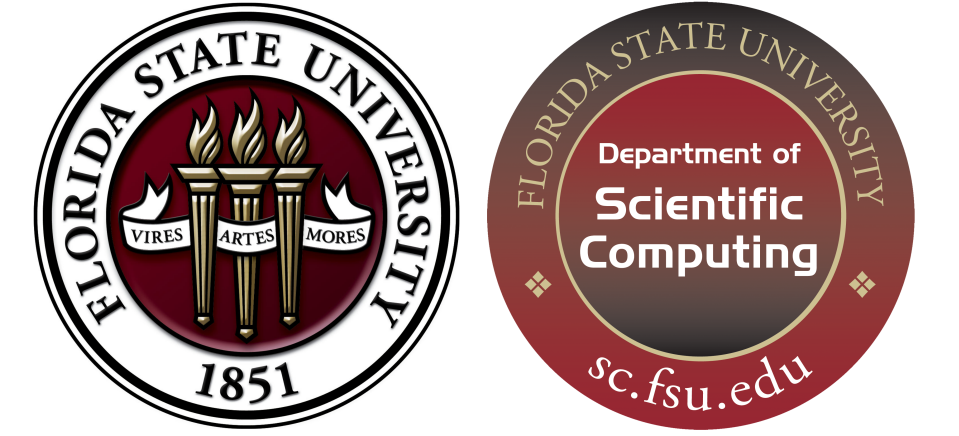


Scaling Up Accurate Electronic Structure Calculations by Patching Exchange-Correlation Potential in Materials

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Background and Motivation

Computer simulations have become invaluable in materials research for solving emerging problems in clean energy, nanotechnology, catalysis, etc. To understand and predict the properties of materials, accurate electronic structures are the prerequisites. The many-body Schrödinger equation is difficult to solve for large-scale materials. Density functional theory (DFT) is the workhorse for material research nowadays, but is severely limited by the approximated exchange-correlation (XC) functionals. In this work, I derive a general way to obtain reliable electronic structure in materials by constructing accurate XC potential.[1] With an accurate XC potential, the Kohn-Sham (KS) DFT becomes accurate.

Step 1. Partition Materials

We start with selecting one atom (call it atom- q) in a material. Some nearby atoms are then selected as its buffer atoms. The atom and its buffer atoms form the cluster, with the rest atoms being the environment. We give an initial guess of the KS potential V_{KS}^{tot} of the material, which yields the total electron density by solving the Kohn-Sham equation. Cluster is defined by projecting V_{KS}^{tot} to its region as

$$V_{KS}^{cluster}(\vec{r}) = w_{cluster}(\vec{r})V_{KS}^{tot}(\vec{r})$$

Environment's KS potential is defined as $V_{KS}^{env} = V_{KS}^{tot} - V_{KS}^{cluster}$. The weight $w_{cluster}$ is designed to satisfy a key requirement for the partitioning that $V_{KS}^{cluster}$ becomes equal to V_{KS}^{tot} inside the cluster.

