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Many-electron theory of laser-assisted surface-ion neutralization

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Abstract. We develop a theoretical framework for investigating charge-transfer processes occurring during the scattering of an ion from a solid surface, in the presence of a pulsed laser field. The theory is based upon the many-electron formalism, previously used by our group, to investigate charge transfer based upon purely electronic mechanisms, but it is here extended to include the additional matrix elements needed to describe laser-assisted transitions. The model is applied to several systems with different scattering behaviours, with the conclusion that the effect of the laser field can be expected to be greatest when the target substrate is one with a relatively narrow valence band. For fixed incident energy, the neutralization probability shows a novel multiple-peaked structure with respect to the laser frequency. These features should be observable at experimentally viable laser intensities.

1. Introduction

When an atom or ion is scattered from the surface of a solid, electronic charge transfer can occur during the collision process, under certain circumstances. In the case of surface-ion neutralization (SIN), a slow-moving positive (negative) ion strikes a surface and rebounds as a neutral atom, having received (given) an electron from (to) the solid during the brief interaction period.

Neutralization can occur by one of several mechanisms [1]. In two-electron Auger transitions, which are not investigated here, an electron is transferred from an occupied level in the solid band into an unoccupied orbital of lower energy on the incoming ion, while a second electron is excited within the solid, so as to ensure energy conservation. In one-electron resonant charge transfer, a positive ion, for example, is neutralized during the collision when an electron is transferred to its empty valence orbital from an occupied orbital of the solid, whose energy is not very different. A similar process is the quasi-resonant transition, so called because neutralization proceeds by the direct transfer of a single electron, but, in this case,

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from a low-lying state of the solid to the vacant valence orbital. The quasi-resonant process is non-adiabatic, because of a difference of 5–10 eV between the two energy levels involved, which results in a small change in the kinetic energy of the projectile, or of the target atom. (This process can occur, for example, in He^+ scattered from Ge and Pb, and H^+ scattered from some alkali halides.)

A popular theoretical framework for ion-scattering studies has been a time-dependent version of the Anderson–Newns (TDAN) model, in which the ion–surface interaction is made time-dependent by imparting a classical trajectory upon the moving particle. The TDAN model has been used extensively to study the interaction of moving particles with surfaces. Although one-electron theories of resonant charge transfer, within the TDAN model, have been quite successful in explaining much of the experimental data, a more rigorous treatment is needed to encompass fully the resonant, quasi-resonant and Auger mechanisms. The need for a many-electron approach was recognized by Tully [2] and was the basis for his classical-path equations describing SIN. Sebastian [3], on the other hand, used a time-dependent version of the coupled-cluster technique, writing the wavefunction in terms of particle-hole excitations on the Slater determinant representing the initial state of the system. He obtained very different results from those for the one-electron theory for certain systems. More recently, Sulston and co-workers [4] formulated a treatment of the TDAN model for ion–surface scattering, using many-electron wavefunctions, which was similar in spirit to that of Tully.

Although considerable attention has been paid to laser effects in gas-phase collisions, because of the importance of laser-induced processes, comparatively little work has been done on laser effects in the related area of ion–surface collisions. George and co-workers [5] showed that the SIN probability at a semiconductor surface is significantly enhanced, when laser radiation excites electrons from the bulk to surface states, where impinging ions have easier access. Kawai and co-workers [6] devised the theory of a new spectroscopy in which an atomic beam in collision with a surface is electronically excited by a high-intensity pulsed laser beam focused on the surface, and performed calculations to demonstrate the experimental feasibility of such a spectroscopy. Milosevic and co-workers [7] formulated a general theory of resonant and Auger processes in (slow) collisions of ions/atoms on metal surfaces, in the presence of a laser field. Although calculations were not done for any particular system, theoretical considerations led to the conclusion that laser-assisted processes should occur at the same magnitudes of laser field intensity (about $10^{12} \text{ W cm}^{-2}$), as in the corresponding processes in atomic collisions.

In this paper, we study the effect of a laser field on the ion-scattering process by incorporating the laser field into the equations of motion, using the many-electron formalism of [4]. Various systems have been studied, so as to get an idea of the magnitude of the effects for different substrates and projectiles. An investigation such as this is of importance because of its potential implications in laser chemistry, in the case where one is specifically interested in stimulating surface reactions.

