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Comparison of localization procedures for applications in crystal embedding

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With the aim of future applications in quantum mechanical embedding in extended systems such as crystals, we suggest a simple and computationally efficient method which enables construction of a set of nonorthogonal highly localized one-electron orbitals for periodic nonmetallic crystals which reflect their chemical nature. The orbitals are also used to build up the Hartree-Fock (HF) electron density of the entire crystals. Our method does not require usage and/or modification of periodic electronic structure codes, and is instead based on the HF calculation of a sequence of finite clusters with subsequent application of a localization procedure to transform the HF canonical molecular orbitals. Two extreme cases of chemical bonding, ionic (MgO crystal) and covalent (Si crystal), are considered for which a number of known localization schemes are applied and compared. With some modifications our method can also be applied to nonperiodic nonmetallic systems as well. Our method can easily be reformulated for the Kohn-Sham orbitals of the density functional theory.

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I. INTRODUCTION

Electronic structure calculations of extended systems with a local perturbation, such as point defects in the bulk of crystals[1] or adsorption of molecules at their surfaces[2] are of fundamental importance in solid state physics and chemistry. Over the last decade a number of effective computational techniques have been developed to study the electronic ground state of such systems which are based on periodic boundary conditions (PBC's) and either Hartree-Fock (HF)[3,4] or density functional theory (DFT)[5,6] approaches. In these methods a local perturbation (e.g., an adsorbed molecule together with a fragment of a crystal surface) is artificially periodically repeated; the periodic cell is chosen to be large enough to ensure that the interaction between periodic images is negligible. These methods can also be applied to study extended (but not infinite) biological systems in which important chemistry is usually associated with a local part of the entire molecule(s).[7]

Another set of methods, commonly referred to as *embedding* techniques, originate from a model in which a single local perturbation is considered in the direct space of the entire system. This makes the model closer to reality at low concentration, but, at the same time, it makes it more challenging since, due to the lack of periodic symmetry, well developed PBC based techniques cannot be applied here. Instead, a number of *hybrid* methods have been developed which treat different parts of the system at different levels of the theory. Most of these methods combine *ab initio* quantum mechanics (QM) methods (based either on the DFT or the HF methods and their extensions) applied to a finite fragment of the system (a quantum cluster), with molecular mechanics (MM) methods based on semiclassical force fields and applied to the rest of the system (environment region). The idea is to consider the most relevant part of the system (e.g., with respect to a process in question) in great detail, while the rest of the system is treated at a substantially lower level. These methods, developed mostly within the quantum chemistry community, and usually referred to as QM/MM have proven to be extremely successful.[8–12] Note that some other embedding schemes[13–20] developed mostly in the solid state community are very close in spirit to the QM/MM methods.

Almost in all embedding methods mentioned above the quantum cluster is surrounded by point charges of the MM region. In addition, in covalent systems the bonds coming out of the cluster are usually terminated by pseudoatoms (see, e.g., Ref. 19), so-called link atoms[9,11,12] or pseudopotentials.[18–22]

Another class of embedding schemes relies on a more "electronic" (less "mechanical") representation of the environment region surrounding the quantum cluster. For instance, in Refs. 9, 23, and 24 this is achieved by a special total energy construction which allows a combination of several electronic structure methods of different complexity applied to different parts of the system; other methods[13–16] rely on a representation of the wavefunction via strongly orthogonal many-electron group functions (see, e.g. Refs. 25 and 26) associated with atoms, bonds, or molecules depending on the specific type of chemical bonding in the system.

We believe that the formalism based on group functions is the most appropriate one for the derivation of any embedding scheme. A rather general method based on overlapping (not strongly orthogonal) group functions[27,28] is presently being developed in our laboratory. Our method which is similar in spirit to some one-electron methods[29–31] is based on construction of strongly localized orbitals which are designed to represent the true electronic density of the entire reference system (normally, a perfect periodic crystal) via a combination of elementary densities associated in simple cases with atoms, ions and/or bonds. Then when considering a defective (nonperiodic) system, the environment region is constructed via a set of the strongly localized orbitals of the reference system as shown schematically in Fig. 1, while the cluster itself is represented using a many-electron wave function.

Our initial effort in this project is focused on the development of an embedding scheme based on the HF approximation and applied to point defects in the bulk or at surfaces of periodic crystals. Our intention is to create a rather general technique which can be valid for systems of different chemical character, ranging from purely ionic to strongly covalent

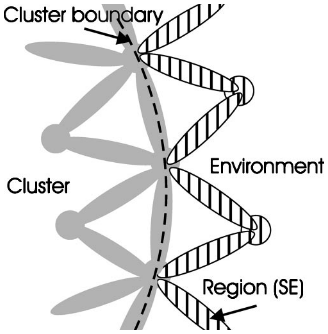

FIG. 1. The philosophy of the embedding: the entire system is split in two parts. One of these is a finite quantum cluster (on the left from the broken line) which is treated in detail, and the other is an infinite environment region (on the right) which is considered approximately.

(note that our method cannot be directly applied to metals). Therefore, the proper choice of the localization technique which can deliver localized orbitals across a wide range of systems with various character of chemical bonding is crucial for our method to work for those systems.

It is the main objective of the present paper to critically analyze and develop further a number of localization methods in order to verify their ability to describe a wide range of different chemical bondings in *periodic crystals*. Two systems are considered in the present paper in detail, MgO and Si bulk crystals, which are examples of extreme ionic and covalent bonding, respectively. Note, however, that the method we suggest is not limited to periodic systems and, with some insignificant modifications, can also be applied, e.g., to infinite amorphous and finite biological systems. The application of the present method to those systems will be a matter of future publications.

It is relevant to mention, as far as the localization methods are concerned, that there are several methods developed[32,33] for obtaining *orthogonal* localized orbitals (i.e., Wannier functions) out of the Bloch-like solutions of the HF or Kohn-Sham (KS) equations[6] for periodic crystals. Due to the built-in orthogonality even strongly localized Wannier functions have long-range tails which make these functions nontransferable to other systems, e.g., when a chemical bond between the same species is placed in a different chemical environment. That is why our interest is focused on construction of nonorthogonal localized orbitals which do not have this disadvantage and thus are more appropriate for our purposes.

The plan of the paper is the following. Our philosophy in constructing localized orbitals as well as a short overview of existing localization methods is given in Sec. II with special emphasis on the methods used in our present work. All the necessary notations are also introduced there. In Sec. III we describe our implementation of some of the methods and their application to MgO and Si crystals. The paper is finished with a short discussion and conclusions in Sec. IV.

II. LOCALIZATION METHODS

A. General philosophy

In order to describe the crystal as a set of overlapping localized functions $\{\widetilde{\varphi}_a(\mathbf{r})\}$ which are given as a linear combination of the original canonical set $\{\varphi_i^c(\mathbf{r})\}$ (and which thus span the same occupied Fock space), one has first to identify the regions of space where each of the functions $\widetilde{\varphi}_a(\mathbf{r})$ has to be localized. This question can be viewed as purely technical since any linear combination of the canonical set will give the same electron density $\rho(\mathbf{r})$. We, however, adopt in our work a strategy based on the chemistry of the system in question. Namely, the choice of the localization regions is based on the type of the chemical bonding, e.g., on atoms in the cases of atomic or ionic systems, on two atoms in the case of covalent bonding, etc. A more complicated choice may be necessary in the cases of intermediate bonding. Several different nonequivalent regions may be necessary to represent a crystal unit cell which can then be periodically translated to reproduce the whole infinite crystal. Note that there could be several localized orbitals associated with every such a region forming together an electronic group.[13,25] For instance, in the case of the Si crystal one needs four localized regions associated with four bonds; each bond is represented by a single double occupied localized orbital.

