A new formulation of the Hartree–Fock–Roothaan method for electronic structure calculations on crystals

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We present a general formulation of the Hartree–Fock–Roothaan method of electronic structure calculations for systems subject to periodic boundary conditions and apply this method to crystals. The derivation of the method does not involve any divergent or conditionally convergent infinite series. The final result for the Hartree–Fock energy per unit cell consists of only absolutely convergent series and can be written in a form whose structure is almost identical to that for the nonperiodic Hartree–Fock energy. A Fock matrix that consists of only absolutely convergent series is also defined. An important feature of the method is that the Ewald potential, which has been used in the past to eliminate divergences in series involving the expectation value of the Coulomb interaction, is introduced in a physically reasonable way at an early stage of the formulation of the quantum mechanical problem. In the final result, the Ewald potential is used not only to express the Coulomb energy, but also to express the exchange energy as an absolutely convergent series, thereby eliminating the problem of slow convergence, or lack of convergence, of the series for the exchange energy. The numerical implementation of this method, which is not discussed in this paper, requires calculation of standard one- and two-electron matrix elements of the electronic kinetic energy and the Coulomb interaction, as well as certain easily calculated moments of basis function overlap charge densities. No integrals involving matrix elements of the Ewald potential between basis functions are required for evaluation of either the energy or the Fock matrix. Instead, Ewald interactions must be evaluated only for point multipoles. The methods used here to formulate the Hartree–Fock problem can be extended to formulate Møller–Plesset perturbation theory and coupled cluster theory for crystals.

I. INTRODUCTION

Ab initio quantum electronic structure methods using localized atomic basis functions and periodic boundary conditions can be used to calculate the Hartree–Fock energy of a crystal. The combination of a periodic Hamiltonian, a periodic system (which in effect implies an infinite number of interacting charges), and long ranged Coulombic interactions leads to energy expressions that are, at best, conditionally convergent infinite series. The physical and mathematical difficulties of this problem have been studied extensively within the context of calculating the Madelung energy of a perfect ionic crystal and of performing classical computer simulations on ionic and dipolar materials. The existence of significant problems has also been recognized by many workers in the quantum mechanical context of formulating Hartree–Fock methods for crystals.

The classical Madelung problem is that of calculating the electrostatic energy of an infinite array of point charges. Usually this array is defined by periodic spatial replication of a finite set of charges called the repeating unit, so the problem involves evaluating an infinite sum of interactions between a specific repeating unit and all other units, as well as the interactions within a repeating unit. Several methods of regrouping the terms of this conditionally convergent infinite series have been proposed, such as those of Madelung, Evjen, and Ewald. It is well known, however, that different methods of regrouping terms in a conditionally convergent series can lead to different values for the sum. More precise formulations of the problem, such as those of Harris and Redlack and Grindlay, involve specifying a finite size and shape of the array of replications, then calculating the electrical potential in the interior of the sample, and then taking the limit as the size of the array approaches infinity with the shape of the array held fixed. These analyses indicate that the specific way in which the repeating unit is chosen for a given crystal structure and the details of the shape of the array of replications can affect the result. Another approach, used by de Leeuw et al., is to apply various convergence factors to the conditionally convergent infinite series to make it absolutely convergent. De Leeuw et al. found that the choice of convergence factor can affect the result obtained for the energy.

Harris and Redlack and Grindlay pointed out that there is a physical basis for the mathematical ambiguities inherent in all of these methods. If a repeating unit is replicated to form a finite sample of a specific size and shape surrounded by a vacuum and if the repeating unit has a dipole moment, then there is a net dipole moment in the sample that is proportional to the size of the system. As a result, there is a net electric field in the sample that leads to a macroscopic electrical potential difference between one side of the material and another and that leads to a contribution to the total energy of the crystal. This contribution is irrelevant to the thermodynamic internal energy of the material in the absence of an applied external electric field, however, because in a real sample something would happen at the surface to eliminate...
this extra contribution. Thus, detailed consideration of what happens at the surface of a replicated array of charges is important for a correct description of its thermodynamic properties. (Note that there are no surfaces in a typical formulation of the lattice energy problem using strictly periodic boundary conditions.)

A further development was made by de Leeuw et al., who showed mathematically that use of the Ewald potential to calculate the energy of a material is physically very closely equivalent to calculating the properties of a spherical sample of the material in a container whose walls are a perfectly conducting material. The walls would establish a constant electrostatic potential at all points on the surface of the material, thereby eliminating the spurious contribution to the energy discussed above. The Ewald method is the method commonly used to calculate electrostatic energies of ionic crystals, and it has become the standard method for computer simulations of ionic fluids, just as it was the method used in the earliest extensive Monte Carlo simulations on plasmas.

More recently, it has been used for computer simulations of dipolar fluids.

The intricacies of the Madelung problem have physical and mathematical relevance for a correct formulation of Hartree–Fock theory for crystals. The Hartree–Fock–Roothaan (HFR) approach to electronic structure of crystals, based on the use of periodic boundary conditions, was first developed by André et al. and del Re et al., but they did not address the complications due to the long ranged nature of the Coulomb potential. Euwema et al. developed a procedure for truncating the sums of Coulomb integrals and applying corrections to account for some of the errors introduced by the truncation. Upton and Goddard developed a similar scheme involving bispherical truncation. Both of these approaches involve rearranging the terms of a conditionally convergent series in order to obtain a rapidly convergent series, so they could lead to incorrect results in cases where the unit cell might have a net dipole moment (i.e., for calculations on crystals with two or more different types of atoms) for reasons discussed above. Harris presented a way of introducing the physical insights discussed above into HFR calculations, relying heavily on Fourier representations for all of the various contributions to the energy of a crystal, but his methods have not been widely adopted or used.

The most commonly used method for performing HFR calculations on crystals is that of Pisani et al., who developed and distributed the CRYSTAL program. In this method, Ewald techniques are applied to the conditionally convergent infinite sums of integrals needed for evaluation of the Coulomb energy. These techniques are introduced in a physically motivated way to convert infinite series into numerically tractable expressions. In the case of the exchange energy, however, they do not use Ewald techniques. Instead they truncate the conditionally convergent exchange series at large distances, and the apparent convergence of the series is very slow. Moreover, the behavior of the exchange energy sum at large distances is dependent on the long ranged behavior of the density matrix or bond order matrix. Previous work by Piela et al. and by Monkhorst and Kertesz has noted the slow convergence of exchange energy sums in HFR calculations, especially for metallic systems.

In this paper, we apply the mathematical and physical understanding gained from studying classical Coulomb systems to the quantum mechanical periodic Hartree–Fock problem. Our formulation of the problem and the ensuing theoretical development contain no conditionally convergent infinite series, and the resulting energy expression contains only absolutely convergent sums. The Ewald potential appears in both the Coulomb and exchange sums, so the exchange sums converge more rapidly than in the method of Pisani et al., and the convergence is not dependent on the density matrix.

An outline of the paper is as follows. In Sec. II, we define our system and discuss our choice of potential energy. In Sec. III, we derive a Hartree–Fock energy expression for a system that is periodic on an arbitrary but large length scale. In Sec. IV, we reformulate this energy expression for a perfect crystalline system. Section V contains a summary of our method and a comparison with other methods. Additional details on this work are contained in Hammes-Schiffer.

II. MECHANICAL DESCRIPTION OF THE SYSTEM AND CHOICE OF POTENTIAL ENERGY

We wish to construct a mechanical theory of a macroscopic (actually, an infinite) system with periodic boundary conditions and long ranged Coulombic forces that does not involve divergent or conditionally convergent infinite series and that provides a correct description of a system in the absence of an applied electric field. In order to do this, it is useful to proceed in the following way. The first step is to calculate the energy of a system with a finite number of mechanical degrees of freedom and finite size, as well as some aspects of periodicity. The second step is to perform an appropriate limiting operation that makes the system become perfectly periodic. The third step (usually called the thermodynamic limit) is to perform another limiting operation in which the number of degrees of freedom and the size of the system approach infinity, and then to calculate the limiting value of the energy per unit volume or per particle. (It will be essential for the following development that the two limiting operations mentioned be distinct and that they be taken in the order specified.) In this section, we discuss the first step of this program.

A. Definition of the system and choice of potential energy function

De Leeuw et al., in the context of formulating a Hamiltonian for classical simulation of particles under periodic boundary conditions, have proposed several formulations of finite periodic systems. One of them is very appropriate for our purposes. With only minor modifications, it is the following. We point out that for simplicity we have specialized to cubic systems for this paper, but the method and results can be generalized to noncubic systems.

Our system is a set of $M$ particles with charges $\{q_i\}_{i=1...M}$, all contained within a cubic cell of side $L$ centered at the origin of a coordinate system. This cell will be called the central cell. $L$ is to be regarded as a macroscopic length, not, for example, the length of a unit cell of a
FIG. 1. Cross section of an array of replicated cells, where \( L \) is the length of the central cell. In this case, \( n_{\text{max}} = 8 \). The array is placed in a spherical vacuum of radius \( a \) surrounded by a perfect conductor. For the calculations described in the text, \( n_{\text{max}} \) is very large and \( a \gg L \).

crystal. The system is electrically neutral. Imagine that the particles in this cell are replicated in adjacent cubes of length \( L \), but this replication does not extend to infinity. It extends only out to cubes whose centers are separated from the origin of the central cell by no more than a distance of \( n_{\text{max}}L \). This spherical array of replicated cells is placed in the center of a spherical vacuum of radius \( a \), which is surrounded by a perfect electrical conductor. (See Fig. 1.) We demand that

\[
\rho \gg L, \tag{1}
\]

\[
n_{\text{max}} \gg 1, \tag{2}
\]

\[
a - n_{\text{max}}L \ll a. \tag{3}
\]

[The first two of these relations are needed because of the order in which two limiting operations will be taken, as discussed in the introduction to Sec. II. The third relation will be needed to prove that the first of the two limiting operations \((a \to \infty)\) leads to an interaction that satisfies periodic boundary conditions.]

From a classical mechanical point of view, the configuration of the system will be specified by giving the values of \( \rho^M \), the positions of the \( M \) particles. These positions are understood to be in the central cell. Each particle is associated with a set of image particles, but these images do not have independent mechanical degrees of freedom associated with them. For example, a particle at \( r_i \) in the central cell has image particles at positions \( r_i + nL \), where \( n \) is any vector with integer components whose magnitude is less than or equal to \( n_{\text{max}} \). As a particle moves in the central cell, its images in the surrounding cells move in the same way.

Let \( r \) and \( r' \) be two positions within the sphere of radius \( a \). The direct Coulomb electrostatic potential at \( r \) caused by a unit charge at \( r' \) is

\[
u_c(r, r') = 1/|r-r'|.
\]

This is not the total electrostatic potential, however, due to the presence of the surrounding perfect conductor. The conductor imposes a boundary condition on electric fields that demands that the electric potential is the same at all points on the surface. Using basic electrostatics, and choosing the boundary condition that the potential be zero on the surface of the conductor, i.e., at \(|r| = a\), it can easily be shown that the total potential \( u_{\text{es}}(r, r') \) at \( r \) caused by a unit charge at \( r' \) is

\[
u_{\text{es}}(r, r') = 1/|r-r'| - \sum_{l=0}^{\infty} \frac{|r|^l|r'|^l}{a^{2l+1}} P_l(\hat{r} \cdot \hat{r}'). \tag{4}
\]

where \( P_l(x) \) are the Legendre polynomials and \( \hat{r} = r/|r| \).

