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Electronic Polarizabilities of Very Small Metallic Particles and Thin Films

M. J. Rice, W. R. Schneider, and S. Strässler

Brown Boveri Research Center, CH-5401 Baden, Switzerland

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This paper presents calculations of the electronic polarizabilities of very small metallic particles and of very thin metallic films. The theoretical model we employ for the metallic particle is simply that of N free electrons trapped by an infinitely deep spherical potential well. The model used for the thin-film problem is that of a system of free electrons constrained to move in the volume enclosed by two infinite parallel planes. Linear-response theory and Poisson's equation are used to calculate the electronic polarizability in terms of the electronic density-density response function. The numerical results provide an idea of just how small, or how thin, a small metallic particle, or thin metallic film, has to be for it to begin to lose its bulk property of being able to screen an externally applied electric field.

I. INTRODUCTION AND SYNOPSIS

The purpose of this paper is to present a model calculation of the electronic polarizabilities α of very small metallic particles and of very thin metallic films. Intimately connected with this problem is the question of the ability of such small or thin metallic systems to screen an externally applied static electric field.

The motivation for these calculations stems from a recently published criticism[1] of the Gorkov-Eliashberg (GE) 1965 prediction[2] that the electronic polarizability of a minute metallic particle should be enormously enhanced with respect to the bulk classical value $\alpha_0 = R^3$, where R denotes the mean radius of the particle. A short résumé of this criticism will serve as a convenient introduction to the formulation of the present problem.

The electric dipole moment $\vec{p}$ developed by an isolated metallic system in response to an externally applied field $\vec{E}_0$ is

$$\vec{p} = \int d^3r\, \vec{r}\, \rho^{in}(\vec{r}) , \tag{1.1}$$

in which $\rho^{in}(\vec{r})$ denotes the induced charge density at the space point $\vec{r}$. Within the framework of linear response,[3] the latter is related to the local electrostatic potential $\Phi(\vec{r})$ by means of the relation

$$\rho^{in}(\vec{r}) = -\int d^3r'\, \Phi(\vec{r}')\chi(\vec{r}, \vec{r}') , \tag{1.2}$$

where $\chi(\vec{r}, \vec{r}')$ denotes the electronic density-density response function characteristic of the metallic system. $\Phi(\vec{r})$ is given by the solution of the Poisson equation $\nabla^2\Phi(\vec{r}) = -4\pi\rho^{in}(\vec{r})$ or, in view of (1.2), by the solution of

$$\nabla^2\Phi(\vec{r}) = 4\pi\int d^3r'\, \Phi(\vec{r}')\chi(\vec{r}, \vec{r}') . \tag{1.3}$$

In terms of $\Phi(\vec{r})$, $\vec{p}$ is

$$\vec{p} = -\int d^3r \int d^3r'\, \vec{r}\, \Phi(\vec{r}')\chi(\vec{r}, \vec{r}') . \tag{1.4}$$

Thus given the appropriate boundary conditions on $\Phi(\vec{r})$, Eqs. (1.3) and (1.4) enable $\vec{p}$, and hence α, to be calculated from the knowledge of the characteristic response function $\chi(\vec{r}, \vec{r}')$.

Now GE were specifically concerned with metallic particles sufficiently minute that the discreteness of their conduction-electron energy levels would have to be taken into account. For such small (but still macroscopic) particles, GE assumed that one would be able to calculate their polarizabilities just as though each behaved as a macroscopic "atom." In terms of the above formulation this meant that GE introduced the drastic assumption that the local field $\vec{E}(\vec{r}) = -\vec{\nabla}\Phi(\vec{r})$ could be identified at every point with the applied field $\vec{E}_0$, so that, for example, in Eq. (1.4) one could write $\Phi(\vec{r}) = -\vec{E}_0 \cdot \vec{r}$. It would then follow[1] from (1.4) that

$$\vec{p} = \vec{E}_0 \Omega \chi_p \tag{1.5}$$

or $\alpha = \Omega\chi_p$, where χ_p denotes the static electronic

susceptibility[1]

$$\chi_p = \tfrac{1}{3} \int \frac{d^3r}{\Omega} \int d^3r' \, \vec{r} \cdot \vec{r}' \, \chi(\vec{r}, \vec{r}') , \qquad (1.6)$$

where Ω denotes the volume of the metallic system, and for the sake of argument, we have assumed an isotropic system. Since for an isolated conduction-electron system of macroscopic extent ($k_F R \gg 1$, where k_F denotes the Fermi wave vector of the conduction-electron system) χ_p can be anticipated to be very large[2] $[\sim (k_F R)^2]$, GE concluded that the electronic polarizability of a minute metallic particle ($\Omega = \tfrac{4}{3}\pi R^3$) would be greatly enhanced with respect to the classical result $\alpha_0 = R^3$.

Clearly, however, the constant-local-field assumption invoked by GE is erroneous, since it completely neglects the screening effect of the system of conduction electrons, an effect that arises irrespectively of whether the electronic energy levels are discrete or continuous, and which effect is, of course, quantitatively determined by the solution of the Poisson equation (1.3). Indeed, for very large $k_F R$, the external field will be always essentially screened $[\vec{E}(\vec{r}) = 0$, almost everywhere in the interior of the metal] even if R is still sufficiently small for the electronic energy levels to be discrete in the sense defined by GE.[2] The polarizability will then be very close to $\alpha_0 = R^3$. Naturally enough, the experimental attempts[4,5] which have been made to confirm GE's enhanced polarizability have failed.[6]

Of course, when $k_F R$ is not too large, the absolute amount of conduction-electron charge present in the metallic system may not be sufficiently large to effect the complete screening of $\vec{E}_0$. In this case, the external field begins to penetrate the interior of the metal; the system is thus less polarized and α will assume a value *less* than α_0. It is particularly this phenomenon—*the limiting tendency of very small metallic objects to lose their bulk screening properties*—that we wish to investigate theoretically in the present paper.

