Electrostatics in Periodic Boundary Conditions and Real-space Corrections

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We address periodic-image errors arising from the use of periodic boundary conditions to describe systems that do not exhibit full three-dimensional periodicity. The difference between the periodic potential, as straightforwardly obtained from a Fourier transform, and the potential satisfying any other boundary conditions can be characterized analytically. In light of this observation, we present an efficient real-space method to correct periodic-image errors, based on a multigrid solver for the potential difference, and demonstrate that exponential convergence of the energy with respect to cell size can be achieved in practical calculations. Additionally, we derive rapidly convergent expansions for determining the Madelung constants of point-charge assemblies in one, two, and three dimensions.

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I. INTRODUCTION

First-principles calculations frequently employ periodic boundary conditions to predict materials properties. Besides constituting a natural choice when studying crystalline systems, periodic boundary conditions allow the use of highly optimized fast Fourier transform (FFT) algorithms, which considerably reduce the computational cost associated with the resolution of electrostatic equations, and allow an efficient evaluation of electronic kinetic energies and interatomic forces when used in conjunction with a plane-wave basis set. Despite these algorithmic advantages, periodic boundary conditions require large supercells when studying aperiodic or partially periodic systems (e.g., isolated molecules, polymer chains, and slabs) in an effort to minimize spurious electrostatic interactions between periodic images. Charged systems are particularly problematic, since conventional algorithms automatically enforce charge neutrality by introducing an artificial jellium background.

In addition to the Makov-Payne asymptotic correction, several schemes have been devised to reduce periodic-image errors. Barnett and Landman proposed to eliminate periodic-image interactions for cluster systems by restricting the plane-wave expansions of the wavefunctions and of the charge density to a spherical domain in reciprocal space. A generalization of this reciprocal-space approach was introduced by Martyna and Tuckerman. The electrostatic-cutoff approach proposed by Jarvis, White, Godby, and Payne suppresses periodic-image effects by damping the electrostatic potential beyond a certain interaction range. The corrective method introduced by Blöchl consists of using atom-centered Gaussian charges and Ewald summation techniques to cancel periodic-image interactions. In the local-moment-countercharge (LMCC) method developed by Schultz, a superposition of Gaussians is employed as a local-moment model for calculating the Coulomb potential analytically up to a certain multipole order, the remaining electrostatic contribution being computed using conventional plane-wave techniques.

In this work, we propose an alternative approach for correcting periodic-image errors and show that exponential energy convergence with respect to cell size can be obtained at tractable computational cost. The approach proceeds by calculating the electrostatic potential in real space, exploiting the periodic solution of the Poisson equation computed using inexpensive FFT techniques. In the following sections, we first discuss and characterize the difference between the open-boundary electrostatic potential and its periodic counterpart, providing a comparative basis for analyzing the relative accuracy of various corrective schemes. Second, we present our correction method and assess its performance. Last, we extend the method to the study of systems exhibiting one- or two-dimensional periodicity, beyond the conventional linear- and planar-average approximations.
II. COMPARISON OF THE OPEN-BOUNDARY AND PERIODIC POTENTIALS

A. Definition of the Corrective Potential

The electrostatic potential $v$ generated by a charge distribution $\rho$ satisfies the Poisson equation:

$$\nabla^2 v(r) = -4\pi \rho(r) \quad (1)$$

(atomic units are used throughout). In the absence of an external electric field, we can solve Eq. 1 subject to open-boundary conditions ($v(r) \to 0$ as $|r| \to +\infty$). As a result, the electrostatic potential $v$ can be computed via Coulomb integration:

$$v = \int \frac{\rho(r')}{|r-r'|}dr'.$$

(2)

(Although this study focuses on open boundary conditions, it should be noted that the contribution from an external field $E$ can be incorporated by adopting the asymptotic boundary conditions $v(r) \to -E \cdot r$, which simply adds a term $-E \cdot r$ to the solution of the Poisson equation.) A differential equation similar to Eq. 1 in the reciprocal-space representation as:

$$\nabla^2 v(r) = -4\pi \rho(r) \quad (3)$$

As a consequence, the periodic potential can be evaluated in the reciprocal-space representation as:

$$v(r) = \sum_{g \neq 0} \frac{4\pi}{g^2} \rho(g)e^{ig \cdot r} \quad (4)$$

where we set the arbitrary component $v'(g = 0) = \langle v' \rangle$ to zero.

It should be noted that the open-boundary potential $v$ and its periodic counterpart $v'$ are distinct. We define the corrective potential $v_{\text{corr}}$ as the difference $v - v'$. The potential $v_{\text{corr}}$ must satisfy:

$$\nabla^2 v_{\text{corr}}(r) = -4\pi \langle \rho \rangle \quad (5)$$

for which we specify Dirichlet boundary conditions:

$$v_{\text{corr}} = v - v' \quad (6)$$

at the cell boundaries. (Note that the solution of this elliptic boundary value problem is uniquely defined.) Eq. 5 indicates that the curvature of the corrective potential is a constant. It should also be noted that, apart from the value of the average $\langle \rho \rangle$, Eq. 5 is independent of the structural details of the charge density $\rho$. Instead, these details are entirely embedded in the Dirichlet boundary conditions, which reflect the electrostatic contributions from compensating jellium and from the surrounding images.

In order to illustrate the implications of Eq. 5, we consider a pyridazine cation in a periodically repeated cubic cell. The open-boundary potential $v$, the periodic potential $v'$, and the corrective potential $v_{\text{corr}}$ are shown in Figure 1. First, we observe that the potential $v'$ is shifted down in energy with respect to $v$, due to the fact that the average $\langle v' \rangle$ is null by construction. In addition to this energy shift, the potential $v'$ is significantly distorted. This distortion results from satisfying the periodicity conditions. Most importantly, we observe that the corrective potential $v_{\text{corr}}$ varies smoothly over space. The smooth spatial dependence of $v_{\text{corr}}$ contrasts markedly with the strong variations in $v$ and in $v'$.

Performing a polynomial regression, we can verify that the potential $v_{\text{corr}}$ is quadratic to good approximation in the proximity of the cell center with departures from parabolicity restricted to the vicinity of the periodic boundaries.

