Electrostatics of charged dielectric spheres with application to biological systems. III. Rigorous ionic screening at the Debye-Hückel level

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The unequivocal role of electrostatic forces in biological (and colloidal) systems underscores the importance of attaining accurate and rapid calculations of electrostatic forces if one wishes to faithfully simulate the electrostatic aspect of a biological system. This paper makes significant progress toward this aspect as it rigorously incorporates ionic screening at the Debye-Hückel level for an electrolyte system containing dielectric spheres of finite radii. We investigated earlier this system without mobile ions via a surface charge method. However, the need for computing a large number of Wigner rotation matrix elements per configuration can significantly slow down the numerical calculations. This difficulty was recently overcome by our Wigner-matrix-free formalism. Unfortunately, in that method ions can only be included individually, making it impractical to investigate, for example, ionic screening in a system modeled by charged dielectric spheres immersed in a solution of mobile ions. Here, we overcome this difficulty by extending the surface charge method to treat ions implicitly. Previous treatments of charged dielectric spheres in a solution of mobile ions did not emphasize the energy reciprocity of electrostatics and are largely limited to a few spheres and/or special symmetries. Our new formalism respects reciprocity and accommodates arbitrarily many dielectric spheres of different dielectric constants and sizes while being rigorous at the Debye-Hückel level. The differences, and the relationship, between our new implicit ion treatment and our previous ion-free (or explicit ion) approach are described. A closed form for the electrostatic energy with implicit ions is also provided. This new formalism speeds up the computation of the electrostatic energy in the presence of ions, and accommodates permanent and induced multipoles that are very important when the polarization effect needs to be correctly included. We also mention how the proposed method can be transformed to a numerical method for use with arbitrary nonspherical surfaces.

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I. INTRODUCTION

Apart from being generally important at the molecular level, electrostatic interactions are crucial for biomolecular systems and colloidal solutions. In both cases there are many charged objects, biomacromolecules in the former and colloids in the latter (and often a large number of small ions), embedded in the (polar) solvent, which for biological system is water. For a colloidal solution with macroscopic colloids the system's energy can be calculated classically, ignoring the quantum effects. Although quantum effects exist in biological systems, except for extremely small systems, it remains impractical to apply precise, full-fledged quantum methods to them due to the exponential increase of Hilbert space dimensions with the degrees of freedom. Therefore, considerable effort has been invested in classical approaches [1], which are often categorized according to how the solvent water is treated. Explicit solvent methods treat each water molecule at the level of atomic detail, while implicit solvent methods replace the individual water molecules with some type of smoothed out version.

Explicit solvent methods, such as TIPnP [2], allow description of biomolecular systems at finer detail, but the absence of mutual polarization of molecules in these models can be a critical deficiency sometimes. The implicit solvent methods [3,4] are in principle less computationally intensive when larger systems are considered; however, their application is limited to systems where fine details of solute-solvent interactions do not play a major role. Both formalisms can take into account ions explicitly when only a few ions are considered; when a large number of ions enter the consideration, even at low concentration level, an implicit ion approach is called for.

Focusing on ion-free or few-ion scenarios, we have earlier devised the surface charge method [5,6]. Although this formalism may be applied to molecular shapes other than spheres [7], we have thus far applied it mainly to the classical systems of dielectric spheres with either a piecewise continuous [8] or a narrow but smooth [9] dielectric function at the spherical boundaries. If the bodies are embedded in a dielectric medium, they provide an implicit solvent model and the bodies represent the biomolecules and ions while the solvent is modeled by the dielectric continuum. If, however, the bodies are considered to be in vacuum, the model becomes an explicit solvent model in which biomolecules, ions, and water molecules are modeled explicitly with their own parameters. These models readily include polarization effects,

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and the model in [8] was previously used to investigate the accuracy of our classical formalism in describing interactions between atomic-sized objects [10]. It was found that this dielectric-sphere model is surprisingly accurate down to distances where chemical bonds start to form. In [8,9], a rigorous formalism allowing a point charge at the center of each sphere was established. In [11], an arbitrary free charge distribution forming higher permanent multipoles was incorporated. It was shown that having the multipole sources inside the dielectric spheres and on the spherical surfaces are equivalent [11]. For later convenience, we denote by "method I-in" the method having multipole sources *in*side the spheres and by "method II-on" the method having multipole sources *on* the spherical surfaces. Although the induced surface charge densities appear different in the two methods, the observable total surface charge densities (induced plus permanent) in either method satisfy the same set of linear equations, implying the same solution. More recently, by further extending a formula mentioned a few decades ago, we managed to bypass the needed computations for Wigner rotation matrix elements [8,11] and were able to significantly speed up the numerical computation [12]. The formalism introduced in [8,9,11,12] allows one to find a solution with arbitrary accuracy for an arbitrary number of interacting dielectric spheres with arbitrary permanent multipoles at their centers or surfaces.

To extend this formalism to incorporate a large number of mobile ions, one needs an implicit ion approach. It is not surprising that systems of dielectric spheres immersed in a solution of mobile ions at low concentration, in addition to being used for modeling biomolecules [13], have long been studied for colloidal [14] and electrolyte [15] systems. For example, the system of two dielectric spheres immersed in electrolyte solution describable by the Debye-Hückel theory has been studied [16–20]. Existing treatments mainly focused on the off-center expansion of spherical harmonics functions, but did not emphasize the important reciprocity property in electrostatics and were largely limited to a few spheres and/or special symmetries. One aim of this paper is to rectify these issues and to provide a rigorous formalism at the Debye-Hückel level. The differences, and the relationship, between our new implicit ion treatment and our previous ion-free (or explicit ion) approach will be described. A useful closed form for the electrostatic energy of an arbitrary number of dielectric spheres of different dielectric constants and sizes with implicit ions will also be provided. Evidently, it is inappropriate to assume all biomolecules to have spherical shape. To this end, we provide a general numerical approach rooted in the current formalism to accommodate arbitrary molecular surfaces.

We should note that the formalism proposed by Lotan and Head-Gordon [13] is similar to ours in many aspects. However, important differences remain. The boundary condition requires reexpansion of spherical harmonics around an arbitrary origin. In the formalism of [13], prior to solving the boundary condition equations, two procedures are required for each pair of spheres: (i) assuming the relative orientation between the two sphere centers are along the $\hat{z}$ direction, reexpand (via numerical iteration) spherical harmonics around one sphere center to that around the other sphere center, and (ii) perform a rotation to bring the local $\hat{z}$ axes to the vector in the laboratory coordinate system. This is similar to our employment of Wigner rotations [8,11] although we provide the Wigner rotation matrix elements analytically. Under the formalism described in this paper, all the needed reexpansions are analytically derived and are completely free from the need of Wigner rotation.

In order to make this paper both self-contained and readable, we begin with an outline section that, in addition to giving an overview of the technical aspects of the paper, provides readers having different levels of interest in the details with corresponding reading paths. Technical derivations that might obstruct the flow of the paper are relegated to the appendices. Before ending the introduction, we would also like to emphasize that the goal of this paper is to provide a rigorous treatment and efficient calculation method of ionic screening at the Debye-Hückel level. Evidently, further development is necessary to achieve the goal of rigorously describing *real* biological systems.

II. OUTLINE

In addition to the introduction, readers are encouraged to read this section before moving to other sections.

The mathematical development of the current paper critically depends on the following two expansion formulas of modified spherical Bessel functions of the second kind (with $r_1 < r_2$ and $\vec{R} = \boldsymbol{r}_1 - \boldsymbol{r}_2$):

$$k_0(\kappa R) = k_0(\kappa|\vec{R}|) = \frac{e^{-\kappa|\boldsymbol{r}_1-\boldsymbol{r}_2|}}{\kappa|\boldsymbol{r}_1-\boldsymbol{r}_2|} = 4\pi\sum_{\ell,m} i_\ell(\kappa r_1)k_\ell(\kappa r_2)Y_\ell^m(\hat{r}_1)Y_\ell^{m*}(\hat{r}_2), \quad (1)$$

$$k_L(\kappa R)Y_L^M(\hat{R}) = \sum_{\ell_1,\ell_2,m_1,m_2} (-1)^{\ell_1+\ell_2} H^{LM}_{\ell_1 m_1 \ell_2 m_2} i_{\ell_1}(\kappa r_1) \times Y_{\ell_1}^{m_1}(\hat{r}_1)\, k_{\ell_2}(\kappa r_2) Y_{\ell_2}^{m_2}(\hat{r}_2), \quad (2)$$

where

$$H^{LM}_{\ell_1 m_1 \ell_2 m_2} \equiv C^{L0}_{\ell_1 0 \ell_2 0} C^{LM}_{\ell_1 m_1 \ell_2 m_2} \sqrt{\frac{4\pi}{2L+1}} \sqrt{(2\ell_1+1)(2\ell_2+1)}; \quad (3)$$

$C^{LM}_{\ell_1 m_1 \ell_2 m_2} = \langle \ell_1 \ell_2; m_1 m_2 | \ell_1 \ell_2; LM\rangle$ is the Clebsch-Gordan coefficient, and $i_\ell(k_\ell)$ is the modified spherical Bessel function of the first (second) kind satisfying the modified Helmholtz equation

$$[\nabla^2 - \kappa^2]\begin{cases} i_\ell(\kappa r)Y_\ell^m(\hat{r}) = 0, \\ k_\ell(\kappa r)Y_\ell^m(\hat{r}) = 0. \end{cases}$$

Formula (1) appears in almost every mathematical physics book; hence we use it as a known result and as the starting point for proving formula (2). A similar form of (2) in terms of the regular spherical Bessel functions can be found in [21] and in Ref. [22]. A proof of (2) is provided in our Appendix A. Identities such as $Y_\ell^{m*}(\hat{r}) = (-1)^m Y_\ell^{-m}(\hat{r})$ and $Y_\ell^m(-\hat{r}) = (-1)^\ell Y_\ell^m(\hat{r})$ yield seemingly different but equivalent forms for (2). It is worthwhile to point out that formula (2) is also a way to expand the spherical harmonics around a different center in the region where the modified Helmholtz equation for the potential is applicable. In fact, the off-center expansions used by [17] and [18], when fully carried out,

must agree with (2). However, taking care of the off-center expansion is only part of the work needed. To complete the theory, one has to obtain the proper substitution rule needed for dielectric spheres of finite radii. This latter part is described in Sec. V in connection with Sec. IV.

Prior to Sec. IV, Sec. III is a comparatively light read. We begin with the Poisson equation, then introduce the inhomogeneous modified Helmholtz equation and then join the two into one equation. We then introduce the reciprocity of the electrostatic energy. This section paves the way for later development. In Sec. IV, we show how the two equivalent surface charge methods in the ion-free case [11] remain equivalent in the presence of mobile ions. Then, in Sec. V, we derive the needed substitution rule for the potential expressions that make possible the treatment of dielectric spheres of finite radii immersed in a dielectric solvent containing mobile ions.

The general formalism including multiple dielectric spheres is given in Sec. VI. In this section, the electrostatic energy of an arbitrary number of dielectric spheres in ionic solvent is derived. Discussed and described in Sec. VII are some important and nontrivial aspects of this new formalism. We also provide here some numerical results of the *correct* energy for two dielectric spheres.

Readers interested in the full details of the derivation should first go through Sec. III and Appendix B. Then go over Secs. IV and V and Appendices C and D. Then go to the formalism Sec. VI and then the results and discussion section (Sec. VII) and Appendix A and then Appendix E, within which the reciprocity is proved for an arbitrary number of charged dielectric spheres. Readers only interested in the content of the new formalism may glance through Sec. III, Eqs. (21) and (27) and the paragraphs leading to and following them, and then go straight to the formalism section, and look at the figures and figure captions in the results and discussion section. Readers who only want to use the formalism may even skip the formalism section but pay attention to Eqs. (14), (27), (37), (38), and (48) and apply them in Eq. (49) to solve for the effectively observable surface charge strength. Then one may obtain the total electrostatic energy via Eq. (58) and the total interaction energy via Eq. (59).

III. UNIFICATION OF POISSON AND INHOMOGENEOUS HELMHOLTZ EQUATIONS AND RECIPROCITY IN ELECTROSTATICS

Let $\Phi(\boldsymbol{r})$ be the electric potential at point $\boldsymbol{r}$. The Poisson equation reads

$$\nabla^2\Phi(\boldsymbol{r}) = -4\pi[\rho_t(\boldsymbol{r}) + \rho_{\rm ion}(\boldsymbol{r})], \tag{4}$$

where $\rho_t = \rho_f + \rho_{\rm ind}$ contains all immobile charge densities including both the freely imposed charge density ρ_f (or, in short, free charge density) and the induced charge density $\rho_{\rm ind}$ in response to the electric field. Assume that the mobile ions of various species are in thermal equilibrium and follow the Boltzmann distribution. That is, for species s ions, each carrying charge q_s, the charge density $\rho_s(\boldsymbol{r})$ is assumed to be

$$\rho_s(\boldsymbol{r}) = c_s q_s e^{-\beta\frac{q_s}{\epsilon_o}\Phi(\boldsymbol{r})},$$

where β equals $1/(k_BT)$ with T being the temperature and k_B being the Boltzmann constant, c_s represents the average particle number density of species s ion, and ϵ_o is the dielectric constant of the fluid populated by mobile ions. The charge density due to mobile ions is thus given by

$$\rho_{\rm ion} = \sum_s c_s q_s e^{-\beta\frac{q_s}{\epsilon_o}\Phi(\boldsymbol{r})}. \tag{5}$$

Keeping only to linear order in Φ, one has

$$\rho_{\rm ion} \approx \left(\sum_s c_s q_s\right) - \frac{\beta}{\epsilon_o}\left(\sum_s c_s q_s^2\right)\Phi(\boldsymbol{r}) = 0 - \frac{1}{4\pi}\kappa^2\Phi(\boldsymbol{r}), \tag{6}$$

where $\kappa^2 \equiv 4\pi\frac{\beta}{\epsilon_o}(\sum_s c_s q_s^2)$. Note that the neutrality of total ion charge demands that $\sum_s c_s q_s = 0$. With (6), the Poisson equation (4) is turned into a *modified* inhomogeneous Helmholtz equation

$$[\nabla^2 - \kappa^2]\Phi(\boldsymbol{r}) = -4\pi\rho_t(\boldsymbol{r}) \tag{7}$$

in the region where mobile ions are present. Equation (7) constitutes the Debye-Hückel description of an electrolyte. Instead of going through Boltzmann distribution, one may arrive at the Debye-Hückel description by directly assuming that the local charge density of s-type ions is

$$c_s(\boldsymbol{r}) = c_s\left[1 - \beta\frac{q_s}{\epsilon_o}\Phi(\boldsymbol{r})\right].$$

Since c_s is the average concentration of the s ion type, integrating over the volume accessible by mobile ions yields

$$\int c_s(\boldsymbol{r})\,d\boldsymbol{r} \to c_s\left(\int d\boldsymbol{r}\right).$$

This means that one needs to have (with s_m being the ion-type of maximum charge magnitude)

$$\left|\int \beta\frac{q_{s_m}}{\epsilon_o}\Phi(\boldsymbol{r})d\boldsymbol{r}\right| \ll \int d\boldsymbol{r}. \tag{8}$$

This is plausible as β can be small, the sign of $\Phi(\boldsymbol{r})$ may vary by region of the space reachable by ions, and in particular $\Phi(\boldsymbol{r}) \to 0$ exponentially as $|\boldsymbol{r}| = r \to \infty$; see Sec. IV.

In the regime without mobile ions, say inside the dielectric spheres, one still has the Poisson equation. One may write a single expression uniting both cases; to proceed, let us begin with some notations. Consider N dielectric spheres, $\mathcal{A}_1, \ldots, \mathcal{A}_N$, immersed in an infinite solvent medium of dielectric constant ϵ_o and with mobile ions present. The jth dielectric sphere $\mathcal{A}_j$, centered at $\boldsymbol{R}_j$ with radius a_j, has a dielectric constant ϵ_j. We may thus write down the equation satisfied by the electric potential

$$[\nabla^2 - \kappa^2(\boldsymbol{r})]\Phi(\boldsymbol{r}) = -4\pi\rho_t(\boldsymbol{r}), \tag{9}$$

where

$$\kappa^2(\boldsymbol{r}) = \kappa^2\prod_{j=1}^{N}\theta(|\boldsymbol{r} - \boldsymbol{R}_j| - a_j),$$

with $\theta(x)$ being the Heaviside theta function: taking value 1 for $x > 0$ and 0 for $x < 0$. The electric potential $\Phi(\boldsymbol{r})$, aside from satisfying Eq. (9) and being continuous across the dielectric boundaries, must satisfy Eq. (19) or Eq. (20) depending on whether one wishes to proceed with method I-in (viewing the permanent multipoles as inside the spheres) or with method

II-on (viewing the permanent multipoles as on the spherical surfaces) [11].

When there are no mobile ions in the system, $\kappa = 0$ everywhere, and Eq. (9) reduces to the starting point of our ion-free (or explicit ion) surface charge method with the net fixed charge density ρ_t also comprising both the induced charge density $\rho_{\rm ind}$ and the *free* charge density ρ_f. The very fundamental idea of the surface charge method is that the electric potential can be written as a linear superposition of the potential produced by both free charge and the yet-to-be-determined induced (surface) charge.

For clarity, let us choose the average position of the dielectric spheres, $\frac{1}{N}\sum_{j=1}^{N}\vec{R}_j$, as the origin. The dielectric spheres are all thus within a finite radius $R_{\rm max}$ of the origin. The space under consideration contains the region $r \gg R_{\rm max}$ within which mobile ions move freely. Designate by $\Phi_1.(\boldsymbol{r})$ $[\Phi_2.(\boldsymbol{r})]$ the potential produced by charge distribution $\rho_n^1 = \rho_f^1 + \rho_{\rm ind}^1 + \rho_{\rm ion}^1 = \rho_t^1 + \rho_{\rm ion}^1$ $(\rho_n^2 = \rho_t^2 + \rho_{\rm ion}^2)$ alone. A simple form of the reciprocity theorem is that (due to $\rho_{\rm ion} = -\kappa^2\Phi/4\pi$)

$$\int_V \rho_t^1(\boldsymbol{r})\Phi_2.(\boldsymbol{r})\,d\boldsymbol{r} = \int_V \rho_t^2(\boldsymbol{r})\Phi_1.(\boldsymbol{r})\,d\boldsymbol{r},$$

which can be proved easily:

$$\begin{aligned}
&\int_V \left[\Phi_2.(\boldsymbol{r})\rho_t^1(\boldsymbol{r}) - \Phi_1.(\boldsymbol{r})\rho_t^2(\boldsymbol{r})\right]d\boldsymbol{r}\\
&= \int_V \{-\Phi_2.(\boldsymbol{r})[\nabla^2 - \kappa^2(\boldsymbol{r})]\Phi_1.(\boldsymbol{r})\\
&\quad + \Phi_1.(\boldsymbol{r})[\nabla^2 - \kappa^2(\boldsymbol{r})]\Phi_2.(\boldsymbol{r})\}\frac{d\boldsymbol{r}}{4\pi}\\
&= \int_V \{\Phi_1.(\boldsymbol{r})\nabla^2\Phi_2.(\boldsymbol{r}) - \Phi_2.(\boldsymbol{r})\nabla^2\Phi_1.(\boldsymbol{r})\}\frac{d\boldsymbol{r}}{4\pi}\\
&= \int_{\partial V} \{\Phi_1.(\boldsymbol{r})\nabla\Phi_2.(\boldsymbol{r}) - \Phi_2.(\boldsymbol{r})\nabla\Phi_1.(\boldsymbol{r})\}\cdot\frac{d\vec{S}}{4\pi} \to 0 \qquad (10)
\end{aligned}$$

because Φ decays exponentially at spatial infinity $r \to \infty$; see Sec. IV. This identity, however, is not very useful as neither $\int_V \rho_t^1(\boldsymbol{r})\Phi_2.(\boldsymbol{r})\,d\boldsymbol{r}$ nor $\int_V \rho_t^2(\boldsymbol{r})\Phi_1.(\boldsymbol{r})\,d\boldsymbol{r}$ represents interaction energy between the two charge distributions.

We now use a physical argument to elucidate a more useful form of reciprocity in electrostatics. As shown in Appendix B, via an energy minimization method, one can see that both $\rho_{\rm ind}^{1(2)}$ and $\rho_{\rm ion}^{1(2)}$ are solely determined by $\rho_f^{1(2)}$. The interaction energy between these two charge distributions, ρ_f^1 and ρ_f^2, may be computed either by

$$U_{\rm int} = \int \rho_f^1(\boldsymbol{r})\Phi_2.(\boldsymbol{r})\,d\boldsymbol{r} \qquad (11)$$

or by

$$U_{\rm int} = \int \rho_f^2(\boldsymbol{r})\Phi_1.(\boldsymbol{r})\,d\boldsymbol{r}. \qquad (12)$$

The former expression corresponds to the energy needed, without counting the self-interaction due to $\rho_{\rm ind}^1$ or $\rho_{\rm ion}^1$ acting on ρ_f^1, to bring ρ_f^1 from spatial infinity to its designated place with ρ_f^2 (hence $\rho_{\rm ind}^2$) already in position; the latter expression corresponds to the same final configuration but with ρ_f^1 (hence $\rho_{\rm ind}^1$) in place first before bringing in ρ_f^2. Since the interaction energy only depends on the free charge configuration, both expressions must yield identical interaction energy. This reciprocity property was not emphasized by most previous treatments on this subject. We shall show that the correct theory at the Debye-Hückel level explicitly respects the reciprocity.

IV. ONE DIELECTRIC SPHERE

We begin with a dielectric sphere $\mathcal{A}$ of radius a with a free charge distribution inside the sphere. The charge and dielectric sphere system is placed in an ionic solution that has no net charge. In this simple system, we will learn about the appropriate boundary condition to use in the limit of negligible ion radii.

For convenience, we shall take the center of the dielectric sphere as the origin. (With $N = 1$, this conforms to our earlier choice of having $\frac{1}{N}\sum_{i=1}^{N}\vec{R}_i$ as the origin.) Assume the radius of the ions to be δ. Let us define, for later convenience, $b = a + \delta$. Evidently, for regime $r < b$, the potential obeys Poisson's equation, while for $r > b$, it follows the modified Helmholtz equation. Consider first some charge distribution $\rho(\boldsymbol{s})$ inside (with $|\boldsymbol{s}| < d < a$) the dielectric sphere with dielectric constant ϵ. Let the region $a < r < b$ have dielectric constant ϵ' and the region $r > b$ ϵ_o. Now consider the $d < r < a$ region. The electric potential due to the charge distribution inside can be written as

$$\begin{aligned}
\int \frac{\rho(\boldsymbol{s})/\epsilon}{|\boldsymbol{s}-\boldsymbol{r}|}\,d\boldsymbol{s} &= \sum_{l,m}\frac{4\pi}{2l+1}\frac{1}{r^{l+1}}Y_l^m(\hat{r})\int\frac{\rho(\boldsymbol{s})}{\epsilon}s^l Y_l^{m*}(\hat{s})\,d\boldsymbol{s}\\
&= \sum_{l,m}\frac{4\pi}{2l+1}\frac{1}{r^{l+1}}Y_l^m(\hat{r})\frac{q_{lm}}{\epsilon}\\
&= \sum_{l,m}\frac{\sqrt{4\pi}}{2l+1}\frac{a^l}{r^{l+1}}Y_l^m(\hat{r})\frac{\overline{Q}_{lm}}{\epsilon}, \qquad (13)
\end{aligned}$$

where the multipole moment is defined in the usual way,

$$q_{lm} \equiv \int \rho(\boldsymbol{s})\,s^l\,Y_l^{m*}(\hat{s})\,d\boldsymbol{s} \qquad (14)$$

and

$$\hat{r} = \frac{\boldsymbol{r}}{|\boldsymbol{r}|} = \frac{\boldsymbol{r}}{r}, \quad \hat{s} = \frac{\boldsymbol{s}}{|\boldsymbol{s}|} = \frac{\boldsymbol{s}}{s}, \quad \overline{Q}_{lm} \equiv \sqrt{4\pi}\,\frac{q_{lm}}{a^l}.$$

Evidently, $\overline{Q}_{lm}$ summarizes the free charge distribution. When a free charge is placed inside the dielectric sphere, there will be induced bound charge that reduces the charge strength by a factor of ϵ. That is why we see the $\overline{Q}_{lm}$ above is divided by ϵ. In [11] we established the equivalence of having q_{lm} inside the sphere (with charge strength screened or reduced by the multiplication factor $\frac{1}{\epsilon}$), and having $\overline{Q}_{lm}$ on the surface of the sphere ($r = a$). Remember that we call the former method I-in and the latter method II-on. The goal of the current section is to describe below that even in the presence of mobile ions, method I-in and method II-on are still equivalent. The detailed proof is provided in Appendix C.

