Many-Body Dispersion in Model Systems and the Surprising Sensitivity of Self-Consistent Screening

Kyle R. Bryenton Dalhousie Department of Physics and Atmospheric Science

Come see my talk: (COMP) Thursday, March 30, 2023 at 10:30am, Room 120 - Indiana Convention Center

Abstract

Standard methods in density-functional theory do not account for dispersion contributions, so a correction such as the exchange-hole dipole moment (XDM) or many-body dispersion (MBD) models must be added. Recent literature has discussed the importance of many-body effects on dispersion, and attention has turned to which methods accurately capture them. Here, we directly compared computed dispersion coefficients and energies from XDM and MBD for model systems, noble gas dimers, molecular dimers, and layered materials. While the results were similar at large separations, MBD was susceptible to a polarization catastrophe at short range. Further, MBD's self-consistent screening formalism (SCS) was shown to be surprisingly sensitive to the choice of input polarizabilities.

Dispersion Corrections and Many-Body Effects

Electronic Many-Body Effects: Refers to the responsiveness of the pairwise dispersion coefficients (C_n's) to changes in the atomic environment. These terms can change by up to 50%.

$$E_{\text{Disp}}^{(2)} = -\sum_{i<j}\left[\frac{C_{6,ij}}{R_{ij}^{6}} + \frac{C_{8,ij}}{R_{ij}^{8}} + \frac{C_{10,ij}}{R_{ij}^{10}} + \dots\right]$$

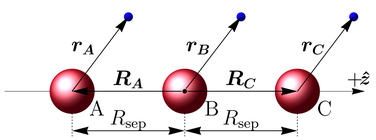
Atomic Many-Body Effects: Refers to the inclusion of dispersion terms that involve more than two atoms, representing a small fraction of the total dispersion energy. The leading-order (ATM) contribution is given by:

$$E_{\text{Disp}}^{(3)} = \sum_{i<j<k}\frac{C_{9,ijk}\left[3\cos(\theta_i)\cos(\theta_j)\cos(\theta_k)+1\right]}{R_{ij}^{3}R_{jk}^{3}R_{ki}^{3}}$$

We compare various post-SCF dispersion corrections. TS uses only an empirically derived C_6 and a Wu-Yang (WY) damping function. XDM includes terms beyond C_6, uses a more sophisticated Becke-Johnson (BJ) damping function, and captures electronic many-body effects through the exchange-hole dipole moment ($d_{X\sigma}$). MBD uses range-separated self-consistent screening (rsSCS) to damp the energy and correct unphysical polarizabilities (α) from its starting point, TS. MBD also implements a coupled fluctuating dipole model (CFDM) Hamiltonian to capture atomic many-body effects.

Disp.	Damp.	C_6	$> C_6$	Elec.	Atom.
TS:	WY	✓	✗	✗	✗
XDM:	BJ	✓	✓	$d_{X\sigma}$	C_9
MBD:	rs	✓	✗	SCS	$\hat{H}_{\text{CFDM}}$

Methods

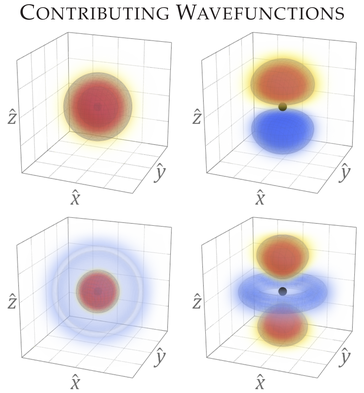


Chains of quantum harmonic oscillators aligned along the z-axis were studied from first principles. The interaction Hamiltonian is

$$\hat{H} = \sum_{p}\left(\hat{T}_p + \hat{V}_p\right) + \sum_{q\neq p}\left(\hat{U}_{pq}^{\text{en}} + \tfrac{1}{2}\hat{U}_{pq}^{\text{ee}} + \tfrac{1}{2}\hat{U}_{pq}^{\text{nn}}\right).$$

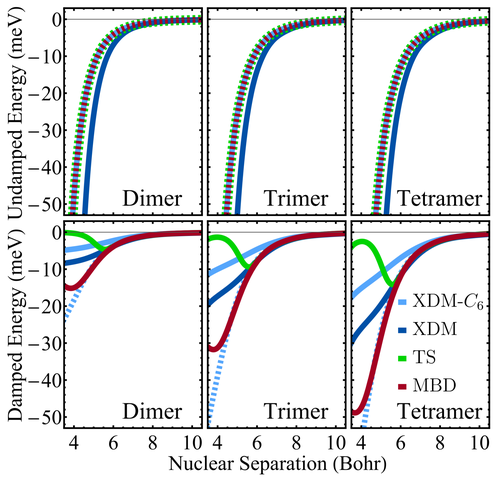
A linear combination of isotropic QHO wavefunctions from the ground and first two excited states were considered, but only those with z-axis symmetry contributed to binding. The total energy was variationally optimized. DFT calculations were performed in FHIaims with a "light" basis, "dense" integration grids for molecules/solids, a "tight" basis for noble gas dimers, and a 12×12×4 **k**-point mesh for layered materials.

