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Theory of Surface Ion Neutralization

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ABSTRACT

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The formal theory of surface ion neutralization is given.
[An electron from a filled state in the conduction band in a
solid tunnels onto a rare gas ion on the surface to neutralize
it, the energy drop $\hbar\omega$ being used to excite another electron
from the band to a sufficiently high state that it can escape
from the metal into a collector.] Because of the large energy
$\hbar\omega$, the Coulomb interaction which is responsible for the pro-
cess is effectively unscreened, but it is shown that the long
range of the unscreened potential does not lead to any diver-
gences which might be expected in calculating the emergent
current. The ejected electrons originate in the first few
atomic layers of the solid and some even outside it. The
variations of the matrix element and of the transmission
coefficient through the surface can explain some directional
dependence observed in the measurements.

I. INTRODUCTION

Fig. 1 shows the potential energy seen by an electron when some free ion such as Ne^+ is near a metallic surface. Electron 'one' can tunnel from a state ϕ_a in the conduction band of the metal to the ground state E_g in the ion, thus neutralizing it. The excess energy $\hbar\omega = E_a - E_g$ is communicated via the Coulomb interaction to electron 'two' in state ϕ_b of the conduction band, which is excited to state ϕ_e and may emerge from the metal with kinetic energy T_e. Such is the general picture of the neutralization process, established by Hagstrum and others[1,2] through their experimental investigations. For instance, the rate is clearly proportional, among other things, to the density of states $n(E)$ at E_a and E_b, and has been used[3] to obtain a picture of $n(E)$ in the conduction band.

However, some questions have remained, in particular, how far below the surface to the emergent electrons originate. One would suppose that the Coulomb interaction is effectively un-screened because of the large energy transfer $\hbar\omega$. However, if one then calculated with it the total emergent current from all electrons, one would obtain a divergent contribution from pro-cesses deep inside the metal, arising from the long range nature of the Coulomb interaction. It therefore seems worth-while to set down a formal theory. Other questions concern

the nature of the matrix element involved in the process and the directional variation of the emergent current.

The rate of the neutralization process is given by

$$(2\pi/\hbar) \sum_{e,a,b} |M_{eab}|^2 \delta(E_e + E_g - E_a - E_b) \qquad (1)$$

where M_{eab} is the matrix element for a particular transition

$$\iint \phi_g^*(r_1) \phi_e^*(r_2) V_{int}(r_1, r_2) \phi(r_2) \phi(r_2) \, dr_1 \, dr_2 \qquad (2)$$

Strictly we should subtract the corresponding exchange contribution, which we shall ignore since it does not affect the following argument. V_{int} is the Coulomb interaction e^2/r_{12} screened as appropriate. It is a very complicated function since the space of r_1, r_2 includes the region outside the metal around the gas ion, as well as the interior of the metal. In (1) transitions from different sets of band states a,b simply add, and it is therefore convenient to consider those involving a particular pair ϕ_a, ϕ_b. The energy of the emergent beam is then fixed at

$$E_e = E_a + E_b - E_g = E_b + \hbar\omega \qquad (3)$$

With ϕ_a fixed we may also perform in principle the r_1 integration in (2). We can treat

$$\nu(\mathbf{r_2}) = \int \phi_g^*(\mathbf{r_1}) \phi_a(\mathbf{r_1}) V_{int}(\mathbf{r_1}, \mathbf{r_2}) d\mathbf{r_1} \qquad (4a)$$

$$= \int \nu(\mathbf{q}) \exp i\mathbf{q} \cdot \mathbf{r} \, d\mathbf{q} \qquad (4b)$$

as a perturbation in the one-electron Hamiltonian of electron 'two'. At large r_2 it is a Coulomb potential, appropriately screened. It is centered at the point of maximum overlap of ϕ_g and ϕ_a, which is somewhere near the center of the surface ion because ϕ_g is so highly localized.

II.   THE COULOMB INTERACTION

The main problem is the long range of $v(r_2)$, i.e., the divergence of $v(q)$ at small q, because the screening is very small for large energy transfers $\hbar\omega$. We can obtain the essential physical picture by taking plane waves for ϕ_b, ϕ_e, and expressing v in terms of a free-electron screening constant $\epsilon(q,\omega)$:

$$v(q) = \frac{4\pi}{q^2 \epsilon(q,\omega)} \tag{5}$$

The matrix element is simply $v(Q)$ where $Q = k_e - k_b$. Here k_b is assumed to be some fixed state and k_e can lie on a sphere of radius k_e determined by (3). The point is that Q can vary from $k_e - k_b$ to $k_e + k_b$, but components $v(q)$ with q $\approx$ o do not contribute to the excitation of electrons at the high energies studied. The minimum value of $\hbar\omega$ for an electron to be observed in this type of experiment, is the work function Φ. Of course other electrons with lower $\hbar\omega$ are produced but cannot escape through the surface. But for these also, Q cannot tend to zero unless $\hbar\omega$ tends to zero as well, and in that limit the screening $\epsilon(q,\omega)$ removes the $1/q^2$ divergence in $v(q)$.

