Strategies in geometry optimization of solids

Claudio M. Zicovich-Wilson
Facultad de Ciencias, U. A. del Edo. de Morelos, México

Ab initio Simulation of Crystalline Systems ASCS2006

September 17-22, 2006 - Spokane, Washington (USA)

Universidad Autónoma del Estado de Morelos
Facultad de Ciencias

CRYSTAL
a computational tool for solid state chemistry and physics

Geometries

Geometries

- The same chemical compound *(same atoms, same bonds)* may have many configurations in what concerns its nuclear positions.

Geometries

- The same chemical compound *(same atoms, same bonds)* may have many configurations in what concerns its nuclear positions.
- In general these nuclear configurations have different energies, and experimentally they appear as an statistical distribution of nuclear arrangements.

Geometries

- The same chemical compound *(same atoms, same bonds)* may have many configurations in what concerns its nuclear positions.
- In general these nuclear configurations have different energies, and experimentally they appear as an statistical distribution of nuclear arrangements.
- What of such configurations **(geometries)** can be adopted as a suitable representative of the compound in order to compute the energy dependent properties?

Geometries

- The same chemical compound *(same atoms, same bonds)* may have many configurations in what concerns its nuclear positions.
- In general these nuclear configurations have different energies, and experimentally they appear as an statistical distribution of nuclear arrangements.
- What of such configurations **(geometries)** can be adopted as a suitable representative of the compound in order to compute the energy dependent properties?

⇓

GEOMETRY
OPTIMIZATION

Potential Energy of a nuclear configuration

According to the Born-Oppenheimer approximation, the *static* total energy depends uniquely on the nuclear positions:

$$E = F(x_1, x_2, \cdots, x_{3N})$$

(x_i Cartesian coordinates of the N núclei)

Invariance under translation-rotations ⟶ Internal degrees of freedom

Internal degrees of freedom

Molecules:

$$M = \underbrace{3N}_{\text{cartesian}} - \overbrace{3}^{\text{translational}} - \overbrace{3[\text{or }2]}^{\text{rotational}}$$

Internal degrees of freedom

Molecules:

$$M = \underbrace{3N}_{\text{cartesian}} - \overbrace{3}^{\text{translational}} - \overbrace{3[\text{or } 2]}^{\text{rotational}}$$

3D Crystals:

$$M = \underbrace{3N}_{\text{cartesian}} - \overbrace{3}^{\text{translational}} + \underbrace{\left(9 - \overbrace{3}^{\text{rotational}}\right)}_{\text{lattice}}$$

Coordinate systems

Coordinate systems

- There are infinite choices to define the M internal coordinates

Coordinate systems

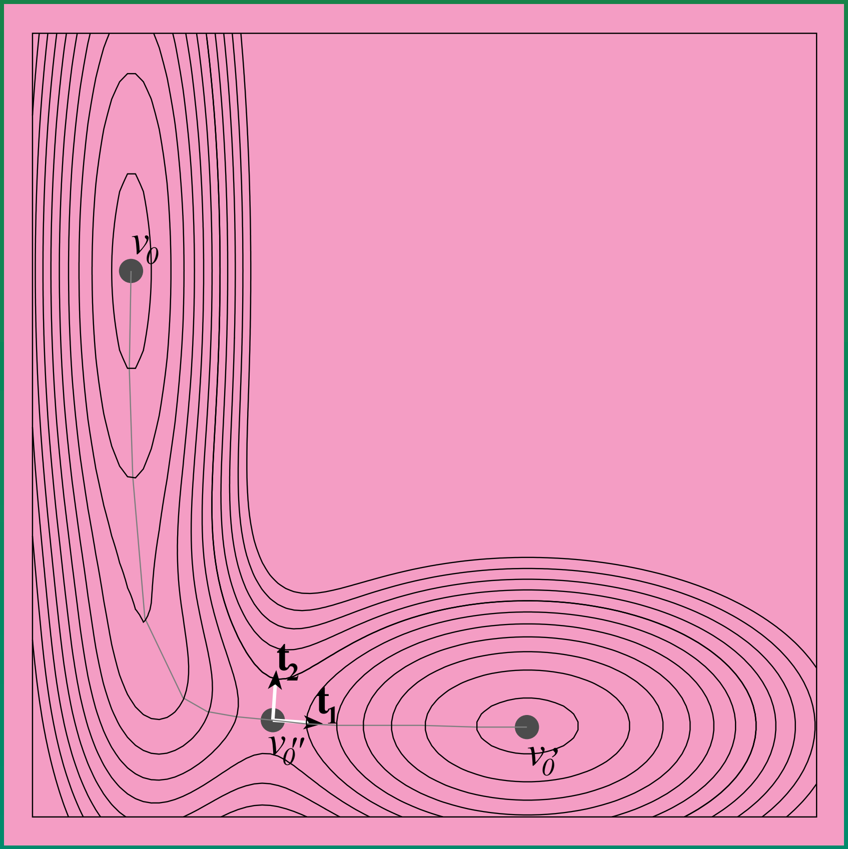
- There are infinite choices to define the M internal coordinates
- The best one should be that who makes easier the study of the potential energy function

Coordinate systems

- There are infinite choices to define the M internal coordinates
- The best one should be that who makes easier the study of the potential energy function
- Let's assume that $\mathbf{v} = (v_1, v_2, \cdots, v_M)$ is the *nuclear configuration* vector in a given coordinate choice

A Potential Energy Hypersurface (PEH)

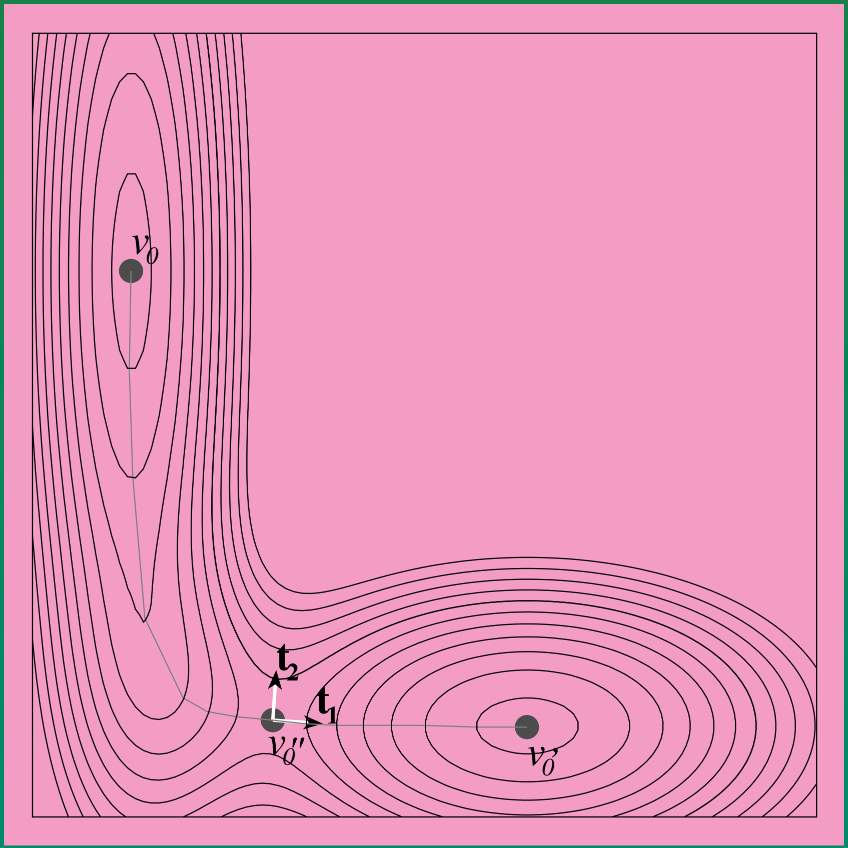
$$E = F(v_1, v_2, \cdots, v_M)$$



How to describe the features of the PEH?

A Potential Energy Hypersurface (PEH)

$$E = F(v_1, v_2, \cdots, v_M)$$



How to describe the features of the PEH?

A relevant information (invariant under the coordinate system choice) is provided by the *critical points* (v_0, v_0' y v_0'')

Critical Points

Condition:

$$\mathbf{g}(\mathbf{v}_0) \equiv g_i(\mathbf{v}_0) = \frac{\partial F}{\partial v_i}(\mathbf{v}_0) = \mathbf{0}$$

If $\mathbf{v}$ is M-dimensional, there are $M + 1$ different types of critical points. The **most relevant** in quantum chemistry are:

Critical Points

Condition:

$$\mathbf{g}(\mathbf{v}_0) \equiv g_i(\mathbf{v}_0) = \frac{\partial F}{\partial v_i}(\mathbf{v}_0) = 0$$

If $\mathbf{v}$ is M-dimensional, there are $M+1$ different types of critical points. The **most relevant** in quantum chemistry are:

- *minima* (v_0, v_0')

Critical Points

Condition:

$$\mathbf{g}(\mathbf{v}_0) \equiv g_i(\mathbf{v}_0) = \frac{\partial F}{\partial v_i}(\mathbf{v}_0) = 0$$

If $\mathbf{v}$ is M-dimensional, there are $M+1$ different types of critical points. The **most relevant** in quantum chemistry are:

- *minima* (v_0, v_0')
- *saddle points* (v_0'')

The Hessian Matrix

$$\boxed{\boldsymbol{H_{ij} = \left.\frac{\partial^2 F}{\partial v_i \partial v_j}\right|_{\mathbf{v}_0}}}$$

Eigenvalue equation:

$$\mathbf{H}\mathbf{t}_\mu = h_\mu \mathbf{t}_\mu$$

h_μ $\longrightarrow$ real (surface curvature in the c. p.).
$\mathbf{t}_\mu$ are special directions in the coordinate space.

The critical point order

The order of a critical point $\mathbf{v}_0$ is the number of negative eigenvalues (n) of the Hessian in that point.

The critical point order

The order of a critical point $\mathbf{v}_0$ is the number of negative eigenvalues (n) of the Hessian in that point.

- $n = 0 \longrightarrow$ minimum

The critical point order

The order of a critical point $\mathbf{v}_0$ is the number of negative eigenvalues (n) of the Hessian in that point.

- $n = 0 \longrightarrow$ minimum
- $n = 1 \longrightarrow$ saddle point

The critical point order

The order of a critical point $\mathbf{v}_0$ is the number of negative eigenvalues (n) of the Hessian in that point.

