PHYSICAL REVIEW B VOLUME 10, NUMBER 2 15 JULY 1974

X-ray excitation of surface plasmons in metallic spheres*

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(Received 11 February 1974)

The cross section for excitation of surface plasmons by x rays is calculated for a free-electron gas confined to a small spherical region and surrounded by a medium having constant dielectric permittivity ϵ_0. The free-electron gas is described in the hydrodynamical approximation, and first-order perturbation theory is used to calculate the transition probability for inelastic scatter. The analogous cross section for volume-plasmon excitation by x rays is also calculated using the hydrodynamical model, and it is compared with a result obtained by Ohmura and Matsudaira using the random-phase approximation. The ratio of cross sections for surface-plasmon and volume-plasmon excitation is also determined.

I. INTRODUCTION

A fast charged particle interacting with a bounded metallic medium will excite both volume plasmons and surface plasmons, as is well known from characteristic energy-loss experiments.[1] Such energy-absorbing processes (i.e., plasmon excitation) are also important when photons interact with this type of system. The purpose of this paper is to assess the importance of surface-plasmon and volume-plasmon excitation in the inelastic scattering of x rays.

The impetus for the present work was provided by the experiment of Miliotis[2] on volume-plasmon dispersion in beryllium targets, and by the experiments of Koumelis *et al.*[3] on the inelastic scattering of x rays from colloidal graphite particles, where the energy loss of the photon was attributed to surface-plasmon excitation.

We calculate first the cross section for volume-plasmon excitation in the inelastic scattering of a photon in a free-electron gas described in the hydrodynamical approximation, and compare this result with the result calculated by treating the free-electron gas in the random-phase approximation. We next calculate the cross section for surface-plasmon excitation in inelastic photon scattering for a dilute collection of small spheres imbedded in a dielectric medium with the spheres modeled as a free-electron gas. The results are used to compare the relative magnitudes expected for volume-plasmon and surface-plasmon effects in x ray scattering experiments.

II. CROSS SECTION FOR VOLUME-PLASMON EXCITATION

For a large volume containing a free-electron gas and an electromagnetic radiation field, the Hamiltonian may be written

$$H = H_e + H_r + V \quad , \tag{1}$$

where H_e is the Hamiltonian for the electron gas, H_r is the Hamiltonian for the electromagnetic field, and V describes the interaction between the electron gas and the electromagnetic field. Following the hydrodynamic approach of Ritchie and Wilems,[4] the interaction term may be written

$$V = \frac{e}{2mc}\int d^3r \left[n(\vec{r}) \left(\frac{e}{c}\vec{A}(\vec{r}) - \vec{p}(\vec{r}) \right) \cdot \vec{A}(\vec{r}) \right] \tag{2}$$

where the integration is over the volume of the system. The constants e and m are the electron charge and mass, respectively; c is the speed of light; $\vec{A}(\vec{r})$ is the vector potential of the electromagnetic field; $\vec{p}(\vec{r})$ is the hydrodynamic momentum; and $n(\vec{r})$ is the hydrodynamic density. For the case of photon inelastic scattering, the interaction term reduces to[5]

$$V' = \frac{e^2}{2mc^2}\int d^3r\, n(\vec{r})\, \vec{A}(\vec{r}) \cdot \vec{A}(\vec{r}) \quad . \tag{3}$$

As long as the frequency of the incoming photon is much greater than the plasma frequency, the term linear in $\vec{A}$ in Eq. (2) may be neglected.[6]

