C. FERMI-DIRAC DISTRIBUTION

Complete derivations of the Fermi-Dirac distribution are found in elementary textbooks on statistical mechanics.[1] We derive the distribution here by a device due to F. Bloch. We consider the inelastic collisions of a conduction electron with a "two-level" impurity atom with which the electron may be imagined to interact. The electron state is labeled by its wavevector $\mathbf{k}$. The impurity atom has two energy states 0 and Δ, as indicated in Fig. C.1; the occupation probabilities of the two levels will be written as $p(0)$ and $p(\Delta)$. We examine those inelastic collisions which connect the electron state $\mathbf{k}$ at electron energy ϵ with the electron state $\mathbf{k}'$ at electron energy $\epsilon + \Delta$.

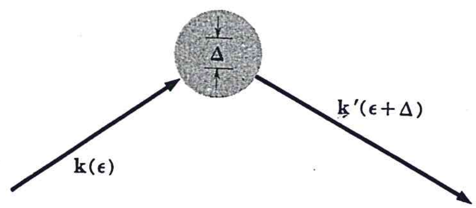

Figure C.1 An electron in a state $\mathbf{k}$ of energy ϵ collides inelastically with an impurity atom initially in an excited state of energy Δ. In the final state shown the electron is in a state $\mathbf{k}'$ with energy $\epsilon + \Delta$. In such collisions the atom loses energy Δ.

The transition rate for a collision in which the electron starts at $\mathbf{k}$ and ends at $\mathbf{k}'$ will be proportional to

$$f(\epsilon)p(\Delta)[1 - f(\epsilon + \Delta)],$$

where $f(\epsilon)$ is the probability that the initial state at $\mathbf{k}$ is occupied; $p(\Delta)$ is the probability the impurity atom is in the state Δ so that it can give up its energy Δ to the electron, and $1 - f(\epsilon + \Delta)$ is the probability that the electron state $\mathbf{k}'$ at $\epsilon + \Delta$ is vacant so that it can receive the scattered electron. The final state $\mathbf{k}'$ *must be vacant if the scattering event is to take place;* this is the special feature introduced by the Pauli principle.

The transition rate for the reverse collision $\mathbf{k}' \rightarrow \mathbf{k}$ is proportional to

$$f(\epsilon + \Delta)p(0)[1 - f(\epsilon)],$$

just reversing the steps in Fig. C.1 and in the preceding argument.

Now in thermal equilibrium the transition rates $\mathbf{k} \rightarrow \mathbf{k}'$ and $\mathbf{k}' \rightarrow \mathbf{k}$ must be equal, so that the two population factors must be equal:[2]

$$f(\epsilon)p(\Delta)[1 - f(\epsilon + \Delta)] = f(\epsilon + \Delta)p(0)[1 - f(\epsilon)], \qquad (1)$$

where the averages are understood to be for thermal equilibrium at a common tempera-

[1] C. Kittel, *Elementary statistical physics*, Wiley, 1958.

[2] The constants of proportionality in the rates of the direct and the inverse processes are exactly equal by the principle of detailed balance, which follows directly from quantum theory.

ture T. The Boltzmann distribution applies to the population of the states of the impurity atom, so that

$$\frac{p(\Delta)}{p(0)} = \exp\,(-\Delta/k_BT). \tag{2}$$

Thus (1) becomes

$$\frac{f(\epsilon + \Delta)}{1 - f(\epsilon + \Delta)} \cdot \frac{1 - f(\epsilon)}{f(\epsilon)} = \exp\,(-\Delta/k_BT). \tag{3}$$

This equation is easily seen to have a solution for all T if

$$\frac{1 - f(\epsilon)}{f(\epsilon)} = e^{(\epsilon-\mu)/k_BT}, \tag{4}$$

where μ is a constant independent of ϵ. From (4) we have the Fermi-Dirac distribution law

$$f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_BT} + 1}. \tag{5}$$

The quantity μ is the chemical potential, as discussed in Chapter 7.

D. TIGHT BINDING APPROXIMATION FOR ELECTRONS IN METALS

It is useful to look at the formation of allowed and forbidden electron bands in another way. We start from the energy levels of the neutral separated atoms and watch the changes in the levels as the charge distributions of adjacent atoms overlap when the atoms are brought together to form the metal. We can understand the origin of the splitting of free atom energy levels into bands as the atoms are brought together by considering two hydrogen atoms, each with its electron in the 1s (ground) state. In Fig. D.1 the wavefunctions ψ_A, ψ_B on the separated atoms are shown in (a). As the atoms are brought closer together and their wavefunctions overlap, we are led to consider the two combi-

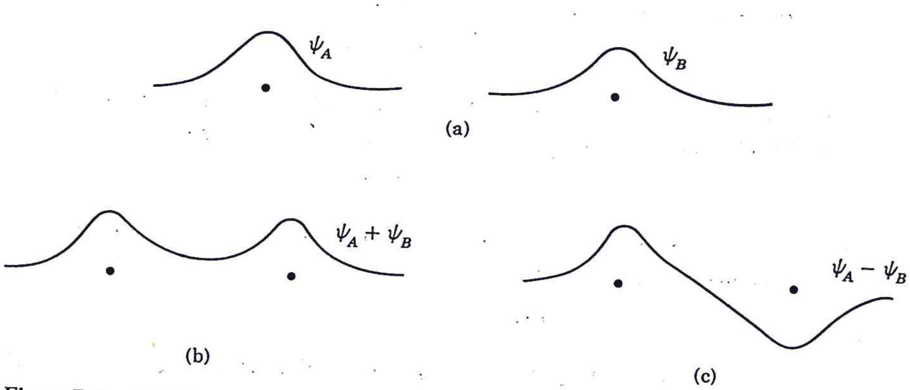

Figure D.1 (a) Schematic drawing of wavefunctions of electrons on two hydrogen atoms at large separation. (b) Ground state wavefunction at closer separation. (c) Excited state wavefunction.