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Numerical Study on the Limit of Quasi-Static Approximation for Plasmonic Nanosphere

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Abstract. Plasmonic nanospheres are often employed as resonant substrates in many nanophotonic applications, like in enhanced spectroscopy, near-field microscopy, photovoltaics, and sensing. Accurate calculation and tuning of optical responses of such nanospheres are essential to achieve optimal performance. Mie theory is widely used to calculate optical properties of spherical particles. Although, an approximated version of Mie approach, the quasi-static approximation (QSA) can also be used to determine the very same properties of those spheres with a lot simpler formulations. In this work, we report our numerical study on the limit and accuracy of QSA with respect to the rigorous Mie approach. We calculated scattering, absorption and extinction spectra of silver and gold nanospheres in air with varying sizes using both QSA and Mie theory. Then, we extracted spectral positions of the resonance peaks from their calculated optical responses and defined the error present in QSA as the difference between the spectral positions of the resonance peaks calculated by QSA and Mie method. Our error analysis reveals that QSA approach yields nonlinear increment in error with linear increment in size of the nanosphere and that the amount of error is significantly less in the case of gold spheres compared to the silver ones. We also provide a polynomial-fitted error function that resembles the qualitative trend in error.

INTRODUCTION

Plasmonic nanospheres are widely used in different nanophotonic applications including surface-enhanced Raman and infrared spectroscopy [1,2], metal-enhanced fluorescence spectroscopy [3], nanobiosensing [4], super-resolution microscopy [5] and photovoltaics [6]. The ease tuning of the plasmon mode of such nanospheres into intended spectral regime by controlling their sizes, makes their application popular in near-field optics [7,8]. Accurate calculation of the optical properties such as scattering, absorption and extinction profiles is essential when optimizing the optical responses of nanospheres. Applying Mie theory of light scattering is one way to do it [7-11]. In Mie formulation, one can determine the optical responses of an isotropic spherical particle by solving Maxwell's equations rigorously for a plane wave excitation and obtain the solution in the form of an infinite series of spherical multipole partial waves [9-11]. An approximated version of Mie theory, the so-called quasi-static approach can also be used to estimate the very same properties of the nanospheres if the size of the sphere is very small compared to the wavelength of light [7,8]. Employment of quasi-static approach can be useful to reduce mathematical complexities in theoretical studies and computational time/resources in numerical approaches since in the quasi-static approximation (QSA), the rigorous electrodynamic approach of Mie theory is reduced to an electrostatic approach by considering the fact that the phase of the electromagnetic wave is constant over the particle volume [7,8].

In this work, we numerically study the limit of the QSA approach and its accuracy compared to the rigorous Mie approach. We calculated scattering, absorption and extinction spectra of silver and gold nanospheres in air with varying sizes from 3 nm to 63 nm over 200 nm – 1000 nm spectral range using both QSA and Mie theory. Then, we estimated the error in the QSA results in terms of the shifts of the spectral peak positions in the scattering, absorption and extinction profiles of the nanospheres from the corresponding peaks calculated with Mie method. Our error analysis reveals that QSA approach yields nonlinear increment in error with linear increment in size of the nanosphere and that the amount of error is significantly less in the case of gold spheres compared to the silver ones. We also provide a polynomial-fitted error function that resembles the qualitative trend in error.

RESULTS AND DISCUSSION

Scattering- , absorption- and extinction cross-sections of silver (Ag) and gold (Au) nanospheres were calculated over a broad spectral range (200 nm – 1000 nm) for 30 different sizes of the spheres (diameters of 3 nm to 63 nm with 2 nm increment) using QSA and Mie approaches. For Mie calculations, an open source Mie scattering calculator MiePlot v4614 [12] was used. For QSA, an in-house made MATLAB code (see *Appendix*) was implemented based on the mathematical expressions obtained in the QSA formulation [7] for the corresponding cross-sections as –

