

Michigan Tech University - Washington State University - University
of Torino

**Ab initio Simulation of Crystalline Systems
ASCS2006**

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Total energy and related quantities

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Outline

Introductory remarks

- Total energy and accurate calculations
- Energy differences and Energy derivatives
- Sources of error

Energy differences: case studies

- Relative stability of silica polymorphs
- Formation energy of the $\text{BeO}:[\text{Li}]^0$ defect
- Relative stability of $\alpha\text{-Al}_2\text{O}_3$ surfaces
- Structure and cohesive energy of crystalline urea

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Accurate calculations in computational chemistry

- The accuracy needed is a relative matter that must be considered for each problem
- The accuracy required in treating larger systems is often lower than with, say diatomics (although not always)
- A celebrated target is 1 kcal/mol (chemical accuracy), but it is better to decide on the accuracy required by considering what the results will be for
- Much of our work is based on *energy differences*

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Fundamentals approximations



$$H\Psi(\mathbf{r}, t) = i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t}$$

- Time independent Schrödinger equation
- Born-Oppenheimer approximation
- Relativistic effects are neglected
- Neglect of higher order effects (e.g. spin-orbit interaction)
- No excited states \Rightarrow **Ground state** (E_0, Ψ_0, ρ_0)

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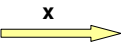



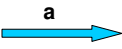
Total energy

- Total energy (and quantities related to it) is in most cases the most important result of the calculation
- Energy is a measure of the quality of the wavefunction
- Good energy does not mean good result for other observables
- Size-extensivity (scaling of the energy with respect to the number of electrons)

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Total energy and related quantities

| | | | |
|-------|---|---|--|
| E |  | Energy differences | <div style="border: 1px solid black; padding: 5px; width: fit-content;"><p>x: atomic coordinates V: unit cell volume a: lattice parameters</p></div> |
| E' |  | Forces (geometry optimisation) | |
| E' |  | Pressure | |
| E'' |  | Force constants (vibrational frequencies) | |
| E'' |  | Bulk modulus | |
| E'' |  | Elastic constants | |

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Total energy calculation in periodic codes

Four main sources of error:

1. Hamiltonian (HF, DFT) (Dispersive forces?)
2. Basis set (... truncated)
3. Numerical approximations (numerical integrations, series truncation, ...)
4. Bugs

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Hamiltonian

Which is the best choice?

Still a matter of debate:

- Molecular quantum chemist would prefer hybrid methods (e.g. B3LYP)
- Many solid state physicists would prefer LDA, GGA or mGGA, or ... and consider HF *completely wrong*
- Post-HF techniques? (see CRYSCOR project – S. Casassa)
- There is not a sharp answer
- Performances vary from system to system
- Experience from molecular quantum chemistry is not fully transferable (different type of bonding)

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Basis set

A gaussian basis set reduces enormously the size of matrices with respect to a plane-wave basis, but requires a careful re-optimisation

In energy differences the basis of system1 and system2 must be of *equivalent* variational quality (e.g. atomic energies in cohesive energy)

Basis sets of different extent are required in order to have good results for different properties (see case studies)

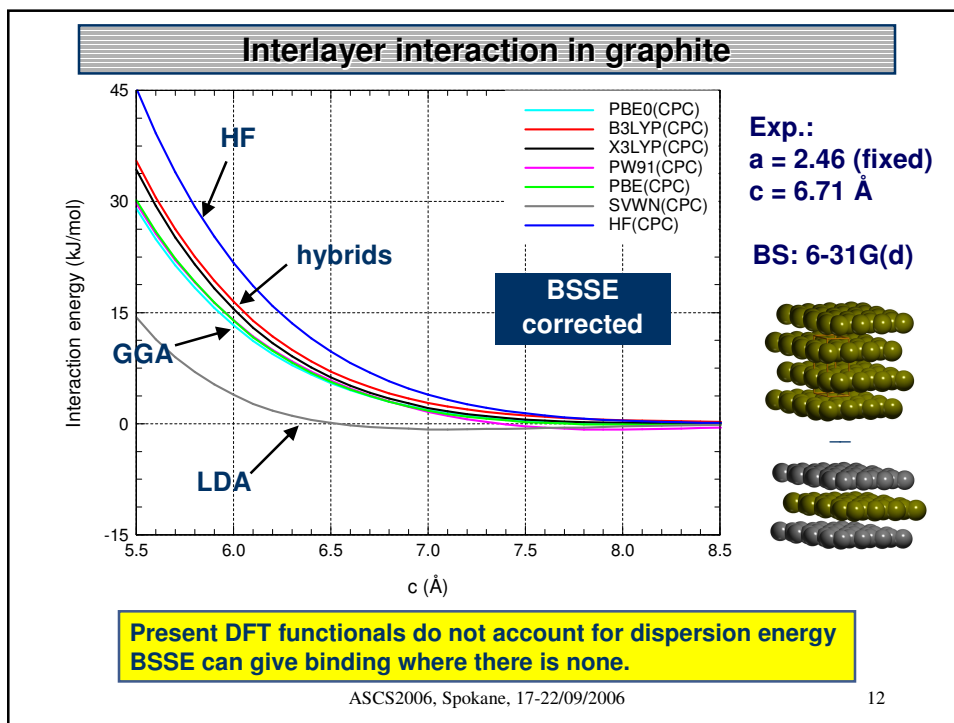
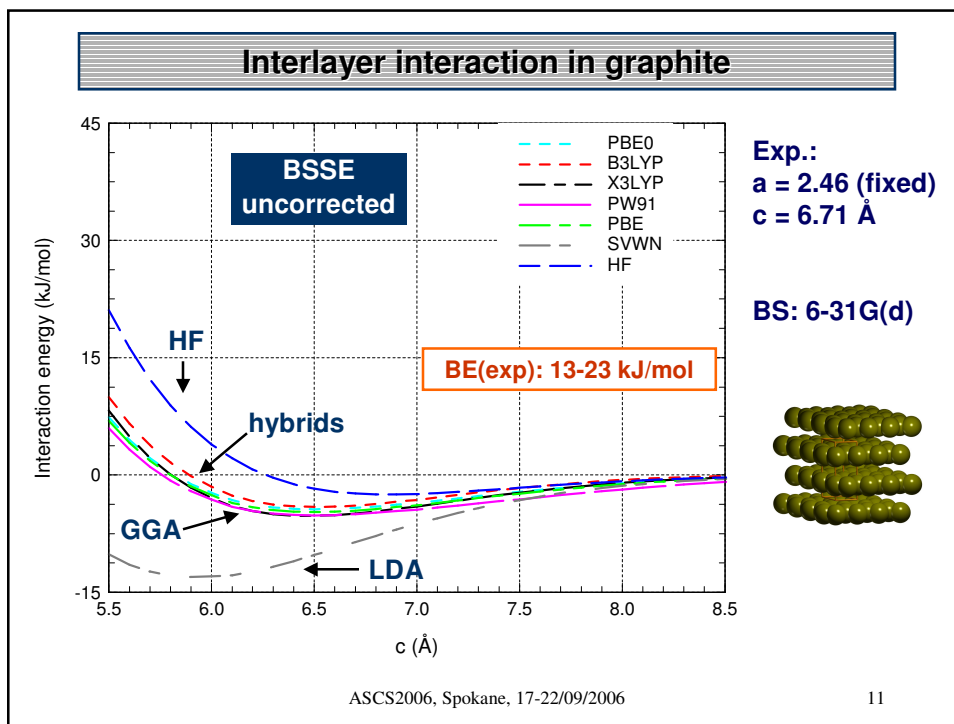
Basis set superposition error (BSSE)

