Calculation of Mie derivatives

Roy G. Grainger, Jonathan Lucas, Gareth E. Thomas, and Graham B. L. Ewen

Analytical expressions are found for the derivatives of commonly used Mie scattering parameters, in particular the absorption and the scattering efficiencies, and for the angular intensity functions. These expressions are based on the analytical derivatives of the Mie scattering amplitudes a_n and b_n with respect to the particle size parameter and complex refractive index. In addition, analytical derivatives are found for the volume absorption and scattering coefficients, as well as for the intensity functions of a population of particles with log normal size distribution. These derivatives are given with respect to the total number density, to the median radius and spread of the distribution, and to the refractive index. Comparison between analytically and numerically computed derivatives showed the analytical version to be 2.5 to 6.5 times as fast for the single-particle and particle-distribution cases, respectively. © 2004 Optical Society of America

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1. Introduction

Many optical measurements of aerosols involve numerical analysis based on the scattering theory for spherical particles developed by Mie.[1] In some cases the analysis requires not only the Mie scattering parameters but also their derivatives with respect to the particle properties (in the case of a single-particle measurement) or the particle distribution properties (in the case of a measurement of an aerosol population). Derivatives are usually required, for instance, if some form of numerical retrieval algorithm is applied to the measurement. Traditionally, the derivatives have been calculated numerically; however, this approach introduces two problems:

1. Numerical techniques require the calculation of the scattering parameters multiple times. Since the calculation of Mie parameters involves an iterative summation of terms involving successive orders of Riccati–Bessel functions (see Section 2), this procedure is computationally expensive.

2. Numerical differentiation techniques are approximations, since the interval over which the local gradient is calculated is always of finite width, and are thus a potential source of error in the analysis.

Analytically derived expressions are presented here for various commonly required derivatives with respect to both particle properties (namely, particle size and complex refractive index), and particle log normal size distribution properties (namely, particle number density, median radius, and distribution spread). These expressions are formulated in such a way as to permit their implementation in computer code with minimal extra computation over that required for calculating the scattering parameters themselves. The expressions have been implemented for both single-particle parameters and log normal distribution parameters by use of the Interactive Data Language (IDL) from Research Systems, Inc. This code is available for download from the worldwide web.[2]

2. Mie Scattering Theory

The results of Mie theory indicate that the scattered light from the sphere can be considered to consist of partial waves radiated by multipoles formed by electric charge constituting the sphere. A dipole emanates the first partial wave, a quadrupole emanates the second, and so on. The amplitudes of the partial waves are given by the coefficients a_n and b_n that are central to Mie's solution. The nth electric partial

The authors are with Atmospheric, Oceanic and Planetary Physics, Clarendon Laboratory, University of Oxford, Parks Road, Oxford OX1 3PU, United Kingdom. G. E. Thomas' e-mail address is gthomas@atm.ox.ac.uk.

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wave has amplitude a_n, and b_n is the amplitude of the nth magnetic partial wave[3]:

$$a_n = \frac{\psi_n(x)\psi_n'(mx) - m\psi_n'(x)\psi_n(mx)}{\zeta_n^{(1)}(x)\psi_n'(mx) - m\zeta_n^{(1)\prime}(x)\psi_n(mx)}, \quad (1)$$

$$b_n = \frac{\psi_n'(x)\psi_n(mx) - m\psi_n(x)\psi_n'(mx)}{\zeta_n^{(1)\prime}(x)\psi_n(mx) - m\zeta_n^{(1)}(x)\psi_n'(mx)}, \quad (2)$$

where m is the complex refractive index; $x = 2\pi r/\lambda$ is the size parameter, given λ is the wavelength of the radiation and r is the radius of the sphere; and prime denotes a derivative with respect to the argument of the function.

$$\psi_n(z) \equiv z j_n(z), \quad (3)$$

$$\zeta_n^{(1)}(z) \equiv z h_n^{(1)}(z). \quad (4)$$

The functions $\psi_n(z)$ and $\zeta_n^{(1)}(z)$ are Riccati–Bessel functions defined in terms of the spherical Bessel function of the first kind, $j_n(z)$, and the spherical Hankel function of the first kind, $h_n^{(1)}(z)$.[4] Spherical Hankel functions of the first kind are used (as opposed to the second kind) in the scattered field amplitudes so as to describe outgoing spherical waves (as in Grandy[5]). Thus, note that the forms of a_n and b_n in Eqs. (1) and (2) differ slightly from that of older texts such as Bohren and Huffman[6] and van de Hulst.[3]

