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Theoretical study of the electric field manipulation of adsorbates using a Scanning Tunnelling Microscope

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Abstract

We study theoretically the behaviour of a Na or a K atom adsorbed on an Al (100) surface when an inhomogeneous electric field is applied to the system by an STM tip. The method presented in this paper overcomes some difficulties associated to the large number of atoms in the system, and avoids the use of unphysical parallel periodicities. Processes like ‘induced surface migration’ or ‘atomic desorption’ are discussed. © 1998 Elsevier Science S.A.

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1. Introduction

Manipulation of adsorbates by STM can be achieved in very different ways. Very roughly, a distinction can be done between methods in which the tip enters in mechanical or chemical contact with the adsorbate (Ref. [1]), and others in which the tip is not close to the adatom, but acts on it via an intense electric field pulse (Refs. [2,3]). The calculations presented in this paper concern this second category. In Section 2 we pose the main difficulty associated with the description of this kind of processes. In Section 3, quantitative results are presented for the STM induced migration and desorption of alkali adsorbates on Al.

2. Method of calculation

The system has been analysed using a Local Density ab initio—Linear Combination of Atomic Orbitals method (details can be found in Ref. [4]). The important aspect that will be treated here is the way in which a very large and inhomogeneous metallic system can be handled selfconsistently. A typical example of such a system is a STM configuration, where the tip breaks completely the symme-

try. If an intense electric field is applied between the tip and the sample, it is necessary to take into account the charge redistribution in a large area, including several hundreds of non equivalent surface and tip atoms (see Fig. 1).

The main hypothesis on which the method relies is that there exists a large part of the system where the charge is a linear function of the potential applied on that region. The linear region has been named ‘zone L’ in Fig. 1, being ‘zone T’ that area where the full response of the system is taken into account. In what follows, we shall label those parts ‘B’ and ‘A’ respectively. Region A represents the area on the metal surface where we assume the ad-atom and the tip to introduce the strongest perturbation; on the other hand, region B is assumed to be only slightly perturbed. Then, we assume that in B, the perturbation potential, V_i^B , induces the following charge, n_i^B :

$$n_i^B = \sum_j \chi_{ij}^{BB} V_j^B \quad (1)$$

where the sum extends to all sites and orbitals belonging only to region B. We have checked that the hypothesis of linearity in region B is valid at least in the range of biases considered here (up to 12 V, being the tip–sample distance 19 a.u.). Furthermore, the whole tip—including the apex atoms, where the field is strongest—exhibits a linear behaviour.

The electronic linear response of the metal can be derived within the Green-function formalism; the unper-

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turbed Green's function, $G_{ij}^{(0)}(\omega)$, is defined by the equation:

$$G_{ij}^{(0)} = \left(\omega \delta_{ij} - H_{ij}^{(0)} \right)^{-1}, \quad (2)$$

where $H_{ij}^{(0)}$ is the unperturbed Hamiltonian of the Al–metal surface. Then, χ_{ij}^{BB} is given by:

$$\chi_{ij}^{BB} = \frac{1}{2\pi} \text{Im} \int_{-\infty}^{E_F} G_{ij}^{(0)}(\omega) G_{ji}^{(0)}(\omega) d\omega. \quad (3)$$

In our calculations, only the diagonal term, $i = j$, contributes substantially to the induced charge, n_i^B , as corresponds to a Fermi–Thomas approximation.

We are going to use Eq. (1) to reduce the total self consistent problem in the region A + B, to an effective selfconsistent one in the reduced area A.

To this end, consider the self consistent potentials, V^A and V^B , and their relation to the induced charges n^A and n^B :

$$V^A = \sum_j v_{ij}^{AA} n_j^A + \sum_j v_{ij}^{AB} n_j^B \quad (4a)$$

$$V^B = \sum_j v_{ij}^{BA} n_j^A + \sum_j v_{ij}^{BB} n_j^B; \quad (4b)$$

where \mathbf{v}^{AA} , \mathbf{v}^{AB} and \mathbf{v}^{BB} define the coulomb potentials created by the different charges. It is convenient to rewrite Eqs. (1), (4a) and (4b) in matrix form:

$$\underline{n}^B = \chi^{BB} \underline{V}^B \quad (5a)$$

$$\underline{V}^A = \mathbf{v}^{AA} \underline{n}^A + \mathbf{v}^{AB} \underline{n}^B \quad (5b)$$

$$\underline{V}^B = \mathbf{v}^{BA} \underline{n}^A + \mathbf{v}^{BB} \underline{n}^B. \quad (5c)$$