Basis Set Superposition Error (BSSE)

In calculation on system AB with a finite basis set, the description of fragment A will be improved by the functions on fragment B, and viceversa

This effect will lower the energy, implying extra binding between A and B. It may even suggest binding where there is none

Most commonly estimated and analyzed (a posteriori) via the *counterpoise correction*: compute the fragment energies not in the individual basis set (A or B) but in the total basis set (A[B], B[A] – ghost functions)



Energy differences

| Computed energy | System1 | System2 | Example |
|----------------------|--------------------|----------------|--|
| Cohesive | Bulk | Atoms | Ionic, covalent crystals |
| Interaction | Bulk | Molecules | Molecular crystals |
| Relative stability | Bulk | Bulk | Polymorphism |
| Solid state reaction | Bulk | Bulk | $\text{MgO} + \text{Al}_2\text{O}_3 \rightarrow \text{MgAl}_2\text{O}_4$ |
| Superexchange | AFM bulk | FM bulk | NiO |
| Surface | Bulk | Slab | MgO(100) |
| Surface stability | Slab | Slab | MgO(100) vs MgO(110) |
| Interface | Slab | Slabs | MgO monolayer on Ag(100) |
| Adsorption | Slab + molecule | Slab, molecule | CO on MgO(100) |
| Adsorption | Bulk (microporous) | molecule | NH_3 in acidic zeolites |
| Substitution | Bulk with defect | Bulk, atoms | C in Si |

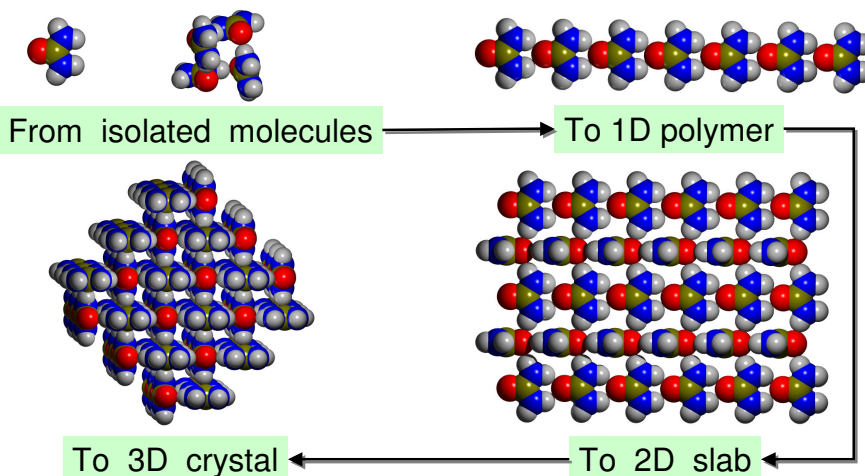
Reliable? It depends...

- Required accuracy
- Big or small numbers
- BSSE (e.g. molecular crystals, adsorption, ...)
- Often System1 and System2 have different dimensionality

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CRYSTAL code: range of applicability



All cases are treated in a consistent way!

