

EXCITATION AND EMISSION OF METAL ELECTRONS IN ATOM-SURFACE COLLISIONS

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Electron-hole pair excitation and ionization probabilities are calculated for atomic collisions with metal surfaces at high incident energies. The method adopted is based on a Sudden Collision Approximation, and a realistic model is employed for the bound and continuum electronic states involved. The parameters used in the calculations are for Ar, He, H atoms impinging on a Li surface at 300 eV. The main results are: (1) Only single electron-hole pair excitations are important; multiple pair contributions are small. (2) The transitions are dominated by the behavior of the electronic wavefunctions in the tunneling region and may serve as a probe of this regime. (3) The excitation efficiency is in the order $H \gg Ar \gg He$, the effectiveness of hydrogen being due to its stronger, longer-range coupling. (4) The maximum excitation probabilities are for electrons ejected with relatively low excess energies. (5) Total transition probabilities are about 0.5 per collision for H, and about 0.1 for Ar, indicating that these are important, easily detectable processes. Experiments in this field should provide important information on electronic wavefunctions at the metal-gas interface, and on gas-metal interactions at high energies.

1. Introduction

The role of electronic excitations in molecular collisions with metal surfaces is a topic of major conceptual interest and of extensive potential relevance to a wide range of experimental phenomena. Thus, the topic bears on the fundamental question as to whether the use of a molecule-surface potential function (in the Born-Oppenheimer sense), as frequently applied in the literature [1], is indeed justified. The possible role of metal electrons is pertinent to processes such as energy accommodation and transfer, and to trapping and adsorption in molecule-surface scattering dynamics. Present theoretical understanding of this field is still at an early formation stage. Several important pioneering studies were made [2-10] aimed mainly at qualitative understanding. For the most part these studies employ very simple, rather unrealistic models for the

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electronic states and for the molecule-surface interaction. Nourtier [2] treated the role of the electrons in the scattering process by a friction force model, and used a contact (delta function) interaction between the molecule and the metal electrons. He proposed a significant role for the electron-phonon coupling in promoting energy transfer from the molecule to the solid. A larger body of work employs time-dependent perturbation methods. Müller-Hartman et al. [3] assumed weak coupling and used a Tomonaga model (representing electron-hole pairs as independent bosons) in describing electronic excitations. Brako and Newns [4] considered the effect of the incoming molecule as affecting a slowly-varying perturbation on the metal electrons. Gadzuk and Metiu [6] considered the effect of the incoming atom perturbation in the limits both of the sudden and of the adiabatic switching model and in the framework of a Tomonaga independent-boson model for the low-lying excitations of the Fermi gas. They estimate sizable effects for electron-hole pair participation in molecule-surface collision and reaction processes [6]. Kumamoto and Silbey [7] employed an adiabatic switching limit in the framework of a time-dependent Hartree approximation to the collision dynamics finding again large energy accommodation coefficients due to electron-hole pair excitations at low temperatures. Several other studies using a time-dependent localized perturbation description of the incoming particle were reported [8,9]. The most quantitative and elaborate approach so far to the problem is due to Gunnarson and Schönhammer [10]. They employ a time-independent, distorted-wave approximation, providing a perturbative estimate of the non-Born-Oppenheimer correction. Applying their model to He scattering from a Cu surface for collision energies of order 0.1 eV, they found essentially negligible electron-hole pair excitation probabilities, in apparent conflict with some of the previous studies mentioned.

In this article we present a method to study the excitation of an electron gas by a high-energy atom impinging upon a metal surface. The main features of this study are: (a) We investigate collisions at very high energies (about 100 eV) where large and conveniently measurable effects associated directly with electronic excitation may be expected, such as electron ejection from the metal. (Note that in low-energy collisions below the ionization threshold there is no direct experimental probe of electron-hole pair excitations because these cannot be distinguished from phonon contributions to the energy accommodation.) The price one pays for exploring processes at high energy is that many other channels will be open (e.g., sputtering). (b) Realistic models are employed for the electronic states involved and for the interaction between metal electrons and the incoming atom. The results obtained will in fact shed light on the influence of the electronic state properties on the excitation probabilities. (c) The collision dynamics are treated by an approximation of reasonable accuracy at the energy regime considered, that is the Sudden Collision Approximation. The fact that main aspects of the problem are treated on a

relatively realistic footing is reflected in a substantial numerical effort being required. The method is applied in this article to several atomic colliders (H, He, Ar), providing insight as to the role of different coupling ranges and strengths.

In section 2 of the article, we first survey the Sudden Approximation and the considerations involved in using it. Then the approximation is applied to atom-metal collisions, and the necessary expressions for the hole pair excitation amplitudes are described. Section 3 describes the systems studied, the electronic states employed, and the interactions. The numerical results are presented and analyzed in section 4. Conclusions are made in section 5.

2. Method

The present study deals with collisions at high energy in systems where many channels are open. (In fact there is a continuum of energetically accessible electron-hole pair states.)

The Sudden Approximation [5,11–17] is a powerful decoupling method that has been successfully applied to the collision dynamics of other problems involving a somewhat similar difficulty. We shall establish that this method with adequate adaptation is a suitable tool for the problem at hand.

The essential aspect of the Sudden Approximation is that the coupled channel equations describing energy transfer in collisions are decoupled by neglecting internal energy changes in the target system in comparison with the collision energy. This approximation is therefore applicable to systems of dense energy level structure, provided that the relevant excitations are well below the collision energy. Thus some of the earliest and most important applications of the Sudden Approximation have been in the treatment of rotationally inelastic atom-molecule collisions where many rotationally excited states are open in typically experimental conditions [11–14]. Later applications of the approximation are in the context of treating the rotational states in vibrational inelastic scattering [19,20], and in reactive molecular collisions [17].

In the framework of the molecule-surface scattering problem, the Sudden Approximation was successful in treating diffraction transitions and a rotationally inelastic scattering [15,16].

Our purpose here is to adopt a version of the Sudden Approximation for generating the S -matrix elements for the Multiple Scattering processes involved in electron-hole pair excitations. In particular it will be found that contributions of two and more electron processes may be represented as products of amplitudes of single electron-hole pair excitations.

In what follows we obtain expressions for the Sudden Approximation in a form suitable for calculating transition probabilities for electronic excitations

in atom-metal surface collisions for realistic potential and with a feasible numerical effort.

