Bulk Plasmon-Assisted Ion Neutralization at Metal Surfaces

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The mechanism for ion neutralization at metal surfaces via surface plasmon excitation was previously suggested. It was shown that this mechanism is of comparable probability as the other two well studied mechanisms, namely, Auger and resonance tunneling neutralizations. In the present work we study the probability of exciting a bulk rather than surface plasmon during the neutralization process. The calculations show that the neutralization rate depends exponentially on the ion distance from the surface. And it is found to be important at small distances from the surface. The theory is applied to the scattering of protons from aluminum surface. Comparison between the transition rate for bulk plasmon-assisted and surface plasmon-assisted ion neutralization shows that the transition rate is lower by two orders of magnitude in the case of bulk plasmon-assisted neutralization as was expected.

I Introduction

It was recently discovered that the neutralization of ions scattered from metal surfaces by surface plasmons is an important electron transfer process especially for ions carrying high potential energy [1-3]. This mechanism was originally suggested by the author as a possible mechanism of neutralization in addition to the fully studied resonance and Auger neutralization mechanisms [4]. The experimentally measured time for neutralization of a proton scattered from a metal surface is about 10^{-15} seconds. For aluminum, for example, the energy of the surface plasmon is about 10.6 eV and that of a bulk plasmon is about 15 eV. This implies a period of oscillation of about 10^{-16} sec. It can be concluded that a collective response from the metal by exciting a surface plasmon or a bulk plasmon is quiet possible. Also plasmons can be excited because the valence electrons cannot respond instantaneously to screen the moving charge. Recently a good number of theoretical papers have been published on potential excitations of surface plasmon during surface neutralization [5-10]. The transition rate for the process is competitive with that for the other two processes [6, 11-12]. It was seen that surface plasmon mediated ion neutralization at metal surfaces is very important. No theoretical work was reported for bulk plasmon-mediated neutralization as far as the author knows. Since plasmons detection in experiment is indirect, relying on the observation of the ejected electrons released from plasmon decay [13], most of the work in this field is done theoretically. However, some experimental work that measures the

energy distribution of electrons ejected by ion impact confirmed the reality of the mechanism of ion neutralization by plasmon excitation. In the case of *He* ions on *Mg* the electron structure due to plasmon decay is more important than that of Auger neutralization [1].

The purpose of this work is to analyze a new neutralization channel whose physical picture is as follows. The ion approaches the surface of the metal, its field attracting electrons in the metal. These electrons move toward the region closest to the ion, leaving uncompensated positive charge behind. This creates a restoring force on the displaced electrons leading to plasma excitation. During the process of exciting a plasmon (taken in this work to be bulk plasmon), the ion picks up an electron, becoming neutralized. The binding energy thereby released is carried away by a bulk plasmon wave, which expands from the point of impact like ripples on a pond.

The Hamiltonian for the process is written down in terms of electron and plasmon annihilation and creation operators. In the calculation a canonical transformation is used in order to able to work with the Hamiltonian of the interaction between the charged particle and the potential of the bulk plasmons. This transformation separates the plasmonic neutralization channel from other scattering and reaction channels. It also introduces appropriate continuum-bound state orthogonality corrections into the matrix elements. This method was used before in the calculations of ion neutralization via the three different mechanisms namely: resonance, Auger, and surface plasmon-assisted ion neutralization [4, 11-12].

II Model

The second quantized Hamiltonian of our model is

$$
\begin{aligned}
\widehat{H} &= \int d\vec{r}\, \widehat{\psi}^\dagger(\vec{r})\, T(\vec{r}) \widehat{\psi}(\vec{r}) \; + \frac{1}{2} \int d\vec{r}\, d\vec{r}\,'\, \widehat{\psi}^\dagger(\vec{r}\,')\, V'_{el-el}(\vec{r}, \vec{r}\,') \widehat{\psi}(\vec{r}\,') \, \widehat{\psi}(\vec{r}) \\
&+ \int d\vec{r}\, \widehat{\psi}^\dagger(\vec{r})\, [V_b(\vec{r}) - |\vec{r} - \vec{s}|^{-1} \widehat{\psi}(\vec{r}) + \sum \omega_s \hat{c}_q^\dagger \hat{c}_q + \int d\vec{r}\, \widehat{\psi}^\dagger(\vec{r}) \widehat{\Phi}_s(\vec{r}) \widehat{\psi}(\vec{r}) \\
&+ \sum \omega_p \hat{a}_q^\dagger \hat{a}_q + \int d\vec{r}\, \widehat{\psi}^\dagger(\vec{r}) \widehat{\Phi}_p(\vec{r}) \widehat{\psi}(\vec{r})
\end{aligned}
\tag{1}
$$