In most practical applications light is measured in the far field. The phase matrix that describes the angular distribution of the scattered radiation can be described in terms of two complex-valued scattering functions[3]

$$S_1(x, m, \theta) = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} [a_n \pi_n(\cos\theta) + b_n \tau_n(\cos\theta)], \quad (5)$$

$$S_2(x, m, \theta) = \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} [a_n \tau_n(\cos\theta) + b_n \pi_n(\cos\theta)], \quad (6)$$

where θ is the angle between the direction of the incident and the direction of the scattered radiation, and π_n and τ_n are given in terms of Legendre polynomials as

$$\pi_n(\cos\theta) = \frac{1}{\sin\theta} P_n^{\,1}(\cos\theta), \quad (7)$$

$$\tau_n(\cos\theta) = \frac{d}{d\theta} P_n^{\,1}(\cos\theta). \quad (8)$$

The summations given in Eqs. (5) and (6) (as well as subsequent expressions) are convergent for large values of n, as the amplitude of the partial waves decreases with increasing order. In practical applications the summation to infinity in these equations is replaced with a value dependent on x as described by Wiscombe.[7]

When unpolarized, natural light of irradiance E_0 is incident on a sphere, the phase matrix has only one nonzero element so that the intensity is given by

$$I = \frac{E_0(i_1 + i_2)}{2k^2R^2}, \quad (9)$$

where $k = 2\pi/\lambda$, R is the distance from the sphere's center, and i_1 and i_2 are, respectively, the intensity of light vibrating perpendicular and parallel to the plane through the directions of propagation of the incident and scattered beams:

$$i_1(x, m, \theta) = |S_1(x, m, \theta)|^2, \quad (10)$$

$$i_2(x, m, \theta) = |S_2(x, m, \theta)|^2. \quad (11)$$

In addition to the angular pattern of scattered radiation it is often also useful to calculate the extinction and scattering efficiency factors. These are dimensionless quantities defined as the ratio of the corresponding cross section to the geometric cross section (πr^2) of the sphere. These are calculated directly from a_n and b_n, i.e.,

$$Q^{\text{ext}} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1)\Re(a_n + b_n), \quad (12)$$

$$Q^{\text{sca}} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1)(|a_n|^2 + |b_n|^2). \quad (13)$$

A. Analytical Expressions for the Mie Terms

The first stage is to find analytic solutions for the derivatives of the coefficients a_n and b_n since all the other quantities are functions of these amplitudes.

Van de Hulst[3] gives the following identities:

$$\psi_n'(x)\zeta_n^{(1)}(x) - \psi_n(x)\zeta_n^{(1)\prime}(x) = i, \quad (14)$$

$$\psi_n''(x)\zeta_n^{(1)}(x) - \psi_n(x)\zeta_n^{(1)\prime\prime}(x) = 0. \quad (15)$$

The Riccati–Bessel functions are solutions of the Riccati differential equation,[4]

$$x^2 w''(x) + [x^2 - n(n+1)]w(x) = 0, \quad (16)$$

where $n = 0, \pm 1, \pm 2, \ldots$ Substituting the terms obtained for $\psi_n(x)$ and $\zeta_n^{(1)}(x)$ from Eq. (16) into Eq. (14), we obtain

$$\psi_n''(x)\zeta_n^{(1)\prime}(x) - \psi_n'(x)\zeta_n^{(1)\prime\prime}(x) = i\left[1 - \frac{n(n+1)}{x^2}\right]. \quad (17)$$

From these expressions it is straightforward to show

$$\frac{\partial a_n}{\partial x} = i\left\{\frac{[\psi_n'(mx)]^2(1 - m^2) + m^2\psi_n(mx)\psi_n''(mx) + m^2[\psi_n(mx)]^2\left[1 - \frac{n(n+1)}{x^2}\right]}{[\zeta_n^{(1)}(x)\psi_n'(mx) - m\zeta_n^{(1)\prime}(x)\psi_n(mx)]^2}\right\}, \tag{18}$$

$$\frac{\partial a_n}{\partial m} = i\left(\frac{mx\{\psi_n(mx)\psi_n''(mx) - [\psi_n'(mx)]^2\} - \psi_n(mx)\psi_n'(mx)}{[\zeta_n^{(1)}(x)\psi_n'(mx) - m\zeta_n^{(1)\prime}(x)\psi_n(mx)]^2}\right), \tag{19}$$

