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Treating periodic systems using embedding: Adams-Gilbert approach

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A direct-space electronic structure method for electronic structure calculations of periodic systems, based on highly localized (noncanonical) molecular orbitals (MOs) and the quantum cluster embedding, is suggested. The method utilizes a modified Adams-Gilbert approach that allows one to find self-consistently (for the given geometry) the system energy and the corresponding localized MOs which give the correct total electron density. The approach suggested here can also be considered as an exact derivation of embedded quantum cluster models. We illustrate this method on a Hartree-Fock calculation of a model periodic He system and the MgO crystal, and the results are compared with a conventional approach based on canonical Bloch-like orbitals as implemented in the CRYSTAL code. Our method, which scales linearly with the system size, can also be used to solve the Kohn-Sham equations of density-functional theory.

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I. INTRODUCTION

A quantum cluster embedding is a powerful computational tool in electronic structure theory of extended systems, such as points defects in the bulk of crystalline[1,2] or amorphous[3] systems, adsorption species on crystal surfaces and surface defects,[4–6] or large biological molecules.[7–10] The embedding methods originate from a model in which a single local perturbation in the direct space of the entire system (the quantum cluster) is considered in great detail using high-quality quantum-mechanical (QM) methods (the QM region), whereas a more approximate method [usually based on molecular mechanics (MM) force fields] is used to account for the rest of the system surrounding the cluster (the MM region).

The main problem in all embedding schemes is related to the correct representation of the cluster boundary. In most methods, especially when applied to ionic systems, the quantum cluster is surrounded by point charges of the MM region. In covalent systems, the bonds coming out of the cluster are usually terminated by pseudoatoms (see, e.g., Ref. 5), so-called link atoms[8,10,11] or pseudopotentials.[12,13] In another family of methods, the environment region surrounding the cluster is better represented by going beyond the simple mechanical models.[8,14,15]

The most natural partitioning of the entire system into the quantum cluster and the environment (and thus the resulting embedding scheme[1,16,17]) can be made using many-electron group function theory (see, e.g., Refs. 18 and 19) when the wave function of the whole system is represented as an antisymmetrized product of strongly orthogonal functions associated with the cluster and electronic groups of the environment surrounding it. Depending on the specific type of chemical bonding in the system, the groups outside the cluster could be atoms (ions), bonds, or molecules.[16,17,20,21] Note that this family of methods rely on wave functions of every group to be "strongly" orthogonal[18,19] to each other which results in their less localized character to accommodate this specific requirement, and thus leads to less computationally efficient schemes.

If one lifts the artificial orthogonality condition, the group functions start to overlap, which makes the calculation of necessary matrix elements highly nontrivial.[22–24] Although in this case a general formulation of the embedding method is still possible,[24] it is very complicated and has not yet been implemented in practice.

In this paper, we suggest a self-consistent method for nonorthogonal one-electron groups (which is equivalent to the one-electron or Hartree-Fock approximation) as the first logical step in this direction. We concentrate here on three-dimensional *periodic systems* as the localized MOs of the perfect bulk crystal are required anyway to represent the environment region in the embedding scheme based on group functions. We have shown previously[20,21,25] that by lifting the orthogonality condition, highly localized molecular orbitals (LMOs) may be obtained that can span the whole occupied Fock space, and thus are capable of representing correctly the system total electron density.[25]

Our method, which is similar in spirit to some existing one-electron methods,[26–28] is based on the partitioning of the entire periodic system into overlapping electronic groups (EGs) corresponding to atoms, ions, bonds, or molecules comprising the entire system. The LMOs are obtained self-consistently by solving Adams-Gilbert equations[29–32] separately for each group within the primitive unit cell. The LMOs obtained in this way should represent the true electronic density of the entire system via a combination of elementary densities associated with each group and are in practice constructed to have transparent chemical meaning, e.g., to represent ions in the case of ionic systems and covalent bonds in covalently bound systems. Note that our method scales linearly with the system size by construction, i.e., it is $O(N)$.

The plan of the paper is as follows. In Sec. II, the main ideas of our method are developed and explained together with the *ab initio* implementation of the method within the MOLCAS package.[33] In Sec. III, we first present a toy-model system which was designed to check the main computational features of our method and the code. Then, our results for a realistic ionic MgO crystal are discussed. Finally, brief conclusions about further possible developments of the method toward more complicated systems are given in Sec. IV.

II. METHOD

A. Adams-Gilbert method

We shall start by briefly reminding the reader of the main ideas of the Adams-Gilbert (AG) method.[29–32] Consider an arbitrary (not necessarily periodic) closed-shell system the energy $E=E[\rho]$ of which is a functional of the nondiagonal density (or density matrix), see, e.g., Refs. 25, 32, and 34:

$$\rho(\mathbf{r},\mathbf{r}') = 2\sum_{ij}^{occ} \psi_i(\mathbf{r})(\mathbf{S}^{-1})_{ij}\psi_j^*(\mathbf{r}'). \tag{1}$$

Here, $\psi_i(\mathbf{r})$ are the (spinless) system MOs which are in general not orthogonal to each other, with the nonsingular overlap matrix $\mathbf{S}=\|S_{ij}\|$, where $S_{ij}=\langle\psi_i|\psi_j\rangle$ is the corresponding overlap integral. The summation in Eq. (1) is performed only over MOs of the occupied subset and the factor of 2 accounts for the spin.

Varying the total energy $E[\rho]$ with respect to the MOs $\{\psi_i(\mathbf{r})\}$, one obtains the following general equations for them:

$$(\hat{F} - \hat{\rho}\hat{F}\hat{\rho})\psi_i(\mathbf{r}) = 0, \tag{2}$$

where $\hat{\rho}$ is the density operator defined via

$$\hat{\rho}\psi_i(\mathbf{r}) = \int \rho(\mathbf{r},\mathbf{r}')\psi_i(\mathbf{r}')d\mathbf{r}'.$$

Note that we have not imposed any conditions on the MOs (including normalization). In the case of the Hartree-Fock (HF) method, $\hat{F}$ is the HF operator, while it is the Kohn-Sham (KS) operator in density-functional theory.