To further examine the characteristics of $v_{\text{corr}}$, we consider the adsorption of carbon monoxide molecules on neutral and charged platinum slabs. Following Neugebauer and Scheffler, the electrostatic correction is calculated along the $z$-direction within the planar-average approximation (that is, from the $xy$-average of the charge distribution). The validity of this approximation is discussed in the last section. For CO molecules adsorbed on a neutral slab (Figure 2a), the periodic potential is shifted up in energy and tilted with respect to the open-boundary potential. The potential correction is seen to be linear, in agreement with the analysis of Neugebauer and Scheffler. For CO molecules adsorbed on a slab of surface charge $\tilde{\sigma}$ (Figure 2b), the real-space potential diverges as $4\pi \tilde{\sigma} |z|$. In this case, the periodic potential $v'$ undergoes a significant energy downshift, which decreases the energy of the positively charged slab. Moreover, we observe that $v'$ is significantly curved in the slab region. Consistent with these observations and with Eq. 5, the corrective potential $v_{\text{corr}}$ is found to be parabolic everywhere in the unit cell.

B. Quasiparabolic Behavior of the Corrective Potential

In order to complete the analysis of the corrective potential, we consider a point charge $q = \pm e$ in a periodically repeated cubic cell of length $L$, as illustrated in Figure 3. The corrective potential generated by the uniform jellium and the surrounding point charges is denoted $v_{0_{\text{corr}}}$. Note that $v_{0_{\text{corr}}}$ cannot be calculated directly as the difference between the potential of a lattice of point charges $v_0$ and the point-charge potential $1/r$ since the representation of a point charge in reciprocal space requires an infinite number of plane-wave components. Instead, to obtain $v_{0_{\text{corr}}}$, we can exploit the cubic symmetry of the system, writing the corrective potential as:

$$v_{0_{\text{corr}}}(r) = v_{0_{\text{corr}}}(r = 0) + \nabla^2 v_0(r = 0) \frac{r^2}{6} + O(|x|^4). \quad (6)$$
This parabolic expansion, valid up to third order, confirms that the point-charge correction \( v_0^{\text{corr}} \) is almost quadratic in the vicinity of \( r = 0 \). For noncubic lattices, due to inversion symmetry, the point-charge corrective potential takes a more general form:

\[
v_0^{\text{corr}}(r) = v_0^{\text{corr}}(r = 0) + \frac{1}{2} \sum_\alpha \left( \frac{\partial^2 v_0^{\text{corr}}}{\partial r_\alpha^2}(r = 0) \right) r_\alpha^2 + O(|r|^4),
\]

(7)

where \( (r_\alpha) \) are the coordinates of \( r \) along the principal axes. Thus, the corrective potential in a noncubic lattice is also quasiparabolic.

Turning now to an arbitrary distribution \( \rho \), we can express the electrostatic correction \( v^{\text{corr}} \) by superposition:

\[
v^{\text{corr}}(r) = \int v_0^{\text{corr}}(r - r')\rho(r') \, dr'.
\]

(8)

As a consequence, defining \( r_{\text{max}} \) as the distance beyond which the parabolic expansion (Eq. 6) ceases to be valid, the corrective potential \( v^{\text{corr}} \) can be considered as nearly parabolic, provided that the spread of the distribution is tolerably lower than \( r_{\text{max}} \).

C. Connection with Existing Schemes

Having justified the general characteristics of the electrostatic-potential correction, we now determine the terms in the expansion of \( v_0^{\text{corr}} \) (Eq. 6). The potential at the origin \( v_0^{\text{corr}}(r = 0) \) can be written in terms of the Madelung constant \( \alpha_0 \) \([22]\) of a cubic lattice of point charges in a compensating jellium background:

\[
v_0^{\text{corr}}(r = 0) = \frac{\alpha_0}{L}.
\]

(9)

(The calculation of the Madelung constant of a jellium-neutralized assembly of point charges is discussed in Appendix A.) Note that \( v_0^{\text{corr}}(r = 0) \) is positive, reflecting the stabilizing contribution from the jellium compensation. The value of \( \nabla^2 v_0^{\text{corr}}(r = 0) \) is then determined from Eq. 5:

\[
\nabla^2 v_0^{\text{corr}}(r = 0) = -\frac{4\pi}{L^3}.
\]

(10)

Hence, the point-charge correction can be expanded as:

\[
v_0^{\text{corr}}(r) = \frac{\alpha_0}{L} - \frac{2\pi}{3L^3} r^2 + O(|r|^4).
\]

(11)

The terms in this parabolic expansion bear a strong resemblance to those entering into the Makov-Payne correction \([3]\). This correspondence is discussed further in Sec. [ID].
A parabolic point-countercharge (PCC) potential may be rewritten:

\[ v_{\text{PCC}}(r) = \sum_{n=1}^{N} q_n \left( \frac{\alpha_0}{L} - \frac{2\pi}{3L^3} (r - r_n)^2 \right). \]  

(12)

This expression may be rewritten:

\[ v_{\text{PCC}}^{\text{corr}}(r) = \frac{\alpha_0 q}{L} - \frac{2\pi q}{3L^3} p \cdot r - \frac{2\pi Q}{3L^3}. \]  

(13)

where \( q = \sum_n q_n \) is the total charge, \( p = \sum_n q_n r_n \) denotes the total dipole moment, and \( Q = \sum_n q_n r_n^2 \) stands for the total quadrupole moment of the countercharge distribution. Eq. (13) indicates that parabolic PCC schemes can correct periodic-image errors up to quadrupole-moment order. Note that no more than \( N_{\text{max}} = 7 \) countercharges are sufficient to obtain the most accurate parabolic correction (one charge for \( q \), two for \( p \), and four for \( Q \)). To obtain higher-order PCC corrections, one would need to determine more terms in the expansion of the point-charge correction, beyond the parabolic contributions. An example of accurate calculations using harmonic expansions can be found in Ref. [21].

