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DYNAMICAL SCREENING AND SURFACE EXCITATIONS IN PLANAR, SPHERICAL AND CYLINDRICAL SOLIDS I GENERAL FORMALISM

ZLATKO PENZAR

Institute of Physics of the University, P. O. B. 304, 41001 Zagreb, Croatia, Yugoslavia

and

JANKA PETRAVIĆ and MARIJAN ŠUNJIĆ

Department of Physics, Faculty of Science, P. O. B. 162, 41001 Zagreb, Croatia, Yugoslavia

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A quantum-mechanical formulation of the dynamical self-consistent electrostatic interaction near metallic surfaces is developed for the case of planar, spherical and cylindrical solids, based on the use of symmetry decomposition of the problem. Analytic expressions are given for the response functions in the jellium *Infinite Barrier Model* in the *Random Phase Approximation.* The knowledge of the interaction propagator enables us to find and discuss various physical properties of the system, in particular the spectrum of elementary (single particle and collective) electronic excitations.

1. Introduction

Dielectric and optical properties of small metallic particles of spherical and other shapes have been extensively studied, especially in connection with the nonretarded electronic excitations and the screening. In the framework of classical electrodynamics one can find the collective electronic modes (surface plasmons) by the standard matching procedure, neglecting the dispersion in the metal, as has been done for a number of different geometries[1,2,3] leading to the results valid in the long wavelength limit. Quantum mechanical calculations present a formidable problem even in the case of planar surfaces and in the *Random Phase Approximation*[4,5], so only a limited number of results has been obtained[6]. In particular, the calculations were restricted, due to the necessary approximations, e. g. to the case of large particles, where one uses the infinite solid (wavevector decomposed) version of the bulk dielectric function in order to obtain the collective modes of spherical particles.

In this paper we want to develop a formalism that exploits the full symmetry of the problem and is valid both in the small particle limit, where the quantization of the electronic states is important, in the transition region, where the collective modes develop, and which also asymptotically gives the large particle results obtained previously[6]. In order to study the surface (collective and single-particle) excitations in small metallic particles with spherical and cylindrical shapes we shall use a generalization of our earlier theory[7] which treats the dynamically screened nonlocal potentials and surface elementary excitations near planar surfaces.

2. *Formulation of the problem*

As before[7], we start with the integral equation for the dynamically screened potential W between two points $\vec{r}$ and $\vec{r}'$:

$$W(\vec{r}, \vec{r}'; \omega) = V(\vec{r}, \vec{r}') + \int d\vec{r}_1 \int d\vec{r}_2 \, V(\vec{r}, \vec{r}_1) \, R(\vec{r}_1, \vec{r}_2) \, W(\vec{r}_2, \vec{r}'; \omega) \tag{1}$$

where V is the bare Coulomb interaction, R is the response function of the solid, and the integrations extend over the solid where $R \neq 0$. V is the solution of the Poisson equation:

$$\Delta V(\vec{r}, \vec{r}') = -4\pi \, \delta(\vec{r} - \vec{r}'). \tag{2}$$

Next, we take account of the symmetry properties of the solid, namely we require that all the quantities appearing in the integral equation (1) have the same symmetry properties as the boundary surfaces of the solid. Therefore, we shall express all these quantities in terms of the Fourier expansions, using as the basis functions the solutions $g_Q(\Omega)$ of the *angular* part of the Laplace equation (3) in the appropriate geometry

$$[\Delta_\Omega + \lambda_Q(r)] \, g_Q(\Omega) = 0. \tag{3}$$

The functions $g_Q(\Omega)$ form a complete and orthonormal set, i. e.:

$$\begin{gathered} \sum g_Q^*(\Omega) \, g_Q(\Omega') = \delta(\Omega - \Omega') \\ \int g_Q^*(\Omega) \, g_{Q'}(\Omega) \, d\Omega = \delta_{QQ'}. \end{gathered} \tag{4}$$

The index Q denotes the conserved quantum numbers, and Ω are the associated coordinates, or degrees of freedom.

In particular, we can write the Coulomb potential in the form:

$$V(\vec{r}, \vec{r}') = \sum_Q g_Q^*(\Omega)\, g_Q(\Omega')\, V_Q(r, r') \tag{5}$$

where we have separated the radial (*broken*) coordinate (r) and the non-radial coordinates (Ω). The *broken* coordinate is the one which defines the boundary surface in the most convenient way.

