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A self-consistent density based embedding scheme applied to the adsorption of CO on Pd(111)

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Abstract

We derive a variant of a density based embedded cluster approach as an improvement to a recently proposed embedding theory for metallic substrates (Govind *et al* 1999 *J. Chem. Phys.* **110** 7677; Klüner *et al* 2001 *Phys. Rev. Lett.* **86** 5954). In this scheme, a local region in space is represented by a small cluster which is treated by accurate quantum chemical methodology. The interaction of the cluster with the infinite solid is taken into account by an effective one-electron embedding operator representing the surrounding region. We propose a self-consistent embedding scheme which resolves intrinsic problems of the former theory, in particular a violation of strict density conservation. The proposed scheme is applied to the well-known benchmark system CO/Pd(111).

1. Introduction

The geometric and electronic structure of surfaces and adsorbate–substrate systems can routinely be calculated by modern quantum mechanical approaches. Continuous development of theoretical concepts and numerical improvement of existing algorithms allow for reliable simulations which have become an integral tool for the interpretation and microscopic understanding of many surface science experiments.

In general, two conceptually different theoretical approaches exist for electronic structure calculations of surfaces and bulk materials. In the first approach, the electronic Schrödinger equation (or Schrödinger-like variational equation for the density) is solved with respect to periodic boundary conditions. However, this supercell ansatz is currently restricted to Hartree–Fock (HF) and density functional theory (DFT). In Hartree–Fock, electron correlation is omitted by definition while in DFT the exact exchange–correlation functional is unknown. Despite recent developments in the construction of new functionals [1–3] and promising proposals of theories beyond Hartree–Fock and DFT including periodic boundary conditions [4, 5], no generally accepted theory exists which provides a well-defined treatment

of electron correlation with respect to periodic boundary conditions, in particular for systems characterized by a delocalized electronic structure.

In the second approach, a representative section of a surface, a cluster, is treated by either DFT or conventional quantum chemical methods [6–9]. The latter approach allows for a well-defined treatment of electron correlation, since taking the HF solution of the electronic Schrödinger equation as a starting point, a systematic hierarchy of approximations exists to eventually arrive at the numerically exact solution (complete configuration interaction). Furthermore, the calculation of electronically excited states via configuration interaction (CI) is straightforward [10–14] in contrast to conventional DFT, although some promising concepts also exist within time-dependent density functional theory and the GW approximation to the self-energy [15–22].

However, a cluster does not obey the translational symmetry of a surface or bulk material, since periodic boundary conditions are not generally applicable to explicitly correlated calculations. This is the well-known main drawback of the cluster approach. Nevertheless, some materials (such as halides and many oxides) exhibit a sufficiently localized electronic structure to be accurately treated by a reasonably small cluster. For these systems, supercell and cluster approaches yield virtually identical results if the same level of theory with respect to the treatment of electron correlation is applied. A necessary condition for this similarity turns out to be a proper embedding of the cluster. In ionic systems a proper embedding can easily be realized by a large array of point charges, which ensures the correct electrostatic potential within the crystal or at the surface. In contrast to this, a proper embedding of systems characterized by a delocalized electronic structure, such as metals, turns out to be far more difficult. Promising approaches have been reported such as ‘dipped adcluster’ embedding [23], and the pioneering cluster-in-cluster ansatz of Whitten *et al* [24–26] certainly offers a valuable perspective. However, the inherent lack of periodic boundary conditions remains, and convergence of properties with respect to cluster size still has to be considered as a severe drawback for systems exhibiting a delocalized electronic structure. Nevertheless, a variety of different embedding schemes have been proposed and successfully applied to systems characterized by completely different electronic structures [25, 27–42].

Recently, a new embedding theory has been proposed which combines the benefits of supercell and cluster approaches, and additionally allows for a reliable calculation of electronically excited states of adsorbates on metal surfaces [43–46].

In the present paper, we re-investigate this approach from a theoretical point of view and propose formal extensions to the existing theory. In particular, we investigate how specific approximations introduced in the current formalism can be improved. The formal analysis of the embedding theory will be presented in the first section of this paper. Subsequently, we will propose an important extension of the current theory concerning a self-consistent treatment of the total density. This extension includes a dynamical update of the total density, similar to the idea of Wesolowski and Warshel [34]. The formalism and its implementation have been introduced by one of us [47] and have subsequently been applied by Huang *et al* [48].

