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Comment on the use of the method of images for calculating electromagnetic responses of interacting spheres

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In this Comment, I argue that the method of images used by Huang, Yu, and Gu [Phys Rev. E **65**, 021401 (2002)] and Huang, Karttunen, Yu, Dong, and Gu [Phys Rev. E., **69**, 051402 (2004)] to calculate electromagnetic properties of interacting spheres at finite frequencies is inapplicable and does not provide a physically meaningful approximation.

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Recently, Huang, Yu, Gu [1] (referred to as HYG below) and Huang *et al.* [2] have applied the method of images to study theoretically the electromagnetic properties of two interacting spherical particles. As is well known, the method of images can be applied to spherical conductors in the electrostatic limit, i.e., when the dielectric constant ϵ can be formally set to $i\infty$ and the Bergman-Milton spectral parameter $s=1/(\epsilon-1)$ is equal to zero. At finite frequencies, when s is not small compared to the generalized depolarization factors s_n, the method of images is not applicable. However, HYG apply the method to dielectric particles at arbitrary frequencies, assuming only that the size of the two-sphere dimer is much smaller than the external wavelength. In particular, they claim to be able to extract the factors s_n and the corresponding oscillator strengths F_n, which characterize the electromagnetic response of a system within the quasistatics. In the first paper of the series [3] and in Ref. [1] the authors mention that their method is approximate. However, in the more recent paper [2] it is presented as exact and used without restriction. In the present Comment, I show that it is impossible to calculate the quantities s_n and F_n using the method of images. Moreover, the expressions for s_n and F_n given by HYG are not consistent with the exact electrostatic solution. Thus, the mathematical formalism developed by HYG is not only not exact, but does not provide a physically meaningful and controllable approximation.

We start with a brief review of mathematical formalism used by HYG. Within the quasistatics, dipole moment of an arbitrary particle characterized by the dielectric function $\epsilon(\omega)$ and excited by a homogeneous external field $\boldsymbol{E}_0\exp(-i\omega t)$ can be written as $\boldsymbol{d}\exp(-i\omega t)$, where $\boldsymbol{d}=\hat{\alpha}\boldsymbol{E}_0$. Here $\hat{\alpha}$ is the polarizability tensor. If polarization of the external field coincides with one of the principal axes of $\hat{\alpha}$, both vectors $\boldsymbol{d}$ and $\boldsymbol{E}_0$ become collinear. The corresponding scalar polarizability can be written in the Bergman-Milton spectral representation [4] as

$$\alpha=\frac{v}{4\pi}\sum_n\frac{F_n}{s+s_n}, \tag{1}$$

where v is the volume of the particle, s_n are the generalized depolarization factors satisfying $0<s_n<1$; and F_n are the corresponding oscillator strengths.

In the case of two spheres, one principal axis of the polarizability tensor coincides with the axis of symmetry and the other two axes are perpendicular to the first one and to each other, but otherwise arbitrary. HYG consider two interacting spheres of the radius R each separated by the center-to-center distance $2L$, obtain the diagonal elements of the polarizability tensor, and derive the following expressions for F_n and s_n:

$$F_n^{(L)}=F_n^{(T)}=F_n=4n(n+1)\sinh^3 a\exp[-(2n+1)a], \tag{2}$$

$$s_n^{(L)}=\tfrac{1}{3}\{1-2\exp[-(2n+1)a]\}, \tag{3}$$

$$s_n^{(T)}=\tfrac{1}{3}\{1+\exp[-(2n+1)a]\},$$

$$n=1,2,3,\ldots, \tag{4}$$

where the upper index (L) denotes longitudinal modes, (T) denotes transverse modes, and a is the solution to $\cosh a=L/R$, or, explicitly, $a=\ln[L/R+\sqrt{(L/R)^2-1}]$ [5]. It can be verified that F_n satisfy the sum rule $\Sigma_n F_n=1$.

Everywhere below we consider only the longitudinal modes, although the results of HYG for the transverse modes are also incorrect. The longitudinal modes are more important physically, since they are known to produce extremely high field enhancements in axially symmetrical arrays of nanospheres [6] and have been extensively studied in conjunction with the single-molecule spectroscopy [7].

