad (77)$$

the form given by (52). The constant  $C$  will be taken to be unity, which follows from the limits in (73):  $1/L$  and  $1/l$ .

## 15 Hopping conduction

If states at the Fermi energy of a condensed electron gas are localized, two conduction mechanisms are possible.

(a) *Excitation of the carrier to a mobility edge.* If interaction with phonons is neglected then we expect the conductivity  $\sigma$  to be of the form

$$\sigma = \sigma_0 \exp\left(-\frac{E_c - E_F}{k_B T}\right),$$

with  $\sigma_0 = 0.03e^2/hL_F$ . For modification of this equation on account of the displacement of the current path from the mobility edge resulting from delocalization by phonons see for instance Overhof and Thomas (1989) and Mott (1988).

(b) *If wave functions are localized, so that  $\langle\sigma(E)\rangle = 0$ , then conduction at low temperatures is by thermally activated hopping.* Every time an electron moves, it hops from one localized state to another, whose wave function overlaps that of the first state. Since the two states have quantized energies, the electron must exchange energy with a phonon (or possibly a spin wave) each time it moves. The hopping processes in which the electron obtains energy from a phonon are rate-determining. Hopping of this kind was first described by Miller and Abrahams (1960) in their theory of impurity conduction. They supposed that an electron on one occupied site would normally jump to a nearest site with energy  $\epsilon_3$  above it, where  $\epsilon_3 \sim [a^3 N(\epsilon)]^{-1}$ . The hopping probability is then of the form

$$v_{\text{ph}} \exp\left(-2\alpha R - \frac{\epsilon_3}{k_B T}\right), \quad (78)$$

where  $v_{\text{ph}}$  depends on the strength of the interaction with phonons and  $\alpha = \xi^{-1}$ , where  $\xi$  is the radius of the states. For large  $\alpha$  the application of percolation theory to the problem of the most-favoured paths has been widely discussed (see e.g. Pollak 1972), but is outside the scope of this book. If  $\alpha$  is small, as it is for  $E = E_F$  in a system near an Anderson transition, then each localized state will overlap a large number of others. The factor  $e^{-2\alpha R}$  may then be neglected over a volume of order  $\xi^3$ , and the electron will normally jump to the site in this volume with the smallest value of  $\epsilon_3$ , which should be given by

$$\epsilon_3 \sim \frac{(a\alpha)^3}{a^3 N(E)} = \frac{\alpha^3}{N(E)}. \quad (79)$$

Figure 5.2 shows some results of Davis and Compton for various forms of conduction in doped germanium, and the drop in  $\epsilon_3$  after an initial rise with decreasing  $a$  may perhaps be ascribed to the mechanism giving rise to (79), though other explanations (e.g. multiple hopping) have been proposed (cf. Pollak and Ortuno 1985).

At sufficiently low temperatures, under all circumstances where  $N(E_F)$  is finite but states are localized near the Fermi energy, we expect the phenomenon of variable-range hopping to set in. If interaction between electrons is not taken into account then the conductivity will follow the formula

$$\sigma = A \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right], \quad (80)$$

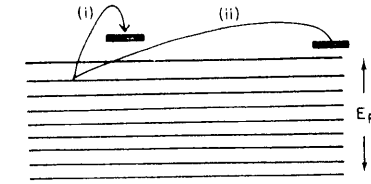


Fig. 1.28 The mechanism of hopping conduction. The electron jumps from a state below the Fermi level to a nearby state (i) or distant state (ii).

(Mott 1968, 1969, Ambegaokar *et al.* 1971, Pollak 1972). Here

$$k_B T_0 = 1.5/\alpha^3 N(E), \quad (81)$$

where  $N(E)$  is the density of states at the Fermi level and  $\alpha$  denotes the rate of fall-off of the envelope of the wave function in Fig. 1.18 ( $\phi \sim e^{-\alpha r}$ ). The constant  $A$ , depends on the assumptions made about electron-phonon interaction. The behaviour from which (80) is deduced is illustrated in Fig. 1.28. An electron just below the Fermi level jumps to a state just above it, the energy required being written as  $\Delta W$ . The farther it jumps, the greater is the choice of states that it has, and in general it will jump to a state for which  $\Delta W$  is as small as possible. If it jumps a distance  $R$ , we can then write

$$\Delta W \sim [4/3 \pi R^3 N(E)]^{-1},$$

so the conductivity is proportional to

$$\exp\left[-2\alpha R - \frac{3}{4\pi k_B T R^3 N(E)}\right]. \quad (82)$$

The formulae (80) and (81) are obtained by maximizing this quantity.