In the Hamiltonian, $\widehat{\psi}$ and $\widehat{\psi}^\dagger$ are the electron annihilation and creation operators, $T(\vec{r})$ is the electron kinetic energy, $V_b(\vec{r})$ is the potential of the positive background, and $V'_{el-el}(\vec{r})$ is the electron-electron interaction. In the equation above $\hat{c}_q$ and $\hat{c}_q^\dagger$ are the surface plasmon annihilation and creation operators. Here s is the position of the proton, $\widehat{\Phi}_s(\vec{r})$ is the second quantized potential of the surface plasmons. Its explicit form is given in related work in a previous paper [4]. The potential $\widehat{\Phi}(\vec{r})$ is the second quantized potential of the bulk plasmons give by

$$
\widehat{\Phi}_p(\vec{r}) == \sum g_p\, e^{-q\,|z|}\, (e^{i\,\vec{q}\cdot\vec{R}}\, \hat{a}_q \, + \, e^{-i\,\vec{q}\cdot\vec{R}}\, \hat{a}_q^\dagger)
\tag{2}
$$

The coupling constant g_p is given by

$$
g_p = \sqrt{\frac{2\,q_z}{\omega_p\, V}}
\tag{3}
$$

where ω_p is the bulk plasmon energy and q_z is the plasmon wave vector in the z-direction.

The interaction term in the Hamiltonian that gives rise to the mechanism being studied is given by the last term in (1), namely,

$$
\int d\vec{r}\, \widehat{\psi}^\dagger(\vec{r})\, \widehat{\Phi}_p(\vec{r})\, \widehat{\psi}(\vec{r})
\tag{4}
$$

In the equations above $\hat{a}_q$ and $\hat{a}_q^\dagger$ are the bulk plasmon annihilation and creation operators. The prime on the summation implies $q < q_c$ where q_c is the plasmon cut-off wave vector (maximum plasmon q). In the Hamiltonian (1), $T(\vec{r})$ is the electron kinetic energy, $V_b(\vec{r})$ is the

potential of the positive background, $V'_{el-el}(\vec{r}, \vec{r}')$ the electron-electron interaction and $\widehat{\psi}(\vec{r})$ and $\widehat{(\psi)}^d ag(\vec{r})$ are the electron annihilation and creation operators. The z-axis is perpendicular to the metal surface, the half plane $z < 0$ constitutes the jellium metal and $z > 0$ constitutes the exterior region. The electron position vector $(\vec{r})$ in (1) may be either inside or outside the metal. This allows for tunneling of the electron. Throughout this paper atomic units will be used.

The electron field operator will be expanded in terms of the complete orthonormal set of orbitals and corresponding annihilation operators $\widehat{\psi}_k$:

$$
\widehat{\psi}(\vec{r}) = \sum \phi_k(\vec{r})\, \widehat{\psi}_k
\tag{5}
$$

Note that $\widehat{\psi}(\vec{r})$ is a an electron field operator, $\phi_k(\vec{r})$ represents electron orbital, while $\widehat{\psi}_k$ represents the corresponding annihilation operator. The metal electrons wave functions would be taken as solutions of the Schrodinger equation with a potential $V(z)$ which is constant inside and outside the metal with a step of height V_0 at the surface ($z = 0$)

$$
V(z) = V_0\, \vartheta(z)
\tag{6}
$$

The step function $\vartheta(z)$ has a value of V_0 for $z \leq 0$, and a value of 0 for $z > 0$. Here $V_0 = F + W$ with F the Fermi energy and W the work function, and energies are measured from the bottom of the conduction band. The corresponding orthonormal eigenfunctions $\phi_k(\vec{r})$ are

$$
\begin{aligned}
\phi_k(\vec{r}) &= \frac{1}{k_\nu\, (V)^{-1/2}} \left\{ e^{i\vec{k}\cdot g\vec{r}} [(k'_z + ik_z)\exp(ik'_z z) + (k'_z - ik_z)\exp(-ik'_z z)] \right\} \quad z < 0 \\
&= \frac{1}{k_\nu\, (V)^{-1/2}} \{ 2\, k_z\, e^{i\vec{k}\cdot g\vec{r}}\, e^{-k_z\, z} \} \qquad z > 0
\end{aligned}
\tag{7}
$$

