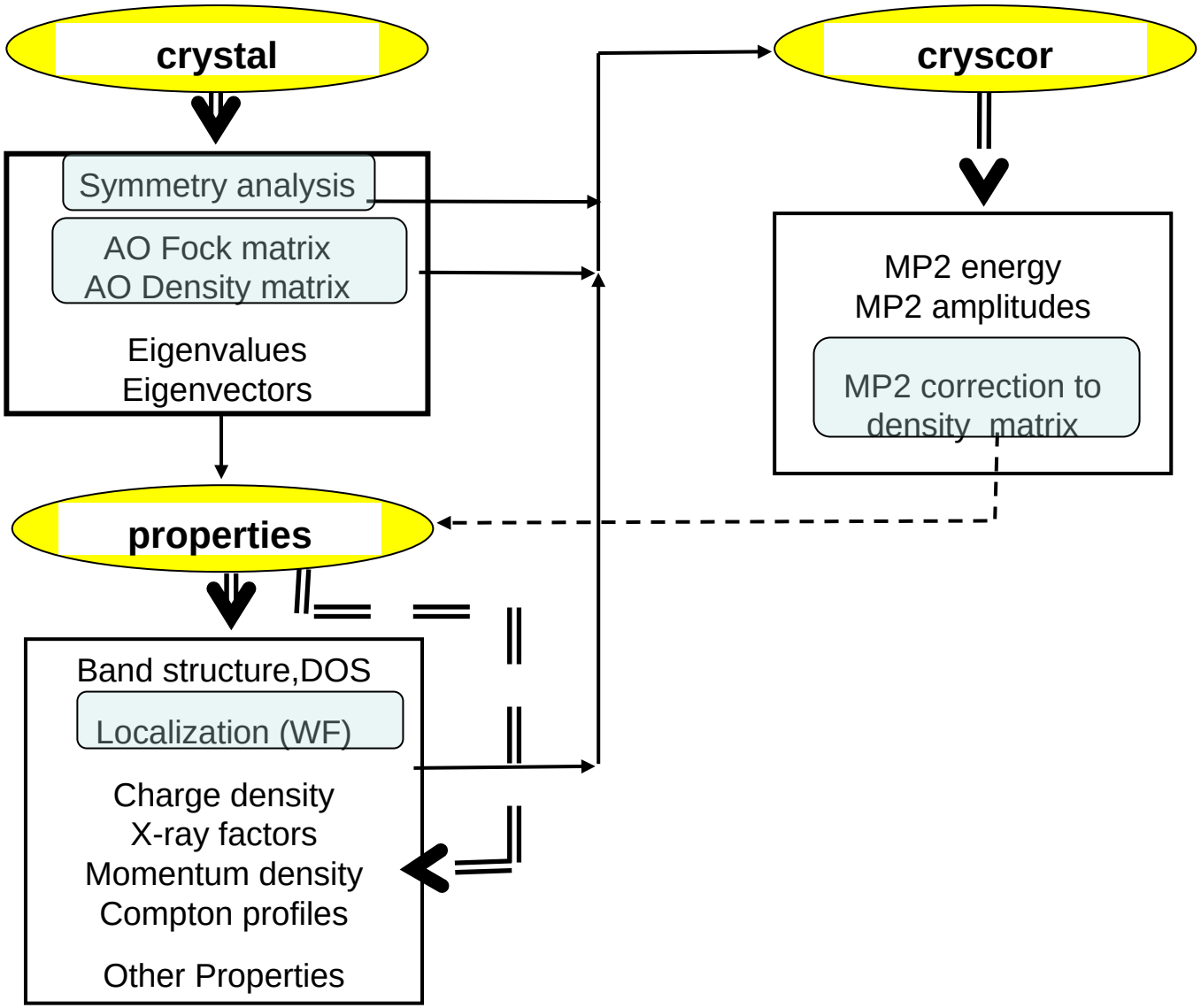
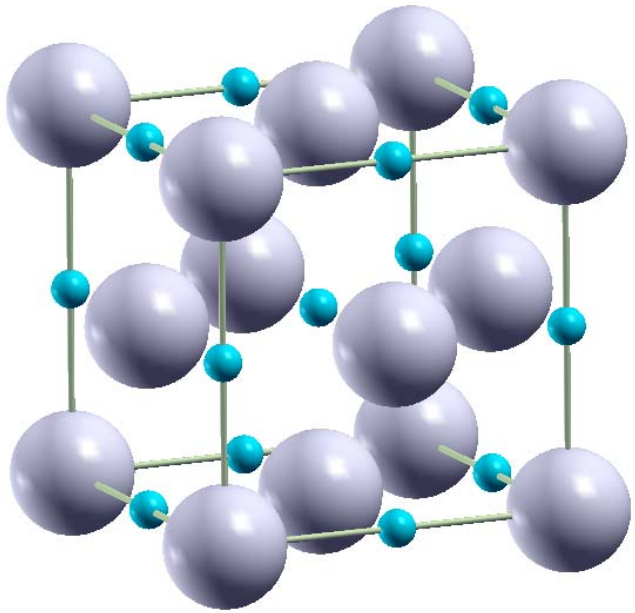
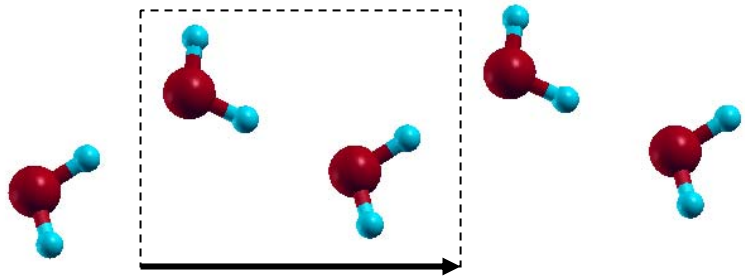
CRYSTAL --- CRYSCOR connection scheme



