Dispersion Interactions from the Exchange-Hole Dipole Moment.
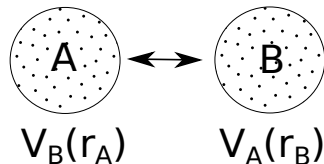
Alberto Otero-de-la-Roza and Erin R. Johnson

School of Natural Sciences, University of California, Merced, 5200 North Lake Road, Merced, California 95343, USA

XDM, basics

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

comes from **perturbation theory**:

$$E^{(2)} = \frac{\langle \hat{V}_{int}^2 \rangle}{\Delta E}$$

$$V_B(r_A) \qquad V_A(r_B)$$

where:

- Interaction between neutral fragments (classical electrostatic interactions already captured at semilocal level).
- Asymptotic expression.

Johnson, E. R. and Becke, A. D., *J. Chem. Phys.* **123** (2005) 024101

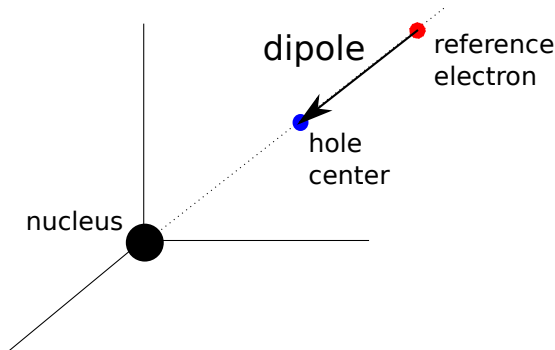Becke, A. D. and Johnson, E. R., *J. Chem. Phys.* **122** (2005) 154104, **127** (2007) 154108

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: $d_{x\sigma}(r) = \int r' h_{x\sigma}(r, r')dr' - r$
- Assumption: dipole oriented to nearest nucleus.
  $\langle M_l^2 \rangle_i = \sum_\sigma \int \omega_i(\mathbf{r}) \rho_\sigma(\mathbf{r})[r_i^l - (r_i - d_{X\sigma})^l]^2 d\mathbf{r}$.
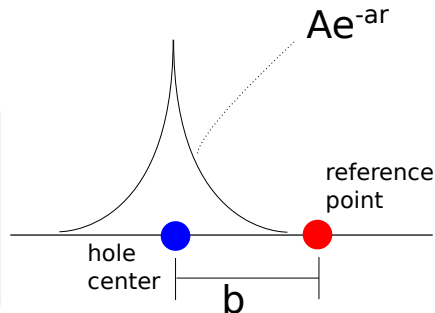
Becke, A. D. and Johnson, E. R., *J. Chem. Phys.* **122** (2005) 154104

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).*

Ae^{-ar}

reference point

hole center

b

Advantages:

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

Becke, A. D. and Roussel, M. R., *Phys. Rev. A* **39** (1989) 3761

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**:

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

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

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

We include: two-body terms C_6, C_8 and C_{10}.

Johnson, E. R. and Becke, A. D., *J. Chem. Phys.* **124** (2006) 174104

Implementation for molecules

XDM implemented post-**Gaussian 09** using the **postg** program. Also **nwchem** (available upon request).

From the wfn file, **postg** gives:

- XDM dispersion coefficients, volumes, polarizabilities
- XDM dispersion energy
- forces for geometry optimization (fixed coefficients)
- second derivatives for frequencies
- Hirshfeld charges

Download **postg** from the XDM page at:
http://faculty1.ucmerced.edu/ejohnson29

Kannemann, F. O. and Becke, A. D., *J. Chem. Theory Comput.* **6** (2010) 1081
Otero-de-la-Roza, A. and Johnson, E. R., *J. Chem. Phys.* **138** (2013) 204109

Implementation for solids

- PS/PW (**Quantum ESPRESSO**)

- Solids – Uniform 3D grid:
  - $d_{x\sigma}$, **valence** τ, ρ.
  - ω_i, **all-electron** ρ, ρ_{at}.

