the present purpose.

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Electronic Surface States of a Dielectric Film on a Metal Substrate*

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An electron near the surface of liquid or solid He, Ne, or H_2 is excluded from the interior of the medium because of a net repulsive interaction with the atoms or molecules composing it. If a layer of such a material is situated on a conductor these electrons may become localized near the insulator-vapor interface, bound there by polarization forces. We discuss the properties of these states and determine their lifetime prior to electron tunneling through the insulator to the metal.

I. INTRODUCTION

It has been known for several years[1,2] that the strongly repulsive interaction between an electron and certain closed-shell atoms or molecules (specifically He, Ne, and H_2) causes an effective exclusion of an excess electron from the interior of a condensed medium composed of such units. On the other hand, when outside the medium, the electron is pulled toward its surface by attractive polarization forces. In view of these considerations, Cohen and the author recently proposed[3,4] that there exist states of excess electrons localized near, but primarily external to, the surface of liquid and solid He, Ne, and H_2.

In this paper a related phenomenon is described. We consider a configuration of a dielectric layer, or film, lying on a metal substrate, as shown in Fig. 1. An electron in the vapor region will be attracted toward the dielectric surface. However, the polarization force will be enhanced relative to the case of an infinitely thick dielectric treated in I. Exclusion from the bulk of the dielectric will occur as it does in that problem. The net result is localization of the extra electron near the medium's surface, but with considerably larger binding energy than occurs in the absence of the metal. These electronic states, however, are not true eigenstates of the system in that the electrons can tunnel quantum mechanically through the insulator to the metal. The lifetime associated with this process must be calculated as well.

Section II utilizes the appropriate electrostatic potential, derived in Appendix A, to obtain the wave equation in a form similar to that of the author's previous treatment. In Sec. III, we discuss the eigenvalues of the most strongly bound states as well as the lifetimes for the tunneling process. Section IV provides further discussion and conclusions.

II. EFFECTIVE POTENTIAL AND RESULTING EIGENFUNCTION

Figure 1 illustrates the experimental configuration of interest. The previous studies of image-potential induced surface states[3,4] concern the case of an infinite dielectric to which the present problem reduces when t tends to infinity.

Experimental[2] and theoretical[1] evidence indicates that the insulators studied here have a negative electron affinity, owing to their filled, tightly bound electronic shells. The repulsive electron-medium interaction causes the conduction band minimum to lie at an energy V_0 which is positive with respect to the vacuum level, which we take to be zero. An energy $E < V_0$ lies in the energy gap so that an electron wave function at that energy decays exponentially with distance into the medium. Outside of the medium, the electron is attracted toward the insulator. At a distance x from the surface large enough for classical electrostatics to apply, the interaction between the electron and an infinite dielectric is[5]

$$V(x, t = \infty) = -\beta e^2/4x, \quad x > b > 0$$
$$\beta = (\epsilon - 1)/(\epsilon + 1),$$
(1)

where b is a cutoff parameter we employ because (1) loses its validity for close approach, and ϵ is the static dielectric constant of the insulator.

In Appendix A, we solve the classical electrostatic problem corresponding to the configuration of Fig. 1 and obtain a generalization of Eq. (1) that includes the influence of the metal. The resulting form for the potential in the vacuum region is a sum of (1) and an infinite series that converges uniformly since $\beta < 1$:

$$V(x, t) = \frac{-\beta e^2}{4x} + \frac{(1 - \beta^2)e^2}{4\beta} \sum_{n=1}^{\infty} \frac{(-\beta)^n}{x + nt},$$
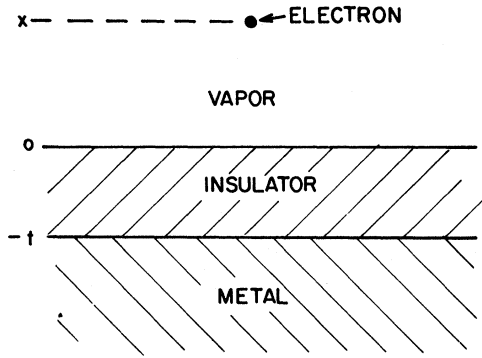$$x \geq b > 0.$$
(2)

FIG. 1. The geometrical configuration under investigation. The metal is semi-infinite and all interfaces are of infinite extent.

