

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 $[j(\omega) - j_0(\omega)]/j_0(\omega) = \text{Im} G_{aa}(\omega) \exp[(-2m\omega/\hbar^2)^{1/2} x_a]$, where $j(\omega)$ and $j_0(\omega)$ are the current densities in energy in the presence and absence of adsorbate, respectively; ω is measured from the vacuum level; x_a is the surface-adsorbate distance; and $\pi^{-1} \text{Im} G_{aa}$ is the local density of states at the adsorbate. This result is general and independent of the explicit form of G_{aa} .

Measurement of the total-energy distribution (TED) of field-emitted electrons from adsorbate-covered surfaces can show the location and shapes of the virtual adsorbate levels and thus constitutes a powerful tool for the study of the chemisorption. Theoretical treatments have been given by Duke and Alferieff¹ (DA) and by Gadzuk,² who considered tunneling of metal electrons through an adsorbate, schematized by a potential. DA considered only one-dimensional cases; their parametrization is difficult to relate to specific systems, nor does it take correlation effects into account. Gadzuk specifically attempted to obtain information on virtual adsorbate levels. However, it is hard to see the justification for the initial-state function used in his Eq. (8) and central to his subsequent development. He uses the external field itself to mix adsorbate and metal states before tunneling occurs, and ignores the fact that the adsorbate is chemisorbed in most cases of interest and has therefore interacted strongly with the substrate prior to tunneling. It is more natural to treat the applied field as a perturbation on the system of metal plus adsorbate.

We wish to calculate the number of electrons per unit energy tunneling from the metal-adsorbate complex to the vacuum in the presence of an external electric field. The appropriate potentials are shown in Fig. 1. We use the transfer-Hamiltonian method³ first introduced by Oppenheimer.⁴ The Hamiltonian is $H = H^{ma} + \hat{V}_f$, where H^{ma} is the many-electron Hamiltonian for the metal-adsorbate complex and \hat{V}_f is defined

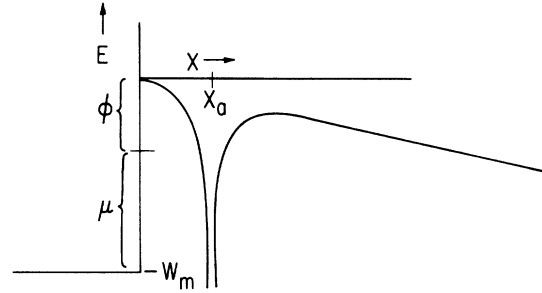


FIG. 1. Schematic diagram of the potentials due to the metal plus adsorbate and to the external electric field. ϕ denotes the work function and x_a is the metal-adsorbate separation.

by

$$\hat{V}_f = V_f \theta(x) = -eFx \theta(x), \quad (1)$$

with $\theta(x) = 1$ for $x > 0$ and $\theta(x) = 0$ for $x < 0$. We define the "left-system" Hamiltonian H_L by

$$H_L = H^{ma} + \Delta \epsilon_a n_a, \quad (2)$$

where $\Delta \epsilon_a = -eFx_a$ is the energy change of the adsorbate caused by \hat{V}_f and x_a is the position of the adsorbate. The "right-system" Hamiltonian H_R consists of the kinetic energy plus the electric field extended over all space. At the energies of interest, eigenfunctions of H_L are largely confined to $x < 0$ and those of H_R to $x > 0$. Tunneling is treated as transitions induced by V_f from "left-system" eigenstates to "right-system" eigenstates. We make use of the method of Appelbaum and Brinkman⁵ to write the tunneling current per unit energy at energy $\hbar\omega$ as

$$j(\omega) = \frac{2f(\omega)}{\hbar} \sum_{i,i'} \langle i' | \tau | f \rangle \langle f | \tau | i \rangle \text{Im} G_{ii'}^L(\omega - i\delta) \delta(\omega - \epsilon_f), \quad (3a)$$

$$\tau = \hat{V}_f - P_a^\dagger \Delta \epsilon_a P_a, \quad (3b)$$

where $f(\omega)$ is the Fermi function, the states $|i\rangle$ form a complete set of one-electron wave functions for the "left system", $|f\rangle$ denote Airy functions which diagonalize H_R , and G^L is the Green's function

for the "left system." Here and later it is assumed that $\delta \rightarrow 0^+$. P_a is a projection operator for the adsorbate states, $|a\rangle\langle a|$.

