

A strictly variational procedure for cluster embedding based on the extended subspace approach

Ulrich Gutdeutsch, Uwe Birkenheuer,^{a)} and Notker Rösch

Lehrstuhl für Theoretische Chemie, Technische Universität München, 85747 Garching, Germany

(Received 18 February 1998; accepted 5 May 1998)

Even if an isolated defect results only in a local perturbation of the electron density, the wave function and the first-order reduced density matrix may still exhibit a long-range response to the defect. We present an axiomatic approach to the construction of a general-purpose embedding scheme which is able to cope with this problem. We start from a list of requirements, which we consider pertinent to an accurate embedding technique, and we proceed to demonstrate that the extended subspace approach recently proposed by Head and Silva [J. Chem. Phys. **104**, 3244 (1996)] is the minimal realization of such an embedding scheme. The variational principle, strict fulfillment of the Pauli exclusion principle, a finite dimensional parameter space, and the possibility to perform the minimization by a standard SCF (self-consistent field) procedure are the key requirements which lead to a constrained SCF procedure. Self-embedding consistency and local completeness of the Hilbert space can then be realized by a mathematically very simple construction principle for the active subspace which can be formulated independent of any basis set. We analyze the spatial structure of the resulting minimal orbital space by means of tight-binding model Hamiltonians. For metal systems, we find active and frozen constrained SCF spaces to necessarily interlock in a strong and complicated fashion. © 1998 American Institute of Physics. [S0021-9606(98)30730-8]

I. INTRODUCTION

The description of localized defects or perturbations in otherwise perfect extended electronic systems represents one of the great challenges of quantum chemistry. There are several approaches to model such systems. Pure cluster model applications have been successful in many respects. However, the finite size of a cluster model can have a significant (negative) impact on the results, e.g., the adsorption energy of atoms or molecules at a metal surface converges rather slowly with cluster size.^{1,2} Another widely used scheme for describing localized defects in solids is the supercell approach;³⁻⁵ there one constructs a model system in which the perturbation is repeated periodically so that standard band structure methods can be used to calculate the electronic and geometrical structure. The interaction of defect sites in neighboring unit cells limits the accuracy of this model strategy. Enlarging the supercell will reduce such artifacts, but the resulting increase of the numerical effort often pushes the model into the range of intractable problems.

A third alternative are embedding schemes where a cluster model is used that includes (at least in part) environmental effects of the extended surroundings.⁶ In general, the cluster model is treated at the maximum level of accuracy while for the remaining part of the defect system additional approximations are introduced. Very often these approximations are based on the properties (and response functions) of the unperturbed environment. Since embedding schemes are designed to describe isolated defects, no artificial defect-

defect interaction can occur. Yet, there are limitations as well. In general, the approximations applied to the external region of a defect system are based on the *assumption* that close to the border of the cluster model the impact of the perturbation has sufficiently declined in some way or another. This requirement naturally provides a lower bound for the size of the embedded cluster which, depending on the nature of the defect, might become quite large.

Very often it is assumed in embedding schemes that the perturbation induced redistributions of the electron charge density as well as the resulting changes in the effective one-electron Hamiltonian are negligible outside some central region around the perturbation. In case of uncharged defects or defects in conducting materials this seems like a reasonable approximation. However, as W. Kohn has recently been put it succinctly, “charge densities are shortsighted, wave functions are not.”⁷ Thus, the physically or chemically intuitive short-range impact of a local perturbation on measurable quantities such as the charge distribution does not necessarily imply similarly short-ranged effects on the wave function or equivalent quantities of a defect system. Particularly ill-behaved are systems which exhibit strong electron delocalization such as metals or aromatics. In such defect systems, the kinetic energy of the system, which directly depends on the first-order reduced density matrix, exhibits slow convergence if evaluated by summing up real space matrix element contributions.^{8,9} This finding can be taken as first indication for the slow decay of the first-order reduced density matrix (further on simply referred to as “density matrix”) of an adsorption system with metal substrate. This long-range wave function response in defect systems has to be taken

^{a)}Author to whom correspondence should be addressed. Electronic mail: birken@theochem.tu-muenchen.de, Fax: x49-89-289-13622.

into account when one intends to construct an embedding scheme that should be applicable to metallic systems as well. The Greens matrix approach⁸ provides one way to take care of such effects. Once the “kernel” of the Dyson equation, $T = \Delta V(1 - G_0 \Delta V)^{-1}$ is solved in the local space of the perturbation ΔV , the long-range tails of the full Greens matrix G are simply mediated by the unperturbed Greens matrix G_0 via the well-known expression $G = G_0 + G_0 T G_0$.

Of course, one may simply *assume* that outside a certain central region of a defect system the contributions of perturbation induced changes in the density matrix may be omitted when calculating measurable quantities of interest, in particular the effective one-particle potential experienced by electrons close to the perturbation. Quite a few recently developed embedding schemes follow this strategy;^{10–13} they have been successfully applied to certain classes of defect systems.^{14–18} Such an *ad hoc* truncation of the density matrix relinquishes the strictly variational spirit of an embedding formalism and bares the risk of introducing “holes” in the variational Hilbert space of the system. It has been demonstrated⁹ that in such a scheme density matrix truncation can completely spoil the evaluation of the total energy even if the charge distribution is reproduced rather well. Hence, a fully variational procedure for restricting the range of the wave function response to local perturbations seems to be much more appropriate. Examples of such variational restrictions are the projection operators which are introduced in some embedding schemes to serve as “penalty” functions for certain regions in the variational space of a defect system (e.g., see Refs. 19–21). Furthermore, experience shows that, compared to many embedding schemes, even moderately large cluster and supercell models often perform surprisingly well. This success may simply be related to the fact that, despite all their intrinsic approximations, these techniques are strictly variational.

