Table II. Contributions to $\langle 0|H|0\rangle$ in cal/mole from the kinetic energy K and from terms proportional to the nth derivative of the potential V^n computed with the ground-state eigenfunctions of the self-consistent $|c,0\rangle$ and the traditional $|h,0\rangle$ harmonic Hamiltonians.

Term	Computed with $\|c,0\rangle$	$\|h,0\rangle$
K	84.7	62.3
V^0	−586.0	−586.0
V^2	45.8	62.3
V^4	14.5	26.8
V^6	2.6	6.5
V^8	0.5	1.4

not minimized with respect to b, but rather $b = 2.74$ Å was chosen to agree with the optimum value reported in Ref. 8. Thus, this theory is compared with other theories. A detailed comparison with experiment will be reported in the future. The value of $-W_0$ is in reasonable agreement with the experimental value[11] 450 ± 10 cal/mole.

It should be noted that the expectation value of the second derivative of the potential is quite different from the second derivative for nearest neighbors but that second-nearest-neighbor and further force constants are not altered much.

Although space limitations do not permit an adequate discussion of this point, an interesting aspect of the numerical procedure used here is that the contributions to W_0 from terms proportional to various derivatives of the potential V are obtained almost trivially. Contributions to $W_0^{(3)}$ and $W_0^{(0)}$ from these terms as well as the kinetic energy K are shown in Table II.

Note that in $W_0^{(3)}$, $K = V^2 + 2V^4 + 3V^6 + \cdots$. The contributions for $W_0^{(0)}$ show clearly that solid neon cannot be treated adequately by the traditional harmonic approximation. Note that $W_0^{(0)}$ as given in Table I equals $K + V^0 + V^2$ here, and that truncation of the Hamiltonian at V^2 results in an error of approximately 35 cal/mole.

One can also show from Eq. (I-54b) that $\langle c; k^\alpha, -k^\beta | H | c, 0\rangle = 0$. Since these matrix elements would normally give rise to the largest correction in perturbation theory, the eigenfunction of $H^{(c)}$ appears to be a logical set with which to begin perturbation calculations.

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"s-d" EXCHANGE MODEL OF ZERO-BIAS TUNNELING ANOMALIES*

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Anomalies in the tunneling conductance centered at zero bias have been found in several experiments.[1] These studies were performed on a large class of p-n junctions, as well as on junctions composed of normal metals separated by an insulating oxide layer.

In particular, Wyatt has observed[2] a peak in the conductance, $G(V)$, centered at zero bias in tunneling junctions where Ta or Nb was separated from Al by a thin oxide layer. Wyatt found that $G(V)$ could be divided into a temperature-independent part $G_0(V)$ and a strongly temperature-dependent part $\Delta G(V) = G(V) - G_0(V)$. $\Delta G(V)/G_0(V)$ varied as $\ln|eV/kT|$ for $eV > kT$, while $\Delta G(0)/G_0(0)$ varied with temperature as $\ln T$. The effect persisted both above and below the superconducting transition temperature, when care was taken to quench the

superconductivity with an applied magnetic field of 9 kG. The effect of varying the magnetic field between 4 and 20 kG was observable only at 1.5°K, where a 10% broadening of $\Delta G(V)$ was observed. Wyatt assumed that the zero-bias anomaly in $G(V)$ was due to a logarithmic singularity in the density of states at the Fermi surface.

Anderson has suggested[3] that the Wyatt anomalies may be caused by magnetic impurities, and recent experiments[4] appear to corroborate his idea. Stimulated by Anderson's suggestion, we have analyzed several microscopic mechanisms; one of these is closely related to the scattering singularities discussed by Kondo.[5]

We begin by remarking that near zero bias and at low temperatures, one expects localized states to contribute to the tunneling current by serving as a momentum reservoir for the tunneling electrons. Such a reservoir is obviously essential, if the initial and final states of the tunneling electron have wave vectors differing by a substantial fraction of a reciprocal lattice vector. This is the case for p-n junctions of Si and Ge, and is probably the case for the junctions studied by Wyatt, considering the nature of the Fermi surfaces of the metals involved.