We assume that the metal-adsorbate complex is described by the many-body Anderson Hamiltonian

$$H^{ma} = \sum_{m\sigma} \epsilon_m n_{m\sigma} + \epsilon_a \sum_{\sigma} n_{a\sigma} + U n_{a\uparrow} n_{a\downarrow} + \sum_{m\sigma} (V_{am} a_{m\sigma}^\dagger d_\sigma + V_{am}^* d_\sigma^\dagger a_{m\sigma}). \quad (4)$$

Equation (4) assumes a single adsorbate level with wave function φ_a and energy ϵ_a . φ_a may be a combination of adsorbate states, i.e., a "hybrid orbital."

H_L is given by (2) after substitution of (4). Thus it is identical to H^{ma} of (4) but with ϵ_a replaced by $\epsilon_a + \Delta\epsilon_a = \epsilon_a - eFx_a$.

By choosing the set of states $\{|i\rangle\} = \{|m\rangle, |a\rangle\}$, we find from (3) that $j(\omega)$ is related to G_{mm}^L , G_{ma}^L , G_{am}^L , and G_{aa}^L . It is easy to show that

$$G^L = g + (1+gV)P_a G^L P_a (Vg+1), \quad (5a)$$

$$g = \sum_m |m\rangle g_m \langle m|, \quad g_m = (\omega - \epsilon_m)^{-1}, \quad (5b)$$

where V is the hopping term in (4) and $V_{aa} = V_{mm} = 0$. Also

$$G_{aa}^L = (\omega - \epsilon_a - \Sigma)^{-1} = G_{aa}^R + iG_{aa}^I, \quad (5c)$$

where $\Sigma = \Sigma_R + i\Sigma_I$ is the self-energy of the adsorbate state. Combining (3) and (5) yields

$$j(\omega) = j_0(\omega) + [2f(\omega)/\hbar] \text{Im}[\sum_f \delta(\omega - \epsilon_f) \langle f|t|a\rangle G_{aa}^L \langle a|\tilde{t}|f\rangle], \quad (6a)$$

where j_0 is the current in the absence of adsorbate:

$$j_0(\omega) = [2\pi f(\omega)/\hbar] \sum_{mf} \delta(\omega - \epsilon_f) \delta(\omega - \epsilon_m) |\langle f|\hat{V}_f|m\rangle|^2, \quad (6b)$$

$$t = \tau + \tau g V, \quad \tilde{t} = \tau + V g \tau. \quad (6c)$$

When $j_0(\omega)$ is evaluated from (6b), under the assumption that the metal potential is the square well shown in Fig. 1, the result is identical to that of Young⁶ obtained by combining a supply function with the WKB barrier-penetration coefficient. The term proportional to $G_{aa}^I \langle f|\tau|a\rangle^2$ in (6a) represents tunneling of an electron from the adsorbate to the vacuum modulated by the density of states G_{aa}^I . The remaining terms in (6) arise because the effective transfer operator is t rather than τ . The $\tau g V$ part of t represents the hopping of an electron from the adsorbate to the metal via V , propagation in the metal, and then tunneling to the vacuum under the influence of τ .

Since the Anderson model involves an overcomplete set of states,⁸ it does not automatically give the correct asymptotic dependence of the eigenstates $\{|i\rangle\}$ of H^{ma} . To compensate for this we give to the state $|a\rangle$ appearing in matrix elements of the form $\langle f|\tau|a\rangle$ the asymptotic dependence which obtains for $\epsilon_a = \epsilon_f$. Upon performing the summation \sum_f in (6a) one finds that

$$j(\omega)/j_0(\omega) = 1 + (u^2 - v^2)G_{aa}^I + 2uvG_{aa}^R, \quad (7a)$$

$$u = [\langle a|\tau + \theta(x)V|s\rangle + \sum_m V_{am} \Gamma_m(\omega)(\omega - \epsilon_m)^{-1}] \{ \pi \sum_m [\Gamma_m(\omega)]^2 \delta(\omega - \epsilon_m) \}^{-1/2}, \quad (7b)$$