Head and Silva have recently proposed an interesting embedding scheme which follows the line of argument presented here.²² The method is based on the constrained SCF (self-consistent field) technique, applied to an orbital space that is constructed in a very specific manner. However, the presentation²² is basis set dependent and interwoven with a variety of technical details, such as pre-orthogonalization, Jacobi rotations for core orbitals, post-orthogonalization, diagonalization of products of density matrices, and an orbital selection criterion. Actually, underneath this elaborate orbital space construction is a very general and powerful concept for establishing a variational embedding scheme which warrants a separate discussion that emphasizes its generality. In particular, we will show in the following that the orbital space construction can be formulated in a basis set independent way. Furthermore, we shall demonstrate that the orbital space proposed by Head and Silva²² is the smallest subspace in the Hilbert space of a defect system which fulfills a set of six requirements that we consider as pertinent, to a general-purpose embedding scheme. The first four conditions lead to a constrained SCF procedure. The remaining two embedding specific requirements result in an orbital space, the minimal realization of which is the variational subspace introduced in Ref. 22.

After introducing and discussing these “intrinsic” embedding requirements, we shall present the formal construction of the minimal variational embedding space. Although mathematically very compact, the construction principle is somewhat abstract. To facilitate physical insight into the properties of this subspace we will illustrate and analyze its shape and extent in real space employing a tight-binding model Hamiltonian. Finally, we shall discuss some aspects of applying this new orbital space to adsorption systems.

II. VARIATIONALLY CONSISTENT EMBEDDING

A. Hartree–Fock and Kohn–Sham based SCF procedures

We will focus on embedding schemes for quantum chemical methods which are based on (effective) one-particle Hamiltonians such as the Hartree–Fock method or the Kohn–Sham formalism of density functional theory. In both cases the total energy E of a system can be regarded as a functional of the density matrix D . (To avoid confusion with projection matrices in the following discussion, the two-fold contra-variant form of the density matrix will be denoted by D rather than by P .) It is related to the (Hermitian) density operator \hat{D} by

$$\hat{D} = \sum_{ij} |i\rangle D_{ij} \langle j|, \quad (1)$$

where $\{|i\rangle\}$ is a (nonorthogonal) spin orbital basis set with overlap matrix S . In the Hartree–Fock technique D is the first-order reduced density matrix of the single determinant wave function, in the Kohn–Sham approach D is the first-order reduced density matrix of the noninteracting reference system which is introduced to evaluate the major part of the kinetic energy functional.²³ In any case, the ground-state energy E_0 results from a minimization of the energy functional $E[D]$

$$E_0 = E[D_0] = \min_{D \in \mathcal{D}} E[D], \quad (2)$$

where the space \mathcal{D} of density matrices is given by

$$\mathcal{D} = \{D | DSD = D \wedge \text{tr}(SD) = N\}. \quad (3)$$

Here N is the number of electrons in the system. The trace condition in Eq. (3) reflects electron conservation; the idempotency condition, $DSD = D$, is a mathematically concise formulation of the *Pauli exclusion principle*, expressing the fact that (in a single determinant wave function) each spin-orbital is either fully occupied or empty. Equations (2) and (3) refer to a restricted (or spin-symmetric) treatment of the defect system. Extension to the unrestricted (or spin-polarized) case is straightforward: The total energy has to be regarded as a functional of both α and a β spin density matrices, and the minimization has to be carried out subject to the conditions of both matrices being Hermitian and idempotent as well as the α and β electron numbers adding to the given number of electrons N .

As mentioned above, cluster-in-cluster embedding calculations⁹ provide strong evidence for requiring that *none* of the unavoidable approximations in a practical embedding

scheme should temper with the *strictly variational* character of the overall procedure. In other words, the self-consistent ground-state density matrix D_0 should minimize precisely that energy functional $E[D]$ which is used for evaluating the total energy of the system. Of course, approximations to the form of the functional are admissible and often necessary. However, additional approximations, which are introduced in many embedding schemes^{10–13,19–21,24} during the SCF procedure for determining the ground-state density matrix, may bare a high risk of seriously violating the variational principle.⁹

B. Constrained SCF method

To arrive at a practical embedding technique some kind of localization has to be introduced in the description of the electronic structure of the total defect system. Within the general scheme of a strictly variational approach [Eq. (2)] this can only be achieved by restricting the search space \mathcal{D} of density matrices to a local search space \mathcal{D}_{loc} without violating the idempotency and trace conditions of Eq. (3). In addition, for practical purposes, it is desirable to restrict the variational freedom by admitting only a *finite-dimensional* search space \mathcal{D}_{loc} . Thus, let

$$D = D_{\text{appr}}(X), \quad (4)$$

where $X \in \mathcal{X}$ is a set of parameters which characterize a set $\mathcal{D}_{\text{appr}}(\mathcal{X})$ of approximate density matrices D_{appr} . Then a strictly variational embedding scheme reads

$$\tilde{E}_0 = \min_{D \in \mathcal{D}_{\text{loc}}} E[D] \quad \text{with} \quad \mathcal{D}_{\text{loc}} = \mathcal{D}_{\text{appr}}(\mathcal{X}) \cap \mathcal{D}. \quad (5)$$

It is most convenient to perform this minimization directly in the parameter space:

$$\tilde{E}_0 = \min_{X \in \mathcal{X}_{\text{loc}}} E[D_{\text{appr}}(X)] \quad \text{with} \quad (6)$$

$$\mathcal{X}_{\text{loc}} = \{X \in \mathcal{X} | D_{\text{appr}}(X) \in \mathcal{D}\}. \quad (7)$$

