Quantum theory of plasmons at metallic spherical surface

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Abstract
In the present work the functional integral technique was applied to the study of the collective excitations of electron gas at a spherical surface. The quanta of these collective excitations are the surface plasmons. Starting from the fundamental principles of the quantum theory, the generating functionals of the many-electron system in a spherical surface were introduced in two different cases, when the electron–electron Coulomb interaction is absent or is present. By means of the Hubbard–Stratonovich transformation, the generating functional of the electron system in the presence of the electron–electron interaction was transformed into that of a scalar field, the effective action of this scalar field was established and the plasmon field was introduced. Then the expression of the Hamiltonian of the quantum field of plasmons was derived and the system of algebraic equations determining the energies of plasmons was established.

Keywords: plasmon, collective excitation, generating functional, canonical quantization
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1. Introduction
Plasmons are quasiparticles exhibiting elementary excitations in the electron gas. They appear as resonances in the collective oscillations of electron gas under the action of a monochromatic electromagnetic field with a suitable frequency called the plasma frequency $\omega_p$. At this frequency the dielectric function $\varepsilon(\omega)$ of the free electron gas vanishes:

$$\varepsilon(\omega_p) = 0.$$

As a rough approximation we can calculate $\varepsilon(\omega)$ by using the classical equation of motion of electrons in a free electron gas under the action of the electrical field of a monochromatic radiation and derive a simple formula for the plasma frequency $\omega_p$. We use the unit system such that the electrostatic potential $V(x)$ created by a charge distribution with the charge density $\rho(x)$ satisfies the Poisson equation

$$\nabla^2 V(x) = -4\pi\rho(x).$$

Then the expression for plasma frequency is determined by the following formula

$$\omega_p^2 = \frac{4\pi^2 N}{M},$$

where $e$ and $M$ are the electron charge and mass, $N$ is the electron density in the electron gas [1]. Rigorous derivation of the formula for the dielectric function $\varepsilon(\omega_p, k)$ depending not only on the frequency $\omega$, but also on the wave vector $k$, required the application of the quantum theory of many-body systems [2–5]. From the condition

$$\varepsilon(\omega_p, k) = 0$$

one then derived the dispersion relation for the plasmon

$$\omega^2 = \omega_p^2 + \frac{6E_F^2}{5M}k^2,$$

where $E_F$ is Fermi level energy of the electron gas [1, 6, 7]. Recently, there has arisen a widespread interest in the study of surface plasmon resonances (SPRs) in nanostructured materials and their interaction processes such as exciton–plasmon coupling [8–20], quantum dot–metal...
nanoparticle interaction [21–23], plasmon-enhanced fluorescence [24–30], plasmon resonance energy transfer etc [31, 32] (see reference [33] for a comprehensive review). In the previous theoretical works on plasmons and their interactions one often used two methods: either one assumed simple phenomenological effective interaction Hamiltonians containing destruction and creation operators of plasmons and other quasiparticles [17], or one wrote the effective Hamiltonian in the form containing the polarization of metallic nanoparticles and used corresponding terms at the plasmon resonance to describe the interaction of plasmon with other quasiparticles [21–23].

In the previous works [34, 35] we have proposed to apply the functional integral technique in quantum field theory for deriving the effective Hamiltonian of plasmons from the fundamental expression of the Hamiltonian of the electron gas. As a clear demonstration of the general method we have considered infinite homogeneous three-dimensional electron gas with Coulomb–electron–electron interaction and derived the results which have been known in conventional theories. In the present work we apply this general method to another electron system—that of interacting electrons at a spherical surface. The quantum field theory of collective excitations in this system will be established. Its quanta are the SPRs in metallic spherical nanoparticles.

Section 2 is devoted to the elaboration of the suitable functional integral technique. The canonical quantization procedure is presented in section 3. As the final result, the explicit expression of the canonical quantum field of SPRs will be established. Section 4 is the conclusion.

