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Cellular solutions for the Poisson equation in extended systems

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The Poisson equation for the electrostatic potential in a solid is solved using three different cellular techniques. The relative merits of these different approaches are discussed for two test charge densities for which an analytic solution to the Poisson equation is known. The first approach uses full-cell multiple-scattering theory and results in the familiar structure constant and multipole moment expansion. This solution is shown to be valid everywhere inside the cell, although for points outside the muffin-tin sphere but inside the cell the sums must be performed in the correct order to yield meaningful results. A modification of the multiple-scattering-theory approach yields a second method, a Green-function cellular method, which only requires the solution of a nearest-neighbor linear system of equations. A third approach, a related variational cellular method, is also derived. The variational cellular approach is shown to be the most accurate and reliable, and to have the best convergence in angular momentum of the three methods. Coulomb energies accurate to within 10^{-6} hartree are easily achieved with the variational cellular approach, demonstrating the practicality of the approach in electronic structure calculations.

I. INTRODUCTION

The electrostatic potential $V(\mathbf{r})$ resulting from a charge density $\rho(\mathbf{r})$ is given by the Poisson equation

$$\nabla^2 V(\mathbf{r}) = -4\pi\rho(\mathbf{r}). \tag{1}$$

The solution of the Poisson equation is an integral part of modern electronic structure calculations. A typical electronic structure calculation utilizes an iterative process in which the Schrödinger equation is solved and its solutions are used to generate a charge density. The Poisson equation is then solved for this charge density and its solution, the electrostatic potential, is used to reconstruct the potential needed for the next iteration of the Schrödinger equation.

Although many techniques can be used to solve the Poisson equation as part of an electronic structure calculation, the procedure which is adopted in practice is often determined by the form of the potential required for the Schrödinger equation and by the form of the charge density that is output from the Schrödinger equation. Thus in techniques, such as the pseudopotential approach,[1] which employ plane wave representations of the wave functions, it is convenient to use Fourier transform techniques to solve the Poisson equation. In the augmented plane wave technique and its derivatives, the wave function is expanded in spherical harmonics inside muffin-tin spheres surrounding each atom and in plane waves outside of these spheres so that it is convenient to use a similar mixed representation when solving the Poisson equation.[2] In this paper we shall discuss techniques for solving the Poisson equation that are appropriate for electronic structure calculations which employ the multiple scattering approach.

In recent years much progress has been made in our understanding of full potential multiple-scattering theory[3–10] (MST). The following results are now clear. (i) Full potential multiple-scattering theory can be viewed as a technique in which locally exact solutions of a differential equation, valid over individual atomic cells, are combined into a global solution valid over all space.[5–7] (ii) These locally exact solutions can be constructed in such a way that (for points inside a given cell) they depend only on the contents of the cell.[3] (iii) The t matrix for a given cell contains all of the information about the contents of a cell necessary to reconstruct the globally exact solution at all points outside the cell.[7] (iv) It is vitally important to converge internal angular momentum sums.[4,5] (v) MST can be converted into a cellular theory with a nearest-neighbor secular matrix.[8] (vi) These results can be easily generalized to relativistic theories.[9,10]

In the multiple-scattering approach to electronic structure calculations the solution to the Schrödinger equation is obtained in terms of an expansion in spherical harmonics, hence the charge density is most naturally expressed in this form. Likewise, the Schrödinger equation potential is most easily used if it is expressed as an expansion in spherical harmonics. Fortunately, many of the full cell

MST techniques developed for treating the Schrödinger equation can be used to facilitate the solution of the Poisson equation.

Although Morgan first attempted a full-cell Poisson solution in 1977,[11] the ℓ convergence of various expansions was not fully understood and the numerical test given by Morgan failed to converge in ℓ. Gonis *et al.*[12] introduced the technique of shifting the center of the multipole expansion and proved that the multipole moments of a cellular charge distribution uniquely determine the potential outside the cell, even within the "moon" region (the region outside the cell but inside the circumscribing sphere of the cell). We shall show that the standard multipole expansion is convergent if summed in the proper order.

Oh *et al.*[13] also employed a scheme that is based on the ideas of multiple-scattering theory. Although their theory appears somewhat different because they avoided using the multipole moments by performing an Ewald summation for the multipole expansion at every point in the cell and incorporating its contribution into the boundary condition of the local solution, their technique is equivalent to the standard multipole expansion specialized to the case of a periodic lattice.

Another recent paper[14] calculated corrections to the usual multipole expansion based on a formula due to Sack.[15] Although these correction terms should satisfy Laplace's equation, they do not, so we suspect that they are incorrect. The numerical results obtained by Schadler do show, however, an improvement when these corrections are truncated at a finite ℓ. The cause of this apparent improvement is unclear to us at present.

We show that the potential can be represented as a local solution plus a series expansion in terms of regular solid harmonics. The coefficients in this expansion can be determined from the multipole moments of the charge density for the cells. If this multipole expansion is used it is important that the internal angular momentum sums be converged. The slow convergence of these internal sums may make the standard multipole expansion impractical. We shall show that these slowly convergent internal sums can be eliminated by the use of surface integrals over the surfaces of neighboring cells. We also show that significantly better convergence as well as the avoidance of internal angular momentum sums can be achieved by means of a cellular technique.

In Sec. II we outline the multiple-scattering approach to the solution of the Poisson equation in a manner that parallels recent developments in full potential MST for the Schrödinger equation. In Sec. III we discuss possible efficiencies and improvements in convergence that may be gained by taking advantage of the fact that there is considerable flexibility in the definition of the locally exact solutions within a given cell. In Secs. IV and V we point out that it is possible to modify the traditional MST approach to generate a cellular approach that can be made to converge faster in angular momentum than the traditional MST approach. In Sec. VI we discuss numerical tests that demonstrate the accuracy and efficiency of the various approaches. Finally, in Sec. VII we summarize our conclusions.

II. MULTIPLE-SCATTERING-THEORY APPROACH TO THE POISSON EQUATION

The Poisson equation, Eq. (1), for a charge distribution ρ and a corresponding Coulomb potential V with the boundary condition $V = V_0$ as $r \to \infty$ is equivalent to

$$V(\mathbf{r}) = V_0 + \int d\mathbf{r}' G(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}'), \tag{2}$$

where the Green function is

$$G(\mathbf{r},\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|}, \tag{3}$$

which satisfies

$$\nabla^2 G(\mathbf{r},\mathbf{r}') = -4\pi\delta(\mathbf{r}-\mathbf{r}'). \tag{4}$$

In the following we shall take $V_0 = 0$.