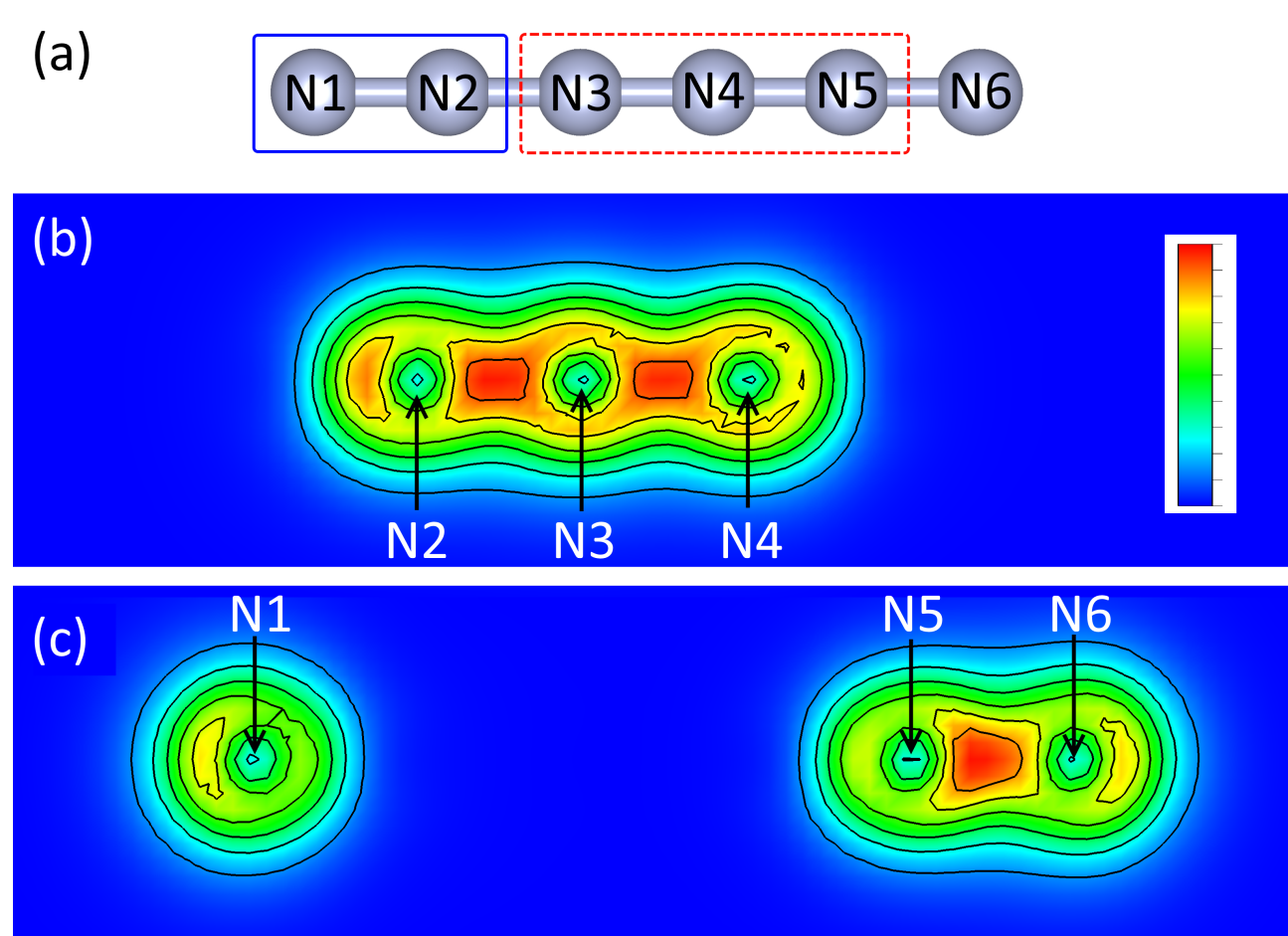


Figure 1: (a) The model N₆ molecule. The nitrogen atoms are equally spaced. (b,c) The partitioned electron densities of the N₂-N₃-N₄ cluster and its environment (N₁, N₅, and N₆). The N₂ and N₄ are the buffer atoms of the N₃.

We use an embedding potential V_{emb} to “glue” the cluster with its environment. By adjusting the embedding potential, the sum of $n_{cluster}(\vec{r})$ and $n_{env}(\vec{r})$ becomes equal to the total density. We demonstrate the density decomposition with a model N₆ molecule (Fig. 1). The cluster consists of atoms “N₂”, “N₃”, and “N₄”, and the rest nitrogen atoms form the environment. Cluster and environment's densities are very localized, which is a must for keeping cluster's Hilbert space as small as possible.

Step 2: Computing Cluster's XC potential

For cluster density $n_{cluster}(\vec{r})$, we solve for its XC potential $V_{xc}^{cluster}$ by inverting the Schrödinger equation. We solve for the external potential $V(\vec{r})$ that yields $n_{cluster}(\vec{r})$. This can be done by constructing the W_e functional

$$W_e = E[V] - \int V(\vec{r})n_{cluster}(\vec{r})d\vec{r}^3,$$

where $E[V]$ is the energy of the cluster with V as an additional external potential. Once we have maximized W_e , $V(\vec{r})$ yields the cluster density. The gradient for maximizing W_e can be easily derived. Cluster's XC potential is obtained as

$$V_{xc}^{cluster}(\vec{r}) = V_{emb}(\vec{r}) + V_{KS}^{cluster}(\vec{r}) - V(\vec{r}) - V_H[n_{cluster}](\vec{r})$$

We then project cluster's XC potential to the atom- q .

Step 3: Patching XC Potential in Entire Material

Steps 1 and 2 are performed for all the atoms in the materials. By stitching the high-level XC potentials of all atoms, we obtain the high-level XC potential of the entire material. We then go back to Step 1 to complete the self-consistent loop. A flowchart is demonstrated (Fig. 2). Our method can be considered as a *local* optimized effective potential (OEP) problem, which consists of two steps: (a) partitioning and (b) patching. The partitioning step can be efficiently parallelized in practice.

