



COMMITTEE MEETING III



Kyle R. Bryenton
Dalhousie Department of Physics & Atmospheric Science
October 22, 2024

PART 1: PROGRESS REPORT

Program Requirements

- Seminars, Courses, and Conferences
- Publications

Projects

- Completed Projects
- Manuscripts in Preparation

Future Work

- Six-Month Research Plan
- The Forces Project

Program Requirements

Seminars, Courses, and Conferences

Publications

Projects

Future Work

SEMINARS, COURSES, AND CONFERENCES

GRADUATE SEMINARS: COMPLETED

COURSES: COMPLETED

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
5. CHEM6360: Kinetics & Catalysis – AUD

CONFERENCES: [NEW: 5-7]

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, GER) Aug 2023
5. Sanibel Symposium (St. Augustine, FL) Feb 2024
6. CCSTC (Halifax, NS) Jul 2024
7. UPEI Seminar (Charlottetown, PE) Aug 2024

PUBLICATIONS

PUBLICATIONS: [NEW: 5-6]

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 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*. *J. Phys. Chem. A*, 127(41), 8712. (2023) doi: 10.1021/acs.jpca.3c04332
6. Ambrosetti, A., **Bryenton, K. R.**, Johnson, E. R., Tkatchenko, A., et al. *Density-Functional Based Methods for Dispersion Interactions*, Submitted to IOP Electronic Structure (2024)

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Projects

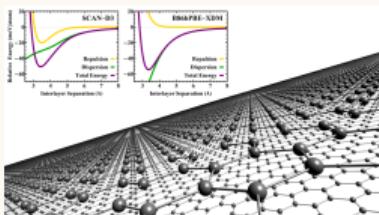
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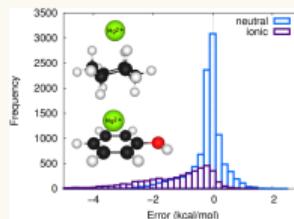
COMPLETED PROJECTS

Requirements for an Accurate Disp.-Corr. Functional



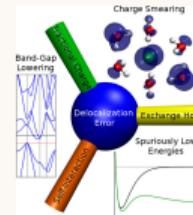
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Comparison of DFT Disp. Corrections on DES15K



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Delocalization Error: Greatest Outstanding Challenge



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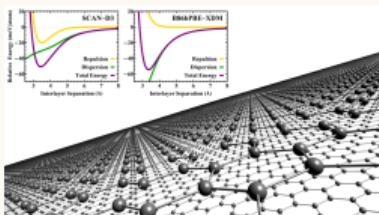
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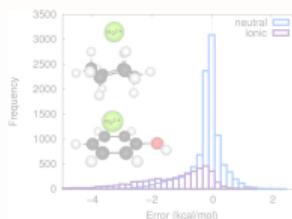
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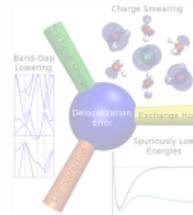
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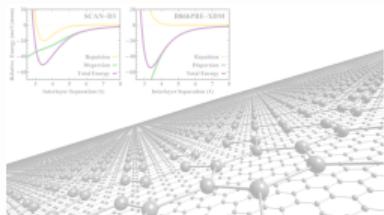
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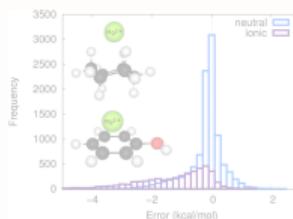
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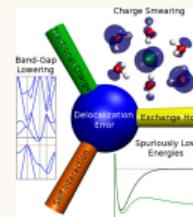
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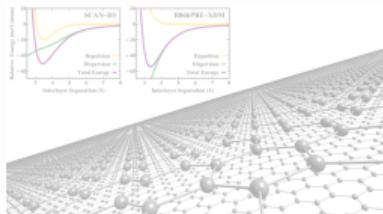
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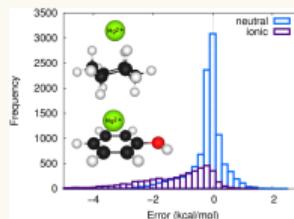
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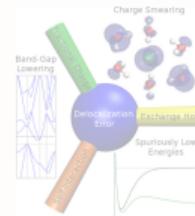
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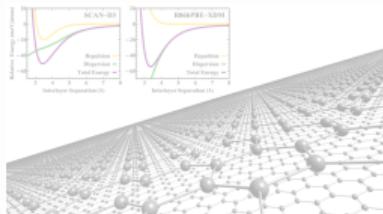
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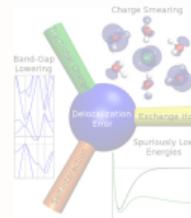
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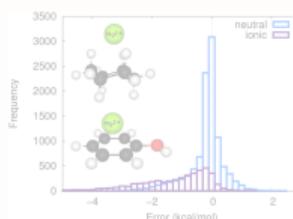
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MANUSCRIPTS IN PREPARATION

