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Self-consistent calculation of the eigenfrequencies for the electronic excitations in small jellium spheres

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The time-dependent local-density approximation is used to formulate the eigenvalue problem for the electronic excitations of small jellium spheres. These spheres provide a model system for the investigation of the response of the conduction electrons in small metal particles. The dynamic response of the sphere to a time-dependent field is continued to complex frequency in order to isolate the eigenmodes of this model system. We are particularly interested in the determination of the frequencies for the collective excitations of these spheres. Computations are reported for the dipolar response of spheres with closed-shell electronic configurations containing from 8 to 198 electrons.

I. INTRODUCTION

The electronic structure[1,2] and polarizability[3–7] of small metal particles have been the subject of a large number of recent theoretical and experimental studies.[8] The electronic structure is calculated using the density-functional formalism,[9] and this formalism in combination with a linear-response approximation provides for a quantum-mechanical calculation of the static polarizability.[10,11] The complexity of the density-functional calculation is reduced by introducing a local-density approximation for the exchange-correlation energy of the interacting electronic system. The time-dependent local-density approximation (TDLDA) is the dynamical extension of this self-consistent procedure and this has been employed with great success in the calculation of the polarization and photoionization of atoms.[10–13] In this paper we employ the TDLDA in a computation of the excitation modes of small jellium spheres which are a model for the behavior of the conduction electrons in small metal particles. In this model the electrons are confined by a positive uniform spherical charge density of radius R and density $n^+ = 3/4\pi r_s^3$. There are two types of excitations for this electronic system—collective and single particle—and we shall focus our attention on the collective modes.[14]

In a single-particle excitation an electron is excited from an occupied ground-state energy level into an occupied level (electron-hole transition) or a continuum state (ionizing transition). These transitions are responsible for most of the prominent features in the response of the system to a time-dependent perturbation, Fig. 1. However, we should not expect the TDLDA to accurately predict the excitation energies for these transitions. The TDLDA gives the linear response of the system to an applied stimulus, and, one assumes that the induced density response, $\delta n(\mathbf{r},t)$, is a "small perturbation" of the ground-state density. It is certainly not possible to argue, convincingly, that an electron hole or ionizing transition, which requires the excitation of an electron and the resulting rearrangement, is only a small perturbation of the ground-state density of these spheres (or atoms[15]). For example, in these calculations the continuum threshold in the imaginary part of the dynamic dipolar polarizability occurs at a frequency corresponding to the energy of the highest occupied level of the ground-state system which

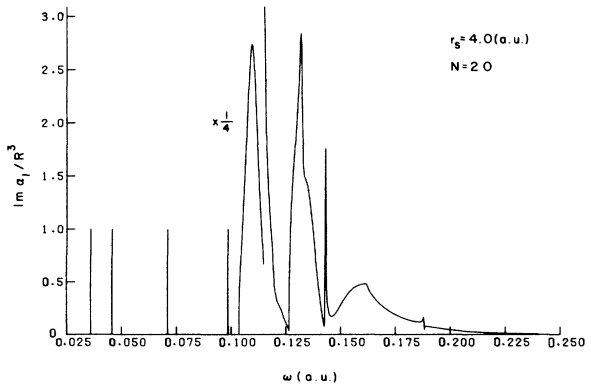

FIG. 1. Imaginary part of the dynamic dipole polarizability for a jellium sphere with $N=20$ and $r_s=4.0$ a.u. The vertical lines, below the continuum threshold at 0.104 a.u., indicate the frequencies for the low-lying excitations.

does not correspond to the frequency determined by the ionization potential (a well-known problem for the LDA). An additional weakness of employing this approximation for these excitations is that the change in the exchange-correlation energy is treated by expanding the local-density expression in a Taylor's series in $\delta n(\mathbf{r},t)$ and retaining only the term proportional to $\delta n(\mathbf{r},t)$ in the effective potential for the electrons.

The collective or "plasma" excitations are excitations where the electronic charge density as a whole is excited and oscillates as a result of the restoring force provided by the rigid positive background. In this type of excitation none of the electrons are transferred from an occupied to an unoccupied energy level and the induced density associated with the excitation can be an infinitesimal perturbation of the ground-state system. Hence, one expects the TDLDA to give an accurate estimate of the energy of this type of excitation. However, the features associated with these excitations tend to be less prominent in the dynamic polarizability than the single-particle features and, consequently, it is difficult to determine their excitation energies.

In Fig. 1 the imaginary part of the dynamic dipolar polarizability for a sphere containing 20 electrons and a positive charge density corresponding to a metal with $r_s=4.0$ a.u. is presented (we use atomic units where $e=\hbar=m=1$; the length unit is the Bohr radius and the energy unit is 27.2 eV). The continuum threshold for this system occurs at $\hbar\omega=0.104$ a.u. or minus the energy of the highest occupied level of the ground-state system. Below this threshold $\alpha_1(\omega)$ is real, since this model has no mechanism for an excitation with energy below the threshold to dissipate its energy. The vertical lines below this threshold indicate the position of the low-lying excitations. The response even for this small highly symmetric system is quite complicated. There are Fano resonances[16] of single-particle modes with the continuum spectrum and features one would associated with single-particle excitations for $\hbar\omega\sim 0.125$ to 0.150 a.u. However, the identification of the features to be associated with the collective modes requires a more extensive analysis. Ekardt[4] identifies the low-lying surface mode by examining the change in phase of the induced density at the edge of the positive background.

