Friedrich-Alexander-Universität
Naturwissenschaftliche Fakultät

43384 – Digital Alchemy

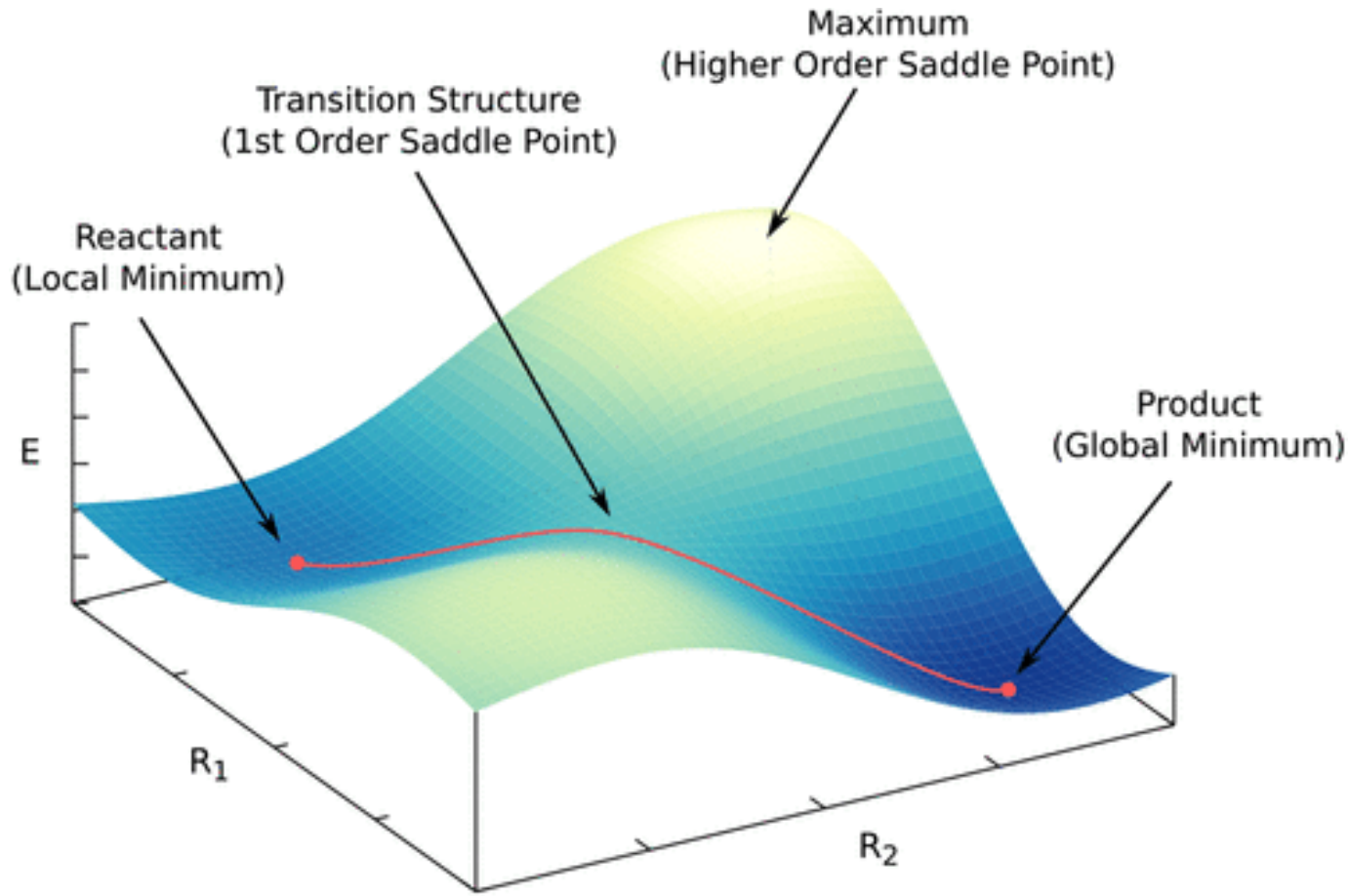
Unit 05 – Molecular Structure Optimization

Prof. Dr. Carolin Müller

November 11, 2025

Optimization of Molecular Structures

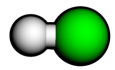
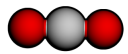
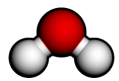
Concept: Potential Energy Surface (PES)



Potential Energy Surfaces (PESs)

Internal degrees of freedom

- A molecule with N atoms has $3N$ degrees of freedom:

Type of molecule	N	$3N$	modes
monoatomic, e.g., Ne 	1	3	
diatomic, e.g., HCl 	2	6	
triatomic linear, e.g. CO_2 	3	9	
triatomic non-linar, e.g. H_2O 	3	9	

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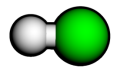
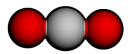
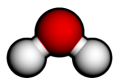
diatomic, e.g., HCl 	2	6	**3** translational
triatomic linear, e.g. CO_2 	3	9	**3** translational
triatomic non-linar, e.g. H_2O 	3	9	**3** translational

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- A molecule with N atoms has $3N$ degrees of freedom:
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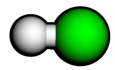
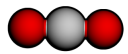
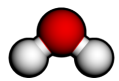
diatomic, e.g., HCl 	2	6	**3** translational
triatomic linear, e.g. CO_2 	3	9	**3** translational
triatomic non-linar, e.g. H_2O 	3	9	**3** translational

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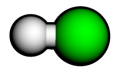
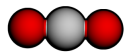
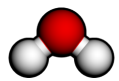
diatomic, e.g., HCl 	2	6	**3** translational **2** rotational
triatomic linear, e.g. CO_2 	3	9	**3** translational **2** rotational
triatomic non-linar, e.g. H_2O 	3	9	**3** translational **3** vibrational

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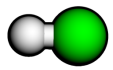
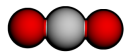
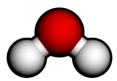
diatomic, e.g., HCl 	2	6	**3** translational **2** rotational
triatomic linear, e.g. CO_2 	3	9	**3** translational **2** rotational
triatomic non-linar, e.g. H_2O 	3	9	**3** translational **3** vibrational

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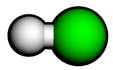
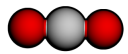
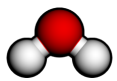
diatomic, e.g., HCl 	2	6	**3** translational **2** rotational **1** vibrational
triatomic linear, e.g. CO_2 	3	9	**3** translational **2** rotational **4** vibrational
triatomic non-linar, e.g. H_2O 	3	9	**3** translational **3** rotational **3** vibrational

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- Once a linear molecule bends, it is no longer linear, so even a linear molecule can have its internal coordinates described by $3N-6$ coordinates.