2. Equations of motion

To solve the time-dependent Schrödinger equation (in atomic units (au), where \hbar , e , m and the Bohr radius are all taken to be one), namely

$$i \frac{\partial \Psi}{\partial t} = H(t) \Psi \quad (1)$$

we work under the assumption that the many-electron wavefunction Ψ can be written as a linear combination of time-independent orthonormal basis functions Ψ_i , i.e.

$$\Psi(t) = \sum_i a_i(t) \Psi_i. \quad (2)$$

Let the solid band consist of N doubly occupied orbitals ϕ_k ($k = 1, \dots, N$). We ignore any unoccupied solid orbitals, so that reionization into these orbitals is neglected. The ion orbital is ϕ_0 and is assumed to be originally unoccupied. The wavefunction for the $2N$ electron system at $t = -\infty$ is a Slater determinant

$$\Psi_0 = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2 \cdots \phi_N \bar{\phi}_N| \quad (3)$$

where unbarred (barred) orbitals indicate occupation by a + (-) spin electron. The wavefunction corresponding to the transfer of an electron from the k th state to the ion is

$$\Psi_k = \frac{1}{\sqrt{2}} \{ |\cdots \phi_k \bar{\phi}_0 \cdots| + |\cdots \phi_0 \bar{\phi}_k \cdots| \}. \quad (4)$$

All other charge-transfer processes are ignored. The set $\{\phi_k\}$ is assumed to be a complete orthonormal set of one-electron functions. Using this basis set, the wavefunction expansion (2) can be rewritten as

$$\Psi(t) = a_0(t) \Psi_0 + \sum_k a_k(t) \Psi_k. \quad (5)$$

Putting (5) into (1), and using the orthonormality of the determinantal wavefunctions, i.e.

$$\langle \Psi_m | \Psi_n \rangle = \int \Psi_m^*(\mathbf{r}) \Psi_n(\mathbf{r}) d\mathbf{r} = \delta_{mn} \quad (6)$$

leads to the following system of equations:

$$i a'_0 = \langle \Psi_0 | H | \Psi_0 \rangle a_0 + \sum_k \langle \Psi_0 | H | \Psi_k \rangle a_k \quad (7a)$$

$$i a'_k = \langle \Psi_k | H | \Psi_0 \rangle a_0 + \sum_l \langle \Psi_k | H | \Psi_l \rangle a_l \quad (7b)$$

where the primes denote differentiation with respect to time t .

The Hamiltonian we use is

$$H = H_0 + H_1. \quad (8)$$

The purely electronic part is the usual TDAN form, namely

$$H_0 = \sum_{\sigma} \epsilon_0 c_{0\sigma}^{\dagger} c_{0\sigma} + \sum_{k,\sigma} \epsilon_k c_{k\sigma}^{\dagger} c_{k\sigma} + \sum_{k,\sigma} V_k(t) (c_{0\sigma}^{\dagger} c_{k\sigma} + c_{k\sigma}^{\dagger} c_{0\sigma}) \quad (9)$$

where $c_{0\sigma}^\dagger$ and $c_{0\sigma}$ are the creation and annihilation operators for the ion valence orbital, with spin σ ($= +$ or $-$), and $c_{k\sigma}^\dagger$ and $c_{k\sigma}$ are the creation and annihilation operators for the k th band orbital. In (9), ε_0 represents the electronic energy of the ion's valence orbital, ε_k the energy of the k th band orbital, and $V_k(t)$ the ion-solid (resonant) electronic coupling. The part of the Hamiltonian (8) describing the laser interaction is

$$H_1 = \sum_{k,\sigma} (W_k(t) c_{0\sigma}^\dagger c_{k\sigma} + W_k^*(t) c_{k\sigma}^\dagger c_{0\sigma}) \quad (10)$$

where $W_k(t)$ represents the ion-surface interaction due to the laser field. Here, we assume that the laser interacts significantly only with the valence electrons of the solid and any electron in the projectile's valence orbital, at least as far as the charge-transfer process is concerned. Any interaction with the core electrons of the ion or the solid is assumed to have a negligible effect upon the charge-transfer process. The inclusion of H_1 in (8) models the presence of the laser by modifying the electronic potential at the surface of the solid, and in this way affecting the charge-transfer process. The specific forms used for the parameters in the Hamiltonian (8)–(10) are discussed in the next section.

