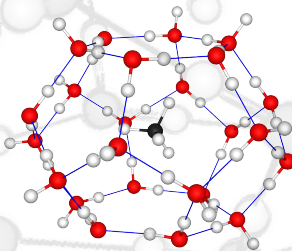


The exchange-hole dipole moment (XDM) dispersion model implementation in FHI-aims

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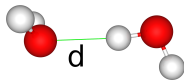
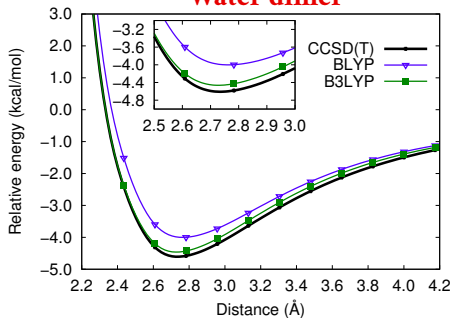
²Dalhousie University, Halifax



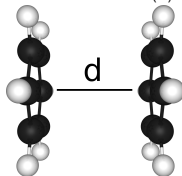
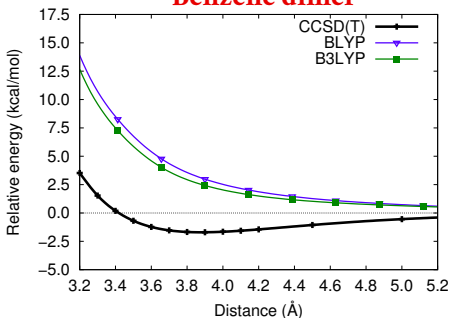
Non-covalent interactions in DFT

The **exchange-hole dipole moment (XDM) model** is a **dispersion correction**, designed to augment DFs to treat NCIs accurately.

Water dimer



Benzene dimer



Dispersion corrections in DFT

- Common exchange-correlation functionals do not model **dispersion**.
- One solution is to **calculate the dispersion energy separately** and then add it to the base DFT energy:

$$E_{\text{total}} = E_{\text{DFT}} + E_{\text{disp}}$$

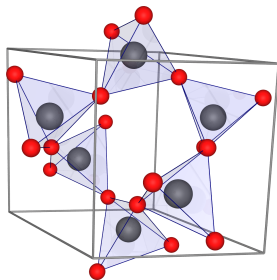
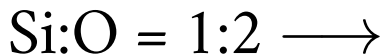
Several **dispersion corrections** have been proposed to address the non-covalent interactions problem:

- Grimme's D2/D3/D4.
- PBE-TS, PBE(0)-MBD and variants (**already in FHI-aims**).
- Exchange-hole dipole moment (XDM) model.
- Others...

Another option is using **nonlocal functionals** like the van der Waals density functionals (vdW-DF).

Motivation for XDM: Crystal structure prediction

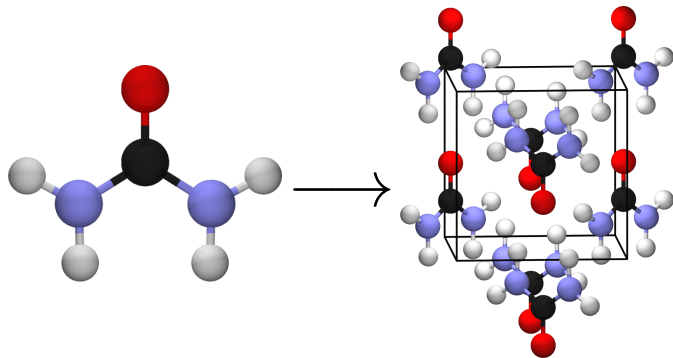
Crystal structure prediction (CSP): Given the chemical composition (formula unit, molecular diagram) of a material, predict its crystal structure.



CSP works by calculating the minimum-energy configuration from a list of randomly generated candidates. It is difficult because it is a **global optimization problem**.

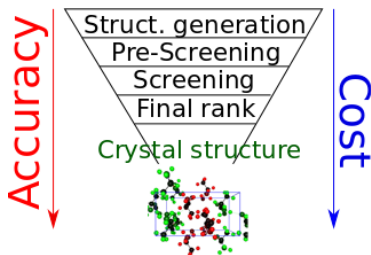
Motivation for XDM: Molecular CSP

Molecular CSP: prediction of the crystal structure of an **organic crystal** from its **molecular diagram**.



