Self-Consistent Density-Functional Embedding: a Systematic Approach for Density Functionals

Uliana Mordovina,1,∗ Teresa E. Reinhard,1 Heiko Appel,1 and Angel Rubio1,2
1Max Planck Institute for the Structure and Dynamics of Matter, Center for Free Electron Laser Science, 22761 Hamburg, Germany
2Center for Computational Quantum Physics (CCQ), Flatiron Institute, 162 Fifth Avenue, New York NY 10010, USA
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A frequently found complaint about popular density-functional approximations is the lack of a systematic path how to improve results obtained with a selected functional. In the present work, we introduce a Self-Consistent Density-Functional Embedding technique, which allows to improve a chosen exchange-correlation functional in a systematic way. Our method adopts ideas from other embedding approaches and combines them with the scheme of density inversion methods, that are based on the rigorous relation of density and potential in density functional theory. With our approach, convergence to exact results can be achieved by increasing the size of the embedded system. While this implies to face exponential cost with the size of the embedded system, we find that already for small embedded fragments accurate results can be reached. We illustrate our approach for molecular bond stretching and demonstrate that it reproduces the known steps and peaks that are present in the exact exchange-correlation potential.

I. INTRODUCTION

Over the past decades, Density Functional Theory (DFT) has become a well established and successful method able to accurately describe molecular and condensed matter systems. One reason for its success can be attributed to its computational efficiency as all physical observables $O[n]$ of interest are functionals of the ground-state density $n(r)$ instead of the many-body wave function $\Psi$. The most popular technique to find the density of the system accurately is the Kohn-Sham (KS) DFT, where the density of the full interacting system is computed via an auxiliary non-interacting system. All interactions and correlations of the interacting system are mimicked by the so-called exchange-correlation potential $v_{xc}[n]$ which can be approximated in many different ways. A remaining challenge is to find the functionals describing the other wanted observables $O[n]$.

Despite its efficiency, there are still open issues in DFT which need to be addressed. One of the big issues is that, once a self-consistent density has been found and an approximate functional for a certain observable $O[n]$ has been selected, a pathway to systematically improve the obtained results is missing.

Another issue with DFT is that, although significant progress in functional development over the years has been achieved, approximate DFT functionals usually still struggle to describe systems with strongly correlated electrons. The dissociation limit of the $H_2$ molecule is a good example for a simple system that is not easy to describe with commonly used approximate DFT functionals. The functionals that are optimized to be able to mimic the dissociation of $H_2$ struggle to describe other physical systems.

There are alternative methods that are able to describe strongly correlated electrons accurately. One big group are wave function methods, such as full configuration interaction (FCI) methods and density-matrix-renormalization group (DMRG). These methods, although becoming more and more efficient, struggle with the problem of having to store the full (approximate) wave function and thus are only able to describe relatively small systems.

A pathway to use accurate (wave-function) methods on a larger scale is provided by embedding theories. The general idea behind embedding consists of dividing a system into one or more fragments of interest and an environment, which is then considered only indirectly. With this partition the need of performing an expensive calculation on the full system is circumvented. An established group of embedding theories are various density-functional embedding methods that have been successfully applied to a large range of complex systems. They provide ways of calculating a system which is weakly bounded to an environment by representing the environment by an external field. Opposed to that, embedding methods such as dynamical-mean-field theory (DMFT) and density-matrix-embedding theory (DMET), and density-embedding theory (DET) consider correlations between system and environment more explicitly and, thus, are successful in describing systems with strongly correlated electrons. In the latter two methods, only a part of the system is described accurately while the rest of the system is described with a lower level calculation. Here, the challenge is the connection between the high-level and the low-level calculation.

All mentioned embedding methods are tailored to describe the behavior of the fragments accurately. Opposed
to that, we use in the present work the embedding idea to improve our large scale description of the full system by including insights from small fragments. To this end we introduce a feedback algorithm, which combines embedding approaches with density inversions based on the one-to-one correspondence of density and potential in exact DFT. This results in a self-consistent density-functional embedding (SDE) technique, which allows to explicitly construct a family of novel density functionals with increasing accuracy. In our method, the global Kohn-Sham system is self-consistently optimized by including findings from accurate wave functions for different fragments. Once the optimal Kohn-Sham system is obtained, we gain information about observables from those interacting fragment wave functions.

