

Electronic Supplementary Information to “Simple accurate approximations for the optical properties of metallic nanospheres and nanoshells”

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S.I. TAYLOR EXPANSIONS AND APPROXIMATIONS

One of the central ideas in this work is to use Taylor expansions up to a certain order in the size parameter x (which is proportional to a/λ), to approximate the results of Mie theory. As we demonstrate explicitly here, there are usually several ways of carrying out these expansions and the resulting approximations may vary dramatically in accuracy. To clarify this point, we discuss in this supplementary section a few tutorial examples illustrating these concepts, and summarized in Fig. S1. We consider a function $f(x)$, which will typically represent a physical parameter such as the extinction coefficient as a function of sphere size. Our goal is to find a simple approximation in the form of a Taylor expansion around $x = 0$ (i.e. a Maclaurin series). The crudest approximation would be to include only the lowest order term in the Taylor expansion, i.e. $f(x) \approx f_0(x)$, where $f_0(x) = \alpha x^n$ for some integer n . Such an approximation is only strictly valid in the limit of $x \rightarrow 0$ and will typically correspond in our case to the electrostatics (or quasi-static) approximation. If for example, $f(x) = x^2/\ln(1+x)$, then $f_0(x) = x$ and the approximation is correct (within 5% relative accuracy) up to $x \approx 0.1$. To increase the range of validity of the approximation, one may use a higher order Taylor expansion, i.e. $f(x) \approx x(1+x/2)$, which is then correct (within 5% relative accuracy) up to $x \approx 1.2$.

If we then want to approximate a function such as $g(x) = \ln(1+x)$, there are two *a priori* equally valid approaches: either we use the Taylor expansion of $g(x)$ as before, or we use the previous approximation of $f(x)$ to compute

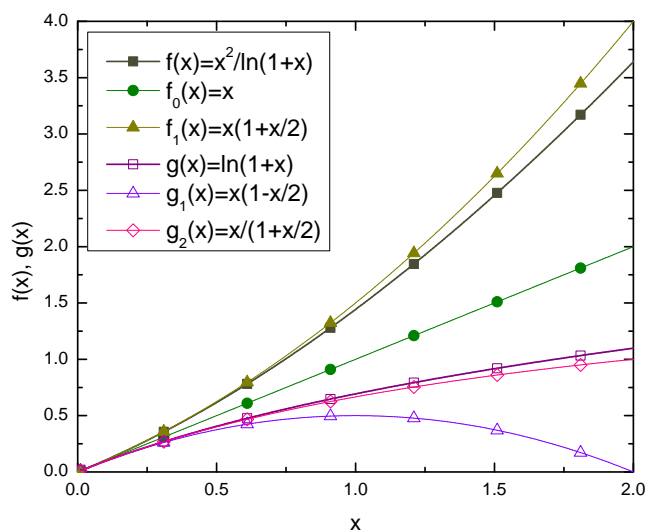


FIG. S1. Illustration of how Taylor expansions can be used to obtain various approximations, with different accuracy, of a function. Note that the best approximation for $g(x)$ is obtained from $g_2(x)$, which correspond to a Taylor expansion of $1/g(x)$, rather than from $g_1(x)$, which is the standard Taylor expansion of $g(x)$.

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$g(x) = x^2/f(x)$. Explicitly, these two approaches give respectively

$$g(x) \approx g_1(x) = x(1 - x/2), \quad (\text{S1})$$

$$g(x) \approx g_2(x) = \frac{x}{1 + x/2}. \quad (\text{S2})$$

Note that these two approximations only differ in higher order terms, or explicitly $g_1(x) = g_2(x) + O(x^3)$. But from a purely practical point of view, $g_2(x)$ is much more accurate, being 95%-correct up to $x \approx 1.2$ while $g_1(x)$ is 95%-correct only up to $x \approx 0.4$. This is also clear in the graph of Fig. S1. As we show in the main text, the same situation happens when searching for approximations of Mie theory, and for a given order of expansion, several expressions can be obtained. These expansions are equivalent at some order in x (like g_1 and g_2) but may be very different in their accuracy, especially if some terms in the series are resonant.