It will be mathematically convenient in the following to define a modified Coulomb potential in the following way. Let

\[
u_{ch}(r, r') = \nu_c(r, r') \quad \text{if} \quad |r-r'| > \Delta
\]

\[= 0 \quad \text{if} \quad |r-r'| \leq \Delta,
\]

where \( \Delta \) is some extremely small but nonzero distance, e.g., \( 10^{-10} \) \( \AA \), and the limit \( \Delta \to 0+ \) will be taken at the end of the calculations. If we write this in the form

\[
u_{ch}(r, r') = \nu_c(r, r') + u_h(r, r'),
\]

then clearly

\[
u_h(r, r') = 0 \quad \text{if} \quad |r-r'| > \Delta
\]

\[= -u_h(r, r') \quad \text{if} \quad |r-r'| \leq \Delta.
\]

For almost all values of the two position arguments, \( u_{ch} \) is equal to the true Coulombic potential. However, if the two position arguments are equal, \( u_{ch} = 0 \) for all \( \Delta \), even as \( \Delta \to 0+ \). A charged particle cannot, of course, interact directly with itself. Thus, when the Coulombic potential energy of a collection of particles is expressed in terms of the interactions between pairs of particles, terms in which a particle interacts with itself must not be included. However, if the Coulombic potential energy is expressed in terms of \( u_{ch} \), it is permissible to include terms in which a particle "interacts" with itself, because \( u_{ch}(r, r) = 0 \). This leads to simplifications in many of the formal expressions below. For example, in Eq. (7) the \( i=j \) terms need not be excluded from the sum. In the calculation of the interactions between distinct particles, use of \( u_h \) rather than \( u_c \) makes a negligible error that goes to zero when the limit \( \Delta \to 0+ \) is taken at the end of the calculation. All the final results that are obtained with this formal procedure can be derived without the use of \( u_h \) or \( u_{ch} \), but the intermediate formulas are more complicated than those presented here.

We now derive expressions for the potential energy of this system. The electrical potential energy of a charged par-
particle with charge $q$ at a point $r$ in the interior of the sphere of radius $a$ can be calculated as the electrical work of a charging process in which the charge of the particle is brought from zero to $q$. Since a charge of magnitude $q'$ at $r$ induces a potential of $q'v_s(r,r)$ at $r$, this work is

$$\int_0^q dq' q' v_s(r,r) = (1/2)q^2v_s(r,r) = (1/2)q^2v_{chs}(r,r),$$

where

$$v_{chs}(r,r') = v_ch(r,r') + v_s(r,r').$$

Thus the potential energy of a particle with charge $q$ at $r$ due to its interaction with the surface of the conductor is $qv_{chs}(r,r)$. Similarly, the potential energy of interaction of a particle of charge $q$ at $r$ and a different particle of charge $q'$ at $r'$ is $qq'v_{chs}(r,r')$. (See Ref. 25.)

Now we can construct the total potential energy for the mechanical system we have defined. Consider the set of all $M$ particles in the central cell of the system as well as the set of all images in the surrounding cells. The potential energy of the central cell can be considered to be the sum of three contributions. The first contribution is the potential energy of each of the $M$ particles in the central cell due to its interaction with the surface of the conductor, which, as derived above, is simply $q^2v_{chs}(r,r)$. The second contribution is the potential energy due to the interaction between each distinct pair of particles, both of which are in the central cell, which can be written as $q^2v_{chs}(r,r')$. The third contribution is one-half of the interaction of each particle in the central cell with each image outside the central cell. (In the case of an interaction between a particle in the central cell and an image outside the central cell, it is reasonable to regard half of the energy as being assigned to the central cell and half as being assigned to the cell that contains the image.) It is easily verified that the sum of all of these contributions is given by the following expression:

$$V_{pchs}(r'^M) = \frac{1}{2} \sum_{i,j=1}^M q_iq_jv_{chs}(r_i,r_j),$$

where

$$v_{uchs}(r,r') = \sum_{u|u|\leq n_{max}} u_{chs}(r,r' + nL).$$

Here the sum is over all vectors $n$ whose components are integers and whose magnitude is less than or equal to $n_{max}$. This result is equivalent to that used by de Leeuw et al. for this system.

Thus, $V_{pchs}$ can be regarded as the electrical potential energy of the central cell when it is embedded in a spherical array of periodic replicas of itself, the whole of which is surrounded by a perfect conductor. It is the potential energy function we adopt for the finite sized mechanical system defined above. Note that the surrounding conducting surface will always redistribute its charge in such a way that the electrical potential is the same at all points on the surface. Thus the system energy calculated with a Hamiltonian that includes this potential energy will be appropriate for comparing with the bulk thermodynamic energy of the material in the absence of an electric field.

B. Properties of the potential energy and its relationship to the Ewald potential

Note that the potential energy in Eq. (7) is written in a form that suggests that there is an effective interaction between a pair of particles in the central cell that is of the form $qq'u_{chs}(r_i,r_j)$. This effective interaction includes not only the direct interaction between the two particles but also the interaction of the first particle with all images of the second. Moreover, it includes both the surface interaction and $1/r^3$ contributions to each of these. This effective interaction is not translationally invariant, i.e., it is not true that $v_{pchs}(r,r') = v_{pchs}(r+\mathbf{r}',r'+\mathbf{r})$ for all $r'$. Moreover, it does not satisfy periodic boundary conditions exactly, i.e., it is not true that $v_{pchs}(r,r') = v_{pchs}(r + \mathbf{m}, r')$ or that $v_{pchs}(r,r') = v_{pchs}(r + \mathbf{m}, r')$. (In the remainder of this paper, vectors like $\mathbf{m}$ will always denote vectors whose components are integers.)

We now derive two different expressions for $v_{pchs}$ that will be useful in the following discussion.

For the first expression, we use Eqs. (5) and (8) to write $v_{pchs}$ as a sum of two parts:

$$v_{pchs}(r,r') = v_{pchs}(r,r') + v_{ps}(r,r'),$$

where

$$v_{pchs}(r,r') = v_{pchs}(r,r') + v_{ps}(r,r'),$$

$$v_{ps}(r,r') = \sum_{u|u|\leq n_{max}} v_{s}(r,r' + nL).$$

Using Eqs. (4) and (5), which provide an explicit expression for $v_s$, and the conditions in Eqs. (1)–(3), it is straightforward to show that

$$v_{ps}(r,r') = \frac{4\pi}{3L^3} [C(a) + r \cdot r' + O(a^{-1})],$$

where $C(a)$ is a constant independent of $r$ and $r'$. Note that this expression is valid only for $r$ and $r'$ both being in or near the central cell. Using this result, we can write

$$v_{pchs}(r,r') = v_{pchs}(r,r') + v_{ps}(r,r') = v_{pchs}(r,r') + \frac{4\pi}{3L^3} [C(a) + r \cdot r' + O(a^{-1})],$$

which is one of the desired expressions for $v_{pchs}$.

The second expression is based on the close connection between $v_{pchs}$ and the Ewald potential. This connection was shown by de Leeuw et al., but we will derive it in a different way and obtain some additional results that will be useful in our following analysis. We define the Ewald potential $v_{el}(r,r')$ as the unique electrical potential that satisfies the...
following conditions. First, the charge density that generates the potential is an electrically neutral perfectly periodic charge density (with period \(l\)) of the form

\[
\rho(r) = \sum_n \delta(r-r'-nl) \frac{1}{l^3},
\]

i.e., a density consisting of a periodic replication of a unit point charge plus a uniform canceling background. (For future convenience, the definition of the Ewald potential given here is for an arbitrarily chosen periodicity length \(l\), which is indicated in the subscript of \(u_{el}\). In this section, we will be concerned with the case that \(l=L\), but in later sections we will also consider \(l=d\), where \(d\) is the length of a crystal unit cell.) Second, the potential is itself perfectly periodic, i.e.,

\[
v_{el}(r,r') = v_{el}(r+ml,r')
\]

for all vectors \(m\) with integer components. Third, the average value of \(u_{el}(r,r')\) over a cube of volume \(l^3\) is zero. From the first condition, it follows that \(u_{el}(r,r')\) satisfies Poisson's equation in the form

\[
\nabla^2 u_{el}(r,r') = -4\pi \left[ \sum_n \delta(r-r'-nl) \right] \frac{1}{l^3}.
\]

(13)

It is straightforward to show that

\[
v_{el}(r,r') = \frac{1}{\pi l} \sum_{n \neq 0} |n|^{-2} \cos(2\pi n \cdot (r-r')/l) \times \exp(-\pi^2 |n|^2/\alpha^2)

\[
+ \sum_n \left[ \text{erfc}(\frac{ar-r'+nl}{l}) \right] \frac{\pi}{l \alpha^2}.
\]

(14)

where \(\text{erfc}(x)\) is the complementary error function and \(\alpha\) is an arbitrary positive number which is usually chosen so that both sums converge reasonably rapidly. Note that \(v_{el}(r,r')\) is independent of \(\alpha\). We point out that this expression is identical to the traditional expression for the Ewald interaction, although the constant term \(-m(l/\alpha)^2\) is often omitted since it does not contribute to the total potential energy for electrically neutral systems.

Note that the Ewald potential, like the Coulomb potential, diverges as \(|r-r'|\to 0\), and it also diverges as \(|r-r'|\to n\) for any \(n\). Accordingly, we define an Ewald-hole function \(v_{eh}(r,r')\) in the following way:

\[
v_{eh}(r,r') = v_{el}(r,r') + \sum_n v_h(r,r'+nl).
\]

(15)

It is straightforward to show that

\[
v_{eh}(0,0) = v_{eh}(r,r) = \frac{1}{l} \sum_{n \neq 0} \left[ \frac{\text{erfc}(\alpha |n|)}{|n|^2} + \frac{1}{\pi |n|^2} \right] \times \exp(-\pi^2 |n|^2/\alpha^2)

\times \left[ \frac{2\alpha}{l \sqrt{\alpha^2}} \right] \frac{\pi}{l \alpha^2}.
\]

(10)

Using these definitions, in Appendix A we derive the second expression for \(V_{pchs}\):

\[
v_{pchs}(r,r') = v_{eh}(r,r') - v_q(r) - v_q(r') + B(a,L) + O(a^{-1}),
\]

(17)

where \(v_q(r) = (2m/3L^3)|r|^2\) and \(B(a,L)\) is a constant independent of \(r\) and \(r'\).

Using this expression, it is straightforward to show that for an electrically neutral system

\[
V_{pchs}(r^M) = \frac{1}{2} \sum_{i,j=1}^M q_i q_j v_{eh}(r_i,r_j) + O(a^{-1}).
\]

From this we see that use of \(V_{pchs}\) followed by taking the limit \(a\to\infty\) is equivalent to using the Ewald potential for a finite sized system of \(M\) particles.

Recall that the Ewald potential satisfies periodic boundary conditions. It is also translationally invariant. This result shows that in the limit \(a\to\infty\), \(V_{pchs}\) has exactly the same properties. This means, for example, that if \(V_{pchs}\) were used to calculate the lattice energy of a cubic ionic crystal (by making the system in the central cell be a large cube of unit cells), the calculated result would be independent of the arbitrary choice of the boundaries for the unit cell, as we should expect from a physically correct theory. If we had not surrounded the system with a perfect conductor, then the potential energy of the central cell would have been

\[
V_{pchs}(r^M) = \frac{1}{2} \sum_{i,j=1}^M q_i q_j v_{eh}(r_i,r_j).
\]

Using Eqs. (12) and (17), it is straightforward to show that

\[
V_{pchs}(r^M) = \frac{1}{2} \sum_{i,j=1}^M q_i q_j v_{eh}(r_i,r_j) + \frac{2\pi}{3L^3} \left[ \sum_{l} q_i |r_i|^2 - \frac{M}{2} \right] + O(a^{-1}).
\]

(18)

Even in the limit of \(a\to\infty\), this expression does not satisfy periodic boundary conditions, is not translationally invariant, and depends on the arbitrary choice of the boundaries for the unit cell, which is not physically reasonable. This is mathematical evidence of the necessity of surrounding the system with a perfect conductor in order to obtain a physically reasonable result. The physical meaning of the extra term in \(V_{pchs}\) as compared to \(V_{pchs}\) was discussed in the introduction. Equation (18), in the \(a\to\infty\) limit, is one of the major results of de Leeuw et al.\(^5\)

We emphasize that the Ewald potential is entering this theory via Eq. (17) not as a device for enhancing the convergence of an infinite series for the expectation value of the Hamiltonian (i.e., the energy of the system), but as part of a mathematical identity involving the Hamiltonian itself. This will lead to the Ewald potential being consistently used in all parts of the energy calculation, e.g., in the calculation of the exchange energy as well as the Coulomb energy in the case of a quantum electronic structure calculation for crystals.

