Fluctuation of electronic density in the plasmon fields excited by a diatomic molecule

J L Gervasoni\textsuperscript{1,2}, S Segui\textsuperscript{1}

\textsuperscript{1} Centro Atómico Bariloche (Comisión Nacional de Energía Atómica), R8402AGP S. C. de Bariloche, Río Negro, Argentina
\textsuperscript{2} Instituto Balseiro (Comisión Nacional de Energía Atómica y Universidad Nacional de Cuyo), R8402AGP S. C. de Bariloche, Río Negro, Argentina
E-mail: gervason@cab.cnea.gov.ar

Abstract. We study the fluctuations of the electronic density due to plasmon field associated to the wake potential generated by a dimer formed by two identical charged particles (such as two nuclei of the ionized hydrogen molecule) traveling through a semi-infinite dielectric medium. We use coherent states to describe plasmons as wave packets that raise fluctuations in the electronic density of the material. We analyze different configurations of interest, regarding the geometry of the surface and the orientation of the dimer.

1. Introduction
The purpose of this work is to study the effects on the plasmon field of a solid when the incident external charged particles have a simple structure, as a diatomic molecule, using coherent states [1, 3]. This formalism provides a very simple tool to analyze different quantities of interest by means of a Hamiltonian formulation of the interaction of the plasmon field with the incident particles. We calculate the wake potential and the fluctuations in the electronic density $\Delta \rho$, and compare them with the results obtained for a single particle. In the present paper, and without loss of generality, rectilinear trajectory is employed. We analyze the case of planar and cylindrical geometries of the solid. We also assume that the valence electrons of the bulk and the electrons at the surface interact independently with the external dimer, generating the bulk and surface plasmons, each with their own characteristic frequencies $\omega_{k}^{b,s}$.

The structure of the paper is as follows: in section 2 we write the basic formulae used to describe the excitation of a plasmon field due to the passage of a swift dimer formed by two identical charged particles. In section 3 we show calculations of the wake potential and the charge density fluctuations, for bulk and surface excitations in aluminum. Finally, we present some concluding remarks in section 4.

2. Coherent states applied to molecules
In this work, we consider a dimer or molecule as formed by two identical point particles with charge $Ze$, separated by a given distance $d$ and traveling along a rectilinear trajectory with constant velocity $v$. We neglect the interaction between the charges, while each charge interacts with the electron gas of the material.
We make use of the coherent states formulation to describe the interaction of the incident particles with the plasmon field. Within this frame, plasmon modes form a set of harmonic oscillators with characteristic frequencies $\omega_k$ determined by the composition and geometry of the studied system [4, 5, 6] and described by an unperturbed hamiltonian $H_0$ in terms of creation and annihilation operators $a_k^\dagger, a_k$ and with $|n_k\rangle$ spanning the possible states of the plasmon field with $n$ plasmons in the mode $k$. The interaction of the incident particles with the electron gas is given by

$$H_{int}(t) = \int d^3r \phi(r, t) \rho_{ext}(r, t)$$

where $\rho_{ext}(r, t)$ is the external charge density,

$$\rho_{ext}(r, t) = Z e (\delta(r - r_1(t)) + \delta(r - r_2(t))),$$

with $r_i$ the position of the $i$th particle, and $\phi(r, t)$ is the potential associated to the plasmon field, in terms of $a_k^\dagger$ and $a_k$. The time evolution of the field interacting with the external particles can be obtained within the interaction representation using the Schrödinger equation

$$i\hbar \frac{\partial |\Psi(t)\rangle}{\partial t} = H_{int} |\Psi(t)\rangle$$

where

$$|\Psi(t)\rangle = e^{-i \sum_k (I_k(t)a_k + I_k^* t)a_k^\dagger)}|\Psi(-\infty)\rangle$$

The coefficients $I_k(t)$ are the evolution operators [2] depending on the trajectory of the incident particle, and $|\Psi(-\infty)\rangle$ is the initial state of the field, in terms of the eigenstates $|n_k\rangle$; the states $|\Psi(t)\rangle$ constitute a set of coherent states, describing the plasmon field as a wave packet that propagates in a classical electromagnetic way. This formalism allows us to calculate the wake potential as:

$$\phi_W(r, t) = \langle \Psi(t) | \phi | \Psi(t) \rangle,$$

as well as the variation of electronic density $\Delta \rho$ as

$$\Delta \rho = -\frac{1}{4\pi} \langle \Psi(t) | \nabla^2 \phi | \Psi(t) \rangle$$

and other quantities of interest such as the energy lost by the incident particles $dW/dt$.

3. Results

3.1. Bulk excitations

First, we consider bulk excitations generated by a dimer of length $d$ traveling along a rectilinear trajectory with constant velocity $v = v \hat{z}$, with its axis forming an arbitrary angle with the $z$-axis, which is perpendicular to the surface.

