

Surface Science Letters

Influence of surface band gaps on the lifetimes of charge transfer states

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Abstract

Using a first principles electronic structure method, we investigate how a band gap in the surface projected density of states of a noble metal influences the resonant tunneling lifetime of an atomic level near the surface. Comparing Li atoms outside Cu(111), where the Li 2s level is within the gap, with Cu(001), where the Li 2s level is below the gap, reveals that the lifetime of the ionization level of Li is longer on Cu(111). This difference is caused both by the decreased final state phase space for the tunneling electron on Cu(111) and by a reduction in intra-atomic hybridization in Li outside a surface whose band gap encompasses the ionization level. Our results are consistent with previous experiments and theory that predict a similar trend for the ionization level of Cs above Cu(111) and Cu(001).

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Charge transfer (CT) processes between adsorbates and solid surfaces are key features in a variety of important phenomena such as catalysis [1,2] corrosion [3] and stimulated desorption [4]. However, even for simple adsorbates such as alkali atoms on metal surfaces, our understanding of the CT process is still incomplete due to the difficulty in developing a theory of charge transfer that properly accounts for the detailed electronic structure of the surface and the adsorbate and their chemical interaction [5–9].

When the energy levels of the adsorbate and the metal overlap, resonance charge transfer becomes the dominant CT mechanism [10]. Formally, the resonance charge transfer (RCT) rate between an adsorbate and a substrate can be determined from the broadening of the ionization level due to interaction with the substrate. This RCT rate is then inversely related to the lifetime of the adsorbate state by the uncertainty principle. Thus, if the resonance width can be

measured or calculated, the RCT rate may be inferred directly from it.

A number of theoretical methods for the calculation of the broadening of atomic levels near metal surfaces have been developed and applied to experimental systems of interest [11–13]. In these approaches, the potential for the tunneling electron is constructed by adding model potentials representing the surface and the atom and empirical correction terms to account for the effects of the atom–surface interaction.

Recent time-resolved 2-photon photoemission (TR-2PPE) experiments have suggested that surface specific electronic effects, such as the surface projected band gap in Cu, can strongly affect the lifetime of charge transfer states of alkali atoms [14–18]. In particular, the lifetimes of alkali atoms adsorbed on Cu(111), where the band gap encompasses the ionization levels, were found to be much longer than on Cu(001), where such levels lie below the surface-projected band gap. These experiments [4,14–17,19] demonstrated that the band gap can suppress charge

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transfer, leading to increased excited state lifetimes of adsorbates on Cu(111).

Few theoretical studies have attempted to model the effects of surface band gaps on the broadening of adsorbate states, mainly due to the complex nature of the potential needed to mimic the surface band gap [6,20]. Borisov and coworkers studied Cs on Cu(111) and Cu(001) using a model potential [7]. Their study conclusively demonstrated that the presence of a band gap decreases the width of the atomic level. The band gap reduces the available final phase space density for the tunneling electron and increases the effective tunneling barrier between the atom and the surface states by forcing the electrons to tunnel into large parallel momentum states. While their calculated one-electron tunneling rates for Cs on Cu(111) and Cu(001) were in qualitative agreement with measurements, they showed that it was necessary to include inelastic electron–electron scattering contributions to the adsorbate lifetimes in order to obtain quantitative agreement.

We recently developed a first principles-based scheme to extract adsorbate widths from self-consistent calculations of the full valence interaction between the ionization level of the adsorbate and a surface [21,22]. The advantage of this approach is that it is parameter-free and makes no assumptions about the form of the potentials representing the atom, the surface, and their interactions. The electronic structure and surface potential is calculated self-consistently in the presence of atom–surface interaction with only the usual approximations within density functional theory (DFT), namely the choice of pseudopotentials representing the nuclei plus core electrons and the exchange–correlation functional representing the quantum mechanical electron–electron interactions. In a recent application to Li on transition metals [23], we showed that the presence of the d-electrons in the substrate can have a pronounced effect on the width of the ionization level by mediating a non-image like intra-atomic hybridization of the Li valence levels. In particular, we showed that the d-band can induce a strong mixing of the relatively short-lived Li 2p state into the predominantly 2s-like ionization level of Li.