$$\frac{\partial b_n}{\partial x} = i\left\{\frac{[\psi_n(mx)]^2\left[1 - \frac{n(n+1)}{x^2}\right] + m^2\psi_n(mx)\psi_n''(mx)}{[m\zeta_n^{(1)}(x)\psi_n'(mx) - \zeta_n^{(1)\prime}(x)\psi_n(mx)]^2}\right\}, \tag{20}$$

$$\frac{\partial b_n}{\partial m} = i\left(\frac{mx\{\psi_n(mx)\psi_n''(mx) - [\psi_n'(mx)]^2\} + \psi_n(mx)\psi_n'(mx)}{[m\zeta_n^{(1)}(x)\psi_n'(mx) - \zeta_n^{(1)\prime}(x)\psi_n(mx)]^2}\right). \tag{21}$$

The complex refractive index can be expressed by $m = m_r + im_i$, allowing the derivatives with respect to real and imaginary parts to be calculated by means of the chain rule:

$$\left(\frac{\partial a_n}{\partial m_r}\right)_{m_i} = \frac{\partial a_n}{\partial m}\left(\frac{\partial m}{\partial m_r}\right)_{m_i} = \frac{\partial a_n}{\partial m}, \tag{22}$$

$$\left(\frac{\partial a_n}{\partial m_i}\right)_{m_r} = \frac{\partial a_n}{\partial m}\left(\frac{\partial m}{\partial m_i}\right)_{m_r} = i\,\frac{\partial a_n}{\partial m}. \tag{23}$$

Differentiation of the quantities S_1 and S_2 is easily achieved since only the coefficients a_n and b_n depend on either x or m. Relating these to i_1 and i_2 requires more thought, since it involves the differentiation of modulus squared terms. Applying the identity for the derivative of the modulus squared of a complex function, we obtain

$$\begin{aligned}\frac{\partial i_1}{\partial z} &= 2\left[\Re(S_1)\Re\left(\frac{\partial S_1}{\partial z}\right) + \Im(S_1)\Im\left(\frac{\partial S_1}{\partial z}\right)\right],\\ &= 2\sum_{n=1}^{\infty}\frac{2n+1}{n(n+1)}\left\{\Re[a_n\pi_n(\cos\theta) + b_n\tau_n(\cos\theta)]\right.\\ &\quad\times\Re\left[\frac{\partial a_n}{\partial z}\pi_n(\cos\theta) + \frac{\partial b_n}{\partial z}\tau_n(\cos\theta)\right]\\ &\quad+\Im[a_n\pi_n(\cos\theta) + b_n\tau_n(\cos\theta)]\\ &\quad\left.\times\Im\left[\frac{\partial a_n}{\partial z}\pi_n(\cos\theta) + \frac{\partial b_n}{\partial z}\tau_n(\cos\theta)\right]\right\},\end{aligned} \tag{24}$$

where the quantity z represents x, m_r, or m_i. The result for i_2 is similar, with S_2 replacing S_1:

$$\begin{aligned}\frac{\partial i_2}{\partial z} &= 2\sum_{n=1}^{\infty}\frac{2n+1}{n(n+1)}\left\{\Re[a_n\tau_n(\cos\theta) + b_n\pi_n(\cos\theta)]\right.\\ &\quad\times\Re\left[\frac{\partial a_n}{\partial z}\tau_n(\cos\theta) + \frac{\partial b_n}{\partial z}\pi_n(\cos\theta)\right]\\ &\quad+\Im[a_n\tau_n(\cos\theta) + b_n\pi_n(\cos\theta)]\\ &\quad\left.\times\Im\left[\frac{\partial a_n}{\partial z}\tau_n(\cos\theta) + \frac{\partial b_n}{\partial z}\pi_n(\cos\theta)\right]\right\}.\end{aligned} \tag{25}$$

To differentiate Q^{ext} with respect to x and m is simple, since apart from the factor $2/x^2$ at the front of Eq. (12) only a_n and b_n depend on x or m. We therefore have, from Eq. (12),

$$\frac{\partial Q^{\text{ext}}}{\partial x} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)\Re\left(\frac{\partial a_n}{\partial x} + \frac{\partial b_n}{\partial x}\right) - \frac{4}{x^3}\sum_{n=1}^{\infty}(2n+1)\Re(a_n + b_n), \tag{26}$$

$$\frac{\partial Q^{\text{ext}}}{\partial m_r} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)\Re\left(\frac{\partial a_n}{\partial m_r} + \frac{\partial b_n}{\partial m_r}\right), \tag{27}$$

$$\frac{\partial Q^{\text{ext}}}{\partial m_i} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)\Re\left(\frac{\partial a_n}{\partial m_i} + \frac{\partial b_n}{\partial m_i}\right). \tag{28}$$