Orbitals $\psi_i(\mathbf{r})$ are in general *noncanonical* and the matrix $\mathbf{S}$ is not the unity matrix. They should be distinguished from the *canonical* orbitals, $\{\varphi_i^c(\mathbf{r})\}$, which are eigenvectors of the operator $\hat{F}$, i.e.,

$$\hat{F}\varphi_i^c(\mathbf{r}) = \varepsilon_i\varphi_i^c(\mathbf{r}). \tag{3}$$

However, since the orbitals $\psi_i(\mathbf{r})$ are some linear combinations of the canonical ones, both sets are equivalent as they span the same occupied Fock space. In particular, both sets give the same electron density [Eq. (1)], although the density looks much simpler if written via canonical orbitals since in this case, the overlap matrix $\mathbf{S}^c=\mathbf{1}$.

Formally, Eq. (2) can be considered as an eigenproblem for the noncanonical orbitals $\psi_i(\mathbf{r})$. These equations are to be solved self-consistently as the operator $\hat{F}$ depends on the density [Eq. (1)] and thus on *all* of the orbitals. The fact that noncanonical MOs are the eigenvectors of the operator with zero eigenvalues means that any linear nonsingular transformation of the orbitals $\{\psi_i(\mathbf{r})\}$ is also a solution. This means that some additional conditions can be imposed on the orbitals to choose the best linear combinations. In particular, one can choose the transformed orbitals to be orthogonal and normalized, in which case the canonical orbitals result.

B. Self-consistent procedure for calculating localized MOs

We shall use the mentioned additional freedom in order to achieve high localization of the orbitals $\{\psi_i(\mathbf{r})\}$. To this end, we shall employ the notion of *localized regions* introduced earlier.[20,21] Briefly, the whole system is broken down into regions each containing one or more atoms that are next to each other. The regions can be chosen arbitrarily; however, in this work, the choice of the localization regions will be based on the type of the chemical bonding in the system, e.g., on atoms in the cases of atomic or ionic systems, on two adjacent atoms in the case of the covalent bonding, etc. A more complicated choice may be necessary in the cases of intermediate bonding. In the case of a periodic system to be considered presently, several different nonequivalent regions may be necessary to represent a crystal unit cell; the chosen "irreducible" regions can then be periodically translated to reproduce the whole infinite crystal. Note that there could be several localized orbitals associated with every such region forming an EG.[20,21] Thus, each region has an EG associated with it, and each EG may contain several doubly occupied localized orbitals. For instance, in the case of the Si crystal, one needs four localized regions associated with four bonds; each bond is represented by an EG containing a single doubly occupied localized orbital,[20] eight valence electrons in total in the primitive cell. In the case of the MgO crystal, the unit cell is represented by a single region containing nearest O and Mg atoms with an EG containing eight electrons distributed over four doubly occupied orbitals.

Consider a primitive unit cell containing several regions (or EGs) A, B, etc. To find the MOs localized in each of the regions, we define *localizing functionals* $\Omega_A[\{\psi_i, i\in A\}]$, $\Omega_B[\{\psi_i, i\in B\}]$, etc., for each of them.[20,21] Various examples of the localization functionals were given in Refs. 20 and 21 (see also references therein). In most cases, the localization functionals contain special *support functions* $\varphi_\lambda \in A$ geometrically located in the corresponding regions and work in such a way as to ensure maximum overlap of the MOs ψ_i with the support functions thus achieving their necessary localization.

If $\chi_\mu(\mathbf{r})$ are atomic orbitals (AOs) centered on atoms of the system, then their linear combinations

$$\psi_i^{(A)} = \sum_\mu c_{i\mu}\chi_\mu \tag{4}$$

will minimize (maximize) the functional Ω_A if the orbitals $\psi_i^{(A)}$ are eigenvectors of the problem $\hat{\Omega}_A\psi_i^{(A)}=\lambda_i\psi_i^{(A)}$. The localization operator $\hat{\Omega}_A$ is defined via the functional derivative, i.e., $\hat{\Omega}_A\psi_i^{(A)}(\mathbf{r})=\frac{\delta\Omega_A}{\delta\psi_i^{(A)}(\mathbf{r})}$. Then, the eigenvalues λ_i will give the indication of the orbital localization (e.g., if the functional Ω_A is minimized, then the lowest eigenfunctions correspond to the maximum localization of the functions $\psi_i^{(A)}$). Since the orbitals $\psi_i^{(A)}$ are eigenvectors of the same operator $\hat{\Omega}_A$, they form an orthonormal set. For definiteness, we shall assume in the following that the maximum localization is achieved in the *minimum* of the functional Ω_A.

In order for the localized orbitals [Eq. (4)] to belong to the Fock space, they should at the same time satisfy the AG equations [Eq. (2)]. This can be achieved by solving the *combined* problem:[31,32]

$$[\hat{F} + \hat{\rho}(\hat{\Omega}_A - \hat{F})\hat{\rho}]\psi_i^{(A)}(\mathbf{r}) = \lambda_i^{(A)}\psi_i^{(A)}(\mathbf{r}). \tag{5}$$

The orbitals satisfying these equations belong to the occupied Fock space and, at the same time, minimize the localization functional Ω_A. This means that they are localized in region A, as indicated by the superscript to the orbitals.

It is important to realize that the orbitals $\{\psi_i^{(A)}\}$ obtained as described above span the *entire*, occupied Fock space, are *orthonormal* and thus can be obtained from the canonical set via some unitary transformation. In practice, only several first (with the smallest eigenvalues $\lambda_i^{(A)}$) of these orbitals will be strongly localized in A. If the localizing functional Ω_A is chosen well using chemical intuition, then the right number of localized functions strongly localized in A can always be chosen.[20,21] We keep these functions and discard the rest.

In order to find orbitals localized in region B, we solve the combined AG problem like in Eq. (5), in which the localization operator $\hat{\Omega}_A$ is replaced with $\hat{\Omega}_B$. In this way, another completely equivalent set of orthonormal orbitals, $\{\psi_i^{(B)}\}$, is obtained, from which we again keep only the necessary number of the first eigenfunctions which are mostly localized in region B. The rest of the functions is discarded. This procedure is repeated for each region within the primitive unit cell. This way, a finite set of MOs, $\{\psi_i^{(A)}(\mathbf{r}), i\in A\}$, $\{\psi_i^{(B)}(\mathbf{r}), i\in B\}$, etc., localized in regions A, B, etc., of the primitive cell are obtained. This concept of representing the Fock space via localized functions is analogous to choosing the Wannier functions instead of the Bloch ones;[34] the difference with our case is that the Wannier functions are orthogonal while the localized MOs here are not if they belong to different groups (regions).

