



PHYC 6802 SEMINAR III:
MANY-BODY DISPERSION IN MODEL SYSTEMS AND THE
SENSITIVITY OF SELF-CONSISTENT SCREENING



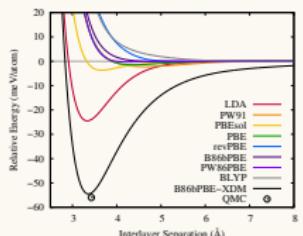
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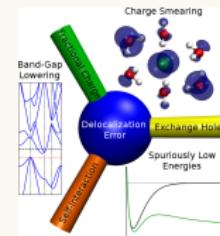
February 14, 2022

Requirements for an Accurate Dispersion-Corrected Density Functional



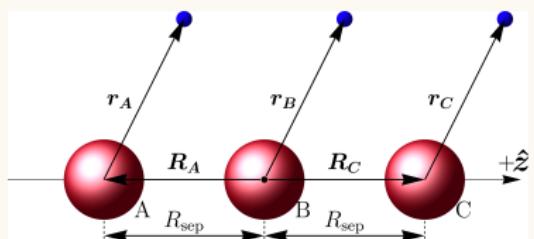
Price, A. J., Bryenton, K. R., & Johnson, E. R. *J. Chem. Phys.* **154**, 230902. (2021) doi: 10.1063/5.0050993

Delocalization Error: The greatest outstanding challenge in Density-Functional Theory



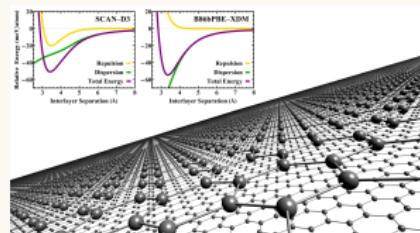
Bryenton, K. R., Adeleke, A. A., Dale, S.G. & Johnson E. R., *WIREs Comput. Mol. Sci.* e1631. (2022) doi: 10.1002/wcms.1631

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



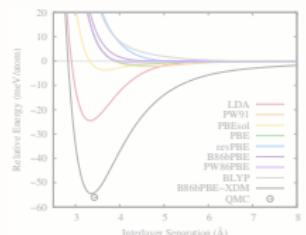
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MBD-XDM Implementation, Improved XDM Forces, and Improved XDM Polarizabilities



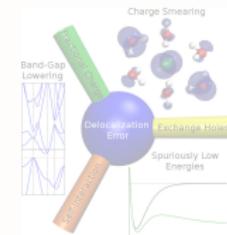
In Progress

Requirements for an Accurate Dispersion-Corrected Density Functional



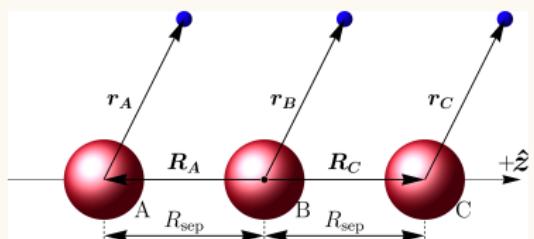
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Delocalization Error: The greatest outstanding challenge in Density-Functional Theory



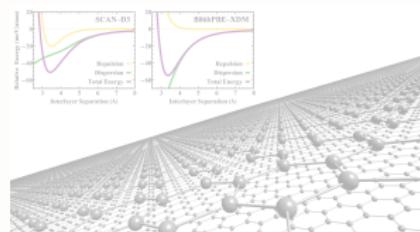
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Many-Body Dispersion in Model Systems and the Sensitivity of Self-Consistent Screening



Bryenton, K. R., & Johnson, E. R. *J. Chem. Phys.* (Submitted). (2023)

MBD-XDM Implementation, Improved XDM Forces, and Improved XDM Polarizabilities



In Progress

Electronic-Structure Theory
○○○

Dispersion
○○○○○○○○○○

Oscillator Systems
○○○○○○○

Results
○○○○○○○○○○

Conclusions
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Electronic-Structure Theory

Wavefunction Theory

Hohenberg-Kohn-Sham DFT

DFT: The Electronic-Structure Multitool

Dispersion

Oscillator Systems

Results

Conclusions

WAVEFUNCTION THEORY

For a general quantum chemical system, the Hamiltonian is given by

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_{i,A} \frac{Z_A}{|\mathbf{r}_i - \mathbf{r}_A|} + \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$

in atomic units, $\hbar = e = a_0 = m_e = 1$.

Instead of dealing with N electrons, we could write everything in terms of the “electron density” instead. For N electrons occupying orbitals $\psi_i(\mathbf{r})$ the electron density is given by

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2.$$

This reduces the dimensionality of our problem from $3N$ to just 3.

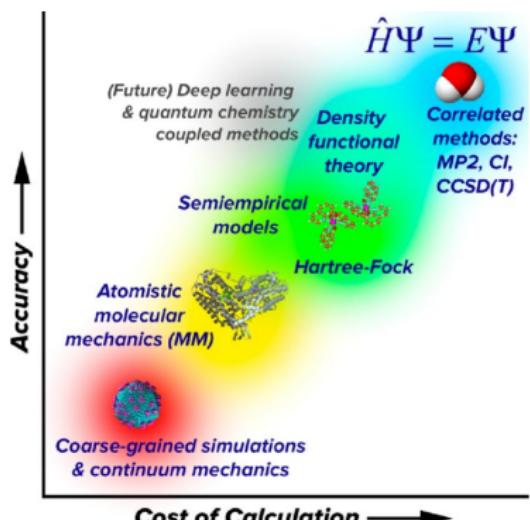
HOHENBERG-KOHN-SHAM DFT

Density-functional theory (DFT) has proven to be one of the most accurate ways of calculating the electronic structure of molecules and solids while maintaining sufficiently low computational requirements.

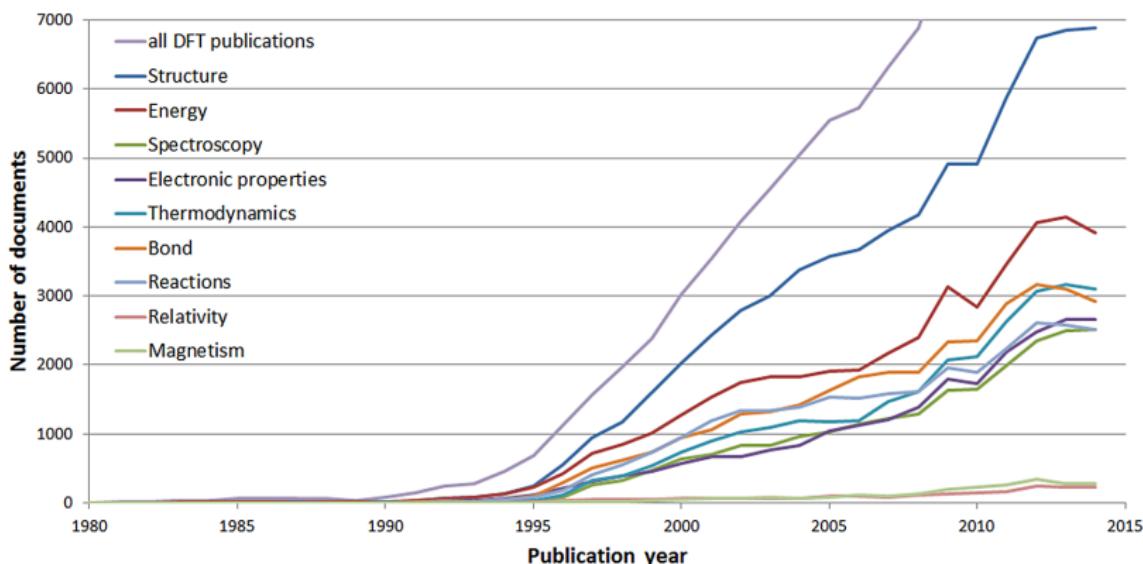
The N -electron problem is greatly simplified by writing the total energy,

$$E[\rho] = T_s[\rho] + \int v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_H[\rho] + E_{\text{xc}}[\rho],$$

as a functional of the electron density.



DFT: THE ELECTRONIC-STRUCTURE MULTITOOL



- In 2019, there were almost 15,000 DFT publications
- In the top 10 most cited papers of all time, #7 and #8 are DFT papers
- One of these was published by Prof. Axel Becke, with almost 100,000 citations

Electronic-Structure Theory

Dispersion

What is Dispersion?