S.II. FULL EXPRESSION FOR THE ELECTRIC DIPOLAR SUSCEPTIBILITY OF A SPHERE

We here provide for reference the exact expression for the electric dipolar susceptibility of a sphere, Δ_1 , as obtained from Mie theory (s and x are defined in Sec. II):

$$\Delta_1 = \frac{-s\left(\frac{\sin(sx)}{sx} - \cos(sx)\right)\left(\frac{\cos(x)}{x} - \frac{\sin(x)}{x^2} + \sin(x)\right) + \left(\frac{\sin(x)}{x} - \cos(x)\right)\left(\frac{\cos(sx)}{sx} - \frac{\sin(sx)}{s^2x^2} + \sin(sx)\right)}{s\left(\frac{\sin(sx)}{sx} - \cos(sx)\right)\left(\frac{\cos(x)}{x} - \frac{\sin(x)}{x^2} + \sin(x)\right) + i\left(\frac{\sin(x)}{x} + \frac{\cos(x)}{x^2} - \cos(x)\right) - \left(\frac{\sin(x)}{x} - \cos(x)\right) + i\left(-\frac{\cos(x)}{x} - \sin(x)\right)\left(\frac{\cos(sx)}{sx} - \frac{\sin(sx)}{s^2x^2} + \sin(sx)\right)}. \quad (\text{S3})$$

S.III. SUPPLEMENTARY FIGURES FOR GOLD NANOSPHERES AND NANOSHELLS IN WATER

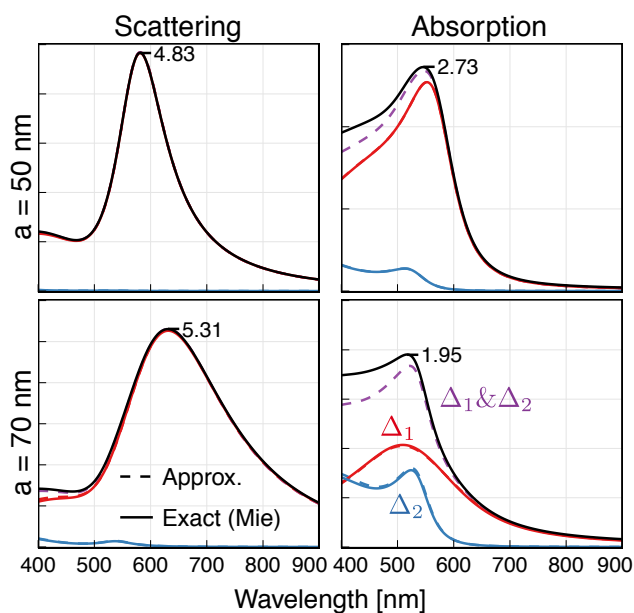


FIG. S2. Equivalent of Fig. 4 but for gold nanospheres immersed in water. Predicted far-field spectra of the scattering and absorption coefficients. Exact results (solid lines) are obtained from Mie theory while the approximated results (dashed lines) are obtained from the expressions obtained in this work. The terms included in the approximation correspond to the electric dipole Δ_1 (Eq. 33; red) and electric quadrupole Δ_2 (Eq. 39; blue). The black solid line, shown for comparison, is the converged Mie solution including contributions from electric and magnetic multipoles of all orders.