Once the occupied Fock space is obtained via a set of canonical orbitals and localized regions are identified, it is necessary to find such linear combinations of canonical orbitals which are localized in each of the regions. The topic of construction of localized (noncanonical) molecular orbitals (MO's) out of delocalized canonical solutions of the HF or Kohn-Sham equations is an old one[34] and many methods have since been developed.

Let us assume that a canonical solution of the restricted HF equations for the entire system (a closed shell crystal) is known[25]

$$\hat{F}\varphi_i^c(\mathbf{r}) = \varepsilon_i\varphi_i^c(\mathbf{r}), \tag{1}$$

$$\varphi_i^c(\mathbf{r}) = \sum_\mu C_{\mu i}^c\chi_\mu(\mathbf{r}), \tag{2}$$

where $\hat{F}$ is the Fock operator, $\varphi_i^c(\mathbf{r})$ is a spin-independent canonical MO (CMO) which is expanded over a set of atomic orbitals (AO's) $\chi_\mu(\mathbf{r})$. The electronic density of the system

$$\rho(\mathbf{r}) = 2\sum_i^{\text{occ}} |\varphi_i^c(\mathbf{r})|^2 \tag{3}$$

contains the summation only over occupied CMO's thus ensuring the correct normalization to the number N of the electrons in the system. If an arbitrary (generally nonunitary) transformation $\mathbf{U}=\|U_{aj}\|$ of the CMO's within the occupied subspace is performed,

$$\widetilde{\varphi}_a(\mathbf{r}) = \sum_j^{\text{occ}} U_{aj}\varphi_j^c(\mathbf{r}) \equiv \sum_\mu \widetilde{C}_{\mu a}\chi_\mu(\mathbf{r}) \tag{4}$$

then the expression for the density via the new set of orbitals should contain the inverse of the overlap matrix $\widetilde{\mathbf{S}}=\|\widetilde{S}_{ab}\|$:[25]

$$\rho(\mathbf{r}) = 2\sum_{ab}^{\text{occ}} \widetilde{\varphi}_a(\mathbf{r})(\widetilde{\mathbf{S}})^{-1}_{ab}\widetilde{\varphi}^{*}_b(\mathbf{r}), \tag{5}$$

where $\widetilde{S}_{ab}=\langle\widetilde{\varphi}_a(\mathbf{r})|\widetilde{\varphi}_b(\mathbf{r})\rangle$ is the overlap integral. Note that the two representations of the electron density, Eqs. (3) and (5), are absolutely equivalent. Moreover, any linear combination (4) of the occupied CMO's leads to the same density. If the transformation is unitary, then the overlap matrix is the unity matrix and the density takes on its "diagonal" form (3).

In general, any localization procedure is equivalent to some transformation **U** of the CMO's. Suppose, we would like to obtain n localized MO's (LMO's) in some region A. To find the necessary transformation, one can formulate an optimization (minimization or maximization) problem for some specific localizing functional $\widetilde{\Omega}_A[\{\widetilde{\varphi}_a\}]$ with the constraint that the LMO's associated with region A are orthonormal (of course, LMO's associated with different regions will not be orthogonal in general). We shall limit ourselves with such functionals which are invariant under arbitrary unitary transformations of LMO's, i.e., which in fact depend on the orbitals $\{\widetilde{\varphi}_a\}$ via invariants in the form of the nondiagonal "density"

$$\sigma_A(\mathbf{r},\mathbf{r}') = \sum_{a=1}^{n} \widetilde{\varphi}_a(\mathbf{r})\widetilde{\varphi}^{*}_a(\mathbf{r}') \tag{6}$$

constructed out of the LMO's associated with region A, i.e., $\widetilde{\Omega}_A[\{\widetilde{\varphi}_a\}]\equiv\Omega_A[\sigma_A]$. We shall see in a moment that this requirement ensures an existence of a simple eigenvaluelike problem for the LMO's. Note in passing that some other types of functionals are also sometimes used which do not fall within this category. For instance, Admiston and Ruedenberg proposed to find the maximum of the self-repulsion energy,[35] while later on von Niessen suggested to maximize the charge density overlap functional.[36] Since the mentioned functionals are not invariant under unitary transformations of LMO's and are also quite expensive computationally, we do not consider them in the following. The quantity $\sigma_A(\mathbf{r},\mathbf{r}')$ will be referred to in the following as the region electron density or region density for short.

To obtain all n LMO's associated with region A, an optimum of the following functional is sought for:

$$\Omega'_A[\sigma_A] = \Omega_A[\sigma_A] - \sum_{a,b=1}^{n} \xi_{ab}(\langle\widetilde{\varphi}_a|\widetilde{\varphi}_b\rangle - \delta_{ab}), \tag{7}$$

where ξ_{ab} are the corresponding Lagrangian multipliers. Because the actual dependence of the functional $\Omega_A[\sigma_A]$ on the orbitals is built-in via the region density (6), the functional derivative $\delta\Omega_A/\delta\widetilde{\varphi}^{*}_a(\mathbf{r})$ can always be written using the operator $\hat{\Omega}_A(\mathbf{r})$ defined through an identity $\delta\Omega_A/\delta\widetilde{\varphi}^{*}_a(\mathbf{x}) = \hat{\Omega}_A\widetilde{\varphi}_a(\mathbf{x})$ since $\delta\sigma_A(\mathbf{r},\mathbf{r}')/\delta\widetilde{\varphi}^{*}_a(\mathbf{x}) = \widetilde{\varphi}_a(\mathbf{r})\delta(\mathbf{x}-\mathbf{r}')$. Examples illustrating this point will be given below. We shall refer to the operator $\hat{\Omega}_A(\mathbf{r})$ as the localization operator in the following. An important property of the localization operator is that it can also be considered as a functional of the region density (6), i.e., it preserves the invariance property of the localizing functional it is built from.

Using standard methods, i.e., setting the variational derivative of the functional (7) with respect to the orbital $\widetilde{\varphi}^{*}_a(\mathbf{r})$ to zero and then performing a unitary transformation of the LMO's which diagonalizes the matrix of Lagrangian multipliers, one can easily obtain the following equations for the LMO's sought for:

$$\hat{\Omega}_A\widetilde{\varphi}_a(\mathbf{r}) = \lambda_a\widetilde{\varphi}_a(\mathbf{r}) \tag{8}$$

or

$$\sum_{j}^{\text{occ}} \Omega^A_{ij}U_{aj} = \lambda_a U_{ai}, \tag{9}$$

where Ω^A_{ij} is given via matrix elements of the operator $\hat{\Omega}_A$ calculated using canonical orbitals $\varphi^c_i(\mathbf{r})$ and $\varphi^c_j(\mathbf{r})$.

Equations (8) resemble an eigenvalue problem for the operator $\hat{\Omega}_A$. Note, however, that in some cases the localization operator may still depend on the region density and thus on the orbitals themselves. Therefore, similarly to the HF or Kohn-Sham problem, the system of equations (8) should be solved self-consistently.