First, let us discuss the small-frequency limit for conductors. In this limit, the dielectric function can be written as $\epsilon=4\pi i\sigma/\omega$, where σ is the static conductivity. Correspondingly, $s\propto\omega\to 0$, and we can expand α into a power series in s. The expansion can be obtained from (1) and reads

$$\alpha=\frac{v}{4\pi}\sum_{k=0}^{\infty}A_k s^k, \tag{5}$$

$$A_k=\sum_n F_n/s_n^{k+1}. \tag{6}$$

The electrostatic polarizability is given by $\alpha_{\rm es}=(v/4\pi)A_0$. The method of images can provide an exact expression for $\alpha_{\rm es}$ and, correspondingly, for A_0. However, since there is an infinite number of different sets of F_n,s_n that produce the

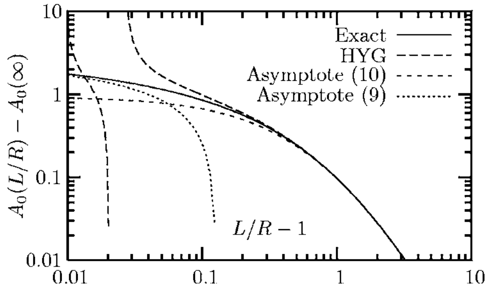

FIG. 1. $A_0(L/R) - A_0(\infty)$ as a function of the relative separation L/R calculated by different methods.

same value of A_0, it is impossible to find these coefficients from the electrostatic solution. We emphasize that this is not possible even if one considers the intersphere separation as an additional degree of freedom, since all quantities (A_k, F_n, and s_n) depend parametrically on L/R. Instead, if the summation in the right-hand side of (6) is truncated at $n=N$, one needs to calculate all coefficients A_k from $k=0$ to $k=2N-1$ in order to make the system of Eqs. (6) sufficiently determined. But the electrostatic solution based on the method of images can provide only one of these coefficients, namely, A_0.

Although one cannot expect that the set of F_n, s_n given by HYG (2) and (3) would produce, on substitution into (6), the correct expansion coefficients A_k for $k > 0$, it is still possible that the value of A_0 obtained in this manner is correct. However, as is demonstrated in Fig. 1, this is not so. In this figure, we plot the function $A_0(L/R) - A_0(\infty)$ [for conducting spheres, $A_0(\infty)=3$] calculated by different methods. The mathematically rigorous result is shown by the solid curve, and the result of HYG by the long dash. We also show in this figure two analytical asymptotes valid for $L \gg R$ (shorter dash) and $L \to R$ (dots). The different curves in Fig. 1 are explained below in more detail. At this point, we note that the result of HYG for $A_0(L/R)$ is accurate at large separations ($L \gg R$), but breaks down when $L/R \approx 1.2$ and becomes grossly inaccurate at $L/R \approx 1.03$. In particular, the HYG curve has a singularity at $L/R = x_c \equiv (2^{2/3}+1)/2^{4/3} \approx 1.026$. This is because the first depolarization factor s_1 defined by (3) crosses zero when $L/R = x_c$. The appearance of negative depolarization factors for smaller intersphere separations is unphysical and can, in particular, result in divergence of the electrostatic polarizability [8].

In the next two paragraphs I explain how the data for different curves shown in Fig. 1 were calculated. The solid curve was obtained by diagonalization of the electromagnetic interaction operator W whose matrix elements are given [9] by

$$W_{il,i'l'} = \frac{l\delta_{ll'}\delta_{ii'}}{2l+1} + (1-\delta_{ii'})(-1)^{l'}[\mathrm{sgn}(z_i - z_{i'})]^{l+l'} \times \sqrt{\frac{ll'}{(2l+1)(2l'+1)}}\frac{(l+l')!}{(L/R)^{l+l'+1}l!l'!}, \tag{7}$$

where $i,i'=1,2$ label the spheres, $l,l'=1,2,\ldots$ and z_i is the z coordinate of the center of ith sphere, assuming the z axis coincides with the axis of symmetry. The depolarization factors s_n are the eigenvalues of W, whereas the oscillator strengths can be found as squared projections of the corresponding eigenvectors $|n\rangle$ on the vector of external field: $F_n = \langle E|n\rangle\langle n|E\rangle$, where $|E\rangle$ is normalized so that $\langle E|E\rangle = 1$ [8]. The matrix defined in (7) was truncated so that $l,l' \leq l_{\max} = 1000$ and diagonalized numerically. In the absence of round-off errors and in the limit $l_{\max} \to \infty$, such diagonalization would produce the infinite set of exact values s_n, F_n. We note that at $l_{\max}=1000$ and $L/R \geq 1.01$, all the modes whose oscillator strength are not very small (i.e., greater than 0.001) have converged with a very high precision, and that the round-off errors do not influence the results in any noticeable way since the matrix W is well conditioned.

