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Bulk plasmon induced ion neutralization near metal surfaces

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ABSTRACT

A novel mechanism is proposed for ion neutralization near metal surfaces, whereby a bulk plasmon is emitted during the electron capture, induced by the presence of the external ion which does not penetrate the metal. In a semiclassical picture of this mechanism the electrons increase their velocity in the field of the ion until they surpass the threshold velocity for collective excitation, emitting the plasmon and getting bound to the ion. Primary evaluations of bulk plasmon transition rates for He^+ interacting with Al surfaces indicate that very close to the image plane the bulk collective channel might become more efficient than the surface plasmon mode to neutralize the ion.

1. Introduction

In recent years a good understanding has been reached for ion neutralization at metal surfaces in the case of H^+ ions impinging on aluminum under grazing incidence conditions and for kinetic energies up to 100 keV [1,2]. In these collisions, the collective (monopole) surface mode [3] plays a significant role to obtain a pretty good agreement between theory and experiments for both the angular distributions (AD) [1,4] and the corresponding neutral fractions (NF) [2,5] of the final hydrogen atoms. Also for low incident energy He^+ ions on Al surfaces, the potential excitation of surface plasmons seems to be at least as important as the single particle Auger mode to obtain theoretical AD of final He atoms [6] which are consistent with the experimental ones [7].

Since experimental reports for electron emission from metal surfaces like Al or Mg after collisional interactions with He^+ ions [8,9] seem to indicate that both surface and bulk plasmons are excited during those interactions, we propose in the present work the novel mechanism of ion neutralization at metal surfaces by potential bulk plasmon emission and compare its corresponding transition rates with those related to the potential surface plasmon neutralization mode [6]. The bulk collective process will take place as long as the potential energy provided by the empty atomic state of the projectile is larger than the bulk plasmon energy [8]. The energy difference between the occupied levels in the conduction band of Al and the empty atomic level of He^+ is in the range (in atomic units) $0.317 \leq \Delta E \leq 0.747$ while the bulk plasmon energy range for the same metal is $0.552 \leq E_{pl} \leq 0.687$ [10] so that the He^+ ion provides enough potential energy to excite the bulk plasmon in Al. This process could contribute to explain the remaining discrepancies between the theoretical results for NF and AD and their experimental counterparts found in our dynamical calculations reported in Ref. [11].

A few comments are in order:

(a) Grazing collisions of interest here ([5] and references therein) correspond to angles of incidence around 1° and energies of a few keV. Therefore the ions are not expected to penetrate significantly the solid so that they cannot excite bulk plasmons directly. However, potential bulk plasmon neutralization (PBPN) near metal surfaces can still proceed indirectly by the acceleration of a metal electron (towards the surface) which, in the field of the external ion, surpasses the electron threshold velocity for collective excitation, emits the bulk plasmon and becomes bound to the external ion. (b) It seems important to note that the PBPN will occur with or without consideration of the electron gas dispersion which makes it possible the kinetic emission of bulk plasmons by charged particles moving outside a metal surface as shown by Bergara et al. [12]. Moreover, their kinetic emission of bulk plasmons by external ions is allowed only above a threshold velocity so that for slow ions which do not penetrate the metal only the PBPN is possible. For velocities above the threshold, the probability they obtained decreases strongly with increasing ion surface distance; something similar occurs for the transition rates of PBPN according to our present primary calculations. (c) The PBPN channel should be also possible for He^+ ions penetrating the metal. In that case our proposed mechanism of bulk plasmon excitation becomes relevant especially in the subthreshold regime where it should compete with second order (or indirect) mechanisms for kinetic plasmon emission, like the one analyzed by Bocan et al. [13] in which the ion excites (through binary collisions) valence electrons that are fast enough to excite plasmons.

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This paper is organized as follows: in Section 2, we present the interaction Hamiltonian corresponding to the novel mechanism proposed here as well as our description of the electronic wavefunctions. Our primary evaluation of the corresponding matrix elements and transition rates is presented in Section 3 while the conclusions are given in Section 4. Atomic units are used throughout unless otherwise indicated.

