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IMAGE-POTENTIAL-INDUCED SURFACE BANDS IN INSULATORS*

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(Received 14 August 1969)

We find that whenever the bottom of the conduction band of an insulator lies at positive energy, the image potential gives rise to bands of surface states. We present lower limits for binding energies of electrons to the surface of liquid and solid ^{3}He, ^{4}He, Ne, H_2, and D_2. Interaction between electrons and surface phonons (solids) or ripplons (liquids) increases the binding. We argue that these states may have in fact been observed in liquid ^{4}He.

We have established theoretically the existence of a new kind of electronic surface state which will be important for the study of excess electrons in certain insulating solids and liquids. In contrast to other known surface states where electrons are primarily located within the medium but are held near the surface by external fields,[1,2] the electrons in the present case stay predominantly outside at a mean distance of 20-100 Å from the surface. Many years ago, Shockley[3] conceived of the possible existence of such extrinsic surface states, but he did not determine the criteria for their existence or elaborate their properties.

Both experiment[4] and theory[5] have revealed that excess electrons in the conduction band of liquid ^{4}He have minimum energy V_0 of order 1 eV above the vacuum level so that this energy is required for electron injection into the liquid. Other studies[6,7] have indicated that the property $V_0 > 0$ is more general, applying to solids or liquids consisting of light and saturated atoms or molecules in which the short-range Hartree-Fock electron-atom repulsion dominates attractive polarization forces.

Outside of the medium, an electron experiences an attractive image potential[8] of the form

$$V_{\text{image}}(x) = -\tfrac{1}{4}e^2(\epsilon-1)/(\epsilon+1)x, \quad x > 0, \tag{1}$$

where ϵ is the static dielectric constant of the material and x is the electron's distance from the surface, which is assumed to be flat. This macroscopic expression becomes inadequate for x less than some d, which is of the order of one interatomic distance.

Because an electron is repelled when inside the medium and weakly attracted when outside, we expect states localized outside the medium but near its surface.

We have found by a self-consistency argument that the effective-mass equation[9] applies to this situation:

$$\left[\frac{P_\parallel^2}{2m_\parallel} + \frac{P_\perp^2}{2m_\perp} + V(x)\right]\psi = E\psi, \tag{2}$$

where $m_\parallel$ and $m_\perp$ are parallel and perpendicular effective masses and we employ the model potential shown in Fig. 1,

$$\begin{aligned} V(x) &= V_0, \quad x < 0, \\ &= -V_1 = -\tfrac{1}{4}e^2(\epsilon-1)/(\epsilon+1)d, \quad 0 < x < d, \\ &= -\tfrac{1}{4}e^2(\epsilon-1)/(\epsilon+1)x, \quad x > d. \end{aligned} \tag{3}$$

The solution to (2) and (3) is given by

$$\psi_{\vec{k}_\parallel, n}(\vec{\rho}, x) = e^{i\vec{k}_\parallel\cdot\vec{\rho}}\varphi_n(x),$$

where $\vec{k}_\parallel$ is an eigenvector and $\vec{\rho}$ a position vector, both in the surface plane, and $\varphi_n(x)$ is the perpendicular wave function which we solve for below. The eigenvalues are

$$E_n(\vec{k}_\parallel) = \hbar^2 k_\parallel^2/2m_\parallel + E_n.$$

We obtain, as a result, two-dimensional bands parallel to the surface with their energy minima

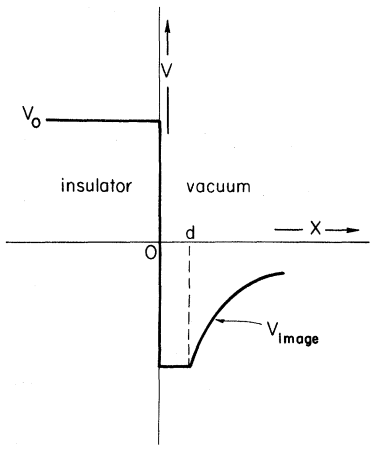

FIG. 1. The model potential used for calculations of electronic surface bands. The mathematical surface lies at $x = 0$.

determined by the solution for the potential of (3). For $x > d$, the equation for φ_n is

$$-\frac{\hbar^2}{2m_\perp}\frac{d^2\varphi_n}{dx^2} - \frac{e^2}{4x}\frac{\epsilon-1}{\epsilon+1}\varphi_n = E_n\varphi_n \tag{4}$$

which is identical in form to the radial Schrödinger equation for $r\psi$ for a Coulomb potential due to a nucleus of charge Ze with $l = 0$, where

$$Z = \tfrac{1}{4}(\epsilon-1)/(\epsilon+1).$$

We may arrive at an approximate solution of (4) by letting $V_0 \to \infty$ and $d \to 0$ so that the boundary condition $\varphi(0) = 0$ results and we obtain hydrogenic solutions

$$E_n^{(0)} = \frac{-Z^2}{n^2}\frac{me^4}{2\hbar^2},$$

where we take $m_\perp$ to be the free-electron mass m.[9]

