Exchange-correlation functionals drawing on first principles, the correlation factor approach, and machine learning

Matthias Ernzerhof

Department of Chemistry, University of Montreal, Canada

Abstract

The widely used approximations to the exchange-correlation (XC) energy, such as GGAs, meta-GGAs, and hybrids, have various shortcomings; they cannot describe bond dissociation correctly, they cannot model multi-configurational open-shell systems, etc. To overcome such limitations, we employ the correlation factor (CF) approach where the XC hole is written as $\rho_{XC}(\mathbf{r},\mathbf{r}+\mathbf{u}) = f(\mathbf{r},\mathbf{r}+\mathbf{u})\, \rho_X(\mathbf{r},\mathbf{r}+\mathbf{u})$ [1-6]. The correlation factor $f(\mathbf{r},\mathbf{r}+\mathbf{u})$ turns an X hole model $\rho_X(\mathbf{r},\mathbf{r}+\mathbf{u})$, yielding the exact exchange energy, into an XC hole. Similarly, $f(\mathbf{r},\mathbf{r}+\mathbf{u})$ can also be used [5] to add dynamic correlation to an exchange-plus-static-correlation (XS) hole, i.e., $\rho_{XC}(\mathbf{r},\mathbf{r}+\mathbf{u}) = f(\mathbf{r},\mathbf{r}+\mathbf{u})\, \rho_{XS}(\mathbf{r},\mathbf{r}+\mathbf{u})$, where $\rho_{XS}(\mathbf{r},\mathbf{r}+\mathbf{u})$ reproduces the XS energy of a MCSCF calculation. More generally, the CFs that we develop can be combined with various X or XS hole models to yield new XC holes and functionals; we discuss specific examples and show that the CF approach solves [5] the above-mentioned problems of strong correlation while solely relying on physical constraints.

Functionals such as those derived from the CF ansatz are becoming increasingly complex and finding appropriate mathematical representations that satisfy all the desired constraints is extremely challenging. To address this problem, starting from a given set of physical constraints, we show how machine learning (ML) can be employed [6] to automate the construction of XC functionals. We provide various examples for how to approximate XC holes and XC functionals through first-principles ML schemes. Furthermore, using ML we introduce new variables into XC functionals; as an example, we consider the fourth derivative of the exact X hole in approximations to the XC energy.

References

[1] Přecechtělová, Bahmann, Kaupp, Ernzerhof, JCP Comm.141, 111102 (2014).
[2] Přecechtělová, Bahmann, Kaupp, Ernzerhof, JCP 143, 144102 (2015).
[3] Wang, Zhou, Ernzerhof, JCP 150, 084107 (2019).
[4] Wang, Zhou, Ernzerhof, JCP 151, 194102 (2019).
[5] Roy, Cuierrier, Ernzerhof, JCP, 152, 211101 (2020).
[6] Cuierrier, Roy, Ernzerhof, JCP, 155, 174121 (2021).