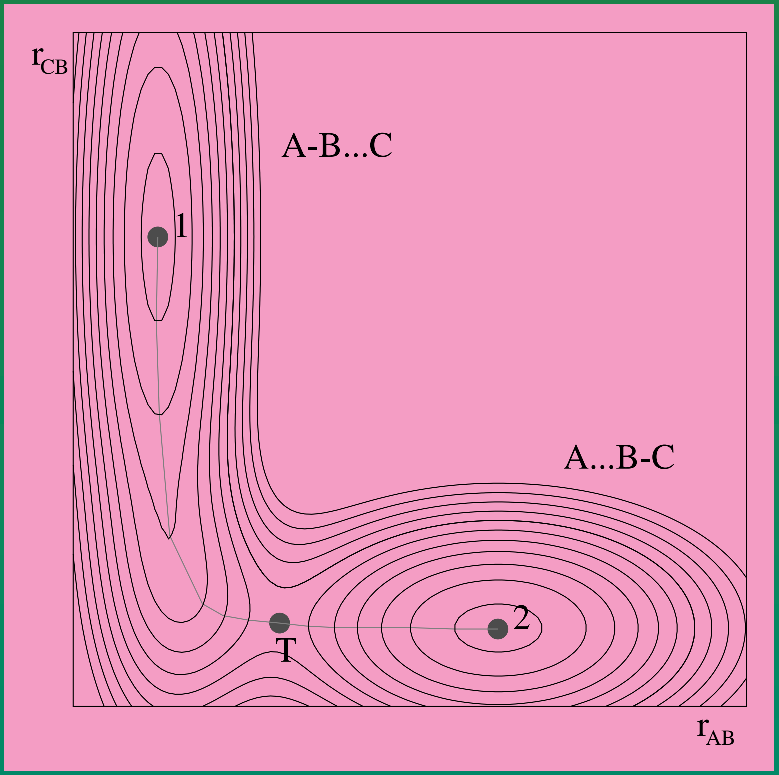
- $n = 0 \longrightarrow$ minimum
- $n = 1 \longrightarrow$ saddle point
- $\ldots$
- $n = M \longrightarrow$ maximum

Reaction path in a bidimensional PEH

$$\mathrm{A - B \cdots C \longrightarrow A \cdots C - B}$$

Reaction path in a bidimensional PEH

$$A - B \cdots C \rightarrow A \cdots C - B$$



The chemical meaning of critical points

Critical points

The chemical meaning of critical points

Critical points

- minima: Clasic → 0 K most stable
  - ↓ temp.
  - ≈ most probable

The chemical meaning of critical points

Critical points

- minima:
  - Clasic → $0\,$K most stable
    - ↓ temp.
    - ≈ most probable
  - Quantum → zero-point correction
    - thermochemistry

The chemical meaning of critical points

Critical points

- minima:
  - Clasic →
    - 0 K most stable
    - ↓ temp.
    - ≈ most probable
  - Quantum →
    - zero-point correction
    - thermochemistry
- saddle point:
  - semi-clasic →
    - Transition state
    - ≈ Activation energy
    - Kinetics
    - Reaction Path

Optimization Methods

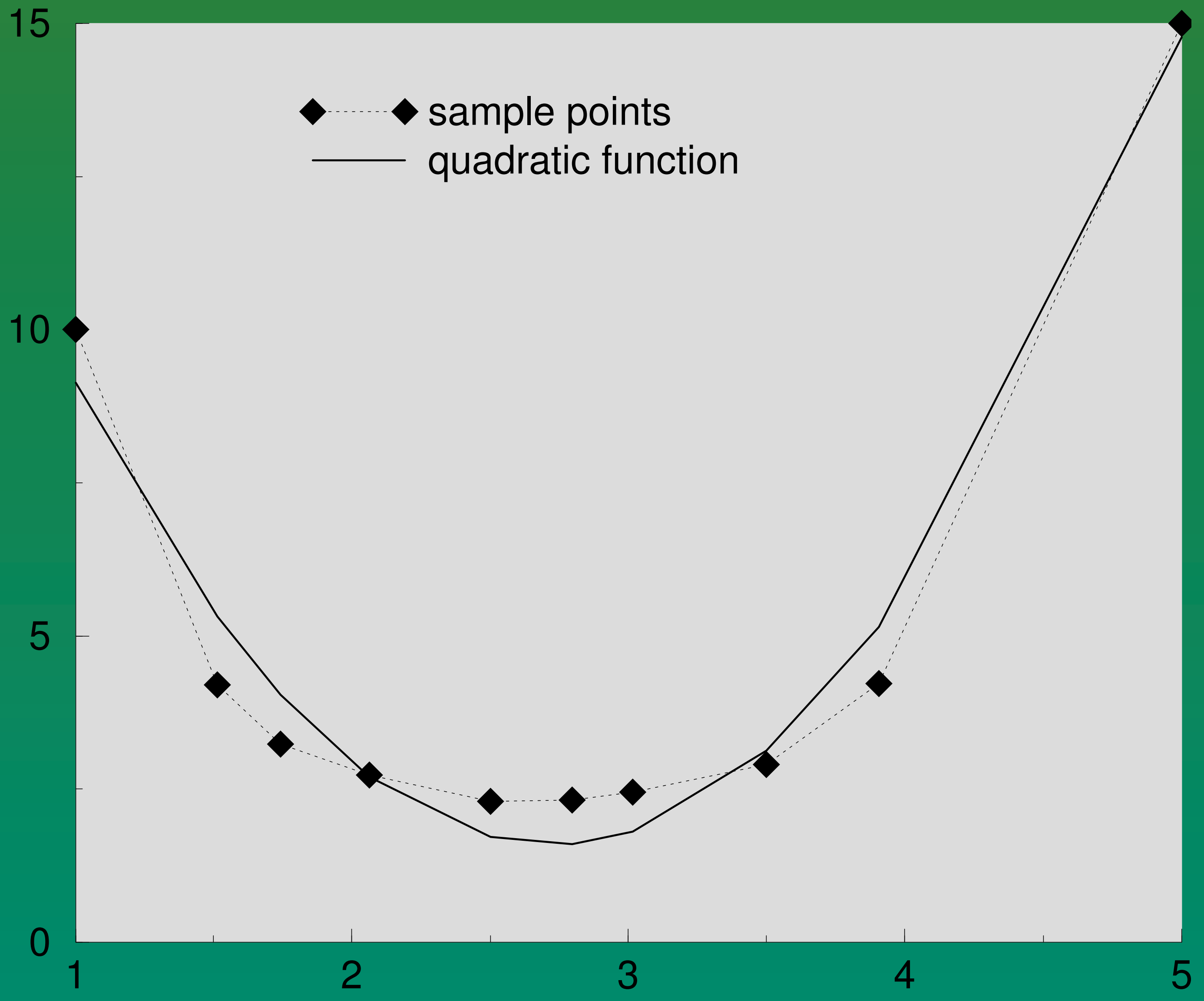
Optimization Methods

- non-gradient

Optimization Methods

- non-gradient
- gradient

Non gradient methods: line optimization



Extension to multiple parameters

Direction set method

Extension to multiple parameters

Direction set method

- Each parameter is separately line-optimized in a given sequence

Extension to multiple parameters

Direction set method

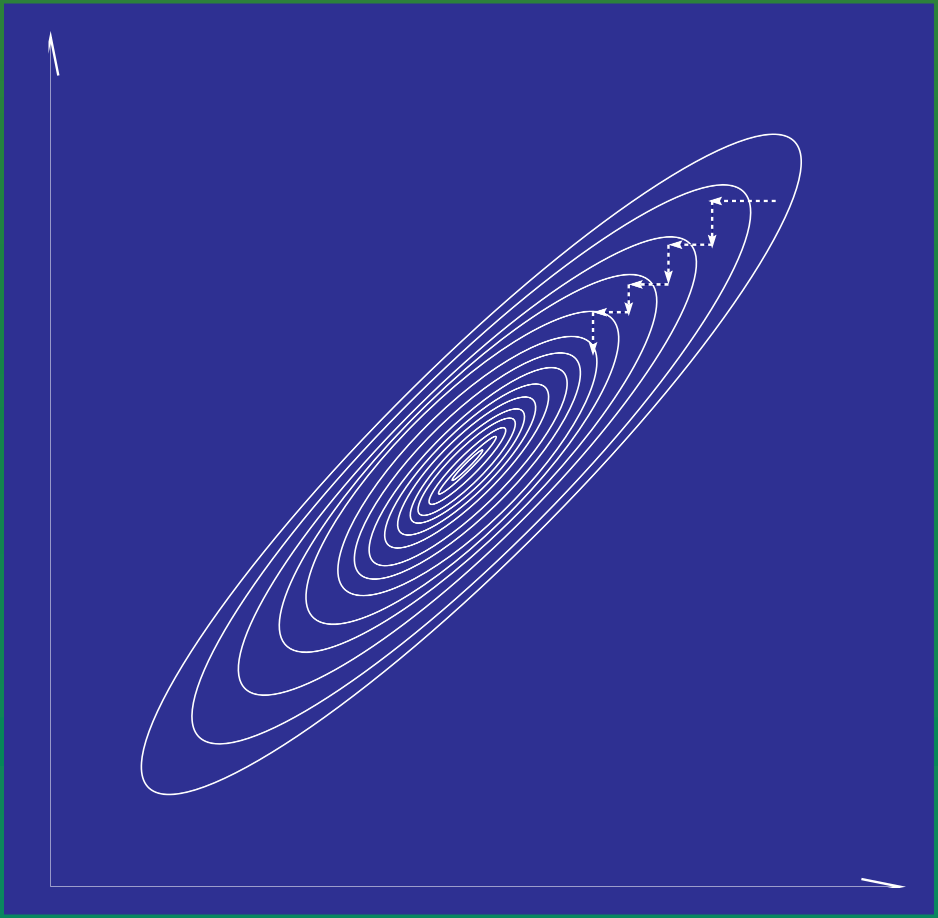
- Each parameter is separately line-optimized in a given sequence
- A cycle finishes when all parameters have been line-optimized

Extension to multiple parameters

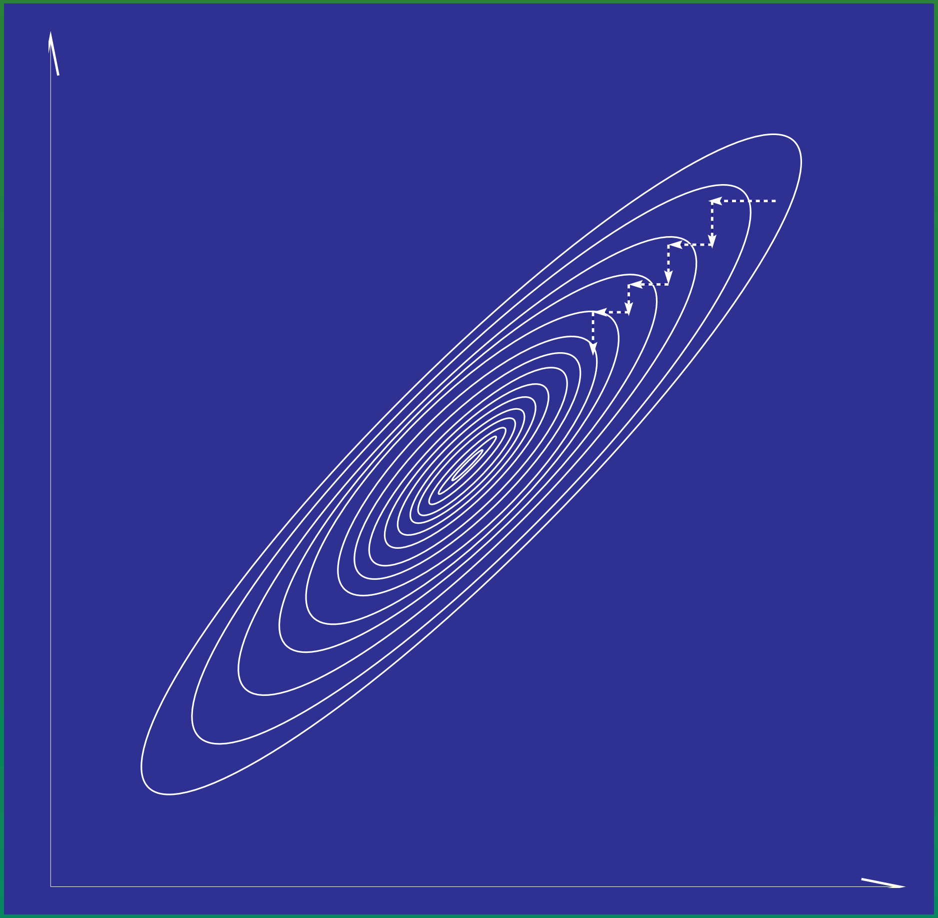
Direction set method

- Each parameter is separately line-optimized in a given sequence
- A cycle finishes when all parameters have been line-optimized
- Convergence is reached when the total energy becomes stable under a given numerical criterion

Convergence of the direction set method in a bidimensional surface.



Convergence of the direction set method in a bidimensional surface.



⟶ **Directions are not fully independent (conjugate)**

The concept of conjugate directions.

Second order Taylor decomposition of F:

$$\begin{aligned}\boldsymbol{F}(\mathbf{u}) &= \boldsymbol{F}(\mathbf{0}) + \sum_i \frac{\partial \boldsymbol{F}}{\partial \boldsymbol{u}_i}\boldsymbol{u}_i + \frac{1}{2}\sum_{ij}\frac{\partial^2 \boldsymbol{F}}{\partial \boldsymbol{u}_i \partial \boldsymbol{u}_j}\boldsymbol{u}_i\boldsymbol{u}_j + \cdots \\ &\approx \boldsymbol{c} - \mathbf{b}\cdot\mathbf{u} + \frac{1}{2}\mathbf{u}\cdot\mathbf{H}\cdot\mathbf{u}\end{aligned}$$

The concept of conjugate directions.

Second order Taylor decomposition of F:

$$\begin{aligned} \boldsymbol{F}(\mathbf{u}) &= \boldsymbol{F}(\mathbf{0}) + \sum_i \frac{\partial \boldsymbol{F}}{\partial \boldsymbol{u}_i} \boldsymbol{u}_i + \frac{1}{2} \sum_{ij} \frac{\partial^2 \boldsymbol{F}}{\partial \boldsymbol{u}_i \partial \boldsymbol{u}_j} \boldsymbol{u}_i \boldsymbol{u}_j + \cdots \\ &\approx \boldsymbol{c} - \mathbf{b} \cdot \mathbf{u} + \frac{1}{2} \mathbf{u} \cdot \mathbf{H} \cdot \mathbf{u} \end{aligned}$$

where

$*$ $\mathbf{u} = \mathbf{v} - \mathbf{v}_0$,	step
$*$ $c = F(\mathbf{0}) = F(\mathbf{v}_0)$,	energy at $\mathbf{v}_0$
$*$ $\mathbf{b} = -\mathbf{g}(\mathbf{v}_0)$,	gradient at $\mathbf{v}_0$
$*$ $\mathbf{H}$,	Hessian matrix

The concept of conjugate directions.

- Approximate gradient:

$$\mathbf{g(v) \equiv g(u) = Hu - b.}$$

The concept of conjugate directions.

- Approximate gradient:

$$\mathbf{g}(\mathbf{v}) \equiv \mathbf{g}(\mathbf{u}) = \mathbf{H}\mathbf{u} - \mathbf{b}.$$

- The function is optimized along direction $\mathbf{t}$. $\longrightarrow$ gradient change along displacement: $\delta\mathbf{t} = \epsilon\mathbf{t}$

$$\boldsymbol{\delta}\mathbf{g} = \mathbf{H} \cdot \boldsymbol{\delta}\mathbf{t} = \boldsymbol{\epsilon}\left(\mathbf{H} \cdot \mathbf{t}\right).$$

The concept of conjugate directions.

- Approximate gradient:

$$\mathbf{g}(\mathbf{v}) \equiv \mathbf{g}(\mathbf{u}) = \mathbf{H}\mathbf{u} - \mathbf{b}.$$

- The function is optimized along direction $\mathbf{t}$. $\longrightarrow$ gradient change along displacement: $\delta\mathbf{t} = \epsilon\mathbf{t}$

$$\delta\mathbf{g} = \mathbf{H} \cdot \delta\mathbf{t} = \epsilon \left(\mathbf{H} \cdot \mathbf{t}\right).$$

- Previously, the function has been optimized along direction $\mathbf{s}$ (the gradient has becomed perpendicular to $\mathbf{s}$).

- To keep that condition it is required that $\mathbf{g} \perp \mathbf{s}$ along all the displacement $\longrightarrow$

$$\mathbf{0} = \mathbf{s} \cdot \delta\mathbf{g} = \mathbf{s}\mathbf{H}\mathbf{t}.$$

Conjugate directions

- Hessian behaves as a metric (quadratic functions):

$$\langle \mathbf{u} \,|\mathbf{v}\rangle = \mathbf{u}\mathbf{H}\mathbf{v}$$

Conjugate directions

- Hessian behaves as a metric (quadratic functions):

$$\langle \mathbf{u} \,|\mathbf{v}\rangle = \mathbf{uHv}$$

- Degree of “dependency” between parameters.

$$\Downarrow$$

Conjugate directions

- Hessian behaves as a metric (quadratic functions):

$$\langle \mathbf{u} | \mathbf{v} \rangle = \mathbf{uHv}$$

- Degree of “dependency” between parameters.

$$\Downarrow$$

$$\text{scalar product: } \langle \mathbf{u} | \mathbf{v} \rangle = \begin{cases} 0 & \text{fully independent (conjugate)} \\ 1 & \text{fully dependent} \end{cases}$$

Powell's quadratically convergent method

Powell's quadratically convergent method

- Scheme similar to direction set method

Powell’s quadratically convergent method

- Scheme similar to direction set method
- Directions are modified along the procedure to be conjugate (within quadratic behavior of the function).

Powell's quadratically convergent method

- Scheme similar to direction set method
- Directions are modified along the procedure to be conjugate (within quadratic behavior of the function).

↓ Dependent on the coordinate system choice

Gradient methods

Gradient methods

- Gradient contains information on what is the direction of the steepest energy descent

Gradient methods

- Gradient contains information on what is the direction of the steepest energy descent
- This permits to improve the minimum search

Gradient methods

- Gradient contains information on what is the direction of the steepest energy descent
- This permits to improve the minimum search
- The numerical calculation of the gradient is costly and a gain in efficiency with respect to non gradient methods is not ensured.

Gradient methods

- Gradient contains information on what is the direction of the steepest energy descent
- This permits to improve the minimum search
- The numerical calculation of the gradient is costly and a gain in efficiency with respect to non gradient methods is not ensured.
- In some *ab initio* methods, the gradient can be obtained through analytic formulae

Gradient methods

- Gradient contains information on what is the direction of the steepest energy descent
- This permits to improve the minimum search
- The numerical calculation of the gradient is costly and a gain in efficiency with respect to non gradient methods is not ensured.
- In some *ab initio* methods, the gradient can be obtained through analytic formulae
- For periodic systems, the implementation of the analytic gradient is not a mere extension to the molecular case, as infinite sums appear that are to be numerically approximated by means of suitable techniques.

Gradient methods

- Gradient contains information on what is the direction of the steepest energy descent
- This permits to improve the minimum search
- The numerical calculation of the gradient is costly and a gain in efficiency with respect to non gradient methods is not ensured.
- In some *ab initio* methods, the gradient can be obtained through analytic formulae
- For periodic systems, the implementation of the analytic gradient is not a mere extension to the molecular case, as infinite sums appear that are to be numerically approximated by means of suitable techniques.
- Crystal2006 includes the implementation of the analytic energy derivatives with respect to
    - ⋆ Atomic positions: K. Doll, V.R. Saunders, N.M. Harrison, *Int. J. Quant. Chem. 82* 1 (2001)
    - ⋆ Cell parameters: K. Doll, R. Dovesi, R. Orlando. *Theor. Chem. Acc. 112*, 394-402 (2004)

Steepest descent method

Steepest descent method

1. How could one exploit the information contained in the gradient?

Steepest descent method

1. How could one exploit the information contained in the gradient?

2. The most straightforward strategy would be the **Steepest descent method**

Steepest descent method

1. How could one exploit the information contained in the gradient?

2. The most straightforward strategy would be the **Steepest descent method**

3. One takes the opposite direction to the gradient

Steepest descent method

1. How could one exploit the information contained in the gradient?
2. The most straightforward strategy would be the **Steepest descent method**
3. One takes the opposite direction to the gradient
4. A line minimization along such a direction is then performed

