Plasmonic excitations in noble metals: The case of Ag.

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The delicate interplay between plasmonic excitations and interband transitions in noble metals is described by means of ab initio calculations and a simple model in which the conduction electron plasmon is coupled to the continuum of electron-hole pairs. Band structure effects, specially the energy at which the excitation of the $d$-like bands takes place, determine the existence of a subthreshold plasmonic mode, which manifests itself in Ag as a sharp resonance at 3.8 eV. However, such a resonance is not observed in the other noble metals. Here, this different behavior is also analyzed and an explanation is provided.

I. INTRODUCTION

In a recent letter, Ku and Eguiluz have shown that band structure effects are responsible for the positive dispersion of the plasmon line width in K. Such a behavior had been previously found by vom Felde, Sprotz-Proch, and Finis in electron energy loss experiments. They interpreted the result as due to short range electron-electron correlations beyond the random phase approximation (RPA). However, Ku and Eguiluz explain the result within the RPA in terms of the extra plasmon decay channels provided by a manifold of unoccupied $d$-symmetry bands. The effect of these localized bands is overlooked when treating K as an homogeneous electron system in the jellium model. Therefore, band structure effects turn out to be decisive in determining, not only the existence interband transitions, but also the properties of plasmonic excitations. Indeed, ab initio calculations of the dynamical response have properly described the experimental plasmon dispersion in a variety of simple metals. On the other hand, the jellium model still provides a qualitative, though not accurate, description of the energy loss spectrum of these systems in the long wavelength limit.

The energy loss spectrum can be obtained either by doing electron energy loss spectroscopy (EELS), inelastic scattering of X-ray photons (IXSS), or indirectly by means of optical measurements. In noble metals this spectrum has a complicate structure, which bears little resemblance to that of simple metals. It is known that such a structure has to do with the existence of a manifold of $d$-like bands a few eV below the Fermi level. These lead to important deviations from even the crudest predictions for an homogeneous electron liquid. Thus, whereas for Ag a narrow resonance is observed at an energy $\approx 3.8$ eV, no well-defined plasmonic excitations appear in the spectra of Cu and Au.

The purpose of this paper is to investigate the structure of the energy loss spectrum in the long wavelength limit, where plasmonic excitations are expected to be important. In particular, we have focused on Ag for our study, but some of our conclusions do also apply to Cu and Au, and could be extended to similar metallic compounds with fully occupied $d$-like bands close to the Fermi level. The spectrum of Cu was studied from first principles in a previous work. In the present work, we show that the structure of the energy loss spectrum of Ag up to $\sim 10$ eV can be understood in terms of a simple model. In particular, we are concerned with the role played by the relative values of the Drude plasma frequency and the threshold energy for the excitation of the $d$-like bands. After clarifying the relevant elements for the existence of a plasmonic excitation below the interband excitation threshold, numerical experiments in an ab initio framework for calculating the dielectric matrix of Ag are performed to confirm this picture. Furthermore, comparison of the ab initio results with experimental data gives good agreement for excitations well above threshold, being able to reproduce all the structure in the loss spectrum up to $\sim 30$ eV. The underestimate of the threshold energy in local density calculations also shows up in our calculations, giving a lower plasma frequency than the experiments (see below for a more detailed discussion).

The question of how band structure alters the properties of plasmons in metals has been previously addressed by a number of authors. Wilson has studied the shift in the Drude plasma frequency by the presence of an optical absorption band that lies above (below) the free electron plasma frequency. He has found that the plasma frequency is shifted downwards (upwards) by the effect of the absorption band. More recently, Sturm has studied within the RPA the corrections to the dielectric function...
of an homogeneous electron gas due to a weak lattice potential. He has shown that the lattice potential can provide the necessary momentum for a plasmon to decay into an electron-hole pair below the Landau cutoff. In other words, when taking into account the lattice structure by folding the free electron bands the first Brillouin zone (BZ), a plasmonic excitation can decay by producing an interband transition. As a consequence, even in th RPA, plasmons acquire a finite lifetime. Core polarization effects on the plasma frequency have been investigated by Zaremba and Sturm. They treated the core polarization as the superposition of the polarizability of the isolated lattice ions. The polarization of core electrons lowers the plasma frequency from its Drude value, bringing it closer to the experimental value.