The dots and short dash in Fig. 1 show the theoretical asymptotes obtained by Mazets, who has derived an expression for A_0 in terms of hypergeometrical functions [10]. He has also provided simple asymptotic expansions, which are valid for small and large intersphere separations. Thus, for longitudinal excitations,

$$A_0 \approx 3\left[2\zeta(3) - \frac{\zeta^2(2)}{C + \ln(2/\sqrt{(L/R)^2 - 1})}\right],$$

$$L \to R, \tag{8}$$

$$A_0 \approx 3\left[1 + \frac{1}{4}\left(\frac{R}{L}\right)^3 + \frac{1}{16}\left(\frac{R}{L}\right)^6\right],$$

$$L \gg R, \tag{9}$$

where $\zeta(x)$ is the Riemann zeta-function and C is the Euler constant. The second term in the right-hand side of (9) is a correction due to the dipole-dipole interaction while the third term describe the next nonvanishing input due to the higher multipole interaction. It can be verified that the asymptotic expansion of the HYG result coincides with (9) at least up to the sixth order in L/R. However, the small-separation asymptote (8) is dramatically different from the one that follows from the HYG formulas.

Next, we compare the coefficients s_n, F_n defined by (2) and (3) according to HYG with respective values obtained by direct diagonalization of the interaction matrix W. The results are shown in Fig. 2. A significant discrepancy already exists at $L/R=1.2$ and becomes more dramatic as this ratio approaches unity. Negative depolarization factors are present in the plot for $L/R=1.01$. We note that the smallest intersphere separation considered by HYG was $L/R = 1+1/30 \approx 1.033$. As was mentioned above, the negative depolarization factors appear for $L/R \leq x_c \approx 1.026$. At these separations, results of any calculation based on the HYG formalism are expected to be grossly inaccurate and unphysical. However, this fact is not explained in Refs. [1,2]. For example, the choice of values for L/R in Fig. 5 of Ref. [1] appears to be random, while, in fact, all these values satisfy the critical condition $L/R > x_c$.

Although it is demonstrated in Fig. 2 that the values of s_n, F_n calculated according to HYG are inaccurate, these coefficients are not directly measurable in an experiment. How-

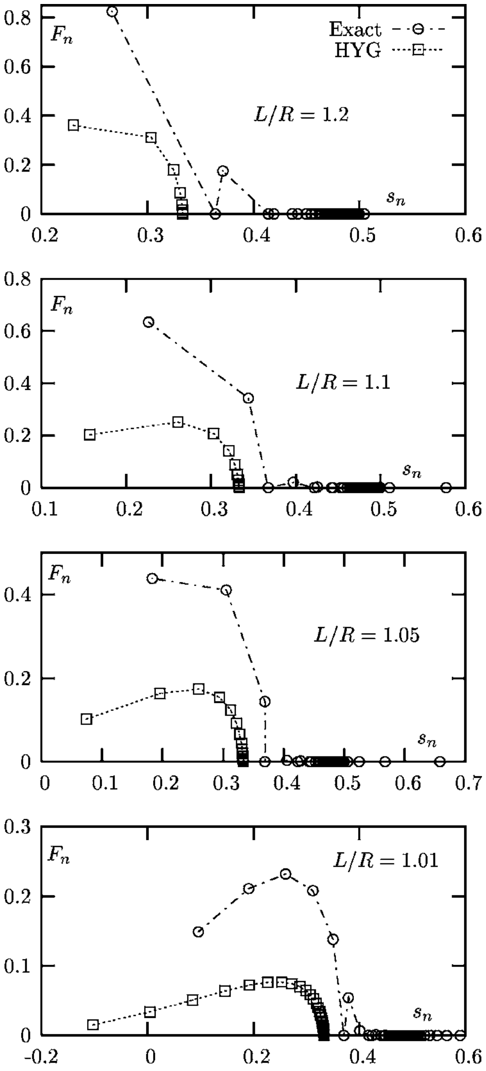

FIG. 2. Bergman-Milton depolarization factors, s_n, and the corresponding oscillator strengths F_n for different relative intersphere separations L/R. Dashed lines are plotted to guide the eye.

