



QUALIFYING EXAM:
IMPROVED CALCULATION OF XDM DISPERSION FORCES
WITH APPLICATIONS TO SURFACES AND INTERFACES



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Theory and Background
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Drude Oscillator Project
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Improved Dispersion Forces
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Proposed Research
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Conclusions
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Theory and Background

Dispersion in DFT

Post-SCF Dispersion Corrections

Research Questions

Drude Oscillator Project

System Setup

Results

Improving Dispersion Forces

The Issue

TS Force Implementation

XDM Force Implementation

Proposed Research

To Do: Drude Oscillator Project

To Do: Improving XDM Forces

Conclusions

Theory and Background

Dispersion in DFT

Post-SCF Dispersion Corrections

The Tkatchenko-Scheffler Model

The Exchange-hole Dipole Moment Model

The Many-body Dispersion Model

Research Questions

Drude Oscillator Project

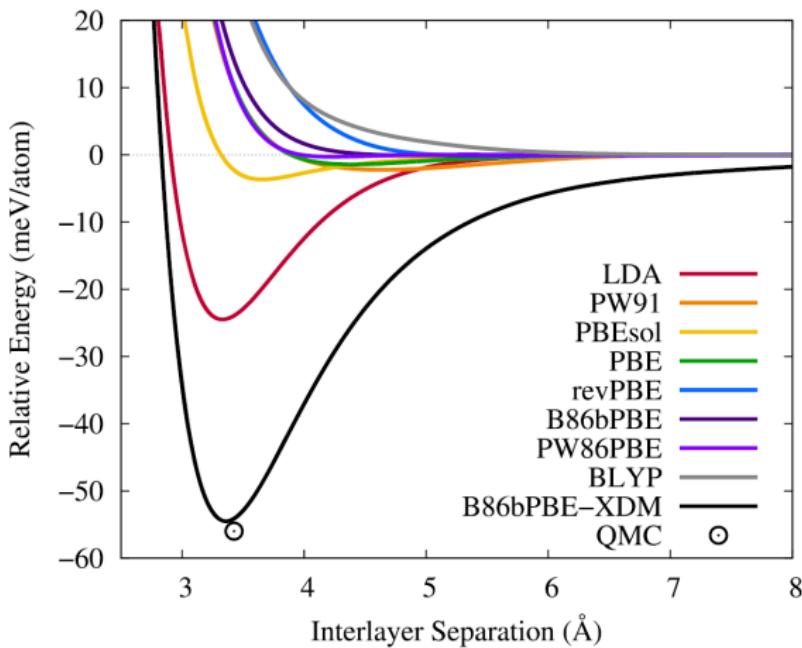
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DISPERSION IN DFT

EXAMPLE: GRAPHITE EXFOLIATION



THE TS MODEL

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

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

where f^{WY} is a Wu-Yang damping function. The heteroatomic dispersion coefficients are obtained from their homoatomic counterparts using the Slater-Kirkwood formula:

$$C_{6,ij}^{\text{TS}} = \frac{2C_{6,ii}C_{6,jj}}{\frac{\alpha_j^0}{\alpha_i^0}C_{6,ii} + \frac{\alpha_i^0}{\alpha_j^0}C_{6,jj}}.$$

In the TS model, 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,

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

Tkatchenko, A. & Scheffler, M. Accurate molecular van der Waals interactions from ground-state electron density and free-atom reference data. *Phys. Rev. Lett.* **102**, 073005. (2009) doi: 10.1103/PhysRevLett.102.073005

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 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, $C_{n,ij}^{\text{XDM}}$.

THE MBD MODEL

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

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

which uses parameters that have been refined through the self-consistent screening (SCS) equation

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

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

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

RESEARCH QUESTIONS

- 1) Does the XDM model implicitly capture many-body effects?

- 2) Can we improve the calculation of the forces in TS and XDM?

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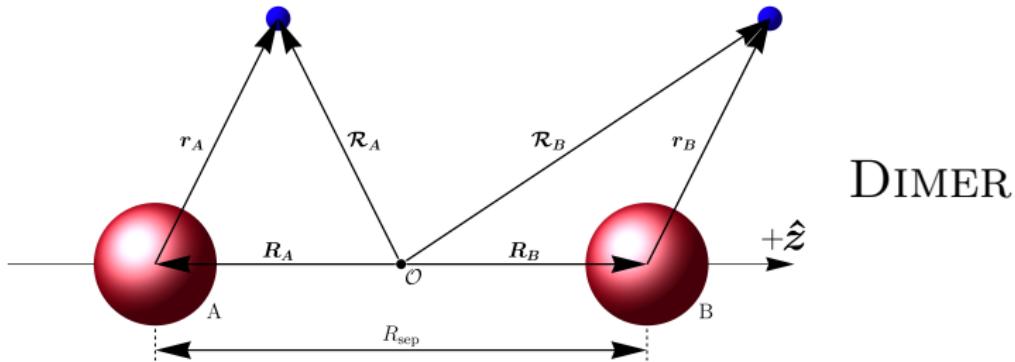
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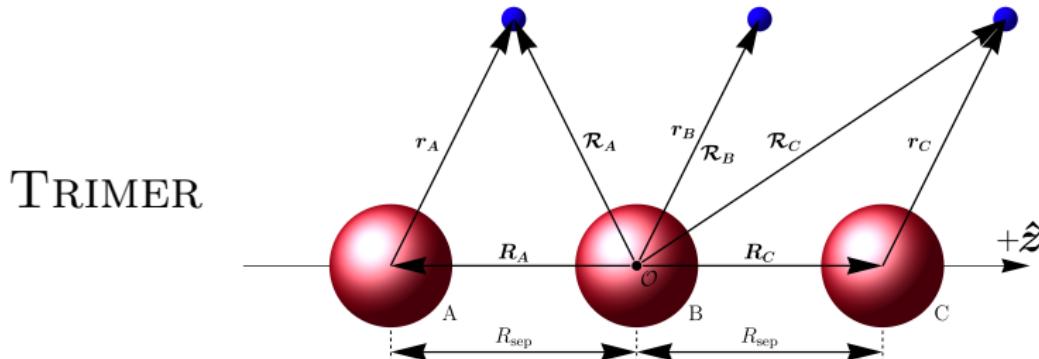
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SYSTEM GEOMETRY