2. Theory

2.1. Ion induced electron-bulk plasmon coupling

The ionic background of the metal is represented here by the jellium model with the jellium occupying the $z\leq 0$ half-space. The Fourier representation of the Coulomb interaction between a monocharged ion at rest at a position $\mathbf{r}_0=(0,0,s)$ outside the jellium edge (JE) and the electrons of the metal is given by [14–16]

$$-\sum_{i=1}^{n}\frac{1}{|\mathbf{r}_i-\mathbf{r}_0|}=-4\pi\sum_{\substack{i=1\\ \tau\neq 0}}^{n}\frac{e^{i\tau\cdot(\mathbf{r}_i-\mathbf{r}_0)}}{\tau^2} \quad (1)$$

with $\mathbf{r}_i$ the coordinates of the metal electrons with respect to the JE as shown in Fig. 1(a). The constraint $\tau\neq 0$ takes into account the interaction of the external ion with the positive background of the solid. Application of the Bohm–Pines transformation [17]

$$e^{i\tau\cdot\mathbf{r}_i}=e^{i\tau\cdot\mathbf{x}_i}+\sum_{q<q_c}\sqrt{\frac{2\pi\omega(\mathbf{q})}{\mathcal{V}q^2}}G(\mathbf{q},\mathbf{p}_i,-\tau)\hat{C}_q e^{i(\mathbf{q}+\tau)\cdot\mathbf{x}_i} - \sum_{q<q_c}\sqrt{\frac{2\pi\omega(\mathbf{q})}{\mathcal{V}q^2}}e^{-i\mathbf{q}\cdot\mathbf{x}_i}\hat{C}_q^{\dagger}G(\mathbf{q},\mathbf{p}_i,-\tau)e^{i\tau\cdot\mathbf{x}_i} \quad (2)$$

where $\mathbf{x}_i$ and $\mathbf{p}_i$ are the transformed [17] position and momentum of the electron i, respectively , $\hat{C}_q^{\dagger}$ and $\hat{C}_q$ are the creation and annihilation operator for bulk plasmons of momentum $\mathbf{q}$ (with $q<q_c$, where q_c is the cut-off value for the plasmon wavevector beyond which the collective mode decays into electron–hole pairs) and energy $\omega(q)$, $\mathcal{V}$ is the elementary solid volume while $G(\mathbf{q},\mathbf{p}_i,\tau)$ is the operator defined by

$$G(\mathbf{q},\mathbf{p}_i,\tau)=\frac{1}{\omega(q)-\mathbf{q}\cdot(\mathbf{p}_i+\tau)}-\frac{1}{\omega(q)-\mathbf{q}\cdot\mathbf{p}_i} \quad (3)$$

Application of Eq. (2) into Eq. (1) will give rise to couplings between bulk plasmons and electrons induced by the ion's field. Indeed, replacement of the third term of Eq. (2) into Eq. (1), followed by the application of the Fock–Tani transformation [15,18] and proceeding along the same lines as those indicated in Ref. [16] allows us to obtain the interaction Hamiltonian $V(a+pl\leftarrow e)$ for bulk plasmon induced ion neutralization at metal surfaces for an ion at rest outside the metal. Its explicit expression, in second quantized form, is

$$V(a+pl\leftarrow e)=\hat{C}_q^{\dagger}\hat{a}_{\mu}^{\dagger}\langle\mathbf{q},\mu|V|\mathbf{k}\rangle\hat{e}_k \quad (4)$$

with $\hat{a}_{\mu}^{\dagger}$ the creation operator for an atom in the state μ and $\hat{e}_{\mathbf{k}}$ the annihilation operator for electrons with momentum $\mathbf{k}$ (with $k\leq k_F$, where k_F is the Fermi wavevector). The matrix elements $\langle\mathbf{q},\mu|V|\mathbf{k}\rangle$ for these transitions are, in coordinate space,

$$\langle\mathbf{q},\mu|V|\mathbf{k}\rangle=\int d^3r\phi_{\mu}^{*}(\mathbf{r}-\mathbf{r}_0)V_{\mathbf{q},\mathbf{k}}^{e-pl}(\mathbf{r})\tilde{\varphi}_{\mathbf{k}}(\mathbf{r}) \quad (5)$$

with $\phi_{\mu}^{*}(\mathbf{r})$ the complex conjugate of the atomic wavefunction of the neutralized ion in the state μ, $\tilde{\varphi}_{\mathbf{k}}(\mathbf{r})$ the wavefunction of the metal electrons which is orthogonal to the atomic wavefunction and with $V_{\mathbf{q},\mathbf{k}}^{e-pl}(\mathbf{r})$ the interaction potential, responsible for the collective process, given by

$$V_{\mathbf{q},\mathbf{k}}^{e-pl}(\mathbf{r})=\sum_{\tau>q_c}\left(-\frac{4\pi}{\mathcal{V}\tau^2}\right)e^{i\tau\cdot\mathbf{r}}\left[\sqrt{\frac{2\pi\omega(q)}{\mathcal{V}q^2}}g(\mathbf{q},\mathbf{k},\tau)e^{-i\mathbf{q}\cdot\mathbf{r}}\right]\theta(-z) \quad (6)$$

where

$$g(\mathbf{q},\mathbf{k},\tau)=\frac{1}{\omega(q)-\mathbf{q}\cdot(\mathbf{k}+\tau)}-\frac{1}{\omega(q)-\mathbf{q}\cdot\mathbf{k}} \quad (7)$$

is a function of the variables $\mathbf{q}$, $\mathbf{k}$, and τ. The spatial constraint accounted for by the unit step function $\theta(-z)$ in Eq. (6) ensures that the plasmon excitation occurs when the electrons are inside the metal.

It is straightforward to verify that the singularity of $g(\mathbf{q},\mathbf{k},\tau)$ for $\omega(q)=\mathbf{q}\cdot\mathbf{k}$ is related—by conservation of energy and momentum—to the excitation of plasmons by electrons in the metal (an equivalent discussion for plasmon excitation by fast ions is given in Ref. [19]). However, since within the bulk $\omega(q)\geq\omega_p>q_c k_F$ (with $\omega_p=(4\pi n_e)^{1/2}$ the

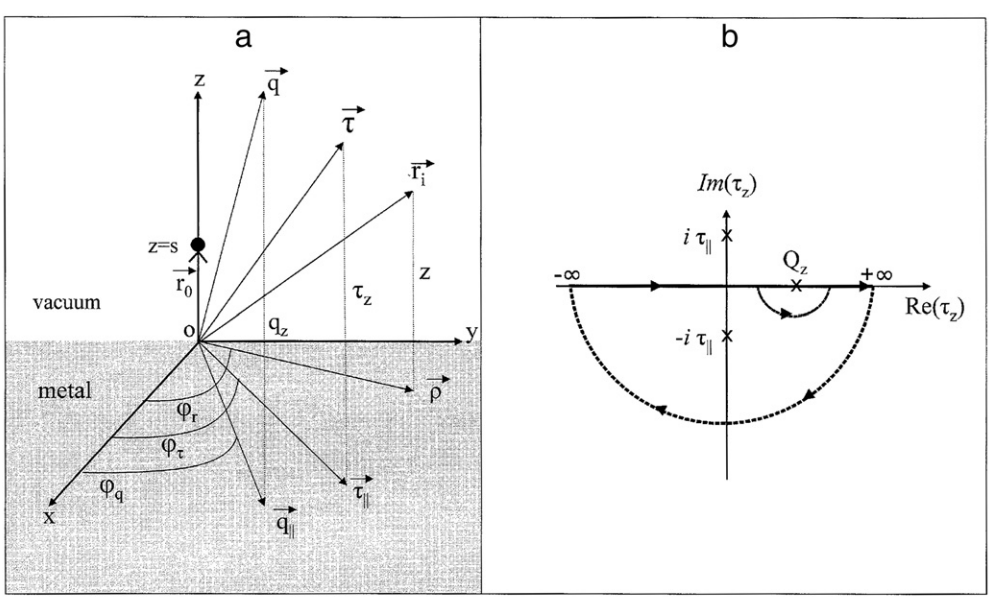

Fig. 1. (a). Reference system for an ion at rest at a distance s from the Jellium Edge. Also drawn are the electron positions $\mathbf{r}_i$, the bulk plasmon momentum wavevector $\mathbf{q}$ and the momentum transfer τ with their corresponding component in cylindrical coordinates (see text). (b). Contour integration to calculate the integral of Eq. (14) showing the poles on real and imaginary axes (see text).

plasma frequency where n_e is the electron gas density [14,16]) the condition for bulk plasmon excitation by electrons is never met for metals within the random phase approximation [14] at zero temperature in the absence of external perturbations. Even more, from Eq. (7) we see that in the absence of the external perturbation ($\tau = 0$) one gets $g(\mathbf{q}, \mathbf{k}, \tau) = 0$ so that $V^{e-pl}_{\mathbf{q},\mathbf{k}}(\mathbf{r})$ vanishes. It is the perturbation produced by the external ion, represented by the momentum transfer τ, which induces a coupling between electrons and plasmons allowing the collective excitation. Indeed, the sum on $\tau > q_c$ contained in $V^{e-pl}_{\mathbf{q},\mathbf{k}}(\mathbf{r})$ allows the existence of a real singularity of $g(\mathbf{q}, \mathbf{k}, \tau)$ for $\omega(q) = \mathbf{q} \cdot (\mathbf{k} + \tau)$ which is the signature for the excitation of a real plasmon. Since the term preceding the square bracket in $V^{e-pl}_{\mathbf{q},\mathbf{k}}(\mathbf{r})$ corresponds to the screened Coulomb interaction between the electrons and the external ion, then in a semiclassical picture of the PBPN mode, the electron is attracted by the screened field of the ion increasing its momentum from $\mathbf{k}$ to $\mathbf{k} + \tau$ (with $\tau > q_c$) surpassing the threshold velocity for plasmon excitation, emitting the plasmon, and getting bound to the ion.

It will become useful to have in mind the general expression of the transition rate Γ_B for the specific case of bulk plasmon mediated neutralization of He^+ ions into the ground state of He near Al surfaces. It is given by

$$\Gamma_B = 2\pi \sum_{\substack{k<k_F \\ q<q_c}} |M|^2 \delta\left(\varepsilon_i - \varepsilon_f\right) \tag{8a}$$

with the matrix elements M given by

$$M = \int d^3 r \phi^*_G(\mathbf{r} - \mathbf{r}_0) V^{e-pl}_{\mathbf{q},\mathbf{k}}(\mathbf{r}) \tilde{\varphi}_{\mathbf{k}}(\mathbf{r}) \tag{8b}$$

where ε_i and ε_f are the initial and final energies of the interacting system respectively, $\phi_G(\mathbf{r})$ is the ground state of the Helium atom near an Al surface and $\tilde{\varphi}_{\mathbf{k}}(\mathbf{r})$ are the metal electron wavefunctions which are orthogonalized with respect to $\phi_G(\mathbf{r})$ [18]. Since, in the continuum limit the sums on k and on q in Eq. (8a) and the sum on τ in Eq. (6) become 3-dimensional integrals [20] therefore evaluation of Γ_B requires the calculation of 12-dimensional integrals, a non-trivial task similar to that faced to evaluate (two-electron) Auger rates [21]. This situation is not surprising since the PBPN mode is one of the complements to the two-electron Auger mode where the energy given up by the captured electron is absorbed by a bulk plasmon (in the PBPN) instead by a second electron (in the Auger case). Nevertheless, the evaluation of Γ_B has the extra complexity of the three-dimensional singularity which is contained in $V^{e-pl}_{\mathbf{q},\mathbf{k}}(\mathbf{r})$. Rewrite $V^{e-pl}_{\mathbf{q},\mathbf{k}}(\mathbf{r})$ as

$$V^{e-pl}_{\mathbf{q},\mathbf{k}}(\mathbf{r}) = -\sqrt{\frac{2\pi\omega(q)}{\mathcal{V}q^2}} e^{-i\mathbf{q}\cdot\mathbf{r}} S_{\mathbf{q}}(\mathbf{r}) \theta(-z) \tag{9}$$

with

$$S_{\mathbf{q}}(\mathbf{r}) = \sum_{\tau > q_c} \left(\frac{4\pi}{\mathcal{V}\tau^2}\right) e^{i\tau\cdot\mathbf{r}} g(\mathbf{q}, \mathbf{k}, \tau) \tag{10}$$

The usual transformation to the continuum for $\tau \left(\sum_\tau \rightarrow \left(\frac{\mathcal{V}}{8\pi^3}\right) \int d^3\tau\right)$ [20] yields with Eq. (7) to

$$S_{\mathbf{q}}(\mathbf{r}) = \frac{1}{2\pi^2} \int d^3\tau \left[\frac{1}{\Omega(\mathbf{q}) - \mathbf{q}\cdot\tau} - \frac{1}{\Omega(\mathbf{q})}\right] \frac{e^{i\tau\cdot\mathbf{r}}}{\tau^2} \tag{11}$$

with $\Omega(\mathbf{q}) \equiv \omega(q) - \mathbf{q}\cdot\mathbf{k}$. Consider cylindrical coordinates as shown in Fig. 1(a) with $\tau = (\tau_\parallel, \varphi_\tau, \tau_z)$, $\mathbf{q} = \left(q_\parallel, \varphi_q, q_z\right)$, $\mathbf{r} = (\rho, \varphi_r, z)(z \le 0)$ and $d^3\tau = \tau_\parallel d\tau_\parallel d\tau_z d\varphi_\tau$ where $0 \le \tau_\parallel \le \infty$, $-\infty \le \tau_z \le \infty$, and $0 \le \varphi_\tau \le 2\pi$. In order to deal with the three-dimensional singularity in Eq. (11), we consider the approximation $\Omega(\mathbf{q}) - \mathbf{q}\cdot\tau \cong \Omega(\mathbf{q}) - q_z\tau_z$ which will allow us to obtain an analytical expression for $V^{e-pl}_{\mathbf{q},\mathbf{k}}$. It amounts to only consider the z-component contribution of the external field to induce the bulk plasmon excitation. Even if the contributions parallel to the surface plane were not negligible we expect that our approximation will give the right order of magnitude for Γ_B. Therefore, with $Q_z \equiv \Omega(\mathbf{q})/q_z$, the expression in square brackets in Eq. (11) reduces to $\tau_z[\Omega(\mathbf{q})(Q_z - \tau_z)]^{-1}$, so that

$$S_{\mathbf{q}}(\mathbf{r}) = \frac{-1}{2\pi^2\Omega(\mathbf{q})} \int_0^\infty d\tau_\parallel \tau_\parallel \int_{-\infty}^\infty \frac{d\tau_z \tau_z e^{iz\tau_z}}{(\tau_z - Q_z)(\tau^2_\parallel + \tau^2_z)} \int_0^{2\pi} d\varphi_\tau e^{i\tau_\parallel \rho \cos(\varphi_\tau - \varphi_r)}; z \le 0 \tag{12}$$

The angular integration in Eq. (12) yields [22] $2\pi J_0(\tau_\parallel\rho)$ with $J_0(x)$ the zeroth-order cylindrical Bessel function. Therefore

$$S_{\mathbf{q}}(\mathbf{r}) = -\frac{1}{\pi\Omega(\mathbf{q})} \int_0^\infty d\tau_\parallel \tau_\parallel J_0(\tau_\parallel\rho) I_{\tau_z} \tag{13}$$

with

$$I_{\tau_z} = \int_{-\infty}^\infty d\tau_z \frac{\tau_z e^{iz\tau_z}}{(\tau_z - Q_z)(\tau^2_\parallel + \tau^2_z)}; \quad z \le 0 \tag{14}$$

The integral I_{τ_z} is solved straightforwardly in the complex plane with the contour shown in Fig. 1(b). Its solution is

$$I_{\tau_z} = \frac{-i\pi}{Q^2_z + \tau^2_\parallel} \left[Q_z e^{izQ_z} - \left(Q_z - i\tau_{||}\right) e^{z\tau_\parallel}\right]; z \le 0 \tag{15}$$

The first term in Eq. (15), coming from the singularity on the real axis in the integrand of Eq. (12) gives, as expected, the most important contribution since the exponential factor $e^{z\tau_\parallel}$ (with $z \le 0$) in the second term makes its contribution to $S_{\mathbf{q}}(\mathbf{r})$ negligible as compared to the first term. Numerical checking confirms that the term proportional to $e^{z\tau_\parallel}$ contributes less than 1% to $S_{\mathbf{q}}(\mathbf{r})$ so that within both our Bohm–Pines Fock–Tani model and the approximation contained in Eq. (12), it is consistent to neglect it. Therefore keeping the first term in Eq. (15) we obtain

$$S_{\mathbf{q}}(\mathbf{r}) = i\frac{Q_z e^{izQ_z}}{\Omega(\mathbf{q})} \int_0^\infty d\tau_\parallel \frac{\tau_\parallel J_0(\tau_\parallel\rho)}{\tau^2_\parallel + Q^2_z} \tag{16}$$

Since the integration in $\tau_\parallel$ yields [22] exactly $K_0(|Q_z|\rho)$ we finally get for the electron plasmon coupling

$$V^{e-pl}_{\mathbf{q},\mathbf{k}}(\mathbf{r}) = -\frac{i}{q_z}\sqrt{\frac{2\pi\omega(q)}{\mathcal{V}q^2}} K_0(|Q_z|\rho) e^{iz(Q_z - q_z)} e^{-i\mathbf{q}_\parallel\cdot\rho} \theta(-z) \tag{17}$$

The presence of the Bessel function K_0 in Eq. (17) is not unusual within the context of collective response of the semi-infinite electron gas. It has appeared connected to the imaginary part of the image potential which accounts for the energy loss of incident particles due to the creation of surface plasmon excitation [23] and also as the oscillatory component of surface wake potential [24]. In our case however it appears as a consequence of the coupling between bulk plasmons and electrons of the metal induced by the external particle. The analytical expression of Eq. (17) for $V^{e-pl}_{\mathbf{q},\mathbf{k}}(\mathbf{r})$ makes it much more tractable the evaluation of Γ_B given by Eqs. (8a) and (8b).

2.2. Electronic wavefunctions

The atomic wavefunction for the ground state of the Helium atom and the corresponding eigenenergy (perturbed by the presence of the metal surface) were evaluated numerically [25] by consideration of the Bottcher model potential [26] to represent the intra-atomic (electron–core) interaction which far from the surface yields unperturbed energy eigenvalues within 0.55% of the experimental results while the Jennings et al. potential [27] was used to represent the electron–surface interaction. The numerical wavefunction was obtained as a linear combination of basis functions which in our case correspond to hydrogenic wavefunctions in parabolic coordinates. In order to simplify the calculations to obtain a primary estimate of Γ_B we have fitted the numerical wavefunction to the hydrogen-like expression $\phi_G^{He}(\mathbf{r}) = (\alpha^3/\pi)^{1/2}\exp(-\alpha r)$ which is also reported in Ref. [25] with the parameter α being a function of the distance d between the ion and the image plane (the image plane is at a distance δ outside the JE so that $s = d + \delta$). For Al, we shall consider the values $\delta = 0.7$, 1.0 and 1.3 to cover the range of values reported in the literature [27]). The values of $\alpha(d)$, tabulated in Ref. [25] for the range $2 \le d \le 20$, include in an average way the perturbation produced by the surface on the atomic state. The corresponding (perturbed) ground state energy defined by $\varepsilon_G(d) = -\frac{1}{2}[\alpha(d)]^2$ reproduces very well the numerical results [25] showing the characteristic $1/4d$ energy shift behavior down to $d = 2$. For $d = 0$ and 1, we have frozen the energy value to $\varepsilon_G(d = 2)$. On the other hand, for the metal electron wavefunctions $\tilde{\varphi}_{\mathbf{k}}$ of Al ($k_F = 0.93$) we have used the usual solution of the step potential [21] orthogonalized [3] to $\phi_G^{He}(\mathbf{r})$.

3. Matrix elements and transition rates: results and discussion

Application of the above wavefunctions together with the analytical expression of Eq. (17) for $V_{\mathbf{q},\mathbf{k}}^{e-pl}$ allows us to reduce the matrix elements M defined in Eq. (8b) from three- to one-dimensional integrals whose explicit expressions are given in Appendix A. Although some of the intermediate steps are non-trivial we did not include them here to avoid unnecessary enlargement of the article. On the other hand, it is also possible to perform both the angular integration on the $\mathbf{k}$-space in Eq. (8a) (since in our approximation the matrix elements do not depend on such variable) and the integration on the delta function. As a consequence one can reduce the evaluation of Γ_B from 9-dimensional integrals into 5-dimensional integrals which are solved by standard numerical routines. Finally we indicate that for this primary estimation of Γ_B the bulk plasmon dispersion for Al has been neglected so that [10] $\omega(q) = \omega_p = 0.552$ with $q_c = 0.582$.

The behavior of Γ_B as a function of the ion-image plane distance d is given in Fig. 2 for the three values of δ already indicated in the previous section. One can observe that smaller values of δ yield larger values of Γ_B although the differences are of not much significance close to the image plane where the contribution of the bulk mode becomes relevant. For purposes of comparison we have also included in Fig. 2 the corresponding results of two reports [28,29] for the multielectron Auger capture mode (MEA) together with those for the excitation of a surface plasmon (SP) [6]. It is important to emphasize that the MEA transition rates reported in Refs. [28,29] contain simultaneously the contributions of both the standard two-electron Auger mode [5] and the surface plasmon excitation [6] but not the bulk plasmon contribution considered here, even when in their case the ion is allowed to enter the metal. In fact, although the formalism used in Refs. [28,29] should in principle contain this latter contribution, it was eliminated in practice [30] probably due to the numerical problems caused by the three-dimensional singularity related to the bulk plasmon excitation. Indeed, the above situation makes it very clear the difficulties introduced by such three-dimensional singularity which we have solved here in an approximated way for an ion which does not get inside the solid.

One can see from Fig. 2 that although for both large and intermediate distances the transition rates for the potential excitation of bulk plasmons do not vanish they appear to be negligible as compared to both MEA and SP rates. However for $d \lesssim 1$ the PBPN transition rates become comparable and even larger than the SP rate which vanishes below that distance due to energetic constraints [6]. It appears then that very close to the surface the PBPN channel would be the only one that could compete with the standard two-electron Auger component of the MEA one in order to neutralize the ion.

4. Conclusions

A novel mechanism for ion neutralization at metal surfaces has been proposed whereby the potential energy given up by the metal electron when it gets bound to the external ion allows the excitation of a bulk plasmon. The important point to be emphasized here is that the bulk plasmon excitation is induced by an external ion traveling outside the solid which is a situation typical of grazing ion surface interactions. The electron-bulk plasmon coupling for such a process has been obtained and a primary calculation of the corresponding transition rate has been performed. These primary results seem to indicate that the bulk plasmon mode rates are comparable to the surface

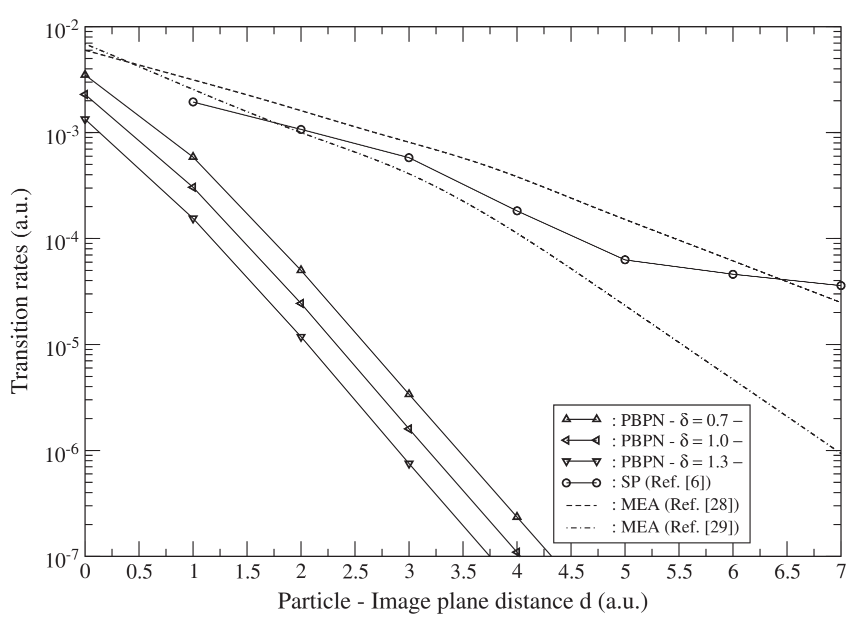

Fig. 2. Static transition rates (in *a.u.*) as a function of the particle-image plane distance d (in *a.u.*). Full lines with open triangles: PBPN transition rates computed in the present work for $\delta = 0.7$ (triangles up), $\delta = 1.0$ (triangles left), and $\delta = 1.3$ (triangles down)—see text. Full line with open circles: Surface plasmon (SP) transition rates computed in Ref. [6]. Dashed line and dot-dashed line: MEA transition rates reported in Refs. [28,29], respectively.

plasmon mode for ion-image plane distances of the order of or smaller than one Bohr radius.

