

## Lifetimes of Stark-Shifted Image States

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The inelastic lifetimes of electrons in image-potential states at Cu(100) that are Stark shifted by the electrostatic tip-sample interaction in the scanning tunneling microscope are calculated using the many-body *GW* approximation. The results demonstrate that in typical tunneling conditions the image state lifetimes are significantly reduced from their field-free values. The Stark shift to higher energies increases the number of inelastic scattering channels that are available for decay, with field-induced changes in the image state wave function increasing the efficiency of the inelastic scattering through greater overlap with final state wave functions.

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The scanning tunneling microscope (STM) is a versatile and powerful probe of surface electronic structure, but it is not ideal. The electric field between the probe tip and the surface of the sample affects the surface. This influence can be exploited to positive effect, most dramatically through the controlled modification of surface atomic structure [1,2]. More prosaically, the influence of the tip must be allowed for interpreting STM measurements, especially at semiconductor surfaces where tip-induced band bending occurs [3].

Recently a significant Stark effect—the shift in energy due to the electric field—has been identified in scanning tunneling spectroscopy (STS) of Shockley surface-state electrons at a metal surface [4]. Surface states, in which the electron is caught between the barrier potential outside the surface and a band gap in the crystal, have been extensively studied by STM and STS, with a particular focus on their dynamics [5–8] and interactions [9], and the recognition of a Stark shift in the case of Shockley states reconciles a discrepancy that has existed between STS-derived binding energies and those from photoelectron spectroscopy [10]. A more pronounced Stark effect has been known for some time [11,12] in the case of a second class of surface electron state, namely, the image-potential states that arise when an electron outside a conductor polarizes the surface and is attracted to the resulting “image charge,” shown schematically in Fig. 1. Image-potential states are more weakly bound than Shockley surface states (which lie close to the Fermi energy  $E_F$ ), forming a hydrogeniclike series with energies

$$E_n = E_v - \frac{0.85 \text{ eV}}{(n + a)^2}, \quad n = 1, 2, \dots, \quad (1)$$

converging on the vacuum level of the surface  $E_v$ . In (1)  $a$  is a quantum defect that depends upon the surface. Tunneling via image states requires significantly greater bias voltages than Shockley states, and the image state electrons are Stark shifted to higher energies by several tenths of an eV [11–13].

The presence of a measurable Stark shift in the surface-state energies raises the important question as to whether there are also changes in the inelastic interactions of the surface-state electrons in the presence of the STM tip. Electronic excitations in the surface-state bands decay on a femtosecond time scale through interactions with the electrons and phonons of the surface and bulk, and there has been considerable activity in recent years directed at an understanding of these interactions [14]. A significant electric-field-induced lifetime change would have important consequences for the interpretation of STM and STS experiments investigating the dynamical properties of image-potential states, for example, in nanostructures where the lateral resolution of the STM is paramount, yet the possible influence of the electric field on the lifetimes measured by the STM has not previously been considered.

To investigate this issue, we have performed many-body calculations of the lifetimes of image-potential states at Cu(100) including for the first time an electric field due to the tip of an STM. Our calculations are an extension of the approach introduced by Chulkov *et al.* [15] and used sub-

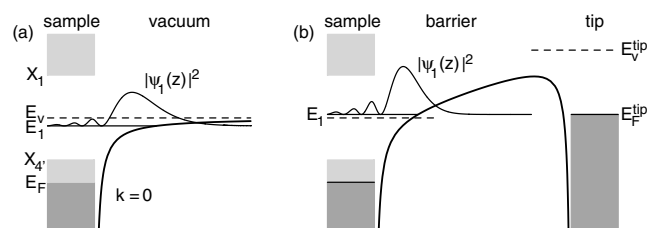


FIG. 1. (a) Schematic energy diagram for the potential at the Cu(100) surface. The vacuum level (dashed line) lies near the center of the projected band gap that extends between the bulk  $X_4'$  and  $X_1$  levels at  $k_{\parallel} = 0$ . The image potential (thick solid line) produces a hydrogeniclike series of states; the  $n = 1$  level and corresponding probability density are shown. (b) Energy diagram in the presence of the STM tip, at the threshold bias for tunneling into the  $n = 1$  image state. The field in the tunnel junction causes a Stark shift of the image state spectrum, with concomitant modification of the state densities.

sequently in numerous surface-state lifetime studies with considerable success [14]. The damping rate or inverse lifetime of the image state is calculated from the expectation value of the imaginary part of the nonlocal self-energy operator

$$\Gamma = \hbar/\tau = -2 \int d\mathbf{r} \int d\mathbf{r}' \psi^*(\mathbf{r}) \text{Im}\Sigma(\mathbf{r}, \mathbf{r}'; E) \psi(\mathbf{r}'). \quad (2)$$