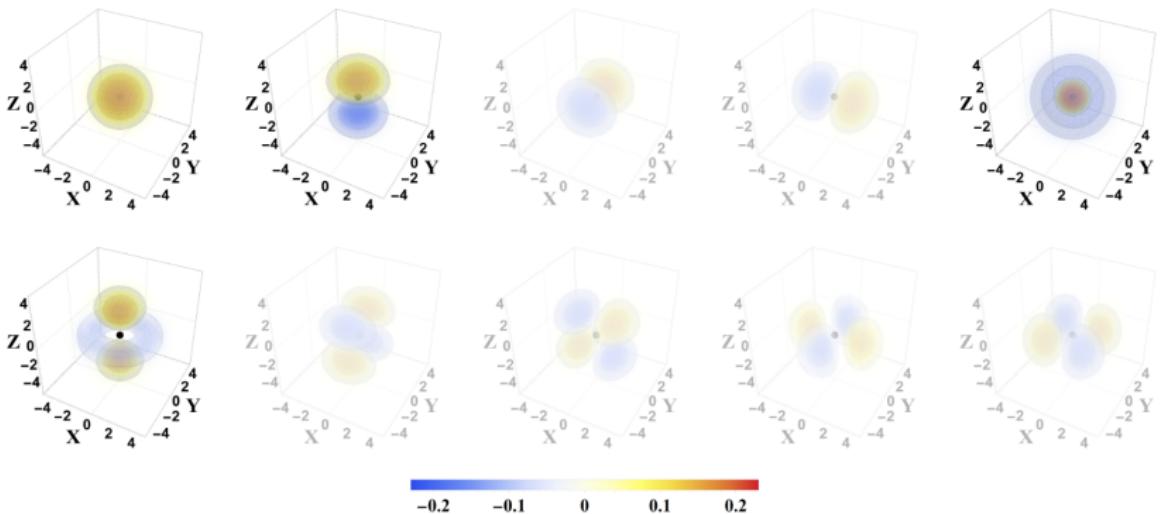
DIMER



TRIMER

HAMILTONIAN AND WAVEFUNCTIONS

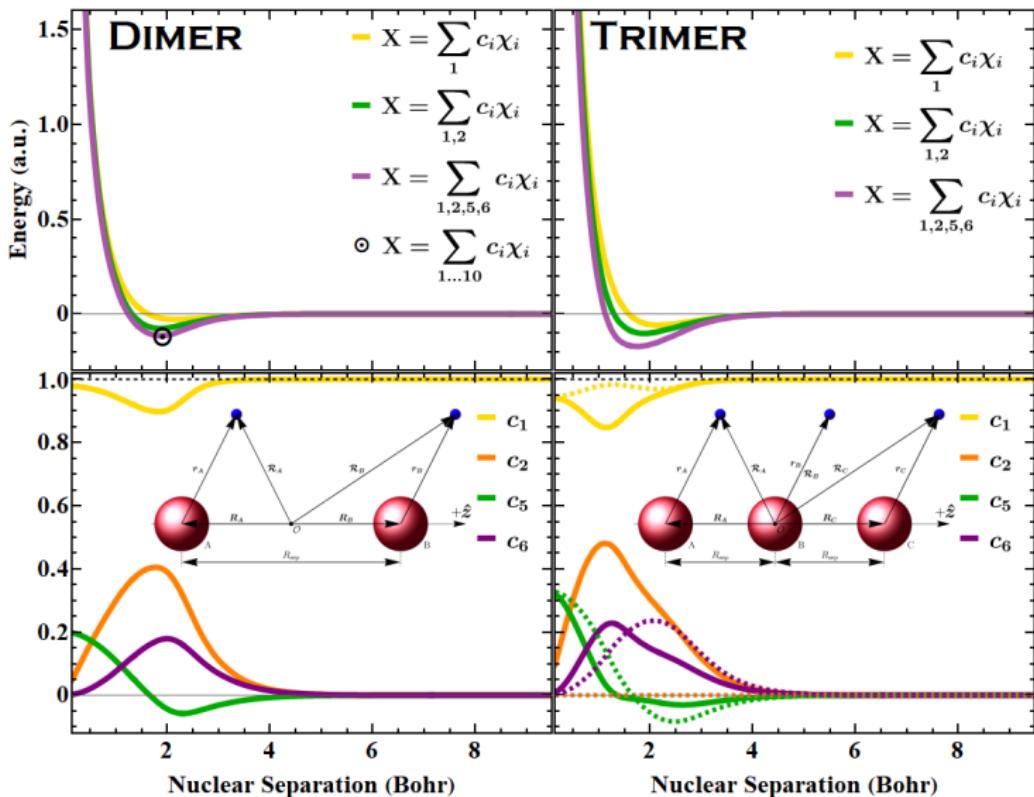
$$\hat{H} = \sum_p \hat{H}_p^{\text{NI}} + \sum_p \sum_{q \neq p} \left(\hat{H}_{pq}^{\text{e-nuc}} + \frac{1}{2} \hat{H}_{pq}^{\text{e-e}} \right) + E_{\text{total}}^{\text{nuc-nuc}}$$



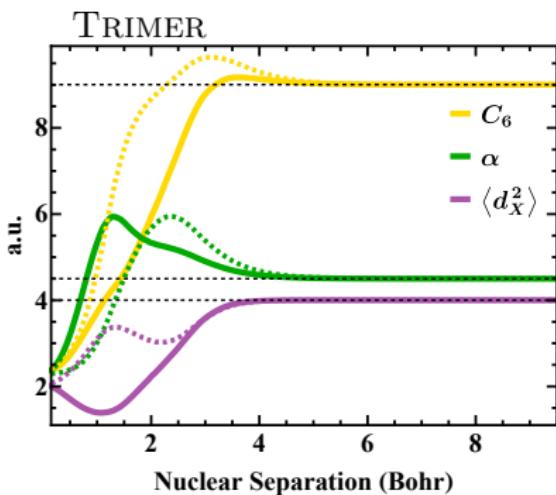
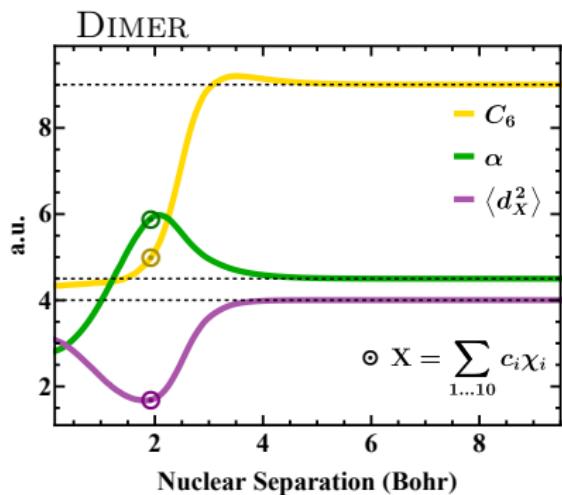
$$\mathbf{X}(\mathbf{r}) = \sum_i c_i \chi_i(\mathbf{r})$$