Moreover, one could imagine proceeding onward to develop a theory using only \(v_{eh}\) and not using \(v_{eh}\). This is in effect what is done when classical computer simulations are performed using the Ewald potential. Such a procedure if applied to quantum electronic structure calculations on solids would lead to a theory that is exactly mathematically equiva-
lent to the one presented below, but it would inevitably require the calculation of quantum mechanical matrix elements of the Ewald potential. Considerable progress has been made by Saunders et al. in developing methods for calculating such matrix elements. The method we present below, which uses both \( v_{\text{peb}} \) and \( v_{\text{eh}} \) and the relationship between them, will lead to a theory in which only standard Coulomb integrals will be needed for numerical calculations of the energy. The Ewald potential will appear in the final energy, but not in integrals involving basis functions.

### III. HARTREE-FOCK THEORY FOR PERIODIC BOUNDARY CONDITIONS

#### A. Formulation of the problem

In this subsection, we formulate the quantum mechanical problem for the electrons in a periodic system. We will assume that our system is electrically neutral, contains \( N \) electrons and \( A \) nuclei, and is the central cell of a spherical array of replicas of itself surrounding by a perfect conductor, as described in the previous section. The dynamical variables of the electrons are \( x_i, \omega_i \), where \( x_i \) denotes the position in the central cell, and \( \omega_i \) denotes the spin coordinate of the electron. The labels for the electrons in the central cell are all those in the set \( e \); e.g., \( i \in C_e \). The nuclear positions in the central cell \( \{ r_i \} \) for \( i \in C_n \) are parameters, not dynamical variables, in the quantum mechanical problem for the electrons. The charges for both electrons and nuclei will be denoted \( \{ q_i \} \). Each electron has charge \( q_e \), where \( q_e = -1 \) in Hartree atomic units.

Using the \( v_{\text{peb}} \) potential described in the previous section, the Hamiltonian for our system (in atomic units) is

\[
H = \sum_{i \in e} t(r_i) + \frac{1}{2} \sum_{i,j \in (e \cup N_c)} q_i q_j v_{\text{peb}}(r_i - r_j),
\]

where \( t(r_i) = -\nabla^2_i/2 \) is the electronic kinetic energy.

The \( N \)-electron wave functions for our system are functions of \( x_1, \ldots, x_N = x^N \) defined for all \( r^N \) for which the electrons are in the central cell. The inner product of two wave functions \( \Psi \) and \( \Psi' \) is

\[
\langle \Psi | \Psi' \rangle = \int_{C_e} dx_1 \int_{C_e} dx_2 \cdots \int_{C_e} dx_N \Psi^*(x^N) \Psi'(x^N)
\]

\[
= \int dx^N \Psi^*(x^N) \Psi'(x^N) \prod_{i=1}^{N} C_0(r_i),
\]

where

\[
C_0(r) = -1 \quad \text{if } r \text{ is in the central cell}
\]

\[
= 0 \quad \text{otherwise.}
\]

On the right side of Eq. (20) each spatial integration is over only the central cell, whereas on the right side of Eq. (21) each spatial integration is over all space.

We specify the boundary conditions for the wave function \( \Psi \) to be such that both \( \Psi \) and its derivatives have the same values at opposite sides of the central cell. One way to satisfy these boundary conditions is to extend the definition of the wave function to all space by demanding that it is a periodic function of each position with period \( L \). In order to do this, we first choose a set of atomic basis functions:

\[
\phi_{\mu}(x) = \sum_{n} \phi_{\mu n}(x),
\]

where \( \mu \) signifies the type of basis function (e.g., the particular atom on which it is centered and the quantum numbers including spin quantum number) and \( r_{\mu} \) is the position of the atom in the central cell. We define \( \sigma(\omega) \) as either the spin up (\( \alpha \)) or spin down (\( \beta \)) function of \( \omega \), where

\[
\int d\omega \alpha^*(\omega) \alpha(\omega) = \int d\omega \beta^*(\omega) \beta(\omega) = 1,
\]

\[
\int d\omega \alpha^*(\omega) \beta(\omega) = \int d\omega \beta^*(\omega) \alpha(\omega) = 0.
\]

Then we construct periodic basis functions from these atomic basis functions:

\[
\Phi_{\mu}(x) = \sum_{n} \phi_{\mu n}(x),
\]

where the sum is over all values of \( n \). These functions are defined for all \( r \) and satisfy periodic boundary conditions. (Note that the periodic basis functions are exactly periodic and are not confined to a sphere of radius \( a \).)

The wave function for our system is then an \( N \)-dimensional Slater determinant constructed from \( N \) orthonormalized periodic molecular orbitals, which are linear combinations of the periodic basis functions:

\[
\psi(x) = \sum_{\mu} c_{\alpha \mu} \Phi_{\mu}(x),
\]

where the \( \{ c_{\alpha \mu} \} \) are the expansion coefficients. (To avoid confusion, we will use Greek letters from the end of the alphabet for periodic basis functions and Greek letters from the beginning of the alphabet for periodic molecular orbitals.) Note that the wave function is perfectly periodic and thus satisfies the boundary conditions specified above.

We shall carry through the derivations without specifying any restrictions on the \( c_{\alpha \mu} \) coefficients. Thus this corresponds to the general Hartree–Fock (GHF) method.27–29 By imposing restrictions on the coefficients, the results for the restricted Hartree Fock (RHF) and unrestricted Hartree–Fock (UHF) methods can be obtained.

#### B. Decomposition of periodic overlap charge densities

The inner product is defined above as an integral over only positions in the central cell. In this section we discuss a procedure that allows these matrix elements to be expressed in terms of standard integrals, involving atomic basis functions, over all space. This procedure involves decomposition of periodic overlap charge densities into various contributions.

The overlap charge density \( \rho_{\mu \nu}(x) \) associated with periodic basis functions \( \Phi_{\mu} \) and \( \Phi_{\nu} \) is
\[ \rho_{\mu \nu}(r) = q_\mu \int d\omega \Phi_\mu^*(x)\Phi_\nu(x) = \sum_{m,n} \rho_{m,n}(r) \]  

(27)

where

\[ \rho_{m,n}(r) = q_\mu \int d\omega \phi_\mu(x) \phi_n(x). \]  

(28)

Note that the integration is over only the spin coordinate.

It will be convenient to consider that there are one or more “sites” to which this overlap charge density might be assigned. (As we will show later in this section, this assignment process will enable us to express the matrix elements of periodic basis functions, which are integrals over the central cell, in terms of integrals of localized atomic basis functions over all space.) The sites might be, for example, the location of one or both of the two atoms, or perhaps the midpoint of the two atoms, or perhaps the center of the unit cell that contains one of the atoms, but they should be reasonably close to the positions where the overlap charge density is largest. After we make a decision as to how to assign the overlap charge densities to sites, we determine the location of all of the possible sites in the central cell and then imagine that there are images of these sites in all periodic replications of the central cell.

Then we decompose the charge density \( \rho_{m,n}(r) \) into contributions associated with the various sites:

\[ \rho_{m,n}(r) = \sum_{i \in C_c} \rho_{m,n,i}(r), \]  

(29)

where \( \rho_{m,n,i}(r) \) is the part of \( \rho_{m,n}(r) \) that is associated with the site of type \( i \) in the cell labeled by \( p \), and \( C_c \) denotes the set of all sites in the central cell to which electronic charge density can be assigned. Typically, the assignment process is chosen so that the sum in Eq. (29) will have only one or two nonzero terms. Moreover, the assignment process must be translationally invariant so that

\[ \rho_{m,n,i}(r) = \rho_{m,n,i}(r - qL). \]

We need not specify the assignment process in greater detail at this point. (For crystals, it will first be worthwhile to discuss the unit cell translational symmetry.) We emphasize that the calculated value of the Hartree–Fock energy for the system [see Eq. (52)] in the limit \( a \to \infty \) is independent of the specific details of the assignment process.

The decomposition of the overlap between two periodic basis functions follows directly:

\[ \rho_{\mu \nu}(r) = \sum_{i \in C_c} \rho_{\mu \nu,i}(r), \]  

where

\[ \rho_{\mu \nu,i}(r) = \sum_{m,n} \rho_{m,n,i}(r) \]

is the part of the overlap of \( \Phi_\mu \) and \( \Phi_\nu \) that is assigned to site \( i \) in cell \( p \).

The part of this overlap that is assigned to sites in the central cell will be denoted \( \rho_{\mu \nu}^{[0]}(r) \). It is clearly given by

\[ \rho_{\mu \nu}^{[0]}(r) = \sum_{i \in C_c} \rho_{\mu \nu,i}(r) = \sum_{i \in C_c} \rho_{m,n,i}(r). \]  

(30)

Note that \( \rho_{\mu \nu}^{[0]}(r) \) is not necessarily zero for \( r \) outside the central cell, but it must go to zero very quickly as \( r \) moves away from the central cell. More generally, the part of this overlap that is assigned to cell \( p \) is

\[ \rho_{\mu \nu}^{[p]}(r) = \sum_{i \in C_c} \rho_{\mu \nu,i}(r) = \sum_{i \in C_c} \rho_{m,n,i}(r). \]  

(31)

The overlap charge density that is relevant for the calculation of matrix elements is the density that is equal to \( \rho_{\mu \nu}(r) \) for \( r \) in the central cell but that is zero outside the central cell. [See Eq. (21).] This is

\[ \rho_{\mu \nu}^{[0]}(r) = C_0(r) \rho_{\mu \nu}(r). \]

The quantities \( \rho_{\mu \nu}^{[0]}(r) \) and \( \rho_{\mu \nu}^{[0]}(r) \) are very closely related, and, using the results above, we define a quantity \( \rho_{\mu \nu}(r) \) equal to their difference:

\[ \rho_{\mu \nu}(r) = \rho_{\mu \nu}^{[0]}(r) - \rho_{\mu \nu}^{[0]}(r) \]

\[ = \sum_{i \in C_c} [C_0(r) - C_0(r_i)] \rho_{m,n,i}(r), \]

(32)

where \( r_i \) is the position of site \( i \) in cell \( p \). Thus the density needed for evaluation of inner products can be expressed as

\[ \rho_{\mu \nu}(r) = \rho_{\mu \nu}^{[0]}(r) + \rho_{\mu \nu}(r). \]

It is clear from Eq. (32) that \( \rho_{\mu \nu}(r) \) has its largest values for \( r \) near the boundaries of the central cell. Moreover, it is easily shown that \( \int d\mathbf{r} \rho_{\mu \nu}(r) = 0 \).

When matrix elements of the potential energy are evaluated using overlap densities like \( \rho_{\mu \nu}(r) \) that are nonzero only in the central cell, the integration region can be extended to all space. For example,

\[ \langle \phi_{\mu} | \phi_{\nu} \rangle = \int_{cc} d\mathbf{r} \rho_{\mu \nu}(r) \]

\[ = \int_{cc} d\mathbf{r} \rho_{\mu \nu}^{[0]}(r), \]  

(34)

where in the first line the integration region is only the central cell, and in the second line the integration region is all space. Moreover, when \( \rho_{\mu \nu}^{[0]}(r) \) is replaced by the right side of Eq. (33), this will generate integrals over intact overlap distributions \( \rho_{\mu \nu}^{[0]}(r) \), in this case the standard overlap integrals calculated in quantum electronic structure calculations, and correction terms containing \( \rho_{\mu \nu}^{[0]}(r) \). In order to illustrate this point, we will temporarily choose a specific method for assigning the charge density to sites, namely, that \( \rho_{m,n} \) is assigned completely to the site of the atom that is the origin of the left basis function. Thus,

\[ \rho_{m,n,i}(r) = \delta_{m,p} \delta_{n,q} \rho_{m,n}(r). \]

(35)

is the part of \( \rho_{m,n} \) that is to be assigned to site \( i \) in cell \( p \). Using this assignment method, we can expand Eq. (34) to get
\[
\int dr \rho_{\mu\nu}(r) = \int dr \rho_{\mu\nu}^{[0]}(r) + \int dr \rho_{\mu\nu}^{[\Delta]}(r)
\]
\[
= \sum \left( \phi_{\mu0} | \phi_{\nu n} \right) \delta_{\sigma_\mu, \sigma_\nu} + \int dr \rho_{\mu\nu}^{\Delta}(r),
\]
(36)

where
\[
\left( \phi_{\mu0} | \phi_{\nu n} \right) = \int dr \phi_{\mu0}^*(r) \phi_{\nu n}(r)
\]
(37)
is a standard spatial integral and \( \delta \) is the Kronecker delta function. The overlap matrix element is a particularly simple and straightforward example, and this result could be obtained using alternative methods (i.e., simple coordinate transformations). Using similar reasoning, however, matrix elements of one-electron and two-electron operators can also be expressed in terms of conventional one-electron and two-electron integrals (i.e., integrals over \( \text{aI} \) space involving intact atomic basis functions), plus, of course, \( \rho^{[\Delta]} \) contributions. Note that this can be shown to be valid not only for this assignment method, which assigns an entire overlap distribution to a single site, but also for any method that assigns fractional multiples of the overlap charge distribution to two or more sites.

