Size-Dependent Plasmons in Metal Clusters

The present theory of size-dependent collective excitation in metal clusters is briefly developed and compared with recent experimental data. Open problems are clearly discussed both on the theoretical side and on the experimental side.

Key Words: *electronic excitation, dynamical response, plasmons, polarizability, giant resonance, collective motion*

1. INTRODUCTION

The optical properties of small metal particles can be derived from the knowledge of the dipolar dynamical polarizability $\alpha(\omega)$. Once $\alpha(\omega)$ is known, the photoabsorption cross section $\sigma(\omega)$ is given by

$$\sigma(\omega) = 4\pi \frac{\omega}{c} \operatorname{Im} \alpha(\omega) . \tag{1}$$

Here Im means the imaginary part of α. Equation (1) can be derived in a straightforward manner using first-order time-dependent perturbation theory with respect to the external radiation field.[1,2] A derivation of Eq. (1) within macroscopic electrodynamics can be found in the monograph by Bohren and Huffman.[3] Although theoretically it is easier to understand the properties of free clusters, to be experimentally investigated in a molecular beam,

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traditionally (for intensity reasons) clusters have been investigated either deposited on a surface or embedded in a so-called matrix (typically one of the rare gases, Xe, Ar, etc.). In this latter case, and within the framework of macroscopic electrodynamics,[4] $\alpha(\omega)$ is given as follows (a spherical shape of the cluster is assumed with radius R):

$$\alpha(\omega) = R^3 \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} . \tag{2}$$

Here the various dielectric constants used (ε_m for the metal particle and ε_d for the dielectric host) are (by definition) the size-independent macroscopic dielectric constants. The only size effect in this formula is the trivial volume term. That this formula is wrong can be immediately inferred from the experimental data shown in Fig. 1, and taken from Ref. 5. According to Eq. (2), the response function blows up at the zeros of the denominator,

$$\varepsilon_m = - 2\varepsilon_d . \tag{3}$$

This equation is the analog for interfaces to the defining equation for surface plasmons of free plasmons of free metal particles.[6]

Inspection of Fig. 1 shows clearly that macroscopic electrodynamics cannot be applied to small metal particles, because there is a strong size dependence of both the peak position and the width of the interface plasmon, whose origin is still the subject of controversy in the existing literature. Whereas some authors assign these features to genuine cluster properties,[7,8] Bo Persson has shown[9] that at least the plasmon width can be quantitatively understood by invoking the coupling of the metal plasmon to particle–hole pairs, where the "particle" state is a chemisorbed state at the interface between the metal cluster and the dielectric host. The situation is much simpler (on the theoretical side) for free clusters, for which Eq. (2) applies for $\varepsilon_d = 1$.

The modern microscopic theory for the optical absorption of free clusters started in 1984 with Ref. 10, and the experimental work on free clusters started two years later with the pioneering work of W. de Heer on free Na_{20}.[11]