XDM Improvements, Tutorial, and FHI-aims Roadmap



Ambrosetti, A., Bryenton, K. R., Johnson, E. R., Tkatchenko, A., et al. Submitted to IOP Electronic Structure (2024)

New Damping Function, Local Hybrids, & GMTKN55

$$\begin{aligned} E_{\text{damp}}^{\text{XDM}} = - \sum_{j>i} \left(\frac{C_{6,ij}}{(3\zeta C_{6,ij}/Z_j^{\text{sum}}) + R_{ij}^6} + \frac{C_{8,ij}}{(3\zeta C_{8,ij}/Z_j^{\text{sum}}) + R_{ij}^8} \right. \\ \left. + \frac{C_{10,ij}}{(3\zeta C_{10,ij}/Z_j^{\text{sum}}) + R_{ij}^{10}} \right), \quad (12) \end{aligned}$$

where the damped contribution from the pair ij at $R_0 = 0$ is $-Z_j^{\text{sum}}/\zeta$ and $Z_j^{\text{sum}} = Z_i + Z_j$ is the sum of the atomic numbers of atoms i and j . As in Eq. (11), each of the $C_{6,ij}$, $C_{8,ij}$, and $C_{10,ij}$ terms is assumed to contribute an equal third to this limit. This scheme has only one nonlinear parameter ζ . Based on GMTKN55 tests, we adopt the value $\zeta = 20\,000$ in atomic units.

Boyer, N., Bryenton, K. R., Johnson, E. R., & Blum, V. Manuscript in Preparation (2024)

B86bPBE0-XDM, PBE0-XDM, and Ne@C70

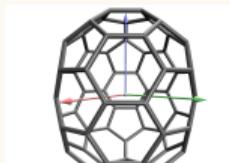
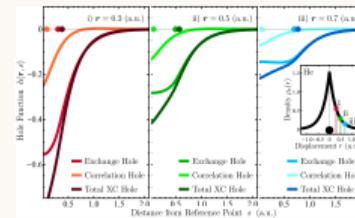


FIG. 1: Orientation of Cartesian x, y, z axes as the red, green and blue arrows within the icosahedron C_{70} cage.

Panchagnula, K., Graf, D., Bryenton, K. R., Johnson, E. R. & Thom, A. J. W. Manuscript in Preparation (2024)

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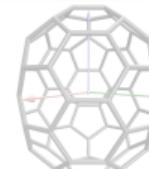
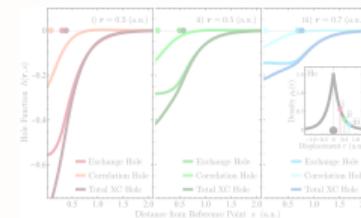


