Ab initio structure prediction for molecules and solids

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Contents

structure prediction:

1) global search on potential surface

   minima correspond to (meta)stable structures

2) search for barriers

method:

simulated annealing:
start from atoms, perform moves until solid is formed
=> change atom positions and lattice constant

examples: LiF (bulk; cluster), BN, CaC_2, GeF_2

Why *ab initio* ?

model potentials good for ionic systems, less for covalent or metallic systems

ab initio calculations more generally applicable, also if type of bond unknown

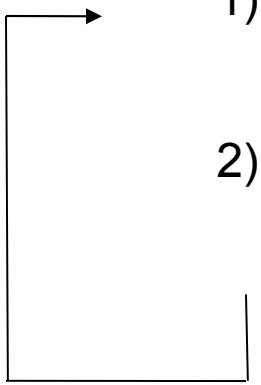
Method, part I

I) simulated annealing with „G42“ code

0) guess structure -> compute energy **(random geometry!)**

1) create new structure
(atoms moved or exchanged, lattice constant changed …),
compute new energy

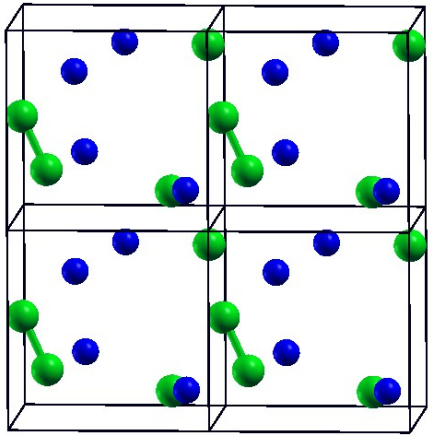
2) accept new structure according to probability $exp\ (-\Delta E / kT)$
(Metropolis algorithm)



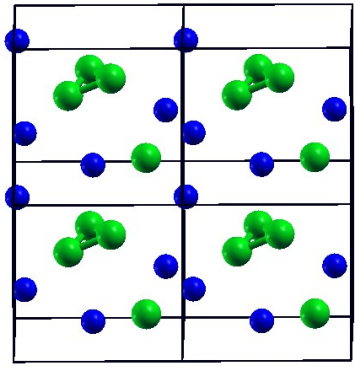
reduce temperature during the run; stop after ~10^4 … 10^6 steps;
followed by quench (~10^4 steps at $T=0$)

J. C. Schön and M. Jansen, Angew. Chem., Int. Ed. Engl. ***35****, 1286 (1996)*

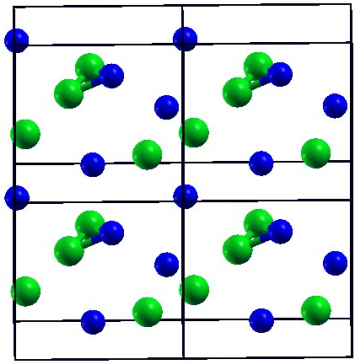
Example



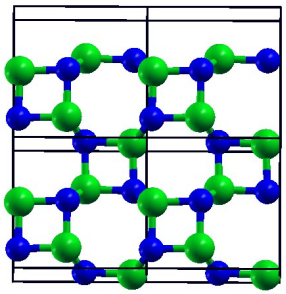
Step 1



Step 2543



Step 2544
(2 atoms exchanged)



Step 22500

Method, parts II, III

II) local optimisation:
start from geometry after quench, optimise with analytical gradients (CRYSTAL code)

analytical gradient with respect to atom positions:
K. Doll, V. R. Saunders, N. M. Harrison, Int. J. Quant. Chem. ***82****, 1 (2001)*
and unit cell:
K. Doll, R. Dovesi, R. Orlando, Theor. Chem. Acc. ***112****, 394 (2004)*

III) symmetry analysis with KPLOT (*R. Hundt, Bonn*)

in total: ~100…1000 runs required (different run=different initialisation of random number generator)

Barrier calculation

Threshold algorithm:

1) Start from minimum, allow all moves up to a certain energy (lid)

2) perform quench, analyse structure

=> transition to other structure possible

Ab initio calculations: with CRYSTAL-Code

Idea: use methods from molecular quantum chemistry for periodic systems
-> Gaussian type functions used (i.e. local basis set)

1975 Turin: Begin of the code development
1988 first release: CRYSTAL88
further releases:1992, 1995, 1998, 2003, 2006

R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, Ph. D'Arco, M. Llunell, ***CRYSTAL2009***

www.crystal.unito.it

CRYSTAL09: some of the new features

phonon dispersion (in CRYSTAL06 for k=0)
dielectric properties (static dielectric tensor)
empirical correction for dispersion

$$E_{\mathrm{disp}} = -s_6 \sum_{i=1}^{N_{\mathrm{at}}-1} \sum_{j=i+1}^{N_{\mathrm{at}}} \frac{C_6^{ij}}{R_{ij}^6} f_{\mathrm{dmp}}(R_{ij}). \qquad f_{\mathrm{dmp}}(R_{ij}) = \frac{1}{1+e^{-d(R_{ij}/R_r-1)}}$$

S. Grimme, J. Comp. Chem. 27, 1787 (2006)

.... various others ....

Ab initio simulated annealing

Idea: connect code for simulated annealing with *ab initio* code
(e.g. CRYSTAL)
use *ab initio* energy instead of energy from model potential

Problems:
1) CPU time
2) numerical stability

Problem 1: CPU time

e.g. LiF bulk: 4 Li atoms, 4 F atoms, experimental geometry

1 calculation with good parameters: 16 seconds
1 calculation with good parameters, no symmetry: 13 minutes

100000 calculations
for 1 simulated annealing and quench run:
13 minutes*100000: ~ 2 years
100 runs: 2 centuries

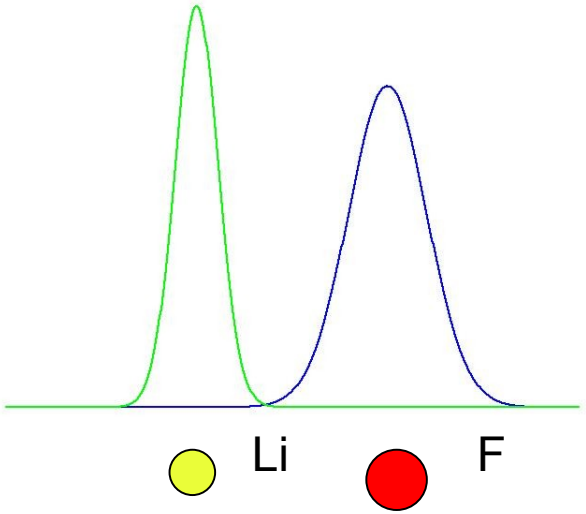
model potential: minutes / hours, with even more steps

How to speed up the *ab initio* calculations?

