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SIMPLE MATHEMATICAL EXPRESSIONS FOR SPECTRAL EXTINCTION AND SCATTERING PROPERTIES OF SMALL SIZE-PARAMETER PARTICLES, INCLUDING EXAMPLES FOR SOOT AND TiO_2

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Abstract—Focusing on small size-parameter particles, this paper compares several easily-computable approximations to the Mie equations, including those by Rayleigh, Penndorf and Wiscombe, with only the first term of Mie-coefficient expansion, and the exact solution. A symbolic algebra algorithm was also developed using Mathematica[tm] for solving the exact Mie equations, which is more than an order of magnitude shorter than an available FORTRAN algorithm for the same purpose. The comparisons of the approximations and the errors incurred are evaluated for a wide range of complex refractive indices ($1.0 \leqslant n \leqslant 5.0$ and $0.001 \leqslant k \leqslant 50$), and for the size-parameter range of $0.0 \leqslant x \leqslant 1.0$. While the choice of approximation depends on the size parameter and the refractive index, the first-term approximation is the best in most cases, with considerable reduction of cpu time. As a specific example, the extinction and scattering coefficients for soot and TiO_2 particle suspensions are computed as a function of the size-parameter by the above-described approximations, by two other available approximations, and by the exact solution.

1. INTRODUCTION

The radiation efficiency factors are usually expressed as the Mie coefficients, which consist of the Riccati-Bessel functions.[1] Although the theoretical formulation was developed long ago, accurate and stable algorithms for computing the efficiency factors for arbitrary size parameter and refractive indices have become available only relatively recently.[2,3] Despite the great advance in computation effectiveness, the formidable Mie equations still pose a significant computation effort, especially when used in models where these coefficients vary in space and time. Since computational schemes for the solution of problems in which these coefficients are used are typically iterative, the effort is compounded greatly.

This paper focuses on small size parameters and examines several leading approximations to the Mie equations, and compares them to the exact solution. A program using the symbolic algebra language Mathematica,‡ was developed for solving the exact Mie equations. The comparisons of the approximations and the errors incurred are evaluated for size parameters up to 1.0 and a wide range of complex refractive indices. When the size parameter and complex refractive index of the particles are known, the presented results allow an easy choice of an approximation for desired error limits. Finally, to provide an example, the extinction and scattering coefficients are computed for soot and TiO_2 particle suspensions.

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2. APPROXIMATIONS FOR RADIATIVE PROPERTIES OF SMALL SIZE-PARAMETER PARTICULATES ($X \leqslant 1$)

2.1. *The radiative properties of a polydispersed medium*

By assuming single, independent scattering, the spectral radiative properties of a polydispersed particulate medium can be obtained from[4]

$$\eta(m, N, \lambda) = \int_0^\infty \pi r^2 Q_\eta(m, r, \lambda) n(r)\, \mathrm{d}r, \tag{1}$$

where η denotes either the extinction (β), the scattering (σ), or the absorption (κ) coefficient, Q_η is the corresponding radiation efficiency factor, m is the complex refractive index of the particles, N is the particle number density, λ is the wavelength, r is particle radius, and $n(r)$ is the particle size distribution function. The extinction and scattering efficiency factors, Q_β and Q_σ, derived from the Mie theory are an infinite series of a function of the Mie coefficients a_n and b_n (*cf* van de Hulst[1]).

2.2. *Approximations for radiative efficiency factors*

Although reliable codes and fast computers are available for computing the efficiency factors (e.g. DBMIE by Dave[2] and MIEV0 by Wiscombe[3]), it is well known[4,5] and confirmed by our past work[6] that the calculation of these Mie coefficients still requires a large computation effort because of the need to evaluate many terms composed of complicated functions with complex arguments. Determination of the radiative properties could be a significant fraction of the entire computational effort when these properties are space and time dependent and when the computation schemes are iterative, such as in modeling coal combustion,[6,7] atmospheric and oceanic radiation transfer, and photocatalytic reactions with small-particle catalyst dispersed in a non-opaque medium. An approximation which requires minimal computational effort but is still sufficiently accurate is thus highly desirable. Several such approximations are described and compared below, for particle size parameters $x \equiv \pi d/\lambda \leqslant 1$.

(1) The Penndorf approximation. For the limiting case of a small size parameter ($x \longrightarrow 0$), the general Mie equations can be expanded into a power series in terms of the size parameter. Penndorf[8] derived the following approximate formulas for small spherical aerosols ($r < \lambda$) by using the series expansion

$$Q_\beta = \frac{24nkx}{z_1} + \left[\frac{4}{15} + \frac{20}{3z_2} + \frac{4.8}{z_1^2}\{7(n^2+k^2) + 4(n^2-k^2-5)\}\right] nkx^3$$
$$+ \frac{8}{3z_1^2}[\{(n^2+k^2)^2 + n^2 - k^2 - 2\}^2 - 36n^2k^2]x^4, \tag{2}$$

$$Q_\sigma = \frac{8x^4}{3z_1^2}[\{(n^2+k^2)^2 + n^2 - k^2 - 2\}^2 + 36n^2k^2]$$
$$\times \left[1 + \frac{6}{5z_1}\{(n^2-k^2)^2 - 4\}x^2 - \frac{8nkx^3}{z_1}\right], \tag{3}$$

where

$$z_1 = (n^2+k^2)^2 + 4(n^2-k^2) + 4, \tag{4}$$

$$z_2 = 4(n^2+k^2)^2 + 12(n^2-k^2) + 9. \tag{5}$$

This approximation was shown to be applicable for small spheres up to $x = 0.8$ with an error within 10%.[9]

(2) The Rayleigh limit approximation. The well-known Rayleigh Limit approximation[1] consists of the leading terms of the above Penndorf approximation, and is valid for the smaller size parameters, $x \leqslant 0.3$ with error within 10%. The efficiency factors estimated by the Rayleigh limit approximation are

$$Q_\kappa = -4x Im\left(\frac{m^2-1}{m^2+2}\right), \tag{6}$$

$$Q_\sigma = \frac{8}{3}x^4\left|\frac{m^2-1}{m^2+2}\right|^2, \tag{7}$$

and

$$Q_\beta = Q_\kappa + Q_\sigma. \tag{8}$$

(3) The small particle approximation (Wiscombe). Considering only the first three Mie equation coefficients, a_1, b_1 and a^2, Wiscombe[10] developed for $x \to 0$ the approximation

$$Q_\beta = 6xRe(\hat{a}_1 + \hat{b}_1 + \tfrac{5}{3}\hat{a}_2), \tag{9}$$

and

$$Q_\sigma = 6x^4(|\hat{a}_1|^2 + |\hat{b}_1|^2 + \tfrac{5}{3}|\hat{a}_2|^2). \tag{10}$$

To avoid the 0/0 singularity as $x \to 0$, the Mie coefficients were scaled as

$$\hat{a}_1, \hat{b}_1, \hat{a}_2 = \frac{a_1}{x^3}, \frac{b_1}{x^3}, \frac{b_2}{x^3}, \tag{11}$$

and the scaled coefficients were expanded in terms of the size parameter as follows

$$\hat{a}_1 = 2i\frac{(m^2-1)}{3}\,\frac{1 - \frac{1}{10}x^2 + \frac{(4m^2+5)}{1400}x^4}{D}, \tag{12}$$

where

$$D \equiv (m^2+2) + \left(1 - \frac{7}{10}m^2\right)x^2 - \frac{(8m^4 - 385m^2 + 350)}{1400}x^4 + 2i\frac{(m^2-1)}{3}x^3\left(1 - \frac{1}{10}x^2\right), \tag{13}$$

and

$$\hat{b}_1 = ix^2\frac{(m^2-1)}{45}\,\frac{1 + \frac{(2m^2-5)}{70}x^2}{1 - \frac{(2m^2-5)}{30}x^2}, \tag{14}$$

$$\hat{a}_2 = ix^2\frac{(m^2-1)}{15}\,\frac{1 - \frac{1}{14}x^2}{2m^2 + 3 - \frac{(2m^2-7)}{14}x^2}. \tag{15}$$

Compared with the exact Mie solutions, this small particle approximation retains an accuracy of 6 significant digits up to $x = 0.1$, and 4–5 digits up to $x = 0.2$, when $|m| \leqslant 2$. It loses accuracy, however, as $|m|$ increases, and is recommended only when $|m|x \leqslant 0.1$.[10]

(4) The first-term approximation. The leading terms in the infinite series defining the efficiency factors are particularly dominant when the size parameter is very small, and therefore the contributions of higher order terms become negligible. For example, a typical size parameter of soot in a coal combustor is $x = 0.1$, and the first terms contribute up to 99.92 and 99.99% of the extinction and scattering efficiency factors, respectively. For such small size parameters one thus needs to evaluate only a_1 and b_1, which is a special case of the Mie solutions with $a_2 = a_3 = \cdots = a_\infty = b_2 = b_3 = \cdots b_\infty = 0$. Although the small particle approximation by Wiscombe is based on the same idea (i.e. only a few leading terms, a_1, b_1 and a_2, as considered), it loses accuracy because of the expansion in x of the three leading terms [Eqs. (12)–(15)] truncates them. To avoid such truncation, we have evaluated an approximation which uses just the first two Mie coefficients a_1 and b_1, but in their exact form.

The efficiency factors can then be written as

$$Q_\beta = \frac{6}{x^2}Re(a_1 + b_1), \tag{16}$$

and

$$Q_\sigma = \frac{6}{x^2}(|a_1|^2 + |b_1|^2), \tag{17}$$

where

$$a_1 = \frac{p}{p + iq}, \tag{18}$$

$$b_1 = \frac{r}{r + is}, \tag{19}$$

and

$$p \equiv \left(1 - \frac{1}{m^2}\right)\frac{1}{x^3}\sin(mx)\sin(x) + m\left[1 - \left(1 - \frac{1}{m^2}\right)\frac{1}{x^2}\right]\cos(mx)\sin(x)$$
$$-\left[1 + \left(1 - \frac{1}{m^2}\right)\frac{1}{x^2}\right]\sin(mx)\cos(x) + \left(1 - \frac{1}{m^2}\right)\frac{m}{x}\cos(mx)\cos(x), \tag{20}$$

$$q \equiv \left(1 - \frac{1}{m^2}\right)\frac{1}{x^3}\sin(mx)\cos(x) + m\left[1 - \left(1 - \frac{1}{m^2}\right)\frac{1}{x^2}\right]\cos(mx)\cos(x)$$
$$+\left[1 + \left(1 - \frac{1}{m^2}\right)\frac{1}{x^2}\right]\sin(mx)\sin(x) - \left(1 - \frac{1}{m^2}\right)\frac{m}{x}\cos(mx)\sin(x), \tag{21}$$

$$r \equiv \left(1 - \frac{1}{m^2}\right)\frac{m}{x}\sin(mx)\sin(x) + \cos(mx)\sin(x) - m\sin(mx)\cos(x), \tag{22}$$

$$s \equiv \left(1 - \frac{1}{m^2}\right)\frac{m}{x}\sin(mx)\cos(x) + \cos(mx)\cos(x) + m\sin(mx)\sin(x). \tag{23}$$

2.3. The approximations applied for computing the extinction and scattering coefficients

As shown in Eq. (1), the efficiency factors are needed for determining the extinction and scattering *coefficients* used in radiative transfer calculations.