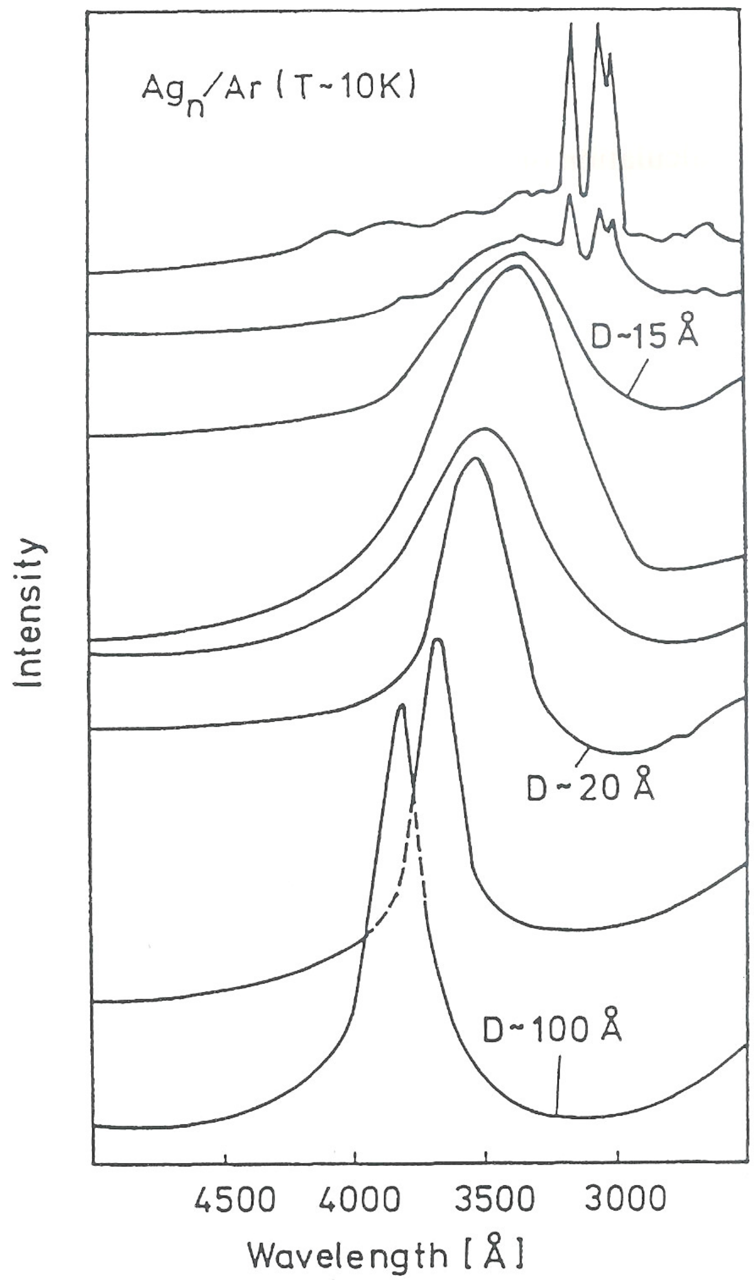

FIGURE 1 Experimental data (absorption for Ag$_n$ clusters embedded in solid Ar (from Ref. 5). The huge hump is understood as an interface plasmon, introduced by the Ag clusters. Neither bulk silver nor solid Ar have any structure in this spectral region; hence it is a size effect. Whereas large clusters show a broad peak, the smallest (upper part of this graph) show an effect which was not fully understood at that time. Nowadays it is considered just one example of fragmentation (discussed in the main text). The interpretation of these data is still controversial (see main text).

2. THEORY

Because clusters constitute a bridge between atoms and solids, one can start in the calculation of the optical properties either from the atomic side or from the solid state point of view. Historically, the latter approach was first; later quantum chemists calculated optical spectra of micro-clusters, but all these methods are far too complicated to study larger aggregates or the transition to the bulk. Furthermore, there seems to be a problem. Whereas the experimental spectra (Fig. 1) show clearly the overwhelming importance of plasmons, there is *no* paper about the quantum-chemical methods showing how collective effects could be identified within this frame.

The solid state point of view for looking at the optical properties of metal clusters starts, consequently, with a cluster model, which has been extremely successful for the study of collective excitations in solids,[12] namely the jellium model,[13] which predicts not only the magic numbers of metal clusters, but also the surface plasmon as the dominating feature in the optical spectra. Having a cluster model for the calculation of the electronic structure, we need in addition a method of calculation of the optical excitations. Because this is intrinsically a very intricate many-body problem, which belongs to the domain of dielectric screening (from the macroscopic point of view), a method which stresses this point should be ideal to study the general dielectric response of metal clusters. When one of us (W.E.) started his activity in this field, a seminal work was published by Zangwill and Soven,[1] which was tailor-made for the study in question, namely the time-dependent local density approximation (TDLDA) applied to closed shell atomic systems (the rare gases). This theory can be applied to systems of any size and is based on density functional theory. Though it lacks a firm theoretical justification (there is *no* theorem like the Hohenberg–Kohn theorem for the ground state[15] which sanctions the use of a time-dependent density functional), it has been shown repeatedly that it "works."[16] Furthermore, there is a perturbational consideration by Gross and Kohn[17] which shows to which extent the

TDLDA can be justified (for a critical discussion of this "method," see also the book by Mahan and Subbaswamy[2]).