Then, eliminating \underline{n}^B and \underline{V}^B from Eqs. (5a), (5b) and (5c) we obtain the following equation:

$$\underline{V}^A = \left[\mathbf{v}^{AA} + \mathbf{v}^{AB} \chi^{BB} (\mathbf{I} - \mathbf{v}^{BB} \chi^{BB})^{-1} \mathbf{v}^{BA} \right] \underline{n}^A. \quad (6)$$

This is the basic equation allowing us to include the effect of region B in the self-consistent equations for region A. In this method we replace the effect of region B by the effective potential, $\mathbf{v}_{\text{eff}}^{AA}$, linking \underline{V}^A and \underline{n}^A ; thus, instead of \mathbf{v}^{AA} we have to use the effective coulomb interaction:

$$\mathbf{v}_{\text{eff}}^{AA} = \mathbf{v}^{AA} + \mathbf{v}^{AB} \chi^{BB} (\mathbf{I} - \mathbf{v}^{BB} \chi^{BB})^{-1} \mathbf{v}^{BA}. \quad (7)$$

Then, we solve the sample–adatom–tip problem in the reduced region A, and introduce the effect of region B through the effective Hartree potential defined by Eqs. (6) and (7). Notice that the main difficulty of this method is to obtain $(\mathbf{I} - \mathbf{v}^{BB} \chi^{BB})^{-1}$; this is calculated only once and used, later on, in each step of the self-consistent procedure. In practice, we can easily introduce in our calculations a region B extending up to 10–14 cells away from the adsorbed atom, and reduce the full non-perturbative self-

consistent calculation to a restricted area, A, having only a 3×3 size.

We should also comment that the electronic structure of the reduced area A is obtained by using the Green-function techniques already presented in Ref. [4] and determining, in a first step, the different components, $G_{ij}^{(0)}(\omega)$, ($i, j \in A$) of the ideal metal surface. In this approach, we neglect the small perturbation that the potential, V^B , introduces in the Green function, $G_{ij}^{(0)}$, of region A. In a further step, this Green function, $G_{ij}^{(0)}$, is perturbed by the different interactions between the metal and the adsorbed atom or the tip. The crucial point to realize is that the combination of this Green function technique and of the effective Coulomb interaction discussed above reduces the general problem appearing in our LCAO-LD approach to selfconsistently calculating V_i and n_i around the reduced region A.

3. Results

The above method has been used to study the behaviour of Na and K atoms adsorbed on an Al (100) surface, under the electric field created by an Al tip. The system is depicted in Fig. 1. We have considered a tip grown in the (100) direction. The tip is modelled as a big pyramid made of seven atomic layers.

The inhomogeneous electric field at the interface is capable of inducing a directional diffusion of the adatom. Also, for high enough bias, the adatom may jump from the surface to the tip. In what follows we shall analyse some magnitudes which characterise these processes.

Fig. 2 illustrates the adequacy of the method for obtaining the self consistent charge of these large systems. We show the electric field obtained at the interface when a bias is applied to the tip. The upper figure corresponds to 3 V applied to a tip whose apex atom is located 19 a.u. over the surface. A sodium atom is located just under the tip, 5 a.u. over the surface, at its equilibrium distance. The lower figure shows the case of an applied bias of -3 V. The

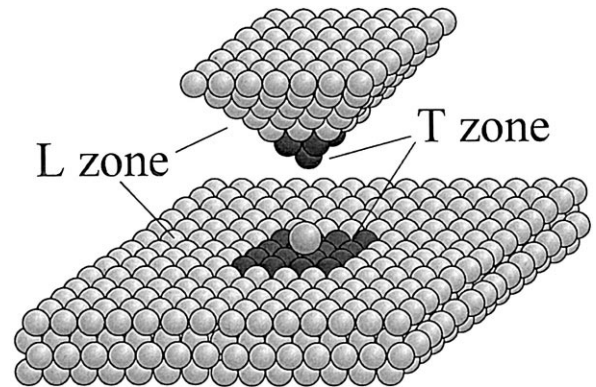


Fig. 1. Model of the surface–tip–adsorbate system considered. The lighter area is treated in linear response (zone ‘L’), while the darker area (zone ‘T’) is treated to all orders.

