J. Phys. C: Solid State Phys. **19** (1986) 5005–5018. Printed in Great Britain

# Interaction of a charged particle with a solid surface: General formalism and spherical geometry

J Mahanty and Marek T Michalewicz
Department of Theoretical Physics, Research School of Physical Sciences,
The Australian National University, GPO Box 4, Canberra, ACT 2601, Australia

Received 10 December 1985

**Abstract.** A formalism for evaluating the interaction potential of a charged particle with a solid is developed using linear response theory. It is applied to study the interaction with a metal sphere. The plasmon modes of the sphere are evaluated using the hydrodynamic model of metallic electrons and used in the general formulae. It is shown that the predominant contributions to the potential for $r \geq R$ is due to a finite number of surface modes for dispersive plasmons. For $r < R$ the bulk modes make the dominant contribution. The first-order quantum correction to the interaction potential is given.

## 1. Introduction

The interaction of a charged particle with a solid surface is a problem of considerable interest in surface physics in view of the implications of the interaction potential on experimental studies of surface properties. Experimental data on image potential surface states in metals (Straub and Himpsel 1984), surface resonance states in metals (reviewed by McRae 1979), scattering of charged particles from surfaces (Ibach, 1977) all require detailed information on the interaction potential for interpretation and analysis. This has stimulated a spurt of theoretical activity in this field in recent years. The literature in this field is vast and growing at an ever-increasing rate.

When the distance between a charged particle and a solid surface is large, the interaction potential can be analysed classically in terms of image theory or variants thereof. At close proximity to the surface the interaction potential saturates mainly for two reasons. The first is the screening of the charge through the induced charge distribution in the solid. The induced charge has a spatial spread arising out of dispersion of the charge oscillation modes in the solid, leading to a finite interaction energy with the charged particle. The second is a polaron-like effect on the self-energy of the charged particle arising out of real or virtual exchange of quanta of the collective charge oscillations of the solid, whose frequencies are bounded at the lower end (e.g., plasmons in metals and optical phonons in dielectrics). These effects have been analysed for a planar geometry of the solid surface in detail, the first by Newns (1969), Heinrichs (1973), Equiluz (1981), and the second by Manson and Ritchie (1981), and Mahanty *et al* (1985), among many others.

The object of this paper is to first give a formalism based on linear response theory

0022-3719/86/255005 + 14 $02.50  

that provides a unified framework for the study of this problem, and secondly, to apply the formalism to evaluate the interaction of a charged particle with a metallic sphere.

## 2. Theory of interaction potential

Tomonaga (1950) had pointed out that the interaction of a local charge with the metal electrons may be considered as one with the electron density fluctuations represented by a Boson field. This approach can obviously be generalised to include the case of interaction with an insulator where the Boson field will represent the polarisation fluctuations associated with optical phonons. In this model the Hamiltonian for a charged particle of mass $M$ and charge $Q$ interacting with a solid would be

$$H = H_0 + H_I \qquad H_0 = H_S + H_P \tag{1a}$$

$$H_S = \sum_\lambda \hbar\omega_\lambda (a_\lambda^\dagger a_\lambda + \tfrac{1}{2}) \tag{1b}$$

$$H_P = p^2/2M \tag{1c}$$

$$H_I = Q\hat{\Phi} = Q\sum_\lambda (\varphi_\lambda^\dagger a_\lambda^\dagger + \varphi_\lambda a_\lambda).$$

Here $\lambda$ is the label of the particular mode of charge oscillation and $a_\lambda^\dagger$, $a_\lambda$ are the creation and annihilation operators thereof. The potential operator $\hat{\Phi}$ has the representation

$$\langle \boldsymbol{r}|\hat{\Phi}|\boldsymbol{r}'\rangle = \delta(\boldsymbol{r}-\boldsymbol{r}')\sum_\lambda [\varphi_\lambda^*(\boldsymbol{r})a_\lambda^\dagger + \varphi_\lambda(\boldsymbol{r})a_\lambda] \tag{2}$$

where $\varphi_\lambda(\boldsymbol{r})$ is the potential due to the $\lambda$th charge oscillation mode of the solid. We shall restrict ourselves here to the electrostatic limit, although the formalism can readily be extended to include retardation effects (Fetter 1973).

According to linear response theory (Kubo 1957) the change in any physical quantity $A$ due to a perturbation $H_I(t)$ is given by,

$$\langle \Delta A\rangle = \frac{1}{i\hbar}\int_{-\infty}^{t} dt' \exp(\eta t')\langle [A(t-t'), H_I(t')]\rangle \qquad \eta \to 0^+ \tag{3}$$

with

$$A(t) = \exp(iH_0 t/\hbar)\, A \exp(-iH_0 t/\hbar). \tag{4}$$

When $H_I$ is time-independent, as in the above example, (3) becomes,

$$\langle \Delta A\rangle = \frac{1}{i\hbar}\int_0^\infty dt \exp(-\eta t)\langle [A(t), H_I]\rangle. \tag{5}$$

Depending on the problem under study $\langle \ldots . \rangle$ in equations (3) and (5) represents either the expectation value in a given state of the system or, more usually, a thermal average over the states of the solid combined with the expectation value in a given state of the particle. The state of the system in the mixed representation is the product $|\{n_\lambda\}\rangle|\boldsymbol{k}\rangle$, where $|\{n_\lambda\}\rangle$ is the state of the solid with $n_\lambda$ quanta in the $\lambda$th mode, and $\boldsymbol{k}$ is the wavenumber of the particle.

When $A = H$, the only non-vanishing term in (5) will be $\langle [H_I(t), H_I]\rangle$. This leads to the second-order energy shift if we multiply by a factor $\frac{1}{2}$. This factor comes from the Hellman–Feynman theorem when applied to perturbation theoretic wavefunctions.

