Density Matrix Embedding Theory(DMET)

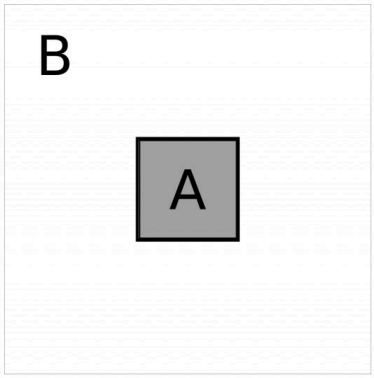
This is a note for static density matrix embedding theory, and some of its clarification through mathematics. It's still a note under construction.

References:

Wouters et al. - 2016 - A Practical Guide to Density Matrix Embedding Theory in Quantum Chemistry

Theoretical Foundation

Imagine a system composed of two parts, a fragment A and an environment B. In some cases, the fragment is the impurity or many body part that we are specifically interested in or relatively hard to solve. In other cases, the fragment is in no sense more important than other parts of the system. Either way, regardless of how we get these two components, we now have the following two components: a fragment A and an environment B, as indicated in the picture below.



Let the Hilbert space of A be $\mathcal{H}_A$, with an orthonormal basis $\{|A_i\rangle\}|_{i=1}^{N_A}$, and correspondingly we have the Hilbert space of B as $\mathcal{H}_B$, with an orthonormal basis $\{|B_j\rangle\}|_{j=1}^{N_B}$. (WLOG, let $N_A < N_B$) Let the Hilbert space of the whole system be $\mathcal{H}$, then we know that $\mathcal{H}$ is the tensor product of $\mathcal{H}_A$ and $\mathcal{H}_B$, i.e.

$$\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B$$

$\mathcal{H}$ is of dimension $N_A \times N_B$, with the following basis:

$$|A_i\rangle \otimes |B_j\rangle, \quad i = 1, \cdots, N_A, \quad j = 1, \cdots, N_B$$

For a quantum state of the system $|\Psi\rangle \in \mathcal{H}$, we have the following decoomposition in the above basis:

$$|\Psi\rangle = \sum_{i=1}^{N_A} \sum_{j=1}^{N_B} M_{ij} |A_i\rangle \otimes |B_j\rangle$$

$c_{i,j}$ could be viewed as the matrix element of a $N_A \times N_B$ matrix M. For matrix M, we have the following singular value decomposition:

$$M = U\Lambda V^*$$

U is a $N_A \times N_A$ unitary matrix, Λ is a $N_A \times N_A$ diagonal matrix, V is a $N_B \times N_A$ matrix, whose N_A column vectors are orthonormal, and V^* means its conjugate transpose . Therefore

$$M_{ij} = \sum_{k=1}^{N_A} \lambda_k U_{ik} V_{kj}^*$$

and then

$$\begin{aligned}
|\Psi\rangle &= \sum_{i=1}^{N_A}\sum_{j=1}^{N_B} M_{ij} |A_i\rangle \otimes |B_j\rangle \\
&= \sum_{i=1}^{N_A}\sum_{j=1}^{N_B}\sum_{k=1}^{N_A} \lambda_k U_{ik} V_{kj}^* |A_i\rangle \otimes |B_j\rangle \\
&= \sum_{k=1}^{N_A} \lambda_k \left(\sum_{i=1}^{N_A} U_{ik} |A_i\rangle\right) \otimes \left(\sum_{i=1}^{N_B} V_{kj}^* |B_j\rangle\right) \\
&= \sum_{k=1}^{N_A} \lambda_k \left|\tilde{A}_k\right\rangle \otimes \left|\tilde{B}_k\right\rangle
\end{aligned}$$

where

$$\left|\tilde{A}_k\right\rangle = \sum_{i=1}^{N_A} U_{ik} |A_i\rangle$$

$$\left|\tilde{B}_k\right\rangle = \sum_{i=1}^{N_B} V_{kj}^* |B_j\rangle$$

It looks like even though $N_B > N_A$, we only need to consider N_A many-body state.

