Optical Response of Arrays of Spheres from the Theory of Hypercomplex Variables

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Transformation from the three-dimensional hypercomplex $X(x, y, z)$ frame to another which has infinite dimensions but has the symmetry properties of an array built in allows the Laplace equation to be solved in structures for which it is nonseparable. The power and practicality of this technique is demonstrated on pairs and chains of spheres of arbitrary complex permittivity in a quasiconstant electric field. New results include strong absorption enhancement at long wavelengths in high density chains due to structurally induced resonances.

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Solutions of Laplace's equation apply to a wide array of physical problems including electrical and thermal transport phenomena, fluid flow, and polarization in an applied electric or magnetic field. Optical properties can also be deduced from these solutions if the characteristic features in a multiphase medium are much smaller in size than wavelength. In this initial presentation of a new, improved technique for exactly solving the Laplace equation (LE), we will focus on the novel insights it gives into the properties of arrays of small (nanoscale) spheres in a quasiconstant external field. We note, however, that the technique has broad potential. For instance, new precision and novel design in larger scale systems including electrode arrays, devices, and materials become possible.

Exact solutions are available for a limited class of structures and particle shapes. These can be represented by coordinate systems which allow the LE to be solved by separation of variables. There are twelve known systems in which this can be done [1]. For some of these, such as touching and separate pairs of spheres, exact results have only been established quite recently when one or more of the materials in the system have complex dielectric constants [2–4]. These results have highlighted the importance of multipolar interactions as particles approach and touch. Small changes in separation can dramatically alter optical absorption response as a function of wavelength. A simple dipole resonance structure for small, absorbing particles which are isolated changes due to the proximity of other particles to quite complex absorption spectra spanning a much broader range of wavelengths. The sensitivity to fine details of geometry means that easy to extract and numerically exact results are needed if we are to understand and model the response of complex arrays.

Earlier works in this field (e.g., [5–9]), while providing general insights into the presence of multipolar resonances were limited in scope and usefulness by the inherent difficulties of the mathematical framework in which they were formulated. The conventional approach is to start with general partial solutions based on individual particle shape, since these were known for the LE. The array is then accounted for by an extra boundary equation relating the potential seen by each particle to the multipoles induced on all the others [7–9]. This approach was originally used by Rayleigh [6]. Our approach is simpler because it uses partial solutions which have the symmetry of the array. Building in the array properties from the outset greatly simplifies solution and improves convergence rates, even for a simple pair. Thus this new technique has much to offer. Ignoring multipole effects has led to some common misconceptions [10] because data fitting is often possible using assumptions about shape distribution or relaxation times.

The powerful technique we present in this paper opens up new systems to exact study as it can provide accurate results for several nonseparable geometries. A basic example is used to introduce the approach which is then applied to the separated sphere pair and the chain of separated spheres. The pair result has been recently obtained with correct symmetry built in at the start using the separable bispherical coordinate system [4]. Our technique gives the same result more simply. However, the chain result is new as this is a nonseparable system. It also represents, we believe, the first practical application and new physical insights provided by the theory of hypercomplex (HC) variables.

We will show how to obtain an exact-integral solution [11] of the LE in 3D space. This approach is not only valid for any dielectric constants of the constituents but we also have results when each particle in an array is itself composite (e.g., a coated sphere). To the best of our knowledge the latter problem in 3D has never been discussed in the literature except in the dipole (lowest order) approximation. It is extremely complex by conventional methods.

We use the theory of functions of the hypercomplex variable X which may be regarded as an n-dimensional generalization of the classical theory of functions of the

two-dimensional complex variable $\mathbf{z}$. This theory originally emerged from the integral representation of the solutions of the LE [11,12]. The particular algebra of the HC numbers was first introduced by Ketchum [13,14] and further developed by Snyder [15] into a theory of hypercomplex analytic functions. We are especially interested in the solution of the LE in three dimensions. Hence we reproduce only their results for 3D HC space. We adopt the symmetry used in Refs. [14,15] rather than that of Ref. [12] so the HC variable X is defined as

$$X = xe_0 + ye_{-1} + ze_1,$$

where e_0, e_{-1}, e_1 are the 3D subspace of the infinite dimensional HC basis e_n. This basis was constructed in such a way that all integral powers of X satisfy the LE [14], that any function $f(X)$ belongs to the ∞D HC space with basis e_n, and for our purposes also means that the x axis becomes the pair or chain axis. It is known that the number of linearly independent solutions of degree n is equal to $2n + 1$. Therefore, the commutative and associative algebra for the basis e_n is introduced so that X^n has $2n + 1$ linearly independent components [14]. They are proportional to the well known spherical harmonics of degree n. As pointed out in Refs. [14,15], the HC algebra is isomorphic to the Banach algebra with the basis