As in I, we will calculate an envelope function $\psi(\vec{r})$ in the effective mass approximation[6,7] for the electron wave function. $\psi(\vec{r})$ is free-electron-like for motion parallel to the surface but localized in the direction normal to the surface:

$$\psi_{\vec{R}}(\vec{r}) = A^{-1/2}\, e^{i\vec{\kappa}\cdot\vec{\rho}}\phi(x), \qquad (3)$$

$$\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V_M(x)\right)\phi(x) = E\phi(x), \qquad (4)$$

where the total energy is

$$E_T = E + \hbar^2\kappa^2/2m. \qquad (5)$$

Here $\vec{\kappa}$ is the wave vector for motion parallel to the surface plane of area A and $\vec{\rho}$ is the component in the plane of electron position vector $\vec{r}$. The one-dimensional model potential for motion perpendicular to this plane is depicted schematically in Fig. 2,

$$V_M(x) = V_0(1-s), \quad x < 0 \qquad (6a)$$

$$= V(b, t), \qquad 0 < x < b \qquad (6b)$$

$$= V(x, t), \qquad b < x. \qquad (6c)$$

The quantity

$$s = e^2/(4\epsilon t\, V_0)$$

is approximately (to order β^2) the fractional reduction, due to the metal, of the barrier potential[8] at $x = 0$.

In the spirit of the usual treatments of quasistationary (QS) states,[9,10] we have chosen V_M as a lowest-order approximation to the potential, which will determine a set of eigenstates. We then consider the necessary corrections to V_M which generate an additional set of states, namely, the Bloch states of the metal. States of the first kind are then truly QS only if they decay slowly to those of the second kind. Later we will investigate the applicability of this approach to the present problem.

Note that we have chosen V_M to be a constant for

the range $0 < x < b$. The cutoff parameter b will be arbitrarily taken as 3 Å for the present calculation, but the results are rather insensitive to this choice.

The solution to Eqs. (4) and (6) which is continuous and has continuous first derivative at $x = 0$ is

$$\phi(x) = e^{K_1 x}, \qquad\qquad x < 0 \qquad (7a)$$

$$= \cos K_2 x + (K_1/K_2)\sin K_2 x, \quad 0 < x < b; \qquad (7b)$$

$$K_1^2 = (2m/\hbar^2)[V_0(1-s) - E],$$

$$K_2^2 = (2m/\hbar^2)[E - V(b, t)].$$

The eigenfunctions and eigenvalues of the localized state are obtained by equating the logarithmic derivative of this solution to that of the corresponding solution for $x > b$ which vanishes at infinity. We have obtained the latter by numerical integration of the Schrödinger equation using the method of Numerov.[11] The asymptotic form used as a starting point is the regular Whittaker function.[12] The relevant properties of this function are derived in I.

III. RESULTS FOR EIGENVALUES AND LIFETIMES

We will perform this calculation for the liquids He, Ne, and H_2. The quantity V_0 is taken from I where it was calculated with the method of Springett et al.[1] The specific values used are given in Table I. The results for the solid will differ only because a somewhat different density would change V_0 and β.
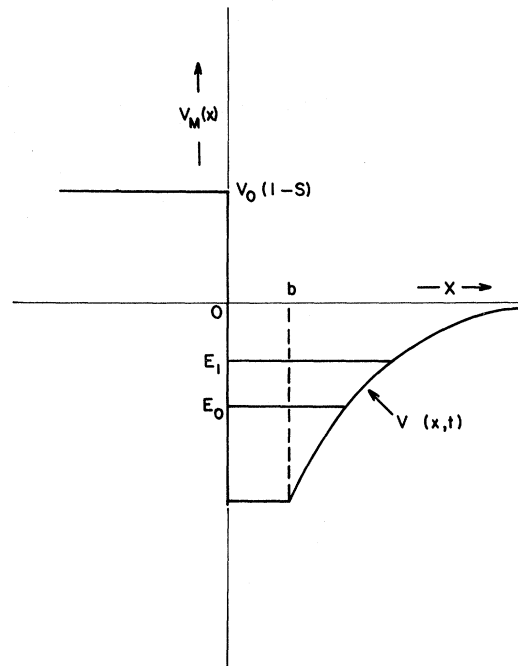

