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Periodic boundary conditions in *ab initio* calculations

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The convergence of the electrostatic energy in calculations using periodic boundary conditions is considered in the context of periodic solids and localized aperiodic systems in the gas and condensed phases. Conditions for the absolute convergence of the total energy in periodic boundary conditions are obtained, and their implications for calculations of the properties of polarized solids under the zero-field assumption are discussed. For aperiodic systems the exact electrostatic energy functional in periodic boundary conditions is obtained. The convergence in such systems is considered in the limit of large supercells, where, in the gas phase, the computational effort is proportional to the volume. It is shown that for neutral localized aperiodic systems in either the gas or condensed phases, the energy can always be made to converge as $O(L^{-5})$ where L is the linear dimension of the supercell. For charged systems, convergence at this rate can be achieved after adding correction terms to the energy to account for spurious interactions induced by the periodic boundary conditions. These terms are derived exactly for the gas phase and heuristically for the condensed phase.

I. INTRODUCTION

Periodic boundary conditions (PBC's) have been applied extensively in theoretical modeling of crystalline solids. Introduction of these boundary conditions is equivalent to considering an infinite Bravais lattice. The shape of the cell to which the PBC's are applied determines the type of lattice, and the contents of the cell determine the lattice basis. In particular, quantum *ab initio* calculations have combined periodic boundary conditions with plane-wave expansions to create a powerful calculational scheme, which has been applied extensively in the study of properties of crystalline solids.[1] There is some interest in extending this method to aperiodic systems such as molecules,[2] defects in solids,[3] and disordered or liquid-condensed matter. This interest arises from the following considerations:

(i) PBC's are a simple way to impose the boundary conditions in calculations of condensed matter. (ii) PBC are compatible with plane-wave expansions, which in turn allow for relatively simple calculations of forces in molecular-dynamics simulations. (iii) Unified numerical schemes can be set up to consider both periodic and aperiodic systems.

There is, however, a major difference between (static) calculations on periodic and on aperiodic systems when PBC's are used. For periodic systems, a calculation on one unit cell can yield all the information that may be obtained. In an aperiodic system, there is no periodic unit cell. Instead the calculation is performed on a portion of the system of interest contained in a supercell, which is then periodically repeated in space for calculational convenience. Only in the limit of an infinitely large supercell do the calculated results converge to the properties of the aperiodic system. If the aperiodicity is local (e.g., a localized defect in a solid, a molecule in a gas), then the difference between results obtained using any finite-sized supercell and those obtained in an infinitely large supercell arises from the spurious interactions of the system with its images in neighboring supercells. If the aperiodicity exists at all length scales, as in the case of a random solid, then, in addition to the above, the energy will fluctuate statistically about its expected value. In this paper we consider only the first of these two possibilities.

Since the results required in a calculation of an aperiodic system are obtained only in the limit $L \to \infty$, where L is the linear dimension of the supercell, it is necessary to consider their convergence. This can depend on the quantity being calculated. In practice, it is often sufficient to consider the convergence of the energy as all the other properties are determined through the variational principle. The convergence of the energy, as the size of the supercell is increased, is determined by the longest-ranged forces, which in general are the electrostatic forces. In solids, the elastic forces can also be long ranged and in principle can be treated similar to the electrostatic forces by the methods described below. The rate of convergence can be very slow, as in the case of a charged species for which the energy converges as L^{-1}. The importance of the rate of convergence lies in the fact that the computational effort is proportional to the volume of the supercell. Typically, in a Kohn-Sham-type calculation using a plane-wave expansion and PBC, the computational effort increases as $V_c \ln V_c$ for an isolated molecular species, where V_c is the supercell volume (i.e., $V_c \sim L^3$).[1] If the exact asymptotic dependence on the linear dimension of the supercell is known, then the energy calculated at finite L can be corrected to provide a better, and more rapidly converging, estimate of the energy in an infinitely large supercell. A step in this direction was taken by Leslie and Gillan[3] who considered the case of a charged defect in a solid and showed heuristically that the leading term in the convergence of the defect formation energy was γL^{-1}, where γ is a calculable constant involving the dielectric constant, for which they used an experimental value.

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To obtain the convergence properties of the electrostatic energy in the limit of infinitely large supercells, it is necessary to have an expression for the electrostatic energy in PBC's. Such expressions were first considered, to our knowledge, early this century in the context of the cohesive energy of ionic solids.[4] However, despite the many years that have passed there is continuing controversy over the exact properties of these expressions.[5] The source of much of this controversy is the fact that electrostatic sums on an infinite lattice are not always absolutely convergent, but for some lattice bases can be only conditionally convergent or even divergent. This can introduce a certain ambiguity into the results, commonly in the form of a constant and unknown potential,[6] but in some cases in the form of a constant and unknown electric field (see Sec. II below). The problem is sometimes compounded by the use of mathematically ill-defined operations involving divergent terms and limits of vectors.[4–6] An important exception to this, was the work of de Leeuw, Perram, and Smith[7] who considered in detail the electrostatic energy of a neutral assembly of classical point charges in a repeated cubic supercell.

In what follows, we present a systematic derivation of the electrostatic energy of an assembly of point charges together with a continuous charge distribution placed in a periodically repeated cell of arbitrary geometry. This derivation is a generalization of the work of de Leeuw, Perram, and Smith.[7] In the course of making this derivation, some conditions for modeling a crystal as an infinite solid by the introduction of PBC's are obtained, in particular with respect to polarized crystals. Then, in Sec. III, the asymptotic convergence of the electrostatic energy of neutral and charged aperiodic systems in PBC is considered. First, we show that for isolated molecular species the rate of convergence can always be reduced to $O(L^{-5})$. This is illustrated with several numerical examples. Then, for the case of aperiodic systems in condensed phases, we show that the same rate of convergence can be achieved if the aperiodic system is neutral. For a charged aperiodic system, the convergence can be reduced to $O(L^{-5})$ by introduction of the dielectric constant, which may be obtained separately or by fitting the data. A short discussion and a summary conclude this paper.

