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Localized description of surface energy gap effects in the resonant charge exchange between atoms and surfaces

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Abstract

The resonant charge exchange between atoms and surfaces is described by considering a localized atomistic view of the solid within the Anderson model. The presence of a surface energy gap is treated within a simplified tight-binding model of the solid, and a proper calculation of the Hamiltonian terms based on a LCAO expansion of the solid eigenstates is performed. It is found that interference terms jointly with a surface projected gap maximum at the Γ point and the Fermi level inside it, lead to hybridization widths negligible around the Fermi level. This result can explain experimental observations related to long-lived adsorbate states and anomalous neutral fractions of low energy ions in alkali/Cu(111) systems.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

A complete description of the interaction of atoms and molecules with a surface, including both the statics and the dynamics, would provide an understanding of several phenomena of fundamental importance in surface science. In particular, the energies and lifetimes of the electronic states of atoms and molecules are the clue to understanding different processes, such as the survival of excited or ionic species produced in electron-, photon-, or particle-induced desorption [1], the neutralization or ionization of particles colliding with surfaces [2] and the spectroscopy of adsorbed species [3–5].

The jellium model is the most basic model for describing a metal surface, and it has been largely used and justified by thinking that the charge transfer processes that determine the survival probabilities of ion or excited species often occur at relatively large distances from the surface [6–13]. On the other hand, the excited states of the adsorbate broaden into resonances as the atom approaches the surface. The wavefunction of these resonances diverges at infinity and the usual bound-state techniques are not applicable. The complex scaling method was found to be the appropriate one to treat these resonances by means of a complex scale transformation in the radial coordinate of the wavefunction [14, 15]. This method has been widely used for calculating resonance widths and shifts of adsorbate electronic states [16–20].

It is now possible to measure the lifetime and the binding energy of excited electronic states by using time-resolved two-photon photoemission spectroscopy (TR-2PPE) [21–25]. This provides a unique method for exploring the electronic properties of unoccupied excited states, including the image potential states, as well as the adsorbate excited states on metal surfaces. Long-lived excited states have been found in alkali atoms adsorbed in Cu(111) and Cu(100) surfaces, with lifetimes that vary from a few tens of femtoseconds (fs) in Cs/Cu(111) to 1.6 and 4 fs in the case of Na adsorbate on Cu(100) and Cu(111) respectively.

Calculations based on the free electron model lead to transient state lifetimes in the 0.5 fs range [18, 26, 27]. Therefore, a new theoretical scenario has appeared, in which the very long-lived state in the Cs/Cu(111) system is related to the presence of a projected energy gap in the electronic band structure of the Cu(111) surface. The wavepacket propagation

(WPP) approach, based on the time evolution of a wavepacket describing the active electron in the resonant charge transfer between atom and surface, has been applied to the study of alkali/Cu(111) systems [26, 28-32]. This calculation includes a potential energy term that reproduces the main features of the (111) surface: the band gap position, the energies of the surface and first image states. On the other hand, the widths of atomic levels near metallic surfaces have also been obtained from the density of states projected on the adsorbate calculated by density functional theory (DFT) using a periodic slab to model the solid surface. [33, 34]. Within this theoretical approach it has been found that the lifetime of Li adsorbate in Cu(111) is greater than the corresponding one in Cu(100). This result is attributed to the energy position of the Li 2s level, which falls inside the surface gap in the (111) surface, while it is below the gap in the (100) case. The shifts of the Li 2s level cannot be easily extracted from the periodic DFT calculations due to hybridization effects at short distances that spread the energy level and make it hard to define the shifts unambiguously. Instead, the same shifts calculated in the complex scaling theory, which essentially follow the classical image potential, were assumed in this calculation [33-35]. But there is experimental evidence showing that the atom levels initially move in energy as the metal surface is approached owing to the image potential, but close to the surface the short range interactions lead to a lowering of their energies [36, 37]. This fact can explain the high neutralization of Li⁺ ions found in the scattering by high workfunction (111) metal surfaces (Ag, Cu, Au) [38–42], but the increase of the neutralization probability found at low energies is not yet completely understood. It is believed that it is mainly associated with the presence of projected energy gaps, surface and image states [38, 40, 42].

In the present work we explore the influence of the band structure features on the charge exchange between atoms and surfaces by using local orbital schemes, which has proved to be very useful in the treatment of chemisorptive bonding theories. The canonical chemisorption theory, due to Grimley [43] and Newns [44], deals with an Anderson Hamiltonian [45]. In the case of dynamical ion-surface scattering, the extension of the chemisorption theory based on the Anderson model is straightforward when the charge exchange is only determined by one-electron hopping processes [46, 47]. The strength of this model is fundamentally the clear physical meaning of each of the parameters of the Hamiltonian, and the possibility of handling them very easily to describe equilibrium and nonequilibrium processes. Then, a proper calculation of the energy and hybridization terms is possible. To this purpose we used the bond-pair model [48–50], which has been successful for describing the interaction between atoms and surfaces in several chemisorption and ion scattering problems [49-57]. In this work we assimilated the interaction parameters calculated in this way to Li-Cu system [56], while a simple firstneighbor tight-binding calculation was used to provide the LCAO expansion of the substrate states. Thus, two bands and a surface projected gap were included in the band structure in order to simulate, very qualitatively, the general trends of the localized d-like and more extended sp-like bands of the Cu(111) surface. The goal of this simplified surface model is to allow one to gain some insight on the interference between surface atoms interacting with the adsorbate (projectile) and its effect on physical magnitudes such as the width and shift of the adsorbate level in a stationary process or the charge state fractions in ion scattering.