where V is the potential appearing in V_{am} of (4), $\tau + \theta(x)V = \theta(x)H^{(1)}$, and where $H^{(1)}$ is the one-particle part of the Hamiltonian. In Eqs. (7a) and (7b)

$$v = \sum_m V_{am} \Gamma_m(\omega) \delta(\omega - \epsilon_m) \{ \pi \sum_m [\Gamma_m(\omega)]^2 \delta(\omega - \epsilon_m) \}^{-1/2}, \quad (7c)$$

$$\Gamma_m(\omega) = (\hbar^2/2m) \int d^2S [(\partial\varphi_m/\partial x) - \xi(\omega)\varphi_m]_{x=0}, \quad (7d)$$

where $\varphi_m = |m\rangle$ is the metal wave function, $\xi(\omega) = (-2m\omega/\hbar^2)^{1/2}$, and the integration is over the metal surface $x=0$. In (7b) the state $|s\rangle = \exp\{\xi(\omega)x - \frac{1}{4}[\alpha x^2/\xi(\omega)]\}$, where $\alpha = 2meF/\hbar^2$, is an asymptotic form of the Airy function.

The relative magnitudes of u and v of (7) can be estimated using the square-well approximation for the metal. The term involving Γ_m in the numerator of (7b) is negligible, and

$$|u/v| \approx (2\pi)^{3/2} (-\omega)^{1/2} (\alpha \Sigma_I \rho_V)^{-1/2} [1 + (\pi g)^{-1}] (1 - \gamma + g) \exp[\xi(\omega)x_a], \quad (8)$$

where ρ_V is the volume per atom in the metal. Σ_I is the broadening of the adsorbate level as seen in $j(\omega)$. The adsorbate wave function $|a\rangle$ is dictated by the specific system. For simplicity we consider

only s states but make allowance for the "polarization" by considering admixtures of p states, i.e., hybridization of the adsorbate orbitals. γ is a measure of the p character: $\gamma=1$ corresponds to equal amounts of s and p character and $\gamma=0$ corresponds to no p character. Only the component of φ_a with zero angular momentum normal to the metal surface will contribute appreciably to $\langle a | \tau + \theta(x) V | s \rangle$. We set $g = \pi^{-1/2} \alpha^{1/2} \xi^{-3/2}$. Substitution of reasonable values for the quantities in Eq. (8) shows that $u/v \sim 10^2-10^3$. This result obtains because the tunneling processes represented by u and v , respectively, are such that the barrier width in u is smaller than that in v . Here, v represents the energy-conserving process "adsorbate-metal-vacuum" while u represents "adsorbate-vacuum" as well as the non-conserving process "adsorbate-metal-vacuum." Thus $u \gg v$, and (7) gives

$$[j(\omega) - j_0(\omega)]/j_0(\omega) \equiv \Delta j(\omega)/j_0(\omega) = u^2 G_{aa}^{-1}, \quad (9a)$$

$$u^2 = \lambda \exp[2\xi(\omega)x_a], \quad (9b)$$

$$\lambda = 4\pi\rho_a(\xi^3/\alpha)W_m[\omega/(\omega + W_m)]^{1/2}(1-\gamma+g)^2[1+(\pi g)^{-1}], \quad (9c)$$

where (9b) and (9c) result from the square-well approximation. ρ_a is the ratio $\pi a^2/S$, where a is the adsorbate radius and S is the surface area seen in the experiment. The exponential factor in (9b) comes about because electrons on the adsorbate "see" a narrower barrier than electrons in the metal. (9a) is valid if $G_{aa}^R \ll 10^2 G_{aa}^{-1}$, which is certainly the case if the adsorbate resonance lies within the metal conduction band.