II. CALCULATION OF THE ELECTROSTATIC ENERGY IN PBC

Consider a finite sample of N periodically repeated cells, each of which contains a charge density $\rho(\mathbf{r})$ comprised of point charges and a continuous charge distribution $n(\mathbf{r})$,

$$\rho(\mathbf{r})=\sum_i z_i\delta(\mathbf{r}-\mathbf{r}_i)+n(\mathbf{r}) \ . \tag{1}$$

This charge density is periodic with the periodicity of the lattice vectors, $\boldsymbol{l}$

$$\rho(\mathbf{r}+\boldsymbol{l})=\rho(\mathbf{r}) \ .$$

The electrostatic potential at an arbitrary point $\mathbf{r}$ in the sample is

$$\begin{aligned}\phi(\mathbf{r})&=\int_{\text{sample}} d^3r'\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\\&=\sum_{\boldsymbol{l}}\int_{\text{cell}} d^3r'\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'+\boldsymbol{l}|} \ ,\end{aligned} \tag{2}$$

where the sum is over all the N cells. The cell in which the point $\mathbf{r}$ is located, is taken as the origin of the lattice. To obtain result (2), it is necessary to assume the existence of zero-potential Dirichlet boundary conditions at infinity.[8]

If the sample is macroscopic, then N is very large and we would like to simplify the mathematics by extending the finite sum over the lattice vectors in Eq. (2) to an infinite sum. This extension is equivalent to introducing periodic boundary conditions and may be performed only if the sum does not diverge. There are two possible cases to be considered.

(i) The sum is absolutely convergent, in which case the potential will have converged for large N and extending the sum to infinity will not affect the results, or in physical terminology the surface terms make a negligible contribution to the potential. (ii) The sum is conditionally convergent, in which case the result depends on the order of summation, or in physical terminology on the contribution of the surface terms.

What are the convergence properties of the sum in Eq. (2) after it has been extended to infinity? These can be obtained by transforming the sum over the lattice vectors $\boldsymbol{l}$ to a sum over spherical shells s of lattice sites at distances $|\boldsymbol{l}|$ from the lattice origin,

$$\sum_{\boldsymbol{l}}\rightarrow\sum_{s}\sum_{\forall \boldsymbol{l}\in s} \ . \tag{3}$$

The convergence will be determined by the contributions of distant shells (large $|\boldsymbol{l}|$) to the sum. In this limit, the asymptotic form of the summand in Eq. (2) is well known to be[8]

$$q_nP_n(\cos\theta)|\boldsymbol{l}|^{-(n+1)} \ , \tag{4}$$

where n is determined by q_n, which is the lowest nonzero multipole of the charge distribution ρ (defined as the nth radial moment of the charge distribution). P_n are the Legendre functions with $\cos\theta=(\mathbf{r}-\mathbf{r}')\cdot\boldsymbol{l}/|\mathbf{r}-\mathbf{r}'||\boldsymbol{l}|$. For odd values of n, the inversion symmetry of the Bravais lattice ensures that the asymptotic contributions from this multipole to the sum are identically zero. If the lowest nonzero multipole is $n=0$, then there is a net charge in the unit cell and the sum of the asymptotic terms in Eq. (3) diverges. If it is $n=3$, or greater, then the sum in Eq. (3) is seen to converge absolutely. If the lowest nonzero multipole is $n=2$, then the sum in Eq. (3) is conditionally convergent by Dirichlet's test.[9] Note that these conclusions require the lattice sum in Eq. (2) to be three-dimensional.

The same approach can be applied to derivatives of the potential: One finds that, e.g., the equivalent sum for the electric field is absolutely convergent if the lowest nonzero multipole is $n=2$ or greater. This sum is conditionally convergent if $n=1$ and diverges if $n=0$. What is the extent of the indeterminacy introduced by the conditional convergence? Consider first the potential: It is conditionally convergent if and only if the lowest nonzero multipole is $n=2$ (quadrupole). This is the lowest multipole if the unit cell is neutral and does not have a dipole. In this case, the sum for the electric field is absolutely convergent, so the potential is undetermined to an additive constant. This constant is determined by the contributions of the charges at the surface of the sample and can be identified as the electrostatic surface barrier. Therefore, this constant cannot be determined by this calculation.[6] Not knowing the value of the constant potential in the lattice does not affect the calculation of the energy of the unit cell because it is charge neutral. It also does not affect the forces on the ions and electrons in the cell as it is independent of position. The exact summation of the potential in an infinite lattice has been obtained in the Appendix and, in this case, it is equal to

$$\phi(\mathbf{r})=\int_{\text{cell}} d^3r'\,\rho(\mathbf{r}')\left[\psi(\mathbf{r},\mathbf{r}')-\frac{2\pi}{3V_c}r'^2\right],$$

$$\psi(\mathbf{r},\mathbf{r}')=\sum_{l}\operatorname{erfc}(\eta|\mathbf{r}-\mathbf{r}'+\mathbf{l}|)+\frac{4\pi}{V_c}\sum_{\mathbf{g}\neq 0}\frac{1}{g^2}e^{-g^2/4\eta^2}e^{i\mathbf{g}\cdot(\mathbf{r}-\mathbf{r}')}\,, \tag{5}$$

where $\mathbf{g}$ are the reciprocal lattice vectors and V_c is the volume of the unit cell.

