# Comparison of DFT dispersion corrections on the DES15K database

**Cameron J. Nickerson**[a], **Kyle R. Bryenton**[a], **Alastair J. A. Price**[b], **and Erin R. Johnson**[b]

[a]*Department of Physics and Atmospheric Science, Dalhousie University, Halifax, NS, Canada*
[b]*Department of Chemistry, Dalhousie University, Halifax, NS, Canada*

While density-functional theory (DFT) remains one of the most widely used tools in computational chemistry, most functionals fail to properly account for the effects of London dispersion. Hence, there are many popular post-self-consistent methods to add a dispersion correction to the DFT energy. Until now, the most popular methods have never been compared on equal footing due to not being implemented in the same electronic structure packages. In this work, we performed a large-scale benchmarking study, directly comparing the accuracy of the XDM, D3BJ, D4, TS, MBD, and MBD-NL dispersion models when applied to the recent DES15K database of nearly 15,000 molecular complexes at both expanded and compressed geometries. Our study showed similarly good performance for all dispersion methods (except TS) when applied to neutral complexes. However, they all performed worse for ionic complexes, particularly those involving dications of alkaline earth metals, due to systematic overbinding by the base PBE0 density functional. Investigation of the largest outliers also revealed that only the MBD and MBD-NL methods demonstrate surprising errors for complexes involving alkali metal cations at compressed geometries, where they tended to significantly overbind. As we would expect minimal dispersion binding for such complexes, we further investigated the origins of these errors for the potential energy curve of a model cation-$\pi$ complex. Overall, there is little to choose between the XDM, D3BJ, D4, MBD, and MBD-NL dispersion methods for most systems. However, the MBD-based methods are not recommended for complexes involving organic species and alkali or alkaline earth metal cations, for example when modeling $Li^+$ intercalation into graphite.