To integrate Eq. (1), the particle size distribution was expressed by the γ-distribution formula[11]

$$n(r) = ar^\alpha e^{-br}, \tag{24}$$

where the size–distribution coefficient a is

$$a = \frac{Nb^{\alpha+1}}{\Gamma(\alpha + 1)}, \tag{25}$$

and the exponent b is found from the condition of extremum at the most probable (modal) particle size r_m,

$$b = \frac{\alpha}{r_m}, \tag{26}$$

where α is determined from experimental data.

For the Rayleigh [Eqs. (6) and (7)] and Penndorf [Eqs. (2)–(5)] approximations, closed from integration of Eq. (1) was performed, and the dimensionless radiative coefficients obtained are:

By the Rayleigh approximation:

$$\kappa^* = \frac{\kappa}{N\pi\bar{r}^2} = \frac{2\pi a}{N\bar{r}^2}\frac{24nk}{[(n^2 - k^2 + 2)^2 + 4n^2k^2]}\frac{\Gamma(\alpha + 4)}{\lambda b^{\alpha+4}}, \tag{27}$$

$$\sigma^* = \frac{\sigma}{N\pi\bar{r}^2} = \frac{2\pi a}{N\bar{r}^2}\frac{8}{3}x^4\left|\frac{m^2 - 1}{m^2 + 2}\right|^2\frac{\Gamma(\alpha + 4)}{\lambda b^{\alpha+4}}, \tag{28}$$

and

$$\beta^* = \kappa^* + \sigma^*. \tag{29}$$

By the Penndorf approximation:

$$\beta^* = \frac{a}{N\bar{r}^2}\left[c_1\left(\frac{2\pi}{\lambda}\right)\frac{\Gamma(\alpha+4)}{b^{\alpha+4}} + c_2\left(\frac{2\pi}{\lambda}\right)^3\frac{\Gamma(\alpha+6)}{b^{\alpha+6}} + c_3\left(\frac{2\pi}{\lambda}\right)^4\frac{\Gamma(\alpha+7)}{b^{\alpha+7}}\right], \tag{30}$$

$$\kappa^* = \frac{a}{N\bar{r}^2}\left[c_1\left(\frac{2\pi}{\lambda}\right)\frac{\Gamma(\alpha+4)}{b^{\alpha+4}} + c_2\left(\frac{2\pi}{\lambda}\right)^3\frac{\Gamma(\alpha+6)}{b^{\alpha+6}} + c_4\left(\frac{2\pi}{\lambda}\right)^4\frac{\Gamma(\alpha+7)}{b^{\alpha+7}} + c_5\left(\frac{2\pi}{\lambda}\right)^5\frac{\Gamma(\alpha+9)}{b^{\alpha+9}} + c_6\left(\frac{2\pi}{\lambda}\right)^7\frac{\Gamma(\alpha+10)}{b^{\alpha+10}}\right], \tag{31}$$

where the constants c_i are

$$c_1 = \frac{24kn}{4k^2n^2 + (2-k^2+n^2)^2}, \tag{32}$$

$$c_2 = 4kn\left\{\frac{1}{15} + \frac{5}{3}\,\frac{1}{16k^2n^2 + [3+2(-k^2+n^2)]^2} + \frac{6}{5}\,\frac{[7(k^2+n^2)^2 + 4(-5-k^2+n^2)]}{[4k^2n^2 + (2-k^2+n^2)^2]^2}\right\}, \tag{33}$$

$$c_3 = \frac{8}{3}\left\{1 + \frac{(1+k^2+n^2)^2 - 4n^2}{4k^2n^2 + (2-k^2+n^2)^2} + \frac{[-2-k^2-n^2+(k^2+n^2)^2]^2 - 36k^2n^2}{[4k^2n^2 + (2-k^2+n^2)^2]^2}\right\}, \tag{34}$$

$$c_4 = \frac{8}{3}\left[1 - \frac{(1+k^2+n^2)^2 - 4n^2}{4k^2n^2 + (2-k^2+n^2)^2}\right], \tag{35}$$

$$c_5 = -\frac{16}{5}\left\{\frac{[(k^2+n^2)^2 - 4][(1+k^2+n^2)^2 - 4n^2]}{[4k^2n^2 + (2-k^2+n^2)^2]^2}\right\}, \tag{36}$$

$$c_6 = -\frac{32}{3}\left\{\frac{2kn[(1+k^2+n^2)^2 - 4n^2]}{[4k^2n^2 + (2-k^2+n^2)^2]^2}\right\}. \tag{37}$$

Closed form integration of Eq. (1) is not possible for the Wiscombe approximation [Eqs. (9)–(15)] and for the first-term approximation [Eqs. (16)–(23)], and neither for the exact solution from the Mie theory. Numerical integration of Eq. (1) was therefore performed in these cases.

Beside the four approximations discussed in this study, two other approximate expressions for the coefficients, suggested by Tien et al[12] and Buckius and Hwang,[13] are also used, and all the results are compared to exact solutions obtained from the Mie theory.

The Tien et al[12] approximation:

$$Q_\beta = 2[1 - e^{-G\rho}], \tag{38}$$

which gives after integration

$$\beta^* = \frac{2a}{N\bar{r}^2}\left\{\frac{\Gamma(\alpha+3)}{b^{\alpha+3}} - \frac{\Gamma(\alpha+3)}{[4\pi(n-1)G/\lambda + b]^{\alpha+3}}\right\}, \tag{39}$$

where

$$G = \frac{6n}{4n^4 - 8n^3 + 8n^2 + 4n + 1} \tag{40}$$

and

$$\rho = \frac{4\pi(n-1)r}{\lambda}. \tag{41}$$

The Buckius and Hwang[13] approximation:

$$\left[\frac{\bar{\beta}}{x_{32}F}\right]^{-1} = \frac{1}{24}\left[1 + \left(\frac{x_{32}F}{0.016}\right)^2\right]^{-1} + \left[\frac{2.25}{(x_{32}F)^{1.1}}\right]^{-1}, \tag{42}$$

$$\left[\frac{\bar{\kappa}}{x_{32}F}\right]^{-1} = \frac{1}{24}\left[1 + \left(\frac{x_{32}F}{0.0275}\right)^2\right]^{-1} + \left[\frac{1}{(x_{32}F)^{1.16}}\right]^{-1}, \tag{43}$$

where

$$x_{32}F = \frac{\pi}{12\lambda}\frac{\int_0^\infty r^3 n(r)\,\mathrm{d}r}{\int_0^\infty r^2 n(r)\,\mathrm{d}r} Im\left(-4\frac{m^2-1}{m^2+2}\right), \tag{44}$$

and the dimensionless coefficients are defined as

$$\bar{\beta}, \bar{\kappa} = \frac{\beta, \kappa}{\int_0^\infty \pi r^2 n(r)\,\mathrm{d}r}. \tag{45}$$

The same particle size distribution expression [Eqs. (24)–(26)] is used to obtain the above radiative coefficients.

3. RESULTS AND DISCUSSION

3.1. The range of investigated parameters and the computational aspects

The approximate expressions are evaluated for a range of complex refractive indices encompassing most common materials, $1.0 \leqslant n \leqslant 5.0$ and $0.001 \leqslant k \leqslant 50$, and for size parameters in the range $0.0 \leqslant x \leqslant 1.0$, and the results are compared to those obtained from the exact Mie equation solutions. It should be noted from the outset that even the exact Mie solution required the computation of only a few of the leading terms when the size parameters are as small as those in the range investigated in this study, and that the computation time increase with the size parameter. Consequently, while the approximations are expressed by only a few lines of FORTRAN code as compared to the approx. 1100 lines in a general Mie solution code such as MIEV0,[3] we found that the cpu (central processing unit) time for computing the efficiency factors using the approximations is only up to 4-fold shorter (for $x = 1$) than that using the MIEV0 code. Average over the range of $0.05 \leqslant x \leqslant 1.0$ and 8 complex refractive indices, $1.5 \leqslant n \leqslant 2.61$ and $0.01 \leqslant k \leqslant 0.93$, the cpu time, depending on the specific approximation, is only 15 to 53% shorter. These are still important cpu time savings, and, combined with the two orders of magnitude reduction in code size, make the use of the appropriate approximations advisable.

Using a 486/33 MHz PC, the Mathematica[tm] program we have developed for solving the Mie equations (and which is only a few lines of code long) took 3.46 sec cpu time to compute the efficiency factors, while the approximations took about 0.05 sec. It is, however, also estimated that it consumes about an order of magnitude more cpu time than MIEV0.

3.2. Comparisons of the suitability of the approximations for the radiative efficiency factors

Figures 1 and 2 show the extinction and the scattering efficiency factors obtained from the approximations and the Mie solutions for a wide range of refractive indices ($n = 1.0, 2.0, 3.0, 5.0$, and $0.001 \leqslant k \leqslant 50$) and 3 different size parameters ($x = 0.1, 0.5, 1.0$). The general trend observed is that the deviation between all approximations except the first-term one, and the exact solution, increases with n, and it also increases with k for the lower range of k-values considered. As k increases further the trend is no longer monotonic and depends on the specific approximation and values of x and n.

For the smallest size parameter, $x = 0.1$ [Fig. 1(a)], all approximations but the Rayleigh limit (for which the error is 14.4% at $k = 6$) yield accurate results for $n \leqslant 2$ and $k \leqslant 6$ (error <0.8%). The first-term approximation is accurate in the entire range of considered variables. The maximal error (it occurs at the highest k evaluated here, $k = 50$), increasing with n, is about 84–95% using the Rayleigh approximation, it is 678–785% using the Penndorf approximation, 255–294% using the Wiscombe approximation, and 0.1% using the first-term approximation.

For a bigger size parameter $x = 0.5$ [Fig. 1(b)], the three approximations show good agreement with the Mie solution up to $k = 3$ for $n \leqslant 2.5$ (errors $\leqslant 1.0\%$). For a larger refractive index, $n \geqslant 2.5$, only the first-term approximation shows excellent results in the entire range of absorptive indices examined, having error $\leqslant 1.2\%$. The maximal error is about 24–27% using the Rayleigh approximation, it is 734% to over 1000% using the Penndorf approximation, and 396% to over 1000% using the Wiscombe approximation.