Now consider a unit cell with a nonvanishing dipole, noting that the value of the dipole can be ill defined when periodic boundary conditions are used.[10] This is illustrated in Fig. 1 for a classical point-charge distribution. As can be seen, the choice of supercell (a) or (b) yields very different dipole moments, while the choice of supercell (c) yields the same dipole moment as (a) (a similar argument can be extended for higher multipoles). In an infinite lattice of unit cells with nonvanishing dipoles, we have shown above that the sum for the electric field is conditionally convergent and that the sum for the potential is divergent. From similar arguments to those used before for the potential, one sees that the derivatives of the electric field with respect to space are absolutely convergent, so the extent of the indeterminacy is an unknown constant electric field. (See also the discussion in Ref. 11.) This means that the energy per unit cell of the infinite sample and the forces on the electrons and ions in the unit cell are indeterminate until the surface contributions have been defined. In the Appendix, we have calculated the potential in a lattice with a dipolar basis under the assumption of spherical boundary conditions and found

$$\phi(\mathbf{r})=\int_{\text{cell}} d^3r'\,\rho(\mathbf{r}')\left[\psi(\mathbf{r},\mathbf{r}')-\frac{2\pi}{3V_c}r'^2\right]+\frac{4\pi}{3V_c}\mathbf{r}\cdot\int_{\text{cell}} d^3r'\,\mathbf{r}'\rho(\mathbf{r}')\,, \tag{6}$$

where ψ is defined in Eq. (5). Comparison with the potential in an infinite lattice without a dipole, (5), shows that only the last term in (6) originates in the dipolar contribution. Indeed it has the form of a constant electric field, the magnitude of which is determined by the shape of the boundary conditions and the definition of the unit cell. In a periodic solid, all choices of supercell geometry relative to the charge distribution should yield equivalent potentials (and energies). This is not the case with Eq. (6); however, this merely reflects the fact that the potential in an infinite lattice with a dipolar basis is not uniquely defined but depends on the contributions of the surface terms, as discussed above.

Some calculations on polarized solids have used periodic boundary conditions with an additional assumption of zero electric field.[12] This means that an external process has caused the potential at different surfaces to be equal. This is often the case in macroscopic samples of polarizable solids where impurities tend to adsorb on the surface and equilibrate the potential. Therefore, one may apply the zero-field condition to calculate static properties of such a polarized crystal using an infinite lattice model. (The results may not necessarily apply to a pure crystalline sample.) The electrostatic energy functional that should be used is that of Eq. (5), which is obtained from the dipolar case, (6), by removing the term linear in the electric field. Calculations of dynamic processes are likely to involve a change in the surface configuration and, therefore, the creation of potential differences and the associated electric fields (i.e., piezoelectric effects). The zero-field approximation can still be applied in such calculations, but this implies the existence of an external process, which rapidly equalizes the potential on the different surfaces of the crystal. The existence of such an external process, and its relevance to the dynamics, must be considered separately for each case.

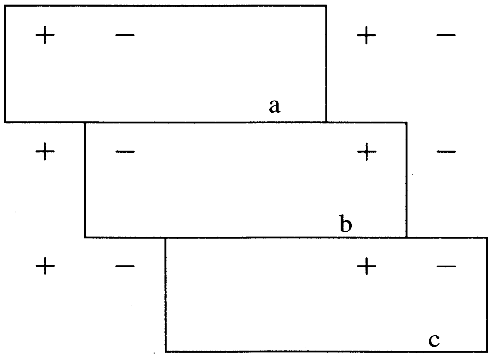

FIG. 1. A section of a periodic classical charge distribution, denoted by the + and − signs, with three possible choices for the supercell.

III. APERIODIC SYSTEMS IN PBC

When calculating the energy of an aperiodic system using periodic boundary conditions, one is interested only in the energy, E_0 in the limit $L\rightarrow\infty$, where L is the linear dimension of the supercell. The energy calculated for a finite supercell $E(L)$ differs from E_0, because of the spurious interactions of the aperiodic charge density with its images in neighboring cells. Furthermore, these interactions induce changes in the aperiodic charge density itself, which depend on L. To estimate E_0 from the calculated $E(L)$, we need to know the asymptotic dependence of the energy on L. For simplicity, we concentrate first on the case of an isolated molecular species in a large supercell, such that the entire molecular charge density is contained in the supercell. In practice, the electron density decays exponentially away from the molecular and the supercell need only be large enough for the density at the surface of the cell to be in this regime. If there was no induced charge density, then the multipole moments would be exponentially convergent with L, while we wish to study the convergence of the electrostatic energy, which will have the form of a power law in L. The leading term in the induced charge density will be the induced dipole, the magnitude of which is determined by the electric field. If the molecule has a permanent dipole then the induced dipole will be $O(L^{-3})$ and its leading contribution to the electrostatic energy $O(L^{-6})$, reflecting the dipole-induced dipole interactions. If the molecule has no dipole moment, then the induced density is $O(L^{-5})$ at least. [This result is also obtained for a molecule with a permanent dipole moment, if the supercell is chosen to be cubic—see below Eq. (9).] As we confine our discussion below to terms in the energy that converge as $O(L^{-5})$, we can ignore the effects of induced charge distributions on the convergence of the energy of an isolated molecular species.

