# XCDM

## THE EXCHANGE-CORRELATION-HOLE
## DIPOLE MOMENT MODEL

Kyle R. Bryenton

Dalhousie Department of Physics & Atmospheric Science

CSTCC 2024 – July 22, 2024

Dispersion and XDM
OOOO

Implementation
OOO

Results
OO

Conclusions
OOO

## 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
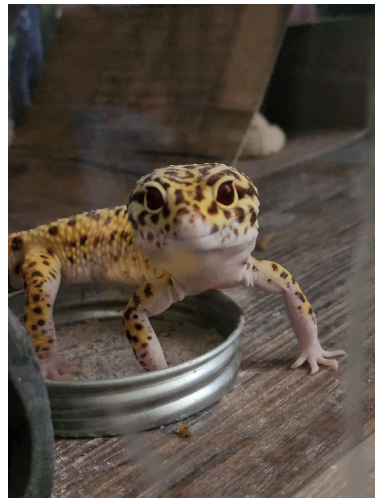


Scamper the Gecko

## THE XDM MODEL

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

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

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

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

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

Becke, A. D. & Johnson, E. R. *J. Chem. Phys.* **127**, 154108. (2007) doi: 10.1063/1.2795701

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

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

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

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

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

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

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.

THE PLAN:
1. Derive same- and opposite-spin correlation hole models
2. Integrate them into XDM in the FHI-aims code
3. Benchmark the results

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.

THE PLAN:
1. Derive same- and opposite-spin correlation hole models
2. Integrate them into XDM in the FHI-aims code
3. Benchmark the results

Dispersion and XDM
OOOO

Implementation
OOO

Results
OO

Conclusions
OOO

Dispersion and XDM
0000

Implementation
●○○

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

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

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

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

where $z$ is the spin-dependent correlation length, $D_\sigma = \tau_\sigma - \tau_\sigma^{\text{W}}$ 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

Dispersion and XDM
0000

Implementation
○●○

Results
○○

Conclusions
○○○

Becke proposed three forms for the normalization function

$$f(\gamma s) = \left\{ \begin{array}{l} \text{sech}(\gamma s) \\ (1 + \gamma s)\,e^{-\gamma s} \\ e^{-(\gamma s)^2} \end{array} \right. .$$

Spherical integration of these correlation hole models lead to the following expressions for the same- and opposite-spin correlation hole dipole moments,
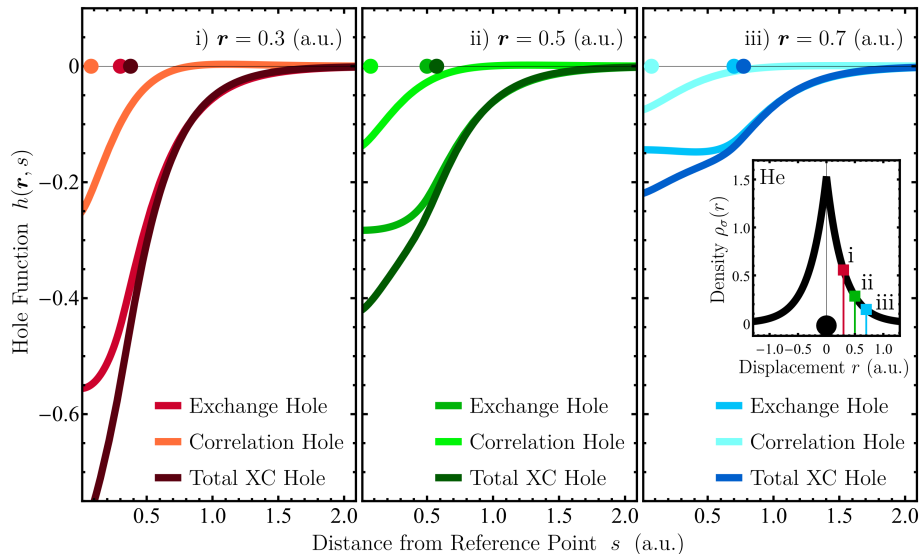
$$d_{C\sigma}^{\sigma\sigma}(\boldsymbol{r}) = \left[ \int h_C^{\sigma\sigma}(\boldsymbol{r}, \boldsymbol{s})\, s\, \mathrm{d}\boldsymbol{s} \right] - \boldsymbol{r} = \frac{c_{\sigma\sigma}\, z_{\sigma\sigma}^7}{2 + z_{\sigma\sigma}} D_\sigma(\boldsymbol{r}) - \boldsymbol{r}\,,$$

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

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:

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

Dispersion and XDM
oooo

Implementation
oo●

Results
oo

Conclusions
ooo

## Plots of the Exchange-Correlation Hole

Dispersion and XDM
OOOO

Implementation
OOO

**Results**
OO

Conclusions
OOO

Dispersion and XDM

Implementation

**Results**
    Benchmark Sets
    Qualitative Results and Observations

Conclusions

Dispersion and XDM
○○○○

Implementation
○○○

Results
●○

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

Dispersion and XDM
○○○○

Implementation
○○○

Results
○●

Conclusions
○○○

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 overbinds and compounds the error

Dispersion and XDM
ooooo

Implementation
ooo

Results
oo

Conclusions
ooo

Dispersion and XDM
0000

Implementation
000

Results
00

Conclusions
●00

KEY TAKEAWAYS

1. For small molecular systems, XDM and XCDM perform equivalently

2. For large molecular systems or crystal structure prediction, use XCDM for the increased accuracy

3. For layered materials or systems with large delocalization error, XDM tends to overbind rather than underbind, so XCDM will likely worsen the error

Dispersion and XDM
oooo

Implementation
ooo

Results
oo

Conclusions
o●o

# Acknowledgements



The Johnson Group:
- Prof. Erin Johnson
- Adrian Rumson
- Cameron Nickerson
- Grace Sparrow

Funding and Resources:
- Mary M. Werner Foundation
- Killam Trusts
- Walter C. Sumner Foundation
- Government of Nova Scotia
- Dalhousie University
- Digital Research Alliance of Canada
- ACENET
- FHI-aims

Dispersion and XDM
○○○○

Implementation
○○○

Results
○○

Conclusions
○○●

# Questions?

## Want My Slides?

Kyle.Bryenton@dal.ca