What is the DMET bath? In fact, $\left\{\left|\tilde{B}_k\right\rangle\right\}_{k=1}^{N_A}$ define an exact DMET bath for the fragment A. To be precise, if $|\Psi\rangle$ is the ground state of the Hamiltonian H, it's also the ground state on the subspace $\mathrm{span}\left(\left\{\left|\tilde{A}_k\right\rangle\right\}_{k=1}^{N_A}\right) \otimes \mathrm{span}\left(\left\{\left|\tilde{B}_k\right\rangle\right\}_{k=1}^{N_A}\right)$ of the following projected Hamiltonian, also called embedded Hamitonian H_{emb}:

$$H_{\mathrm{emb}} = PHP, \quad P = \sum_{k_1=1}^{N_A}\sum_{k_2=1}^{N_A} \left(\left|\tilde{A}_{k_1}\right\rangle \otimes \left|\tilde{B}_{k_2}\right\rangle\right)\left(\left\langle\tilde{A}_{k_1}\right| \otimes \left\langle\tilde{B}_{k_2}\right|\right)$$

DMET utilizes this simple fact: the solution of the embedded problem, i.e., finding global minimum on the subspace with the projected Hamiltonian, has the same solution as the ground state of full system.

However, knowing this subspace or the projection operator P requires knowing the exact ground state Ψ and do Schmidt decomposition on it. But, if we know the exact ground state in the first place, we don't have to bother doing all these things.

In practice, we use an approximate low-level $|\Phi\rangle$ to derive an approximate bath and then self-consistently improve it based on the information from solving the small embedded problem with the previous bath, which leads to a high level $|\Psi\rangle$. Different self-consistency rules and different initial $|\Phi\rangle$ leads to different kinds of DMET methods.

If the system is not an impurity-like system but a big system divided into multiple local fragments, each local fragment A_i is associated with its own embedded problem and high-level wave function $|\Psi_i\rangle$. Consistency between the different $|\Psi_i\rangle$ is reached by the self-consistency loop with a single low-level $|\Phi\rangle$ to describe the whole system.

Constructing DMET Bath of Slater Determinant

We now consider this problem under the lattice setting. Assume that there are L orthonormal spin-orbitals in total, L_A orbitals in the fragment A (as a result $L - L_A$ ones in environment B) . By spin-orbitals, we mean that we combine the lattice site and spin indices into one index, thus we no longer need to specifically worry about spin. We use k, l, m, n to denote there orbitals.

Assume that there are N_{occ} electrons, therefore there are N_{occ} orthonormal occupied orbitals, denoted by μ, ν. The creation operator of these occupied orbitals could be written in terms of the fragment and environment orbitals:

$$\hat{a}_\mu^\dagger = \sum_{k=1}^{L} \hat{a}_k^\dagger C_{k\mu}$$

Then the quantum state of these N_{occ} occupied orbitals could be expressed as a Slater determinant constructs by the above creation operator:

$$|\Phi_0\rangle = \prod_{\mu \in \text{occ}} \hat{a}_\mu^\dagger |-\rangle$$

where $|-\rangle$ is the vacuum. Note that $|\Phi_0\rangle$ is unchanged when we orthonormally rotate the N_{occ} orbitals. We now try to rotate them so that it can divided into two kinds: orbitals with and without overlapping with the fragment A.

In fact, the coefficient $C_{k\mu}$ forms a $L \times N_{occ}$ matrix C, which can be divided into two parts:.

$$C = \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

where C_1 is a $L_A \times N_{occ}$ matrix corresponding to the L_A fragment orbitals, while C_2 is a $(L - L_A) \times N_{occ}$ matrix corresponding to the $(L - L_A)$ environment orbitals. For now, we assume $L_A < N_{occ}$, which is indeed the case when we use a large basis set.