An alternative approach is to employ countercharges whose corrective potential can be computed handily. A popular choice is to use Gaussian densities, as proposed by Blöchl [11]. Repeating the preceding analysis for a Gaussian density of charge \( q = +e \), we can expand the Gaussian corrective potential \( v_{\sigma,L}^{\text{corr}} \) as:

\[ v_{\sigma,L}^{\text{corr}}(r) = \frac{\alpha_{\sigma/L}}{L} - \frac{2\pi}{3L^3} r^2 + O(|r|^4), \]  

(14)

where \( \alpha_{\sigma/L} \) is the Madelung constant of an assembly of Gaussians of width \( \sigma \) immersed in a compensating jellium in a cubic cell of length \( L \). It is more convenient, however, to write the corrective potential directly as:

\[ v_{\sigma,L}^{\text{corr}}(r) = v_{\sigma}(r) - v_{\sigma,L}(r) \]

\[ = \frac{\text{erf}(r/\sigma)}{r} - \frac{1}{L^3} \sum_{g \neq 0} \frac{4\pi}{g^2} e^{-\sigma^2 g^2/4} e^{i\mathbf{g} \cdot \mathbf{r}}, \]  

(15)

where \( v_{\sigma} \) is the electrostatic potential of an isolated Gaussian charge, and \( v_{\sigma,L} \) is the potential corresponding to a periodically repeated Gaussian in a jellium background.
The sum in the right-hand side of the equation converges very rapidly, and can be calculated using FFT techniques. Superimposing \( N \) compensating charges, the Gaussian-countercharge (GCC) corrective potential \( \psi_{GC}^{corr}(r) \) can be expressed as:

\[
\psi_{GC}^{corr}(r) = \sum_{n=1}^{N} q_n \psi_{\sigma,L}^{corr}(r - r_n).
\]

This results in the following approximation for the open-boundary potential \( v(r) \):

\[
v(r) \approx v'(r) + \psi_{GC}^{corr}(r).
\]

We underscore that this scheme is equivalent to the Gaussian scheme introduced by Blöchl [11] and the LMCC method proposed by Schultz [12]. The equivalence with LMCC approach can be established by recasting Eq. 17 as:

\[
\begin{aligned}
    v(r) &\approx v_{PBC}(r) + v_{GCC}(r) \\
    v_{PBC}(r) &= v'(r) - v_{GCC}(r),
\end{aligned}
\]

where \( v_{GCC}(r) = \sum q_n \psi_{\sigma}^L (r - r_n) \) is the electrostatic potential generated by the isolated countercharge distribution, and \( v_{GCC}(r) = \sum q_n \psi_{\sigma,L}^L (r - r_n) \) is the corresponding periodic potential.

We are now in a position to compare the corrective potentials \( \psi_{PCC}^{corr} \) and \( \psi_{GCC}^{corr} \) with the potential \( \psi^{corr} \), obtained as the direct difference between the open-boundary potential and its periodic counterpart. For our comparative analysis, we refer to the exact corrective potential \( \psi^{corr} \) as the density-countercharge (DCC) potential. The DCC potential is obtained by evaluating the Coulomb integral defining \( v \) at each grid point in the unit cell. (A cheaper alternative to this procedure is presented in the next section.) The PCC, GCC, and DCC potentials for a charged pyridazine cation in a cubic cell of length \( L = 15 \) bohr are plotted in Figure 4. The PCC and GCC corrections are computed up to dipole order. First, it should be noted that the maximal energy of the PCC potential is slightly above its GCC counterpart, reflecting the fact that the Madelung energy of an array of point charges immersed in a jellium is higher than that of a jellium-neutralized array of Gaussian charges (cf. Appendix A). In addition, the maximal DCC energy is found to be approximately 0.05 Ry above \( \alpha_0 q/L \), indicating that the dipole PCC and GCC corrections tend to underestimate the energy of the system. Moreover, the parabolic PCC potential is not as steep as its GCC counterpart, suggesting that the energy underestimation will be more significant for the GCC correction. Owing to the cubic symmetry of the cell, the PCC and GCC potentials display the same curvature in each direction of space, equal to one third of \(-4\pi \rho\). In contrast, the curvature of the DCC potential is not uniform, due to the nonspherical nature of the molecular charge density. This shape dependence suggests that the accuracy of the GCC correction could be improved by optimizing the ge-
omometry of the Gaussian countercharges.

In summary, we have shown that the PCC (Makov-Payne), GCC (LMCC), and DCC corrections belong to the same class of periodic-image corrections. The analysis of the corrective potential has established that the parabolic PCC correction cannot eliminate periodic-image interactions beyond quadrupole order. Difficulties inherent in the GCC scheme have also been evidenced. To overcome these limitations, an efficient implementation of the DCC correction is presented in Sec. III.

D. Energy Correction

To conclude this preliminary analysis, we give the expression of the energy correction $\Delta E_{corr}$ in terms of the corrective potential $v_{corr}$. The total electrostatic energy of the system being equal to:

$$E = \frac{1}{2} \int v(r)\rho(r)dr,$$

the corrective energy can be expressed as [17]:

$$\Delta E_{corr} = \frac{1}{2} \int v_{corr}(r)\rho(r)dr. \quad (20)$$

it is worth mentioning that in the case of a single point countercharge $q = \int \rho(r)dr$, the PCC energy correction can be written as:

$$\Delta E_{0}^{corr} = \frac{1}{2} \int q_{0}v_{corr}(r)\rho(r)dr$$

$$= \frac{\alpha_0 q^2}{2L} - \frac{\pi qQ}{3L^3}. \quad (21)$$

III. IMPLEMENTATION OF THE DENSITY-COUNTERCHARGE CORRECTION

A. Density-countercharge Algorithm

The first term corresponds to the Madelung energy correction, as proposed by Leslie and Gillian [4]. Note that the second term differs from Eq. 15 in Ref. 3 by a factor 1/2. The validity of the energy correction given by Eq. 21 is illustrated in Figure 5.

FIG. 5: Electrostatic energy of two Gaussians of unit charge and unit spread calculated via (a) real-space integration, (b) reciprocal-space integration with the PCC energy correction given by Eq. 21 and (c) reciprocal-space integration with the energy correction given by Eq. 15 in Ref. 3. The Gaussian charges are positioned at $r_0 = (-5, -5, -5)$ and $r_1 = (5, 5, 5)$ (corresponding to a quadrupole moment $Q$ of 153 a.u.).

