

Towards a general purpose code for the evaluation of correlation in crystalline solids: the CRYSCOR project. Theory, current status and prospects.

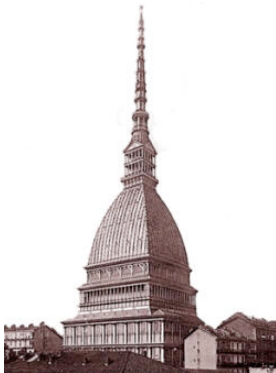
**Lorenzo Maschio**

Dipartimento di Chimica I.F.M. and N.I.S. centre of excellence Università di Torino

# The **CRYStalCOR**relation Project

The Cryscor project started in Torino in the year 2000, and it is aimed to the post-HF evaluation of electron correlation in crystalline solids.

The Cryscor group today is mainly composed by:

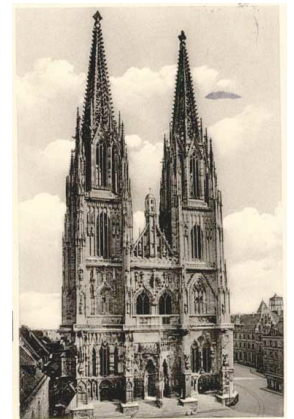


## Torino

Cesare Pisani  
Silvia Casassa  
Lorenzo Maschio  
Migen Halo

## Regensburg

Martin Schütz  
Denis Usvyat



...with fundamental contributions by:

Roberto Dovesi  
Fred Manby  
Claudio Zicovich-Wilson

# The **CRY**stal**COR**relation Project

The strategy is to combine two well assessed, robust,  
**compatible** technologies

## **CRYSTAL 2006**

**Dovesi, Saunders, Roetti,  
Orlando, Zicovich-Wilson,  
Pascale, Civalleri...**

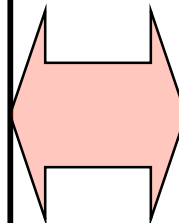
<http://www.crystal.unito.it>

**Atomic Gaussian Type  
Orbital basis set**

Geometrical and structural  
analysis of **periodic** system

Accurate **HF** and **DFT**  
solution

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



## **MOLPRO 2006.1**

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

<http://www.molpro.net>

**Atomic Gaussian Type  
Orbital basis set**

Correlation techniques for  
**molecules**, at various  
sophistication levels:

HF, MP2, CCSD(T), ...

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

# The CRYStalCORrelation Project

Our aim is to:

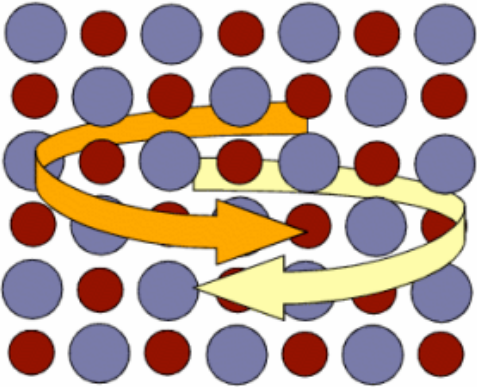
- ✓ Describe electron correlation in non-conducting crystals (bulk and surfaces), using standard *ab initio* **post-HF methods**
- ✓ Use technology and HF solution from the **CRYSTAL** program
- ✓ Adopt linear-scaling **Local Correlation** techniques, which have been successfully implemented in MOLPRO
- ✓ Produce a **public domain**, general purpose, robust, efficient code
- ✓ Adopt **fast** integral evaluation techniques

As a first step, an MP2 code has been prepared <sup>(1)</sup>

(1) Pisani, Busso, Capecchi, Casassa, Dovesi, Maschio, Zicovich-Wilson, Schütz  
*J. Chem. Phys.* 122, 094113 (2005)

# The **CRYStalCOR**relation Project

The program, together with preliminary results on simple test systems, was presented for the first time in Torino in 2004, during the first edition of the LCC Workshop.



**LCC 2004: Workshop on  
Local Correlation methods:  
from molecules to Crystals**

September 9-11, 2004 - Torino, Italy

Director: Cesare Pisani and Roberto Dovesi, University of Torino

<http://www.theochem.unito.it/lcc2004>

Since then we have improved the code in many ways, improving its stability and efficiency, and we are able now to study systems of general interest.

**We are looking for beta testers !!**

This talk will mainly focus on the new features of the code, in particular Density Fitting and other techniques for the fast evaluation of Integrals.

# The **CRYStalCOR**relation Project

Are post-HF *ab initio* treatments of crystalline **solids** and their **surfaces** really needed?

HF is **often** inadequate for ground state characterization:  
equilibrium structure, solid state reactions, **reactions at surfaces**,  
vibrational properties, magnetic and electric properties.

And **always** inadequate for excited state properties:  
band structure, electronic response properties...

DFT exists but is it the final answer ?

“DFT is the ultimate semiempirical theory” [Pulay]

# The CRYStalCORrelation Project

DFT is accurate, but often not accurate enough;

- ✓ It can't account for dispersive interactions between remote parts of the system.
- ✓ Different functionals must be adopted according to the system to be studied.

Post-HF ab initio treatments of crystals and their surfaces are useful

## Do ab-initio periodic correlation codes already exist?

Several approaches are presently adopted by different research groups...

However, a simple, reliable, easily accessible code, could serve the purpose of:

*providing reference data,*  
*exploring the role of computational parameters,*  
*checking the usefulness of alternative techniques,*  
*opening the route to progressively more sophisticated techniques...*

# The **CRY**stal**COR**relation Project

## Why MP2?

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

Yet, it has several merits:

- 1) The MP2 energy  $E^{(2)}$  is **size consistent**;
- 2) MP2 provides an adequate treatment of **long-range** interactions;
- 3) It allows the assessment of techniques, basis sets, etc., before introducing a more adequate treatment of short-range interactions (**MP4, CCSD, ...**);
- 4) the MP2 correlation energy estimates can be corrected using the simple **Grimme SCS** (Spin-Component-Scaled) MP2 formula [**Grimme, *J. Chem. Phys.* 118 (2003) 9095**], which has proved very efficient in a molecular context [**Hill, Platts, Werner, *PCCP* 8 (2006) 4072**].



# Outline of the Presentation

**The  
current  
status**  
**Integrals  
evaluation**  
**LMP2**

- Local MP2 in crystals
- Post-HF Density Matrix

- Multipolar Approximation
- Lennard-Jones extrapolation to infinity
- Density Fitting for Periodic systems

- Feasibility of different systems
- Work to do and Prospects

# MP2 in Crystals : The Ingredients

We start from the **local** non-canonical formulation of MP2 energy for closed shell systems:

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

$$K_{ab}^{ij} = (ia|jb) = \int \phi_i(\mathbf{r}_1)\phi_a(\mathbf{r}_1) \frac{1}{r_{12}} \phi_j(\mathbf{r}_2)\phi_b(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

In this formulation the total MP2 energy is evaluated as a sum of local contributions, that is doubly excited configurations.

The excitation of a pair of electrons occurs from occupied local orbitals to virtual space.

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

The amplitudes are obtained through self-consistent iterations

$$K_{ab}^{ij} = (ia|jb) = \int \phi_i(\mathbf{r}_1)\phi_a(\mathbf{r}_1) \frac{1}{r_{12}} \phi_j(\mathbf{r}_2)\phi_b(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

$$R_{ab}^{ij} = K_{ab}^{ij} + \sum_{cd} \left\{ F_{ac} T_{cd}^{ij} S_{db} + S_{ac} T_{cd}^{ij} F_{db} - S_{ac} \left[ \sum_k (F_{ik} T_{cd}^{kj} + T_{cd}^{ik} F_{kj}) \right] S_{db} \right\} = 0$$

In this formulation the total MP2 energy is evaluated as a sum of local contributions, that is doubly excited configurations.

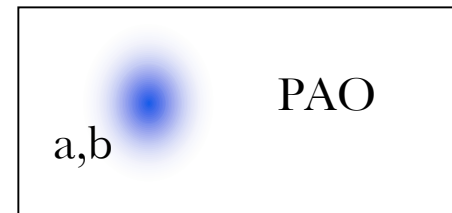
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The main ingredients of our method are **Symmetry Adapted Wannier Functions** (SAWFs), here and in the following indicated with latin letters (i,j) and **Projected Atomic Orbitals** (PAOs), indicated as (a,b).

•LMP2 in crystals

•Post-HF Density Matrix

•Multipolar Approximation

•Lennard-Jones extrapolation

•Density Fitting in Crystals

•Feasibility of different systems

•Work to do and Prospects

# MP2 in Crystals : The Ingredients

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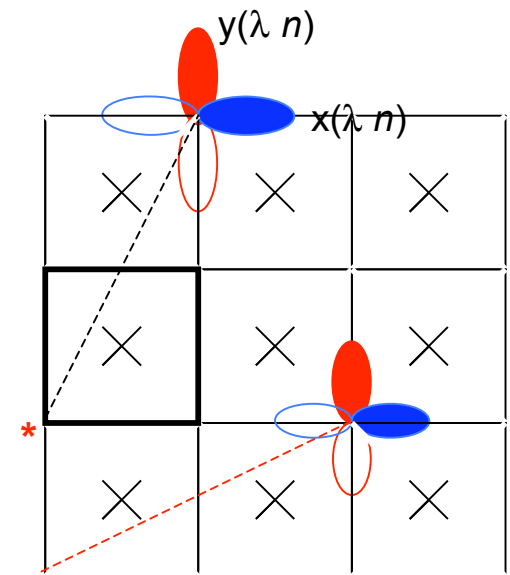
- Feasibility of different systems

- Work to do and Prospects

A peculiar feature of CRYSCOR, inherited from CRYSTAL, is the full exploitation of translational **and** point symmetry

The point symmetry requires in particular that all “objects” or “groups of objects” (AOs, shells, PAOs, ...) transform into one another for any symmetry operation of the crystal.