2. Functional integral technique

Let us apply the functional integral technique elaborated in the previous works [34, 35] to the system of electrons moving on the surface $S$ of a sphere with the center at the point $O$ and the radius $R$. We chose the center $O$ to be the origin of the coordinate system. The angular coordinates of each point $M$ on the surface $S$ are the same as those of the unit vector

$$n = \frac{OM}{OM},$$

and each function $f$ on the surface $S$ can be considered as a function of $n$ and denoted $f(n)$. The generating functional of the electron system on the surface $S$ contains the surface integrals over this surface. In the calculation of the integral of some function $f(n)$ on the surface $S$ it is convenient to use the following identity

$$\int_S f(n) d\Omega_n = \int f\left(\frac{x}{x}\right) \frac{\delta(x - R)}{R^2} \, dx,$$

with $x = |x|$, and to replace each surface integral by a corresponding volume integral over the whole three-dimensional space with the measure

$$\frac{\delta(x - R)}{R^2} \, dx.$$

Without the loss of generality we can omit the spin index of electron wave function and consider electron as a spinless fermion. Denote $\psi\left(\frac{x}{x}, t\right)$ and $\bar{\psi}\left(\frac{x}{x}, t\right)$, $x = |x|$, the Grassmann variables describing the electron field on spherical surface $S$ and its Hermitian conjugate. Introducing corresponding Grassmann parameters $\eta\left(\frac{x}{x}, t\right)$ and $\bar{\eta}\left(\frac{x}{x}, t\right)$, we have the following expression of the generating functional of the non-interacting electron system on the spherical surface $S$

$$Z^\psi_0[\eta, \bar{\eta}] = \int [D\psi][D\bar{\psi}] \exp \left\{ i \int dt \int \frac{\delta(x - R)}{R^2} \, dx \right\} \times \left\{ \left[ \bar{\eta}\left(\frac{x}{x}, t\right) \psi\left(\frac{x}{x}, t\right) + \bar{\psi}\left(\frac{x}{x}, t\right) \eta\left(\frac{x}{x}, t\right) \right] \right\},$$

$$\times \exp \left\{ i \int dt \int \frac{\delta(x - R)}{R^2} \, dx \bar{\psi}\left(\frac{x}{x}, t\right) \right\} \times \left[ \frac{i}{\partial t} - \bar{H}_0 \right] \psi\left(\frac{x}{x}, t\right) \right\},$$

(1)

where $\bar{H}_0$ is quantum-mechanical Hamiltonian of the free electron on the spherical surface $S$:

$$\bar{H}_0 = \frac{\hat{L}^2}{2MR^2}.$$

\(\hat{L}\) being the vector operator of orbital momentum of electron. Each eigenstate of $\bar{H}_0$ is characterized by the value $l$ of the orbital momentum and the value $m$ of its projection onto the $Oz$ axis, $-l \leq m \leq l$. The corresponding eigenvalue of $\bar{H}_0$ depends only on $l$

$$\bar{H}_0 u_{lm} \left(\frac{x}{x}\right) = E_l u_{lm} \left(\frac{x}{x}\right).$$

Eigenvunctions $u_{lm} \left(\frac{x}{x}\right)$ are the spherical functions

$$u_{lm} \left(\frac{x}{x}\right) = Y_{lm} \left(\frac{x}{x}\right).$$

(4)

The generating functional (1) has following explicit form

$$Z^\psi_0[\eta, \bar{\eta}] = Z^\psi_0[0, 0],$$

$$\times \int dt' \int \frac{\delta(x' - R)}{R^2} \, dx' \bar{\eta}\left(\frac{x}{x}, t\right) \psi\left(\frac{x}{x}, t\right) \right\},$$

(5)

where

$$Z^\psi_0 \left(0, 0\right) = \frac{1}{2\pi} \int [d\omega] \sum_{lm} \eta_{lm} \left(\frac{x}{x}\right) u_{lm} \left(\frac{x}{x}\right) \times \left\{ \frac{1 - n_l}{\omega - E_l + i\omega} + \frac{n_l}{\omega - E_l - i\omega} \right\},$$

