PHYSICAL REVIEW B
CONDENSED MATTER

THIRD SERIES, VOLUME 42, NUMBER 6 15 AUGUST 1990-II

Photoabsorption of small metal clusters: Surface and volume modes

Vitaly Kresin
Department of Physics, University of California, Berkeley, California 94720

(Received 27 December 1989; revised manuscript received 22 February 1990)

The size-dependent dynamic polarizability of small clusters of simple metals is calculated analytically. It is predicted that the photoabsorption spectrum should consist of two peaks, one corresponding to surface, and the other to volume collective excitations. Unlike the case of bulk matter, the volume mode in small clusters can be excited by photons; its oscillator strength decreases with increasing cluster size. The derived oscillator-strength distribution is shown to satisfy exact energy-weighted sum rules. The results are used to explain experimental photoabsorption data.

I. INTRODUCTION

Many properties of small clusters of simple metals are governed by the behavior of the delocalized valence electrons. They determine cluster stabilities, shapes, and the electromagnetic response.[1]

Collective oscillations of the valence-electron cloud[2,3] dominate the optical spectra of small alkali-metal clusters. In recent publications, an analytical derivation of the surface-plasma resonance frequencies of neutral[4,5] and ionized[6] metal clusters was presented. The calculation was based on the random-phase approximation (RPA), and made use of the statistical Thomas-Fermi description of the valence electrons in metal clusters, developed in Ref. 7. Excellent agreement with experimental data was obtained. In the present paper, this approach will be extended to an evaluation of the dynamic polarizability of metal clusters.

The analysis described below leads to the prediction that, in addition to the surface-plasma resonance, in small particles there should appear a higher-frequency dipole resonance peak, corresponding to the volume plasma oscillation in bulk metals. In small clusters, as opposed to the bulk, this excitation is capable of coupling to photons. Our calculation explains the observation[2] that in sodium clusters the surface-plasma resonance does not exhaust 100% of the valence electron oscillator strength. In addition, the dynamic polarizability will be shown to satisfy some general and rigorous sum rules.

The plan of the paper is as follows. In Sec. II, the existence of the second resonance mode is demonstrated. Section III describes the calculation of the dynamic polarizability and the photoabsorption cross section. Oscillator-strength distribution and sum rules are the subject of Sec. IV, which also addresses the static electric polarizability of metal clusters.

II. RESONANCE FREQUENCIES

A. Equation of linear response

We begin by writing down a general equation describing a cluster in an external potential $v_0(\mathbf{r})\exp(i\omega t)$. The effective field, $V(\mathbf{r},\omega)\exp(i\omega t)$ is the solution of the integral equation

$$V(\mathbf{r},\omega)=v_0(\mathbf{r})+e^2\int\int\frac{1}{|\mathbf{r}-\mathbf{r}_1|}\Pi(\mathbf{r}_1,\mathbf{r}_2,\omega)V(\mathbf{r}_2,\omega)d^3r_1\,d^3r_2\ . \tag{1}$$

The second term on the right-hand side is the potential due to the induced cluster charge. $\Pi(\mathbf{r}_1,\mathbf{r}_2,\omega)$ is the irreducible polarization operator,[8,9] which describes the screening of the external field by the valence electrons (see Fig. 1). (We set $\hbar=1$ throughout the paper; also, we use the convention that the electron charge is $-e$.)

It has been shown[10] (see also the discussion in Ref. 5) that when the RPA expression for Π is expanded in powers of Δ/ω, where Δ is the single-particle level spacing (in metal clusters $\Delta\lesssim 0.1-0.3$ eV), the first-order result for Eq. (1) is

$$\left[1-\frac{4\pi n(\mathbf{r})e^2}{m\omega^2}\right]V(\mathbf{r})=v_0(\mathbf{r})-\frac{e^2}{m\omega^2}\int d^3r_1\,\mathbf{V}(\mathbf{r}_1)\nabla_{\mathbf{r}_1}\left[\frac{1}{|\mathbf{r}_1-\mathbf{r}|}\right]\cdot\nabla_{\mathbf{r}_1}n(\mathbf{r}_1)\ , \tag{2}$$

