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Kinetic excitation of solids: The concept of electronic friction

M. Lindenblatt [a], E. Pehlke [a], A. Duvenbeck [b], B. Rethfeld [c,d], A. Wucher [b,*]

[a] *Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany*
[b] *Fachbereich Physik, Universität Duisburg-Essen, Lotharstr. 1, D-47048 Duisburg, Germany*
[c] *Institut für Kernphysik, Technische Universität Darmstadt, Schlossgartenstrasse 9, D-64289 Darmstadt, Germany*
[d] *Gesellschaft für Schwerionenforschung, mbH Planckstrasse 1, D-64291 Darmstadt, Germany*

Abstract

The energy dissipation into electron–hole pairs has been simulated ab initio within time-dependent density-functional theory for hydrogen atoms with a low kinetic energy in the range below 10 eV impinging on an Al(111) surface. The H-atoms penetrate into the crystal via the fcc-hollow site and are backscattered by the third atomic layer. The energy dissipation rate due to electronic friction fits well to known bulk data. The electron–hole pair excitation spectra are characterized by an approximately exponentially decaying tail of the electron energy distribution, with a fictitious temperature describing the slope of the spectra in the range of 2000–3000 K, depending on the initial kinetic energy of the incident H-atom.
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1. Introduction

If a ground state atom, molecule, or cluster collides with a metal surface, part of its kinetic energy and, in case it sticks to the surface, also part of its chemisorption energy is converted into electronic excitations. The implications of this are twofold: first, the incoming particle will experience an energy loss, which in the simplest approximation can be described as a friction force acting on the particle to slow down its motion. This electronic stopping effect is well known in the field of particle–solid interaction, where the respective energy loss per unit distance traveled within the solid is described as the electronic stopping power of the solid for the particular projectile. Second, the process leads to the excitation of electron–hole pairs which, depending on the electronic properties of the solid and the total energy deposited, can in turn undergo further

scattering processes. One of the most prominent manifestations of this excitation is the particle bombardment induced emission of electrons from the surface into, e.g., the surrounding gas or vacuum. It is apparent that this process requires electron excitation energies in excess of the surface work function. In the case of chemically inert projectiles, such excitations are generated at appreciable rate only if the kinetic energy of the projectile exceeds values of the order of keV. In situations with strongly exothermic chemical reactions between the projectile and the solid, a chemically induced exo-electron emission can occur [1]. Quite recently, the kinetically and chemically induced internal emission of electrons has been detected experimentally using metal–insulator–metal tunnel junctions [2,3] or Schottky diodes [4–6]. In these experiments, electrons chemically excited at a metal surface into states with energies below the vacuum level are detected as a particle induced internal current into an underlying substrate, provided the energy of the electron or hole is large enough to overcome the respective internal energy barrier. The results

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* Corresponding author. Tel.: +49 203 379 2292; fax: +49 203 379 2289.
 E-mail address: wucher@uni-essen.de (A. Wucher).

obtained with these experimental techniques clearly demonstrate the conversion of kinetic or chemical energy into the excitation of electron–hole pairs even at energies of the incident particle down to the eV level. It has been demonstrated that even a simple adsorption reaction, where gas atoms at thermal energies approach a surface, gaining solely the chemical adsorption energy of the order of 1–2 eV, is accompanied by the generation of electron–hole pairs within the solid [4–6]. These findings manifest that chemically induced electronic excitations represent a ubiquitous energy dissipation channel at metal surfaces, the fundamentals of which, though explored since long, are still matter of intense research [7–14].

