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Theory of electronic excitations in coated metal particles: Jellium-on-jellium model

W. Ekardt
*Abteilung Elektronenmikroskopie, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6,
D-1000 Berlin 33, West Germany*

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Electronic excitations in coated metal particles are investigated within the framework of a self-consistent spherical jellium-on-jellium model (the spherical analog to Lang's chemisorption model for flat surfaces). With use of the calculated single-electron potential in the ground state, the time-dependent local-density approximation is applied to study the existence of a variety of collective modes such as surface modes, interface modes, and overlayer-volume modes. The results are compared with the Eguiluz's work, which used the same model to study collective motion in flat metallic overlayers.

I. INTRODUCTION

The study of the dielectric properties of coated metallic particles has a rather long history. Beginning with the classical work by Aden and Kerker,[1] who studied the problem because of its relevance to radar meteorology, there has been renewed interest in theoretical work in the late 1970s,[2-5] when the systematic experimental investigation of small metal particles began. In these studies one is very often confronted either with naturally grown oxide layers on small metallic nuclei or with metallic particles grown on a dielectric core. Hence there is a natural interest in the dielectric properties not only of the *bare* metal particles but also in the dielectric properties of the *coated* ones.

There is no doubt that in the case of a large nucleus and a thick coating classical optics can be applied to understand the gross features of the experimental data. However, for a detailed understanding of the dielectric properties of coated metal particles having diameters of some 10 Å or so, a microscopic theory is inevitably required because—as has been shown before for "bare" metallic particles[6-11]—classical, macroscopic electrodynamics does not hold down to those dimensions. Hence all the research results obtained on the basis of using macroscopic dielectric constants[2-5] must be considered with care and, possibly, revised.

Of course, the understanding of the dynamical electronic properties at a truly microscopic level of, e.g., an Ag nucleus coated with, e.g., Xe is strictly impossible for the time being. The best we can do at this level is an all-electron calculation for the *ground-state properties* of a cluster consisting of a very small number of atoms[12] and *dynamical* calculations for very simple molecules.[13,14] Hence we have either to stop or to resort to some simplifying microscopic model systems aimed at an understanding of only certain features of the dynamical response of coated metal particles. Experience has shown that, in the case of bare clusters of the alkaline-earth metals, the spherical jellium model[8-10,15-17] seems to be able to contribute to an understanding of a variety of experimental results such as abundance numbers in the beam,[18,19] the static polarizability,[20] and certain features in the number dependence of the photoionization threshold.[21] Because there is a strong corroboration of the approximate validity of the jellium description of small metal particles by recent pseudopotential calculation for Na (Ref. 22) and Li (Ref. 23) (if the number of atoms is not too small and assuming the cluster has a high symmetry), it seems to be promising to extend the jellium description to coated particles. Hence the model we are going to discuss is a spherical analog to what has been done quite recently by Eguiluz for flat surfaces,[24] namely, to study the dynamical electronic properties of Lang's chemisorption model.[25]

The actual reason for doing these calculations is that experiments on clusters of mixtures of two alkalis are presently underway.[19] One of the main issues here is the following: Given N_1 atoms of alkaline metal 1 and N_2 atoms of alkaline metal 2, there are at least three simple structure alternatives: Either species 1 (2) coats species 2 (1) *or* the two form a structureless alloy. Which of these alternatives will be experimentally observed cannot be said *a priori*, not even on an energetic argument, because it is generally unclear whether energetics alone is responsible for the observed cluster formation or whether kinetic factors lead to an explanation of the observed abundances.[26] Aside from these principal remarks, it is an interesting problem in itself to see how different (or how similar) the dynamical response is if a low-density jellium coats a high-density one or vice versa.

Among the key problems concerning the dynamical response of a coated metal particle is the following: Classical optics tells us[2-5] that for a coated (metal-on-metal) particle two collective modes are formed which, generally, are coupled interface-surface modes. In a *planar* geometry and in the thick-coating limit the classical frequency of the interface mode is $\frac{1}{2}(\omega_1^2+\omega_2^2)^{1/2}$ with $\omega_i^2=4\pi n_i e^2/m$ and n_i $(i=1,2)$ the electronic densities. Hence this mode is—in a description *with* spatial dispersion—inevitably in the volume plasmon continuum of the lower-density metal and, for this reason, heavily damped. As remarked by Paranjape,[27] it is therefore now generally realized that *localized* collective modes cannot exist at the interface between two extended metals. The only wave we can expect is a resonancelike structure.