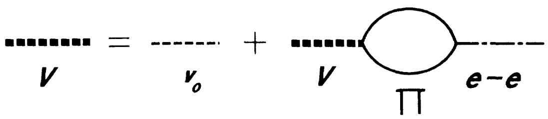

FIG. 1. Diagrammatic representation of Eq. (1). The external field v_0 is screened by the delocalized electrons in a cluster; the line "*e-e*" represents their Coulomb interaction. RPA consists of taking the lowest-order expression for the polarization operator Π.

where $n(r)$ is the number density of the valence electrons and m is the electron mass (the ω dependence of V is implied, but no longer explicitly indicated).

We consider spherical clusters, containing closed shells of valence electrons.[1] The electron density is then a function of the radial coordinate only: $n(\mathbf{r})=n(r)$. We define the dimensionless electron-cloud shape factor

$$g(r)\equiv n(r)/\rho_+ \;, \tag{3}$$

where ρ_+ is the number density of the positive background, treated as a uniform sphere of radius $R=a_0 r_s N_e^{1/3}$. Here N_e is the number of valence electrons in the cluster, r_s is the Wigner-Seitz electron-density parameter, and a_0 is the Bohr radius.

We are interested in electric dipole transitions; therefore, we take the external field to be

$$v_0(\mathbf{r})=-eE_0 z=-eE_0 r\cos\theta \;, \tag{4}$$

and the effective field

$$V(\mathbf{r})=f(r)\cos\theta \;. \tag{5}$$

Choosing the z_1 axis in Eq. (2) to lie along $\mathbf{r}$, we arrive, after some manipulations, at the following integral equation (cf. Ref. 5):

$$\frac{1}{r^2}\int_0^r dr_1\, r_1^2 g'(r_1)f(r_1)-2r\int_r^\infty dr_1\,\frac{1}{r_1}g'(r_1)f(r_1) = -3\frac{\omega^2}{\omega_p^2}eE_0 r+3\left[g(r)-\frac{\omega^2}{\omega_p^2}\right]f(r) \;, \tag{6}$$

where

$$\omega_p^2=\frac{4\pi\rho_+ e^2}{m} \tag{7}$$

is the bulk plasma frequency.

Differentiating (6) with respect to r, we obtain

$$\frac{2}{r^3}\int_0^r dr_1\, r_1^2 g'(r_1)f(r_1)+2\int_r^\infty dr_1\,\frac{1}{r_1}g'(r_1)f(r_1) = -3\frac{\omega^2}{\omega_p^2}eE_0-3\left[g(r)-\frac{\omega^2}{\omega_p^2}\right]f'(r) \;. \tag{8}$$

Together, Eqs. (6) and (8) suffice to determine $f(r)$.

When there is no external field present ($E_0=0$), these equations will have a nontrivial solution for certain values of ω. These eigenvalues are the resonance frequencies of the valence electron system. In Secs. II B and II C we consider the limits of a large sphere and a small cluster, respectively.

B. Macroscopic limit

The limit of a large spherical particle corresponds to the unit-step-function electron-density profile: $g(r)=1$ for $r<R$ and $g(r)=0$ for $r>R$. In this case, the derivative of $g(r)$ is a δ function: $g'(r)=-\delta(r-R)$, and Eq. (6) (with $E_0=0$) becomes

$$f(R)=\begin{cases}\dfrac{3R}{2r}\left[1-\dfrac{\omega^2}{\omega_p^2}\right]f(r) & \text{for } r<R \;,\\[2ex] \dfrac{3r^2}{R^2}\dfrac{\omega^2}{\omega_p^2}f(r) & \text{for } r>R \;.\end{cases} \tag{9}$$

These equations have two roots: $\omega=\omega_p/\sqrt{3}$ and $\omega=\omega_p$. The former corresponds to the surface plasmon and the latter to the volume plasmon. (In the first case, the solution is of the form $f(r)\sim r$ inside the sphere and $f(r)\sim r^{-2}$ outside. This is the dipole field of classical surface charge oscillations. In the second case, $f(r)$ vanishes outside and grows to a finite value on the inside. This implies that oscillations are taking place in the interior of the sphere; they do not involve the appearance of a surface charge.) There is also the root $\omega=0$, but it is easily shown to correspond to the trivial solution $f(r)\equiv 0$.