Assume C_1 has the following singular value decomposition:

$$C_1 = \bar{U}\bar{\Lambda}\bar{V}^*$$

where $\bar{U}$ is a $L_A \times L_A$ unitary matrix, $\bar{\Lambda}$ is a $L_A \times L_A$ diagonal matrix, $\bar{V}$ is a $N_{occ} \times L_A$ matrix, whose L_A column vectors are orthonormal, and $\bar{V}^*$ means its conjugate transpose . Therefore

$$(C_1)_{k\mu} = \sum_{p=1}^{L_A} \lambda_p \bar{U}_{kp} \bar{V}^*_{p\mu}$$

Let us add $(N_{occ} - L_A)$ columns to $\bar{V}$ to get an orthogonal $N_{occ} \times N_{occ}$ matrix $\widetilde{V} = [\bar{V}, \bar{V}']$. We use $\widetilde{V}$ to rotate the occupied orbital space:

$$\widetilde{C} = CW$$

i.e.

$$\widetilde{C}_{kp} = \sum_{\mu=1}^{N_{occ}} C_{k\mu} W_{\mu p}$$

and the new corresponding creation operator is:

$$\begin{aligned}\widehat{\widetilde{a}}_p^\dagger &= \sum_{k=1}^{L} \hat{a}_k^\dagger \widetilde{C}_{kp} = \sum_{k=1}^{L}\sum_{\mu=1}^{N_{occ}} \hat{a}_k^\dagger C_{k\mu} W_{\mu p} = \sum_{\mu=1}^{N_{occ}}\sum_{k=1}^{L} \hat{a}_k^\dagger C_{k\mu} W_{\mu p} \\ &= \sum_{\mu=1}^{N_{occ}} \widehat{a}_\mu^\dagger W_{\mu p}\end{aligned}$$

We take a closer look at $\widetilde{C}$. Let

$$\widetilde{C} = \begin{pmatrix} \widetilde{C}_1 \\ \widetilde{C}_2 \end{pmatrix}$$

where $\widetilde{C}_1$ is a $L_A \times N_{occ}$ matrix, while $\widetilde{C}_2$ is a $(L - L_A) \times N_{occ}$ matrix. Therefore

$$\widetilde{C}_1 = C_1 W = C_1[\bar{V}, \bar{V}'] = \bar{U}\bar{\Lambda}\bar{V}^*[\bar{V}, \bar{V}'] = [\bar{U}\bar{\Lambda}, 0]$$

which means $\widetilde{C}_1$ is $\bar{U}\bar{\Lambda}$ for the left $L_A \times L_A$ block but zero for the right $L_A \times (N_{occ} - L_A)$ columns. Therefore these $(N_{occ} - L_A)$ columns in matrix C corresponds to the occupied orbitals that doesn't have overlapping with the fragment, while the first L_A columns are those that have overlapping with the fragment.

In other words, we now rewrite $|\Phi_0\rangle$ as

$$|\Phi_0\rangle = \left(\prod_{p=1}^{L_A} \widehat{\widetilde{a}}_p^\dagger\right)\left(\prod_{p=L_A+1}^{N_{occ}} \widehat{\widetilde{a}}_p^\dagger\right)|-\rangle$$

Now back to what we talked about in the first section. Recall that for any $\Psi \in \mathcal{H}$, we have the decomposition

$$|\Psi\rangle = \sum_{i=1}^{N_A}\sum_{j=1}^{N_B} M_{ij}\,|A_i\rangle \otimes |B_j\rangle$$

and after the transformation

$$|\Psi\rangle = \sum_{k=1}^{N_A} \lambda_k \left|\tilde{A}_k\right\rangle \otimes \left|\tilde{B}_k\right\rangle$$

Recall our notation in the previous section. Here $\mathcal{H}_A$ is the Fock space of the L_A orbitals in the fragment A, therefore it is a 2^{L_A}-dimensional space, i.e. $N_A = 2^{L_A}$. Similarly, $\mathcal{H}_B$ is the Fock space of the $(L - L_A)$ orbitals in the environment B, i.e. $N_B = 2^{L-L_A}$.