The performance of our new approach will be demonstrated by the calculation of adsorption energies of the benchmark system CO/Pd(111). Finally, we will provide future perspectives and an outlook to further improvements with respect to the generalization of the existing embedding theory.

2. Theory

In this section, we will summarize the status of the embedding theory as proposed in [43–46]. The analysis of the current formalism will reveal significant drawbacks of the original approach but will simultaneously demonstrate how to improve the existing concept.

The central idea of any embedding theory is the partitioning of the total system in (at least) two subsystems. The region of interest which might be an adsorption site on a surface or a defect in a crystal will be denoted as region I. This region should be treated as accurately as possible while the remainder of the system (region II) can be calculated using less accurate methods. Thus, region II is not of interest as such but only its influence on region I has to be considered. According to this approach, the system Hamiltonian \hat{H} is composed of the Hamiltonians of the two subsystems (\hat{H}_I, \hat{H}_{II}) and an interaction Hamiltonian \hat{H}_{INT} , respectively:

$$\hat{H} = \hat{H}_I + \hat{H}_{II} + \hat{H}_{INT}. \quad (1)$$

This definition furthermore implies a partitioning of the total energy, i.e.

$$E_{\text{tot}} = E_I + E_{II} + E_{INT}. \quad (2)$$

Thus, the interaction energy can be expressed as

$$E_{INT} = E_{\text{tot}}[\rho_{\text{tot}}] - E_I[\rho_I] - E_{II}[\rho_{II}], \quad (3)$$

where we introduce the total electron density of the system, ρ_{tot} , and the densities of the subsystems ρ_I and ρ_{II} , respectively. Of course, the total density should be the sum of the subsystem densities, i.e.

$$\rho_{\text{tot}}(r) = \rho_I(r) + \rho_{II}(r). \quad (4)$$

Now, the effective embedding operator acting on region I is defined by the functional derivative of the interaction energy with respect to the density in region I,

$$\hat{v}_{\text{emb}}(r) = \frac{\delta E_{INT}}{\delta \rho_I(r)} = \frac{\delta E_{\text{tot}}}{\delta \rho_I(r)} - \frac{\delta E_I}{\delta \rho_I(r)} - \frac{\delta E_{II}}{\delta \rho_I(r)}, \quad (5)$$

where the explicit dependence of the energies on the corresponding densities has been omitted for reasons of simplicity. Using the chain rule for functional derivatives results in the following expression:

$$\hat{v}_{\text{emb}}(r) = \int \frac{\delta E_{\text{tot}}}{\delta \rho_{\text{tot}}(r')} \frac{\delta \rho_{\text{tot}}(r')}{\delta \rho_I(r)} dr' - \frac{\delta E_I}{\delta \rho_I(r)} - \int \frac{\delta E_{II}}{\delta \rho_{II}(r')} \frac{\delta \rho_{II}(r')}{\delta \rho_I(r)} dr'. \quad (6)$$

Next, equation (4) can be inserted in equation (6) resulting in:

$$\begin{aligned} \hat{v}_{\text{emb}}(r) &= \int \frac{\delta E_{\text{tot}}}{\delta \rho_{\text{tot}}(r')} \frac{\delta(\rho_I(r') + \rho_{II}(r'))}{\delta \rho_I(r)} dr' - \frac{\delta E_I}{\delta \rho_I(r)} - \int \frac{\delta E_{II}}{\delta \rho_{II}(r')} \frac{\delta \rho_{II}(r')}{\delta \rho_I(r)} dr' \\ &= \int \frac{\delta E_{\text{tot}}}{\delta \rho_{\text{tot}}(r')} \left(\frac{\delta \rho_I(r')}{\delta \rho_I(r)} + \frac{\delta \rho_{II}(r')}{\delta \rho_I(r)} \right) dr' - \frac{\delta E_I}{\delta \rho_I(r)} - \int \frac{\delta E_{II}}{\delta \rho_{II}(r')} \frac{\delta \rho_{II}(r')}{\delta \rho_I(r)} dr' \\ &= \int \frac{\delta E_{\text{tot}}}{\delta \rho_{\text{tot}}(r')} \delta(r - r') dr' + \int \frac{\delta E_{\text{tot}}}{\delta \rho_{\text{tot}}(r')} \frac{\delta \rho_{II}(r')}{\delta \rho_I(r)} dr' \\ &\quad - \frac{\delta E_I}{\delta \rho_I(r)} - \int \frac{\delta E_{II}}{\delta \rho_{II}(r')} \frac{\delta \rho_{II}(r')}{\delta \rho_I(r)} dr' \\ &= \frac{\delta E_{\text{tot}}}{\delta \rho_{\text{tot}}(r)} - \frac{\delta E_I}{\delta \rho_I(r)} + \int \left(\frac{\delta E_{\text{tot}}}{\delta \rho_{\text{tot}}(r')} - \frac{\delta E_{II}}{\delta \rho_{II}(r')} \right) \frac{\delta \rho_{II}(r')}{\delta \rho_I(r)} dr'. \end{aligned} \quad (7)$$