In Ref. 10, only the surface plasmon was identified as the solution to Eq. (6) in the macroscopic limit. In fact, it is clear that a large metal sphere should support both surface and volume plasma waves. The latter have vanishingly small oscillator strength (i.e., they do not couple to photons, see Sec. III A), but nevertheless represent a well-defined excitation.

C. Resonance frequencies in clusters

As discussed in Ref. 5, Eqs. (6) and (8) (with $E_0=0$) can be solved analytically. One makes use of the rapid decrease of $g(r)$ at the edge of the positive background sphere ($r=R$) and expands the integrands about this point. Two eigenvalues (resonance frequencies) are obtained:

$$6\left[\frac{\omega_\pm}{\omega_p}\right]^2=3g(R)+1\pm\{[3g(R)-1]^2+24q(1-3q)\}^{1/2} \;, \tag{10}$$

where the quantity

$$q\equiv\frac{1}{R}\int_R^\infty g(r)dr \tag{11}$$

measures the extent of the spill out of the valence electron cloud outside the positive background. Equation (10) is a general result, independent of the precise form of $g(r)$.

In Ref. 5, we focused on the root with the minus sign on the right-hand side, ω_-: in the macroscopic limit ($q\rightarrow 0$) it is the surface plasma resonance frequency. Based on the analysis in Sec. II B, we can now identify the physical meaning of the root ω_+. In the large-particle limit, we set $g(r)=1$ and $q=0$ (no spill out) in

Eq. (10), and recover the bulk-plasma frequency. Therefore, ω_+ corresponds, in the large-sphere limit, to the volume plasmon, and ω_- to the surface plasmon.

To obtain numerical results for the resonance frequencies, we employ the density distribution given by the Thomas-Fermi statistical description of the electronic structure of metal clusters developed in Ref. 7. The surface-plasma resonance frequencies calculated on the basis of this approach (see Refs. 5 and 6) are in excellent agreement with the experimental data for both neutral[2] and ionized[3] clusters. In contrast to the surface resonance frequency, ω_-, which increases rather fast with increasing cluster size, the volume-plasmon energy, ω_+, varies only very slowly with size, being $\approx 0.75\omega_p$ for clusters from a few up to hundreds of atoms in size. The reason for the decrease in resonance frequencies in clusters compared to macroscopic systems ("red shifts") is that the average electron density in clusters is smaller than in bulk, because of the spill-out effect.

III. PHOTOABSORPTION OF METAL CLUSTERS

A. Dynamic polarizability and absorption cross section

The dynamic polarizability[10,11] of the valence electron system is given by

$$\alpha(\omega) = -e^2 \sum_n \left[\frac{|\langle n|Z|0\rangle|^2}{\omega - \epsilon_{n0} + i\delta} - \frac{|\langle n|Z|0\rangle|^2}{\omega + \epsilon_{n0} + i\delta} \right]$$

$$= -2e^2 \sum_m \frac{\epsilon_{n0} |\langle n|Z|0\rangle|^2}{\omega^2 - \epsilon_{n0}^2 + i\delta} , \tag{12}$$

where the coordinate operator is $Z = \sum z_i$, the sum being over all the electrons.