(9) is a remarkably simple result: It shows that TED measures the local density of states at the adsorbate. We estimate u^2 from (9b) and (9c) for the Plummer-Young⁷ (PY) experiment of Ba adsorbed on W; they estimate $10^{-4} < \rho_a < 10^{-3}$, $eF = 0.2 \text{ eV } \text{\AA}^{-1}$, $W_m = 10 \text{ eV}$, and $-\omega = 5 \text{ eV}$. We take $\gamma = 0.8$ and $2 \text{ \AA} < x_a < 3 \text{ \AA}$. These values yield $50 < u^2 < 5 \times 10^3$. At the adsorbate resonance ϵ_r , $G_{aa}^{-1}(\epsilon_r) = 1/\Sigma_I$; Σ_I may be estimated from the adsorbate peak width observed by PY to be $\sim 1 \text{ eV}$. Thus we estimate⁹ $51 < j(\epsilon_r)/j_0(\epsilon_r) < 5 \times 10^3$. The experimental result is $j(\epsilon_r)/j_0(\epsilon_r) \sim 2-5$. The high calculated value is largely due to omission of the image potential in our calculation. Its inclusion would increase $j_0(\epsilon_r)$ by $\sim 6 \times 10^2$, while tunneling from the adsorbate would be much less affected. In addition, the overcompleteness of the basis states in the Anderson model would introduce pseudopotentials (see Kanamori, Terakura, and Yamada⁸) which may affect $j(\omega)$. Thus λ in Eq. (9) should be regarded as a parameter.

We stress that $\Delta j(\omega)/j_0(\omega) \propto G_{aa}^{-1}$ depends only on $u \gg v$, as is clear from (7). The corrections to the asymptotic behavior of $|a\rangle$ made in calculating $\langle a | \tau + \theta(x) V | s \rangle$ do not influence v and this gives additional confidence in the result $u \gg v$. We further check the consistency of this point as follows. If $u \gg v$ then from (7), $u^2 = (\Delta j/j_0) \times (G_{aa}^{-1})^{-1}$. As stated above, PY observe $\Delta j/j_0 \sim 1-4$ at $\omega = \epsilon_r$ and $G_{aa}^{-1}(\epsilon_r) \approx 1 \text{ eV}$. Thus $u \sim 1-2$.

The quantity v^2 is given by

$$v^2 \approx (1/2\pi^2)\rho_a W_m(\omega + W_m)^{-1/2}(-\omega)^{-1/2}\Sigma_I \xi^3 \rho_v \quad (10)$$

for the square-well approximation. For the PY experiment we estimate $v < 1.5 \times 10^{-3}$ from (10) which is much smaller than the value for u estimated above.

If the adsorbate resonance ϵ_r is below the metal conduction band, $G_{aa}^{-1} \sim 0$ for $\omega \sim \epsilon_F$ and then $\Delta j/j_0 \approx G_{aa}^R 2uv$, where now $G_{aa}^R \approx (\omega - \epsilon_r)^{-1}$; also $uv < 0$ so that $\Delta j/j_0 < 0$. This result is 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.

Although the energy dependence of $\Delta j(\omega)/j_0(\omega)$ is primarily determined by G_{aa}^{-1} , an additional dependence comes from the factor $\exp[2\xi(\omega)x_a]$ [see (9b)]. Assuming that G_{aa}^{-1} is represented by

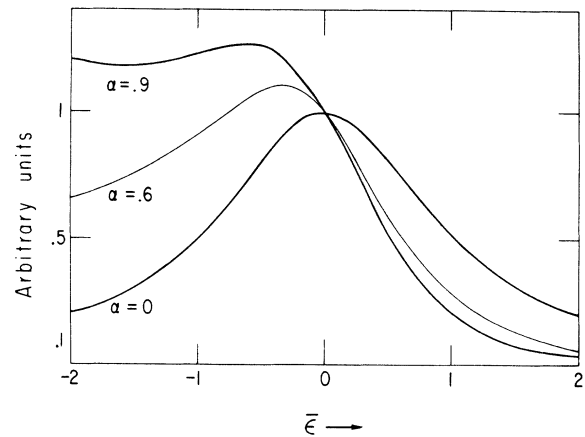


FIG. 2. Plots of $j(\omega)/j_0(\omega)$ as given by Eq. (11) for the cases $\alpha = 0, 0.6,$ and 0.9 .

a Lorentzian, we may write

$$\Delta j/j_0 \propto G_{aa}^{-1} \exp[2\xi(\omega)x_a] \propto (1 + \bar{\epsilon}^2)^{-1} \exp(-\alpha\bar{\epsilon}), \quad (11a)$$

$$\bar{\epsilon} = (\omega - \epsilon_r)/\Gamma, \quad (11b)$$

$$\alpha = x_a \xi(\epsilon_r)\Gamma/|\epsilon_r|, \quad (11c)$$

where the resonance is at $\epsilon_r < 0$, and Γ is the width of the resonance.