We shall assume for the present that we can solve the Poisson equation for a localized region of space containing cell n. Techniques for obtaining such solutions are discussed in Sec. III. Let us denote the electrostatic potential calculated for this region by $v_n(\mathbf{r}_n)$. The only property of $v_n(\mathbf{r}_n)$ which we need at present is that it satisfies the Poisson equation $\nabla^2 v_n(\mathbf{r}_n) = -4\pi\rho(\mathbf{r}_n)$ for all points $\mathbf{r}_n$ in cell n. Here and in the following we use the notation $\mathbf{r}_n$ to denote a position relative to the expansion center in cell n. In an electronic structure calculation, this expansion center would normally coincide with the position of the nucleus.

We would like to write the total electrostatic potential in cell n, $V_n(\mathbf{r}_n)$, as the local solution $v_n(\mathbf{r}_n)$ plus corrections (e.g., due to charges outside the cell). Thus we can write

$$V_n(\mathbf{r}_n) = v_n(\mathbf{r}_n) - \frac{1}{4\pi}\sum_{n'}\int_{n'} d\mathbf{r}'[G(\mathbf{r}_n,\mathbf{r}'_{n'})\nabla'^2 v_{n'}(\mathbf{r}'_{n'}) - v_{n'}(\mathbf{r}'_{n'})\nabla'^2 G(\mathbf{r}_n,\mathbf{r}'_{n'})]. \tag{5}$$

Here the first term in the integrand is simply Eq. (2) with $\rho(\mathbf{r}_{n'})$ substituted by $-\nabla^2 v_{n'}(\mathbf{r}_{n'})/4\pi$ for points in cell n'. The second term simply gives $-v_n(\mathbf{r}_n)$ by virtue of the definition of the Green function, Eq. (4). These volume integrals over the cells can be converted into surface integrals using Green's theorem,

$$V_n(\mathbf{r}_n) = v_n(\mathbf{r}_n) - \frac{1}{4\pi}\sum_{n'}\int_{n'} d\mathbf{S}_{n'}\cdot[G(\mathbf{r}_n,\mathbf{r}'_{n'})\nabla' v_{n'}(\mathbf{r}'_{n'}) - v_{n'}(\mathbf{r}'_{n'})\nabla' G(\mathbf{r}_n,\mathbf{r}'_{n'})]. \tag{6}$$

If the point $\mathbf{r}$ is inside the *inscribed* sphere of cell n, the Green function can be expanded in a convergent series of solid harmonics, so that Eq. (6) can be written as

$$V_n(\mathbf{r}_n) = v_n(\mathbf{r}_n) - \sum_L \frac{J_L(\mathbf{r}_n)}{2\ell+1}\sum_{n'}[H_L^n, v_{n'}]_{n'}. \tag{7}$$

Here the regular and irregular solid harmonics are defined as $J_L(\mathbf{r}) = r^\ell Y_L(\hat{\mathbf{r}})$ and $H_L(\mathbf{r}) = r^{-\ell-1}Y_L(\hat{\mathbf{r}})$, respectively, and $Y_L(\hat{\mathbf{r}})$ is a real spherical harmonic. We have used the notation $[f^n, g_{n'}]_{n'}$ to represent the Wronskianlike surface integral over the surface of cell n' of a function centered on site n and a function centered on site n'. Thus

$$[H_L^n, v_{n'}]_{n'} \equiv \int_{n'} d\mathbf{S}_{n'} \cdot [H_L(\mathbf{r}'_n)\nabla' v_{n'}(\mathbf{r}'_{n'}) - v_{n'}(\mathbf{r}'_{n'})\nabla' H_L(\mathbf{r}'_n)]. \tag{8}$$

Since, for given $v_n(\mathbf{r})$, the expansion in solid harmonics is unique, it follows that if this expansion is convergent the expression correctly gives the potential even at points, $\mathbf{r}$, outside the inscribed sphere. We shall show in Sec. III B and the Appendix that for a particular choice of the local solution, $v_n(\mathbf{r}_n)$, the sum over L in Eq. (7) always converges for all points $\mathbf{r}$ within the cell.

Equation (7) can be converted into the standard multipole expansion by using the expansion of the irregular solid harmonic centered in cell n in terms of regular solid harmonics centered in cell n',

$$H_L(\mathbf{r}_n) = \sum_{L'} G_{LL'}^{nn'} J_{L'}^{n'}(\mathbf{r}_{n'}), \tag{9}$$

where the zero-energy structure constants $G_{LL'}^{nn'}$ are given by[16]

$$G_{LL'}^{nn'} = (-1)^{\ell'} 4\pi \frac{(2\ell+2\ell'-1)!!}{(2\ell-1)!!(2\ell'+1)!!} \sum_{m''} \frac{Y_{\ell+\ell'\,m''}(\hat{\mathbf{R}}_{nn'})}{R_{nn'}^{\ell+\ell'+1}} \times \int Y_{\ell m}(\hat{\mathbf{r}}') Y_{\ell' m'}(\hat{\mathbf{r}}') Y_{\ell+\ell'\,m''}(\hat{\mathbf{r}}') d\Omega'. \tag{10}$$

If we make the observation that the multipole moments for each cell are given by

$$Q_L^n = -\frac{1}{4\pi} \int_n d\mathbf{S}_n \cdot [J_L(\mathbf{r}_n)\nabla v_n(\mathbf{r}_n) - v_n(\mathbf{r}_n)\nabla J_L(\mathbf{r}_n)], \tag{11}$$

then the solution for the coefficients can be cast into the more familiar form,

$$V_n(\mathbf{r}_n) = v_n(\mathbf{r}_n) - \sum_L \frac{J_L(\mathbf{r}_n)}{2\ell+1} \int_n d\mathbf{S}_n \cdot [H(\mathbf{r}_n)\nabla v_n(\mathbf{r}_n) - v_n(\mathbf{r}_n)\nabla H(\mathbf{r}_n)] + \sum_L \frac{4\pi J_L(\mathbf{r}_n)}{2\ell+1} \sum_{n'\neq n} \left[\sum_{L'} G_{LL'}^{nn'} Q_{L'}^{n'}\right]. \tag{12}$$

The sum over L' in Eq. (12) can be shown to converge if $R_{nn'}$ is larger than the largest distance from the origin of cell n' to any point within cell n'. This condition is satisfied for reasonably close packed systems. Even when this condition is satisfied, the convergence may be slow. Moreover, the maximum value of L' required for a given level of convergence will generally increase with increasing L. The issue of the convergence of the final sum (over L) is subtle and may depend on the choice that is made for the local solution, v_n. We shall return to this point in Sec. III.

Equation (12) has a simple physical interpretation. The first two terms on the right hand side represent the contribution to the electrostatic potential from the charge in cell n as will be discussed in Sec. III. The third term involving the sums over L, n', and L' represent the contributions to the potential from charges on the sites other than n. These results agree with those of Gonis *et al.*,[12] who pointed out that the multipole moments of a cellular charge distribution are sufficient to define the electrostatic potential due to that charge distribution at all points outside the cell.