Recently, the dielectric matrix as well as the energy loss spectrum have been evaluated numerically within a first principles framework. In these calculations, one usually starts from a set of LDA[25] orbitals and energies, using time-dependent density functional theory (TDDFT)[26] an approximation to the density correlation function can be calculated. Hence, The energy loss spectrum is obtained from the imaginary part of the density correlation function, as dictated by the fluctuation dissipation theorem.[27] To mention a few examples of these studies besides the above mentioned work by Ku and Eguiluz[18] Quong and Eguiluz[19] have investigated the anisotropy in the plasmon dispersion of aluminum. Aryasetiawan and Karlsson[20] have studied the excitations in the energy loss spectra of Li. The negative dispersion of bulk plasmons in Cs has been explained by Fleszar and co-workers[21]. In general, specific details of the band structure of metals as the presence of band gaps in the conduction band region are needed to describe the experimental energy loss spectra in some simple[22] and noble metals.[23]

The behavior of noble metals has been considered by Ehrenreich and Phillipp.[12] These authors used the data obtained in experimental measurements of the reflectivity from Cu and Ag[24] to obtain the optical and energy loss spectra. They separated the Drude and interband contributions to the optical response, thus shedding light on the reason why the energy of the plasma resonance in Ag is shifted down in energy. In a later work, Cooper, Ehrenreich and Phillipp[13] extended this analysis to Au. They touched upon the question of assigning interband transitions to the most relevant features observed in the optical spectrum. To further clarify this point, Mueller and Phillipp[14] performed, within the RPA, based on band structure calculations by Burdick[15] a numerical calculation of the imaginary part of interband contribution to the optical response of Cu. Thus, they could give a more correct identification of the interband transitions that contribute to the optical spectrum at a given energy. Their interpretation is consistent with the optical data obtained in a number of reflectivity measurements from Ag and Ag alloys.[16]

As we have mentioned above, the energy loss function of Cu has been recently evaluated from first principles by Campillo, Rubio, and Pitarke.[28] These authors solved the Kohn-Sham equations on a plane wave basis using a norm conserving pseudopotential.[29] Subsequently, they evaluated the dielectric and energy loss functions. The method is shown to give an accurate description of the energy loss spectrum of Cu once the fully occupied $d$-like bands are taken into account as part of the valence electron complex. The remaining core electrons do not take an active part in the excitations and would only act as a global dielectric background as long as the excitation energy remains small compared to their binding energy. In the present work, we obtain the energy loss spectrum for Ag using the same ab initio techniques but, this time, we focus on the plasmonic excitations of noble metals. In the case of Ag, the appearance of a plasma resonance at $\approx 3.8$ eV can be also qualitatively understood with help of a simple model, which provides a new perspective on how a subthreshold plasmonic mode can appear, and what are the parameters controlling the existence of this type of excitations.

The outline of the paper is as follows. In the following section, we discuss a model which provides a qualitative explanation for some features in the energy loss spectrum up to $\sim 10$ eV. The details of the ab initio computation of the spectrum can be found in Sect. III. A description and discussion of the results is given in Sect. IV. Finally, the main conclusions of the present paper are summarized in Sect. V. Atomic units ($\hbar = e^2 = m_e = 1$) are used in all mathematical expressions.

II. A SIMPLE MODEL

In order to estimate the plasma frequency in Ag the classical expression $\omega_p \approx \sqrt{4\pi n}$ can be used. If we set $n = n_e$, the density of conduction electrons, i.e., those coming from the atomic 5$s$ orbital, we find that $\omega_p = 8.98$ eV. However, if we furthermore include those coming from the atomic 4$d$ orbitals it turns out that $\omega_p = 32.6$ eV. In both cases, we obtain values clear disagreement with the experiment, which gives a value of 3.8 eV. Thus, as we have remarked in the previous section, Ag does not seem to behave as a “simple” metal whose plasmonic excitations can approximately understood within the jellium model. Ehrenreich and Phillipp[12] considered this issue, concluding that it is also necessary to take into account the effect of electrons coming from the atomic 4$d$ orbitals in a more subtle way. In fact, it is necessary to account for the full band structure of Ag in order to explain what is observed in the experiments. In what follows, we shall study how the interband transitions affect the collective motion of conduction electrons, leading to the existence of a subthreshold plasmonic excitation.

The usual way to find out the energy plasmonic excitations goes as follows. Disregarding crystal local field effects, plasmonic excitations correspond to zeroes in the
macroscopic dielectric function. In the $|q| = 0$ limit we have that:

$$
\epsilon(\Omega) = 0,
$$

(1)

for some complex $\Omega$. Using the Sellmeyer-Drude expressions for $\epsilon(\omega)$, and neglecting damping effects,

$$
\epsilon(\omega) = 1 - \frac{\omega_p^D}{\omega^2} + \delta\epsilon^{(ib)}(\omega),
$$

(2)

where last term corresponds to the interband contribution:

$$
\delta\epsilon^{(ib)}(\omega) = \sum_{\omega_n > 0} \frac{f_n}{\omega_n^2 - \omega^2}.
$$

(3)

The condition in Eq. (1) can be written as

$$
\Omega^2 - (\omega_p^D)^2 + \Omega^2\delta\epsilon^{(ib)}(\Omega) = 0.
$$

(4)

The oscillator strength, $f_n$ in Eq. (3), is a measure of the effective number of electrons that participate in the excitation of a given mode ‘$n’$, with energy $\omega_n$. The dominant contribution at frequencies below $\omega_n$ comes from the excitation of conduction electrons. The Drude plasma frequency $\omega_p$ is 9.2 eV, is slightly higher than $\omega_n$. The ratio of the two plasma frequencies is usually expressed in terms of the “optical” mass, $m_{opt}$ (recall that $m_e = 1$ in atomic units):

$$
\left(\frac{\omega_n}{\omega_p}\right)^2 = m_{opt} = 0.95
$$

(5)

for Ag and $m_{opt} = 1.35$ for Cu in the RPA, $m_{opt}$ corresponds to the effective mass of electrons averaged over the occupied part of the conduction band.