FIG. 6: DCC total energy as a function of cell size for a pyridazine cation varying the coarse-grid cutoff $E_{cut}$ from 10 Ry ($M = 13 \times 13 \times 13$) to 250 Ry ($M = N = 73 \times 73 \times 73$). Also depicted is the corrective potential $v_{corr}$ in the plane of the molecule as a function of the coarse-grid resolution at a cell size of 15 bohr.

DCC energy as a function of cell size for a pyridazine cation varying the coarse-grid cutoff $E_{cut}$ from 10 Ry ($M = 13 \times 13 \times 13$) to 250 Ry ($M = N = 73 \times 73 \times 73$). Also depicted is the corrective potential $v_{corr}$ in the plane of the molecule as a function of the coarse-grid resolution at a cell size of 15 bohr.
equation for \( v^{\text{corr}} \) (Eq. 5) and the fact that \( v^{\text{corr}} \) is smoothly varying.

First, we note that taking into account appropriate boundary conditions, Eq. 5 can be solved efficiently using multigrid solvers \([22, 23, 24, 25]\). Multigrid algorithms typically scale as \( O(N \log N) \), that is, comparable to the scaling of an FFT computation. Hence, the overall cost of the calculation can be reduced from \( O(N^5) \) to \( O(N^{5/3}) \), corresponding to the expense arising from the determination of the boundary conditions. Although a similar approach may be employed to directly solve the electrostatic equation defining \( v \) (Eq. 1), we emphasize that Eq. 5 allows a considerable reduction in the overall cost of the calculation can be reduced from \( O(N^5) \) to \( O(M^{5/3}) \). It should also be mentioned that the DCC algorithm can be used in combination with multipole-expansion methods for a rapid evaluation of the Dirichlet boundary conditions \([31]\). The performance the multipole-expansion approach is reported in Appendix B.

Further exploiting this idea, it is possible to solve Eq. 5 on a grid much coarser than that used to discretize the charge density. To illustrate this fact, we consider a pyridazine cation in a periodic cubic cell of varied size (Figure 5). The total energy of the system is calculated using density-functional theory \([29]\). An energy cutoff \( E_{\text{cut}} = 250 \text{ Ry} \) is applied to the plane-wave expansion of \( v^{\text{corr}} \). Reducing the energy cutoff \( E_{\text{cut}}^{\text{corr}} \) from 250 to 40 Ry, the corrected energies are observed to depart by less than \( 5 \times 10^{-3} \text{ Ry} \) from their converged values for cell sizes greater than 13 bohr. The ability to decrease the number of grid points without a significant loss of accuracy enables a substantial reduction of the additional computational cost from \( O(N^{5/3}) \) to \( O(M^{5/3}) \), where \( M \) is the number of coarse-grid points. Note that diminishing the plane-wave energy cutoff from 250 to 40 Ry at \( L = 15 \text{ bohr} \) reduces the cost of the boundary-condition calculation by a factor \( 29^5/73^5 \approx 1/100 \).

Before presenting the algorithm, we draw attention to the fact that the DCC scheme relies on the central idea that most of the structural characteristics of the open-boundary potential \( v \) can be removed by subtracting out its periodic counterpart \( v' \). The residual \( v^{\text{corr}} \) (that is, the amount by which \( v' \) fails to reproduce \( v \)) is smooth and can be determined on a coarse grid at low computational cost. Additional computational savings come from the ability to avoid updating the potential \( v^{\text{corr}} \) at each step of the self-consistent-field (SCF) calculation, but instead at fixed interval between electronic iterations.

The DCC algorithm for a typical electronic-structure calculation can be described as follows. Let \( N^{\text{corr}} \) denote the number of SCF steps between each update of the corrective potential.

1. Start from an initial charge distribution \( \rho \) on the fine grid.

2. Calculate the periodic potential \( v' \) corresponding to \( \rho \).

3. Transfer \( \rho \) and \( v' \) on the coarse grid (tricubic interpolation \([30]\)) to obtain the coarse-grid density \( \tilde{\rho} \) and coarse-grid periodic potential \( \tilde{v}' \).

4. Calculate the real-space potential \( \tilde{v} \) at the boundaries of the coarse grid from \( \tilde{\rho} \) to obtain the Dirichlet boundary conditions \( \tilde{v}^{\text{corr}} = \tilde{v} - \tilde{v}' \).

5. Solve \( \nabla^2 \tilde{v}^{\text{corr}} = -4\pi \langle \rho \rangle \) (multigrid techniques) to obtain the corrective potential \( \tilde{v}^{\text{corr}} \).

6. Transfer \( \tilde{v}^{\text{corr}} \) on the fine grid (tricubic interpolation) to obtain \( v^{\text{corr}} \), and calculate \( v = v^{\text{corr}} + v' \).

7. Perform \( N^{\text{corr}} \) electronic SCF steps.

8. Iterate from Step 2 until reaching SCF convergence.

Note that we employ real-space tricubic interpolation techniques in order to avoid oscillatory distortions inherent in Fourier-transform interpolation schemes. We also underscore that the DCC algorithm can be efficiently parallelized, since its most expensive step (namely, the calculation of the Dirichlet boundary conditions) scales linearly with the number of processors.

The above procedure can be adapted to one- and two-dimensional systems by considering the linear or planar average of the charge density for calculating the corrective potential \([13]\). The validity the linear- or planar-average approximations will be discussed in the final section. The computational cost of this approach is moderate, on the order of \( O(M^{1/3}) \) and \( O(M) \) for one and two dimensions, respectively.

It should also be mentioned that the DCC algorithm can be used in combination with multipole-expansion methods for a rapid evaluation of the Dirichlet boundary conditions (Step 4). The accuracy of this approach depends on the precision of the multipole expansion at the boundary of the supercell. (A mathematical discussion on the long-range accuracy of multipole expansions is presented in Sec. 3.4. of Greengard’s dissertation [31].) The performance the multipole-expansion approach is reported in Appendix B.