Similarly, we can expand W and R:

$$W(\vec{r}, \vec{r}'; \omega) = \sum_Q W_Q(r, r'; \omega)\, g_Q^*(\Omega')\, g_Q(\Omega) \tag{6}$$

$$R(\vec{r}, \vec{r}'; \omega) = \sum_Q R_Q(r, r'; \omega)\, g_Q^*(\Omega')\, g_Q(\Omega) \tag{7}$$

and the fact that the Fourier expansions (5), (6) and (7) are diagonal in the Q components reflects the symmetry of the problem.

Inserting (5), (6) and (7) into (1) and integrating over Ω we obtain a system of integral equations for each set of quantum numbers Q:

$$W_Q(r, r'; \omega) = V_Q(r, r') + \int f(r_1)\, \mathrm{d}r_1 \int f(r_2)\, \mathrm{d}r_2\, V_Q(r, r_1)\, R_Q(r_1, r_2; \omega) \cdot \\ \cdot W_Q(r_2, r'; \omega) \tag{8}$$

where $f(r)\,\mathrm{d}r$ are the differentials of the radial coordinate in different geometries.

Now we turn to the specific geometries in which the above symmetry decomposition is possible, namely the planar, spherical and cylindrical surfaces.

In Tables 1 and 2 we give all the quantities and functions mentioned above, calculated for these three cases.

The Poisson equation for the Fourier components of the Coulomb potential now becomes:

$$[\Delta r - \lambda_Q(r)]\, V_Q(r, r') = \frac{4\pi}{f(r)}\, \delta(r - r') \tag{9}$$

and the solution is:

$$V_Q(r, r') = v_Q\, [\psi_Q^{>}(r)\, \psi_Q^{<}(r')\, \Theta(r - r') + \psi_Q^{>}(r')\, \psi_Q^{<}(r)\, \Theta(r' - r)] \tag{10}$$

where $\psi_Q^{>}$, $\psi_Q^{<}$ are the solutions of Laplace equation:

$$[\Delta r - \lambda_Q(r)]\, \psi_Q^{\lessgtr} = 0$$

TABLE 1

	Planar	Spherical	Cylindrical
Invariant coordinates (Ω)	x, y	ϑ, φ	z
Conserved quantities	p_x, p_y	L^2, L_z	p_z, L_z
Corresponding symmetry operations	translation along x and y axis	rotation by ϑ, φ	translation along and rotation around z axis
Conserved quantum number (Ω)	k_x, k_y $\vec{K} = \vec{k}_x + \vec{k}_y$	l, m	k, m
Eigenfunctions $g_Q(\Omega)$	$\frac{1}{(2\pi)^2} e^{i\vec{K}\cdot\vec{\varrho}}$	$Y_{lm}(\vartheta, \varphi)$	$\frac{1}{(2\pi)^2} e^{ikz} e^{im\varphi}$
$\lambda_Q(r)$	$\lambda_{\vec{k}} = K^2 = k_x^2 + k_y^2$	$\lambda_{lm} = \frac{l(l+1)}{r^2}$	$\lambda_{km} = k^2 + \frac{m^2}{a^2}$
Broken coordinate (r) and the boundary condition	z $z = 0$	r $r = a$	ϱ $\varrho = a$
Differential of the radial coordinate $f(r)\,dr$	dz	$r^2\,dr$	$\varrho\,d\varrho$

TABLE 2

	Planar	Spherical	Cylindrical
$V_Q(r, r')$	$\frac{2\pi^2}{K} e^{-K\|z-z'\|}$	$\frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}}$	$4\pi I_m(k\varrho_<) K_m(k\varrho_>)$
v_Q	$\frac{2\pi^2}{K}$	$\frac{4\pi}{2l+1}$	4π
$\psi_Q^>(r)$	e^{-Kz}	r^{-l-1}	$K_m(k\varrho)$
$\psi_Q^<(r)$	e^{Kz}	r^l	$I_m(k\varrho)$