The equations describing the system are now written in the second quantization formalism. The expression for $n(\vec{r})$ is given by

$$n(\vec{r}) = \sum_{\vec{k}} \left(\frac{n_0 \hbar k^2}{2m\omega_k \mathcal{V}} \right)^{1/2} e^{i\vec{k}\cdot\vec{r}} (b_{\vec{k}} + b^{\dagger}_{-\vec{k}}) \quad , \tag{4}$$

where $\mathcal{V}$ is the volume of the system, n_0 is the equilibrium electron density in the electron gas, $b_{\vec{k}}(b^{\dagger}_{\vec{k}})$ is the plasmon annihilation (creation) operator, and ω_k is related to the plasma frequency $\omega_p = (4\pi n_0 e^2/m)^{1/2}$ by

$$\omega_k^2 = \omega_p^2 + \beta^2 k^2 \quad . \tag{5}$$

For Eq. (5) to correspond to the Bohm-Pines dispersion relation for the volume plasmon, we take $\beta = (\frac{3}{5})^{1/2} v_F$, where v_F is the Fermi speed of the electron gas of density n_0.[7]

The vector potential can be written in terms of annihilation and creation operators, $c_{\vec{s},\lambda}$ and $c^{\dagger}_{-\vec{s},\lambda}$, for photons of wave vector $\vec{s}$ and polarization λ.

The unit vectors $\hat{e}_{\vec{s},\lambda}$, for $\lambda = 1$ and 2, define the two polarization directions for the field and, with $\vec{s}$, define a mutually orthogonal set of vectors. With the photon frequency given by $\omega_s = sc$, the vector potential is given by

$$\vec{A}(\vec{r}) = \sum_{\vec{s},\lambda} \left(\frac{2\pi\hbar c^2}{\omega_s \mathcal{V}}\right)^{1/2} \hat{e}_{\vec{s},\lambda} e^{i\vec{s}\cdot\vec{r}} (c_{\vec{s},\lambda} + c^\dagger_{-\vec{s},\lambda}) \quad . \tag{6}$$

With Eqs. (4) and (6), the matrix element of V' between an initial state with one photon of wave vector $\vec{s}$, polarization λ, and a final state with one plasmon of wave vector $\vec{k}$ and one photon of wave vector $\vec{s}'$, polarization λ', is given by

$$\langle 0 \mid c_{\vec{s}',\lambda'} b_{\vec{k}} V' c^\dagger_{\vec{s},\lambda} \mid 0 \rangle$$

$$= 2 \frac{e^2}{2mc^2} \left(\frac{2\pi^2\hbar^3 n_0 c^4 k^2}{m\omega_s \omega_{s'} \omega_k \mathcal{V}}\right)^{1/2} (\hat{e}_{-\vec{s}',\lambda'} \cdot \hat{e}_{\vec{s},\lambda})\, \delta_{\vec{s},\vec{s}'+\vec{k}} \; . \tag{7}$$

The transition rate for the process, γ_{fi}, for the given initial (subscript i) and final (subscript f) states is obtained by using the standard golden rule formula from perturbation theory, $\gamma_{fi} = (2\pi/\hbar) \times |V'_{fi}|^2 \delta(E_f - E_i)$ where $E_f(E_i)$ is the final-(initial-) state energy. The transition rate is thus

$$\gamma_{fi} = \frac{\pi^2 e^2 \hbar k^2 \omega_p^2}{m^2 \omega_s \omega_{s'} \omega_k \mathcal{V}} (\hat{e}_{-\vec{s}',\lambda'} \cdot \hat{e}_{\vec{s},\lambda})^2$$

$$\times \delta_{\vec{s},\vec{s}'+\vec{k}}\, \delta(\omega_s - \omega_{s'} - \omega_k) \quad . \tag{8}$$

