

1.3.2 Exact analytical and numerical methods

The general statement of the single-particle scattering problem is rather simple and can be described as follows. A field \mathbf{E}_0 is incident on a scattering particle of volume V and excites the field \mathbf{E}_i inside V . Outside V , an additional field, the diffraction field \mathbf{E}_s , is generated. It is required to calculate, on the basis of Maxwell's equations, the complete field \mathbf{E} , which equals \mathbf{E}_i inside V , and $\mathbf{E}_0 + \mathbf{E}_s$ outside V , and that satisfies the boundary conditions at the particle surface as well as the radiation conditions at infinity. The general scheme being simple, a concrete solution to the problem depends essentially on the geometry of the scatterer and on the properties and structure of its substance. For example, the solution cannot be obtained in a general closed form even for a *spherical* particle with an anisotropic refractive index of a general type.¹² Therefore, in the theory of scattering by small particles various methods have been developed whose scope and effectiveness depend on the particular statement of a problem. From a current standpoint, an effective numerical algorithm realized on a personal computer is equivalent to an analytical solution, which as a rule also calls for nontrivial calculations. In this section, we will look briefly only at those methods that are most intensively used in biological applications. A more detailed discussion of the calculation methods can be found in a recent review.¹⁶

1.3.2.1 Separation of variables and T-matrix methods (SVM and TM)

The most important analytical solution is the theory of scattering by a homogeneous isotropic sphere, called the Mie theory^{1,12} (the pioneering work on this problem is associated with a constellation of names⁴⁰⁻⁴⁴). To illustrate the basic results of the Mie theory, we give formulas for the extinction cross section, the scattering cross section, and the anisotropy parameter, following the designations¹²

$$\sigma_e = \frac{2\pi}{k^2} = \sum_{n=1}^{\infty} (2n+1) \operatorname{Re}(a_n + b_n), \quad (1.15)$$

$$\sigma_s = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n+1) (|a_n|^2 + |b_n|^2), \quad (1.16)$$

$$g = \frac{4\pi}{k^2 \sigma_s} \left\{ \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} \operatorname{Re}(a_n b_n^*) + \sum_{n=1}^{\infty} \frac{n(n+2)}{n+1} \operatorname{Re}(a_n a_{n+1}^* + b_n b_{n+1}^*) \right\}, \quad (1.17)$$

where the coefficients a_n and b_n are called Mie coefficients.¹² The Mie theory is generalized for the case of concentrated spheres, particles with an

inhomogeneous profile of refractive index or with the optical activity of the substance, and also for the case of illumination by a focused laser beam. The relevant literature citations and effective computer codes can be found in Refs. 16 and 23.

For an infinite circular cylinder an exact solution at perpendicular incidence was first obtained by Rayleigh,⁴⁵ who addressed this problem once again in his last work written shortly before his death.⁴⁶ Though an infinite cylinder is not a three-dimensional (3-D) scatterer, this model is helpful in understanding light scattering and extinction by an anisotropic dispersion medium (see Section 1.7 below). References to literature that generalizes a simplest model can be found in Ref. 16. The Mie solution is also generalized to an arbitrary collection of spheres, but this subject concerns the problem of scattering by particle aggregates and will be treated separately in Section 1.4.

In Helmholtz's scalar equation, the variables are separated into 11 physically interesting coordinate systems.⁴⁷ But for a vector field containing *three* scalar functions, a complete separation of variables is possible only in six systems: (1) Cartesian, (2–4) three cylindrical, (5) conical, and (6) spherical. Therefore, Möglich's⁴⁸ formal solution for spheroidal coordinates was useless for all practical purposes until the method for separation of variables was adapted by Asano and Yamamoto⁴⁹ for numerical calculations via cutoff of infinite coupled (i.e., not fully separated) equations. Farafonov⁵⁰ improved the method described in Ref. 49 by using an ingenious scheme of splitting fields into two types with an invariant angular part. By now, a large body of factual material has been assembled on the application of SVM in the calculation of scattering by spheroidal particles.^{15,51}