Necessary: fast
reasonably stable (convergence at random geometry required!)

Important: energy does not have to be very accurate

Faster: 1) Gaussian basis set used:
=> increase thresholds for integral selection
e.g. neglect integrals with
Overlap < 10^{-4} (default: 10^{-6})



2) small basis set (no polarisation functions, outermost exponents less diffuse)

3) stop SCF cycles earlier (full convergence not necessary)

4) fewer k-points ...

Problem 2: How to achieve stability?

Difficulties: a) initial geometry is obtained RANDOMLY
Kohn-Sham equations have to be solved
=> expect convergence problems!

> 10000 subsequent geometries are generated, calculations performed at all these geometries!

b) weak computational parameters, instabilities more likely

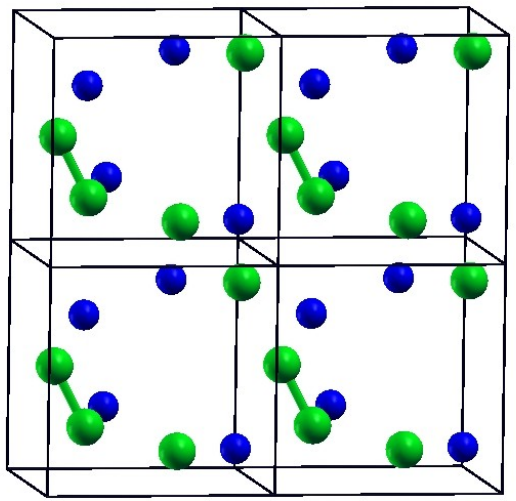
How to achieve stability?

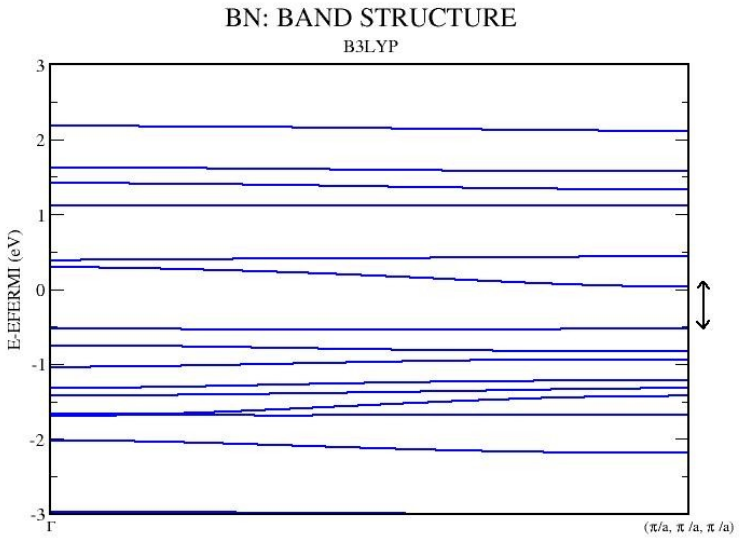
use a method which is not so difficult to converge:

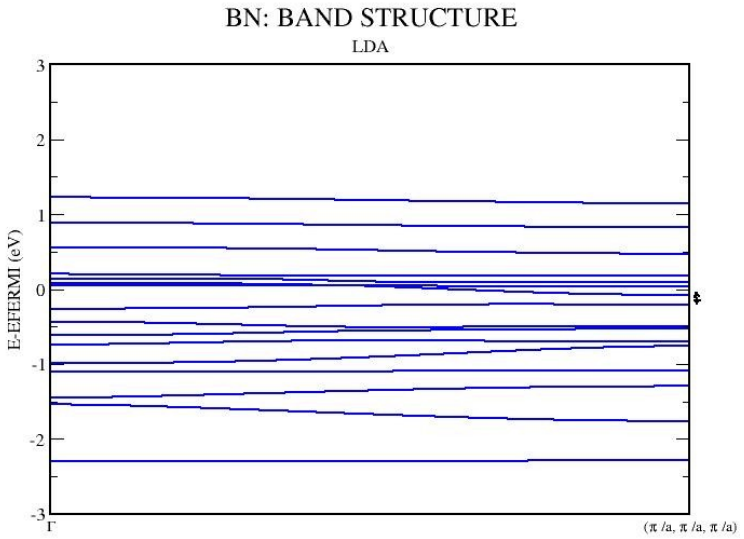
1) Hartree-Fock approach quickest: large gap helps to converge
2) hybrid functional B3LYP takes much longer than HF
3) LDA very difficult to converge (small gap)

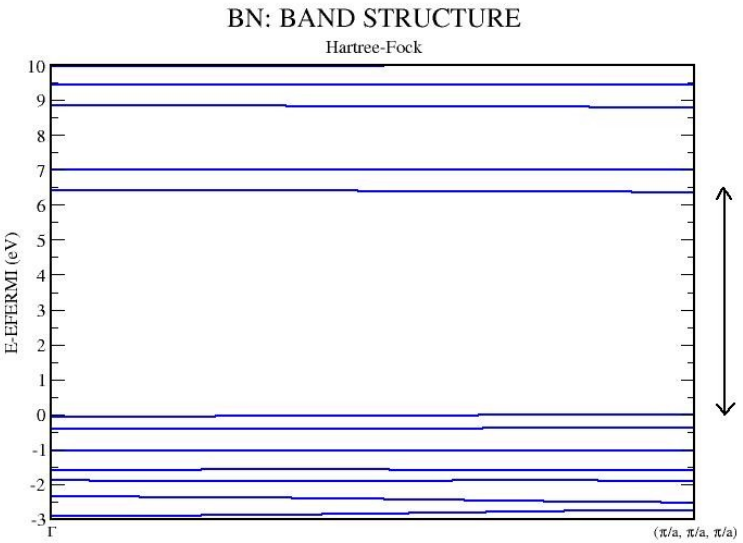
=> 1) Hartree-Fock can be used for global optimisation
2) local optimisation is very quick, no problem:
compare various functionals, use good parameter values