In case of a spin-polarized calculation two spin dependent parametrizations $D_{\text{appr}}^\alpha(X_\alpha)$ and $D_{\text{appr}}^\beta(X_\beta)$ have to be used with individually restricted parameters spaces $\mathcal{X}_{\text{loc}}^\alpha$ and $\mathcal{X}_{\text{loc}}^\beta$ which are coupled in such a way that electron conservation is obeyed. Unfortunately, a minimization of such general form will be rather difficult to implement. Thus at this stage additional approximations are often introduced. However, there is a way of arriving at a tractable scheme without further approximations if it is possible to recast the local parameter space \mathcal{X}_{loc} in a form similar to Eq. (3), albeit referring to a ‘local’ subspace U of the total Hilbert space. To this end, one identifies X with the relevant subblock D_U of D_{appr} , requiring in analogy to Eq. (3)

$$\mathcal{X}_{\text{loc}} = \{D_U | D_U S_U D_U = D_U \wedge \text{tr}(S_U D_U) = N_U\}, \quad (8)$$

where S_U is the overlap matrix within subspace U , and N_U the partial electron number attributed to the subsystem. In this form the minimization of Eq. (6) can directly be carried out by a *standard SCF procedure* within the subspace U .

There may very well exist a sophisticated parametrization $D_{\text{appr}}(D_U)$ which generates changes in *all* elements of

the approximative density matrix and still guarantees D_{appr} to be idempotent and electron conserving for each admissible subblock D_U . However, if all matrix elements D_{ij}^{appr} of D_{appr} are taken constant where none of its indices i and j refer to the subspace U , then the strategy of switching to the alternative characterization, Eq. (8), of the local parameter space \mathcal{X}_{loc} directly leads to the well-known constrained SCF method.^{22,25,26} In this case, D_{appr} is defined by the matrix blocking scheme

$$D_{\text{appr}}(D_U) = \begin{pmatrix} D_U & 0 \\ 0 & D_V^{\text{fix}} \end{pmatrix}. \quad (9)$$

Here, V is the orthogonal complement to subspace U , and D_V^{fix} is a fixed contribution to the approximate density matrix D_{appr} . The ‘penalty’ projectors in the embedding scheme of Refs. 20 and 21 are essentially introduced to favor such a blocked form of D_{appr} . Note, however, that it is crucial for the constrained SCF approach to keep the active and frozen subspaces U and V *strictly* orthogonal. Thus, with the special ansatz of Eq. (9) in mind one aims at a local parameter space \mathcal{X}_{loc} that fulfills the alternative definition given in Eq. (8). To ensure the equivalence of these characterizations, it is necessary and sufficient that D_V^{fix} be idempotent itself, and that the partial electron number N_U be chosen properly

$$D_V^{\text{fix}} S_V D_V^{\text{fix}} = D_V^{\text{fix}} \wedge N_U = N - \text{tr}(S_V D_V^{\text{fix}}). \quad (10)$$

In this way, it is guaranteed that for any local density matrix D_U of the parameter space \mathcal{X}_{loc} the approximate density matrix $D_{\text{appr}}(D_U)$ of the total defect system obeys the idempotency and trace conditions for an appropriate density matrix [Eq. (3)].

C. Self-embedding consistency

We consider two further aspects as important for high-quality embedding schemes. First, in absence of any defect, the embedding scheme should perfectly reproduce the electronic structure of the unperturbed extended reference system. For a strictly variational approach this *self-embedding consistency* requires the density matrix D^f of the unperturbed system (f, free) to be accessible *via* the ansatz of the approximate density matrices [Eq. (9)] which is used to minimize the energy functional. Put differently, D^f has to be of the form $D_{\text{appr}}(D_U^f)$ with a suitable local density matrix D_U^f from \mathcal{X}_{loc} . As a consequence the density matrix of the unperturbed reference system must be block diagonal

$$D^f = \begin{pmatrix} D_U^f & 0 \\ 0 & D_V^f \end{pmatrix}, \quad (11)$$

with respect to the subspace partitioning $U \oplus V$ which underlies the constrained SCF method. Furthermore, D_V^f must coincide with the constant contribution D_V^{fix} to the ansatz matrices [Eq. (9)]. For a spin-polarized description, the blocking scheme must hold separately for each spin density matrix. Hence two different spin-dependent sets of orthogonal subspaces (U_α, V_α) and (U_β, V_β) will be necessary. Although possibly surprising at first glance, different active spaces for

each spin component are quite reasonable, e.g., for reflecting the different amount of electron localization in systems with ferro-magnetic spin coupling.

Using the density operator \hat{D}^f instead of the density matrix D^f , the blocking condition may be rewritten as

$$\hat{D}^f U \subseteq U \wedge \hat{D}^f V \subseteq V. \quad (12)$$

This self-embedding condition is not easy to fulfill. It actually implies that one has to construct a set of occupied orbitals for the unperturbed system such that they entirely fall either into the subspace U or into its orthogonal complement V .

D. Local completeness

The final condition for a practical embedding scheme, *local completeness*, has already been discussed in Ref. 22: The embedding scheme should not restrict the variational degrees of freedom of the defect. If an embedding scheme is constructed by superposition of atomic basis sets, at least all basis functions localized in the defect region (i.e., on the embedded cluster) have to be included in the active subspace U of the constrained SCF partitioning. With C being the variational space spanned by those ‘‘cluster’’ basis functions, the local completeness condition thus reads

$$C \subseteq U. \quad (13)$$

Note that this condition is not easy to implement in a computational scheme. In any case, it reflects a strategy quite different from those often pursued when a given density matrix, here D^f , is transformed to block diagonal form in certain localized basis sets.^{20,21,27,28} In the following, we advocate an alternative procedure that allows one to comply with *all* conditions discussed in a computationally feasible way.