Since  $\alpha$  in (81) is the reciprocal of the localization length  $\xi$ , measurements of  $T_0$  near to the (Anderson) metal-insulator transition can determine how  $\xi$  varies with  $n_c - n$ . Thus Castner and co-workers (Shafarman and Castner 1986, Shafarman *et al.* 1986) have made measurements in Si:P and found, as expected, that for systems just below the Anderson transition  $\xi$  varies as  $(n_c - n)^{-\nu}$ , with  $\nu \sim 1$ .

However, it is now realized that it is only near the transition that (80) is valid—and even this is not certain. Efros and Shklovskii (1975) showed that the Coulomb repulsion between carriers led to a form of hopping for which

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_0'}{T}\right)^\nu\right], \quad \nu = \frac{1}{2}, \quad (83)$$

where (Shklovskii and Efros 1984)

$$k_B T_0' = 2.8e^2/\kappa a. \quad (84)$$

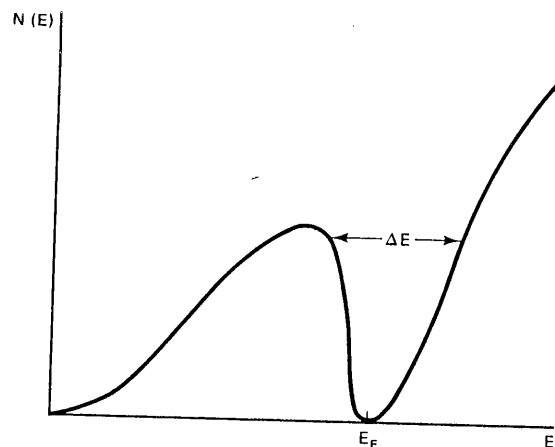


Fig. 1.29 Density of states  $N(E)$  as a function of energy  $E$  in a disordered material in the localized regime, showing the Coulomb gap of width  $\Delta E$ .

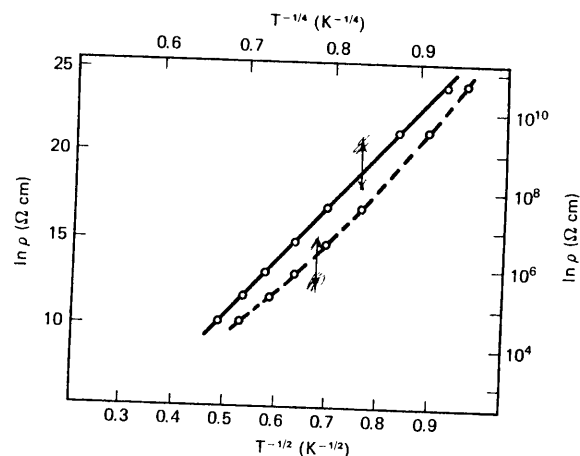


Fig. 1.30 Temperature dependence of variable-range hopping in a sample of Si:P: —, plotted against  $T^{-1/2}$ ; ---, plotted against  $T^{-1/4}$  (Ionov *et al.* 1985).

The analysis first given by these authors depends on the proof that the *one-electron* density of states vanishes at  $E_F$ , showing the so-called “soft” Coulomb gap, illustrated in Fig. 1.29. This analysis is limited to systems far from the transition, where the overlap between wave functions is small. Here there is rather