Two examples of CRYSCOR use and results : LiH and poly-H_2O

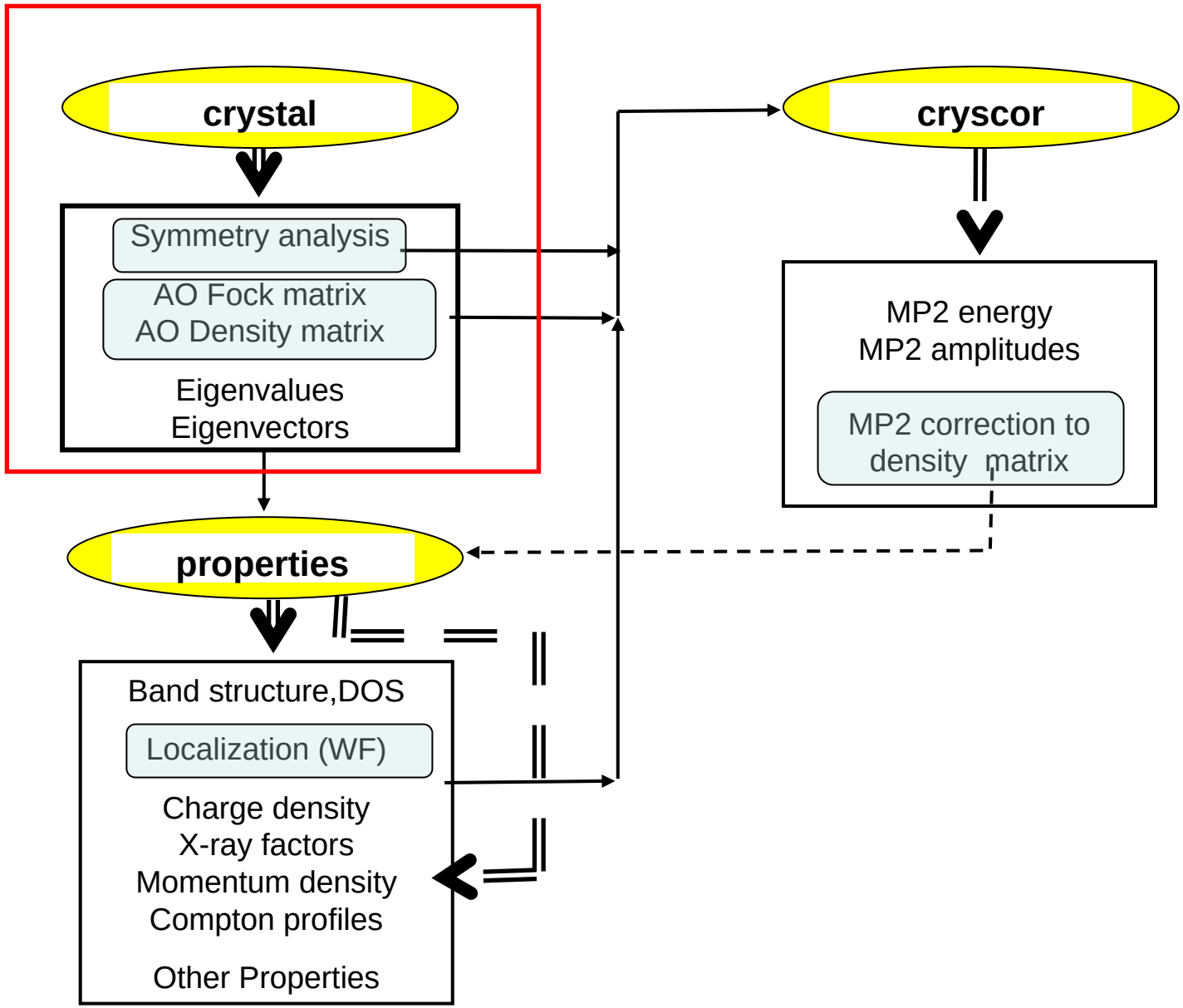


Li H (conventional cell)



poly-H_2O (yz view)

poly-H_2O (xz view)