Since we are primarily interested in the limit $\delta \to 0$ (or $b \to a$), we will summarize the results in Appendix C under such a limit. Let us emphasize again that, with Q_{lm} denoting the induced surface charge strengths, the net surface

charge strengths $\breve{Q}_{lm}$ equal $Q_{lm} + \frac{\overline{Q}_{lm}}{\epsilon}$ for method I-in and equal $Q_{lm} + \overline{Q}_{lm}$ for method II-on. For $r < a$, we have two expressions (C8) and (C9), displayed again below, corresponding to method I-in and method II-on, respectively,

$$\Phi^{\text{I-in}}(r<a) = \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) \left[\left(Q_{lm}^{<} + Q_{lm}^{>} \left(\frac{a}{b}\right)^{l+1} \right) \frac{r^l}{a^{l+1}} + \frac{\overline{Q}_{lm}}{\epsilon} \frac{a^l}{r^{l+1}} \right]$$

$$= \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) \left[Q_{lm} \frac{r^l}{a^{l+1}} + \frac{\overline{Q}_{lm}}{\epsilon} \frac{a^l}{r^{l+1}} \right], \tag{15}$$

$$\Phi^{\text{II-on}}(r<a) = \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) \left[Q_{lm}^{<} + Q_{lm}^{>} \left(\frac{a}{b}\right)^{l+1} + \overline{Q}_{lm} \right] \frac{r^l}{a^{l+1}}$$

$$= \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) [Q_{lm} + \overline{Q}_{lm}] \frac{r^l}{a^{l+1}} = \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r})\, \breve{Q}_{lm} \frac{r^l}{a^{l+1}}. \tag{16}$$

Those two expressions coincide at $r = a$, yielding

$$\Phi(r=a) = \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) \frac{\breve{Q}_{lm}}{a}.$$

In the region $r > a$, the potential satisfies the modified Helmholtz equation and is supposed to decay to zero as $r \to \infty$. Hence the general solution should be

$$\Phi^{\text{out}}(r>a) = \sum_{l,m} D_{lm}\, k_l(\kappa r)\, Y_l^m(\hat{r}). \tag{17}$$

Matching the values of both potential expressions at $r = a$ allows one to determine D_{lm}, leading to

$$\Phi^{\text{out}}(r>a) = \sum_{l,m} D_{lm}\, k_l(\kappa r)\, Y_l^m(\hat{r})$$

$$= \sum_{l,m} \frac{\sqrt{4\pi}}{2l+1} \frac{k_l(\kappa r)}{k_l(\kappa a)} \frac{\breve{Q}_{lm}}{a} Y_l^m(\hat{r}). \tag{18}$$

The other boundary condition for method I-in is written as

$$\epsilon_o \frac{\partial \Phi^{\text{out}}}{\partial r}\bigg|_{r=a^+} = \epsilon \frac{\partial \Phi^{\text{I-in}}}{\partial r}\bigg|_{r=a^-} \tag{19}$$

and for method II-on as

$$\epsilon_o \frac{\partial \Phi^{\text{out}}}{\partial r}\bigg|_{r=a^+} = \epsilon \frac{\partial \Phi^{\text{II-on}}}{\partial r}\bigg|_{r=a^-} - 4\pi\sigma_f, \tag{20}$$

where

$$\sigma_f(\hat{s}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sqrt{4\pi}\, \sigma_{flm} Y_l^m(\hat{s}) \quad \text{and} \quad \overline{Q}_{lm} = 4\pi a^2 \sigma_{flm}.$$

After summarizing the results from Appendix C, let us now apply the boundary conditions from method I-in and method II-on to obtain the induced surface charge strengths, and hence the solvation energy. Let us first solve for Q_{lm} in method I-in via (19):

$$\epsilon_o \sum_{l,m} \frac{\sqrt{4\pi}}{2l+1} \kappa \frac{k_l'(\kappa a)}{k_l(\kappa a)} \frac{\breve{Q}_{lm}}{a} Y_l^m(\hat{r})$$

$$= \epsilon \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) \left[Q_{lm} \frac{l}{a^2} - \frac{\overline{Q}_{lm}}{\epsilon} \frac{l+1}{a^2} \right]$$

$$= \epsilon \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) \left[\breve{Q}_{lm} \frac{l}{a^2} - \frac{\overline{Q}_{lm}}{\epsilon} \frac{2l+1}{a^2} \right]$$

$$= \epsilon \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) \breve{Q}_{lm} \frac{l}{a^2} - \sqrt{4\pi} \sum_{lm} Y_l^m(\hat{r}) \frac{\overline{Q}_{lm}}{a^2},$$

leading to

$$\breve{Q}_{lm} = \frac{2l+1}{\epsilon\, l - \epsilon_o(\kappa a) \frac{k_l'(\kappa a)}{k_l(\kappa a)}} \overline{Q}_{lm} \tag{21}$$

or (because here $\breve{Q}_{lm} = Q_{lm}^{\text{I-in}} + \frac{\overline{Q}_{lm}}{\epsilon}$)

$$Q_{lm}^{\text{I-in}} = \left[\frac{2l+1}{\epsilon\, l - \epsilon_o(\kappa a) \frac{k_l'(\kappa a)}{k_l(\kappa a)}} - \frac{1}{\epsilon} \right] \overline{Q}_{lm}$$

$$= \sqrt{4\pi} \left[\frac{2l+1}{\epsilon\, l - \epsilon_o(\kappa a) \frac{k_l'(\kappa a)}{k_l(\kappa a)}} - \frac{1}{\epsilon} \right] \frac{q_{lm}}{a^l}. \tag{22}$$

Not surprisingly, when we use (20) to solve for Q_{lm} in method II-on, we also obtain

$$\breve{Q}_{lm} = \frac{2l+1}{\epsilon\, l - \epsilon_o(\kappa a) \frac{k_l'(\kappa a)}{k_l(\kappa a)}} \overline{Q}_{lm}$$

except that now $\breve{Q}_{lm} = Q_{lm}^{\mathrm{II-on}} + \overline{Q}_{lm}$. Hence, for method II-on,

$$Q_{lm}^{\mathrm{II-on}} = \left[\frac{2l+1}{\epsilon\, l - \epsilon_o(\kappa a)\frac{k_l'(\kappa a)}{k_l(\kappa a)}} - 1\right]\overline{Q}_{lm} = \sqrt{4\pi}\left[\frac{2l+1}{\epsilon\, l - \epsilon_o(\kappa a)\frac{k_l'(\kappa a)}{k_l(\kappa a)}} - 1\right]\frac{q_{lm}}{a^l}. \quad (23)$$

In the multiple-sphere case, $\Phi^{\mathrm{I-in}}$ and $\Phi^{\mathrm{II-on}}$ will contain contributions from other spheres. However, the contribution from sphere j will always appear through the observable surface charge strengths $\breve{Q}_{lm}^j$ and thus does not affect the proof above.

It is worthwhile to ponder the difference

$$Q_{lm}^{\mathrm{II-on}} - Q_{lm}^{\mathrm{I-in}} = \left[\frac{1}{\epsilon} - 1\right]\overline{Q}_{lm} = \sqrt{4\pi}\left[\frac{1}{\epsilon} - 1\right]\frac{q_{lm}}{a^l}.$$

This extra part comes from smearing to the surface the induced bound charges that are originally attached to the free charges inside the sphere. These induced bound charges must be excluded from calculation of solvation energy. That is, computation of solvation energy under method II-on is less direct as shown below.

Under method I-in, the solvation energy is simply given by

$$\begin{aligned} U_s^{\mathrm{I-in}} &= \frac{1}{2}\int \rho_f(\boldsymbol{r})\left[\sum_{lm}\frac{\sqrt{4\pi}\,Q_{lm}^{\mathrm{I}}}{2l+1}Y_l^m(\hat{r})\frac{r^l}{a^{l+1}}\right]d\boldsymbol{r} \\ &= \frac{1}{2}\sum_{lm}\frac{\sqrt{4\pi}}{2l+1}\frac{q_{lm}^* Q_{lm}^{\mathrm{I}}}{a^{l+1}} \\ &= \frac{1}{2}\sum_{lm}\frac{4\pi}{2l+1}\left[\frac{2l+1}{\epsilon\, l - \epsilon_o\,\kappa a\frac{k_l'(\kappa a)}{k_l(\kappa a)}} - \frac{1}{\epsilon}\right]\frac{q_{lm}^* q_{lm}}{a^{2l+1}} \\ &= \frac{1}{2}\sum_{lm}\left[\frac{2l+1}{\epsilon\, l - \epsilon_o\,\kappa a\frac{k_l'(\kappa a)}{k_l(\kappa a)}} - \frac{1}{\epsilon}\right]\frac{\overline{Q}_{lm}^*\overline{Q}_{lm}}{(2l+1)a}. \end{aligned} \quad (24)$$

On the other hand, under method II-on, when computing solvation energy the smeared induced bound charges must be removed from consideration, leading to using Q_{lm}^{I} instead of Q_{lm}^{II}:

$$\begin{aligned} U_s^{\mathrm{II-on}} &= \frac{1}{2}\int \sigma_f(\hat{r})\left[\sum_{lm}\frac{\sqrt{4\pi}\,Q_{lm}^{\mathrm{I}}}{2l+1}Y_l^m(\hat{r})\frac{1}{a}\right]dS \\ &= \frac{1}{2}\sum_{lm}\frac{4\pi a^2}{2l+1}\frac{\overline{\sigma}_{lm}^* Q_{lm}^{\mathrm{I}}}{a} = \frac{1}{2}\sum_{lm}\frac{\overline{Q}_{lm}^* Q_{lm}^{\mathrm{I}}}{(2l+1)a} \\ &= \frac{1}{2}\sum_{lm}\frac{4\pi}{2l+1}\left[\frac{2l+1}{\epsilon\, l - \epsilon_o\,\kappa a\frac{k_l'(\kappa a)}{k_l(\kappa a)}} - \frac{1}{\epsilon}\right]\frac{q_{lm}^* q_{lm}}{a^{2l+1}} \\ &= \frac{1}{2}\sum_{lm}\left[\frac{2l+1}{\epsilon\, l - \epsilon_o\,\kappa a\frac{k_l'(\kappa a)}{k_l(\kappa a)}} - \frac{1}{\epsilon}\right]\frac{\overline{Q}_{lm}^*\overline{Q}_{lm}}{(2l+1)a}. \end{aligned} \quad (25)$$

Having obtained the solvation energy of the sphere, we are ready to proceed to the second goal.

V. SYSTEM EQUIVALENCE AND THE SUBSTITUTION RULE

As mentioned in the introduction, the equivalence between method I-in (putting the multipole sources *in*side of a sphere) and method II-on (putting the multipole sources *on* the surface of the same sphere) was established for the ion-free case in [11]. In Sec. IV and Appendix C, we further demonstrate the equivalence of these two methods when the dielectric spheres are immersed in an ionic solution that is describable by the Debye-Hückel theory. Consequently, we may consider only the case where the multipole sources, when present, are on the spherical surfaces. Remember that although the total observable surface charge strengths $\breve{Q}_{lm}$ equal $Q_{lm} + \frac{\overline{Q}_{lm}}{\epsilon}$ for method I-in and equal $Q_{lm} + \overline{Q}_{lm}$ for method II-on, both methods yield identical equations for $\breve{Q}_{lm}$. Hence the physically observable $\breve{Q}_{lm}$ is the same for both methods. For our development here, it is slightly easier to use method II-on.

In our system, the presence of dielectric spheres of finite radii introduces spherical regions having $\kappa^2 = 0$. Following our surface charge method, we may write down the potential produced by the free charge distribution and the yet to be determined induced charge distribution in the spatial region where $\kappa^2 \neq 0$, and apply the boundary conditions to obtain the induced surface charge distribution, hence the potential in the $\kappa^2 \neq 0$ region. As for the potential inside the spheres, because it satisfies the Laplace equation, one may write down the most general solution and determine the coefficients by demanding continuity with the potential outside the spheres.

For example, if one wishes to calculate the potential near the outside of a dielectric sphere caused by a free point charge outside the sphere in the mobile ion reachable region, one needs to add the contribution from the point charge using Eq. (1) and the contribution from the induced surface charge. This task will be easier if one can build an equivalent system with κ^2 constant everywhere while computing the potential outside the dielectric spheres. The spherical symmetry of (18) offers such a possibility, and the goal of the current section is to use the single-sphere example to bring out the correspondence principle needed for finite a.

Placing permanent multipoles q_{lm} on the surface, the potential outside the sphere is given by the expression (18)

$$\begin{aligned} \Phi^{\mathrm{out}}(r > a) &= \sum_{l,m}\frac{\sqrt{4\pi}}{2l+1}\frac{k_l(\kappa r)}{k_l(\kappa a)}\frac{\breve{Q}_{lm}}{a}Y_l^m(\hat{r}) \\ &= \sum_{l,m}\frac{\sqrt{4\pi}}{2l+1}\frac{k_l(\kappa r)}{k_l(\kappa a)}\frac{\overline{Q}_{lm} + Q_{lm}}{a}Y_l^m(\hat{r}). \end{aligned}$$

Now remember from (C2) that $\overline{Q}_{lm} = 4\pi a^2\sigma_{f\,lm} = \sqrt{4\pi}\frac{q_{lm}}{a^l}$ corresponds to the permanent multipole q_{lm} placed on the spherical surface while $Q_{lm} = 4\pi a^2\sigma_{lm}$ corresponds to the induced multipole that exists only on the spherical surface.

The spherical symmetry in (18) prompts us to compare it with a similar system of a spherical shell of charge density $\sigma_t = \sigma_f + \sigma$ (with $\breve{Q}_{lm} = 4\pi a^2\sigma_{t\,lm}$) in a solution of mobile

ions. Namely, using Eq. (1),

$$\Phi^{\rm pseudo}(\boldsymbol{r}, r > a) = \int \frac{\sigma_t(\hat{r}')}{|\boldsymbol{r} - a\hat{r}'|} e^{-\kappa|\boldsymbol{r}-a\hat{r}'|} dS' = \sum_{lm} (4\pi a^2 \kappa)\, k_l(\kappa r) Y_l^m(\hat{r}) i_l(\kappa a) \times \int \sigma_t(\hat{r}') Y_l^{m*}(\hat{r}') d\Omega' = \sum_{lm} \sqrt{4\pi}\, [(\kappa a) i_l(\kappa a)] k_l(\kappa r) \frac{\breve{Q}_{lm}}{a} Y_l^m(\hat{r}). \tag{26}$$

By comparing (26) with (18),

$$\Phi^{\rm out}(\boldsymbol{r}) = \sum_{l,m} \frac{\sqrt{4\pi}}{2l+1} \frac{1}{k_l(\kappa a)} k_l(\kappa r) \frac{\breve{Q}_{lm}}{a} Y_l^m(\hat{r}),$$

we find that by introducing a substitution rule

$$\breve{Q}_{lm} \Rightarrow \breve{Q}^+_{lm} \equiv \frac{\breve{Q}_{lm}}{(\kappa a)(2l+1) i_l(\kappa a) k_l(\kappa a)}, \tag{27}$$

we can turn $\Phi^{\rm pseudo}$ into the true Φ. Let $\hat{T}$ denote such an operation. We thus have

$$\hat{T}\,\Phi^{\rm pseudo}(\boldsymbol{r}, r > a) = \sum_{lm} \sqrt{4\pi}\,(\kappa a)\, i_l(\kappa a)\, k_l(\kappa r) \frac{\hat{T}\,[\breve{Q}_{lm}]}{a} Y_l^m(\hat{r}) = \sum_{lm} \sqrt{4\pi}\,(\kappa a)\, i_l(\kappa a)\, k_l(\kappa r) \frac{\breve{Q}^+_{lm}}{a} Y_l^m(\hat{r}) = \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} \frac{k_l(\kappa r)}{k_l(\kappa a)} \frac{\breve{Q}_{lm}}{a} Y_l^m(\hat{r}) = \Phi^{\rm out}(\boldsymbol{r}).$$

This substitution rule in effect introduces a multipole-dependent correction factor (for both Q_{lm} and $\overline{Q}_{lm}$, and hence $\breve{Q}_{lm}$)

$$T_l(a) = \frac{1}{(\kappa a)(2l+1) i_l(\kappa a) k_l(\kappa a)} \tag{28}$$

due to the dielectric sphere having a finite radius. Note that $T_l \geqslant 1$ always. To justify this point, let us first make the following observation. As $a \to 0$, the presence of the dielectric inside the spherical shell becomes less and less important, and we expect the correction factor $T_l(a) \to 1$ as $a \to 0$. We find this is exactly the case because when $x \ll 1$, $i_l(x) \approx x^l/(2l+1)!!$, $k_l(x) \approx (2l-1)!!/x^{l+1}$. That is, in terms of the multipole potential, one may use the substitution rule (i.e., the correction factor) to correct the calculated potential (outside the dielectric spheres) while assuming mobile ions are present everywhere.

In a system containing N spheres, at a spatial point $\boldsymbol{r}$ not inside any of the spheres, one may thus write down the potential as the sum of the contribution from each sphere. In other words, one may compute the potential at $\boldsymbol{r}$ from N spherical shells of charge distributions in a space filled with mobile ions and then apply the substitution rule (27). However, in order to compute the induced surface charge strength on sphere $\mathcal{A}_k$, for example, we will need to compute the radial derivative of the potential due to all other spheres $j \neq k$ while using $\boldsymbol{R}_k$, the center of $\mathcal{A}_k$, as the origin. It is tempting simply to use Eq. (2) to obtain the expansion of the potential due to other spheres $\mathcal{A}_{j\neq k}$ around $\boldsymbol{R}_k$. However, because $\mathcal{A}_k$ is a dielectric sphere without mobile ions inside, such an expansion is valid only when $|\boldsymbol{r} - \boldsymbol{R}_k| \geqslant a_k$, that is, when $\boldsymbol{r}$ is outside $\mathcal{A}_k$.

To examine if the substitution rule (27) is all we need, we check, in Appendix D, reciprocity in electrostatics: Interaction energy $V_{\rm int}^{(1)}$ is the work done to bring to $\boldsymbol{r}_0$ charge multipoles $q'_{l'm'}$ when multipoles q_{lm} were already placed either inside or exactly on the surface of the sphere; interaction energy $V_{\rm int}^{(2)}$ is the work done to bring the multipoles q_{lm} to the inside or the surface of the sphere when $q'_{l'm'}$ were already placed at $\boldsymbol{r}_0$. Reciprocity demands that $V_{\rm int}^{(1)} = V_{\rm int}^{(2)}$.

As shown in Appendix D, the condition of reciprocity reduces to the following rule:

$$\frac{(\kappa a)^2}{\epsilon_o} \epsilon_o \frac{i_l'(\kappa a) - i_l(\kappa a) \frac{k_l'(\kappa a)}{k_l(\kappa a)}}{\epsilon\, l - \epsilon_o \frac{k_l'(\kappa a)}{k_l(\kappa a)} (\kappa a)} \Rightarrow \frac{1}{\epsilon\, l\, k_l(\kappa a) - \epsilon_o k_l'(\kappa a)\,(\kappa a)}.$$

This turns out to be an exact identity. If one defines $F_l(x) \equiv i_l'(x) k_l(x) - k_l'(x) i_l(x)$, one has [because both i_l and k_l satisfy the differential equation $f_l'' + \frac{2}{x} f_l' - (1 + \frac{l(l+1)}{x^2}) f_l = 0$]

$$\frac{dF_l}{dx} = k_l(x) i_l''(x) - i_l(x) k_l''(x) = -\frac{2}{x} F_l(x) \Rightarrow F_l(x) = \frac{C_l}{x^2}.$$

By using the fact that when $x \ll 1$, $i_l(x) \approx x^l/(2l+1)!!$, $k_l(x) \approx (2l-1)!!/x^{l+1}$, one sees that $C_l = 1$, that is,

$$(\kappa a)^2 [i_l'(\kappa a) k_l(\kappa a) - k_l'(\kappa a) i_l(\kappa a)] = 1. \tag{29}$$

Therefore, we have explicitly verified the reciprocity:

$$V_{\rm int}^{(2)} = V_{\rm int}^{(1)}. \tag{30}$$

The substitution rule (27) is all we need for making easy the calculation of the system's total and interaction energies.

VI. FORMALISM FOR ANY NUMBER OF DIELECTRIC SPHERES

After establishing the substitution rule (27), we now describe the general formalism for an arbitrary number of dielectric spheres. Let us first review some notations. We consider N dielectric spheres, $\mathcal{A}_1, \ldots, \mathcal{A}_N$, immersed in an infinite medium of dielectric constant ϵ_o. Except for the regions occupied by the N dielectric spheres, mobile ions are present everywhere in the medium. The vector from the center of $\mathcal{A}_l$ to an arbitrary point P is $\boldsymbol{r}_l$. The angle between $\boldsymbol{r}_l$ and the z axis is θ_l; the azimuthal angle of $\boldsymbol{r}_l$ with respect to the coordinate system is ϕ_l. The jth dielectric sphere $\mathcal{A}_j$, centered at $\boldsymbol{R}_j$ with radius a_j, has an effective *free* permanent surface charge density $\sigma_f^j(\hat{r}_j)$ and consists of a material with dielectric constant ϵ_j. The induced surface charge density on sphere $\mathcal{A}_j$ is $\sigma_i^j(\hat{r}_j)$. When considering the boundary condition imposed on $\mathcal{A}_k$, we need to consider the potential produced by charges, be they permanent or induced, from all spheres. For later convenience, we introduce the vector $\vec{L}_{k\to j} = \boldsymbol{R}_j - \boldsymbol{R}_k$ that points from the center of $\mathcal{A}_k$ to the center of $\mathcal{A}_j$.

The objective is to find the total electrostatic energy and the interaction energy of such a system of N dielectric spheres

embedded in an unbounded dielectric ionic solution. To that end, one wishes to calculate for an arbitrary point in space the electrical potential, which is a linear superposition of the potentials of the free surface charge distributions σ_f^j $(j = 1, \ldots, N)$ and the induced surface charge densities σ_i^j $(j = 1, \ldots, N)$:

$$\Phi^{\text{pseudo}}(\boldsymbol{r}) = \sum_{j=1}^{N} \int_{\mathcal{A}_j} \frac{\sigma_f^j(\hat{r}_j) + \sigma_i^j(\hat{r}_j)}{|\boldsymbol{r} - \boldsymbol{R}_j - a_j\hat{r}_j|} e^{-\kappa|\boldsymbol{r}-\boldsymbol{R}_j-a_j\hat{r}_j|} dS_j$$
$$= \sum_{j=1}^{N} \int_{\mathcal{A}_j} \frac{\sigma_t^j(\hat{r}_j)}{|\boldsymbol{r} - \boldsymbol{R}_j - a_j\hat{r}_j|} e^{-\kappa|\boldsymbol{r}-\boldsymbol{R}_j-a_j\hat{r}_j|} dS_j, \quad (31)$$

where we have used $\hat{r}_j \equiv \boldsymbol{r}_j/|\boldsymbol{r}_j|$ to represent an arbitrary unit vector, hence its associated polar angles, emanating from the center of $\mathcal{A}_j$. As mentioned in [5,8,11,12], the induced surface charge densities are not known; rather, they are obtained by enforcing the boundary condition at the surface of each sphere. Application of the boundary condition requires that the total potential of the known free surface charge distributions $[\sigma_f^j(\hat{r}_j)$'s] and the still unspecified surface charge densities $[\sigma_i^j(\hat{r}_j)$'s] be calculated just inside and just outside the surface of each sphere. When the total potential near a sphere $\mathcal{A}_k$ is expressed in terms of a set of spherical harmonics with $\boldsymbol{R}_k$ as the origin, the boundary conditions will yield algebraic equations which, when solved, give the induced surface charge densities in terms of known quantities.

Starting with Eq. (31), let us consider the potential at a point $\boldsymbol{r}$ outside sphere $\mathcal{A}_j$, meaning that $|\boldsymbol{r} - \boldsymbol{R}_j| > a_j$. The contribution from sphere $\mathcal{A}_j$ to the potential at $\boldsymbol{r}$ has two parts: one from the permanent surface charge distribution σ_f^j and the other from the induced surface charge density σ_i^j on the spherical surface of $\mathcal{A}_j$. As in [8], we write $\sigma_{i(f)}^j(\hat{\boldsymbol{r}}_i)$ as

$$\sigma_{i(f)}^j(\hat{\boldsymbol{r}}_j) = \sigma_{i(f)}^j(\theta_j, \phi_j) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sqrt{4\pi}\, \sigma_{i(f)lm}^j Y_l^m(\theta_j, \phi_j)$$

and define the induced and permanent surface charge strengths

$$Q_{lm}^j = 4\pi a_j^2 \sigma_{ilm}^j, \quad \overline{Q}_{lm}^j = 4\pi a_j^2 \sigma_{flm}^j.$$

Writing via (1) (with $\boldsymbol{r}_j = a_j\hat{r}_j$ and $|\boldsymbol{r} - \boldsymbol{R}_j| > a_j$)

$$\frac{e^{-\kappa|\boldsymbol{r}-\boldsymbol{R}_j-a_j\hat{r}_j|}}{|\boldsymbol{r} - \boldsymbol{R}_j - a_j\hat{r}_j|} = 4\pi\kappa \sum_{l,m} i_l(\kappa a_j)\, Y_l^{m*}(\hat{r}_j)\, k_l(\kappa|\boldsymbol{r} - \boldsymbol{R}_j|) \times Y_l^m\left(\frac{\boldsymbol{r} - \boldsymbol{R}_j}{|\boldsymbol{r} - \boldsymbol{R}_j|}\right),$$

we may express the potential contribution from sphere $\mathcal{A}_j$ at $\boldsymbol{r}$ as

$$\Phi_j^{\text{pseudo}}(\boldsymbol{r}) = \int_{\mathcal{A}_j} \frac{\sigma_t^j(\hat{r}_j) e^{-\kappa|\boldsymbol{r}-\boldsymbol{R}_j-a_j\hat{r}_j|}}{|\boldsymbol{r} - \boldsymbol{R}_j - a_j\hat{r}_j|} dS_j$$
$$= 4\pi\kappa \sum_{l,m} i_l(\kappa a_j)\, k_l(\kappa|\boldsymbol{r} - \boldsymbol{R}_j|)\, Y_l^m\left(\frac{\boldsymbol{r} - \boldsymbol{R}_j}{|\boldsymbol{r} - \boldsymbol{R}_j|}\right) a_j^2 \times \int_{\mathcal{A}_j} \sigma_t^j(\hat{r}_j) Y_l^{m*}(\hat{r}_j) d\Omega_i$$
$$= \sqrt{4\pi}\kappa \sum_{l,m} i_l(\kappa a_j)\, k_l(\kappa|\boldsymbol{r} - \boldsymbol{R}_j|) \times Y_l^m\left(\frac{\boldsymbol{r} - \boldsymbol{R}_j}{|\boldsymbol{r} - \boldsymbol{R}_j|}\right) \breve{Q}_{lm}^j. \quad (32)$$

As expected, one may turn this expression into the true potential contribution from sphere j by applying $\hat{T}$:

$$\Phi_j(\boldsymbol{r}) = \hat{T}\left[\Phi_j^{\text{pseudo}}(\boldsymbol{r})\right] = \sqrt{4\pi}\kappa \sum_{l,m} i_l(\kappa a_j)\, k_l(\kappa|\boldsymbol{r} - \boldsymbol{R}_j|) \times Y_l^m\left(\frac{\boldsymbol{r} - \boldsymbol{R}_j}{|\boldsymbol{r} - \boldsymbol{R}_j|}\right) \breve{Q}_{lm}^{j+}. \quad (33)$$