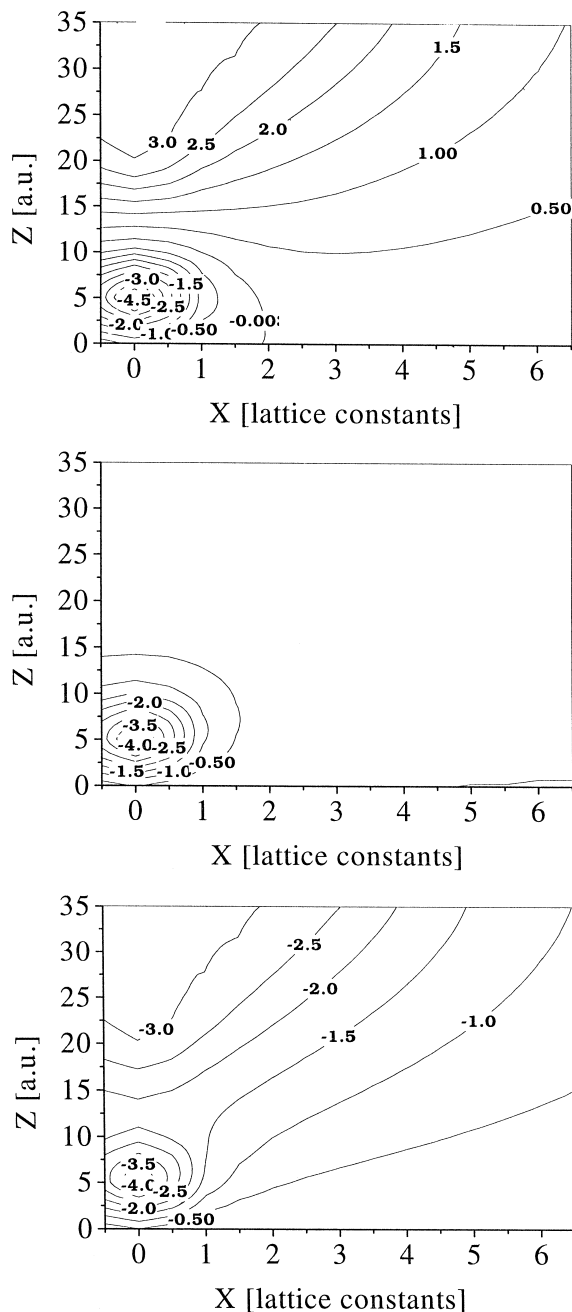


Fig. 2. Electrostatic potential at the interface, as seen by a negative point charge, when +3 V are applied (top); 0 V and the tip has been removed (middle); or -3 V applied (bottom).

case when the tip is absent is shown in the central figure. It is evident, from these figures, that the adatom is more ionic in the first case, while there is a ‘neutralising’ effect for the adatom in the third case.

The lateral movement of the adatom over the surface is determined by the diffusion energy barriers. When the electric field created by the tip is acting on the system, those barriers are modified. Due to the inhomogeneous character of the field, the barrier overcome by the adatom when jumping between two sites will be different from that overcome when the adatom jumps in the opposite

direction. This determines a net flux probability in a given direction. We have calculated the change of barrier heights when a positive bias is applied to the tip. This is shown in Fig. 3a and b. The stable adsorption sites have been numbered from 0 to 3. Site 0 corresponds to the site located just under the tip. Its neighbouring adsorption site is called site 1 (there are four equivalent ones). The next site in the same direction is called site 2, and so on. The barrier heights overcome during each jump are shown in Fig. 3 as a function of the applied bias. The upper graphs show the barrier heights corresponding to diffusion towards the tip. Those heights decrease when the voltage increases. On the other hand, the barriers corresponding to outwards diffusion increase in the ‘1–2’ and ‘2–3’ processes, but decrease in the case of the ‘0–1’ jump (‘ x – y ’ process means a jump from site x to site y). The different behaviour in the third case is explained by the presence of two counteracting effects operating simultaneously in the barrier height reduction phenomenon: firstly, the field gradient tends to increase all the barriers in outward diffusion; on the other hand, if the field were homogeneous, barrier heights tend to be reduced in alkali adsorbates (as shown experimentally in Ref. [5], for potassium) when the field is positive (and they decrease when it is negative). The field just under the tip is rather constant, and therefore the dominant effect is that of the barrier height reduction for the jump ‘0–1’. For the other cases, the field gradient dominates the process, and thus the barrier heights ‘1–2’ and ‘2–3’ increase.