$R_Q(r, r'; \omega)$	
Planar	$R_{\mathbf{K}}(z, z') = \sum_{\mathbf{K}'} \sum_{k\, k'>0} \sin kz \sin k'z \sin k'z' \sin kz' \frac{1}{2L^4 l^2} \frac{f(E_{\mathbf{K}+\mathbf{K}',k}) - f(E_{\mathbf{K},k})}{\omega - E_{\mathbf{K}+\mathbf{K}',k'} + E_{\mathbf{K},k} + i\eta}$
Spherical	$R_L(r, r') = \sum_{\substack{ll'\\nn'}} \frac{4}{a^6} \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \frac{(2l+1)(2l'+1)}{4\pi} \frac{j_l\left(x_{ln}\frac{r}{a}\right)}{j_{l+1}(x_{ln})} \frac{j_{l'}\left(x_{l'n'}\frac{r}{a}\right)}{j_{l'+1}(x_{l'n'})} \frac{j_{l'}\left(x_{l'n'}\frac{r'}{a}\right)}{j_{l'+1}(x_{l'n'})} \frac{j_l\left(x_{ln}\frac{r'}{a}\right)}{j_{l+1}(x_{ln})} \frac{f(E_{ln}) - f(E_{l'n'})}{\omega - E_{ln} + E_{l'n'} + i\eta}$
Cylindrical	$R_{KM}(\varrho, \varrho') = \int_{-\infty}^{+\infty} dk \sum_{\substack{m\\nn'}} \frac{1}{a^2\pi^2} \frac{\mathcal{J}_m\left(x_{mn}\frac{\varrho}{a}\right)}{\mathcal{J}_{m+1}(x_{mn})} \frac{\mathcal{J}_{m+M}\left(x_{m+M,n'}\frac{\varrho}{a}\right)}{\mathcal{J}_{m+M+1}(x_{m+M,n'})} \frac{\mathcal{J}_m\left(x_{mn}\frac{\varrho'}{a}\right)}{\mathcal{J}_{m+1}(X_{mn})} \frac{\mathcal{J}_{m+M}\left(x_{m+M,n'}\frac{\varrho'}{a}\right)}{\mathcal{J}_{m+M+1}(x_{m+M,n'})} \frac{f(E_{kmn}) - f(E_{k+K,m+M,n'})}{\omega - E_{kmn} + E_{k+K,m+M,n'} + i\eta}$

with the boundary conditions:

$$\lim_{r\to\infty} \psi_Q^{>}(r) = 0 \qquad \lim_{r\to 0} \psi_Q^{<}(r) < \infty .$$

The explicit results for these functions are given in Table 2.

The integral equation (8) can be formally written in the matrix form

$$W = V + VRW \tag{11}$$

and solved for W:

$$W = W + VR(1 - VR)^{-1}\, V \tag{12}$$

or, explicity for each Q component:

$$W(r, r') = V(r, r') + W_{ind}(r, r') \tag{13}$$

$$W_{ind}(r, r') = \int f(r_1)\, \mathrm{d}r_1 \int f(r_2)\, \mathrm{d}r_2\, V(r, r_1)\, [R(1 - VR)^{-1}]_{r_1 r_2}\, V(r_2, r') \tag{14}$$

where we have omitted writing the conserved quantities Q and ω.

The first term on the r. h. s. of (13) is the direct (vacuum) Coulomb interaction between r and r', and W_{ind} is the induced interaction due to the presence of electronic excitations in the solid[7)].

Let us now study the induced dynamical potential W_{ind} in the region outside the solid, so that r and r' are always larger then r_1 and r_2, which are restricted to the region inside the boundary surface. This surface is in fact determined by the condition that the electronic density response function R becomes negligible at the boundary surface. In the *Infinite Barrier Model*, this will also be the location of the barrier.

Therefore, in the integrand in (14):

$$\begin{aligned} V(r, r_1) &= v_Q\, \psi^{>}(r)\, \psi^{<}(r_1) \\ V(r_2, r') &= v_Q\, \psi^{>}(r')\, \psi^{<}(r_2) \end{aligned} \tag{15}$$

and we can completely separate the spatial dependence of the induced potential:

$$W_{ind} = v_Q\, \psi^{>}(r)\, D\, \psi^{>}(r') \tag{16}$$

where $D \equiv D(Q, \omega)$ depends only on the frequency and the conserved quantum numbers Q.

$D(\Omega, \omega)$ plays the role of the propagator, or the boson Green's function, of the dynamically screened induced Coulomb interaction[7)].

In the long wavelength limit this gives the classical propagator of the surface plasmons for each of the geometries in question. $D(Q, \omega)$ will be the key quantity in the further discussion, and its evaluation will provide information about a number of interesting physical quantities, as was already discussed for the planar geometry[7].