Many-Body Dispersion Effects

Post-SCF Dispersion Corrections

The Tkatchenko-Scheffler Model

The Exchange-hole Dipole Moment Model

The Many-body Dispersion Model

Motivation: XDM vs. MBD

Oscillator Systems

Results

Conclusions

WHAT IS DISPERSION

London dispersion is a weak, attractive, intermolecular force that occurs due to interactions between instantaneous dipole moments of neighbouring atoms.

Properties Determined by Dispersion:

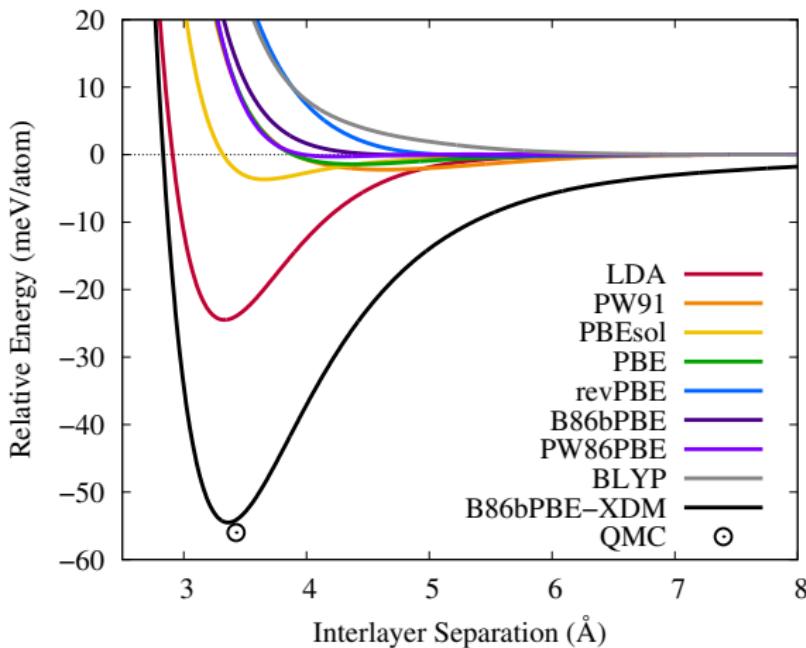
- Adhesion
- Friction
- Surface adsorption
- Phase-change conditions
- Packing in molecular crystals
- Shapes of biomolecules
- Stability of supramolecular complexes



Scamper the Gecko

DISPERSION IN DFT

EXAMPLE: SEPARATING GRAPHITE LAYERS



ELECTRONIC MANY-BODY EFFECTS

Refers to the responsiveness of the pairwise dispersion coefficients to changes in the atomic environment.

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

ATOMIC MANY-BODY EFFECTS

Refer to terms in the perturbation-theory expansion of the dispersion energy that involve more than two atoms. These represent <1% of the total dispersion energy.

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

THE TS MODEL

The Tkatchenko-Scheffler (TS) model only considers the lowest-order dispersion term, corresponding to instantaneous dipole-dipole contributions of the form

$$E_{\text{TS}} = - \sum_i \sum_{j < i} f_{\text{TS}}^{\text{WY}}(R_{ij}) \frac{C_{6,ij}^{\text{TS}}}{R_{ij}^6},$$

where f^{WY} is a Wu-Yang damping function with $R_{ij}^0 = R_i^0 + R_j^0$, and the heteroatomic dispersion coefficients are obtained using the Slater-Kirkwood formula:

$$f^{\text{WY}}(R_{ij}) = \frac{1}{1 + \exp \left[-d \left(\frac{R_{ij}}{\beta R_{ij}^0} - 1 \right) \right]}, \quad C_{6,ij}^{\text{TS}} = \frac{2C_{6,ii}C_{6,jj}}{\frac{\alpha_j^0}{\alpha_i^0}C_{6,ii} + \frac{\alpha_i^0}{\alpha_j^0}C_{6,jj}}.$$

The homoatomic dispersion coefficients, static polarizabilities, and vdW radii are determined from their free values and effective volumes $v_i = \langle r^3 \rangle_i$ as,

$$C_{6,ii} = \left(\frac{v_i}{v_i^{\text{free}}} \right)^2 C_{6,ii}^{\text{free}}, \quad \alpha_i^0 = \left(\frac{v_i}{v_i^{\text{free}}} \right) \alpha_i^{\text{free}}, \quad R_i^0 = \left(\frac{v_i}{v_i^{\text{free}}} \right)^{\frac{1}{3}} R_i^{\text{free}}.$$

THE XDM MODEL

The exchange-hole dipole moment (XDM) model calculates the dispersion energy via

$$E_{\text{XDM}} = - \sum_i \sum_{j < i} \sum_{n=6,8,10} f_n^{\text{BJ}}(R_{ij}) \frac{C_{n,ij}^{\text{XDM}}}{R_{ij}^n}$$

using the Becke-Johnson damping function, $f_n^{\text{BJ}}(R_{ij})$, defined in terms of the van der Waals radius, $R_{\text{vdW},ij} = (a_1 R_{c,ij} + a_2)$, and the critical damping radius

$$f_n^{\text{BJ}} = \frac{R_{ij}^n}{R_{ij}^n + R_{\text{vdW},ij}^n}, \quad R_{c,ij} = \frac{1}{3} \left[\left(\frac{C_{8,ij}^{\text{XDM}}}{C_{6,ij}^{\text{XDM}}} \right)^{\frac{1}{2}} + \left(\frac{C_{10,ij}^{\text{XDM}}}{C_{6,ij}^{\text{XDM}}} \right)^{\frac{1}{4}} + \left(\frac{C_{10,ij}^{\text{XDM}}}{C_{8,ij}^{\text{XDM}}} \right)^{\frac{1}{2}} \right].$$

The exchange-hole dipole moment for a reference electron at point \mathbf{r}_1 is obtained by integrating the exchange hole over \mathbf{r}_2 via

$$d_{X\sigma}(\mathbf{r}_1) = \left[\frac{1}{\rho_\sigma(\mathbf{r}_1)} \sum_{ij} \psi_{i\sigma}(\mathbf{r}_1) \psi_{j\sigma}(\mathbf{r}_1) \int \mathbf{r}_2 \psi_{i\sigma}(\mathbf{r}_2) \psi_{j\sigma}(\mathbf{r}_2) d\mathbf{r}_2 \right] - \mathbf{r}_1.$$

The multipole moment integral is defined in terms of the Hirshfeld weights and the exchange-hole dipole moment

$$\langle M_\ell^2 \rangle = \sum_{\sigma} \int w_i(\mathbf{r}) \rho_{\sigma}(\mathbf{r}) \left[r^\ell - (r - d_{X\sigma})^\ell \right]^2 d\mathbf{r},$$

which is then used to solve for the heteroatomic dispersion coefficients:

$$C_{6,ij}^{\text{XDM}} = \frac{\alpha_i \alpha_j \langle M_1^2 \rangle_i \langle M_1^2 \rangle_j}{\alpha_i \langle M_1^2 \rangle_j + \alpha_j \langle M_1^2 \rangle_i}$$

$$C_{8,ij}^{\text{XDM}} = \frac{3}{2} \frac{\alpha_i \alpha_j \left(\langle M_1^2 \rangle_i \langle M_2^2 \rangle_j + \langle M_2^2 \rangle_i \langle M_1^2 \rangle_j \right)}{\alpha_i \langle M_1^2 \rangle_j + \alpha_j \langle M_1^2 \rangle_i}$$

$$C_{10,ij}^{\text{XDM}} = 2 \frac{\alpha_i \alpha_j \left(\langle M_1^2 \rangle_i \langle M_3^2 \rangle_j + \langle M_3^2 \rangle_i \langle M_1^2 \rangle_j \right)}{\alpha_i \langle M_1^2 \rangle_j + \alpha_j \langle M_1^2 \rangle_i} + \frac{21}{5} \frac{\alpha_i \alpha_j \langle M_2^2 \rangle_i \langle M_2^2 \rangle_j}{\alpha_i \langle M_1^2 \rangle_j + \alpha_j \langle M_1^2 \rangle_i}.$$

