Surface Science 137 (1984) 527–550
North-Holland, Amsterdam

DYNAMICS OF METAL ELECTRON EXCITATION IN ATOM–SURFACE COLLISIONS: A QUANTUM WAVE PACKET APPROACH

Z. KIRSON

Department of Physical Chemistry and The Fritz Haber Research Center for Molecular Dynamics, Hebrew University, Jerusalem 91904, Israel
and
Institute of Chemistry, Tel-Aviv University, Ramat-Aviv, Tel Aviv, Israel

R.B. GERBER

Department of Physical Chemistry and The Fritz Haber Research Center for Molecular Dynamics, Hebrew University, Jerusalem 91904, Israel

A. NITZAN

Institute of Chemistry, Tel-Aviv University, Ramat-Aviv, Tel Aviv, Israel

and

M.A. RATNER

Department of Chemistry, Northwestern University, Evanston, Illinois 60201, USA

Received 26 October 1983

Electron–hole pair excitations upon atom impact on a metal surface are studied in a framework of a one-dimensional independent-electron model. The method employed treats electron dynamics quantum mechanically and the atom motion classically, and the two are coupled through the time-dependent self-consistent field (TDSCF) approximation. A variational method is used to calculate the time evolution of the electronic wave packet. Calculations were carried out for the colliders, He, Ar and H; the surface parameters were chosen to model Li. Some of the results obtained are: (1) Electron excitation by H is much more efficient than for a rare-gas collider. Experimental search for hole–pair excitations should thus be best pursued with H as a collider. (2) At 0 K surface temperature $\Delta E/E$, the fraction of collision energy converted to hole-pair excitations, decreases as the collision energy increases for energies up to ~1 eV. At collision energy $E = 0.01$ eV, the fraction of energy transferred is ~0.2% for He and ~10% for H. (3) Atom trapping due to energy transfer to electrons occurs with high probability (50–100%) at sufficiently low collision energies. Ar trapping takes place at energies below 1 K and H trapping below 20 K. (4) The calculations show a pronounced transition from atom de-excitation to atom excitation by electron–hole pairs as surface temperature increases. (5) Perturbation theory is tested against the present method. It breaks down mainly for trapping and for temperature effects.

1. Introduction

Establishing the role of conduction electrons in collisional energy transfer between molecules and metal surfaces is a problem of major importance in the study of gas–solid interactions. Most studies of neutral molecule scattering from metals ignore electron–hole pair excitation and assume that phonons are the only significant energy-receiving modes of the solid [1]. Evidence is very insufficient, however, as to which are the processes and systems for which such an assumption is valid, and quantitative estimates are still scarce as to the magnitude of electron participation in aspects such as energy accommodation, trapping and desorption. Important pioneering studies on this topic were made in recent years [2–10], leading to the formation of several models. However, in some cases, estimates of electron contribution to accommodation effects differ by order of magnitude for different models [2–10]. One difficulty in treating the problem is the unavailability as yet of direct evidence from experiments that could serve as a useful guide. The main obstacles in formulating a quantitative approach are, however, the many-body nature of the problem, the complicated dynamics of the electron undergoing excitation in the band, and the poorly known interaction potentials. The approaches taken thus far necessarily introduced drastic simplifications in treating most of these aspects or all of them. Thus, in one of the earliest studies of this problem, Nourtier [2] treated the effect of the metal electrons through a phenomenological friction force and employed a delta function model for the interaction between the metal electrons and the molecule. He estimated a major effect of electron–hole pair excitation on accommodation and diffraction phenomena. Various types of time-dependent perturbation methods were used by several authors in the field to describe the excitation dynamics. Müller-Hartman et al. [3] applied the weak-coupling limit. Brako and Newns [4] modelled the effect of the incoming molecule as a slowly varying perturbation on the electrons. Gadzuk and Metiu [5] provided estimates for accommodation effects due to electron–hole pairs, examining the perturbation by the incoming atom in the sudden, in the adiabatic and in other switching limits. Several other studies representing the incoming atom as some time-dependent perturbation on the electrons were reported [6,7], Kumamoto and Silbey [8] treated the coupling between the motion of the atom and that of the metal electrons by the time-dependent Hartree approximation. They used a very simple model Hamiltonian for the electrons, and evaluated the dynamics in special limits (e.g., sudden switching) [8]. Probably the most quantitative studies to date employ time-independent treatments of the dynamics. Gunnarson and Schönhammer [9] employed a distorted-wave approximation to calculate electron–hole pair excitations in He scattering from a Cu surface at low energies (~ 0.01 eV). They found extremely low excitation probabilities differing considerably from some previous estimates. Kirson et al. [10] studied electron–hole pair excitations in very high

energy ($E > 100$ eV) atom–surface collisions, using the "Sudden Approximation". At these very high energies, electrons can be ejected from the metal, and experiments studying this effect (and in particular the energy distribution of the emitted electrons) are in progress [11]. However, the Sudden Approximation for electron excitations is not applicable for collisions at the energy range typical of chemical interest.

The purpose of the present article is to contribute to the development of a quantitative theory of collisional excitation of metal electrons by providing a more refined treatment of the dynamical behaviour of the eletron undergoing excitation. More specifically, the time evolution of the wave packet describing the electron is solved numerically, to reasonable accuracy, by a variational procedure. This should offer an adequate description of the exciting dynamics at the single (independent) electron level. It is thus a useful step towards understanding the behaviour of the real (many-electron) system. An important advantage of the method used is that the time evolution of the electron wave packet offers detailed physical insight into the development of the process. In coupling the motion of the electron and the colliding atom, the time-dependent Hartree approximation will be used, as in the formalism of ref. [8]. However, in this framework the equation of motion will be solved without further approximations. The resulting scheme can describe adequately also atom trapping due to energy transfer to the electron. We are not aware of any previous demonstration of trapping dynamics in this process. (Perturbation models always break down in the description of trapping.)

The article proceeds as follows. Section 2 formulates the method used, including the time-dependent Hartree approximation and the variational technique used to obtain the time evolution of the wave function. Section 3 outlines the calculations carried out. Section 4 presents the results and their analysis.

2. The method

We restrict the treatment for simplicity to a model system of an atom colliding with a one-dimensional metal, the motion of the atom being along the axis collinear with the lattice. Extention to 3D is straightforward in principle, but involves increased numerical effort. In a recent study of electron–hole pair excitation in very high energy collisions [12], 1D and 3D models of the metal electrons were compared and also examined against experimental data [11]. It was found that an appropriate 1D model provides satisfactory results for the excitation probabilities [12]. Another drastic simplification that will be made in the following development is to neglect phonon participation in the process. The aim is obviously to focus on the role of the electrons, but it should clearly be desirable in future studies to examine the extent to which conclusions on the electron excitation are affected by the simultaneous occurrence of energy

transfer to phonons. In any case, there have been suggestions that electron–hole pair excitations could be partly due to phonon–electron coupling, following excitation of phonons by the projectile [2]. Such a mechanism is neglected here. Also neglected in the present study are processes involving electron exchange between the atom and the metal. For the applications studied here such channels are improbable.

Finally, another extremely important simplification that will be employed here is to treat the process in an independent-electron framework. The Pauli principle is imposed, but essentially only on the counting of initial and final states. The "intermediate stage" dynamics during the collision will be described strictly at the one (metal) electron level. The emphasis of this article is thus on providing insight into the dynamics of single-electron behaviour in collisional excitation of metal surfaces.

2.1. TDSCF approximation

Consider at the outset a single electron in a 1D extended potential box with which an atom is colliding. Extension of the treatment to allow for N independent electrons in the well is described later. To describe the collision between the atom and the electron in the 1D potential field, the time-dependent self-consistent field (TDSCF) approximation will be used. In this approximation each particle (or mode) is described as moving in a spatially-averaged time-dependent potential due to the other modes. The mean fields in which the different particles move are determined self-consistently with the motions of the particles. This approximation was found to adequately describe cases of weak as well as of substantial energy transfer, while retaining many advantages of formal separability of modes. The TDSCF dates from the early days of quantum mechanics [13], and was used in different versions and adaptations to describe dynamical phenomena in a wide range of disciplines, e.g., excitation spectra and dynamics of many-electron systems [14], nuclear reactive collisions [15–17], inelastic molecular collisions [18–20], intramolecular dynamics and molecular dissociation [21], and electron–hole pair excitations in atom–surface collisions. An advantage of the TDSCF is that one can treat all particles quantum-mechanically [14,15], or all classically [22d], or some classically and others quantum mechanically [22a,22b,8]. In the present problem it appears natural to apply a mixed classical–quantum-mechanical TDSCF method, and treat the dynamics of the electron quantum-mechanically and the motion of the atom classically.

We formulate now the TDSCF approximation for the collision of an atom with an electron in a one-dimensional potential field. Measuring the position from some arbitrary reference point (e.g., the edge atom of the 1D metal), x will denote the coordinate of the electron and x_A the coordinate of the atom.