The function D, defined by:

$$D(Q, \omega) = v_Q \int f(r_1)\, \mathrm{d}r_1 \int f(r_2)\, \mathrm{d}r_2\, \psi_Q^{\lessgtr}(r_1)\, [R(1 - VR)]^{-1}_{r_1 r_2}\, \psi_Q^{\lessgtr}(r_2) \tag{17}$$

can be evaluated in real space, but it is more convenient to introduce the Fourier transforms with respect to the *broken* variable. We shall again take account of the symmetry of the problem, and expand the quantities in (16) in terms of the functions $h_q(r)$ which are the solutions of the equation:

$$[\Delta_r - \lambda_Q(r)]\, h_q(r) = \lambda_q\, h_q(r) \tag{18}$$

with the boundary condition:

$$h_q(r \text{ on the surface } S) = 0. \tag{19}$$

It is convenient to choose the eigenfunctions that vanish at the boundary surface S because the response function R also has this property.

We note that (18) is in fact the Schrödinger equation for the electronic wave functions in the *Infinite Barrier Model*. These functions are complete and orthonormal:

$$\int h_q^*(r)\, h_{q'}(r)\, f(r)\, \mathrm{d}r = \delta_{qq'}$$

$$\sum_q h_q(r)\, h_q^*(r') = \frac{\delta(r - r')}{f(r)}. \tag{20}$$

The response function can now be expanded:

$$R(r, r'; \omega) = \sum_{qq'} R_{qq'}\, h_{q'}^*(r')\, h_q(r) \tag{21}$$

and the Fourier coefficients are:

$$R_{qq} = \int f(r)\, \mathrm{d}r \int f(r')\, \mathrm{d}r'\, R(r, r')\, h_q^*(r)\, h_q^{\prime}(r'). \tag{22}$$

Inserting the expansion (21) into the definition of the propagator (17), we get:

$$D(Q, \omega) = v_Q \sum_{qq'} \int f(r_1)\, \mathrm{d}r_1 \int f(r_2)\, \mathrm{d}r_2\, \psi^{<}(r_1)\, h_q(r_1)\, R_{qq'}\, h_{q'}(r_2)\, \psi^{<}(r_2) +$$

$$+ v_Q \sum_{\substack{q_1 q_2 \\ q_3 q_4}} \int f(r_1)\, \mathrm{d}r_1 \int f(r_2)\, \mathrm{d}r_2 \int f(r_3)\, \mathrm{d}r_3 \int f(r_4)\, \mathrm{d}r_4 \cdot$$

$$\cdot\, \psi^{<}(r_1)\, h_{q1}^*(r_1)\, R_{q1q2}\, h_{q2}(r_2)\, V(r_2, r_3)\, h_{q3}^*(r_3)\, R_{q3q4}\, h_{q4}(r_4)\, \psi^{<}(r_4) + \ldots. \tag{23}$$

Defining the Fourier coefficients:

$$\psi_q^< = \int f(r)\,\mathrm{d}r\,\psi^<(r)\,h_q^*(r)$$

$$\psi_q^> = \int f(r)\,\mathrm{d}r\,\psi^>(r)\,h_q^*(r) \tag{24}$$

$$V_{qq'} = \int f(r)\,\mathrm{d}r \int f(r')\,\mathrm{d}r'\,V(r, r')\,h_q^*(r)\,h_{q'}(r')$$

we see that (23) becomes:

$$D(Q, \omega) = v_Q\,(\sum_{q_1q_2} \psi_{q1}^< R_{q_1q_2}\,\psi_{q2}^< + \sum_{\substack{q_1q_2\\ q_3q_4}} \psi_{q1}^< R_{q_1q_2}\,V_{q_2q_3}\,R_{q_3q_4}\,\psi_{q4}^< + \ldots). \tag{25}$$

This expression is obviously a matrix sum:

$$D(Q, \omega) = v_Q\,\{\psi^<(R + RVR + RVRVR + \ldots)\,\psi^<\} =$$

$$= v_Q\,\{\psi^< R\,(1 - VR)^{-1}\,\psi^<\} \tag{26}$$

where the curly brackets denote the summation over all internal q-variables.

In Tables 3 and 4 we give the explicit expressions for the Coulomb potentials and their Fourier components in the specific coordinate systems.

3. Generalized Fourier transform of the Coulomb potential

Now we want to show that the generalized Fourier transform $V_{qq'}$ of the Coulomb potential, defined by (24), consists of a diagonal part and a separable part, i. e.:

$$V_{qq'} = b_q\,\delta_{qq'} + c\,\psi_q^*\,\psi_{q'} \tag{27}$$

or in the matrix form

$$V = b\,I + c\,\psi^*|\psi$$

where the bar denotes the break in matrix multiplication.

