

Advanced School on
QUANTUM MODELLING
of Materials with CRYSTAL

The Geometry Optimizer: More than just the Equilibrium Structure



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Geometry Optimizer for:

MOLECULES AND SOLIDS:

- 1) Finding the equilibrium nuclear configuration (useful *per se* for structural analysis but also as a starting point for more advanced calculations: harmonic frequencies, elastic constants, ...);
- 2) Finding and characterizing Transition States;

SOLIDS:

- 3) Including the effect of Pressure on computed properties of materials (structure, elasticity, ect.);
- 4) Accounting for nuclear-relaxation effects on strain-related tensorial response properties of materials (elastic, piezoelectric, photoelastic, etc.);



Some Initial Assumptions

In most quantum chemistry/physics simulations, we aim at solving the static Schroedinger equation for the electronic ground state of the system:

$$\mathcal{H}\Psi = E\Psi$$

Many approximations:

- 1) Time-independent “static” formulation;
- 2) Electrostatic, non-relativistic (or scalar-relativistic) Hamiltonian;
- 3) Single-determinantal representation of the ground-state wave function;
- 4) Approximated description of electron-electron repulsion (HF, DFT, ...);
- 5) Adiabatic, **Born-Oppenheimer approximation** (decouples electronic from nuclear motion)

$$\mathcal{H}(R)\Psi(R) = E(R)\Psi(R)$$

where R is a nuclear configuration.



Static vs. Dynamic Geometries

With the BOA, one fixes the atomic positions, solves the electronic Schroedinger equation, and computes the energy of that nuclear configuration.

In order to determine the properties of the “**equilibrium structure**” of a system, the typical approach consists in performing a geometry optimization to find “**the**” equilibrium configuration. This is a static approach.

In reality, the picture is dynamic. **Atoms are never at rest** in their equilibrium positions, which can only be interpreted as those positions in space where they are most likely to be found.

Each configuration has a different energy, and **equilibrium properties are in fact the result of a Boltzmann average** over them all.

The **static approach** assumes that equilibrium properties can be evaluated on a **single configuration**, provided that one makes sure to select **the most probable one**, the minimum energy one (the one that dominates the Boltzmann average).

This is what a geometry optimizer is typically used for.



Geometry Optimizer

In particular, we are going to discuss:

- 1) Some of the fundamental concepts related to the formal understanding of a geometry optimizer for solids;
- 2) Some specific aspects of the implementation of the geometry optimizer in the CRYSTAL program.

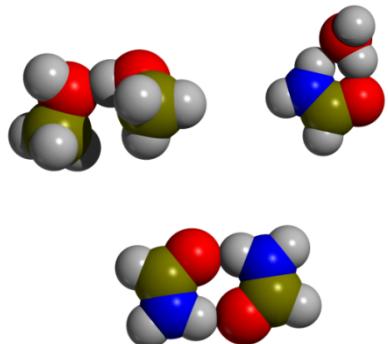
The main ingredient of a geometry optimizer are **coordinates**. The same lattice configuration can be represented by different sets of coordinates and this has a significant impact on:

- 1) The type of optimization that can be performed (constraints);
- 2) The computational efficiency of the geometry optimization process.

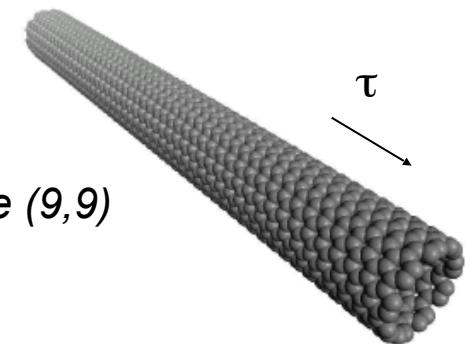


Chemical structures

Molecule/Cluster (0D)

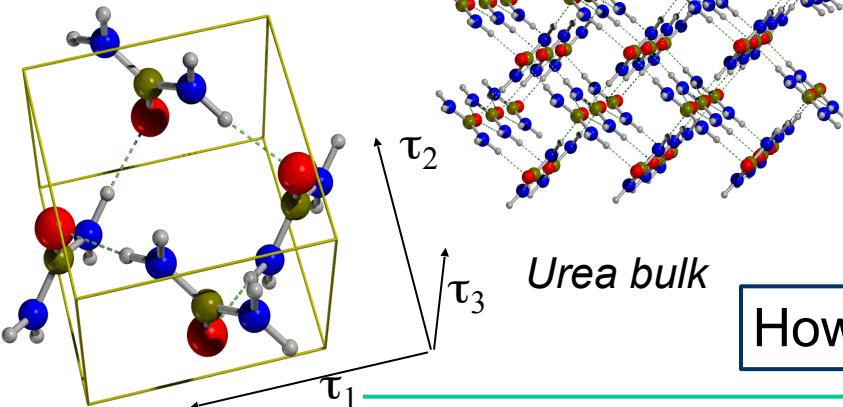


Polymer (1D)



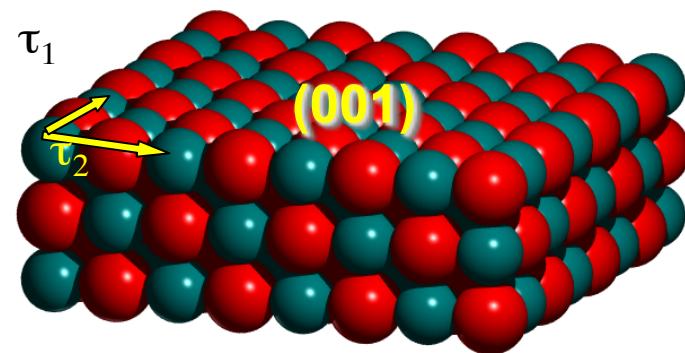
Carbon nanotube (9,9)

Crystal (3D)



Urea bulk

Surface (2D)

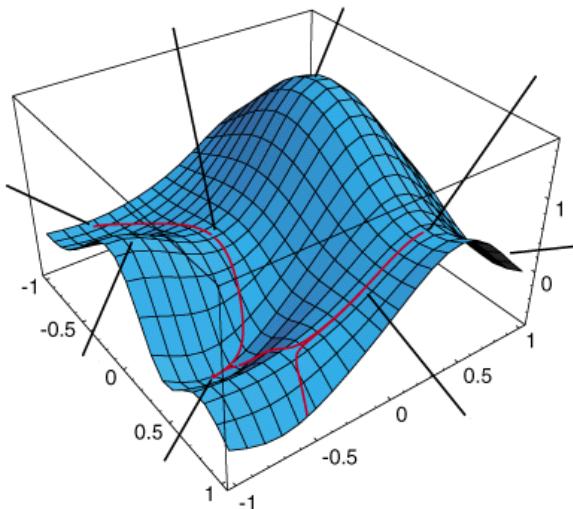


Slab model of the (001) MgO surface

How can one define a chemical structure?



Potential Energy (Hyper)Surface (PES)



$$E=f(x_1, x_2, x_3, \dots, x_{3N})$$

- PES describes the energy of the system as a function of its geometry (\Rightarrow *hypersurface*)
- PES arises naturally from the Born-Oppenheimer approximation
- PES makes it possible to discuss chemical structures