For the spherical analog of this problem the situation changes a little. Since for a sphere every mode is size quantized, a *continuum* of volume plasmon modes does not exist.[9,10,28] Hence, from *this* point of view, an interfacial mode could be expected to exist. However, as we know from our earlier study,[8,9,29] Landau decay is an efficient damping mechanism for every kind of collective motion as—due to the very presence of the spherical surface—all the excitations are coupled together. Therefore, the interfacial mode can be expected to be heavily damped out, as it will be generally located within various bound-continuum single-electron transition regions. Because the number of these channels and the coupling matrix elements will be different in the two differing situations, $n_i \gtrless n_{\text{ex}}$, it might happen that in one case the interfacial mode is completely destroyed, whereas in the other case it is merely a heavily damped resonance. Hence we see that even within a microscopic approach a general answer concerning the existence of the interfacial mode cannot be given.

There is yet another important effect which, in the limit of a very thin coating, can prevent any kind of collective interfacial mode from existing. Classically, we have, by definition, a sharp density edge between the spherical core and the coating density shell. Quantum mechanically we need a certain thickness for the formation of an interfacial step in the electronic density.[24,30] As we shall see below, for too thin a shell the electrons relax across the jellium double step in very much the same way as they do across a single step (but, of course, with a different exponential decay parameter). Therefore, from this point of view the formation of an interfacial mode is not to be expected if there is no genuine interfacial electronic density because of the very gentle electronic charge relaxation across the double step (as if there were only *one* step to screen out).

The method we are going to apply is self-consistent in a twofold sense. First, the ground-state electronic charge density and potential are determined by solving the Kohn-Sham equations[31] for the jellium-background double-step problem up to self-consistency. On top of this first step the electronic response properties to external fields are determined within self-consistent-field theory by a method which has become known as time-dependent local-density approximation (TDLDA).[32] This method, which has a structure similar to the random-phase approximation with exchange (RPAE),[33] is on a firm theoretical basis only for zero frequency. Its use for finite frequencies is nothing other than an *unproven* extrapolation out of $\omega = 0$. However, its repeated use in understanding and explaining various dynamical processes in atoms,[32,34–36] molecules,[13,14] metal clusters,[9,10] planar metal surfaces,[37] and metallic overlayers[24] has made it clear that the method "works." Even more important in the context in which we are going to use the TDLDA is the following: As important as the exchange-correlation interaction V_{xc} generally is, in the frequency range in which we are interested, it is *not* decisive for the formation of collective behavior (in sharp contrast to the excitonic effects in the spectrum where it is certainly not allowed to use the form of V_{xc} which we adapt here). The direct Coulomb interaction would, qualitatively, do the job—which means simple RPA, based on the Kohn-Sham orbitals. For the latter there is increasing agreement regarding in which sense they can be used to calculate the excitation spectrum.[38–40] From this point of view the most serious flaw of the TDLDA is the frequency independence of the exchange-correlation interaction, which mainly amounts to a neglect of relaxation effects in the single-particle levels. For the latter effect, Zangwill and Liberman have shown (empirically)[35] how it can be accounted for in cases where it is important. For the problem at hand, these effects are not very important because the relaxation of the occupied valence levels is, due to the extended nature of all the orbitals, nearly level independent.[41] Hence, in a first approximation, one could take into account those effects by a rigid shift of, e.g., the absorption spectrum.

Due to the specific approximation for V_{xc} within the TDLDA, the asymptotic Rydberg states are missing in the spectrum. For a discussion of this point the interested reader is referred to the original paper by Zangwill and Soven.[32]

The rest of this work is organized as follows: Sec. II contains the ground-state results for the various model systems, Sec. III gives a discussion of the static and dynamical polarizability, Sec. IV turns to a discussion of thin-film size effects, and Sec. V is the conclusion.

II. GROUND-STATE PROPERTIES

A. The model

The homogeneous, one-component spherical jellium model is uniquely defined by two parameters, the electron density parameter in the bulk, r_s, and the number of atoms to be described, N. The radius R follows then as $R = N^{1/3} r_s$, and the problem can be solved as described in detail in Ref. 17.

For the coated spherical jellium problem we need at least one further piece of information. As mentioned in the Introduction, for a two-component system of N_1 atoms with electronic density parameter $r_{s,1}$ and N_2 atoms with electronic density parameter $r_{s,2}$, we have at least three different alternative "structures" to consider: "1" coats "2," or vice versa, and the homogeneous "alloy." In the first two cases we need more information whenever there are no atoms to build an integer number of coating layers. In this case we have, at least, two alternatives: First, Warner's model,[42] which determines the thickness d of the outermost shell from the number N and the *bulk* density r_s via

$$[(R_i + d)^3 - R_i^3]/r_s^3 = N$$

or second, Lang's model[25] which assumes d to be given from the lattice plane distance and, consequently, calculates for an incomplete number of layers a mean density r_s' for the outermost layer (for details see Ref. 25). Of course, for a complete number of layers both models agree.

