Comment on “Accurate and fast numerical solution of Poisson's equation for arbitrary, space-filling Voronoi polyhedra: Near-field corrections revisited”

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Phys. Rev. B **86**, 127101 — Published 20 September 2012

DOI: 10.1103/PhysRevB.86.127101

Comment on: Accurate and fast numerical solution of Poisson's equation for arbitrary, space-filling Voronoi polyhedra: Near-field corrections revisited

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This is a comment on the paper by Aftab Alam, Brian G. Wilson, and D. D. Johnson [1], proposing the solution of the near-field corrections (NFC's) problem for the Poisson equation for extended, e.g., space filling, charge densities. We point out that the problem considered by the authors can be simply avoided by means of performing certain integrals in a particular order, while their method does not address the genuine problem of NFC's that arises when the solution of the Poisson equation is attempted within multiple scattering theory. We also point out a flaw in their line of reasoning leading to the expression for the potential inside the bounding sphere of a cell that makes it inapplicable to certain geometries.

PACS numbers: 41.20.Cv, 71.15.Dx, 02.30.Em
Keywords: Near-field corrections, Poisson equation, space filling cells, muffin-tin sphere

The problem of near-field corrections (NFC's) arises when one attempts to solve the linear, second-order partial differential equations of mathematical physics. e.g., the Poisson and Schrödinger equations, through the formalism of multiple scattering theory (MST) [2–4] expressed in the *angular momentum representation*.

Consider, for example, the Poisson equation associated with a charge density, $\rho(\mathbf{r})$, and divide the charge into a set of contiguous but non-overlapping cells, see Fig. 1. The global solution for the total charge is now to be constructed in terms of the *asymptotic solutions* of the individual cells, describing the potential at points outside the bounding sphere of a cell, calculated in the angular momentum representation, i.e., in terms of the multipole moments of the charge in the cell.

Because the use of the multipole moments in the moon region, Fig. 1, violates the condition in the expansion about a shifted center of the spherical Hankel (or Neumann) functions [5] (the solutions of the free-space Laplace equation irregular at the origin), the unmodified use of the expansions for the potential outside the bounding sphere (given in terms of the cell multipole moments) diverge in the *near field region* (the moon region). One can only conjecture that the expression in terms of multipole moments must be corrected in the moon region, hence the suggestive term *near-field corrections* [6]. Furthermore, because the problem is encountered immediately in the case of extended charge densities when treated within MST, particularly charges that fill all space, one may further conjecture that these corrections are connected to the charge in the moon region of a cell. This latter viewpoint is evidently also adopted by Alam, et. al.[1]

The presence of charge in the moon region of a cell has no effect on the description of the potential anywhere in space due to the charge in that cell alone, regardless of how that potential is described. As was pointed out initially by Gonis [7], and further developed in Gonis, et. al., [8–10], as well as by other authors [11], the problem is *strictly* one of geometric origin, having to do with the choice of the centers of expansion [7] of the irregular spherical functions. Indeed the problem appears in full force in the case of a single cell. The realization of the true nature of the problem ultimately led to its solution that has been amply discussed in the literature [10]. By contrast, Alam, et al., [1] propose the solution of a non-existent problem.

Equation (2) in [1] for the potential inside the bounding sphere of a cell is an elementary result and is, of course, correctly stated. In the authors' view, however, NFC's seem to be necessary in the calculation of the parameter, α_L, in that equation.

The authors express α_L as the sum of two terms, one that counts the contribution of the charge inside all cells other than the one at the origin, (using a method that evidently can perform such sums efficiently), and one that removes the contribution of the charge inside the moon region of the central cell, i.e., inside the bounding sphere but outside the cell (because this contribution to the potential has been accounted for in the term, $V^{\rm ex}(\mathbf{r})$, in Eq. (2)). It is this second term, (the integral in Eq. (8) in [1]) that the authors refer to as NFC's.

In terms of the cells in Fig. 1 , the authors calculate α_L as an integral of the charge in in Ω_2 minus that in the moon region. Alternatively, α_L can be calculated as a single integral over the region, B, in Fig. 1 (inside Ω_2 but outside the sphere bounding Ω_1). Clearly, the so-called NFC's are simply the integral over the moon region that is completely avoided in the integral over B.

On the other hand, consider the problem of determining the potential in Ω_1 contributed by the charge in Ω_2, Fig. 1, expressed strictly in terms of the multipole moments of the charge in Ω_2. This problem cannot be avoided through the performance of integrations in a particular order. This is the problem addressed and solved in [7–10].

