Quantum electrodynamics and plasmonic resonance of metallic nanostructures

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Abstract
Plasmonic resonance of a metallic nanostructure results from coherent motion of its conduction electrons driven by incident light. At the resonance, the induced dipole in the nanostructure is proportional to the number of the conduction electrons, hence $10^7$ times larger than that in an atom. The interaction energy between the induced dipole and fluctuating virtual field of the incident light can reach a few tenths of an eV. Therefore, the classical electromagnetism dominating the field may become inadequate. We propose that quantum electrodynamics (QED) may be used as a fundamental theory to describe the interaction between the virtual field and the oscillating electrons. Based on QED, we derive analytic expressions for the plasmon resonant frequency, which depends on three easily accessible material parameters. The analytic theory reproduces very well the experimental data, and can be used in rational design of materials for plasmonic applications.

Keywords: localized surface plasmonic resonance frequency, red shift, vacuum virtual electromagnetic field, lamb shift, shape and size dependence

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(Some figures may appear in colour only in the online journal)
Suppose that a metallic ellipsoid with a dielectric function \( \varepsilon_1 = \varepsilon'_1 + i\varepsilon''_1 \) is embedded in a medium with a dielectric function \( \varepsilon_2 = \varepsilon'_2 + i\varepsilon''_2 \), and the electric field of the incident photon, \( E^\text{ext}_z \), is along the \( z \)-axis of the ellipsoid. If the longest dimension of the ellipsoid, \( L_{\text{max}} \), is much smaller than \( \lambda \varepsilon''_2^{-1/2} \) (\( \lambda \) is the wavelength), the beam width \( W \) of the incident light [14], and the skin-depth \( \delta = \lambda(2\pi\varepsilon''_2^{-1/2})^{-1} \), the quasi-static approximation is valid [15]. The quasi-static approximation implies the phase change across the nanostructure should be small, i.e. \( 2\pi L_{\text{max}}(\lambda \varepsilon''_2^{-1/2}) \ll \pi/2 \). For the violet light with \( \lambda = 4000 \) Å in vacuum (\( \varepsilon'_2 = 1 \)), one arrives at \( L_{\text{max}} < 100 \) nm. The phase retardation effect can be observed when the particle size is larger than 20 nm, and becomes important when \( L_{\text{max}} > 100 \) nm. Under the quasi-static approximation, the total induced dipole moment in the ellipsoid is given by [15, 16]:

\[
P_{\text{total}} = \alpha V \varepsilon_0 E^\text{ext}_z, \quad \text{with} \quad \alpha = \frac{\varepsilon_2(\varepsilon_2 - 1)}{\varepsilon_2 + (\varepsilon_1 - \varepsilon_2)\varepsilon_0^{-1}}.
\]

Here \( V \) is the volume of the ellipsoid; \( \varepsilon_0 \) is the permeability of free space and \( \varepsilon_0^{-1} \) is the depolarization factor along the \( z \)-axis. Note that equation (4) corresponds to \((\pi L_{\text{max}}\varepsilon''_2^{-1/2}/\lambda)^3\) terms in the Mie theory [16]. To capture the phase retardation effect in larger nanostructures (\( L_{\text{max}} > 100 \) nm), one can include the higher terms such as \((\pi L_{\text{max}}\varepsilon''_2^{-1/2}/\lambda)^5\) in the Mie theory, which correspond to the induced electric quadrupole and magnetic dipole of the nanostructure [15]. We now make two assumptions: (1) \( \varepsilon'_2 \) is a constant, which is a reasonable assumption for commonly used media, such as vacuum, SiO2 and polyvinyl alcohol, in plasmonic applications. (2) The dielectric functions of the nanostructures are primarily determined by the conduction electrons [18], which is also a reasonable approximation. Under these assumptions, the dielectric functions of the nanostructure can be expressed as:

\[
\varepsilon'_1 = 1 - \frac{S\omega_p^2}{\omega^2 + \gamma^2}, \quad \varepsilon''_1 = \frac{S\gamma\omega_p^2}{\omega^2 + \gamma^2}.
\]