Thus, the second-order energy shift is,

$$(\Delta E)_2 = \frac{1}{2i\hbar}\int_0^\infty dt \exp(-\eta t)\langle[H_I(t), H_I]\rangle. \tag{6}$$

Let us consider a physical quantity $A$ having the form

$$A = \sum_\lambda [A_\lambda^*(\boldsymbol{R})a_\lambda^\dagger + A_\lambda(\boldsymbol{R})a_\lambda]. \tag{7}$$

To evaluate $A(t)$ from (4) we must distinguish among a few cases. Firstly, if $\boldsymbol{R}$ is not the coordinate of the particle (as would be the case, for instance, if $\boldsymbol{R}$ were a field point), the time evolution of $A$ will occur only through $H_S$ of (1*b*). Secondly, if the mass of the charged particle is very large so that the effect of $H_P$ of equation (1*c*) is negligible, then also the time evolution of $A$ will occur mainly through $H_S$, irrespective of whether or not $\boldsymbol{R} = \boldsymbol{r}$, the coordinate of the particle. This gives the classical limit for the response as measured through $\langle\Delta A\rangle$. Finally, if $\boldsymbol{R} = \boldsymbol{r}$ and $M$ is not too large, both $H_S$ and $H_P$ will determine the time evolution. In the first two cases,

$$A(t) = \sum_\lambda [A_\lambda^*(\boldsymbol{R})a_\lambda^\dagger \exp(i\omega_\lambda t) + A_\lambda(\boldsymbol{R})a_\lambda \exp(-i\omega_\lambda t)] \tag{8}$$

so that

$$[A(t), H_I] = \sum_\lambda [-A_\lambda^*(\boldsymbol{R})\varphi_\lambda \exp(i\omega_\lambda t) + A_\lambda(\boldsymbol{R})\varphi_\lambda^\dagger \exp(-i\omega_\lambda t)]. \tag{9}$$

Then (5) becomes,

$$\langle\Delta A\rangle = -\sum_\lambda \left(\frac{1}{\hbar\omega_\lambda}\right)\langle\{A_\lambda^*(\boldsymbol{R})\varphi_\lambda + A_\lambda(\boldsymbol{R})\varphi_\lambda^\dagger\}\rangle. \tag{10}$$

When the expectation value is taken in a mixed representation $|\{n_\lambda\}\,|\boldsymbol{k}\rangle$, using (2) we get

$$\langle\Delta A\rangle = \int d^3r\langle\boldsymbol{k}|\boldsymbol{r}\rangle A_I(\boldsymbol{R}, \boldsymbol{r})\langle\boldsymbol{r}|\boldsymbol{k}\rangle \tag{11}$$

where

$$A_I(\boldsymbol{R}, \boldsymbol{r}) = -\sum_\lambda \left(\frac{1}{\hbar\omega_\lambda}\right) 2\,\mathrm{Re}[A_\lambda^*(\boldsymbol{R})\varphi_\lambda(\boldsymbol{r})]. \tag{12}$$

This depends on the particle coordinate $\boldsymbol{r}$ and the field point $\boldsymbol{R}$, and its expectation value in the particle state $\langle\boldsymbol{r}|\boldsymbol{k}\rangle$ gives the induced change $\langle\Delta A\rangle$. If $A_\lambda(\boldsymbol{R}) \equiv \varphi_\lambda(\boldsymbol{R})$ for instance, $A_I(\boldsymbol{R}, \boldsymbol{r})$ would give the induced potential at $\boldsymbol{R}$ when the particle is at $\boldsymbol{r}$.

If $A$ is set equal to $H_I$ and (6) is used, we get in the same approximation as above (i.e., neglecting the time evolution of $H_I$ through $H_P$),

$$(\Delta E)_2 = \int d^3r\langle\boldsymbol{k}|\boldsymbol{r}\rangle \Sigma_c(\boldsymbol{r})\langle\boldsymbol{r}|\boldsymbol{k}\rangle, \tag{13}$$

where the classical self-energy of the charge, i.e., its interaction potential with the solid is given by,

$$\Sigma_c(\boldsymbol{r}) = -Q^2\sum_\lambda \left(\frac{1}{\hbar\omega_\lambda}\right)|\varphi_\lambda(\boldsymbol{r})|^2. \tag{14}$$

This is independent of the state of the particle and represents the interaction potential of a static particle.

Finally, in the general case when the time evolution of $A$ is determined by both $H_S$ and $H_P$, we can write

$$\langle \Delta A \rangle = \int \mathrm{d}^3 r \langle \boldsymbol{k}|\boldsymbol{r}\rangle \, V_A(\boldsymbol{r};\boldsymbol{k}) \langle \boldsymbol{r}|\boldsymbol{k}\rangle \tag{15}$$

where the generalised potential whose expectation value in the particle state $|\boldsymbol{k}\rangle$ gives $\langle \Delta A \rangle$ is,

$$V_A(\boldsymbol{r};\boldsymbol{k}) = \frac{1}{\mathrm{i}\hbar} \int_0^\infty \mathrm{d}t \exp(-\eta t) \left( \frac{1}{\langle \boldsymbol{r}|\boldsymbol{k}\rangle} \int \mathrm{d}^3 r' \, \langle \boldsymbol{r}|\langle [A(t), H_I]\rangle_s |\boldsymbol{r}'\rangle \times \langle \boldsymbol{r}'|\boldsymbol{k}\rangle \right). \tag{16}$$

$\langle \ldots \rangle_s$ stands for the expectation value in a state $|\{n_\lambda\}\rangle$ of the solid.

When $\langle \Delta A \rangle$ is the second-order energy $(\Delta E)_2$, the corresponding interaction potential is the self-energy of the particle,

$$\Sigma_k(\boldsymbol{r}) \equiv \tfrac{1}{2} V_{H_I}(\boldsymbol{r};\boldsymbol{k}). \tag{17}$$

Using (16) and some straightforward algebra we get,

$$\Sigma_k(\boldsymbol{r}) = \left(\frac{Q^2}{2}\right) \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}) \sum_\lambda \left[ n_\lambda \varphi_\lambda^*(\boldsymbol{r}) \int \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}') G\left(\boldsymbol{r}-\boldsymbol{r}'; \frac{\hbar^2 k^2}{2M} + \hbar\omega_\lambda\right) \right.$$

$$\times \varphi_\lambda(\boldsymbol{r}') \, \mathrm{d}^3 r' + (n_\lambda + 1)\varphi_\lambda(\boldsymbol{r})$$

$$\left. \times \int \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}') \, G\left(\boldsymbol{r}-\boldsymbol{r}'; \frac{\hbar^2 k^2}{2M} - \hbar\omega_\lambda\right) \varphi_\lambda^*(\boldsymbol{r}') \, \mathrm{d}^3 r' \right]. \tag{18}$$