Of course, the localized MOs discussed so far will not span the whole occupied Fock space as they belong to the central unit cell only. The whole set of the localized functions that do span the entire occupied part of the Fock space is obtained by accepting the images of these functions in every unit cell of the periodic system, i.e., by adding translated functions $\{\psi_i^{(A)}(\mathbf{r}-\mathbf{L}), i\in A\}$, $\{\psi_i^{(B)}(\mathbf{r}-\mathbf{L}), i\in B\}$, etc., where $\mathbf{L}$ is a translation vector. Therefore, due to translational symmetry of the periodic system, the complete (occupied) Fock space can be constructed using a finite number of localized functions from the central unit cell. All other functions can be obtained by applying lattice translations.

This brings us to another important point of our method which is *self-consistency*. The procedure described above would be impractical computationally, if the Fock operator $\hat{F}$ depended on orbitals in a rather complicated way because in this case, we would have to make a full self-consistent-field (SCF) calculation for every combined AG problem using in each case *all* orbitals. Fortunately, both in the HF and the KS cases, $\hat{F}$ depends on the orbitals only via the *electron density* [Eq. (1)] which allows running a single SCF problem for all localized orbitals inside the central cell at the same time. Indeed, the (nondiagonal) electron density can be written entirely via the localized functions of the *central cell* as follows:

$$\rho(\mathbf{r},\mathbf{r}') = 2\sum_{\mathbf{L}Ai}\sum_{\mathbf{L}'A'i'}\psi_i^{(A)}(\mathbf{r}-\mathbf{L})\mathbf{G}_{Ai,A'i'}^{\mathbf{L}-\mathbf{L}'}\psi_{i'}^{(A')}(\mathbf{r}'-\mathbf{L}'), \tag{6}$$

where the first sum runs over all cells $\mathbf{L}$, regions $A\in\mathbf{L}$ inside them and the localized MOs $i\in A$ associated with each region (similarly for the second sum). The quantity $\mathbf{G}_{Ai,A'i'}^{\mathbf{L}-\mathbf{L}'} = (\mathbf{S}^{-1})_{Ai,A'i'}^{\mathbf{L}-\mathbf{L}'}$ is the element of the inverse of the overlap matrix

$$S_{Ai,A'i'}^{\mathbf{L}\mathbf{L}'} = \langle\psi_i^{(A)}(\mathbf{r}-\mathbf{L})|\psi_{i'}^{(A')}(\mathbf{r}-\mathbf{L}')\rangle \equiv S_{Ai,A'i'}^{\mathbf{L}-\mathbf{L}'}$$

that depends only on the difference of the lattice vectors $\mathbf{L}-\mathbf{L}'$ due to periodic symmetry. The inverse of the overlap matrix can be calculated exactly by going into the reciprocal space[25] as follows:

$$\mathbf{G}_{Ai,A'i'}^{\mathbf{L}-\mathbf{L}'} = \frac{1}{N}\sum_{\mathbf{k}}[\mathbf{S}^{-1}(\mathbf{k})]_{Ai,A'i'}e^{-i\mathbf{k}(\mathbf{L}-\mathbf{L}')}, \tag{7}$$

where $\mathbf{S}^{-1}(\mathbf{k})$ is the inverse of the overlap matrix $\mathbf{S}(\mathbf{k}) = \|S_{Ai,A'i'}(\mathbf{k})\|$ at the point $\mathbf{k}$ of the Brillouin zone, and

$$S_{Ai,A'i'}(\mathbf{k}) = \sum_{\mathbf{L}} S_{Ai,A'i'}^{-\mathbf{L}}e^{i\mathbf{k}\mathbf{L}} \tag{8}$$

can be calculated as a simple lattice sum of overlap integrals between the orbitals in the central and surrounding cells. This summation can be quite limited if the orbitals are well localized in their regions due to exponential decay of the overlap integrals with distance. Note that the size of the square matrix $\mathbf{S}(\mathbf{k})$ is equal to the total number of localized orbitals within the unit cell.

Finally, the per-cell total energy of the periodic system within the HF approximation can be written in the following way:

$$E = \sum_{Ai}\sum_{\mathbf{L}'A'i'}\mathbf{G}_{Ai,A'i'}^{-\mathbf{L}'}(\tilde{h}_{Ai,A'i'}^{0\mathbf{L}'} + F_{Ai,A'i'}^{0\mathbf{L}'}) + \frac{1}{2}\sum_n Z_n V_n^{Mad}, \tag{9}$$

where $\tilde{h}_{Ai,A'i'}^{0\mathbf{L}'}$ is the matrix element of the one-electron part of the Hamiltonian in which atomic pseudopotentials have been stripped off their long-range parts (indicated by tilde). The latter are included separately in the last (Madelung) term together with the nuclei-nuclei interaction. This rearrangement of terms has been done to avoid divergence of the Coulomb interaction. Finally, $F_{Ai,A'i'}^{0\mathbf{L}'}$ is the matrix element of the Fock operator for the entire system which depends on the total electron density matrix $\rho(\mathbf{r},\mathbf{r}')$.

The summation in the last term in Eq. (9) is run over all nuclei n (atomic cores) of charge Z_n in the central unit cell and $V_n^{Mad}=V^{Mad}(\mathbf{R}_n)$ is the exact Madelung potential from the whole system calculated at the position $\mathbf{R}_n$ of the nucleus n as follows:

$$V^{Mad}(\mathbf{R}_n) = {\sum_{\mathbf{L}'n'}}' \frac{Z_{n'}}{|\mathbf{R}_n-\mathbf{L}'-\mathbf{R}_{n'}|} - \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{R}_n-\mathbf{r}'|}, \qquad (10)$$

where the first sum accounts for the electrostatic potential due to all nuclei of the system with the prime indicating that the self-interaction is to be avoided ($n'\neq n$ when $\mathbf{L}'=0$), and the second term provides a similar contribution from the electronic charge; $\rho(\mathbf{r})=\rho(\mathbf{r},\mathbf{r})$ is the diagonal element of the density matrix $\rho(\mathbf{r},\mathbf{r}')$. Note that the latter term in Eq. (10) is represented entirely via LMOs because of Eq. (6).