This paper is organized as follows. In section 2 the Anderson model is presented and the *ab initio* calculation to obtain the Hamiltonian parameters is described. The simple surface model used and the Green function formalism for calculating the physical magnitudes of interest in both the adsorption and dynamical surface scattering processes are also introduced in this section. Section 3 is devoted to a comprehensive analysis of the interference and surface gap effects on the energy dependence of the hybridization widths, and also on the behavior of the charge fractions at low incoming projectile energies. A summary is presented in section 4.

2. Theory

The Anderson model has three main ingredients: a localized atomic state with energy ϵ_a , an on-site Coulomb repulsion U in the atomic shell and a hybridization matrix element $V_{\tilde{k},a}^{\sigma}$ between the atomic state and the conduction states of the metal. The Hamiltonian is

$$\hat{H} = \sum_{\vec{k},\sigma} \epsilon_{\vec{k}} \hat{n}_{\vec{k},\sigma} + \sum_{\sigma} \left(\epsilon_a + \frac{1}{2} U \hat{n}_{a\bar{\sigma}} \right) \hat{n}_{a\sigma} + \sum_{\vec{k},\sigma} (V^{\sigma}_{\vec{k},a} \hat{c}^{\dagger}_{\vec{k},\sigma} \hat{c}_{a,\sigma} + \text{h.c}).$$
(1)

Here, $\hat{c}_{a\sigma}^{\dagger}$ creates one electron in the atomic orbital *a* with spin projection σ and energy ϵ_a , $\hat{c}_{\vec{k}\sigma}^{\dagger}$ creates one electron in the conduction band state with wavevector \vec{k} and spin projection σ and energy $\epsilon_{\vec{k}\sigma}$; $\hat{n}_{q\sigma} = \hat{c}_{q\sigma}^{\dagger}\hat{c}_{q\sigma}$ is the number operator. The index \vec{k} includes the band index, which can be also referred to inner and localized surface bands.

An important quantity deeply related to the physics of the Anderson model is the hybridization width $\Gamma_a^{\sigma}(\epsilon) =$ $\pi \sum_{\vec{k}} |V_{\vec{k},a}^{\sigma}|^2 \delta(\epsilon - \epsilon_{\vec{k},\sigma})$, which is the imaginary part of the adsorbate self-energy $\Sigma_{\sigma}^{0}(\omega) = \sum_{\vec{k}} \frac{|V_{\vec{k},a}^{\sigma}|^{2}}{\omega - \epsilon_{\vec{k},\sigma} + i\eta}$ in the U = 0 case. In this case, the real part of $\Sigma_{\sigma}^{0}(\omega)$, evaluated in $\omega = \epsilon_a$, provides the atomic level shift caused by the interaction with the band states, and the hybridization width evaluated in the shifted atom energy, $\Gamma_a^{\sigma}(\tilde{\epsilon}_a)$, measuring the energy half-width of the atomic resonance. These concepts continue being valid in the interacting case $(U \neq 0)$ provided the adsorbate self-energy can be assumed as $\Sigma_{\sigma}(\omega)$ = $\Sigma^0_{\sigma}(\omega) + \Sigma^U_{\sigma}(\omega)$. The knowledge of the energy dependence of the hybridization width and the atom energy level position allow us to completely determine the resonant electron transfer between atoms and surfaces within the Anderson model framework. Therefore, ab initio calculations of the on-site energy and hopping terms are desirable in order to make use of the full potential of the Anderson model.

2.1. Calculation of Hamiltonian terms: bond-pair model

A model Hamiltonian previously developed to describe pairs of interacting atoms [48] was generalized to any atom–surface system by assuming that one of the two atoms consists of a system having a quasicontinuum basis of states (including extended valence and 'localized' or core-like flat band states). A symmetrically orthogonalized [58] mixed basis set of localized adatom orbitals and extended surface states is used in this case to finally reduce the Hamiltonian to the form of the Anderson model. The one electron hybridization term $V_{\vec{k},a}^{\sigma}$ includes one and two electron contributions consistently with a mean-field approximation of the many body Hamiltonian. Basically, the $V_{\vec{k},a}^{\sigma}$ term is expanded according to the overlap expansion of the orthogonal \vec{k} - and *a*-states:

$$V_{\vec{k},a}^{\sigma} = V_{\vec{k},a}^{\sigma(0)} - \frac{1}{2}S_{\vec{k},a}(V_{\vec{k},\vec{k}}^{\sigma(0)} + V_{a,a}^{\sigma(0)}) + \cdots$$
(2)