For $x = 1.0$ [Fig. 1(c)], the maximal errors of the Rayleigh Limit and the Penndorf approximation are, depending on the magnitude of n, 26 to 182% and 653 to >1000%, respectively. The Rayleigh approximation is thus acceptable only for approximately $5 \leqslant k \leqslant 9$, and the Penndorf approximation is only acceptable for $k \leqslant \sim 6$ and $n \approx 1.0$. The maximal error in the first-term approximation is 4.6–12.0%. The accuracy of the small-particle approximation for $n \leqslant \sim 2$ and

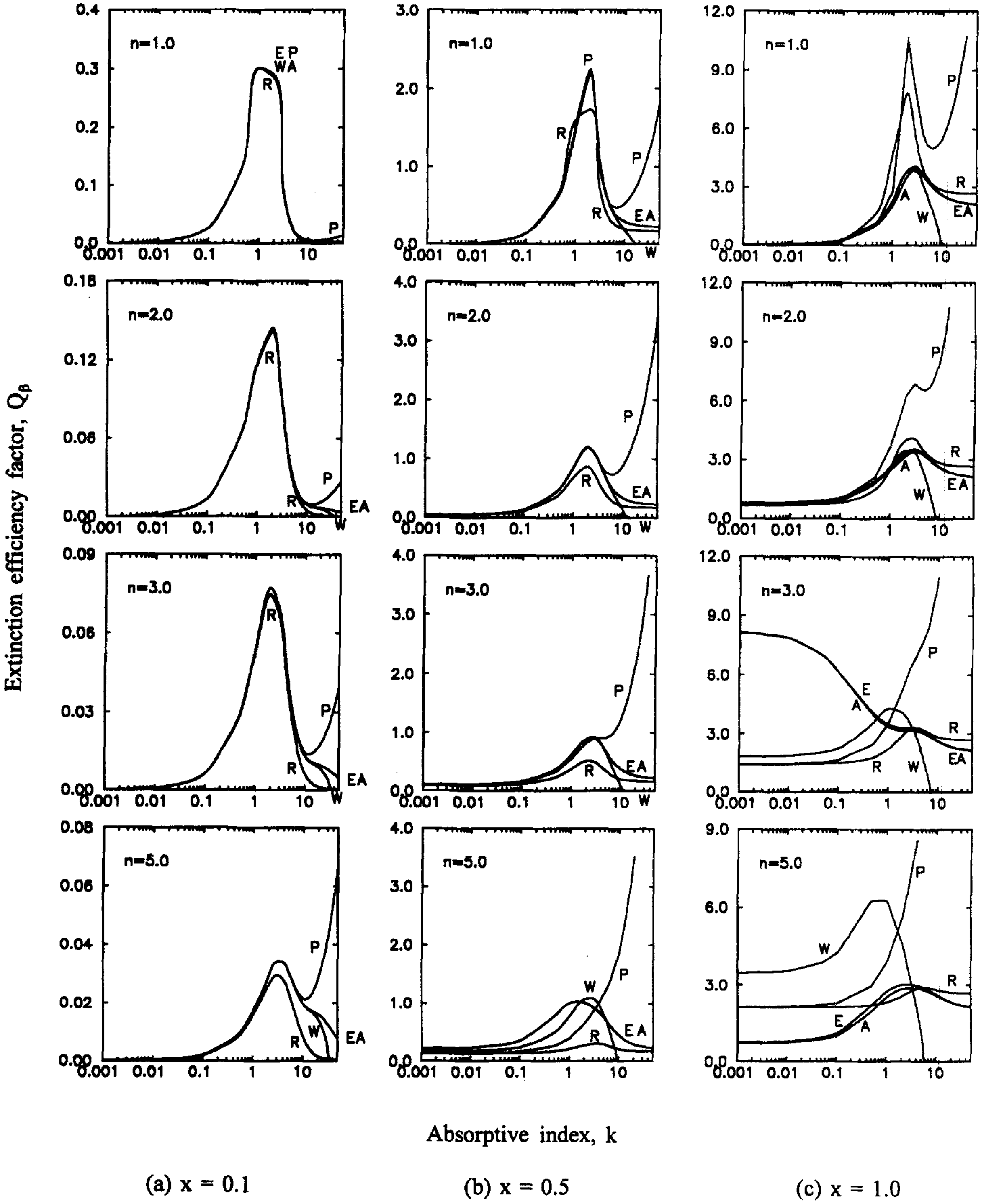
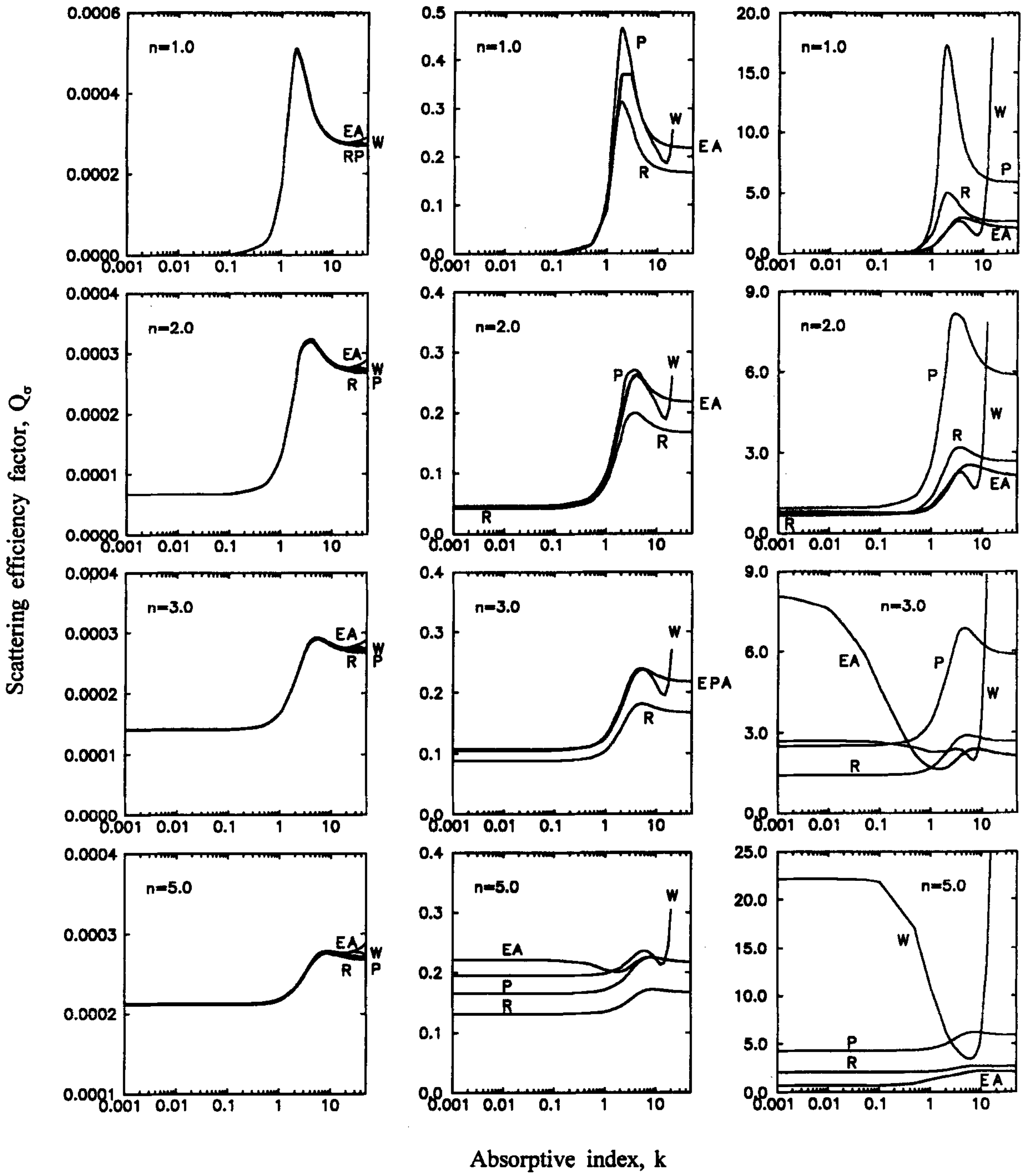


Fig. 1. The effect of the absorptive index k on the extinction efficiency factor Q_β, as computed by the Mie theory (E), and the approximations by Rayleigh (R), Penndorf (P), Wiscombe (W) and the first term (A). (a) $x = 0.1$; (b) $x = 0.5$; (c) $x = 1.0$, for $n = 1.0$, 2.0, 3.0, 5.0.



(a) x = 0.1 (b) x = 0.5 (c) x = 1.0

Fig. 2. The effect of the absorptive index k on the scattering efficiency factor Q_σ, as computed from the Mie theory (E), and from the approximations by Rayleigh (R), Penndorf (P), Wiscombe (W) and the first term (A). (a) $x = 0.1$; (b) $x = 0.5$; (c) $x = 1.0$, for $n = 1.0, 2.0, 3.0, 5.0$.

$k \leqslant \sim 3$ is comparable to that of the first-term approximation. For $n > 2$, however, only the first-term approximation shows excellent agreement with the Mie solutions.

Qualitatively similar results are observed for the scattering efficiency factor (Fig. 2). As in the case for the extinction efficiency factor, the first-term approximation for the scattering efficiency factor is accurate (here within 0.6%) in the full range of refractive indices and size parameters investigated.