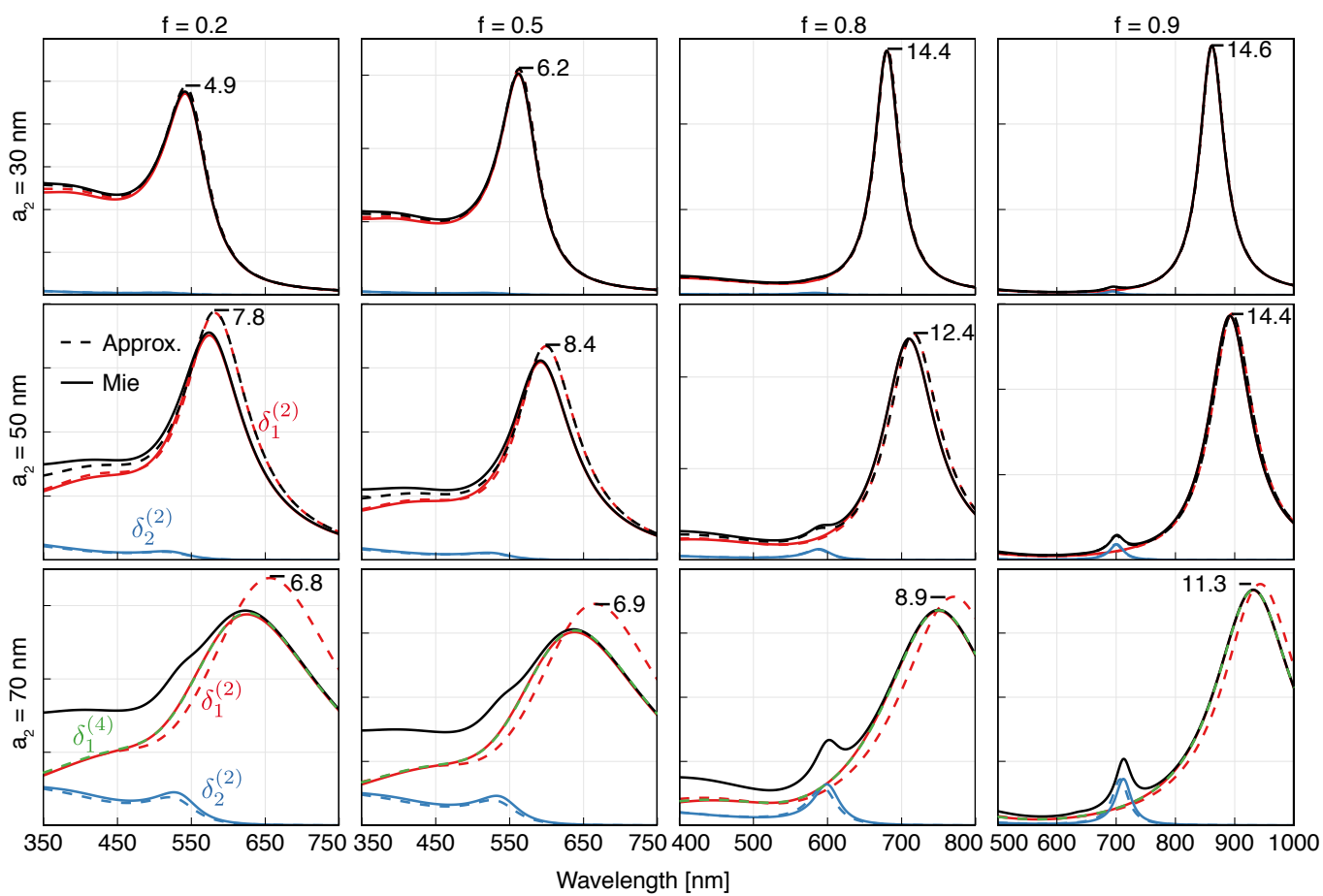


FIG. S3. Equivalent of Fig. 6 but for gold nanoshells (core refractive index 1.5) immersed in water showing the far-field extinction coefficients with varying filling ratio $f = 0.2$ to $f = 0.9$. The black solid line is the fully converged result from Mie theory, including electric and magnetic multipoles 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 (Eq. 53; red) and δ_2 (Eq. 54; blue) to the corresponding term from Mie theory (solid lines). For the larger particle size $a_2 = 70$ nm, we also compare the second order (Eq. 53) and fourth-order (Eq. 54) approximations to δ_1 (red and green dashed lines, respectively). Note how in all cases the agreement between the exact and the approximate expressions improves as f increases.

S.IV. PROCEDURE FOR OBTAINING APPROXIMATE EXPRESSIONS FOR NANOSHELLS

Here we outline the procedure we used to manipulate the Taylor series expansion for δ_1^X when seeking approximate expressions for shells. By analogy, one could use the same procedure to approximate higher order Mie susceptibilities (i.e. δ_n and γ_n with $n > 1$). We begin by rewriting the exact expression given in equation (43) of the manuscript as:

$$\delta_1^X(x, s_s, x_1, s_1) = \frac{A(s_s, x) + \Delta_1^X(s_1, x_1)B(s_s, x)}{C(s_s, x) + \Delta_1^X(s_1, x_1)D(s_s, x)}, \quad (\text{S4})$$

where A , B , C and D are combinations of the Riccati-Bessel functions, which can be Taylor expanded about $x = 0$:

$$\left. \begin{aligned} A(s_s, x) &= \psi_1(x)\psi_1'(s_s x) - s_s \psi_1(s_s x)\psi_1'(x) = x^3 \left[\sum_{m=0}^M A_m(s_s)x^{2m} + O(x^N) \right], \\ B(s_s, x) &= \psi_1(x)\chi_1'(s_s x) - s_s \chi_1(s_s x)\psi_1'(x) = \sum_{m=0}^M B_m(s_s)x^{2m} + O(x^N), \\ C(s_s, x) &= s_s \psi_1(s_s x)\chi_1'(x) - \chi_1(x)\psi_1'(s_s x) = \sum_{m=0}^M C_m(s_s)x^{2m} + O(x^N), \\ D(s_s, x) &= s_s \chi_1(s_s x)\chi_1'(x) - \chi_1(x)\chi_1'(s_s x) = x^{-3} \left[\sum_{m=0}^M D_m(s_s)x^{2m} + O(x^N) \right], \end{aligned} \right\} \quad (\text{S5})$$