(6)

$$n_l$$ being the occupation number in each state with the wave function $u_{lm} \left(\frac{x}{x}\right)$, $-l \leq m \leq l$. By using formula (5), it is straightforward to calculate the average of the products of fermionic fields $\psi\left(\frac{x}{x}, t\right)$ and $\bar{\psi}\left(\frac{x}{x}, t\right)$ at different points $\frac{x}{x}, \frac{x}{x}$.
and different times $t_i$ over all field configurations
\[
\left\langle \psi \left( \frac{x}{x_1}, t_1 \right) \psi \left( \frac{x_2}{x_2}, t_2 \right) \ldots \psi \left( \frac{x_n}{x_n}, t_n \right) \psi \left( \frac{x'_m}{x'_m}, t'_m \right) \cdots \psi \left( \frac{x'_n}{x'_n}, t'_n \right) \right\rangle
\]
\[
= \frac{1}{Z_0^R} \int [D\psi] [D\tilde{\psi}] \psi \left( \frac{x_1}{x_1}, t_1 \right) \cdots \psi \left( \frac{x_n}{x_n}, t_n \right) \times \tilde{\psi} \left( \frac{x'_1}{x'_1}, t'_1 \right) \cdots \tilde{\psi} \left( \frac{x'_m}{x'_m}, t'_m \right) \exp \left\{ i \int dt \right\}
\times \int \delta(x - R) \mathcal{D}x \tilde{\psi} \left( \frac{x}{x}, t \right) \left[ i \frac{\partial}{\partial t} - H_0 \right] \psi \left( \frac{x}{x}, t \right)
\times \int \delta(x' - R) \mathcal{D}x' \tilde{\psi} \left( \frac{x'}{x'}, t' \right) \psi \left( \frac{x'}{x'}, t' \right)
\times \int \delta(x' - R) \mathcal{D}x' \tilde{\psi} \left( \frac{x}{x}, t \right) V(x - x') \psi \left( \frac{x'}{x'}, t' \right)
\times \left( \frac{x'}{x'}, t' \right) \right\}.
\] (8)

In particular, it is easy to derive the Wick theorem expressing the $2n$-point Green function
\[
G \left( \psi \left( \frac{x_1}{x_1}, t_1 \right) \psi \left( \frac{x_2}{x_2}, t_2 \right) \ldots \psi \left( \frac{x_n}{x_n}, t_n \right) \right) = \left\langle \psi \left( \frac{x_1}{x_1}, t_1 \right) \psi \left( \frac{x_2}{x_2}, t_2 \right) \ldots \psi \left( \frac{x_n}{x_n}, t_n \right) \right\rangle
\]
\[
= iS \left( \frac{x}{x}, \frac{x'}{x'}, t - t' \right)
\] (9)

Consider now the interacting electron system, the electron–electron interaction being the Coulomb interaction, and denote $V(x - x')$ the Coulomb energy potential of the system of two electrons located at two points $x$ and $x'$. This interacting electron system has the following functional integral
\[
Z_0^R = \int [D\varphi] \exp \left\{ \frac{i}{2} \int \mathcal{D}x \mathcal{D}x' \frac{\delta(x - R) \mathcal{D}x}{R^2} \tilde{\varphi} \left( \frac{x}{x}, t \right) V(x - x') \varphi \left( \frac{x'}{x'}, t \right) \right\}
\times \left( \frac{x'}{x'}, t' \right) \right\}.
\] (10)

We can linearize the interaction Hamiltonian with respect to the electron density $\varphi \left( \frac{x}{x}, t \right)$ by introducing a scalar field $\varphi \left( \frac{x}{x}, t \right)$ playing the role of the order parameter of the collective excitations of the electron system and using
\[
Z = \sum_{\psi} \int [D\varphi] \exp \left\{ \frac{i}{2} \int \mathcal{D}x \mathcal{D}x' \frac{\delta(x - R) \mathcal{D}x}{R^2} \tilde{\varphi} \left( \frac{x}{x}, t \right) V(x - x') \varphi \left( \frac{x'}{x'}, t \right) \right\}
\times \left( \frac{x'}{x'}, t' \right) \right\}.
\] (11)

