



## COMMITTEE MEETING II



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

Program Requirements  
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Dispersion  
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The Oscallot Code  
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Results  
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Improved Dispersion Forces  
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Conclusions  
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## 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

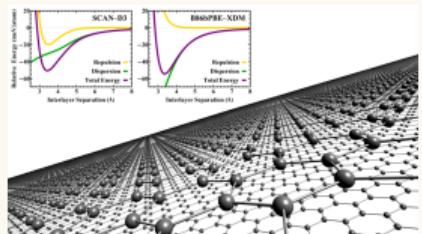
3. Seminar III - 2023-02-14

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

## SIX-MONTH RESEARCH PLAN:

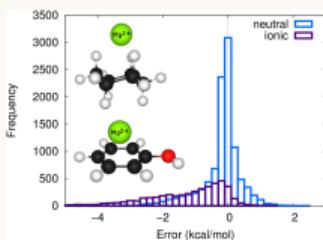
1. Complete XDM forces implementation in FHI-aims and publish.
2. Derive an XDM polarizability functional free of empiricism and publish.
3. Audit: *Advanced Module on Solid State Modeling and Relativistic Effects in Chemistry*
4. Audit: *Advanced Module on Thermochemistry and Kinetics*
5. Self-study 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



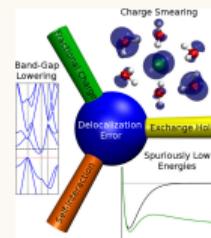
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## Comparison of DFT Disp. Corrections on DES15K



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

## Delocalization Error: Greatest Outstanding Challenge



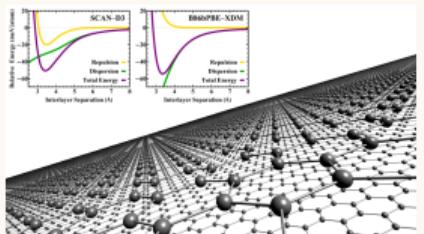
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## Many-Body Dispersion and the Sensitivity of SCS



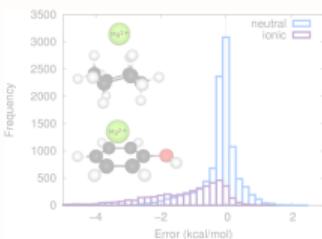
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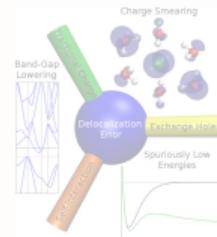
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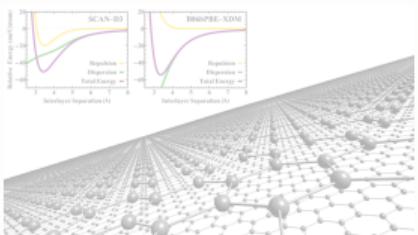
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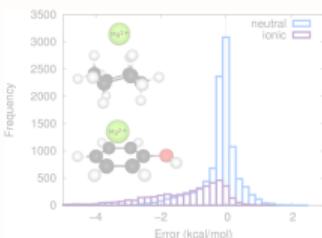
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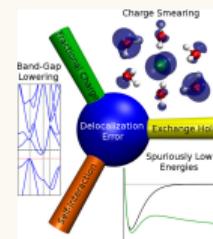
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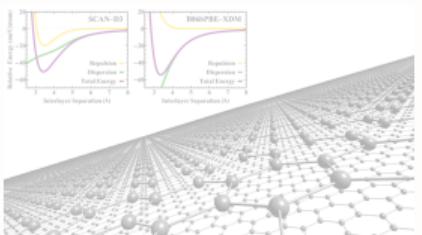
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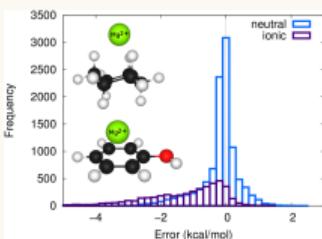
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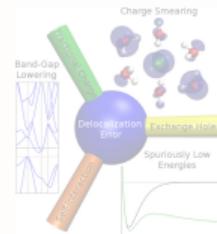
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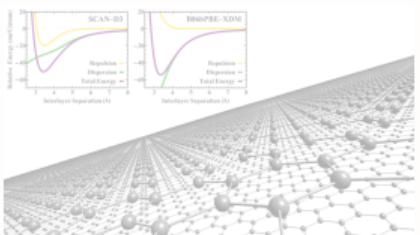
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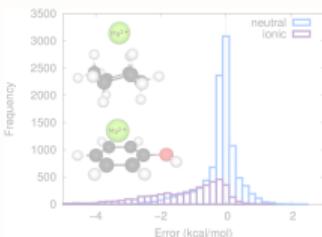
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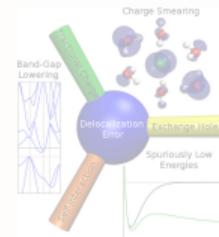
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The Oscallot Code  
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Results  
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Improved Dispersion Forces  
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Conclusions  
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## 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