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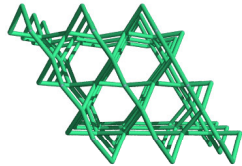
Relative stability of silica polymorphs

In silica the linearization barrier for Si-O-Si is close to zero

A large number of different all-silica polymorphs exists (from dense phases to microporous and mesoporous structures)

At the static limit α -Quartz is the most stable polymorph

For microporous polymorphs, The experimental range of stability with respect to α -Quartz is from 5 to 16 kJ/mol

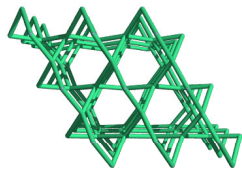


α -Q

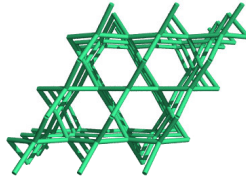
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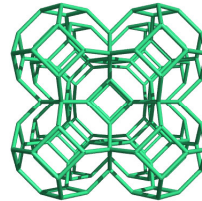
Dense and microporous silica polymorphs



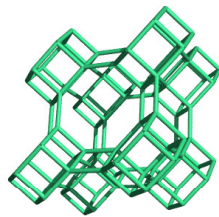
α -Q



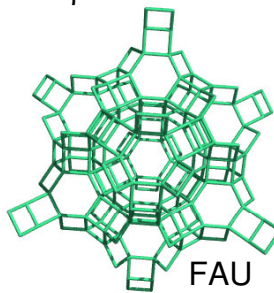
β -Q



SOD



CHA



FAU

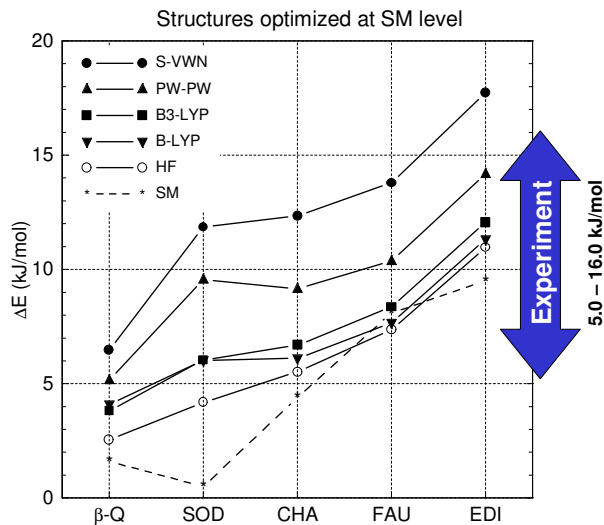


EDI

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Relative stability of silica polymorphs



- DFT//SM energy
- HF, BLYP, B3LYP similar
- LDA overestimates the instability
- SM//SM critical for SOD
- DFT GGA and B3LYP in good agreement with experiment

B. Civalleri, *et al.*, *Chem. Phys. Lett.* 292 (1998) 394

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Dense silica polymorphs relative stability

| Method | α -Cristobalite | α -Tridymite |
|---------------|------------------------|---------------------|
| HF | 0.0 | 1.5 |
| HF+corr | 2.2 | 3.5 |
| SVWN | 9.3 | 12.6 |
| B3LYP | 1.4 | 4.0 |
| HF//SM-HF | 0.5 | 1.8 |
| B3LYP//SM-B3 | 0.9 | 3.3 |
| HF//SM-Exp | -1.1 | -0.5 |
| B3LYP//SM-Exp | 2.4 | 3.7 |
| SM-HF | -3.8 | -3.0 |
| SM-B3 | 1.6 | 7.4 |
| SM-Exp | 3.5 | 4.9 |
| Experiment | 2.8±2.2 | 3.2±2.6 |
| Experiment' | 2.6 | 2.9 |

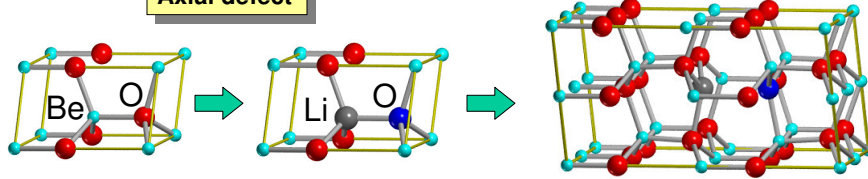
Relative energies with respect to α -Quartz (kJ/mol/SiO₂)

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M. Catti, B. Civalleri, P. Ugliengo, *J. Phys. Chem. B* 104 (2000) 7259

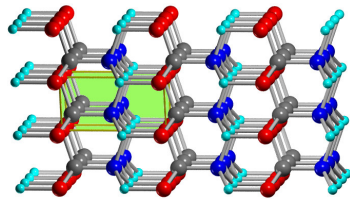
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[Li]⁰ center in beryllium oxide

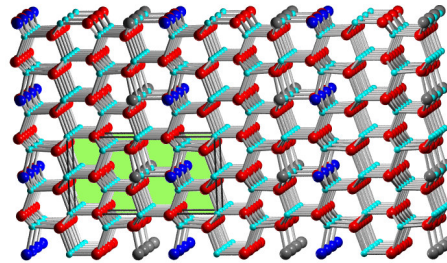
Axial defect



Defect-defect interactions?