The eigenvalue problem (8) or (9) may give a set of solutions from which only the first (in the case when Ω_A is minimized) or the last (maximized) n solutions should be chosen. If the localization criterion (i.e., the functional Ω_A) used is appropriate, then (i) the chosen n solutions would have close eigenvalues λ_a which correspond to their similar localization in region A and (ii) the gap in the eigenvalues λ_a between the chosen n and other solutions is considerable, i.e., the other solutions have much worse localization in region A (cf. see Ref. 37). By collecting LMO's from all regions in the unit cell and then translating those over the whole crystal it should be possible to span the whole occupied Fock space and thus construct the total electron density (5).

One point is in order now. So far we have assumed that the set of canonical MO's which span the occupied part of the Fock space is already known. In other words, the procedure consists of two steps: first, a HF (or Kohn-Sham) problem is solved and thus the occupied Fock space is determined, and, secondly, the LMO's are obtained by finding appropriate linear combinations of the canonical orbitals within this space. However, it is also possible to formulate the problem in such a way that LMO's are obtained together with the set of canonical orbitals in a single step.[34] In this method a localization criterion is considered alongside the energy minimization leading to a set of so-called Adams-Gilbert (AG) equations (see, e.g., Ref. 38) which are solved in a self-consistent manner. For instance, a projection operator on the subspace of the LMO's was used by Stoll *et al.*[39] as the specific localization method. This technique was implemented in Ref. 40 for the embedded molecular cluster calculations. The LMO's resulting from a single AG calculation are orthogonal as solutions of a single secular problem. The first eigenvectors obtained will show strong localization within the chosen region A; other eigenvectors will be much less localized and can usually be distinguished by a gap in their eigenvalues as explained above. To obtain LMO's strongly localized in a different region A', one has to solve the AG equations once again using another localization criterion and then pick up the necessary number of the most localized orbitals. Repeating this procedure across the entire system, the whole occupied Fock space can be split into sets of mutually nonorthogonal LMO's. Of course, in the case of the perfect crystals this procedure should only be applied to various localization regions within the primitive unit cell owing to crystals periodic symmetry.

Note that it is also possible to obtain all the LMOs corresponding to several localization regions at once within the same self-consistent calculation by solving the necessary sets of eigenproblems associated with each region.[30,31] The LMO's obtained using this technique are known as extremely localized MO's. This method is quite expensive computationally since the overlap between LMO's localized in different regions in space changes in the course of the iteration procedure and this affects the convergence.

There are many ways in which a localizing functional Ω_A can be chosen. Some of these methods which will be utilized in the present work will be considered below in more detail.

B. Methods based on functionals linear in region density

In a number of methods[41] the localizing functional is proportional to the nondiagonal density (6) and thus can be represented as a Hermitian bilinear functional with respect to the LMO's of the following general form:

$$\Omega_A = \int [\hat{\Omega}_A \sigma_A(\mathbf{r},\mathbf{r}')]_{\mathbf{r}'\to\mathbf{r}} d\mathbf{r} = \sum_{a=1}^{n} \int \tilde{\varphi}_a^*(\mathbf{r}) \hat{\Omega}_A \tilde{\varphi}_a(\mathbf{r}) d\mathbf{r}$$

$$\equiv \sum_{a=1}^{n} \sum_{jk}^{\mathrm{occ}} U_{aj}^* \Omega_{jk}^A U_{ak}, \qquad (10)$$

where $\hat{\Omega}_A$ is some localization operator and the Hermitian matrix $\mathbf{\Omega}^A = \|\Omega_{jk}^A\|$ can easily be written in terms of the canonical MO's using the definition (2):

$$\Omega_{jk}^A = \langle \varphi_j^c | \hat{\Omega}_A | \varphi_k^c \rangle = \sum_{\mu,\nu} C_{\mu j}^{c*} C_{\nu k}^c \langle \chi_\mu | \hat{\Omega}_A | \chi_\nu \rangle. \qquad (11)$$

For all methods of this group both the operator $\hat{\Omega}_A$ and the matrix $\mathbf{\Omega}^A$ do not depend on the LMO's sought for so that in order to obtain the localized orbitals one has simply to find the eigenvectors of the matrix $\mathbf{\Omega}^A$ using Eq. (9). Two methods of this group are implemented in our work and will be considered in the following in more detail.

Mulliken's net population (method M). Magnasco-Perico criterion maximizes Mulliken's[42] net atomic population produced by the LMO's in the selected region.[41,43] In this case the matrix $\mathbf{\Omega}^A$ is chosen in the following form:

$$\Omega_{jk}^A = \sum_{\mu,\nu\in A} C_{\mu j}^{c*} S_{\mu\nu} C_{\nu k}^c, \qquad (12)$$

where $S_{\mu\nu}$ is the overlap integral between two AO's χ_μ and χ_ν. The summation here is performed over AO's which are centered in the chosen region A. Thus, in practice the localization region in this method is specified by a selection of AO's in Eq. (12). This way one can make the LMO's to have the maximum contribution from the specified AO's in region A. Sometimes a different choice of AO's may lead to physically identical localization (see the next section). This method will be referred to as method M.

The projection on the atomic subspace (method P). The Roby's population maximization[44] gives LMO's for which the projection on the subspace spanned by the basis orbitals centered within the selected region is a maximum, or is at least stationary.[41] In this method the localization operator $\hat{\Omega}_A$ in Eq. (10) is chosen in the form of a projection operator

$$\hat{\Omega}_A = \sum_{\mu,\nu\in A} |\chi_\mu\rangle (\mathbf{S}_A^{-1})_{\mu\nu} \langle \chi_\nu|, \qquad (13)$$

where $\mathbf{S}_A^{-1}$ stands for the inverse of the overlap matrix $\mathbf{S}_A$ defined on all AO's μ, $\nu \in A$. Note that operator $\hat{\Omega}_A$ is idempotent: $(\hat{\Omega}_A)^2 = \hat{\Omega}_A$. It projects any orbital into a subspace spanned by the AO's associated with region A only. In particular, $\hat{\Omega}_A |\chi_\mu\rangle = |\chi_\mu\rangle$. The detailed expression for the matrix $\mathbf{\Omega}^A$ is then

$$\Omega_{jk}^A = \sum_{\lambda,\tau} C_{\lambda j}^{c*} C_{\tau k}^c \left[\sum_{\mu,\nu\in A} S_{\lambda\mu} (\mathbf{S}_A^{-1})_{\mu\nu} S_{\nu\tau} \right]. \qquad (14)$$

Here the first double summation is performed over all AO's of the system. Region A is also defined via a subset of AO's: by choosing particular AO's one ensures the maximum overlap of the LMO's with them. It is seen that this method, which will be referred to as method P, although different in the implementation, is very similar in spirit to the previous method M.

Other methods. Note that several other methods[41] also belong to this class of methods. Since we are not using them here, we shall only mention some of them. Bader's method (see also Ref. 45) is computationally expensive and leads to LMO's with discontinuities at the border of the localization regions. The widely used Pipek-Mezey localization scheme[46] could be described as the maximization of the Mulliken's gross atomic population. The Pipek-Mezey functional corresponds also to a minimization of the number of atoms over which the LMO is to be spread. This method is very similar to the Mulliken's net population method considered above, although is slightly more computationally expensive. All population methods have an advantage of being very simple in the implementation which results in fast non-self-consistent algorithms: indeed, only overlap integrals are to be computed. Note that instead of the overlap, one can also maximize an exchange interaction of the LMO's with a set of AO's in region A.[37]

Perhaps the most widely used, due to its relatively low computational cost, is the Foster-Boys[47] method in which the dipole moment matrix element between so-called exclusive orbitals is maximized. The efficiency of the HF method was improved in Ref. 48 by using localized orbitals constructed from the Foster-Boys method as AO's. Recently[33] the Wannier functions were calculated for periodic Si and MgO crystals using the modified version of the Foster-Boys method which ensured better localization within the cell volume. Note that, according to Ref. 41, the Pipek-Mezey functional, unlike the Fosters-Boys method, preserves the σ/π separation of double bonds, which is in chemistry usually preferred over the τ picture (where the orbitals are proportional to the linear combinations $\sigma+\pi$ and $\sigma-\pi$) associated with the Fosters-Boys localization procedure.