Our program will be to solve (1.3) and (1.4) for simple microscopic models of a small metallic particle and a thin metallic film. The model that we shall introduce for the metallic particle will be that of a system of N free electrons trapped by an infinite spherical potential well of radius R. For the film, we shall consider a system of free electrons constrained to move within the volume enclosed by two infinite parallel planes (separated by distance d). For either model the electronic density-density response function $\chi(\vec{r}, \vec{r}')$ will be of the form[3]

$$\chi(\vec{r}, \vec{r}') = 2e^2 \sum_{nn'} \sum \frac{f(\epsilon_n) - f(\epsilon_{n'})}{\epsilon_{n'} - \epsilon_n}$$

$$\times \phi_n^*(\vec{r}) \, \phi_n(\vec{r}') \, \phi_{n'}^*(\vec{r}') \, \phi_{n'}(\vec{r}) , \qquad (1.7)$$

in which the $\phi_n(\vec{r})$ and ϵ_n denote, respectively, the appropriate single-electron wave functions and energy eigenvalues, and $f(\epsilon_n)$ denotes the usual Fermi-Dirac function. The factor 2 accounts for the spin degeneracy.

The layout of the paper will be as follows. In Secs. II and III we reduce the problems of calculating α and the local field $\vec{E}(\vec{r})$ for the spherical particle and film to the numerical solution of a system of linear equations. We have found it convenient to outline in Sec. IV an approximate calculation of α and $\vec{E}(\vec{r})$ based on a Thomas-Fermi (TF) approximation in which the right-hand side of the integro-differential equation (1.3) is replaced by

$$k_s^2(\vec{r}) \, \phi(\vec{r}) , \qquad (1.8)$$

where $k_s(\vec{r})$ denotes the TF screening wave vector appropriate to the actual electronic density at the point $\vec{r}$. In Sec. V numerical results for α/α_0 and $\vec{E}(\vec{r})$ as functions of both the dimensions R or d and the value of the mean electronic density r_s will be presented and discussed. For large enough R or d we find that the TF approximation (1.8) closely approximates the results of the exact (and time consuming) methods of calculation presented in Secs. II and III.

The microscopic models employed in the present calculations are too simplified to do proper justice to *actual* small metallic particles and thin films. From the standpoint of the calculation of α the most important shortcoming of the models is probably their inherent neglect of a realistic treatment of the electronic density in the surface region. This criticism would be of particluar relevance to very small dimensions, such as R or d, where the amount of charge situated in the surface regions would amount to an appreciable fraction of the metal's total charge. In his pioneering work on the thermodynamic properties of minute metallic particles, Kubo[7] has stressed the importance of surface shape irregularities that would remove the extremely high degeneracy of the bound electronic states of a particle of perfect sphericity. The retention of the high degeneracy of electronic states in the present work on the spherical particle is probably not too serious for the calculation of α, since the change in the distribution of the electronic charge density that would be brought about by the removal of the degeneracy can be expected to be minor.[8]

The present numerical results should, however, give us a semiquantitative idea of just how small, or how thin, a small metallic particle, or thin film, has to be for it to lose, or partially lose, its normal bulk screening property. The degree to which this happens is specified by the amount

by which the radio α/α_0 is less than unity. For example, in order for a small metallic particle of mean electronic density $r_s = 4$ to have its polarizability reduced to, say, 70% of its classical value, we find its diameter would have to be as small as 26 Å. For a thin film of the same density, we find that a similar reduction in electronic polarizability would occur if the film were as thin as approximately 10 Å. Detailed results of this nature will be found in Sec. V.

II. FORMAL SOLUTION FOR SPHERICAL PARTICLE

The wave functions and energy eigenvalues of the bound electronic states of an infinitely deep spherical potential well of radius R are

$$\psi_{nlm}(\vec{r}) = c_{ln} j_l(\alpha_{ln} r/R) Y_{lm}(\vec{e}), \quad (2.1)$$

$$\epsilon_{ln} = (\hbar^2/2mR^2)\alpha_{ln}^2, \quad (2.2)$$

in which α_{ln} denotes the nth zero of the spherical Bessel function j_l ($n = 1, 2, \ldots$; $l = 0, 1, 2, \ldots$), Y_{lm} the mth spherical harmonic $[m = -l, -(l-1), \ldots, (l-1), l]$, and c_{ln} are the normalizing coefficients

$$c_{ln} = 2^{1/2}/R^{3/2} j_l'(\alpha_{ln}), \quad (2.3)$$

where $j_l'(x)$ denotes the derivative of $j_l(x)$ with respect to x. In (2.1), $\vec{e}$ denotes the unit vector $\vec{r}/r$, and the origin of the coordinate system is the center of the sphere. The response function $\chi(\vec{r}, \vec{r}')$, (1.7), is

$$\chi(\vec{r}, \vec{r}') = 2e^2 \sum_{lnm} \sum_{l'n'm'} \frac{f(\epsilon_{ln}) - f(\epsilon_{l'n'})}{\epsilon_{l'n'} - \epsilon_{ln}}$$
$$\times \psi_{lnm}^*(\vec{r})\psi_{lnm}(\vec{r}')\psi_{l'n'm'}^*(\vec{r}')\psi_{l'n'm'}(\vec{r}). \quad (2.4)$$