To continue the decomposition of the densities, we construct a point multipole representation of \( \rho_{\mu\nu\sigma\tau} \). First we calculate the net charge, dipole moment vector, traceless quadrupole moment tensor, and spheropole moment of this density relative to its site at \( \mathbf{r}_p \). The spheropole moment of a general charge density \( \rho(r) \) is defined as \( \int dr \rho(r) | \mathbf{r} |^2 \). Then we construct a point monopole, point dipole, point quadrupole, and point spheropole with these values centered at \( \mathbf{r}_p \). (A point spheropole is a charge distribution that has a nonzero spheropole moment but no nonzero multipoles.) The charge density for this point multipole representation of \( \rho_{\mu\nu\sigma\tau} \) will be denoted \( \rho_{\mu\nu\sigma\tau}^{[m]} \). We then define
\[
\rho_{\mu\nu\sigma\tau}^{[m]}(r) = \rho_{\mu\nu\sigma\tau}(r) - \rho_{\mu\nu\sigma\tau}^{[p]}(r).
\]
(38)

As a result of this construction, the correction term \( \rho_{\mu\nu\sigma\tau}^{[p]}(r) \) has zero net charge, zero dipole moment, zero quadrupole moment, and zero spheropole moment. Moreover, it has its largest values for \( r \) near \( \mathbf{r}_p \), the location of the site to which this density was assigned.

Using Eqs. (30) and (38), we can perform a further decomposition of \( \rho_{\mu\nu}\(r) \):
\[
\rho_{\mu\nu}(r) = \rho_{\mu\nu}^{[0]}(r) + \rho_{\mu\nu}^{[\Delta]}(r),
\]
where
\[
\rho_{\mu\nu}^{[0]}(r) = \sum_{i(\text{C\&e})} \rho_{\mu\nu}^{[p]}(r),
\]
\[
\rho_{\mu\nu}^{[\Delta]}(r) = \sum_{i(\text{C\&e})} \rho_{\mu\nu}^{[m]}(r).
\]

Hence, we have broken up each overlap electron charge density in the central cell into three parts:

Note that we are not attempting to represent the overlap density with a multipolar expansion, which would require all higher order multipoles. Instead, we are representing the density exactly as a sum of three parts, one of which has the same low order multipole moments as the entire density. We will see that for our method to work, it is necessary that the point multipole representation \( \rho_{\mu\nu}^{[0]} \) have the same charge, dipole moment, quadrupole moment, and spheropole moment as \( \rho_{\mu\nu}^{[0]} \), but it need not have the same values for higher order multipole moments. We will use Eq. (39) in the next subsection to evaluate the expectation value of the Hamiltonian.

Before doing this, we define the nuclear charge density. The nuclei are treated classically and can be viewed as point charges, so the nuclear charge density \( \rho_{n}(r) \) in the central cell is simply
\[
\rho_{n}(r) = \sum_{i(\text{C\&e})} q_i \delta(r - \mathbf{r}_i).
\]
(40)

C. Derivation of the Hartree–Fock energy

We break up the Hamiltonian into zero-, one-, and two-electron contributions:
\[
H = H_0 + H_1 + H_2.
\]
(41)
The zero-electron contribution \( H_0 \) contains the nuclear–nuclear repulsion, which is a constant:
\[
H_0 = \frac{1}{2} \sum_{i,j(\text{C\&e})} q_i q_j v_{\text{pchs}}(\mathbf{r}_i, \mathbf{r}_j).
\]
(42)
The one-electron contribution \( H_1 \) contains the electron kinetic energy, the electron–nuclear potential energy, and the \( i=j \) terms in the electron–electron interaction:
\[
H_1 = \sum_{i(\text{C\&e})} t(\mathbf{r}_i) + \frac{1}{2} \sum_{i,j(\text{C\&e})} q_i q_j v_{\text{pchs}}(\mathbf{r}_i, \mathbf{r}_j)
\]
\[
+ \sum_{i(\text{C\&e})} \sum_{j(\text{C\&e})} q_i q_j v_{\text{pchs}}(\mathbf{r}_i, \mathbf{r}_j) + \frac{1}{2} \sum_{i(\text{C\&e})} q_i^2 v_{\text{pchs}}(\mathbf{r}_i, \mathbf{r}_i)
\]
\[
= \sum_{i(\text{C\&e})} [t(\mathbf{r}_i) + h_{1n}(\mathbf{r}_i) + h_{1s}(\mathbf{r}_i)]
\]
\[
+ \sum_{i(\text{C\&e})} t(\mathbf{r}_i) + H_{1n} + H_{1s},
\]
(43)

where
\[
H_{1n} = \sum_{i(\text{C\&e})} h_{1n}(\mathbf{r}_i),
\]
(44)
\[
H_{1s} = \sum_{i(\text{C\&e})} h_{1s}(\mathbf{r}_i),
\]
(45)
\[
h_{1n}(\mathbf{r}_i) = \frac{q_i}{2} \sum_{j(\text{C\&e})} q_j [v_{\text{pchs}}(\mathbf{r}_i, \mathbf{r}_j) + v_{\text{pchs}}(\mathbf{r}_j, \mathbf{r}_i)],
\]
(46)
The two-electron contribution $H_2$ contains the $i \neq j$ terms in the electron–electron interaction:

$$H_2 = \frac{1}{2} \sum_{i \neq j} q_i q_j \psi_{pcch}(r_i, r_j) = \frac{1}{2} \sum_{i \neq j} h_2(r_i, r_j),$$  \hspace{1cm} (48)$$

where

$$h_2(r_i, r_j) = q_i^2 \psi_{pcch}(r_i, r_j).$$

Now we can take the expectation value of $H$:

$$\langle H \rangle = H_0 + \sum_{\alpha} \left[ \langle \psi_\alpha | \hat{H}_1 | \psi_\alpha \rangle + \langle \psi_\alpha | \hat{H}_2 | \psi_\alpha \rangle + \langle \psi_\alpha | \hat{H}_3 | \psi_\alpha \rangle \right] + \sum_{\sigma C} \left[ \langle \psi_\sigma \psi_\sigma | \hat{H}_2 | \psi_\sigma \psi_\sigma \rangle - \langle \psi_\sigma \psi_\sigma | \hat{H}_3 | \psi_\sigma \psi_\sigma \rangle \right] - H_0 + \sum_{\mu, \nu} P_{\mu \nu} \left[ \langle \mu | \hat{H}_1 | \nu \rangle + \langle \mu | \hat{H}_2 | \nu \rangle + \langle \mu | \hat{H}_3 | \nu \rangle \right] + \frac{1}{2} \sum_{\eta, \xi} P_{\eta \xi} \left[ \langle \mu \eta | \hat{H}_2 | \nu \xi \rangle - \langle \mu \eta | \hat{H}_3 | \nu \xi \rangle \right],$$  \hspace{1cm} (50)$$

where

$$P_{\mu \nu} = \sum_{\sigma C} \psi_{\sigma \alpha}^* \psi_{\sigma \beta}$$

and for notational convenience we denote the periodic basis functions only by their subscript. Note that the inner product was defined as an integral over only the central cell.

The energy expression can be conveniently broken into three parts. One part will contain only the kinetic energy $E_T = \sum_{\mu, \nu} P_{\mu \nu} \langle \mu | \nu \rangle$. Another part will be

$$E_E = \frac{1}{2} \sum_{\mu, \nu} P_{\mu \nu} \left[ \langle \mu | \hat{H}_1 | \nu \rangle + \langle \mu | \hat{H}_2 | \nu \rangle + \langle \mu | \hat{H}_3 | \nu \rangle \right].$$

We will call these the exchange terms for reasons that will become clear below. The remaining terms will be called the Madelung terms and will be denoted $E_M$.

This expression for the expectation value of the Hamiltonian is subject to the orthonormality condition of the periodic molecular orbitals:

$$\langle \psi_\alpha | \psi_\beta \rangle = \sum_{\mu, \nu} c_{\mu \alpha}^* c_{\beta \nu} \langle \mu | \nu \rangle = \delta_{\alpha \beta}.$$  \hspace{1cm} (51)$$

We now discuss a simplification of the expression for the expectation value of the Hamiltonian. First we extend the integration region to all space by using overlap densities like $\rho_\mu^{(0)}(r)$ that are nonzero only in the central cell. This introduces no error. [See Eq. (34).] For each matrix element, we break up the electronic charge density $\rho_\mu^{(0)}(r)$ into its three parts using Eq. (39). We then express $\psi_{pcch}(r_i, r_j)$ as either a sum of two contributions using Eq. (11) or as a sum of four contributions using Eq. (17). [We use Eq. (17) for $H_0$ and for all parts of the $\langle \mu | \hat{H}_3 | \nu \rangle$ matrix elements. For the $\langle \mu | \hat{H}_1 | \nu \rangle$ matrix elements, we use Eq. (17) for the $p$ and $\Delta$ densities and Eq. (11) for the $c$ densities. For the $\langle \mu | \hat{H}_2 | \nu \rangle$ matrix elements, we use Eq. (11) for terms containing at least one $c$ density but no $\Delta$ density and Eq. (17) for all other terms.] This will create a large number of terms, many of which will be identically zero or of order $a^{-1}$ for reasons given in Appendix B or will cancel with other terms due to the charge neutrality of the system. (See Ref. 20 for details of this calculation.) The final result can be written in a form that closely resembles the traditional nonperiodic Hartree–Fock energy:

$$\langle H \rangle = \frac{1}{2} \sum_{i \neq j} q_i q_j \psi_{elch}(r_i, r_j) + \frac{N V_{elch}(0, 0)}{2} + \sum_{\mu, \nu} P_{\mu \nu} \left[ \langle \mu | \nu \rangle + \langle \mu | \nu \rangle \right] + \frac{1}{2} \sum_{\eta, \xi} P_{\eta \xi} \left[ \langle \mu \eta | \nu \xi \rangle - \langle \mu \eta | \nu \xi \rangle \right] + O(a^{-1})$$

$$= E_T + E_M + E_E + O(a^{-1}),$$  \hspace{1cm} (52)$$

where the notation is defined below. The exchange terms are now

$$E_E = \frac{N V_{elch}(0, 0)}{2} \sum_{\mu, \nu, \eta, \xi} P_{\mu \nu} P_{\eta \xi} \langle \mu \eta | \nu \xi \rangle,$$

and the Madelung terms $E_M$ contain the rest of the terms, other than the kinetic energy $E_T$.

The first two terms in Eq. (52) are just constants: the first term contains the nuclear–nuclear repulsion of all nuclei in $H_0$ (we will refer to the $i=j$ term as the nuclear self-interaction); and the second term arises from the $i=j$ electron interaction terms involving $h_{1S}$ (which we will refer to as the electron self-interaction). The third term is the electron kinetic energy term.