Here \( \omega_p = (ne^2/\pi\varepsilon_0)^{1/2} \) is the plasmon frequency. \( n \) and \( m \) denote the electron number density and mass of the electron. \( S(\omega) \) represents intra-band oscillator strength of the conduction electrons. \( \gamma \) is the decay rate of the quasiparticles, given by [18–21]:

\[
\gamma = \gamma_0 + \text{Av}_p I_{\text{eff}}.
\]

where \( \text{Av}_p = \hbar(3\pi^2n)^{1/3}/m \) is the Fermi velocity of the metal and \( I_{\text{eff}} \) is the effective dimension of the ellipsoid along the polarization direction. \( A \) is a dimensionless, positive constant on the order of one. \( \gamma_0 \) is the decay rate resulting from electron–phonon, electron-impurity, and electron–electron interactions [18], and can be estimated by \( \gamma_0 = ne^2/\text{m}\sigma \) with \( \sigma \) as the conductivity of the metal. The second term in equation (6) stems from electron scattering with the surface, and is the only term dependent on the size of the nanostructure.

Note that the derivation of equation (5) is based on the free electron model where the wave-functions of the single particle states are Bloch waves. On the other hand, if the shortest dimension of the metallic nanostructure, \( L_{\text{min}} \), is small, the corresponding
wave-functions are best described standing waves. To ensure that the wave-vectors at the Brillouin zone boundary have an acceptable error (<10%), \(L_{\text{mn}}\) has to be greater than 2 nm. Therefore, our analytical results are valid in the size range of \(2 \text{nm} < L < 100 \text{nm}\). In the classical electromagnetism, the extinction cross-section \(\sigma_{\text{ex}}(\omega)\) of the nanostructure is [15] proportional to \([\epsilon_2^2 + (\epsilon_1 - \epsilon_2)n^2]^{-1} + [\epsilon_2'' + (\epsilon_1'' - \epsilon_2'')n^2]^{-1}\). We show in the supplementary information (stacks.iop.org/JPhysCM/28/155302/mmedia) that the eigenfrequency \(\omega_{\text{m}}\) maximizes \(\sigma_{\text{ex}}(\omega)\). Therefore \(\omega_{\text{m}}\) is the root of the following equation [22–31]:

\[
\epsilon_2^2 + (\epsilon_1 - \epsilon_2)n^2 = 0.
\]

Equation (7) yields the expression for the eigenfrequency \(\omega_{\text{m}}\):

\[
\omega_{\text{m}} = \omega_0\sqrt{\frac{S}{1 + \epsilon_2^2/n(1 - 1)}} - \left(\frac{\gamma}{\omega_p}\right)^2/2.
\]

Here and later we drop the superscript \(z\) for brevity when there is no confusion.

Based on non-perturbative many-body quantum theory, the frequency shift \(\Delta\) can be determined from the Green’s function of the Hamiltonian (1). Specifically, \(\hbar \Delta = \text{Re}(R)\) and \(R\) is the shift-operator of the Green’s function, given by [9]

\[
R = \sum_{\alpha\beta\kappa\xi} \frac{|\langle \alpha; \kappa | U | \Psi_{\text{in}}; 0 \rangle|^2}{E_{\alpha} - E_{\kappa} - \hbar \omega_{\kappa\xi}} + \sum_{\alpha\beta\kappa\xi} \sum_{\alpha'\beta'\kappa'\xi'} \frac{\langle \Psi_{\text{in}}; 0 | U | \alpha; \kappa \rangle \langle \alpha; \kappa | U | \alpha'; \kappa' \rangle \langle \alpha'; \kappa' | U | \Psi_{\text{in}}; 0 \rangle}{(E_{\alpha} - E_{\xi} - \hbar \omega_{\kappa\xi})(E_{\alpha'} - E_{\xi'} - \hbar \omega_{\kappa'\xi'})} + \ldots,
\]

where \(E_{\alpha}\) is the energy of the eigenstate \(\Psi_{\alpha}\); \(\Psi_{\text{in}}; 0\) represents the many-body state at which the incident photon is absorbed and the plasmon is excited. \(|\alpha; \kappa\rangle\) denotes direct-product state of a many-electron state \(|\alpha\rangle\) and a virtual photon state with a wave-vector \(\kappa\) and a polarization vector \(\xi\). Finally, we arrive at

\[
\Delta = -\frac{\omega_{\text{m}}}{4} \frac{\beta_2}{1 + \beta_2},
\]

with

\[
\beta_2 = \frac{V}{\lambda_{\text{mn}}^2} \left\{ \epsilon_2^2 \left( \frac{1}{n^2} + \frac{\epsilon_1 - 1}{\epsilon_1''} \right) \right\}.
\]

