Influence of adsorbed atoms on the charge transfer in atom/ion — surface collision

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The ionization probability of an atom scattered on the atom adsorbed on a metal surface has been studied theoretically within the time-dependent Anderson–Newns model and the time -evolution operator technique. The influence of different parameters describing the investigated system on the dynamics of the charge transfer between the moving atom and the metal surface with an adsorbed atom has been investigated and the comparison with the results obtained for scattering on a clean metal surface has been made.

1. Introduction

Charge exchange processes play a fundamental role in atom/ion — metal surface collisions. The knowledge of the dynamics of the charge transfer is necessary for understanding of a number of physical processes in many surface analysis techniques, for example, in ion scattering spectroscopy (ISS), in electron- or photo-stimulated desorption (ESD, PSD). Especially, the resonant charge transfer (RCT) between a low-energy ion/atom beam and a metal surface has been a subject of many experimental and theoretical studies, *e.g.*, [1] − [9].

Usually, the time-dependent Anderson–Newns (AN) model is used for a theoretical description of the charge transfer process. The AN model is sufficiently good to give a reasonable explanation of many experimental studies concerning the clean and perfect surfaces. However, realistic surfaces have adsorbed impurities and the presence of additional atoms at the surface can affect the charge transfer process [10]. For example, the presence of oxygen at the silicon surface enhances the ionization probability of sputtered Si atoms [11]. The RCT process is sensitive to whether the atom is backscattered from the adsorbate or from the substrate atom. As the electron occupancy of atoms scattered from a given adsorbed atom or a substrate atom can be measured by experiment [11] − [13], then it should be interesting to investigate theoretically the RCT process during scattering of atoms/ions on the atoms adsorbed on the surface. In this case the electron can be transferred from the moving atom to the surface both directly and indirectly through the adsorbed atom level. The final charge state of the scattered atom should depend on the position of the metal surface Fermi energy, the adsorbed atom energy level ε_A, the moving atom level ε_0 and the atom velocity.

The aim of this paper is to study the RCT process for the above-mentioned system within the time-dependent AN model and the time-evolution operator technique [5] − [7], [14], and to determine the influence of different system parameters on the final occupancy of the scattered atom.

2. Theory

The Hamiltonian of the considered system can be written in the form

$$H = H_0 + V \tag{1}$$

where

$$H_0 = \sum_k \varepsilon_k c_k^+ c_k + \varepsilon_A c_A^+ c_A + \varepsilon_0(z) c_0^+ c_0, \tag{2}$$

$$V = \sum_k (V_{kA} c_k^+ c_A + V_{k0}(z) c_k^+ c_0 + \text{h.c.}) + V_{A0}(z) c_A^+ c_0 + \text{h.c.} \tag{3}$$

The operators c_A, c_0, $c_k (c_A^+, c_0^+, c_k^+)$ are the electron annihilation (creation) operators for the adsorbed and incident atom orbitals and for the surface electron state, respectively. $V_{A0}(z)$, $V_{kA}(V_{k0}(z))$ are the matrix elements of the interaction between the scattered and adsorbed atoms and between the adsorbed (moving) atom and the k-th level of the surface electron band. The incident and adsorbed atoms are characterised by their valence electron levels ε_A and $\varepsilon_0(z)$, respectively, and the dispersion of the surface electron band is described by ε_k.

We assume that

$$\varepsilon_0(z) = \varepsilon_0(0) + az \tag{4}$$

where: $a = -\varepsilon_0(0)/z_c$, $z_c = 3$ a.u., and z_c − denotes the distance from the surface at which the energy of the moving atom level coincides with the centre of the surface band. The z-dependence $V_{A0}(z)$ and $V_{k0}(z)$ is taken in the exponential form, usually used in literature [8]

$$V_{A0}(z) = V_{A0} \exp(-z/\lambda), \tag{5}$$

$$V_{k0}(z) = V_{k0} \exp(-z/\lambda) \tag{6}$$

where λ is the interaction range (we assume $\lambda = 2.5$ a.u., $V_{A0} = 2$ eV and $V_{k0} = 1$ eV).