The Hamiltonian of the system is:

$$H = T_e + T_A + U_e(x) + V_{MA}(x_A) + V_{Ae}(x - x_A), \tag{1}$$

where T_e and T_A are respectively the kinetic energy operators of the metal electron and the incoming atom, $U_e(x)$ is the potential field for the electron in the metal, $V_{MA}(x_A)$ is the static part of the atom interaction with the metal surface and $V_{Ae}(x - x_A)$ denotes the interaction potential between the electron and the atom. In the TDSCF approximation, the following ansatz is made for the time-dependent wave function of the total system:

$$\Psi(x, x_A, t) \approx \phi_e(x,t)\, \phi_A(x_A,t) \exp[i\gamma(t)]. \tag{2}$$

The value of $\gamma(t)$ is chosen so as to simplify the equations obtained, but is of no physical significance. The equations obtained with an adequate choice of $\gamma(t)$ are:

$$i\frac{\partial \phi_e(x,t)}{\partial t} = \left[T_e + U_e(x) + V_e^{SCF}(x,t)\right] \phi_e(x,t), \tag{3a}$$

$$i\frac{\partial \phi_A(x_A,t)}{\partial t} = \left[T_A + V_{MA}(x_A) + V_A^{SCF}(x_A,t)\right] \phi_A(x_A,t), \tag{3b}$$

where

$$V_e^{SCF}(x,t) = \int |\phi_A(x_A,t)|^2\, V_{Ae}(x - x_A)\, dx_A, \tag{4a}$$

$$V_A^{SCF}(x_A,t) = \int |\phi_e(x,t)|^2\, V_{Ae}(x - x_A)\, dx. \tag{4b}$$

Eq. (3) is the familiar TDSCF approximation. It appears reasonable in this problem to treat the motion of the atom classically. Following previous mixed classical–quantum-mechanical TDSCF schemes [20,22a,22b,8], the classical TDSCF equation for the trajectory of the atom is:

$$m_A \frac{d^2 x_A}{dt^2} = -\frac{\partial V_A^{SCF}(x_A,t)}{\partial x_A} - \frac{\partial V_{MA}(x_A)}{\partial x_A}, \tag{5}$$

m_A denoting the mass of the atom. The electron satisfies eq. (3a) with the classical approximation for $V_e^{SCF}(x, t)$:

$$V_e^{SCF}(x,t) \approx V_{Ae}(x - x_A(t)). \tag{6}$$

Note that the initial conditions for the collision of the atom with the solid require only a single trajectory for the atom. The average in (4a) is thus replaced in the classical limit by a classical trajectory approximating the motion of the wave packet $\phi_A(x, t)$. In the TDSCF scheme employed, one thus solves self-consistently the classical trajectory equation (5) and the time-dependent Schrödinger equation (3a) for the electron. The scheme conserves the total energy of the system, although energy is of course transferred between the atom and the electron.

2.2. Variational method for calculating the time-dependent wave function

Calculation of $\phi_e(x, t)$ involves several difficulties. The electron in the energy band has a continuous spectrum. Expansion of $\phi_e(x, t)$ in a basis of stationary states will therefore involve a continuum of unknown time coefficients to be determined, which is an extremely difficult problem to handle. Also, for electrons as opposed to atomic-mass particles, a semiclassical description of the wave packet dynamics [23] is not applicable in general [23].

The approach we shall take for solving eq. (3a) is based on using a time-dependent variational principle. This variational method was introduced by Frenkel in the early years of quantum-mechanics [24], with much useful insight provided by recent studies of McLachlan [25] and Heller [26]. Assume that the solution $\psi(x,t_0)$ at $t = t_0$ of the Schrödinger equation is known. The variational method seeks to approximate the wave function at later times $t_0 + \Delta t$, where Δt is small. Using atomic units ($\hbar = 1$):

$$\psi(t_0 + \Delta t) \approx \psi(t_0) - i\theta(t_0)\,\Delta t, \tag{7}$$

where θ is to be taken as the "best" approximation to $i(\partial\psi/\partial t)_{t=t_0}$. To this effect, one considers the following functional of θ and ψ [26]:

$$I(\psi,\theta) = \int |\mathscr{H}\psi - \theta|^2 \,\mathrm{d}x. \tag{8}$$

The functional I vanishes if $\theta = i(\partial\psi/\partial t)$, when $\mathscr{H}\psi = \theta$. The variational property of $I(\psi, \theta)$ is that it is stationary to first order in $\delta\theta$ when a small change is made, $\theta \to \theta + \delta\theta$, about the time solution, i.e., to first order in $\delta\theta$:

$$\delta I = \int \delta\theta^*(\mathscr{H}\psi - \theta)\,\mathrm{d}x + \int \delta\theta\,(\mathscr{H}\psi^* - \theta^*)\,\mathrm{d}x$$

$$= 2\,\mathrm{Re}\int \delta\theta^*(\mathscr{H}\psi - \theta)\,\mathrm{d}x = 0. \tag{9}$$

Solving eq. (9) for θ (at $t = t_0$), eq. (7) is used and the process is repeated for $t = t_0 + \Delta t$. The solution is propagated in this way until the full time evolution is obtained.

To apply the principle (9) in practice, $\psi(x,t)$ must be approximated by some explicit form that depends on a small number of time-dependent parameters. Substitution in (9) yields equations from which the parameters are calculated [26].

The variational principle was applied to the determination of $\psi_e(x, t)$ as follows. Consider the unperturbed states of the electron in the metal:

$$[T_e + U_e(x)]\, f_k(x) \equiv H_e^0 f_k(x) = E_k f_k(x), \tag{10}$$

where the wave vector k is used to label the states. To obtain the time

development of $\psi_e(x, t)$, which evolve according to the Hamiltonian:

$$\mathscr{H}_e^{SCF}(x,t) = H_e^0(x) + V_e^{SCF}(x,t), \tag{11}$$

the following wave packet form is assumed:

$$\psi_e(x,t) = \int_{k=0}^{\infty} g_k(t - t_0)\, f_k(x) \exp\left[-iE_k(t - t_0)\right] dk, \tag{12}$$

where $g_k(t - t_0)$ was taken to be a Gaussian in the wave vector, with time-dependent parameters:

$$g_k(\tau) = \left[\frac{2c(\tau)}{\pi}\right]^{1/4} \exp\left\{-c(\tau)\left[k - k_0(\tau)\right]^2\right\}. \tag{13}$$

In the above equations, t_0 is the time at which the centre of the wave packet arrives at $x = 0$, a point which we choose to coincide with the surface edge (the position at which $U_e(x)$ has a barrier defining the metal/vacuum interface). Below we shall see that t_0 is a convenient parameter for describing initial conditions for the electron wave packet.

The time development of the wave packet is determined by the evolution of $c(t)$, the inverse width in wave vector space of the wave packet, and of $k_0(t)$, the centre of the packet in k-space. Physically, to represent an electron within the given energy band, the half-width of the Gaussian in k-space must be narrower than the value of the Fermi wavenumber:

$$|\Delta k| = 2/\left[c(t)\right]^{1/2} < k_F. \tag{14}$$

This condition implies that only a limited range of k-values contribute significantly to the wave packet [12].

We specialize the considerations now to a specific model choice of the potential field in the metal:

$$U_e(x) = \begin{cases} U_0(>0), & \text{for} \quad x > 0, \\ 0, & \text{for} \quad x < 0, \end{cases} \tag{15}$$

i.e., the electron is free inside the metal but experiences a finite barrier at the surface edge. The stationary states of the energy band are, in this case:

$$2f_k(x) = \begin{cases} e^{ikx} + R(k)\, e^{-ikx}, & x \leqslant 0, \\ T(k)\, e^{-\alpha(k)x}, & x > 0, \end{cases} \tag{16}$$

where

$$\alpha(k) = \left[2m(U_0 - E_k)\right]^{1/2}, \quad E_k = k^2/2m, \tag{17}$$

with m the electronic mass. $T(k)$ and $R(k)$ are given by:

$$R(k) = \frac{ik + \alpha(k)}{ik - \alpha(k)}, \quad T(k) = \frac{2ik}{ik - \alpha(k)}. \tag{18}$$

We substitute now the ansatz (12)-(13) into the variational principle (9) to obtain the equations for the nonlinear variational parameters $k_0(t)$ and $c(t)$, representing, respectively, the centre position and (inverse) spread in k-space of $\psi_e(x, t)$. We skip the details of the algebra, and present the equations obtained:

$$\dot{c}(t)\int_0^{+\infty}\left(\frac{\partial g_k}{\partial c}\right)^2 \mathrm{d}k + \dot{k}_0(t)\int_0^{+\infty}\left(\frac{\partial g_k}{\partial c}\right)\left(\frac{\partial g_k}{\partial k_0}\right)\mathrm{d}k$$

$$= \mathrm{Re}\left\{-\mathrm{i}\int_0^{+\infty}\mathrm{d}k\int_0^{+\infty}\mathrm{d}k'\left(\frac{\partial g_k}{\partial c}\right) g_{k'}\exp\left[\mathrm{i}(E_k - E_{k'})(t-t_0)\right]\right.$$

$$\left.\times\int f_k^*(x)\, V_e^{\mathrm{SCF}}(x,t)\, f_{k'}(x)\,\mathrm{d}x\right\}, \tag{19}$$

$$\dot{c}(t)\int_0^{+\infty}\left(\frac{\partial g_k}{\partial k_0}\right)\left(\frac{\partial g_k}{\partial c}\right)\mathrm{d}k + \dot{k}_0(t)\int_0^{+\infty}\left(\frac{\partial g_k}{\partial k_0}\right)^2\mathrm{d}k$$

$$= \mathrm{Re}\left\{-\mathrm{i}\int_0^{+\infty}\mathrm{d}k\int_0^{+\infty}\mathrm{d}k'\left(\frac{\partial g_k}{\partial k_0}\right) g_{k'}\exp\left[\mathrm{i}(E_k - E_{k'})(t-t_0)\right]\right.$$

$$\left.\times\int f_k^*(x)\, V_e^{\mathrm{SCF}}(x,t)\, f_{k'}(x)\,\mathrm{d}x\right\}. \tag{20}$$