In order to facilitate the isolation of the contributions of the various excitations of the system to the dynamic response, we have formulated the TDLDA as an eigenvalue problem and computed the eigenfrequencies for the spheres. In Table I we have listed some of the dipolar eigenfrequencies for the sphere treated in Fig. 1, and, for comparison, the excitation frequencies computed from the Kohn-Sham independent-particle model of the ground-state system are also listed. For frequencies above the continuum threshold an excitation can dissipate its energy and decay, hence the higher eigenfrequencies are complex. Their computation, therefore, requires the continuation of the response into the complex frequency plane which greatly complicates the search for the eigenmodes.

Our identification of the character of the excitation associated with each of the eigenfrequencies is inferred from the induced electronic density perturbation. The induced-dipole-density responses for four of the modes identified as electron-hole excitations are presented in Fig. 2 and those for four modes identified as collective excitations are presented in Fig. 3. The features of the induced densities for most of the single-particle modes are quite regular and the disturbance is principally confined to the interior of the particle. The induced densities for the collective modes have more prominent surface features which extend well beyond the positive charge.

The identification of the collective modes is complicated by a number of factors. There are single-particle excitations of electrons to resonancelike states in the continuum spectrum and the induced densities for these excitations also extend beyond the positive charge. A further complication is the coupling between excitation modes which prevent the unique determination of the character of the coupled modes;[4] for example the mode with $\mathrm{Re}z=0.110$ a.u. [Fig. 2(c)] has a prominent surface feature which can be attributed to the coupling of this "single-particle" excitation and the "collective" excitation with $\mathrm{Re}z=0.099$ a.u. [Fig. 3(a)].

Our calculation of the static polarizability of these spheres contains a description of the procedures and numerical methods employed, and the details of the formalism have been thoroughly expounded[10,11] so only a brief description of the TDLDA formalism and notation is provided in Sec. II. Section II also contains our formulation of the eigenvalue problem and a discussion of the analytic structure of the complex continuation of the generalized susceptibility.

II. FORMALISM

We consider a spherically symmetric system subjected to an infinitesimal time-dependent perturbation

TABLE I. Eigenfrequencies for the dipole excitations in a jellium sphere with $N=20$ and $r_s=4.0$ a.u. The probable identification of the excitation is indicated and the excitation energies ($\Delta\varepsilon=\varepsilon_{n'l}-\varepsilon_{n,l\pm1}$) for the ground state Kohn-Sham system are given for comparison. The ionization potential for this sphere is 0.0918 a.u. The highest occupied level for the ground-state system is -0.1036 a.u. and the lowest occupied level is -0.1882 a.u.

z (a.u.)	Excitation ($l_1\rightarrow l_2$)	$\Delta\varepsilon$ (a.u.)
$0.036-i0$	$2\rightarrow3$	0.0415
$0.046-i0$	$0\rightarrow1$	0.0443
$0.071-i0$	$2\rightarrow1$	0.0675
$0.099-i0$	coll.	
$0.110-i0.004$	e-h	
$0.132-i0.001$	$0\rightarrow1$	0.1288
$0.137-i0.009$	$1\rightarrow2$	0.1420
$0.142-i0.021$	coll.	
$0.143-i0.000$	$1\rightarrow0$	0.1449
$0.155-i0.047$	e-h	
$0.177-i0.031$	e-h	
$0.188-i0.000$	$0\rightarrow1$	
$0.203-i0.044$	coll.	
$0.277-i0.054$	coll.	
$0.390-i0.089$	coll.	
$0.559-i0.129$	coll.	

$$\delta V_M(\mathbf{r},t)=\lambda^0 r^M Y_M^0(\hat{\mathbf{r}})e^{-i\omega t}$$

which develops an Mth order moment,

$$P_M=\lambda^0\alpha_M(\omega)=\frac{4\pi}{2M+1}\int d\mathbf{r}\, r^M Y_M^{0*}(\hat{\mathbf{r}})\delta n(\mathbf{r},\omega)\ . \tag{1}$$

Here $Y_M^N(\hat{\mathbf{r}})$ is a spherical harmonic and the linear density response of the system is given by

$$\delta n(\mathbf{r},\omega)=\int d\mathbf{r}'\chi^0(\mathbf{r},\mathbf{r}';\omega)v_{\rm SCF}(\mathbf{r}',\omega)\ . \tag{2}$$

The random-phase-approximation (RPA) expression for the generalized susceptibility of the Kohn-Sham independent-particle system is[11]

$$\chi^0(\mathbf{r},\mathbf{r}';\omega)=\sum_{i,j}[f(\varepsilon_i)-f(\varepsilon_j)]\frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{\varepsilon_i-\varepsilon_j+\omega}$$
$$=\sum_{i\ (\rm occup)}\{\psi_i^*(\mathbf{r})\psi_i(\mathbf{r}')G(\mathbf{r},\mathbf{r}';\varepsilon_i+\omega)+[\psi_i^*(\mathbf{r})\psi_i(\mathbf{r}')G(\mathbf{r},\mathbf{r}';\varepsilon_i-\omega^*)]^*\} \tag{3}$$

where ω has a small positive imaginary part in order to define the retarded response. The self-consistent-field potential for the TDLDA is given by

$$v_{\rm SCF}(\mathbf{r},\omega)=\lambda^0 r^M Y_M^0(\hat{\mathbf{r}})+\int d\mathbf{r}'\frac{\delta n(\mathbf{r},'\omega)}{|\mathbf{r}-\mathbf{r}'|}+\delta n(\mathbf{r},\omega)\frac{d^2}{dn^2}[n\varepsilon_{\rm xc}(n)]\ . \tag{4}$$