Finally, we comment on the line of reasoning followed by Aftab, et. al., in developing the form of α_L. The alternative procedure for calculating α_L suggested above is independent of the existence of a spherical region centered at the center of the cell at the origin and lying outside the bounding spheres of adjacent cells. The only parameter necessary in defining α_L is the radius of the bounding sphere [12]. As such, the alternative method applies to cells of arbitrary geometry, whereas the formalism in [1] is inapplicable to cells of elongated, or prism-like shape where the bounding sphere of a cell may overlap the

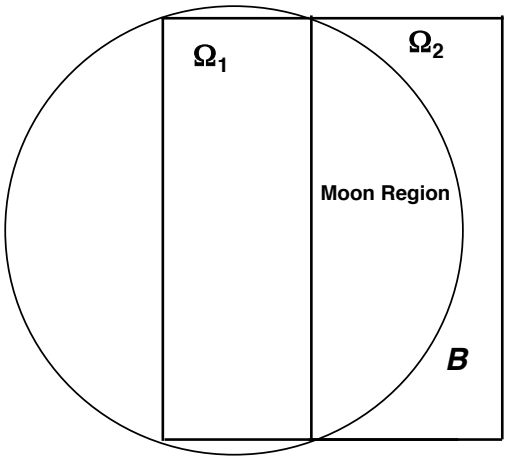

FIG. 1. Illustrating the artificial nature of the problem of NFC's as treated in [1]. Note the imposibility of defining $r_{\min}$.

center of some of its neighboring cell. If such prism-like cells were chosen in the case of muffin-tin spheres, each containing several muffin tins, the NFC's defined by the authors would need to be calculated in a case where no NFC's arise in the first place!

Reference 10 in [1] presents a method for performing integrations over convex cells that may be of interest to the electronic structure community. However, a technical matter should not be confused with conceptual challenges in mathematical physics such as those arising within multiple scattering theory, especially when these problems have been solved some years ago.

Discussions with D. M. Nicholson, Patrice Turchi and M. Däne are gratefully acknowledged. Work supported by the U.S. DOE under Contract DE-AC52-07NA27344 with LLNS, LLC, and by the Office of User Facilities, U.S. DOE at the Center for Nanophase Materials Sciences, Oak Ridge National Laboratory.

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[12] The authors of Ref. [1] perform a single shifted-center expansion of $H_0(\mathbf{r}-\mathbf{r}')$, hence for $r < r_{\rm BS}$ they need only the condition, $r' > r_{\rm BS}$, to guarantee the convergence of the expansion, $H_0(\mathbf{r}-\mathbf{r}') = \sum_L J_L(\mathbf{r})H_L(\mathbf{r}')$. A second condition would be necessary if $H_L(\mathbf{r}')$ were to be further expanded about the center, $\mathbf{R}$, of an adjacent cell. Provided that a spherical region about the center of a cell of radius $r_{\min}$ could be defined, setting $r \leq r_{\min}$ and writing $\mathbf{r}' = \mathbf{R}+\mathbf{r}'$, where $\mathbf{r}'$ is measured from $\mathbf{R}$, we have, $H_0(\mathbf{r}-(\mathbf{R}+\mathbf{r}')) = \sum_{LL'} J_J(\mathbf{r})S_{LL'}(\mathbf{R})J_{L'}(\mathbf{r}')$, where the sums over angular momentum states can be performed in arbitrary order. Here, $S_{LL'}(\mathbf{R})$ are the so-called zero-energy structure constants of MST. Integrating over $\mathbf{r}'$ and summing over $\mathbf{R}$, leads to the expression, $a_L = \sum_{\mathbf{R}}\sum_{LL'} S_{LL'}Q^{\mathbf{R}}_{L'}$, where $Q^{\mathbf{R}}_{L'}$ denotes the multipole moments of the charge in the cell at $\mathbf{R}$. This expression double counts the potential inside the bounding sphere, and the use of multipole moments violates the smaller over larger condition that justified the expansion, $H_0(\mathbf{r}-\mathbf{r}') = \sum_L J_L(\mathbf{r})H_L(\mathbf{r}')$. If the charge in the cell is given, then the term under the integral sign in Eq. (8) in the paper by Alam, et. al. [1] would remove the double-counting. *However*, the authors make no use of multipole moments, and no need for correcting for double counting exists (unless artificially introduced in performing integrations over the charge density).