An intriguing branching of the maximum position of the absorption cross section in Mie theory explained

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A potential control over the position of maxima of scattering and absorption cross-sections can be exploited to better tailor nanoparticles for specific light-matter interaction applications. Here we explain in detail the mechanism of an appreciable blue shift of the absorption cross-section peak relative to a metal spherical particle localized surface plasmon resonance (LSPR) and remaining scattering and extinction cross sections. Such a branching of cross sections maxima requires a certain threshold value of size parameter \( x \approx 0.7 \) and is a prerequisite for obtaining high fluorescence enhancements, because the spectral region of high radiative rate enhancement becomes separated from the spectral region of high non-radiative rate enhancement. A consequence is that the maximum of the absorption cross section cannot be used as the definition of the LSPR position for \( x \gtrsim 0.7 \).

The electromagnetic theory of light scattering from small particles with sizes comparable with the wavelength of the incident illumination has the long history [1]. In a number of applications, the control of the absorption is preferable, which led to the extensive theoretical and numerical works in this direction [2–8], as well as various experimental applications [9–12]. Our recent study [13] has revealed that optimal metallo-dielectric core-shell particles designed to obtain the highest possible fluorescence enhancements have the spectral region of high radiative rate enhancement red-shifted and well separated from the blue-shifted spectral region of high non-radiative rate enhancement [Fig. 4]. Herein and below, any red or blue shift, unless specified otherwise, refers relative to the particle localized surface plasmon resonance (LSPR). For the purpose of this letter, a LSPR will be identified as a maximum of the total (extinction) cross section. The maximum of radiative rate enhancement coincides with the maximum of near-field (NF) [13] and the NF peak red shift has been known for a long time [14]. Contrary to that, there seem to be no reports of a blue shift of the maximum of the absorption cross section, \( \sigma_{\text{abs}} \), responsible for the maximum of non-radiative rate enhancement [13]. Below we explain in detail the mechanism underlying the puzzling and appreciable, yet so far overlooked, blue shift of the absorption cross-section peak. Because Fig. 1 shows that such a pronounced blue shift of the absorption cross section is intrinsic already for a homogeneous spherical metal particle of sufficiently large radius \( r_s \), we shall here, for the sake of simplicity, focus only on homogeneous particles.

The resulting cross sections in the Mie theory are given as an infinite sum over all momentum channels \( \ell \geq 1 \) and both polarizations [15, 16]. According to Eqs. (2.135-8) of Ref. [15], any given angular momentum channel \( \ell \) of one of polarizations \( A = E \) for electric (or TM) polarization, and \( A = M \) for magnetic (or TE) polarization contributes the following partial amount to the resulting cross sections shown in Fig. 1(a).

![Fig. 1.](image-url)
where \( T_{\ell \ell} \) are the T-matrix elements, \( \Re \) takes the real part, \( k = 2\pi/\lambda \) is the wavenumber, and \( \lambda \) is the incident wavelength in the host medium. For \( \ell = 1 \), the above expressions can be easily rephrased in terms of a particle polarizability, \( \alpha \), on substituting \( 2ik^3\alpha/3 \) for \( T_{E1} \). In the case of a homogeneous sphere, the respective T-matrix elements in a given \( \ell \)-th angular momentum channel are [Eqs. (2.127) 15]

\[
T_{\ell \ell} = -\frac{m[xj_\ell(x)][j_\ell(x) - j_{\ell+1}(x)]}{m[xh_\ell(x)][j_\ell(x) - h_{\ell+1}(x)]} \quad (4)
\]

with high-frequency permittivity limit \( \varepsilon_\infty = 9.5 \), the bulk plasma frequency \( \omega_p = 8.9488 \) eV, and damping constant \( \gamma = 0.06909 \) eV, which is optimized to fit experimental data of Johnson and Christy [18]. The host medium will be assumed to be air (\( \varepsilon_\infty = 1 \)).

As seen in Fig. 2(a), with increasing particle radius up to \( r_s \approx 70 \) nm, the maxima of all cross sections of the dipole term of the Mie series experience initially monotonically increasing red shift from the initial quasi-static LSPR position at \( \omega_{101} \). Thereafter the maximum of the absorption cross section (2) gradually reverses its red shift relative to \( \omega_{101} \) into an increasing blue shift, which for \( r_s \approx 100 \) nm can be as large as 200 nm. The position of the maximum of the absorption cross section becomes eventually nearly constant with increasing size parameter \( x \) in a blue shifted region (centered around the frequency implicitly given by Eq. (11) below) relative to \( \omega_{101} \).