This is generally **not** true for WFs (or localized molecular orbitals) resulting from a localization procedure



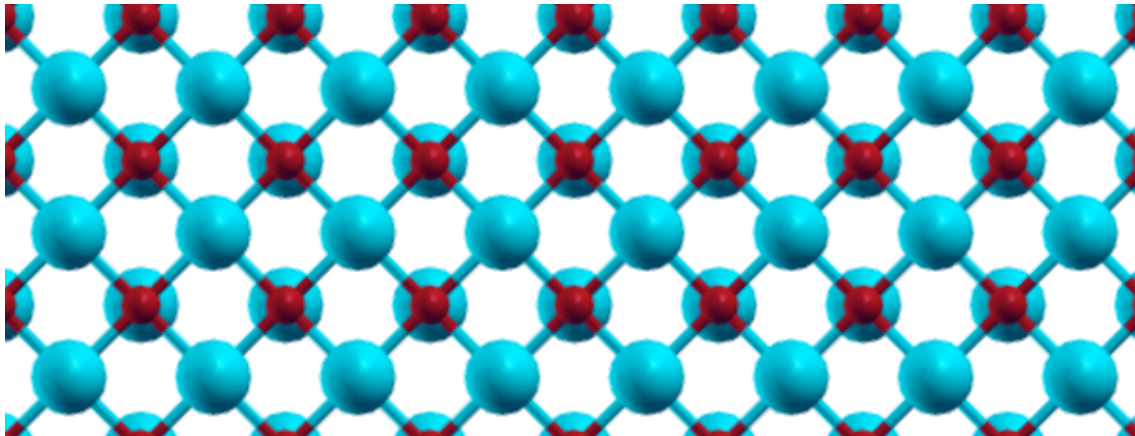
A symmetrization step of WFs is preliminarily required

# MP2 in Crystals

Since all the quantities of interest (Fock matrix, overlap matrix, amplitudes, integrals) are *translationally invariant*, we redefine the correction energy as an *energy per cell*:

$$E_2 = LE_2^{cell}$$

$$E_2^{cell} = \sum_{i_0 j_g} E_2^{i_0 j_g}$$



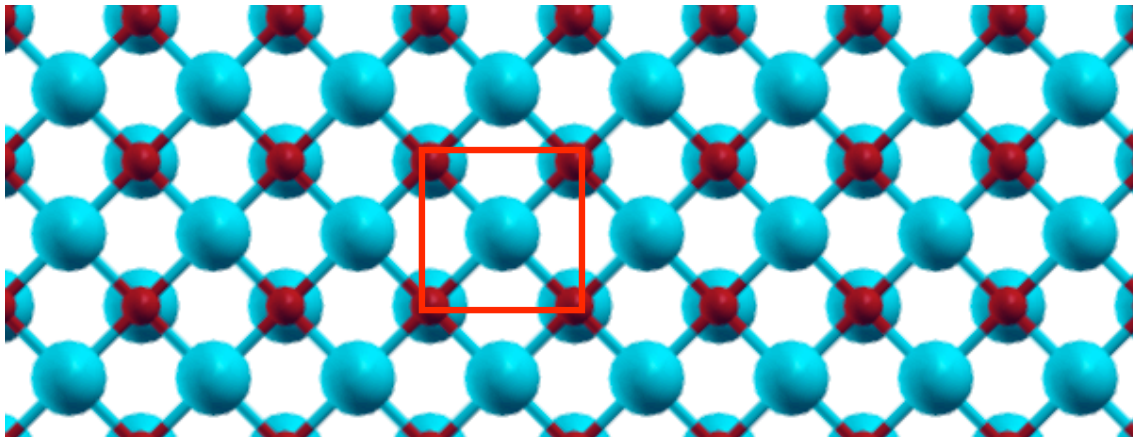
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The first WF index is always in the zero cell



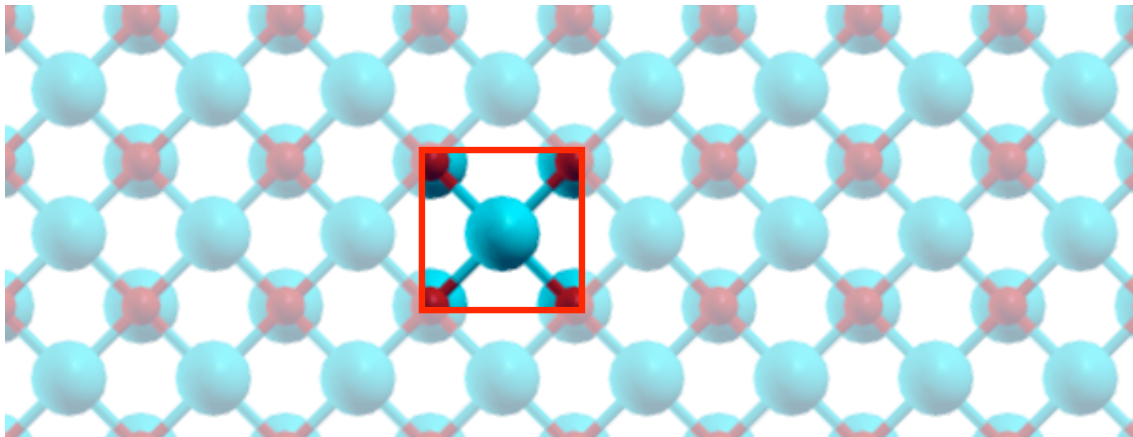
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We are confined *in a vicinity of the reference cell*. The computation becomes  $\mathcal{O}(0)$  with respect to  $L$ , and  $\mathcal{O}(n)$  with the size of the *irreducible part* of the reference cell. We are able to describe an *infinite system*.



# MP2 in Crystals

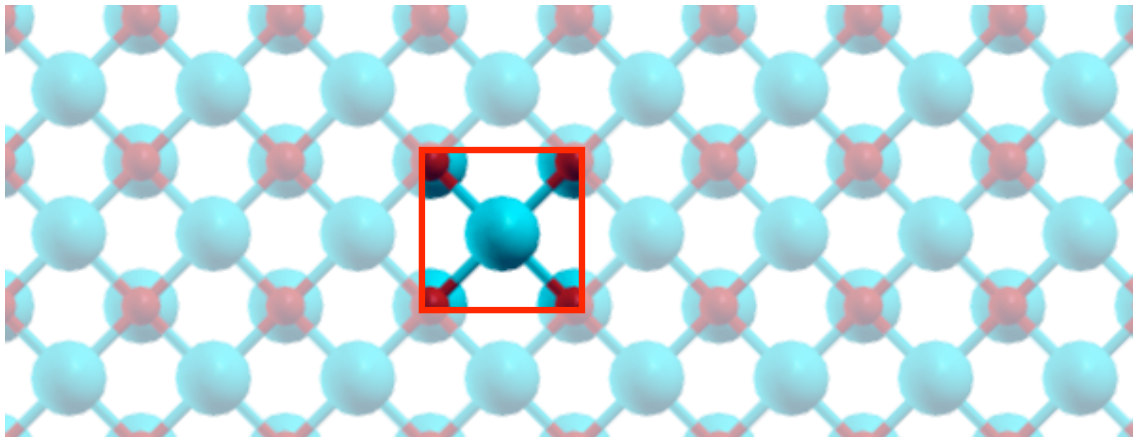
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$$E_2^{cell} = \sum E_2^{i_0 j_g}$$

The sum is restricted to symmetry irreducible pairs

The first WF index is always in the zero cell



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Since all the quantities of interest (Fock matrix, overlap matrix, amplitudes, integrals) are *translationally invariant*, we redefine the correction energy as an *energy per cell*:

$$E_2 = LE_2^{cell}$$

$$E_2^{cell} = \sum_{i_0 j_g} E_2^{i_0 j_g} = \sum_{ij} E_2^{ij}$$

In order to simplify the notation, from now on we will adopt **single indices** instead of double, **implying that the summation is performed over lattice vectors** also. It is implicit that the first WF is always in the reference cell.

