Removed sphere method for Poisson's equation

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Abstract
We propose a straightforward method for solving the Poisson equation that is
appropriate for charge densities expressed as spherical harmonic expansions,
for example, electron densities in full potential multiple scattering electronic
structure codes. The method is conceptually simple, is accurate, has
computation times that scale linearly with the number of expansion centres
(atoms) up to thousands of atoms and can be efficiently implemented on
massively parallel processor computers.

1. Introduction

Solving the Poisson equation (in Hartree atomic units),

$$\nabla^2 v(\boldsymbol{r}) = -4\pi\rho(\boldsymbol{r}), \tag{1}$$

for the electrostatic potential, $v(\boldsymbol{r})$, in terms of the charge density, $\rho(\boldsymbol{r})$, is important in the
context of first principles density functional (DF) calculations.

In DF theory the electron density is often represented by a sum of plane waves or augmented
plane waves. The k-space nature of these representations is well suited to the calculation of
the Hartree potential. This has facilitated the development of full potential electronic structure
codes based on plane wave representations. In an alternative set of methods based on multiple
scattering theory (MST) it is assumed that the electron density and one-electron potential
are well represented by spherical harmonic expansions about the nuclear positions. Methods
that express the electron density as spherical harmonic expansions include the Korringa–
Kohn–Rostoker (KKR) [1], the quadratic KKR [2], locally selfconsistent multiple scattering
(LSMS) [3, 4], locally selfconsistent Green function (LSGF) [5], layer KKR [6], linearized
muffin-tin orbital (LMTO) [7], Green function impurity method [8] and others. The optimum
method for solving the Poisson equation in MST codes is yet to be determined. Although
there are several techniques that purport to conveniently construct the Hartree potential
corresponding to an electron density expanded in this manner, no technique has emerged
as preeminent. In this paper we propose a method that is particularly straightforward. We
argue its merits and present an example of its application to an exactly solvable problem. We
also relate it to the widely used method of Gonis *et al* [9].

Electron densities found in materials and the corresponding Hartree potentials have expansions that converge rapidly in angular momentum[1]. Hence, we shall assume that the electron density is supplied up to a sufficiently high angular momentum, $l_{max\text{-}\rho}$, to converge it, and that the task at hand is to find the Lth component of the potential expanded about a nucleus taken, for simplicity, to be at the origin. The potential components are sought up to $l_{max\text{-}v}$ which is typically equal to $l_{max\text{-}\rho}$. Our method introduces an additional parameter, $l = l_{max\text{-}neighbour}$, the angular momentum cut-off of the truncated electron density on the sites neighbouring the origin. The convergence of the potential with respect to this parameter is investigated by comparison to an exactly solvable model introduced by Morgan [10].

At the time of early full potential multiple scattering calculations [2] there were serious questions [11–14] about the applicability of MST to potentials that are non-zero beyond the region formed by non-overlapping spheres centred at each scatterer. There were questions about whether or not the MST solution could be cast in terms of the atomic scattering matrices alone. In the zero-energy limit where the Schrödinger equation becomes the Poisson equation the issue becomes whether or not the potential outside a Wigner–Seitz cell can be given in terms of the moments of the cell charge alone. The resolution of these questions [15, 16] has motivated development of several methods to accurately determine the potential for site expanded electron densities [9, 17–20]. These methods are not approximations; they claim to provide solutions of arbitrary accuracy if the various sums are properly converged. These proposed methods should therefore give accurate results if internal parameters are taken to convergence. The method of Gonis has the convenience of requiring only the electron density in the local cell and the multipole moments of all other cells. Furthermore, its specification of the solution in terms of the moments alone directly supports and sheds light on the solution on the Schrödinger equation in terms of the single-site scattering matrices alone. Because the ultimate accuracy of all methods should be comparable, the utility of the techniques will be determined by ease of coding, memory requirements and the number of operations required to reach the desired level of accuracy. We believe that the method proposed here is conceptually simpler and easier to implement than other methods. Furthermore, the computation time scales linearly with the number of atoms with the exception that the Ewald procedure to account for the isotropic contribution to atomic potentials from surrounding monopoles requires operations of $O(N^2)$. This $O(N^2)$ term is small for systems as large as thousands of atoms. Furthermore, this method can be parallelized efficiently because very little communication between processors is required. Because it is essentially $O(N)$ and efficiently implemented on massively parallel processor computers it requires a small amount of time compared with the solution of the MST equations.