$$C_{sca} = 42.67\pi^5\lambda^{-4}r^6[((\epsilon_1^2 + \epsilon_1\epsilon_m + \epsilon_2^2 - 2\epsilon_m^2)^2 + 9\epsilon_m^2\epsilon_2^2)/(\epsilon_1^2 + 4\epsilon_1\epsilon_m + \epsilon_2^2 + 4\epsilon_m^2)^2], \qquad (1)$$

$$C_{abs} = 24\pi^2\lambda^{-1}r^3[(\epsilon_m\epsilon_2)/(\epsilon_1^2 + 4\epsilon_1\epsilon_m + \epsilon_2^2 + 4\epsilon_m^2)], \qquad (2)$$

$$C_{ext} = [C_{sca} + C_{abs}], \qquad (3)$$

where C_{sca}, C_{abs}, and C_{ext} are the scattering- , absorption- and extinction cross-sections, respectively. The parameter r is the radius of the nanosphere, λ is the wavelength of incident light, ϵ_1 and ϵ_2 are the real and imaginary part of the dielectric function of the metal, respectively, while ϵ_m is the nondispersive dielectric constant of the surrounding medium. In both QSA and Mie calculations, nanospheres were considered as homogeneous (perfect) spheres surrounded by air (refractive index is 1) and illuminated by unpolarized plane wave while the complex dielectric function of the metals were extracted from Johnson and Christy [13].

The main goal behind the above-mentioned calculations was to determine the trend in 'error' present in the QSA results with respect to the Mie results, when the size of the sphere is increasing. Such systematic study could provide a qualitative limit for QSA, i.e. the point where the approximation becomes invalid due to the retardation effect [7]. We extracted scattering, absorption, and extinction peak positions of the nanospheres from both QSA and Mie results. Then, we defined 'error' in the QSA results as the difference between the spectral peak positions calculated by QSA and Mie method. Figure 1 pictorially illustrates the definition of 'error' in nm as the difference between the extinction peak positions calculated by the QSA and Mie method in the case of Ag nanosphere having a diameter of 61 nm.

To visualize the trend of the 'error' in the QSA results, errors of the scattering, absorption and extinction profiles of the Ag and Au spheres are plotted over the sizes of the spheres in Fig. 2, Fig. 3, and Fig. 4, respectively.
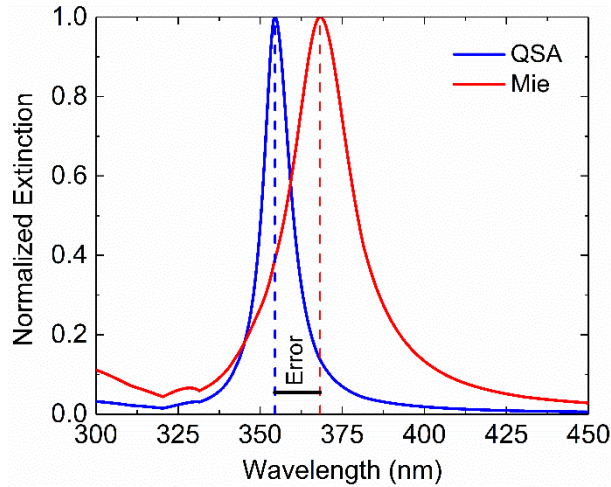

