



CAP 2023:
MANY-BODY DISPERSION IN MODEL SYSTEMS AND THE
SENSITIVITY OF SELF-CONSISTENT SCREENING



Kyle R. Bryenton

Supervisor: Prof. Erin Johnson

Dalhousie Department of Physics & Atmospheric Science

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Dispersion

What is Dispersion?

Many-Body Dispersion Effects

Post-SCF Dispersion Corrections

Motivation: XDM vs. MBD

Model Oscillator Systems

Results

Conclusions

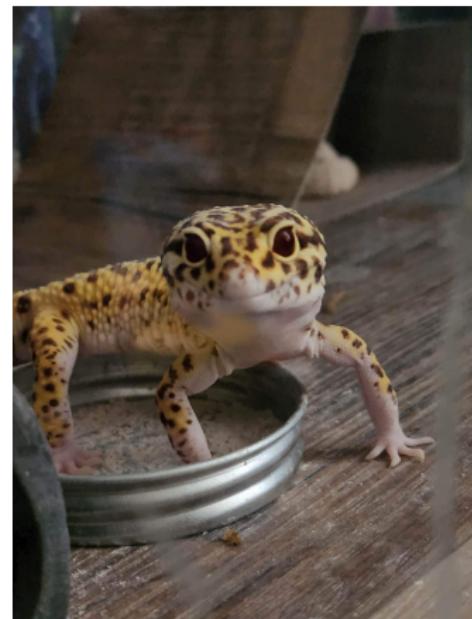
WHAT IS DISPERSION

London dispersion is a weak, attractive, intermolecular force.

It is caused by instantaneous dipole moments between 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

ELECTRONIC MANY-BODY EFFECTS

Refer to the responsiveness of the 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 typically contribute negligibly to 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 dipole-dipole interactions, and determines $C_{6,ii}$, α_i^0 , and R_i^0 from their free-atom reference values using effective volumes.

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

THE XDM MODEL

The exchange-hole dipole moment (XDM) model includes higher-order terms and determines $C_{6,ii}$ and R_{vdW} via multipole moment integrals. The α_i is determined from free-atom reference values using effective volumes.

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

THE MBD@rssCS MODEL

The many-body dispersion (MBD) model refines its coefficients through range-separated self-consistent screening (rssCS).

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

The dispersion energy is calculated through the use of the coupled fluctuating dipole model (CFDM) Hamiltonian.

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

THE MBD-NL MODEL

The imprecisely named non-local (NL) MBD model uses Vydrov and Van Voorhis's 2010 (VV10) model as a starting point, forgoing SCS, and extending applicability to ions, metals, and interfaces.

$$\alpha^{\text{VV}}[\rho](\mathbf{r}, i\omega) = \frac{\rho(\mathbf{r})}{\frac{4\pi}{3} + C \frac{|\nabla \rho(\mathbf{r})|^4}{\rho(\mathbf{r})^4} + \omega^2}$$

Tkatchenko, A., et al. *Phys. Rev. Lett.* **108**, 236402. (2012) doi: 10.1103/PhysRevLett.108.236402
Hermann, J., & Tkatchenko, A. *Phys. Rev. Lett.* **124**, 146401. (2020) doi: 10.1103/PhysRevLett.124.146401

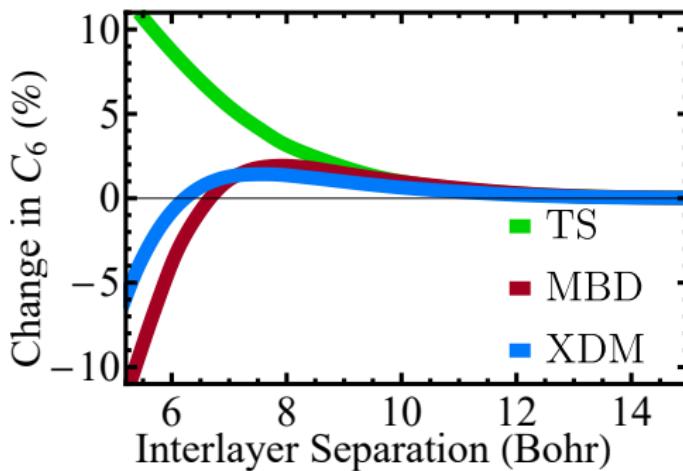
SUMMARY OF DISPERSION CORRECTIONS

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
VV10	Vydrov and Van Voorhis	MBD-NL	Non-Local MBD Dispersion Model