Here $G(\boldsymbol{r}-\boldsymbol{r}';E)$ is the Green function of the particle,

$$G(\boldsymbol{r}-\boldsymbol{r}';E) \equiv \sum_{k'} \frac{\langle \boldsymbol{r}|\boldsymbol{k}'\rangle\langle \boldsymbol{k}'|\boldsymbol{r}'\rangle}{E - (\hbar^2 k'^2/2M)}$$

$$= -\left(\frac{M}{2\pi\hbar^2}\right) \frac{\exp[-|\boldsymbol{r}-\boldsymbol{r}'|(2M|E|/\hbar^2)^{1/2}]}{|\boldsymbol{r}-\boldsymbol{r}'|} \qquad E<0 \tag{19a}$$

$$= -\left(\frac{M}{2\pi\hbar^2}\right) \frac{\exp[\mathrm{i}|\boldsymbol{r}-\boldsymbol{r}'|(2ME/\hbar^2)^{1/2}]}{|\boldsymbol{r}-\boldsymbol{r}'|} \qquad E>0. \tag{19b}$$

If the solid is in thermal equilibrium, $n_\lambda$ in (18) is replaced by its thermal average,

$$\bar{n}_\lambda = 1/[\exp(\hbar\omega_\lambda/k_B T) - 1]. \tag{20}$$

In the ground state of the solid, or at $T = 0$ only the second term in (18) contributes to the interaction potential,

$$\Sigma_k(\boldsymbol{r}) = \left(\frac{Q^2}{2}\right) \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}) \sum_\lambda \left[ \varphi_\lambda(\boldsymbol{r}) \int G\left(\boldsymbol{r}-\boldsymbol{r}'; \frac{\hbar^2 k^2}{2M} - \hbar\omega_\lambda\right) \right.$$

$$\left. \times \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}') \varphi_\lambda^*(\boldsymbol{r}') \, \mathrm{d}^3 r' \right]. \tag{21}$$

We shall use equations (18) to (21), together with their classical limit (14) to evaluate the interaction of a charged particle with a metal sphere, the collective charge oscillation modes of which are evaluated in the electrostatic limit in the hydrodynamic model of the metallic electrons. Other cases of practical interest will be considered in a later paper.

## 3. The plasmon modes of a metallic sphere

We consider a jellium sphere of radius $R$ with an equilibrium electron density which is a constant $n_0$ within the sphere and drops to zero at the surface. The linearised equation of motion for the density fluctuation $n(\boldsymbol{r}, t)$ in the time-independent form is given by (Barton 1979),

$$(\omega_P^2 - \beta^2\nabla^2)n = \omega^2 n \qquad \omega_P^2 = 4\pi n_0 e^2/m. \tag{22}$$

$\omega_P$ is the plasma frequency and $\beta$ is the parameter describing the dispersion of plasmons. The eigenvalue $\omega_\lambda$ obtained for a solution $n_\lambda(\boldsymbol{r})$ of (22) with the boundary condition of vanishing of the radial current at the surface gives the frequency of the $\lambda$th plasmon mode. The parameter $\beta^2$ equals $\frac{3}{5}v_F^2$ at high frequencies (Jackson 1962), and is $\frac{1}{3}v_F^2$ at low frequencies—here we shall treat it as a parameter.

In (22) there are two distinct frequency regions $\omega^2 < \omega_P^2$ and $\omega^2 > \omega_P^2$. With the above boundary condition, which in terms of $n$ can be written as

$$\frac{\partial}{\partial r}\left[-n_0 e^2 \int_{r' \le R} \frac{n(\boldsymbol{r}')\,\mathrm{d}^3 r'}{|\boldsymbol{r} - \boldsymbol{r}'|} - m\beta^2 n(\boldsymbol{r})\right]_{r \to R} = 0 \tag{23}$$

we get the following solutions and dispersion relations in the two regions, assuming that

$$n(\boldsymbol{r}) \equiv n_{l,m}(\boldsymbol{r}) = n_l(r) Y_l^m(\theta, \varphi) \qquad 0 < r < R. \tag{24}$$

(i) For $\omega^2 < \omega_P^2$,

$$n_l^S(r) = N_l^S m_l(\kappa_l r) \qquad \kappa_l^2 = \frac{\omega_P^2 - \omega_l^2}{\beta^2} \qquad m_l(z) \equiv \sqrt{\frac{\pi}{2z}}\, I_{l+\frac{1}{2}}(z). \tag{25}$$

The corresponding frequency $\omega_l$ is the root of the equation

$$\frac{m_l(\kappa R)}{\kappa R} = \left[1 - \left(\frac{2l+1}{l+1}\right)\frac{\kappa^2\beta^2}{\omega_P^2}\right]\frac{m_l'(\kappa R)}{l} \qquad \kappa^2 = \frac{\omega_P^2 - \omega^2}{\beta^2}. \tag{26}$$

$N_l^S$ is a normalisation factor. It is easy to show that $l = 0$ does not give a root for $\omega$ in (26), and the solutions start with $l = 1$. It can also be shown that for finite $\beta$ there is an upper limit $l_{\max}$,

$$l_{\max} \cong \frac{(36 + 16y^2)^{1/2} - 6}{8} \qquad y^2 = \frac{\omega_P^2}{\beta^2} R^2 \equiv k_0^2 R^2 \tag{27}$$

beyond which solutions of (26) for $\omega^2 < \omega_P^2$ cannot arise. $k_0^{-1} = (\beta/\omega_P)$ is the Thomas–Fermi screening length. In the non-dispersive limit $\beta \to 0$ the frequencies obtained from (26) are the well known result,

$$\lim_{\beta \to 0} \omega_l^2 = \omega_P^2 \left(\frac{l}{2l+1}\right). \tag{28}$$

We shall call these solutions the surface modes, denoted by the superscript S, since $m_l(\kappa_l r)$ vanishes at the centre of the sphere and monotonically goes to a maximum at the surface for all $l$ in the range $1 \leqslant l < l_{\max}$.

