CRYSCOR, a public program for the post-Hartree Fock treatment of electron correlation in nonconducting solids and surfaces.

http://www.cryscor.unito.it

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The CRYStalCORrelation Project

The Cryscor project started in Torino in the year 2000.

A first public version of cryscor will be released in autumn 2009.

The Cryscor group today is composed by:

Torino	Regensburg
Cesare Pisani Silvia Casassa Lorenzo Maschio Migen Halo Alessandro Erba	Martin Schütz Denis Usvyat Marco Lorenz

…with fundamental contributions by:

Roberto Dovesi
Fred Manby
Claudio Zicovich-Wilson

Context

The CRYStalCORrelation Project

CRYSTAL 06

Dovesi, Saunders, Roetti, Orlando, Zicovich-Wilson, Pascale, Civalleri, et al.

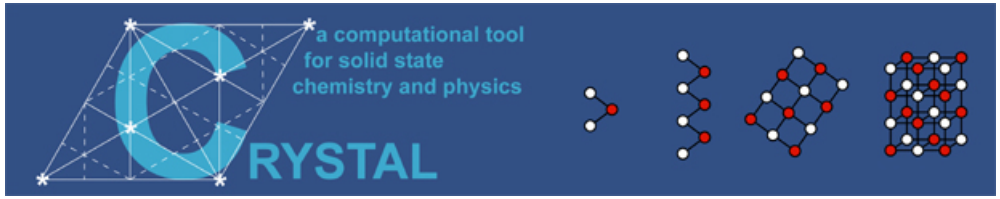
http://www.crystal.unito.it

Atomic Gaussian Type Orbital basis set (Different from Plane Waves)

Geometrical and structural analysis of **periodic** systems (3D, 2D, 1D ... 0D)

Accurate **HF** and **DFT Periodic** (no embedding) nonrelativistic solution

Local representation of occupied manifold (**WF**)



CRYSTAL 09 will be released in late 2009 with new features:

- Transition state search
- Phonon dispersion
- Linear and non-linear dielectric properties through the CPHF/CPKS scheme
- Automated calculation of EOS and elastic constants
- Exploitation of special symmetry for nanotubes and helices

The CRYStalCORrelation Project

MOLPRO 2008

(Pulay) **Werner, Schütz, Manby, Knowles**…

http://www.molpro.net

HF and DFT solution for molecules

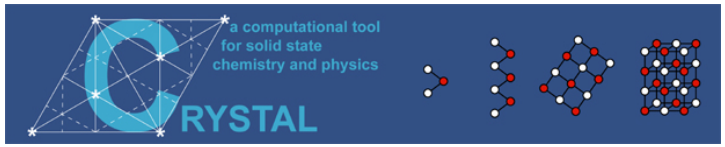
Atomic Gaussian Type Orbital basis set

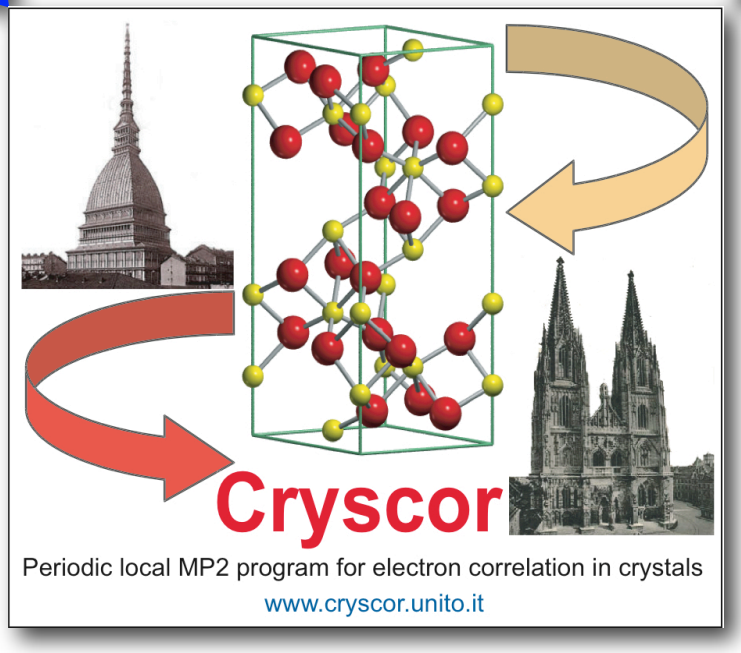
Local correlation techniques for **molecules,** allow high sophistication levels:

MP2, MP4, CCSD, CCSD(T), …

$\mathcal{O}(N)$ **scaling** thanks to the **local approach** and to efficient algorithms for **fast integrals evaluation** (density Fitting)

The CRYStalCORrelation Project





The CRYStalCORrelation Project

✓Describe electron correlation in non-conducting crystals (bulk and surfaces), using standard *ab initio* post-HF methods

✓Improve upon the HF solution from CRYSTAL

✓Adopt well assessed, popular linear-scaling Local Correlation techniques, which have been successfully implemented in MOLPRO

✓Produce a public domain, general purpose, robust, fast, linear scaling, efficient code

As a first step, a Local-MP2 code has been prepared [1]

[1] C. Pisani, L. Maschio *et al.*, J. Comp. Chem. **29**, 2113 (2008).