THE MBD MODEL

The many-body dispersion (MBD) model revolves around solving the coupled fluctuating dipole model (CFDM) Hamiltonian

$$\hat{H} = -\frac{1}{2} \sum_i^N \nabla_{\xi_i}^2 + \frac{1}{2} \sum_i^N \left(\omega_i^{SCS} \xi_i \right)^2 + \sum_i^N \sum_{j < i}^N \omega_i^{SCS} \omega_j^{SCS} \sqrt{\alpha_i^{SCS} \alpha_j^{SCS}} \xi_i \mathbf{T}'_{ij} \xi_j ,$$

which uses refines its coefficients through self-consistent screening (SCS):

$$\boldsymbol{\alpha}_i^{SCS}(i\omega) = \boldsymbol{\alpha}_i^{TS}(i\omega) + \boldsymbol{\alpha}_i^{TS}(i\omega) \sum_{j \neq i} \mathbf{T}_{ij} \boldsymbol{\alpha}_j^{SCS}(i\omega) \quad \mathbf{T}_{ij} = \nabla_{\mathbf{R}_i} \otimes \nabla_{\mathbf{R}_j} v_{ij}$$

$$C_{6,ij}^{SCS} = \frac{3}{\pi} \int_0^\infty \alpha_i^{SCS}(i\omega) \alpha_j^{SCS}(i\omega) d\omega \quad \omega_i^{SCS} = \frac{4}{3} \frac{C_{6,ii}^{SCS}}{(\alpha_i^{SCS})^2} .$$

The CFDM eigenvalues and SCS excitation frequencies are used to calculate the MBD energy

$$E_{MBD} = \frac{1}{2} \sum_{i=1}^{3N} \sqrt{\lambda_i} - \frac{3}{2} \sum_{i=1}^N \omega_i^{SCS} .$$

RSSCS: RANGE-SEPARATED SELF-CONSISTENT SCREENING

The MBD model also makes use of rsSCS, which is effectively just implementing a Wu-Yang damping function.

First, the dipole-dipole interaction tensor elements is converted into a short-range version via a Wu-Yang damping function,

$$\mathcal{T}_{\text{SR},ij}^{ab} = \left[1 - f_{\text{rsSCS}}^{\text{WY}}(R_{ij}) \right] \mathcal{T}_{ij}^{ab}.$$

Substituting this into the SCS equation generates the short-range screened parameters, α^{rsSCS} and ω^{rsSCS} . These are then combined with a long-range interaction tensor,

$$\mathcal{T}_{\text{LR},ij}^{ab} = f_{\text{rsSCS}}^{\text{WY}}(R_{ij}) \frac{R_{ij}^2 \delta_{ab} - 3R_{ij}^a R_{ij}^b}{R_{ij}^5},$$

to calculate the CFDM Hamiltonian's eigenvalues and ultimately calculate the MBD@rsSCS dispersion energy.

SUMMARY OF DISPERSION CORRECTIONS

α	Polarizability	SCS	Self-Consistent Screening
C_n	Dispersion Coefficients	CFDM	Coupled-Fluctuating Dipole Model
R_{vdw}	van der Waals Radius	TS	Tkatchenko-Scheffler Model
WY	Wu-Yang Damping	XDM	Exchange-Hole Dipole Moment
BJ	Becke-Johnson Damping	MBD	Many-Body Dispersion Model

Disp.	Damping	C_6	$> C_6$	Empirical	Elec.	Atom.
TS:	WY	✓	✗	$\alpha, C_6, R_{\text{vdw}}$?	✗

SUMMARY OF DISPERSION CORRECTIONS

α	Polarizability	SCS	Self-Consistent Screening
C_n	Dispersion Coefficients	CFDM	Coupled-Fluctuating Dipole Model
R_{vdw}	van der Waals Radius	TS	Tkatchenko-Scheffler Model
WY	Wu-Yang Damping	XDM	Exchange-Hole Dipole Moment
BJ	Becke-Johnson Damping	MBD	Many-Body Dispersion Model

Disp.	Damping	C_6	$> C_6$	Empirical	Elec.	Atom.
TS:	WY	✓	✗	α, C_6, R_{vdw}	?	✗
XDM:	BJ	✓	✓	α	?	✓

SUMMARY OF DISPERSION CORRECTIONS

α	Polarizability	SCS	Self-Consistent Screening
C_n	Dispersion Coefficients	CFDM	Coupled-Fluctuating Dipole Model
R_{vdw}	van der Waals Radius	TS	Tkatchenko-Scheffler Model
WY	Wu-Yang Damping	XDM	Exchange-Hole Dipole Moment
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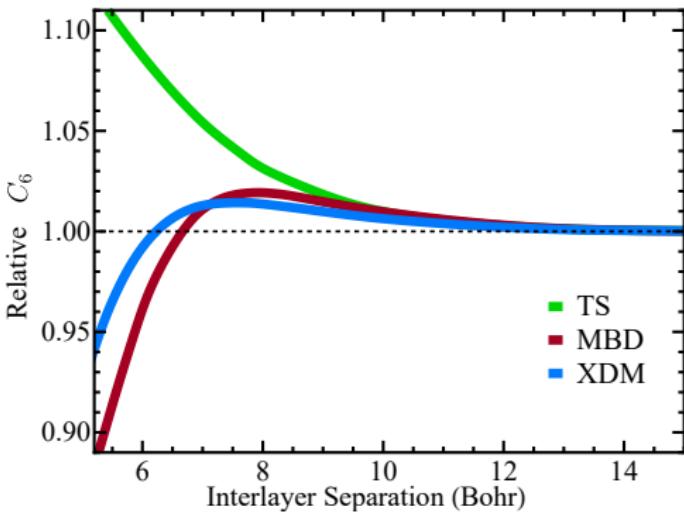
Disp.	Damping	C_6	$> C_6$	Empirical	Elec.	Atom.
TS:	WY	✓	✗	α, C_6, R_{vdw}	?	✗
XDM:	BJ	✓	✓	α	?	✓
MBD:	rsSCS	✓	?	TS+SCS	?	✓

SUMMARY OF DISPERSION CORRECTIONS

α	Polarizability	SCS	Self-Consistent Screening
C_n	Dispersion Coefficients	CFDM	Coupled-Fluctuating Dipole Model
R_{vdw}	van der Waals Radius	TS	Tkatchenko-Scheffler Model
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Disp.	Damping	C_6	$> C_6$	Empirical	Elec.	Atom.
TS:	WY	✓	✗	α, C_6, R_{vdw}	?	✗
XDM:	BJ	✓	✓	α	?	✓
MBD:	WY+ 	✓	?	TS+SCS	?	✓

MOTIVATION: XDM vs. MBD SEPARATING GRAPHITE LAYERS



ORIGINAL RESEARCH GOALS:

1. Compare XDM and MBD on systems of harmonic oscillators
2. Investigate if XDM captures electronic many-body dispersion effects
3. Investigate if MBD captures higher-order dispersion effects

Adapted with permission from:

Otero-de-la-Roza, A. et al. *J. Phys. Chem. Lett.*, **11** 6, 2298–2302. (2020) doi: 10.1021/acs.jpclett.0c00348

Electronic-Structure Theory
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Dispersion
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Oscillator Systems
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Results
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Conclusions
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Electronic-Structure Theory

Dispersion

Oscillator Systems

System Geometry

Single-Oscillator Hamiltonian & Wavefunctions

Multi-Oscillator Hamiltonian & Wavefunctions

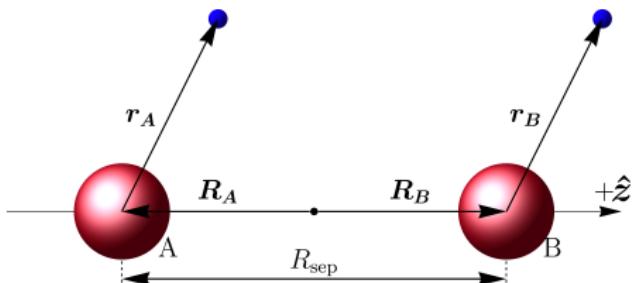
Variational Minimization

Results

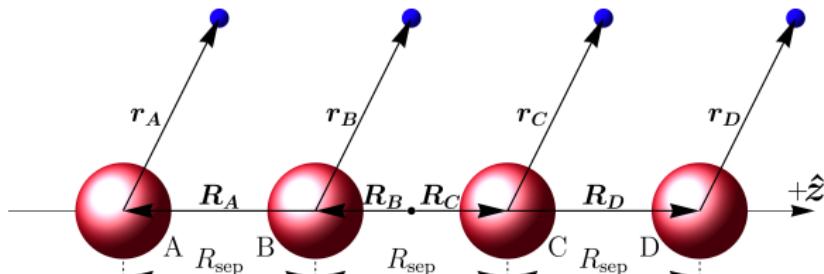
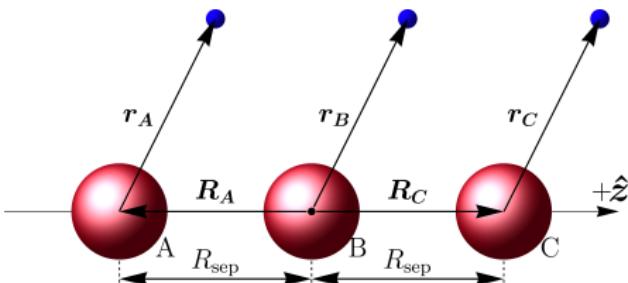
Conclusions