$$i = i_0$$

$$j = j_g$$

# Standard Scheme of CRYSCOR

•LMP2 in crystals

•Post-HF Density Matrix

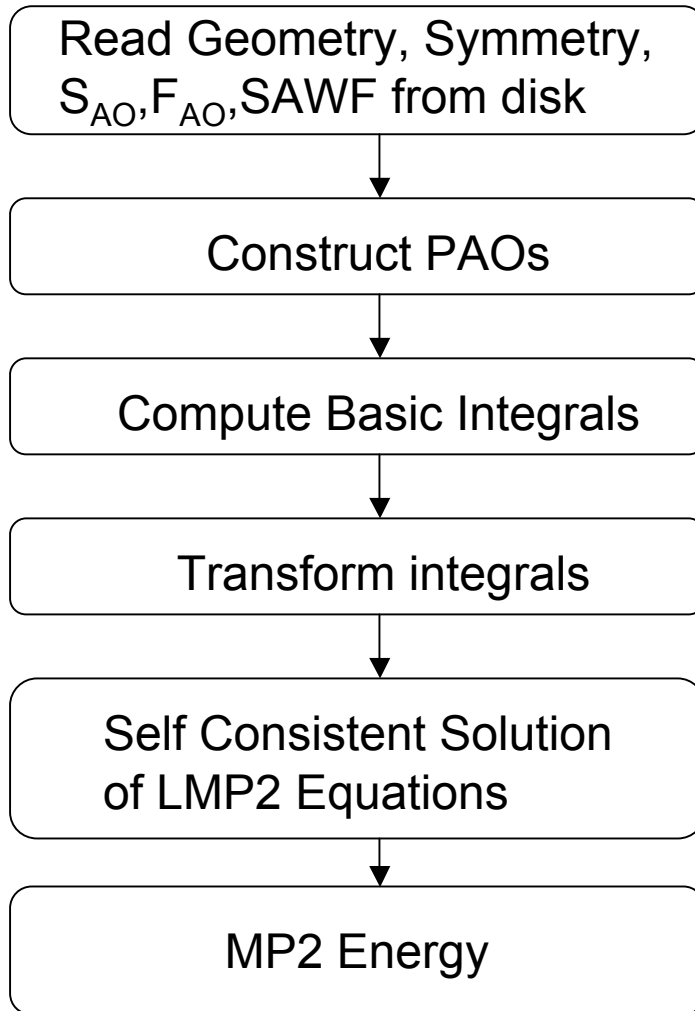
•Multipolar Approximation

•Lennard-Jones extrapolation

•Density Fitting in Crystals

•Feasibility of different systems

•Work to do and Prospects



$$\chi_{\alpha} = \sum_{\beta} (1 - \hat{P})_{\alpha,\beta} \chi_{\beta} \rightarrow a$$

$$(\mu\nu|\rho\tau) = \int \frac{\phi_{\mu}(\mathbf{r}_1)\phi_{\nu}(\mathbf{r}_1)\phi_{\rho}(\mathbf{r}_2)\phi_{\tau}(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

$$K_{ia}^{jb} = \sum_{\mu,\nu,\rho,\tau} c_{\mu}^i c_{\nu}^a c_{\rho}^j c_{\tau}^b (\mu\nu|\rho\tau)$$

$$R_{ab}^{ij} \leq \epsilon$$

$$E_2^{cell} = \sum_i^{(cell\ 0)} \sum_j \sum_{ab} K_{ij}^{ab} (2T_{ij}^{ab} - T_{ij}^{ab})$$

# The Role of Computational Parameters

- LMP2 in crystals

- Post-HF Density Matrix

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- Lennard-Jones extrapolation

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The most interesting feature of the local approach is that we are allowed to truncate summations according to thresholds. Here we present the most critical parameters for our calculation.

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Truncation on WFs and PAOs coefficients

$$K_{ia}^{jb} = \sum_{\mu, \nu, \rho, \tau} c_{\mu}^i c_{\nu}^a c_{\rho}^j c_{\tau}^b (\mu\nu|\rho\tau)$$

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$$K_{ia}^{jb} = \sum_{\mu, \nu, \rho, \tau} c_{\mu}^i c_{\nu}^a c_{\rho}^j c_{\tau}^b (\mu\nu|\rho\tau)$$

Threshold on convergence

$$R_{ab}^{ij} \leq \epsilon$$

$$E_2^{cell} = \sum_i^{(cell\ 0)} \sum_j \sum_{ab} K_{ij}^{ab} (2T_{ij}^{ab} - T_{ij}^{ab})$$

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Size of WF domains

$$E_2^{cell} = \sum_i^{(cell\ 0)} \sum_j \sum_{ab} K_{ij}^{ab} (2T_{ij}^{ab} - T_{ij}^{ab})$$

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Threshold on convergence

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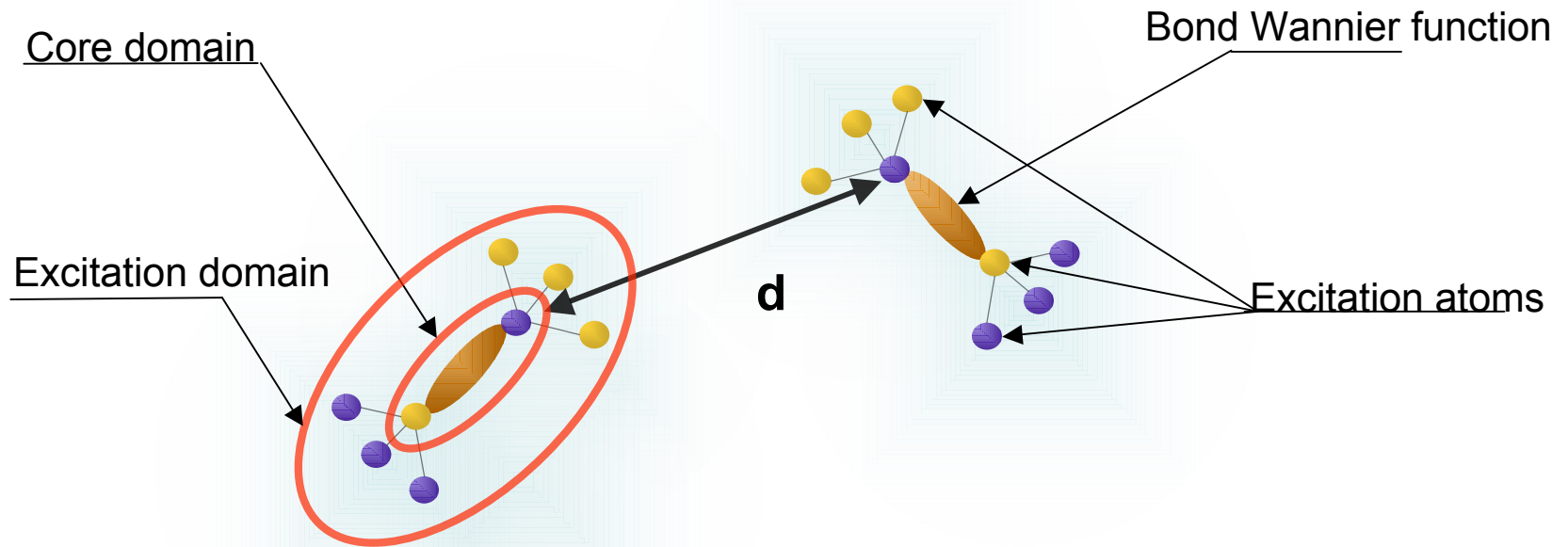
Number of pairs included

Size of WF domains

$$E_2^{cell} = \sum_i^{(cell\ 0)} \sum_j \sum_{ab} K_{ij}^{ab} (2T_{ij}^{ab} - T_{ij}^{ab})$$



# The Role of Computational Parameters



From our experience, “good” values for the computational parameters (errors  $\cong 10^{-5}$  Ha) are:

- ✓ Maximum distance between core domains :  $d \leq d_{\max} \cong 10 \text{ \AA}$  (extrapolation to infinite distance feasible with Lennard-Jones-Fitting Technique!)
- ✓ Excitation domain  $\cong 2$  stars of neighbors for ionic and covalent crystals, one molecule in the case of a molecular crystal
- ✓ Threshold on coefficients truncation =  $10^{-3} \div 10^{-4}$

# Post-HF Density Matrix

- LMP2 in crystals

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From the knowledge of the first-order correction to the HF wavefunction ( $|\Psi^{(1)}\rangle$ ), information can be obtained on how correlation effects may influence the electron distribution.

A size consistent expression of the MP2 correction to the HF **one-electron density matrix** has been recently proposed and implemented in CRYSCOR.

Pisani, Casassa, Maschio, Z. Phys. Chem. **220** (2006) 913

Casassa, Halo, Maschio, Pisani, Theor. Chem. Acc. 117 (2007) 781

It can be used for obtaining „correlated“ **X-ray structure factors** and **directional Compton profiles** which can be compared to the experiment.

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The problem of computing the corrected density matrix  $\gamma'(r, r')$  is non trivial, due to *size-consistency* problems.

$$\gamma'(r, r') = \gamma^{HF}(r, r')$$

We need to define a “local one density”

$$\gamma'_{loc}(r, r') = \gamma^{HF}(r, r') + \gamma_{loc}^{MP2}(r, r'; 0)$$

And make a “periodization” ansatz:

$$\gamma'_{per}(r, r') = \gamma^{HF}(r, r') + \gamma_{per}^{MP2}(r, r')$$

$$\gamma_{per}^{MP2}(r, r') = \sum_g \gamma_{loc}^{MP2}(r, r'; g)$$

A different technique, based on a perturbative approach, has been very recently implemented by Denis Usvyat.