The fourth term arises from the electron–nuclear interactions $h_{1S}$ and is defined as follows:

$$\langle \mu | 1 N \nu \rangle = \langle \mu | 1 N_{elch} | \nu \rangle + \langle \mu | 1 N_{pch} | \nu \rangle,$$

where

$$\langle \mu | 1 N_{elch} | \nu \rangle = \int dr_1 \int dr_2 \rho_\mu^{(0)}(r_1) \times \rho_\nu^{(0)}(r_2) \psi_{elch}(r_1, r_2),$$

$$\langle \mu | 1 N_{pch} | \nu \rangle = \int dr_1 \int dr_2 \rho_\mu^{(0)}(r_1) \times \rho_\nu^{(0)}(r_2) \psi_{pch}(r_1, r_2),$$

$$\langle \mu | 1 N_{elch} | \nu \rangle = \sum_{\eta, \xi} \int dr_1 \int dr_2 \rho_\mu^{(0)}(r_1) \times \rho_\nu^{(0)}(r_2) \psi_{elch}(r_1, r_2),$$

$$\langle \mu | 1 N_{pch} | \nu \rangle = \sum_{\eta, \xi} \int dr_1 \int dr_2 \rho_\mu^{(0)}(r_1) \times \rho_\nu^{(0)}(r_2) \psi_{pch}(r_1, r_2).$$
where $U$ denotes the set of all vectors with integer components. Note that the integration region in these definitions is all space. The first term of Eq. (53) is an Ewald interaction between the nuclear charge $\rho^0_n(r)$ in the central cell and the point multipole representation of an electron charge distribution, $\rho^m_{\mu \nu}(r)$. The second term in Eq. (53) is the short range part of the Coulomb interaction between the nuclear charge $\rho^0_n(r)$ and the electron charge distribution $\rho_{\mu \nu}(r)$. The leading multipole of the difference charge density in square brackets in the integrands of Eqs. (55) and (56) is an octopole moment. Thus the leading contribution to these integrands is a charge-octopole interaction, as in Eqs. (55) and (56). Again, the infinite series in Eq. (56) is absolutely convergent.

Finally, the last term arises from the electron-electron interactions $h_2$, and is defined as follows:

$$\langle \mu \eta | 2 e L h | \nu \zeta \rangle = \langle \mu \eta | 2 e L h | \nu \zeta \rangle + \langle \mu \eta | 2 p c h | \nu \zeta \rangle,$$

where

$$\langle \mu \eta | 2 e L h | \nu \zeta \rangle = \int dr_1 \int dr_2 \rho^{[\mu]}(r_1) \rho^{[\mu]}(r_2) u_{elh}(r_1, r_2),$$

$$\langle \mu \eta | 2 p c h | \nu \zeta \rangle = \int dr_1 \int dr_2 \rho^{[0]}(r_1) \rho^{[0]}(r_2) u_{pch}(r_1, r_2).$$

The first term of Eq. (57) is an Ewald interaction between the point multipole representations $\rho^{[\mu]}(r)$ and $\rho^{[\mu]}(r)$. The second term in Eq. (57) is the short range part of the Coulomb interaction between the electron charge distributions $\rho^{[0]}(r)$ and $\rho^{[0]}(r)$. The leading multipole of the expression in square brackets in the integrands of Eqs. (59) and (60) is an octopole moment, so the leading contribution to these integrands is a charge-octopole interaction, as in Eqs. (55) and (56). Again, the infinite series in Eq. (56) is absolutely convergent, and the magnitude of the terms falls off as $O(|n|^{-6})$.

Now let lower case letters from the beginning of the alphabet (e.g., $a, b$) denote the type of basis function in a unit cell, and let boldface letters (e.g., $f, g$) denote vectors with integer components. Then the symbol $\mu$ from the previous section contains information about the unit cell and the particular type of basis function in the unit cell, i.e., $\mu \in \{ a, f \}$ for $f \in U_C$, and $\mu \in \{ b, g \}$ for $b, g \in U_C$. Using this notation, $\rho^{[0]}(r)$ is replaced by $\rho^{[0]}(r) = \sum_{f \in U_C} \sum_{x \in \mathcal{N}_f} q_{x} S_{x}^f(r - r_x + \mathbf{f} d)$. Here $r_x$ is the position of nucleus $x$ in the central unit cell, and hence $r_x + \mathbf{f} d$ is the position of the corresponding nucleus in the unit cell labeled by $\mathbf{f}$. Note that lower case letters from the beginning of the alphabet (e.g., $a, b$) denote the type of basis function in a unit cell, and let boldface letters (e.g., $f, g$) denote vectors with integer components. Then the symbol $\mu$ from the previous section contains information about the unit cell and the particular type of basis function in the unit cell, i.e., $\mu \in \{ a, f \}$ for $f \in U_C$, and $\mu \in \{ b, g \}$ for $b, g \in U_C$. Using this notation, $\rho^{[0]}(r)$ is replaced by $\rho^{[0]}(r) = \sum_{f \in U_C} \sum_{x \in \mathcal{N}_f} q_{x} S_{x}^f(r - r_x + \mathbf{f} d)$. Note that only point multipoles and intact overlap distributions appear (i.e., no $\Delta$ terms exist in the final expression; they have canceled one another completely and exactly). Also note that due to the hole contributions to $v_{elh}$ and $v_{ch}$, there are no divergences in the Coulomb and Ewald interactions when a site of an overlap happens to coincide with a nucleus or with the site of another overlap. Finally, note that Eqs. (56) and (60) are the first places in which an infinite series has appeared in this theoretical development, and both series are absolutely convergent.

IV. HARTREE-FOCK THEORY FOR PERFECT CRYSTALS WITH AN ASSUMED UNIT CELL STRUCTURE

In this section we apply the theory from the previous section to infinite crystalline systems with an assumed unit cell structure.

A. Unit cell symmetry

Let us assume that our system is a crystal with a cubic unit cell that has sides of length $d$, and that there are $Q$ unit cells in each row of the central cell. Thus, $L = Q d$. One unit cell has its origin at the origin of the coordinate system. Other unit cells have their origins at points whose coordinates are integer multiples of $d$. A three-dimensional vector with integer components, e.g., $\mathbf{f}$, thereby provides a label for unit cells, such that the origin of the unit cell labeled by $\mathbf{f}$ is at $\mathbf{f} d$. Let $U$ denote the set of all vectors with integer components, and let $U_C$ denote the subset of all such vectors that correspond to unit cells located in the central cell. In addition, let $\mathcal{N}_f$ be the set of nuclei in the central unit cell. We now introduce new notation that exploits the unit cell symmetry.

First we break up the nuclear charge density into contributions associated with each unit cell:

$$\rho^{[0]}(r) = \sum_{f \in U_C} \sum_{x \in \mathcal{N}_f} q_x S_{x}^f(r - r_x + \mathbf{f} d).$$

Here $r_x$ for $x \in \mathcal{N}_f$ is the position of nucleus $x$ in the central unit cell, and hence $r_x + \mathbf{f} d$ is the position of the corresponding nucleus in the unit cell labeled by $\mathbf{f}$. Using this notation, $\rho^{[0]}(r)$ is replaced by $\rho^{[0]}(r) = \sum_{f \in U_C} \sum_{x \in \mathcal{N}_f} q_x S_{x}^f(r - r_x + \mathbf{f} d)$. Note that only point multipoles and intact overlap distributions appear (i.e., no $\Delta$ terms exist in the final expression; they have canceled one another completely and exactly). Also note that due to the hole contributions to $v_{elh}$ and $v_{ch}$, there are no divergences in the Coulomb and Ewald interactions when a site of an overlap happens to coincide with a nucleus or with the site of another overlap. Finally, note that Eqs. (56) and (60) are the first places in which an infinite series has appeared in this theoretical development, and both series are absolutely convergent.
\[ \rho_{\omega a b \sigma}(r) = q \int d \omega^* \phi_{\omega a}(x) \phi_{\omega b}(x) \]
\[ (64) \]
and
\[ \tilde{\rho}_{ab}(r) = q \int d \omega^* \phi_{\omega x}(x) \phi_{\omega b}(x). \]
\[ (65) \]
Finally, \( P_{\mu \nu} \) is replaced by \( \tilde{\rho}_{ab} \).

Previously we used \( i \) as the label for a site to which electronic charge density is assigned. Since each unit cell contains exactly the same set of sites, the label \( i \) can be replaced by \( z \) and \( h \), where \( z \) denotes the particular site in a unit cell and \( h \) denotes a unit cell. Let \( C_u \) be the set of sites in the central unit cell to which electronic charge density can be assigned.

We now address the question of how overlap charge densities are to be assigned to specific sites. We start by defining a method of assigning the \( \tilde{\rho}_{ab}(r) \) to sites, independent of any considerations of periodicity on the length scale \( L \). Again we emphasize that the calculated Hartree–Fock energy for the system [see Eq. (83)] in the limit \( a \to 0 \) is independent of the specifics of the assignment process.

For simplicity we will choose a specific method of assignment, where \( \tilde{\rho}_{ab}(r) \) is assigned completely to the site of the atom that is the origin of the left basis function, namely that of basis function \( a \) in unit cell \( f \). This method is closely related to that of Pisani et al.31) Thus,
\[ \tilde{\rho}_{ab}(x) = \delta_{ih} \delta_{x,z} \tilde{\rho}_{ab}(r) \]
\[ (66) \]
is the part of \( \tilde{\rho}_{ab}(r) \) that is to be assigned to site \( zh \). For a more general treatment and a discussion of other possible assignment methods, the reader is referred to Ref. 20.

Note that
\[ \tilde{\rho}_{ab}(r) = \sum_{z(C_u),h(C_u)} \tilde{\rho}_{ab}(r), \]
\[ (67) \]
and, using Eqs. (63), (66), and (67) we have
\[ \tilde{\rho}_{ab}(r) = \sum_{h(C_u),z(C_u)} \tilde{\rho}_{ab}(r), \]
\[ (68) \]
where
\[ \tilde{\rho}_{ab}(r) = \sum_{m,n(C_u)} \tilde{\rho}_{a,t+m,Q,b,g+nQ,z,h}(r) \]
\[ = \sum_{m,n(C_u)} \delta_{t+m,Q,b,g+nQ,z,h}(r). \]
\[ (69) \]
Then the part of an overlap of periodic basis functions that is assigned to the central simulation cell is easily expressed as
\[ \tilde{\rho}^{[0]}_{ab}(r) = \sum_{n(C_u),z(C_u)} \tilde{\rho}_{ab}(r). \]
\[ (70) \]
The notation for point multipole representations of these densities is straightforward. Let \( \tilde{\rho}_{ab}(r) \) be the point multipole representation of \( \tilde{\rho}_{ab}(r) \), and define
\[ \tilde{\rho}_{ab}(r) = \sum_{\mu \nu} \tilde{\rho}_{\mu \nu}(r). \]
\[ (71) \]

**B. Bloch orbitals**

A fundamental assumption made in applying the Hartree–Fock method to crystals is that each occupied orbital is a linear combination of Bloch basis functions of the same wave vector \( k \). For this purpose, we define a Bloch basis function
\[ \Psi_{ak}(x) = \sum_{\alpha} \Phi_{ak}(x)e^{ik \cdot \alpha} \]
\[ (72) \]
for each \( a \) (i.e., for each type of basis function in a unit cell) and for each wave vector \( \mathbf{k} \in \mathbb{B} \), where \( \mathbb{B} \) is the set of all wave vectors \( \mathbf{k} = (2\pi/L)m \) for all \( m \in U \). We also define the first Brillouin zone (denoted \( \mathbb{B}_1 \)) as the set of all wave vectors \( \mathbb{B} \) that have a smaller magnitude than any other wave vector that differs from it by a vector integer multiple of \( 2\pi/L \). We point out that there are \( Q^3 \) wave vectors in \( \mathbb{B}_1 \).