C. Methods based on functionals bilinear in region density

More complicated localization procedures can be constructed if the localizing functional is bilinear in nondiagonal density (6) of region A in question, i.e., is of the fourth order with respect to the LMO's sought for. Three important general points should be mentioned: (i) for all methods of this group the localizing operator $\hat{\Omega}_A$ is linear in the density $\sigma_A(\mathbf{r},\mathbf{r}')$ and (ii) is thus invariant under any unitary transformation of the LMO's; (iii) therefore, one still has the secular problem (8) or (9) for the LMO's in this case; however, it is to be solved self-consistently.

Minimization of the HF energy of a structure element (method E). In this paper we shall only apply one method of this group in which the functional Ω_A is chosen as the HF energy of a finite fragment of the system. The fragment, which is usually called a *structure element* (SE), (see Ref. 13), comprises all electrons belonging to region A and the corresponding nuclei (or their parts, see below). Note that if a SE is positively charged or electrically neutral, then every electron in it can be approximately viewed as moving in a potential well of a finite depth. This is also true if the SE is negatively charged (e.g., an oxygen ion O^{2-} in the MgO crystal); however, in this case one has to add the Madelung field of the rest of the crystal to stabilize it. This method, which will be referred to as method E in the following, in its simplest version of the localization on a single atom originates from Adams.[49] It was recently used in Ref. 50 to derive an embedding potential provided by a part of a molecule. Method E is based on an intuitive idea that every stable finite system, e.g., a SE, will try to find an energetically favorable ground state which will be localized in space. Indeed, the ground state wavefunction for an electron in a potential well is known to be strongly localized in the well. The SE could be an atom, group of atoms or a bond. In the latter case the SE for the Si crystal represents essentially a hydrogen-like molecule consisting of fragments of two nearest atomic cores each of charge $+e$ ($-e$ is the electron charge) and two electrons of opposite spins (see the next section).

The eigenvalue problem (9) in this case is nothing but the usual Hartree-Fock-Roothaan (HFR) problem[25] for molecular orbitals of region A, i.e., the elements of the matrix $\mathbf{\Omega}^A$ are

$$\Omega^A_{jk} = \langle \varphi^c_j | \hat{\Omega}_A | \varphi^c_k \rangle,$$

where $\hat{\Omega}_A \equiv \hat{F}_A$ is the usual HF operator of the SE containing both electron-electron and electron-core interactions. The peculiarity of this case is that the MO's (which are, in fact, LMO's) are expanded not via AO's but rather via canonical HF orbitals for the whole system which, in turn, are linear combinations of AO's of the whole system as in Eq. (2). In other words, the difference with the usual setup of the HFR problem is that in our case the preset linear combinations (2) of the AO's of the whole system are used in place of the AO's themselves. Correspondingly, this method is computationally expensive since all the one- and two-electron integrals which are necessary for the construction of the Fock matrix $\mathbf{\Omega}^A$ are expressed as double and quadruple sums of the corresponding AO integrals.

D. Localization criteria

Application of the various schemes described above results in LMO's which may be localized in 3D space differently. It is therefore useful to have a simple criterion (or criteria) which identifies the degree of their localization. In this paper we shall use two methods. The first one, the so-called localization index, is the measure of localization proposed by Pipek and Mezey[46] which is based on the gross Mulliken populations. Qualitatively, it gives the number of atoms where the orbital $\widetilde{\varphi}_a(\mathbf{r})$ is predominantly localized and is defined by the formula

$$d_a = \left[\sum_A (\Omega^A_a)^2 \right]^{-1}, \tag{15}$$

with

$$\Omega^A_a = \sum_{\mu} \sum_{\nu \in A} \widetilde{C}^*_{\mu a} S_{\mu\nu} \widetilde{C}_{\nu a}. \tag{16}$$

Here $\widetilde{C}_{\nu a}$ are the expansion coefficients of the LMO in question, see Eq. (4). Note that this criterion is similar, but not identical, to the method of participation ratio proposed by Bell and Dean.[53]

Alternatively, the overlap between localized orbitals gives also an important information about their localization. That is why as the second criterion we shall consider the maximum eigenvalue of the overlap matrix. Note that for periodic structures it is more convenient to use the Fourier transformation of the overlap matrix[54]

$$S_{ab}(\mathbf{k}) = \sum_{\mathbf{L}} \langle \widetilde{\varphi}_a(\mathbf{r}) | \widetilde{\varphi}_b(\mathbf{r}-\mathbf{L}) \rangle e^{i\mathbf{kL}}, \tag{17}$$

where $\mathbf{k}$ is a point in the Brillouin zone, $\widetilde{\varphi}_a(\mathbf{r})$ and $\widetilde{\varphi}_b(\mathbf{r})$ are LMO's in the elementary cell and $\mathbf{L}$ is the lattice translation vector. Note, that if any of the eigenvalues of the overlap matrix $\mathbf{S}=\|S_{ab}(\mathbf{k})\|$ is larger than 2 it is impossible to obtain the total crystal density in this basis via the Löwdin's expansion method.[54] Therefore, existence of large eigenvalues of the matrix $\mathbf{S}$ correspond to weak localization of the corresponding LMO's. In practice, when applying this criterion, we apropriately sample the Brillouin zone, calculate the eigenvalues of the $\mathbf{S}(\mathbf{k})$ matrix at every $\mathbf{k}$ point and then pick up the largest eigenvalue. It is worth noting that the overlap matrix has all its eiegenvalues equal to unity in the case of orthogonal orbtals, so that this criterion is only applicable to the case of nonorthogonal orbitals.

III. LOCALIZED MOLECULAR ORBITALS FOR Si and MgO BULK CRYSTALS

In this section we shall examine LMO's obtained using three methods described above. Two crystalline systems with extreme types of chemical binding will be considered: MgO (ionic) and Si (covalent).

A. General method

We are interested in calculating LMO's for perfect periodic solids. In this case the canonical MO's are Bloch-like solutions of the HF or Kohn-Sham equations. This means that the eigenvalue problem (9) is of an infinite dimension which makes the calculation quite complicated; in addition, it would be necessary to use (and modify) a periodic electronic structure code. To avoid these difficulties, we suggest a very simple procedure based on a cluster method. The basic idea relies on the fact that when the cluster size is increased, the distribution of the electron density in its central region should become closer to the actual electron distribution of the infinite periodic system.

Our method is based on the following steps.

(1) Analyze the known electron charge density $\rho(\mathbf{r})$ of the 3D periodic system in question to identify regions *A*, *B*, *C*, etc., which can each be associated with even numbers of localized electrons, e.g., atoms, ions, bonds; the density $\rho(\mathbf{r})$ can be found in the literature or our own calculations.

(2) Consider a quantum cluster which contains region *A* in its center (or close to it); terminate the cluster using pseudoatoms (see below) and/or an array of point charges to reproduce the correct Madelung field; obtain the occupied canonical orbitals $\varphi_i^c(\mathbf{r})$ for the whole cluster.

(3) Then consider a localization problem for region *A* using one of the methods of the previous section; this should give the necessary number of LMO's $\widetilde{\varphi}_a(\mathbf{r})$ $(a=1,\ldots,n)$ as a linear combination of the occupied canonical MO's $\{\varphi_i^c(\mathbf{r})\}$, Eq. (4); note that in some cases when, e.g., pseudoatoms are used to terminate the cluster, their contribution to the LMO's should be removed and the orbitals renormalized.

(4) Repeat procedures 2 and 3 for larger clusters to ensure that the LMO's obtained have converged.

(5) If other types of regions exist, repeat steps 2–4 for those regions as well; when finished, LMO's for the whole unit cell should be available; sometimes (as is the case for silicon), LMO's of some other regions can be obtained without additional calculation by simply translating and possibly rotating the LMO's of a single region.

(6) The LMO's within the primitive cell can be displaced by all possible lattice translations to obtain the complete set of crystal LMO's spanning the complete occupied Fock space; these can now be employed for the calculation of the density according to Eq. (5). We shall denote the electron density calculated in this way $\widetilde{\rho}(\mathbf{r})$. We distinguish it from the actual periodic density $\rho(\mathbf{r})$ calculated using a periodic code and identical basis set by a tilde since the two densities will not be exactly the same due to a number of approximations employed here in calculating the LMO's (see below).

Some general comments of our general method are necessary at this point. First, the convergence of our procedure with the cluster size depends on the "boundary conditions" used in every case, i.e., it depends on the way the cluster is terminated; it is nothing but the embedding method itself. The latter is, however, unknown. Therefore, our procedure can be considered only as the first iteration and thus larger cluster sizes are expected. In principle, when the LMO's are obtained, one can use them for a new set of embedding calculations to obtain a better approximation for them, etc. In this case smaller cluster sizes may only be necessary.

Secondly, it has already been mentioned that any linear combination of the canonical set of MO's should lead to the same electron density. Therefore, one may think that the density $\widetilde{\rho}(\mathbf{r})$ obtained using the procedure outlined above will always result in the correct electron density $\rho(\mathbf{r})$. This is, however, do not need to be the case due to a number of approximations adopted. Indeed, we only consider finite clusters with *ad hoc* boundary conditions; in addition, the contribution of boundary cluster atoms may be modified when pseudoatoms are used. Finally, the cluster size may be insufficient to accommodate completely the LMO's. Therefore, the obtained occupied Fock space will never be exactly the same as that obtained using the periodic calculation. Hence, the comparison of the electron densities $\widetilde{\rho}(\mathbf{r})$ and $\rho(\mathbf{r})$ may indicate on the quality of the calculated LMOs, and this method will be used in this paper.

The calculation of $\widetilde{\rho}(\mathbf{r})$ is performed by exploiting the periodic symmetry and representing the LMO's as an integral over the Brillouin zone.[54] This method is exact and does not depend on the degree of localization of the LMO's. It also allows exact handling of the inverse of the overlap matrix in Eq. (5). To calculate the reference density $\rho(\mathbf{r})$, we used our cluster calculations in the following way: (i) a parallelepiped in the central part of the cluster with the sides along the primitive lattice translations $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ which is equivalent to the primitive unit cell is identified; its density is denoted $\rho_c(\mathbf{r})$. (ii) The density of the whole 3D crystal is then modeled as $\rho(\mathbf{r}) \equiv \rho_c(\mathbf{r}_1)$, where $\mathbf{r}_1$ is obtained from $\mathbf{r}$ by removing any lattice translations (this is most conveniently performed by first calculating fractional coordinates of $\mathbf{r}$ in terms of $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ and then removing integral parts from them). The larger size of the cluster is used in the calculations, the better approximation for the density $\rho(\mathbf{r})$ will be obtained in this way. All numerical calculations reported in this paper were done using the HF method and the Gamess-UK (Ref. 51) code within the pseudopotential approximation.

B. Localized orbitals for the MgO bulk

MgO crystal has a face centered cubic lattice with the distance between magnesium and oxygen ions of 2.122 Å.[55] Each Mg atom donates its both valence electrons to the O sublattice resulting in effective atomic charges of $\pm 2e$. For the investigation we have chosen a sequence of three finite clusters of increased size, Mg_6O, $Mg_{38}O_{13}$, and $Mg_{44}O_{19}$, containing 7, 51, and 63 atoms, respectively; each of the clusters was surrounded by an array of nearly 10^3 point charges of $\pm 2e$ to simulate the Madelung field. The largest cluster used is shown in Fig. 2.

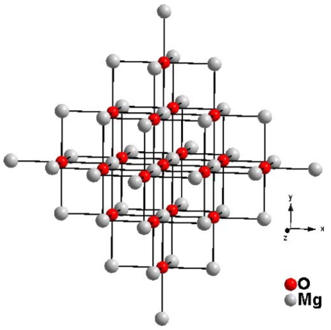

FIG. 2. (Color online) The largest quantum cluster used in our HF calculations to model the MgO crystal. Point charges surrounding the MgO cluster to simulate the Madelung field are not shown.

To consider explicitly only the valence electrons, for both Mg and O we used coreless Hartree-Fock pseudopotentials (CHF) with LP-31G basis set from Ref. 52. The number of electrons in each cluster was calculated by adopting a well known ionic character of the MgO crystal, i.e., by assuming that every Mg^{2+} ion is associated with no electrons, while every O^{2-} ion has eight electrons. The LP-31G basis set was used in all our calculations.

After the HF solution was obtained for every cluster, we applied the three localization procedures (methods *M*, *P*, and *E*) considered in the previous section to obtain the LMO's for this system. Since there are only two atoms in the primitive cell, Mg and O, and it is well known that the valence electron density is localized predominantly on the O atoms, one can choose essentially a single region *A* within the primitive unit cell to localize the LMO's into, namely, on the O atom. We should expect four LMOs localized on every O atom: one of the *s* type $\tilde{\varphi}_s(\mathbf{r})$ and three of the *p* type $\tilde{\varphi}_{px}(\mathbf{r})$, $\tilde{\varphi}_{py}(\mathbf{r})$, and $\tilde{\varphi}_{pz}(\mathbf{r})$.

Therefore, when applying the methods *M* and *P* we used the *s* and p_x, p_y, and p_z type AO's centered on the O atom in the center of every cluster when applying Eqs. (12) and (14). In the case of method *E*, we considered the HF problem for a single oxygen ion O^{2-} in the basis set of all occupied canonical MOs of the entire cluster. In every case exactly four LMO's were obtained as having the smallest eigenvalues; other states were found to be separated by a considerable gap.

We find that the density is perfectly converged already for the smallest of the clusters. This means that the electron density in the center of any of the clusters can be considered as being very close to the density of the actual 3D periodic crystal calculated in the HF approximation using the same basis set. The HF electron density through the central O atom for the largest cluster is shown in Fig. 3(b).

The partial oxygen electron density

$$\rho_O(\mathbf{r}) = \tilde{\varphi}_s^2(\mathbf{r}) + \tilde{\varphi}_{p_x}^2(\mathbf{r}) + \tilde{\varphi}_{p_y}^2(\mathbf{r}) + \tilde{\varphi}_{p_z}^2(\mathbf{r}) \tag{18}$$

can be conveniently used to characterize the localization of the obtained LMO's $\tilde{\varphi}_s(\mathbf{r})$, $\tilde{\varphi}_{p_x}(\mathbf{r})$, etc. Note that we have omitted the factor of two here (due to spin) since it is not essential in assessing the localization of the LMO's. We compare $\rho_O(\mathbf{r})$ obtained for all clusters using method *M* in Fig. 3(a). Note that other methods give practically identical densities. It is seen that all four LMO's are extremely well localized on the O atom (as one would expect for such an extremely ionic system) and converge very quickly with the cluster size. The LMO's are essentially identical for all three methods. These findings are also confirmed by both localization criteria (Sec. II D) as shown in Table I. The localization indices for the LMO's calculated using either of the methods *E*, *M*, and *P* are only slightly larger than one which confirms the predominant localization of the LMO's on the single O atom. Moreover, the largest eignevalues of the overlap matrix **S** are found to be all smaller than 2 which demonstrates that the overlap between neighbouring LMO's is very small.

Obviously, LMO's associated with any other unit cell can now be obtained simply by moving the calculated four LMO's by the appropriate lattice translation. We have made a careful comparison of the total electron density $\tilde{\rho}(\mathbf{r})$ constructed using Eq. (5) with the density $\rho(\mathbf{r})$ calculated using the central part of the largest cluster. In particular, such a comparison is shown in Fig. 3(b) along the (001) direction across the central O atom. One can see that either method

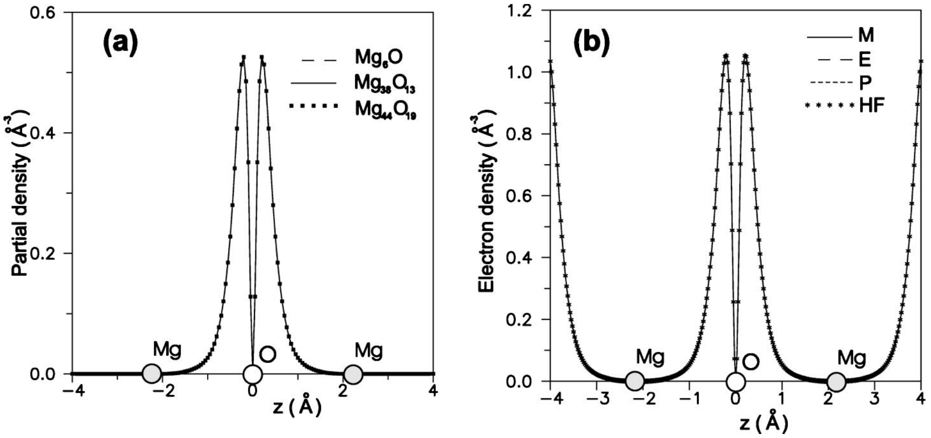

FIG. 3. (a) Partial density $\rho_{\mathrm{O}}(\mathbf{r})$, Eq. (18), calculated using method *M* for all clusters, (b) electron densities of the MgO crystal constructed from LMO's obtained using methods *M*, *P*, and *E* (lines) are compared with the HF density calculated from the middle of the largest cluster (stars). All densities are shown along the Mg-O-Mg direction. Mg and O atoms are indicated on the picture.

TABLE I. Localization criteria for the LMO's of the MgO and Si crystals calculated using both the localization index and the maximum eigenvalue of the overlap matrix methods. Note that in the case of MgO there are four LMO's altogether; the data in the table correspond to the least localized orbital. The largest clusters were used in each case.

	Localization scheme	Localization index *d*	Max. eigenvalue of **S** matrix
MgO	*E*	1.286	1.798
	M	1.211	1.738
	P	1.220	1.572
Si	*E*	19.345	27.155
	M	2.078	2.860
	P	2.107	2.074

results in the perfect matching between the density $\tilde{\rho}(\mathbf{r})$ obtained using the LMO's (indistinguishable on the plot) and the reference density $\rho(\mathbf{r})$. Thus, all three localization techniques work equally well in the case of MgO and require clusters of very moderate sizes.

C. Localized orbitals for the Si bulk

Crystalline Si has the diamond-type lattice with the distance between the nearest Si atoms of 2.35 Å. Each Si atom is surrounded by four neighbors forming four covalent bonds with them. There are two Si atoms, and thus eight electrons (within the valence approximation), to be assigned to every primitive cell. Since each bond is associated with two electrons, there should be four bonds per cell. We expect that well localized orbitals can be constructed for this crystal if localization regions are associated with every two-electron bond. Therefore, in this case we have four regions *A*, *B*, *C*, and *D* of identical nature in the primitive cell as shown schematically in Fig. 4.

Note that the choice of four inequivalent bonds is not unique. In our choice shown in the figure all four bonds share atom 1 and can be obtained from any single bond (e.g., the central bond between atoms 1 and 2) by applying appropriate displacements and rotations.

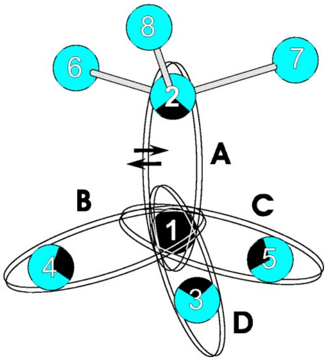

FIG. 4. (Color online) Four two-electron bonds associated with a primitive unit cell in the Si crystal.

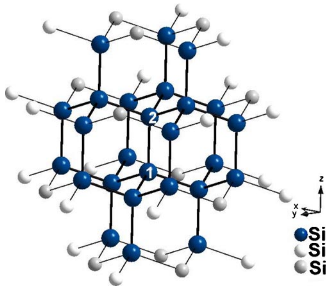

FIG. 5. (Color online) The largest quantum cluster used in our HF calculations to model the Si crystal. One electron Si* and two electron Si** pseudoatoms were used to saturate bonds with the boundary Si atoms (see text).

Three quantum clusters $Si_2Si^*_6$, $Si_8Si^*_{18}$, and $Si_{26}Si^*_{18}Si^{**}_{12}$, containing 2, 8, and 26 Si atoms were used in our calculations; every cluster contains a single Si-Si pair in its center as shown in Fig. 5. The core electrons of all Si atoms were described using the Hay-Wadt pseudopotential.[56] To terminate unsaturated bonds of the Si atoms located at the boundary of the clusters, we used pseudoatoms which have the same pseudopotentials as the Si atoms. The Si* pseudoatoms contribute a single electron to the cluster and are positioned at the correct Si-Si distance to saturate a single dangling bond. Si** atoms have two electrons and were used in the same way to saturate two dangling bonds from two nearest boundary Si atoms (see Fig. 5). Since the Si crystal is a highly covalent system, the Madelung field can be considered of a secondary importance and thus was neglected. The 66-21G basis set[57] was used on the Si atoms in most cases so that the density we shall be referring to in the following corresponds to the valence electron density. The basis set on pseudoatoms Si* and Si** included only *s* type AO's.

To construct the LMO's for the Si crystal, we oriented the coordinate system in such a way that the *z* axis would pass along the central Si-Si bond of every cluster. This particular choice of the coordinate system is merely needed to simplify the choice of the AO's to be associated with the localization region *A*. Then, the HF solution was obtained which demonstrated a good degree of the sp^3 hybridization, as expected. When applying the localization methods *M* and *P*, AO's of the *s* and p_z types centered on the two central Si atoms were chosen as belonging to region *A*. In order to apply method *E*, the following SE was considered in place of the central Si-Si molecule: it consisted of two electrons and two pseudoatoms with the Si pseudopotential and the total charge $+e$ each. Effectively, this way the SE was chosen as a pseudohydrogen molecule with pseudohydrogen atoms at the Si-Si distance described each by the Si pseudopotential.

