

Introduction

Density Functional Theory (DFT) has been instrumental in understanding the electronic structure of materials, but accurately modelling the exchange-correlation (XC) energy in strongly correlated systems remains challenging. In this study, we propose a novel method to treat the on-site XC energies in strongly correlated systems. Our method involves partitioning a system's electron density onto individual atoms to enable a more accurate treatment of on-site correlations, such as the correlation between *d* and *f* electrons in transition metals and rare earth elements. This allows us to better capture the complex on-site correlations essential for understanding strongly correlated materials, such as transition metals oxides.

Our method presents a potential solution to the limitations of existing methods like the local density approximation (LDA) + U method and the exact exchange for correlated electrons (EECE) method, which are two major methods for treating on-site correlations. One limitation of these two methods is that they rely on the choice of local projectors for defining local correlated orbitals, while our density partitioning scheme is first-principle and unique. Another more prominent limitation with LDA+U and EECE is that they cannot treat on-site correlation by using advanced orbital-based correlation energy functionals, since they only have access to occupied orbitals from the projection. Our method is able to employ any advanced correlation functional, such as the random phase approximation correlation energy functional, since each embedded atom is a complete Kohn-Sham system. With our method, it is possible to fully calculate the on-site correlation energy without any empirical parameter.

In this poster, we demonstrate some preliminary results of this new method by performing non-self-consistent calculations on CO and N₂ molecules. To treat the on-site XC energies, a range-separated hybrid functional is used as the high-level XC functional. The binding energy curves and bond lengths agree with the benchmarks very well. The development of a fully self-consistent version of this new method is in progress in our group.

Method

Our method employs a partitioning approach, where the system's electron density is distributed onto individual atoms, requiring the summation of individual atom densities through a patching scheme to derive the total density.

$$\rho_{\text{total}}(\vec{r}) = \sum_{i=1}^{N_{\text{atom}}} \rho_{\text{atom},i}(\vec{r}) \quad (1)$$

Following this, density functional theory (DFT) simulations are conducted using a suitable high-level exchange-correlation (XC) energy functional. The calculation of the embedded atom approximation (EAA) for current study is described as follows:

$$E_{\text{total}}^{\text{EAA}} = E_{\text{total}}^{\text{PBE}} - \sum_{i=1}^{N_{\text{atom}}} (E_{\text{XC}}^{\text{PBE}}[\rho_{\text{atom},i}] - E_{\text{XC}}^{\text{HSE}}[\rho_{\text{atom},i}]) \quad (2)$$

In this equation, the total energy of the system is computed using the Perdew-Burke-Ernzerhof (PBE) method. The on-site XC energies are then corrected by the Heyd-Scuseria-Ernzerhof (HSE) functional, which uses an error function-screened Coulomb potential.

In our current study, we have employed EAA to determine the bond lengths of two systems: CO and N₂. Energy calculations are performed for various bond lengths, and the minima of the energy versus bond length curve are used to determine the equilibrium energy and bond length. These results are then validated against benchmark experimental values.

We conducted density functional theory (DFT) simulations using the ABINIT software. The computational parameters employed in these simulations were as follows: a k-point mesh of 1 × 1 × 1 was utilized, with a total of 10 bands included in the calculations. The cutoff energy was set to 800 eV, ensuring convergence of the computations. These parameters were chosen to accurately model the atomic interactions and electronic properties of the system while maintaining computational efficiency.

Results

As depicted in Fig. 1, the total electron density of the CO molecule is partitioned onto individual atoms. The left part of the figure illustrates the density distribution for carbon (C), indicated by the yellow color, while the right part shows the density distribution for oxygen (O), indicated by the blue color.

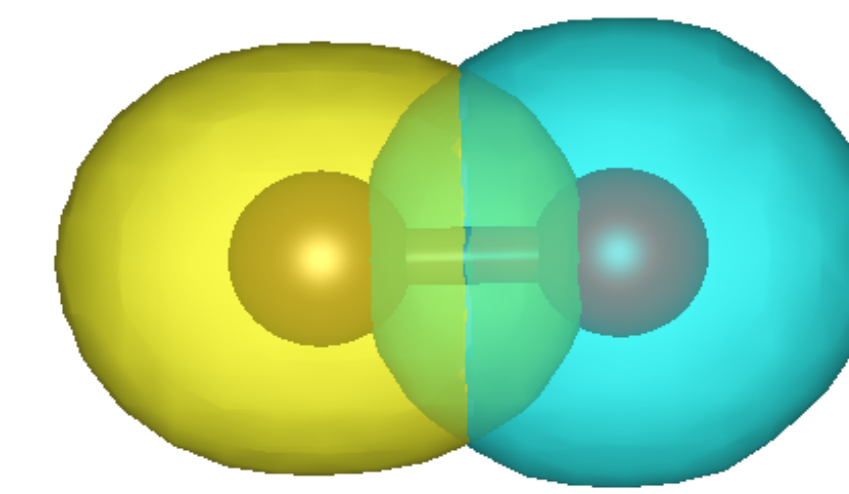


Figure 1. Atomic electron densities on carbon (yellow) and oxygen (blue) from density partitioning.

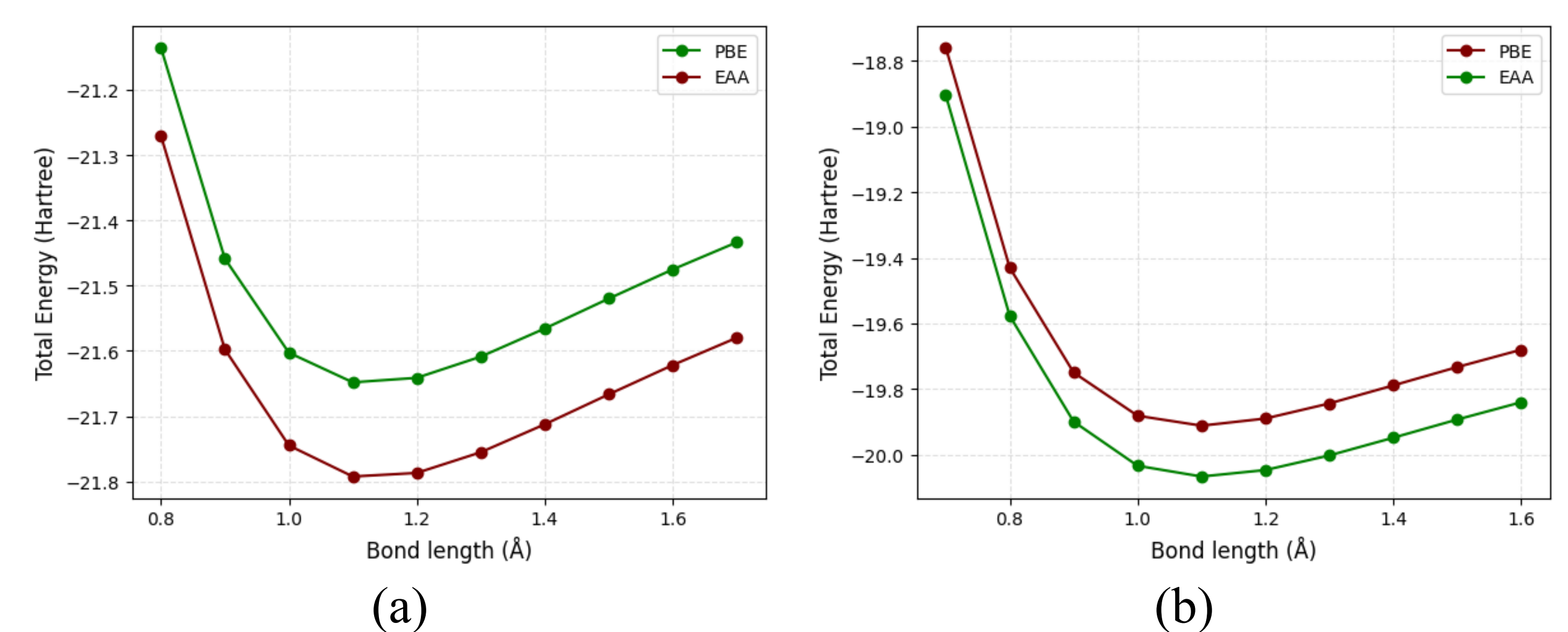


Figure 2. Energy versus bond lengths for (a) CO and (b) N₂ calculated using EAA and PBE.

Figures 2a and 2b display the energy values as a function of bond length for CO and N₂, respectively, using both the PBE functional and EAA. The energy gap between these two methods remains consistent throughout, indicating the stability of our approach. These curves are fitted, and the equilibrium energy is determined. The bond length corresponding to this equilibrium energy represents the required bond length for our molecules.

	PBE	EAA	Exp. value
CO	1.127	1.127	1.128
N ₂	1.104	1.107	1.098

Table 1. Comparison of EAA and PBE bond lengths with experimental values. All values are in Å.

The calculated bond lengths for the CO and N₂ molecules obtained using our method are 1.1275 Å and 1.1045 Å, respectively, which closely align with the experimental benchmarks and PBE method.

Discussion and Future Work

The obtained results convincingly demonstrate the effectiveness of our method in accurately reproducing experimental findings. As we continue to develop a fully self-consistent version, our aim is to expand its application to more intricate and highly correlated systems. This advancement promises deeper insights into the complexities of correlated systems, representing a significant stride in broadening the scope of our methodology. One of the key challenges ahead lies in optimizing our method to not only enhance accuracy in exchange-correlation (XC) energy calculations but also ensure computational efficiency.

References

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