We continue with a brief presentation of the basic formalism of the TDLDA as applied to metal clusters, where we always focus on the physics behind the formalism presented. If we neglect for a moment the electron–electron interaction and if the cluster is placed in an external electromagnetic field, an induced charge density is set up in the following way:

$$\varrho_{ind}(\mathbf{r},\omega) = \int d\mathbf{r}_1 \chi_0(\mathbf{r},\mathbf{r}_1;\omega) V_{ex}(\mathbf{r}_1,\omega) . \tag{4}$$

V_{ex} is the external potential. Here χ_0 is by assumption the independent-particle electronic susceptibility

$$\chi_0(\mathbf{r},\mathbf{r}_1;\omega) = \sum_{i,j} (f_i - f_j) \frac{\psi_i(\mathbf{r}_1)\psi_j^*(\mathbf{r}_1)\psi_j(\mathbf{r})\psi_j^*(\mathbf{r})}{\hbar\omega - (\varepsilon_j - \varepsilon_i) + i\delta} \tag{5}$$

and the positive infinitesimal δ guarantees the causality of the response (that is, the response is *retarded*). The interpretation of this formula is evident.

The external perturbation creates particle–hole pairs with energies $\varepsilon_j - \varepsilon_i$ and wave-functions $\psi_j\psi_i^*$; unfortunately this is *not* the complete story, simply because once the induced charge density is established, the electrons (and holes) feel an additional induced field, which consists of an induced Coulomb part

$$V_{ind,C}(\mathbf{r},\omega) = \int d\mathbf{r}_1 \frac{\varrho_{ind}(\mathbf{r}_1,\omega)}{|\mathbf{r} - \mathbf{r}_1|} , \tag{6}$$

and an induced exchange-correlation part:

$$V_{ind,xc}(\mathbf{r},\omega) = \left[\frac{\partial V_{xc}}{\partial \varrho}\right]_{\varrho_0} \varrho_{ind} \cdot \tag{7}$$

Whereas there is absolutely *no* doubt about the Coulomb part of the induced potential, the same is unfortunately not true for the exchange-correlation part. The special form, Eq. (7), was introduced by Zangwill and Soven intuitively, by assuming that the same functional as in the ground state can be used in the presence of a time-dependent induced charge density; and because $\delta\varrho_{ind}$ is assumed to be small, a Taylor expansion around the density in the ground state ϱ_0 leads immediately to Eq. (7). Because of this induced field, the induced charge density is no longer determined by Eq. (4), but instead by the following equation:

$$\varrho_{ind}(\mathbf{r},\omega) = \int d\mathbf{r}_1 \chi_0(\mathbf{r},\mathbf{r}_1;\omega) V_{eff}(\mathbf{r}_1,\omega), \qquad (8)$$

with the total effective potential given by $V_{eff} = V_{ex} + V_{ind,C} + V_{ind,xc}$. Hence, the TDLDA is conceptually a self-consistent field theory, as is the random phase approximation (RPA) or the random phase approximation with exchange (RPAE): Indeed, the TDLDA is the density functional theory (DFT)-based analog to the RPAE. The underlying basic assumption is that all many-body effects can be stored in an effective field to which the electrons respond as independent particles.