Figures 3 and 4 show the effect of size parameter on the extinction and scattering efficiency factors, respectively, as computed by the exact solution and by each of the approximations. Generally, both efficiency factors increase with the size parameter, with the exception of the oscillatory behavior in the exact solution and in the first-term and small-particle approximations which occurs for the combination of the smallest k ($k = 0.01$) and largest n ($n = 5$) examined. With some local exceptions, the deviation between the exact solution and the approximations rises with

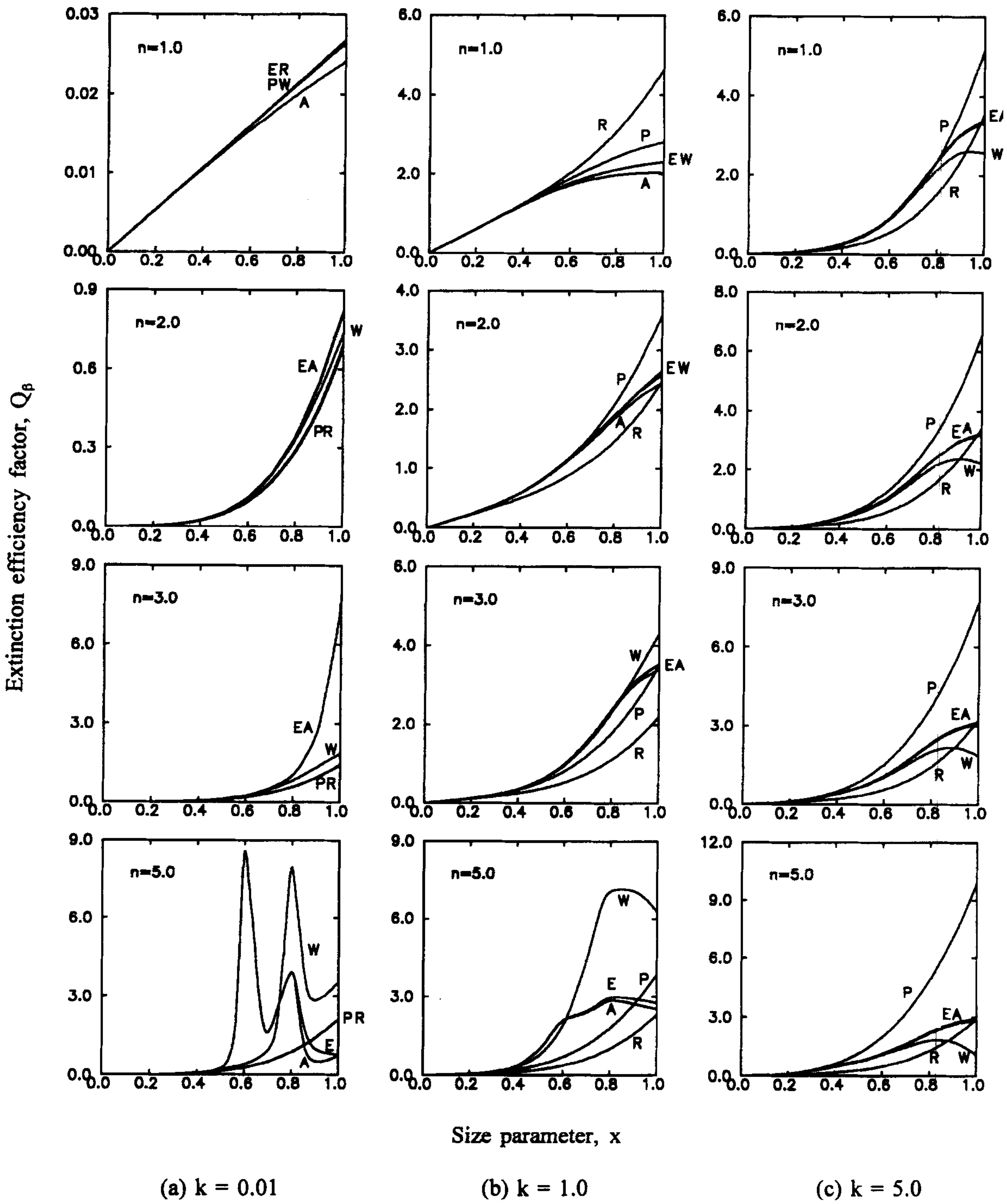


Fig. 3. The effect of the size parameter x on the extinction efficiency factor Q_β, as computed from the Mie theory (E), and from the approximations by Rayleigh (R), Penndorf (P), Wiscombe (W) and the first term (A). (a) $k = 0.01$; (b) $k = 1.0$; (c) $k = 5.0$, for $n = 1.0$, 2.0, 3.0, 5.0.

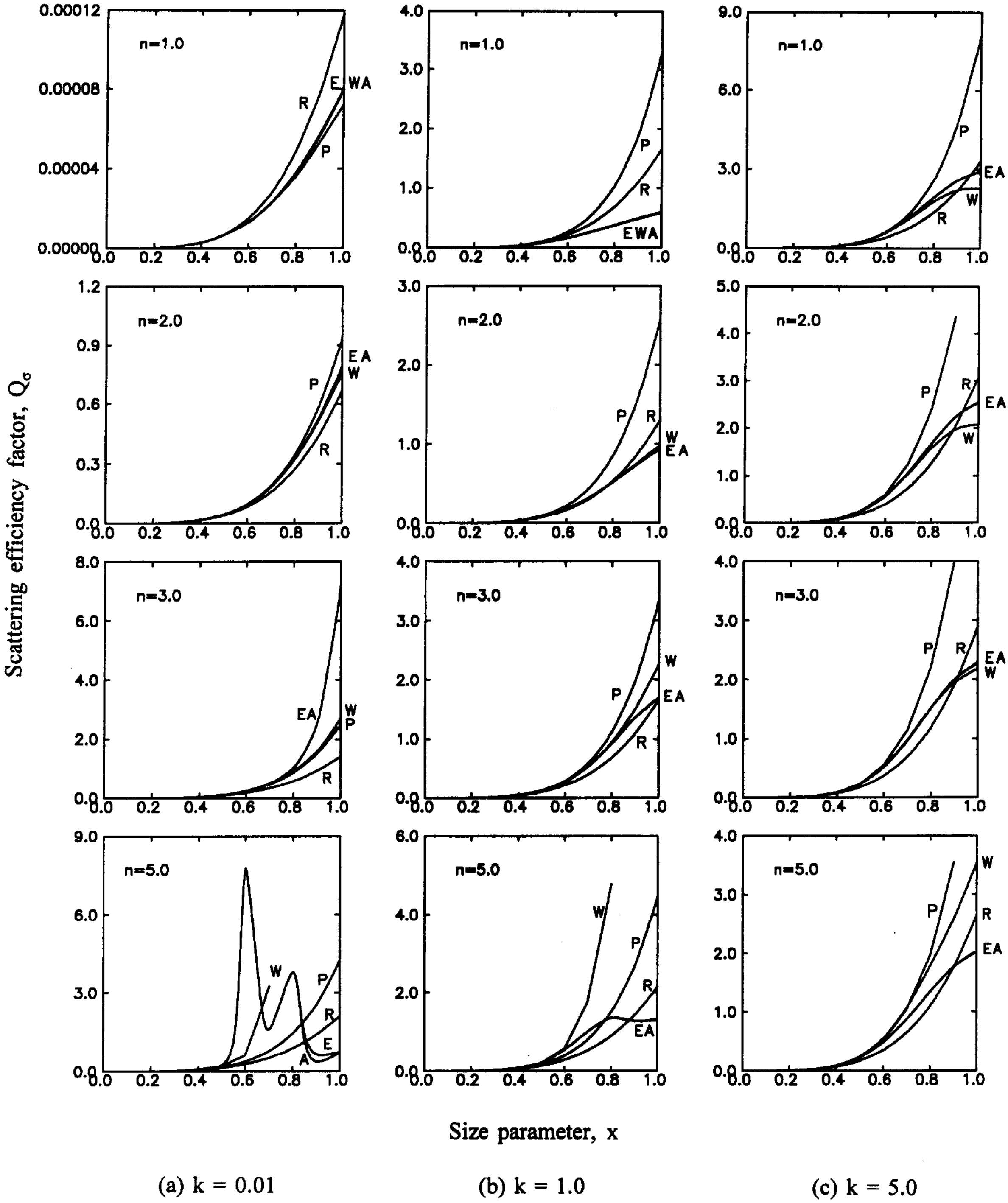


Fig. 4. The effect of the size parameter x on the scattering efficiency factor Q_σ, as computed from the Mie theory (E), and from the approximations by Rayleigh (R), Penndorf (P), Wiscombe (W), and the first term (A). (a) $k = 0.01$; (b) $k = 1.0$; (c) $k = 5.0$, for $n = 1.0$, 2.0, 3.0, 5.0.

k and n, but all of the approximations are accurate for $x \leqslant 0.4$. Again with a few exceptions, the first-term approximation follows the exact solution values and trends (including the oscillatory trend with x at low k and high n) most closely. The small-particle approximation is similarly accurate for the smaller range of approximately $n \leqslant 2$, $k \leqslant 1$.

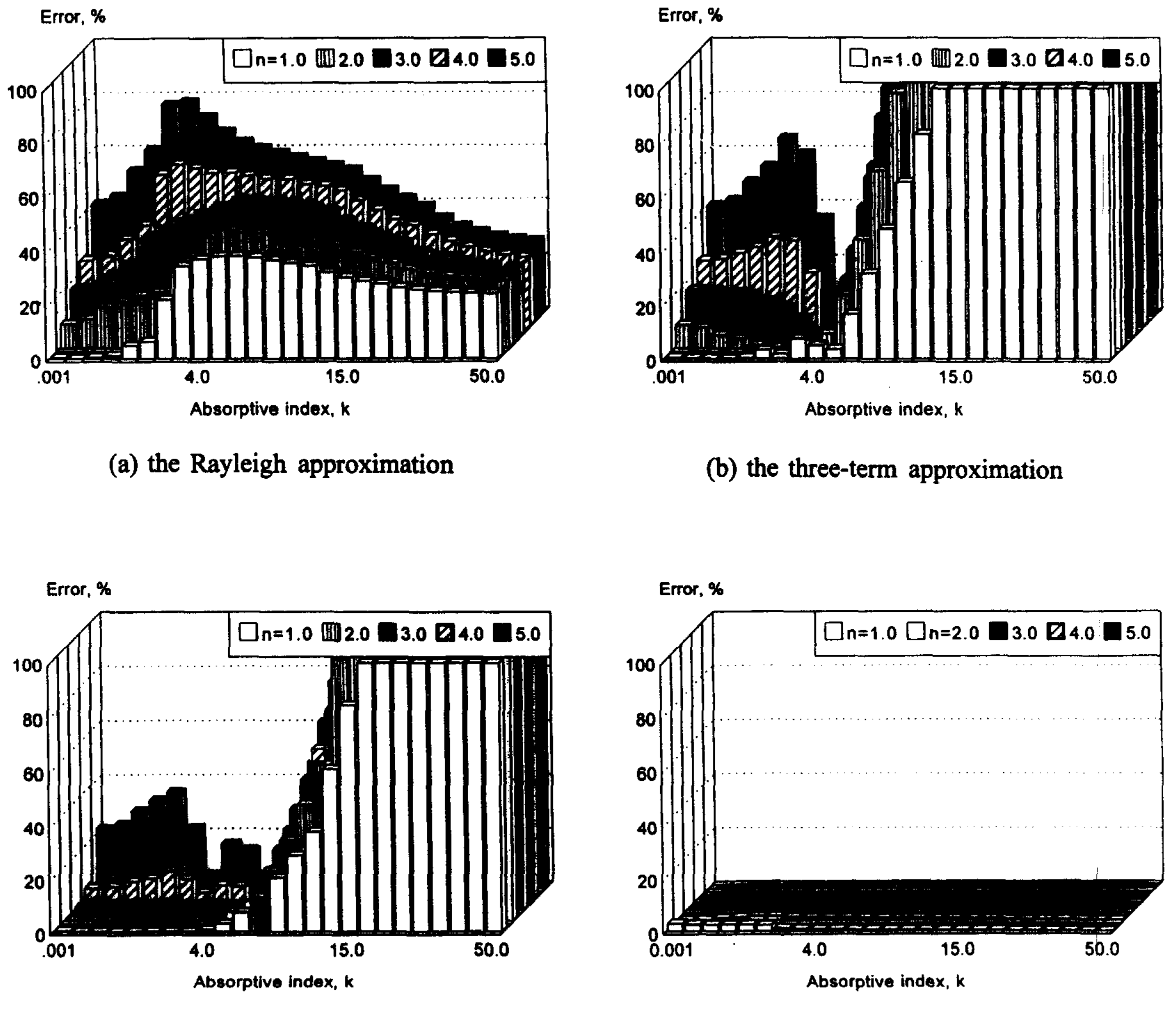
The absolute percentage error ($= |Q_E - Q_{APPX}|/Q_E \times 100\%$) in the extinction efficiency factor as computed by each of the approximations is plotted in Fig. 5 as a function of k and n, for $x = 0.5$.