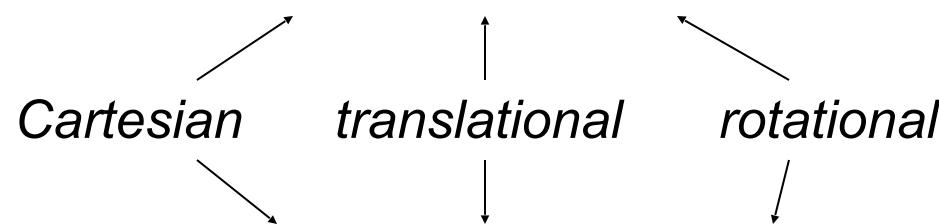
Minimum Number of Variables, M

$$E = f(x_1, x_2, x_3, \dots, x_M)$$

The energy is invariant under translations and rotations

Molecules:

$$M = 3N - 3 - 3(2)$$



3D crystals:

$$M = 3N - 3 + (9 - 3)$$

lattice



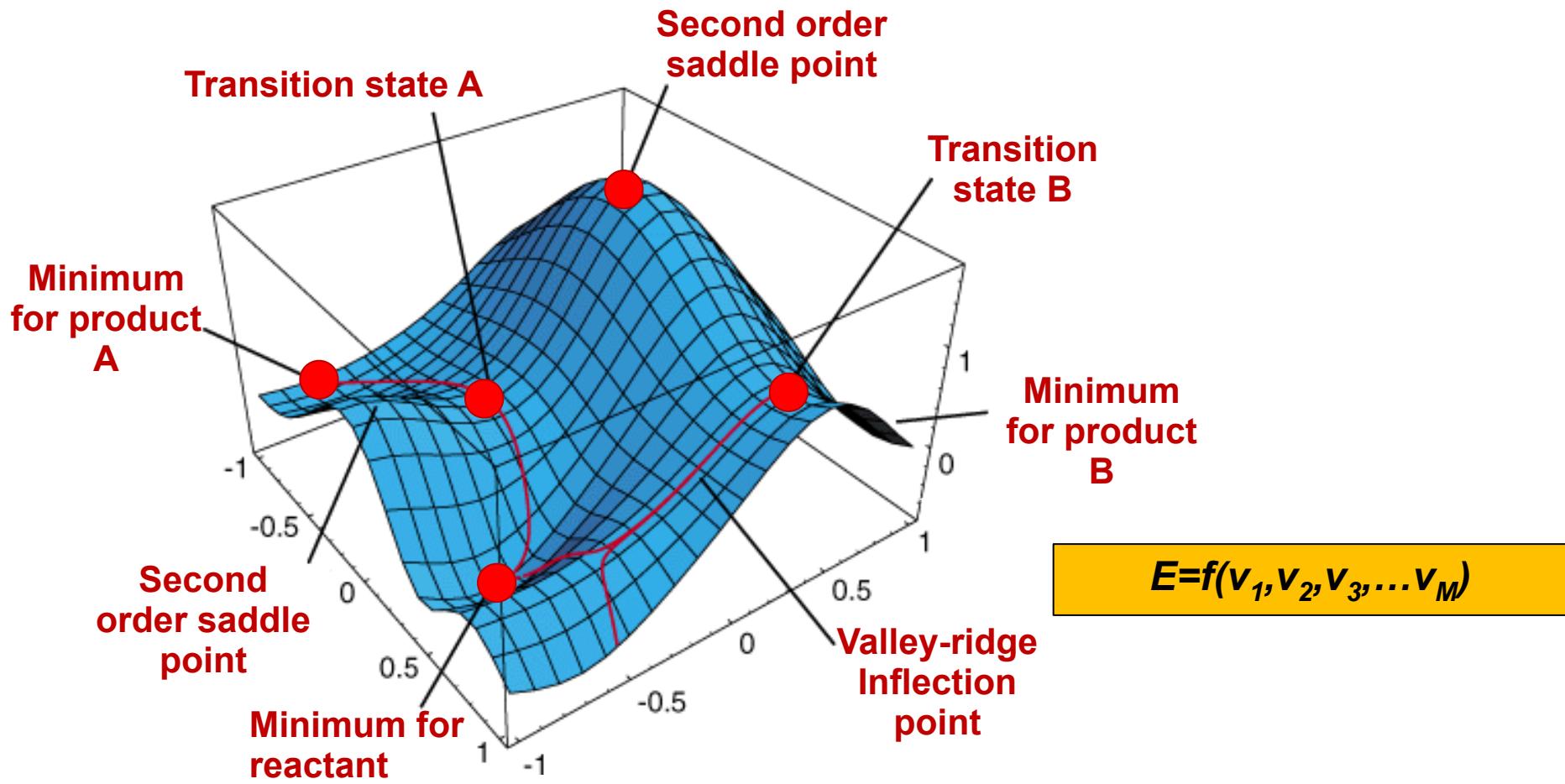
Coordinate Systems

- There are infinite choices to define the coordinates;
- **The shape of the PES depends on the adopted coordinate system;**
- The best set of coordinates should be the one that makes it easiest to study the potential energy surface;
- Let's assume that $\mathbf{v} = (v_1, v_2, \dots, v_M)$ is the nuclear configuration vector in a given coordinate choice



PES: Relevant Information

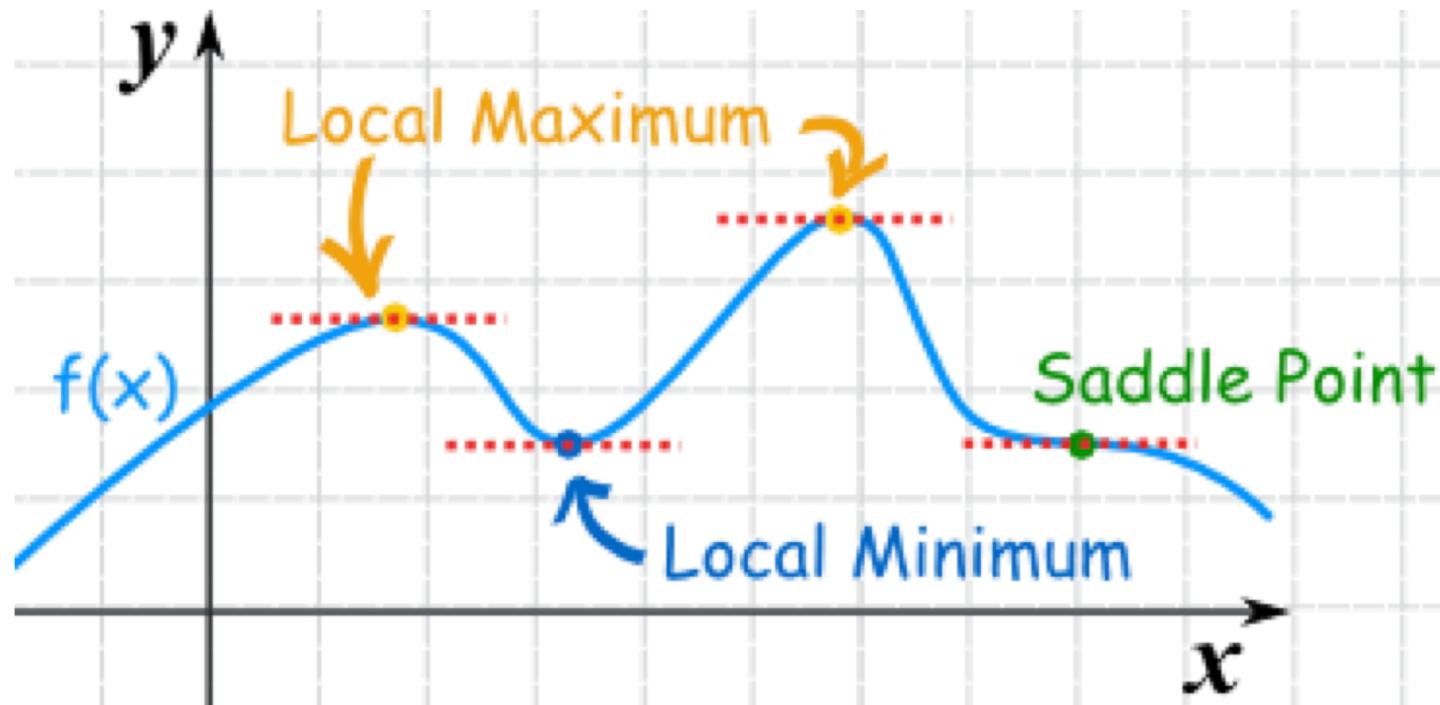
Relevant **chemical structures** correspond to some specific features of the PES (i.e. some of its **critical points**, invariant under transformations of the coordinate system). A **topological analysis** of the PES is required.



PES: Relevant Information

Critical points are defined as those points in space where the function has a vanishing gradient.

For functions of a single variable $f(x)$:



Minima, maxima and saddle points are characterized by a zero first-derivative (gradient) and by positive, negative and zero second-derivative.