When $\boldsymbol{r}$ is close to the surface of another sphere $\mathcal{A}_k$ $(k \neq j)$, that is, when $\boldsymbol{r} = \boldsymbol{R}_k + \boldsymbol{r}_k$ with $r_k \approx a_k$, we shall write $\Phi_j(\boldsymbol{r})$ purposely as $\Phi_{j\to k}(\boldsymbol{R}_k + \boldsymbol{r}_k)$. Let us rewrite $\Phi_{j\to k}(\boldsymbol{R}_k + \boldsymbol{r}_k)$ as (using (33), (2) and with $a_k \leqslant r_k < |\vec{L}_{k\to j}|$)

$$\Phi_{j\to k}(\boldsymbol{R}_k + \boldsymbol{r}_k, r_k > a_k) = \sqrt{4\pi}\kappa \sum_{\ell_1,m_1} i_{\ell_1}(\kappa a_j)\, k_{\ell_1}(\kappa|\boldsymbol{r}_k + \boldsymbol{R}_k - \boldsymbol{R}_j|)\, Y_{\ell_1}^{m_1}\left(\frac{\boldsymbol{r}_k + \boldsymbol{R}_k - \boldsymbol{R}_j}{|\boldsymbol{r}_k + \boldsymbol{R}_k - \boldsymbol{R}_j|}\right) \breve{Q}_{\ell_1 m_1}^{j+}$$
$$= \sqrt{4\pi}\kappa \sum_{\ell_1,m_1} i_{\ell_1}(\kappa a_j)\, k_{\ell_1}(\kappa|\boldsymbol{r}_k - \vec{L}_{k\to j}|)\, Y_{\ell_1}^{m_1}\left(\frac{\boldsymbol{r}_k - \vec{L}_{k\to j}}{|\boldsymbol{r}_k - \vec{L}_{k\to j}|}\right) \breve{Q}_{\ell_1 m_1}^{j+} \quad (34)$$
$$= \sqrt{4\pi}\kappa \sum_{\ell_1,m_1} i_{\ell_1}(\kappa a_j)\, \breve{Q}_{\ell_1 m_1}^{j+} \sum_{l,\ell_2,m,m_2} (-1)^{l+\ell_2} H_{lm\ell_2 m_2}^{\ell_1 m_1} i_l(\kappa r_k) Y_l^m(\hat{r}_k)\, k_{\ell_2}(\kappa L_{k\to j}) Y_{\ell_2}^{m_2}(\hat{L}_{k\to j})$$
$$= \sqrt{4\pi}\kappa \sum_{lm} i_l(\kappa r_k) Y_l^m(\hat{r}_k) \left[\sum_{\ell_1,m_1} i_{\ell_1}(\kappa a_j)\, \breve{Q}_{\ell_1 m_1}^{j+} \sum_{\ell_2,m_2} (-1)^{l+\ell_2} H_{lm\ell_2 m_2}^{\ell_1 m_1}\, k_{\ell_2}(\kappa L_{k\to j}) Y_{\ell_2}^{m_2}(\hat{L}_{k\to j})\right]. \quad (35)$$

The expression above is for $r_k > a_k$. The potential produced by the surface charge σ_t^j in the region $r_k < a_k$ satisfies the Laplace equation. It has the following general solution:

$$\Phi_{j\to k}(r_k < a_k) = \sum_{l,m} B_{lm}^{j\to k} \frac{r_k^l}{a_k^{l+1}} Y_l^m(\hat{r}_k).$$

By matching the expression above with (35) at $r_k = a_k$, we see that

$$B_{lm}^{j\to k} = \sqrt{4\pi}\,(\kappa a_k)\, i_l(\kappa a_k) \sum_{\ell_1,m_1} i_{\ell_1}(\kappa a_j)\, \breve{Q}_{\ell_1 m_1}^{j+} \sum_{\ell_2,m_2} (-1)^{l+\ell_2}\, H_{lm\ell_2 m_2}^{\ell_1 m_1}\, k_{\ell_2}(\kappa L_{k\to j}) Y_{\ell_2}^{m_2}(\hat{L}_{k\to j}).$$

That is, $\Phi_{j\to k}(\boldsymbol{R}_k + \boldsymbol{r}_k)$ takes, when $r_k < a_k$, the following form which we will need for the boundary condition calculation:

$$\Phi_{j\to k}(\boldsymbol{R}_k + \boldsymbol{r}_k, r_k < a_k) = \sqrt{4\pi}\,(\kappa a_k) \sum_{l,m} i_l(\kappa a_k)\, \frac{r_k^l}{a_k^{l+1}} Y_l^m(\hat{r}_k) \times \left[\sum_{\ell_1,m_1} i_{\ell_1}(\kappa a_j)\, \breve{Q}_{\ell_1 m_1}^{j+} \sum_{\ell_2,m_2} (-1)^{l+\ell_2}\, H_{lm\ell_2 m_2}^{\ell_1 m_1}\, k_{\ell_2}(\kappa L_{k\to j}) Y_{\ell_2}^{m_2}(\hat{L}_{k\to j}) \right]. \tag{36}$$

Note that

$$\breve{Q}_{lm}^j = \overline{Q}_{lm}^j + Q_{lm}^j, \tag{37}$$

$$\overline{Q}_{lm}^j = \sqrt{4\pi}\, \frac{q_{lm}^j}{a_j^l}, \tag{38}$$

with the conventional notation for the spherical multipole moment (14), and

$$\breve{Q}_{lm}^{j+} = \hat{T}\left[\breve{Q}_{lm}^j\right] = T_l(a_j)\left(\overline{Q}_{lm}^j + Q_{lm}^j\right) = \overline{Q}_{lm}^{j+} + Q_{lm}^{j+}. \tag{39}$$

That is, when a charge distribution inside sphere $\mathcal{A}_j$ yields multipole q_{lm}^j, this charge distribution may be effectively replaced by $\overline{Q}_{lm}^j$ on the surface, see [11,12] and Sec. IV, and it appears as $\overline{Q}_{lm}^{j+}$ if one pretends that everywhere in the space is accessible by mobile ions. Recall that in terms of effectively observable surface charge strengths, $\breve{Q}_{lm}^j = Q_{lm}^j + \overline{Q}_{lm}^j/\epsilon_j$ for method I-in and $\breve{Q}_{lm}^j = Q_{lm}^j + \overline{Q}_{lm}^j$ for method II-on. The boundary conditions for the two methods are different but both boundary condition equations reduce to the same one, despite the fact that the Q_{lm}^j (induced surface charge strengths) appear different in the two cases.

Let us now focus on method II-on and write down the total electrostatic energy

$$U^{\text{II-on}} = \frac{1}{2}\int \rho_f(\boldsymbol{r})\,\Phi(\boldsymbol{r}) d\boldsymbol{r} = \frac{1}{2}\sum_{k=1}^N \int_{\mathcal{A}_k} \sigma_f^k(\hat{r}_k)\,\Phi_{\text{e}}(\boldsymbol{R}_k + a_k\hat{r}_k) dS_k, \tag{40}$$

where by taking the analog from (18) we have defined Φ_{e} as

$$\Phi_{\text{e}}(\boldsymbol{R}_k + \boldsymbol{r}_k) = \sum_{j\neq k} \Phi_{j\to k}(\boldsymbol{R}_k + \boldsymbol{r}_k) + \begin{cases} \sum_{l,m} \frac{\sqrt{4\pi}}{2l+1} \frac{k_l(\kappa r_k)}{a_k\, k_l(\kappa a_k)} Q_{lm}^k Y_l^m(\hat{r}_k), & [r_k > a_k], \\ \sum_{l,m} \frac{\sqrt{4\pi}}{2l+1} \frac{r_k^l}{a_k^{l+1}} Q_{lm}^k Y_l^m(\hat{r}_k), & [r_k < a_k], \end{cases}$$
$$= \sum_{j\neq k} \Phi_{j\to k}(\boldsymbol{R}_k + \boldsymbol{r}_k) + \begin{cases} \sqrt{4\pi}\kappa \sum_{l,m} i_l(\kappa a_k)\, k_l(\kappa r_k)\, Y_l^m(\hat{r}_k)\, Q_{lm}^{k+}, & [r_k > a_k], \\ \sqrt{4\pi}\kappa \sum_{l,m} i_l(\kappa a_k)\, k_l(\kappa a_k)\, \frac{r_k^l}{a_k^l} Y_l^m(\hat{r}_k)\, Q_{lm}^{k+}, & [r_k < a_k]. \end{cases} \tag{41}$$

Before moving on, let us further note that

$$\Phi_{\text{f}}^{\text{II-on}}(\boldsymbol{R}_k + \boldsymbol{r}_k) = \begin{cases} \sum_{l,m} \frac{\sqrt{4\pi}}{2l+1} \frac{k_l(\kappa r_k)}{a_k\, k_l(\kappa a_k)} \overline{Q}_{lm}^k Y_l^m(\hat{r}_k), & [r_k > a_k], \\ \sum_{l,m} \frac{\sqrt{4\pi}}{2l+1} \frac{r_k^l}{a_k^{l+1}} \overline{Q}_{lm}^k Y_l^m(\hat{r}_k), & [r_k < a_k], \end{cases}$$
$$= \begin{cases} \sqrt{4\pi}\kappa \sum_{l,m} i_l(\kappa a_k)\, k_l(\kappa r_k)\, Y_l^m(\hat{r}_k)\, \overline{Q}_{lm}^{k+}, & [r_k > a_k], \\ \sqrt{4\pi}\kappa \sum_{l,m} i_l(\kappa a_k)\, k_l(\kappa a_k)\, \frac{r_k^l}{a_k^l} Y_l^m(\hat{r}_k)\, \overline{Q}_{lm}^{k+}, & [r_k < a_k], \end{cases} \tag{42}$$

is not included in the computation of $\Phi_{\text{e}}(\boldsymbol{r}_k)$ because the free charges are treated as frozen in place and the potential energy associated with the frozen configuration within each sphere is a constant, albeit possibly infinite, that can be excluded. However, this term cannot be dropped when applying the boundary condition near the surface of $\mathcal{A}_k$ because it is the total potential that must be used for computing the derivatives near the outside of the spherical dielectric interface. That is, when applying the boundary condition near the surface of $\mathcal{A}_k$, we need to use

$$\Phi_{\text{b}}(\boldsymbol{R}_k + \boldsymbol{r}_k) = \Phi_{\text{e}}(\boldsymbol{R}_k + \boldsymbol{r}_k) + \Phi_{\text{f}}^{\text{II-on}}(\boldsymbol{R}_k + \boldsymbol{r}_k) \equiv \sum_{j\neq k} \Phi_{j\to k}(\boldsymbol{R}_k + \boldsymbol{r}_k) + \Phi_{k\to k}(\boldsymbol{R}_k + \boldsymbol{r}_k). \tag{43}$$

The last term above, which we call $\Phi_{k\to k}$, has been worked out in Sec. IV [see Eqs. (16) and (18)]. Basically,

$$\Phi_{k\to k}(\boldsymbol{R}_k+\boldsymbol{r}_k)=\begin{cases}\sum_{l,m}\frac{\sqrt{4\pi}}{2l+1}\frac{k_l(\kappa r_k)}{a_k\,k_l(\kappa a_k)}\breve{Q}^k_{lm}Y^m_l(\hat{r}_k), & [r_k>a_k],\\ \sum_{l,m}\frac{\sqrt{4\pi}}{2l+1}\frac{r_k^l}{a_k^{l+1}}\breve{Q}^k_{lm}Y^m_l(\hat{r}_k), & [r_k<a_k],\end{cases}$$
$$=\begin{cases}\sqrt{4\pi}\kappa\sum_{l,m}i_l(\kappa a_k)\,k_l(\kappa r_k)\,Y^m_l(\hat{r}_k)\,\breve{Q}^{k+}_{lm}, & [r_k>a_k],\\ \sqrt{4\pi}\kappa\sum_{l,m}i_l(\kappa a_k)\,k_l(\kappa a_k)\,\frac{r_k^l}{a_k^l}Y^m_l(\hat{r}_k)\,\breve{Q}^{k+}_{lm}, & [r_k<a_k].\end{cases}\tag{44}$$

We are now ready to apply the boundary condition

$$\epsilon_o\frac{\partial\Phi_{\rm b}(\boldsymbol{r}_k)}{\partial r_k}\bigg|_{a_k^+}=\epsilon_k\frac{\partial\Phi_{\rm b}(\boldsymbol{r}_k)}{\partial r_k}\bigg|_{a_k^-}-4\pi\sigma_f^k=\epsilon_k\frac{\partial\Phi_{\rm b}(\boldsymbol{r}_k)}{\partial r_k}\bigg|_{a_k^-}-\frac{\sqrt{4\pi}}{a_k^2}\sum_{lm}\overline{Q}^k_{lm}Y^m_l(\hat{r}_k).\tag{45}$$

For later convenience, we shall multiply the boundary condition equation above by a_k^2. We shall first work out the equation for the component having angular dependence $Y^m_l(\hat{r}_k)$. We begin by considering the left-hand side:

$$\epsilon_o\,a_k^2\frac{\partial\Phi_{\rm b}(\boldsymbol{r}_k)}{\partial r_k}\bigg|_{a_k^+}\to\epsilon_o\sqrt{4\pi}\,(\kappa a_k)^2\Bigg\{i_l(\kappa a_k)k_l'(\kappa a_k)\breve{Q}^{k+}_{lm}+\sum_{j\neq k}i_l'(\kappa a_k)$$
$$\times\Bigg[\sum_{\ell_1m_1\ell_2m_2}i_{\ell_1}(\kappa a_j)\,\breve{Q}^{j+}_{\ell_1m_1}(-1)^{l+\ell_2}\,H^{\ell_1m_1}_{lm\ell_2m_2}\,k_{\ell_2}(\kappa L_{k\to j})Y^{m_2}_{\ell_2}(\hat{L}_{k\to j})\Bigg]\Bigg\}.\tag{46}$$

The right-hand side becomes

$$\epsilon_k a_k^2\frac{\partial\Phi_{\rm b}(\boldsymbol{r}_k)}{\partial r_k}\bigg|_{a_k^-}-4\pi\sigma_f^k a_k^2\to\epsilon_k\sqrt{4\pi}\,(\kappa a_k)\Bigg\{l\,i_l(\kappa a_k)k_l(\kappa a_k)\breve{Q}^{k+}_{lm}-\frac{\overline{Q}^k_{lm}}{(\kappa a_k)\,\epsilon_k}+\sum_{j\neq k}l\,i_l(\kappa a_k)$$
$$\times\Bigg[\sum_{\ell_1m_1\ell_2m_2}i_{\ell_1}(\kappa a_j)\,\breve{Q}^{j+}_{\ell_1m_1}(-1)^{l+\ell_2}\,H^{\ell_1m_1}_{lm\ell_2m_2}\,k_{\ell_2}(\kappa L_{k\to j})Y^{m_2}_{\ell_2}(\hat{L}_{k\to j})\Bigg]\Bigg\}.$$

Equating the left-hand side and the right-hand side of the boundary condition equation, we thus have (after getting rid of the common factor $\sqrt{4\pi}$)

$$\overline{Q}^k_{lm}=(\kappa a_k)i_l(\kappa a_k)k_l(\kappa a_k)\Bigg[l\,\epsilon_k-\frac{(\kappa a_k)\,k_l'(\kappa a_k)}{k_l(\kappa a_k)}\epsilon_o\Bigg]\breve{Q}^{k+}_{lm}+\sum_{j\neq k}(\kappa a_k)\Bigg[l\,\epsilon_k-\frac{(\kappa a_k)i_l'(\kappa a_k)}{i_l(\kappa a_k)}\epsilon_o\Bigg]$$
$$\times\Bigg[\sum_{\ell_1m_1\ell_2m_2}i_l(\kappa a_k)\,i_{\ell_1}(\kappa a_j)\,\breve{Q}^{j+}_{\ell_1m_1}(-1)^{l+\ell_2}\,H^{\ell_1m_1}_{lm\ell_2m_2}\,k_{\ell_2}(\kappa L_{k\to j})Y^{m_2}_{\ell_2}(\hat{L}_{k\to j})\Bigg].\tag{47}$$

For later convenience, let us define

$$D_j(\ell)\equiv\frac{1}{(\kappa a_j)}\frac{1}{\ell\epsilon_j-\frac{(\kappa a_j)i_\ell'(\kappa a_j)}{i_\ell(\kappa a_j)}\epsilon_o}\quad\text{and}\quad V_j(\ell)=i_\ell(\kappa a_j)k_\ell(\kappa a_j)+\epsilon_o D_j(\ell).\tag{48}$$

We may thus rewrite the boundary condition equation as

$$\overline{Q}^k_{lm}=D_k^{-1}(l)i_l(\kappa a_k)\,k_l(\kappa a_k)\frac{l\,\epsilon_k-\frac{(\kappa a_k)\,k_l'(\kappa a_k)}{k_l(\kappa a_k)}\epsilon_o}{l\,\epsilon_k-\frac{(\kappa a_k)i_l'(\kappa a_k)}{i_l(\kappa a_k)}\epsilon_o}\breve{Q}^{k+}_{lm}+\sum_{j\neq k}D_k^{-1}(l)$$
$$\times\Bigg[\sum_{\ell_1m_1\ell_2m_2}i_l(\kappa a_k)i_{\ell_1}(\kappa a_j)\,\breve{Q}^{j+}_{\ell_1m_1}(-1)^{l+\ell_2}\,H^{\ell_1m_1}_{lm\ell_2m_2}\,k_{\ell_2}(\kappa L_{k\to j})Y^{m_2}_{\ell_2}(\hat{L}_{k\to j})\Bigg]$$
$$=D_k^{-1}(l)V_k(l)\breve{Q}^{k+}_{lm}+\sum_{j\neq k}\sum_{\ell_1m_1}D_k^{-1}(l)$$
$$\times i_l(\kappa a_k)i_{\ell_1}(\kappa a_j)\Bigg[\sum_{\ell_2m_2}(-1)^{l+\ell_2}\,H^{\ell_1m_1}_{lm\ell_2m_2}\,k_{\ell_2}(\kappa L_{k\to j})Y^{m_2}_{\ell_2}(\hat{L}_{k\to j})\Bigg]\breve{Q}^{j+}_{\ell_1m_1},\tag{49}$$

where we have applied (29) to

$$i_l(\kappa a_k)\,k_l(\kappa a_k)\frac{l\,\epsilon_k-\frac{(\kappa a_k)k_l'(\kappa a_k)}{k_l(\kappa a_k)}\epsilon_o}{l\,\epsilon_k-\frac{(\kappa a_k)i_l'(\kappa a_k)}{i_l(\kappa a_k)}\epsilon_o}=i_l(\kappa a_k)\,k_l(\kappa a_k)\left[1+\epsilon_o\frac{\frac{(\kappa a_k)i_l'(\kappa a_k)}{i_l(\kappa a_k)}-\frac{(\kappa a_k)k_l'(\kappa a_k)}{k_l(\kappa a_k)}}{l\,\epsilon_k-\frac{(\kappa a_k)i_l'(\kappa a_k)}{i_l(\kappa a_k)}\epsilon_o}\right]$$

$$=i_l(\kappa a_k)\,k_l(\kappa a_k)+\frac{\epsilon_o}{(\kappa a_k)}\frac{1}{l\,\epsilon_k-\frac{(\kappa a_k)i_l'(\kappa a_k)}{i_l(\kappa a_k)}\epsilon_o}=i_l(\kappa a_k)\,k_l(\kappa a_k)+\epsilon_o D_k(l). \tag{50}$$

We may rewrite (49) as (with $l\to\ell_k, m\to m_k, \ell_1\to\ell_j, m_1\to m_j, \ell_2\to l, m_2\to m$)

$$\overline{Q}^k_{\ell_k m_k}=D_k^{-1}(\ell_k)\,V_k(\ell_k)\breve{Q}^{k+}_{\ell_k m_k}+\sum_{j\neq k}D_k^{-1}(\ell_k)\left[\sum_{\ell_j m_j lm}i_{\ell_k}(\kappa a_k)i_{\ell_j}(\kappa a_j)\,\breve{Q}^{j+}_{\ell_j m_j}(-1)^{l+\ell_k}\,H^{\ell_j m_j}_{\ell_k m_k lm}\,k_l(\kappa L_{k\to j})Y_l^m(\hat{L}_{k\to j})\right]. \tag{51}$$

By defining the matrix $M^{(k,j)}$ having elements

$$M_{\ell_k m_k,\ell_j m_j}\equiv\sum_{lm}i_{\ell_k}(\kappa a_k)i_{\ell_j}(\kappa a_j)\,(-1)^{l+\ell_k}\,H^{\ell_j m_j}_{\ell_k m_k lm}\,k_l(\kappa L_{k\to j})Y_l^m(\hat{L}_{k\to j}), \tag{52}$$

the expression inside square bracket of (51) can be written as

$$M_{\ell_k m_k,\ell_j m_j}\,\breve{Q}^{j+}_{\ell_j m_j}.$$

Note that we may rewrite (52) as (using $\ell_k+\ell_j+l$ needing to be even by $H^{\ell_j m_j}_{\ell_k m_k lm}$ and $\sum_m H^{\ell_j m_j}_{\ell_k m_k lm}Y_l^m=\sum_m H^{\ell_k m_k}_{\ell_j m_j lm}Y_l^{m*}$)

$$M_{\ell_k m_k,\ell_j m_j}\equiv\sum_{lm}i_{\ell_k}(\kappa a_k)i_{\ell_j}(\kappa a_j)\,(-1)^{\ell_k}H^{\ell_j m_j}_{\ell_k m_k lm}\,k_l(\kappa L_{j\to k})Y_l^m(\hat{L}_{j\to k})$$

$$=\sum_{lm}i_{\ell_k}(\kappa a_k)i_{\ell_j}(\kappa a_j)\,(-1)^{\ell_j+l}H^{\ell_k m_k}_{\ell_j m_j lm}\,k_l(\kappa L_{j\to k})Y_l^{m*}(\hat{L}_{j\to k})=M^*_{\ell_j m_j,\ell_k m_k}, \tag{53}$$

implying that

$$M^{(k,j)^\dagger}=M^{(j,k)}.$$

One may rewrite the boundary condition equation in yet another form that is useful solely for analytical development:

$$D_k(\ell_k)\overline{Q}^k_{\ell_k m_k}=V_k(\ell_k)\breve{Q}^{k+}_{\ell_k m_k}+\sum_{j\neq k}\left[\sum_{\ell_j m_j lm}i_{\ell_k}(\kappa a_k)i_{\ell_j}(\kappa a_j)\,\breve{Q}^{j+}_{\ell_j m_j}(-1)^{l+\ell_k}\,H^{\ell_j m_j}_{\ell_k m_k lm}\,k_l(\kappa L_{k\to j})Y_l^m(\hat{L}_{k\to j})\right]. \tag{54}$$

Equation (49) or Eq. (51) allows us to solve for $\breve{Q}^{k+}_{lm}$ (hence $\breve{Q}^k_{lm}$) in terms of permanent multipole sources $\overline{Q}^k_{lm}$ with $k=1,2,\ldots,N$.

Note that knowing $\breve{Q}^k_{lm}$ is equivalent to knowing $\sigma_t^k(\hat{r}_k)$. Because $\sigma_f^k(\hat{r}_k)$ is the input, hence known, we thus may learn about the induced surface charge density $\sigma^k(\hat{r}_k)=\sigma_t^k(\hat{r}_k)-\sigma_f^k(\hat{r}_k)$, hence Q^k_{lm}. Having obtained $\breve{Q}^k_{lm}$ (hence $Q^k_{lm}=\breve{Q}^k_{lm}-\overline{Q}^k_{lm}$), we may wish to use (40) to compute the total electrostatic energy. However, caution needs to be exercised as this is incorrect. As explained near the end of Sec. IV, the extra induced surface charge strength $-[1-\frac{1}{\epsilon}]\overline{Q}_{lm}$ comes from smearing to the surface the induced bound charges that are originally attached to the free charges inside the sphere. These induced bound charges must be excluded from energy calculation. In expression (40), however, the interaction energy between this extra induced surface charge strength and the effective permanent surface charge strength is included. Hence, technically speaking, (40) does not give the correct total electrostatic energy. However, if one defines an auxiliary solvation energy (for sphere k)

$$U^{k,\mathrm{II-on}}_{s;\mathrm{aux}}=\frac{1}{2}\int\sigma_f(\hat{r})\left[\sum_{lm}\frac{\sqrt{4\pi}\,Q^{k;\mathrm{II-on}}_{lm}}{2l+1}Y_l^m(\hat{r}_k)\frac{1}{a_k}\right]dS_k=\frac{1}{2}\sum_{lm}\frac{4\pi a_k^2}{2l+1}\frac{\overline{\sigma}^{k*}_{lm}\,Q^{k;\mathrm{II-on}}_{lm}}{a_k}$$

$$=\frac{1}{2}\sum_{lm}\frac{\overline{Q}^{k*}_{lm}\,Q^{k;\mathrm{II-on}}_{lm}}{(2l+1)a_k}=-\frac{1}{2}\sum_{lm}\frac{4\pi}{2l+1}\left[\frac{2l+1}{(\kappa a_k)\,\epsilon_o\frac{k_l'(\kappa a_k)}{k_l(\kappa a_k)}-\epsilon\,l}+1\right]\frac{q^{k*}_{lm}\,q^k_{lm}}{a_k^{2l+1}}, \tag{55}$$

then one may subtract $\sum_{i=1}^N U^{i,\mathrm{II-on}}_{s;\mathrm{aux}}$ from (40) to arrive at the correct interaction energy. A simple calculation shows that the extra energy contained in $U^{\mathrm{II-on}}$ is simply

$$\sum_{k=1}^N\left[U^{k,\mathrm{II-on}}_{s;\mathrm{aux}}-U^{k,\mathrm{II-on}}_s\right]=\frac{1}{2}\sum_{k=1}^N\sum_{lm}\frac{4\pi}{2l+1}\left(\frac{1}{\epsilon_k}-1\right)\frac{q^{k*}_{lm}q^k_{lm}}{a_k^{2l+1}}=\frac{1}{2}\sum_{k=1}^N\sum_{lm}\frac{1}{2l+1}\left(\frac{1}{\epsilon_k}-1\right)\frac{\overline{Q}^{k*}_{lm}\overline{Q}^k_{lm}}{a_k}. \tag{56}$$

Hence, we may write the total electrostatic energy of the system as

$$U = U^{\text{II-on}} - \frac{1}{2}\sum_{k=1}^{N}\sum_{lm}\frac{1}{2l+1}\left(\frac{1}{\epsilon_k}-1\right)\frac{\overline{Q}_{lm}^{k*}\overline{Q}_{lm}^{k}}{a_k} = U^{\text{II-on}} - \sum_{k=1}^{N}U_{s;\text{aux}}^{k,\text{II-on}} + \sum_{k=1}^{N}U_{s}^{k,\text{II-on}}. \tag{57}$$

And not surprisingly,

$$U_{\text{int}} = U - \sum_{k=1}^{N}U_{s}^{k,\text{II-on}} = U^{\text{II-on}} - \sum_{i=1}^{N}U_{s;\text{aux}}^{i,\text{II-on}}.$$