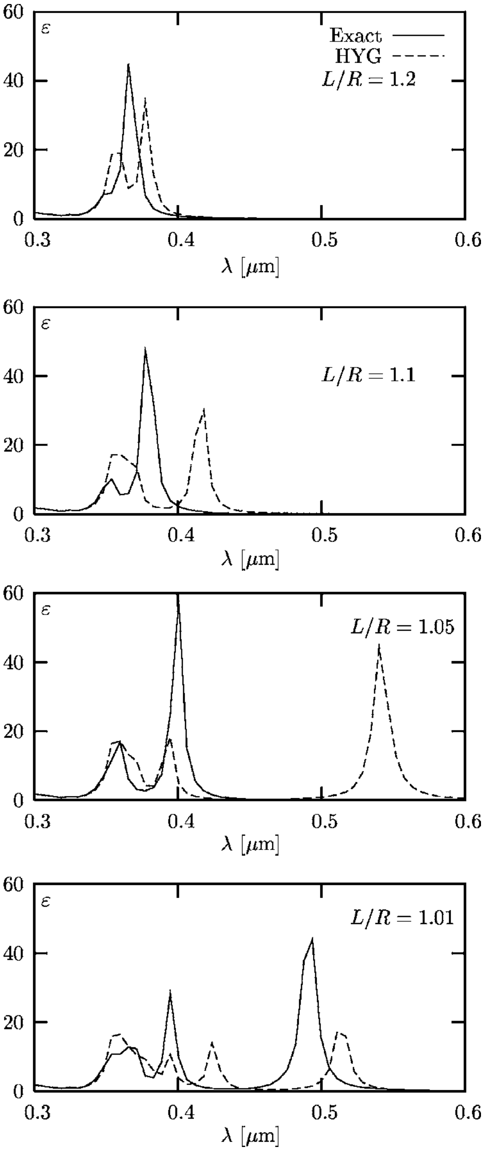

FIG. 3. Dimensionless extinction parameter $\varepsilon = \sigma_e / kv$ as a function of wavelength λ, where σ_e is the extinction cross section, $k = 2\pi/\lambda$, v is the total volume of the scatterer, plotted for different relative intersphere separations L/R. Polarization of the incident field is parallel to the axis of symmetry.

ever, they can be used to calculate various physically measurable quantities. For example, the extinction cross section is given by $\sigma_e = 4\pi kv \, \mathrm{Im} \sum_n F_n / (s + s_n)$. In Fig. 3 we plot the extinction spectra of two silver nanoparticles obtained for the same intersphere separations as in Fig. 2 and for the longitudinal polarization of the external field. Interpolated data for silver from Ref. [11] have been used to calculate the spectral parameter s as a function of wavelength. It can be seen that the spectra calculated using the formulas (2) and (3), for s_n, F_n differ dramatically from those calculated with the use of exact values of these coefficients. The discrepancy is evident even at relatively large separation, $L/R = 1.2$. It should be noted that in the case $L/R = 1.01$, the HYG spectra exhibit unlimited growth with the wavelength, which starts in the near-IR region (data not shown). This is due to the appearance of negative depolarization factors and contradicts the general sum rules for extinction spectra, which imply that σ_e must decrease faster than $1/\lambda$ in the limit $\lambda \to \infty$ [8]. Note that the presence of negative depolarization factors can result in even more severe anomalies of extinction spectra in dielectrics whose static dielectric permeability is positive, as well as the value of s in the limit $\lambda \to \infty$.

The papers [1,2] contain a number of other less significant inaccuracies. In particular, HYG confuse orientational averaging (for randomly oriented bispheres) with the averaging over polarization of the incident light. Thus, for example, Eq. (2) in Ref. [1] is presented as a result of averaging over polarization for a fixed bisphere. However, such averaging should clearly depend on the direction of the incident wave vector relative to the axis of symmetry of the bisphere. In fact, the first equality in this formula gives the result of orientational averaging, except that HYG are mistaken in stating that $\langle \cos^2 \theta \rangle = \langle \sin^2 \theta \rangle = 1/2$. It is easy to check that $\langle \cos^2 \theta \rangle = 1/3$ and $\langle \sin^2 \theta \rangle = 2/3$. Note that the second equality in Eq. (2) of Ref. [1] would be correct if the averaging is done over polarizations of the incident beam for a fixed bisphere, assuming that the incident wave vector is perpendicular to the axis of symmetry.

It should be noted that on p. 4 of Ref. [1], the authors acknowledge that the method of images is only approximate, but state that the approximation is very good and make a reference to the earlier work [3] to support that statement. However, in Ref. [3] verification of accuracy of the method of images is only done for relatively large separations, namely, $L/R \geqslant 1.5$ (Figs. 3 and 4 in Ref. [3]). At these separations, the multipole effects are generally not important, which clearly follows from the data shown in these figures. However, in later publications, HYG have used the method for much smaller separations, typically, $L/R = 1 + 1/30$.

Finally, also on p. 4 of Ref. [1], the authors write: "More accurate calculations based on bispherical coordinates can be attempted." This was, in fact, done in the above-referenced paper by Mazets [10], although only for perfect conductors. More general analytical results can be obtained with the use of the theory of hypercomplex variables (a generalization of the conformal mapping) [12].

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[5] A slight change of notations compared to those of HYG is adopted in this Comment. Namely, the parameter α of HYG is denoted by a in order to avoid confusion with the polarizability; the spectral parameter is defined as $s = 1/(\epsilon - 1)$ instead of $s = 1/(1 - \epsilon)$ and the coefficients F_n (2) differ from those of HYG by the overall factor -3.

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