III. THE EXTENDED SUBSPACE APPROACH

A. The concept

Having set up a set of minimal intrinsic conditions for an applicable embedding scheme we will now address the construction of the smallest variational space U that is compatible with all these requirements. To construct the subspaces U and V one has to render a given density matrix D^f of the unperturbed system block diagonal. This can be done by applying an orthogonalization procedure, e.g., by Jacobi rotations as in Ref. 27, or by any other unitary localization transformation.^{29,30} However, for embedding purposes it is more advantageous to *augment* the original orbital space C (see also Sec. IV) as originally suggested by Head and Silva.²² However, whereas these authors have implemented the augmentation of the cluster space C by a rather involved procedure of subspace diagonalizations and selection criteria,²² we will focus here on the basic concept of the construction. To this end a basis set independent formulation of the minimal subspace U will be presented. We will refrain from discussing implementational details like a special treatment of core orbitals etc.²²

Starting point for the construction of U is the variational subspace C of the defect region referred to as (original) clus-

ter space in the following. According to the local completeness condition the final embedding space U , which will be referred to as the active (variational) subspace, has to encompass at least the cluster space C . Using the projection operator \hat{P}_{occ}^f onto the manifold of all occupied one-particle states of the unperturbed extended reference system and the orthogonal projector

$$\hat{P}_{\text{vir}}^f = \hat{I} - \hat{P}_{\text{occ}}^f, \quad (14)$$

onto the unoccupied (virtual) states, one can split each spin basis function $|i\rangle$ of the subspace C into an occupied and a virtual contribution

$$|i\rangle = \hat{P}_{\text{occ}}^f |i\rangle + \hat{P}_{\text{vir}}^f |i\rangle = |i_{\text{occ}}\rangle + |i_{\text{vir}}\rangle. \quad (15)$$

In methods which are based on an effective one-particle Hamiltonian the projector \hat{P}_{occ}^f is directly given by the total density operator

$$\hat{P}_{\text{occ}}^f = \hat{D}^f = \hat{D}^{f,\alpha} + \hat{D}^{f,\beta}. \quad (16)$$

In general, each basis function $|i\rangle$ yields two linear independent functions $|i_{\text{occ}}\rangle$ and $|i_{\text{vir}}\rangle$ (see below for a discussion of exceptions). The target space U is therefore defined as the span of all these individual functions

$$U = \left\{ \psi \left| \psi = \sum_i a_i |i_{\text{occ}}\rangle + \sum_i b_i |i_{\text{vir}}\rangle \right. \right\}, \quad (17)$$

where a_i and b_i are arbitrary coefficients. Actually, the resulting space U is independent of the basis set $|i\rangle$. This is most easily seen from the following formulation which summarizes the above construction in a more abstract form:

$$U = \hat{P}_{\text{occ}}^f C \oplus \hat{P}_{\text{vir}}^f C = C + \hat{P}_{\text{occ}}^f C \quad (18)$$

$$= C + \hat{D}^f C. \quad (19)$$

The right hand side of Eq. (18) results from the fact that each linear combination of $|i_{\text{occ}}\rangle$ and $|i_{\text{vir}}\rangle$ can equally well be written as linear combination of $|i\rangle = |i_{\text{occ}}\rangle + |i_{\text{vir}}\rangle$ and $|i_{\text{occ}}\rangle$, and *vice versa*. The second row, finally, is simply a consequence of Eq. (16).

If for some reason (e.g., as discussed in Sec. V) the density operator \hat{D}^f is not perfectly idempotent, a constrained SCF procedure based on the subspace U defined in Eq. (19) and its orthogonal complement V is still possible. However, problems are likely to arise. For one, (perfect) self-embedding consistency cannot be achieved since the density matrix D^f of the unperturbed reference system is no longer block diagonal with respect to the subspace partitioning $U \oplus V$ [Eq. (11)]. Yet, the main problem is connected to the fact that the subblock D_V^f which serves as the constant part D_V^{fix} of the density matrix parametrization $D_{\text{appr}}(D_U)$ in Eq. (9) is no longer idempotent. This can lead to serious violations of the Pauli exclusion principle which is manifested in the idempotency condition for the full trial densities [Eq. (3)], and thus bares a high risk of violating the variational character of the embedding scheme.

As evident from Eqs. (18) and (19), the original cluster space C is a subspace of U and the dimension of U is at most twice that of C . The dimension will actually be smaller as

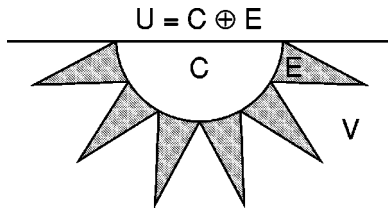


FIG. 1. Schematic representation of the Hilbert space partitioning within the extended subspace approach: the original cluster subspace C , the active subspace U , the required extension $E=U \cap C^\perp$, and the frozen orthogonal complement V .

soon as there exist some linear combinations of occupied orbitals of the unperturbed reference system which are completely localized in C (e.g., core states); for them the projector \hat{P}_{occ}^f would yield nothing “new,” i. e. a linear dependent function. Similarly, there also might exist some linear combinations of “cluster” basis functions (most likely highly oscillatory wave functions) which are perfectly orthogonal to all occupied states of the unperturbed reference system. Evidently such a linear combination within C can not contribute any new basis function to U either.

