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Density-functional calculation of the static electronic polarizability of a small metal sphere

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The response of a small metal sphere to a uniform electrostatic field is calculated within density-functional theory. The gradient-expansion approximation is used for the kinetic-energy functional, while exchange and correlation are treated in the local-density approximation. A jellium model is assumed and the electron density is determined by a variational method. Calculations were performed for spheres containing between 5 and 8000 electrons. The applied field was found to induce a substantial amount of charge outside the sphere. This causes the electronic polarizability α to be larger than the classical value R^3, where R is the radius of the sphere. Our calculations give $\alpha=(R+\delta)^3$, where $R+\delta$ plays the role of an effective radius, and δ is approximately 2.0 a.u. for the electron-radius parameter $r_s=2$ and is approximately 1.0 a.u. for $r_s=4$. Our calculated values of δ are nearly independent of R. As R approaches infinity, δ approaches the image-plane distance for the problem of a flat surface. It is shown that there is a force sum rule that is not well satisfied by previous calculations, and is approximately satisfied by most of our calculations.

I. INTRODUCTION

The response of a small metal sphere to an electric field is an area of great current interest.[1] Theoretical calculations of the response to time-dependent[2–6] and static[4–8] electric fields have appeared, but none of these calculations provide a fully self-consistent quantum-mechanical treatment of the electrons. In this paper we present a density-functional calculation of the electronic response of a small metal sphere to a uniform electrostatic field. Except for approximations introduced by a variational procedure our calculation is self-consistent.

Although we treat only the static case, the results can also be used to determine approximately the induced electric field around a small metal sphere exposed to infrared radiation in the "quasistatic" or "nonretarded" regime.[6] This is the regime where the radius of the sphere is much less than both the wavelength of radiation and the skin depth.[9] The results for the static case are therefore relevant to the problem of infrared absorption by adsorbed molecules on a metal sphere, where, for example, the radius is smaller than about 50 Å and the wavelength is on the order of 50 000 Å or more.[6,10]

A self-consistent quantum-mechanical calculation of the electronic response to an applied static field is a difficult task. An approach based on the random-phase approximation[11] (RPA) suggests itself, but such an approach leads to considerable calculational complexity. In the RPA one first calculates the self-consistent electronic wave functions for the system in the absence of the applied electric field. These wave functions are then used to obtain the RPA response function, and a new self-consistent problem must be solved with the applied field present. Rice, Schneider, and Strässler[8] calculated the static polarizability within the RPA, but used an infinite-barrier model to obtain the zero-field wave functions. The first phase of their RPA calculation, therefore, is not self-consistent. Furthermore, as we shall see, their values for the electronic polarizability are artificially small because the electrons are effectively held back by the infinite barrier. A similar effect occurs in the calculations of Lushnikov and Simonov[4] and Dasgupta and Fuchs,[5] where the electrons are confined by a sharp boundary which is taken to be the radius of the sphere. In all of these calculations the effective radius of the induced surface charge is less than the radius of the particle. In our calculation, the electrons are allowed to penetrate into the vacuum, and consequently, the effective radius turns out to be greater than the particle radius.

The density-functional theory[12,13] provides a powerful framework for a self-consistent calculation of the static electronic polarizability. In its wave-mechanical version,[13,14] the theory is as difficult to implement as the RPA. However, in one of its more approximate versions, the theory becomes quite tractable. In this version, the kinetic-energy functional is treated in a density-gradient expansion, while exchange and correlation are included in a local-density approximation.[13] We have recently used this model to calculate the work function of small metal spheres.[15] In this paper we apply the model to calculate the electronic polarizability. We express our results in terms of an effective radius, which allows us to make contact with image-plane calculations for the response of a flat metallic surface to a uniform electrostatic field. Along the way, we develop a sum rule for the electrostatic forces exerted upon the positive-charge background. It is pointed out that none of the previous calculations of the static electronic polarizability of metallic spheres satisfies the sum rule. This failure of the previous calculations is a consequence of their lack of self-consistency.

The organization of this paper is as follows. Section II describes our model. A rigid jellium background is assumed. The energy functional is presented and expanded to second order in the applied electric field. Section III describes the variational calculation of the electron density. The form of the trial function is specified. The polarizability is expressed in terms of an effective-radius shift δ which is related to the dipole moment of the induced charge and which can also be related to that part of the energy that is second order in the applied electric field. A discussion of the results of the calculation is given in Secs. IV A–IV E. The induced charge and electric field are discussed in Sec. IV A. The electronic polarizability is discussed in Sec. IV B. It is shown in Sec. IV C that for large spheres the parameter δ reduces to the image-plane distance for the problem of a semi-infinite metal. In Sec. IV D the sum rule is discussed. The reliability of the variational calculation is considered in Sec. IV E. Finally, Sec. V provides a summary and conclusion.

