Inelastic energy loss in low-energy ion-surface collisions

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Recent measurements showed a previously unobserved sharp thresholdlike inelastic excitation occurring in low-energy ion-metal surface collisions when varying the energy of the incident ion. Using a relativistic Dirac-Fock-Slater approach we deduce that the inelastic energy loss of the ion beam can be traced to the fast diabatic promotion of specific molecular levels to the continuum. [S0163-1829(97)03534-0]

Low-energy ion-metal surface collisions allow for a variety of electronic processes to occur. Extensive investigations have been undertaken to quantify the involved charge exchange, ionization, neutralization, and inelastic loss processes which play a fundamental role in areas such as ion-scattering spectroscopy and sputtering.[1–7] A common theoretical ansatz for an ion-metal surface encounter is the jellium approximation for the conduction-band electrons.[8–12] This model allows for an understanding of ionization and neutralization processes happening at larger ion-surface distances but fails in the region of strong overlap between the ionic orbitals and the atomic orbitals of the surface atoms. Experimental evidence has been found recently for a sharp thresholdlike behavior in the inelastic energy loss in low-energy ions (Ne^+) colliding with various metal surfaces such as Fe, Ni, and Cu.[13,14] The inelastic energy loss shows a sharp increase with increasing incident energy which cannot be attributed to the excitation of low-energy electrons along the path of the incoming and outgoing ion. It was therefore proposed that the threshold could be due to inner-shell electron promotion occurring in the close encounter between the ion and a surface atom.[13,14]

In this work we investigate the proposed electron promotion process employing a twofold procedure. In a first step we use an *ab initio* relativistic linear combination of atomic orbitals-molecular orbitals (LCAO-MO) Dirac-Fock-Slater approach to get accurate single-particle molecular levels formed during the slow encounter of the incoming ion and a surface atom. These level diagrams allow for the detailed study of electron promotion occurring at small ion-surface distances R. As we are interested in the close encounter ($R \approx 0.5$ Å) between the projectile and a specific surface atom, the influence of neighbor atoms, which in a typical metal are at least 3–5 Å away, can be neglected and a two-center ansatz is appropriate. In a second step we use the one-electron kinetic-emission model proposed by Sroubek *et al.*[15–17] and Fine *et al.*[18] to understand the projectile energy loss. The Sroubek-Fine picture states that core-level promotion in binary collisions generates localized molecular orbitals with energies above the ionization threshold. Subsequently these diabatically promoted states interact with continuum states and the promoted electrons can be ejected with fairly high energies. This approach should hold as long as the initial binding energy of the promoted electron is high enough and the promotion time is short compared to the orbiting time of the active electron, i.e., the state stays localized during the promotion process. Sroubek *et al.*[15–17] and Fine *et al.*[18] used this ansatz to understand electron emission spectra in slow ion-surface collisions. During the core-level promotion and subsequent ionization of the promoted electron, energy is taken out of the projectile kinetic energy leading to a significant inelastic energy loss of the projectile. Direct ionization through inner-shell promotion was previously investigated by Wille.[19]

We briefly outline our theoretical ansatz:[20–23] The two-center single-particle Dirac-Fock-Slater equation for the projectile-surface atom system to be solved is given as

$$\left[c\hat{\vec{\alpha}}\cdot\hat{\vec{p}} + (\hat{\beta}-1)m_e c^2 + \frac{Z_T e^2}{|\vec{r}-\vec{R}_T|} + \frac{Z_P e^2}{|\vec{r}-\vec{R}_P|} + \int \frac{\rho^{\mathrm{MO}}(\vec{r})}{|\vec{r}-\vec{r}'|} d\vec{r}' - 3\mathcal{X}_\alpha \left(\frac{3}{8\pi}\rho^{\mathrm{MO}}(\vec{r}) \right)^{1/3} \right] \phi_j(\vec{r};\vec{R}) = \varepsilon_j(\vec{R})\phi_j(\vec{r};\vec{R}), \quad (1)$$

where $\phi_j(\vec{r};\vec{R})$ are the adiabatic molecular orbitals.