In order to calculate $\vec{p}$ we shall have to solve

$$\nabla^2 \Phi(\vec{r}) = 4\pi \int d^3r' \chi(\vec{r}, \vec{r}')\Phi(\vec{r}') \quad (2.5)$$

$$= -4\pi\rho^{in}(\vec{r}) \quad (2.6)$$

for $\Phi(\vec{r})$. If we take the constant external field $\vec{E}_0$ to be directed along the z axis, we may write, in spherical coordinates (r, θ, ϕ),

$$\Phi(\vec{r}) = -E_0 r \cos\theta + \Phi^{in}(\vec{r}), \quad (2.7)$$

defining the induced potential $\Phi^{in}(\vec{r})$. The latter must satisfy

$$\lim \vec{\nabla}\Phi^{in}(\vec{r}) = 0 \text{ as } |\vec{r}| \to \infty. \quad (2.8)$$

Also, Φ^{in} and its associated field $-\vec{\nabla}\Phi^{in}$ must be continuous. Since, in view of the definition of our model, $\rho^{in}(\vec{r}) = 0$ for $|\vec{r}| > R$, it follows from (2.6) that

$$\nabla^2\Phi^{in}(\vec{r}) = 0, \quad |\vec{r}| > R. \quad (2.9)$$

Equations (2.9) and (2.8) are satisfied by

$$\Phi^{in}(\vec{r}) = (c_0 E_0 R^3/r^2)\cos\theta, \quad (2.10)$$

where c_0 is a constant. For $|\vec{r}| < R$, a solution for $\Phi^{in}(\vec{r})$ may be written in the form

$$\Phi^{in}(\vec{r}) = E_0[c_0 r + Rf(r)]\cos\theta, \quad (2.11)$$

where $f(r)$ is some function of r. In view of (2.6), (2.11) implies

$$\rho^{in}(\vec{r}) = (E_0 R/4\pi)g(r)\cos\theta, \quad (2.12)$$

where

$$g = -[f'' + (2/r)f' - 2f/r^2]. \quad (2.13)$$

The continuity of Φ^{in} and $\vec{E}^{in}$ at $r = R$ will, in view of (2.10) and (2.11), impose the conditions

$$f(R) = 0, \quad (2.14)$$

$$Rf'(R) = -3c_0. \quad (2.15)$$

Before going ahead with the solution $f(r)$, let us first demonstrate that the polarizability of the sphere will be just $\alpha = R^3 c_0 = \alpha_0 c_0$; i.e., the constant c_0 measures the deviation of α from the classical polarizability R^3. To see this, we insert (2.12) into (1.1). After evaluating the angular integrals, we obtain

$$\vec{p} = \vec{E}_0(\tfrac{1}{3}R)\int_0^R dr\, r^3 g(r).$$

Using (2.13) and partially integrating twice leads to

$$\vec{p} = \vec{E}_0(\tfrac{1}{3}R^3)[f(R) - Rf'(R)]$$

or, on using (2.14) and (2.15),

$$\vec{p} = \vec{E}_0 R^3 c_0 \equiv \alpha\vec{E}_0. \quad \text{(Q. E. D.)}$$

We now expand the function $f(r)$ in terms of the complete orthogonal set $j_1(\alpha_{1n}r/R)$ ($n = 1, 2, \ldots$):

$$f(r) = \sum_{n=1}^{\infty} c_n j_1(\alpha_{1n}r/R). \quad (2.16)$$

Equation (2.14) is automatically satisfied, whereas (2.15) leads to

$$c_0 = -\tfrac{1}{3}\sum_{n=1}^{\infty} c_n j_1'(\alpha_{1n})\alpha_{1n}. \quad (2.17)$$

The function $g(r)$ becomes

$$g(r) = \sum_{n=1}^{\infty} c_n \left(\frac{\alpha_{1n}}{R}\right)^2 j_1\left(\frac{\alpha_{1n}r}{R}\right). \quad (2.18)$$

If we equate the right-hand sides of Eqs. (2.5) and (2.6), we obtain

$$g(r) = \int_0^R ds\, s^2 q(r, s)[(c_0 - 1)s/R + f(r)], \quad (2.19)$$

where

$$q(r, s) = 4\pi \int d\Omega(\vec{e}) \int d\Omega(\vec{e}') Y_{10}(\vec{e}) Y_{10}(\vec{e}')\chi(r\vec{e}, s\vec{e}'). \quad (2.20)$$

Inserting (2.16), (2.18), and (2.20) into (2.19), and making use of the explicit form (2.4) for $\chi(\vec{r}, \vec{r}')$, we obtain, after considerable algebra, the following system of linear equations for the coefficients c_n ($n = 1, 2, \ldots$):

$$\sum_{n=1}^{\infty} A_{mn}c_n = a_m, \quad m = 1, 2, \ldots \quad (2.21)$$

with

$$a_m = 4\bar{R} \sum_{ln_1n_2} \left(\frac{f_{ln_1} - f_{(l-1)n_2}}{\alpha_{ln_1}^2 - \alpha_{(l-1)n_2}^2} \frac{l}{\gamma_{ln_1}\gamma_{(l-1)n_2}} B_m^1(ln_1n_2)C^1(ln_1n_2) + \frac{f_{ln_1} - f_{(l+1)n_2}}{\alpha_{ln_1}^2 - \alpha_{(l+1)n_2}^2} \frac{(l+1)}{\gamma_{ln_1}\gamma_{(l+1)n_2}} B_m^2(ln_1n_2)C^2(ln_1n_2) \right),$$

$$(2.22)$$

$$A_{mn} = 4\bar{R} \sum_{ln_1n_2} \left(\frac{f_{ln_1} - f_{(l-1)n_2}}{\alpha_{ln_1}^2 - \alpha_{(l-1)n_2}^2} \frac{l}{\gamma_{ln_1}\gamma_{(l-1)n_2}} B_m^1(ln_1n_2)B_n^1(ln_1n_2) + \frac{f_{ln_1} - f_{(l+1)n_2}}{\alpha_{ln_1}^2 - \alpha_{(l+1)n_2}^2} \frac{(l+1)}{\gamma_{ln_1}\gamma_{(l+1)n_2}} B_m^2(ln_1n_2)B_n^2(ln_1n_2) \right)$$

$$- \tfrac{1}{3} a_m \, \alpha_{ln} j_1'(\alpha_{lm}) - \delta_{mn} \alpha_{ln}^2 \gamma_{ln} \ . \quad (2.23)$$