Eq. (4) can be read in the following way. We assume that the term $\Omega^2\delta\epsilon^{(ib)}(\Omega)$ plays the role of a “self-energy” for the Drude plasmon. In simple metals, this term is usually small and varies slowly with $\omega$. This leads to a small shift of the Drude frequency. The plasma frequency also acquires a small imaginary part, which accounts for the fact that the plasmon state is degenerate in energy with other configurations of the system involving one or several electrons excited from one band to another. This idea can be easily realized in a model in which the plasmon is viewed as a boson coupled to an energy continuum. In an independent electron picture, the continuum corresponds to the electron-hole pair excitations. A simple model Hamiltonian that can be set up to describe this situation is the following:

$$
H = \sum_q \omega_p^D b_q^\dagger b_q + \sum_{k,q} \omega_{k,q} m_{k,q}^\dagger m_{k,q} + \sum_{q,k} g_{q,k} (b_q + b_q^\dagger)(m_{k,q}^\dagger + m_{-k,-q}).
$$

(6)

In this model, plasmons are presented as a field of oscillators carrying momentum $q$. Thus, $b_q^\dagger$ and $b_q$ are plasmon creation and annihilation operators, respectively. To keep the model as simple as possible, but retaining all the important physical effects, the energy continuum is also represented by a set of harmonic oscillators whose quanta are created and annihilated by the operators $m_{k,q}^\dagger$, $m_{k,q}$. The label $k$ stands for the additional quantum numbers (spin, relative momentum, band indices...) carried by a given continuum mode. The operator $m_{-k,-q}$ ($m_{k,-q}$) annihilates (creates) a continuum mode with all the momentum quantum numbers reversed. The assumed interaction between plasmons and the energy continuum conserves the momentum $q$. Terms connecting plasmons and modes with momentum differing by a finite reciprocal lattice vector are therefore neglected. This approximation amounts to disregarding crystal local field corrections, which in general is a good approximation for metals. Indeed, in the frequency range in which we are interested, namely $\omega \sim \omega_p^D$, as it can be seen from the ab initio calculations in Cu and Ag (see below), the local field effects at small $q$ amount to a few percent correction.

The above model, Eq. (6), can be solved exactly. Indeed, it is related to the models introduced by Fano and Anderson to study the coupling of a discrete state to a continuum. More precisely, the present model can be thought of as an extension of Gadzuk’s work to a localized vibrational mode in an electron liquid. Thus, the energies of the plasmonic modes are given by the solutions of the following equation:

$$
\Omega^2 - (\omega_p^D)^2 + 2\omega_p^D M(q, \Omega) = 0,
$$

(7)

where $M(q, \omega)$ is the plasmon self-energy. It can be expressed in terms of its imaginary part:

$$
\text{Im} M(q, \omega) = \pi \sum_k |g_{k,q}|^2 [\delta(\omega - \omega_{k,q}) - \delta(\omega + \omega_{k,q})],
$$

(8)

by means of the expression:

$$
M(q, \omega) = \int \frac{d\omega'}{\pi} \frac{\text{Im} M(q, \omega')}{\omega' - \omega - i\eta},
$$

(9)

with $\eta \rightarrow 0^+$. Working by analogy with Eq. (6), leads us to tentatively identify

$$
M(|q| \rightarrow 0, \omega) = \frac{\omega^2}{2\omega_p^D} \delta\epsilon^{(ib)}(\omega).
$$

(10)

If the RPA expression of $\delta\epsilon^{(ib)}(\omega)$ is used, we can express it in terms of single-electron orbitals, $|n k\rangle$, and energies, $\varepsilon_{nk}$:

$$
\text{Im} M(|q| \rightarrow 0, \omega) = \frac{2\pi^2}{3V\omega_p^D} \sum_{k \in BZ} \sum_{m \neq n} f(\varepsilon_{nk}) \times [1 - f(\varepsilon_{mk})] |\langle m k | p | n k \rangle|^2 \delta(\omega - \varepsilon_{mk} + \varepsilon_{nk}),
$$

