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Local electrostatic moments and periodic boundary conditions

Peter A. Schultz

Sandia National Laboratories, Albuquerque, NM 87185

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Electronic structure calculations frequently invoke periodic boundary conditions to solve for electrostatic potentials. For systems that are electronically charged, or contain dipole (or higher) moments, this artifice introduces spurious potentials due to the interactions between the system and multipole moments of its periodic images in aperiodic directions. I describe a method to properly handle the multipole moments of the electron density in electronic structure calculations using periodic boundary conditions. The density for which an electrostatic potential is to be evaluated is divided into two pieces. A local density is constructed that matches the desired moments of the full density, and its potential computed treating this density as isolated. With the density of this local moment countercharge removed from the full density, the remainder density lacks the troublesome moments and its electrostatic potential can be evaluated accurately using periodic boundary conditions.

I. Introduction

An integral part of many electronic structure methods is the assumption of periodic boundary conditions (PBC) to solve for the electrostatic potential. The use of fast Fourier transforms (FFT) is frequently a convenient and efficient means to solve Poisson's equation, and is central to density functional methods such as those using plane wave basis expansions. The application of PBC is straightforward for uncharged bulk crystalline systems. Systems that are not periodic, however, such as slabs or molecular clusters, require the use of a supercell approximation, where the full three-dimensional periodicity is artificially created in aperiodic directions via making periodic copies of the supercell. The difficulty is illustrated in Figure 1. For supercells of finite dimensions, this procedure does not accurately represent the electrostatic potential of an isolated system, shown in Figure 1(a). The computed potential of the system derives not only from its internal charge distribution, but also contains the spurious interactions with the multipole moments of the periodic images of the system (in aperiodic directions), as in Figure 1(b). From practical considerations, it is desirable to make the supercells as small as possible to reduce the computational cost. However, the errors due to image multipoles reduces the accuracy of the resulting electrostatics. This paper describes a method for removing, rigorously and exactly, the spurious interactions of multipole moments from the artificial system images, as illustrated in Figures 1(c) and 1(d), and yields a procedure that is both computationally simple and efficient.

The difficulty in treating charged systems in PBC has long been recognized. The problem of a periodic array of charges cannot be solved exactly and the supercell approach for a charged system fails because of the energy of a periodic array of interacting charges diverges. For a finite molecular cluster, the true electrostatic potential and energy is well-defined: that of an isolated charged cluster. The most common approach for dealing with charged systems within PBC involves immersion in a neutralizing jellium background,[1] the energetic consequences of which were pointed out by Leslie and Gillan,[2] and later given a formal foundation by Makov and Payne.[3] Its formal justification stems from the equivalence of an isolated charged system with the limit of an infinite supercell with a jellium background charge that exactly cancels the ionic charge. For a finite supercell, Makov and Payne[3] describe how to evaluate the electrostatic energy to $O(L^{-5})$, where L is the linear dimension of the supercell. The correct evaluation of the energy requires the calculation of the volume dependent Madelung energy of a lattice of point charges in a neutralizing jellium background and other complex integrals that can only be evaluated readily on a cubic lattice.

In addition to charge, Makov and Payne[3] also describe how to correct the electrostatic energy expression for unphysical dipole interactions in aperiodic systems using PBC. This correction addresses only the energy and not the potential, and neglects the effects of induced moments. For two-dimensional slab systems, Neugebauer and Scheffler[4] described a procedure to correct not the energy but the electrostatic *potential* for the unphysical contributions generated by the dipole moments present in periodic slab images and communicated through the vacuum region separating the slabs. They introduce a planar dipole in the middle of the vacuum region to cancel the artificial dipole field. However, this procedure does not generalize to non-slab systems. The common thread connecting these approaches is the attempt to correct *a posteriori* the electrostatic potential and energy for the unphysical interactions with the multipole moments of system images across supercell boundaries.