It is important to remember that the internal angular momentum sum over L' in Eq. (12) must be converged before the sum over L is performed. For cells n' whose bounding spheres overlap cell n, the double sum over L and L' is, for general charge densities, only conditionally convergent. The sums must be performed in the order indicated. Alternatively, the problem of slow and conditional convergence may be avoided by using the surface integral expression of Eq. (7) for the contributions to the potential from the charge density in neighboring cells.

The existence of a convergent angular momentum expansion of the potential can be demonstrated if the electron density can be expanded to sufficient accuracy using a finite Fourier series because if the charge density is given by

$$\rho(\mathbf{r}) = \sum_{\mathbf{R}_n} Q_n \delta(\mathbf{r} - \mathbf{R}_n) + \sum_{\mathbf{G}_m}^{\mathbf{G}_{\max}} B_m e^{i\mathbf{G}_m \cdot \mathbf{r}}, \tag{13}$$

then the potential will be given by

$$v(\mathbf{r}) = \sum_{\mathbf{R}_n} \frac{Q_n}{|\mathbf{r} - \mathbf{R}_n|} + 4\pi \sum_{\mathbf{G}_m}^{\mathbf{G}_{\max}} \frac{B_m}{G_m^2} e^{i\mathbf{G}_m \cdot \mathbf{r}}. \tag{14}$$

The first series in this equation can be expanded in terms of regular solid harmonics centered at the origin [except for the term with $R_n = 0$ which can be represented by $H_0(\mathbf{r})$]. If the system is infinite the infinite contribution coming from large values of R_n will be canceled by the $\mathbf{G}_m = 0$ term in the second series. Each term in the second series can be represented by a convergent expansion of regular solid harmonics. We show in the Appendix that a convergent angular momentum expansion for the potential exists for charge distributions more general than that of Eq. (13) if one uses a local solution to the Poisson equation based on the extended charge density as defined in the next section.

III. USING TRUNCATED OR EXTENDED ρ TO CALCULATE V_N

A. Truncated ρ

If the local solution to the Poisson equation, $v_n(\mathbf{r}_n)$, is calculated using a charge density that is truncated at the boundaries of cell n, i.e., the $\rho(\mathbf{r})$ used for calculating $v_n(\mathbf{r}_n)$ does not extend outside cell n, then

$$\int_n d\mathbf{S}_n \cdot [H(\mathbf{r}_n)\nabla v_n(\mathbf{r}_n) - v_n(\mathbf{r}_n)\nabla H(\mathbf{r}_n)] = 0. \tag{15}$$

Equation (15) can be proved by noting that the surface integral can (by virtue of Green's theorem) be evaluated on the circumscribing sphere where

$$v_n^t(\mathbf{r}_n) = \sum_L \frac{4\pi}{2\ell+1} H_L(\mathbf{r}_n) \int_0^R d\mathbf{r}'_n J_L(\mathbf{r}'_n)\rho(\mathbf{r}'_n)\theta_n(\mathbf{r}'_n). \tag{16}$$

Thus $[H_L^n, v_n^t]_n$ vanishes because $[H_L^n, H_{L'}^n]_n = 0$.

Thus for truncated ρ, the potential is given by

$$V_n(\mathbf{r}_n) = v_n^t(\mathbf{r}_n) - \sum_L a_L^n \frac{J_L(\mathbf{r}_n)}{2\ell+1}, \tag{17}$$

where

$$a_L^n = \sum_{n' \neq n} [H_L^n, v_{n'}^t]_{n'}, \tag{18}$$

or by

$$V_n(\mathbf{r}_n) = v_n^t(\mathbf{r}_n) + \sum_L \frac{4\pi}{2\ell+1} J_L(\mathbf{r}_n) \sum_{n' \neq n} \left[\sum_{L'} G_{LL'}^{nn'} Q_{L'}^{n'}\right], \tag{19}$$

where $v_n^t(\mathbf{r}_n)$ is given by

$$\sum_L \frac{4\pi}{2\ell+1} [q_L^{nt}(r_n) H_L(\mathbf{r}_n) + s_L^{nt}(r_n) J_L(\mathbf{r}_n)]. \tag{20}$$

The superscript t indicates that ρ has been truncated and we have defined

$$q_L^{nt}(r_n) = \int_0^{r_n} d\mathbf{r}'_n J_L(\mathbf{r}'_n)\rho(\mathbf{r}'_n)\theta_n(\mathbf{r}'_n) \tag{21}$$

and

$$s_L^{nt}(r_n) = \int_{r_n}^R d\mathbf{r}'_n H_L(\mathbf{r}'_n)\rho(\mathbf{r}'_n)\theta_n(\mathbf{r}'_n). \tag{22}$$

The step function $\theta_n(\mathbf{r}_n)$ is defined to be unity if the point $\mathbf{r}_n$ is inside cell n and zero if it is outside.

B. Extended ρ

We can also calculate $v_n(\mathbf{r}_n)$ without truncating ρ with the step function. In this case, the particular solution to the inhomogeneous equation is

$$v_n^e(\mathbf{r}_n) = \sum_L \frac{4\pi}{2\ell+1} [q_L^{ne}(r_n) H_L(\mathbf{r}_n) + s_L^{ne}(r_n) J_L(\mathbf{r}_n)], \tag{23}$$

where the "extended" q_L^n and s_L^n are defined without the step functions used in calculating the truncated versions

$$q_L^{ne}(r_n) = \int_0^{r_n} d\mathbf{r}'_n J_L(\mathbf{r}'_n)\rho(\mathbf{r}'_n), \tag{24}$$

$$s_L^{ne}(r_n) = \int_{r_n}^R d\mathbf{r}'_n H_L(\mathbf{r}'_n)\rho(\mathbf{r}'_n). \tag{25}$$

The solution to the homogeneous equation is given by $-\sum_L a_L^{ne} \frac{J_L^n(\mathbf{r})}{2\ell+1}$ with

$$a_L^{ne} = \sum_{n'} [H_L^n, v_{n'}^e]_{n'}. \tag{26}$$

Note that now there is no exclusion of site n in the sum over n'; thus

$$a_L^{ne} = a_L^n + [H_L^n, v_n^e]_n, \tag{27}$$

since for $n' \neq n$

$$\begin{aligned} [H_L^n, v_{n'}^e]_{n'} &= [H_L^n, v_{n'}^t]_{n'} \\ &= \int_{n'} d\mathbf{r}' H_L^n(\mathbf{r}')[-4\pi\rho(\mathbf{r}')]. \end{aligned} \tag{28}$$

