Brief Reports

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Image states of a corrugated metal surface

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Quantum states of the image potential due to a corrugated metal surface and a coincident hard-wall boundary are developed in perturbation theory through second order in the corrugation height or profile function $h(\mathbf{r}_{||})$. It is shown how these wave functions can be useful in analyzing data from inverse photoemission and two-photon photoemission. In addition, an analogous approximate wave function for a soft-wall corrugated metal surface is derived and applied to scanning tunneling microscopy.

In the past few years a number of investigators have reported observations involving the image potential experienced by an electron in the vicinity of a metal surface.[1-3] These experiments, inverse photoemission,[1] two-photon photoemission,[2] and scanning tunneling microscopy,[3] all involve unoccupied surface and bulk states of the metal and in particular involve electron quantum states of the image potential. In the case of photoemission (PES) the methods are spectroscopic in nature and hence the image states are observed via binding energies, $\mathbf{k}_{||}$ dispersion, $\mathbf{k}_{||}$ line broadening, and photon polarization. The scanning tunneling microscope (STM), on the other hand, directly probes the surface electron density of states and its manifestations in the tunneling conductance.[3] The image potential is apparently observed through its effect on the tunneling electrons as they pass from probe to target through the vacuum.

Our goal in the present report is to point out that the electron image states are profoundly influenced by corrugations in the metal surface. Both the image plane and the boundary plane exhibit corrugations and these in turn effect the quantum states of the electrons. The correct image potential due to a corrugated metal surface has been worked out in detail in our previous work.[4] There we also discussed how the quantum states are to be affected if the boundary surface upon which the electron wave functions vanish remained planar. In our most recent work, we have carried out a detailed study of the quantum states of a nonplanar image potential for both periodic and aperiodic deformations of the conducting surface with a coincident boundary surface.[5] Here we present a preliminary report of our wave functions which we feel might be useful to workers in the previously mentioned fields.

In Fig. 1(a) we define the coordinate system and surface profile function $h(x,y)$. We consider a conducting surface (image surface) defined by $h(x,y)$, coincident with the boundary surface upon which we require the electron wave function to vanish. The present model should have many of the features appropriate to a real metal, and it has the distinct advantage of being analytically and numerically tractable. Our problem now is to solve the Schrödinger equation for an electron in the above prescription.

In our first report[4(a)] on the nonplanar image potential, it was shown how the electrostatic problem is modified through first order in the surface deformation defined by $h(x,y)$. In a later report[4(b)] we presented more general expressions for the modified image potential formally valid to all orders in $h(x,y)$. There, we also presented the

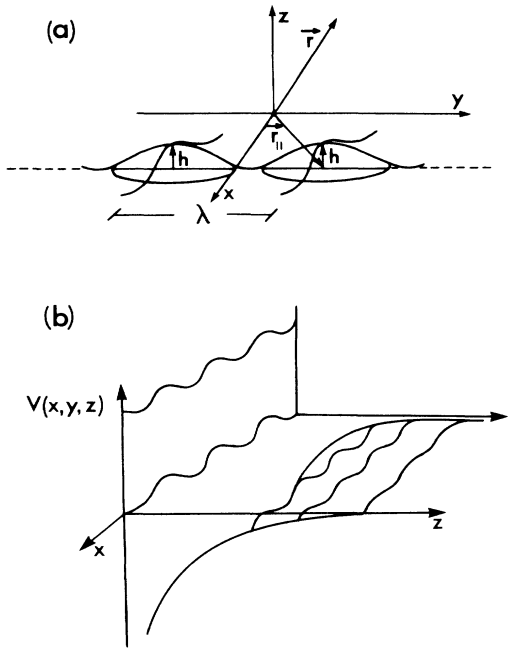

FIG. 1. (a) Coordinate system for the surface corrugation. (b) Corrugated image potential vs z and x.