The self-consistent, noninteracting, single-particle wave functions are obtained from a density-functional calculation using the Kohn-Sham procedure.[9] They satisfy the Schrödinger equation

$$[-\tfrac{1}{2}\nabla^2+v_{\rm eff}(n;\mathbf{r})-\varepsilon_i]\psi_i(\mathbf{r})=0 \tag{5}$$

with an effective potential

$$v_{\rm eff}(n;\mathbf{r})=v(\mathbf{r})+\int d\mathbf{r}\frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}+\frac{d}{dn}[n\varepsilon_{\rm xc}(n)]$$

and a self-consistent density given by

$$n(\mathbf{r})=\sum_{i\ (\rm occup)}|\psi_i(\mathbf{r})|^2\ .$$

The external potential, $v(\mathbf{r})$, for this calculation is provided by a uniform sphere of positive charge;

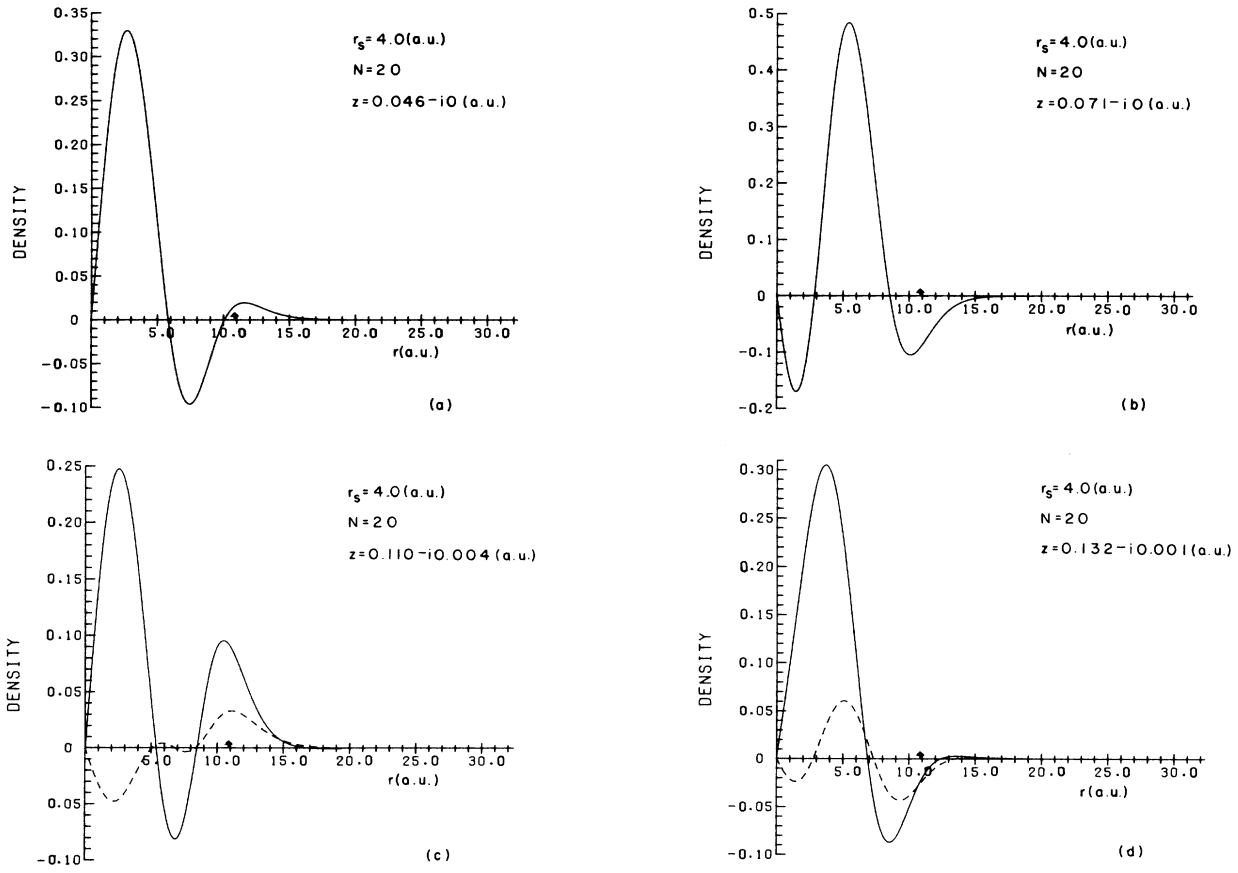

FIG. 2. Complex electronic density perturbations associated with single-particle eigenmodes of a jellium sphere with $N=20$ and $r_s=4.0$ a.u. The real and imaginary parts are indicated by the solid and dashed curves, respectively, and the arrow marks the edge of the uniform positive charge density. The physical units for the density are arbitrary since the density is adjusted so that Eq. (14) is satisfied.