SYSTEM GEOMETRY

DIMER



TRIMER



TETRAMER

SINGLE OSCILLATOR

We start by solving the isotropic quantum harmonic oscillator

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 + \frac{1}{2} \mu \omega^2 r^2 \quad E = \hbar \omega \left(2k + \ell + \frac{3}{2} \right) \quad n = 2k + \ell$$

with eigenvector solutions given by

$$\psi_{k\ell m}(r, \theta, \phi) = N_{k\ell} r^\ell e^{-\nu r^2} L_k^{\ell+\frac{1}{2}}(2\nu r^2) Y_\ell^m(\theta, \phi) \quad \nu = \mu\omega/2\hbar$$

We take a linear combination of wavefunctions

$$\Psi(\mathbf{r}) = \sum_i c_i \psi_i(\mathbf{r}) \quad \sum_i c_i^2 = 1$$

for use in the oscillator systems of interest.

MULTI-OSCILLATOR HAMILTONIAN

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

ENERGY TERMS

$$\hat{T}_p + \hat{V}_p = -\frac{\hbar^2}{2\mu_p} \nabla_p^2 + \frac{1}{2} \mu_p \omega_p^2 r_p^2$$

$$\hat{U}_{pq}^{\text{en}} = \frac{e^2}{4\pi\epsilon_0} \frac{-Z_q}{|(\mathbf{R}_p + \mathbf{r}_p) - \mathbf{R}_q|}$$

$$\hat{U}_{pq}^{\text{ee}} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{|(\mathbf{R}_p + \mathbf{r}_p) - (\mathbf{R}_q + \mathbf{r}_q)|}$$

$$\hat{U}_{pq}^{\text{nn}} = \frac{e^2}{4\pi\epsilon_0} \frac{Z_p Z_q}{|\mathbf{R}_p - \mathbf{R}_q|}$$

MULTI-OSCILLATOR HAMILTONIAN

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

1-ELECTRON ENERGY

$$E_p^{\text{1e}} = \left\langle \Psi_p \left| \hat{T}_p + \hat{V}_p + \sum_{q \neq p} \hat{U}_{pq}^{\text{en}} \right| \Psi_p \right\rangle$$

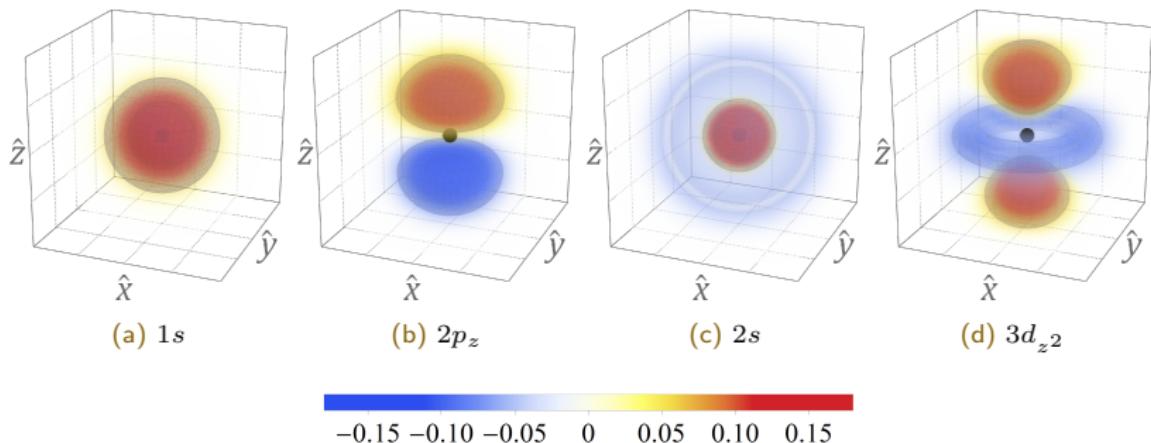
2-ELECTRON ENERGY

$$E_{pq}^{\text{2e}} = \left\langle \Psi_p \Psi_q \left| \frac{1}{2} \hat{U}_{pq}^{\text{ee}} \right| \Psi_p \Psi_q \right\rangle$$

TOTAL ENERGY

$$E = \sum_p E_p^{\text{1e}} + \sum_{q \neq p} E_{pq}^{\text{2e}} + \sum_{q \neq p} \frac{1}{2} \hat{U}_{pq}^{\text{nn}}$$

MULTI-OSCILLATOR WAVEFUNCTIONS



The explicit forms of the wavefunctions are written in terms of $\nu = \mu\omega/2\hbar$

$$\psi_{1s}(\mathbf{r}) = \frac{2^{3/4} \nu^{3/4}}{\pi^{3/4}} e^{-\nu r^2}$$

$$\psi_{2p_z}(\mathbf{r}) = \frac{2^{7/4} \nu^{5/4}}{\pi^{3/4}} e^{-\nu r^2} r \cos(\theta)$$

$$\psi_{2s}(\mathbf{r}) = \frac{2^{1/4} \nu^{3/4}}{\sqrt{3} \pi^{3/4}} e^{-\nu r^2} (3 - 4\nu r^2)$$

$$\psi_{3d_{z^2}}(\mathbf{r}) = \frac{2^{3/4} \nu^{7/4}}{\sqrt{3} \pi^{3/4}} e^{-\nu r^2} r^2 (3 \cos(2\theta) + 1)$$

VARIATIONAL MINIMIZATION

Minimizing the energy is a constrained optimization problem, suitable for the method of Lagrange multipliers. The Lagrangian for each of our systems is given by

Dimer:

$$\mathcal{L}(\{c_i\}, \lambda) = E - \lambda \left(1 - \sum_i c_i^2 \right)$$

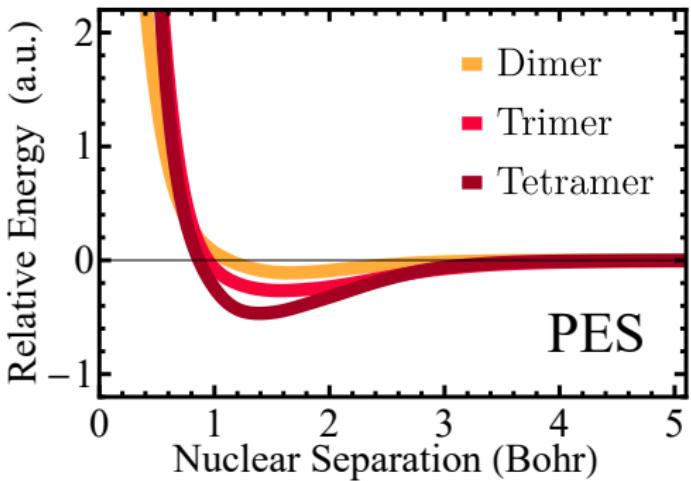
Trimer or Tetramer:

$$\mathcal{L}(\{c_i\}, \{d_i\}, \lambda_1, \lambda_2) = E - \lambda_1 \left(1 - \sum_i c_i^2 \right) - \lambda_2 \left(1 - \sum_i d_i^2 \right)$$

The critical points on our potential energy surface may be found by solving for the expansion coefficients, $\{c_i\}$ and $\{d_i\}$, in the equations generated by

$$\nabla \mathcal{L} = 0.$$

POTENTIAL ENERGY SURFACES



Now that the energies and electron densities have been determined, we may compute properties of interest, such as our dispersion corrections.