The energy of the image state is  $E$ , and  $\psi$  is the wave function. The imaginary part of the self-energy is calculated in the  $GW$  approximation of many-body theory, which uses the first term only in the series expansion of  $\Sigma$  in terms of the screened Coulomb interaction  $W$ :

$$\text{Im}\Sigma(\mathbf{r}, \mathbf{r}'; \epsilon) = -\frac{1}{\pi} \int_{E_F}^{\epsilon} d\epsilon' \text{Im}G(\mathbf{r}, \mathbf{r}'; \epsilon') \text{Im}W(\mathbf{r}, \mathbf{r}'; \epsilon - \epsilon'). \quad (3)$$

We use the zeroth order approximation to the Green function; in the spectral representation

$$G(\mathbf{r}, \mathbf{r}'; \epsilon) = \sum_i \frac{\psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')}{\epsilon - E_i + i\delta}, \quad (4)$$

where the  $\psi_i(\mathbf{r})$  are one-electron eigenfunctions with eigenenergies  $E_i$  and  $\delta$  a positive infinitesimal. The screened interaction is evaluated in the random phase approximation (RPA)

$$W(\mathbf{r}, \mathbf{r}'; \omega) = V(\mathbf{r} - \mathbf{r}') + \int d\mathbf{r}_1 \int d\mathbf{r}_2 V(\mathbf{r} - \mathbf{r}_1) \times \chi^0(\mathbf{r}_1, \mathbf{r}_2; \omega) W(\mathbf{r}_2, \mathbf{r}'; \omega), \quad (5)$$

where  $V(\mathbf{r})$  is the bare Coulomb interaction and  $\chi^0(\mathbf{r}, \mathbf{r}'; \omega)$  is the density-density response function of the noninteracting electron system:

$$\chi^0(\mathbf{r}, \mathbf{r}'; \omega) = -\frac{2}{\pi} \int_{E_F}^{\epsilon} d\epsilon \text{Im}G(\mathbf{r}, \mathbf{r}'; \epsilon) [G(\mathbf{r}, \mathbf{r}'; \epsilon + \omega) + G^*(\mathbf{r}, \mathbf{r}'; \epsilon - \omega)]. \quad (6)$$

This  $GW$ -RPA approach has been shown to give decay rates for image states at Cu surfaces that are within 1 meV of those found using the more complete  $GW$ T-TDLDA approximation [16], in which exchange-correlation effects that are omitted in  $GW$ -RPA are included in both (5) and (6). Note that the phonon contribution to the decay rate of image-potential states at Cu(100) is  $<0.5$  meV and so safely ignored here [17].

We calculate the Green function using a one-dimensional pseudopotential which by construction reproduces the Cu(100) bulk band edge energies  $X_4'$  and  $X_1$ , and the energies of the unoccupied surface resonance and first image state at the field-free surface, and which also accurately predicts the energies of the higher image states [18]. In the direction parallel to the surface we assume parabolic dispersion with effective masses ( $m^*$ ) fitted to *ab initio* band structures. To model the influence of the STM we

follow Limot *et al.* [4] and include a linear potential due to the bias voltage between the STM tip and the sample, and modify the image potential to include the multiple images in the tunnel junction geometry. Using this potential we are able to reproduce the sequence of Stark-shifted image state energies and increments in the tip-sample distance observed at Cu(100) in  $z(V)$  spectroscopy by Wühl *et al.* [13], who were also able to describe them using a model that omitted multiple images.

In Fig. 2 we show the calculated damping rates (inverse lifetimes) of the Stark-shifted  $n = 1$  image-potential state at Cu(100). Calculation parameters have been systematically varied to ensure that decay rates are converged to within 1 meV. At the field-free Cu(100) surface, the image state lies at an energy of  $-0.57$  eV relative to the vacuum energy, and we find  $\Gamma = 18 \pm 1$  meV for this state, corresponding to a lifetime of  $\tau = 37 \pm 2$  fs. This compares well with the lifetime  $\tau = 40 \pm 6$  fs measured using time-resolved two-photon photoemission (2PPE) [19,20], and  $\tau = 38$  fs found in previous  $GW$  calculations [16]. In the presence of the electric field due to the STM tip, the image state electrons are Stark shifted to higher energies. At currents of 0.1–1 nA the  $n = 1$  level is observed in  $z(V)$  spectroscopy at bias voltages near 4.7 V, corresponding to an energy  $E_1 \simeq E_v + 0.1$  eV [13]. For the results in Fig. 2 the tip-sample separation has been varied so that the bias voltage coincides with the  $n = 1$  image state energy in the presence of the electric field. This situation corresponds to the onset of tunneling into the  $n = 1$  level [Fig. 1(b)]. In these conditions the resulting image state energy increases linearly with the applied electric field, and we find that the decay rates also increase linearly. The rate of change is  $d\Gamma/dE_1 = 0.037 \pm 0.002$ , so that when the image state is