Disp.	Damping	C_6	$> C_6$	Empiricism	Elec.	Atom.
TS:	WY	✓	✗	$\alpha, C_6, R_{\text{vdw}}$?	✗
XDM:	BJ	✓	✓	α	?	C_9
MBD:	rsSCS	✓	?	TS@SCS	?	✓
MBD-NL:	rs	✓	?	VV10	?	✓
MBD-Free:	rsSCS	✓	?	Free@SCS	?	✓
MBD-XDM:	rsSCS	✓	?	$\alpha+SCS$?	✓

MOTIVATION: XDM vs. MBD

SEPARATING GRAPHITE LAYERS



RESEARCH GOALS:

1. Investigate if XDM captures electronic many-body dispersion effects
2. Investigate if MBD captures higher-order dispersion effects
3. Compare XDM and MBD on model systems, molecular systems, and layered materials

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

Dispersion
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Model Oscillator Systems
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Results
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Conclusions
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Dispersion

Model Oscillator Systems

System Geometry

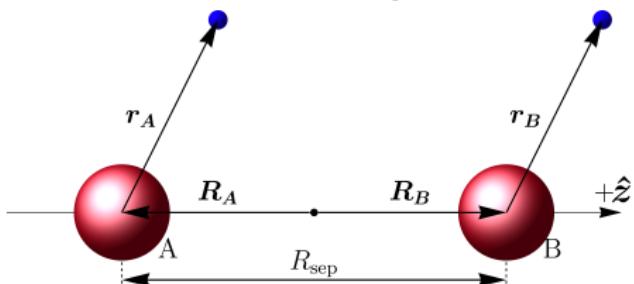
Multi-Oscillator Wavefunctions

Results

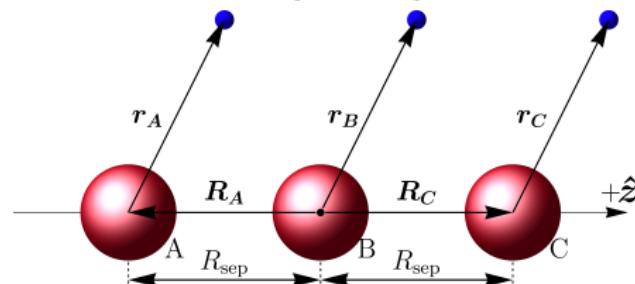
Conclusions

SYSTEM GEOMETRY

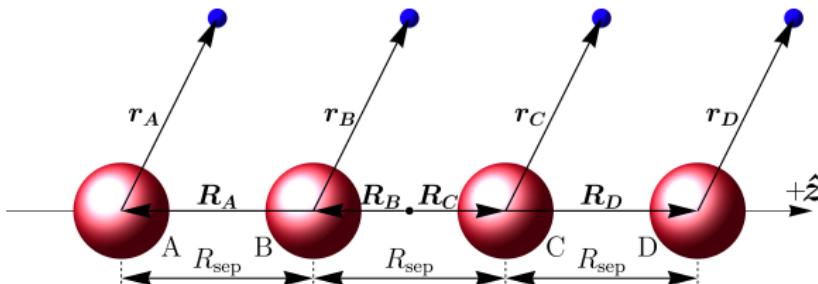
DIMER



TRIMER



TETRAMER



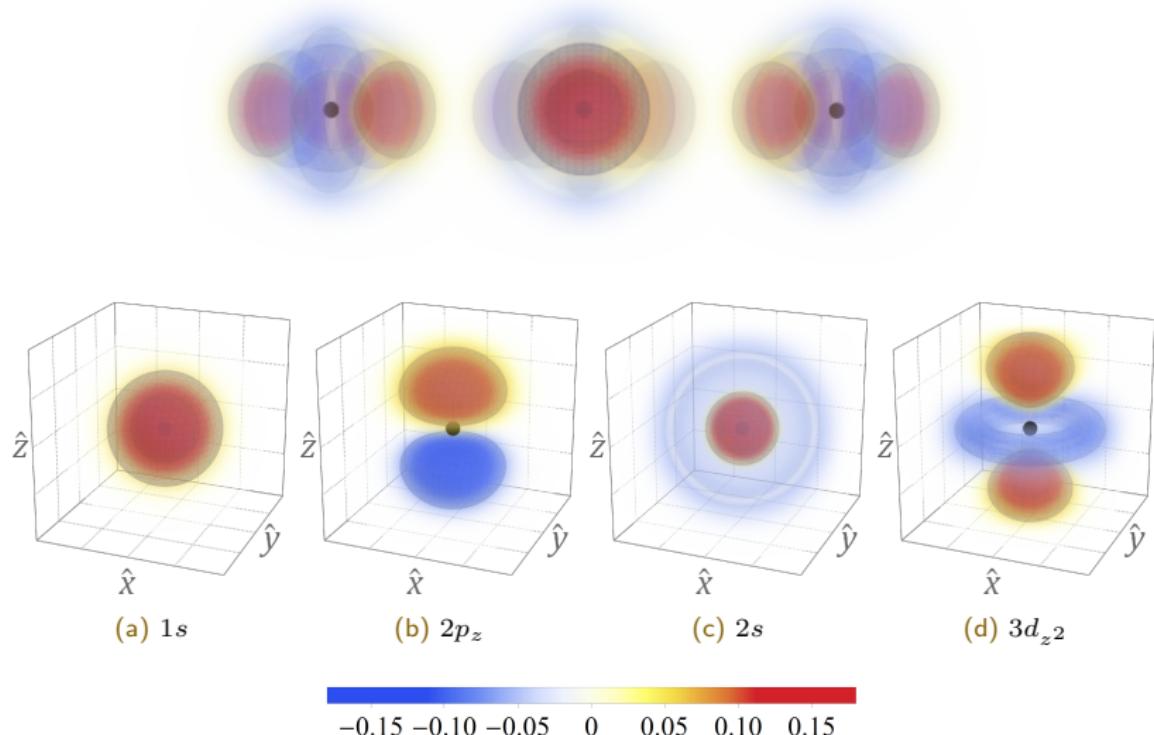
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MULTI-OSCILLATOR WAVEFUNCTIONS



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Dispersion

Model Oscillator Systems

Results

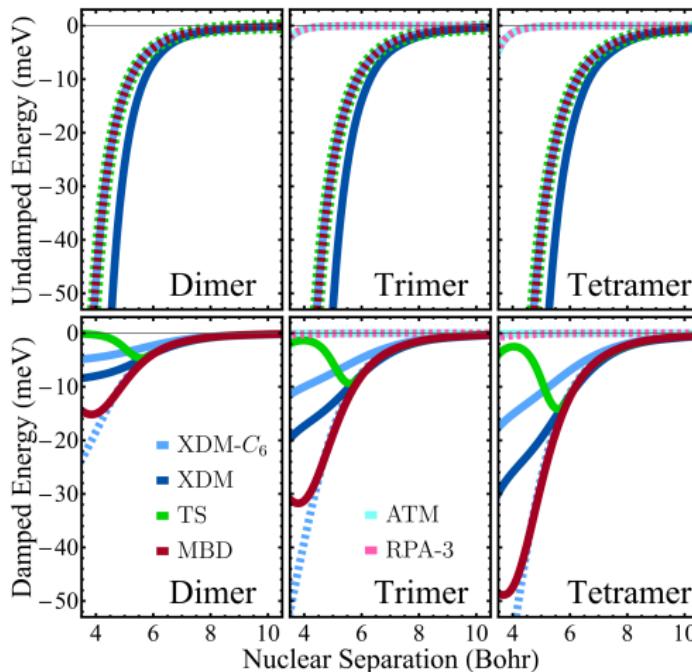
Model Oscillator System Results

Comparison to Noble Gasses

Connection with Molecular Dimers and Layered Materials

Conclusions

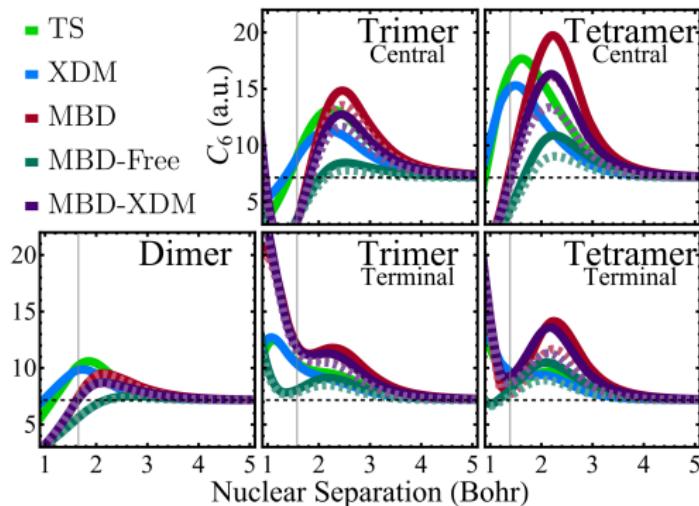
UNDAMPED/DAMPED ENERGY COMPARISON



- MBD seems to only be a C_6 -only method
- C_6 -only corrections compensate by underdamping
- The 3-body dispersion energy contributions (ATM/RPA) are negligible