2.1. The Sudden Approximation

The Infinite Order Sudden (IOS) approximation which we adopt here was derived in the literature [12–18] by several approaches and we shall outline its most essential features only in the CRS (Coordinate Representation Sudden) [13,15,16] version of the approximation.

We consider an atom of mass M normally incident upon a metallic surface at collision energy E . The metal is considered to be flat and phononless and the electron gas is noninteracting except for Fermi correlations which are introduced by antisymmetrization of the electronic wave functions. Electronic excitations of the atom will be also neglected.

We note that while phonon excitation and sputtering processes occur with high probability at the collision energy considered, it appears reasonable to neglect them in a study focusing on electronic excitations. We believe that processes associated with these other channels will not qualitatively affect our general conclusion on ionization and excitation of electrons.

The full Hamiltonian is given by

$$H = H_0 + V_0(Z) + V(r^N, Z) + K, \quad (1)$$

where K is the kinetic energy of the incident atom,

$$K = \frac{\hbar^2}{2M} \frac{\partial^2}{\partial Z^2}. \quad (2)$$

H_0 is the Hamiltonian of the internal electrons with eigenfunctions $\phi_\alpha(r^N)$ and eigenvalues ϵ_α ,

$$H_0 \phi_\alpha(r^N) = \epsilon_\alpha \phi_\alpha(r^N). \quad (3)$$

$r^N = \{r_i\}$, $i = 1, \dots, N$, is used as a shorthand notation for all the electronic coordinates while r_i is the position vector of the i th electron. Z is the distance of the atom from the surface and $V_0(Z)$ is the potential between the atom and the metal ions. We neglect all effects of surface corrugations as well as phonon participation. Consequently $V_0(Z)$ does not lead to any inelastic processes. $V(r^N, Z)$ is the interaction between the incident atom and the metal electrons assumed for simplicity to be a sum of pairwise potentials,

$$V(r^N, Z) = \sum_{i=1}^N v_i(r_i, Z). \quad (4)$$

The familiar complex-channel equations are obtained by expanding the exact scattering wavefunction in a series of eigenfunctions of the target metal:

$$\phi(Z, r^N) = \sum_{\alpha} \psi_{\alpha}(Z) \phi_{\alpha}(r^N). \quad (5)$$

Proceeding in the standard fashion one obtains a system of coupled equations for $\psi_\alpha(z)$:

$$\left(\frac{\hbar^2}{2m} \frac{\partial^2}{\partial Z^2} + V_0(Z) + E_\alpha \right) \psi_\alpha(Z) = \sum_\beta V_{\alpha\beta}(Z) \psi_\beta(Z), \quad (6)$$

where

$$E_\alpha = E - \epsilon_\alpha, \quad (7)$$

E being the incident energy, and where

$$V_{\alpha\beta}(Z) = \int dr^N \phi_\alpha^*(r^N) V(r^N, Z) \phi_\beta(r^N). \quad (8)$$

Our first objective is to calculate the scattering matrix elements $S_{\alpha\beta}$ associated with the coupled channel problem (6). The Sudden Approximation decoupling is based on the assumption that the collision energy E is large compared with the energies of the electronic states that are significantly populated by the collision. With this assumption, we get $E_\alpha = E$ for each α in eq. (6). The infinite matrix $V_{\alpha\beta}(Z)$ may then be analytically diagonalized by a transformation that amounts to going from the $\langle\alpha\rangle$ state representation back to the coordinate $\langle r \rangle$ representation. Indeed, the latter is a representation in which the potential is diagonalized.

The essence of all Sudden Approximation approaches is to obtain the S -matrix in the uncoupled system described above (where the interaction is diagonalized). The diagonal elements of S represent elastic scattering in each of the decoupled channels. The scattering amplitudes for transitions between the internal target states ϕ_α and ϕ_β (eq. (5)) is then given by the off-diagonal elements $S_{\alpha\beta}$ after transforming back to the representation of the ϕ_α basis.

Since the infinite matrix $V_{\alpha\beta}(Z)$ is diagonal in the r^N coordinate representation where it becomes $V(r^N, Z) \delta(r^N - r^{N'})$, eq. (6) in the Sudden Approximation leads to

$$\left(\frac{\hbar^2}{2m} \frac{\partial^2}{\partial Z^2} - V_0(Z) - V(r^N, Z) + E \right) \psi_r(Z) = 0. \quad (9)$$

$\psi_r(Z)$ depends here parametrically on the electron coordinates r^N . We note that eq. (9) may be obtained directly from the Hamiltonian (1) by neglecting the electronic Hamiltonian H_0 relative to E . The diagonal elements $S(r^N)$ of the scattering matrix are now determined by the asymptotic behavior of the solutions $\psi_r(Z)$ of eq. (9) in the form

$$S(r^N) = \exp[2i\eta(r^N)], \quad (10)$$

where $\eta(r^N)$ is the elastic phase shift for scattering by a fixed potential $V(r^N, Z)$ for each value of r^N .

It may be readily shown [13,15,16] that the desired transition amplitudes $S_{\alpha\beta}$

may be obtained from $S(r^N)$ by

$$S_{\alpha\beta} = \langle \phi_\alpha(r^N) | S(r^N) | \phi_\beta(r^N) \rangle, \quad (11)$$

which is the Secrest-type result [13] for the transition amplitudes in the coordinate representation Sudden Approximation.

2.2. WKB treatment of the Sudden phase shifts

To evaluate the transition amplitude (11) the element $S(r^N)$ will be written explicitly by using the WKB approximation for the phase shift in eq. (10),

$$\eta(r^N) = \frac{1}{\hbar} \int_{Z_i}^{\infty} [P(r^N, Z) - P_0] dZ - P_0 Z_i, \quad (12)$$

where

$$P^2(r^N, Z) = 2M [E - V_0(Z) - V(r^N, Z)] \quad (13)$$

is the local momentum of the atom and

$$P_0^2 = 2ME \quad (13a)$$

is the initial momentum, Z_i is the classical turning point corresponding to (13).