II. MODEL

We assume a jellium model for the spherical particle, i.e., the metallic ions are modeled by a uniform positive background filling a sphere of radius R. We take the energy functional to be the one used by Smith,[16] Appelbaum and Hamann,[17] and others.[13,15,18] Exchange and correlation are treated in a local-density approximation, with correlation given by Wigner's interpolation formula.[13] In terms of the electron density $n(\vec{r})$, the energy functional has the form[13]

$$E=E_{\rm kin}+E_{\rm xc}+E_{\rm Coul}+E_{\rm ext}\ , \tag{1}$$

where the kinetic, exchange-correlation, Coulomb, and external-field contributions are, respectively,

$$E_{\rm kin}=a_1\int n^{5/3}(\vec{r})d^3r+a_2\int\frac{|\vec{\nabla}n(\vec{r})|^2}{n(\vec{r})}d^3r\ , \tag{2}$$

$$E_{\rm xc}=-\int n^{4/3}(\vec{r})\left[a_3+\frac{a_4}{a_5+n^{1/3}(\vec{r})}\right]d^3r\ , \tag{3}$$

$$E_{\rm Coul}=\frac{1}{2}\int\frac{[n(\vec{r})-n_+(\vec{r})][n(\vec{r}\,')-n_+(\vec{r}\,')]}{|\vec{r}-\vec{r}\,'|}d^3r\,d^3r'\ , \tag{4}$$

$$E_{\rm ext}=\int[n(\vec{r})-n_+(\vec{r})]\vec{\mathcal{E}}_0\cdot\vec{r}\,d^3r\ , \tag{5}$$

where the coefficients a_i have the following values: $a_1=2.8712$, $a_2=\frac{1}{72}$, $a_3=0.7386$, $a_4=0.056\,41$, and $a_5=0.079\,53$. Atomic units are used throughout ($e=\hbar=m=1$, energy unit $=27.2$ eV, and length unit $=0.529$ Å). The positive jellium background density is $n_+(\vec{r})$, which is taken to be a constant for $r\leq R$ and zero for $r>R$. The term $E_{\rm ext}$ explicitly contains the applied electric field $\vec{\mathcal{E}}_0$ and represents the Coulomb interaction between the metal sphere and the sources of the applied field. For definiteness we may imagine these sources to be oppositely charged sheets at $z=\pm L$, where $L\gg R$. Then $\vec{\mathcal{E}}_0=\mathcal{E}_0\hat{z}$, where $\hat{z}$ is a unit vector along the z axis, and the energy E given above is the total energy of the isolated system consisting of the metal sphere and the charged sheets except that we ignore the uninteresting, $n(\vec{r})$-independent Coulomb interaction energy of the charged sheets in the absence of the metal sphere.

Our goal is to determine $n(\vec{r})$ for the case of a weak applied field $\vec{\mathcal{E}}_0$. To this end, we write

$$n(\vec{r})=n_0(r)+\delta n(\vec{r})\ , \tag{6}$$

where $n_0(r)$ is the density in the absence of the field and $\delta n(\vec{r})$ is the perturbation arising from the external field. We now expand the integrands in Eqs. (2)–(4) to second order in δn. The zeroth-order expression for E is the sum $E_{\rm kin}+E_{\rm xc}+E_{\rm Coul}$, with $n(\vec{r})$ replaced by $n_0(r)$. The first-order expression for E is equal to

$$\int\{\delta E[n]/\delta n(\vec{r})\}\,|_{n=n_0}\delta n(\vec{r})d^3r\ ,$$

which vanishes because the functional derivative $\delta E[n]/\delta n(\vec{r})=\mu$, which is a constant,[13] and $\int\delta n(\vec{r})d^3r=0$ by particle conservation. Finally, there is the part of E which is second order in δn, or equivalently second order in $\vec{\mathcal{E}}_0$. Denoting this quantity by δE, we have

$$\delta E=\delta E_{\rm kin}+\delta E_{\rm xc}+\frac{1}{2}\int\frac{\delta n(\vec{r})\delta n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d^3r\,d^3r' + \int\delta n(\vec{r})\vec{\mathcal{E}}_0\cdot\vec{r}\,d^3r\ , \tag{7}$$

where $\delta E_{\rm kin}$ and $\delta E_{\rm xc}$ are the second-order terms in the expansion of the integrands in Eqs. (2) and (3), respectively, in powers of δn.

