have to be matched by more intense dc field pulses with short rise and fall times for off-resonance observations. From this point of view the choice of Teflon appears to be a rather poor one since the nonsecular terms in this compound are surprisingly large in the range of rf fields used. As compared to sample rotation and multiple-pulse-sequence techniques the continuous rotating field approach has the disadvantage that the signal is not observable in the presence of the rf field.

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Energy Distribution in Field Emission from Adsorbate-Covered Surfaces*

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A calculation of the total energy distribution of field-emitted electrons in the presence of chemisorbed atoms shows that $[j(\omega)-j_0(\omega)]/j_0(\omega)=u(\omega)^2\,\mathrm{Im}G_{aa}(\omega)$ if the adsorbate resonance level lies within the conduction band of the metal. $j(\omega)$ and $j_0(\omega)$ are the current densities per unit energy in the presence and absence of the adsorbate, respectively; the energy ω is measured from the vacuum level; x_a is the surface-adsorbate distance; and $(1/\pi)\,\mathrm{Im}G_{aa}$ is the local density of states at the adsorbate. $u(\omega)^2\propto\exp\{2(-2m\omega/\hbar^2)^{1/2}x_a+[\frac{4}{3}(2m/\hbar^2)^{1/2}(-\omega)^{3/2}(eF)^{-1}\times(v(y)-1)]\}$, where F is the electric field and $v(y)$ is the image-potential correction factor. The expression given above for the tunneling current is general and independent of the explicit form of G_{aa}. If the adsorbate resonance lies below the bottom of the conduction band, then $[j(\omega)-j_0(\omega)]/j_0(\omega)<0$, in agreement with the results of Duke and Alferieff.

I. INTRODUCTION

Measurements of total energy distribution (TED) of field-emitted electrons from adsorbate-covered surfaces can show the location and shapes of the virtual impurity levels associated with the adsorbate, and thus constitute a powerful tool for the study of chemisorption. Theoretical treatments of tunneling through adsorbates have been given by Duke and Alferieff[1] (DA) and by Gadzuk.[2] Both DA and Gadzuk formulated the problem in terms of tunneling of metal electrons through an adsorbate schematized in terms of a potential. DA considered only one-dimensional cases, and their parametrization does not easily lend itself to interpretations of specific systems nor does it take correlation effects into account. Gadzuk has attempted to attack the problem specifically from the point of view of obtaining information on virtual adsorbate levels. However, it is hard to see the justification for his initial state function $|m\rangle+GV_F|m\rangle$ used in Eq. (8) of his paper and central to his subsequent development, since G is the Green's function appropriate to the total field-free Hamiltonian, metal plus adsorbate, while $|m\rangle$ is an eigenfunction of the metal Hamiltonian only, and V_F, the external electric field, is in this context a higher-order perturbation. In the case of chemisorption, however, the

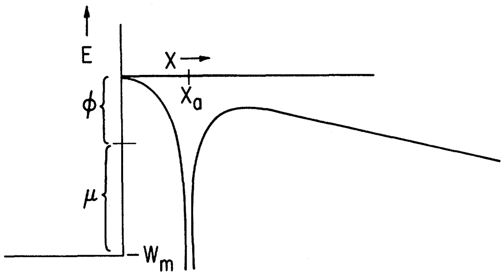

FIG. 1. Schematic diagram of the potentials due to the metal plus adsorbate and the external electric field. ϕ denotes the work function, μ is the Fermi energy of the metal, $W_m = \mu + \phi$, and x_a is the metal-adsorbate distance.

adsorbate wave function is already mixed with the metal wave function even in the absence of a field. It is more natural therefore to treat the applied field as a perturbation on the metal plus adsorbate system and to consider tunneling from system states.

The metal-adsorbate system is characterized by its Green's function; we adopt the many-body form of the Anderson Hamiltonian to describe the system with the result that the metal-adsorbate Green's function is directly related to $G_{aa}(\omega)$, the adsorbate Green's function. All information relevant to the adsorbate binding is contained in $G_{aa}(\omega)$. $G_{aa}(\omega)$ is determined by the adsorbate level shift Σ_R and the broadening of the virtual adsorbate level Σ_I. We use the transfer Hamiltonian method to calculate the tunneling current per unit energy $j(\omega)$, and find that it is directly related to $G_{aa}(\omega)$. More specifically, the ratio of the excess tunneling current to that in the absence of the adsorbate is directly proportional to the real and imaginary parts of $G_{aa}(\omega)$; $\Delta j/j_0 = \alpha_a G^R_{aa} + \beta_a G^I_{aa}$. An estimate of α_a and β_a reveals that $\beta_a \gg \alpha_a$; thus TED experiments can provide a direct measurement of G^I_{aa}. In the case of adsorbate resonances well below the Fermi energy of the metal, we find a current decrease in accord with the results of DA.

The present approach is general and independent of the explicit form of G_{aa}. A short account of this work has previously appeared.[3]

II. FORMULATION

We wish to calculate the current per unit energy due to the tunneling of electrons from the metal-adsorbate complex to the vacuum in the presence of an external electric field. The appropriate potentials are shown in Fig. 1. For simplicity the metal potential is drawn as a square well. The transfer Hamiltonian method[4,5] is used to compute the tunneling current. The Hamiltonian for the system has the form $H = H^{ma} + V^>_f$, where H^{ma} is the many-electron Hamiltonian for the metal-adsorbate complex and $V^>_f$ is the potential due to the constant electric field:

$$V^>_f = V_f\,\theta(x) = -eFx\theta(x)\,, \tag{1a}$$

where

$$\theta(x) = 1\,, \quad x > 0 \tag{1b}$$

$$\theta(x) = 0\,, \quad x < 0\,. \tag{1c}$$

Consider a "left system" for which the Hamiltonian is

$$H_L = H^{ma} + \Delta\epsilon_a n_a\,, \tag{2a}$$

where

$$\Delta\epsilon_a = -eFx_a \tag{2b}$$

is the energy shift of the adsorbate caused by $V^>_f$. Here n_a is the number of electrons on the adsorbate and x_a is the position of the adsorbate. The one-electron part of H_L is shown in Fig. 2(a). H_L governs the motion of an electron in the "left system" throughout all space; similarly the Hamiltonian of the "right system," H_R, consists of the kinetic energy plus the external field extended over all space. The external potential $V_f = -eFx$ is shown in Fig. 2(b).

At the energies of interest eigenfunctions of H_L are largely confined to $x < 0$ and those of H_R to $x > 0$. Thus tunneling may be treated as transitions induced by V_f from "left-system" eigenstates to "right-system" eigenstates. In particular, we can make use of the method of Appelbaum and Brinkman[6] to write the tunneling current per unit energy at energy ω as

$$j(\omega) = [2f(\omega)/\pi\hbar] \sum_{ii'jj'} \langle i|\tau|j\rangle\langle j'|\tau|i'\rangle$$

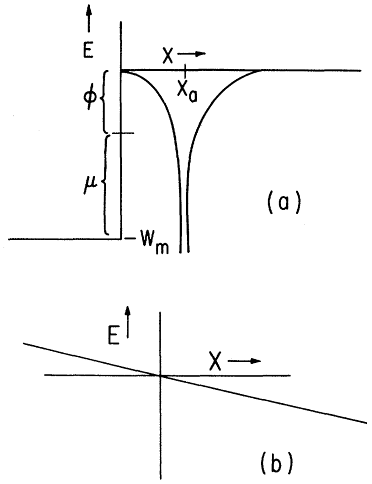

FIG. 2. (a) Potentials of the "left system" consisting of the metal and adsorbate; (b) the potential of the "right system," $v_f = -efx$.

$$\times \mathrm{Im}\, G^{L}_{i'i}(\omega - i\delta)\, \mathrm{Im}\, G^{R}_{jj'}(\omega - i\delta)\ , \tag{3a}$$

where

$$\tau = H - H_{L} = V^{>}_{f} - \underline{\mathrm{P}}_{a} \Delta\epsilon_{a} \underline{\mathrm{P}}_{a} \tag{3b}$$

and $\underline{\mathrm{P}}_a$ is the projection operator for the adsorbate states. $f(\omega)$ is the Fermi function; the states $|i\rangle$ form a complete set of one-electron wave functions for the "left system"; $|j\rangle$ form a complete set for the "right system"; G^L and G^R are the Green's functions for the left and right systems, respectively. (Here and later in the paper it is assumed that $\delta \to 0^+$.) Expression (3) holds for the general many-body system. The derivation of an analogous expression for $j(\omega)$ in the noninteracting electron case illustrates the method without introducing the complications associated with a many-body formalism and is given in Appendix A.