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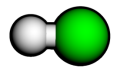
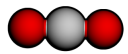
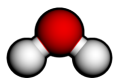
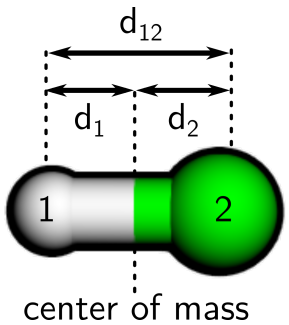
diatomic, e.g., HCl 	2	6	**3** translational **2** rotational **1** vibrational
triatomic linear, e.g. CO_2 	3	9	**3** translational **2** rotational **4** vibrational
triatomic non-linar, e.g. H_2O 	3	9	**3** translational **3** rotational **3** vibrational

PESs of diatomic molecules: 1D case

Example: HCl

Internal coordinate in HCl: d(H,Cl)



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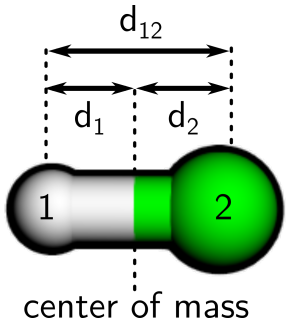

Scan of internal coordinate with VeloxChem:

```
1  import veloxchem as vlx
2
3  # Molecule specification
4  hcl_xyz ='2
5  XYZ of HCl
6  H    0.00 0.00 0.00
7  Cl   0.00 0.00 1.10'
8  hcl_mol = vlx.Molecule.
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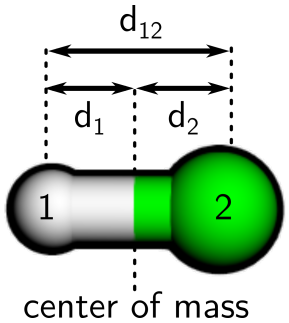

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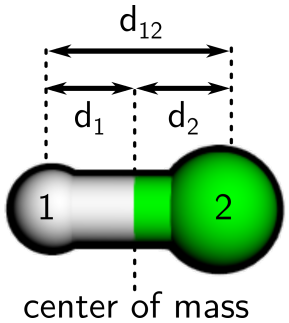

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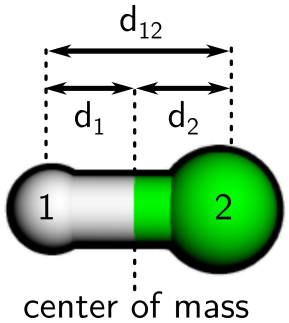

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17 opt_res_scan = opt_drv.compute(