strong experimental evidence that  $\nu = \frac{1}{2}$ , particularly through the work of the Leningrad school. Figure 1.30 shows plots of the log resistivity of Si:P “without any special compensation” and  $n = 2.5 \times 10^{18} \text{ cm}^{-3}$  plotted against  $T^{-1/4}$  and  $T^{-1/2}$ . The results are due to Ionov *et al.* (1985). It will be seen that  $\nu = \frac{1}{2}$  is favoured, even though the concentration is quite near the transition, which is stated to be at  $3.74 \times 10^{18} \text{ cm}^{-3}$ . Zabrodskii (1980) found in Ge with  $(5-7) \times 10^{17} \text{ donors cm}^{-3}$  that the conductivity followed the hopping law with  $\nu = \frac{1}{2}$ . At the metal-insulator transition the concentration is about  $10^{18}$ , so again the results are for specimens not far from the transition. Rentzsch *et al.* (1986) found  $\nu = \frac{1}{2}$  in GaAs. Zabrodskii and Zinov’eva (1984) found  $\nu = \frac{1}{2}$  in compensated n-Ge near the transition. On the other hand, there is some evidence that near the transition the index  $\nu = \frac{1}{4}$  is valid. Thus Biskupski and Briggs (1987) and Biskupski *et al.* (1988) showed that when compensated barely insulating InP is subject to a magnetic field, driving it further from the transition by contracting the orbits, the hopping index changes from  $\frac{1}{4}$  to  $\frac{1}{2}$ . Similar results for Si:P were obtained by Shafarman and Castner (1986) and Shafarman *et al.* (1986).

That the Coulomb gap might disappear, leading to  $\nu = \frac{1}{4}$ , can be understood in the following way.  $\kappa$  in (84) tends to infinity with  $\zeta$  (see Chapter 5, Section 8). The width of the Coulomb gap is given by

$$\Delta E = [4\pi a \zeta^2 N(E_F)]^{-1},$$

which tends to zero as  $\zeta \rightarrow \infty$ . If

$$k_B T > \Delta E \sim \left( \frac{n - n_c}{n_c} \right)^2 / 4\pi a^3 N(E_F)$$

then we may expect that  $\nu = \frac{1}{4}$  will be observed.

Apart from its effect on hopping conduction, there is direct evidence for a Coulomb gap in various materials. Thus Franz and Davies (1986) found evidence in sodium tungsten bronzes in the non-metallic state from the optical absorption coefficient. In a series of papers Whall *et al.* (1984, 1986, 1987) traced its influence in the conduction and thermopower of ferrites. Monroe *et al.* (1987) injected excess charge into p-type compensated GaAs, forming a layer of a metal-insulator semiconductor heterostructure. They found, in the delayed response to applied voltage, evidence for the Coulomb gap. Weng *et al.* (1983) found evidence for a Coulomb gap in their study of granular palladium films.

Whall *et al.* (1984, 1986) studied the electrical conductivity and thermopower of nickel ferrous ferrites ( $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ ) with  $0 < x < 0.9$ . The thermopower for  $x$  between 0.1 and 0.8 tends to zero with temperature below 40 K, suggesting variable-range hopping (Whall *et al.* 1986). For higher temperatures they imply nearest-neighbour hopping. Whall *et al.* (1986, Fig. 3), in plots of  $d \ln(\sigma T) / d(1/T)$  against  $T$ , showed an increase in the hopping energy round 300 K, which they ascribed to a Coulomb gap.

The Hall effect for hopping conduction is discussed in Chapter 5.

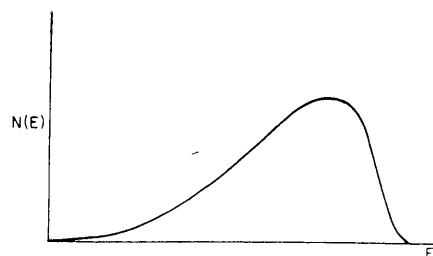


Fig. 1.31 Density of states  $N(E)$  for a band with lateral disorder.

### 16 Pseudogaps and metal-insulator transitions

There have been many calculations of the density of states in various kinds of disordered material; we are concerned in this book mainly with narrow bands and thus with the tight-binding approximation. When the disorder is in the positions of the wells and not due to a random potential as in Fig. 1.17, the simple approximation (40) for  $N(E)$  is not applicable. Some calculations have been made by Rousseau *et al.* (1970) and by Gaspard and Cyrot-Lackmann (1972, 1973). The type of density of states found by Gaspard and Cyrot-Lackmann is shown in Fig. 1.31, with low-energy tails due to groups of wells closer together than the average and an absence of Van Hove singularities. The minimum in the density of states predicted by Lifshitz (1964) is not found. These calculations do not distinguish between localized and non-localized states. Some rough estimates of the range of localized states for simple models have also been made (Mott 1970, Mott and Davis 1979). Two kinds of disorder can lead to localization. One is the random positions of the atoms, and this we believe gives a very narrow range of localization in liquids or glasses when the atomic functions are s-like, as in liquid rare gases (Mott and Davis 1979, Chap. 5). The other is the random orientation of p- or d-like functions, which should give a wider range of localization, perhaps a few tenths of an electron volt in an amorphous semiconductor.

