Kinetic excitation of solids: The concept of electronic friction

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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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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

\[
\Delta E_{\text{max}} = 2k_F v, \tag{1}
\]

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(111). 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(111) 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 \( \Gamma \) point. While the H-atom is represented by its \(-1/r\)
Coulomb potential, the Al-atoms are described by norm-conserving ionic pseudopotentials for the three valence electrons [38,39]. Basically no Fermi-surface smearing is used, thus the time-evolution of a pure quantum state is described. The Kohn–Sham states are expanded into plane waves with a kinetic energy cut-off of 10 Ry. A spin-unpolarized system is assumed throughout the whole simulation. The adiabatic approximation is applied to the time-dependent exchange-correlation potential, i.e. the instantaneous electron density \( n(r,t) \) is inserted into the Perdew–Burke–Ernzerhof form of the generalized gradient approximation (PBE-GGA) [40] for the exchange-correlation functional from static density-functional theory.

For the preparation of the initial configuration we have relaxed the atomic positions of the clean Al-slab until the residual forces are below \( 10^{-3} \) H/bohr. Then two hydrogen atoms have been added to the supercell. They were positioned above the fcc-hollow site, one H-atom on either side of the slab. The H-atoms are located in such a way that the distance to the nearest neighbor Al-atoms amounts to 6 bohr. The initial velocity of all Al-atoms was set to zero, while a finite velocity corresponding to a kinetic energy of 2.0 eV, 5.0 eV, or 10.0 eV was assigned to the H-atoms. It should be noted here that the trajectory starts with the H-atom not far away from the surface, but still within the chemisorption well. Thus, neglecting the energy dissipation along the outer part of the trajectory, the initial kinetic energy has to be corrected by \(-0.24\) eV to obtain the kinetic energy of the respective H-atom infinitely far away from the surface. The TDDFT and Ehrenfest equations were integrated until the H-atom was reflected and returned back to the same z-coordinate perpendicular to the surface where it started from. Only in case of the run with 2 eV initial kinetic energy of the H-atom the integration had to be stopped somewhat earlier, because the H-atom reached an outer (on the vacuum side) reflection point of its trajectory due to the strong energy dissipation. During the simulation, Kohn–Sham wave-functions \( |\psi_{\mathbf{k}}(t)\rangle \) and ionic coordinates \( \mathbf{R}(t) \) are stored at equidistant time steps \( \Delta t \). A posteriori, these configurations are relaxed electronically down onto the Born–Oppenheimer surface at frozen-in ionic positions \( \mathbf{R}(t) \). The difference in electronic total-energy \( E_{\text{TDDFT}}(t) - E_{\text{BO}}(\mathbf{R}(t)) \) equals the energy \( E_{\text{diss}} \) that is dissipated into electron–hole pairs. The Kohn–Sham excitation spectra are calculated by projecting the \( n \) time-dependent Kohn–Sham states from the TDDFT run onto the Kohn–Sham eigenstates \( |\phi_{j}(\mathbf{R}(t),\mathbf{k})\rangle \) with eigenenergies \( \epsilon_j(\mathbf{R}(t),\mathbf{k}) \) of the system after relaxation onto the Born–Oppenheimer surface [36]:

\[
n(\epsilon,t) = 2 \sum_{f} \sum_{j} \int d\mathbf{k} \frac{1}{\Omega_{BZ}} \left| \langle \psi_{f}(\mathbf{k},t) | \phi_{j}(\mathbf{R}(t),\mathbf{k}) \rangle \right|^2 \\
\times \delta(\epsilon - \epsilon_j(\mathbf{R}(t),\mathbf{k}))
\]

The integral over the Brillouin zone is represented by a special \( \mathbf{k} \)-point. The calculated spectrum consists of a discrete finite set of eigenenergies, thus it is convoluted with a Gaussian with a width of 50 meV. In this way the electronic energy dissipation along the trajectory can be quantified and studied in detail.

3. Results and discussion

The calculations were done for a hydrogen atom approaching and penetrating into a (111) oriented aluminum surface. As a test case for this study, a specific trajectory was initiated by placing the hydrogen atom at some distance above the threefold Al(111) fcc-hollow site, with the separation between the H-atom and its nearest-neighbor Al-atoms equal to 6 bohr.

This choice of the starting point ensures that the projectile, being attracted and accelerated towards the surface, will penetrate the top atomic layer of the solid before being reflected by an inner atomic Al-layer. To examine the velocity dependence of the electronic excitation exerted by the projectile motion, three different cases were treated where the projectile starts with an initial kinetic energy of 2 eV, 5 eV or 10 eV. The velocity vector is directed towards the surface. Along the trajectory of the particle within the solid, the excitation spectrum of electron–hole pairs was analysed and the total energy dissipated into electron–hole pairs was calculated for the two trajectories with \( E_{\text{kin}}^{\text{init}} = 2 \) eV and 10 eV.