To establish a numerically elegant strategy for detecting these non-contributing functions we temporarily switch to a basis set description of the given cluster space C which is built from the natural spin orbitals $|\nu\rangle$ of the local density operator

$$\hat{D}_C^f = \hat{P}_C \hat{D}^f \hat{P}_C \quad \text{with} \quad \hat{P}_C = \sum_{i,j \in C} |i\rangle \langle i| S_C^{-1} |j\rangle \langle j|. \quad (20)$$

The two-fold co-variant matrix elements $\langle i | \hat{D}_C^f | j \rangle$ are directly given by the corresponding matrix elements $\langle i | \hat{D}^f | j \rangle$ of the complete density operator \hat{D}^f . Only *partially* occupied natural orbitals yield *two* nonvanishing functions $\hat{P}_{\text{occ}}^f |\nu\rangle$ and $\hat{P}_{\text{vir}}^f |\nu\rangle$, and it can be shown that the set of all non-vanishing projections actually provides an orthogonal basis set of subspace U . Thus, we have accomplished our task. This selection procedure also permits a direct evaluation of the number of electrons N_U which are associated with the active subspace of a defect system. Let N_d be the number of electrons added (or removed) by the defect, then the total number of electrons N of the defect system is given by $\text{tr}(SD^f) + N_d$. Using Eq. (10) and the fact that D^f is block diagonal [Eq. (11)] directly leads to $N_U = \text{tr}(S_U D_U^f) + N_d$. With the help of the special basis set $\{|\nu_{\text{occ}}\rangle, |\nu_{\text{vir}}\rangle\}$ it can easily be shown that $\text{tr}(S_U D_U^f)$ precisely corresponds to twice the number of the nondiscarded basis functions $|\nu_{\text{occ}}\rangle$ (or the sum of the nondiscarded spin-dependent basis functions $|\nu_{\text{occ}}^\alpha\rangle$ and $|\nu_{\text{occ}}^\beta\rangle$ in cases where the defect system is treated unrestrictedly). Figure 1 illustrates the construction principle of U in a schematic way. It shows the original cluster space C , its extension $E = \hat{P}_C^\perp (\hat{P}_{\text{occ}}^f C)$, and the orthogonal complement $V = U^\perp$ of the active subspace $U = C \oplus E$. The embedding procedure outlined so far is straightforward to implement in any effective one-particle scheme such as the Hartree–Fock technique (as used in Ref. 22) or the Kohn–Sham approach to density functional theory. However, the overall efficiency of such an embedding method will strongly depend on the spe-

cific features of the active subspace U , especially its extension in real space, and the effort required for evaluating the resulting matrix elements. Below we will illustrate the spatial shape of the relevant subspaces for tight-binding Hamiltonians; in a subsequent section the construction will be discussed for adsorption systems.

However, before doing so we will first demonstrate that the construction of the active variational subspace U given above fulfills the self-embedding condition as formulated in Eq. (12). From Eq. (19) and the fact that \hat{D}^f is a projector, it is evident that $\hat{D}^f U \subseteq U$ which is the first part of the self-embedding condition. The second part is actually equivalent to the first one

$$\hat{D}^f U \subseteq U \Leftrightarrow \langle v | \hat{D}^f u \rangle = 0 \Leftrightarrow \langle \hat{D}^f v | u \rangle = 0 \Leftrightarrow \hat{D}^f V \subseteq V, \quad (21)$$

where $u \in U$ and $v \in V$ are arbitrary. From Eq. (19) is also evident that, by construction, subspace U is the *smallest* subset of the Hilbert space of a defect system that satisfies the following two important conditions. On the one hand, it completely contains the original cluster space C and, on the other hand, it obeys the relationship $D^f C \subseteq U$ which is a crucial pre-requisite for achieving self-embedding consistency once C is contained in U . Hence in any embedding scheme which complies with the six requirements announced above, the active embedding space must at least contain the subset U defined in Eq. (18). For some systems, this is actually a rather severe condition as we will show in the following section: At least for metal substrates, subspace U is not as localized in real space as one might expect at first glance.

B. Examples

The projector onto the occupied one-particle states of the unperturbed extended reference system is the key quantity in the construction of the minimal active subspace U . Since this projector is directly related to the density matrix of the system the specific properties of subspace U are very likely to depend quite significantly on the electronic structure of the extended surrounding. Metal systems are expected to yield the most diffuse active subspaces; support for this statement comes from the observation that localization procedures do not perform particularly well on large Al clusters.²¹ To illustrate this point within the present formalism, we will discuss the construction of subspace U and its basis functions for various s -type tight-binding Hamiltonians.

We start with a linear chain of s -type orbitals. The basis functions $|n\rangle$ are assumed to constitute an orthonormal basis set, $\langle n | m \rangle = \delta_{nm}$, and the model Hamiltonian for the infinite chain is set up in simple Hückel fashion (with $\beta < 0$)

$$H = \begin{pmatrix} \ddots & \beta & & \\ \beta & 0 & \beta & \\ & \beta & 0 & \beta \\ & & \beta & \ddots \end{pmatrix}. \quad (22)$$

The well-known eigen functions and eigen values of this particular model Hamiltonian are

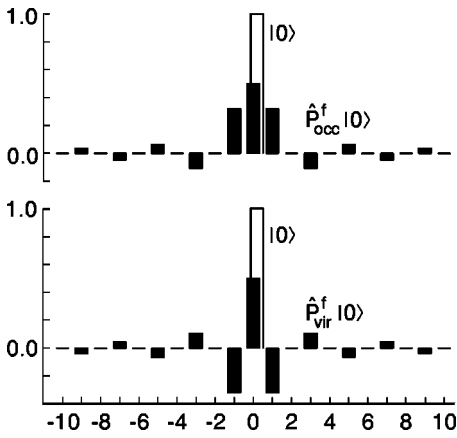


FIG. 2. Projections $\hat{P}_{\text{occ}}^f|0\rangle$ and $\hat{P}_{\text{vir}}^f|0\rangle$ of a site function $|0\rangle$ onto the occupied and virtual states of a metallic chain of s -type orbitals.

$$|\psi_k\rangle = \sum_n e^{ikna} |n\rangle \quad \text{and} \quad \varepsilon_k = 2\beta \cos(ka) \quad (23)$$

where k is the one-dimensional Bloch vector and a the lattice constant of the chain. To simulate metallic behavior the energy band is chosen half filled by setting the Fermi level to zero. The matrix elements of the resulting density operator \hat{D}^f and the related projectors can be easily evaluated

$$\langle n | \hat{P}_{\text{occ}}^f | m \rangle = \begin{cases} 1/2 & \text{for } n=m \\ \frac{(-1)^{(n-m-1)/2}}{\pi(n-m)} & \text{for } n-m \text{ odd.} \\ 0 & \text{else} \end{cases} \quad (24)$$