As suggested by Figs. 2(c) and 3, the modified long-wavelength approximation (MLWA) agrees very well with the exact Mie theory over an entire size range up to \( x \approx 5 \) not only for dipole, but also for higher multipole contributions. Therefore, the essentials of the blue shift can be captured by the MLWA.

The usual MLWA [19-21] is a limiting form of the Mie dipole term, that, unlike the usual quasi-static Rayleigh approximation, keeps both dynamic depolarization (\( \sim x^3 \)) and radiative reaction (\( \sim x^5 \)) terms. This is why the MLWA can account for a size-dependent red shift of the dipole LSPR, whereas the Rayleigh approximation cannot. Here we use the following MLWA form of the \( T \)-matrix which is valid in any given channel \( \ell \) (cf. Eq. (A3) of [21] for \( \ell = 1 \)),

\[
T_{E\ell} \sim \frac{iR(x)}{F + D(x) - iR(x)}, \quad F = \frac{\xi_s + \frac{\ell + 1}{\ell}}{\frac{\ell + 1}{\ell}}, \quad D(x) = \left( \frac{\ell - 2}{\ell + 1} - \frac{1}{\ell} \right) \frac{(\ell + 1)(2\ell + 1)}{(2\ell - 1)(2\ell + 3)} x^2, \quad R(x) = \frac{\ell + 1}{(2\ell - 1)!!(2\ell + 1)!!} (\xi_s - 1)^{2\ell + 1} \quad (6)
\]

Eq. (6) is derived by using asymptotic expressions for spherical Bessel and Hankel functions used in (4). It makes transparent that \( T_{E\ell} \) in any given channel is determined solely by a size independent quasi-static Fröhlich term \( F \), a dynamic depolarization term \( D \) (\( \sim x^3 \)), and a radiative reaction term \( R \) (\( \sim x^{2\ell + 1} \)).

The vanishing of the size independent \( F \) in the denominator yields the usual quasi-static Fröhlich LSPR condition, which
determines the quasi-static LSPR frequencies $\omega_{\text{LSR}}$. In the case of Drude fit (5) of $\varepsilon_s$ one finds $\omega_{\text{LSR}} = \omega_p/\sqrt{\varepsilon_{\infty} + [(\ell+1)\varepsilon_h/\ell]}$.

One refers, somewhat misleadingly, to a unitarity, if the substitution of a given approximation to $T_E$ into the above equations yields $\sigma_{\text{ext}} = \sigma_{\text{scat}} + \sigma_{\text{abs}}$. The MLWA can be shown to satisfy unitarity. In contrast, the usual Rayleigh limit, which amounts to setting $D(x) = R(x) \equiv 0$ in the denominator of the dipole MLWA $T_E$ in (6), yields a purely imaginary $T_E$ for real $\varepsilon_s$ (i.e., a purely real polarizability) and violates the unitarity [21].

In what follows we shall focus on the dipole MLWA. The higher order multipole MLWA can be treated similarly. On substituting Eq. (6) into Eq. (1) – Eq. (3), one finds the following cross sections of the dipole MLWA contribution:

$$\sigma_{\text{abs},1} = \frac{4\pi}{15k^2} \left( \frac{9}{2} x^3 (2x^2 + 5) \Im(\varepsilon_s) \right) \left( \varepsilon_s + 2 \frac{3}{2} (\varepsilon_s - 2)x^2 - i\frac{3}{2} (\varepsilon_s - 1)x^3 \right)$$ \hspace{1cm} (7)

$$\sigma_{\text{scat},1} = \frac{4\pi}{15k^2} \left( \frac{10}{6} \varepsilon_s - 1 \right)^2 \left( \varepsilon_s + 2 \frac{3}{2} (\varepsilon_s - 2)x^2 - i\frac{3}{2} (\varepsilon_s - 1)x^3 \right)^2$$ \hspace{1cm} (8)

$$\sigma_{\text{ext},1} = \frac{4\pi}{15k^2} \left( \frac{9}{2} x^3 (2x^2 + 5) \Im(\varepsilon_s) + 10x^6 |\varepsilon_s - 1|^2 \right) \left( \varepsilon_s + 2 \frac{3}{2} (\varepsilon_s - 2)x^2 - i\frac{3}{2} (\varepsilon_s - 1)x^3 \right)^2$$ \hspace{1cm} (9)

where $\Im(\varepsilon_s)$ denotes the imaginary part of $\varepsilon_s$. For $\Im(\varepsilon_s) = 0$, the common denominator $|\Delta|^2$ of the dipole MLWA cross-sections (7)-(9) vanishes at

$$\varepsilon_s \approx -2 - \frac{12x^2}{5}$$ \hspace{1cm} (10)

up to the order $x^3$, in which case $\Delta \approx O(x^3)$. For $\Im(\varepsilon_s) \neq 0$, one can approximate $|\Delta|^2$ as

$$|\Delta|^2 \approx \left( 1 - \frac{3x^2}{5} \right) \Im(\varepsilon_s) + 2x^3 \left( \frac{3}{5} \Im(\varepsilon_s) \right)^2$$

