XCDM

THE EXCHANGE-CORRELATION-HOLE
DIPOLE MOMENT MODEL

Kyle R. Bryenton
Dalhousie Department of Physics & Atmospheric Science
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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
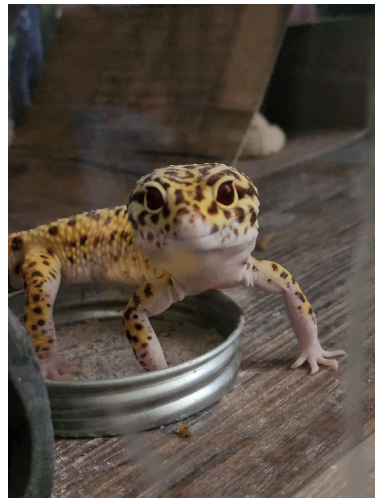
Scamper the Gecko

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 convergence at small interatomic separations, R_{ij}. The XDM model calculates the dispersion coefficients, C_n, using exchange-hole dipole moments,

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

which are obtained by integrating the exchange hole, $h_{\text{X}\sigma}$, 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, ρ_σ, 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, α_i, to solve for the heteroatomic dispersion coefficients,

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

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

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

Dispersion and XDM
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Implementation
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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

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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

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

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

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

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

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Becke proposed three forms for the normalization function

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

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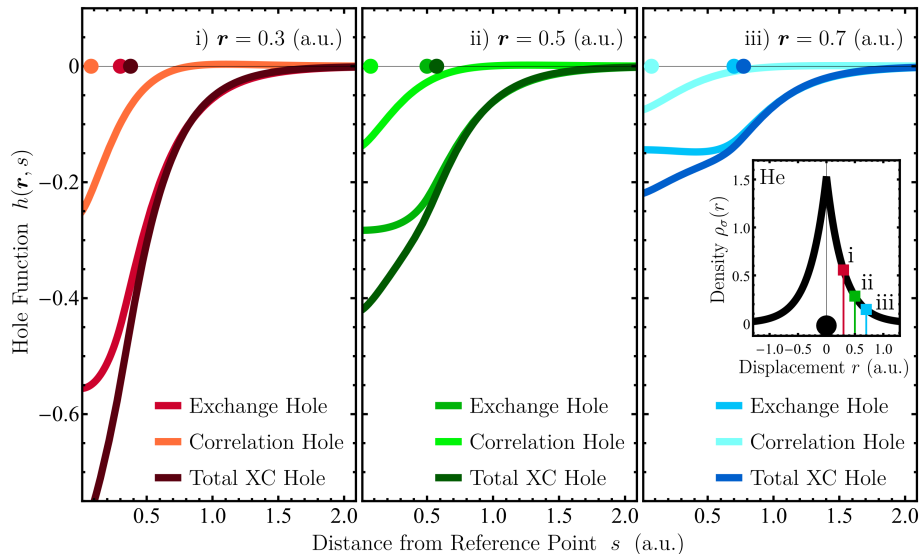
$$d_{C\sigma}^{\sigma\sigma}(\boldsymbol{r}) = \left[\int h_C^{\sigma\sigma}(\boldsymbol{r}, \boldsymbol{s}) \, s \, \mathrm{d}\boldsymbol{s} \right] - \boldsymbol{r} = \frac{c_{\sigma\sigma} \, z_{\sigma\sigma}^7}{2 + z_{\sigma\sigma}} D_\sigma(\boldsymbol{r}) - \boldsymbol{r} \, ,$$

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

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:

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

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PLOTS OF THE EXCHANGE-CORRELATION HOLE

i) $\boldsymbol{r} = 0.3$ (a.u.)

ii) $\boldsymbol{r} = 0.5$ (a.u.)

iii) $\boldsymbol{r} = 0.7$ (a.u.)

Hole Function $h(\boldsymbol{r}, s)$

Distance from Reference Point s (a.u.)

Density $\rho_\sigma(r)$

He

i ii iii

Displacement r (a.u.)

Exchange Hole
Correlation Hole
Total XC Hole

Exchange Hole
Correlation Hole
Total XC Hole

Exchange Hole
Correlation Hole
Total XC Hole

Dispersion and XDM
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Dispersion and XDM
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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
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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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- ACENET
- FHI-aims

QUESTIONS?

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KYLE.BRYENTON@DAL.CA