- Computational cost.
  - Comparable to DFT-D.
  - E_{disp} fast compared to E_{DFT}.

- Optimization: atomic forces and stresses.

Insensitive to grid density (CO_2)			
$n_{grid} =$	64	80	120
C_6 (C-C)	22.300	22.425	22.426
C_6 (O-O)	11.580	11.627	11.627
E_{disp} (Ry)	-0.062965	-0.063374	-0.063374

Otero-de-la-Roza, A. and Johnson, E. R., *J. Chem. Phys.* **136** (2012) 174109

Damping function parametrization

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

$$f_n(R_{ij}) = \frac{R_{ij}^n}{R_{ij}^n + (\mathbf{a_1} R_{ij,c} + \mathbf{a_2})^n}$$
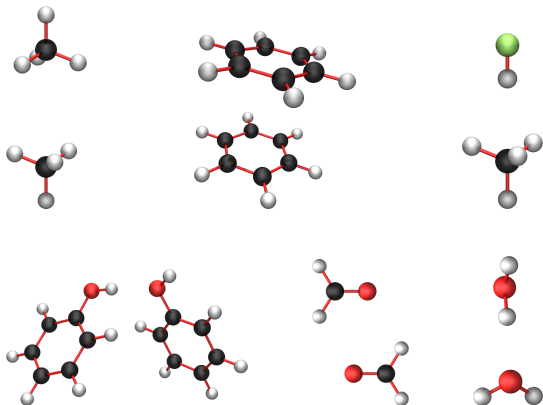
Kannemann-Becke 65-set.
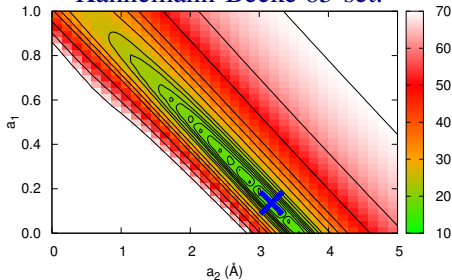
Supercell calculations.
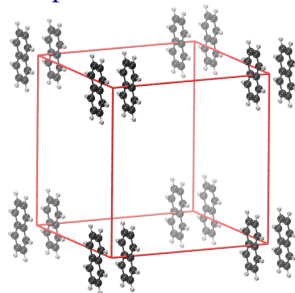
Parametrization set

49 gas-phase dimers from Kannemann and Becke; JCTC **6** (2010) 1081.

- noble gases
- dispersion
- π-stacking
- dipole - induced dipole
- mixed
- dipole - dipole
- hydrogen-bonding

Statistics of the fit (solids)

*Statistics for **supercell (PS/PW)** and **Gaussian** calculations.*

	Training set (KB49)				
	B86bPBE	*PW86PBE*		*BLYP*	
a_1	*0.684*	*0.407*	*0.934*	*0.267*	*0.774*
a_2(Å)	*1.368*	*2.415*	*0.965*	*2.227*	*0.839*
MAE (kcal/mol)	*0.41*	*0.46*	*0.42*	*0.41*	*0.31*
MAPE	*11.3*	*13.8*	*11.8*	*14.3*	*9.8*
	S22				
MAE (kcal/mol)	*0.43*	*0.46*	*0.35*	*0.32*	*0.22*
MAPE	*7.00*	*8.12*	*5.92*	*8.24*	*4.85*

Statistics of the fit (molecules)

XDM with aug-cc-pVTZ; mean absolute errors in kcal/mol.

Pure functionals:

Quantity	BLYP	PW86	PBE
MAE	0.31	0.40	0.50
MA%E	9.8	11.8	14.3

Hybrid and range-separated functionals:

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

Role of exchange

The exact exchange potential decays as $-1/r$ far from a molecule.

In terms of the exchange hole, h_X remains on the molecule as the reference point moves away from it.

The $-1/r$ asymptotic dependence was used to design the B88 exchange functional.