The CRYStalCORrelation Project

What is **MP2**?

MP2 (Møller-Plesset Perturbation theory at second order) is the ***simplest post-HF correlation technique***
Though inadequate in many respects (in particular, it is non variational, it has several merits:

1) The MP2 energy $E^{(2)}$ is **size consistent**;
2) MP2 provides an adequate treatment of **long-range** interactions, dispersive interactions, hydrogen bonds and so on;
3) It allows the assessment of techniques, basis sets, etc., before introducing a more adequate treatment of short-range interactions (**MP4, CCSD**, …);

Are there other periodic MP2 codes available?

GAUSSIAN - Laplace Transformed MP2 (Scuseria)

Ayala, Kudin, Scuseria, J. Chem. Phys., 115, 21, (2001)

VASP - canonical MP2 (Kresse)

Marsman, Grüneis, Paier, and Kresse, J. Chem. Phys. 130, 184103 (2009)

Method of Increments - Stoll, Paulus - uses CRYSTAL and MOLPRO

Paulus, Phys Rep 428, 1 (2006)

The CRYStalCORrelation Project

CRYSCOR presently allows to compute

- Local-MP2 energy
- Local-MP2-corrected (orbital unrelaxed) Density Matrix and related quantiities, like X-ray structure factors and compton profiles Pisani, *et al.*, Z. Phys. Chem. **220** (2006) 913; Usvyat, J.Phys. **117** (2008)
- Spin Component Scaling - LMP2 energy

Features include:

- Full exploitation of point and translational symmetry at all levels
- Density Fitting for the fast evaluation of two-electron integrals
- Dual Basis Sets to improve virtual space description
- Freezing of local quantities for Geometry Optimization
- Evaluation of long-range dispersive forces through extrapolation of pair energies to infinity
- Frequencies LMP2 correction by means of the ANHARM program by P. Ugliengo

Few things about the program

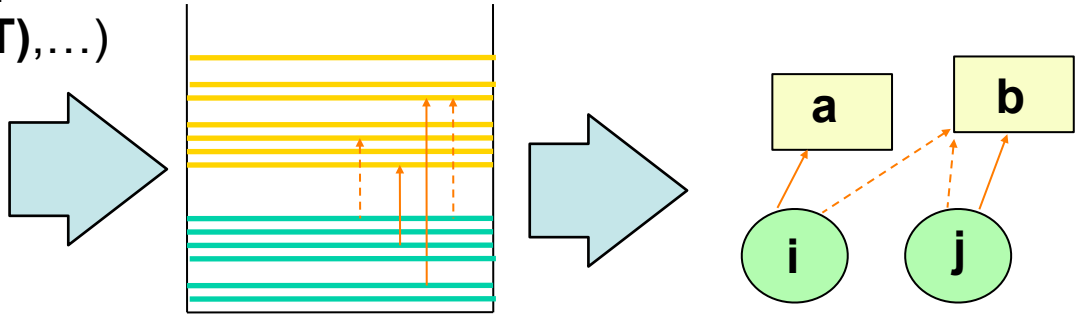
Local Methods from Molecules to Crystals

Local, orthonormal represent. of **occupied HF** manifold … **i j k (SAWF)**

Local, non-orthonormal, representation of **virtual** space … **a b c** **(PAO)**

Reformulation of standard approaches (**MPn, CCSD(T)**,…)

Bloch Functions



Zicovich-Wilson, Dovesi, Saunders, J. Chem. Phys., 115 (**21**) (2001)

TRUNCATION STRATEGY

$$E_2 = \Sigma_{(ij)} \Sigma_{ab \in (ij)} (i\ a \mid j\ b)\ (2\ T^{ij}_{ab} - T^{ij}_{ba})$$

*Dynamical correlation effects are **short-ranged.***

***N*--SCALING** → ***n*--SCALING**

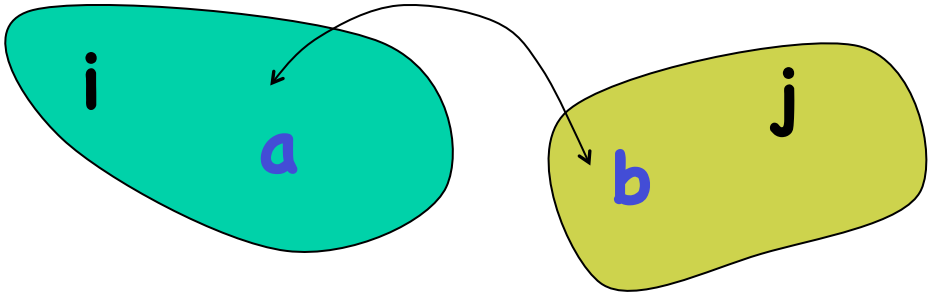
N: molecular size

n : size of irred. part of crystal cell

The problem of integrals evaluation

The bottleneck of LMP2 calculations is the evaluation of 2 electron integrals **K = (i a | j b)** giving the Coulomb interaction between two occupied x virtual product-distributions

