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Quantum plasmonics for next-generation optical and sensing technologies

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ABSTRACT

Classical plasmonics has mostly focused on structures characterized by large dimension, for which the quantum-mechanical effects have nearly no impact. However, recent advances in technology, especially on miniaturized plasmonics devices at nanoscale, have made it possible to imagine experimental applications of plasmons where the quantum nature of free charge carriers play an important role. Therefore, it is necessary to use quantum mechanics to model the transport of charge carriers in solid state plasma nanostructures. Here, a non-local quantum model of permittivity is presented by applying the Wigner equation with collision term in the kinetic theory of solid state plasmas where the dominant electron scattering mechanism is the electron-lattice collisions. The surface plasmon resonance of ultra-small nanoparticles is investigated using this non-local quantum permittivity and its dispersion relation is obtained. The successful application of this theory in ultra-small plasmonics structures such as surface plasmon polariton waveguides, doped semiconductors, graphene, the metamaterials composed of alternating layers of metal and dielectric, and the quantum droplets is anticipated.

Keywords: Quantum plasmonics, non-local effects, surface plasmons, metallic nanoparticles

1. INTRODUCTION

The recent advances in nanophotonics have made it possible to squeeze light on miniaturized metallic devices as the compact photon finally approaches to the order of the electron wave function (EWF) [1,2]. The light-matter interaction in ultra-small plasmonic structures (USPS) is an interesting phenomenon and the new physical fundamentals are expected in the new field which called quantum plasmonics [3] and important technological advances become visible. Such phenomena have so far been poorly understood, particularly on the experimental front, while classical case have mostly focused on structures characterized by no size dependence. When the light is shrunk to USPS, there is no way to describe collective electron oscillations using classical Drude model

$$\varepsilon(\omega) = \varepsilon_{IB} + \chi_C(\omega), \quad (1)$$

where $\chi_C(\omega) = -\omega_p^2 / (\omega(\omega + i\nu))$ is the classical susceptibility of electrons, ω is the photon frequency, ω_p is the plasma frequency of metal, ν is the collision frequency of electrons in metal, and ε_{IB} is the corrective interband term [4]. In this range, the quantum-mechanical effects start dominating and become relevant with changing the plasmons oscillation frequency. Therefore, a quantum model of metal permittivity is required to understanding this size-dependent changing.

The behaviour of plasmon resonances of individual silver metallic nanoparticles has been investigated by a local quantum model of susceptibility known as Lorentz-Drude model [5]

$$\chi_{LD}(\omega) = \omega_p^2 \sum_i \sum_j \frac{S_{if}}{\omega_{if} - \omega^2 - i\gamma\omega}, \quad (2)$$

where the sum is taken over all initial and final states of the electrons. Here ω_{if} is the frequency of the transitions from the occupied to excited states, S_{if} is the oscillator strength terms collectively sum to unity, γ is the scattering frequency

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of electrons. This model has provided a straightforward method of understanding the size-dependent changing in the resonance of plasmonic waves in USPS [5,6], however, the infinite potential barrier model and the only electron-lattice interactions simplifying assumptions were necessary to make this model. While, the barrier may be have in a more finite model with spill-out effects in experimental systems that involve structures with quantum size [7]. Also, the dominant mode of plasmon relaxation in USPS is the Landau damping process [8], which leads to the formation of interaction between energetic EWF with plasmonic waves. On the other hand, the plasmon resonance can occur at certain ‘magic number’ collections of atoms even down to the smallest cluster sizes [9]. In such systems, quantum effects such as nonlocality [10] cannot be ignored because they produce the spatial localization of EWF, which is extended due to the sizeable plasmon-frequency shifts, and a non-local model of permittivity is needed for plasmon excitation.

The semi-classical permittivity, as a non-local model, has been studied in degenerate plasma using the solution of kinetic equations for the Boltzmann system [11]. In fact, this semi-classical model was obtained by applying the Fermi distribution function as a quantum distribution of electrons in Boltzmann equation which is a classical kinetic equation.