Here \(\lambda_{\text{mn}} = 2\pi c/\omega_{\text{m}}\). In equation (11), \(\epsilon_1\) and \(\epsilon_1''\) are evaluated at \(\omega = \omega_{\text{m}}\). As \(\beta_2 > 0\), the frequency shift \(\Delta\) is less than 1/4 of \(\omega_{\text{m}}\). The central aim of this work is to demonstrate that the interaction of the induced dipole and the vacuum fluctuation of the electromagnetic field causes a red shift \(\Delta\) of the resonance frequency with increasing the volume of a nanostructure. The equations (7), (10) and (11) are valid for arbitrary dielectric functions. Using Drude model, we have derived an analytical expression for the dielectric functions in equation (5) and ultimately a simple analytical expression for \(\omega_{\text{m}}\) in equation (8). However, one should bear in mind that the Drude model is only valid for free-electron like metals, such as Na. For noble metals such as Ag and Au, only low-energy plasmonic excitations involving x-electrons can be described correctly by the Drude model. We find that for the energy range (<3.5 eV) examined in this paper, the x-electrons dominate the plasmonic excitations in Ag and Au, and thus the Drude model is appropriate. According to equations (8) and (10), there are three contributions to \(\omega_{\text{res}}\). Among them, the dominant one is the first term in equation (8) since \(\omega_{\text{m}} \ll \omega_{\text{p}}\); the second term in equation (8) is the smallest among them. The dominant term depends only on the shape of the nanostructure through the depolarization factor, \(n(\gamma)^3\). Hence the resonant frequency \(\omega_{\text{res}}\) of the nanostructure is determined primarily by its shape as opposed to its size. This fact has been well established and exploited in plasmonics [22, 23]. More importantly, \(\gamma\) in equation (8) is a monotonically decreasing function of \(L_{\text{eff}}\) as indicated in equation (6), hence \(\omega_{\text{m}}\) is a weakly increasing function of the particle size. If there were no correction term \(\Delta\), the resonant frequency \(\omega_{\text{res}} (=\omega_{\text{m}})\) would have been a monotonically increasing function of the particle size, which is opposite to the experimental observations [21, 24, 25, 30]. The QED correction term, \(\Delta\), as a decreasing function of the particle size, reverses the incorrect size-dependence of the classical electromagnetic theory and renders \(\omega_{\text{res}}\) consistent with the experiments. The failure of the classical theory has also been discussed by Scholl et al [25] who attributed the opposite size-dependence to the inappropriate use of macroscopic dielectric functions in the nanoparticles. The macroscopic dielectric functions failed to capture the effects of discrete energy levels and the fact that only certain electronic or plasmonic transitions are allowed in the nanoparticles. To remedy the classical theory, Scholl et al proposed a phenomenological model based on discrete energy levels. Although the model yielded an improved agreement to the experimental data, it did not consider the quantum effect of the electromagnetic field. As a result, the model cannot guarantee the monotonically decreasing size-dependence of \(\omega_{\text{res}}\), as revealed in experiments and the present theory. Nonetheless, Scholl’s model is valuable contribution and could be combined with the present theory to form a more comprehensive microscopic picture of plasmonic resonance.

If the electric field of the incident light is perpendicular to the \(z\)-axis, the depolarization factor in the normal direction has to be worked out. We have derived the corresponding equations, which are included in the supplementary information. Moreover, if the electric field of the incident light is along an arbitrary direction, the total induced dipole is a vector sum of the components in each major axis [15, 16]. Finally, for a spheroid with its rotational axis along \(z\), the depolarization factors \(n^3(\gamma), n^5(\gamma), n^7(\gamma)\) and the resonant frequency \(\omega_{\text{res}} (\mathbf{E}_{\text{ext}} \perp \mathbf{L})\) and \(\omega_{\text{res}} (\mathbf{E}_{\text{ext}} \perp \mathbf{z})\) can be calculated analytically as well. For a general ellipsoid, the corresponding quantities have to be evaluated numerically.