The paper is organized as follows. In section II we introduce the proposed SDE method step by step. In section III we present the Hamiltonian for two electrons in a heteroatomic model system in one and two dimensions, which we use to benchmark our approach. The results for the energy and the Kohn-Sham potential of the introduced systems are shown in section IV and our findings are summarized in section V.

II. THEORY

The fundamental idea of the SDE approach is to improve the KS description of a system by including results from wave function methods, thus being able to describe strongly correlated systems. By dividing the system into small parts, which we from now on call fragments or impurities, and solving each of these parts independently, the calculation becomes feasible even for big system sizes.

The SDE method is depicted schematically in Fig. 1. It consists of the following parts, to each of which we will assign a distinct subsection:

1. The full system is described in terms of its ground-state density \( n(r) \) by means of KS DFT. The foundations of KS DFT are given in subsection II.A.

2. In SDE, the system has to be divided into fragments. Our kind of partition differs significantly from e.g. partition DFT[33, 34] and we will introduce our ‘continuous partition’ in subsection II.B.

3. For each impurity, the full system is projected onto an embedded system, where the impurity is embedded into an effective bath. In this paper, the choice for the projector is based on the DMET approach, which we explain in detail in subsection II.C.

4. For each impurity, an accurate calculation is performed with a wave-function method. The impurity wave functions are then used to calculate accurate densities and other properties on the impurity (see subsection II.D).

5. Finally, accurately calculated properties of the fragments are used to improve the KS description of the full system. This procedure is done in a self-consistent manner and we explain the algorithm in subsection II.E.

As we divide our system into fragments in real space, we will, for the sake of convenience, consider only systems that are discretized on a real space lattice throughout the paper.

A. Density Functional Theory

The mathematical foundation of ground-state DFT is the Hohenberg-Kohn theorem [1]. This theorem states, that there is a one-to-one correspondence between the external potential \( v_{\text{ext}}(r) \) of a given system and its ground-state wave function \( |\Psi\rangle \), as well as there is a one-to-one correspondence between the ground-state wave function of this system and its ground-state density \( n(r) \). This implies that all observables \( O \) of a many-body system...
are uniquely determined by its ground-state density, although the functionals $\mathcal{O}[n]$ themselves are in general unknown. Specifically, when trying to find a functional for the ground-state energy $E[n]$, the kinetic energy contribution $T[n]$ of this functional is the most difficult part and all direct approximations are so far insufficient. Although difficult to approximate directly in the interacting system of interest, there is a method to indirectly approximate this term through the KS construction [2].

This construction is based on the Hohenberg-Kohn theorem, from which follows that for any interacting system there exists one and only one auxiliary non-interacting system with local multiplicative potential, which has the same density, but different ground-state wave function and external potential.

Based on this connection, the ground-state density of an interacting system is found by solving the uncoupled one-body KS equations (atomic units are used throughout the paper)

\[
\left(-\frac{\nabla^2}{2} + v_S(r)\right) \varphi_j(r) = \varepsilon_j \varphi_j(r), \tag{1}
\]

\[
v_S[v_{\text{ext}}, n](r) = v_{\text{ext}}(r) + v_{\text{Hxc}}[n](r). \tag{2}
\]

The ground state of the auxiliary KS system is given by a Slater determinant built from the orbitals $\varphi_i(r)$, from which the kinetic energy (of the non-interacting system) can be obtained in a straightforward manner. The term $v_S(r)$ is the KS potential. It includes not only the external potential of the interacting system $v_{\text{ext}}(r)$ but also an additional term, the Hartree-exchange-correlation potential $v_{\text{Hxc}}[n](r)$ that accounts for the missing interactions and the kinetic correlations.

In the KS scheme, $v_{\text{Hxc}}[n](r)$ is the only term which has to be approximated. Hence, the two important goals in KS DFT are to find an accurate approximation for this mapping and then to describe the observables of interest, such as the energy.

The energy and other observables can, but don’t have to be obtained from the Hartree-exchange-correlation potential. Within our approach, we will provide an algorithm to find the mapping $v_{\text{Hxc}}[n](r)$ but calculate observables in a different manner as will be explained in section IID.