Here $\bar{R} = R/a_B$, where $a_B = \hbar^2/me^2$ denotes the Bohr radius and

$$\gamma_{ln} = \tfrac{1}{2}[j_1'(\alpha_{ln})]^2 \ . \quad (2.24)$$

The quantities $B_n^1(ln_1n_2)$, $B_n^2(ln_1n_2)$, $C^1(ln_1n_2)$, and $C^2(ln_1n_2)$ are defined by

$$B_n^1(ln_1n_2) = \int_0^1 dx \, x^2 j_1(\alpha_{ln}x) j_l(\alpha_{ln_1}x) j_{l-1}(\alpha_{(l-1)n_2}x) \ ,$$

$$B_n^2(ln_1n_2) = \int_0^1 dx \, x^2 j_1(\alpha_{ln}x) j_l(\alpha_{ln_1}x) j_{l+1}(\alpha_{(l+1)n_2}x) \ ,$$

$$(2.25)$$

$$C^1(ln_1n_2) = \int_0^1 dx \, x^3 j_l(\alpha_{ln_1}x) j_{l-1}(\alpha_{(l-1)n_2}x) \ ,$$

$$C^2(ln_1n_2) = \int_0^1 dx \, x^3 j_l(\alpha_{ln_1}x) j_{l+1}(\alpha_{(l+1)n_2}x) \ .$$

Finally, the f_{ln} denote the Fermi-Dirac functions $f(\epsilon_{ln})$ which we shall take as step functions ($T = 0$):

$$f_{ln} = \begin{cases} 1, & \alpha_{ln} < \alpha_F \\ 0, & \alpha_{ln} > \alpha_F \end{cases} \quad (2.26)$$

α_F defines the Fermi level $E_F = (\hbar^2/2mR^2)\alpha_F^2$ and determines the number of electrons N by

$$2 \sum_{ln} (2l+1) f_{ln} = N \ . \quad (2.27)$$

The components of the local field are

$$E_r = -\frac{\partial \Phi}{\partial r} = E_0 f_1(r) \cos\theta \ ,$$

$$(2.28)$$

$$E_\theta = -\frac{1}{r}\frac{\partial \Phi}{\partial \theta} = E_0 f_2(r) \sin\theta \ ,$$

where

$$f_1(r) = 1 - c_0 - \sum_{n=1}^{\infty} c_n \alpha_{ln} j_1'(\alpha_{ln}r/R) \ ,$$

$$(2.29)$$

$$f_2(r) = 1 + c_0 + (R/r) \sum_{n=1}^{\infty} c_n j_1(\alpha_{ln}r/R) \ .$$

Here c_0 is given by (2.17), which may be reexpressed as

$$c_0 = -\frac{1}{3} \sum_{n=1}^{\infty} \frac{(-1)^n c_n \alpha_{ln}}{(1 + \alpha_{ln}^2)^{1/2}} \ . \quad (2.30)$$

III. FORMAL SOLUTION FOR FILM

Our microscopic model of the metallic film consists of a system of free electrons confined to move in the volume enclosed by two parallel planes separated by the distance d. We choose Cartesian coordinates (x, y, z) in which the planes are given by $z = \pm a$, where $a = \tfrac{1}{2}d$. The electronic wave functions and energy eigenvalues are

$$\psi_{\vec{k}}(\vec{r}) = (1/2\pi) e^{-ik_x x} e^{-ik_y y} (1/a)^{1/2} \sin k_z(z + a), \quad (3.1)$$

$$\epsilon_{\vec{k}} = (\hbar^2/2m)(k_x^2 + k_y^2 + k_z^2) \ , \quad (3.2)$$

where k_x and k_y are arbitrary real numbers, while k_z is quantized according to

$$k_z = (\pi/d)N, \quad N = 1, 2, \dots \ . \quad (3.3)$$

The response function $\chi(\vec{r}, \vec{r}')$ for the film is

$$\chi(\vec{r}, \vec{r}') = 2e^2 \int dk_x \int dk_y \int dk_x' \int dk_y'$$

$$\times \sum_{k_z} \sum_{k_z'} \frac{f(\epsilon_{\vec{k}}) - f(\epsilon_{\vec{k}'})}{\epsilon_{\vec{k}'} - \epsilon_{\vec{k}}}$$

$$\times \psi_{\vec{k}}^*(\vec{r}) \psi_{\vec{k}}(\vec{r}') \psi_{\vec{k}'}^*(\vec{r}') \psi_{\vec{k}'}(\vec{r}) \ . \quad (3.4)$$

We shall consider the polarization of the film resulting from the application of a constant external field E_0 in the z direction, i.e., perpendicular to the plane of the film. The resulting induced charge density will only depend on the z coordinate, in which case we may define a polarizability per unit area:

$$\alpha = (1/E_0) \int_{-a}^{a} dz \, z \, \rho^{in}(z) \ . \quad (3.5)$$

The Poisson equation will be of the form

$$\frac{d^2}{dz^2} \Phi(z) = -4\pi \rho^{in}(z) \quad (3.6)$$

$$= \int_{-a}^{a} dz' \, q(z, z') \Phi(z') \ , \quad (3.7)$$

with

$$q(z, z') = 4\pi \int dx' \int dy' \, \chi(\vec{r}, \vec{r}') \quad (3.8)$$

[the right-hand side of (3.8) depends only on z and z' as is seen by inserting (3.4), (3.2)]. We may write