Clearly, there are some important intrinsic deficiencies in the formalism developed so far. First of all, the TDLDA suffers from self-interaction effects, in very much the same way as the local density approximation (LDA) for the ground state. These effects can be removed, as has been shown by two of us.[18,19] As already mentioned, all many-body effects (plasmons, giant resonances, resonant photoemission, etc.) are stored in V_{eff}, whereas χ_0, as an independent-particle response function, does not contain any many-body effects. But, of course, we can define alternatively a response function with respect to the external field which contains all these many-body effects:

$$\varrho_{ind}(\mathbf{r},\omega) = \int d\mathbf{r}_1 \chi(\mathbf{r},\mathbf{r}_1;\omega) V_{ex}(\mathbf{r}_1,\omega) \,. \qquad (9)$$

By comparing all definitions introduced so far, one can show that χ is obtained by solving the following integral equation[10]:

$$\chi(\mathbf{r},\mathbf{r}_1;\omega) = \chi_0(\mathbf{r},\mathbf{r}_1;\omega) + \int\int d\mathbf{r}'d\mathbf{r}''\chi_0(\mathbf{r},\mathbf{r}';\omega) \times K(\mathbf{r}',\mathbf{r}'')\chi(\mathbf{r}'',\mathbf{r}_1;\omega)\,. \tag{10}$$

Here the kernel K, sometimes called residual interaction or irreducible particle–hole interaction, is given as follows:

$$K(\mathbf{r},\mathbf{r}_1) = \frac{e^2}{|\mathbf{r}-\mathbf{r}_1|} + \left[\frac{\partial V_{xc}}{\partial \varrho}\right]_{\varrho_0} \delta(\mathbf{r}-\mathbf{r}_1)\,. \tag{11}$$

Finally, from the dipole part of χ, $\alpha(\omega)$ is obtained as described in Ref. 10.

From a general point of view, expression (11) is oversimplifying the irreducible particle–hole interaction, first of all, because it is frequency independent, which seems to "work" whenever one studies plasmon-type excitations. But we have the feeling that this crude approximation would completely fail whenever one has to study excitonic-type collective excitations. That means, in order to study the size dependence of excitons in rare gases[20] or semiconductors, one should use a better approximation to K or a different method.

3. RESULTS AND DISCUSSION

In Fig. 2 we reproduce a typical result for the absorption of a jellium sodium cluster Na_n (with $100 < n < 200$). The frequency is scaled with the classical surface-plasmon frequency $\tilde{\omega} = \omega_p/\sqrt{3}$. Generally, the absorption curve has a rich structure, due to the various excited states of the clusters. Among these, two different collective states can be identified, namely, the surface plasmon, which peaks around $\tilde{\omega} \approx 0.88$ (a little red-shifted from the classical curve, which peaks trivially at $\tilde{\omega} \approx 1$). This red-shift is a consequence of the quantum mechanical spill-out of the valence electrons leading to a reduced mean electronic density. The fact that this excitation is a surface mode can be seen directly by inspection of the induced charge density; at the resonance frequency, its imaginary part displays a pronounced peak centered at the surface of the cluster. On the other hand, the fact that it is collective can be recognized because the plasmon resonance peak has an associated oscillator strength very close to N, the number of delocalized electrons, thereby nearly exhausting the associated sum rule.[29] This value is comparable to the "classical" value shown as a continuous curve in Fig. 2. We would like to stress that all other modes of excitation gain only very little oscillator strength (e.g., the various cusps which are dressed electron–hole pairs, or the weak hump around $\omega = \sqrt{3}$). Furthermore, the TDLDA applied to the jellium model for metal clusters brings about another qualitative prediction which was confirmed experimentally, several years later, by the Orsay group for Na,[21] K[22] and Li.[23] As already shown in 1985,[10] the features of the photoabsorption spectrum change, for $n < 100$ with respect to the size range $n > 100$, in which it is dominated by a single peak. Indeed, for these smaller clusters, the surface plasmon is sometimes located in the proximity of a single pair line, which is collectively enhanced, and gains comparable oscillator strength as the surface plasmon. In those cases it is a rather intricate task to identify the "character" of the excitation. Nevertheless, it can be done by comparing the TDLDA absorption with the absorption of the free electrons, which do not show any collective mode. This is demonstrated for the case of Na_{20} in the bottom part of Fig. 3. Comparing the free-particle response (dashed line) with the dressed response (TDLDA, continuous line). we see not only a pronounced reshuffling of oscillator strength from the low-frequency region to the high-frequency one, but (as a consequence of the residual interaction) a pronounced new spectral feature in the proximity of the classical surface plasmon (inspection of the charge density shows[10] that it is indeed a surface excitation which is strongly coupled to the particle–hole pair in its neighborhood). Because this is the analog to Landau damping for the case of a discrete spectrum, we termed this behaviour Landau fragmentation. It