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

1) HF solution: CRYSTAL

```
LiH bulk
CRYSTAL
0 0 0
225
3.876
2
 1 0.    0.    0.
 3 0.5   0.5   0.5
ENDG
```

BS: A, C

```
ENDBS
TOLINTEG
7 7 7 9 11
SHRINK
8 8 8
FMIXING
30
MAXCYCLE
100
END
```

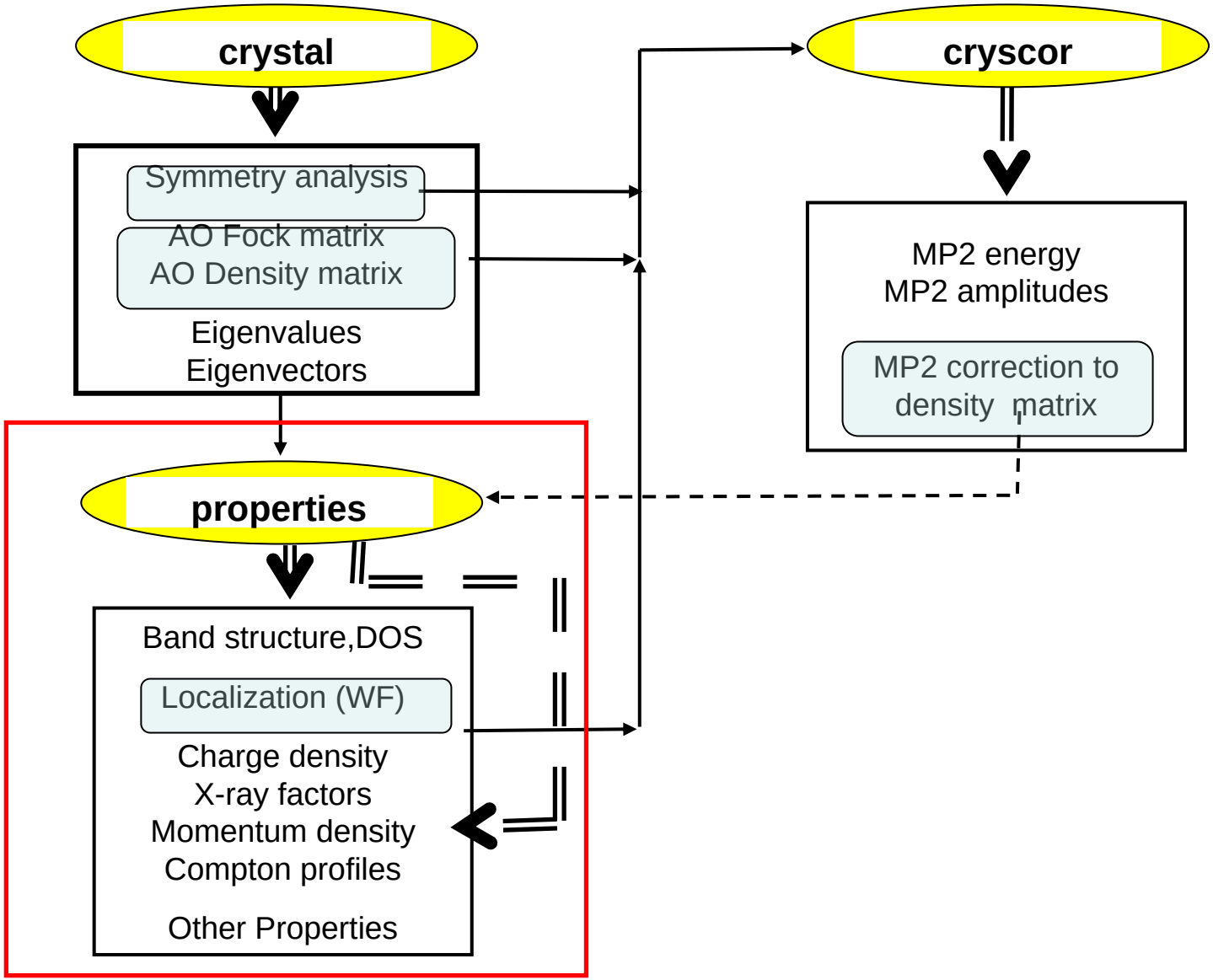
A

```
1   4
0  0  5  2.  1.
120.0  0.000267
 40.0  0.002249
 12.0  0.006389
  4.0  0.032906
  1.2  0.095512
0  0  1  0.  1.
  0.5  1.
0  0  1  0.  1.
  0.13 1.
0  2  1  0.  1.
  0.3  1.



3   3
0  0  6  2.  1.
 700.00    0.001421
 220.00    0.003973
  70.00    0.016390
  20.00    0.089954
   5.00    0.315646
   1.5     0.494595
0  0  1  0.  1.
   0.50  1.0
0  2  1  0.  1.
   0.6   1.0
```

