Exact Solution of the Poisson–Boltzmann Equation for Two Spheres with Fixed Surface Potentials[1]

EYTAN BAROUCH AND SANJEEV KULKARNI

Department of Mathematics and Computer Science and Institute of Colloid and Surface Science, Clarkson University, Potsdam, New York 13676

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An iteration scheme for the Poisson–Boltzmann equation for two spheres with constant surface potentials is devised. The scheme yields an exact solution to this problem, and it is uniformly convergent.

I. INTRODUCTION

The Poisson–Boltzmann (PB) equation has been a major theoretical tool (1–5) in understanding and interpreting properties of colloidal systems immersed in electrolitic solutions. The most elementary geometry of two particles consists of two parallel plates, since the PB equation for such system becomes a classical ordinary differential equation. This simplification enables one to obtain a useful intuition about the system at hand. On the other hand it has some serious limitations, particularly due to the fact that most systems of interest are not one-dimensional. Furthermore, geometry and curvature effect embedded in a system of interest can at best be approximated with little information on improvement of these estimates. Thus, it is highly desirable to obtain a systematic solution of the PB equation for a realistic nontrivial geometry.

It is the purpose of this paper to provide an exact solution for a system of spheres with unequal surface potentials immersed in 1–1 electrolyte. Once the solution is obtained, one may use it directly to compute electrostatic interaction energies, forces, stability parameters, escape probabilities, potential profiles, etc. This method enables one to obtain a solution to systems of spheres with different boundary conditions as well, provided a good approximation is available.

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II. FORMULATION

Consider (6) a system of two spheres of radii a_1, a_2, surface-to-surface separation H_0, and fixed dimensionless surface potentials $0 < \psi_1 < \psi_2$, immersed in 1–1 electrolite with Debye's inverse length κ satisfying the PB equation

$$\Delta\Psi = \kappa^2 \sinh \Psi \qquad [1]$$

$$\Psi \text{ (on sphere 1)} = \psi_1$$

$$\Psi \text{ (on sphere 2)} = \psi_2. \qquad [2]$$

Suppose that a good approximation to [1] is obtained by some independent method as Ψ_0. Since the charge density in the bulk is approximately known it is reasonable to expect that the potential associated with this charge density satisfies the Poisson equation approximately,

$$\Delta\Psi_1 = \kappa^2 \sinh \Psi_0 \qquad [3]$$

with conditions [2] applied to Ψ_1, as well as Ψ_0. If the method used to obtain Ψ_1 is independent of Ψ_0 one may repeat the process indefinitely, as long as it converges. In other words one may define the iterative process

$$\Delta\Psi_{n+1} = \kappa^2 \sinh \Psi_n \quad n = 0, 1, 2, \cdots \qquad [4]$$

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with conditions [2] imposed. When the process converges uniformly, $\lim_{n\to\infty} \Psi_n = \Psi$ becomes an exact solution of [1]. Equation [4] can be rewritten as

$$\Delta\Psi_{n+1} = \kappa^2 \sinh \Psi_{n+1} + \kappa^2(\sinh \Psi_n - \sinh \Psi_{n+1}). \quad [5]$$

Let $\Psi_n \equiv \Psi_{n+1} + \epsilon_n$. If ϵ_n is systematically decreasing the limit exists, since [5] can be expressed as

$$\Delta\Psi_{n+1} = \kappa^2 \sinh \Psi_{n+1} + 2\kappa^2 \sinh\left(\frac{\epsilon_n}{2}\right)\cosh\left(\Psi_{n+1} + \frac{\epsilon_n}{2}\right). \quad [6]$$

Therefore, $\lim_{n\to\infty} \epsilon_n = 0$ is equivalent to $\lim_{n\to\infty} \Psi_n = \Psi$ as long as $|\epsilon_n| \ll |\psi_{n+1}|$.