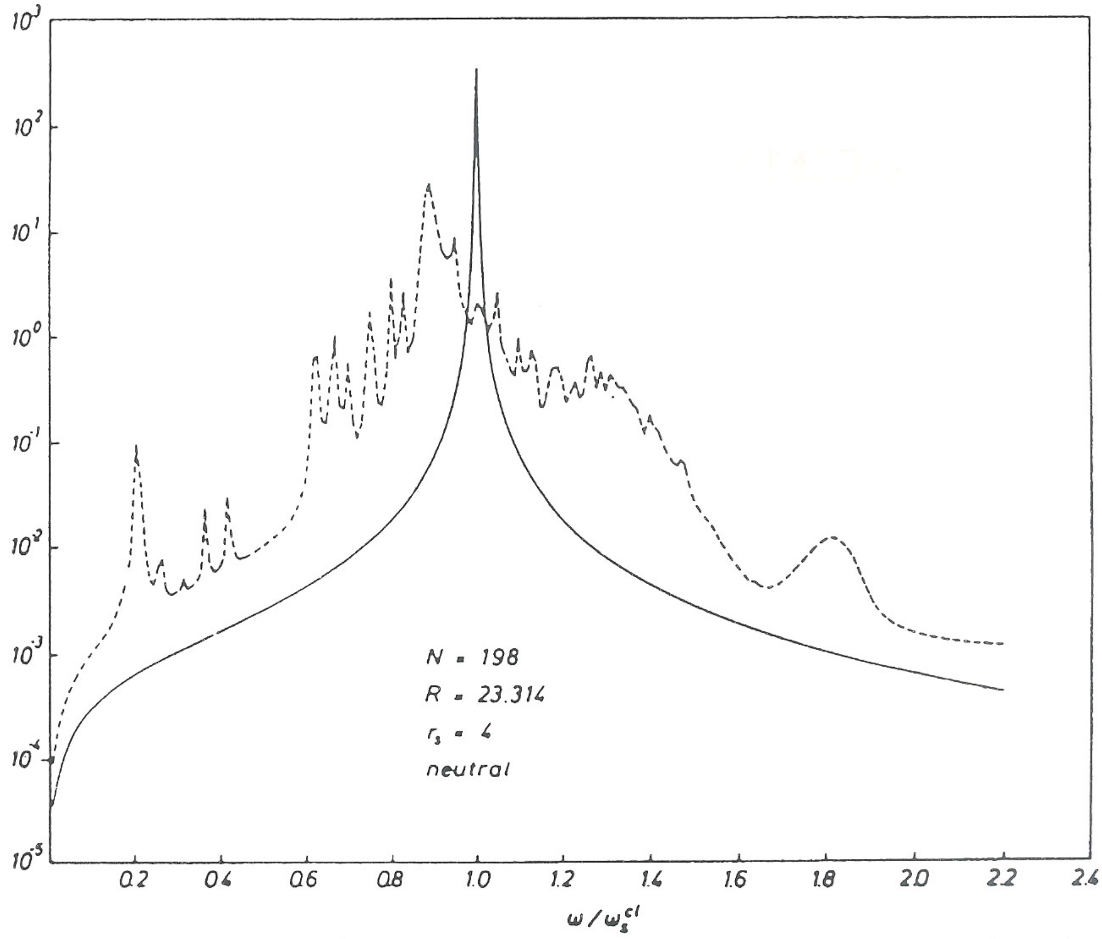

FIGURE 2 Typical absorption curve for the TDLDA applied to the jellium model for the specific example of Na_{198}. Continuous curve: Size-independent classical absorption; dashed curve: size-dependent quantum correction. The character of the various types of excitations can be inferred from inspection of the induced charge density (Ref. 10). In this way three different types can be identified: (1) surface plasmon (peak at 0.88), (2) the precursor of the volume plasmon (hump at $\sqrt{3}$), and (3) various dressed single pair lines (the many spikes). Only the surface excitation has considerable oscillator strength; the optical excitation of the other modes is a so-called quantum size effect. Within the jellium model the particle radius R, the number N of delocalized electrons ($N = 198$) and the Wigner–Seitz radius $r_s = 4$ in a.u. are interrelated by $R = N^{1/3} r_s$. The frequency ω of the incoming photons is scaled with the classical surface plasmon frequency ω_s^{cl}.

is a general phenomenon for particle numbers below 100 (Na_{40} has already been discussed in the literature[24,25]). But in contrast to Ref. 25, we found a considerable fragmentation even in Na_{92} and in