However, for $n' = n$, we must evaluate $[H_L^n, v_n^e]_n$, which can be written as the sum of two surface integrals, one over the muffin-tin sphere and the other which encloses the surface of the region outside the muffin-tin sphere but inside the cell,

$$\begin{aligned} &\int_n d\mathbf{S}_n \cdot [H_L(\mathbf{r}_n)\nabla v^e(\mathbf{r}_n) - v^e(\mathbf{r}_n)\nabla H_L(\mathbf{r}_n)] \\ &= r_{\mathrm{MT}}^2 \int d\Omega_n \left[\frac{Y_L(\hat{\mathbf{r}}_n)}{r_n^{\ell+1}} \frac{\partial v^e(\mathbf{r}_n)}{\partial r} \right. \\ &\quad \left. +(\ell+1)\frac{Y_L(\hat{\mathbf{r}}_n)}{r_n^{\ell+2}} v^e(\mathbf{r}_n)\right]_{r_{\mathrm{MT}}} \\ &\quad + \int_{r_{\mathrm{MT}}}^R d\mathbf{r} \frac{Y_L(\hat{\mathbf{r}})}{r^{\ell+1}} [-4\pi\rho(\mathbf{r})]\theta_n(\mathbf{r}), \end{aligned} \tag{29}$$

where the last term arises from the use of Green's theorem to convert the surface integral over the region bounded by the muffin-tin sphere and the cell boundary into a volume integral. This term is equal to $-4\pi s_L^{nt}(r_{\mathrm{MT}})$. The first term can be evaluated by substituting (23) for v^e. The contributions involving $q_L^e(r)$ cancel leaving $4\pi s_L^{ne}(r_{\mathrm{MT}})$.

Thus $V_n(\mathbf{r}_n)$ can be calculated as

$$\begin{aligned} V_n(\mathbf{r}_n) = &\sum_L \frac{4\pi}{2\ell+1} \{q_L^{ne}(r_n) H_L(\mathbf{r}_n) [s_L^{ne}(r_n) + s_L^{nt}(r_{\mathrm{MT}}) \\ &- s_L^{ne}(r_{\mathrm{MT}})] J_L(\mathbf{r}_n)\} + \sum_L a_L^n \frac{J_L(\mathbf{r}_n)}{2\ell+1}. \end{aligned} \tag{30}$$

This may be compared with the version which uses the truncated ρ

$$\begin{aligned} V_n(\mathbf{r}_n) = &\sum_L \frac{4\pi}{2\ell+1} [q_L^{nt}(r_n) H_L(\mathbf{r}_n) + s_L^{nt}(r_n) J_L(\mathbf{r}_n)] \\ &+ \sum_L a_L^n \frac{J_L(\mathbf{r}_n)}{2\ell+1}. \end{aligned} \tag{31}$$

Note that the coefficients a_L^n in (30) and (31) are given by (18). One advantage of Eq. (30) is that integrals over the step function do not have to be performed for variable limits. The integrals can be performed, for example, by Gauss-Legendre quadrature over each analytic piece of the step function defined by

$$\theta_L(r) = \int_r d\Omega Y_L(\hat{\mathbf{r}})\theta(\mathbf{r}). \tag{32}$$

A second important advantage is the fact that the angular momentum expansion can be shown to converge throughout the cell regardless of the the charge distribution. This result is shown in the Appendix.

The present discussion shows that there is considerable flexibility in the choice of the local solution $v_n(\mathbf{r}_n)$. This flexibility arises from the fact that the local solution v_n is only required to satisfy Poisson's equation within cell n. The effect of external charge distributions is to add terms which are analytic and satisfy Laplace's equation within the cell. It is easy to see that such terms cancel out between the first and second terms on the right hand side of Eq. (7). An analogous property of certain solutions to the Schrödinger equation was pointed out recently by Nesbet.[3] Note that we use the phrase "solutions to Poisson's equation" advisedly. This is not the same as the physical electrostatic potential, which, of course, does depend on the charge density outside the cell.

IV. THE GREEN-FUNCTION CELLULAR METHOD

The Green-function cellular method (GFCM) for the Schrödinger equation was developed[8] as a variation of the MST method which eliminates the structure constants and yields a strictly nearest-neighbor secular equation. The GFCM can also be applied to solve Poisson's equation. To derive the GFCM for Poisson's equation, we write Poisson's equation, Eq. (2), in the integral form

$$\sum_{n'} \int_{n'} d\mathbf{r}'_{n'} [G(\mathbf{r},\mathbf{r}'_{n'})\nabla'^2 V(\mathbf{r}'_{n'}) - V(\mathbf{r}'_{n'})\nabla'^2 G(\mathbf{r},\mathbf{r}'_{n'})] = 0, \tag{33}$$

by use of Eqs.(1) and (4). By means of Green's theorem this can be written as

$$\sum_{n'} \int_{n'} d\mathbf{S}'_{n'} \cdot [G(\mathbf{r},\mathbf{r}'_{n'})\nabla' V(\mathbf{r}'_{n'}) - V(\mathbf{r}'_{n'})\nabla' G(\mathbf{r},\mathbf{r}'_{n'})] = 0. \tag{34}$$

If $\mathbf{r}$ is inside the muffin-tin sphere inscribed within cell n, it is clear that we can write the above equation as

$$\sum_L J_L^n(\mathbf{r}_n) \sum_{n'} [H_L^n, V_{n'}]_{n'} = 0. \tag{35}$$

This implies that the solution to the Poisson equation must satisfy

$$\sum_{n'} [H_L^n, V_{n'}]_{n'} = 0 \tag{36}$$

for all n and L. The MST solution for the Poisson equation derived in Sec. II can be obtained by writing the solution as the sum of a local solution to the Poisson equation plus a solution to Laplace's equation with coefficients that are to be determined,

$$V_n(\mathbf{r}_n) = v_n(\mathbf{r}_n) - \sum_L a_L^n \frac{J_L(\mathbf{r}_n)}{2\ell+1}. \tag{37}$$

Substituting this expression into Eq. (36) and solving for a_L^n with the aid of the identity

$$[H_L^n, J_{L'}^{n'}] = (2\ell+1)\delta_{nn'}\delta_{LL'} \tag{38}$$

yields the MST result

$$a_L^n = \sum_{n'} [H_L^n, v_{n'}]_{n'}, \tag{39}$$

which may be compared with Eqs. (18) and (26).

The GFCM equations for the Poisson equation also begin with (36), but by carefully choosing which cell center one uses for expanding V on the various cell boundaries, one can cancel all contributions to the surface integrals, except those from the surface of cell n. This process is the same as was used to derive the GFCM formula for the Schrödinger equation.[8] One can obtain

$$[H_L^n, V_n]_n + \sum_{n'=n+\delta} [H_L^n, V_{n'}]_{n'\to n} = 0. \tag{40}$$

Here $n' = n + \delta$ means that n' only runs over the neighbors of n, i.e., over the atoms that share a cell face with atom n. The notation $[H_L^n, V_{n'}]_{n'\to n}$ represents a surface integral over the face separating cells n and n' with the normal to the surface pointing from cell n' to cell n.