If we now sum the transition rate over final states and divide by the incident photon flux through a given area for an unpolarized incident photon beam, we arrive at a differential probability for scattering a photon into solid angle $d\Omega$ (at an angle θ from the incident photon direction) due to volume-plasmon excitation. This differential probability is given by

$$\frac{dP_{vp}}{d\Omega} = \frac{\alpha^5}{32\pi}\left(\frac{\hbar\omega_p}{\mathcal{R}}\right)^2 \frac{\omega_p}{\omega_k} \frac{\omega_s - \omega_k}{\omega_s}$$

$$\times \frac{a\omega_p}{c}\left(\frac{kc}{\omega_p}\right)^2 \left(\frac{1}{2}\sum_\lambda \sum_{\lambda'} (\hat{e}_{-\vec{s}',\lambda'} \cdot \hat{e}_{\vec{s},\lambda})^2\right) , \tag{9}$$

where $\mathcal{R} \equiv e^2/2a_0$, $a_0 \equiv \hbar^2/me^2$, $\alpha \equiv e^2/\hbar c$, a is the thickness of the target along the incident photon direction, and $(kc/\omega_p)^2$ is given from energy and momentum conservation by

$$\left(\frac{kc}{\omega_p}\right)^2 = \left(\frac{\omega_k}{\omega_p}\right)^2 + [4\omega_s(\omega_s - \omega_k)/\omega_p^2] \sin^2 \tfrac{1}{2}\theta \, . \tag{10}$$

For the unpolarized incident photon beam we find

$$\frac{1}{2}\sum_\lambda \sum_{\lambda'} (\hat{e}_{-\vec{s}',\lambda'} \cdot \hat{e}_{\vec{s},\lambda})^2 = \tfrac{1}{2}(1 + \cos^2\theta) \quad .$$

For small-angle scattering of the photons ($\theta \ll 1$), the differential probability may be written

$$\frac{dP_{vp}}{d\Omega} \approx \frac{\alpha^5}{32\pi}\left(\frac{\hbar\omega_p}{\mathcal{R}}\right)^2 \frac{a\omega_p}{c} \frac{\omega_k}{\omega_p}$$

$$\times \frac{\omega_s - \omega_k}{\omega_s}\left[1 + \theta^2\left(\frac{\omega_s^2}{\omega_k^2} - \frac{\omega_s}{\omega_k} - \frac{1}{2}\right)\right] \quad . \tag{11}$$

Thus the forward scattering intensity (i.e., around $\theta = 0$) is nonzero, and the scattering probability increases quadratically with θ for small θ. If k is also small so that $\omega_k \approx \omega_p$ and $\omega_s \gg \omega_p$ (as for photons in the x-ray region), Eq. (11) reduces to

$$\frac{dP_{vp}}{d\Omega} \approx \frac{\alpha^5}{32\pi}\left(\frac{\hbar\omega_p}{\mathcal{R}}\right)^2 \frac{a\omega_p}{c}\left(1 + \theta^2 \frac{\omega_s^2}{\omega_p^2}\right) \tag{12}$$

to the lowest order in k^2.

The results found in the analysis here may be compared with the work of Ohmura and Matsudaira,[5] who treated the electron gas in the random-phase approximation. From their Eqs. (2.5), (2.5′), and (5.2), the differential scattering cross section for volume-plasmon excitation is (with $\hbar = 1$)

$$\frac{d\sigma_{vp}}{d\Omega} = \frac{e^2 V \omega_k}{4\pi^2 m^2 c^4} (\hat{e}' \cdot \hat{e})^2 \frac{k^2}{\omega_s}$$

$$\times \int d\omega' \, \tfrac{1}{2}\pi\omega' \, \delta(\omega_s - \omega' - \omega_k) \quad , \tag{13}$$

where V is the sample volume. The vectors $\hat{e}$ and $\hat{e}'$ are the polarization vectors of the photon in the initial and final states. The simple integration in Eq. (13) may readily be performed to yield

$$\frac{d\sigma_{vp}}{d\Omega} = \frac{e^2 V}{8\pi m^2 c^4} \frac{\omega_k}{\omega_s} (\hat{e}' \cdot \hat{e})^2 k^2 (\omega_s - \omega_k) \quad . \tag{14}$$