To illustrate the method of convergence, it is useful to exhibit the asymptotic behavior for the cylindrically symmetric PB equation. It takes the form (for $\kappa = 1$)

$$\frac{1}{r}\frac{d}{dr} r \frac{d}{dr} \Psi = \Psi + (\sinh \Psi - \Psi). \quad [7]$$

Consider the linear equation as the equation utilized to obtain Ψ_0. That is to say that

$$\Psi_0(r) = AK_0(r) \quad [8]$$

with K_0 being modified Bessel function of the third kind. Variation of parameters yields

$$\Psi_1(r) = A(K_0(r) + \tfrac{1}{2}K_0^2(r) + 0(K_0^3) \quad [9]$$

which indeed illustrates the above discussion after one iteration. Furthermore, since the system has absence of movable critical points, the behavior at finite distances is completely determined by the asymptotic region.

III. DETERMINATION OF THE STARTING SOLUTION Ψ_0

Recently, a uniform approximation *consisted* of scale balancing was introduced (6), making use of the fact that the parameter κ is very large. The PB equation for the two-sphere system is cylindrically symmetric, thus it can be written as

$$\frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial}{\partial r} \Psi + \frac{\partial^2}{\partial z^2} \Psi = \kappa^2 \sinh \Psi. \quad [10]$$

Upon scaling

$$R = \kappa r$$
$$Z = \kappa^2(z - a_1)$$
$$H_0 = \kappa^{-2} h \quad [11]$$

the equation takes the approximate form

$$\kappa^2 \frac{\partial^2}{\partial Z^2} \Psi_0 = \sinh \Psi_0 \quad [12]$$

and its linearized form becomes

$$\kappa^2 \frac{\partial^2}{\partial Z^2} \Psi_{0,l} = \Psi_{0,l} \quad [13]$$

with boundary conditions

$$\Psi(Z_1) = \Psi_0 \text{ (on } Z \cong -R^2/2a_1) = \psi_1 \quad [14a]$$

$$\Psi(Z_2) = \Psi_0 \text{ (on } Z \cong h + R^2/2a_2) = \psi_2. \quad [14b]$$

The solution of [13] is immediate and could serve as a starting solution. It is given explicitly by

$$\Psi_{0,l} = \{\psi_1 \sinh[\kappa H_0 + (\kappa r)^2/2(\kappa a_2) - \kappa(z - a_1)] + \psi_2 \sinh[\kappa(z - a_1) + (\kappa r)^2/2(\kappa a_1)]\}/\{\sinh[\kappa H_0 + (1/\kappa a_1 + 1/\kappa a_2)(\kappa r)^2/2]\}. \quad [15]$$

However, the convergence is slow if one intends to solve the nonlinear system. Since $\Psi_{0,l}$ is a linear combination of two hyperbolic sines, it could be monotonic with z or contain an extremal point. Thus, two cases must be distinguished for [12].

(i) $\dfrac{d\Psi_0}{dZ} > 0$ for $-R^2/2a_1 \leqslant Z \leqslant h + R^2/2a_2$.

One integration of [12] yields

$$\frac{d\Psi_0}{dZ} = 2^{1/2}\kappa^{-1}[\cosh \Psi_0(Z, R) - \phi_1(R)]^{1/2} \quad [16]$$

with $\phi_1(r)$ determined from

$$\int_{\psi_1}^{\psi_2} d\psi'[\cosh\psi' - \phi_1(R)]^{-1/2} = 2^{1/2}\kappa^{-1}[h + \tfrac{1}{2}R^2(1/a_1 + 1/a_2)]. \quad [17]$$

The second integration is a well-known classical inversion problem.

(ii) $\dfrac{d\psi_0}{dZ} = 0$ for some $Z = Z_0(R)$.

