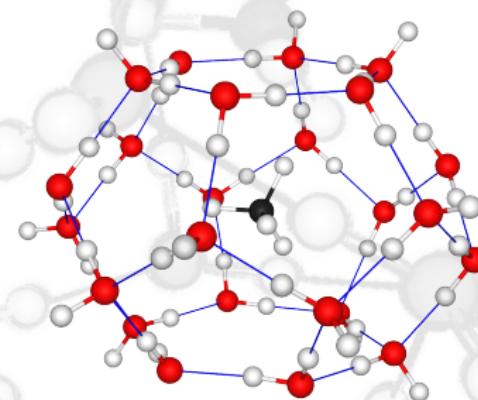
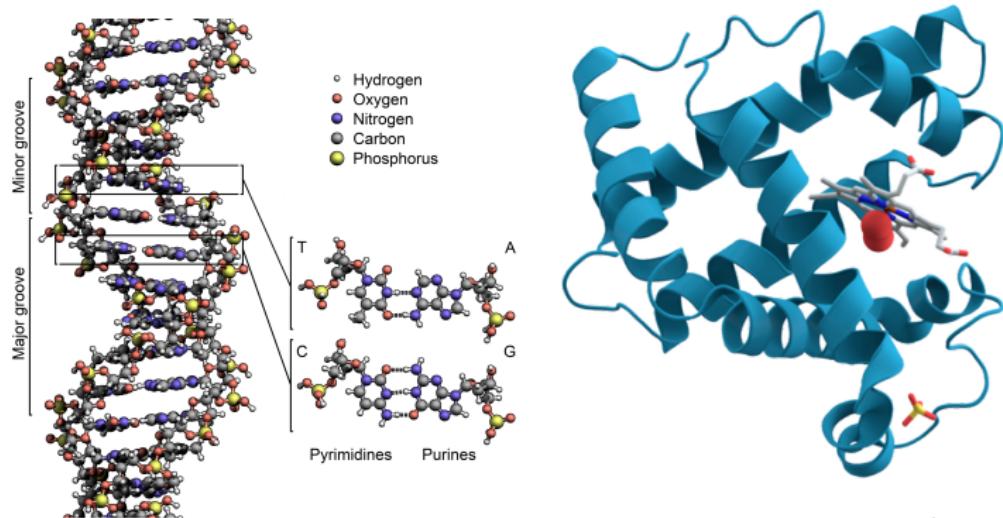


Non-covalent interactions in density-functional theory with the exchange-hole dipole moment (XDM) model

Alberto Otero de la Roza
University of Oviedo, Spain



Importance of non-covalent interactions



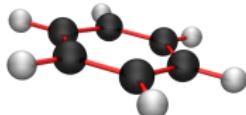
Source: Wikipedia

- Non-covalent interactions are ubiquitous in nature.
- They control the structure and function of biological molecules.
- Important in many fields of science.

Some examples of non-covalent interaction motifs



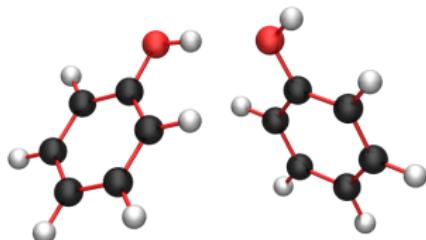
Methane dimer
0.5 kcal/mol



Benzene π -stack
1.7 kcal/mol



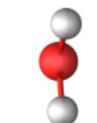
Methane-HF
1.6 kcal/mol



Phenol dimer
7.1 kcal/mol



Acetaldehyde dimer
3.4 kcal/mol

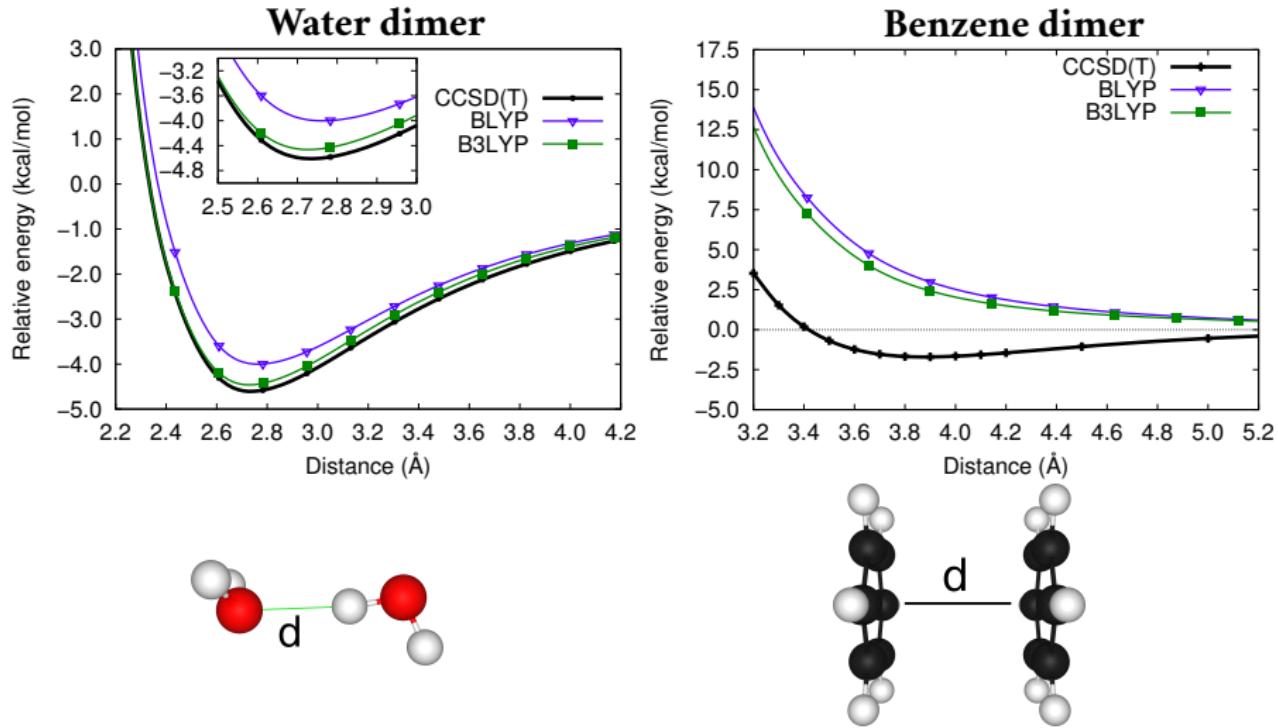


Water dimer
5.0 kcal/mol

Classification of intermolecular forces

- **Electrostatic interactions:** between permanent multipoles on the interacting molecules—charges, dipoles, quadrupoles, etc.
- **Exchange-repulsion:** the repulsion between the closed shells in different molecules arising from Pauli exclusion principle.
- **Induction:** changes in the electronic structure of one molecule caused by the electric field of the other.
- **Charge transfer:** electron transfer between molecules.
- **Dispersion:** interaction between instantaneous dipoles on the two fragments.

Non-covalent interactions in DFT



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 DFT energy:

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

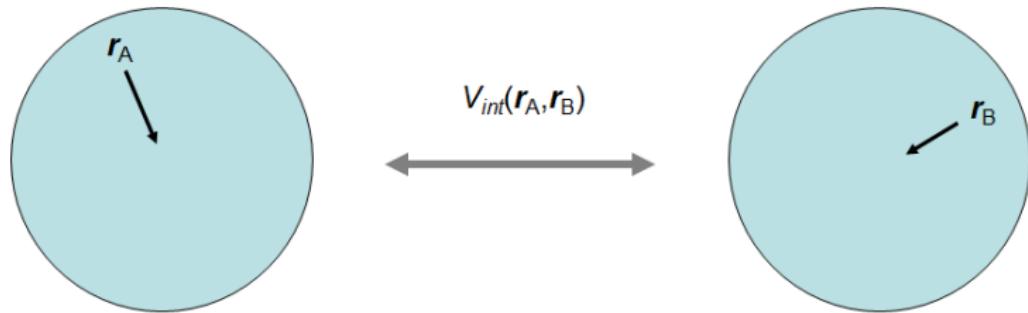
Several **dispersion corrections** have been proposed to address the non-covalent interactions problem:

- Grimme's D2/D3/D4.
- PBE(0)-MBD and variants.
- Exchange-hole dipole moment (XDM) model.