Following the method presented in previous work [34, 35] and calculating the functional integral over the Grassmann variables $\varphi \left( \frac{x}{x}, t \right)$ and $\varphi \left( \frac{x}{x}, t \right)$, we derive expression of $Z$ in the form of a functional integral over the scalar function $\varphi \left( \frac{x}{x}, t \right)$
\[
Z = \frac{Z_0^R}{Z_0^R} \int [D\varphi] \exp \left\{ i \mathcal{F}[\varphi] \right\}
\] (12)
with the effective action

\[ I[\varphi] = -\int dt \left[ \frac{\delta(x - R)}{R^2} \right] \delta(x - \varphi(x', t)) \]

\[ \times n \left( \frac{\varphi(x)}{x} \right) V(x - x') \varphi \left( \frac{x'}{x'} \right) t + \frac{1}{2} \int dr \int \delta(x - \varphi(x', t)) \]

\[ + \frac{i}{2} \int dt \int \delta(x_1 - R) \frac{\delta(x - \varphi(x', t))}{R^2} \]

\[ \times \int dr \int \delta(x_2 - x_1) \frac{\delta(x - \varphi(x', t))}{R^2} \]

\[ \times \int dr \int \delta(x_3 - x_2) \frac{\delta(x - \varphi(x', t))}{R^2} \]

\[ \times \int dr \int \delta(x_4 - x_3) \frac{\delta(x - \varphi(x', t))}{R^2} \]

\[ \times S \left( \frac{x_1}{x_1}, \frac{x_2}{x_2}, \frac{x_3}{x_3}; t_1 - t_2 \right) S \left( \frac{x_2}{x_2}, \frac{x_3}{x_3}, \frac{x_4}{x_4}; t_2 - t_3 \right) \]

\[ \times S \left( \frac{x_3}{x_3}, \frac{x_4}{x_4}; t_3 - t_4 \right) S \left( \frac{x_4}{x_4}, \frac{x_1}{x_1}; t_4 - t_1 \right) \]

\[ \times V(x_1 - x_0) V(x_2 - x_1) V(x_3 - x_2) V(x_4 - x_3) \varphi \]

\[ \times \left( \frac{\varphi(x_1)}{x_1}, \frac{\varphi(x_2)}{x_2}, \frac{\varphi(x_3)}{x_3}, \frac{\varphi(x_4)}{x_4}, \ldots \right) \] (16)

\[ n \left( \frac{x}{x} \right) = \lim_{\epsilon \to 0^+} \left( \varphi \left( \frac{x}{x}, t + \epsilon \right) - \varphi \left( \frac{x}{x}, t \right) \right) \]

\[ = -\int dt \lim_{\epsilon \to 0^+} \left( \frac{x}{x} \right) \varphi \left( \frac{x}{x}, t \right) \] (17)

From formula (7) for \( S \left( \frac{x}{x}, \frac{x}{x}; -\epsilon \right) \) it follows that

\[ n \left( \frac{x}{x} \right) = \sum n_i \left[ A \left( \frac{x}{x}, \frac{x}{x}, \frac{x}{x}, \frac{x}{x} \right) \right]^2 . \] (18)

This means that \( n \left( \frac{x}{x} \right) \) is the electron density at the spherical surface.

In the second order approximation with respect to the scalar field \( \varphi \left( \frac{x}{x}, t \right) \) we have following effective action

\[ I_0[\varphi] = -\int dt \delta(x - \varphi(x', t)) \int \delta(x' - \varphi(x', t)) \]

\[ \times \varphi \left( \frac{x}{x}, \frac{x}{x} \right) V(x - x') + \frac{1}{2} \int dt \int \delta \varphi \left( \frac{x}{x}, \frac{x}{x} \right) \]

\[ \times \int \delta(x - \varphi(x', t)) \int \delta(x' - \varphi(x', t)) \]

\[ \times \varphi \left( \frac{x}{x}, t \right) A \left( x, x', t - t' \right) \varphi \left( \frac{x'}{x'}, t' \right) . \] (19)

where

\[ A \left( x, x'; t - t' \right) = V \left( x - x' \right) \delta(t - t') \]

\[ + \int \frac{\delta(y - \varphi(x', t))}{R^2} \int \frac{\delta(y' - \varphi(x', t))}{R^2} \]

\[ \times V(x - y) \Pi \left( \frac{y}{y}, \frac{y}{y}; t - t' \right) V(y' - x') . \] (20)

\[ \Pi \left( \frac{y}{y}, \frac{y}{y}; t - t' \right) = i S \left( \frac{y}{y}, \frac{y}{y}; t - t' \right) \]

\[ \times S \left( \frac{y}{y}, \frac{y}{y}; t - t' \right) . \] (21)