$$\ldots, i^n \sin(n\, u), \ldots, i \sin(u), 1, i \cos(u), \ldots, i^n \cos(n\, u), \ldots,$$

which is the usual algebra of Fourier series. Therefore, the expansion of $F(X)$ over the basis $\ldots e_{-n}, \ldots, e_{-1}, e_0, e_1, \ldots, e_n, \ldots$ is just the Fourier series of the function

$$F(x + i\cos(u)y + i\sin(u)z)$$

$$= \sum_{n=0}^{\infty} i^n [\cos(n\, u)\, f_n(x, y, z) + \sin(n\, u)\, f_{-n}(x, y, z)]. \tag{1}$$

According to Eq. (1), $F(X)$ as well as all its $f_n(x, y, z)$ components are solutions of the LE.

To the best of our knowledge this formalism has never been used for obtaining solutions for any particular electrostatic problem, as given mathematically by (all evaluated at $\mathbf{r}$ =surface)

$$\nabla^2 \Phi(\mathbf{r}) = 0,$$
$$\Phi_{\text{out}}(\mathbf{r}) = \Phi_{\text{in}}(\mathbf{r}), \tag{2}$$
$$\epsilon\, \partial\Phi_{\text{in}}(\mathbf{r})/\partial\mathbf{n} = \partial\Phi_{\text{out}}(\mathbf{r})/\partial\mathbf{n},$$

where $\mathbf{n}$ is a normal vector to the given surface. We will first illustrate the power of this formalism using two of the known rotational coordinate systems which allow us to separate variables in the LE. We then go further and apply it to a nonseparable case.

The simplest example of a 3D separable coordinate system is a spherical one. Let us obtain the well known partial solutions of LE in this system in terms of HC variables. We will use a method which is quite similar to one widely used in the 2D complex representation of the usual polar frame. In the complex coordinate system given by the transformation

$$\omega = \ln(\mathbf{z})$$

the partial solution of the LE can be written as

$$\Phi(\mathbf{z}) = \exp(\pm n\omega) \equiv \mathbf{z}^{\pm n}.$$

For the spherical system we can follow the same sequences of steps. First, we introduce a "transformation"

$$\Omega = \ln(X).$$

The function $\ln(X)$ as well as other functions used in this study can be treated as ordinary analytic functions [14,15]. Thus each partial solution of the LE can be written as

$$\Phi_{\pm}(X) = \exp[\pm n\Omega(X)] \equiv X^{\pm n}. \tag{3}$$

The explicit form of Eq. (3) can be obtained by evaluating the Fourier series of $[x+iy\cos(u)+iz\sin(u)]^n$. The result is widely known (see [1,12]),

$$\Phi_+(X) \equiv X^n = R^n P_n(\cos(\theta)) + 2R^n \sum_{m=1}^{n} i^m \frac{n!}{(n+m)!} P_n^m(\cos(\theta)) \cos m(\phi - u), \tag{4a}$$

$$\Phi_-(X) \equiv X^{-n} = (1/R^n)P_{n-1}(\cos(\theta)) + (2/R^n) \sum_{m=1}^{n} i^m \frac{(n)!}{(n-m)!} P_{n-1}^m(\cos(\theta)) \cos m(\phi - u)$$

$$+ (2/R^n) \sum_{m=n+1}^{\infty} i^m \frac{(n)!}{(n-m)!} C_{n-1}^m(\cos(\theta)) \cos m(\phi - u), \tag{4b}$$

where R, θ, ϕ are the spherical coordinates, $P_n^m(\cos(\theta))$ are the associated Legendre polynomials, and $C_n^m(\cos(\theta))$ are the Gegenbauer polynomials.

From this simple example one can see the difference between the partial solutions of the LE for the polar frame in two dimensions and the spherical one in 3D. In the 2D case the $\mathbf{z}^n$ and $\mathbf{z}^{-n}$ solutions have the same rotational symmetry while in the 3D case the X^n and X^{-n-1}

solutions give equivalent rotational symmetry solutions. To solve the full electrostatic problem (2) we need to consider the partial solutions with equivalent symmetry properties. The easiest way to do this is to introduce the simple shift for the negative powers $n \to n + 1$ from the very beginning. From now on we will follow this procedure, referring to it as the "$n \to n+1$" rule, in which the second partial solution (4b) is multiplied by $1/X$.