The size dependence of plasmonic resonance frequency in metallic nanostructures has been studied extensively and several physical origins have been proposed, including size-dependent dielectric functions [25, 32, 33], phase retardation [34, 35], and nonlocal response of current to the electromagnetic field [36–43], etc. However, in all previous works, the electromagnetic field was treated classically.
To validate the proposed theory, we apply it to various metallic nanostructures including nano-spheres, nano-rods, and nano-plates. First, we examine the size-dependence of \( \omega_{\text{res}} \) in nano-spheres. Since all spheres have the same shape or the depolarization factors \( n = 1/3 \), the nano-spheres of the same metal would yield the same \( \omega_{\text{in}} \) for a given surrounding medium. According to equations (10) and (11), \( \Delta \) depends only on the volume of a sphere, thus \( \omega_{\text{res}} \) is a monotonically decreasing function of the sphere diameter \( D \). When comparing to experimental results for nanoparticles, one should be cautious. This is because in most experiments where plasmon resonance of nanoparticles is measured, the nanoparticles are often covered by ligands. Since the ligands tend to attract electrons from the nanoparticles, the measured resonant energies may deviate considerably from their intrinsic values, for which the theoretical model is developed. More importantly, nanoparticles with different sizes are affected differently by the ligands (the smaller the particle, the greater the effect), thus yielding different size-dependence of the resonance energy. To avoid this problem, we choose to focus on experiments where the nanoparticles are ligand-free. One such experiment which has attracted a lot attention is the work of Scholl et al [25] who have measured the plasmon resonance of individual ligand-free Ag nanoparticles using aberration-corrected transmission electron microscope (TEM) and mono-chromated scanning TEM electron energy-loss spectroscopy. In figure 1(a), we compare the theoretical prediction to the experimental data taken from figure 3(b) of Scholl’s paper [25]. The dielectric constant of the surrounding medium \( \varepsilon_0^\mathrm{s} \) is 1.69 as measured in the experiment. We find that the theoretical prediction agrees very well to the experimental data as long as the two fitting parameters \( A \) and \( S \) are chosen reasonably, in this case \( A = 0.03 \), \( S = 1 \). It is important to point out that the present theory predicts the correct experimental trend—a monotonic redshift as \( D \) increases, regardless of the choice of \( A \) and \( S \). As displayed in figure 1(b), the size dependence of \( \omega_{\text{res}} \) is entirely contained in \( \Delta \) while \( \omega_{\text{in}} \) is essentially flat. Thus the size-dependence of the nano-spheres originates exclusively from the quantum nature of the electromagnetic field. To the best of our knowledge, the present theory is the only one that yields the correct experimental trend for ligand-free nanoparticles in the range between 2 nm and 20 nm. For Ag nanowires, self-consistent hydrodynamic model reproduced the same trend as in Scholl’s work on Ag nanoparticles [44]. However, for Na nanowires, the same method predicted a redshift first then a blueshift as the nanowire radius increases. For Na nanoparticles, the quantum mechanical time-dependent orbital-free density functional theory (TD-OFDFT) calculations reported a redshift first, then a blueshift and then a redshift again as the particle diameter varies from 1 nm to 12 nm [45]. The time-dependent DFT calculations reported a blueshift for small particles less than 2 nm [46] for Ag nanoparticles. It is important to point out, however, that the electric quadrupole, magnetic dipole and phase retardation can also lead to the redshift, but for much larger particles (>100 nm) [16]. Similar comparison is made for gold nano-spheres embedded in water whose dielectric constant \( \varepsilon_0^\mathrm{s} = 1.78 \). As shown in figures 1(c) and (d), the fitting parameters are \( A = 0.01, S = 0.54 \).

Second, we compare the theoretical prediction to the experimental results for Au nano-rods embedded in silica [23] (\( \varepsilon_0^\mathrm{s} = 2.15 \)). In figure 2(a), the experimental resonance frequency \( \omega_{\text{res}}^\parallel \) as function of the length \( L \) and diameter \( D \) of the nano-rods is shown in circles, while the theoretical prediction is on the surface. In this case, the two fitting parameters are \( A = 0.6, S = 1.4 \). Because \( L \) is \( \sim 32–70 \) nm [23], larger than the size of the nano-spheres, the electron scattering at the surface becomes more important, thus \( A \) is larger. For the similar reason, the oscillator strength \( S \) is also larger than the nano-spheres, as discussed in the supplementary information. There is an overall good agreement between the theory and experiment, down to the size of 8.5 nm [23]. The theoretical prediction for the polarization direction perpendicular to the nano-rod axis is displayed in figure 2(b). We next demonstrate the validity of \( \omega_{\text{in}} \), which cannot be measured directly by experiments. Hence, we compare the theoretical prediction of \( \omega_{\text{in}} \) to a set of computational results obtained from TD-OFDFT simulations [45, 47] for a Na nano-rod embedded in vacuum (\( \varepsilon_0^\mathrm{s} = 1 \)). A number of \((L, D)\) combinations including \((5.79, 0.86), (5.79, 1.41), (5.79, 1.93), (5.79, 2.23), (5.79, 3.54), (5.79, 4.76), \) and \((5.79, 5.46), \) in the unit of nm, are considered. The two fitting parameters are \( A = 0.6, S = 0.8 \) for \( \mathbf{E}^\parallel \) axis and \( A = 0.6, S = 0.92 \) for \( \mathbf{E}^\perp \) axis. There is an excellent agreement between the theoretical
owing to the
are compared to the experimental results [22]. The
\(8\) and
\(60\) is due to the oppo-
\(180\)
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\(60\) \(\hbar\). Taking
\(4\) \(F\) \(1/2\) \(100\) \(6\) results are no longer size-dependent. This condition leads to
\(L\)\(\text{dependence of their respective depolarization factors.}