where the supra-index (0) indicates that the matrix elements are referred to the states of the isolated subsystems (atom and solid) and $S_{\vec{k},a}$ is the overlap between them. The LCAO expansion of the unperturbed surface states is then performed,

$$\phi_{\vec{k},\sigma}(\vec{r}) = \sum_{i,\vec{R}_s} C_i^{\vec{k},\sigma}(\vec{R}_s)\varphi_i(\vec{r}-\vec{R}_s)$$
(3)

and the three-center integrals are approximated consistently with the overlap expansion. In this way the non-dimeric contributions are canceled and finally the hybridization term is recovered as a superposition of the atomic hopping integrals $V_{i,a}^{\sigma(\dim)}$ calculated with functions only orthogonalized within each dimeric subspace (\vec{R}_s, \vec{R}_a) (see equations (12) and (13) of [49]):

$$V_{\vec{k},a}^{\sigma} = \sum_{i,\vec{R}_s} C_i^{\vec{k},\sigma}(\vec{R}_s) V_{i,a}^{\sigma(\dim)}.$$
(4)

The coefficients $C_i^{\vec{k},\sigma}(\vec{R}_s)$ determine the density matrix of the unperturbed solid whose elements are $\rho_{i,j}^{\sigma}(\vec{R}_s, \vec{R}_{s'}; \epsilon) = \sum_{\vec{k}} C_i^{\vec{k},\sigma*}(\vec{R}_s) C_j^{\vec{k},\sigma}(\vec{R}_{s'}) \delta(\epsilon - \epsilon_{\vec{k},\sigma})$. How many atoms of the substrate contribute to the expansion given by equation (4) depends on the magnitude of the atomic hopping integral $V_{i,a}^{\sigma(\dim)}$; and the weight of each dimeric contribution is directly related to the band structure through the coefficient $C_i^{\vec{k},\sigma}(\vec{R}_s)$. In summary, two main ingredients are required for an *ab initio* calculation of $V_{\vec{k},a}^{\sigma}$: (i) a good atomic basis set [59, 60] and (ii) an appropriate calculation of the band structure based on a localized description of the solid [61, 62]. The adsorbate energy level, calculated following the same procedure, includes the orthogonalization effects and the adsorbate–substrate two-electron interactions within a meanfield approximation (see equation (9) of [49]).

The bond-pair model has allowed for a general satisfactory description of experimental results in adsorption and surface scattering processes in many different atom–surface combinations [49–57]. In all these works only the diagonal on-site elements of the surface density matrix (the

surface local density of states, LDOS) have been conserved in the calculation of quantities such as the hybridization width:

$$\Gamma_{a}^{\sigma}(\epsilon) = \pi \sum_{i,j} \sum_{\vec{R}_{s}, \vec{R}_{s'}} \rho_{i,j}^{\sigma}(\vec{R}_{s}, \vec{R}_{s'}; \epsilon) V_{i,a}^{\sigma*}(\vec{R}_{s}) V_{j,a}^{\sigma}(\vec{R}_{s'}).$$
(5)

Very good agreement between experiment and theory has been found for colliding ions having large velocity components along the normal to the surface, while this theoretical description seems to fail when the interaction has more time to incorporate the details of the surface band structure. In the Li/Cu system the differences between theory and experiment become dramatic at low energies [56]. In the light of these results, it is very important to explore the effect of the crossed on-site terms of $\rho_{i,j}^{\sigma}(\vec{R}_s, \vec{R}_{s'}; \epsilon)$ in the resonant charge exchange process.

2.2. Band-states calculation

The $\phi_{\vec{k},\sigma}(\vec{r})$ eigenstates of the solid are calculated within a firstneighbor tight-binding approximation by assuming a simple cubic symmetry and one atomic state per site. The coefficients of the LCAO expansion are given by

$$C_i^{\vec{k},\sigma}(\vec{R}_s) = \sqrt{2}\sin(mk_z b)\exp(i\vec{k}_{\parallel}\cdot\vec{R}_s)$$
(6)

where *m* is the index denoting the plane parallel to the surface, *b* is the lattice parameter (b = 7 au) and $\vec{k} = (\vec{k}_{\parallel}, k_z)$. The presence of a Shockley-like surface state as the one existing in the Cu(111) surface is disregarded in this case, because the interest in this work is to isolate the effects originating from the presence of surface energy gaps. The eigenenergy of the extended \vec{k} -state is given by

$$\epsilon_{\vec{k},\sigma} = E_1 + 2V_1[\cos(k_x b) + \cos(k_y b) + \cos(k_z b)].$$
(7)

The tight-binding parameters E_1 and V_1 are the site energy and the coupling between the first neighbors, respectively. In this form we constructed a solid with two non-hybridized bands, one (E_1, V_1) of more localized character than the other (E_2, V_2) , in an attempt to mimic the d- and sp-bands of a Cu(111) surface. The atomic hopping parameters $V_{j,a}(\vec{R}_s, z)$ are consistently chosen as the coupling between the orbitals $j = d_{z^2}$ and p_z of Cu and a = 2s of Li.