To illustrate the typical shape of the projected basis functions $|n_{\text{occ}}\rangle = \hat{P}_{\text{occ}}^f |n\rangle$ and $|n_{\text{vir}}\rangle = \hat{P}_{\text{vir}}^f |n\rangle$ we compare in Fig. 2 the two projections $|0_{\text{occ}}\rangle$ and $|0_{\text{vir}}\rangle$ to the generating basis function $|0\rangle$. Other projections $|n_{\text{occ}}\rangle$ and $|n_{\text{vir}}\rangle$ look precisely the same, except for the displacement corresponding to the transition from $|0\rangle$ to $|n\rangle$. For each generating function $|n\rangle$ of the cluster subspace C , both projected functions $|n_{\text{occ}}\rangle$ and $|n_{\text{vir}}\rangle$ will belong to the active subspace U . The occupied part $|0_{\text{occ}}\rangle$ of the original basis function exhibits bonding nearest-neighbor overlap at the site of the generating basis function, while the virtual part $|0_{\text{vir}}\rangle$ clearly is of anti-bonding character there. The mutual orthogonality of the two functions is comprehensible (Fig. 2). As expected the wave function amplitudes of the projections are most dominant at the central site, and they decay symmetrically to both sides. However, this decay is not of short-range nature. Inspection of Eq. (24) reveals that the site amplitudes of the new wave functions only decrease by $1/r$ with increasing distance $r = a(n-m)$ from their origin. Yet, these functions have to be added to the original cluster space to set up subspace U for the constrained SCF procedure. Obviously a very delicate interlocking between the active subspace U and its ‘‘frozen’’ complement V is necessary to achieve that none of the defect induced modifications within the subspace U can interfere with the idempotency condition which reflects the Pauli exclusion principle within of the entire defect system.

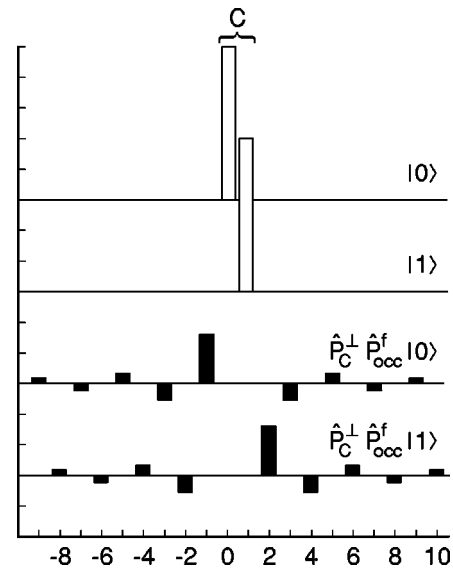


FIG. 3. Basis functions of a finite cluster subspace $C = \{|0\rangle, |1\rangle\}$ within a metallic chain of s -type orbitals in comparison to the augmentation functions $\hat{P}_C^\perp \hat{P}_{\text{occ}}^f |i\rangle$ of the orthogonal complement of C which are necessary for setting up the corresponding active subspace $U = C + \hat{P}_{\text{occ}}^f C$.

The active subspace U is defined as the span of C and its image space $\hat{P}_{\text{occ}}^f C$. The image space, of course, is not orthogonal to C . Thus, to make evident how the cluster space C is actually *expanded*, in the sense of a direct sum

$$U = C \oplus E \quad \text{with} \quad E = U \cap C^\perp, \quad (25)$$

it is convenient to isolate those contributions to the basis functions in $\hat{P}_{\text{occ}}^f C$ which belong to the orthogonal complement C^\perp of C . We shall illustrate this construction for the two-dimensional cluster space $C = \{|0\rangle, |1\rangle\}$ and the resulting active subspace $U = \{|0\rangle, |0_{\text{occ}}\rangle, |1\rangle, |1_{\text{occ}}\rangle\}$. In Fig. 3 we, therefore, depict those contributions to the projected basis functions which belong to $E = U \cap C^\perp$: $\hat{P}_C^\perp \hat{P}_{\text{occ}}^f |0\rangle$ and $\hat{P}_C^\perp \hat{P}_{\text{occ}}^f |1\rangle$. For comparison the original basis functions of the cluster space are shown as well. No wave function amplitudes within C persist in the two augmentation functions $\hat{P}_C^\perp \hat{P}_{\text{occ}}^f |0\rangle$ and $\hat{P}_C^\perp \hat{P}_{\text{occ}}^f |1\rangle$. Of course, both functions exhibit the characteristic $1/r$ decay. Again a rather complicated spatial interlocking of the two augmentation functions is discernible. The subspace extension $E = U \cap C^\perp$ has been schematically depicted in Fig. 1 in such a peculiar manner in order to emphasize this interlocking aspect of the construction procedure set forth in Eq. (18).

