The CRYSCOR program: an overview

C. Pisani, L. Maschio, M. Halo, A. Erba, S. Casassa
M. Lorenz, D. Usvyat, M. Schütz
C. Zicovich-Wilson

MSSC2011 Turin, September 5-9, 2011
Electron Correlation (EC)

- Lowdin definition (1959):
  \[ E_{\text{corr}} = E_0 - E_{\text{HF}} \]

- the difference between the exact energy of the fundamental state \( E_0 \) and the Hartree-Fock energy \( E_{\text{HF}} \) calculated by means of the variational method.

- Within the HF framework we miss DYNAMIC correlation due to the lack of instantaneous correlation in the motion of the electrons.
Why Post-HF techniques are needed?

Despite the fact that EC is often a small percentage of the total energy, its evaluation can be of fundamental importance:

- in the evaluation of cohesive energies and relative stabilities in van der Waals solids, weak hydrogen bonds solids, molecular crystals;
- in the study of physisorption phenomena as adsorption of small molecules on ionic or covalent surfaces;
- for accurate estimation of one-electron properties that do not depend directly from the one-electron density function.

→ The HF limits are universally well known
HF and Physisorption phenomena

- He (2x2) monolayer interacting with a slab of MgO(100).
Cohesive energy ($\mu\text{Ha}$) as a function of the lattice parameter (Ang)

The CRYSCOR project: an overview

Turin, September 2011
Why Post-HF techniques are needed?

- Despite the fact that EC is often a small percentage of the total energy, its evaluation can be of fundamental importance:
  - in the evaluation of cohesive energies and relative stabilities in van der Waals solids, weak hydrogen bonds solids, molecular crystals;
  - in the study of physisorption phenomena as adsorption of small molecules on ionic or covalent surfaces;
  - for accurate estimation of one-electron properties that do not depend directly from the one-electron density function.

→ DFT is often able to predict accurate geometry and electron density but...

- does not correctly describe the van der Waals dispersion;
- does not allow for a systematic improvement of the results;
- need for parametrizations.

The CRYSCOR project: an overview

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DFT and Rare Gas Crystals

Cohesive energy ($\mu$Ha) as a function of the lattice parameter (Ang)

The CRYSCOR project: an overview

Turin, September 2011
DFT and the relative stability of cubic versus hexagonal BN

Calculated energy vs volume data for c-BN (left) and h-BN (right). In red BS-A (1d), in blue BS-B (3d, 1f).

For h-BN two curves are drawn in each case: the shallower one corresponds to changing c with a fixed at its experimental minimum, the other one vice-versa.

Functionals: PBE0, PBE, PBEsol.

+ Exp for c-BN
| Exp for h-BN

The CRYSCOR project: an overview
The CRYSCOR project: an overview

**DFT and the relative stability of Aluminium Hydroxides**

![DFT Diagram](image)

<table>
<thead>
<tr>
<th>Formula Unit</th>
<th>$\text{Al}_2\text{O}_3\text{(H}_2\text{O)}$</th>
<th>$\text{Al}_2\text{O}_3\text{(H}_2\text{O)}$</th>
<th>$\text{Al}_2\text{O}_3\text{(H}_2\text{O)}_3$</th>
<th>$\text{Al}_2\text{O}_3\text{(H}_2\text{O)}_3$</th>
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<td>$N_{\text{atoms}}$ per cell</td>
<td>16</td>
<td>8</td>
<td>56</td>
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<table>
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<tr>
<th>Technique</th>
<th>Mono-hydrates: (1)-(2)</th>
<th>Try-hydrates: (4)-(3)</th>
<th>Relative Stability at 0 K (kJ/mol $\text{Al}_2\text{O}_3$)</th>
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<tr>
<td>SVWN</td>
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<td>PW91</td>
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<td>Exp*</td>
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</table>

*Corrected for zero-point and thermal energy

* by courtesy of R. Demichelis
The CRYSCOR Project

aim at a public, improvable tool capabes, with few well established approximations, to perform post-HF calculations.

The Cryscor project started in Torino in the year 2000.

The first public version of Cryscor has be released in March 2009.