In this formalism, each occupied orbital is characterized by its wave vector \( \mathbf{k}_1 \) and some other quantum number \( \alpha \), as opposed to just \( \sigma \) as in the previous section. Using our new notation to rewrite Eq. (26), we have
\[ \tilde{\rho}_{ab}(x) = \sum_{\alpha, \lambda} \tilde{\rho}_{ab}(x) \tilde{\rho}_{a \lambda}(x). \]
\[ (73) \]
Incorporating the insight that the occupied orbitals are linear combinations of Bloch basis functions, we also have
\[ \tilde{\rho}_{ab}(x) = \sum_{\alpha} \tilde{\rho}_{ab}(x) \Phi_{ak}(x) e^{ik \cdot \alpha}. \]
\[ (74) \]
This equation imposes the following restriction on the \( c_{ak} \):
\[ c_{ak} = \sum \tilde{\rho}_{ab}(x). \]
\[ (75) \]
We now discuss how these restrictions on the coefficients affect the density matrix. For the general problem, the density matrix was defined as
\[ \rho_{\mu \nu} = \sum_{a} c_{a \mu} c_{a \nu}. \]
\[ (76) \]
In the present case, the corresponding expression is
\[ \rho_{ab} = \sum_{k} c_{ak} c_{ak}, \]
\[ (77) \]
where the sum is understood to be over occupied orbitals \( k \). Thus use of Bloch basis functions imposes restrictions on the
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coefficients such that the density matrix depends only on the difference between the two vectors that denote unit cells. Moreover,

\[ P_{abfg} = P_{a,f+h,b,g+h} \quad \text{for} \quad f,g,f+h,g+h \in U_c. \quad (77) \]

For convenience, we extend the definition of \( P_{abfg} \) to all vectors \( f,g \in U \) so that

\[ P_{a,b+nQ,d+i+mQ} = P_{abdl} \quad \text{for} \quad h,i \in U_c, \quad n,m \in U. \quad (78) \]

As a consequence of this extended definition of \( P_{abfg} \), Eq. (77) now holds for all \( f,g,h \in U \).

We also define

\[ P_{ab}(k) = \left( \frac{L}{2\pi} \right)^3 \sum_{\alpha} d_{k\alpha a}^* d_{k\alpha b} \quad \text{for} \quad k \in B_1, \quad (79) \]

and we extend this definition so that

\[ P_{ab}(k+2\pi n/d) = P_{ab}(k) \quad \text{for} \quad n \in U. \quad (80) \]

Thus

\[ P_{abfg} = \left( \frac{2\pi}{L} \right)^3 \sum_{k \in (U/U_c)} P_{ab}(k)e^{-ik\cdot(q-\delta d)}. \quad (81) \]

Due to the normalization constraint on the molecular orbitals, \( p_{ab}(k) \) will approach a finite limit as \( L \to \infty \). We will also define

\[ d_{k\alpha a} = \left( \frac{L}{2\pi} \right)^{3/2} d_{k\alpha a}, \quad (82) \]

which will also approach a finite limit as \( L \to \infty \).

C. Expectation value of the Hamiltonian

Using the notation described in the previous two subsections, we can rewrite Eq. (52) as

\[
\langle H \rangle = \frac{1}{2} \sum_{i,j \in (U/U_c)} q_{i} q_{j} P_{e \L} (r_{i}, r_{j}) + \frac{N v_{e \L}(0, 0)}{2} \\
 + \sum_{\mathbf{f}, \mathbf{g} \in U} P_{abfg} (\langle af|bf \rangle + \langle af|1N|bg \rangle) \\
+ \frac{1}{2} \sum_{\mathbf{f}, \mathbf{g}, \mathbf{h}, \mathbf{i} \in U} P_{abfg} P_{cdhl} (\langle af|ch \rangle 2|bgd \rangle) \\
- \frac{1}{2} \sum_{\mathbf{f}, \mathbf{g}, \mathbf{h}, \mathbf{i} \in U} P_{abfg} P_{cdhl} (\langle af|ch \rangle 2|dbg \rangle) \\
+ O(a^{-1}) = E_T + E_M + E_E + O(a^{-1}), \quad (83)
\]

where \( E_T \) is the kinetic energy, \( E_R \) is the exchange energy [the \( v_{e \L}(0, 0) \) term and the last summation term], and \( E_M \) is the Madelung energy (all of the remaining terms). Each of these contributions can be analyzed and presented in a form suitable as a starting point for numerical computations. The derivations are detailed but straightforward and are based primarily on the translational symmetry properties of the various quantities. Some of the relevant considerations are presented in Appendix C. We will just present the results here. For more information and detailed derivations, see Ref. 20.

We define the energy per unit cell as \( E_U = \langle H \rangle / Q^2 \) and then we take the thermodynamic limit of large system size. As discussed in Sec. II A, the limit of \( a \to \infty \) must be taken before the limit of \( L \to \infty \). Finally, the limit \( \Delta \to 0+ \) should be taken to account properly for the fact that a point charge cannot interact directly with itself. The energy per unit cell in the thermodynamic limit is:

\[
E_U = \frac{1}{2} \sum_{\mathbf{x}, \mathbf{y} \in (N_U)} q_{\mathbf{x}} q_{\mathbf{y}} v_{edh} (\mathbf{r}_{\mathbf{x}}, \mathbf{r}_{\mathbf{y}}) + \sum_{\mathbf{a}, \mathbf{b} \in U} \sum_{\mathbf{c}, \mathbf{d} \in U} \delta_{\sigma_a \sigma_b} P_{a \mathbf{b} \mathbf{c} \mathbf{d}} \left[ (\mathbf{a} \mathbf{0}|\mathbf{b} \mathbf{f} + \mathbf{g}|\mathbf{p}) + \sum_{\mathbf{y} \in (U/U_c)} (\langle \mathbf{a} \mathbf{0}|\mathbf{y} \mathbf{e} \mathbf{d} \mathbf{h}|\mathbf{b} \mathbf{g}|\mathbf{p}) \right] + \sum_{\mathbf{r} \in U} \left[ (\mathbf{a} \mathbf{0}|\mathbf{y} \mathbf{e} \mathbf{d} \mathbf{h}|\mathbf{b} \mathbf{g}|\mathbf{p}) \right] \left[ (\mathbf{a} \mathbf{0}|\mathbf{y} \mathbf{e} \mathbf{d} \mathbf{h}|\mathbf{b} \mathbf{g}|\mathbf{p}) \right] \\
- (\langle \mathbf{a} \mathbf{0}|\mathbf{y} \mathbf{e} \mathbf{d} \mathbf{h}|\mathbf{b} \mathbf{g}|\mathbf{p} \rangle) + \sum_{\mathbf{a}, \mathbf{b} \in U} \sum_{\mathbf{c}, \mathbf{d} \in U} \delta_{\sigma_a \sigma_b} \delta_{\sigma_c \sigma_d} P_{a \mathbf{b} \mathbf{c} \mathbf{d}} \left[ (\mathbf{a} \mathbf{0}|\mathbf{b} \mathbf{g} |\mathbf{e} \mathbf{d} \mathbf{h} |\mathbf{c} \mathbf{0} \mathbf{d} |\mathbf{p}) + \sum_{\mathbf{h} \in U} \left[ (\mathbf{a} \mathbf{0}|\mathbf{b} \mathbf{g} |\mathbf{c} \mathbf{h} \mathbf{d} \mathbf{h} + \mathbf{i} |\mathbf{p}) \right] - \delta_{\sigma_a \sigma_d} \delta_{\sigma_c \sigma_b} \sum_{\mathbf{h} \in U} \mathbf{P}_{\mathbf{c} \mathbf{d} \mathbf{h} \mathbf{i}} \left[ (\mathbf{a} \mathbf{0}|\mathbf{d} \mathbf{l} |\mathbf{w} \mathbf{r} (\mathbf{c} \mathbf{a} \mathbf{'} )|\mathbf{c} \mathbf{h} \mathbf{b} \mathbf{g} |\mathbf{p} + (\mathbf{a} \mathbf{0}|\mathbf{d} \mathbf{l} |\mathbf{c} \mathbf{b} \mathbf{g} |\mathbf{p} - (\mathbf{a} \mathbf{0}|\mathbf{d} \mathbf{l} |\mathbf{c} \mathbf{b} \mathbf{g} |\mathbf{p}) \right] \\
- \frac{1}{2} \int_{B_1} d\mathbf{k} \int_{B_1} d\mathbf{q} \sum_{\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{d} \in U} P_{a \mathbf{b} \mathbf{c} \mathbf{d}} (\mathbf{k} + \mathbf{q}) e^{i \mathbf{q} \mathbf{a} \mathbf{b} \mathbf{c} \mathbf{d} + i(k + q) \cdot \mathbf{r} \mathbf{c} \mathbf{d} \mathbf{h} \mathbf{i} \mathbf{a} \mathbf{b} \mathbf{c} \mathbf{d} + i \mathbf{u} \mathbf{v} \mathbf{c} \mathbf{d} \mathbf{h} \mathbf{i} \mathbf{a} \mathbf{b} \mathbf{c} \mathbf{d} + i \mathbf{v} \mathbf{c} \mathbf{d} \mathbf{h} \mathbf{i} \mathbf{a} \mathbf{b} \mathbf{c} \mathbf{d}) \left[ (\mathbf{a} \mathbf{0}|\mathbf{d} \mathbf{l} |\mathbf{w} \mathbf{r} (\mathbf{c} \mathbf{a} \mathbf{'} )|\mathbf{c} \mathbf{b} \mathbf{g} |\mathbf{p} \right], \quad (84)
\]

where the notation is defined below and \( \delta \) is the Kronecker delta function. [Recall from Eq. (22) that \( \sigma_a \) is the spin associated with basis function \( \mathbf{a} \).] Note that \( v_{edh} \) is the Ewald potential with periodicity \( d \). [See Eq. (C16) for an identity relating \( v_{edh} \) and \( v_{e \L b} \) that was used to derive Eq. (84).] Standard integrals involving basis functions depending only on the spatial quantum numbers and not on the spin quantum numbers will be denoted using parentheses to distinguish them from the closely related quantities designated with angular brackets. In Eq. (84), the limit \( \Delta \to 0+ \) is understood to be taken.

The definitions of the one-electron matrix elements are:
is a standard kinetic energy integral;

\[
(a|f|b) = \int dr \, \phi_a^*(r-r_a) \left( -\frac{1}{2} \nabla^2 \phi_b(r-r_b - gd) \right)
\]

is the Ewald interaction (with periodicity \(d\)) between nucleus \(y\) in the central unit cell and the point multipole representation of the overlap of the two atomic basis functions \(a\) and \(b\), according to Eq. (66), is assigned to the central unit cell; 

\[
(a|y|0|edh|b)=\int dr \, q_y^p \phi_a^*(r) v_{eda}(r, r)
\]

is the overlap electronic charge density with a nucleus of type \(y\) in the unit cell denoted \(j\) and; and

\[
(a|y|j|bg)^p = \int dr \, \tilde{\rho}_{ajb}(r) \left( q_y^{y} \frac{q_y}{|r-(r_y+jd)|+q_y u_h(r_y+jd)} \right)
\]

denotes a one-electron spatial integral for the interaction of an overlap electronic charge density with a nucleus of type \(y\) in the unit cell denoted \(j\) and; and

\[
(a|y|j|bg) = \int dr \, \tilde{\rho}_{ajb}(r) \left( q_y^{y} \frac{q_y}{|r-(r_y+jd)|+q_y u_h(r_y+jd)} \right)
\]

is equivalent to Eq. (87) with the overlap density replaced by its point multipole representation and \(v_{ch}\) replaced by \(v_{ch}\).

The definitions of the two-electron matrix elements that are analogous to Eqs. (86)–(88) are:

\[
(a|0|b|c|d|e|0|d) = \int dr_1 \int dr_2 \, \tilde{\rho}_{ab}(r_1) \tilde{\rho}_{cd}(r_2) \left( q_y^{y} \frac{q_y}{|r_1-(r_1+jd)|+q_y u_h(r_1+jd)} \right)
\]

Note that we have followed the standard chemist's notation for two-electron integrals, with the basis functions involved in a single overlap being grouped together on the same side of the vertical line. The exchange terms are defined and derived in Appendix D.

Each matrix element in Eq. (84) with an \(edh\) operator is evaluated using Eqs. (14) and (15), which involves choosing a value for \(\alpha\). The value of \(\alpha'\) does not need to be the same as the value of \(\alpha\). However, the same value of \(\alpha'\) must be used for both \(wr(\alpha')\) and \(wf(\alpha')\) matrix elements.