High density defective system



Low density defective system

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BeO:[Li]⁰: effect of the supercell size

Axial defect

UHF

$$\Delta E = (E_{\text{def}} + E_{\text{Be}}) - (E_{\text{per}} + E_{\text{Li}})$$

| Supercell | | $E_{\text{tot}}(\text{BeO})$ | E_{BeO} | $E_{\text{tot}}(\text{BeOLi})$ | ΔE |
|------------------|---------|------------------------------|------------------|--------------------------------|------------|
| S ₃₂ | (2 2 2) | -1435.23633 | -89.70227 | -1427.83826 | 0.25818 |
| S ₄₈ | (2 2 3) | -2152.85450 | -89.70227 | -2145.45400 | 0.26061 |
| S ₆₄ | (2 2 4) | -2870.47266 | -89.70227 | -2863.07115 | 0.26162 |
| S ₇₂ | (3 3 2) | -3229.28175 | -89.70227 | -3221.89975 | 0.24211 |
| S ₁₀₈ | (3 3 3) | -4843.92262 | -89.70227 | -4836.53959 | 0.24314 |
| S ₁₄₄ | (3 3 4) | -6458.56349 | -89.70227 | -6451.18019 | 0.24341 |
| S ₁₈₀ | (3 3 5) | -8073.20437 | -89.70227 | -8065.82080 | 0.24368 |
| S ₂₁₆ | (3 3 6) | -9687.84524 | -89.70227 | -9680.46139 | 0.24396 |
| S ₂₅₂ | (3 3 7) | -11302.48612 | -89.70227 | -11295.10206 | 0.24417 |
| S ₁₂₈ | (4 4 2) | -5740.94533 | -89.70227 | -5733.56656 | 0.23888 |
| S ₁₉₂ | (4 4 3) | -8611.41799 | -89.70227 | -8604.03731 | 0.24079 |
| S ₂₅₆ | (4 4 4) | -11481.89066 | -89.70227 | -11474.50982 | 0.24095 |
| S ₃₀₀ | (5 5 3) | -13455.34061 | -89.70227 | -13447.96104 | 0.23968 |

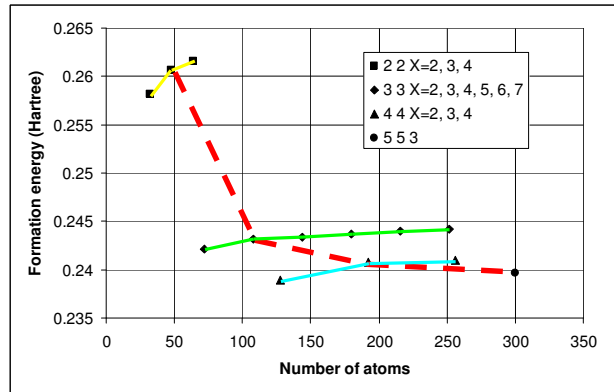
$E_{\text{BeO}} = -89.70227$; $E_{\text{Be}} = -14.56948$; $E_{\text{Li}} = -7.42959$

Energies in Hartree

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BeO:[Li]⁰: effect of the supercell size



Axial defect

UHF

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Surface formation energy

$$E_{surf} = \frac{E_{slab} - E_{bulk}}{2A}$$

E_{slab} = Total energy of the slab

E_{bulk} = Total energy of the perfect crystal

A = Area of the two-dimensional cell

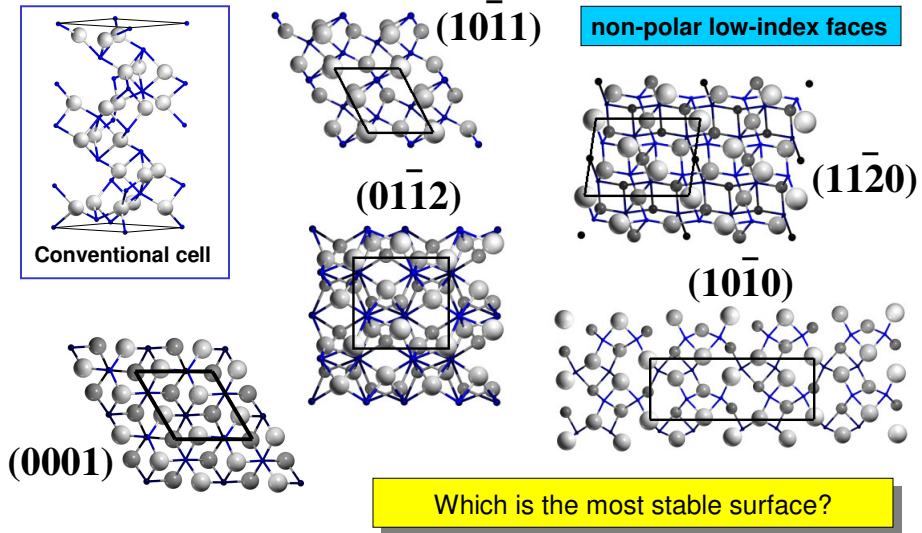
Check for:

- Slab thickness
- Relaxation and reconstruction effects

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Relative stability of different surfaces of $\alpha\text{-Al}_2\text{O}_3$



G. Mallia, B. Civalleri, R. Orlando, R. Dovesi, unpublished

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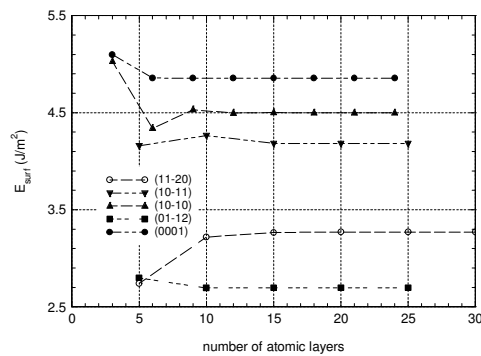
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Relative stability of different surfaces of $\alpha\text{-Al}_2\text{O}_3$

RHF - Al: 85-11G(d), O: 8-411G(d)