modified image potential in its Fourier representation, the form of which will prove very useful in our present discussion. For example to first order in $h(x,y)$ we found

$$V_I(\mathbf{r}_{||}z)=-\frac{1}{4z}-\frac{1}{8}\int\frac{d^2k_{||}}{(2\pi)^2}\tilde{h}(\mathbf{k}_{||})e^{i\mathbf{k}_{||}\cdot\mathbf{r}_{||}}k_{||}^2K_2(k_{||},z)\ , \tag{1}$$

where atomic units are used throughout and $h(\mathbf{k}_{||})$ is the Fourier transform of the surface profile function $h(\mathbf{r}_{||})=h(x,y)$ and K_2 is the modified Bessel function. If $h(\mathbf{r}_{||})$ represents a periodic deformation (corrugation) then Eq. (1) becomes a discrete Fourier series over the reciprocal-lattice vectors of the two-dimensional net $\{\mathbf{k}_{||}\}$.

In Ref. 4(b), Eq. (1) was also used in a short discussion of nearly-free-electron theory of surface image corrugation states with plane hard-wall boundary conditions. The matrix element $\langle\mathbf{k}_{||},n\,|\,V_I^{(1)}\,|\,\mathbf{k}_{||},n\rangle$ was calculated between planar image states, $\langle\mathbf{r}\,|\,\mathbf{k}_{||},n\rangle=\exp(i\mathbf{k}_{||}\cdot\mathbf{r}_{||})\phi_n(z)$, where $\phi_n(z)$ is an eigenstate of $H^{(0)}=-\frac{1}{2}\nabla^2-\frac{1}{4}z$. The matrix elements were then used to discuss the possibility of observing a gap

$$\begin{aligned}\Delta E_n&=2\,|\,\langle\mathbf{k}_{||},n\,|\,V_I^{(1)}\,|\,\mathbf{k}_{||},n\rangle\,|\\&=\tfrac{1}{4}\,|\,\tilde{h}(\mathbf{k}_{||})k_{||}^2I_n(\mathbf{k}_{||})\,|\ ,\end{aligned} \tag{2}$$

where $I_n(\mathbf{k}_{||})=\int dz\,|\,\phi_n(z)\,|^2K_2(\mathbf{k}_{||},z)$. We showed that if a typical corrugation height for a sinusoidal $h(\mathbf{r}_{||})$ is 0.2 Å then $\Delta E_n\simeq 2.0$ eV, which is a value that is easily within the capabilities of inverse photoemission experiments. We will return to this calculation later in this report using the full image and boundary plane perturbations.

We next turn to a discussion of perturbation theory when both the potential and the boundary condition are involved. In a quantum-mechanical problem where only the boundary condition on the wave function changes it was shown by Froelich[6] that boundary terms arise which lead to a change in the energy of the form

$$\Delta E=\int_{S_0}\psi^*\frac{\partial\psi^{(0)}}{\partial n}dS=-\int_S\psi^{(0)*}\frac{\partial\psi}{\partial n}dS\ , \tag{3}$$

where $\partial/\partial n$ denotes the normal derivative and $\psi^{(0)}$ vanishes on the initial surface S_0 while ψ vanishes on the final surface S. Equation (3) is exact, and a first-order result is obtained when ψ is replaced by $\psi^{(0)}$.

In the corrugated-metal-surface problem one must consider the more general problem where both the image potential and the boundary condition are changed from the plane-metal surface. We have considered the simplest case where the electron is subject to a hard-wall boundary condition that is coincident with the corrugated image plane [depicted in Fig. 1(b)]. This general class of problems can be treated elegantly using the Feshbach-Clogston (FC) method of the boundary transformation operator.[7] We thus discuss their method in the context of our problem as defined above.