The potential $\varphi^{\mathrm{S}}_{l,m}(\boldsymbol{r})$ corresponding to the mode $(l, m)$ is obtained by solving Poisson's equation

$$\nabla^2 \varphi^{\mathrm{S}}_{l,m}(\boldsymbol{r}) = 4\pi e n^{\mathrm{S}}_{l,m}(\boldsymbol{r}) \equiv 4\pi e n^{\mathrm{S}}_l(r) Y^m_l(\theta, \varphi). \tag{29}$$

The normalisation of $n^{\mathrm{S}}_{l,m}$ and of $\varphi^{\mathrm{S}}_{l,m}$ can be done exactly as indicated by Barton (1979), and we get

$$\varphi^{\mathrm{S}}_{l,m}(\boldsymbol{r}) = 4\pi e \left(\frac{\hbar n_0}{2mR}\right)^{1/2} [\kappa_l R(\omega_l \Delta^{\mathrm{S}}_l)^{1/2}]^{-1} \left[\frac{m_l(\kappa_l r)}{m_{l+1}(\kappa_l R)} - \left(\frac{l+1}{2l+1}\right)\left(a_l + \frac{\kappa_l R b_l}{l+1}\right)\left(\frac{r}{R}\right)^l\right] Y^m_l(\theta, \varphi) \qquad r < R \tag{30a}$$

$$= -4\pi e \left(\frac{\hbar n_0}{2mR}\right)^{1/2} [(2l+1)(\omega_l \Delta^{\mathrm{S}}_l)^{1/2}]^{-1} \times \left(\frac{R}{r}\right)^{l+1} Y^m_l(\theta, \varphi) \qquad r > R. \tag{30b}$$

Here

$$\Delta^{\mathrm{S}}_l = \frac{b_l}{l} - \tfrac{1}{2}(a_l^2 - c_l) \tag{31a}$$

and $a_l$, $b_l$ and $c_l$ are defined through the equations

$$m_l(\kappa_l R) = a_l m_{l+1}(\kappa_l R) \tag{31b}$$

$$m'_l(\kappa_l R) = b_l m_{l+1}(\kappa_l R) \tag{31c}$$

$$m_{l-1}(\kappa_l R) = c_l m_{l+1}(\kappa_l R). \tag{31d}$$

Using (26) and the recursion relations for modified spherical Bessel functions we can write

$$a_l = \frac{\kappa_l R}{l}\left[\left(\frac{l+1}{2l+1}\right)\frac{k_0^2}{\kappa_l^2} - 1\right] \tag{32a}$$

$$b_l = \left(\frac{l+1}{2l+1}\right)\frac{k_0^2}{\kappa_l^2} \tag{32b}$$

$$c_l = \left(\frac{l+1}{l}\right)\left(\frac{k_0^2}{\kappa_l^2} - 1\right). \tag{32c}$$

(ii) For $\omega^2 \geqslant \omega_{\mathrm{P}}^2$,

$$n^{\mathrm{B}}_{l,\nu}(r) = N^{\mathrm{B}}_{l,\nu} j_l(k_{l,\nu} r) \qquad k^2_{l,\nu} = \frac{\omega^2_{l,\nu} - \omega^2_{\mathrm{P}}}{\beta^2} \qquad 0 < r < R. \tag{33}$$

Here, $j_l$ being spherical Bessel functions, the modes have nodes between the centre and the surface of the sphere. We shall denote these modes as bulk modes with the superscript

B. The frequencies $\omega_{l,\nu}$ are roots of the equation

$$\frac{j_l(kR)}{kR} = \left[1 + \frac{\beta^2 k^2}{\omega_P^2}\left(\frac{2l+1}{l+1}\right)\right]\frac{j_l'(kR)}{l} \qquad k = \frac{\omega^2 - \omega_P^2}{\beta^2}. \tag{34}$$

This equation has an infinite number of solutions for each $l$, and hence the second index $\nu$ is introduced in (33).

It may be mentioned here that unlike the surface modes, bulk modes also exist for $l = 0$. They are the roots of

$$j_0'(kR) = j_1(kR) = 0. \tag{35}$$

One root occurs at $k = 0$, i.e., for $\omega^2 = \omega_P^2$. The other roots correspond to the zeros of $j_1(kR)$.

The corresponding normalised potential for $l \neq 0$ is,

$$\varphi^B_{l,\nu;m}(\boldsymbol{r}) = -4\pi e\left(\frac{\hbar n_0}{2mR}\right)^{1/2}[k_{l,\nu}R(\omega_{l,\nu}\Delta^B_{l,\nu})^{1/2}]^{-1}$$
$$\times\left[\frac{j_l(k_{l,\nu}r)}{j_{l+1}(k_{l,\nu}R)} - \left(\frac{l+1}{2l+1}\right)\left(\frac{k_{l,\nu}R\beta_{l,\nu}}{l+1} + \alpha_{l,\nu}\right)\left(\frac{r}{R}\right)^l\right]$$
$$\times Y_l^m(\theta,\varphi) \qquad r < R \tag{36a}$$

$$= -4\pi e\left(\frac{\hbar n_0}{2mR}\right)^{1/2}[(2l+1)(\omega_{l,\nu}\Delta^B_{l,\nu})^{1/2}]^{-1}\left(\frac{R}{r}\right)^{l+1}$$
$$\times Y_l^m(\theta,\varphi) \qquad r > R. \tag{36b}$$

Here

$$\Delta^B_{l,\nu} = \tfrac{1}{2}(\alpha^2_{l,\nu} - \gamma_{l,\nu}) - \frac{\beta_{l,\nu}}{l} \tag{37a}$$

and $\alpha_{l,\nu}, \beta_{l,\nu}$ and $\gamma_{l,\nu}$ are defined through the equations

$$j_l(k_{l,\nu}R) = \alpha_{l,\nu}j_{l+1}(k_{l,\nu}R) \tag{37b}$$

$$j_l'(k_{l,\nu}R) = \beta_{l,\nu}j_{l+1}(k_{l,\nu}R) \tag{37c}$$

$$j_{l-1}(k_{l,\nu}R) = \gamma_{l,\nu}j_{l+1}(k_{l,\nu}R). \tag{37d}$$

Using (34) and the recursion relations for spherical Bessel functions we get,

$$\alpha_{l,\nu} = \frac{k_{l,\nu}R}{l}\left[1 + \frac{k_0^2}{k_{l,\nu}^2}\left(\frac{l+1}{2l+1}\right)\right] \tag{38a}$$

$$\beta_{l,\nu} = \frac{k_0^2}{k_{l,\nu}^2}\left(\frac{l+1}{2l+1}\right) \tag{38b}$$

$$\gamma_{l,\nu} = \left(\frac{l+1}{l}\right)\left(1 + \frac{k_0^2}{k_{l,\nu}^2}\right). \tag{38c}$$