PES: Relevant Information

For functions of many variables $f(x_1, x_2, \dots, x_M)$ the gradient becomes the **gradient vector**:

$$\nabla f = \begin{pmatrix} \frac{\partial f}{\partial x_1} \\ \frac{\partial f}{\partial x_2} \\ \vdots \\ \frac{\partial f}{\partial x_M} \end{pmatrix}$$

Therefore, critical points are those points in space where the gradient vector vanishes (i.e. all of its M components simultaneously vanish).



PES: Relevant Information

For functions of many variables $f(x_1, x_2, \dots, x_M)$ the second-derivative becomes the **Hessian matrix (MxM)**:

$$\mathbf{H} = \nabla^2 f = \begin{pmatrix} \frac{\partial^2 f}{\partial x_1^2} & \frac{\partial^2 f}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 f}{\partial x_1 \partial x_M} \\ \frac{\partial^2 f}{\partial x_2 \partial x_1} & \frac{\partial^2 f}{\partial x_2^2} & & \frac{\partial^2 f}{\partial x_2 \partial x_M} \\ \vdots & \ddots & & \vdots \\ \frac{\partial^2 f}{\partial x_M \partial x_1} & \frac{\partial^2 f}{\partial x_M \partial x_2} & \cdots & \frac{\partial^2 f}{\partial x_M^2} \end{pmatrix}$$

The Hessian matrix is **diagonalized**, its M eigenvalues obtained and analyzed.



PES: Relevant Information

If all the M eigenvalues are positive, the critical point is a minimum.

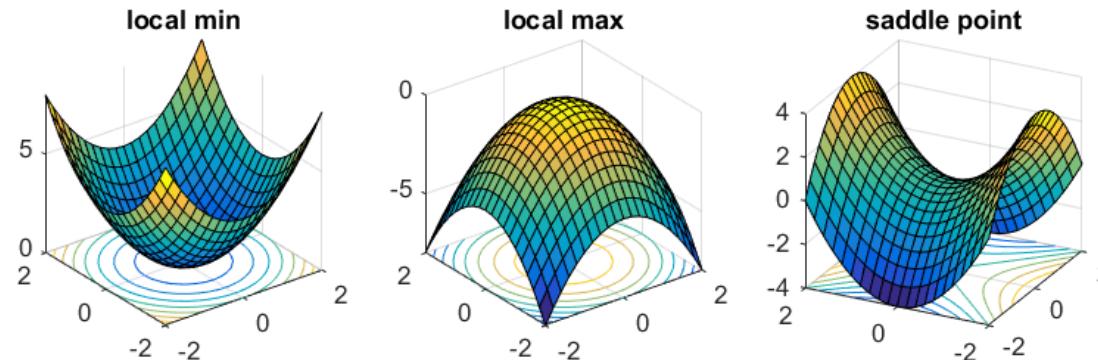
If all the M eigenvalues are negative, the critical point is a maximum.

There are many intermediate cases:

If all the M eigenvalues are positive but one negative, the critical point is a first-order saddle point.

If all the M eigenvalues are positive but two negative, the critical point is a second-order saddle point.

For a function of just two variables $f(x_1, x_2)$:



PES: Relevant Information

Chemical Structures

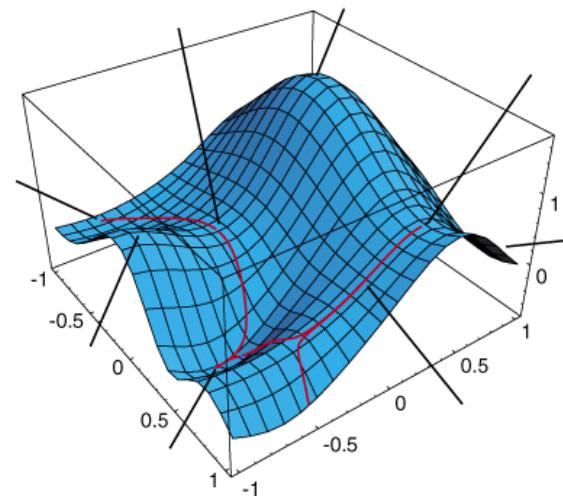
- **Equilibrium geometries:** are local minima on the PES (e.g. conformers, isomers, polymorphs, reactants, intermediates and products of a chemical reaction)
- **Transition states:** correspond to first-order saddle points on the PES (e.g. transition structures of a chemical reaction)



PES and related quantities (derivatives)

Many physical properties can be obtained from the analysis of the PES:

- $E(\mathbf{x}, a_i)$  Energy differences
- $\frac{\partial E}{\partial \mathbf{x}}, \frac{\partial E}{\partial a_i}$  Forces (geometry optimisation)
- $\frac{\partial^2 E}{\partial x_i \partial x_j}$  Vibrations (Phonons)
- $\frac{\partial^2 E}{\partial a_i \partial a_j}$  Elastic constants
- $\frac{\partial E}{\partial V}$  Pressure
- $\frac{\partial^2 E}{\partial V^2}$  Bulk modulus



x : atomic coordinates
 a_i : lattice parameters
 V : cell volume



What is the meaning of Geometry Optimization?

It is the process of finding minima and saddle points on the PES

How to do that?



Geometry Optimization

The process of finding minima (or saddle points) of the PES. Different ingredients can be used: **energy, forces, Hessian** of **increasing effectiveness and computational cost**:

$$E < g \ll H$$

- Energy-based methods (e.g. line optimization, ...)
Simple, widely applicable, very slow convergence
- Gradient-based methods (e.g. conjugate gradient, **quasi-Newton**,...)
Good convergence, expensive
- Second derivative methods (e.g. Newton, Newton-Raphson,...)
Very fast, very expensive

Most **QM packages for solids** compute **forces analytically** and the **Hessian, numerically**.



Newton and Quasi-Newton Methods

The **PES** is approximated as a **quadratic function** (Taylor expansion centered around an initial configuration \mathbf{v}_0 and truncated to second-order):

$$E(\mathbf{v}) = E_0 + \mathbf{g}_0^\top \Delta\mathbf{v} + \frac{1}{2} \Delta\mathbf{v}^\top \mathbf{H}_0 \Delta\mathbf{v}$$

where $\Delta\mathbf{v} = \mathbf{v} - \mathbf{v}_0$ so that:

$$\mathbf{g}(\mathbf{v}) = \mathbf{g}_0 + \mathbf{H}_0 \Delta\mathbf{v}$$

Now, we **look for a critical point** so **we impose the condition**:

$$\mathbf{g}(\mathbf{v}) = \mathbf{g}_0 + \mathbf{H}_0 \Delta\mathbf{v} = 0$$

which leads to the **Newton step to be taken to get to the minimum**:

$$\Delta\mathbf{v} = -\mathbf{H}_0^{-1} \mathbf{g}_0$$



Newton and Quasi-Newton Methods

For a **quadratic PES**, a **single optimization step** would be needed from \mathbf{g} and \mathbf{H} .