(11)
where \( V \) is the volume of the system and \( p \) the momentum operator. We have assumed cubic symmetry and a local pseudopotential; if the pseudopotential is not local, the matrix element of \( p \) must be replaced by a more complicated expression. For \( \omega = \omega_p^D \) this equation matches the Golden Rule result for the plasmon line width in the \( |q| \rightarrow 0 \) limit [3], which confirms the identification made above in Eq. (1). For arbitrary \( \omega \), however, it is better to look at \( \text{Im} M(q, \omega) \) as a weighted density of the continuum modes, cf. Eq. (6). Thus, it follows from Eqs. (6) and (9) that if \( \omega_p^D \) lies above (below) the region where \( \text{Im} M(q, \omega) / \omega_p^D \) is large (provided \( \text{Im} M(q, \omega_p^D) / \omega_p^D \) be small), the plasma frequency will be blue (red) shifted. This result is in disagreement with the above mentioned work of Wilson [4]. When \( \text{Im} M(q, \omega_p^D) / \omega_p^D \) is large, we will not observe a well-defined plasma resonance in the spectrum. This seems to be the case of noble metals due to the presence of a manifold of occupied \( d \)-like bands, which gives rise to a broad band of modes extending from the interband threshold energy \( \omega_T \approx 3.9 \text{ eV} \) (for Ag and 2.1 eV for Cu), to well above the Drude plasma frequency (9.2 eV for Ag and 9.3 eV for Cu). If we assumed that the onset of interband transitions in Ag took place so sharply as to produce a discontinuity in the weighted density of continuum modes:

\[
\text{Im} \, M(|q| \rightarrow 0, \omega) \sim \theta(\omega_T - \omega)
\]

for \( \omega \sim \omega_T \), then \( \text{Re} \, M(q \rightarrow 0, \omega) \) would develop a logarithmic behavior \( \sim -\log(\omega - \omega_T) \) for \( \omega < \omega_T \). This means that Eq. (11) would have a dampingless solution just below the threshold, \( \omega_T \). This polaronic-like solution corresponds to an hybrid plasmonic mode, in which the conduction electrons oscillate coherently without exciting the electrons in the \( d \)-like bands. These are just polarized by the electric field set up by plasmonic mode, so that the plasma frequency is lowered. This point of view agrees well with more phenomenological approaches [3,4,5,6] which simply assume that the red shift in the plasma frequency can be accounted for by an effective dielectric function \( \epsilon_d \) for the electrons in the \( d \)-like bands so that \( \omega_p^D = \omega_p^D / \sqrt{\epsilon_d} \approx 3.8 \text{ eV} \).

Additionally, there is another complex solution of Eq. (6), for which the conduction electrons move as an overdamped oscillator, rapidly decaying into an electron hole-pair. For \( |q| \rightarrow 0 \), this excitation corresponds to an optical interband transition. Two types of optical transitions may occur above the threshold [2]. Two examples have been indicated by arrows in Fig. 2, which represents the calculated first-principles LDA band structure of Ag. Type A corresponds to the excitation of an electron from one flat \( d \)-like band to an unoccupied state in the conduction band or above. The other type (B), whose threshold occurs at approximately the same energy in the three noble metals, corresponds to the excitation from an occupied state in the conduction band (near \( L \) point in the BZ) to the flat part of an unoccupied band or above. This type of transitions seems to be responsible for the damping of the plasmon when the \( 4d \) electrons are included in the pseudocore, i.e., they are considered to be frozen. In Sect. 4 we shall explain this issue more in detail. These two types of transitions are important because they often involve flat bands, which may lead to van Hove singularities in the joint density of states.

In the case of Ag, the onsets for the transitions of type A and B nearly overlap in energy. This produces a sharp interband onset and gives rise to the pronounced peak that \( \text{Im} \, \epsilon(\omega) \) exhibits around 4 eV. From Eq. (10), it follows then that \( \text{Im} \, M(|q| \rightarrow 0, \omega) \) will also have a maximum at the same energy. The onset of the interband transitions at \( \omega_T \) is not as sharp as suggested by Eq. (3). However, it still leads to a zero of \( \Omega^2 - (\omega_p^D)^2 + 2 \omega_p^D \text{Re} \, M(|q| \rightarrow 0, \Omega) \) for a real \( \Omega \), which occurs below the threshold, where the density of continuum modes is very small. This point is illustrated by Fig. 5, which displays the graphical solution of Eq. (6). This provides an explanation for the existence of a subthreshold plasma resonance in Ag. However, it remains to be explained why a similar phenomenon is not observed in the spectra of Cu or Au. The difference stems from the specific details of the band structure and, in particular, from the value of the threshold energy. In Fig. 6 we have plotted the graphical solution of Eq. (6) in the case of Cu. The threshold for the excitation of \( d \)-like bands occurs this time at a lower energy (2.1 eV) because the onset for the interband transitions of type A and B does not overlap. Comparison of Figs. 2 and 6 shows the important role played by the value of the threshold energy, cf. Eq. (11), in enhancing the maximum of \( \text{Im} \, M(|q| \rightarrow 0, \omega) \), and thus in \( \text{Re} \, M(|q| \rightarrow 0, \omega) \). Therefore, for Cu no zero of Eq. (6) close to the real axis exists below the threshold, where this plasma mode would have a small density of continuum modes to decay. A similar conclusion can be drawn for the case of Au.