The conclusions remain valid when we take Bloch waves $\phi(k_b,\ n_b;\ r_2)$ and $\phi(\mathbf{k}_e,\ n_e;\ r_2)$ where $\mathbf{k}$ is now the reduced wave vector and n the band index. It is now perfectly possible to have $k_e = k_b$ and for small q terms in (5) to contribute. Let us focus attention this time on transitions from all ϕ_b in a filled band n_b to a particular final state ϕ_e in the higher band n_e. The number of emergent electrons in ϕ_e is proportional to

$$\int [v(q)\, M(q)]^2\, dq \tag{6}$$

where

$$M(q) = \int \phi^*(k_e+q, n_b)\, exp(iq \cdot r)\, \phi(k_e, n_e)\, dr \tag{7}$$

$M(q)$ must vanish by orthogonality for q = o, and from $\mathbf{k \cdot p}$ pertur-bation theory we have $M(q) \propto q$, which kills one of the factors of q in (5). The other, when squared, disappears with the volume element $dq = 4\pi q^2 dq$.

Finally it remains to consider the effect in the real situation of terminating the wave function ϕ_b at the surface of the metal, with some tail overlapping the surface ion. ϕ_e exists both inside and outside the metal. If we choose cylindri-

cal coordinates ρ , θ , γ with axis perpendicular to the surface, we see that the $\rho\,d\rho$ in the volume element is not strong enough to give a divergence with $1/r$ in the matrix element

$$\int \phi_e^*(\underset{\sim}{r})\, v(\underset{\sim}{r})\, \phi_b(\underset{\sim}{r})\, d\underset{\sim}{r} \tag{8}$$

when we integrate over the volume just outside the surface of the metal.

We note incidentally that since the center of $v(\underset{\sim}{r})$ lies near the surface ion, an appreciable fraction of (8) may come from the region between the metal surface and the ion. Thus, some of the emergent electrons may be regarded as generated outside the metal proper, for the complete emergent wave packet originating from a particular ϕ_b may be written[4] (treating the ϕ_e as free waves for simplicity)

$$\phi(\underset{\sim}{r}) = \int \frac{4\pi \exp i\, k_e |\underset{\sim}{r} - \underset{\sim}{r_2}|}{|\underset{\sim}{r} - \underset{\sim}{r_2}|}\, v(\underset{\sim}{r_2})\phi(\underset{\sim}{r_2})\, d\underset{\sim}{r_2} \tag{9}$$

where in classical terms $v(r)\, \phi_b\,(r_2)$ is the source of the wave. As regards the inside of the metal, we have already shown that the long range part of v, corresponding to low q, does not contribute anything substantial. Only the high q components contribute effectively, and the emergent electrons originating in the first few atomic layers.

III. INTENSITY VARIATIONS

Two orientational effects arise from the surface. In the free-electron model the total number of electrons excited to $\underset{\sim}{k}_e$ is independent of its direction. However, states with $\underset{\sim}{k}_e$ perpendicular to the surface have the largest transmission coefficient through it. Further, the magnitude of the tail of ϕ_b outside the metal is largest when $\underset{\sim}{k}_b$ is perpendicular to the surface, and the extra contribution to the matrix element from outside the metal makes the largest contribution to the current when $\underset{\sim}{k}_e$ is also perpendicular to the surface, for then q is smallest, v(q) largest. Both effects give an orientational dependence relative to the direction of the surface as observed,[2,5] the former probably being dominant.

With a real band structure there can also be directional effects with respect to the crystal axes. All states ϕ_b of energy E_b contribute to the emergent current in a particular state ϕ_e, giving a factor $n(E_b)$ in the current if all ϕ_b are weighted equally. However, in the nearly-free-electron pseudopotential model, the ϕ_b with dominant wave vector $\underset{\sim}{k}_b$ parallel to, or otherwise closest to, the strongest component $\underset{\sim}{k}_e$ of ϕ_e, will have the largest v(q) factor. Thus, the correctly weighted density of states, $\bar{n}(E_b)$ say, depends somewhat[2,5] on the final state ϕ_e.