The integral transformation with the kernel \( A \left( x, x'; t - t' \right) \) in the r.h.s. of equation (19) is symmetric in the sense that

\[ A \left( x', x; t' - t \right) = A \left( x, x'; t - t' \right) . \] (22)

From the principle of the extreme action

\[ \frac{\delta I_0[\varphi]}{\delta \varphi \left( \frac{x}{x}, t \right)} = 0 \] (23)

it follows that the values \( \varphi_0 \left( \frac{x}{x}, t \right) \) of the field \( \varphi \left( \frac{x}{x}, t \right) \) corresponding to the extreme of the action \( I_0[\varphi] \) must be the solution of the integral equation

\[ \int dt' \int \frac{\delta(x' - R)}{R^2} \int \frac{\delta(x' - x)}{R^2} \]

\[ \times A \left( x, x', t - t' \right) \varphi \left( \frac{x}{x}, t' \right) \]

\[ = \int \frac{\delta(x' - R)}{R^2} \int \frac{\delta(x - x)}{R^2} V \left( x - x' \right) \varphi \left( \frac{x}{x}, t' \right) . \] (24)
Let us verify that the solution \( \varphi_0 \left( \frac{x}{t}, t \right) \) of this equation is time-independent

\[
\varphi_0 \left( \frac{x}{t}, t \right) = \varphi_0 \left( \frac{x}{t} \right)
\]  
(25)

For this purpose we perform the Fourier transformation of the functions \( \varphi_0 \left( \frac{x}{t}, t \right) \) and \( A(x, x'; t - t') \) with respect to the time variable

\[
\varphi_0 \left( \frac{x}{t}, t \right) = \frac{1}{2\pi} \int \! d\omega e^{-i\omega t} \varphi_0 \left( \frac{x}{\omega} \right)
\]  
(26)

\[
A(x, x'; t - t') = \frac{1}{2\pi} \int \! d\omega e^{-i\omega (t - t')} A(x, x'; \omega)
\]  
(27)

In terms of the Fourier transform \( \varphi_0 \left( \frac{x}{\omega}, \omega \right) \) and \( \tilde{A}(x, x'; \omega) \) the integral equation (24) becomes

\[
\begin{aligned}
\frac{1}{2\pi} \int \! d\omega e^{-i\omega t} \int \! \frac{\delta(x' - R)}{R^2} \, d\omega' \tilde{A}(x, x'; \omega) \varphi_0 \left( \frac{x'}{\omega}, \omega \right) & = \int \! \frac{\delta(x' - R)}{R^2} \, d\omega' V(x - x') n \left( \frac{x'}{\omega} \right).
\end{aligned}
\]  
(28)

This equation shows that \( \varphi_0 \left( \frac{x}{\omega}, \omega \right) \) must be proportional to \( \delta(\omega) \) and therefore \( \varphi_0 \left( \frac{x}{t}, t \right) \) does not depend on \( t \), equation (25). It describes the background state of the electron system on the spherical surface. The difference

\[
\zeta \left( \frac{x}{t}, t \right) = \varphi \left( \frac{x}{t}, t \right) - \varphi_0 \left( \frac{x}{t} \right)
\]  
(29)

is the field of the fluctuation of \( \varphi \left( \frac{x}{t}, t \right) \) around the background field \( \varphi_0 \left( \frac{x}{t} \right) \). In term of \( \varphi_0 \left( \frac{x}{t} \right) \) and \( \zeta \left( \frac{x}{t}, t \right) \) the effective action \( I_0[\varphi] \) has following expression

\[
\begin{aligned}
I_0[\varphi] & = I_0[\varphi_0] + \frac{1}{2} \int \! dt \int \! dt' \int \! \frac{\delta(x - R)}{R^2} \, dx \\
& \times \int \! \frac{\delta(x' - R)}{R^2} \, dx' \zeta \left( \frac{x}{t}, t \right) \\
& \times A(x, x'; t - t') \zeta \left( \frac{x'}{t}, t' \right).
\end{aligned}
\]  
(30)