Consider now the separable bispherical system. The transformation is (replacing ω and z in the 2D bicylindrical system with Ω and X)

$$\Omega = \ln\left(\frac{X+a}{X-a}\right),$$

where a is a pole distance [1]. Therefore, we seek the solutions in the form

$$\Phi_n^\pm(X) = \frac{1}{X \mp a}\exp(\pm n\Omega) \equiv \frac{(X \pm a)^n}{(X \mp a)^{n+1}}$$

(once again applying the $n \to n+1$ rule). The "zero" Fourier term is

$$\Phi_0^\pm(\mathbf{r}) = \frac{|\,\mathbf{r} \pm a\,|^n}{|\,\mathbf{r} \mp a\,|^{n+1}}P_n(\cos(\nu)),$$

where $\nu = \pi - \Theta_1 - \Theta_2$ with Θ_1, Θ_2 the angles of the point $\mathbf{r}$ seen from the poles $\pm a$, respectively. If now one transforms this formula from Cartesian coordinates into bispherical ones, the final expression will be

$$\Phi_0^\pm(\mu,\nu) = \sqrt{\cosh(\mu) - \cos(\nu)}\,e^{\pm(1/2+n)\mu}P_n(\cos(\nu)).$$

This is the known exact solution in the bispherical frame [4]. The other Fourier terms are just combinations of the expressions

$$\Phi_n^\pm(\mu,\nu,\phi) = \sqrt{\cosh(\mu) - \cos(\nu)}\,e^{\pm(1/2+n)\mu}$$
$$\times P_n^m(\cos(\nu))\begin{bmatrix}\cos(m\phi)\\\sin(m\phi)\end{bmatrix}, \qquad (5)$$

which are also solutions.

We have also solved, quite simply, the generalized touching sphere problem by this method based on the transformation $\Omega = 1/X$. Using separation, the general solution only appeared for the first time just last year [2] despite many previous attempts.

We now turn to the chain of spheres where our hypercomplex technique provides a direct solution, despite the LE being nonseparable. Applying the results shows clearly that going from a pair to a chain can have a very significant impact on the spectral resonance character. This has not been clearly demonstrated before.

An important new feature must be noted for the chain (or other extended systems such as a lattice) in the 3D hypercomplex approach. The surface of the particles does not have to be defined by one of the coordinates as is common in 2D conformal methods. Even in 2D the standard approach breaks down at higher densities in a chain [16]. The frame here determines the symmetry properties of the partial solutions. Boundary conditions are imposed on the original surfaces of particles, but expressed in the new frame variables. Thus we can take the 2D contours of potential and field arising from a line of alternating positive and negative charges placed at $x = 2na$ with n an integer, as the starting point. Rotation about the x axis leads to the desired hypercomplex

frame. In practice we can just replace $\mathbf{z}$ by $\mathbf{X}$ as before. The transformation becomes

$$\bar{\Omega} = \frac{a}{\pi}\ln\left[\tan\left(\frac{\pi\mathbf{X}}{a}\right)\right],$$

where Ω and $\mathbf{X}$ are hypercomplex variables.

We proceed exactly as before to establish partial solutions of desired symmetry using the $n \to n+1$ rule for negative powers of X. Then comes application of boundary conditions and some specific results for a pair and a chain.

For each system the general solution is the sum or the integral over the partial solutions, namely,

$$F_{\text{in,out}}(X) = \sum_{m=-\infty,k=\pm}^{\infty} \alpha_{m,k}^{\text{in,out}}\Phi_m^k(X). \qquad (6)$$

Now we rewrite the boundary conditions (2) using HC functions. For that purpose we shift where necessary, $X + a \to X$, so as to have one of the particles in the center of the coordinate system. Then, for spherical particles the normal derivative is

$$\frac{\partial F(X)}{\partial \mathbf{n}} \equiv \frac{\partial F(X)}{\partial R} = \frac{\partial F(X)}{\partial X}\frac{\partial X}{\partial R} = \frac{X}{R}\frac{\partial F(X)}{\partial X},$$

where R is the radial distance. The definition of the derivatives of the functions of the HC variables are also given in Ref. [15]. For our purposes we should know only that they are formally differentiable like the functions of 2D complex variables. The system of boundary conditions becomes (both evaluated at $R = R_0$)

$$\begin{aligned}F_{\text{in}}(X) &= F_{\text{out}}(X),\\\epsilon\,F_{\text{in}}'(X) &= F_{\text{out}}'(X).\end{aligned} \qquad (7)$$

R_0 is the sphere radius. To solve we first expand the partial solutions $\Phi^\pm(X)$ in Eq. (6) over X truncating at some order, then substitute these expansions into Eqs. (7), and finally solve the linear matrix equation for the coefficients $\alpha_n^\pm$. This procedure is nothing more than matching coefficients for the Legendre polynomials of the same order. The last step is to extract the coefficient in front of the term $1/X^2$ in the outer solution to get the polarizability.