Errors over 100% are truncated and therefore not shown in the figures. It is clear that the first-term approximation is generally the most accurate, and its error rises up to about 3% at small m.

To compare more directly the effect of the size parameter on the error incurred when using these approximations, a side-by-side presentation is made for $m = 1.0 - ik$ [in Fig. 6(a)] and $m = 2.0 - ik$ [in Fig. 6(b)], where $k = 0.01$, 1.0 and 5.0. Altogether, the first-term approximation incurs the smallest errors, which are $\leqslant 2\%$ in all cases except for $m = 1.0 - 0.01i$ and $m = 1.0 - 1.0i$ where the maximal error is of the order of 10%, and for $m = 2.0 - 1.0i$ where it is of the order of 5%. The Wiscombe approximation is better than the first-term approximation in these three cases, but is much worse in the other cases, reaching errors of about 32% for $m = 2.0 - 5.0i$. The Rayleigh and Penndorf approximations are better than the first-term approximation only for the lowest $|m|$, here of the order of 1; for the highest values of $|m|$ they produce errors which reach about 44% for the Rayleigh approximation and 52% for the Penndorf approximation, but the latter approximation is generally better than the former.

3.3. Comparisons of the suitability of the approximations for the extinction and scattering coefficients

The sensitivity of the dimensionless extinction and scattering coefficients to k and x, as computed from the exact Mie solution and the approximations (using for the size distribution the values $\alpha = 4$



(a) the Rayleigh approximation (b) the three-term approximation

(c) the small particle approximation (d) the first-term approximation

Fig. 5. The sensitivity of the absolute percentage error in the extinction efficiency factor to the absorptive index k, as computed by (a) the Rayleigh approximation, (b) the three-term (Penndorf) approximation, (c) the small particle (Wiscombe) approximation, and (d) the first-term approximation; for $n = 1.0$, 2.0, 3.0, 4.0, 5.0; $x = 0.5$.

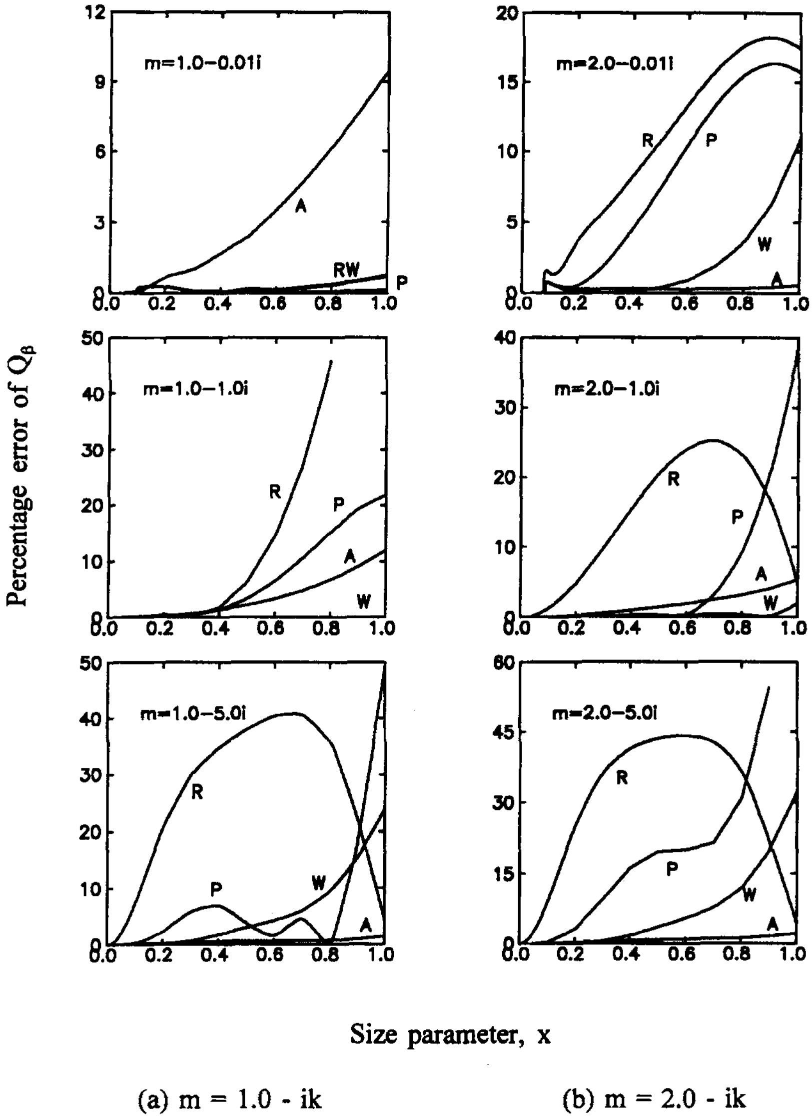


Fig. 6. The sensitivity of the absolute percentage error in the extinction efficiency factor Q_β to the size parameter x as computed from the approximations by Rayleigh (R), Penndorf (P), Wiscombe (W) and the first term (A). (a) $m = 1.0 - ik$ (b) $m = 2.0 - ik$, for $k = 0.01$, 1.0, 5.0.

and $r_m = 0.03\ \mu$m, typical of soot) is presented in Figs. 7–10. For a small size parameter [$x = 0.1$, Fig. 7(a)], the Wiscombe and the first-term approximations are most accurate, up to $k = 10$ with a maximal error of 6.8%. The empirical correlation by Buckius and Hwang[13] produces a large error when $n = 1$ at around $k = 1.0$, and, as n increases, it gradually approaches the Rayleigh approximation. For $x = 0.5$ [Fig. 7(b)], only the first-term approximation shows a good agreement with the exact solution (maximal error is about 4.7%). When $n \leqslant 2$, the Wiscombe approximation has an accuracy comparable to the first-term approximation up to $k = 3$. As pointed out by Wiscombe[10] and shown in the figures for $n \geqslant 3$, the approximation, however, loses accuracy as $|m|$ increases. Figure 7(c) shows the results for $x = 1.0$. Except for the case of $n = 1$, all approximations have large errors, including the first-term approximation. This can be explained by the fact that, unlike the computation of the efficiency factors at $x = 1.0$, the radiative coefficients [evaluated by integration over a size parameter distribution around the value $x = 1$, Eq. (1)] include efficiency factors for $x > 1.0$. For such larger values of x the number of terms used in the approximations should be increased beyond what is used in the approximations evaluated in this paper. The scattering coefficients are shown in Fig. 8, and the behaviors of the approximations are quite similar to those observed for the extinction coefficients.

The same results are presented in Figs. 9 and 10 as a function of the size parameter. As can be seen from the figures, especially for $n \geqslant 3$ in Figs. 9(a) and 10(a), the first-term approximation shows a reasonably good agreement over a wide range of parameters examined here. However, even the

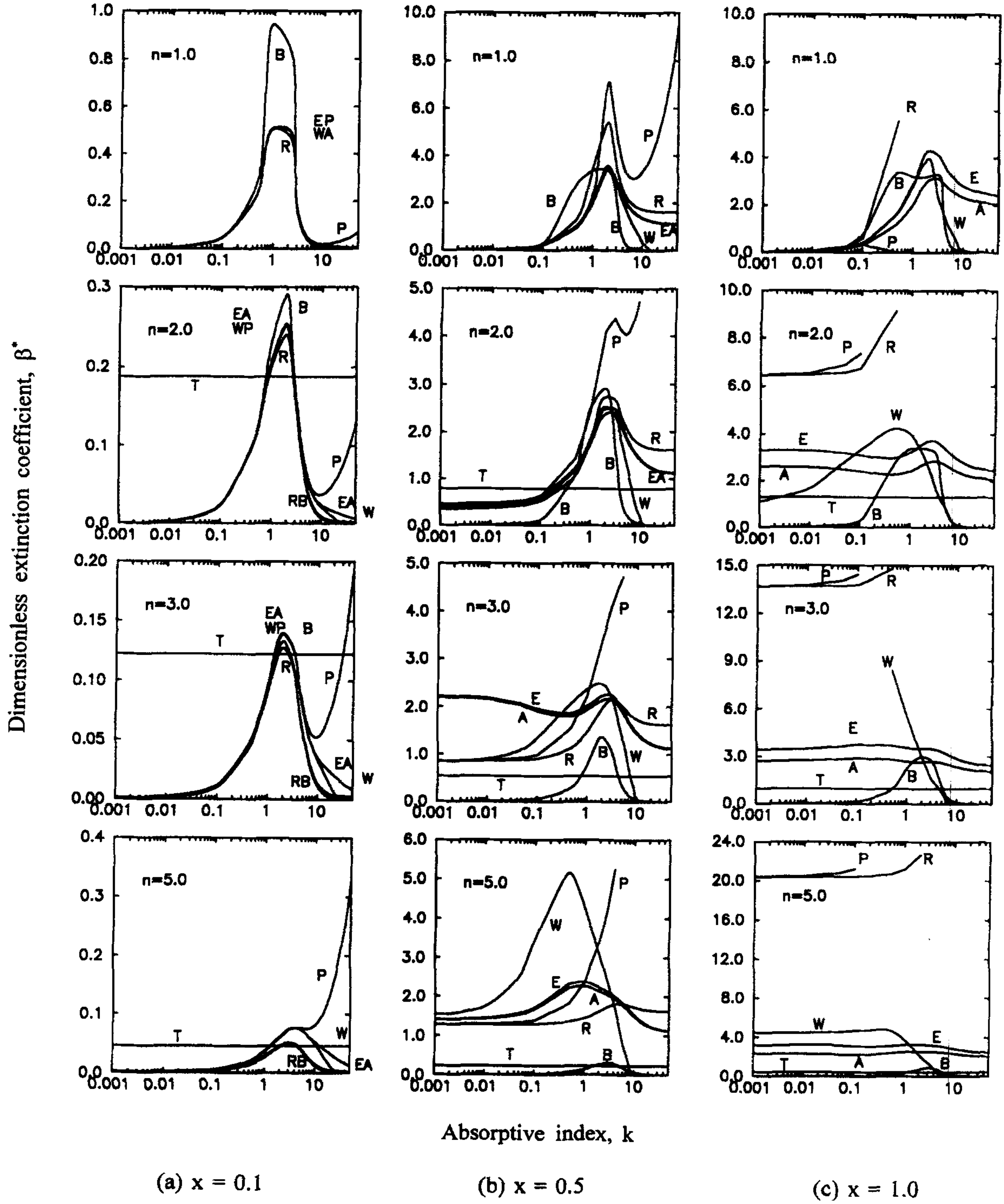


Fig. 7. The effect of the absorptive index k on the extinction coefficient β^*, as computed by the Mie theory (E), and the approximations by Rayleigh (R), Penndorf (P), Wiscombe (W), Tien et al (T), Buckius and Hwang (B) and the first term (A). (a) $x = 0.1$; (b) $x = 0.5$; (c) $x = 1.0$, for $n = 1.0$, 2.0, 3.0, 5.0.