An important simplification will now be introduced based on an estimate that the electronically inelastic part of the potential is weak in comparison with the collision energy, so that, not too close to Z_i ,

$$V(r^N, Z) \ll E - V_0(Z). \quad (14)$$

Using this in a first order expansion for the phase shift leads to

$$\eta(r^N) = \eta^0 + \eta^1, \quad (15)$$

$$\eta^0 = \frac{1}{\hbar} \left(\int_{Z_i}^{\infty} \left(\sqrt{2M [E - V_0(Z)]} - \sqrt{2ME} \right) dZ - P_0 Z_i \right), \quad (16)$$

$$\eta^1 = \frac{1}{\hbar} \sqrt{2M} \int_{z_i^0}^{\infty} \frac{V(r^N, Z)}{\sqrt{E - V_0(Z)}} dZ = \sum_{i=1}^N \eta_i^1(r_i), \quad (17)$$

with

$$\eta_i^1(r_i) = \frac{1}{\hbar} \sqrt{2M} \int_{z_i^0}^{\infty} \frac{v_i(r_i, Z)}{\sqrt{E - V_0(Z)}} dZ. \quad (18)$$

Z_i^0 is now the turning point associated with $V_0(Z)$.

The transition amplitude is given by eq. (11). This assumes the form

$$S_{\alpha\beta} = \langle \phi_\alpha(r_1, \dots, r_N) | \prod_{i=1}^N s_i(r_i) | \phi_\beta(r_1, \dots, r_N) \rangle \times \exp(i\eta_0), \quad (19)$$

where

$$s_i(\mathbf{r}_i) = \exp[2i\eta_i^+(\mathbf{r}_i)]. \quad (20)$$

The contribution of the individual electron-atom interactions to the total phase shift is additive under the previous assumption of pairwise potential model for $V(\mathbf{r}^N, Z)$ (eq. (4)). This makes it possible to separate out the contributions to $S_{\alpha\beta}$ from n -electron excitation for different values of n . To this end we expand the product $\prod_{i=1}^N s_i(\mathbf{r}_i)$ in (18) to the familiar multiple scattering series. Define

$$t_i(\mathbf{r}_i) = 1 - s_i(\mathbf{r}_i), \quad (21)$$

where 1 is the identity operator and t_i is the single-particle transition operator responsible for inelastic transfer. Using (21) we get for the S -matrix in eq. (19)

$$\begin{aligned} 1 - S(\mathbf{r}_1, \dots, \mathbf{r}_N) &= 1 - \prod_i [1 - t_i(\mathbf{r}_i)] \\ &= \sum_{i=1}^N t_i(\mathbf{r}_i) - \sum_{i \neq j} t_i(\mathbf{r}_i) t_j(\mathbf{r}_j) + \dots, \end{aligned} \quad (22)$$

where t_i is given by (20) and (21).

The terms in (22) correspond to single, double, etc., scattering. Each term consists of products of single-particle operators which act in the noninteracting electron gas model, on antisymmetrized products of single-electron wavefunctions. This leads to the appearance of products of n single-electron amplitudes in all higher order terms which correspond to n -electron excitations. This makes it possible in principle to estimate these contributions to the total amplitude.

The single-electron part of the transition amplitude obtained from the first term of the series (22) is given by

$$T_{\alpha\beta}^{(1)} = \langle \phi_\alpha | t | \phi_\beta \rangle = \langle \phi_\alpha(\mathbf{r}) | 1 - s(\mathbf{r}) | \phi_\beta(\mathbf{r}) \rangle = \delta_{\alpha\beta} - S_{\alpha\beta}^{(1)}, \quad (23)$$

where $s(\mathbf{r})$ is defined by (20), and where now ϕ_α and ϕ_β denote initial (bound) and final (bound or free) single electron states. $\delta_{\alpha\beta}$ is the Kronecker δ .

The contribution of two-electron excitation to the amplitude resulting from the second term in (22) takes the form

$$\begin{aligned} T_{\alpha_1, \alpha_2, \beta_1, \beta_2}^{(2)} &= \frac{1}{2} (\langle \phi_{\alpha_1} | t | \phi_{\beta_1} \rangle \langle \phi_{\alpha_2} | t | \phi_{\beta_2} \rangle \\ &\quad - \langle \phi_{\alpha_1} | t | \phi_{\beta_2} \rangle \langle \phi_{\alpha_2} | t | \phi_{\beta_1} \rangle). \end{aligned} \quad (24)$$

Here $\alpha_{1,2}$ and $\beta_{1,2}$ stand for the initial and final states of the two particles respectively. This has to be summed over all pairs.

Similarly we may in principle evaluate all the terms in (22) in terms of single-electron amplitudes. The total transition probability includes contributions from all these terms together with interference among them. In what

follows we shall focus on the lowest order (single-electron) term (23). Our results indicate that, with the possible exception of hydrogen as an incident atom, this term is dominant.

2.3. The energy transfer probabilities

Having obtained the S -matrix elements for the electronic state-to-state ($\alpha \rightarrow \beta$) transitions in the Sudden Approximation framework, we proceed to construct from these elements the transition probabilities for the electrons to gain an amount of energy ΔE in the collision. In this calculation we shall set the metal temperature to zero, thereby avoiding the need for thermal averaging over initial states.

A state α is characterized by the unit vector \hat{k}_α pointing in the direction of the momentum, the magnitude of the momentum k_α (or equivalently the energy E_α) and any other quantum number j_α .

The probability $P(\Delta E)$ for energy transfer ΔE may now be written in terms of the S -matrix elements in the form

$$P(\Delta E) = \left(\frac{\mathcal{N}}{(2\pi)^2} \right)^2 \sum_{j_\alpha, j_\beta} \int \delta(\Delta E + \epsilon_\alpha - \epsilon_\beta) |S_{\alpha\beta}|^2 d^3k_\alpha d^3k_\beta. \quad (25)$$

The summation is carried out over all hole ($\epsilon_\alpha < E_F$) and electron ($\epsilon_\beta > E_F$) final states. \mathcal{N} is the normalization volume of the electrons and E_F is the Fermi energy. ϵ_α is the electron energy in the state α .