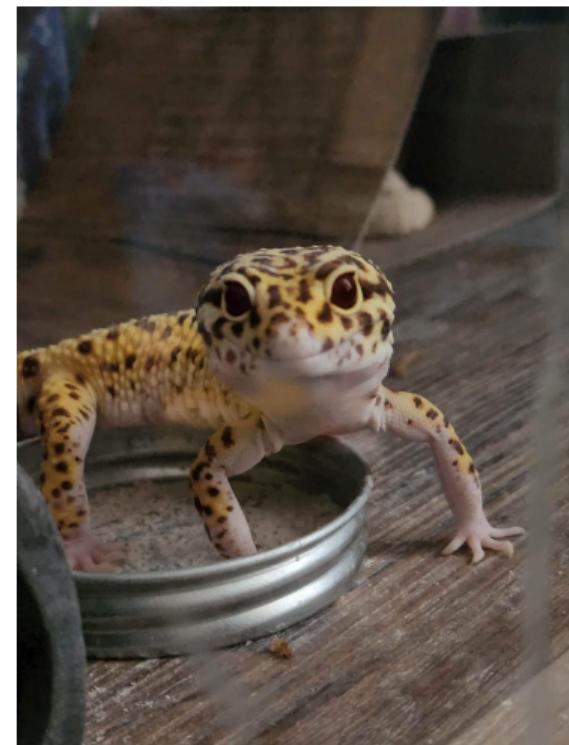
## WHAT IS DISPERSION

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.

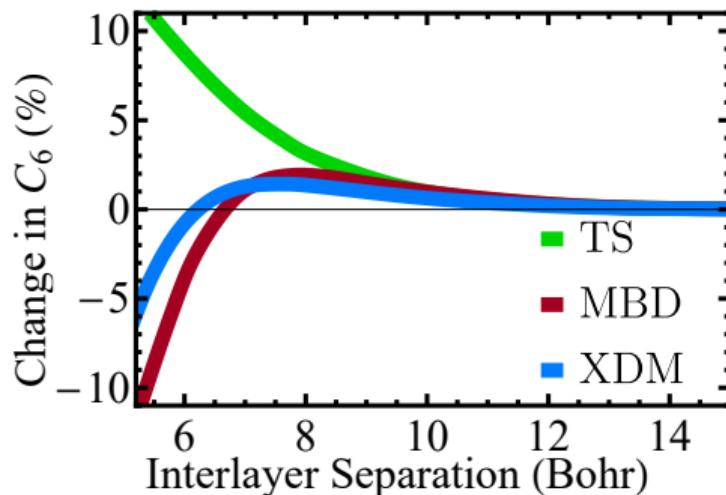
$$\alpha^{\text{VV}}[\rho](\mathbf{r}, i\omega) = \frac{\rho(\mathbf{r})}{\frac{4\pi}{3} + C \frac{|\nabla \rho(\mathbf{r})|^4}{\rho(\mathbf{r})^4} + \omega^2}$$