The Cryscor group is composed by:

Torino
Cesare Pisani
Silvia Casassa
Lorenzo Maschio
Migen Halo
Alessandro Erba

Regensburg
Martin Schütz
Denis Usvyat
Marco Lorenz

...with fundamental contributions by:

Roberto Dovesi
Fred Manby
Claudio Zicovich-Wilson

Turin, September 2011
The hierarchy of post-HF methods

Not saying anything about multiconfigurational methods ...

Perturbative techniques

<table>
<thead>
<tr>
<th>MP2</th>
<th>MP4</th>
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</table>

Convergence not Guaranteed

Coupled Cluster

<table>
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<tr>
<th>CC2</th>
<th>CCSD</th>
<th>CCSD(T)</th>
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</table>

“Full” CC

Configuration Interaction

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<tr>
<th>CIS</th>
<th>CISD</th>
<th>CIS(D)</th>
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<tbody>
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</tr>
</tbody>
</table>

“Full” CI
Second order Möller-Plesset Perturbation theory (MP2)

- It is inadequate in many respects: in particular, it is non-variational, but..

- is the simplest post-HF correlation technique,

- MP2 energy is size consistent;

- it provides an adequate treatment of long-range interactions, dispersive interaction, hydrogen bonds and so on;

- it allows the assessment of techniques, basis sets, etc., before introducing a more adequate treatment of short-range interactions (MP4, CCSD,..);

Post-HF methods are well known from decades, but never became routine, in solid state field, due to their tremendous computational cost.
Local Post-HF Methods

→ Since dynamical electron correlation is essentially a local effect, the huge scaling of post-HF methods is shown to be an artifact of their formulation in terms of canonical orbitals.

An efficient reformulation:
♥ in terms of local BASIS SETS
♥ adopting local criteria for reducing the variational space
♥ and local criteria for truncating summations

→ \( O(N^5) \rightarrow O(N) \)

\[
\text{can lean to linear scaling with respect to the size of the system.}
\]
Local MP2 for Periodic System
Exploitation of the SHORT-RANGE character of EC

LOCAL basis set to describe the occupied manifold

Wannier Functions (WFs), $\omega(r)$
Wannier Functions

WFs, $\omega_i^T(r)$ are obtained through a unitary transformation of the crystalline orbitals $\Psi_i(r, k)$:

$$\rightarrow \omega_i(r - T) = \frac{V}{2\pi^3} \int_{BZ} e^{ik T} \Psi_i(r, k) dk$$

$$\rightarrow \langle \omega_s^T | \omega_p^{T'} \rangle = \delta_{sp} \delta_{TT'}$$

$$\rightarrow \omega_s^T(r) = \omega_s^0(r - T)$$
Symmetrized Wannier Functions

MgO bulk, 8 valence electrons, 4 WFs centered on Oxygen

I bunch: A1
1 flower
1 petal

II bunch: T1
1 flower
3 petals
Symmetrized Wannier Functions

Hexagonal Argon, 2 atoms in the unit cell, 16 valence electrons.

8 WFs

IRREP A1
IRREP E
IRREP A2

I  bunch: 2 flowers, 2 petals
II bunch: 2 flowers, 4 petals
III bunch: 2 flowers, 2 petals
Exploitation of the SHORT-RANGE character of EC

- LOCAL basis set to describe the occupied manifold
  - Wannier Functions (WFs), $\omega(r)$

- LOCAL basis set to describe the virtual manifold
  - Projected Atomic Orbitals (PAOs): $\tilde{\chi}(r)$
Exploitation of the SHORT-RANGE character of EC

PAOs, \( \tilde{\chi}(r) \) are obtained by projecting out the occupied part from each atomic orbital \( \chi(r) \):

\[
\rightarrow |\tilde{\chi}(r)\rangle = (\hat{I} - \hat{P})|\chi(r)\rangle
\]
The LMP2 Equations

\[ E_2 = \sum_{ij} \sum_{ab} K_{ab}^{ij} (2T_{ab}^{ij} - T_{ba}^{ij}) \]

\[ K_{ab}^{ij} = \int \frac{\omega_i(r_1)\tilde{\chi}_a r_1}{r_{12}} \frac{1}{\omega_j(r_2)\tilde{\chi}_b r_2} dr_1 dr_2 = (i a| j b) \]