The right Green's function G^R is diagonalized by Airy functions. Letting the set $\{|j\rangle\}$ be the set of Airy functions $\{|f\rangle\}$ yields

$$j(\omega) = [2f(\omega)/\hbar] \sum_{ii'f} \langle i' | \tau | f \rangle \langle f | \tau | i \rangle$$

$$\times\, \mathrm{Im}\, G^{L}_{ii'}(\omega - i\delta)\, \delta(\omega - \epsilon_f)\ , \tag{4}$$

where ϵ_f is the energy associated with the state $|f\rangle$.

In order to test the transfer Hamiltonian method as formulated above, we apply it to a particular one-dimensional model considered by DA, their model 1. They carried out an exact calculation of the tunneling current by a direct solution of the Schrödinger equation for the case where the adsorbate is represented by an attractive δ-function potential. As shown in Appendix B, the transfer Hamiltonian method agrees with the DA calculation [their Eqs. (30) and (41)] with the minor difference that $\nu_2 = [B_e/(\mu_m + \phi - E - Fd)]^{1/2}$ in their Eq. (28) is replaced by $[B_e/(\mu_m + \phi - E)]^{1/2}$.

In order to gain some insight into the dependence of j on ω, we first consider the limiting case in which the external field as well as the metal-adatom interaction is very weak. In this case $H_L \simeq H^{ma} \simeq H_m + H_a$, with $H_m \Psi_m = \epsilon_m \Psi_m$ and $H_a \Psi_a = \epsilon_a \Psi_a$, where H_m is the Hamiltonian of the metal and H_a describes a free adsorbate atom. Equation (4) yields

$$j(\omega) = \frac{2f(\omega)}{\hbar}\, \mathrm{Im}\Big[\sum_{fm} |\langle f | \tau | m \rangle|^2\, G^{L}_{mm}(\omega - i\delta)\ \delta(\omega - \epsilon_f)$$

$$+ \sum_{fa} |\langle f | \tau | a \rangle|^2\, G^{L}_{aa}(\omega - i\delta)\Big]\, \delta(\omega - \epsilon_f)$$

$$= \frac{2\pi f(\omega)}{\hbar}\Big[\sum_{fm} |\langle f | \tau | m \rangle|^2\ \delta(\epsilon_f - \epsilon_m)\delta(\epsilon_f - \omega)$$

$$+ \sum_{fa} |\langle f | \tau | a \rangle|^2\, \delta(\epsilon_f - \epsilon_a)\delta(\epsilon_f - \omega)\Big]\ . \tag{5}$$

The first term in the brackets represents the current $j_0(\omega)$ in the absence of the adsorbate. There is typically very little structure in $j_0(\omega)$, and the ω dependence is dominated by the exponential $\exp[-(2m/\hbar^2)^{1/2}(4/3eF)(-\omega)^{3/2}]$. The second term represents tunneling from the adsorbate level; electrons can tunnel from the adsorbate to the vacuum only if they have energy $\omega = \epsilon_a$. In the presence of the metal-adatom interactions the atomic level will be broadened, and G^L will acquire off-diagonal matrix elements G^L_{ma}, G^L_{am} which represent a mixing of metal and adsorbate states.

The expression (4) for $j(\omega)$ is quite general. We next assume that the metal-adatom complex is described by the many-body Anderson Hamiltonian

$$H^{ma} = \sum_{m\sigma} \epsilon_m n_{m\sigma} + \epsilon_a \sum_{\sigma} n_{a\sigma} + U n_{a\uparrow} n_{a\downarrow}$$

$$+ \sum_{m\sigma} (V_{am} a^{\dagger}_{m\sigma} d_{\sigma} + V^{*}_{am} d^{\dagger}_{\sigma} a_{m\sigma})\ . \tag{6}$$

The first term represents the metal, the second and third terms represent the adsorbate, and the last term describes electron hopping between the metal and the adsorbate. This Hamiltonian ignores Coulomb interactions between adsorbate electrons and metal electrons as well as quantities like $V_{mm'}$. The former can be taken into account in a rough way in terms of image potentials modified by finite screening lengths, $V_{\mathrm{image}} \simeq e^2/4(d+\lambda)$, and thus renormalizing U and ϵ_a. Equation (6) assumes a single adsorbate level with wave function ϕ_a and energy ϵ_a. However, this level should not be thought of as the free-adsorbate level. The metal will interact with the higher-energy adsorbate states as well as the lowest one, and this may be taken into account by considering ϕ_a to be a "hybrid orbital," i.e., a linear combination of atomic states. Formally, the metal-induced interaction between the lowest unperturbed adsorbate state and the higher ones can be removed by a canonical transformation.

It is also easy to generalize the present theory to include several levels explicitly. This generalization is required to understand some of the details of the experimental data of Plummer and Young[7] (PY).

The Hamiltonian of the left system is given by (2) after substitution of (6). Thus, the "left-system" Hamiltonian is identical to H^{ma} of (6) but with ϵ_a replaced by $\epsilon_a + \Delta\epsilon_a = \epsilon_a - eFx_a$.

By choosing the set of states $\{|i\rangle\} = \{|m\rangle, |a\rangle\}$, Eq. (4) takes the form

$$j(\omega) = [2f(\omega)/\hbar]\, \mathrm{Im} \sum_{f} \delta(\omega - \epsilon_f)\Big[\, |\langle f | \tau | a \rangle|^2\, G^{L}_{aa}$$

$$+ \sum_{m} (\langle f | \tau | a \rangle\, G^{L}_{am}\, \langle m | V^{>}_{f} | f \rangle$$

$$+ \langle f | V^{>}_{f} | m \rangle\, G^{L}_{ma}\, \langle a | \tau | f \rangle)$$

$$+\sum_{mm'} \langle f|\, V_f^{>}|\, m\rangle G^L_{mm'} \langle m'|\, V_f^{>}|\, f\rangle] . \quad (7)$$

It is straighforward to show that

$$G^L_{mm'} = \delta_{mm'}\, g_m + g_m V_{ma} G_{aa} V_{am'} g_{m'} , \quad (8a)$$

$$G^L_{ma} = g_m V_{ma} G_{aa} , \quad (8b)$$

$$G^L_{am} = G_{aa} V_{am} g_m , \quad (8c)$$

where

$$g_m = (\omega - \epsilon_m)^{-1} , \quad (8d)$$

$$G^L_{aa} \equiv (\omega - \epsilon_a - \Sigma)^{-1} \equiv G^R_{aa} + iG^I_{aa} , \quad (8e)$$

where G^R_{aa} is the real part of G_{aa} and should not be confused with G^R, the Green's function of the "right system." Making use of (8) in (7):

$$j(\omega) = j_0(\omega) + [2f(\omega)/\hbar]\,\mathrm{Im}\sum_f \delta(\omega - \epsilon_f)\,[(\langle f|\,\tau\,|\,a\rangle$$

$$+\sum_m \langle f|\, V_f^{>}|\, m\rangle g_m V_{ma}) G_{aa} (\langle a|\,\tau\,|f\rangle$$

$$+\sum_m \; V_{am} g_m \langle m|\, V_f^{>}|f\rangle)] , \quad (9a)$$

where

$$j_0(\omega) = [2\pi f(\omega)/\hbar] \sum_{mf} \delta(\omega - \epsilon_f) \delta(\omega - \epsilon_m) \;|\,\langle f|\, V_f^{>}|\, m\rangle|^2 . \quad (9b)$$

Equation (9) may be written in a more transparent form by introducing the operators T and $\tilde{T}$,

$$T = \tau + \tau g V , \quad \tilde{T} = \tau + V g \tau , \quad (10)$$

where g is the metal Green's function and V is the potential appearing in the matrix element V_{am}. We find

$$j(\omega) = j_0(\omega) + [2f(\omega)/\hbar]$$

$$\times\ \mathrm{Im}\sum\nolimits_f \delta(\omega - \epsilon_f)\,(\langle f|\, T|\, a\rangle G_{aa} \langle a|\, \tilde{T}|f\rangle). \quad (11)$$