In the present study we choose Warner's model because of its correspondence to what has been done before in all the *classical studies*.[2–5] But, of course, there would be no intrinsic problem in solving the spherical analog to Lang's model *if* the "spherical" lattice constant were known. Such a number can, ideally, be inferred from extended x-ray-absorption fine structure measurements. But to the best of my knowledge, those results are not yet published. In the universal example we are going to discuss, this problem does not matter at all, because the numbers correspond *approximately* to full monolayers.

The model system we are studying in this section corresponds to 40 atoms of Na, $r_s=4$, and 18 atoms of Cs, $r_s=6$.[43] The total radius, R_{ex}, corresponding to the spherical jellium model is given by (in Bohr a.u.)

$$R_{ex}=(4^3\times 40+6^3\times 18)^{1/3}\approx 18.613\ .$$

The inner radius, or the radius of the core, is given either by

$$R_i=4\times(40)^{1/3}\approx 13.680$$

or by

$$R_i=6\times(18)^{1/3}\approx 15.724\ ,$$

depending on the case under study.

In the first case (Cs coats Na) the example corresponds to approximately one spherical monolayer coverage of Cs because

$$4\pi R_i^2/\pi(r_s^{\text{Cs}})^2\approx 20.8\ .$$

In the second case to consider we have

$$4\pi R_i^2/\pi(r_s^{\text{Na}})^2\approx 61.81\ .$$

Hence it is in this case where Warner's model and Lang's model would give slightly different results. In the third case, the "alloy," no core radius is needed but, instead, we define a mean ionic background density as

$$r_{s,\text{alloy}}^3=(N_1r_{s,1}^3+N_2r_{s,2}^3)/(N_1+N_2)\ ,$$

which gives $r_{s,\text{alloy}}\approx 4.808$. As we shall see below, all three alternatives give rather different results, not only concerning the ground state but also concerning the response properties to external fields.

B. Results

To obtain the ground-state electronic density and single-particle potential, we had to solve the Kohn-Sham equations pertaining to the various background potentials following from the three alternatives discussed in Sec. II A. This procedure was discussed at length in Ref. 17 and will not be repeated here. The interested reader is referred to that work (see also Refs. 10, 15, and 16).

(i) Cs covers Na: The result of this "natural" coating is shown in Fig. 1. We see that the Cs edge does not produce any visible peculiarity in the electronic charge density. Instead, the electrons relax across the double edge in a very soft and gentle way. Especially, there is no visible hint of two different exponential decay lengths (or tunneling rates into the vacuum), and a glance at the potential shows why: There is *no* constant potential region which could produce any kind of constant electronic density. The filled one-particle levels in this example are 1*S*, 1*P*, 1*D*, 2*S*, 1*F*, 2*P*, and 1*G*, in that order.[44] Thus the level ordering is the same as in the case of 58 atoms of Na. We believe this to be quite natural as the "adsorption" of Cs fits ideally the formation of the selvedge. The sole, yet important, effect is that the surface barrier is considerably softer than in the case of pure Na (which *does* have consequences on the level scheme for a larger number of atoms, see below). Most important is the following observation (conjecture): Both from the charge density and from the potential there is no pronounced hint of the formation of an interface and, as a consequence, the formation of an interfacial mode is *not* to be expected. We shall confirm this conjecture in the next section.

(ii) Na covers Cs: The charge density and single-particle potential are shown in Fig. 2. This is a rather unusual surface behavior (compared to the bare surface) which has a rather unusual consequence. First of all, if the same quantum states are filled as in case (i), the resulting level ordering is as follows: 1*S*, 1*P*, 1*D*, 1*F*, 1*G*, 2*S*, and 2*P*. However, with these levels occupied the *unoccupied* level 1*H* is *below* the uppermost filled level 2*P*. If, therefore, the level 1*H* is partially filled with just six electrons, the now *unoccupied 2P level is below the fractionally filled level 1H*. Hence both configurations contradict the "Aufbau principle" and we have evidently to allow fractional occupation numbers[45] to obtain a stable ground state. Instead of going into this very intricate and fundamental problem, we leave the density as it is—mainly because there is *no* significant difference between the two