C

```
1   5
0  0  5  2.  1.
120.0  0.000267
 40.0  0.002249
 12.0  0.006389
  4.0  0.032906
  1.2  0.095512
0  0  1  0.  1.
  0.5  1.
0  0  1  0.  1.
  0.13 1.
0  2  1  0.  1.
  0.3  1.
0  3  1  0.  1.
  0.8   1.0
3   4
0  0  6  2.  1.
 700.00    0.001421
 220.00    0.003973
  70.00    0.016390
  20.00    0.089954
   5.00    0.315646
   1.5     0.494595
0  0  1  0.  1.
   0.50  1.0
0  2  1  0.  1.
   0.6   1.0
0  3  1  0.  1.
  0.8   1.0
```

basis set	HF		
	E_{coe}	a_0	B_0
A	0.3423	4.126	27.7
C	0.3425	4.121	28.3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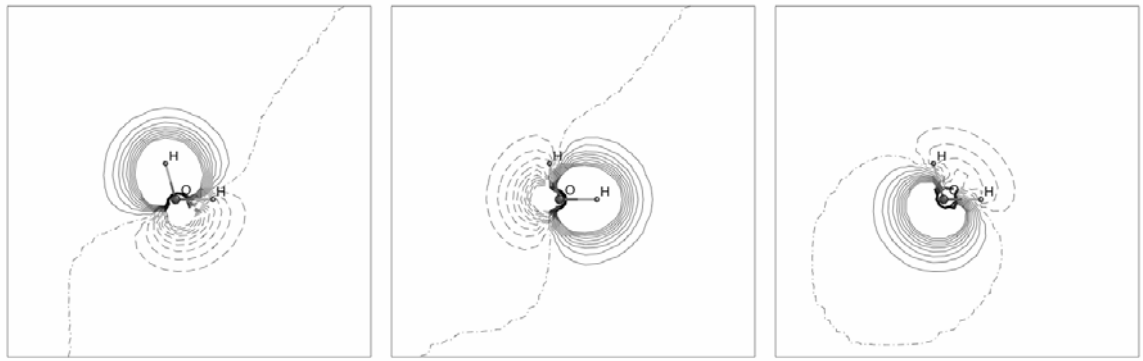
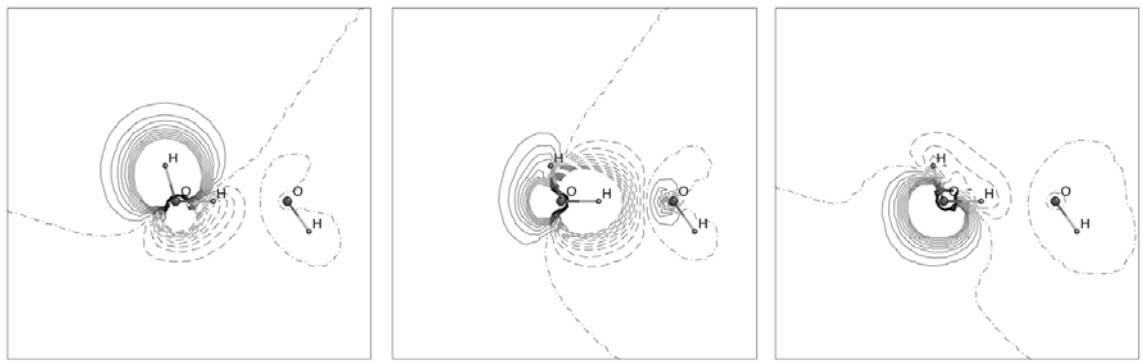
2) WFs preparation: PROPERTIES