If this expression is summed over final-state polarizations, averaged over initial-state polarizations, reduced to a differential probability by multiplication by a/V, and then denoted $dP_{vp}/d\Omega]_{\mathrm{OM}}$, we have

$$\left.\frac{dP_{vp}}{d\Omega}\right]_{\mathrm{OM}} = \left(\frac{\omega_k}{\omega_p}\right)^2 \left.\frac{dP_{vp}}{d\Omega}\right]_{\mathrm{Eq.\,(9)}} \quad . \tag{15}$$

To the lowest order in k^2, exact agreement is predicted by Eq. (15) for these two different approaches. Further discussion of x-ray inelastic scattering within the context of the linear-response theory may be found in a recent paper by Kliewer and Raether.[8]

III. CROSS SECTION FOR SURFACE-PLASMON EXCITATION ON A SPHERE

The calculation of surface-plasmon excitation on a sphere in photon inelastic scattering is carried out in basically the same manner as the volume-plasmon excitation described in Sec. II. The same interaction term V' [Eq. (3)] is applicable, and the vector potential is given by Eq. (6), but a different $n(\vec{r})$ is required.

The density operator is obtained by quantizing the scalar potential on a sphere and connecting this quantized scalar potential to $n(\vec{r})$ through Poisson's equation.[9] The use of Poisson's equation is appropriate for the case of small spheres where the effects of retardation are expected to be negligible. This procedure, shown in detail in the Appendix, leads to the density-fluctuation operator for a sphere of radius r_0,

$$n(\vec{r}) = -\frac{\delta(r-r_0)}{4\pi e} \sum_{l,m,p} \left(\frac{2\pi\hbar\omega_l}{[\epsilon_0(l+1)+l]\,r_0^3}\right)^{1/2} \times (2l+1)\, Y_{lmp}(\theta,\varphi)\,(b_{lmp}+b_{lmp}^\dagger) \quad , \tag{16}$$

where ϵ_0 is the dielectric constant of the medium surrounding the sphere. The spherical harmonics Y_{lmp}'s are defined in the Appendix and

$$\omega_l^2 = \frac{\omega_p^2 l}{\epsilon_0(l+1)+l} \quad . \tag{17}$$

The δ function in Eq. (16) indicates that the polarization charge resides only on the surface of the sphere. The quantity $b_{lmp}(b_{lmp}^\dagger)$ is the annihilation (creation) operator for surface-plasmon momentum states on the sphere.

The calculation of V'_{fi} for an initial state with one photon of wave vector $\vec{s}$, and a final state with one photon of wave vector $\vec{s}'$ and one surface plasmon in an (l, m, p) momentum state, yields

$$V'_{fi} = \frac{2\pi\hbar e i^l}{m\mathfrak{V}} \left(\frac{2\pi\hbar r_0\omega_l(2l+1)^2}{\omega_s\omega_{s'}[\epsilon_0(l+1)+l]}\right)^{1/2} \times (\hat{e}_{-\vec{s}',\lambda'}\cdot\hat{e}_{\vec{s},\lambda})\, j_l(kr_0)\, Y_{lmp}(\theta_k,\varphi_k) \quad , \tag{18}$$

where $j_l(kr_0)$ is the spherical Bessel function of order l, $k \equiv |\vec{s}-\vec{s}'|$, and (θ_k, φ_k) specify the direction of $\vec{k}$.

The differential cross section $d\sigma_l/d\Omega$ for exciting a surface plasmon in an angular momentum state l, energy $\hbar\omega_l$, by scattering of a photon into solid angle $d\Omega$ about the incident photon direction is obtained from the sum over final states of the transition rate divided by $c/\mathfrak{V}$. We find

$$\frac{d\sigma_l}{d\Omega} = 2\pi\alpha^3 a_0^2 \frac{r_0\omega_p}{c}\frac{\omega_l}{\omega_p}\frac{\omega_s-\omega_l}{\omega_s} S_\lambda \times \frac{(2l+1)^2}{\epsilon_0(l+1)+l}\, j_l^2(kr_0) \sum_{m,p} Y_{lmp}^2(\theta_k,\varphi_k) \quad , \tag{19}$$

where S_λ is defined by $S_\lambda \equiv \sum_{\lambda'}(\hat{e}_{-\vec{s}',\lambda'}\cdot\hat{e}_{\vec{s},\lambda})^2$.