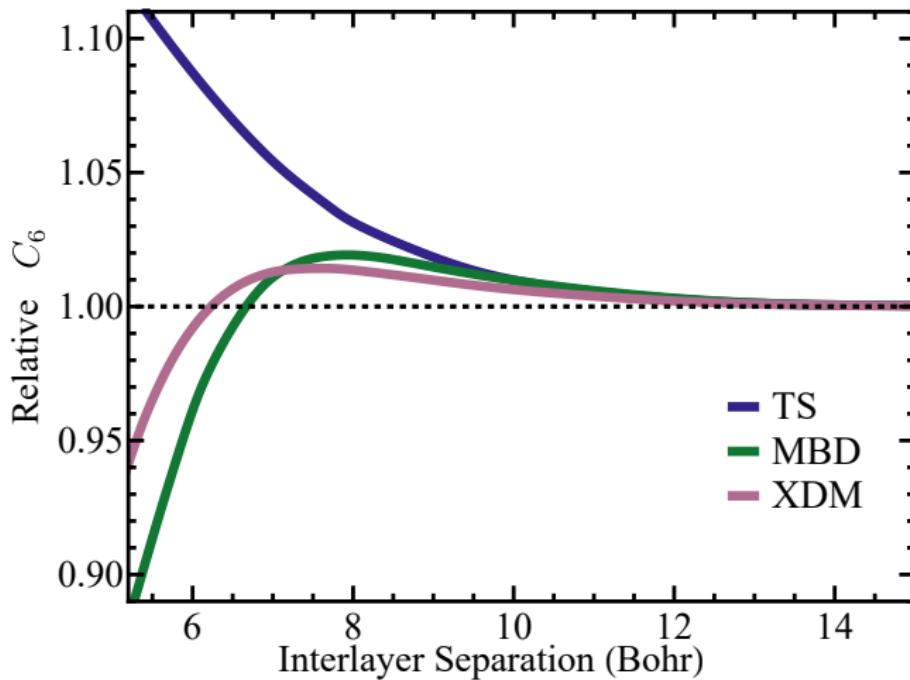
$$\sum_i c_i^2 = 1$$

MINIMIZED ENERGY



CALCULATED XDM PARAMETERS



COMPARISON TO LITERATURE
FOR GRAPHITE EXFOLIATION

Adapted with permission from:

Otero-de-la-Roza, A., LeBlanc, L. M., & Johnson, E. R. Asymptotic pairwise dispersion corrections can describe layered materials accurately, *J. Phys. Chem. Lett.*, **11** 6, 2298–2302. (2020) doi: 10.1021/acs.jpclett.0c00348

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The Issue

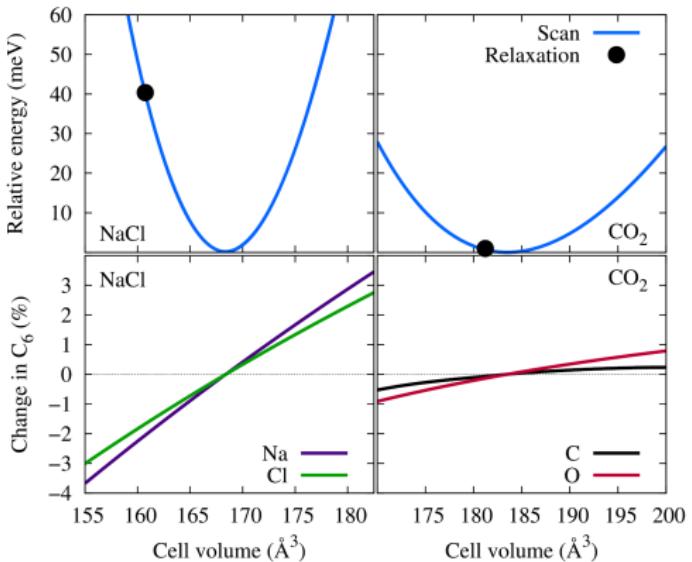
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THE ISSUE



TAKEAWAYS FROM CS8 BENCHMARKING:

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

TS FORCES: CURRENT IMPLEMENTATION

ENERGY:

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

HELLMANN-FEYNMAN FORCE:

$$\mathbf{F}_i^{\text{TS}} = \sum_{\mathbf{L}} \sum_{j'} \left[-6f^{\text{WY}} \frac{C_{6,ij}^{\text{TS}}}{R_{ij,\mathbf{L}}^7} + (f^{\text{WY}})' \frac{C_{6,ij}^{\text{TS}}}{R_{ij,\mathbf{L}}^6} \right] \hat{\mathbf{R}}_{ij,\mathbf{L}}$$

TS FORCES: PROPOSED IMPLEMENTATION

$$\mathbf{F}_i^{\text{TS}} = \sum_{\mathbf{L}} \sum_{j'} \left[-6f^{\text{WY}} \frac{C_{6,ij}^{\text{TS}}}{R_{ij,\mathbf{L}}^7} + (f^{\text{WY}})' \frac{C_{6,ij}^{\text{TS}}}{R_{ij,\mathbf{L}}^6} + f^{\text{WY}} \frac{(C_{6,ij}^{\text{TS}})'}{R_{ij,\mathbf{L}}^6} \right] \hat{\mathbf{R}}_{ij,\mathbf{L}}$$

DERIVATIVE OF f^{WY}

$$f^{\text{WY}}(R_{ij}) = \frac{1}{1 + \exp \left[-d \left(\frac{R_{ij}}{s R_{\text{vdW},ij}} - 1 \right) \right]}$$

$$(f^{\text{WY}})' = \frac{d (R_{\text{vdW},ij} - R_{ij,\mathbf{L}} (R_{\text{vdW},ij})')}{2s R_{\text{vdW},ij}^2} \left(1 + \cosh \left[d \left(\frac{R_{ij,\mathbf{L}}}{s R_{\text{vdW},ij}} \right) - 1 \right] \right)^{-1}$$

TS FORCES: PROPOSED IMPLEMENTATION

$$\mathbf{F}_i^{\text{TS}} = \sum_{\mathbf{L}} \sum_{j'} \left[-6f^{\text{WY}} \frac{C_{6,ij}^{\text{TS}}}{R_{ij,\mathbf{L}}^7} + (f^{\text{WY}})' \frac{C_{6,ij}^{\text{TS}}}{R_{ij,\mathbf{L}}^6} + f^{\text{WY}} \frac{(C_{6,ij}^{\text{TS}})'}{R_{ij,\mathbf{L}}^6} \right] \hat{\mathbf{R}}_{ij,\mathbf{L}}$$