where $N = 2(M + 1)$. The Taylor coefficients $A_m(s_s)$, $B_m(s_s)$, $C_m(s_s)$ and $D_m(s_s)$ can be readily written down in terms of s_s if needed. Following the same procedure as in the approximation B for spheres, we first Taylor expand the inverse of $\Delta_1^X(s_1, x_1)$ about $x_1 = 0$ and obtain:

$$\Delta_1^X(s_1, x_1) = x_1^3 \left[\sum_{m=0}^M E_m(s_1)x_1^{2m} + O(x_1^N) \right]^{-1}, \quad (\text{S6})$$

where the Taylor coefficients $E_m(s_1)$ can be explicitly written down in terms of $s_1 = s_c/s_s$. Now, after substituting $x_1 = f s_s x$, we can manipulate the series and write δ_1^X as

$$\begin{aligned} \delta_1^X &= x^3 \times \frac{\left[\sum_{m=0}^M A_m x^{2m} + O(x^N) \right] \left[\sum_{m=0}^M E_m \{f s_s x\}^{2m} + O(x^N) \right] + \{f s_s\}^3 \left[\sum_{m=0}^M B_m x^{2m} + O(x^N) \right]}{\left[\sum_{m=0}^M C_m x^{2m} + O(x^N) \right] \left[\sum_{m=0}^M E_m \{f s_s x\}^{2m} + O(x^N) \right] + \{f s_s\}^3 \left[\sum_{m=0}^M D_m x^{2m} + O(x^N) \right]} \\ &= x^3 \times \frac{\sum_{m=0}^M \left[\{f s_s\}^3 B_m + \sum_{\substack{k,l \\ k+l=m}} A_k E_l \{f s_s\}^{2l} \right] x^{2m} + O(x^N)}{\sum_{m=0}^M \left[\{f s_s\}^3 D_m + \sum_{\substack{k,l \\ k+l=m}} C_k E_l \{f s_s\}^{2l} \right] x^{2m} + O(x^N)}, \end{aligned} \quad (\text{S7})$$

where the indices k and l are non-negative integers in the range $[0, M]$.

Isolating the lowest order term, we then have:

$$\delta_1^X = x^3 \times \frac{\left[\{f s_s\}^3 B_0 + A_0 E_0 \right]}{\left[\{f s_s\}^3 D_0 + C_0 E_0 \right]} \times \left[\frac{1 + \sum_{m=1}^M G_m x^{2m} + O(x^N)}{1 - \sum_{m=1}^M F_m x^{2m} + O(x^N)} \right]^{-1}, \quad (\text{S8})$$

where we introduced auxiliary coefficients

$$F_m = - \frac{\{f s_s\}^3 B_m + \sum_{\substack{k,l \\ k+l=m}} A_k E_l \{f s_s\}^{2l}}{\{f s_s\}^3 B_0 + A_0 E_0},$$

and

$$G_m = + \frac{\{f s_s\}^3 D_m + \sum_{\substack{k,l \\ k+l=m}} C_k E_l \{f s_s\}^{2l}}{\{f s_s\}^3 D_0 + C_0 E_0}.$$

At this point it is worthwhile to explicitly write the expressions for A_0 , B_0 , C_0 , D_0 and E_0 :

$$\begin{aligned} A_0(s_s) &= -\frac{2s_s(s_s^2 - 1)}{9}, & B_0(s_s) &= +\frac{2s_s^2 + 1}{3s_s^2}, \\ C_0(s_s) &= +\frac{s_s(s_s^2 + 2)}{3}, & D_0(s_s) &= -\frac{s_s^2 - 1}{s_s^2}, \\ E_0(s_1) &= -\frac{3(s_1^2 + 2)}{2(s_1^2 - 1)}, \end{aligned}$$

which can be used to check that the lowest order term is

$$x^3 \times \left[\frac{\{f s_s\}^3 B_0 + A_0 E_0}{\{f s_s\}^3 D_0 + C_0 E_0} \right] = i\delta_1^{(0)}, \quad (\text{S9})$$

where $\delta_1^{(0)}$ is the lowest-order approximation (i.e. the electrostatic expression) given in equation (44) of the manuscript. When Taylor expanding susceptibilities of n -th order, i.e. δ_n^X or γ_n^X , one will be able to factor out $i\delta_n^{(0)} \propto x^{2n+1}$ or $i\gamma_n^{(0)} \propto x^{2n+3}$ and obtain an expression analogous to that in (S8).