Since the contributions to the k-integral are highly localized around k_0 (see eq. (14)), no sigificant error is made by extending the lower limits of the integrals in (19) and (20) to $k \to -\infty$. Furthermore, in carrying out the k-integrations, advantage may be taken of the fact that $R(k)$ and $T(k)$ of eq. (18), which appear as factors in $f_k(x)$, and similarly α_k of (17) are expected to vary more slowly in k than g_k. Using the above observations, together with eqs. (13) and (14), one finds, after some algebra:

$$\dot{c} = \left(\frac{2c}{\pi}\right)^{1/2}|T(k_0)|^2\,\mathrm{Im}\left\{\left[2cG_-^0 - 8c^2\left(F^0 - 2k_0H^0 + k_0^2G_-^0\right)\right]G_+^0\right\}$$

$$\times\int_0^{\infty} V_e^{\mathrm{SCF}}(x,t)\,\mathrm{e}^{-2\alpha(k_0)x}\,\mathrm{d}x + \left(\frac{2c}{\pi}\right)^{1/2}|T(k_0)|^2$$

$$\times\left\{\int_{-\infty}^{0} V_e^{\mathrm{SCF}}(x,t)\left[2c\left(G_-^i + R(k_0)G_+^i\right)^* - 8c^2\left(\left(F_-^i + R(k_0)F_+^i\right)^*\right.\right.\right.$$

$$\left.\left.\left.-2k_0\left(H_-^i + R(k_0)H_+^i\right)^* + k_0^2\left(G_-^i + G_+^i\right)^*\right)\right]\left[G_+^i + R(k_0)G_-^i\right]\mathrm{d}x\right\}, \tag{21}$$

$$\dot{k}_0 = 2\left(\frac{2c}{\pi}\right)^{1/2} |T(k_0)|^2 \,\mathrm{Im}\left[\left(H^0 - k_0 G_-^0\right) G_+^0\right] \int_0^\infty V_e^{\mathrm{SCF}}(x,t)\, \mathrm{e}^{-2\alpha(k_0)x}\, \mathrm{d}x$$

$$+ 2\left(\frac{2c}{\pi}\right)^{1/2} |T(k_0)|^2 \,\mathrm{Im}\left\{\int_{-\infty}^0 V_e^{\mathrm{SCF}}(x,t)\left[\left(H_-^i + R(k_0) H_+^i\right)^*\right.\right.$$

$$\left.\left. - k_0\left(G_-^i + R(k_0) G_+^i\right)^*\right]\left[\left(G_+^i + R(k_0) G_-^i\right)\right] \mathrm{d}x\right\}, \tag{22}$$

where c, k_0, $G_\pm^0$, H^0, F^0, etc. in eqs. (21) and (22) are all taken at the time value $t - t_0$ (only the potential V_e^{SCF} is evaluated at time t). The x-independent quantities $G_\pm^0$, H^0 and F^0 are defined by:

$$G_\pm^0 = \pi^{1/2} \frac{1}{\left[c(\tau) \pm \frac{1}{2}\mathrm{i}\tau\right]^{1/2}} \exp\left[-ck_0^2\left(1 - \frac{1}{1 \pm \frac{1}{2}\mathrm{i}\tau/c}\right)\right], \tag{23}$$

$$H^0 = \frac{ck_0}{c - \frac{1}{2}i\tau}\left(\frac{\pi}{c - \frac{1}{2}\mathrm{i}\tau}\right)^{1/2} \exp\left[-ck_0^2\left(1 - \frac{1}{1 - \frac{1}{2}\mathrm{i}\tau/c}\right)\right], \tag{24}$$

$$F^0 = \frac{1}{2\left(c - \frac{1}{2}\mathrm{i}\tau\right)}\left(\frac{\pi}{c - \frac{1}{2}\mathrm{i}\tau}\right)^{1/2}\left(1 + 2\frac{ck_0^2}{c - \frac{1}{2}\mathrm{i}\tau}\right)$$

$$\times \exp\left[-ck_0^2\left(1 - \frac{1}{1 - \frac{1}{2}\mathrm{i}\tau/c}\right)\right], \tag{25}$$

with $\tau = t - t_0$. $G_\pm^i$, $H_\pm^i$ and $F_\pm^i$ depend on x and are given by:

$$G_\pm^i = \pi^{1/2} \frac{1}{c + \frac{1}{2}\mathrm{i}\tau} \exp\left[-ck_0^2 + \frac{\left(ck_0 \pm \frac{1}{2}\mathrm{i}x\right)^2}{c + \frac{1}{2}\mathrm{i}\tau}\right], \tag{26}$$

$$H_\pm^i = \frac{ck_0 \pm \mathrm{i}x}{\left(c + \frac{1}{2}\mathrm{i}\tau\right)^{1/2}}\left(\frac{\pi}{c + \frac{1}{2}\mathrm{i}\tau}\right)^{1/2} \exp\left[-ck_0 + \frac{\left(ck_0 \pm \frac{1}{2}\mathrm{i}x\right)^2}{c + \frac{1}{2}\mathrm{i}\tau}\right], \tag{27}$$

$$F_\pm^i = \frac{1}{2\left(c + \frac{1}{2}\mathrm{i}\tau\right)}\left(\frac{\pi}{c + \frac{1}{2}\mathrm{i}\tau}\right)^{1/2}\left[1 + 2\frac{\left(ck_0 \pm \mathrm{i}x\right)^2}{c + \frac{1}{2}\mathrm{i}\tau}\right]$$

$$\times \exp\left[-ck_0 + \frac{\left(ck_0 \pm \frac{1}{2}\mathrm{i}x\right)^2}{c + \frac{1}{2}\mathrm{i}\tau}\right]. \tag{28}$$

In conclusion, in the framework of the specific variational ansatz chosen here, the TDSCF equations for the atom collision with a metal electron consist of the atom trajectory equation (5) combined with eqs. (21) and (22) for the parameters $c(\tau)$ and $k_0(\tau)$ of the electronic wave function.

3.3. Choice of initial conditions

For the incoming atom, the initial conditions were chosen to represent an idealized experimental situation of an incoming beam of well-defined momentum directed towards the surface:

$$p_A(t \to -\infty) \equiv m\dot{x}_A(t \to -\infty) = (2m_A E)^{1/2}, \tag{29}$$

where E is the collision energy, and

$$x_A(t \to -\infty) \to \infty, \tag{30}$$

i.e., the initial distance from the surface was taken extremely large compared with the interaction range. The choice of initial conditions for $\psi_e(x, t)$ presents, however, some difficulty. The most straightforward approach may appear to be to take $\psi_e(x, t \to -\infty)$ as one of the eigenstates $f_k(x)\, e^{-i\varepsilon_k t}$ of the electron in the energy band (with calculations carried out, in principle, for all k-values, and with appropriate thermal averaging over all possible initial k-states). However, such an initial condition cannot be applied in numerical practice with the variational ansatz (12)–(13). That form coincides with one of the well-defined k-states of (10) only, provided $c(\tau) \to \infty$. In that case eqs. (21) and (22) become numerically unstable, and the solutions cannot be propagated for increasing time values. To avoid this difficulty, initial wave packets were chosen that are superpositions of band eigenstates, i.e., corresponding to a finite value of $c(\tau)$ at $\tau \to -\infty$, but where the width of the k-distribution is narrow (on the scale of k_F). The energy of such a wave packet is, to good approximation, $\frac{1}{2}k_0^2$. The corresponding initial c-values are of the order of 10^2 in atomic units. These initial wave packets are not completely delocalized as the band eigenstates $f_k(x)$, but have a spatial extension of more than 10 Å. To cover all possible initial states in this localized set, one must sample over all independent packets (i.e., packets that do not overlap extensively) and, of course, over their mean energies $\frac{1}{2}k_0^2$ with appropriate Fermi–Dirac weighting. The peak positions in x-space of the initial wave packets must be so chosen as to sample all the metal ($x \leqslant 0$), but two neighbouring peak positions in the sample set should be separated by about the wave packet width distance, to exclude large overlap. (Such sampling of initial conditions for localized wave packets is similar to sampling over initial particle positions in classical trajectory calculations.) The wave packets are, of course, not strictly confined to a finite region and any such two wave packets have some overlap, at least. In principle, the effect of overlap should have been projected out in calculating the initial states. We have, however, neglected this effect, following numerical tests that have shown that it is unimportant. Rather than sample packets with different peak positions at some t, $t \to -\infty$, the following equivalent procedure is taken: The centre of the wave packet (12), located at point x at time t, reaches the surface edge $x = 0$ at time t_0. We therefore sample over different t_0

values as the equivalent to sampling over peak positions at some given time t, $t \to -\infty$. The method employed corresponds to the following physical picture: An independent sequence of wave packets, each representing an electron with different initial conditions, travels towards the metal edge. At the same time an atom undergoes (a much slower) collision with the surface. The electron and the atom will not necessarily hit the surface region at the same time, but if both reach, during their respective motions, a mutual distance smaller than the interaction range, then energy transfer may occur.