A. Neutral molecular species

Consider first the case of an isolated neutral molecule that has no dipole moment. The energy is absolutely convergent and is given by Eq. (A14) in the Appendix or equivalent by direct summation of Eq. (2) and integration. The exact details need not concern us here as it is sufficient to note that the asymptotic behavior is determined by the quadrupole-quadrupole interaction, which has the functional dependence of $|l|^{-5}$. For large supercells, the quadrupoles will be independent of L and the energy will be

$$E(L)=E_0+O(L^{-5}) \; . \tag{7}$$

Consider next an isolated neutral molecule that has a dipole moment. In this case, we first have to define what energy is being calculated, because the energy of an infinite lattice with a basis that has a dipole moment is not well defined, as discussed above in Sec. II. However, in a calculation of an aperiodic system the infinite lattice is merely a device and is not meant to correspond to any physical reality. Therefore, the order of summation of the electrostatic sum (i.e., the surface) can be chosen for convenience. Choice of summation over spherical shells is considered in the Appendix and the electrostatic energy functional is found to be

$$E=\tfrac{1}{2}\int_{\text{cell}} d^3r\,\rho(\mathbf{r})\int_{\text{cell}} d^3\mathbf{r}'\,\rho(\mathbf{r}')\psi(\mathbf{r},\mathbf{r}') + \frac{2\pi}{3V_c}\left|\int_{\text{cell}} d^3r\,\mathbf{r}\rho(\mathbf{r})\right|^2 , \tag{8}$$

where if there are point charges in the charge distribution, the modified functional in Eq. (A14) of the Appendix should be used. Two comments should be made about Eq. (8).

(i) It differs from commonly used energy functional (e.g., that in Ref. 1) in having an additional dipole-dependent term. In the case of an infinite periodic solid, the same arguments apply as those used above in discusssing the potential. For an aperiodic system, the absence of this term will not change the value of the energy in the limit $L\rightarrow\infty$, E_0, as the additional term is $O(L^{-3})$. However, if the dipole term in Eq. (8) is not included then the energy will converge to E_0 with an additional $O(L^{-3})$ term. Furthermore, since this additional term in the energy functional contains the position coordinate explicitly, it will also mean that the forces will converge more slowly to their limiting value.

(ii) It has been noted[10] that the dipole moment is ill defined in PBC's. In a periodic solid, all choices of supercell geometry relative to the charge distribution should yield equivalent energies. This is not the case with Eq. (8) as different choices of supercell will yield different values of the dipole moment and, therefore, different energies. However, this is not really a problem as it merely reflects the fact that an infinite periodic solid with a dipolar basis does not have a well-defined energy. However, in a calculation of an aperiodic system, different choices of supercell need not be equivalent. The relevant choice of supercell geometry relative to the charge distribution is determined by the system to be considered in the limit $L\rightarrow\infty$. The supercell chosen must include the entire aperiodic system in the same configuration as it would be in the bulk limit. If this condition is obeyed, then the dipole moment is invariant to the choice of supercell as in choices (a) and (c) in Fig. 1. Choosing supercell (b) would imply choosing to study a different aperiodic system in the limit $L\rightarrow\infty$.

What is the asymptotic convergence of the energy with increasing supercell size in this case? From the same considerations as above, the energy is dominated by the dipole-dipole interactions, which have the functional dependence $|l|^{-3}$ and, therefore, in general, would lead to an $O(L^{-3})$ convergence. However, by choosing the supercell to be a cube we can make use of the special symmetry of the Legendre functions on a cube, first pointed out in this context by Nijboer and deWette.[11] The contribution of the dipoles on a spherical shell of radius $|l|$ to the electric field at the origin is

$$\sum_{l\in|l|}\frac{3(\mathbf{p}\cdot l)^2}{l^2}-p^2=3\sum_{j=x,y,z}p_j^2\sum_{l\in|l|}\frac{l_j^2}{l^2}-p^2=0 \; , \tag{9}$$

where l_j is the cartesian component of l in direction j. This result implies that dipoles on a cubic lattice do not interact and, therefore, the energy in such a calculation will converge $O(L^{-5})$. If it is necessary to use a supercell with a shape other than a cube, then the contribution to the energy arising from the dipole interactions may be calculated by performing the relevant lattice sum, which depends on the specific lattice geometry.

As an example, we have calculated the potential energy of stretching a NaCl molecule by 0.3 A from equilibrium. The calculations were based on the Kohn-Sham

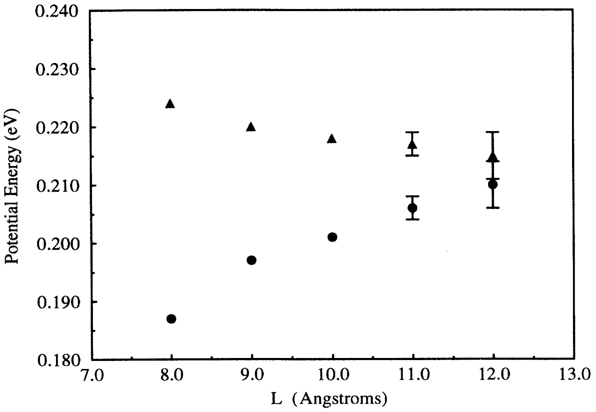

FIG. 2. The potential energy of stretching a NaCl molecule by 0.3 A from equilibrium calculated for cubic supercells of side L. The triangles refer to the electrostatic energy functional in Eq. (8), while the filled circles refer to the same functional without the dipole term.

method,[13] using pseudopotentials to represent the core electrons and the nuclei, periodic boundary conditions, and a plane-wave representation of the electron wave functions.[1] The supercell was chosen to have a cubic geometry and the molecule was located at the center of the cube. The calculations were performed using the program CASTEP, the principles of which have been described elsewhere.[1] The calculation was performed both with the dipolar term in the electrostatic energy functional and without. Therefore, we expect the results to converge as $O(L^{-5})$ and $O(L^{-3})$, respectively. The results are shown in Fig. 2, where one can clearly see that the energy calculated without the dipole term in Eq. (8) converges more slowly than the energy calculated with this term. Also, note that both calculations converge to the same result within numerical accuracy. (The numerical error increases with cell size due to an instability associated with the representation of the electrostatic potential in reciprocal space.)[1]

B. Nonneutral molecular species.

Calculation of the energy of a charged system is of interest for ions or charged impurities in crystalline solids. However, the energy of a periodically repeated electrically charged system diverges. For an aperiodic system, practical interest is restricted to the limit of an infinitely large supercell, which contains the charged system. This limit is identical to that obtained from a similar system, which consists of the original charged system immersed in a jellium background which fills the supercell and neutralizes the charge, so that the net charge is zero.[3] For this new system, the calculation can proceed as discussed in the previous section. The energy of the unit cell in this calculation will converge slowly, reflecting the decreasing interaction between the charge species and the jellium background as the supercell is taken to be larger and larger. This convergence will have the form of a power law in L, and in this section we obtain the asymptotic dependence on supercell size of the electrostatic energy of a charge species to $O(L^{-5})$.