At the limit $kV_F \ll \omega$, the semi-classical susceptibility reduces to the simple form

$$\chi_{SC}(\omega, k) = -\frac{\omega_p^2}{\omega^2 + i\nu\omega - \frac{3}{5}k^2V_F^2}, \quad (3)$$

where k is the wave number of electrons and V_F is the Fermi velocity of the electrons in metals. This simple semi-classical generalized non-local optical response theory has been investigation for optical properties of individual metallic particles [12]. The simple model (3) is valid for nanoparticles with quantum size down to 5 nm in diameter for metals. In realistic plasmonic nanostructures, this minimum size depends on actual dimension. For smaller structures, electrons will move between the surfaces of the structure, and surface scattering might be important. Although the plasmon excitations has been extensively studied by above permittivity models, a fully quantum model of permittivity requires further investigations in USPS (where only just a few electrons are available).

Here, the non-local quantum (NLQ) model of permittivity is theoretically investigated by applying the Wigner equation with the collision term in the kinetic theory of quantum plasmas. This theory is applied for the modelling of plasmonic waves in USPS that shows how the quantum effects dominate in such structures.

2. PHYSICAL REGIMES IN PLASMA SOLID STATE

The typical relation between parameter scales in classical or quantum plasma solid state can be represented by a number of dimensionless parameters which allow us to discriminate between different physical regimes. The parameters that define a plasma as classical or quantum, and if it collisionless or collisional, are [13]

$$\zeta = \frac{1}{2} \left(3\pi^2 \right)^{2/3} \frac{\lambda_B^2}{d^2}, \quad g_C = \frac{e^2}{k_B T \epsilon_0 d}, \quad \text{and} \quad g_Q = \frac{2}{(3\pi^2)^{2/3}} \frac{e^2 m d}{\hbar^2 \epsilon_0}, \quad (4)$$

where $\lambda_B = \hbar / \sqrt{mk_B T}$ is the thermal de Broglie wavelength of electrons that roughly represents the spatial extension of EWF due to quantum uncertainty, m is the mass of the electron, k_B is the Boltzmann’s constant, T is the temperature, $d = N^{-1/3}$ is the average interparticle distance, N is the density number of electrons, e is the electron charge, and ϵ_0 is the electric permittivity of vacuum. These three parameters determine whether the plasma is classical or quantum, and, in either case, whether it is collisional or collisionless:

1. In solid state plasmas, quantum effects become important when $\zeta \geq 1$. One can postulate that quantum effects play a significant role when λ_B is similar to or larger than the average interparticle distance d . While, in classical case, λ_B is small and particles can be considered as point-like; therefore, there is no quantum interference and no overlapping of EWF in classical solid state.

2. When the expression g_C (which is known as the classical coupling parameter) is small, the plasma is classical dominated by thermal effects and is collisionless. On the other hand, the binary collisions cannot be neglected when $g_C \sim 1$ or larger, and the classical plasma is collisional. In other words, classical plasmas are collisional at high densities and low temperatures.
3. The quantum plasma is collisionless when the quantum coupling parameter g_Q is small. It became visible that the quantum plasma is 'more collective' at larger densities, opposite to the classical plasmas. It can be understood by invoking Pauli's exclusion principle, which two electrons cannot occupy the same quantum state. If we add one more electron to the quantum plasma, it will necessarily assume a higher energy state, since all lower energy states are occupied by other electrons. Therefore, the average kinetic energy of electrons is increased by rising the density, which reduces the value of g_Q .

The straight lines corresponding to $\zeta = g_C = g_Q = 1$ are plotted in Fig. 1 on a T - N plane diagram divided into four regions, identified by the kinetic models that are relevant to each regime. As seen, for collisional classical plasmas (e.g., weakly ionized plasmas, electrolytes, and low-doped semiconductors), the electron distribution function is governed by Maxwell-Boltzmann distribution [14]. For collisional quantum plasmas, such as high-doped semiconductors, graphene, diamond, and metals on the other hand, Fermi-Dirac distribution quantifies the electron distribution function and the Wigner equation with collisions represents the appropriate model for kinetic equation. In plasmonic nanostructures, in fact, the interaction of electrons with the external environment should be taken into account and cannot be ignored. g_Q for such nanostructures is larger than unity; therefore, electron collisions (e.g., electron-electron and electron-lattice collisions) are as important as collective effects.

