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Simple accurate approximations for the optical properties of metallic nanospheres and nanoshells†

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This work aims to provide simple and accurate closed-form approximations to predict the scattering and absorption spectra of metallic nanospheres and nanoshells supporting localised surface plasmon resonances. Particular attention is given to the validity and accuracy of these expressions in the range of nanoparticle sizes relevant to plasmonics, typically limited to around 100 nm in diameter. Using recent results on the rigorous radiative correction of electrostatic solutions, we propose a new set of long-wavelength polarizability approximations for both nanospheres and nanoshells. The improvement offered by these expressions is demonstrated with direct comparisons to other approximations previously obtained in the literature, and their absolute accuracy is tested against the exact Mie theory.

1 Introduction

Small particles of noble metals in the size range of about 5 nm to 100 nm present unique optical characteristics, owing to the excitation of localised surface plasmon resonances (LSPRs). This resonant coupling between light and the free conduction electrons[1,2] is strongly dependent on the material properties—the plasma frequency of the metal[3,4] in particular—but also on the size and geometry of the nanoparticle, as well as the refractive index of the embedding medium.[5,6]

The excitation of LSPRs is readily observed in the far-field as a magnified interaction with the incident light, where both scattering and absorption cross-sections are greatly enhanced at resonance. Naturally, LSPRs also intensify the local electric field in close proximity to the metal surface. It is the combination of these two crucial features—amplification of the electromagnetic field and focussing of far-field radiation to subwavelength near-field regions—that justifies their use as "nanoantennas"[7,8] with a wide range of practical applications. The excitation of LSPRs is indeed crucial to the field of surface-enhanced Raman spectroscopy (SERS) and surface-enhanced fluorescence.[4,9,10] LSPRs can also be exploited for refractive-index sensing and bio-sensing (both relying on the large sensitivity of the LSPRs to changes in the surrounding medium),[11,12] and also for applications such as photo-thermal therapy[13,14] or imaging.[15]

The optical properties of the bulk metal, characterised by its dielectric function, partly determine: (i) the range of wavelengths over which LSPRs can be excited: it is always below the plasma frequency; and (ii) the strength or the quality factor of the resonance, related to the optical absorption at the resonance wavelength.[16] The majority of studies have focused on silver and gold as plasmonic materials, which exhibit the best optical properties in the visible/NIR range for this purpose. For example, silver nanoparticles can sustain intense LSPRs across the visible range. Gold is less suitable for applications in the blue/green part of the spectrum because of strong interband absorption, but offers performances comparable to silver in the red/NIR. Gold is in fact often preferred to silver in this range because of its greater chemical stability and biocompatibility. For a given metal, the key properties of the LSPR such as resonance wavelength and maximum field enhancement can be further tuned by changing the nanoparticle shape and size. Increasing the size results in a redshift of the resonance, also accompanied by a detrimental broadening and damping of the resonance.[17,18] Varying the particle shape allows for a much greater tunability of the resonance,[19] and methods for synthesis of metallic nanoparticles with a wide variety of shapes have been developed.[20–22]

An alternative approach to tuning the resonance is the use of composite particles, the simplest and most successful of which are dielectric–core/metal–shell structures, also called nanoshells. By altering the ratio of core-to-shell radii, the LSPR can be tuned over a large range,[23–25] while retaining the simple

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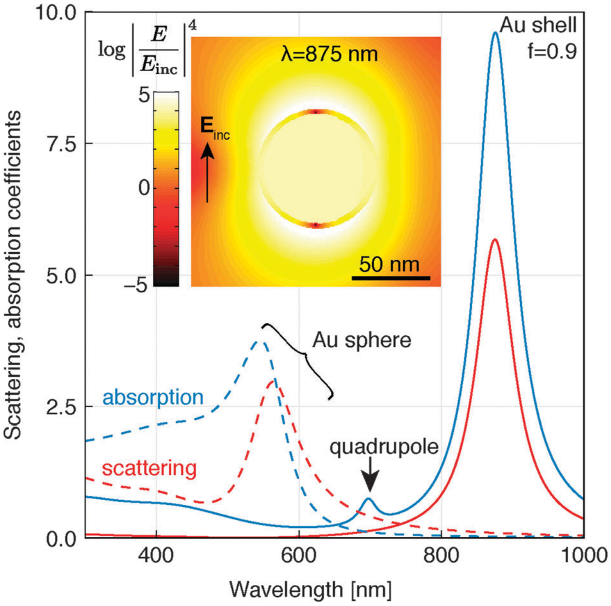

Fig. 1 Far-field scattering (red) and absorption (blue) spectra of a 40 nm radius gold nanosphere immersed in water (dashed lines), and a 40 nm gold nanoshell (solid lines) with a glass core (refractive index = 1.5, core-to-shell ratio $f = 0.9$). Scattering and absorption cross-sections are normalised by the geometrical cross-section. For both types of particles a strong peak in scattering and absorption is observed in the visible-NIR region of the spectrum, associated with the excitation of a dipolar plasmon resonance; the nanoshell has a resonance frequency red-shifted with respect to the homogeneous sphere, and its quality factor is enhanced. A small contribution from a quadrupolar resonance appears at around 700 nm for the nanoshell. The colormap displayed as an inset presents the SERS enhancement factor $|E/E_{inc}|^4$ in the vicinity of the nanoshell at resonance (λ = 875 nm). These graphs were produced with the freely available SERS and plasmonics codes for Matlab.[4,28]

spherical geometry, which facilitates both fabrication of uniform monodisperse solutions and interpretations of the results. Nanoshells have been used in various contexts, including SERS,[26] refractive index sensing,[27] and photothermal therapy.[13]

For applications and further developments, it is important to be able to theoretically understand and predict the optical properties of metallic nanoparticles, and much effort has been dedicated to this problem. For non-spherical particles, it is necessary to turn to numerical methods, such as finite-difference-time-domain (FDTD) simulations,[29] finite element modelling (FEM),[30] discrete-dipole approximation (DDA),[31,32] semi-analytic approaches like the T-matrix method,[18,33,34] or empirical approximations.[35] Nanospheres and nanoshells enjoy the advantage that they can be readily modelled in the exact framework of Mie theory.[2,36] Thanks to existing implementations (such as the SPlaC[4,28] used here), it is possible to predict with minimum time and effort all properties of such structures, including the details of the local field distribution, as shown in the example of Fig. 1. However, such implementations, although accurate and efficient, remain numerical in essence. Closed-form expressions, even approximate, are still important for developing a physical intuition about the system and for rapid and easy analysis of experimental data. In the case of nanoparticles, the small dimensions (of order a) compared to the wavelength (λ) present a natural route to such an approximation. Indeed the electrostatics or quasi-static approximation[1,2,36] provides a simple analytical expression for spheres (and nanoshells) that is valid in the limit of zero-size ($a/\lambda \to 0$)[37] and useful for qualitative understanding.

