Implementation of orbital-free density functional theory for transition metals

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Introduction

Alloys stand as the backbone of modern engineering, indispensable in critical applications spanning aerospace to industrial manufacturing. Renowned for their blend of strength, durability, and resilience, alloys form the bedrock of essential components such as rocket engines and high-caliber parts. Orbital-free density functional theory (OF-DFT) is a promising method for large-scale metal simulations. While OF-DFT has been well-established for main-group metals, it is still challenging to apply it to transition metals due to the presence of localized *d* and *f* electrons. To address this issue, Huang and Carter proposed a density-decomposition scheme in which the electron density of a transition metal atom is partitioned into the localized and delocalized components.[1] During OF-DFT simulations, the localized component remains fixed in the space, and only the delocalized part is optimized. In this work, we integrate the localized electron density into an open-source, Python-based OF-DFT program "DFTpy". We first defined the atomic localized electron density and then performed the Fourier transformation to transform it into the Fourier space. This localized density is then efficiently constructed in the bulk using the structure factor.

Method

The structure factor of a crystal is defined as[2]

$$S(\vec{G}) = \sum_{i=1}^{N_{ions}} e^{i\vec{G}\cdot\vec{R}_i}$$

where $\vec{R}_i$ is the position of atom i. The structure factor can be considered as a Fourier transformation of the lattice sites. We then decompose an atom's electron density into localized and delocalized parts. We multiply the localized part with the structure factor to obtain the localized electron density in the bulk (but in the Fourier space)

$$\rho_{bulk}^{localized}(\vec{G}) = S(\vec{G})\rho_{atom}^{localized}(\vec{G})$$

The real-space bulk localized density is obtained by Fourier transforming $\rho_{bulk}^{localized}(\vec{G})$ back to the real space.

Results

To make sure that the localized densities from different atoms do not overlap, a cutoff radius r_{cut} is defined. To make the localized electron density, we first generate the delocalized electron density based on the following formula

$$\rho_{atom}^{deloc} = e^{-c_1 r}(c_2 r^4 + c_3 r^5)$$

where c_1, c_2, and c_3 control the shape of the delocalized electron density. They are determined to satisfy two conditions: (1) the derivative of the delocalized electron density matches the atomic density at cutoff radius r_{cut} and (2) delocalized electron density matches the atomic electron density at r_{cut}. Once the optimal parameters are determined, the delocalized electron density is generated. This delocalized density represents the electron distribution that is not localized around specific atomic nuclei but instead extends outside. The localized density is defined based on the formula:

$$\rho_{atom}^{loc}(\vec{r}) = \rho_{atom}(\vec{r}) - \rho_{atom}^{deloc}(\vec{r})$$

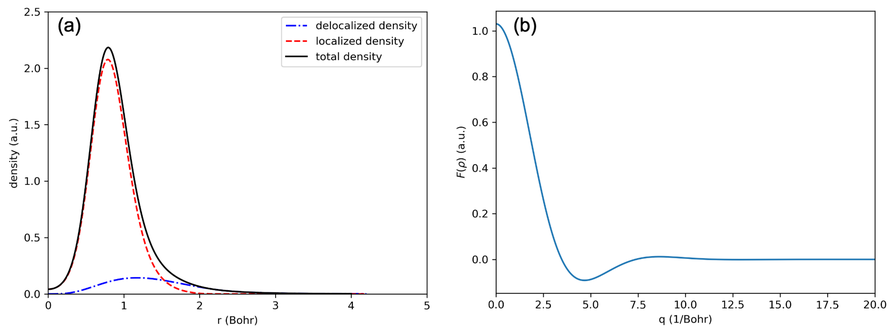

Figure 1. (a) Silver's atomic density, the delocalized density, and the localized density. (b) The Fourier transformation of the localized density.

We applied the above procedure to silver, for which the valence electrons contain the entire 4th and 5th shells. r_{cut} is set to 2.2 Bohr. In Figure 1(a), we show the electron density of silver and its decomposition to the localized and delocalized parts. The large peak from the atomic density is mainly due to the 4*d* electrons. The localize density is well localized within r_{cut}. Figure 1(b) shows the Fourier transformation of the localized electron density, which is later combined with the structure factor to build localized electron density in bulk.

In Figure 3(a), we show the bulk structure of silver. It has a face-centered cubic (FCC) structure. There are four inequivalent atoms in the unit cell. However, we see 14 atoms in the figure. The reason is the inherent translational symmetry within the structure. Figure 3(b) shows the localized electron density in the bulk. The blue shells denote one isosurface of the localized electron density. We see that these densities are around each atom.

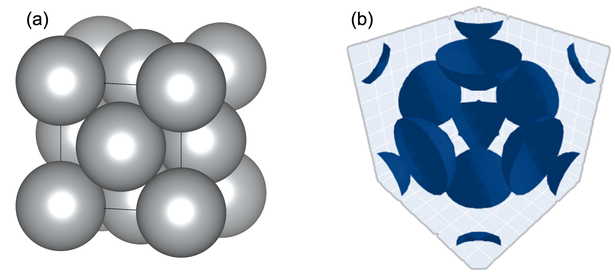

Figure 3: (a) Bulk structure of silver. (b) Constructed localized density in the silver bulk

Conclusion

We successfully implemented atomic localized electron density in the DFTpy program. This work is one step closer to OF-DFT simulations of alloys, which can potentially help us design high-performance alloys essential for various industries, including aerospace and manufacturing.

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References

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