$N=4\pi n^{+}R^{3}/3$. The local density approximation for the exchange-correlation energy, $\varepsilon_{xc}(n)$, of Gunnarsson and Lundqvist[17] is used in the computations. The Green's functions in Eq. (3) satisfy

$$\left[-\frac{\nabla^2}{2}+v_{\text{eff}}(n,\mathbf{r})-\omega\right]G(\mathbf{r},\mathbf{r}';\omega)=-\delta(\mathbf{r}-\mathbf{r}') \ . \tag{6}$$

For a closed-shell (spherically symmetric) system the only nonzero terms in the expansion of $\delta n(\mathbf{r},\omega)$ and $v_{\text{SCF}}(\mathbf{r},\omega)$ in terms of spherical harmonics are those with the same symmetry as the perturbation,[3,12] hence

$$\delta n(\mathbf{r},\omega)=\delta n_M(r,\omega)Y_M^0(\hat{\mathbf{r}})=\lambda r^M\eta_M(r,\omega)Y_M^0(\hat{\mathbf{r}})$$

and

$$v_{\text{SCF}}(\mathbf{r},\omega)=v_M(r,\omega)Y_M^0(\hat{\mathbf{r}})=\lambda r^M\nu_M(r,\omega)Y_M^0(\hat{\mathbf{r}}) \ .$$

Introducing

$$\psi_i(\mathbf{r})=u_{nl}(r)Y_l^m(\hat{\mathbf{r}}) \ ,$$

where i denotes the quantum numbers $(nlms)$, we can reduce Eqs. (2) and (3) to

$$\eta_M(r,\omega)=\int_0^\infty r'^2dr'\chi_M^0(r,r';\omega)(r'/r)^M\nu_M(r',\omega) \ , \tag{7}$$

where

$$\chi_M^0(r,r';\omega)=(2s+1)\sum_{n,l,l'}c(M;l,l')\{u_{nl}^*(r)G_{l'}(r,r';\varepsilon_{nl}+\omega)u_{nl}(r')+[u_{nl}^*(r)G_{l'}(r,r';\varepsilon_{nl}-\omega^*)u_{nl}(r')]^*\} \tag{8}$$

and $c(M;l,l')$ is a Gaunt coefficient.[18] The radial Green's function satisfies

$$\left[-\frac{1}{2r^2}\frac{d}{dr}r^2\frac{d}{dr}-\frac{l(l+1)}{2r^2}+v_{\text{eff}}(r)-\omega\right]G_l(r,r';\omega)=\frac{-\delta(r-r')}{r^2} \ . \tag{9}$$

Equation (4) for $v_{\text{SCF}}(\mathbf{r})$ yields

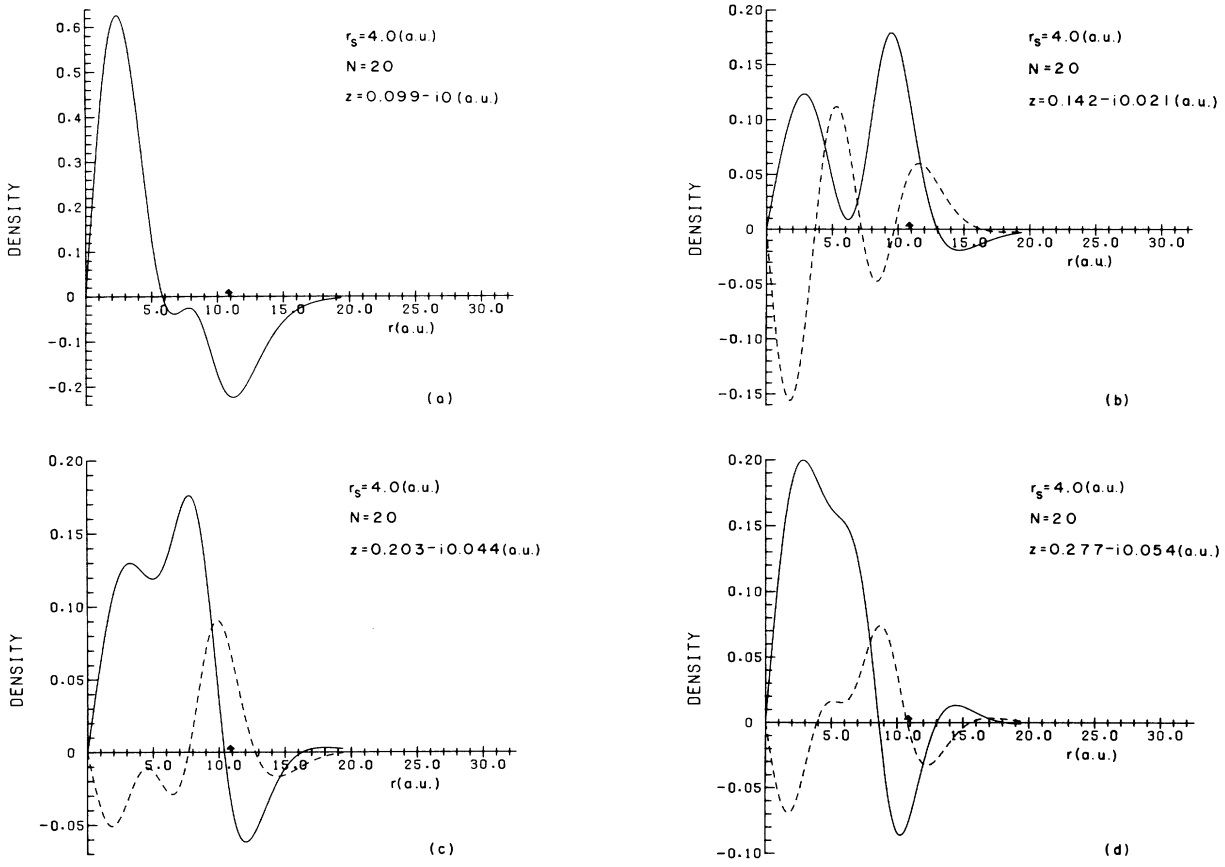

FIG. 3. Complex electronic density perturbations associated with plasma eigenmodes of a jellium sphere with $N=20$ and $r_s=4.0$ a.u. The real and imaginary parts are indicated by the solid and dashed curves, respectively, and the arrow marks the edge of the uniform positive charge density. The physical units for the density are arbitrary since the density is adjusted so that Eq. (14) is satisfied.