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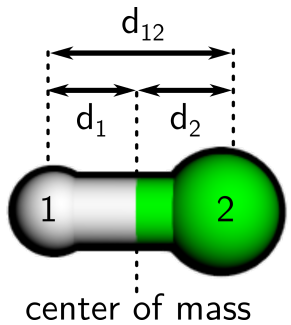

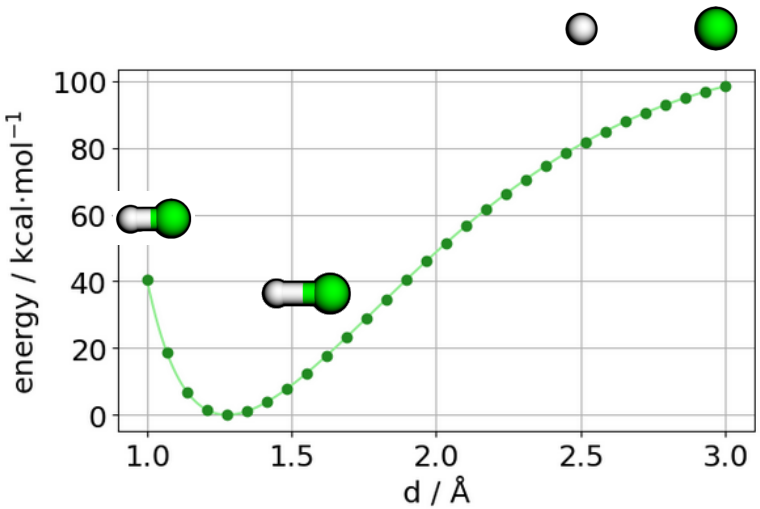

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PESs triatomic non-linear molecules

Example: Water

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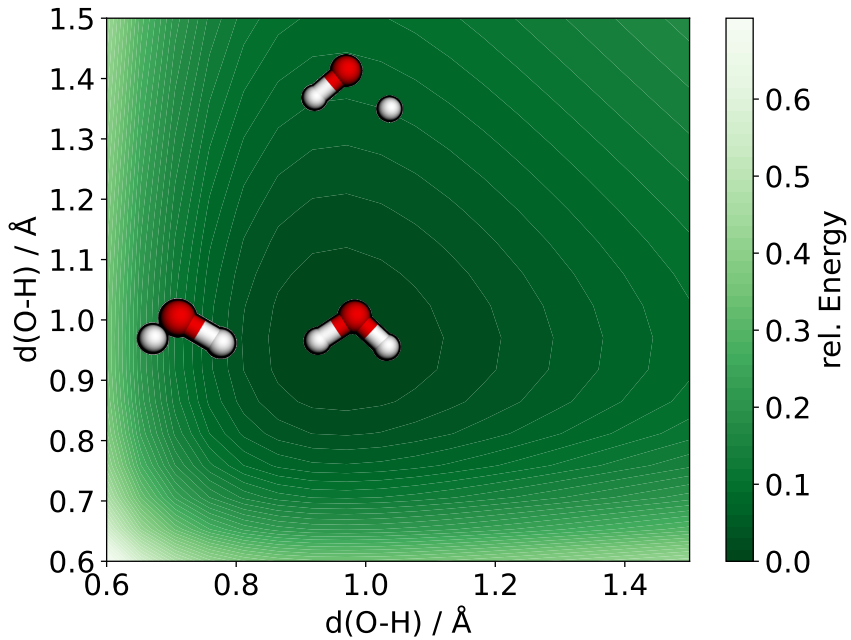
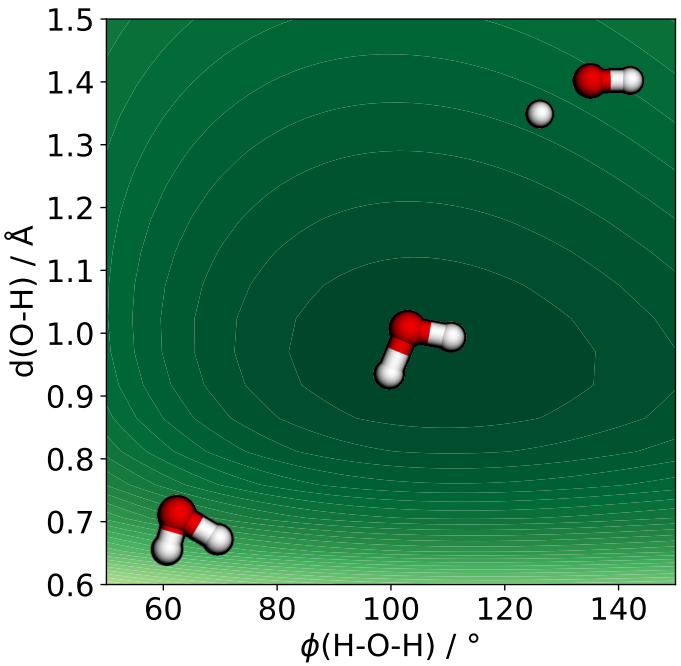
Symmetric stretching mode:



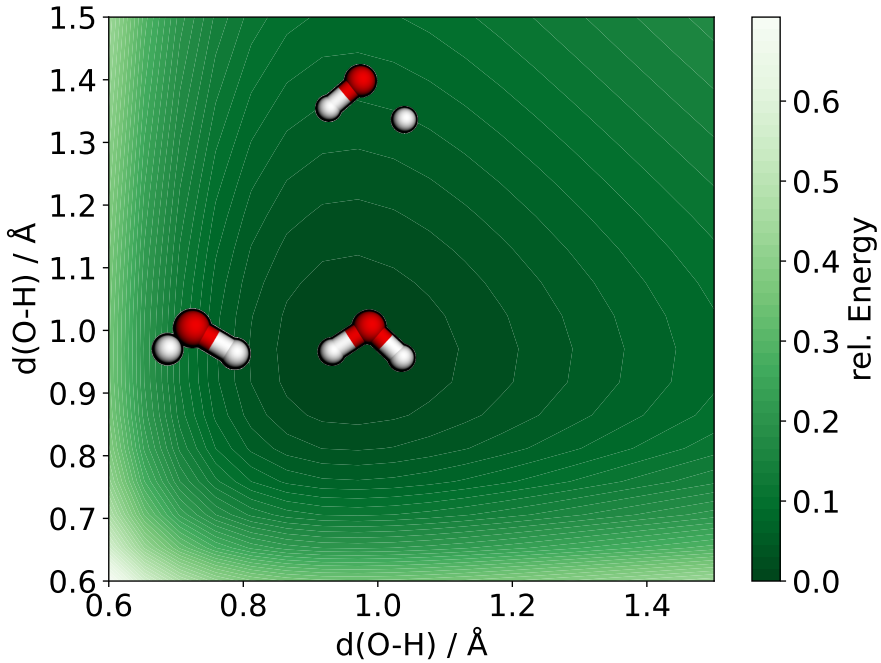
PESs triatomic non-linear molecules

Example: Water

Asymmetric stretching and bending modes:



Symmetric stretching mode:



PESs 4-atomic non-linear molecules

Example: Hydrogen peroxide (H_2O_2)

- 12 degrees of freedom:

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  - 3 rotational

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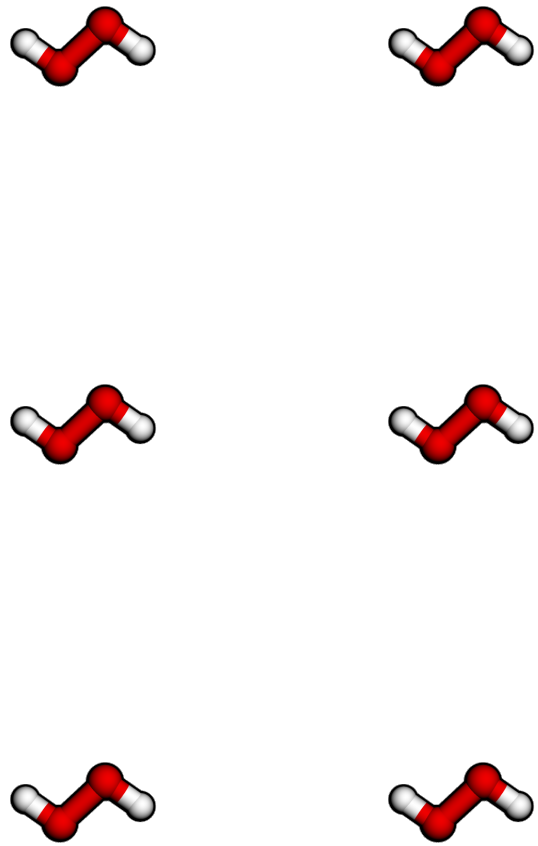

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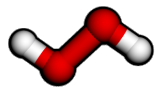
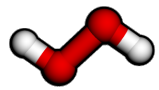
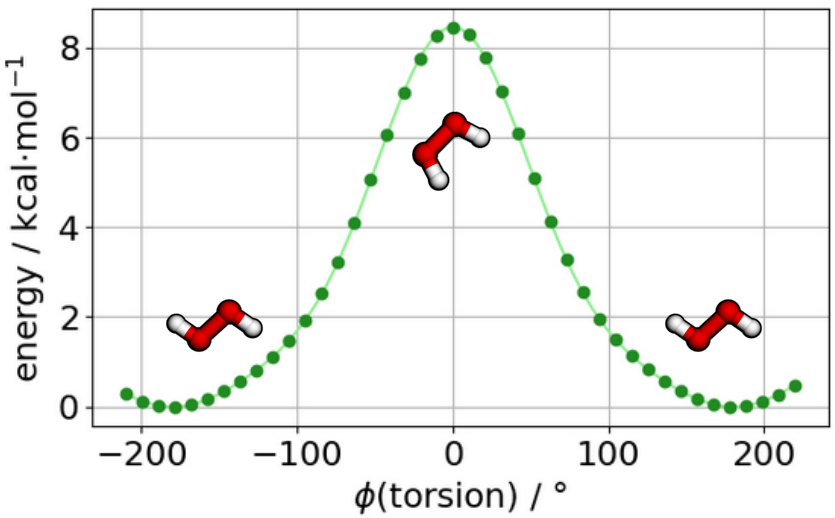
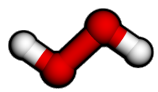
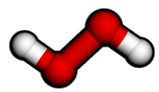
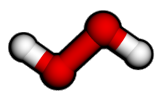
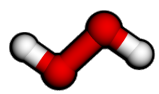



Torsion scan, δ(H-O-O-H):