\[ = \sum_{\mu \nu \sigma} c_{i \mu}^{occ} c_{a \rho}^{vir} c_{j \nu}^{occ} c_{b \sigma}^{vir} (\mu \rho|\nu \sigma) \]

\[
K_{ab}^{ij} = \int \omega_i(r_1) \tilde{\chi}_a r_1 \frac{1}{r_{12}} \omega_j(r_2) \tilde{\chi}_b r_2 \, dr_1 \, dr_2
\]
The LMP2 Equations

\[ E_2 = \sum_{ij} \sum_{ab} K_{ij}^{ab} \left( 2T_{ab}^{ij} - T_{ba}^{ij} \right) \]

\[ K_{ij}^{ab} = (i a | j b) = \sum_{\mu \rho \nu \sigma} c_{i \mu}^{occ} c_{\alpha \rho}^{vir} c_{j \nu}^{occ} c_{b \sigma}^{vir} (\mu \rho | \nu \sigma) \]

\[ R_{ij}^{ab} = K_{ij}^{ab} + \sum_{cd} \left[ f_{ac} T_{cd}^{ij} S_{db} + S_{ac} T_{cd}^{ij} f_{dc} \right] - \sum_{cd} \sum_{k} \left( f_{ac} T_{cd}^{kj} + T_{cd}^{ik} f_{kj} \right) S_{cb} = 0 \]
The LMP2 Equations

\[ E_2 = \sum_{ij} \sum_{ab} K^{ij}_{ab} \left( 2T^{ij}_{ab} - T^{ij}_{ba} \right) \]

\[ K^{ij}_{ab} = (i a | j b) = \sum_{\mu \nu \sigma} c^{\text{occ}}_{i \mu} c^{\text{vir}}_{a \rho} c^{\text{occ}}_{j \nu} c^{\text{vir}}_{b \sigma} (\mu \rho | \nu \sigma) \]

\[ R^{ij}_{ab} = K^{ij}_{ab} + \sum_{cd} \left[ f_{ac} T^{ij}_{cd} S_{db} + S_{ac} T^{ij}_{cd} f_{dc} \right] - \sum_{cd} \left[ S_{ac} \sum_{k} (f_{ac} T^{k}_{cd} + T^{ik}_{cd} f_{kj}) S_{cb} \right] = 0 \]
The LMP2 Equations

\[ E_2 = \sum_{ij} \sum_{ab} K_{ab}^{ij} (2T_{ab}^{ij} - T_{ba}^{ij}) \]

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\[ R_{ab}^{ij} = K_{ab}^{ij} + \sum_{cd} [f_{ac} T_{cd}^{ij} S_{db} + S_{ac} T_{cd}^{ij} f_{dc}] - \sum_{cd} [S_{ac} \sum_{k} (f_{ac} T_{cd}^{kj} + T_{cd}^{ik} f_{kj}) S_{cb}] = 0 \]
Local MP2 Method in Periodic systems

\[ \sum_{ij} \rightarrow \sum_{iJ} \sum_{ab} \rightarrow \sum_{AB} \]

\[ R_{ij}^{ab} = K_{ij}^{ab} + \sum_{cd} \left[ f_{ac} T_{ij}^{cd} S_{db} + S_{ac} T_{ij}^{cd} f_{dc} \right] - \sum_{cd} \left[ S_{ac} \sum_{k} \left( f_{ac} T_{kj}^{cd} + T_{ik}^{cd} f_{kj} \right) S_{cb} \right] = 0 \]
Local MP2 Method in Periodic systems

\[ \sum_{ij} \rightarrow \sum_{iI_jJ} \quad \sum_{ab} \rightarrow \sum_{aA_bB} \]

\[ E_2 = \sum_{ij} \sum_{IJ} \sum_{ab} \sum_{AB} K_{il_jJ}^{iA_bB} (2 T_{il_jJ}^{iA_bB} - T_{il_jJ}^{iB_aA}) \]

\[ K_{il_jJ}^{iA_bB} = \sum_{\mu\nu\sigma} \sum_{MRNS} c_{i\mu}^{\text{occ}} c_{l\nu}^{\text{vir}} c_{aA}^{\text{occ}} c_{j\nu}^{\text{vir}} c_{bB}^{\text{vir}} S \left( \mu^M \rho^R | \nu^N \sigma \right) \]
Exploitation of the SHORT-RANGE character of EC