The charge density of the immersed system consists of the density of the charged species, $\rho_c(\mathbf{r})$ and the jellium density, n_0;

$$\rho(\mathbf{r})=\rho_c(\mathbf{r})+n_0 \ . \tag{10}$$

Assuming a total charge q on the charged species, then $n_0=-q/V_c$ to ensure charge neutrality. The density may be split into two contributions by adding and subtracting a point charge q at $\mathbf{r}_0$,

$$\rho(\mathbf{r})=[q\delta(\mathbf{r}-\mathbf{r}_0)+[\rho_c(\mathbf{r})-q\delta(\mathbf{r}-\mathbf{r}_0)] \ . \tag{11}$$

The density in the first brackets on the right-hand side of Eq. (11) will be denoted as ρ_1 and the density in the second brackets as ρ_2. $\mathbf{r}_0$ can be chosen to be any point in the supercell. A useful choice, which we make use of below, is to choose $\mathbf{r}_0$ so that ρ_2 has no dipole, and the origin of the coordinates is chosen to be at the center of the unit cell.

We wish to obtain the asymptotic contributions to the energy in the limit of large supercells. The electrostatic energy can now be considered to be the sum of three energies: ρ_1 on a lattice interacting with itself, E_{11}; ρ_2 on a lattice interacting with itself, E_{22}; and ρ_1 and ρ_2 on a lattice interacting only with each other, E_{12}. E_{11} is well known to be the Madelung energy of a lattice of point charges immersed in neutralizing jellium[4]

$$E_{11}=-\frac{q^2\alpha}{2L} \ , \tag{12}$$

where α is the lattice-dependent Madelung constant. E_{22} is the interaction energy of a neutral charge density on a lattice. Since the ρ_2 has no dipole moment (due to the choice of $\mathbf{r}_0$), E_{22} will converge as $O(L^{-5})$ as discussed above.

Last, consider E_{12}: This is the interaction energy between two different neutral charge densities, which at first might be expected to also have an $O(L^{-5})$ asymptotic form. However, this result was obtained under the assumption that the charge densities are localized and independent of supercell size. While for ρ_2 this assumption holds, it does not hold for ρ_1, where n_0 is obviously dependent on the supercell volume. The explicit form of E_{12}, by simple generalization of the results of the Appendix, is

$$E_{12}=\lim_{s\to 0}\int_{\text{cell}} d^3r\,\rho_1(\mathbf{r}) \times\int_{\text{cell}} d^3r'\,\rho_2(\mathbf{r}')\psi(\mathbf{r}-\mathbf{r}',s) \ , \tag{13}$$

where ψ is defined in Eq. (A9), and ρ_j refers to density j of Eq. (11). ρ_2 does not have a dipole moment, because of the choice of $\mathbf{r}_0$, which implies that the lattice sum in ψ is absolutely convergent up to an irrelevant constant potential. This allows us to separate the energy in Eq. (13) into two parts; that arising from the interaction between ρ_2 and the point charge in ρ_1, and that arising from the interaction of ρ_2 and n_0. The interaction of the point charge with ρ_2 can be considered in the limit of the convergence parameter $\eta \rightarrow 0$, i.e., in the limit of a lattice sum over the lattice vectors $\boldsymbol{l}$. The leading term in this interaction is between the point charge q and the quadrupole (second radial) moment of ρ_2, Q. If the lattice is chosen to be simple cubic, then this interaction vanishes for the same symmetry reasons as discussed for the dipole-dipole interaction at Eq. (10) above. The interaction of the jellium with ρ_2 can be considered in the opposite limit of $\eta \rightarrow \infty$, which means a lattice sum over the reciprocal vectors $\mathbf{g}$. The jellium has no spatial structure and, therefore, only the $\mathbf{g}=0$ contribution to the potential (see Appendix) need be considered. This leads to the L dependent contribution

$$E_{12}=\frac{2\pi q}{3V_c}\int_{\text{cell}} d^3r\, \rho_2(\mathbf{r}) r^2+O(L^{-5}) , \tag{14}$$

where $V_c=L^3$ for a cube. The asymptotic result for the total electrostatic energy of a charged species on a cubic lattice is