# 1st Summary - Periodic LMP2



- LMP2 in crystals
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- ✓Based on CRYSTAL HF solution
- ✓Local-MP2 energy
- ✓SCS correction
- ✓Full symmetry exploitation
- ✓MP2 correction to Density Matrix

# The problem of integrals evaluation

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The bottleneck of the whole Local-MP2 method is represented by the calculation of **4 index** integrals, which constitutes by itself about **99%** of the whole time 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.

$$K_{ab}^{ij} = (ia|jb) = \int \phi_i(\mathbf{r}_1)\phi_a(\mathbf{r}_1)\frac{1}{r_{12}}\phi_j(\mathbf{r}_2)\phi_b(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2$$

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

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PAOs

WFs

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# The Multipolar Approximation

Pisani, Capecchi, Casassa and Maschio, Mol. Phys 103-18(2005) 2527-2536

- LMP2 in crystals
- Post-HF Density Matrix

## •Multipolar Approximation

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The product distribution between Wannier function  $i$  and PAO  $a$  can be represented by a set of electric multipoles,  $\{\mathbf{m}_{(ia)}\}_C^l$  of multipole 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 :

$$(ia|jb) = (\{\mathbf{m}_{(ia)}\}_{C_1}^l | \{\mathbf{m}_{(jb)}\}_{C_2}^l)$$

Due to translational invariance only the multipoles in the zero cell need to be computed, all the others being the same.

Multipoles can be used for distances larger than 6 Å.

# Lennard-Jones Extrapolation

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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.

This makes the multipolar approach itself inefficient for distances larger than, say, 12 Å.

On the other hand the distribution of atoms as a function of distance is known, and the energy contributions obey the  $r^{-6}$  law.

This allows us to extrapolate contribution up to large distances.

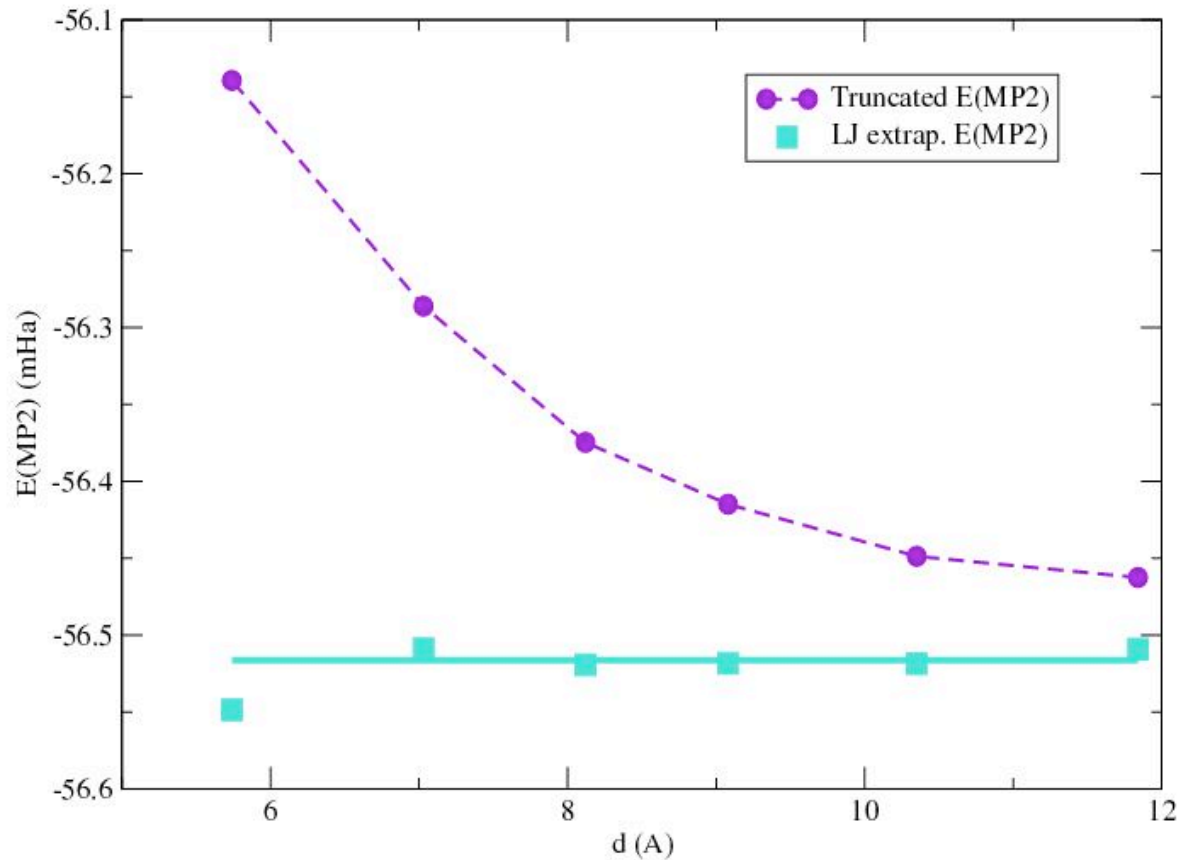
$$E_2^{LJ} \approx \frac{4\pi}{3} \frac{1}{r_0^3 V_{cell}} \sum_{ij} c_{ij} n_{ij}$$

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  $r_0$ .



# Lennard-Jones Extrapolation

## LiH Bulk



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# Density Fitting in molecules

Schuetz, Manby, PCCP (2003) 5, 3349-3358

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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  $\{\Xi\}_i$ ). We will from now on refer to these functions with latin capital letters P,Q.

$$\rho_{ia}(\mathbf{r}) = \phi_i(\mathbf{r})\phi_a(\mathbf{r}) \approx \tilde{\rho}_{ia}(\mathbf{r}) = \sum_P d_{ia}^P \Xi_P(\mathbf{r})$$

Fitting coefficients are determined by minimizing the error functional  $\Delta$

$$\Delta = (\rho_{ia} - \tilde{\rho}_{ia} | w_{12} | \rho_{jb} - \tilde{\rho}_{jb}) \quad \boxed{w_{12} = r_{12}^{-1}}$$

leading to the linear equation system

$$\sum_P d_{ia}^P (P|Q) = (ia|Q)$$

# Density Fitting in molecules

- LMP2 in crystals

- Post-HF Density Matrix

- Multipolar Approximation

- Lennard-Jones extrapolation

- Density Fitting in Crystals

- Feasibility of different systems

- Work to do and Prospects

So that the 4-index integrals are finally approximated as :

$$(ia|jb) \approx (\widetilde{ia|jb}) = \sum_{P,Q} (ia|P)[J^{-1}]_{PQ}(Q|jb)$$

where:

$$(ia|P) = \int \phi_i(\mathbf{r}_1)\phi_a(\mathbf{r}_1)r_{12}^{-1}\Xi_P(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2$$

and:

$$J_{PQ} = (P|Q) = \int \Xi_P(\mathbf{r}_1)r_{12}^{-1}\Xi_Q(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2$$

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Only 3-center Coulomb integrals are needed.

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Only 3-center Coulomb integrals are needed.

The inverse matrix of 2-center coulomb integrals has the size of the number of auxiliary functions in the system.

where:

$$(ia|P) = \int \phi_i(\mathbf{r}_1)\phi_a(\mathbf{r}_1)r_{12}^{-1}\Xi_P(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2$$

and:

$$J_{PQ} = (P|Q) = \int \Xi_P(\mathbf{r}_1)r_{12}^{-1}\Xi_Q(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2$$

# Density Fitting in Periodic Systems

We have seen that, thanks to translational symmetry, 4-index integrals are always referred to the zero cell

$$(ia|jb) \rightarrow (i_0a_g|j_{\bar{g}}b_{\bar{g}'})$$

$g, \bar{g}, \bar{g}'$  are lattice vector labels

This leads to the following expression for approximated integrals:

$$(i_0a_g|\widetilde{j_{\bar{g}}b_{\bar{g}'}}) = \sum_{P,g_P,Q,g_Q} (i_0a_g|P_{g_P})[J^{-1}]_{P_{g_P},Q_{g_Q}} (Q_{g_Q}|j_{\bar{g}}b_{\bar{g}'})$$

- LMP2 in crystals
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Maschio, Usvyat, Manby *et al.* PRB **76**, 075101 (2007)  
Usvyat, Maschio, Manby *et al.* PRB **76**, 075102 (2007)

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3-index integrals are referred to the zero cell, all the others can be obtained by translation. In addition 3-center objects have, generally, higher point symmetry than 4-center ones

Maschio, Usvyat, Manby *et al.* PRB **76**, 075101 (2007)  
Usvyat, Maschio, Manby *et al.* PRB **76**, 075102 (2007)


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This leads to the following expression for approximated integrals:

$$(i_0 a_g | \widetilde{j_{\bar{g}} b_{\bar{g}'}}) = \sum_{P, g_P, Q, g_Q} (i_0 a_g | P_{g_P}) [J^{-1}]_{P_{g_P}, Q_{g_Q}} (Q_{g_Q} | j_{\bar{g}} b_{\bar{g}'})$$


Indices  $g_P, g_Q$  over lattice vectors should go very far, since they must, at least in principle, cover all the space spanned by *all the possible i-j Wannier pairs*, with their relative domains.

Maschio, Usvyat, Manby *et al.* PRB **76**, 075101 (2007)  
Usvyat, Maschio, Manby *et al.* PRB **76**, 075102 (2007)

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This leads to the following expression for approximated integrals:

$$(i_0a_g|\widetilde{j_{\bar{g}}b_{\bar{g}'}}) = \sum_{P,g_P,Q,g_Q} (i_0a_g|P_{g_P}) \underbrace{[J^{-1}]_{P_{g_P},Q_{g_Q}}}_{\text{Inversion of a NxN matrix}} (Q_{g_Q}|j_{\bar{g}}b_{\bar{g}'})$$

Inversion of a NxN matrix scales as  $\mathcal{O}(N^3)$ .  
Inversion of such a big J matrix has high computational costs. Translational invariance is not preserved.