An examination of (9) reveals that $\langle f|\tau|a\rangle$ is real; also $\sum_m \langle f|\, V_f^{>}|\, m\rangle g_m V_{ma}$ is real for $\epsilon_f < 0$ (see Appendix D). Hence, $\langle a|\tilde{T}|f\rangle = \langle f|\, T|\, a\rangle$ and (11) becomes

$$j(\omega) = j_0(\omega) + [2f(\omega)/\hbar] \sum\nolimits_f \delta(\omega - \epsilon_f)\, \mathrm{Im}(G_{aa} \langle f|\, T|\, a\rangle^2), \quad (12a)$$

where

$$\langle f|\, T|\, a\rangle = \langle f|\,\tau\,|\, a\rangle + \sigma_f , \quad (12b)$$

$$\sigma_f = \sigma^R_f + i\sigma^I_f = \sum\nolimits_m \langle f|\, V_f^{>}|\, m\rangle V_{ma} (\omega - \epsilon_m)^{-1}$$

$$+ i\pi \sum\nolimits_m \langle f|\, V_f^{>}|\, m\rangle V_{ma}\, \delta(\omega - \epsilon_m) , \quad (12c)$$

and

$$\langle f|\,\tau\,|\, a\rangle = \langle f|\, V_f^{>} - \Delta\epsilon_a|\, a\rangle . \quad (12d)$$

Taking the imaginary part indicated in (12a) yields

$$j(\omega) = j_0(\omega) + [2f(\omega)/\hbar]$$

$$\times \sum\nolimits_f \delta(\omega - \epsilon_f)\,[(x^2 - y^2)\, G^I_{aa} + 2xyG^R_{aa}] , \quad (13a)$$

where

$$x = \langle f|\,\tau\,|\, a\rangle + \sigma^R_f , \quad (13b)$$

$$y = \sigma^I_f . \quad (13c)$$

The expression (13) for $j(\omega)$ treats the Hamiltonian of (6) exactly.

The term $j_0(\omega)$ in (13) represents the current in the absence of the adatom. The term proportional to $\langle f|\tau|a\rangle^2 G^I_{aa}$ represents the tunneling of an electron from the adsorbate to the vacuum, as moderated by the density of adsorbate state G^I_{aa}. The remaining terms in (13) arise because the effective transfer operator is T of Eq. (10) rather than τ. The $\tau g V$ part of T represents the hopping of an electron from the adsorbate to the metal via V; it propagates in the metal and then tunnels to the vacuum under the influence of V_f.

The matrix element $\langle f|\, V_f^{>}|\, m\rangle$ of (12c) can be written in a more convenient form by noting

$$V_f^{>} = \theta(x) V_f = (T + V_f)\theta(x) - \theta(x) T + [\theta(x), T]$$

$$= H_f \theta(x) - \theta(x) H_m + [\theta(x), T] . \quad (14a)$$

Thus,

$$\langle f|\, V_f^{>}|\, m\rangle = (\epsilon_f - \epsilon_m)\, \langle f|\,\theta(x)|\, m\rangle + \langle f|\, J|\, m\rangle , \quad (14b)$$

$$\langle f|\, J\,|\, m\rangle = \langle f|\, [\theta(x), T]|\, m\rangle$$

$$= \left(\frac{\hbar^2}{2m}\right) \int d^2S \left(\phi_f \frac{\partial\phi_m}{\partial x} - \phi_m \frac{\partial\phi_f}{\partial x}\right)_{x=0} , \quad (14c)$$

where the integration $\int d^2S$ is over the metal surface. Use of (14b) and (12c) yields

$$\sigma^R_f = \langle f|\,\theta(x) V|\, a\rangle + \sum\nolimits_m \langle f|\, J\,|\, m\rangle V_{ma} (\omega - \epsilon_m)^{-1} , \quad (15a)$$

$$\sigma^I_f = \pi \sum\nolimits_m \langle f|\, J|\, m\rangle V_{ma}\, \delta(\omega - \epsilon_m) , \quad (15b)$$

where V in (15a) is the potential appearing in the matrix element V_{ma} and we have used the fact that $\omega = \epsilon_f$, as dictated by (12a).

III. EVALUATION OF TUNNELING CURRENT

The Anderson model uses the set of states $\{|m\rangle, \; |a\rangle\}$ as a basis set and thus describes the metal-adsorbate eigenstates $\{|i\rangle\}$ by a linear combination of $\{|m\rangle\}$ and $|a\rangle$. The set $\{|m\rangle, \; |a\rangle\}$ is, however, overcomplete since the set of states $\{|m\rangle\}$ is complete. It can be shown[8] that because the Anderson model ignores this overcompleteness it gives an incorrect asymptotic dependence of the metal-adsorbate eigenstates. To compensate for this, we always give the states $|a\rangle$ inside matrix elements of the form $\langle f|\tau|a\rangle$ the asymptotic dependence on position which obtains for ϵ_a equal to ϵ_f; this better represents the exact eigenstates $\{|i\rangle\}$ inside the tunneling barrier.

We next evaluate $\langle f|\tau|a\rangle$ and $\langle f|J|m\rangle$. The primary contribution to these matrix elements comes from a region of space in which $|f\rangle$ may be replaced by the asymptotic form

$$\Psi_f(\vec{r}) \equiv s(\vec{r}, \epsilon_{\perp f}) e^{-\lambda_{\perp f}}$$

$$= \exp\{-\lambda_{\perp f} + \xi(\epsilon_{\perp f})\, x - [\tfrac{1}{4}\alpha x^2/\xi(\epsilon_{\perp f})] + i\vec{k}_{\parallel f}\cdot\vec{\rho}\}\,, \tag{16a}$$

$$\epsilon_f = \epsilon_{\perp f} + (\hbar^2/2m)\, k_{\parallel f}{}^2\,, \tag{16b}$$

$$\lambda_{\perp f} = (2/3\alpha)\xi(\epsilon_{\perp f})^3\,, \tag{16c}$$

$$\xi(\epsilon_{\perp f}) = (-2m\epsilon_{\perp f}/\hbar^2)^{1/2}\,, \tag{16d}$$

$$\alpha = 2meF/\hbar^2\,. \tag{16e}$$

Making use of (14c) and (16) gives

$$\langle f|J|m\rangle = \Gamma_m(\epsilon_f)\, e^{-\lambda_{\perp f}}\,, \tag{17a}$$

$$\Gamma_m(\epsilon_f) = \left(\frac{\hbar^2}{2m}\right) \int d^2S \left(\frac{\partial\phi_m}{\partial x} - \xi(\epsilon_f)\phi_m\right)_{x=0}\,. \tag{17b}$$

In deriving (17a) we have replaced $\epsilon_{\perp f}$ by ϵ_f in all terms of (16) except $e^{-\lambda_{\perp f}}$. This replacement is justified because the summation $\sum_f$ in (13) is dominated by $e^{-\lambda_{\perp f}}$, which has its maximum at $\epsilon_{\perp f} = \epsilon_f$. Use of (17) in (15) gives

$$\sigma_f^R = [\gamma(\epsilon_f) + b^R(\epsilon_f)]\, e^{-\lambda_{\perp f}}\,, \tag{18a}$$

$$\sigma_f^I = b^I(\epsilon_f)\, e^{-\lambda_{\perp f}}\,, \tag{18b}$$

$$\gamma(\epsilon_f) = \langle a|\theta(x)V|s(\epsilon_f)\rangle\,, \tag{18c}$$

$$b^R(\epsilon_f) = \sum_m \Gamma_m(\epsilon_f) V_{ma}/(\omega - \epsilon_m)\,, \tag{18d}$$

$$b^I(\epsilon_f) = \pi \sum_m \Gamma_m(\epsilon_f) V_{ma}\, \delta(\omega - \epsilon_m)\,, \tag{18e}$$

where s in (18c) is defined by (16a). The matrix element $\langle f|\tau|a\rangle$ of (12d) is given by

$$\langle f|\tau|a\rangle = \Delta(\epsilon_f)\, e^{-\lambda_{\perp f}}\,, \tag{19a}$$

$$\Delta(\epsilon_f) = \langle a|\tau|s(\epsilon_f)\rangle\,. \tag{19b}$$

It has been assumed that $|a\rangle$ has zero angular momentum about an axis normal to the metal; if this were not the case the matrix element $\langle a|\tau|f\rangle$ would be very small.