Effect of the slab thickness

Unrelaxed



Order of stability

$(01-12) < (11-20) < (10-11) < (10-10) < (0001)$

J/m^2

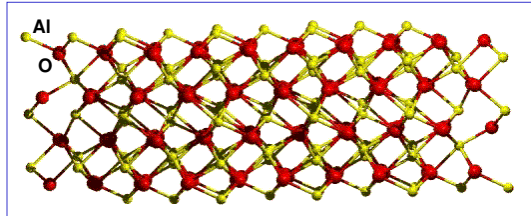
2.696 3.270 4.183 4.498 4.854

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Relaxation effects in $\alpha\text{-Al}_2\text{O}_3(0001)$

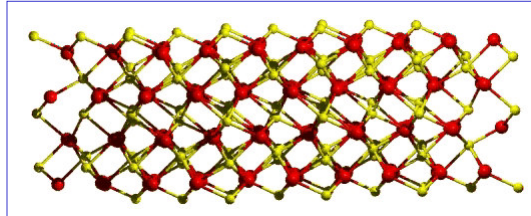
unrelaxed



$\alpha\text{-Al}_2\text{O}_3(0001)$

12 layer slab model

relaxed



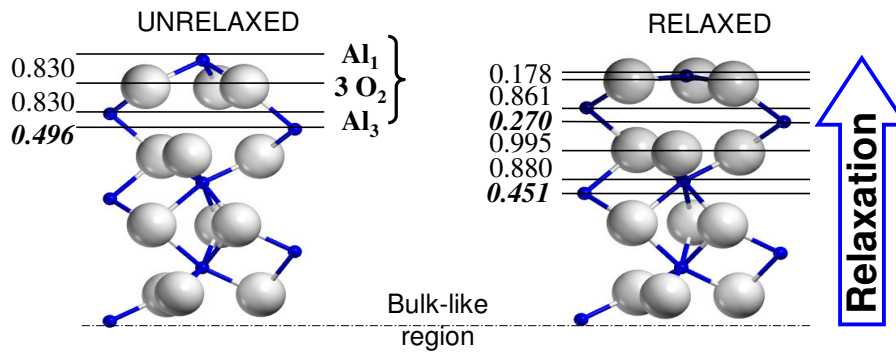
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Relaxation effects on $\alpha\text{-Al}_2\text{O}_3(0001)$

HF

INTERLAYER DISTANCE (Å)



| | HF | LDA ^a | B3LYP ^a |
|--------------|-------|------------------|--------------------|
| d_{12} (%) | -78.6 | -89.2 | -81.9 |

^aJ.R.B. Gomes et al., Chem. Phys. Lett. 341 (2001) 412 (Numerical gradients)

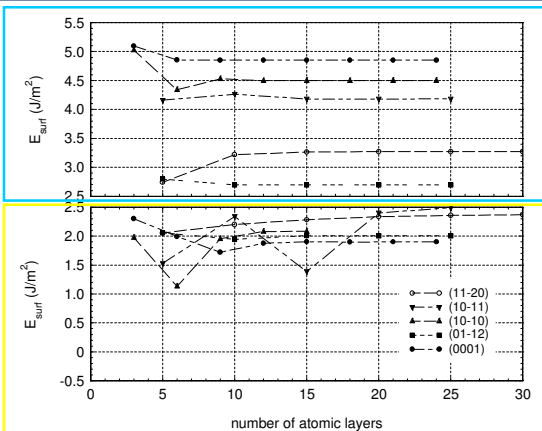
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Relaxation effects on surface stability

Unrelaxed

Relaxed



| Order of stability | relaxed | unrelaxed |
|--------------------|--|--|
| | (0001) < (10-12) < (10-10) < (11-20) < (10-11) | (01-12) < (11-20) < (10-11) < (10-10) < (0001) |
| | J/m ² | J/m ² |
| | 1.898 2.004 2.080 2.367 2.490 | |

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Cohesive energy in molecular crystals

$$\Delta E = \frac{E_{bulk}}{n} - E_{mol}$$

E_{bulk} = total energy of the unit cell

E_{mol} = total energy of the molecule in gas-phase

n = nr. of molecules in the unit cell

ΔE can be considered as the energy of condensation of a molecule from gas-phase to the solid and can be compared to the experimental sublimation energy

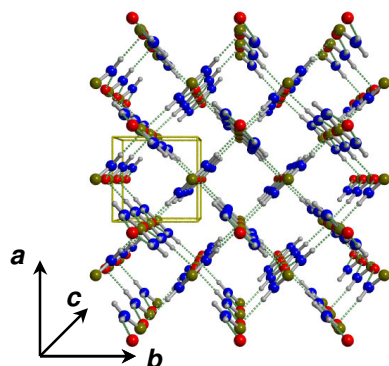
Check for:

- Relaxation effects
- Conformation energy of the molecule
- BSSE

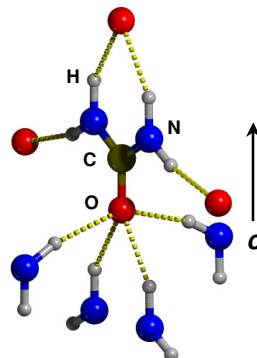
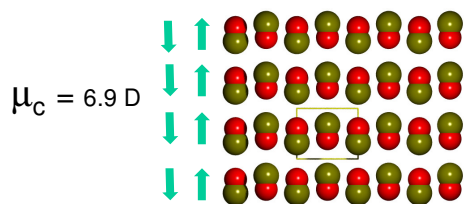
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Crystalline structure of urea