In equation (7) all three densities $\rho_I(r)$, $\rho_{II}(r)$ and $\rho_{\text{tot}}(r)$ are used to calculate the embedding operator. From a self-consistent cluster calculation and from the density conservation as stated in equation (4), it is just possible to determine two densities at most. Therefore, it is necessary to introduce the following approximation as one possible choice at this point:

$$\left. \frac{\delta \rho_{II}(r')}{\delta \rho_I(r)} \right|_{r=r'} = 0. \quad (8)$$

Equation (8) states the densities of regions I and II to be linearly independent functions, implying that a variation of the electron density in region I does not affect the density attributed to the surrounding region II. Note that this approximation does not imply the neglect of interaction between the two regions, since the presence of the background density yields the effective embedding potential. However, the approximation introduced by equation (8) already implies that great care has to be taken in the construction of the background density. Since it will not be influenced by variations of the density in region I, it should be chosen as accurately as possible at the beginning of the calculation. This issue will be addressed in detail in section 4. The assumption of equation (8) leads to a neglect of the integral in equation (7), resulting in the following embedding operator:

$$\hat{v}_{\text{emb}}(r) = \frac{\delta E_{\text{tot}}}{\delta \rho_{\text{tot}}(r)} - \frac{\delta E_{\text{I}}}{\delta \rho_{\text{I}}(r)}. \quad (9)$$

The total energy and the energy of region I contain different contributions each of which can be expressed within DFT and resulting in the following functional form of the embedding operator [45, 46]:

$$\begin{aligned} \hat{v}_{\text{emb}}(r) &= \frac{\delta T_{\text{S}}[\rho_{\text{tot}}]}{\delta \rho_{\text{tot}}} - \frac{\delta T_{\text{S}}[\rho_{\text{I}}]}{\delta \rho_{\text{I}}} + \frac{\delta E_{\text{NE}}[\rho_{\text{tot}}]}{\delta \rho_{\text{tot}}} - \frac{\delta E_{\text{NE}}[\rho_{\text{I}}]}{\delta \rho_{\text{I}}} \\ &\quad + \frac{\delta E_{\text{XC}}[\rho_{\text{tot}}]}{\delta \rho_{\text{tot}}} - \frac{\delta E_{\text{XC}}[\rho_{\text{I}}]}{\delta \rho_{\text{I}}} + \frac{\delta J[\rho_{\text{tot}}]}{\delta \rho_{\text{tot}}} - \frac{\delta J[\rho_{\text{I}}]}{\delta \rho_{\text{I}}} \\ &= \frac{\delta T_{\text{S}}[\rho_{\text{tot}}]}{\delta \rho_{\text{tot}}} - \frac{\delta T_{\text{S}}[\rho_{\text{I}}]}{\delta \rho_{\text{I}}} + (V_{\text{NE}}^{\text{tot}} - V_{\text{NE}}^{\text{I}}) + (V_{\text{XC}}^{\text{tot}} - V_{\text{XC}}^{\text{I}}) + (V_{\text{H}}^{\text{tot}} - V_{\text{H}}^{\text{I}}). \end{aligned} \quad (10)$$

Here, T_{S} , E_{NE} , E_{XC} , J denote the kinetic, electron–nuclear attraction, exchange–correlation and Coulomb repulsion energy functionals, respectively.

