

LETTER TO THE EDITOR

Image-potential-induced surface states, binding energies and lifetimes

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Abstract. An analysis of recent experimental results on image-potential-induced surface states is presented. Plasmon dispersion and single-particle effects in the medium response are included as well as the bound-state nature of the electron creating its own image potential. The formalism is accurate enough to explain well the existing experimental binding energy data. We predict a peak width narrower than the experimental one. This should be confirmed with increasing experimental resolution.

It has long been recognised that electrons can be trapped at surfaces (Tamm 1932, Shockley 1939). The electrons in such a state do not have enough energy to escape into the vacuum and cannot penetrate into the crystal because their energy lies in a band gap of the crystal. A special case arises if such states are localised in a gap containing the vacuum level. Then the electron might be trapped by its own image potential (i.e. the potential created by the polarisation charge it induces at the surface). These states are sometimes called surface-barrier-induced surface states to distinguish them from different sorts of other surface states, the ones most studied up to now; for example, the 'dangling bond' surface states on silicon, which are directly connected with the electronic properties of the bulk crystals.

Theoretical studies of barrier-induced states have used the classical image potential with a cut-off for the surface barrier. This approximation uses a potential induced by a point charge as the one felt by the electron in the surface state whereas it is precisely the bound electron which is the one creating the image potential binding itself. Recent experimental measurements (Straub and Himpsel 1984, Reihl *et al* 1984) have made a more sophisticated treatment of the localisation process important. In this Letter, we present a formalism including the bound-state nature of the electron creating its image potential, together with a treatment of the surface response which takes into account both plasmon dispersion and single-particle effects in the response of the medium. We find that dispersion effects strongly affect the binding energy. Our calculation reproduces well the recent experimental results of Straub and Himpsel and Reihl and co-workers.

Surface-induced-state characteristics are mainly decided by the surface potential and have a very mild dependence on the crystal structure of the materials. These states are not restricted to metals with s, p band gaps or to materials with metallic screening. Due to the universal nature of the image potential these states present a widespread

occurrence and appear on many insulators, molecular solids, and liquids. In fact the coulombic tail of the image potential, Z_1/z , falling as the inverse of the distance from the surface, z ($Z_1 = \frac{1}{2}[(\epsilon - 1)/(\epsilon + 1)]$), ϵ is the static dielectric constant, $\frac{1}{2}$ for a metal of course) allows an infinite Rydberg-type series to exist.

These states are of importance in a very wide range of phenomena in physics. Electronic states of this kind in insulators were first suggested on theoretical grounds by Cole and Cohen (1969) and Cole (1970) who noted that liquid helium showed total reflectivity to electrons near the vacuum zero in energy. Garcia and Solana (1973) have studied the role of the surface potential shape on surface states in a one-dimensional Kronig-Penney model. They are also important in low-energy electron diffraction (Rundgren and Malmstrom 1977, McRae 1979) experiments where they produce a detailed structure on the intensity versus energy curves before the emergence of a new beam.

A clear picture of surface states is obtained in terms of scattering theory, as suggested by Pendry and Gurman (1975). A surface state is created by multiple reflections between the atomic potentials of the crystal and the surface potential; i.e. reflection at the crystal gap and the barrier. If $r_c e^{i\varphi_c}$ and $r_b e^{i\varphi_b}$ are the reflection coefficients of the crystal and the barrier respectively, the conditions for a surface state are $r_c r_b = 1$ and $\varphi_c + \varphi_b = 2\pi n$. A trapped electron beam can lose flux via scattering with the bulk crystal, diffraction into another beam and, due to its energy parallel to the surface, by interaction with surface excitations. Echenique and Pendry (1978) calculated the binding energy and lifetime broadening of these states. They discussed observability of these states and proved that they could, in principle, be resolved for all members of the Rydberg series. Echenique and Pendry were interested in the possibility of resolving the Rydberg series and not in the actual binding energy. They presented a very simplified model calculation to evaluate the binding energy of the states in which the z -dependent local image potential was approximated by its asymptote $(4z)^{-1}$ for distances greater than a certain distance z_0 from the surface and by a constant potential $(-4z_0)^{-1}$ for distances smaller than z_0 .

In this Letter we present the results of a many-body calculation of the surface-state binding energy using a self-energy formalism (Hedin and Lundqvist 1969). Nieminen and Hodges (1978) have used this method, together with an undispersed response function to represent the medium response to study positron surface states at metal surfaces. Identical results can be obtained by a different approach to the self-energy problem recently proposed by Manson and Ritchie (1981). Our formalism takes into account both plasmon dispersion and single-particle effects in the medium response together with the bound-state nature of the electron creating its own image potential and reproduces well the existing experimental data.