COMPARISON OF C_6 DISPERSION COEFFICIENTS

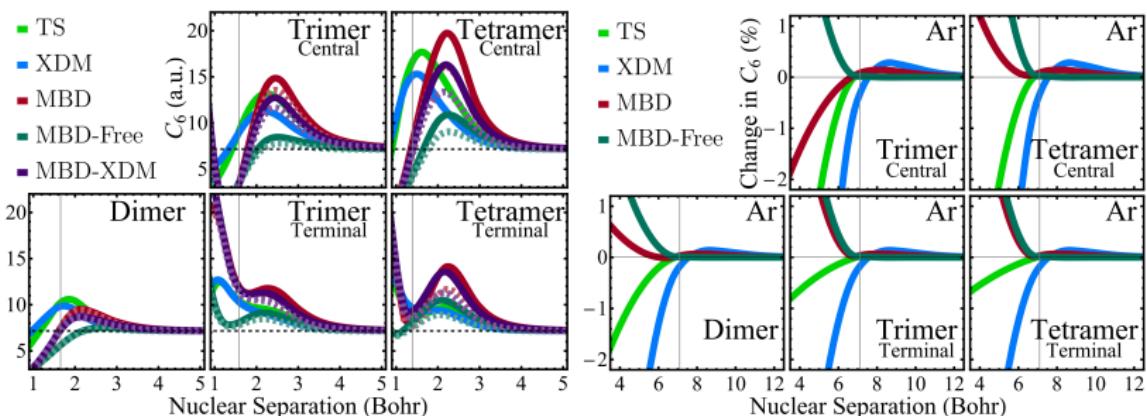
We look at the C_6 coefficients directly as we change inter-oscillator separation. The equilibrium separation for each system is indicated by a vertical line.



- TS, MBD, and XDM capture similar changes in C_6 for oscillator chains
- MBD's SCS routine is very sensitive to starting conditions

OSCILLATOR CHAINS VS. ARGON CHAINS

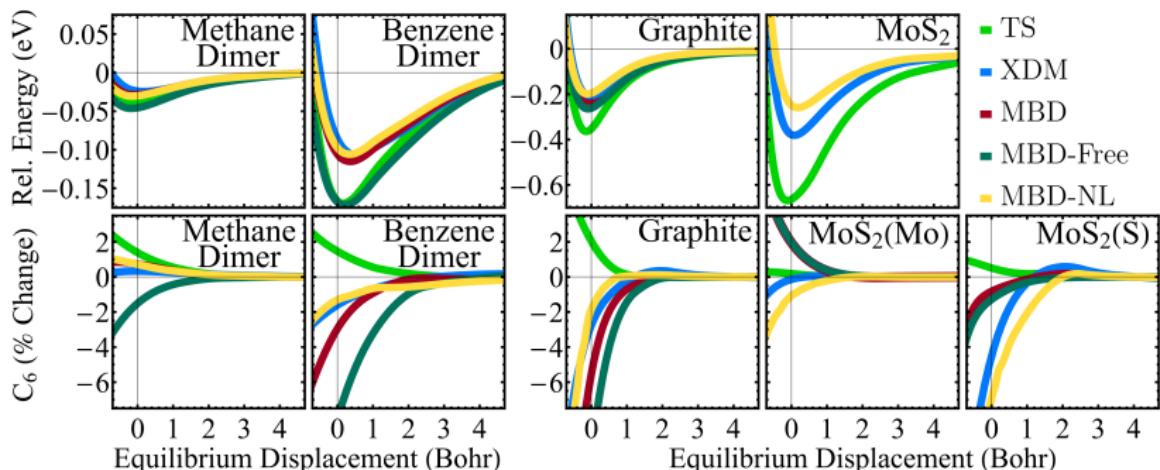
We compare to Ar chains as this model system will be bound by dispersion.
Computed in FHI-aims using Tight basis settings and the PBE functional.



- 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

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, $12 \times 4 \times 4$ \mathbf{k} -point meshes were used.



- MBD and MBD-Free fail for MoS₂
- 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

Table: Computed binding energies, in kcal/mol for the molecular dimers and in meV/Å² for the layered materials. Also, mean absolute errors (MAE) for the S66×8 benchmark of molecular complexes and two benchmarks of layered materials.