NON-LOCAL QUANTUM MODEL OF PERMITIVITY FOR PLASMONIC NANOSTRUCTURES

Investigating the optical properties of plasmonic nanostructures requires solving the kinetic and Maxwell's equations to describe the excitation of electrons by light. Also, with considering the density of electronic states in these structures at room temperature, the quantum effects cannot be ignored [13], since quantum effects arise from the quantum nature of electrons and the dynamic response of these structures to self-consistent electromagnetic fields. Therefore, the kinetic equation for the distribution function f in nanostructures with ion background can be governed by the Wigner equation with the collision term

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} - \frac{iem^3}{(2\pi)^3 \hbar^4} \iint d^3s d^3v' \exp \left[i \frac{m}{\hbar} (\mathbf{v} - \mathbf{v}') \cdot \mathbf{s} \right] \left[\phi \left(\mathbf{r} + \frac{\mathbf{s}}{2}, t \right) - \phi \left(\mathbf{r} - \frac{\mathbf{s}}{2}, t \right) \right] f(\mathbf{v}') = C(f), \quad (5)$$

Figure 1. Plasma diagram in the T - N plane.

where $\mathbf{v}$ is velocity vector of electron, ϕ is the potential at the position of the electron $\mathbf{r}$, $\mathbf{s}$ is the space over which the integral is taken, t is time, and $C(f)$ describes the rate of change in distribution function (the collision integral). We model it by a relaxation term of the Bhatnagar-Gross-Krook type [15] as $C(f) = -\nu(f - f_0)$, where f_0 is the distribution function in the steady state and ν is the velocity independent and constant collision frequency describing the electron-lattice collisions, which occurs due to lattice vibrations (phonons). We ignore electron-electron collisions in our model, since the electron-electron interaction lifetime is in order 10^{-10} s which is much larger than the typical time scale for the electron-lattice collisions 10^{-14} s [13]. The solution of Eq. (5) in the stationary state, f_0 , is the equilibrium Fermi distribution function [13,15].

We introduce a perturbed field into the equilibrium of the quantum plasma as $\delta f = f - f_0$, where $\delta f \ll f_0$ and also δf and ϕ are proportional to $\exp(-i\omega t + i\mathbf{k} \cdot \mathbf{r})$. Assuming that the associated fields are small and by applying the Fourier transform to Eq. (5), we obtain the first-order linear kinetic equation [16]. Substituting the first-order linear kinetic equation into Maxwell's equations and following the standard procedure (see ref. [16]), one finally obtains the k -dependent NLQ model of susceptibility for plasmonic structures as

$$\chi_{NLQ}(E_\omega, E) = \frac{3E_p^2}{16EE_F} \frac{\left\{ 2 - \frac{1}{E\sqrt{EE_F}} \left[EE_F - \left(\frac{E_\omega + iE_v + E}{2} \right)^2 \right] \ln \left| \frac{E_\omega + iE_v - 2\sqrt{EE_F} + E}{E_\omega + iE_v + 2\sqrt{EE_F} + E} \right| \right\}}{\left\{ + \frac{1}{E\sqrt{EE_F}} \left[EE_F - \left(\frac{E_\omega + iE_v - E}{2} \right)^2 \right] \ln \left| \frac{E_\omega + iE_v - 2\sqrt{EE_F} - E}{E_\omega + iE_v + 2\sqrt{EE_F} - E} \right| \right\}}, \quad (6)$$

where $E_\omega = \hbar\omega$ is the photon energy, $E_p = \hbar\omega_p$ is the plasmon energy, E_F is the Fermi energy, $E_v = \hbar\nu$ is the collision energy of electrons, and $E = \hbar^2 k^2 / 2m$ is the EWF energy. In the limit of $E \rightarrow 0$, NLQ model (6) reduces to the classical Drude model (1).

Here we introduce the parameter $\eta = \sqrt{EE_F} / E_\omega$ which leads to spatial quantum non-locality in plasmonic nanostructures. At small values of this parameter ($\eta \ll 1$), NLQ model (6) reduce to the simple non-local quantum (SNLQ) model which can be written as

$$\chi_{SNLQ}(E_\omega, E) = - \frac{E_p^2}{E_\omega^2 + iE_\omega E_v - 2.4EE_F - (1 + \alpha)E^2}, \quad (7)$$

where $\alpha = (192/175)E_F^2/E_p^2$ is in the order of ~ 0.4 for a typical metal, while it is much smaller for doped semiconductors and can safely be dropped compared with unity in Eq. (7).