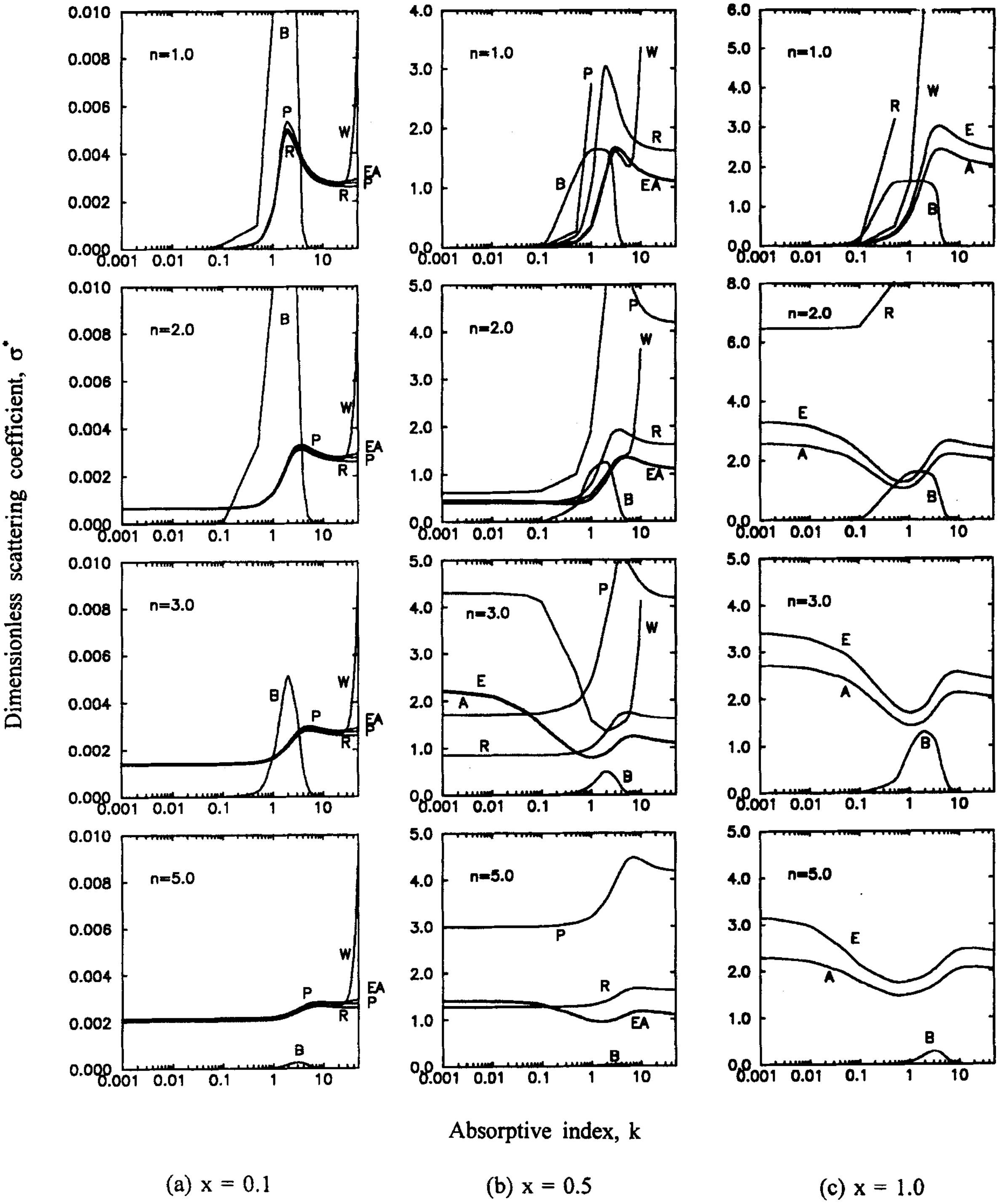


Fig. 8. The effect of the absorptive index k on the scattering coefficient σ^*, as computed from the Mie theory (E), and from the approximations by Rayleigh (R), Penndorf (P), Wiscombe (W), Tien et al (T), Buckius and Hwang (B) and the first term (A). (a) $x = 0.1$; (b) $x = 0.5$; (c) $x = 1.0$, for $n = 1.0, 2.0, 3.0, 5.0$.

first-term approximation produces a large error as the size parameter approaches 1.0, due to the above-discussed reasons. The figures also demonstrate the improvement which the Penndorf approximation offers over the Rayleigh approximation as k increases; for small k [Fig. 9(a), $k = 0.01$], the two approximations give almost the same results.

To facilitate the choice of approximations as a function of the parameters x, k and n, the results of the comparisons of the approximations with the exact solution are summarized in Tables 1 and 2. These tables show, for different values of x and n, the range of k within which each approximation produces an error within 10%, which we found is acceptable and reasonable in most computations which use these radiative coefficients.

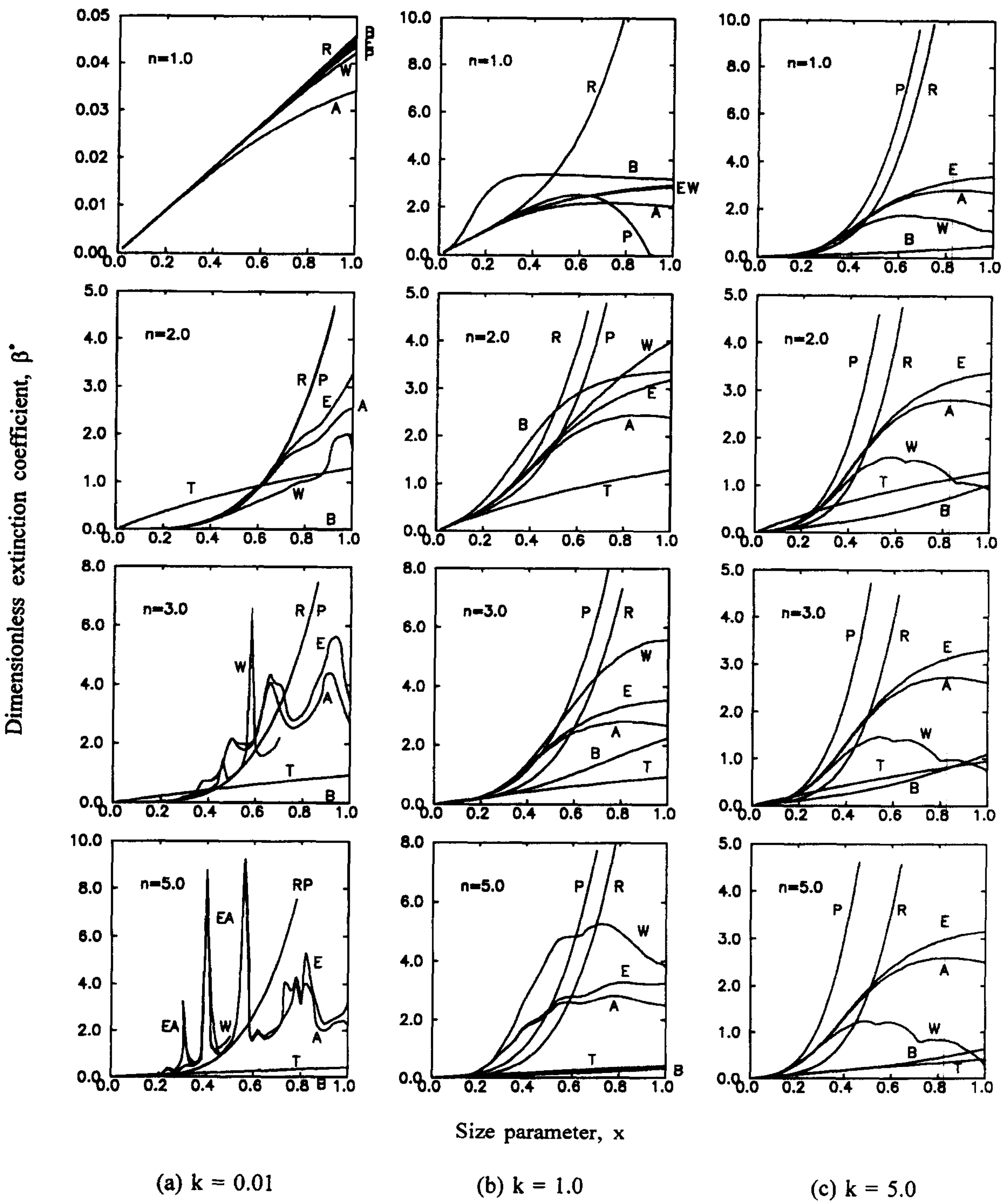


Fig. 9. The effect of the size parameter x on the extinction coefficient β^*, as computed from the Mie theory (E), and from the approximations by Rayleigh (R), Penndorf (P), Wiscombe (W), Tien et al (T), Buckius and Hwang (B) and the first term (A). (a) $k = 0.01$; (b) $k = 1.0$; (c) $k = 5.0$, for $n = 1.0$, 2.0, 3.0, 5.0.