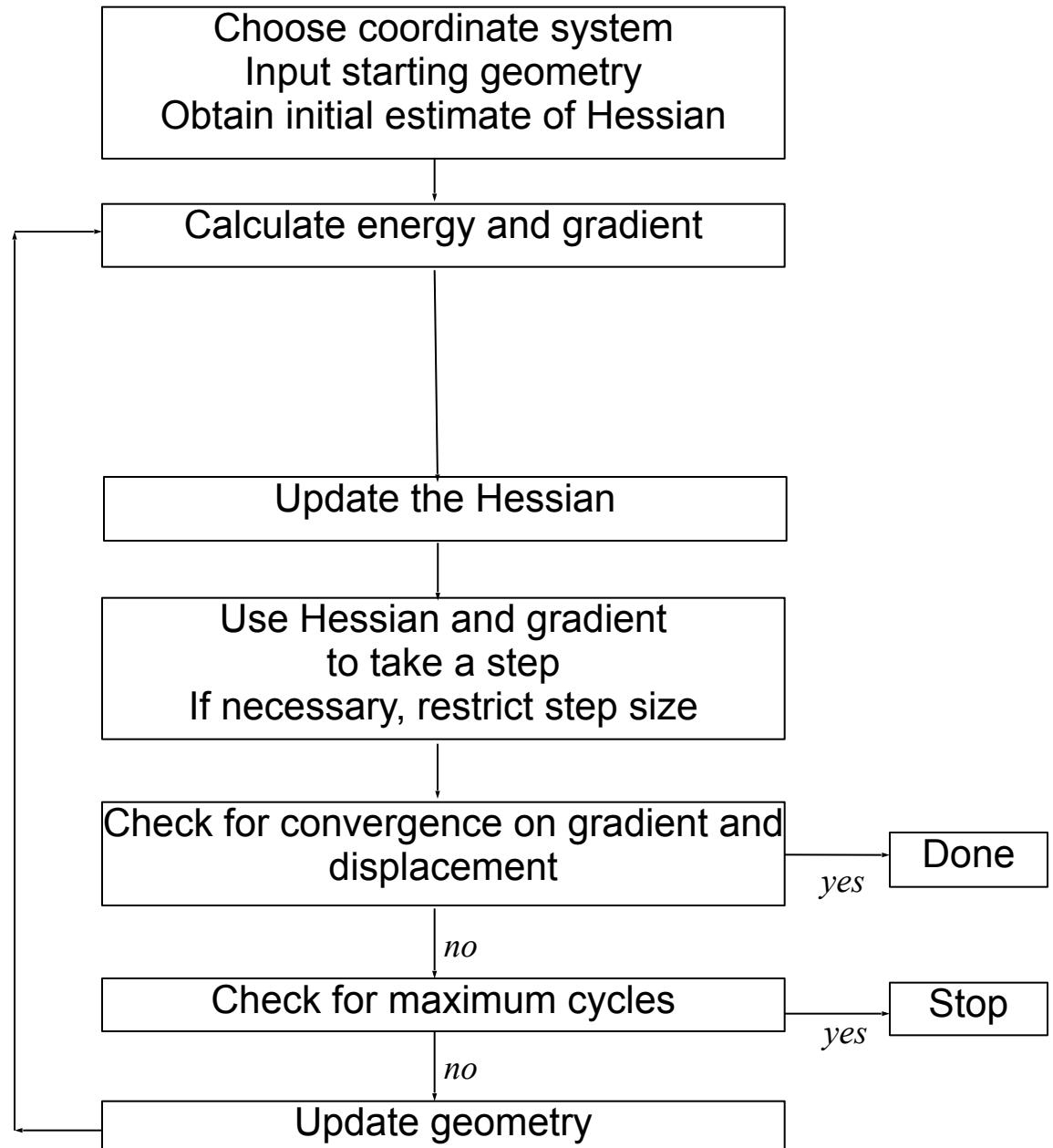
The **Hessian is very computationally expensive**. With **Quasi-Newton methods** one avoids its explicit calculation.

During the optimization process, the changes in the gradient between steps provide useful information on the surface curvature (second derivatives). An approximation to the Hessian matrix, \mathbf{H} is built during the optimization process by using information from gradients. Several methods for this approximation exist:

- Fletcher-Powell
- Murtagh-Sargent (SR1)
- Powell-Symmetric-Broyden (PSB)
- **Broyden-Fletcher-Goldfarb-Shanno (BFGS)**



Flow chart for Quasi-Newton algorithms



Efficiency of a geometry optimization

The efficiency (i.e. *number of steps*) depends on several factors:

- 1) *Initial geometry* (experiment, GUI/Molecular Modelling, Molecular Mechanics, lower level QM)
- 2) *Coordinate system* (Cartesian, internal (redundant, natural, ...))
- 3) *Hessian initial guess* (Identity, Molecular Mechanics, lower level QM, numerical)
- 4) *Hessian updating* (Bergy, MS, DFP, BFGS, ...)
- 5) *Step size control* (simple rescaling, trust radius, RFO, ...)



Hessian matrix (Initial Guess)

A good estimate of the initial Hessian can drastically improve the optimization process

⌚ *Identity Matrix* [**HESSIDEN**]

No structure information, hence very inefficient

⌚ *Numerical Hessian* [**HESSNUM**]

Close to exact, hence fast convergence. However, high calculation cost
(good for difficult cases, e.g. transition state searches)

😊 *Model Hessian* [**HESSMOD1,HESSMOD2**]

Good and cheap approximation. Based on valence force fields (Lindh,
Schlegel). Significant improvement with respect to the Identity matrix (>50%
speed-up).



Step size control

- When the step size is too large a simple scaling can be applied (too crude)
- In non-quadratic functions the Newton step may not be the best choice and should be controlled:

- **Level-shift trust region:** A **trust radius** of an hyper-sphere in which the function is expected to behave quadratically. A parameter, μ , is computed so that the displacement:

$$\mathbf{v}_{i+1} - \mathbf{v}_i = (\mathbf{H}_i - \mathbf{I}\mu)^{-1} \mathbf{g}(\mathbf{v}_i)$$

is kept within the trust region.

Ensured to be the best direction within the hyper-sphere of radius,
 $\tau = |\mathbf{v}_{i+1} - \mathbf{v}_i|$

- **Line search:** A scale factor α_i is computed as to reach a minimum along the Newton step direction, according to:

$$|\mathbf{v}_{i+1} - \mathbf{v}_i| = -\alpha_i \mathbf{H}_i^{-1} \mathbf{g}(\mathbf{v}_i)$$



Choice of coordinate system

- Good Performance \leftrightarrow Quadratic behaviour
- Ideal set of coordinates yields a PES that behaves quadratically close to the critical point
- Coordinate systems suitable for crystals:
 - Fractionary coordinates + elastic distortions
 - Internal valence coordinates (redundant)



Coordinate systems for crystals (I)

Fractionary coordinates + elastic cell distortions

- Atom coordinates defined in the basis set of the lattice vectors.
 - Cell parameters obtained from elastic distortions (expansion matrix applied on the lattice vectors)
- ☺ Easy to keep special positions and cell parameters by imposing symmetry
- ☹ Delocalised by definition. Not useful for chemical reactivity.
- ☹ In general, non-quadratic
- ☹ Low dependence between coordinates and lattice parameters



Coordinate systems for crystals (II)

Redundant internal coordinates

- All valence coordinates (bond distances, angles and torsions) are considered to form a set of redundant coordinates ($N_{RC} \gg M$);
- Cell parameters are embedded into the redundant coordinates;
- Hessian, gradient and geometry displacements are built in terms of the redundant coordinates;
- The redundancies are eliminated to obtain the actual geometry (in Cartesian space) using numerical approximations

- ☺ Quadratic behaviour
- ☺ Easy choice of geometrical parameters
- ☺ Easy to constrain 'chemical' degrees of freedom (bond lengths angles or dihedrals) → Good for reactivity studies
- ☹ The size of redundant space may be very large
- ☹ The back-transformation from redundant to non-redundant space is difficult

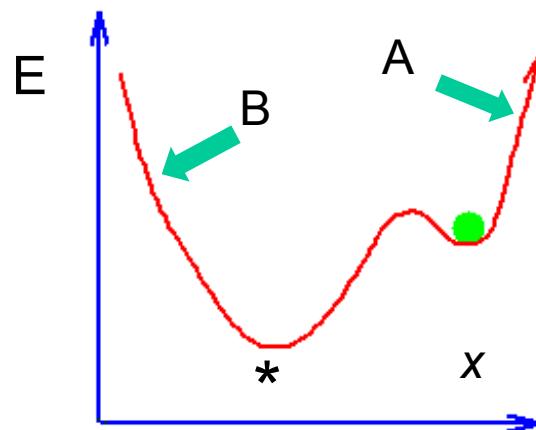


Comparison between Frac.+Cell and Redundant

System	Dim	Theor. Method	Frac+Cell	Redundant	C-R
			Nstep	Nstep	$\Delta E (\mu Ha)$
α -Quartz	3D	B3LYP	8	7	-0.05
β -Quartz	3D	LDA	13	22	2.15
All silica Faujasite	3D	PBE	27	16	-7.26
KNbO ₃ tetragonal	3D	BLYP	21	16	-0.46
BaTiO ₃ orthoromb.	3D	LDA	24	21	2.14
Bohemite	3D	PW91	6	5	0.09
Calcite	3D	B3PW91	8	7	1.01
NaNO ₂	3D	BP86	18	18	0.00
TiO ₂	3D	PW91	5	4	0.01
ZnGeP ₂	3D	LDA/ECP	6	6	0.00
ZrO ₂	3D	PBE	3	3	0.02
Formamide	3D	B3LYP	22	16	2.28
Ice	3D	PW91	17	12	1.40
Oxalic acid	3D	B3LYP	29	27	-0.05
Oxalic acid	3D	HF	29	22	2.07
Al ₂ O ₃ (0001) 12-layer	2D	B3LYP	22	19	-1.09
EDI(100)/NH ₃	2D	B3LYP	15	10	1.70
H ₂ O infinite chain	1D	PBE0	16	13	0.17
Li doped PA	1D	B3LYP	12	9	0.01
Tot			301	253	