We first define the function of two variables:

$$F(r, r') = h_q(r)\,h_q^*(r') \tag{28}$$

and use the divergence theorem on the product of $F(r, r')\,V(r, r')$:

$$(\Delta_r F)\,V - (\Delta_r V)\,F \doteq \nabla_r\,[(\nabla_r F)\,V - (\nabla_r V)\,F]. \tag{29}$$

TABLE 3

	Planar	Spherical	Cylindrical
$h_q(r)$	$\left(\frac{2}{a}\right)^{1/2} \sin kz, \ k = \frac{n\pi}{a} (n \in N)$	$\left(\frac{2}{a^3}\right)^{1/2} \frac{j_l\left(x_{ln}\frac{r}{a}\right)}{j_{l+1}(x_{ln})}$	$\frac{\sqrt{2}}{a} \frac{\mathcal{J}_m\left(x_{mn}\frac{\varrho}{a}\right)}{\mathcal{J}_{m+1}(x_{mn})}$
q	k	n	n
λ_q	$\lambda_k = k^2$	$\lambda_n = -\frac{x_{ln}^2}{a^2}$	$\lambda_n = k^2 + \frac{x_{mn}^2}{a^2}$
Ω	L^2	4π	$2L\pi$
$\left.\frac{\mathrm{d}h_q}{\mathrm{d}r}\right\vert_{r=a}$	$\left(\frac{2}{a}\right)^{1/2} k(-1)^{n-1}$	$\left(\frac{2}{a^5}\right)^{1/2} \frac{x_{ln}}{2l+1}\left[l\frac{j_{l-1}(x_{ln})}{j_{l+1}(x_{ln})} - l - 1\right]$	$\frac{\sqrt{2}}{2a^2} x_{mn}\left[\frac{\mathcal{J}_{m-1}(x_{mn})}{\mathcal{J}_{m+1}(x_{mn})} - 1\right]$
b_q	$\frac{4\pi}{k}$	$-\frac{4\pi a^2}{x_{ln}^2}$	$\frac{4\pi}{k^2 + x_{mn}^2/a^2}$
c	$\frac{2\pi^2}{K} e^{-2Ka}$	$\frac{4\pi}{2l+1} a^{-2l-1}$	$4\pi \frac{I_m(ka)}{K_m(ka)}$
Energy E_q	$E_k = \frac{\hbar^2(k^2+K^2)}{2m_e}$	$E_{ln} = \frac{\hbar^2 x_{ln}^2}{2m_e a^2}$	$E_{kmn} = \frac{\hbar^2}{2m_e}\left(k^2 + \frac{x_{mn}^2}{a^2}\right)$
$\psi_q^<$	$\left(\frac{2}{a}\right)^{1/2} \frac{1}{K^2+k^2} [k + e^{-Ka}(-K \sin ka + k \cos ka)]$	$\frac{(2a^{2l+3})^{1/2}}{x_{ln}^2}\left[l\frac{j_{l-1}(x_{ln})}{j_{l+1}(x_{ln})} - l - 1\right]$	$\frac{x_{mn}}{\sqrt{2}\,a} \frac{I_m(ka)}{k^2 + x_{mn}^2/a^2}\left[\frac{\mathcal{J}_{m-1}(x_{mn})}{\mathcal{J}_{m+1}(x_{mn})} - 1\right]$
$V_{qq'}$	$\frac{4\pi}{k}\delta_{kk'} + \frac{2\pi^2}{K}\frac{e^{-Ka}}{e^{Ka}}\psi_k^< \psi_{k'}^<$	$-\frac{4\pi a^2}{x_{ln}^2}\delta_{nn'} + \frac{4\pi a^{-2l-1}}{2l+1}\psi_{ln}^< \psi_{ln'}^<$	$\frac{4\pi}{k^2 + x_{mn}^2/a^2}\delta_{nn'} + 4\pi\frac{I_m(ka)}{K_m(ka)}\psi_{kmn}^< \psi_{kmn'}^<$