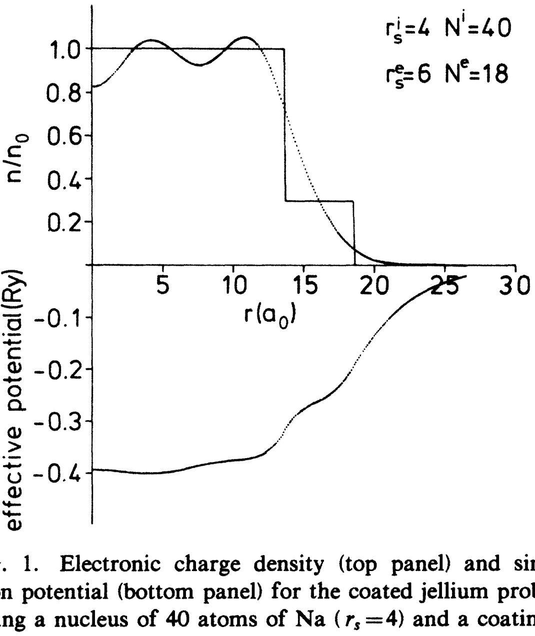

FIG. 1. Electronic charge density (top panel) and single-electron potential (bottom panel) for the coated jellium problem modeling a nucleus of 40 atoms of Na ($r_s=4$) and a coating of 18 atoms of Cs ($r_s=6$). The electronic charge density is in units of the bulk density of Na, $n_0=1/[(4\pi/3)r_s^3(\text{Na})]$, and the potential is given in units of Ry. The spatial coordinate is in Bohr atomic units, a_0. The straight double edge in the top panel gives the jellium-background double edge. For the determination of the radii see text.

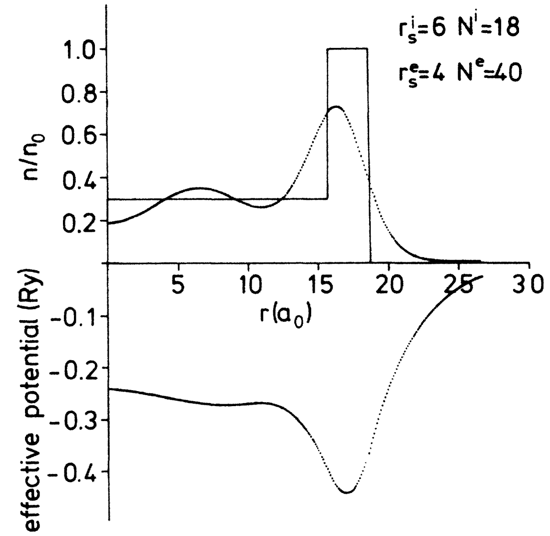

FIG. 2. Same as Fig. 1, but for a nucleus of 18 atoms of Cs and 40 coating atoms of Na.

configurations. For the main problem we are interested in, namely, the formation of collective motion, this point is of marginal importance. Again, already a glance at the charge density and the single-particle potential makes it clear that a formation of an interface mode is most unlikely. Even the formation of a "simple" surface mode seems to be greatly hampered, simply because the charge density is in every way too inhomogeneous. We shall see in the next section to what extent these qualitative conclusions are confirmed by the detailed calculations to follow.

(iii) Cs-Na alloy: Electronic charge density and single-particle potential pertaining to this example are shown in Fig. 3. Although the charge density is rather inhomogeneous, a surface region can be defined in a meaningful way and, for this reason, a surface mode *is* to be expected.

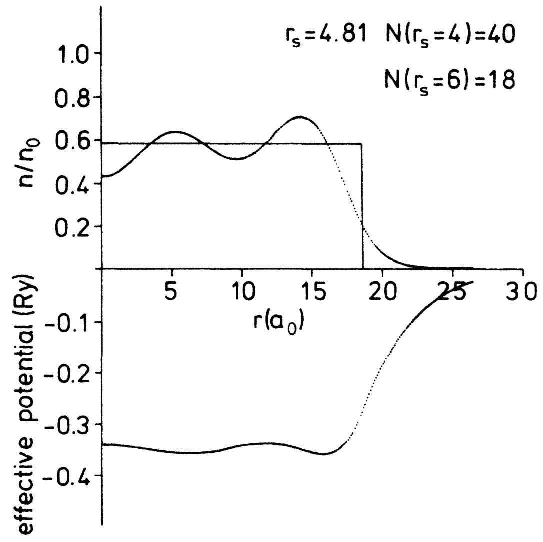

FIG. 3. Charge density and potential for a "jellium alloy" consisting of 40 atoms of Na and 18 atoms of Cs.

For all three examples presented above, the following general complication comes into play: As we observed for the homogeneous[9,29] one-component spherical jellium problem, in small physical objects such as atoms, molecules, and clusters, collective motion interferes strongly with single-pair motion. For this reason it is difficult—eventually impossible, for very small particles—to identify collective peaks. The general problem does not change due to coating the particle. Therefore, we expect for the coated particle again a strong mixing between single pairs and collective excitations. With this remark in mind we turn to a discussion of the dynamical properties.