This probability may be written as summation over all final (hole and electron) energy values

$$P(\Delta E) = \frac{\mathcal{N}^2}{(2\pi)^6} \left(\frac{2m}{\hbar^2} \right)^3 \int d\epsilon_\alpha \sqrt{\epsilon_\alpha} \sqrt{\epsilon_\alpha + \Delta E} P(\epsilon_\alpha \rightarrow \epsilon_\beta), \quad (26)$$

with $P(\epsilon_\alpha \rightarrow \epsilon_\beta)$ being the transition probability from the initial electronic state with energy $\epsilon_\alpha < E_F$ to a final excited state with energy $\epsilon_\beta > E_F$. We ignore here band structure and assume a spherical Fermi surface to simplify energy momentum relations. $P(\epsilon_\alpha \rightarrow \epsilon_\beta)$ is given by

$$P(\epsilon_\alpha \rightarrow \epsilon_\beta) = \sum_{j_\alpha, j_\beta} \int |T_{\alpha\beta}^{(1)}|^2 d\Omega_\alpha d\Omega_\beta. \quad (27)$$

Integration is over the angular direction of k_α and k_β . The sums include summation over spin states which result in a factor of 2 and over the two degenerate states attached to each energy value in the continuum (see section 2.4). $T^{(1)}$ is given by eq. (23).

2.4. Wavefunctions and potentials

In an atom-surface collision it should be expected that coupling with the electron is predominantly in the vicinity and outside of the metal surface so that penetration of the electron wavefunction through the surface barrier is of dominant importance to its excitation by the incoming atom.

The metal is represented by a step potential

$$U(z) = \begin{cases} 0, & z \leq 0, \\ E_f + W, & z \geq 0, \end{cases} \quad (28)$$

where W is the work function, and z is the electron coordinate normal to the surface. In our model calculations we shall use parameters corresponding to Li: $E_f = 5.25$ eV and $W = 2.90$ eV.

Both free and bound state wavefunctions are considered for the electron. The bound states are

$$\phi_a(x, y, z) = \sqrt{2/\mathcal{N}} e^{ik_x x} e^{ik_y y} f(k_z, z), \quad (29)$$

where

$$f(k_z, z) = \begin{cases} \sin(k_z z + \theta), & z \leq 0, \\ A \exp(-\alpha z), & z > 0, \end{cases} \quad (30)$$

and where

$$A = k_z / \sqrt{k_z^2 + \alpha^2}, \quad (31)$$

$$\hbar\alpha = \sqrt{2m(E_f + W) - \hbar^2 k_z^2}, \quad (32)$$

$$\theta = \tan^{-1}(k_z/\alpha).$$

For the continuum we have two degenerate wavefunctions for each energy value corresponding to incoming and outgoing motion of the electron. For $f(k_z, z)$ in (29) we then have:

$$f_1(k_z, z) = \begin{cases} \frac{1}{2} \left(e^{ik_z z} + \frac{k_z - k_{0z}}{k_z + k_{0z}} e^{-ik_z z} \right), & z < 0, \\ \frac{k_z}{k_z + k_{0z}} e^{ik_{0z} z}, & z > 0, \end{cases} \quad (33)$$

$$f_2(k_z, z) = \begin{cases} \frac{k_{0z}}{k_z + k_{0z}} e^{-ik_z z}, & z < 0, \\ \frac{1}{2} \left(e^{-ik_{0z} z} - \frac{k_{0z} - k_z}{k_{0z} + k_z} e^{ik_{0z} z} \right), & z > 0. \end{cases} \quad (34)$$

k_{0z} is the normal component of the momentum outside the metal surface,

$$\hbar k_{0z} = \sqrt{\hbar^2 k_z^2 - 2m(E_i + W)}. \quad (34a)$$

For the interaction between the atom and the metal surface (which scatter the atom elastically) we chose a repulsive exponential

$$V_0(Z) = E e^{-C(Z-Z_i^0)}, \quad (35)$$

Z being the distance of the atom from the surface, Z_i^0 its classical turning point, and E the collision energy, taken to be 10 au (270 eV) in our calculations. It is found that the inelastic scattering is hardly affected by range of the static potential as given by C . The value of $C = 0.6 \text{ bohr}^{-1}$ is chosen for the inverse range parameter. The preexponential coefficient in eq. (35) is determined by setting Z_i^0 to be the sum of the radii of the incident and the surface ion. In so doing we disregard the energy dependence of the turning point. This is a good approximation for the high collision energy employed in the present calculation.

Our numerical calculations can be carried out without further simplifying restrictions on the atom–electron potential function (in contrast to most previous studies dealing with electron excitation in surface–atom collisions) and a realistic potential function could be chosen. For He and Ar collision with the Li surface we adopt the electron–atom effective potential of Green et al. [22,23]. These authors use two parameter potential functions to represent the electron–atom interaction where the parameters can be adjusted experimentally or by using results of Hartree–Fock calculations [21] for the description of the atom. This potential is given (in atomic units) by

$$v(R) = -R^{-1} Z_A \Omega(R), \quad (36)$$

where R is the distance between the electron and the center of the atom, Z_A is the atomic number and where

$$\Omega(R) = \{\mathcal{Q} D Z_A^\nu [\exp(R/D) - 1] + 1\}^{-1}, \quad (37)$$

the parameter ν is taken to be 0.4 for all elements and the parameters D and \mathcal{Q} are found [22] by adjustment to HF energies and are given by $\mathcal{Q} = 1$, $D = 0.215$ for He and $\mathcal{Q} = 1$ and $D = 0.862$ for Ar. For the electron–hydrogen interaction we use an effective potential derived in an adiabatic approximation [24], appropriate when the electron energy is below the lowest hydrogen excitation energy,

$$v(R) = -\frac{1}{2R^4} \left[\frac{9}{2} - \frac{2}{3} e^{-2R} \left(R^5 + \frac{9}{2} R^4 + 9R^3 + \frac{27}{2} R^2 + \frac{27}{2} R + \frac{27}{4} \right) \right], \quad (38)$$

where v and R are again given in atomic units. This approximation attempts to account for both polarization and exchange effects. $v(R)$ behaves as R^{-4} for large R . This dependence is typical of the dipole contribution due to polarization of the atom by the electron.

Such effective local potentials are expected to be sufficient for our purpose though they fail when the electron enters the atomic charge distribution. Our calculations indeed indicate that most of the contributions to the transition probabilities come from regions where the electrons are not that close to the atom.