[**i,j** : occupied **a,b** : virtuals]



Accurate and **cheap** estimates of the K integrals are obtained:

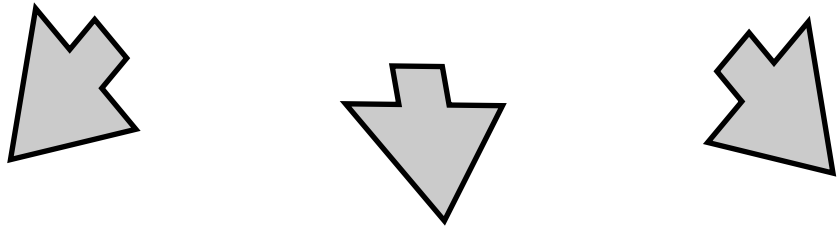
for **close-by** pairs, by a density-fitting-periodic (**DFP**) approximation;

for **well separated** WF pairs, by a **multipolar** approximation;

(not needed for **very distant** pairs due to **Lennard-Jones** extrapolation to infinity).

Density Fitting in Periodic Systems

Three approaches



Reciprocal Space

Correction of the density

Instead of the true density, we fit a corrected density, suitably constructed so that it has no multipoles.

Direct Space

Local Direct Fitting

(Almost) completely analogous to the one used in molecules

Reciprocal AND Direct Space

Direct Reciprocal Decoupled fitting

Two mutually orthogonal fitting sets are used, one in reciprocal space and another in direct space, and two fitting procedures are performed indipendently.

Direct Reciprocal Decoupled Density Fitting

Two fitting sets are defined:

1) Spans the whole direct space, made of Poisson functions only, treated in reciprocal space

2) Is made of GTFs and confined in a local-fit domain

To make the two fittings independent, the two sets must be orthogonal.

$$\mathbf{J} = \begin{bmatrix} (\mathbf{G}|\mathbf{G}) & (\mathbf{G}|\mathbf{P}) \\ (\mathbf{P}|\mathbf{G}) & (\mathbf{P}|\mathbf{P}) \end{bmatrix} \Rightarrow \begin{bmatrix} (\mathbf{\Gamma}|\mathbf{\Gamma}) & \mathbf{0} \\ \mathbf{0} & (\mathbf{P}|\mathbf{P}) \end{bmatrix} \equiv \begin{bmatrix} \mathbf{J}^{[\Gamma]} & \mathbf{0} \\ \mathbf{0} & \mathbf{J}^{[\mathbf{P}]} \end{bmatrix}$$

and also the fitting of the four-index integral can be performed in two separate steps, one in reciprocal space and one in direct space.

$$\tilde{K} = \tilde{K}^{P} + \tilde{K}^{\Gamma}$$

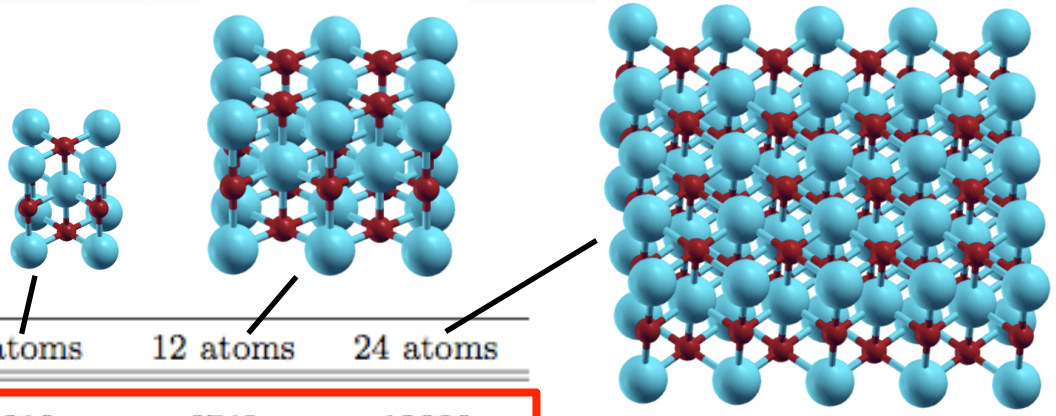
Performance of DFP

System	Basis set	Time LMP2	Time DF-LMP2	% Error on Energy
Diamond	6-21G*	16 days	4 min.	0.03%
Ice	6-311G**	4 days	15 min.	0.01%
CO_2	6-311G(3d)	2 days	30 min.	0.01%
MgO	8-511G*/8-411G*	19 h.	8 min.	0.01%
Ar	ECP/[4s4p3d2f]	10 days	5 min.	0.02%