III. RESPONSE PROPERTIES

The response properties are calculated within the TDLDA.[32] Because the application of the formalism to the problem under discussion was described at length in Refs. 8–10 and 29, it will not be repeated here. We only sketch the underlying physics, with a few remarks.

Being a self-consistent-field theory, all the many-particle aspects of the problem are stored in an effective field to which the electrons respond as if they were independent. Since due to their quantum nature the electrons have both *direct* Coulomb interaction and additional exchange interactions (plus correlations), the effective field is made up from the external field, the induced Coulomb field, and the induced exchange-correlation field.

For the static case, $\omega=0$, we have again a ground-state problem to solve. If the problem is solved with *linear-response* theory and if local-density approximation is considered to give a good description of the response, we immediately come up with

$$(dV_{\rm xc}/d\rho)\delta(\mathbf{r}-\mathbf{r}')$$

as an additional interaction between particle-hole pairs in the *excited* state (with respect to the field-free ground state). Here, $dV_{\rm xc}/d\rho$ is the density derivative of the exchange-correlation potential in the field-free ground state and $\delta(\mathbf{r})$ is the δ function. We see that the response properties of the system are uniquely defined in terms of the field-free ground state.

Up to this point the formalism is on a firm theoretical basis. It is from a formal point of view very similar to the old-fashioned RPA with exchange. The static polarizabilities obtained in this way are certainly directly comparable with experimental data. For $\omega\neq0$ there is *no* formal proof for the validity of the formalism. It requires *simple faith* to rely on the utility of the procedure. However, as we have indicated in the Introduction, there is increasing evidence that results obtained in this way *do* agree with the gross features of the response in a variety of rather *different* systems. Hence it seems to be not unwarranted to apply the formalism for the problem under discussion.

To obtain the absorption spectrum we must calculate the dynamical polarizability $\alpha(\omega)$, whose imaginary part is the key quantity for lossy processes.[9,29] Therefore, we concentrate on this quantity. Excitation modes of the system show up as humps or spikes in Im$\alpha(\omega)$ and their character as being collective or single-pair can be analyzed with methods discussed at length in Refs. 8, 9, and 29. For reasons of brevity, the discussion is not repeated here; only the results are presented.

Figure 4 shows the Im$\alpha(\omega)$ (continuous line) in units of the classical, static polarizability of the sphere, R^3, as a function of the normalized frequency $\omega/\omega_s^{\rm cl}({\rm Na})$ with $\omega_s^{\rm cl}({\rm Na})$ the classical dipolar surface plasmon frequency of a Na sphere. Note that Imα is given on a logarithmic scale. The spectrum consists of just one collective mode around 0.6 and a number of particle-hole pair-related structures. The character of the collective mode is neither surface nor interface; it is a true mixed mode. The important feature to note is that there is definitely *no* second collective mode. The spectrum is compared with the classical one, shown as thick dots. As anticipated above, the classical spectrum consists of two collective modes which are coupled surface-interface modes. They are obtained in a straightforward way by solving Maxwell's equations in the nonretarded limit for the electrostatic potential

$$V_l(r,\theta)=V_l(r)P_l(\theta)\ .$$

Here, l is the angular momentum and P_l means the Legendre polynomial of order l:

$$V_l(r)=\begin{cases} A_l r^l, & r\le R_i \\ B_l r^l + C_l r^{-(l+1)}, & R_i\le r\le R_{\rm ex} \\ -r^l + D_l r^{-(l+1)}, & r\ge R_{\rm ex}\ . \end{cases}$$

In these equations, D_l is, by definition, the classical polarizability. If $\epsilon_i(\omega)$ and $\epsilon_{\rm ex}(\omega)$ denote the classical dielectric constants of the nucleus and the coating material, the l-pole polarizability can be shown to be given as follows (with $L\equiv(l+1)/l$)

$$D_l/R_{\rm ex}^{2l+1}=\frac{[(\epsilon_{\rm ex}-1)(\epsilon_i+L\epsilon_{\rm ex})(R_{\rm ex}/R_i)^{2l+1}+(\epsilon_i-\epsilon_{\rm ex})(1+L\epsilon_{\rm ex})]}{[(\epsilon_{\rm ex}+L)(\epsilon_i+L\epsilon_{\rm ex})(R_{\rm ex}/R_i)^{2l+1}+L(\epsilon_i-\epsilon_{\rm ex})(\epsilon_{\rm ex}-1)]}\ .$$