The only non-zero matrix elements of H can be shown to be

$$\begin{aligned} \langle \Psi_0 | H_0 | \Psi_0 \rangle &= E_0 - \varepsilon_0 \\ \langle \Psi_k | H_0 | \Psi_k \rangle &= E_0 - \varepsilon_k \\ \langle \Psi_0 | H_0 | \Psi_k \rangle &= \langle \Psi_k | H_0 | \Psi_0 \rangle^* = \sqrt{2} V_k \\ \langle \Psi_0 | H_1 | \Psi_k \rangle &= \langle \Psi_k | H_1 | \Psi_0 \rangle^* = \sqrt{2} W_k^* \end{aligned} \quad (11)$$

where $E_0 = 2 \sum_k \varepsilon_k + \varepsilon_0$. With these elements, the equations of motion (7) become

$$\begin{aligned} i\dot{a}_0' &= (E_0 - \varepsilon_0) a_0 + \sum_k (\sqrt{2} V_k + \sqrt{2} W_k^*) a_k \\ i\dot{a}_k' &= (E_0 - \varepsilon_k) a_k + (\sqrt{2} V_k + \sqrt{2} W_k) a_0 \end{aligned} \quad (12)$$

with similar equations for the complex conjugates, and subject to the initial conditions

$$a_0(-\infty) = 1 \quad a_k(-\infty) = 0 \quad (13)$$

which correspond to the system being in the state Ψ_0 at $t = -\infty$. Once values have been chosen for the parameters, it is straightforward to solve the equations of motion numerically for the coefficients a_0 and a_k , to determine their final values at $t = \infty$. From these values can be found the probabilities for the occurrence of the various charge states of the system; in particular, one is interested in the ion-neutralization probability, i.e. the probability that an electron from a solid orbital has transferred to the ion's valence orbital, creating a neutral atom:

$$P^0 = 1 - |a_0(\infty)|^2. \quad (14)$$

The corresponding ion-survival probability is

$$P^+ = |a_0(\infty)|^2. \quad (15)$$

3. Description of the model

In order to perform calculations it is necessary to assign values to the parameters appearing in equations (12), namely ε_0 , ε_k , V_k and W_k . The electronic energy, ε_0 , of the ion valence orbital is typically assumed to have the time-dependent form

$$\varepsilon_0(t) = -I_p + F(t) \quad (16)$$

where I_p is the ionization potential of the isolated projectile. $F(t)$ is the time variation of the energy, due to changing image forces (if present), as the projectile approaches and leaves the surface, and is assumed to have the form

$$F(t) = 1/4(z(t) + z_0) \quad (17)$$

where $z(t)$ is the ion-surface separation at time t and z_0 is a constant with a value of about 4 au. (The trajectory $z(t)$ is discussed below.)

The energies ε_k of the band states can be modelled in a number of ways, the simplest being to assume that the solid consists of a chain of N atoms, each with a single valence orbital, with Coulomb integral α and resonance integral β . Within one-electron tight-binding theory, the molecular orbitals for the solid have energies [8]

$$\varepsilon_k = \alpha + 2\beta \cos\left(\frac{k\pi}{N+1}\right) \quad (18)$$

and surface coefficients

$$v_k = \left(\frac{2}{N+1}\right)^{1/2} \sin\left(\frac{k\pi}{N+1}\right). \quad (19)$$

The lowest and highest of the energies ε_k determine the band edges ε_l and ε_u . Physically, α and $4|\beta|$ correspond to the centre and width of the solid band, so that these parameters can be chosen empirically to mimic the solid's electronic structure. This model allows the band edges and Fermi level to be fixed accurately (in agreement with experimentally observed values), and these energies are the most important part of the band structure, with regards to determining the scattering behaviour of the surface [9]. For this reason, simple models of the density of states are usually used in the theory of surface-ion neutralization, thus avoiding the computational complications resulting from using a more sophisticated electronic structure. Inclusion of the fine structure of the density of states does not affect the general dependencies of the charge-transfer probabilities upon their parameters. Thus, although this model is a simplification of the substrate's actual band structure, it is adequate for a qualitative analysis of scattering phenomena.