where V is the volume of the metal and and k_ν are defined by

$$(k'_z)^2 = 2\,E'_k\,;\;\; k_z^2 = 2\,(V_0 - E'_k)\,;\;\; k_\nu^2 + (k'_z)^2 = 2\,V_e 0$$

with

$$E'_k = E_k - (1/2)K^2$$

E_k is the eigenvalue of ϕ_k and $\vec{K}$ is the component of $\vec{k}$ parallel to the surface. Within the conduction band $E_k < F$ one has

$$0 < E'_k < E_k < F < V_0$$

The wave functions will be oscillatory inside the metal and decay into z direction outside. The same is true for the unfilled levels with $F < E_k < V_0 + \frac{1}{2}K^2$. The wave functions with $E_k > V_0 + \frac{1}{2}K^2$ oscillate with z outside as well as inside the metal. They also require a different normalization, but this is irrelevant since the plasmonic neutralization matrix element will involve conduction band electrons. Since ϕ_k constitute a complete set, the bound atomic wave function ϕ_{at} in the final states can be expended in terms of them.

In order to overcome the problem of lack of orthogonality between the final atomic wave function and the initial conduction band wave function, a unitary transformation to a new representation is being used. In this representation the atom is described by a state orthogonal to all conduction band states was used. The appropriate unitary transformation is of the form

$$\widehat{U} = e^{(\frac{\pi}{2})\,\widehat{F}} \tag{8}$$

where the appropriate unitary operator is

$$\widehat{F} = \sum (\widehat{A}^\dagger_\nu \widehat{\psi}_\nu - \widehat{\psi}^\dagger_\nu \widehat{A}_\nu) \tag{9}$$

and

$$\widehat{A}^\dagger_\nu = \int d\vec{r}\, \phi_\nu(\vec{r} - \vec{s})\, \widehat{\psi}^\dagger_\nu(\vec{r}) \tag{10}$$

This unitary transformation rotates the Fock space by $\pi\,/\,2$ into a new space called the ideal space. The transformation being unitary preserves the matrix elements and the Hermiticity of the Hamiltonian. The problem of the final atomic state being not orthogonal to the initial band function is solved automatically in this formalism. The final atomic states will be taken as the unperturbed ground $1\,s$ state of hydrogen

$$\phi_{1s} = \frac{1}{\sqrt{2}}\, e^{-\left|\vec{r} - \vec{s}\right|} \tag{11}$$

Acting on the Hamiltonian in (1) a transformed Hamiltonian in which the matrix elements of the possible reactive channels are orthogonalized will be produced. Each matrix element will contain two parts, the first being the usual matrix element of the process, and the second is the orthogonalization term. In (10) $A^\dagger_\nu$ is the creation operator for an electron in a bound hydrogen orbital $\phi_\nu(\vec{r} - \vec{s})$ centered on the proton (position s) and ν stands for the atomic quantum numbers $\nu = (n\,l\,m)$.

The physical states on which the transformed Hamiltonian acts are of the form

$$|\ldots\rangle = \widehat{U}^{-1}\,\widehat{\psi}^\dagger(\vec{r}) \tag{12}$$

where $|\ldots\rangle$ is any standard Fock state represented in terms of electron creation operators $\widehat{\psi}^d ag(\vec{r})$ acting on the vacuum state $|o\rangle$

Using (8-10) and making use of the commutation rules of $\widehat{\psi}_\nu$ and , $\widehat{\psi}(\vec{r})$ the electron field operators transform as follows

$$\widehat{U}^{-1}\,\widehat{\psi}(\vec{r})\,\widehat{U} = \widehat{\psi}(\vec{r}) - \int d\vec{r'}\,\Delta(\vec{r} - \vec{s}, \vec{r'} - \vec{s})\,\widehat{\psi}(\vec{r'}) + \sum \phi_\nu(\vec{r} - \vec{s})\widehat{\psi}_\nu \tag{13}$$

where $\Delta(\vec{r} - \vec{s},\ \vec{r}\,' - \vec{s})$ is the hydrogen bound state kernel

$$\Delta(\vec{r} - \vec{s}, \vec{r'} - \vec{s}) = \sum \phi_\nu(\vec{r} - \vec{s})\,\phi^*_\nu(\vec{r'} - \vec{s}) \tag{14}$$

Transforming the Hamiltonian in (1) using the unitary transformation in (8), it can be seen that all channels of scattering are represented; including those of reactive scattering that are sought. Transforming the last term in the Hamiltonian, the bulk plasmon-mediated ion neutralization channel would arise.