We emphasize the fact that the present results represent a first attempt to face the non-trivial task of evaluating transition rates for the here proposed novel mechanism of potential bulk plasmon excitation for external ion neutralization under grazing incidence conditions. Indeed, the present qualitative and quantitative results obtained in the static case must be corroborated by calculations containing the effect of the parallel ion velocity which has been found to significantly modify both the plasmon and MEA transition rates [11]. Only then one might attempt to use the bulk plasmon rates to evaluate physical variables (like angular distributions or neutral fractions) that can be finally compared to experimental data. The results reported in this work indicate that such calculations might be worth the effort.

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Appendix A

After two of the three integrations for the matrix elements M defined in Eq. (8b) are performed, within the orthogonalized Born approximation, it can be written as $M = M_1 - M_{21}M_{22}$ where the first Born term M_1 is given by

$$M_1 = \sqrt{\frac{\alpha^3}{\pi}} A(q_\parallel, q_z) B(k_z) I_1 \tag{A1}$$

with

$$A(q_\parallel, q_z) = \frac{ie^{i(Q_z - q_z)}}{q_z} \sqrt{\frac{2\pi\omega}{\mathcal{V}q^2}}, \tag{A2}$$

$$B(k_z) = \frac{k_z + i\sqrt{2V_0 - k_z^2}}{\sqrt{2\mathcal{V}V_0}} e^{ik_z}, \tag{A3}$$

$$I_1 = 2\pi\alpha \int_0^\infty du \frac{uf(u)}{\beta^2} \frac{e^{-[\beta + i(Q_z - q_z + k_z)]s}}{[\beta + i(Q_z - q_z + k_z)]} \left[s + \frac{1}{\beta} + \frac{1}{[\beta + i(Q_z - q_z + k_z)]} \right] \tag{A4}$$

and

$$f(u) = \frac{1}{\sqrt{u^4 + 2u^2\left(Q_z^2 - (\mathbf{k}_\parallel - \mathbf{q}_\parallel)^2\right) + \left(Q_z^2 + (\mathbf{k}_\parallel - \mathbf{q}_\parallel)^2\right)}} \tag{A5}$$

while the orthogonalization correction product $M_{21}M_{22}$ is:

$$M_{21}M_{22} = \left(\frac{\alpha^3}{\pi}\right)^{3/2} A(q_\parallel, q_z) B(k_z) I_{21} I_{22} \tag{A6}$$

with

$$I_{21} = 4\pi\alpha \int_0^\infty du \frac{u\tilde{f}(u)}{\tilde{\beta}^2} \frac{e^{-\left[\tilde{\beta} + i(Q_z - q_z)\right]s}}{\left[\tilde{\beta} + i(Q_z - q_z)\right]} \left[s + 1\tilde{\beta} + \frac{1}{\left[\tilde{\beta} + i(Q_z - q_z)\right]} \right], \tag{A7}$$

$$\tilde{f}(u) = \frac{1}{\sqrt{u^4 + 2u^2\left(Q_z^2 - q_\parallel^2\right) + \left(Q_z^2 + q_\parallel^2\right)}}, \tag{A8}$$

and

$$I_{22} = \frac{2\pi\alpha}{h^2} \frac{e^{-[h + ik_z]s}}{[h + ik_z]} \left[s + \frac{1}{h} + \frac{1}{[h + ik_z]} \right] \theta(k_\parallel), \tag{A9}$$

where $\beta = \sqrt{\alpha^2 + u^2}$, $\tilde{\beta} = \sqrt{4\alpha^2 + u^2}$ and $h = \sqrt{\alpha^2 + k_\parallel^2}$.

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