Feshbach and Clogston show that the equations,

$$H\psi=E\psi\ ,\quad \psi\,|_S=0 \tag{4}$$

are equivalent to the transformed equations,

$$\tilde{H}\phi=E\phi\ ,\quad \phi\,|_{S_0}=0\ , \tag{5}$$

where

$$\tilde{H}=THT^{-1}\ ,\quad \phi=T\psi\ .$$

T is the boundary transformation operator, $T=\exp(\sigma)$ and $\sigma=h(x,y)\partial/\partial z$. One can then use $T=1+\sigma+\cdots$ to generate a perturbation theory for the function ϕ from which $\psi=T^{-1}\phi=(1-\sigma+\cdots)$ can be calculated in any given order in the profile function $h(x,y)$ once ϕ is known. Thus, for example, if $H=H^{(0)}+V^{(1)}+\cdots$, then $\tilde{H}=H^{(0)}+H^{(1)}+\cdots$, where

$$H^{(1)}=V^{(1)}+[\sigma,H^{(0)}]\ , \tag{6}$$

and so on. The algorithm proceeds by first calculating ϕ using $\tilde{H}=H^{(0)}+H^{(1)}+\cdots$ in the usual perturbation theory from which one then calculates $\psi=T^{-1}\phi$. For example,

$$\psi_n=(1-\sigma)\psi_n^{(0)}+\sum_{n'(\neq n)}\frac{\langle n'\,|\,V^{(1)}+[\sigma,H^{(0)}]\,|\,n\rangle}{E_n^{(0)}-E_{n'}^{(0)}}\psi_{n'}^{(0)} \tag{7}$$

is the modified wave function through first order. Here we note what may be not entirely obvious and is just one example of what occurs when boundary surfaces are perturbed. Namely, $\langle n'\,|\,[\sigma,H^{(0)}]\,|\,n\rangle\neq(E_n^{(0)}-E_{n'}^{(0)})\langle n'\,|\,\sigma\,|\,n\rangle$ in the usual way, since $(\sigma\psi_n^{(0)})$ and $\psi_n^{(0)}$ do not satisfy the same boundary conditions and therefore the standard manipulations with Hermitian operators are different. In particular the $\partial\psi_n^{(0)}/\partial z$ term does not vanish on the original surface S_0 and therefore additional surface terms arise. In the specific examples to follow this will be

made more evident. We next present several applications of the FC method.

1. Surface band gap. This calculation extends our earlier discussion to include the boundary effects. We obtain for the energy gap

$$\Delta E_n = 2 \mid \langle \mathbf{k}_{\parallel}, n \mid V_I^{(1)} + [\sigma, H^{(0)}] \mid \mathbf{k}_{\parallel}, n \rangle \mid$$
$$= 2 \mid \langle \mathbf{k}_{\parallel}, n \mid V_I^{(1)} + h(\mathbf{r}_{\parallel}) \frac{dV_I^{(0)}}{dz} \mid \mathbf{k}_{\parallel}, n \rangle \mid . \quad (8)$$

The reason the commulator simplifies so, is the fact that the matrix element $\langle n \mid d/dz \mid n \rangle = 0$, and therefore, terms involving $[h, H^{(0)}]$ vanish. The terms in Eq. (8) are easily calculated analogous to Eq. (2). For corrugation heights of 0.6 and 1.0 a.u. for Cu(100), we calculated the dispersion curves and gaps indicated in Fig. 2. The experimental data has not as yet been extended as far as the gap.

2. Surface binding energies. Here we carried out a much more detailed calculation since second order perturbation theory was required and the image potential had to be calculated to the same order. The details will appear in our elaborated report.[5] Again we applied our results to Cu, Au, and Ag (100) and (111) surface states recently reported in inverse and two-photon photoemission experiments.[1,2] We find that reasonable corrugation heights (0.3 to 0.15 Å) allow the data to be interpreted in terms of a raising of the $n = 1$ level in agreement with the interpretation of Smith,[8] Wienert *et al.*,[9] and Echenique and coworkers.[10] We find for example, in atomic units: Cu(100), $E = h^2/86.965$; Ag(100), $E = h^2/125.87$; Au(100), $E = h^2/118.73$ for the binding-energy shifts.