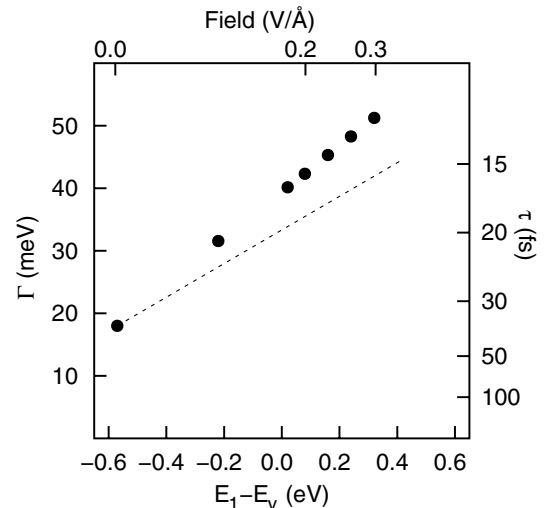


FIG. 2. Calculated decay rates ( $\Gamma$ ) and lifetimes ( $\tau$ ) of the Stark-shifted  $n = 1$  image state at Cu(100) (filled circles).  $E_1$  is the image state energy in the presence of the electric field, and  $E_v$  the field-free vacuum level of Cu(100). The significance of the dashed line is explained in the text.

Stark shifted to  $E_1 = E_v + 0.1$  eV the lifetime is only 15 fs, a reduction of 60% from the field-free value.

Recently the phase relaxation time of electrons in the  $n = 1$  image state at Cu(100) has been studied using the STM by Wühl *et al.* [13], who measured the spatial decay of quantum interference patterns near steps. This technique measures the lifetime of electrons with nonvanishing momentum  $\hbar\mathbf{k}_{\parallel}$  parallel to the surface, corresponding to energies above the image state band minimum:  $E(\mathbf{k}_{\parallel}) = E_1 + \hbar^2 k_{\parallel}^2 / 2m^*$ . In Fig. 3 we compare calculated decay rates as a function of lateral energy with those reported in Ref. [13]. There it was concluded that the STM tip did not substantially alter the dynamical properties of the image-potential states, but subsequently an error has been recognized in the identification of the phase relaxation length that was used [21] so that the values displayed in Fig. 3 have been multiplied by 2 to correct for this. The calculations are performed for fields which give  $E_1 = 4.7$  eV. Also shown are calculated results for the field-free case, along with values from the 2PPE measurements [20] that correspond to this case. The overall agreement between theoretical and experimental lifetimes shown in Fig. 3 is very good and confirms the existence of a significant field-induced change in the inelastic lifetimes of the image state electrons.

We now consider the origin of this effect. In Fig. 4 we compare the probability density  $|\psi|^2$  and the imaginary part of the self-energy  $\text{Im}\Sigma$  at the Cu(100) surface calculated both with and without the electric field caused by the

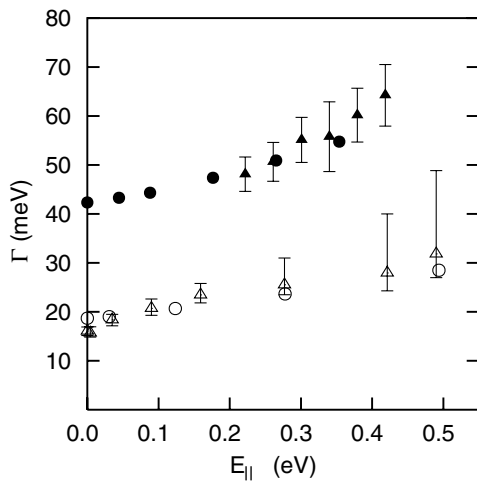


FIG. 3. Decay rates of electrons in the  $n = 1$  image state band at Cu(100) as a function of lateral energy  $E(\mathbf{k}_{\parallel}) - E_1$ . Filled symbols correspond to Stark-shifted electrons with energy  $E_1 = 4.7$  eV at  $k_{\parallel} = \mathbf{0}$ ; circles are calculated decay rates and triangles plus associated error bars are experimental decay rates from Ref. [13] multiplied by 2 to correct for an error in the phase relaxation length used in that work [21]. Open symbols are field-free results; circles are calculated decay rates, triangles plus associated error bars are decay rates from 2PPE experiments [20].

tip of the STM. The changes in  $|\psi|^2$  show that accompanying the Stark shift to higher energies is a redistribution of the weight of the surface state towards the metal surface, which increases the spatial overlap with the nonlocal self-energy. By displacing the image state electron towards the surface, the inelastic scattering channels are rendered more efficient. Calculating  $\Gamma$  using the wave function of the Stark-shifted state but the self-energy of the field-free surface at the unperturbed image state energy accounts for approximately three-quarters of the full increase in  $\Gamma$ , as shown by the dashed line in Fig. 2.