$$\Phi(z) = -E_0 z + \Phi^{in}(z) \ , \quad (3.9)$$

defining the induced potential Φ^{in}. The induced field E^{in}, given by

$$E^{in} = -\frac{d}{dz} \Phi^{in} \ , \quad (3.10)$$

has to satisfy the conditions

$$\lim E^{\text{in}}(z) = 0 \text{ as } |z| \to \infty \qquad (3.11)$$

and

$$E^{\text{in}}(-z) = E^{\text{in}}(z), \qquad (3.12)$$

the latter expressing the symmetry of the problem. As Φ, and hence Φ^{in}, is only determined up to an additive constant, (3.12) may be replaced by

$$\Phi^{\text{in}}(-z) = -\Phi^{\text{in}}(z). \qquad (3.13)$$

Since $\rho^{\text{in}}(z) = 0$ for $|z| > a$, it follows from (3.6) that

$$\frac{d^2}{dz^2}\Phi^{\text{in}}(z) = 0, \quad |z| > a. \qquad (3.14)$$

Equations (3.11)–(3.14) are satisfied by

$$\Phi^{\text{in}}(z) = E_0 a c_0 \operatorname{sgn} z, \qquad (3.15)$$

where c_0 is some constant. For $|z| < a$, a solution for Φ^{in} may be written in the form

$$\Phi^{\text{in}}(z) = E_0[c_0 z + df(z)], \qquad (3.16)$$

with some function $f(z)$, which in view of (3.13) has to be odd. Equations (3.6) and (3.16) give

$$\rho^{\text{in}}(z) = -(E_0 d/4\pi) f''(z). \qquad (3.17)$$

The continuity of Φ^{in} and E^{in} at $z = \pm a$ will, in view of (3.15) and (3.17), impose the conditions

$$f(a) = f(-a) = 0, \qquad (3.18)$$

$$2af'(a) = 2af'(-a) = -c_0. \qquad (3.19)$$

Inserting (3.17) into (3.5) leads, after a partial integration, to

$$\alpha = (d/4\pi)[f(a) - f(-a) - af'(a) - af'(-a)] \qquad (3.20)$$

or, using (3.18) and (3.19),

$$\alpha = (d/4\pi)c_0. \qquad (3.21)$$

Hence c_0 measures the deviation from the classical polarizability per unit area $\alpha_0 = d/4\pi$.

We now expand the function $f(z)$ in terms of the orthogonal set $\sin(\pi n z/a)$, $n = 1, 2, \dots$:

$$f(z) = \sum_{n=1}^{\infty} (-1)^n c_n \sin(\pi n z/a). \qquad (3.22)$$

Equation (3.18) is automatically satisfied, whereas (3.19) leads to

$$c_0 = -2\pi \sum_{n=1}^{\infty} n c_n. \qquad (3.23)$$

If we equate the right-hand sides of Eqs. (3.6) and (3.7), we obtain, using (3.16) and (3.17),

$$f''(z) = \int_{-a}^{a} dz' \, q(z, z')[(c_0 - 1)(z'/d) + f(z')]. \qquad (3.24)$$

Inserting (3.22) and (3.8) into (2.24), we obtain the following system of linear equations for the coefficients c_n $(n = 1, 2, \dots)$:

$$\sum_{n=1}^{\infty} A_{mn} c_n = a_m, \quad m = 1, 2, \dots \qquad (3.25)$$

with

$$A_{mn} = 16(d/a_B) \sum_{NN'} a(N, N') I(N, N', m)$$
$$\times [I(N, N', n) - 2\pi n J(N, N')] - \tfrac{1}{2}(2\pi m)^2 \delta_{mn}, \qquad (3.26)$$

$$a_m = 16(d/a_B) \sum_{N,N'} a(N, N') I(N, N', m) J(N, N'), \qquad (3.27)$$

in which

$$a(N, N') = \frac{(F^2 - N^2)\,\theta\,(F^2 - N^2) - (F^2 - N'^2)\,\theta(F^2 - N'^2)}{N^2 - N'^2}, \qquad (3.28)$$

$$J(N, N') = \frac{1}{\pi^2} S(N, N')\left(\frac{1}{(N+N')^2} - \frac{1}{(N-N')^2}\right), \qquad (3.29)$$

$$I(N, N', n) = \frac{1}{2\pi} S(N, N')\left(\frac{1}{N - N' + 2n} - \frac{1}{N - N' - 2n}\right.$$
$$\left. - \frac{1}{N + N' + 2n} + \frac{1}{N + N' - 2n}\right). \qquad (3.30)$$

Here θ is the usual unit step function and

$$S(N, N') = \begin{cases} 1, & N - N' \text{ odd} \\ 0, & N - N' \text{ even}. \end{cases} \qquad (3.31)$$

The quantity F is related to k_F through

$$F = k_F d/\pi. \qquad (3.32)$$

The local field $E(z) = E_0 + E^{\text{in}}(z)$ for $|z| < a$ may be expressed as follows:

$$E(z) = E_0\left(1 + 2\pi \sum_{n=1}^{\infty} n c_n[1 - (-1)^n \cos(n\pi z/a)]\right), \qquad (3.33)$$

using (3.16), (3.22), and (3.23).

IV. A THOMAS-FERMI APPROXIMATION

We *define* a "Thomas-Fermi" approximation (TFA) by replacing the actual Poisson equation (1.3) by the equation

$$\nabla^2 \Phi(\vec{r}) = k_s^2(\vec{r})\, \Phi(\vec{r}), \qquad (4.1)$$

where

$$k_s^2(\vec{r}) = n_0(\vec{r}) k_s^2 \qquad (4.2)$$

in which

$$n_0(\vec{r}) = n(\vec{r})/n,$$
$$k_s^2 = (4/a_B)(3n/\pi)^{1/3}. \qquad (4.3)$$

Here $n(r)$ denotes the local electronic density, n is the mean electronic density $(n = N/\Omega)$, and k_s is the standard Thomas-Fermi wave vector of a bulk electron gas of uniform density n. We give no formal justification for this particular definition of a TF approximation. For sufficiently large

values of the dimensions R and d, we have found the scheme to closely approximate the numerical results of the exact methods of calculation outlined in Secs. II and III.