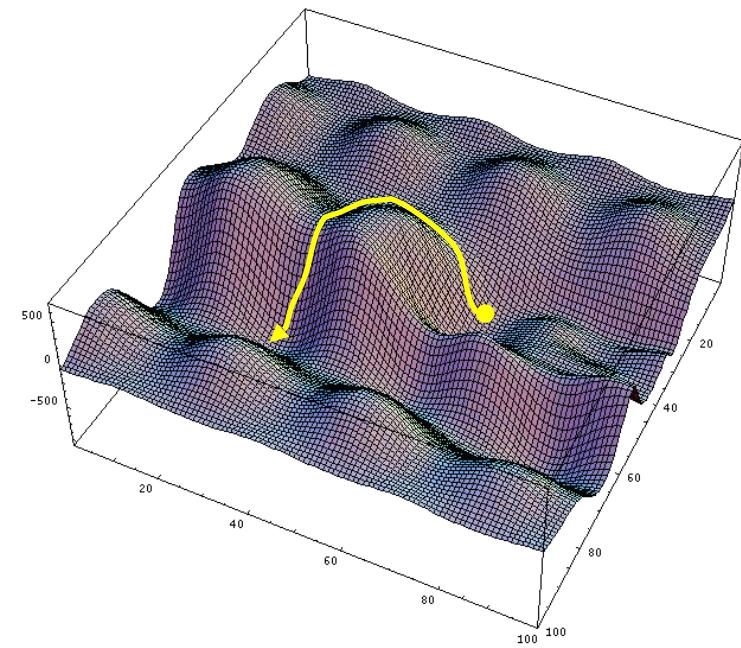
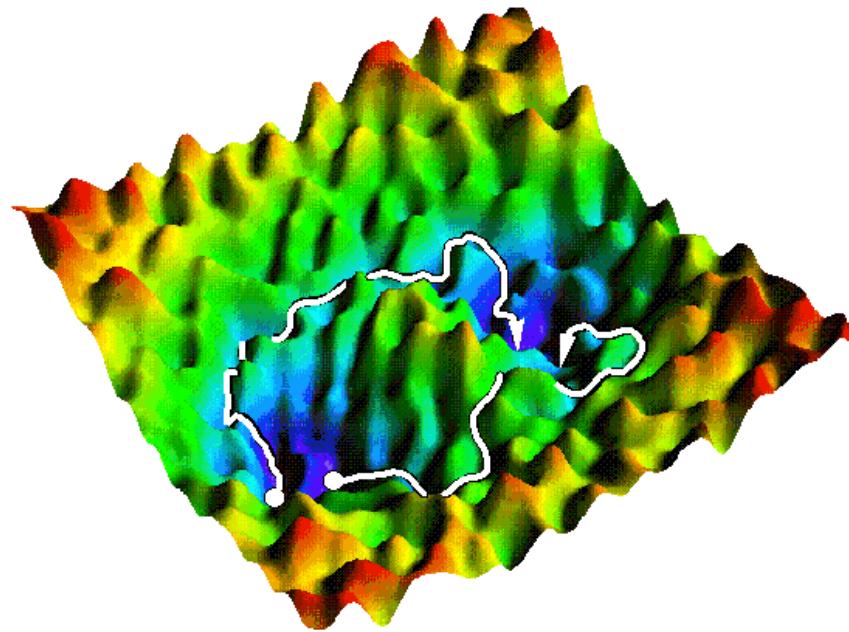


Warning! Local vs. Global Minima



When starting from A we will fall into the minimum denoted as a dot, while starting from B we will arrive at minimum indicated with a star.

In general, for a very complex PES the search for the global minimum is rather difficult and time-consuming. Specific algorithms that sample the PES have been proposed to locate the global minimum, but they will not be discussed here.



Geometry optimization input block

E.g.: α -Quartz - hexagonal cell – RHF/STO-3G

```
a-QUA (in. geom. expt.)  
CRYSTAL  
0 0 2  
154  
0 0 16  
4.916 5.4054  
2  
14 0.4697 0. 0.  
8 0.4135 0.2669 0.1191  
OPTGEOM  
Optional keywords  
END  
ENDG
```

Title
Dimensionality of the system
Crystallographic information (3D only)
Space Group (*Fm3m* – 154)
Shift of the origin
Lattice parameters (*hexagonal*)
Number of non equivalent atoms
Atomic number and fractional coordinates

Geometry optim. input block
Optimization of atomic positions + cell
End of geom. opt. input block
End of geometry input section

Optional keywords are related to:

- Modification of the algorithm (Initial Hessian, Hessian updating,...)
 - Convergence criteria and tolerances (**TOLDEE**, **TOLDEX**, **TOLDEG**)
 - Constrained geometry optimization
- See CRYSTAL Tutorials
(Geometry Optimization)



Geometry optimization input block

E.g.: α -Quartz - hexagonal cell – RHF/STO-3G

Full geometry optimization of atomic positions and lattice param.s

Redundant internal coordinates

```
a-QUA (in. geom. expt.)  
CRYSTAL  
0 0 2  
154  
0 0 16  
4.916  5.4054  
2  
14 0.4697  0.          0.  
 8 0.4135  0.2669  0.1191  
OPTGEOM  
INTREDUN  
Optional keywords  
END  
ENDG
```



Constrained geometry optimization

Optimization in **Cartesian/fractionary coordinates** (*default*)

1. Fixing Cartesian coordinates (FRAGMENT)
2. Constant volume geometry optimization (CVOLOPT)
3. Fixing a lattice parameter (CRYDEF – FIXDEF)
4. Constant pressure geometry optimization (EXTPRESS)

Optimization in **redundant internal coordinates** (INTREDUN)

1. Fixing a set of internal coordinates (FREEZINT)
2. Adding a new internal coordinate (DEFLNGS, ...)
3. Fixing a given internal coordinate (LNGSFROZEN, ...)



FRAGMENT

E.g.: Urea bulk - tetragonal cell – RHF/STO-3G

Urea (expt.) STO-3G

CRYSTAL

0 0 0

113

5.565 4.684

5

6 0.0 0.5 0.326

8 0.0 0.5 0.5953

7 0.1459 0.6459 0.1766

1 0.2575 0.7575 0.2827

1 0.1441 0.6441-0.0380

KEEP SYMM

OPT GEOM

FRAGMENT

2

9 13

END

END

Title

Dimensionality of the system

Crystallographic information (3D only)

Space Group (P4₁21 – 113)

Lattice parameters (tetragonal)

Number of non equivalent atoms

Atomic number and fractional coordinates

Keyword to preserve the symmetry

Geometry optim. input block

Keyword to optimize a fragment of the structure

Number of atoms free to relax

Labels of the atoms free to relax (see output)

End of geometry optimization input block

End of the geometry input section



Effect of Pressure

FROM PRESSURE-CONSTRAINED OPTIMIZATIONS

Through an external hydrostatic pre-stress added to the stress tensor.

FROM VOLUME-CONSTRAINED OPTIMIZATIONS

Through an Equation-of-State approach.