To sum up, band structure effects modify the original Drude plasmon, which turns out to be no longer a well defined plasmonic excitation. Thus, it shows up in the Ag spectrum as broad peak with a maximum around 8 eV. Moreover, a combination of a high value for \( \omega_T \) along with the sudden onset of interband transitions produces a narrow plasma resonance in Ag. In this respect, our conclusions agree with those of Ehrenreich and Phillips [2]. Furthermore, the line width of this “delicate” feature in the energy loss spectrum also depends on the sharpness of the interband onset. The sharper onset the narrower the resonance, which in any case has very little oscillator strength. This makes this plasmonic excitation very sensitive to changes in the band structure, impurities or defects. This is consistent with the experimental data from alloying experiments [1,2,4] which indicate that the plasmon is strongly damped by increasing the concentration of the other component in the alloy. Finally, it is worth pointing out that the existence of this resonance also depends on the value of the Drude plasma frequency. If the value of \( \omega_p^D \) is increased, for example by increasing the electron density in the system, the resonance could dis-
appear from the spectrum. This prediction is confirmed by our ab initio results (shown below) for the energy loss spectrum of Ag under externally applied hydrostatic pressure.

III. DETAILS OF THE AB INITIO CALCULATIONS

By measuring the energy lost by electrons or X-ray photons in their interaction with matter, one can access the dynamical structure factor of a system. The fluctuation-dissipation theorem allows us to relate \( S(q, \omega) \) to the density correlation function:

\[
\chi(r, r', t) = -i \theta(t) \langle \{n_H(r, t), \delta n_H(r', 0)\} \rangle,
\]

where \( n_H(r, t) = n_H(r, t) - \langle n_H(r, t) \rangle \), and suffix \( H \) means that operators are in the Heisenberg picture. The brackets mean that the average is taken over the ground state of the system. Now, time-dependent density functional theory (TDDFT) provides us with a method to compute this correlation function by solving the following integral equation:

\[
\chi_{GG'}(q, \omega) = \chi_{GG'}^0(q, \omega) + \sum_{G_1, G_2} \chi_{GG_1'}^0(q, \omega) \times [v_{G_1G_2}(q) + K_{GG'}^{xc}(q)] \chi_{G_2G'}(q, \omega).
\]

Here, we have exploited crystal symmetry and time translation invariance by introducing:

\[
\chi_{GG'}(q, \omega) = \frac{1}{V} \int dt \, d^3r \, d^3r' e^{-i(q+G') \cdot r} e^{i(q-G) \cdot r} \chi(r, r', t),
\]

where \( q \) belongs to the BZ, and \( G, G' \) to the reciprocal lattice. Similar definitions hold for the other functions that appear in Eq. (14). For example,

\[
v_{GG'}(q) = \frac{4\pi}{|G + G'|^2} \delta_{G, G'}
\]

corresponds to the Fourier components of the Coulomb interaction between metal electrons. The function

\[
\chi_{GG'}^0(q, \omega) = \frac{1}{V} \sum_{k \in BZ, n,m} \frac{f(\varepsilon_{nk}) - f(\varepsilon_{nk+q})}{\omega - \varepsilon_{nk} - \varepsilon_{nk+q} + i\eta} \times |n \, k| e^{-i(q+G') \cdot r} |m \, k + q\rangle \times \langle m \, k + q| e^{i(q+G') \cdot r} |n \, k\rangle
\]

with \( \eta \to 0^+ \), is the density correlation function for a system of independent particles, with single-particle energies \( \varepsilon_{nk} \) and orbitals \( |n \, k\rangle \). These are eigenvalues and eigenstates of a single-particle Hamiltonian. The potential energy in this Hamiltonian is given by the Kohn-Sham potential. In our case, the Kohn-Sham potential has been calculated within LDA.

We have used a plane wave basis to expand the Bloch eigenstates. For this procedure to be computationally efficient, it is necessary to replace the lattice potential by a superposition of ionic pseudopotentials having the same scattering properties. However, as electrons in the outer atomic 4d shell play an important role in the response of noble metals, they are treated as a part of the valence electrons. The remaining core electrons are replaced by a frozen pseudocore using a norm-conserving pseudopotential scheme. Therefore, electrons included in the pseudocore will not respond to an external perturbation. This is not an important drawback as long as the excitation energy remains below the typical excitation energies of core electrons \( \sim 100 \text{ eV} \).

Including 4d electrons in the valence produces a pseudopotential that requires a relatively high number of plane waves to get good convergence. Here, we have used a scalar relativistic pseudopotential generated according to the scheme of Troullier and Martins. It requires \( \approx 1, 400 \) plane waves per Bloch state up to a cutoff energy of \( \approx 1.1 \text{ keV} \) in order to obtain a well converged ground state energy (less than 0.01 eV), and single-electron energies and orbitals up to \( \approx 100 \text{ eV} \). The lattice constant has been set to the experimental value of the FCC crystal structure of Ag, namely \( a = 4.09 \text{ Å} \). We have also solved the Kohn-Sham equations with \( a = 3.70 \text{ Å} \), which corresponds to an externally applied hydrostatic pressure of 63 GPa.