In *ab initio* quantum chemical cluster calculations, Hartree–Fock (HF) theory serves as a starting point for more accurate calculations in which electron correlation effects are explicitly accounted for. Given the functional form of the embedding potential as an effective one-electron operator (cf equation (9)), it enters the HF-equations as an additive term to the Fock matrix, i.e.

$$\sum_{\nu} (F_{\mu\nu} + M_{\mu\nu}) C_{\nu,i} = \varepsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu,i}. \quad (11)$$

$F_{\mu\nu}$ and $S_{\mu\nu}$ denote the Fock and overlap matrix elements in the Gaussian atomic orbital basis, whereas ε_i and $C_{\nu,i}$ are the orbital energies and molecular orbital expansion coefficients for the i th molecular orbital, respectively. $M_{\mu\nu}$ is the matrix representation of the embedding operator \hat{v}_{emb} in the atomic orbital (AO) basis set, i.e.

$$M_{\mu\nu} = \langle \chi_{\mu} | \hat{v}_{\text{emb}} | \chi_{\nu} \rangle. \quad (12)$$

Details of the explicit implementation of the various terms in equation (9) can be found elsewhere [45, 46] and will not be discussed in the present paper.

However, one further approximation was introduced in previous studies and should be noted: the total density, ρ_{tot} , was evaluated only once at the beginning of an embedding calculation and was kept frozen (FR) during the self-consistent (SC) solution within region I for convenience, resulting in a partially self-consistent embedding potential, i.e.

$$\hat{v}_{\text{emb}}(r) = \left(\frac{\delta E_{\text{tot}}}{\delta \rho_{\text{tot}}(r)} \right)_{\text{FR}} - \left(\frac{\delta E_{\text{I}}}{\delta \rho_{\text{I}}(r)} \right)_{\text{(SC)}}. \quad (13)$$

Note, that in addition to all terms containing the total density, the kinetic energy contribution $\frac{\delta T_{\text{S}}[\rho_{\text{I}}]}{\delta \rho_{\text{I}}}$ was kept frozen as well. This approximation is indicated by the index in parenthesis ‘(SC)’ and was justified in our earlier studies [43, 44].

The frozen density approximation for $\rho_{\text{tot}}(r)$ might seem reasonable at first glance, since a sufficiently small region I might not severely modify the total density of the system. However, we will now demonstrate that it necessarily violates the density conservation introduced in equation (4).

In fact, equation (13) implies an imbalanced treatment of the potential arising from the total density and the potential due to region I, since only in the hypothetical case of an infinitely small region I does this equation result in the exact limiting case.

In the realistic case of a finite region I, this analysis reveals a dilemma of the current embedding theory according to the potential introduced in equation (13). In any embedding theory, a faithful treatment of the embedded system should be improved by an extension of the region I, which—as the region of interest—is treated as accurately as possible. Region I should not only be investigated at the currently highest level of theory (e.g. CCSD(T) or MRCISD), but also the cluster size representing region I should be as large as possible only limited by computational resources. However, a substantial spatial increase of region I is prohibited by the results of the preceding analysis. In other words, an increase of cluster size representing region I might not necessarily improve the description of the embedded system since the aforementioned conditions may not be fulfilled. In particular, equation (13) implies a violation of the density conservation as stated in equation (4). If the electron density in region II is not affected by a change of the density in region I, as equation (8) implies, and the total electron density is constant by definition according to equation (13), then equation (4) cannot be fulfilled since $\rho_{\text{I}}(r)$ is self-consistently updated (e.g. in a Hartree–Fock self-consistent field (SCF) scheme), while $\rho_{\text{tot}}(r)$ and $\rho_{\text{II}}(r)$ are constant by definition with respect to a variation of $\rho_{\text{I}}(r)$.