All of the matrix elements with a superscript \(p\) involve point multipole representations of the densities, which include point charges, dipoles, quadrupoles, and spheropoles. However, the total contribution to the Madelung energy of the point spheropoles in the point multipole representations is zero. Moreover, the contribution of the point spheropoles in the point multipole representations to the Coulomb-hole part of the exchange energy is also zero. Thus the point spheropoles have to be included only in the \(wr\) and \(wf\) matrix elements. See Ref. 20 for details.

Although the structure of Eq. (84) is affected by some choices made in the derivation of the result, the final result for the total energy is in fact not affected by these choices. First, Eq. (84) was obtained by introduction of the \(v_h\) potential at the beginning of the calculation (as a bookkeeping device to reflect the fact that a charged particle cannot interact with itself) with the understanding that the limit \(\Delta \to 0^+\) is to be taken at the end of the calculation. It would be possible to get an equivalent result without introduction of \(v_h\) and the limiting operations involving \(\Delta\), but at the cost of greatly complicating the notation and the derivation. To confirm this, note that Eq. (84) can, in fact, be expressed in a form in which \(v_h\) does not explicitly appear. Second, Eq. (84) was derived using a specific method of assignment of overlap charge distributions to sites [see Eq. (66)]. Other methods of assignment could be used, however, and results equivalent to Eq. (84) would be obtained.

D. Fock matrix formalism

We now use the results above to derive a Fock matrix and an analog to the traditional Hartree–Fock–Roothaan equations. First define

\[
C_{aobg} = A_{aobg} + B_{aobg},
\]

and

\[
\]
Finally, define 

$$G_{ab}(k) = -\frac{1}{2} \sum_{\mu \in (CN_u)} \sum_{\nu \in (k+q)} \int d\mathbf{r} \sum_{\beta} \tilde{d}_{k+q,\nu,\beta,\varepsilon} e^{i(k+q)\cdot r} \delta_{a,\nu,\beta,\varepsilon} e^{i(k+q)\cdot r} \times \langle \mathbf{a} | \mathbf{a} | \mathbf{b} \rangle$$

and then the Fock matrix in $k$ space is defined as 

$$F(k) = C(k) + G(k).$$

The construction of the Fock matrix involves the calculation of infinite series containing molecular integrals for electron-electron repulsion and electron-nuclear attraction. Whenever such an integral appears, such as $(a|f|y|bg)$ in $A_{a|b|g}$ or $(a|bg|ch|di)$ in $B_{a|b|g}$, the corresponding integral with the point multipole representations of the overlaps also appears with the opposite sign. For the same reason that the infinite series in Eqs. (56) and (60) are absolutely convergent (the reader is referred to the discussion after each of these equations), all of the infinite series in the Fock matrix will be absolutely convergent.

We now obtain the Roothaan equations for this problem. In the present notation, the energy per unit cell is 

$$E_{uc} = \int d\mathbf{k} \sum_{\alpha} F_{ab}(k) \tilde{d}_{ab}$$

Using Lagrange's method of undetermined multipliers and the functional variational technique, as described in Ref. 32, we minimize the following functional with respect to the coefficients $\tilde{d}_{k\alpha\alpha}$:

$$L(k) = \sum_{\alpha} \sum_{\alpha} \left[ \tilde{d}_{k\alpha\alpha} F_{ab}(k) \tilde{d}_{ab} - \sum_{\beta} \epsilon_{k\alpha,\beta} \tilde{d}_{k\alpha\alpha} S_{ab}(k) \tilde{d}_{k\beta\beta} \frac{d}{2\pi} \delta_{\alpha\beta} \right],$$

where the $\epsilon_{k\alpha,\beta}$ are Lagrange multipliers. This gives us the following equation:

$$F_{ab}(k) \tilde{d}_{k\alpha\beta} = \sum_{\beta} S_{ab}(k) \tilde{d}_{k\beta\beta} \epsilon_{k\alpha,\beta}.$$

or, diagonalizing the $\epsilon$ matrix and defining $\tilde{e}_{k\alpha} \equiv \epsilon_{k\alpha,\alpha}$, we get an expression of similar form as the traditional Hartree-Fock equations:

$$F_{ab}(k) \tilde{d}_{k\alpha\beta} = S_{ab}(k) \tilde{d}_{k\alpha\alpha} \epsilon_{k\alpha}.$$

We can write this in matrix form as follows:

$$F(k)D(k) = S(k)D(k)E(k).$$

where the elements of the eigenvector matrix \( D(k) \) are \( D_{ba}(k) = \delta_{kab} \), and the diagonal elements of the eigenvalue matrix \( E(k) \) are \( E_{aa}(k) = \epsilon_k \) (and the off-diagonal elements are zero).

At this point, the traditional SCF (self-consistent field) procedure can be applied to this matrix equation.

V. SUMMARY AND DISCUSSION

In this paper, we have presented a method for evaluating the Hartree–Fock energy per unit cell for an infinite crystalline system. At all points in the formulation of the problem and the derivation of the result, all of the series that appear are either finite series or absolutely convergent infinite series. No conditionally convergent series appear. No truncations, which are commonly used in Hartree–Fock schemes, are employed. Moreover, this method provides a unified description of the Coulomb and exchange energies. All terms other than the long ranged part of the exchange terms are evaluated in real space. The long ranged part of the exchange terms is evaluated in Fourier space. As a result, the convergence of the exchange sums does not depend on the density matrix.

Our method compares favorably with other methods. As mentioned earlier, methods in which the Coulomb sums are truncated, such as that of Euwema et al.\(^{14}\) and that of Upton and Goddard,\(^{15}\) will be incorrect if the unit cell contains a net dipole moment. Harris’ Fourier representation method\(^6\) is similar to our method in that Ewald techniques are applied to both the Coulomb and exchange terms, but it has the disadvantage that it requires complicated Fourier techniques for the evaluation of all of the terms. In the method used in CRYSTAL,\(^6\) the electrostatic Coulomb terms are evaluated in a similar way as in our method, but the CRYSTAL method has the drawback that the exchange sums are truncated, they converge slowly (if at all), and their convergence depends on the density matrix. As discussed above, in our method the exchange sums are absolutely and rapidly convergent, and their convergence does not depend on the density matrix. Thus, we believe that our method will give the same results as CRYSTAL for the electrostatic Coulomb terms but will not give the same results as CRYSTAL for the exchange energy in some situations. (See Ref. 20 for a detailed comparison of our method and the truncation method used in CRYSTAL for evaluating the exchange energy.) Saunders et al.\(^{26}\) have presented methods for evaluating matrix elements of the Ewald potential. We have shown that our method is mathematically equivalent to evaluating matrix elements of the Ewald potential. Our method is likely to be computationally faster, however, because it involves the evaluation of the Ewald interaction only between point multipoles.

The periodic Hartree–Fock method presented in this paper can be applied to many different kinds of systems ranging from crystals to amorphous materials. Moreover, correlation can be included by applying this method to Møller–Plesset perturbation theory and coupled cluster theory. In addition to calculating the energy of static periodic systems, this method can also be applied to \textit{ab initio} dynamics simulations of materials.

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APPENDIX A

In this Appendix, we show that

\[
\nu_{\text{pcq}}(\mathbf{r}_1, \mathbf{r}_2) = \nu_{\text{ELH}}(\mathbf{r}_1, \mathbf{r}_2) - \nu_q(\mathbf{r}_1) - \nu_q(\mathbf{r}_2) + B(a, L) + O(a^{-1}),
\]

\( A1 \)

where

\[
\nu_q(r) = \frac{2\pi}{3L^3} |r|^2.
\]

Define

\[
\nu_{\text{pcq}}(\mathbf{r}_1, \mathbf{r}_2) = \nu_{\text{pcq}}(\mathbf{r}_1) + \nu_q(\mathbf{r}_1) + \nu_q(\mathbf{r}_2),
\]

\( A3 \)

which is defined only for \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \) in or near the central cell so that a sphere of radius \( n_{\text{max}}L \) centered at each coordinate lies completely in the conducting sphere of radius \( a \). It is straightforward to show that except for an error term of order \( a^{-2} \) or smaller, \( \nu_{\text{pcq}} \) is symmetric in its two arguments. It is also straightforward to show that

\[
u_{\text{pcq}}(\mathbf{r}_1 + \hat{\mathbf{m}}L, \mathbf{r}_2) = -\frac{4\pi}{3L^3} \left( \frac{L}{2}\hat{\mathbf{m}} \right) \cdot \hat{\mathbf{m}} + O(a^{-1})
\]

\( A4 \)

and

\[
\nu_q(\mathbf{r}_1 + \hat{\mathbf{m}}L) - \nu_q(\mathbf{r}_1) = -\frac{4\pi}{3L^3} \left( \frac{L}{2}\hat{\mathbf{m}} \right) \cdot \hat{\mathbf{m}},
\]

\( A5 \)

where \( \hat{\mathbf{m}} \) is a unit vector in either the positive or negative \( x, y, \) or \( z \) directions. Thus,

\[
u_{\text{pcq}}(\mathbf{r}_1 + \hat{\mathbf{m}}L, \mathbf{r}_2) - \nu_{\text{pcq}}(\mathbf{r}_1, \mathbf{r}_2) = O(a^{-1}).
\]

\( A6 \)

This same procedure can be applied to the second argument.

Now we calculate the Laplacian of \( \nu_{\text{pcq}} \) with regard to \( \mathbf{r}_1 \):

\[
\nabla^2 \nu_{\text{pcq}}(\mathbf{r}_1, \mathbf{r}_2)
\]

\[
= \nabla^2 \nu_{\text{pcq}}(\mathbf{r}_1, \mathbf{r}_2) + \nabla^2 \nu_q(\mathbf{r}_1)
\]

\[
= -4\pi \sum_{n \in \text{int}} \frac{\delta(r_1 - r_2 - nL) - \frac{1}{L^3}}{L^3}.
\]

\( A7 \)

The corresponding boundary condition is that

\[
u_{\text{pcq}}(a\hat{\mathbf{r}}, \mathbf{r}_2) = \nu_q(a\hat{\mathbf{r}}) + \nu_q(\mathbf{r}_2),
\]

\( A8 \)

for all \( \hat{\mathbf{r}} \) and all \( \mathbf{r}_2 \).

Recall that the differential equation satisfied by the Ewald potential is

\[
\nabla^2 \nu_{\text{EL}}(\mathbf{r}_1, \mathbf{r}_2) = -4\pi \sum_{n \neq 0} \frac{\delta(r_1 - r_2 - nL) - \frac{1}{L^3}}{L^3}.
\]

\( A9 \)
which is subject to periodic boundary conditions and to the condition that the average value of \( v_{el}(r_1, r_2) \) over one cell is zero.

Consider the difference
\[
\Delta v_d(r_1, r_2) = v_{per}(r_1, r_2) - v_{el}(r_1, r_2),
\]
which is again only defined for \( r_1 \) and \( r_2 \) in or near the central cell. Clearly,
\[
\nabla \Delta v_d(r_1, r_2) = 0
\]
exactly, i.e., with no error term. Using the result in Eq. (A6) and the fact that \( v_{per}(r_1, r_2) \) satisfies periodic boundary conditions exactly, the values of \( v_d(r_1, r_2) \) on the boundaries of the central cell deviate from satisfying periodic boundary conditions by an amount of order \( a^{-1} \).

Consider fixed \( r_2 \) in the interior or at the surface of the central cell and regard \( v_d \) as a function of \( r_1 \). The differential equation in the interior of the cell plus the values at the surface of the central cell determine \( v_d \) completely. We find that
\[
v_d(r_1, r_2) = (\text{constant independent of } r_1) + O(a^{-1}).
\]

Since \( v_d(r_1, r_2) \) is symmetric in its arguments at least to order \( a^{-1} \), the constant is independent of both \( r_1 \) and \( r_2 \) at least to order \( a^{-1} \), and if we call this constant \( B(a, L) \), we get
\[
v_d(r_1, r_2) = B(a, L) + O(a^{-1}).
\]
We can use Eqs. (A3), (A10), and (A13) to get
\[
v_{per}(r_1, r_2) = v_{el}(r_1, r_2) - v_{d}(r_1) - v_{d}(r_2) + B(a, L) + O(a^{-1}),
\]
and we can add the hole potential to both sides to get Eq. (A1), which is valid as written only for both arguments inside the central cell.