For the subject matter of this book, it is of particular interest to consider the situation for a non-crystalline system analogous to that of crystalline ytterbium or strontium under pressure, namely that when a valence and conduction band are separate or overlap slightly. If the degree of overlap can be changed by varying the mean distance between atoms, the composition or the coordination number then a metal-insulator transition can occur. Many examples will be discussed in this book, particularly amorphous films of composition  $(Mg_{1-x})_2(Bi_x)_3$ , liquid mercury at low densities, and liquid tellurium alloys in which the coordination number changes with temperature. The transition is, we believe, of Anderson type.

If a conduction and valence band overlap slightly then a "pseudogap" or minimum in the density of states (Fig. 1.32) is expected, as first suggested by Mott (1966). As long as the overlap is small, one would expect the density of states, all

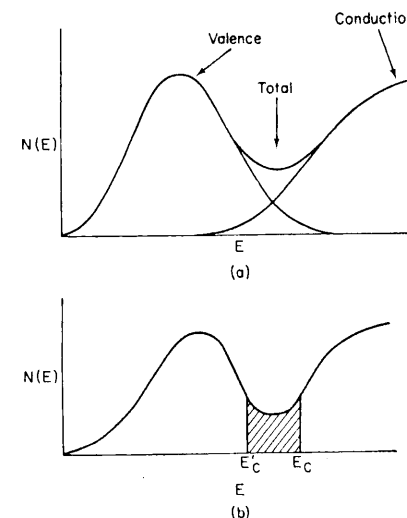


Fig. 1.32 (a) Overlapping bands forming a pseudogap, with localized states at the Fermi energy. (b) Total density of states, with localized states shaded.

localized, to be the sum of the contributions by the two bands. As the overlap increases, a point will be reached at which states at  $E_F$  are no longer localized. At this point a metal-insulator transition of Anderson type is expected. For weak localization, conduction by hopping according to (80) and (83) will occur. For extended states just above the transition, the conductivity will behave in a manner that we shall now discuss.

As in previous sections, we introduce the Mott  $g$ -factor, though here we must define it as being proportional to the density of states at the Fermi level, and normalized so that

$$\sigma = S_F e^2 a g^2 / 12 \pi^3 \hbar$$

without quantum interference as in (37). Putting  $S_F = 4\pi k^2$ ,  $k = \pi/a$ , this gives

$$\sigma = g^2 e^2 / 3 \hbar a.$$

We emphasize that the use of  $g$  in these equations may be justified only if  $l \sim a$ , because of the Edwards cancellation theorem (Section 6). We should expect a metal-insulator transition to occur for some value of  $g$  in the neighbourhood of  $\frac{1}{3}$ . For several liquid systems there is experimental evidence that the interference term in (52) is absent. Thus for liquid TeTl alloys, with variation of composition and temperature, for  $\sigma$  less than the Ioffe-Regel value  $e^2/3\hbar a$ , the conductivity is proportional to the square of the Pauli paramagnetic susceptibility and then to  $g^2$ . These results are due to Cutler (1977). Warren (1970a, b, 1972a, b) examined

the Knight shift in liquid  $\text{In}_2\text{Te}_3$  and  $\text{Ga}_2\text{Te}_3$ , from which he deduced  $g$ . He found  $\sigma$  to be proportional to  $g^2$ ,  $g$  decreasing with decreasing temperature until  $g$  reaches a value of about 0.2; it then drops more rapidly, suggesting that localization occurs. These results are discussed further in Chapter 10.

Mott (1985, 1989a) proposed that in liquids all collisions are inelastic, so that  $l = L_i$  and the interference term in (52) vanishes. Thus, in a sense,  $\sigma_{\min}$  exists for liquids (see Chapter 10). We have to ask, however, whether localization exists under these conditions. The same problem exists in certain amorphous solids, where strong phonon interaction leads over a certain temperature range to the relation  $L_i \sim a$ . We find that, as the energy drops into a region of small density of states,  $\tau_i$  increases and the normal localization condition again becomes valid.

Pseudogaps in liquids are discussed in Chapter 10. Examples of pseudogaps in solids ( $\text{Mg}_{2-x}\text{Bi}_{2+x}$ ) are also described in Chapter 7.