One correlation factor to unify them all

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ABSTRACT

The correlation factor (CF) [1, 2, 3] approach to the generalized Kohn-Sham density functional theory (KS-DFT), developed in our group, has proven to be a powerful tool to generate non-empirical and generalizable approximations to the exchange-correlation functional by transforming approximate or exact exchange (plus static correlation). In the CF approach, a starting exchange (plus static correlation) hole, denoted as $\rho_{X(S)}(\mathbf{r}, u)$, which depends on the reference position $\mathbf{r}$ and interelectronic separation u, is modeled from a simple auxiliary wavefunction. This model is then transformed into an exchange-correlation hole, $\rho_{XC}(\mathbf{r}, u)$, by applying a correlation factor $f_C(\mathbf{r}, u)$. This methodology has been successfully applied to meta-GGA exchange (CFBR_H) [3], exact exchange (CFX) [1], and exchange plus with static correlation obtained from an MCSCF reference wavefunction (CFXStatic) [2]. These applications have led to a series of highly accurate XC functionals, increasingly generalizable and suitable for systems with delocalization errors and strong static correlation. However, while these models yield similar results in normal systems where the exact exchange hole is fairly localized, differences arise due to certain simplifications made for implementation. The presentation will introduce a unified approach to these models, aimed at establishing a consistent methodology where the auxiliary wavefunction can be adjusted as necessary. We will also discuss the self-consistent implementation of this approach using automatic differentiation libraries, representing a significant step forward in computational efficiency and accuracy.

References

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[3] Roy, P.O.; Cuierrier, E.; Ernzerhof, M. *J. Phys. Chem. A* **2023**, *127,8*, 2026–2033.