Formalism. The self-energy of an electron of energy E_0 is given by

$$\Sigma(r, r', E_0) = \frac{i}{2\pi} \int d\omega W(r, r', \omega) G(r, r', E_0 - \omega).$$

The effective potential felt by the electron is then defined as

$$V_{\text{eff}}(r)\Psi_0(r) = \int \Sigma(r, r', E_0)\Psi_0(r') dr'$$

where W is the screened interaction given by

$$W(r, r', \omega) = \frac{1}{(2\pi)} \int \frac{\epsilon_s(\omega, Q) - 1}{\epsilon_s(\omega, Q) + 1} \frac{1}{Q} e^{-i\cdot Q(\rho - \rho')} e^{-Q(z+z')} dQ$$

Here $\varepsilon_s(\omega, Q)$ is related to the bulk dielectric constant $\varepsilon(\omega, k)$ via the specular reflection model of Ritchie and Marusak (1966)

$$\varepsilon_s(\omega, Q) = \frac{Q}{\pi} \int_{-x}^x \frac{dk_z}{k^2 \varepsilon(\omega, k)} \quad k^2 = Q^2 + k_z^2 \quad (4)$$

and the one-particle Green function is

$$G(r, r', \omega) = \frac{1}{(2\pi)^2} \int d^2k'' \sum_{n \neq 0} \frac{\Psi_n^*(z') \Psi_n(z)}{E_n + (k_{\parallel}''/2) - (\omega + i\delta)} e^{i\mathbf{k}'' \cdot \mathbf{r} - i\omega t} \quad (5)$$

$$\mathbf{r} = (\rho, z).$$

Ψ_n is the set of eigenstates of the effective potential. The mean potential energy of an electron in the ground state is then

$$\Delta = \frac{i}{2\pi} \int d\omega \int d\mathbf{r} \int d\mathbf{r}' W(\mathbf{r}, \mathbf{r}', \omega) G(\mathbf{r}, \mathbf{r}', E_0 - \omega) \Psi_0^*(\mathbf{r}) \Psi_0(\mathbf{r}'). \quad (6)$$

A good approximation to $\varepsilon_s(\omega, Q)$ —the surface plasmon pole approximation, including single-particle effects and plasmon dispersion in the medium response—has been proposed by Echenique *et al* (1981). Using their expressions in our calculation we get (using atomic units throughout)

$$\Delta = \frac{-\omega_s^2}{2} \sum_n \int_0^\infty \frac{\langle 0|e^{-Qz}|n\rangle \langle n|e^{-Qz}|0\rangle \theta[(\omega_s(Q) + Q^2/2 + E_{n0}) - Qk_{\parallel}]}{\omega_s(Q)[(\omega_s(Q) + Q^2/2 + E_{n0})^2 - (Qk_{\parallel})^2]} dQ. \quad (7)$$

Here θ is the step function, ω_s is the surface plasmon energy and $\omega_s(Q)$ is given by

$$\omega_s^2(Q) = \omega_s^2 + \alpha Q + \beta Q^2 + Q^4/4 \quad (8)$$

$\alpha = (3/5)^{1/2} \omega_s v_F$; v_F being the Fermi velocity and $\beta = 0.0026 + (2.6798/r_s^{1.85})$ where r_s is the electron gas parameter; $E_{n0} = E_n - E_0$ is the energy difference between the n th state and the ground state associated with the motion normal to the surface.

Since for high n -values, wavefunction overlap with the ground state will be small and in any case for the discrete states $E_{n0} \ll \omega_s$, a good approximation to Δ might be obtained by taking $E_{n0} = 0$ in the integrand of equation (8), then the sum over intermediate states is approximately done by using the closure relation. We have

$$\Delta = \frac{-\omega_s^2}{2} \int_0^\infty \frac{\langle 0|e^{-2Qz}|0\rangle \theta[(\omega_s(Q) + Q^2/2) - Qk_{\parallel}]}{\omega_s(Q)[(\omega_s(Q) + Q^2/2)^2 - (Qk_{\parallel})^2]^{1/2}} dQ. \quad (9)$$

To assess the importance of including plasmon dispersion and single-particle effects on the medium response, we have evaluated variationally for $k_{\parallel} = 0$ the binding energy, using a trial wavefunction of the form $\Psi_0(z) = Cz e^{-\Gamma z}$, as a function of the electron gas density parameter Γ_s for both the dispersed and the undispersed model. The results of our calculations are shown in figure 1, showing that inclusion of dispersion in the surface response alters significantly the binding energy. This trial wavefunction and its boundary conditions at the surface are not very realistic. They correspond to an infinite-barrier model for the crystal, the phase of the crystal reflectivity being π . Instead of an infinite barrier, there is a band gap, and the phase of the crystal reflectivity will change by π as we go across the gap. So to compare with the experimental results, we have calculated the binding energy variationally, using a trial wavefunction of the form $\Psi_0(z) = (az +$