Two important magnitudes can be obtained from the behaviour of the adsorption energy as a function of the bias: the dipole moment and the polarisability, which are obtained from the first and second coefficients of the Taylor expansion of the energy vs. field curve (see Refs. [5–8]). An estimation of these quantities when the adatom is under the tip (site ‘0’) yields $\mu = 2.0$ a.u. for Na, and $\mu = 2.3$ a.u. for K; the polarisability is estimated to be about 8 \AA^3 for Na, and 20 \AA^3 for K. The experimental value for Na/W(110) provided by Ref. [9] gives a polarisability of 5 \AA^3 , while we have not found any experimental estimation for K. Regarding the dipole moment, it has been experimentally measured by Porteus (Ref. [10]) for the system Na/Al, which corresponds to the case treated here, yielding 2.8 a.u. Other theoretical calculations on jellium have obtained values between 1.3 and 1.5 a.u. (Refs. [11,12]) while a value of 4.1 a.u. has been obtained in a cluster calculation (Ref. [13]; in this reference, however, the author recognises that such a value is an overestimation, and should be closer to the experimental one given by Porteus (Ref. [6–8])). Regarding potassium, the dipole moment of the system K/W(110) has been measured experimentally (Ref. [9]), yielding a value around 2.1 a.u. Theoretical studies on jellium yield values of 2.1 and 2.6 a.u. for $r_s = 2$ and 1.5 respectively [12].

If the voltage is increased more and more, finally the adatom can desorb, jumping to the tip. Our analyses

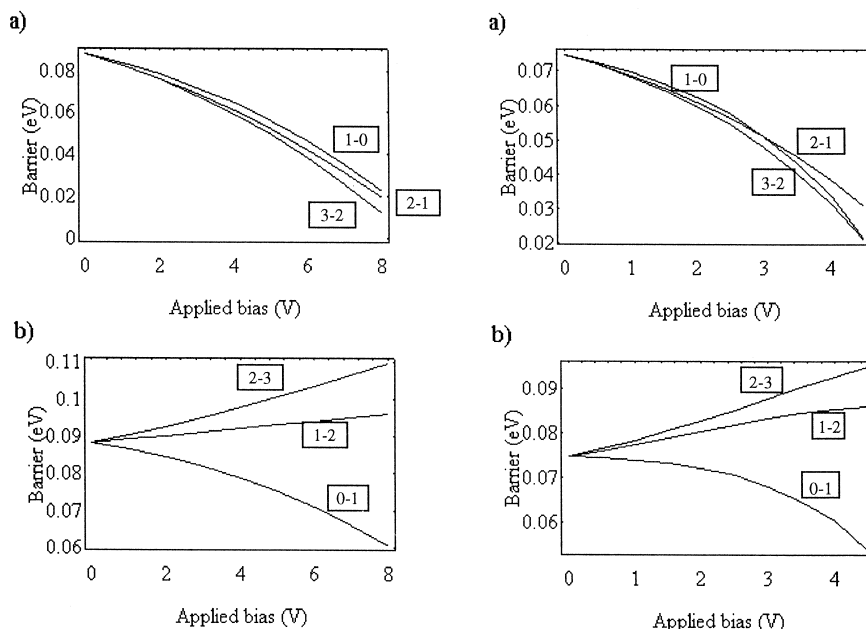


Fig. 3. Surface diffusion barriers corresponding to jumps between neighbouring adsorption sites. Left: case of Na. Right: case of K. (a) The atom moves away from the tip. (b) The atom jumps towards the tip.

indicate that a desorption channel is formed in the potential energy surface of the system. In this way, a diffusion assisted mechanism could take place, where atoms first migrate to the position under the tip, and once there, they jump to the tip through the desorption channel.

From the analysis of the desorption barrier for the systems considered, we have estimated a desorption field of $0.6 \text{ V}/\text{\AA}$ for the case of Na/Al (100), and $0.3 \text{ V}/\text{\AA}$ for K/Al. Such fields are obtained at the adsorption site under the tip (site '0') when 12 or 6 Volts are respectively applied to the tip, that is located 19 a.u. over the surface. Other calculations performed for homogeneous fields have yielded desorption fields close to those estimated here: Neugebauer and Scheffler (Ref. [14]) estimate $0.8 \text{ V}/\text{\AA}$ for the Na/Al desorption, while Kahn and Ying (Ref. [12]) obtain $0.7 \text{ V}/\text{\AA}$ for Na and $0.4 \text{ V}/\text{\AA}$ for K, both on Al. Experimental results have been reported [15] for Na and K on W (110), yielding desorption fields of 0.6 and $0.36 \text{ V}/\text{\AA}$ respectively.

4. Conclusions

We have presented a method that simplifies the self-consistent calculation of large inhomogeneous metallic systems under long range electrostatic fields. This is done by projecting a large area of the system, which responds linearly to the applied field, onto a smaller part which responds nonlinearly. This method is appropriate for describing the STM manipulation of adatoms when the electric field effects are long ranged, as is the case of STM

induced adatom migration, or the atomic transfer between far enough electrodes (see Refs. [6–8]). The calculated diffusion and desorption barriers indicate the feasibility of a low temperature experimental study of those processes for atoms adsorbed on metals.

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