The d-bands in transitional metals do not contribute as strongly, relative to the plane wave bands, as in optical excitation.[2,5] Firstly, the amplitude of the tail of ϕ_a overlapping the ion is smaller,[2,5] and secondly, the matrix element (7) does not have the enhancement provided in the optical case by the momentum operator, i.e., by differentiating once.

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FIGURE CAPTION
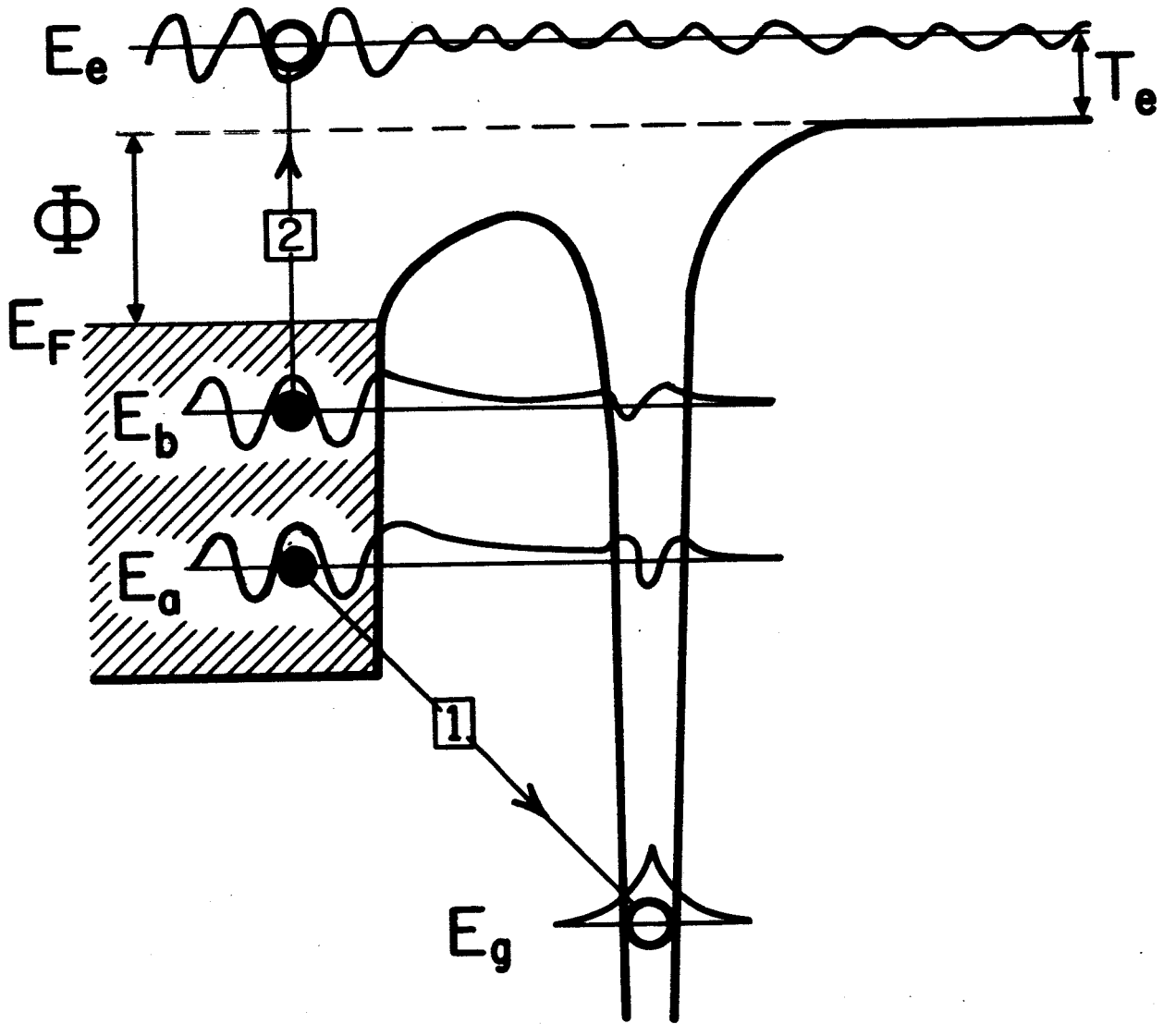
Fig. 1.   Surface ion neutralization process.

Fig. I