3. Calculations

In calculating probabilities for a one-electron-hole excitation we use the first term in the multiple scattering expansion for the S -matrix (eq. (22)) as given by (cf. eqs. (18) and (20))

$$s(\mathbf{r}) = \exp\left[2i\eta^l(r_{\parallel}, z)\right], \quad (39)$$

$$\eta^l(\mathbf{r}) = \eta^l(r_{\parallel}, z) = \frac{1}{\hbar} \sqrt{2M} \int_{Z_1^0}^{\infty} \frac{v(r_{\parallel}, |z - Z|)}{\sqrt{E - V_0(Z)}} dZ. \quad (40)$$

Here we have denoted the electronic coordinate as $\mathbf{r} = (r_{\parallel}, z)$ where z is the coordinate normal to the surface and r_{\parallel} is the two-dimensional coordinate parallel to the surface. The position of the atom in the (x, y) plane is taken as the origin for the r_{\parallel} coordinate.

The probability of energy transfer to the electron is expected (and will be numerically shown) to be extremely sensitive to the strength of the electron

Table 1

Parameters used in the transition probability calculations (for definition see text); the atom-surface distance at the turning point Z_1^0 is determined as the sum of the atomic radius of the colliding atom and the atomic radius of Li (1.28 bohr); B is determined from the electron-atom interaction so as to replace the distance dependence of this interaction in the xy direction by a step function having the same maximum and the same area under the curve; C and A parametrize the phase of the S -matrix element given in eqs. (43) and (46)

Incident atoms	Phase parameters		Atom-metal distance at Z_1^0 (bohr)	Atomic radius (bohr)	B (bohr)
	C	A			
Ar	1.74	1.5	4.5	3.21	2.25
He	0.048	2.3	3.7	2.45	1.75
H	2.1	0.75	1.9	0.566	2.3

penetration out of the metal surface. Therefore, to simplify the final expression for the transition amplitude, only the dependence of $v(r_{\parallel}, z - Z)$ on $z - Z$ is used exactly in the calculation. The dependence of v on r_{\parallel} is treated in an approximate manner: v is taken to be constant over a typical interaction length B for each atom (see table 1),

$$v(b, |z - Z|) = \begin{cases} V(|z - Z|), & b \leq B, \\ 0, & b > B, \end{cases} \quad (41)$$

where we have denoted $b \equiv r_{\parallel}$. For B we have chosen reasonable interaction lengths for each atom (see table 1). The phase function in eq. (40) assumes the form

$$\eta^l(b, z) = \begin{cases} \frac{1}{2} u(z) \equiv \frac{1}{\hbar} \sqrt{2M} \int_{z_i^0}^{\infty} \frac{v(|z - Z|)}{\sqrt{E - V_0(Z)}} dZ, & b \leq B, \\ 0, & b > B, \end{cases} \quad (42)$$

where $V_0(Z)$ of eq. (35) is used and $v(z - Z)$ is given by eqs. (36) and (37) for

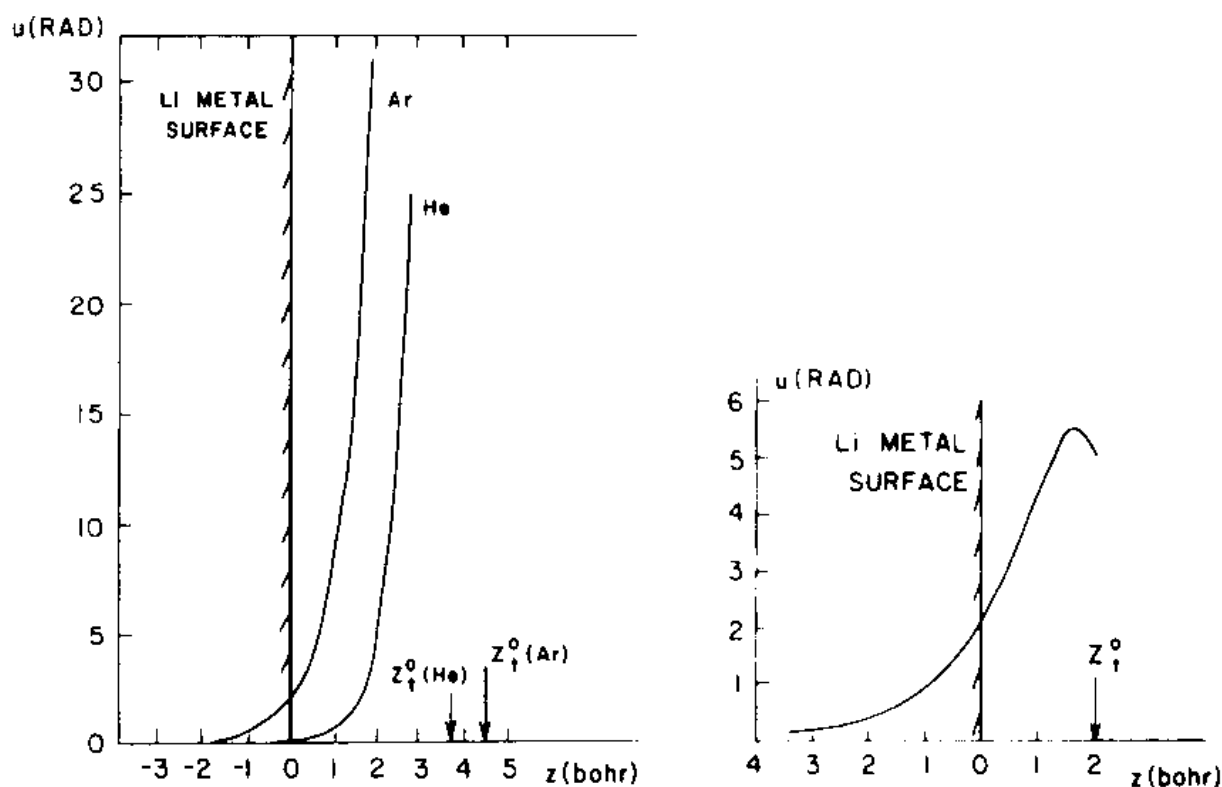


Fig. 1. Calculated phase-shift $u(z)$ as a function of the electron normal coordinate z using the effective potential of ref. [21] (see section 2.4). An exponential function (eq. (43)) with the parameters of table 1 coincides with that part of the calculated phases shown in fig. 1. $Z_i^0(\text{He}) = 3.7$ bohr and $Z_i^0(\text{Ar}) = 4.5$ bohr are the locations of He and Ar centers at the corresponding turning points.

