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Band gap effect on H^- ion survival near Cu surfaces

B. Bahrim [a], B. Makarenko [b], J.W. Rabalais [a,b,*]

[a] Department of Chemistry and Physics, Lamar University, P.O. Box 10022, Beaumont, TX 77710, United States
[b] Department of Chemistry, University of Houston, Houston, TX 77204, United States

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Abstract

The presence of a band gap in the direction normal to the surface, such as the L-gap in the case of the Cu(1 1 1) surface, should dramatically influence various experimental results on electron capture (loss) in atom–surface collisions. The main goal of this joint theoretical and experimental work is to investigate the impact of the L-gap on the survival probability of hydrogen negative ions interacting with a copper surface. We show that the ion survival probability strongly depends on the collision velocity. At low velocities the electron loss is increased by the collision velocity, whereas at high velocities the Cu(1 1 1) surface behaves like a jellium surface and the shorter the interaction time, the smaller the decay.

Keywords: Ion–solid interactions; Ion scattering; Atomistic dynamics; Copper

1. Introduction

Electron charge transfer during the interaction between an atomic projectile and a metal surface is of both fundamental and practical interest. The charge transfer process plays a very important role in a variety of processes at surfaces, such as desorption, fragmentation of adsorbates, chemical reactions, and quenching of metastable states [1–4]. The most efficient type of charge transfer is one-electron transfer between energetically degenerate electronic levels of the atom and the solid, also called resonant charge transfer (RCT). The RCT process governs negative ion formation in atom–surface collisions.

The RCT process involving negative ions is very sensitive to the geometry of collision, including the scattering angle, projectile distance of closest approach to the surface [5], and crystallographic band structure of the metal [6,7]. It has also been shown that the RCT process is strongly influenced by the presence of a band gap in the direction normal to the surface, such as the L-gap in the Cu(1 1 1) surface [8,9]. The effect of such a band

* Corresponding author. Tel.: +1 409 880 7904; fax: +1 409 880 8270.
E-mail address: rabalaisjw@hal.lamar.edu (J.W. Rabalais).

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gap is to forbid electrons with energies in a certain range to be transferred into the metal along the surface normal. After experiencing the metal potential, the electrons are reflected back from the surface toward the projectile. Depending on the reflectivity of the surface and its ability to localize electrons, surface states may be "built" inside the band gap as a result of several electron transitions back and forth between the surface and the projectile. The interest in studying these states is due to their major role in the electron dynamics at surfaces [8]. Projectile energy levels falling inside the band gap will mainly decay into the surface state continuum rather than into the valence band continuum. To the best of our knowledge, no detailed studies have been carried out regarding the band gap influence on the measured ion fractions at different collision energies. The presence of a band gap should dramatically influence various experimental results on electron capture or loss in ion/atom–surface collisions. This combined theoretical and experimental work investigates the impact of the Cu(1 1 1) L-gap on the survival probability of hydrogen negative ions (H^-) during collisions with the copper surface. The L-gap in Cu(1 1 1) extends below the vacuum level in the range -0.69 to -5.83 eV [11]. The electron reflecting ability of this surface is capable of localizing a surface state whose energy falls inside the band gap at $E = -5.33$ eV. Hydrogen is an excellent projectile choice to test the band gap effect since its unique negative ion energy level is located just below the upper edge of the gap at $E = -0.75$ eV. Thus, we expect the negative ion survival probability during collisions with the copper surface to be strongly affected by the presence of the band gap.

We have performed a detailed investigation of the RCT process between H^- and the Cu(1 1 1) surface by using the Crank–Nicholson wave packet propagation method [10]. The wave packet propagation technique is proliferating rapidly in various areas of theoretical physics, including atomic physics and chemical physics. The technique has become an extremely powerful tool for studying atom–surface collisions since (1) it provides an exact solution to the dynamical problem without making use of the commonly used approximations and (2) it naturally includes non-adiabatic effects. Thus, the method is very well suited to treat the charge transfer not only on clean metal surfaces, but on adsorbate-covered surfaces as well, where non-adiabatic effects are brought into discussion. This propagation technique can be used in two different contexts: (1) Static case: fixed projectile–surface distance. This provides an understanding of the decay of the atomic state into the metal and allows calculation of the level characteristics (energy and width). (2) Dynamic case: By following the wave packet evolution in time, it is possible to obtain the atomic survival probabilities resulting from the collision.

2. Theoretical approach

The basis of the wave packet propagation technique is the study of the time evolution of the wave function of the active electron during the RCT process. The existence of a few active electrons at the same time, could bring into discussion many-body effects. In our approach, the electron is evolving in a compound potential formed by a superposition of the electron–hydrogen core potential $V_{\text{e-H}}(r)$ and the electron–Cu(1 1 1) surface potential $V_{\text{e-surf}}(z)$. The Cu(1 1 1) surface is modeled by using the one-electron pseudopotential suggested by Chulkov and coworkers [11]. It consists of a local potential that is periodic along the surface normal (z-axis) and is independent of the two coordinates parallel to the surface. We place the origin of the potential at the outermost surface atomic layer, so that $V_{\text{e-surf}}(z) = V_1(z) + V_2(z) + V_3(z) + V_4(z)$ will have the following form:

$$V_1(z) = A_{10} + A_1 \cos\left[\frac{2\pi}{a_s}(z+D)\right]; \quad z < 0$$

$$V_2(z) = A_{20} + A_2 \cos(\beta z); \quad 0 < z < z_1$$

$$V_3(z) = A_3 \exp[-\alpha(z - z_1)]; \quad z_1 < z < z_{\text{im}}$$

$$V_4(z) = \frac{\exp[-\alpha(z - z_1)] - 1}{4(z - z_{\text{im}})}; \quad z > z_{\text{im}}$$

The parameter D is the distance between the outermost surface atomic layer and the central atomic layer position, $D = [(n-1)/2]a_s$. In this formula, n is the number of Cu layers used in the calculations