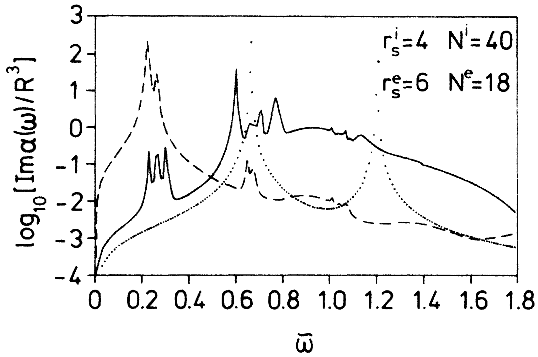

FIG. 4. Imaginary part of the dynamical polarizability $\alpha(\omega)$ of a coated metal sphere consisting of a nucleus of 40 atoms of Na and 18 coating atoms of Cs. The polarizability is scaled with the corresponding static classical result R^3, with $R=\{40[r_s({\rm Na})]^3+18[r_s({\rm Cs})]^3\}^{1/3}$, where $r_s({\rm Na})=4$ and $r_s({\rm Cs})=6$. The frequency ω is scaled with the classical dipolar surface plasmon frequency of Na, $\omega_s^{\rm cl}({\rm Na})=\omega_p({\rm Na})/\sqrt{3}$. TDLDA: solid line. Classical result: black dots. LDA: dashed line. In sharp contrast to the classical result, the TDLDA does not reveal a high-frequency collective pole. The reason is discussed in the text. On comparing the LDA with the TDLDA we clearly see how collective motion is formed at the cost of single pair oscillator strength.

Poles in the polarizability give, by definition, the eigenmodes of the system. Using free-electron dielectric constants ϵ_i and $\epsilon_{\rm ex}$ with plasma frequencies pertaining to $r_{s,i}=4$ and $r_{s,{\rm ex}}=6$ and using a "numerical" damping[46] of 10 meV, the dotted line of Fig. 4 is obtained for ${\rm Im}(D_l/R_{\rm ex}^{2l+1})$ in the case of $l=1$.

The dashed line in the figure gives the independent electron result and shows how collective modes are formed at the cost of single pairs. For a general discussion of this point see Refs. 9 and 29.

The next figure (Fig. 5) shows the spectrum at various levels of sophistication for the opposite case, namely, Na coats Cs. Qualitatively, the same result is obtained as before. However, the particle-hole pair structures are much more pronounced (because they carry more oscillator strength) and a glance at the corresponding single-particle potential, Fig. 2, makes immediately clear the reason. Compared to the potential in Fig. 1, the potential barrier is much steeper, which means the momentum providing "surface scattering" (in a dynamical picture) is more efficient.[47] Especially remarkable is the huge broad hump around 1.3 on the left of the classical high-frequency mode which has no counterpart in the independent electron spectrum (dashed line).

Finally, Fig. 6 shows the results for the "alloy" with $r_s'=4.808$. This figure is very similar to results published earlier for $r_s=4$,[8,9] hence no further comment will be given.

As to the *static* screening properties, both the application of sum rules[48,49] and direct calculations show that the

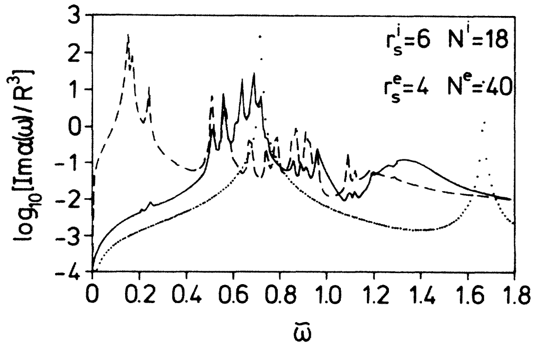

FIG. 5. Same as Fig. 4, but for a nucleus of 18 atoms of Cs and 40 coating atoms of Na.

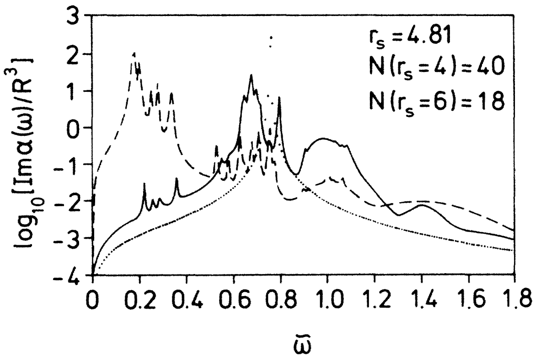

FIG. 6. Same as Fig. 4, but for the jellium alloy. Note that the hump around $\tilde{\omega} \approx 1.0$ does not mean a collective effect because the dashed curve shows a similar behavior. In contrast, the hump around 1.4 *is* a collective volume plasmon excitation belonging to a jellium with $r_s^{\mathrm{alloy}} = 4.808$. The huge peak around 0.68 corresponds to the considerably red-shifted dipolar surface plasmon frequency of a jellium sphere with $r_s = 4.808$. Its classical frequency in those units is at 0.761.