Functionals based on B88 or range-separated hybrids with the full exact-exchange limit (LC-ωPBE) give more accurate intermolecular exchange contributions.

Benchmark sets

Mean absolute errors in XDM binding energies with aug-cc-pVTZ

(kcal/mol)	BLYP	PW86	B3LYP	LC-ωPBE
S22	*0.22*	*0.35*	*0.31*	*0.31*
S66	*0.22*	*0.29*	*0.25*	*0.20*
HSG	*0.20*	*0.17*	*0.12*	*0.23*

S22 and HSG reference data: Marshall *et al.* JCP **135** (2011) 194102.

S66 reference data: Rezac *et al.* JCTC **7** (2011) 2427.

See JCP **138** (2013) 204109 for additional data.

Graphite

Otero-de-la-Roza, A. and Johnson, E. R., *J. Chem. Phys.* **136** (2012) 174109

A. Otero & E. Johnson (UC Merced) XDM ACS Meeting (April 2013) 15 / 29
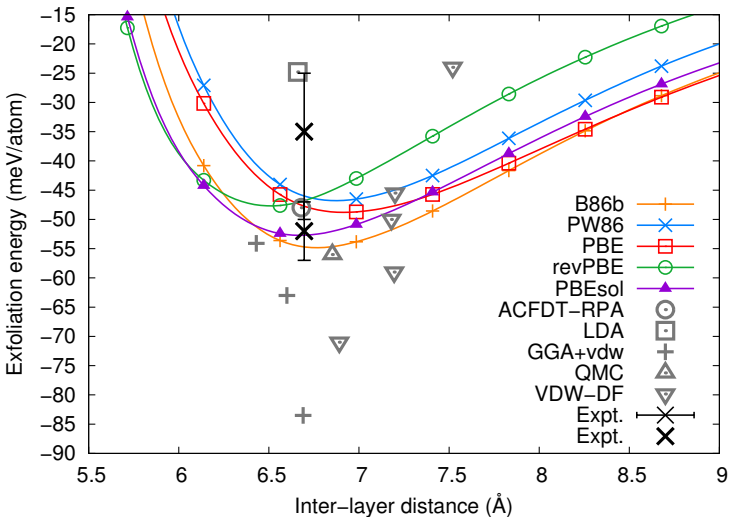
Prediction of sublimation enthalpies

Benchmark:

- No reference wave-function data.
- Experimental **sublimation enthalpies** not directly comparable.

- 21 crystals, small systems, low polymorphism.
- Well known sublimation enthalpies at or below room temperature.
- Different intermolecular interactions.

ΔH_{sub}: zero-point and thermal correction

$$\Delta H_{sub}(V, T) = E_{el}^{mol} + E_{trans} + E_{rot} + E_{vib}^{mol} + pV$$
$$- \left(E_{el}^{crys} + E_{vib}^{crys} \right)$$

- $E_{\text{el}}^{\text{crys}} \longrightarrow$ DFT+dispersion
- $E_{\text{el}}^{\text{mol}} \longrightarrow$ DFT+dispersion, supercell
- $E_{\text{trans}} + E_{\text{rot}} + pV \longrightarrow 4RT$ ($7/2RT$)
- Rigid molecule approximation $E_{\text{vib}}^{\text{mol}} = E_{\text{vib}}^{\text{crys}}$ for intramolecular
- Intermolecular $E_{\text{vib}}^{\text{crys}} \longrightarrow$ Dulong-Petit $6RT$ ($5RT$)
- Zero-point vibrational contributions neglected
- Approximations tested for CO_2 crystal. Average experimental accuracy ≈ 1 kcal/mol.