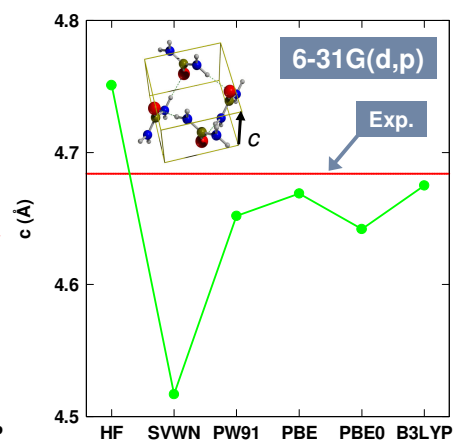
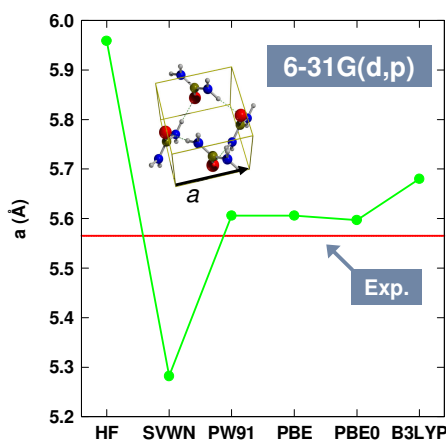
- SG: $P-42_1m$ (Tetragonal)
- Non-centrosymmetric
- 8 H-bonds per molecule
- Long-range dipole-dipole interactions
- Dispersion forces are not negligible



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Crystal cell parameters vs Hamiltonian



- Cell parameters are well reproduced by GGA and hybrid functionals
- In all cases the agreement is better for c than for a
- A very satisfactory performance of the hybrid approach, especially PBE0

Exp. data (NPD 12K): S. Swaminathan, B.N. Craven, R.K. McMullan *Acta Crystallogr.* **B40** (1984) 300

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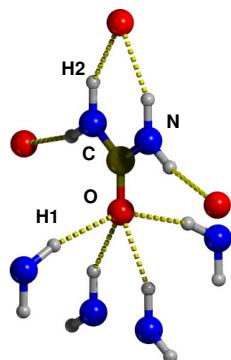
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Geometrical features vs Hamiltonian

| 6-31G(d,p) | HF | SVWN | PW91 | PBE | PBE0 | B3LYP | Exp. |
|------------|------|-------|------|------|------|-------|-------|
| C-O | -2.4 | 2.7 | 2.1 | 2.1 | 0.5 | 0.9 | 126.2 |
| C-N | -0.7 | -1.0 | 0.8 | 0.9 | -0.3 | 0.4 | 134.5 |
| N-H1 | -1.5 | 2.9 | 1.4 | 1.5 | 0.5 | 0.5 | 100.9 |
| N-H2 | -0.9 | 2.8 | 1.8 | 1.8 | 0.9 | 1.0 | 100.5 |
| H1...O | 29.9 | -23.6 | -0.7 | -0.5 | 1.1 | 6.2 | 199.2 |
| H2...O | 7.9 | -16.5 | -6.0 | -4.7 | -4.7 | -2.5 | 205.8 |

Deviations from experiment (in pm)

Basis: 6-31G(d,p) - 132 AOs x cell

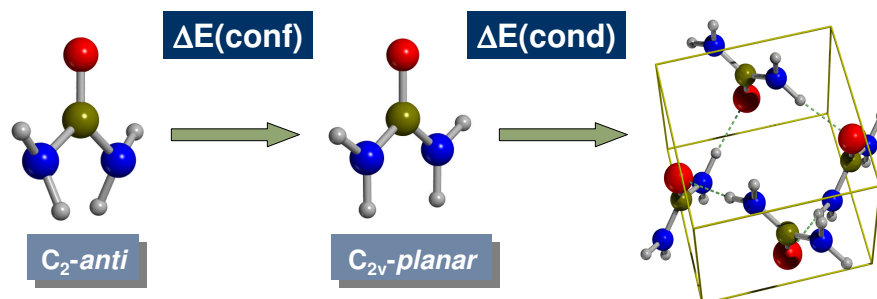


- HF largely overestimates H-bonds while LDA largely underestimates, both inadequate
- Pure GGA overestimate NH and underestimates H...O
- Hybrids improve over GGA

Exp. data (NPD 12K): S. Swaminathan, et al. *Acta Crystallogr.* **B40** (1984) 300
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Crystal formation energy



$$\Delta E = \Delta E(\text{cond}) + \text{BSSE} + \Delta E(\text{conf})$$

$$\Delta H^0(0) = \Delta E + \Delta \text{ZPE}$$

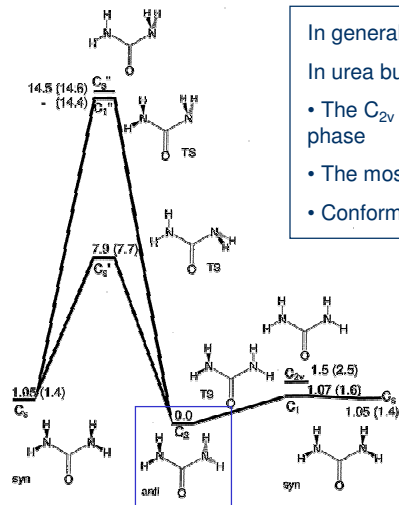
$$\Delta_{\text{sub}} H^0(298) = 87.7 \text{ kJ/mol}$$

K. Suzuki, et al. *Bull. Chem. Soc. Jpn.* **29** (1956) 127

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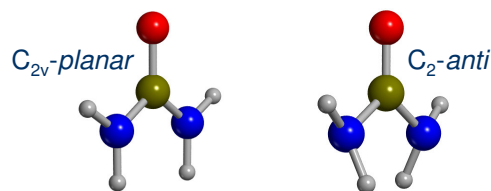
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Conformers of urea molecule