The resonant interaction coupling $V_k(t)$ has been modelled in several ways in the literature. As is usually done, we assume that the energy and time dependencies separate, so that the interaction can be written as

$$V_k(t) = v_k V(t) \quad (20)$$

where v_k is given by (19), and [10]

$$V(z(t)) = V_0 z \exp(-\mu z) \quad (21)$$

with $z(t)$ the projectile's trajectory. The empirical values for the parameters in (21) are

$$V_0 = I_p^{1/2} I_s^{1/2} \mu \quad (22)$$

and

$$\mu = \frac{1}{2}(\sqrt{2I_p} + \sqrt{2I_s}) \quad (23)$$

where I_p and I_s are the ionization potentials (in atomic units) of the projectile and the target surface atom.

To calculate the form of the Hamiltonian term H_1 in (10), we take the vector potential to be

$$A(t) = \hat{e} \frac{c}{\omega} \mathcal{E}_0 \cos(\omega t + \delta) \quad (24)$$

where \hat{e} is the unit vector along the direction of the vector potential, \mathcal{E}_0 is the field amplitude, ω the frequency, δ the phase and c the speed of light. Then, in coordinate representation [11],

$$H_1 = \frac{e}{mc} A \cdot p = \frac{e}{m\omega} \mathcal{E}_0 \cos(\omega t + \delta) \hat{e} \cdot p \quad (25)$$

where $p = -i\hbar\nabla$, e is the charge on a proton, and m the mass of an electron. Using (10) and (25), we obtain

$$W_k(t) = \langle \phi_0 | H_1 | \phi_k \rangle = -\frac{i\hbar e}{m\omega} \mathcal{E}_0 \cos(\omega t + \delta) \langle \phi_0 | \hat{e} \cdot \nabla | \phi_k \rangle. \quad (26)$$

Taking the solid orbital to be a linear combination of atomic orbitals

$$|\phi_k\rangle = \sum_n c_{kn} |\chi_n\rangle \quad (27)$$

we make the assumption that the dominant contribution to the integral in (26) comes from the term in (27) associated with the surface target atom, putting $n = s$, where $c_{ks} \equiv v_k$, so that

$$\langle \phi_0 | \hat{e} \cdot \nabla | \phi_k \rangle \approx v_k \langle \phi_0 | \hat{e} \cdot \nabla | \chi_s \rangle = v_k \int \phi_0^*(\mathbf{r} - \mathbf{R}) \hat{e} \cdot \nabla \chi_s(\mathbf{r}) d\mathbf{r} \quad (28)$$

where $\mathbf{R} = (0, 0, z)$, assuming the motion is normal to the surface. In spherical coordinates, the atomic orbital χ_s (and, similarly, ϕ_0) is taken to be of the form

$$\chi_s(\mathbf{r}) = F_n(r) Y_{l0}(\theta, \phi) \quad (29)$$

where the radial part is a Slater-type orbital

$$F_n(r) = C_n r^{n-1} e^{-\zeta r} \quad (30)$$

with

$$C_n = \frac{(2\zeta)^{n+1/2}}{(2n)!^{1/2}} \quad (31)$$

and the angular part is a spherical harmonic (with $m = 0$, so that it is independent of ϕ), i.e.

$$Y_{l0}(\theta, \phi) = \left(\frac{2l+1}{4\pi}\right)^{1/2} P_l^0(\cos \theta) \quad (32)$$

where P_l^0 is an associated Legendre polynomial. Standard values for the Slater exponents ζ are available in the literature [12]. Taking the component of \hat{e} in the z direction to be $\cos \eta$, (26) can be rewritten as

$$W_k(t) = -\frac{i\hbar e}{m\omega} \mathcal{E}_0 \cos(\omega t + \delta) v_k 2\pi \cos \eta C_{n'} \left(\frac{2l'+1}{4\pi}\right)^{1/2} C_n \left(\frac{2l+1}{4\pi}\right)^{1/2} I \quad (33)$$

where I is a double integral which, in coordinates r and $s = |r - R|$, can be evaluated analytically using the symbolic manipulation program MAPLE, to give a complicated expression of the general form

$$I = (\text{rational in } z)e^{-\zeta_0 z} + (\text{rational in } z)e^{-\zeta_1 z} \quad (34)$$

where $z = z(t)$ is again the projectile trajectory. The field amplitude \mathcal{E}_0 is related to the intensity \mathcal{I} through

$$\mathcal{I} = \frac{1}{2} \epsilon_0 \mathcal{E}_0^2 c \quad (35)$$

where ϵ_0 is the permittivity.