Example: BN, **initial** structure:



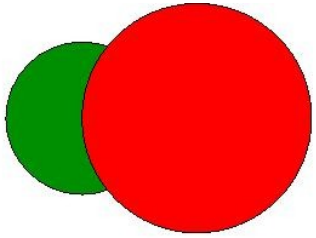






gap: LDA ~0.1 eV; B3LYP ~ 0.5 eV; HF ~6 eV

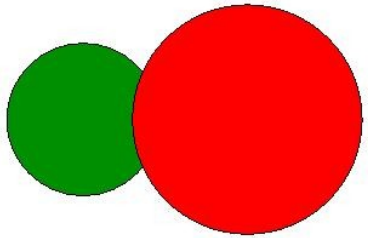
How to achieve stability?



atoms too close: discard geometry

discard unrealistic geometries:

minimum distance between atoms required
(use atomic/ionic radii, Mulliken charge)



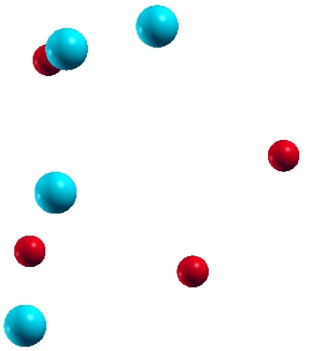
atoms not too close: perform calculation

if no convergence after maximum number of SCF iterations:

-> discard geometry: assign infinite energy

CPU times (one single CPU):

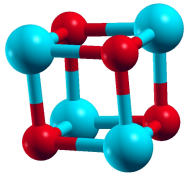
LiF cluster (4 formula units):



Single energy, initial geometry: 0.2 s

(large volume, many integrals discarded)

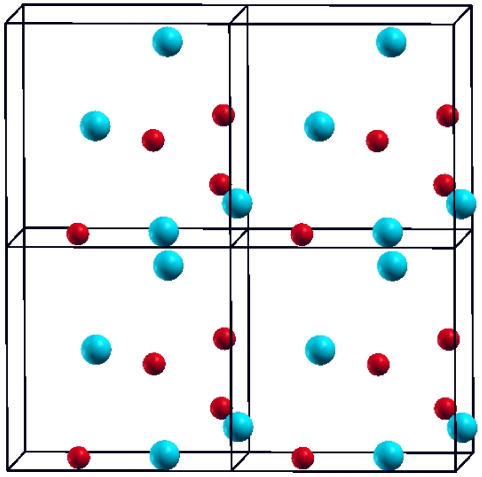
final geometry: 2 s



1 Simulated annealing run, 45000 steps: a few hours (<10)

1 Threshold run for 1 lid, 400000 steps: order of one week

CPU times (one single CPU):

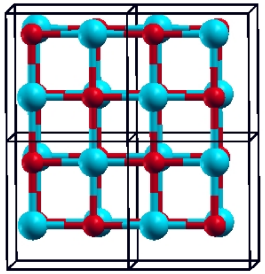


LiF bulk (4 formula units)

single energy, initial geometry: 1 s

(large volume, many integrals discarded)

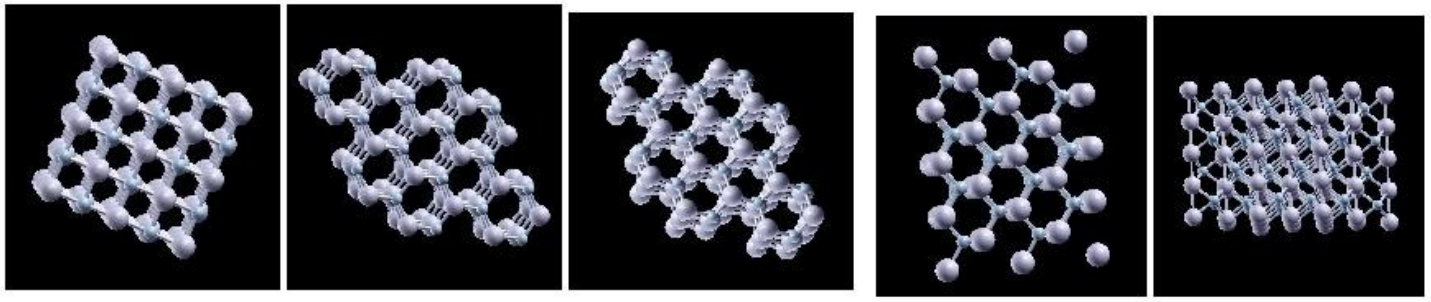
final geometry: 30 s



1 Simulated annealing run, 12500 steps: 3 days

1 Threshold run: ???

LiF: proof of principle



NaCl 5-5 Wurtzite zinc blende NiAs

others, space group: *Pnma (62)* *Pc (7)* *$Cmc2_1$ (36)*

Confirmation of the calculations with model potential

Model potential: *J. C. Schön and M. Jansen, Comput. Mater. Sci.* ***4****, 43 (1995)*

ab initio: K. Doll, J. C. Schön, M. Jansen, Phys. Chem. Chem. Phys. ***9****, 6128 (2007)*

experiment (new LiBr structure: wurtzite):

Y. Liebold Ribeiro, D. Fischer, M. Jansen, Angew. Chemie, ***120****, 4500 (2008)*

A covalent system: BN bulk

Difficulties:

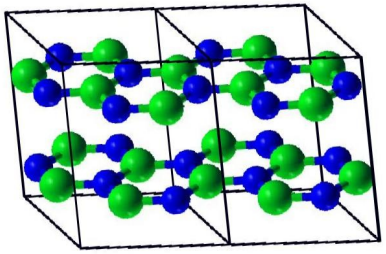
1) solution of Schrödinger equation for ***random*** geometry necessary
(much more difficult for covalent system than for ionic system)

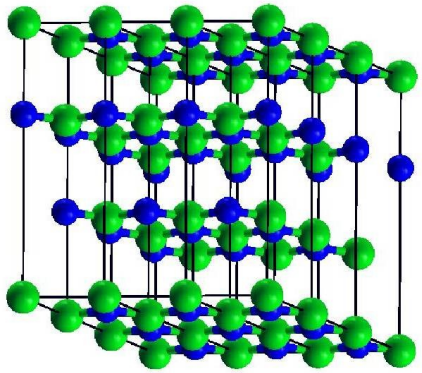
2) experiment: layered structures (similar to graphite)
and „3d“ structures (zinc blende,wurtzite)