3.4. Extension to many independent electrons, and the evaluation of mean energy transfer

For a single electron with given initial conditions, the energy transfer ΔE can be obtained as follows from the results of the TDSCF wave packet calculation outlined in sections 3.1 to 3.3:

$$\Delta E\{x_0,\epsilon\} = \tfrac{1}{2}k_0^2(t=+\infty) - \tfrac{1}{2}k_0^2(t=-\infty), \tag{31}$$

where $\epsilon = \frac{1}{2}\mathbf{k}_0^2(t=-\infty)$. Here, x_0 is the initial position of the wave packet centre at some large negative time; x_0 is related to the t_0, over which the wave packets were actually sampled, by $x_0 = k_0 t_0$ (k_0 being the electron velocity in atomic units). Energy transfer depends on the initial x_0 (or t_0) since, as pointed out in section 3.3, this parameter determines whether the wave packet and the atom arrive at the surface region at the same time.

To obtain the *average* energy transfer from the atom to the electrons, it is necessary to: (i) average over ϵ, the initial energy of the wave packte, and x_0, its initial position; (ii) sum contributions from all the independent electrons, subject, however, to the Pauli exclusion. Straightforward considerations yield the following expression for the average energy transfer $\langle \Delta E \rangle$ in terms of transfer for sample events $\Delta E(x_0, \epsilon)$:

$$\langle \Delta E \rangle = 2n \int\int f_T(\epsilon)\left[1 - f_T(\epsilon + \Delta E\{x_0,\epsilon\})\right] \Delta E\{x_0,\epsilon\} \frac{D(\epsilon)}{N} \mathrm{d}\epsilon \, \mathrm{d}x_0. \tag{32}$$

Here n is the electron density per unit length,

$$f_T(\epsilon) = \left\{1 + \exp\left[(\epsilon - \epsilon_F)/k_B T\right]\right\}^{-1}$$

is the Fermi–Dirac distribution at temperature T, and $D(\epsilon)$ is the three-dimensional electron density of states, normalized by

$$N = \int_0^{\epsilon_F} D(\epsilon)\, \mathrm{d}\epsilon,$$

where N is the total number of electrons. The factor 2 in eq. (32) arises from spin degeneracy. Attention should be drawn to the similarity in structure between eq. (32) and the expression obtained for conductivity in the standard

semiclassical theory of electron conduction in metals [27]. In actual applications, due to the $f_T(\epsilon)$ factors only electrons from the Fermi surface contribute to (32), so $D(\epsilon) \approx D(\epsilon_F)$ in the integral (32).

4. Calculations and results

Numerical calculations were carried out for He, Ar and H colliding with a Li surface, in the energy range 0–1.0 eV. The same systems were previously studied at very high collision energies ($E > 100$ eV) using the Sudden Approximation [10]. In modelling the interaction between a metal electron and the atoms, $V_{Ae}(x - x_A)$, we assumed that it is approximately the same as the corresponding free electron–atom (gas phase) interaction. We thus ignore screening effects, which for electrons at the close vicinity of the surface are probably not very large. He–electron and Ar–electron effective potentials were given by Green et al. [28] based on Hartree–Fock calculations. A suitable e–H effective potential was obtained by Brandsen [29] from an adiabatic approximation. We fitted the potntials of refs. [8,29] to a form convenient for our calculations. In carrying out the fitting, we used the fact that the results are sensitive to $V_{eA}(x - x_A)$ only in a very limited range of $x - x_A$ values: very short $(x - x_A)$ ranges are excluded by the fact that the atom is stopped by the repulsive wall of the interaction with the solid in configurations where the penetration of $\psi_e(x, t)$ outside the metal $(x > 0)$ is very weak. For large $(x - x_A)$, the potential is in any case too weak to cause significant energy transfer. Analysis has shown that the pertinent range of $(x - x_A)$ values falls in the region where V_{eA} is attractive, and over the limited range of importance it could be fitted by:

$$V_{eA}(x - x_A) = -A_0 \exp\left[-\mu(x - x_A)^2\right], \tag{33}$$

for all three atoms. The values of the parameters A_0 and μ are listed in table 1.

Table 1
Parameters used for the static interaction of the atom with the metal surface, eq. (34), and electron–atom interaction, eq. (33)

Incident atoms	Electron–atom interaction		Atom–surface interaction	
	A_0 (a.u.)	μ (bohr^{-2})	D (eV)	x_m (bohr)
H	0.18	0.18	1.8	3
Ar	0.25	0.17	0.15	8
He	0.1	0.3	0.002	7.2

For the static atom–surface interactions $V_{MA}(x_A)$, we employed the form:

$$V_{MA}(x_A) = D\left[(x_m/x_A)^9 - 3(x_m/x_A)^3\right], \tag{34}$$

widely used in the literature [1]. The values of D and x_m for He/Li(surface) were taken from Kohn and Sham [30] who calculated the potential for that system using a Hartree–Fock method for the repulsive part and a polarization approximation for the attractive component. Several electronic energy curves for the H/Li(001) were given by Vojtik et al. [31] from Li cluster calculations. The one-dimensional model we use is in fact somewhat questionable in this case, since D and x_m vary significantly with the position upon the cluster where H strikes [32]. We estimated average values. As far as we are aware, quantitative data on the Ar/Li(surface) interaction are not available. We very crudely estimate D and x_m for this system based on the differences between the polarizability of Ar and of He (for which case the parameters are known). The values of D and x_m used in the calculations are listed in table 1.

In the calculations we carried out, the trajectory equation (5) for the atom, and the equations (21) and (22) for the electron wave packet parameters were solved self-consistently by numerical integration, subject to the initial conditions $c(t \to -\infty) = 500$ bohr^2 and $k_0(t \to -\infty) = k_F$. As noted in section 3.4, other k_0, or $\epsilon = \frac{1}{2}k_0^2$, values do not contribute significantly to the integral equation (32). The sampling over initial t_0 (or equivalently x_0) was taken typically over the order of 10^2 points. In practical terms the sampling was dense enough so that a "smooth" numerical function $\Delta E = \Delta E\{t_0\}$ was obtained. Each calculation for fixed value of t_0 takes only a few seconds cpu on the CDC 6600. The method is therefore not expensive computationally.

4.1. Excitation and de-excitation for different initial conditions

We consider first the energy transferred to a single electron $\Delta E\{k_F, t_0\}$ as a function of the initial condition t_0, the time when the wave packet centre reached the metal surface $x = 0$. Fig. 1 shows the results for $\Delta E\{k_F, t_0\}$ in the case of He/Li(surface) at collision energies $E = 0.004$ eV and $E = 0.014$ eV, and fig. 2 shows corresponding results in the case of H/Li(surface) at $E = 0.1$ eV. At the single electron level, before the Pauli exclusion weighting is introduced, both excitation and de-excitation of the electron are possible, and as seen in figs. 1 and 2 the two processes are of similar (though not identical) magnitude. If t_0 is such that the wave packet reaches the surface region ($x \approx 0$) while the atom is still approaching the metal, the result will be *de-excitation* since, as the electron is reflected from the surface, the atom will get nearer and a *stronger attractive interaction* $V_A(x - x_A)$ will be experienced by the reflected electron. Similarly for t_0, such that the atom reaches the surface before the electron the attraction $V_A(x - x_A)$ experienced by the electron during its

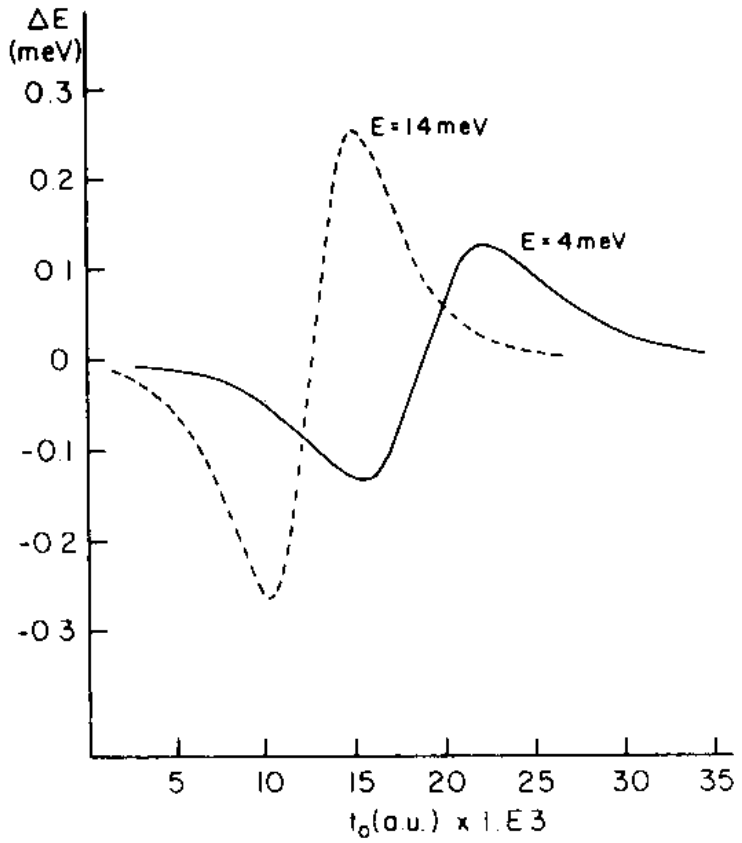

Fig. 1. Dependence of energy transfer to single electron on arrival time t_0 of wave packet: case of He/Li(surface). Sampling over t_0 covers the initial condition values for the wave packet. (———) Collision energy $E = 4$ meV. (— — —) Collision energy $E = 14$ meV.