Now we want to choose the new $\left|\tilde{A}_k\right\rangle_{k=1}^{N_A}, \left|\tilde{B}_k\right\rangle_{k=1}^{N_A}$ for $|\Phi_0\rangle$, which is what we have theoretically derived for general $|\Psi\rangle$. To do this, we need to do SVD on the $N_A \times N_B$ matrix. However, we didn't do that, instead we do SVD on the coefficient matrix, which is of size $L_A \times N_{\text{occ}}$, and use it to get new coefficient $\widetilde{C}$

$$\widetilde{C} = \begin{pmatrix} \bar{U}\bar{\Lambda} & 0 \\ C_2\bar{V} & C_2\bar{V}' \end{pmatrix} = \begin{pmatrix} \widetilde{C}_1 \\ \widetilde{C}_2 \end{pmatrix}$$

Here $\widetilde{C}$ is $L \times N_{\text{occ}}$, $\bar{U}\bar{\Lambda}$ is $L_A \times L_A$, $C_2\bar{V}$ is $(L - L_A) \times L_A$, $C_2\bar{V}'$ is $(L - L_A) \times (N_{\text{occ}} - L_A)$.

We take a close look at $\widetilde{C}_2 = C_2\bar{V}$. Define new creation operators using columns of $\widetilde{C}_2$:

$$\hat{\mathbf{a}}_r^\dagger = \frac{1}{\sqrt{\sum_{l=L_A+1}^{L} |\widetilde{C}_{lr}|^2}} \sum_{k=L_A+1}^{L} \hat{a}_k^\dagger \widetilde{C}_{kr}$$

Here $1 \le r \le L_A$. This is what we call the bath orbitals here.

In practice, the above bath constructions could be done through density matrix. Let

$$D = CC^* = \widetilde{C}\widetilde{C}^*$$

This is a $L \times L$ matrix and an idempotent matrix (with only 0 or 1 as eigenvalues), and $\text{trace}(D) = N_{occ}$.

Constructing bath orbitals using linear algebra

We provide a more mathematical description about the above part. For the $L \times N_{occ}$ matrix C, we know that C has orthogonal columns, i.e.

$$C^\dagger C = I_{\text{occ}}$$

For this kind of matrix C, we always have the following CS decomposition:

$$C = \begin{pmatrix} U_A\Sigma_A V^\dagger \\ U_B\Sigma_B V^\dagger + U_{\text{core}}\, V_\perp^\dagger \end{pmatrix}$$

where U_A is $L_A \times L_A$, U_B is $(L - L_A) \times L_A$, U_{core} is $(L - L_A) \times (N_{\text{occ}} - L_A)$, V is $N_{\text{occ}} \times L_A$, $V_\perp$ is $N_{\text{occ}} \times (N_{\text{occ}} - L_A)$, all of them are column orthogonal matrices, and $U_B^\dagger U_{\text{core}} = 0$, $V^\dagger V_\perp = 0$. And Σ_A, Σ_B are $L_A \times L_A$ non-negative diagonal matrices and $\Sigma_A^2 + \Sigma_B^2 = I_{L_A}$.

Using this decompositions, we have the following orbitals:

$$\Phi_x^{\text{frag}} = \begin{pmatrix} I_{L_A} \\ 0 \end{pmatrix}, \quad \Phi_x^{\text{bath}} = \begin{pmatrix} 0 \\ U_B \end{pmatrix}, \quad \Phi_x^{\text{core}} = \begin{pmatrix} 0 \\ U_{\text{core}} \end{pmatrix}$$

Φ_x^{frag} are the L_A fragment orbitals, Φ_x^{bath} are the L_A bath orbitals, Φ_x^{core} are the $(N_{\text{occ}} - L_A)$ core orbitals. There should be L orbitals in total, the rest $(L - L_A - N_{\text{occ}})$ orbitals are called virtual orbitals, which will not be used explicitly here.