TABLE 4

Spherical	$M^{LN}_{lnl'n'} = \int_0^1 r^2 \, \mathrm{d}r \, \frac{j_l(x_{ln} r) j_{l'}(x_{l'n'} r) j_L(x_{LN} r)}{j_{l+1}(x_{ln}) j_{l'+1}(x_{l'n'}) j_{L+1}(x_{LN})}$
Cylindrical	$M^{MN}_{mnn'} = \int_0^1 \varrho \, \mathrm{d}\varrho \, \frac{\mathcal{J}_m(x_{mn}\varrho) \mathcal{J}_{m+M}(x_{m+M,n'}\varrho) \mathcal{J}_M(x_{MN}\varrho)}{\mathcal{J}_{m+1}(x_{mn}) \mathcal{J}_{m+M+1}(x_{m+M,n'}) \mathcal{J}_{M+1}(x_{MN})}$

Integrals appearing in $R_{Qqq'}(\omega)$

$R_{Qqq'}(\omega)$

Planar	$R_{\mathbf{K}kk'} = \frac{1}{8L^2 a^2} \sum_{\mathbf{K}'} \Big\{ \sum_{q=-\infty}^{+\infty} \frac{f(E_{\mathbf{K}',q}) - f(E_{\mathbf{K}'+\mathbf{K},q+k})}{\omega - E_{\mathbf{K}',q} + E_{\mathbf{K}'+\mathbf{K},q+k} + \mathrm{i}\eta} \delta_{kk'} - \frac{f(E_{\mathbf{K}',1/2(k+k')}) - f(E_{\mathbf{K}'+\mathbf{K},1/2(k-k')})}{(E_{\mathbf{K}+\mathbf{K}',1/2(k-k')} - E_{\mathbf{K}',1/2(k+k')} + \omega + \mathrm{i}\eta} - - \frac{f(E_{\mathbf{K}',1/2(k+k')}) - f(E_{\mathbf{K}'+\mathbf{K},1/2(k-k')})}{E_{\mathbf{K}'+\mathbf{K},1/2(k-k')} - E_{\mathbf{K}',1/2(k+k')} + \omega + \mathrm{i}\eta} \Big\}$
Spherical	$R_{LNN'} = \left(\frac{2}{a^3}\right)^3 \sum_{ll'nn'} \frac{f(E_{ln}) - f(E_{l'n'})}{\omega - E_{ln} + E_{l'n'} + \mathrm{i}\eta} \frac{(2l+1)(2l'+1)}{4\pi} \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix}^2 M^{LN}_{lnl'n'} M^{LN'}_{lnl'n'}$
Cylindrical	$R_{KMNN'} = \frac{2}{a^4 \pi^2} \int_{-\infty}^{+\infty} \mathrm{d}k \sum_{mnn'} \frac{f(E_{kmn}) - f(E_{k+K,m+M,n'})}{\omega - E_{kmn} + E_{k+K,m+M,n'} + \mathrm{i}\eta} M^{MN}_{mnn'} M^{MN'}_{mnn'}$

Matrix elements of response function $R_{Qqq'}(\omega)$

Let us evaluate the l. h. s. of (29):

$$(\Delta_r F)\, V - (\Delta_r V)\, F = \lambda_q F(r, r')\, V(r, r') - \frac{4\pi}{f(r)}\, \delta(r - r')\, F(r, r').$$

Integrating this over the solid and using the Poisson equation (9) for V, we obtain:

$$\lambda_q \int \mathrm{d}\Omega\, \mathrm{d}\Omega'\, f(r)\, \mathrm{d}r\, f(r')\, \mathrm{d}r'\, h_q(r)\, h_q^*(r')\, V(r, r') -$$

$$- 4\pi \int \mathrm{d}\Omega\, \mathrm{d}\Omega'\, \delta(r - r')\, F(r, r')\, f(r)\, \mathrm{d}r\, f(r')\, \mathrm{d}r' = \Omega^2 (\lambda_q V_{qq'} - 4\pi\, \delta_{qq'}). \quad (30)$$

The r. h. s. gives, after integration:

$$\Omega^2 \int_0^a f(r)\, \mathrm{d}r \int_0^a f(r)\, \mathrm{d}r'\, \nabla_r [(\nabla_r F)\, V - (\nabla_r V)\, F] =$$

$$= \Omega^2 f(a) \int_0^a f(r')\, \mathrm{d}r' \left[\left.\frac{\mathrm{d}F}{\mathrm{d}r}\right|_{r=a} V(r = a, r') - \left.\frac{\mathrm{d}V(r, r')}{\mathrm{d}r}\right|_{r=a} F(r = a, r') \right].$$