Note that a similar expression can be obtained in the KS case as well. In either case, it is important to see that the total energy (per cell) can also be expressed entirely via the LMOs.

Thus, for our method to work, we do not actually need the discarded parts of the orbitals from each combined AG problem; only those orbitals which are actually kept in each case are directly utilized.

C. Practical implementation

From the technical point of view, AG equations [Eq. (5)] are quite complicated. When written in the matrix form with respect to the AOs, see Eq. (4), they contain products of various matrix elements of $\hat{F}$ and $\hat{\rho}$ summed over the lattice. These summations, however, can be terminated very quickly due to the localization character of the LMOs and, consequently, fast decay of the matrix elements.

Although our method can be used in both the HF and KS methods, in this paper, we shall describe its implementation in the HF case only. Then, the Fock operator $\hat{F}$ contains the Coulomb and exchange parts. The exchange part is short ranged and requires lattice summations to be performed only within a limited region around the central cell. The situation with the Coulomb part is more complex as it contains matrix elements of the long-ranged Madelung potential $V^{Mad}(\mathbf{r})$, Eq. (10).

In order to deal with this term, we notice that the electron density of Eq. (6) can also be written as a lattice sum:

$$\rho(\mathbf{r},\mathbf{r}') = \sum_{\mathbf{L}} \bar{\rho}(\mathbf{r}-\mathbf{L},\mathbf{r}'-\mathbf{L}), \qquad (11)$$

$$\bar{\rho}(\mathbf{r},\mathbf{r}') = 2\sum_{Ai}\sum_{(\mathbf{L}'A'i')} \psi_i^{(A)}(\mathbf{r})\mathbf{G}_{Ai,A'i'}^{-\mathbf{L}'}\psi_{i'}^{(A')}(\mathbf{r}'-\mathbf{L}'). \qquad (12)$$

Because of the localized character of the LMOs, the lattice summation $\mathbf{L}'$ in the expression for $\bar{\rho}(\mathbf{r},\mathbf{r}')$ may actually be limited to the cells nearest to the central cell associated with the zero lattice vector (indicated by round brackets under the sum), and hence $\bar{\rho}(\mathbf{r},\mathbf{r}')$ will be localized well around this cell. Consequently, $\bar{\rho}(\mathbf{r}-\mathbf{L},\mathbf{r}'-\mathbf{L})$ is well localized around the unit cell $\mathbf{L}$. Therefore, $\bar{\rho}(\mathbf{r},\mathbf{r}')$ can be interpreted as the zero unit-cell density matrix, and $\bar{\rho}(\mathbf{r}-\mathbf{L},\mathbf{r}'-\mathbf{L})$ as the $\mathbf{L}$ unit-cell density matrices. Then, the electronic contribution to the Madelung potential [the second term in Eq. (10)] can be represented as a lattice sum of contributions associated with different unit cells of the crystal. Since when calculating the matrix elements $F_{Ai,A'i'}^{0\mathbf{L}'}=\langle\psi_i^{(A)}(\mathbf{r})|\hat{F}|\psi_{i'}^{(A')}(\mathbf{r}-\mathbf{L}')\rangle$ of the Fock operator between LMOs of the zero and $\mathbf{L}'$ cells, one is interested in the Madelung potential within a small region surrounding the central (zero) cell only, the contribution from the remote cells can be represented by *point charges*. This is combined with the corresponding contribution of the nuclei of the remote cells [arising from the first term in Eq. (10)] to produce a point-charge Madelung potential associated with the remote region of the crystal, as explained in more detail below. The point charges can be calculated from the LMOs since they are sufficient to represent the density adequately. In this study, we obtained charges from the Mulliken analysis during the SCF procedure.

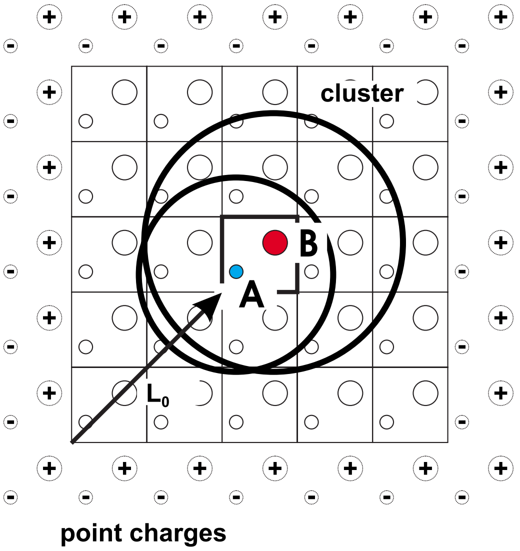

FIG. 1. (Color online) Schematic representation of the periodic system from the "point of view" of the central cell (indicated). It is assumed in this schematics that the unit cell contains two electronic groups A and B. The quantum cluster containing a finite number of primitive unit cells (indicated) is surrounded by point charges.

Therefore, in the actual implementation of the method, we consider a *quantum cluster* containing a finite number of complete primitive cells with the central cell in the middle of it, see Fig. 1. The cluster is used to account for the detailed distribution of the electron density. The cluster is surrounded by a finite number of point charges that reproduce correctly the Madelung field inside the cluster due to the outside region. In the present implementation of the method, the inverse of the overlap matrix, $\mathbf{G}_{Ai,A'i'}^{-\mathbf{L}'}$, is calculated not via the $\mathbf{k}$-point method (which is exact) as outlined in the previous section, but rather approximately as the inverse of the finite overlap matrix calculated on the LMOs within the quantum cluster region. This approximation may affect the convergence of calculated LMOs and the total energies with the size of the quantum clusters.

Our implementation is similar in spirit to commonly used cluster models. However, there are major differences: (i) the total electron density we use in the Fock and density operators, $\hat{F}$ and $\hat{\rho}$, corresponds to the whole infinite system, not to the cluster; (ii) a more complicated AG operator $\hat{F}+\hat{\rho}(\hat{\Omega}_A-\hat{F}_A)\hat{\rho}$ is used instead of the Fock operator $\hat{F}$ that is employed in any of the common cluster methods; (iii) as a result, the MOs found in our method correspond to noncanonical solutions for the whole *infinite system*; (iv) finally, the orbitals overlap with each other, while in the commonly used cluster methods, the orbitals are canonical and form an orthonormal set.