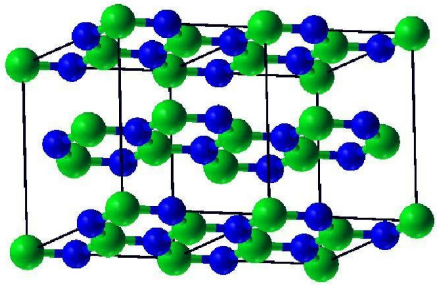
*K. Doll, J. C. Schön, M. Jansen, Phys. Rev. B **78**, 144110 (2008)*

BN

structures found:
wurtzite, zinc blende, hexagonal BN …., **no** roc







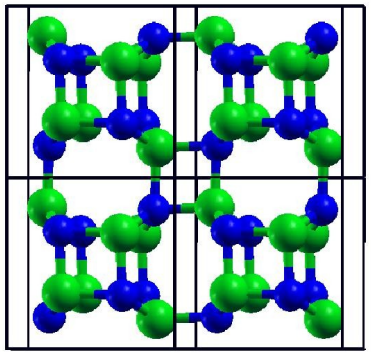
$P6_3/mmc$ (194)

$R3m$ (160)

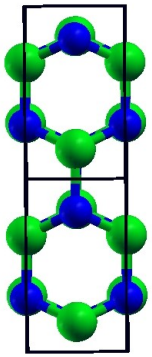
$P6m2$ (187)

space group $P4_2/mnm$:

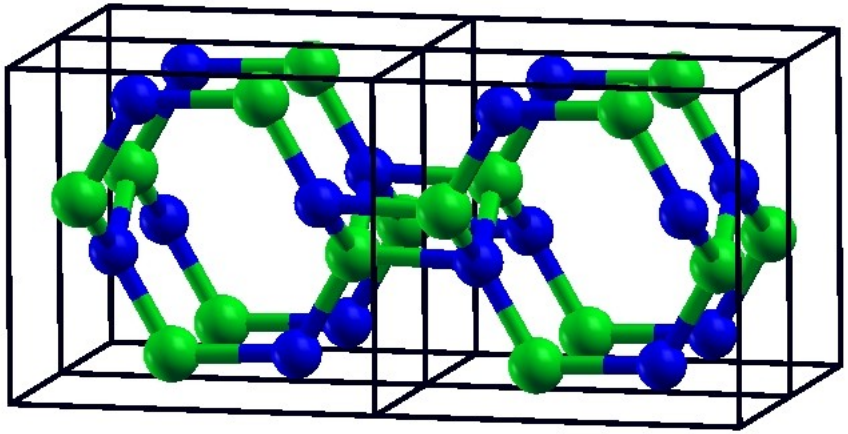
β-BeO
(isoelectronic
with BN)



different view:



$SrAl_2$ like structure:



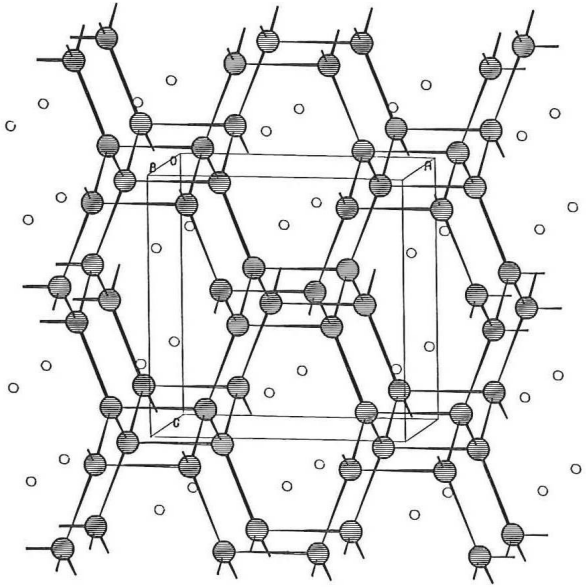


Abb. 2. Perspektivische Ansicht der Struktur der $SrAl_2$(ND)-Modifikation.
Gestrichelte Kreise ≙ Al-Atome, kleine Kreise ≙ Sr-Atome.