In order to solve this apparent dilemma, we introduce a refined embedding theory which partially removes the restrictions imposed by previous approaches and resolves the aforementioned contradiction. In fact, we keep the restriction of $\rho_{\text{II}}(r)$ being independent with respect to a variation of $\rho_{\text{I}}(r)$ (as stated above, this approximation is valid for the surface–adsorbate system discussed here), but we do not impose any restriction on the total electron density, $\rho_{\text{tot}}(r)$, i.e. the embedding operator is evaluated through:

$$\hat{v}_{\text{emb}}(r) = \left(\frac{\delta E_{\text{tot}}}{\delta \rho_{\text{tot}}(r)} \right)_{\text{SC}} - \left(\frac{\delta E_{\text{I}}}{\delta \rho_{\text{I}}(r)} \right)_{\text{SC}} . \quad (14a)$$

Note, that in equation (14) all terms are treated self-consistently except for the kinetic energy contribution $\frac{\delta T_{\text{S}}[\rho_{\text{I}}]}{\delta \rho_{\text{I}}}$. For comparison we will also investigate an embedding operator in which, in addition to $\frac{\delta T_{\text{S}}[\rho_{\text{I}}]}{\delta \rho_{\text{I}}}$, the kinetic energy term of the total density, i.e. $\frac{\delta T_{\text{S}}[\rho_{\text{tot}}]}{\delta \rho_{\text{tot}}}$, is kept frozen as well, resulting in the following embedding operator:

$$\hat{v}_{\text{emb}}(r) = \left(\frac{\delta E_{\text{tot}}}{\delta \rho_{\text{tot}}(r)} \right)_{\text{SC}} - \left(\frac{\delta E_{\text{I}}}{\delta \rho_{\text{I}}(r)} \right)_{\text{SC}} . \quad (14b)$$

The idea of a self-consistent update of all densities involved in an embedding scheme was proposed by Wesolowski and Warshel [34] and has been successfully applied in recent studies [33, 48].

Actually, a first approximation of the total electron density is evaluated in the first step of our embedding calculation, and is subsequently updated during the self-consistent solution within region I according to equation (4). Thus, $\rho_{\text{II}}(r)$ is calculated in the very first step of the iterative scheme using equation (4). In the subsequent execution of the iterative SC scheme, the total density (and all terms arising in the embedding potential corresponding to the total density, cf equation (10)) is updated iteratively. Therefore, density conservation according to equation (4) is inherently ensured by definition. Note that this update of the total density represents a significant step towards a fully self-consistent embedding scheme,

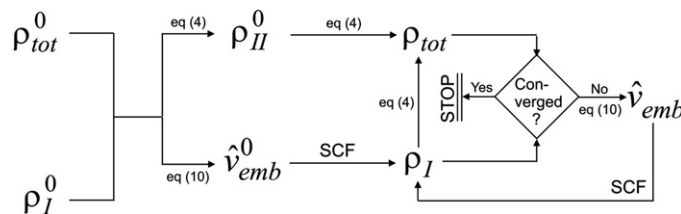


Figure 1. Schematic representation of a Hartree-Fock calculation within a self-consistent embedding scheme using a dynamically updated total density. SCF denotes a Hartree-Fock-SCF calculation. The equations for the construction of potentials and densities are denoted by equations (4) and (10), respectively.

since the restriction that terms containing the total density (half of all contributions to the embedding potential) are frozen is removed. In figure 1, we demonstrate the scheme of this refined embedding calculation opposed to the previously introduced theory. From a formal point of view, the main advantage consists of the strict electron density conservation.

In order to elucidate the consequences of this refined embedding scheme, we will present investigations on the benchmark system Pd(111)/CO which has been the subject of many investigations over recent years [49–58].