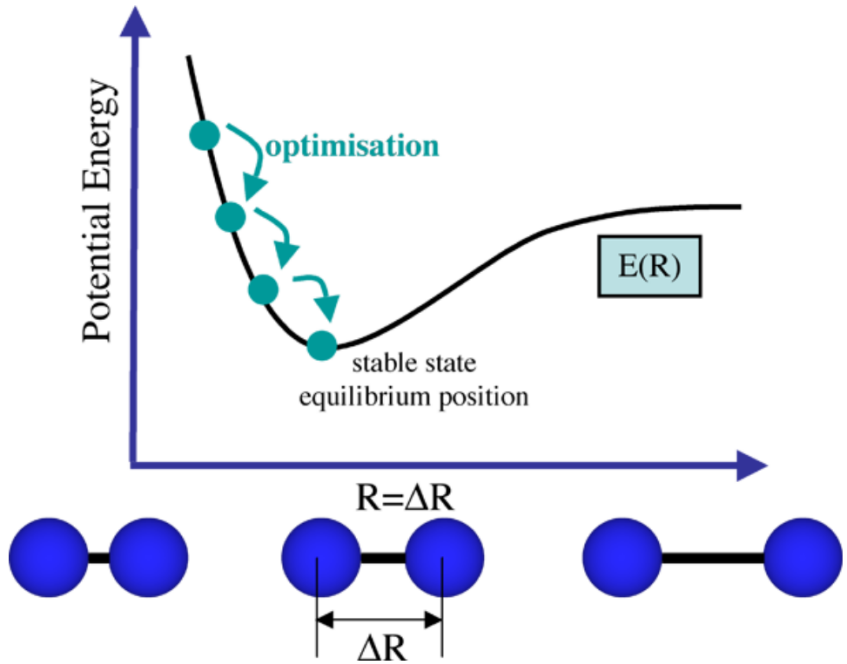





Optimization of Molecular Structures

Ingredients of structure optimization

Structure Optimization

Structure optimization refers to the process of finding the **atomic coordinates** that **minimize** the **energy** of a molecular system, typically corresponding to a local energy minimum on the potential energy surface (PES). A local minimum represents an equilibrium molecular structure, where the first-order energy derivative vanishes, and the Hessian matrix has only positive eigenvalues.



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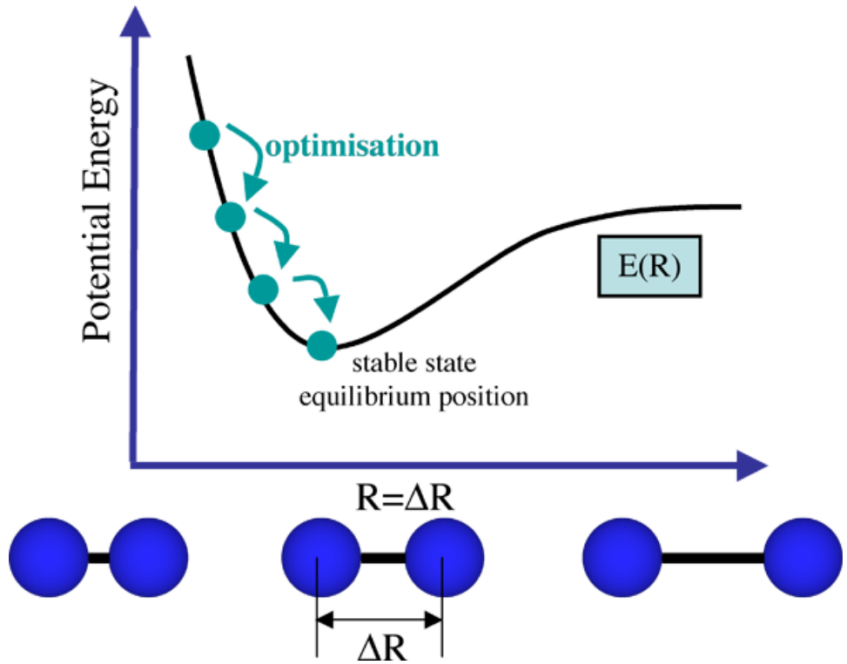
1. initial molecular coordinates



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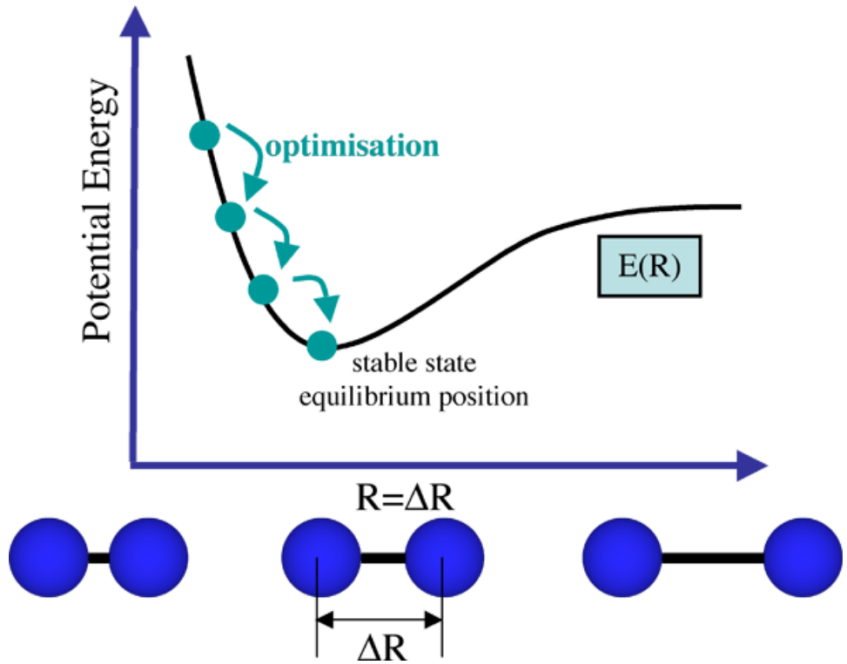
Ingredients of structure optimization:

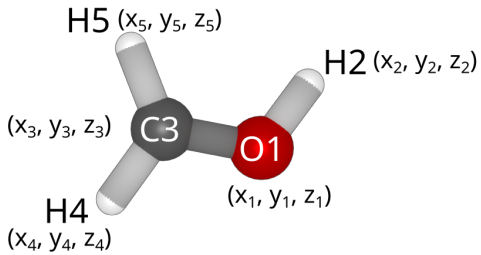
1. initial molecular coordinates
2. choice of coordinate system



Optimization of Molecular Structures

Choice of coordinates

Cartesian coordinates



3N = 15

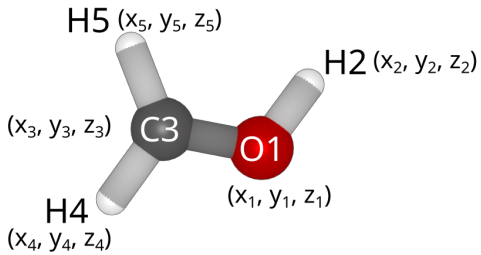
- Each atomic position is specified by its x, y, and z coordinates.

O	x_1	x_1	x_1
H	x_2	x_2	x_2
C	x_3	x_3	x_3
H	x_4	x_4	x_4
H	x_5	x_5	x_5

Optimization of Molecular Structures

