triangles. Reasonable agreement is thus obtained between the experimental form factor values and those computed assuming the unpaired electrons to be in a state of pure e_g symmetry.

It is important to observe that the scale factor, k, here determined experimentally, is such as to make the unpaired $3d$ charge distribution for Ni^{++} much more compact in the solid than it is for the free atom. This is in contrast to the case of Mn^{++} where experiments[13] show that the charge distribution is expanded in the solid.

These experimental results may be compared with the recent calculations of Watson and Freeman[5] for the Ni^{++} ion. These Hartree-Fock self-consistent field calculations allow the wave functions of electrons with opposite spins to have different radial dependencies (spin polarization) and lead to a contraction of the charge distribution (both for the free-atom case and the case where the Ni^{++} ion is placed in an octahedral array of point charges).[14] Unfortunately, the magnitude of the contraction is much too small to explain the observations reported here. Nevertheless, the important fact that the relation of the observed f_S to the free-atom f_S is just opposite for the cases of Ni^{++} and Mn^{++} would lead one to look for the origin of this effect in the outstanding difference between the two ions: namely their differing spin configurations. These experimental results also serve to suggest that whereas effects such as spin polarization and crystalline environment have a large influence on f_S, their effect on f_A is small.

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TUNNELLING FROM A MANY-PARTICLE POINT OF VIEW*

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Giaever[1] and more recently Nicol, Shapiro, and Smith[2] have observed the tunnelling current flowing between two metals separated by a thin oxide layer. The most interesting results are obtained when one or both of the metals are superconducting, in which case they find direct evidence for a gap in the quasi-particle spectrum of the superconductor. They were able to account for the data quantitatively on the assumption that the only relevant factor is the density of states in energy. This is to be expected if the transition probability for transfer of an electron from one side to the other is given by the familiar expression $(2\pi/\hbar)|M|^2\rho_f$, where M is the matrix element and ρ_f the energy density of final states, and if it is further assumed that M can be treated as a constant. It is implied that M is not only independent of energy for the small energy differences involved, but is also unchanged when the metal goes from normal to superconducting.

However, it is not immediately obvious that these assumptions are justified. We give here a discussion of tunnelling from a many-particle point of view and show that it is plausible to treat M as a constant in the interpretation of the experiments.

We suppose that the barrier extends from x_a to x_b, with metal a to the left of x_a and metal b to the right of x_b. Consider two many-particle states of the entire system, Ψ_0 and Ψ_{mn}, which differ in the transfer of an electron from a to b. We suppose that Ψ_0 and Ψ_{mn} may be defined in terms of quasi-particle occupation numbers of metals a and b, so that Ψ_{mn} differs from Ψ_0 in the transfer of an electron from state m in a to state n in b, all other occupation numbers remaining the same. Of course m may correspond to a normally occupied state, in which case there will be a hole in m in Ψ_{mn}.

The quasi-particles do not correspond to plane waves, but to waves which are reflected at the barrier and which drop exponentially with distance into the barrier region. For example, in the free-electron approximation for the normal state the wave function would be of the form (WKB approximation):

$$\psi_m = Cp_x^{-1/2} e^{i(p_y y + p_z z)} \sin(p_x x + \gamma), \quad x < x_a \tag{1a}$$

$$\psi_m = \tfrac{1}{2} C |p_x|^{-1/2} e^{i(p_y y + p_z z)} \times \exp\left(-\int_{x_a}^{x} |p_x| dx\right), \quad x_a < x < x_b \tag{1b}$$

where $C = (2p_x/L)^{1/2}$ is a normalization constant, and in the barrier region, $|p_x| = (2\mu U - p_y^2 - p_z^2)^{1/2}$, where $U(x)$ is the potential energy. We have taken units such that $\hbar = 1$. Beyond x_b, we assume that the wave function representing the electron in state m drops smoothly to zero, instead of oscillating, so that it is not a good solution for $x > x_b$.

Thus we assume that Ψ_0 is a solution of the Schrödinger equation with energy W_0 for $x < x_b$, but there is a region to the right of x_b where it is not a good solution. Similarly, we assume that Ψ_{mn} with energy W_{mn} is a solution for $x > x_a$, but not for the region to the left of x_a where the wave function for quasi-particle n drops to zero. Both Ψ_0 and Ψ_{mn} are good solutions in the barrier region $x_a < x < x_b$.

We form a time-dependent solution as a linear combination of Ψ_0 and various final states, Ψ_{mn}, by the usual method:

$$\Psi = a(t)\Psi_0 e^{-iW_0 t} + \sum_{mn} b_{mn}(t)\Psi_{mn} e^{-iW_{mn} t}, \tag{2}$$

and substitute into the Schrödinger equation. This gives for the matrix element for the transition

$$M_{mn} = \int \Psi_0^* (H - W_{mn}) \Psi_{mn} d\tau. \tag{3}$$

Since the integrand vanishes except over a region to the left of x_a, we need to integrate only over this region.