2.3. Green function technique

In dynamical ion–surface scattering processes we are interested in calculating the probability of ion neutralization. Within the spinless approximation, this is given by the average atom state occupation $\langle n_a(t) \rangle = \langle c_a^{\dagger}(t)c_a(t) \rangle$. This quantity is obtained from the following Green function [63, 64]:

$$F_{aa}(t,t') = i\langle\Phi|[c_a^{\dagger}(t'), c_a(t)]|\Phi\rangle \to i[2\langle n_a(t)\rangle - 1]_{t\to t'}$$
(8)

where [] indicates the commutator and Φ is the dynamical state in the Heisenberg picture. The function $F_{aa}(t, t')$ is calculated by solving the equation of motion given by

$$i\frac{\mathrm{d}}{\mathrm{d}t}F_{aa}(t,t') = \epsilon_a F_{aa}(t,t') + \int_{-\infty}^{\infty} \mathrm{d}\tau \ \Sigma_0^R(t,\tau)F_{aa}(\tau,t') + \int_{-\infty}^{\infty} \mathrm{d}\tau \ \Omega_0(t,\tau)G_{aa}(\tau,t').$$
(9)



Figure 1. The atom energy level (triangles) measured with respect to the Fermi energy ($\varepsilon_F = 0$) and the $V_{j,a}(z, \vec{R}_s)$ hopping terms as a function of atom–surface distance. Inset: central atom (1) and its first neighbors (2 and 3).

In equation (9) $G_{aa}(t, t')$ is the advanced Green function, and the introduced self-energies are

$$\Sigma_{0}^{R}(t,\tau) = -i\Theta(t-\tau)\sum_{\vec{k},n} V_{a,\vec{k}n}(t)V_{\vec{k}n,a}(\tau)$$

$$\times \exp[-i\epsilon_{\vec{k}n}(t-\tau)]$$

$$\Omega_{0}(t,\tau) = -i\sum_{\vec{k},n} V_{a,\vec{k}n}(t)V_{\vec{k}n,a}(\tau)$$

$$\times \exp[-i\epsilon_{\vec{k}n}(t-\tau)][1-\langle n_{\vec{k}n}(t)\rangle]$$
(11)

where $\langle n_{\vec{k}n}(t) \rangle$ is given by the Fermi function. The boundary condition required to solve equation (9) is $F_{aa}(t_0, t') = (2\langle na(t_0) \rangle - 1)G_{aa}(t_0, t')$, with t_0 being the initial time value.

3. Results and discussion

3.1. Atomic couplings and energy level

In figure 1, the hopping integrals $V_{j,a}(z, R_s)$ and the level energy calculated by using the bond-pair model in the case of Li/Cu(111) [56] are shown as a function of atom–surface distance (z). The adsorbate on-top position considered is shown in the inset of figure 1.

We can observe from figure 1 that the localized d-band states allow for a significant coupling of the adsorbate only with the central atom, while the more extended p-surface band involves the interaction of the adsorbate with the first neighbors too.

3.2. Stationary process: hybridization widths

The hybridization width given by the imaginary part of the Fourier transform of equation (10) can be separated into contributions from each band, $\Gamma_a(\varepsilon, z) = \Gamma_a^1(\varepsilon, z) + \Gamma_a^2(\varepsilon, z)$, where $\Gamma_a^n(\varepsilon, z)$ is

$$\Gamma_{a}^{n}(\varepsilon, z) = \operatorname{Im} \sum_{\vec{k}} \frac{|V_{a,\vec{k}n}(z)|^{2}}{\varepsilon - \varepsilon_{\vec{k},n} - \mathrm{i}\eta} = \pi \sum_{\vec{k}} \left| \sum_{\vec{R}_{s}} \sqrt{2} \sin\left(mk_{z}b\right) \right| \times \exp(\mathrm{i}\vec{k}_{\parallel} \cdot \vec{R}_{s\parallel}) V_{a,n}(z, \vec{R}_{s}) \right|^{2} \delta(\varepsilon - \varepsilon_{\vec{k},n}).$$
(12)



Figure 2. $E_2 = 3 \text{ eV}$ case. (a) Level widths for n = 1 (black lines) and n = 2 (gray lines). Solid lines correspond to the calculation by equation (12) and dash lines to the one by equation (14). The inset shows the surface projected band structure of the two bands, n = 1 (black lines) and n = 2 (gray lines). (b) Shifted energy level variation with distance: the complete calculation derived from equation (12) (solid black curve) and the calculation derived from equation (14) (gray dash curve). The surface LDOS is shown for the two bands, n = 1 (black line) and n = 2 (gray line). The inset is an expanded view of the atom level behavior around the Fermi energy $\varepsilon_F = 0$.

Here, $V_{a,n}$ means V_{a,d_z} for n = 1 and V_{a,p_z} for n = 2. The energy level width $\Gamma_a(\tilde{\varepsilon}_a, z)$ is calculated as the hybridization width evaluated at the atom energy shifted by the interaction with the surface, $\tilde{\varepsilon}_a(z) = \varepsilon_a(z) + \Lambda(\varepsilon_a, z)$. The energy shift $\Lambda(\varepsilon_a, z)$ is calculated as

$$\Lambda(\varepsilon_a, z) = \frac{P}{\pi} \int_{-\infty}^{\infty} d\omega \, \frac{\Gamma_a(\omega, z)}{\varepsilon_a - \omega} \tag{13}$$

where P denotes the Cauchy principal value.