FIG. 2. The one-dimensional model potential $V_M(x)$ depicted schematically. The two lowest eigenvalues E_0 and E_1 are included. The curves terminate at a thickness $t_{\min}$ given in Table I and calculated in the text.
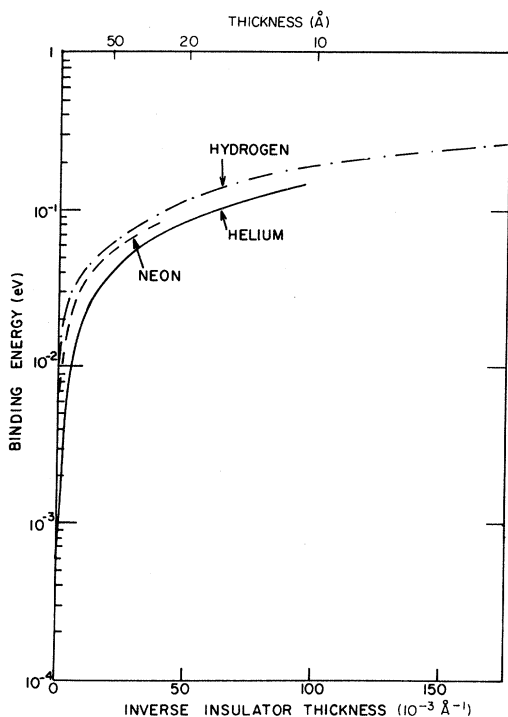
FIG. 3. Binding energy of the ground state for motion perpendicular to the surface as a function of the inverse of the insulator's thickness.

Figure 3 shows the binding energy $-E_0$ of the ground state of the system for the three insulators of interest, as a function of t. In Fig. 4 we give the energy ΔE of excitation to the first excited state. We observe, as predicted, that the presence of the metal considerably strengthens the binding to the surface region. Although we have not calculated the normalization integral for ϕ, we have estimated it and determined the fractional penetration of the wave function into the insulator. As in I this is of order 1% for all cases studied, which means that the electron remains primarily outside of the medium.

As mentioned earlier, these states are unstable with respect to tunneling through the insulating barrier to the metal. The lifetime τ associated with this process is calculated in Appendix B using the WKB approximation, taking into account the "varia-

TABLE I. Parameters for liquid insulators under investigation.

	$10^{-22} \times$density (cm^{-3})	V_0 (eV)	$10^2\beta$	$t_{\min}$ (Å)	$\delta E(t_{\min})$ (eV)
He	2.18	1.30	0.27	10.5	1.0×10^{-4}
Ne	3.72	0.47	0.88	26.1	2.5×10^{-4}
H$_2$	2.17	2.20	1.04	5.5	1.1×10^{-3}

tion of V in the barrier region" associated with the metal-induced potential. The result is expressed in the form

$$\tau^{-1} = e^{-J}/T_{cl} \quad ,$$

where T_{cl} is the classical period of oscillation in the quasistationary state, given in (B3), and the exponential is a tunneling probability factor. The quantity J has the value

$$J = [8mt^2(V_0 - E)/\hbar^2]^{1/2} \{(1 - y^{-2})^{1/2}$$

$$- y^{-2}\ln[y + (y^2 - 1)^{1/2}]\}, \quad \text{(B2')}$$

where

$$y^2 = 4\epsilon t(V_0 - E)/e^2 \approx s^{-1} \quad ,$$

since $V_0 \gg E$. For the case of sufficiently thin dielectric, we will have $y < 1$ so that the insulating "barrier" vanishes completely and the state decays almost immediately. In fact, the QS state method requires for its validity that y be somewhat greater than unity. If we arbitrarily choose $y = 2$ to be the minimum value imposed by this requirement, this corresponds to a minimum thickness $t_{\min}$ amenable to treatment by this approach. Table I includes this value, computed for the ground state of the system, as well as the energy broadening $\delta E(t_{\min})$ that corresponds to τ according to the uncertainty principle. We observe that these values of δE (≈ 1 meV)
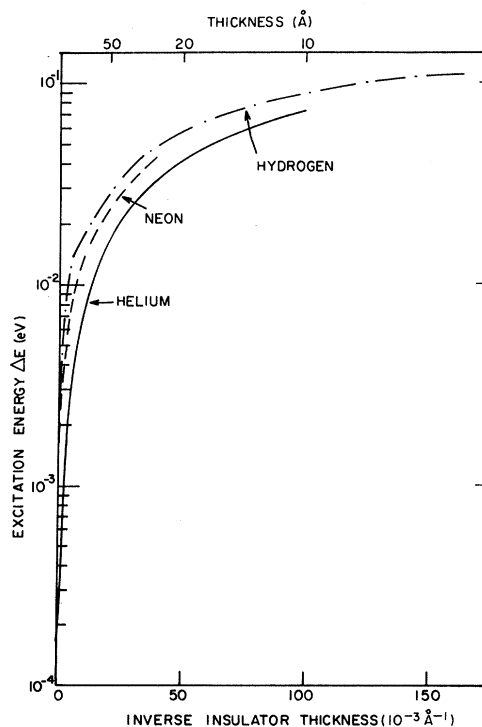