$SrAl_2$ is isoelectronic: ignore Sr^{2+} , then: Al isoelectronic with B

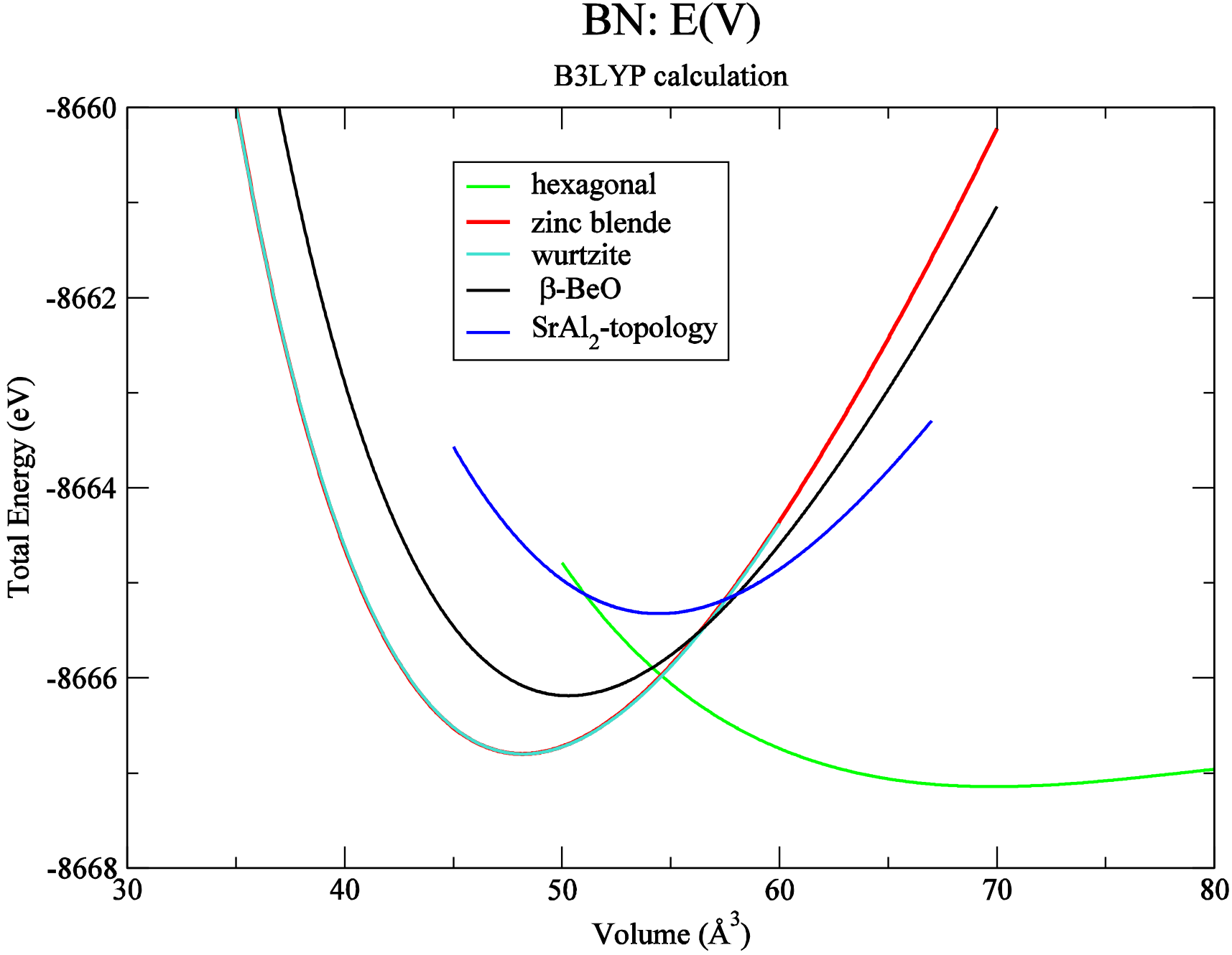
Al^{2-} isoelectronic with N

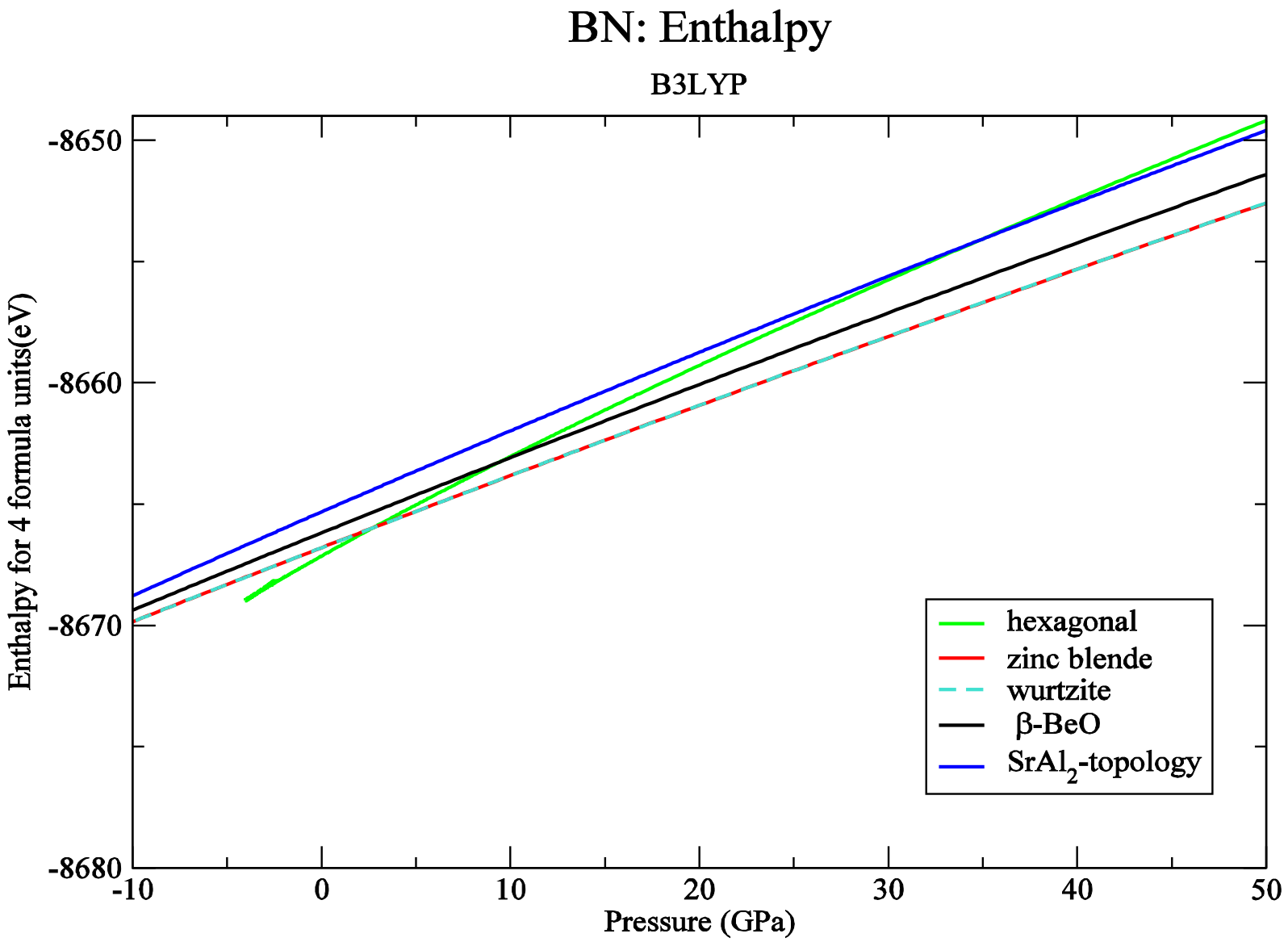
note: BN has space group *Pnma* (62)

$SrAl_2$ has space group *Imma* (74)