When one differentiates Q^{sca} the identity for differentiation of the square modulus of complex functions is again applied:

$$\frac{\partial Q^{\text{sca}}}{\partial x} = \frac{4}{x^2}\sum_{n=1}^{\infty}(2n+1)\left[\Re(a_n)\Re\left(\frac{\partial a_n}{\partial x}\right) + \Im(a_n)\Im\left(\frac{\partial a_n}{\partial x}\right) + \Re(b_n)\Re\left(\frac{\partial b_n}{\partial x}\right) + \Im(b_n)\Im\left(\frac{\partial b_n}{\partial x}\right)\right] - \frac{4}{x^3}\sum_{n=1}^{\infty}(2n+1)(|a_n|^2 + |b_n|^2), \tag{29}$$

$$\frac{\partial Q^{\text{sca}}}{\partial m_r} = \frac{4}{x^2}\sum_{n=1}^{\infty}(2n+1)\left[\Re(a_n)\Re\left(\frac{\partial a_n}{\partial m_r}\right) + \Im(a_n)\Im\left(\frac{\partial a_n}{\partial m_r}\right) + \Re(b_n)\Re\left(\frac{\partial b_n}{\partial m_r}\right) + \Im(b_n)\Im\left(\frac{\partial b_n}{\partial m_r}\right)\right], \tag{30}$$

$$\frac{\partial Q^{\text{sca}}}{\partial m_i} = \frac{4}{x^2}\sum_{n=1}^{\infty}(2n+1)\left[\Re(a_n)\Re\left(\frac{\partial a_n}{\partial m_i}\right) + \Im(a_n)\Im\left(\frac{\partial a_n}{\partial m_i}\right) + \Re(b_n)\Re\left(\frac{\partial b_n}{\partial m_i}\right) + \Im(b_n)\Im\left(\frac{\partial b_n}{\partial m_i}\right)\right]. \tag{31}$$

We thus have expressions for the derivatives of all the important quantities in Mie theory in terms of just the derivatives of the coefficients a_n and b_n.

B. Expressing the Derivatives in Suitable Form

For numeric values for the derivatives of a_n and b_n, values for the Riccati–Bessel functions, $\psi_n(mx)$ and $\zeta_n^{(1)}(x)$, and their derivatives, as in Eqs. (18)–(21), must be computed. Dave[8] shows that a_n and b_n can be expressed

$$a_n = \frac{\left[\dfrac{A_n(y)}{m} + \dfrac{n}{x}\right]\psi_n(x) - \psi_{n-1}(x)}{\left[\dfrac{A_n(y)}{m} + \dfrac{n}{x}\right]\zeta_n^{(1)}(x) - \zeta_{n-1}^{(1)}(x)}, \tag{32}$$

$$b_n = \frac{\psi_{n-1}(x) - \left[mA_n(y) + \dfrac{n}{x}\right]\psi_n(x)}{\zeta_{n-1}^{(1)}(x) - \left[mA_n(y) + \dfrac{n}{x}\right]\zeta_n^{(1)}(x)}, \tag{33}$$

where $y = mx$ and the logarithmic derivative

$$A_n(y) = \frac{\psi_n'(y)}{\psi_n(y)}.$$

The Riccati–Bessel functions $\psi_n(x)$ and $\zeta_n^{(1)}(x)$ can both be generated with the upward recurrence relation

$$\psi_n(x) = \frac{2n-1}{x}\psi_{n-1}(x) - \psi_{n-2}(x), \tag{34}$$

and equivalently for $\zeta_n^{(1)}(x)$, where $\psi_{-1}(x) = \cos x$, $\psi_0(x) = \sin x$, $\zeta_{-1}^{(1)}(x) = \cos x + i\sin x$, and $\zeta_0^{(1)}(x) = \sin x - i\cos x$. Additionally, the recurrence relation for the Riccati–Bessel functions[9]

$$\psi_n'(x) = \psi_{n-1}(x) - \frac{n}{x}\psi_n(x) \tag{35}$$

follows immediately from the recurrence relations of the spherical Bessel functions.[4]

Dave[10] also states that the function $A_n(y)$ is best calculated with downward recurrence from

$$A_n(y) = \frac{n+1}{y} - \frac{1}{A_{n+1}(y) + \dfrac{n+1}{y}}. \tag{36}$$

We therefore need to be able to express the derivatives of the coefficients in terms of just the Riccati–Bessel functions and $A_n(y)$ since we have a method of working these out by computation.