FIG. 4. Energy of excitation from the ground state to the first excited state as a function of the inverse of the insulator's thickness.

are small in comparison to the energy differences between levels for $t = t_{\min}$. Hence, we may regard the $t_{\min}$ chosen to be a reasonable limit of the regime of validity of the QS state method used here.

IV. DISCUSSION

The energy spectrum associated with these surface states is quasicontinuous and free-electron-like for motion parallel to the surface and quantized in discrete levels for perpendicular motion. We observe that both the binding energy of the electrons in these states and the separation ΔE between the discrete levels increase rapidly as the thickness of the dielectric decreases. However the lifetime of the states is limited by the process of tunneling, the rate of which also increases with decreasing thickness. These properties may be investigated with experiments involving electromagnetic radiation in the infrared or longer wavelength region, or in mobility experiments that probe the various possible scattering mechanisms.[4]

APPENDIX A

In this Appendix, we derive the attractive potential $V(x, t)$ associated with a charge q situated at position $(\vec{p} = 0, x > 0)$ in the vacuum region shown in Fig. 1. We let $\vec{r} = (\vec{p}, d)$ denote the radius vector to a general point in space. The electrostatic potential $U(\vec{r})$ satisfies Laplace's equation, appropriate continuity conditions at the interfaces, and has cylindrical symmetry. We separate the solution in vacuum (region I) into U_0, the potential which q would produce in the absence of dielectric and metal[13] and δU, the induced potential which we determine,

$$U_{\mathrm{I}} = U_0 + \delta U, \quad x > 0 \tag{A1}$$

$$U_0(\vec{p}, d) = q \int_0^\infty dk \, J_0(k\rho) e^{-k|x-d|}, \tag{A2}$$

$$\delta U(\vec{p}, d) = q \int_0^\infty dk \, J_0(k\rho) e^{-kd} s(k), \tag{A3}$$

where J_0 is the zero-order Bessel function, and $s(k)$ will be determined. In the dielectric (region II), we choose expansion coefficients for U_{II} which guarantee that it goes continuously at $x = -t$ to the potential of the perfect conductor, $U_{\mathrm{III}} = 0$:

$$U_{\mathrm{II}}(\vec{p}, d) = q \int_0^\infty dk \, J_0(k\rho) (e^{-kd} - e^{k(d+2t)}) a(k).$$

Continuity at $x = 0$ of the potential and the normal component of the electrostatic displacement vector give

$$e^{-kx} + s(k) = a(k) (1 - e^{2kt}),$$

$$e^{-kx} - s(k) = \epsilon \, a(k) (-1 - e^{2kt}),$$

with solution

$$s(k) = -e^{-kx} (1 + \beta e^{2kt}) / (\beta + e^{2kt}).$$

One may easily verify that this solution reduces to standard ones for the limiting cases of infinite di-

electric and no dielectric, respectively.

In general the attractive image potential is given by

$$V(x, t) = \tfrac{1}{2} q \, \delta U(\vec{p} = 0, x)$$

$$= -\beta q^2 / 4x - \tfrac{1}{4}(1 - \beta^2) q^2 \, I(x),$$

$$I(x) = 2 \int_0^\infty dk \, e^{-2kx} / (\beta + e^{2kt}),$$

in which the first term corresponds to the case of an infinite dielectric and the second indicates the metal's influence. We may evaluate $I(x)$ by expanding its denominator and integrating term by term. There results an infinite series which converges if $\beta < 1$, yielding the final expression

$$V(x, t) = \frac{-\beta q^2}{4x} + \frac{q^2(1 - \beta^2)}{4\beta} \sum_{n=1}^\infty \frac{(-\beta)^n}{x + nt}. \tag{A4}$$