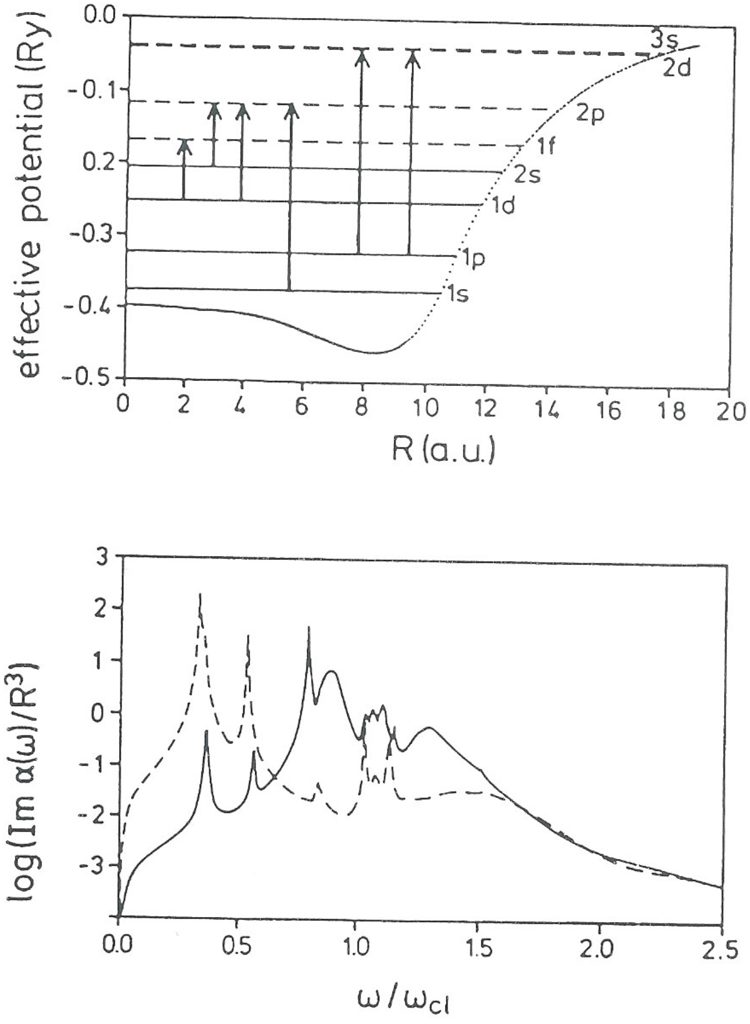

FIGURE 3 The absorption in Na_{20} (bottom part) and its interpretation. Continuous line: TDLDA, the nature of the double structure between 0.5 and 1.0 can be understood in two steps. In order to facilitate the character of the various humps and spikes, we show as a dashed line the independent particle response. This is the response at the LDA level (the analog to Hartree–Fock). Each of the spikes in this curve is a bare particle–hole pair, which corresponds exactly to one of the transitions marked as an arrow in the upper part of the figure, which shows both the occupied levels (continuous lines) and the empty levels (dashed lines) of the Kohn–Sham potential of Na_{20}. Upon turning on the residual interaction, two different things happen: First the bare pairs are transformed into dressed pairs (the spikes in the continuous TDLDA curve), and second there are new structures in the interacting curve: one hump between 0.75 and 1.0 and a further hump around 1.25. Both humps are collective in nature. The low-frequency hump together with the low-lying dressed particle–hole pair constitutes the fragmented surface plasmon, whereas the hump around 1.25 relates to higher multipoles (analog to a similar phenomenon for a flat jellium surface). The reshuffling of low-frequency oscillator strength can clearly be seen (of course, *both* curves obey the so-called f-sum rule).

Na_{91}^{-},[26] which is roughly in agreement with recent experimental data of H. Haberland.[27]

Recently, two of us have investigated the effect of the ionic skeleton on surface plasmons in jellium clusters.[28] The preliminary result is that the effect of the ions is essentially to change the volume of delocalization for the loosely bound electrons with the effect that it improves the performance of the TDLDA with respect to experiment. In a recent work,[25] Yannouleas has explicitly demonstrated within an equivalent formulation to the TDLDA (namely the matrix-RPA, which detours via determination of wave functions and eigenvalues, and calculates the optical absorption afterwards, whereas the TDLDA focuses directly on the polarization propagator) that the bulk limit towards the classical Mie plasmon is properly approached by this type of theory. Hence, in our view, the only thing which is missing now is a quantitative theory of surface-plasmon damping for large- and intermediate-size clusters. Such a theory can be developed along the line of Ref. 28 (and Ref. 9 in this work).