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

$$C_{6,ij}^{\text{TS}} = \frac{2C_{6,ii}C_{6,jj}}{\frac{\alpha_j^0}{\alpha_i^0}C_{6,ii} + \frac{\alpha_i^0}{\alpha_j^0}C_{6,jj}}$$

$$\begin{aligned} (C_{6,ij}^{\text{TS}})' &= \frac{2(C_{6,ii})'C_{6,jj}}{\frac{\alpha_j^0}{\alpha_i^0}C_{6,ii} + \frac{\alpha_i^0}{\alpha_j^0}C_{6,jj}} + \frac{2C_{6,ii}(C_{6,jj})'}{\frac{\alpha_j^0}{\alpha_i^0}C_{6,ii} + \frac{\alpha_i^0}{\alpha_j^0}C_{6,jj}} - \frac{2C_{6,ii}C_{6,jj}}{\left(\frac{\alpha_j^0}{\alpha_i^0}C_{6,ii} + \frac{\alpha_i^0}{\alpha_j^0}C_{6,jj},\right)^2} \times \\ &\left[\frac{\alpha_j^0}{\alpha_i^0}(C_{6,ii})' + \frac{\alpha_i^0}{\alpha_j^0}(C_{6,jj})' + \frac{\alpha_i^0(\alpha_j^0)' - (\alpha_i^0)' \alpha_j^0}{(\alpha_i^0)^2} C_{6,ii} + \frac{(\alpha_i^0)' \alpha_j^0 - \alpha_i^0(\alpha_j^0)'}{(\alpha_i^0)^2} C_{6,jj} \right] \end{aligned}$$

TS FORCES: PROPOSED IMPLEMENTATION

$$\mathbf{F}_i^{\text{TS}} = \sum_{\mathbf{L}} \sum_{j'} \left[-6f^{\text{WY}} \frac{C_{6,ij}^{\text{TS}}}{R_{ij,\mathbf{L}}^7} + (f^{\text{WY}})' \frac{C_{6,ij}^{\text{TS}}}{R_{ij,\mathbf{L}}^6} + f^{\text{WY}} \frac{(C_{6,ij}^{\text{TS}})'}{R_{ij,\mathbf{L}}^6} \right] \hat{\mathbf{R}}_{ij,\mathbf{L}}$$

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

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

$$(C_{6,ii})' = 2 \frac{(v_i)'}{v_i} C_{6,ii} \quad (\alpha_i^0)' = \frac{(v_i)'}{v_i} \alpha_i^0 \quad (R_{\text{vdW},ij})' = R_i^0 + R_j^0 \\ = \frac{1}{3} \left(\frac{(v_i)'}{v_i} R_i^0 + \frac{(v_j)'}{v_j} R_j^0 \right)$$

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

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:

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

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 f^{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 $C_{6,ij}^{\text{XDM}}$

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

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

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

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RESEARCH PROGRESS

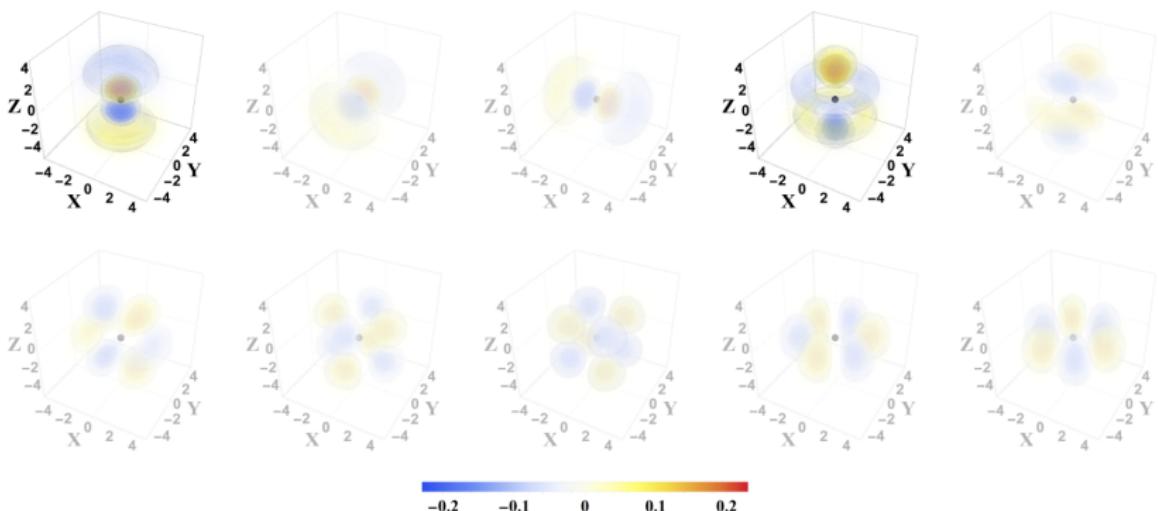
1) Does the XDM model implicitly capture many-body effects?

- ✓ Solved the isotropic quantum harmonic oscillator
- ✓ Created a Mathematica code, batch-runner for efficient computation
- ✓ Modelled a dimer and trimer systems for the first 3 energy states
- ✓ Implemented XDM
- ✗ Test higher-energy wavefunctions
- ✗ Implement a tetramer oscillator system
- ✗ Implement MBD

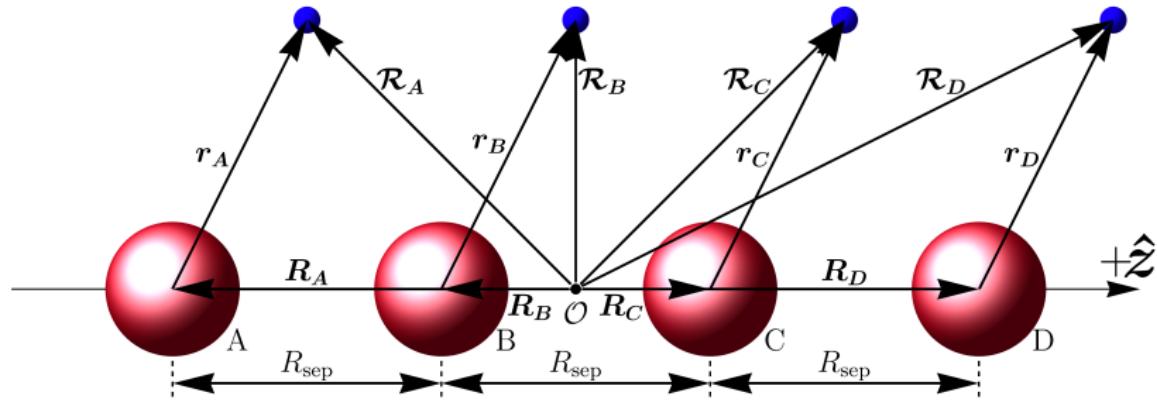
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- ✓ Confirmed the issue is present for both TS and XDM in various codes
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- ✗ Test and benchmark the new implementations

INCLUSION OF HIGHER-ENERGY WAVEFUNCTIONS



TETRAMER OSCILLATOR SYSTEM IMPLEMENTATION



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.

RESEARCH PROGRESS

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IMPLEMENT THE CODE

Easier said than done. Thankfully, there are resources available:

- Otero de la Roza, A., & Johnson, E. R., *Van der Waals interactions in solids using the exchange-hole dipole moment model*, J. Chem. Phys. **136**, 174109 (2012) doi: 10.1063/1.4705760
- Price, A. J., Otero de la Roza, A., & Johnson, E. R., *XDM dispersion with local orbitals: Implementation in the FHlaims package*, Work In Progress (2022).

MAY
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ACENET: Modern Fortran for
scientific programming

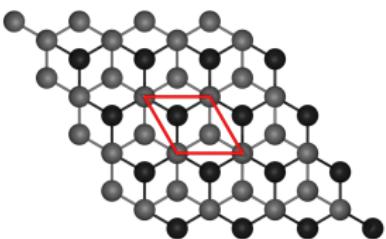
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Free order #2805150499 placed on Mon, Feb 14,
5:08 PM

TESTING AND BENCHMARKING

CS8 BENCHMARK

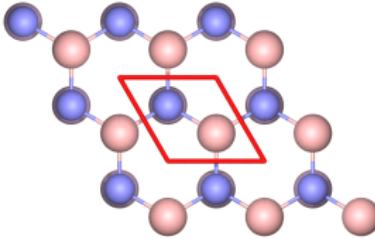
- CO₂
- Diamond
- Si
- GaAs
- Ni
- Cu
- NaCl
- MgO



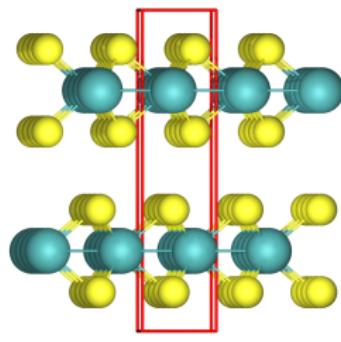
Graphite

LM11 BENCHMARK

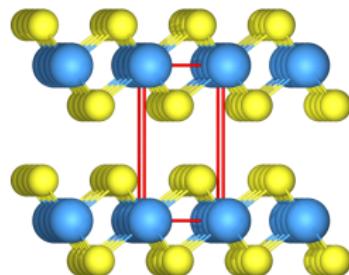
- Graphene
- Boron Nitride
- MoS₂
- MoSe₂
- MoTe₂
- WS₂
- PdTe₂
- TaS₂
- HfS₂
- HfSe₂
- HfTe₂



h-BN



Mo{S,Se,Te}₂, WS₂



TaS₂, HF{S,Se,Ts}₂, PdTe₂

Theory and Background
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Drude Oscillator Project
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Improved Dispersion Forces
ooooo

Proposed Research
oooooooo

Conclusions
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Theory and Background

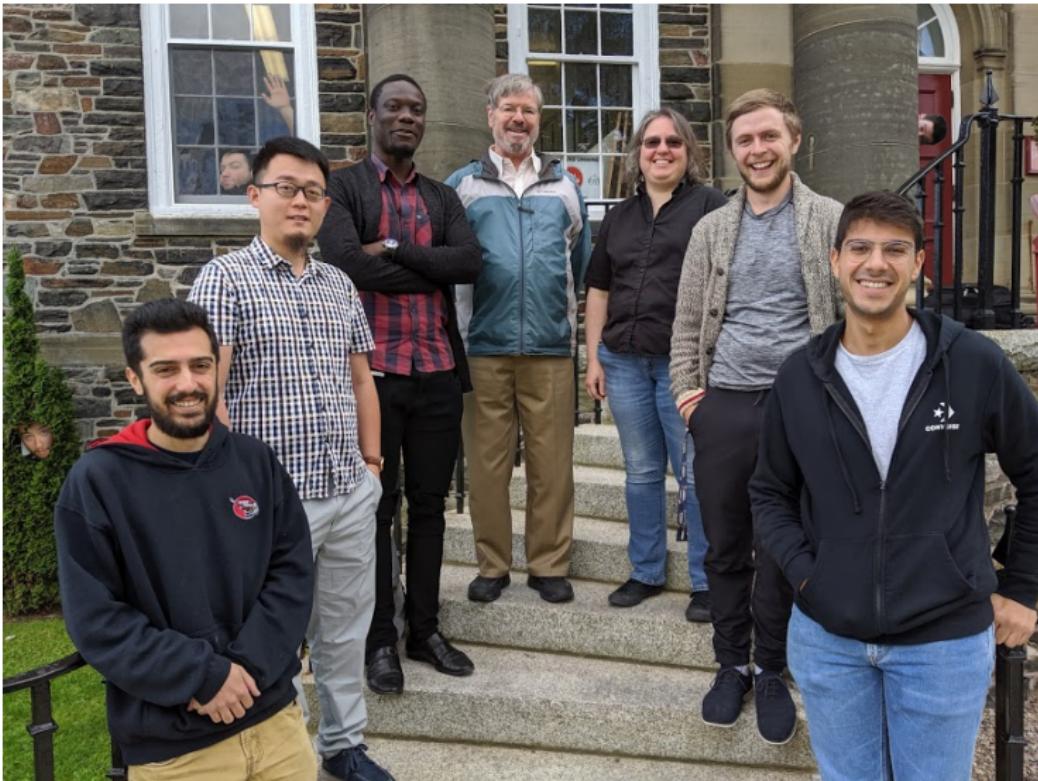
Drude Oscillator Project

Improving Dispersion Forces

Proposed Research

Conclusions

ACKNOWLEDGEMENTS



Theory and Background
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Drude Oscillator Project
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Improved Dispersion Forces
ooooo

Proposed Research
oooooooo

Conclusions
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QUESTIONS?

WANT MY SLIDES?



KYLE.BRYENTON@DAL.CA

APPENDIX

Program Requirements

Intro

Hohenberg-Kohn-Sham DFT

Project 1

Energy Terms

Confinement Potentials

Project 2

Damping Function

CS8 Benchmarking

C_n Derivatives

PROGRAM REQUIREMENTS

COMPLETED SEMINARS

Title	Grade
Seminar 1: Stress Tensors	4.55/5
Seminar 2: DM 2021 Functional	4.75/5
Total:	4.65/5

AWARDS & HONOURS

Award Name	Value
Killam Predoctoral Schol.	\$90,000
Nova Scotia Graduate Schol.	\$50,000
Dalhousie President's Award	\$12,294
W. C. Sumner Memorial Fell.	\$16,400

COMPLETED COURSEWORK

Univ.	Description	CH	Grade
GWPI	Quantum Mechanics	3.0	B+
GWPI	Statistical Mechanics	3.0	B+
GWPI	Solid State Physics	3.0	B
GWPI	Scientific Computing	3.0	A
AARMS	Math. Sci. Chaos	3.0	A
Dal	Theory Chem. Bond.	3.0	A
Dal	Dens.-Funct. Theory	1.5	A+
Dal	Elec. Struct. Theory	1.5	A
Total:			A–

PUBLICATIONS

- 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
- **Bryenton, K. R.**, Adeleke, A. A., Dale, S. G., & Johnson, E. R. Delocalization error: the greatest outstanding challenge in density-functional theory. *Submitted to Wiley Interdiscip. Rev.: Comput. Mol. Sci.* (2022)

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,

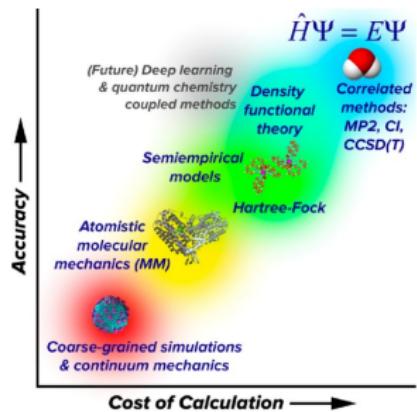
$$E[\rho] = T_s[\rho] + \int v_{\text{ext}}\rho(\mathbf{r})d\mathbf{r} + E_{\text{H}}[\rho] + E_{\text{xc}}[\rho],$$

as a functional of the electron density,

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

for N electrons occupying orbitals $\psi_i(\mathbf{r})$. Forces are calculated via the Hellmann-Feynman theorem

$$\mathbf{F}_r = - \left\langle \frac{\partial \hat{H}}{\partial \mathbf{r}} \right\rangle = - \frac{\partial E}{\partial \mathbf{r}}$$



Borges et al., *Chem. Rev.* **121** 10, 5633–5670. (2021) doi: 10.1021/acs.chemrev.0c00901

WAVEFUNCTIONS

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

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

We take a linear combination of wavefunctions

$$X(\mathbf{r}) = \sum_i c_i \chi_i(\mathbf{r}) \sum_i c_i^2 = 1$$

for use in the dimer and trimer systems of interest.

ENERGY EXPRESSION

$$\hat{H}_{\text{total}} = \sum_p \hat{H}_p^{\text{NI}} + \sum_{pq} \hat{H}_{pq}^{\text{e-nuc}} + \frac{1}{2} \sum_{pq} \hat{H}_{pq}^{\text{e-e}} + E_{\text{total}}^{\text{nuc-nuc}}$$

DIMER AND TRIMER HAMILTONIANS

$$\hat{H}_{\text{dimer}} = \hat{H}_A^{\text{NI}} + \hat{H}_B^{\text{NI}} + \hat{H}_{AB}^{\text{e-nuc}} + \hat{H}_{BA}^{\text{e-nuc}} + \frac{1}{2} (\hat{H}_{AB}^{\text{e-e}} + \hat{H}_{BA}^{\text{e-e}}) + E_{\text{total}}^{\text{nuc-nuc}}$$

$$\begin{aligned} \hat{H}_{\text{trimer}} = & \hat{H}_A^{\text{NI}} + \hat{H}_B^{\text{NI}} + \hat{H}_C^{\text{NI}} \\ & + \hat{H}_{AB}^{\text{e-nuc}} + \hat{H}_{AC}^{\text{e-nuc}} + \hat{H}_{BA}^{\text{e-nuc}} + \hat{H}_{BC}^{\text{e-nuc}} + \hat{H}_{CA}^{\text{e-nuc}} + \hat{H}_{CB}^{\text{e-nuc}} \\ & + \frac{1}{2} (\hat{H}_{AB}^{\text{e-e}} + \hat{H}_{AC}^{\text{e-e}} + \hat{H}_{BA}^{\text{e-e}} + \hat{H}_{BC}^{\text{e-e}} + \hat{H}_{CA}^{\text{e-e}} + \hat{H}_{CB}^{\text{e-e}}) \\ & + E_{\text{total}}^{\text{nuc-nuc}} \end{aligned}$$

ENERGY EXPRESSION

$$\hat{H}_{\text{total}} = \sum_p \hat{H}_p^{\text{NI}} + \sum_{pq} \hat{H}_{pq}^{\text{e-nuc}} + \frac{1}{2} \sum_{pq} \hat{H}_{pq}^{\text{e-e}} + E_{\text{total}}^{\text{nuc-nuc}}$$

NON-INTERACTING COMPONENT

$$\begin{aligned}
 \left\langle \hat{H}_A^{\text{NI}} \right\rangle &= \left\langle \sum_i c_i \chi_{A,i} \left| \hat{H}_A^{\text{NI}} \right| \sum_j c_j \chi_{A,j} \right\rangle \\
 &= \sum_{ij} c_i c_j \delta_{ij} \left\langle \chi_{A,i} \left| -\frac{\hbar^2}{2\mu_A} \nabla_A^2 + \frac{1}{2} \mu_A \omega_A^2 r_A^2 \right| \chi_{A,j} \right\rangle \\
 &= \sum_i c_i^2 \left\langle \chi_{A,i} \left| -\frac{\hbar^2}{2\mu_A} \nabla_A^2 + \frac{1}{2} \mu_A \omega_A^2 r_A^2 \right| \chi_{A,i} \right\rangle
 \end{aligned}$$

ENERGY EXPRESSION

$$\hat{H}_{\text{total}} = \sum_p \hat{H}_p^{\text{NI}} + \sum_{pq} \hat{H}_{pq}^{\text{e-nuc}} + \frac{1}{2} \sum_{pq} \hat{H}_{pq}^{\text{e-e}} + E_{\text{total}}^{\text{nuc-nuc}}$$

ELECTRON-NUCLEAR COMPONENT

$$\begin{aligned}\left\langle \hat{H}_{AB}^{\text{e-nuc}} \right\rangle &= \left\langle \sum_i c_i \chi_{A,i} \left| \hat{H}_{AB}^{\text{e-nuc}} \right| \sum_j c_j \chi_{A,j} \right\rangle \\ &= \sum_{ij} c_i c_j \left\langle \chi_{A,i} \left| \frac{e^2}{4\pi\epsilon_0} \frac{-Z_B}{|\mathcal{R}_A - \mathbf{R}_B|} \right| \chi_{A,j} \right\rangle\end{aligned}$$

ENERGY EXPRESSION

$$\hat{H}_{\text{total}} = \sum_p \hat{H}_p^{\text{NI}} + \sum_{pq} \hat{H}_{pq}^{\text{e-nuc}} + \frac{1}{2} \sum_{pq} \hat{H}_{pq}^{\text{e-e}} + E_{\text{total}}^{\text{nuc-nuc}}$$

ELECTRON-ELECTRON COMPONENT

$$\begin{aligned} \left\langle \hat{H}_{AB}^{\text{e-e}} \right\rangle &= \frac{1}{2} \left\langle \sum_{i_1} c_{i_1} \chi_{A,i_1} \sum_{i_2} d_{i_2} \chi_{B,i_2} \left| \hat{H}_{AB}^{\text{e-e}} \right| \sum_{i_3} c_{i_3} \chi_{A,i_3} \sum_{i_4} d_{i_4} \chi_{B,i_4} \right\rangle \\ &= \frac{1}{2} \sum_{i_1 i_2 i_3 i_4} c_{i_1} d_{i_2} c_{i_3} d_{i_4} \left\langle \chi_{A,i_1} \chi_{B,i_2} \left| \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathcal{R}_A - \mathcal{R}_B|} \right| \chi_{A,i_3} \chi_{B,i_4} \right\rangle \end{aligned}$$

ENERGY EXPRESSION

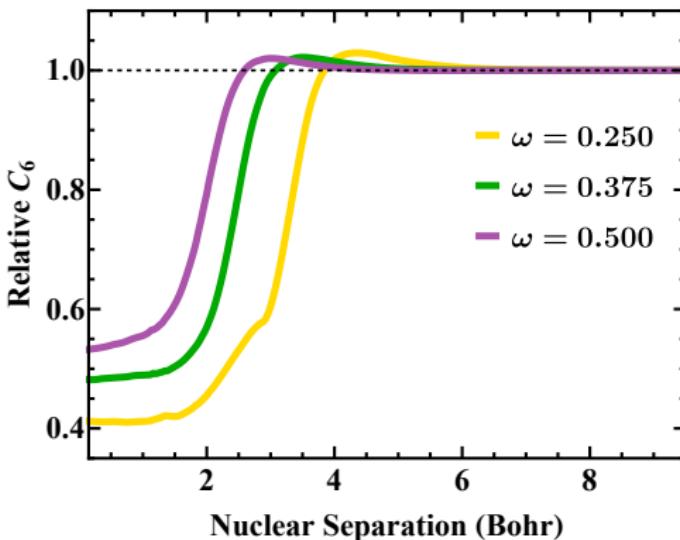
$$\hat{H}_{\text{total}} = \sum_p \hat{H}_p^{\text{NI}} + \sum_{pq} \hat{H}_{pq}^{\text{e-nuc}} + \frac{1}{2} \sum_{pq} \hat{H}_{pq}^{\text{e-e}} + E_{\text{total}}^{\text{nuc-nuc}}$$

NUCLEAR-NUCLEAR COMPONENT

$$E_{\text{total}}^{\text{nuc-nuc}} = \sum_p \sum_{q < p} \frac{e^2}{4\pi\epsilon_0} \frac{Z_p Z_q}{|\mathbf{R}_p - \mathbf{R}_q|}$$

VARYING ω AND CONFINEMENT POTENTIALS

The results above used $\omega = 0.375$ to match hydrogen excitation energy.



A recent study by Kozłowska et al., looked at effects of a confinement potential, $V_{\text{conf}} = \frac{1}{2}\omega_{\text{conf}}^2 r^2$, on intermolecular interactions. Confinement compacts the density, reducing the moment integrals and C_6 coefficient.

VARIATIONAL MINIMIZATION

$$\hat{H} = \sum_p \hat{H}_p^{\text{NI}} + \sum_p \sum_{q \neq p} \left(\hat{H}_{pq}^{\text{e-nuc}} + \frac{1}{2} \hat{H}_{pq}^{\text{e-e}} \right) + E_{\text{total}}^{\text{nuc-nuc}}$$

Minimizing $\langle \hat{H} \rangle$ is a constrained optimization problem, suitable for the method of Lagrange multipliers. The Lagrangian of our two systems are determined by

$$\mathcal{L}(\{c_i\}, \lambda) = \langle \hat{H}_{\text{dimer}} \rangle - \lambda \left(1 - \sum_i c_i^2 \right)$$

$$\mathcal{L}(\{c_i\}, \{d_i\}, \lambda_1, \lambda_2) = \langle \hat{H}_{\text{trimer}} \rangle - \lambda_1 \left(1 - \sum_i c_i^2 \right) - \lambda_2 \left(1 - \sum_i d_i^2 \right)$$

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

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

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

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

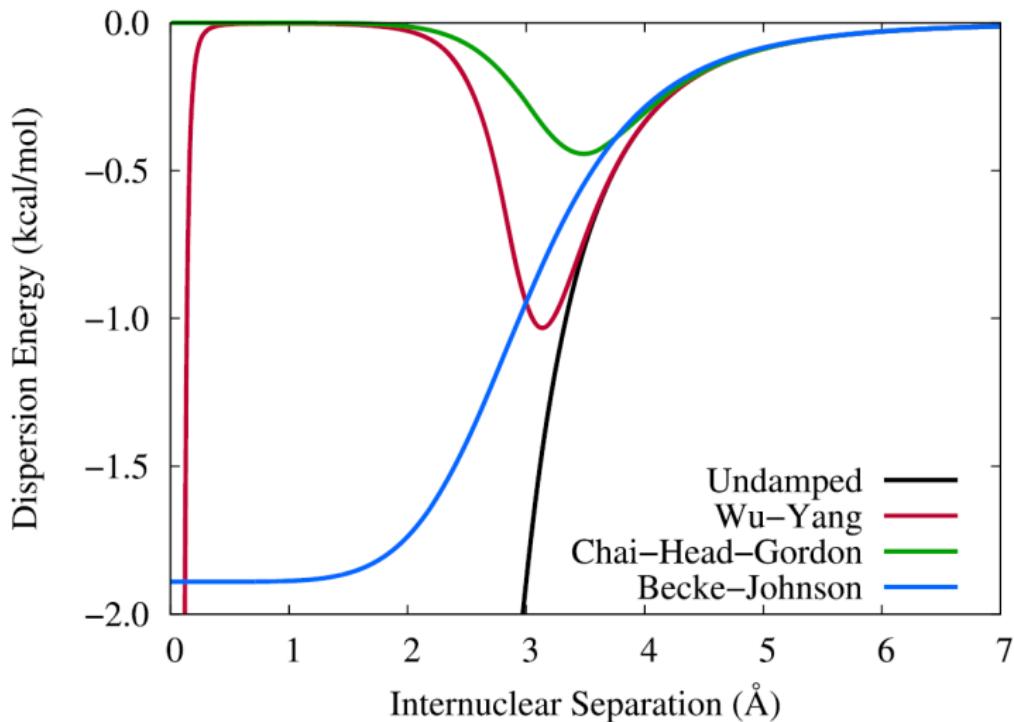
where the TS polarizabilities are

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

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

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

DAMPING FUNCTIONS



CS8 BENCHMARKING

a_{latt}^{\min} : Manual PES scan (Å)

$a_{\text{latt}}^{\text{rel}}$: From VC-relax (Å)

ΔE : VC-relax energy error (eV)

FHI: light basis & PBE

QE: PAW & B86bPBE

Material	TS (FHI)			XDM (FHI)			XDM (QE)		
	a_{latt}^{\min}	$a_{\text{latt}}^{\text{rel}}$	ΔE	a_{latt}^{\min}	$a_{\text{latt}}^{\text{rel}}$	ΔE	a_{latt}^{\min}	$a_{\text{latt}}^{\text{rel}}$	ΔE
CO ₂	5.93	5.93	<.001	5.93	5.93	<.001	5.69	5.66	0.001
Diamond	3.57	3.56	0.008	3.57	3.56	0.002	3.57	3.56	0.009
Si	5.49	5.46	0.007	5.49	5.44	0.011	5.46	5.42	0.020
GaAs	5.71	5.73	0.004	5.71	5.67	0.023	5.71	5.66	0.036
Ni	3.41	3.41	<.001	3.48	3.45	0.016	3.51	3.47	0.034
Cu	3.54	3.54	<.001	3.61	3.56	0.021	3.62	3.58	0.026
NaCl	5.40	5.40	<.001	5.56	5.55	0.007	5.52	5.44	0.040
MgO	4.22	4.20	0.005	4.26	4.22	0.012	4.23	4.19	0.036

TAKEAWAYS:

- 1) The issue is present in both corrections, but to a lesser extent in TS.
- 2) The issue is present in both codes, but to a lesser extent in FHI-aims.