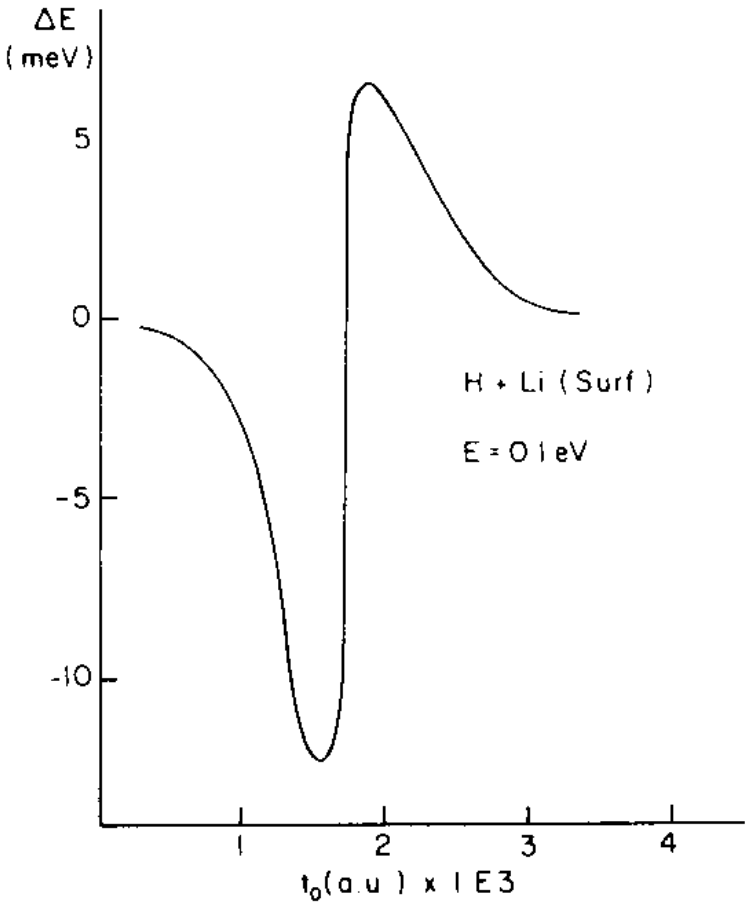

Fig. 2. Dependence of energy transfer to single electron on arrival time t_0 of wave packet: case of H/Li(surface). Sampling over t_0 covers the initial condition values for the wavepacket. Results shown are for collision energy 10 meV.

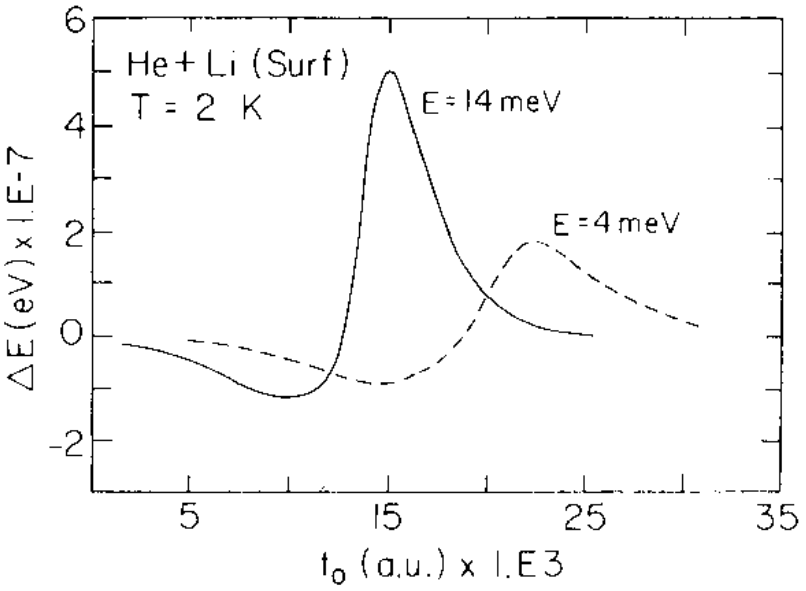

Fig. 3. Dependence of energy transfer on arrival time t_0 of the wave packet: effect of Pauli exclusion: case of He/Li(surface). $\Delta\hat{E}(t_0)$ shown here is the energy transfer $\Delta E(t_0)$ multiplied by the Pauli exclusion factor $\rho_T(\Delta E)$. (———) Collision energy $E = 14$ meV. (— — —) Collision energy $E = 4$ meV.

approach to the surface is stronger, leading to acceleration and excitation. For a many-electron system, *the balance between excitation and de-excitation is affected, however, strongly by the Pauli exclusion*. Indeed at $T = 0$ de-excitation of the electron is, of course, forbidden. To examine this quantitatively at temperature T, it is convenient to consider the quantity

$$\Delta\hat{E}\{x_0, T\} \equiv \Delta E\{x_0\}\, \rho_T(\Delta E), \tag{35}$$

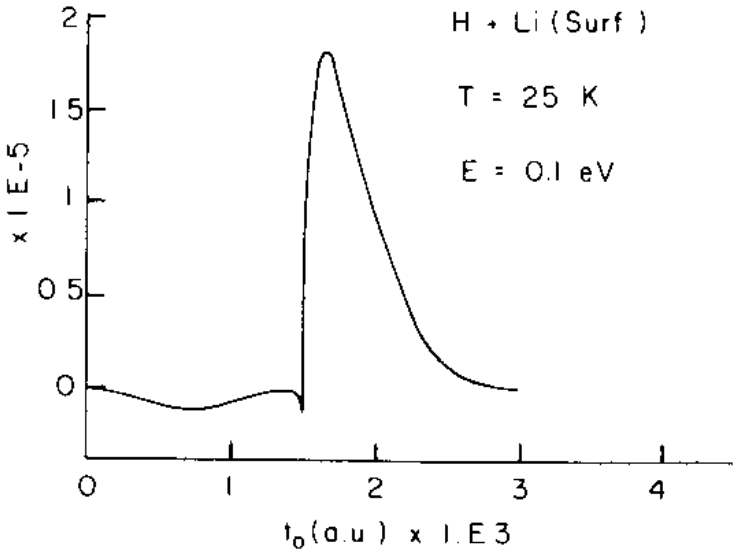

Fig. 4. Dependence of energy transfer on arrival time t_0 of the wave packet: effect of Pauli exclusion: case of Hi/Li(surface). $\Delta\hat{E}(t_0)$ shown here is the energy transfer $\Delta E(t_0)$ (in eV) multiplied by the Pauli exclusion factor $\rho_T(\Delta E)$. The results are for collision energy $E = 0.01$ eV.

where $\rho_T(\Delta E)$ is the Pauli exclusion factor

$$\rho_T(\Delta E\{x_0\}) = \int f_T(\epsilon)\left[1 - f_T(\epsilon + \Delta E\{x_0\})\right]\frac{D(\epsilon)}{N}\,\mathrm{d}\epsilon. \tag{36}$$

$\Delta\hat{E}\{x_0,T\}$ is essentially the contribution from x_0 to the average energy transfer $\langle\Delta E\rangle$. Indeed, using the fact that the only significant contributions in (32) are from $\epsilon \approx \epsilon_F$, one can set there

$$\Delta E\{x_0,\epsilon\} \approx \Delta E\{x_0,\epsilon_F\} \equiv \Delta E\{x_0\},$$

one then has

$$\langle\Delta E\rangle = 2n\int \Delta\hat{E}\{x_0,T\}\,\mathrm{d}x_0. \tag{37}$$

Through the scaling $x_0 = k_0 t_0$ (here $k_0 = k_F$), $\Delta\hat{E}$, like ΔE can be also regarded as a function of t_0. Fig. 3 shows $\Delta\hat{E}\{t_0,T\}$ versus t_0 for He/Li(surface) at the same collision energies as in fig. 1, and for surface temperature $T = 2$ K. Similarly, fig. 4 shows $\Delta\hat{E}\{t_0,T\}$ versus t_0 for H/Li(surface) at the collision energy of fig. 2 (0.1 eV), and for surface temperature $T = 25$ K. Quite obviously, *the near-balance between excitation and de-excitation in $\Delta E\{t_0\}$ of figs. 1 and 2 is shifted very heavily by the Pauli factor in favour of the excitation process*. The effect of the Pauli factor is stronger when the excitation and de-excitation at the single electron level is pronounced. The effect of the Pauli factor is therefore larger for the higher collision energy in the two calculations shown for He/Li, and the effect is most striking for H/Li, since the single-electron excitation (and de-excitation) probabilities are very high. The strong effect of the Pauli factor on the balance between excitation and de-excitation indicates that temperature effects on atom-to-metal electron energy transfer may be large. This will be confirmed in detail in a subsequent section.