The imaginary part of $\alpha(\omega)$ is related to the photoabsorption cross section:

$$\sigma(\omega) = \frac{4\pi\omega}{c} \mathrm{Im}\alpha(\omega) . \tag{13}$$

The dynamic polarizability can be calculated as follows. It is defined as the ratio of the induced electric dipole moment to the external electric field:

$$\alpha(\omega) = \frac{-e}{E_0} \int d^3r \, z n_{\mathrm{ind}}(\mathbf{r}) , \tag{14}$$

where n_{ind} is the induced valence electron density given by [cf. Eq. (1) for the effective field]

$$n_{\mathrm{ind}}(\mathbf{r}) = -\int \Pi(\mathbf{r}, \mathbf{r}_1, \omega) V(\mathbf{r}_1, \omega) d^3 r_1 . \tag{15}$$

The integral in Eq. (14) is similar to that in Eq. (1), and can be simplified in the same way. As a result, we obtain

$$\alpha(\omega) = \frac{-1}{3eE_0} \frac{\omega_p^2}{\omega^2} \int dr \, r^2 f(r) g'(r) , \tag{16}$$

$$= \frac{1}{3eE_0} \frac{\omega_p^2}{\omega^2} R^2 f(R) . \tag{17}$$

The function $f(r)$ is the solution of Eqs. (6) and (8). To obtain Eq. (17), we again made use of the sharpness of $g'(r)$ by expanding $r^2 f(r)$ around the point $r = R$. The quantity $f(R)$ can be found in a way, similar to the case of no external field (see Sec. II C and Ref. 5). Substituting this $f(R)$ into Eq. (17), we obtain the following result for the dynamic polarizability of the valence electrons in a spherical metal cluster:

$$\alpha(\omega) = -\frac{N_e e^2}{m} \left[(1-\eta) \frac{1}{\omega^2 - \omega_-^2} + \eta \frac{1}{\omega^2 - \omega_+^2} \right] , \tag{18}$$

where $\omega_\pm$ are given by Eq. (10), and

$$\eta = \frac{1 + \{[3g(R) - 1]^2 + 24q(1-3q)\}^{1/2} - 3g(R) - 6q}{2\{[3g(R) - 1]^2 + 24q(1-3q)\}^{1/2}} . \tag{19}$$

To find the imaginary part of $\alpha(\omega)$, and hence the photoabsorption cross section, we need to take into account the fact that the resonances corresponding to $\omega_\pm$ are in reality damped. Therefore the denominators in Eq. (18) contain small imaginary terms that give the resonance lifetimes. Consequently, the photoabsorption cross section consists of two Lorentzian peaks:

$$\sigma(\omega) = \frac{4\pi N_e e^2}{mc} \left[(1-\eta) \frac{\Gamma_- \omega_-^2 \omega}{(\omega^2 - \omega_-^2)^2 + \Gamma_-^2 \omega_-^4} + \eta \frac{\Gamma_+ \omega_+^2 \omega}{(\omega^2 - \omega_+^2)^2 + \Gamma_+^2 \omega_+^4} \right] , \tag{20}$$

where Γ_- and Γ_+ are the dimensionless damping constants.

From Eq. (19) one can see that as the cluster becomes large ($q \to 0$), the weight of the surface-plasma resonance peak approaches unity, and that of the volume plasmon vanishes. This is in accord with the fact[12] that in the bulk, volume plasmons do not couple to photons: light