First integral is the same as [16] with $\phi_2(R)$ replacing $\phi_1(R)$, and it is determined from

$$-2^{1/2}\kappa^{-1}[h + R^2(1/a_1 + 1/a_2)/2] = \int_{\Delta_1}^{\phi_2(R)} du[(u^2 - 1)(u - \phi_2(R)]^{-1/2} + \int_{\Delta_2}^{\phi_2(R)} du[(u^2 - 1)(u - \phi_2(R)]^{-1/2}. \quad [18]$$

The function $\phi_2(R)$ satisfies the relation

$$\cosh[\Psi_0(Z_0(R), R)] = \phi_2(R). \quad [19]$$

Note that for $Z_1 \leqslant Z < Z_0$ $d\psi_0/dZ < 0$ and for $Z_0 < Z \leqslant Z_2$ $d\Psi_0/dZ > 0$. Again, once $\phi_2(R)$ is obtained from the transcendental Eq. [18], inversion of the elliptic integrals yields the desired explicit starting solution $\Psi_0(Z, R)$ for $Z_1 \leqslant Z \leqslant Z_2$.

IV. BISPHERICAL COORDINATES

A system of two unequal spheres of radii a_1, a_2 and center-to-center separation $|l_1| + |l_2|$, surface-to-surface separation H_0, is conveniently parameterized in terms of bispherical coordinate system (7).

Let the interfocal distance a be defined by

$$l_1^2 = a^2 + a_1^2$$
$$l_2^2 = a^2 + a_2^2 \quad [20]$$

and upon elimination of l_1, l_2, one obtains the parameter a in terms of the physical parameters of the system as

$$2a = [H_0(H_0 + 2a_1)(H_0 + 2a_2) \times (H_0 + 2a_1 + 2a_2)]^{1/2}(a_1 + a_2 + H_0)^{-1}. \quad [21]$$

The bispherical coordinate system (μ, η, ϕ) is defined in terms of the interfocal distance a and the Cartesian system (x, y, z). Explicitly one defines

$$r = [x^2 + y^2]^{1/2}$$
$$\phi = \arctan(y/x)$$
$$\mu = \tanh^{-1}[2az/(a^2 + z^2 + r^2)]$$
$$\eta = \arctan[2ar/(z^2 + r^2 - a^2)] \quad [22]$$

and the Cartesian system (x, y, z) takes the form

$$u \equiv [\cosh\mu - \cos\eta]^{-1}$$
$$x = u\,a \sin\eta \cos\phi$$
$$y = u\,a \sin\eta \sin\phi$$
$$z = u\,a \sin\mu. \quad [23]$$

The range of the bispherical system is $-\infty < \mu < \infty$, $0 < \eta < \pi$, $0 \leqslant \phi \leqslant 2\pi$. The surface $\mu = \mu_i$ is a sphere of radius $a|\mathrm{csch}\ \mu_i|$ whose center is at $(x, y, z) = (0, 0, a\ \coth\mu_i)$, $i = 1, 2$.

When bispherical coordinate system is imposed on Laplace's equation, one may employ separation of variables to obtain the elementary necessary solutions. Unfortunately the Helmholtz equation does not separate. It is precisely for this reason that a very accurate starting solution is needed, in order for an iteration scheme to become useful.

V. GREEN-FUNCTION FORMULATION

Consider two continuous functions g_1, g_2, defined on and outside the two spheres, whose Laplacians Δg_1, Δg_2 are defined as well. If g_1 and g_2 vanish at infinity, one may employ Green's identity as

$$\int_\tau d\tau[g_1\Delta g_2 - g_2\Delta g_1] = \int_S dS[g_1\mathbf{n}\cdot\nabla g_2 - g_2\mathbf{n}\cdot\nabla g_1] \quad [24]$$

where τ is the exterior volume, S the total surface area, $\mathbf{n}$ the normal vector to the surface, ∇g_i the gradient of g_i and $\mathbf{n}\cdot\nabla g_i = \partial g_i/\partial n$ the

normal derivative of g_i at the surface. Equation [24] is used to generate solutions of Poisson's equation.

Define the Green's function as the solution of

$$\Delta G = -4\pi\delta(\mathbf{r} - \mathbf{r}_0) \qquad [25]$$

with $\mathbf{r}$ being the observation point, $\mathbf{r}_0$ the source point, and $\delta(\mathbf{r} - \mathbf{r}_0)$ a Dirac delta function whose volume integral is unity. Since [25] has many solutions, one must specify boundary conditions. Of particular interest are the homogeneous boundary conditions, namely G vanishes on the surfaces of the spheres. From this stage on, G is assumed vanishing on the boundaries, unless otherwise specified.