To first order in $\mathcal{E}_0$, the density perturbation has the form

$$\delta n(r,\theta)=f(r)\mathcal{E}_0\cos\theta\ , \tag{8}$$

where we use spherical coordinates with the polar axis along $\vec{\mathcal{E}}_0$. This form follows from spherical symmetry and the assumed linearity in the response. When the form (8) is used in Eq. (7) the angular integrals can be done immediately. One obtains

$$\delta E=\frac{4\pi}{3}\mathcal{E}_0^2\int\left[g_1f^2+g_2f\frac{df}{dr}+g_3\left[\frac{df}{dr}\right]^2+\left[r-\frac{v}{2}\right]f\right]r^2dr\ , \tag{9}$$

where the g_i are functions which depend only on $n_0(r)$ and $dn_0(r)/dr$. Explicitly,

$$g_1=\frac{5}{9}a_1n_0^{-1/3}+\frac{a_2}{n_0}\left[\left[\frac{1}{n_0}\frac{dn_0}{dr}\right]^2+\frac{2}{r^2}\right]+h(n_0)\ ,$$

$$g_2=-(2a_2/n_0^2)dn_0/dr\ ,$$

and

$$g_3=a_2/n_0\ ,$$

where

$$h(n_0)=-\frac{1}{9}n_0^{-2/3}\left[2a_3+a_4a_5\frac{(2a_5+n_0^{1/3})}{(a_5+n_0^{1/3})^3}\right].$$

The $(r-v/2)f$ term in Eq. (9) is $\delta E_{\rm ext}+\delta E_{\rm Coul}$, where the electrostatic potential due to $\delta n(r,\theta)$ is written as $v(r)\mathscr{E}_0\cos\theta$. In terms of $f(r)$, we have

$$v(r)=-\frac{4\pi}{3}\left[\frac{1}{r^2}\int_0^r f(r')(r')^3dr'+r\int_r^\infty f(r')dr'\right] . \quad (10)$$

The total electrostatic potential arising from the applied field and δn is given by

$$V(r,\theta)=-r\mathscr{E}_0\cos\theta+v(r)\mathscr{E}_0\cos\theta , \quad (11)$$

from which one obtains the electric field $\vec{\mathscr{E}}(r,\theta)$ using

$$\vec{\mathscr{E}}(r,\theta)=-\vec{\nabla}V(r,\theta) . \quad (12)$$

By this definition, $\vec{\mathscr{E}}$ is the part of the electric field that is linear in the applied field, and does not contain the field due to n_0 or n_+.

III. CALCULATION

The electron density $n(\vec{r})$ could be obtained by numerical solution of the Euler-Lagrange equations appropriate to the energy functional given in Eq. (1).[13] Rather than follow this laborious course we obtain an appropriate $n(\vec{r})$ by means of a variational calculation. The correct $n(\vec{r})$ is the function that minimizes E.[13] We proceed by assuming a trial function for $n_0(r)$ and varying its parameters to minimize the energy in the absence of the applied field $\vec{\mathscr{E}}_0$. We then use this variationally determined $n_0(r)$ to calculate the g_i functions in expression (9) for δE. Finally, we assume a trial function for $f(r)$, and vary its parameters to minimize δE using Eqs. (9) and (10). The variationally determined $f(r)$ then gives $\delta n(r,\vartheta)$ for our problem by Eq. (8).

The variational calculation for $n_0(r)$ has been described in detail elsewhere.[15] Our trial function was assumed to have the form

$$n_0(r)=\frac{c}{1+\exp[2b(r-R-a)]+\exp[-2b(r+R+a)]} , \quad (13)$$

where a and b are two variational parameters and c is a normalization constant. Our trial function is similar in form to the trial function chosen by Appelbaum and Hamann[17] for the problem of a plane surface. They chose the function

$$n_0(z)=c/[1+\exp(2bz)] .$$

Our function is a smooth two-parameter function which can reduce to the Appelbaum-Hamann form near the surface of a very large sphere. The second exponential term in the denominator of our $n_0(r)$ assures that our $n_0(r)$ behaves correctly at the origin ($dn_0/dr=0$ at $r=0$).

Values of a and b were numerically obtained by evaluating the energy E in the absence of the external field ($\mathscr{E}_0=0$), and searching for the a,b pair that gave the minimum value for E. Results for the a,b parameters for spheres of different radii R are shown in Table I. Calculations were performed for two choices of the bulk electron-density parameter r_s, where $(\frac{4}{3}\pi r_s^3)^{-1}$ equals the jellium background density. ($r_s=2$ corresponds to aluminum; $r_s=4$ corresponds to sodium.) The number N of electrons in a sphere of radius R equals $(R/r_s)^3$. This number, rounded off to the nearest integer, is listed for each R in Table I. Also listed are the parameters relevant to the trial function $f(r)$ for the perturbed density, which we now describe.

Our choice of a trial function for $f(r)$ is guided by the following physical considerations. The classical electron distribution is $f_{\rm cl}(r)=3\delta(r-R)/4\pi$, which corresponds to a surface charge that completely screens $\vec{\mathscr{E}}_0$ from the interior of the sphere. The quantum-mechanical distribution is expected to have a finite width, and to be peaked near, but not precisely at, the jellium radius $r=R$. Also we must allow for field penetration even to $r=0$ for small spheres. These considerations suggest a three-parameter function, with one parameter, A, governing the location of the peak, another parameter, B, governing the width of the peak, and a third parameter, C, governing the normalization of $f(r)$, or the amount of field penetrating to $r=0$.