$$v_M(r,\omega)=\frac{\lambda^0}{\lambda}+\frac{4\pi}{2M+1}\int r'^2dr'\left[\frac{r'}{r}\right]^M\eta_M(r',\omega)\frac{r_<^M}{r_>^{M+1}}+\eta_M(r,\omega)\frac{d^2}{dn^2}[n\varepsilon_{xc}(n)]$$

or

$$v_M(r,\omega)=1+\frac{4\pi}{2M+1}\int_0^r r'dr'\left[\left[\frac{r'}{r}\right]^{2M+1}-1\right]\eta_M(r',\omega)+\eta_M(r,\omega)\frac{d^2}{dn^2}[n\varepsilon_{xc}(n)] \tag{10}$$

where we have set

$$\lambda=\lambda^0\left[1-\frac{4\pi}{4M+1}\int_0^\infty r\,dr\,\eta_M(r,\omega)\right]^{-1}. \tag{11}$$

Inserting Eq. (7) into Eq. (10), we obtain the integral equation,

$$v_M(r,\omega)=1+\int_0^\infty r'^2dr'K_M(r,r';\omega)v_M(r',\omega)\,, \tag{12}$$

with the kernel,

$$K_M(r,r';\omega)=\int_0^{r^+}r''dr''\chi_M^0(r'',r';\omega)\left[\frac{r'}{r''}\right]^M\left\{\frac{4\pi}{2M+1}\left[\left[\frac{r''}{r}\right]^{2M+1}-1\right]+\frac{\delta(r''-r)}{r''}\frac{d^2}{dn^2}n\varepsilon_{xc}(n)\right\}. \tag{13}$$

Using the solutions of this integral equation one can obtain the multipole polarizability for the response of the system to an external disturbance from Eqs. (1) and (7),

$$\alpha_M(\omega)=\frac{\lambda}{\lambda^0}\frac{4\pi}{2M+1}\int_0^\infty dr\,r^{2M+2}\eta_M(r,\omega)\,.$$

Our approach to isolating the contributions to the excitation spectra of these jellium spheres is to seek their eigenfrequencies. Below the continuum threshold these frequencies are real and correspond to self-sustained excitations of the system. Above the continuum threshold the excitations are damped and the eigenfrequencies are complex with a negative imaginary part. Thus we seek nontrivial solutions of our system of equations when no external field is applied, $\lambda^0\to 0$. Such solutions require that λ, Eq. (11), remains finite when $\lambda^0\to 0$ or that

$$\xi(z_j)=\frac{4\pi}{2M+1}\int_0^\infty r\,dr\,\eta_M(r,z_j)=1 \tag{14}$$

for the set of complex eigenfrequencies, z_j, so that we obtain a finite induced density even for an infinitesimal external perturbation. The computational procedure is to search for solutions of Eq. (14) along the real z axis for frequencies below the continuum threshold and in the lower half of the complex z plane above the threshold.

The Green's function for a particular value of angular momentum, can be represented by

$$G_l(r,r';z)=-\sum_n\frac{u_{nl}^0(r)u_{nl}^{0*}(r')}{\varepsilon_{nl}-z}\,, \tag{15}$$

where $u_{nl}^0(r)$ is a solution of the homogeneous differential equation corresponding to the equation satisfied by $G_l(r,r';\omega)$, Eq. (6). The Green's function will have poles at the bound-state energies ε_{nl} and the physical sheet for $G_l(z)$ is obtained by introducing a cut along the positive real axis, from $z=0$ to ∞. The analytic continuation to complex frequencies ($\mathrm{Im}z<0$) is then on the physical sheet for $\mathrm{Re}z<0$ and, through the cut, onto the second sheet for $\mathrm{Re}z>0$. Since we require $G_{l'}(\varepsilon_{nl}+z)$ to form $\chi_M^0(r,r';z)$, Eq. (8), we introduce cuts among the line from $z=-\varepsilon_{nl}$ to $z=-\varepsilon_{nl}-i\infty$ in order to define each of the contributions to the sum over n and l in Eq. (8).

The computations presented in this manuscript are for the dipole response of these spheres; $M=1$. For this problem the dynamic force sum rule[19] can be expressed in terms of the electrical potential, and one obtains

$$(4\pi/3)\left[R^{-2}\int_0^R dr\,r^3\delta n_1(r,\omega)+R\int_R^\infty dr\,\delta n_1(r,\omega)\right]+\lambda^0R=(4\pi\omega^2R/3N)\int_0^\infty dr\,r^3\delta n_1(r,\omega)$$

or

$$(4\pi/3)\int_0^R dr\,r[(r/R)^3-1]\eta_1(r,\omega)+1=(4\pi\omega^2/3N)\int_0^\infty dr\,r^4\eta_1(r,\omega)\,,$$

which provides for a useful numerical check on the accuracy of the self-consistent solution.