Consider the Poisson equation

$$\Delta U = -4\pi\rho \qquad [26]$$

with ρ being the known charge density, and U is given on the spheres, namely

$$U = u_i \quad \text{on } S_i, \quad i = 1, 2. \qquad [27]$$

One way to solve [26] is composed of a solution of [26] with vanishing U on the surfaces, U_H, and a solution of Laplace equation which satisfies [27], U_L. Then U is given by

$$U = U_H + U_L. \qquad [28]$$

If the solution of [25] is known, U_H can be obtained immediately from [24] by identifying $G \equiv g_1$, $U_H = g_2$, and due to the vanishing of both functions on the surface, the RHS of [24] vanishes. Explicitly one obtains

$$\int_\tau [-G(\mathbf{r}, \mathbf{r}_0)\rho(\mathbf{r}_0) + \delta(\mathbf{r} - \mathbf{r}_0)U_H(\mathbf{r}_0)]d^3\mathbf{r}_0 = 0. \qquad [29]$$

Equation [28], upon integration of the delta function yields

$$U_H(\mathbf{r}) = \int_\tau G(\mathbf{r}, \mathbf{r}_0)\rho(\mathbf{r}_0)d^3\mathbf{r}_0. \qquad [30]$$

As [28] takes the form

$$U = U_L + \int_\tau G(\mathbf{r}, \mathbf{r}_0)\rho(\mathbf{r}_0)d^3\mathbf{r}. \qquad [31]$$

To complete the determination of U_1 one must also solve the Laplace equation for U_L that satisfies [27]. A somewhat more efficient way of obtaining U can be obtained from [24] directly, again once G is known, using the boundary conditions [27] directly. More precisely, one may define in [24] $G = g_1$, $U = g_2$ to obtain

$$4\pi \int_\tau [G(\mathbf{r}, \mathbf{r}_0)\Delta U + \delta(\mathbf{r} - \mathbf{r}_0)U(\mathbf{r}_0)]d^3\mathbf{r}_0 = -U_1 \int_{S_1} \mathbf{n}_1 \cdot \nabla G(\mathbf{r}, \mathbf{r}_0)dS - U_2 \int_{S_2} \mathbf{n}_2 \cdot \nabla G(\mathbf{r}, \mathbf{r}_0)dS \qquad [32]$$

and after the delta function integration [32] takes the form

$$U(\mathbf{r}) = \int_\tau G(\mathbf{r}, \mathbf{r}_0)\rho(\mathbf{r}_0)d^3\mathbf{r}_0 - U_1 \int_{S_1} (\partial G/\partial n_1) \times dS/4\pi - U_2 \int_{S_2} (\partial G/\partial n_2)dS/4\pi. \qquad [33]$$

If one compares [33] and [31] and employs the uniqueness of the solution, it is evident that the sum of the two surface integrals is actually U_L. In other words, one has a choice between carrying out an integration of the normal derivative of the Green's function and direct solution of Laplace equation. However, in principle it is sufficient to obtain G, since U in [33] is dependent only on G and known functions, once ρ is identified properly. The iteration scheme thus takes the form

$$\psi_{n+1}(\mathbf{r}) = -\kappa^2 \int_\tau G(\mathbf{r}, \mathbf{r}_0)\sinh[\psi_n(\mathbf{r}_0)]d^3\mathbf{r}_0 - \left[\psi_1 \int_{S_1} (\partial G/\partial n_1)dS + \psi_2 \int_{S_2} (\partial G/\partial n_2)dS\right] \Big/ 4\pi. \qquad [34]$$

At this juncture, it should be emphasized that all functions in the integrands are given in Cartesian coordinate systems. Since the it-

erations as well as the Green function are expressed in bipolar system, the Jacobian must be employed upon change of variables. This will be done later on. It is straightforward to express $\psi_0(\mathbf{r})$ in Cartesian system, even though it is originally obtained in cylindrical coordinates.