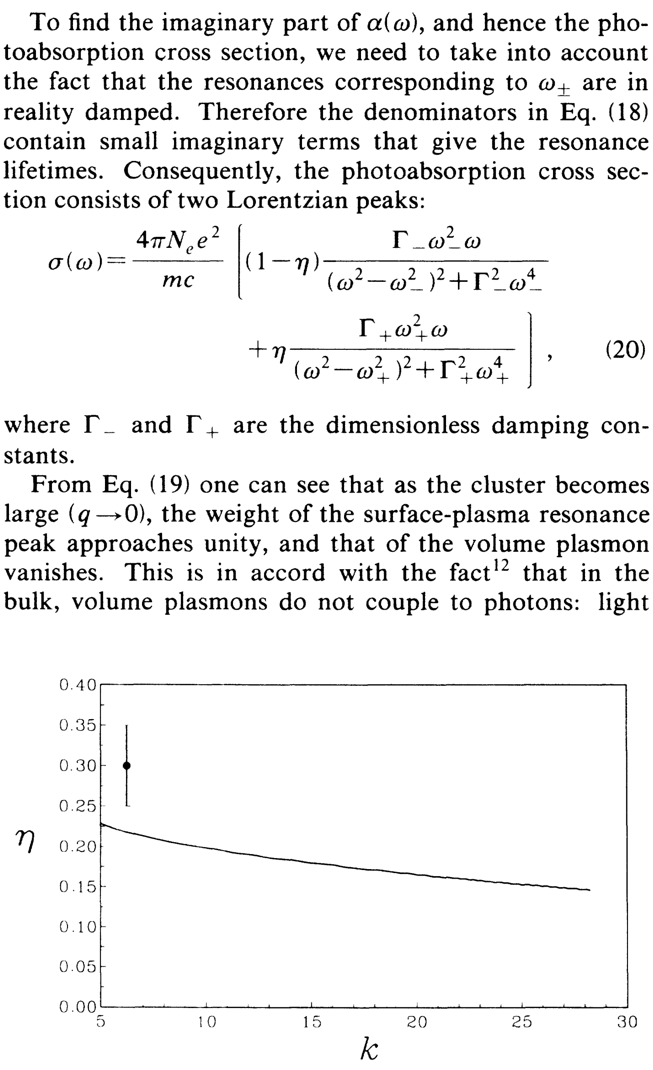

FIG. 2. Size-dependent fraction, η, of dipole oscillator strength contained in the volume mode [Eq. (19) in the text]. Cluster sizes are given in terms of the dimensionless parameter $k \equiv (12/\pi)^{1/3} r_s^{1/2} N_e^{1/3}$, which, in the statistical description, uniquely determines the valence electron density distribution (for example, for Na_n, $k = 3.11 n^{1/3}$; see Ref. 7 for details). Circle: $(1-\xi)$, where ξ is the measured oscillator strength contained in the surface-plasma resonance line of the Na_8 cluster, data from Ref. 2.

waves are transverse, whereas plasma waves in an infinite medium are longitudinal. In finite-sized particles, on the other hand, the volume mode can couple to light.

The weight factor η can be calculated from the density distribution given by the statistical Thomas-Fermi method.[7] Figure 2 displays this factor as a function of cluster size, and shows the results to be in agreement with the observation[2] that the surface-plasma resonance does not exhaust 100% of the oscillator strength in small sodium clusters. The oscillator-strength distribution in metal clusters is discussed in more detail below.

B. Discussion

There have been, to our knowledge, no direct observations of the volume dipole mode in the optical spectra of small (containing from a few to several hundred atoms) metal clusters, particularly free ones, where interaction with the substrate does not complicate the picture. The photoabsorption spectra of potassium cluster ions[3] suggest that most strength is concentrated in the surface mode, but the accuracy of these measurements is stated to be about 25%. Consequently, it would be interesting to carry out a spectroscopic search for the high-frequency volume dipole absorption peak in size-selected clusters.

A feature in a numerically calculated[13] time-dependent local-density approximation curve of the dynamic polarizability of sodium clusters has been termed a volume plasmon. However, this calculation predicted that the feature would be prominent in large clusters, and disappear in clusters with less than $N \cong 92$ atoms. Our conclusion, on the other hand, is that in small clusters the higher-lying resonance should be quite prominent, and should account for the oscillator strength missing from the surface-plasma resonance peak (see earlier).

Calculations based on the hydrodynamic model and the Drude dielectric function have predicted that in metallic spheres with diffuse electronic profiles, there would exist a number of additional higher-lying dipole surface modes[14,15] as well as many dipole volume modes,[16] the latter having frequencies higher than ω_p (the calculation in Ref. 13 also predicted a "blue shift" of the volume plasmon). Our calculation does not indicate any additional surface resonances, while predicting a red-shifted volume mode.

There is some experimental[2] as well as theoretical[17] indication that the surface collective resonance may in fact be split into two or more closely spaced lines. Within the framework of the method used here, this could come about if one took into account higher-order terms in the expansion of the polarization operator $\Pi(\mathbf{r},\mathbf{r}_1,\omega)$. In this case, the contribution of higher-energy single particle-hole transitions may split the resonance peak, while maintaining the average resonance excitation energy at the value given by Eq. (10).