III. COLLECTIVE EXCITATIONS

A classical description of a metal sphere where the positive and negative charge densities are uniform will have a multipole surface plasma mode (nonretarded) at a frequency given by

$$\omega_M^c=\omega_P\sqrt{M/2M+1}$$

where ω_P is the bulk plasma frequency,

$$\omega_P=(4\pi ne^2/m)^{1/2}=(3/r_s^3)^{1/2}\ \text{a.u.}$$

The induced density associated with this mode is localized at the surface of the sphere, $\delta n_M(r) \propto \delta(r-R)$. In the model of the metal sphere used in this calculation the electronic charge density can "spill out" from the rigid positive background charge, and the hydrodynamic calculations[20] using a diffuse electron surface density obtain a size-dependent "red shift" of the frequency for this "surface" plasma mode with decreasing sphere size; i.e., $\mathrm{Re}z < \omega_M^c$. We might also expect to find additional "surface" plasma modes[21] which for the classical sphere would be degenerate with ω_M^c. In addition there are theoretical predictions[22] and experimental results[23] which indicate the presence of "bulk" plasma modes at frequencies above ω_P.

Because of the complexity of the structure spectrum, $\xi(z)$, in Eq. (14), one cannot guarantee that all of the eigenfrequencies in a given region of the complex z plane have been located. Also, as we stated in the Introduction, it is often not possible to make a completely unambiguous identification of the collective modes. Nonetheless, we have attributed a number of the eigenfrequencies to dipolar plasma modes for the closed shell configurations of jellium spheres from $N=8$ to $N=198$ electrons. The positive charge densities for $r_s=2.0$ and 4.0 a.u. are approximately the conduction electron densities for bulk aluminum and sodium (2.07 and 3.99, respectively). The complex eigenfrequencies for some of the dipolar plasma modes in these spheres are tabulated in Tables II and III. The unique identification of many of these eigenmodes is complicated by the coupling with "nearby" single-particle excitations and in these cases the coupled eigenfrequency is also given.

There are additional eigenmodes with prominent surface features and eigenfrequencies in the interval, $\omega_1^c < \mathrm{Re}z < \omega_P$. However, the cuts introduced to define the G_l's, Eq. (15), and the single-particle excitations complicate the analytic structure of the response and prevent the unique identification of these modes. For the spheres with $r_s=2.0$ a.u. it was possible to isolate an additional eigenmode with $\mathrm{Re}z < \omega_P$ ($\omega_P=0.6124$ a.u. for $r_s=2.0$ a.u.) above the low-lying surface mode and to trace its dependence on sphere radius, and the eigenfrequencies for this mode in these spheres are also tabulated in Table III. The eigenfrequencies for the surface mode show only a slight "red shift" with decreasing sphere size when $r_s=4.0$ a.u. However, the "red shift" of this mode is more pronounced for the smallest spheres with $r_s=2.0$ a.u. All of the bulk eigenfrequencies for these spheres demonstrate the "blue shift" with decreasing sphere size that was reported in Ekardt's calculation of the polarizability.[4,14] The Imz or the damping of these bulk modes decreases with increased sphere radius which correlates with the appearance of a peak in $\mathrm{Im}\alpha_1(\omega)$ near ω_P for the larger spheres.[4]

The dipole density perturbations for a set of modes identified as plasma excitations of a sphere with $N=20$ and $r_s=4.0$ a.u. are presented in Fig. 3, and the induced densities for these modes in a sphere containing $N=186$ electrons are presented in Fig. 4. The dipole density disturbances for the mode with $\mathrm{Re}z=0.099$ and 0.142 a.u. in Fig. 3 clearly have a surface character while the modes with $\mathrm{Re}z=0.203$ and 0.277 a.u. have large bulk contributions ($\omega_P=0.2165$ a.u. for $r_s=4.0$ a.u.). The perturbed dipole densities for eigenmodes in a jellium sphere with $r_s=2.0$ a.u. and $N=20$ are presented in Fig. 5.

IV. DISCUSSION

Most of the experimental results which relate to the plasma modes in metal particles have been obtained using samples which contain a distribution of particle sizes, and the median radii for the particles in these samples are usually large compared to the radii of the spheres studied in our computation. This distribution of particle size will

TABLE II. Eigenfrequencies for dipolar plasma modes in closed-shell jellium spheres with $r_s=4.0$ a.u. The bulk plasma frequency for $r_s=4.0$ is $\omega_P=0.2165$ a.u. and the classical surface frequency is $\omega_1^c=0.1250$ a.u. The frequencies in parentheses are for eigenmodes which are coupled with the mode above them.

N	z (a.u.) (surface)	z (a.u.) (bulk)	z (a.u.) (bulk)
8	$0.101-i0$	$0.230-i0.057$	$0.367-i0.094$
18	$0.103-i0$	$0.201-i0.043$	$0.276-i0.054$
20	$0.099-i0$	$0.203-i0.044$	$0.277-i0.054$
	$(0.110-i0.004)$		
34	$0.106-i0$	$0.225-i0.042$	$0.272-i0.050$
40	$0.100-i0$	$0.231-i0.039$	$0.277-i0.048$
	$(0.096-i0)$		
58	$0.105-i0$	$0.193-i0.044$	$0.246-i0.024$
		$(0.189-i0.051)$	$(0.216-i0.051)$
92	$0.117-i0.000$	$0.192-i0.045$	$0.240-i0.018$
			$(0.235-i0.039)$
132	$0.113-i0$	$0.181-i0.036$	$0.235-i0.038$
138	$0.114-i0.000$	$0.178-i0.036$	$0.237-i0.036$
	$(0.112-i0.000)$		
186	$0.113-i0$	$0.169-i0.026$	$0.229-i0.043$
	$(0.108-i0)$		$(0.217-i0.039)$

TABLE III. Eigenfrequencies for dipolar plasma modes in closed-shell jellium spheres with $r_s=2.0$ a.u. The bulk plasma frequency for $r_s=2.0$ is $\omega_P=0.6124$ a.u. and the classical surface frequency is $\omega_1^c=0.3536$ a.u. The frequencies in parentheses are for eigenmodes which are coupled with the mode above them.