Attempts have been made to improve this approximation by expanding the solution of Mie theory to higher orders in the size parameter (a/λ), both for nanospheres[38,39] and nanoshells.[40,41] We however believe that none of these previous works have succeeded in providing expressions that are both relatively simple and accurate in the range of interest (*i.e.* for diameters up to $\approx$100 nm). Moreover, although several approximate expressions have been proposed, to the best of our knowledge a comparative analysis of their respective merits has not been carried out. We here argue that the choice of which expression is the most appropriate to use should be guided by:

• The accuracy of these expressions (or equivalently, their range of validity).

• The simplicity of the expressions; indeed there is no interest in finding an approximation that is as complicated to compute and manipulate as the original one.

• The compatibility with physical constraints. For example, we can compute within Mie theory the extinction and scattering coefficients Q_{ext} and Q_{sca}, from which the absorption coefficient is derived as $Q_{abs} = Q_{ext} - Q_{sca}$. The latter must be zero for non-absorbing spheres and positive otherwise. If Q_{abs} is small, an approximation may accurately predict Q_{ext} and Q_{sca}, but predict a non-physical negative Q_{abs}, and such a situation is clearly not desirable as it violates energy conservation.

In fact, most of the expressions so far proposed in the literature for nanospheres and nanoshells fail one or more of these three criteria.

In this article, we compare the accuracy of a number of possible small-size expansions of the Mie coefficients to predict far-field optical properties (extinction, scattering, and absorption) of metallic nanospheres. We in particular highlight how various forms of these expansions can be written, which, although equivalent to a given order, vary significantly in their accuracy for predicting LSPR properties. We also use recent developments in the understanding of the radiative correction[39,42] to propose simple and accurate new expressions for nanospheres, and study their range of validity. These results are then extended to the case of nanoshells. These expressions should prove very useful for a quick comparison with experimental results and may provide further physical insight into the behaviour of LSPR in nanospheres and nanoshells.

2 Metallic nanospheres

2.1 Brief review of Mie theory

Without going into the full details of Mie theory (see *e.g.* Ch. 4 in ref. 2 or App. H in ref. 4), we first define for completeness the main notations and recall the expressions most relevant to this work.

We consider first a homogeneous, non-magnetic and isotropic sphere of radius a with relative dielectric function ε_s

(possibly complex and wavelength dependent) in a non-absorbing embedding medium of relative dielectric constant ε_m (which is real and positive and $\varepsilon_m = n_m^2$, where n_m is the refractive index) and define the relative refractive index as:

$$s = \frac{\sqrt{\varepsilon_s}}{\sqrt{\varepsilon_m}}. \quad (1)$$

For time-harmonic excitation at wavelength λ, the wave-vector in the medium is $k = 2\pi\sqrt{\varepsilon_m}/\lambda$ and we define the dimensionless size parameter x,

$$x = ka = 2\pi\sqrt{\varepsilon_m}\frac{a}{\lambda}. \quad (2)$$

In this work, we will only consider silver and gold spheres, and use for $\varepsilon_s(\omega)$ the corresponding bulk dielectric functions, given by analytical fits to experimental data as given in ref. 4, 43 and 44. Note that any small-size effects[2] on ε_s are neglected for simplicity. It would however be straightforward to include, for example, electron surface scattering effects[45,46] within our formalism.

The optical response of the sphere is then entirely defined by the Mie susceptibilities Γ_n and Δ_n (note that $n = 1,2,\ldots$ defines the multipole order), which will be conveniently expressed here as:

$$\Gamma_n = -C_n^{\psi}/C_n^{\xi}, \quad \Delta_n = -D_n^{\psi}/D_n^{\xi}, \quad (3)$$

where

$$C_n^{\psi} = s\psi_n(x)\psi_n'(sx) - \psi_n'(x)\psi_n(sx), \quad (4)$$

$$C_n^{\xi} = s\xi_n(x)\psi_n'(sx) - \xi_n'(x)\psi_n(sx), \quad (5)$$

$$D_n^{\psi} = \psi_n(x)\psi_n'(sx) - s\psi_n'(x)\psi_n(sx), \quad (6)$$

$$D_n^{\xi} = \xi_n(x)\psi_n'(sx) - s\xi_n'(x)\psi_n(sx). \quad (7)$$

The functions $\psi_n(x)$, $\chi_n(x)$, and $\xi_n(x)$ are the Riccati–Bessel functions[2] defined in terms of the spherical Bessel and Hankel functions as:

$$\psi_n(x) = xj_n(x), \quad \chi_n(x) = xy_n(x), \quad (8)$$

$$\xi_n(x) = xh_n^{(1)}(x) = \psi_n(x) + i\chi_n(x). \quad (9)$$

In the standard case of plane wave excitation, the extinction, scattering, and absorption coefficients (*i.e.* cross-sections normalised to the geometrical cross-section) are obtained as:

$$Q_{\rm ext} = -\frac{2}{x^2}\sum_n (2n+1)[\mathrm{Re}(\Gamma_n) + \mathrm{Re}(\Delta_n)], \quad (10)$$

$$Q_{\rm sca} = \frac{2}{x^2}\sum_n (2n+1)\left[|\Gamma_n|^2 + |\Delta_n|^2\right], \quad (11)$$

$$Q_{\rm abs} = Q_{\rm ext} - Q_{\rm sca} = -\frac{2}{x^2}\sum_n (2n+1) \times \left[|\Gamma_n|^2\mathrm{Re}\left(1+\Gamma_n^{-1}\right) + |\Delta_n|^2\mathrm{Re}\left(1+\Delta_n^{-1}\right)\right]. \quad (12)$$

The latter equation is a consequence of energy conservation,[2] expressed as $Q_{\rm ext} = Q_{\rm sca} + Q_{\rm abs}$. For physical solutions, we must have $Q_{\rm abs} \geq 0$ for any type of incident excitation, which is equivalent to:[47]

$$1 + \mathrm{Re}(\Delta_n^{-1}) \leq 0 \quad (13)$$

(and an identical relation for Γ_n) with the equality for non-absorbing spheres (for which s is real).