For the spherical particle problem (see Sec. II) we have

$$n(r) = 2 \sum_{lmn} f(\epsilon_{ln}) \left| \psi_{lnm}(\vec{r}) \right|^2$$

$$= 2 \sum_{ln} f(\alpha_{ln}) \frac{(2l+1)}{4\pi} c_{ln}^2 [j_l(\alpha_{ln} r/R)]^2 . \qquad (4.4)$$

For $r > R$ we have from (2.7) and (2.10)

$$\Phi(\vec{r}) = -E_0(r - c_0 R^3/r^2)\cos\theta , \qquad (4.5)$$

while for $r < R$ we set

$$\Phi(\vec{r}) = E_0 h(r)\cos\theta , \qquad (4.6)$$

where, in view of (4.1),

$$h'' + (2/r)h' - (2/r^2)h = n_0 k_s^2 h . \qquad (4.7)$$

The continuity of Φ and $-\vec{\nabla}\Phi$ at $r = R$ leads to

$$h(R) = R(c_0 - 1), \quad h'(R) = -(2c_0 + 1). \qquad (4.8)$$

In addition, $h(r)$ has to be regular at $r = 0$. Now from (4.7) it follows that $h(r)$ vanishes linearly with r as $r \to 0$. Hence we can solve (4.7) by setting

$$h(r) = a h_1(r) , \qquad (4.9)$$

where $h_1(r)$ satisfies (4.7) with the initial conditions

$$h_1(0) = 0, \quad h_1'(0) = 1. \qquad (4.10)$$

This can be done numerically on an electronic computer. From (4.8) and (4.9),

$$c_0 = \frac{Rh_1'(R) - h_1(R)}{Rh_1'(R) + 2h_1(R)} \qquad (4.11)$$
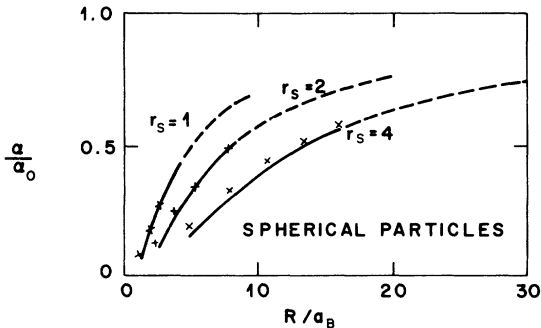
and

$$a = -3R/[Rh_1'(R) + 2h_1(R)] . \qquad (4.12)$$

FIG. 1. α/α_0 vs R/a_B for small spherical metallic particles with various values of r_s. Full curves denote the SCF calculation, broken curves and the points × the TF approximation.
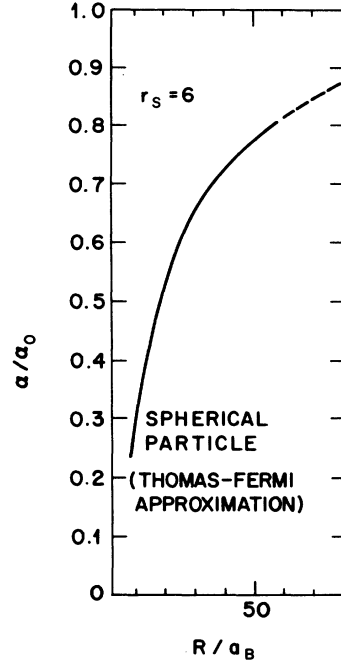

FIG. 2. α/α_0 vs R/a_B for a spherical particle in the TF approximation with $r_s = 6$. The broken curve is an extrapolation of the calculated values.

As in Sec. II, c_0 determines α/α_0. The local field $-\vec{\nabla}\phi(\vec{r})$ is easily obtained from (4.5) or (4.6).

In the case of the film we have

$$n(\vec{r}) = 2 \int dk_x \int dk_y \sum_{k_z} f(\epsilon_{\vec{k}}) \left| \psi_{\vec{k}}(\vec{r}) \right|^2$$

$$= \frac{1}{2\pi a} \sum_{k_z < k_F} (k_F^2 - k_z^2)\sin^2 k_z(z + a) . \qquad (4.13)$$

Correspondingly, the mean electronic density n is given by

$$n = \frac{1}{4\pi a} \sum_{k_z < k_F} (k_F^2 - k_z^2)$$

$$= (1/4\pi a)[N_F k_F^2 - \tfrac{1}{6}(\pi/d)^2 N_F(N_F + 1)(2N_F + 1)] , \qquad (4.14)$$

where N_F is the largest integer smaller than $F = \pi k_F/d$. For $|z| > a$, we have from (3.9) and (3.15),

$$\Phi(z) = -E_0 z + E_0 a c_0 \operatorname{sgn} z , \qquad (4.15)$$

while for $|z| < a$ we set

$$\Phi(z) = E_0 h(z) , \qquad (4.16)$$

with $h(-z) = -h(z)$ and

$$h'' = n_0 k_s^2 h , \qquad (4.17)$$

in view of (4.1). The continuity of Φ and Φ' at $|z| = a$ leads to
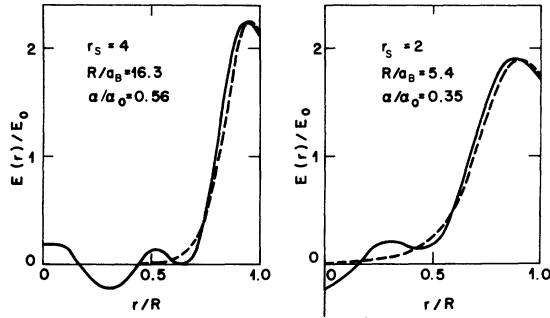
FIG. 3. Local field $E(r)/E_0$ vs r/R for various small spheres: the full curve denotes the SCF calculation, the broken curve the TF approximation.