3. Canonical quantization procedure

In order to establish the relationship between the fluctuation field \( \zeta \left( \frac{x}{t}, t \right) \) of the order parameter \( \varphi \left( \frac{x}{t}, t \right) \) and its canonical coordinates and momenta as those of a classical physical system, we must study the explicit expression of the term quadratic with respect to the fluctuation field \( \zeta \left( \frac{x}{t}, t \right) \) in the effective action (30). Together with the Fourier transformation (27) of \( A(x, x'; t - t') \) we use also that of \( \zeta \left( \frac{x}{t}, t \right) \)

\[
\zeta \left( \frac{x}{t}, t \right) = \frac{1}{2\pi} \int \! d\omega' e^{-i\omega t} \zeta \left( \frac{x}{\omega'}, \omega' \right)
\]  
(31)

and obtain

\[
I_0[\varphi] = I_0[\varphi_0] + I_{\text{eff}}[\zeta],
\]  
(32)

\[
I_{\text{eff}}[\zeta] = \frac{1}{4\pi} \int \! d\omega \int \! \frac{\delta(x - R)}{R^2} \, dx \int \! \frac{\delta(x' - R)}{R^2} \, dx' \\
\times \int \! d\omega' \zeta \left( \frac{x}{\omega'}, \omega' \right) \tilde{A}(x, x'; \omega) \zeta \left( \frac{x'}{\omega}, \omega \right).
\]  
(33)

Introduce also the Fourier transformation of \( S \left( \frac{x}{t}, \frac{x'}{t}; t - t' \right) \) and \( \Pi \left( \frac{x}{t}, \frac{x'}{t}; t - t' \right) \):

\[
\begin{aligned}
S \left( \frac{x}{t}, \frac{x'}{t}; t - t' \right) & = \frac{1}{2\pi} \int \! d\omega e^{-i\omega t} S \left( \frac{x}{t}, \frac{x'}{t}; \omega \right), \\
\Pi \left( \frac{x}{t}, \frac{x'}{t}; t - t' \right) & = \frac{1}{2\pi} \int \! d\omega e^{-i\omega t} \tilde{S} \left( \frac{x}{t}, \frac{x'}{t}; \omega \right).
\end{aligned}
\]  
(34)

(35)

From the definition (21) of \( \Pi \left( \frac{x}{t}, \frac{x'}{t}; t - t' \right) \) it follows that

\[
\begin{aligned}
\Pi \left( \frac{x}{t}, \frac{x'}{t}; \omega \right) & = \frac{i}{2\pi} \int \! d\varepsilon \tilde{S} \left( \frac{x}{t}, \frac{x'}{t}; \varepsilon + \omega \right) \\
& \times S \left( \frac{x}{t}, \frac{x'}{t}; \varepsilon \right).
\end{aligned}
\]  
(36)

According to the expression (7) of the function \( S \left( \frac{x}{t}, \frac{x'}{t}; t - t' \right) \) and the equality (4) we have

\[
\begin{aligned}
S \left( \frac{x}{t}, \frac{x'}{t}; \omega \right) & = \sum_{lm} Y_{lm} \left( \frac{x}{t} \right) Y_{lm}^* \left( \frac{x'}{t} \right) \\
& \times \left[ \frac{1 - n_l}{\omega - E_l + io} + \frac{n_l}{\omega - E_l - io} \right].
\end{aligned}
\]  
(37)

Substituting expression of the form (37) into the rhs of formula (36), we obtain

\[
\begin{aligned}
\Pi \left( \frac{x}{t}, \frac{x'}{t}; \omega \right) & = \sum_{lm} \sum_{lm'} Y_{lm} \left( \frac{x}{t} \right) Y_{lm}^* \left( \frac{x'}{t} \right) \\
& \times \tilde{\Pi}_{ll'}(\omega) Y_{lm} \left( \frac{x'}{t} \right) Y_{lm}^* \left( \frac{x}{t} \right).
\end{aligned}
\]  
(38)

where

\[
\tilde{\Pi}_{ll'}(\omega) = \frac{(1 - n_l) n_{l'} - (1 - n_{l'}) n_l}{\omega + E_l - E_{l'}}.
\]  
(39)