N	z (a.u.) (surface)	z (a.u.) (surface)	z (a.u.) (bulk)	z (a.u.) (bulk)
8	$0.202-i0$[a]	$0.359-i0.095$	$0.641-i0.159$	$0.917-i0.220$
18	$0.231-i0.041$	$0.376-i0.087$	$0.611-i0.131$	$0.836-i0.185$
20	$0.242-i0.043$	$0.384-i0.088$	$0.603-i0.141$	$0.825-i0.186$
34	$0.243-i0.035$	$0.383-i0.075$	$0.587-i0.126$	$0.778-i0.156$
40	$0.271-i0.034$	$0.373-i0.078$	$0.592-i0.129$	$0.784-i0.158$
58	$0.262-i0.035$	$0.388-i0.074$	$0.571-i0.122$	$0.740-i0.122$
68	$0.290-i0.026$	$0.402-i0.079$	$0.579-i0.124$	$0.746-i0.123$
70	$0.296-i0.024$	$0.407-i0.079$	$0.583-i0.125$	$0.750-i0.125$
92	$0.273-i0.027$	$0.390-i0.073$	$0.570-i0.117$	$0.721-i0.091$
	$(0.303-i0.013)$			
106	$0.300-i0.018$	$0.416-i0.072$	$0.574-i0.142$	$0.725-i0.091$
			$(0.597-i.0.119)$	
138	$0.317-i0.004$	$0.399-i0.063$	$0.577-i0.103$	$0.706-i0.068$
156	$0.321-i0.004$	$0.414-i0.054$	$0.590-i0.093$	$0.706-i0.067$
198	$0.311-i0.006$	$0.398-i0.050$	$0.570-i0.083$	$0.695-i0.052$
	$(0.291-i0.009)$			

[a]The best determination of this frequency places it at the continuum threshold.

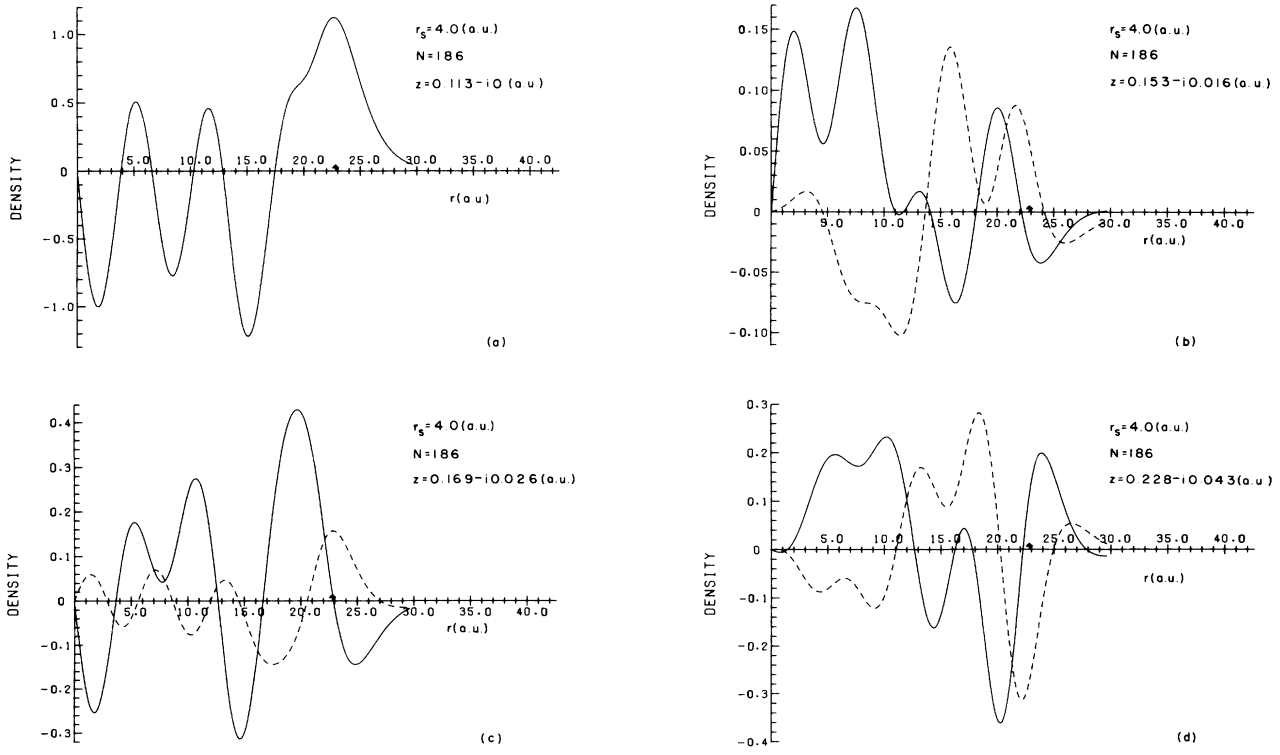

FIG. 4. Complex electronic density perturbations associated with plasma eigenmodes of a jellium sphere with $N=186$ and $r_s=4.0$ a.u. The real and imaginary parts are indicated by the solid and dashed curves, respectively, and the arrow marks the edge of the uniform positive charge density. The physical units for the density are arbitrary since the density is adjusted so that Eq. (14) is satisfied.