We shall assume that the localized states (which may be associated specifically with impurities or with the metal-oxide interface) are paramagnetic and are coupled to the conduction electrons by an exchange interaction of the following form:

$$H = H_1 + H_2, \tag{1}$$

$$H_1 = T_J \sum_{\vec{k},\vec{k}'} S_z [(a_{\vec{k}+}^* b_{\vec{k}'+} - a_{\vec{k}-}^* b_{\vec{k}'-}) + (b_{\vec{k}'+}^* a_{\vec{k}+} - b_{\vec{k}'-}^* a_{\vec{k}-})] + T_J \sum_{\vec{k},\vec{k}'} S^+ (a_{\vec{k}-}^* b_{\vec{k}'+} + b_{\vec{k}'-}^* a_{\vec{k}+}) + T_J \sum_{\vec{k},\vec{k}'} S^- (a_{\vec{k}+}^* b_{\vec{k}'-} + b_{\vec{k}'+}^* a_{\vec{k}-}), \tag{2}$$

$$H_2 = +J \sum_{\vec{k},\vec{k}'} S_z [(a_{\vec{k}+}^* a_{\vec{k}'+} - a_{\vec{k}-}^* a_{\vec{k}'-}) + (b_{\vec{k}+}^* b_{\vec{k}'+} - b_{\vec{k}-}^* b_{\vec{k}'-})] + J \sum_{\vec{k},\vec{k}'} S^+ (a_{\vec{k}-}^* a_{\vec{k}'+} + b_{\vec{k}-}^* b_{\vec{k}'+}) + J \sum_{\vec{k},\vec{k}'} S^- (a_{\vec{k}+}^* a_{\vec{k}'-} + b_{\vec{k}+}^* b_{\vec{k}'-}), \tag{3}$$

where S_z, S^+, and S^- are the spin operators of the localized states. Electrons on the left-hand side (a) of the junction which have momentum $\vec{k}$ and spin σ are described by the creation and annihilation operators $a_{\vec{k}\sigma}^*$, $a_{\vec{k}\sigma}$, respectively, while the operators $b_{\vec{k}'\sigma'}^*$, $b_{\vec{k}'\sigma'}$ have similar meanings for electrons on the right-hand side (b) of the junction.

J is an exchange coupling for electrons which remain on the same side of the junction after scattering off the localized spin. T_J is similarly an exchange coupling, except it is defined in terms of electrons on opposite sides of the junction. It will, consequently, be smaller than J by a factor, the order of the overlap of the exponential tails of the wave functions on opposite sides of the junction. The two terms, H_1 and H_2, represent, respectively, the two possible outcomes of an electron scattering off a localized spin; either the electron scatters to the other side of the junction or remains on the same side. Thus, the interaction described by H is confined to within a mean free path of the junction.

H contains the interaction of conduction electrons with a single localized spin. We assume that we may neglect interference effects between localized spin states. To obtain the total current J_{ab} between sides a and b we multiply j_{ab}, the current calculated from H, by N, the number of localized spins.

We obtain j_{ab} from

$$j_{ab} = e \sum_{\substack{\vec{k}\sigma \\ \vec{k}'\sigma'}} \{W_{\vec{k}\sigma;\vec{k}'\sigma'} f(\epsilon_{\vec{k}\sigma})[1 - f(\epsilon_{\vec{k}'\sigma'})] - W_{\vec{k}'\sigma';\vec{k}\sigma} f(\epsilon_{\vec{k}'\sigma'})[1 - f(\epsilon_{\vec{k}\sigma})]\}, \tag{4}$$

where $f(\epsilon_{\vec{k}\sigma})$ is the Fermi-Dirac distribution function and $W_{\vec{k}\sigma;\vec{k}'\sigma'}$ is the transition probability for an electron scattering from state $(\vec{k}, \sigma)$ on side a to $(\vec{k}', \sigma')$ on side b.