2.2 Small sphere expansions and radiative corrections

There have been many attempts to find suitable small-argument expansions of these susceptibilities, notably in the context of plasmonics for the study of localised surface plasmon resonances (LSPR) in metallic nanospheres, where $|s|$ may be relatively large. As $x \to 0$, one can show that the susceptibilities scale as

$$\Gamma_n \propto x^{2n+3}, \quad \Delta_n \propto x^{2n+1}. \quad (14)$$

The dominant contribution is therefore governed by Δ_1 (electric dipole) of order x^3, the lowest term of which corresponding to the quasi-static approximation.[2] The next lowest order includes contribution from Δ_2 (electric quadrupole) and Γ_1 (magnetic dipole), both of order x^5. All other terms are of order at least x^7. The far field properties may therefore be approximated as:

$$Q_{\rm ext} = -\frac{2}{x^2}\mathrm{Re}(3\Delta_1 + 3\Gamma_1 + 5\Delta_2 + O(x^7)) \quad (15)$$

$$Q_{\rm sca} = \frac{2}{x^2}\left[3|\Delta_1|^2 + 3|\Gamma_1|^2 + 5|\Delta_2|^2 + O(x^7)\right]. \quad (16)$$

When carrying out approximations of the susceptibilities, it is important for physical reasons to retain the validity of the energy conservation condition given above (eqn (13)). In order to enforce this condition, we first write (a similar argument is valid for Γ_n):

$$1 + \frac{1}{\Delta_n} = \frac{i}{\Delta_n^{\chi}}, \quad (17)$$

where we have defined

$$\Delta_n^{\chi} = -\frac{D_n^{\psi}}{D_n^{\chi}}, \quad (18)$$

similar to Δ_n, except for the substitution of ξ by χ, *i.e.* $D_n^{\chi} = \chi_n(x)\psi_n'(sx) - s\chi_n'(x)\psi_n(sx)$. The energy conservation condition (eqn (13)) is then expressed conveniently as:

$$\mathrm{Im}(\Delta_n^{\chi}) \leq 0 \quad (= 0 \text{ for } s \text{ real}). \quad (19)$$

In the special case of a non-absorbing scatterer (s real) $\chi(sx)$ is also real, and the latter condition, which reduces to Δ_n^{χ} real, is therefore trivially satisfied by inspection of eqn (18). It is not so obvious to show that the equivalent expression on Δ_1 (eqn (13)) is also satisfied. We have therefore argued recently[42] that this alternative condition is much easier to check in approximate treatments, and it provides a simple procedure for finding approximations of the susceptibility that satisfy energy conservation, namely: first find an approximation of $\Delta_n^{\chi} \approx \tilde{\Delta}_n^{\chi}$ that satisfies eqn (19) (at least in the desired range of validity), and then deduce the approximate Δ_n^{RC} from eqn (17), or explicitly:

$$\Delta_n^{\mathrm{RC}} = \left(-1 + \frac{i}{\tilde{\Delta}_n^{\chi}}\right)^{-1}. \tag{20}$$

We will demonstrate in the following sections that this operation improves the accuracy of approximate polarizability expressions. This procedure is in fact a generalisation of the commonly used radiative correction, previously introduced for a dipole,[39] and is a special case of a recently proposed general formalism for radiative corrections applicable to arbitrary scatterers.[42]

2.3 Electric dipole contribution

For metallic nanospheres, the optical response is largely dominated by a main dipolar LSPR, described by Δ_1 and it is therefore interesting to consider its approximation independently of the other terms. Its resonant character is evident in the wavelength-dependence of the far-field properties, given by:

$$Q_{\mathrm{ext}} \approx -\frac{6}{x^2}\mathrm{Re}(\Delta_1) \tag{21}$$

$$Q_{\mathrm{sca}} \approx \frac{6}{x^2}|\Delta_1|^2 \tag{22}$$

The full expression for Δ_1 in terms of trigonometric functions is given in Section SII† for reference. The lowest order approximation to Δ_1 is

$$\Delta_1^{(0)} = \frac{2i}{3}\frac{s^2-1}{s^2+2}x^3, \tag{23}$$

which is simply equivalent to the electrostatics approximation (recall that $s^2 = \varepsilon_s/\varepsilon_m$).

However, as highlighted in ref. 42, this approximation is only valid up to very small sizes of $\approx$5 nm for metallic spheres, and in fact violates the optical theorem (it predicts a negative absorption) as x increases.[47] Moreover, since the electrostatics approximation is size-independent (apart from a trivial scaling factor), it does not predict the redshift and broadening of the LSPR as the size increases, which originates from radiation damping and a gradual dephasing of the field across the particle.[48] The radiative correction to this dipolar polarizability can be obtained from the earlier considerations by noticing that the lowest order approximation to Δ_1^{χ} is simply $\tilde{\Delta}_1^{\chi} \approx i\Delta_1^{(0)}$, since $\Delta_1^{(0)}$ is of lowest order x^3 in eqn (17). Substituting this into eqn (20), we obtain the radiative correction to Δ_1 at lowest order as

$$(\Delta_1^{(0)-\mathrm{RC}})^{-1} = (\Delta_1^{(0)})^{-1} - 1, \tag{24}$$

which can be written in the more familiar form

$$\Delta_1^{(0)-\mathrm{RC}} = \frac{\Delta_1^{(0)}}{1-\Delta_1^{(0)}}. \tag{25}$$

This formula is equivalent to the one proposed by Wokaun and coworkers;[39] the radiative correction of the lowest order polarizability presents a characteristic term $\Delta_1^{(0)}$ of relative order x^3 in the denominator. However, as pointed out in ref. 42, the improvement is marginal and not quantitative. It corrects the problem of negative absorption as expected, but does not predict the observable size-induced redshift of the LSPR.

Higher order expansions, up to third relative order, have therefore been proposed, notably:[35]

$$\Delta_1^{\mathrm{A}} = \Delta_1^{(0)}\frac{1-\frac{x^2}{10}(s^2+1)+O(x^4)}{1-\frac{x^2}{10}\frac{s^2-1}{s^2+2}(s^2+10)-\Delta_1^{(0)}+O(x^4)}. \tag{26}$$

In this expression, the Taylor expansions of the numerator and the denominator are each exact to order 3. However, other equally valid expansions to the same order could be obtained, for example:[4]

$$\Delta_1^{\mathrm{B}} = \Delta_1^{(0)}\frac{1}{1-\frac{3x^2}{5}\frac{s^2-2}{s^2+2}-\Delta_1^{(0)}+O(x^4)}, \tag{27}$$

which corresponds to a Taylor expansion of Δ_1^{-1}, or

$$\Delta_1^{\mathrm{C}} = \Delta_1^{(0)}\left[1+\frac{3x^2}{5}\frac{s^2-2}{s^2+2}+\Delta_1^{(0)}+O(x^4)\right], \tag{28}$$

which corresponds to a direct Taylor expansion of Δ_1. Another alternative, which amounts to a partial re-arrangement of Δ_1^{A} has also been proposed:[38,48]

$$\Delta_1^{\mathrm{D}} = \Delta_1^{(0)}\frac{1-\frac{x^2}{10}+O(x^4)}{1-\frac{x^2}{10}\frac{7s^2-10}{s^2+2}-\Delta_1^{(0)}+O(x^4)} \tag{29}$$

It is interesting to note that all these expressions are equivalent to third relative order, *i.e.* they only differ in terms of fourth relative order or higher (see also the general discussion of Taylor expansions in Section SI†). Which one of these expansions, if any, best describes the LSPR and is the most physical, is an important question, which has not been investigated. In terms of predicting the far-field properties of metallic nanospheres, case C fails badly even for the smallest sizes (not shown here). As shown in Fig. 2, cases A and B seem to have a larger range of validity, up to $a \approx$ 20–30 nm, but then fail to predict the correct redshift for B or the correct magnitude for A. Case D (not shown here) is similar to case B (although marginally worse). In fact, even if expressions A, B, and D contain a term in the denominator of order x^3 corresponding to the radiative correction of the lowest order term, closer inspection reveals that cases A and D do not strictly satisfy eqn (13). This is also evident in the negative absorption predicted at larger sphere sizes (see Fig. 2).