4.2. Electron excitation efficiency of different colliders

Table 2 shows the average excitation energy $\langle\Delta E\rangle$ of Li electrons due to impact at energy $E = 0.01$ eV of He, Ar and H, for surface temperature $T = 0$ K. Both He and Ar give extremely low energy transfer, on a scale that would be experimentally negligible. *On the other hand, energy transfer to electrons by H collisions is substantial*, and as we shall also see further below, likely to be of significant experimental consequence (e.g., in causing high atom capture probabilities). The reasons for the large differences between H and He or Ar are, first, that H penetrates much more into regions where the density of surface electrons, $|\psi(x, t_0)|^2$ is substantial, and second, that the H–Li interaction has a deep attractive well, and H is therefore accelerated to much higher effective collision energies than the rare gas atoms. The similarity between He and Ar is

Table 2
Fractional energy transfer with fixed collision energy $E = 0.01$ eV for all three colliders at zero surface temperature

	H	He	Ar
$\frac{\Delta E}{E}$	0.28	0.00175	0.009

due to partial cancellation of opposing effects: He penetrates deeper into regions of significant surface electron density, but Ar as a larger atom has a stronger coupling to the electrons, and (because of the larger well depth of its interaction with the metal) is accelerated more than He by V_{MA}. It is of interest to note that calculations at very high collision energies ($E > 100$ eV) and using a completely different method (Sudden Approximation) predicted a similar order of excitation efficiencies H > Ar ≫ He [10]. The main new conclusions in this section, as far as possible experimental relevance is concerned, is that H seems of great efficiency (relative to other atoms) in exchanging energy with electron–hole pairs. *It should be desirable in searches of evidence for hole-pair excitation in molecule–surface collisions to carry out experiments with H as a collider.* Our conclusion on the very poor energy transfer in He collisions is qualitatively in line with the earlier finding of Gunnarson and Schönhammer [9] (they did not study H or Ar collisions). The potentials used here are quite different from those of ref. [9], but for similar potentials our results are in reasonable quantitative agreement with that study.

4.3. Dependence of electron excitation on the collision energy

In the case of H/Li(surface), $\langle \Delta E \rangle$ is almost independent of the incident collision energy, at least in the range $0 < E < 0.2$ eV, since the velocity of the H atom upon impact at the surface is in any case determined mainly by its acceleration in the deep attractive well. We focus therefore on the result of He/Li(surface). Fig. 5 shows for that system the fraction of the collision energy transferred to the electrons $\langle \Delta E \rangle / E$ as a function of the collision energy in the range $10^{-3} < E < 1.0$ eV, and for several values of the surface temperature. For $T = 0$ K, the fractional energy tranfer falls off monotonically as E increases, i.e., although energy tranfer is greater at higher collision energies, the effect of the transfer on the dynamics of the atom (of which $\langle \Delta E \rangle / E$ is some indicator) is more significant for slow collisions. For $T > 0$ K, the behaviour is different: $\langle \Delta E \rangle / E$ first increases sharply with E, reaches a maximum, and then falls off monotonically and slowly, the behaviour in that range being as in the $T = 0$ K case. The higher the surface temperature, the larger is the E-value at which the maximum occurs. The explanation for the

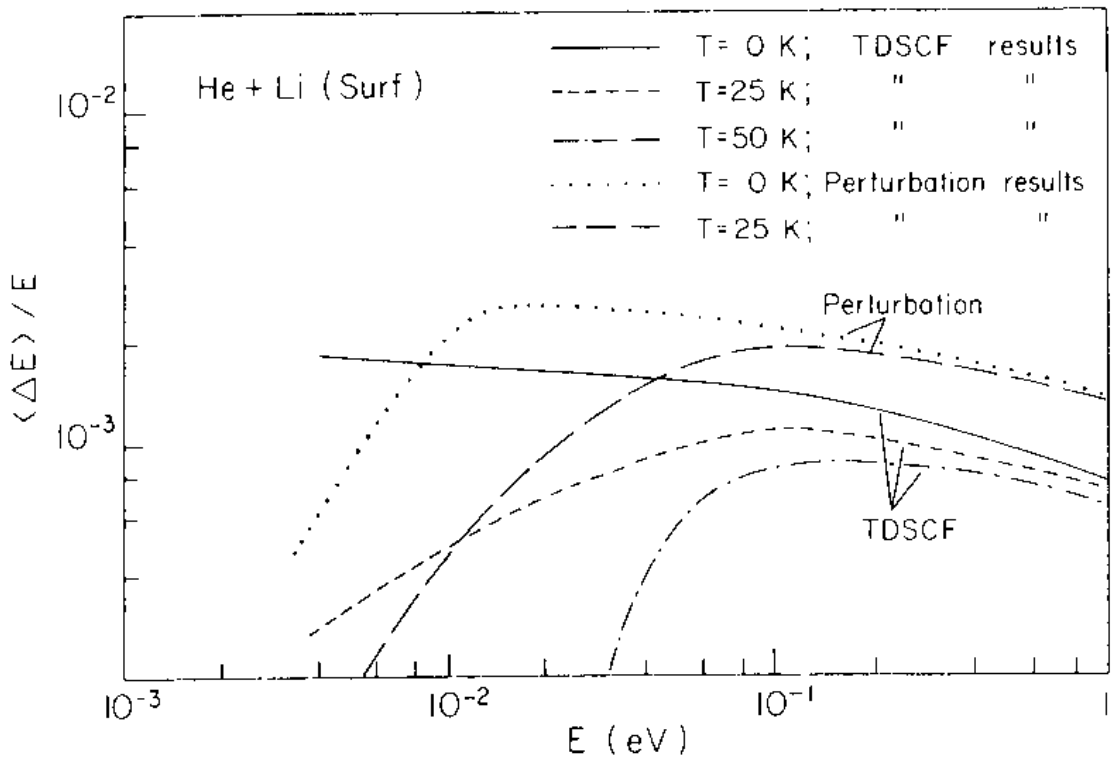

Fig. 5. Fraction of collision energy $\langle \Delta E \rangle / E$ transferred to electrons versus E. Results shown are for He/Li(surface) for several surface temperatures T. (———) $T = 0$ K, TDSCF calculation; (— — —) $T = 25$ K, TDSCF calculation; (– · – · –) $T = 50$ K, TDSCF calculation; (· · · · · ·) $T = 0$ K, perturbation calculation; (– – –) $T = 25$ K, perturbation calculation.

temperature effect on $\langle \Delta E \rangle / E$ is that, *as surface temperature increases, energy transfer from the electron to the atom plays an increasingly important role*, and *reduces* the average energy transfer $\langle \Delta E \rangle$ (which for He/Li is positive, corresponding to net excitation, for all T values shown). At sufficiently low energies $E \to 0$ for given $T > 0$, electron excitation and de-excitation are nearly balanced, with $\langle \Delta E \rangle / E \to 0$. As E increases, electron excitation increases very rapidly compared with de-excitation, leading to a steep rise of $\langle \Delta E \rangle / E$ with increasing E. For sufficiently large E, the electron de-excitation becomes unimportant and the close balance between excitation and de-excitation disappears. $\langle \Delta E \rangle$ which corresponds to excitation still increases with collision energy but more slowly than E itself, thus in this range $\langle \Delta E \rangle / E$ falls off as in the $T = 0$ K case. The lower T is, the larger is the net excitation probability at given E, hence the shift in the maxima in fig. 5 with increasing T.

4.4. Atom trapping at low energies due to metal electron excitation

Trapping of the atom will occur if the energy transferred to metal electrons exceeds the initial collision energy. The TDSCF seems to be the only approach available so far that is capable of calculating such trapping correctly; in particular it can follow the dynamical evolution of the atom–electron system in

a trapping event (perturbation-type approaches cannot provide such a description of trapping). H atoms in particular are expected to give a pronounced effect, since for this projectile $\langle \Delta E \rangle$ is independent of E for $E < 0.2$ eV. (The effective collision velocity with the metal is dominated by the acceleration of the atom in the deep potentials well.) For sufficiently low E, a regime where $\langle \Delta E \rangle > E$ is thus expected. The well-depth $2D$ of the atom–metal interaction is of critical importance in the trapping, so we carried out calculations for trapping in H collisions for two values of D: 1.9 and 0.5 eV. In the calculations, trapping was considered as a collision during which the atom carries out at least one oscillation in the attractive potential well of its interaction with the surface. The trapping probability versus the collision energy $P(E)$ was calculated as the probability of finding an electron (at energy ϵ_F) in the range of values that lead to the trapping event:

$$P(E) = 2n \int_{x_1}^{x_2} \rho_T(\Delta E\{x_0\})\, \mathrm{d}x_0, \tag{38}$$

where $\rho_T(\Delta E)$ is the Pauli exclusion factor, eq. (36), and $\Delta E(x_0) > E$ for $x_1 > x_0 > x_2$.