The RPA is equivalent to solving Eq. (17) with \( K^{xc} = 0 \). Therefore, all the exchange correlation effects beyond the RPA are contained in the kernel \( K_{GG'}^{xc}(q, \omega) \). Consistently with the use of LDA eigenstates and eigenvalues in the calculation of \( \chi^0 \), this function is approximated by the following expression:

\[
K_{GG'}^{xc} = \frac{1}{V} \int d^3r \, e^{-i(G-G')} \cdot r \, f_{xc}(r),
\]

where

\[
f_{xc}(r) = \left[ \frac{dV_{xc}(n)}{dn} \right]_{n_{gs}(r)}.
\]

Here \( V_{xc} \) is the exchange correlation part of the Kohn-Sham LDA potential, and \( n_{gs}(r) \) is the ground state density. This approximation is usually called adiabatic local density approximation (ALDA). However, it is observed that for metals in the long wavelength limit, ALDA and RPA yield very similar results. This has been found in simple metals and also in Cu. Thus, when computing the spectrum, we have used the RPA.

Instead of solving Eq. (17), we have evaluated the RPA dielectric matrix:

\[
\epsilon_{GG'}(q, \omega) = \delta_{G', G'} - v_{GG'}(q) \chi_{GG'}^0(q, \omega).
\]
To calculate the dielectric matrix we have used a cutoff of 41 eV in $G$, $G'$, which amounts to using 59 × 59 matrices.

To evaluate $\chi_0$ using Eq. (17), we have cut off the sum over $n$ and $m$ using bands up to an energy of ≈ 100 eV. The integration over the first BZ has been performed using a $20 \times 20 \times 20$ Monkhorst-Pack mesh in the irreducible BZ, which allows to deal effectively with the topology of the Fermi surface of Ag. Indeed, this is a very dense mesh and the calculation of $\chi_0$ becomes certainly time and memory consuming. However, if one is to resolve the very narrow plasma resonance that Ag presents near the interband excitation threshold, it is then necessary to work with such a fine mesh.

In order to further reduce the numerical damping $\eta$ we have also computed $\chi_0$ on the imaginary frequency axis by making the replacement $\omega \rightarrow i \nu$ in Eq. (17). Analytic continuation to the real axis has been carried out by using a Padé approximant. This procedure allows us to use a numerical damping as small as 0.001 eV. This is to be compared with the 0.2 eV value used in the real frequency calculations also presented in this work. However, we shall show the results of both types of calculations together, to indicate that one must be very careful with the analytic continuation procedure using Padé approximants. Thus, the results obtained using this method tend to be smoother than what is obtained with a calculation with real frequencies and larger values of $\eta$. Thus, it usually happens that some features of the spectrum, as obtained in a real frequency calculation, are completely missing from the analytically continued result (see following section). In fact, although we have used Lentz algorithm(4) to evaluate the corresponding continued fraction, we have been unable to ensure that the procedure converges by increasing the number of points over the same interval of $\nu$. When fitting the Padé approximant(2) to the calculated values of $c_{G,G}(q, i \nu)$, we have found that the results are unstable with respect to increasing the number of points. Thus, we have obtained differences of the order of 10 % when the number of points over the same interval was simply doubled. Finally, we have decided to use the modulus of the remainder of the truncated continued fraction to estimate the error, and always compare the outcome with a real frequency calculation prior to consider it as reliable.

**IV. RESULTS**

In Fig. 4 we have plotted the band structure of Ag as calculated within the LDA. Two examples of the main types of interband transitions (A and B) which couple to plasmons at energies $\omega \sim \omega_p^D$ are indicated by arrows. In the LDA, we obtain a threshold energy for type A transitions $\approx 3$ eV, whereas experimentally it is found 4 eV. Since LDA eigenvalues enter the expression for $\chi_0$, this turns out to be the reason for underestimating the threshold frequency, $\omega_T$, as shown in Figs. 4 and 5. An underestimate of this kind was already observed for Cu, where $\omega_T \approx 1.5$ eV in contrast with the experimental value of 2.1 eV. The source of such an underestimate may be either a failure of the LDA or an indication that a frequency dependent and perhaps nonlocal $K^{\infty}$ may be required to fully account for the experimental value of $\omega_T$. In our opinion, however, it is related to a failure of the LDA, which may not be taken into account the strong correlations occurring amongst the electrons in the flat $d$-like bands of Ag. Therefore, a more detailed description of correlation for the $d$-like bands seems to be required(5).