To third order in the exchange coupling, W

is given by

$$W_{i;j}=\frac{2\pi}{\hbar}\left[\sum_{k\neq i}\frac{H_{ik}H_{kj}H_{ij}}{E_i-E_k}+\text{complex conjugate}+|H_{ij}|^2\right]\delta(E_i-E_j), \tag{5}$$

where E_i and E_j are the energies of the initial and final states of the electron–localized-spin system. We shall be interested in only those terms of $W_{i;j}$ which are first order[6,7] in T_J. We assume there is a magnetic field $\vec{H}$ present, so that the localized spins have a Zeeman energy Δ equal to $g|\mu_B|H$, where g is the g factor of the localized spin, and μ_B, the Bohr magneton. The Zeeman energies of the conduction electrons were found to have no effect on the current.

Typical scattering processes which contribute to ΔG are shown in Fig. 1. Following an analysis similar to that of Kondo,[5] one obtains for the processes shown in Fig. 1 the following:

$$W_{\vec{k}+M\to\vec{k}-',M+1}$$
$$=-2T_J^2J[S(S+1)-M(M+1)][g^{(a)}(\epsilon_{\vec{k}+}-\Delta)+g^{(a)}(\epsilon_{\vec{k}+})+g^{(b)}(\epsilon_{\vec{k}-})+g^{(b)}(\epsilon_{\vec{k}-'}+\Delta)]\delta(\epsilon_{\vec{k}+}+eV-\epsilon_{\vec{k}-'}-\Delta), \tag{6}$$

where M is the component of localized spin along the magnetic field, and S is the total spin of the localized state. We assume the Fermi energy on the a side has been raised by an energy eV, the applied potential. $g^{(n)}(\omega)$ is defined by

$$g^{(n)}(\omega)=\sum_{k^{(n)}}\frac{f(\epsilon_k)}{\epsilon_k-\omega}=\int_{\epsilon_F-E_0}^{\epsilon_F+E_0}\frac{\rho^{(n)}(\epsilon)f(\epsilon)d}{\epsilon-\omega},\qquad n=a,b, \tag{7}$$

where the index n specifies whether the above sum is carried out over states from the a or b sides. $\epsilon_{\vec{k}\sigma}$ is the energy of an electron with momentum $\vec{k}$ and spin σ before the external electric field is applied, and the Fermi energy appearing in $f(\epsilon_{\vec{k}})$ is the common Fermi energy of sides a and b when $V=0$.

We have limited the sum over states to a narrow energy region of width $2E_0$ centered at the Fermi energy. This reflects the fact that only in a narrow energy is our assumption valid, that the exchange couplings J and T_J appearing in Eqs. (1)-(3) are constant. It is difficult to estimate E_0, and it will be taken as an adjustable parameter.

When all terms which contribute to $W_{i;f}$ are evaluated, the $\vec{k}$-space sums in Eq. (4) performed, and the derivatives with respect to V taken, one obtains[8] for $G(V)$

$$G(V)=G_0(V)+\Delta G(V), \tag{8}$$

where

$$G_0(V)=C\left[1+\frac{\langle M\rangle}{2S(S+1)}\left(\tanh\frac{eV+\Delta}{2k_BT}-\tanh\frac{eV-\Delta}{2k_BT}\right)\right], \tag{9a}$$

$$\Delta G(V)=-J[\rho^a(\epsilon_F)+\rho^b(\epsilon_F)]C[\Delta G_1(V)+\Delta G_2(V)+\Delta G_3(V)]; \tag{9b}$$