Conceptually the simplest picture of the interaction between a projectile atom moving in a solid environment involves the treatment of the solid as a free, degenerate electron gas. This case has first been treated in an approximative way by Fermi and Teller [15], followed by Ritchie et al. [16], and by Lindhard and coworkers [17,18], who used linear response theory to calculate the respective scattering cross section. These results show that the electronic energy loss indeed manifests as a friction force proportional to the particle velocity v, provided the value of v is small compared to the average velocity of valence electrons in the system. The latter condition is violated only in the limit of very high kinetic impact energies of the order of 100 keV or above, which are far outside the energy range of a few eV considered here. During the years, numerous corrections to the Lindhard formalism have been published in order to account for higher order terms in the perturbation expansion and for the electronic properties of the solid in a more realistic manner [19–23]. Prevailing descriptions are based on full quantum mechanical calculations of the scattering cross section. They yield a velocity-proportional friction force acting on the moving particle with, however, modified friction coefficients. Recently the energy loss of a localized charge propagating through a material with constant velocity has been calculated using TDDFT by Pruneda et al. [24].

Apart from the influence that the electronic energy loss exerts on the motion of the projectile, an important question regards the excitation spectrum produced in the electronic system of the solid. A proper description of this quantity is of fundamental interest for the interpretation of phenomena in surface chemistry, in particular for the prediction of the efficiency of processes like external or internal electron emission. Again, the conceptually simplest model involves the scattering of single electrons by the projectile, the latter being represented as a pseudopotential moving with constant velocity v through a degenerate electron gas [28]. This scenario has been described in numerous publications, ranging from simple classical treatments to quantum mechanical scattering theory [27–31]. In the case of the homogeneous electron gas, energy and momentum conservation considerations imply a maximum possible excitation energy for a single scattering event, which is given (in atomic units) by

$$\Delta\varepsilon_{max} = 2k_F v, \tag{1}$$

where k_F is the Fermi wave vector characterizing the homogeneous electron gas [28]. In the framework of kinetic electron emission, Eq. (1) leads to a minimum kinetic impact energy of the projectile in order to allow an excited electron to overcome the surface barrier and be emitted. While many early experiments on kinetic electron emission have indeed indicated the existence of such a threshold, more recent experimental data clearly reveal electron emission well below the threshold velocity calculated by equating (1) with the work function, obviating the need for a more realistic description of the excitation process. This ultimately requires a treatment of the scattering within the solid beyond the jellium model, and velocity changes the particle experiences due to its interaction with the atoms in the solid ought to be accounted for. Moreover, the projectile may displace atoms in the solid from their equilibrium lattice positions and induce secondary motions of these particles, which in turn may again contribute to the resulting electronic excitation spectrum. As a consequence, it appears desirable to combine a complete molecular dynamical description of the particle dynamics with an ab initio treatment of the resulting electronic excitation. In the present work, we employ this concept in order to calculate the excitation spectrum and the energy dissipation rate for a specific system of a low-energy hydrogen atom approaching and penetrating a metallic surface, the Al(1 1 1). The electron dynamics of the system will be described numerically by time-dependent density-functional theory (TDDFT) [32,33], while the Ehrenfest approximation [34] will be used for the dynamics of the nuclei.

2. Description of the calculation

To simulate the coupled dynamics of electrons and ions, we have implemented the simultaneous integration of the time-dependent Kohn–Sham equations [32,33] for the dynamics of the electrons and the Ehrenfest equation for the motion of the nuclei into the plane-wave total-energy program-package [35] from the Fritz–Haber Institute in Berlin [36]. The time step of the integration needed for the H/Al simulations is determined by the electron dynamics and amounts to about 0.003 fs in case of the present simulations. This renders the numerical simulations extremely time consuming and effectively limits the size of the supercell as well as, e.g., the size of the basis set that can be employed in the calculations.

To describe the chemisorption of hydrogen atoms on the Al(1 1 1) surface, a slab geometry with a periodically repeated $2\sqrt{3} \times 2\sqrt{3}$ supercell containing 14 layers of Al-atoms is used. Two H-atoms are contained in the simulation cell, one impinging from either side of the Al-slab. The integration over the Brillouin zone is approximated by a single special **k**-point [37], which differs from the Γ point. While the H-atom is represented by its $-1/r$