3. Details of calculations

3.1. DFT supercell calculations

In order to obtain the total electron density, $\rho_{\text{tot}}(r)$, of a system, the first step in an embedding calculation is a periodic supercell DFT calculation, for which a commercial version of the CASTEP program package [59] as implemented in Cerius² has been used¹. The Pd(111) surface was modelled by a three-layer slab containing eight atoms per layer. A three-layer slab was found to be sufficiently thick to give converged results for adsorption energies and geometries with respect to the number of layers used. One CO molecule was placed at the experimentally preferred fcc hollow site on one side of the slab simulating a coverage of 0.125 monolayers. The simulation cell was large enough ($5.52 \text{ \AA} \times 9.55 \text{ \AA} \times 16.00 \text{ \AA}$) to prevent an artificial interaction between adjacent periodic slab images normal to the Pd(111) surface. A full geometry optimization was performed for the adsorbed CO molecule, while the slab geometry was chosen to be identical to the experimental bulk lattice constant. Surface relaxation effects were found to be of minor importance for the properties of interest such as adsorption energies. In all calculations a plane wave cut-off energy of $E_{\text{cut}} = 700 \text{ eV}$ and a surface Brillouin zone sampling with nine special k -points was found to be sufficient to obtain accurate adsorption energies with an estimated maximum error of about 0.1 eV. Nonlocal norm-conserving pseudopotentials [60] were used to replace the nuclei and core electrons, and the PW91-GGA functional for exchange and correlation was chosen. All parameters of the calculations (supercell size, k -point sampling, plane-wave cut-off) have been subject to convergence studies. Within this model, an adsorption energy of $\Delta E_{\text{slab}}^{\text{DFT}} = -1.71 \text{ eV}$ and a linear adsorption geometry of the CO molecule were obtained. Experimental results of Guo *et al* [50] and Conrad *et al* [49] predict a lower binding energy of $E = -1.54$ and -1.47 eV . The internal CO distance was found to be $d(\text{C-O}) = 1.172 \text{ \AA}$ and the distance of the carbon molecule from the surface turned out to be $d(\text{C-surface}) = 1.362 \text{ \AA}$. This is in reasonable agreement with other theoretical and experimental data [49–58].

¹ Cerius² is provided by Accelrys Inc.

3.2. Embedded cluster calculations

After the total density ρ_{tot} has been obtained from a periodic DFT calculation, *ab initio* embedded cluster calculations were performed as the second step of our embedding approach. The smallest cluster to model the adsorption of CO at a fcc hollow site of a Pd(111) surface consists of three Pd atoms (Pd_3) and the CO molecule. For consistency with the periodic DFT calculations, the core electrons and nuclei were replaced by large core effective core potentials (ECP) [61]. For an accurate description of the valence electrons, a double-zeta basis set turned out to be sufficient [47]. The basis set superposition error (BSSE) was estimated by the counterpoise correction scheme of Boys and Bernardi [62] to be about 0.1 eV for interaction energies [44]. All calculations have been performed with a modified version of the HONDO quantum chemical program package [59]. For the calculation of adsorption energies, the HF and MP-*n* level of theory has been applied.

3.3. Embedding potential and local correction of the total DFT energy

As already discussed in previous publications, all contributions to the effective embedding potential as given by equation (10) can be calculated straightforwardly [43–46]. In particular, the evaluation of the kinetic energy potentials by application of the locally truncated conventional gradient expansion (CGE) has been shown to be a practical and sufficiently accurate approach.

Once an embedded cluster calculation has been performed in region I, the total embedding energy, $E_{\text{tot}}^{\text{emb}}$, is obtained according to equation (15)

$$E_{\text{tot}}^{\text{emb}} = E_{\text{tot}}^{\text{DFT}} + (E_{\text{I}}^{\text{ab}} - E_{\text{I}}^{\text{DFT}}), \quad (15)$$

where $E_{\text{tot}}^{\text{DFT}}$ denotes the total DFT energy of the preceding slab calculation. E_{I}^{ab} and $E_{\text{I}}^{\text{DFT}}$ are defined as the *ab initio* and DFT energy in region I in the presence of the embedding potential. Again, details of the derivation of equation (15) and the explicit calculation of the various terms can be found elsewhere [43–46]. Note, that equation (15) represents a local correction to periodic density functional theory within region I.

4. Results

As already mentioned in section 2, the refined embedding theory introduced in the present paper removes the limitation of our former approach of $\rho_{\text{tot}}(r)$ being constant irrespective of a variation of $\rho_{\text{I}}(r)$. This approach is favourable from a formal point of view, since it ensures density conservation as implied by equation (4) and does not result in contradictions pointed out in section 2. However, $\rho_{\text{II}}(r)$ is frozen by definition as implied by equation (8) and can be obtained as the difference of the total density and the density in region I, which have to be determined before the embedded calculation, according to equation (4). Naturally, the question arises of which density $\rho_{\text{II}}(r)$ should be used in actual applications. One possible choice would be to calculate the density of region II according to equation (16)

$$\rho_{\text{II}}(r) = \rho_{\text{tot}}^{\text{DFT}}(r) - \rho_{\text{I}}^{\text{DFT}}(r). \quad (16)$$