Eq. (10) imposes restriction on the real part of $\varepsilon_s$ [Eq. (B1) 21] explaining the observed initial size-dependent red shift of all cross sections (Fig. 2(a)). At the MLWA branching point at $r_s \approx 90$ nm in Fig. 2(b), where the peak position of $\sigma_{\text{abs},1}$ begins to deviate from the remaining cross sections, the size parameter $x \approx 0.975$ (cf. $x \approx 0.8$ and the internal size parameter $x \approx \sqrt{\varepsilon_s} = 1.1$ for the branching point at $r_s \approx 70$ in the Mie theory in Fig. 2(a)). The appearance of the branching point and ensuing blue shift of the absorption cross section (2) can be explained within the dipole MLWA as follows:

(i) For $x^2 \gg x^3$ the maxima positions are governed by the first two terms of the complex root of $\Delta$ on the rhs of Eq. (10), as was already observed by Bohren and Huffman [Sec. 12.1.1 16], yielding the red-shifted behaviour of the maximum of $1/\Delta$ relative to $\omega_{\text{LSPR}}$ with increasing $x$. The latter is the chief cause of the synchronized red-shifted behaviour of the maxima of all three fundamental scattering cross-section relative to $\omega_{\text{LSPR}}$ with increasing $x$ up to $x \approx 1$. This is why, unlike the Rayleigh approximation, the MLWA can account for the size-dependent red shift of the dipole LSPR.

(ii) As soon as $x^3 \sim x^2$, the $x^3$-term of $\Delta$ in Eqs. (7) – (9) begins to dominate. One can achieve another maximum of $1/\Delta$ if the $x^2$-term is rendered as small as possible, i.e., $\varepsilon_s$ has to be ideally +1. The latter can, in the case of dissipative media

Fig. 4. Evolution of the blue-shifted maximum of the dipole $\sigma_{\text{abs},1}$ with increasing $x$. (a) The minimum of denominator and (b) a corresponding value of the numerator for absorption and scattering cross sections of Eq. (7) and Eq. (8). A double peak of $1/\Delta^2$ for $r_s = 170$ nm, with the maximum at the frequency implicitly given by Eq. (11), can be clearly identified. Note that the numerator of $\sigma_{\text{scat},1}$ is smaller than that of $\sigma_{\text{abs},1}$ at (11). Panels (a) and (b) also illustrate the well-known fact why smaller particles have much larger absorption than larger particles [16].

$$\Re(\varepsilon_{\text{max,abs}}) \approx 1,$$ \hspace{1cm} (11)

which means that the blue-shifted maximum of $\sigma_{\text{abs},1}$ coincides with the condition of minimizing the radiative reaction (Fig. 4(a)). This causes a maximum of $\sigma_{\text{abs},1}$ but not of $\sigma_{\text{scat},1}$ (Fig. 1). The reason why the maximum of $1/\Delta$ does not cause a maximum of $\sigma_{\text{scat},1}$ is that the latter has $|\varepsilon_s - 1|$ in its numerator, which becomes very small, in contrast to $\sigma_{\text{abs},1}$ having $\Im(\varepsilon_s)$ in its numerator (Fig. 4(b)). Note, $\Re(\varepsilon_{\text{max,abs}}) \approx -1.5$ for $r_s \approx 91.5$ nm, and $\Re(\varepsilon_{\text{max,abs}}) \approx 1$ for $r_s \gtrsim 107$ nm.