Substituting the logarithmic derivative into $\partial a_n/\partial x$ in Eq. (18) yields

$$\frac{\partial a_n}{\partial x} = i\left\{\frac{[A_n(y)]^2(1-m^2) + m^2\dfrac{\psi_n''(y)}{\psi_n(y)} + m^2\left[1 + \dfrac{n(n+1)}{x^2}\right]}{[\zeta_n^{(1)}(x)A_n(y) - m\zeta_n^{(1)\prime}(x)]^2}\right\}. \tag{37}$$

From the Riccati differential Eq. (16), we make the observation

$$\frac{\psi_n''(y)}{\psi_n(y)} = \left(1 - \frac{n(n+1)}{y^2}\right), \tag{38}$$

then substituting the foregoing into Eq. (37) yields

$$\frac{\partial a_n}{\partial x} = i\left\{\frac{[A_n(y)]^2(1-m^2) + m^2 n(n+1)\left(\dfrac{1}{y^2} - \dfrac{1}{x^2}\right)}{[\zeta_n^{(1)}(x)A_n(y) - m\zeta_n^{(1)\prime}(x)]^2}\right\}. \tag{39}$$

Now, using the recurrence relation [Eq. (35)] for $\zeta_n^{(1)}(x)$ and then simplifying we obtain

$$\frac{\partial a_n}{\partial x} = i\left\{\frac{[A_n(y)]^2\left(\dfrac{1}{m^2} - 1\right) + n(n+1)\left(\dfrac{1}{y^2} - \dfrac{1}{x^2}\right)}{\left[\left(\dfrac{A_n(y)}{m} + \dfrac{n}{x}\right)\zeta_n^{(1)}(x) - \zeta_{n-1}^{(1)}(x)\right]^2}\right\}. \tag{40}$$

Near identical manipulations give similar forms for the other derivatives:

$$\frac{\partial a_n}{\partial m_r} = i\left(\frac{\frac{n(n+1)}{y} - y\{1 + [A_n(y)]^2\} - A_n(y)}{\left\{\left[A_n(y) + \frac{nm}{x}\right]\zeta_n^{(1)}(x) - m\zeta_{n-1}^{(1)}(x)\right\}^2}\right), \tag{41}$$

$$\frac{\partial a_n}{\partial m_i} = -\left(\frac{\frac{n(n+1)}{y} - y\{1 + [A_n(y)]^2\} - A_n(y)}{\left\{\left[A_n(y) + \frac{nm}{x}\right]\zeta_n^{(1)}(x) - m\zeta_{n-1}^{(1)}(x)\right\}^2}\right), \tag{42}$$

$$\frac{\partial b_n}{\partial x} = i\left(\frac{1 - m^2 + n(n+1)\left(\frac{m^2}{y^2} - \frac{1}{x^2}\right)}{\left\{\left[mA_n(y) + \frac{n}{x}\right]\zeta_n^{(1)}(x) - \zeta_{n-1}^{(1)}(x)\right\}^2}\right), \tag{43}$$

$$\frac{\partial b_n}{\partial m_r} = i\left(\frac{\frac{n(n+1)}{y} - y\{1 + [A_n(y)]^2\} + A_n(y)}{\left\{\left[A_n(y) + \frac{nm}{x}\right]\zeta_n^{(1)}(x) - m\zeta_{n-1}^{(1)}(x)\right\}^2}\right), \tag{44}$$

$$\frac{\partial b_n}{\partial m_i} = -\left(\frac{\frac{n(n+1)}{y} - y\{1 + [A_n(y)]^2\} + A_n(y)}{\left\{\left[A_n(y) + \frac{nm}{x}\right]\zeta_n^{(1)}(x) - m\zeta_{n-1}^{(1)}(x)\right\}^2}\right). \tag{45}$$

C. Derivatives for the Properties of an Aerosol Distribution

Thus far we have concentrated on the derivatives of Mie parameters with respect to the properties of an individual particle. Often, however, measurements are made of a distribution of particles, and it is the properties of the distribution that are of interest. If we have a distribution of particles, the optical properties of the population will simply be the summation of the properties of each individual particle. If the population is made up of particles with the same composition but a distribution of radii, such that

$$N_0 = \int_0^\infty n(r)\mathrm{d}r, \tag{46}$$

where N_0 is the total number density of the particles and $n(r)$ is the number density of particles in the infinitesimal radius interval $[r, r + dr]$, the bulk optical properties can be expressed in terms of integrals of the single-particle properties weighted by this distribution.