TABLE I. Parameters used in the spherical particle calculations.

| Number of electrons N | R/a_B | | | |
	$r_s = 1$	$r_s = 2$	$r_s = 4$	$r_s = 6$[a]
2	1.26	2.52	5.04	7.56
8	2.00	4.00	8.00	12.00
20	2.71	5.43	10.86	16.29
40	3.42	6.84	13.68	20.52
68	4.08	8.16	16.33	24.45
92	4.51	9.03	18.06	27.09
138	5.17	10.34	20.67	31.01
186	5.71	11.42	22.83	34.25
306[a]	6.74	13.48	26.96	40.43
912[a]	9.70	19.40	38.79	58.19

[a]Used only in the Thomas-Fermi approximation.

$$h(a) = -h(-a) = a(c_0 - 1) , \qquad (4.18)$$

$$h'(a) = h'(-a) = -1 . \qquad (4.19)$$

Setting

$$h(z) = bh_1(z) \qquad (4.20)$$

and imposing the initial conditions

$$h_1(0) = 0, \quad h_1'(0) = 1 , \qquad (4.21)$$

Eq. (4.17) for h_1 can be integrated numerically. From (4.18)–(4.20) we get

$$c_0 = 1 - h_1(a)/ah_1'(a) \qquad (4.22)$$

and

$$b = -1/h_1'(a) . \qquad (4.23)$$

V. NUMERICAL RESULTS AND DISCUSSION

We shall refer to the "exact" methods of calculation presented in Secs. II and III as the self-consistent-field (SCF) calculation. In these calculations the sets of linear equations (2.21) (for spherical particles) and (3.11) (for thin films) have to be solved. We have solved both sets of equa-

tions on the basis of a numerical procedure in which the infinite matrix A_{nm} is replaced by a finite 10×10 matrix ($n = 1, 2, \ldots, 10$; $m = 1, 2, \ldots, 10$). As discussed in Sec. IV the numerical work involved in the TFA consists of first calculating the local electronic density and then numerically integrating a differential equation. The results of these numerical calculations are as follows.

A. Small Spherical Particles

For the particle calculation it is convenient first to choose a particular mean electronic density r_s and a specific number N of electrons. The radius R of the sphere is then fixed by the relation

$$R/a_B = r_s N^{1/3} . \qquad (5.1)$$

We recall that the usual electronic density parameter r_s is related to the mean electronic density n by the relation $r_s = (3/4\pi n)^{1/3}/a_B$, where a_B = $\hbar^2/me^2$ = 0.53 Å. The values of N and r_s used in the present calculations, together with the corresponding values of R, are shown in Table I. The
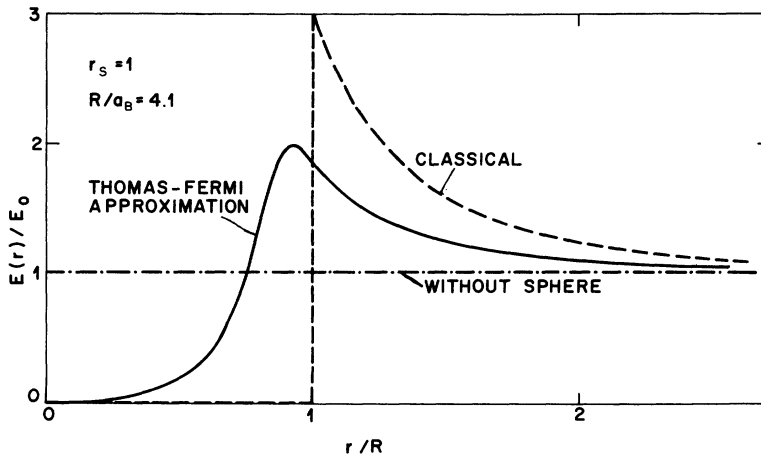

FIG. 4. $E(r)/E_0$ vs r/R for a spherical particle of radius $R = 4.1a_B$ and $r_s = 1$, calculated with the TFA and compared with the classical field distribution.
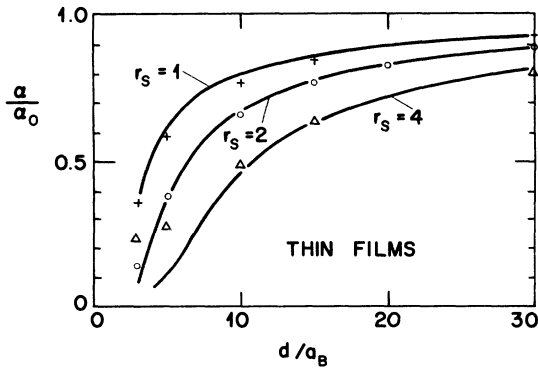
FIG. 5. α/α_0 vs d/a_B for thin films with various values of r_s. The full curves denote the SCF calculation while the points +, O, and Δ denote α/α_0 calculated within the TF approximation for $r_s = 1$, 2, and 4, respectively.

upper limits of the values shown for N, and consequently for R, were dictated merely by the computing facilities available to us.