**B. Continuous partition**

We continue by considering the problem of dividing the full problem into fragments. Generally, the fragments have to cover the full system and should be selected small enough to be calculated with required accuracy.

In embedding approaches like subsystem DFT [22] and also in the framework of partition DFT [32], the system is divided into non-overlapping fragments, which are weakly bounded to one another. In other words, the partition is dictated by density distribution and correlations within the system and cannot be chosen arbitrarily. Therefore, those approaches are applicable to a small range of (weakly correlated) systems.

In DMET [26–28] the system is also divided into non-overlapping fragments, which are called impurities. The partition itself can be chosen arbitrarily, as particle transfer between impurity and the rest of the system is possible within this approach. The size of the fragments is dictated mostly by the correlation length in the system [26]. The amount of correlation, which can be described with the DMET method is limited by the size of the impurity. Thus, by increasing the impurity size a convergence towards the exact solution can be achieved, which makes the method systematically improvable. However, in DMET, dividing the system into non-overlapping fragments causes artificial discontinuities in local observables [31], which we would like to avoid.

In SDE, we include correlations as in DMET (see section IID) and we also introduce a partition that guarantees that all impurities connect smoothly to one another. We define a continuous partition, where the system is covered by overlapping impurities as is depicted in Figure 2. In practice, we sweep through the system by just going one site forward for each impurity calculation. Then, only the physical properties of the centering site are taken into account when considering local observables. The upper image (a) shows the partition in 1D, whereas the lower image (b) illustrates the partition in 2D. Projections $P_1$ onto embedded systems as well as effective bases depicted by different kinds of crosses are explained in section IID. This partition procedure can be extended to 3D in a straightforward manner (not shown).
have an intrinsic discontinuity (due to discretization of the real space) and our partition procedure is constructed such that the local observables remain as continuous as they can possibly be on a real space lattice. By selecting the lattice spacing appropriately, the accuracy can then be improved to reach the desired accuracy. In practice, this has to be balanced with the computational cost as for any real-space method.

C. Projection onto the embedded system

Having decided on how to divide the system into impurities, we now treat each impurity separately and find an effective description for the corresponding embedded system (see Figure 1). We want the embedded system to be such that it describes the physics on the impurity as accurately as possible. As depicted in Figure 1, we have to project the full system onto an embedded system for each impurity.

Out of a manifold of possible projections [21][22][23][24] we adopt here the the projection used in DMET [20][25] as it provides an efficient way of including static correlations between impurity and the rest of the system, which we call bath from now on.

The DMET method can be understood as a complete active space (CAS) calculation under the assumption that the impurity basis functions are always in the active space. What then remains to be found are the orbitals that build up the remaining part of the active space.

We are solving a system with the general Hamiltonian \( \hat{H} \) which includes one-particle terms, accounting for the kinetic energy and the external potential of the system, and two-particle terms describing the electron-electron interaction. In the following, we will denote the number of lattice sites of our real-space basis by \( N \) and the number of impurity lattice sites by \( N_{\text{imp}} \).

The ground state wave function of \( \hat{H} \) can be exactly split up as [26]

\[
|\Psi\rangle = \sum_{i}^{4^{N_{\text{imp}}}} \Sigma_{i} |A_{i}\rangle |B_{i}\rangle = \sum_{i}^{4^{N_{\text{imp}}}} \Sigma_{i} |A_{i}\rangle |\tilde{B}_{i}\rangle , \tag{3}
\]

Here, the \( |\tilde{A}_{i}\rangle \) (which in Figure 1 are depicted in orange) are the many body states located on the impurity and the \( |\tilde{B}_{i}\rangle \) (which in Figure 1 in the middle are depicted in turquoise) are defined on the bath.

To project the bath states onto a basis which is optimized with respect to the interaction of the bath with the impurity, we use the Schmidt decomposition [26]. The wave function is written in terms of many-body states \( |A_{i}\rangle |B_{i}\rangle \), where \( \Sigma_{i} \) is a diagonal matrix containing the singular values of the decomposition. The number of states needed to describe the wave function in this new basis is \( 4^{2-N_{\text{imp}}} \) opposed to the \( 4^{N} \) basis functions needed to set up the full Fock space of the problem.