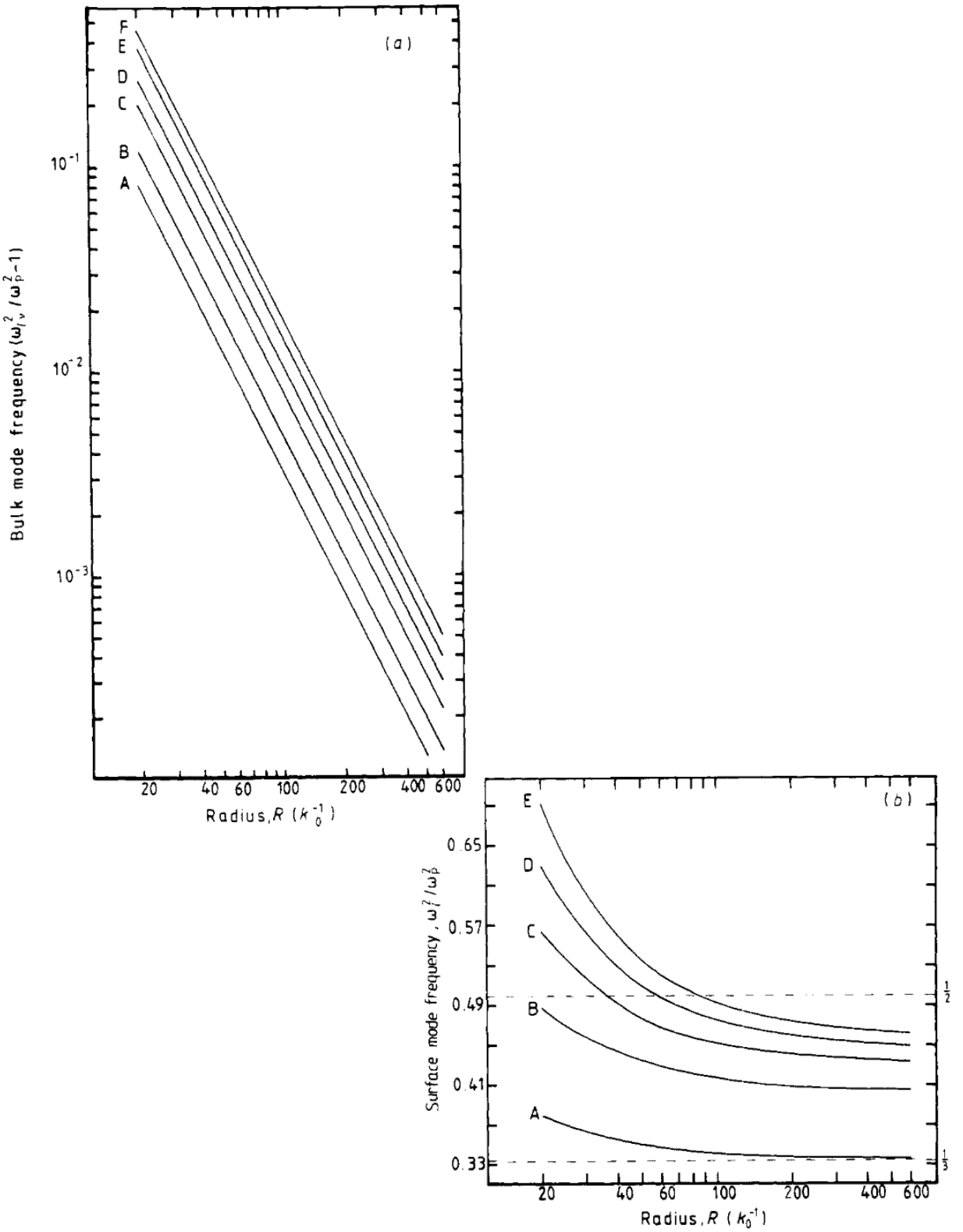


**Figure 1.** (*a*) The bulk mode eigen-frequencies $(\omega_{l\nu}^2/\omega_p^2 - 1)$ against radius of the sphere $R$ for the first $l = 1, 2$ and $\nu = 1, 2, 3$ bulk modes of the sphere. For curve A: $l = 1$, $\nu = 0$; for C: $l = 1$, $\nu = 1$; for E: $l = 1$, $\nu = 2$; for B: $l = 2$, $\nu = 0$; for D: $l = 2$, $\nu = 1$; and for F: $l = 2$, $\nu = 2$. For a fixed radius the eigen-frequencies of increasing order interlace in the same way as the zeros of the spherical Bessel functions. (*b*) The surface mode eigen-frequency $\omega_l^2/\omega_p^2$ against radius of the sphere $R$ for the $l = 1$ (line A), $l = 2$ (line B), $l = 3$ (line C), $l = 4$ (line D) and $l = 5$ (line E) modes. The screening length $\lambda = \beta/\omega_p = 0.8$ nm corresponds to an Al sphere. The horizontal lines for $(\omega_l^2/\omega_p^2) = \frac{1}{2}$ and $\frac{1}{3}$ indicate the non-dispersive limit of surface plasmons ($\beta = 0$) which is formally equivalent to the limit $R \to \infty$ (flat surface). All the eigen-frequencies are then contained in the interval $(\frac{1}{3}, \frac{1}{2})$.

For $l = 0$, the bulk mode potential is

$$\varphi^{B}_{0,\nu}(r) = -4\pi e\left(\frac{\hbar n_0 k_{0,\nu}}{m\omega_{0,\nu}}\right)^{1/2}[k_{0,\nu}R - \tfrac{1}{2}\sin(2k_{0,\nu}R)]^{-1/2}$$
$$\times\left[\frac{\sin(k_{0,\nu}r)}{k_{0,\nu}r} - \cos(k_{0,\nu}R)\right] \qquad r < R \tag{39a}$$

$$= -4\pi e\left(\frac{\hbar n_0 k_{0,\nu}^3}{m\omega_{0,\nu}}\right)^{1/2}[k_{0,\nu}R - \tfrac{1}{2}\sin(2k_{0,\nu}R)]^{-1/2}$$
$$\times j_1(k_{0,\nu}R)\,(R^2/r) \equiv 0 \qquad r > R. \tag{39b}$$

The last result follows from (35) which implies $j_1(k_{0,\nu}R) \equiv 0$ for all $\nu$.