As already noted, the first term in (13), $j_0(\omega)$, is the current in the absence of the adsorbate. Equations (9b), (14b), and (17) give

$$j_0(\omega) = [2f(\omega)/\hbar]\, c(\omega) \sum_f \delta(\omega - \epsilon_f)\, e^{-2\lambda_{\perp f}}\,, \tag{20a}$$

where $\lambda_{\perp f}$ is defined in (16c) and

$$c(\omega) = \pi \sum_m \delta(\omega - \epsilon_m)\, \Gamma_m(\omega)^2\,. \tag{20b}$$

This expression for $j_0(\omega)$ is evaluated in Appendix C, assuming that the metal potential is the square well shown in Fig. 1. The resulting expression is identical to that which would be obtained by combining the supply function with the Fowler-Nordheim expression[9] for the barrier-penetration coefficient in the WKB approximation limit. It is thus essentially identical with an expression previously derived by Young.[10] Use of (18)–(20) in (13) gives the final result

$$j(\omega)/j_0(\omega) = 1 + (u^2 - v^2) G_{aa}^I + 2uv G_{aa}^R\,, \tag{21a}$$

$$u = [\Delta(\omega) + \gamma(\omega) + \sum_m \Gamma_m(\omega) V_{ma} (\omega - \epsilon_m)^{-1}]/c(\omega)^{1/2}\,, \tag{21b}$$

$$v = \pi \sum_m \Gamma_m(\omega) V_{ma}\, \delta(\omega - \epsilon_m)/c(\omega)^{1/2}\,. \tag{21c}$$

By definition, $V_{ma} = \langle m|H_L^{(1)}|a\rangle$, where $H_L^{(1)}$ is the one-particle part of the "left-system" Hamiltonian. Thus, in (21b), $\Delta + \gamma = \langle a|\tau + \theta(x)V|s\rangle = \langle a|\theta(x)H^{(1)}|s\rangle$, where $H^{(1)}$ is the one-electron part of the total Hamiltonian for the metal, adsorbate, and electric field. We remark that the summations $\sum_m$ in (20b) and (21b) do not include a summation over $\vec{k}_{\parallel m}$, the momentum parallel to the surface which is zero by (17b).

The interpretation of (21) is the same as that of (13). The term $(\Delta^2/c)G_{aa}^I$ is associated with the direct tunneling of adsorbate electrons, and the other terms arise from the more complicated processes previously mentioned.

In Appendix D we estimate the magnitudes of $\Delta(\omega)$, $\gamma(\omega)$, $\sum_m \Gamma_m(\omega) V_{ma} (\omega - \epsilon_m - i\delta)^{-1}$ of (21). We find

$$\Delta(\omega) \approx 4\pi(-\omega)\alpha^{-1/2}(1 - \gamma_a + g)(1 + \tfrac{1}{3}\gamma_a^2)^{-1/2} e^{\xi(\omega)x_a}\,, \tag{D2a}$$

where α, ξ are defined in (16) and $g = \pi^{-1/2}\alpha^{1/2}\xi^{-3/2}$. γ_a is a measure of the polarization of the adsorbate by the metal; γ_a satisfies $0 < \gamma_a < 1$ and large polarization corresponds to large γ_a. We also find from (D2a) and (D4) that

$$\gamma(\omega) \approx [\pi^{-1/2}\xi(\omega)^{3/2}\alpha^{-1/2}]\,\Delta(\omega)\,. \tag{22}$$

Also, (D7) and (D8) give

$$\sum_m \Gamma_m(\omega) V_{ma}/(\omega - \epsilon_m) = (\Sigma_I \rho_V W_m/\pi)^{1/2} (W_m + 2\omega)/[2W_m(W_m + \omega)]^{1/2}\,, \tag{23a}$$

$$\pi \sum_m \Gamma_m(\omega) V_{ma}\, \delta(\omega - \epsilon_m) = -(-2\omega\Sigma_I \rho_V/\pi)^{1/2}\,, \tag{23b}$$

where Σ_I is the broadening of the adsorbate resonance as determined from experiment and ρ_V is metal volume per atom. We estimate a minimum value of $|u/v|$ of (21a) from (D2a), (22), and (23) by the choices $x_a = 2$ Å, $\gamma_a = 0.8$, $eF = 0.2$ eV Å^{-1}, $W_m = 10$ eV, $\Sigma_I = 4$ eV. The energies of greatest interest are 0–3 eV below the Fermi energy so we choose $\omega = -5$ eV (the choice $\omega = -8$ eV would not make a substantial difference). For the values of the parameters given above $\Delta(\omega)$, $\gamma(\omega) \gg \sum_m \Gamma_m(\omega)(\omega - \epsilon_m - i\delta)^{-1}$ and $|u/v| \simeq 10^2$. The result is due to the fact that the tunneling processes represented by u and v, respectively, are such that the barrier width in u is smaller than that in v. v represents the energy-conserving process "adsorbate-metal vacuum" while u represents the tunneling of an electron directly from the adsorbate to the vacuum as well as the process "adsorbate-metal vacuum" where the energy of the electron in the metal can be different from its energy in the adsorbate or in the vacuum.

For $u \gg v$, Eq. (21a) becomes

$$[j(\omega) - j_0(\omega)]/j_0(\omega) \equiv \Delta j(\omega)/j_0(\omega) = u^2 G^I_{aa}\,, \tag{24a}$$

$$u^2 = \lambda\, e^{2\xi(\omega)x_a}\,, \tag{24b}$$

$$\lambda = 4\pi\rho_a(\xi^3/\alpha)\, W_m[\omega/(\omega + W_m)]^{1/2} \times (1 - \gamma_a + g)^2[1 + (\pi g)^{-1}]\,, \tag{24c}$$

where $\rho_a = \pi a^2/S$, a is the adsorbate radius, and S is the surface area seen in the experiment. (24b) and (24c) result from (21b), (D2a), (22), and (C2). (22a) is valid if $G^I_{aa} \gg 10^{-2} G^R_{aa}$, which is certainly the case if the adsorbate resonance lies within the metal conduction band.

(24a) is a remarkably simple result; it shows that TED essentially measures the density of states near the adsorbate as determined by G^I_{aa}. We stress that the result $\Delta j/j_0 = u^2 G^I_{aa}$ obtains if $u \gg v$. v does not involve $\langle f|\tau|a\rangle$ and is thus not affected by the ansatz of correcting the asymptotic behavior of $|a\rangle$ discussed in the beginning of this section. This gives additional confidence in the result $u \gg v$ obtained above. The consistency of the result $u \gg v$ may be checked by obtaining a value for u from the Plummer-Young experiment[7] of Ba adsorbed on W. At the adsorbate resonance ϵ_r, $G^R_{aa}(\epsilon_r) = 0$ and $G^I_{aa}(\epsilon_r) = 1/\Sigma_I(\epsilon_r)$. From (21a), $u^2 - v^2 = \Sigma_I(\epsilon_r)\Delta j(\epsilon_r)/j_0(\epsilon_r)$. $\Sigma_I(\epsilon_r)$ is estimated from the broadening of the peak in $j(\omega)$ to be $\Sigma_I \sim 1$ eV and $\Delta j(\epsilon_r)/j_0(\epsilon_r) \sim 1 - 4$, depending on the experimental conditions. Thus, $u^2 - v^2 \simeq 1 - 4$. v^2 obtained from (21c), (D7c), and (C2) is

$$v^2 \approx (1/2\pi^2)\rho_a W_m(\omega + W_m)^{-1/2}(-\omega)^{-1/2}\textstyle\sum_I \xi^3\rho_V \tag{25}$$

for the square-well approximation. PY estimate ρ_a to be at most 10^{-3}; thus (25) gives $v^2 < 1.5 \times 10^{-3}$ and $u^2 \gg v^2$.

Finally, we estimate u^2 from the theoretical expressions (24b) and (24c). Again, we use $-\omega = 5$ eV, $W_m = 10$ eV, $eF = 0.2$ eV Å^{-1}, $\gamma_a = 0.8$. PY estimate $10^{-3} < \rho_a < 10^{-4}$. We estimate 2 Å $< x_a <$ 3 Å. These values of the parameters give $50 < u^2 < 5 \times 10^3$. At the adsorbate resonance, $G^I_{aa}(\epsilon_r) = 1/\Sigma_I(\epsilon_r) \sim 1$ eV as stated above, and thus (24a) yields $50 < \Delta j(\epsilon_r)/j_0(\epsilon_r) < 5 \times 10^3$. The experimental result is $\Delta j(\epsilon_r)/j_0(\epsilon_r) \simeq 1 - 4$, depending on the experimental conditions. The high calculated value is largely due to omission of the image potential in our work.