In this paper, I propose a method for solving for the electrostatics that does not introduce the error from artificial multipoles into the potential *a priori*. This is accomplished by removing from the total charge distribution $\rho_{PBC}(r)$ of the system, Figure 1(b), a periodically reproduced countercharge $n_{LM}(r)$, Figure 1(c), that exactly cancels the local moments within each supercell that cause difficulty within PBC:

$$\rho_{PBC}(r) = \sum_{l_a} \sum_{l_b} \sum_{l_c} \rho_{uc}(r + l_a + l_b + l_c) \tag{1}$$

$$= \sum_{l_a} \sum_{l_b} \sum_{l_c} \{ \rho'_{uc}(r + l_a + l_b + l_c) + n_{LM}(r + l_a + l_b + l_c) \} \tag{2}$$

where $\rho_{uc}(r)$ is the charge distribution within a single unit cell. In the limit that the local moment countercharge (LMCC) reproduces all the multipole moments within a supercell, the remainder charge distribution $\rho'_{uc}(r)$, as schematically depicted in Fig. 1(d), will have no moments, and the electrostatic potential ϕ'_{PBC} computed in the usual manner within PBC will not be contaminated by moments from periodic images. To complete the electrostatic potential, one needs to compute the potential ϕ_{LM} from the LMCC, and for this one does not use PBC, but rather computes the potential due the local moments within the volume of the supercell treating the moments as *isolated*, as illustrated in Fig. 1(d). The total potential

$$\phi(r) = \phi'_{PBC}(r) + \phi_{LM}(r) \tag{3}$$

is then truly the electrostatic potential of the isolated cluster (or slab), at least within the unit cell used in the calculation. The forces computed with this potential will be variational. The remainder of this paper is devoted to a particular implementation of this idea - a description of how one can construct $n_{LM}(r)$ and compute $\phi_{LM}(r)$ for clusters and slabs geometries - and application to a couple of illustrative examples.

As a practical matter, one needs only be concerned with the lowest moments: the net charge, of course, and the dipole. The quadrupole and other moments introduce errors of $O(L^{-5})$, and can usually be neglected. Hence, I limit my discussion to dipole moments and charges (in clusters). It is straightforward, however, to extend the LMCC methodology to higher moments, if desired. The construction of $n_{LM}(r)$ admits a great deal of flexibility. For an computationally effective method the following conditions must be fulfilled:

(a) $n_{LM}(r)$ can readily be constructed to contain the moments desired to be removed from the supercell

(b) $n_{LM}(r)$ be spatially slowly varying (so as not to introduce into $\rho'_{uc}(r)$ spatial variations that would require denser grids or higher energy cutoffs in an FFT)

(c) The isolated potential $\phi_{LM}(r)$ from it be readily computable (and slowly varying)

(d) The density is localized within the supercell (i.e., not overlap supercell boundaries in aperiodic directions)

The approach I adopt is to build the LMCC using combinations of Gaussians. Gaussians are not the only means to build $n_{LM}(r)$, one could just as well have chosen any other distribution which satisfies the above conditions, but they are a uniquely convenient form for all the usual reasons.

Point charges violate (b) and (c), and a jellium background violates (c) and (d). For this study, Gaussians are particularly convenient as the electronic structure code implements a Gaussian-based method,[5] and much of the necessary machinery is already in place. The Gaussian-based LMCC is equally applicable to plane wave based methods, however.

The first step in the process is to identify the moments to be removed. The charge state q (for a cluster system) is an externally specified parameter. With the cluster system placed in such as way so that it is fully contained within the supercell (note that this unit cell need not be a cube or any other special shape), the dipole (and higher multipoles) can be uniquely computed from the charge distribution given on a computational grid (typically a regular FFT grid). For a charged system, $n_{\mathrm{LM}}(r)$ takes the form of a single Gaussian, normalized to integrate to a charge q, and can be located in the unit cell in such a way as to exactly cancel the system dipole.

For a neutral system, to remove the dipole the $n_{\mathrm{LM}}(r)$ takes the form of a pair of spherical Gaussians, opposite in sign, and centered about the center of the existing dipole in the unit cell. The latter condition guarantees that the dipole LMCC does not introduce a new, and possibly significant, quadrupole into the remainder density. The system dipole determines the charge and orientation of the Gaussians. The Gaussian decay constant (at 0.3/bohr^2) and distance between the Gaussians (3.0 bohr) is fixed. One could use these latter as degrees of freedom to better represent higher moments. To compute the density, and potential, of an array of localized spherical Gaussians is straightforward, involving the evaluation of Gaussians and error functions.