Sublimation enthalpies

(kJ/mol)		XDM		DFT-D2	TS09	vdw-DF	
	B86b	PW86	PBE	PBE	PBE	v1	v2
MAE	4.81	6.50	5.35	9.05	16.97	10.22	10.11
MAPE	6.23	8.00	6.74	11.94	22.08	13.53	13.11
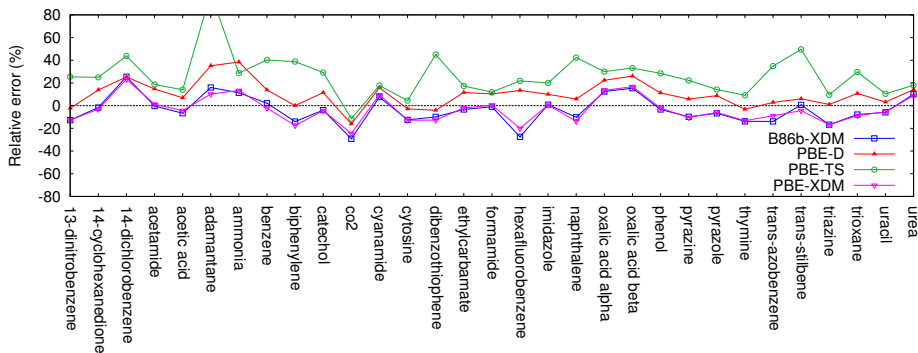
Otero-de-la-Roza, A. and Johnson, E. R. *J. Chem. Phys.* **137** (2012) 054103

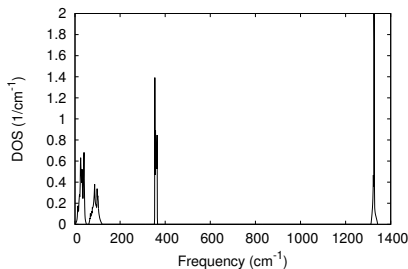## Prediction of crystal structures

- Vibrational Helmholtz free energy:

$$F_{\text{vib}}(V, T) = \sum_{j=1}^{3n} \left[\frac{\omega_j}{2} + k_B T \ln \left(1 - e^{-\omega_j/k_B T} \right) \right]$$

- Thermal pressure:

$$p_{\text{th}} = -\frac{\partial F_{\text{vib}}}{\partial V}$$

- Equilibrium condition:

$$\frac{\partial E}{\partial V} = p_{\text{th}} = -p_{\text{sta}}$$

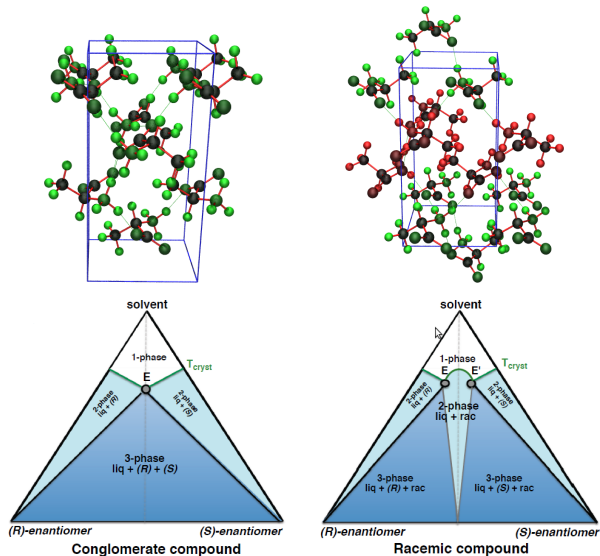**Relax the crystal under negative pressure p_{th}**