We can also write this as

$$\sum_{n'=n+\delta} [H_L^n, V_n - V_{n'}]_{n\to n'} = 0. \tag{41}$$

This form makes it clear that the equation will be satisfied by a set of V_n's which are continuous and have continuous derivatives across the cell boundaries.

Using Eq. (37) for V_n and $V_{n'}$, we have

$$[H_L^n, v_n]_n - \sum_{n'=n+\delta} [H_L^n, v_{n'}]_{n\to n'} - \sum_{L'} [H_L^n, J_{L'}^n]_n \frac{a_{L'}^n}{2\ell'+1} + \sum_{n'=n+\delta} \sum_{L'} [H_L^n, J_{L'}^{n'}]_{n\to n'} \frac{a_{L'}^n}{2\ell'+1} = 0. \tag{42}$$

Using Eq.(38), we have,

$$[H_L^n, v_n]_n - \sum_{n'=n+\delta} [H_L^n, v_{n'}]_{n\to n'} - a_L^n + \sum_{n'=n+\delta} \sum_{L'} [H_L^n, J_{L'}^{n'}]_{n\to n'} \frac{a_{L'}^n}{2\ell'+1} = 0. \tag{43}$$

This is the GFCM approach to the Poisson equation. It seems to converge in angular momentum about as well as the Korringa-Kohn-Rostoker (KKR) approach as we show in Sec. VI. Either the truncated or extended version of the local solution, v_n can be used in Eq. (43). We find it more convenient to use the extended version.

Note that although Eq. (43) has the form of a simple linear system,

$$\sum_{n'L'} M_{LL'}^{nn'} a_{L'}^{n'} = X_L^n, \tag{44}$$

the matrix M is generally singular. This is easiest to see for the case of a periodic system with one atom per unit cell. Then, a is independent of n and

$$\sum_{n'} M_{L0}^{nn'} a_0 = -a_0 \delta_{\ell 0} + \sum_{n'=n+\delta} [H_L^n, J_0^{n'}]_{nn'} a_0, \tag{45}$$

but since $J_0^{n'} = 1$, which is independent of n',

$$\sum_{n'} M_{L0}^{nn'} a_0 \equiv 0. \tag{46}$$

In other words, the linear equations do not contain the coefficient a_0. This simply reflects the fact that the potential is undetermined up to an overall constant. This problem can be handled by eliminating the first row and column of the linear system. For the case of a nonperiodic system, or a periodic system with more than one atom per unit cell, one has to be more careful to distinguish two possibilities. In these cases either the $\ell = 0$ row for only one sublattice vanishes and therefore one removes this row and the corresponding column, or several $\ell = 0$ rows are linearly dependent, in which case one removes any one row among them and the corresponding column. These situations can be easily identified from the geometry of the system.

In the GFCM approach one avoids the cumbersome internal ℓ sum of Eq. (12). Instead one performs a set of surface integrals and solves a system of linear equations. Although in the KKR approach the multipole expansion of Eq. (12) can be avoided by using the cell surface integrals, Eq. (7), these surface integrals involve the evaluation of the irregular solid harmonics and the normal derivatives of the solution from a neighboring cell on all the surfaces of the central cell. This is a rather cumbersome process compared with that in the GFCM where one only needs the surface integrals on the surface between the two cells. However, because the GFCM approach is nonvariational, its convergence with respect to ℓ truncation is rather slow, similar to the KKR approach which is also nonvariational.[17]

V. VARIATIONAL CELLULAR METHOD

In this section we consider a variation of the GFCM in which the irregular solid harmonics (the H_L^n's) are replaced by regular solid harmonics, (J_L^n's), thus

$$[J_L^n, v_n]_n - \sum_{n'=n+\delta} [J_L^n, v_{n'}]_{n\to n'} + \sum_{n'=n+\delta} \sum_{L'} [J_L^n, J_{L'}^{n'}]_{n\to n'} \frac{a_{L'}^{n'}}{2\ell' + 1} = 0. \tag{47}$$

We shall show later that this set of equations yields solutions which are much more accurate than either the KKR approach or the GFCM approach at the same ℓ truncation. The reason that this particular technique works so well is that it can be derived from a variational principle.[18] Consider the electrostatic energy as a functional of the potential

$$U[V] = \int d\mathbf{r} \rho(\mathbf{r}) V(\mathbf{r}) - \frac{1}{8\pi} \int d\mathbf{r} \nabla V(\mathbf{r}) \cdot \nabla V(\mathbf{r}). \tag{48}$$

The variational principle $\frac{\delta U}{\delta V} = 0$ yields the Poisson equation, Eq. (1). We would like to set up Rayleigh-Ritz equations by expanding V using Eq. (37) and then evaluate $\frac{\delta U}{\delta a_L^n}$. Before we can do that, however, it is necessary to deal with the fact that in practice, because of ℓ truncation, the expansion for $V(\mathbf{r})$, Eq. (37), is in general discontinuous in value and derivative at the boundaries between the cells. Thus when the Coulomb integral in Eq. (48) is partitioned into cellular integrals, the contributions to the integral from the discontinuities at the cell boundaries have to be considered.

Consider first the integral of the square of the derivative of the discontinuous function

$$f(x) = \begin{cases} f_1(x) & \text{for } x < x_0; \\ f_2(x) & \text{for } x > x_0. \end{cases} \tag{49}$$

One can show that this integral is given by

$$\int_{-L_1}^{L_2} dx \left(\frac{df(x)}{dx}\right)^2 = \int_{-L_1}^{x_0} dx \left(\frac{df_1(x)}{dx}\right)^2 + \int_{x_0}^{L_2} dx \left(\frac{df_2(x)}{dx}\right)^2 + 2[f_2(x_0) - f_1(x_0)] \left(\frac{df_1(x_0)}{dx} + \frac{df_2(x_0)}{dx}\right) + \lim_{\epsilon\to 0} \frac{[f_1(x_0) - f_2(x_0)]^2}{2\epsilon}. \tag{50}$$

If one excludes the last term, which is singular but of second order in the discontinuity, then the contribution from the discontinuity agrees with the formula of Schlosser and Marcus.[19] When applied to the Schrödinger equation, the Schlosser-Marcus functional allows false roots in addition to the true solutions because of the exclusion of the divergent term. An observed property of the false solutions is that the function and its derivative are discontinuous at the cell boundary. The derivative changes sign but not magnitude at the cell boundary, causing the vanishing of the second to last term in Eq. (50). The last term in Eq. (50) would prohibit the false solution by adding an infinite penalty to a discontinuous function. In fact it has been shown for the Schrödinger equation in one dimension, where the effect of the divergent term and the $\epsilon \to 0$ limit can be studied analytically, that false roots are no longer found if the contribution of the divergent term is added to the secular equation.[24]

In contrast to the variational cellular method (VCM) solution of the Schrödinger equation,[18] the VCM solution of the Poisson equation produces a unique solution with no false roots. This can be understood by observing that the VCM solution to the Poisson equation is like the VCM solution to the Schrödinger equation with both $\mathbf{k} = 0$ and $E = 0$. By fixing both E and $\mathbf{k}$ one precludes the possibility of a false root which by definition would, if $\mathbf{k}$ were fixed, occur at another energy. Since the only effect of the divergent term is to prohibit false roots which are not present in our solution to the Poisson equation it can be ignored.

