

Ongoing Improvements to the Exchange-hole Dipole Moment Model

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Density-functional theory (DFT) allows first-principles computational modelling of the electronic structure of large-scale quantum systems. The combination of DFT’s high efficiency and accuracy has positioned it as the workhorse of computational chemistry in recent years. Standard DFT methods neglect dispersion, a weak intermolecular force that determines properties like friction, adhesion, crystal structure packing, and the shapes of biomolecules. To capture dispersion interactions, we incorporate corrections, such as the exchange-hole dipole moment (XDM) model.¹ In recent studies, we demonstrated that XDM correctly captures dispersion physics and exhibits best-in-class performance on a benchmark of 15,000 chemical systems.^{2,3}

Rather than using exact exchange, most implementations of the XDM model use the localized Becke-Rousell (BR) hole to calculate the exchange-hole dipole moments. This choice of model hole is more computationally efficient, especially for solid-state systems, but it also captures non-dynamical correlation from chemical bonding, thereby improving accuracy for many molecular systems. However, this approach fails to capture short-range dynamical correlation, which may hamper XDM’s accuracy in systems like bulk metals.⁴

When the XDM model calculates the forces and stresses, we assume that the dispersion coefficients are constant with respect to changing chemical environment. However, this assumption can occasionally lead to slight inaccuracies in system geometry in specific solid-state applications, where dispersion coefficients are highly sensitive to changes in unit-cell volume.⁵ Further, this assumption hinders XDM’s use in molecular dynamics, where it could cause a force-energy inconsistency in simulations over time.

We are currently developing an improved version of XDM that accounts for changes in the dispersion coefficients in the evaluation of the forces and stress tensor. Further, we are also investigating whether it is worthwhile to explicitly capture the correlation hole and account for that contribution to the dispersion energy and forces. This work will discuss recent progress towards these two goals.

References

- [1] A. D. Becke, E. R. Johnson, *Exchange-hole Dipole Moment and the Dispersion Interaction Revisited*, J. Chem. Phys. **127**, 154108 (2007)
- [2] K. R. Bryenton, E. R. Johnson, *Many-Body Dispersion in Model Systems and the Sensitivity of Self-Consistent Screening*, J. Chem. Phys. **158**, 204110 (2023). doi: [10.1063/5.0142465](https://doi.org/10.1063/5.0142465)
- [3] C. J. Nickerson, K. R. Bryenton, A. J. Price, E. R. Johnson, *Comparison of DFT Dispersion Corrections for the DES15K Database*. J. Phys. Chem. (In Press, 2023). doi: [10.1021/acs.jpca.3c04332](https://doi.org/10.1021/acs.jpca.3c04332)
- [4] K. R. Bryenton, A. A. Adeleke, S. G. Dale, E. R. Johnson, *Delocalization Error: The Greatest Outstanding Challenge in Density-functional Theory*, WIREs Comput. Mol. Sci. **13** e1631, (2023). doi: [10.1002/wcms.1631](https://doi.org/10.1002/wcms.1631)
- [5] A. J. Price, K. R. Bryenton, E. R. Johnson, *Requirements for an Accurate Dispersion-corrected Density Functional*, J. Chem. Phys. **154**, 23, 230902, (2021). doi: [10.1063/5.0050993](https://doi.org/10.1063/5.0050993)