Table I gives the ground-state energy $E_1^{(0)}$ in this approximation for a number of liquid and solid insulators for which we believe this electronic surface state to be important. We have used the Clausius-Mossotti relation for ϵ as a function of number density, N, an accurate approximation due to the tight-binding character of the valence wave functions.[10] The theoretical values of V_0 are either taken from the paper of Springett et al.[5] with numerical errors corrected, or calculated using the method of that paper. Other published values[5,7] do not differ significantly. Table I also includes the expectation value $\langle x\rangle$ of the distance from the surface, computed in the hydrogenic approximation.

We have improved upon this approximation and calculated analytic solutions to the full potential (4), using the method of Wannier[11] modified here to accomodate a finite V_0. The resulting values of ground-state binding energy obtained with the cutoff d chosen as the bulk interatomic distance are shown as $|E_1|$ in Table I. Variation of d by a factor of 2 from the assumed value changes $|E_1|$ by less than 20%, the sensitivity being largest for small V_0. Other reasonable forms for the transition-region potential would also modify E_1.

Those substances having $V_0 > 0$ should both pre-

Table I. Numerical test for existence of electronic surface bands.

	T	10^{-22} N	10^3 Z	$\lvert E_1^{(0)}\rvert$	$\lvert E_1\rvert$	V_0(eV)		$\langle x\rangle$
	(°K)	(cm^{-3})		(meV)	(meV)	Thry.	Expt.	(Å)
^{3}He (liq)	1.0	1.64	5.14	0.36	0.39	0.90		103
(sol)	1.0	2.56	8.00	0.87	0.94	1.61		66
^{4}He (liq)	1.0	2.18	6.82	0.63	0.68	1.30	1.05±0.05[a]	78
(sol)	1.0	3.01	9.39	1.20	1.30	2.01		56
Ne (liq)	25.0	3.72	22.12	6.65	9.55	0.46		24
(sol)	4.2	4.60	27.16	10.03	14.67	0.61		19
H_2 (liq)	19.0	2.17	25.99	9.19	10.75	2.25	0.3±0.2[b]	20
(sol)	4.2	2.66	31.62	13.60	15.76	3.27		17
D_2 (liq)	19.0	2.59	30.82	12.92	15.00	3.11		17
(sol)	4.2	3.08	36.37	17.99	20.67	4.33		15

[a] See Ref. 4.

[b] B. Halpern and R. Gomer, to be published.

sent a barrier to electron injection and be characterized by excess electronic surface states. Substances having $0 > V_0 > E_1$ should also exhibit bands of surface states. Some experimental information is available for liquid ^{4}He, where such a barrier has been found.[4] In Sommer's injection experiment, he observed that charge remained near the surface but had a high parallel mobility. Unfortunately, external fields complicate analysis of his experiment. Careri, Fasoli, and Gaeta[12] and later Bruschi, Maraviglia, and Moss[13] measured electron current above 1°K from liquid ^{4}He through its surface. The latter found that of the total current arriving at the surface, part flowed parallel to the surface and the remainder escaped from the surface with a temperature dependence indicative of an activation energy corresponding to 25°K, or 2.3 meV.

In bulk ^{4}He the electron-atom repulsion creates a cavity, or bubble, in which the electron is localized.[5, 14, 15] The total energy of formation of an electron bubble relative to an electron at rest in vacuum is 0.1-0.3 eV.[16] Part of this energy is dissipated during the process of bubble annihilation upon arrival at the surface. If one hypothesizes that the probability of subsequent capture into an electronic surface state is high, then thermionic emission from these states would give a possible explanation of the experimental observations. The ground-state binding energy in the case of liquid ^{4}He, 0.68 meV, is about $\frac{1}{3}$ of the observed activation energy. The difference might arise from the interaction between the excess electron and capillary waves (ripplons[17]). We have quantized these waves using the technique of Pitaevskii[18] and have computed the electron-ripplon interaction.[19] The problem is analogous to that of the polaron in polar crystals. In simplest approximation the liquid surface is found to bulge out in the vicinity of the electron, lowering its self-energy. The effect appears to be strong enough to account for the discrepancy.[19]

One expects these dynamic effects to increase the binding energy of electrons in image-potential–induced surface states over the values listed in Table I, for both liquids and solids. The correction should be larger for liquids because the energy for ripplons in the region of interest is of the form $k^{3/2}$ while for phonons it is proportional to k, where k is the excitation wave vector.