Interestingly, case B, which corresponds to a Taylor expansion of $(\Delta_1^{\chi})^{-1}$ to order 5 (second relative order) followed by the radiative correction as given by eqn (20), does satisfy exactly

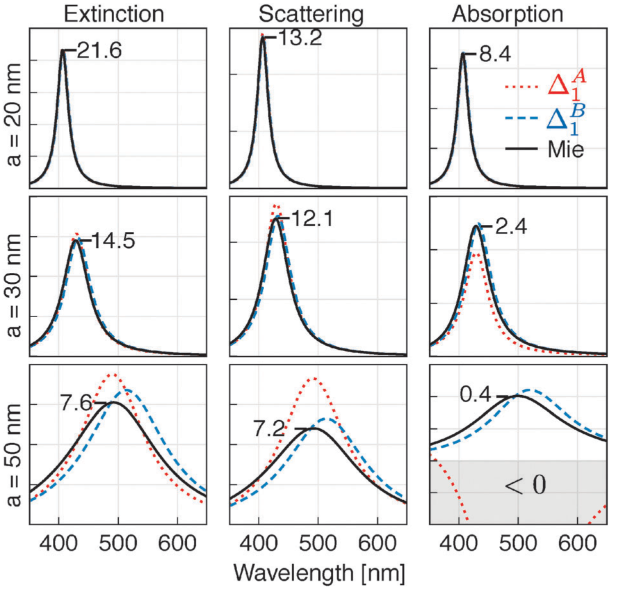

Fig. 2 Predictions of the dipolar localised surface plasmon resonance for a silver nanosphere in water, as evidenced by the wavelength dependence of the far-field properties: extinction, scattering, and absorption. Only the dominant electric dipole response (corresponding to Δ_1) was included in these calculations. We compare the exact result (bold/black lines) with the approximate results using Δ_1^{A} from eqn (26) (red/dotted lines) and Δ_1^{B} from eqn (27) (blue/dashed lines). The vertical scales have been adjusted in each panel to improve the visualisation; the magnitude of the maximum Q_{ext}, Q_{sca}, and Q_{abs} in each case is indicated for information.

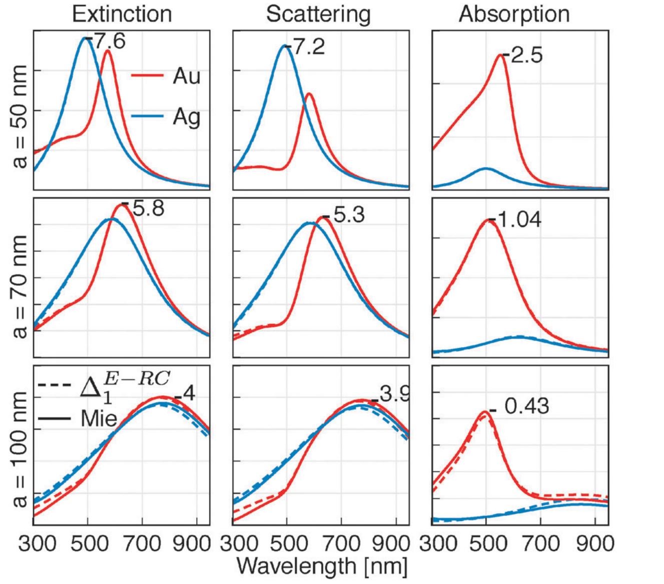

Fig. 3 Predictions of the dipolar localised surface plasmon resonance for silver (blue) and gold (red) nanospheres in water, as evidenced by the wavelength dependence of the far-field properties: extinction, scattering, and absorption. Only the dominant electric dipole response (corresponding to Δ_1) was included in these calculations. We compare the exact result (solid lines) with the simple fourth order approximation proposed in this work $\Delta_1^{E-\mathrm{RC}}$ from eqn (32) (dashed lines).

eqn (13) for all s and x. To see this, one may notice that we have in this case

$$\tilde{\Delta}_1^{\chi} = -\frac{2}{3}x^3\frac{s^2-1}{s^2+2-\dfrac{3}{5}x^2(s^2-2)}. \qquad (30)$$

For s real, it is obvious that $\tilde{\Delta}_1^{\chi}$ is real. It is also possible to show that $\mathrm{Im}(\tilde{\Delta}_1^{\chi}) \leq 0$ provided that $\mathrm{Im}(s^2) \geq 0$ (which is the case for materials with no gain). Eqn (19) is therefore satisfied by the approximated $\tilde{\Delta}_1^{\chi}$, which automatically implies eqn (13) for $\Delta_1^{\mathrm{B}} = -i\tilde{\Delta}_1^{\chi}/(1 + i\tilde{\Delta}_1^{\chi})$ derived from eqn (20). Case B is therefore arguably the most physical approximate expression of the susceptibility that has been proposed when restricting oneself to third relative order expansions.

Ideally, an approximation valid up to at least $a \approx 50$ nm would be desirable to cover the majority of relevant experimental cases in plasmonics. We therefore seek to extend the approximation obtained for Δ_1^{B} to fourth relative order. Writing first $(\Delta_1^{\chi})^{-1}$ as:

$$\frac{1}{\Delta_1^{\chi}} = \frac{1}{i\Delta_1^{(0)}}\left[1 - \frac{3x^2}{5}\frac{s^2-2}{s^2+2} - \frac{3x^4}{350}\frac{s^4-24s^2+16}{s^2+2} + O(x^6)\right], \qquad (31)$$

and applying the radiative correction formula (eqn (20)), we get:

$$\Delta_1^{E-\mathrm{RC}} = \frac{\Delta_1^{(0)}}{1 - \dfrac{3x^2}{5}\dfrac{s^2-2}{s^2+2} - \Delta_1^{(0)} - \dfrac{3x^4}{350}\dfrac{s^4-24s^2+16}{s^2+2}}, \qquad (32)$$

or, substituting the value of $\Delta_1^{(0)}$:

$$\Delta_1^{E-\mathrm{RC}} = \frac{\dfrac{2}{3}ix^3(s^2-1)}{s^2+2-\dfrac{3x^2}{5}(s^2-2)-\dfrac{2}{3}ix^3(s^2-1)-\dfrac{3x^4}{350}(s^4-24s^2+16)}. \qquad (33)$$

As shown in Fig. 3, this relatively simple formula predicts almost perfectly the dipolar LSP resonance profiles of extinction, scattering and absorption of silver and gold nanospheres up to a diameter of at least $2a$ = 140 nm and even semi-quantitatively up to $2a$ = 200 nm. While the exact Mie coefficient for the dipolar term could also be calculated with simple trigonometric functions (see Section SII†), the polynomial expansion given in eqn (33) can provide a more direct assessment of the different correction terms in connection to the electrostatic result, as a function of the size parameter.