We can allow for an image potential V_{im} in our calculation by including it in the metal potential, H_m. Repeating the calculation of Sec. II gives the current $j'(\omega)$ as

$$j'(\omega) = j_0'(\omega) + [2f(\omega)/\hbar] \times \textstyle\sum_f \delta(\omega - \epsilon_f)[(x'^2 - y'^2)G^I_{aa} + 2x'y'G^R_{aa}]\,, \tag{26a}$$

$$x' = \langle f|\tau + \theta(x)V|a\rangle + \sum_{m'}\langle f|J + V_{im}|m'\rangle V_{m'a}(\omega - \epsilon_{m'})^{-1}\,, \tag{26b}$$

$$y' = \textstyle\sum_{m'}\langle f|J + V_{im}|m'\rangle V_{m'a}\,\delta(\omega - \epsilon_{m'})\,, \tag{26c}$$

$$j_0'(\omega) = [2\pi f(\omega)/\hbar]\textstyle\sum_{m'f}\delta(\omega - \epsilon_f)\delta(\omega - \epsilon_{m'}) \times |\langle f|J + V_{im}|m'\rangle|^2\,, \tag{26d}$$

where it is understood that $|m'\rangle$ is an eigenfunction of the metal Hamiltonian with V_{im} included. WKB calculations indicate that for the parameters relevant to the PY experiment $j_0'(\epsilon_r)$ is larger than the metal current without image correction $j_0(\omega)$ by a factor $\sim 5 \times 10^2$. A similar analysis to that carried out in Appendix D yields the result $x' \gg y'$ and $x' \simeq \langle f|\tau + \theta(x)V|a\rangle$ for values of the parameters typical in field emission. Equations (26) give

$$j'(\omega) \simeq j_0'(\omega) + [2f(\omega)/\hbar] \times \textstyle\sum_f \delta(\omega - \epsilon_f)\,\langle f|\tau + \theta(x)V|a\rangle^2 G^I_{aa}\,. \tag{27}$$

The enhancement due to the adsorbate is given by the second term on the right-hand side of (27) and is not changed by the inclusion of the image potential, except to the extent that $|a\rangle$ is modified via the interaction of the excited adsorbate states with the metal. This effect is very small compared to the effect of the image potential on the metal tunneling as given by j_0'. Nordheim[11] and Burgess[12] have determined $j_0'(\omega)/j_0(\omega)$ to exponential accuracy:

$$j_0'(\omega)/j_0(\omega) = \exp\{[4\xi(\omega)^3/3\alpha][1 - v(y)]\}\,, \tag{28a}$$

$$y = (e^3F)^{1/2}/(-\omega)\,, \tag{28b}$$

and $v(y)$ is defined in Ref. 11. Values for it are given in Table I. These considerations show that

TABLE I. Functions $v(y)$, $t(y)$ appearing in Eqs. (28)–(30) of the text.

y	$v(y)$	$t(y)$
0	1.000	1.000
0.1	0.982	1.004
0.2	0.937	1.011
0.3	0.872	1.021
0.4	0.789	1.032
0.5	0.690	1.044
0.6	0.577	1.057
0.7	0.450	1.070
0.8	0.312	1.083
0.9	0.161	1.097
1.0	0	1.111

image-potential corrections change Eq. (24) to

$$[j'(\omega)-j_0'(\omega)]/j_0'(\omega)\equiv \Delta j'(\omega)/j_0'(\omega)=u'^2G^I_{aa}\ , \tag{29a}$$

$$u'^2=\lambda\exp\{2\xi(\omega)x_a+[4\xi(\omega)^3/3\alpha][v(y)-1]\}\ , \tag{29b}$$

where we have assumed that λ is still given by (24c); this should be correct to ~ 10% accuracy. Use of Eqs. (29) changes our previous estimate of $\Delta j/j$ for the PY experiment from $50<\Delta j(\epsilon_r)/j_0(\epsilon_r)<5\times10^3$ to $10^{-1}<\Delta j'(\epsilon_r)/j_0'(\epsilon_r)<10$; the experimental value is $\Delta j(\epsilon_r)/j_0(\epsilon_r)\sim 1-4$. Thus we have achieved quite reasonable agreement with experiment, granted the uncertainties in the parameters entering our theory.

The overcompleteness of the basis states in the Anderson model will introduce pseudopotentials[13] which may affect $j(\omega)$. Thus λ in (29b) or (24c) should be regarded as a parameter.

In the case in which the adsorbate resonance is below the metal conduction band, $G^I_{aa}(\omega)\sim 0$ for $-\omega\sim\phi$ and $\Delta j/j_0\simeq 2uvG^R_{aa}$, where now $G^R_{aa}\sim(\omega-\epsilon_r)^{-1}$. Also, $uv<0$ so $\Delta j/j_0<0$, in agreement with DA. However, our theory should be most reliable when ϵ_r lies near energies observable in TED, i.e., 0–3 eV below the Fermi level.

The experimental $j(\omega)$ will give $G^I_{aa}(\omega)$; in Appendix E we discuss the form of $G^I_{aa}(\omega)$ as determined by the Anderson Hamiltonian (6). We conclude that $G^I_{aa}(\omega)$ will often be well represented by a Lorentzian near the adsorbate resonance ϵ_r.

Although the enhancement factor $j(\omega)/j_0(\omega)$ will have an energy dependence determined primarily by G^I_{aa}, there is some additional energy dependence from the factor $\exp\{2\xi(\omega)x_a+[4\xi(\omega)^3/3\alpha][v(y)-1]\}$ which multiplies G^I_{aa}, Eq. (29b). For energies near the resonant energy ϵ_r (which is the case of interest in field emission) one has

$$\exp[2\xi x_a+(4\xi^3/3\alpha)(v-1)]\sim A\exp[B(|\omega|-|\epsilon_r|)]\ , \tag{30a}$$

$$A=\exp\{2\xi(\epsilon_r)x_a+[4\xi^3(\epsilon_r)/3\alpha][v(e^{3/2}F^{1/2}/|\epsilon_r|)-1]\}\ , \tag{30b}$$

$$B=(2m/\hbar^2)^{1/2}\{(x_a/|\epsilon_r|^{1/2}) + (2\phi^{1/2}/eF)[t(e^{3/2}F^{1/2}/|\epsilon_r|)-1]\}\ , \tag{30c}$$

where t is given in Table I. In the absence of image-potential corrections, $v=1$ and $t=1$ in (30). Assuming G^I_{aa} is represented by a Lorentzian (E3a) gives

$$G^I_{aa}\exp[2\xi x_a+(4\xi^3/3\alpha)(v-1)] \simeq\frac{(A/\Gamma^2)}{\bar\epsilon^2+1}\exp(B\Gamma\bar\epsilon)\ , \tag{31a}$$

$$\bar\epsilon=(|\omega|-|\epsilon_r|)/\Gamma\ . \tag{31b}$$

For values of Γ, x_a, ϵ_r, and eF equal to 1 eV, 2.5 Å, − 5 eV, and 0.2 eV Å^{-1}, respectively, $B\Gamma\approx 0.9$. A plot of $(\bar\epsilon^2+1)^{-1}e^{B\Gamma\bar\epsilon}$ is shown in Fig. 3. For $B\Gamma=0.6$ and 0.9, the peaks are shifted by 0.33Γ and 0.62Γ below the actual resonance, and the curves are not Lorentzian in shape. Thus $G^I_{aa}(\omega)$ must be "unfolded" from the experimental curves.