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

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

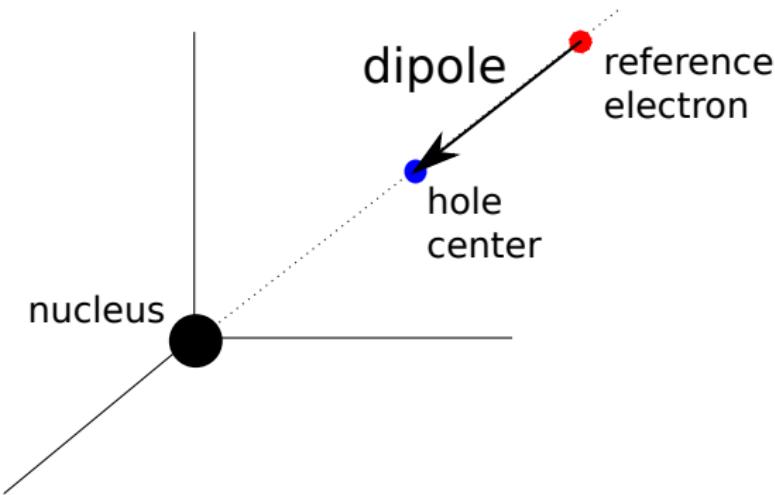
The exchange-hole model

The exchange hole:

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

- 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.

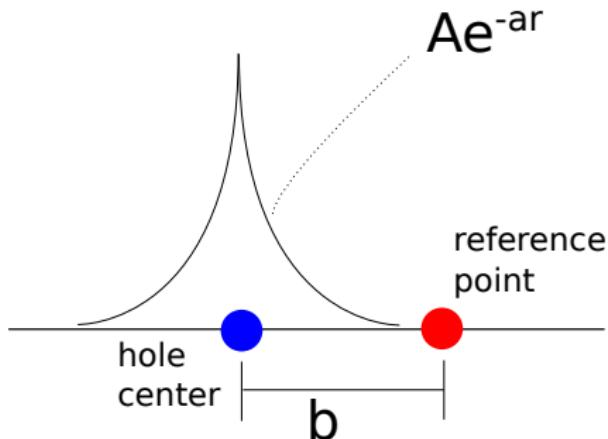
The Becke-Roussel model of exchange-hole

- **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 → 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:

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

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 linear 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

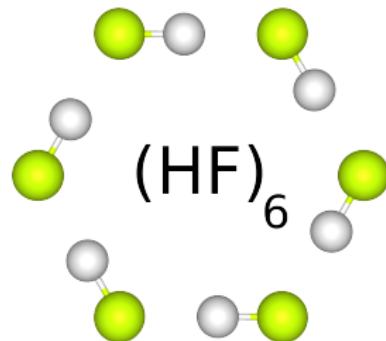
Challenge: rational design of xc-functionals for NCIs

Challenge: no dispersion-corrected functional gives good across-the-board results, particularly for large molecular aggregates (e.g. water hexamers). Such functional is essential for supramolecular chemistry and *ab initio* molecular dynamics simulations.

Desideratum: *a (GGA?) functional that achieves good across-the-board performance for small systems and presents small error scaling in larger systems.*

Source of NCI errors in DFT

- Repulsion error
- Delocalization error
- Relaxation error



The exchange-hole dipole moment (XDM) model

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

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

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.



Accuracy of XDM

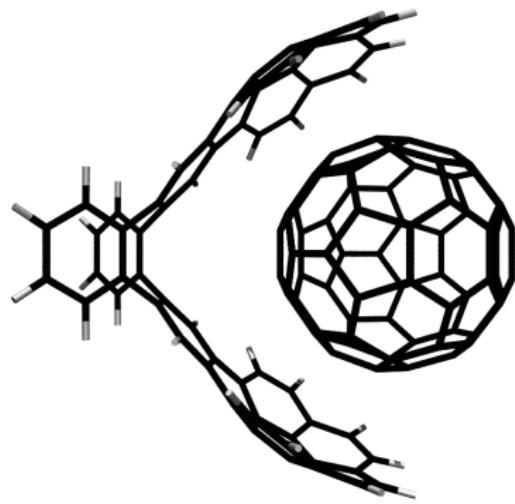
Benchmark sets: sets of accurate reference energies for non-covalent interactions in model systems.

- **Kannemann-Becke set (KB49):** binding energies of 49 small molecular dimers.
- **X23 set:** crystal lattice energies derived from sublimation enthalpies.

Functional	Mean absolute error (kcal/mol) KB49	Mean absolute error (kcal/mol) X23
B86bPBE	0.41	0.85
PW86PBE	0.41	0.88
BLYP	0.43	1.31
PBE	0.50	1.11
B3LYP	0.28	1.29
PBE0	0.41	0.83

Accuracy of XDM

Accuracy. XDM works in many different types of systems (dimers, crystals, surfaces, etc.). Small gas-phase dimers: **0.25–0.5 kcal/mol.**



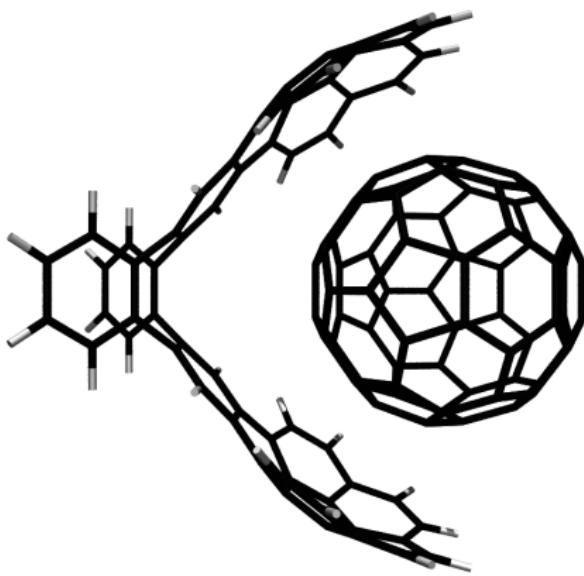
Host-guest complexes

S12L set (only QMC data)	
Functional	MAE (kcal/mol)
PBE-XDM	1.2
RPA-PBE	3.9
PBE-dDsC	4.6
PBE-D2	3.5
PBE-D3	2.3
M06-L	1.9
PBE-MBD	1.8

Challenges: accurate modeling of large systems

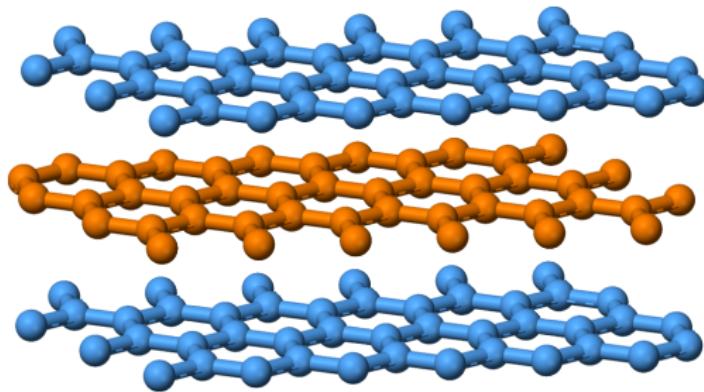
Accuracy of DFT-XDM limited by the size of the basis set used to represent the orbitals. **Large basis** sets are required for non-covalent interactions.

- Large systems (> 100 atoms) can not be run with complete basis sets.
- **Basis-set superposition error**
- Alternative DFT-based semiempirical methods like DFTB.
- Using empirical potentials to correct for BSSE.



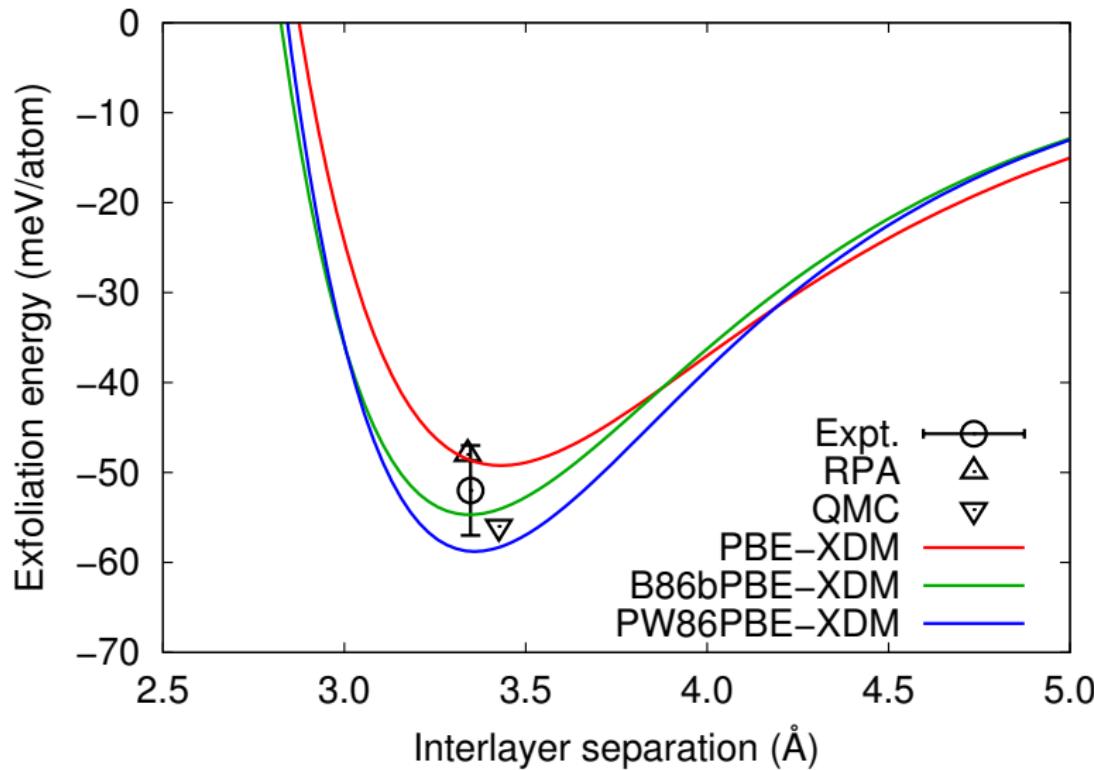
Graphite and layered materials

The simplest material that is bound by non-covalent interactions is **graphite**. Graphite is composed of stacked layers of carbon, individually called graphene:

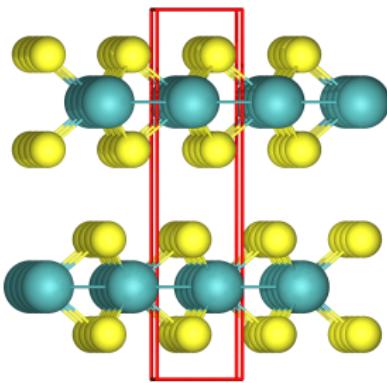
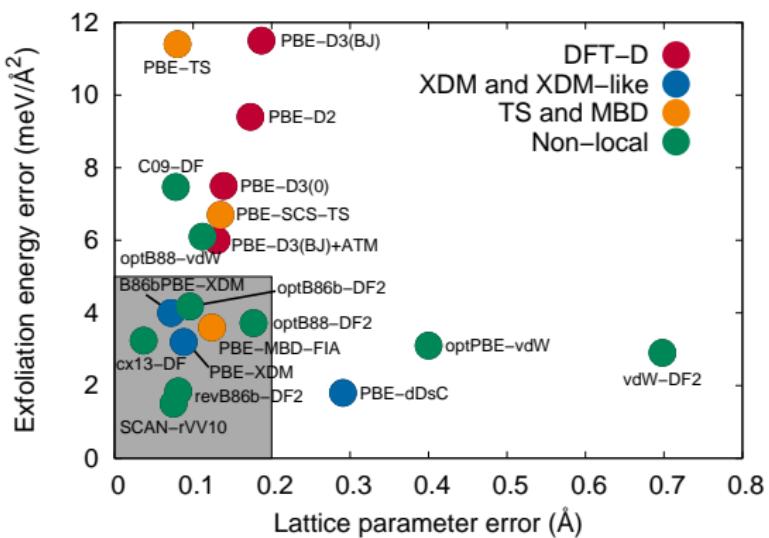


A simple quantity whose value is controlled by non-covalent interactions is the **exfoliation energy**.