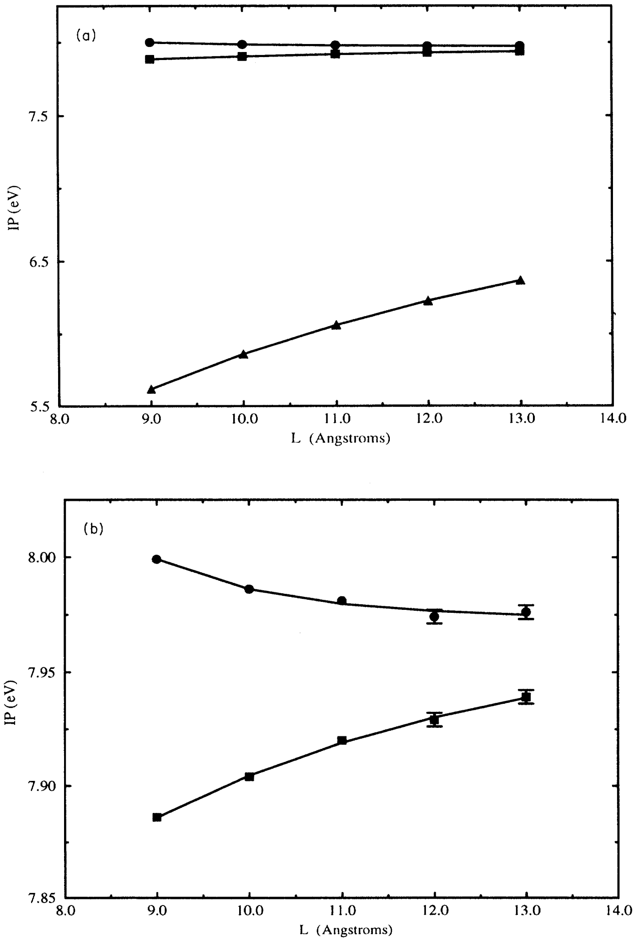

FIG. 3. (a) The ionization potential of a Mg atom calculated in cubic supercells of side L (filled triangles). The same after application of the Madelung correction Eq. (12) (filled squares). The same after application of the present correction Eq. (15) (filled circles). (b) Expanded section of (a).

$$E=E_0-\frac{q^2\alpha}{2L}-\frac{2\pi q Q}{3L^3}+O(L^{-5}) , \tag{15}$$

where Q is the quadrupole moment given by the integral in Eq. (14) and E_0 is the desired electrostatic energy of the isolated species.

An example illustrating the size dependence of the energy on cell size in Eq. (15) is shown in Fig. 3. The ionization energy of an Mg atom has been calculated by the methods described above using the electrostatic energy of Eq. (8). Also shown are the convergence after the application of the Madelung correction of Eq. (12) and after the more extended correction of Eq. (15). It is clear that as the corrections are applied, convergence increases rapidly.

C. Aperiodic system in condensed matter

Consider first a localized (point) defect in a crystalline solid. In this case, the charge density can be considered to be the sum of two contributions—the periodic charge density of the underlying crystalline solid $\rho_p(\mathbf{r})$, and the charge density of the aperiodic defect $\rho_{\text{ap}}(\mathbf{r})$;

$$\begin{aligned}&\rho(\mathbf{r})=\rho_p(\mathbf{r})+\rho_{\text{ap}}(\mathbf{r}) ,\\ &\rho_p(\mathbf{r}+\boldsymbol{l})=\rho_p(\mathbf{r}) .\end{aligned} \tag{16}$$

The aperiodic density $\rho_{\text{ap}}(\mathbf{r})$ will be a localized charge density similar to a molecular density. The electrostatic energy can then be considered to be the sum of the interactions between (i) the periodic charge density and itself, which is independent of L; (ii) the periodic and aperiodic charge densities, which is also independent of L (and equal to the interaction of a single isolated aperiodic density with an infinite periodic density); and (iii) the aperiodic densities located in different supercells, which is L dependent. Note that the periodic part of the density must fulfill the conditions of Sec. II, namely, it should not contribute a net charge in the unit cell or a net dipole. It is reasonable to assume that this model will be valid for modeling any species in a condensed phase that is homogeneous beyond some length scale (e.g., an ion in a solution).

What is the asymptotic dependence of the aperiodic density and its multipoles on the supercell dimensions? The aperiodic density depends on L through two mechanisms. One mechanism, as in the case of the isolated molecule, is changes in the charge distribution induced by interactions of the aperiodic charge with its images. The convergence with L of this case has been discussed above, and was found to converge faster than $O(L^{-5})$. The other source of L dependence in ρ_{ap} is the dielectric response of the periodic medium to the aperiodic density. The asymptotic term arising from this response cannot be obtained by the methods used above for the isolated molecule as it involves the induced charge density, which implies nonelectrostatic contributions to the energy. Instead, the phenomenological approach of Leslie and Gillan[3] in which the potential is reduced by the dielectric constant ε can be applied. This correction is exact in the limit of large L, and we apply it to the results of Sec.

III B to obtain, for the case of a charged aperiodic system in a cubic supercell,

$$E=E_0-\frac{q^2\alpha}{2L\varepsilon}-\frac{2\pi qQ}{3L^3\varepsilon}+O(L^{-5})\ . \tag{17}$$

In this case, Q is the second radial moment only of that part of the aperiodic density that does not arise from dielectric response or from the jellium, i.e., is asymptotically independent of L. The two parameters ε and Q are properties of the periodic density and the aperiodic density, respectively. They may either be calculated explicitly (ε can be obtained separated by considering the response of the periodic density to a point test charge, $q \ll e$, where e is the unit charge and for which $Q=0$), or by fitting the data to expression (17). For neutral aperiodic systems, the size dependence will be unaffected by the introduction of the dielectric constant and will remain $O(L^{-5})$, assuming a square supercell for dipolar aperiodic densities.

IV. SUMMARY AND DISCUSSION

In this paper, we have derived exactly the electrostatic energy functional for an infinite periodic lattice with a basis, by generalizing and extending the work of de Leeuw, Perram, and Smith.[7] In doing so we obtained conditions for using an infinite solid as a model for a real solid. These conditions are that the unit cell should be neutral and have no dipole moment. If these conditions are not fulfilled, then the energy per unit cell of the solid diverges or is indeterminate unless further boundary conditions at the surface are imposed. However, static properties of a polarized solid can still be calculated under the assumption of zero electric field. This reflects the existence of external processes that can cause the potential at all the surfaces to be equal. Calculations of dynamical processes under the zero-field assumption, imply the existence of a faster external mechanism, which equilibrates the potential over the crystal surfaces.

