Usage Report for Fiscal Year 2020

Project Title: Development of new long-range corrected density functional theory

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1. Background and purpose of the project, relationship of the project with other projects

Density functional theory (DFT) has developed so markedly in recent years that not only can many experimental results be almost exactly reproduced but also numerical material designs before experimental synthesis are gradually becoming possible. In fact, many recent theoretical studies have been devoted to periodic boundary condition (PBC) solid state materials. The minimum requirement to establish DFT as a reliable tool for designing solid state materials is that the method should be able to safely and confidently predict the physical phenomena regardless of the physical and chemical systems of the theoretical target. There remain, however, a number of serious problems to be resolved.

The mechanism by which carbon monoxide (CO) is adsorbed on the Cu(111) surface is one of the most difficult and controversial problems that has been attracting considerable attention for many years [2]. This is because the system poses at least two chemical challenges that need to be tackled.

The first problem is the so-called “back-donation” of electrons from the Cu surface orbital to the CO molecular orbital. The first reasonable model proposed for this is known as Blyholder’s model. The significant finding of this model is that bonding of the CO molecule on metal surfaces stems from the bonding originating from electron transfer from the filled 5σ orbital of CO to an unfilled d orbital of the metal, and by π bonding due to back-donation of electrons from the filled t_{2g} band of the transition metal to the unfilled 2π* orbital of CO. This scenario was further confirmed by the chemisorption model proposed by Nørskov and by DFT calculations carried out by Neef and Doll.

The second problem posed by the CO/Cu(111) system has long been known as the so-called “CO adsorption puzzle”. In short, CO is experimentally observed to be placed on a top site of the Cu(111) surface. However, many numerical calculations, e.g., the local-density approximation (LDA) and the generalized gradient approximation (GGA), have erroneously predicted that CO is adsorbed on a hollow site. It is known that both LDA and GGA tend to underestimate the band gap or, equivalently, the HOMO–LUMO gap. However, the random phase approximation (RPA) formulated in the framework of the adiabatic connection fluctuation-dissipation theorem has successfully predicted that CO will be preferentially adsorbed on the top site [9], with a stabilization energy ~0.2 eV compared to the hybrid density functionals PBE0 and HSE03.

As to the present status of the issue described above, researchers are still uncertain as to which density functionals should be used for describing the back-donation correctly and for predicting the correct site preference for CO/metallic surface systems.

Recently, we reported that the long-range corrected (LC) DFT functional, which utilizes

$$O^{\mathrm{HF}}\left(r_{12}\right)=\frac{\operatorname{erf}(\mu r_{12})}{r_{12}}$$

(1)

as a modified two-electron HF exchange operator with an error function, satisfies Koopman’s theorem [16]. Here, the modified exchange operator, O^{HF}, is defined through the decomposition of the Coulomb operator, $1/r_{12}$, of the exchange energy as

$$\frac{1}{r_{12}}=O^{\mathrm{HF}}\left(r_{12}\right)+\left[\frac{1}{r_{12}}-O^{\mathrm{HF}}\left(r_{12}\right)\right]_{\mathrm{DFT}}$$

(2)

where r_{12} = | $\mathbf{r}_1 - \mathbf{r}_2$ | is the distance between electrons $\mathbf{r}_1$ and $\mathbf{r}_2$ and μ is a parameter that controls the inclusion ratio between HF and DFT exchange dependent on r_{12}. In other words, LC-DFT correctly calculates HOMO and LUMO energies and the HOMO–LUMO gaps of molecular systems, which conventional DFT functionals significantly underestimate. It is reported that this underestimation of molecular orbitals is responsible for the many electron self-interaction errors (SIEs) of conventional exchange functionals in the long-range region, and LC-DFT is known for being free from many electron SIEs in the inter-electronic long-range region, which results in improvements in its performance in calculating reaction barrier heights and orbital energies.

More recently, we have developed modified LC-DFT functionals, namely, LC-ωPBE(2Gau) and LC-BLYP(2Gau), which utilizes a modified two-electron HF exchange operator consisting of two Gaussian functions, instead of the error function operator of Eqn. (1) as

$$O^{\mathrm{HF}}_{LC-DFT(2Gau)}\left(r_{12}\right) = \beta_S e^{-\alpha_S r_{12}^2} + \beta_L e^{-\alpha_L r_{12}^2} \quad .$$

(3)

where the first Gaussian function with a set of two parameters, α_S and β_S, is for the short-range region of the HF exchange operator and the other Gaussian function with α_L and β_L covers the long-range HF exchange region of LC-DFT. Note that the usage of two-electron Gaussian operator let Gamma-point calculation of functionals free from singularity problem at $r_{12} \rightarrow 0$ specially in case of plane-wave basis calculations. We reported LC-DFT(2Gau) has similar performances to LC-DFT at significantly lower cost. Their advantages and reliability have been demonstrated in practice by several researchers, whose calculations show the improvements obtained by LC-DFT.