APPENDIX A

We derive the independent-electron version of (3). H_L has the form

$$H_L=T+V_{ma}+\underline{P}_a\,\Delta\epsilon_a\underline{P}_a\ , \tag{A1}$$

as stated in Sec. II; its eigenfunctions and eigenvalues are denoted by Ψ_L and E_L, respectively. H_R is given by

$$H_R=T-efx\equiv T+V_f\ , \tag{A2}$$

with eigenfunctions and eigenvalues Ψ_R and E_R. The Hamiltonian for the metal-adsorbate complex in the presence of the external field is

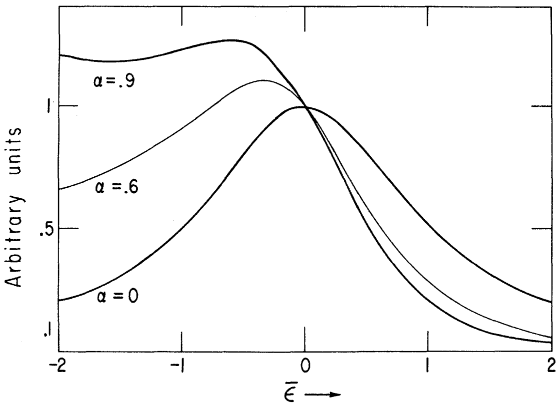

FIG. 3. Plots of $j'(\omega)/j_0'(\omega)$ as given by Eq. (31) for the cases $\alpha\equiv B\Gamma=0$, 0.6, 0.9.

$$H = T + V_{ma} + V_f^{>} \ . \qquad \text{(A3)}$$

Prior to turning on the field V_f, at time $t = 0$ electrons are governed by H_L. Application of V_f induces an electron in state Ψ_L to tunnel to a state described approximately by a wave function Ψ_R. The wave function of an electron is thus assumed to be

$$\Psi = a(t)\,\Psi_L e^{-iE_L t/\hbar} + b(t)\,\Psi_R e^{-iE_R t/\hbar} \ , \qquad \text{(A4)}$$

where

$$a(0) = 1, \quad b(0) = 0 \ . \qquad \text{(A5)}$$

Using $H\Psi = i\hbar(\partial\Psi/\partial t)$ with (A4), and recognizing that for small $t, a(t) \simeq 1$, $\dot{a}(t) \simeq 0$, $b(t) \simeq 0$, we find

$$\frac{d}{dt} b(t) = \left(\frac{1}{i\hbar}\right) \langle \Psi_R | H - E_L | \Psi_L \rangle \ . \qquad \text{(A6)}$$

The matrix element in (A6) is small due to the small overlap of Ψ_R with Ψ_L. Thus the usual methods of second-order perturbation theory yield

$$P_{LR} = (2\pi/\hbar) |\langle \Psi_R | H - E_L | \Psi_L \rangle|^2 \delta(E_L - E_R) \qquad \text{(A7)}$$

as the probability per unit time for tunneling. The current density at energy ω is obtained by summing (A7) over all states such that the final states have energy ω. One finds

$$j(\omega) = (2\pi/\hbar) \sum_{LR} |\langle R | H - E_L | L \rangle|^2 \times \delta(E_L - E_R)\delta(\omega - E_R) f(E_L) \ , \qquad \text{(A8)}$$

where the Fermi function ensures that the initial state is occupied. Equations (A1) and (A3) yield

$$H - E_L = H_L - E_L + H - H_L = H_L - E_L + V_f^{>} - \underline{\mathrm{P}}_a \Delta\epsilon_a \underline{\mathrm{P}}_a \ . \qquad \text{(A9)}$$

Use of (A9) in (A8) gives

$$j(\omega) = [2\pi f(\omega)/\hbar] \sum_{LR} |\langle R | \tau | L \rangle|^2 \delta(E_L - E_R)\delta(\omega - E_R) \ , \qquad \text{(A10a)}$$

$$\tau = H - H_L = V_f^{>} - \underline{\mathrm{P}}_a \Delta\epsilon \underline{\mathrm{P}}_a \ . \qquad \text{(A10b)}$$

Equation (A10) may be written as

$$j(\omega) = \frac{2\pi f(\omega)}{\hbar} \sum_{LR} |\langle R | \tau | L \rangle|^2 \times \frac{1}{\pi} \operatorname{Im} \langle L | G^L(\omega - i\delta) | L \rangle \times \frac{1}{\pi} \operatorname{Im} \langle R | G^R(\omega - i\delta) | R \rangle \ , \qquad \text{(A11)}$$

where G^L, G^R are the one-electron Green's functions

$$G^L = (\omega - H_L)^{-1} \ , \quad G^R = (\omega - H_R)^{-1} \ . \qquad \text{(A12)}$$

Introducing the complete sets of states $|i\rangle$, $|j\rangle$ for the left and right systems, respectively, we have

$$\begin{aligned} j(\omega) &= [2f(\omega)/\pi\hbar]\, T_R(\mathrm{Im}G^L \,\tau\, \mathrm{Im}G^R \,\tau) \\ &= [2f(\omega)/\pi\hbar] \sum_{ii'jj'} \langle i' | \mathrm{Im}G^L | i \rangle \langle i | \tau | j \rangle \times \langle j | \mathrm{Im}G^R | j' \rangle \langle j' | \tau | i' \rangle \ , \end{aligned} \qquad \text{(A13)}$$

which is identical in form to (3).

APPENDIX B

We calculate here the tunneling current by means of the transfer Hamiltonian technique for a model in which the metal is represented by a square well and the adsorbate is represented by an attractive δ-function potential. This is model 1 studied by DA.

The prescription for defining H_L, H_R in Sec. II gives

$$H_L = T + V_m + V_a^{(1)} + \underline{\mathrm{P}}_a V_f(x_a) \underline{\mathrm{P}}_a \ , \qquad \text{(B1a)}$$

$$H_R = T + V_f(x) \ , \qquad \text{(B1b)}$$

where $V_a^{(1)} = \lambda\delta(x - x_a)$ is the adsorbate potential given by DA [Eq. (4)]. The current density is calculated from (A10):

$$j(\omega) = [2\pi f(\omega)/\hbar] \sum_{if} |\langle f | \tau | i \rangle|^2 \delta(\omega - \epsilon_f)\delta(\epsilon_i - \epsilon_f) \ , \qquad \text{(B2a)}$$

$$\tau = V_f^{>} - \underline{\mathrm{P}}_a \Delta\epsilon_a \underline{\mathrm{P}}_a = V_f^{>} - \underline{\mathrm{P}}_a V_f(x_a) \underline{\mathrm{P}}_a \ , \qquad \text{(B2b)}$$

where $|f\rangle$ is an eigenfunction of H_R, i.e., an Airy function, and where $|i\rangle$ is an eigenfunction of H_L. Following the procedure that led to (14) we write

$$\begin{aligned} \langle f | \tau | i \rangle &= \langle f | \theta(x)(T + V_f) | i \rangle + \langle f | \theta(x) V_a^{(1)} | i \rangle - \langle f | \theta(x) H_L | i \rangle \ , \\ &= \langle f | J + \theta(x) V_a^{(1)} | i \rangle + (\epsilon_f - \epsilon_i) \langle f | \theta(x) | i \rangle \ , \end{aligned} \qquad \text{(B3a)}$$

where

$$\langle f | J | i \rangle = \left(\frac{\hbar^2}{2m}\right) \left(\phi_f \frac{\partial \phi_i}{\partial x} \ \phi_i \frac{\partial \phi_f}{\partial x}\right)_{x=0} \ . \qquad \text{(B3b)}$$

By (B2a), $\epsilon_f = \epsilon_i$, and the term $(\epsilon_f - \epsilon_i)\langle f | \theta(x) | i \rangle$ of (B3a) gives no contribution to $j(\omega)$. Thus

$$\langle f | \tau | i \rangle \to -\lambda\phi_f(x_a)\phi_i(x_a) + \left(\frac{\hbar^2}{2m}\right)\left(\phi_f \frac{\partial \phi_i}{\partial x} - \phi_i \frac{\partial \phi_f}{\partial x}\right)_{x=0} \ . \qquad \text{(B4)}$$

The asymptotic form of ϕ_f may be used in evaluating (B4); this is given by (16a) combined with a normalization factor $N(\omega)$ which is discussed in Appendix C immediately preceding Eq. (C3).

It is trivial to solve for $\phi_i(x)$; one obtains

$$\phi_i(x) = C e^{k_2 x} + D e^{-k_2 x} \ , \quad 0 < x < x_a \qquad \text{(B5a)}$$

$$\phi_i(x) = E e^{-k_2 x} \ , \qquad x_a < x \qquad \text{(B5b)}$$

$$C = E \gamma_0 e^{-2k_2 x_a} \ , \qquad \text{(B5c)}$$

$$D = E(1 - \gamma_0) \ , \qquad \text{(B5d)}$$

$$E = (2/L_m)^{1/2} \left\{ [1 - \gamma_0(1 - e^{-2k_2 x_a})]^2 + \gamma_1^2 [1 - \gamma_0(1 + e^{-2k_2 x_a})]^2 \right\}^{-1/2} \ , \qquad \text{(B5e)}$$

$$k_2 = (2m/\hbar^2)^{1/2}(-\epsilon_i)^{1/2} , \tag{B5f}$$

$$\gamma_0 = B_e^{1/2}/(-\epsilon_i)^{1/2}, \quad \gamma_1 = (-\epsilon_i)^{1/2}/(\phi + \mu + \epsilon_i)^{1/2} , \tag{B5g}$$

where B_e is the binding energy of the lowest state of $V_a^{(1)}$ and the metal has length L_m. Use of (B5) in (B4) yields

$$\langle f | \tau | i \rangle = -2N(\omega)(\hbar^2/2m)^{1/2}(-\omega)^{1/2} E\, e^{-2\xi^3/3\alpha} , \tag{B6}$$

where $\xi = \xi(\omega)$ is defined in (16d) and $\alpha = 2meF/\hbar^2$.