- LOCAL basis set to describe the occupied manifold
  - Wannier Functions (WFs), $\omega(r)$

- LOCAL basis set to describe the virtual manifold
  - Projected Atomic Orbitals (PAOs): $\tilde{\chi}(r)$

- truncation of the occupied space
  - Wannier-Wannier pairs (WW-pairs)

- reduction of the virtual space
  - Wannier domain and WW-pairs domain
Inside the Equations

An infinite crystal.
Inside the Equations

A bond WF.
PAOs centered on the selected ATOMS are included in WF domain.
Inside the Equations

\[ E_2 = \sum_{ij} \sum_{ab} \cdots \rightarrow E_2 = \sum_{i (j < \text{dist})} \sum_{ab \in (ij)} \]
Inside the Equations

$$E_2 = \sum_{ij} \sum_{ab} \sum_{IJ} \sum_{AB} \ldots \rightarrow \sum_{ij} \sum_{ab\in(ij)} \sum_{0(J<d)} \sum_{A\in0} B_{\in J}$$
Inside the Equations

The calculations are performed inside a cluster, around the reference cell: exploitation of translational symmetry.
Only irreducible quantities are evaluated: exploitation of point symmetry.
The Code
The CRYSTAL-CRYSCOR suite of programs

CRystal
- Symmetry analysis
- AO Fock matrix
- AO Density matrix
  - Eigenvalues
  - Eigenvectors

PropertiEs
- Band structure, DOS
- Localization (WF)
- Charge density
- X-ray factors
- Momentum density
- Compton profiles
- Other Properties

CRYScor
- MP2 energy
- MP2 amplitudes
- MP2 correction to density matrix
The CRYSTAL-CRYSCOR suite of programs

CRYSTAL

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PROPERTIES

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PROPERTIES
- Band structure, DOS
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- Momentum density
- Compton profiles
- Other Properties
\[
\omega_i(r - T) = \frac{V}{2\pi^3} \int_{\text{BZ}} e^{i k T} \Psi_i(r, k) \, dk
\]

NEWK
8 8 8
LOCALWF
SYMMWF
..
..
\[ \omega_i(r) = \sum_{\mu g} c_i^g \chi_i(r - g) \]

KNET
8
MEMORY
4000
TOBJ
0.001 0.001
..
\[ \langle \tilde{\chi}(r) \rangle = (\hat{I} - \hat{P})\chi(r) \]

KNET
8
MEMORY
4000
.. 
..

The Code
Turin, September 2011
Flow Chart

\[ \rightarrow |\chi(\vec{r})\rangle = \sum_{ag} c_g^a \chi_a(r - g) \]

KNET
8
MEMORY
4000
TOBJ
0.001 0.001
..
Flow Chart

\[ K_{ab}^{ij} = \sum_{\mu \nu \sigma} c_{i\mu}^{occ} c_{ap}^{vir} c_{j\nu}^{occ} c_{b\sigma}^{vir} (\mu|\nu\sigma) \]

- KNET
- 8
- MEMORY
- 4000
- DFITTING
- DIRECT
- PG-VTZ
- ...

The Code

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Flow Chart

read geometry, symmetry, $S_{AO}$, $F_{AO}$ and WFs

construct PAOs

compute integrals

solve self consistent the LMP2 equations

LMP2 energy

LMP2 correction to the Density Matrix

KNET
8
MEMORY
4000
CONTOL
6 0.000001

$\rightarrow R_{ab}^{ij} \cdots

\rightarrow R_{ab}^{ij} < \epsilon$
\[ E_2 = \sum_{i,j < d} \sum_{ab} K_{ab}^{ij} \left( 2T_{ab}^{ij} - T_{ba}^{ij} \right) \]
\[ E_2 = \sum_{ij} \sum_{ab \in \text{Dom}} K_{ab}^{ij} \left(2T_{ab}^{ij} - T_{ba}^{ij}\right) \]
The bottleneck of the whole Local-MP2 method is represented by the calculation of 4 index integrals, which constitutes by itself about 99% needed for a calculation.