Fig. 6 shows the trapping probability at $T = 0$ K. Trapping probability exceeds 10% for collisions at energies lower than 70 K, and exceeds 50% for $E < 20$ K in the calculation with $D = 1.9$ eV. In the case of $D = 0.5$ eV, the trapping exceeds 50% only for $E < 5$ K. The steepness of $P(E)$ versus E becomes very large as $E \to 0$. *The results suggest very major trapping effects due*

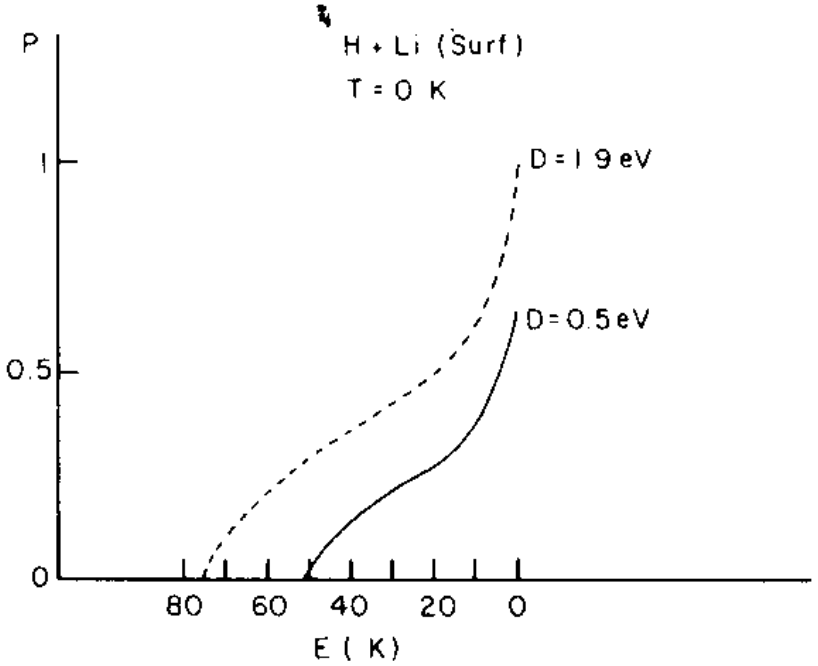

Fig. 6. Trapping probability as function of collision energy for H/Li(surface). Results shown are for surface at $T = 0$ K. Collision energy E is given in K. (———) Results for calculation with potential well depth $2D = 1$ eV. (— — —) Results for calculation with potential well depth $2D = 3.8$ eV.

to electron–hole participation in low energy atom–surface collisions for systems where the interaction potential is of the order of an eV or more. The experimental relevance of this depends, however, on establishing whether and how this conclusion is affected by the inclusion of phonon effects (which, perhaps, may give rise to even larger trapping effects or which may cause fast desorption). Studies of this question seem very desirable.

Trapping takes place also in the calculations on Ar/Li(surface), but the effect becomes large only at energies $E < 0.5$ K. Trapping probabilities for He remain small even for lower collision energies. Unlike the case of H, metal electron excitation in rare-gas collision is too inefficient to induce trapping in collisions energies of practical interest.

Another interesting aspect of the calculations involves the time evolution of the trapping events. This requires propagating the TDSCF solutions beyond the primary trapping event (the first bounded vibration of the atom in the potential well of its interaction with the surface). It was found that the collisions leading to trapping almost invariably leave the atom just slightly below the dissociation energy (typically, E after the first collision is -10^{-3} eV), at a highly excited level of the atom–surface potential well. As the atom carries out vibrations, it gradually loses more energy to metal electrons. Cascading of the vibrational energy in the well continued in the TDSCF calculations for about (typically) 1000 vibrations, at which stage the atom was relaxed to the bottom of the potential well. The pattern of H (vibrational) energy lost as a function of time to the surface electrons during the relaxation is shown in fig. 8. We note that in this calculation each encounter of the atom with the surface (during its vibration) is considered as an independent collision process with new, independent wave packets.

4.5. Effect of surface temperature on the switchover from electron excitation to de-excitation

The influence of surface temperature in shifting the balance between excitation to de-excitation of the metal electrons in the collision process was already discussed briefly for He/Li(surface) in section 4.2. We examine now more detailed results on this in the more striking example of H collisions. Fig. 7 shows $\langle \Delta E \rangle$ (energy transfer from electrons to atom) as a function of the surface temperature for fixed collision energy $E = 0.01$ eV. $\langle \Delta E \rangle$ increases monotonically with T throughout the temperature range. Up to about $T = 200$ K, atom collisions cause more excitation than the de-excitation of the electron and $\langle \Delta E \rangle < 0$. As surface temperature increases, contributions of energy tranfer *from* metal electrons *to* the incoming atoms begin to dominate over the electron excitation processes, and the total $\langle \Delta E \rangle$ keeps increasing. Energy transfer in the electron excitation regime is 3×10^{-3} eV or less. Energy tranfer from the electrons to the atom reaches 10^{-2} eV in the high T range.

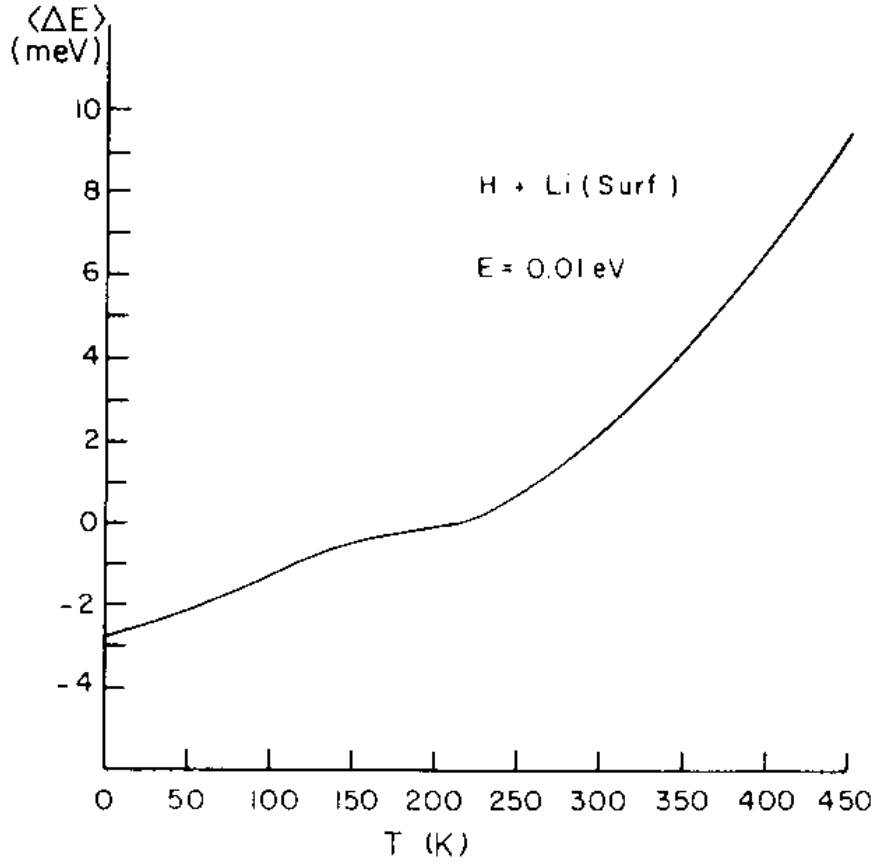

Fig. 7. Dependence of mean energy transfer (to the atom) $\langle \Delta E \rangle$ on surface temperature for H/Li(surface). Result shown is for collision energy $E = 0.01$ eV. Potential well depth is $2D = 3.8$ eV.

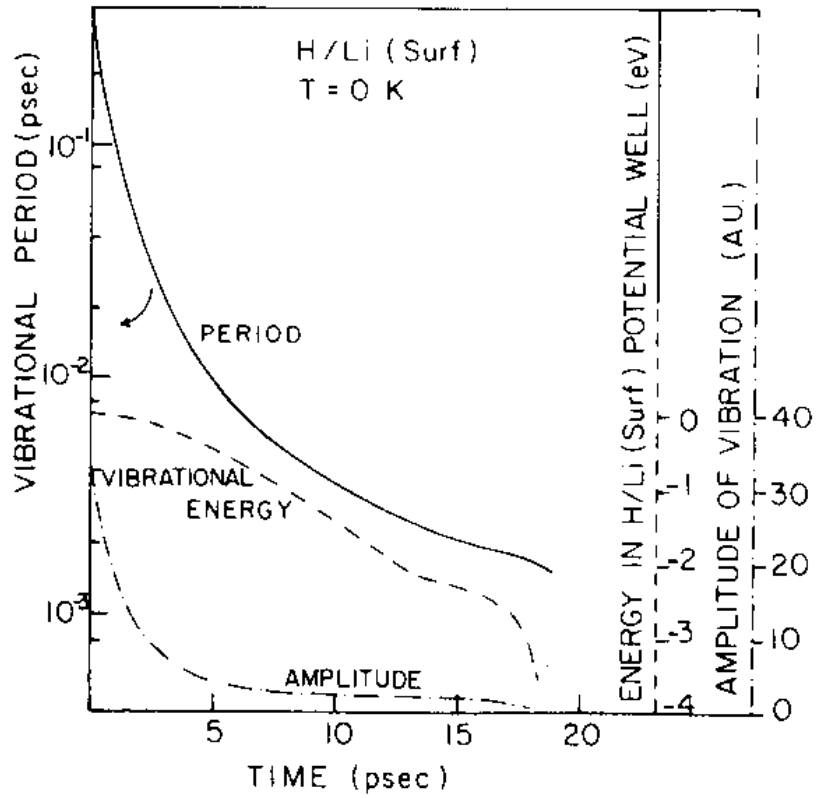

Fig. 8. Time evolution of the trapping process for H/Li(surface). (— — —) Energy of vibrating atom in surface potential well as a function of time. (———) Vibrational period versus time. (– · – · –) Amplitude versus time. Potential well depth is $2D = 3.8$ eV.