# Density Fitting in Periodic Systems

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The local domain approach is not desirable for several reasons.

- It doesn't preserve the translational periodicity.
- In some crystals (i.e. ionic) the fitting domains can be difficult to define.
- Due to close packing, domains can be very large and the method might be not efficient.

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# Solution: reformulate Density Fitting in reciprocal space

Let us obtain the Fourier transform of the needed integrals

$$J(\mathbf{k})_{PQ} = \sum_{\mathbf{g}'} (P|Q_{\mathbf{g}'})e^{-i\mathbf{k}\mathbf{g}'}$$

$$J'_{i_0 a_g}{}^P(\mathbf{k}) = (i_0 a_g|P)(\mathbf{k}) = \sum_{\mathbf{g}'} (i_0 a_g|P_{\mathbf{g}'})e^{-i\mathbf{k}\mathbf{g}'}$$

4-index approximated integrals can now be expressed as:

$$(i_0 a_g|\widetilde{j_{\bar{g}}b_{\bar{g}'}}) = \sum_{\mathbf{k}} \left[ \sum_{P,Q} J'_{i_0 a_g}{}^P(\mathbf{k}) [J(\mathbf{k})^{-1}]_{PQ} J'_{j_0 b_{\bar{g}' - \bar{g}}}{}^Q(\mathbf{k}) \right] e^{-i\mathbf{k}\bar{g}}$$

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4-index approximated integrals can now be expressed as:

$$(i_0 a_g|\widetilde{j_{\bar{g}}b_{\bar{g}'}}) = \sum_{\mathbf{k}} \left[ \sum_{P,Q} J'_{i_0 a_g}{}^P(\mathbf{k}) [J(\mathbf{k})^{-1}]_{PQ} J'_{j_0 b_{\bar{g}' - \bar{g}}}{}^Q(\mathbf{k}) \right] e^{-i\mathbf{k}\bar{g}}$$

The 4-index integrals are achieved through a back-transform. Assembly for each k point can be done separately (easy parallelization of the code).

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4-index approximated integrals can now be expressed as:

$$(i_0 a_g|\widetilde{j_{\bar{g}}b_{\bar{g}'}}) = \sum_{\mathbf{k}} \left[ \sum_{P,Q} J'_{i_0 a_g}{}^P(\mathbf{k}) \underbrace{[J(\mathbf{k})^{-1}]_{PQ}}_{\text{matrix inversion}} J'_{j_0 b_{\bar{g}' - \bar{g}}}{}^Q(\mathbf{k}) \right] e^{-i\mathbf{k}\bar{g}}$$

For each  $\mathbf{k}$  point the size of the matrix to be inverted is given by the number of auxiliary functions in the reference cell.

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Let us obtain the Fourier transform of the needed integrals

$$J(\mathbf{k})_{PQ} = \sum_{\mathbf{g}'} (P|Q_{\mathbf{g}'})e^{-i\mathbf{k}\mathbf{g}'}$$

$$J'^P_{i_0 a_g}(\mathbf{k}) = (i_0 a_g|P)(\mathbf{k}) = \sum_{\mathbf{g}'} (i_0 a_g|P_{\mathbf{g}'})e^{-i\mathbf{k}\mathbf{g}'}$$

4-index approximated integrals can now be expressed as:

$$(i_0 a_g|\widetilde{j_{\bar{g}}b_{\bar{g}'}}) = \sum_{\mathbf{k}} \left[ \sum_{P,Q} J'^P_{i_0 a_g}(\mathbf{k}) [J(\mathbf{k})^{-1}]_{PQ} J'^Q_{j_0 b_{\bar{g}' - \bar{g}}}(\mathbf{k}) \right] e^{-i\mathbf{k}\bar{g}}$$

The convolution over auxiliary function indices is restricted to the reference cell

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# The problem of Linear dependencies in the auxiliary fitting basis set

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Atoms are packed considerably closer in crystalline systems than in molecules.

Large auxiliary basis sets, or diffuse exponents, can easily lead to quasi-linear dependence, causing so the inversion of the matrix

$$[J(k)^{-1}]$$

to become unstable or critical.

Solution to this problem has been found by diagonalizing the J matrix, and then inverting the diagonal elements.

This allows to remove linear dependencies by eliminating eigenvectors whose eigenvalue is below a given threshold ( default is  $10^{-4}$  ).

# The problem of Coulomb series convergence

However this scheme cannot be adopted as it is, due to the behaviour of Coulomb series involving Gaussian functions.

For  $s$ -type functions the series is divergent, for  $p$ -type it is only conditionally convergent. For higher order functions the series converge but very slowly, and thus we need to compute integrals up to large distance.

A solution is offered by the use of Poisson-type functions as an auxiliary basis set.

Manby, Knowles, Lloyd, *J. Chem. Phys.*, 115(2001), 20

Since these functions hold no charge nor multipoles of any order, their mutual interaction vanishes fast, and therefore are suitable for our purposes.

Unfortunately, for the same reasons, they are unable to fit correctly Coulomb interactions, so we nevertheless need to introduce a few “true” Gaussian Functions in the basis set.

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# The “Two-Step Moment Constrained DF”

- LMP2 in crystals
- Post-HF Density Matrix

- Multipolar Approximation

- Lennard-Jones extrapolation

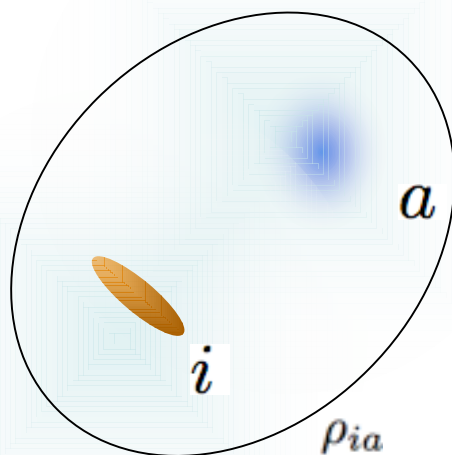
- Density Fitting in Crystals

- Feasibility of different systems

- Work to do and Prospects

On each atom **A** of the local fitting domain we put a set of correcting functions  $\{\Pi_A^\mu\}$  centered on atoms.

$$\mu = s, p, d, f, g$$



# The “Two-Step Moment Constrained DF”

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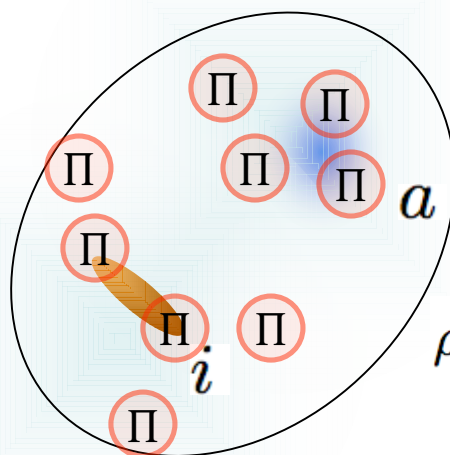
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On each atom **A** of the local fitting domain we put a set of correcting functions  $\{\Pi_A^\mu\}$  centered on atoms

$$\mu = s, p, d, f, g$$



$$\rho'_{ia} = \rho_{ia} - \sum_A \sum_{\mu} d_{ia}^{\mu A} \Pi_A^{\mu}$$

We obtain a *corrected product distribution*,  $\rho'_{ia}$ , which has zero multipoles up to a given order.

# The “Two-Step Moment Constrained DF”

On each atom **A** of the local fitting domain we put a set of correcting functions  $\{\Pi_A^\mu\}$  centered on atoms, having multipole moments  $\mathbf{m}_\nu^{\mu A}$

$$\int \frac{1}{r_{12}} \left[ \rho_{ia}(\mathbf{r}_1) - \sum_A \sum_\mu d_{ia}^{\mu A} \Pi_A^\mu(\mathbf{r}_2) \right]^2 d\mathbf{r}_1 d\mathbf{r}_2 - \\ + \sum_\nu \lambda_{ia}^\nu \left( \sum_A \sum_\mu d_{ia}^{\mu A} \mathbf{m}_\nu^{\mu A} - D_{ia}^\nu \right)$$

The formulation is very similar to the usual density fitting functional.

The constraints guarantee that the multipoles  $D_{ia}^\nu$  are cancelled up to order  $\nu$ , while the resulting density is as smooth as possible.

Good results are obtained with reasonably small domains for the local fitting (8 - 15 atoms).

- LMP2 in crystals
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# The “Two-Step Moment Constrained DF”

We perform in reciprocal space the fitting of the integrals  $\widetilde{K}'_{ab}{}^{ij}$  between corrected densities.

At the end of the procedure the needed integrals are obtained through:

$$\begin{aligned}\widetilde{K}_{ab}{}^{ij} = & \widetilde{K}'_{ab}{}^{ij} + (\rho_{ia} | \sum_B \sum_{\mu} d_{jb}^{\mu B} \Pi_B^{\mu}) + \\ & + (\sum_A \sum_{\mu} d_{ia}^{\mu A} \Pi_A^{\mu} | \rho_{jb}) - (\sum_A \sum_{\mu} d_{ia}^{\mu A} \Pi_A^{\mu} | \sum_B \sum_{\mu} d_{jb}^{\mu B} \Pi_B^{\mu})\end{aligned}$$

Up to now we successfully implemented and tested only correcting gaussians of s and p type.