Steepest descent method

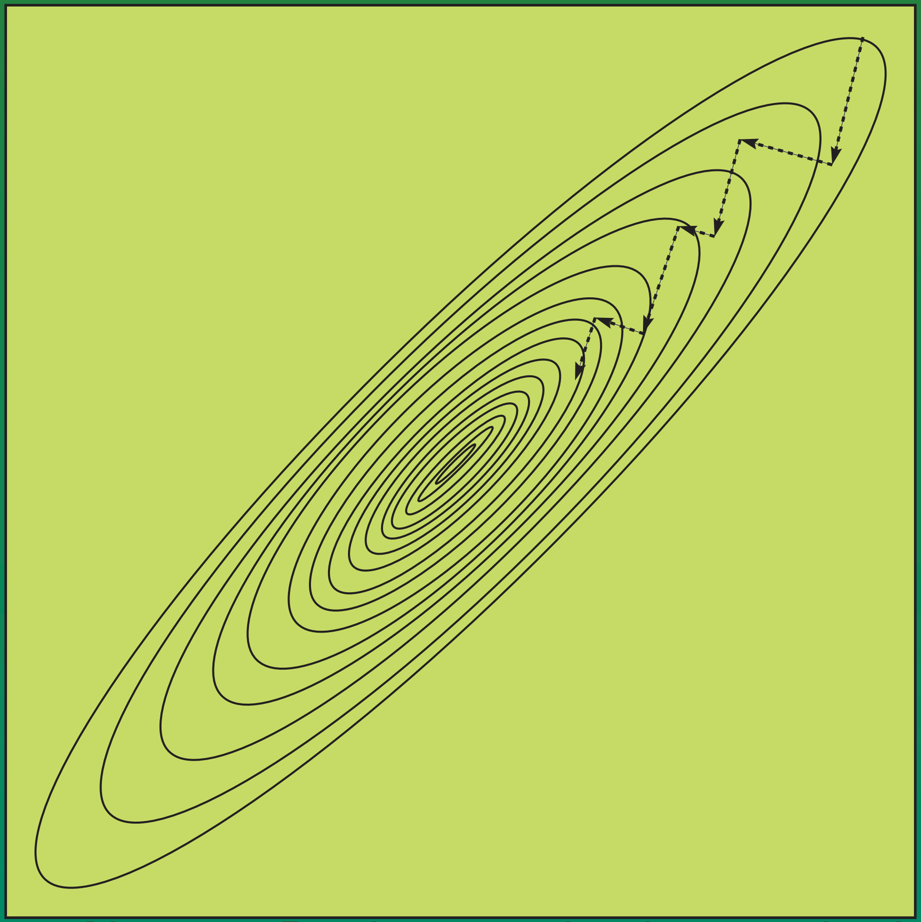
1. How could one exploit the information contained in the gradient?
2. The most straightforward strategy would be the **Steepest descent method**
3. One takes the opposite direction to the gradient
4. A line minimization along such a direction is then performed
5. Iterate since a given convergence criterion (on Energy or gradient norm) is attained

Steepest descent method

1. How could one exploit the information contained in the gradient?
2. The most straightforward strategy would be the **Steepest descent method**
3. One takes the opposite direction to the gradient
4. A line minimization along such a direction is then performed
5. Iterate since a given convergence criterion (on Energy or gradient norm) is attained

Independent on the coordinate system choice

Convergence of the steepest descent method in a bidimensional surface.



⟶Newton-Raphson and other methods.

Quadratic behavior

Points $\mathbf{v}_0 \longrightarrow \mathbf{v}$.

Quadratic behavior

Points $\mathbf{v}_0 \longrightarrow \mathbf{v}$.
Within the second order approximation of the energy, the gradient in $\mathbf{v}$ reads

$$\mathbf{g}(\mathbf{v}) = \mathbf{H} \times (\mathbf{v} - \mathbf{v_0}) + \mathbf{g}(\mathbf{v}_0)$$

Quadratic behavior

Points $\mathbf{v}_0 \longrightarrow \mathbf{v}$.
Within the second order approximation of the energy, the gradient in $\mathbf{v}$ reads

$$\mathbf{g}(\mathbf{v}) = \mathbf{H} \times (\mathbf{v} - \mathbf{v_0}) + \mathbf{g}(\mathbf{v}_0)$$

Being $\mathbf{v}$ the minimum $\Rightarrow \mathbf{g}(\mathbf{v}) = \mathbf{0}$

$$(\mathbf{v} - \mathbf{v_0}) = -\mathbf{H}^{-1}\mathbf{g}(\mathbf{v}_0)$$

Quadratic behavior

Points $\mathbf{v}_0 \longrightarrow \mathbf{v}$.
Within the second order approximation of the energy, the gradient in $\mathbf{v}$ reads

$$\mathbf{g}(\mathbf{v}) = \mathbf{H} \times (\mathbf{v} - \mathbf{v_0}) + \mathbf{g}(\mathbf{v}_0)$$

Being $\mathbf{v}$ the minimum $\Rightarrow \mathbf{g}(\mathbf{v}) = \mathbf{0}$

$$(\mathbf{v} - \mathbf{v_0}) = -\mathbf{H}^{-1}\mathbf{g}(\mathbf{v}_0)$$

Within the quadratic approximation the minimum can be reached in **ONE** step, known the gradient vector and the Hessian matrix

Newton-Raphson method

The minimum search is made in steps i, in which the following equation is solved:

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

Newton-Raphson method

The minimum search is made in steps i, in which the following equation is solved:

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

↑ A few cycles are required to reach the minimum even in non quadratic PEHs

Newton-Raphson method

The minimum search is made in steps i, in which the following equation is solved:

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

↑ A few cycles are required to reach the minimum even in non quadratic PEHs

↓ The hessian calculation is costly from the computational point of view.

Newton-step control

In non-quadratic functions the Newton step may not be the best choice and should be controlled:

Newton-step control

In non-quadratic functions the Newton step may not be the best choice and should be controlled:

- **level-shift trust region**: A trust radius τ of an hypersphere into which the function is supposed quadratically behaved. 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.

Newton-step control

In non-quadratic functions the Newton step may not be the best choice and should be controlled:

- **level-shift trust region**: A trust radius τ of an hypersphere into which the function is supposed quadratically behaved. 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.

- **Line search:** A parameter α_i is found so that a minimum is found along the Newton step direction:

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

Improvements to gradient methods

Along the optimization the changes in the gradient between steps provide useful information on the surface curvature (second derivatives):

Improvements to gradient methods

Along the optimization the changes in the gradient between steps provide useful information on the surface curvature (second derivatives):

∗ Conjugate gradient: the information is accumulated implicitly (Polak-Ribiere, Berny –implemented in CRYSTAL–)

Improvements to gradient methods

Along the optimization the changes in the gradient between steps provide useful information on the surface curvature (second derivatives):

- Conjugate gradient: the information is accumulated implicitly (Polak-Ribiere, Berny –implemented in CRYSTAL–)
- Variable metric: an approximation to the inverse of the Hessian matrix $\mathbf{H}^{-1}$ is built during the optimization process.

Improvements to gradient methods

Along the optimization the changes in the gradient between steps provide useful information on the surface curvature (second derivatives):

$\ast$ Conjugate gradient: the information is accumulated implicitly (Polak-Ribiere, Berny –implemented in CRYSTAL–)

$\ast$ Variable metric: an approximation to the inverse of the Hessian matrix $\mathbf{H}^{-1}$ is built during the optimization process. Several updating formulae:

- Fletcher-Powell
- Murtagh-Sargent (SR1)
- Powell-Symetric-Broyden (PSB)
- Broyden-Fletcher-Godfarb-Shanno (BFGS)

A quite good Hessian to start the procedure may drastically reduce the optimization process

A quite good Hessian to start the procedure may drastically reduce the optimization process

↓ **Identity matrix:** positive definite, no structure: very inefficient.

A quite good Hessian to start the procedure may drastically reduce the optimization process

↓ **Identity matrix:** positive definite, no structure: very inefficient.

→ **Numerical Hessian:** close to exact, fast convergence, high calculation cost (good for very difficult cases: Transition State –see later–)

A quite good Hessian to start the procedure may drastically reduce the optimization process

↓ **Identity matrix:** positive definite, no structure: very inefficient.

→ **Numerical Hessian:** close to exact, fast convergence, high calculation cost (good for very difficult cases: Transition State –see later–)

↑ **Model Hessian:** good and cheap approximation to the actual Hessian. Based on valence forcefields. Significant improvement with respect to Identity matrix.

Transition state (TS) optimization

Transition state (TS) optimization

TS $\longrightarrow$ critical point $\longrightarrow \mathbf{g}(\mathbf{v}) = \mathbf{0}$

$$\downarrow$$

$$(\mathbf{v} - \mathbf{v}_0) \quad = \quad -\mathbf{H}^{-1}\mathbf{g}(\mathbf{v}_0)$$

Transition state (TS) optimization

- TS ⟶ critical point ⟶ $\mathbf{g}(\mathbf{v}) = \mathbf{0}$

$$\downarrow$$

$$(\mathbf{v} - \mathbf{v}_0) \quad = \quad -\mathbf{H}^{-1}\mathbf{g}(\mathbf{v}_0)$$

- Hessian is not positive definite ⟶ search is not always downwards

Transition state (TS) optimization

- $$\boxed{\text{TS} \longrightarrow \text{critical point} \longrightarrow \mathbf{g}(\mathbf{v}) = \mathbf{0}}$$

$$\downarrow$$

$$(\mathbf{v} - \mathbf{v_0}) = -\mathbf{H}^{-1}\mathbf{g}(\mathbf{v}_0)$$

- Hessian is not positive definite ⟶ search is not always downwards

- Much more costly than minima optimization

Necessary conditions for a TS optimization

- The starting point must be close to the TS (*Pre-optimization:* systematic exploration, L(Q)ST, etc)

Necessary conditions for a TS optimization

- The starting point must be close to the TS (*Pre-optimization:* systematic exploration, L(Q)ST, etc)

- Start from an accurately estimated Hessian (analytically or numerically).

Necessary conditions for a TS optimization

- The starting point must be close to the TS (*Pre-optimization:* systematic exploration, L(Q)ST, etc)
- Start from an accurately estimated Hessian (analytically or numerically).
- Some techniques can help in the search (–Eigenvalue Following, Step Walking Surface, NEB–)

Choice of the coordinate system

- Good performance ⟷ Quadratical behavior.

- Coordinate transformation:

$$v_i = v_i(s_1, s_2, \cdots, s_M)$$

- Transformation of $F(\mathbf{v})$ results in a new function F':

$$\begin{aligned} F'(s_1, s_2, \ldots, s_M) = \; & F(v_1(s_1, s_2, \ldots, s_M), v_2(s_1, s_2, \ldots, s_M), \\ & \ldots, v_M(s_1, s_2, \ldots, s_M)) \end{aligned}$$

- One would like the transformation to give rise to function F' that behaves quadratically around the critical point.