Thus, the whole procedure can be summarized in the following scheme:

(1) Choose several localized regions (groups) A, B, etc., that adequately represent the unit cell of the periodic system; an even number of electrons, $2n_A$, $2n_B$, etc., should be associated with each EG on the basis of *chemical intuition*.

(2) Choose localizing operators $\hat{\Omega}_A$, $\hat{\Omega}_B$, etc., for each region that allow for the efficient localization of the MOs; in practice, this also means that one has to choose the support AO (or AOs) within each region with which the maximum "overlap" (in the sense of the particular localizing operator) of the LMOs is sought during the localization.

(3) As the initial guess, select some localized functions for each region: n_A functions $\psi_i^{(A)}$ belonging to region A (where $i=1,\ldots,n_A$), n_B functions $\psi_i^{(B)}$ belonging to region B (with $i=1,\ldots,n_B$), etc.

(4) Choose the point charges associated with each unit cell (e.g., Mulliken charges of the HF problem for the central cell); the LMOs and the point charges obtained in this way serve as the initial approximation to the whole problem.

(5) Once the LMOs in the central cell are known, they can be used as "bricks" to build up the whole system; hence, the total electron density can be constructed according to Eqs. (6)–(8).

(6) A quantum cluster containing an integer number of complete unit cells is considered which is surrounded by the point charges.

(7) Start the *AG iterations* keeping the same charges; these electronic iterations consist of the following steps:

(a) Using the LMOs and the point charges, calculate the necessary matrix elements of the Fock and density operators $\hat{F}$ and $\hat{\rho}$; these include matrix elements between LMOs within the central cell, as well as the ones between the central cell and the surrounding cells of the quantum cluster.

(b) Solve the combined eigenproblem for region A; pick up the first n_A solutions and ignore the rest.

(c) Repeat the last step for all regions (EGs) comprising the unit cell, one after another.

(d) Check consistency (e.g., compare the current total energy and the Mulliken charges with those calculated on the previous iteration).

(e) If necessary, repeat the cycle by going back to step 7a; otherwise, go out of the AG loop to step 8 with converged LMOs for each region.

(8) Recalculate the Mulliken charges and construct a new set of point charges around the quantum cluster.

(9) Go back to step 7; stop if the convergence with respect to the charges (i.e., within the "charge iterations") is reached; note that the outer iteration procedure with respect to the point charges of steps 7–9 is to be distinguished from the electronic AG iterations performed during step 7.

Thus, the procedure is iterative and consists of the outer loop (steps 7–9) with respect to the point charges and the inner loop (steps 7a–7e) with respect to the LMOs; it is performed until convergence is achieved. For systems with neutral atoms, the outer loop may be omitted.

The total energy (per cell) of Eq. (9) can be modified to account for the partition of the system into the cluster and the outside regions. Indeed, firstly, the $\mathbf{L}'$ lattice summation in the first term of the energy [Eq. (9)] can be limited to the cluster cells only similarly to the density in Eq. (12). Secondly, the matrix element $\tilde{h}^{0\mathbf{L}'}_{Ai,A'i'}$ contains the sum over short-range parts of the pseudopotentials of all atoms in the system. Due to the localized character of the LMOs and the pseudopotentials, this sum can be limited to atoms within the cluster only. Next, we add to the one-electron matrix elements $\tilde{h}^{0\mathbf{L}'}_{Ai,A'i'}$ in the energy the long-range parts of the pseudopotentials for all cluster atoms; at the same time, the Coulomb potential $V_{out}(\mathbf{r})$ of all point charges representing the outside region is also added. This results in modification of the one-electron matrix elements $\tilde{h}^{0\mathbf{L}'}_{Ai,A'i'}\to H^{0\mathbf{L}'}_{Ai,A'i'}$. To compensate for the added terms, we subtract them from the energy which results in two additional terms in it: (i) $E^{(1)}_{add}$ due to point charges inside the cluster (atomic cores) and (ii) $E^{(2)}_{add}$ due to the point charges outside the cluster (atomic charges). Using the exact representation of the unit-cell electron density of Eq. (12), these extra terms can actually be written via point charges, and this is consistent with the cluster approximation we adopted here. We shall demonstrate this point by considering the second extra term, arising due to the field $V_{out}(\mathbf{r})$:

$$E^{(2)}_{out}=\sum_{Ai}\sum_{(\mathbf{L}'A'i')}\mathbf{G}^{-\mathbf{L}'}_{Ai,A'i'}\langle\psi_i^{(A)}(\mathbf{r})|V_{out}(\mathbf{r})|\psi_{i'}^{(A')}(\mathbf{r}-\mathbf{L}')\rangle$$

$$=\frac{1}{2}\int V_{out}(\mathbf{r})\bar{\rho}(\mathbf{r})d\mathbf{r},$$

where $\bar{\rho}(\mathbf{r})\equiv\bar{\rho}(\mathbf{r},\mathbf{r})$ and we have made use of Eq. (12) for the cell density matrix. This energy contribution can then be written explicitly via the summation over all cells (and charges inside them) which are located in the outside region (indicated by the square brackets under the sum):

$$E^{(2)}_{out}\simeq\frac{1}{2}\int\left(\sum_{[\mathbf{L}n]}\frac{q_n}{|\mathbf{r}-\mathbf{L}-\mathbf{R}_n|}\right)\bar{\rho}(\mathbf{r})d\mathbf{r}$$

$$=\frac{1}{2}\sum_n q_n\left(\sum_{[\mathbf{L}']}\int\frac{\bar{\rho}(\mathbf{r}-\mathbf{L}')}{|\mathbf{r}-\mathbf{R}_n|}d\mathbf{r}\right).$$