Our technique is applied to the polarizability of a pair and a chain of NaCl spheres with centers a unit distance apart. The NaCl pair has been previously discussed [4] based on a bispherical solution but the chain is new to the hypercomplex work. The dielectric constant depends on frequency as $\epsilon(\omega) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/[1 - (\omega/\omega_T)^2 - i\gamma(\omega/\omega_T)]$, where $\epsilon_0 = 5.934$, $\epsilon_\infty = 2.328$, $\omega_T = 164$ cm^{-1}, and $\gamma = 0.02$. In Fig. 1 each $R_0 = 0.4$; in Fig. 2 each $R_0 = 0.48$ and the absorption spectrum is shown using the imaginary part of polarizability. The strong convergence improvement for our pair result over conventional (Rayleigh) methods, especially at close approach, has been already outlined in Ref. [4]. Conventional re-
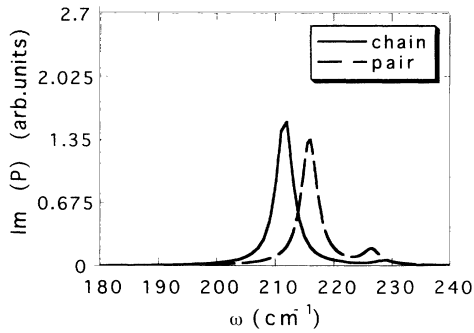
FIG. 1. Imaginary part of the infrared polarizability of a pair and a chain of equal NaCl spheres, separated by unit distance and with each $R_0 = 0.4$.
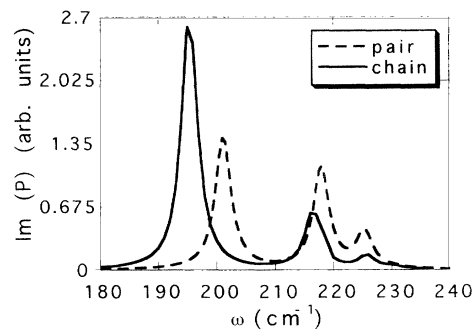

FIG. 2. Same as for Fig. 1 with each $R_0 = 0.48$.

sults are not even available in that regime for a chain. We can typically achieve convergence for absorbing particles in a chain with just 30 terms, when the spacing is 0.01 (so $R_0 = 0.495$) .

For the pair we see in Fig. 1 that higher order multipolar resonances appear to play a minor role at moderate separations but they are strong at close approach in Fig. 2. Three features stand out for the chain relative to the pair on which it is based. (a) The dominant dipole resonance shifts substantially at both separations to longer wavelengths and by similar amounts but also important is that adjacent multipolar resonance peaks are more widely separated, (b) at close separation only the leading resonance peak is strongly amplified, and (c) higher order resonances are damped out in the chain relative to the pair. Thus changes due to the presence of additional neighbors can be quite large and strongly enhanced absorption is possible at wavelengths where absorption is weak in a pair. Similar effects are also found in metallic particles.

There is an important new feature in the chain of spheres which has not shown up in earlier studies. While the resonance wavelengths of the low order poles shift to longer wavelengths in all cases with both additional neighbors and decreasing particle separation, the spectral weight of these poles commonly falls off or shifts up slightly. For the chain, in contrast, a substantial increase occurs at longer wavelengths. One major practical consequence concerns the chain of metal spheres. Our results show that a very strong enhancement in infrared absorption can result. Thus the resonance properties of a chain of spheres is a strong contender to explain the well known infrared absorption enhancement in some fine particle systems.

A new approach to solving the Laplace equation in complex arrays has been established. The theory of functions of hypercomplex variables developed in Refs. [14,15] plus use of a frame which builds in translational symme-

try at the outset are the key features. Numerical calculation is simple and rapidly convergent. The way is open to new insights into a number of important physical problems and technologies, as we have demonstrated in the case of the electromagnetic resonance behavior of chains of spheres.

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