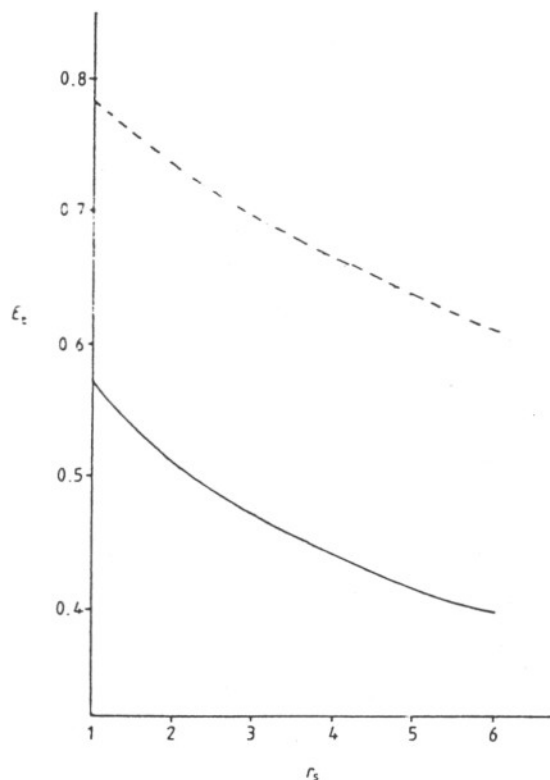


Figure 1. Binding energy in eV of an electron trapped by its own image potential and an infinite barrier to represent the crystal as a function of the electron gas density parameter r_s for a dispersed (—) and an undispersed model (---) for the surface response.

b) $e^{-\Gamma z}$. The crystal boundary conditions are fixed by the crystal reflectivity which we obtained from a simplified treatment of the crystal wavefunctions at the gap (Inglesfield 1982). As stated, the phase of the crystal reflectivity will change by π as we go across the gap. For our calculation, we take the value at the middle of the gap which is where the experiments show the vacuum zero to lie. We find, for the state at the bottom of the band, a binding energy of 0.65 eV for copper and 0.61 for silver. They compare well with the experimental findings.

A word of caution should, however, be added. Although the penetration of the wavefunction in the crystal is generally small, a quantitative estimation depends on the position of the state at the gap and on the particular surface face. This effect results in an extra contribution to the binding energy due to the roughness of the potential (García *et al* 1985). On the other hand the position of the image plane, or the coefficient of the linear term in Q in the surface response function, can be varied thus effectively changing the calculated binding energy.

The correction to the effective mass in the parallel direction due to the many-body interaction between the bound state and the surface can be evaluated by expanding equation (9) in powers of k_{\parallel}^2 . We find the correction to be less than 1%. While inclusion of small-energy electron-hole pairs in the medium response will increase this contribution, their effect, we believe, cannot explain the experimentally observed masses of 1.2 and 1.3.

So far, we have concentrated on the position of the state, and we have assumed $r_c = 1$. There are three effects of which we must take account: real surface excitations, the absorption in the crystal due to decay of the state into excitations of the crystal, and, in a general case, the fact that flux can also be lost by diffraction into other beams which escape from the surface, thus reducing r_c to being less than unity even in the absence of absorption due to inelastic effects. These processes were discussed by Echenique and Pendry (1978) in their paper. They gave 0.32 eV for the width of the first state which agrees well, as remarked by Straub and Himpsel, with their experimental findings. However, at the energies of the inverse photoemission experiment of Straub and Himpsel and for the state at the bottom of the image-state band, the only contribution to the width comes from decay to the crystal states and is small because of the small overlap between the wavefunctions. Even assuming that the electron feels the total imaginary part of the self-energy in the bulk, the phase of the barrier reflectivity (equations (34) and (35) of the Echenique and Pendry (1978) paper) is big enough to lead to a small energy broadening. In other words, the Rydberg state's wavefunctions are effectively decoupled from the crystal wavefunctions and thus the small broadening. This is precisely why these states can be observed. An upper limit of 0.1 eV for the state width results from the same parameters as used by Echenique and Pendry. Note that because of this finite width a tunnelling current can be established throughout these states in spite of their localised character (Binning *et al* 1985, Becker *et al* 1985, Louis *et al* 1986).

A very recent experiment (Giesen *et al* 1985) has confirmed our prediction of an upper limit of 0.1 eV for the width of the state. Also, a detailed experimental study of such states over a wide range of materials and energies will give much experimental information about the detailed nature of electron surface interactions and the form of the image potential.

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