The computational time amounts to several days even for the simplest system.

This is due to the four index contraction over atomic orbitals needed to compute this integral between composite objects.

In order to be able to study systems of general interest it is mandatory to implement fast techniques to approximate these integrals.

\[
K_{ab}^{ij} = \int \omega_i(r_1) \tilde{\chi}_a r_1 \frac{1}{r_{12}} \omega_j(r_2) \tilde{\chi}_b r_2 \, dr_1 \, dr_2
\]

\[
K_{aA_bB}^{iM} = \sum_{\mu \nu \sigma} \sum_{MRNS} c_{i \mu M}^{occ} c_{aA \rho R}^{vir} c_{j \nu N}^{occ} c_{bB \sigma S}^{vir} (\mu M^\rho R | \nu N^\sigma S)
\]
Hierarchy of integrals

\[ \rho_{ia}(r) \approx \sum_{F} d_{F}^{ia} F(r) \]

(L. Maschio and D. Usvyat, Phys. Rev. B, 78, 073102 (2008).)
Density Fitting

Density Fitting is a powerful technique for integral evaluation that has widely proved its efficiency in molecular codes like MOLPRO.

The basic idea is to expand product distributions in an Auxiliary Basis (e.g. Gaussian functions \(\{ F(r) \}\)):

\[
\rho_{ia}(r) = \langle \omega_i(r) \tilde{\chi}_a(r) \rangle \approx \tilde{\rho}_{ia}(r) = \sum_F d_{ia}^F F(r)
\]

Fitting coefficients are determined by minimizing the error functional

\[
\Delta = \langle \rho_{ia}(r) - \tilde{\rho}_{ia}(r) | r_{12}^{-1} | \rho_{jb}(r) - \tilde{\rho}_{jb}(r) \rangle
\]
Hierarch of integrals

\[ \rho_{ia}(r) \approx \langle \{m_{ia}\}'_{C_1} \rangle \]
The multipolar Approximation

- The product distribution between WF $\omega_i$ and PAO $\tilde{\chi}_a$ can be represented by a set of electric multipoles, $\{m_{(ia)}\}^l_C$, of maximum order $l$ and centered in C.

- If the two distributions are sufficiently apart to be entirely contained in separate spheres, their electrostatic interaction can be approximated by a sum of interactions between the respective multipoles:

$$\rho_{ia}(r) = \langle \omega_i \tilde{\chi}_a | \omega_j \tilde{\chi}_b \rangle \approx \langle \{m_{(ia)}\}^l_{C_1} | \{m_{(jb)}\}^l_{C_2} \rangle$$

- Due to translational invariance only the multipoles in the zero cell need to be computed, all the others being the same. Multipoles can be safely used for distances larger than 6 Ang.
Hierarchy of integrals

\[ E_{2}^{LJ} \approx \frac{1}{r^6} \]
Lennard-Jones Extrapolation

In molecular local correlation calculations very distant pairs can be safely neglected. In crystalline systems, these pairs can contribute significantly to the correlation energy. This is due to the fact that the number of pairs included within a sphere grows quadratically with distance.

The contributions of atoms up to large distance obey the $r^{-6}$ law.

This allows us to extrapolate these contributions as following:

$$E_{2}^{LJ} \approx \frac{4\pi}{3} \frac{1}{r_0^3 V_{cell}} \sum_{ij} c_{ij} n_{ij}$$

where $ij$ labels the individual WF pair, $n_{ij}$ is the multiplicity, and the LJ coefficient $c_{ij}$ is determined by fitting of all the computed contributions below $r_0$.
LiH Bulk.

Tests and Benchmarks
### Performance of Periodic Density Fitting

Calculations performed on AMD Opteron, 64 bit, 2200 MHz CPU (4G).

(Maschio, Usvyat, PRB, 78 (2008).)