The time-independent Dirac-Fock-Slater equation (1) is solved in the framework of an MO-LCAO (molecular orbitals-linear combination of atomic orbitals) ansatz therefore writing:

$$\phi_j(\vec{r};\vec{R}) = \sum_{k=1}^{A} c_{jk}(\vec{R})\chi_k(\vec{r}). \quad (2)$$

The states $\chi_k(\vec{r};\vec{R})$ are atomic four-component spinors

$$\langle \vec{r}|\chi_k\rangle \equiv \chi_{n\kappa m_j}(r,\Omega) = \frac{1}{r}\begin{pmatrix} F_{n\kappa}(r) & \mathcal{Y}_{+\kappa,m_j}(\Omega) \\ iG_{n\kappa}(r) & \mathcal{Y}_{-\kappa,m_j}(\Omega) \end{pmatrix}.$$

Using the ansatz (2) the solution of the Dirac-Fock-Slater equation (1) is reduced to the secular equation

$$\mathbf{h}^{\mathrm{MO}}\mathbf{c} = \varepsilon \mathbf{S}\mathbf{c}^T, \quad (3)$$

which is to be solved self-consistently for all relevant projectile-surface atom distances. The relativistic molecular orbitals $\phi_j(\vec{r};\vec{R})$ are ordered with respect to the magnetic quantum number m_j and their binding energy [i.e., $11(1/2)\pm$ stands for the 11th level of the $m_j=+1/2$ or $m_j=-1/2$ manifold which are energetically degenerate].

For the present study we focused on the collision systems Ne^+-Ni and Ne^+-Cu as experimentally analyzed by Li and

MacDonald.[13,14] For these collision systems Li and MacDonald measured the total inelastic energy loss Q_{total} experienced by the projectile while colliding with the metal surface at steep incident angles (45° and 90°). Subsequently the experimental data were analyzed by supposing the total inelastic energy loss Q_{total} to be given as

$$Q_{\text{total}} = Q_e + Q_{\text{inner}}^{\text{exp}}, \tag{4}$$

where Q_e and $Q_{\text{inner}}^{\text{exp}}$ are the inelastic energy losses due to continuous electron excitation and inner-shell excitation, respectively.[14] The inelastic energy loss due to mean electron excitation Q_e was estimated in a model based on first-principles calculations by Närmann *et al.*[11] This theoretical approach gives a monotonic increase of the energy loss Q_e as a function of the incident energy of the projectile. In a second step Li and MacDonald[13,14] extracted the inelastic energy loss due to inner-shell excitation $Q_{\text{inner}}^{\text{exp}}$ by subtracting the theoretical value for Q_e from the total inelastic energy loss Q_{total}. For all studied collision systems $Q_{\text{inner}}^{\text{exp}}$ rises steeply from a value near zero at incident energies in the range of 2 to 4 keV. The maximum measured energy loss is in the order of 140 eV. Finally the incident energies were converted to a distance of closest approach by using the universal scattering potential,[24,25] therefore yielding the inelastic energy loss $Q_{\text{inner}}^{\text{exp}}$ as a function of the distance of closest approach.

The measurements on the inelastic energy loss of Ne^+ scattering from a metal surface were performed in the incident energy range of 1–9 keV.[13,14] We therefore expect a close encounter of the incoming ion with a surface atom to be well described by our molecular approach. We assume that the incoming projectile is neutralized at larger distances during its initial approach towards the surface. The effective neutralization of slow ions interacting with metal surfaces taking place at ion-surface distances, large compared to the close encounter studied in this work, has been experimentally confirmed in several studies.[26,27] We therefore perform our subsequent analysis of the close encounter based on a neutral projectile interacting with a surface atom. Figures 1 and 2 show the correlation diagrams of the molecular levels for the Ne-Ni and Ne-Cu collision system in the range of $0 \leqslant R \leqslant 2$ Å. It should be said that the relativistic approach used in the present work is not an absolute necessity for the collision systems Ne-Ni and Ne-Cu. Nonrelativistic calculations reveal that relativistic contribution to the binding energies of the molecular levels of interest are in the order of 0.1 eV. Relativistic effects can be important for collision systems involving heavy partners as Au or Pb where deviations from nonrelativistic calculations are at the percent level.

The molecular $9(1/2)\pm$ state correlates asymptotically to the $\text{Ne}(2s_{1/2})$ state whereas the molecular $11(1/2)\pm$ state merges for large internuclear distances into the $\text{Ne}(2p_{1/2})$ projectile state. For both collision systems one clearly sees that the $9(1/2)\pm$ state [$\text{Ne}(2s_{1/2})$ state] as originally proposed by Li and MacDonald,[13,14,28] is a bad candidate to be responsible for any significant inelastic energy loss. This molecular level is strongly demoted with decreasing internuclear distance R and has only a slight promotion setting in below $R = 0.35$ Å. Neither is this level promoted near to the continuum to contribute to a significant inelastic loss. On the basis of these results we expect the asymptotic $\text{Ne}(2s_{1/2})$ level not to be responsible for the sharp thresholdlike increase in the inelastic energy loss.