Choice of coordinates

Cartesian coordinates



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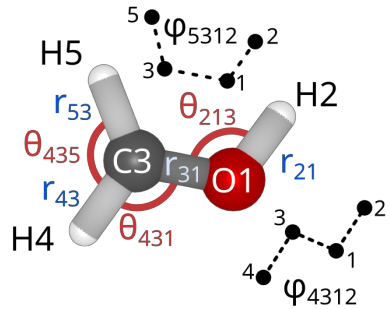
Internal coordinates



3N-6 = 9

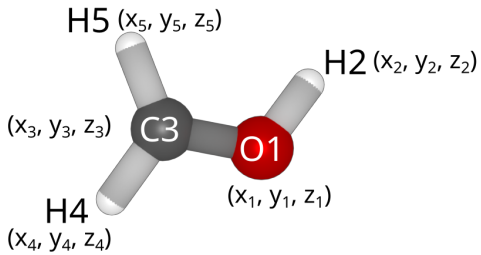
- bond lengths, valence angles, and dihedrals instead of atomic positions (e.g. Z-matrix)

O						
H	1	r_{21}				
C	1	r_{31}	2	Θ_{213}		
H	3	r_{43}	1	Θ_{431}	2	φ_{4312}
H	3	r_{53}	1	Θ_{531}	2	φ_{5312}

Optimization of Molecular Structures

Choice of coordinates

Cartesian coordinates



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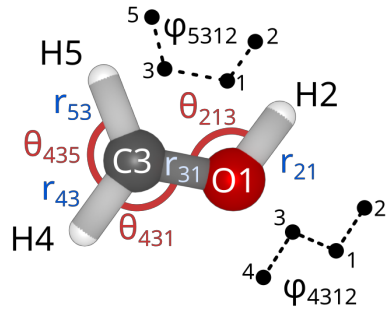
- Each atomic position is specified by its x, y, and z coordinates.
- Advantage: Simplifies calculations of total energy and energy gradients.
- Disadvantage: Not ideal for geometry optimization due to strong coupling between coordinates.

Internal coordinates



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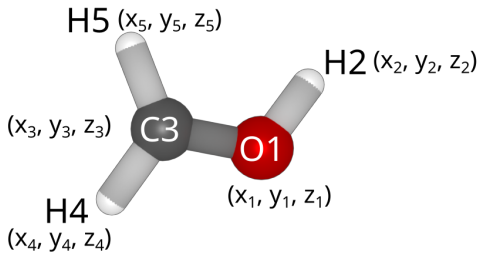

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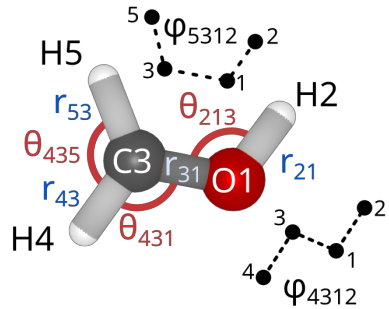

3N-6 = 9

- bond lengths, valence angles, and dihedrals instead of atomic positions (e.g. Z-matrix)
- Advantage: More suitable for geometry optimization.
