Numerical Analysis of Quantum Plasmonic Metasuraface by Time-Dependent Density Functional Theory

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Abstract—**We theoretically investigate optical properties of a quantum plasmonic metasurface composed of metallic nanoparticles that are arranged in a two-dimensional matrix form with a sub-nanometer gap. We employ a time-dependent density functional theory approach to calculate optical properties of the metasurface. They show characteristic features at gap distance smaller than 0.4 nm due to the tunneling currents that flow through the gaps.**

I. Introduction

A plasmonic metasurface in which metallic nano-objects are periodically placed on a plane has been attracting substantial attention in terms of its exotic optical characteristics [1]. Although investigations have been devoted mostly to metasurfaces with periodic structures of sub-wavelength length, there have been reported recent experimental studies of periodic structures with much smaller gap distances between nano-objects, reaching to *sub-nanometer* [2]. In isolated systems with a sub-nanometer gap such as a metallic nanodimer, it has been revealed that there appears substantial differences between theoretical descriptions using classical and quantum theories [3]. The difference becomes substantial for gap distances less than 0.4 nm [4] where the quantum tunneling across the gap becomes sizable. In the studies of metasurfaces, however, to the best of our knowledge, there have not been any theoretical reports discussing quantum effects, although measurements have been carried out for the metasurface with the gap distance as small as 0.45nm [2].

In this paper, we theoretically and numerically investigate the quantum plasmonic metasurface with sub-nanometer gaps. To take into account quantum mechanical effects in the analysis, we employ time-dependent density functional theory (TDDFT) treating the constituent nano-particles by a jellium model. We will show transmission, reflection, and absorption rates of the metasurface to elucidate quantum effects for the optical properties. Our results show that there appear qualitative differences between the classical and the quantum results for systems with the gap distance less than 0.4 nm, which is consistent with the previous study dealing with isolated systems.

II. Theory

In Fig. 1, we illustrate the metasurface of our calculation and define parameters that characterize the geometry. Parameters a, d, and l, denote the diameter of the spheres, the gap distance, and the length of the period, respectively. We treat the constituent nano-particles by a jellium model with the Wigner-Seitz radius of 4.01 Bohr that correspond to the valence electron density of Na. We set the diameter of the jellium sphere as $a = 3.1$ nm. This jellium nanosphere accommodates 398 electrons with a closed shell configuration. The jellium model is known to provide a reasonable
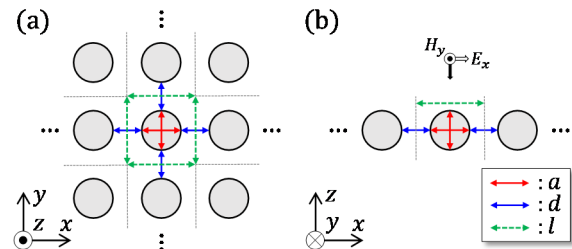

Fig. 1. Schematic illustration of the studied metasurface consisting of jellium nanospheres. (a) Top view. (b) Side view.

description for metallic nanoparticles [3] with a moderate computational costs.

Since the thickness of the metasurface is much smaller than typical optical wavelength, we may regard the metasurface as a two-dimensional material. Then, optical properties of the metasurface can be described using the two-dimensional conductivity as defined below.

We consider that a uniform electric field $\mathbf{E}(t)$ is applied to the metasurface and an electric current density $\mathbf{j}(\mathbf{r}, t)$ is induced in the metasurface. From the induced current, we define the macroscopic 2D electric current density $\mathbf{J}_{2D}(t)$ as

$$\mathbf{J}_{2D}(t) = \int_{cell} \frac{dxdy}{l^2} \int dz \, \mathbf{j}(\mathbf{r}, t). \tag{1}$$

In linear response regime, the two-dimensional conductivity σ_{2D} connects the 2D electric current density and the applied electric field,

$$\mathbf{J}_{2D}(t) = \int^t dt' \, \sigma_{2D}(t - t')\mathbf{E}(t'). \tag{2}$$

Using the Fourier transform of the 2D conductivity $\sigma_{2D}(\omega)$ we can obtain the transmission, reflection, and the absorption rates of the metasurface, T, R, A, as follows [5].

$$T(\omega) = \frac{1}{|1 + 2\pi\sigma_{2D}(\omega)/c|^2}, R(\omega) = \left|\frac{2\pi\sigma_{2D}(\omega)/c}{1 + 2\pi\sigma_{2D}(\omega)/c}\right|^2 \tag{3}$$

$$A(\omega) = 1 - T(\omega) - R(\omega) \tag{4}$$

Next, we consider a microscopic calculation of the 2D conductivity. In classical electromagnetism, we can easily extract the 2D conductivity once we specify the geometry of the metasurface and the medium property using, for example, the Drude model. In quantum description, we carry out electron dynamics calculations in the metasurface based on TDDFT. We solve the following time-dependent Kohn–Sham equation in real space and real time,

$$i\hbar \frac{\partial u_{n\mathbf{k}}(\mathbf{r}, t)}{\partial t} = \left[\frac{1}{2}\left(-i\hbar\nabla + \hbar\mathbf{k} + \frac{e}{c}\mathbf{A}(t)\right)^2\right.$$
$$\left. -e\phi(\mathbf{r}, t) + V_{jm}(\mathbf{r}) + V_{XC}(\mathbf{r}, t)\right] u_{n\mathbf{k}}(\mathbf{r}, t), \tag{5}$$