Now let us write down $U^{\text{II-on}}$ explicitly by using (40), (41), and (35):

$$\begin{aligned}
U^{\text{II-on}} &= \frac{1}{2}\sum_{k=1}^{N}\int_{\mathcal{A}_k}\sigma_f^k(\hat{r}_k)\,\Phi_{\text{e}}(\boldsymbol{R}_k + a_k\hat{r}_k)dS_k \\
&= \frac{1}{2}\sum_{k=1}^{N}\left\{\sum_{lm}\frac{\overline{Q}_{lm}^{k*}\left(\breve{Q}_{lm}^{k} - \overline{Q}_{lm}^{k}\right)}{(2l+1)\,a_k} + \sum_{j\neq k}\int_{\mathcal{A}_k}\sigma_f^k(\hat{r}_k)\,\Phi_{j\to k}(\boldsymbol{R}_k + a_k\hat{r}_k)dS_k\right\} \\
&= \frac{\kappa}{2}\sum_{k=1}^{N}\sum_{lm}\left[i_l(\kappa a_k)k_l(\kappa a_k)\overline{Q}_{lm}^{k*}\breve{Q}_{lm}^{k+} - \frac{\overline{Q}_{lm}^{k*}\overline{Q}_{lm}^{k}}{(2l+1)\,(\kappa a_k)}\right] \\
&\quad + \frac{\kappa}{2}\sum_{k=1}^{N}\sum_{j\neq k}\left\{\sum_{lm}i_l(\kappa a_k)\overline{Q}_{lm}^{k*}\left[\sum_{\ell_1,m_1}i_{\ell_1}(\kappa a_j)\breve{Q}_{\ell_1m_1}^{j+}\sum_{\ell_2,m_2}(-1)^{l+\ell_2}\,H_{lm\ell_2m_2}^{\ell_1m_1}\,k_{\ell_2}(\kappa L_{k\to j})Y_{\ell_2}^{m_2}(\hat{L}_{k\to j})\right]\right\}.
\end{aligned}$$

Applying this result to (57), one has the total electrostatic energy

$$\begin{aligned}
U &= \frac{\kappa}{2}\sum_{k=1}^{N}\sum_{lm}\left[i_l(\kappa a_k)k_l(\kappa a_k)\overline{Q}_{lm}^{k*}\breve{Q}_{lm}^{k+} - \frac{\overline{Q}_{lm}^{k*}\overline{Q}_{lm}^{k}}{(2l+1)\,(\kappa a_k)\,\epsilon_k}\right] + \frac{\kappa}{2}\sum_{k=1}^{N}\sum_{j\neq k}\left\{\sum_{lm}i_l(\kappa a_k)\overline{Q}_{lm}^{k*}\right. \\
&\quad \left.\times\left[\sum_{\ell_1,m_1}i_{\ell_1}(\kappa a_j)\breve{Q}_{\ell_1m_1}^{j+}\sum_{\ell_2,m_2}(-1)^{l+\ell_2}\,H_{lm\ell_2m_2}^{\ell_1m_1}\,k_{\ell_2}(\kappa L_{k\to j})Y_{\ell_2}^{m_2}(\hat{L}_{k\to j})\right]\right\}.
\end{aligned} \tag{58}$$

The interaction energy is obtained via

$$\begin{aligned}
U_{\text{int}} &= U - \sum_{k=1}^{N}U_{s}^{k,\text{II-on}} \\
&= \frac{\kappa}{2}\sum_{k=1}^{N}\sum_{lm}\left(i_l(\kappa a_k)k_l(\kappa a_k)\overline{Q}_{lm}^{k*}\breve{Q}_{lm}^{k+} - \frac{\overline{Q}_{lm}^{k*}\overline{Q}_{lm}^{k}}{\left[\epsilon_k\,l - \epsilon_o\,\kappa a\,\frac{k_l'(\kappa a)}{k_l(\kappa a)}\right](\kappa a_k)}\right) \\
&\quad + \frac{\kappa}{2}\sum_{k=1}^{N}\sum_{j\neq k}\left\{\sum_{lm}i_l(\kappa a_k)\overline{Q}_{lm}^{k*}\left[\sum_{\ell_1,m_1}i_{\ell_1}(\kappa a_j)\breve{Q}_{\ell_1m_1}^{j+}\sum_{\ell_2,m_2}(-1)^{l+\ell_2}\,H_{lm\ell_2m_2}^{\ell_1m_1}\,k_{\ell_2}(\kappa L_{k\to j})Y_{\ell_2}^{m_2}(\hat{L}_{k\to j})\right]\right\}.
\end{aligned} \tag{59}$$

VII. RESULTS AND DISCUSSION

Our main Eqs. (58) and (59) here are similar to Eqs. (21) and (23) of [12] where ions are not considered or have to be included explicitly. The boundary condition equation (49) here corresponds to Eq. (20) of [12]. In the ion-free case [8,9,11,12], the convergence of the potential multipole expansion and the energy expression is controlled as follows. For a localized charge distribution inside a sphere of radius a centered around the origin, the multipole potential is equivalent to an effective Coulomb term $\overline{Q}_{lm}/r$ multiplied by a^l/r^l when observed at a distance $r > a$ away. In the interaction energy expression, the effective charge strength $\overline{Q}_{lm}$ corresponding to multipole q_{lm} is always combined with a factor of $\frac{a^l}{L^l}$ where a is the sphere radius and L is the distance between two spherical centers.

In the implicit ion method, the convergence property is less transparent. We will first discuss this point by examining the *exact* potential expansion outside a sphere (18):

$$\Phi^{\text{out}}(r > a) = \sum_{l,m}\frac{\sqrt{4\pi}}{2l+1}\frac{k_l(\kappa r)}{k_l(\kappa a)}\frac{\breve{Q}_{lm}}{a}Y_l^m(\hat{r}).$$

First, the factor $1/(2l+1)$ there simply reflects that there are $2l+1$ values of m for a particular l. This factor somewhat

averages out the contributions from the $2l+1$ values of m. Next, for a given l, we notice that the radial function is given by

$$\frac{k_l(\kappa r)}{[ak_l(\kappa a)]}.$$

We know that for large κr, all $k_l(\kappa r)$ have similar values, while at a fixed finite x the function $k_l(x)$ increase with l. This means that $\frac{k_l(\kappa r)}{[ak_l(\kappa a)]}$ decrease with l when $r > a$, indicating a decrease of importance of higher multipoles. When $\kappa a \ll 1$, $k_l(\kappa a) \approx (2l-1)!!/(\kappa a)^{l+1}$ and the scaling factor $1/[ak_l(\kappa a)] \propto a^l/\xi^{l+1}$ where $\xi = 1/\kappa$ is the effective decay length. That is, instead of a^l/r^{l+1} for the radial function, one has an exponential decay function $\approx e^{-\kappa r}/(\kappa r)$ multiplied by a^l/ξ^{l+1}. This shows the convergence of the sum is given by powers of a/ξ, not powers of a/r, illustrating the difference between the ion-free case and the Debye-Hückel level theoretical result. As for electrostatic interaction energy, we find the effective charge strengths $\breve{Q}_{lm}$ or $\overline{Q}_{lm}$ are accompanied by the factor

$$\frac{1}{(\kappa a)k_l(\kappa a)} \overset{\kappa a \ll 1}{\propto} \left(\frac{a}{\xi}\right)^l.$$

These analyses show that when mobile ions are considered, the convergence is controlled primarily by the ratio $a/\xi = \kappa a$. This tells us that in the case of small κa, the total (interaction) energy calculated by the series expressions (58) and (59) will converge faster than the large-κa case at small intersphere separations. That is, the theory becomes more powerful for small κa. Interestingly, one may remember that having a small κ is one starting criterion for a valid Debye-Hückel theory.

The readers must be curious about the relationship between this implicit ion approach (rigorous at the Debye-Hückel level) and our rigorous ion-free result [12]. The answer is simply that by taking the $\kappa^2 \to 0$ limit, one mathematically removes the Debye-Hückel ion charge density, and the electrical potential is governed once again by the Poisson equation, not the modified inhomogeneous Helmholtz equation. It turns out that one may show this explicitly, although the procedure is a bit tedious. To convince the readers but not bore them with the lengthy algebra, we shall illustrate but one nontrivial point in detail. If we compare the interaction energy expression (59) here with the corresponding Eq. (23) of [12], we find that the effective charge strengths $\overline{Q}^{k*}_{lm}$ and $\breve{Q}^{j}_{\ell_1 m_1}$ on two distinct spheres k and j seem to interact differently. In the current formalism, we have

$$\kappa\, i_l(\kappa a_k)\,\overline{Q}^{k*}_{lm}\, i_{\ell_1}(\kappa a_j)\breve{Q}^{j+}_{\ell_1 m_1}\left[\sum_{\ell_2,m_2}(-1)^{l+\ell_2} H^{\ell_1 m_1}_{lm\ell_2 m_2}\, k_{\ell_2}(\kappa L_{k\to j}) Y^{m_2}_{\ell_2}(\hat{L}_{k\to j})\right]$$

$$= \kappa\,\frac{i_l(\kappa a_k)\,\overline{Q}^{k*}_{lm}\breve{Q}^{j}_{\ell_1 m_1}}{(\kappa a_j)\,(2\ell_1+1)\,k_{\ell_1}(\kappa a_j)}\left[\sum_{\ell_2,m_2}(-1)^{l+\ell_2} H^{\ell_1 m_1}_{lm\ell_2 m_2}\, k_{\ell_2}(\kappa L_{k\to j}) Y^{m_2}_{\ell_2}(\hat{L}_{k\to j})\right]. \tag{60}$$

This is to be compared with the corresponding part in Eq. (23) of [12],

$$q^{k*}_{lm}\,\frac{4\pi(-1)^{\ell_1+m}\breve{Q}^{j}_{\ell_1 m_1}}{(2l+1)(2\ell_1+1)}\,\frac{a_j^{\ell_1}}{L^{l+\ell_1+1}_{k\to j}}\,\Lambda_{l,\ell_1,-m,m_1}\, Y^{-m+m_1}_{l+\ell_1}(\hat{L}_{k\to j})$$

$$= \frac{\overline{Q}^{k*}_{lm}}{2l+1}\,\frac{\breve{Q}^{j}_{\ell_1 m_1}}{2\ell_1+1}\,\frac{a_k^l a_j^{\ell_1}}{L^{l+\ell_1+1}_{k\to j}}\sqrt{4\pi}(-1)^{\ell_1+m}\Lambda_{l,\ell_1,-m,m_1}\, Y^{-m+m_1}_{l+\ell_1}(\hat{L}_{k\to j}). \tag{61}$$

We see that the previous result contains no summation over ℓ_2. So how does the summation over ℓ_2 disappear? To see this, let us remember again as $\kappa \to 0$, $\kappa a \to 0$ and $k_l(\kappa a) \to (2l-1)!!/(\kappa a)^{l+1}$ and $i_l(\kappa a) \to (\kappa a)^l/(2l+1)!!$. Expression (60) becomes

$$\overline{Q}^{k*}_{lm}\breve{Q}^{j}_{\ell_1 m_1}\kappa\,\frac{(\kappa a_k)^l}{(2l+1)!!}\,\frac{(\kappa a_j)^{\ell_1}}{(2\ell_1+1)!!}\left[\sum_{\ell_2,m_2}(-1)^{l+\ell_2} H^{\ell_1 m_1}_{lm\ell_2 m_2}\,\frac{(2\ell_2-1)!!}{(\kappa L_{k\to j})^{\ell_2+1}} Y^{m_2}_{\ell_2}(\hat{L}_{k\to j})\right]. \tag{62}$$

Because $H^{\ell_1 m_1}_{lm\ell_2 m_2}$ contains the Clebsch-Gordan coefficient $C^{\ell_1 m_1}_{lm\ell_2 m_2}$, the range of ℓ_2 is between $|l-\ell_1|$ and $l+\ell_1$. For any $\ell_2 < l+\ell_1$, there will be a positive power of κ in the expression above, rendering zero value upon taking the $\kappa \to 0$ limit. Hence, the $\kappa \to 0$ limit forces $\ell_2 = l+\ell_1$ and the sum over ℓ_2 disappears. As a bonus, we also see how the factor

$$\frac{a_k^l a_j^{\ell_1}}{L^{l+\ell_1+1}_{k\to j}}$$

of (61) arises from (62). When $\ell_2 = l+\ell_1$,

$$\kappa\,\frac{(\kappa a_k)^l(\kappa a_j)^{\ell_1}}{(\kappa L_{k\to j})^{\ell_2+1}} \to \frac{a_k^l a_j^{\ell_1}}{L^{l+\ell_1+1}_{k\to j}}.$$

Another property of the Wigner $3j$ symbol

$$C^{00}_{lml-m} = (-1)^{l-l+0}\sqrt{2\times 0+1}\begin{pmatrix} l & l & 0 \\ m & -m & 0\end{pmatrix} = \frac{(-1)^{l-m}}{\sqrt{2l+1}},$$

leading to the following useful expression,

$$H^{00}_{lml-m} = C^{00}_{l0l0} C^{00}_{lml-m} \sqrt{\frac{4\pi}{2\times 0+1}} \sqrt{(2l+1)(2l+1)} = \sqrt{4\pi}(-1)^m,$$

which helps in proving the equivalence between [12] and the current formalism as $\kappa \to 0$.

The main purpose of this paper is to describe an implicit ion formalism rigorous at the Debye-Hückel level. The system under consideration consists of an arbitrary number of dielectric spheres of finite radii immersed in a dielectric solvent that contains mobile ions. To the best of our knowledge, except for the formalism described here, no other formalism emphasizes reciprocity and offers a rigorous, closed form for the electrostatic energy. Comparison with other methods remains important, but since this paper is already lengthy we prefer to do so in a separate publication [23]. Here, we content ourselves by showing the correct results for the frequently studied case of two dielectric spheres [16–20].

Prior to computing the energy of the two-sphere system, let us first elucidate the reciprocity property further. The full exposition of reciprocity for an arbitrary number of spheres is provided in Appendix E. Here we only summarize the results for two spheres. With the general definitions given in Eq. (48) let us denote by D_1 (D_2) the diagonal matrix with elements $D_1(\ell_1)$ [$D_2(\ell_2)$]. We also abbreviate by V_1 (V_2) the diagonal matrix with elements $V_1(\ell_1) = \epsilon_o D_1(\ell_1) + i_{\ell_1}(\kappa a_1)\, k_{\ell_1}(\kappa a_1)$ [$V_2(\ell_2) = \epsilon_o D_2(\ell_2) + i_{\ell_2}(\kappa a_2)\, k_{\ell_2}(\kappa a_2)$].

The boundary conditions can now be written as a matrix equation of the following form:

$$\begin{pmatrix} V_1 & M \\ M^\dagger & V_2 \end{pmatrix} \begin{pmatrix} \breve{Q}_1^+ \\ \breve{Q}_2^+ \end{pmatrix} = \begin{pmatrix} D_1 \overline{Q}_1 \\ D_2 \overline{Q}_2 \end{pmatrix},$$

where $\breve{Q}_i^+$ ($\overline{Q}_i$) denotes the vector with components $\breve{Q}_{lm}^{i+}$ ($\overline{Q}_{lm}^i$) for all l up to $l_{\max}$ (the maximum l value considered) and elements of M are given by Eq. (E3). For the two-sphere system, the first form and the second form of the reciprocity interaction energies, proven identical for any $l_{\max}$ in Appendix E, may be expressed as

$$U_{\rm int}^{r(1)} = \kappa\, \overline{Q}_1^{*T} [(V_1 - \epsilon_o D_1)\breve{Q}_1^+ + M\breve{Q}_2^+], \tag{63}$$

$$U_{\rm int}^{r(2)} = \kappa \overline{Q}_2^{*T} [(V_2 - \epsilon_o D_2)\breve{Q}_2^+ + M^\dagger \breve{Q}_1^+]. \tag{64}$$

In Fig. 1, we provide readers with concrete numerical verification of reciprocity: equivalence between the two expressions (63) and (64) above, corresponding to (E7) and (E11) in Appendix E, for whatever choice of $l_{\max}$.

A particularly simple case is when $l_{\max} = 0$. As shown in Appendix E, with $l_{\max} = 0$, we have for a two-sphere system the reciprocity interaction energy

$$U_{\rm int}^r(l_{\max}=0) = \frac{q_1\, q_2}{\epsilon_o L} \frac{e^{-\kappa(L-a_1-a_2)}}{(1+\kappa a_1)(1+\kappa a_2)} \times \left[1 - G_{12}\left(\frac{e^{-\kappa(L-a_1-a_2)}}{\kappa L}\right)^2\right]^{-1}$$

with

$$G_{12} = G_{21} = \frac{(\kappa a_1)(\kappa a_2)[T_0(a_1) - (1+\kappa a_1)][T_0(a_2) - (1+\kappa a_2)]}{T_0(a_1)(1+\kappa a_1) T_0(a_2)(1+\kappa a_2)}.$$

Note that when L is large so that $\frac{e^{-\kappa(L-a_1-a_2)}}{\kappa L} \ll 1$, we have

$$U_{\rm int}^r(l_{\max}=0) \approx \frac{q_1\, q_2}{\epsilon_o L} \frac{e^{-\kappa(L-a_1-a_2)}}{(1+\kappa a_1)(1+\kappa a_2)}, \tag{65}$$

which is the celebrated long-range interaction term of Verwey and Overbeek [24].

Even though the Verwey-Overbeek term appears as the dominant term in the reciprocity interaction energy, we must emphasize that it is incorrect to use (E14) for computation of the force. That is, the derivative with respect to L of (E14), led by the Verwey-Overbeek term, does not yield the correct force between the two dielectric spheres. The actual force comes from the derivative of the total energy with respect to L. The computed interaction energy in either (E9) or (E11) does not

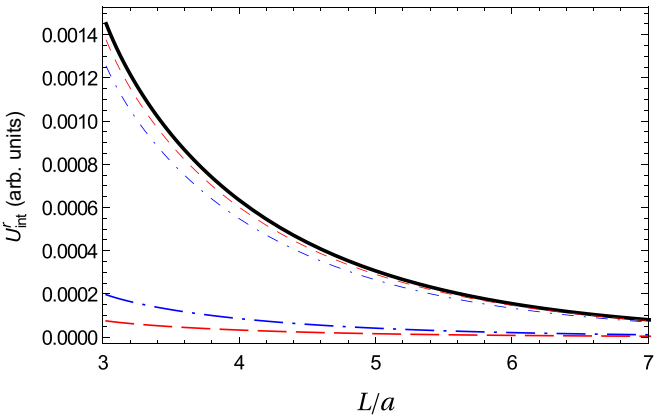

FIG. 1. The reciprocity interaction energy of a system of two spheres versus their separation. Each sphere contains a unit charge at its center; sphere 1 has radius $a_1 = a$ while sphere 2 has radius $a_2 = 2a$. The other parameters are chosen to mimic two spherical proteins immersed in a rather strong ionic solution with water as solvent: $\epsilon_1 = \epsilon_2 = 4$, $\epsilon_o = 80$, and $\kappa = 0.5$. There are two forms, (E7) and (E11), of the reciprocity interaction energy, each containing two components. The $\kappa\, \overline{Q}_1^{*T}(V_1 - \epsilon_o D_1)\breve{Q}_1^+$ component of (E7) is plotted using a thick red dashed line while the $\kappa\, \overline{Q}_1^{*T} M \breve{Q}_2^+$ component of (E7) is plotted using thin red dashed line. The $\kappa\, \overline{Q}_2^{*T}(V_2 - \epsilon_o D_2)\breve{Q}_2^+$ component of (E11) is plotted using a thick blue dot-dashed line while the $\kappa\, \overline{Q}_2^{*T} M^\dagger \breve{Q}_1^+$ component of (E11) is plotted using thin blue dot-dashed line. Although the components all have different values, as shown in the plot, the sums of the two components belonging to either (E7) or (E11) yield identical values shown using a solid black line. As proved in Appendix E, reciprocity holds for an arbitrary $l_{\max}$ cutoff. The numerical values in this plot are produced using $l_{\max} = 10$ throughout.

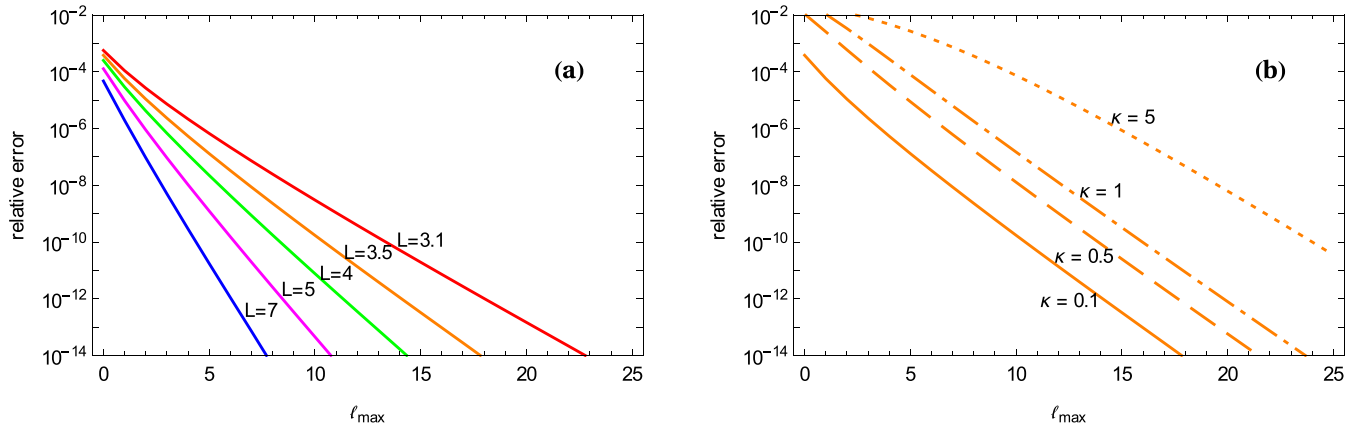

FIG. 2. The relative errors of the computed interaction energy, (59), between two spheres versus l_{max}. The system consists of two spheres, the first one with radius $a_1 = a$ while the other with radius $a_2 = 2a$; each sphere has a point charge q at its center. In panel (a), the relative error curves—when the two sphere centers are separated by $L = 3.1a$, $3.5a$, $4.0a$, $5.0a$, and $7.0a$, and for $\kappa = 0.1$—are each labeled by the corresponding L and shown in different colors: red ($L = 3.1a$), orange ($L = 3.5a$), green ($L = 4.0a$), magenta ($L = 5.0a$), and blue ($L = 7.0a$). In panel (b), we display the relative error versus l_{max} for various κ when $L = 3.5a$. We find that as κ increases, the relative error, for the same l_{max} value, also increases.

include the force due to self-interaction. For example, one may consider a point charge near a conducting plane. There is apparently a real force on the point charge produced by its image charge. However, such a force is not accounted for by computing the derivative of the *reciprocity interaction* energy with respect to L.

While calculating the interaction energy U_{int} using (59), one may control the accuracy of the energy obtained by varying l_{max}. For practical purposes, it is desirable to know what l_{max} to use for a desired accuracy requirement. In Fig. 2, we display the relative error versus l_{max} when the two spheres, the first one with radius $a_1 = a$ and the second $a_2 = 2a$, have their centers separated by $3.1a$, $3.5a$, $4.0a$, $5.0a$, and $7.0a$ for $\kappa = 0.1$. For $L = 3.5a$, we also display the relative error versus l_{max} for various κ. We note that as κ increases, the relative error, for the same l_{max} value, also increases. This means that when one applies the rigorous formalism for ionic screening at the Debye-Hückel level to the large-κ regime, the convergence gets worse (needing more terms) as κ increases. One also observes, from Fig. 2, that for a given κ and separation distance L, the relative error in the computed interaction energy decreases exponentially with l_{max}. For most applications up to $\kappa \leqslant 1$, we find $l_{max} = 10$ sufficient.

With l_{max} fixed at 10, we show in Fig. 3 the computed interaction energy, (59), as a function of separation distance between two sphere centers for various values of κ. Two expected trends are observed. First, the interaction energy magnitude decreases with κ for the same separation distance. Second, the decay rate with respect to the separation distance increases with κ.

Some readers might be interested in knowing whether the same level of rigor can be kept if one wishes to treat the ion radius δ as finite. The answer is affirmative. In this case, for every sphere, say sphere k, there are two spherical interfaces, $r_k = a_k$ and $r_k = a_k + \delta = b_k$, hence two boundary conditions and two sets of induced surface charge strengths: $Q_{lm}^{k<}$ for $r_k = a_k$ and $Q_{lm}^{k>}$ for $r_k = b_k$. Having already proved the equivalence between methods I-in and II-on in Appendix C for finite δ, we shall use only method II-on to describe the modifications required. For convenience, we shall define

$$Q_{lm}^{k} \equiv Q_{lm}^{k<} + \left(\frac{a_k}{b_k}\right)^{l+1} Q_{lm}^{k>}$$

and $\breve{Q}_{lm}^{k} = Q_{lm}^{k} + \overline{Q}_{lm}^{k}$. Because it is our plan to investigate the effect of finite ion radii in a separate publication [25], we outline only the modifications required to perform the boundary condition matching without displaying all the final expressions of solvation energy and interaction energy. This is because the energy expressions are readily attainable once the variables in the boundary equations are solved for and because the energy expressions might become so unnecessarily cumbersome that the essence of the proposed method in this paper is masked.