From the addition theorem for the spherical harmonics (see Appendix) we have

$$\sum_{m,p} Y_{lmp}^2(\theta_k,\varphi_k) = (2l+1)/4\pi \quad . \tag{20}$$

Equation (19) thus reduces to

$$\frac{d\sigma_l}{d\Omega} = \tfrac{1}{2}\alpha^3 a_0^2 \frac{r_0\omega_p}{c}\frac{\omega_l}{\omega_p}\frac{\omega_s-\omega_l}{\omega_s} S_\lambda \times \frac{(2l+1)^3}{\epsilon_0(l+1)+l}\, j_l^2(kr_0) \quad . \tag{21}$$

Consider now a target composed of spheres of radius r_0 distributed at random in a dielectric medium with an average number density N. Assume N is small enough so that the scattered fields add incoherently. If the target thickness in the direction of photon incidence is a, the differential scattering probability is given by

$$\frac{dP_l}{d\Omega} = \tfrac{1}{2}\alpha^3 N a a_0^2 \frac{r_0\omega_l}{c}\frac{\omega_s-\omega_l}{\omega_s} S_\lambda \times \frac{(2l+1)^3}{\epsilon_0(l+1)+l}\, j_l^2(kr_0) \tag{22}$$

for excitation of a surface plasmon in the angular momentum state l. For an unpolarized incident photon beam, $\frac{1}{2}\sum_\lambda S_\lambda = \frac{1}{2}(1+\cos^2\theta)$.

IV. COMPARISON OF SURFACE-PLASMON AND VOLUME-PLASMON EXCITATION PROBABILITIES

Consider two targets of the same material with plasma frequency ω_p. One target is assumed to be solid, with a thickness a along the direction of the incident photon beam, while the second is made up of spheres of radius r_0 and density N, with the same target thickness. The ratio of the surface-plasmon excitation probability for the target composed of spheres [Eq. (22)] to the volume-plasmon excitation probability for the solid target [Eq. (9)] is given for an unpolarized photon beam by

$$\mu_l \equiv \frac{dP_l}{d\Omega}\Big/\frac{dP_{vp}}{d\Omega} = 4\pi r_0^3 N \frac{\omega_l\omega_k}{\omega_p^2} \times \frac{\omega_s-\omega_l}{\omega_s-\omega_k}\frac{(2l+1)^3}{\epsilon_0(l+1)+l}\frac{j_l^2(kr_0)}{(kr_0)^2} \quad . \tag{23}$$

For $\omega_s \gg (\omega_l, \omega_k)$, $\omega_k \approx \omega_p$, and $kr_0 \ll 1$, we find that for the $l=1$ surface-plasmon mode (dipole term),

$$\mu_1 \approx 9(\tfrac{4}{3}\pi r_0^3 N)/(2\epsilon_0+1)^{3/2} \equiv 9F/(2\epsilon_0+1)^{3/2} \ , \tag{24}$$

where the small argument expansion for $j_l(kr_0)$ has been used. The constant F is approximately the fraction of the target volume that is occupied by the spheres. For a typical value[10] $F \approx 10^{-2}$, which is consistent with the incoherency assumption, $\mu_1 \approx 0.02$ for $\epsilon_0 = 1$ (vacuum).

There seems to be no experimental data available in the literature from which cross sections comparable to those displayed in Eq. (22) may be inferred. It is hoped that future experimental work might be done using colloidal suspensions of metallic particles,[9] or using techniques developed by Kreibig[11] for forming small metallic spheres in glass media, so that x-ray inelastic scatter on surface plasmons may be studied in detail.