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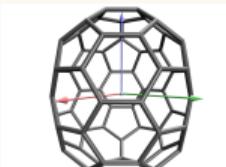
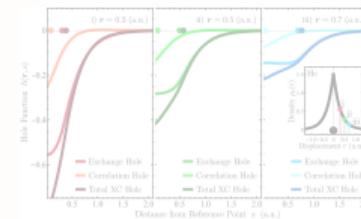


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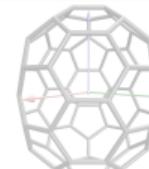
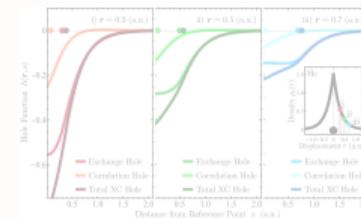


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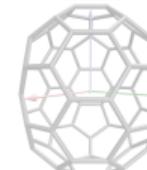
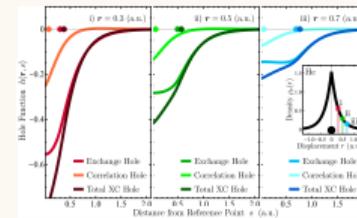


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Future Work
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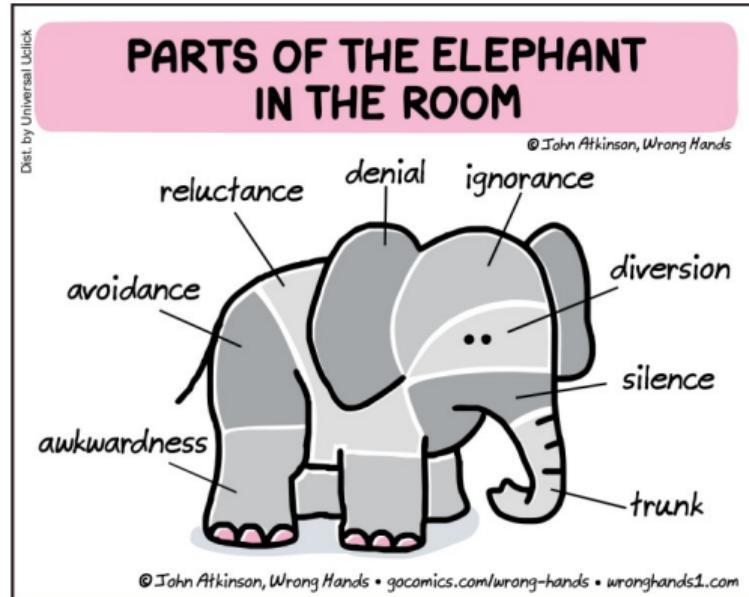
Six-Month Research Plan

The Forces Project

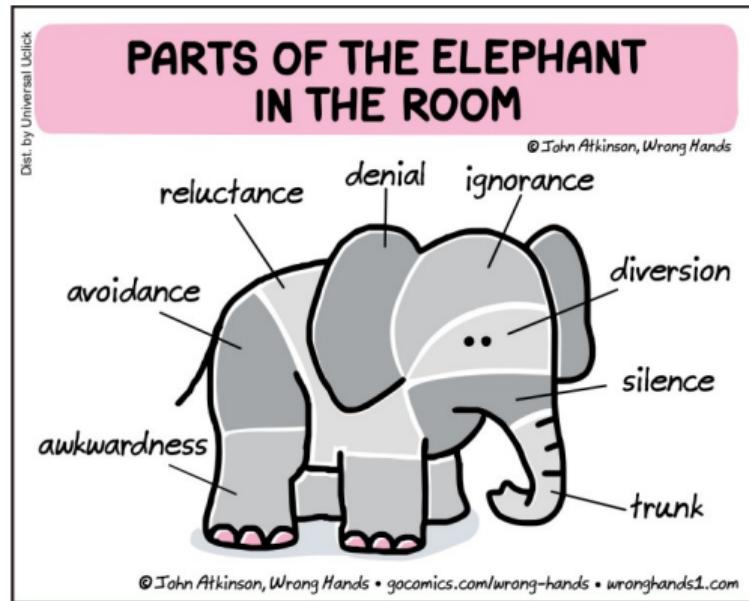
SIX-MONTH RESEARCH PLAN

1. Complete my contribution to the Ne@C70 manuscript
2. Implement Becke's new one-parameter damping function for XDM
Test XDM's new damping function with local hybrids on GMTKN55
3. Complete XCDM project
4. Thesis draft by March 2025
5. Defend in time for spring convocation