The transformed term takes the form

$$\int d\vec{r}\, \widehat{U}^{-1}\,\widehat{\psi}^\dagger(\vec{r})\,\widehat{\Phi}_p(\vec{r})\,\widehat{\psi}(\vec{r})\,\widehat{U} \tag{15}$$

This can be manipulated by inserting an identity operator $\widehat{U}^{-1}\,\widehat{U}$ in between the operators in this way

$$\int d\vec{r}\, \widehat{U}^{-1}\,\widehat{\psi}^\dagger(\vec{r})\,\widehat{U}\,\widehat{U}^{-1}\,\widehat{\Phi}_p(\vec{r})\,\widehat{U}\,\widehat{U}^{-1}\,\widehat{\psi}^\dagger(\vec{r})\,\widehat{U} \tag{16}$$

The terms for bulk plasmon-mediated ion neutralization channel take the form

$$\widehat{T}_{11} = \sum \int d\vec{r} \, \phi_\nu^*(\vec{r} - \vec{s}) \, \widehat{\psi}_\nu^\dagger \, \widehat{\Phi}_p(\vec{r}) \, \widehat{\psi}(\vec{r}) \tag{17}$$

$$\widehat{T}_{12} = -\sum \iint d\vec{r} \, d\vec{r}^{\,\prime} \, \phi_\nu^*(\vec{r} - \vec{s}) \, \Delta(\vec{r} - \vec{s}, \vec{r}^{\,\prime} - \vec{s}) \widehat{\psi}_\nu^\dagger \, \widehat{\Phi}_p(\vec{r}) \, \widehat{\psi}(\vec{r}) \tag{18}$$

Inserting (7) in the two terms $\widehat{T}_{11}$, $\widehat{T}_{12}$ one finds the following expressions for the perturbation $\widehat{H}_{in}$ leading to the channel of neutralization. For bulk plasmon-mediated neutralization

$$\widehat{H}_{in} = \sum (\nu, q \, |H_4| \, k) \, \widehat{\psi}_\nu^\dagger \, \widehat{a}_q^\dagger \, \widehat{\psi}_k \tag{19}$$

where the matrix elements are given by

$$\begin{aligned}
(\nu, q \, |H_4| \, k) = {} & g_p \int d\vec{r} \, \phi_\nu^*(\vec{r} - \vec{s}) \, \phi_k(\vec{r}) \, e^{-q|z|} \, e^{-i \vec{q} \cdot \vec{r}} \\
& - \iint d\vec{r} \, d\vec{r}^{\,\prime} \, \phi_\nu^*(\vec{r} - \vec{s}) \, \Delta^*(\vec{r} - \vec{s}, \vec{r}^{\,\prime} - \vec{s}) \, \phi_k(\vec{r}^{\,\prime}) \, e^{-q|z|} \, e^{-i \vec{q} \cdot \vec{r}}
\end{aligned} \tag{20}$$

This form of the matrix elements shows clearly the advantage of using the unitary transformation. It includes (the second term) an orthogonalization term that comes out automatically with the theory. The orthogonalization term takes care of orthogonalizing the metal orbitals to all bound atomic orbitals. The matrix elements in (20) are corrected forms of the Born approximation to the exact T-matrix elements for the scattering process, and due to the inclusion of the orthogonalization term it is a better approximation. This term was found to be important in the ion neutralization at surfaces [4, 11-12].

III   Calculations

The evaluation of the matrix elements will be carried out using (20). The transition rate of the scattering P is given by

$$P = 2\pi \sum \left| (1s \, |H_{in}| \, k)^2 \right| \delta(\varepsilon_i - \varepsilon_f) \tag{21}$$

where the final hydrogen state has been taken to be the $1s$ state. The prime on the summation sign indicates the restriction that the k sum is over the interior of the filled Fermi sea only. The matrix elements M for the neutralization channel are now taken from the actual evaluations, thus giving

$$P = 2\pi \sum |g_p|^2 \, |M|^2 \, \delta(\tfrac{1}{2} k^2 - E(1s) - \omega_p) \tag{22}$$

Changing the sum into an integral we get

$$P = \frac{4\pi V^2}{(2\pi)^6} \int d\vec{k} \, d\vec{q} \, |g_p|^2 \, |M|^2 \, \delta(\tfrac{1}{2} k^2 - E(1s) - \omega_p) \tag{23}$$