In order to calculate the occupancy of the moving atom we describe the dynamical evolution of the system in terms of the time-evolution operator $U(t, t_0)$ (in the interaction representation) given by the equation $(\hbar = 1)$

$$i \frac{\partial}{\partial t} U(t, t_0) = \tilde{V}(t) U(t, t_0) \tag{7}$$

where:

$$\tilde{V}(t) = U_0(t, t_0) V(t) U_0^+(t, t_0), \tag{8}$$

$$U_0(t,t_0) = \exp\left[i\int_{t_0}^{t} H_0(\tau)d\tau \right]. \tag{9}$$

The occupancy of the moving atom reads

$$n_0(t) = n_0(t)\,|U_{00}(t,t_0)|^2 + n_A(t_0)|U_{0A}(t,t_0)|^2 + \sum_{\mathbf{k}} n_{\mathbf{k}}(t_0)|U_{0\mathbf{k}}(t,t_0)|^2 \tag{10}$$

where $n_0(t_0)$, $n_A(t_0)$ and $n_{\mathbf{k}}(t_0)$ are the initial occupancies of moving and adsorbed atoms and substrate energy levels, respectively. $U_{ij}(t,t_0) \equiv \langle i|U(t,t_0)|j\rangle$ denote the appropriate matrix elements of the evolution operator U calculated within the set of basis functions $|A\rangle$, $|0\rangle$ and $|\mathbf{k}\rangle$. We consider ε_0 as an affinity level of the moving atom, then $n_0(t)$ (Eq. (10)) denotes the probability of the negative ionization.

3. Results and discussion

We performed the numerical calculations of the negative ionization probability of the atom scattered on the atom adsorbed on the surface. The obtained results are compared with those calculated for the clean surface. We use the broad rectangular density of states $D(\varepsilon)$ with the band width $D = 8$ eV. In our calculations we place the adsorbed atom energy level ε_A in different regions of the energy band: in the lower part $\varepsilon_A = -D/4$, in the middle of the band $\varepsilon_A = 0$, and in the higher part of the band $\varepsilon_A = D/4$. In all figures the parts **b**), **c**) and **d**) represent the above-mentioned three cases, and the parts **a**) correspond to the results obtained for the clean surface.
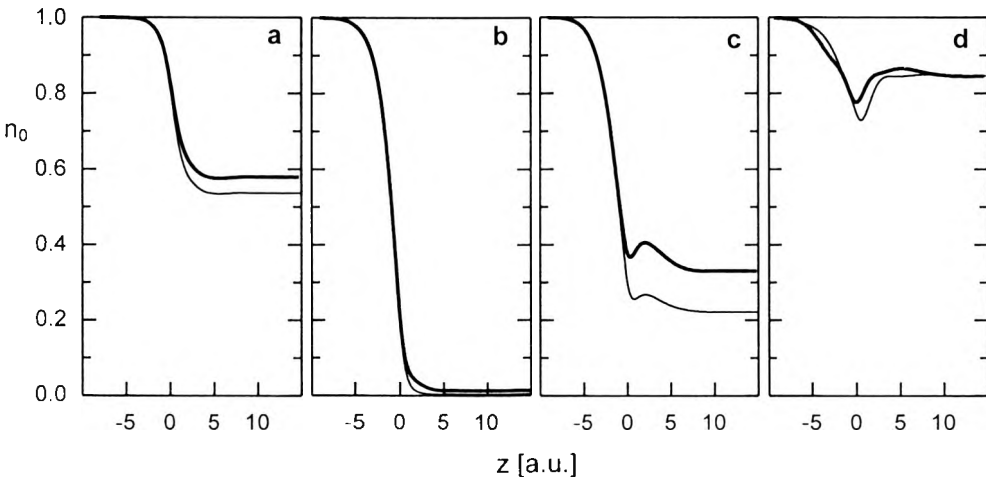

Fig. 1. Probability of the negative ionization of the moving atom *vs.* the distance from the clean surface (**a**) and the surface with the adsorbed atom (**b**, **c**, **d**) for different values of the adatom energy levels: $\varepsilon_A = -D/4$ (**b**), $\varepsilon_A = 0$ (**c**) and $\varepsilon_A = D/4$ (**d**). The distance dependence of $\varepsilon_0(z)$ was taken in the linear form (Eq. (4)) with $z_c = 3$ a.u. and $\varepsilon_0(0) = -2$ eV (thick lines) and $\varepsilon_0(z) = -1$ eV (thin lines). The atom velocity $v = 0.11$ a.u. and empty surface energy band ($D = 8$ eV) was assumed.