Different electronic systems will certainly exhibit differently extended real space representation of \hat{P}_{occ}^f . This point is easily demonstrated by considering a two level tight-binding model of an insulator with one band completely occupied and the other one completely empty. In that case, as expected, the wave function amplitudes of the projections $\hat{P}_{\text{occ}}^f |i\rangle$ decrease much faster with increasing distance r ; actually an exponential decay is found. The (effective) dimensionality of an electronic system will also influence the real space decay behavior of the density matrix. To explore this aspect, we have studied a two-dimensional square lattice of

s -type orbitals as a tight-binding model for a metallic film or surface system. The long-range behavior of the projections strongly depends on the shape of the Fermi "area." In fact, the projector $\langle nn' | P_{\text{occ}}^f | mm' \rangle$ viewed as a function of the distance vector $(x, y) = [a(n-m), a(n'-m')]$ turns out to be the reciprocal space analogue to the field amplitude of the Fraunhofer diffraction pattern of the specific Fermi area (regarded as a diffraction hole). For a square shaped Fermi area an asymptotic r^{-1} behavior (with $r = |(x, y)|$) is found in directions normal to the borders of the Fermi area and an r^{-2} behavior in all other directions. For a circular Fermi area the decay follows a $r^{-3/2}$ law. Similar considerations for arbitrary d -dimensional lattices reveal that for a metallic system a $r^{-\alpha}$ long-range behavior is to be expected for the projected basis functions $\hat{P}_{\text{occ}}^f |i\rangle$ of a tight-binding model system with α ranging from 1 to d depending on the details of the shape of the Fermi "body."

The analysis of these simple model systems has clearly demonstrated that the minimal active subspace U of a metallic system, although of finite dimension, cannot simply be assumed as short ranged in real space. Unfortunately, this finding (together with some computational experience^{21,31-33}) has to be taken as harbinger for serious computational efforts which necessarily will accompany an implementation of a cluster embedding scheme that is aimed at metal substrates.

IV. APPLICATION TO ADSORPTION SYSTEMS

Adsorbates on well-ordered surfaces represent a type of defect often treated by embedding techniques. In order to describe the electronic structure of such a system within a linear combination of atomic orbitals (LCAO) scheme it will be necessary to augment the cluster space C by additional basis functions centered on the adsorbate. Also, displacements of atomic orbitals in the cluster space C can occur if substrate relaxation is considered. Substitutional defects may even lead to the exchange of basis functions in the cluster space C . For simplicity, we will address the first case only: inclusion of an adsorbate space A spanned by the additional orbital basis functions anchored on the atoms of the adsorbate. Similar considerations apply for the other types of basis set modifications. Furthermore, the following discussion for an adsorption system may easily be carried over to substitutional or interstitial defects.

One way of setting up the active variational subspace U' of an adsorption system is to simply take the sum

$$U' = U + A, \quad (26)$$

of the adsorbate space A and the active variational subspace U of the clean surface system (e.g., see Ref. 22). This is the most convenient approach since U can be constructed without reference to any specific adsorbate. However, in the strict sense, this ansatz violates the idempotency condition which the approximative density matrices $D_{\text{appr}}(X)$ must obey [Eq. (7)]. In general, the added orbitals in A will not be orthogonal to the complement V of U , which is to be kept fixed. Hence, there may exist some basis functions in the active subspace U' which are no longer strictly orthogonal to the

frozen occupied states of the extended surroundings. For rather compact basis sets and for sufficiently extended cluster spaces C , this nonorthogonality apparently does not lead to serious problems.²² However, if orbital overlap between the adsorbate space A and the frozen orbital space V can not be neglected (e.g., when rather flexible basis sets are used), special measures have to be taken. There are two ways to proceed: (a) Either U' is constructed by applying the extended subspace procedure Eq. (18) to the complete cluster space $C' = C + A$ which encompasses both adsorbate and substrate, or (b) the adsorbate subspace A has to be orthogonalized to the frozen orbital space V (or at least to the occupied orbitals in V) *before* being added to the active subspace U of the clean surface.

Both methods have their advantages and disadvantages. Approach (a) guarantees that the variational freedom of the adsorbate space is maintained in the final active subspace U' while approach (b) bares the risk that some tails of the frozen orbitals in V will cover the adsorbate space and in this way restrict the variational flexibility of the system close to the adsorbate. This may present a potential conflict with the local completeness criterion (see above) and may even, as pointed out by Whitten,²⁰ result in an effective model potential for an embedded cluster which is far too repulsive. However, the Hilbert space partitioning $U' \oplus V'$ derived from C' in approach (a) will result in subspaces U' and V' which both depend on the structure of the adsorbate. In cases where the adsorbate geometry has to be optimized, this feature will increase the numerical effort since the subspaces U' and V' have to be re-constructed for each adsorbate geometry. This procedure also introduces an adsorbate dependent approximation which might very well lead to uncertainties in the quality of the embedding calculations (e.g., spurious trends in the energy potential surface). In addition, for the analytical evaluation of consistent total energy derivatives one has to consider new energy corrections which arise from the geometry dependence of the underlying approximation. The orthogonalization approach (b) does not exhibit such dependencies since the substrate active subspace U is setup once and for all before the adsorbate is actually introduced.

V. DISCUSSION

Next we shall elaborate three aspects of the present embedding strategy that are relevant for practical calculations.

(a) The embedding scheme has been explicitly formulated for the case of a spin-restricted system; extension to the spin-unrestricted case has been addressed. Cluster models of adsorption on metal substrates are often treated by employing fractional occupation numbers in combination with level broadening³⁴ which is physically motivated, but *ad hoc* from a formal point of view. It is not easy to introduce fractional occupation numbers within the density matrix in the context of the present embedding strategy. The partially filled occupied states of the unperturbed reference system restrict the freedom of localization transformations tremendously. A strictly blocked density matrix D^f as required for self-embedding consistency is, therefore, hardly possible for any reasonably "localized" active subspace U and its complement V . Similar problems can arise if the k -space integration

used to evaluate the density matrix of the extended reference system is carried out by means of interpolation techniques (e.g., tetrahedron methods^{35,36}). For such integration schemes, the density matrix D^f is not guaranteed to be idempotent. On the other hand, once the Hilbert space partitioning $U \oplus V$ is set up, one may employ level broadening within the active subspace as part of the defect induced response during the minimization procedure [Eq. (5)].