with

$$\Delta G_1(V)=2\left[1-\frac{\langle M^2\rangle}{S(S+1)}+\frac{\langle M\rangle}{2S(S+1)}\left(\tanh\frac{\Delta-eV}{2k_BT}+\tanh\frac{\Delta+eV}{2k_BT}\right)\right]\ln\frac{|eV|+k_BT}{E_0}, \tag{10a}$$

$$\Delta G_2(V)=\left[1+\frac{\langle M^2\rangle}{S(S+1)}+\frac{\langle M\rangle}{S(S+1)}\tanh\frac{\Delta-eV}{2k_BT}\right]\ln\frac{|eV-\Delta|+k_BT}{E_0}, \tag{10b}$$

$$\Delta G_3(V)=\left[1+\frac{\langle M^2\rangle}{S(S+1)}+\frac{\langle M\rangle}{S(S+1)}\tanh\frac{\Delta+eV}{2k_BT}\right]\ln\frac{|eV+\Delta|+k_BT}{E_0}, \tag{10c}$$

$$C=\frac{4\pi e^2}{\hbar}T_J^{\,2}\rho^a(\epsilon_F)\rho^b(\epsilon_F)S(S+1).$$

To order JT_J^2, only terms with a strong temperature and voltage dependence have been retained. $\langle M^2\rangle$ and $\langle M\rangle$ refer to appropriate statistical averages of $S_z^{\,2}$ and S_z, respectively. Terms of the form $\ln(kT+|\omega|)/E_0$ which appear above are interpolative approximations to the function $F(\omega)$, where

$$\rho^n(\epsilon_F)F(\omega)=\int_0^\infty d\epsilon\, g^{(n)}(\epsilon)\frac{\partial}{\partial\epsilon}f(\epsilon+\omega). \qquad (11)$$

We have assumed throughout that $\rho^{(n)}(\epsilon)$, the density of states, is a slowly varying function of energy, and where it has appeared in integrals, we have replaced it by its value at ϵ_F, the Fermi energy.

For $H=0$ ($\Delta=0$), $G(V)$ simplifies to

$$G(V)=C\{1-4J[\rho^a(\epsilon_F)+\rho^b(\epsilon_F)]\}\times\ln[(|eV|+k_BT)/E_0], \qquad (12)$$

whence

$$\Delta G(0)/G(0)=-4J[\rho^a(\epsilon_F)+\rho^b(\epsilon_F)]\ln(k_BT/E_0). \qquad (13)$$

This is precisely the temperature and voltage dependence found by Wyatt. Fitting his data we obtain $E_0=10.6$ meV and $J(\rho^a+\rho^b)=0.012$. Little significance should be attached to the small values of E_0 and J obtained from the data, as these parameters will be renormalized when, e.g., the current from nonmagnetic localized states is considered. Notice also that J is positive, which implies antiferromagnetic coupling between the conduction electrons and the localized spins, and that ferromagnetic coupling in Eq. (12) implies a dip in $G(V)$ instead of a peak.

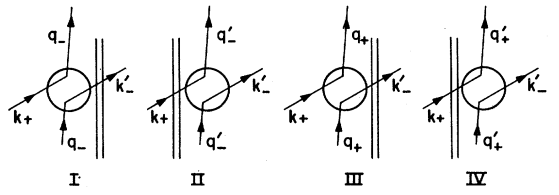

FIG. 1. Diagram I represents a second-order scattering process in which an electron in state $\vec{k}+$ scatters into the virtual state $\vec{q}-$. The localized spin state, represented in the diagram by a circle, changes its $\vec{z}$ component of spin by one unit. The virtual state $\vec{q}-$ then scatters into the final state $\vec{k}-'$. Such a process may also occur in the reverse order: e.g., $\vec{q}-$ first scattering $\vec{k}-$, then $\vec{k}+$ scattering $\vec{q}-$. The double vertical lines represent the junction interface. Diagrams II-IV are similarly interpreted.