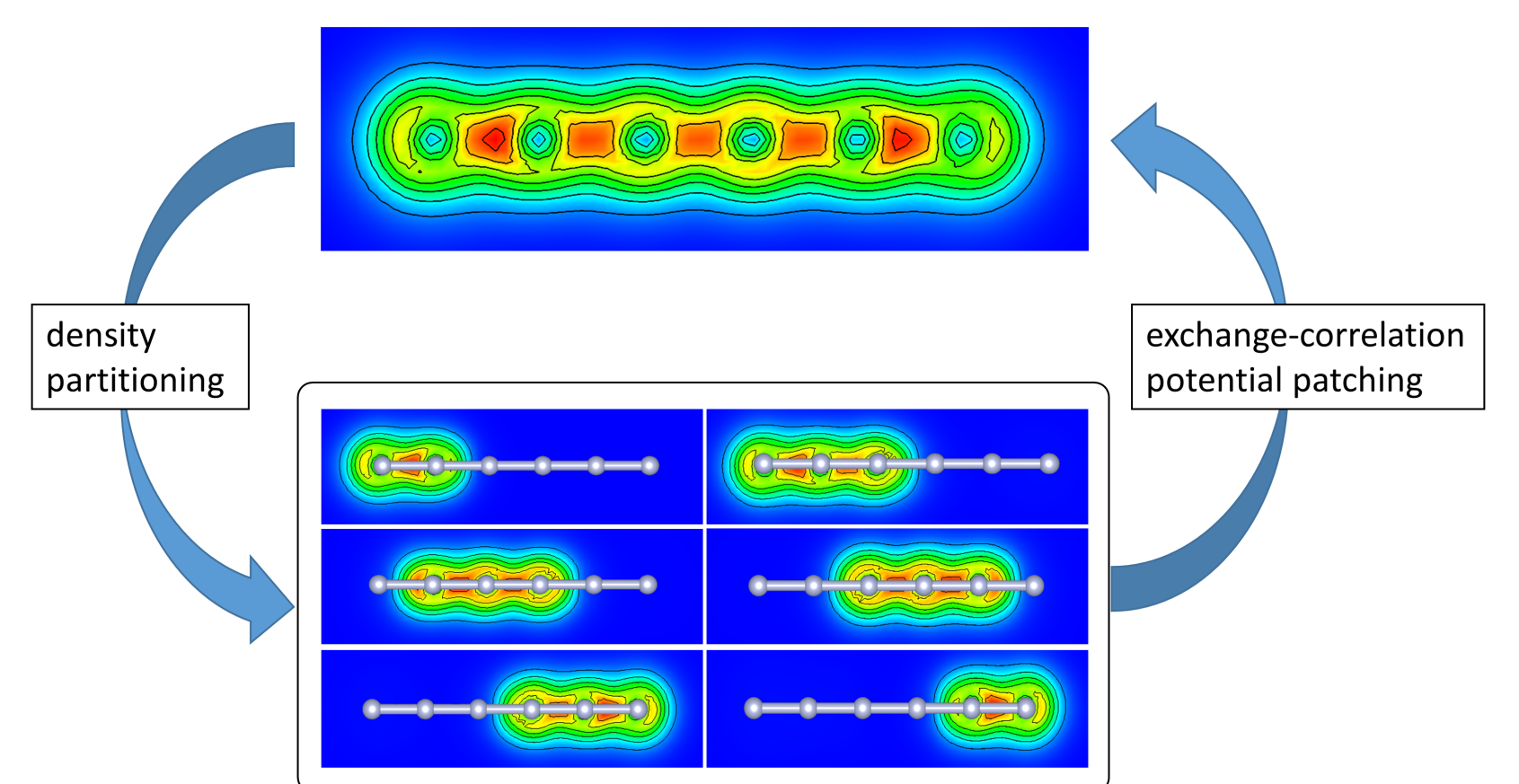


Figure 2: The flowchart of solving the N₆ model molecule using the XC-patching method. We have six “cluster-environment” pairs, since we have six N atoms.

Outlook and Acknowledgment

We are building a software based on the XC-patching method developed here, with the aim to predict electronic structure of large-scale (strongly) correlated materials *completely* based on computer simulations in a parameter-free way. We are grateful for the financial support from the Florida State University.

References

- [1] Chen Huang. *Journal of Chemical Theory and Computation*. doi:10.1021/acs.jctc.6b00051 (2016) in press.