The $\Gamma_a^n(\tilde{\varepsilon}_a, z)$ calculated by using equation (12) is shown as a function of the distance to the surface in figures 2–4 for three different values of E_2 . The parameters E_1 , V_1 , V_2 are chosen equal to -2 eV, -1 eV and 1.5 eV respectively, in order to have the lower band (n = 1) more localized than the upper one (n = 2). The projected band structure $\varepsilon_{\vec{k},n}(\vec{k})$ as a function of \vec{k}_{\parallel} for $k_z = \frac{\pi}{b}$ and 0; the LDOS on the surface atom (m = 1)and the distance dependence of the shifted energy level have also been included in these figures.

It can be observed from figures 2 to 4 that the contribution of the n = 1 band to the level width is more significant for distances close to the surface (z < 4 au), while the n = 2 band contributes more appreciably to the level width at distances larger than 4 au. This can be correlated to the corresponding atomic hopping integrals shown in figure 1, and also with the energy position of the shifted energy level. The energy resonance with the n = 2 band states occurs at distances for which the atom level is near the Fermi energy (see figures 2(b), 3(b) and 4(b)). This resonance becomes more effective for small values of E_2 . In this way we can understand



Figure 3. The same as in figure 2 for $E_2 = 7$ eV.



Figure 4. The same as in figure 2 for $E_2 = 11$ eV.

the predominant contribution of the n = 2 band to the level width at large distances in the $E_2 = 3$ eV case, the value comparable to the n = 1 band contribution for $E_2 = 7$ eV, and the negligible contribution in the $E_2 = 11$ eV case.

In the same figures the level width calculated from

$$\Gamma_{a}^{n}(\varepsilon, z) \approx \pi \sum_{\vec{R}_{s}} |V_{a,n}(z, \vec{R}_{s})|^{2} \times \sum_{\vec{k}} |\sqrt{2}\sin(mk_{z}b)|^{2} \delta(\varepsilon - \varepsilon_{\vec{k},n})$$
(14)

is shown. This is obtained from equation (12) by conserving only the diagonal on-site terms. This calculation leads to a larger and more extended in distance contribution of the n = 2band, which rules the level width at large distances in the cases $E_2 = 3$ and 7 eV. Instead, small differences between the widths calculated by using either equation (12) or (14) are observed in the case of the more localized d-like band n = 1. At short distances the expression (14) leads to a diminution of the level



Figure 5. Hybridization width as a function of energy calculated by using equation (12) (solid lines) and by using equation (14) (dash lines). Black curves correspond to n = 1 and gray curves to n = 2. The distance z = 2 au was considered for the n = 1 case and z = 5.8 au for the n = 2 case. The arrows indicate the corresponding energy positions of the shifted atom level. (a) $E_2 = 3$ eV; (b) $E_2 = 7$ eV; (c) $E_2 = 11$ eV.

width in this case. The differences in the level shift between both calculations are only appreciable around the Fermi level, where the incidence of the n = 2 band is more important (see insets in figures 2(b), 3(b) and 4(b)).

In figure 5 the hybridization widths $\Gamma_a^n(\varepsilon, z)$ are shown as a function of energy at distance values where each band contribution to the level width is significant, z = 2 au in the n = 1 band and z = 5.8 au in the n = 2 case. The results obtained from equations (12) and (14) are compared. For the d-like band both calculations lead to similar results, although it is observed that the hybridization width function is slightly shifted towards lower energy values in the case of considering the \vec{k}_{\parallel} dependence of $|V_{a,\vec{k}n}(z)|^2$ according to equation (12). In contrast, pronounced differences are observed between both calculations in the p-like band case. The peaked structure is narrowed and shifted to higher energies when the \vec{k}_{\parallel} dependence of $|V_{a,kn}(z)|^2$ is taken into account. An increasing surface energy gap means a decreasing contribution of the n = 2 band to the hybridization width around the Fermi level. Therefore, a diminution of the energy level widths is expected when going from $E_2 = 3$ to 11 eV because of the shifted energy level positions (indicated by arrows in figures 5) at the corresponding z value in each case.

The differences between the results obtained by using either equation (12) or (14) can be understood by looking at



Figure 6. (a) Surface contour plot of $|V_{a,\vec{k}n}(z)|^2$ as a function of the \vec{k} -components: perpendicular to the surface in the vertical axis and parallel to the surface in the horizontal axis, for the n = 2 band case. The gray scale is used to indicate the variation of the square modulus of $V_{a,\vec{k}n}(z)$. (b) $|V_{a,\vec{k}n}(z)|^2$ as a function of \vec{k}_{\parallel} according to equation (12) for $k_z = \frac{\pi}{2b}$, m = 1. The black curve corresponds to n = 1 and gray curve to n = 2. The same z values as figure 5. The dash horizontal lines are the $|V_{a,\vec{k}n}(z)|^2$ calculated by neglecting the \vec{k}_{\parallel} dependence (see text). (c) The surface projected band structure for n = 1 and 2; the dot-dash line corresponds to $k_z = \frac{\pi}{2b}$ and the dot line to the Fermi energy $\varepsilon_{\rm F} = 0$ ($E_2 = 7$ eV).