<table>
<thead>
<tr>
<th>System</th>
<th>Basis set</th>
<th>Time LMP2</th>
<th>Time DF-LMP2</th>
<th>% Error on Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>6-21G*</td>
<td>16 days</td>
<td>4 min.</td>
<td>0.03%</td>
</tr>
<tr>
<td>Ice</td>
<td>6-311G**</td>
<td>4 days</td>
<td>15 min.</td>
<td>0.01%</td>
</tr>
<tr>
<td>CO2</td>
<td>6-311G(3d)</td>
<td>2 days</td>
<td>30 min.</td>
<td>0.01%</td>
</tr>
<tr>
<td>MgO</td>
<td>8-511G*/8-411G*</td>
<td>19 h.</td>
<td>8 min.</td>
<td>0.01%</td>
</tr>
<tr>
<td>Ar</td>
<td>ECP[4s4p3d2f]</td>
<td>10 days</td>
<td>5 min.</td>
<td>0.02%</td>
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</table>

Tests and Benchmarks

Turin, September 2011
Timing

Tests and Benchmarks

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Accuracy

Tests and Benchmarks

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Applications
Rare Gas Crystals

**Cohesive energies in Ha/mol, 4s4p3d1f(2f) basis set.**

(M. Halo, S. Casassa, L. Maschio and C. Pisani, PCCP 11 (2009).)

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**Applications**

Turin, September 2011
Argon crystal

Cohesive energies in Ha/mol, 4s4p3d1f(2f) basis set.

## Molecular crystals

**Cohesive energies in kJ/mol aug(d,f)-TZPP basis set.**


<table>
<thead>
<tr>
<th>System</th>
<th>atoms per unit cell</th>
<th>HF</th>
<th>LMP2</th>
<th>B3LYP</th>
<th>Exp.</th>
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<td>-4.4</td>
<td>-25.1</td>
<td>-23.1</td>
<td>-31.1</td>
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<td>-35.2</td>
<td>-36.3</td>
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<td>HCN</td>
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<td>-40.0</td>
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<td>Ice XI</td>
<td>12</td>
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<td>-60.1</td>
<td>-59.2</td>
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<td>-96.8</td>
<td>-100.3</td>
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<td>23.0</td>
<td>-57.3</td>
<td>-46.3</td>
<td>-49.8</td>
</tr>
</tbody>
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DFT and the relative stability of cubic versus hexagonal BN
Helium on MgO

Physisorption of He on MgO(100).


Applications

Turin, September 2011
### Relative stability of Aluminium Hydroxides: DFT vs LMP2

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<tr>
<td>PBE</td>
<td>-0.5</td>
<td>-12.0</td>
</tr>
<tr>
<td>PW91</td>
<td>-2.2</td>
<td>-12.0</td>
</tr>
<tr>
<td>PBESOL</td>
<td>-10.5</td>
<td>-11.4</td>
</tr>
<tr>
<td>B3LYP</td>
<td>+4.5</td>
<td>-9.1</td>
</tr>
<tr>
<td>PBE0</td>
<td>+1.0</td>
<td>-7.21</td>
</tr>
<tr>
<td>LMP2</td>
<td>-8.7</td>
<td>-5.1</td>
</tr>
<tr>
<td>Exp*</td>
<td>-3.5/-12.5</td>
<td>-3.0/-10.5</td>
</tr>
</tbody>
</table>

*Corrected for zero-point and thermal energy

Relative Stability at 0 K (kJ/mol Al$_2$O$_3$)

LMP2 gives usually correct indications of the relative stability of crystalline allotropes.
..have a look in the Kitchen!

- CRYSTAL HF wavefunction must be of higher quality than usual - tighten ITOL4 and ITOL5. (For instance: 7 7 7 15 50)

- Choose carefully the local excitation domains. If you compute binding energies, cohesive energies, relative stabilities, domains in different calculations must be compatible.

- Try to understand how the localization has localized the orbitals, and if the domains are suitable according to chemical considerations.

- Choose a basis set which is suitable for correlation - very good HF basis sets can be very poor for post-HF. Role of diffuse and polarization functions is very important!

- The fitting basis set should match the quality of the HF basis set
Conclusions
Features

- MP2 Energy from the CRYSTAL HF solution
- MP2 Correction to the Density Matrix
- FULL exploitation of point and translational symmetry
- Fast evaluation of integrals
- Extrapolation of pair energies to infinite distance
- Fixing of indices (e.g. for lattice parameter optimizations)
- Possibility of Dual Basis Set technique to improve upon the HF basis set
Acknowledges

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