To match the boundary conditions on the two interfaces of sphere k, we will need [see Eq. (43)]

$$\Phi_b(\boldsymbol{R}_k + \boldsymbol{r}_k) = \sum_{j\neq k} \Phi_{j\to k}(\boldsymbol{R}_k + \boldsymbol{r}_k) + \Phi_{k\to k}(\boldsymbol{R}_k + \boldsymbol{r}_k).$$

The electrostatic potential contribution from sphere k to its nearby location is now given by

$$\Phi_{k\to k}(\boldsymbol{R}_k + \boldsymbol{r}_k) = \begin{cases} \sum_{l,m} D_{lm}^k\, k_l(\kappa r_k)\, Y_l^m(\hat{r}_k), & [r_k > b_k], \\ \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}_k)\left[\frac{a_k^l}{r_k^{l+1}} \breve{Q}_{lm}^k + \left(r_k^l - \frac{a_k^{2l+1}}{r_k^{l+1}}\right)\frac{Q_{lm}^{k>}}{b_k^{l+1}}\right], & [a_k < r_k < b_k], \\ \sum_{l,m} \frac{\sqrt{4\pi}}{2l+1} \frac{r_k^l}{a_k^{l+1}} \breve{Q}_{lm}^k Y_l^m(\hat{r}_k), & [r_k < a_k], \end{cases}$$

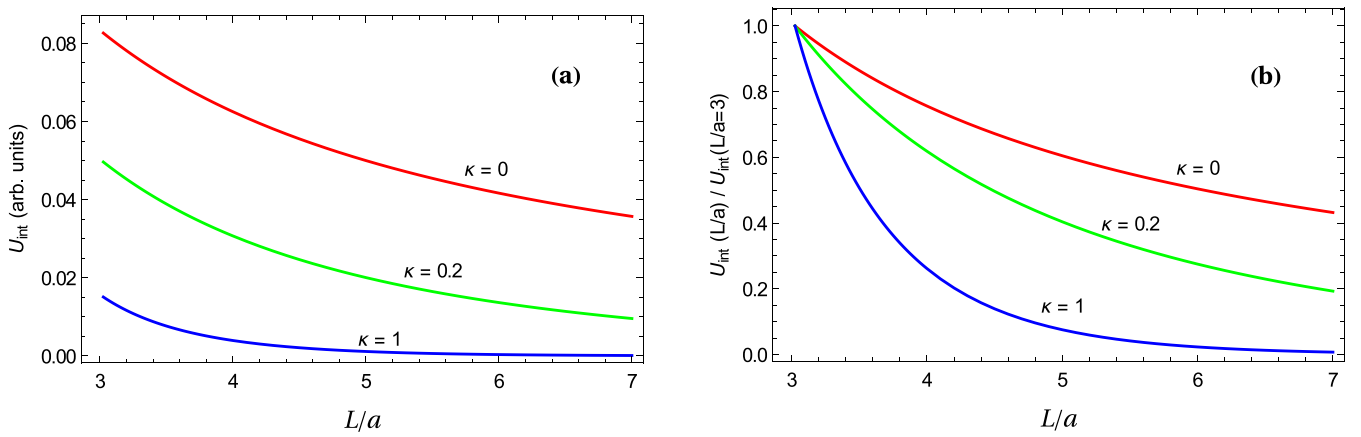

FIG. 3. Interaction energy (59) for a system of two spheres versus their separation distance. The first sphere has radius $a_1 = a$, while the second one has radius $a_2 = 2a$. Each sphere has a point charge q at its center. Displayed in panel (a) is the interaction energy versus separation distance for various κ values. It is obvious that the magnitude of the interaction energy at a fixed separation decreases as κ increases. In panel (b), the interaction energies are scaled by their values at contact distance. This allows us to see clearly the trend that the interaction energy decreases with the separation distance more rapidly for larger κ values.

where, similarly to (C14),

$$D^k_{lm} = \frac{1}{k_l(\kappa b_k)} \frac{\sqrt{4\pi}}{2l+1} \left[\frac{a_k^l}{b_k^{l+1}} \breve{Q}^k_{lm} + \frac{1}{b_k} \left(1 - \frac{a_k^{2l+1}}{b_k^{2l+1}} \right) Q^{k>}_{lm} \right].$$

And the potential contribution from sphere j at the region near sphere k is

$$\begin{aligned}
\Phi_{j\to k}(\boldsymbol{R}_k + \boldsymbol{r}_k, r_k > b_k) &= \sum_{\ell_1,m_1} D^j_{\ell_1 m_1} k_{\ell_1}(\kappa|\boldsymbol{r}_k + \boldsymbol{R}_k - \boldsymbol{R}_j|) Y^{m_1}_{\ell_1} \left(\frac{\boldsymbol{r}_k + \boldsymbol{R}_k - \boldsymbol{R}_j}{|\boldsymbol{r}_k + \boldsymbol{R}_k - \boldsymbol{R}_j|} \right) \\
&= \sum_{\ell_1,m_1} D^j_{\ell_1 m_1} k_{\ell_1}(\kappa|\boldsymbol{r}_k - \vec{L}_{k\to j}|) Y^{m_1}_{\ell_1} \left(\frac{\boldsymbol{r}_k - \vec{L}_{k\to j}}{|\boldsymbol{r}_k - \vec{L}_{k\to j}|} \right) \\
&= \sum_{\ell_1,m_1} D^j_{\ell_1 m_1} \sum_{l,\ell_2,m,m_2} (-1)^{l+\ell_2} H^{\ell_1 m_1}_{lm\ell_2 m_2} i_l(\kappa r_k) Y^m_l(\hat{r}_k) k_{\ell_2}(\kappa L_{k\to j}) Y^{m_2}_{\ell_2}(\hat{L}_{k\to j}) \\
&= \sum_{lm} i_l(\kappa r_k) Y^m_l(\hat{r}_k) \left[\sum_{\ell_1,m_1} D^j_{\ell_1 m_1} \sum_{\ell_2,m_2} (-1)^{l+\ell_2} H^{\ell_1 m_1}_{lm\ell_2 m_2} k_{\ell_2}(\kappa L_{k\to j}) Y^{m_2}_{\ell_2}(\hat{L}_{k\to j}) \right], \qquad (66)
\end{aligned}$$

$$\Phi_{j\to k}(\boldsymbol{R}_k + \boldsymbol{r}_k, a_k < r_k < b_k) = \sum_{lm} \tilde{B}^{j\to k}_{lm} \left[\frac{(\epsilon' - \epsilon_k) l}{\epsilon_k\, l + \epsilon'(l+1)} \left(\frac{a_k}{b_k} \right)^{l+1} \frac{a_k^l}{r_k^{l+1}} + \frac{r_k^l}{b_k^{l+1}} \right] Y^m_l(\hat{r}_k), \qquad (67)$$

$$\Phi_{j\to k}(\boldsymbol{R}_k + \boldsymbol{r}_k, r_k < a_k) = \sum_{lm} \tilde{B}^{j\to k}_{lm} \left[\frac{(\epsilon' - \epsilon_k) l}{\epsilon_k\, l + \epsilon'(l+1)} \left(\frac{a_k}{b_k} \right)^{l+1} \frac{r_k^l}{a_k^{l+1}} + \frac{r_k^l}{b_k^{l+1}} \right] Y^m_l(\hat{r}_k), \qquad (68)$$

and $\tilde{B}^{j\to k}_{lm}$ are determined via matching the potential $\Phi_{j\to k}(\boldsymbol{R}_k + \boldsymbol{r}_k)$ at $r_k = b_k$. The two boundary conditions for sphere k are taken with $\boldsymbol{R}_k = 0$:

$$\begin{aligned}
\epsilon_o \frac{\partial \Phi_b(\boldsymbol{r}_k)}{\partial r_k}\bigg|_{b_k^+} &= \epsilon' \frac{\partial \Phi_b(\boldsymbol{r}_k)}{\partial r_k}\bigg|_{b_k^-}, \\
\epsilon' \frac{\partial \Phi_b(\boldsymbol{r}_k)}{\partial r_k}\bigg|_{a_k^+} &= \epsilon_k \frac{\partial \Phi_b(\boldsymbol{r}_k)}{\partial r_k}\bigg|_{a_k^-} - 4\pi\sigma_f^k.
\end{aligned}$$

Before ending this paper, we would like to touch on a question that probably will have occurred to an avid reader: how can we proceed when the biomolecular shapes are nonspherical? The answer is quite simple. Without spherical symmetry, although the analytical expressions are lost, we can still tackle this problem numerically. With Eq. (B20) given, one may discretize Eq. (B19) and obtain the charge densities numerically. The molecular shapes now can be arbitrary. The space occupied by a biomolecule now is signified by zero mobile ion density. However, the computational cost inevitably increases with the number of representative spatial points in discretization.

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APPENDIX A: DERIVATION OF EQUATION (2)

Let O_A be an arbitrary point and O_1 be a local origin. The vector from O_1 to an observation point P is denoted by $\vec{r}_1$. The vector from O_1 to O_A is denoted by $\vec{r}_2$. For our applications, $r_1 < r_2$. Let $\vec{R} = \vec{r}_1 - \vec{r}_2$ be the vector from O_A to P. The derivation below utilizes an argument that was originally in [26] (page 578), although the original argument requires correction, which we provide here.

Consider the analytic continuation of $h_0^{(1)}$ (shown on page 577 of [26]) by taking $|\vec{k}| = k = i\kappa$:

$$k_0(\kappa R) = \frac{e^{-\kappa R}}{\kappa R} = \int_1^\infty e^{-\kappa R\eta} d\eta = \frac{1}{2\pi}\int_0^{2\pi}\int_1^\infty e^{-\kappa R\cos\gamma} d(\cos\gamma) d\psi. \quad \text{(A1)}$$

This expression is like laying $\vec{R} = R\hat{z}$, $\gamma \to \theta_k$, and $\psi \to \phi_k$. Evidently, $d\cos\gamma\, d\psi$ is a surface element (on the unit sphere) which coincides with $d\cos\theta_k\, d\phi_k$ due to choosing $\vec{R} = R\hat{z}$. If one were to get a general $\vec{R}$ by rotating $R\hat{z}$ to yield $\vec{R} = R(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta) = R\hat{R}$, then $\cos\gamma = \hat{k}\cdot\hat{R} = \cos\theta\cos\theta_k + \sin\theta\sin\theta_k\cos(\phi - \phi_k)$. This *fixed* rotation will also change the course of the θ_k integral. That is, if one were rotate the integration paths using the fixed rotation, one will not be using the same limits as before but requiring a new integration limit or domain. That is, one may still write

$$\frac{e^{-\kappa R}}{\kappa R} = \frac{1}{2\pi}\int_{D_k} e^{-\kappa R\cos\gamma} d(\cos\theta_k) d\phi_k \quad \text{(A2)}$$

with

$$\int_{D_k} d\Omega_k \neq \int_0^{2\pi} d\phi_k \int_1^\infty d\cos\theta_k. \quad \text{(A3)}$$

The exact form of $\int_{D_k}$ does not matter. All one needs to know is that once the fixed rotation that brings $R\hat{z}$ to $\vec{R} = R(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$ is found, D_k is fixed and its details matter little.

With $\vec{R} = \vec{r}_1 - \vec{r}_2$, we have $\vec{k}\cdot\vec{R} = \vec{k}\cdot\vec{r}_1 - \vec{k}\cdot\vec{r}_2$. The plane wave expansion states

$$e^{i\vec{k}\cdot\vec{r}} = e^{ikr\hat{k}\cdot\hat{r}} = 4\pi\sum_{\ell,m} i^\ell j_\ell(kr) Y_\ell^m(\hat{r}) Y_\ell^{m*}(\hat{k}).$$

With $kr \to i\kappa r$ and using $i_\ell(x) = i^{-\ell} j_\ell(ix)$, we have

$$e^{-\kappa r\hat{k}\cdot\hat{r}} = 4\pi\sum_{\ell,m}(-1)^\ell i_\ell(\kappa r) Y_\ell^m(\hat{r}) Y_\ell^{m*}(\hat{k}). \quad \text{(A4)}$$

We also note the Green's function expansion

$$\frac{e^{-\kappa|\vec{r}_> - \vec{r}_<|}}{\kappa|\vec{r}_> - \vec{r}_<|} = 4\pi\sum_{\ell,m} i_\ell(\kappa r_<) k_\ell(\kappa r_>) Y_\ell^m(\hat{r}_<) Y_\ell^{m*}(\hat{r}_>). \quad \text{(A5)}$$

We have already considered $r_1 < r_2$. Now there are two cases: $R^2 > r_2^2$ or $R^2 < r_2^2$. In this proof, we focus on $R > r_2$ for now. We shall investigate the validity of the formula when $R < r_2$ at least numerically.

The main idea is to first express $k_0(\kappa r_1)$ in two different ways and then link the identity. From (A5), we have

$$k_0(\kappa r_1) = \frac{e^{-\kappa|\vec{r}_2 + \vec{R}|}}{\kappa|\vec{r}_2 + \vec{R}|} = 4\pi\sum_{L,M}(-1)^L i_L(\kappa r_2) k_L(\kappa R) Y_L^M(\hat{r}_2) Y_L^{M*}(\hat{R}). \quad \text{(A6)}$$

Here, the factor $(-1)^L$ comes from $Y_L^M(\hat{R}) = (-1)^L Y_L^M(-\hat{R})$. Applying (A2) to $k_0(\kappa r_1)$, we have

$$\frac{e^{-\kappa|\vec{r}_2 + \vec{R}|}}{\kappa|\vec{r}_2 + \vec{R}|} = \frac{1}{2\pi}\int_{D_k} e^{-\kappa r_1\hat{k}\cdot\hat{r}_1} d(\cos\theta_k) d\phi_k = \frac{1}{2\pi}\int_{D_k} e^{-\kappa r_2\hat{k}\cdot\hat{r}_2} e^{-\kappa R\hat{k}\cdot\hat{R}} d(\cos\theta_k) d\phi_k. \quad \text{(A7)}$$

Replacing the integrand $e^{-\kappa r_2\hat{k}\cdot\hat{r}_2}$ by (A4), one has

$$k_0(\kappa r_1) = \frac{e^{-\kappa|\vec{r}_2 + \vec{R}|}}{\kappa|\vec{r}_2 + \vec{R}|} = \frac{4\pi}{2\pi}\int_{D_k}\left[\sum_{L,M}(-1)^L i_L(\kappa r_2) Y_L^M(\hat{r}_2) Y_L^{M*}(\hat{k})\right] \times e^{-\kappa R\hat{k}\cdot\hat{R}} d\Omega_k. \quad \text{(A8)}$$

Equating the coefficient function of $(-1)^L i_L(\kappa r_2) Y_L^M(\hat{r})$ between expressions (A6) and (A8), one arrives at an integral expression for $k_L(\kappa R) Y_L^{M*}(\hat{R})$:

$$k_L(\kappa R) Y_L^{M*}(\hat{R}) = \frac{1}{2\pi}\int_{D_k} Y_L^{M*}(\hat{k})\, e^{-\kappa R\hat{k}\cdot\hat{R}} d\Omega_k. \quad \text{(A9)}$$

Note that $\kappa R\hat{k}\cdot\hat{R} = \kappa r_1\,\hat{k}\cdot\hat{r}_1 - \kappa r_2\,\hat{k}\cdot\hat{r}_2 = \kappa r_1\,\hat{k}\cdot\hat{r}_1 + \kappa r_2\,\hat{k}\cdot(-\hat{r}_2)$.

Rewriting $e^{-\kappa R\hat{k}\cdot\hat{R}}$ as above,

$$\begin{aligned} k_L(\kappa R) Y_L^{M*}(\hat{R}) &= \frac{1}{2\pi}\int_{D_k} Y_L^{M*}(\hat{k})\, e^{-\kappa r_1\hat{k}\cdot\hat{r}_1 - \kappa r_2\hat{k}\cdot(-\hat{r}_2)} d\Omega_k \\ &= \frac{4\pi}{2\pi}\int_{D_k} Y_L^{M*}(\hat{k}) \sum_{\ell_1,m_1}(-1)^{\ell_1} i_{\ell_1}(\kappa r_1) Y_{\ell_1}^{m_1}(\hat{r}_1) \\ &\quad \times Y_{\ell_1}^{m_1*}(\hat{k})\, e^{-\kappa r_2\hat{k}\cdot(-\hat{r}_2)} d\Omega_k \\ &= \frac{4\pi}{2\pi}\sum_{\ell_1,m_1}(-1)^{\ell_1} i_{\ell_1}(\kappa r_1) Y_{\ell_1}^{m_1}(\hat{r}_1)\int_{D_k} Y_L^{M*}(\hat{k}) \\ &\quad \times Y_{\ell_1}^{m_1*}(\hat{k})\, e^{-\kappa r_2\hat{k}\cdot(-\hat{r}_2)} d\Omega_k. \end{aligned}$$

Using Eq. (3.7.72) on page 216 of [27], one has

$$\begin{aligned} Y_L^{M*}(\hat{k}) Y_{\ell_1}^{m_1*}(\hat{k}) &= \sum_{\ell_2,m_2}\sqrt{\frac{4\pi}{2\ell_2+1}}\frac{\sqrt{(2L+1)(2\ell_1+1)}}{4\pi} \\ &\quad \times C_{LM\ell_1 m_1}^{\ell_2 m_2} C_{L0\,\ell_1 0}^{\ell_2 0} Y_{\ell_2}^{m_2*}(\hat{k}) \\ &\equiv \sum_{\ell_2,m_2}\frac{H_{LM\ell_1 m_1}^{\ell_2 m_2}}{4\pi} Y_{\ell_2}^{m_2*}(\hat{k}). \end{aligned} \quad \text{(A10)}$$

Therefore,

$$\begin{aligned} k_L(\kappa R)Y_L^{M*}(\hat{R}) &= \frac{4\pi}{2\pi}\sum_{\ell_1,m_1}(-1)^{\ell_1} i_{\ell_1}(\kappa r_1)Y_{\ell_1}^{m_1}(\hat{r}_1)\int_{D_k} Y_L^{M*}(\hat{k})\,Y_{\ell_1}^{m_1*}(\hat{k})\,e^{-\kappa r_2\,\hat{k}\cdot(-\hat{r}_2)}\,d\Omega_k \\ &= (4\pi)\sum_{\ell_1,m_1,\ell_2,m_2}\frac{H_{LM\ell_1m_1}^{\ell_2 m_2}}{4\pi}(-1)^{\ell_1}\,i_{\ell_1}(\kappa r_1)Y_{\ell_1}^{m_1}(\hat{r}_1)\,k_{\ell_2}(\kappa r_2)Y_{\ell_2}^{m_2*}(-\hat{r}_2) \\ &= \sum_{\ell_1,m_1,\ell_2,m_2}H_{LM\ell_1m_1}^{\ell_2 m_2}(-1)^{\ell_1+\ell_2}\,i_{\ell_1}(\kappa r_1)Y_{\ell_1}^{m_1}(\hat{r}_1)\,k_{\ell_2}(\kappa r_2)Y_{\ell_2}^{m_2*}(\hat{r}_2). \end{aligned} \tag{A11}$$

Note the relation between Wigner $3j$ symbols and the Clebsch-Gordan coefficient (see Eq. (3.7.44) on page 210 of [27]):

$$C_{j_1m_1j_2m_2}^{jm} = (-1)^{j_1-j_2+m}\sqrt{2j+1}\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix}. \tag{A12}$$

Here $m = m_1 + m_2$ and the $3j$ symbol has the beautiful cyclic invariance. Utilizing this, one may make $\vec{L}$ the sum of $\vec{\ell}_1$ and $\vec{\ell}_2$.

Let us rework the coefficients [here $m_2 = (m_1 + M)$]:

$$\begin{aligned} H_{LM\ell_1m_1}^{\ell_2 m_2} &= \sqrt{\frac{4\pi}{2\ell_2+1}}\sqrt{(2L+1)(2\ell_1+1)}\,C_{LM\ell_1m_1}^{\ell_2 m_2}C_{L0\,\ell_10}^{\ell_2 0} \\ &= \sqrt{\frac{4\pi}{2\ell_2+1}}\sqrt{(2L+1)(2\ell_1+1)}(-1)^{m_2}(2\ell_2+1)\begin{pmatrix} L & \ell_1 & \ell_2 \\ M & m_1 & -m_2 \end{pmatrix}\begin{pmatrix} L & \ell_1 & \ell_2 \\ 0 & 0 & 0 \end{pmatrix} \\ &= \sqrt{(4\pi)(2\ell_2+1)}\sqrt{(2L+1)(2\ell_1+1)}(-1)^{m_2}\begin{pmatrix} \ell_1 & \ell_2 & L \\ m_1 & -m_2 & M \end{pmatrix}\begin{pmatrix} \ell_1 & \ell_2 & L \\ 0 & 0 & 0 \end{pmatrix} \\ &= \sqrt{\frac{4\pi}{2L+1}}\sqrt{(2\ell_1+1)(2\ell_2+1)}(-1)^{m_2}(-1)^{(M=m_2-m_1)}C_{\ell_10\,\ell_20}^{L0}\,C_{\ell_1m_1\ell_2\,-m_2}^{L\,-M} \\ &= \sqrt{\frac{4\pi}{2L+1}}\sqrt{(2\ell_1+1)(2\ell_2+1)}(-1)^{m_1}C_{\ell_10\,\ell_20}^{L0}\,C_{\ell_1m_1\ell_2\,-m_2}^{L\,-M}. \end{aligned}$$

Note that $(-1)^{m_1}Y_{\ell_1}^{m_1}(\hat{r}_1) = Y_{\ell_1}^{-m_1*}(\hat{r}_1)$. Furthermore,

$$\begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} = (-1)^{\ell_1+\ell_2+\ell_3}\begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \end{pmatrix}. \tag{A13}$$

Because the $3j$ symbol

$$\begin{pmatrix} \ell_1 & \ell_2 & L \\ 0 & 0 & 0 \end{pmatrix}$$

arises from integral of $\int_{-1}^{1} dx P_{\ell_1}(x)P_{\ell_2}(x)P_L(x)$ and given that $P_\ell(x) = (-1)^\ell P_\ell(-x)$, it will vanish if $\ell_1 + \ell_2 + L$ is odd.

That is, we may rewrite the expression as

$$\begin{aligned} k_L(\kappa R)Y_L^{M*}(\hat{R}) &= \sum_{\ell_1,m_1,\ell_2,m_2}\sqrt{\frac{4\pi}{2\ell_2+1}}\sqrt{(2L+1)(2\ell_1+1)}C_{LM\ell_1m_1}^{\ell_2 m_2}C_{L0\,\ell_10}^{\ell_2 0}(-1)^{\ell_1+\ell_2}\,i_{\ell_1}(\kappa r_1)Y_{\ell_1}^{m_1}(\hat{r}_1)\,k_{\ell_2}(\kappa r_2)Y_{\ell_2}^{m_2*}(\hat{r}_2) \\ &= \sum_{\ell_1,m_1,\ell_2,m_2}\sqrt{\frac{4\pi}{2L+1}}\sqrt{(2\ell_1+1)(2\ell_2+1)}(-1)^{m_1}C_{\ell_10\ell_20}^{L0}\,C_{\ell_1m_1\ell_2\,-m_2}^{L\,-M}(-1)^{\ell_1+\ell_2}\,i_{\ell_1}(\kappa r_1)Y_{\ell_1}^{m_1}(\hat{r}_1)\,k_{\ell_2}(\kappa r_2)Y_{\ell_2}^{m_2*}(\hat{r}_2) \\ &= \sum_{\ell_1,m_1,\ell_2,m_2}\sqrt{\frac{4\pi}{2L+1}}\sqrt{(2\ell_1+1)(2\ell_2+1)}C_{\ell_10\ell_20}^{L0}\,C_{\ell_1m_1\ell_2\,-m_2}^{L\,-M}(-1)^{\ell_1+\ell_2}\,i_{\ell_1}(\kappa r_1)Y_{\ell_1}^{-m_1*}(\hat{r}_1)\,k_{\ell_2}(\kappa r_2)Y_{\ell_2}^{m_2*}(\hat{r}_2). \end{aligned} \tag{A14}$$

Renaming m_1 by $-m_1'$ and later renaming $m_1' \to m_1$, we thus have

$$k_L(\kappa R)Y_L^{M*}(\hat{R}) = \sum_{\ell_1,m_1',\ell_2,m_2} \sqrt{\frac{4\pi}{2L+1}}\sqrt{(2\ell_1+1)(2\ell_2+1)}C^{L0}_{\ell_1 0\ell_2 0}\, C^{L\,-M}_{\ell_1\,-m_1'\ell_2\,-m_2}(-1)^{\ell_1+\ell_2}\, i_{\ell_1}(\kappa r_1)Y_{\ell_1}^{m_1'\,*}(\hat{r}_1)\, k_{\ell_2}(\kappa r_2)Y_{\ell_2}^{m_2*}(\hat{r}_2)$$

$$= \sum_{\ell_1,m_1',\ell_2,m_2} \sqrt{\frac{4\pi}{2L+1}}\sqrt{(2\ell_1+1)(2\ell_2+1)}C^{L0}_{\ell_1 0\ell_2 0}\,(-1)^{\ell_1+\ell_2+L}C^{LM}_{\ell_1 m_1'\ell_2 m_2}$$

$$\times (-1)^{\ell_1+\ell_2}\, i_{\ell_1}(\kappa r_1)Y_{\ell_1}^{m_1'\,*}(\hat{r}_1)\, k_{\ell_2}(\kappa r_2)Y_{\ell_2}^{m_2*}(\hat{r}_2). \tag{A15}$$

Because the factor $(-1)^{\ell_1+\ell_2+L} = 1$, by naming m_1' back to m_1, we have

$$k_L(\kappa R)Y_L^{M*}(\hat{R}) = \sum_{\ell_1,m_1,\ell_2,m_2} H^{LM}_{\ell_1 m_1\ell_2 m_2}(-1)^{\ell_1+\ell_2}\, i_{\ell_1}(\kappa r_1)Y_{\ell_1}^{m_1\,*}(\hat{r}_1)\, k_{\ell_2}(\kappa r_2)Y_{\ell_2}^{m_2*}(\hat{r}_2). \tag{A16}$$

Or by taking the complex conjugate on both sides, one has

$$k_L(\kappa R)Y_L^{M}(\hat{R}) = \sum_{\ell_1,m_1,\ell_2,m_2} H^{LM}_{\ell_1 m_1\ell_2 m_2}(-1)^{\ell_1+\ell_2}\, i_{\ell_1}(\kappa r_1)Y_{\ell_1}^{m_1}(\hat{r}_1)\, k_{\ell_2}(\kappa r_2)Y_{\ell_2}^{m_2}(\hat{r}_2). \tag{A17}$$

In our applications, it is possible that the expression (A11) can be more useful. Equation (A17) has been extensively verified numerically for all positive R values, including $R < r_1$.

APPENDIX B: ENERGY MINIMIZATION FORMULATION

Previously [9] we considered the problem of charges in a polarizable medium. We express the energy U as a functional of the polarization vector $\mathbf{P}$,

$$U[\mathbf{P}] = U_{\rm C}[\mathbf{P}] + W[\mathbf{P}], \tag{B1}$$

where $U_{\rm C}[\mathbf{P}]$ is the electrostatic energy of interaction of all charges present in the system, and $W[\mathbf{P}]$ is the energy required to create the given polarization vector field $\mathbf{P}(\boldsymbol{r})$.