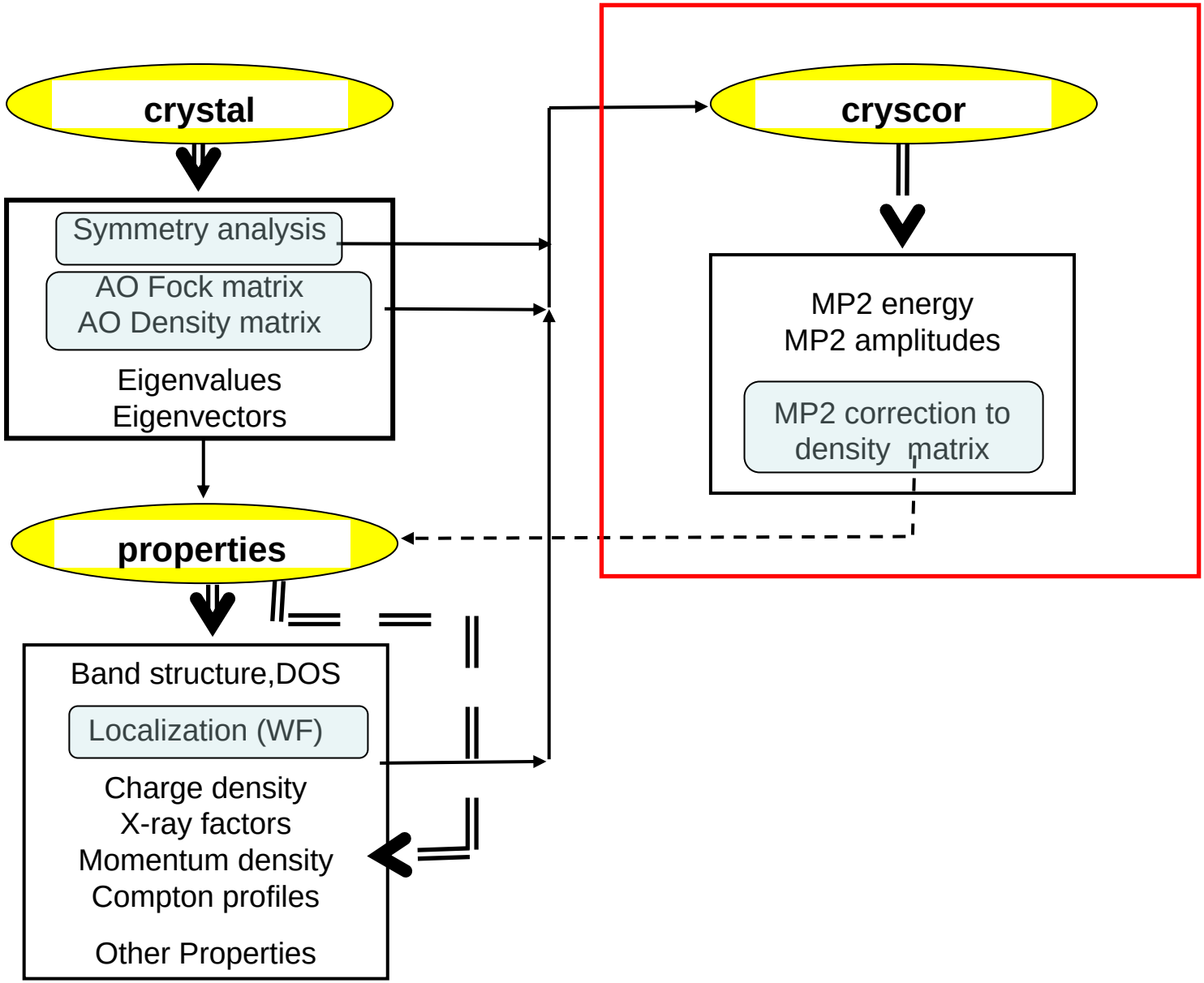
```
NEWK
8 8 8
1 0
LOCALWF
SYMMWF
VALENCE
END
END
END
```

water molecule symmetrized WFs



water polymer symmetrized WFs

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3) MP2 calculation: CRYSCOR

NEWK
12 12 12
1 0

*** FLOWERs DOMAINs ***
FLOW n. 1
Atom 1 H - n. of G: 1 --> 1

*** PAIRs CLASSIFICATION ***
STRONG PAIRS: 1
WEAK PAIRS: 0
DISTANT PAIRS: 0

DOMDEF
STARS
1
1 2
1 2 3

*** FLOWERs DOMAINs **
FLOW n. 1
Atom 1 H - n. of G: 13 --> 1 2 3 4 5 6
7 8 9 10 11 12 13
Atom 2 LI - n. of G: 6 --> 2 8 12 26 30 40

PAIR
4. 6.

*** PAIRs CLASSIFICATION ***
STRONG PAIRS: 1
WEAK PAIRS: 2
DISTANT PAIRS: 2

TOBJ
0.001 0.001
END

improve description of WF and PAO tails !!!

(default: 0.01 0.01)

N. int (10^6)	E-time (sec)
3.5	45
19	87
108	560
2952	14617 (4 hours)

c') density-fitting option for LiH

```
DFITTING
8   (shrinking Factor)
20  (fitting radius A)
!H FITTING SET
---
!Li FITTING SET
---
99 0
END
```

```
!H FITTING SET
1 12
0 0 1 1
  4.242065 1.
0 0 1 1
  1.928212 1.
0 0 1 1
  0.876460 1.
0 0 1 1
  0.398391 1.
0 2 1 1
  2.574000 1.
0 2 1 1
  1.170000 1.
0 2 1 1
  0.531818 1.
0 3 1 1
  1.561851 1.
0 3 1 1
  0.709932 1.
0 3 1 0
  1. 1.
0 4 1 1
  0.947700 1.
0 4 1 0
  1. 1.
```

```
!Li FITTING SET
3 16
0 0 1 1
85.451043 1.0
0 0 1 1
17.875674 1.0
0 0 1 1
4.471934 1.0
0 0 1 1
2.715449 1.0
0 0 1 1
1.181735 1.0
0 0 1 1
0.428376 1.0
0 0 1 1
0.168385 1.0
0 2 1 1
7.134624 1.0
0 2 1 1
2.650729 1.0
0 2 1 1
0.687662 1.0
0 2 1 1
0.336802 1.0
0 2 1 1
0.158526 1.0
0 3 1 1
3.669560 1.0
0 3 1 1
0.632956 1.0
0 3 1 1
0.147632 1.0
0 3 1 0
1. 1.
```

Use of the DF option reduces the integral step from 14137 to 540 secs, with a gain in speed by a factor 26.

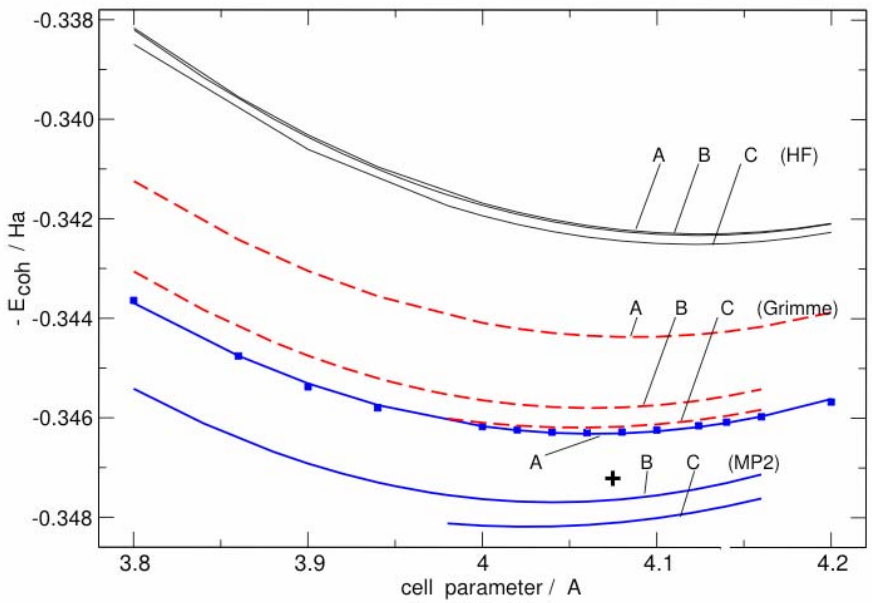
Use of the DF option + multipolar option with **good** tolerances

(domain size 19 atoms TOBJ: 0.001 0.001 8+12 irred. pairs)

reduces the computation time from 6 days to 30 minutes with no loss of accuracy!

Some CRYSCOR results : LiH

Casassa, Halo, Maschio, Roetti and Pisani, TCA, in press



Cohesion energy of LiH as a function of the lattice parameter,

of the basis set adopted:

A : H(3s,3p), Li(2s,1p)

B : H(3s,3p.1d), Li(2s,1p)

C : H(3s,3p,1d), Li(2s,1p,1d)

and of computational method:

HF ———

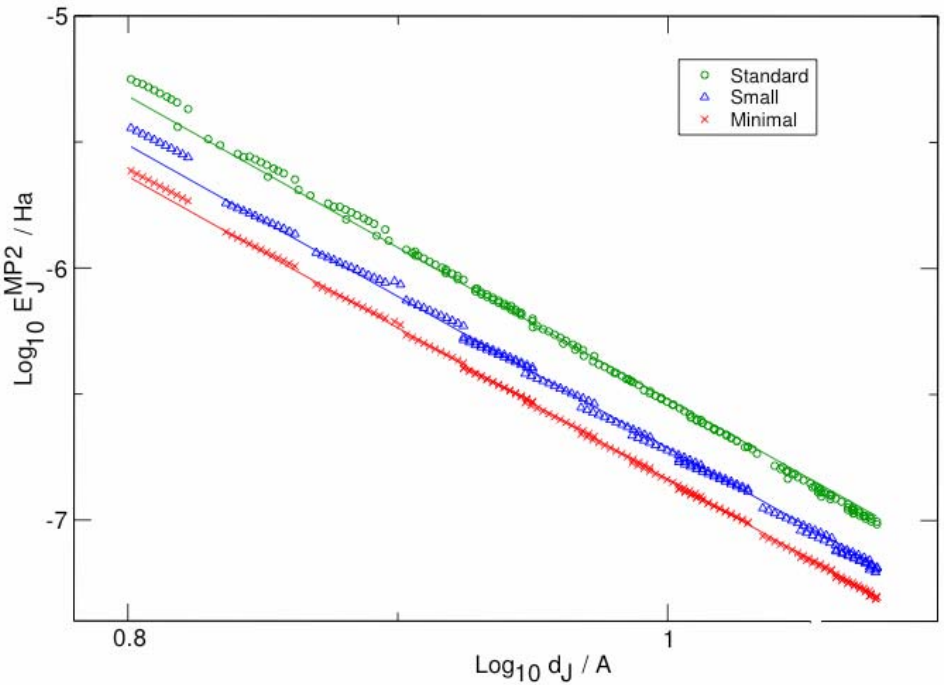
MP2 ———

Grimme (corrected MP2) - - - - -

\+ experimental values

Some CRYSCOR results : LiH

Casassa, Halo, Maschio, Roetti and Pisani, TCA, in press



Contribution to MP2 energy by excitations from a WF pair

$(\omega^0\omega^j)$ in LiH, for basis set A,

as a function of the distance d_j between the two WF centers

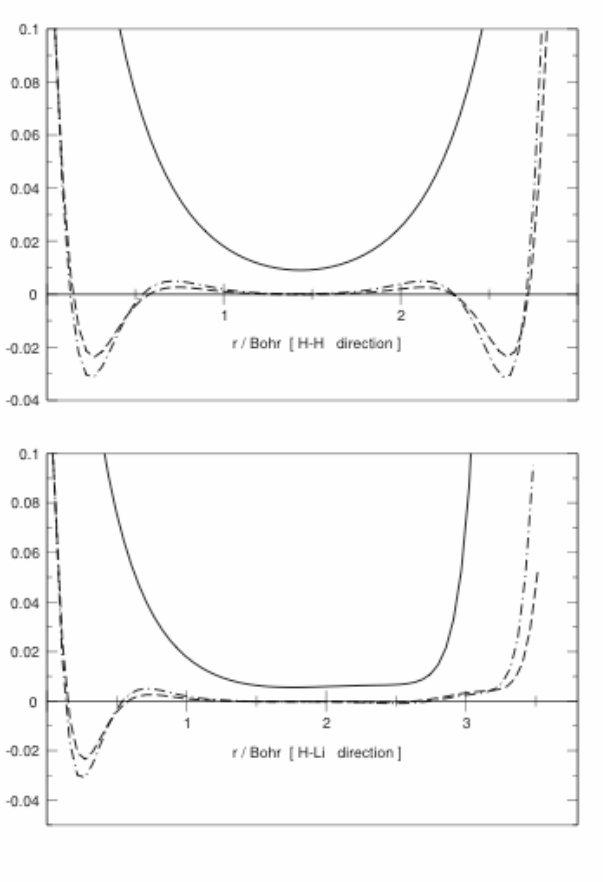
$$\log E_j = -6 \log d_j + \text{const} ,$$

and of the size of the WF domains:

- □ 19 atoms
- △ 7 atoms
- × 1 atom

Some CRYSCOR results : LiH

Casassa, Halo, Maschio, Roetti and Pisani, TCA, in press



Profile of the HF electron density (a.u.)

(———),

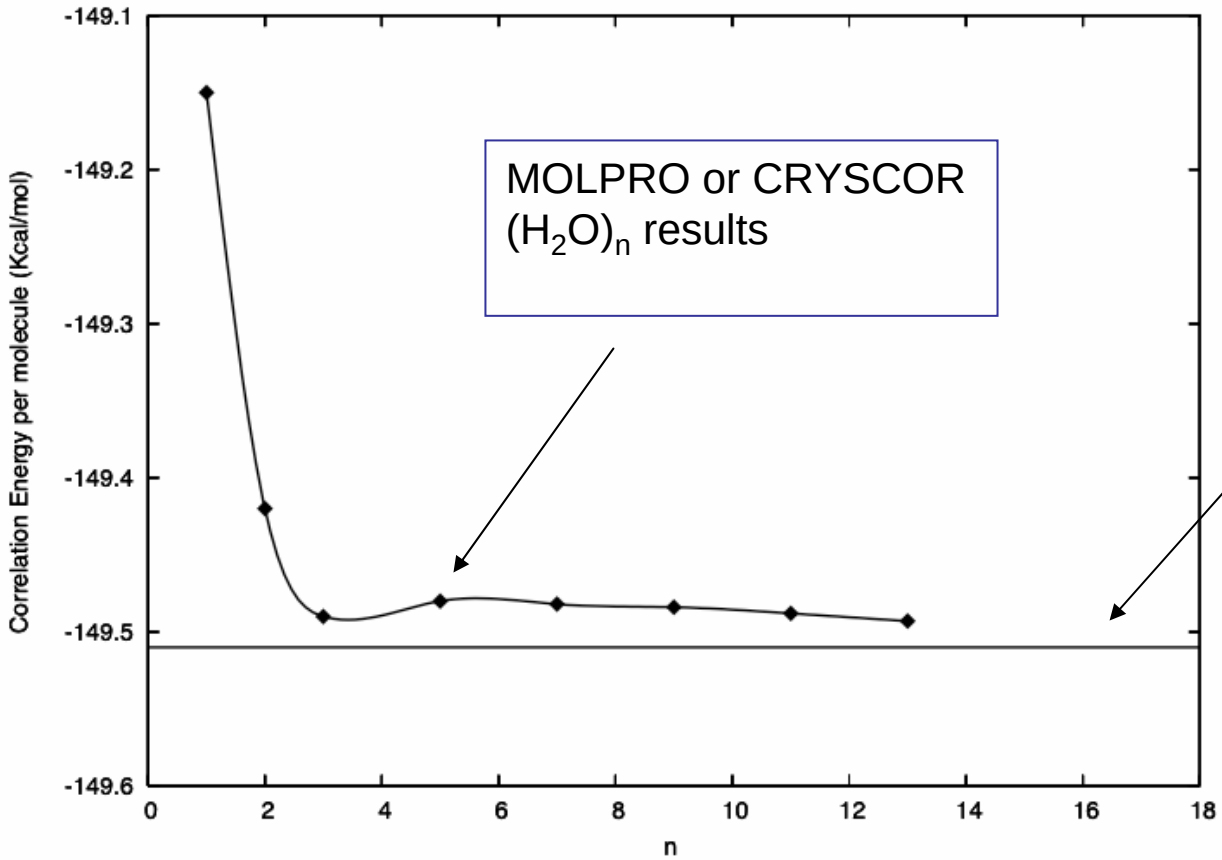
and of the MP2 correction ($\times$ 10)

(- - - - -) bs A , (- · - · - ·) bs C

along the H---H line (plot above)

and the H---Li line (plot below)

Some CRYSCOR results : the H_2O polymer

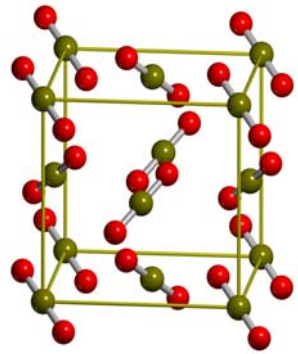


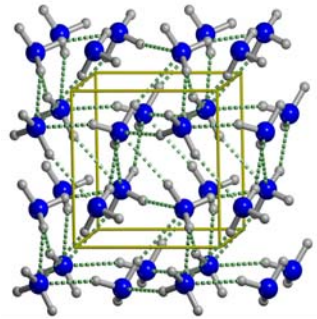
L-MP2 results: CO_2 and NH_3 molecular crystals

Single-point energy calculations on experimental geometries

Experimental lattice energy:

$$\Delta E = \Delta H^0(298)+2RT$$





6-31G(d,p)	CO_2	NH_3
PBE	-5.8	-33.2
PBE0	-7.2	-32.2
HF(WL)	-23.5	-47.1
HF-WL	-21.8	-44.7
L-MP2	-14.1	-30.0
Exp.t	-31.1	-36.0

CONCLUSIONS AND PROSPECTS

Current work :

* **Refinement and standardization of "basic" program**

Higher efficiency, parallelization
Preparation and test of Public (beta) version and User's manual

* **Tests**

Different systems (Ionic and molecular crystals, Layered compounds, Slabs, Adsorption on crystalline surfaces,…)
Assessing basis set quality
Providing standard sets for the density fitting technique

Open problems and lines of development :

* Auxiliary basis set (to complement the HF set)
* Extension to other local correlation schemes (CCSD, MP4, …)
* Improved estimates of electron density matrix

Acknowledgments

* CRYSCOR team