In this Letter, we use this periodic DFT-based scheme to investigate the effects of a Cu surface band gap on the lifetimes of the ionization level of Li. We find that the width of the Li ionization level is strongly influenced by the presence of a band gap. The mechanism is both a band-gap-induced reduction in the available phase space for the tunneling electron, as originally predicted by Borisov et al. [24], and a band-gap-induced reduction in the d-band-mediated intra-atomic hybridization of the valence orbitals of the Li atom. This latter effect has not been noted before and cannot be modeled without specific inclusion of the d-electrons in the substrate.

We investigate the band gap effect by comparing the self-consistent valence electronic structure of Li above Cu(111) and Cu(001) using the periodic DFT program CASTEP_3.2 [25]. The Cu(111) and Cu(001) supercells contained 9 atoms per layer (p-3×3) and 8 atoms per layer

(c-2×2), respectively. Electron exchange and correlation is described by the local density approximation (LDA) [26,27]. The pseudopotentials for Cu and Li are taken from the Trouiller–Martins libraries created by Allan and Teter [28,29]. We employ a planewave basis kinetic energy cutoff of 850 eV. The Cu(111)-(3×3) and the Cu(001)-c(2×2) supercells contained k-point spacings of 0.0376 1/a.u. and 0.0343 1/a.u., respectively. These numerical parameters converge the Li energy level widths to within 0.05 eV. Periodic images of the surfaces are separated by 49 a.u. of vacuum. Li–Li lateral interactions due to periodic images are negligible for these supercell sizes [21]. We use seven layers of Cu atoms to properly mimic the crystalline surface [21], and exploit symmetry by placing a Li atom on each side of the slab. Equilibrium bulk-terminated structures as predicted by DFT–LDA were employed, since surface relaxations were found to be small.

Previously, we noted that the main source of error in our approach is the use of ground state DFT–LDA, which does not properly describe the image potential for an adsorbate near a metal surface [21]. The image potential plays an important role in determining the broadening and shift of the adsorbate levels near a metallic surface, since it is determines the electron tunneling barrier. However, DFT–LDA tends to overestimate one contribution while underestimating another contribution to the image potential, such that the errors tend to cancel. We therefore proceed within the DFT–LDA framework for our subsequent analysis.

Once the Kohn–Sham DFT orbitals are obtained, the width of the atomic resonance can be calculated from the projected density of states (PDOS).

$$\Pi_l(\varepsilon) = 2\pi \sum_m |\langle \phi_m | \phi_l \rangle|^2 \delta(\varepsilon - \varepsilon_m) \quad (1)$$

The PDOS ($\Pi_l(\varepsilon)$) in Eq. (1) is a function of the energy ε and the state l onto which we are projecting. This function is evaluated by calculating the overlap of the m Kohn–Sham orbitals ϕ_m of the adsorbate–surface interacting system with the isolated Li orbital ϕ_l . The Dirac delta functions $\delta(\varepsilon - \varepsilon_m)$, where ε_m is the energy of orbital m , are then broadened using a small parameter and the width can be extracted using a deconvolution procedure which is independent of the broadening parameter [21,22].

Often this procedure leads to one distinct peak in the PDOS. However, as mentioned above, we recently found that the d-band in transition metal surfaces can mediate an effective interaction between the energy levels of the adsorbate resulting in a hybridization of the Li 2s and 2p orbitals. The width of the hybridized ionization level must therefore be estimated differently than what would be done for a pure atomic 2s state [23]. As an example, the PDOS displayed in Fig. 1 for Li 8 a.u. above Cu(001) contains two distinct Lorentzian-like peaks. The appearance of these two peaks is the result of the intra-atomic hybridization between the Li 2s and 2p states.