THE FORCES PROJECT



THE FORCES PROJECT



- FHI-aims' implementation of the Hirshfeld weight derivatives is broken and has never worked
- The developer that implemented it now works at Microsoft
- We are reaching out to this developer to see if they will be willing to help us
- In the meantime, we've had requests to implement in both Quantum ESPRESSO and CASTEP

PART 2: CSTCC2024 TALK – XCDM

Dispersion and XDM

What is Dispersion?

XDM: The Exchange-hole Dipole Moment Model

Motivation

Implementation

Short-Range Dynamical Correlation Models

Plots of the Exchange-Correlation Hole

Results

Benchmark Sets

Qualitative Results and Observations

Conclusions

Dispersion and XDM

What is Dispersion?

XDM: The Exchange-hole Dipole Moment Model

Motivation

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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

THE XDM MODEL

The exchange-hole dipole moment (XDM) model calculates the dispersion energy via a pairwise sum over all atoms,

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

Here, $f_n^{\text{BJ}}(R_{ij})$ is the Becke-Johnson damping function to prevent divergence at small interatomic separations, R_{ij} . The XDM model calculates the dispersion coefficients, C_n , using exchange-hole dipole moments,

$$d_{X\sigma}(\mathbf{r}) = \left[\int h_{X\sigma}(\mathbf{r}, \mathbf{s}) s d\mathbf{s} \right] - \mathbf{r},$$

which are obtained by integrating the exchange hole, $h_{X\sigma}$, over its reference point, \mathbf{s} .

These exchange-hole dipole moments are used along with Hirshfeld weights, w_i , and the electron density, ρ_σ , to compute the multipole moment integrals,

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

These are then combined with atom-in-molecule polarizabilities, α_i , to solve for the heteroatomic dispersion coefficients,

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

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

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

MOTIVATION

"Why does XDM only use the exchange hole and not the exchange-correlation hole?"

REASONS:

1. The contribution from exchange dominates over correlation
2. XDM uses the BR-hole, which partially models non-dynamical correlation
3. The contribution from dynamical correlation has been shown to be small

... Though, it'd be nice to properly include dynamical correlation.

WHAT WE'VE DONE:

1. Derived same- and opposite-spin correlation hole models
2. Integrated them into XDM in the FHI-aims code
3. Extensive Benchmarking

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Dispersion and XDM
oooo

Implementation
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Results
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Conclusions
ooo

Dispersion and XDM

Implementation

- Short-Range Dynamical Correlation Models
- Plots of the Exchange-Correlation Hole

Results

Conclusions

SHORT-RANGE DYNAMICAL CORRELATION MODELS

We can simply expand the hole term from the previous slide to include terms for the same- and opposite-spin dynamical correlation holes

$$d_{XC\sigma}(\mathbf{r}) = \left[\int h_{XC}(\mathbf{r}, \mathbf{s}) s d\mathbf{s} \right] - \mathbf{r} = \left[\int \left(h_{X\sigma}(\mathbf{r}, \mathbf{s}) + h_{C\sigma}^{\sigma\sigma}(\mathbf{r}, \mathbf{s}) + h_{C\sigma}^{\alpha\beta}(\mathbf{r}, \mathbf{s}) \right) s d\mathbf{s} \right] - \mathbf{r}.$$