One of us (R.H.R.) would like to acknowledge the kind hospitality of K. Alexopoulos, D. M. Miliotis, C. Koumelis, and D. Leventouri, during which helpful conversations about the experimental work described in Refs. 2 and 3 were held.

APPENDIX: SURFACE-PLASMON OPERATORS FOR SPHERICAL SYSTEMS

For a sphere of radius R, the electrostatic potential due to a superficial-charge-density distribution may be written in terms of the real spherical harmonics $Y_{lmp}(\theta, \varphi)$ as[9]

$$\Phi(\vec{r}, t) = \sum_{l=0}^{\infty} \sum_{m=0}^{l} \sum_{p=\pm 1} A_{lmp}(t)\, g_l(r)\, Y_{lmp}(\theta, \varphi) , \quad (A1)$$

where

$$g_l(r) = \begin{cases} r^l , & r < R \\ R^{2l+1}/r^{l+1} , & r > R \end{cases} . \quad (A2)$$

With $g_l(R) = R^l$, Φ is continuous across the surface $r = R$. The real spherical harmonics are defined in terms of the Legendre polynomials P_l by

$$Y_{lmp}(\theta, \varphi) = \left(\frac{\epsilon_m (2l+1)\,(l-m)!}{4\pi (l+m)!}\right)^{1/2} \times P_l^m(\cos\theta) \times \begin{Bmatrix} \cos m\varphi \\ \sin m\varphi \end{Bmatrix} \quad \begin{Bmatrix} p = +1 \\ p = -1 \end{Bmatrix} , \quad (A3)$$

where

$$P_l^m(x) \equiv (1-x^2)^{m/2} \frac{d^m}{dx^m} P_l(x) \quad (A4)$$

and ϵ_m is defined by $\epsilon_0 = 1$ and $\epsilon_m = 2$, $m \geq 1$. This form for the spherical harmonics may be found in Ref. 12.

These spherical harmonics satisfy the orthogonality relation

$$\int d\Omega\, Y_{lmp}(\theta, \varphi)\, Y_{l'm'p'}(\theta, \varphi) = \delta_{l,l'}\, \delta_{m,m'}\, \delta_{p,p'} , \quad (A5)$$

where $d\Omega$ is the solid angle. They also form a complete set as indicated by the equation

$$\sum_{l=0}^{\infty} \sum_{m=0}^{l} \sum_{p=\pm 1} Y_{lmp}(\theta, \varphi)\, Y_{lmp}(\theta', \varphi') = \delta(\varphi - \varphi')\, \delta(\cos\theta - \cos\theta') . \quad (A6)$$

The addition theorem

$$P_l(\cos\gamma) = \frac{4\pi}{2l+1} \sum_{m=0}^{l} \sum_{p=\pm 1} Y_{lmp}(\theta, \varphi)\, Y_{lmp}(\theta', \varphi') , \quad (A7)$$

where $\cos\gamma \equiv \cos\theta \cos\theta' + \sin\theta \sin\theta' \cos(\varphi - \varphi')$, provides the useful sum rule

$$\sum_{m=0}^{l} \sum_{p=\pm 1} [Y_{lmp}(\theta, \varphi)]^2 = \frac{2l+1}{4\pi} . \quad (A8)$$

The potential, Eq. (A1), is a solution of Laplace's equation at all points in space except on the surface of the sphere. From Poisson's equation,

$$\nabla^2 \Phi = -4\pi\rho , \quad (A9)$$

it can be shown that

$$\rho = \frac{1}{4\pi} \sum_{lmp} A_{lmp}\, Y_{lmp}(\theta, \varphi)\, (2l+1)\, R^{l-1}\, \delta(r - R) . \quad (A10)$$