The convergence of the energy of a localized aperiodic system with respect to supercell size was also considered in detail. The convergence is dominated by the electrostatic interactions of the species under consideration and its images. We have shown that by suitable choice of supercell geometry, as well as the employment of the exact electrostatic energy functionals, the energy can be calculated so that it will converge to its limiting value as $O(L^{-5})$. For neutral systems without a dipole, this is always the case. For systems with a dipole moment, this is the case only if a cubic supercell is used and if the electrostatic energy functional is derived correctly. In particular, the commonly used electrostatic energy functional was found to be missing a dipolar term, the addition of which increases the rate of convergence from $O(L^{-3})$ to $O(L^{-5})$. For nonneutral isolated molecular systems, we found the explicit asymptotic dependence on L to order $O(L^{-5})$ for a cubic supercell. Correcting the calculated energy by adding these terms we found it converged rapidly, as expected. For an aperiodic system in condensed matter, we argued that the gas-phase terms may be generalized by introducing an empirical dielectric constant.

These results for calculations on aperiodic systems make the use of PBC highly competitive compared to the isolated system on a grid approach.[14] The main benefit of this approach was that spurious interactions with the lattice images were avoided. We have shown that these interactions can be converged rapidly with supercell size. This allows efficient use of PBC in the study of aperiodic systems in the condensed phase. It is also our belief that considerations similar to those employed in this work can be applied to the convergence of long-ranged elastic forces in microscopically deformed solids, which are similar in their form to electrostatic forces.

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APPENDIX

In this appendix the electrostatic energy per cell of a charge distribution in a periodically repeated supercell, is calculated by the method of de Leeuw, Perram, and Smith[7] who studied the related problem of point charges in a cubic lattice. The expression for the electrostatic energy is

$$\begin{aligned}E&=\tfrac{1}{2}\int_{\text{cell}} d^3r\,\rho(\mathbf{r})\phi(\mathbf{r})\\&=\tfrac{1}{2}\int_{\text{cell}} d^3r\,\rho(\mathbf{r})\sum_{l}\int_{\text{cell}} d^2r'\,\rho(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'+\boldsymbol{l}|}\ ,\end{aligned} \tag{A1}$$

and the cell is charge neutral

$$\int_{\text{cell}} d^3r\,\rho(\mathbf{r})=\int_{\text{cell}} d^3r\,n(\mathbf{r})+\sum_i z_i=0\ , \tag{A2}$$

where $n(\mathbf{r})$ is the continuous part of the density and there are also point charges, with the ith point charge having a charge z_i and located at $\mathbf{r}_i$.

As discussed in the main body of this work, the lattice sum for the potential in (A1) can be conditionally convergent. To make the sum absolutely convergent, we introduce the convergence factor $e^{-s|l|^2}$. In the absolutely convergent sum we are allowed to exchange the sum and the integrals; therefore, we consider the sum

$$\psi(\mathbf{x},s)=\sum_{l} e^{-s|l|^2}\frac{1}{|\mathbf{x}+\boldsymbol{l}|}\ . \tag{A3}$$

This sum can be transformed into a double sum as in Eq. (3) in the main body of the paper. Then the sum over $|\boldsymbol{l}|$ is a one-dimensional conditionally convergent series, for which the introduction of a convergence factor induces convergence to a definite limit.[7] The choice of how to transform the lattice sum to a one-dimensional sum is arbitrary and reflects the surface geometry. The present choice corresponds to a sum over spherical shells.

Introducing the integral expression for the Gamma function $\Gamma(n)$, which after simple rearrangement is

$$y^{-2a}=\frac{1}{\Gamma(a)}\int_0^{\infty}dt\,e^{-ty^2}t^{a-1}\,. \tag{A4}$$

$\psi(\mathbf{x},s)$ can be rewritten as

$$\psi(\mathbf{x},s)=\pi^{-1/2}\sum_{l}\int_0^{\infty}t^{-1/2}e^{-t(\mathbf{x}+\boldsymbol{l})^2}\mathrm{e}^{-s|\boldsymbol{l}|^2}dt\,. \tag{A5}$$

The integral in (A5) is singular when $s=0$, and this singularity is at the $t=0$ limit of the integral. If the integration range is split arbitrary into two ranges $[0,\eta^2]$ and $[\eta^2,\infty]$, then the second integral is immediate and $\psi(\mathbf{x},s)$ becomes equal to

$$\psi(\mathbf{x},s)=\pi^{-1/2}\sum_{l}\int_0^{\eta^2}t^{-1/2}e^{-\mathrm{t}(\mathbf{x}+\boldsymbol{l})^2}e^{-s|\boldsymbol{l}|^2}dt + \sum_{l}\frac{\operatorname{erfc}(\eta|\mathbf{x}+\boldsymbol{l}|)}{|\mathbf{x}+\boldsymbol{l}|}e^{-s|\boldsymbol{l}|^2}\,. \tag{A6}$$

Erfc(z) is the complementary error function, which for large z has the asymptotic form, $\pi^{-1/2}z^{-1}e^{-z^2}$. This ensures that the second lattice sum in (A6) is absolutely convergent for all values of s, or in other words, that the singularity at $s=0$ is in the first lattice sum as expected. Applying the θ transformation, valid for all Bravais lattices[15]

$$\sum_{l}\mathrm{e}^{-\mathrm{t}|\mathbf{x}+\boldsymbol{l}|^2}=\frac{\pi^{3/2}}{V_c t^{3/2}}\sum_{\mathbf{g}}e^{-g^2/4t}e^{i\mathbf{g}\cdot\mathbf{x}}\,, \tag{A7}$$

to the first lattice sum, we obtain a new lattice sum over the reciprocal lattice vectors $\mathbf{g}$ and the first term on the right-hand side of (A6) becomes

$$\frac{\pi}{V_c}\sum_{\mathbf{g}}\int_0^{a^2}dt(t+s)^{-3/2}t^{-1/2} \times e^{[g^2/4(s+t)]}e^{i\mathbf{g}\cdot\mathbf{x}t/(t+s)}e^{-[st/(t+s)]x^2}\,. \tag{A8}$$