VI. DETERMINATION OF THE GREEN-FUNCTION

Fortunately, the general nonhomogeneous Green's function $\tilde{G}$ for two spheres is given in Morse and Feshbach (7) in bipolar coordinates

$$\tilde{G}(\mu, \eta, \phi, \mu_0, \eta_0, \phi_0) = a^{-1} \times [(\cosh \mu - \cos \eta)(\cosh \mu_0 - \cos \eta_0)]^{1/2} \times \sum_{n=0}^{\infty} \sum_{m=0}^{n} \epsilon_m \frac{(n-m)!}{(n+m)!} \cos[m(\phi - \phi_0)] \times P_n^m(\cos \eta_0) P_n^m(\cos \eta) e^{-(n+1/2)|\mu - \mu_0|} \quad [35]$$

with P_n^m being Legendre functions and $\epsilon_0 = 1$, $\epsilon_m = 2$ for $m > 0$. A solution of Laplace's equation H must be subtracted from $\tilde{G}$. If $H(\mu_1) = \tilde{G}(\mu_1)$, $H(\mu_2) = \tilde{G}(\mu_2)$ than

$$G = \tilde{G} - H \quad [36]$$

is the required homogeneous Green's function. Since Laplace's equation separates in bispherical coordinate system, a typical solution H_p is of the form

$$H_p = (\cosh \mu - \cos \eta)^{1/2} P_n^m(\cos \eta) \times \exp[\pm im\phi \pm (n + 1/2)\mu]. \quad [37]$$

In other words, the most general solution H can be expressed as

$$H = (\cosh \mu - \cos \eta)^{1/2} \sum_{n=0}^{\infty} \sum_{m=0}^{n} P_n^m(\cos \eta) \times \{[A_{mn} e^{(n+1/2)\mu} + B_{mn} e^{-(n+1/2)\mu}] \cos m\phi + [C_{mn} e^{(n+1/2)\mu} + D_{mn} e^{-(n+1/2)\mu}] \sin m\phi\}. \quad [38]$$

It is convenient to define

$$S_{kl} \equiv a^{-1}(\cosh \mu_0 - \cos \eta_0)^{-1/2} \times \epsilon_k P_l^k(\cos \eta_0) \frac{(l-k)!}{(l+k)!} \quad [39]$$

where a is the interfocal distance given in [21].

The conditions $H_p(\mu_i) = \tilde{G}(\mu_i)$, $(i = 1, 2)$, together with the orthogonality of the Legendre functions yield the equations

$$A_{kl} + \exp[-2(l + 1/2)\mu_1] B_{kl} = S_{kl} \cos(k\phi_0) \exp[-(l + 1/2)\mu_0] \quad [40a]$$

$$C_{kl} + \exp[-2(l + 1/2)\mu_1] D_{kl} = S_{kl} \sin(k\phi_0) \exp[-(l + 1/2)\mu_0] \quad [40b]$$

$$\exp[2(l + 1/2)\mu_2] A_{kl} + B_{kl} = S_{kl} \cos(k\phi_0) \exp[(l + 1/2)\mu_0] \quad [40c]$$

$$\exp[2(l + 1/2)\mu_2] C_{kl} + D_{kl} = S_{kl} \sin(k\phi_0) \exp[(l + 1/2)\mu_0] \quad [40d]$$

with the solution

$$\begin{pmatrix} A_{kl} \\ C_{kl} \end{pmatrix} = S_{kl} \left(\frac{e^{(2\mu_1 - \mu_0)(l+1/2)} - e^{\mu_0(l+1/2)}}{e^{2(l+1/2)\mu_1} - e^{2(l+1/2)\mu_2}} \right) \times \begin{pmatrix} \cos(k\phi_0) \\ \sin(k\phi_0) \end{pmatrix} \quad [41]$$

$$\begin{pmatrix} B_{kl} \\ D_{kl} \end{pmatrix} = S_{kl} \left(\frac{e^{-\mu_0(l+1/2)} - e^{(l+1/2)(\mu_0 - 2\mu_2)}}{e^{-2(l+1/2)\mu_1} - e^{-2(l+1/2)\mu_2}} \right) \times \begin{pmatrix} \cos(k\phi_0) \\ \sin(k\phi_0) \end{pmatrix} \quad [42a]$$