G. Cordier, E. Czech, H. Schäfer, Z. Naturforsch. ***37*** *b, 1442 (1982)*

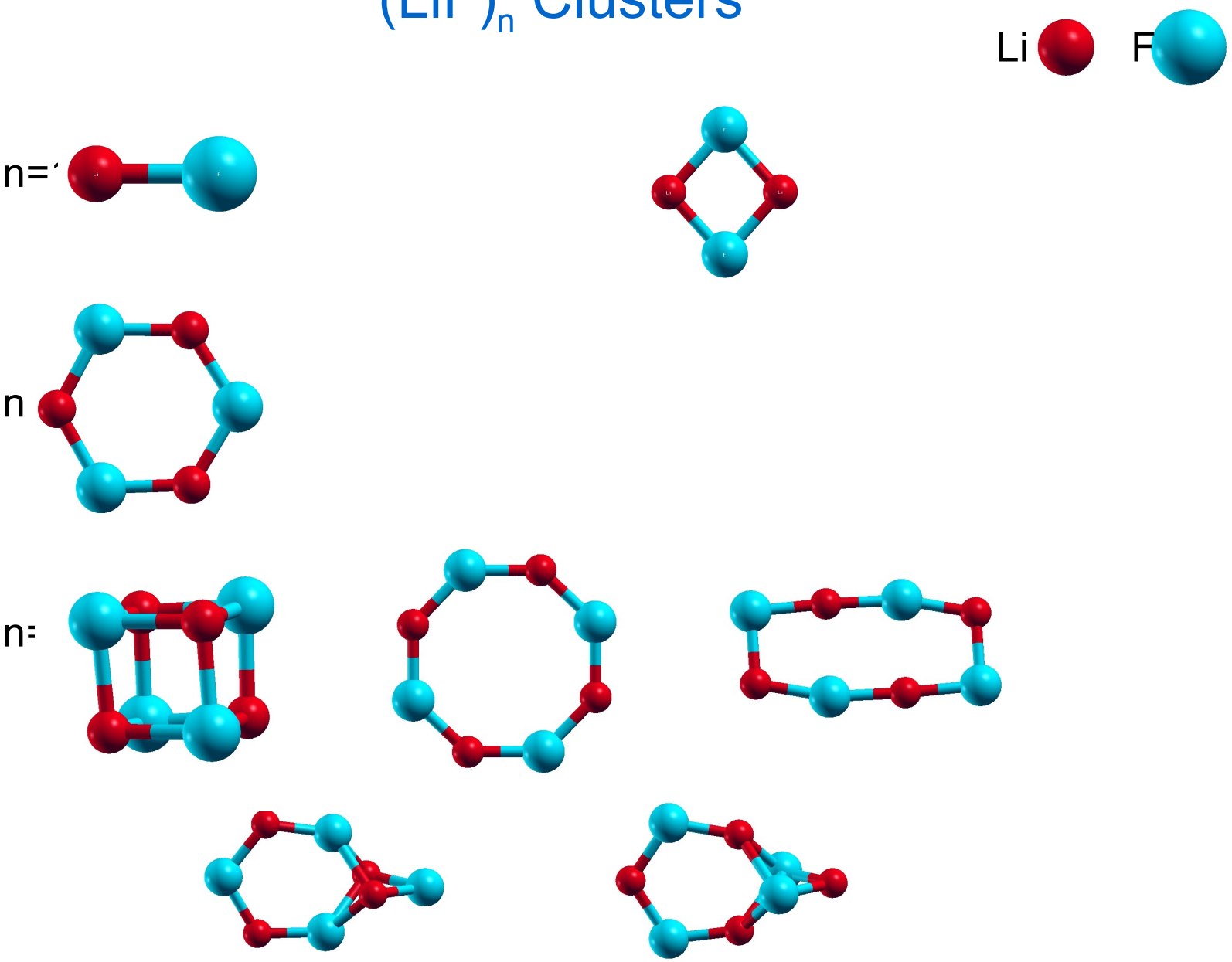
identified with TOPOS software *(V. A. Blatov, A. P. Shevchenko, V.N. Serezhkin, Samara, Russia)*


BN: E(V)
B3LYP calculation
hexagonal
zinc blende
wurtzite
β-BeO
SrAl2-topology
Total Energy (eV)
-8660
-8662
-8664
-8666
-8668
30
40
50
60
70
80
Volume (Å3)

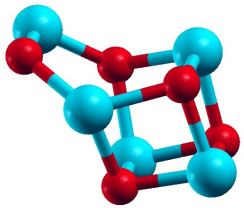


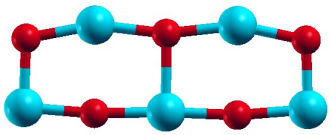
Synthesis of the new β - BeO phase: not feasible by just applying pressure