2. Method

To simplify discussion we temporarily remove the nucleus at the origin so that only electrons contribute to the charge density around the origin and the potential is nonsingular. The nuclear potential Z/r can be added at the end of the discussion. Nuclei are assumed to occupy all other atomic sites. We shall also assume that the problem of determining the electrostatic potential near the origin from a collection of point multipole moments of any extent is obtainable by techniques described elsewhere [21–23] provided the multipole expression for the potential at the origin from each site individually converges in angular momentum. This will hold for site i provided its moments are derived from the charge density inside its Wigner–Seitz cell, Ω_i, and provided its circumscribing sphere, $r_{c,i}$ does not enclose the origin [24]. In many cases determining the multipole potential may be as simple as applying the Ewald procedure [25]

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[1] It is necessary in some lattices to introduce empty or vacancy sites that do not contain a nucleus.

for the monopole moments and either a straightforward summing of the contributions from higher multipole moments or an extended Ewald method [21,22]. For nonperiodic collections of moments, fast multipole methods have been developed [23].

A simple and fast algorithm (algorithm I) gives the potential anywhere within the unit cell but leaves the constant multiplying the homogeneous solution unspecified. In algorithm I the charge is divided into that which is interior to the circumscribing sphere of the cell at the origin and that which is exterior. The Lth component of the potential contributed by the charge, ρ_L^e (extended charge density), inside the circumscribing sphere of radius r_c is simple to calculate at all radii inside the sphere. A solution to the Poisson equation for ρ_L^e is [26]

$$v_L^e(r) = \frac{4\pi}{2l+1}\left(\int_0^r r'^2\,\mathrm{d}r'\,\frac{r'^l}{r^{l+1}}\rho_L^e(r') + \int_r^{r_c} r'^2\,\mathrm{d}r'\,\frac{r^l}{r'^{l+1}}\rho_L^e(r')\right). \tag{2}$$

The charge outside r_c contributes to the potential at radii inside r_c in a particularly simple way. The charge outside the sphere determines the coefficient, a_L, of the homogeneous solution, $a_L r^l$. If the single number a_L were known the Lth component of the potential would be known at all points in the sphere and our problem would be solved. The total potential is [18]

$$v_L(r) = v_L^e(r) + a_L r^l. \tag{3}$$

Another simple and fast algorithm (algorithm II) gives the potential, but only at points near the origin. First, the electron density is truncated at the Wigner–Seitz cell boundaries using the spherical harmonic expansion, about the nuclear position, of the cell step function $\sigma(\mathbf{r})$ [27] to obtain spherical harmonic expansions of the truncated electron densities about their respective nuclei.

$$\rho_L^t(r) = \sum_{L',L''}^{L_{\max-\rho},L'+L}\int_0^{r_c}\mathrm{d}\Omega_r\,\rho_{L'}^e(\mathbf{r})Y_{L'}(\mathbf{r})\sigma_{L''}(\mathbf{r})Y_{L''}(\mathbf{r})Y_L^*(\mathbf{r}). \tag{4}$$

Second, the potential, $v_L^t(r)$, associated with the truncated density centred at the origin is calculated 'l by l,' using equation (2) but with ρ_L^e replaced by ρ_L^t. Third, the multipole moments, $q_{i,L}^t$, of the truncated electron density on each site are calculated. The potential near the origin is the sum of v^t and the potential of the surrounding multipole moments:

$$v_L^{l_{max-neighbour}}(r) = v_L^t(r) + v_L^{mult}(\{q_L^t\},r,l_{max-neighbour}); \tag{5}$$

$$v_L^{mult}(r) = \int\mathrm{d}\Omega_r\sum_{i,L'}^{l_{max-neighbour}}\frac{4\pi}{2l+1}\frac{q_{i,L}^t Y_{L'}(\mathbf{r}-\mathbf{R}_i)Y_L(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_i|^{l+1}}. \tag{6}$$

The multipole moments can be obtained from v^t on each site:

$$\frac{4\pi}{2l+1}\frac{q_{i,L}^t}{r_c^{l+1}} = v_{i,L}^t(r_c). \tag{7}$$

Performing the angular integration in equation (6) gives

$$v_L^{mult}(r) = a_L^{mult}(l_{max-neighbour})r^l \tag{8}$$

where

$$a_L^{mult}(l_{max-neighbour}) = \sum_i\sum_{L'}B_L^{L'}Y_{l+l',m'-m}^*(\mathbf{R}_i)(q_{i,L'}^t + \delta_{l=0}Z_i Y_{0,0})/R_i^{l+l'+1} \tag{9}$$

and

$$B_L^{L'} = (4\pi)^{3/2}\left(\frac{(l+l')!(2l+2l'-1)!!}{l!(2l+1)!!l'!(2l'+1)!!}\right)^{1/2}(-)^{l'+m'}\begin{pmatrix} l & l' & l+l' \\ -m' & m & m'-m \end{pmatrix}. \tag{10}$$

The last factor is the Wigner $3j$-symbol.

The limitation of algorithm II is that it is convergent only near the origin. But convergence near the origin is all that is required to determine the coefficient, a_L, that is unspecified by algorithm I. Algorithms I and II work together to give a final expression for the potential:

$$v_L(r) = v_L^e(r) + \text{limit}_{r_f \to 0; l_{max\text{-}neighbour} \to \infty} (v_L^{l_{max\text{-}neighbour}}(r_f) - v_L^e(r_f))\left(\frac{r}{r_f}\right)^l. \tag{11}$$

$$v_L(r) = v_L^e(r) + \text{limit}_{l_{max\text{-}neighbour} \to \infty}$$
$$\times \left(\frac{4\pi}{2l+1} \int r^2 \, \mathrm{d}r \, \frac{(\rho_L^t(r') - \rho_L^e(r'))}{r^{l+1}} + a_L^{mult}(l_{max\text{-}neighbour})\right) r^l. \tag{12}$$

The method of Gonis [9] which we shall refer to as the removed cell method, RCM, relies on similar concepts although its derivation had a different motivation. The motivation for the RCM was to prescribe the potential outside a cell in terms of only the charge moments. The full solution is given by superposition. Here we provide a derivation that closely follows the above derivation of the RSM. First the charge is divided into that which is within the Wigner–Seitz cell at the origin, Ω_0 and that which is not. The total potential is

$$v_L(r) = v_L^t(r) + b_L r^l \Theta(r_{ins} - r) + f_L(r)\Theta(r - r_{ins}). \tag{13}$$

The last term on the right-hand side is a homogeneous solution that matches $b_l r^l$ at the inscribed sphere radius, r_{ins}, and matches the potential at the cell boundary. This is more complicated than the RSM where the form $a_l r^l$ is used throughout. In order to find the potential contributed by charge outside the cell at the origin, the charge is broken into contributions from each Wigner–Seitz cell, Ω_i. The cells whose circumscribing spheres do not intersect the cell at the origin contribute a potential of the far field multipole form given by equation (6). The neighbouring cells also contribute as far multipole fields for points outside their circumscribing spheres but the situation inside the circumscribing sphere of Ω_i and also inside Ω_0 (the moon region) must be treated more carefully. For each point, r_0, in the moon region we can pick a point, $R(r_0)$, outside the $r_{c,i}$ such that a sphere centred at $R(r_0)$ does not intersect Ω_i. Inside this sphere the potential can be expanded as $\sum_L c_L (r - R(r_0))^l$. The point $R(r_0)$ is outside the circumscribing sphere so the potential near $R(r_0)$ can be evaluated with the simple far field multipole expression. This allows the c_L to be determined and the potential at r_0 to be evaluated by summation over L. Removing a cell instead of a sphere has required the use of a different expansion point, $R(r_0)$, for each r_0 whereas in the RSM the origin can be used for all $R(r_0)$. The RCM has, in a somewhat circuitous way, provided the value of the potential at all points inside Ω_0. If one is interested in the spherical harmonic expansion of the extended potential inside $r_{c,0}$ there is an integral over angles that requires values of the potential from Ω_0 and neighbouring cells Ω_i. If the expansion of the truncated potential is required then the spherical expansion of the step function must be used to avoid the use of the RCM expression for $V(r_0)$ outside Ω_0 because $V(r_0)$ is valid only inside Ω_0. The RSM requires one convergent sum over angular momentum to obtain $V_L(r)$ whereas the RCM requires two sums one of which is conditionally convergent. Gonis and others have successfully implemented the RCM so it is clear that its complexities can be mastered. Here, we point out that a simpler procedure is possible if one makes the choice of removing a sphere instead of a cell.

3. Morgan test

Morgan [10] introduced a test density and its exact solution:

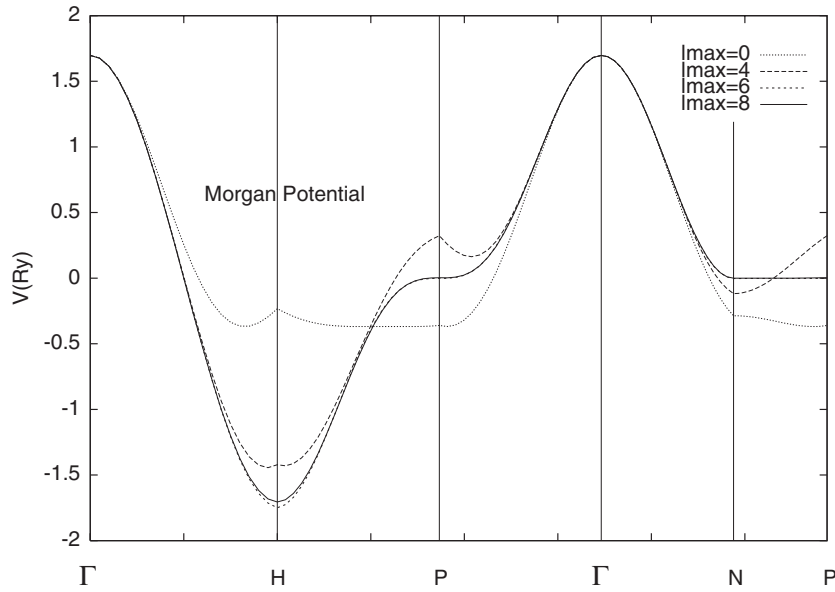$$\rho(r) = B \sum_n \mathrm{e}^{\mathrm{i}T_n r}; \tag{14}$$

Figure 1. Convergence w.r.t. the maximum l used in summing the exact spherical harmonic expansion of the Morgan potential. Symbols on the abscissa label symmetry points of the fcc Wigner–Seitz cell. The solid line represents both the exact result and the sum up to $l = 8$ of the exact spherical harmonic expansion.

T_n are the nearest neighbour fcc reciprocal lattice vectors. The corresponding potential is

$$v(r) = 4\pi\rho(r)/T^2 + \text{constant.} \tag{15}$$

We choose the lattice constant and B equal to 1.0. The potential and density are easily expanded in spherical harmonics

$$\rho_L(r) = 4\pi j_l(\text{Tr})\text{i}^l \sum_n Y_L(T_n) \tag{16}$$

and

$$v_L(r) = (4\pi)^2 j_l(\text{Tr})\text{i}^l \sum_n Y_L(T_n)/T^2 + \text{constant } \delta_{l,0}. \tag{17}$$

The potential at any point in the central cell can be calculated via equations (14) and (15) by summing over n or via equation (17) by summing over L and n; however, the exact potential as calculated from equations (14) and (15) will be approached only in the limit $l \to \infty$. In figure 1 we compare the exact potential from equation (15) with the potential reconstructed from the exact v_L given by equation (17) but summed up to values of $l = 2, 4, 6$ and 8. Observe that the potential converges rapidly in angular momentum; the $l = 8$ values agree with the exact values to within the thickness of the line.

In figure 2, the potential calculated with $l_{max\text{-}v} = l_{max\text{-}\rho} = 8$ is shown as a function of $l_{max\text{-}neighbour}$ beginning at $l_{max\text{-}neighbour} = 10$. Even for low values of $l_{max\text{-}neighbour}$ the potential is reasonable throughout most of the cell volume. However near the cell boundary and particularly at the corners of the cell disagreement is substantial. For $l_{max\text{-}neighbour} = 8$ (not shown) the error at H is 0.21, hence the usefulness of potentials calculated with low values of $l_{max\text{-}neighbour}$ is questionable. When $l_{max\text{-}neighbour} = 10$ the error at H is down to a few per cent and the potential is adequate for many applications. The potential converges to the exact result as $l_{max\text{-}neighbour}$ is further increased.
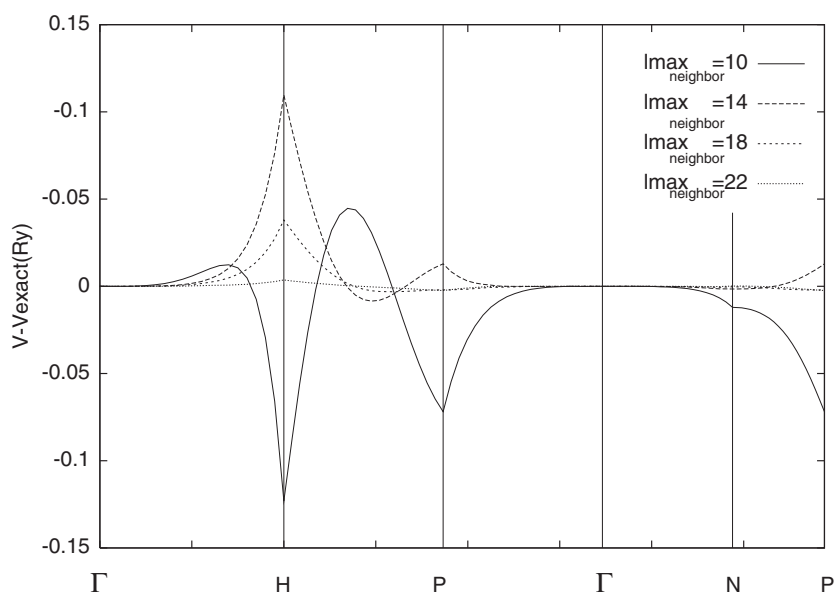
Figure 2. Error in the calculated Morgan potential as a function of $l_{max-neighbour}$.
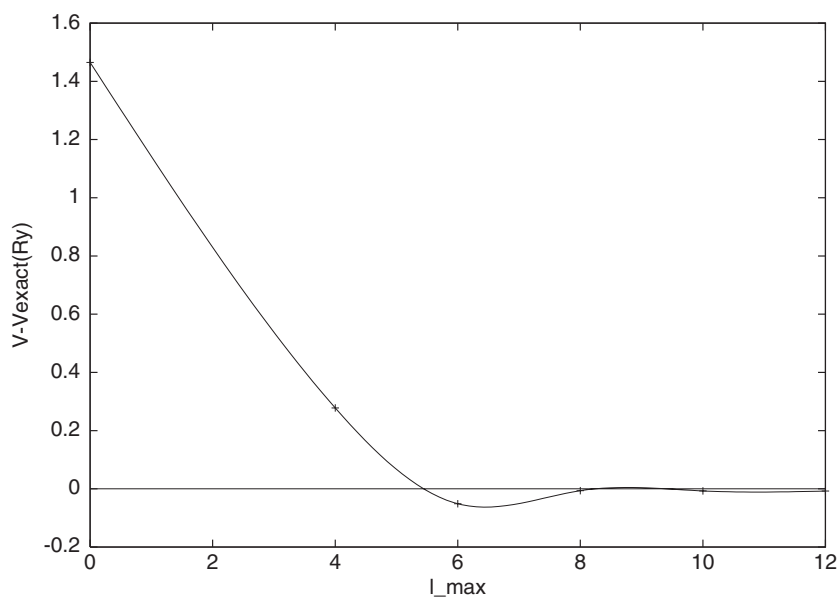

Figure 3. Error in potential at $H = (100)/2$ as a function of $l_{max-\rho}$ for $l_{max-neighbour} = 22$.

In figure 3, $l_{max-neighbour}$ has been set equal to 22 and the error in the potential at the 'H-point' is plotted as a function of $l_{max-\rho}$. We observe that the potential is well converged at $l_{max-\rho} = 8$.

4. Implementation

This algorithm has been implemented within the LSMS [3,4]. Each atom is assigned a process. Each process computes $= v_L^e(r)$ of its assigned atomic nucleus. The values of the moments are exchanged among all processes so that each process can construct the Madelung contribution to its local potential. Monopole contributions are handled by the Ewald method. If there are dipole terms that cannot be converged by the direct summation in equation (8) they can also be incorporated via an Ewald procedure.

The method is 'order N' except for the Ewald procedure which is O[N^2] where N is the number of atoms in the system or unit cell.

5. Conclusions

We have presented a straightforward procedure for calculating the solution to Poisson's equation when the charge density is represented by a spherical harmonic expansion. We have demonstrated the precision of the method by comparing with exact results for the Morgan density.

This method is specifically for those situations in which the potential and charge density are well represented by site expansion in spherical harmonics. It is assumed that the charge density and potential within the circumscribing sphere of each Voronoi polyhedron are rapidly convergent in l about some point inside each cell. If this situation is not attainable by any choice of cells including the introduction of empty cells, then the procedure is not applicable. However, if such a choice of cells is not obtainable then multiple scattering methods, likewise, are not applicable. If the charge and potential can be expanded in spherical harmonics the method proposed has one parameter, $l_{max\text{-}neighbour}$, with respect to which it must be converged. The convergence with respect to this parameter is demonstrated for an exactly solvable case.

In this paper we have calculated the Hartree potential without taking advantage of a reference charge density. It should be remembered that in practice it is useful to subtract from the electron density a reference charge density. A reference electron density can be any density for which the exact solution is easily obtained. This can increase the accuracy by lessening the demands on the cell shape function and thereby accelerating the convergence in $l_{max\text{-}neighbour}$ of the potential contributions from the neighbouring sites. Simple choices for a reference charge density are a uniform density with compensating point charges, overlapped atomic charge densities, or a potential previously calculated to high precision with this or another method for a similar system. Another modification that would accelerate the l convergence is the use of 'fuzzy' cell shape functions that go to zero continuously and overlap in such a manner that the sum over all cell shape functions is equal to unity at every point in space.

Acknowledgments

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