The T-matrix method, which is well known in quantum theory,¹³ was introduced into electromagnetic scattering by Waterman.¹⁴ Contrary to the Green function method, the T-matrix relates not the fields themselves in a coordinate representation, but the expansion coefficients of the incident and scattered fields over some complete set of vector basis functions. For example, if one expands all fields in vector spherical harmonics (VSH) $\mathbf{Y}_{mnp}^{(\tau)}$ ^{13,47,52}

$$\mathbf{Y}_{mn1}^{(\tau)} = \mathbf{N}_{mn}^{(\tau)}(k\mathbf{r}), \mathbf{Y}_{mn2}^{(\tau)} = \mathbf{M}_{mn}^{(\tau)}(k\mathbf{r}), \quad (1.18)$$

of the first and third kind ($\tau=1,3$), then the expansion coefficients for scattered (a_{mnp}) and incident (exciting, $p_{\mu\nu q}$) fields are related by

$$a_{mnp} = \sum_{\nu=1}^{\infty} \sum_{\mu=-\nu}^{\nu} \sum_{q=1}^2 T_{mnp,\mu\nu q} p_{\mu\nu q}. \quad (1.19)$$

After being published in Ref. 53, the T-matrix method began to be used commonly in the scattering theory.^{54–56} An important strong point of the method is the possibility that the problem on the orientational averaging of

the observed scattering characteristics may be solved analytically.^{57,58} To illustrate, the extinction and scattering cross sections averaged over random particle orientations are expressed directly in terms of a T-matrix

$$\langle C_e \rangle = -\frac{2\pi}{k^2} \text{Re}[\text{Sp}(T)], \quad (1.20)$$

$$\langle C_s \rangle = \frac{2\pi}{k^2} \sum_{ab} |T_{ab}|^2, \quad (1.21)$$

where the symbol Sp in Eq. (1.20) stands for a spur over all T-matrix indices, and the symbol a or b in Eq. (1.21) signifies a combined multi-index (nmp).

1.3.2.2 Integral equation method

The integral equation method (IEM) occupies a special place in the range of theoretical methods, since it is a general approach in which, by using the affiner Green function¹³

$$G(\mathbf{r}, \mathbf{r}') = (1 + k^{-2} \nabla \nabla) \frac{\exp[i\mathbf{k}(\mathbf{r} - \mathbf{r}')] }{4\pi|\mathbf{r} - \mathbf{r}'|}, \quad (1.22)$$

a boundary problem is reduced to an integral equation that includes the boundary condition and radiation condition at infinity^{13,59,60}

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + k^2 \int G(\mathbf{r}, \mathbf{r}') [\varepsilon(\mathbf{r}') - \hat{1}] \mathbf{E}(\mathbf{r}') d^3\mathbf{r}'. \quad (1.23)$$

Therefore, the IEM is not merely a numerical approach, but also an efficient basis for the formulation of other methods [e.g., the method of moments,⁶¹ the T-matrix method,^{53,62} or the Rayleigh–Debye–Gans (RDG) method^{6,13,59,63}]. In Eq. (1.23), the scattered field is expressed by way of an unknown distribution of *bulk* sources induced by an external field. In the electromagnetic theory, another approach is also used,^{60,62} in which the scattered field is calculated by way of a *surface* source distribution.

The presence of singularity in Green's function (1.22) gives rise to a “self-term” that accounts for the difference between the average Maxwell field and the local (effective) Lorenz field.⁵⁹ The various formulations of IEM are in many ways different only in the methods for allowing for the self-term and in the methods for replacing the integral equation by its discrete counterpart.^{64–67} The singular equation (1.23) can be represented, by the Fourier transform, as a nonsingular Fredholm integral equation (FIE) of the second kind,^{68,69} which is solved numerically after the discrete-analogue substitution. It is interesting that the FIE kernel coincides with the second Born approximation for the integral equation obtained in Ref. 63. References to papers on the application of various IEM versions in problems of single-particle scattering are available for review.¹⁶