- Disadvantage: choice of internal coordinates is not unique, back-conversion to Cartesian coordinates for energy and gradient computations

Optimization of Molecular Structures

Ingredients of structure optimization

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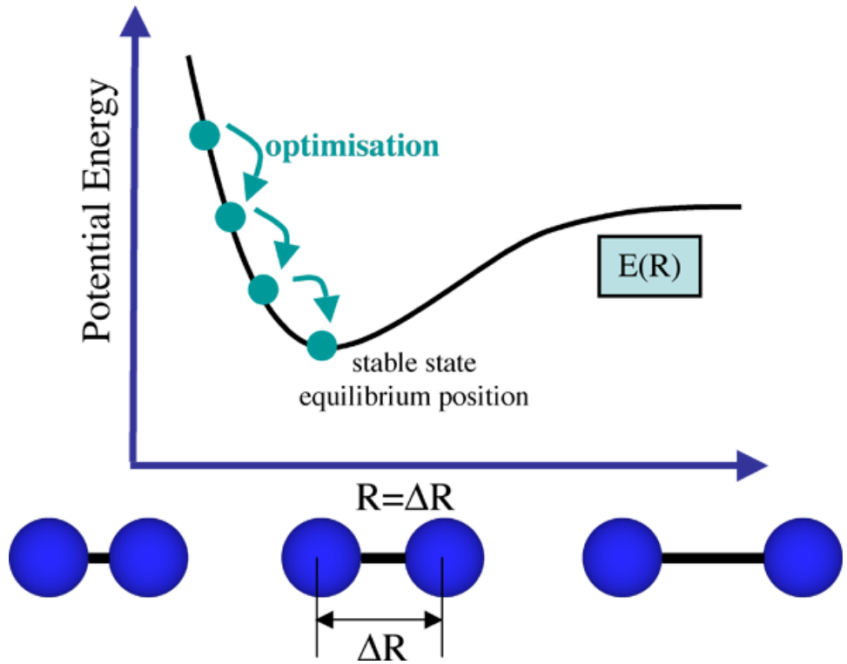

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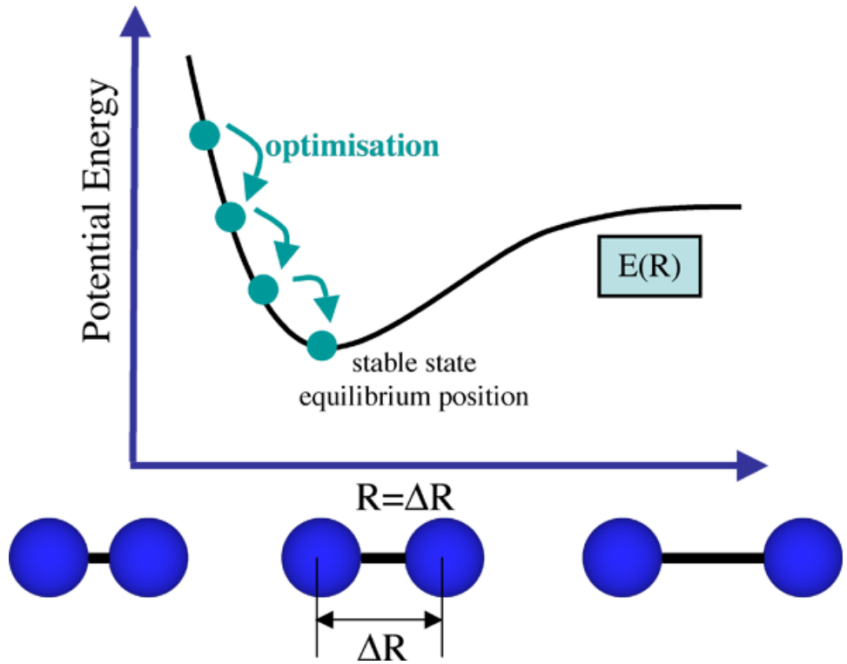
3. energy at a specific geometry $E(R)$



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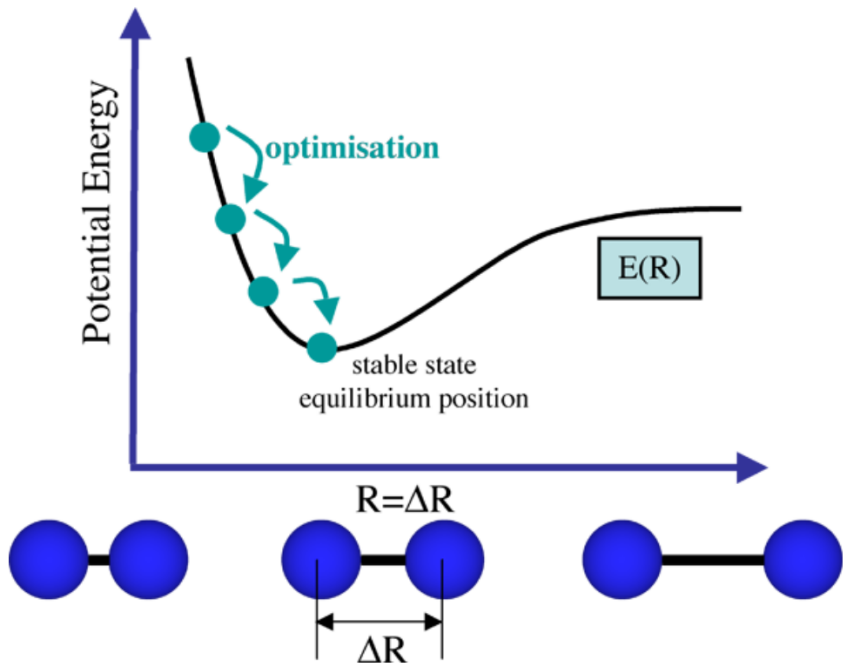
3. energy at a specific geometry $E(R)$
4. gradient $g(R) = \nabla E(R)$



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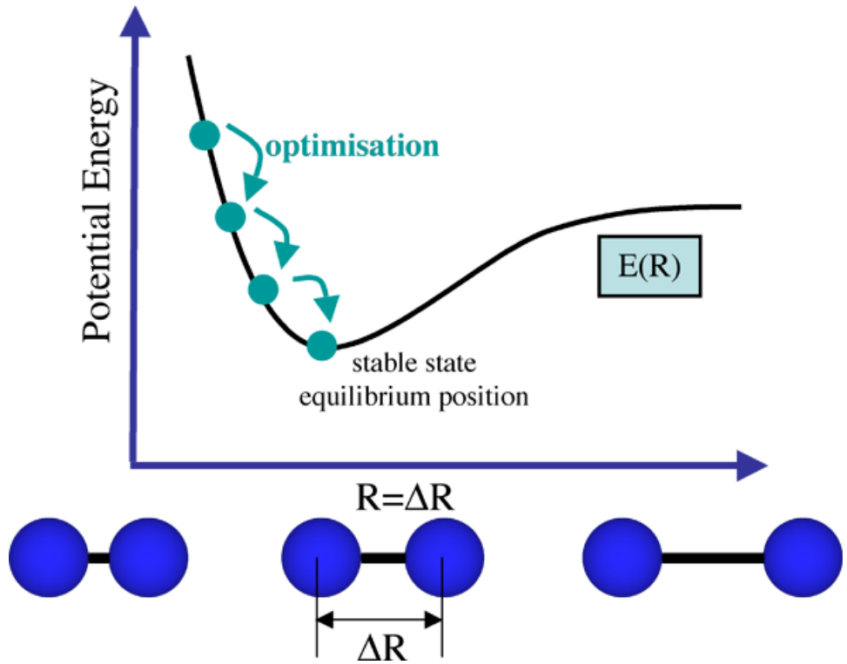

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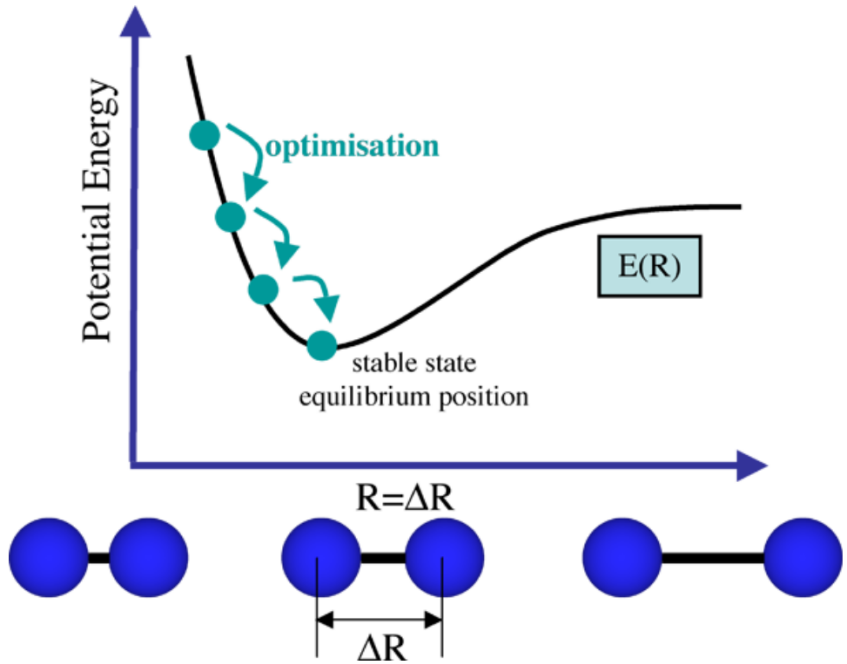
Ingredients of structure optimization:

1. initial molecular coordinates
2. choice of coordinate system
3. energy at a specific geometry $E(R)$
4. gradient $g(R) = \nabla E(R)$
5. Hessian, and
6. procedure to update the coordinates and Hessian and move on the potential energy surface towards lower energy



Optimization of Molecular Structures

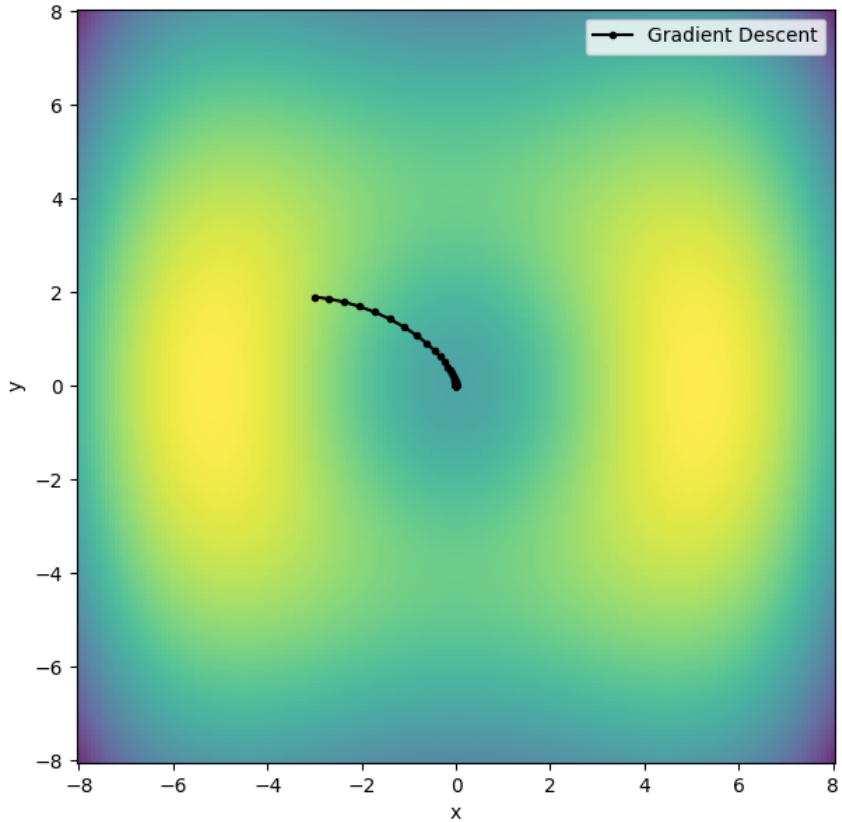
Optimization algorithm

Gradient Descent Algorithm