Fig. 5 presents our results for the energy loss function for $q = (0.05 \ 0.0)/2\pi/a$ as obtained from the LDA band structure. Since our interest is focused on the plasmonic excitations, which occur for small $q$, we need not consider exactly the $|q| = 0$ limit. Thus, for the small $q$ considered, the theory developed in Sect. 4 still applies. The continuous line in this figure corresponds to the $\omega_p$-like band. The important role played by the $\omega_p$-like bands of Ag. Therefore, a more detailed description of correlation for the $d$-like bands seems to be required (6).

As it can be seen in Fig. 5, although the calculation using a Padé approxim-
To modify the threshold energy on the plasma resonance in its energy loss spectrum, while Cu (and Au) is to understand why Ag presents a narrow plasma resonance. The motivation of these experiments has been remarked in the previous section, this leads to the excitation of interband transitions. The experimental results, full circles for the imaginary parts of \( \epsilon \) is further investigated below.

In this figure, continuous lines correspond to calculations for real frequencies with \( \eta = 0.2 \text{ eV} \), while dashed lines correspond to the analytic continuation using a Padé approximant from the results obtained on the imaginary frequency axis. Both calculations show the same tendency. On the other hand, when the threshold energy is further decreased, from its LDA value \( \approx 3 \text{ eV} \), \( \omega_F \approx 1.5 \text{ eV} \), the plasma resonance disappears and the spectrum becomes more “Cu-like”.

Finally, in Fig. 8 we show the energy loss spectrum of Ag under an external pressure of 63 GPa. As in previous cases, the continuous line corresponds to a calculation using real frequencies while the dashed line is the result of an analytical continuation using a Padé approximant. Notice that in this case the lattice constant is \( a_{\text{press}} = 3.7 \text{ Å} \) so that now \( q = (0.05 0 0)/(2\pi/a_{\text{press}}) \), corresponds to a slightly larger momentum \( (|q_{\text{press}}| = 8.5 \times 10^{-2} \text{ Å}^{-1} \text{ vs } |q| = 7.7 \times 10^{-2} \text{ Å}^{-1}) \).

Decreasing the lattice constant changes the width of the bands so that they disperse more rapidly with \( k \) (i.e., the band width becomes larger). Furthermore, electronic density also increases. This shifts the maximum previously at \( \omega_{\text{max}} \approx 7.5 \text{ eV} \) to \( \omega_{\text{max}} \approx 8.8 \text{ eV} \). Since this maximum is related to the Drude plasmon, whose bare frequency scales with the lattice parameter as \( a^{-3/2} \), we could understand the shift (neglecting the change in the optical mass) as due to the increase in the electronic density. Indeed, this argument works reasonably well as \( (a_{\text{press}}/a)^{-3/2} = 1.16 \), and \( \omega_{\text{press}}/\omega_{\text{max}} \approx 1.17 \).

More, as the bands become wider, specially those corresponding to excited states, more oscillator strength is transferred to higher energies. This decreases the density of modes at the Drude frequency, and thus the corresponding peak is now less broad. What is more, in this spectrum the subthreshold plasmon is not present any more. Again, this is due to the increased electronic density, which yields a higher value for the Drude plasma frequency so that Eq. 7 has no longer a solution close to the real axis. The behavior under pressure predicted here remains to be confirmed by experiments.

\[ \begin{align*}
\chi & = \frac{\omega}{\epsilon} \\
\epsilon & = \epsilon_0 + \frac{\omega}{\epsilon}
\end{align*} \]

\[ \begin{align*}
\omega_0(q, \omega) &= (0.05 0 0)/(2\pi/a) \\
\omega_{\text{max}} &= 8 \text{ eV} \\
\omega_{\text{press}} &= 10^2 \text{ Å}^{-1}
\end{align*} \]
tion. We have also shown the important role played by the $d$ symmetry bands in determining the existence of the plasma resonance at 3.8 eV, just below the interband excitation threshold. By using a simple model, it is shown that the appearance of this excitación has to do with the sharpness of the interband onset and the relative values of the threshold energy and the Drude plasma frequency. Since it contains very little oscillator strength, it is very sensitive to impurities, defects, and changes in the band structure. Thus, we have demonstrated by performing numerical experiments that its presence depends on the value of the threshold energy. Finally, we have also computed the energy loss spectrum of Ag under pressure, and found that its features can be also understood in terms of the simple model presented here. We remark that the techniques used and analysis carried out in this work are not specific of Ag, and could be readily extended to other metallic compounds with fully occupied $d$ symmetry bands close to the Fermi level.

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**FIG. 1.** Calculated LDA band structure of Ag. Arrows indicate the two examples (A and B) of the types of interband transitions that couple to the plasmonic excitations in the long wavelength limit, for energies above the interband excitation threshold. The crystal structure is FCC with lattice parameter equal to \( a = 4.09 \) Å. The zero energy corresponds to the Fermi level.