A question of great interest is the origin of the line width $\Gamma_\pm$. The measured width of the surface-plasma resonance[2] ($\sim 10\%$ of the resonance frequency) is in disagreement with the simple $1/R$ scaling law proposed for larger particles.[18] As discussed in Ref. 2, there are probably several contributions to the damping of the collective excitations of the valence electrons, among them: excitation of electron-hole pairs [described by higher-order terms in the expansion of $\Pi(\mathbf{r},\mathbf{r}_1,\omega)$, see Ref. 10], coupling of the electrons to ion vibrations (vibronic interaction[19]) and to cluster shape oscillations,[20] and escape of cluster fragments into the continuum.

IV. OSCILLATOR STRENGTHS AND SUM RULES

A. Energy-weighted sum rules

The oscillator strength of state $|n\rangle$ of the cluster valence electron system is defined as $f_{n0}=2m\epsilon_{n0}|\langle n|Z|0\rangle|^2$. From Eqs. (12) and (18), or alternatively, (13) and (20), one can write

$$f_{n0}=\begin{cases}(1-\eta)N_e & \text{for } \epsilon_{n0} \text{ near } \omega_- \,,\\ \eta N_e & \text{for } \epsilon_{n0} \text{ near } \omega_+ \,,\\ 0 & \text{otherwise} \,.\end{cases} \tag{21}$$

We can use this result to check whether our calculation satisfies two rigorous sum rules for many-electron systems. The first of these is the well-known Thomas-Reiche-Kuhn sum rule[21]

$$S_0 \equiv \sum_n f_{n0} = N_e \,. \tag{22}$$

Clearly, this sum rule is satisfied by (21).

The other sum rule reads[21]

$$S_2 \equiv \sum_n \epsilon_{n0}^2 f_{n0} = \frac{4\pi}{3}\frac{e^2}{m}\int \rho_+(\mathbf{r})n(\mathbf{r})d^3r \,. \tag{23}$$

For a cluster with a spherical uniform positive background, this can be rewritten as

$$S_2 = \frac{N_e}{3}\omega_p^2\left[1-\frac{\Delta N}{N_e}\right] , \tag{24}$$

where we have used Eq. (7), and ΔN is the amount of the valence electron spill out:

$$\Delta N = 4\pi\int_R^\infty n(r)r^2\,dr \,. \tag{25}$$

We use Eq. (3), integrate Eq. (25) by parts, and then once again employ the fact that $g'(r)$ is sharply peaked near $r=R$. Expanding the factor r^2 in the integrand about this point and integrating, we find the following relation between the spill out and the parameter q defined in Eq. (11):

$$\Delta N = 3qN_e \,. \tag{26}$$

Thus the sum rule (24) can be written as

$$S_2 = \frac{N_e}{3}\omega_p^2(1-3q) \,. \tag{27}$$

One can see that Eqs. (21), together with the results (10) for the resonance frequencies and (19) for the weight factor η, satisfy the equality (27) exactly.

In Refs. 22 and 23, the sum rules (22) and (23) were used to extract the centroid and variance of the strength function for clusters. However, these quantities cannot be used to calculate the position and the width of a cluster absorption resonance. Since, as we have shown, there are two distinct peaks in the absorption spectrum, the centroid and the variance will give only the position of the "center of mass" of the peaks, and a measure of the distance between them. In fact, it is easy to see that the sum rule (24) could not possibly be satisfied if only the red-shifted surface plasma resonance peak, ω_- [see Eq. (10)], were present in small clusters.

Thus, in this section we have shown that our two-peak result is in precise agreement with two rigorous energy-weighted oscillator-strength sum rules, S_0 and S_2.

B. Static polarizability

In Ref. 5, we calculated the static electric polarizabilities, α_0, of metal clusters, under the assumption that the surface-plasma resonance exhausts 100% of the valence electron oscillator strength. The results were in excellent agreement with the experimental data.[24] Here we would like to analyze what effect the oscillator-strength distribution (21) will have on α_0.