$h_{X\sigma}$ is currently captured via the framework of the BR hole, which we can leverage to capture $d_{XC\sigma}$. Becke proposed analogous models for the same- and opposite-spin dynamical correlation holes of the form

$$h_{C\sigma}^{\sigma\sigma}(\mathbf{r}, \mathbf{s}) = \frac{s^2 (s - z_{\sigma\sigma}) D_\sigma(\mathbf{r})}{3(2 + z_{\sigma\sigma})} f(\gamma_{\sigma\sigma} s) \quad h_{C\sigma}^{\alpha\beta}(\mathbf{r}, \mathbf{s}) = \frac{(s - z_{\alpha\beta}) \rho_\sigma(\mathbf{r})}{1 + z_{\alpha\beta}} f(\gamma_{\alpha\beta} s),$$

where z is the spin-dependent correlation length, $D_\sigma = \tau_\sigma - \tau_\sigma^W$ is the difference between the exact kinetic-energy density and the von Weizsäker approximation, and $f(\gamma s)$ is a function that serves to normalize these correlation holes to 0 electrons.

Becke, A. D., *J. Chem. Phys.* **88**, 2, 1053–1062 (1988) doi: 10.1063/1.454274

Becke, A. D., *Int. J. Quantum Chem.* **52**, S28, 625–632 (1994) doi: 10.1002/qua.560620855

Becke proposed three forms for the normalization function

$$f(\gamma s) = \begin{cases} \operatorname{sech}(\gamma s) \\ (1 + \gamma s) e^{-\gamma s} \\ e^{-(\gamma s)^2} \end{cases} .$$

Spherical integration of these correlation hole models lead to the following expressions for the same- and opposite-spin correlation hole dipole moments,

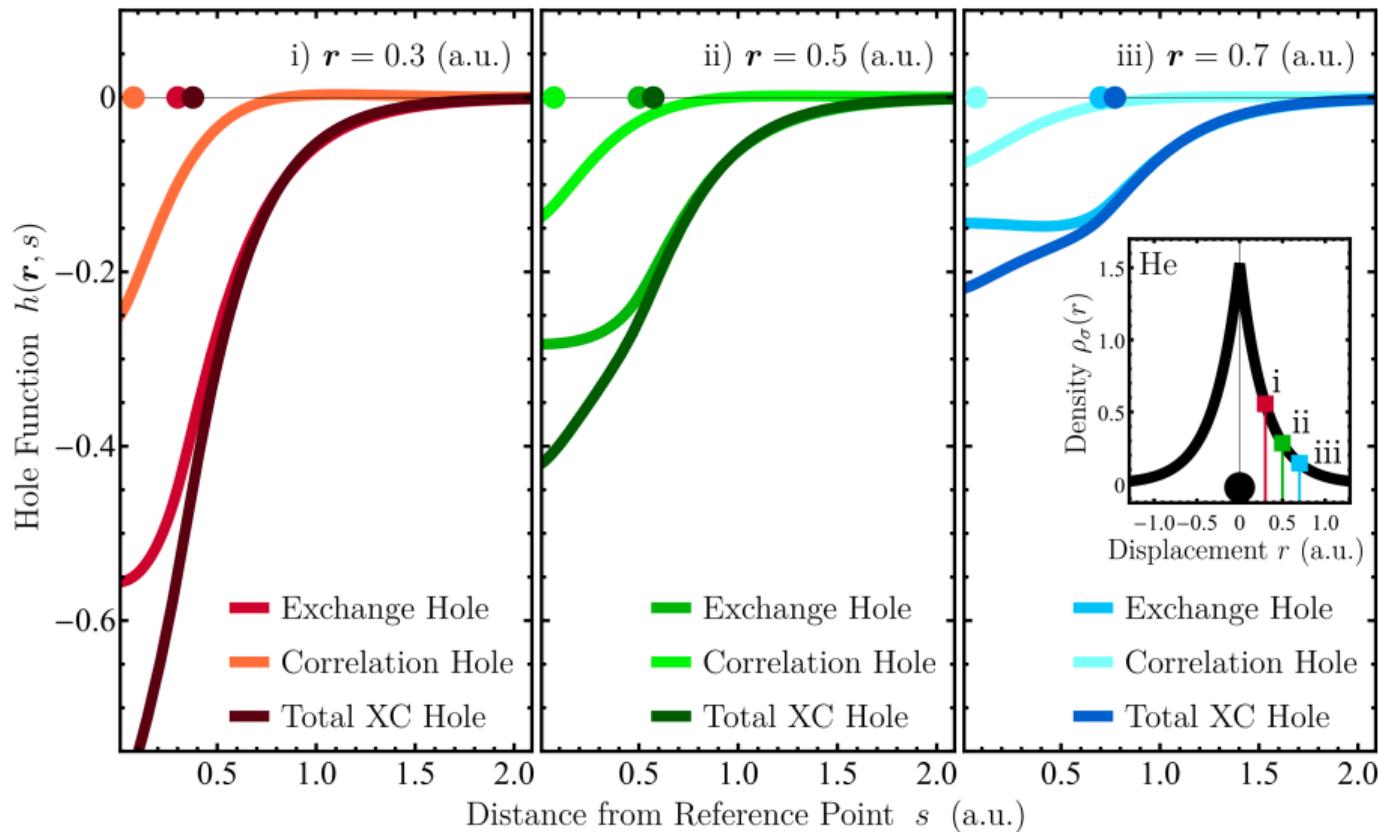
$$d_{C\sigma}^{\sigma\sigma}(\mathbf{r}) = \left[\int h_C^{\sigma\sigma}(\mathbf{r}, \mathbf{s}) s d\mathbf{s} \right] - \mathbf{r} = \frac{c_{\sigma\sigma} z_{\sigma\sigma}^7}{2 + z_{\sigma\sigma}} D_\sigma(\mathbf{r}) - \mathbf{r} ,$$