Crystal structures
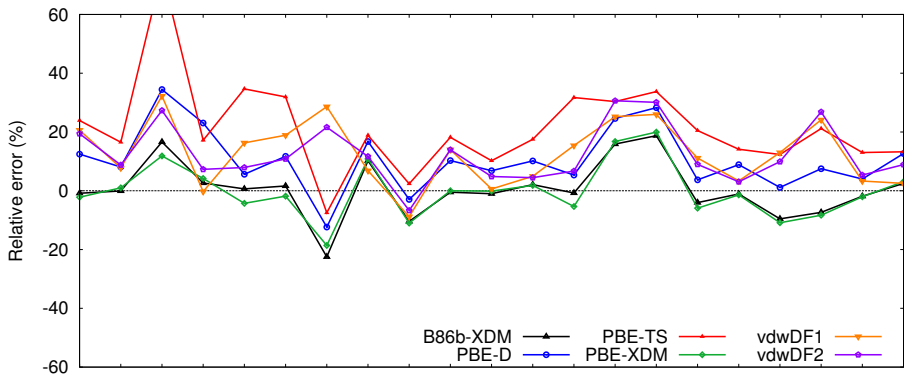
		XDM		DFT-D2	TS	vdw-DF	
(a.u.)	B86b	PW86	PBE	PBE	PBE	v1	v2
MAE	0.12	**0.06**	0.20	0.11	0.10	0.31	0.14
MAPE	1.76	**0.90**	2.75	1.31	1.58	4.40	1.88

Otero-de-la-Roza, A. and Johnson, E. R. *J. Chem. Phys.* **137** (2012) 054103

Enantiomeric excess of amino-acids

Conglomerate compound

Racemic compound

Enantiomeric excess of amino-acids

A simple model

- Same solvation energies.
- Same crystal temperature effects.
- $\Delta E = E_{dl} - E_l$
- Predicted ee:

$$ee = \frac{\beta^2 - 1}{\beta^2 + 1} \times 100$$

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

Amino acid	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

Enantiomeric excess
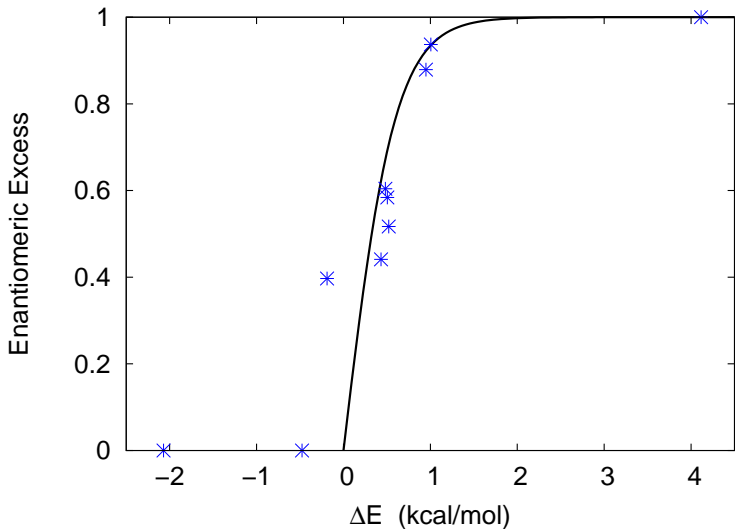
Electrides

An electride is an ionic substance in which a localized electron acts as an anion.

Existing electrides require a cage like structure to stabilise the cation: crown ethers and cryptands.

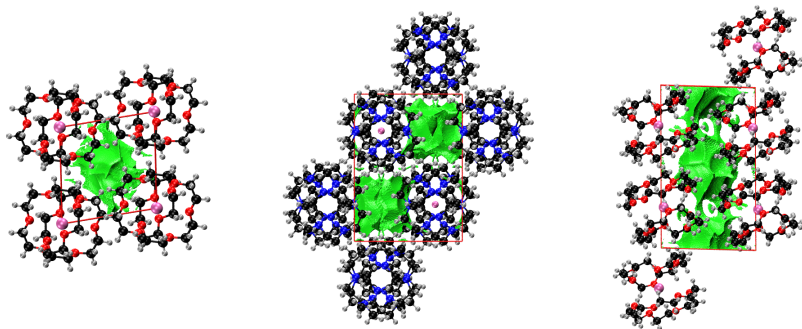High magnetic susceptibilities, variable conductivities, very strong reducing agents.
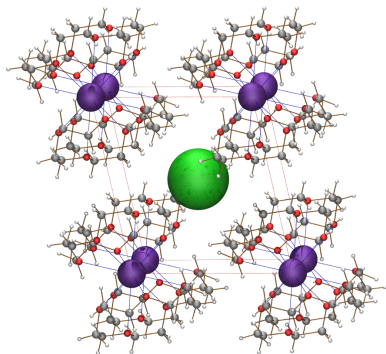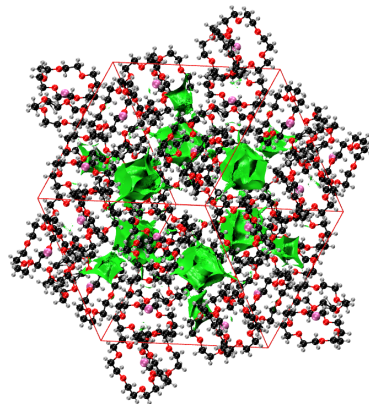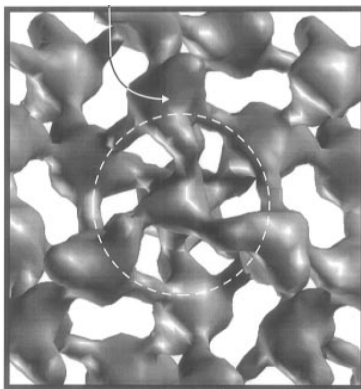
Electrides