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

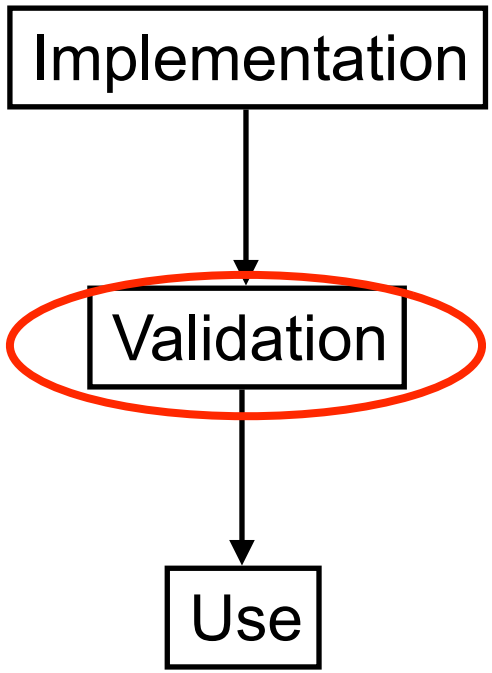
Is it really Linear Scaling?

Increasing size of the *unit cell*



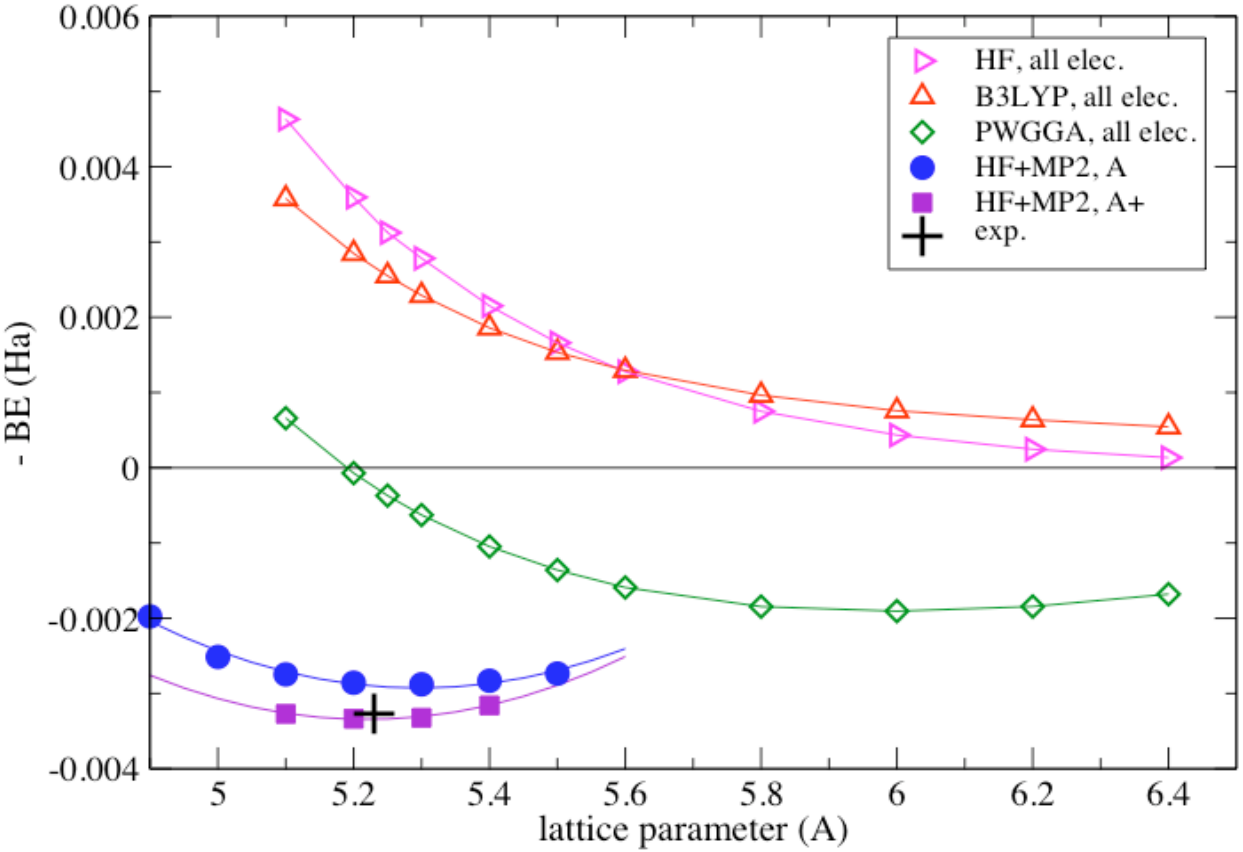
		6 atoms	12 atoms	24 atoms
Elap. time	Hartree-Fock	3210	6748	12666
	Localization/ Symmetrization	175	1286	11673
	E_{HF}	-823.991859	-823.991861	-823.991862
Direct-reciprocal decoupled DF				
Elapsed time	Fit-domain constr.	40	132	765
	3-index integrals	889	1575	3883
	Projection	44	64	227
	DF coefficients	18	66	331
	Assembly	202	393	1012
	Total DF	1181	2305	6427
	Total LMP2	2208	4935	11274
	E_2	-0.838846	-0.838878	-0.838866