This charge density is composed of two parts. With the contribution to the charge density due to the material inside the sphere denoted by ρ', and that due to the material outside the sphere by ρ'', we may write

$$\rho = \rho' + \rho'' . \quad (A11)$$

This charge density will be different from that for a sphere in vacuum due to the depolarizing effect of the surrounding medium. From simple electrostatics considerations the contribution ρ'' due to the surrounding medium of dielectric constant ϵ_0 is given by

$$\rho'' = -\frac{\epsilon_0 - 1}{4\pi} \sum_{lmp} A_{lmp}\, Y_{lmp}(\theta, \varphi)\, (l+1)\, R^{l-1} \delta(r - R) \quad (A12)$$

and thus

$$\rho' = \frac{1}{4\pi} \sum_{lmp} A_{lmp} [\epsilon_0 (l+1) + l]\, Y_{lmp}(\theta, \varphi)\, R^{l-1}\, \delta(r - R) . \quad (A13)$$

The energy in the fields inside the sphere, W_F, may be calculated from

$$W_F = \tfrac{1}{2} \int dV \rho' \Phi , \quad (A14)$$

where the integration extends over the volume of the sphere. We find

$$W_F = \frac{1}{8\pi} \sum_{lmp} [\epsilon_0 (l+1) + l]\, R^{2l+1} A_{lmp}^2 . \quad (A15)$$

The energy due to particle motion in the sphere will be calculated from an examination of the microscopic equations of motion. We assume that electrons are bound isotropically to randomly located positions in the sphere with a single force constant $m\omega_0^2$. This model may be generalized to a many-oscillator system. If $\vec{\xi}$ is the displacement of an oscillator of frequency ω_0, charge e, and mass m from its equilibrium position, we have

$$\ddot{\vec{\xi}} + \omega_0^2 \vec{\xi} = -(e/m) \vec{E}_i = (e/m) \nabla \Phi_i , \quad (A16)$$

where the subscript i indicates that Φ and $\vec{E}$ are the potential and the electric field inside the sphere. The charge density ρ' is related to the displacement vector through

$$\rho' = -e n_0 \nabla \cdot [\vec{\xi} \theta(R - r)] , \quad (A17)$$

where n_0 is the density of the oscillators. If σ' is the surface-charge density, then $\sigma' \delta(r - R) = \rho'$, and we have

$$\sigma' = -e n_0 \hat{e}_r \cdot \vec{\xi} \big]_{r=R} , \quad (A18)$$

where $\hat{e}_r$ is a unit vector in the direction of increasing r. Equation (A16) thus leads to

$$\ddot{\sigma}' + \omega_0^2 \sigma' = -\frac{n_0 e^2}{m} \frac{\partial \Phi_i}{\partial r}\bigg]_{r=R} . \quad (A19)$$

If we introduce the definitions $\Phi_l \equiv \sum_{lmp} \Phi_{lmp}$ and $\sigma' = \sum_{lmp} \sigma'_{lmp}$, we find

$$\sum_{lmp}\left(\ddot{\sigma}'_{lmp} + \omega_0^2 \sigma'_{lmp} + \frac{n_0 e^2}{m} A_{lmp} Y_{lmp} l R^{l-1}\right) = 0 \ . \quad \text{(A20)}$$

Using Eq. (A13) we can relate σ'_{lmp} to A_{lmp} by

$$A_{lmp} Y_{lmp} = 4\pi\sigma'_{lmp}/[\epsilon_0(l+1)+l]\, R^{l-1} \quad \text{(A21)}$$

and find from Eq. (A20)

$$\ddot{\sigma}'_{lmp} + \left(\omega_0^2 + \frac{l\omega_p^2}{\epsilon_0(l+1)+l}\right)\sigma'_{lmp} = 0 \quad , \quad \text{(A22)}$$

where $\omega_p^2 = 4\pi n_0 e^2/m$. Equation (A22) may also be written in the form

$$\ddot{A}_{lmp} + \omega_l^2 A_{lmp} = 0 \quad , \quad \text{(A23)}$$

with

$$\omega_l^2 \equiv \omega_0^2 + [l\omega_p^2/\epsilon_0(l+1)+l] \quad . \quad \text{(A24)}$$

Note that this equation may be written[13] $\epsilon + [(l+1)/l] \times \epsilon_0 = 0$, where $\epsilon = 1 + \omega_p^2/(\omega_0^2 - \omega_l^2)$ is the dielectric permittivity of the system of bound electrons which we consider.