In Figure 1 we present the z-dependence of the probability of the negative ionization of the ion scattered on a surface with the adsorbed atom for two values of $\varepsilon_0(0) = -1$ eV (thin lines) and $\varepsilon_0(0) = -2$ eV (thick lines). The atom velocity $v = 0.11$ a.u. and the surface energy band was assumed to be empty. Figure 2 shows
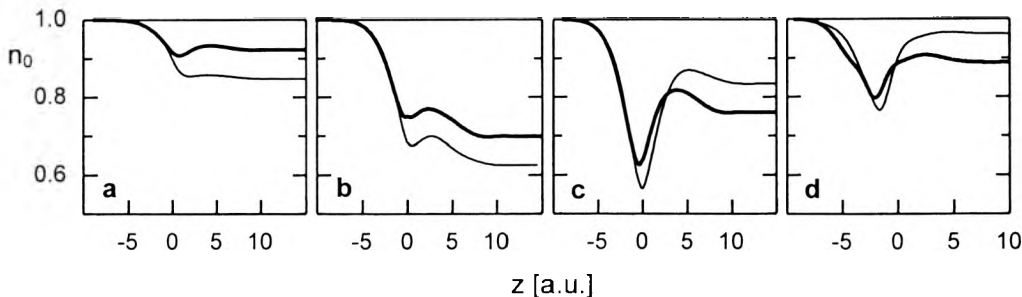

Fig. 2. The same as in Fig. 1, but for the half-filled energy band.

the results obtained for the same parameters as in Fig. 1, but for the half-filled energy band. The results in Figs. 1 and 2 show that the probability of the negative ionization of the scattered ion strongly depends on the relative position of ε_0 and ε_A. The smaller is the difference between $\varepsilon_0(z)$ (for small values of z) and ε_A the larger increase in the probability of the electron hopping between the scattered atom and the surface is observed. Note that the electrons can tunnel between the surface and the moving atom directly, as well as through the adatom level, and the latter tunneling channel can be more efficient than the direct tunneling for the same cases (see Fig. 1 a, b).

Comparing the results presented in the figures **b**, **c** and **d** with those obtained for the clean surface (**a**) we can conclude that the presence of the adsorbed atom can enhance (for example, Fig. 1 a, b) or damp (Fig. 1 c) the charge transfer, depending on the relative position of the energies ε_0 and ε_A.

In the case of partly filled surface energy band the charge transfer from the moving negative ion is considerably smaller due to the smaller number of available states in this band (Fig. 2).

Figure 3 presents the results obtained for the same parameters as in Fig. 1 but for $v = 0.05$ a.u. Now we observe greater differences between the curves obtained for different values of $\varepsilon_0(0)$ (Fig. 3 c,d). Such behaviour can be easily understood, as in this case the incident atom is present on the surface long enough and electronic characteristics of both atom and metal surface (relative position of the atom levels and Fermi level) have greater influence on the charge transfer and final charge state of the scattered atom.

In summary, we have calculated the ionization probability of the negative ion scattered on the atom adsorbed on metal surface. We found that this probability depends strongly on the relative position of the adsorbed and moving atoms energy levels and surface Fermi energy, as well as on the scattered atom velocity. For
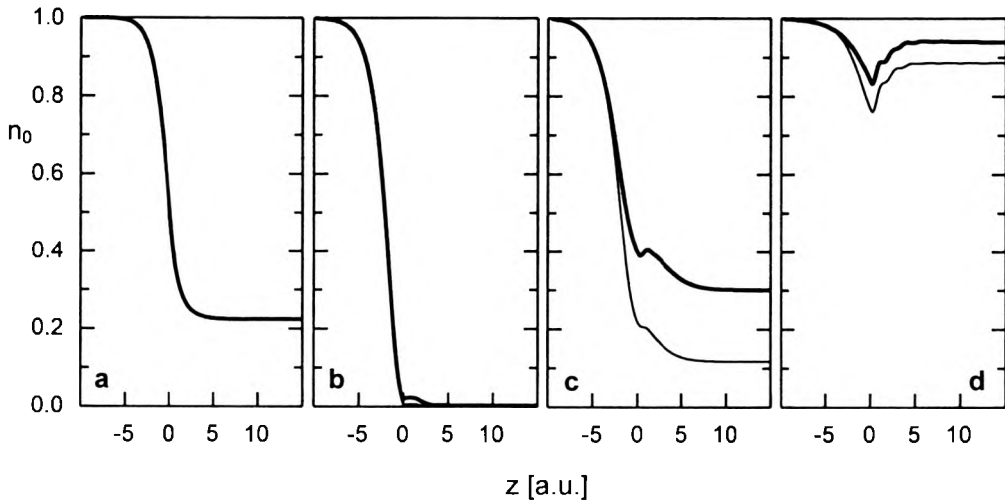
Fig. 3. The same as in Fig. 1, but for the atom velocity $v = 0.05$ a.u.

smaller velocities the functional dependence of the moving atom affinity level on the distance from the surface is more important and relative differences between $\varepsilon_0(z)$ (for small values of z) and ε_A have greater influence on the charge transfer. Moreover, we concluded that the presence of the adsorbed atom can enhance as well as damp (Fig. 1c) the charge transfer depending on the relative position of the energy levels of the scattered atom and the adsorbed atom.

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