\section*{APPENDIX B}

In this Appendix, we list the general reasons that terms will be zero or \( O(a^{-1}) \) for the derivation of Eq. (52).

(1) Any term with a \( \Delta \) density and the \( v_{elh}(r_1, r_2) \) interaction is zero because the Ewald interaction satisfies periodic boundary conditions and because of the properties of a \( \Delta \) density.

(2) Any term with a \( \Delta \) or \( c \) density and the \( B(a, L) \) interaction is zero because \( \Delta \) and \( c \) distributions have no net zeroth moment.

(3) Any term with a \( v_{d}(r_1) \) interaction for a general density \( \rho[r_1] \), where the other density is either \( \rho^{[\Delta]}(r_2) \) or \( \rho^{[c]}(r_2) \), is zero since both \( \Delta \) and \( c \) distributions have no net zeroth moment.

(4) Any term with a \( c \) density and a \( v_{elh}(r_1, r_2) \) interaction is at most \( O(a^{-1}) \) because a \( c \) distribution has no charge or dipole moment.

\section*{APPENDIX C}

In this Appendix, we discuss the principles that are relevant for the derivation of the energy per unit cell of a crystal. For the kinetic energy and overlap matrix elements, we can either use simple coordinate transformations or express the inner product as an integral over a large number of cells divided by the number of cells and then let the number of cells approach infinity. The net result is that matrix elements can be expressed in terms of integrals over all space of overlaps of atomic basis functions. For the other matrix elements, the following symmetry properties can be used to derive the results quoted in Sec. IV.

\section*{APPENDIX D}

In this appendix, we derive the exchange terms in going from Eq. (83) to Eq. (84). The exchange energy in Eq. (83) is
\[
E_E = E_{E3} + E_{E2elh} + E_{E2pCH},
\]
where \( E_{E3} \) is the electron self-interaction term and the other contributions are labeled by the type of matrix element needed for their evaluation.

The electron self-interaction term can be written as
since \( N/Q^3 \), the number of electrons in a unit cell, is independent of \( L \) and \( v_{\text{el}}(0,0) \propto L^{-1} \).

To evaluate \( E_{\text{E2eLh}} \), we use the Fourier representation of the density matrix [Eq. (81)]:

\[
E_{\text{E2eLh}} = -\frac{1}{2} \sum_{abghcd(fgh,lc)\in U} P_{abgh} P_{chcd} (afch|2eLh|dbg) = -\frac{Q^3}{2} \sum_{a'bghcd(fgh,lc)\in U} \left( \frac{2\pi}{L} \right)^6 \sum_{k(\in B_1)} \sum_{q(\in B_1)} P_{ab}(k) P_{cd}(k+q) e^{i(k-g)L} d\frac{e^{i(k+q)(K-h)L}}{d}
\]

\[
\times \sum_{j,a(\in c_{h0})} \int dr_1 \int dr_2 \tilde{[\rho_{gh}]}_a(r_1) P_{a'bghcd}(r_2) w(r_1, r_2; q)
\]

\[
= E_{\text{E2eLhr}} + E_{\text{E2eLhf}} + E_{\text{E2eLlh}},
\]

where

\[
w(r_1, r_2; q) = \sum_{j(\in c_{h0})} e^{i\tilde{q}j} v_{el}(r_1 + jd, r_2),
\]

and the three terms come from the real space, constant, and Fourier space parts of \( w \), which are obtained by evaluating Eqs. (14) and (15) for \( \alpha' = Q\alpha' \):

\[
w(r_1, r_2; q) = w^{[r]}(r_1, r_2; q; \alpha') + w^{[c]}(r_1, r_2; q; \alpha') + w^{[f]}(r_1, r_2; q; \alpha'),
\]

where

\[
w^{[r]}(r_1, r_2; q; \alpha') = \sum_{m(\in U)} e^{i\tilde{q}m} \left( \frac{\text{erfc}(\alpha' | r_1 + m + r_2j/d)}{|r_1 + m + r_2j/d|} + v_h(r_1 + m + r_2j/d) \right).
\]

\[
w^{[c]}(r_1, r_2; q; \alpha') = -\frac{\pi}{\alpha' \sqrt{d}} \sum_{m(\in U)} \delta \left( q + \frac{2\pi m}{d} \right).
\]

\[
w^{[f]}(r_1, r_2; q; \alpha') = \sum_{m(\in U), qd(2\pi)} \frac{1}{wd} |m - qd/(2\pi)|^{-2} \exp(-\pi|m - qd/(2\pi)|^2/\alpha'^2)
\]

\[
\times \exp(2\pi i[m - qd/(2\pi)] \cdot (r_1 - r_2)/d).
\]

Note that \( w(r_1, r_2; q) \) is independent of the choice of \( \alpha' \), but the three parts in Eq. (D6) are not.

The real space part can be evaluated as follows.

\[
E_{\text{E2eLhr}} = -\frac{Q^3}{2} \sum_{a,b,c,d,ghcd(gh,lc)\in U} P_{a'0b} P_{chcd} \delta_{s_a} \delta_{s_d} \delta_{s_c} (a0d1| wr(\alpha') | chbg)[\rho],
\]

where

\[
(a0d1| wr(\alpha') | chbg)[\rho] = \int dr_1 \int dr_2 \tilde{[\rho]}_a(r_1) \tilde{[\rho]}_b(r_2) \left( \frac{\text{erfc}(\alpha' | r_1 - r_2j/d)}{|r_1 - r_2j/d|} + v_h(r_1, r_2) \right).
\]

The constant part can be expressed as

\[
E_{\text{E2eLhf}} = \frac{N\pi}{2d\alpha' \sqrt{Q^3} Q^6} = O(L^{-3}).
\]

In order to evaluate the Fourier space part, we use the following expression:

\[
w^{[f]}(r_1, r_2; q; \alpha') = w^{[f]}_0(r_1, r_2; q; \alpha') + w^{[f]}_1(r_1, r_2; q; \alpha') + w^{[f]}_2(r_1, r_2; q; \alpha') + w^{[f]}_3(r_1, r_2; q; \alpha'),
\]

where
\[
\omega^\alpha_{\beta}(r_1, r_2; q; \alpha') = \sum_{m \in U \neq 0} \frac{1}{\pi d} |m - q d/(2\pi)|^{-2} \exp(\pi |m - q d/(2\pi)|^{-1} (r_1 - r_2)/(d \pi) \exp(-\pi |m - q d/(2\pi)|^{-1/2} (r_1 - r_2)^2/\alpha' 2),
\]
\[
\omega_{00}^\alpha(r_1, r_2; q; \alpha') = (1 - \delta_{0,0}) \frac{1}{\pi d} |q d/(2\pi)|^{-2} \exp(-\pi |q d/(2\pi)|^{-1/2} (r_1 - r_2)^2/\alpha' 2),
\]
\[
\omega_{01}^\alpha(r_1, r_2; q; \alpha') = (1 - \delta_{0,0}) \frac{1}{\pi d} |q d/(2\pi)|^{-2} \exp(-\pi |q d/(2\pi)|^{-1/2} (r_1 - r_2)^2/\alpha' 2),
\]
\[
\omega_{02}^\alpha(r_1, r_2; q; \alpha') = (1 - \delta_{0,0}) \frac{1}{\pi d} |q d/(2\pi)|^{-2} \exp(-\pi |q d/(2\pi)|^{-1/2} (r_1 - r_2)^2/\alpha' 2). \]

(These formulas are correct for \( q \) in the first Brillouin zone.) The terms \( \omega_{01}^\alpha \) and \( \omega_{02}^\alpha \) have no net contribution, as can be shown using the orthonormality condition. Thus,
\[
E_{\text{Hartree-Fock}} = \frac{-Q^3}{2} \sum_{a,b,c,d \in \mathcal{U}} \left( \frac{2\pi}{L} \right)^6 \sum_{k \in \mathcal{B}} \sum_{q \in \mathcal{K}} p_{ab}(k)p_{cd}(k + q) \delta_{k - q, 0} \delta_{\sigma_a \sigma_d} \delta_{\sigma_c \sigma_b} \langle a0d|w_f(q; \alpha')|c0bg \rangle \langle \rho_{abg}(r_2) \rangle_{\sigma_a = \sigma_b} \ni \omega_{00}^\alpha(r_1, r_2; q; \alpha') + \omega_{01}^\alpha(r_1, r_2; q; \alpha') \rangle. \quad (D11)
\]

where
\[
\langle a0d|w_f(q; \alpha')|c0bg \rangle \langle \rho_{abg}(r_2) \rangle_{\sigma_a = \sigma_b} \ni \omega_{00}^\alpha(r_1, r_2; q; \alpha') + \omega_{01}^\alpha(r_1, r_2; q; \alpha') \rangle. \quad (D12)
\]

Note that \( E_{\text{Hartree-Fock}} \) contains no divergences.

The 2pc contribution to the exchange energy is
\[
E_{\text{exchange}} = -\frac{1}{2} \sum_{a,b,c,d \in \mathcal{U}} P_{abg} P_{cdh} \langle a \sigma c h \rho_{abg}(r_1) \rho_{cdh}(r_2) \rangle \langle b \sigma d g \rangle_{\sigma_a = \sigma_d} \ni \omega_{00}^\alpha(r_1, r_2; q; \alpha') + \omega_{01}^\alpha(r_1, r_2; q; \alpha') \rangle. \quad (D13)
\]

When we define the energy per unit cell as \( E_{\text{cell}} = E_{\text{Hartree-Fock}} + E_{\text{exchange}} \), the factors of \( Q^3 \) are canceled. In the limit of \( a \to \infty \), the correction term \( O(a^{-1}) \) vanishes. In the limit \( L \to \infty \), the correction term \( O(L^{-1}) \) vanishes, and the sums over wave vectors in \( E_{\text{Hartree-Fock}} \) become integrals over wave vectors, introducing a factor of \( (L/2\pi)^p \) that cancels the \( (2\pi/L)^p \).
electron the exclusion of a small volume near the nucleus makes an error that goes to zero as $\Delta \to 0^+$, because of the $r^2 \, dr$ factor in the integrand. A similar conclusion also applies to electron-electron interactions.


An alternative is to have just one site in each unit cell. Various ways of choosing the unit cell to which an overlap is assigned could be chosen. The results in this paper can easily be adapted for the case where $\rho_{dfq}$ is assigned to the site contained in the unit cell $f$.

31 Pisani et al. (Ref. 16) organize the charge density into shells, i.e., the various charge densities assigned to the same site are divided into different groups depending on the quantum number of the basis functions involved. In our formulation, this is equivalent to having more than one site at each atomic location.


33 The value of $\alpha$ does not need to be the same for different matrix elements. Moreover, the value of $\alpha'$ also need not be the same for different matrix elements, with the restriction that $wr$ and $wf$ matrix elements with identical indices must have the same value of $\alpha'$.

34 The potential $\nu_A$ appears in Eq. (84) in various ways: as part of $e_{ab}$ in the Ewald contributions to the Madelung energy, in certain Coulombic matrix elements of the Madelung and exchange energy [see Eqs. (88) and (91)], and in certain matrix elements in the real space part of the exchange energy [see Eq. (D8)]. An analysis of Eq. (84) shows that $\nu_A$ has a nonzero effect on the values of only a finite number of terms. It has a nonzero effect only for the interactions of nuclear charges and point multipole representations when both of the two charge distributions are in the central cell and both are at exactly the same point. Thus, without changing the value of $E_{ac}$ as given in Eq. (84), it could be reexpressed in a form in which $\nu_A$ does not appear in any term, but the limits on the sums are more complicated and/or the values of some terms in the sums depend on whether the point charges and point multipoles in the terms are at the same point or not.