IMPLEMENTING DISPERSION

Disp.	Damping	C_6	$> C_6$	Empirical	Elec.	Atom.
TS:	WY	✓	✗	$\alpha, C_6, R_{\text{vdw}}$?	✗
XDM:	BJ	✓	✓	α	?	✓
MBD:	rsSCS	✓	?	TS+SCS	?	✓
MBD-Free:	rsSCS	✓	?	Free+SCS	?	✓
MBD-XDM:	rsSCS	✓	?	$\alpha+SCS$?	✓

The MBD-Free variant uses a free-atom starting point rather than implementing TS's volume scaling.

$$C_{6,ii} = \left(\frac{v_i}{v_i^{\text{free}}} \right)^2 C_{6,ii}^{\text{free}}, \quad \alpha_i^0 = \left(\frac{v_i}{v_i^{\text{free}}} \right) \alpha_i^{\text{free}}, \quad R_i^0 = \left(\frac{v_i}{v_i^{\text{free}}} \right)^{\frac{1}{3}} R_i^{\text{free}}.$$

Conversely, MBD-XDM uses the XDM dispersion model as a starting point. Here, the starting C_6 coefficients and polarizabilities are given by

$$C_{6,ii} = C_{6,ii}^{\text{XDM}}, \quad \alpha_i^0 = \alpha_i^{\text{free}} \sqrt{\frac{C_{6,ii}^{\text{XDM}}}{C_{6,ii}^{\text{free}}}}.$$

Electronic-Structure Theory
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Dispersion
oooooooooooo

Oscillator Systems
oooooooooooo

Results
oooooooooooo

Conclusions
oooo

Electronic-Structure Theory

Dispersion

Oscillator Systems

Results

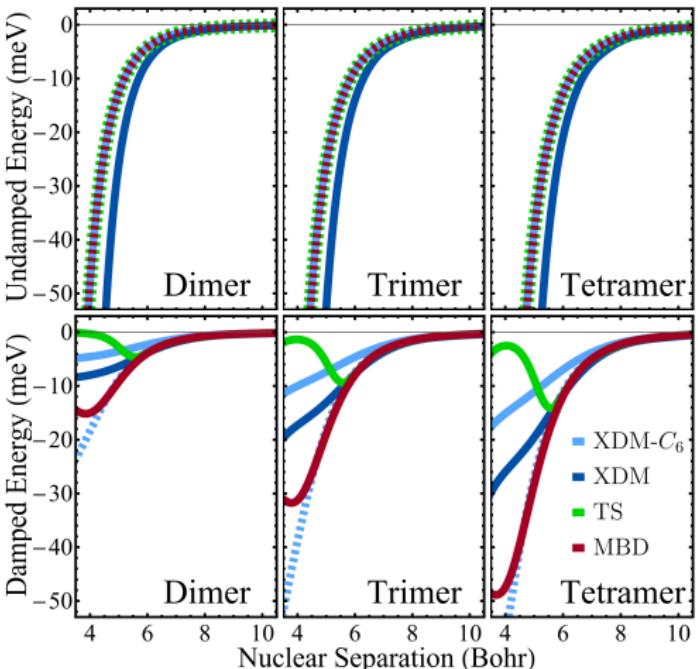
Oscillator System Results

Investigation of MBD's Self-Consistent Screening

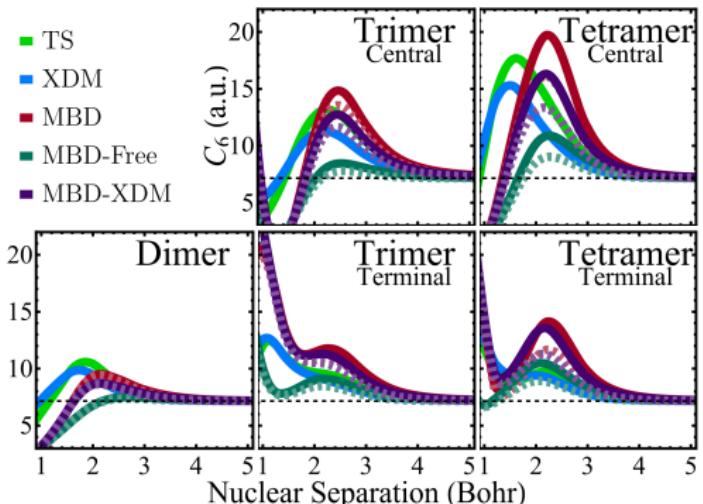
Connection with Molecular Dimers and Layered Materials

Conclusions

ENERGY COMPARISON



- All damping functions were reparameterized on noble gas dimers
- MBD seems to only be a C_6 -only method
- Reparameterized XDM- C_6 behaves similarly to MBD in mid/long range

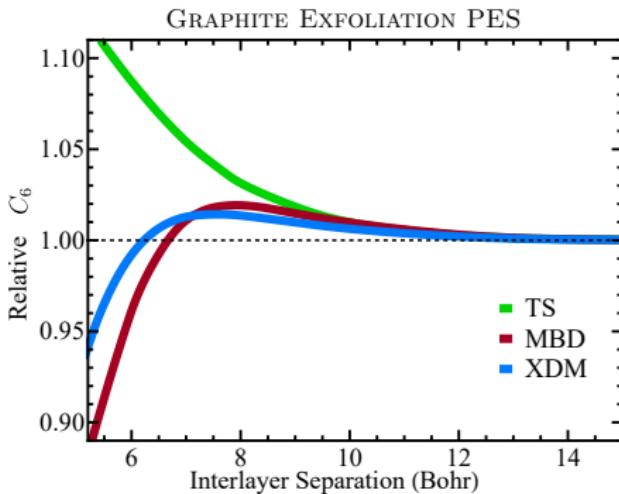
COMPARISON OF C_6 DISPERSION COEFFICIENTS

- TS, MBD, and XDM capture similar changes in C_6 for oscillator chains
- XDM has the lowest C_6 coefficients aside from MBD-Free
- rsSCS seems to have a lowering effect on C_6
- MBD's SCS routine is very sensitive to starting conditions

BACK TO RESEARCH GOALS

ORIGINAL RESEARCH GOALS:

1. Compare XDM and MBD on systems of harmonic oscillators
2. Investigate if XDM captures electronic many-body dispersion effects
3. Investigate if MBD captures higher-order dispersion effects



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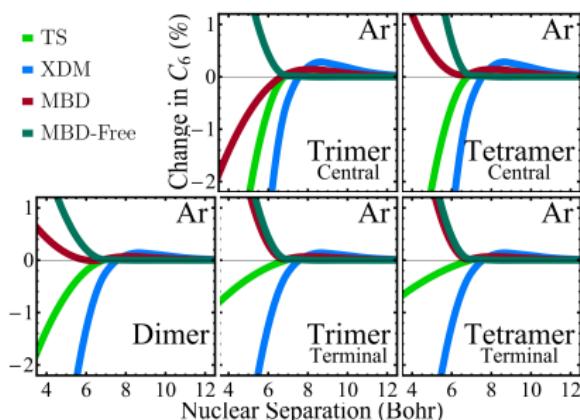
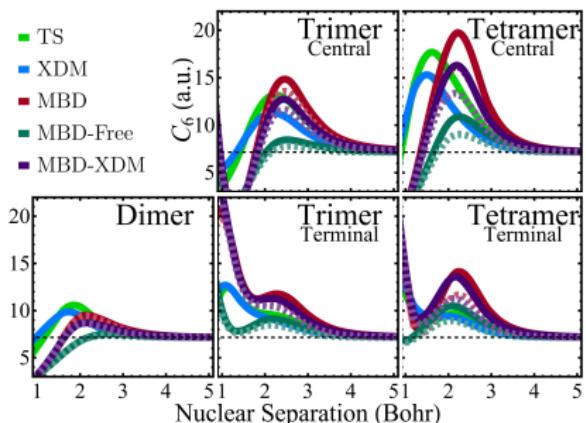
Perhaps oscillators aren't the best model system for dispersion?