Applications:

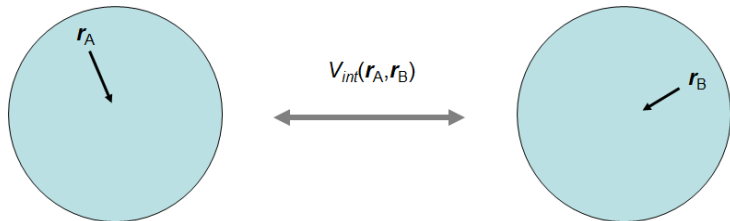
- **Drug design** (bioavailability and patenting)
- **Organic electronics** (properties of the material)
- **Energetic materials, phase change materials,...**



- **DFT** is successful but **expensive**. Each candidate out of a list of many thousands requires a local optimization.
- **Curse of dimensionality**: the number of degrees of freedom increases with molecular size but the energy differences in the energy landscape do not.
- **XDM**: very accurate energy landscapes.
- **FHI-aims**: hybrid functionals, linear scaling, easy access to vibrational free energies.

The XDM method

Dispersion arises from **interaction of induced dipoles**.



The source of the instantaneous dipole moments is taken to be the **dipole moment of the exchange hole**.

Becke and Johnson, J. Chem. Phys. **127** (2007) 154108

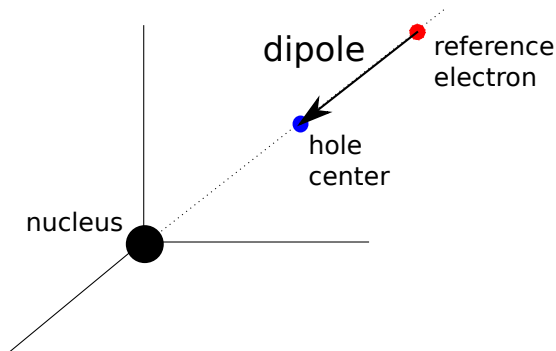
The exchange-hole model

The **exchange hole**:

$$h_{x\sigma}(\mathbf{1}, \mathbf{2}) = -\frac{|\rho_{1\sigma}(\mathbf{1}, \mathbf{2})|^2}{\rho_{1\sigma}(\mathbf{1})}$$

- Conditional probability of exclusion of same-spin electron.
- On-top depth condition: $h_{x\sigma}(\mathbf{1}, \mathbf{1}) = -\rho_{1\sigma}(\mathbf{1})$
- Normalization: $\int h_{x\sigma}(\mathbf{1}, \mathbf{2})d\mathbf{2} = -1$ for all $\mathbf{1}$.
- $\rho_{1\sigma}(\mathbf{1}, \mathbf{2}) = \sum_i^\sigma \psi_i^*(\mathbf{1})\psi_i(\mathbf{2})$

The exchange-hole model



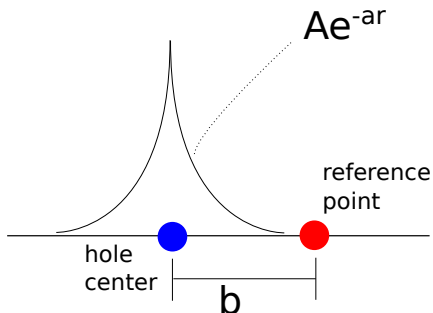
- **Model for dispersion: interaction of electron-hole dipoles.**
- Dipole: $\mathbf{d}_{x\sigma}(\mathbf{r}) = \int \mathbf{r}' h_{x\sigma}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' - \mathbf{r}$
- **Assumption:** dipole oriented to nearest nucleus.

The Becke-Roussel model of exchange-hole

- **Becke-Roussel model** of h_x .
(PRA 39 (1989) 3761)

Parameters (A, a, b) obtained:

- Normalization
- Value at reference point.
- Curvature at reference point (reqs. kinetic energy density).



Advantages:

- 1 Semilocal model of the dipole ($d_x = b$).
- 2 XDM dispersion model \rightarrow meta-GGA.
- 3 Better performance than exact hole (HF) version in molecules.

The XDM equations: interaction coefficients

Multipole moments

$$\langle M_l^2 \rangle_i = \sum_{\sigma} \int \omega_i(\mathbf{r}) \rho_{\sigma}(\mathbf{r}) [r_i^l - (r_i - d_{X\sigma})^l]^2 d\mathbf{r}$$

use **Hirshfeld atomic partition**:

$$\omega_i(\mathbf{r}) = \frac{\rho_i^{\text{at}}(\mathbf{r})}{\sum_j \rho_j^{\text{at}}(\mathbf{r})}$$

Non-empirical dispersion coefficients. ***n*-body and any order**. For instance:

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

Canonical XDM: two-body terms C_6 , C_8 and C_{10} are included.

The exchange-hole dipole moment (XDM) model

The XDM model uses a **damped asymptotic expression** for the dispersion energy:

$$E_{\text{total}} = E_{\text{disp}} + E_{\text{base}}$$

The XDM dispersion energy is:

$$E_{\text{disp}} = -\frac{1}{2} \sum_{ij} \frac{C_6 f_6(R_{ij})}{R_{ij}^6} + \frac{C_8 f_8(R_{ij})}{R_{ij}^8} + \frac{C_{10} f_{10}(R_{ij})}{R_{ij}^{10}} + \dots$$

where the damping function is:

$$f_n(R_{ij}) = \frac{R_{ij}^n}{R_{ij}^n + (\mathbf{a}_1 R_{ij,c} + \mathbf{a}_2)^n}$$

Two parameters, a_1 and a_2 , in the damping function are **fit for use with a particular XC functional**.

Damping function parametrization: statistics

$$f_n(R_{ij}) = \frac{R_{ij}^n}{R_{ij}^n + (\mathbf{a}_1 R_{ij,c} + \mathbf{a}_2)^n}$$

The **damping function parameters** are determined for a given functional by fitting to a **parametrization set** composed of reference binding energies for small molecular dimers (the Kanneman-Becke set, KB49). The parameters are then **used for all systems unchanged**.

Results for **XDM parametrization** with some xc functionals (kcal/mol):

| Quantity | B3LYP | BH&HLYP | PBE0 | CAM-B3LYP | LC- ω PBE |
|----------|-------|---------|------|-----------|------------------|
| MAE | 0.28 | 0.37 | 0.41 | 0.39 | 0.28 |
| MA%E | 6.7 | 7.8 | 10.2 | 8.3 | 7.8 |

The exchange-hole dipole moment (XDM) model

Extended to ***n*-body and any order**. For instance, 3-body coefficients:

$$C_{9,ijk} = \frac{\langle M_1^2 \rangle_i x_i \times \langle M_1^2 \rangle_j x_j \times \langle M_1^2 \rangle_k x_k}{x_i + x_j + x_k} \quad ; \quad x_a = \frac{\langle M_1^2 \rangle_a}{\alpha_a^0}$$

are the coefficients in the leading three-body dispersion term:

$$E_{\text{ATM}}^{(3)} = \sum_{i < j < k} \frac{C_{9,ijk} [3 \cos(\theta_i) \cos(\theta_j) \cos(\theta_k) + 1] f_9(R_{ij}, R_{jk}, R_{ki})}{R_{ij}^3 R_{jk}^3 R_{ki}^3}$$

- **Electronic many-body effects:** arise from the changes in atomic moments, volumes, and pairwise C_n due to the chemical environment. C_6 can change by more than 50%.
- **Atomic many-body effects:** three-body and higher-order dispersion. Less than 1% of the dispersion energy. Much less important than pairwise C_8 , C_{10} . Choice of functional has greater impact.

XDM: summary and other advantages

- **Simple.** Although the calculation of the dispersion coefficients depend in a complex way on the density and kinetic energy density, the XDM energy and derivatives is as a simple pairwise expression.
- **Efficient.** XDM is formally a meta-GGA. The computational cost is negligible compared to a semilocal DFT calculation.
- **Available** in several quantum chemistry programs:
 - 1 Quantum ESPRESSO.
 - 2 Gaussian, psi4, ... using the postg interface.
 - 3 NWChem.
 - 4 **FHI-aims**



github.com/aoterodelaroza

XDM implementation in FHI-aims

Details of the **XDM implementation in FHI-aims**:

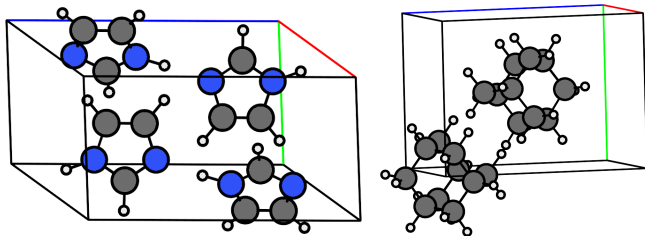
- Activate using XDM with the **xdm keyword** in `control.in`.
- **Available functionals** for combination with XDM (MAPE light/tight): PBE (19.0/14.1), B86bPBE (14.9/11.0), HSE06 (13.6/11.1), PBE0 (12.5/10.2), PBE-50 (9.8/9.6), B86bPBE-25 (9.7/8.4), B86bPBE-50 (8.5/8.5).
More can be parametrized easily.
- **XDM calculation steps**: i) Atomic volumes, moments, polarizabilities, ii) Atomic dispersion coefficients, iii) lattice sum for the dispersion energies.
- The contribution to the **energy, forces, and stress** are calculated.

Work to do:

- Implement exact **density-dependent forces**.
- Improve **lattice sums** for linear scaling.

Molecular crystal lattice energies

Strict test of performance for NCIs in molecular crystals is the calculation of **lattice energies**: crystal minus gas-phase molecule energy difference. Reference data can be obtained by **back-correcting experimental sublimation enthalpies**. Examples: **C21 set**, **X23 set**.



Molecular crystal lattice energies

Mean absolute errors (MAE) for X23 in kcal/mol per molecule.

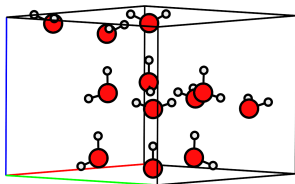
| Functional | Dispersion | Light | Tight |
|---------------------------------------|------------|-------------|-------------------|
| Full Geometry Relaxation | | | |
| PBE | TS | 4.17 | 3.14 |
| PBE | MBD | 1.61 | 0.94 |
| PBE0 | MBD | 1.98 | 0.84 ^a |
| B86bPBE | XDM | 0.83 | 0.72 |
| B86bPBE-25 | XDM | 0.81 | — |
| B86bPBE-50 | XDM | 1.06 | — |
| Single Points at GGA/Light Geometries | | | |
| B86bPBE-25//B86bPBE | XDM | 0.66 | 0.48 |
| B86bPBE-50//B86bPBE | XDM | 0.70 | 0.53 |

Ice lattice energies

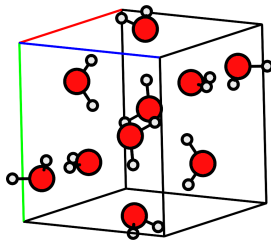
Even stricter test of performance for NCIs: **lattice energies of ice phases:**

- Cooperative (many-body induction) effects.
- Existence of **delocalization error** precludes obtaining good absolute and relative lattice energies.

ICE13 set: Della Pia et al. recently obtained Diffusion Monte Carlo (DMC) data for 13 ice phases.



Ice Ih



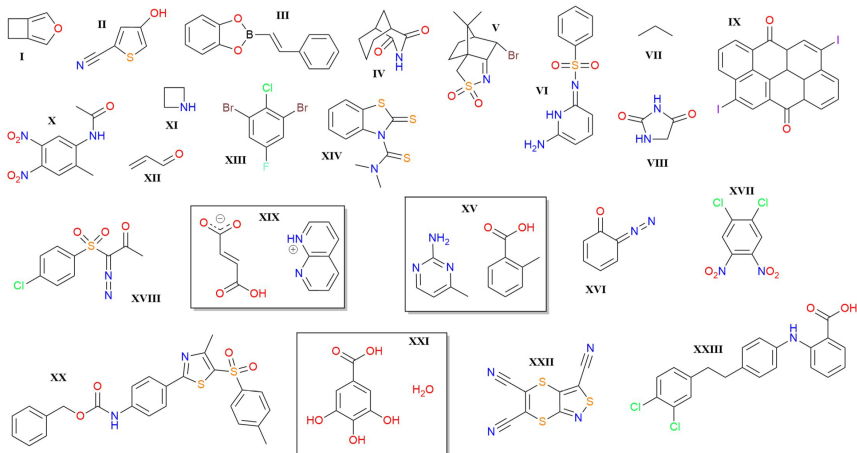
Ice VI

Mean absolute errors (MAE) for X23 in kcal/mol per molecule.

| Functional | Dispersion | Absolute | | Relative | |
|---------------------------------------|------------|-------------|-------------|-------------|-------------|
| | | Light | Tight | Light | Tight |
| Full Geometry Relaxation | | | | | |
| PBE | TS | 3.69 | 2.18 | 0.56 | 0.51 |
| PBE | MBD | 3.70 | 2.19 | 0.66 | 0.60 |
| PBE0 | MBD | 2.38 | — | 0.37 | |
| B86bPBE | XDM | 2.69 | 1.78 | 0.67 | 0.45 |
| B86bPBE-25 | XDM | 1.16 | — | 0.53 | |
| B86bPBE-50 | XDM | 0.55 | — | 0.42 | |
| Single Points at GGA/Light Geometries | | | | | |
| B86bPBE-25//B86bPBE | XDM | 0.93 | 0.19 | 0.49 | 0.28 |
| B86bPBE-50//B86bPBE | XDM | 0.32 | 1.20 | 0.31 | 0.19 |

Molecular CSP: blind tests

To measure progress in the field, **blind test competitions** are periodically run by the **Cambridge Crystallographic Data Centre (CCDC)**: BT1 (2000), BT2 (2002), BT3 (2005), BT4 (2009), BT5 (2011), BT6 (2016), **BT7 (2022, unpublished)**.



Molecular CSP: blind tests

Recalculated structures:

- BT1–5: first three structures submitted by all participants.
- BT6: first three structures + Neumann's 100-structure submissions + POLY59.

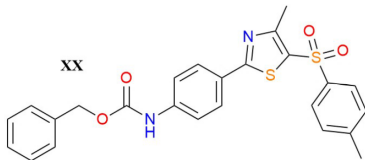
| Compound | B86bPBE | | 25% hyb. | | 50% hyb. | |
|-----------|----------|------------|----------|------------|----------|------------|
| | Rank | ΔE | Rank | ΔE | Rank | ΔE |
| II | 4 | 1.1 | 2 | 0.7 | 2 | 0.5 |
| V | 4 | 1.9 | 4 | 1.9 | 4 | 1.5 |
| X | 2 | 0.9 | 2 | 0.4 | 1 | 0.0 |
| XV | 2 | 0.3 | 2 | 0.8 | 2 | 1.2 |
| XIX | 6 | 4.3 | 4 | 2.2 | 2 | 0.1 |
| XX | 4 | 6.7 | 4 | 6.5 | 6 | 6.7 |
| XXII | 9 | 2.7 | 3 | 0.4 | 2 | 0.1 |
| XXIII | 3 | 0.8 | 2 | 0.0 | 2 | 0.0 |
| XXIV | 8 | 2.0 | 3 | 0.7 | 2 | 0.4 |

Molecular CSP: blind tests

Results with B86bPBE-50:

- 18/26 experiment as **first rank**.
- 6/26 experiment as **second rank**.
- All “failed” cases are **within 1.5 kJ/mol** from the energy minimum, except XX.
- XX: experiment is 6.7 kJ/mol above the minimum. **Large floppy molecule**: lack of thermal contribution or kinetic effects.

In summary, B86bPBE-50-XDM **improves significantly upon B86bPBE-XDM**: it fixes intermolecular delocalization error and improves the treatment of molecular conformational energies.

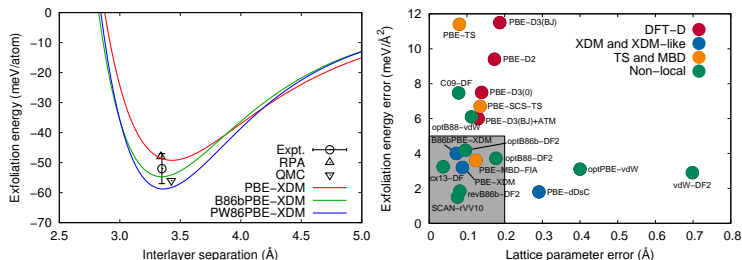


XDM for systems other than molecular crystals

A good thing about XDM-corrected functionals is that they **improve the treatment of NCIs for very disparate systems** without reparametrization.

XDM has been used for:

- Formation energies of **supramolecular systems**.
- Molecular **surface adsorption** on metals and ionic solids.
- **Clathrate hydrates**.
- Graphite and **graphene heterostructures**.
- **Layered materials** (transition metal dichalcogenides).
- Geometries and bulk moduli of **ionic solids**.



Conclusions

The **exchange-hole dipole moment (XDM) model** is a dispersion correction recently **implemented in FHI-aims**:

- **Simple and efficient.** The calculation of the XDM contribution takes a small fraction of an SCF cycle.
- **Physically grounded.** The dispersion coefficients are calculated non-empirically from the self-consistent wavefunction and react to the chemical environment.
- **Very accurate for non-covalent interactions of any kind.** Particularly B86pPBE-XDM and hybrids based on it.
- **Easy to use.** Simply include the xdm keyword.

Thanks!