The simplest optimization procedure is to repeatedly take a step in the direction opposite to the local gradient:

$$\mathbf{R}_{i+1} = \mathbf{R}_i - k_i \cdot g(\mathbf{R}) \quad ,$$

where $\mathbf{R}_{i+1}$ is the new coordinate and $\mathbf{R}_i$ are the coordinates at the previous step i, k_i is the step size and $g(\mathbf{R})$ is the gradient. The step size can either be kept constant, or adjusted at each iteration, e.g. by the line search procedure.



Optimization of Molecular Structures

Optimization algorithm

Conjugate Gradient Algorithm

An improved method over the gradient-descent approach is to use the "gradient history" (steps i and $i-1$) to determine the coordinates at step $i+1$:

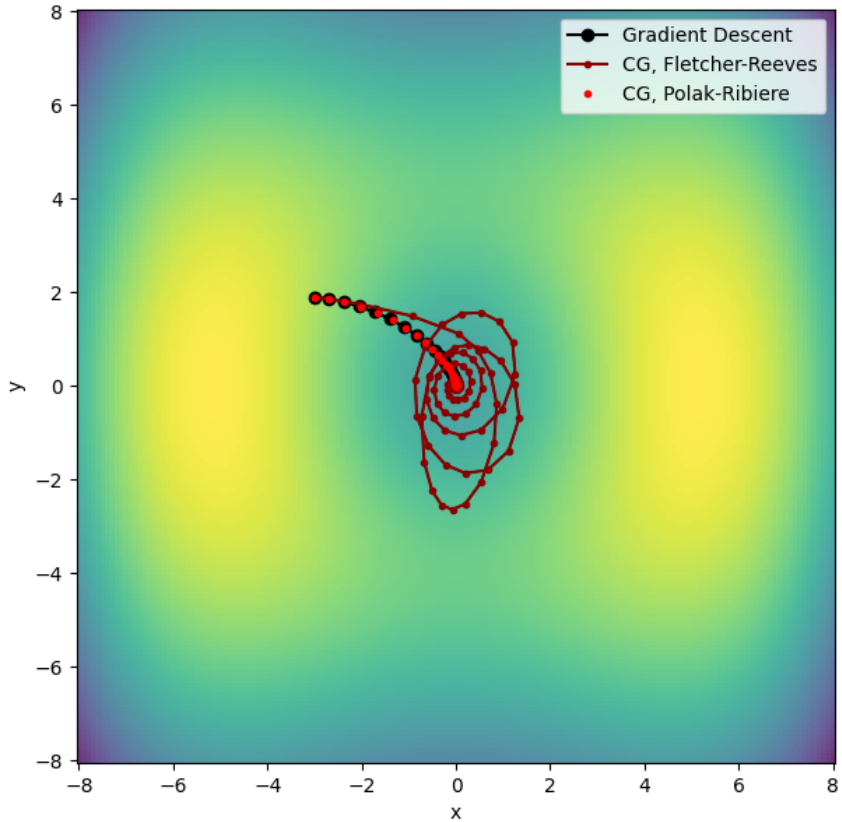
$$\mathbf{R}_{i+1} = \mathbf{R}_i - k_i \cdot \mathbf{h}_i \quad ,$$

with

$$\mathbf{h}_i = g(\mathbf{R}_i) + \gamma_i \cdot \mathbf{h}_{i-1}$$

The function γ_i contains gradient information from steps i and $i-1$, e.g. Fletcher-Reeves conjugate gradient method:

$$\gamma_i = \frac{|g(\mathbf{R}_i)|^2}{|g(\mathbf{R}_{i-1})|^2}$$



Optimization of Molecular Structures

Optimization algorithm

Newton-Raphson Algorithm

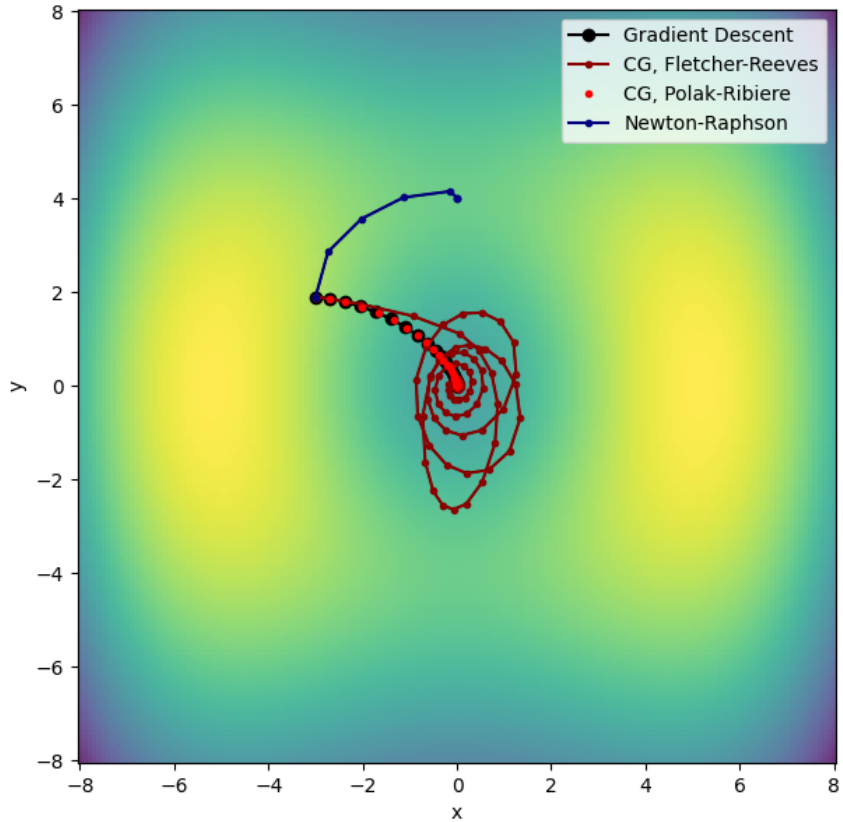