### B. Applications

The energy of a pyridazine molecule as a function of cell size \( L \) for each countercharge correction is reported in Figure 6. For this neutral species, the uncorrected energy shows a characteristic minimum at \( L = 14 \text{ bohr} \) before slowly approaching its asymptotic value. In contrast, the corrected energies are seen to converge monotonically towards their common energy limit. Although the three schemes demonstrate comparable convergence, it should be noted that the PCC method is slightly more accurate. In addition to further validating the energy expansion given by Eq. [21] this comparison suggests that the PCC correction can be preferred for studying neutral species.
with the notable exception of elongated systems (e.g., polymer fragments or terminated nanotubes).

We now consider the energy of a pyridazine cation as a function of cell size (Figure 8). We use energy cutoffs of 35 and 250 Ry for expanding the wavefunctions and the charge density, and select a coarse-grid cutoff of 35 Ry for calculating the DCC correction. Expectedly, the uncorrected energy converges very slowly with respect to $L$ (at 19 bohr, the energy error is still larger than 0.15 Ry). The PCC and GCC corrections substantially improve the convergence of the total energy, reducing periodic-image errors by one order of magnitude. Using the DCC scheme, the energy is observed to converge even more rapidly, reflecting the exponential disappearance of energy errors arising from charge density spilling across periodic cells: at a cell size of 15 bohr, which is barely larger than the size of the molecule, the DCC energy is converged within $10^{-4}$ Ry. The performance of each scheme as a function of the total computational time is shown on a logarithmic energy scale in Figure 9. Each curve corresponds to cell sizes in the range 12-19 bohr. For meaningful comparison with the DCC scheme, the PCC and GCC corrective potentials are also updated at fixed SCF intervals. We observe that the computational cost of the corrected calculations is comparable to that without correction for a considerable improvement in accuracy. For this charged system, the DCC approach constitutes the most advantageous alternative, improving the energy precision by two orders of magnitude over the PCC and GCC corrections for cell sizes above 15 bohr.

The performance of the DCC and GCC corrective schemes for a neutral polyvinylidene fluoride (PVDF) chain is reported in Figure 10. The comparison shows a significant improvement of energy convergence for both schemes. As shown in the inset, the performance of the DCC scheme is perceptibly superior to that of the GCC scheme. We emphasize that for systems exhibiting one dimensional periodicity, the additional computational cost due to the electrostatic correction is moderate, on the order of $O(M)$ at most.

The DCC scheme can also be used in the calculation of work functions, as it solves energy-reference issues by automatically setting the vacuum level to zero. Figure 11 depicts the convergence of the opposite Fermi energy of a Pt(100) slab as a function of transverse cell size. The wavefunction, charge-density, and corrective potential energy cutoffs are 25, 200, and 150 Ry, respectively. We use a shifted $5 \times 5 \times 1$ mesh with a cold-smearing occupation function [36] (smearing temperature of 0.03 Ry) to sample the Brillouin zone. Without correction, the relative error in the Fermi energy stays above 100% for all cell sizes in the considered range. Using the GCC scheme,
the convergence of the Fermi level improves greatly: at
150 bohr, the relative error reduces to approximately 0.1
eV. Employing the DCC corrective scheme, the calcu-
lated Fermi energy is converged within 2 meV at 60 bohr
and 0.1 meV at 150 bohr. Thus, the DCC scheme al-
 lows to directly determine the work function of a metal
as the opposite of the calculated Fermi energy using
supercells of minimal size. A similar convergence im-
provement is obtained for the work function of carbon
nanotubes [35]. Besides improving the convergence of total
energies, the DCC approach can be employed to correct
structural and vibrational properties [32], and to calcu-
late linear-response characteristics with a reduced com-
putational effort [32, 33, 34].

IV. BEYOND THE LINEAR- AND
PLANAR-AVERAGE APPROXIMATIONS

A. Treating Systems with Partial Periodicity

In the preceding sections, we have assumed that the
corrective potential of a one- or two-dimensional system
can be obtained by homogenizing the system along its pe-
riodicity directions, as initially proposed by Baldereschi,
Baroni, and Resta [13]. This approach, referred to as
the linear- or planar-average approximation, has been
frequently employed in electronic-structure calculations
[13, 14, 17, 20, 37].

Alternative schemes adapting the Ewald method to
evaluate conditionally convergent lattice sums [38] or
generalizing the FMM approach [39, 40] have also been
proposed for systems exhibiting partial periodicity. Such
schemes are particularly suited to localized-orbital cal-
culations but are of relatively limited applicability for
plane-wave implementations. Here, we propose an effi-
cient method to calculate the electrostatic potential for
partially periodic systems, taking into account the full
three-dimensional structure of the charge distribution.
In addition to presenting this methodological extension,
we discuss how to assess the validity of the linear- and
planar-average approximations a priori in terms of struc-
tural characteristics of the system.

B. DCC Scheme for One-dimensional Periodicity

To introduce the DCC approach for one-dimensional
systems, we first study the electrostatic problem corre-
sponding to an isolated sinusoidal-density line:
\[ \rho(r) = \delta^{(2)}(r_\perp) \exp(ig_zz), \]  
where \( \delta^{(2)} \) stands for the two-dimensional Dirac delta
function and \( r_\perp \) denotes the transverse coordinates \((x, y)\).
Making the ansatz \( v(r) = \mathcal{G}(r_\perp; g_z) \exp(ig_zz) \) for
the Green’s function, we obtain:
\[ (\nabla_\perp^2 - g_z^2)\mathcal{G}(r_\perp; g_z) = -4\pi\delta^{(2)}(r_\perp). \]
The solution of this generalized electrostatic problem can be written as:

\[
\begin{align*}
    G(r_\perp; 0) &= -2 \ln |r_\perp|, \\
    G(r_\perp; g_z) &= 2K_0(g_z |r_\perp|) \quad \text{for } g_z \neq 0
\end{align*}
\]