It is well known that $\rho_{\rm ind}(\boldsymbol{r}) = -\nabla\cdot\mathbf{P}(\boldsymbol{r})$ is the induced charge density. Therefore, the total charge density $\rho_t(\boldsymbol{r})$ in the medium is the sum of the free charge density $\rho_f(\boldsymbol{r})$ and $\rho_{\rm ind}(\boldsymbol{r})$:

$$\rho_t(\boldsymbol{r}) = \rho_f(\boldsymbol{r}) + \rho_{\rm ind}(\boldsymbol{r}). \tag{B2}$$

We then have

$$U_{\rm C}[\mathbf{P}] = \frac{1}{2}\int [\rho_f(\boldsymbol{r}) - \nabla\cdot\mathbf{P}(\boldsymbol{r})]\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} \times [\rho_f(\boldsymbol{r}') - \nabla\cdot\mathbf{P}(\boldsymbol{r}')]d\boldsymbol{r}d\boldsymbol{r}' \tag{B3}$$

and employ the simple quadratic work functional

$$W[\mathbf{P}] = \frac{1}{2}\int \frac{\mathbf{P}\cdot\mathbf{P}}{\chi(\boldsymbol{r})}d\boldsymbol{r}. \tag{B4}$$

That is,

$$U[\mathbf{P}] = U_C[\mathbf{P}] + \frac{1}{2}\int \frac{\mathbf{P}(\boldsymbol{r})\cdot\mathbf{P}(\boldsymbol{r})}{\chi(\boldsymbol{r})}d\boldsymbol{r}. \tag{B5}$$

Performing a functional variation with respect to $\mathbf{P}$, we arrive at

$$\frac{\mathbf{P}(\boldsymbol{r})}{\chi(\boldsymbol{r})} + \nabla_r\int \frac{\rho_f(\boldsymbol{r}') - \nabla\cdot\mathbf{P}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}' = 0, \tag{B6}$$

which implies

$$\mathbf{P}(\boldsymbol{r}) = \chi(\boldsymbol{r})\int [\rho_f(\boldsymbol{r}') - \nabla\cdot\mathbf{P}(\boldsymbol{r}')]\frac{\boldsymbol{r}-\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|^3}d\boldsymbol{r}' = \chi(\boldsymbol{r})\mathbf{E}(\boldsymbol{r}). \tag{B7}$$

Thus the constitutive relation for a linear dielectric is obtained as a result of functional minimization, with the expansion coefficient $\chi(\boldsymbol{r})$ turning out to be the dielectric susceptibility. Inserting the equilibrium polarization (B7) in (B5) results in the well-known expression for the total energy of the system:

$$U = \frac{1}{2}\int \rho_f(\boldsymbol{r})\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}[\rho_f(\boldsymbol{r}') - \nabla\cdot\boldsymbol{P}(\boldsymbol{r}')]d\boldsymbol{r}d\boldsymbol{r}'. \tag{B8}$$

When we add mobile ions at the Debye-Hückel level, we also have a linear relation $\rho_{\rm ion} = -\kappa^2\Phi/4\pi$. This prompts us to use the following simple energy functional:

$$U[\mathbf{P}, \rho_{\rm ion}] = U_{\rm C}[\mathbf{P}, \rho_{\rm ion}] + W[\mathbf{P}] + W'[\rho_{\rm ion}], \tag{B9}$$

with

$$U_{\rm C}[\mathbf{P}, \rho_{\rm ion}] = \frac{1}{2}\int [\rho_f(\boldsymbol{r}) - \nabla\cdot\mathbf{P}(\boldsymbol{r}) + \rho_{\rm ion}(\boldsymbol{r})]\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} \times [\rho_f(\boldsymbol{r}') - \nabla\cdot\mathbf{P}(\boldsymbol{r}') + \rho_{\rm ion}(\boldsymbol{r}')]d\boldsymbol{r}d\boldsymbol{r}' \tag{B10}$$

and

$$W'[\rho_{\rm ion}] = \frac{4\pi}{2}\int \frac{\rho_{\rm ion}(\boldsymbol{r})\cdot\rho_{\rm ion}(\boldsymbol{r})}{\kappa^2(\boldsymbol{r})}d\boldsymbol{r}. \tag{B11}$$

Performing functional variations with respect to $\rho_{\rm ion}$ and $\mathbf{P}$, we arrive at

$$\rho_{\rm ion}(\boldsymbol{r}) = -\frac{\kappa^2(\boldsymbol{r})}{4\pi}\int \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}[\rho_f(\boldsymbol{r}') - \nabla\cdot\mathbf{P}(\boldsymbol{r}') + \rho_{\rm ion}(\boldsymbol{r}')]d\boldsymbol{r}'$$

$$= -\frac{\kappa^2(\boldsymbol{r})}{4\pi}\Phi(\boldsymbol{r}) \tag{B12}$$

and

$$\frac{\mathbf{P}(\boldsymbol{r})}{\chi(\boldsymbol{r})} + \nabla_r\int \frac{\rho_f(\boldsymbol{r}') - \nabla\cdot\mathbf{P}(\boldsymbol{r}') + \rho_{\rm ion}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}d\boldsymbol{r}' = 0, \tag{B13}$$

implying

$$\mathbf{P}(\boldsymbol{r}) = \chi(\boldsymbol{r}) \int [\rho_f(\boldsymbol{r}') - \nabla \cdot \mathbf{P}(\boldsymbol{r}') + \rho_{\text{ion}}(\boldsymbol{r}')] \frac{\boldsymbol{r}-\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|^3} d\boldsymbol{r}' = \chi(\boldsymbol{r})\mathbf{E}(\boldsymbol{r}). \tag{B14}$$

Equations (B12) and (B14) form two coupled integro-differential equations with $\rho_f(\boldsymbol{r})$ as the source. Thus the constitutive relation for a linear dielectric medium inside a linear electrolytic solution is obtained as a result of functional minimization, with the expansion coefficients $\chi(\boldsymbol{r})$ and $\kappa(\boldsymbol{r})$ turning out to be respectively the dielectric susceptibility and the inverse Debye length. Inserting the equilibrium ion charge density (B12) and polarization (B14) in (B9) result in the well-known expression for the total energy of the system:

$$U = \frac{1}{2}\int \rho_f(\boldsymbol{r}) \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}[\rho_f(\boldsymbol{r}') - \nabla \cdot \boldsymbol{P}(\boldsymbol{r}') + \rho_{\text{ion}}(\boldsymbol{r}')] d\boldsymbol{r}' d\boldsymbol{r} = \frac{1}{2}\int \rho_f(\boldsymbol{r})\, \Phi(\boldsymbol{r})\, d\boldsymbol{r}. \tag{B15}$$

To provide a flavor of how equations (B12) and (B14) are used simultaneously, let us first rewrite (B14) into

$$\begin{aligned}
\rho_{\text{ind}}(\boldsymbol{r}) = -\nabla \cdot \mathbf{P}(\boldsymbol{r}) &= -\nabla\chi(\boldsymbol{r}) \cdot \int [\rho_f(\boldsymbol{r}') - \nabla \cdot \mathbf{P}(\boldsymbol{r}') + \rho_{\text{ion}}(\boldsymbol{r}')] \frac{\boldsymbol{r}-\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|^3} d\boldsymbol{r}' \\
&\quad - \chi(\boldsymbol{r}) \int [\rho_f(\boldsymbol{r}') - \nabla \cdot \mathbf{P}(\boldsymbol{r}') + \rho_{\text{ion}}(\boldsymbol{r}')] \nabla_{\boldsymbol{r}} \cdot \left(\frac{\boldsymbol{r}-\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|^3} \right) d\boldsymbol{r}' \\
&= -\nabla\chi(\boldsymbol{r}) \cdot \mathbf{E}(\boldsymbol{r}) - \chi(\boldsymbol{r}) \int [\rho_f(\boldsymbol{r}') - \nabla \cdot \mathbf{P}(\boldsymbol{r}') + \rho_{\text{ion}}(\boldsymbol{r}')][4\pi\delta(\boldsymbol{r}-\boldsymbol{r}')] d\boldsymbol{r}' \\
&= -\nabla\chi(\boldsymbol{r}) \cdot \mathbf{E}(\boldsymbol{r}) - 4\pi\chi(\boldsymbol{r})[\rho_f(\boldsymbol{r}) + \rho_{\text{ind}}(\boldsymbol{r}) + \rho_{\text{ion}}(\boldsymbol{r})],
\end{aligned} \tag{B16}$$

leading to [with $\epsilon(\boldsymbol{r}) = 1 + 4\pi\chi(\boldsymbol{r})$ and defining $\rho_n(\boldsymbol{r}) = \rho_t(\boldsymbol{r}) + \rho_{\text{ion}}(\boldsymbol{r})$]

$$\epsilon(\boldsymbol{r})[\rho_t(\boldsymbol{r}) + \rho_{\text{ion}}(\boldsymbol{r})] = \rho_f(\boldsymbol{r}) + \rho_{\text{ion}}(\boldsymbol{r}) - \nabla\chi(\boldsymbol{r}) \cdot \int \frac{\boldsymbol{r}-\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|^3} [\rho_t(\boldsymbol{r}') + \rho_{\text{ion}}(\boldsymbol{r}')] d\boldsymbol{r}', \tag{B17}$$

and we rewrite Eq. (B12) as

$$\rho_{\text{ion}}(\boldsymbol{r}) = -\frac{\kappa^2(\boldsymbol{r})}{4\pi} \int \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} [\rho_t(\boldsymbol{r}') + \rho_{\text{ion}}(\boldsymbol{r}')] d\boldsymbol{r}'. \tag{B18}$$

Plugging Eq. (B18) into Eq. (B17), one obtains

$$\rho_n(\boldsymbol{r}) = \frac{\rho_f(\boldsymbol{r})}{\epsilon(\boldsymbol{r})} - \int C(\boldsymbol{r}, \boldsymbol{r}') d\boldsymbol{r}' \rho_n(\boldsymbol{r}'), \tag{B19}$$

$$C(\boldsymbol{r}, \boldsymbol{r}') = \frac{\kappa^2(\boldsymbol{r})}{4\pi\epsilon(\boldsymbol{r})|\boldsymbol{r}-\boldsymbol{r}'|} + \frac{\nabla\chi(\boldsymbol{r})}{\epsilon(\boldsymbol{r})} \cdot \frac{\boldsymbol{r}-\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|^3}. \tag{B20}$$

Equations (B18), (B19), and (B20) form the foundation for approximate solutions via iteration. This aspect is beyond the scope of the current paper and will be discussed in detail in a separate publication.

APPENDIX C: BOUNDARY CONDITIONS WITH MOBILE IONS PRESENT

In method I-in, the multipoles $q_{lm} \equiv \overline{Q}_{lm} a^l / \sqrt{4\pi}$ are inside the sphere and Eq. (13) yields the potential in the region close to (but inside) the spherical surface:

$$\Phi_\rho^{\text{I-in}}(r < a) = \sum_{l,m} \frac{\sqrt{4\pi}}{2l+1} \frac{a^l}{r^{l+1}} Y_l^m(\hat{r}) \frac{\overline{Q}_{lm}}{\epsilon}. \tag{C1}$$

In method II-on, we have $\overline{Q}_{lm}$ on the surface of the sphere ($r = a$) and the resulting potential at $r < a$ is

$$\int \frac{\sigma_f(\hat{s})}{|a\hat{s}-\boldsymbol{r}|} dS = \sum_{l,m} \frac{4\pi a^2}{2l+1} \frac{r^l}{a^{l+1}} Y_l^m(\hat{r}) \int \sigma_f(\hat{s}) Y_l^{m*}(\hat{s})\, d\Omega = \sum_{l,m} \frac{\sqrt{4\pi}}{2l+1} \frac{r^l}{a^{l+1}} Y_l^m(\hat{r})\, \overline{Q}_{lm},$$

where

$$\sigma_f(\hat{s}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sqrt{4\pi}\, \sigma_{flm} Y_l^m(\hat{s}) \quad \text{and} \quad \overline{Q}_{lm} = 4\pi a^2 \sigma_{flm}. \tag{C2}$$

Hence

$$\Phi_\rho^{\text{II-on}}(r < a) = \sum_{l,m} \frac{\sqrt{4\pi}}{2l+1} \frac{r^l}{a^{l+1}} Y_l^m(\hat{r}) \overline{Q}_{lm}. \tag{C3}$$

Similarly, for $a < r < b$, we have

$$\Phi_\rho^{\text{I-in}}(a < r < b) = \sum_{l,m} \frac{\sqrt{4\pi}}{2l+1} \frac{a^l}{r^{l+1}} Y_l^m(\hat{r}) \frac{\overline{Q}_{lm}}{\epsilon}. \tag{C4}$$

In method II-on, we have $\overline{Q}_{lm}$ on the surface of the sphere ($r = a$) and hence

$$\Phi_\rho^{\text{II-on}}(a < r < b) = \sum_{l,m} \frac{\sqrt{4\pi}}{2l+1} \frac{a^l}{r^{l+1}} Y_l^m(\hat{r}) \overline{Q}_{lm}. \tag{C5}$$

To continue the proof that methods I-in and II-on remain equivalent in the presence of mobile ions, we note that another source of the potential comes from the *induced* surface charge density $\sigma^<(\theta, \phi)$ [$\sigma^>(\theta, \phi)$] on the dielectric interface $r = a$ ($r = b$). As in [8], we write

$$\sigma^{<(>)}(\theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sqrt{4\pi}\, \sigma_{lm}^{<(>)} Y_l^m(\theta, \phi)$$

and define the induced surface charge strengths

$$Q_{lm}^< = 4\pi a^2 \sigma_{lm}^<, \quad Q_{lm}^> = 4\pi b^2 \sigma_{lm}^>.$$

This surface charge distribution produces a different potential when $r < a$ and when $r > a$:

$$\Phi_{\rm s}(\boldsymbol{r}) = \int \frac{\sigma^{<}(\hat{\boldsymbol{s}})}{|\boldsymbol{r} - a\hat{\boldsymbol{s}}|} dS^{<} + \int \frac{\sigma^{>}(\hat{\boldsymbol{s}})}{|\boldsymbol{r} - b\hat{\boldsymbol{s}}|} dS^{>} = \sum_{l,m} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) \begin{cases} \frac{a^l}{r^{l+1}} Q_{lm}^{<} + \frac{r^l}{b^{l+1}} Q_{lm}^{>}, & a < r < b, \\ \frac{r^l}{a^{l+1}} Q_{lm}^{<} + \frac{r^l}{b^{l+1}} Q_{lm}^{>}, & r < a. \end{cases} \tag{C6}$$

We introduce for later convenience the effective induced surface charge strengths

$$Q_{lm} = Q_{lm}^{<} + Q_{lm}^{>} \left(\frac{a}{b}\right)^{l+1}. \tag{C7}$$

Let us emphasize that the net surface charge strengths $\breve{Q}_{lm}$ equal $Q_{lm} + \frac{\overline{Q}_{lm}}{\epsilon}$ for method I-in and equal $Q_{lm} + \overline{Q}_{lm}$ for method II-on.

Note that the net potential arises from $\Phi_{\rm s} + \Phi_\rho$. That is, for method I-in (II-on), we will write $\Phi^{\rm I-in(II-on)}(\boldsymbol{r}) = \Phi_{\rm s}(\boldsymbol{r}) + \Phi_\rho^{\rm I-in(II-on)}(\boldsymbol{r})$. Therefore, using Eq. (C6), we have

$$\begin{aligned} \Phi^{\rm I-in}(r < a) &= \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) \left[\left(Q_{lm}^{<} + Q_{lm}^{>} \left(\frac{a}{b}\right)^{l+1} \right) \frac{r^l}{a^{l+1}} + \frac{\overline{Q}_{lm}}{\epsilon} \frac{a^l}{r^{l+1}} \right] \\ &= \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) \left[Q_{lm} \frac{r^l}{a^{l+1}} + \frac{\overline{Q}_{lm}}{\epsilon} \frac{a^l}{r^{l+1}} \right], \end{aligned} \tag{C8}$$

$$\begin{aligned} \Phi^{\rm II-on}(r < a) &= \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) \left[Q_{lm}^{<} + Q_{lm}^{>} \left(\frac{a}{b}\right)^{l+1} + \overline{Q}_{lm} \right] \frac{r^l}{a^{l+1}} \\ &= \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) [Q_{lm} + \overline{Q}_{lm}] \frac{r^l}{a^{l+1}} = \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) \breve{Q}_{lm} \frac{r^l}{a^{l+1}}, \end{aligned} \tag{C9}$$

$$\begin{aligned} \Phi^{\rm I-in}(a < r < b) &= \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) \left[\frac{a^l}{r^{l+1}} \left(Q_{lm}^{<} + \frac{\overline{Q}_{lm}}{\epsilon} \right) + \frac{r^l}{b^{l+1}} Q_{lm}^{>} \right] \\ &= \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) \left[\frac{a^l}{r^{l+1}} \left(Q_{lm} + \frac{\overline{Q}_{lm}}{\epsilon} \right) + \left(r^l - \frac{a^{2l+1}}{r^{l+1}} \right) \frac{Q_{lm}^{>}}{b^{l+1}} \right] \\ &= \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) \left[\frac{a^l}{r^{l+1}} \breve{Q}_{lm} + \left(r^l - \frac{a^{2l+1}}{r^{l+1}} \right) \frac{Q_{lm}^{>}}{b^{l+1}} \right], \end{aligned} \tag{C10}$$

$$\begin{aligned} \Phi^{\rm II-on}(a < r < b) &= \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) \left[\frac{a^l}{r^{l+1}} (Q_{lm}^{<} + \overline{Q}_{lm}) + \frac{r^l}{b^{l+1}} Q_{lm}^{>} \right] \\ &= \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) \left[\frac{a^l}{r^{l+1}} (Q_{lm} + \overline{Q}_{lm}) + \left(r^l - \frac{a^{2l+1}}{r^{l+1}} \right) \frac{Q_{lm}^{>}}{b^{l+1}} \right] \\ &= \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) \left[\frac{a^l}{r^{l+1}} \breve{Q}_{lm} + \left(r^l - \frac{a^{2l+1}}{r^{l+1}} \right) \frac{Q_{lm}^{>}}{b^{l+1}} \right]. \end{aligned} \tag{C11}$$

Evidently, for both methods, the potential is continuous across $r = a$, with

$$\Phi(r = a) = \sum_{lm} \frac{\sqrt{4\pi}}{2l+1} Y_l^m(\hat{r}) \frac{\breve{Q}_{lm}}{a}.$$

We next note the second boundary condition for method I-in and II-on at $r = a$:

$$\epsilon' \frac{\partial \Phi^{\rm I-in}}{\partial r}\bigg|_{r=a^+} = \epsilon \frac{\partial \Phi^{\rm I-in}}{\partial r}\bigg|_{r=a^-}, \quad \epsilon' \frac{\partial \Phi^{\rm II-on}}{\partial r}\bigg|_{r=a^+} = \epsilon \frac{\partial \Phi^{\rm II-on}}{\partial r}\bigg|_{r=a^-} - 4\pi\sigma_f^{<} = \epsilon \frac{\partial \Phi^{\rm II-on}}{\partial r}\bigg|_{r=a^-} - \frac{\sqrt{4\pi}}{a^2} \sum_{lm} \overline{Q}_{lm} Y_l^m(\hat{r}).$$

Note that the expressions for $\Phi^{\mathrm{I-in}}(r>a)$ and $\Phi^{\mathrm{II-on}}(r>a)$ are identical provided that the $\breve{Q}_{lm}$ are the same in both expressions. Therefore, if we hold $\breve{Q}_{lm}$ the same in both methods, and if one can show

$$\epsilon\frac{\partial\Phi^{\mathrm{I-in}}}{\partial r}\bigg|_{r=a^-}=\epsilon\frac{\partial\Phi^{\mathrm{II-on}}}{\partial r}\bigg|_{r=a^-}-\frac{\sqrt{4\pi}}{a^2}\sum_{lm}\overline{Q}_{lm}\,Y_l^m(\hat{r})=\epsilon\sum_{lm}\frac{\sqrt{4\pi}\,l}{2l+1}Y_l^m(\hat{r})\frac{\breve{Q}_{lm}}{a^2}-\sqrt{4\pi}\sum_{lm}\frac{\overline{Q}_{lm}}{a^2}\,Y_l^m(\hat{r}),$$

then we have shown the equivalence of the two methods. We work on the left-hand side of this equation using (C8) and by adding and subtracting the same term, $\epsilon\sum_{lm}\frac{\sqrt{4\pi}}{2l+1}\frac{\overline{Q}_{lm}}{\epsilon}\frac{l}{a^2}Y_l^m(\hat{r})=\sum_{lm}\frac{\sqrt{4\pi}}{2l+1}\overline{Q}_{lm}\frac{l}{a^2}Y_l^m(\hat{r})$:

$$\begin{aligned}
\epsilon\frac{\partial\Phi^{\mathrm{I-in}}}{\partial r}\bigg|_{r=a^-}&=\epsilon\sum_{lm}\frac{\sqrt{4\pi}}{2l+1}Q_{lm}\frac{l}{a^2}Y_l^m(\hat{r})-\sum_{lm}\frac{\sqrt{4\pi}}{2l+1}\overline{Q}_{lm}\frac{l+1}{a^2}Y_l^m(\hat{r})\\
&=\epsilon\sum_{lm}\frac{\sqrt{4\pi}}{2l+1}Q_{lm}\frac{l}{a^2}Y_l^m(\hat{r})-\sum_{lm}\frac{\sqrt{4\pi}}{2l+1}\overline{Q}_{lm}\frac{l+1}{a^2}Y_l^m(\hat{r})\\
&\quad+\epsilon\sum_{lm}\frac{\sqrt{4\pi}}{2l+1}\frac{\overline{Q}_{lm}}{\epsilon}\frac{l}{a^2}Y_l^m(\hat{r})-\sum_{lm}\frac{\sqrt{4\pi}}{2l+1}\overline{Q}_{lm}\frac{l}{a^2}Y_l^m(\hat{r})\\
&=\epsilon\sum_{lm}\frac{\sqrt{4\pi}}{2l+1}\left[Q_{lm}+\frac{\overline{Q}_{lm}}{\epsilon}\right]\frac{l}{a^2}Y_l^m(\hat{r})-\sum_{lm}\frac{\sqrt{4\pi}}{2l+1}\overline{Q}_{lm}\frac{2l+1}{a^2}Y_l^m(\hat{r})\\
&=\epsilon\sum_{lm}\frac{\sqrt{4\pi}\,l}{2l+1}Y_l^m(\hat{r})\frac{\breve{Q}_{lm}}{a^2}-\sqrt{4\pi}\sum_{lm}\frac{\overline{Q}_{lm}}{a^2}\,Y_l^m(\hat{r}).
\end{aligned}\tag{C12}$$

In the region ($r>a+\delta=b$) where mobile ions are present, the potential satisfies the modified Helmholtz equation and is supposed to decay as $r\to\infty$. Hence the general solution should be

$$\Phi^{\mathrm{out}}(r>b)=\sum_{l,m}D_{lm}\,k_l(\kappa r)\,Y_l^m(\hat{r}).\tag{C13}$$

On the boundary $r=b$, continuity of the potential demands that

$$D_{lm}\,k_l(\kappa b)=\frac{\sqrt{4\pi}}{2l+1}\left[\frac{a^l}{b^{l+1}}\breve{Q}_{lm}+\frac{1}{b}\left(1-\frac{a^{2l+1}}{b^{2l+1}}\right)Q_{lm}^{>}\right]$$

or

$$D_{lm}\;=\;\frac{1}{k_l(\kappa b)}\,\frac{\sqrt{4\pi}}{2l+1}\left[\frac{a^l}{b^{l+1}}\breve{Q}_{lm}+\frac{1}{b}\left(1-\frac{a^{2l+1}}{b^{2l+1}}\right)Q_{lm}^{>}\right].\tag{C14}$$

Because we do not have any free charge density on the surface $r=b$, the second boundary condition takes the form

$$\epsilon_o\frac{\partial\Phi^{\mathrm{out}}}{\partial r}\bigg|_{r=b^+}=\epsilon'\,\frac{\partial\Phi^{\mathrm{I-in(II-on)}}}{\partial r}\bigg|_{r=b^-}.$$

We next calculate

$$\begin{aligned}
&\frac{\partial\Phi^{\mathrm{I-in(II-on)}}}{\partial r}\bigg|_{r=b^-}-\frac{\partial\Phi^{\mathrm{I-in(II-on)}}}{\partial r}\bigg|_{r=a^+}\\
&=\sum_{lm}\frac{\sqrt{4\pi}}{2l+1}Y_l^m(\hat{r})\left\{(l+1)\left(\frac{1}{a^2}-\frac{a^l}{b^{l+2}}\right)\breve{Q}_{lm}+\left[l(b^{l-1}-a^{l-1})+(l+1)\left(\frac{a^{2l+1}}{b^{l+2}}-a^{l-1}\right)\right]\frac{Q_{lm}^{>}}{b^{l+1}}\right\}
\end{aligned}$$

and find it approaching zero upon taking the limit $\delta\to 0$ (or $b\to a$). Thus, under this limit we have

$$\epsilon_o\frac{\partial\Phi^{\mathrm{out}}}{\partial r}\bigg|_{r=b^+}=\epsilon'\,\frac{\partial\Phi^{\mathrm{I-in(II-on)}}}{\partial r}\bigg|_{r=b^-}\to\begin{cases}\epsilon'\,\frac{\partial\Phi^{\mathrm{I-in}}}{\partial r}\big|_{r=a^+}=\epsilon\,\frac{\partial\Phi^{\mathrm{I-in}}}{\partial r}\big|_{r=a^-},\\ \epsilon'\,\frac{\partial\Phi^{\mathrm{II-on}}}{\partial r}\big|_{r=a^+}=\epsilon\,\frac{\partial\Phi^{\mathrm{II-on}}}{\partial r}\big|_{r=a^-}-4\pi\sigma_f.\end{cases}$$

That is, if we view the q_{lm} as inside the sphere, method I-in, we have the ($\delta\to 0$ limit) boundary condition

$$\epsilon_o\frac{\partial\Phi^{\mathrm{out}}}{\partial r}\bigg|_{r=a^+}=\epsilon\,\frac{\partial\Phi^{\mathrm{I-in}}}{\partial r}\bigg|_{r=a^-},\tag{C15}$$

while if we place $\overline{Q}_{lm}$ on the sphere surface, method II-on, we have the ($\delta \to 0$ limit) boundary condition

$$\epsilon_o \frac{\partial \Phi^{\rm out}}{\partial r}\bigg|_{r=a^+} = \epsilon \frac{\partial \Phi^{\rm II-on}}{\partial r}\bigg|_{r=a^-} - 4\pi\sigma_f. \tag{C16}$$

Under this $\delta \to 0$ limit, the induced surface charge strengths $Q^<_{lm}$ and $Q^>_{lm}$ coalesce into $Q_{lm} = Q^<_{lm} + Q^>_{lm}$. That is, one may forget about the middle layer $a < r < b$ dielectric altogether.

APPENDIX D: SUBSTITUTION RULE AND RECIPROCITY

To examine whether the substitution rule (27) is all we need, we check reciprocity in electrostatics: Interaction energy $V^{(1)}_{\rm int}$ is the work done to bring to $\boldsymbol{r}_0$ charge multipoles $q'_{l'm'}$ when multipoles q_{lm} were already placed either inside or exactly on the surface of the sphere; interaction energy $V^{(2)}_{\rm int}$ is the work done to bring the multipoles q_{lm} to the inside or the surface of the sphere when $q'_{l'm'}$ were already placed at $\boldsymbol{r}_0$. Reciprocity demands that $V^{(1)}_{\rm int} = V^{(2)}_{\rm int}$.