(b) The analysis of the long-range behavior of density matrices presented in Sec. III B leads to the following conclusion: although the minimal active subspace U is of finite dimension and although it mainly serves to ensure a variationally consistent response to a local perturbation, for metal systems U is by no means localized in real space. One way to overcome the problem associated with the long-range tails of the active subspace U in a metal system is to apply the six embedding requirements to a *simplified* total energy functional $\tilde{E}[D]$. If chosen properly, the corresponding strictly variational effective one-particle Hamiltonian can be much easier to evaluate. In this context the energy approximation used in Feibelman's Greens matrix formalism⁸ is of interest. It is based on the standard assumption of Greens function techniques for defect systems, namely that at least the electron density and the resulting effective one-particle potential only exhibit a short-range response to a local perturbation. All contributions to the total energy arising from defect induced changes in density matrix elements D_{ij} which refer to basis functions $|i\rangle$ or $|j\rangle$ outside some central region are, therefore, taken into account in linearized manner only. As a consequence, only variations of density matrix elements D_{ij} with both indices associated with the central region actually contribute to the effective one-particle Hamiltonian. All long-range contributions, no matter how far reaching they may be, can be treated as an additional fixed external potential (possibly nonlocal) during the SCF procedure. It seems worthwhile to investigate an implementation of these ideas in the context of the extended subspace approach for metal substrates.

(c) At first glance, the constrained SCF methodology may be thought of as the most questionable aspect of the general embedding scheme outlined here. Within a constrained SCF approach, the density matrix response of the extended system to a local defect is *de facto* limited to a finite-dimensional subspace [see Eq. (9)]. This is at variance with pure Greens function methods which do not impose any restriction on the density (or Greens) matrix beyond the assumption that the defect induced changes in the effective one-particle potential is localized. Thus, one may ask how an embedded cluster description which only leads to a finite number of well-separated effective eigenstates can account for the proper coupling of cluster states to the continuum of bulk states (e.g., as exhibited by the formation of broad surface resonances). Key to the answer is the subspace partitioning $U \oplus V$: It can be regarded as a bond preparation procedure whereby occupied (as well as the virtual) states of the unperturbed reference system are hybridized to yield linear combinations which are more appropriate for the interaction with a defect. Among these linear combinations there are wave functions which are more or less localized around the

defect site as well as Bloch waves which are "scattered" back into the bulk at distances rather far from the defect. Only the former type of functions is actually included in the active subspace and thus allowed to interfere with the defect orbitals. The latter states are considered as less important for the description of the defect and hence kept frozen. None of the newly formed "frontier" orbitals will in general be an eigenstate of the extended system. Instead, re-expressed as a linear combinations of the eigenstates of the reference system, they will cover a certain energy range. As a matter of fact, this spreading in energy may be regarded as the intrinsic level broadening of each of the states gathered in the active subspace of the constrained SCF approach. In this way, coupling to a broad manifold of different continuum states is *implicitly* included in the constrained SCF approach from the very beginning, at least to the extent permitted by the specific choice of the cluster space C and the resulting active subspace $U = C + P_{\text{occ}}^f C$.

(d) Adding those localized orbitals of the unperturbed extended surroundings to the cluster space basis which participate in the cluster–environment interaction represents one way of setting up a finite-dimensional active variational subspace for embedding purposes. An alternative strategy is pursued in the wave function based embedding scheme developed by Whitten;^{19,20} recently it has been adapted for density functional calculations as well.²¹ In this scheme, one starts from a somewhat enlarged embedded cluster and actually *freezes* all localized orbitals from the surroundings which penetrate the cluster region. This selection is guided by the notion that the rejected orbitals are already "consumed" (in the sense of variational freedom) by the cluster–environment interaction. In other words, the external subspace V , rather than U , is explicitly constructed starting from the span of all atomic basis functions which are assigned to the *surrounding*, and the active subspace U is then taken as the orthogonal complement. Although similar in spirit, this approach is mathematically not strictly equivalent to the present embedding scheme. For example, the construction principle proposed by Whitten may imply restrictions of the variational freedom in the close proximity of the defect site by the frozen cluster–environment bond orbitals (see the discussion in Ref. 20). On the other hand, from a chemical point of view, it is hard to judge which way is actually more appropriate to take care of the cluster–environment boundary conditions.

VI. SUMMARY

We have outlined a procedure for constructing a variationally stable general-purpose embedding scheme which is applicable to practical calculations. This scheme follows the concepts recently proposed by Head and Silva.²² However, we have taken a more axiomatic approach, starting from a set of requirements which may be considered pertinent for an efficient and high-quality embedding scheme. We contend that an embedding method should be

- strictly variational,
- in accordance with the Pauli exclusion principle,
- restricted to a finite variational space,
- solvable by means of a standard SCF procedure,

- self-embedding consistent, and
- variationally complete close to the defect site.

The first four conditions directly lead to a constrained SCF procedure with an arbitrary partitioning $U \oplus V$ of the underlying Hilbert space into active and frozen subspaces U and V , respectively. Self-embedding consistency requires the partitioning to “respect” the electronic structure of the unperturbed reference system (f) in the sense that the density matrix D^f of the reference system has to become block-diagonal in U and V . Finally, local completeness with respect to a given local defect-relevant cluster subspace C leads to the fact that the recently proposed²² orbital space U is a minimal realization of a variationally consistent active subspace for embedding. In Eq. (19), we have derived a mathematically compact formulation for that space: $U = C + \hat{D}^f C$. To maintain variational completeness and accordance with the Pauli exclusion principle, i.e., with the idempotency condition for the blocked density matrix of the entire defect system, special care is required if the embedding scheme outlined so far has to be extended due to defect mediated changes in the basis functions of the cluster subspace C . Either post-orthogonalization may be employed or one has to accept that the construction of the active subspace depends on the defect.

ACKNOWLEDGMENTS

We thank S. Krüger for valuable discussions. This work has been supported by the Deutsche Forschungsgemeinschaft via SFB 338 and by the Fonds der Chemischen Industrie.

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