# Bridging Classical and Quantum Plasmons via an FDTD-TDDFT Hybrid Model

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## Abstract

The interaction between classical plasmons of a gold bowtie nanoantenna and quantum plasmons of graphene nanoflakes (GNF) placed in the narrow gap of the nanoantenna is studied by a proposed FDTD-TDDFT hybrid numerical method. Our analysis shows that the quantum plasmon response of a molecular-scale GNF can be enhanced by more than two orders of magnitude in this hybrid system. This finding can be particularly useful for applications to molecular sensors and quantum optics.

## 1. Introduction

Recently, plasmons in two-dimensional (2D) materials, such as graphene, have attracted increasing research interest, primarily because of the new rich physics characterizing these materials. However, when the geometrical size of plasmonic nanoparticles is less than about 10 nm, the description of their optical properties becomes more challenging because quantum effects begin to play an important role. At this scale, plasmon resonances become more sensitive to the quantum nature of the conduction electrons [1], thus the theoretical predictions of classical approaches based entirely on the Maxwell equations are less successful in describing experimental results [2]. The shortcomings of the classical theory stem chiefly from neglecting three quantum effects: i) spill-out of electrons at medium boundaries, ii) surface-enabled electron-hole pair creation, and iii) nonlocal effects of electron wavefunction. These quantum effects can significantly change the features of plasmon spectra predicted by the classical theory [3]. To overcome these shortcomings of the classical theory, a new research area that combines plasmonics with quantum mechanics, known as quantum plasmonics, has recently emerged [4]. In this paper, we apply an FDTD-TDDFT hybrid numerical method [5] to study the classical-quantum plasmon interaction of a multiphysics system in the weak-coupling regime.

## 2. Physical System

The physical system used to illustrate the main features of our numerical method is shown in Fig. 1. It consists of a gold bowtie nanoantenna placed on a silica substrate and a molecular-scale GNF located in the narrow gap of the nanoantenna. The nanoantenna is made of two triangular gold plates with angle, $\alpha$, length, $L$, and thickness, $t$, the separation distance between the tips of the gold plates being $\Delta$. In all our simulations $\alpha$=12°, $\Delta$=10 nm, and $t$=30 nm, but $L$ will be varied. Moreover, the GNF has a triangular shape, too, with side length, $a$=1.23 nm, namely there are six carbon atoms along each side of the triangle. It should be noted that triangular GNFs is one of the stable configurations in which they exist [6]. The GNF is positioned in such a way that its symmetry axis coincides with the longitudinal axis of the nanoantenna. The bowtie nanoantenna has plasmon resonances associated with the triangular plates and strongly localized (hot-spot) plasmons generated in the narrow gap of the nanoantenna.

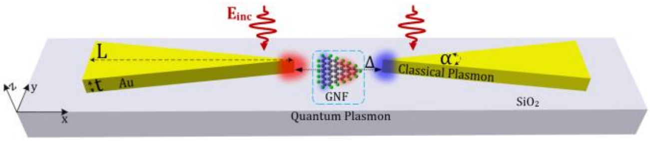


Figure 1: A classical and quantum plasmon multiphysical system, where the quantum plasmon of a graphene nanoflake interacts with the classical plasmon of a gold bowtie nanoantenna via the optical near-field.

## 3. Results and Discussion

### 3.1. Quantum plasmons of graphene nanoflakes

We considered first the GNFs described in the preceding section and used the TDDFT method to investigate their optical spectra. More specifically, we used the Octopus code package [7]. The GNF is freestanding and it only interacts with an external time-dependent and spatially constant electric field. We assumed that the time dependence of the field was described by a delta-function. In the right-side inset of Fig. 2, we have performed a calculation for a GNF with charge doping concentration of 15%. Here, the charge doping concentration is defined as the ratio of the number of excess charges to the number of carbon atoms in the GNF. The quantum response of the GNF is quantified by the dipole strength function $S(\omega)$. It can be seen in this figure that the main resonance peak of this GNF is located in the infra-red region. Moreover, we have also calculated the distribution of the net charge density at the resonance frequencies, as compared to that in the ground state. The blue and red colors correspond to the negative and positive net charge density, respectively. This net charge distribution does prove that this resonance peak corresponds to collective electron density oscillations, i.e. it can be viewed as a quantum plasmon.