System	TS	MBD	MBD-NL	XDM	Ref.
(CH ₄) ₂	72%	25%	32%	7.5%	0.53 ^[1]
(C ₆ H ₆) ₂	39%	-6%	-13%	-12%	2.81 ^[1]
Graphite	88%	19%	2.7%	6.8%	18.32 ^[2]
MoS ₂	88%	—	-27%	7.2%	20.53 ^[2]
RMSPE	75%	18%	22%	8.6%	
S66×8 (kcal/mol) ^[3]	0.60	0.44	0.43	0.45	—
LM11 (meV/Å ²) ^[4]	12.5	—	5.0	3.7	—
LM26 (meV/Å ²) ^[2]	13.1	—	4.6	4.9	—

- Again, XDM, MBD, and MBD-NL are in agreement while TS overbound
- Clearly, XDM proves to be the most reliable with these test systems
- XDM and MBD-NL performed best on the benchmark sets

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

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

[3] Brauer et al. *Phys. Chem. Chem. Phys.*, **18**, 20905–20925 (2016) doi: 10.1039/C6CP00688D

[4] Tawfik et al. *Phys. Rev. Mater.*, **2**, 034005 (2018) doi: 10.1103/PhysRevMaterials.2.034005

TABULATED C_6 COEFFICIENTS

Table: Computed homoatomic C_6 dispersion coefficients, in a.u. for single isolated molecules and selected layered materials at large interlayer separation.

System	Atom	Free	TS	MBD	MBD-NL	XDM
CH_4	C	46.6	26.0	31.7	27.6	18.7
C_6H_6	C	46.6	32.6	30.7	28.6	21.4
Graphite	C	46.6	35.4	33.3	27.7	20.2
MoS_2	Mo	1029	1060	627	260	388
MoS_2	S	134.0	132	80.3	101	78.5

- Wild variation in C_6 due to chemical bonding not seen in model systems
- XDM seems to consistently underestimate C_6
- Future Work: Improve XDM by implementing a polarizability functional

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Dispersion

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Key Takeaways

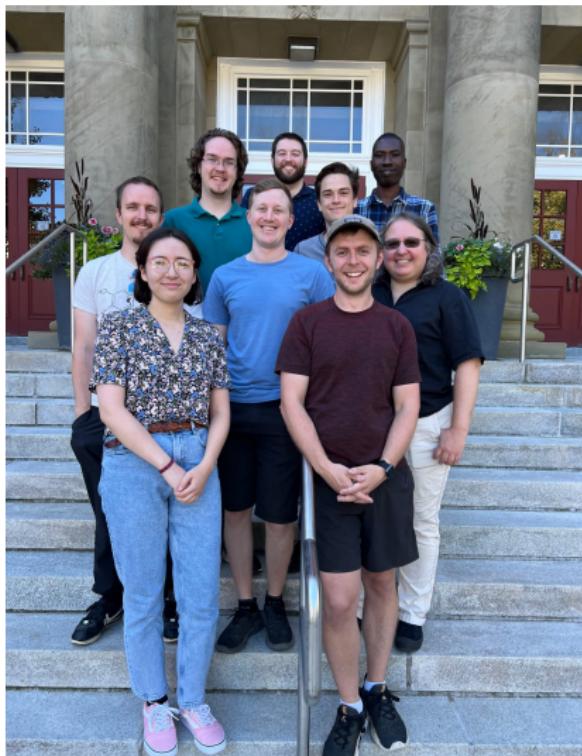
Acknowledgements

KEY TAKEAWAYS

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

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

ACKNOWLEDGEMENTS



- Prof. Erin Johnson
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- Nick Roberts
- Cameron Nickerson

QUESTIONS?

READ THE PAPER:

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

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KYLE.BRYENTON@DAL.CA

APPENDIX SLIDES

Density-Functional Theory

Dispersion in DFT

Optimized Damping Parameters

Geometry Optimization

Dispersion Corrections

The Tkatchenko-Scheffler Model

The Exchange-hole Dipole Moment Model

The Many-body Dispersion Model

MBD-Free and MBD-XDM

Oscillator Model

Single-Oscillator Hamiltonian & Wavefunctions

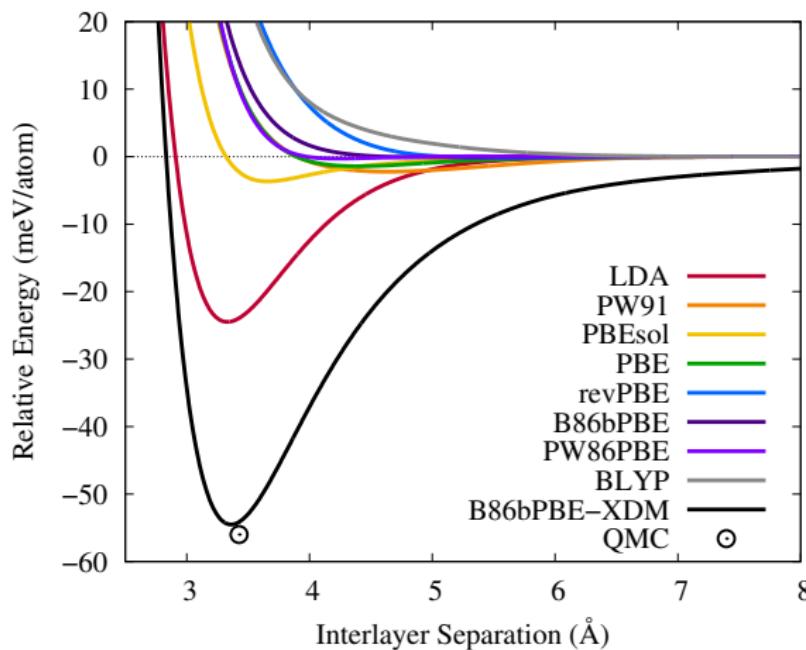
Multi-Oscillator Hamiltonian & Wavefunctions