Finally, we must prescribe a trajectory $R(t)$ for the projectile, i.e. its separation from the target atom. As is commonly done, we assume that the projectile strikes the surface normally, so that we only need a single component, i.e. $R(t) = (0, 0, z(t))$. If we take the interaction between the incident and target atoms to be governed by a Born-Mayer (BM) potential

$$V(z) = Ae^{-az} \quad (36)$$

then this leads [13] to a classical trajectory of the form

$$z(t) = (2/a) \ln[\cosh(az_0 t/2)] - (1/a) \ln \rho \quad (37)$$

where

$$\rho = K_0/A \quad (38)$$

with the ion's initial kinetic energy K_0 related to its initial velocity \dot{z}_0 by

$$K_0 = \frac{1}{2} M \dot{z}_0^2 \quad (39)$$

where M is the ion's mass. The BM parameters A and a for the pair of (unlike) projectile and target atoms can be found using standard values [14] for like pairs, and the combining rules

$$A = (A_p A_s)^{1/2} \quad (40)$$

$$a = \left(\frac{a_p^{-1} + a_s^{-1}}{2} \right)^{-1}. \quad (41)$$

The trajectory (37), describing the motion of the projectile, is used in (17), (21) and (34).

The model described in this section is applicable to a variety of scattering systems, where there are several parameters ($\alpha, \beta, I_p, I_s, a, A$) that are chosen so as to model the specific system under study, and three parameters are variable within the system: the incident energy K_0 , the intensity \mathcal{I} and the laser frequency ω . The term K_0 is typically taken to be within the range 10–1000 eV. The intensity should not be too high, to avoid damaging the surface—we estimate that if the laser is pulsed (in the picosecond range), then intensities up to about $10^{12} \text{ W cm}^{-2}$ should be viable. The frequency ω is variable, but should be of the same order of magnitude as $\epsilon_0 - \alpha$, to maximize the effect of the laser field. The phase δ and polarization η are relatively unimportant for our calculations, and are given the constant values 0 and $\pi/4$, respectively. The number, N , of orbitals used to model the solid is chosen so as to ensure convergence of the results, and is typically in the range 20–40.

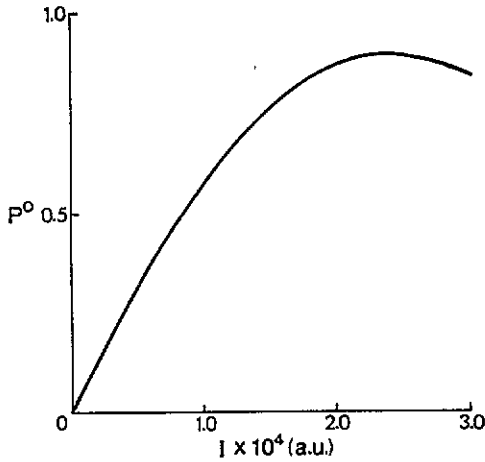
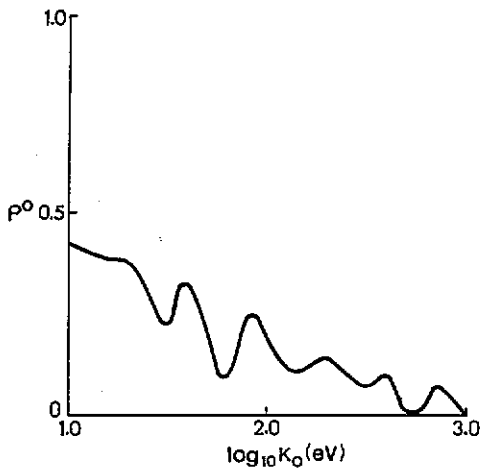
4. Results and discussion

Using the above theory, we have performed calculations of the neutralization probabilities P^0 for several scattering systems: Li^+ scattered from KBr, Cu and Si, and K^+ scattered from W. The parameters used to model these systems are given in table 1. We have studied the variation of the ion neutralization probability with the laser intensity \mathcal{I} , laser frequency ω and ion kinetic energy K_0 . We have also drawn comparisons with the probabilities in the absence of the laser field ($\mathcal{I} = 0$), so that the size of the laser's effect can be observed.