(24)

where \(K_0\) is the modified Bessel function of the second kind. Note that \(K_0(g_z |r_\perp|) = -\ln |r_\perp| + \ldots\) when \(g_z |r_\perp|\) approaches zero, reflecting the fact that a sinusoidal-density line can be considered as uniform when seen from a distance much smaller than its wavelength. Knowing the electrostatic potential generated by a single line (the Green’s function characterizing the generalized electrostatic problem), the potential of an arbitrary one-dimensional charge distribution can be determined analytically, as illustrated in Figure 12. The general procedure consists of calculating the one-dimensional Fourier transform of \(\rho\) to obtain its longitudinal Fourier components \(\rho(r_\perp; g_z)\) (step 1). Each individual component is then convoluted with the electrostatic potential generated by a sinusoidal density, as expressed in Eq. (24) to obtain the Fourier components \(v(r_\perp; g_z)\) of the open-boundary potential (step 2):

\[
\begin{align*}
    v(r_\perp; 0) &= -2 \int \ln |r_\perp - r'_\perp| \rho(r'_\perp; 0) dr'_\perp, \\
    v(r_\perp; g_z) &= 2 \int K_0(g_z |r_\perp - r'_\perp|) \rho(r'_\perp; g_z) dr'_\perp \quad \text{for } g_z \neq 0.
\end{align*}
\]

(25)
Finally, the open-boundary potential is transformed back to real space (step 3). We underscore that this procedure directly extends the linear-average approximation since the linear average of the charge density corresponds to the first term of the one-dimensional Fourier decomposition. Thus, averaging the charge density along the axis of periodicity amounts to restricting the Fourier series to its \( g_z \neq 0 \) term.

To estimate errors resulting from this truncation, we analyze the asymptotic behavior of \( v(r_\perp; g_z) \) at large \( g_z \rvert r_\perp \rvert \)
\[
v(r_\perp; g_z) \approx \sqrt{\frac{\pi}{2}} \frac{e^{-g_z r_\perp}}{g_z r_\perp} \text{ when } g_z \rvert r_\perp \rvert \gg 1. \tag{26}
\]

From Eq. 26, the validity of the linear-average approach can be assessed by calculating the ratio of the cell size in the transverse direction \( L_\perp \) (that is, the distance between periodic replicas) to the typical wavelength \( \lambda_\parallel \) characterizing longitudinal inhomogeneities in the system. For large values of the dimensionless parameter \( L_\perp/\lambda_\parallel \), periodic-image interactions are predominantly due to the logarithmic first-order contribution \( v(r_\perp; 0) \) corresponding to the linear average of the charge density. Thus, as expected intuitively, the linear-average approximation is valid in this situation. In contrast, when \( \lambda_\parallel \) is comparable to the distance \( L_\perp \) between periodic images, higher-order Fourier components \( v(r_\perp; g_z) \) corresponding to \( g_z \approx 2\pi/\lambda_\parallel \) must also be taken into consideration.

Despite its merit in discussing the validity of the linear-average approximation, determining the open-boundary potential using the preceding approach requires expensive summations for each point \( r_\perp \) of the two-dimensional grid and for each longitudinal wavevector \( g_z \). Along the same methodological lines as those of the DCC algorithm, a substantial reduction of computational cost can be achieved by exploiting the periodic potential \( v' \), whose longitudinal Fourier components can be computed inexpensively using FFT techniques:

\[
\begin{aligned}
\left\{ v'(r_\perp; 0) &= \sum_{g_\perp \neq 0} \frac{4\pi}{g_\perp} \rho(g_\perp) e^{i g_\perp r_\perp}, \\
v'(r_\perp; g_z) &= \sum_{g_\perp} \frac{4\pi}{g_\perp^2 + g_z^2} \rho(g_\perp + g_z \hat{z}) e^{i g_\perp r_\perp} \text{ for } g_z \neq 0.
\end{aligned}
\tag{27}
\]

After coarse-grid interpolation, the component of the open-boundary potential \( v(r_\perp; g_z) \) can be calculated at the boundaries of the domain, yielding Dirichlet boundary conditions for the smooth corrective components \( v'_{\text{corr}}(r_\perp; g_z) = v'(r_\perp; g_z) - v'(r_\perp; g_z) \). The corresponding \( g_z \)-dependent electrostatic problems read:
\[
\begin{aligned}
\nabla^2 v'_{\text{corr}}(r_\perp; 0) &= -4\pi \rho \\
(\nabla^2 - g_z^2) v'_{\text{corr}}(r_\perp; g_z) &= 0 \text{ for } g_z \neq 0
\end{aligned}
\tag{28}
\]

These differential equations can be solved using efficient multigrid techniques. Once calculated, the longitudinal Fourier components of the electrostatic correction are added to those of the periodic potential, thereby recovering \( v(r_\perp; g_z) \). Finally, the potential \( v(r) \) is computed via an inverse Fourier transform.

C. DCC Scheme for Two-dimensional Periodicity

The electrostatic potential of a slab can be calculated in real space using a scheme similar to that presented above. The formalism is to a great extent analogous to that developed by Lang and Kohn for studying interactions between localized external charges and metallic surfaces [41], and to the Green’s function approach recently proposed by Otani and Sugino [42]. The prescription consists of performing two-dimensional Fourier transforms to obtain the charge-density profile \( \rho(z; g_\parallel) \) associated with each wavevector \( g_\parallel = (g_z, g_\parallel) \) parallel to the surface. Solving the electrostatic problem for sinusoidal density layers, the two-dimensional Green’s functions \( G(z; g_\parallel) \) can be written as:
\[
\begin{aligned}
G(z; 0) &= -2\pi |z|, \\
G(z; g_\parallel) &= \frac{2\pi}{g_\parallel} e^{-g_\parallel |z|} \text{ for } g_\parallel \neq 0.
\end{aligned}
\tag{29}
\]

Hence, as in the one-dimensional case, the density-average approximation is valid provided that the geometrical parameter \( L_\perp/\lambda_\parallel \) is large—this criterion is identical to that derived by Natan, Kronik, and Shapira [19]. In addition, the above expressions allow one to determine the corrective potential of a two-dimensional system by integrating the differential equations:
\[
\begin{aligned}
\frac{d^2}{dz^2} v'_{\text{corr}}(z; 0) &= -4\pi \rho \\
(\frac{d^2}{dz^2} - g_\parallel^2) v'_{\text{corr}}(z; g_\parallel) &= 0 \text{ for } g_\parallel \neq 0
\end{aligned}
\tag{30}
\]