The NQL permittivity of bulk silver is plotted in Fig. 2. As can be seen, NLQ model approaches to the classical Drude model, specially at optical and ultraviolet range, when E decreases. One can also see the difference between NLQ and SNLQ models at high EWF energy E and low photon energy E_ω , due to change in non-local parameter η .

There are two different resonance frequencies for bulk plasmon ($\text{Re}[\varepsilon_{IB} + \chi(E_\omega, E)] = 0$). The low-resonance frequency mode is in the infrared and terahertz ranges, while the high-resonance frequency mode is in the visible and ultraviolet range. The imaginary part of NLQ shows that the low-resonance frequency mode of plasmons cannot propagate, because of strong absorption, compared to the high-resonance frequency mode with less absorption. In the quantum case, NLQ is strongly depends on the EWF energy E and Bulk plasmon resonance occurs at higher energies as E increases.

Figure 2. Real and imaginary parts of bulk silver permittivity with $E_F = 5.57$ eV, $E_p = 9.01$ eV, and $E_v = 16$ meV at various EWF energies (the corrective interband term ε_{IB} [4] included). Solid lines: corresponding to NLQ model; dashed lines: corresponding to SNLQ model; dotted line: classical Drude model (1).

APPLICATIONS

Quantum metallic nanoparticles (i.e., less than 10 nm in diameter [5]) may revolutionize the field of nanophotonics. In this range, the quantum effects play an important role, become relevant with changing the plasmons oscillation frequency. Here the dispersion relation of surface plasmon resonance is investigated by NLQ model in silver nanoparticle with diameters from low-nanometer to atomic size.

The resonance energy obtained by NLQ model in Fig. 3a is showing excellent agreement with the experimental data [5] for both surface and bulk plasmons. One can see the strong blueshift of the surface plasmons resonance due to quantum effects such as non-locality at diameters less than 10 nm. This shift is caused by higher-order conduction electron transitions from deeper within the Fermi sphere to immediately outside it. They create additional spectral resonance in quantum size and this additional energy increases for smaller particles because their oscillator strengths are relatively greater than those of larger spheres.

The oscillations of EWF can be attributed to the stronger wave-like properties and plasmon propagation length becomes comparable to the size of quantum well (nanoparticle) at low-nanometer scale. So, there is a possibility of existing higher resonance energy level and the probability of finding EWF outside the quantum well (see Fig. 1b). Therefore, one needs to solve the Schrodinger equation for the finite potential well as in the experimental systems that involve colloidal particles with stabilizing ligands.

Figure 3. **a)** The absorption efficiency of silver nanoparticles obtained by NLQ model at the first energy level based on the solution of infinite quantum well; in inset compared to experimental data [5] (the black points corresponding to surface plasmon resonance and grey points corresponding to bulk plasmon resonance); the grey lines corresponding to bulk plasmon resonance; and classical plasmon resonance theory, obtained from classical Drude model (1), is given by the dashed lines. **b)** The schematic of non-local radial EWF at low-nanometer diameter (the black ring represents the diameter of quantum well, D). **c)** The spectrum energy of surface plasmons (and the energy of EWF in inset) at the first energy level based on the solution of both infinite and finite quantum well.

Figure 1c shows that there is no surface plasmon resonance of particles with diameters under 1 nm based on the solution of infinite quantum well, because of strong damping in metals, while the energy spectrum approaches close to the Fermi energy of electrons at atomic sizes in the solution of the finite quantum well. In this range, the electrons are sufficiently hot (i.e., around 1 eV) and Interesting effects such as partial lattice disassembly and warm dense matter may be induced by non-equilibrium and electron delocalization.

The advantage of NLQ model, compared to the previous studies [5,12] on quantum surface plasmon resonance of individual metallic nanoparticle, is shown in table 1. Applications NLQ model can be successfully anticipated in other USPS such as plasmonic nanoparticles, surface plasmon polariton waveguides, doped semiconductors, graphene, metamaterials composed of alternating layers of metal and dielectric, quantum droplets, etc.

Table 1. Comparison of NQP with previous theories in quantum effects on surface plasmon resonance in nanoparticles.

works	Permittivity model	Quantum well	Validity of size	Detail of EWF
Scholl et al. [5]	Local quantum	Infinite	Down to 2 nm	No
Mortensen et al. [12]	Non-local semi-classic	No quantum well	Down to 4 nm	No
NLQ model	Non-local quantum	Infinite and finite	Atomic size	Yes

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