

## 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 compare computed dispersion coefficients and energies from XDM and MBD for model systems, noble gas dimers, molecular dimers, and layered materials. While the results are similar at large separations, MBD's polarizabilities proved to be prone to error and sensitive to starting conditions.

## MANY-BODY EFFECTS AND POST-SCF DISPERSION CORRECTIONS

**ELECTRONIC MANY-BODY EFFECTS:** Refers to the responsiveness of the dispersion coefficients ( $C_n$ 's) to changes in the atomic environment, which can vary by up to 50%. The pairwise dispersion energy has the form

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

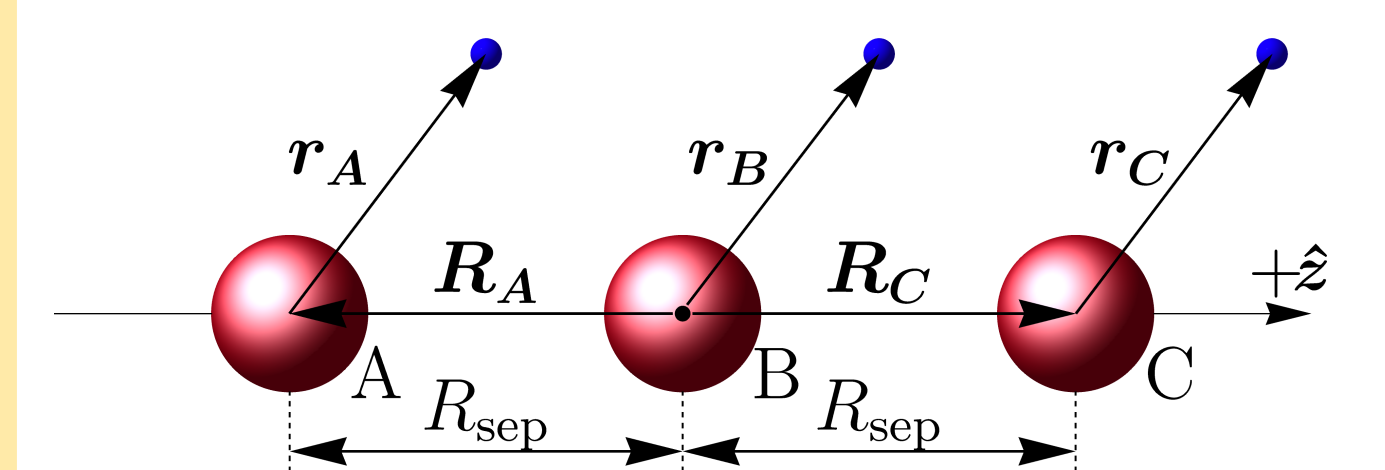
**ATOMIC MANY-BODY EFFECTS:** Refers to the inclusion of dispersion terms that involve more than two atoms, representing a small fraction of the total dispersion energy. The leading-order (ATM) contribution is given by

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

TS uses 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 ( $d_{\chi\sigma}$ ). MBD is based on random phase approximation (RPA) formalism and uses range-separated self-consistent screening (rsSCS) to damp the energy and attenuate the polarizabilities ( $\alpha$ ) 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	✓	✓	$d_{\chi\sigma}$	$C_9$
MBD:	rs	✓	✗	SCS	$\hat{H}_{\text{CFDM}}$

## METHODS

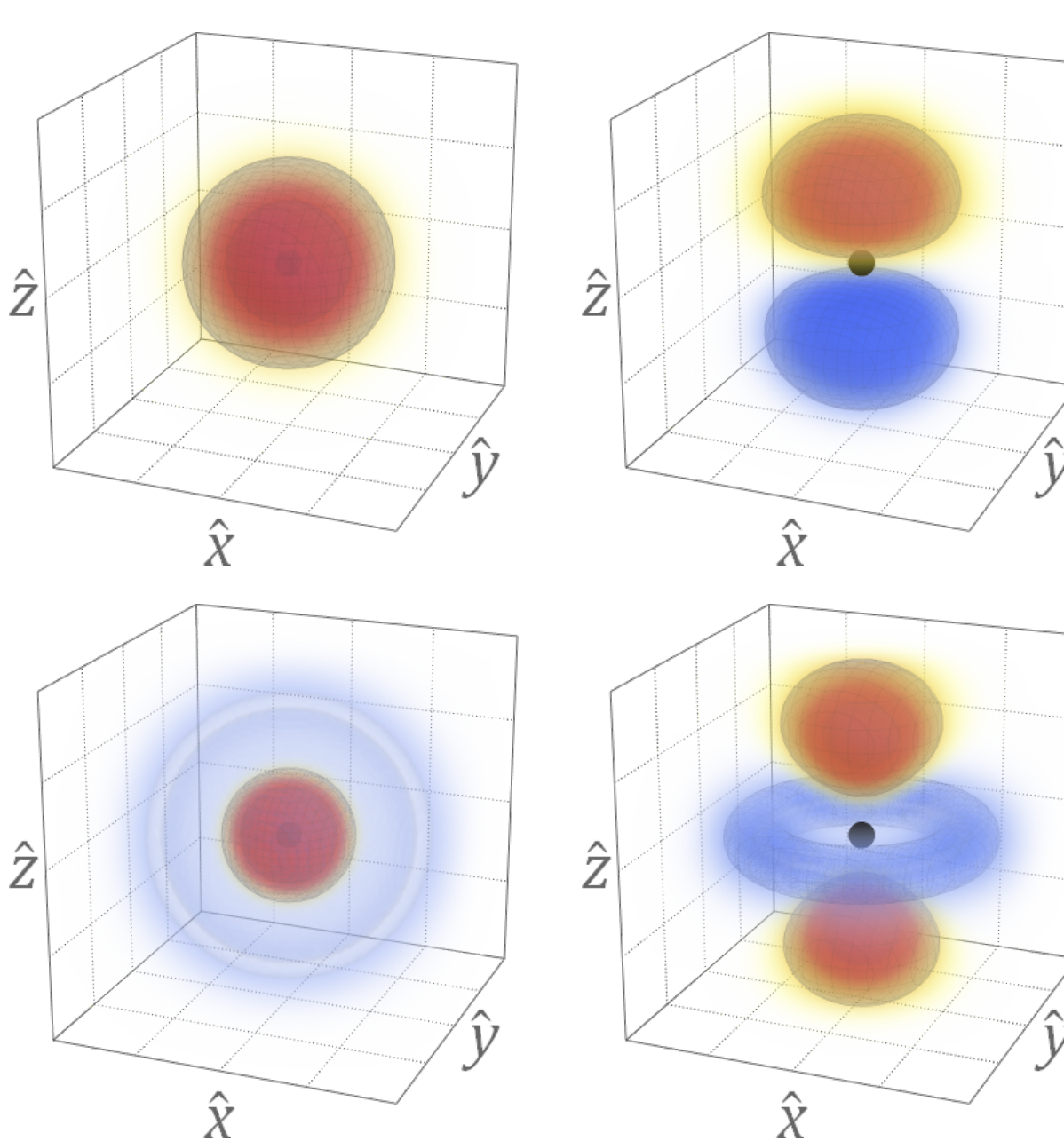


Chains of quantum harmonic oscillators aligned along the  $z$ -axis were studied from first principles. This system's Hamiltonian has the form

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

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 energy was calculated and variationally minimized by the `Oscallot` code. Accompanying DFT calculations were performed in FHI-aims with a "light" basis, "dense" integration grids for molecules/solids, a "tight" basis for noble gas dimers, and a  $12 \times 12 \times 4$   $k$ -point mesh for layered materials.

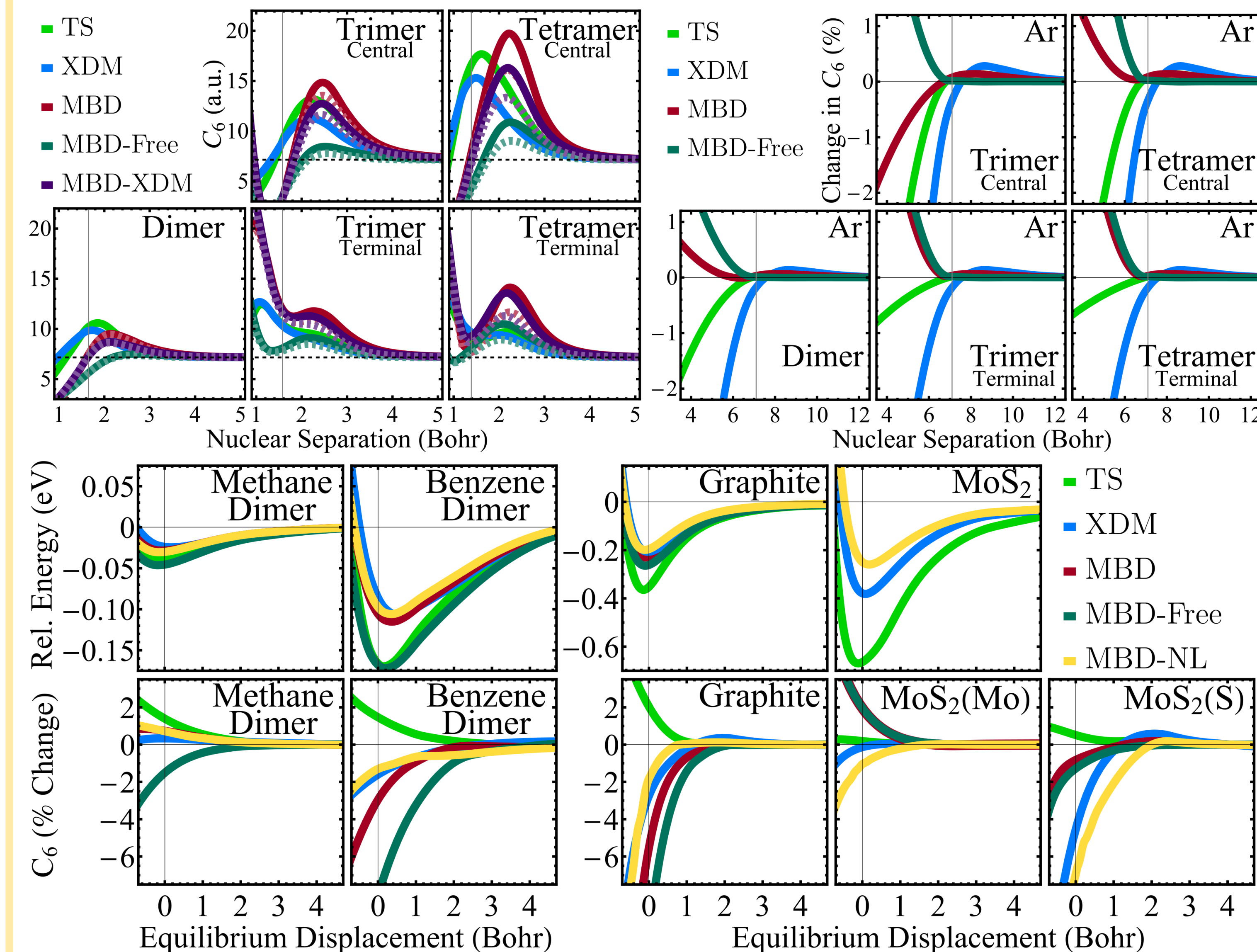
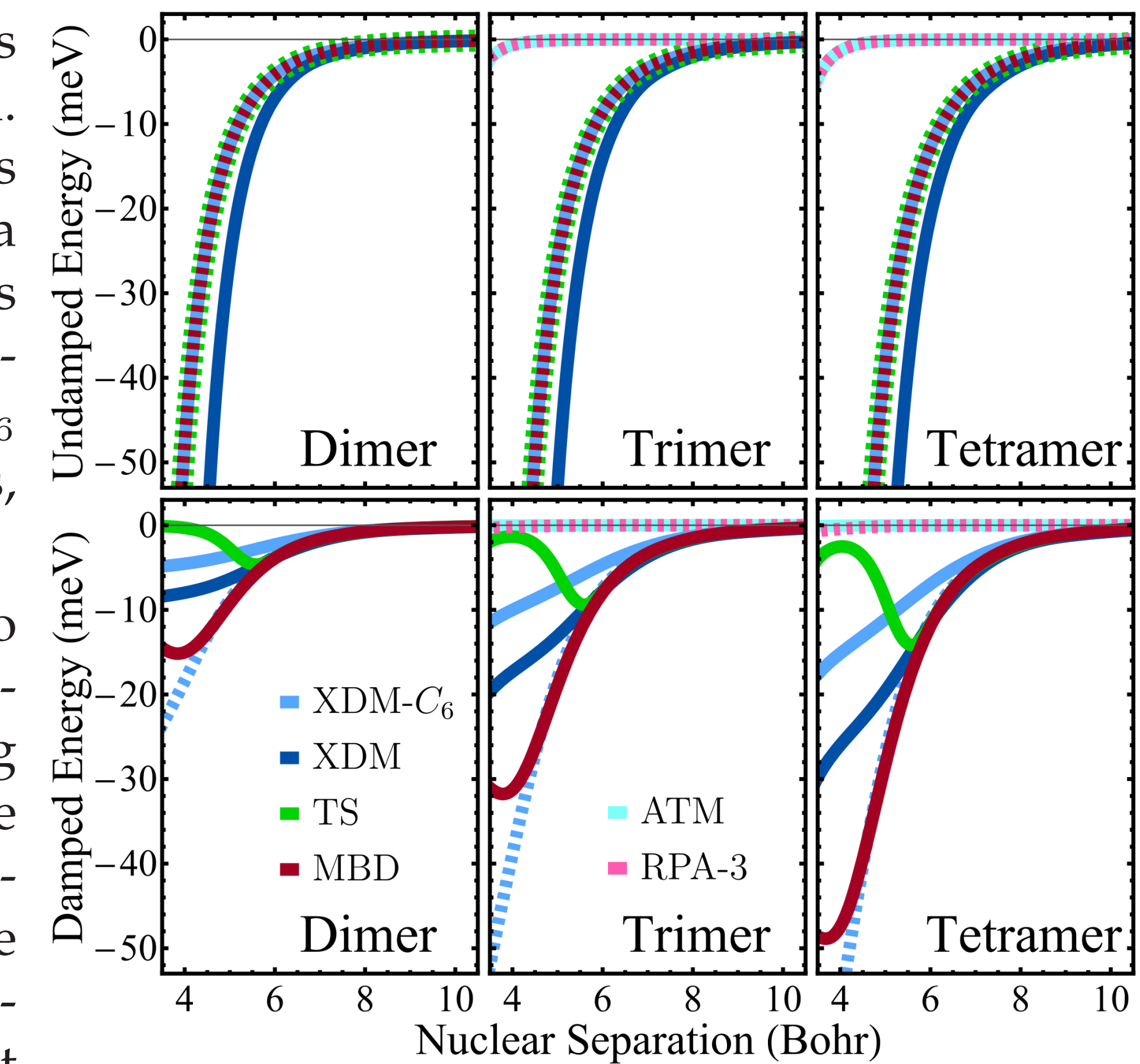
CONTRIBUTING WAVEFUNCTIONS



## 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. 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. Also shown are the 3-body RPA and ATM terms, which contribute negligibly to the total dispersion energy.

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  $\text{MoS}_2$ , MBD and MBD-Free predicted complex-valued energies and thus are not reported. The MBD-NL method (which uses VV10's polarizability functional as a starting point) is suggested for such systems. Here, we see that TS poorly captures electronic many-body effects on its  $C_6$  dispersion coefficient. In contrast, MBD-NL and XDM performed well in all systems and achieved similar accuracy to each other. On the molecular dimer,  $\text{S66} \times 8$ , and layered material,  $\text{LM26}(\text{LM11})$ , benchmarks, the MAEs were 0.60 kcal/mol and  $13.1(12.5) \text{ eV/\AA}^2$  for TS, 0.43 kcal/mol and  $4.6(5.0) \text{ meV/\AA}^2$  for MBD-NL, and 0.45 kcal/mol and  $4.9(3.7) \text{ meV/\AA}^2$  for XDM, respectively.

## CONCLUSION

XDM clearly captures electronic many-body effects through exchange-hole dipole moments and is highly accurate. MBD neglects higher-order terms and compensates with weaker damping, permitting similar accuracy to XDM at long range. At short range, MBD exhibits a "polarization catastrophe" due to the SCS routine and is surprisingly sensitive to the starting point. Forgoing SCS, MBD-NL performs well in all systems. Lastly, the 3-body ATM and RPA effects did not meaningfully contribute to the total energy.

• K R Bryenton, "Oscallot" (Version 2023-05-16), Github. (2023), doi: 10.5281/zenodo.7942358

• 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

## CONTACT INFORMATION

**PRESENTER:** KYLE BRYENTON  
**EMAIL:** KYLE.BRYENTON@DAL.CA  
**SUPERVISOR:** PROF. ERIN JOHNSON  
**EMAIL:** ERIN.JOHNSON@DAL.CA