The last expression can be interpreted as the energy of point charges q_n in the central cell placed in the Coulomb potential due to the electron distribution in the outside region. Thus, the potential due to the outside electron charge should be replaced (consistently with our cluster model) with "electronic" point charges P_n on atoms in every cell (for each atom n, we have the total charge as $q_n = Z_n - P_n$), which results in the following point-charge representation of this contribution to the energy:

$$\begin{aligned} E^{(2)}_{out} &= \frac{1}{2}\sum_n q_n \sum_{[\mathbf{L}'n']} \frac{P_{n'}}{|\mathbf{R}_n - \mathbf{L}' - \mathbf{R}_{n'}|} \\ &= \frac{1}{2}\sum_{n'} P_{n'} \sum_{[\mathbf{L}n]} \frac{q_n}{|\mathbf{R}_n + \mathbf{L} - \mathbf{R}_{n'}|} \\ &= \frac{1}{2}\sum_n P_n V_{out}(\mathbf{R}_n). \end{aligned}$$

The other contribution, $E^{(1)}_{out}$, can be worked out along similar lines. Finally, we get the following expression for the energy per unit cell:

$$\begin{aligned} E = \sum_{Ai} \sum_{(\mathbf{L}'A'i')} \mathbf{G}^{-\mathbf{L}'}_{Ai,A'i'} [H^{0\mathbf{L}'}_{Ai,A'i'} + F^{0\mathbf{L}'}_{Ai,A'i'}] + E^{QC}_{nn} \\ + \frac{1}{2}\sum_n (Z_n + P_n) V_{out}(\mathbf{R}_n), \end{aligned} \tag{13}$$

where E^{QC}_{nn} is the interaction energy between nuclei within the cluster (per cell). The first and the second terms in the energy, if multiplied by the number of cells in the cluster, coincide with the total energy of the cluster placed in an external field of point charges, the quantity that is calculated routinely by any quantum chemistry code. The last term in the energy is a necessary correction which takes account of the long-range Coulomb interactions across the infinite periodic system.

Using the MOLCAS package[33] as the development platform, we have written a general-purpose *ab initio* computer code that realizes the scheme drawn above. The code uses localized basis set, periodic boundary conditions, and the pseudopotential method to take account of the core electrons. Several localization methods[20] have been implemented. At present, the code works only within the HF method treating exchange explicitly. However, the corresponding implementation for the KS scheme is straightforward. The code utilizes the translational symmetry across the quantum cluster.

Two particular localization methods have been used in our calculations, which will be described in the next section: (i) the Magnasco-Perico method that maximizes Mulliken's[35] net atomic population produced by the LMOs in the selected region[20,36,37] and (ii) the Adams method,[20,30] in which the localization operator $\hat{\Omega}_A$ coincides with the Fock operator of region A. In practice, both methods give very similar LMOs and the same total electron density, so that we shall not show any detailed comparison of them.

III. RESULTS

A. He "crystal:" A toy model

In order to check the main computational aspects of our method and efficiency of the code, we have first considered an artificial "toy" model which contains He atoms in a simple cubic lattice (i.e., a single atom in the cell) with lattice constants of 1.0, 1.5, and 2.0 Å. We have used a standard 3-21G basis set from Ref. 38 which consists of two s AOs (with the effective radius of 1.3 Å) on every atom.

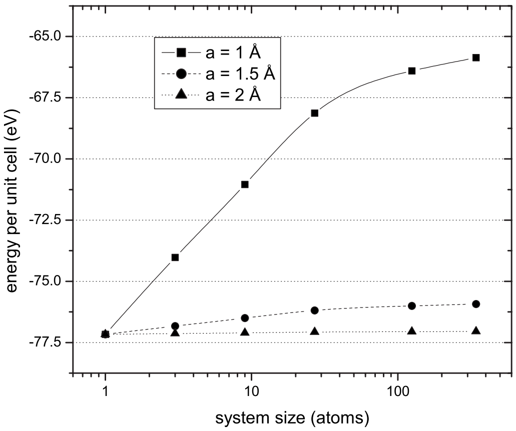

FIG. 2. Total energy (per cell) of the model simple cubic lattice He crystal with the He-He nearest neighbor distance $a=1.0$, 1.5, and 2.0 Å (squares, circles, and triangles, respectively), calculated as a function of the number of atoms in the quantum clusters used, the sizes of which start from a single atom and go up to 343 atoms.

Each He atom is considered as a group with one doubly occupied LMO whose localization is controlled by the second s AO centered on the atom; hence, the AO serves as the support function for the localization functional. For the lattice constants of 1.0 and 1.5 Å, we expect a considerable overlap between neighboring AOs, so that one would expect that the central cell LMO should have noticeable contributions on neighboring atoms. The simplicity of the system allows us to perform calculations on large clusters comprising hundreds of primitive cells (=He atoms), so that convergence of the calculations with respect to the actual spread of the LMO can be tested. Due to the neutral nature of this system, in these calculations, we did not add point charges to represent the rest of the system outside the quantum cluster. The second s orbital of the central He atom was taken as the initial approximation for the LMO in the SCF procedure.

We find that either of the localization operators gives practically identical results for the LMO orbital in each case. To check the convergence of our calculations with respect to the direct space available to the LMO (the cluster size), we performed calculations on several quantum clusters $N \times M \times L$ containing N, M, and L unit cells in the three perpendicular directions. In particular, these included quantum clusters $3 \times 3 \times 3$ (27 atoms), $5 \times 5 \times 5$ (125 atoms), and $7 \times 7 \times 7$ (343 atoms).

The energy (per cell) for different clusters and all three values of the lattice parameter a are shown in Fig. 2. One can see that in the cases of $a=1.5$ and 2.0 Å, a very good convergence with the cluster size is observed (−75.9 and 77.0 eV, respectively). Moreover, the calculated per-cell total energies agree extremely well with the energies of −76.0 and −77.0 eV for these systems obtained using the periodic CRYSTAL (Ref. 39) calculations which employed exactly the same basis set. The CRYSTAL code employs periodic boundary conditions and Bloch-like combinations of AOs (i.e., the canonical set of MOs), and thus can be used as an independent reference to validate our method.