Thus, for example

$$\beta^{\text{ext}} = \int_0^\infty \sigma^{\text{ext}}(r)n(r)\mathrm{d}r, \tag{47}$$

$$\beta^{\text{sca}} = \int_0^\infty \sigma^{\text{sca}}(r)n(r)\mathrm{d}r, \tag{48}$$

where β^{ext} and β^{sca} are the volume extinction and scattering coefficients, respectively.

In general, it will be the properties of the particle distribution that will be of interest, and since the single scattering parameters are independent of these, the differentiation of these values is reasonably simple. As an example, the result for a log normal distribution is presented here.

A log normal distribution is described

$$n(r) = \frac{N_0}{\sqrt{2\pi}}\frac{1}{\ln S}\frac{1}{r}\exp\left[-\frac{(\ln r - \ln r_m)^2}{2\ln^2 S}\right], \tag{49}$$

where r_m is the median radius of the distribution and the standard deviation of $\ln r$ is $\ln S$. Thus a log normal distribution is completely described by N_0, r_m, and S, and it is these parameters that are treated as the independent variables in the derivatives.

Substituting for $n(r)$ in Eq. (47) and replacing σ^{ext} by $\pi r^2 Q^{\text{ext}}$ yields

$$\beta^{\text{ext}} = \frac{N_0}{\ln S}\sqrt{\frac{\pi}{2}}\int_0^\infty rQ^{\text{ext}}\exp\left[-\frac{(\ln r - \ln r_m)^2}{2\ln^2 S}\right]\mathrm{d}r. \tag{50}$$

One obtains the corresponding expression for β^{sca} by simply exchanging Q^{sca} for Q^{ext} in Eq. (50).

The intensity functions for a log normal distribution, $i_1^{\ln}$ and $i_2^{\ln}$, can also be found:

$$i_1^{\ln} = \frac{N_0}{\sqrt{2\pi}\ln S}\int_0^\infty \frac{i_1}{r}\exp\left[-\frac{(\ln r - \ln r_m)^2}{2\ln^2 S}\right]\mathrm{d}r, \tag{51}$$

$$i_2^{\ln} = \frac{N_0}{\sqrt{2\pi}\ln S}\int_0^\infty \frac{i_2}{r}\exp\left[-\frac{(\ln r - \ln r_m)^2}{2\ln^2 S}\right]\mathrm{d}r. \tag{52}$$

Differentiation of Eq. (50) with respect to N_0 yields

$$\frac{\partial \beta^{\text{ext}}}{\partial N_0} = \frac{1}{\ln S} \sqrt{\frac{\pi}{2}} \int_0^\infty r Q^{\text{ext}} \exp\left[-\frac{(\ln r - \ln r_m)^2}{2 \ln^2 S} \right] \mathrm{d}r. \tag{53}$$

The derivative with respect to r_m can be expressed

$$\begin{aligned} \frac{\partial \beta^{\text{ext}}}{\partial r_m} &= \frac{N_0}{\ln S} \sqrt{\frac{\pi}{2}} \int_0^\infty \frac{\partial}{\partial r_m} \left\{ r Q^{\text{ext}} \right. \\ &\quad \left. \times \exp\left[-\frac{(\ln r - \ln r_m)^2}{2 \ln^2 S} \right] \right\} \mathrm{d}r, \\ &= \frac{N_0}{\ln^3 S} \frac{1}{r_m} \sqrt{\frac{\pi}{2}} \int_0^\infty r Q^{\text{ext}} (\ln r - \ln r_m) \\ &\quad \times \exp\left[-\frac{(\ln r - \ln r_m)^2}{2 \ln^2 S} \right] \mathrm{d}r, \end{aligned} \tag{54}$$

whereas differentiation of β^{ext} with respect to S results in

$$\begin{aligned} \frac{\partial \beta^{\text{ext}}}{\partial S} &= \frac{N_0}{S \ln^2 S} \sqrt{\frac{\pi}{2}} \left\{ \frac{1}{\ln^2 S} \int_0^\infty r Q^{\text{ext}} (\ln r \right. \\ &\quad - \ln r_m)^2 \exp\left[-\frac{(\ln r - \ln r_m)^2}{2 \ln^2 S} \right] \mathrm{d}r \\ &\quad \left. - \int_0^\infty r Q^{\text{ext}} \exp\left[-\frac{(\ln r - \ln r_m)^2}{2 \ln^2 S} \right] \mathrm{d}r \right\}. \end{aligned} \tag{55}$$