The results are displayed in Fig. 1 as a function of time after the start of the trajectory calculation. The circles denote the data extracted from the TDDFT calculation. The simulation stops at a time where the projectile has completed one cycle, i.e. has penetrated into the Al-slab, been reflected at the third layer, crossed the surface again and returned close to the initial height above the Al-surface (this means that only part of the full scattering trajectory is simulated). At this final point of the simulation, a total energy of about 1.2 eV, 1.5 eV, and 2.2 eV has been transferred into the electronic system per incident H-atom for an

![Fig. 1. Energy \( E_{\text{diss}} \) dissipated into electron–hole pair excitations as a function of time for initial kinetic energies of the H-atom of 2 eV and 10 eV. The dissipated energy \( E_{\text{diss}} \) refers to a single hydrogen atom. The results from the TDDFT simulation (circles) are compared to the empirical bulk-friction ansatz (full lines), Eq. (4).](image-url)
initial kinetic energy of 2 eV, 5 eV, and 10 eV, respectively. Considering even the acceleration of the H-atom in the chemisorption well (the chemisorption energy is of the order of 2 eV), we note that a sizeable fraction of the total energy available in the system has been dissipated by electronic friction. This finding is in accord with recent experimental data on internal exoelectron emission, or chemicurrents, induced by hydrogen adsorption on silver surfaces [4,6].

Following the concept of electronic friction, the energy dissipated into the electronic system per unit path length \(\frac{dE}{dx}\) of a particle (either an H- or Al-atom, enumerated here by the index \(i\)) moving in a homogeneous electron gas is assumed to be proportional to its velocity \(v_i\),

\[
\left(\frac{dE}{dx}\right)_i = -k_i v_i, \tag{3}
\]

the constant \(k_i\) depending on the electron density and the nature of the moving particle. This yields the overall energy dissipation rate

\[
\frac{dE}{dt} = - \sum_i k_i \frac{2}{m_i} E_{kin}^{i} = - \sum_i A_i E_{kin}^{i}, \tag{4}
\]

where the sum is taken over all particles with mass \(m_i\) moving in the system. Integrating this expression over time, the total energy transferred into the electronic system can be estimated from the kinetic energies of all moving particles which, in turn, can be directly taken from the calculated trajectory. In order to evaluate Eq. (4), the constants \(A_i\) were approximated by experimental data for the electronic stopping power of H- and Al-ions moving through Al-foils by Ormrod et al. [25] and Ward et al. [26] as collected by Echenique et al. in their Fig. 10 of [19]. In particular, the value of \(A_{Al}\) was set equal to 0.0021 fs\(^{-1}\) and \(A_{H}\) was chosen equal to 0.011 fs\(^{-1}\). Note that these values originally describe the electronic energy loss of particles moving in bulk aluminum. In order to allow a fair comparison between Eq. (4) and the TDDFT simulation, we restrict the energy integration to the time interval between those points where the H projectile crosses the uppermost atomic layer of the Al-crystallite. The resulting predictions of Eq. (4) are displayed as full lines in Fig. 1. The contribution from the motion of the Al-atoms turned out to be negligible for the initial conditions studied in this paper. It is evident that the data are in good agreement with the results of the TDDFT calculations. Since no further fitting procedure is involved, this agreement even holds in a semi-quantitative manner. As a consequence, we conclude that – at least for the case studied here – the concept of electronic friction using published data on the bulk friction coefficients \(k_j\) provides an astonishingly good description of the energy transfer processes governing the conversion of kinetic into electronic excitation energy close to the solid surface.

Snapshots of the resulting electronic excitation spectra \(n(\varepsilon, t) - n^0(\varepsilon, R(t))\) along the trajectory are depicted in Fig. 2 for the run with 2 eV initial kinetic energy of the H-atom. For reasons of presentation, the hole part of the spectra has been multiplied with \(-1\), and the spectra are displayed on a logarithmic scale. In detail, the data roughly correspond to the moments where the H-atom crosses the first atomic Al-layer at \(t_1 = 13\) fs, where the H-atom crosses the second atomic Al-layer at \(t_2 = 23\) fs, where the H-atom is reflected at the third layer close to \(t_3 = 29\) fs, and the end of the simulation at \(t_4 = 75\) fs. The buildup of the electron-hole pair excitation density in the solid becomes apparent.

