We present a quantitative many-body analysis using the GW approximation of the decay rate $\Gamma$ due to electron-electron scattering of excitations in the Shockley surface state band of Ag(111), as measured using the scanning tunnelling microscope (STM). The calculations include the perturbing influence of the STM, which causes a Stark-shift of the surface state energy $E$ and concomitant increase in $\Gamma$. We find $\Gamma$ varies more rapidly with $E$ than recently found for image potential states, where the STM has been shown to significantly affect measured lifetimes. For the Shockley states, the Stark-shifts that occur under normal tunnelling conditions are relatively small and previous STM-derived lifetimes need not be corrected.

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Theoretical analysis of STM-derived lifetimes of excitations in the Shockley surface state band of Ag(111)

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The femtosecond lifetimes $\tau$ of electronic excitations in noble metal surface bands can be determined using the scanning tunnelling microscope (STM). The STM-based techniques complement those that use photoexcitation such as photoemission spectroscopy (PES) and two-photon photoemission, being applicable to both electron-like and hole-like excitations in combination with the advantages of atomic-scale spatial resolution. There are two principal methods available. The first is based upon line shape analysis of differential conductivity $(dI/dV)$ measurements, along with artificial or naturally occurring nanoscale resonator structures which are used to induce spectral structure over a wide range of energies. The second approach is based upon the spatial variation of quantum interference patterns that are visible in $dI/dV$ measurements. These are analysed to determine the phase coherence length $L_\phi$, which can be converted to the lifetime via the group velocity $v_g$: $\tau = L_\phi/v_g$.

An analysis of Ag(111) Shockley lifetime values determined using these two different STM techniques has demonstrated that considerable agreement exists, over a range of energies. The lifetimes are also comparable to state-of-the-art many-body calculations using the GW method, but decrease more rapidly with increasing energy. In comparing theoretical and experimental lifetimes no consideration has yet been given to the possible consequences of the perturbing influence of the STM tip, which is known to cause a measurable Stark-shift in the surface state energy $E$. Many-body GW calculations have shown that in the case of the higher-lying image potential states this Stark-shift is accompanied by a significant increase in the inelastic decay rate, the electric field between the STM tip and sample leads to a doubling of the decay rate under normal tunnelling conditions. Here we perform a quantitative study using the many-body GW method to quantify for the first time the impact of the STM tip on the electron-electron scattering rate of Shockley state electrons. We discount the possibility of a significant Stark-shift induced change to the electron-phonon contribution, which has previously been shown to be constant for excitations with energies in excess of 20 meV.

Our calculations are based upon the approach developed by Chulkov and coworkers, and used widely in calculations of surface state dynamics including the lifetimes of Stark-shifted image potential states. The damping rate or inverse lifetime of an excitation in the state $\psi(r)$ with energy $E$ is obtained from the expectation value of the imaginary part of the electron self-energy, $\Sigma(r, r'; E)$:

$$\Gamma = \frac{1}{\tau} = -2\int dr dr' \psi^*(r) \text{Im}\Sigma(r, r'; E)\psi(r').$$  \hspace{1cm} (1)

In the GW approximation of many-body theory the imaginary part of the self energy is calculated in terms of the screened Coulomb interaction $W$ and the Green function $G$

$$\text{Im}\Sigma(r, r'; \epsilon) = -\frac{1}{\pi} \int_{E_F}^{\infty} d\epsilon' \text{Im}G(r, r'; \epsilon')\text{Im}W(r, r'; \epsilon - \epsilon').$$  \hspace{1cm} (2)

A successful account of the decay rates of the noble metal Shockley surface states is possible using for the Green function its non-interacting counterpart

$$G(r, r'; \epsilon) = \sum_i \frac{\psi_i(r)\psi_i^*(r')}{\epsilon - E_i + i0^+},$$  \hspace{1cm} (3)

and evaluating the screened Coulomb interaction in the random phase approximation (RPA),

$$W(r, r'; \omega) = \frac{\omega}{v(r-r')} + \int dr_1 \int dr_2 v(r-r_1) \times \chi^0(r_1, r_2; \omega) W(r_2, r'; \omega)$$  \hspace{1cm} (4)

where $v$ is the bare Coulomb interaction and $\chi^0$ is the density-density response function of the non-interacting electron system.
In the calculations reported here we have therefore used surface state crossing the band edge, which is incorrect. be seen in Fig. 1. The parabolic dispersions result in the effective masses of interest here these provide a poor description of the intrinsic surface state and the lower band edge respectively, but we find that over the extended energy range in Fig. 2 is primarily due to the change in the rate of in-
traband scattering, the process by which the hole is filled by an electron from within the surface state band itself. The integral in Eqn. (2) is over final states, and by isolating contributions to the imaginary self energy due to the surface state band (2) is over final states, and by isolating contributions to

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\frac{\partial \Gamma}{\partial E} = 0
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The rate of increase is comparable to that found for image state electrons, with \(\frac{d\Gamma}{dE} = 0.050\), compared to \(d\Gamma/dE_1 = 0.037\) for the Cu(001) n = 1 image state, although the range of accessible Stark-shifted energies is significantly smaller so that the absolute change in decay rates that occurs for the Shockley state is much smaller. The integral in Eqn. (2) is over final states, and by isolating contributions to the imaginary self energy due to the surface state band and using just those to calculate the decay rate allows \(\Gamma\) to be decomposed into intraband and interband contributions. We find that the variation in the decay rate shown in Fig. 2 is primarily due to the change in the rate of intraband scattering, the process by which the hole is filled by an electron from within the surface state band itself. The interband contribution, in which the hole is filled by an electron from the bulk continuum, contributes less than 6% of the overall decay rate.