Applying Eq. (50), and neglecting the singular term to $U[V]$, for the case where V may not be continuous or have continuous derivatives at the boundaries separating cells one arrives at the following variational expression for $U[V]$:

$$\begin{aligned} U[V] = \sum_n \int_n d\mathbf{r} \left[\rho(\mathbf{r}) V_n(\mathbf{r}) - \frac{1}{8\pi} \nabla V_n(\mathbf{r}) \cdot \nabla V_n(\mathbf{r}) \right] \\ - \frac{1}{8\pi} \sum_n \sum_{n'=n+\delta} \int_{n\to n'} d\mathbf{S} \cdot [V_{n'}(\mathbf{r}) - V_n(\mathbf{r})] \\ \times \nabla_{n\to n'} [V_n(\mathbf{r}) + V_{n'}(\mathbf{r})]. \end{aligned} \tag{51}$$

It is straightforward to show that the functional is now stationary with respect to variations in $V_n(\mathbf{r})$. This variational functional is precisely the one that would be derived from the formalism of Schlosser and Marcus.[19] This approach first partitions the Coulomb energy into a sum over cell integrals and then constructs a functional which is stationary even when the trial expansions may have discontinuous values and derivatives at the cell boundary. Expanding $V_n(\mathbf{r})$ in the form given by Eq. (37) and taking the variation with respect to a_L^n gives Eq. (47).

VI. NUMERICAL TESTS

In this section we describe tests of the formalism presented in preceding sections. One test case is provided by the work of Slater and de Cicco,[20] who calculated to great precision, using the Ewald approach, the electrostatic potential of a uniform positive charge density and balancing negative unit point charges on an fcc lattice of unit lattice constant. The Ewald method is often used for muffin-tin charge densities where the interstitial charge is a constant.[23] This "Slater–de Cicco" test becomes a rather rigorous test of a full-potential method for the Poisson equation if one views the system as a collection of cellular charge distributions, each of which has a multipole expansion to infinite order due to the nonspherical shape of the cells.

Slater tabulated the electrostatic potential on a uniform mesh of points spanning the fcc Wigner-Seitz cell.[20] Figure 1 shows the *nonspherical* part of this potential. We have plotted the potential along symmetry lines of the fcc Wigner-Seitz cell. Since the fcc Wigner-Seitz cell has the same shape as the bcc Brillouin zone we use the notation that is commonly used to label points in reciprocal space for a bcc lattice. We emphasize, however, that the figures are plots in real space. The point labeled Γ is at the origin, the point labeled H is at (0.5,0.0,0.0), the point labeled N is at (0.25,0.25,0.0), and the point labeled P is at (0.25,0.25,0.25). All of these are in units of the lattice constant.

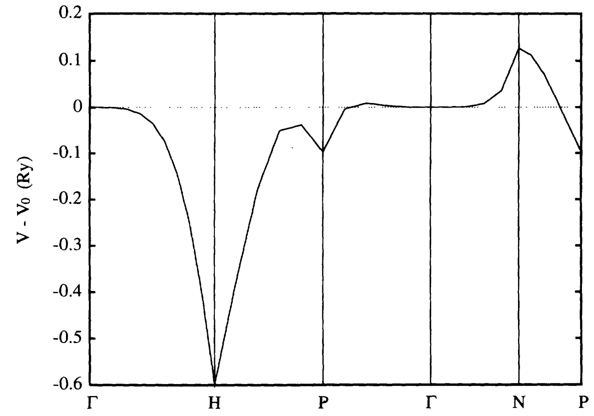

FIG. 1. Nonspherical part of the electrostatic potential for a uniform charge density with balancing point charges on an fcc lattice as calculated by Slater and de Cicco (Ref. 20). Symbols on the abscissa label symmetry points of the fcc Wigner-Seitz cell.

Figure 2 shows the difference between the exact results obtained by Slater and de Cicco and the results obtained using Eq. (31) for differing values of $l_{\max}$. In calculating the contribution from neighboring cells, we found it to be necessary to take the maximum value of l' in the sum on L' in Eq. (12) to be approximately three times the maximum value of l used in the sum in Eq. (30). The large number of multipoles needed results from the discontinuities at the cell boundaries. A scheme which could partition the charge density on each site without introducing radial or angular discontinuities would probably not need such high values of l'. The results using Eq. (30) are denoted by KKR on the figure since this technique for solving the Poisson equation is closely analogous to the Korringa-Kohn-Rostoker technique[21,22] for

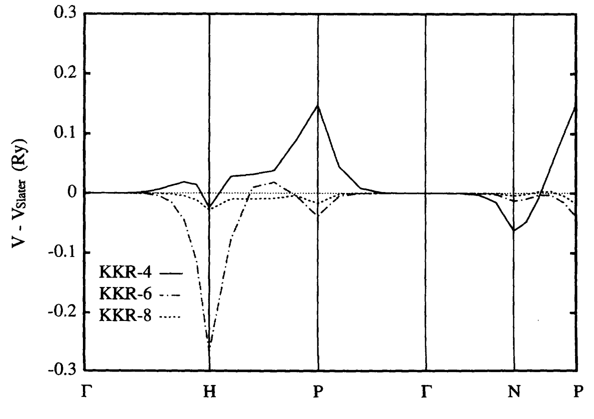

FIG. 2. Test of KKR technique for solving the Poisson equation using the Slater–de Cicco model. The internal angular momentum sums used in calculating the multipole contributions from neighboring sites were truncated at three times $\ell_{\max}$ in each case.