Application Examples



Weakly Bound Rare Gas Crystals : Argon

Basis set: [4s4p3d1f(2f)]



Casassa, Halo, Maschio, Journal of Physics: Conference Series **117** (2008)

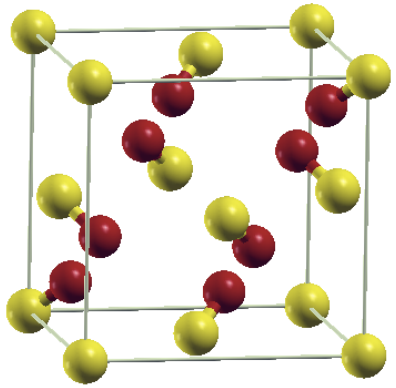
M.Halo, S.Casassa, L.Maschio and C.Pisani, Chem. Phys. Lett. 467 (2009) 294–298

M.Halo, S.Casassa, L.Maschio and C.Pisani, PCCP 11(2009) 568–574

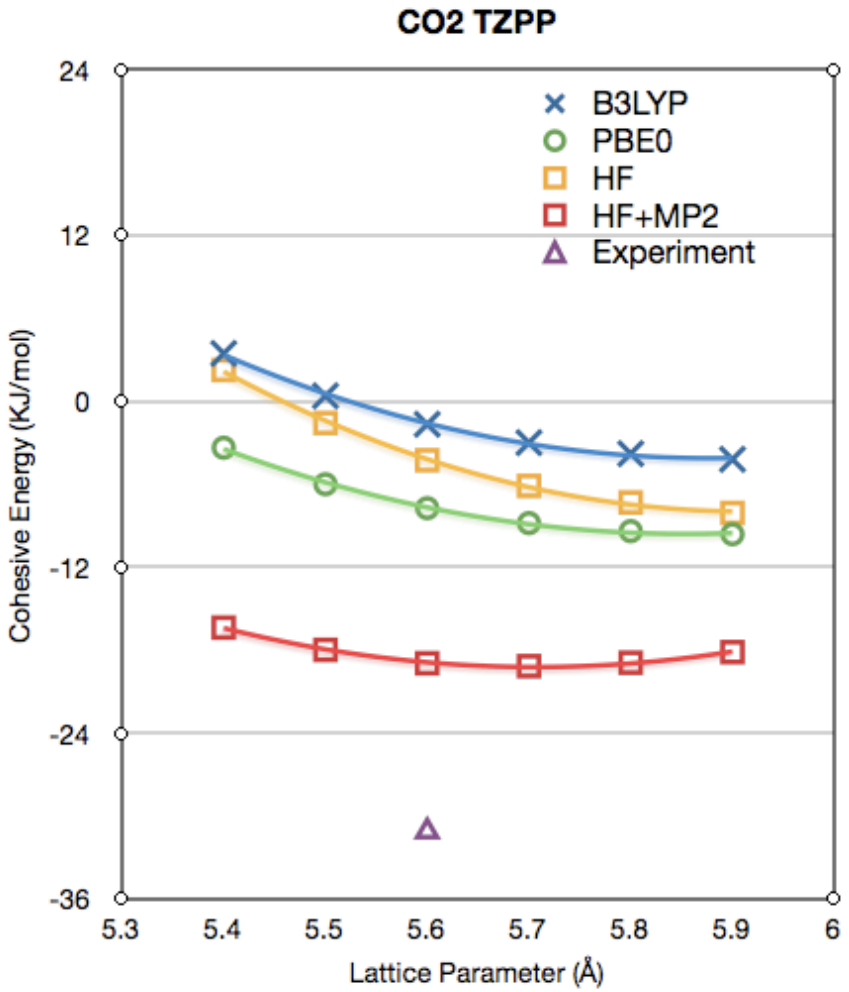
Molecular Crystals : Carbon Dioxide

The cohesive energy and lattice parameter obtained by LMP2 is compared to that obtained with different methods.

L. Maschio, D. Usvyat and B. Civalleri, in preparation



We have also investigated Ice, stability of its different phases and vibrational modes.



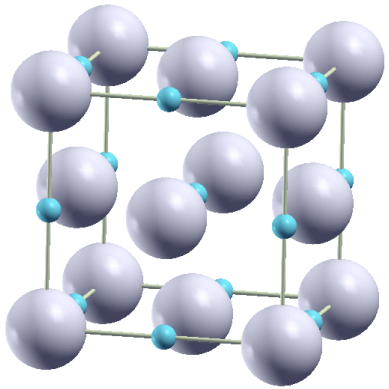
A. Erba, S. Casassa, R. Dovesi, L. Maschio, and C. Pisani, J. Chem. Phys. 130, 074505(2009)
A. Erba, S. Casassa, L. Maschio, and C. Pisani, *J. Phys. Chem. B*, 113 (8), 2347-2354 (2009).