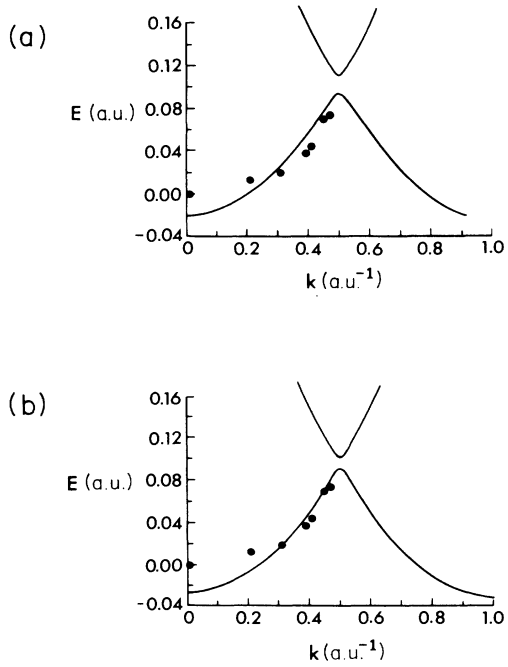

FIG. 2. Dispersion curves: (a) $h^{\max} = 1.0$ a.u.; (b) $h^{\max} = 0.6$ a.u.

These values also lead to an interpretation that the effective mass deviates from unity by less than 1%.

3. Boundary perturbations of self-consistent jellium wave functions: scanning tunneling microscopy. The importance of image states in both scanning tunneling microscopy (STM) and spectroscopy (STS) has been recently emphasized.[11] Here we discuss an application of wave functions closely related to the ones presented in the preceding discussion of photoemission. Namely it involves generating an approximate wave function $\psi(\mathbf{r}_{\parallel}, z)$, for a corrugated surface S, by replacing z with $z - h(\mathbf{r}_{\parallel})$ in the wave function $\psi^{(0)}(\mathbf{r}_{\parallel}, z)$ for the planar surface S_0, i.e., $\psi(\mathbf{r}_{\parallel}, z) = \psi^{(0)}(\mathbf{r}_{\parallel}, z - h(\mathbf{r}_{\parallel}))$. This wave function is just the FC operator $T^{-1} = \exp(-\sigma)$ applied to $\psi^{(0)}(\mathbf{r})$, namely

$$\psi(\mathbf{r}) = \exp(-\sigma)\psi^{(0)}(\mathbf{r}) , \quad (9)$$

which differs from the usual FC result in that T^{-1} is applied to eigenfunctions of $H^{(0)}$, rather than those of $\tilde{H}$.[12] We now proceed to establish the range of validity of the preceding expression for $\psi(\mathbf{r})$.

We begin by noting that in the STM problem, the hard-wall boundary condition used in the photoemission problem, $\psi(\mathbf{r}_{\parallel}, z = h(\mathbf{r}_{\parallel})) = 0$, may not be appropriate, but rather a finite potential barrier at the metal-vacuum interface may be more suitable. For the soft-wall boundary condition, ordinary perturbation theory is applicable.

We have shown[4(b)] that for a corrugated surface of wavelength λ and amplitude h_0, the planar image potential $V^{(0)}(z)$ goes to $V^{(0)}(z - h(\mathbf{r}_{\parallel}))$, for $z/h < 1$ and $z/\lambda \to 0$. Assuming that the potential close to the metal surface, and within the metal, also follows the corrugation, i.e., $V(z) = V^{(0)}(z - h(\mathbf{r}_{\parallel}))$ for all z,[13] it can be shown[14] by applying ordinary perturbation theory that in the limit of $z/\lambda \to 0$, the wave function can be approximated by $\psi(\mathbf{r}_{\parallel}, z) = \psi^{(0)}(\mathbf{r}_{\parallel}, z - h(\mathbf{r}_{\parallel}))$. In the following application to STM, we will use the aforementioned approximation for the wave function.