Effect of Pressure

FROM PRESSURE-CONSTRAINED OPTIMIZATIONS

The stress tensor is defined as follows in terms of cell gradients:

$$\sigma_{ij} = \frac{1}{V} \frac{\partial E}{\partial \epsilon_{ij}} = \frac{1}{V} \sum_{k=1}^3 \frac{\partial E}{\partial a'_{ki}} a_{kj}$$

The stress tensor can be modified by adding a pre-stress in the form of a hydrostatic pressure:

$$\sigma_{ij}^{\text{pre}} = P \delta_{ij}$$

By inverting the first expression above, one gets the expression of the cell gradients contained by the applied pressure. By using them within the geometry optimization process, one basically minimizes the enthalpy of the system:

$$\frac{\partial H}{\partial a_{ij}} = \frac{\partial E}{\partial a_{ij}} + P V(\mathbf{A}^{-1})_{ji}$$



Effect of Pressure

FROM PRESSURE-CONSTRAINED OPTIMIZATIONS

A **specific value of pressure is specified** (input parameter) and a pressure-constrained geometry optimization performed. At the end, one gets the optimized structure at the desired pressure.

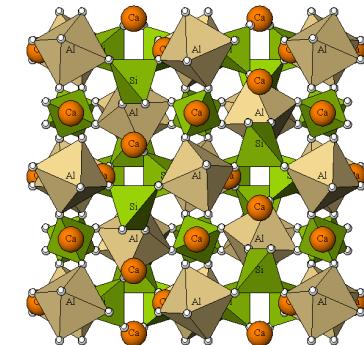
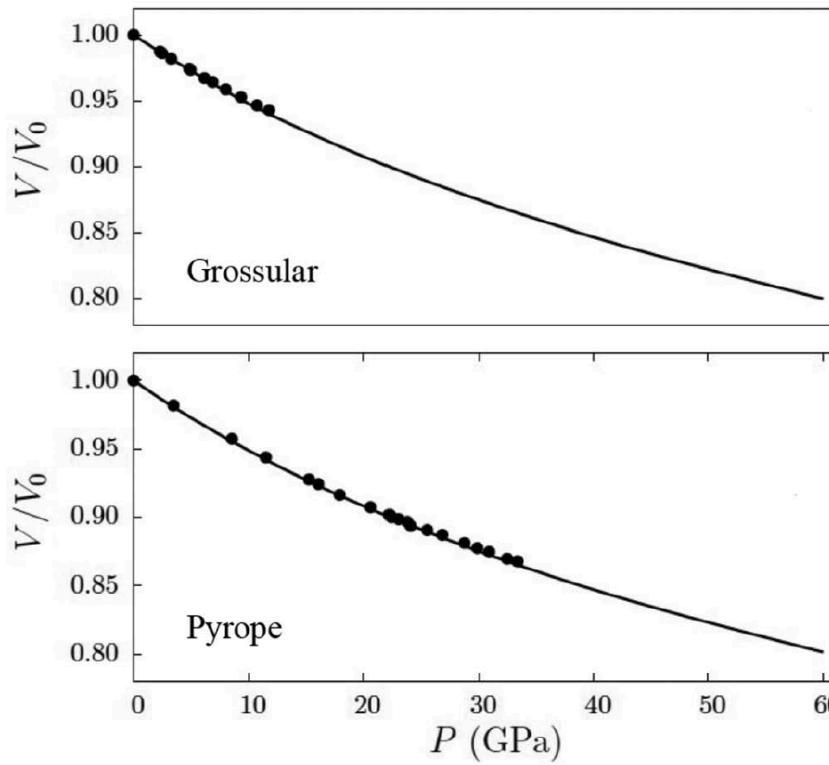
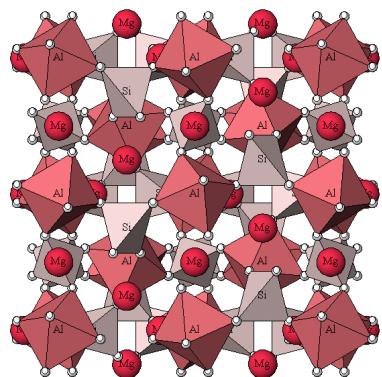
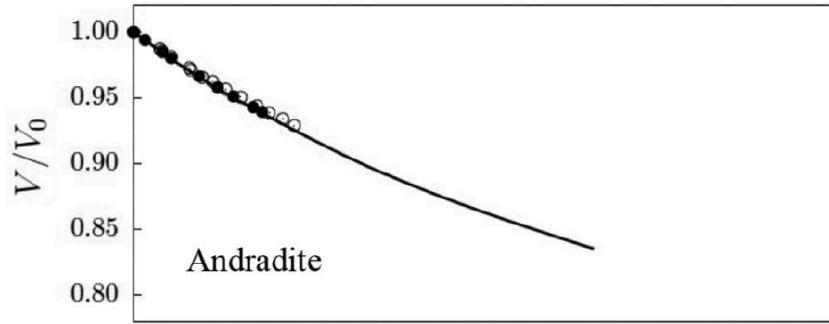
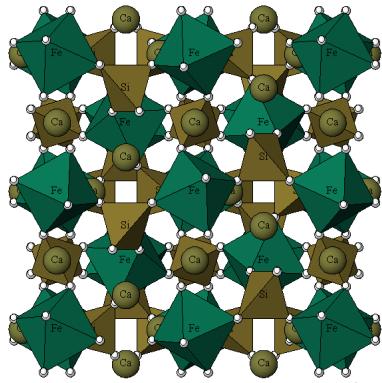
This approach is therefore very effective when one wants to determine the equilibrium structure of the system at one specific value of pressure.

If one wants to determine the **$V(p)$ relation** (i.e. to know how the volume, and structure, changes with pressure p) then one needs to run many pressure-constrained geometry optimizations at different pressures.



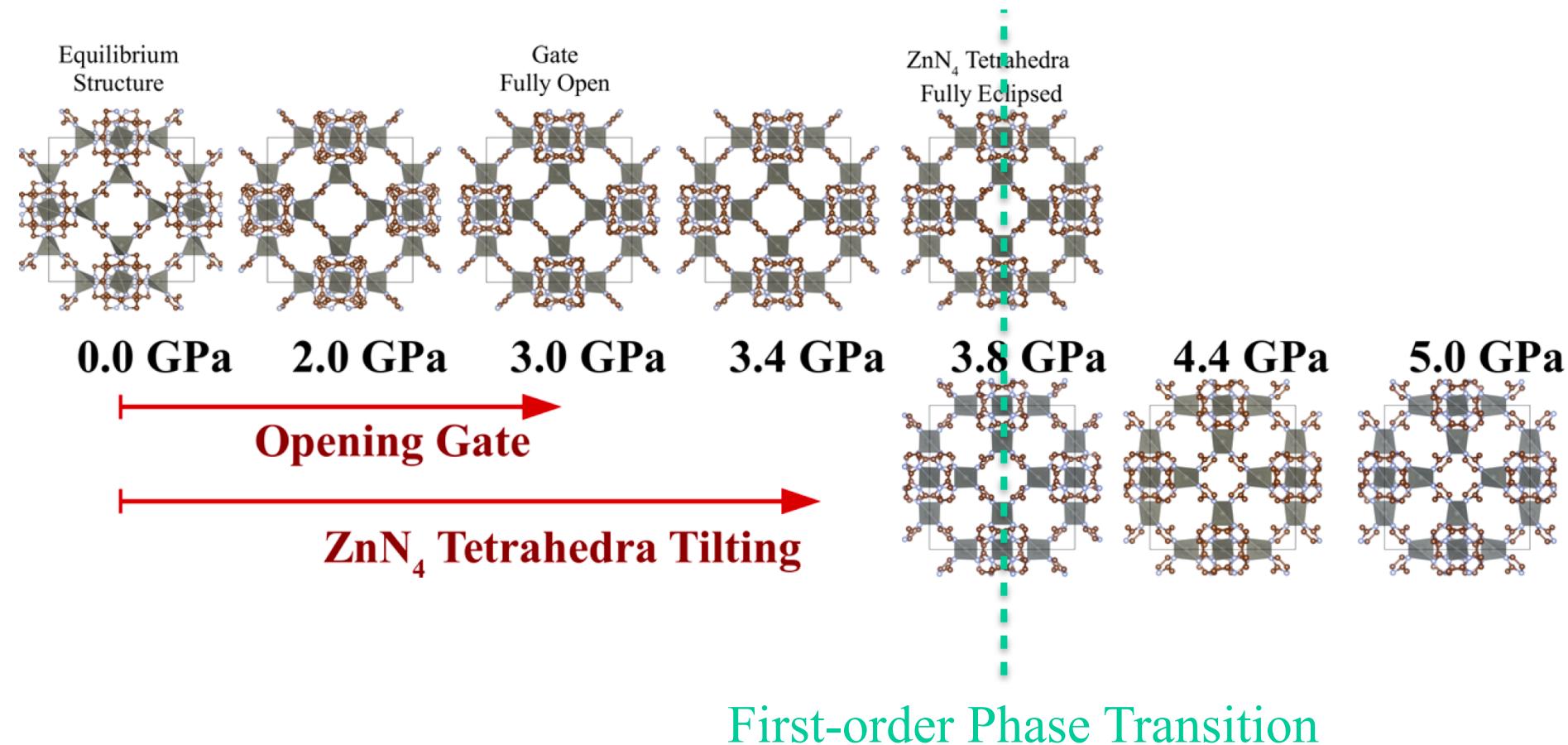
Effect of Pressure

FROM PRESSURE-CONSTRAINED OPTIMIZATIONS



Effect of Pressure

FROM PRESSURE-CONSTRAINED OPTIMIZATIONS



Effect of Pressure

FROM PRESSURE-CONSTRAINED OPTIMIZATIONS

EXTPRESS is the keyword that allows to apply a given pressure to the system and optimize the structure.