2.4 Higher order multipoles

We have so far considered only the optical response associated with the electric dipole term Δ_1, which is dominant for small spheres. However, for sphere sizes increasing up to $a \approx 50$ nm, the electric quadrupole Δ_2 and magnetic dipole Γ_1 terms are no longer negligible in metal particles. Their respective lowest order expansions have also been considered in approximate treatment of nanospheres.[17,38] These are:

$$\Delta_2^{(0)} = \frac{i}{30}\frac{s^2-1}{s^2+3/2}x^5, \qquad (34)$$

and

$$\Gamma_1^{(0)} = \frac{i}{45}(s^2 - 1)x^5. \quad (35)$$

Note that for metallic spheres, $\Delta_2^{(0)}$ exhibits a resonance for $\mathrm{Re}(s^2) = -3/2$, corresponding to the quadrupolar LSPR, but $\Gamma_1^{(0)}$ has no such feature.[2] As a result, the latter is for most purposes negligible. It is only when the LSP resonances are strongly damped (*e.g.* for larger gold particles with resonances below 550 nm) that it may be worth including it in the approximation. In such cases, one could use the radiatively-corrected lowest order approximation:

$$\Gamma_1^{(0)-\mathrm{RC}} = \frac{\frac{i}{45}(s^2-1)x^5}{1 - \frac{i}{45}(s^2-1)x^5}. \quad (36)$$

As for Δ_1, the lowest order approximation $\Delta_2^{(0)}$ fails pretty rapidly as the size increases, even when including a radiative correction. Following the previous procedure, we therefore expand to next order to get

$$(\Delta_2^{\chi})^{-1} = \left(i\Delta_2^{(0)}\right)^{-1} \times \left[1 + \frac{5}{14}x^2\frac{1}{s^2+3/2} + O(x^4)\right], \quad (37)$$

and apply the radiative correction formula (eqn (20)) to obtain:

$$\Delta_2 \approx \frac{\frac{1}{30}ix^5(s^2-1)}{s^2 + 3/2 + \frac{5x^2}{14} - i\frac{x^5}{30}(s^2-1)}. \quad (38)$$

Note that the x^5 term in the denominator is the radiative correction terms and is here necessary (even if some lower order x^4 term have been neglected) to ensure that the optical theorem is satisfied. This approximation is accurate for gold spheres in water up to a = 50 nm and silver spheres in water up to a = 25 nm.

Perhaps unexpectedly, it is necessary to go to an even higher order to model accurately the quadrupolar LSP of larger silver spheres (a > 25 nm). We then need to use:

$$\Delta_2 \approx \frac{\frac{1}{30}ix^5(s^2-1)}{s^2 + 3/2 + \frac{5x^2}{14} - \frac{5x^4}{2646}(s^4 + 30s^2 - 45) - i\frac{x^5}{30}(s^2-1)}. \quad (39)$$

In such nanospheres, the octupolar LSPR, characterised by Δ_3 is also visible in the far-field properties. In most cases of interest, its contribution is neglected, but we nevertheless include its expansion here for completeness. As for the dipolar and quadrupolar cases, an expansion to fourth relative order is necessary to account properly for the size-induced redshift, and we therefore have (including radiative correction):

$$\Delta_3 \approx \frac{\frac{4}{4725}ix^7(s^2-1)}{s^2 + 4/3 + \frac{7x^2}{135}(s^2+4) - \frac{7x^4}{10\,692}(s^4 + 8s^2 - 32) - i\frac{4x^7}{4725}(s^2-1)}. \quad (40)$$

The validity of these approximations is illustrated in Fig. 4 by comparison with exact results from Mie theory for silver nanospheres in water. We find that it is not necessary to include the magnetic dipole term (Γ_1) as the LSP resonances strongly dominate the spectra. As shown in Fig. 3, the dipolar LSP resonance is well described by Δ_1 approximated by eqn (33), but higher order resonances must be included to describe accurately the overall spectrum. Adding the electric quadrupole term (Δ_2, approximated by eqn (39)) is sufficient up to at least a = 30 nm, but for a = 50 nm and above, one may also want to add the octupolar term (Δ_3, approximated by eqn (40)), in particular to model the absorption cross-section. The approximated expressions are found to be in excellent agreement up to at least a = 50 nm and in reasonable agreement up to a = 70 nm.

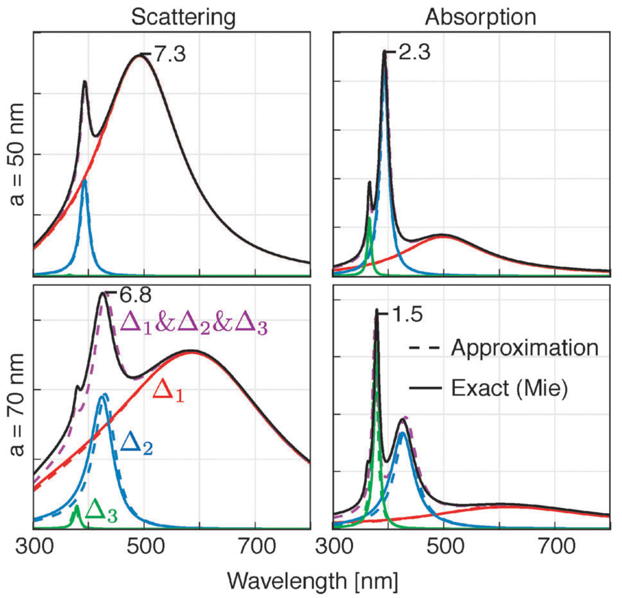

Fig. 4 Predicted far-field spectra of the scattering and absorption coefficients of silver nanospheres in water. Exact results (solid lines) are obtained from Mie theory while the approximated results (dashed lines) are obtained from the expressions obtained in this work. The terms included in the approximation correspond to the electric dipole Δ_1 (approximated by eqn (33)), electric quadrupole Δ_2 (eqn (39)), and electric octupole Δ_3 (eqn (40)). The black solid line is the converged Mie solution including multipoles of all orders, shown for comparison.

In the case of gold nanospheres in water (see Fig. S2†), only the electric dipole term (Δ_1, approximated by eqn (33)) needs to be included, as the higher order resonances are strongly damped by the large absorption below ~550 nm. One may also include the magnetic dipole term (Γ_1, approximated by eqn (36)) for a slightly better quantitative agreement. The proposed approximation of the far field properties is then extremely good up to a = 50 nm (100 nm diameter), and even to some extent up to a = 70 nm, where it only fails to predict the absorption coefficient.