Equations (11) are valid for $|\omega - \epsilon_r|/|\epsilon_r| \ll 1$. For values of Γ , x_a , and ϵ_r equal to 1, 2.5, and -5 eV, respectively, $\alpha = 0.6$. A plot of (11a) is shown in Fig. 2 for $\alpha = 0, 0.6$, and 0.9 . For $\alpha = 0.6$ and 0.9 , the peak is shifted by 0.33Γ and 0.62Γ below the actual position of the adsorbate resonance and the curves are not Lorentzian in shape; thus $G_{aa}^{-1}(\omega)$ must be "unfolded" from the experimental curves.

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¹C. B. Duke and M. E. Alferieff, *J. Chem. Phys.* **46**, 923 (1967).

²J. W. Gadzuk, *Phys. Rev. B* **1**, 2110 (1970).

³M. H. Cohen, L. M. Falicov, and J. C. Phillips, *Phys. Rev. Lett.* **8**, 316 (1961).

⁴J. R. Oppenheimer, *Phys. Rev.* **31**, 66 (1928).

⁵J. A. Appelbaum and W. F. Brinkman, *Phys. Rev.* **186**, 464 (1969).

⁶R. D. Young, *Phys. Rev.* **113**, 110 (1959).

⁷E. W. Plummer and R. D. Young, *Phys. Rev. B* **1**, 2088 (1970).

⁸J. Kanamori, K. Terakura, and K. Yamada, *Progr. Theor. Phys.* **41**, 1426 (1969).

⁹The transfer-Hamiltonian method gives a smaller value for the ionization probability of a hydrogen atom (see Ref. 4) than that given by the calculation of C. Tancozos [*Z. Phys.* **68**, 204 (1931)].

Identification of Auger Electrons in GaAs

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Auger electrons resulting from across-the-gap recombination are believed to have been identified by their velocity distribution which does not depend on the energy of the exciting photons.

One of the mechanisms responsible for nonradiative recombination of electron-hole pairs in semiconductors is sometimes believed to be Auger recombination. In the Auger process to be considered, the energy released by the recombination of an electron-hole pair is transferred to a second electron which can dissipate this energy by multiphonon emission within the conduction band.

The occurrence of the Auger effect in across-the-gap recombination in semiconductors has been surmised on theoretical grounds; but, at best, its manifestation has been indirect: the emission of photons having an energy higher than expected from thermodynamic consideration.^{1,2} The much shorter carrier lifetime than calculated from detailed balance,³ the temperature-dependent reduction of carrier lifetime,^{4,5} and the carrier concentration dependence of radiative efficiency⁶ are other indirect plausible consequences of Auger recombination.

In this Letter we report the direct observation of the hot electrons believed to be generated by Auger interaction. The hot electrons are emitted

into vacuum where their kinetic energy distribution is measured. From the characteristic distribution of emitted electrons and its dependence on the excitation energy, it is possible to differentiate between Auger electrons and other hot electrons. In other words, it is possible to identify that component of the emission current which is due to Auger excitation.

Wafers of *p*-type GaAs doped to have a net hole concentration of $8 \times 10^{16} \text{ cm}^{-3}$ and $2 \times 10^{17} \text{ cm}^{-3}$ were used; *n*-type material was avoided to permit reducing the electron affinity by surface treatment. Heavily doped *p*-type material was also avoided for two reasons: (1) to increase the nonequilibrium electron concentration (the lifetime decreases with increasing doping), and (2) to reduce the competing process in which an Auger interaction between one electron and two holes results in the generation of a hot hole. The GaAs was polished and etched and then mounted in the vacuum chamber illustrated in Fig. 1 where it could be cesiated. The photoluminescence spectrum of the specimen used reveals transitions attributed to band-to-band as well as