The condition (11) explains why the position of the blue-shifted maximum of $\sigma_{\text{abs},1}$ remains substantially constant with increasing $r_s$, soon after it branched off from the position of maxima of other two cross sections. With the parameters of the Drude fit (5), the zero of $\Re(\varepsilon_s)$ occurs at $\omega_s = \omega_p/\sqrt{\varepsilon_{\infty}} = \omega_p/\sqrt{9.5} \approx 2.99144$ eV. The $\Re(\varepsilon_s) = 1$ occurs at $\omega_s = \omega_p/\sqrt{8.5} \approx 3.0694$ eV. One can clearly observe in Figs. 2 and 4(a) how the blue-shifted maximum of $\sigma_{\text{abs},1}$ stabilizes around $\omega_s$ with increasing $x$. Obviously, the blue shift of absorption is possible only if $\Im(\varepsilon_s)$ at the frequency implicitly given by Eq. (11) is sufficiently small, as in the present case of Au. Provided that $\Im(\varepsilon_s)$ at (11) is sufficiently large, this may prevent $\Delta$ from acquiring a local minimum and the blue shift of absorption may be absent. The situation for $\ell > 1$ is analogous to that for $\ell = 1$ in that the radiative reaction term $R$ in Eq. (6) maintains its factor $\varepsilon_s - 1$. A slight modification to $\ell = 1$ case results from that the $\ell$-dependent factor $(\ell + 1)/[(2\ell - 1)!!][2\ell + 1]!!$ of $R(x)$ in Eq. (6) decreases much faster with increasing $\ell$ that the $\ell$-dependent factor $(\ell + 1)(2\ell + 1)/[(2\ell - 1)(2\ell + 3)]$ of $D(x)$. Therefore, the threshold size parameter $x$ value required for the MLWA $\sigma_{\text{abs}}$ to exhibit a blue-shifted maximum necessarily increases with increasing $\ell$. Again, this is clearly seen in Fig. 3. Consequently, the build-up of the blue-shifted maxima of $\sigma_{\text{abs}}$ is not uniform in $\ell$. For a given fixed $x$, only the lowest multipoles have blue-shifted maximum, whereas the maxima of the remaining multipoles

(Au), be in principle achieved only with a suitably tailored gain. In the present case we are left with the condition

$$\Re(\varepsilon_{\text{max,abs}}) \approx 1,$$ \hspace{1cm} (11)
continue to be red-shifted. The latter causes a rearrangement of the natural order of the $\ell$-pole absorption maxima: the lowest absorption peak of $\sigma_{abs}$ may be due to $\ell = 3$ followed by $\ell = 4$, and only later the absorption maxima of $\ell = 1, 2$ appear (Fig. 1). Overall, the above condition (11) defines a rare location at which the total $\sigma_{abs}$ is the dominant contribution to $\sigma_{ext}$ and the single-scattering albedo (the ratio of scattering efficiency to total extinction efficiency) acquires its minimum (Fig. 1(a)).

To conclude, the properties of small metal particles continue to surprise. Whenever one thinks a full understanding has been reached, some unexpected connection, or an unnoticed property appears. We have demonstrated that at the size parameter value $x = 0.7$ the maximum of the absorption cross section $\sigma_{abs}$ can be appreciably blue shifted relative to the quasi-static position $\omega_{0q}$ of the dipole LSPR. An obvious consequence is that the maximum of $\sigma_{abs}$ can no longer be used as the definition of the LSPR position for $x > 0.7$. A threshold size parameter value required to exhibit a blue-shifted maximum of $\sigma_{abs}$ for an $\ell$-pole increases with increasing $\ell$. The latter causes a rearrangement of the natural order of $\ell$-pole absorption maxima (e.g. the lowest absorption peak of $\sigma_{abs}$ may be due to octupole ($\ell = 3$) as shown in Fig. 1(a)). The blue shift of absorption is possible only if $I_3(\bar{\epsilon}_s)$ at the frequency implicitly given by Eq. (11) is sufficiently small, as in the present case of Au nanoparticles. Our results bring us one step closer to an ideal world scenario, where one would be able to achieve a control over the position of maxima of basic cross-sections in order to better tailor nanoparticles to specific light-matter interaction applications. They could be of immediate interest not only for enhanced fluorescence [13], but also for nonlinear optics [6], surface enhanced Raman spectroscopy [22, 23], heat management, thermophotovoltaic, [23], but also for nonlinear optics [6], surface enhanced Raman spectroscopy [22, 23], heat management, thermophotovoltaic, [21], plasmonic heating [11], opto-plasmonic evaporation, or solar vapor generation enabled by nanoparticles [12].

It is worthwhile to mention that recent work [24] deals with a related issue within the electrostatic approximation (i.e. the Rayleigh limit), without any use of MLLWA, and without any comparison with the exact Mie results. Under these limitations, it is difficult to argue for a blue shift if already the well-known size-dependent red shift (10) relative to $\omega_{0q}$ cannot be properly accounted for.

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