ADDITIONAL RESEARCH GOALS:

4. Investigate the sensitivity of MBD's self-consistent screening (SCS)
5. Study these corrections on molecular systems and layered materials

OSCILLATOR CHAINS VS. ARGON CHAINS

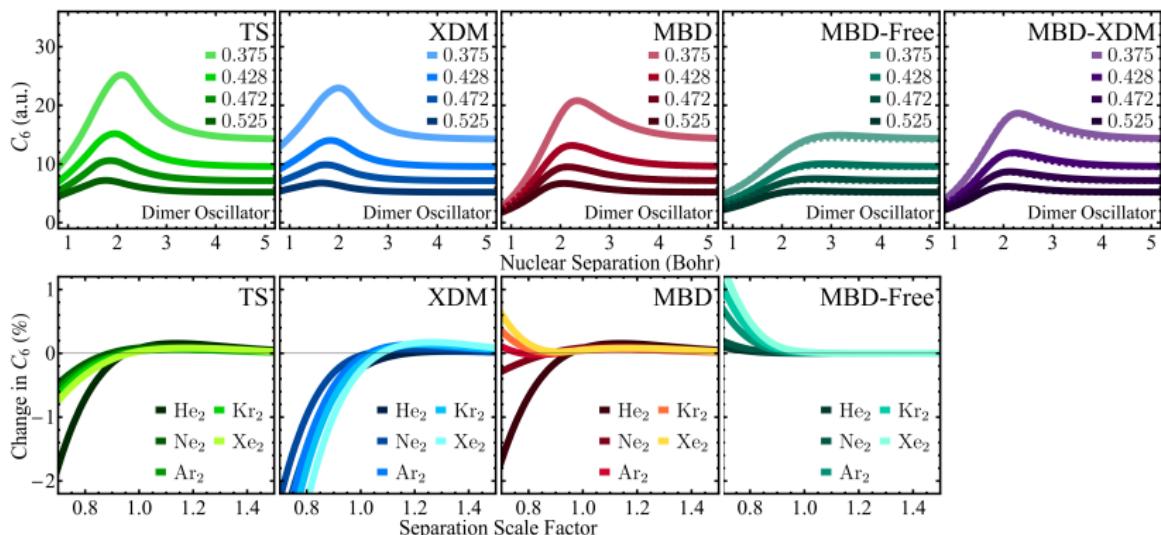
We compare to Ar chains as this model system will be bound by dispersion.
Computed in FHI-aims using Tight basis settings and the PBE functional.



- We see very different behaviour between the two model systems
- MBD behaves as a competing mixture between MBD-Free and TS
- We see a “polarization catastrophe” in the SCS methods

EFFECT OF OSCILLATOR FREQUENCY

For large frequencies, the electron is strongly bound to the oscillator resulting in low polarizability. Conversely, for low frequencies, the electron is weakly bound to the oscillator resulting in high polarizability.



- The noble gas dimers behave like the high- ω oscillators
- XDM most clearly recovers the trend seen with the oscillators
- MBD and MBD-Free suffer from a polarization catastrophe

Electronic-Structure Theory
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Dispersion
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Oscillator Systems
○○○○○○

Results
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Conclusions
○○○○

CONNECTION WITH MOLECULAR DIMERS AND LAYERED MATERIALS

So... there was an issue.

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The resolution: MBD-NL.

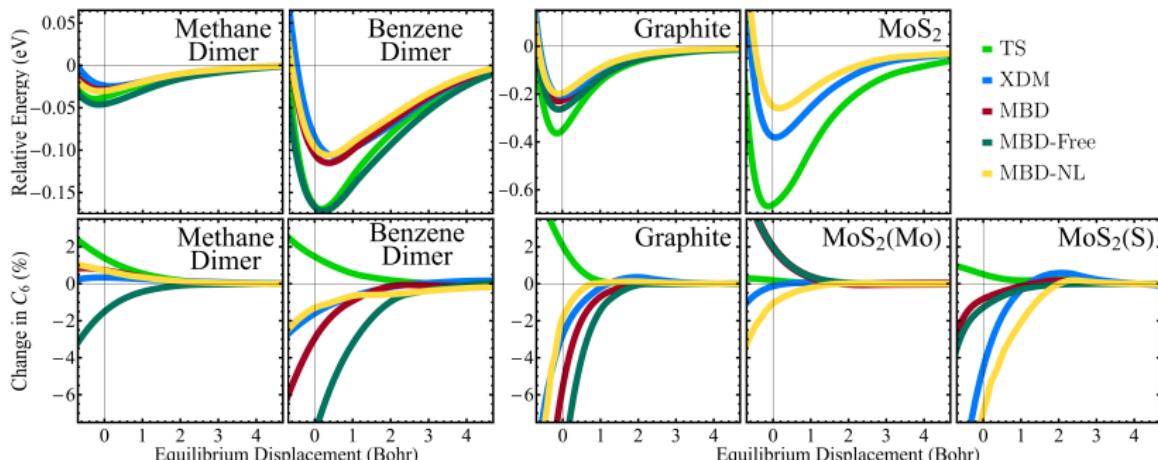
	Disp.	Damping	C_6	$> C_6$	Empirical	Elec.	Atom.
TS:	WY	✓		✗	α, C_6, R_{vdw}	?	✗
XDM:	BJ	✓		✓	α	✓	✓
MBD:	rsSCS	✓		✗	TS+SCS	✓	✓
MBD-Free:	rsSCS	✓		✗	Free+SCS	✓	✓
MBD-XDM:	rsSCS	✓		✗	$\alpha+SCS$	✓	✓
MBD-NL:	rs	✓		✗	VV10	✓	✓

For MBD-NL

- The new starting point is the non-local VV10 dispersion model
- VV10 uses a polarizability functional, removing some empiricism
- Doesn't use SCS, avoiding the "polarization catastrophe" issues
- Instead uses cutoffs to refine the polarizability

CONNECTION WITH MOLECULAR DIMERS AND LAYERED MATERIALS

Computed in FHI-aims using the PBE functional, light basis sets and dense integration grids. For the layered materials, $12 \times 4 \times 4$ k-point meshes were used.



- MBD and MBD-Free fail for MoS_2
- TS, MBD, and MBD-Free all suffer from polarization issues
- TS is no longer showing the same responsiveness as in the model systems
- XDM, MBD, and MBD-NL are in general agreement

TABULATED BINDING ENERGIES

Computed binding energies, in kcal/mol for the molecular dimers and in meV/Å for the layered materials. Literature reference data is shown for comparison.

System	TS	MBD-Free	MBD	MBD-NL	XDM	Ref.
(CH ₄) ₂	0.91	1.07	0.66	0.70	0.57	0.53 ^[1]
(C ₆ H ₆) ₂	3.91	3.96	2.65	2.44	2.46	2.81 ^[1]
Graphite	34.47	25.02	21.78	18.82	19.56	18.32 ^[2]
MoS ₂	38.62	—	—	14.98	22.01	20.53 ^[2]
RMSPE	75%	67%	18%	22%	8.6%	

- Again, XDM, MBD, and MBD-NL are in general agreement
- TS and MBD-Free both overbound all systems
- MoS₂ proved to be the most challenging system to model
- Clearly, XDM proves to be the most reliable with these test systems

[1] Björkman, *J. Chem. Phys.* **141**, 074708. (2014) doi: 10.1063/1.4893329

[2] Gráfová et al. *J. Chem. Theory Comput.* **6**, 8, 2365–2376 (2010) doi: 10.1021/ct1002253

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Computed binding energies, in kcal/mol for the molecular dimers and in meV/Å for the layered materials. Literature reference data is shown for comparison.

System	TS	MBD-Free	MBD	MBD-NL	XDM	Ref.
(CH ₄) ₂	72%	102%	25%	32%	7.5%	0.53 ^[1]
(C ₆ H ₆) ₂	39%	41%	-6%	-13%	-12%	2.81 ^[1]
Graphite	88%	37%	19%	2.7%	6.8%	18.32 ^[2]
MoS ₂	88%	—	—	-27%	7.2%	20.53 ^[2]
RMSPE	75%	67%	18%	22%	8.6%	

- Again, XDM, MBD, and MBD-NL are in general agreement
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TABULATED C_6 COEFFICIENTS

Computed homoatomic C_6 dispersion coefficients, in a.u. for the selected molecular dimers and layered materials at their equilibrium separations. The homoatomic free C_6 values for C, S, and Mo, are 46.6, 134.0, and 1028.73 a.u.