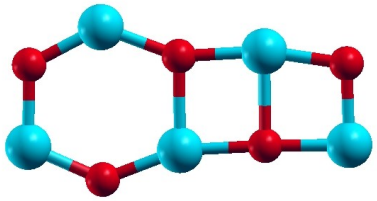
$(LiF)_n$ Clusters

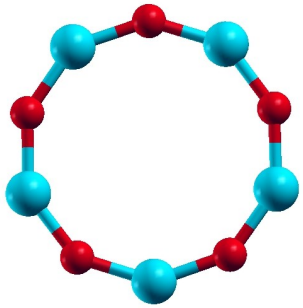


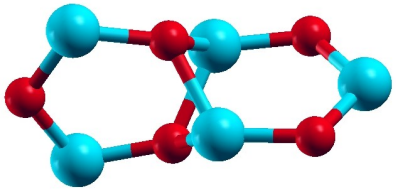
n=5

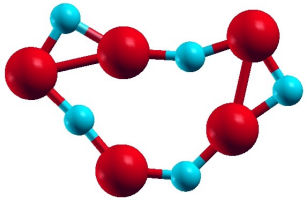


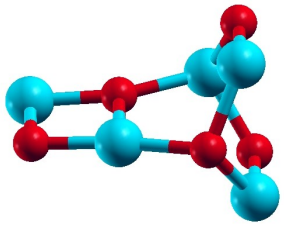












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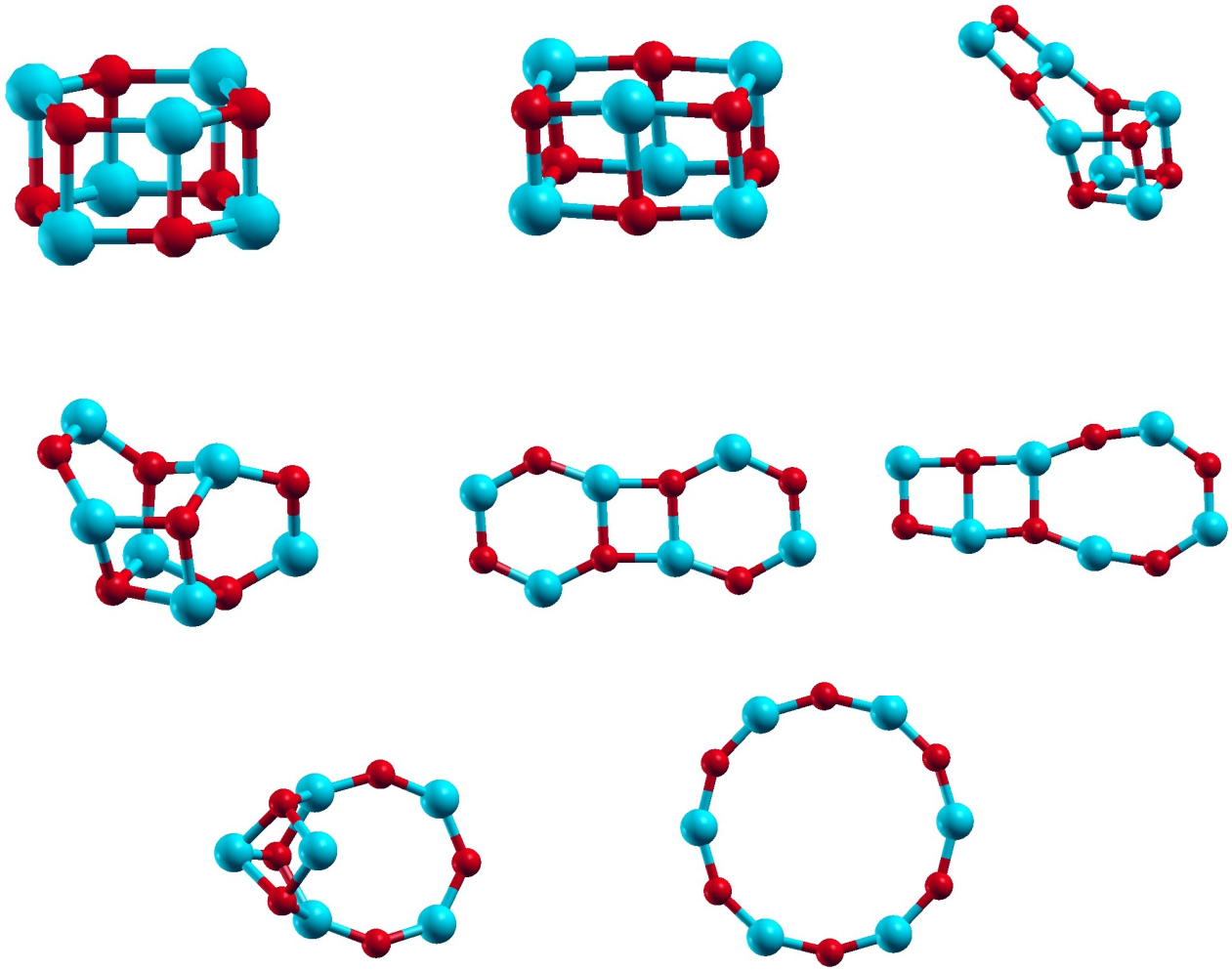
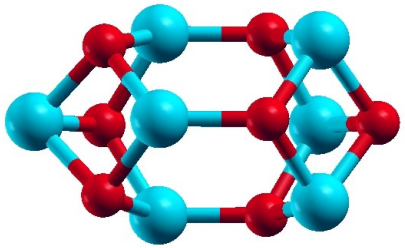
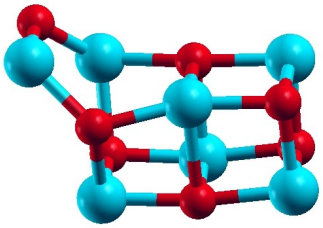
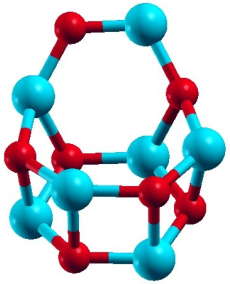
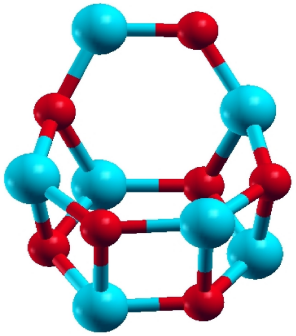
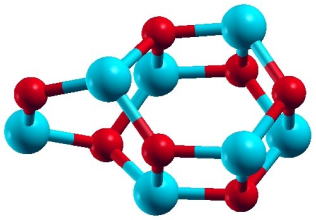
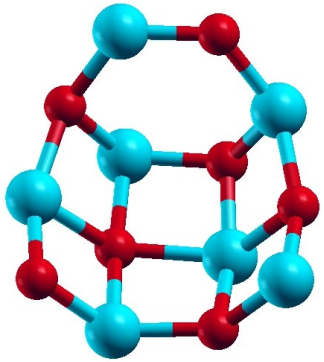
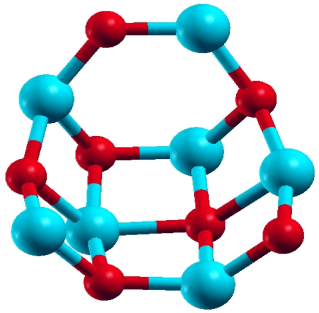
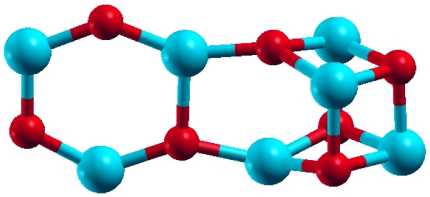
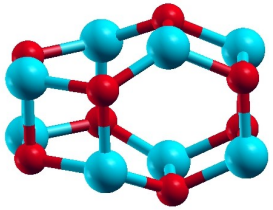
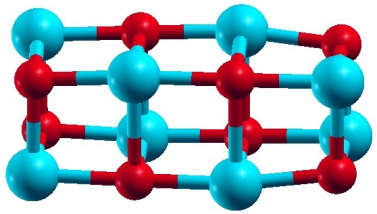