Here, $\rho_{\text{I}}^{\text{DFT}}(r)$ is obtained by a DFT cluster calculation within region I in the presence of an embedding potential in which all contributions containing the total density are kept frozen (cf equations (10) and (13)). It has been demonstrated, that such a DFT-in-DFT embedding scheme results in a reasonably accurate representation of $\rho_{\text{I}}^{\text{DFT}}(r)$ when compared with $\rho_{\text{tot}}^{\text{DFT}}(r)$ within region I [44]. Thus, application of equation (16) in order to calculate $\rho_{\text{II}}(r)$ will result in a faithful representation of the electron density in region II.

Table 1. Adsorption energies of CO/Pd(111). The different embedding schemes are defined in equations (14a), (14b) and (13).

Embedding scheme	$E(\text{HF})$ (eV)	$E(\text{MP-2})$ (eV)	$E(\text{MP-4})$ (eV)
DTD-14a	-1.44	-1.63	-1.79
DTD-14b	-1.84	-1.94	-2.09
FTD-13 [43, 44]	-2.13	-1.42	-1.55
Experiment (eV) [49, 50]		-1.47 to -1.54	

Note, that $\rho_{\text{II}}(r)$ is calculated only once and subsequently used in a self-consistent update of the total density. Therefore, in each iteration k of a Hartree–Fock self-consistent field calculation, the total density is updated via

$$\rho_{\text{tot}}(r)^k = \rho_{\text{II}}(r) + \rho_{\text{I}}(r)^k \quad (17)$$

and all corresponding terms of the embedding operator are updated. In previous calculations using the embedding operator of equation (13), the kinetic energy potential arising from region I was never subject to a self-consistent embedding treatment, but was evaluated once at the beginning of an embedded cluster calculation using an *ab initio* electron density obtained from a bare, i.e. non-embedded, Hartree–Fock cluster calculation. This approximation was rationalized in recent publications [43–46] and will not be discussed further in this paper.

Table 1 contains adsorption energies for the CO/Pd(111) system at different levels of theory. In all calculations the PW91 exchange–correlation functional and the locally truncated conventional gradient expansion for the kinetic energy (CGE) have been used in the corresponding terms of the embedding potential. In general, the embedding operator containing a dynamic total density (DTD-14a) as defined in equation (14a) is used. However, table 1 also contains results where all kinetic energy terms in the embedding potential are kept frozen (DTD-14b), equation (14b). For comparison, we also include results obtained by the frozen total density (FTD-13) embedding operator as defined by equation (13) and as used in previous studies [43, 44].

On the MP-4 level of theory, the use of embedding operators as defined by equation (14b) does not yield satisfactory results. Evidently, the self-consistent calculation of $\frac{\delta T_{\text{S}}[\rho_{\text{tot}}]}{\delta \rho_{\text{tot}}}$ is mandatory for a faithful description of the embedding potential (equation (14a)). Given the fact that the adsorption energies are not corrected for the BSSE, an overestimation of the adsorption energy of about 0.1–0.2 eV can be expected. Therefore, the results obtained within our refined embedding theory are in very good agreement with experimental data.

However, the question arises whether a complete self-consistent treatment of the embedding operator in which also $\frac{\delta T_{\text{S}}[\rho_{\text{I}}]}{\delta \rho_{\text{I}}}$ is dynamically updated further improves the results obtained. Unfortunately, this is not the case. While the inclusion of this term in the former, partially self-consistent, embedding theory (FTD-13) resulted in severe convergence problems, the situation is improved in the refined theory (DTD-14a). However, the results obtained are not in agreement with the experimental data. The calculated CO binding energy at the MP-2 level of theory is strongly underestimated ($E = -0.73$ eV). This fact underlines the sensitivity of kinetic energy terms in the embedding potential with regard to the actual details of the calculation.