We have solved the former case exactly by beginning with the *free* multipoles inside the sphere and matching the boundary conditions. We found via Eqs. (18) and (21)

$$\begin{aligned}
\Phi^{\rm out}(\boldsymbol{r}) &= \sum_{l,m} \frac{\sqrt{4\pi}}{2l+1} \frac{k_l(\kappa r)}{k_l(\kappa a)} \frac{\breve{Q}_{lm}}{a} Y^m_l(\hat{r}) = \sum_{l,m} \frac{\sqrt{4\pi}}{2l+1} \frac{k_l(\kappa r)}{k_l(\kappa a)} \frac{(2l+1)\sqrt{4\pi}}{\epsilon l - \epsilon_o(\kappa a)\frac{k'_l(\kappa a)}{k_l(\kappa a)}} \frac{q_{lm}}{a^{l+1}} Y^m_l(\hat{r}) \\
&= \sum_{l,m} \frac{k_l(\kappa r)}{k_l(\kappa a)} \frac{4\pi Y^m_l(\hat{r})\, q_{lm}/a^{l+1}}{\epsilon l - \epsilon_o(\kappa a)\frac{k'_l(\kappa a)}{k_l(\kappa a)}} = \sum_{l,m} \frac{k_l(\kappa r)}{k_l(\kappa a)} \frac{4\pi\, k_l(\kappa a)}{\epsilon l\, k_l(\kappa a) - \epsilon_o(\kappa a) k'_l(\kappa a)} Y^m_l(\hat{r})\, \frac{q_{lm}}{a^{l+1}} \\
&\equiv \sum_{l,m} A_{lm}\, q_{lm}\, k_l(\kappa r)\, Y^m_l(\hat{r}),
\end{aligned}$$

meaning

$$A_{lm} = \frac{4\pi/a^{l+1}}{\epsilon l\, k_l(\kappa a) - \epsilon_o(\kappa a) k'_l(\kappa a)}.$$

Given that the point multipoles $q'_{l'm'}$ are at $\boldsymbol{r}_0$, one may imagine these multipoles resulted from a charge distribution within an infinitesimal radius s around $\boldsymbol{r}_0$. This suggests that, with $s < \eta$ and $\eta \to 0$, the first form of the interaction energy between the two charge distributions should be computed by

$$V^{(1)}_{\rm int} = \sum_{lm} A_{lm}\, q_{lm} \int d\boldsymbol{s}\, \rho'(\boldsymbol{r}_0 + \boldsymbol{s})\, k_l(\kappa|\boldsymbol{r}_0 + \boldsymbol{s}|)\, Y^m_l\!\left(\frac{\boldsymbol{r}_0 + \boldsymbol{s}}{|\boldsymbol{r}_0 + \boldsymbol{s}|}\right).$$

By using (2) [with $\boldsymbol{s} \to \boldsymbol{r}_1$ and $\boldsymbol{r}_0 \to -\boldsymbol{r}_2$ in mind],

$$\begin{aligned}
k_l(\kappa|\boldsymbol{r}_0 + \boldsymbol{s}|) Y^m_l\!\left(\frac{\boldsymbol{r}_0 + \boldsymbol{s}}{|\boldsymbol{r}_0 + \boldsymbol{s}|}\right) &= \sum_{\ell_1,\ell_2,m_1,m_2} (-1)^{\ell_2} H^{lm}_{\ell_1 m_1 \ell_2 m_2} (-1)^{\ell_1+\ell_2} i_{\ell_1}(\kappa s) Y^{m_1}_{\ell_1}(\hat{s})\, k_{\ell_2}(\kappa r_0) Y^{m_2}_{\ell_2}(\hat{r}_0) \\
&\equiv \sum_{\ell_1,\ell_2,m_1,m_2} (-1)^{\ell_1} H^{lm}_{\ell_1 m_1 \ell_2 m_2}\, i_{\ell_1}(\kappa s) Y^{m_1}_{\ell_1}(\hat{s})\, k_{\ell_2}(\kappa r_0) Y^{m_2}_{\ell_2}(\hat{r}_0),
\end{aligned} \tag{D1}$$

and since as $s < \eta \to 0$, $i_{\ell_1}(\kappa s) \to (\kappa s)^{\ell_1}/(2\ell_1+1)!!$, one obtains the *correct* interaction energy

$$\begin{aligned}
V^{(1)}_{\rm int} &= \sum_{l,m,\ell_1,m_1} \sum_{\ell_2,m_2} A_{lm} q_{lm} (-1)^{\ell_1} H^{lm}_{\ell_1 m_1 \ell_2 m_2} \frac{\kappa^{\ell_1} q'^*_{\ell_1,m_1}}{(2\ell_1+1)!!} k_{\ell_2}(\kappa r) Y^{m_2}_{\ell_2}(\hat{r}) \\
&\equiv \sum_{l,l',m,m'} q_{lm} q'^*_{l'm'} G_{l,l',m,m'} = \sum_{l,l',m,m'} q^*_{lm} q'_{l'm'} G^*_{l,l',m,m'},
\end{aligned} \tag{D2}$$

meaning

$$G_{l,l',m,m'} = A_{lm} \frac{(-1)^{l'}\kappa^{l'}}{(2l'+1)!!} \sum_{\ell_2 m_2} H^{lm}_{l'm'\ell_2 m_2} k_{\ell_2}(\kappa r) Y^{m_2}_{\ell_2}(\hat{r}) = \frac{4\pi(-1)^{l'}\kappa^{l'}/[a^{l+1}(2l'+1)!!]}{\epsilon l\, k_l(\kappa a) - \epsilon_o(\kappa a) k'_l(\kappa a)} \sum_{\ell_2 m_2} H^{lm}_{l'm'\ell_2 m_2} k_{\ell_2}(\kappa r) Y^{m_2}_{\ell_2}(\hat{r})$$

and

$$G^*_{l,l',m,m'} = \frac{4\pi(-1)^{l'}\kappa^{l'}/[a^{l+1}(2l'+1)!!]}{\epsilon l\, k_l(\kappa a) - \epsilon_o(\kappa a) k'_l(\kappa a)} \sum_{\ell_2 m_2} H^{lm}_{l'm'\ell_2 m_2} k_{\ell_2}(\kappa r) Y^{m_2 *}_{\ell_2}(\hat{r}).$$

To obtain the second form of the interaction energy, let us place a tight charge distribution yielding multipoles $q'_{l'm'}$ at $\boldsymbol{r}_0$ outside the sphere and calculate the potential everywhere in the region $r < r_0$, including $r < a$. One writes the potential contribution from multipoles around $\boldsymbol{r}_0$ near the spherical surface but with $r \geqslant a$ as

$$\begin{aligned}\Phi_{\rho'}(\boldsymbol{r}, r \geqslant a) &= \int d\boldsymbol{s}\, \rho'(\boldsymbol{r}_0+\boldsymbol{s})\, \frac{e^{-\kappa|\boldsymbol{r}_0+\boldsymbol{s}-\boldsymbol{r}|}}{\epsilon_o\,|\boldsymbol{r}_0+\boldsymbol{s}-\boldsymbol{r}|} \\ &= \frac{4\pi\kappa}{\epsilon_o}\sum_{l'm'}(-1)^{l'}k_{l'}(\kappa|\boldsymbol{r}_0-\boldsymbol{r}|)Y_{l'}^{m'}\left(\frac{\boldsymbol{r}_0-\boldsymbol{r}}{|\boldsymbol{r}_0-\boldsymbol{r}|}\right)\int d\boldsymbol{s}\,\rho'(\boldsymbol{r}_0+\boldsymbol{s})Y_{l''}^{m'*}(\hat{s})i_{l'}(\kappa s) \\ &= \frac{4\pi\kappa}{\epsilon_o}\sum_{l'm'}(-1)^{l'}k_{l'}(\kappa|\boldsymbol{r}_0-\boldsymbol{r}|)Y_{l'}^{m'}\left(\frac{\boldsymbol{r}_0-\boldsymbol{r}}{|\boldsymbol{r}_0-\boldsymbol{r}|}\right)\frac{\kappa^{l'}q'_{l'm'}}{(2l'+1)!!} \\ &= \sum_{\ell_1,m_1} i_{\ell_1}(\kappa r)Y_{\ell_1}^{m_1}(\hat{r})\frac{4\pi\kappa}{\epsilon_o}\sum_{l'm'}(-1)^{l'}\frac{\kappa^{l'}q'_{l'm'}}{(2l'+1)!!}\sum_{\ell_2,m_2}H_{\ell_1m_1\ell_2m_2}^{l'm'}k_{\ell_2}(\kappa r_0)Y_{\ell_2}^{m_2}(\hat{r}_0),\end{aligned}$$

where in the last line we have used the identity (2) (with $\boldsymbol{r}_1 \to -\boldsymbol{r}$ and $\boldsymbol{r}_2 \to -\boldsymbol{r}_0$),

$$\begin{aligned}k_{l'}(\kappa|\boldsymbol{r}_0-\boldsymbol{r}|)Y_{l'}^{m'}\left(\frac{\boldsymbol{r}_0-\boldsymbol{r}}{|\boldsymbol{r}_0-\boldsymbol{r}|}\right) &= \sum_{\ell_1,\ell_2,m_1,m_2}(-1)^{\ell_1+\ell_2}\,H_{\ell_1m_1\ell_2m_2}^{l'm'}\,i_{\ell_1}(\kappa r)Y_{\ell_1}^{m_1}(-\hat{r})\,k_{\ell_2}(\kappa r_0)Y_{\ell_2}^{m_2}(-\hat{r}_0) \\ &= \sum_{\ell_1,\ell_2,m_1,m_2}H_{\ell_1m_1\ell_2m_2}^{l'm'}\,i_{\ell_1}(\kappa r)Y_{\ell_1}^{m_1}(\hat{r})\,k_{\ell_2}(\kappa r_0)Y_{\ell_2}^{m_2}(\hat{r}_0).\end{aligned}$$

The potential $\Phi_{\rho'}(\boldsymbol{r})$ must remain continuous across $r = a$ into $r < a$. Inside the sphere, because the potential produced by $q'_{l'm'}$ must satisfy the Laplace equation rather than the modified Helmholtz equation, its general solution is of the form

$$\Phi_{\rho'}(\boldsymbol{r}, r \leqslant a) = \sum_{lm} B_{lm}\frac{r^l}{a^{l+1}}Y_l^m(\hat{r}).$$

Hence by demanding continuity of the potential produced by q'_{lm} at $r = a$, we have

$$\frac{B_{lm}}{a} = \frac{4\pi\kappa}{\epsilon_o}i_l(\kappa a)\sum_{l'm'\ell_2m_2}(-1)^{l'}\frac{\kappa^{l'}q'_{l'm'}}{(2l'+1)!!}H_{lm\ell_2m_2}^{l'm'}\,k_{\ell_2}(\kappa r_0)Y_{\ell_2}^{m_2}(\hat{r}_0) \tag{D3}$$

and

$$\Phi_{\rho'}(\boldsymbol{r}, r < a) = \sum_{lm}\frac{4\pi(\kappa a)}{\epsilon_o}i_l(\kappa a)\frac{r^l}{a^{l+1}}Y_l^m(\hat{r})\left[\sum_{l'm'\ell_2m_2}(-1)^{l'}\frac{\kappa^{l'}q'_{l'm'}}{(2l'+1)!!}H_{lm\ell_2m_2}^{l'm'}\,k_{\ell_2}(\kappa r_0)Y_{\ell_2}^{m_2}(\hat{r}_0)\right].$$

Now let us denote by Q_{lm} the induced surface charge strengths on the sphere due to charge distribution around $\boldsymbol{r}_0$. This induced surface charge will produce a potential of different forms for outside and inside the sphere:

$$\Phi_{\rm ind}(r \geqslant a) = \sum_{lm}\frac{\sqrt{4\pi}}{2l+1}\frac{k_l(\kappa r)}{k_l(\kappa a)}\frac{Q_{lm}}{a}Y_l^m(\hat{r}), \quad \Phi_{\rm ind}(r \leqslant a) = \sum_{lm}\frac{\sqrt{4\pi}}{2l+1}\frac{r^l}{a^{l+1}}Q_{lm}Y_l^m(\hat{r}). \tag{D4}$$

One may then solve for Q_{lm} by imposing the following boundary condition (since there is no free charge on the sphere surface):

$$\epsilon_o\frac{\partial}{\partial r}[\Phi_{\rho'}(r>a)+\Phi_{\rm ind}(r>a)]|_{r\to a} = \epsilon\frac{\partial}{\partial r}[\Phi_{\rho'}(r<a)+\Phi_{\rm ind}(r<a)]|_{r\to a}$$

leading to

$$\begin{aligned}&4\pi\kappa^2 i'_l(\kappa a)\left[\sum_{l'm'\ell_2m_2}(-1)^{l'}\frac{\kappa^{l'}q'_{l'm'}}{(2l'+1)!!}H_{lm\ell_2m_2}^{l'm'}\,k_{\ell_2}(\kappa r_0)Y_{\ell_2}^{m_2}(\hat{r}_0)\right]+\epsilon_o\frac{\sqrt{4\pi}(\kappa a)}{2l+1}\frac{k'_l(\kappa a)}{k_l(\kappa a)}\frac{Q_{lm}}{a^2} \\ &= \epsilon\left\{\frac{4\pi(\kappa a)}{\epsilon_o}i_l(\kappa a)\frac{l}{a^2}\left[\sum_{l'm'\ell_2m_2}(-1)^{l'}\frac{\kappa^{l'}q'_{l'm'}}{(2l'+1)!!}H_{lm\ell_2m_2}^{l'm'}\,k_{\ell_2}(\kappa r_0)Y_{\ell_2}^{m_2}(\hat{r}_0)\right]+\frac{\sqrt{4\pi}}{2l+1}\frac{l}{a^2}Q_{lm}\right\}\end{aligned} \tag{D5}$$

or

$$\frac{\sqrt{4\pi}\,Q_{lm}}{(2l+1)}\left[\epsilon\,l-\epsilon_o\frac{k'_l(\kappa a)}{k_l(\kappa a)}(\kappa a)\right] = 4\pi(\kappa a)\left[(\kappa a)i'_l(\kappa a)-l\frac{\epsilon}{\epsilon_o}i_l(\kappa a)\right]\left[\sum_{l'm'\ell_2m_2}(-1)^{l'}\frac{\kappa^{l'}q'_{l'm'}}{(2l'+1)!!}H_{lm\ell_2m_2}^{l'm'}\,k_{\ell_2}(\kappa r_0)Y_{\ell_2}^{m_2}(\hat{r}_0)\right] \tag{D6}$$

or

$$\frac{\sqrt{4\pi}\,Q_{lm}}{(2l+1)} = \frac{4\pi(\kappa a)}{\epsilon_o}\frac{\epsilon_o i_l'(\kappa a)(\kappa a) - \epsilon\, l\, i_l(\kappa a)}{\epsilon\, l - \epsilon_o \frac{k_l'(\kappa a)}{k_l(\kappa a)}(\kappa a)}\left[\sum_{l'm'\ell_2 m_2}(-1)^{l'}\frac{\kappa^{l'} q'_{l'm'}}{(2l'+1)!!}H^{l'm'}_{lm\ell_2 m_2}\,k_{\ell_2}(\kappa r_0)Y^{m_2}_{\ell_2}(\hat{r}_0)\right]. \tag{D7}$$

The net potential with $r \leqslant a$, $\Phi_{\rm ind}(\boldsymbol{r}, r \leqslant a) + \Phi_{\rho'}(\boldsymbol{r}, r \leqslant a)$, is thus

$$\sum_{lm}\frac{r^l}{a^{l+1}}Y_l^m(\hat{r})\left\{\frac{\sqrt{4\pi}Q_{lm}}{2l+1} + \frac{4\pi(\kappa a)}{\epsilon_o}i_l(\kappa a)\left[\sum_{l'm'\ell_2 m_2}(-1)^{l'}\frac{\kappa^{l'}q'_{l'm'}}{(2l'+1)!!}H^{l'm'}_{lm\ell_2 m_2}\,k_{\ell_2}(\kappa r_0)Y^{m_2}_{\ell_2}(\hat{r}_0)\right]\right\}$$
$$= \frac{4\pi(\kappa a)}{\epsilon_o}\sum_{lm}\frac{r^l}{a^{l+1}}Y_l^m(\hat{r})\left(\frac{\epsilon_o i_l'(\kappa a)(\kappa a) - \epsilon\, l\, i_l(\kappa a)}{\epsilon\, l - \epsilon_o\frac{k_l'(\kappa a)}{k_l(\kappa a)}(\kappa a)} + i_l(\kappa a)\right)\left[\sum_{l'm'\ell_2 m_2}(-1)^{l'}\frac{\kappa^{l'}q'_{l'm'}}{(2l'+1)!!}H^{l'm'}_{lm\ell_2 m_2}\,k_{\ell_2}(\kappa r_0)Y^{m_2}_{\ell_2}(\hat{r}_0)\right]. \tag{D8}$$

If we integrate over the charge distribution $\rho_f(\boldsymbol{r})$ [whether confined to the inside the sphere or $\propto \delta(r-a)$, meaning only on the spherical surface], we obtain the second form of the interaction energy:

$$V^{(2)}_{\rm int} = \frac{4\pi(\kappa a)}{\epsilon_o}\sum_{lm}\frac{q^*_{lm}}{a^{l+1}}\left(\frac{\epsilon_o i_l'(\kappa a)(\kappa a) - \epsilon\, l\, i_l(\kappa a)}{\epsilon\, l - \epsilon_o\frac{k_l'(\kappa a)}{k_l(\kappa a)}(\kappa a)} + i_l(\kappa a)\right)\left[\sum_{l'm'\ell_2 m_2}(-1)^{l'}\frac{\kappa^{l'}q'_{l'm'}}{(2l'+1)!!}H^{l'm'}_{lm\ell_2 m_2}\,k_{\ell_2}(\kappa r_0)Y^{m_2}_{\ell_2}(\hat{r}_0)\right]. \tag{D9}$$

We next show that

$$\sum_{m_2}H^{l'm'}_{lm\ell_2 m_2}\,k_{\ell_2}(\kappa r_0)Y^{m_2}_{\ell_2}(\hat{r}_0) = \sum_{m_2}H^{lm}_{l'm'\ell_2 m_2}\,k_{\ell_2}(\kappa r_0)Y^{m_2 *}_{\ell_2}(\hat{r}_0). \tag{D10}$$

To prove this identity, first recall that

$$H^{l'm'}_{lm\ell_2 m_2} = C^{l'\,0}_{l\,0\,\ell_2\,0}C^{l'\,m'}_{l\,m\,\ell_2\,m_2}\sqrt{\frac{4\pi}{2l'+1}}\sqrt{(2l+1)(2\ell_2+1)}$$

and that the Clebsch-Gordan coefficient can be expressed by Wigner's $3j$ symbol as follows (with $m = m_1 + m_2$):

$$C^{l\,m}_{\ell_1\,m_1\,\ell_2\,m_2} = (-1)^{\ell_1-\ell_2+m}\sqrt{2l+1}\begin{pmatrix}\ell_1 & \ell_2 & l\\ m_1 & m_2 & -m\end{pmatrix}.$$

Some symmetry property of the Wigner's $3j$ will be useful:

$$\begin{pmatrix}\ell_1 & \ell_2 & \ell_3\\ m_1 & m_2 & m_3\end{pmatrix} = (-1)^{\ell_1+\ell_2+\ell_3}\begin{pmatrix}\ell_3 & \ell_2 & \ell_1\\ m_3 & m_2 & m_1\end{pmatrix} = (-1)^{\ell_1+\ell_2+\ell_3}\begin{pmatrix}\ell_1 & \ell_2 & \ell_3\\ -m_1 & -m_2 & -m_3\end{pmatrix}. \tag{D11}$$

Also, the Legendre polynomial $P_l(x) = (-1)^l P_l(-x)$ and the Clebsch-Gordan coefficient

$$C^{l'\,0}_{l\,0\,\ell_2\,0} \propto \int_{-1}^{1}P_{l'}(x)P_l(x)P_{\ell_2}(x)$$

is nonzero only when $(l + l' + \ell_2)$ is an even integer. We thus write

$$\sum_{m_2}H^{l'm'}_{lm\ell_2 m_2}\,k_{\ell_2}(\kappa r)Y^{m_2}_{\ell_2}(\hat{r}) = \sum_{\ell_2 m_2}C^{l'\,0}_{l\,0\,\ell_2\,0}C^{l'\,m'}_{l\,m\,\ell_2\,m_2}\sqrt{\frac{4\pi}{2l'+1}}\sqrt{(2l+1)(2\ell_2+1)}\,k_{\ell_2}(\kappa r)Y^{m_2}_{\ell_2}(\hat{r})$$
$$= \sum_{m_2}(-1)^{m'}\begin{pmatrix}l & \ell_2 & l'\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l & \ell_2 & l'\\ m & m_2 & -m'\end{pmatrix}\sqrt{4\pi(2l'+1)(2l+1)(2\ell_2+1)}\,k_{\ell_2}(\kappa r)Y^{m_2}_{\ell_2}(\hat{r})$$
$$= \sum_{m_2}(-1)^{m'}\begin{pmatrix}l' & \ell_2 & l\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l' & \ell_2 & l\\ -m' & m_2 & m\end{pmatrix}\sqrt{4\pi(2l'+1)(2l+1)(2\ell_2+1)}\,k_{\ell_2}(\kappa r)Y^{m_2}_{\ell_2}(\hat{r})$$
$$= \sum_{m_2}(-1)^{m'}\begin{pmatrix}l' & \ell_2 & l\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l' & \ell_2 & l\\ m' & -m_2 & -m\end{pmatrix}\sqrt{4\pi(2l'+1)(2l+1)(2\ell_2+1)}\,k_{\ell_2}(\kappa r)Y^{m_2}_{\ell_2}(\hat{r})$$
$$= \sum_{m_2}(-1)^{m'-m}C^{l\,0}_{l'\,0\,\ell_2\,0}C^{l\,m}_{l'\,m'\,\ell_2\,-m_2}\sqrt{\frac{4\pi}{2l+1}}\sqrt{(2l'+1)(2\ell_2+1)}\,k_{\ell_2}(\kappa r)Y^{m_2}_{\ell_2}(\hat{r})$$
$$= \sum_{m_2'}(-1)^{m_2'}C^{l\,0}_{l'\,0\,\ell_2\,0}C^{l\,m}_{l'\,m'\,\ell_2\,m_2'}\sqrt{\frac{4\pi}{2l+1}}\sqrt{(2l'+1)(2\ell_2+1)}\,k_{\ell_2}(\kappa r)Y^{-m_2'}_{\ell_2}(\hat{r})$$

$$= \sum_{m_2'} C^{l\,0}_{l'\,0\,\ell_2\,0} C^{l\,m}_{l'\,m'\,\ell_2\,m_2'} \sqrt{\frac{4\pi}{2l+1}} \sqrt{(2l'+1)(2\ell_2+1)}\, k_{\ell_2}(\kappa r) Y^{m_2'\,*}_{\ell_2}(\hat{r})$$

$$= \sum_{m_2} C^{l\,0}_{l'\,0\,\ell_2\,0} C^{l\,m}_{l'\,m'\,\ell_2\,m_2} \sqrt{\frac{4\pi}{2l+1}} \sqrt{(2l'+1)(2\ell_2+1)}\, k_{\ell_2}(\kappa r) Y^{m_2\,*}_{\ell_2}(\hat{r})$$

$$= \sum_{m_2} H^{lm}_{l'm'\ell_2 m_2}\, k_{\ell_2}(\kappa r) Y^{m_2\,*}_{\ell_2}(\hat{r}),$$

which exactly proves (D10).

Hence, by comparing (D9) with (D2), despite their rather complicated expressions, we find that, for them to exactly match, all one needs is the following correspondence:

$$\frac{(\kappa a)^2}{\epsilon_o} \epsilon_o \frac{i_l'(\kappa a) - i_l(\kappa a) \frac{k_l'(\kappa a)}{k_l(\kappa a)}}{\epsilon\, l - \epsilon_o \frac{k_l'(\kappa a)}{k_l(\kappa a)} (\kappa a)} \Rightarrow \frac{1}{\epsilon\, l\, k_l(\kappa a) - \epsilon_o k_l'(\kappa a)\, (\kappa a)}. \tag{D12}$$

In the main text near the end of Sec. V, we show that the correspondence relation above in fact is an identity.

APPENDIX E: RECIPROCITY FOR ANY NUMBER OF DIELECTRIC SPHERES

To lighten the notation for the two-sphere case, we shall choose the origin at the midpoint between the two spherical centers. Hence, $\boldsymbol{R}_1 = \vec{L}/2$ while $\boldsymbol{R}_2 = -\vec{L}/2$. We therefore have $\vec{L}_{1\to 2} = \boldsymbol{R}_2 - \boldsymbol{R}_1 = -\vec{L}$ and $\vec{L}_{2\to 1} = \boldsymbol{R}_1 - \boldsymbol{R}_2 = \vec{L}$. We may begin with the boundary condition equation (54) and the definition (48):

$$D_1(\ell_1) \overline{Q}^1_{\ell_1 m_1} = V_1(\ell_1) \breve{Q}^{1+}_{\ell_1 m_1} + \sum_{\ell_2 m_2} \left[\sum_{lm} i_{\ell_1}(\kappa a_1)\, i_{\ell_2}(\kappa a_2)\, (-1)^{\ell_1 + l}\, H^{\ell_2 m_2}_{\ell_1 m_1 l m}\, k_l(\kappa L) Y^m_l(\hat{L}_{1\to 2}) \right] \breve{Q}^{2+}_{\ell_2 m_2}, \tag{E1}$$

$$D_2(\ell_2) \overline{Q}^2_{\ell_2 m_2} = V_2(\ell_2) \breve{Q}^{2+}_{\ell_2 m_2} + \sum_{\ell_1 m_1} \left[\sum_{lm} i_{\ell_1}(\kappa a_1)\, i_{\ell_2}(\kappa a_2)\, (-1)^{\ell_2 + l}\, H^{\ell_1 m_1}_{\ell_2 m_2 l m}\, k_l(\kappa L) Y^m_l(\hat{L}_{2\to 1}) \right] \breve{Q}^{1+}_{\ell_1 m_1}. \tag{E2}$$

One uses the boundary condition equations above to express $\breve{Q}^{1+}_{lm}$ and $\breve{Q}^{2+}_{lm}$ in terms of $\overline{Q}^1_{lm}$ and $\overline{Q}^2_{lm}$. Note that $H^{\ell_1 m_1}_{\ell_2 m_2 l m}$ requires $\ell_1 + \ell_2 + l$ to be an even integer. Thus, $(-1)^{l+\ell_2} = (-1)^{\ell_1}$. Further note that from Eq. (D10) of Appendix D, $\sum_m H^{\ell_1 m_1}_{\ell_2 m_2 l m} Y^m_l(\hat{L}) = \sum_m H^{\ell_2 m_2}_{\ell_1 m_1 l m} Y^{m\,*}_l(\hat{L})$. If we define the matrix elements

$$M_{\ell_1 m_1, \ell_2 m_2} \equiv \sum_{lm} i_{\ell_1}(\kappa a_1)\, i_{\ell_2}(\kappa a_2)\, (-1)^{\ell_1 + l}\, H^{\ell_2 m_2}_{\ell_1 m_1 l m}\, k_l(\kappa L) Y^m_l(\hat{L}_{1\to 2}) \tag{E3}$$

and

$$M_{\ell_2 m_2, \ell_1 m_1} \equiv \sum_{lm} i_{\ell_1}(\kappa a_1)\, i_{\ell_2}(\kappa a_2)\, (-1)^{\ell_2 + l}\, H^{\ell_1 m_1}_{\ell_2 m_2 l m}\, k_l(\kappa L) Y^m_l(\hat{L}_{2\to 1}), \tag{E4}$$

we see that

$$M_{\ell_2 m_2, \ell_1 m_1} = M^*_{\ell_1 m_1, \ell_2 m_2}. \tag{E5}$$

Note that $M_{\ell_1 m_1, \ell_2 m_2}$ left multiplies to $\breve{Q}^{2+}$ while $M_{\ell_2 m_2, \ell_1 m_1}$ left multiplies to $\breve{Q}^{1+}$.