3 Nanoshells

3.1 General principle

We now show how these arguments can be extended to the more complicated case of a nanoshell, *i.e.* a composite scatterer

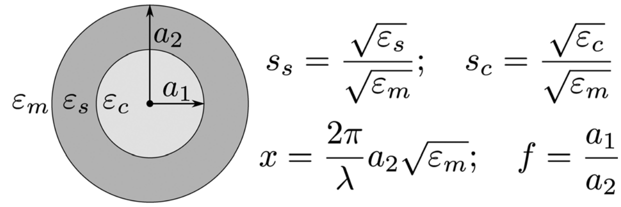

Fig. 5 The geometry of a nanoshell, defined by two concentric spherical surfaces partitioning space into three disjointed regions. The core (ε_c), the shell (ε_s) and the outer medium (ε_m) are each characterised by a distinct dielectric constant. We also define reduced variables used in the text.

consisting of two concentric spheres as illustrated in Fig. 5. The exact solution can be found again from a simple extension of Mie theory to the case of multiple spherical interfaces.[49] More elaborate models have also been used to study non-local effects.[50] Taylor expansions of the Mie solution have been provided by Alam and Massoud,[40] and further developed by Li *et al.*[41] In both of these studies, no attempts were made to find the simplest, most accurate expansions at a given (low) order. As a result, the approximate expressions end up being more complicated than the original expressions they approximate. To remedy this problem, we here use what we have learnt in the previous section in the case of nanospheres to obtain both simple and accurate expressions. We will in particular carry out Taylor expansions of the *inverse* susceptibilities, and apply again the concept of radiative correction.[42] Moreover, in ref. 40 and 41 Taylor expansions are carried out with respect to both sphere radii, a_1 and a_2, which makes it very difficult to isolate the electrostatics limit ($a_1, a_2 \to 0$ with a_1/a_2 constant). In fact, expansions to third relative order are then necessary to obtain the electrostatics limit. We here instead consider a fixed ratio $f = a_1/a_2$, which defines the internal structure of the nanoshell, and carry out expansion with respect to the overall nanoshell size characterized by a_2, at a fixed f. The electrostatics limit then arises naturally as the lowest order term. This considerably simplifies the expressions obtained, and their use for further physical analysis of the scattering problem.

The validity of the obtained expressions will be tested for model structures of interest: silica core (refractive index of 1.5)/metal shell (silver or gold).

3.2 Mie theory solution for nanoshells

We consider a spherical shell (see Fig. 5), characterised by two concentric radii $a_1 < a_2$ and three dielectric constants ε_c (core), ε_s (shell) and ε_m (embedding medium). The size-independent internal structure is determined by the filling ratio $f = a_1/a_2 \in (0,1)$. The size parameter is determined by the outer radius and defined as $x = 2\pi a_2\sqrt{\varepsilon_m}/\lambda$ and for a fixed f corresponds to uniform scaling of the entire particle. We also define relative refractive indices $s_s = \sqrt{\varepsilon_s}/\sqrt{\varepsilon_m}$ and $s_c = \sqrt{\varepsilon_c}/\sqrt{\varepsilon_m}$. For simplicity, we focus here only on the electric Mie susceptibilities, denoted by δ_n:[4,40,41]

$$\left.\begin{aligned} \delta_n \quad & n_n^{\xi}/d_n^{\xi}, \\ n_n^{\xi} &= \psi_n(x)\left[\psi_n'(s_s x) + \Delta_n(s_1,x_1)\xi_n'(s_s x)\right] \\ &\quad - s_s[\psi_n(s_s x) + \Delta_n(s_1,x_1)\xi_n(s_s x)]\psi_n'(x), \\ d_n^{\xi} &= s_s[\psi_n(s_s x) + \Delta_n(s_1,x_1)\xi_n(s_s x)]\xi_n'(x) \\ &\quad - \xi_n(x)\left[\psi_n'(s_s x) + \Delta_n(s_1,x_1)\xi_n'(s_s x)\right], \end{aligned}\right\} \tag{41}$$

where $\Delta_n(s_1,x_1)$ is the single-sphere Mie susceptibility of the core sphere embedded in an infinite shell, *i.e.* eqn (3) with $x_1 = fs_s x$, $s_1 = s_c/s_s$.

One may notice that the four expressions in brackets can be simplified as for example: $[\psi_n(s_s x) + \Delta_n(s_1,x_1)\xi_n(s_s x)] = i[\psi_n(s_s x) + \Delta_n^{\chi}(s_1,x_1)\chi_n(s_s x)]$, *i.e.* this amounts to replacing ξ by $i\chi$. Since χ has a simpler Taylor expansion than ξ (for example it has a well-defined parity, but not ξ), it is beneficial here to use this equivalent formulation.

Moreover, following the method we used for spheres for radiative correction, we will also rewrite the electric susceptibility of the nanoshell as:

$$(\delta_n)^{-1} = -1 + i(\delta_n^{\chi})^{-1}, \tag{42}$$

where δ_n^{χ} can be expressed as:

$$\left.\begin{aligned} \delta_n^{\chi} &= n_n^{\chi}/d_n^{\chi}, \\ n_n^{\chi} &= \psi_n(x)\left[\psi_n'(s_s x) + \Delta_n^{\chi}(s_1,x_1)\chi_n'(s_s x)\right] \\ &\quad - s_s\left[\psi_n(s_s x) + \Delta_n^{\chi}(s_1,x_1)\chi_n(s_s x)\right]\psi_n'(x), \\ d_n^{\chi} &= s_s\left[\psi_n(s_s x) + \Delta_n^{\chi}(s_1,x_1)\chi_n(s_s x)\right]\chi_n'(x) \\ &\quad - \chi_n(x)\left[\psi_n'(s_s x) + \Delta_n^{\chi}(s_1,x_1)\chi_n'(s_s x)\right]. \end{aligned}\right\} \tag{43}$$

3.3 Lowest order and electrostatics approximation

Assuming the particle is small compared to the wavelength in the incident medium, we now seek approximate expressions to the dipolar electric susceptibility δ_1 by means of Taylor expansion about $x = 0$. The general procedure for this is detailed in Section SIV.†

It can be shown that the lowest order approximation to δ_1 is

$$\delta_1^{(0)} = \frac{2i}{3}\left[\frac{s_s{}^2\varepsilon_a - \varepsilon_b}{s_s{}^2\varepsilon_a + 2\varepsilon_b}\right]x^3, \tag{44}$$

where

$$\left.\begin{aligned} \varepsilon_a &= s_c{}^2(1+2f^3) + 2s_s{}^2(1-f^3), \\ \varepsilon_b &= s_c{}^2(1-f^3) + s_s{}^2(2+f^3), \end{aligned}\right\} \tag{45}$$

which is equivalent to the electrostatic expression obtained by Averitt *et al.*[45] (hence the nomenclature). Note that when: (i) $f = 0$, $s_s = s$; (ii) $s_s = s_c = s$; and (iii) $f = 1$, $s_c = s$, we should recover $\Delta_1^{(0)}$ given in eqn (23). To make this more explicit, we define the ratio:

$$r = \frac{\varepsilon_a}{\varepsilon_b}, \tag{46}$$

and rewrite $\delta_1^{(0)}$ as

$$\delta_1^{(0)} = \frac{2i}{3}\left[\frac{r{s_s}^2 - 1}{r{s_s}^2 + 2}\right]x^3. \tag{47}$$

Since $r = 1$ if $f = 0$ or $s_s = s_c$, and $r{s_s}^2 = {s_c}^2$ if $f = 1$, these three special cases reduce naturally to $\Delta_1^{(0)}$, as expected.