4. SUMMARY AND CONCLUSION

The TDLDA applied to the jellium model for metal clusters is able to account for the main features of the dynamical response of metal clusters, especially in the case of the alkaline metals. This is true because pseudopotential perturbation theory[28] shows that the monopole part of the potential is quite similar to the jellium potential. Consequently, for these metals, the present theory gives not only qualitatively, but also quantitatively, all the main features of the dynamical response, except for the surface-plasmon damping, which can only be obtained by a better description of the ionic structure. The situation is different for the noble metals (Cu, Ag, Au). Here, due to the presence of the d-electrons, we need to couple the free s-electrons to the deeper-lying d-electrons in very much the same way as we know it from, e.g., bulk silver.

As already discussed above, the TDLDA should be able to work in these materials, too, if the proper wave functions for the single-particle states are used. At the very end we want to comment about some confusion in the literature.

Whereas there is absolutely *no* doubt that very small clusters (e.g., Na_8) show collective excitations of the eight delocalized electrons, one *can* argue whether or not one should use the term "plasmon" for this excitation mode. We think one should, because physically it is exactly the same driving force, namely the electrostatic attraction, caused by the charge imbalance, which is active in both cases; and the kinematic features are the same in both cases: Essentially *all* the electrons are moving against a rigid ionic background. So whereas microscopically there is *no* reason to avoid the term "plasmon," macroscopically, one should be a bit careful, because the volume plasmon is a longitudinal excitation, whereas microscopically it is a mixed mode [this is the reason for its weak excitation (see in Fig. 2 the hump around 1.0)]. Of course, in cases like Na_{20}, the problem is very complex, because it is a new phenomenon—typically for clusters—that the plasmon is *not* above the particle–hole part of the spectrum, but within. Here we have a problem very similar to that with the volume plasmon at large wave vectors in the NFE-metals. In order to contrast it to the simpler situation, we introduced the term "fragmented plasmon."

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