An analogous procedure produces $n_{\mathrm{LM}}(r)$ for a slab system, but the form of that density and the computation requires some elaboration. Unlike the cluster system, the dipole of concern is not the full three-dimensional dipole, but the component of the dipole normal to the slab. Without loss of generality, I can assume the z-axis is normal to the surface. Under the condition that the supercell boundaries in the z-direction are in vacuum, the dipole normal to the surface can be uniquely computed (the component of the dipole within the plane of the surface is ill-defined). The $n_{\mathrm{LM}}(r)$ is not composed of spherical Gaussians, but has a one-dimensional Gaussian profile in the z-direction, and is constant parallel to the plane of the slab:

$$n_{\mathrm{LM}}(r) = n_{\mathrm{LM}}(z) = c_{\mathrm{LM}}\ [\ e^{-\alpha(z - Z_+)^2} - e^{-\alpha(z - Z_-)^2}\ ]. \tag{4}$$

Unlike the spherical Gaussians used for clusters, the potential cannot be calculated as the sum of the potentials of the Gaussians, because the potentials from these charged infinite planar Gaussian sheets individually diverges. Only the sum yields a finite potential, which takes the following form with Gaussians and error functions (in Rydberg energy units):

$$\phi_{\mathrm{LM}}(z) = 4\pi c_{\mathrm{LM}}\ \{\ \alpha^{-1}\ [\ e^{-\alpha(z - Z_+)^2} - e^{-\alpha(z - Z_-)^2}\ ] + (\pi/\alpha)^{1/2}\ [\ |z - Z_+|\ \mathrm{erf}(\ \alpha^{1/2}\ |z - Z_+|\ ) - |z - Z_-|\ \mathrm{erf}(\ \alpha^{1/2}\ |z - Z_-|\ )\ ]\ \}. \tag{5}$$

This potential approaches asymptotically a constant value, equal and opposite sign going into the vacuum on either side of slab, and introduces a discontinuity in the potential at the supercell boundary, as expected for a planar dipole field. This discontinuity is inconsequential to the solution as the wave functions, by construction, have no amplitude at the aperiodic supercell boundaries. For a one dimensional (linear) system, one can do an analogous procedure, except using a two-dimensional Gaussian profile for the LMCC.

This approach was tested for a small sample of molecular and slab systems. The calculations used a Gaussian based pseudopotential code,[5] within the local density functional approximation[6] to density functional theory.[7] The specific details are unimportant outside of the observation that the part of the electrostatics containing all the moments of the system is solved self-consistently with PBC in a supercell using FFT's. The cases considered included the NaCl molecule, OH radical, OH^- and CH_4^+ ions, and a model slab calculation with a hexagonal array of K and CO, depicted in Figure 2. Only methane lacks a significant dipole. The LMCC extended only to remove dipole moments - quadrupole moments and beyond were neglected.

For convenience of description, the unit cells were made cubic for the molecular tests, and linear dimension varied from 14.4 to 30.0 bohr for OH, to 16.8 to 30.0 bohr for NaCl, and from 18.0 to 30.0 bohr for methane. For the neutral molecules, OH and NaCl, and CH_4^+ the energy convergence as a function of unit cell size was on the order of a few tens if μeV even for the smallest unit cell sizes, where the self-consistent wave functions (and densities) begin to impinge significantly on the supercell boundaries. In contrast, the error for NaCl without any dipole correction was 0.144 eV for the smallest unit cell and 0.024 eV for the largest unit cell, following closely the L^{-3} scaling expected of interacting dipoles. The variation with unit cell size was greater for OH^- due to interaction of the charge with the neglected quadrupole moment, but even so the error for the smallest unit cell amounted to only ~1 meV. Not only does the total energy converge in these tests, but the decomposition of the energy converges to the same level. The total electrostatic energy, kinetic energy, exchange-correlation energy all converge to the same accuracy as the total energy, as do the computed forces, illustrating the level of convergence and accuracy in the computation of the potential of the isolated molecules.

The convergence behavior in the slab calculations was equally good. The dipole LMCC result gave total energies accurate to within 1 μeV down to slab separations where the densities of the slab impinged significantly on the supercell boundaries. The energy analysis and computed forces also were fully converged even for the smallest slab separations considered.