The static polarizability of a metal cluster, due to the valence electron cloud, is given by[11]

$$\alpha_0=2e^2S_{-2}\equiv 2e^2\sum_n \epsilon_{n0}^{-2}f_{n0}\ . \tag{28}$$

With the help of Eqs. (10), (19), and (21), this becomes

$$\alpha_0=R^3\frac{g(R)+q}{g(R)-2q(1-3q)}\ . \tag{29}$$

In the large-particle limit ($q\rightarrow 0$), this approaches the macroscopic result $\alpha_0=R^3$. In small clusters, the fraction in Eq. (29) is greater than unity, so that the static polarizability is enhanced with respect to the macroscopic value.

Before discussing the numerical results, it is essential to note that there exists yet another contribution to the static electric polarizability, coming from the low-frequency part of the electronic spectrum. The result for the oscillator-strength distribution, Eq. (21), was derived under the assumption that one was dealing with resonance frequencies much higher than the single-particle level spacing [$\omega \gg \Delta$, see the discussion following Eq. (1)]. However, in addition to the plasma resonances, clusters may display transitions in the low-frequency region ($\omega\sim\Delta$), which are not contained in the strength function (21). A calculation of the exact low-energy spectrum of electrons in small metal clusters is difficult, since it requires an analysis of the polarization operator $\Pi(\mathbf{r},\mathbf{r}_1,\omega)$ for small ω. (Approximate treatments of the low-energy behavior of photoabsorption of small metal particles is presented, e.g., in Refs. 10 and 25.)

Since the two collective resonance peaks exhaust the sum rules, Eqs. (22) and (23), the oscillator strengths of the low-lying transitions must be very small, but they will come into Eq. (28) with small energy denominators. As a result, their contribution to the static polarizability will increase its value.

TABLE I. Static electric polarizabilities (in units of R^3) of Na and K clusters. *SV*: including both surface and volume terms [Eq. (29) in the text]; *S*: including only the surface term (see Ref. 5); Expt.: experimental data from Ref. 24.

		α_0/R^3	
Cluster	*SV*	*S*	Expt.
Na_8	1.54	1.81	1.77±0.03
Na_{20}	1.41	1.62	1.68±0.10
Na_{40}	1.33	1.51	1.61±0.03
Na_{58}	1.29	1.46	
Na_{92}	1.25	1.40	
K_8	1.49	1.74	1.79±0.09
K_{20}	1.37	1.57	1.66±0.13
K_{40}	1.30	1.46	
K_{58}	1.26	1.42	
K_{92}	1.23	1.36	

Numerical values for Eq. (29) can be obtained by using the valence electron density distribution calculated in the statistical Thomas-Fermi approach.[7] Table I lists the results for some clusters; the agreement with experiment is good. Note that even better agreement is obtained if one includes only the surface collective state in Eq. (28), with a strength of 1. (Static polarizabilities calculated in this way are also in excellent agreement with recent data on aluminum clusters with 40 and more atoms.[26])

In view of the preceding discussion, this can be understood as follows. Suppose one started out with 100% of the oscillator strength concentrated in the surface resonance state and calculated the polarizability. Next, one takes into account the existence of the volume plasmon; this leads to Eq. (29) and a reduced value of α_0. However, it is necessary at the same to remember the presence of the low-lying energy levels, whose contribution will increase α_0 and move it close to the starting value.

V. CONCLUSION

We analyze photoabsorption by small metallic clusters, and present an analytical calculation of cluster dynamic polarizabilty in the random-phase approximation. The absorption spectrum consists of two resonances: a surface mode and a volume mode. In small particles, as opposed to bulk matter, the volume-plasma oscillation can be excited by photons. The oscillator strength distribution, deduced from the dynamic polarizability, is shown to satisfy rigorous energy-weighted sum rules. With increasing cluster size, the resonance frequencies move up and approach their macroscopic values, while the oscillator strength is transferred from the volume to the surface collective mode.