In order to write the exact decomposition Eq. (3) explicitly, the wave function \( |\Psi\rangle \) has to be known which makes it unfeasible for realistic systems. Thus, the projection has to be obtained from an approximated wave function. In practice, the bath orbitals \( |B_{i}\rangle \) are obtained from a non-interacting system described by a Slater determinant \( |\Phi\rangle \).

Similar to the interacting system, we split up the Slater determinant into impurity and bath like in Eq. (3). For any Slater determinant, it can be shown [28] that this equation can then further be decomposed as (see Figure 3)

\[
|\Phi\rangle = \sum_{i,l}^{4^{N_{\text{imp}}}} \Phi_{i,l} |A_{i}\rangle |B_{l}\rangle + \sum_{i}^{4^{N-2N_{\text{imp}}}} |\tilde{B}_{i}\rangle . \tag{4}
\]

Here, the embedding part and the environment part do not interact with each other. Hence, in order to describe the physics on the impurity, only the embedding part of the full system has to be considered.

The two contributions in the embedding part, \( |A_{i}\rangle \) and \( |B_{l}\rangle \), on the other hand are fully correlated, and also particle transfer between \( |A_{i}\rangle \) and \( |B_{l}\rangle \) is possible. From the decomposed Kohn-Sham Slater determinant, we define a projection

\[
P = \sum_{i,l}^{4^{N_{\text{imp}}}} |A_{i}\rangle |B_{l}\rangle \langle B_{l}| |A_{i}| \tag{5}
\]

Which, applied to the original Hamiltonian \( \hat{H} \) yields

\[
P^{\dagger} \hat{H} P = \hat{H}_{\text{emb}} \tag{6}
\]

The Hamiltonian \( \hat{H}_{\text{emb}} \) now approximately describes the physics on the impurity and the interaction of the bath with the impurity. Its ground state can be calculated accurately with wave-function based methods.

Note that, while the projection \( P \) is approximated, as it is built from a Slater determinant, we apply it to the
exact Hamiltonian \( \hat{H} \) including interactions. Therefore, also the embedding Hamiltonian \( \hat{H}_{\text{emb}} \) includes interactions.

The difference between the projector in SDE and DMET is the choice of the underlying mean-field system. While in the DMET scheme, any Slater determinant can be chosen, we use the KS Slater determinant to obtain the projection. This makes our calculation of the full system in principle exact, as the KS Slater determinant reproduces the density of the interacting system and, hence, is sufficient to obtain all other observables (knowing their functionals \( O[\hat{n}] \)). We will also use the one-to-one relation between ground-state density and ground-state wave function to improve the projection, which we explain in the section IIE.

### D. Impurity calculation

Given a projection, we obtain the embedding Hamiltonian \( \hat{H}_{\text{emb}}^i \) for each impurity \( i \) as described in section [II C] and then diagonalize it to obtain the embedding wave function \( |\Psi_{\text{emb}}^i \rangle \) of this embedded system.

In the present work, we use exact diagonalization (ED) to solve for the ground-state wave function of the embedded system. We emphasize that also other solvers, such as DMRG [16, 37, 38], coupled cluster [39–41], selective CI approaches [42], or Monte-Carlo methods [43, 44] can be used for the impurity calculation.

The correlated embedding wave functions can then be used to calculate the energy of the full system \( E \) or any other non-local local observable. As described in reference [27], the energy of the full system \( E \) can be approximated as a sum of impurity energies, which are calculated by taking a partial trace of the corresponding embedding density matrix \( \hat{\rho}_{\text{emb}}^i \). As in the SDE approach for each impurity \( i \) only one site \( \alpha_i \) is considered for obtaining properties of the full system (see section [II E]), we adopt the energy formula from reference [27] to

\[
E = \langle \hat{H} \rangle \simeq \sum_{i}^{N} E_{\alpha_i} = \sum_{i}^{N} \text{Tr}_{\text{CAS} - \alpha_i} \left( \hat{\rho}_{\text{emb}}^i \hat{H}_{\text{emb}}^i \right). \tag{7}
\]

The formula above can be applied to any other observable. Thus, we circumvent the usual problem in DFT of finding explicit functional dependence \( O[\hat{n}] \) between an observable of interest \( O \) and the density \( \hat{n} \) by simply using the embedding wave functions instead of the density.