For large $\mathbf{g}$, the sum in (A8) is absolutely convergent independent of s. However, the $\mathbf{g}=\mathbf{O}$ term is singular for $s=0$; therefore, we separate it from the sum and change variables from t to $u=t/(s+t)$. Then we take the limit $s\rightarrow 0$ for the remaining, absolutely convergent sum over $\mathbf{g}\neq\mathbf{0}$ and the absolutely convergent sum in (A6) over $\boldsymbol{l}$, to obtain

$$\psi(\mathbf{x},s)=\sum_{l}\frac{\operatorname{erfc}(\eta|\mathbf{x}+\boldsymbol{l}|)}{|\mathbf{x}+\boldsymbol{l}|}+\frac{4\pi}{V_c}\sum_{\mathbf{g}\neq 0}\frac{1}{g^2}e^{g^2/4\eta^2}e^{i\mathbf{g}\cdot\mathbf{x}} + \frac{\pi}{V_c s}\int_0^{\eta^2/(\eta^2+s)}\mathrm{d}u\mathrm{e}^{-sux^2}u^{-1/2}\,. \tag{A9}$$

Note that the entire singularity in s is contained in the third term on the right-hand side of (A9). Expanding the third term for the case of small s, we obtain

$$\frac{2\pi}{V_c s}-\frac{\pi}{V_c\eta^2}-\frac{2\pi}{3V_c}x^2+O(s)\,. \tag{A10}$$

Using (A10) and (A9) in (A1) and taking the limit $s\rightarrow 0$, we obtain

$$\phi(\mathbf{r})=\int_{\text{cell}}d^3r'\,\rho(\mathbf{r})\left[\psi(\mathbf{r},\mathbf{r}')-\frac{2\pi}{3V_c}(r^2-2\mathbf{r}\cdot\mathbf{r}')\right], \tag{A11}$$

$$\psi(\mathbf{r},\mathbf{r}')=\sum_{l}\frac{\operatorname{erfc}(\eta|\mathbf{r}-\mathbf{r}'+\boldsymbol{l}|)}{|\mathbf{r}-\mathbf{r}'+\boldsymbol{l}|} + \frac{4\pi}{V_c}\sum_{\mathbf{g}\neq 0}\frac{1}{g^2}e^{-g^2/4\eta^2}\mathrm{e}^{i\mathbf{g}\cdot(\mathbf{r}-\mathbf{r}')}\,. \tag{A12}$$

For the special case of a neutral charge distribution, we obtain for the energy

$$E=\tfrac{1}{2}\int_{\text{cell}}d^3r\,\rho(\mathbf{r})\int_{\text{cell}}^{3}\mathbf{r}'\,\rho(\mathbf{r}')\psi(\mathbf{r},\mathbf{r}') + \frac{2\pi}{3V_c}\left|\int_{\text{cell}}d^3r\,\mathbf{r}\rho(\mathbf{r})\right|^2, \tag{A13}$$

where use of the charge neutrality condition (A2) was also made. This result for the energy depends on the fact that we chose a spherical surface for the performance of the sum. This choice was implicit in our choice of convergence factor as mentioned above. It should be noted that the choice of the convergence factor $e^{-s|\mathbf{r}+\boldsymbol{l}|^2}$ leads to the same result only without the unusual dipole term in (A13). However, in this case the convergence factor does not apply to a one-dimensional sum and is not known to have a definite limit as $s\rightarrow 0$. Thus, the result should be considered as a coincidence rather than one of mathematical significance.

If the charge distribution contains discrete point charges, additional care needs to be taken in applying equation (A12) as it contains unphysical, and diverging self-interaction terms when $\boldsymbol{l}=\mathbf{0}$. For this case the energy is found to be

$$E=\tfrac{1}{2}\int_{\text{cell}}d^3r\,n(\mathbf{r})\int_{\text{cell}}d^3r'\left[n(\mathbf{r}')+2\sum_{i}z_i\delta(\mathbf{r}'-\mathbf{r}_i)\right] \times\psi(\mathbf{r},\mathbf{r}') + \frac{2\pi}{3V_c}\left|\int_{\text{cell}}d^3r\,\mathbf{r}\rho(\mathbf{r})\right|^2 + \tfrac{1}{2}\sum_{i}\sum_{j\neq i}z_i z_j\psi(\mathbf{r}_i,\mathbf{r}_j)+\frac{\xi}{2}\sum_{i}z_i^2\,, \tag{A14}$$

with ξ defined as

$$\xi=\lim_{\mathbf{r}\rightarrow\mathbf{r}'}\left\{\sum_{l}\frac{\operatorname{erfc}(\eta|\mathbf{r}-\mathbf{r}'+\boldsymbol{l}|)}{|\mathbf{r}-\mathbf{r}'+\boldsymbol{l}|} + \frac{4\pi}{V_c}\sum_{\mathbf{g}\neq 0}\frac{1}{g^2}e^{g^2/4\eta^2}e^{i\mathbf{g}\cdot(\mathbf{r}-\mathbf{r}')}-\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right\} = \sum_{l\neq 0}\frac{\operatorname{erfc}(\eta|\boldsymbol{l}|)}{|\boldsymbol{l}|}+\frac{4\pi}{V_c}\sum_{\mathbf{g}\neq 0}\frac{1}{g^2}e^{-g^2/4\eta^2}-\frac{2\eta}{\sqrt{\pi}}\,. \tag{A15}$$

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