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# Performance of DFP

- LMP2 in crystals

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- Multipolar Approximation

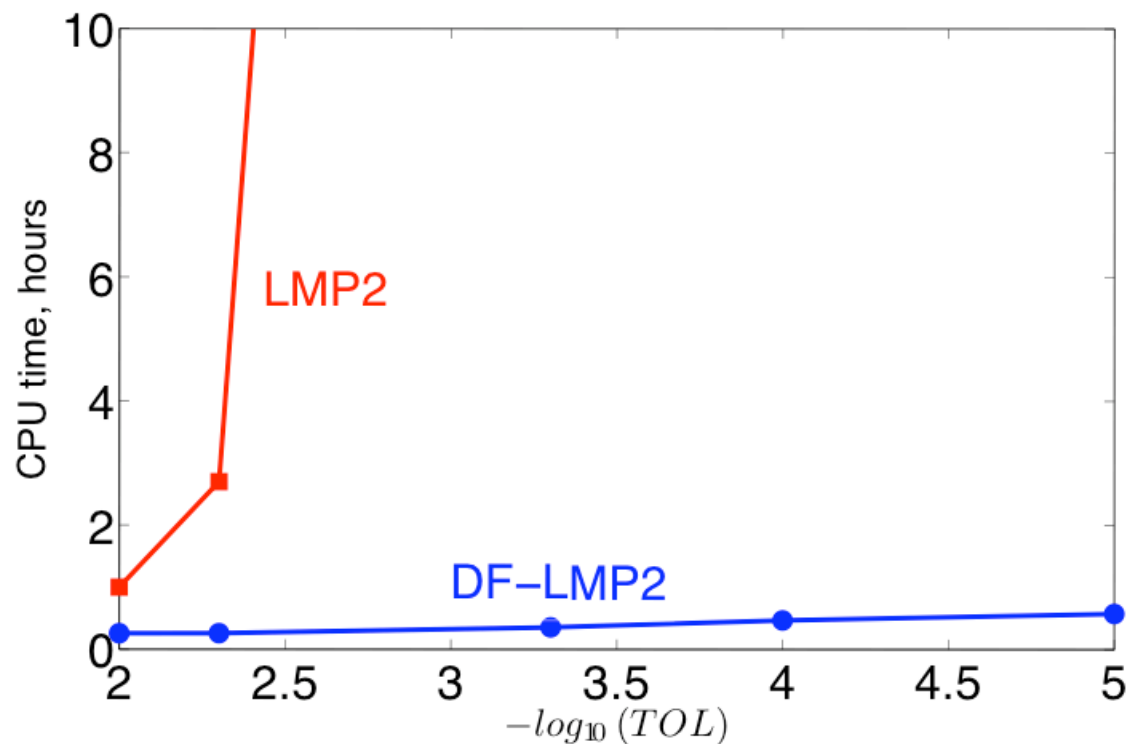
- Lennard-Jones extrapolation

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Timings for LMP2 calculations for diamond with 6-21G\*  
Dependence on the Wannier functions truncation threshold



# Performance of DFP

It is often difficult to estimate how much the DF approach is performing better. In some cases an exact calculation with reasonable thresholds is simply unfeasible.

System / technique		Diamond		CO <sub>2</sub>		MgO-3Layer slab	
		LMP2	DF-LMP2	LMP2	DF-LMP2	LMP2	DF-LMP2
d <sub>max</sub> =4 Å	time/min	23288	11	610	43	6247	10
	E2/Ha	-0.22865	-0.22875	-1.75366	-1.75401	-0.57774	-0.57774
d <sub>max</sub> =11 Å	time/min	Too long!	38	Too long!	50	Too long!	42
	E2/Ha	Too long!	-0.25765	Too long!	-1.76360	Too long!	-0.61002

- LMP2 in crystals
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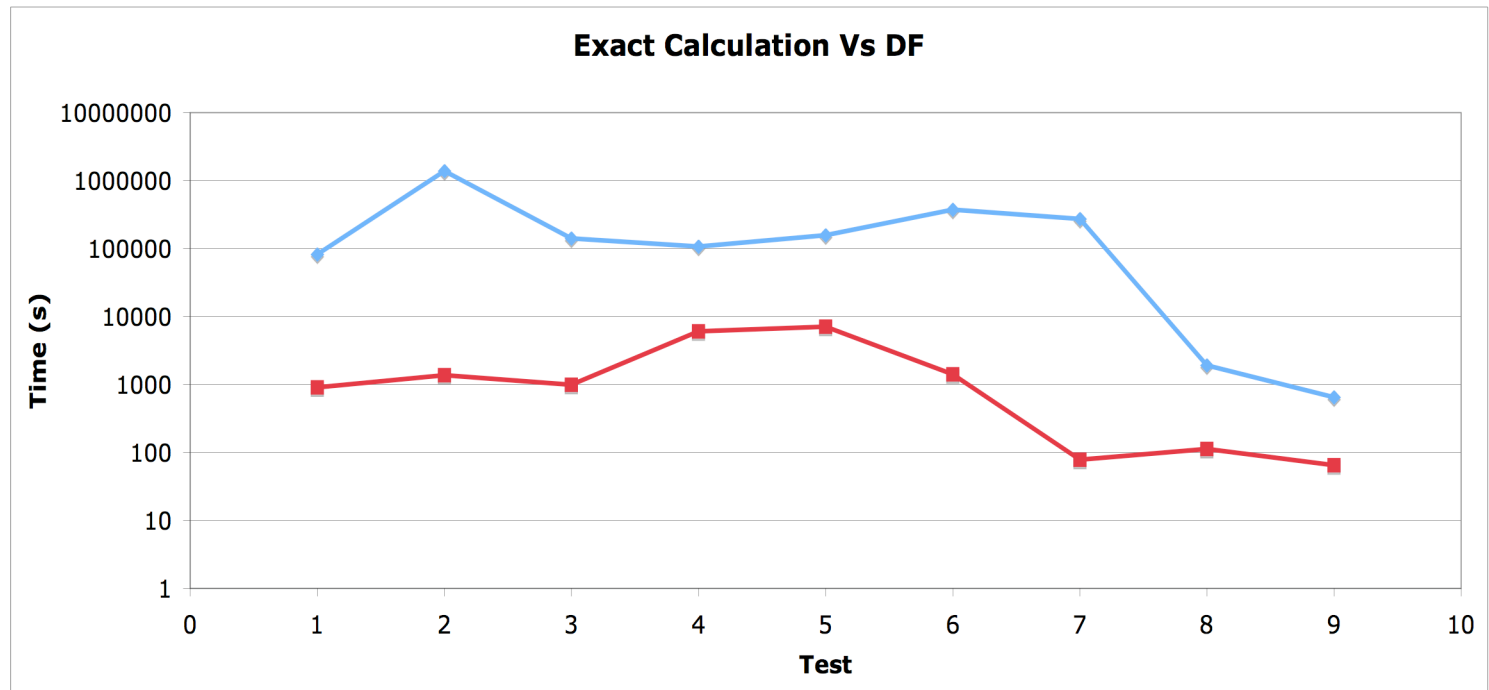
- Density Fitting in Crystals

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# Performance of DFP

Let us take a look to the performance of our approach on some test cases.



- LMP2 in crystals

- Post-HF Density Matrix

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- Lennard-Jones extrapolation

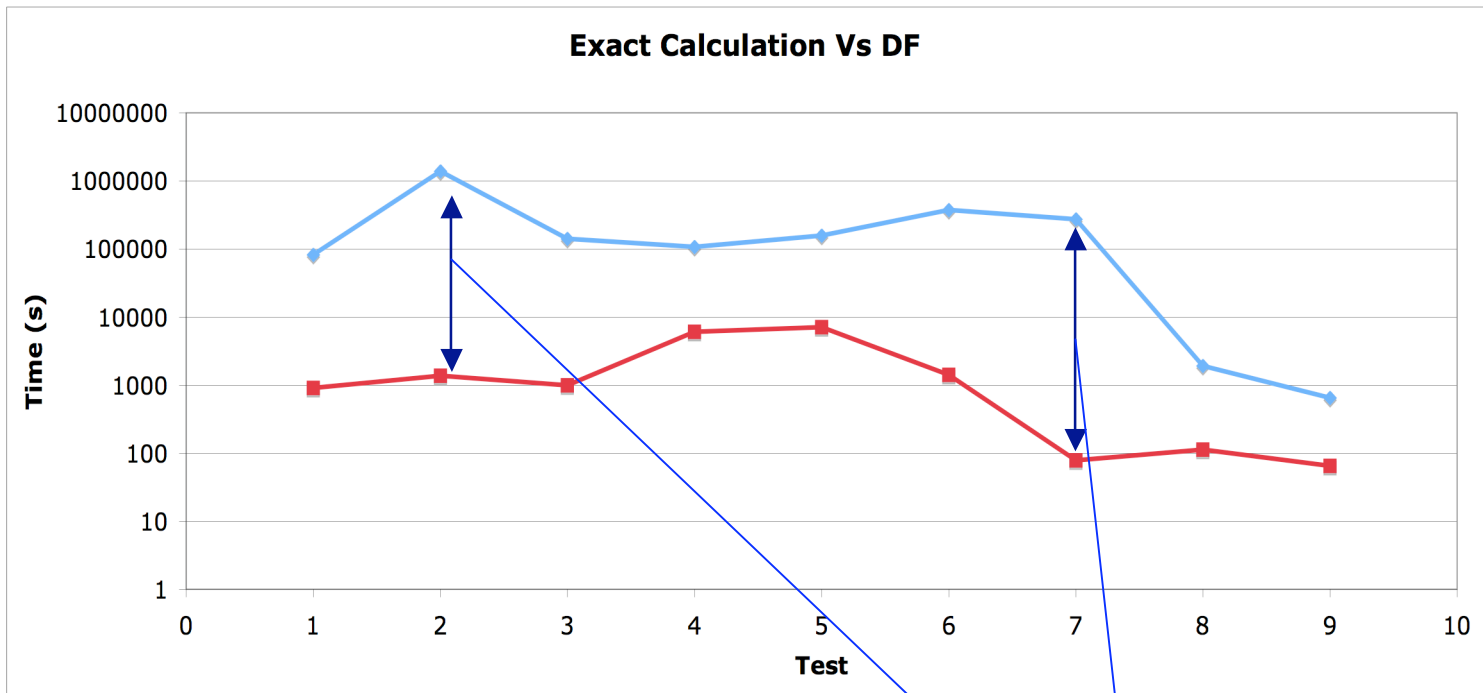
- Density Fitting in Crystals

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# Performance of DFP

Let us take a look to the performance of our approach on some test cases.