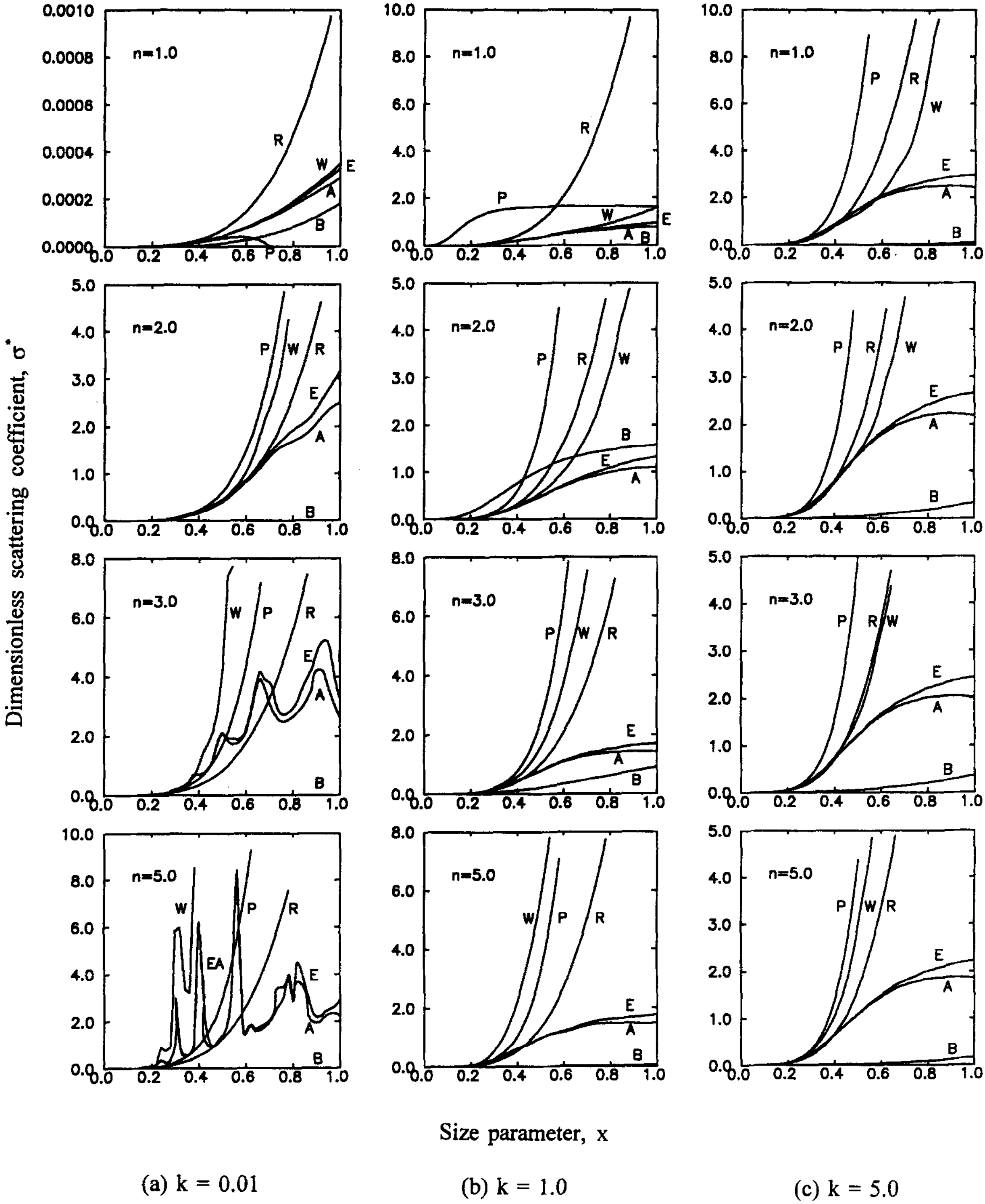


Fig. 10. The effect of the size parameter x on the scattering coefficient σ^*, as computed from the Mie theory (E), and from the approximations by Rayleigh (R), Penndorf (P), Wiscombe (W), Tien et al (T), Buckius and Hwang (B) and the first term (A). (a) $k = 0.01$; (b) $k = 1.0$; (c) $k = 5.0$, for $n = 1.0, 2.0, 3.0, 5.0$.

3.4. *A specific example: the extinction and scattering coefficients for soot and small particles of* TiO_2

The accuracy of the coefficients as computed by the approximations was evaluated for two technologically-relevant particle suspensions in which the size parameter $x \leqslant 1$:

(i) soot particles found in coal combustors (typically $\bar{d} = 0.06\,\mu m$, $\alpha = 3$,[14] $m = 1.98 - 0.93i$), and

Table 1. The range of k with 10% error in the extinction and scattering coefficients ($\bar{d} = 0.06\,\mu$m, $\alpha = 4$).

		$n = 1.0$	$n = 2.0$	$n = 3.0$	$n = 5.0$
*Nondimensional extinction coefficients, β**					
$x = 0.1$	R	0.001–4.0	0.001–3.0	0.001–2.0	0.001–0.001
	T	N/A	OR	OR	OR
	B	0.001–0.1	0.05–0.5	0.5–3.0	OR
	P	0.001–6.0	0.001–6.0	0.001–6.0	0.001–6.0
	W	0.001–10.0	0.001–10.0	0.001–10.0	0.001–10.0
	A	0.001–50.0	0.001–50.0	0.001–50.0	0.001–50.0
$x = 0.5$	R	0.001–0.1	1.0–5.0	3.0–7.0	5.0–9.0
	T	N/A	OR	OR	OR
	B	0.001–0.05	OR	OR	OR
	P	0.001–1.0	0.05–0.1	OR	0.001, 1.0
	W	0.001–3.0	0.5–3.0	3.0	0.001, 3.0
	A	0.001–50.0	0.001–50.0	0.001–50.0	0.001–50.0
$x = 1.0$	R	0.001–0.01	OR	OR	OR
	T	N/A	OR	OR	OR
	B	0.001–0.01	0.5–2.0	OR	OR
	P	0.001–0.05	OR	OR	OR
	W	0.001–2.0	0.1	OR	OR
	A	N/A	OR	OR	OR
*Nondimensional extinction coefficients, σ**					
$x = 0.1$	R	0.001–50.0	0.001–35.0	0.001–35.0	0.001–35.0
	T	N/A	N/A	N/A	N/A
	B	0.001–0.1	N/A	N/A	N/A
	P	0.001–50.0	0.001–50.0	0.001–50.0	0.001–50.0
	W	0.001–30.0	0.001–30.0	0.001–30.0	0.001–30.0
	A	0.001–50.0	0.001–50.0	0.001–50.0	0.001–50.0
$x = 0.5$	R	0.001	0.05–0.1	0.05	0.001–0.1
	T	N/A	N/A	N/A	N/A
	B	0.001	0.5	N/A	N/A
	P	0.001, 0.1	N/A	0.05	N/A
	W	0.001–7.0	0.001–6.0	N/A	N/A
	A	0.001–50.0	0.001–50.0	0.001–50.0	0.001–50.0
$x = 1.0$	R	N/A	N/A	N/A	N/A
	T	N/A	N/A	N/A	N/A
	B	N/A	N/A	N/A	N/A
	P	N/A	N/A	N/A	N/A
	W	0.01	N/A	N/A	N/A
	A	0.001	N/A	N/A	N/A

N/A, not applicable; OR, out of range; *R*, Rayleigh approximation; *T*, Tien et al approximation; *B*, Buckius and Hwang approximation; *P*, Penndorf approximation; *W*, Wiscombe approximation; *A*, the first-term approximation.

(ii) TiO_2 particle used as a catalyst in photocatalytic detoxification of contaminated water (typically $\bar{d} = 0.03\,\mu$m, $\alpha = 2$,[15] $m = 2.57 - 1.28i$).

Dimensionless size distribution curves based on these parameters are shown in Fig. 11. The size parameter x was calculated in the wavelength range of $1\,\mu\text{m} \leqslant \lambda \leqslant 10\,\mu\text{m}$ for the soot particles, corresponding to combustion chamber conditions, and $0.3\,\mu\text{m} \leqslant \lambda \leqslant 0.4\,\mu\text{m}$ for the TiO_2 particles, corresponding to their use as catalysts in the u.v. light spectrum.

The size-parameter sensitivity of the dimensionless extinction and scattering coefficients thus computed for these particles from the exact Mie solution and the approximations is presented in Fig. 12. For soot particles [Fig. 12(a)], the first-term approximation is the best overall, giving a negligible error for $x \leqslant \sim 0.4$ (as seen in Fig. 11, $x \leqslant 0.3$ for soot in typical combustors), and a maximal extinction coefficient error of about -30% for $x = 1.0$, with smaller errors ($\leqslant -21\%$) in the scattering coefficient. The Wiscombe approximation also gives negligible errors for $x \leqslant \sim 0.4$, but produces unacceptably large errors in the scattering coefficient for $x \geqslant \sim 0.5$. The Penndorf and Rayleigh approximations produce negligible errors only for $x \leqslant \sim 0.1$, but produce unacceptably large errors for $x \geqslant \sim 0.4$ using the Penndorf approximation, and for $x \geqslant \sim 0.5$ using the

Table 2. The maximum values of x with 10% error in the extinction and scattering coefficients ($\bar{d} = 0.06\,\mu m$, $\alpha = 4$).

		$n = 10$		$n = 2.0$		$n = 3.0$		$n = 5.0$	
		β^*	σ^*	β^*	σ^*	β^*	σ^*	β^*	σ^*
$k = 1.0$	R	0.30	0.14	0.18	0.34	0.12	0.18	0.04	0.12
	T	N/A	N/A	0.10	N/A	0.00	N/A	0.00	N/A
	B	0.02	0.00	0.08	0.00	0.12	0.00	0.04	0.00
	P	0.68	0.12	0.38	0.18	0.24	0.24	0.12	0.18
	W	1.00	0.66	0.68	0.46	0.44	0.32	0.26	0.18
	A	0.56	0.80	0.66	0.82	0.68	0.84	0.68	0.84
$K = 5.0$	R	0.06	0.12	0.06	0.12	0.04	0.12	0.02	0.12
	T	N/A	N/A	0.00	N/A	0.00	N/A	0.00	N/A
	B	0.06	0.00	0.04	0.00	0.04	0.00	0.02	0.00
	P	0.34	0.24	0.14	0.24	0.14	0.24	0.12	0.24
	W	0.36	0.40	0.34	0.54	0.34	0.42	0.34	0.22
	A	0.78	0.82	0.76	0.82	0.74	0.82	0.74	0.84

N/A, not applicable; *R*, Rayleigh approximation; *T*, Tien et al approximation; *B*, Buckius and Hwang approximation; *P*, Penndorf approximation; *W*, Wiscombe approximation; *A*, the first-term approximation.

Rayleigh approximation. At $x = 0.1$, a typical average size parameter for soot in a coal combustor, the errors for the extinction coefficient are smaller than 4.2% (Rayleigh) and 0.2% (Penndorf), respectively.