$$\phi_{\text{sp hybrid}} = c_{2s}\phi_{2s} + c_{2p}\phi_{2p} \quad (2)$$

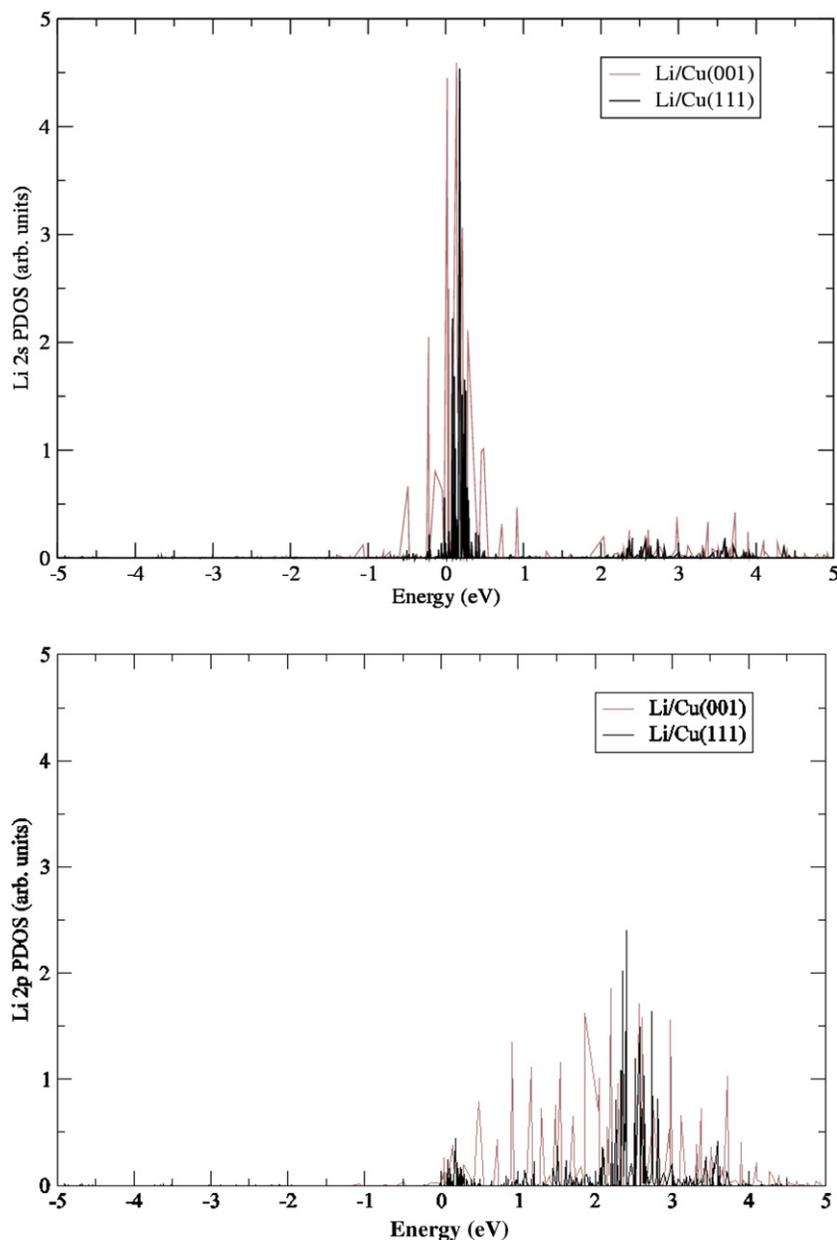


Fig. 1. The 2s (top) and 2p (bottom) PDOS for a Li atom 8 a.u. above the Cu(001) surface (brown) and above the Cu(111) surface (black). Peaks corresponding to both the pure Li 2s (at 0.1 eV) and pure Li 2p (at ~ 2.5 eV) levels exist in both projections, indicating that intra-atomic hybridization of Li has occurred. The energies are referenced (at 0 eV) to the highest occupied orbital energy (mostly the Li valence state) in the Li/Cu interacting system. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

This hybridization produces two new “adiabatic” states that are linear combinations of the pure (“diabatic”) Li 2s and 2p atomic states. We are only concerned with the hybrid state pointed at the surface ($s - p_z$), since the other one pointing away from the surface ($s + p_z$) will contribute little to the charge transfer rate. The dominant Lorentzian peaks occurring at ~ 0.1 eV (Fig. 1 top) and at ~ 2.5 eV (Fig. 1 bottom) correspond to the Li 2s and 2p states, respectively. The Taylor–Nordlander [22] deconvolution method can be applied separately to each of these two dominant peaks to extract diabatic energy level widths for each of the Li 2s and 2p states.

Fig. 2 displays these diabatic 2s and 2p widths as a function of distance from the Cu(111) and Cu(001) surfaces. We see that the diabatic widths for Li near Cu(111) are considerably narrower than for Li near Cu(001). This suggests that RCT is considerably slower for Li above Cu(111) than above Cu(001) and in turn the lifetime of a CT state should be larger for Li/Cu(111) than for Li/Cu(001), as discussed further below.