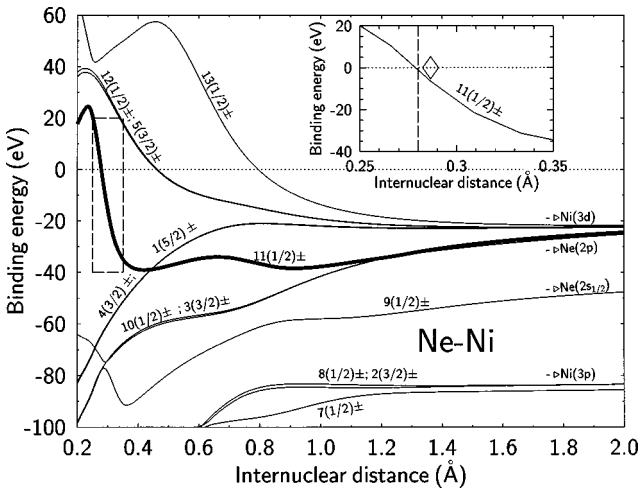

FIG. 1. Correlation diagram for the Ne-Ni collision system. The molecular $11(1/2)\pm$ state (thick line) corresponds asymptotically to the atomic $\text{Ne}(2p_{1/2})$ projectile state whereas the molecular $9(1/2)\pm$ state merges for large R into the $\text{Ne}(2s_{1/2})$ state. The inset shows the molecular $11(1/2)\pm$ state at the ionization threshold marked as a vertical broken line. The diamond in the inset gives the experimental threshold distance for the onset of the Ne^{++} yield (Ref. 13). The area of the inset is marked with broken lines on the main graph.

A closer look at the molecular $11(1/2)\pm$ level suggests the following mechanism to take place: As can be seen in the Ne-Ni correlation diagrams the molecular $11(1/2)\pm$ level has no avoided crossing which could lead to an electronic redistribution over the whole range of internuclear distances R shown. For the Ne-Cu system the molecular $11(1/2)\pm$ level exhibits an avoided crossing with the $12(1/2)\pm$ level at $R = 0.27$ Å. To investigate to what extent this avoided crossing is passed in a diabatic manner at projectile energies in the range of 3 to 9 keV, we have calculated *ab initio* dynamic coupling matrix elements between all molecular levels.[21,22] In the upper part of Fig. 2 the radial coupling matrix elements, acting between the molecular $11(1/2)\pm$ and $12(1/2)\pm$ level, is shown. It is peaked at the avoided crossing and has a very large magnitude therefore allowing an electron to diabatically follow the energy curve (dashed line). For the case of Ne-Ni and Ne-Cu the molecular $11(1/2)\pm$ level is in contrast to the $9(1/2)\pm$ level only slightly demoted. Below a threshold distance of $R = 0.4$ Å a strong promotion of the $11(1/2)\pm$ state sets in leading to ionization at $R = 0.28$ Å for Ne-Ni and $R = 0.25$ Å for Ne-Cu. The main emphasis of this work is to show that the inelastic energy loss Q_{inner} attributed to the inner-shell promotion[14,15] can be tentatively explained by the diabatic promotion of the $11(1/2)\pm$ molecular state. One should recall that the collision energies for the presently investigated collision systems are in the range of 1 to 10 keV and therefore additional inelastic energy loss channels due to inner-shell excitation (K, L shell of a metal atom) are not available. The latter have been studied extensively by Kessel and Everhart[29,30] and Schmidt and Garcia[31] for ion-atom collision systems.