Using expressions (38) and (39), from the definition (20) of \( A(x, x'; t - t') \), we obtain the following expression of the
Fourier transform $\tilde{A}(x, x'; \omega)$:

$$
\tilde{A}(x, x'; \omega) = V(x - x') + \int \frac{\delta(y - R)}{R^2} \, dy
$$

$$
\int \frac{\delta(y' - R)}{R^2} \, dy' V(x - y) \sum_{lm} Y_m(l) Y_{-m}(l) Y_{-m}(l) Y_{-m}(l)
$$

$$
\left( \frac{y'}{y} \right) \frac{\tilde{\Pi}_L(\omega)}{\tilde{Y}_{-m}(l)} \left( \frac{y'}{y} \right) \frac{\tilde{Y}_{-m}(l)}{\tilde{Y}_{-m}(l)} V(y' - x').
$$

Introducing the Fourier transformation of the Coulomb potential

$$
V(x - x') = \frac{1}{(2\pi)^3} \int dk \; e^{ik(x-x')} \tilde{\nabla}(k),
$$

with $k = |k|$, and using following formula

$$
e^{ikx} = 4\pi \sum_{lm} (i)^l g_l(kx) Y_m(l) Y_{-m}(l) Y_{-m}(l),
$$

with

$$
g_l(kx) = \frac{\pi}{\sqrt{2kx}} J_{\frac{l}{2}}(kx),
$$

$J_p(z)$ being the Bessel functions, we represent the Coulomb potential in the form

$$
V(x - x') = \sum_{lm} Y_m(l) V_l(x, x') Y_{-m}(l),
$$

where

$$
V_l(x, x') = \frac{2}{\pi} \int k^2 \, dk \; \tilde{\nabla}(k) g_l(kx) g_l(kx').
$$

The Fourier transform $\zeta(x, \omega)$ of the scalar field $\zeta(x, t)$ can be also expanded in terms of the spherical functions $Y_m(l)$:

$$
\zeta(x, \omega) = \sum_{lm} Y_m(l) \zeta_{lm}(\omega).
$$

Substituting the expansions (40), (44) and (46) into the rhs of formula (33) and setting

$$
\tilde{\sigma}_{lm}(\omega) = \sqrt{V_l} \zeta_{lm}(\omega),
$$

$$
V_l = \int x^2 \, dx \int y^2 \, dy \; V_l(x, y),
$$

we obtain the effective action $I_{pl}[\sigma]$ of the scalar field $\sigma$ with the components $\tilde{\sigma}_{lm}$:

$$
I_{pl}[\sigma] = \frac{1}{4\pi} \int d\omega \sum_{LM,LM'} \tilde{\sigma}_{LM}(\omega)^* \delta_{LL'} \delta_{MM'}
+ \sqrt{V_L} U_{LM,LM'}(\omega) \sqrt{V_{L'}} \tilde{\sigma}_{LM'}(\omega),
$$

and

$$
U_{LM,LM'}(\omega) = \sum_{lm} \sum_{LM} \left( C_{LM,LM'}^{lm} \tilde{Y}_{lm}(l) \tilde{Y}_{lm}(l) \tilde{Y}_{lm}(l) \tilde{Y}_{lm}(l). \right.
$$

Constants $C_{LM,LM'}^{lm}$ in the expression (50) are the Clebsch–Gordan coefficients. From the expression (49) of the effective action it follows the system of algebraic equations determining the scalar field $\sigma(x, t)$ with the components $\tilde{\sigma}_{LM}(\omega)$:

$$
\sum_{LM'} \left\{ \delta_{LL'} \delta_{MM'} + \sqrt{V_L} U_{LM,LM'}(\omega) \sqrt{V_{L'}} \right\} \tilde{\sigma}_{LM'}(\omega) = 0. \quad (51)
$$

This system of linear algebraic equations has a nontrivial solution if and only if its determinant vanishes

$$
det \left\{ \delta_{LL'} \delta_{MM'} + \sqrt{V_L} U_{LM,LM'}(\omega) \sqrt{V_{L'}} \right\} = 0. \quad (52)
$$

By solving equation (52) we obtain the discrete spectrum of energies (angular frequencies) $\omega_l$ of plasmons.

4. Conclusion

In the present work we have elaborated the quantum theory of plasmons at the metallic spherical surface by means of the functional integral technique. Starting from the principles of electrodynamics and quantum mechanics we have established the effective action of the scalar field describing the quantum fluctuation of the electron density in the harmonic approximation. Then we have derived the system of algebraic equations determining the discrete spectrum of energies (angular frequencies) of the surface plasmons. The solution of this system of equations requires the application of suitable simulation calculations.

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