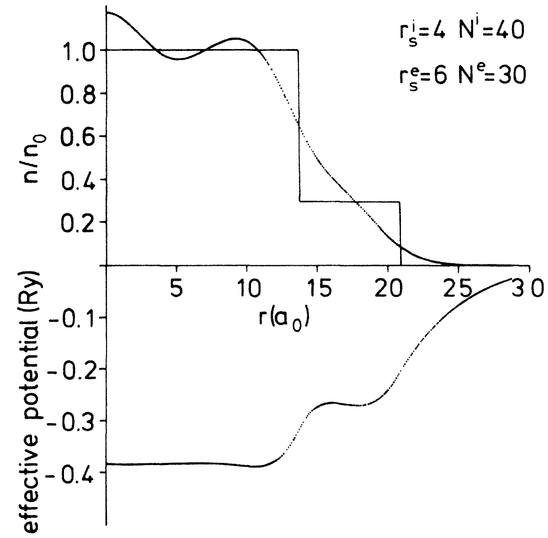

FIG. 7. Same as Fig. 1, but for 30 atoms of coating Cs instead of 18. In contrast to Fig. 1, we observe two different decay lengths of the electronic charge screening the double edge of the jellium background.

static polarizability $\alpha(0)/R_{\mathrm{ex}}^3$ is biggest for the case Na covers Cs. The specific results are as follows: Na/Cs 1.24; Cs/Na 1.04; alloy 1.16. Thus one should have a chance to decide—by the experimental determination of the static polarizability of a *series* of alkali mixtures—which case is realized. These experiments are underway.

IV. THIN-FILM SIZE EFFECTS

In this section we discuss thin-film size effects with Cs on Na as an example. Because the calculations are very time consuming, only three different film thicknesses are discussed, with the example already given as a reference. As we have seen, for a thickness of 4.93 a.u. the electrons relax with *one* decay length across the double jellium-background edge without any *visible* indication of two separate inhomogeneity steps. (See Fig. 1.) For this reason it is not too surprising that in the dynamical TDLDA spectrum, shown in Fig. 4, a second surface or interface mode cannot be detected. Perhaps the tiny hump around 1.1 is a remainder of the classical peak around 1.2.

The next thickness investigated (with the 40 core atoms of Na held fixed) corresponds to 30 atoms of Cs, which means a thickness of 7.15 a.u. The specific number results from the demand to have a uniquely defined ground state with only *completely* filled spherical shells (see discussion above). To be specific, the filled levels are (in this order) $1S$, $1P$, $1D$, $2S$, $1F$, $1G$, $3S$, and $2P$, with the last three levels nearly degenerate at -0.17360, -0.17196, and -0.17175 (in units of Ry). The potential (see Fig. 7) shows a pronounced double step around the inner radius, $R_i = 13.680$ a.u., and the charge density shows clearly *two* exponential decay lengths. However, there is definitely *no* constant-density region in the interfacial area from which a *dynamical separation* of the two surface decay lengths could be deduced. Hence it is not too surprising that in this case again the dynamical spectrum (Fig. 8) does not reveal a second "interface-derived" collective peak. The surface mode around 0.53 is red shifted compared to the case discussed before, and this seems to be a natural consequence of the fact that the surface of the coated particle becomes more and more Cs like.

Interestingly enough, even at a ("spherical") thickness of 7.15 a.u., with a core radius of 13.68 a.u., we have a *qualitatively* different excitation spectrum than we would expect on the basis of the classical picture, shown as black dots in the figure. Similar results were obtained by Eguiluz[24] for the dynamical behavior of *planar* alkaline metal films. Thus this result does not seem to depend on the details of the excitation spectrum of the substrate but only on whether or not there is a constant-density region, separating the interface from the surface. From this point of view it is a natural result that classically at every thickness a double-peak structure is obtained, whereas quantum

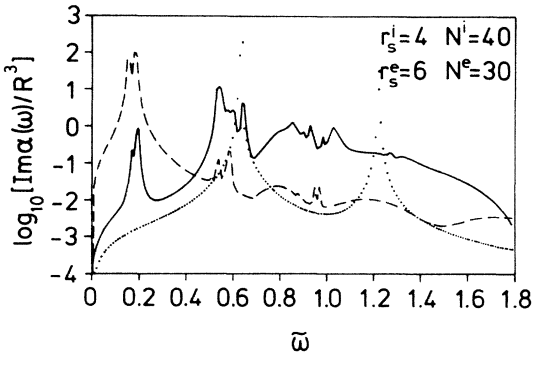

FIG. 8. Same as Fig. 4, but corresponding to the ground state shown in Fig. 7. As discussed in the text, even for a coating width of ~ 7.15 a.u. there is no hint of formation of a second collective peak, corresponding to the classical peak at ~ 1.2.