or alternatively

$$\begin{pmatrix} B_{kl} \\ D_{kl} \end{pmatrix} = S_{kl} e^{2\mu_1(l+1/2)} \frac{e^{(l+1/2)\mu_0} - e^{(2\mu_2 - \mu_0)(l+1/2)}}{e^{2(l+1/2)\mu_1} - e^{2(l+1/2)\mu_2}} \times \begin{pmatrix} \cos(k\phi_0) \\ \sin(k\phi_0) \end{pmatrix}. \quad [42b]$$

The solution H is therefore obtained as

$$H = a^{-1}[(\cosh \mu - \cos \eta)(\cosh \mu_0 - \cos \eta_0)]^{1/2} \times \sum_{n=0}^{\infty} \sum_{m=0}^{n} \epsilon_m \frac{(n-m)!}{(n+m)!} \cos[m(\phi - \phi_0)] \times P_n^m$$

$$\times (\cos\eta)P_n^m(\cos\eta_0)[1 - e^{2(n+1/2)(\mu_2-\mu_1)}]^{-1}$$
$$\times \{2\cosh[(n+1/2)(\mu-\mu_0)]$$
$$- e^{-(n+1/2)(\mu+\mu_0-2\mu_2)} - e^{(n+1/2)(\mu+\mu_0-2\mu_1)}\}. \quad [43]$$

Combining [43] and [35] yields the desired homogeneous Green's function as

$$G = a^{-1}$$
$$\times [(\cosh\mu - \cos\eta)(\cosh\mu_0 - \cos\eta_0)]^{1/2}$$
$$\times \sum_{n=0}^{\infty}\sum_{m=0}^{n}\left\{\epsilon_m \frac{(n-m)!}{(n+m)!}\cos[m(\phi-\phi_0)]\right.$$
$$\times P_n^m(\cos\eta)P_n^m(\cos\eta_0)[e^{-(n+1/2)|\mu-\mu_0|}$$
$$+ [1 - e^{2(n+1/2)(\mu_2-\mu_1)}]^{-1} \times (e^{-(n+1/2)(\mu+\mu_0-2\mu_2)}$$
$$+ e^{(n+1/2)(\mu+\mu_0-2\mu_1)} - 2\cosh$$
$$\left.\times [(n+1/2)(\mu-\mu_0)])]\right\}. \quad [44]$$

The solution ψ_L of Laplace's equation that satisfies the boundary conditions $\psi = \psi_i$ on S_i is obtained in a similar fashion, taking into account the radial symmetry of the system which induces independence of ϕ (only the $m = 0$ term survives). After some labor ψ_L takes the form

$$\psi_L = \sqrt{2}(\cosh\mu - \cos\eta)^{1/2}$$
$$\times \sum_{n=0}^{\infty}\left\{\left[\left(\frac{\psi_2 - e^{2(n+1/2)\mu_1}\psi_1}{e^{2(n+1/2)\mu_2} - e^{2(n+1/2)\mu_1}}\right)e^{(n+1/2)\mu}\right.\right.$$
$$\left.\left. + \left(\frac{\psi_1 - e^{-2(n+1/2)\mu_2}\psi_2}{e^{-2(n+1/2)\mu_1} - e^{-2(n+1/2)\mu_2}}\right)e^{-(n+1/2)\mu}\right]$$
$$\left.\times P_n(\cos\eta)\right\} \quad [45]$$

where $P_n(\cos\eta)$ is the nth Legendre polynomial.