Internal valence coordinates

- Defined in terms of bond distances, bond angles, and bond torsions.
- Expected that the functional dependence on them is more or less factorized into additive terms.
- The behavior is assumed to be close to quadratic (good for optimizations)
- The most widely used → $\boxed{\text{Z-MATRIX}}$

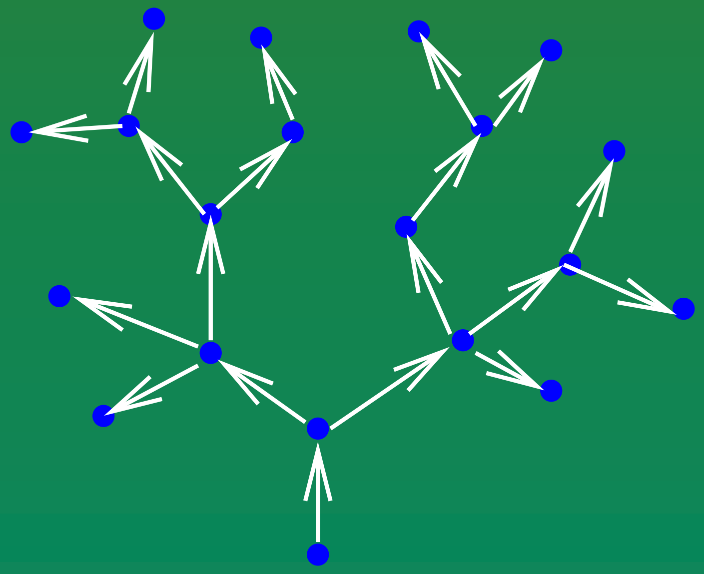
Z-Matrix coordinate system

- Ordered definition of the atomic positions in terms of distances, angles and torsions with reference to previously defined atoms

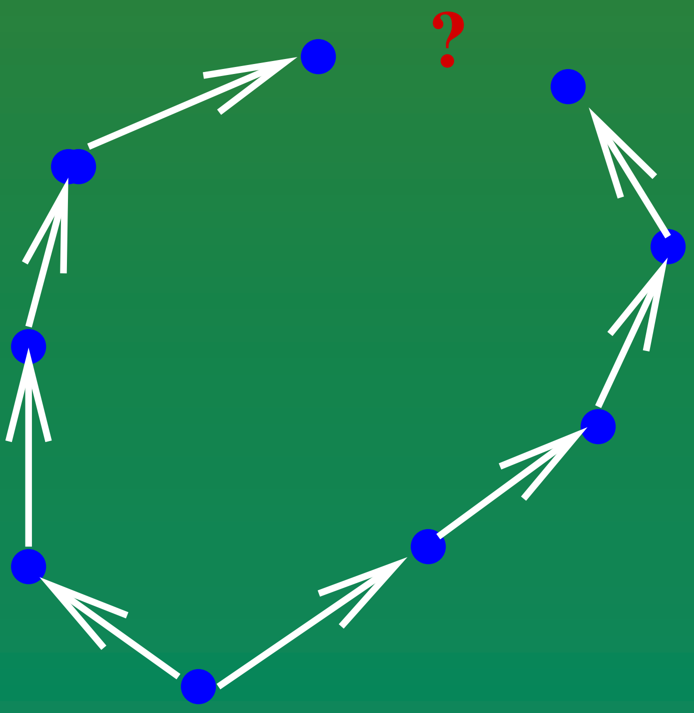
- Easy way to obtain non-redundant *internal* valence coordinates

- The choice is in general arbitrary

Scheme of the Z-matrix logic



TREE STRUCTURE



LOOP STRUCTURE

→ arbitrariness in the definition

Internal valence coordinates for periodic systems

- Periodic systems feature in most cases an infinite number of valence loops (unless molecular crystals, or 1D polymers)
- The arbitrariness of the Z-Matrix valence coordinates is higher than in molecules.

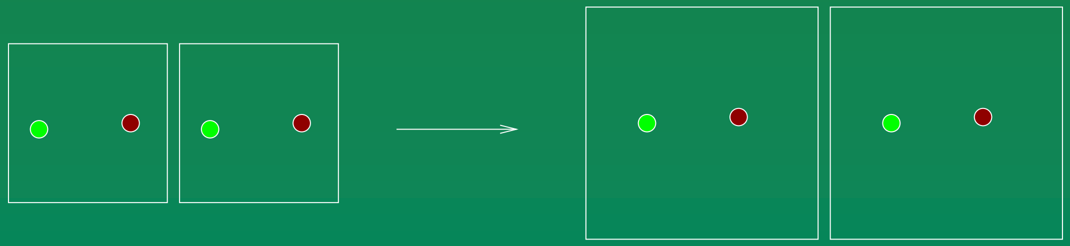
Coordinate systems suitable for crystals

Cartesian coordinates + lattice parameters

↑ Easy definition

↓ Non quadratic behavior (in general)

↓ When the cell is not kept fixed during optimization → high degree of dependency between coordinates and lattice parameters



Coordinate systems suitable for crystals

Fractionary coordinates + lattice parameters

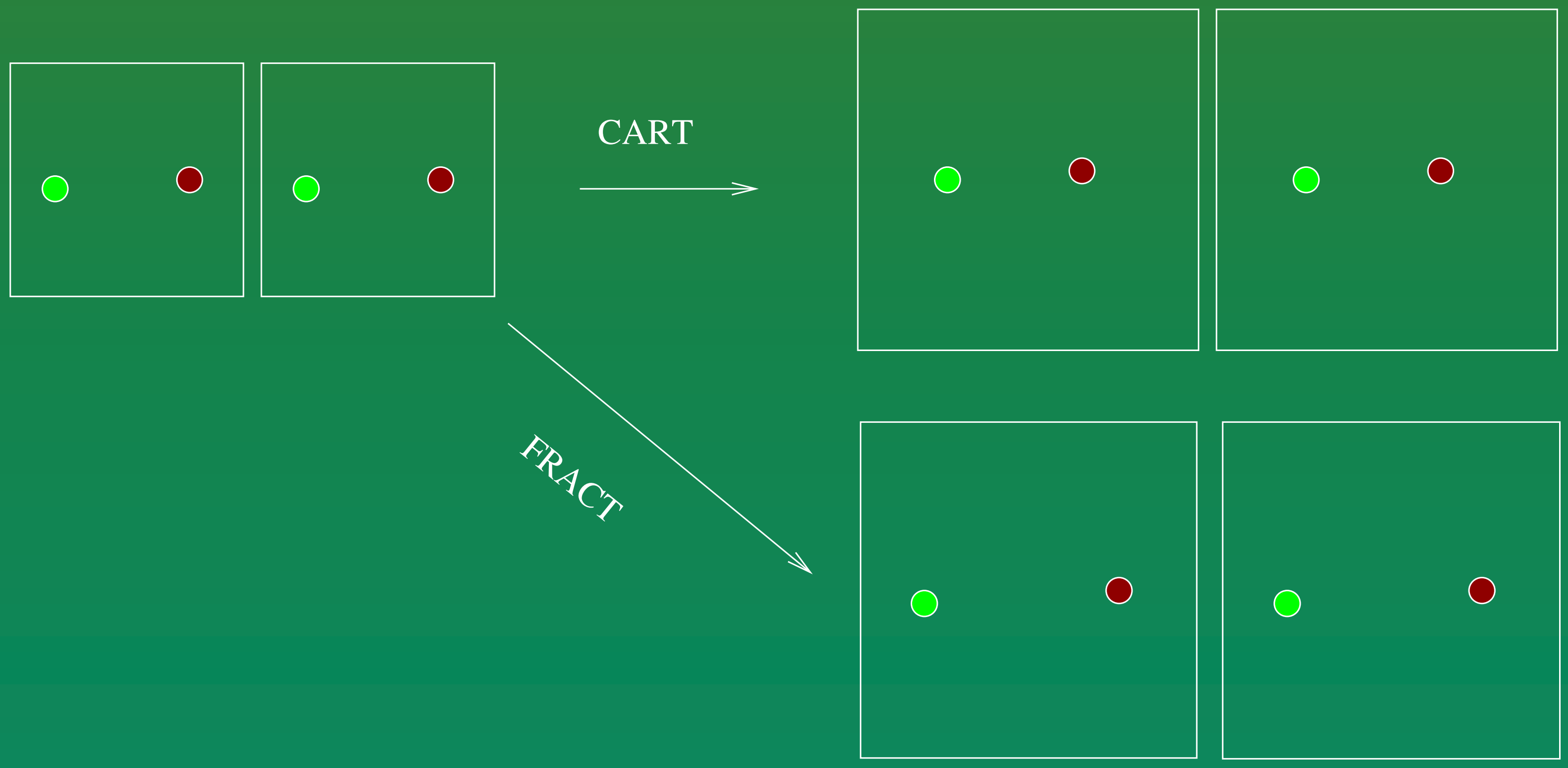
Atomic coordinates are defined in the basis set of the lattice vectors.

↑ Easy to keep fixed special symmetry positions.

↓ In general, non quadratic behavior

↑ Not too high degree of dependency between coordinates and lattice parameters

Dependency of cartesian and fractionary systems on the lattice parameters



Coordinate systems suitable for crystals

Redundant internal coordinates

- All valence coordinates (bond distances, angles and torsions) are considered to form a set of 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 the cartesian non-redundant space) using numerical approximations

Coordinate systems suitable for crystals

Redundant internal coordinates

↑ Quadratic behavior.

↑ Easy choice of the geometrical parameters

↑ Easy to constrain “chemical” degrees of freedom (bond length, angles or dihetrals)

(!!) control optimization for reactivity studies

↓ The size of the redundant space may be very large

↓ The back-transformation from the redundant to the non-redundant (real) space, is a very tricky task.

Comparison between redundant and fractionary+latt coordinate systems. Schlegel Model Hessian

Compound	Dim	Hamil	Num Steps		E_{red} - E_{fr-l}
			N_{red}	N_{fr-l}	(μHartree)
ZrO_2(cubic)	3D	PBE0	3	5	-0.2
TiO_2 (rutile)	3D	PW91	5	5	0.0
α-quartz	3D	B3LYP	7	8	-0.2
β-quartz	3D	LDA	7	7	0.1
Si-Faujasite	3D	PBE0	16	17	-1.7
Edingtonite (100)+NH_3	2D	B3LYP	8	10	-18.1
Corundum(001)12 layers	2D	B3LYP	21	18	-6240.9
$NaNO_2$	3D	B3PW91	18	18	-0.0
$CaCO_3$	3D	B3PW91	7	8	0.3
$ZnGeP_2$	3D	LDA	6	4	-361.5
Formaldehyde	3D	B3LYP	17	19	1.9
Oxalic Acid	3D	B3LYP	25	56	4.7
Ice	3D	PW91	12	19	1.4
Li-dopped PA	1D	B3LYP	12	14	0.3
H_2O polymer	1D	PBE0	18	19	-0.6

Optimization in CRYSTAL2006. Implementation.