We turn first to the scattering of Li^+ from KBr, an insulator with a narrow valence band of width of about 0.54 eV. This system has the particular advantage that, in the absence of a laser field (i.e. ordinary scattering), there is essentially no neutralization of Li^+ within the usual range of kinetic energies (10–1000 eV), so that once the field is switched on, any observed neutrals can be attributed to a laser-assisted (or perhaps, more accurately, laser-induced) process. In figure 1, the neutralization probability P^0 is plotted as a function of field intensity \mathcal{I} (in atomic units, for which $\mathcal{I}_0 = 6.436 \times 10^{15} \text{ W cm}^{-2}$), for a typical incident kinetic energy of 100 eV. The laser frequency was taken to be 0.1168 au, so as to match the energy difference between the ion's valence level and the band centre. As can be seen from the graph, measurable quantities (greater than a few per cent) of neutrals are found when the intensity reaches a magnitude of about 10^{-5} au , which is less than what we estimate to be the maximum acceptable intensity ($10^{12} \text{ W cm}^{-2} \approx 10^{-4} \text{ au}$), and indeed, for the maximum intensity, the neutrals constitute the majority of the product. When $\mathcal{I} \approx 2 \times 10^{-4}$ the curve exhibits a local maximum, and for increasing

Table 1. Table of parameter values (in atomic units) for various systems.

	Li ⁺ -KBr	K ⁺ -W	Li ⁺ -Cu	Li ⁺ -Si
α	-0.315	-0.2481	-0.34058	-0.3996
β	-0.005	-0.0322	-0.08594	-0.1153
I_p	0.1982	0.1595	0.1982	0.1982
I_s	0.4342	0.2933	0.2839	0.2995
a	1.99788	1.88467	2.00269	2.04
A	104.0726	743.9033	90.7717	54.796

**Figure 1.** Neutralization probabilities against $I \times 10^4$ (in au), for Li⁺ scattered from KBr, with $K_0 = 100$ eV and $\omega = 0.1168$ au.**Figure 2.** Neutralization probabilities against $\log_{10} K_0$ (in eV), for Li⁺ scattered from KBr, with $I = 3 \times 10^{-5}$ au and $\omega = 0.1168$ au.

values of I , the curve shows an oscillatory behaviour, as would be expected from the corresponding atomic structure calculations.

The graph of figure 1 is quite encouraging, since it demonstrates the plausibility of the laser-assisted process at reasonable field intensities. We can try to understand this process by considering that the ion's valence level is situated 3.2 eV above the valence band centre (and 2.9 eV above the upper band edge), which is apparently too large an energy gap to permit an electron to undergo a resonant transition. However, a photon in the laser field has the energy to reduce this gap to approximately zero, so that the transition becomes energetically possible. This is dependent, of course, upon the laser field having sufficient intensity, so that there is a high probability that a surface electron will absorb a photon during the short time period (about 10^{-14} s) that the ion is within interaction distance of the surface.

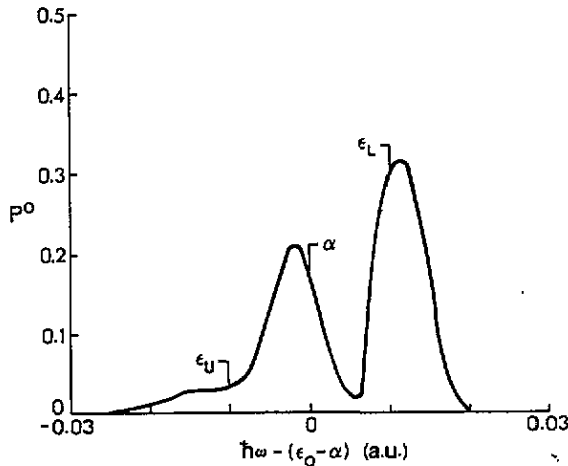


Figure 3. Neutralization probabilities against $\hbar\omega - (\epsilon_0 - \alpha)$ (in au), for Li^+ scattered from KBr, with $K_0 = 100$ eV and $\mathcal{I} = 3 \times 10^{-5}$ au.

In figure 2, the neutralization probability has been graphed as a function of the incident kinetic energy K_0 (in the range 10–1000 eV), for $\mathcal{I} = 3 \times 10^{-5}$ and $\omega = 0.1168$. We see an interesting oscillatory structure, reminiscent of the sort seen in experimental observations [15] of quasi-resonant neutralization. This might suggest that the induced electron transfer is occurring via a mechanism similar to that of the quasi-resonant process, where multiple electron transfers produce the observed oscillations, although such an interpretation is perhaps concluding more from the similarity than is actually warranted.

The variation of the neutralization probability with laser frequency is shown in figure 3; we have actually plotted P^0 against $\hbar\omega - (\epsilon_0 - \alpha)$, so that zero on the horizontal axis corresponds to a laser frequency chosen to align the ion level with the band centre, and thus locate the band edges at ± 0.01 . The observed structure is rather unexpected, in that there are two local maxima, approximately corresponding to alignment with the band centre and lower band edge. Moreover, the 'tailing off' of the curve from the maxima is asymmetrical, being quite sharp at the upper end, but very gradual at the opposite end. In fact, in the region corresponding to alignment with the upper band edge (near -0.01), there is a flat 'plateau', which almost forms a third (smaller) local maximum. In the analogous ion-atom scattering system, a single peak would be observed, corresponding to $\hbar\omega$ being taken equal to the difference in

the two energy levels, $\varepsilon_0 - \varepsilon_1$. The replacement of the target atom by a target solid has caused a splitting of the single peak into two, which seem to be associated with the band centre and the lower band edge, although there are shifts in their positions.

The next system we investigated was the scattering of K^+ from W, a transition metal with an occupied valence-band width of about 3.5 eV. Again, in the absence of a laser field, the neutralization probability is zero at all incident energies of interest. Some representative values of P^0 for different intensities are given in table 2, where K_0 was chosen to be 100 eV and $\omega = \varepsilon_0 - \alpha = 0.153$. Note that, for $\mathcal{I} < 0.01$, the dependence of P^0 upon \mathcal{I} is virtually linear. For the magnitude of \mathcal{I} considered acceptable ($\leq 10^{-4}$ au), there is less than 1% neutralization, and \mathcal{I} must be increased by a couple of orders of magnitude to get significant amounts of charge transfer to occur. It seems that the quantitative differences in the amount of neutrals produced, between this system and the previous one, can be traced to the difference in band widths in the two systems, KBr having a very narrow band, and W a much wider one. If one refers back to (33), then one can see that the matrix element W_k , corresponding to a laser-assisted transition, is proportional to the surface coefficient v_k , which is (roughly) inversely proportional to the band width, and P^0 itself goes approximately as v_k^2 , so that increasing band width generally leads to a corresponding decrease in laser-assisted neutralization (all other parameters being roughly equal).

Table 2. Neutralization probabilities against intensity (in au), for K^+ scattered from W, with $K_0 = 100$ eV and $\omega = 0.153$ au.

\mathcal{I}	P^0
0.0	0.0
0.00001	0.0003
0.0001	0.003
0.001	0.029
0.01	0.260

Table 3. Neutralization probabilities against frequency (in au), for K^+ scattered from W, with $K_0 = 100$ eV and $\mathcal{I} = 0.003$ au.

ω	P^0
0.02	0.00003
0.04	0.0027
0.06	0.032
0.08	0.076
0.10	0.051
0.12	0.036
0.14	0.054
0.16	0.077
0.18	0.058
0.20	0.052
0.22	0.026
0.24	0.0016

The variation of P^0 with frequency ω is given in table 3, for $K_0 = 100$ eV, and $\mathcal{I} = 0.003$, the latter parameter being unrealistically large, but chosen so as to give

non-zero values to study. The double-peak structure of figure 3 is clearly present here, and the two local maxima again occur when the frequency is aligned with either $\epsilon_0 - \alpha$ or $\epsilon_0 - \epsilon_1$. Additional calculations (not shown) for ω close to $|\epsilon_0 - \epsilon_u|$ indicate that there is a third, very small, peak similar to the 'plateau' of figure 3. We can conclude that this feature is not an anomaly of a particular system, but something quite general to these systems.

We turn now to the scattering of Li^+ from Cu, for which non-zero neutralization probabilities are obtained in the absence of the laser. Calculations indicate that the neutralization occurs primarily through resonant interaction with the 4s band, having an occupied width of about 9 eV. The variation of P^0 with \mathcal{I} is shown in table 4 for some characteristic intensities, with $K_0 = 100$ eV and $\omega = 0.0977$. With $\mathcal{I} = 0$ (i.e. no laser field), the neutralization probability is about 20%. At small but non-zero intensities, the number of extra neutrals produced is insignificant, but at the maximum 'allowable' intensity of 10^{-4} , the neutralization probability is raised to 26%, which is not negligible, and perhaps detectable experimentally. As in table 2, P^0 depends almost linearly upon \mathcal{I} , for all but the highest intensities. For this system, P^0 seems to be relatively independent of the frequency ω , so it is difficult to tell whether the multi-peak structure of the other systems reappears here as well.

