

## COMMITTEE MEETING II



Kyle R. Bryenton  
Dalhousie Department of Physics & Atmospheric Science  
September 01, 2023

Program Requirements  
ooo

Dispersion  
oooooo

The Oscallot Code  
oo

Results  
oooooooo

Improved Dispersion Forces  
oooo

Conclusions  
oo

## Program Requirements

## Dispersion

## The Oscallot Code

## Results

## Improving Dispersion Forces

## Conclusions

## PROGRESS SINCE LAST MEETING & SIX-MONTH PLAN

### COURSES [NEW: NONE]:

1. AARMS5900 - Math. & Sci. of Chaos – A
2. CHEM5301 - Theory Chem. Bond – A
3. CHEM6353 - Dens.-Funct. Theory – A+
4. CHEM6363 - Elec. Struct. Theory – A

### CONFERENCES [NEW: 1-4]:

1. CCAM (Virtual) Aug 2022
2. ACS Spring Meeting (Virtual) Mar 2023
3. CAP Congress (Fredericton, NB) Jun 2023
4. FHI-aims Dev. Meeting (Hamburg, Germany) Aug 2023

### PUBLICATIONS [NEW: 2-5]:

1. Price, A. J., **Bryenton, K. R.**, & Johnson, E. R. *Requirements for an accurate dispersion-corrected density functional*. J. Chem. Phys. 154, 230902. (2021) doi: 10.1063/5.0050993
2. **Bryenton, K. R.**, Adeleke, A. A., Dale, S. G., & Johnson, E. R. *Delocalization Delocalization error: the greatest outstanding challenge in density-functional theory*. WIREs Comput Mol Sci. 13, e1631 (2022) doi: 10.1002/wcms.1631
3. **Bryenton, K. R.**, & Johnson, E. R. *Many-Body Dispersion in Model Systems and the Sensitivity of Self-Consistent Screening*. J. Chem. Phys. 158, 204110 (2023) doi: 10.1063/5.0142465
4. **Bryenton, K. R.** Oscallot (Version 2023-05-16), Github, (2023) doi: 10.5281/zenodo.7884604
5. Nickerson, C. J. **Bryenton, K. R.**, Price, A. J. & Johnson, E. R. *Comparison of DFT Dispersion Corrections for the DES15K Database*. Submitted to J. Phys. Chem. 2023

## GRADUATE SEMINARS [NEW: 3]:

1. Seminar I - 2021-02-09

What The Flip Are Stress Tensors? How do I use them, and why do I care?

2. Seminar II - 2022-02-01

The DeepMind 2021 Functional; Simulating matter on the quantum scale with AI

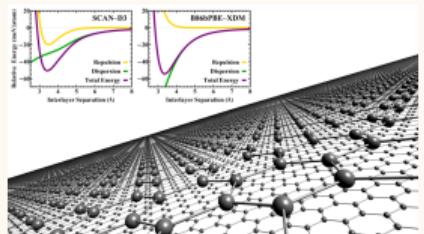
3. Seminar III - 2023-02-14

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

## SIX-MONTH RESEARCH PLAN:

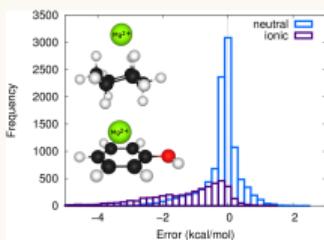
1. Complete XDM forces implementation in FHI-aims and publish.
2. Derive an XDM polarizability functional free of empiricism and publish.
3. Audit: *Advanced Module on Solid State Modeling and Relativistic Effects in Chemistry*
4. Audit: *Advanced Module on Thermochemistry and Kinetics*
5. Self-study Python and machine learning in Tensorflow
6. Attend the Sanibel Symposium (St. Augustine, FL) Feb 2023
7. Give invited talks at UPEI
8. Start working on thesis draft

## Requirements for an Accurate Disp.-Corr. Functional



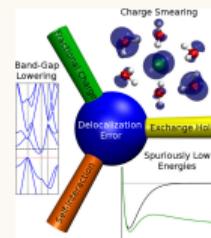
A. J. A. Price, K. R. Bryenton, & E. R. Johnson, *J. Chem. Phys.* 154, 230902 (2021).  
doi: 10.1063/5.0050993

## Comparison of DFT Disp. Corrections on DES15K



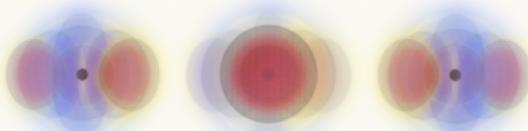
C. J. Nickerson, K. R. Bryenton, A. J. Price, & E. R. Johnson, Submitted to *J. Phys. Chem.* (2023)

## Delocalization Error: Greatest Outstanding Challenge



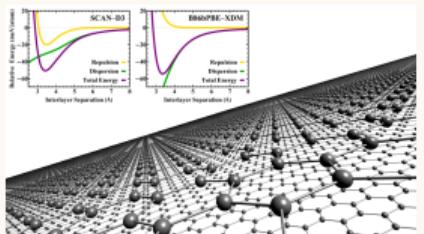
K. R. Bryenton, A. A. Adeleke, S. G. Dale, & E. R. Johnson, *WIREs Comp. Mol. Sci.* 13, e1631 (2023). doi: 10.1002/wcms.1631

## Many-Body Dispersion and the Sensitivity of SCS



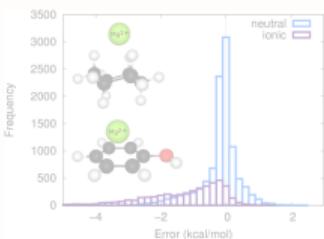
K. R. Bryenton & E. R. Johnson, *J. Chem. Phys.* 158 204110 (2023). doi: 10.1063/5.0142465

## Requirements for an Accurate Disp.-Corr. Functional



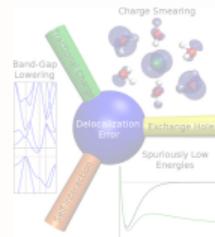
A. J. A. Price, K. R. Bryenton, & E. R. Johnson, *J. Chem. Phys.* 154, 230902 (2021).  
doi: 10.1063/5.0050993

## Comparison of DFT Disp. Corrections on DES15K



C. J. Nickerson, K. R. Bryenton, A. J. Price, & E. R. Johnson, Submitted to *J. Phys. Chem.* (2023)

## Delocalization Error: Greatest Outstanding Challenge



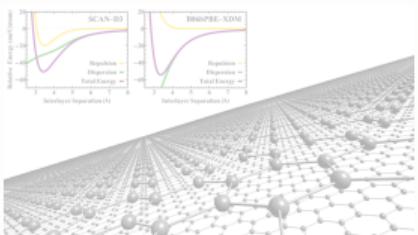
K. R. Bryenton, A. A. Adeleke, S. G. Dale, & E. R. Johnson, *WIREs Comp. Mol. Sci.* 13, e1631 (2023). doi: 10.1002/wcms.1631

## Many-Body Dispersion and the Sensitivity of SCS



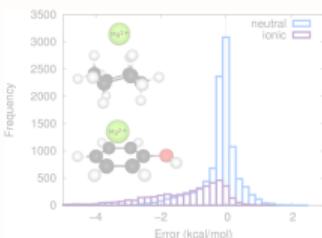
K. R. Bryenton & E. R. Johnson, *J. Chem. Phys.* 158 204110 (2023). doi: 10.1063/5.0142465

## Requirements for an Accurate Disp.-Corr. Functional



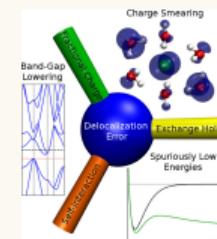
A. J. A. Price, K. R. Bryenton, & E. R. Johnson, *J. Chem. Phys.* 154, 230902 (2021).  
doi: 10.1063/5.0050993

## Comparison of DFT Disp. Corrections on DES15K



C. J. Nickerson, K. R. Bryenton, A. J. Price, & E. R. Johnson, Submitted to *J. Phys. Chem.* (2023)

## Delocalization Error: Greatest Outstanding Challenge



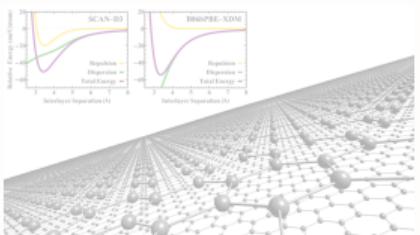
K. R. Bryenton, A. A. Adeleke, S. G. Dale, & E. R. Johnson, *WIREs Comp. Mol. Sci.* 13, e1631 (2023). doi: 10.1002/wcms.1631

## Many-Body Dispersion and the Sensitivity of SCS



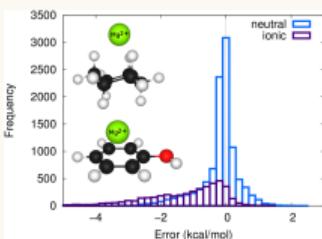
K. R. Bryenton & E. R. Johnson, *J. Chem. Phys.* 158 204110 (2023). doi: 10.1063/5.0142465

## Requirements for an Accurate Disp.-Corr. Functional



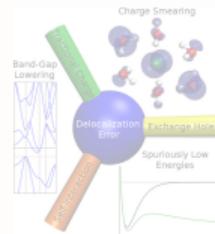
A. J. A. Price, K. R. Bryenton, & E. R. Johnson, *J. Chem. Phys.* 154, 230902 (2021). doi: 10.1063/5.0050993

## Comparison of DFT Disp. Corrections on DES15K



C. J. Nickerson, K. R. Bryenton, A. J. Price, & E. R. Johnson, Submitted to *J. Phys. Chem.* (2023)

## Delocalization Error: Greatest Outstanding Challenge



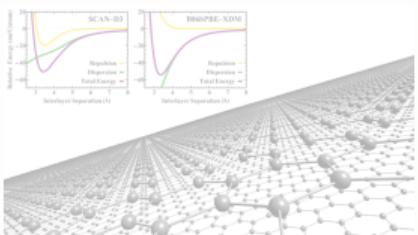
K. R. Bryenton, A. A. Adeleke, S. G. Dale, & E. R. Johnson, *WIREs Comp. Mol. Sci.* 13, e1631 (2023). doi: 10.1002/wcms.1631

## Many-Body Dispersion and the Sensitivity of SCS



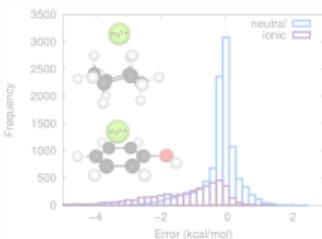
K. R. Bryenton & E. R. Johnson, *J. Chem. Phys.* 158 204110 (2023). doi: 10.1063/5.0142465

## Requirements for an Accurate Disp.-Corr. Functional



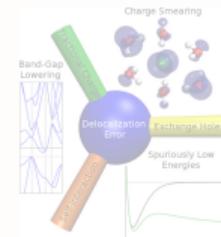
A. J. A. Price, K. R. Bryenton, & E. R. Johnson, *J. Chem. Phys.* 154, 230902 (2021).  
doi: 10.1063/5.0050993

## Comparison of DFT Disp. Corrections on DES15K



C. J. Nickerson, K. R. Bryenton, A. J. Price, & E. R. Johnson, Submitted to *J. Phys. Chem.* (2023)

## Delocalization Error: Greatest Outstanding Challenge



K. R. Bryenton, A. A. Adeleke, S. G. Dale, & E. R. Johnson, *WIREs Comp. Mol. Sci.* 13, e1631 (2023). doi: 10.1002/wcms.1631

## Many-Body Dispersion and the Sensitivity of SCS



K. R. Bryenton & E. R. Johnson, *J. Chem. Phys.* 158 204110 (2023). doi: 10.1063/5.0142465

Program Requirements  
ooo

Dispersion  
oooooo

The Oscallot Code  
oo

Results  
oooooooo

Improved Dispersion Forces  
oooo

Conclusions  
oo

## Program Requirements

## Dispersion

What is Dispersion?

Many-Body Dispersion Effects

Post-SCF Dispersion Corrections

Motivation: XDM vs. MBD

## The Oscallot Code

## Results

## Improving Dispersion Forces

## 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  $C_{6,ii}$ ,  $\alpha_i^0$ , 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  $R_{\text{vdW}}$  via multipole moment integrals. The polarizability 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.

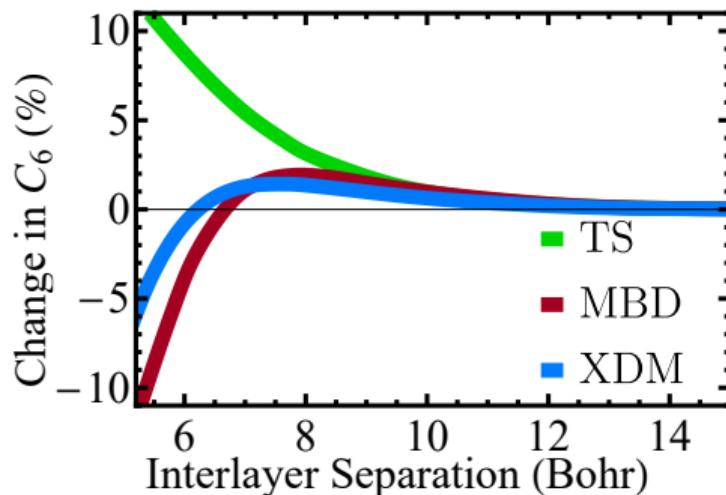
$$\alpha^{\text{VV}}[\rho](\mathbf{r}, i\omega) = \frac{\rho(\mathbf{r})}{\frac{4\pi}{3} + C \frac{|\nabla \rho(\mathbf{r})|^4}{\rho(\mathbf{r})^4} + \omega^2}$$

## SUMMARY OF DISPERSION CORRECTIONS

$\alpha$	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	✓	✗	$\alpha, C_6, R_{vdw}$	?	✗
XDM:	BJ	✓	✓	$\alpha$	?	$C_9$
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 et al. *J. Phys. Chem. Lett.*, **11** 6, 2298–2302. (2020) doi: 10.1021/acs.jpclett.0c00348

Program Requirements  
ooo

Dispersion  
oooooo

The Oscallot Code  
oo

Results  
oooooooo

Improved Dispersion Forces  
oooo

Conclusions  
oo

## Program Requirements

## Dispersion

## The Oscallot Code

System Geometry

Multi-Oscillator Wavefunctions

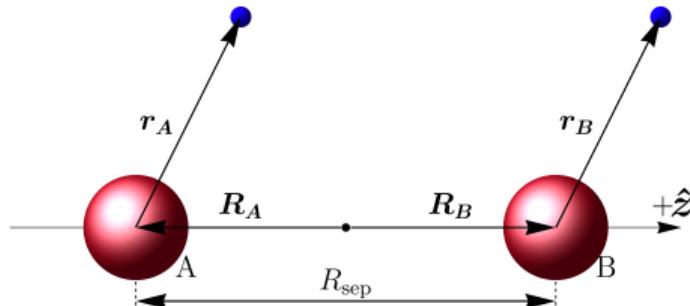
## Results

## Improving Dispersion Forces

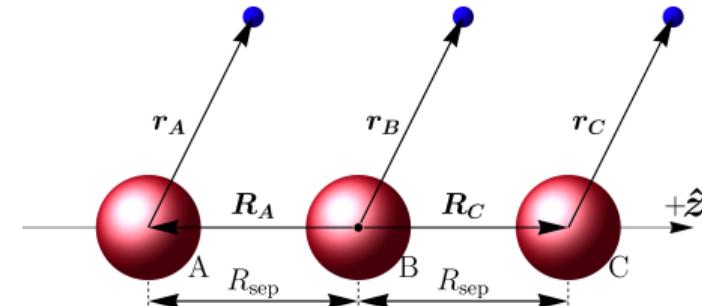
## Conclusions

## SYSTEM GEOMETRY

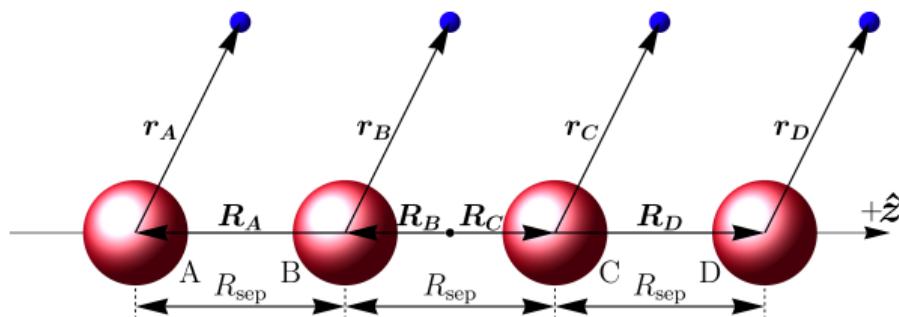
DIMER



TRIMER



TETRAMER



Program Requirements  
○○○

Dispersion  
○○○○○

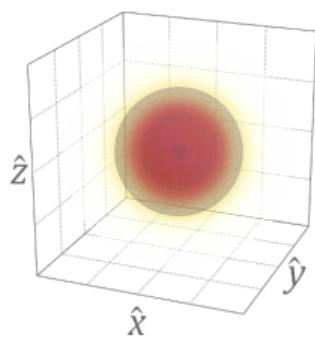
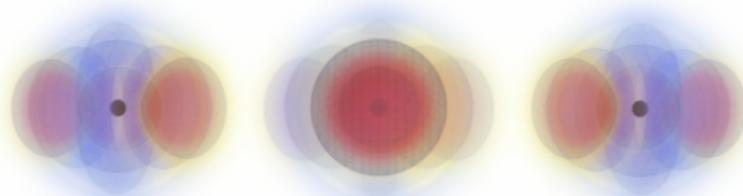
The Oscillator Code  
○●

Results  
○○○○○○○

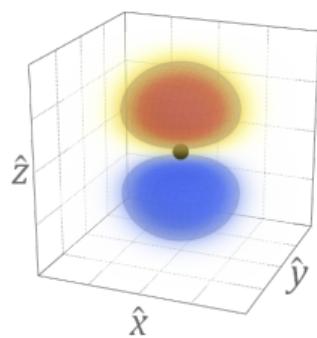
Improved Dispersion Forces  
○○○○

Conclusions  
○○

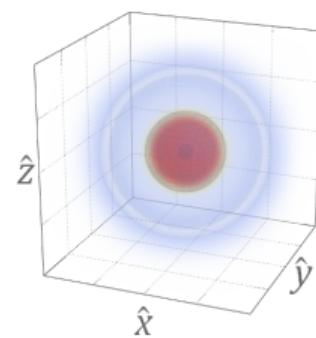
## MULTI-OSCILLATOR WAVEFUNCTIONS



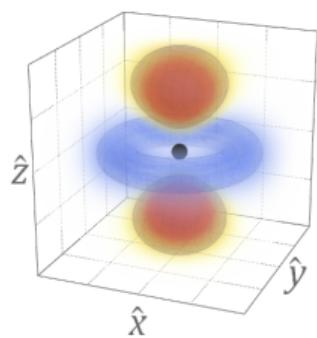
(a)  $1s$



(b)  $2p_z$



(c)  $2s$



(d)  $3d_{z^2}$



Program Requirements  
ooo

Dispersion  
oooooo

The Oscallot Code  
oo

Results  
oooooooo

Improved Dispersion Forces  
oooo

Conclusions  
oo

## Program Requirements

## Dispersion

## The Oscallot Code

## Results

Model Oscillator System Results

Comparison to Noble Gasses

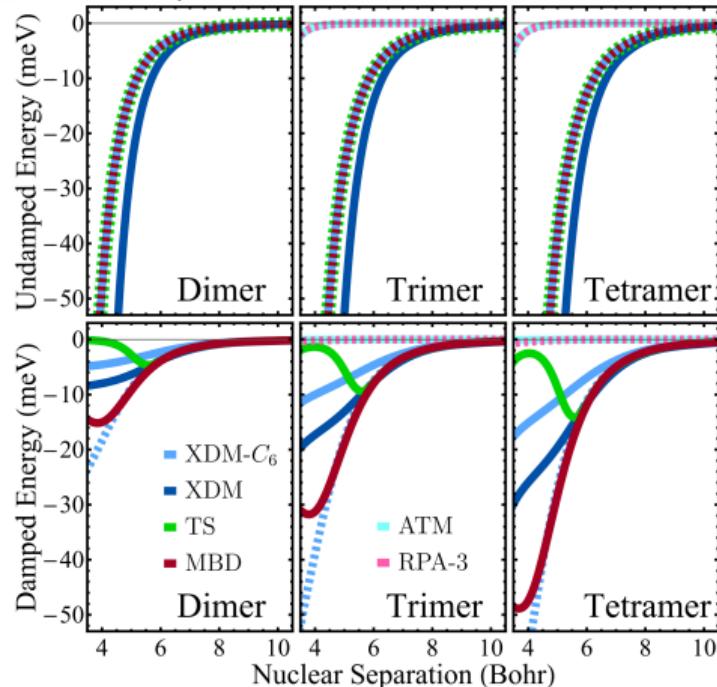
Connection with Molecular Dimers and Layered Materials

Key Takeaways

## Improving Dispersion Forces

## Conclusions

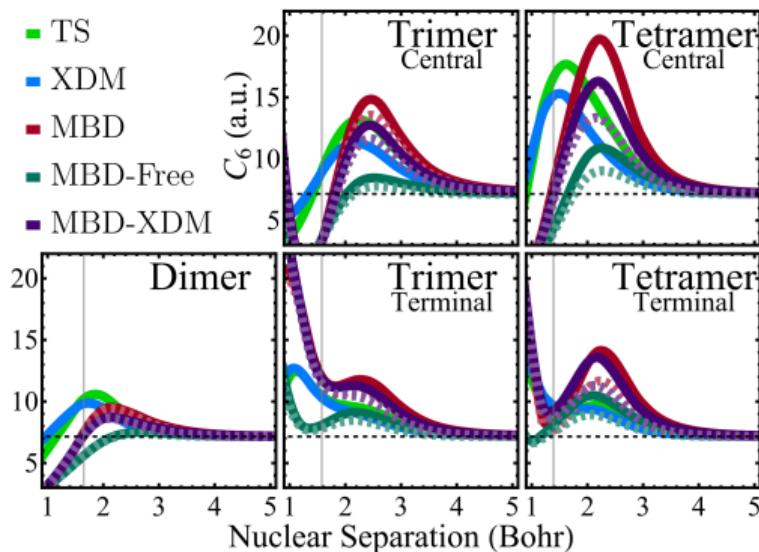
## UNDAMPED/DAMPED ENERGY COMPARISON



- 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

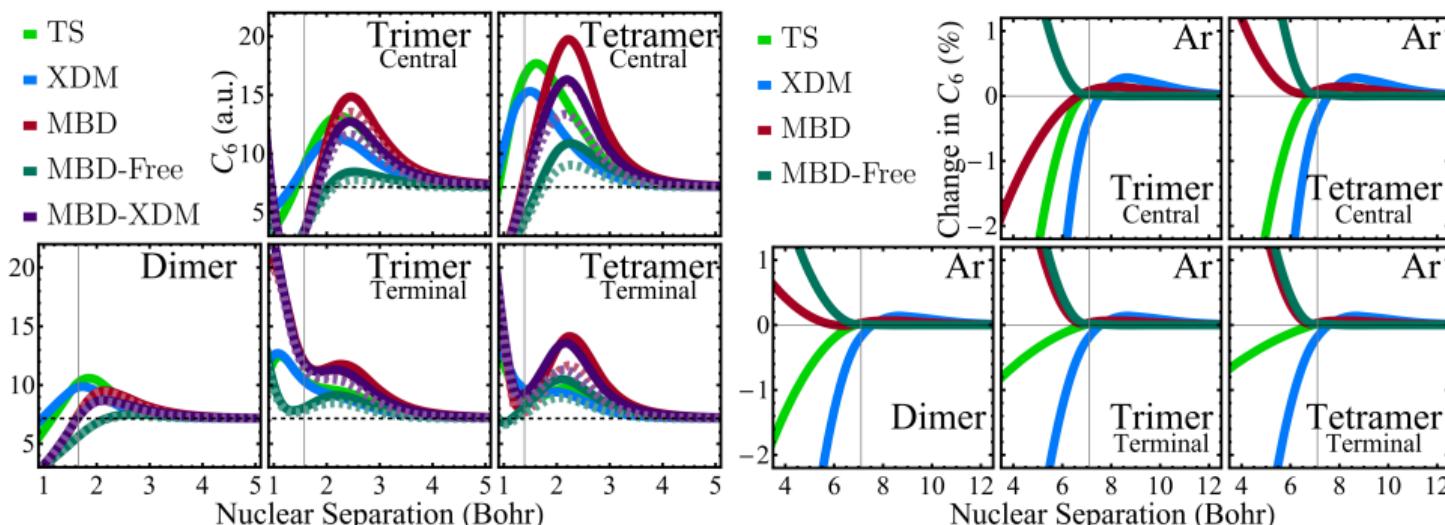
We look at the  $C_6$  coefficients directly as we change inter-oscillator separation. The equilibrium separation for each system is indicated by a vertical line.



- 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

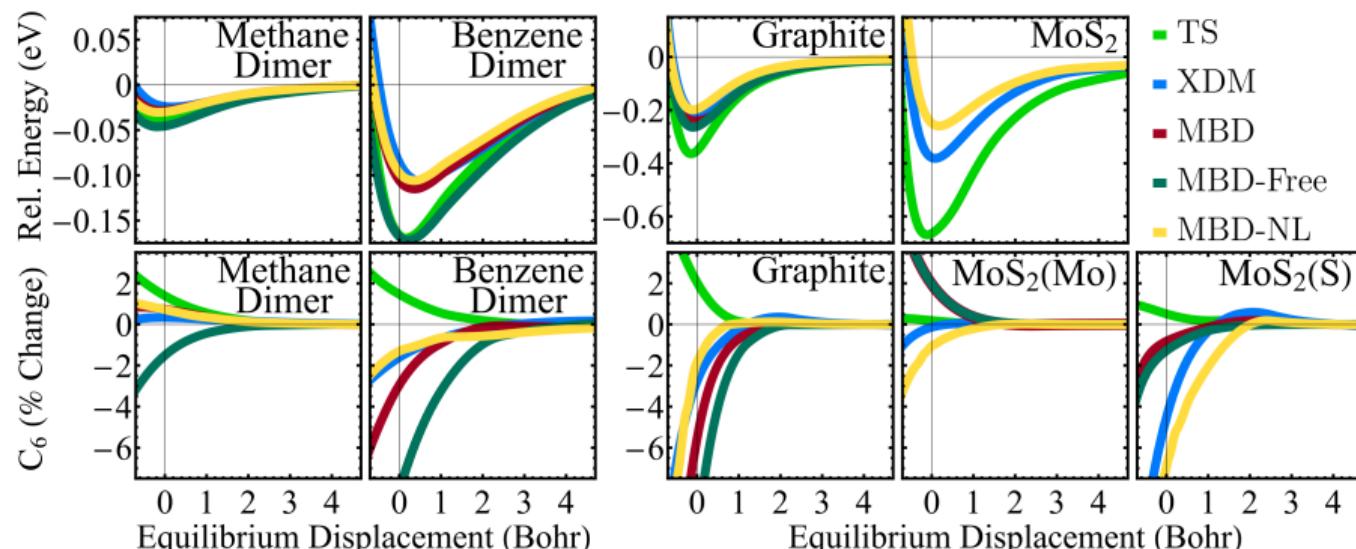
We compare to Ar chains as this model system will be bound by dispersion.  
Computed in FHI-aims using Tight basis settings and the PBE functional.



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



- MBD and MBD-Free fail for  $\text{MoS}_2$
- 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/Å<sup>2</sup> 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 <sub>4</sub> ) <sub>2</sub>	72%	25%	32%	7.5%	0.53 <sup>[1]</sup>
(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	39%	-6%	-13%	-12%	2.81 <sup>[1]</sup>
Graphite	88%	19%	2.7%	6.8%	18.32 <sup>[2]</sup>
MoS <sub>2</sub>	88%	—	-27%	7.2%	20.53 <sup>[2]</sup>
RMSPE	75%	18%	22%	8.6%	
S66×8 (kcal/mol) <sup>[3]</sup>	0.60	0.44	0.43	0.45	—
LM11 (meV/Å <sup>2</sup> ) <sup>[4]</sup>	12.5	—	5.0	3.7	—
LM26 (meV/Å <sup>2</sup> ) <sup>[2]</sup>	13.1	—	4.6	4.9	—

- 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
$\text{CH}_4$	C	46.6	26.0	31.7	27.6	18.7
$\text{C}_6\text{H}_6$	C	46.6	32.6	30.7	28.6	21.4
Graphite	C	46.6	35.4	33.3	27.7	20.2
$\text{MoS}_2$	Mo	1029	1060	627	260	388
$\text{MoS}_2$	S	134.0	132	80.3	101	78.5

- XDM seems to consistently underestimate  $C_6$
- Future Work: Improve XDM by implementing a polarizability functional

## 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	✓	✓	$\alpha$	$d_{X\sigma}$	$C_9$
MBD:	rsSCS	✓	✗	TS@SCS	SCS	$\hat{H}_{\text{CFDM}}$
MBD-NL:	rs	✓	✗	VV10	VV10	$\hat{H}_{\text{CFDM}}$
MBD-Free:	rsSCS	✓	✗	Free@SCS	SCS	$\hat{H}_{\text{CFDM}}$
MBD-XDM:	rsSCS	✓	✗	$d_{X\sigma} + \text{SCS}$	$d_{X\sigma} + \text{SCS}$	$\hat{H}_{\text{CFDM}}$

Program Requirements  
ooo

Dispersion  
oooooo

The Oscallot Code  
oo

Results  
oooooooo

Improved Dispersion Forces  
oooo

Conclusions  
oo

## Program Requirements

## Dispersion

## The Oscallot Code

## Results

## Improving Dispersion Forces

### The Issue

### Proposed Implementation

### Testing and Benchmarking

## Conclusions

## XDM FORCES: CURRENT IMPLEMENTATION

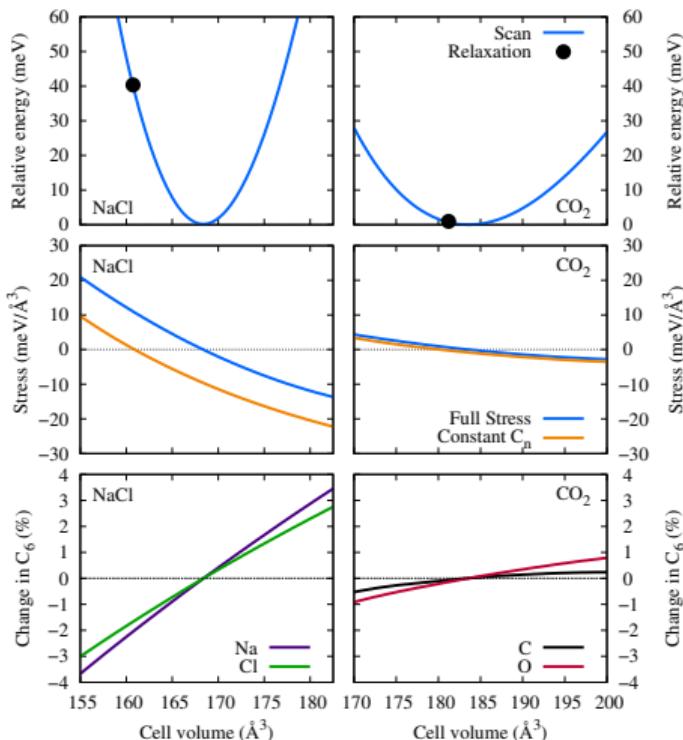
ENERGY:

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

HELLMANN-FEYNMAN FORCE:

$$\mathbf{F}_i^{\text{XDM}} = \sum_{\mathbf{L}} \sum_{j'} \sum_{n=6,8,10} \frac{n C_{n,ij}^{\text{XDM}} R_{ij,\mathbf{L}}^{n-1}}{\left( R_{\text{vdW},ij}^n + R_{ij,\mathbf{L}}^n \right)^2} \hat{\mathbf{R}}_{ij,\mathbf{L}},$$

## THE ISSUE



**Table:** Lattice constant ( $a_{\text{latt}}$  in Å) and corresponding energy errors ( $\Delta E$  in meV) computed by FHI-aims with the PBE functional and LightDense basis.

	TS			MBD-NL			XDM		
	$a_{\text{latt}}^{\min}$	$a_{\text{latt}}^{\text{rel}}$	$\Delta E$	$a_{\text{latt}}^{\min}$	$a_{\text{latt}}^{\text{rel}}$	$\Delta E$	$a_{\text{latt}}^{\min}$	$a_{\text{latt}}^{\text{rel}}$	$\Delta E$
CO <sub>2</sub>	5.92	5.93	01	5.92	5.93	<1	5.93	5.93	<1
Diam.	3.55	3.56	<1	3.56	3.56	<1	3.57	3.56	01
Si	5.47	5.46	<1	5.47	5.44	08	5.47	5.44	13
GaAs	5.73	5.73	<1	5.71	5.69	03	5.72	5.67	23
Ni	3.41	3.41	<1	3.47	3.47	<1	3.48	3.45	17
Cu	3.55	3.54	<1	3.60	3.60	<1	3.60	3.56	25
NaCl	5.38	5.40	02	5.62	5.63	<1	5.56	5.51	13
MgO	4.20	4.20	<1	4.26	4.24	02	4.24	4.22	15

TAKEAWAYS:

- 1) The issue affects XDM, (and to a lesser extent) MBD-NL, and TS
- 2) The issue is present in both Quantum ESPRESSO and FHI-aims

## XDM FORCES: PROPOSED IMPLEMENTATION

$$\mathbf{F}_i^{\text{XDM}} = \sum_{\mathbf{L}} \sum_{j'} \sum_{n=6,8,10} \left[ -n f_n^{\text{BJ}} \frac{C_{n,ij}^{\text{XDM}}}{R_{ij,\mathbf{L}}^n} + (f_n^{\text{BJ}})' \frac{C_{n,ij}^{\text{XDM}}}{R_{ij,\mathbf{L}}^n} + f_n^{\text{BJ}} \frac{(C_{n,ij}^{\text{XDM}})'}{R_{ij,\mathbf{L}}^n} \right] \hat{\mathbf{R}}_{ij,\mathbf{L}}$$

### DERIVATIVE OF $f^{\text{BJ}}$

$$f_n^{\text{BJ}} = \frac{R_{ij}^n}{R_{ij}^n + R_{\text{vdW},ij}^n}, \quad R_{\text{vdW},ij} = \frac{a_1}{3} \left[ \left( \frac{C_{8,ij}^{\text{XDM}}}{C_{6,ij}^{\text{XDM}}} \right)^{\frac{1}{2}} + \left( \frac{C_{10,ij}^{\text{XDM}}}{C_{6,ij}^{\text{XDM}}} \right)^{\frac{1}{4}} + \left( \frac{C_{10,ij}^{\text{XDM}}}{C_{8,ij}^{\text{XDM}}} \right)^{\frac{1}{2}} \right] + a_2$$

$$(f_n^{\text{BJ}})' = \frac{n R_{ij,\mathbf{L}}^{n-1} R_{\text{vdW},ij}^{n-1} [R_{\text{vdW},ij} - R_{ij,\mathbf{L}} (R_{\text{vdW},ij})']}{(R_{\text{vdW},ij}^n + R_{ij,\mathbf{L}}^n)^2}$$

$$(R_{\text{vdW},ij})' = \frac{a_1}{6} \left[ \frac{C_{6,ij}(C_{8,ij})' - (C_{6,ij})'C_{8,ij}}{C_{6,ij}^{3/2} C_{8,ij}^{1/2}} + \frac{C_{6,ij}(C_{10,ij})' - (C_{6,ij})'C_{10,ij}}{2C_{6,ij}^{5/4} C_{10,ij}^{3/4}} \right. \\ \left. + \frac{C_{8,ij}(C_{10,ij})' - (C_{8,ij})'C_{10,ij}}{C_{6,ij}^{3/2} C_{10,ij}^{1/2}} \right]$$

## XDM FORCES: PROPOSED IMPLEMENTATION

$$\mathbf{F}_i^{\text{XDM}} = \sum_{\mathbf{L}} \sum_{j'} \sum_{n=6,8,10} \left[ -n f_n^{\text{BJ}} \frac{C_{n,ij}^{\text{XDM}}}{R_{ij,\mathbf{L}}^{n+1}} + (f_n^{\text{BJ}})' \frac{C_{n,ij}^{\text{XDM}}}{R_{ij,\mathbf{L}}^n} + f_n^{\text{BJ}} \frac{(C_{n,ij}^{\text{XDM}})'}{R_{ij,\mathbf{L}}^n} \right] \hat{\mathbf{R}}_{ij,\mathbf{L}}$$

### DERIVATIVE OF $C_{6,ij}^{\text{XDM}}$

$$C_{6,ij}^{\text{XDM}} = \frac{\alpha_i \alpha_j \langle M_1^2 \rangle_i \langle M_1^2 \rangle_j}{\alpha_i \langle M_1^2 \rangle_j + \alpha_j \langle M_1^2 \rangle_i}, \quad \langle M_\ell^2 \rangle_i = \sum_{\sigma} \int \omega_i \rho_{\sigma}(\mathbf{r}) [r^\ell - (r - d_{X,\sigma})^\ell]^2 d\mathbf{r}$$

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

$$\langle M_\ell^2 \rangle_i' = \sum_{\sigma} \int (\omega_i)' \rho_{\sigma}(\mathbf{r}) [r^\ell - (r - d_{X,\sigma})^\ell]^2 d\mathbf{r}.$$

## XDM FORCES: PROPOSED IMPLEMENTATION

$$\mathbf{F}_i^{\text{XDM}} = \sum_{\mathbf{L}} \sum_{j'} \sum_{n=6,8,10} \left[ -n f_n^{\text{BJ}} \frac{C_{n,ij}^{\text{XDM}}}{R_{ij,\mathbf{L}}^{n+1}} + (f_n^{\text{BJ}})' \frac{C_{n,ij}^{\text{XDM}}}{R_{ij,\mathbf{L}}^n} + f_n^{\text{BJ}} \frac{(C_{n,ij}^{\text{XDM}})'}{R_{ij,\mathbf{L}}^n} \right] \hat{\mathbf{R}}_{ij,\mathbf{L}}$$

DERIVATIVES OF  $C_{6,ii}^{\text{TS}}$ ,  $\alpha_i^0$ ,  $R_i^0$ , AND  $v_i$

$$\alpha_i^0 = \frac{v_i}{v_i^{\text{free}}} \alpha_i^{\text{free}}$$

$$v_i = \int r^3 \omega_i \rho_i(\mathbf{r}) d\mathbf{r} .$$

$$(\alpha_i^0)' = \frac{(v_i)'}{v_i} \alpha_i^0$$

$$(v_i)' = \int r^3 (\omega_i)' \rho_i(\mathbf{r}) d\mathbf{r} .$$

---

Heßelmann, Geometry optimisations with a nonlocal density-functional theory method based on a double Hirshfeld partitioning *J. Chem. Phys.* **149**, 044103. (2018) doi: 10.1063/1.5032175

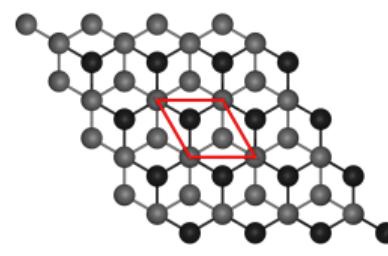
## TESTING AND BENCHMARKING

## CS8 BENCHMARK

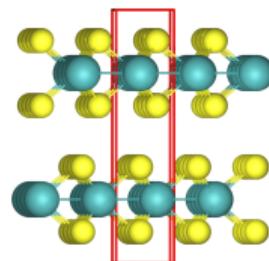
- CO<sub>2</sub>
- Diamond
- Si
- GaAs
- Ni
- Cu
- NaCl
- MgO

## LM11/LM26 BENCHMARKS

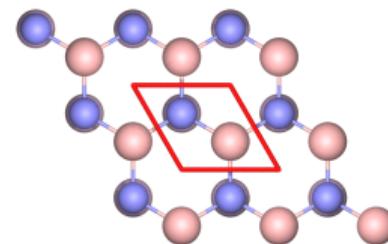
- Graphite
- Boron Nitride
- MoS<sub>2</sub>
- MoSe<sub>2</sub>
- MoTe<sub>2</sub>
- WS<sub>2</sub>
- PdTe<sub>2</sub>
- TaS<sub>2</sub>
- HfS<sub>2</sub>
- HfSe<sub>2</sub>
- HfTe<sub>2</sub>



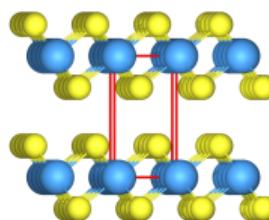
Graphite



Mo{S,Se,Te}2, WS2



h-BN



TaS2, HF{S,Se,Ts}2, PdTe2

Program Requirements  
ooo

Dispersion  
oooooo

The Oscallot Code  
oo

Results  
oooooooo

Improved Dispersion Forces  
oooo

Conclusions  
oo

Program Requirements

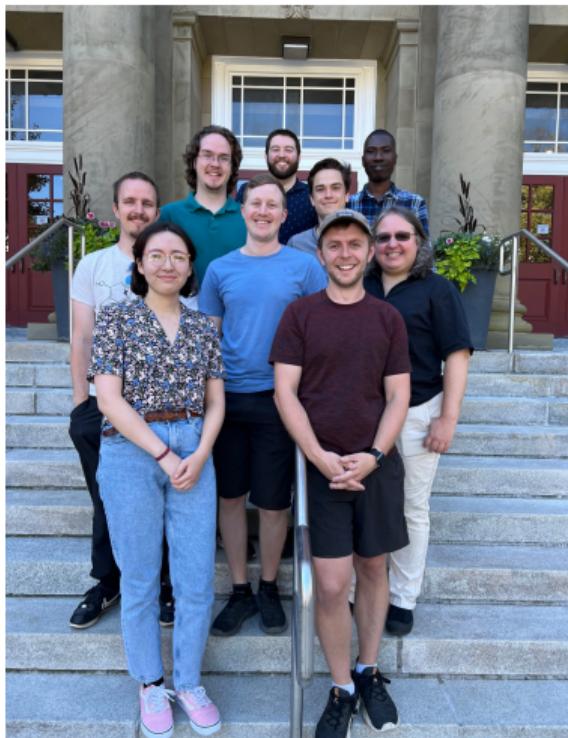
Dispersion

The Oscallot Code

Results

Improving Dispersion Forces

Conclusions



# ACKNOWLEDGEMENTS

## The Johnson Group:

- Prof. Erin Johnson
- Prof. Alberto Otero de la Roza
- Emeritus Prof. Axel Becke
- Dr. Adebayo Adeleke
- Dr. Alastair Price
- Dr. R. Alex Mayo
- Adrian Rumson
- Cameron Nickerson
- Nick Roberts
- Sarah Clarke

## Funding and Resources:

- Killam Trusts
- Walter C Sumner Foundation
- Government of Nova Scotia
- Dalhousie University
- Digital Research Alliance of Canada

Program Requirements  
○○○

Dispersion  
○○○○○○

The Oscallot Code  
○○

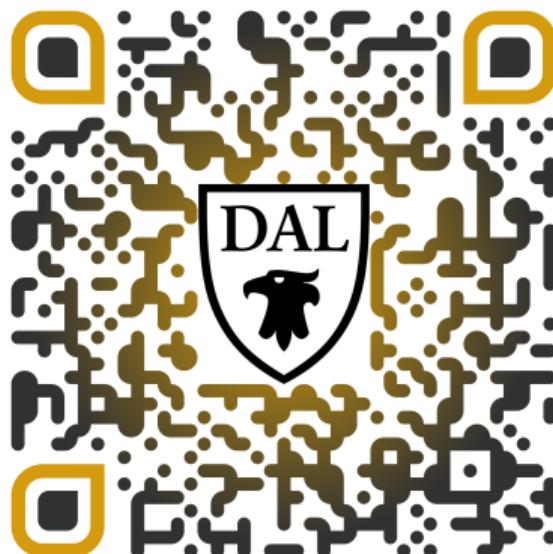
Results  
○○○○○○○

Improved Dispersion Forces  
○○○○

Conclusions  
○●

# QUESTIONS?

WANT MY SLIDES?



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

KYLE.BRYENTON@DAL.CA