The derivatives of β^{sca} take the same form as Eqs. (53)–(55) with Q^{sca} replacing Q^{ext}. The derivative of $i_1^{\ln}$, and similarly for the derivative of $i_2^{\ln}$, with respect to N_0 is

$$\frac{\partial i_1^{\ln}}{\partial N_0} = \frac{1}{\sqrt{2\pi} \ln S} \int_0^\infty \frac{i_1}{r} \exp\left[-\frac{(\ln r - \ln r_m)^2}{2 \ln^2 S} \right] \mathrm{d}r. \tag{56}$$

The derivatives of $i_1^{\ln}$ with respect to r_m and S are

$$\begin{aligned} \frac{\partial i_1^{\ln}}{\partial r_m} &= \frac{N_0}{\sqrt{2\pi}\, r_m \ln^3 S} \int_0^\infty i_1 \frac{(\ln r - \ln r_m)^2}{r} \\ &\quad \times \exp\left[-\frac{(\ln r - \ln r_m)^2}{2 \ln^2 S} \right] \mathrm{d}r, \end{aligned} \tag{57}$$

$$\begin{aligned} \frac{\partial i_1^{\ln}}{\partial S} &= \frac{N_0}{\sqrt{2\pi}\, S \ln^2 S} \left\{ \frac{1}{\ln^2 S} \int_0^\infty i_1 \frac{(\ln r - \ln r_m)^2}{r} \right. \\ &\quad \times \exp\left[-\frac{(\ln r - \ln r_m)^2}{2 \ln^2 S} \right] \mathrm{d}r \\ &\quad \left. - \int_0^\infty \frac{i_1}{r} \exp\left[-\frac{(\ln r - \ln r_m)^2}{2 \ln^2 S} \right] \mathrm{d}r \right\}. \end{aligned} \tag{58}$$

Interchanging the derivative and the integral operators in Eqs. (54), (55), (57), and (58) is possible because the integrand of each equation is a continuous function of both r and the considered parameter (either r_m or S for $S > 1$) and the integrals converge uniformly. Thus the Leibniz Integral Rule holds.[11]

If the derivatives of any of the above quantities with respect to the refractive index (m_r or m_i) are required, the derivative of the appropriate single-particle scattering parameter simply replaces the parameter itself. This replacement is possible as the scattering parameters themselves are the only quantities that have a refractive-index dependence in the above expressions. So, for example,

$$\frac{\partial \beta^{\text{ext}}}{\partial m_r} = \frac{N_0}{\ln S} \sqrt{\frac{\pi}{2}} \int_0^\infty r \frac{\partial Q^{\text{ext}}}{\partial m_r} \exp\left[-\frac{(\ln r - \ln r_m)^2}{2 \ln^2 S} \right] \mathrm{d}r, \tag{59}$$

where $\partial Q^{\text{ext}}/\partial m_r$ is as defined in Eq. (27), and the differentiation can be performed under the integral sign because the integral on the right-hand side of Eq. (59) is uniformly convergent with respect to the refractive index and the integrand is continuous in both r and m.

We thus have derivatives for all the properties of interest for a log normal distribution. Values for all of these expressions are straightforward to compute, as most of the factors involved are calculated during the computation of the Mie parameters. Therefore the addition of the derivative expressions adds very little computational overhead to code that calculates the scattering parameters. The derivation outlined above can also be applied to any continuous distribution; hence analytical calculation of the derivatives is possible for any such distribution.

3. Applications

A. Scattering from Natural Unpolarized Light

An example of an application in which the derivatives with respect to a single-particle's properties would be of use is the analysis of measurements from particle levitation instruments[12–14] or multiangle optical particle counters.[15–17] Such instruments make measurements of the intensity of scattered radiation from single particles, over a range of scattering angles. Because of the highly nonlinear nature of the relation between the particle properties and the corresponding scattering pattern, producing such estimates can involve a complex retrieval scheme. These schemes involve the iterative minimization of a cost function and often use the local gradient of the function to provide the next guess to the minima. In such circumstances the availability of analytical expressions for the derivative of the Mie intensity functions offers the potential for significant savings in computation time.