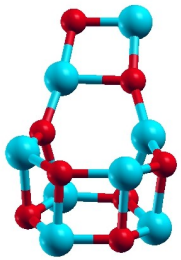
n=7

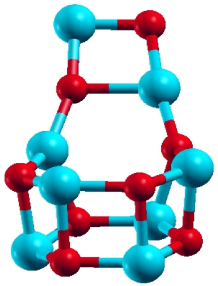









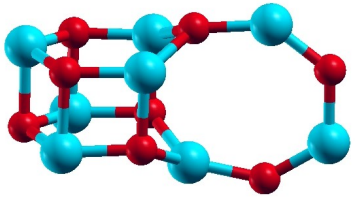
n=8

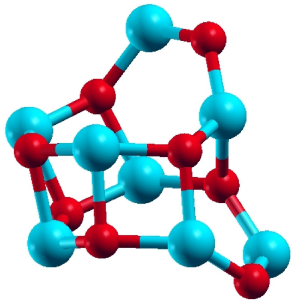


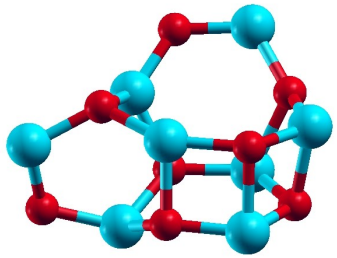






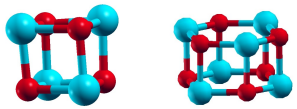


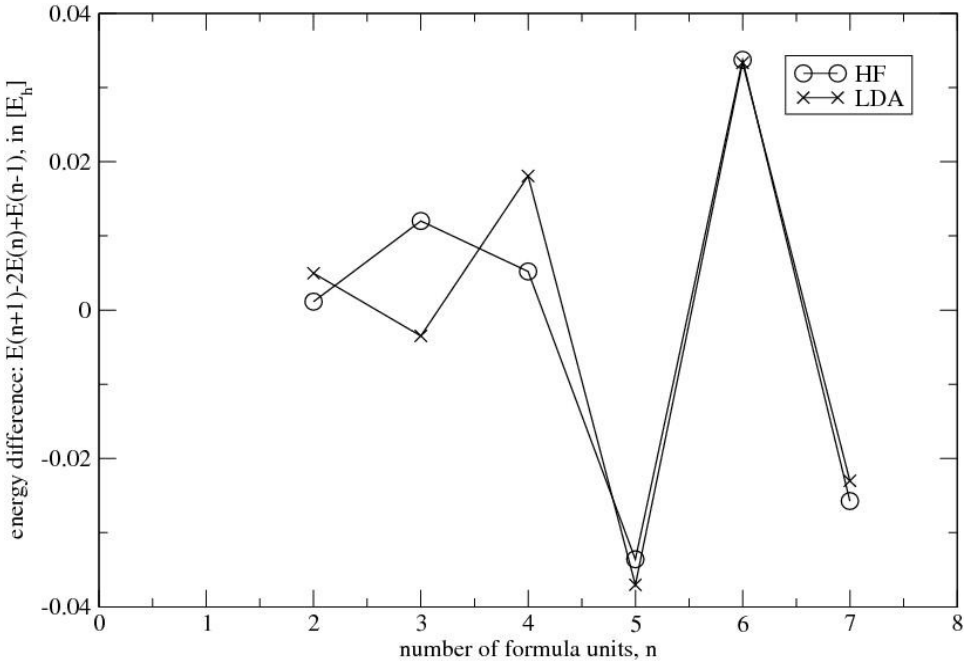


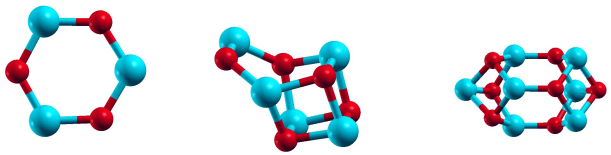


important: the relevant minima are found

Clusters $(LiF)_{2n}$ are more stable:

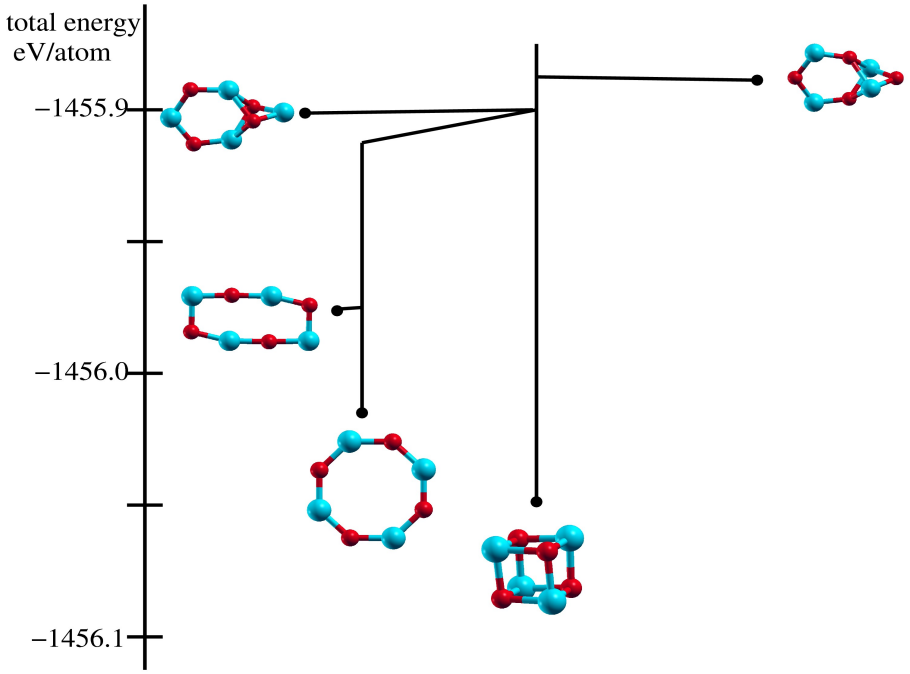






Tree graph from threshold run

Threshold run: start from one structure
accept all moves up to a certain value, then quench
-> possible transition to new structure after quench



two lowest lying minima with large barriers → observable ?

K. Doll, J. C. Schön, M. Jansen, J. Chem. Phys. ***133****, 024107 (2010)*

Conclusion

structure prediction based on simulated annealing and *ab initio* energies in all the steps feasible

LiF: *ab initio* results agreed with earlier results based on empirical potentials (proof of principle)

BN: example for a covalent system, new modifications

CaC_2: mixed covalent/ionic system

GeF_2: chain like+3d-structures

LiF clusters: barriers can be computed