4.6. Validity of first-order perturbation theory for energy transfer to metal electrons

As noted in the Introduction, many of the available estimates of electron–hole pair excitation in atom–surface collisions are based on various versions of first-order time-dependent perturbation theory, which indeed appears in view of its simplicity an attractive tool to apply. The availability of the more refined TDSCF calculations makes it possible to test the validity of the perturbation-theoretic (PT) treatment. In time-dependent PT approach, the "back reaction" of the electrons undergoing excitations on the incoming atom is neglected. The trajectory $x_A(t)$ of the atom then pertains to elastic scattering and is easily computed for the potential $V_{MA}(x_A)$. Substituting the trajectory in the electron–atom coupling, first-order perturbation theory is used to calculate transitions between the states $f_k(x)$ of the metal electrons under the time-dependent interaction $V_{eA}(x - x_A(t))$.

The familiar expression for the probability of transition from initial state $f_k(x)$ to final state $f_{k'}(x)$ as a result of the collisions is, in atomic units [32]:

$$P_{k\to k'} = \left| \int_{-\infty}^{+\infty} \exp\left[i(E_{k'} - E_k)t \right] V_{k'k}(t)\, dt \right|^2, \tag{39}$$

where

$$V_{k'k}(t) = \langle f_{k'} | V_{eA}(x - x_A(t)) | f_k \rangle. \tag{40}$$

The mean energy transfer is

$$\langle \Delta E \rangle = \underset{k}{\mathrm{Av}} \sum_{k'} (E_{k'} - E_k)\, P_{k\to k'}. \tag{41}$$

Av denotes the thermal averaging over initial electron states, and the k' summation is an integration over all-final states. In the calculations the integrals (39) and (41) are carried out numerically. Comparison between the PT results and those of TDSCF is shown in fig. 5 for the variation of $\langle \Delta E \rangle / E$ with E in the case of He/Li(surface) at $T = 0$ K and $T = 25$ K. PT seems to yield the correct trend of the curves and is within a factor of ~ 2 of the TDSCF results in the range $E > 0.1$ eV. On the other hand, PT fails even qualitatively at very low energies ($E < 0.005$ eV). For the 0 K case the PT results decrease with decreasing E unlike the TDSCF $\langle \Delta E \rangle / E$ which increase in that direction. Mainly, the failure of PT at low energies may be due to the fact that the true atom trajectory at very low energies is very sensitive even to very small amounts of energy transferred, so that use of an elastic trajectory $x_A(t)$ leads to serious error. Next, in the present problem PT is in error in always yielding higher electron excitation than de-excitation due to the fact that $V_{k'k}(t)$, for given initial k, is larger for $E_{k'} > E_k$ than for $E_{k'} < E_k$ (simple

consequence of overlap properties of the $f_k(x)$). Since temperature effects are mainly reflected in the balance between excitation and de-excitation, PT is qualitatively wrong on the T-dependence. Finally, PT cannot describe trapping dynamics which is definitely not first-order in the coupling, and where the changes in the atom trajectory due to energy transfer are extremely important.

In conclusion, PT has better than order-of-magnitude validity provided the collision energies are not too low ($E \gg 0.01$ eV in the case of He). The approximation breaks down, sometimes qualitatively, at very low energies for several properties and effects of importance (e.g., T-dependence).

5. Concluding remarks

In this article, a model based on the TDSCF approximation was introduced for energy transfer between an atom colliding with a metal–surface and the conduction electrons of the metal. A time-dependent variational principle was employed to calculate the electron wave packets, and the resulting description of the dynamics appears very convenient for physical interpretation.

The main results obtained were, first, that energy transfer to metal electrons is predicted to be of substantial, experimentally detectable magnitudes for H atom collisions although not for rare-gas projectiles. Secondly, it was demonstrated that at high surface temperature and extremely low collision energy, excitation of the atom by energy transfer from the electron–hole pairs becomes appreciable. Thirdly, atom trapping due to energy transfer to electrons was found to occur (for H atoms) at extremely low collision energies ($\sim$ 30 K) and for very low surface temperatures. Finally, time-dependent perturbation theory was tested and found to apply provided the collision energy is not very low, but to break down qualitatively otherwise.

The results obtained in this work must be viewed as tentative in part, since phonons were not incorporated in the treatment. This has been a limitation also in previous studies, and we believe that it will be extremely important to include both phonons in future investigations and to elucidate the role and effects associated with each of the two types of modes.

Another limitation of the present study to which attention is called is that the dynamics was treated at the independent electron level, even the Pauli exclusion being introduced only in the summation over final and initial states (but not included in the dynamics itself). It seems to us that this is a reasonable approximation for the conditions and systems examined here. Estimates of Pauli effects on the dynamics, should, however, be very useful in providing a test for the validity of the independent electron dynamics model.

Acknowledgements

This work was partially supported by the ARO and partly by the Chemical Division of the NSF. A.N. acknowledges support from the US-Israel-Binational Science Foundation. The Fritz Haber Center at the Hebrew University is supported by the Minerva Gesellschaft für Forschung, München, FRG.

References

[1] F.O. Goodman and H.Y. Wachman, Dynamics of Gas–Surface Scattering (Academic Press, New York, 1976).
[2] S. Nourtier, J. Physique 38 (1977) 479.
[3] E. Müller-Hartman, T.V. Ramakrishman and G. Toulouse, Phys. Rev. B3 (1971) 1102.
[4] R. Brako and D.M. Newns, J. Phys. C14 (1981) 305.
[5] J.N. Gadzuk and H. Metiu, Phys. Rev. B22 (1980) 2603;
H. Metiu and J.W. Gadzuk, J. Chem. Phys. 74 (1981) 2641.
[6] P. Nozières and C.T. de Dominics, Phys. Rev. 178 (1969) 5164.
[7] K. Schönhammer and O. Gunnarson, Z. Physik 38 (1980) 127.
[8] D. Kumamoto and R. Silbey, J. Chem. Phys. 75 (1981) 5164.
[9] O. Gunnarson and K. Schönhammer, Phys. Rev. B25 (1982) 2514.
[10] Z. Kirson, R.B. Gerber and A. Nitzan, Surface Sci. 124 (1983) 279.
[11] T.A. Delchar, unpublished results.
[12] Z. Kirson, A. Nitzan and R.B. Gerber, to be published.
[13] P.A.M. Dirac, Proc. Cambridge Phil. Soc. 26 (1930) 376.
[14] H. Ehrenreich and M.H. Cohen, Phys. Rev. 115 (1959) 786.
[15] P. Bonche, S. Koonin and J.W. Negele, Phys. Rev. C13 (1976) 1226.
[16] J.N. Negele, S. Koonin, N. Heller, R. Nix and A.J. Sierk, Phys. Rev. C17 (1978) 1098.
[17] J.J. Grifin, P.C. Lichtner and M. Dwozecka, Phys. Rev. C21 (1980) 1351.
[18] K. Goeke and P.-G. Reinhard, Eds., Time-Dependent Hartree–Fock and Beyond (Springer, Berlin, 1982).
[19] J.T. Muckerman, I. Rusinek, R.E. Roberts and M. Alexander, J. Chem. Phys. 65 (1976) 2416.
[20] D.J. Locker and D. Wilson, J. Chem. Phys. 52 (1970) 271.
[21] G.C. Schatz, Chem. Phys. 24 (1977) 263.
[22] (a) R.B. Gerber, V. Buch and M.A. Ratner, J. Chem. Phys. 77 (1982) 3022;
(b) R.B. Gerber, V. Buch and M.A. Ratner, in: Intramolecular Dynamics, Proc. 15th Jerusalem Symp. on Quantum Chemistry, Eds. J. Jortner and B. Pullman (Reidel, Dordrecht, 1982);
(c) R.B. Gerber, M.A. Ratner and V. Buch, Chem. Phys. Letters 91 (1982) 173;
(d) G.C. Schatz, V. Buch, M.A. Ratner and R.B. Gerber, J. Chem. Phys. 79 (1983) 1808.
[23] E.J. Heller, J. Chem. Phys. 62 (1975) 1544.
[24] J. Frenkel, Wave Mechanics (Clarendon, Oxford, 1934).
[25] A.D. McLachlan, Mol. Phys. 8 (1964) 39.
[26] E.J. Heller, J. Chem. Phys. 64 (1976) 63.
[27] N.W. Ashcroft and N.D. Mermin, Solid State Physics (Saunders, Philadelphia, PA, 1976).
[28] A.E.S. Green, D.L. Sellin and A.S. Zachor, Phys. Rev. 184 (1969) 1;
A.E.S. Green, D.L. Sellin and G. Darewych, Phys. Rev. A3 (1971) 169.
[29] B.H. Brandsen, Atomic Collision Theory (Benjamin, New York, 1970).
[30] W. Kohn and L.J. Sham, Phys. Rev. A140 (1965), 1133.
[31] J. Vojtik, J. Fiser and R. Polak, Chem. Phys. Letters 80 (1981) 569.
[32] L.D. Landau and E.M. Lifshitz, Quantum Mechanics, 2nd ed. (Pergamon Oxford, 1965).