A natural function to choose is the derivative of the Fermi function, e.g., the r derivative of $C/\{1+\exp[2B(r-R-A)]\}$. This form, however, will not behave properly at the origin because a single-valued $\delta n(\vec{r})$ requires $f(0)=0$. We must modify the Fermi function so that $f(0)=0$. We elect to do this by symmetrizing the denominator. Our choice for $f(r)$ is

TABLE I. Results of variational calculation. R is the sphere radius, N is the number of electrons in the sphere, a,b are variational parameters for the zero-field density $n_0(r)$, and A,B,K are variational parameters for the field-dependent density $\delta n(\vec{r})$. The quantity δ measures the location of the effective radius relative to R. Atomic units assumed.

r_s	2	2	2	2	4	4	4
R	4	7	14	40	7	14	40
N	8	43	343	8000	5	43	1000
a	−0.258	−0.168	−0.088	−0.031	−0.302	−0.155	−0.054
b	0.854	0.840	0.835	0.834	0.847	0.849	0.852
A	1.412	1.625	1.754	1.826	0.266	0.444	0.552
B	0.665	0.649	0.640	0.633	0.670	0.668	0.668
K	1.098	1.058	1.028	1.010	1.174	1.071	1.022
δ	1.921	2.014	2.029	2.010	0.923	0.909	0.886

$$f(r)=\frac{d}{dr}\left[\frac{C}{1+\exp[2B(r-R-A)]+\exp[-2B(r+R+A)]}\right] . \tag{14}$$

For very large spheres, the second exponential in the denominator is irrelevant since there will be negligible induced charge at $r=0$. In this case, our function reduces to the derivative of the Fermi function.

Rather than deal with the variational parameter C directly, it is more convenient to introduce the variational parameter K defined by

$$K=-\frac{4\pi}{3}\int_0^\infty f(r)dr . \tag{15}$$

For our choice of trial function, it follows that

$$C=\frac{3K}{4\pi}\{1+2\exp[-2B(R+A)]\} . \tag{16}$$

The parameter K is a measure of the screening effectiveness of the polarization charge. The electric field at the origin is given by

$$\vec{\mathscr{E}}(r=0)=(1-K)\vec{\mathscr{E}}_0 , \tag{17}$$

which follows from Eqs. (10)–(12) and (15) regardless of the form chosen for the trial function. Thus, $K=1$ corresponds to perfect screening of the external field at the origin.

Values of A, B, and K were obtained by numerically evaluating δE and searching for the A,B,K set that gave the minimum value of δE. Results are given in Table I. For the case $r_s=2$ and $R=7$ a.u., Fig. 1 presents the electron densities and the electric field. All other values of r_s and R that we have considered would result in graphs qualitatively similar to Fig. 1.

The electronic polarizability α is defined in terms of the dipole moment $\vec{p}$ according to $\vec{p}=\alpha\vec{\mathscr{E}}_0$. This gives

$$\alpha=-\frac{1}{\mathscr{E}_0}\int \delta n(r,\theta)r\cos\theta\, d^3r=-\frac{4\pi}{3}\int_0^\infty f(r)r^3dr . \tag{18}$$

It is useful to define an effective radius[6] R_{eff} by $R_{\text{eff}}\equiv\alpha^{1/3}$. This choice is motivated by the fact that the classical polarizability of a metal sphere equals R^3. A small metal sphere therefore is polarized as if it were a classical conducting sphere of radius R_{eff}. It also follows that the electric field outside the region where δn is appreciable is given by the electric field outside a classical metal sphere of radius R_{eff}. To see this, apply Eqs. (10) and (11) to this exterior region where $f(r)$ is assumed to be negligible, and introduce α using Eq. (18). The potential in this exterior region becomes

$$V(r,\theta)=-\mathscr{E}_0\left[r-\frac{\alpha}{r^2}\right]\cos\theta , \tag{19}$$

where the calculated electronic response enters only in $\alpha=R_{\text{eff}}^3$.

It is convenient to specify the location of the effective radius relative to the jellium edge, and to introduce the parameter $\delta\equiv R_{\text{eff}}-R$. By definition,

$$\alpha=(R+\delta)^3 . \tag{20}$$

Values of δ obtained through Eqs. (18) and (20) are shown in Table I.