Because of the boundary conditions on $h_q(r)$, $F(r = a, r')$ obviously vanishes, and the r. h. s. reduces to:

$$\Omega^2 f(a) \int f(r')\, \mathrm{d}r'\, v_Q\, \psi^>(a)\, \psi^<(r') \left.\frac{\mathrm{d}h_q(r)}{\mathrm{d}r}\right|_{r=a} h_{q'}^*(r') =$$

$$= \Omega^2 f(a)\, v_Q\, \psi^>(a) \left.\frac{\mathrm{d}h_q(r)}{\mathrm{d}r}\right|_{r=a} \int_0^a f(r')\, \mathrm{d}r'\, \psi^<(r')\, h_{q'}^*(r'). \quad (31)$$

The integral in (31) is readily recognized as the Fourier coefficient $\psi_{q'}^<$. Using the divergence and Gauss' theorems on the product $\psi^<(r)\, h_q^*(r)$ we similarly get: L. h. s.:

$$\int \mathrm{d}\Omega \int_0^a \mathrm{d}r [(\Delta_r \psi^<)\, h_q^* - (\Delta_r h_q)\, \psi^<] = \Omega \int_0^a \mathrm{d}r [\lambda_Q(r)\, \psi^< h_q^* - [\lambda_Q(r) + \lambda_q]\, \psi^< h_q^*] =$$

$$= -\Omega \int_0 f(r)\, \mathrm{d}r\, \lambda_q\, \psi^<(r)\, h_q^*(r) = -\Omega\, \lambda_q\, \psi_q^< \quad (32)$$

R. h. s.:

$$\int \mathrm{d}\Omega \int_0^a f(r)\,\mathrm{d}r\,\nabla_r\,[(\nabla_r\,\psi^<)\,h_q^* - (\nabla_r\,h_q^*)\,\psi^<] = -\,\Omega\,f(a)\,\frac{\mathrm{d}h_q^*(r)}{\mathrm{d}r}\bigg|_{r=a}\psi^<(a). \quad (33)$$

Equating (32) and (33) we get for $\psi_q^<$:

$$\psi_q^< = \frac{f(a)}{\lambda_q}\,\frac{\mathrm{d}h_q^*(r)}{\mathrm{d}r}\bigg|_{r=a}\psi^<(a). \quad (34)$$

From (30) and (31) we find

$$V_{qq'} = \frac{4\pi}{\lambda_q}\,\delta_{qq'} + v_Q\,\frac{f(a)}{\lambda_q}\,\psi^<(a)\frac{\mathrm{d}h_q(r)}{\mathrm{d}r}\bigg|_{r=a}\psi_{q'}^< \quad (35)$$

and replacing the r. h. s. of (34) with $\psi_{q'}^<$ in (35), we finally obtain

$$V_{qq'} = \frac{4\pi}{\lambda_q}\,\delta_{qq'} + v_Q\,\frac{\psi^>(a)}{\psi^<(a)}\,\psi_q^{*<}\,\psi_{q'}^<. \quad (36)$$

So we see that (27) holds if we define:

$$b_q = \frac{4\pi}{\lambda_q} \quad (37)$$

$$c = v_Q\,\frac{\psi^>(a)}{\psi^<(a)}. \quad (38)$$

4. *Evaluation of the propagator D (Q, ω)*

Now we start evaluating the propagator $D(Q,\omega)$ given in (26)

$$D(Q,\omega) = v_Q\,\{\psi^<\,R\,(1 - VR)^{-1}\,\psi^<\}. \quad (26)$$

We define the function:

$$\Phi = \sqrt{c}\,\psi_q^< \quad (39)$$

and insert into (26) so that:

$$D(\mathrm{Q},\omega) = \frac{v_Q}{c}\,\{\Phi\,R\,(1 - b\,R - \Phi\,|\,\Phi\,R)\,\Phi\}.$$

After some matrix manipulations we find:

$$D(Q, \omega) = \frac{v_Q}{c} \left\{ \frac{1}{\left| 1 - \Phi R \frac{1}{1 - b R} \Phi \right|} \Phi R \frac{1}{1 - b R} \Phi \right\}. \tag{40}$$

If we define:

$$A = \Phi R \frac{1}{1 - b R} \Phi \tag{41}$$

the expression (40) becomes:

$$D(Q, \omega) = \frac{v_Q}{c} \frac{\{A\}}{1 - \{A\}}. \tag{42}$$

In this way we have shown that the propagator of electronic excitations can be written in a general form (42) which is much simpler then the equivalent form (17).