1.3.2.3 Discrete dipole approximation

In the theory of scattering by small particles, this method began to be employed intensively after the publication of a paper by Pursell and Pennypacker,⁷⁰ though undoubtedly its physical basis was known and applied elsewhere previously.³⁰ Yurkin et al. (see, e.g., Ref. 71, and references therein) developed an alternative discrete dipole approximation code (ADA version) with enhanced efficiency. A detailed consideration of discrete dipole approximation (DDA) or ADDA capabilities and limitations can be found in Ref. 71. The basic physical approximation is in substitution of the actual scatterer for an ensemble of discrete elements with volume V_i , polarizability α_i , and dipole moments $\mathbf{d}_i = \mathbf{d}(\mathbf{r}_i)$, $i = 1 - N$. All the other calculations, e.g., those of the dipole amplitudes, the scattered field, the integral cross sections, and the scattering matrix may be done absolutely rigorously. The equations for dipole moments are not hard to write from simple considerations based on the concept of an exciting field equal to the sum of the incident wave and the fields of other dipoles at a given point

$$\mathbf{d}_i(\mathbf{r}_i) = \alpha_i \left[\mathbf{E}_0(\mathbf{r}_i) + k^3 \sum_{j \neq i} G_{ij} \mathbf{d}_j(\mathbf{r}_j) \right]. \quad (1.24)$$

The tensor of dipolar scattering G_{ij} is determined by the known formulas³⁰

$$G_{ij} = \exp(ikr_{ij}) [G_1(kr_{ij}) + G_2(kr_{ij}) \mathbf{R}_{ij} \cdot \mathbf{R}_{ij}], \quad (1.25)$$

$$G_n(z) = (-1)^n [-z^{-1} - (2n-1)(iz^{-2} - z^{-3})], \quad n = 1, 2, \quad (1.26)$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $\mathbf{R}_{ij} = \mathbf{r}_{ij}/r_{ij}$, and $\mathbf{a} \cdot \mathbf{b}$ is a dyadic. The solution of the system of linear equations (1.24) allows the calculation of all basic optical characteristics of an aggregate: the vector scattering-amplitude, $\mathbf{S}(\mathbf{k}_0, \mathbf{k}_s)$

$$\mathbf{S}(\mathbf{k}_0, \mathbf{k}_s) = k^3 \sum_i [\mathbf{d}_i - \mathbf{s}(\mathbf{s} \cdot \mathbf{d}_i)] \exp(-i\mathbf{k}_s \cdot \mathbf{r}_i), \quad (1.27)$$

and the integral cross sections of extinction C_e , absorption C_a , and scattering $C_s = C_e - C_a$

$$C_e = 4\pi k \text{Im} \sum_i (\mathbf{e}_0 \cdot \mathbf{d}_i) \exp(-i\mathbf{k} \cdot \mathbf{r}_i), \quad (1.28)$$

$$C_e = 4\pi k \sum_i \eta_i |\mathbf{d}_i|^2, \quad \eta_i = \frac{4\pi \text{Im}(\epsilon_i)}{V_i |\epsilon_i - 1|^2}. \quad (1.29)$$

The important question about the choice of model polarization is left beyond the limits of the phenomenological scheme just described. It is well known¹ that the simplest choice based on the Mossotti–Clausius formula does not satisfy the optical theorem. Therefore, various approximations have been proposed in

the literature^{64,70,72–75} that allow for the dipole-energy radiation losses and lead to complex polarizability even for the nonabsorbing dipole particle.

At first glance, it seems that the bulk IEM and DDA methods are based on different physical principles. Therefore, it is important to emphasize that the solution of Eq. (1.23) by the method of moments and the DDA solution actually lead to *identical* systems of linear equations for dipoles if equivalent assumptions have been made for polarizability in the DDA and for the self-term in the IEM.⁶⁶

If a basis lattice has been specified and the algorithm of finding polarizability found, it remains only to fill the lattice nodes by the corresponding dipoles with regard to the inhomogeneity and shape of the scatterer. Essentially no limitations are placed on the geometry and, to a degree, on the properties of the material. This is the chief value of the method, particularly as applied to structurally complex biological objects.⁷⁶ The limitations of DDA are associated with the provision of convergence and accuracy of the results, which are impaired for optically rigid structures.