Optimization in CRYSTAL2006. Implementation.

- Analitic gradient cell+atoms

Optimization in CRYSTAL2006. Implementation.

- Analitic gradient cell+atoms
  - Several Hamiltonians (HF and DFT)
  - Periodicity 0D, 1D, 2D and 3D at the same level of theory.
  - All-electron or pseudopotentials.

Optimization in CRYSTAL2006. Implementation.

- Analitic gradient cell+atoms
  - ⋆ Several Hamiltonians (HF and DFT)
  - ⋆ Periodicity 0D, 1D, 2D and 3D at the same level of theory.
  - ⋆ All-electron or pseudopotentials.
- Coordinate systems

Optimization in CRYSTAL2006. Implementation.

- Analitic gradient cell+atoms
  - ⋆ Several Hamiltonians (HF and DFT)
  - ⋆ Periodicity 0D, 1D, 2D and 3D at the same level of theory.
  - ⋆ All-electron or pseudopotentials.
- Coordinate systems
  - ⋆ Choices
    - ♣ Cartesian/fixed cell
    - ♣ Fractionary+cell
    - ♣ redundant internal valence coordinates

Optimization in CRYSTAL2006. Implementation.

- Analitic gradient cell+atoms
  - Several Hamiltonians (HF and DFT)
  - Periodicity 0D, 1D, 2D and 3D at the same level of theory.
  - All-electron or pseudopotentials.
- Coordinate systems
  - Choices
    - Cartesian/fixed cell
    - Fractionary+cell
    - redundant internal valence coordinates
  - Constraints
    - some atoms fixed
    - some cell parameters fixed
    - fix cell shape (volume optimization or partial fixing) + atoms
    - fix symmetrized fractionary coordinates
    - fix internal valence coordinates
    - symmetry constraints

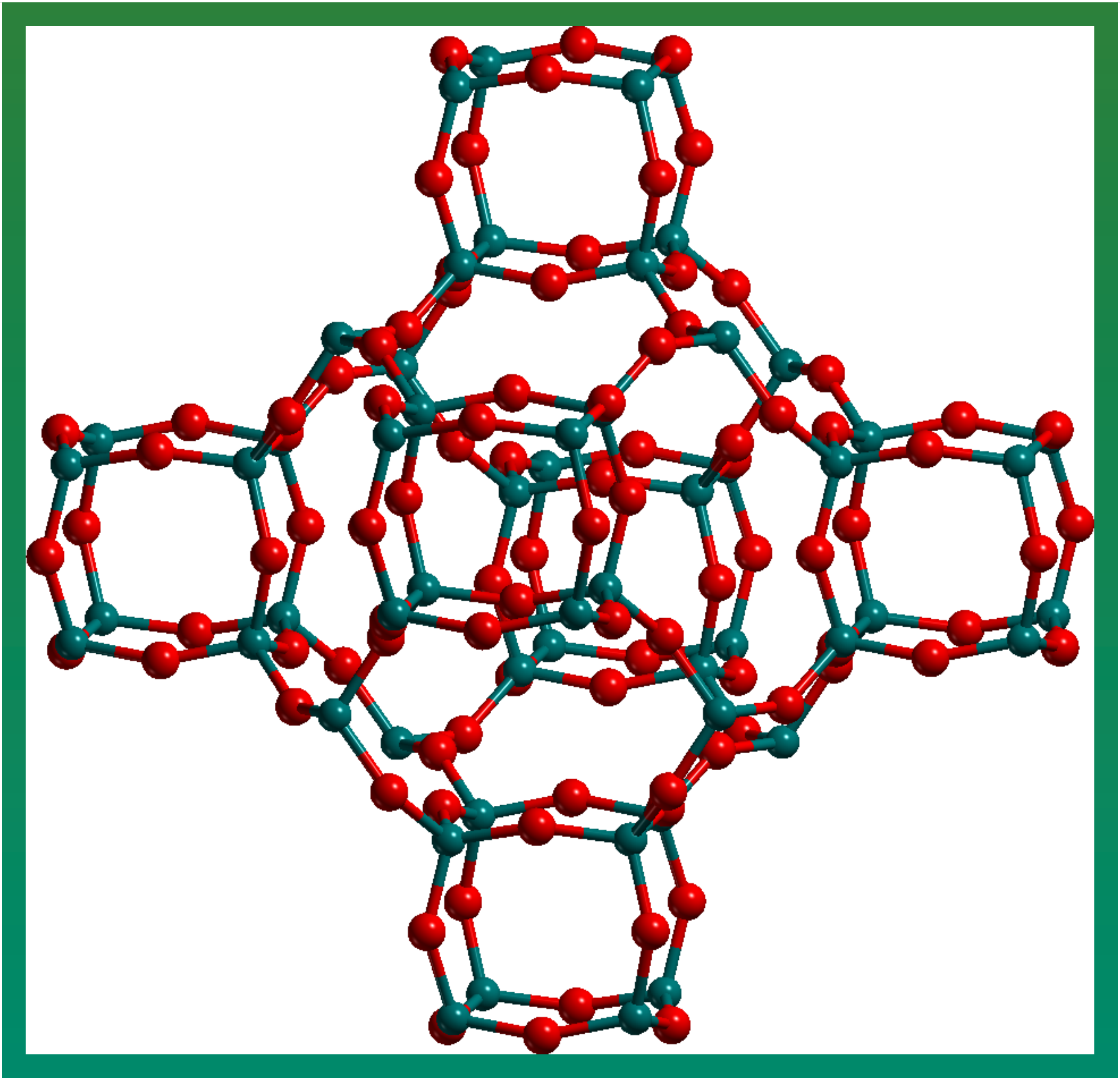
Optimization in CRYSTAL2006. Implementation.

- Analitic gradient cell+atoms
  - Several Hamiltonians (HF and DFT)
  - Periodicity 0D, 1D, 2D and 3D at the same level of theory.
  - All-electron or pseudopotentials.
- Coordinate systems
  - Choices
    - Cartesian/fixed cell
    - Fractionary+cell
    - redundant internal valence coordinates
  - Constraints
    - some atoms fixed
    - some cell parameters fixed
    - fix cell shape (volume optimization or partial fixing) + atoms
    - fix symmetrized fractionary coordinates
    - fix internal valence coordinates
    - symmetry constraints
- Different Hessian updating schemes: Berny, BFGS, Powell,. . .

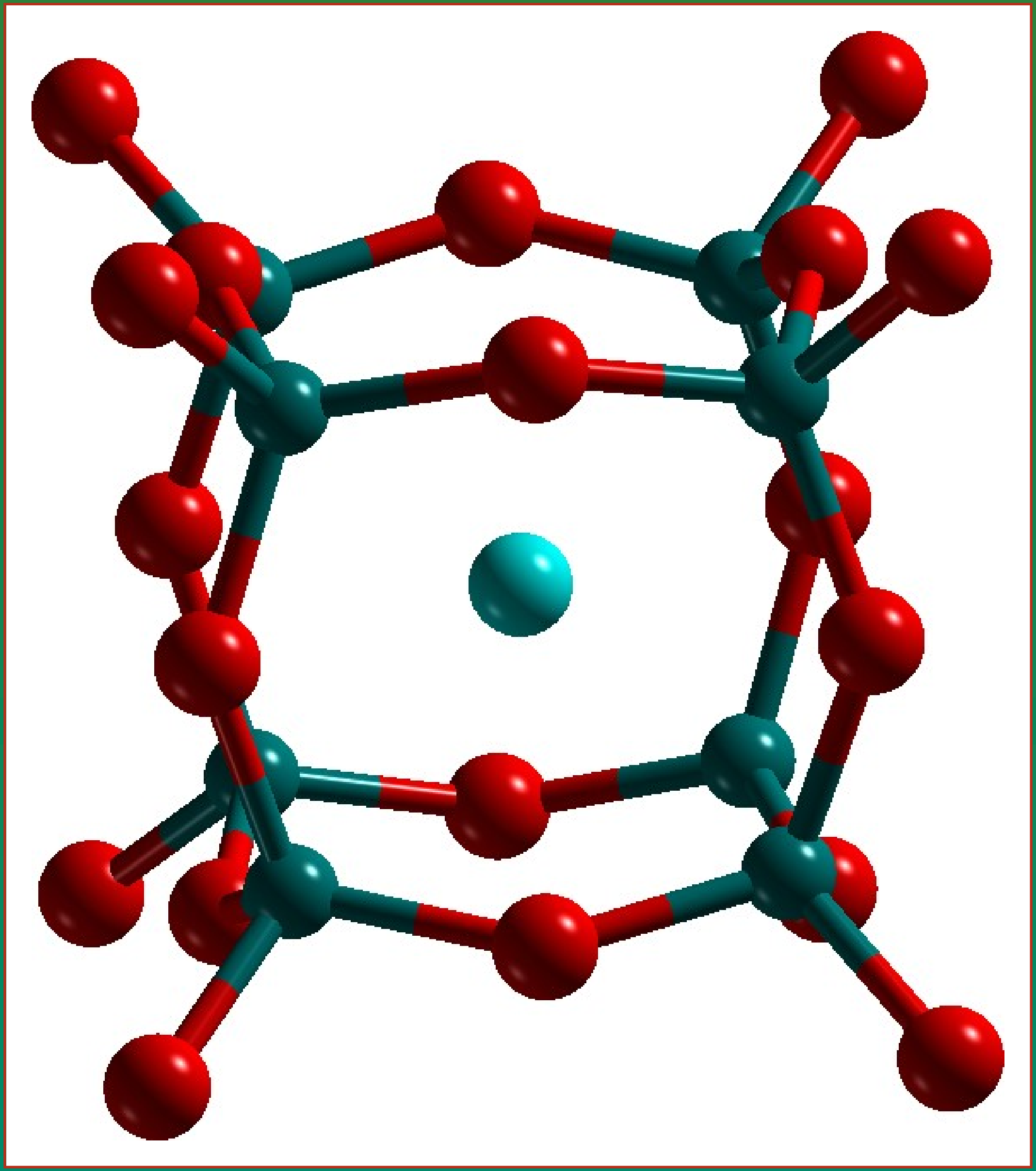
Optimization in CRYSTAL2006. Implementation.