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To understand the origin of the change in the decay
FIG. 2: Decay rate $\Gamma$ due to electron-electron scattering of hole-like excitations at the bottom of the Shockley surface state band on Ag(111), as a function of Stark-shifted energy $E_0$. Filled triangles show the total decay rate, and open triangles the intraband contribution. The inset illustrates intraband and interband decay processes.

rate we have performed a number of auxiliary calculations, focusing on the dominant intraband decay rate. These show that the physical basis for the increase in the decay rate is the increased number of final states available for decay. The calculations are as follows. At the field-free surface we find $\Gamma_{\text{intra}} = 2.66$ meV, and when the surface state is Stark-shifted to a binding energy of $-80$ meV we find $\Gamma_{\text{intra}} = 3.41$ meV. If we calculate the decay rate using the Stark-shifted eigenvalues but replace the corresponding wave functions by their unperturbed counterparts, we find $\Gamma_{\text{intra}} = 3.37$ meV, which is close to the result of the calculation using the field-perturbed wave functions, and conversely using the Shockley wave functions calculated in the presence of the applied field, but the unperturbed energies, gives $\Gamma_{\text{intra}} = 2.67$ meV, close to the field-free decay rate. Hence changes in the wave functions of the surface and bulk states due to the STM-induced electric field are of minor importance, which is different to the situation found for the $n = 1$ image state at Cu(001) where changes in the wave function are the most important contributor to the increased decay rate.

Next we have also calculated the decay rate using the field-free energies and wave functions, but with the surface state wave function in the Green function Eqn. scaled by $\sqrt{80/63}$; 80/63 is the ratio of the number of electrons in the surface state band in the perturbed and unperturbed systems. The resulting decay rate is $\Gamma_{\text{intra}} = 3.41$ meV. This simple re-normalisation of the contribution of the surface state to the sum (integral) over final states in the evaluation of the self-energy, Eqn. is sufficient to reproduce the result of the calculation using the properly Stark-shifted states, and indicates that it is only the change in the total number of states available to fill the hole that matters, and not their changed energies.

We have extended this study to also consider the decay rate of excitations at energies further up the Ag(111) Shockley surface state band. These have been measured experimentally using line shape analysis in nanoscale resonators and from studies of quantum interference patterns near steps and in triangular adatom corrals. We consider energies between 0 and 1 eV where the surface state is well defined. Physically this energy range is of interest as within it there is a cross-over in the primary decay channel from intraband to interband dominated decay. In these calculations we keep the tip-sample separation fixed at 8 Å as the bias voltage is varied (this distance results in a 4 meV Stark-shift of the band edge, as was presented in Ref. [3]), and we once again calculate the decay rate of the surface state at the tunnelling threshold, where the energy of the Stark-shifted state coincides with the Fermi energy of the tip.

The results are presented in Fig. Using this fixed tip-sample separation we find that the Stark-shift $\Delta E$ of the surface state energy increases linearly with the bias over the range of voltages considered, and reaches 22 meV when the bias is 1 V (Fig. inset). However, accompanying the field-induced modification of the surface state we find a rather small change in the decay rate. The additional numerical complexity associated with the reduced symmetry of an excitation with a finite wave vector

FIG. 3: Calculated change in the decay rate induced by the electric field of the STM, for Ag(111) surface state electrons at the tunnelling threshold ($E - E_F = eV$). A tip-sample separation of 8 Å has been used. The inset shows the size of the Stark-shift.
results in a greater uncertainty in the calculated decay rate away from the band edge. Allowing for this, we find that the change in the decay rate is less than 0.3 meV over most of the range, only reaching 0.7 ± 0.15 meV for a bias of 1 V.

We now consider our results as a whole and in the context of experimental studies. In the case of holes at the bottom of the surface state band, in the measurements of Kliewer et al., the onset was observed at −67 meV for Ag(111), corresponding to a Stark-shift of 4 meV from the PES field-free value. Our calculations reported here (Fig. 2) show that the corresponding decay rate is increased by 0.2 meV above the field-free value, which is within the experimental uncertainty. For electron-like excitations in the surface state band the decay rate increases with energy due to the increase in available decay channels, and for an energy 1 eV above $E_F$ the corresponding contribution to the linewidth is approximately 40 meV. The STM-induced increase of $\sim 0.7$ meV is small in comparison, and again well within the experimental uncertainty.

Therefore, to conclude, on the basis of our quantitative theoretical many-body analysis using the GW approximation we have demonstrated that in contrast to the case of image potential states, the lifetimes of excitations in noble metal Shockley surface state bands determined using the STM are not sufficiently affected by the electric field of the STM tip that previously reported values need to be corrected. We have identified that relative changes of up to 30% can occur under extreme but experimentally accessible tunnelling conditions, and the decay rate actually changes more rapidly as a function of the Stark-shift for Shockley states than for image potential states. However the significantly smaller Stark-shifts that occur when tunnelling via the lower-lying Shockley states under normal tunnelling conditions mean that the absolute changes in the decay rate lie within experimental uncertainties previously reported.

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assuming parabolic dispersion $E(k) = E_0 + \hbar^2 k^2/(2m^*)$:

$v_g = \hbar k/m^*$. Fitting a parabola to our \textit{ab initio} surface state dispersion (Fig. [1]) to obtain $m^*$ and comparing $\hbar k/m^*$ with $(1/\hbar) dE(k)/dk$ shows differences can exceed 10\%.