Before moving on to improving the KS description of the full system, we have to add an additional constrain to the impurity calculations. As in DMET [28] or partition DFT [41], we have to make sure that, when patching the system back together, we retain the correct particle number \( \mathcal{N} \) in the full system

\[
\langle \mathcal{N} \rangle - \mathcal{N} = 0. \tag{8}
\]

Following reference [28], we achieve this by adding and self-consistently optimizing a chemical potential \( \mu \) to the embedding Hamiltonian of each impurity

\[
\hat{H}_{\text{emb}}^i \rightarrow \hat{H}_{\text{emb}}^i + \mu \sum_{\alpha \in \mathcal{N}_{\text{imp}}} \hat{n}_{\alpha}, \tag{9}
\]

where \( \hat{n}_{\alpha} \) denotes the density operator on site \( \alpha \) and the index \( \alpha \) runs over all impurity sites. The constant \( \mu \) in Eq. (9) is added only to the impurity part of the embedding Hamiltonian in order to achieve a correct particle distribution between impurity and environment. In other words, the chemical potential is a Lagrange multiplier, which assures that the constraint in Eq. (8) is fulfilled.

### E. Self-consistency

A remaining question is how to improve the KS description of the full system with correlated embedding wave functions. From the embedding wave functions, we calculate the density \( \hat{n}_{\text{emb}}^i \) of the embedded system \( i \). From the Hohenberg-Kohn theorem it follows that in real space to every interacting density \( \hat{n}_{\text{emb}}^i \) there belongs a local KS potential \( \hat{v}_{\text{ext}, \text{emb}}^i = \hat{v}_{\text{ext}}^i + \hat{v}_{\text{Hxc,emb}}^i \) with an identical non-interacting density.

The Hartree-exchange-correlation potential \( \hat{v}_{\text{Hxc}} \) for
each embedded system can be obtained either by analytical [45] or numerical inversion [46][48], or with any robust minimization as in DMET [28].

We represent the global density and potential on each site $\alpha_i$ by their value obtained in the corresponding embedded system $i$

$$n(\alpha_i) = n_{\text{emb}}^i(\alpha_i), \quad \hat{v}_{\text{Hxc}}(\alpha_i) = \hat{v}_{\text{Hxc, emb}}(\alpha_i). \quad (10)$$

This yields the new KS Hamiltonian $\hat{h} + \hat{v}_{\text{Hxc}}$, which is then used to calculate a new set of projections $P_i$. This is done until convergence (see algorithm in Figure 4).

Eventually, we obtain an accurate density and KS potential for the considered systems as well as for observables, which are calculated with embedding wave functions as described in Eq. (7).

The SDE algorithm can be improved systematically by increasing the impurity size and it converges to the exact solution.

III. $H_2$ IN ONE AND TWO DIMENSIONS

The SDE approach so far is valid for all closed systems that can be represented by a time independent Schrödinger equation. In order to benchmark our method and to show its efficiency, we describe the two-electron bond stretching of a heteroatomic molecule in one and two dimensions (see Fig. 5).

We model this system with the following Hamiltonian [49] on a 1D/2D real-space lattice [50]

$$\hat{H} = -\frac{1}{2}\Delta x^2 \sum_{i,\sigma} \left( \hat{c}_{i+1,\sigma} \hat{c}_{i,\sigma} + \hat{c}_{i,\sigma} \hat{c}_{i+1,\sigma} - 2\hat{n}_{i,\sigma} \right) + \sum_{i,\sigma} v_{i,\text{ext}} \hat{n}_{i,\sigma} + \sum_{i,j,\sigma,\sigma'} \frac{\hat{n}_{i,\sigma} \hat{n}_{j,\sigma'}}{2\sqrt{(\Delta x (i-j))^2 + \alpha}}. \quad (11)$$