- Analitic gradient cell+atoms
  - Several Hamiltonians (HF and DFT)
  - Periodicity 0D, 1D, 2D and 3D at the same level of theory.
  - All-electron or pseudopotentials.
- Coordinate systems
  - Choices
    - Cartesian/fixed cell
    - Fractionary+cell
    - redundant internal valence coordinates
  - Constraints
    - some atoms fixed
    - some cell parameters fixed
    - fix cell shape (volume optimization or partial fixing) + atoms
    - fix symmetrized fractionary coordinates
    - fix internal valence coordinates
    - symmetry constraints
- Different Hessian updating schemes: Berny, BFGS, Powell,. . .
- Starting Model Hessians: Lindh, Schlegel.

Structure of Si-Octadecasyl (AST)



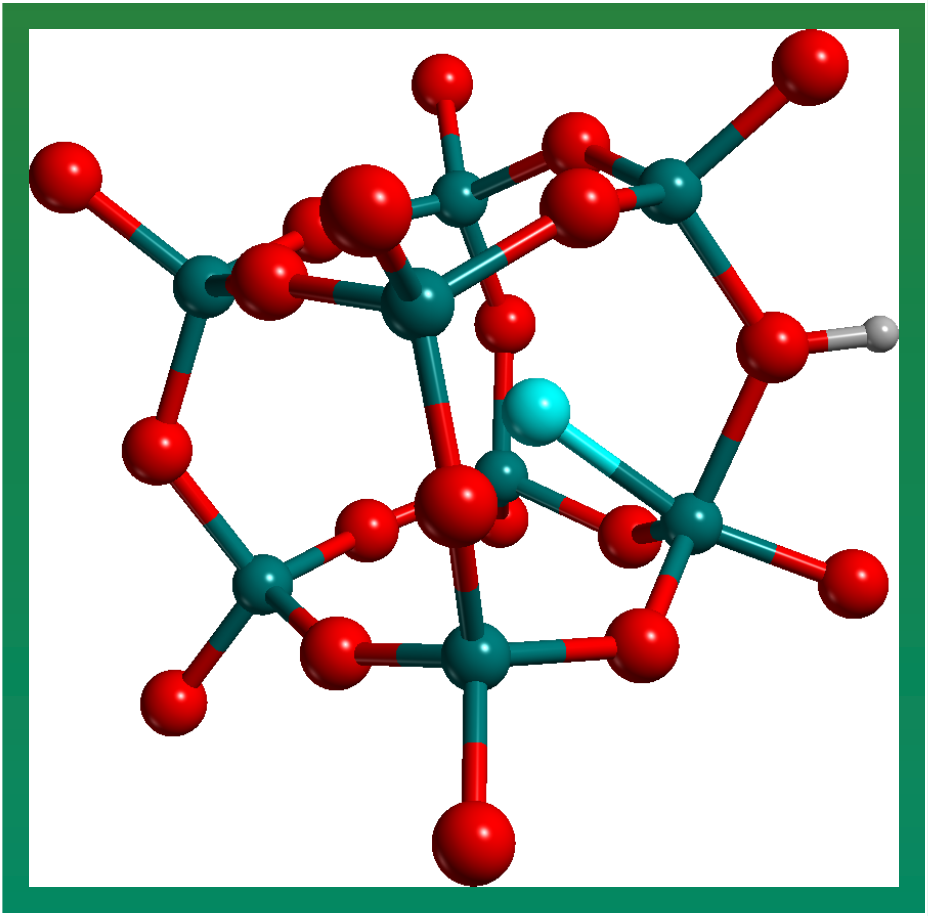
F^- occluded in a D4R unit in as-synthesized zeolites



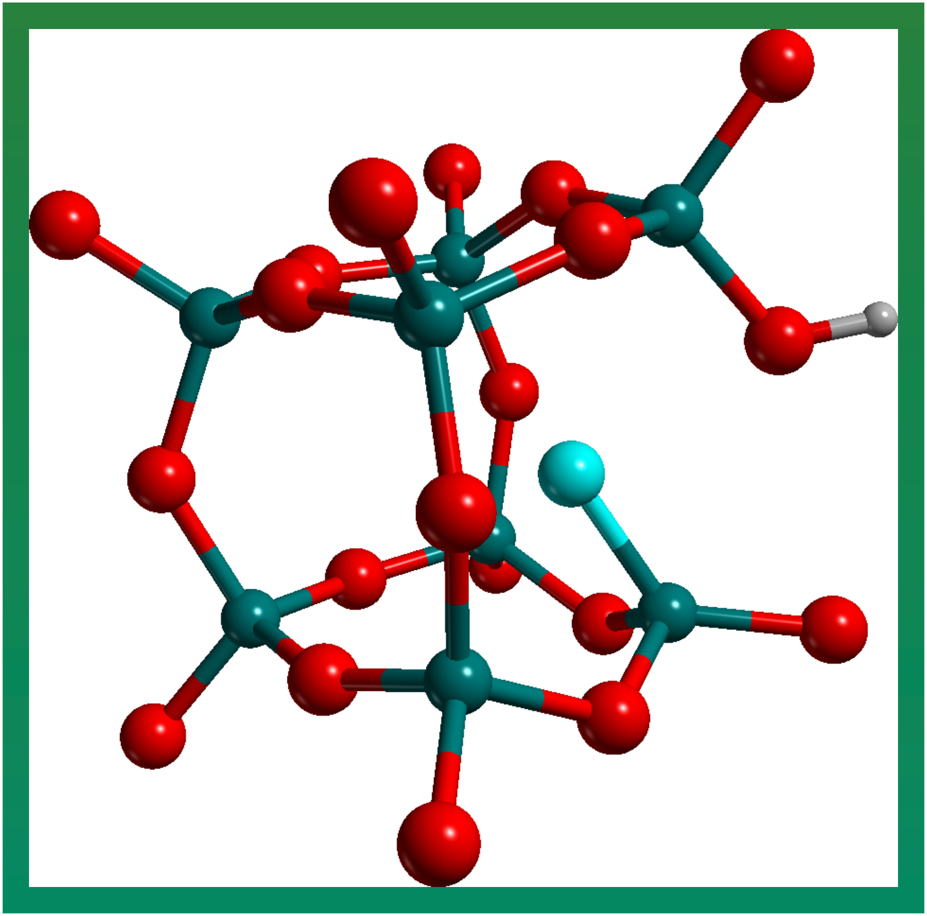
Seeking for a mechanism of F$^-$ elimination

- Octadecasyl has been chosen because of a previous experimental work (Villaescusa *et al*, 1998)
- The unit cell consists of 30 atoms
- Cell parameters has been kept fixed in the experimental values
- Atomic positions were fully optimized; all stationary points has been characterized as minima or transition states by means of the ab initio vibrational analysis
- Methodological level: B3LYP/DZVP//TZVP.
- All energies corrected by ZPE (at DZVP level) and BSSE (at TZVP)
- The starting point of the path has been chosen to be the protonated F-D4R unit, as it is assumed these species are present at the final steps of the template decomposition.