The remaining change in the decay rate originates in the increase in the magnitude of  $\text{Im}\Sigma$  that can also be seen in Fig. 4. We find that calculating the self-energy using in (3) either the screened interaction  $W(\mathbf{r}, \mathbf{r}'; \epsilon)$  of the field-free surface or of the surface in the presence of the electric field gives comparable results; i.e., the changes in the electron wave functions caused by the electric field of the STM tip do not have a significant effect on the screening of the Coulomb interactions that dominate the inelastic scattering of the image state. Instead, the change in  $\text{Im}\Sigma$  is due to the increase in the number of final states into which the image state can decay, i.e., the number of states between  $E_F$  and the image state energy, which is Stark shifted to higher energies by the tip-surface interaction of the STM. Thus the decreased lifetime of the Stark-shifted image-potential states results from an increase in the number of final states available for inelastic scattering along with increased efficiency of inelastic channels due to the greater spatial overlap of initial and final state wave functions.

Given the magnitude of the tip-induced change in the lifetimes of image-potential states, it is worthwhile to consider whether similar changes affect STM-derived life-

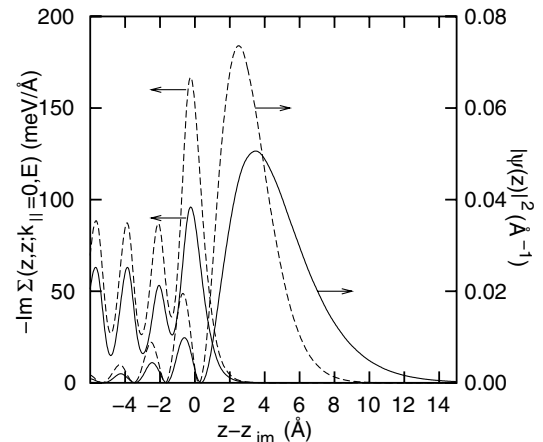


FIG. 4. Probability density  $|\psi|^2$  of the  $n = 1$  image state normal to the Cu(100) surface ( $\hat{z}$ ;  $z_{\text{im}}$  is the position of the image plane) and the negative imaginary part of the self-energy  $-\text{Im}\Sigma$  evaluated for  $\mathbf{k}_{\parallel} = \mathbf{0}$  and at the image state energy, shown for  $z = z'$ . Solid lines are for the unperturbed image state,  $E_1 = E_v - 0.57$  eV, and dashed lines for the surface where the image state is Stark shifted to an energy  $E_1 = E_v + 0.08$  eV.

times of Shockley surface states [5–8]. A calculation for the  $k_{\parallel} = 0$  state at Cu(111) indicates that for this state the effect is much smaller. The Shockley state lies at  $E_F - 0.435$  eV, which means that under typical tunneling conditions the electrostatic tip-surface interaction gives rise to fields that are 5–10 times smaller than those present when tunneling into image-potential states, and the resulting Stark shift is much smaller: 10–15 meV [22]. This causes only a minor change in the number of final states that are available for decay. Furthermore, unlike image-potential states that lie predominantly outside the surface, much of the Shockley state lies inside the metal and is screened from the tip-induced electric field; there is a negligible change in the wave function penetration in the presence of the fields. Overall the electron-electron scattering decay rate that contributes two-thirds of the total decay rate of  $\approx 21$  meV [14] changes by less than 5% in the electric field. Although the effect of the Stark shift is not quantitatively significant in this particular case, the physical picture that has been presented for the mechanism underlying the lifetime change in an electric field makes it clear that the tip-induced field will have an increasing and potentially important effect on the lifetimes of Shockley states that lie further from  $E_F$ , especially at positive energies [7].

To conclude, we have used the many-body *GW*-RPA method to calculate the inelastic lifetimes of electrons in image states at Cu(100) including for the first time the electric field due to the tip-surface interaction in the STM. We find that under typical tunneling conditions the lifetime of electrons in the  $n = 1$  image state band is reduced by some 60% compared to in the absence of the STM tip. The Stark shift to higher energies increases the number of inelastic decay channels that are available, while the electric field moves the image state electrons closer to the metal surface, which significantly increases the efficiency of the scattering channels due to increased spatial overlap with final state wave functions. This tip-induced change in electron lifetimes must be taken into account when using the STM to study the dynamical properties of higher-lying surface electron states.

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