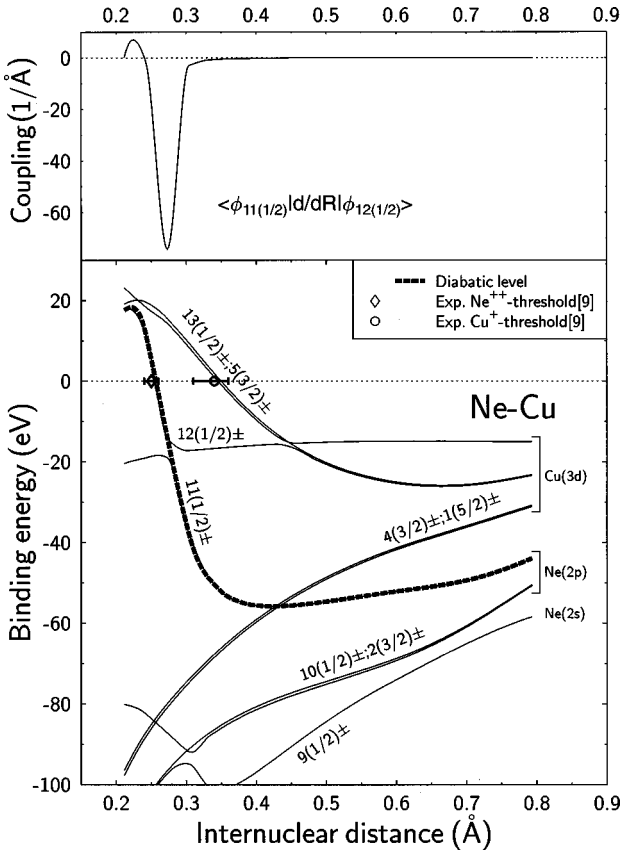

FIG. 2. Same as Fig. 1 for the Ne-Cu collision system. The diamond marks the onset for the experimental Ne^{++} production (Ref. 13). The circle marks the onset for the experimental Cu^{+} recoil yield (Ref. 13). The upper graph shows the *ab initio* radial coupling matrix element between the molecular 11(1/2) and 12(1/2) levels.

The theoretical inelastic energy loss $Q_{\text{inner}}^{\text{theo}}$ due to inner shell promotion of *one* electron is now obtained in the following manner:

$$Q_{\text{inner}}^{\text{theo}} = E_{\text{MO}}(R) - E_{\text{AO}}, \tag{5}$$

i.e., we subtract the negative atomic binding energy of the $Ne(2p_{1/2})$ projectile state from the ion-atom distance dependent $11(1/2)\pm$ eigenstate energy. As long as the distance of closest approach does not undergo the ionization threshold, no inelastic loss is generated. Once the $11(1/2)\pm$ level is promoted to the continuum a strong interaction with the conduction band sets in, leading to resonant ionization of the quasimolecular level and subsequent loss of kinetic energy of the projectile which is transferred to the ejected electron.[15–18] The minimum energy loss is given by the asymptotic binding energy of the $Ne(2p_{1/2})$ electron plus the metal work function which together amount to 20 eV. The promotion of the $11(1/2)\pm$ level happens in a diabatic manner over a short period of time as compared to the velocity of the quasimolecular electron. For a 5 keV incoming Ne projectile the time for promotion of the $11(1/2)\pm$ level is in the order of $t = 0.25$–0.5 a.u. whereas the typical orbiting time for a $Ne(2p_{1/2})$ electron is in the order of $t = 0.7$ a.u. According to Sroubek *et al.*[15–17] and Fine *et al.*[18] this is the crucial criterion for the molecular level to stay localized during the promotion. We therefore expect most of the resonant loss to the continuum of the promoted electron to take place at the distance of closest approach. The only parameter in our theoretical inelastic energy loss is the number of electrons promoted to the continuum which cannot be deduced *a priori* from our one-electron ansatz. As we assume that the incoming projectile is neutralized before having a close encounter with a specific surface atom, up to two electrons can be promoted to the continuum out of the asymptotic $Ne(2p_{1/2})$ state. By matching the maximum in the theoretical inelastic energy loss $Q_{\text{inner}}^{\text{theo}}$ with the experimental maximum for $Q_{\text{inner}}^{\text{exp}}$, we found both for the case of Ne^{+}-Ni and Ne^{+}-Cu that two $Ne(2p_{1/2})$ electrons are promoted to the continuum. Figures 3 and 4 show the corresponding inelastic energy loss $Q_{\text{inner}}^{\text{theo}}$ versus the experimental result for $Q_{\text{inner}}^{\text{exp}}$. Good quantitative agreement is reached over the whole range of incident energies, i.e., distances of closest approach.