Fig. 2. Calculated phase-shift as a function of the electron normal coordinate z using the adiabatic effective hydrogen-electron potential (eq. (38)). This calculated phase is replaced in further calculations by the exponential function (eq. (43)) with the parameters of table 1. $Z_i^0 = 1.9$ bohr is the location of H center at its turning point.

Ar and He and by eq. (38) for electron–hydrogen interaction. We note that the effect of the collision energy E on the transition amplitude results from the denominator of the phase in (42).

The calculated phases $u(z)$ in eq. (42) for H, He, Ar are shown in figs. 1 and 2 as function of z . In these figures $z = 0$ coincides with the metal surface (represented by the position of the potential barrier) and Z_i^0 is given by table 1.

Numerical effort is considerably reduced if we replace the numerically calculated phase $u(z)$ (eq. (42)) by a simple analytical function. An exponential function representation was found adequate;

$$u(z) = C e^{Az}, \quad (43)$$

where values of the parameters A and C (determined such that (43) fits the numerically calculated phase-shifts) are given in table 1. This function coincides with the numerically calculated phase shifts if the electron surface distance z is not too large (see figs. 1 and 2).

The phases $u(z)$ and the electron wavefunctions (eqs. (29) and (30) or (33) and (34)) are now substituted into the expression for the transition amplitude, eq. (27a). The assumption (41) makes the $r_{\parallel} = (x, y)$ integration trivial. The desired T -matrix element takes the form

$$T_{\alpha\beta}^{(1)} = \frac{2\pi B^2}{\mathcal{N}} \frac{J_1(|q_{\parallel}|B)}{|q_{\parallel}|B} F_{\alpha\beta}, \quad (44)$$

where J_1 is the Bessel function of order 1, q_{\parallel} is defined by

$$q_{\parallel} = (k_{\beta x} - k_{\alpha x}, k_{\beta y} - k_{\alpha y}), \quad (45)$$

and where

$$F_{\alpha\beta} = \int_{-\infty}^{\infty} dz f_{\beta}^*(k_{\beta z}, z) [1 - \exp(iu(z))] f_{\alpha}(k_{\alpha z}, z). \quad (46)$$

In eq. (46) f_{β} and f_{α} are the functions f (eqs. (30), (33) and (34)) corresponding to the initial (α) and final (β) states.

4. Analysis of the results

In figs. 3–5 we present calculated probabilities $P(\epsilon_i \rightarrow \epsilon_f)$, eq. (27), for a one-electron excitation in atom–surface collision as a function of the electron final state energy ϵ_f , taking fixed initial energy values. Calculations were carried out for collisions of H, He, Ar with a Li surface to test different types of atom interaction with metal electrons. Collision energy in all systems is 10 au (~ 270 eV). The transition probability per unit energy, $P(\Delta E)$, for energy transfer ΔE per collision is shown in fig. 6 for the Ar–Li surface collision. The

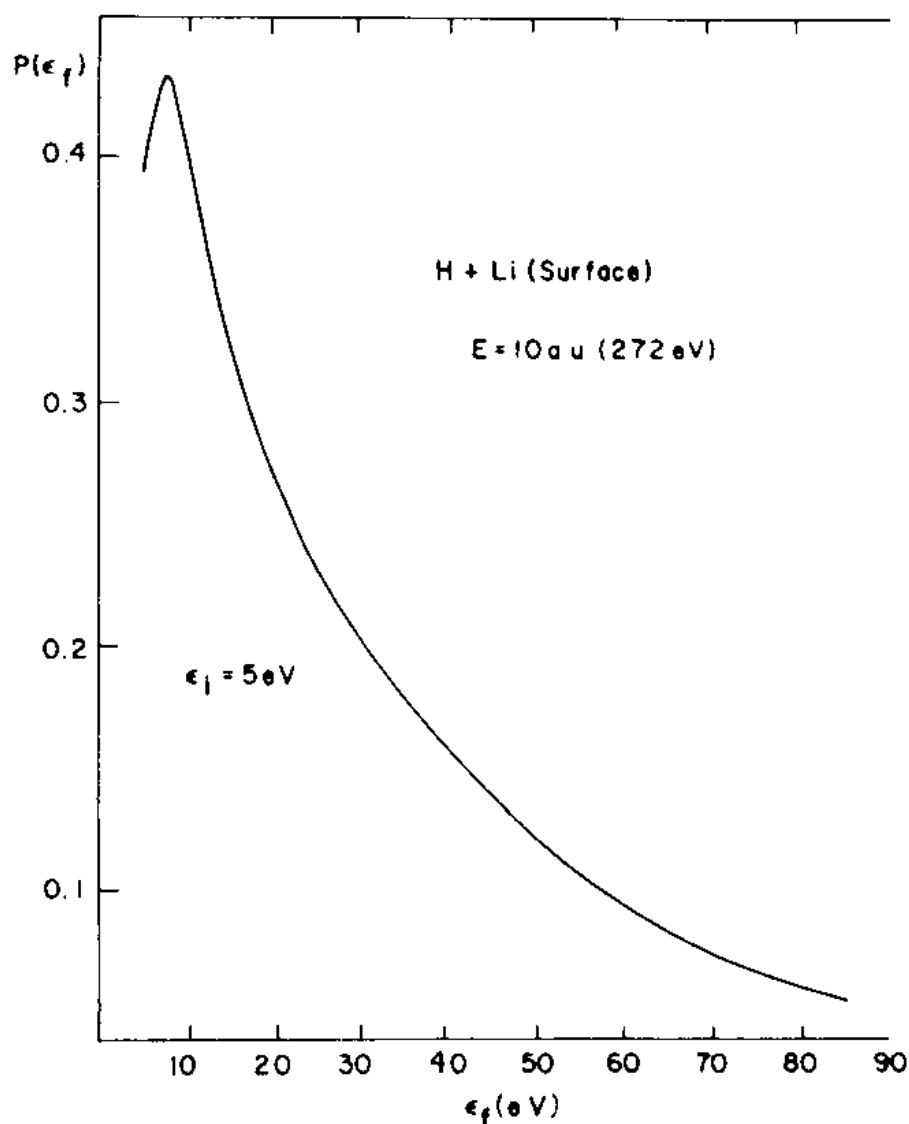


Fig. 3. Single electron-hole excitation "probability" $P(\epsilon_i \rightarrow \epsilon_f)$ (eq. (27)) (arbitrary scale) as a function of the electron final energy ϵ_f for an initial electronic energy $\epsilon_i = 5$ eV in H + Li(surface) collision.