the \vec{k}_{\parallel} dependence of $|V_{a,\vec{k}n}(z)|^2$ shown in figure 6. A peaked function around the Γ point is found, being more localized at $\vec{k}_{\parallel} = 0$ when the number of surface atoms involved in the interaction with the adsorbate is larger (this is the case of the n = 2 band). By comparing this result with that obtained by neglecting the \vec{k}_{\parallel} dependence, keeping only the diagonal onsite terms $(|V_{a,\vec{k}n}(z)|^2 \approx \sum_{\vec{k}_s} |V_{a,n}(z, \vec{R}_s)|^2 |\sqrt{2} \sin(mk_z b)|^2)$, the different energy behaviors of the hybridization widths observed in figure 5 can be easily understood. Figure 6(c) shows clearly that, due to the presence of the gap, the hybridization widths calculated by using equation (12) are narrowed and shifted to higher energies in the case of the p-band and to lower energies in the case of the d-band, with respect to the hybridization widths obtained by equation (14).

As a general result we have that an increasing number of surface atoms involved with similar atomic couplings means a rather strong localization of $|V_{a,\vec{k}n}(z)|^2$ around $\vec{k}_{\parallel} = 0$. This fact, jointly with a surface energy gap maximum at the Γ point and the Fermi level located inside it, give rise to a hybridization width localized at energies far from the Fermi level. This

picture can explain qualitatively the long-lived adsorbate states in systems such as alkali/Cu(111) [21–24].

By looking at charge exchange processes, the n = 2band contribution to the level width is mainly associated with electron loss occurring at large distances where the atom energy level is above the Fermi level, while the contribution of the n = 1 band is related to electron capture at distances closer to the surface (see figures 2–4). In the case of $E_2 = 7$ eV (figure 3) a qualitative change of behavior can be observed between cases considering and neglecting the \vec{k}_{\parallel} dependence of $|V_{a,\vec{k}n}(z)|^2$. In the case where the dependence on \vec{k}_{\parallel} is ignored, the electron loss becomes more effective than the electron capture. This result is reversed when taking into account the localization effect around $\vec{k}_{\parallel} = 0$ obtained by using equation (12).

3.3. Collision process: neutral fraction

The interplay between loss and capture processes is decisive in determining the final charge state of an incoming positive ion scattered by a surface. The neutral fraction is calculated by considering an ion trajectory normal to the surface, described by the time dependent function z = z(t). Different velocity values are considered in the incoming and outgoing paths in order to simulate the perpendicular component of velocity corresponding to an angle of 24° with respect to the surface in the incoming trajectory and 90° in the exit one. This is the scattering geometry used in the Li⁺/Cu(111) experiments of [38].

Figures 7–9 show the neutral fraction $\langle n_a(\infty) \rangle$ as a function of the exit ion energy, the distance behavior of the energy levels and their widths shown as error bars. Both calculations, including and neglecting the \vec{k}_{\parallel} dependence of $V_{a,\vec{k}n}(t)V_{\vec{k}n,a}(\tau)$ in equations (10) and (11), are compared. In the range of low kinetic energies analyzed, the position of the ion energy level with respect to the Fermi level and its width allow us to infer the qualitative behavior of the neutral fraction with the incoming energy. It can be assumed that there are characteristic distances to the surface at which the final charge state of the projectile is defined that depend on its velocity. If the motion with respect to the surface is slower, these characteristic distances are larger and the dynamical charge exchange process occurs close to an adiabatic evolution. Note that, in the analyzed situation the incoming ion velocity is always smaller than the exit one. This fact means that the ion has enough time along the incoming trajectory to be partially neutralized due to the down-shift and width of the energy level near to the surface. The final charge state is defined by the balance between loss and capture processes along the outgoing part, as can be observed in figures 8(b)and (c), where the evolution of the neutral fraction along the ion trajectory is shown in the case of a low exit energy (200 eV). For $E_2 = 3$ eV the discharge at large distances dominates in the two cases, whether considering the \vec{k}_{\parallel} dependence or not, leading in this way to a marked drop of the neutral fraction at low kinetic energies. The larger neutralization on including the interference terms is related to the diminution of the n = 2band contribution to the level width due to the localization effects around small values of k_{\parallel} (see figure 2).



Figure 7. $E_2 = 3 \text{ eV}$ case. (a) The neutral fraction as a function of the projectile exit energy; black squares correspond to the complete calculation and gray circles to the one that neglects the \vec{k}_{\parallel} dependence of $V_{a,\vec{k}n}(t)V_{\vec{k}n,a}(\tau)$ in equations (10) and (11). (b) and (c) The energy level and the total width shown as error bars as a function of *z*: (b) width calculated by equation (12), (c) width calculated by equation (14). The dot line indicates the Fermi energy level.