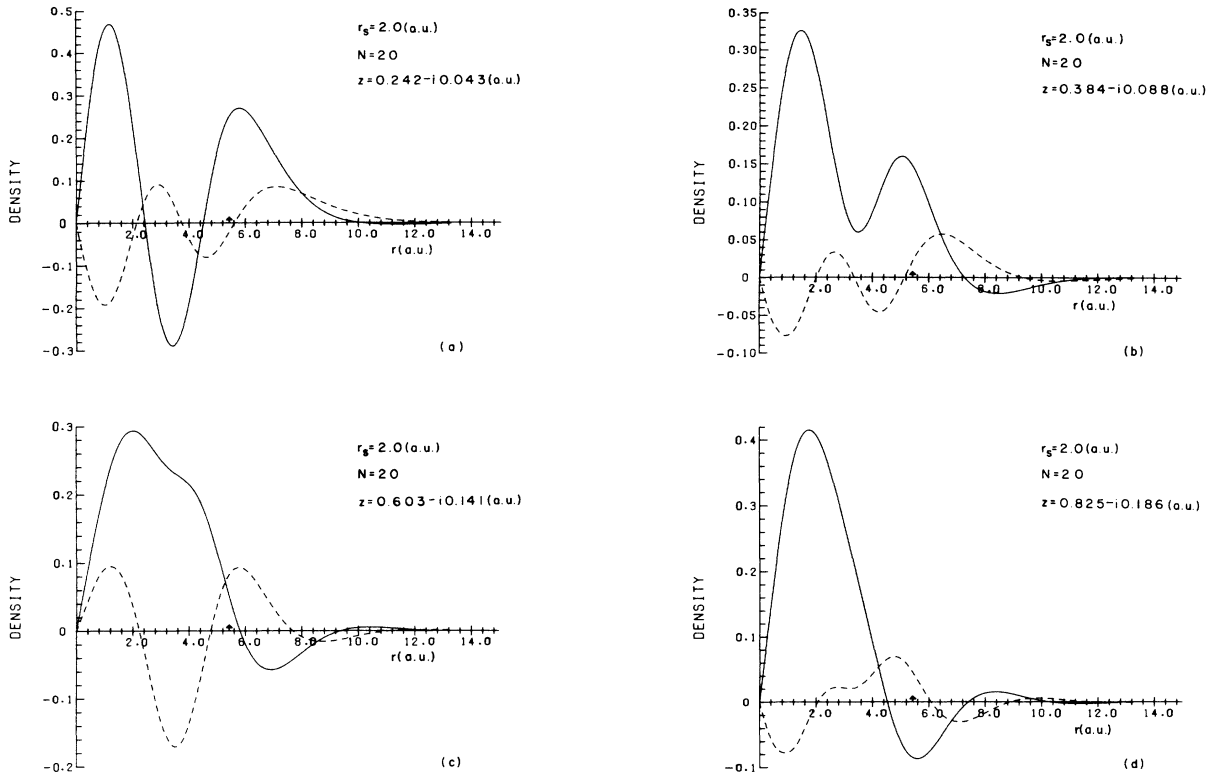

FIG. 5. Complex electronic density perturbations associated with plasma eigenmodes of a jellium sphere with $N=20$ and $r_s=2.0$ a.u. The real and imaginary parts are indicated by the solid and dashed curves, respectively, and the arrow marks the edge of the uniform positive charge density. The physical units for the density are arbitrary since the density is adjusted so that Eq. (14) is satisfied.

certainly average the effects due to the single-particle excitations of the individual particles. In addition, the very high symmetry of the jellium model is certainly broken by the ion cores in the real metal clusters which results in the splitting of the energy levels and a greater number of single-particle excitations with diminished amplitudes. In contrast, the plasma modes show only a very small dependence on sphere size and the low-lying surface mode should be a prominent feature of the experimental data.

Duthler *et al.*[23] using sodium particles of "less than 100 Å in diameter" reported a blue shift of 15% from ω_1^c for the low-lying peak in their light scattering data. Their data also has a peak at a shorter wavelength corresponding to ω_P. The mode we designate as the surface plasmon for our largest sphere with $r_s=4.0$ ($R=22.83$ a.u.) is red-shifted 11%. This eigenfrequency lies just below the continuum threshold for ionizing transitions from the "conduction band," and, as the sphere size increases, one expects this eigenfrequency to increase and move above the threshold (bandwidth ~ 0.102 a.u.). In this frequency range the contribution of the single-particle excitations broadens the response,[4] hence, attributing the experimental peak solely to the surface plasmon greatly oversimplifies the response of these sodium particles.

The computation of the complex eigenfrequencies permits the isolation of the various contributions to the complicated dynamic polarizability (or photoabsorption cross section[11]) and facilitates the characterization of the excitations. The proper identification of the collective modes and their incorporation into macroscopic descriptions of the particle response will permit the transfer of the information obtained in the self-consistent, microscopic calculations for small particles to larger particles[24] where such calculations would be very expensive. However, as we have emphasized, it is often difficult to provide a unique characterization of the eigenmodes because of the overlap of the single particle and surface plasma modes and the large number of single-particle excitations.

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