## 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

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## Program Requirements

## Dispersion

## The Oscallot Code

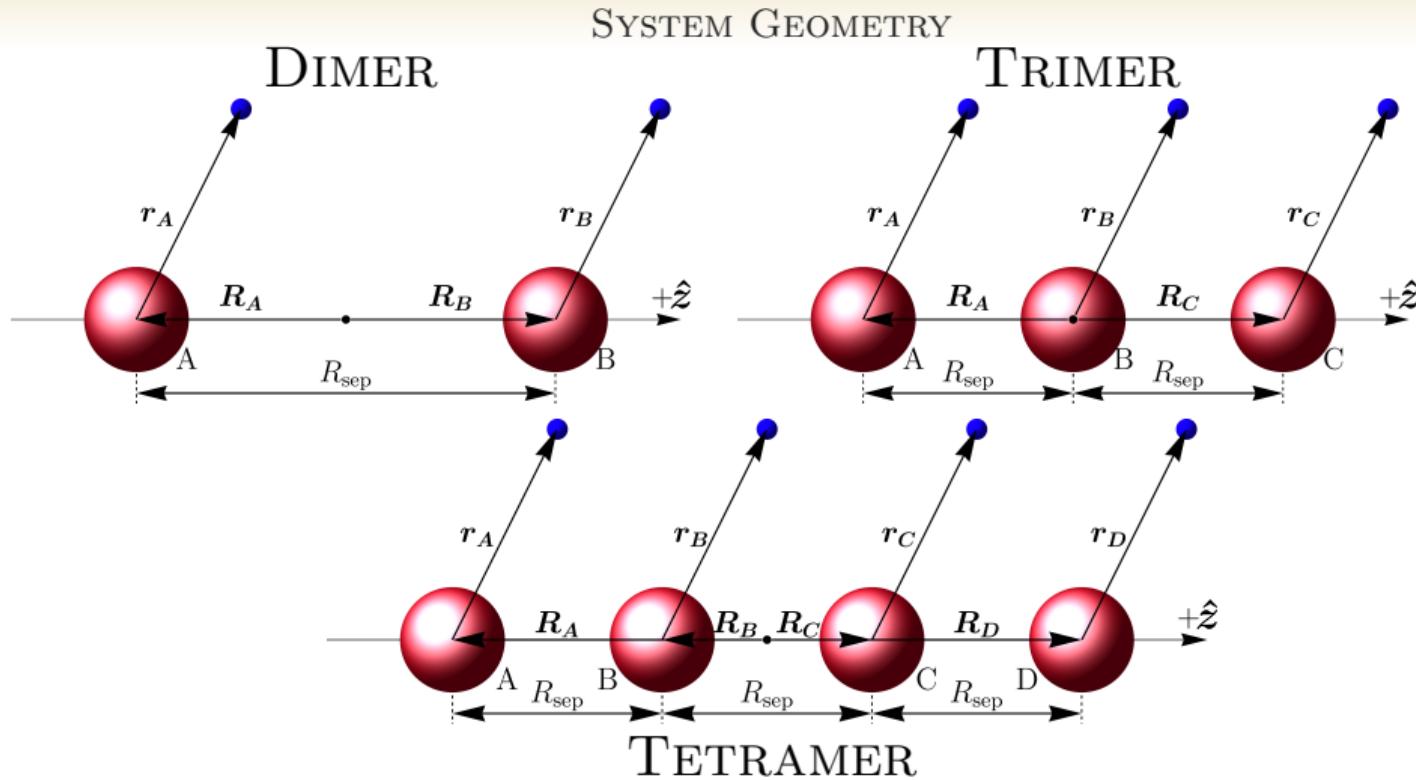
System Geometry

Multi-Oscillator Wavefunctions

## Results

## Improving Dispersion Forces

## Conclusions



Program Requirements  
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Dispersion  
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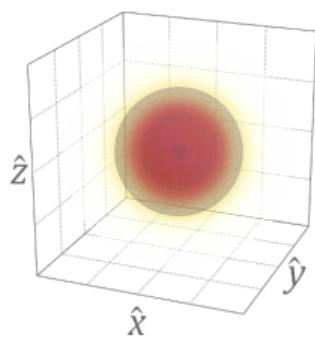
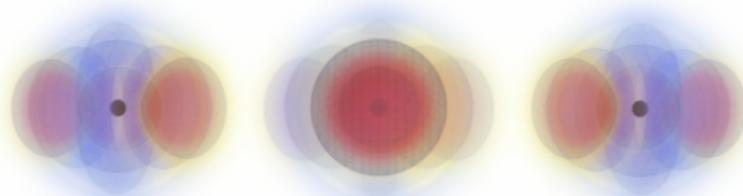
The Oscillator Code  
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Results  
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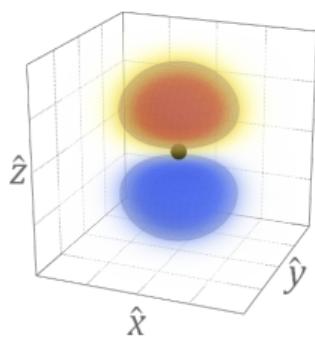
Improved Dispersion Forces  
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Conclusions  
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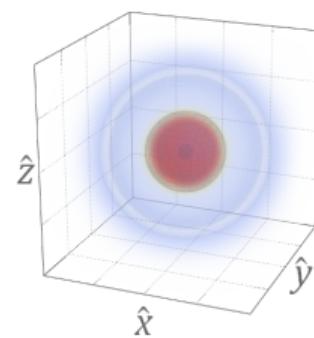
## MULTI-OSCILLATOR WAVEFUNCTIONS



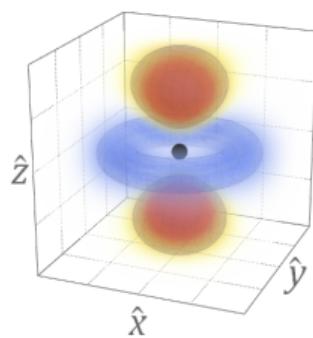
(a)  $1s$



(b)  $2p_z$



(c)  $2s$



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



Program Requirements  
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## Program Requirements

## Dispersion

## The Oscallot Code

## Results

Model Oscillator System Results

Comparison to Noble Gasses

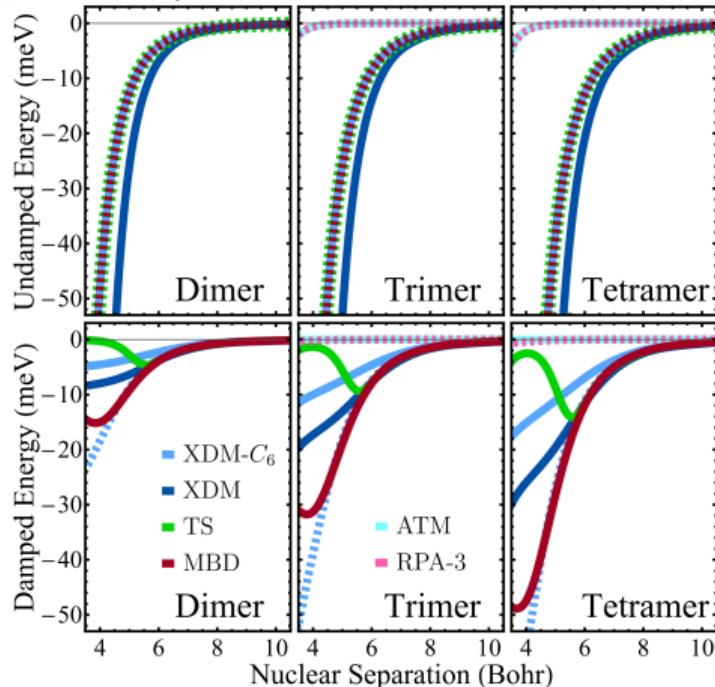
Connection with Molecular Dimers and Layered Materials

Key Takeaways

## Improving Dispersion Forces

## Conclusions

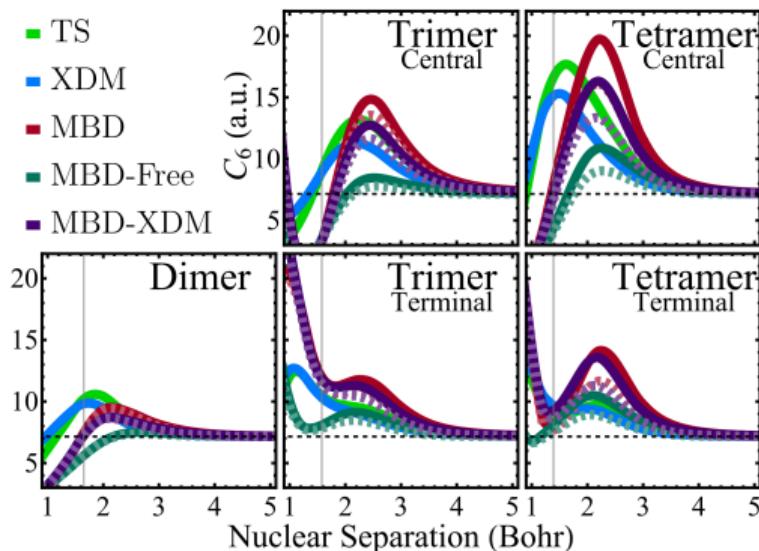
## UNDAMPED/DAMPED ENERGY COMPARISON



- 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

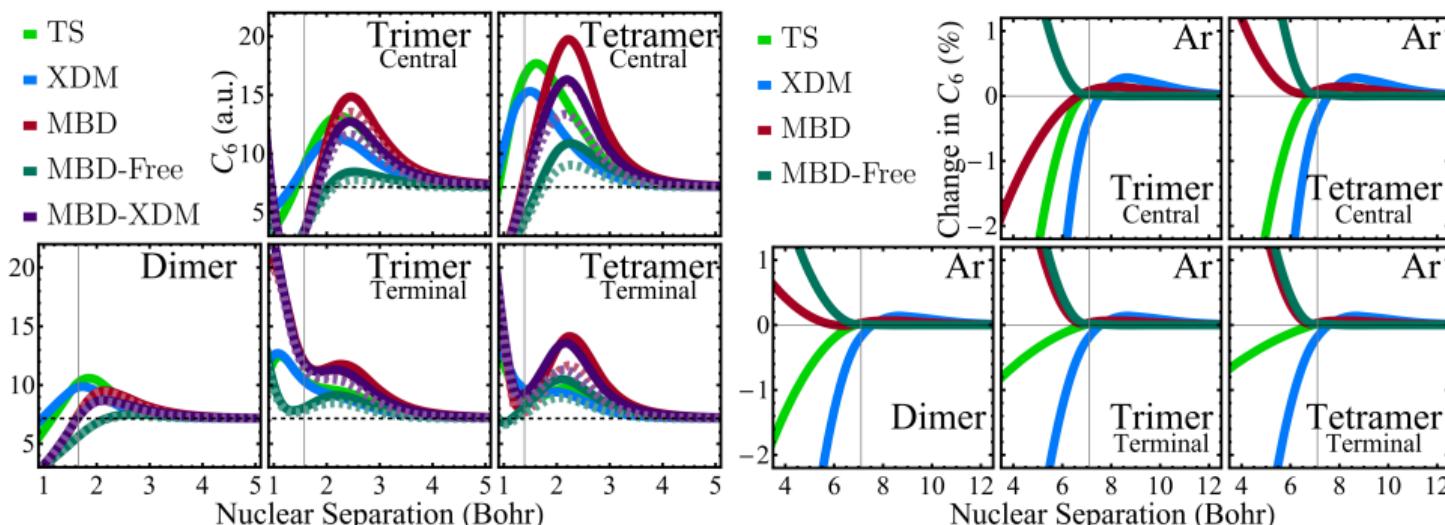
We look at the  $C_6$  coefficients directly as we change inter-oscillator separation. The equilibrium separation for each system is indicated by a vertical line.



- 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

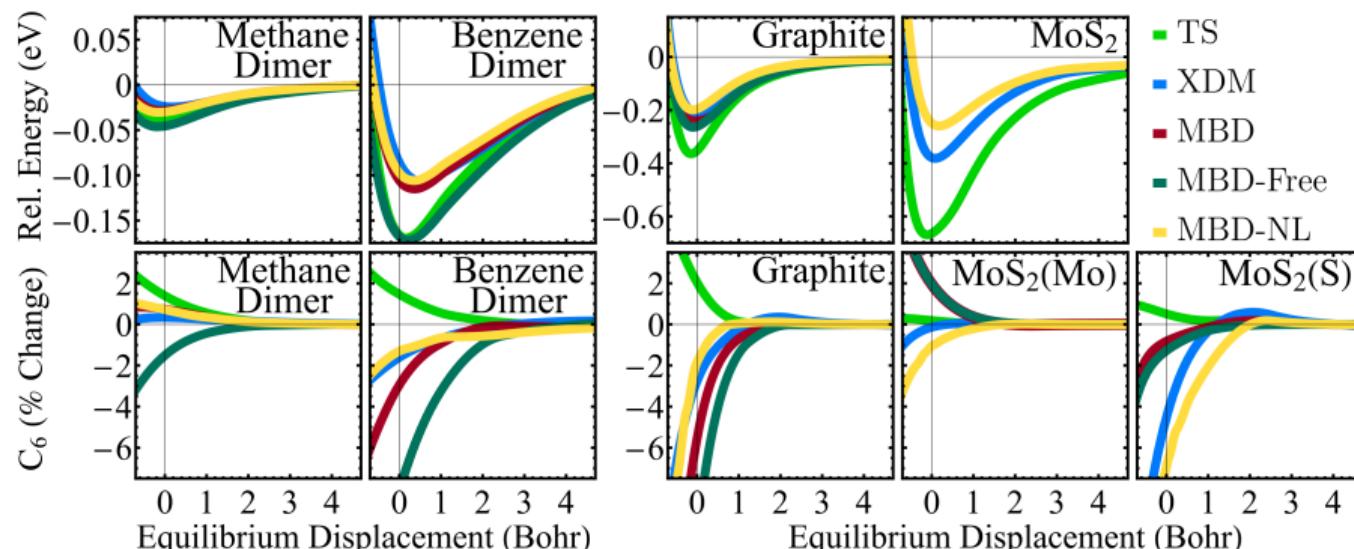
We compare to Ar chains as this model system will be bound by dispersion.  
Computed in FHI-aims using Tight basis settings and the PBE functional.



- 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  
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Dispersion  
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The Oscallot Code  
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Results  
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Improved Dispersion Forces  
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Conclusions  
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## Program Requirements

## Dispersion

## The Oscallot Code

## Results

## Improving Dispersion Forces

**The Issue**

**Proposed Implementation**

**Testing and Benchmarking**

## Conclusions

## XDM FORCES: CURRENT IMPLEMENTATION

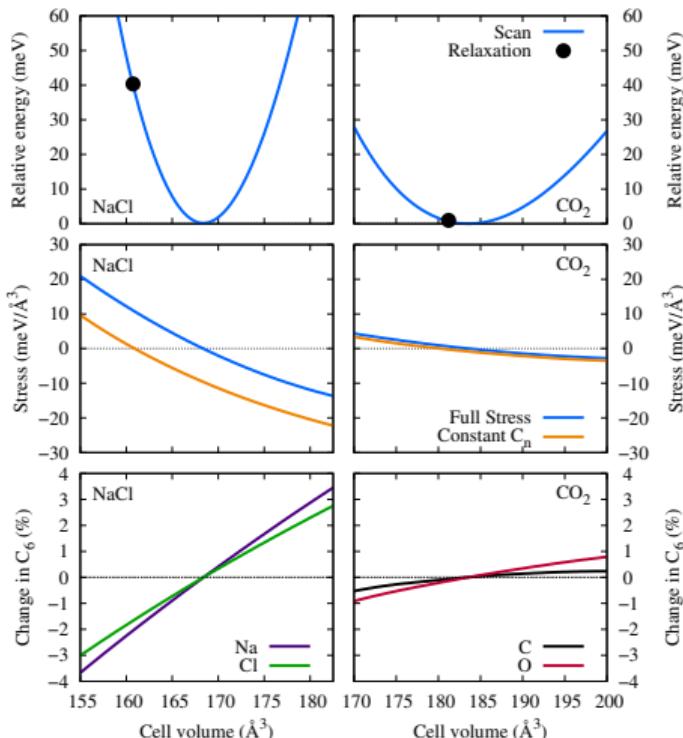
ENERGY:

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

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  $v_i$

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

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

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

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

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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

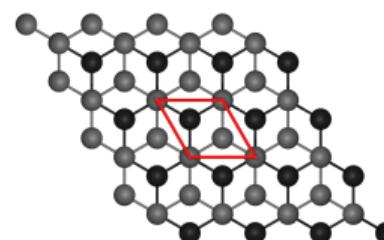
## TESTING AND BENCHMARKING

## CS8 BENCHMARK

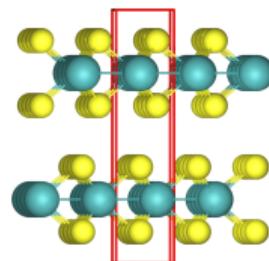
- CO<sub>2</sub>
- Diamond
- Si
- GaAs
- Ni
- Cu
- NaCl
- MgO

## LM11/LM26 BENCHMARKS

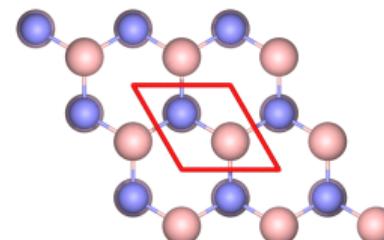
- Graphite
- Boron Nitride
- MoS<sub>2</sub>
- MoSe<sub>2</sub>
- MoTe<sub>2</sub>
- WS<sub>2</sub>
- PdTe<sub>2</sub>
- TaS<sub>2</sub>
- HfS<sub>2</sub>
- HfSe<sub>2</sub>
- HfTe<sub>2</sub>



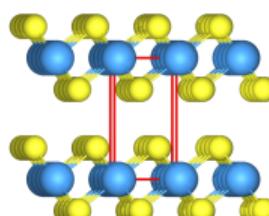
Graphite



Mo{S,Se,Te}2, WS2



h-BN



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

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Program Requirements

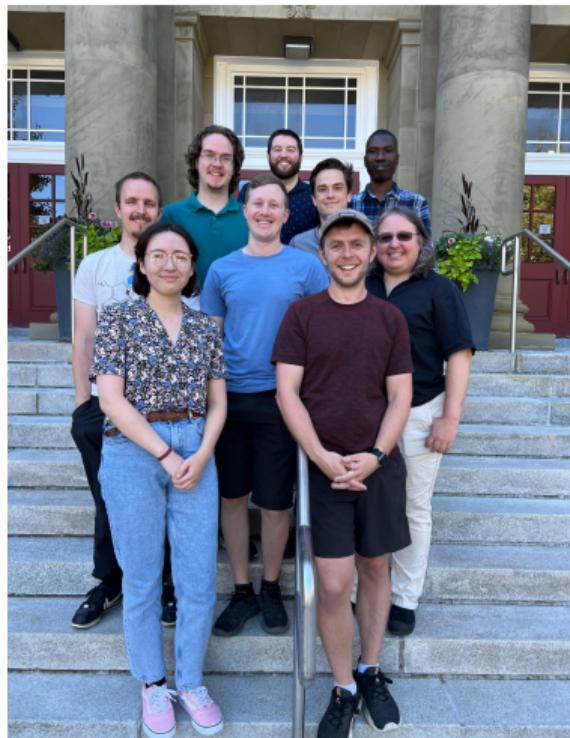
Dispersion

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Improving Dispersion Forces

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Program Requirements  
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Improved Dispersion Forces  
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Conclusions  
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# QUESTIONS?

WANT MY SLIDES?



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

KYLE.BRYENTON@DAL.CA