We may express the integral in a more symmetric form by subtracting $\Psi_{mn}(H - W_0)\Psi_0^*$, which vanishes to the left of x_b. Since we are interested only in final states such that $W_{mn} \simeq W_0$, the result may be written

$$M_{mn} = \int_a [\Psi_0^* H \Psi_{mn} - \Psi_{mn} H \Psi_0^*] d\tau, \tag{4}$$

where the subscript a indicates that the integration is to be taken over the region to the left of x_a.

The matrix element may be expressed in terms of that of the current density operator, J, in the barrier region as follows. We introduce into the integrand a step function $S(x)$ which is equal to unity between a point x_0 to the left of the important region of integration and a point x_1 in the barrier and which vanishes elsewhere. Then integrations with respect to y_i and z_i vanish and integration with respect to x_i gives

$$M_{mn} = -\frac{1}{2\mu} \sum_i \int \cdots \int (\Psi_0^* \nabla_i^2 \Psi_{mn} - \Psi_{mn} \nabla_i^2 \Psi_0^*) S(x_i) d\tau_1 \cdots d\tau_N$$

$$= -i[J_{mn}(x_1) - J_{mn}(x_0)], \tag{5}$$

where $J_{mn}(x)$ is the matrix element of the x component of the current density operator defined by

$$J_{mn}(x) = -\frac{i}{2\mu} \sum_i \int \cdots \int [\Psi_0^* \partial \Psi_{mn}/\partial x_i - \Psi_{mn} \partial \Psi_0^*/\partial x_i] \delta(x - x_i) d\tau_1 \cdots d\tau_N. \tag{6}$$

According to our assumptions, $J_{mn}(x_0) = 0$ and further, $J_{mn}(x_1)$ is independent of position as long as x_1 is in the barrier region. Thus

$$M_{mn} = -iJ_{mn}(x_1). \tag{7}$$

It is easily verified that this method leads to the usual results for barrier penetration problems.

The quasi-particle energy in a superconductor is $E = (\epsilon^2 + \Delta^2)^{1/2}$, where $\epsilon(k)$ is the normal state energy measured from the Fermi surface. In calculating the density of final states, it is simplest to take the conventions that $f = 1$ and E is negative for the normally occupied states in the Fermi sea, so that for $k < k_F$, the probability of a hole excitation is $1-f$ and the energy of a hole is $-E$. This is the procedure which has been used in the interpretation of the experimental data.[1,2] In each region of k space the density of states in energy in the superconductor differs from that in the normal metal by the factor

$$\rho_S = \rho_n[|E|/(E^2 - \Delta^2)^{1/2}], \tag{8}$$

with $\rho_S = 0$ in the gap, $|E| < \Delta$. Agreement with experiment is obtained if it is assumed that M_{mn} (or J_{mn}) is the same for the corresponding transitions in normal and superconducting states.

Usually coherence factors, which have a marked effect on transition probabilities, are introduced in calculations of matrix elements between quasi-particle states of a superconductor.[3] To see why such factors are not expected to occur in tunnelling, one must consider the pairing in the vicinity of the barrier. Coherence factors would be introduced if one simply paired complex conjugate wave functions of the type (1a), (1b), so that pairing extends into the barrier region. However, if one looks at the problem more closely, from the viewpoint of the more general Gor'kov equations[4] which allow for a variation of the energy gap parameter with position, one sees that Δ will drop to zero very rapidly in the barrier. In effect electrons in this region are not paired and the wave function is essentially the same as in the normal state.

For an effective interaction $v(\vec{r}_1, \vec{r}_2)$, the position-dependent energy gap function is defined by

$$\Delta(\vec{r}_1, \vec{r}_2) = \langle N-2|\psi(\vec{r}_1)\psi(\vec{r}_2)|N\rangle_{\mathrm{av}}\, v(\vec{r}_1, \vec{r}_2). \tag{9}$$

Simply from the fact that ψ is very small in the barrier region, one expects that $\Delta(\vec{r}_1, \vec{r}_2)$ is small when either $\vec{r}_1$ or $\vec{r}_2$ is in the barrier. Note that the tail in the barrier of the wave function of a typical electron at the Fermi surface is very much smaller than that of one of the few electrons moving normal to the interface which has an appreciable probability of penetrating. However, $\Delta(\vec{r}_1, \vec{r}_2)$ is expected to rise very rapidly to normal values in the superconductor, $\Delta(\vec{r}_1, \vec{r}_2) \simeq \delta(\vec{r}_1 - \vec{r}_2)\Delta$, with $\Delta = \text{const}$.

Since, according to (6), the matrix element depends only on the wave function in the barrier, it would be expected to be the same as for the corresponding transition in the normal state. Actually, the wave function in the barrier would be changed slightly because of the difference in quasi-particle energies in normal and superconducting states, but this would have a negligible effect on the matrix elements. Thus the only significant difference in the tunnelling current comes from the density of states factor.

The method described here can also be used for calculating the tunnelling current between the valence and conduction bands of a semiconductor, as observed in the Esaki diode. It can be generalized to take indirect transitions into account.

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