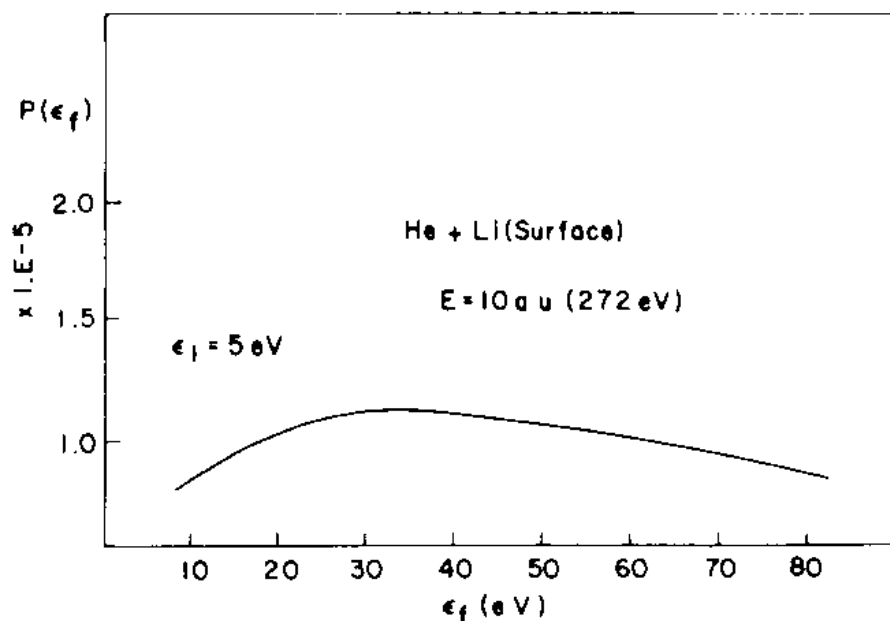


Fig. 4. Single electron-hole excitation "probability" $P(\epsilon_i \rightarrow \epsilon_f)$ (eq. (27)) as a function of the electron final energy in He + Li (surface) collision for an initial electronic energy $\epsilon_i = 5$ eV. The vertical scale is the same as in fig. 3.

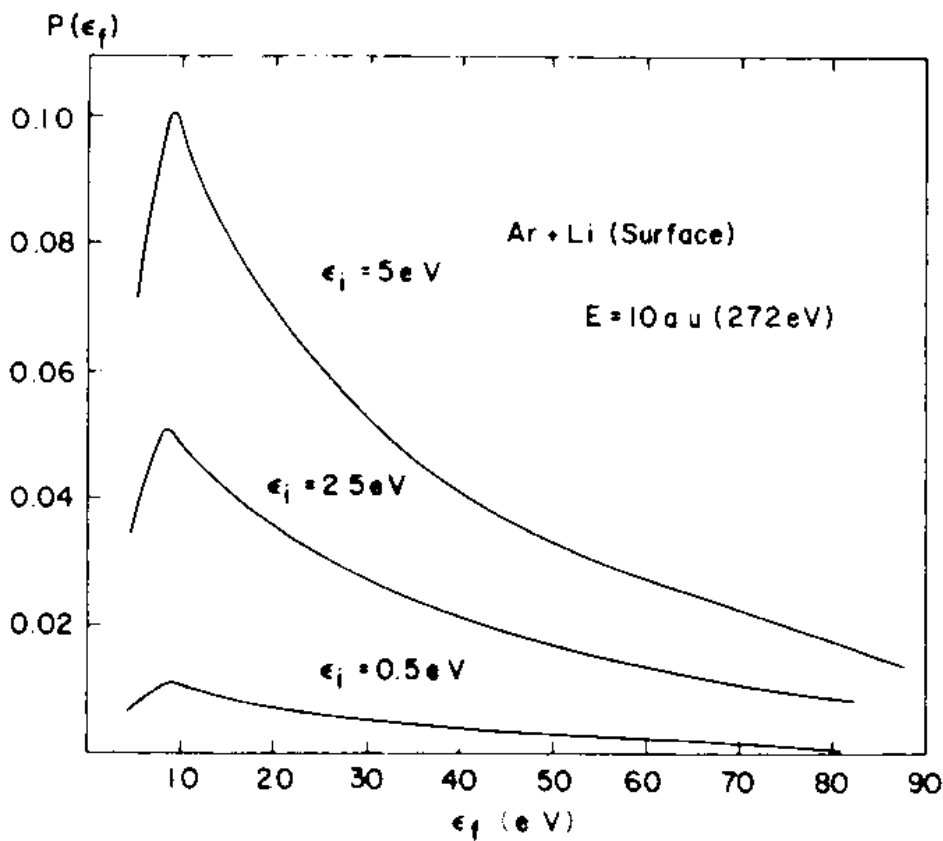


Fig. 5. Single electron-hole pair excitation "probability" for an Ar+Li(surface) collision as a function of the electron final energy, for three values of the electron initial energy: $\epsilon_i = 0.5, 2.5$ and 5 eV. The vertical scale is the same as in fig. 3.