A similar method applied to the electric quadrupolar susceptibility δ_2 yields:

$$\delta_2^{(0)} = \frac{i}{30}\left[\frac{{s_s}^2\tilde{\varepsilon}_a - \tilde{\varepsilon}_b}{{s_s}^2\tilde{\varepsilon}_a + \frac{3}{2}\tilde{\varepsilon}_b}\right]x^5 = \frac{i}{30}\left[\frac{\tilde{r}{s_s}^2 - 1}{\tilde{r}{s_s}^2 + \frac{3}{2}}\right]x^5, \tag{48}$$

where

$$\left.\begin{aligned} \tilde{r} &= \tilde{\varepsilon}_a/\tilde{\varepsilon}_b, \\ \tilde{\varepsilon}_a &= {s_c}^2\left(2 + 3f^5\right) + 3{s_s}^2\left(1 - f^5\right), \\ \tilde{\varepsilon}_b &= 2{s_c}^2\left(1 - f^5\right) + {s_s}^2\left(3 + 2f^5\right). \end{aligned}\right\} \tag{49}$$

Again note that $\tilde{r} = 1$ if $f = 0$ or $s_s = s_c$, and $r{s_s}^2 = {s_c}^2$ if $f = 1$, so that setting: (i) $f = 0$, $s_s = s$; (ii) $s_s = s_c = s$; and (iii) $f = 1$, $s_c = s$ in eqn (48) and (49) naturally yields the expression for $\Delta_2^{(0)}$ obtained earlier in eqn (34) as expected.

3.4 Higher order corrections

As for the sphere, the lowest order approximations rapidly fail as the nanoshell size increases. There are many possible routes to obtaining higher-order polynomial approximations to δ_1. Alam and Massoud[40] and Li *et al.*[41] heroically derived analytic expressions for δ_1 by Taylor expansion of the numerator and the denominator, each up to the sixth order in both a_1 and a_2. Although this procedure yields results that are close to the exact Mie theory, it involves cumbersome polynomials that are not really *easier* to deal with than the exact expressions. By following the procedure used for spheres and expanding only in x (at a fixed f), we can derive considerably simpler yet accurate expressions. The derivation involves expanding first $(\delta_1^\chi)^{-1}$ as:

$$\left(\delta_1^\chi\right)^{-1} = \left(i\delta_1^{(0)}\right)^{-1}\left[1 - \frac{3}{5}\alpha_1 x^2 + O\left(x^4\right)\right]. \tag{50}$$

The factor $-3/5$ is included by analogy with the sphere result (eqn (27)). Part of the difficulty here is to write α_1 in a form that is simple enough to be usable. To this end, we chose to reuse the expressions already defined in the electrostatics approximation, and in particular express the results in terms of r as before. We obtained:

$$\alpha_1 = \frac{\left({s_s}^2 - 1\right)\left[(3r - 2){s_s}^2 - 2\right] + \frac{3f^2{s_s}^4}{\varepsilon_b}(r - 1)\left({s_c}^2 - 2{s_s}^2\right)}{\left(r{s_s}^2 - 1\right)\left(r{s_s}^2 + 2\right)}. \tag{51}$$

Note that for $r = 1$ (*i.e.* if $f = 0$ or $s_c = s_s$), we directly recover the sphere result (eqn (27)). If $f = 1$, then $r{s_s}^2 = {s_c}^2$ and $3f^2{s_s}^4/\varepsilon_b = {s_s}^2$, so the sphere result is also recovered after simple algebraic simplifications.

After radiative correction, the Mie susceptibility therefore has the form (correct to third relative order):

$$\delta_1^{RC} = \frac{\delta_1^{(0)}}{1 - \frac{3x^2}{5}\alpha_1 - \delta_1^{(0)}}, \tag{52}$$

or explicitly:

$$\delta_1^{RC} = \frac{\frac{2i}{3}x^3\left(r{s_s}^2 - 1\right)}{r{s_s}^2 + 2 - \frac{3x^2}{5}\frac{\left({s_s}^2 - 1\right)\left[(3r - 2){s_s}^2 - 2\right] + \frac{3f^2{s_s}^4}{\varepsilon_b}(r - 1)\left({s_c}^2 - 2{s_s}^2\right)}{\left(r{s_s}^2 - 1\right)} - \frac{2i}{3}x^3\left(r{s_s}^2 - 1\right)}. \tag{53}$$

As illustrated in Fig. 6, this second order approximation predicts almost exactly the dipolar LSP resonances of silver nanoshells up to at least $a_2 = 30$ nm, for all values of the filling factor f. However, as for nanospheres, the approximation loses accuracy for nanoshells of radius $a_2 = 50$ nm, except in the case of thin shells (f close to 1), where it remains valid. We therefore also provide for completeness the expression for the fourth-order correction of the dipolar susceptibility of nanoshells, following the same method as that used for the second order (see Section SIV† for details). We obtained:

$$\delta_1^{RC} = \frac{\delta_1^{(0)}}{1 - \frac{3x^2}{5}\alpha_1 - \frac{3}{350}\alpha_2 x^4 - \delta_1^{(0)}}, \tag{54}$$

where

$$\begin{aligned} \alpha_2 = {} & \frac{1}{(r{s_s}^2 - 1)(r{s_s}^2 + 2)} \\ & \times\Bigg\{\frac{{s_s}^2 - 1}{2}\left[(43r^2 - 73r + 32){s_s}^4 + (25 - 73r){s_s}^2 + 32\right] \\ & + \frac{3f^4{s_s}^4}{\varepsilon_b}(r - 1)({s_c}^4 - 24{s_c}^2{s_s}^2 + 16{s_s}^4) \\ & + \frac{126{s_s}^2({s_s}^2 - 1)(r - 1)}{r{s_s}^2 - 1}\left[\frac{1}{6}((4 - 3r){s_s}^2 + 1) + \frac{f^2{s_s}^2}{\varepsilon_b}({s_c}^2 - 2{s_s}^2)\right]^2\Bigg\} \end{aligned} \tag{55}$$

This expression is then very accurate (see Fig. 6) up to at least $a_2 = 70$ nm for all types of nanoshells (low and large f).