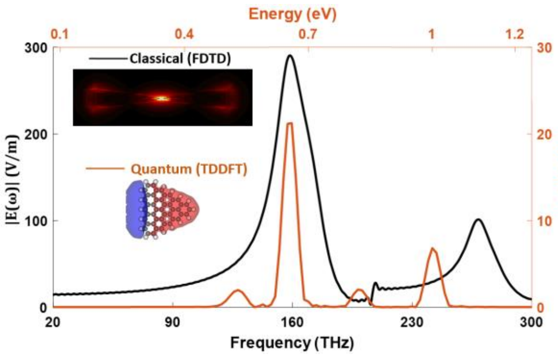


Figure 2: Spectra of the bowtie nanoantenna (black line) and GNF. In insets, the profile of the optical near-field of the hot-spot plasmon and the charge distribution of the quantum plasmon, calculated at the resonance frequency.

### 3.2. Classical plasmons of gold bowtie

The second part of our study consists of the calculation of the optical spectra of the bowtie nanoantenna. The nanoantenna is illuminated by a normally incident plane wave. Based on FDTD method, the electric field at center of the gap of a nanoantenna with $L$ = 280 nm is given in Fig. 2, where the spectra $|E(\omega)|$ has been normalized to the amplitude of the incident electric field. The spectra reveal that the amplitude of the optical near-field could be enhanced by more than two orders of magnitude. To gain more physical insights, we have calculated the electric field profile corresponding to the frequency of the major spectral peak. The result, shown as left-side inset in Fig. 2, shows this main resonance corresponds to a strongly localized plasmon formed in the narrow gap of the nanoantenna (a so-called hot-spot plasmon). Moreover, particularly relevant to our study is the fact that the hot-spot plasmon is strongly confined in the gap of the bowtie nanoantenna, which would lead to a strong field overlap and implicitly enhanced interaction with the quantum plasmon of a GNF placed in the gap.

### 3.3. Interaction between classical and quantum plasmons

The interaction between the classical and quantum plasmons can be characterized quantitatively by analyzing the combined hybrid plasmonic system. In Fig. 2, we show the two plasmon resonances are located at the same frequency of 159 THz. To assess the influence of the field enhancement effect induced by the classical plasmon resonance of bowtie nanoantenna on the quantum plasmon of the GNF, we place such a GNF at the center of the gap of the optimized bowtie nanoantenna, as illustrated in Fig. 3(a). For reference, we also calculated the spectrum of the GNF without the nanoantenna but under the same pulsed plane wave excitation conditions, as depicted in Fig. 3(b). In Fig. 3(c), we show the spectra of the amplitude of the dipole moments, $|p_a|$ and $|p_b|$, corresponding to the two systems. For a better comparison, we plot in the inset of Fig. 3(c) the ratio $|p_a|/|p_b|$. The two spectra suggest that the frequency of the quantum plasmon of the GNF is not affected by the excitation of the hot-spot plasmon, which means that, as expected, the effects of the quantum plasmon on the classical one are negligible. More importantly, however, it can be seen that the response of the quantum plasmon of the GNF can be enhanced by more than two orders of magnitude upon interaction with the hot-spot plasmon of a specially designed gold bowtie nanoantenna.

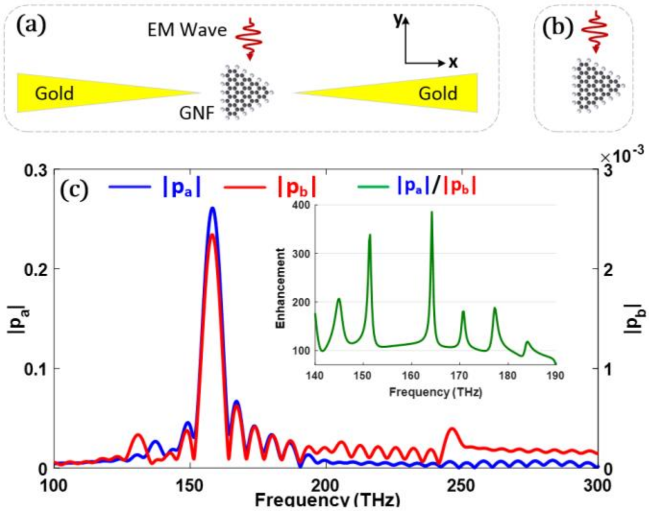


Figure 3: (a), (b) Schematics of a GNF placed in the gap of a bowtie nanoantenna and of an isolated GNF, respectively. (c) Spectra of the dipole moments $|p_a|$ and $|p_b|$ corresponding to the configurations shown in panels Fig.3(a) and 3(b), respectively.


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