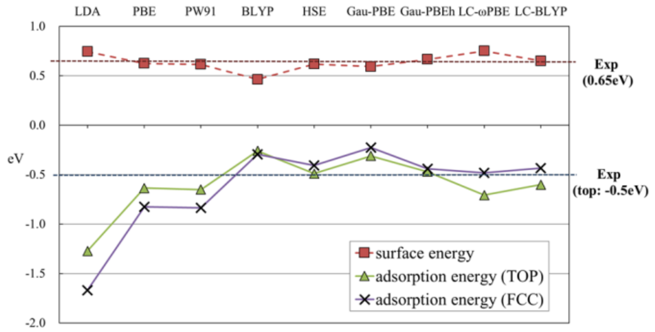
In this project, we will show that the LC DFT methods are some of the powerful tools for estimating physical and chemical properties at least of closed-shell PBC systems. In other words, not only can the correct CO adsorption site be reasonably predicted but also physical quantities such as lattice constants, surface energies, adsorption energies, bond lengths, the HOMO–LUMO gap, and the projected density of states (PDOS) of the CO/Cu(111) system can be reproduced by LC DFT much better than by other DFT functionals.

2. Specific usage status of the system and calculation method

In this project, we used 24.8% of bwmpc (726,722 hour) for this project and other researches which will be submitted to publications.

3. Result

Figure below shows the adsorption energies of CO on the Cu(111) surface for top and fcc binding sites and the surface energies of Cu(111) obtained using several different DFT functionals, along with the experimental results. We can see that LDA overestimates the adsorption energies for both the top and fcc sites. The numerical values obtained by GGA, such as PW91 and BLYP, deviate less from the experimental results, by comparison. The screened hybrid functionals, such as HSE, Gau-PBE, and Gau-PBEh, predict improved numerical adsorption energies close to the experimental adsorption energy of 0.5 eV, and a slight preference for the top-site adsorption energies compared to those of the fcc sites. Therefore, we can infer that inclusion of the short-range HF exchange integral appears to improve the results of the adsorption energy calculations. The LC-DFT functionals, LC-ωPBE(2Gau) and LC-BLYP(2Gau), show the adsorption energies of the top sites, with a definite large gap to those of the fcc sites, which suggests that the long-range HF exchange integral widens the adsorption energy gap between the top sites and the fcc sites. The surface energies show a tendency quite similar to that of the adsorption energies described above. This shows that LC-DFT is a versatile tool for reproducing the physical quantities correctly.



4. Conclusion

We have applied LC hybrid density functionals to DFT calculations of a periodic boundary system: CO adsorbed on the Cu(111) surface. We have demonstrated that the CO adsorption puzzle, namely, the preference of CO for a top site rather than an fcc site, can be explained using the LC hybrid density functionals. It has been shown that the fundamental factors for determining the site preference are the HOMO–LUMO gap of CO and the HOMO and LUMO positions relative to the Fermi level, which have already been emphasized by other researchers. This indicates that our proposed LC DFT method will become an invaluable tool for investigating periodic boundary condition (PBC) systems as well as large molecular systems. In addition, it should be emphasized that LC-DFT enables quite accurate quantum chemistry calculations to be performed while simultaneously reducing computation times. These two beneficial aspects should help to guarantee the future of advanced applications of LC-DFT for a variety of physical, chemical, and biological systems.

5. Schedule and prospect for the future

6. If no job was executed, specify the reason.

Usage Report for Fiscal Year 2020

Fiscal Year 2020 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

1. “Peptoid-Conjugated Magnetic Field-Sensitive Exciplex System at High and Low Solvent Polarities” Dongkyum Kim, Yen Jea Lee, Dae-Hwan Ahn, Jong-Won Song,* Jiwon Seo,* and Hohjai Lee,* J. Phys. Chem. Lett. 11, 4668-4677 (2020).
2. “Core Level Excitation Energies of Nucleic Acid Bases Expressed as Orbital Energies of Kohn–Sham Density Functional Theory with Long-Range Corrected Functionals” Kimihiko Hirao, Takahito Nakajima, Bun Chan, Jong-Won Song, and Han-Seok Bae, J. Phys. Chem. A 124, 10482 (2020).
3. “Charge-Transfer Excitation Energies Expressed as Orbital Energies of Kohn–Sham Density Functional Theory with Long-Range Corrected Functionals” Kimihiko Hirao, Bun Chan, Jong-Won Song, and Han-Seok Bae, J. Phys. Chem. A 124, 8079 (2020).
4. ″Application of Accelerated Long-range Corrected Exchange Functional to Periodic Boundary Condition Systems: CO Adsorption on Cu(111) Surface” Kenji Mishima, Masanori Kaneko, Jong-Won Song,* Hiroki Kawai, Koichi Yamashita, and Kimihiko Hirao, J. Chem. Phys. 152, 104105 (2020).
5. “Predicting whether aromatic molecules would prefer to enter a carbon nanotube — A density functional theory study” Dae-Hwan Ahn, Chiyoung Park, and Jong-Won Song,* J. Compt. Chem. 41, 1261-1270 (2020).
6. ″Excitation energies expressed as orbital energies of KS-DFT with LC functionals” Kimihiko Hirao, Bun Chan, Jong-Won Song, Kamala Bhattarai, and Subrata Tewary, J. Compt. Chem. 41, 1368-1383 (2020).

[Conference Proceedings]

[Oral presentation]

[Poster presentation]

[Others (Book, Press release, etc.)]