Table 4. Neutralization probabilities against intensity (in au), for Li^+ scattered from Cu, with $K_0 = 100$ eV and $\omega = 0.0977$ au.

\mathcal{I}	P^0
0.0	0.2032
0.0000001	0.2032
0.000001	0.2038
0.00001	0.2092
0.0001	0.2616
0.001	0.6587

Table 5. Neutralization probabilities against incident kinetic energy (in au), for Li^+ scattered from Cu, with $\mathcal{I} = 0$ (laser off) and 0.00003 (laser on) and $\omega = 0.0977$ au.

K_0	P^0 (laser off)	P^0 (laser on)
10	0.4840	0.5283
50	0.2130	0.2183
100	0.2032	0.2210
200	0.1634	0.1717
300	0.1956	0.2027
400	0.1794	0.1853
500	0.1524	0.1580
600	0.1366	0.1417
700	0.1340	0.1387
800	0.1408	0.1451
900	0.1528	0.1568
1000	0.1674	0.1710

The variation of P^0 with the incident kinetic energy K_0 is shown in table 5, for $\mathcal{I} = 0$ and 3×10^{-5} . At all energies, the effect of the laser field is to enhance

Table 6. Neutralization probabilities against intensity (in au), for Li^+ scattered from Si, with $K_0 = 100 \text{ eV}$ and $\omega = 0.1 \text{ au}$.

\mathcal{I}	P^0
0.0	0.8133
0.000001	0.8134
0.00001	0.8146
0.0001	0.8235
0.001	0.7793

the neutralization process, although to varying degrees at different values of K_0 . The greatest enhancement is certainly at the lowest incident energy (10 eV), which is due to the ion's longer interaction time at the surface allowing for an increased probability of a surface electron absorbing a photon and using the extra energy to make the resonant transition.

Finally, we turn to the scattering of Li^+ from Si, a solid whose valence band has a width of about 12.5 eV, and is a hybrid of s and p orbitals. (The latter feature was incorporated into our calculation of W_k in (33).) The neutralization probabilities for several values of \mathcal{I} are given in table 6. Again, for the lower intensities, P^0 depends almost linearly upon \mathcal{I} . For intensities within the acceptable limits, there is essentially no change in the neutralization probability from the zero-intensity value of about 81%. When \mathcal{I} becomes somewhat larger than 10^{-4} , P^0 undergoes a local maximum and starts to decrease with increasing intensity, so that when $\mathcal{I} = 10^{-3}$ the neutralization probability has been lowered to 78%. Again we attribute the relative weakness of the effect of the laser field to the width of the solid band. As was the case for the Cu substrate, P^0 seems to be virtually independent of the frequency ω , (generally between 81–82%), so that the double-peaked structure of figure 3 is not detectable. The structure therefore appears to be associated with substrates with relatively narrow valence bands, at least for the purpose of experimental observation.

5. Conclusions

In this paper, we have extended the many-electron theory of ion neutralization at solid surfaces, so as to incorporate the mechanism of a laser-assisted transition. The modification of the equations of motion, and their numerical solution, is straightforward, but it was necessary to derive approximate expressions for the matrix elements $W_k(t)$, by assuming Slater-type forms for the atomic orbitals, and then evaluating the appropriate integrals. Several scattering systems were modelled, and the calculated results indicated that observable quantities of neutrals should be produced by this mechanism, at experimentally feasible laser intensities (up to $10^{12} \text{ W cm}^{-2}$, for a pulsed laser), at least for some systems. The effect of the laser field should be greatest for systems in which the substrate's valence band is very narrow (as with alkali halides), due to the larger density of electrons at the required energy, and in this respect the process is very similar to the analogous process in ion-atom scattering. Qualitatively, the ion-surface scattering results differ from those of ion-atom scattering in that, in the former, the neutralization probability, as a function of laser frequency, shows two (or perhaps three) local maxima, which is due to the fact that the ion's valence level is interacting with a band of energy levels, rather than just a single one. It is hoped that the results presented here will stimulate

some experimental investigations into the laser-assisted transitions, as well as further theoretical work.

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