An alternative way to calculate α, and hence δ, is from the energy δE rather than from the dipole moment as in Eq. (18). Within the framework of linear response, the exact value of the energy δE is equal to the classical Coulomb interaction energy between the polarizable sphere and the applied electric field.[19] But this classical Coulomb interaction energy is just $-\frac{1}{2}\vec{p}\cdot\vec{\mathscr{E}}_0=-\frac{1}{2}\alpha\mathscr{E}_0^2$, so that

$$\alpha=-2\delta E/\mathscr{E}_0^2 . \tag{21}$$

If the variational calculation is consistent, Eq. (21) will agree with Eq. (18). However, for a poor choice of trial function in a variational calculation, Eqs. (21) and (18) may give significantly different values of α. This is not the case for our trial function. We find that Eqs. (18) and (21) give values of α that agree to better than one-tenth of a percent. However, when we attempted to use a two-parameter trial function, the agreement was poor (see Sec. IV E).

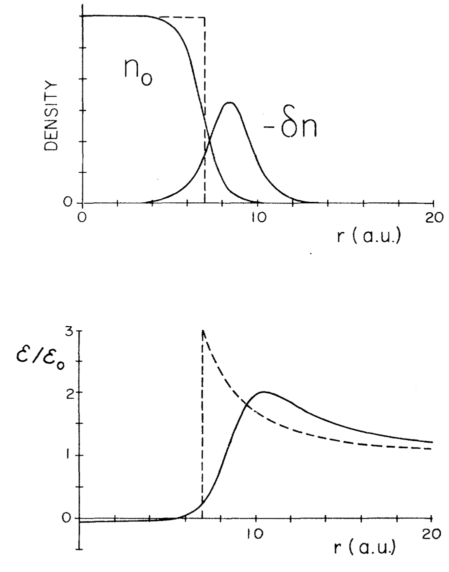

FIG. 1. Electron densities and electric field for the case $r_s=2$ and $R=7$ a.u. In the upper panel the unperturbed electron density $n_0(r)$ is drawn on the same scale as the jellium density, which is the dashed step. Perturbation in the electron charge $-\delta n(r,0)$ is drawn greatly enlarged on an arbitrary scale. In the lower panel the solid line is $\mathscr{E}_r(r,0)$, the radial component of the electric field plotted along the polar axis, and the dashed line is the corresponding electric field for a classical metal sphere. Both curves are normalized to the applied field strength $\mathscr{E}_0$.

IV. DISCUSSION

A. Induced charge and electric field

The applied electric field causes electronic charge to be pulled out of the metal out to distances on the order of a few a.u. from the jellium edge (see Fig. 1). The peak in the induced charge density $-\delta n$ is approximately at $r=R+A$ for our trial function (14). From Table I we see that this peak is on the order of 1.6 a.u. beyond the jellium edge for $r_s=2$ and is on the order of 0.5 a.u. beyond the jellium edge for $r_s=4$. The variation of A with R is surprisingly small for spheres containing more than 40 electrons. (Results of calculations for spheres having radii between values of R listed in Table I can be found reliably by interpolation, and so are not listed.)

The width of the induced charge density is governed by the parameter B. This parameter shows only slight variation with R. From the values of A and B in Table I, we can infer that as the particle size increases there is a tendency for the charge to be pulled out slightly further, while the width of the charge distribution is nearly unchanged.

Most remarkable is the *very* small variation of the parameter δ with radius. There is only a few percent variation in δ between the smallest and largest spheres. This variation is smaller than the variation in the parameter A. [The quantities δ and A are determined by different moments of $f(r)$.]

As discussed earlier, the electric field in the exterior region where δn is negligible is equal to the electric field outside a classical conducting sphere of radius $R_{\text{eff}}=R+\delta$. For our trial function (14) the exterior region roughly begins at $r=R+A+B^{-1}$, or about $R+3.5$ a.u. for $r_s=2$ and $R+2.0$ a.u. for $r_s=4$. For r greater than these values, the electrostatic potential is well approximated by Eq. (19) with $\alpha=(R+\delta)^3$.

In Fig. 1 we plotted the radial electric field component $\mathscr{E}_r(r,0)$ for the case $r_s=2$ and $R=7$ a.u. Also shown is the corresponding classical field, which equals $[1+2(R/r)^3]\mathscr{E}_0$ for $r>R$ and zero for $r<R$. The electric field is smaller than the classical value just outside the jellium surface, but is larger than the classical value in the exterior region where δn is negligible. The larger field in the exterior region arises because δ is positive.

The electric field inside the sphere is noteworthy. Figure 1 shows a large region of a small negative value of $\mathscr{E}_r(r,0)$ for $r<R$. This implies that δn is slightly overscreening the external field, giving rise to a total electric field in the interior which is opposite to the external field. This overscreening effect is correlated with the parameter K [see Eq. (17)], and as one can see from Table I, is largest for the smallest spheres, and larger for $r_s=4$ than for $r_s=2$. That is, the field in the interior becomes more classical for larger spheres and higher electron density. The fact that there is a reversed electric field within the sphere is discussed further in Sec. IV D.