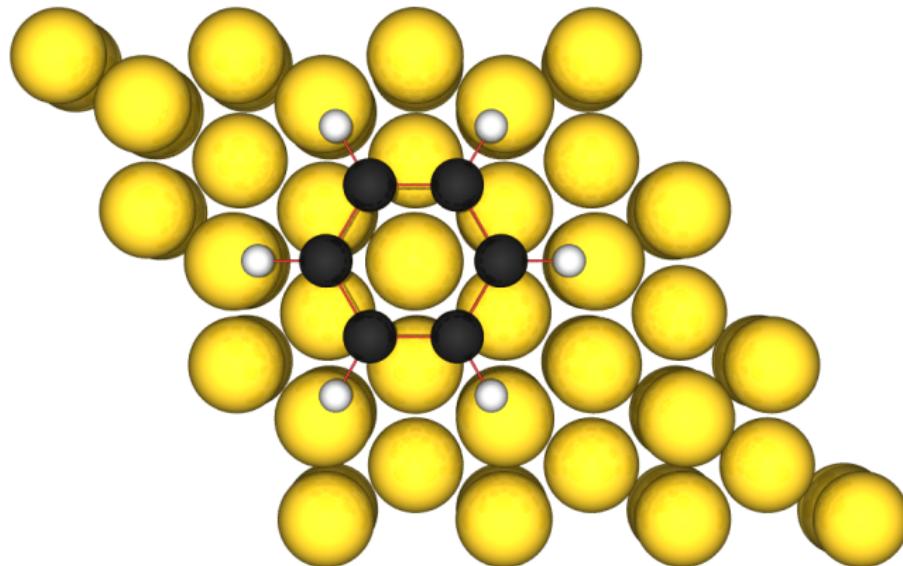
Graphite exfoliation energy



Layered materials



Surface adsorption

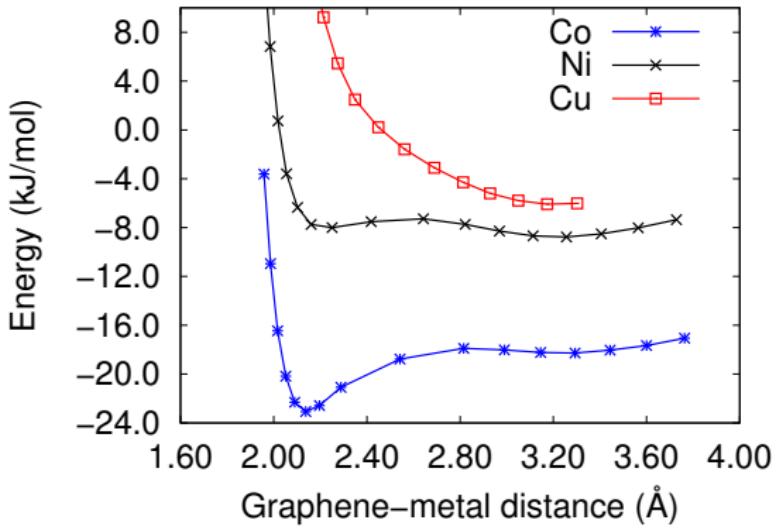
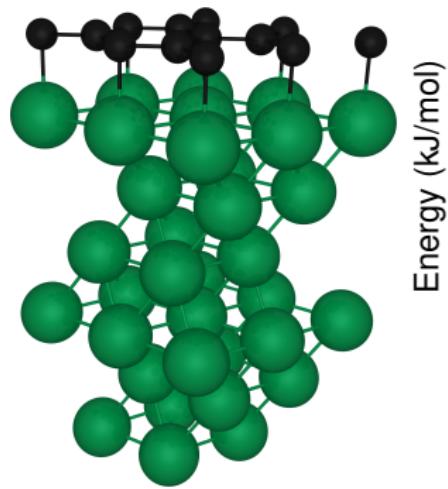


- **Molecular surface adsorption:** important in catalysis, self-assembled materials, etc.
- Dispersion interactions are important in chemisorption and physisorption.

Surface adsorption

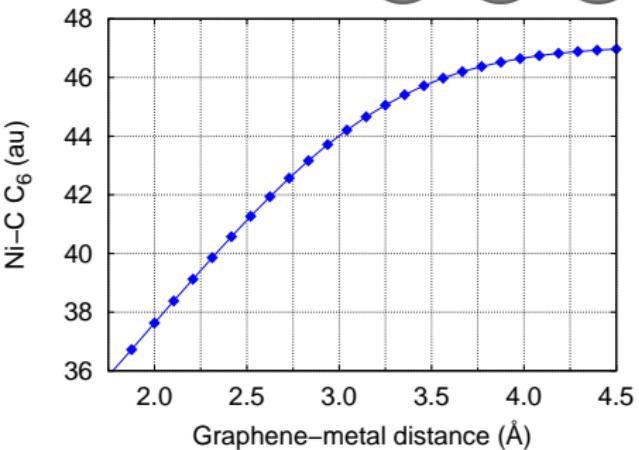
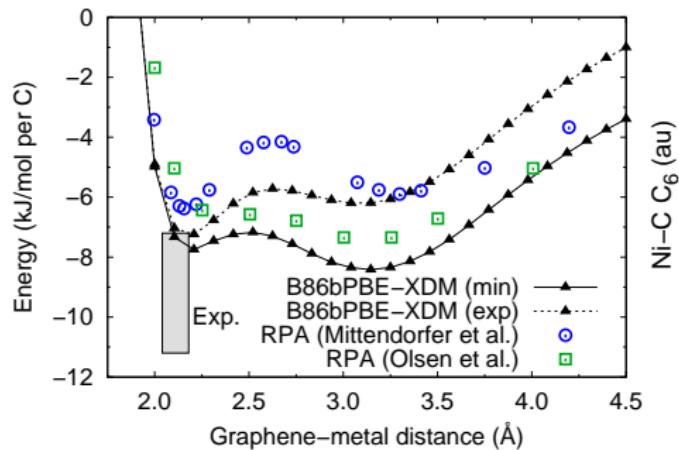
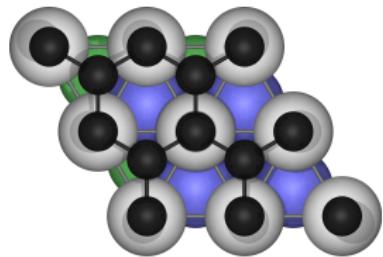
Base	Disp.	Cu	Ag	Au	MAE
PBE	none	0.08	0.08, 0.09	0.08, 0.15	0.57–0.59
PBE	D2	0.86	—	1.35	—
PBE	D3	0.99	0.74	0.86	0.19
PBE	D3(ABC)	0.79	0.61	0.73	0.08
PBE	TS	1.02, 1.07	0.82, 0.87	0.80, 0.84	0.20–0.25
PBE	TS ^{surf}	0.79, 0.86	0.73, 0.75	0.73, 0.74	0.08–0.11
PBE	MBD	0.63	0.57	0.56	0.09
opt-B86b	vdw-DF	0.82	0.76	0.86	0.14
opt-PBE	vdw-DF	0.68	0.71	0.71	0.03
rPW86	vdw-DF	0.49	0.52	0.55	0.15
B86bPBE	XDM	0.59	0.68	0.64	0.04
Expt.		0.69±0.04	0.68±0.05	0.65±0.03	

Surface adsorption: graphene on metals



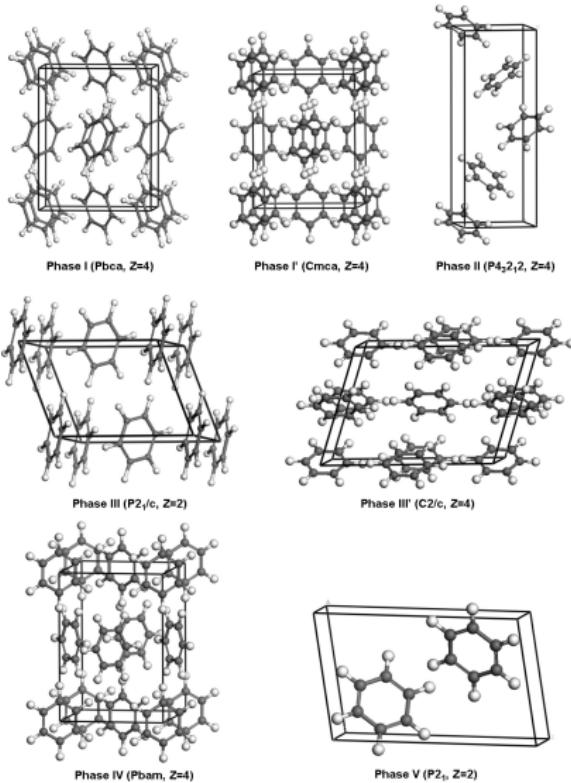
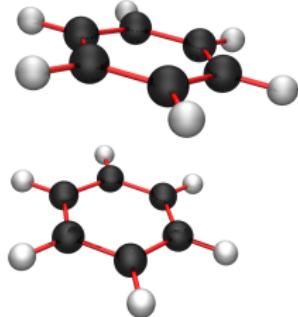
Surface adsorption: graphene on metals

- **Electronic many-body effects** are important in graphene-Ni interaction.
- The onset of chemisorption is marked by **surface charge transfer**.

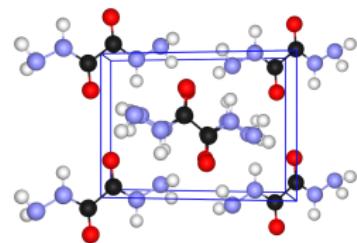
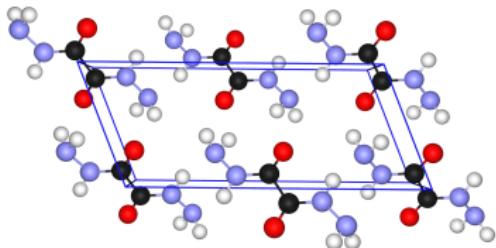
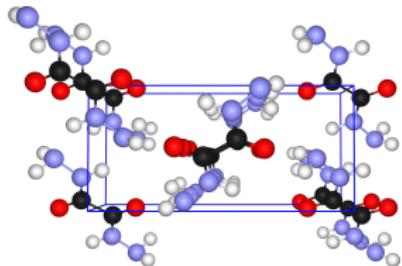


Molecular crystals: polymorphism

The structure of molecular crystals are the result of a very delicate balance of non-covalent interaction. Simple molecules can crystallize in **polymorphs**, many of which are very close in energy.



Oxalyl dihydrazide



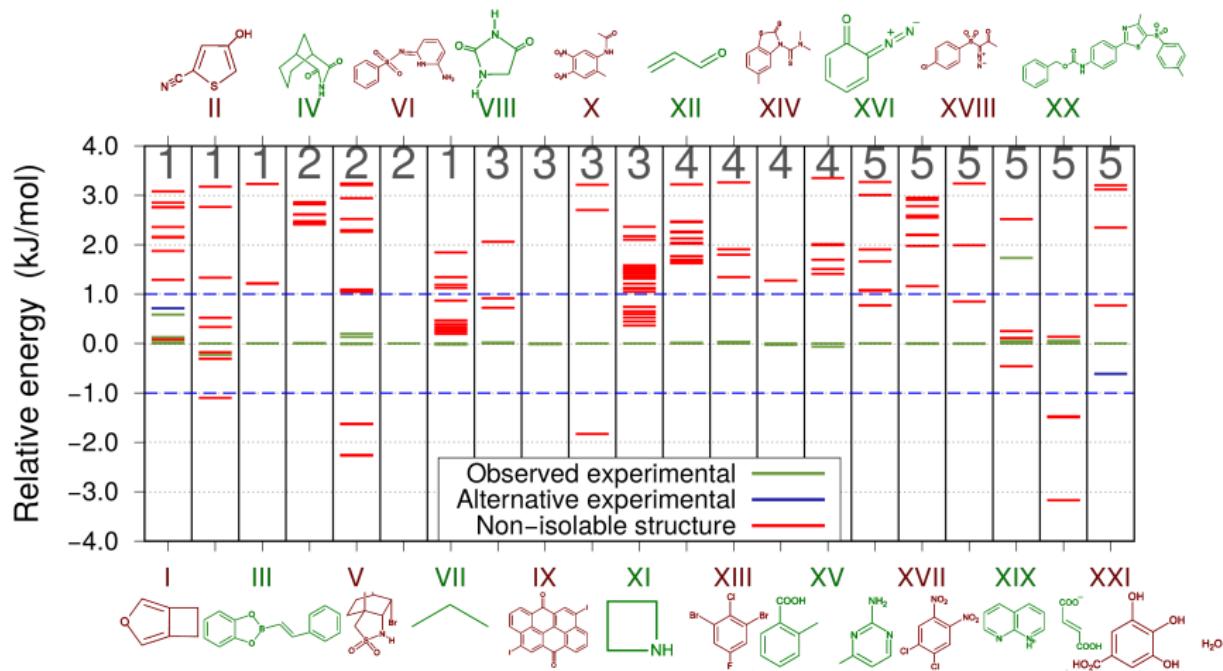
Five known polymorphs; experimentally, the order of stabilities is:

$$\alpha, \delta, \epsilon < \gamma < \beta$$

Relative energies (kcal/mol per molecule):

Form	Base	XDM
β	1.1	2.9
γ	-0.1	2.5
δ	-0.2	1.9
ϵ	1.6	1.2
α	0.0	0.0

CSP ranking functions



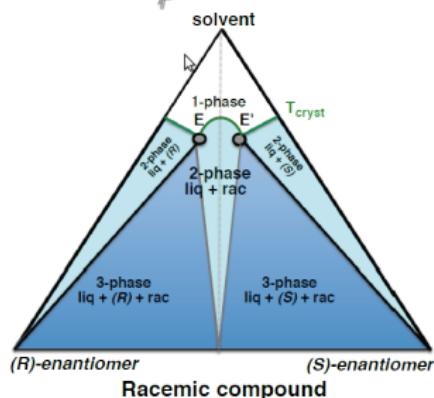
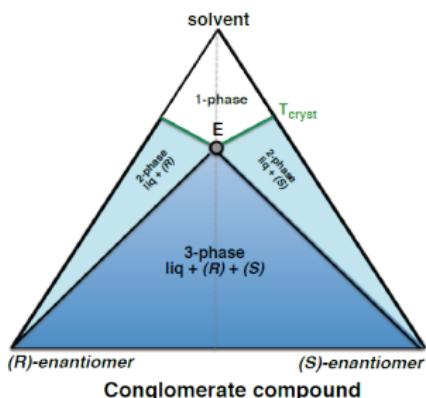
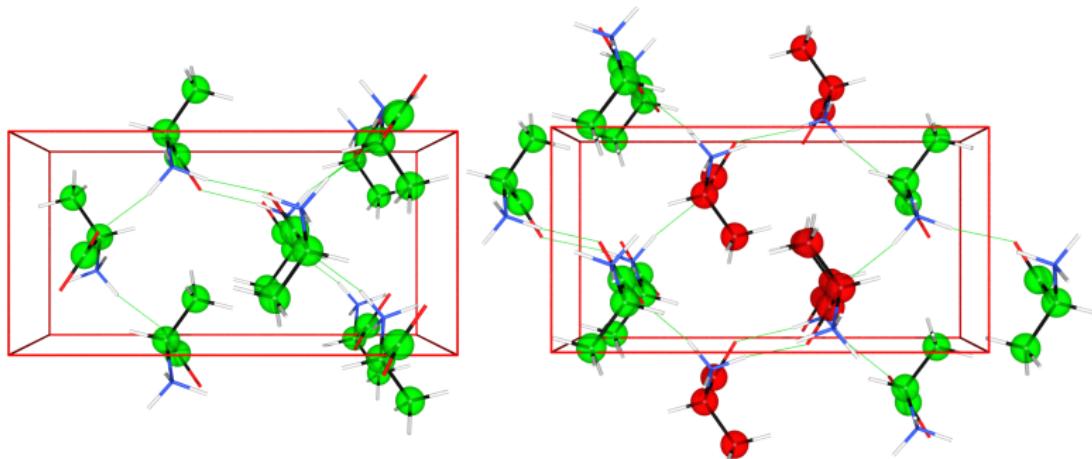
Unsolved difficulties in DFT for molecular crystals

There are a number of **problematic systems**:

- **Organic salts:** due to delocalization error, DFT tends to overstabilized charge transfer states. Relative energies in organic salts are biased towards **maximum charge transfer**.
- **Conformational energies:** the molecular conformation in the crystal is, in general, not the same as in the gas phase (e.g. urea). GGA functionals sometimes have problems with these energies.
- **Cooperative effects:** many-body induction effects. Important in multiple hydrogen-bonded systems. (e.g. ranking of ice phases).

Better: **hybrid functionals**, but expensive.

Enantiomeric excess in solution



Enantiomeric excess in solution

A simple model

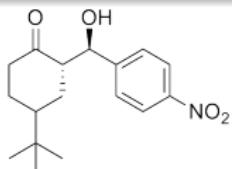
$$\Delta E = E_{dl} - E_l$$

$$ee = \frac{\beta^2 - 4}{\beta^2 + 4} \times 100$$

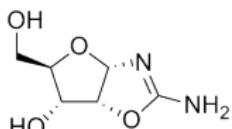
$$\beta = e^{-\Delta E/RT}$$

*Thanks:

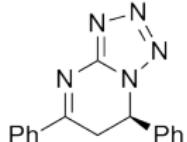
Matthew Fuchter,
Jason Hein, Ivy
Price.



A



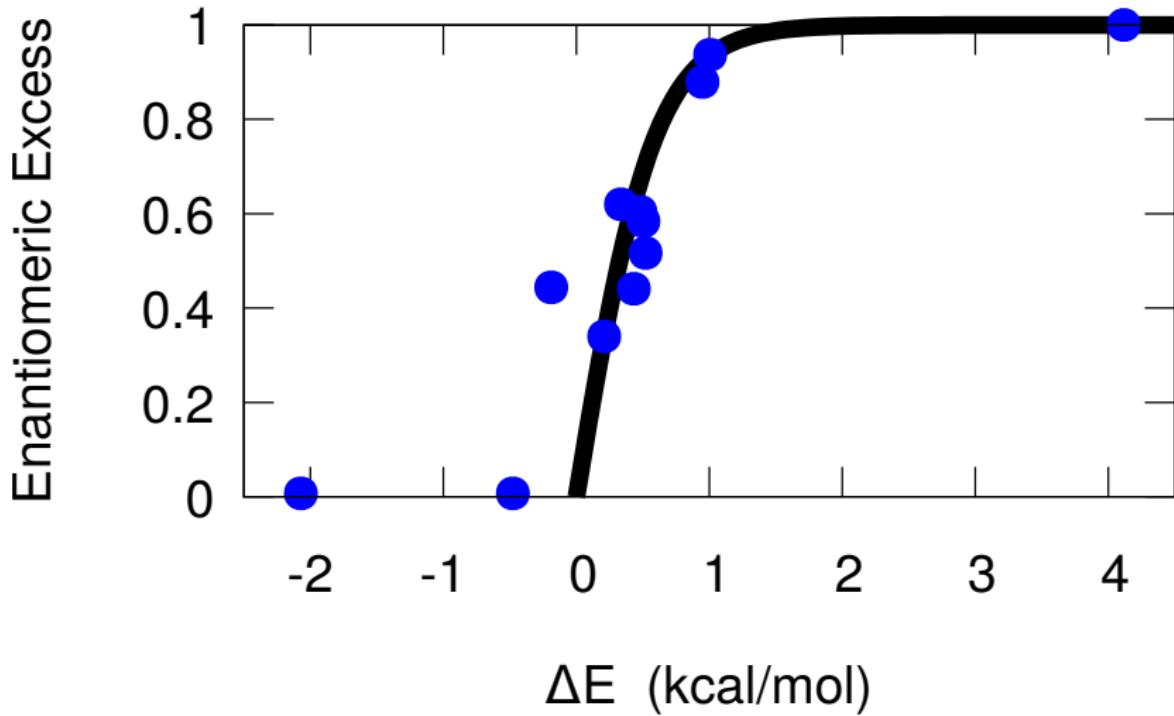
B



C

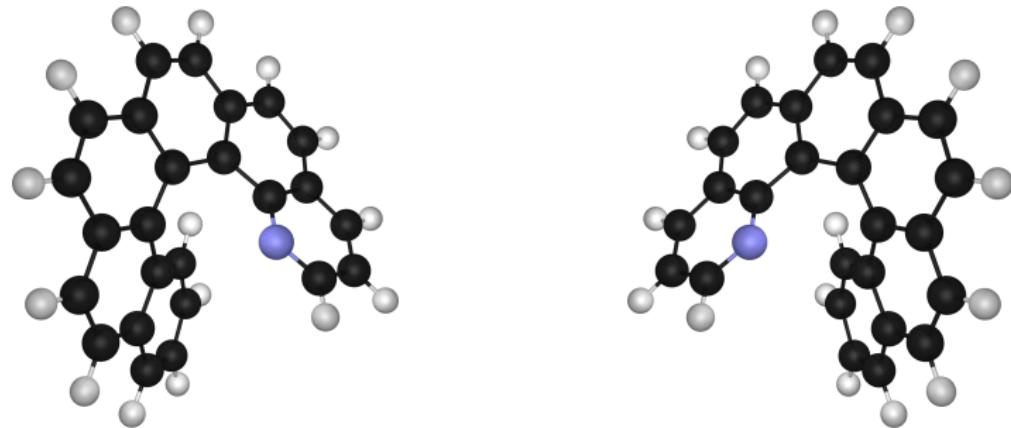
Molecule	DFT	Expt.
Serine	100.0	100.0
Histidine	93.5	93.7
Leucine	92.2	87.9
Alanine	67.1	60.4
Cysteine	69.2	58.4
Tyrosine	70.6	51.7
Valine	62.3	44.1
Proline	0.0	39.7
Aspartic acid	0.0	0.0
Glutamic acid	0.0	0.0
1-aza[6]helicene*	90.6	74
A	35.5	34
B	51.3	62
C	100.0	100.0

Enantiomeric excess in solution



XDM applied to CSP: helicenes

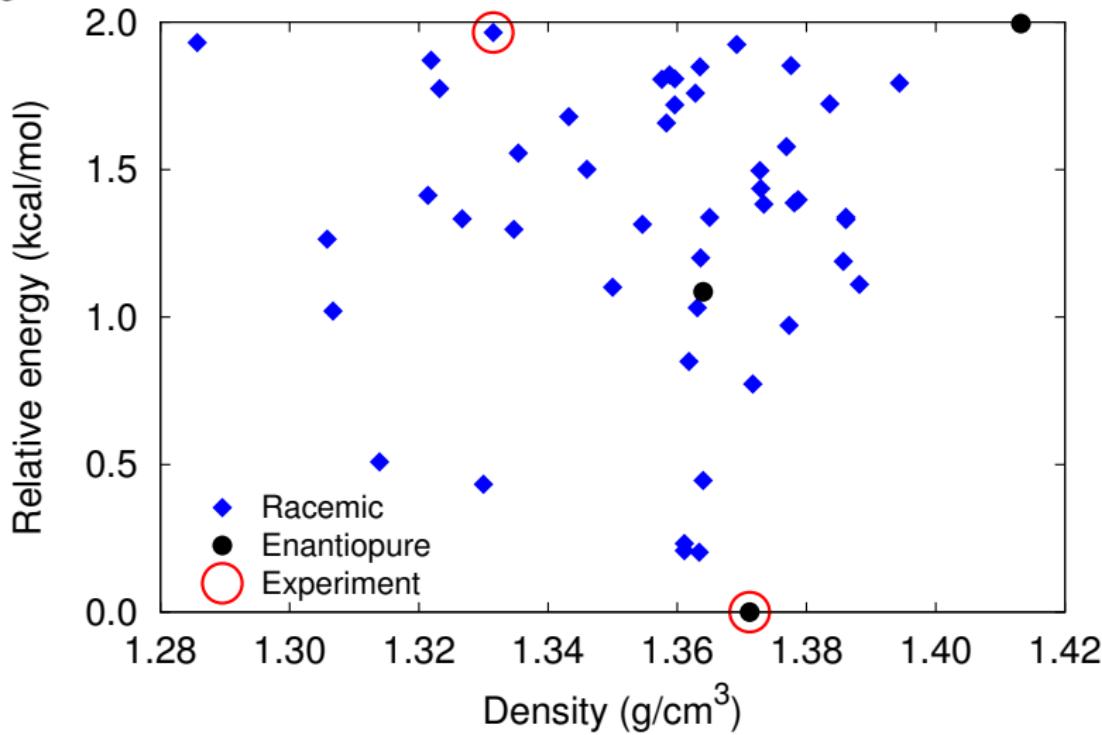
Use XDM in conjunction with a classical force field to predict the homochiral and heterochiral crystal phases of 1-aza[6]helicene (OFETs).



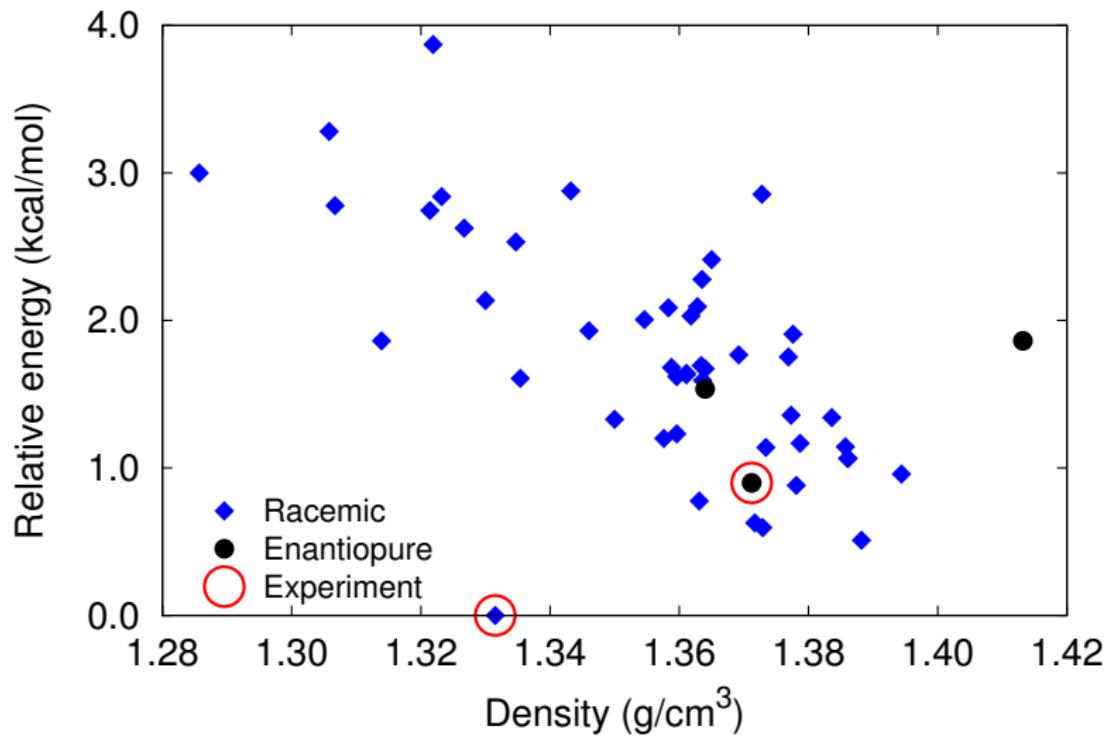
The heterochiral form has 80-fold higher carrier mobility than the homochiral form.

Azahelicenes: Force field results

Fifty low-energy structures from the W99 force field (Kim Jelfs, Imperial College, London).

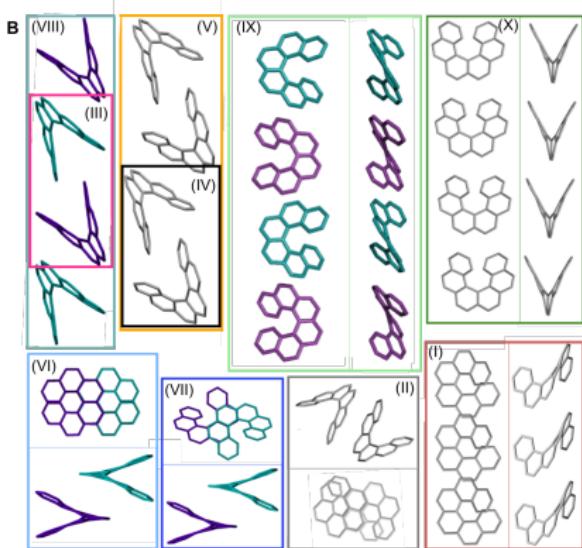
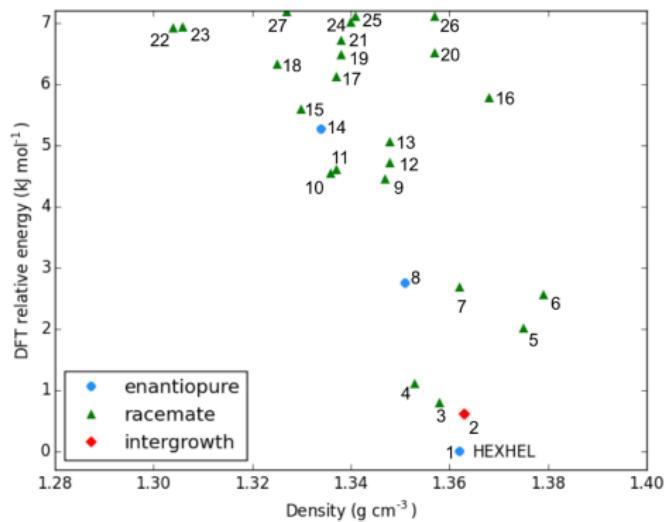


Azahelices: DFT-XDM results

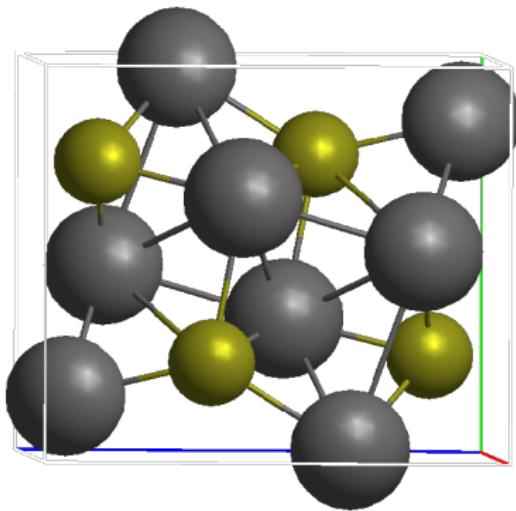


Helicenes

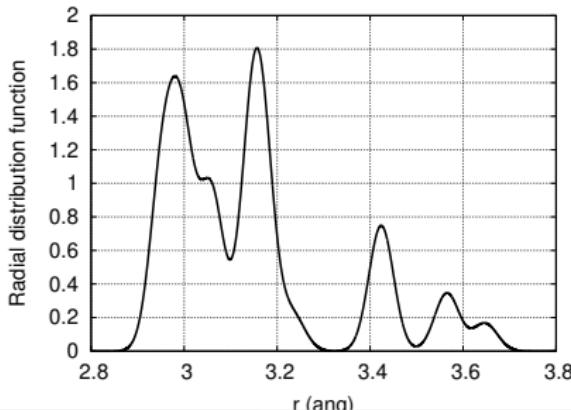
Another example: [6]helicenes. Exploration of the energy landscape and identification of the relevant motifs.



Silver (I) sulfide (Ag_2S)



- Silver (I) sulfide has an **anti-cotunnite** (anti-PbCl_2) structure.
- The bulk modulus and EOS **do not agree with experiment** ($B_0^{\text{calc}} = 14.4$, $B_0^{\text{exp}} = 38$).
- S is in **coordination 9** with Ag.
- **Nearest-neighbor (Ag-S) distance distribution:**



Silver(I) sulfide, structure & experimental data

Silver(I) sulfide (Ag_2S)—Inorg. Chem. **51 (2012) 5289.**

Experiments: synchrotron X-ray powder diffraction data.

Inorganic Chemistry

Article

pubs.acs.org/IC

Compression of Silver Sulfide: X-ray Diffraction Measurements and Total-Energy Calculations

David Santamaría-Pérez,^{*,†,‡} Miriam Marqués,^{‡,§,||} Raquel Chuliá-Jordán,[†] José M. Menendez,^{‡,§,||} Oscar Gomis,^{§,||} Javier Ruiz-Fuertes,^{||,‡} Juan A. Sans,^{||,‡} Daniel Errandonea,^{||,‡} and José M. Recio^{‡,§,||}

[†]Departamento de Química Física I, Universidad Complutense de Madrid, 28040 Madrid, Spain

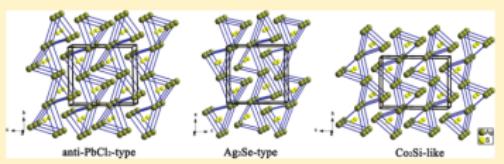
[‡]Departamento de Química-Física y Analítica, Universidad de Oviedo, 33007 Oviedo, Spain

[§]Centro de Tecnologías Físicas:Acústica, Materiales y Astrofísica, Universitat Politècnica de València, 46022 Valencia, Spain

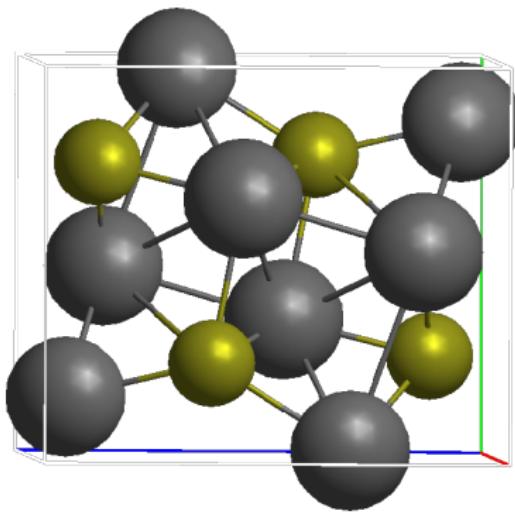
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 Supporting Information

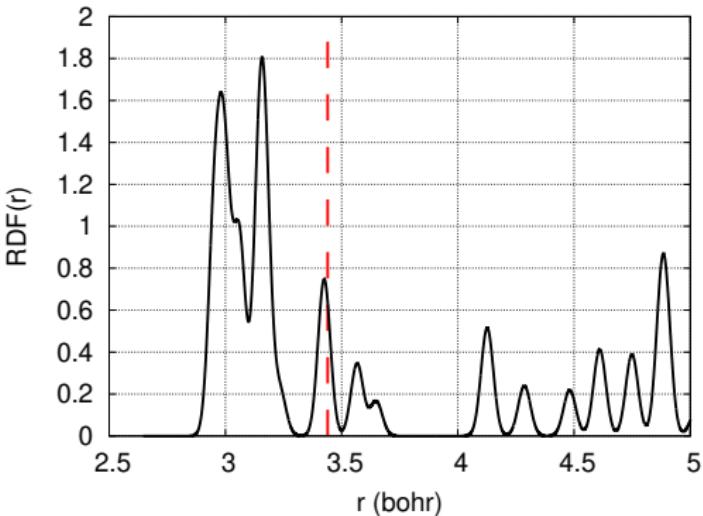
ABSTRACT: Angle-dispersive X-ray diffraction measurements have been performed in acanthite, Ag_2S , up to 18 GPa in order to investigate its high-pressure structural behavior. They have been complemented by ab initio electronic structure calculations. From our experimental data, we have determined that two different high-pressure phase transitions take place at 5 and 10.5 GPa. The first pressure-induced transition is from the initial anti- PbCl_2 -like monoclinic structure (space group $P2_1/n$) to an orthorhombic



Silver (I) sulfide



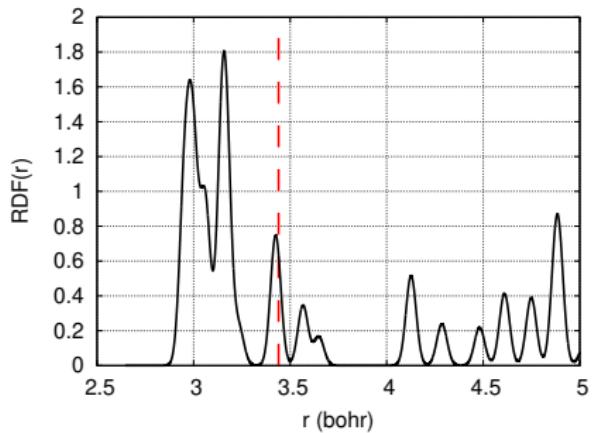
Ag-Ag RDF shows close second-nn contacts:



There are **two non-equivalent Ag atoms**. Each has a **4-fold coordination with the S** and **7-fold coordination with the other Ag atoms** around them, in a range 2.54 Å to 3.44 Å (sum of van der Waals radii = 3.44 Å).

Silver (I) sulfide

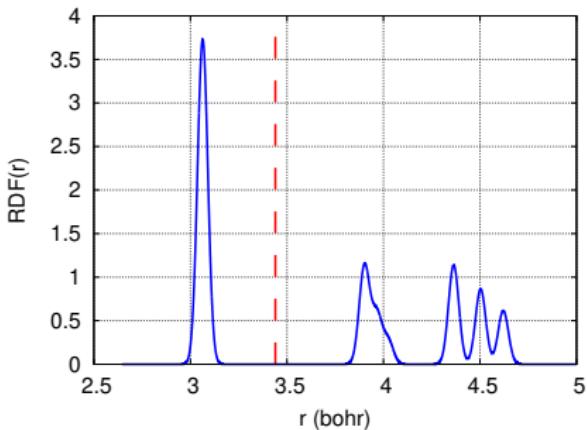
Experimental Ag-Ag RDF:



Ag-Ag (bohr):

5.583	5.969
5.665	5.991
5.753	6.455
5.783	6.473
5.945	

Calculated Ag-Ag RDF (PBE):



Ag-Ag (bohr):

5.789
5.791
5.787
5.794

Silver (I) sulfide

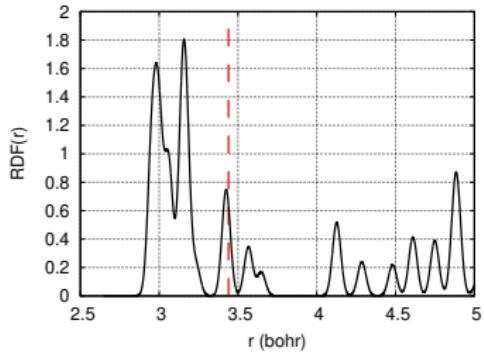
There is a significant effect caused by including **dispersion effects** in the calculation, because of the importance of Ag-Ag interactions:

Method	V_0 (a.u.)	B_0 (GPa)
Expt	1441.3	38
PBE-D3BJ	1522.9	22.8
PBE-D2	1626.1	39.9
PBE-D3	1641.7	32.0
PBE-XDM	1659.2	32.0
rVV10	1725.6	24.7
PBE	1811.6	17.2
vdW-DF1	1939.6	16.9
vdW-DF2	2010.4	19.5

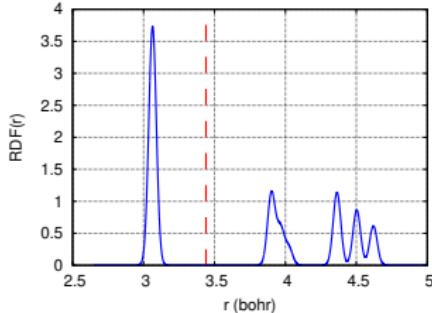
This is evidence of a large effect of **metallophilic interactions** on the equilibrium structure of this system.

Silver (I) sulfide

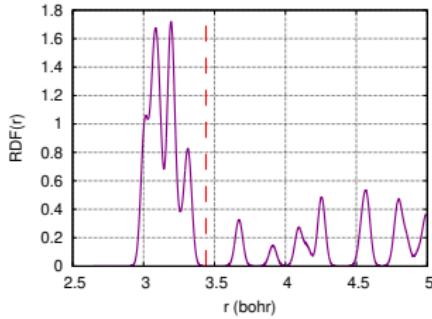
Experimental Ag-Ag RDF:



Without dispersion:



With dispersion (XDM):



The dispersion-corrected result is **correct (7-coordinated)** but the positions of the atoms and RDF depend on the type of dispersion correction.

Conclusions

XDM is a simple, efficient, accurate, and physically motivated dispersion functional.

Applications

- Lattice energies of molecular crystals.
- Layered materials.
- Surface adsorption.
- Enantiomeric excess in solution.
- Polymorph energy landscapes for molecular crystal structure prediction (CSP).
- Metallophilic effects.