For TiO_2 particles [Fig. 12(b)], the Rayleigh approximation is best for the extinction coefficient in the range of $0 \leqslant x \leqslant 0.44$ with a maximal error of 18%. It is also the best, producing errors $\leqslant 3.6\%$ in the range of size parameters relevant to an u.v. light photocatalytic process (Fig. 11). The error decreases until x reaches 0.66 and then increases again, producing errors within 27%; it is less than 58% for that photocatalytic process. It is noteworthy that since the approximation error depends on x, and the particle size distribution contributes to the definition of x, the size distribution function parameters (α and r_m) also affect the error. For example, the first-term approximation for TiO_2 ($\alpha = 2$) was found to produce larger errors than those obtained for $\alpha = 4$ (Figs. 9 and 10).

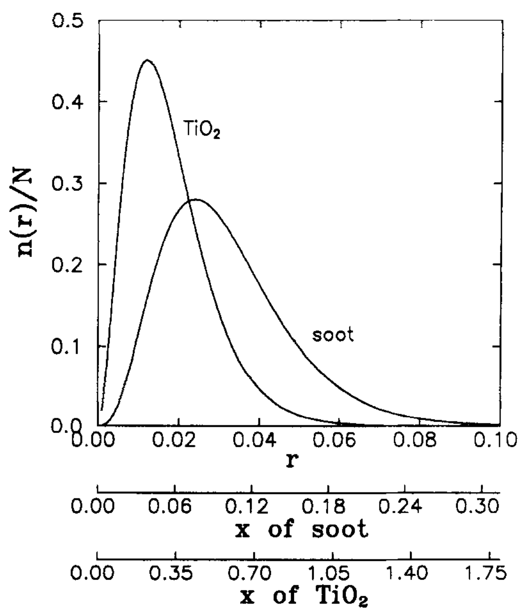


Fig. 11. Dimensionless size distribution curves of soot ($\alpha = 3$, $\bar{d} = 0.06\,\mu m$, $\lambda = 2\,\mu m$) and TiO_2 ($\alpha = 2$, $\bar{d} = 0.03\,\mu m$, $\lambda = 0.35\,\mu m$) particles.

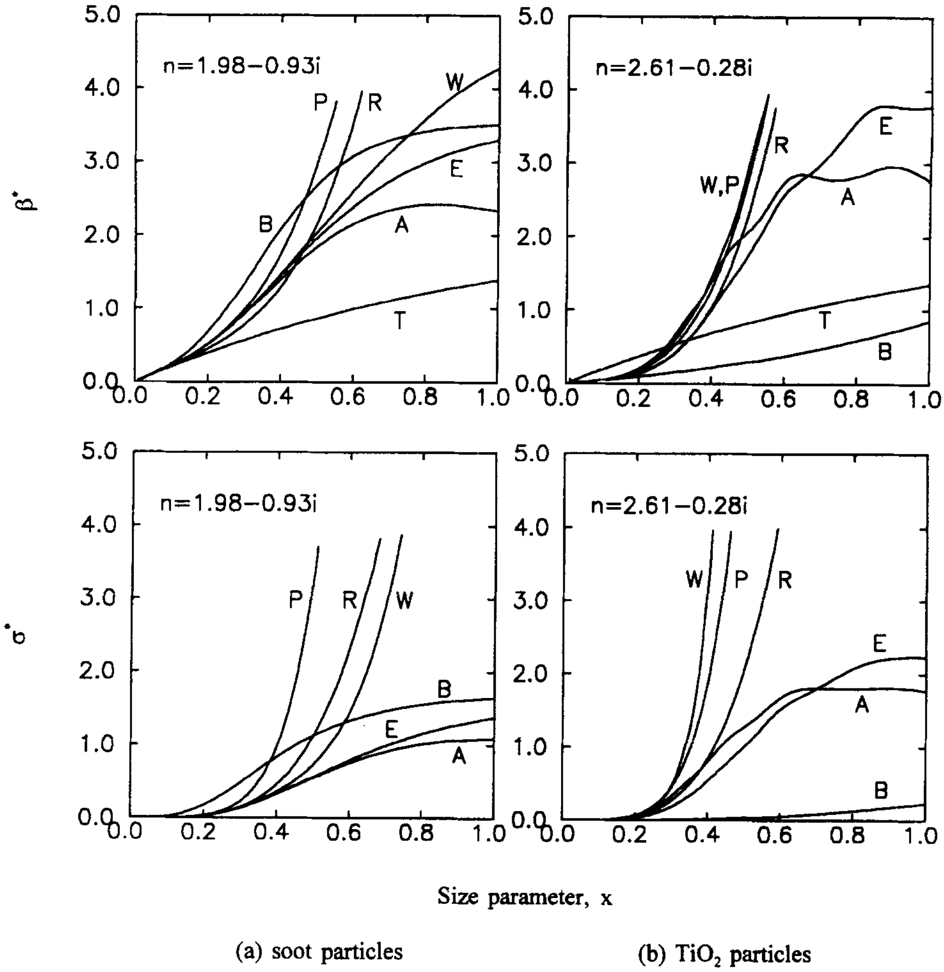


Fig. 12. The effect of the size parameter x on the dimensionless extinction and scattering coefficients, for (a) soot particles ($\bar{d} = 0.06\,\mu$m, $\alpha = 3$, $m = 1.98 - 0.93i$), and (b) TiO_2 particles ($\bar{d} = 0.03\,\mu$m, $\alpha = 2$, $m = 2.57 - 1.28i$), as computed by the Mie theory (E), and the approximations by Rayleigh (R), Penndorf (P), Wiscombe (W), Tien et al (T), Buckius and Hwang (B) and the first term (A).

The error of the Buckius and Hwang approximation is negligible only for $0.1 \leqslant x \leqslant 0.15$, but increases rapidly to unacceptable levels for other size parameters. For the scattering coefficient, the Rayleigh approximation produces errors within 46% for $x \leqslant 0.32$, in which range the first-term approximation is second best, producing errors up to 76%. For $x > 0.4$, the first-term approximation is the best, producing errors of up to 50%. The errors decrease till $x = 0.7$, and errors within 10% are produced only by the first-term approximation in the very narrow range of $0.6 \leqslant x \leqslant 0.8$.

CONCLUSIONS

(1) Detailed information is provided for facilitating selection of a mathematically-simplified expression for computing the radiative efficiency factors.

(2) The approximations require only a few lines of computer code and require less cpu time than the full Mie-equations solution code.

(3) A symbolic algebra code, using Mathematica^{tm} and thus consisting of about two orders of magnitude fewer lines of code than available FORTRAN programs, was developed and successfully used for solving the full Mie equations.

(4) The first-term approximation for the extinction efficiency factor agrees with the Mie solutions within 10% in a wide range of the complex refractive index ($1.0 \leqslant n \leqslant 5.0$ and $0.01 \leqslant k \leqslant 50.0$) for size parameter $x \leqslant 0.8$. For a maximal error of 12%, the valid limit is extended to $x = 1.0$, with

$1.0 \leqslant n \leqslant 5.0$ and $1.0 \leqslant k \leqslant 50.0$. For the scattering efficiency factor, the approximation has a much wider range of applicability, up to $x = 1.0$ with a maximal error of 1.2%, for $1.0 \leqslant n \leqslant 5.0$ and $1.0 \leqslant k \leqslant 50.0$.

(5) The small-particle approximation by Wiscombe[10] has better accuracy than the first-term approximation only for the extinction efficiency factor in the cases of $n = 1, k \leqslant 1$, and $n = 2, k = 1$ (for example, the errors at $x = 1.0$ are 0.2 and 12%, respectively, when $m = 1.0 - 1.0i$). However, it loses accuracy as the size parameter or the complex refractive index increase.

(6) The advantage of the Penndorf approximation over the Rayleigh approximation is limited to a few small seemingly arbitrary regions of the refractive index and size parameter. As well-known, both are satisfactory only in the smallest of the size-parameter values examined here.

(7) The first-term approximation for the extinction coefficient agrees with the Mie solutions within 7.3% in the range of $1.0 \leqslant n \leqslant 5.0$ and $0.001 \leqslant k \leqslant 50.0$ for size parameter $x \leqslant 0.5$. For the scattering coefficient, the approximation has smaller errors, maximal 1.8%, in the same range.

(8) The small-particle approximation by Wiscombe has better accuracy than the first-term approximation for the limited cases of $1.0 \leqslant n \leqslant 3.0$ and $0.05 \leqslant k \leqslant 5.0$ for the extinction coefficient at $x = 0.1$. For the scattering coefficient, both approximations have equally accurate results in the same range.

(9) The Penndorf approximation is better than the Rayleigh approximation only in the cases of $1.0 \leqslant n \leqslant 5.0$ and $0.001 \leqslant k \leqslant 10.0$ when computing the extinction coefficient, and for $2.0 \leqslant n \leqslant 5.0$ and $8.0 \leqslant k \leqslant 50.0$ when computing the scattering coefficient, for $x = 0.1$. For other cases, there is no substantial advantage of the Penndorf extension over the Rayleigh approximation.

(10) Amongst the different approximations analyzed here, the first-term approximation is the best for computing the radiative coefficients of soot for $x \leqslant 1.0$, incurring a maximal error of -29% for soot at $x = 1.0$. The error is $\leqslant 10\%$ for $x \leqslant \sim 0.6$. For TiO_2 particles of $x \leqslant 0.47$, the Rayleigh approximation is best (error $\leqslant 21\%$). For $x > 0.47$, the first-term approximation is best with errors smaller than 27%. The Buckius and Hwang approximation gives results for TiO_2 particle somewhat better than those of the first-term solution of approx. $0.75 \leqslant x \leqslant 1.0$.

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NOMENCLATURE

a—Particle size distribution coefficient, dimensionless
b—Exponent in size distribution function, dimensionless
a_n, b_n—Mie coefficients, dimensionless

H—Hankel function of the second kind
J—Bessel function of the first kind
k—Absorptive index, dimensionless
m—Complex refractive index ($= n - ik$), dimensionless
N—Total number of particles in unit volume (#/m^3)
n—Refractive index, dimensionless
Q—Radiation efficiency factor, dimensionless
r—Radius of a particle (μm)
$\bar{r}$—Mean radius of particles (μm)
r_m—Modal particle size (μm)
x—Size parameter ($x = \pi d/\lambda$), dimensionless

Greek symbols

α—Size distribution parameter
β—Extinction coefficient ($= \kappa + \sigma$) (m^{-1})
Γ—Gamma function
ζ—Riccati–Bessel function
κ—Absorbtion coefficient (m^{-1})
λ—Wavelength (μm)
σ—Scattering coefficient (m^{-1})
ψ—Riccati–Bessel function

Subscripts

E—Exact solution from the Mie theory
APPX—Approximate solution
β—Extinction
κ—Absorption
σ—Scattering
λ—Spectral

Superscript

$*$—Dimensionless
$\wedge$—Scaling by x_3
$-$—Average