In this minimization method both, the first and second order energy derivatives (*i.e.* gradient and Hessian $\mathbf{H}$) are used in determining the next step in conformation space.

This is based on a quadratic approximation for the local shape of the PES

$$E(\mathbf{R} + \Delta\mathbf{R}) \approx E(\mathbf{R}) + g(\mathbf{R})\nabla\mathbf{R} + \frac{1}{2}\nabla\mathbf{R}^T\mathbf{H}\nabla\mathbf{R}$$

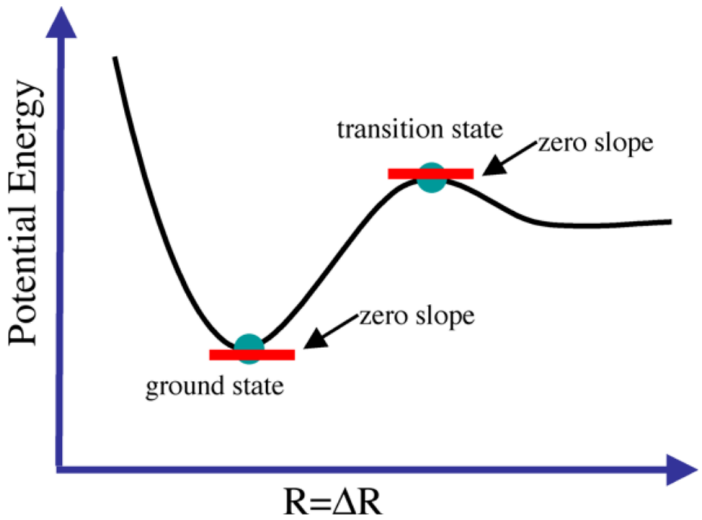
Here, $\nabla\mathbf{R}$ is the Newton step used for updating the coordinates:

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

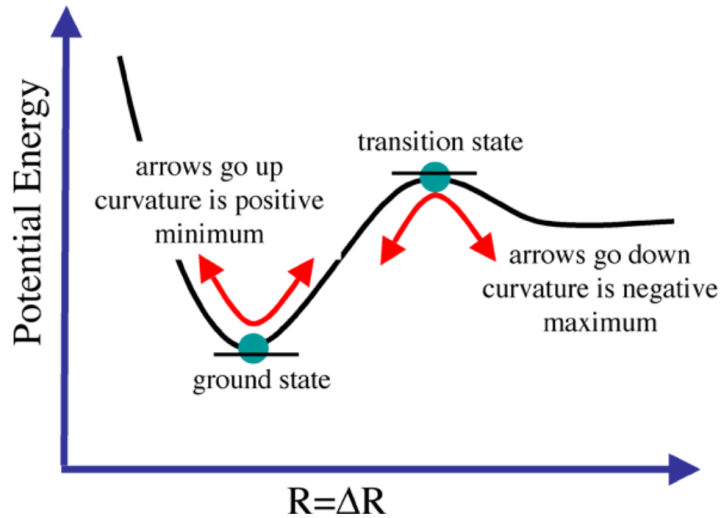


Optimization of Molecular Structures

Summary



Minima, transition states: geometries with zero-gradient



Minima: only positive values in Hessian
transition states: 1 negative value in Hessian

Hands-On Session

Working with VeloxChem

Ethanol

- optimize geometry (global minimum)
- scan internal coordinates

Vinyl Alcohol

- optimize geometries of isomers (two local minimum geometries)
- scan coordinates between the two minima

Ethylene Glycol

- optimize geometries of conformers (multiple local minima)
- scan coordinates between local minima
- interpolate coordinate between local minima