Fig. 2 also includes a rough estimate of the adiabatic width of the sp -hybridized Li level. This is obtained from the following weighted sum of the widths of the two peaks comprising the Li 2s PDOS (e.g., in the top panel of Fig. 1)

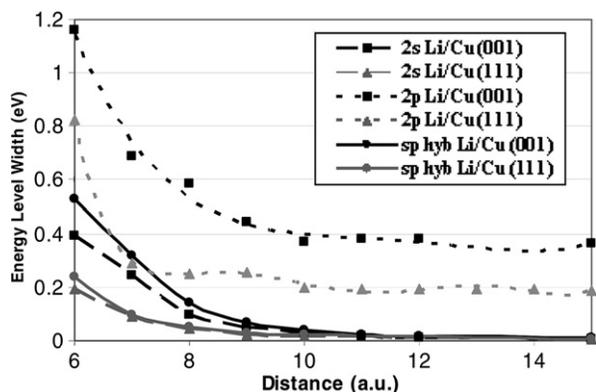


Fig. 2. Widths for Li 2s and 2p energy levels as a function of distance to the on-top sites on Cu(001) and Cu(111). The diabatic Li 2s widths, dashed lines with grey triangles and dashed lines with black squares, are broader above Cu(001) than Cu(111). In addition, the diabatic Li 2p widths are also broader for Cu(001) (dotted black lines with squares) vs. Cu(111) (dotted grey lines with triangles). The sp-hybridized widths (mixture of the diabatic 2s and 2p states given by Eq. 3) for the Li charge transfer state are also broader above Cu(001) (solid black lines with circles) than Cu(111) (solid grey lines with circles). These variations can be attributed to the band gap displayed in Fig. 3.

$$\Gamma_{\text{sp hybrid}} = \lambda_{2s}\Gamma_{2s} + \lambda_{2p}\Gamma_{2p}, \quad (3)$$

where λ_{2s} and λ_{2p} are the squares of the amplitudes c_{2s} and c_{2p} in Eq. (2) and can be obtained from the relative height of the 2s and 2p peaks in the calculated PDOS (Eq. (1)). Accounting for the hybridization via Eq. (3) increases the ionization level (2s) widths significantly as the Li atom approaches the surface, as seen in Fig. 2. As we now discuss, the adiabatic (hybridized state) width given by Eq. (3) is an underestimate, which further highlights the importance of accounting for this hybridization in calculating the widths.

The approximate adiabatic width of the hybridized level given in Eq. (3) neglects interference effects between the 2s and 2p states. A more rigorous width may be extracted by projecting the DOS onto an adiabatic basis consisting of a hybrid orbital comprised of an optimal linear combination of the isolated 2s and 2p atomic orbitals. This optimal linear combination is the one that produces a single Lorentzian peak in the PDOS.¹ Inclusion of these interference effects in this way results in widths that are up to ~60% larger (not shown), though the dependence on Li – surface separation remains similar.

The difference in our predicted RCT lifetimes for the two surfaces is consistent with alkali level lifetimes measured above Cu(111) and Cu(001). Since experimental lifetimes are unavailable for Li above Cu, we compare our predicted lifetimes to experimentally measured TR-2PPE data for Cs above Cu. Bauer et al. [14,15] measured the lifetimes of excited Cs states to be 15 and 6 fs above Cu(111) and Cu(001), respectively. Petek et al. [16,19], using similar TR-2PPE experimental techniques, found the Cs/Cu(111)

¹ These coefficients turn out to be intuitive: c_{2s} and c_{2p} from Eq. (2), forming an sp-hybrid pointing towards the surface.

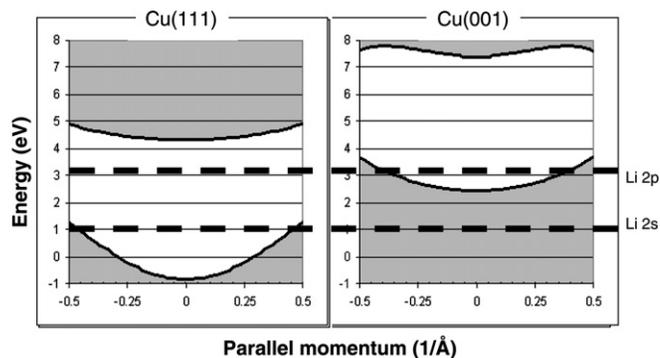


Fig. 3. Schematic band gap diagram for Cu(001) and Cu(111), after reference [7]. The band gap is present at the Fermi level (0 eV) in Cu(111), but not in Cu(001). The dashed lines correspond to the position of the 2s and 2p levels of an isolated Li atom, with respect to the Fermi level of Cu.