**FIG. 2.** Graphical solution of Eq. (7) for the subthreshold plasmonic modes in Ag. Data for \( \delta \epsilon^{(0)}(\omega) \) (i.e., for Re \( M(|q| \to 0, \omega) \)) are from Ref. [42]. The continuous line cuts the dashed line at the point indicated by the black dot. This point lies just below the threshold, where the density of continuum modes is small. As a consequence, a narrow plasma resonance appears in the spectrum.

**FIG. 3.** Graphical solution of Eq. (7) for the subthreshold plasmonic modes in Cu. Data for \( \delta \epsilon^{(0)}(\omega) \) (i.e., for Re \( M(|q| \to 0, \omega) \)) are from Ref. [42]. The continuous line does not cut the dashed line, indicating that no subthreshold plasmonic modes exist in Cu. A similar situation is expected to hold for Au.

**FIG. 4.** Energy loss spectrum of Ag for \( q = (0.05\,00)(2\pi/a) \), \( |q| = 7.7 \times 10^{-2} \text{ Å}^{-1} \). The continuous line is imaginary part of \( \epsilon_{00} \) element of the inverse dielectric matrix, namely the energy loss function \( \text{Im} \left[ -\epsilon_{00}(q, \omega) \right] \), whereas the dashed line corresponds to (the imaginary part of) one over the \( \epsilon = \epsilon' = 0 \) element of the dielectric matrix \( \text{Im} \left[ -1/\epsilon_{00}(q, \omega) \right] \). Differences between them are due to crystal local field effects. Dots are the experimental data from Ref. [44]. As they were obtained from optical data and do not include crystal local field corrections, they must be compared to the dashed line.

**FIG. 5.** Energy loss spectrum of Ag for \( q = (0.05\,00)(2\pi/a) \), \( |q| = 7.7 \times 10^{-2} \text{ Å}^{-1} \). The continuous line is a calculation for real frequencies with \( \eta = 0.2 \) eV, cf. Eq. (7). The dot-dashed line, however, is obtained by analytically continuing to the real axis an imaginary frequency calculation, using a Padé approximant. As it can be seen, the results obtained by analytical continuation cannot reproduced all the features in the spectrum obtained using a real \( \omega \) (but higher numerical damping \( \eta \)). The dashed line is a calculation of the loss function including the \( 4d \) electrons of Ag in the frozen pseudocore that replaces the true ionic core. Then, these electrons cannot be excited, thus showing the important role that they actually play in modifying the spectrum. Notice that the intensity of this peak is five times what is represented here.

**FIG. 6.** Dielectric function \( \epsilon_{00}(q, \omega) \) of Ag for \( q = (0.05\,00)(2\pi/a), |q| = 7.7 \times 10^{-2} \text{ Å}^{-1} \). The continuous line corresponds to the imaginary part as obtained by analytically continuing an imaginary frequency calculation, using a Padé approximant. The dashed line is the real part obtained by the same method. We checked that the results are consistent with a real frequency calculation (not showed here for clarity). Full circles (imaginary part) and open squares (real part) correspond to experimental data from Ref. [44].

**FIG. 7.** Results of the scaling procedure described in Sect. [14]. The continuous line are the results as calculated for real \( \omega \) with \( \eta = 0.2 \) eV, while the dashed lines are obtained by analytical continuation using Padé approximants. When the occupied bands are scaled so that the interband threshold energy increases, the subthreshold plasmon appears more defined. However, when threshold energy is decreased the plasmon disappears from the energy loss spectrum.

**FIG. 8.** Energy loss spectrum of Ag for \( q = (0.05\,00)(2\pi/a \text{ press}) \), \( |q| = 8.5 \times 10^{-2} \text{ Å}^{-1} \) with \( a \text{ press} = 3.7 \) Å, which corresponds to an externally applied hydrostatic pressure of 63 GPa. The continuous line is a calculation for real frequencies with \( \eta = 0.2 \) eV, cf. Eq. (7). The dashed line, however, is obtained by analytically continuing to the real axis an imaginary frequency calculation, using a Padé approximant.
$2 \text{Re} M(q = 0, \omega) / \omega_d^p$

$1 - \frac{\omega^2}{(\omega_d^p)^2}$

Interband threshold energy $\omega_T$
$$2 \Re M(q=0,\omega) / \omega_p^D$$

$$1 - \omega^2 / (\omega_p^D)^2$$

Interband threshold energy $\omega_T$
Energy loss function $\omega \text{(eV)}$
$q = (0.05 \ 0 \ 0 \ (2\pi/a)$
\[ \varepsilon_{00}(q, \omega) \]
Im \varepsilon^{-1}_{\infty}(q, \omega)

\begin{align*}
q &= (0.05 \ 0 \ 0) (2\pi/a) \\
\omega_T &= 3.5 \text{ eV} \\
\omega_T &= 3 \text{ eV (LDA)} \\
\omega_T &= 1.5 \text{ eV}
\end{align*}
\[ q = (0.05 \ 0 \ 0) \ (2\pi/a_{\text{press}}) \]

\[ P = 63 \text{ GPa} \]