Use of (B6) in (B2a) yields an expression for $j(\omega)$ which is identical to that of DA [Eqs. (30b) and (41)] with the trivial difference that they find $\lambda_0 = B_e^{1/2}/(-\epsilon_i - Fd)^{1/2}$ rather than $B_e^{1/2}(-\epsilon_i)^{1/2}$ (our zero of energy is the vacuum level).

APPENDIX C

The expression (9b) for the current in the absence of an adsorbate, $j_0(\omega)$, is evaluated in this Appendix assuming the metal potential is a square well of depth W_m. The metal wave functions ψ_m are given by

$$\psi_m(\vec{r}) = M(\epsilon_{\perp m}) \exp[-\xi(\epsilon_{\perp m})x + i\vec{k}_{\parallel m} \cdot \vec{\rho}\,] \tag{C1a}$$

in the region $x > 0$. Here

$$M(\epsilon_{\perp m}) = 2(W_m + \epsilon_{\perp m})^{1/2}(2SL_m W_m)^{-1/2} , \tag{C1b}$$

$$\xi(\epsilon_{\perp m}) = (2m/\hbar^2)^{1/2}(-\epsilon_{\perp m})^{1/2} , \tag{C1c}$$

$$\epsilon_m = \epsilon_{\perp m} + (\hbar^2/2m)k_{\parallel m}{}^2 . \tag{C1d}$$

The region $x < 0$ is taken to be a cylinder of length L_m and surface area S. Only those states m with $\vec{k}_{\parallel m} = 0$ and $\epsilon_m = \epsilon_{\perp m}$ enter the summation in (20b). We find

$$C(\omega) = \pi[N(\omega)M(\omega)(\hbar^2/m)\xi(\omega)S]^2 \times (L_m/\pi)(m/2\hbar^2)^{1/2}(\omega + W_m)^{-1/2} . \tag{C2}$$

$N(\omega)$ is a normalization factor for the function ψ_f of (16a);

$$N(\omega) = (\omega + W_f)^{1/4}(-\omega)^{-1/4}(2L_f S)^{-1/2} .$$

This result is obtained by replacing $V_f = -eFx$ by a square well of depth W_f for large x,

$$V_f > \rightarrow -eFx\theta[W_f/eF) - x] - W_f\theta[x - (W_f/eF)] . \tag{C3}$$

The asymptotic form of the wave function corresponding to the potential (C3) is given correctly by (16). $N(\omega)$ is the normalization factor assuming the region $x > 0$ is a cylinder of surface area S and length L_f. W_f does not appear in the final expression for $j_0(\omega)$, which is unaffected by the truncation of $V_f^{>}$ as given by (C3).

After converting the summation in (20a) to an integration, the resulting integral may be evaluated by replacing $\epsilon_{\perp f}$ by ϵ_f in all nonexponential terms. This is justified by the strong dependence of $e^{-2\lambda_{\perp f}}$ on $\epsilon_{\perp f}$. We thus obtain

$$\sum_f e^{-2\lambda_{\perp f}}\delta(\omega - \epsilon_f) = (SL_f/2^3\pi^2)(m/\hbar^2)^2 eF[(\omega + W_f)(-\omega)]^{-1/2} \times \exp[-(4/3eF)(2m/\hbar^2)^{1/2}(-\omega)^{3/2}] . \tag{C4}$$

Use of (C2) and (C4) in (20a) yields

$$j_0(\omega) = Sf(\omega)eF(\omega + W_m)^{1/2}(2^{3/2}\pi^2\hbar W_m)^{-1}(m/\hbar^2)^{1/2} \times \exp[-(4/3eF)(2m/\hbar^2)^{1/2}(-\omega)^{3/2}] . \tag{C5}$$

APPENDIX D

In this Appendix we evaluate $\Delta(\omega)$, $\gamma(\omega)$, $\sum_m \Gamma_m(\omega)V_{am}(\omega - \epsilon_m - i\delta)^{-1}$, $u(\omega)$, and $v(\omega)$ of (21).

$\Delta(\omega)$ is given by (19b), where $\tau = -eF(x - x_a)$. The Airy function is defined in (16). ϕ_a appearing in (19b) represents a polarized adsorbate state with asymptotic behavior $e^{-\xi(\omega)x}$ for large x. In order to estimate $\Delta(\omega)$ we assume ϕ_a is given by the s-p hybrid

$$\phi_a(r) = N_a[1 - \gamma(x - x_a)/r]e^{-\xi(\omega)r} , \tag{D1a}$$

$$r^2 = (x - x_a)^2 + y^2 + z^2 , \tag{D1b}$$

$$N_a = \pi^{-1/2}\xi(\omega)^{3/2}(1 + \tfrac{1}{3}\gamma_a^2)^{-1/2} , \tag{D1c}$$

and γ_a is a parameter satisfying $0 \lesssim \gamma_a \lesssim 1$. γ_a must be positive if ϕ_a is to be a bonding state, and γ_a must be less than 1 if ϕ_a is to have no nodes. Making use of (D1) and (16) in (19b) we find[14]

$$\Delta(\omega) = 4\pi\omega\alpha^{-1/2}(1 - \gamma_a + g)(1 + \tfrac{1}{3}\gamma_a^2)^{-1/2}e^{\xi(\omega)x_a}, \tag{D2a}$$

where

$$g = \pi^{-1/2}\alpha^{1/2}\xi(\omega)^{-3/2} . \tag{D2b}$$

$\gamma(\omega)$, as given by (18c), is

$$\gamma(\omega) = \langle a | \theta(x)V | s \rangle = \langle a | \theta(x)H^{ma} | s \rangle \approx \omega\langle a | \theta(x) | s \rangle . \tag{D3}$$

Use of (D1), and (16) in (D3) yields

$$\gamma(\omega) \approx 4\pi^{1/2}\xi(\omega)^{3/2}\alpha^{-1}\omega(1 - \gamma_a + \tfrac{1}{2}\pi g) . \tag{D4}$$

The quantity $\sum_m \Gamma_m(\omega)V_{ma}/(\omega - \epsilon_m - i\delta)$ is evaluated by noting

$$\sum_m \frac{\Gamma_m(\omega)V_{ma}}{(\omega - \epsilon_m - i\delta)} = \left(\frac{\hbar^2}{2m}\right)\iint d^3r'\, d^2S\, \theta_a(r')V(r')\left[\left(\frac{\partial}{\partial x} - \xi(\omega)\right)\sum_m \frac{\phi_m(x')\phi_m(x)}{\omega - \epsilon_m - i\delta}\right]_{x=0} , \tag{D5}$$

where (17b) has been used and $V(r')$ is the potential appearing in V_{ma}. It is easily shown that

$$\textstyle\sum_m \varphi_m(x)\phi_m(x')/(\omega-\epsilon_m-i\delta)\equiv G(x,x')$$
$$=m(S\hbar^2\xi)^{-1}\{e^{-\xi|x-x'|}+[(\xi+ik)/(\xi-ik)]e^{-\xi(x+x')}\},\qquad x,x'>0 \tag{D6a}$$

where $\xi=\xi(\omega)$ and

$$k=[2m(W_m+\omega)/\hbar^2]^{1/2}\ . \tag{D6b}$$

Use of (D6) in (D5) yields

$$\textstyle\sum_m \Gamma_m(\omega)V_{ma}/(\omega-\epsilon_m-i\delta)$$
$$=-[N(\omega)/M(\omega)][(\xi+ik)/(\xi-ik)]V_{ma}\ ; \tag{D7a}$$

equivalently,

$$\textstyle\sum_m \Gamma_m(\omega)V_{am}/(\omega-\epsilon_m)$$
$$=(L_mS)^{1/2}V_{ma}(W_m+2\omega)/[2W_m(\omega+W_m)]^{1/2}\ , \tag{D7b}$$

$$\pi\textstyle\sum_m \Gamma_m V_{ma}\,\delta(\omega-\epsilon_m)=-(L_mS)^{1/2}V_{ma}(-2\omega)^{1/2}W_m^{-1/2}\ , \tag{D7c}$$

where $M(\omega)$ in (D7a) is given by (C1b) and it is understood that $|m\rangle$ appearing in V_{ma} [on the right-hand sides of (D7a)–(D7c)] has energy $\epsilon_m=\omega$. V_{ma} is estimated by assuming that broadening of the adsorbate level is given roughly by the Hartree-Fock expression for the broadening. That is,

$$\Sigma_I(\omega)\approx\pi V_{am}^2\rho_m(\omega)\ , \tag{D8a}$$

where the metal density $\rho_m(\omega)$ is approximately

$$\rho_m(\omega)\simeq L_mS/W_m\rho_v\ , \tag{D8b}$$

and where ρ_v is volume per atom of the metal. (D8a) is probably correct to within a factor of 2.