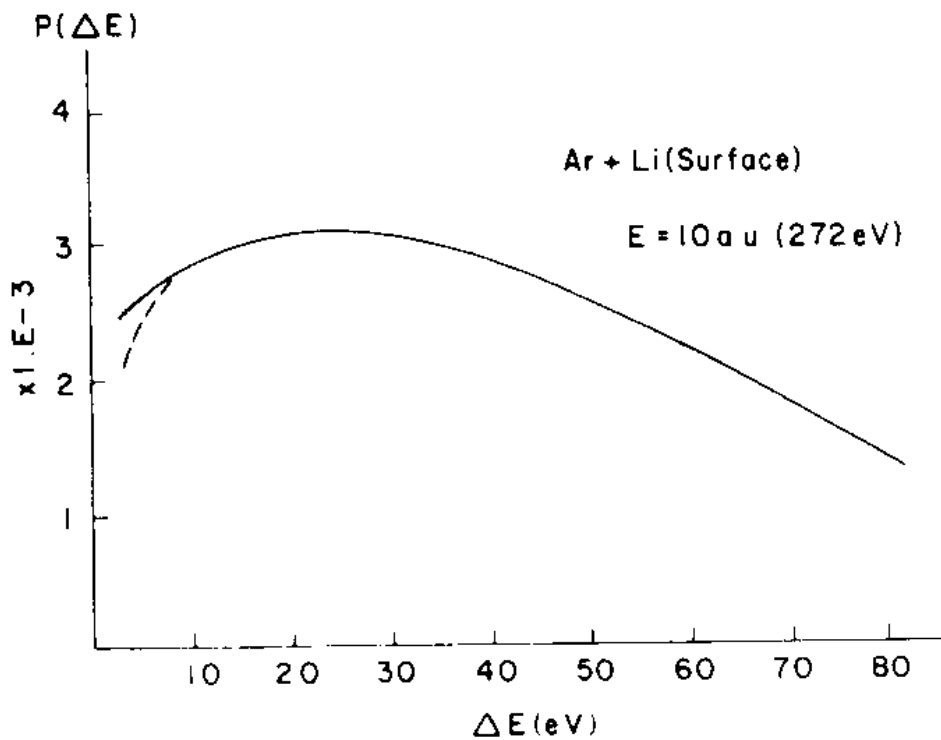


Fig. 6. Solid line: probability per unit energy, $P(\Delta E)$, of energy transfer ΔE for Ar-Li surface collision. Dashed line: probability per unit energy for energy transfer ΔE resulting in electron excitation beyond the Li threshold (the two curves coincide for energies above the work function W).

following points should be noticed:

(a) Figs. 3–6 show that the maximum energy transfer occurs in the 10–30 eV range. For this energy range the Sudden Approximation is expected to be valid. However, the high-energy tails of these distributions, where the energy transfer becomes comparable to the total initial energy, are not reliable.

(b) Hydrogen is seen to be more effective than the rare gases in transferring energy to the solid's electrons. He is by far the least effective and in fact the transition probabilities obtained for it are of the same order of magnitude as that calculated by Gunnarson et al. [10] for the low-energy collision of He with a Cu surface.

(c) The dependence of the electron excitation probabilities on the initial energy of the electron (fig. 5) emphasizes the role played by the penetration of the electronic wavefunction through the surface barrier. A larger initial energy corresponds to a larger tunneling tail of the initial electronic wavefunction which implies a stronger coupling with the colliding atom. Indeed the coupling strength is determined by the degree of overlap between the initial and final electronic wavefunctions and between the phase shift functions $u(z)$ depicted in figs. 1 and 2.

(d) The sensitivity of the transition probability to the behavior of the tails of the electronic wavefunctions outside the metal suggest that the process will be strongly dependent on the metal work function. Consequently, large external field effects on the efficiency of energy transfer to the metal electrons are expected.

(e) The efficiency of energy transfer is strongly affected also by the range and strength of the interaction potential between the atom and the metal electrons. This is reflected by the differences between the excitation probabilities obtained from H, He, and Ar as colliders. The coupling in the case of hydrogen is more "chemical" and hence is stronger and has longer range than that for He or Ar. This results in the stronger transition probabilities obtained with H. The relatively high efficiency of Ar results again from a stronger and longer-range interaction potential compared to that of He.

(f) For longer-range interaction potentials the phase shifts as functions of the electron coordinate (figs. 1 and 2) penetrate deeper into the metal. The stronger this penetration is, the smaller is the role played by the tunneling tail of the electronic wavefunctions. This is reflected in the fact that the transition probability as a function of final energy peaks at lower energy for hydrogen than for Ar, and for Ar than for He.

(g) The peak in the transition probability versus energy transfer results from the combined effect of the tunneling tail of the electronic wavefunctions (which promotes larger probability for larger energy transfer) and of the effective overlap between the initial and final electronic wavefunctions which yields smaller matrix elements for wavefunctions largely separated in energy, thereby reducing the transition probability for very large energy transfers.

(h) At the collision energy considered, ionization (excitation to final levels above the threshold of 8.5 eV for Li) is a likely process and may be experimentally observable. This in fact seems to be the only possibility to demonstrate that electronic excitation indeed takes place in neutral atom-surface collisions (energy transfer always combines electron and phonon contributions).

(i) Integrating the transition probability versus energy transfer curve of fig. 6 we obtain a value of about 0.1 for the total one-electron excitation probability for Ar-Li surface collision. This relatively small number suggests that multiple-electron excitations (which are higher order in the atom-surface interaction) are not very probably. This conclusion certainly holds also for He, while for H (with total transition probability for one-electron excitation estimated to be about 0.5) we cannot exclude multiple-electron excitations. Physically, one-electron processes are expected to be dominant in collisions characterized by short-time and short-range interactions: the volume in the metal which "sees" the colliding atom is of the order of a single unit cell or smaller and is thus associated with a single valence electron.

5. Conclusions

The present article studied electron-hole pair excitations in high-energy collisions of atoms with metals. Electron excitation to the continuum is energetically allowed, and its efficiency was pursued in detail. The study employed the Sudden Collision Approximation, and the numerical results established its consistency. One of the major conclusions is that the efficiency of excitation varies greatly (within orders of magnitude) with the nature of the atom involved, as reflected in the metal electron-atom interaction. We thus concluded that for a weak coupling system such as He/Li(surface), the excitation probability is so low that the Born-Oppenheimer approximation remains practically valid even at 300 eV. In the case of H/Li scattering, on the other hand, there is a relatively large probability of electron excitation and/or ionization per collision, due to the long-range "chemical" type interaction. We anticipate experimental detectability of the electrons ejected from the metal. Another factor of great importance is the degree of electron tunneling into the classical forbidden regime outside the metal. The implication is that scattering processes as discussed here (including ionization) may be a sensitive probe of electronic wavefunction at the solid-gas interface, especially in the little understood tunneling regime.

Finally it is very important to note that the present study involved major simplification in ignoring other important channels such as sputtering, atom penetration, and energy transfer to phonons. While our belief is that the inclusion of these channels will not affect our main physical conclusions (as far

as electron excitation is concerned) this point clearly deserves critical examination in future studies.

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