In order to further clarify this point, we investigated the influence of the kinetic energy functional used. Table 2 contains adsorption energies using the CGE up to first and second order, respectively. In the former case, only the Thomas–Fermi (TF) functional as the leading term of the expansion is included, while in the latter case (CGE), gradient corrections are applied by the use of the von Weizsäcker term. Interestingly, the refined embedding theory

Table 2. Adsorption energies of CO/Pd(111). Results obtained with different kinetic energy functionals in embedding schemes defined in equations (14a) and (13).

Embedding scheme	$E(\text{HF})$ (eV)	$E(\text{MP-2})$ (eV)	$E(\text{MP-4})$ (eV)
DTD-14a TF only	-1.43	-1.78	-1.93
DTD-14a CGE	-1.44	-1.63	-1.79
FTD-13 TF only	-1.77	-2.28	-2.37
FTD-13 CGE	-2.13	-1.42	-1.55

Table 3. Adsorption energies of CO/Pd(111). Comparison of two embedding schemes using different densities $\rho_{\text{II}}(r)$ (equation (16); equation (18)).

$\rho_{\text{II}}(r)$	$E(\text{HF})$ (eV)	$E(\text{MP-2})$ (eV)	$E(\text{MP-4})$ (eV)
DTD-14a (equation (16))	-1.44	-1.63	-1.79
DTD-14a (equation (18))	-2.10	-1.55	-1.69

(DTD-14a) is much less sensitive to the actual choice of the kinetic energy functional as compared to the partially self-consistent embedding scheme (FTD-13). The MP- n energy difference between calculations using the Thomas–Fermi functional and calculations using the CGE within a completely self-consistent embedding operator is (with $\Delta E = 0.15$ eV) much smaller than the difference using the partially self-consistent embedding operator ($\Delta E = 0.8$ eV). This relative insensitivity can be regarded as a further advantage of the current scheme, which seems to be more robust with respect to model parameters.

An important feature of the completely self-consistent embedding scheme is the choice of $\rho_{\text{II}}(r)$. In order to elucidate how the explicit construction of $\rho_{\text{II}}(r)$ influences the results obtained, we performed alternative calculations using the following equation for the density in region II:

$$\rho_{\text{II}}(r) = \rho_{\text{tot}}^{\text{DFT}}(r) - \rho_{\text{I}}^{\text{HF}}(r) \quad (18)$$

i.e. $\rho_{\text{II}}(r)$ is calculated by using a Hartree–Fock density in region I, again obtained under the presence of an embedding potential as defined by equation (10). The results for the CO binding energy are shown in table 3.

Although $\rho_{\text{II}}(r)$ is calculated using different evaluation methods for $\rho_{\text{I}}(r)$, the obtained MP- n results are in good agreement with the results using equation (16) and the experimental results. The important feature in the determination of $\rho_{\text{II}}(r)$ is therefore to use an embedded density $\rho_{\text{I}}(r)$. This is confirmed by the results using a bare cluster density obtained from a non-embedded DFT calculation to calculate $\rho_{\text{II}}(r)$. Such an approach is not expected to give a reasonable representation of $\rho_{\text{II}}(r)$, since the density in region I will strongly differ depending on the presence or absence, respectively, of an embedding potential. Thus, if such a bare DFT cluster density is used to construct $\rho_{\text{II}}(r)$, the CO binding energy of $E(\text{MP-2}) = -3.79$ eV is strongly overestimated as compared with experiment. Although such a scheme has been proposed in a recent study [48], our results strongly discourage the use of a bare cluster density to calculate $\rho_{\text{II}}(r)$.

5. Conclusions

In this paper we report on a refined embedding theory in which virtually all terms are subject to a self-consistent treatment, only excluding $\frac{\delta T_{\text{S}}[\rho_{\text{I}}]}{\delta \rho_{\text{I}}}$ from a dynamical update. We demonstrate that this new scheme not only removes a formal inconsistency of our previous approach,

but also yields adsorption energies for the benchmark system CO/Pd(111) which are in good agreement with experimental data. Nevertheless, further improvements of the theory are still possible. Note, that even in our new scheme the electron density of region II is kept frozen during an embedding calculation. This can be regarded as a drawback of the current approach and work is in progress to lift this approximation with a perspective of a completely self-consistent embedding potential including all densities. Such a scheme has been proposed recently [47], and will be summarized in a forthcoming publication [63].

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