To provide a quantitative measure of the computational gains made by employing the analytical derivatives derived here, we performed a direct comparison between analytical and numerical methods. Derivatives were calculated for a series of 100 particles with evenly spaced radii between 0.1 and 10 μm and a refractive index of $1.4 + 0.1i$. The derivatives of the extinction parameter, scattering parameter, and intensity functions (for 180 scattering angles between 0 and π) were calculated with respect to particle size and both parts of the complex refractive index. The numerical differentiation method used was the simple finite-difference equation

$$\frac{\partial f}{\partial x} = \frac{f(x + h) - f(x - h)}{2h}, \qquad (60)$$

where h is a small perturbation term. All computation was performed with double-precision floating point numbers in IDL on an Athlon XP 2000+ processor. Using this configuration we found that the analytical form of the derivatives were approximately 2.5 times faster to compute than the numerical ones. In addition, the numerical derivatives of the scattering functions were prone to error, with a change in the size of the h parameter, resulting in large changes in the value of the derivative.

B. Scattering from a Distribution of Particles

The measurement of the properties of an ensemble of particles is a more common situation than the measurements of single particles. Such measurements might take the form of aerosol extinction at different wavelengths[18–20] (a measurement that is made by many satellite-based radiometers and spectrometers) or scattered intensity at different angles.[21,22] Often it is of interest to know the properties of the aerosol size distribution in such cases or possibly the refractive index of the particles making up the ensemble. The determination of such information will again require a numerical retrieval scheme. Once again the ability to calculate the appropriate derivatives analytically and in conjunction with the Mie parameters themselves should significantly reduce the computation time and may result in improved retrieval accuracy.

As with the single-particle case, a comparison between the numerical and the analytical methods of calculating the derivatives was performed on a log normal particle distribution. In this case the derivatives were performed on a log normal distribution with $N_0 = 100$, $r_m = 2$ μm, $S = 1.5$ μm, and the wave number of the illumination $k = 10{,}000$ cm^{-1}. To obtain the integrations that are required for generating the scattering parameters for the bulk aerosol, we calculated the scattering parameters at 200 different sizes. Derivatives of the volume extinction and scattering coefficients, as well as the intensity functions, were performed with respect to the number density, median radius, and distribution spread. The numerical derivatives were again calculated by use of Eq. (60). Here it was found that the analytical derivatives were computed approximately 6.5 times as quickly, and once again the numerical derivatives of the intensity functions were found to be prone to error.

4. Conclusion

Expressions have been found for the Mie coefficients a_n and b_n with respect to the particle size parameter and the real and the imaginary parts of the refractive index. These have then been used to produce analytical derivatives of the extinction and the scattering efficiency factors, Q^{ext} and Q^{sca}, as well as the intensity functions, i_1 and i_2. In addition, analytical expressions for the derivatives of volume extinction and scattering coefficients, β^{ext} and β^{sca}, and the net intensity functions, i_1^{ln} and i_2^{ln}, have been derived for a log normal particle size distribution, with respect to the total number density, mean radius, and spread of the distribution, as well as the complex refractive index. The methodology used in deriving the derivatives for the log normal distribution are readily adaptable to other continuous aerosol distributions.

The availability of such analytical expressions will be of great use in the analysis of optical measurements of both single particles and aerosol ensembles. The foregoing is particularly true when scattering or extinction measurements are used to estimate aerosol properties, for which iterative numerical retrieval schemes that require derivatives of the measured quantities are often used. The derivative expressions derived here can be calculated with little increase in computation over the calculation of the Mie parameters themselves; hence their use would represent a significant computational saving over numerically calculated derivatives. In trial runs of both numerical and analytical derivatives of the Mie parameters, the analytical expressions were found to reduce computation time by a factor of approximately 2.5 in the single-particle scattering case and 6.5 in the particle-distribution case (for the particular range of particle sizes used). In addition, note that the use of analytically derived derivatives could offer further computational savings and could result in improvements in the accuracy of the retrieval because errors introduced by numerical differentiation are eliminated. This point was also illustrated by the trial comparison, in which the numerical derivatives of the intensity functions were found to be prone to instability in both single-particle and particle-distribution cases.

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