APPENDIX B

We calculate here the rate of tunneling through the insulator for QS electronic surface states localized primarily in the vacuum region. For elastic tunneling the transverse wave vector $\vec{k}$ is conserved, and the problem reduces to one dimension.[10] Except within a few atomic layers of each interface,[14] the effective potential $V_i(x)$ of an electron in the insulator can be taken as V_0 modified by the metal's image potential

$$V_i(x) \approx V_0 - e^2 / 4\epsilon \, (x + t), \quad x < 0. \tag{B1}$$

We find in the WKB approximation[15] that the tunneling rate τ^{-1} is a product of an "attempt rate," equal to the inverse of the classical period of motion T_{cl} in the QS state, and a tunneling probability given by the usual integral over the classically forbidden region, which we may evaluate immediately:

$$\tau = T_{\mathrm{cl}} \, e^J,$$

$$J = 2 \int_{x_0}^0 dx \left(\frac{2m[V_i(x) - E]}{\hbar^2} \right)^{1/2},$$

$$= \left(\frac{8m(V_0 - E)t^2}{\hbar^2} \right)^{1/2} \{ (1 - y^{-2})^{1/2}$$

$$- y^{-2} \ln[y + (y^2 - 1)^{1/2}] \}, \tag{B2}$$

where x_0 is the classical turning point on the metal side of the insulator,

$$x_0 = -t(1 - y^{-2}),$$

$$y^2 = 4t\epsilon (V_0 - E) / e^2 \cong s^{-1}.$$

We note that the parameter y^2 is the ratio of $(V_0 - E)$ to the magnitude of the metal's contribution to the image potential at $x = 0$. If $y < 1$, then the barrier is completely eliminated and the QS-state picture becomes invalid.

The quantity T_{cl} is given by an integral over the classically allowed range, between $x = 0$ and $x = x_m$, the classical turning point[16]

$$T_{cl} = 2 \int_0^{x_m} dx \; \left(\frac{m}{2[E - V(x)]} \right)^{1/2} .$$

Since $V(x)$ is not of simple form we cannot calculate this integral exactly by other than numerical means. However, we can find functions $V_u(x)$ and $V_l(x)$ which are upper (u) and lower (l) bounds for $V(x)$ and permit exact integration of T_{cl}.:

$$V_u(x) > V(x) > V_l(x),$$

$$V_l(x) \equiv - e^2/4x,$$

$$V_u(x) \equiv V(x_m) - V'(x_m)(x_m - x)$$

$$= E - V'(x_m)(x_m - x),$$

where the prime denotes differentiation. The resulting upper and lower bounds for the period are, respectively,

$$T_{cl}^{(u)} = \left(\frac{2m x_m}{V'(x_m)} \right)^{1/2} ,$$

$$T_{cl}^{(l)} = \left[\frac{me^4}{32 |E|^3} \right]^{1/2} [(u + u^2)^{1/2} \\ - \ln((1+u)^{1/2} + u^{1/2})], \qquad (B3)$$

$$u = 4 |E| x_m/e^2 .$$

Comparison of these quantities shows that $T_{cl}^{(u)}$ is a factor of 5–10 larger than $T_{cl}^{(l)}$. For convenience we will take the actual value to be

$$T_{cl} \approx \tfrac{1}{2} T_{cl}^{(u)} . \qquad (B4)$$

This imprecision is not significant for an order-of-magnitude estimate since T_{cl} is only a preexpotential factor.

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[13] D. Newns [J. Chem. Phys. 50, 4572 (1969)] has used a similar method.

[14] The classical solution is not reliable within a few angstroms of either interface. Since Eq. (B1) is the solution for the infinite dielectric problem, by using it we neglect the influence of the vapor, a satisfactory approximation. Neither of these oversimplifications affects the results significantly.

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Infrared Absorption of Small NaCl Crystals*

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Results of recent measurements of the infrared absorption of small NaCl crystals are compared with calculated absorption spectra.

The infrared absorption in the reststrahlen region of small crystals of NaCl has recently been measured by Martin.[1] The samples used were rectangular in shape, with two of their sides of length 10 μ and the third one shorter. (This size represents, however, only the average over a wide experimental size distribution.[2]) The crystallites were embedded in polyethylene and were well separated. The spectra observed at 7 and 290 °K are shown in Fig. 1.

As noted by Martin,[1] the highest-frequency (frequency here measured in wave-number units) secondary minima (at about 216 cm⁻¹ for 290 °K and at about 232 cm⁻¹ for 7 °K) are probably due to two-