where $\hat{c}_{i,\sigma}^\dagger$ and $\hat{c}_{i,\sigma}$ are the usual creation and annihilation operators of an electron with spin $\sigma$ on lattice site $i$ and $\hat{n}_{i,\sigma} = \hat{c}_{i,\sigma} \hat{c}_{i,\sigma}$ is the corresponding density operator. In 2D the index $i$ becomes a double index with

$$i \rightarrow (i_x, i_y)$$

$$i + 1 \rightarrow (i_x + 1, i_y), (i_x, i_y + 1)$$

$$i - j \rightarrow (i_x - j_x)^2 + (i_y - j_y)^2 \quad (12)$$

The lattice spacing $\Delta x$ is determined by the box size $L$ in direction $x$ and the number of lattice points $N$ and as external potential we employ a double well potential $v_{\text{ext}}$.

The first part of the Hamiltonian takes into account the kinetic energy of the molecule by means of a next-neighbors hopping term. The second term in Eq. (11) is the external potential which mimics the ions of the molecule and depends on the considered dimension. In the one dimensional case, the external potential on each point is given by

$$v_{i,\text{ext}}^{1D} = -\frac{z_1}{\sqrt{(x_i - \frac{\Delta x}{2})^2 + \alpha}} - \frac{z_2}{\sqrt{(x_i - \frac{\Delta x}{2})^2 + \alpha}} + \frac{z_1 z_2}{2\sqrt{(d^2 + \alpha)}}$$

with $x_i = \Delta x (i - \frac{N_x}{2})$. The numbers $z_1$ and $z_2$ determine the depth of each well respectively. In our case they take values between 0 and 2 and we will characterize the potential by their difference $\Delta z = z_1 - z_2$. In the two-dimensional case the external potential takes the form

$$v_{i,\text{ext}}^{2D} = v_{i,\text{ext}}^{1D} \cdot \frac{1}{\sqrt{\Delta x^2 \left(i_y - \frac{N_y}{2} - \frac{1}{2}\right)^2 + \alpha}}$$

accounting for both, the charge distribution of the ions in $x$ and $y$ direction.

The third term of the Hamiltonian takes into account the interaction of the electrons. We model the electronic interaction as well as the core potentials by the soft-Coulomb interaction, which avoids the singularity at zero distance. In order to do so, we include a softening parameter $\alpha = 1$.

One reason for choosing a problem that only includes two electrons is that for this example we can analytically invert the density $n$ of the problem to yield the Hartree-exchange-correlation potential $\hat{v}_{\text{Hxc}}$. As the ground state of a two-electron problem is always a singlet it is valid that

$$n(r) = 2 |\varphi_0(r)|^2. \quad (15)$$

Inserting this property into the Kohn-Sham equations Eq. (1) yields [45]

$$\hat{v}_{\text{Hxc}}(r) = \frac{1}{2} \nabla^2 \sqrt{n(r)} + \epsilon_0. \quad (16)$$

The formula above is given in the real space domain but it can be applied to any quantum lattice system, as there is a one-to-one correspondence between density and potential for those systems [51]. The exact inversion formula
can therefore be applied to every embedded system with two electrons, hence, to every embedded system resulting from our model.

IV. RESULTS

A. Dissociation of the $H_2$ molecule

Common DFT functionals like the local density approximation (LDA [2]), or generalized gradient approximations (GGA [3, 4]) fail to describe the dissociation limit of the $H_2$ molecule. This failure is attributed to the so-called static correlation error, which is related to fractional spin states [14]. These states arise, when we consider the parts into which the closed-shell $H_2$ molecule dissociates. One half of the molecule is given by an $H$ atom with half of electron with spin up and half of electron with spin down. For the exact functional this artificial atom has the same energy as the usual $H$ atom with one electron with either spin up or spin down [22] so that the total energy of the dissociated $H_2$ is twice the energy of an $H$ atom. Common approximate functionals, however, violate this condition and predict wrong energies for fractional spin states resulting in the wrong dissociation limit.

Although there are methods such as the strictly-correlated electron functional [9], functionals based on the random phase approximation (RPA) [8, 53] and on GW combined with RPA [54], or the exchange-correlation potential by Baerends et al. [55, 56], which were designed to overcome these issues, modeling the bond stretching of $H_2$ remains a challenging test for any new functional.