Using these orbitals, we can define a decomposition corresponding to this very setting. Let $\hat{c}_1^\dagger, \ldots, \hat{c}_{L_A}^\dagger$ corresponds to all the creation operators in fragment A, $\hat{c}_{L_A+1}^\dagger, \ldots, \hat{c}_{2L_A}^\dagger$ corresponds to those bath orbitals, and $\hat{c}_{2L_A+1}^\dagger, \ldots, \hat{c}_{N_{\text{occ}}}^\dagger$ corresponds to those core orbitals. Then the low-level wave function $|\Psi\rangle$ could be written as

$$|\Psi\rangle = \left|\Psi^{\text{act}}\right\rangle \otimes \left|\Psi^{\text{inact}}\right\rangle$$

Here $\left|\Psi^{\text{act}}\right\rangle \in \mathcal{F}^{\text{act}}$, $\left|\Psi^{\text{inact}}\right\rangle \in \mathcal{F}^{\text{inact}}$, where $\mathcal{F}^{\text{act}}$ is the active Fock space generated by $\hat{c}_1^\dagger, \ldots, \hat{c}_{2L_A}^\dagger$ while $\mathcal{F}^{\text{inact}}$ is the inactive space generated by core orbitals $\hat{c}_{2L_A+1}^\dagger, \ldots, \hat{c}_{N_{\text{occ}}}^\dagger$.

Based on this decomposition, we define the following subspace:

$$\mathcal{F}_A = \mathcal{F}^{\text{act}} \otimes \text{span}(|\Psi^{\text{inact}}\rangle)$$

therefore we have in fact $\mathcal{F}_A \simeq \mathcal{F}_{\text{act}}$. There is no doubt that $|\Psi\rangle \in \mathcal{F}_A$. What we said we want to do in the first section is that we want to project the Hamiltonian onto this space $\mathcal{F}_A$.

How to reach self-consistency

In lattice applications of DMET, the low-level Hamiltonian is termed the lattice Hamiltonian, and the high-level embedding Hamiltonian is termed the impurity Hamiltonian.

Let us assume that the whole system S is divided into a few fragments $\{A_i\}_{i \in I}$. We have $S = \cup_{i \in I} A_i$, $A_i \cap A_j = \emptyset (i \neq j)$.

We start with the real system Hamiltonian:

$$\hat{H} = E_{\text{nuc}} + \sum_{k,l=1}^{L} t_{kl} \hat{a}_k^\dagger \hat{a}_l + \frac{1}{2} \sum_{k,l,m,n=1}^{L} (klmn) \hat{a}_k^\dagger \hat{a}_m^\dagger \hat{a}_n \hat{a}_l$$

We aim to find the ground state $|\Psi_0\rangle$ of the $\hat{H}$. In DMET, this is done by the self-consistency loop between the low-level wavefuction $|\Phi\rangle$ from the low-level Hamiltonian $\hat{h}'$ and the high level wavefunction $|\Psi_i\rangle$ for the fragment A_i from the high-level embedding Hamiltonian $\hat{H}_{emb}^i$.

Both $\hat{h}'$ and $\hat{H}^i_{emb}$ are derived from the real Hamiltonian $\hat{H}$.

$\hat{h}'$ has the following form:

$$\hat{h}' = \hat{h} + \sum_i \hat{u}_i$$

where $\hat{C}_i$ is one-particle operators acting only on A_i:

$$\hat{u}_i = \sum_{k,l \in A_i} u^i_{kl} \hat{a}^\dagger_k \hat{a}_l$$

Here u^i_{kl} are the matrix element waiting to be fit to accomplish the self-consistency loop.

$\hat{h}$ is a fixed single-particle Hamiltonian, which could be the one-particle part of $\hat{H}$ or the Hartree-Fock approximation of $\hat{H}$. These two are equivalent when the Coulomb terms of $\hat{H}$ act in each fragment separately (for example, in the Hubbard model).

As $\vec{u}$ is the undetermined variable here, we define several functions of $\vec{u}$. The low-level wavefunction from $\hat{h} + \hat{u}$ is denoted as $|\Phi_0(\vec{u})\rangle$

The determination of embedding Hamiltonian $\hat{H}^i_{emb}$ has the following two kinds: