PRF#: 59480-DNI5

Understanding the asymptotic dependence of van der Waals density functionals for heterogeneous catalysis

Principal Investigator: Jianwei Sun

Department of Physics & Engineering Physics, Tulane University, New Orleans, LA 70118 USA

Heterogeneous catalysts are essential for generating petroleum products from crude oil. To study mechanisms of the catalysis where organic molecules meet solid surfaces, the van der Waals (vdW) interaction has to be considered. Various approaches have been proposed to correct conventional approximations of density functional theory (DFT) by adding a long-range vdW correction that recovers the leading orders and their coefficients (e.g., C_6) of the vdW asymptotic series between two atoms. Unlike the semi-empirical approaches, the vdW density functionals are based only on the electron density and hence are conceptually applicable to any chemical environment with general geometry. However, these approaches usually significantly overestimate the leading order coefficient C_3 of the asymptotic series between a molecule and a surface. This is one of the error sources for the overestimation of molecular adsorption energies on metal surfaces.

Our proposal proposed to include the kinetic energy density, □, for modeling the nonlocal vdW correlation functional to better treat different chemical environments and to recover both C_6 and C_3, since τ has been successfully used by the strongly-constrained and appropriately-normed (SCAN) density functional [1] to recognize different chemical bonds. We have made progress towards this goal following the steps outlined in the proposal: 1) a τ-dependent local polarizability model has been constructed. Our preliminary results show the τ-dependent local polarizability model is equally or more accurate than the successful VV09 model [2] (see Fig. 1) for the Ar atom, and yields encouraging C_6 coefficients for several atoms as shown in Table I; 2) extracted from the binding energy curve, the C_3 coefficient of SCAN+rVV10 [3] has been calculated to be 590.0 for Xe/Cu(111), which is almost the same as that of DFT/vdw-DF2 result (589.0) [4] and much better than DFT+D_2 (1048.3) and DFT+D_3 (1381.8). All these C_3 values are overestimated in comparison with the reference C_3 data (488), as expected.