We use the plasmon pole approximation to describe the dielectric properties of the material, with a hydrodynamic dispersion relation, $\omega_k = (\omega_p^2 + \beta k^2 + \hbar^2 k^4/2m)^{1/2}$ (where $\omega_p$ is the plasma frequency, $m$ is the electron mass and $\beta = v_F/\omega_p$; with $v_F$ the Fermi velocity). The wake potential calculated from equation 4 yields

$$\phi_W^b(r, t) = \frac{Ze\omega_p^2}{2\pi^2} \Re \left[ \int \frac{d^3k}{k^2\omega_k} \cos(k \cdot r_0) \frac{e^{i k \cdot (r - vt)}}{k \cdot v - \omega_k t + i\eta} \right]$$

$$= 2\Re \left[ \int d^3k \cos(k \cdot r_0) \phi_b^{\dagger}(r, t) \right]$$

(6)
where \( r_0 \) is the position of one of the particles constituting the dimer with respect to the center of mass (CM). \( \phi^b_w \) corresponds to the wake potential generated by a single charge \( Ze \) following the trajectory of the center of mass, being \( \eta \) the damping parameter.

Figure 1 shows the wake potential generated by the dimer along the \( z \) axis for two separations \( d \), being \( d = 0 \) the limit case of one single particle. The dimer moves with velocity \( v = 2 \) a.u. perpendicularly to the surface of an homogeneous aluminum medium (\( \omega_p = 0.55 \) a.u.). The surface is located in \( z = 0 \).

It is important to point that, when the movement of the dimer is parallel to the surface, the interatomic distance for which differences with the case of a point particle start to be significative varies with the distance between the external charged particle and the surface.

### 3.2. Surface excitations

Now, we turn to the case of a cylindrical geometry, which is important for the study of nanowires and tubes. In previous works we analyzed in detail the interaction of single external charged particle with nanostructures [7, 8]. In this work, we consider only the case of a dimer travelling parallel to the surface of the cylinder, with a fixed distance \( z_0 \) from the CM. In this configuration, different orientations can be of interest; as an illustrative example, we calculate the wake potential due to the passage of the dimer with its two particles moving on a plane parallel to the axis of the wire. We solve the equations with a simple dependence for the dispersion relation (\( \omega_k = \omega_s = \omega_p/\sqrt{2} \)), and obtain the following expression for \( \phi^s_w \):

\[
\phi^s_w(r, t) = \frac{Z}{4\pi} 2\omega_s e^{-\gamma t} R \left\{ i \int d^2q \frac{e^{-qz_0}}{q} 2\cos(q \cdot r_0) \frac{e^{iq(vt-r)}}{q \cdot v - \omega_s + i\gamma} \right\}
\]

with \( \gamma \) a damping rate which accounts for the finite lifetime of the plasmons. Figure 2 shows the variation of the electronic density due to surface excitations for different interatomic distances, along a line following the trajectory of the dimer on the interface with velocity \( v = 2 \) au. The distance from the trajectory to the surface is \( z_0 = 1 \) u.a., with its axis parallel to \( v \).

The induced charge density is obtained from equation 5, which is easily evaluated when combined with the result of equation 7 for the wake potential. \( \Delta \rho \) accompanies the wake potential on the surface and has approximately the same dependence with the distance to the surface and orientation of the incident molecule.

### 4. Conclusions

We have applied the coherent states formalism to describe the bulk and surface plasmon excitation for a diatomic molecule with two identical charges interacting with a semi-infinite solid in different configurations. Note that for a flat surface, the largest contribution to the energy loss

![Figure 1. Wake potential for a dimer traveling with velocity \( v = 2 \) a.u. and different distance \( d \) between the particles.](image)
Figure 2. Variation of the electronic density induced by a dimer \((2Z_e)\) of velocity \(v = 2\) au on the surface of a metallic wire \((w_p = 15.5\) eV\) of 5 a.u. radius. The distance between the charges is \(d = 4\) a.u. and the distance between the trajectory and the axis of the wire is 6 a.u.

is given by bulk plasmons, but for cylindrical geometry, the relationship is reversed. Because of this fact we have prioritized in this work to show bulk plasmon excitation for flat surface (considering neighborhood effects to surface in the results), and surface plasmons excitations for cylindrical surface. This example is of relevance due to that surface plasmons are the principal contributions to interaction of molecules with nanostructures.

Within a first order of approximation, the calculations are useful to determine critical values of the parameters for which it is important to take into account the structure of the incident particles.

We conclude that the coherent states formalism used to describe the interaction of the plasmon field with the incident charges has proved to be adequate for a straightforward evaluation of different quantities of interest, providing an insight into the contribution of the different excited modes. The present results and their potential applications motivate us to go on with the study of new configurations and geometries of the surface.

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References
[1] Merzbacher E 1970 Quantum Mechanics (New York: Wiley)
[2] Landau L. D. and Lifshitz E. M. 1976 Quantum Mechanics (Pergamon Press, Oxford, 1976)
[3] Echenique P M, Ashley J C, Ritchie R H 1982 Eur. J. Phys. 3 25
[4] Denton C D, Gervasoni J L, Barrachina R O and Arista N R, Phys. Rev. A 57 4498
[5] Arista N R and Fuentes M A 2001 Phys. Rev. B 63 165401
[6] Gervasoni J L and Arista N R 2003 Phys. Rev. B 68 235302
[7] Segui S, Gervasoni J L and Arista N R 2007 Surf. Sci. 601 4169
[8] Mowbray D J, Segui S, Gervasoni J L, Mišković Z L and Arista N R 2010 Phys. Rev. B 82 035405