lifetime to be 50 fs and the Cs/Cu(001) lifetime to be considerably shorter. Our calculated lifetimes are 2–3 times longer for Li above Cu(111) than above Cu(001) at all Li-surface distances considered in this study. For chemisorbed Li at 6 a.u. above Cu(111) and Cu(001), our calculated RCT lifetimes are 17 and 8 fs, respectively. These results agree well with the above-mentioned measurements by Bauer et al. [14,15] and previous theory [7], suggesting RCT is a controlling factor for alkali lifetimes.

The significant difference in Li energy level widths above Cu(111) and Cu(001) can be explained by the simple phase space argument introduced by Borisov et al. [24]. Fig. 3 displays an overlay of the Li 2s and 2p levels for an isolated Li atom on schematic surface band structure diagrams for Cu(111) and Cu(001). We see that the Li 2s and 2p levels lie within the surface band gap of Cu(111). In particular, the Li 2p level lies entirely within the Cu(111) band gap, whereas the Li 2p level overlaps the Cu(001) valence band near the edges of the first Brillouin zone. Consequently, we expect Li 2p energy level widths to be narrower for Li above Cu(111) than Cu(001) due to the lack of resonant metallic states for Li/Cu(111). The upward image shift of the Li levels with decreasing surface separation will not alter this conclusion. Although the Li 2s level will shift into the band gap outside the Cu(001) surface, the phase space will remain larger than for Li 2s outside Cu(111).

The finding of longer RCT lifetimes for Li on Cu(111) than on Cu(001) is also supported by the presence of greater electron density in the region between Li and Cu(001) than between Li and Cu(111). Fig. 4 displays the degree of hybridization λ_{2p} , calculated from Eq. (1), as a function of the Li distance above Cu(001) and Cu(111). We see that s–p hybridization is greater for Li/Cu(001) than Li/Cu(111) at all distances considered. Increased hybridization is known to correlate strongly with decreased adsorbate lifetimes [13], due to polarization of the valence orbitals facilitating CT. Thus we suggest that these longer lifetimes for Li above Cu(111) are also due to a decrease of s–p hybridization of the Li ionization level. The smaller hybridization for Li outside Cu(111) is caused by a lack of

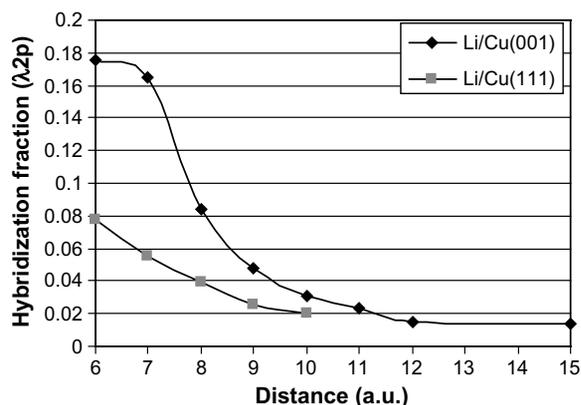


Fig. 4. Hybridization fraction (λ_{2p} from Eq. 2) as a function of Li distance from the surface. The Li *sp* hybridization is larger for Li above Cu(001) (black triangles) than for Li above Cu(111) (grey squares) at all distances. This difference in hybridization can be attributed to the Cu band gap illustrated in Fig. 3.

overlap of the Li levels with the surface valence states, as shown in Fig. 3. Without this overlap, the effective interaction mediated by the *d*-band is reduced, resulting in smaller mixing of the Li 2*s* and 2*p* orbitals.

In conclusion, using a parameter-free first principles DFT-based approach, we have investigated the width of the ionization level of Li on Cu surfaces exhibiting band gaps in their surface projected density of states. We find that the broadening of the Li level is significantly smaller on a surface with a projected band gap that encompasses the ionization level. The presence of a substrate surface band gap increases the lifetime of the ionization level both by reducing the available phase space of the electron for tunneling and by reducing the *sp*-hybridization of the Li valence orbital. We predict the ionization lifetime for Li above Cu(111) to be 2–3 times longer than for Li above Cu(001), consistent with measured lifetimes for other alkali adsorbates above Cu(111) and Cu(001) [14,15].

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