In Fig. 6, we show how our SDE methods performs in this test case. We plot the ground-state energy of the Hamiltonian described in section IV calculated with exact diagonalization, and compare with energies obtained with one dimensional LDA-DFT [57] and with SDE. Our method quantitatively agrees with the exact solution at a much lower cost than the exact diagonalization technique. While the costs grow exponentially with the number of orbitals $N$ in the exact case ($4^N$), in the SDE method, only the costs of impurity calculations are growing exponentially with the impurity size. The costs for the underlying mean field calculation are growing quadratically with the amount of orbitals, multiplied by the amount of impurities, which is also $N$, and the needed self-consistency iterations $\eta$ yielding a scaling of $4^{2 N_{\text{imp}}} \cdot N^3 \cdot \eta$. For comparison, the numerical costs of an LDA calculation grow quadratically with the amount of lattice sites times the self-consistency iterations ($N^2 \cdot \eta$). We can therefore state that SDE is quantitatively accurate for the present case, but with a much lower cost than the exact method.

B. Peaks and steps in the Kohn-Sham potential

For the $H_2$ model, the Kohn-Sham system needs to describe the repulsion of the two electrons. As the system does not include an actual interaction term, this repulsion needs to be mimicked by the Kohn-Sham potential. As has been investigated in previous work [45, 58, 59], we expect to see a peak that prevents the two electrons from being at the same atom. In Fig. 7, we plot the density and the Kohn-Sham potential obtained with SDE for impurity sizes of 5 and 9 sites and compare them with the exact density and the exact Kohn-Sham potential. The density from the SDE calculations for both impurity sites agrees quantitatively with the exact density. We also see peaks at position $x = 0$ in the Kohn-Sham potential for both SDE calculations. This peak is overestimated for small impurity sizes ($N_{\text{imp}} = 5$), but agrees quantitatively with the exact solution for bigger impurity sizes ($N_{\text{imp}} = 9$).

Additionally, by considering an asymmetric external potential, we can study more general models such as the bond stretching of heteroatomic molecules. In Fig. 8, also accurately agreeing with the exact solution, we observe that the electron density is not symmetric anymore. In addition to the peak observed in the symmetric case in Fig. 7, in the asymmetric case we observe a step between the two wells in the Kohn-Sham potential that accounts for the asymmetric density distribution.
cases and for both chosen properties, we observe a de-
and strong correlation between the electrons. In both
distances (17), the exact and the SDE solution
agree quantitatively. The SDE Kohn-Sham potential shows
the expected peak in the center which mimics the electron-
interaction. For small impurity sizes, this behavior
is overestimated, but converges quickly to a quantitatively
exact result for bigger impurity sizes. The following set of
parameters has been used: \( N = 120, L = 20, d = 10 \)

C. Convergence behavior

The assumption made in the presented SDE method is
due to the projection \( P \) which is not defined with the ex-
act wave function but with the Kohn-Sham Slater deter-
minant. As we do not project the impurity, this assump-
tion is only made for the bath, i.e. for the interactions
of the rest of the system with the impurity. In contrast
to conventional DFT functionals, we can therefore im-
prove our SDE functional systematically by increasing
the impurity size. Once the investigated property of the
system \( M \) does not change any more (with respect to the
required accuracy), we know that we have an accurate
estimate for this property.

In Fig. 9 and 10, we see the deviation of our results
from the exact solution for different properties of the sys-
tem, integrated over the whole lattice:

\[
\Delta M = \sum_i |M_i^{\text{SDE}} - M_i^{\text{exact}}| \cdot \Delta x,
\]

where \( \Delta x \) is the lattice constant.

In Fig. 9, we plot the deviation of the density \( \Delta n \)
and the Kohn-Sham potential \( \Delta v_S \) between the SDE calcula-
tion and the exact result. We consider two different core
distances (\( d = 0 \) and \( d = 10 \)), which correspond to weak
and strong correlation between the electrons. In both
cases and for both chosen properties, we observe a de-
crease in \( \Delta M \) with increasing impurity size up to a quan-
titative agreement of the two solutions, with \( \Delta M \leq \epsilon \)
within the wanted accuracy. Already for the smallest
considered impurity size \( N_{\text{imp}} = 3 \), the deviations are
relatively small, that is of the order of the fourth digit
for the density \( \Delta n \leq 10^{-4} \) and of the order of the first
digit for the Kohn-Sham potential \( \Delta v_S = 10^{-1} \).