Figures 1(*a*) and (*b*) give the variation of some of the surface and bulk plasma frequencies with the radius of the sphere.

## 4. The interaction potential

We shall consider first the interaction potential between the charged particle and the sphere in the classical limits given by (14). Using the potentials given in equations (30), (36) and (39) we get for the surface mode and volume mode contributions to the interaction potential the following expressions.

$$\Sigma^{S}_{c}(r) = -Q^2\sum_{l=1}^{l_{max}}\sum_{m=-l}^{l}\left(\frac{1}{\hbar\omega_l}\right)|\varphi^{S}_{l,m}(r)|^2$$

$$= -\frac{Q^2}{2R}\sum_{l=1}^{l_{max}}\left(\frac{\omega_P^2}{\omega_l^2}\right)\frac{1}{(2l+1)\Delta^{S}_{l}}\left(\frac{R}{r}\right)^{2(l+1)} \qquad r > R \tag{40a}$$

$$= -\frac{Q^2}{2R}\sum_{l=1}^{l_{max}}\left(\frac{\omega_P^2}{\omega_l^2}\right)\frac{1}{\kappa_l^2 R^2\Delta^{S}_{l}}\left[\frac{m_l(\kappa_l r)}{m_{l+1}(\kappa_l R)}\right.$$
$$\left. -\left(\frac{l+1}{l(2l+1)}\right)\kappa_l R\left(\frac{k_0^2}{\kappa_l^2} - 1\right)\left(\frac{r}{R}\right)^{l}\right]^2 \qquad r < R. \tag{40b}$$

This vanishes at $r = 0$ and at $r = \infty$, and has a minimum at the surface. For large $r$ the value converges to that of the interaction potential of $Q$ with a charge-neutral insulated sphere obtained by image theory (Stratton 1941).

The contribution to the classical interaction potential from the bulk modes is

$$\Sigma^{B}_{c}(r) = -Q^2\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\sum_{\nu=0}^{\infty}\left(\frac{1}{\hbar\omega_{l,\nu}}\right)|\varphi^{B}_{l,\nu;m}(r)|^2$$

$$= -\frac{Q^2}{2R}\sum_{l=1}^{\infty}\sum_{\nu=0}^{\infty}\frac{\omega_P^2}{\omega_{l,\nu}^2\Delta^{B}_{l,\nu}}\left(\frac{1}{2l+1}\right)\left(\frac{R}{r}\right)^{2l+2} \qquad r > R \tag{41a}$$

$$= -\frac{Q^2}{2R}\sum_{l=1}^{\infty}\sum_{\nu=0}^{\infty}\frac{\omega_P^2}{\omega_{l,\nu}^2\Delta_{l,\nu}^B}\frac{(2l+1)}{(k_{l,\nu}R)^2}\left[\frac{j_l(k_{l,\nu}r)}{j_{l+1}(k_{l,\nu}R)}\right.$$
$$\left.-\left(\frac{l+1}{l(2l+1)}\right)k_{l,\nu}R\left(\frac{k_0^2}{k_{l,\nu}^2}+1\right)\left(\frac{r}{R}\right)^l\right]^2$$
$$-\frac{Q^2}{R}\sum_{\nu=1}^{\infty}\left(\frac{\omega_P^2}{\omega_{0,\nu}^2}\right)\frac{\{j_0(k_{0,\nu}r)-\cos(k_{0,\nu}R)\}^2}{\{1-j_0(2k_{0,\nu}R)\}} \qquad r<R. \tag{41b}$$

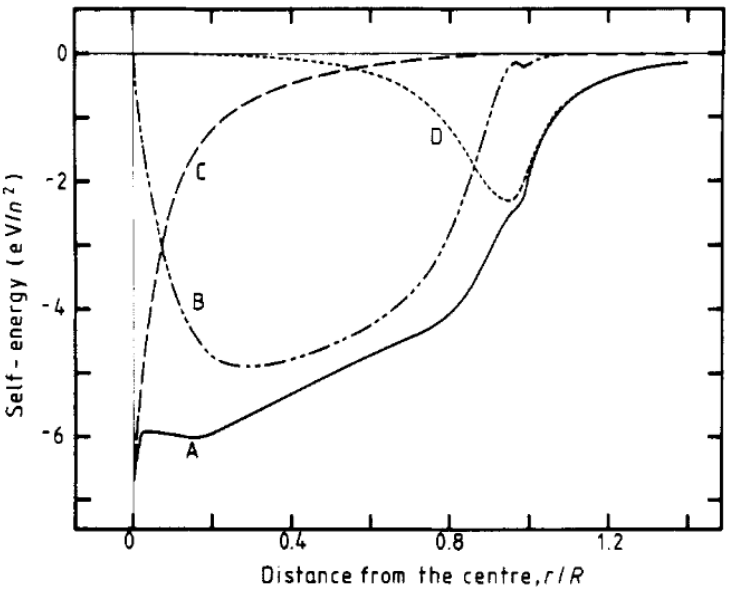


**Figure 2.** The contributions from different types of modes to the total self-energy of a static charge against distance from the centre of the sphere $r/R$, for an Al sphere of radius $R$ = 2 nm. B, bulk modes contribution; C, $l = 0$ bulk modes contribution; D, surface modes contribution; A, total self-energy. The units are eV/$n^2$, where $n = Q/e$ is the multiple of the electronic charge.

The second term in (41*b*) is the contribution from the $l = 0$ mode. At the centre of the sphere the value of the potential is given only by the $l = 0$ mode and has the form

$$\Sigma_c^B(r\to 0) = -\frac{Q^2}{R}\sum_{\nu=1}^{\infty}\left(\frac{\omega_P^2}{\omega_{0,\nu}^2}\right)\frac{[1-\cos(k_{0,\nu}R)]^2}{[1-j_0(2k_{0,\nu}R)]}. \tag{42}$$

For a large sphere this tends to the value,

$$\lim_{R\to\infty}\Sigma_c^B(r\to 0)\to\lim_{R\to\infty}\left(-\frac{Q^2k_0}{2}\tanh(Rk_0)\right) = -\frac{Q^2k_0}{2} \tag{43}$$

which is the well known value of the self-energy of a charged particle embedded in a homogeneous dispersive plasma. Figure 2 gives a plot of the contributions of various mode types to the total self-energy. The self-energy of a static charge outside and inside the sphere, for different sphere radii $R$ is plotted in figure 3.