In general, for flexible molecules different conformers exist
 In urea bulk, molecules have a C_{2v} planar structure, but:

- The C_{2v} conformer is not a minimum on the PES in gas-phase
- The most stable is the C_2 -anti conformer
- Conformation energy must be taken into account



| HF(kJ/mol) | C_{2v} | C_s | C_2 |
|------------|----------|----------|----------|
| 6-31G(d,p) | 4.81 (2) | 4.37 (1) | 0.00 (0) |

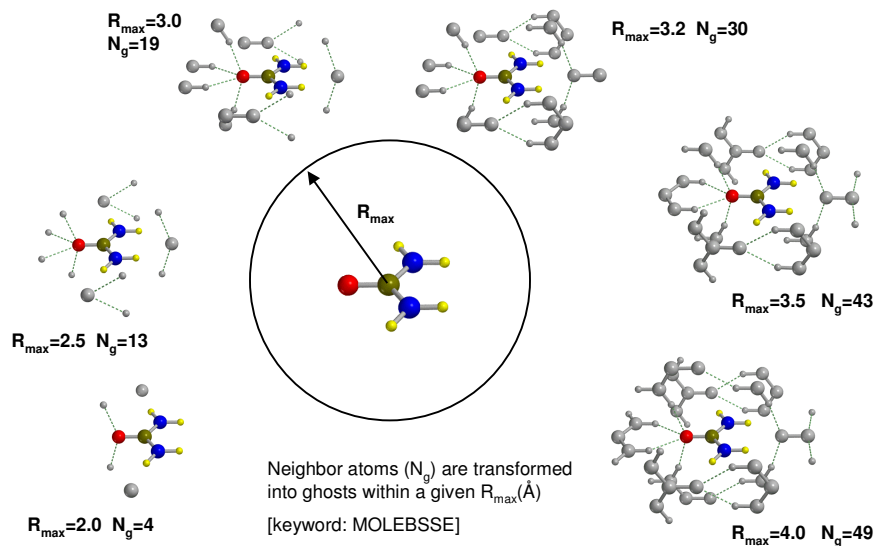
A. Masunov, J.J. Dannenberg, *J. Phys. Chem. A* **103** (1999) 178

In parentheses the number of imaginary frequencies is indicated

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CP correction in CRYSTAL

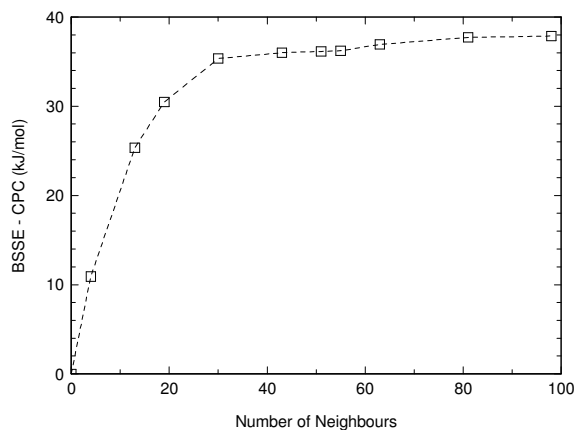


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CP correction dependence on R_{\max}

S-VWN/6-31G(d,p) - experimental geometry – energies in kJ/mol

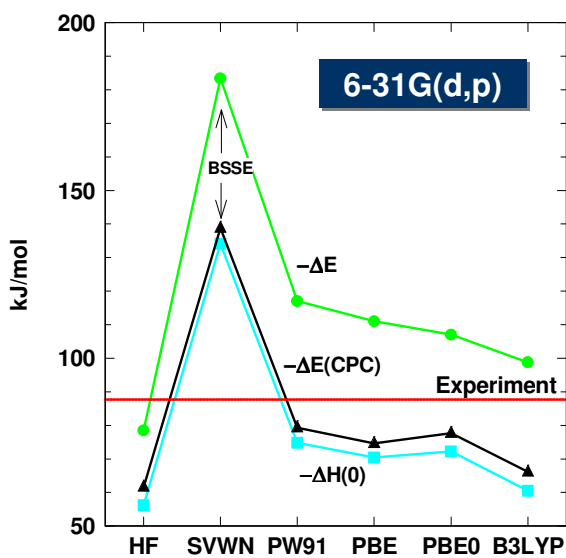


- Quite regular convergence of the CP correction with the number of ghosts
- At least 30 ghost atoms have to be included

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Interaction energy



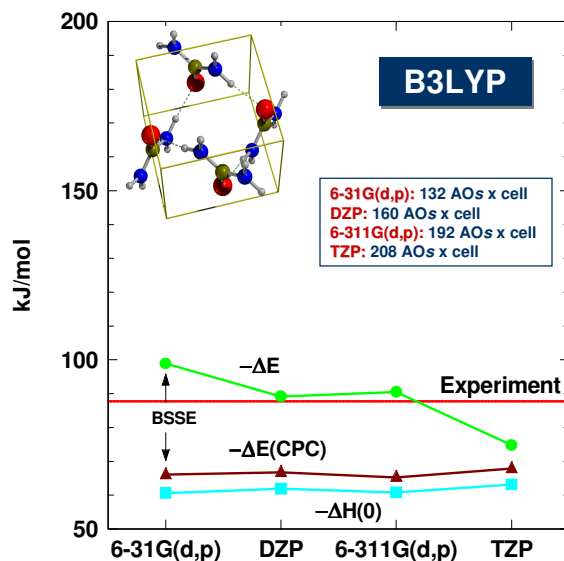
- Electron correlation increases the binding energy (LDA > GGAs > Hybrids)
- DFT methods suffer from a BSSE larger than HF
- Both GGA and hybrid methods underestimate $\Delta_{\text{sub}}H^0(298) = 87.7 \text{ kJ/mol}$
- The trend in binding energy is similar to hydrogen bonded molecular adducts
- DFT methods do not include dispersive interactions