FIGURE 1. Pictorial description of an error present in the QSA results. The blue and red solid curves are the normalized extinction profiles of Ag nanosphere with a diameter of 61 nm calculated by QSA and Mie method, respectively. The blue and red (vertical) dashed lines are presenting the spectral positions of the extinction peaks in the corresponding spectra, and the black solid line between them shows the error as the difference between the peak positions calculated by the two different methods
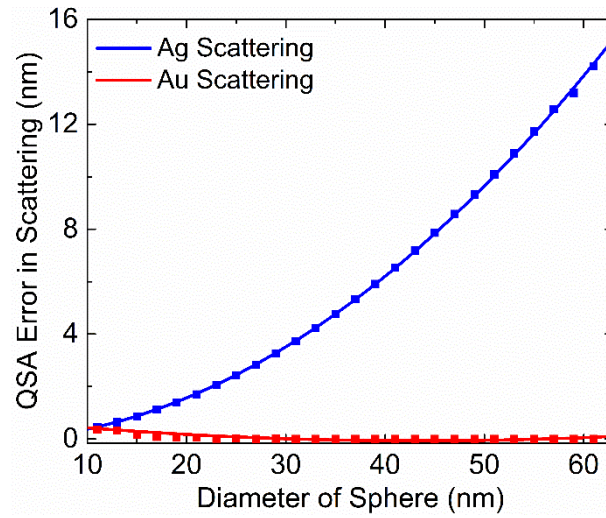
FIGURE 2. Error in the QSA results for the scattering calculations. The blue and red solid curves represent the fitted error trend in the scattering profiles of Ag and Au spheres, respectively. The blue and red squares are the actual data points of errors fitted by the corresponding curves
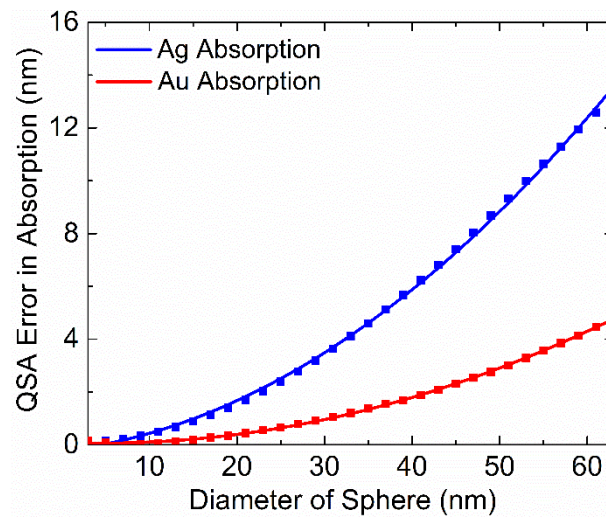

FIGURE 3. Error in the QSA results for the absorption calculations. The blue and red solid curves represent the fitted error trend in the absorption profiles of Ag and Au spheres, respectively. The blue and red squares are the actual data points of errors fitted by the corresponding curves
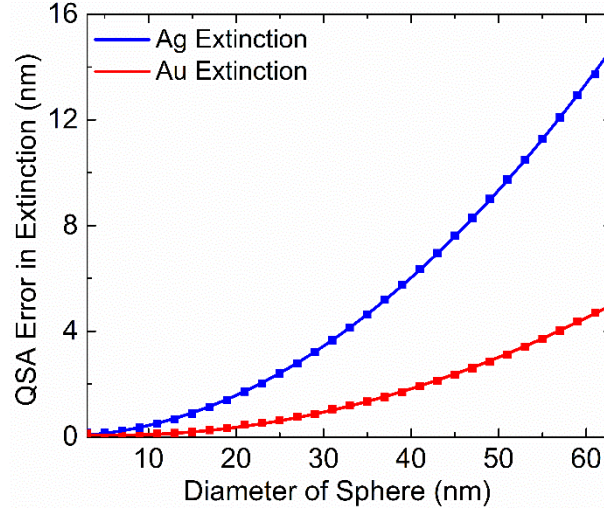
FIGURE 4. Error in the QSA results for the extinction calculations. The blue and red solid curves represent the fitted error trend in the extinction profiles of Ag and Au spheres, respectively. The blue and red squares are the actual data points of errors fitted by the corresponding curves

In Fig. 2 to Fig. 4, the blue and red squares represent the actual data points of the errors while the blue and red solid curves joining them show a polynomial fit ($ax^2 + bx + c$ with x as the diameter of the sphere) which resembles the trend in error. The fitting parameters (a, b, and c) for the corresponding spectra are reported in Table 1.