This paper illustrates the design and use of the LMCC for aperiodic systems, but a few comments about the possible extension of this concept to periodic systems are merited. First, multipole moments are generally ill-defined in bulk systems, although for some cases of high-symmetry defects, it is possible to associate local moments with the defect. Second, the use of LMCC, in general, introduces discontinuities in the potential at the supercell boundaries. For aperiodic systems, this does not cause difficuly, for the discontinuities occur in vacuum. For a bulk problem there is no vacuum, and the discontinuities introduced by the simple transference of the LMCC method as described above for aperiodic systems cause unphysical effects.

It is possible to avoid the discontinuities from multipole moment potentials in special cases of multipole oriented properly in high symmetry supercells (imagine the potential of a quadrupole moment in the center of a cubic unit cell, aligned along one of primitive axes). Moreover, it is always possible to avoid the discontinuities generated by a local charge. Rather than computing the potential of the charge within the volume of the supercell in which the charge resides, the potential must be computed within a primitive Wigner-Seitz cell produced by the lattice of local charges. Then all the boundaries are equidistant from neighboring charges, and, hence, the potential at the boundary is continuous (though the derivative of the potential is not continuous). Hence, it is possible to construct an internally consistent LMCC for charged bulk systems.

The viability of a bulk LMCC depends on the charge in bulk being truly strongly localized. The position of the charge must be properly identified (and incorrect position would lead to a large image dipole error). The errors are much greater than for a molecular cluster, depending on how well the charge and the perturbation to the bulk lattice is indeed localized within the Wigner-Seitz cell. Overly confining supercells will result in artificial charge buildup/depletion of electrons at the boundaries, with unknown consequences. It would be an interesting exercise to investigate the convergence of such a LMCC for charged bulk systems, compared to the standard neutralizing jellium approach.

In summary, I have presented a method to remedy the problem in using PBC for aperiodic systems that have multiple moments. The error of incorporating spurious potentials from artificial periodic images of system multipoles is avoided by evaluating the potential from the moments locally. The LMCC method is rigorous, easily computable and not dependent on using special supercell geometries, and straightforwardly extends to moments beyond dipoles. The *a priori* removal of the troublesome moments leads to a method where more than an *a posteriori* correction to the energy is made: the proper isolated local potential is generated, and the multipole moment correction is incorporated self-consistently because the multipole moment error is never made at the outset. The LMCC approach leads to a method that is more rapidly convergent with supercell size and, hence, more efficient calculations.

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Figure Captions.

Figure 1. An schematic illustration of the use of and problem with periodic boundary conditions to compute the electrostatic potential for an isolated system, and . (a) The idealized charge distribution for an isolated system to be studied, with an internal dipole. (b) Application of periodic boundary conditions, showing the interaction of the periodic dipole images. (c) Local moment countercharge which exactly reproduces the dipole of the system, and for which the potential can be computed within the boundaries of the unit cell, treating the LMCC as isolated. (d) The remainder density with the LMCC removed. The use of periodic boundary conditions no longer incurs the error of interacting dipole moments.

Figure 2. Schematic of an ionic slab of KCO. (a) Slab symmetry is hexagonal with a lattice parameter of 5.03 bohr. The triangles position the CO (normal to the slab plane). The dashed line indicates the position of the plane normal to the surface used to illustate the positions of K and CO in (b).