Contributing Wavefunctions

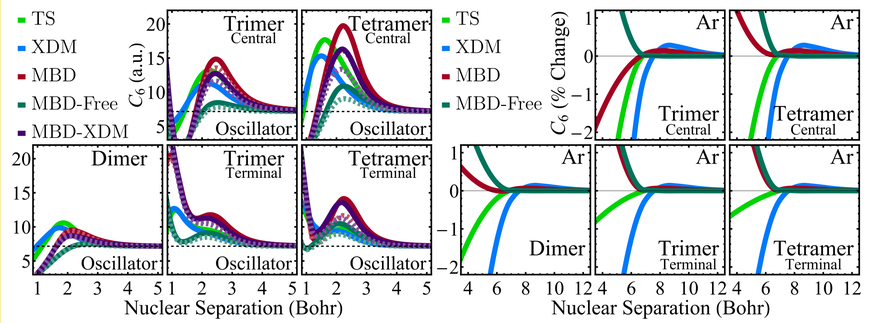


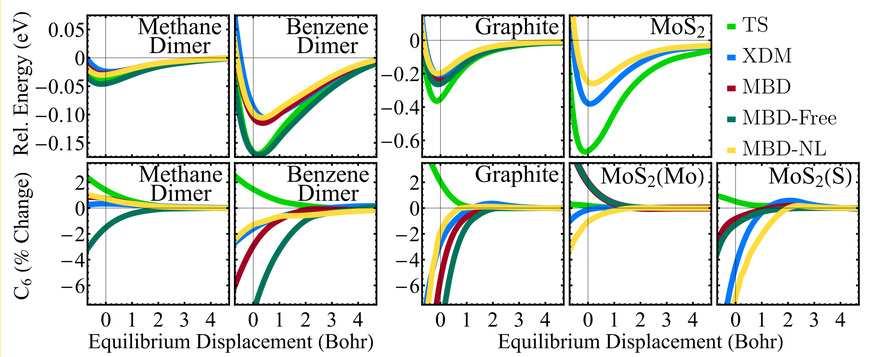
Results

First, we compare the oscillator systems' undamped and damped dispersion energies. In the undamped case, MBD follows XDM's C_6-only energy contribution, indicating it is a C_6-only method. For a fair comparison of damped energies, all damping functions were reparameterized at a 5Z level of theory on a set of noble gas dimers. The light-blue dashed line represents a C_6-only version of XDM. Here we see that the C_6-only methods all underdamp to compensate for the lack of higher-order dispersion terms, following the full version of XDM rather than its C_6 contribution.



Next, we compare the C_6 coefficients from the oscillator data to Ar chains. Here, we implemented two variants of MBD: MBD-Free and MBD-XDM, which use free-atom and XDM starting points. For the MBD methods, solid and dashed lines indicate SCS- and rsSCS-derived C_6 coefficients respectively. The C_6 coefficients of these MBD methods diverge at short range due to the "polarization catastrophe" associated with the SCS routine. Further, the SCS routine shows a concerning sensitivity to the input polarizability, suggesting TS may be a non-ideal starting point.





Lastly, we compare to molecular dimers and layered materials. For MoS_2, MBD and MBD-Free predicted complex-valued energies and thus are not reported. The MBD-NL method (which uses the VV10 model as a starting point) is suggested for such materials. Here, we see TS poorly captures electronic many-body effects on its C_6 dispersion coefficient, while MBD, MBD-NL, and XDM are in general agreement. MBD and MBD-NL tended to have about 50% higher C_6 coefficients than XDM, which is not unexpected as $1.5\times C_6$ has been shown to improve C_6-only XDM's performance. The RMSPE for these systems' binding energies were 75% (TS), 67% (MBD-Free), 22% (MBD-NL), 18% (MBD), and 8% (XDM).

Conclusion

XDM clearly captures electronic many-body effects through the use of the exchange-hole dipole moments. MBD cancels the error from lacking higher-order dispersion effects through a weaker damping function and overestimating C_6 coefficients, achieving similar results to XDM at both intermediate and long range. At short range, MBD exhibits a "polarization catastrophe" due to the SCS routine, which has been shown to be highly sensitive to the starting point. While XDM performs consistently well, no one starting point appears suitable for MBD. Perhaps the MBD-XDM scheme, considered here only for the oscillator model systems, may present a more general solution for MBD.

Contact Information

Presenter: Kyle Bryenton
Email: kyle.bryenton@dal.ca
Supervisor: Prof. Erin Johnson
Email: erin.johnson@dal.ca