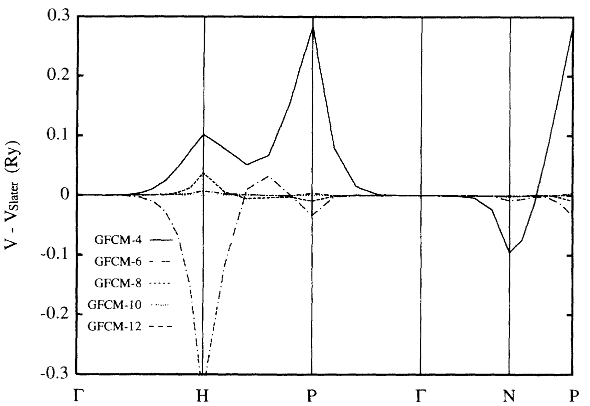

FIG. 3. Test of GFCM technique for solving the Poisson equation using the Slater–de Cicco model.

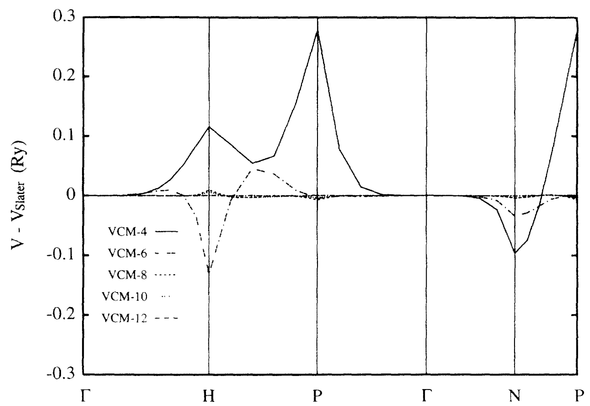

FIG. 4. Test of VCM technique for solving the Poisson equation using the Slater–de Cicco model.

solving the Schrödinger equation for a periodic potential.

The fcc crystal structure has cubic (O_h) symmetry; hence there is no contribution from odd values of ℓ or from $\ell = 2$. In addition, there are single independent coefficients for $\ell = 4$, 6, 8, and 10 and two independent coefficients for $\ell = 12$ and $\ell = 14$. This observation reflects the fact that the potential can be expanded in cubic harmonics belonging to the a_{1g} or Γ_1 representation of the O_h group.

The agreement between Slater's results and the KKR results truncated at $\ell_{\max} = 4$ is fair. There are significant errors for fairly small values of r even within the muffin-tin radius ($r = 0.353\,55$, i.e., the distance of the point N from the origin), implying incomplete convergence at $\ell_{\max} = 4$. For $\ell_{\max} = 6$, the agreement is much better at small values of r, but appears to be worse for points in the interstitial region. At $\ell_{\max} = 8$, the agreement is good but there are still discernible discrepancies especially for the larger radii near the corners of the fcc cell.

Since the GFCM approach does not require convergence of internal ℓ sums, it is easier to use a higher value of $\ell_{\max}$ in the expansion of the potential. Figure 3 shows a comparison between Slater's results and the nonvariational GFCM approach, Eq. (42) for $\ell_{\max} = 4, 6, 8, 10$, and 12. The results appear to be of comparable accuracy to those obtained from the KKR approach for a given value of ℓ truncation except perhaps for the $\ell_{\max} = 4$ results which seem to be fortuitously good in the corner of the cell (near H) for the KKR technique. However, as can be seen from Fig. 3, the overall quality of the potential improves consistently as $\ell_{\max}$ is increased. A quantitative measure of the fit, given in Table I, confirms this observation.

Figure 4 shows a comparison between Slater's results and the VCM approach, Eq. (47). The agreement can be seen to be very good especially for ℓ truncations of 8, 10, and 12. Table I shows the root mean square error over the cell for the various approaches. It can be seen that aside from the KKR $\ell_{\max} = 4$ results, the VCM approach gives better agreement at every level of truncation and is of sufficient accuracy to be used in electronic structure calculations.

Another numerical test for which the exact solution is known is the model used by Morgan,[11] with the charge density given by

$$\rho(\mathbf{r}) = B \sum_n e^{i\mathbf{T}_n \cdot \mathbf{r}} \tag{52}$$

distributed over a fcc lattice. $\mathbf{T}_n$ are the nearest-neighbor reciprocal lattice vectors. The Coulomb potential for this charge density is

$$V(\mathbf{r}) = 4\pi\rho(\mathbf{r})/T^2 + \text{const}, \tag{53}$$

where T is the length of the vectors $\mathbf{T}_n$. Unlike the work of Morgan,[11] we chose $B = 1$ and a lattice constant of unity since this produced a nonspherical potential of roughly the same magnitude as that found for the Slater potential. Figure 5 shows the comparison between the exact results and those calculated using the VCM approach at various levels of ℓ truncation. The level of agreement is generally very good. Table II shows the variation in the Coulomb energy and cell charge with $\ell_{\max}$. The last column indicates the exact results. By ℓ=10 convergence of the Coulomb energy to better than 10^{-6} hartree is achieved.

TABLE I. Comparison of the root mean square error for different techniques and different angular momentum truncations for solving Poisson's equation for Slater's test of an fcc lattice of point charges in a compensating uniform background.

$\ell_{\max}$	4	6	8	10	12	14
KKR	0.028 467	0.034 474	0.004 392			
GFCM	0.053 001	0.044 885	0.004 572	0.004 609	0.001 005	
VCM	0.053 631	0.018 641	0.001 476	0.001 100	0.000 193	0.000 167 8

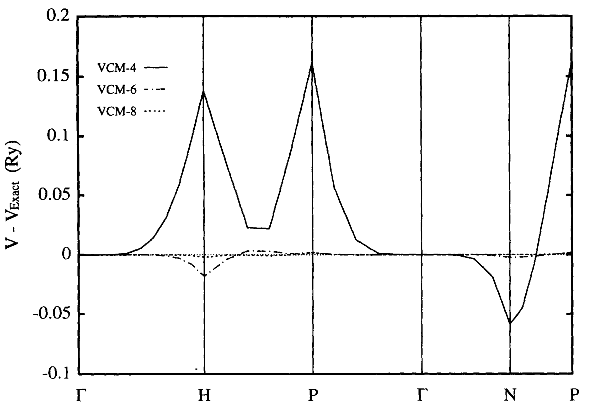

FIG. 5. Test of VCM technique for solving the Poisson equation using Morgan's model for $\ell_{\max} = 4{,}6{,}8$.

Notice that at the same ℓ truncation the agreement of the VCM and the exact potentials is much better than in the Slater test. This is due to the fact that the ℓ convergence for the cell potential is more rapid in the Morgan test than in the Slater test. In the Morgan test the potential converges in ℓ at the same rate as the charge density, which has converged at $\ell = 8$. This convergence can be judged by looking at the net charge in the cell which should, of course, be exactly zero (see Table II). In the Slater test while the charge density converges at $\ell = 0$, the potential converges at a much slower rate. In view of this, we believe that the Slater test is a much more rigorous test of a full-cell electrostatic solution.