The error on energy is in all cases  $10^{-4}$  Ha or lower

In some cases we gain more than 3 orders of magnitude!

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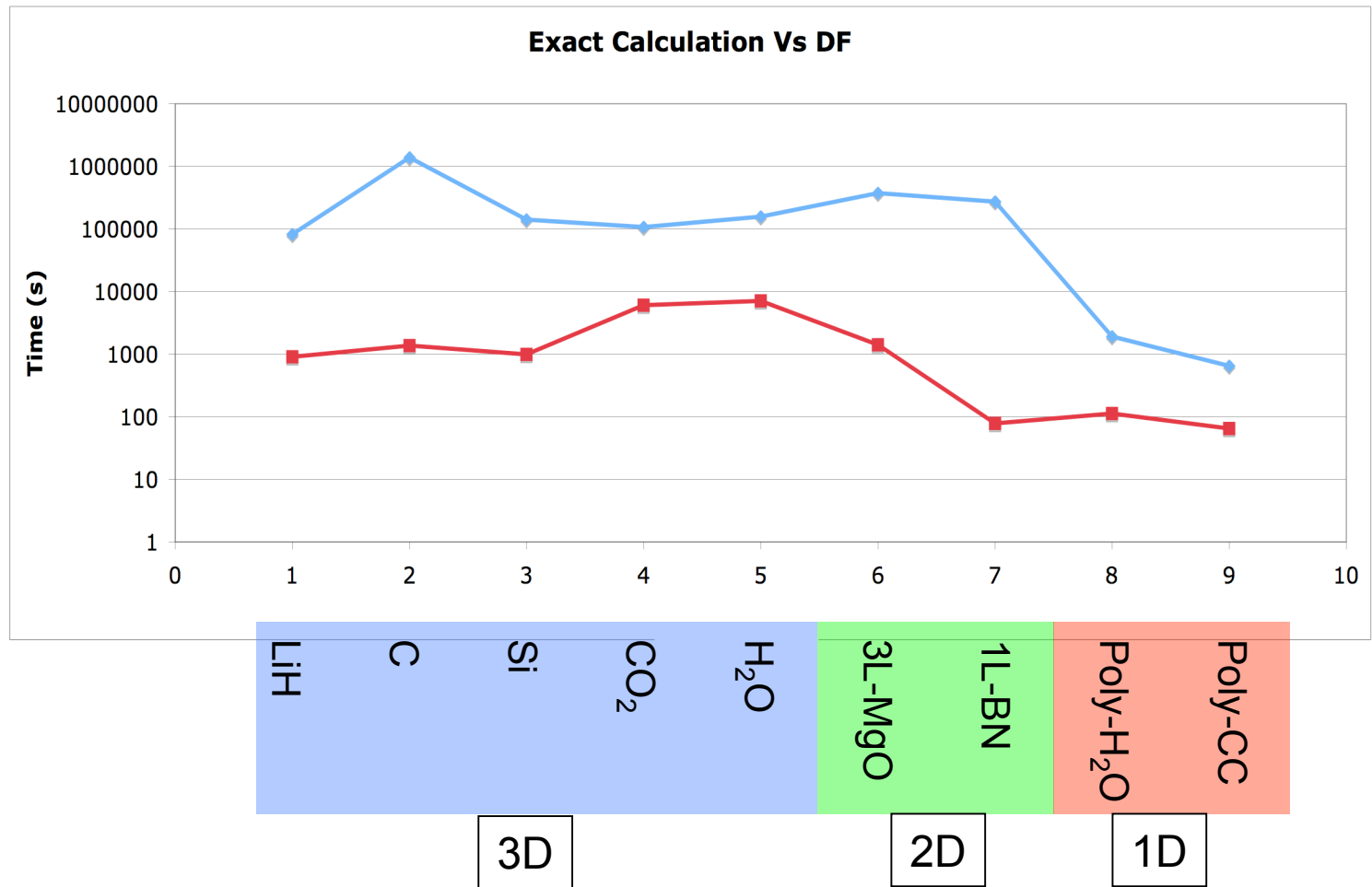
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# 2nd Summary- Fast Integrals Evaluation

- LMP2 in crystals
- Post-HF Density Matrix

•Multipolar Approximation

•Lennard-Jones extrapolation

•Density Fitting in Crystals

•Feasibility of different systems

•Work to do and Prospects

We have successfully adapted the popular Density Fitting technique to approximate two electron repulsion integrals in crystalline systems.

**This implementation features:**

- ✓ Reciprocal space formulation
- ✓ Use of Poisson Functions
- ✓ Two-step Fitting

The gain in time is up to three orders of magnitude.

**Our recipe:**

- ✓ 0-6Å : Density Fitting
- ✓ 6Å-10Å : Multipolar Approximation
- ✓ 10Å- ∞ : Lennard-Jones Extrapolation

# What Cryscor can do today:

- LMP2 in crystals
- Post-HF Density Matrix

- Multipolar Approximation

- Lennard-Jones extrapolation

- Density Fitting in Crystals

- Feasibility of different systems

- Work to do and Prospects

We present here in the following a series of test systems which have been successfully studied with Cryscor.

We won't provide results, since a full study of each of this systems would imply careful basis set analysis, deep insight and experience. An overview of applications will be presented by Denis Usvyat in the forthcoming talk.

This list is intended to provide an insight into what is today feasible with Cryscor.

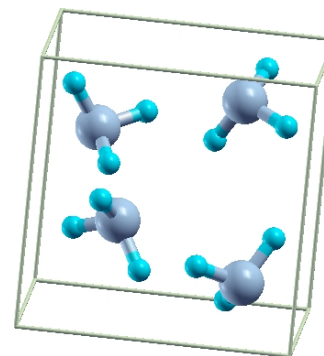
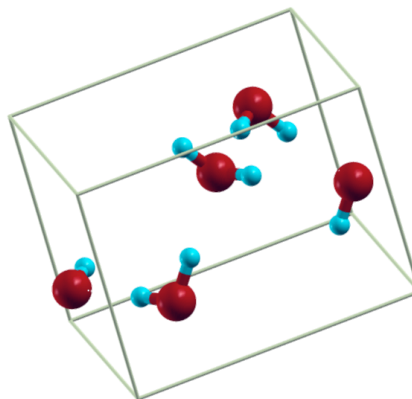
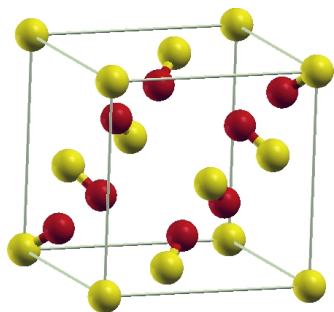
# Molecular Crystals

- LMP2 in crystals
- Post-HF Density Matrix
- Multipolar Approximation
- Lennard-Jones extrapolation
- Density Fitting in Crystals

System	Space Group	n. atoms per cell
Cubic Apolar Ice	tetragonal (P 41 21 2)	12
Cubic Polar Ice	tetragonal (I 41md)	6
Hexag. Apolar Ice	orthorombic (Pna21)	24
Hexag. Polar Ice	orthorombic (Cmc21)	12
N2	cubic (Pa3)	8
Urea	tetragonal (P-421m)	16
Acetyl	cubic (Pa3)	16
CO2	cubic (Pa3)	12
Ammonia	cubic (P 213)	16
KNH	orthorombic (C 2221)	24

•Feasibility of different systems

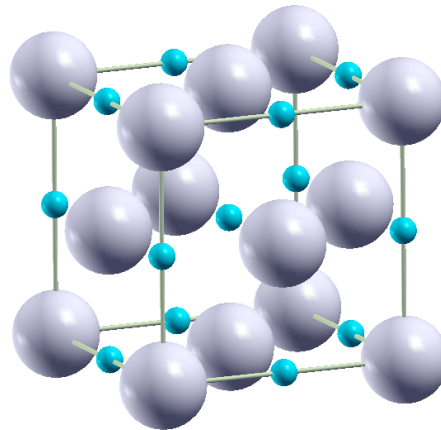
•Work to do and Prospects



# Ionic Crystals

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- Multipolar Approximation
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- Density Fitting in Crystals
- Feasibility of different systems
- Work to do and Prospects