The LiH Bulk Crystal and the Basis set Limit

HF Basis : VQZ quality for H and VTZ for Li.

LMP2 Basis : [6s5p5d4f] (provides result comparable to those obtained by other authors[1] with cc-pVQZ basis set). Singles excitation have to be taken into account. All the parameters of the local method have been pushed as far as possible.

Results in good agreement with the very accurate calculations at the basis set limit performed by other authors,[1,2] recovering 98.5% of the canonical frozen-core MP2 energy.

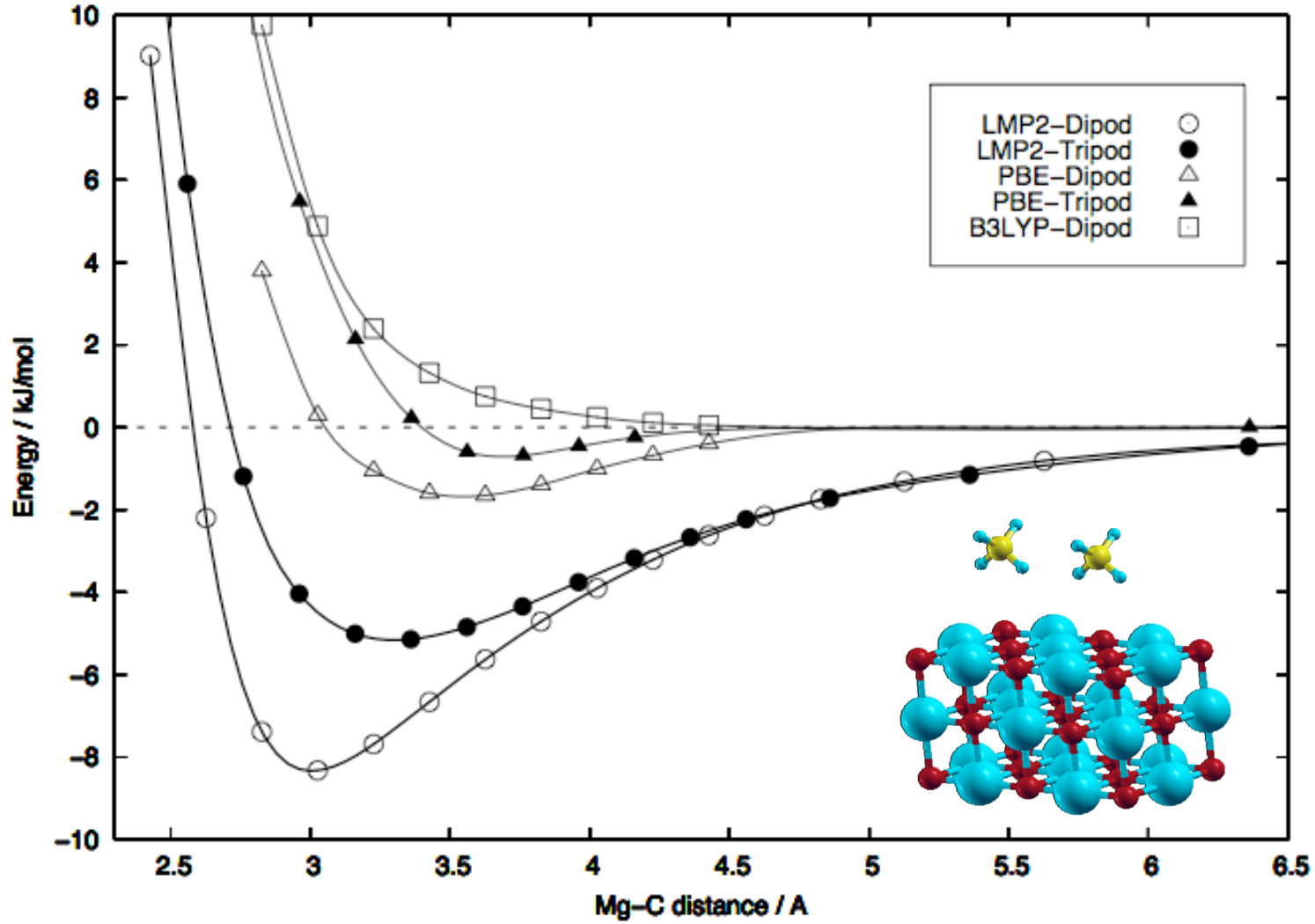


E_{HF}	-8.064592
E_{MP2}	-0.040906
$E_{singles}$	-0.000124
Total E	-8.105622

[1] M. J. Gillan, D. Alfè, S. de Gironcoli, F.R. Manby, J Comput Chem 29, 2098–2106 (2008).
[2] M. Marsman, A. Grüneis, J. Paier, and G. Kresse, J. Chem. Phys. 130, 184103 (2009).
[3] B. Paulus, Phys Rep 2006, 428, 1.