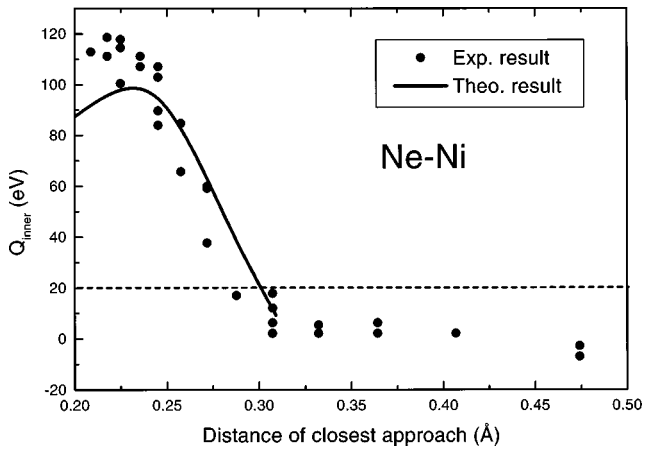

FIG. 3. Theoretical inelastic energy loss $Q_{\text{inner}}^{\text{theo}}$ versus the experimental inelastic energy loss due to inner shell promotion $Q_{\text{inner}}^{\text{exp}}$ as a function of the distance of closest approach for the Ne^{+}-Ni system. The dashed horizontal line marks the minimum energy loss due to excitation of one electron to the continuum.

Further evidence for the atomic $Ne(2p_{1/2})$ projectile state to be the right candidate for the thresholdlike features in the energy-loss spectra and ion yield can be seen from the experimental Ne^{++} yield.[14,15] This yield shows for both sys-

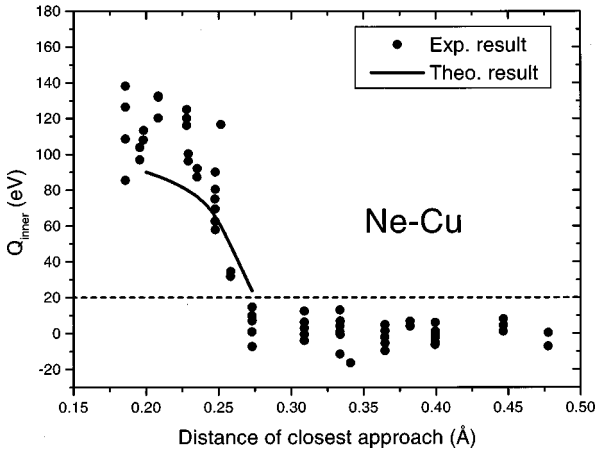

FIG. 4. Same as Fig. 3 for Ne^{+}-Cu.

tems a very sharp onset at about 3.5 keV for Ne^+-Ni and 4 keV for Ne^+-Cu. Similarly from our calculations we get for the Ne-Cu system a higher threshold incident energy for the $11(1/2)\pm$ level to be ionized as for Ne-Ni. Converting the experimental incident energies to distances of closest approach[13,14] gives $R=0.28$ Å and $R=0.25$ Å as the threshold distances for the onset of the production of Ne^{++} ions in the Ne^+-Ni and Ne^+-Cu systems, respectively. These values are in almost perfect agreement with the ionization threshold distance of the molecular $11(1/2)\pm$ level as can be seen from the inset in Fig. 1 and the diamond in Fig. 2, the deviation being in both cases in the order of 5×10^{-3} Å. This method could be used to calibrate the widely used various empirical surface scattering potentials.[25] Finally we focused on the experimental Cu^+ recoil yield measured in Ne^+-Cu collisions. It shows a sharp threshold at incident energies of 2–3 keV. Converting these energies to distances of closest approach gives a mean distance of $R=0.34$ Å, which is in perfect agreement with the Cu($3d$) ionization threshold (circle in Fig. 2), and further evidence for the correct description of the close encounter between an ion and a surface atom by means of an *ab initio* two-center ansatz.

We have investigated the sharp thresholdlike behavior of the inelastic energy loss in low-energy Ne^+-metal surface collisions. We found the inner-shell promotion of single quasimolecular states created in the close encounter of the ion with a surface atom to be responsible for the sharp increase in the inelastic energy loss with increasing incident energy. Using a relativistic Dirac-Fock-Slater approach, we deduced that the inelastic energy loss and energetic broadening of the ion beam can be precisely traced back to the promotion to the continuum of specific molecular levels. For the collision systems studied in this work the asymptotic atomic Ne($2p_{1/2}$) projectile state is responsible for a thresholdlike behavior in both the inelastic energy-loss spectra and the Ne^{++} yields.

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