It is noted that including the volume mode in a calculation of the static electric polarizability tends to reduce its value, and it is pointed out that it is essential to take into account the low-energy part of the excitation spectrum.

Numerical values for the resonance frequencies and the relative oscillator strengths are calculated with the use of the Thomas-Fermi statistical description of metal clusters.[7] The results allow to explain the available experimental data on surface plasma resonances in small clusters.[2] It would be interesting to verify the predictions by carrying out a search for the volume resonance peak in cluster photoabsorption spectra.

ACKNOWLEDGMENTS

I would like to thank W. D. Knight, V. Z. Kresin, S. Stringari, and K. Selby for very valuable discussions. This work was supported by the U.S. National Science Foundation under Grant No. DMR-89-13414.

---

[1] W. A. de Heer, W. D. Knight, M. Y. Chou, and M. L. Cohen, in *Solid State Physics,* edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1987), Vol. 40, p. 93.

[2] K. Selby, M. Vollmer, J. Masui, V. Kresin, W. A. de Heer, and W. D. Knight, Z. Phys. D **12**, 477 (1989); K. Selby, M. Vollmer, J. Masui, V. Kresin, W. A. de Heer, and W. D. Knight, Phys. Rev. B **40**, 5417 (1989).

[3] C. Bréchignac, Ph. Cahuzac, F. Carlier, and J. Leygnier, Chem. Phys. Lett. **164**, 433 (1989).

[4] Vitaly Kresin, Phys. Lett. A **133**, 89 (1988).

[5] Vitaly Kresin, Phys. Rev. B **39**, 3042 (1989).

[6] Vitaly Kresin, Phys. Rev. B **40**, 12 507 (1989).

[7] Vitaly Kresin, Phys. Rev. B **38**, 3741 (1988).

[8] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, San Francisco, 1971).

[9] A. B. Migdal, *Theory of Finite Fermi Systems and Applications to Atomic Nuclei* (Wiley, New York, 1967).

[10] A. Lushnikov and A. Simonov, Z. Phys. **270**, 17 (1974); A. Lushnikov, V. Maksimenko, and A. Simonov, in *Electromagnetic Surface Modes,* edited by A. Boardman (Wiley, New York, 1982).

[11] E. Lipparini and S. Stringari, Phys. Rep. **175**, 103 (1989).

[12] R. A. Ferrell, Phys. Rev. **111**, 1214 (1958).

[13] W. Ekardt, Phys. Rev. B **31**, 6360 (1985).

[14] A. D. Boardman and B. V. Paranjape, J. Phys. F **7**, 1935 (1977).

[15] B. Giovannini and R. Saniz, Helv. Phys. Acta **61**, 566 (1988).

[16] R. Ruppin, J. Phys. Chem. Solids **39**, 233 (1978).

[17] C. Yannouleas, R. A. Broglia, M. Brack, and P. F. Bortignon, Phys. Rev. Lett. **63**, 255 (1989).

[18] U. Kreibig and L. Genzel, Surf. Sci. **156**, 678 (1985).

[19] G. Fischer, *Vibronic Coupling* (Academic, New York, 1984).

[20] J. M. Pacheco and R. A. Broglia, Phys. Rev. Lett. **62**, 1400 (1989).

[21] O. Bohigas, A. M. Lane, and J. Martorell, Phys. Rep. **51**, 267 (1979).

[22] M. Brack, Phys. Rev. B **39**, 3533 (1989).

[23] Ll. Serra, F. Garcias, M. Barranco, J. Navarro, C. Balbás, and A. Mañanes, Phys. Rev. B **39**, 8247 (1989).

[24] W. D. Knight, K. Clemenger, W. A. de Heer, and W. A. Saunders, Phys. Rev. B **31**, 2539 (1985); K. Clemenger, Ph.D. thesis, University of California, Berkeley, 1985.

[25] E. Zaremba and B. N. J. Persson, Phys. Rev. B **35**, 596 (1987).

[26] W. A. de Heer, P. Milani, and A. Châtelain, Phys. Rev. Lett. **63**, 2834 (1989).