Note that the wiggly structure of the spectra is due to the fact that there are only a finite number of discrete eigenstates contained in the supercell calculation; the corresponding delta-function contributions in the excitation spectra are convoluted with a Gaussian of 50 meV width in order to obtain a reasonably continuous representation of the spectra. We attribute the larger width of the spectra in comparison to the jellium result, Eq. (1), to lattice effects in the electronic structure of the Al substrate and the spectrum of the time-dependent perturbation potential. To analyse the excitation spectra in more detail, the function

\[
\Phi(\varepsilon_jk) = -\ln \left( \frac{1}{f_{jk}} - 1 \right) \tag{5}
\]

suggested by Rethfeld et al. [41], with the occupation numbers \(f_{jk}\) with respect to the Kohn-Sham eigenstate \(|\phi_j(R(t), k)\rangle\) defined by the expression

\[
f_{jk} = \sum_{n} \left| \langle \psi_i(k, t)|\phi_j(R(t), k) \rangle \right|^2, \tag{6}
\]

is plotted versus the discrete set of Kohn–Sham eigenergies in Fig. 3. Areas where the data are suspected to be superposed by numerical noise, e.g. due to residual excitations in the initial configuration, are gray-shaded. They have been estimated from calculated excitation spectra at small simulation times. Note that in thermodynamic
equilibrium $f_j^k$ would equal Fermi occupation numbers and $\Phi(e)$ would become a simple linear function of $e$. Deviation from linearity including the scattering of the $f_j^k$ indicate non-equilibrium electron energy distributions.

Looking particularly at the energy range around the Fermi level (the zero of the energy axis in Fig. 2 and the following), it is seen that the energy spectrum of hot electrons is dominated by low energy excitations closely above and below the Fermi level. In principle, this finding has been predicted by earlier theoretical studies and, therefore, constitutes no real surprise. Theoretical model-Hamiltonians for electron–hole pair-excitation spectra after chemisorption have been analysed since long [7–9], and a DFT-calculation of the electronic friction during chemisorption of H/Cu(111) has been carried through by Trail et al. [10]. What we observe from our simulations is that the spectra can be coarsely approximated by an exponentially decaying tail in the energy range between 0.1 eV and 1–2 eV above or below the Fermi level. This is also evident in the last panel of Fig. 3, where we find linearity within an energy interval exceeding $\pm 1.6$ eV around the Fermi edge. A purely empirical two parameter fit, $n(e,t) - n^{BO}(e,R(t)) = A \exp \left(-e/k_B T\right)$, has been applied to the excitation spectra independently for holes and electrons after the H-atom has performed its full scattering cycle, see Fig. 4.

While on first sight resembling something like equilibrium, it should be emphasized that these fits are not representing any true thermodynamic equilibrium distribution, in particular as thermal equilibrium is represented by only a single parameter, the temperature, as opposed to the two fit parameters we have introduced. For completeness, the fictitious temperatures from the fit in Fig. 4 are summarized in Table 1. Data in the energy range from $\pm 0.05$ eV to $\pm 2$ eV have been included in this least-squares fit. Decreasing the energy range used for fixing the fit parameters reveals a relative uncertainty of the temperature parameter of 10%. Thus the temperature parameters for electrons and holes are to be considered the same within the error bars.

In judging this finding, one has to keep in mind that the femtosecond time scale of the dynamics leading to the formation of the energy distributions is considered to be too short to establish thermodynamical equilibrium among the electronic degrees of freedom. Moreover, as pointed out recently by Veksler [42], the mean free path for electron–electron scattering is significant, since it exceeds the dimensions of our supercell, thus precluding the establishment of a local equilibrium on that length scale. The spectra shown in this work therefore represent the source distribution of electronic excitations generated by the perturbation due to the motion of both the hydrogen projectile and the atoms contained in the model aluminum crystallite.

### Table 1

<table>
<thead>
<tr>
<th>$E_{kin}^{init}$ [eV]</th>
<th>$T$ [K] holes</th>
<th>$T$ [K] electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>2050</td>
<td>2070</td>
</tr>
<tr>
<td>5.0</td>
<td>2160</td>
<td>2330</td>
</tr>
<tr>
<td>10.0</td>
<td>2770</td>
<td>2850</td>
</tr>
</tbody>
</table>
Alterations of the spectra due to electron–electron scattering processes are not reliably described (presumably grossly underestimated as no explicit two-particle scattering is included) in our simulations due to the adiabatic approximation to exchange and correlation.

4. Conclusion

The important message of this work is that, presumably irrespective of the actual equilibration by electron-scattering events, the excitation energy distributions displayed in Figs. 2 and 4 of hot electrons and holes generated by atomic motion in solids can be roughly approximated by an exponentially decaying tail characterized by a fictitious electron “temperature”. Even for extremely low kinetic energies of only a few eV, the resulting excitation “temperature” is shown to be of the order of $10^3$ K. Higher kinetic starting energy of the projectile leads to a higher excitation “temperature”, as detailed in Table 1. As becomes apparent from Fig. 2, the slope of the spectra varies only slightly after the energy distribution has been established, in particular after the reflection of the projectile at the inner Al atomic layer (time $t_3$ in Fig. 2).

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