Third, we switch to a Au nano-plate whose rotational symmetric axis is along \(\mathbf{z}\). The theoretical predictions for \(\omega_{\text{res}}(D)\) are compared to the experimental results [22]. The circular nano-plate has a height \(L = 20\text{nm}\) embedded in a medium with a refractive index of 1.26. The fitting parameters \(A = 0.6, S = 0.86\) yield an excellent agreement between the theoretical predictions and the experimental data as shown in Figure 4. Similar agreement between the theory and experiments is also observed for Al and Pt nano-plates which is presented in the supplementary information. The opposite \(D\)-dependence between \(\omega_{\text{res}}(D)\) and \(\omega_{\text{res}}^+(D)\) is due to the opposite \(D\)-dependence of their respective depolarization factors.

Although size-dependent dielectric functions could be invoked to explain the size-dependence of \(\omega_{\text{res}}\), such explanation is restricted to small nanoparticles. One can estimate the maximum radius \(R\) of the nanoparticles above which the size-dependent dielectric functions become indistinguishable from the bulk dielectric functions. It is known that the presence of discrete energy levels is the origin of the size-dependent dielectric functions [25]. Hence if the level spacing becomes comparable or smaller than \(\hbar \gamma_0\) (\(\gamma_0 = \nu_F l\)) where \(l\) is the mean free path of bulk material), the dielectric functions are no longer size-dependent. This condition leads to 
\[R \sim \pi (\hbar/8m\nu_F)^{1/2}.\]
Taking \(l \sim 10^3\ \text{ Å}, \nu_F \sim 3 \times 10^6\ \text{ m s}^{-1}\), we have \(R \sim 2.2\ \text{nm}\). Clearly, for the size range \(2 < L_{\text{max}} < 100\ \text{nm}\) discussed in this work, the size-dependence of \(\omega_{\text{res}}\) cannot be described by the size-dependent dielectric functions.

The QED formalism provides a plausible framework whose predictions agree well with the experimental observations. QED could have more profound implications in plasmonics than what is presented in this paper. For example, it is known that when a nano-antenna is placed next to a metallic nano-structure, there is an interaction between the nano-antenna (an emitter) and the virtual field. The interaction could change the directional radiation pattern of the antenna [48], analogous to cavity QED [49]. The present work, on the other hand, focuses on the interaction between an absorber (the plasmonic nano-structure) and the virtual field. Such interaction could also change the induced magnetic moment of the metallic nano-structure, as well as the polarization of the incident light.

To summarize, we propose that QED is important to understand the plasmonic resonance in metallic nanostructures, specially nanoparticles. The coherent motion of the conduction electrons in the nanostructure could lead to a large induced dipole moment, which interacts with the virtual field and results in a significant shift in the resonant frequency. The frequency shift is the key to reconciling the theoretical predictions and experimental observations on size-dependent plasmonic resonance. Based on QED, we have derived analytic expressions for the plasmonic resonant frequency, which depends on three easily accessible material parameters—the dielectric constant \(\epsilon_\infty\) of the surrounding medium, the number density \(n\) of electrons and the conductivity \(\sigma\) of the metal. The analytic expression are shown to reproduce very well the experimental data for nano-spheres, nano-rods and nano-plates, and can be used readily for estimating the resonant frequency of plasmonic nanostructures as a function of their geometry, composition and surrounding medium.

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