In Fig. 9, we show the deviation of the total energy \( E_0 \)
of the SDE method from the exact calculation. Again,
we consider one example with weakly static correlated
electrons and one example with strongly static correlated
electrons. For weakly correlated electrons, the difference
in energy decreases and already for an impurity size of
\( N_{\text{imp}} = 7 \), the deviation from the exact solution is below
chemical accuracy of 1.6 mhartree.

For strongly correlated electrons, we observe that the
SDE energy becomes smaller than the exact energy for a range of impurities between \( N_{\text{imp}} = 9 \) and \( N_{\text{imp}} = 20 \).
This is because the SDE method is not variational. While
for each single considered impurity, we create a wave
function (that is variational), we do not have the inter-
acting wave function of the whole system and calculate
the energy (and every other observable) of each impurity
individually. The total energy is then, due to the con-
tinuous overlapping of the impurities, the sum of all site
energies. This is why the estimate can also be lower than
the real energy. Also for this observable though, already
for small impurities our estimate is of order \( \Delta E_0 \leq 10^{-5} \)
which is far below chemical accuracy.

As discussed in section 11B we do not have a wave
function for the whole system, but a wave function for
every impurity. As consequence, the total particle number is not necessarily correct. The employed optimization of the chemical potential leads to the correct number for \( \langle N \rangle \) up to a desired accuracy (\( |\langle N \rangle - \langle \mathcal{N} \rangle| < 10^{-5} \)). As the energy difference is of the same order of magnitude, we further rescale the energy with respect to the particle number

\[
E_0^{\text{SDE}} \to E_0^{\text{SDE}} \cdot \langle \mathcal{N} \rangle / \langle N \rangle, \tag{18}
\]

to achieve a better convergence behavior, as can also be seen in Fig. 10. Nonetheless, the calculated energy can still be lower than the exact energy, meaning that we still observe the non-variational nature of our approximation.

### D. Application to lattice systems in 2D

It is straightforward to apply our SDE method to higher-dimensional models. To demonstrate the universality of our approach, we here discuss the \( H_2 \) molecule and a model heteroatomic molecule in two dimensions.

In Fig. 11, we plot the density \( n \), the Kohn-Sham potential \( v_\text{S} \), the external potential \( v_\text{ext} \), the Hartree-exchange-correlation potential \( v_\text{Hxc} \), and deviations from the exact solution \( \Delta n \) and \( \Delta v_\text{Hxc} \) for the two-dimensional \( H_2 \) model.

We observe a homogeneous density distribution around the two core potentials that is consistent with the external potential. The Hartree-exchange-correlation potential which mimics the interactions of the electrons as well the kinetic correlations in the interacting case, shows a peak in the middle of the molecule. Our observations are consistent with the exact solution of this problem.

For a model heteroatomic molecule, we also plot the same properties as for \( H_2 \). The density for the heteroatomic molecule in the two-dimensional case is asymmetrically distributed between the two cores, again consistent with the external potential. In the Hartree-exchange-correlation potential, additional to the peak accounting for the interaction of the electrons, we also observe a step that accounts for the asymmetric distribution of the density.
We expect to face one challenge with respect to the treatment of larger systems and that is the storage and projection of the electron-electron interaction term $\hat{W}$ of the Hamiltonian in Eq. (11), which numerically is stored in a large tensor of fourth order (and thus is also growing by fourth order with respect to the system size). In order to treat larger systems, we either have to find an efficient way of storing the interaction tensor of the original system and then project it to the embedded system or we have to employ the non-interacting bath picture from DMET [28], that circumvents the treatment of the interaction tensor for the full system altogether.

In this work we provide a first benchmark for a promising group of methods that combine functional methods with embedding schemes, yielding systematically improvable functionals that converge to the exact ones. Work to extend the method to larger systems is underway.

VI. ACKNOWLEDGMENTS

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[59] O. V. Gritsenko, R. van Leeuwen, and E. J. Baerends, Phys. Rev. A 52, 1870 (1995)