APPENDIX E

We discuss the form of $G_{aa}^I(\omega)$ as determined by the Anderson Hamiltonian (6). We are primarily interested in energies near the adatom resonance level in contrast to the Kondo problem, where one is concerned with energies very close to the Fermi energy.

In general,

$$G_{aa}^I(\omega)=\Sigma_I(\omega)/\{[\omega-\epsilon_d-\Sigma_R(\omega)]^2+[\Sigma_I(\omega)]^2\}\ , \tag{E1}$$

where $\epsilon_d=\epsilon_a-eFx_a$ is the adatom energy level in the presence of the external field and Σ_R, Σ_I are the real and imaginary parts of the self-energy. The resonant adatom levels ϵ_r are determined by

$$\epsilon_R-\epsilon_d-\Sigma_R(\epsilon_r)=0\ . \tag{E2}$$

This equation may have more than one solution, as will be discussed later. In the case that Σ_R, Σ_I vary slowly near a resonant energy ϵ_r, one may write

$$G_{aa}^I(\omega\sim\epsilon_R)\simeq\beta\Gamma/[(\omega-\epsilon_R)^2+\Gamma^2]\ , \tag{E3a}$$

where

$$\Gamma=\Sigma_I(\epsilon_r)\Big/\left(1-\frac{d}{d\omega}\Sigma_I(\epsilon_R)\right) \tag{E3b}$$

and

$$\beta=1\Big/\left(1-\frac{d}{d\omega}\Sigma_I(\epsilon_r)\right)\ . \tag{E3c}$$

Thus, under fairly general conditions the peak or peaks in G_{aa}^I will have Lorentzian shapes with widths Γ given by (E3b).

We now distinguish two regimes according to whether $U/\rho_m V_{am}^2$ is greater or less than one. In the case $U/\rho_m V_{am}^2\ll 1$, the adsorbate does not exhibit magnetic behavior, and the Hartree-Fock treatment of the Coulomb interaction is valid. In this case Anderson has shown

$$\Sigma_R^{\mathrm{HF}}=\tfrac{1}{2}Un_a+\textstyle\sum_m V_{am}^2/(\omega-\epsilon_m)\ , \tag{E4a}$$

$$\Sigma_I^{\mathrm{HF}}=\pi V_{am}^2\rho_m(\omega)\ , \tag{E4b}$$

where n_a is the average number of electrons on the adsorbate. In the Hartree-Fock case there will normally be one solution ϵ_r of (E2), although Newns[15] has shown that if V_{am} is large and ϵ_a lies near the center of the band, then (31) yields two solutions, both at energies far from the band center. In general, (33) indicates that Σ_R^{HF}, Σ_I^{HF} are slowly varying and $G_{aa}^I(\omega\simeq\epsilon_r)$ is well described by the Lorentzian (E3a), with $\Gamma\simeq\Gamma_0=\pi V_{am}^2\rho_m(\epsilon_r)$.

In the case $U/\rho_m V_{am}^2\gtrsim 1$ the adsorbate may exhibit magnetic behavior, i.e., have a net spin above the Kondo temperature. $G_{aa}^I(\omega)$ will then have two peaks. For example, in the limit $V_{am}\to 0$, the adsorbate is free and $G_{aa}^I(\omega)$ is the sum of two δ functions, one at energy ϵ_a and the other at energy ϵ_a+U. No rigorous theory exists in this regime, and we shall make use of an approximate theory developed by Appelbaum and Penn.[16] Their solution for $G_{aa}^I(\omega)$ takes a particularly simple form in the case that the metal conduction bands is described by a Lorentzian density of states, is half-filled, and $U=2\epsilon_d$, where the zero of energy is taken to be the Fermi level. In other words, there are two levels when V_{am} is zero, one below the Fermi energy at ϵ_d, the other above the Fermi level at ϵ_d+U, with the Fermi level midway between the two levels. They found

$$G_{aa}^I(\omega)=\Gamma_0^{-1}(\tilde{\omega}^2+9+3\tilde{\epsilon}_d^2)/[(\tilde{\omega}-3-\tilde{\epsilon}_d^2)^2+(4\tilde{\omega})^2]\ , \tag{E5a}$$

where

$$\tilde{\omega} = \omega/\Gamma_0\ , \quad \tilde{\epsilon}_d = \epsilon_d/\Gamma_0\ , \tag{E5b}$$

$$\Gamma_0 = \pi V_{am}^2 \rho_m(0)\ . \tag{E5c}$$

The approximate G_{aa}^I given by (E5) has the following properties:

(a) In the limit $V_{am} = 0$ it reproduces the correct atomic density of states:

$$G_{\text{atomic}}^I = \tfrac{1}{2}\,\delta(\omega - \epsilon_d) + \tfrac{1}{2}\,\delta(\omega + \epsilon_d)\ . \tag{E6}$$

(b) In the limit $U/\Gamma_0 \ll 1$ it reproduces the Hartree-Fock approximation to $G_{aa}^I(\omega)$ for energies ω near the resonance (which is located at $\epsilon_d = \mu = 0$).

(c) For $\tilde{\epsilon}_d = \epsilon_d/\Gamma_0 = U/2\Gamma_0 < 1.95$, the quantity G_{aa}^I exhibits one peak. If $\tilde{\epsilon}_d \ll 1$, the peak is Lorentzian and has width $\Gamma_0\,(1 + \frac{1}{3}\tilde{\epsilon}_d)$.

(d) For $U/2\Gamma_0 > 1.95$, the quantity G_{aa}^I exhibits two peaks; this is the magnetic limit. For $U/\Gamma_0 \gg 1$, the peaks are separated by an energy U, and they have Lorentzian shapes of width $2\Gamma_0$.

Thus, in the large Coulomb interaction limit as well as in the weak interaction limit, we expect a Lorentzian peak or peaks in $G_{aa}^I(\omega)$.

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Stress Effects in the Paraelectric Resonance of KCl : Li[†]

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The paraelectric resonance of KCl : Li was studied in the presence of uniaxial stress applied along the crystallographic [110] direction. The results are interpreted in terms of the simple tunneling model proposed by Gomez, Bowen, and Krumhansl and yield a coupling coefficient for coupling to T_{2g} symmetry strain of − 0.185 ± 0.03 GHz/bar.

I. INTRODUCTION

KCl, doped in the 1–100 ppm molecular range with lithium, has been extensively studied using paraelectric resonance, thermal conductivity, specific heat, electrocaloric effect, acoustic attenuation, dielectric constant, and NMR.[1]

The singly ionized lithium goes in substitutionally for a potassium, but sits off-center in a crystal-field potential characterized by minima in the eight equivalent ⟨111⟩ directions. The eight low-lying tunnel split levels of this system, having a permanent electric dipole moment of 5.6 D, couple strongly to an applied electric (both dc and microwave) field. They also couple strongly to distortions from cubic symmetry of the cubic host KCl lattice. In particular, T_{2g} components of lattice strain are the dominant ones which produce energy-level shifts within the eight-level ground-state multiplet. The nature of this coupling is predicted by a logical extension of the tunneling model of Gomez, Bowen, and Krumhansl (GBK),[2] assuming equal zero-field tunnel splittings.

The object of this work was to determine whether the GBK model is adequate to describe the stress effects and to measure the magnitude and sign of this coupling between the T_{2g} lattice strain and the tunneling levels of the ground-state multiplet. We used paraelectric resonance measurements at 4.2 and 1.9 °K and at 56 and 64 GHz in the presence of an applied uniaxial stress.

II. SAMPLE PREPARATION

KCl doped in the melt with Li was grown using