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B3LYP interaction energy: effect of the basis set

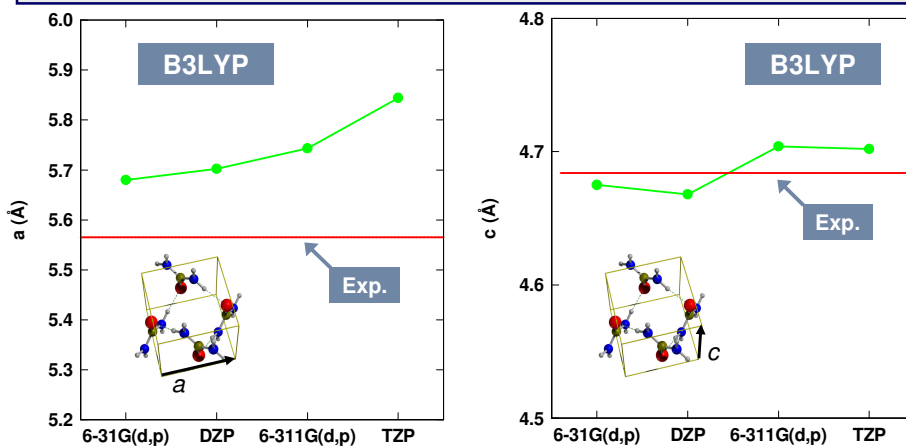
- Basis set mainly affects BSSE uncorrected condensation energy
- Enlarging the basis set reduces the BSSE, even if a very large basis set is needed to reduce it to 10% of ΔE
- Final BSSE corrected ΔH^0 is insensitive to the quality and the size of the basis set
- Trusting B3LYP ΔH^0 value, about 30 kJ/mol dispersive ($\Delta_{\text{sub}} H^0 = 87.7 \text{ kJ/mol}$)



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Crystal cell parameters vs basis set at B3LYP



- Basis set effects are marked on a while small on c
- The molecular geometry is still well reproduced
- Inter-chain H-bonds increase while intra-chain H-bonds in good agreement
- Behaviour for other functionals expected to be similar

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Gaussian BS vs Plane-Wave BS

| | PW91 AE TZP | PW91 [1] PAW (800 eV) | PBE AE TZP | PBE NC-TM (1200 eV) | Exp. [2] |
|------------|-------------------|-----------------------------|------------------|---------------------------|-------------|
| <i>a</i> | 5.759 (3.5) | 5.788 (4.0) | 5.765 (3.6) | 5.803 (4.3) | 5.565 |
| <i>c</i> | 4.700 (0.3) | 4.703 (0.4) | 4.701 (0.4) | 4.699 (0.3) | 4.684 |
| <i>c/a</i> | 0.816 (-3.1) | 0.812 (-3.6) | 0.816 (-4.4) | 0.810 (-3.8) | 0.842 |
| <i>V</i> | 155.9 (7.5) | 157.6 (8.6) | 156.3 (7.8) | 158.3 (9.1) | 145.1 |
| ΔE | | | 77.6 | 73.5 | |

- PP-PW calculations do not suffer from BSSE
- Good agreement between GTFs and PWs
- Results are independent of the computational approach (GTFs or PWs)
- *a* is in both cases markedly overestimated
- Errors due to inherently lack of dispersion forces in DFT

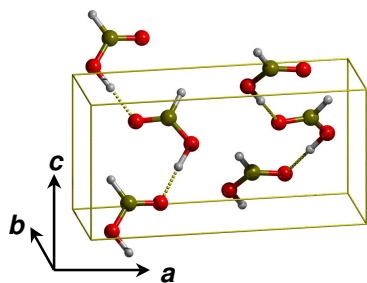
[1] T. Bucko, J. Hafner, J.G. Angyan, *J. Chem. Phys.* **122** (2005) 124508

[2] NPD (12 K): S. Swaminathan, B.N. Craven, R.K. McMullan *Acta Cryst.* **B40** (1984) 300

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Formic Acid: B3LYP/TZP



$$a = 11.3 \text{ (+10.4\%)}$$

$$b = 4.2 \text{ (+19.3\%)}$$

$$c = 5.4 \text{ (+0.8\%)}$$

$$\Delta H^0(0) = 35 \text{ kJ/mol}$$

- *a* and *b* largely overestimated (dispersion) while *c* (H-bonds) in good agreement
- $\Delta H^0(0)$ definitely underestimated with respect to $\Delta_{\text{sub}} H^0(298) = 60.5 \text{ kJ/mol}$
- Harmonic frequency shifts overestimated (anharmonic even worse)

$$\Delta\omega(\text{OH}) = 750 \text{ cm}^{-1}$$

$$\Delta\omega(\text{CO}) = 150 \text{ cm}^{-1}$$

$$\Delta\nu(\text{OH}) = 600 \text{ cm}^{-1}$$

$$\Delta\nu(\text{CO}) = 150 \text{ cm}^{-1}$$

Mikawa et al *J. Mol. Spect.* **24**, 314 (1967)

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Useful references

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