By analyzing the electron density in the central region of every cluster, we find that the largest cluster we considered is sufficient for our purposes. As an example, we show in Fig. 6 the electron densities across the central Si-Si bond for the three clusters. Note that we have carefully checked that the comparison of the densities (orbitals) along the central Si-Si bond reflects well the extent in which the densities (orbitals) match each other. The single LMO's calculated for the central Si-Si bond of the three clusters using methods *M* and *E*

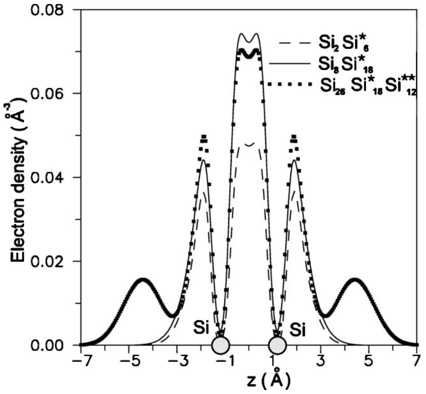

FIG. 6. The HF electron densities for the Si crystal across the central Si-Si bond for the three clusters studied. Positions of atoms are indicated.

are shown in Fig. 7. The LMO's calculated using method *P* are very similar to those calculated using method *M* and thus are not shown here. The important conclusion which can be drawn from these pictures is that the LMO obtained using method *M* for the largest cluster is practically converged with the cluster size. On the contrary, the LMO calculated using method *E* is not yet converged becoming more and more delocalized with the increase of the cluster size.

Even bigger clusters are thus needed to converge the LMO using this method. However, as was mentioned earlier in Sec. II C, larger clusters require a very expensive procedure of calculating two-electron integrals, and thus we did not consider larger systems. Note that another way of circumventing the convergence problem in method *E* might be to add some potential well to the HF problem for region *A* to enforce a stronger localization; although we did not pursue this idea in this work, we may consider it in the future.

Our conclusions concerning the localization of the LMO's obtained using different localization methods are also well illustrated by the application of the localization criteria of Sec. II D. These are summarized in Table I. One can see that both criteria indicate to an extremely weak localization of the LMO for the Si crystal obtained using method *E*. On the contrary, the LMO's obtained by either of the other two methods demonstrate a very good localization. Moreover, the localization index is just above 2 which means that the orbitals are predominantly localized on only two Si atoms, as expected.

To construct the electron density $\widetilde{\rho}(\mathbf{r})$ of the whole Si crystal we need other three LMO's assigned to the same primitive cell. These are obtained by appropriate rotations and displacements of the central bond LMO considered above. The LMO's corresponding to other crystal cells are then obtained by applying appropriate lattice translations. The electron densities $\widetilde{\rho}(\mathbf{r})$ obtained using the three localization methods for the largest cluster have been thoroughly compared with the reference density $\rho(\mathbf{r})$ obtained by translating the central part of the same cluster, and are shown in Fig. 8(a). One can see that both methods *M* and *P* lead to the electron density of the Si crystal which is very close to the reference density $\rho(\mathbf{r})$. However, the density $\widetilde{\rho}(\mathbf{r})$ calculated from the LMO's obtained using method *E* shows an unphysical oscillatory behavior which is due to their poor localization and thus an insufficient cluster size used to construct them.

IV. DISCUSSION AND CONCLUSIONS

We have seen in the previous section that for an ionic system such as MgO all localization procedures give identical results and do not require large cluster sizes. This is because a natural localization takes place in those systems. In fact we find that practically identical LMO's can be obtained for MgO using methods *M* and *P* if in addition to the AO's centered on the central O atom one also adds AO's of any of the nearest Mg atoms to define region *A*. This means that these localization procedures are sufficiently flexible in terms of the AO's used to define the localization regions. Note also that the localization indices calculated for the LMO's obtained by either of the localization methods are very close to those reported in Ref. 33 where a different localization method was used.

We find that the localization procedures for covalent systems with strong hybridization in its chemical bonding are more sensitive to the choice of the localization region and the particular localization method. We have seen above that method *E* fails for this system since the LMO's it produces

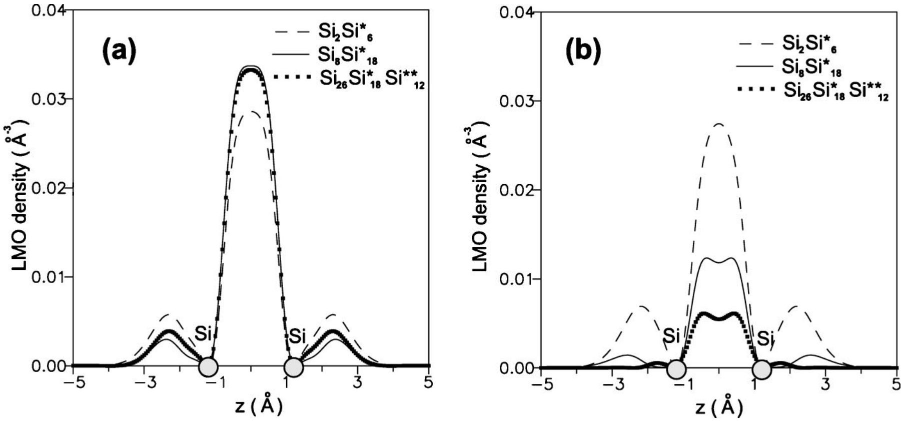

FIG. 7. LMO's partial densities $\widetilde{\varphi}^2(\mathbf{r})$ calculated across the Si-Si bond for every cluster using methods *M* (a) and *E* (b).

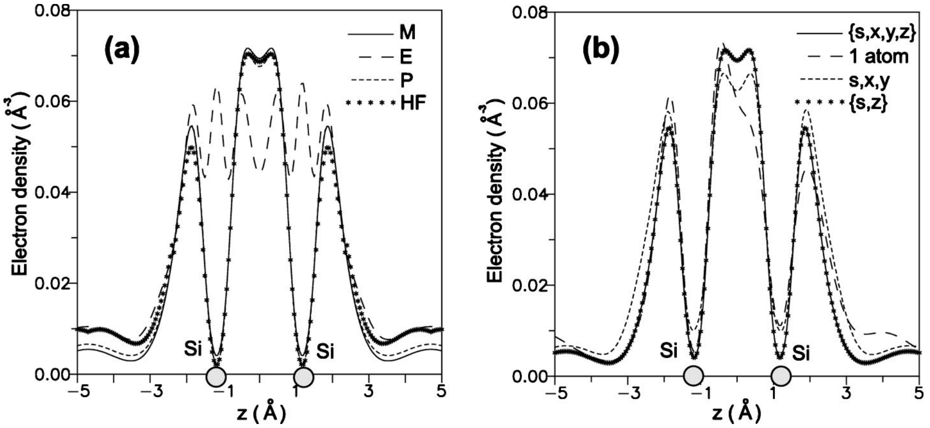

FIG. 8. Electron densities of the Si crystal constructed from LMO's obtained using different methods based on the largest Si cluster. All densities are shown along the central Si-Si bond. Positions of the two Si atoms are also indicated. (a) $\widetilde{\rho}_{sz}$ based on s and p_z types of AO's using methods M (solid line), P (small dashes), and E (long dashes) are compared with the HF density calculated from the middle of the largest cluster (stars), (b) $\widetilde{\rho}_1$–all AO's centered on a *single* central Si atom (long dashes); $\widetilde{\rho}_{sz}$ (stars), $\widetilde{\rho}_{sxy}$ (small dashes), and $\widetilde{\rho}_{sxyz}$ (solid line) were obtained using $\{s,p_z\}$, $\{s,p_x,p_y\}$, and $\{s,p_x,p_y,p_z\}$ types of AO's centered on *both* central Si atoms, respectively; method M was used for all cases in (b).

are not sufficiently localized within the cluster sizes we use. This fact is also reflected in a very large both the localization index and overlap matrix eigenvalues (see Table I).