B. Electronic polarizability

Our calculations yield electronic polarizabilities which are greater than the classical values. This follows from Eq. (20) and the fact that our δ values are positive. Hence, our results conflict with previous calculations,[4,5,7,8] where it was concluded that α is smaller than the classical value R^3. As remarked earlier, the problem with these previous calculations is that they were not self-consistent. Either an infinite barrier was assumed at some stage in the calculation[8] or electronic response functions were approximated to be nearly bulk metalliclike in the region $r<R$ while the region $r>R$ was treated as vacuum.[4,5,7] The net effect is to prevent the electrons from being pulled out of the jellium background. As a result, δ turned out to be negative and α was smaller than R^3.

When $R \gg \delta$, Eq. (20) gives

$$\alpha \cong R^3(1+3\delta/R) . \tag{22}$$

For our calculated values of δ, Eq. (22) is a reasonable approximation for the case $r_s=2$ when $R\geq 14$ a.u. and for the case $r_s=4$ when $R\geq 7$ a.u.

C. Connection with image plane

On physical grounds it is clear that as $R\rightarrow\infty$, the electrostatic potential and charge density near $r=R$ and $\theta=0$ must approach the corresponding quantities for the problem of an electric field applied perpendicular to the plane surface of a semi-infinite metal. This follows from considering a section of a very large sphere in the region near the surface where $\theta\approx 0$. As $R\rightarrow\infty$, this part of the sphere locally resembles a plane surface which is subjected to an applied field perpendicular to the surface.

When a field is applied perpendicular to a plane surface, the electron response can be characterized by an image plane.[13,20] Lang and Kohn[20] showed that the image plane is located at the centroid of the induced electron density. If the position of the image plane relative to the jellium background is δ_p, the Lang-Kohn result is[20]

$$\delta_p=\frac{\int_{-\infty}^{\infty}\delta n_p(z)z\,dz}{\int_{-\infty}^{\infty}\delta n_p(z)dz} , \tag{23}$$

where $z=0$ is the jellium edge and δn_p is the induced electron density for the problem of a plane surface.

We now consider the case of a very large sphere and show that $\delta\rightarrow\delta_p$ as $R\rightarrow\infty$. We perform a change of variable $r=R+\xi$ in the integrand of Eq. (18), and assume the large-R expansion $(R+\xi)^3\cong R^3+3\xi R^2$. This gives

$$\alpha\cong-\frac{4\pi}{3}\int_{-R}^{\infty}\tilde{f}(\xi)(R^3+3\xi R^2)d\xi , \tag{24}$$

where $\tilde{f}(\xi)=f(R+\xi)$ is the function f after a shift of origin to the surface of the sphere. The assumption that $\xi \ll R$ is justified because $f(r)$ is appreciable only in a finite range around R.

As $R\rightarrow\infty$, Eq. (24) yields the form (22), with a value of δ given by

$$\delta=\frac{\int_{-\infty}^{\infty}\tilde{f}(\xi)\xi\,d\xi}{\int_{-\infty}^{\infty}\tilde{f}(\xi)d\xi} . \tag{25}$$

In obtaining (25) we used the result that $\int_{-\infty}^{\infty}\tilde{f}(\xi)d\xi\rightarrow-3/4\pi$ as $R\rightarrow\infty$, which follows from Eqs. (15) and (17) and the fact that as $R\rightarrow\infty$, the electric field vanishes at the center of the sphere. (The bulk-limit result of perfect shielding is approached.)

Now in the $R \to \infty$ limit the functions $\tilde{f}$ and δn_p become identical (apart from differences in normalization). That is, the induced electron distribution in the vicinity of the radius of the sphere (with $\theta \approx 0$) goes over to the induced electron distribution in the vicinity of a plane surface. We conclude that the right-hand sides of Eqs. (23) and (25) are equal, and so $\delta \to \delta_p$ as $R \to \infty$.

Our calculations show that δ varies little between $R = 7$ a.u. and 40 a.u. It is reasonable to assume that the δ value for $R = 40$ a.u. is close to the δ value for $R \to \infty$. It then follows from our calculations that $\delta_p \approx 2.0$ a.u. for $r_s = 2$ and $\delta_p \approx 0.9$ a.u. for $r_s = 4$. The corresponding results of Lang and Kohn's wave-mechanical calculation[20] are 1.6 a.u. for $r_s = 2$ and 1.3 a.u. for $r_s = 4$.

Presumably the wave-mechanical form of the density-functional formalism is superior to the density-gradient form. However, the density-gradient form probably indicates the correct variation of δ, if not the correct value. Since it indicates that δ is nearly *independent of* R we might reverse the previous arguments (to incorporate the wave-mechanical value of δ_p) and obtain

$$\alpha \cong R^3(1 + 3\delta_p / R) \ . \tag{26}$$

A similar result can be obtained in the large -R limit from an expression given by Ljungbert and Apell.[3] To apply their expression, one must assume that the metal sphere is described by a dielectric constant ϵ, where $|\epsilon| \gg 1$ for the static case.