The expression in (S8) essentially corresponds to Taylor expansion of the numerator and the denominator each up to $O(x^N)$. In order to obtain an approximation of type B (cf. equations 27 and 50 in the manuscript), the next step in the procedure would be to rearrange (S8) so that all terms in the expansion of $(\delta_1^X)^{-1}$ are in the numerator. Even though this can be done for expansions to arbitrary (even) order N , for illustration we first consider the case of $M = 2$ ($N = 6$):

$$\begin{aligned} (\delta_1^X)^{-1} &= (i\delta_1^{(0)})^{-1} \times \left[\frac{1 + G_1 x^2 + G_2 x^4 + O(x^6)}{1 - F_1 x^2 - F_2 x^4 + O(x^6)} \right] \\ &= (i\delta_1^{(0)})^{-1} \times [1 + G_1 x^2 + G_2 x^4 + O(x^6)] \times [1 + F_1 x^2 + (F_1^2 + F_2)x^4 + O(x^6)] \\ &= (i\delta_1^{(0)})^{-1} \times [1 + \beta_1 x^2 + \beta_2 x^4 + O(x^6)], \end{aligned}$$

where we used $(1 - y)^{-1} = 1 + y + y^2 + O(y^3)$, and introduced

$$\begin{aligned} \beta_1 &= G_1 + F_1 \\ \beta_2 &= G_2 + F_2 + F_1(G_1 + F_1). \end{aligned}$$

Note that β_1 and β_2 differ from α_1 and α_2 in equation (54) of the manuscript only by a multiplicative constant: $\beta_1 = -\frac{3}{5}\alpha_1$ and $\beta_2 = -\frac{3}{350}\alpha_2$. By explicitly writing out the necessary coefficients F_m and G_m in terms of f , s_s and $s_1 = s_c/s_s$, the expressions for α_1 and α_2 given in the manuscript can be recovered. In doing so one will find that the resultant expressions for β_1 and β_2 are quite cumbersome, but they can be simplified greatly by introducing different variables such as ϵ_a , ϵ_b and r defined in equations (45) and (46) of the manuscript.

However, even then, expressions for higher order ($N \geq 8$) approximations cease to be simple, though there may well be a more convenient set of variables that could be used to simplify approximations of arbitrary order in a more systematic and consistent manner. For completeness, we nevertheless return to the general case of arbitrary order M

and make use of the infinite geometric series to manipulate (S8):

$$\begin{aligned} \frac{1}{1 - \sum_{m=1}^M F_m x^{2m} + O(x^N)} &= \sum_{k=0}^M \left(\sum_{m=1}^M F_m x^{2m} \right)^k + O(x^N) \\ &= 1 + \sum_{k=1}^M \left(\sum_{m=1}^M F_m x^{2m} \right)^k + O(x^N) \\ &= 1 + \sum_{m=1}^M H_m x^{2m} + O(x^N), \end{aligned}$$

where in the last step the series has been rearranged, and the newly introduced auxiliary coefficients H_m are related to F_m via the multinomial formula. Now we can write $(\delta_1^X)^{-1}$ up to order $N = 2(M+1)$ in x :

$$\begin{aligned} (\delta_1^X)^{-1} &= x^{-3} \times \left[\frac{\{fs_s\}^3 D_0 + C_0 E_0}{\{fs_s\}^3 B_0 + A_0 E_0} \right] \\ &\quad \times \left[\left(1 + \sum_{m=1}^M G_m x^{2m} + O(x^N) \right) \left(1 + \sum_{m=1}^M H_m x^{2m} + O(x^N) \right) \right] \\ &= x^{-3} \times \left[\frac{\{fs_s\}^3 D_0 + C_0 E_0}{\{fs_s\}^3 B_0 + A_0 E_0} \right] \times \left[1 + \sum_{m=1}^M \sum_{\substack{j,k \\ j+k=m}} G_j H_k x^{2m} + O(x^{2(M+1)}) \right], \end{aligned}$$

which has the same form as equation (50) in the manuscript. Again we stress that, as m increases, the coefficients

$$\beta_m = \sum_{\substack{j,k \\ j+k=m}} G_j H_k \quad (\text{S10})$$

rapidly become complicated functions of s_1 , s_s and f , yielding relatively simple expressions only for $M < 3$. Without being able to express higher order ($M \geq 3$) approximations in compact form, the utility in using them is somewhat questionable.