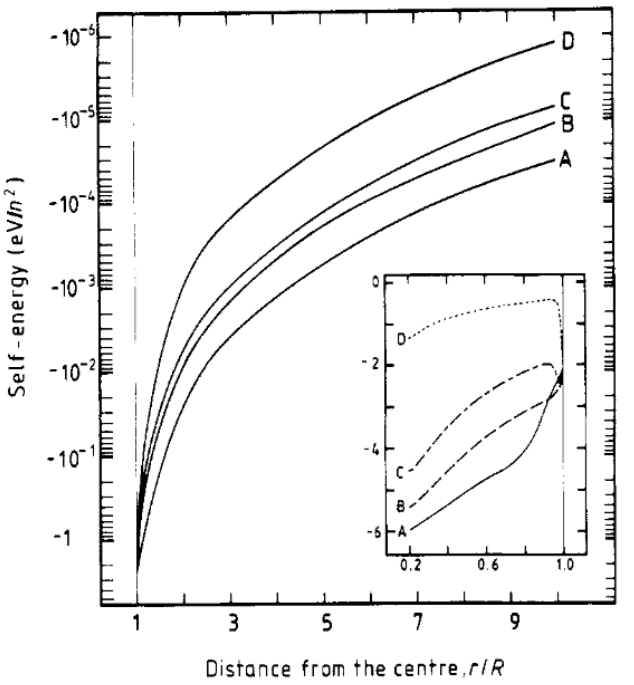


**Figure 3.** The interaction potential of a static charged particle outside the Al sphere against distance from the centre $r/R$ for spheres of various radii: $R = 2$ nm (A); $R = 6$ nm (B); $R = 10$ nm (C); $R = 60$ nm (D). The inset figure shows the interaction potential inside the sphere. The description is the same as that of the main figure.

## 5. The interaction potential: quantum correction

The quantum correction to the self-energy of a massive particle is obtained by substituting the following expansion for the Green function (19):

$$G(\boldsymbol{r}-\boldsymbol{r}';E) \simeq -\frac{1}{\hbar\omega_\lambda}\left(\delta(\boldsymbol{r}-\boldsymbol{r}')+\frac{\hbar}{2M\omega_\lambda}\left[k^2\delta(\boldsymbol{r}-\boldsymbol{r}')+\nabla^2\delta(\boldsymbol{r}-\boldsymbol{r}')\right]\right) \tag{44}$$

in expression (21). This leads to the correction to the self-energy of the form

$$\Sigma_Q(\boldsymbol{r}) = -Q^2\sum_\lambda \frac{1}{M\omega_\lambda^2}\left\{\mathrm{i}\varphi_\lambda(\boldsymbol{r})\boldsymbol{k}\cdot\bar{\nabla}\varphi_\lambda^*(\boldsymbol{r})+2\pi e\varphi_\lambda(\boldsymbol{r})n_\lambda^*(\boldsymbol{r})\right\} \tag{45}$$

which, in the static limit $\boldsymbol{k} = 0$ reduces further to

$$\lim_{k\to 0}\Sigma_Q(\boldsymbol{r}) = -Q^2\sum_\lambda \frac{2\pi e}{M\omega_\lambda^2}\varphi_\lambda(\boldsymbol{r})n_\lambda^*(\boldsymbol{r}). \tag{46}$$

The contribution of the surface modes in the above correction term calculated for the case of a charged particle interacting with the plasmons in the sphere is given by

$$\Sigma_Q^S(r) = -\frac{Q^2}{2R}(Rk_P)^{-2}\sum_{l=1}^{l_{max}}\frac{\omega_P^3}{\omega_l^3}\frac{(2l+1)}{\Delta_l^S}$$
$$\times\left[\frac{m_l(\kappa_l r)}{m_{l+1}(\kappa_l R)}-\frac{(l+1)}{l(2l+1)}\kappa_l R\left(\frac{k_0^3}{\kappa_l^3}-1\right)\left(\frac{r}{R}\right)^l\right]\frac{m_l(\kappa_l r)}{m_{l+1}(\kappa_l R)} \tag{47a}$$

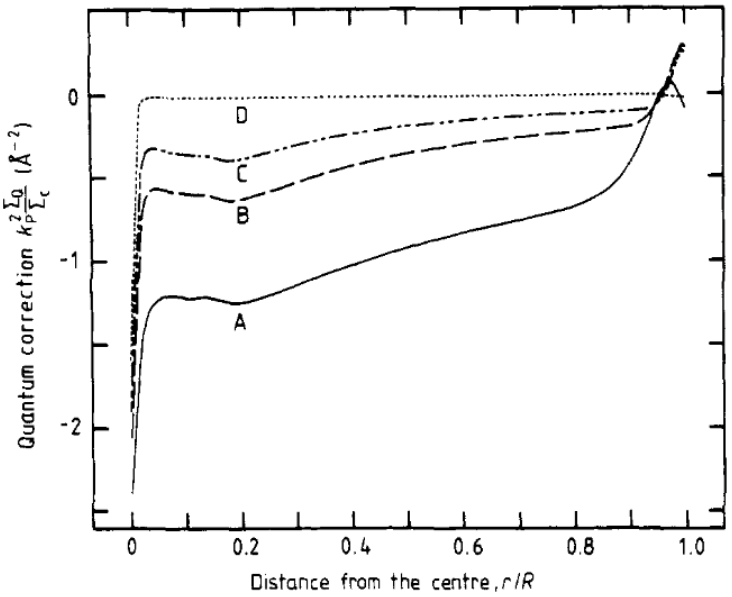


**Figure 4.** The relative quantum contribution $k_P^2\Sigma_Q(r)/\Sigma_c(r)$ of self-energy for a static charge inside the Al sphere of radius: $R = 2$ nm (A), 6 nm (B), 10 nm (C), 60 nm (D) against distance from the centre of the sphere $r/R$. The correction is less than 0.05% at the centre of the smallest sphere of radius $R = 2$ nm.