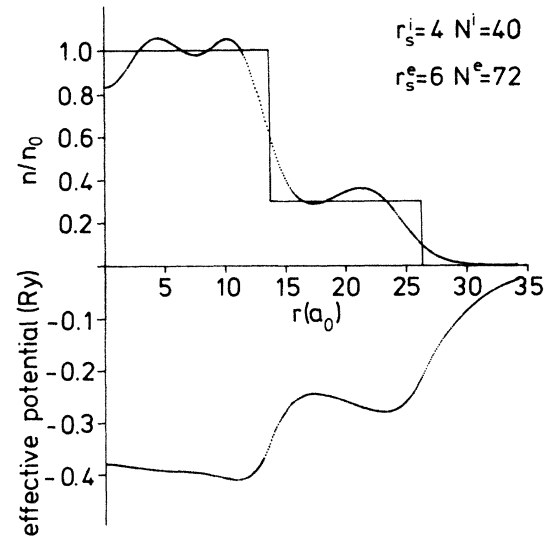

FIG. 9. Same as Fig. 1, but for 72 atoms of coating Cs instead of 18. We now see a pronounced plateau of electronic charge indicating the formation of a quasihomogeneous electronic Cs film. The coating width in this case is ~12.58 a.u.

mechanically we need a minimum thickness and a minimum size (see below) for a second peak to appear.

This interpretation is confirmed by results we obtained for the third example, namely, 72 atoms of Cs coating 40 atoms of Na. Here, the thickness of the shell is 12.58 a.u. and the total radius of the sphere is 26.26 a.u. The filled electronic levels are, in this order, 1*S*, 1*P*, 1*D*, 2*S*, 1*F*, 2*P*, 3*S*, 2*D*, 1*G*, 2*F*, 3*P*, and 1*H*. Ground-state charge density and single-electron potential are shown in Fig. 9 and the dynamical results are presented in Fig. 10.

The striking feature of these results is the following: Despite the fact that both the electronic charge density and the potential show up a pronounced double-step structure there is positively *no* hint of a second collective mode. This seems to indicate the *complete* breakdown of the classical picture and shows explicitly how misleading qualitative conclusions can be made solely on the basis of the (static) charge density. With this recognition in mind it does not seem too surprising that up to now even a qualitative understanding is lacking for such simple systems as (planar) Na on Al or Cs on Na. The excitation peaks found by electron-energy-loss-spectroscopy (EELS) measurements[50] do not fit the theoretical jellium-on-jellium TDLDA results by Eguiluz and Campbell[24] obtained for coverages up to two monolayers. This finding seems to indicate that—because of the *general* importance of single-pair transitions in extremely inhomogeneous configurations like thin films—the *dynamical* properties of the corresponding jellium model deviate considerably from the behavior at a truly microscopic level. This result is puzzling insofar as all-electron results obtained, e.g., for Cs on $W(001)$[51] gave an interfacial charge density which corresponds more or less to a polarized *metallic* bond. Even so, the dynamical experimental results obtained by Soukiassian *et al.*[52] show explicitly the breakdown of a simple jellium-on-jellium description and indicate the need for a fully microscopic dynamical response calculation.

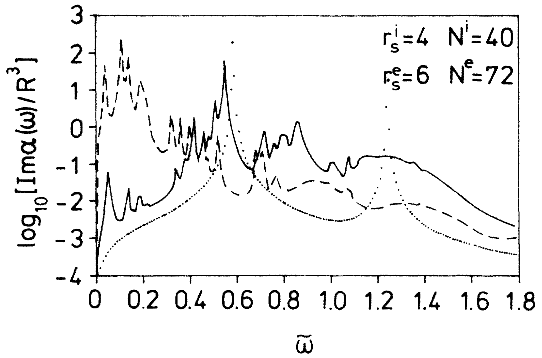

FIG. 10. Same as Fig. 4, but corresponding to the ground state shown in Fig. 9. Again, no second collective peak, corresponding to the classical one at ~1.2, can be detected. For further discussion see text.

IV. CONCLUSION

The dynamical properties of coated jellium spheres are investigated within the framework of the TDLDA. The results show clearly the breakdown of the very popular classical description based on the use of local dielectric constants. Even worse, there are serious hints that for planar—and probably also for spherical—films even a description like the "dynamical jellium model" based on the TDLDA is not adequate to account for the complex collective motion of the real response.

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