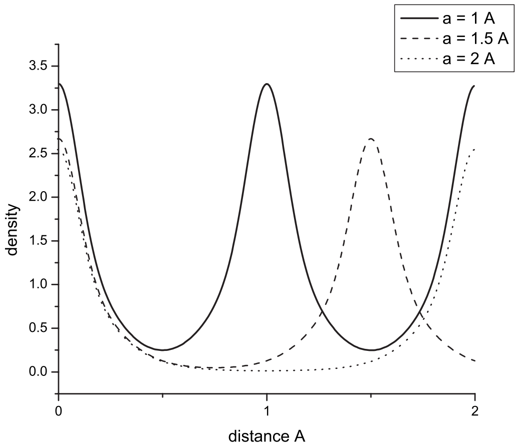

FIG. 3. Calculated total electron density along the [100] direction for the model simple cubic lattice He crystal with the He-He nearest neighbor distance $a=1.0$, 1.5, and 2.0 Å.

One can also see from Fig. 2 that calculations with our AG method for the lattice parameter of $a=1.0$ Å display a much slower convergence. In this case, He atoms are positioned much closer to each other (this situation corresponds to the crystal under compression). Our CRYSTAL calculations become unstable indicating a much more diffusive character of the crystalline orbitals. In this case calculations using our method also demonstrate much slower convergence with the cluster size.

Total electron densities along the [100] direction around the central atom for the largest quantum cluster and the three values of the lattice parameter considered here are shown in Fig. 3. One can see a strong peak on the crystal atoms with some noticeable density also between atoms in the cases of $a=1.0$ and 1.5 Å.

In addition, following the main ideas of our previous work,[20,21] we also considered a fairly large isolated cluster ($5\times5\times5$, containing 125 atoms) and calculated its total electron density using the standard HF method based on Eq. (3). The electron density in the central region of the isolated cluster can be directly compared to the total density of the infinite periodic system obtained using the AG method, as described above. The comparison (not shown) demonstrates an excellent agreement already for the AG density obtained using the $5\times5\times5$ cluster.

As we know, the total density is composed of the LMOs. Generally, we observe that the LMO decays very fast with the distance from the central atom, demonstrating excellent localization (not shown): it has a strong peak on the atom it is centered on, but there are also some appreciable contributions on the neighboring atoms of the first and the second sphere. As the size of the cluster is increased, the LMO becomes slightly more diffuse. Nevertheless, we find that in all cases the orbital remains very well localized around the central atom. Moreover, the orbital obtained using the smallest cluster can in fact serve as a very good approximation to the more correct orbital obtained employing the largest cluster.

The number of the AG iterations needed to reach SCF convergence is a good criterion for assessing the efficiency of our method. Just a single iteration is required in the case of the smallest cluster consisting of only a single He atom. However, the number of iterations was found to increase for bigger clusters although we did observe some stabilization of the required number of AG iterations after some specific cluster sizes (depending on the value of a) were reached. This is an encouraging result: the electronic convergence of the AG problem, which is much more complicated than the corresponding canonical problem, is not greatly influenced by the size of the quantum clusters used. The convergence has also been found to improve as the value of a is increased.

B. MgO crystal

MgO is an ionic crystal with the face-centered-cubic lattice and distance between Mg and O atoms of 2.122 Å.[40] Since the valence electron density is mostly localized around O atoms, we consider a pair of nearest Mg and O atoms (comprising a single unit cell) as a group.[20] AOs centered on the O atom within the group are used as the support functions in the localization operators to control localization of the LMOs. We used the pseudopotentials and a (slightly reduced) basis set proposed in Ref. 41: for O atoms, the basis set consists of two s and two sets of p orbitals (with the effective radius of about 3 Å), while for Mg atoms, only two s AOs are included. Altogether, there are ten AOs in every unit cell, containing eight valence electrons. It is expected that these valence electrons are localized on the O atom, thus forming four doubly occupied LMOs in every unit cell, all localized on oxygens.

In comparison with the previous toy model, in this case, it is necessary to take account of the point charges outside the quantum cluster to represent the rest of the system when calculating the Coulomb part of the Fock operator. In the present calculations, we used nearly 27 000 point charges which surrounded the quantum cluster. The set of charges was constructed out of complete cubes of eight charges to make sure that the total dipole moment is zero[3] (see also Fig. 1).

Seven quantum clusters $N\times M\times L$, containing N, M, and L unit cells along the three basic lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ of the face-centered-cubic lattice, were considered: $1\times1\times1$ (2 atoms), $1\times1\times3$ (6 atoms), $1\times3\times3$ (18 atoms), $3\times3\times3$ (54 atoms), $3\times3\times5$ (90 atoms), $3\times5\times5$ (150 atoms), and, finally, the biggest cluster, $5\times5\times5$, containing 250 atoms.

The partial density,

$$\rho_A(\mathbf{r}) = 2\sum_{j=1}^{4} [\psi_j^A(\mathbf{r})]^2, \tag{14}$$

associated with the four LMOs corresponding to the central cell, is shown in Fig. 4 for the three (out of four) biggest clusters. Similarly to the previous result for the He crystal, the density is mostly localized on the central O atom; however, it also has small bumps at the positions of the nearest O atoms. Although for all three clusters the partial densities are qualitatively similar, there are some small differences in details. Remarkably, the contribution of the second sphere O orbitals to the LMOs is very small, as expected for this highly ionic system.

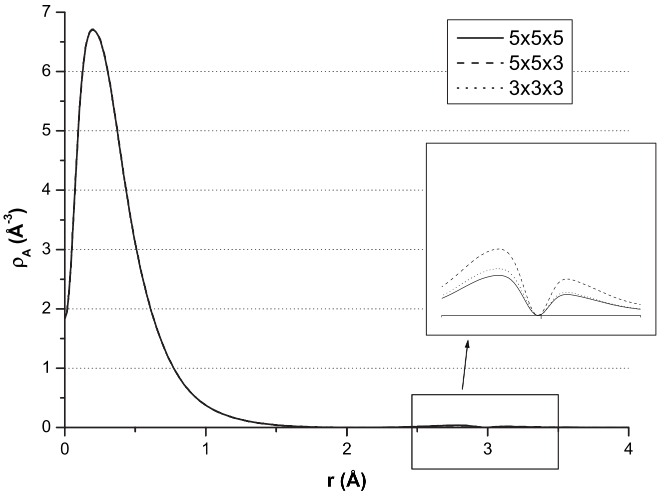

FIG. 4. The partial electron densities of Eq. (14), corresponding to the four LMOs of the central cell of the MgO crystal, shown along the [110] direction for the three quantum clusters $3\times3\times3$, $5\times5\times3$, and $5\times5\times5$. Inset: details of the densities around the O atom in the second sphere.