We did not perform a careful study of the computer time necessary to calculate the potential as a function of $\ell_{\max}$ and other parameters for each of these methods because it depends on other considerations such as programming technique and optimization as well as the inherent efficiency of the technique. Generally, we found that the KKR calculations required more computer time than the GFCM and VCM calculations because of the need to calculate internal sums to high values of angular momentum. The GFCM and the VCM calculations at the same ℓ truncation take exactly the same time. The largest VCM calculations required approximately two minutes on an IBM RS-6000 model 370.

VII. CONCLUSIONS

We have shown that the techniques of full-cell multiple-scattering theory can be applied to the solution of Poisson's equation. The global solution can be written in terms of a local solution plus other terms which contain the contribution to the potential from charges in other cells and which ensure the continuity and smoothness of the global solution. In calculating the local solution one can use either a truncated charge density, which vanishes outside the cell, or an extended charge density. Use of the latter can be shown to lead to a series representation of the potential which is convergent at all points within the cell. The contributions to the potential at points within a given cell due to charges outside that cell can be written in terms of a sum over the multipole moments of those cells provided that the cells are sufficiently compact that the intercellular distance exceeds the radii of both of the circumscribing spheres.

We have shown that a cellular method (the GFCM) can also be derived from the MST formalism and used to solve the Poisson equation. Moreover, a variational cellular method (the VCM) appears to offer the best convergence of the techniques that we have investigated. The GFCM and the KKR approaches show similar convergence rates in terms of ℓ truncation. The slow rate of convergence for the KKR approach is consistent with the previous work. In both Refs. 12 and 13 reasonable convergence was achieved only at about $\ell_{\max} > 30$. However, the convergence of the variational cellular approach is much faster. This is because at any ℓ truncation, although the KKR method calculates each a_L, and therefore V_L, more accurately, provided all the internal sums are converged, the cellular method gives a set of approximate a_L's that fit the exact potential better at that level of truncation since the solution is one which tries to minimize the Coulomb energy.

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TABLE II. Convergence of Coulomb energy (U) in hartrees and net cell charge (Q) calculated using the VCM approach for Morgan's test charge density.

$\ell_{\max}$	4	6	8	10	12	Exact
U	0.096 132 9	0.106 708 5	0.106 141 7	0.106 103 7	0.106 103 2	0.106 103 3
Q	1.6×10^{-2}	-4.2×10^{-4}	-4.4×10^{-5}	-9.9×10^{-7}	3.0×10^{-8}	0.0

No. W-7405-Eng-48 with Lawrence Livermore National Laboratory.

APPENDIX: CONVERGENCE OF THE SPHERICAL HARMONIC EXPANSION OF THE POTENTIAL

Here we show that the angular momentum expansion converges quite generally when one uses a local solution based on the extended charge density. The electrostatic-potential due to charge density $\rho(\mathbf{r})$ can be written as an integral over all space,

$$V(\mathbf{r}) = \int G(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}'. \tag{A1}$$

If $\mathbf{r}$ is restricted to be within cell n then the electrostatic potential $V(\mathbf{r})$ can be written in the form

$$V(\mathbf{r}) = -\frac{1}{4\pi}\int_0^R \nabla'^2 G(\mathbf{r},\mathbf{r}')V(\mathbf{r}')d\mathbf{r}', \tag{A2}$$

where the integral is over the region enclosed by a spherical surface of radius R which circumscribes cell n. To this equation we can add zero in the form of an integral over $\nabla^2 V + 4\pi\rho$,

$$\begin{aligned} V(\mathbf{r}) = &-\frac{1}{4\pi}\int_0^R \nabla'^2 G(\mathbf{r},\mathbf{r}')V(\mathbf{r}')d\mathbf{r}' \\ &+\frac{1}{4\pi}\int_0^R G(\mathbf{r},\mathbf{r}')[\nabla'^2 V(\mathbf{r}') + 4\pi\rho(\mathbf{r}')]d\mathbf{r}'. \end{aligned} \tag{A3}$$

Thus, rearranging terms, we have,

$$\begin{aligned} V(\mathbf{r}) = &\int_0^R G(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}' \\ &+\frac{1}{4\pi}\int_0^R [G(\mathbf{r},\mathbf{r}')\nabla'^2 - \nabla'^2 G(\mathbf{r},\mathbf{r}')]V(\mathbf{r}')d\mathbf{r}'. \end{aligned} \tag{A4}$$

The last two terms can be converted by means of Green's theorem into an integral over the circumscribing surface of radius R,

$$\begin{aligned} V(\mathbf{r}) = v_n^e(\mathbf{r}) + \frac{1}{4\pi}\int_R d\mathbf{S}' \cdot [G(\mathbf{r},\mathbf{r}')\nabla' \\ -\nabla' G(\mathbf{r},\mathbf{r}')]V(\mathbf{r}'). \end{aligned} \tag{A5}$$

Since all points on the surface satisfy $r' > r$ we can expand the Green function in a convergent expansion and obtain

$$V(\mathbf{r}) = v_n^e(\mathbf{r}) + \sum_L \frac{J_L^n(\mathbf{r})}{2\ell + 1}[H_L^n, V]_R. \tag{A6}$$

Comparison with Eq. (7) for the case $v_n = v_n^e$ yields

$$[H_L^n, V]_R = -\sum_{n'}[H_L^n, v_{n'}^e]_{n'}. \tag{A7}$$

This can also be shown directly by observing that for any finite charge distribution confined within a surface S, the surface integral $[H_L^n, V]_S = 0$ vanishes. Therefore we can write,

$$[H_L^n, V]_R = -\sum_{n' \neq n}[H_L^n, v_{n'}^e]_{n'} + [H_L^n, v_n^e]_M, \tag{A8}$$

where the subscript M indicates that the second surface integral is over the "moon" region bounded by the surface of cell n and the surface of the sphere circumscribing this cell. However, since

$$[H_L^n, v_n^e]_S = [H_L^n, v_n^e]_n + [H_L^n, v_n^e]_M = 0, \tag{A9}$$

it follows that the $[H_L^n, v_n^e]_M = -[H_L^n, v_n^e]_n$ from which follows Eq. (A7).

It is easy to find charge densities for which the angular momentum expansion does not converge if one uses the local solution v_n^t for the truncated charge density but does converge for the extended version v_n^e. One such example would be the case where there is a point charge in the moon region. The requirements on the charge distribution sufficient to ensure convergence when the truncated version of the local solution is used are unclear to us, but we speculate that continuity of the charge density and its spatial derivatives should suffice. It should be noted that Brown and Ciftan[25,26] have advocated use of the "extended" solutions for the Schrödinger equation as well as the Poisson equation.

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