$$d_{C\sigma}^{\alpha\beta}(\mathbf{r}) = \left[\int h_C^{\alpha\beta}(\mathbf{r}, \mathbf{s}) s d\mathbf{s} \right] - \mathbf{r} = \frac{c_{\alpha\beta} z_{\alpha\beta}^5}{1 + z_{\alpha\beta}} \rho_\sigma(\mathbf{r}) - \mathbf{r} .$$

Here, $c_{\sigma\sigma} \approx 0.02$ and $c_{\alpha\beta} \approx 0.6$; the exact value depends on the chosen form of $f(\gamma s)$. Now, our description of the exchange-correlation-hole dipole moment is complete:

$$d_{XC\sigma}(\mathbf{r}) = \left[\int h_{X\sigma}(\mathbf{r}, \mathbf{s}) s d\mathbf{s} + \frac{c_{\sigma\sigma} z_{\sigma\sigma}^7}{2 + z_{\sigma\sigma}} D_\sigma(\mathbf{r}) + \frac{c_{\alpha\beta} z_{\alpha\beta}^5}{1 + z_{\alpha\beta}} \rho_\sigma(\mathbf{r}) \right] - \mathbf{r} .$$

PLOTS OF THE EXCHANGE-CORRELATION HOLE



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oooo

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Results
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Conclusions
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Dispersion and XDM

Implementation

Results

Benchmark Sets

Qualitative Results and Observations

Conclusions

BENCHMARKING

Basis Sets:

- Light
- LightDense
- Intermediate
- Tight

Functionals:

- B86bPBE
- B86bPBE-25
- B86bPBE-50
- PBE
- PBE0
- PBE-50
- HSE06

XCDM is currently implemented into a private version of the FHI-aims code.