Pressure is given as Hartree/Bohr³ (1 Hartree/Bohr³ = 29421 GPa)

E.g.

```
OPTGEOM
EXTPRESS
0.001
END
```



CVOLOPT

E.g.: α -Quartz - hexagonal cell – constant volume optimization

a-QUA (in. geom. expt.)

CRYSTAL

0 0 2

154

0 0 16

4.916 5.4054

2

14 0.4697 0. 0.
8 0.4135 0.2669 0.1191

OPTGEOM

CVOLOPT

END

ENDG

Title

Dimensionality of the system

Crystallographic information (3D only)

Space Group ($Fm\bar{3}m - 154$)

Shift of the origin

Lattice parameters (*hexagonal*)

Number of non equivalent atoms

Atomic number and fractional coordinates

Geometry optim. input block

Keyword to run a constant volume opt.

End of geom. optim. input block

End of geometry input section

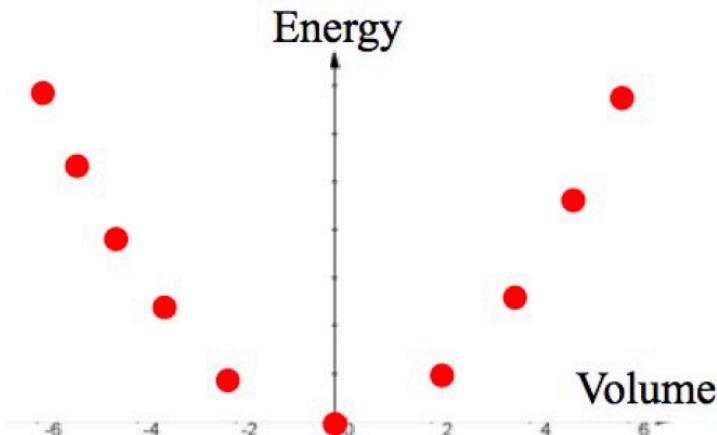
Useful to compute E vs V curves (e.g. for EoS)



Effect of Pressure

FROM VOLUME-CONSTRAINED OPTIMIZATIONS

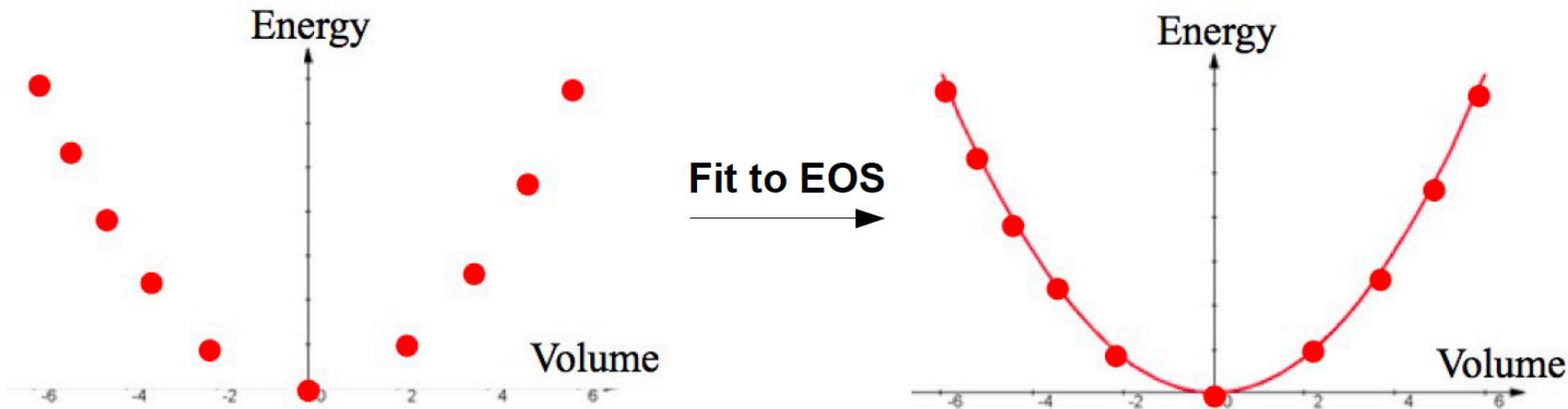
Constant-volume optimizations are performed at different volumes to get a E-V curve, that is then fitted to evaluate the slope (**pressure**) and curvature (bulk modulus).



Effect of Pressure

FROM VOLUME-CONSTRAINED OPTIMIZATIONS

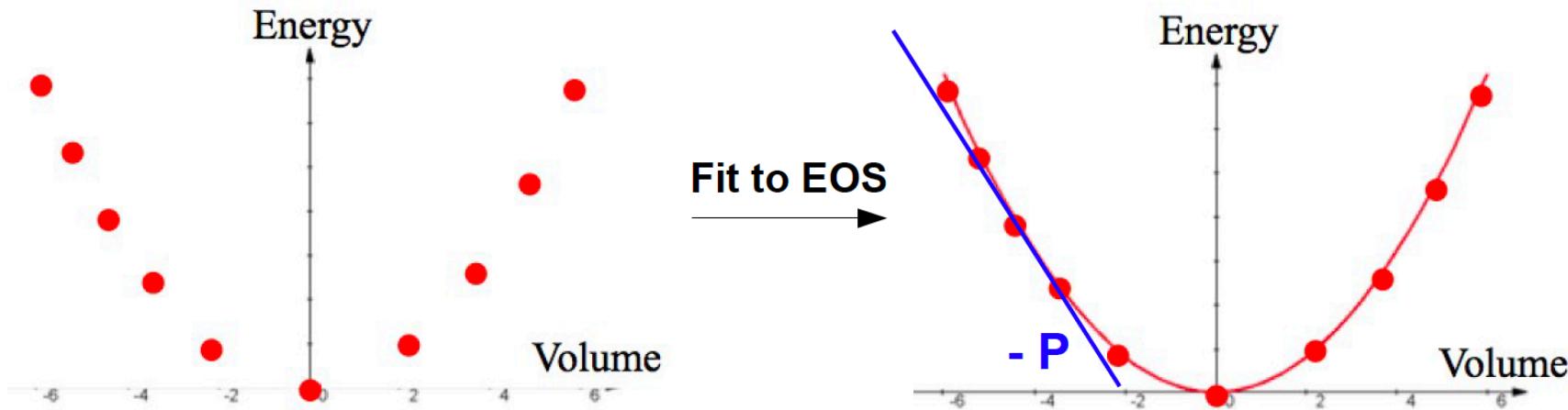
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Effect of Pressure

FROM VOLUME-CONSTRAINED OPTIMIZATIONS

Constant-volume optimizations are performed at different volumes to get a E-V curve, that is then fitted to evaluate the slope (**pressure**) and curvature (bulk modulus).