Parenthetically, it is important to note that Eq. 30 can be solved analytically, taking into account the boundary
The convergence of the total energy with respect to transverse cell size for a −[CH\textsubscript{2}CF\textsubscript{2}]\textsubscript{3}−[CF\textsubscript{2}CH\textsubscript{2}]\textsubscript{3}− polymer chain without correction, corrected using the density-countercharge scheme with full Fourier decomposition (DCC), and by limiting the density-countercharge decomposition to the linear-average \( \mathbf{g} = 0 \) component (DCC/LA).

conditions calculated by superposition—that is, by convoluting the longitudinal components of \( \mathcal{G} \) and \( \rho \) (similarly to Eq. 25), then subtracting out the components of \( \nu' \). Therefore, the additional cost of the two-dimensional DCC correction is negligible.

### D. Applications

The convergence of the total energy with respect to transverse cell size for a fluoropolymer chain −[CH\textsubscript{2}CF\textsubscript{2}]\textsubscript{3}−[CF\textsubscript{2}CH\textsubscript{2}]\textsubscript{3}− of long periodicity \( \lambda_\parallel \approx 24 \) bohr is depicted in Figure 13. We employ ultrasoft pseudopotentials [43] with energy cutoffs of 50 and 500 Ry for the plane-wave expansions of the electronic wavefunc-

![FIG. 13: Total energy as a function of transverse cell size for a −[CH\textsubscript{2}CF\textsubscript{2}]\textsubscript{3}−[CF\textsubscript{2}CH\textsubscript{2}]\textsubscript{3}− polymer chain without correction, corrected using the density-countercharge scheme with full Fourier decomposition (DCC), and by limiting the density-countercharge decomposition to the linear-average \( \mathbf{g} = 0 \) component (DCC/LA).](image1)

![FIG. 14: Force on one of the fluorine atoms along a transverse lattice direction as a function of transverse cell size for a −[CH\textsubscript{2}CF\textsubscript{2}]\textsubscript{3}−[CF\textsubscript{2}CH\textsubscript{2}]\textsubscript{3}− polymer chain without correction, corrected using the density-countercharge scheme with full Fourier decomposing (DCC), and by limiting the density-countercharge decomposition to the linear-average \( \mathbf{g} = 0 \) component (DCC/LA).](image2)

![FIG. 15: Longitudinal density response coefficient \( \chi(g_\parallel) = \partial n(g_\parallel)/\partial v(g_\parallel) \) as a function of transverse cell size for a graphene sheet without correction, and corrected using the density-countercharge scheme with full Fourier decomposition (DCC).](image3)

To conclude this study, we consider the electronic density response of a graphene sheet subject to a perturbation field. Figure 15 reports the dependence of the linear-response coefficient \( \chi(g_\parallel) = \partial n(g_\parallel)/\partial v(g_\parallel) \) with respect to the interplane distance \( L_\perp \) for a longitudinal sinusoidal perturbation of wavevector \( q_\parallel = 1/25 \) bohr\(^{-1} \). The wavelength of the perturbation field being large (\( \lambda_\parallel = 157 \) bohr), the uncorrected response coefficient does not converge until reaching cell sizes on the order of hundreds of bohrs. Contrary to uncorrected calculations, the
DCC-corrected linear response shows considerable convergence improvement with a negligible increase in computation cost. For comparison, at an interplane distance of \( L_1 = 50 \text{ bohr} \), the relative error in the uncorrected linear-response coefficient \( \chi(g_1) \) is on the order of 25%, while it is lower than 1% using the DCC correction.

V. CONCLUSION

We have studied the analytical properties of the corrective potential, defined as the difference between the electrostatic potential and its periodic counterpart, unifying the Makov-Payne (PCC) and LMCC (GCC) schemes in the same class of periodic-image corrections and suggesting possible improvements for both methods. Based on these properties, we have shown that the periodic-image cost of these properties, we have shown that the periodic-image errors can be eliminated at a moderate computational cost of \( O(M^{5/3}) \), where \( M \) is the number of points of the mesh used in the calculation the corrective potential, which is generally about two orders of magnitude smaller than the number of points of the charge-density grid. The resulting density-countercharge (DCC) scheme owes its improved efficiency to the determination of the exact boundary conditions characterizing the electrostatic potential. In several cases of interest, we have shown that the DCC algorithm represents a beneficial compromise between cost and accuracy. The validity of the linear- and planar-average approximations routinely employed in the study of partially periodic systems has also been discussed. An efficient scheme going beyond these conventional approximations for inhomogeneous systems has been proposed and validated.

Relevant applications for the DCC algorithm include the study of molecular adsorption at solid-vacuum interfaces in the constant-charge regime, the determination of structural parameters, the correction of vibrational spectra, the inexpensive calculation of work functions, and the determination of linear-response properties with a reduced computational effort.

Acknowledgments

The calculations in this work have been performed using the Quantum-Espresso package [44] (GNU General Public License), and the conjugate-gradient multigrid solver developed by M. Holst, as part of the Parallel algebraic Multigrid/Finite-element Toolkit [45]. Both software packages are licensed for use under the GNU General Public License.

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APPENDIX A: MADELUNG CONSTANTS AND GAUSSIAN POTENTIALS

In this appendix, we determine the Madelung constants of periodic point charges immersed in a compensating jellium background in one, two, and three dimensions for lattices characterized by a single geometric parameter \( L \). A compilation of high-precision values for these fundamental constants is generally not found in the literature.