Benchmarks:

- | | |
|------------|--|
| • KB49 | – Intermolecular Complexes |
| • MolC6 | – Molecular C_6 Coefficients |
| • S22×5 | – Small Molecular Dimers & Non-Eq. Geoms |
| • S66×8 | – Small Molecular Dimers & Non-Eq. Geoms |
| • 3B-69 | – Small Molecular Trimers |
| • Heavy28 | – Complexes with Heavy Atom Hydrides |
| • L7 | – Large Molecular Complexes |
| • S6L | – Large Molecular Complexes |
| • X23 | – Molecular Crystals |
| • Ice13 | – Ice Crystal Phases |
| • HalCrys4 | – Halogen Crystals |
| • LM26 | – Layered Materials |

QUALITATIVE RESULTS AND OBSERVATIONS

XCDM compared to XDM: Mean Absolute Error % Change

Benchmark	MAE Chg.	Description
KB49	↓ 1%	Intermolecular Complexes
MolC6	↓ 15%	Molecular C_6 Coefficients
S22×5	~	Small Molecular Dimers & Non-Eq. Geoms
S66×8	~	Small Molecular Dimers & Non-Eq. Geoms
3B-69	↓ 2%	Small Molecular Trimers
Heavy28	↓ 3%	Complexes with Heavy Atom Hydrides
L7	↓ 2%	Large Molecular Complexes
S6L	↓ 10%	Large Molecular Complexes
X23	↓ 5%	Molecular Crystals
Ice13	~	Ice Crystal Phases
HalCrys4	↑ 1%	Halogen Crystals
LM26	↑ 5%	Layered Materials

Observations:

- Our previous conjecture that dynamical correlation doesn't matter much was generally correct
- MolC6's improvement shows we're accurately modelling the physics
- XCDM typically captures an additional 0.02-0.10 kcal/mol binding energy
- If XDM overbinds, XCDM often (but not always) compounds the error

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KEY TAKEAWAYS

1. For small molecular systems, XDM and XCDM perform about equivalently
2. For large molecular systems or crystal structure prediction, use XCDM for increased accuracy
3. For layered materials, systems with large delocalization error, or other systems where XDM overbinds, using XCDM might worsen the error

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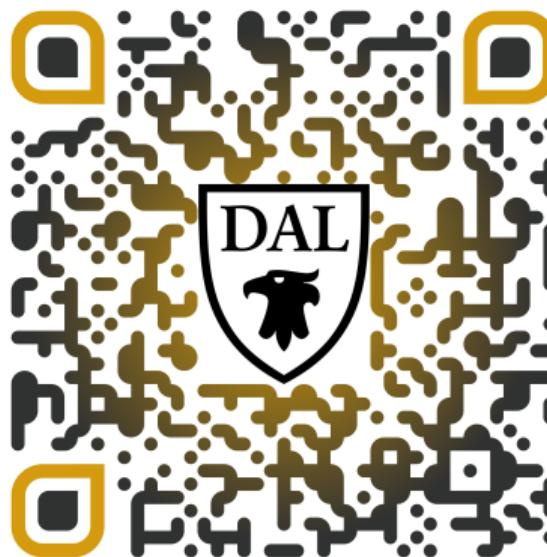
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- Government of Nova Scotia
- Dalhousie University
- Digital Research Alliance of Canada
- ACENET
- FHI-aims

QUESTIONS?

WANT MY SLIDES?



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

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SIX-MONTH RESEARCH PLAN

SIX-MONTH RESEARCH PLAN

1. Complete my contribution to the Ne@C70 manuscript
2. Implement Becke's new one-parameter damping function for XDM
Test XDM's new damping function with local hybrids on GMTKN55
3. Complete XCDM project
4. Thesis draft by March 2025
5. Defend in time for spring convocation

ADDITIONAL PROJECTS (TIME PERMITTING)

1. Complete XDM forces implementation in FHI-aims / Quantum ESPRESSO / CASTEP
2. Test MBD-NL's polarizability functional in XDM
3. Test K_2Se_x system with XDM, TS predicted nuclear fusion due to overbinding