System	Space Group	n. atoms per cell
MgO	Cubic (Fm3m)	2
LiH	Cubic (Fm3m)	2
LiF	Cubic (Fm3m)	2
NaCl	Cubic(Fm3m)	2
TiO <sub>2</sub>	Tetragonal (P 42m nm)	6



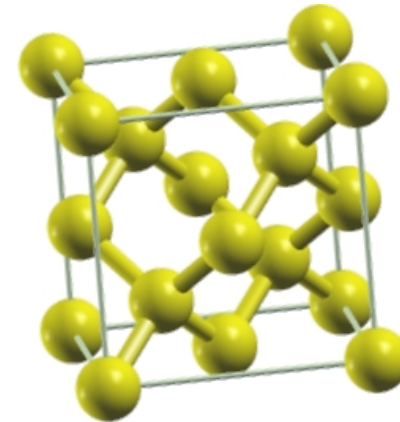
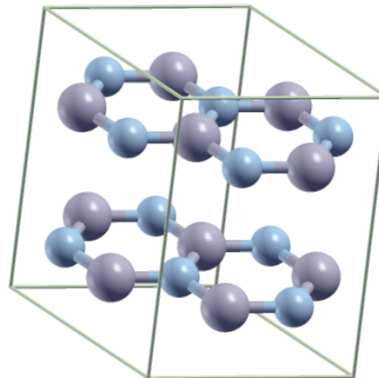
# Covalent Crystals

- LMP2 in crystals
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- Lennard-Jones extrapolation
- Density Fitting in Crystals

System	Space Group	n. atoms per cell
BeS	cubic (F-43m)	2
Diamond	cubic (Fd3m)	2
Si	cubic (Fd3m)	2
Alpha-Quartz	hexagonal (P32 21)	9
Hexag. BN	hexagonal (P63mmc)	4

•Feasibility of different systems

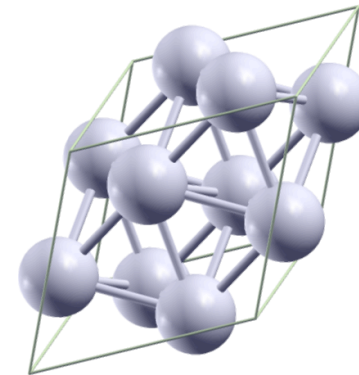
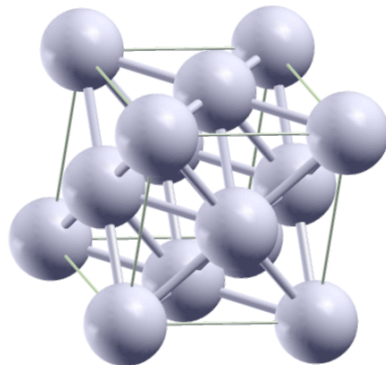
•Work to do and Prospects



# Weakly Bound Rare Gas Crystals

- LMP2 in crystals
- Post-HF Density Matrix
- Multipolar Approximation
- Lennard-Jones extrapolation
- Density Fitting in Crystals
- Feasibility of different systems
- Work to do and Prospects

System	Space Group	n. atoms per cell
Argon	cubic (Fm3m)	1
Hexag. Ar	hexagonal (P63mmc)	2



# 2D Slabs and adsorption of molecules

- LMP2 in crystals
- Post-HF Density Matrix

- Multipolar Approximation

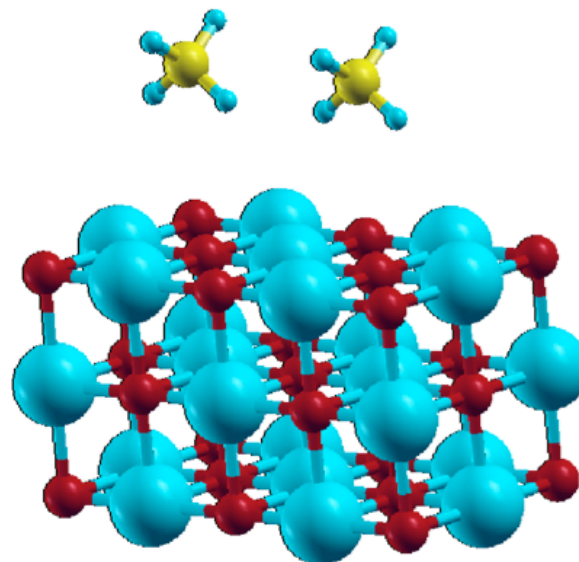
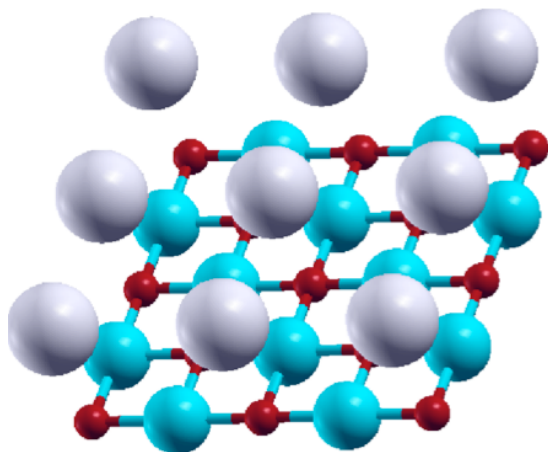
- Lennard-Jones extrapolation

- Density Fitting in Crystals

- Feasibility of different systems

- Work to do and Prospects

System	Space Group	N. Atoms per Cell
HBN 1L	hexagonal (P -6m2)	2
MgO 3L	square (P 4mmm)	6
CH4/MgO3L	no symmetry	11
corundum 2L	hexagonal (R -3c)	10



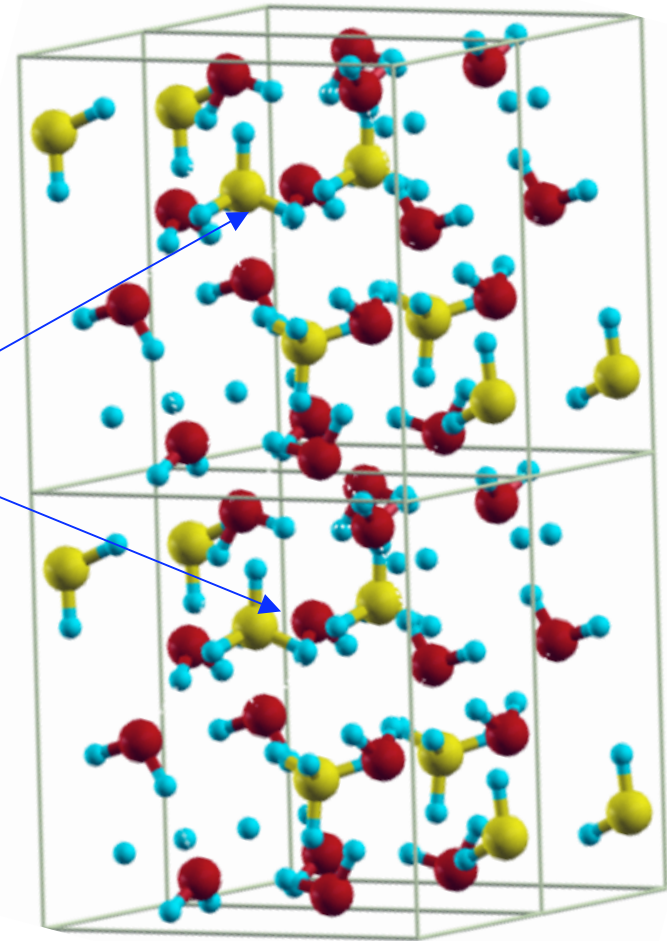


# Interaction of molecules inside crystalline bulk cages

- LMP2 in crystals
- Post-HF Density Matrix
- Multipolar Approximation
- Lennard-Jones extrapolation
- Density Fitting in Crystals
- Feasibility of different systems
- Work to do and Prospects

System	Space Group	N. Atoms per Cell
Clathrate MH-III	Pna2 <sub>1</sub>	11

CH<sub>4</sub> molecules are trapped inside an Ice structure



# Conclusions and Prospects

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•LMP2 in crystals

•Post-HF Density Matrix

•Multipolar Approximation

•Lennard-Jones extrapolation

•Density Fitting in Crystals

•Feasibility of different systems

•Work to do and Prospects

## Current work :

- ✓ Refinement and standardization of “basic” program
- ✓ Preparation and test of Public (beta) version and User’s manual
- ✓ Tests, tests, tests
- ✓ Release of public version in 2008
- ✓ Cryscor Web site

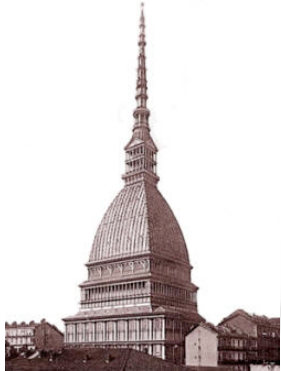
## In the next future...

- ✓ Auxiliary basis set (to complement the HF set)
- ✓ Providing optimized basis sets for our new two-step density fitting technique
- ✓ Improved estimates of electron density matrix
- ✓ Higher efficiency, parallelization
- ✓ Assessing basis set quality

## ...and more distant in time:

- ✓ Extension to other local correlation schemes (CCSD, MP4, ...)
- ✓ Automatic geometry optimization.

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