Variational Minimization

Results Supplement

DISPERSION IN DFT

EXAMPLE: SEPARATING GRAPHITE LAYERS



OPTIMIZED DAMPING PARAMETERS

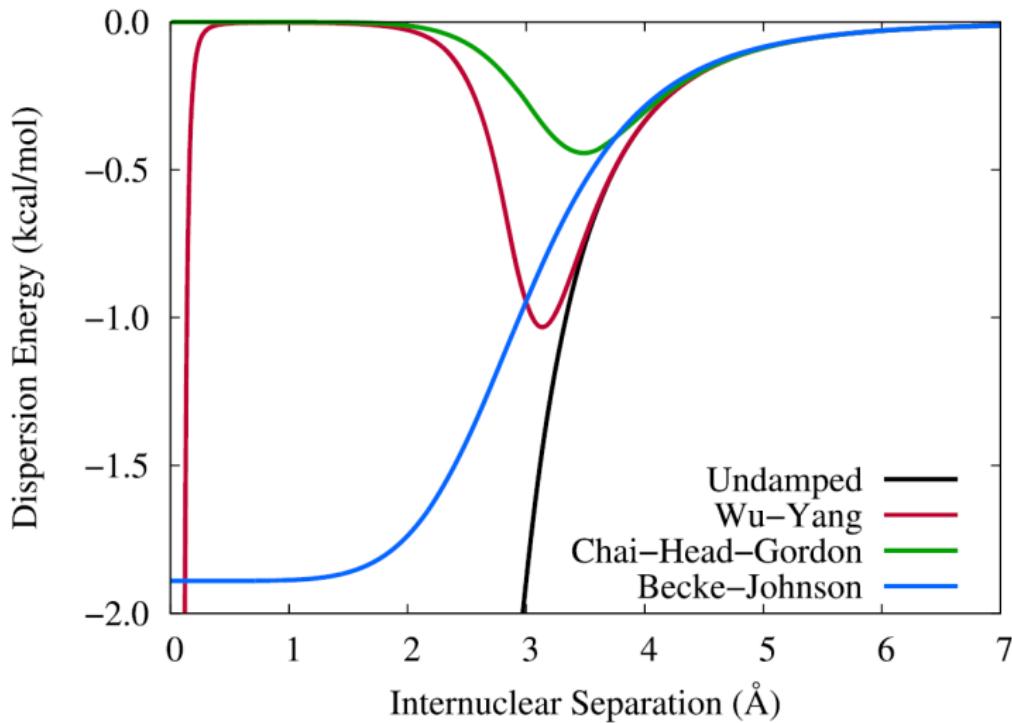
The XDM and MBD damping parameters were optimized on the KB65(6) subset of noble gas dimers of He, Ne, and Ar pairs.