Tersoff and Hamann[15] have shown that the tunneling conductance in STM is proportional to the local density of unoccupied states (LDOS) of the target at the Fermi level, E_F, evaluated at the probe position $\mathbf{R}$,

$$I \sim \rho_{\mathrm{LDOS}}(\mathbf{R}, E_F) = \sum_{\mathbf{k}} \mid \psi_{\mathbf{k}}(\mathbf{R}) \mid^2 \delta(E_{\mathbf{k}} - E_F) . \quad (10)$$

Substituting our wave function into (10), we obtain

$$\rho_{\mathrm{LDOS}}(\mathbf{R}, E_F) = \sum_{\mathbf{k}} \mid \psi_{\mathbf{k}}(\mathbf{R}_{\parallel}, Z - h) \mid^2 \delta(E_{\mathbf{k}} - E_F) . \quad (11)$$

For the case that $\psi^{(0)}(\mathbf{r}_{\parallel}, z) = \exp(i\mathbf{k}_{\parallel} \cdot \mathbf{r}_{\parallel}) \phi_{k_z}(z)$, we obtain for the conductance

$$I \sim \sum_{k_z} \mid \phi_{k_z}(Z - h(\mathbf{R}_{\parallel})) \mid^2 \delta(E_{\mathbf{k}} - E_F) . \quad (12)$$

Equation (12) indicates that the contours of constant conductance follow the surface corrugation function $h(\mathbf{R}_{\parallel})$, i.e., the change in the probe position, ΔZ, is given by $\Delta Z = h(\mathbf{R}_{\parallel})$.[16]

In summary, we have determined wave functions for a corrugated metal surface. We presented specific expressions for the wave functions in terms of the corrugation function $h(x,y)$ and suggested how they might be useful in several types of electron-surface experimental probes. In particular all of these methods are capable of determining the theoretically significant function $h(x,y)$.[17]

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[12]We note that to first order in h, $\psi^{(0)}(\mathbf{r}_{||},z-h(\mathbf{r}_{||}))=(1-\sigma)\psi^{(0)}(\mathbf{r}_{||},z)$, a result which may be useful for evaluating certain types of matrix elements.

[13]In the present context this assumption is only necessary in very close to the surface where the potential saturates and becomes very non-image-like, and within the metal. In general, however, the conditions under which any potential $V(\mathbf{r})$ can be approximated by $V^{(0)}(\mathbf{r}_{||},z-h(\mathbf{r}_{||}))$ is very important. The reason for this is that very good self-consistent one-dimensional calculations involving planar surfaces have been made (see Ref. 9) wherein one could generate "very easily" approximate three-dimensional wave functions for slowly varying corrugated surfaces simply with the replacement $z\rightarrow z-h(\mathbf{r}_{||})$.

[14]V. B. Shikin, Zh. Eksp. Teor. Fiz. **60**, 713 (1971) [Sov. Phys.—JETP **33**, 387 (1971)]; W. L. Clinton, M. A. Esrick, and W. S. Sacks (unpublished).

[15]J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1985); see also M. C. Payne, J. Phys. C **19**, 781 (1986), where explicit image-potential corrections are applied in the transfer Hamiltonian formalism. In a specific example, he shows the corrections to the tunneling matrix element range between 10 and 20%. We have not included these since they will not effect our qualitative results.

[16]A necessary and sufficient condition for $I((Z-h(\mathbf{R}_{||}))$ to be constant is that $Z-h(\mathbf{R}_{||})$ be independent of $\mathbf{R}_{||}$ provided only that $\sum_{k_z}|\phi^{(0)}_{k_z}(Z-h(\mathbf{R}_{||}))|^2\delta(E_{\mathbf{k}}-E_F)$ is a monotonic function of $Z-h(\mathbf{R}_{||})$. It may also be appropriate to note here that our results do not predict the exponential decay in Z of the contours of constant conductance. Apparently this can only result from higher-order terms in the Shikin perturbation operator.

[17]We note here that in the model where the image and boundary planes are coincidental, $h(x,y)$ is precisely defined and is just the position of the "image" plane relative to a plane surface at $z=0$. This is also the average position of the screening charge $\delta\rho(\mathbf{r}_{||},z)$; $h(\mathbf{r}_{||})=\int dz\,\delta\rho(\mathbf{r}_{||},z)z$. See, for example, N. D. Lang and W. Kohn, Phys. Rev. B **7**, 3541 (1973).