We have also experimented with localization methods M and P by trying to use different definitions of region A in order to find the LMO. First of all, we used all AO's on the two central Si atoms. Similarly to the case of MgO, in this case an LMO practically identical to the one which we calculated using only s and p_z types AO's was obtained. The $\widetilde{\rho}$ densities calculated in these two cases are also the same as is demonstrated in Fig. 8(b) by the good match between $\widetilde{\rho} \equiv \widetilde{\rho}_{sxyz}$ and $\widetilde{\rho} \equiv \widetilde{\rho}_{sz}$. The two methods succeeded since the chemical bonding is essentially correctly reproduced by either choice of region A. This is confirmed by the contour plot of the partial density $\widetilde{\varphi}^2(\mathbf{r})$ associated with the LMO and calculated using all AO's centered on the two central Si atoms: as shown in Fig. 9, the LMO essentially corresponds to the Si-Si bond.

In contrast, when assuming a wrong character of the chemical bonding in Si, we obtained LMO's which were either not very well localized or had completely unexpected (unphysical) spatial distribution. For instance, assuming atomic character of the chemical bonding, we attempted to use AO's on a *single* Si atom to define the single localization region in the primitive cell. This assumption gave four LMOs similarly to the MgO case. We find, however, that these LMO's become much less localized and, as a result, the constructed electron density $\widetilde{\rho} \equiv \widetilde{\rho}_1$ is very different from $\widetilde{\rho}_{sz}$ as is obvious from Fig. 8(b). Another example of an "unwise" choice of the localization region is to use only s, p_x, and p_y AOs of the two central Si atoms to define region A (recall that the two Si atoms are positioned along the z axis). In this case the total electron density $\widetilde{\rho} \equiv \widetilde{\rho}_{sxy}$ also shown in Fig. 8(b) along the central Si-Si bond, somewhat differs from $\widetilde{\rho}_{sz}$, but, at the same time, reproduces all its main features. However, the LMO itself appears to have a completely different spatial distribution (see Fig. 9): it is not anymore localized on the Si-Si bond, but instead was found to be delocalized over a large volume around it. This explains why the total density $\widetilde{\rho}_{sxy}$ was found quite different from the reference one: much larger cluster should be considered to accommodate fully the LMO obtained using this particular choice of region A. Therefore, the proper choice of the localization regions which reflect the chemistry of the given crystal results in more localized orbitals and thus much smaller cluster sizes needed to construct them.

It is also instructive to compare the LMO we obtained for the Si crystal [its square is shown, e.g., in Fig. 7(a)] with the one calculated in Ref. 33 using the all-electron method (i.e., without pseudopotentials) for the upper valence band. The LMO of Ref. 33 shows characteristic spikes around the Si atoms and thus differs considerably from the one calculated here. Although in our method the LMOs of different regions

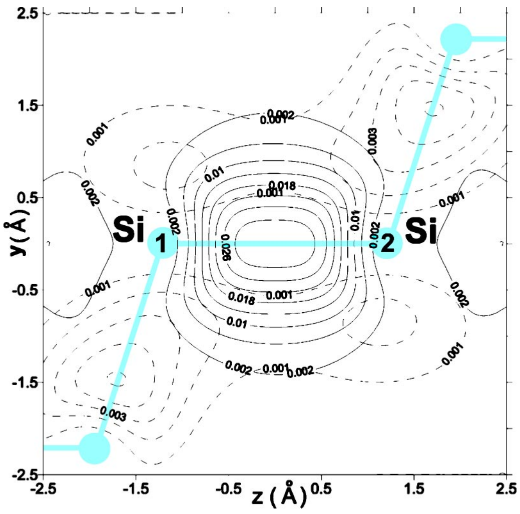

FIG. 9. (Color online) Contour plots of the LMO partial densities $\widetilde{\varphi}^2(\mathbf{r})$ obtained using method M for the two choices of region A: (i) all AO's of the two central Si atoms (solid line) and (ii) only $\{s,p_x,p_y\}$ AO's (dashed lines). The plots are calculated in the plane passing through the Si atoms and two of their nearest neighbors.

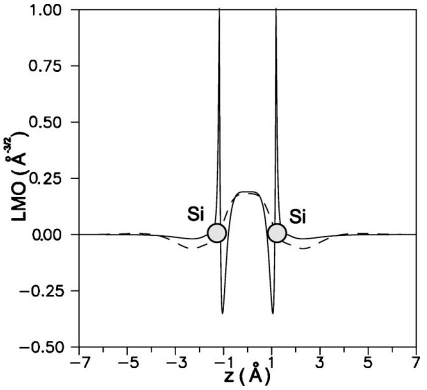

FIG. 10. The localized valence molecular orbitals calculated with (dashed line) and without (solid line) pseudopotentials on Si atoms. In the case of the all-electron calculation the 6-31G basis set was used.

are not orthogonal, whereas those of Ref. 33, which correspond to the Wannier functions, are orthogonal with each other, it appears that the main difference comes from the pseudopotential method. Indeed, as demonstrated in Fig. 10, when we use the all-electron method as well, the calculated LMO for the upper valence band is found to be almost identical to the one reported in Ref. 33 using a different method. Interestingly, the orthogonality of the LMO's does not affect the central part of the orbitals. We also found that the localization index of Eq. (15) for our LMO is very close to the one reported in Ref. 33 (see Table I).

Concluding, a simple method based on a cluster approach was suggested in order to construct localized molecular orbitals (LMO's) for a periodic solid. Our method does not require usage of periodic codes, is thus much easier to implement in practice and also, in addition, can also be applied to nonperiodic systems. The work in this direction is presently in progress and will be published elsewhere.

Several localization procedures were analyzed and two crystals were considered in detail (MgO and Si) which correspond to the two cases of extreme types of chemical bonding—ionic and covalent. We find that two localization procedures considered, one based on the Mulliken populations (method M) and another on a projection operator (method P), give well localized orbitals with the expected conventional meaning adopted in chemistry, using already quite moderate cluster sizes. The third procedure, based on the minimization of the HF energy of a structural element (one or two atoms) demonstrated a much slower convergence with the cluster size and is found to be also computationally expensive.

Two cases considered here, MgO and Si crystals, have a well known type of chemical bonding and thus the choice of the localization regions in these two cases was obvious. At the same time, we find that there is a certain degree of flexibility in choosing the localization regions and this can be exploited in the cases of more complicated (e.g., intermediate) types of chemical bonding. This work is being done in our laboratory at present and will be a matter of future publications.

We finally note that the usage of the HF orbitals is not essential for our method which can equally be applied to the Kohn-Sham orbitals of the density functional theory.

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