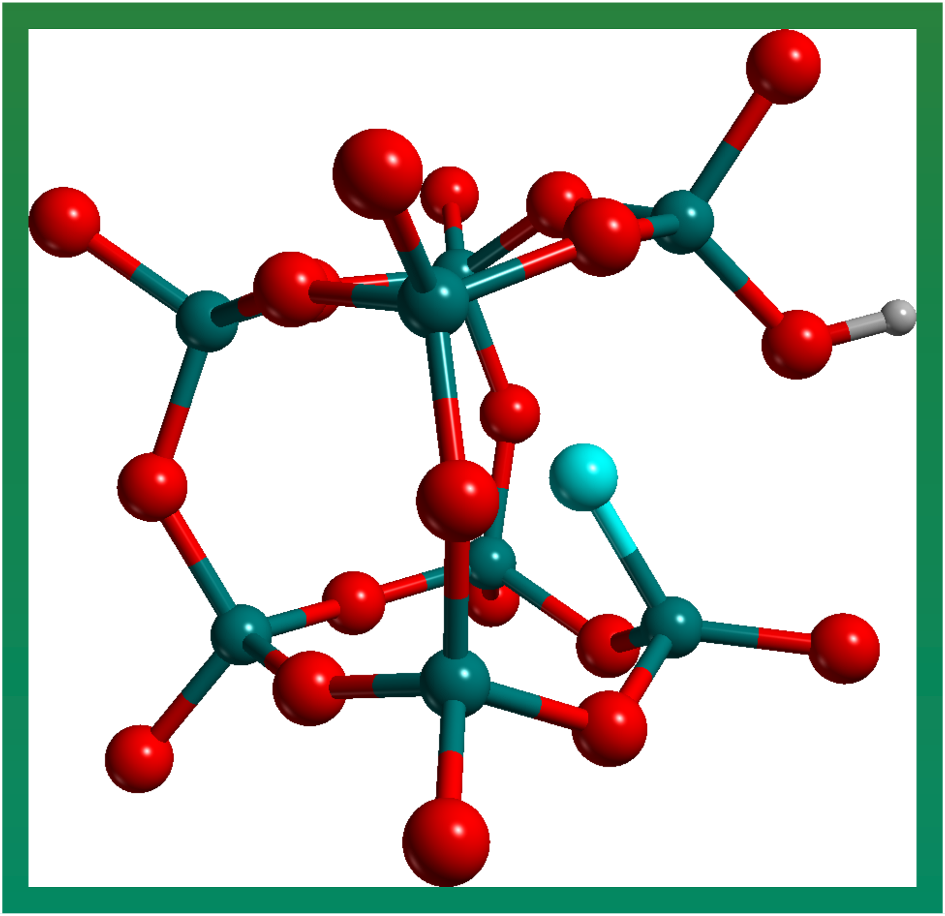
Protonated F-D4R: reactant



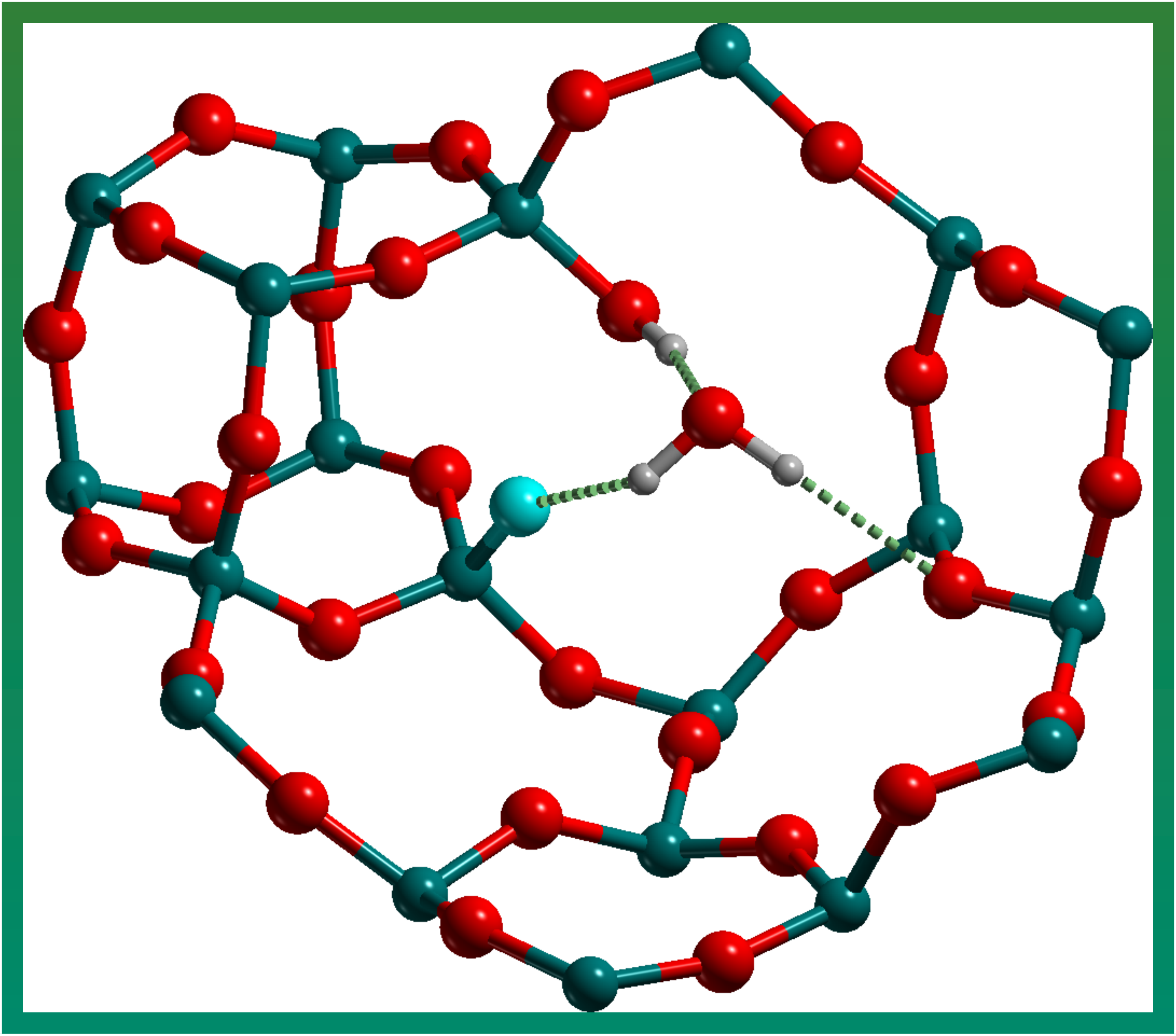
Protonated F-D4R: transition state



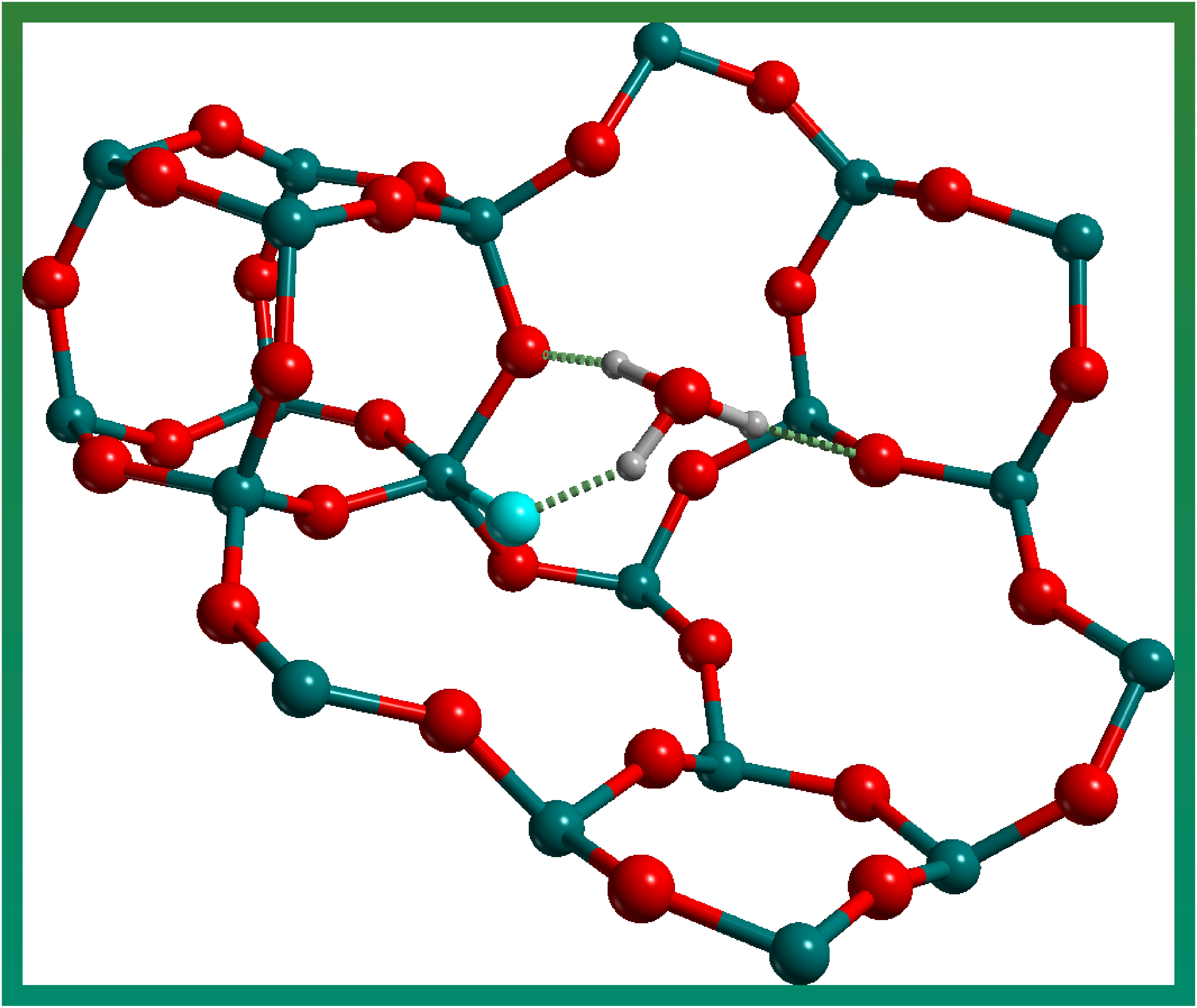
Protonated F-D4R: product



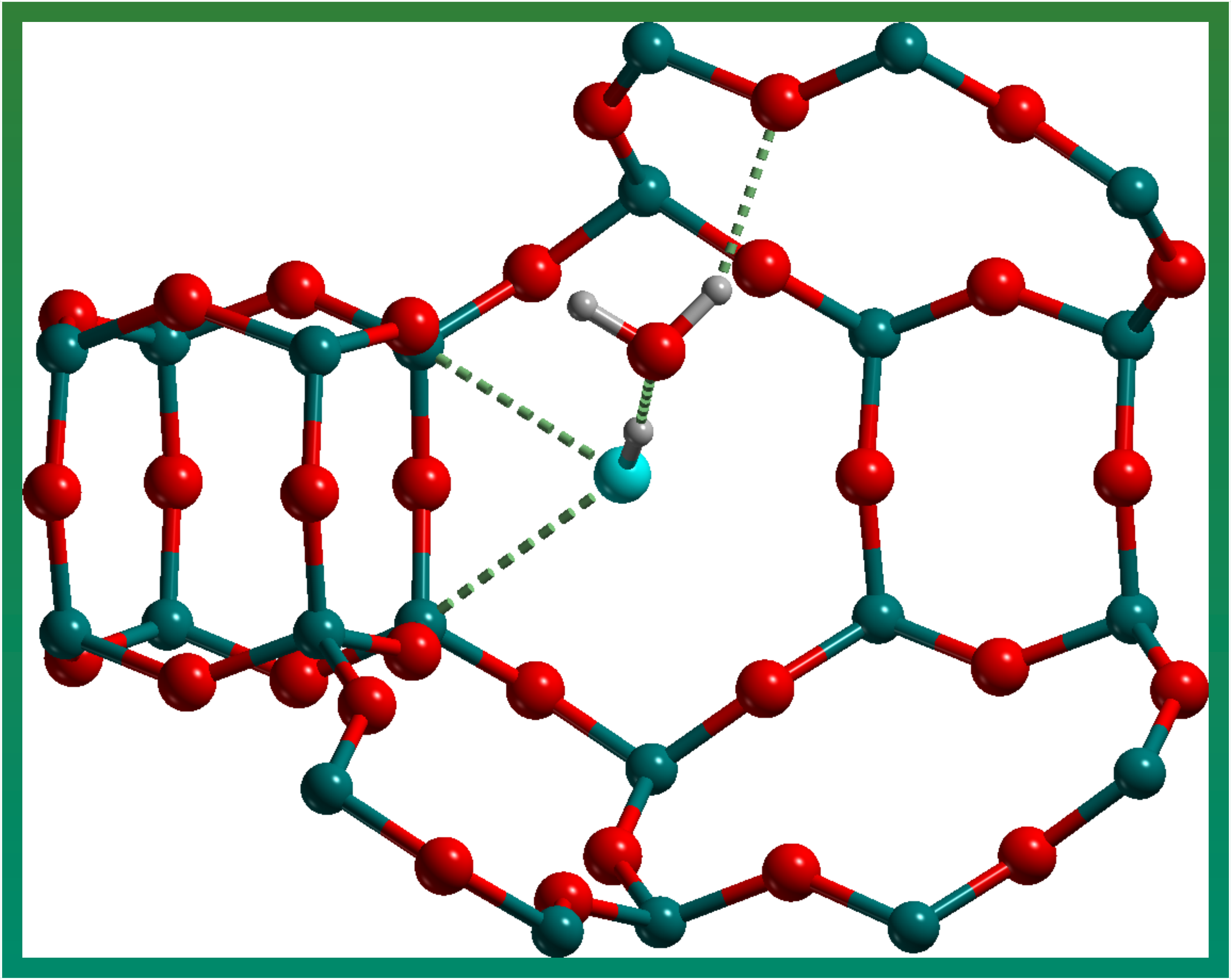
The role of a water molecule



HF elimination and Si-O-Si bridge condensation: transition state



HF elimination and Si-O-Si bridge condensation: product



Periodic B3LYP reaction profile for the F⁻ elimination (energies in kJ/mol)