Use the NCI index to visualize the electrons - JACS **132** (2010) 6498.

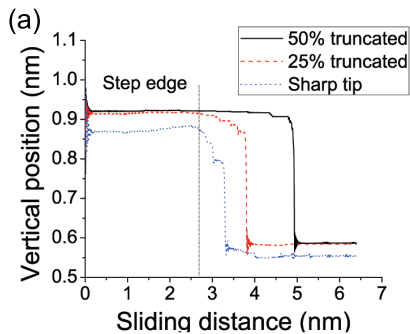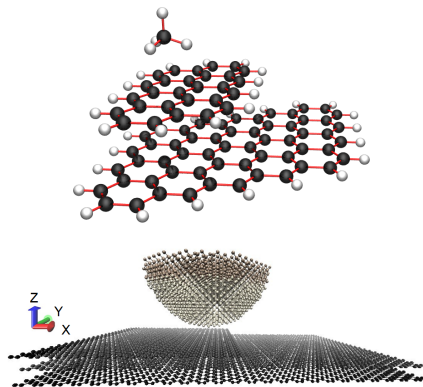Plots regions with low electron density and reduced density gradient.

Electrides

J. L. Dye used van der Waals radii to generate approximate channels and vacancies of electrons - JACS 1996, **118** (1996) 7329.
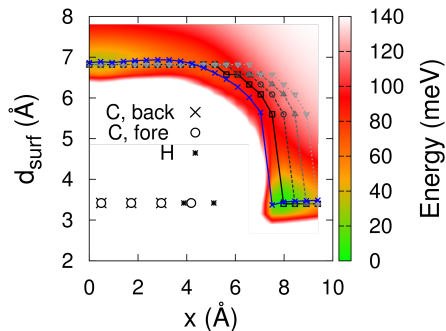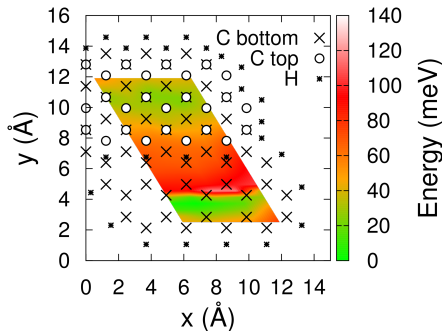
Graphite step edges

Ye, Zhijiang et al. *Appl. Phys. Lett.*, (2013) (in press).

Graphite step edges

Summary

1. XDM implemented for gas-phase and solid-state.
2. Excellent benchmarking results.
3. Very accurate lattice energies and crystal geometries.
4. Accurate enough to predict ee in solution.
5. More: electrides, tribology,...

Download **postg**, QE+XDM, and CRITIC2 from:

http://faculty1.ucmerced.edu/ejohnson29