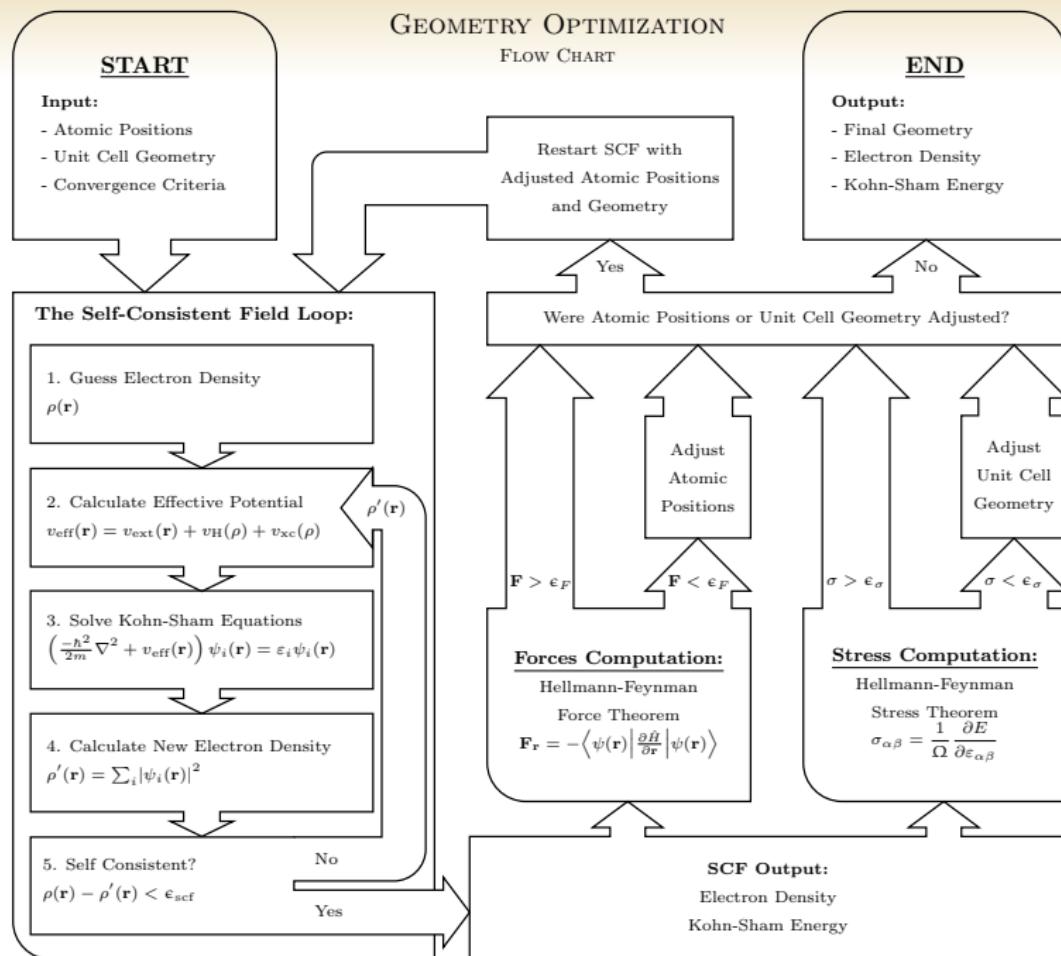
PW86PBE was the most accurate of the functionals tested, and reaches the CBS limit at the quintuple-zeta level of theory.

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





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.

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

$$\boldsymbol{\alpha}_i^{\text{SCS}}(\imath\omega) = \boldsymbol{\alpha}_i^{\text{TS}}(\imath\omega) + \boldsymbol{\alpha}_i^{\text{TS}}(\imath\omega) \sum_{j \neq i} \mathbf{T}_{ij} \boldsymbol{\alpha}_j^{\text{SCS}}(\imath\omega)$$

where the TS polarizabilities are

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

$\mathbf{T} = \nabla_{\mathbf{R}_i} \otimes \nabla_{\mathbf{R}_j} v_{ij}$ 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,

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

The diagonal elements of α_i^{SCS} may be substituted into the Casimir-Polder integral to determine the effective MBD C_6 values.

MBD-FREE AND MBD-XDM

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

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

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

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

EXPLICIT WAVEFUNCTIONS

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

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

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

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

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

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

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

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:

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

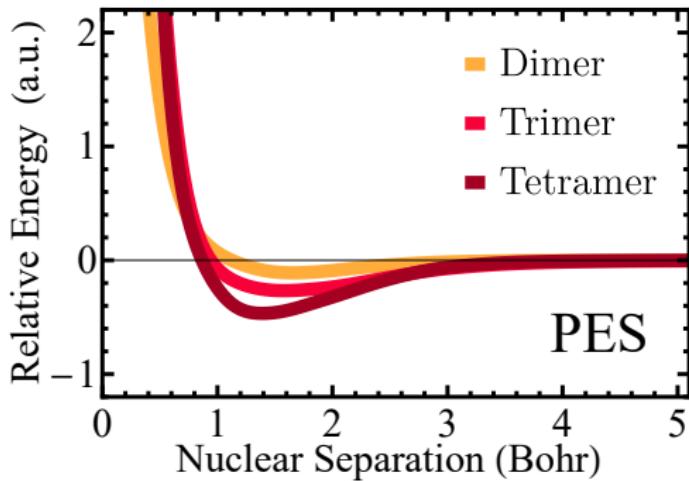
Trimer or Tetramer:

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

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

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

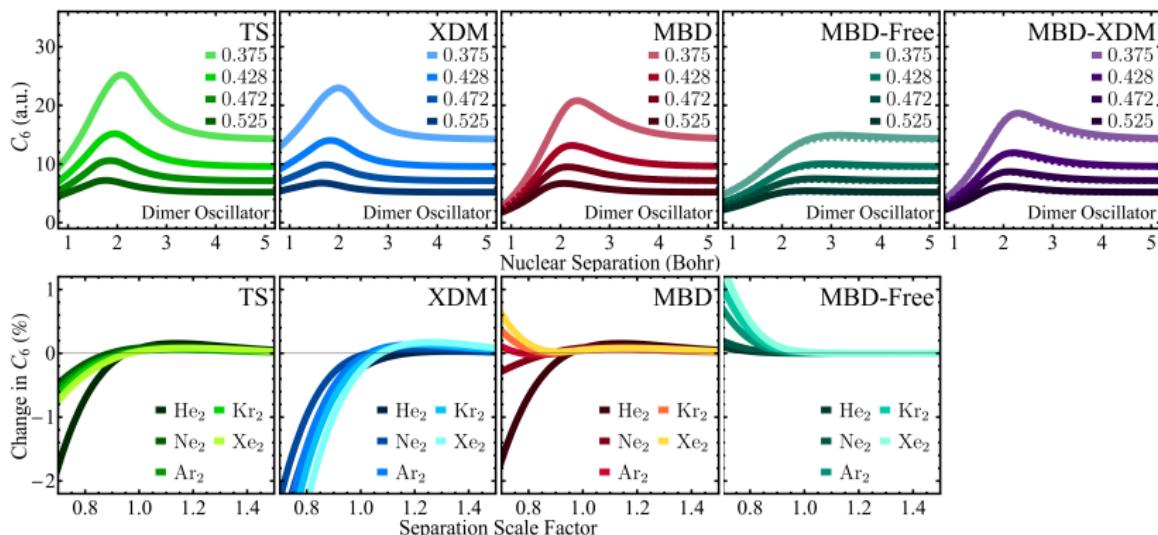
POTENTIAL ENERGY SURFACES



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

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

TABULATED BINDING ENERGIES

Table: Computed binding energies, in kcal/mol for the molecular dimers and in meV/Å² for the layered materials. Also, mean absolute errors (MAE) for the S66×8 benchmark of molecular complexes and two benchmarks of layered materials.

System	TS	MBD	MBD-NL	XDM	Ref.
(CH ₄) ₂	0.91	0.66	0.70	0.57	0.53 ^[1]
(C ₆ H ₆) ₂	3.91	2.65	2.44	2.46	2.81 ^[1]
Graphite	34.47	21.78	18.82	19.56	18.32 ^[2]
MoS ₂	38.62	—	14.98	22.01	20.53 ^[2]
RMSPE	75%	18%	22%	8.6%	
S66×8 (kcal/mol) ^[3]	0.60	0.44	0.43	0.45	—
LM11 (meV/Å ²) ^[4]	12.5	—	5.0	3.7	—
LM26 (meV/Å ²) ^[2]	13.1	—	4.6	4.9	—

- Again, XDM, MBD, and MBD-NL are in agreement while TS overbound
- Clearly, XDM proves to be the most reliable with these test systems
- XDM and MBD-NL performed best on the benchmark sets

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

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

[3] Brauer et al. *Phys. Chem. Chem. Phys.*, **18**, 20905–20925 (2016) doi: 10.1039/C6CP00688D

[4] Tawfik et al. *Phys. Rev. Mater.*, **2**, 034005 (2018) doi: 10.1103/PhysRevMaterials.2.034005

TABULATED C_6 COEFFICIENTS

Table: Computed homoatomic C_6 dispersion coefficients, in a.u. for single isolated molecules and selected layered materials at large interlayer separation. Also included are mean absolute percent errors (MAPE) and mean percent errors (MPE) for a set of 20 homomolecular C_6 dispersion coefficients ($\text{Mol}C_6$).

System	Atom	Free	TS	MBD	MBD-NL	XDM
CH_4	C	46.6	26.0	31.7	27.6	18.7
C_6H_6	C	46.6	32.6	30.7	28.6	21.4
Graphite	C	46.6	35.4	33.3	27.7	20.2
MoS_2	Mo	1029	1060	627	260	388
MoS_2	S	134.0	132	80.3	101	78.5
$\text{Mol}C_6$ MAPE (%)		–	12.7	13.1	7.3	20.1
$\text{Mol}C_6$ MPE (%)		–	2.5	-3.2	-2.2	-18.2

- 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
- In FHI-aims, XDM seems to consistently underestimate C_6