and for the contribution of the bulk modes,

$$\Sigma_Q^B(r) = -\frac{Q^2}{2R}(Rk_P)^{-2}\sum_{l=1}^{\infty}\sum_{\nu=0}^{\infty}\frac{\omega_P^3}{\omega_{l,\nu}^3}\frac{(2l+1)}{\Delta_{l,\nu}^B}$$
$$\times\left[\frac{j_l(k_{l,\nu}r)}{j_{l+1}(k_{l,\nu}R)} - \frac{(l+1)}{l(2l+1)}k_{l,\nu}R\left(\frac{k_0^2}{k_{l,\nu}^2}+1\right)\left(\frac{r}{R}\right)^l\right]\frac{j_l(k_{l,\nu}r)}{j_{l+1}(k_{l,\nu}R)}$$
$$-\frac{Q^2}{R}(Rk_P)^{-2}\sum_{\nu=1}^{\infty}\frac{\omega_P^3}{\omega_{0,\nu}^3}(Rk_{0,\nu})^2 j_0(k_{0,\nu}r)$$
$$\times\frac{[j_0(k_{0,\nu}r)-\cos(k_{0,\nu}R)]}{[1-j_0(2k_{0,\nu}R)]} \qquad (47b)$$

where $k_P^{-2} = \hbar/(2M\omega_P)$. The second term in (47*b*) describes the contribution due to the $l = 0$ mode.

The relative magnitude of the quantum correction for a stationary particle, $k_P^2\Sigma_Q(r)/\Sigma_c(r)$, is plotted in figure 4 for different sphere radii $R$.

## 6. Discussion

The purpose of the paper was twofold. First, the generalisation of the method of evaluating the interaction between a charged particle and a solid through the self-energy formalism, using linear response theory has been given. Using the formalism, we have then studied the case of a charged particle interacting with a metallic sphere.

The two distinct types of normal plasma modes of the sphere were classified and the dispersion relations were given in some detail, to stress some features not given in

existing literature (Ogale *et al* 1978, Agarwal and O'Neil, 1983). It was found that only a finite number of surface modes exist in the dispersive sphere.

We have computed all the eigen-frequencies for the surface modes (up to 299 solutions for the sphere $R = 60$ nm). In the case of bulk modes the first 1200 eigen-frequencies were computed ($l = 30$, $\nu = 40$), and for the bulk $l = 0$ mode terms up to $\nu = 3000$ were included in the sums for self-energy.

The main results depicted in figures 2 and 3 are exact outside the sphere, due to a finite sum in the surface part contribution to self-energy. However the error range in the numerical values of the self-energy inside the sphere are 30% for small $r$ and 10% near the surface for spheres of radii $R < 10$ nm whereas for a sphere of radius $R = 60$ nm (line D in the inset of figure 3) the calculated values are far from their saturation. This is due to the truncation of the sum in expression (41*b*) after the first $l = 30$, $\nu = 40$ terms. The effect of truncation is less drastic for a smaller sphere (2–6 nm) but is quite large for a bigger sphere ($R = 60$ nm) (inset of figure 3).

It should be emphasised that the hydrodynamic model breaks down for very high frequencies and so the sum in (41*b*) is not infinite; there should be cut-off indices $l_c$ and $\nu_c$, where the sum is to be terminated. By inspection of figure 1(*a*) one notices that for bigger spheres the number of terms in the sum (41*b*) will be drastically higher:

$$l_c(R_1) \ll l_c(R_2) \quad \text{and} \quad \nu_c(R_1) \ll \nu_c(R_2) \quad \text{for} \quad R_1 < R_2.$$

The quantum correction introduces the additional screening parameter $k_P^{-1} = (\hbar/2M\omega P)_{1/2}$, in analogy with the polaron problem and with the case of planar geometry with non-dispersive surface plasmons (Manson and Ritchie 1981). The complete quantum result for $\Sigma(r)$ can, of course, be worked out from equations (18) and (19). But as has been pointed out in the case of planar geometry (Mahanty *et al* 1985), the effect of screening due to plasmon dispersion on $\Sigma(r)$ near the surface of a metal is more dominant than polaronic screening, and hence we have given only the leading order quantum correction term. The screening parameter $k_P^{-1} \simeq 1.4 \times 10^{-2}$ Å for a proton incoming to an Al target, therefore the quantum correction is found to be less than 0.05% even for the smallest sphere of radius 2 nm.

The discontinuity of the quantum correction at the surface (figure 4) results from the boundary condition of abrupt vanishing of the electronic density fluctuation at the surface (see (46)). By relaxing this boundary condition and allowing diffuse electronic density at the surface the continuity of the quantum correction is recovered. However its magnitude is smaller by one order and it rapidly vanishes in the close proximity of the surface. In a later paper we shall present the results for other geometries of experimental interest.

## Acknowledgments

One of us (MTM) would like to thank Dr S Prakash and Dr A Radlinski for discussions during the course of this work.

## References

Agarwal G S and O'Neil S V 1983 *Phys. Rev.* B **28** 487–93
Barton G 1979 *Rep. Prog. Phys.* **42** 963–1016

Equiluz A G 1981 *Phys. Rev.* B **23** 1542–58
Fetter A L 1973 *Ann. Phys.* **81** 367–93
Heinrichs J 1973 *Phys. Rev.* B **8** 1346–64
Ibach H 1977 *Electron Spectroscopy for Surface Analysis* (Berlin: Springer)
Jackson J D 1962 *Classical Electrodynamics* (New York: Wiley) ch 10 § 10.9
Kubo R 1957 *J. Phys. Soc. Japan* **12** 570–86
McRae E G 1979 *Rev. Mod. Phys.* **51** 541–68
Mahanty J, Pathak K N and Paranjape V V 1985 *Solid State Commun.* **54** 649–52
Manson J R and Ritchie R H 1981 *Phys. Rev.* B **24** 4867–70
Newns D M 1969 *J. Chem. Phys.* **50** 4572–5
Ogale S B, Bhoraskar V N and Panat P V 1978 *Pramana* **11** 135–44
Stratton J A 1941 *Electromagnetic Theory* (New York: McGraw-Hill) ch III § 3.22
Straub D and Himpsel F J 1984 *Phys. Rev. Lett.* **52** 1922–4
Tomonaga S 1950 *Prog. Theor. Phys.* **5** 544–69