These values are computed using the asymptotic expansion of the Madelung constant \( \alpha_{\sigma/L} \) of an array of Gaussian charges of spread \( \sigma \) in a compensating jellium, which is defined as:

\[
\alpha_{\sigma/L} = (v_\sigma(0) - v'_{\sigma,L}(0))L^{d-2},
\]

where \( d \) is the spatial dimension. To obtain the expansion of \( \alpha_{\sigma/L} \) in the limit \( \sigma/L \to 0 \), we may write \( v'_{\sigma,L}(0) \) as:

\[
v'_{\sigma,L}(0) = \frac{L^{2-d}}{\Omega_d}w_d(\frac{\sigma^2}{L^2}),
\]

where \( \Omega_d \) is the volume of \( d \)-dimensional unit cell, and \( g' = Lg \) denotes the dimensionless wavevector. Differentiating \( w_d \) with respect to \( \sigma^2/L^2 \), we obtain:

\[
\frac{dw_d}{d(\sigma^2/L^2)} = -\pi \sum_{g' \neq 0} \exp(-\frac{g'^2}{4} \cdot \frac{\sigma^2}{L^2}),
\]

In the limit \( \sigma/L \to 0 \), this derivative becomes:

\[
\frac{dw_d}{d(\sigma^2/L^2)} = -\pi \frac{\Omega_d}{\pi^{d-1}} \left( \frac{\sigma^2}{L^2} \right)^{-d/2} \int_{R^d} e^{-u^2}du + ...
\]

Integrating this expression, we obtain the asymptotic expansions of \( v'_{\sigma,L}(0) \) and \( \alpha_{\sigma/L} \) listed in Table [54].

Hence, the Madelung constant \( \alpha_0 \) can be calculated with high accuracy from the expansion of \( \alpha_{\sigma/L} \). In the case of a cubic lattice of point charges, we obtain:

\[
\alpha_0 \approx \alpha_{\sigma/L} + \frac{\pi \sigma^2}{L^2} - \sum_{n \neq 0} \frac{1}{|n|} \operatorname{erfc}(\frac{L}{\sigma}|n|)
\]
frequently found in the literature:

\[ \alpha \approx \frac{4\pi e^{-\sigma^2 g^2/4}}{g^2} \left( -\frac{2L}{\sqrt{\pi \sigma}} L^2 \right) \]

\[ + \frac{\pi \sigma^2}{L^2} \sum_{n \neq 0} \frac{1}{|n|} \text{erfc} \left( \frac{L}{\sigma} |n| \right) \]

(A6)

where \( n = (i, j, k) \) denotes an integer vector. Figure 16 illustrates the rapid convergence of the Madelung constant calculated from Eq. (A6) for a cubic unit cell. This expression converges considerably faster than the expression frequently found in the literature:

\[ \alpha = \frac{4\pi e^{-\sigma^2 g^2/4}}{g^2} \left( -\frac{2L}{\sqrt{\pi \sigma}} \right) \]

\[ \sum_{n \neq 0} \frac{1}{|n|} \text{erfc} \left( \frac{L}{\sigma} |n| \right). \]

(A7)

Although a similar procedure can be applied without additional difficulty for any dimensionality, we draw attention to the fact that in two dimensions, \( \alpha_{\sigma/L} \) is not equal to the Madelung constant \( \alpha \) in the limit \( \sigma/L \to 0 \), due to the logarithmic divergence of the potential. For a more complete discussion of the two-dimensional case, we refer the reader to the study of Cichocki and Felderhof [21]. As a final remark, we note that the one-dimensional Madelung constant can be determined analytically from the relation:

\[ \sum_{n=1}^{+\infty} \frac{1}{n^2} = \zeta(2) = \frac{\pi^2}{6}, \]

where \( \zeta \) stands for the Riemann zeta function.

APPENDIX B: PERFORMANCE OF THE MULTIPOLe-EXPANSION METHOD

The performance of the multipole-expansion adaptation of the DCC scheme—the multipole-countercharge (MCC) correction—for a pyridazine cation is compared to that of the PCC and GCC schemes in Figure 17. The size of the calculation cell ranges from 12 to 19 bohr. The labels \( D \) (dipole) and \( Q \) (quadrupole) indicate the order of the multipole expansion. For each scheme the corrective potential is updated every five SCF iterations.

![Figure 16: Convergence of the Madelung constant as a function of the geometric parameter \( L/\sigma \) for a cubic unit cell using the approximation given by Eq. (A6). (The black curve is Eq. (A6) without the \( \pi \sigma^2/L^2 \) and the complementary-error-function terms, the red curve is Eq. (A6) without the complementary-error-function term, and the blue curve is Eq. (A6). Note the negligible contribution of the complementary-error-function term beyond \( L/\sigma = 3 \) and the improvement in convergence brought about by the term \( \pi \sigma^2/L^2 \).)](image)

![Figure 17: Accuracy of the total energy of a pyridazine cation as a function of computational time using the PCC, GCC, and MCC schemes for cell sizes above 17 bohr. The labels \( D \) (dipole) and \( Q \) (quadrupole) indicate the order of the multipole expansion. For each scheme the corrective potential is updated every five SCF iterations.)](image)

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| 3 D lattice | α₀ | 2 D lattice | α | 1 D lattice | α₀ |
|-------------|----|-------------|---|-------------|----|
| cubic       | 2.837 297 479 | squared     | 2.621 065 852 | linear | −π/3 |
| body-centered | 3.639 233 449 | hexagonal   | 2.786 075 893 |         |     |
| face-centered | 4.584 862 074 |             |              |         |     |

\[ v_\sigma(r) = \frac{1}{\sqrt{2\pi}} \text{erf}(\frac{r}{\sqrt{\sigma}}) \]
\[ v'_\sigma(L) = \frac{1}{\sqrt{2\pi}} \sum_{g \neq 0} \frac{4\pi e^{-\frac{1}{\sigma} g^2/4+ig\cdot r}}{g} \]
\[ v_\sigma(0) = \frac{2\sqrt{\pi\sigma}}{\sqrt{\sigma}-\alpha_0 + \frac{\sigma}{2} + ...} \]
\[ v'_\sigma(0) = \ln(\frac{2\sqrt{\pi\sigma}}{\sigma_0}) - \alpha + \frac{\sigma}{2} + ... \]
\[ \alpha_\sigma/L = \alpha_0 + \frac{\sigma}{2} + ... \]

TABLE I: Madelung constants in one, two, and three dimensions computed using the procedure described in Appendix A, along with the quantities used in the calculation. Ei denotes the exponential integral and \( \gamma = 0.577 215 665 \) is the Euler constant.