$$P(V) = - \left(\frac{\partial E}{\partial V} \right)$$

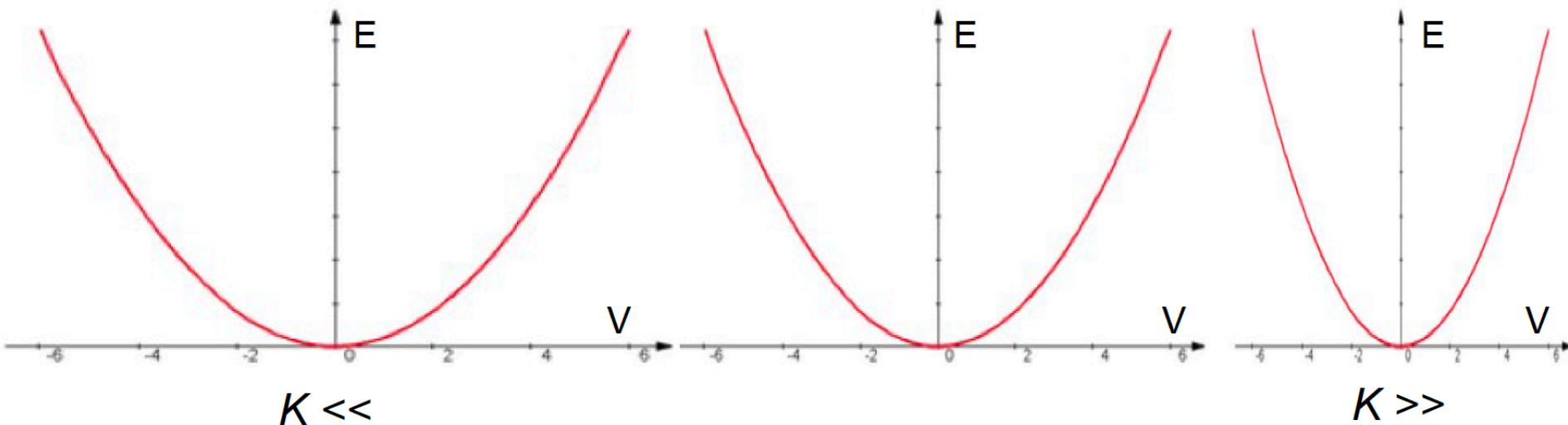


Effect of Pressure

FROM VOLUME-CONSTRAINED OPTIMIZATIONS

Constant-volume optimizations are performed at different volumes to get a E-V curve, that is then fitted to evaluate the slope (pressure) and curvature (**bulk modulus**).

$$K = V \left(\frac{\partial^2 E}{\partial V^2} \right)$$



Effect of Pressure

FROM VOLUME-CONSTRAINED OPTIMIZATIONS

In CRYSTAL, this whole process is fully-automated and can be run by using the EOS keyword:

Geometry Input

EOS

[optional sub-keywords]

END



Effect of Pressure

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THERMODYNAMIC FUNCTIONS OBTAINED WITH EOS: VINET 1987
+++++

V = VOLUME, P = PRESSURE, E = ENERGY, G = GIBBS FREE ENERGY, B = BULK MODULUS

V (A^3)	P (GPa)	E (a.u.)	G (a.u.)	B (GPa)
136.37	-5.00	-1319.73967343	-1319.89603452	21.96
131.93	-4.21	-1319.74437012	-1319.87175596	25.86
128.22	-3.42	-1319.74762603	-1319.84821045	29.53
125.02	-2.63	-1319.74985141	-1319.82528837	33.03
122.21	-1.84	-1319.75129893	-1319.80290843	36.40
119.70	-1.05	-1319.75213646	-1319.78100994	39.65
117.43	-0.26	-1319.75248193	-1319.75954364	42.81
115.35	0.53	-1319.75242166	-1319.73847018	45.89
113.45	1.32	-1319.75202088	-1319.71775646	48.90
111.68	2.11	-1319.75133026	-1319.69737458	51.86
110.04	2.90	-1319.75038992	-1319.67730070	54.75
108.51	3.69	-1319.74923235	-1319.65751494	57.61
107.06	4.47	-1319.74788404	-1319.63799827	60.41
105.71	5.26	-1319.74636708	-1319.61873479	63.18
104.42	6.05	-1319.74470011	-1319.59971153	65.91
103.20	6.84	-1319.74289869	-1319.58091375	68.61
102.04	7.63	-1319.74097644	-1319.56233179	71.28
100.94	8.42	-1319.73894489	-1319.54395405	73.91
99.89	9.21	-1319.73681430	-1319.52577266	76.53
98.88	10.00	-1319.73459329	-1319.50777698	79.11



FIXDEF

E.g.: α -Quartz - hexagonal cell – fixing c lattice constant

a-QUA (in. geom. expt.)

CRYSTAL

0 0 2

154

0 0 16

4.916 5.4054

2

14 0.4697 0. 0.
8 0.4135 0.2669 0.1191

OPTGEOM

FULLOPTG

CRYDEF

FIXDEF

1

0 2 0.0 0.0

END

ENDG

Title

Dimensionality of the system

Crystallographic information (3D only)

Space Group ($Fm\bar{3}m - 154$)

Shift of the origin

Lattice parameters (*hexagonal*)

Number of non equivalent atoms

Atomic number and fractional coordinates

Geometry optim. input block

Full optimization of cell param.s and atoms

Setting crystallographic deformations

Keyword to fix a given deformation

Number of constraints

Fixing c lattice constant

End of geom. optim. input block

End of geometry input section



INTREDUN

E.g.: Ice - orthorombic cell – Fractionary vs Internal

Ice Cmc21 setting expt.

CRYSTAL

0 0 0

36

4.523 7.834066 7.367

5

8 0.00000 -0.33333 -0.4371

8 0.50000 -0.16667 -0.5629

1 0.50000 -0.16667 -0.6989

1 0.50000 -0.04490 -0.5182

1 0.18265 -0.27245 -0.4818

OPTGEOM

INTREDUN

ENDOPT

END (ENDG)

Title

Dimensionality of the system

Crystallographic information (3D only)

Space Group (36)

Lattice parameters (*orthorombic*)

Number of non equivalent atoms

Atomic number and fractional coordinates

Geometry optim. input block

Full optimization of cell param.s and atoms
in redundant internal coordinates

End of geometry input section

Note: **INTREDUN** performs a full optimization of cell param. and atomic positions

Before running the calculation it is better to run a test to check the consistency of the set of internal
coordinates (keyword **TESTREDU**)

Automatic generation of the internal coordinates depends on the definition of covalent radii (see
keyword **RAYCOV**)



INTREDUN - FREEZINT

Example: (Ice - Freezing a set of internal coordinates)

Modify the previous input for Ice XI to freeze internal coordinates (keyword **FREEZINT**).

This allows users to fix a set of internal coordinates according to the list of bonds, angles and torsions printed in the output file.

FREEZINT fix internal coord.s by specifying how many bonds, angles and torsions are frozen (in this order) according to the list.

E.g.

```
ATOMORDE  
OPTGEOM  
INTREDUN  
FREEZINT  
3 8 0  
END
```

Note that this corresponds to a rigid body geometry optimization.
Repeat the exercise for crystalline urea.



INTREDUN – LNGSFROZEN/ANGSFROZEN

Example: (a-Quartz – rigid tetrahedra geom. optimization)

Modify the previous input for α -Quartz to freeze given internal coordinates (keyword **LNGSFROZEN** and **ANGSFROZEN**). This allows users to fix a given internal coordinate by specifying the atoms that define the bond or the angle. If the specified internal coordinate does not exist, it is created, first, and then added on top of the list of coordinates.

E.g.

OPTGEOM

INTREDUN

ANGSFROZEN

4

5 1 -1 0 0 8 0 0 0

4 1 0 0 0 8 1 0 0

4 1 0 0 0 7 0 0 0

4 1 0 0 0 5 1 0 0

LNGSFROZEN

2

4 1 0 0 0

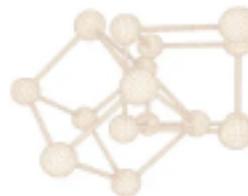
5 1 -1 0 0

END

This corresponds to a rigid tetrahedra (SiO_4) geometry optimization.

Repeat the previous exercise for Ice by using **LNGSFROZEN** and **ANGSFROZEN**.





Advanced School on
QUANTUM MODELLING
of Materials with CRYSTAL

Thank you