Adsorption of CH_4 molecules on MgO Slab

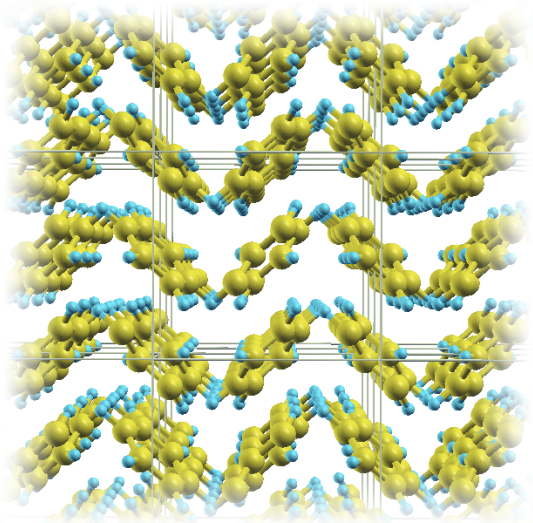
Maschio, Usvyat, Manby *et al. PRB*, **76** (2007)



Work in progress - very preliminary results

Benzene Crystal

48 atoms per cell
6-31G(d,p) basis

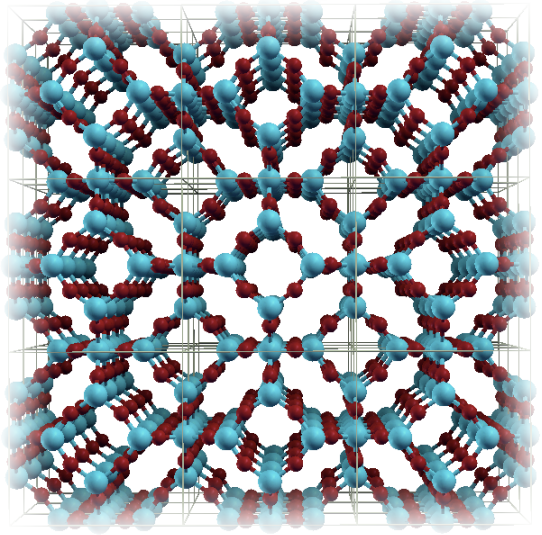


Cohesive energy

```
HF+MP2    : 36.4 KJ/mol
Exp.      : 49.8 KJ/mol
```

Sodalite - SiO_2

36 atoms per cell
Si [5s4p2d1f] /
O [4s3p2d1f] basis

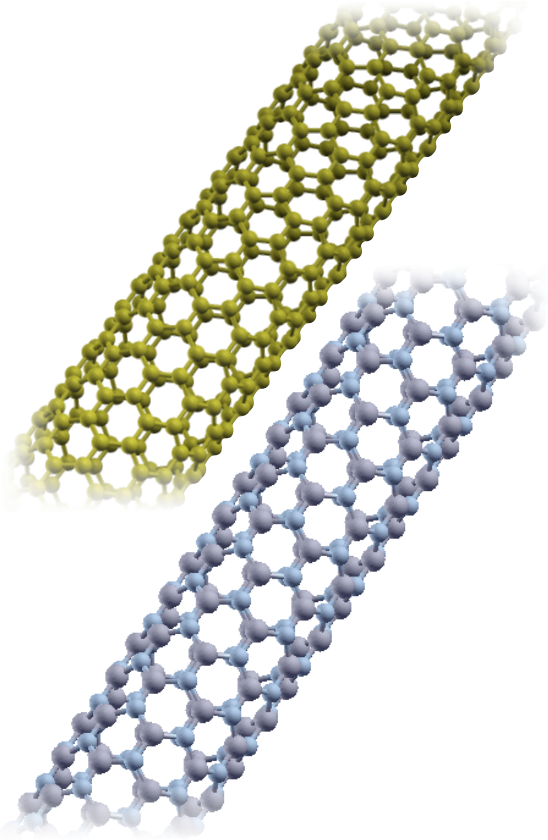


Total energy

```
HF+MP2    : -6.49273
Time : 8 hours
(single processor)
```

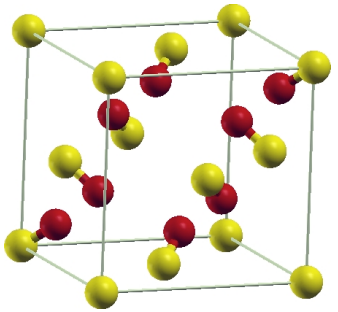
Carbon and BN Nanotubes

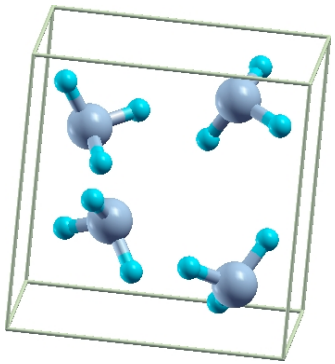
with different radiuses



System Tested - Molecular Crystals

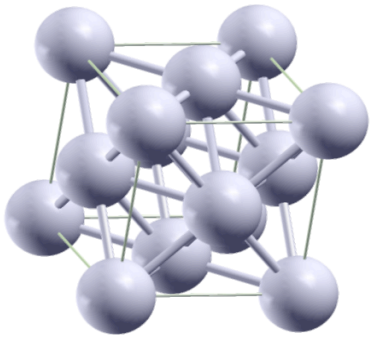
System	Lattice	N_{atoms} per Cell
Cubic Apolar Ice	Tetragonal	12
Cubic Polar Ice	Tetragonal	6
Hexagonal Apolar Ice	Orthorombic	24
Hexagonal Polar Ice	Orthorombic	12
N2	Cubic	8
CO2	Cubic	12
NH3	Cubic	16
Urea	Tetragonal	16
Acetylene	Cubic	16
KNH	Orthorombic	24
Benzene	Orthorombic	48