System	Atom	TS	MBD-Free	MBD	MBD-NL	XDM
$(\text{CH}_4)_2$	C	26.0	48.2	31.7	27.6	18.7
$(\text{C}_6\text{H}_6)_2$	C	32.6	41.2	30.7	28.6	21.4
Graphite	C	35.4	42.1	33.3	27.7	20.2
MoS_2	Mo	1060	610	627	260	388
MoS_2	S	132	82.1	80.3	101	78.5

- Wild variation in C_6 due to chemical bonding not seen in model systems
- MBD & MBD-NL have C_6 coefficients 50% larger than XDM
- Unsurprising, as $1.5 \times C_6^{\text{XDM}}$ is similar to full XDM

Electronic-Structure Theory
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Dispersion
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Oscillator Systems
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Results
oooooooooooo

Conclusions
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Electronic-Structure Theory

Dispersion

Oscillator Systems

Results

Conclusions

Results Summary

Future Work

Acknowledgements

RESULTS SUMMARY

1. XDM- C_6 and MBD are comparable at intermediate and long range
2. XDM captures electronic many-body effects in both model and real systems
3. MBD does not capture higher-order dispersion effects, resulting in underdamping
4. MBD's SCS is prone to error and is surprisingly sensitive to the starting point
5. Quantum harmonic oscillators seem to be too simple to capture dispersion

Disp.	Damping	C_6	$> C_6$	Empirical	Elec.	Atom.
TS:	WY	✓	✗	α, C_6, R_{vdw}	✗	✗
XDM:	BJ	✓	✓	α	$d_{X\sigma}$	C_9
MBD:	rsSCS	✓	✗	TS+SCS	SCS	\hat{H}_{CFDM}
MBD-Free:	rsSCS	✓	✗	Free+SCS	SCS	\hat{H}_{CFDM}
MBD-XDM:	rsSCS	✓	✗	$d_{X\sigma}+SCS$	$d_{X\sigma}+SCS$	\hat{H}_{CFDM}
MBD-NL:	rs	✓	✗	VV10	VV10	\hat{H}_{CFDM}

FUTURE WORK

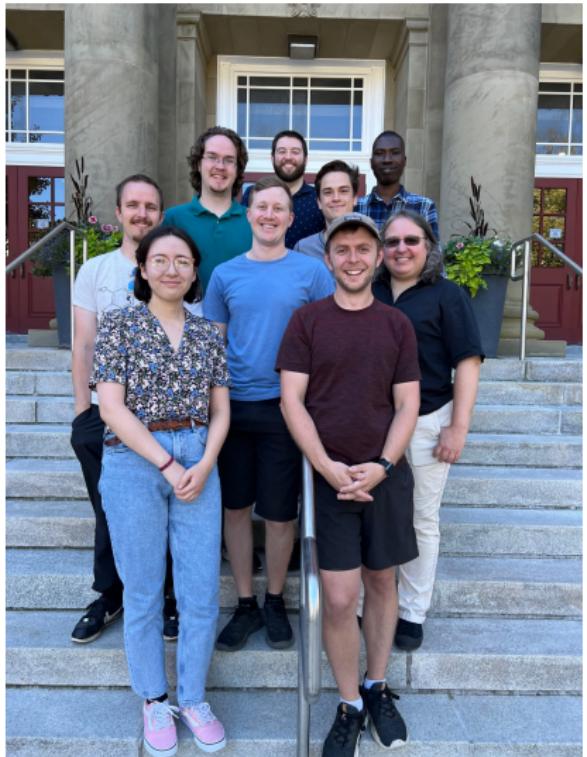
INSPIRED FROM THIS WORK:

1. Test MBD-XDM and MBD-NL with and without rsSCS in FHI-aims
2. Implement the VV10 polarizability functional in XDM

ALSO ON THE TO-DO LIST:

3. Improving the accuracy of XDM's calculation of dispersion forces

ACKNOWLEDGEMENTS



- Prof. Erin Johnson
- Emeritus Prof. Axel Becke
- Dr. Adebayo Adeleke
- Alastair Price
- Alex Mayo
- Sarah Clarke
- Adrian Rumson
- Nick Roberts
- Cameron Nickerson

QUESTIONS?

WANT MY SLIDES?



[HTTPS://GITHUB.COM/KYLEBRYENTON/SLIDES-POSTERS](https://github.com/KyleBryenton/slides-posters)

KYLE.BRYENTON@DAL.CA

IMPLEMENTATION OF MBD

To implement MBD, we need to derive “MBD” C_6 coefficients. To do that, we need to solve for the SCS polarizabilities

$$\alpha_i^{\text{SCS}}(\omega) = \alpha_i^{\text{TS}}(\omega) + \alpha_i^{\text{TS}}(\omega) \sum_{j \neq i} \mathbf{T}_{ij} \alpha_j^{\text{SCS}}(\omega)$$

where the TS polarizabilities are

$$\alpha_i^{\text{TS}}(\omega) = \frac{\alpha_i^0}{1 - (\omega/\omega_i)^2}$$

$\mathbf{T} = \nabla_{\mathbf{R}_i} \otimes \nabla_{\mathbf{R}_j} v_{ij}$ is a fourth-rank (modified) dipole-dipole interaction tensor. Thankfully, we have the form of its elements as used in MBD:

$$\begin{aligned} \mathcal{T}_{ij}^{ab} &= -\frac{3\mathbf{R}_a \mathbf{R}_b - R_{ij}^2 \delta_{ab}}{R_{ij}^5} \left(\operatorname{erf} \left[\frac{R_{ij}}{\sigma_{ij}} \right] - \frac{2}{\sqrt{\pi}} \frac{R_{ij}}{\sigma_{ij}} e^{-R_{ij}^2/\sigma_{ij}^2} \right) \\ &\quad + \frac{4}{\sqrt{\pi}} \frac{\mathbf{R}_a \mathbf{R}_b}{\sigma_{ij}^3 R_{ij}^3} e^{-R_{ij}^2/\sigma_{ij}^2} \end{aligned}$$

IMPLEMENTATION OF MBD

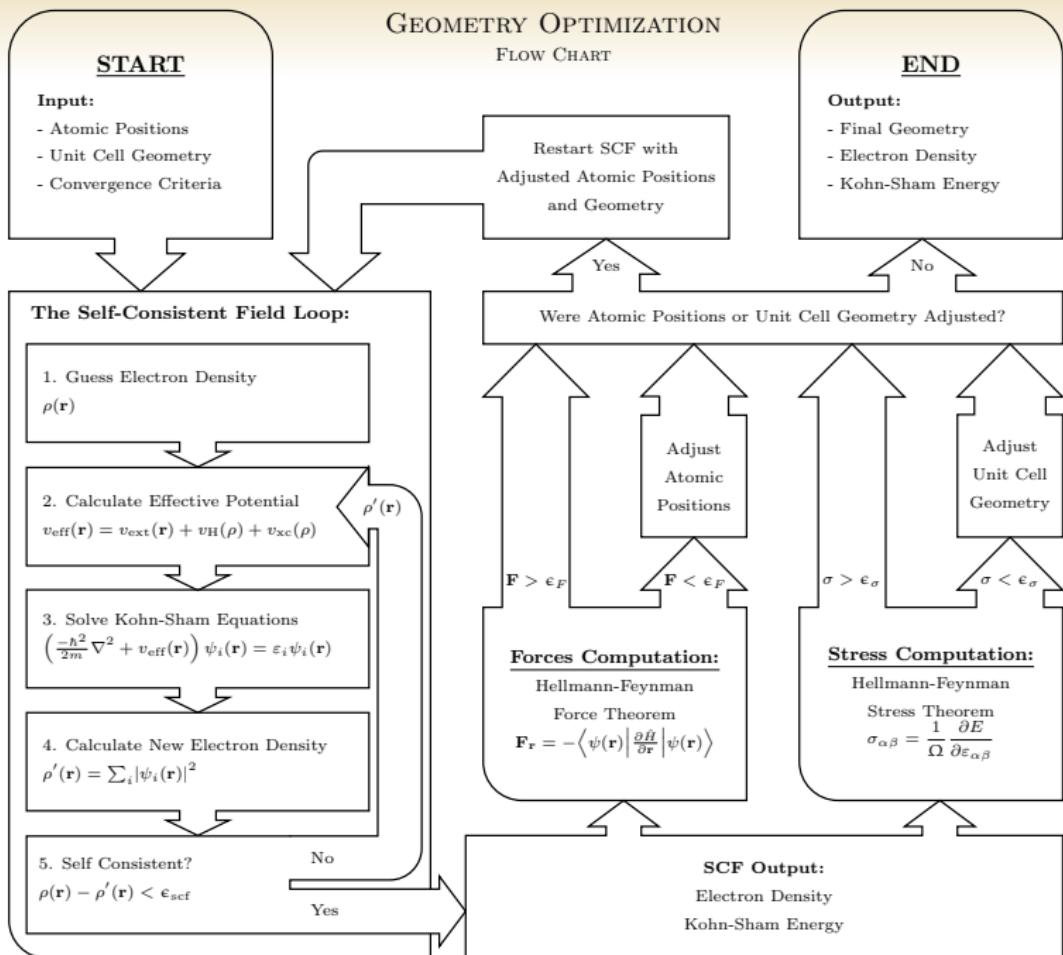
To implement MBD, one can construct a $3N \times 3N$ matrix, \mathbf{A} , which is partitioned by 3×3 sub-blocks representing each atom pair in the system.