D. Sum rule

The electrostatic field within the jellium sphere must satisfy a certain sum rule or electrostatic balance theorem. The sum rule states that the sum of all the electrostatic forces on the positive background of an isolated neutral object in a uniform external field vanishes. This sum rule has been derived for isolated molecules[21]; it is also true for current-carrying conductors.[22] Although these derivations make use of the exact quantum-mechanical equations of motion of the electrons, we have also shown that the sum rule holds if the electron system is characterized by an approximate energy functional.[23] The mathematical statement of the sum rule is

$$\int n_+(\vec{r})\vec{\mathscr{E}}(\vec{r})d^3r = \vec{0} \ . \tag{27}$$

The sum rule (27) holds whether or not the positive background density is assumed to be rigid. In our calculations we assumed a rigid uniform background. When we calculate $\vec{\mathscr{E}}$ from the potential using Eqs. (11) and (12), we find that the sum rule (27) leads to the interesting result

$$V(R,\theta) = 0 \ , \tag{28}$$

where we have made use of our convention that $V(r=0)=0$. We emphasize that the potential V is due only to the external field and induced charges; it does not include the contributions from n_+ and n_0. Alternatively, we can express the condition (28) in terms of the radial component of field for $\theta = 0$, as follows:

$$\int_0^R \mathscr{E}_r(r,0)dr = 0 \ . \tag{29}$$

As far as we are aware, none of the previously reported calculations within the jellium model satisfy conditions (28) or (29). The failure to satisfy the sum rule is particularly obvious in the semiclassical or Thomas-Fermi—type calculations that confine the electrons to $r < R$.[24] In those calculations $\vec{\mathscr{E}}$ is parallel to $\vec{\mathscr{E}}_0$ everywhere along the polar axis. The sum rule requires that along $\theta = 0$ within the jellium, the electric field is parallel to $\vec{\mathscr{E}}_0$ in some regions and antiparallel to $\vec{\mathscr{E}}_0$ in others. The average field along $\theta = 0$ vanishes according to Eq. (29). In our calculations we do find a region within the sphere where the field is parallel to $\vec{\mathscr{E}}_0$ and another region where it is antiparallel to $\vec{\mathscr{E}}_0$. This can be seen in Fig. 1. Note, however, that for our calculations the antiparallel component dominates in this $r_s = 2$, $R = 7$ a.u. case. We find that the radius r_0 for which $V(r_0,\theta) = 0$ is within a fraction of an a.u. from R, and that the agreement with the sum rule is better for $r_s = 4$ than for $r_s = 2$. Table II gives values of r_0 for various cases.

E. Reliability of variational calculations

Our numerical results are approximate for two reasons. First, our chosen trial functions may not be accurate representations of the true electron distribution that minimizes the energy functional. Second, the energy functional that we use is only an approximation to the exact, but unknown, energy functional. We discuss these two points in the remainder of this section.

1. Accuracy of trial functions

One indication that our trial function (14) for $f(r)$ is a good one is the excellent agreement of the values of δ calculated by means of Eq. (20) and each of the two equations, (18) and (21). If δ_{energy} is the value of δ obtained from the energy δE by means of Eqs. (20) and (21), then

$$\delta_{\text{energy}} = R - (-2\delta E / \mathscr{E}_0^2)^{1/3} \ . \tag{30}$$

If δ_{field} is the value of δ obtained from the induced dipole field using Eqs. (18) and (20), then

$$\delta_{\text{field}} = R - \left[\frac{1}{\mathscr{E}_0} \int \delta n(r,\theta) r \cos\theta \, d^3r \right]^{1/3} \ . \tag{31}$$

For our three-parameter trial function we found that

TABLE II. Calculated values of the radius r_0 for which $V(r_0,\theta) = 0$.

r_s	2	2	2	4	4
R	4	7	40	7	40
r_0	4.48	7.56	40.45	7.12	40.00

δ_{energy} and δ_{field} agree to four-figure accuracy, so that only one value δ is reported in Table I.

In general, δ_{energy} and δ_{field} may differ significantly. To investigate this and to test the importance of the overscreening effect ($K>1$) we performed a two-parameter variational calculation. We used the same form of the trial function $f(r)$ as before but we fixed $K=1$. Results for the very small spheres are given in Table III. (For larger spheres, the optimal K approaches unity, and the results are in better agreement with the three-parameter calculation.) We note that the δ values shown in Table III are only approximately equal. This is an indication that the three-parameter trial function with variable K is a good one, and the two-parameter trial function with $K=1$ is considerably less accurate. In other words, the overscreening effect needs to be included for small spheres.