There are other advantages of the form (42) with respect to the form (17). The Fourier-transformed quantity A is dependent on the discrete set of q-points, which become farther away from each other, as the particle gets smaller. Thus, this representation is more suitable for the numerical matrix inversion procedure (40), which requires the use of a set of discrete representative points for the matrix $1 - b R$. It can also be argued that in this picture the smaller matrix size is needed, since the contributions of highly oscillating functions for large q to the response function become very small. Thus, although the matrix $R_{qq'}$ is strictly speaking infinite, there exists natural cut-off for larger q's. These arguments are confirmed by our preliminary calculations of D[8].

The quantities needed in the definitions (41) and (42) are given in Tables 3 and 4 for various geometries. The difficult part obviously is to calculate the density response function R and its Fourier transforms. We have done that for the planar geometry elsewhere[9] in the *Random Phase Approximation* and using the wave functions $h_q(r)$ in the *Infinite Barrier Model.* Here we give in Table 4 the results in the other two cases that can be treated in the same general formalism, namely for the spherical and cylindrical solids.

5. *Conclusion*

We have shown that the propagator of electronic excitations near metallic surfaces — which in the long wavelength limit becomes the surface plasmon propagator, can be factorized in such a way that the dielectric function can be deduced easily, whenever the surface of the solid has some overall symmetry which permits the separation of one coordinate dependence from the others.

The knowledge of the generalized response function $D(Q, \omega)$ in (42) corresponding to a certain multipole symmetry, provides the description of the fully screened electrostatic interaction between the metallic particle and the external charge distribution of the same multipolar symmetry. Therefore our present formalism can be applied to a number of cases, involving real transitions, as e. g. in the (electron or atom) scattering experiments, or virtual processes, contributing to the energy shifts of the system, as in the image potential or the van der Waals interaction between two neutral conducting particles (spheres, cylinders, thin films, and their combinations).

Furthermore we can establish the connection between the spectrum of the elementary surface electronic excitations in the metallic particle and the poles of the generalized response function $D(Q, \omega)$, which are defined by:

$$1 - \{A\} = 0.$$

This condition gives the real and imaginary frequencies of the surface plasmon mode of a certain symmetry. The spectral function of the mode of Q-symmetry, defined by:

$$S(Q, \omega) = -\frac{1}{\pi} \operatorname{Im} D(Q, \omega)$$

contains the more or less well defined peak due to the collective (surface plasmon) excitation, but also the continuum of single particle excitations.

For small particles (radius $\leqslant 1$ nm) containing a few hundreds of electrons at the usual metallic density, the surface plasmon frequencies can substantially deviate from their classical values[1] because most of the spectral weight is in the single particle excitations. But, as the particles get larger, the spectra gradually approach their known classical limits[1]. This can also be shown analytically, by taking the limit of (42) for large radii of the sphere or cylinder[8].

It is especially interesting to follow this gradual build-up of the coherent collective excitation at the expense of incoherent single particle excitations, with increasing particle size.

The main difficulty is presented by numerical evaluation of the quantities in (41) and (42), namely, the matrix inversion. It is argued that the form (42) for D is much more convenient for the matrix inversion than the form (17). However, this problem requires further numerical calculations, which will be presented elsewhere[8].

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DINAMIČKO ZASJENJENJE I POVRŠINSKA POBUĐENJA U RAVNINSKIM, SFERNIM I CILINDRIČNIM TIJELIMA I OPĆI FORMALIZAM

ZLATKO PENZAR

Institut za fiziku Sveučilišta, P. p. 304, 41001 *Zagreb*

i

JANKA PETRAVIĆ i MARIJAN ŠUNJIĆ

Fizički odjel, Prirodoslovno-matematički fakultet, P. p. 162, 41001 *Zagreb*

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Kvantnomehanički opis dinamičkog samosuglasnog elektrostatskog međudjelovanja u blizini metalnih površina izveden je za slučaj ravninskih, sfernih i cilindričnih tijela, pomoću rastava koji dozvoljava simetrija problema. Dati su analitički izrazi za odzivnu funkciju u *modelu beskonačne barijere* za jellium u *aproksimaciji slučajnih faza*. Poznavanje propagatora međudjelovanja omogućuje nam proračun i analizu različitih fizičkih svojstava sistema, posebno spektra elementarnih (jednočestičnih i kolektivnih) elektronskih pobuđenja.