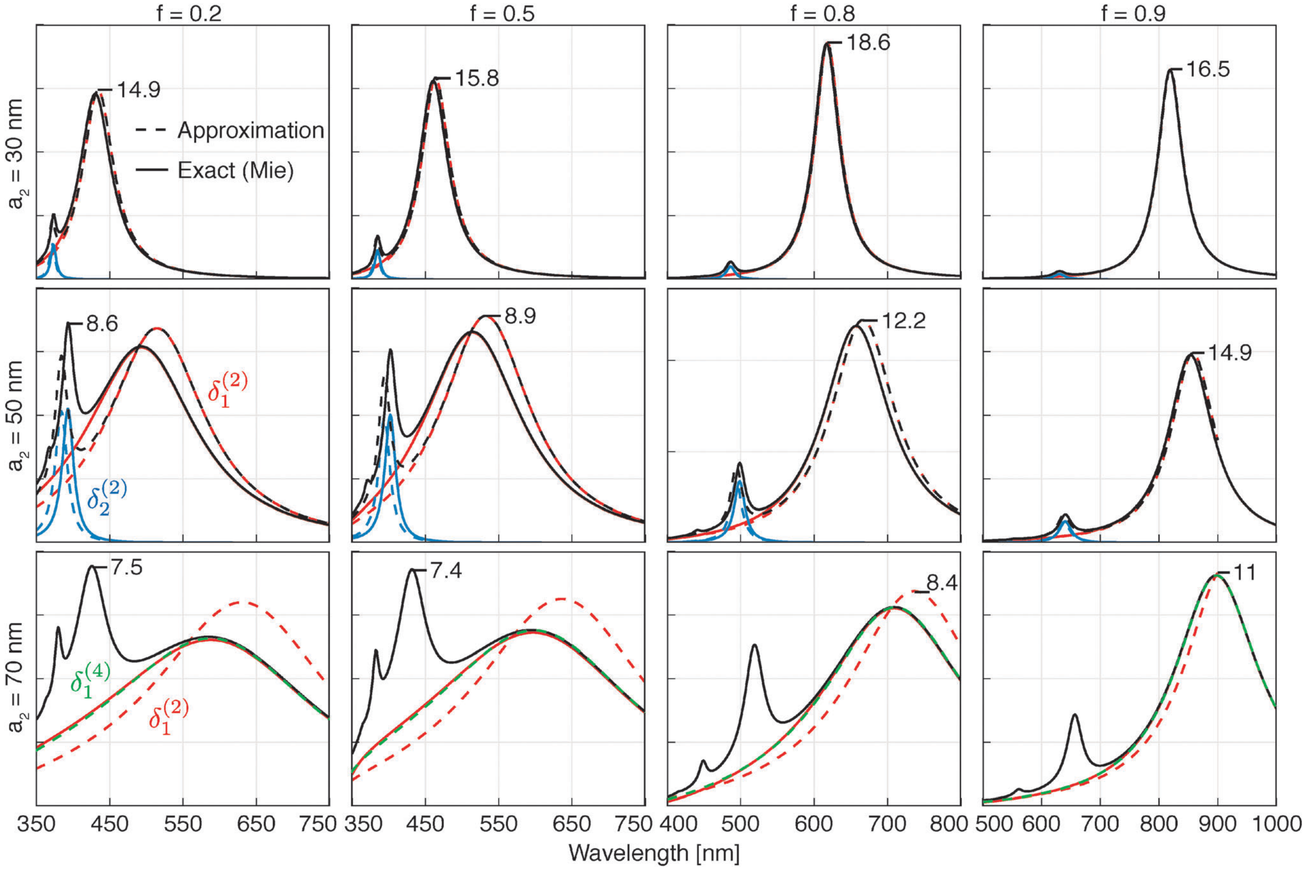

Fig. 6 Far-field extinction coefficients for silver nanoshells (core refractive index 1.5) immersed in water, with varying filling ratios $f = 0.2$ to $f = 0.9$. The black solid line is the fully converged result from Mie theory, including multipoles of all orders. For the radii $a_2 = 30$ nm and $a_2 = 50$ nm (first two rows), we compare the second-order expressions (dashed lines) for δ_1 (eqn (53); red) and δ_2 (eqn (56); blue) to the corresponding term from Mie theory (solid lines). For the larger particle size $a_2 = 70$ nm, only the dipolar term is shown, with a comparison between the second order (eqn (53)) and fourth-order (eqn (54)) approximations (red and green dashed lines, respectively). Note how in all cases the agreement between the exact and the approximate expressions improves as f increases.

As for spheres, larger shells also exhibit a non-negligible quadrupolar LSP resonance associated with the electric quadrupolar susceptibility δ_2. We may follow the same procedure for this term to get (to second-relative order):

$$\delta_2^{\mathrm{RC}} = \frac{\dfrac{i}{30}x^5(\tilde{r}{s_\mathrm{s}}^2 - 1)}{\tilde{r}{s_\mathrm{s}}^2 + \dfrac{3}{2} + \dfrac{5x^2}{14}\dfrac{({s_\mathrm{s}}^2 - 1)\left[(1-\tilde{r}){s_\mathrm{s}}^2 + 1\right] + \dfrac{5f^2{s_\mathrm{s}}^6}{\tilde{\varepsilon}_\mathrm{b}}(\tilde{r} - 1)}{(\tilde{r}{s_\mathrm{s}}^2 - 1)} - \dfrac{i}{30}x^5(\tilde{r}{s_\mathrm{s}}^2 - 1)}, \quad (56)$$

which reduces to eqn (38) for spheres if $\tilde{r} = 1$ (*i.e.* $f = 0$ or $s_\mathrm{s} = s_\mathrm{c}$) or if $f = 1$. As shown in Fig. 6, this expression accurately predicts the quadrupolar LSP resonance up to at least $a_2 = 30$ nm and even up to $a_2 = 50$ nm for thinner shells ($f \geq 0.8$).

Finally, we provide in Fig. S3† a figure equivalent to Fig. 6 but for gold nanoshells in water. It is clear that these expressions are also valid to model the optical properties of gold nanoshells up to at least $a_2 = 50$ nm.

4 Conclusion

We believe the new analytic approximations proposed in this work will be valuable for rapid, yet quantitative, comparison with experimental results in optical studies of plasmonic nanoparticles with spherical symmetry, *i.e.* spheres or shells. They could also provide the basis for further theoretical description of LSPRs in such structures. This detailed comparison moreover highlights a number of often overlooked, yet important features of such analytic expansions. Firstly, the fact that various forms of these expansions can be written, which, although equivalent to a given order, vary significantly in their accuracy for predicting LSPR properties. Secondly, the results highlight the effectiveness of the recently-introduced general radiative correction scheme[39,42] to improve the accuracy of such expansions and maintain the physical requirement of energy conservation.

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