A particular solution to Eq. (A16) is given by

$$\vec{\xi} = \sum_{lmp} \frac{e}{m}\,\frac{\epsilon-1}{\omega_p^2}\,\nabla\Phi_{lmp} \quad . \quad \text{(A25)}$$

No solution to the homogeneous equation is included since it will add only a constant term to the energy. With the equations derived above we may calculate the total kinetic plus displacement energy for the oscillators in the sphere, W_p, as

$$W_p = \frac{mn_0}{2}\int dV\,\dot{\vec{\xi}}\cdot\dot{\vec{\xi}} + \frac{mn_0\omega_0^2}{2}\int dV\,\vec{\xi}\cdot\vec{\xi}$$

$$= \frac{1}{8\pi\omega_p^2}\sum_{lmp}[\epsilon_0(l+1)+l]\,R^{2l+1}(1-\epsilon)\,(\dot{A}_{lmp}^2 + \omega_0^2 A_{lmp}^2) \ . \quad \text{(A26)}$$

The total energy for the particles plus the fields, $W_p + W_F = W$, is given by

$$W = \frac{1}{8\pi\omega_p^2}\sum_{lmp}(1-\epsilon)[\epsilon_0(l+1)+l]\,R^{2l+1} \times (\dot{A}_{lmp}^2 + \omega_l^2 A_{lmp}^2) \quad . \quad \text{(A27)}$$

For $\omega_0 = 0$, Eq. (A27) gives the energy density for the free-electron gas, and new coefficients, b_{lmp} and b^*_{lmp}, defined through the equations

$$A_{lmp} = (\alpha_l/2\omega_l)\,(b_{lmp} + b^*_{lmp}) \quad ,$$
$$\dot{A}_{lmp} = -i\tfrac{1}{2}\alpha_l\,(b_{lmp} - b^*_{lmp}) \quad , \quad \text{(A28)}$$

give

$$W = \frac{1}{8\pi\omega_p^2}\sum_{lmp}(1-\epsilon)[\epsilon_0(l+1)+l]\,R^{2l+1} \times \alpha_l^2\,\tfrac{1}{2}\,(b_{lmp}b^*_{lmp} + b^*_{lmp}b_{lmp}) \quad . \quad \text{(A29)}$$

If the b's are now interpreted as boson operators, i.e., $b_{lmp} \to b_{lmp}$ (an operator) and $b^*_{lmp} \to b^\dagger_{lmp}$ (an operator), and write, assuming $\omega_0 \to 0$,

$$\alpha_l = \{8\pi\hbar\omega_l^3/[\epsilon_0(l+1)+l]\,R^{2l+1}\}^{1/2} \quad , \quad \text{(A30)}$$

Eq. (A29) becomes

$$W = \sum_{lmp}\hbar\omega_l(b^\dagger_{lmp}b_{lmp} + \tfrac{1}{2}) \quad . \quad \text{(A31)}$$

From Eq. (A10), the number density $n = -\rho/e$ may be written as an operator in the form

$$n(r) = -\frac{1}{4\pi e}\sum_{lmp}\left(\frac{2\pi\hbar\omega_l}{R^3[\epsilon_0(l+1)+l]}\right)^{1/2} \times (2l+1)\,\delta(r-R)\,Y_{lmp}(\theta,\varphi)\,(b_{lmp} + b^\dagger_{lmp}) \quad . \quad \text{(A32)}$$

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*Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation.

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