One can test for the existence of these surface bands by a variety of experiments. Their common difficulty is the low concentration of electrons to be expected at the surface. Perhaps the most sensitive will be measurement of frequency dependence of surface mobility by microwave absorption techniques, comparing the results for electric vector parallel and perpendicular to the surface.

Other materials than those listed in Table I may satisfy the requirement $V_0 > 0$. In cases of surfaces with absorbed layers, the surface potential may have this property but would require more complicated treatment than we have employed.[20] The concept of image-potential–induced surface bands is likely to be of wide importance for insulators.

We have benefitted greatly from discussion with Professor Joshua Jortner.

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*Research supported in part by the National Aeronautics and Space Administration and Office of Naval Research, and aided through general support of materials science by the Advanced Research Projects Agency.

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WEAK FORM OF THE GRIFFITHS THEOREM FOR THE FERROMAGNETIC HEISENBERG MODEL*

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(Received 18 August 1969)

A weaker form of Griffiths' theorem is established for the ferromagnetic Heisenberg model.

Griffiths[1] has shown that, for an Ising ferromagnet in zero field, with arbitrary crystal structure and range of interaction, the spin correlation is a monotonically increasing function of the interactions. Recently it was pointed out[2] that this theorem does not hold for the ferromagnetic Heisenberg model because of the existence of a counter example. However, we shall show that the theorem holds for certain bounds of the Heisenberg model.

Consider an arbitrary Heisenberg model of N spins, with a Hamiltonian $H=-\sum_{i<j}J_{ij}(\vec{\sigma}_i\cdot\vec{\sigma}_j-1)$ and $J_{ij}\geqslant 0$. Let $\{\psi\}$ be the complete set of orthonormal states of N noninteracting spins. It is clear that the ground-state energy $E_0=0$, and $\langle\psi|H|\psi\rangle\geqslant 0$. One can also show that[3]

$$e^{-\beta\langle\psi|H|\psi\rangle}\leqslant\langle\psi|e^{-\beta H}|\psi\rangle\leqslant e^{-\beta\langle\psi|H|\psi\rangle a}\leqslant 1,\qquad(1)$$

where $a=\exp(-\beta\langle\psi|H^2|\psi\rangle/\langle\psi|H|\psi\rangle)$. From Eq. (1) and the fact that the spin correlation is non-negative[2] we can find the bounds of $\langle\sigma_{kz}\sigma_{lz}\rangle$ $(=\frac{1}{3}\langle\vec{\sigma}_k\cdot\vec{\sigma}_l\rangle)$ as

$$2^{N-2}\Big(\sum\nolimits_A e^{-\beta\langle\psi|H|\psi\rangle}\Big)^{-1}-\tfrac{1}{2}\geqslant\langle\sigma_{kz}\sigma_{lz}\rangle\geqslant 2^{-N}\sum\nolimits_P e^{-\beta\langle\psi|H|\psi\rangle}-\tfrac{1}{2},\qquad(2)$$

where $\sum_P$ ($\sum_A$) indicates summation over those states of $\{\psi\}$ in which $|k\rangle$ and $|l\rangle$ are "parallel" ("antiparallel"). Also, if (m,n) represent different spins from (k,l), all sums in Eq. (2) are functions of J_{mn} in the form

$$\sum\exp(-\beta\langle\psi|H|\psi\rangle)=C_1+C_2\exp(-2\beta J_{mn}),$$

where C_1, C_2 are positive and independent of J_{mn}. This immediately implies that the upper bound of $\langle\sigma_{kz}\sigma_{lz}\rangle$ is a monotonically increasing function of J_{mn}. The lower bound in Eq. (2) is, however, a trivial one, as it is always nonpositive.

Monotone bounds are interesting and quite useful. If a monotone upper bound indicates the absence of a long-range order in a certain lattice structure, all lattice structures which can be constructed by subtracting ferromagnetic bonds must also exhibit no phase transition. On the other hand, if a monotone lower bound indicates the existence of a long-range order in a certain lattice structure, all lattice structures which can be constructed by adding ferromagnetic bonds must also exhibit a phase transition, with a higher transition temperature.

Another way to study the behavior of spin correlation is by constructing simple and accurate bounds. The bounds of Eq. (1) are quite accurate for high temperatures. From Eq. (1), a nontrivial lower bound of spin correlation can be constructed as

$$\langle\sigma_{kz}\sigma_{lz}\rangle\geqslant 2^{-N}\Big[\sum\nolimits_P e^{-\beta\langle\psi|H|\psi\rangle}-\sum\nolimits_A e^{-\beta\langle\psi|H|\psi\rangle a}\Big].\qquad(3)$$

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*Work supported by a faculty research fellowship from the Research Foundation of The State University of New York.

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