C_6 : At energy min. (a.u.)

$$|\Delta C_6|: \left| C_6^{(-5\%)} - C_6^{(+5\%)} \right|$$

FHI: light basis & PBE

QE: PAW & B86bPBE

Bond	(Material)	TS (FHI)		XDM (FHI)		XDM (QE)	
		C_6	$ \Delta C_6 $	C_6	$ \Delta C_6 $	C_6	$ \Delta C_6 $
C-O	(CO ₂)	19.80	1.2	15.63	2.0	15.10	.17
C-C	(Diamond)	38.55	.96	15.42	3.8	14.16	3.6
Si-Si	(Si)	271.9	6.9	129.1	27.	99.50	24.
Ga-As	(GaAs)	302.1	6.9	184.7	34.	156.5	31.
Ni-Ni	(Ni)	361.7	14.	136.3	26.	112.2	24.
Cu-Cu	(Cu)	295.2	2.5	144.9	30.	105.7	19.
Na-Cl	(NaCl)	220.3	7.4	87.38	12.	75.53	9.5
Mg-O	(MgO)	67.01	.50	25.82	5.8	26.60	5.4

TAKEAWAYS:

- 1) TS's C_6 coefficient is drastically higher than XDM's.
- 2) XDM's coefficients are more sensitive geometry changes.
- 3) XDM's C_6 differs for large atoms when comparing FHI-aims and QE.

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

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

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

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

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

DERIVATIVE OF $C_{8,ij}^{\text{XDM}}$

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

$$\begin{aligned}
 \left(C_{8,ij}^{\text{XDM}} \right)' &= \frac{3}{2} \frac{\alpha_i \alpha_j \left[\langle M_1^2 \rangle_j \langle M_2^2 \rangle'_i + \langle M_1^2 \rangle_i \langle M_2^2 \rangle'_j + \langle M_1^2 \rangle'_i \langle M_2^2 \rangle_j + \langle M_1^2 \rangle'_j \langle M_2^2 \rangle_i \right]}{\alpha_i \langle M_1^2 \rangle_j + \alpha_j \langle M_1^2 \rangle_i} \\
 &+ \frac{3}{2} \frac{\alpha'_i \alpha_j \left[\langle M_1^2 \rangle_j \langle M_2^2 \rangle_i + \langle M_1^2 \rangle_i \langle M_2^2 \rangle_j \right] + \alpha_i \alpha'_j \left[\langle M_1^2 \rangle_j \langle M_2^2 \rangle_i + \langle M_1^2 \rangle_i \langle M_2^2 \rangle_j \right]}{\alpha_i \langle M_1^2 \rangle_j + \alpha_j \langle M_1^2 \rangle_i} \\
 &- \frac{3}{2} \frac{\alpha_i \alpha_j \left[\langle M_1^2 \rangle_j \langle M_2^2 \rangle_i + \langle M_1^2 \rangle_i \langle M_2^2 \rangle_j \right] \left[\alpha_i \langle M_1^2 \rangle'_j + \alpha_j \langle M_1^2 \rangle'_i + \alpha'_i \langle M_1^2 \rangle_j + \alpha'_j \langle M_1^2 \rangle_i \right]}{\left(\alpha_i \langle M_1^2 \rangle_j + \alpha_j \langle M_1^2 \rangle_i \right)^2}
 \end{aligned}$$

DERIVATIVE OF $C_{10,ij}^{\text{XDM}}$

$$\begin{aligned}
 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} \\
 (C_{10,ij}^{\text{XDM}})' &= 2 \frac{\alpha_i \alpha_j \left[\langle M_1^2 \rangle_j \langle M_3^2 \rangle'_i + \langle M_1^2 \rangle_i \langle M_3^2 \rangle'_j + \langle M_1^2 \rangle'_i \langle M_3^2 \rangle_j + \langle M_1^2 \rangle'_j \langle M_3^2 \rangle_i \right]}{\alpha_i \langle M_1^2 \rangle_j + \alpha_j \langle M_1^2 \rangle_i} \\
 &\quad + 2 \frac{\alpha'_i \alpha_j \left[\langle M_1^2 \rangle_j \langle M_3^2 \rangle_i + \langle M_1^2 \rangle_i \langle M_3^2 \rangle_j \right] + \alpha_i \alpha'_j \left[\langle M_1^2 \rangle_j \langle M_3^2 \rangle_i + \langle M_1^2 \rangle_i \langle M_3^2 \rangle_j \right]}{\alpha_i \langle M_1^2 \rangle_j + \alpha_j \langle M_1^2 \rangle_i} \\
 &\quad - 2 \frac{\alpha_i \alpha_j \left[\langle M_1^2 \rangle_j \langle M_3^2 \rangle_i + \langle M_1^2 \rangle_i \langle M_3^2 \rangle_j \right] \left[\alpha_i \langle M_1^2 \rangle'_j + \alpha_j \langle M_1^2 \rangle'_i + \alpha'_i \langle M_1^2 \rangle_j + \alpha'_j \langle M_1^2 \rangle_i \right]}{\left(\alpha_i \langle M_1^2 \rangle_j + \alpha_j \langle M_1^2 \rangle_i \right)^2} \\
 &\quad + \frac{21}{5} \frac{\alpha_i \alpha_j \left[\alpha_i \langle M_1^2 \rangle_j + \alpha_j \langle M_1^2 \rangle_i \right] \left[\langle M_2^2 \rangle_i \langle M_2^2 \rangle'_j + \langle M_2^2 \rangle_j \langle M_2^2 \rangle'_i \right]}{\left(\alpha_i \langle M_1^2 \rangle_j + \alpha_j \langle M_1^2 \rangle_i \right)^2} \\
 &\quad - \frac{21}{5} \frac{\langle M_2^2 \rangle_i \langle M_2^2 \rangle_j \left[\alpha_i \alpha_j^2 \langle M_1^2 \rangle'_i + \alpha_i^2 \alpha_j \langle M_1^2 \rangle'_j - \alpha'_i \alpha_j^2 \langle M_1^2 \rangle_i - \alpha_i^2 \alpha'_j \langle M_1^2 \rangle_j \right]}{\left(\alpha_i \langle M_1^2 \rangle_j + \alpha_j \langle M_1^2 \rangle_i \right)^2}.
 \end{aligned}$$