$$\mathbf{A} = \begin{bmatrix} 1/\alpha_1^{\text{TS}} & 0 & 0 & \mathcal{T}_{12}^{xx} & \mathcal{T}_{12}^{xy} & \mathcal{T}_{12}^{xz} & \mathcal{T}_{13}^{xx} & \mathcal{T}_{13}^{xy} & \mathcal{T}_{13}^{xz} \\ 0 & 1/\alpha_1^{\text{TS}} & 0 & \mathcal{T}_{12}^{yx} & \mathcal{T}_{12}^{yy} & \mathcal{T}_{12}^{yz} & \mathcal{T}_{13}^{yx} & \mathcal{T}_{13}^{yy} & \mathcal{T}_{13}^{yz} \\ 0 & 0 & 1/\alpha_1^{\text{TS}} & \mathcal{T}_{12}^{zx} & \mathcal{T}_{12}^{zy} & \mathcal{T}_{12}^{zz} & \mathcal{T}_{13}^{zx} & \mathcal{T}_{13}^{zy} & \mathcal{T}_{13}^{zz} \\ \hline \mathcal{T}_{21}^{xx} & \mathcal{T}_{21}^{xy} & \mathcal{T}_{21}^{xz} & 1/\alpha_2^{\text{TS}} & 0 & 0 & \mathcal{T}_{23}^{xx} & \mathcal{T}_{23}^{xy} & \mathcal{T}_{23}^{xz} \\ \mathcal{T}_{21}^{yx} & \mathcal{T}_{21}^{yy} & \mathcal{T}_{21}^{yz} & 0 & 1/\alpha_2^{\text{TS}} & 0 & \mathcal{T}_{23}^{yx} & \mathcal{T}_{23}^{yy} & \mathcal{T}_{23}^{yz} \\ \mathcal{T}_{21}^{zx} & \mathcal{T}_{21}^{zy} & \mathcal{T}_{21}^{zz} & 0 & 0 & 1/\alpha_2^{\text{TS}} & \mathcal{T}_{23}^{zx} & \mathcal{T}_{23}^{zy} & \mathcal{T}_{23}^{zz} \\ \hline \mathcal{T}_{31}^{xx} & \mathcal{T}_{31}^{xy} & \mathcal{T}_{31}^{xz} & \mathcal{T}_{32}^{xx} & \mathcal{T}_{32}^{xy} & \mathcal{T}_{32}^{xz} & 1/\alpha_3^{\text{TS}} & 0 & 0 \\ \mathcal{T}_{31}^{yx} & \mathcal{T}_{31}^{yy} & \mathcal{T}_{31}^{yz} & \mathcal{T}_{32}^{yx} & \mathcal{T}_{32}^{yy} & \mathcal{T}_{32}^{yz} & 0 & 1/\alpha_3^{\text{TS}} & 0 \\ \mathcal{T}_{31}^{zx} & \mathcal{T}_{31}^{zy} & \mathcal{T}_{31}^{zz} & \mathcal{T}_{32}^{zx} & \mathcal{T}_{32}^{zy} & \mathcal{T}_{32}^{zz} & 0 & 0 & 1/\alpha_3^{\text{TS}} \end{bmatrix}$$

Inverting \mathbf{A} permits quick computation of the SCS polarizability tensor,

$$\boldsymbol{\alpha}_i^{\text{SCS}} = \sum_{j=1}^N [\mathbf{A}^{-1}]_{ij} .$$

The diagonal elements of $\boldsymbol{\alpha}_i^{\text{SCS}}$ may be substituted into the Casimir-Polder integral to determine the effective MBD C_6 values.



OPTIMIZED DAMPING PARAMETERS

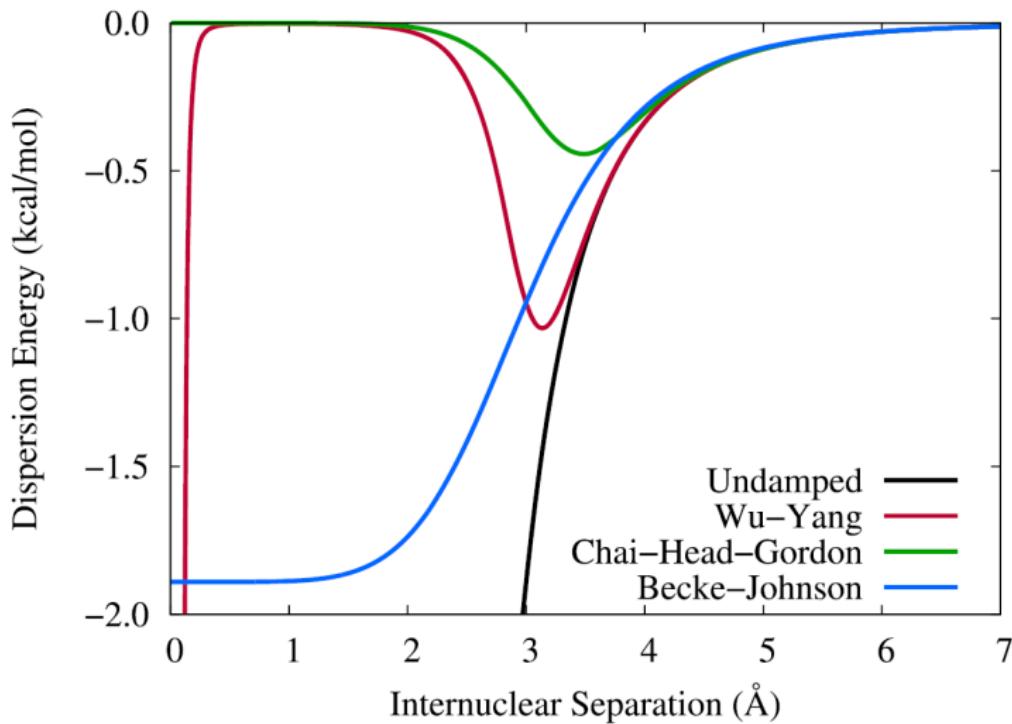
The XDM and MBD damping parameters were optimized on the KB65(6) subset of noble gas dimers of He, Ne, and Ar pairs.

PW86PBE was the most accurate of the functionals tested, and reaches the CBS limit at the quintuple-zeta level of theory.

XDM was parametrized by minimizing the RMSPD of CP-corrected PW86PBE-XDM/aug-pV5Z binding energies.

MBD's contribution was calculated using FHIaims with a 'tight' basis using the PBE functional.

DAMPING FUNCTIONS



ORIGINAL RESEARCH GOALS

1. Compare XDM and MBD on systems of harmonic oscillators

They are comparable for long range. MBD's damping function is weaker than XDM, causing it to emulate higher-order dispersion coefficients in the intermediate range. At short range, MBD exhibits a "polarization catastrophe" due to the SCS routine.

2. Investigate if XDM captures electronic many-body dispersion effects

XDM clearly captures electronic many-body effects through the use of the exchange-hole dipole moments. TS seems to also capture these effects for model systems, but does not for molecules and materials.

3. Investigate if MBD captures higher-order dispersion effects

MBD does not capture higher-order dispersion effects. Its similar performance to XDM can be attributed to overestimating C_6 by about 50% while also under-damping.

ADDITIONAL RESEARCH GOALS

4. Investigate the sensitivity of MBD's self-consistent screening (SCS)

SCS shows concerning sensitivity to input polarizability. TS has shown to suffer from polarization issues in molecules and materials, making it perhaps a less-than-optimal starting point for MBD.

5. Study these corrections on molecular systems and layered materials

No one starting point appears suitable for MBD, while XDM performs consistently well. Perhaps the MBD-XDM scheme, considered here only for the oscillator model systems, may present a more general solution.

Disp.	Damping	C_6	$> C_6$	Empirical	Elec.	Atom.
TS:	WY	✓	✗	α, C_6, R_{vdw}	✗	✗
XDM:	BJ	✓	✓	α	$d_{X\sigma}$	C_9
MBD:	rsSCS	✓	✗	TS+SCS	SCS	\hat{H}_{CFDM}
MBD-Free:	rsSCS	✓	✗	Free+SCS	SCS	\hat{H}_{CFDM}
MBD-XDM:	rsSCS	✓	✗	$d_{X\sigma}+SCS$	$d_{X\sigma}+SCS$	\hat{H}_{CFDM}
MBD-NL:	rs	✓	✗	VV10	VV10	\hat{H}_{CFDM}