Our calculations clearly demonstrate the importance of recalculating the point charges around the cluster region during the SCF procedure of the AG problem. During the very first iteration, the $\pm 2e$ point charges were used. Then, during the course of the SCF procedure, the charges very quickly converge to their final values, which appear to depend on the cluster dimension and size. The calculated atomic charges for clusters of different sizes are shown in Fig. 5. One can see that the atomic charge has converged for the four biggest clusters considered here ($3\times3\times3$, $3\times3\times5$, $5\times5\times3$, and $5\times5\times5$) and reached the value of $\pm 1.85e$. The importance of having quantum clusters with the central cell surrounded by at least one sphere of other cells in all three directions is clearly recognized from these results. Note that the atomic charge cannot be defined uniquely. However, the obtained charge falls within the values obtained by other methods (see, e.g., Ref. 42).

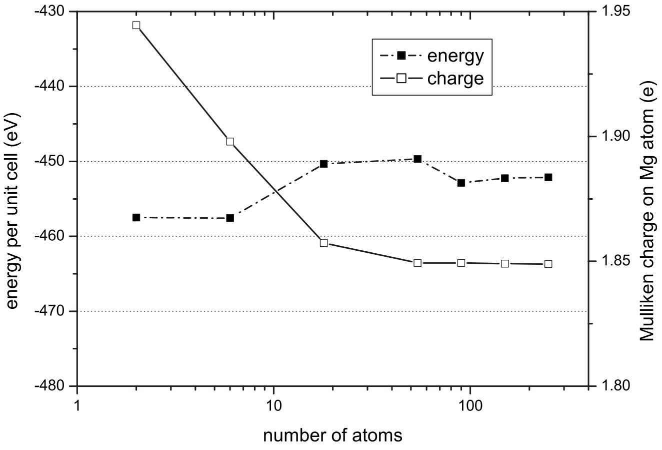

FIG. 5. Energy (per cell) of the periodic MgO crystal (left vertical axis) and the absolute value of the Mulliken charges on Mg and O atoms (right axis) for different quantum clusters used in our AG calculations (indicated). The size of the system starts from a single cell (2 atoms) and goes up to 250 atoms (the $5\times5\times5$ cluster).

On the same graph, one can also see the HF energy per unit cell calculated for all clusters using Eq. (13). The energy starts to converge from the fourth biggest cluster, i.e., similarly to the atomic charges, when the central cell is surrounded by at least one sphere of adjacent cells. We also see that the energy is more sensitive to the cluster shapes than the charges, which results in a slightly nonmonotonous behavior of the energy. This may also be related to the way the energy is calculated: as a bigger cluster is considered, point charges surrounding the smaller cluster are replaced by the actual electron density. A more rigorous procedure is needed here, which would allow for a more gradual change of the electron density representation across the cluster boundary, however, this is not yet implemented in the present method.

A real test to our AG method would be to compare the energy and the atomic charges with those obtained by the CRYSTAL code,[39] keeping all numerical parameters the same (i.e., the lattice constant, basis set, and pseudopotentials). Our CRYSTAL calculations gave the total energy (per cell) of −453.66 eV and the Mulliken charges of $\pm 1.72e$, which are very close to those obtained using our largest cluster (−452.1 eV and $\pm 1.85e$, see Fig. 5). The discrepancy can be explained by an approximate character of our computational scheme in which the part of the crystal outside the quantum clusters is replaced by point charges and the way the overlap matrix is calculated. This is to be compared with a very careful account of the Coulomb and exchange lattice sums and the **k**-point summation, respectively, as implemented in the CRYSTAL code.[39] This means that in order to have the exact agreement with the CRYSTAL calculations, we should consider even bigger quantum clusters (e.g., $7\times7\times7$). Unfortunately, this option is computationally very expensive at the moment. Nevertheless, the agreement with the calculations based on the periodic boundary conditions and Bloch-like canonical orbitals, a very different computational scheme as compared to that suggested in this paper, is extremely encouraging and suggests that our method is correct.

IV. CONCLUSIONS

In this paper, we suggest an *ab initio* self-consistent method that can be used to obtain electronic structure of periodic systems within either Hartree-Fock or Kohn-Sham methodologies using essentially a cluster approach. The method is based on calculating localized nonorthogonal molecular orbitals within each unit cell that are used to construct the exact electron density of the whole system. Our method is advantageous over other embedding approaches mentioned in the Introduction as it provides an exact route of *deriving* the boundary conditions for the quantum cluster model. Since the current implementation is based on the Hartree-Fock model, it also opens a way to go beyond the HF approximation and, e.g., consider excited states using well-known methods developed in quantum chemistry.[18]

The proposed method is similar in spirit to techniques[43,44] designed to find the Wannier functions. However, there are important differences: (i) the localized orbitals in our method are not orthogonal to each other and (ii) they are found during a self-consistency procedure (the Wannier functions are normally obtained by a unitary transformation from the Bloch orbitals of the canonical problem).

The main difficulty of our method is related to strong nonlinearity of the AG equations [Eq. (5)] with respect to the AO coefficients in the LMO expansion [Eq. (4)]. As a result, it is a nontrivial computational task to obtain a self-consistent solution of the AG problem, so that care should be taken in choosing the initial approximation for the LMOs and the point charges. Two examples considered (the He and the MgO crystals) show that the method works if a favorable initial approximation and sufficiently large quantum regions are chosen.

However, still more effort is needed to make the method efficient. The present implementation based on the HF approach requires calculation of all one- and two-electron integrals, and thus it is computationally very expensive to increase the size of the quantum regions. Implementation within the KS method should computationally be more advantageous. A possible direction to improve the numerical scheme is related to incorporating the charge convergency into the AG cycle by updating the point charges "on the fly" during the electronic iterations. One can also incorporate symmetry in the direct space to reduce the computational work: some of the LMOs may be related to each other by symmetry, so that only some "irreducible" ones need to be calculated. Finally, implementation of the direct energy minimization with subsequent localization of LMOs at every step may help to improve the efficiency of the SCF cycle in our method.

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