The dynamical neutral fractions calculated by including or neglecting the \vec{k}_{\parallel} dependence in the $E_2 = 7$ eV case, show a change of behavior consistent with that observed in the level width (figure 3). In this case the localization in \vec{k}_{\parallel} leads to a less significant discharge compared to the charge process, promoting in this way an increase of the neutral fraction at low energies. This negligible level width at large distances, due to both localization effects around small values of \vec{k}_{\parallel} and the presence of a surface gap, provides a possible explanation for the low energy dependence of the Li⁺ neutral fraction measured in the scattering by the Cu(111) surface [38].

In the case of a very small overlap between the two bands, $E_2 = 11$ eV, only the more localized d-like band determines the charge exchange. Therefore, the dominant electron capture process leads to an increase of the ion neutralization at low energies. Since in this case only one surface atom is practically involved, the interference effects do not play a significant role.

Another interesting point is the memory effect with reference to the initial state. The final neutral fraction in the case of $E_2 = 7$ eV is presented in figure 10 for neutral and positive initial charge states. The calculation by conserving only the diagonal on-site terms in $V_{a,\vec{k}n}(t)V_{\vec{k}n,a}(\tau)$ shows a loss



Figure 8. The same as in figure 7 for $E_2 = 7$ eV. (b) and (c) include the evolution of the atom state occupation probability along the ion trajectory when considering (b) and neglecting (c) the \vec{k}_{\parallel} dependence of $V_{a,\vec{k}n}(t)V_{\vec{k}n,a}(\tau)$. Negative (positive) values of z denote the incoming (outgoing) part of the trajectory.

of memory of the initial state. Instead, the smaller level width obtained at large distances on considering the \vec{k}_{\parallel} dependence (see figure 8) increases the survival probability of incoming neutral atoms, as can be observed in figure 10. A very slow motion along the incoming trajectory is required to produce a loss of memory in this situation.

4. Conclusions

The atom-surface interaction is described within the framework of the Anderson model and the Hamiltonian terms are obtained from an *ab initio* theoretical proposal. The localized atom-atom interactions, together with the extended features of the solid band structure, determine the hybridization term of the Anderson model. The general trends of the Li/Cu(111) system, related to the different localization character of the band states and the presence of a surface gap, are reproduced in a very qualitative way. It is found that the interference between surface atoms interacting with the adsorbate (projectile) leads to a modulus of the hybridization function more localized around $k_{\parallel} = 0$. Consequently, a surface gap maximum at the Γ point and the Fermi level location inside it, lead to a reduction of the hybridization widths around the Fermi level. This means small widths of the atom levels whose energies are near the Fermi level. This result can explain the measured long-lived excited states of alkali atoms adsorbed in Cu(111), and also the increasing neutralization found at low velocities



Figure 9. The same as in figure 7 for $E_2 = 11$ eV.



Figure 10. $E_2 = 7$ eV case. Atomic state occupation probability as a function of the exit energy. Black symbols correspond to the correct calculation of $V_{a,\vec{k}n}$; gray symbols to the calculation that neglects the \vec{k}_{\parallel} dependence. Closed (open) symbols are for the case of an incoming ion (incoming neutral atom).

in the case of Li⁺ scattered by a Cu(111) surface. It is not expected that the 'Shockley-like' surface state on Cu(111), which lies partly below the Fermi level around the Γ point and is strongly localized close to the surface, will change this picture appreciably.