VII. ANALYTICAL ITERATION SCHEME

Consider the starting solution Ψ_0 as determined in section III, expressed in bispherical coordinates, i.e.,

$$\Psi_0 = \psi_0(\mu, \eta) \quad [46]$$

and consider the charge density as

$$\rho = -(1/4\pi)\sinh[\psi_0(\mu, \eta)]. \quad [47]$$

Direct substitution of [44], [47], [45] in [31] taking into account the expression for the Jacobian

$$J(\mu_0, \eta_0) = a^3\sin\eta_0(\cosh\mu_0 - \cos\eta_0)^{-3} \quad [48]$$

yield the first iterate $\Psi_1(\mu, \eta)$ as

$$\Psi_1(\mu, \eta) = \psi_L(\mu, \eta) - \frac{\kappa^2}{4\pi}\int_{\mu_1}^{\mu_2} d\mu_0 \int_0^{\pi} d\eta_0$$
$$\times \int_0^{2\pi} d\phi_0\{\sinh[\psi_0(\mu_0, \eta_0)]J(\mu_0, \eta_0)$$
$$\times G(\mu, \eta, \phi, \mu_0, \eta_0, \phi_0)\} \quad [49]$$

since both $J(\mu_0, \eta_0)$ and $\psi_0(\mu_0, \eta_0)$ are ϕ_0 independent, the integration $d\phi_0$ of G term by term yields $2\pi\delta_{m,0}$. It is another manifestation of the importance of an accurate starting solution. If one starts with ψ_0 dependent on ϕ_0, the convergence rate is extremely slow. In [49] one may replace $\Psi_1(\mu, \eta)$ by $\Psi_{j+1}(\mu, \eta)$, $\psi_0(\mu, \eta)$ by $\Psi_j(\mu, \eta)$ and the desired iteration scheme emerges. Explicitly it takes the form

$$\Psi_{j+1}(\mu, \eta) = (\cosh\mu - \cos\eta)^{1/2}$$
$$\times \sum_{n=0}^{\infty} P_n(\cos\eta)W_{j,n}(\mu) \quad [50]$$

where $W_{j,n}(\mu)$ is given by

$$W_{j,n}(\mu) = \sqrt{2}\left(\frac{\psi_2 - e^{2(n+1/2)\mu_1}\psi_1}{e^{2(n+1/2)\mu_2} - e^{2(n+1/2)\mu_1}}\right)e^{(n+1/2)\mu}$$
$$+ \sqrt{2}\left(\frac{\psi_1 - e^{-2(n+1/2)\mu_2}\psi_2}{e^{-2(n+1/2)\mu_1} - e^{-2(n+1/2)\mu_2}}\right)e^{-(n+1/2)\mu}$$
$$- \frac{\kappa^2 a^2}{2}\int_{\mu_1}^{\mu_2} T_{j,n}(\mu_0)F_n(\mu, \mu_0)d\mu_0 \quad [51]$$

with ψ_1, ψ_2 being the boundary conditions and $T_{j,n}(\mu_0)$, $F_n(\mu, \mu_0)$ are given by

$$F(\mu, \mu_0) = e^{-(n+1/2)|\mu-\mu_0|}$$
$$+ [1 - e^{2(n+1/2)(\mu_2-\mu_1)}]^{-1}\{e^{-(n+1/2)(\mu+\mu_0-2\mu_2)}$$
$$+ e^{(n+1/2)(\mu+\mu_0-2\mu_1)} - 2\cosh$$
$$\times [(n+1/2)(\mu-\mu_0)]\} \quad [52]$$

$$T_{j,k}(\mu_0) = \int_0^{\pi} \times \frac{\sin \eta_0 P_k(\cos \eta_0)\sinh[\Psi_j(\mu_0, \eta_0)]d\eta_0}{[\cosh \mu_0 - \cos \eta_0]^{5/2}}. \quad [53]$$

The iteration [50] is a uniformly convergent scheme. However, the rate is largely dependent on the accuracy of the initial approximation. These mathematical details are beyond the scope of this paper, and will be reported elsewhere together with detailed numerical evaluations and analysis of this approach.

An alternative method was suggested by Tung (8). Since the approximation ψ_0 of the linear system is an elementary function, one may iterate the Helmholtz instead of the PB equation thus improving on the starting solution of the desired equation. Then, after desired accuracy is achieved, [50] can be employed with a faster convergent rate, or a simple numerical scheme may be implemented in a similar fashion that the asymptotic perturbation is obtained. These ideas are the subject of future investigations.

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