TABLE 1. Fitting parameters of the polynomial fit ($ax^2 + bx + c$) for the error in QSA

Optical Properties	a	b	c
Ag Extinction	0.003624	0.005154	0.021005
Ag Absorption	0.002878	0.037439	- 0.231469
Ag Scattering	0.003752	0.006840	- 0.072302
Au Extinction	0.001531	- 0.018788	0.126045
Au Absorption	0.001376	- 0.012493	0.089692
Au Scattering	0.000445	- 0.038658	0.771106

The QSA approach clearly yields nonlinear increment in error with increasing size of the nanosphere and the amount of error is significantly less in the case of gold spheres compared to the silver ones. The polynomial-fitted error function almost resembles the qualitative trend in error for all cases. In contrast with others, only Au scattering shows insignificant (almost zero) error in QSA over a broad range of particle size. Of particular note is that, the scattering from the Ag and Au spheres was insignificant and the extinction was almost equal to the absorption, for spheres with diameter less than 10 nm. Due to this these values are omitted from Fig. 2.

CONCLUSIONS

Concisely, we calculated optical properties of Ag and Au nanospheres having different sizes (3 nm – 63 nm) over a broad wavelength regime (200 nm – 1000 nm) with the help of two different approaches, rigorous Mie theory and its quasi-static approximated form. We extracted spectral positions of the resonance peaks from their calculated optical responses and defined an error present in QSA as the difference between the spectral positions of the resonance peaks calculated by QSA and Mie method. Our numerical study on error revealed that (except in the case of Au scattering) the error increment takes a nonlinear form (quadratic) with increasing sphere size. For Au scattering, surprisingly the error was almost zero over a broad range of particle size. In general, Au spheres yielded much less error (6 nm or less) compared to the silver ones (16 nm or less) in all cases. We also provided an error function in the form of a polynomial fit, which is able to depict the qualitative trend of error in QSA with respect to the size of the sphere. Certainly, depending on the application-specific requirements, one can set the acceptance 'limit' of error in QSA i.e. the upper limit of nanosphere size after which employment of QSA can induce substantial amount of error in desired outcomes.

APPENDIX

The MATLAB code for the QSA is implemented as a user-defined function based on the mathematical expressions presented in Eq. (1) to Eq. (3).

```
%% Quasi-Static Approximation (QSA) code for nanosphere
% s_sc=scattering cross-section (normalized by geometrical cross-section)
% s_abs=absorption cross-section (normalized by geometrical cross-section)
% s_ext=extinction cross-section (normalized by geometrical cross-section)
% l_min=lowest wavelength (nm)
% l_max=highest wavelength (nm)
% l_step=step size of wavelength (nm)
% r=radius of the nanosphere (nm)
% x=wavelengths from the material model (nm)
% n=refractive index from the material model
% k=extinction coefficient from the material model
% e_m=dielectric constant of the surrounding medium

function [s_sc,s_abs,s_ext] = QSA(l_min,l_max,l_step,r,x,n,k,e_m)
lambda=(l_min:l_step:l_max); % wavelength start at l_min, end at l_max with step
size of l_step

%% Material Model
n_material=interp1(x,n,lambda); % linear interpolation of experimental n
k_material=interp1(x,k,lambda); % linear interpolation of experimental k
e1=(n_material.^2)-(k_material.^2); % real part of dielectric function
e2=2.*n_material.*k_material; % imaginary part of dielectric function

%% Scattering, Absorption and Extinction Cross-Sections [based on Eq. (1) to Eq.
(3)]
A=(42.67*pi^5*r^6)./(lambda.^4);
B=(e1.^2)+(e1.*e_m)-(2*e_m.^2)+(e2.^2);
C=9*e_m.^2*e2.^2;
D=(e1.^2)+(4*e_m.^2)+(4*e1.*e_m)+(e2.^2);
P=(24*pi^2*r^3*e2.*e_m)./lambda;
c_g=pi*(r^2); % geometrical cross-section of the nanosphere
s_sc=(A.*((B.^2)+C)./(D.^2))./c_g;
s_abs=(P./D)./c_g;
s_ext=s_sc+s_abs;
end
```

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