where $u_{n\mathbf{k}}$, $\mathbf{k}$, V_{jm}, and V_{XC} represent the Bloch orbitals, 2D crystalline momentum vector, jellium potential, and exchange-correlation potential, respectively. The vector potential $\mathbf{A}(t)$ describes the applied electric field $\mathbf{E}(t)$ by $\mathbf{E}(t) = -(1/c)d\mathbf{A}(t)/dt$ and $\phi(\mathbf{r}, t)$ expresses the Hartree

potential. The microscopic electric current density **j** in the metasurface is obtained from the Bloch orbitals as follows:

$$\mathbf{j}(\mathbf{r}, t) = -\text{Re}\left[\sum_{nk} u^*_{n\mathbf{k}}\left(-i\hbar\nabla + \hbar\mathbf{k} + \frac{e}{c}\mathbf{A}\right) u_{n\mathbf{k}}\right]. \quad (6)$$

To solve the time-dependent Kohn–Sham equation (5), SALMON, an open-source code (https://salmon-tddft.jp/) developed in our group [6], has been employed.

III. COMPUTANTINAL RESULTS

Fig. 2 shows calculated transmission, reflection, and absorption rates of the metasurfaces for various gap distances, $d = -0.1 - 0.4$ nm, where the horizontal-, and vertical-axes are the photon energy and the rates, respectively. We show results using TDDFT in (a-c). For comparison, we show results of classical electromagnetic analysis in (d-f) where we carry out FDTD calculations with the same geometry of the nano-particles and assuming the Drude model.

We first look at results of (d-f) using classical electromagnetism. We find there appear two types of peaks. Peaks that appear in lower energy region are considered to originate from the so-called bonding dipole plasmon (BDP) mode, while those in higher energy region are from the bonding quadrupole plasmon (QDP) mode. These plasmon modes show red-shifts as d decreases. This is caused by the reduction of the anti-electric fields inside the sphere, as the distance between the spheres decreases. At $d \leqq 0.0$ nm, sudden blue-shifts are observed for the two plasmon peaks. They are considered as the appearance of the void plasmon- and its higher-modes (VP and HVP) that are newly emerged when the nanospheres start to contact to each other. Summarizing the above results, the plasmon modes exited on the metasurfaces are always clearly classified into two cases: (i) BDP and QDP for $d > 0$ nm. (ii) VP and HVP for $d \leqq 0$ nm.

Compared with the above classical results, we find there appear qualitative differences in (a-c) calculated by the TDDFT. The peaks become smaller and much broader as d decreases. No blue-shifts are observed from stem to stern. We consider these qualitative differences are caused by the tunneling currents that flow in the gap region between nanospheres. By the tunneling effects, the metasurfaces are considered to have not only BDP and QDP but also VP and HVP modes even in $d > 0$ nm region. Optical responses of the metasurfaces are formed by the superposition of those four plasmon modes, resulting in a number of small and broad peaks. Furthermore, we find another interesting characteristics at $d = 0$ nm: the reflection almost vanishes while the absorption survives for a wide range of spectral region. This characteristics may be useful as an optical absorbers.

IV. CONCLUSION

We have investigated a quantum plasmonic metasurface with sub-nanometer gap distances based on TDDFT as well as ordinary electromagnetic analysis. Transmission, reflection, and absorption rates have been calculated and analyzed. Although optical responses by classical theory are characterized by clear signals of various plasmons, it has been shown that the quantum effects smear the plasmon features and produce broad structures. In particular, the reflection showed a rapid attenuation as the gap distance decreases. This characteristics may be suitable for optical absorbers. In the presentation, we will further discuss the effect of the tunneling currents in detail.
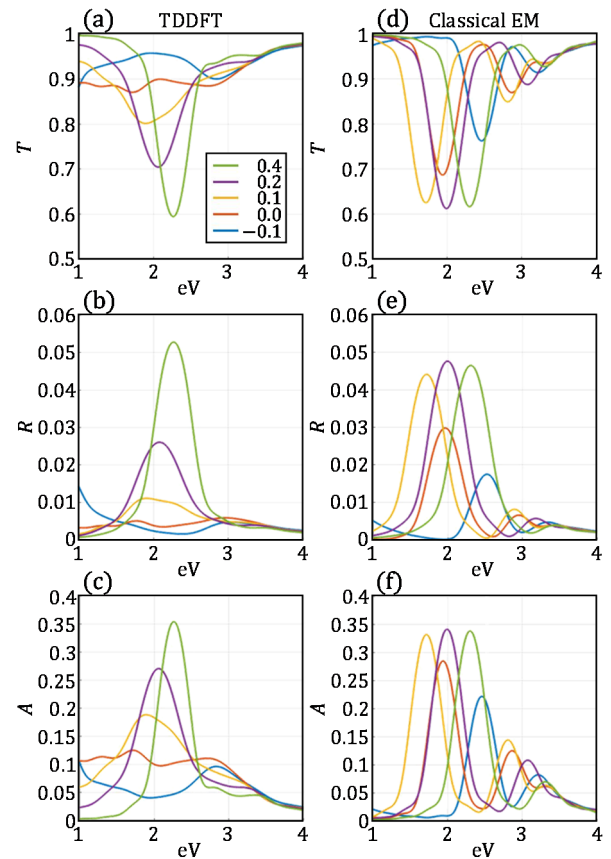

Fig. 2. Spectral distributions of the transmission, reflection, and absorption of the metasurfaces calculated by the TDDFT (a-c) and the classical electromagnetic analysis (d-f), respectively.

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