Numerical results for α/α_0 as a function of R/a_B for various values of r_s are shown in Fig. 1. The full curves denote the SCF calculation while the broken curves and the discrete crosses depict the results obtained from the TFA. It is seen that for a given value of r_s, the TFA will approximate very closely the SCF results, provided R is sufficiently large. In Fig. 2, α/α_0 vs R/a_B has been
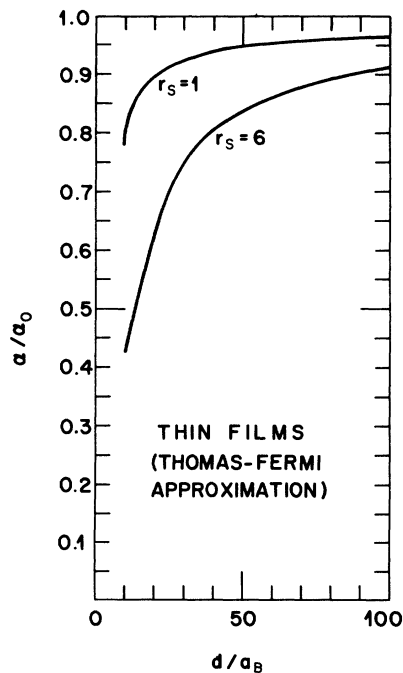
FIG. 6. α/α_0 vs d/a_B for thin films with $r_s = 1$ and $r_s = 6$, calculated within the TFA.

TABLE II. Diameter D of a small spherical metallic particle at which its polarizability is reduced to 70% of the classical value, $D^3/8$, for various values of the mean electronic density r_s.

r_s	1	2	4	6
$D(\text{Å})$	10.5	17	27.5	36.5

calculated in the TFA for the particular electronic density $r_s = 6$. Not surprisingly, the relatively small spherical particles that we have studied $(R \leq 58.\ 2a_B \simeq 31\ \text{Å})$ all exhibit appreciable deviations of α/α_0 from 1. The local field $E(r)$, for $\vec{r}$ directed along the direction of $\vec{E}_0$, is shown in Fig. 3 as a function of r/R for two different spherical particles $(R/a_B = 16.\ 3,\ r_s = 4;\ R/a_B = 5.\ 4,\ r_s = 2)$. Note that the closer α/α_0 is to unity, the less the electric field penetrates the interior of the sphere. The full curves in Fig. 3 denote the SCF calculation while the broken curves denote the TFA. The oscillations exhibited by the SCF calculations for $r < \sim \frac{1}{2}R$ are erroneous and reflect our finite truncation of the matrix equation (2. 21). In Fig. 4 the behavior of $E(r)$ for both $r < R$ and $r > R$ is shown for the particle with $R = 4.\ 1a_B$ and $r_s = 1$, and is compared with the corresponding classical calculation of $E(r)$. [In the classical problem the value of $E(r)$ at $r = R$ is always $3E_0$.]

B. Thin Metallic Films

Numerical results for α/α_0 as a function of d/a_B for various values of r_s are shown in Fig. 5. The full curves denote the SCF calculations while the symbols +, O , and Δ denote specific values of α/α_0 calculated with the TFA. As a rough rule, the TFA reproduces the SCF values of α/α_0 for $d/a_B > \sim 10$, independently of r_s. Figure 6 shows α/α_0 calculated in the TFA for the electronic densities $r_s = 1$ and $r_s = 6$, for the wider range of d/a_B values $10 \leq d/a_B \leq 100$. The internal field $E(z)$ vs z/d is shown in Fig. 7 for various film thicknesses and r_s values. The full curves denote the SCF calculation and the crosses the TFA. Again the small oscillations in $E(z)$ obtained with the SCF calculation for the thicker films reflect the finite truncation procedure employed in our numerical calculations.

The present numerical results indicate that the radius R or thickness d of a small spherical metal-

TABLE III. Thickness d of a thin metallic film at which its polarizability is reduced to 90% of the classical value, $d/4\pi$, for various values of the mean electronic density r_s.

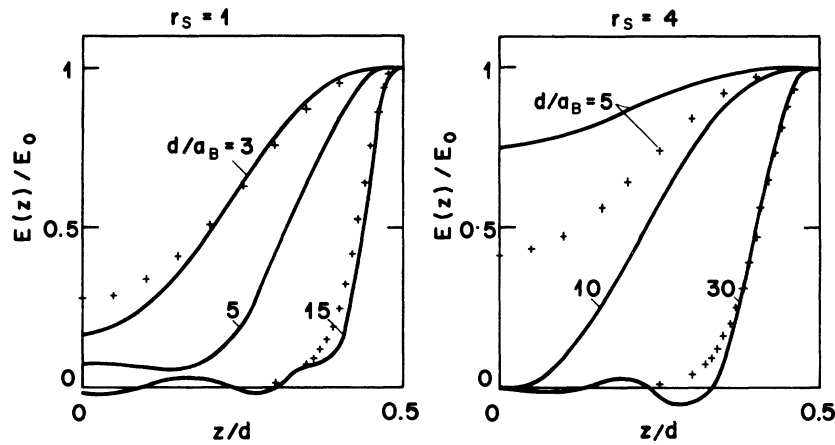| r_s	1	2	4	6
$d(\text{Å})$	12	20	32	46.5

FIG. 7. Internal field $E(z)/E_0$ vs z/d for various thin films. The full curves denote the SCF approximation, and the crosses the TF approximation.

lic particle or thin metallic film has to be quite small for α/α_0 to deviate very significantly from unity. In Table II we have listed values of the diameter D at which the electronic polarizability of the spherical metallic particle is reduced to (say) 70% of its classical polarizability. Even for the lowest metallic electronic density that we have considered, $r_s = 6$, this D would have to be as small

as 36. 5 Å.

In Table III we have given values of the thickness d at which the polarizability of the thin metallic film is reduced to 90% of its classical value. For $r_s = 6$, the value of d would have to be 46. 5 Å.

It would be interesting to know whether or not the reduced polarizabilities considered in this paper could be observed experimentally.

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