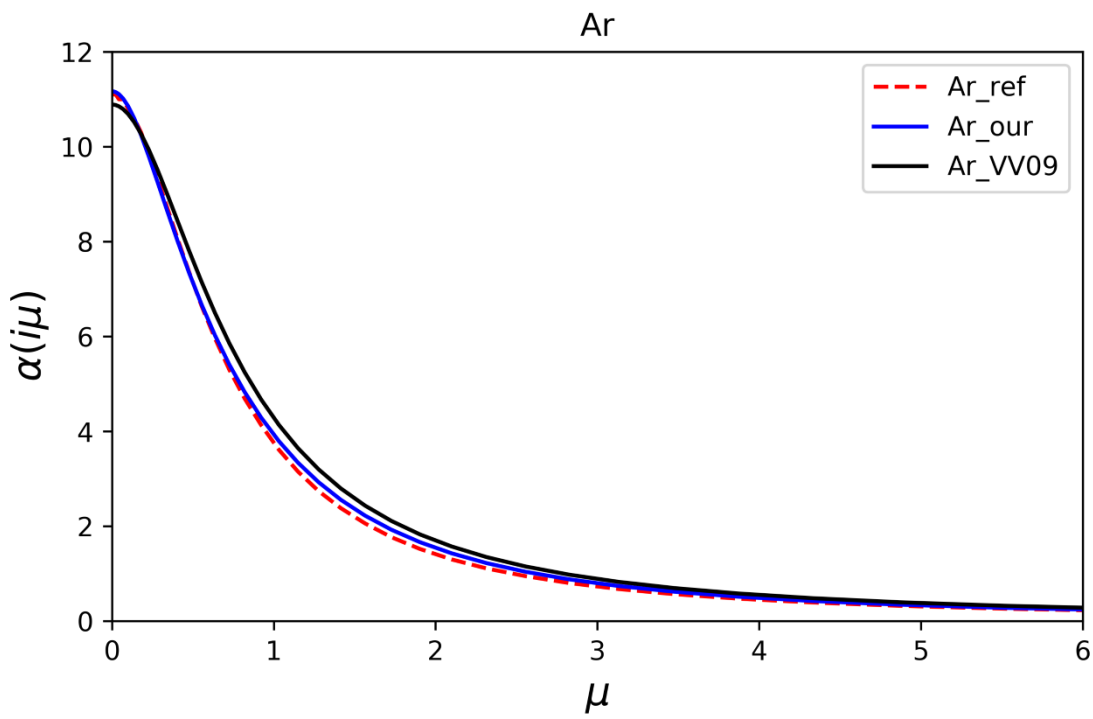

Figure 1. The average dynamic dipole polarizabilities calculated from our τ-dependent local polarizability model and the VV09 model [2] in comparison with the accurate reference values [2].

In the following year, we will apply the τ-dependent local polarizability model to calculate C_6 and C_3 for more systems. Since a τ-dependent local polarizability model accurate for both C_6 and C_3 is critical for the success of this project, refinements of the τ-dependent local polarizability model will be continued. Once a satisfactory τ-

dependent local polarizability model is obtained, it will be built into a vdW nonlocal correlation functional by following the VV10 nonlocal correlation functional construction principles [5]. The resulting vdW nonlocal correlation functional will be implemented into different electronic structure codes and tested for molecular adsorption problems.

Table 1. C_6 coefficients of several atoms calculated by different models. The second column data are from our τ-dependent local polarizability model. The third ones are from the VV09 model [2]. The last column is the accurate reference data [2].

Name	Our model	VV09	Accurate
He	1.39	1.45	1.46
Be	210.12	186.00	214.00
Ne	5.81	8.44	6.35
Ar	65.77	70.08	64.42

This grant was initially planned to fully support a single graduate student in 2018-2020. However, the graduate student joining my group in September 2018, Luis Lopez, obtained a fellowship of $10,000/year for three years from the Louisiana Board of Regents/Southern Regional Education Board Doctoral Scholars Program, freeing up the ACS-PRF funding to be used to support several students of various levels working on the project. With the partial support from ACS-PRF, Luis Lopez has been able to learn density functional theory (DFT) and focus on the DFT development. Another graduate student, Manish Kothakonda, partially supported by a teaching assistantship from Tulane, is working on molecular adsorption problems related to this grant and made progress in computation and understanding the underlying physics. The grant also supported one undergraduate student, Jamin Kidd, during the summer of 2019, which enabled him to learn how to apply computational electronic structure methods to real materials problems. In 2018-2019, the PI has not been able to recruit a postdoc qualified for this project until recently. Dr. Ruiqi Zhang joined the PI's group and is now partially supported by this grant as well. With the support of ACS-PRF, the PI has been able to train both undergraduate and graduate students and to make innovative attempts in this important direction of density functional theory development (i.e., the τ-dependent vdW nonlocal correlation functional).

As there will be a significant carryover to the next year, due to Luis Lopez's fellowship and the delay recruiting a postdoc, the PI plans to use the carryover to partially support another graduate student, Kanun Pokharel, and another postdoc, Dr. Jinliang Ning, to accelerate the progress. Pokharel is in his fourth year of graduate study and works on DFT development using machine learning, which can be potentially used in this project. Dr. Ning is working on catalysis problems with layered materials, which is highly relevant to this project, and he will contribute to testing the vdW density functional developed under the support of this grant for molecular adsorption on surfaces.

[1] J. Sun, A. Ruzsinszky, and J. Perdew, Phys. Rev. Lett. 115, 036402 (2015).
[2] O. A. Vydrov and T. Van Voorhis, Phys. Rev. A 81, 062708 (2010).
[3] H. Peng, Z. H. Yang, J. P. Perdew, and J. Sun, Phys. Rev. X 6, 1 (2016).
[4] A. Ambrosetti and P. L. Silvestrelli, Phys. Rev. B 85, 073101 (2012).
[5] O. A. Vydrov and T. Van Voorhis, J. Chem. Phys. 133, 244103 (2010).