Here $\varepsilon_i = \tfrac{1}{2} k^2$ is the metal electron energy, ω_p is the bulk plasmon energy and $E(1s)$ is the atomic electron energy, V is the volume and 2 is for the double spin of the electron.

$$P(s) = \frac{V}{\omega_p \, \pi^2} \iiint \int d\vec{Q} \, dq_z \, d\vec{K} \, dk_z \, \vec{Q} \, \vec{K} \, q_z \, |M|^2 \, \delta(\varepsilon_i - \varepsilon_f) \tag{24}$$

In the integral above $\vec{Q}$ is the plasmon wave vector in the parallel to the surface direction. The delta function is used now to evaluate the integral over $\vec{K}$ where $\vec{K}$ is the component of $\vec{k}$ parallel to the surface.

$$P(s) = \frac{V}{\omega_p \, \pi^2} \iiint d\vec{K} \, dk_z \, dq_z \, \vec{Q} \, q_z \, |M|^2 \tag{25}$$

with the matrix element evaluated at

$$\tfrac{1}{2} K^2 = \varepsilon_f - \tfrac{1}{2} k_0^2 = E(1s) + \omega_p - \tfrac{1}{2} k_z^2 \tag{26}$$

It should be stated that the atomic energies are shifted upward by V since energies are measured from the bottom of the conduction band. Hence the value of $E(1s)$ should be given by
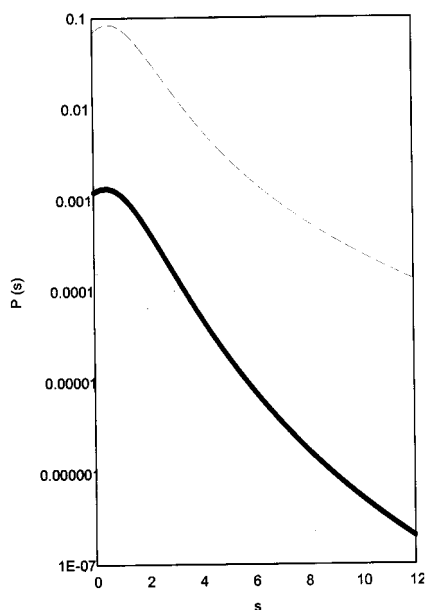
$$E(1s) = V_0 - 1/2 = F + W - 1/2 \tag{27}$$

Figure 1. Transition rate P as a function of the distance s from the metal surface for a proton scattered from aluminum surface (solid curve for the case when a bulk plasmon is excited while the dashed curve represents the case when a surface plasmon is excited).

Transition rate P as a function of the distance s from the metal surface for a proton scattered from aluminum surface (solid curve for the case when a bulk plasmon is excited while the dashed curve represents the case when a surface plasmon is excited).

IV   Results and Discussion

To apply the theory developed here we assume the scattering system

$$H + e^- \, (Al \, metal) \rightarrow H(1s) \qquad (28)$$
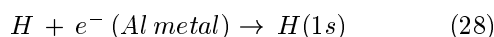
The aluminum is chosen because it best satisfies the assumptions made in the theory. First, it can be well approximated by a jellium model. Second, its Fermi surface is very close to the free electron surface for a face centered cubic monatomic Bravais lattice with three conduction electrons per atom. Third, plasmons are well defined for aluminum and their existence has been demonstrated experimentally. Fourth, the existence of experimental work on this system [15]. This is in addition to the theoretical work for the different mechanisms of neutralization [16-22].The parameters used for aluminum are: 0.9261 for the Fermi wave vector k , 0.5862 for the surface potential V. The ground state in the hydrogen atom $H(1s)$ lies energetically within the conduction band of aluminum. All other states lie above the Fermi level.

Equation (23) is used to calculate the transition rate P as a function of the distance s of the proton from the surface. The integration over k is calculated numerically. All other calculations are done analytically using the inverse Fourier transform integrals and making use of the calculus of residues [4, 11-12].

The figure shows the Transition rate P as a function of the distance s from the metal surface for a proton scattered from aluminum surface (solid curve for the case when a bulk plasmon is excited while the dashed curve represents the case when a surface plasmon is excited). From the figure it is seen that the neutralization rate depends exponentially on the ion distance from the surface. And it is found to be important at small distances from the surface. Comparison between the transition rate for bulk plasmon-assisted and surface plasmon-assisted ion neutralization shows that the transition rate is lower by two orders of magnitudes in the case of bulk plasmon-assisted neutralization as expected. The reason is clearly simple, since electrons on the surface are more easily excited to form a surface plasmon than those in the bulk of the metal.

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