With the general definitions given in Eq. (48) let us denote by D_1 (D_2) the diagonal matrix with elements $D_1(\ell_1)$ [$D_2(\ell_2)$]. We also abbreviate by V_1 (V_2) the diagonal matrix with elements $V_1(\ell_1) = \epsilon_o D_1(\ell_1) + i_{\ell_1}(\kappa a_1)\, k_{\ell_1}(\kappa a_1)$ [$V_2(\ell_2) = \epsilon_o D_2(\ell_2) + i_{\ell_2}(\kappa a_2)\, k_{\ell_2}(\kappa a_2)$].

The boundary conditions can now be written as a matrix equation of the following form:

$$\begin{pmatrix} V_1 & M \\ M^\dagger & V_2 \end{pmatrix} \begin{pmatrix} \breve{Q}^+_1 \\ \breve{Q}^+_2 \end{pmatrix} = \begin{pmatrix} D_1 \overline{Q}_1 \\ D_2 \overline{Q}_2 \end{pmatrix}, \tag{E6}$$

where $\breve{Q}^+_i$ ($\overline{Q}_i$) denotes the vector with components $\breve{Q}^{i+}_{lm}$ ($\overline{Q}^i_{lm}$) for all l up to the maximum l value considered. Hence the dimension of $\breve{Q}^+_i$ is $\sum_{l=0}^{l_{\max}} (2l+1) = (l_{\max}+1)^2$. For example, when $l_{\max} = 3$, the dimension of $\breve{Q}^+$ is $1+3+5+7 = 16 = (l_{\max}+1)^2$.

To explicitly show reciprocity, we need to show equivalence of two forms of computing the energy. First, we set $\overline{Q}^1_{lm} = 0$ and compute the corresponding $\breve{Q}^+_1$ and $\breve{Q}^+_2$. Then the first form of the interaction energy is given by

$$U^{r(1)}_{\text{int}} = \kappa\, \overline{Q}^{*T}_1 [(V_1 - \epsilon_o D_1) \breve{Q}^+_1 + M \breve{Q}^+_2]. \tag{E7}$$

When $\overline{Q}_1$ is set to zero, we have

$$V_1 \breve{Q}^+_1 + M \breve{Q}^+_2 = 0 \Rightarrow \breve{Q}^+_1 = -(V_1)^{-1} M \breve{Q}^+_2,$$
$$M^\dagger \breve{Q}^+_1 + V_2 \breve{Q}^+_2 = D_2 \overline{Q}_2 \Rightarrow [V_2 - M^\dagger (V_1)^{-1} M] \breve{Q}^+_2 = D_2 \overline{Q}_2.$$

To compute the first form of the interaction energy, we first simplify the quantity

$$\begin{aligned}&(V_1-\epsilon_o D_1)\breve{Q}_1^+ + M\breve{Q}_2^+\\&\quad=-\epsilon_o D_1\breve{Q}_1^+ = \epsilon_o D_1 V_1^{-1} M\breve{Q}_2^+\\&\quad=\epsilon_o D_1 V_1^{-1} M\big[V_2 - M^\dagger V_1^{-1} M\big]^{-1} D_2\overline{Q}_2.\end{aligned}\tag{E8}$$

Hence, the first form of the interaction energy is simply given by

$$\begin{aligned}U_{\rm int}^{r(1)} &= \kappa\overline{Q}_1^{*T}[(V_1-\epsilon_o D_1)\breve{Q}_1^+ + M\breve{Q}_2^+]\\&=\kappa\epsilon_o\overline{Q}_1{}^{*T} D_1 V_1^{-1} M\big[V_2 - M^\dagger V_1^{-1} M\big]^{-1} D_2\overline{Q}_2\\&=\kappa\epsilon_o\overline{Q}_1{}^{*T} D_1 V_1^{-1} M\big[I - V_2^{-1} M^\dagger V_1^{-1} M\big]^{-1} V_2^{-1} D_2\overline{Q}_2.\end{aligned}\tag{E9}$$

The second form of the interaction energy is obtained by first setting $\overline{Q}_2 = 0$ to obtain $\breve{Q}_2^+$ and $\breve{Q}_1^+$. We obtain

$$\begin{aligned}\breve{Q}_2^+ &= -V_2^{-1} M^\dagger \breve{Q}_1^+,\\ \breve{Q}_1^+ &= \big[I - V_1^{-1} M V_2^{-1} M^\dagger\big]^{-1} V_1^{-1} D_1\overline{Q}_1,\end{aligned}\tag{E10}$$

and the interaction energy is given by

$$\begin{aligned}U_{\rm int}^{r(2)} &= \kappa\overline{Q}_2^{*T}[(V_2-\epsilon_o D_2)\breve{Q}_2^+ + M^\dagger\breve{Q}_1^+] = -\kappa\epsilon_o\overline{Q}_2^{*T} D_2\breve{Q}_2^+\\&=\kappa\epsilon_o\overline{Q}_2^{*T} D_2 V_2^{-1} M^\dagger[I - V_1^{-1} M V_2^{-1} M^\dagger]^{-1} V_1^{-1} D_1\overline{Q}_1.\end{aligned}\tag{E11}$$

Let us take the complex conjugate of the interaction energy above; due to realness of the energy, we should get the same energy:

$$\begin{aligned}U_{\rm int}^{r(2)*} &= \big\{\kappa\epsilon_o\overline{Q}_2^{*T} D_2 V_2^{-1} M^\dagger\big[I - V_1^{-1} M V_2^{-1} M^\dagger\big]^{-1} V_1^{-1} D_1\overline{Q}_1\big\}^* = \kappa\epsilon_o\overline{Q}_1^{*T} D_1 V_1^{-1}\big[I - M V_2^{-1} M^\dagger V_1^{-1}\big]^{-1} M V_2^{-1} D_2\overline{Q}_2\\&=\kappa\epsilon_o\overline{Q}_1{}^{*T} D_1 V_1^{-1} M\big[I - V_2^{-1} M^\dagger V_1^{-1} M\big]^{-1} V_2^{-1} D_2\overline{Q}_2 = U_{\rm int}^{r(1)},\end{aligned}\tag{E12}$$

which agrees exactly with (E9). We have thus formally proved that the reciprocity theorem holds for any arbitrary $l_{\rm max}$ cutoff for a system of two dielectric spheres. The general proof of reciprocity for an arbitrary number of spheres is given in the latter part of this Appendix.

A case that is particularly simple for a two-sphere system is when $l_{\rm max} = 0$. We have

$$\begin{aligned}M^\dagger = M &= i_0(\kappa a_1) i_0(\kappa a_2) k_0(\kappa L) = \frac{T_0(a_1)^{-1} T_0(a_2)^{-1}}{(\kappa a_1)(\kappa a_2)}\frac{k_0(\kappa L)}{k_0(\kappa a_1)k_0(\kappa a_2)} = \frac{e^{-\kappa(L-a_1-a_2)}}{(\kappa L)T_0(a_1)T_0(a_2)},\\ D_1 &= -\frac{i_0(\kappa a_1)}{\epsilon_o}\frac{1}{(\kappa a_1)^2 i_0'(\kappa a_1)} = -\frac{i_0(\kappa a_1)}{\epsilon_o}\frac{k_0(\kappa a_1)}{1+\frac{(\kappa a_1)}{T_0(a_1)}\frac{k_0'(\kappa a_1)}{k_0(\kappa a_1)}} = -\frac{1}{\epsilon_o}\frac{k_0(\kappa a_1)/(\kappa a_1)}{T_0(a_1)k_0(\kappa a_1) + (\kappa a_1)k_0'(\kappa a_1)},\\ D_2 &= -\frac{i_0(\kappa a_2)}{\epsilon_o}\frac{1}{(\kappa a_2)^2 i_0'(\kappa a_2)} = -\frac{i_0(\kappa a_2)}{\epsilon_o}\frac{k_0(\kappa a_2)}{1+\frac{(\kappa a_2)}{T_0(a_2)}\frac{k_0'(\kappa a_2)}{k_0(\kappa a_2)}} = -\frac{1}{\epsilon_o}\frac{k_0(\kappa a_2)/(\kappa a_2)}{T_0(a_2)k_0(\kappa a_2) + (\kappa a_2)k_0'(\kappa a_2)},\\ V_1 &= i_0(\kappa a_1)k_0(\kappa a_1) + \epsilon_o D_1 = \frac{1}{T_0(a_1)(\kappa a_1)}\left[1 - \frac{1}{1+\frac{(\kappa a_1)}{T_0(a_1)}\frac{k_0'(\kappa a_1)}{k_0(\kappa a_1)}}\right]\\&= \frac{1}{T_0(a_1)(\kappa a_1)}\frac{(\kappa a_1)k_0'(\kappa a_1)}{T_0(a_1)k_0(\kappa a_1) + (\kappa a_1)k_0'(\kappa a_1)} = \frac{1}{T_0(a_1)}\frac{k_0'(\kappa a_1)}{T_0(a_1)k_0(\kappa a_1) + (\kappa a_1)k_0'(\kappa a_1)},\\ V_2 &= i_0(\kappa a_2)k_0(\kappa a_2) + \epsilon_o D_2 = \frac{1}{T_0(a_2)(\kappa a_2)}\left[1 - \frac{1}{1+\frac{(\kappa a_2)}{T_0(a_2)}\frac{k_0'(\kappa a_2)}{k_0(\kappa a_2)}}\right]\\&= \frac{1}{T_0(a_2)(\kappa a_2)}\frac{(\kappa a_2)k_0'(\kappa a_2)}{T_0(a_2)k_0(\kappa a_2) + (\kappa a_2)k_0'(\kappa a_2)} = \frac{1}{T_0(a_2)}\frac{k_0'(\kappa a_2)}{T_0(a_2)k_0(\kappa a_2) + (\kappa a_2)k_0'(\kappa a_2)},\\ \frac{D_1}{V_1} &= -\frac{T_0(a_1)}{\epsilon_o}\frac{k_0(\kappa a_1)}{(\kappa a_1)k_0'(\kappa a_1)} = \frac{T_0(a_1)}{\epsilon_o}\frac{1}{1+\kappa a_1},\quad \frac{D_2}{V_2} = -\frac{T_0(a_2)}{\epsilon_o}\frac{k_0(\kappa a_2)}{(\kappa a_2)k_0'(\kappa a_2)} = \frac{T_0(a_2)}{\epsilon_o}\frac{1}{1+\kappa a_2},\\ \frac{MM^\dagger}{V_2V_1} &= \frac{(\kappa a_1)(\kappa a_2)[T_0(a_1)-(1+\kappa a_1)][T_0(a_2)-(1+\kappa a_2)]}{T_0(a_1)(1+\kappa a_1)T_0(a_2)(1+\kappa a_2)}\left(\frac{e^{-\kappa(L-a_1-a_2)}}{\kappa L}\right)^2\\&\equiv G_{12}\left(\frac{e^{-\kappa(L-a_1-a_2)}}{\kappa L}\right)^2 = G_{21}\left(\frac{e^{-\kappa(L-a_1-a_2)}}{\kappa L}\right)^2.\end{aligned}\tag{E13}$$

Hence, with $l_{\max} = 0$, we have the reciprocity interaction energy [using (E7), (E9), (E11), or (E12)]:

$$U^r_{\rm int}(l_{\max}=0) = \frac{q_1\,q_2}{\epsilon_o L}\frac{e^{-\kappa(L-a_1-a_2)}}{(1+\kappa a_1)(1+\kappa a_2)}\left[1 - G_{12}\left(\frac{e^{-\kappa(L-a_1-a_2)}}{\kappa L}\right)^2\right]^{-1}$$
$$= \frac{q_1\,q_2}{\epsilon_o L}\frac{e^{-\kappa(L-a_1-a_2)}}{(1+\kappa a_1)(1+\kappa a_2)}\left\{1 + G_{12}\left(\frac{e^{-\kappa(L-a_1-a_2)}}{\kappa L}\right)^2 + \left[G_{12}\left(\frac{e^{-\kappa(L-a_1-a_2)}}{\kappa L}\right)^2\right]^2 + \ldots\right\}. \tag{E14}$$

And one sees the exact symmetry between indices 1 and 2 as expected.

For the general N-sphere case, one may place arbitrarily $n = 1, 2, \ldots, n_A$ spheres into group A and the rest of the spheres, labeled by $m = 1, 2, \ldots, m_B = N - n_A$, into group B. The goal of this Appendix is to show that the two forms of computing the interaction energy between the free charge distribution associated with group A and the free charge distribution associated with group B are equivalent.

The boundary conditions can now be written as a matrix equation of the following form:

$$\begin{pmatrix} M_{AA} & M_{AB} \\ M^\dagger_{AB} & M_{BB} \end{pmatrix}\begin{pmatrix} \breve{Q}^+_A \\ \breve{Q}^+_B \end{pmatrix} = \begin{pmatrix} D_A\overline{Q}_A \\ D_B\overline{Q}_B \end{pmatrix}. \tag{E15}$$

We explain the notation below. First,

$$\breve{Q}^+_A = \begin{pmatrix} \breve{Q}^+_1 \\ \breve{Q}^+_2 \\ \vdots \\ \breve{Q}^+_{n_A} \end{pmatrix}, \quad \breve{Q}^+_B = \begin{pmatrix} \breve{Q}^+_{n_A+1} \\ \breve{Q}^+_{n_A+2} \\ \vdots \\ \breve{Q}^+_{n_A+m_B} \end{pmatrix}, \quad \overline{Q}_A = \begin{pmatrix} \overline{Q}_1 \\ \overline{Q}_2 \\ \vdots \\ \overline{Q}_{n_A} \end{pmatrix}, \quad \overline{Q}_B = \begin{pmatrix} \overline{Q}_{n_A+1} \\ \overline{Q}_{n_A+2} \\ \vdots \\ \overline{Q}_{n_A+m_B} \end{pmatrix},$$

where $\breve{Q}^+_i$ ($\overline{Q}_i$) denotes the vector with components $\breve{Q}^{i+}_{lm}$ ($\overline{Q}^i_{lm}$) for all l, m up to the maximum l value considered. Namely, $\breve{Q}^+_i$ is a $\sum_{l=0}^{l_{\max}} 2l+1 = (l_{\max}+1)^2$ dimensional column vector. If $l_{\max} = 2$, then

$$\breve{Q}^+_i = \left(\breve{Q}^{i+}_{0,0}, \breve{Q}^{i+}_{1,-1}, \breve{Q}^{i+}_{1,0}, \breve{Q}^{i+}_{1,1}, \breve{Q}^{i+}_{2,-2}, \breve{Q}^{i+}_{2,-1}, \breve{Q}^{i+}_{2,0}, \breve{Q}^{i+}_{2,1}, \breve{Q}^{i+}_{2,2}\right)^T. \tag{E16}$$

The diagonal matrices D_A and D_B are represented by

$$D_A = \mathrm{diag}(D_1, D_2, \ldots, D_{n_A}), \quad D_B = \mathrm{diag}(D_{n_A+1}, D_{n_A+2}, \ldots, D_{n_A+m_B}),$$

where the diagonal matrix D_j has again linear dimensions $(l_{\max}+1)^2$ and is expressed as

$$D_j = \mathrm{diag}\left(D^j_0, D^j_1, \ldots, D^j_{l_{\max}}\right),$$

and D^j_ℓ is a $(2\ell+1)\times(2\ell+1)$ identity matrix multiplied by

$$D_j(\ell) \equiv \frac{1}{(\kappa a_j)}\frac{1}{\ell\,\epsilon_j - \frac{(\kappa a_j) i'_\ell(\kappa a_j)}{i_\ell(\kappa a_j)}\epsilon_o}.$$

For later convenience, let us also introduce another diagonal matrix V_j that also has linear dimensions $(l_{\max}+1)^2$ and is expressed as

$$V_j = \mathrm{diag}\left(V^j_0, V^j_1, \ldots, V^j_{l_{\max}}\right)$$

with V^j_ℓ being a $(2\ell+1)\times(2\ell+1)$ identity matrix multiplied by

$$V_j(\ell) \equiv \epsilon_o D_j(\ell) + i_\ell(\kappa a_j) k_\ell(\kappa a_j).$$

Hence, if $l_{\max} = 2$,

$$V_j = \mathrm{diag}(V_j(0), V_j(1), V_j(1), V_j(1), V_j(2), V_j(2), V_j(2), V_j(2), V_j(2)). \tag{E17}$$

If we define the matrix elements in the submatrix $M^{(i,j)}$ (i and j are sphere indices)

$$M_{\ell_i m_i, \ell_j m_j} \equiv \sum_{lm} i_{\ell_i}(\kappa a_i) i_{\ell_j}(\kappa a_j)(-1)^{\ell_i + l} H^{\ell_j m_j}_{\ell_i m_i l m} k_l(\kappa L_{ij}) Y^m_l(\hat{L}_{i\to j}) \tag{E18}$$

and elements in submatrix $M^{(j,i)}$

$$M_{\ell_j m_j,\ell_i m_i} \equiv \sum_{lm} i_{\ell_i}(\kappa a_i) i_{\ell_j}(\kappa a_j)(-1)^{\ell_j+l} H^{\ell_i m_i}_{\ell_j m_j lm} k_l(\kappa L_{ij}) Y_l^m(\hat{L}_{j\to i}), \tag{E19}$$

we see that [because $(-1)^l Y_l^m(\hat{L}_{i\to j}) = Y_l^m(\hat{L}_{j\to i})$, $\ell_i + \ell_j + l$ must be even due to $H^{\ell_j m_j}_{\ell_i m_i lm}$, and $\sum_m H^{\ell_j m_j}_{\ell_i m_i lm} Y_l^m(\hat{L}_{j\to i}) = \sum_m H^{\ell_i m_i}_{\ell_j m_j lm} Y_l^{m*}(\hat{L}_{j\to i})$]

$$M_{\ell_j m_j,\ell_i m_i} = M^*_{\ell_i m_i,\ell_j m_j}, \tag{E20}$$

implying $M^{(j,i)} = M^{(i,j)\dagger}$. Note that in the boundary condition equation the submatrix $M^{(i,j)}$ (with elements $M_{\ell_i m_i,\ell_j m_j}$) left multiplies to $\breve{Q}_j$ while the submatrix $M^{(j,i)}$ (with elements $M_{\ell_j m_j,\ell_i m_i}$) left multiplies to $\breve{Q}_i$.

We now come to the other symbols in the boundary condition equation (E15), with the M matrix in the main text now represented by M_{12},

$$M_{AA} = \begin{pmatrix} V_1 & M^{(1,2)} & \dots & M^{(1,n_A)} \\ M^{(1,2)\dagger} & V_2 & \dots & M^{(2,n_A)} \\ \vdots & \vdots & \ddots & \vdots \\ M^{(1,n_A)\dagger} & M^{(2,n_A)\dagger} & \dots & V_{n_A} \end{pmatrix} = M^\dagger_{AA},$$

$$M_{BB} = \begin{pmatrix} V_{n_A+1} & M^{(n_A+1,n_A+2)} & \dots & M^{(n_A+1,n_A+m_B)} \\ M^{(n_A+1,n_A+2)\dagger} & V_{n_A+2} & \dots & M^{(n_A+2,n_A+m_B)} \\ \vdots & \vdots & \ddots & \vdots \\ M^{(n_A+1,n_A+m_B)\dagger} & M^{(n_A+2,n_A+m_B)\dagger} & \dots & V_{n_A+m_B} \end{pmatrix} = M^\dagger_{BB},$$

$$M_{AB} = \begin{pmatrix} M^{(1,n_A+1)} & M^{(1,n_A+2)} & \dots & M^{(1,n_A+m_B)} \\ M^{(2,n_A+1)} & M^{(2,n_A+2)} & \dots & M^{(2,n_A+m_B)} \\ \vdots & \vdots & \ddots & \vdots \\ M^{(n_A,n_A+1)} & M^{(n_A,n_A+2)} & \dots & M^{(n_A,n_A+m_B)} \end{pmatrix} = M^\dagger_{BA}.$$

To explicitly show reciprocity, we need to show equivalence of two forms of computing the energy. In the first form, we set all components of $\overline{Q}_A$ to 0 and compute the corresponding $\breve{Q}^+_A$ and $\breve{Q}^+_B$. Then the first form of the interaction energy, see (58), is given by

$$U_{\rm int} = \kappa \overline{Q}^{*T}_A [M_{AA}\, \breve{Q}^+_A - \epsilon_o D_A \breve{Q}^+_A + M_{AB}\, \breve{Q}^+_B]. \tag{E21}$$

When $\overline{Q}_A$ is set to zero, we have

$$M_{AA}\breve{Q}^+_A + M_{AB}\breve{Q}^+_B = 0 \Rightarrow \breve{Q}^+_A = -M^{-1}_{AA} M_{AB} \breve{Q}^+_B,$$
$$M^\dagger_{AB}\breve{Q}^+_A + M_{BB}\breve{Q}^+_B = D_B \overline{Q}_B \Rightarrow \breve{Q}^+_B = \left[M_{BB} - M^\dagger_{AB} M^{-1}_{AA} M_{AB}\right]^{-1} D_B \overline{Q}_B.$$

One therefore has

$$\begin{aligned} U_{\rm int} &= -\epsilon_o \kappa\, \overline{Q}^{*T}_A D_A \breve{Q}^+_A = \epsilon_o \kappa\, \overline{Q}^{*T}_A D_A M^{-1}_{AA} M_{AB} \left[M_{BB} - M^\dagger_{AB} M^{-1}_{AA} M_{AB}\right]^{-1} D_B \overline{Q}_B \\ &= \epsilon_o \kappa\, \overline{Q}^{*T}_A D_A M^{-1}_{AA} M_{AB} \left[\mathbf{I} - M^{-1}_{BB} M^\dagger_{AB} M^{-1}_{AA} M_{AB}\right]^{-1} M^{-1}_{BB} D_B \overline{Q}_B. \end{aligned} \tag{E22}$$

The second form of the interaction energy is obtained by first setting $\overline{Q}_B = 0$ to obtain $\breve{Q}_A$ and $\breve{Q}_B$ and has the form

$$U_{\rm int} = \kappa \overline{Q}^{*T}_B [M^\dagger_{AB}\, \breve{Q}^+_A - \epsilon_o D_B \breve{Q}^+_B + M_{BB}\, \breve{Q}^+_B]. \tag{E23}$$

When $\overline{Q}_B$ is set to zero, we have

$$M^\dagger_{AB}\breve{Q}^+_A + M_{BB}\breve{Q}^+_B = 0 \Rightarrow \breve{Q}^+_B = -M^{-1}_{BB} M^\dagger_{AB} \breve{Q}^+_A,$$
$$M_{AA}\breve{Q}^+_A + M_{AB}\breve{Q}^+_B = D_A \overline{Q}_A \Rightarrow \breve{Q}^+_A = \left[M_{AA} - M_{AB} M^{-1}_{BB} M^\dagger_{AB}\right]^{-1} D_A \overline{Q}_A.$$

One therefore has

$$\begin{aligned} U_{\rm int} &= -\epsilon_o \kappa\, \overline{Q}^{*T}_B D_B \breve{Q}^+_B = \epsilon_o \kappa\, \overline{Q}^{*T}_B D_B M^{-1}_{BB} M^\dagger_{AB} \left[M_{AA} - M_{AB} M^{-1}_{BB} M^\dagger_{AB}\right]^{-1} D_A \overline{Q}_A \\ &= \epsilon_o \kappa\, \overline{Q}^{*T}_B D_B M^{-1}_{BB} M^\dagger_{AB} \left[\mathbf{I} - M^{-1}_{AA} M_{AB} M^{-1}_{BB} M^\dagger_{AB}\right]^{-1} M^{-1}_{AA} D_A \overline{Q}_A \\ &= \epsilon_o \kappa\, \overline{Q}^{*T}_B D_B \sum_{n=0}^{\infty} M^{-1}_{BB} M^\dagger_{AB} \left[M^{-1}_{AA} M_{AB} M^{-1}_{BB} M^\dagger_{AB}\right]^n M^{-1}_{AA} D_A \overline{Q}_A \end{aligned}$$

$$= \epsilon_o \kappa \, \overline{Q}_B^{*T} D_B \sum_{n=0}^{\infty} M_{BB}^{-1} \left[M_{AB}^{\dagger} M_{AA}^{-1} M_{AB} M_{BB}^{-1} \right]^n M_{AB}^{\dagger} M_{AA}^{-1} D_A \overline{Q}_A$$

$$= \epsilon_o \kappa \, \overline{Q}_B^{*T} D_B M_{BB}^{-1} \left[\mathbf{I} - M_{AB}^{\dagger} M_{AA}^{-1} M_{AB} M_{BB}^{-1} \right]^{-1} M_{AB}^{\dagger} M_{AA}^{-1} D_A \overline{Q}_A . \tag{E24}$$

The realness of the interaction energy allows us to take its complex conjugate without changing its value. Taking the complex conjugate of the above, we obtain

$$\left\{ \epsilon_o \kappa \, \overline{Q}_B^{*T} D_B M_{BB}^{-1} \left[\mathbf{I} - M_{AB}^{\dagger} M_{AA}^{-1} M_{AB} M_{BB}^{-1} \right]^{-1} M_{AB}^{\dagger} M_{AA}^{-1} D_A \overline{Q}_A \right\}^*$$

$$= \epsilon_o \kappa \overline{Q}_A^{*T} D_A M_{AA}^{-1} M_{AB} \left[\mathbf{I} - M_{BB}^{-1} M_{AB}^{\dagger} M_{AA}^{-1} M_{AB} \right]^{-1} M_{BB}^{-1} D_B \overline{Q}_B . \tag{E25}$$

This is exactly the same as (E22). We have thus proved the reciprocity of the interaction energy.

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