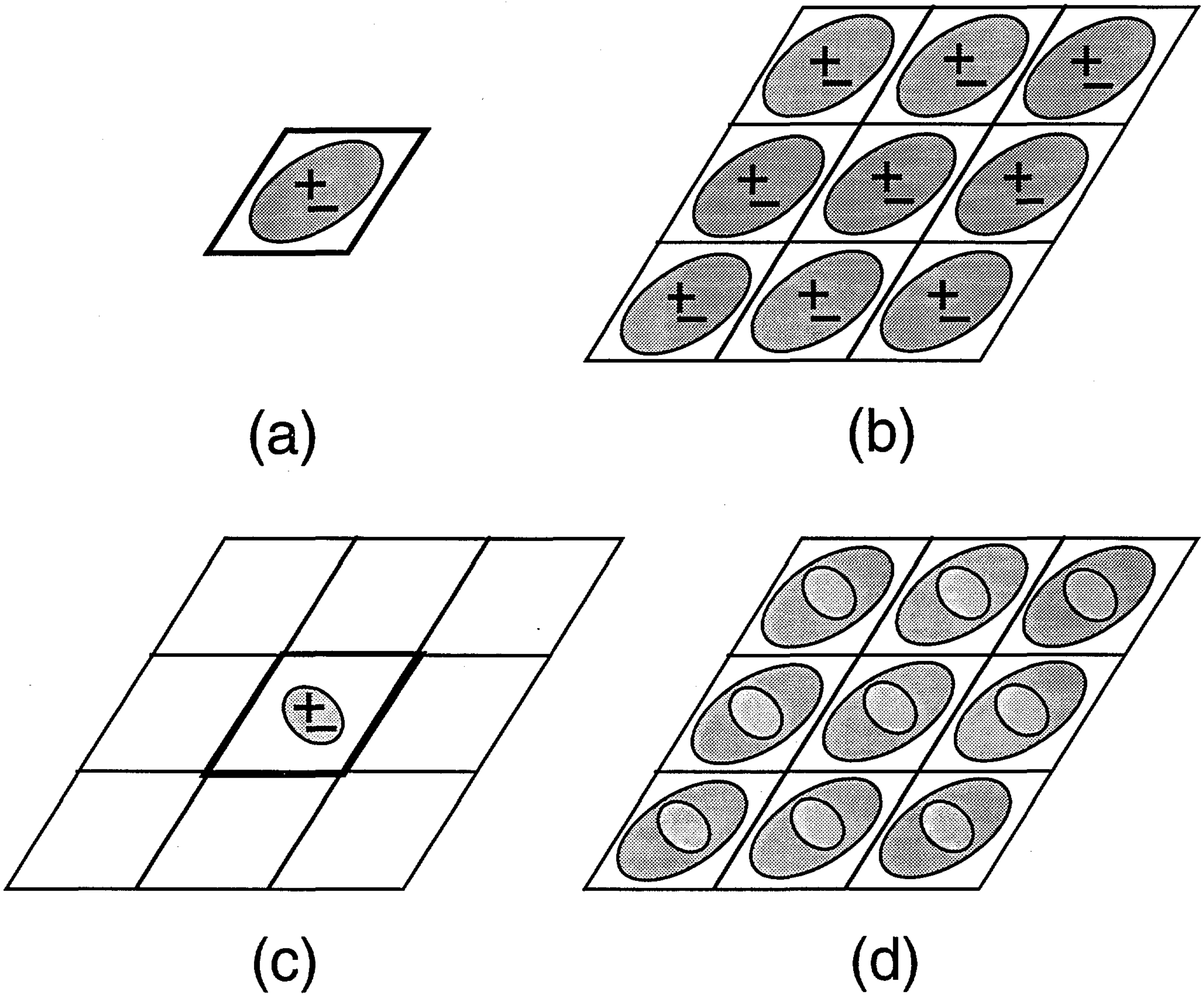
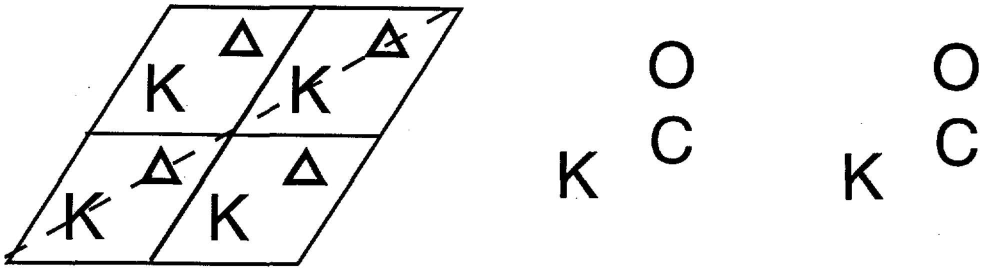


Figure 1 - Schultz (Phys. Rev. B)



(a) (b)

Figure 2 - Schultz (Phys. Rev. B)