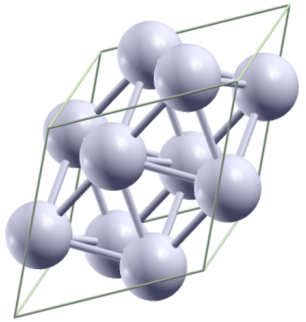




System Tested - Rare gases

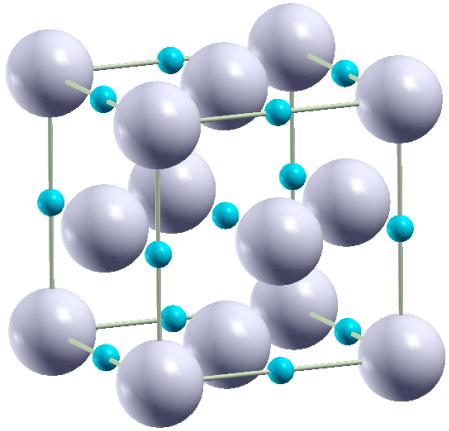
System	Lattice	N_{atoms} per Cell
Argon	Cubic	1
Argon	Hexagonal	2
Neon	Cubic	1
Kripton	Cubic	1
Xeon	Cubic	1





System Tested - Ionics

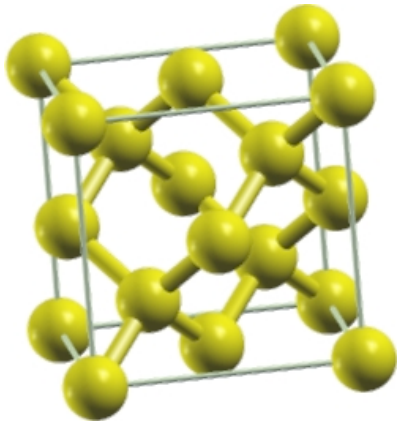
System	Lattice	N_{atoms} per Cell
MgO	Cubic	2
LiH	Cubic	2
LiF	Cubic	2
NaCl	Cubic	2
TiO2	Tetragonal	6
MgO Slab - 1 layer	Cubic	2
MgO Slab - 3 layer	Cubic	6

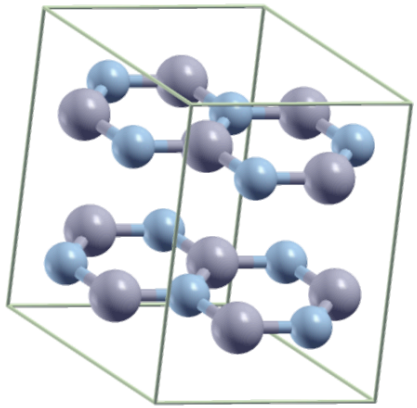


System	Lattice	N_{atoms} per Cell
α-quartz	Hexagonal	9
β-quartz	Cubic	6
sodalite	Cubic	36
chabazite	Hexagonal	36

System Tested Covalent Crystals

System	Lattice	N_{atoms} per Cell
Diamond	Cubic	2
Silicon	Cubic	2
BN	Cubic	2
BN	Hexagonal	4
C Nanotube	Polymer	32 - more
BN nanotube	Polymer	32 - more
BN slab	Hexagonal	2





Conclusions and Prospects

What CRYSCOR can do today...

✓LMP2 Energy from the CRYSTAL HF solution
✓LMP2 Correction to the density matrix (orbital unrelaxed)
✓Fast evaluation of integrals - Linear scaling code
✓Full exploitation of the point and translational symmetry at all levels

...in the near future…

✓MP2 automatic geometry optimization (numerical gradients)
✓CIS approach for excited states (Correction to the HF Band Gap)
✓Improved estimates of electron density matrix correction (orbital relaxation)
✓Parallel version

…and more distant in time

✓Extension to other local correlation schemes (CC2, CCSD, MP4, …)
✓MP2 analytical gradients.
✓Explicitly correlated methods (F12)
✓Vibrational frequencies a a correlated level

Acknowledgements

Thanks once more to all the Cryscor group:

Cesare Pisani
Silvia Casassa
Lorenzo Maschio
Migen Halo
Alessandro Erba

Martin Schütz
Denis Usvyat
Marco Lorenz

Roberto Dovesi
Fred Manby
Claudio Zicovich-Wilson

And thank You for your kind attention!