1.3.3 Approximate theories

With advances in computer facilities and new algorithms many approximate methods of the scattering theory lost their initial value. Despite this, they often give useful information for the qualitative understanding of the physics of phenomena and quantitative tendencies. In this section, we look briefly at only the basic physical principles of certain approximations. A closer look at the approximate theories and abundant references are available in Refs. 16, 77, and 78.

1.3.3.1 Rayleigh approximation

The basic ideas of all approximate methods are associated with definite regions of values of the most important diffraction parameters: the size parameter ka and the relative refractive index $m = n/n_0$. For example, if $ka \ll 1$ and $ka|m| \ll 1$, we are dealing with Rayleigh scattering, in which a particle scatters like an infinitesimal dipole $\mathbf{d} = \alpha \mathbf{e}_0$

$$\mathbf{E}_{sR} = k^3 [\mathbf{d}_i - \mathbf{s}(\mathbf{s} \cdot \mathbf{d}_i)] \frac{\exp(ikr)}{kr}. \quad (1.30)$$

The dipole moment and the corresponding polarizability tensor are estimated from electrostatic equations.^{1,12} The possibility of using an electrostatic approximation to calculate the dipole moment allows particles of virtually all shapes to be considered in the Rayleigh scattering theory.⁷⁹ The accuracy of the Rayleigh approximation has received in-depth treatment in Refs. 80 and 81.

Stevenson^{82,83} generalized the Rayleigh theory by expanding the fields in powers of ka . This approximation was used to calculate the Mueller matrix of light scattering by random spheroids.⁸⁴ This chapter refers to other applications of the Stevenson approximation, as does Ref. 16.

1.3.3.2 Rayleigh–Debye–Gans approximation

In a large number of practically important cases, the relative refractive index of particles m is close to 1. In particular, for the overwhelming majority of biological structures, $m \sim 1$.⁷⁶ This condition is valid in an even greater number of cases for x-radiation or neutron scattering. Such particles are called “optically soft,” and the corresponding approximation can be called an “approximation of optically soft particles.”

The condition $|m - 1| \ll 1$ itself is not sufficient for the development of the theory, since the ratio between size and light wavelength and the phase-shift magnitude $\rho = 2ka(m - 1)$ are of major importance. The RDG approximation is applicable when two conditions are simultaneously fulfilled

$$|m - 1| \ll 1, \quad |\rho| \ll 1. \quad (1.31)$$

There are a number of names for the theory that is based on the assumptions in Eq. (1.31). The best-known name is the Rayleigh–Gans (RG) approximation.¹ We believe that the term RDG is best suited for the following reasons. The fundamental ideas of the method (including the derivation of successive approximations based on the integral relation for a scattered field) were formulated by Rayleigh in his 1881 paper,⁴⁵ and the formula for the sphere-scattering cross section was obtained by him in 1914.⁸⁵ In 1915, Debye⁸⁶ derived a general formula for the intensity of x-rays scattered by a randomly oriented particle ensemble. Later, Debye applied this approach to light scattering by polymer solutions,⁸⁷ which had a profound impact on the development of this trend.⁷ In quantum mechanics, an analogue to Rayleigh iterations was developed by Born;⁸⁸ his name is rightly associated with this approximation. Thus, retaining the name of Gans in the name of the theory (RDG) makes sense only because the name RG approximation has received wide acceptance thanks to van de Hulst.¹

The RDG approximation can be obtained by various means. For example, one may use general integral relation (1.23), assuming that the field inside the particle is the incident-wave field.¹³ Another mean is based on the physical interpretation of scattering as a result of interference from the independent-dipole fields excited by an incident wave in particle volume V .^{1,7} In either case, the scattered field is represented as

$$\mathbf{E}_s = \mathbf{E}_{sR} G(\mathbf{q}), \quad (1.32)$$

where \mathbf{E}_{sR} is the Rayleigh scattered field (1.30), $\mathbf{q} = \mathbf{k}_s - \mathbf{k}_0$ is the scattering vector, and $G(\mathbf{q})$ is the interference function or the scattering form-factor

$$G(\mathbf{q}) = \frac{1}{V} \int \exp(-i\mathbf{q}\mathbf{r}) d^3\mathbf{r}. \quad (1.33)$$