Note that for the two-parameter trial function δ_{energy} is closer than δ_{field} to the value of δ for the three-parameter trial function. This is to be expected because δE satisfies a minimum principle and hence δE and δ_{energy} are relatively insensitive to changes in the trial function when one is near the minimum. Furthermore, because the true value of δE is less than or equal to the value of δE calculated by using a trial function, we deduce that δ_{energy} calculated from a trial function satisfies the extremum principle

$$\delta_{\text{true}} \geq \delta_{\text{energy}}\ , \tag{32}$$

where δ_{true} is the value of δ for the true charge density. Thus, as we improve the trial function, δ_{energy} should increase. Comparison of the results in Tables I and III shows that this is the case. Because of the extremum principle (32), δ_{energy} is a more reliable estimate of δ_{true} than is δ_{field}. The relatively small change in δ_{energy} as we go from a two-parameter to a three-parameter variational calculation also indicates that we are probably near the minimum δE and therefore the values of δ in Table I are close to δ_{true}.

The fact that the sum rule (27) is not accurately obeyed for some cases indicates that some details of our $\delta n(r,\theta)$ are in error. Note, however, that the field in the exterior region depends only on δ by Eqs. (19) and (20). We conclude that our results for the exterior field should be approximately correct.

There may also be some error in the calculation of $\delta n(r,\theta)$ that is introduced by relying on the trial function (13) for $n_0(r)$. Although we experimented with a limited number of other trial functions for $n_0(r)$, we did not find them to be significantly better.

2. *Accuracy of energy functional*

It has been suggested that the energy functional which we are considering is not accurate in treating the kinetic energy term E_{kin}.[25] The choice $a_2=\frac{1}{72}$ in the gradient expansion (2) for E_{kin} may be an underestimate.[25,26] To investigate the sensitivity of our calculations to a_2, we chose $a_2=\frac{1}{36}$ as a reasonable upper limit to this coefficient.[26] We then repeated the calculations. The results are shown in Table IV. The values of δ for $r_s=2$ are lowered by about 15% and the values of δ for $r_s=4$ are raised by about 10%. The near constancy of δ as a function of R is still observed. The δ values for the large spheres are closer to the values of δ_p calculated by Lang and Kohn for the plane surface. In general, the sum-rule condition (29) is also better obeyed.

The use of a gradient expansion for E_{kin} excludes effects due to discrete quantum levels and Friedel oscillations. A treatment of such effects requires an RPA calculation or a density-functional calculation in wave-mechanical form. It is reasonable to expect that the weak R dependence of δ which we have found will also be found, at least in some average sense,[27] in the wave-mechanical calculations.

V. CONCLUSION

Our variational calculation has proven to be conceptually simple and numerically tractable. The calculations that we have described can be readily performed on a microcomputer.

We find that the applied field pulls out electronic charge from the jellium region by a significant amount. The effective radius of the polarization charge lies a distance δ beyond the jellium radius R, where δ is nearly independent of particle size for R in the range between 7 a.u. and 40 a.u. From the results in Tables I and IV we estimate $\delta \approx 1.7-2.0$ a.u. for $r_s=2$ and $\delta \approx 0.9-1.1$ a.u. for $r_s=4$.

The electronic polarizability is given by $\alpha=(R+\delta)^3$, and it is larger than the classical value R^3 since δ is positive. In the limit of large spheres, δ approaches the image-plane distance δ_p for a flat surface. This fact and the near constancy of δ with R suggests the approximation $\alpha \cong (R+\delta_p)^3$ for $R \gg \delta_p$.

The effective-radius shift δ can be directly related to the energy as in Eq. (30), and as a result satisfies an extremum principle given by expression (32).

The electric field outside the region of induced charge is

TABLE III. Results of two-parameter variational calculation ($K=1$).

r_s	2	2	4
R	4	7	7
A	1.510	1.688	0.416
B	0.673	0.655	0.683
δ_{field}	1.82	1.90	0.65
δ_{energy}	1.91	2.01	0.88

TABLE IV. Results of variational calculation when $a_2=\frac{1}{36}$ in the kinetic-energy functional.

r_s	2	2	4	4
R	7	40	7	40
a	−0.235	−0.040	−0.500	−0.359
b	0.767	0.783	0.665	0.693
A	1.285	1.458	0.229	0.608
B	0.586	0.588	0.523	0.542
K	1.067	1.011	1.226	1.026
δ	1.752	1.664	1.159	1.027
r_0	7.11	40.05	7.10	39.92

equal to the field outside a classical conducting sphere of radius $R_{\text{eff}}=R+\delta$. This equivalence allows one to use classical expressions, for example, in approximating the field experienced by an adsorbed molecule on a small metal sphere that is exposed to infrared radiation.[6,10]

A general sum rule was developed for the jellium model of a sphere. Equation (28) holds for an exact calculation based on any assumed form for the energy functional. None of the previous calculations satisfies this sum rule; our calculations satisfy this sum rule approximately in the majority of cases as can be seen from Tables II and IV.

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