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References

- Tolk N H et al 1984 Nucl. Instrum. Methods Phys. Res. B 2 457–60
- [2] Los J and Geerlings J J C 1990 Phys. Rep. 133 190
- [3] Avouris P and Persson B N J 1984 J. Phys. Chem. 88 837
- [4] Néel N, Kröger J, Limat L, Palotas K, Hofer N A and Berndt R 2007 *Phys. Rev. Lett.* 98 016801
- [5] Merino J and Gunnarsson O 2004 Phys. Rev. Lett. 93 156601
- [6] Blandin A, Nourtier A and Hone D 1976 J. Physique 37 369
- [7] Norskov J K and Lundquist B I 1979 Phys. Rev. B 19 5661
- [8] Brako R and Newns D M 1981 Surf. Sci 108 253
- [9] Brako R 1984 *Phys. Rev.* B **30** 5629
- [10] Wunnik J N M, Geerlings J J and Los J 1983 Surf. Sci 131 1
- [11] Burgdörfer J and Kupfer E 1986 Phys. Rev. Lett. 57 2649
- [12] Brako R and Newns D M 1982 Vacuum 32 39
- [13] Yu M L and Lang N D 1983 Phys. Rev. Lett. 50 127
- [14] Junker B R 1982 Adv. At. Mol. Phys. 18 207
- [15] Reinhardt W P 1982 Ann. Rev. Phys. Chem. 33 223
- [16] Nordlander P and Tully J C 1988 Phys. Rev. Lett. 61 990
- [17] Nordlander P and Tully J C 1989 Surf. Sci. 211/212 207
- [18] Nordlander P and Tully J C 1990 Phys. Rev. B 42 15564
- [19] Borisov A G, Teillet-Billy D and Gauyacq J P 1992 Phys. Rev. Lett. 68 2842
- [20] Gauyacq J P and Borisov A G 1998 J. Phys.: Condens. Matter 10 6585
- [21] Bauer M, Pawlik S and Aeschilmann M 1997 Phys. Rev. B 55 10040
- [22] Bauer M, Pawlik S and Aeschilmann M 1999 Phys. Rev. B 60 5016
- [23] Ogawa S, Nagano H and Petek H 1999 Phys. Rev. Lett. 82 1931
- [24] Petek H, Weida M J, Nagano H and Ogawa S 2000 Science 288 1402
- [25] Zhao J et al 2008 Phys. Rev. B 78 085419
- [26] Borisov A G, Teillet-Billy D, Gauyacq J P, Winter H and Dierkes G 1996 Phys. Rev. B 54 17166
- [27] Lang N D and Williams A R 1978 Phys. Rev. B 18 616
- [28] Borisov A G, Kazansky A K and Gauyacq J P 1999 Surf. Sci. 430 165
- [29] Gauyacq J P, Borisov A G, Rassev G and Kazansky A K 2000 Faraday Discuss. 117 15
- [30] Borisov A G, Kazansky A K and Gauyacq J P 1999 Phys. Rev. B 59 10935
- [31] Borisov A G, Gauyacq J P, Chulkov E V, Silkin V M and Echenique P M 2002 *Phys. Rev.* B **65** 235434
- [32] Sjakste J, Borisov A G and Gauyacq J P 2004 Phys. Rev. Lett. 92 156101
- [33] Niedfeldt K, Carter E and Nordlander P 2004 J. Chem. Phys. 121 3751
- [34] Niedfeldt K, Nordlander P and Carter E 2006 Phys. Rev. B 74 115109
- [35] Niedfeldt K, Carter E and Nordlander P 2006 Surf. Sci. 600 L291
- [36] Lankaster J C, Kontur F J, Watters G K and Dunning F B 2003 Phys. Rev. B 67 115413
- [37] Wetherkam S and Winter H 2005 Surf. Sci. 59 L319
- [38] Canario A R, Kravchuk T and Esaulov V A 2006 *New J. Phys.* 8 227
- [39] Kravchuk T, Bandourine Y, Hoffman A and Esaulov V A 2006 Surf. Sci. 600 L265
- [40] Canario A R, Borisov A G, Gauyacq J P and Esaulov V A 2005 Phys. Rev. B 71 121404
- [41] Hamoudi H, Dablemont C and Esaulov V A 2008 Surf. Sci. 8 2486
- [42] Hecht T, Winter H, Borisov A G, Gauyacq J P and Kazanszky A K 2000 Phys. Rev. Lett. 84 2517
- [43] Grimley T B 1967 Proc. Phys. Soc. Lond. 90 751

- [44] Newns D M 1969 Phys. Rev. B 178 1123
- [45] Anderson P W 1961 Phys. Rev. B 41 1123
- [46] Muda Y and Newns D M 1988 Phys. Rev. B 37 7048
- [47] Muda Y and Hanawa T 1980 Surf. Sci. 97 283
- [48] Bolcatto P G, Goldberg E C and Passeggi M C G 1994 Phys. Rev. A 50 4643
- [49] Bolcatto P G, Goldberg E C and Passeggi M C G 1998 Phys. Rev. B 58 5007
- [50] Bolcatto P G, Goldberg E C and Passeggi M C G 2000 J. Phys.: Condens. Matter 12 8369
- [51] Goldberg E C, Monreal R, Flores F, Brongersma H and Bauer P 1999 *Surf. Sci.* **440** L875
- [52] Torralba M C, Bolcatto P G and Goldberg E C 2003 Phys. Rev. B 68 075406
- [53] García E A, Pascual C G, Bolcatto P G, Passeggi M C G and Goldberg E C 2006 Surf. Sci. 600 2195
- [54] Bonetto F, Romero M A, García E A, Vidal R, Ferrón J and Goldberg E C 2007 *Europhys. Lett.* **80** 53002

- [55] Bonetto F, Romero M A, García E A, Vidal R, Ferrón J and Goldberg E C 2008 Phys. Rev. B 78 075422
- [56] García E A, Romero M A, González C and Goldberg E C 2009 Surf. Sci. 603 597
- [57] Bajales N, Cristina L, Mendoza S, Baragiola R A, Goldberg E C and Ferrón J 2008 Phys. Rev. Lett. 100 227604
- [58] Lowdin P O 1950 J. Chem. Phys. 18 365
- [59] Huzinaga S 1965 J. Chem. Phys. 42 1293
- [60] Huzinaga S et al 1984 Gaussian Basis Set for Molecular Calculation (Amsterdam: Elsevier)
- [61] James J P, Glaesemann K R, Voth G A, Fritsch J, Demkok A A, Ortega J and Sankey O F 2001 Phys. Rev. B 64 195103
- [62] Jelinek P, Wang H, Lewis J P, Sankey O F and Ortega J 2005 Phys. Rev. B 71 235101
- [63] Keldysh L V 1964 Zh. Eksp. Teor. Fiz. 47 1515
- [64] Keldysh L V 1965 Sov. Phys.—JETP 20 1018