For $\vec{H}\neq 0$, $G(V)$ assumes the rather complicated form given in Eqs. (8)-(10). For weak magnetic fields (those for which $\Delta/2k_BT\ll 1$), $\vec{H}$ should have no noticeable effect on $G(V)$. This is expected to be the case for all temperatures studied by Wyatt except $T=1.5$°K. (We have assumed $g=1$ in evaluating Δ.) At this temperature the essential effect of $\vec{H}$ is to broaden the peak.[12] This can be seen from Eq. (10), where the single logarithmic peak centered on zero bias for $\vec{H}=0$ is split into three peaks, two of which are displaced by Δ to either side of zero bias. We see, therefore, that the magnetic field dependence of $G(V)$ is consistent with that found by Wyatt.

In the limit $eV, k_BT\ll\Delta$, we expect H to have a more noticeable effect on $\Delta G(0)/G_0(0)$. This effect will be different, depending on whether the main contribution to G_0 comes from magnetic or nonmagnetic scattering. In the former case, Eq. (13) is replaced by

$$\Delta G(0)/G(0)=-4J[\rho^a(\epsilon_F)+\rho^b(\epsilon_F)]\times\ln[(k_BT+\Delta)/E_0], \qquad (14)$$

while in the latter, one should use instead of Eq. (13)

$$\Delta G(0)/G(0)=-4J[\rho^a(\epsilon_F)+\rho^b(\epsilon_F)][S/(S+1)]\times\ln[(k_BT+\Delta)/E_0] \qquad (15)$$

in the high-field limit.

Experimental studies in the above regime should serve to test the proposed exchange model.

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LOCALIZED MAGNETIC STATES AND FERMI-SURFACE ANOMALIES IN TUNNELING

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The purpose of this paper is to provide a physical model for the interactions proposed by Appelbaum which he used to explain Fermi-surface anomalies in tunneling. We also evaluate these interactions and show why the anomalous conductance need not be small compared to the direct tunneling.

Appelbaum[1] has recently explained some of the anomalous variations of the tunneling conductance which are frequently observed near zero-bias voltage in terms of exchange interactions between tunneling electrons and magnetic states in, or near, the insulating layer of the tunnel junction. These anomalous variations are observed both in tunneling between degenerate semiconductors[2,3] and between metals,[4,5] and in the latter case depend to some extent on the metal, on the insulator, and on junction preparation.[5] Characteristically, in the simplest cases, a peak in conductance, logarithmic in some homogeneous function of V and T, is observed.[5]

The purpose of this Letter is to provide a physical model for the interactions postulated by Appelbaum, which also evaluates them and demonstrates why the anomalous conductance need not be small compared to the direct tunneling.

Appelbaum's explanation assumed an exchange type of interaction between a localized spin $\vec{S}$, somewhere near the tunneling layer, and electrons in the two degenerate Fermi gases described by operators $a_{k\sigma}^*, a_{k\sigma}$ for metal 1, $b_{q\sigma}^*, b_{q\sigma}$ for metal 2:

$$\mathcal{H}_{\text{int}} = \sum_{kk'\sigma\sigma'} \{\vec{S}\cdot(\vec{\tau})_{\sigma\sigma'}[J(a_{k\sigma}^* a_{k'\sigma'}) + T_J(a_{k\sigma}^* b_{k'\sigma'} + b_{k\sigma}^* a_{k'\sigma'})]\}. \quad (1)$$

(Appelbaum's Hamiltonian is symmetric in the two metals, but this is neither necessary nor, as we shall see, likely). $\vec{\tau}$ is the Pauli spin operator, and J and T_J are exchange and exchange-tunneling interactions between the local moment and the metals.

The anomalous term appears to order JT_J^2 and is, in the simplest case, of the form

$$\Delta G(0) = J\rho_a(0)[(16\pi e^2/\hbar)T_J^2 S(S+1)\rho_a(0)\rho_b(0)] \times \ln[E_0/(|eV|+kT)]. \quad (2)$$

ρ_a and ρ_b are the metallic densities of states;