Geometry Optimization

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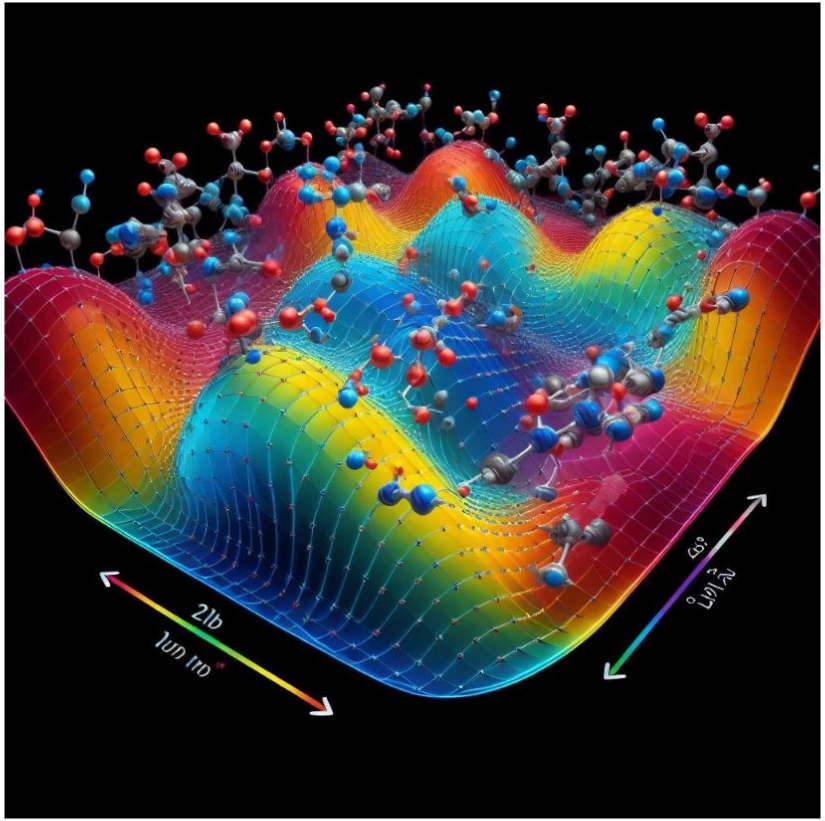
Zero kelvin geometry

-Minimum on the potential energy surface

For a system treated using the Born-Oppenheimer approximation, the geometry of a system at zero absolute temperature correspond to a minima on potential energy surface.

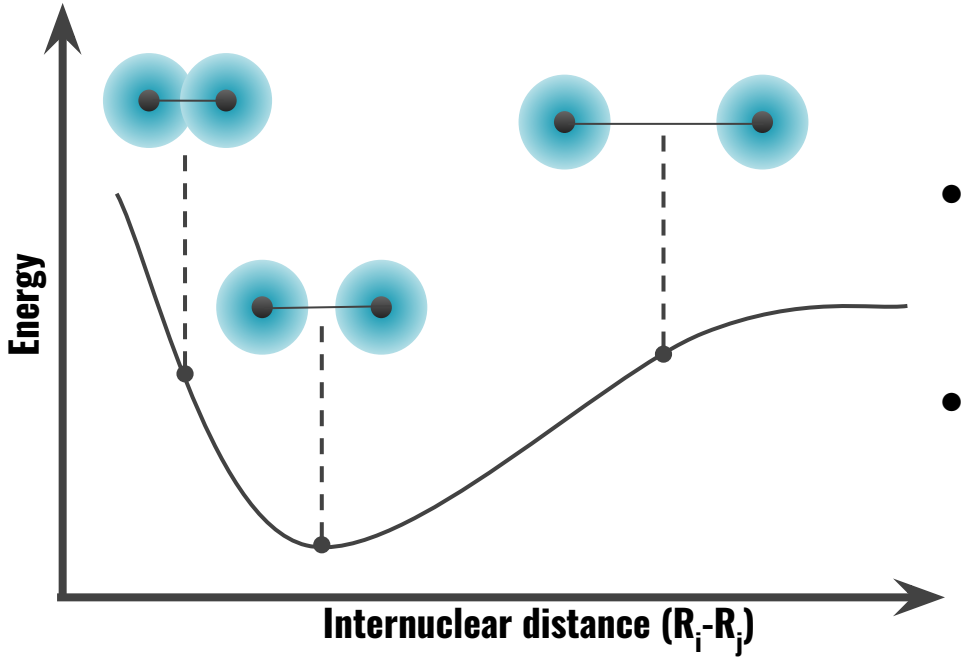
The process of locating such minima is known as geometry optimization and usually constitute the first step in a simulation.

The image was generated using AI (DALL E3).
Notice the artistic labels on the axis!



Potential energy surface

-Reading the force from the curve



- For a given nuclear configuration $\{\mathbf{R}_1,\mathbf{R}_2,...,\mathbf{R}_N\}$, there is an unique electronic energy E. (Born-Oppenheimer approximation)
- As nuclei move continuously, the points of electronic energy join to form a potential energy surface on which nuclei move.
- The force, **F**, acting on a nuclei is related to the derivative (gradient) on this surface. In the general case, it has components along x,y, and z. Ex:

$$\mathbf{F}_{x_i} = -\frac{\partial E}{\partial x_i} \qquad \mathbf{R}_i = [x_i, y_i, z_i]$$

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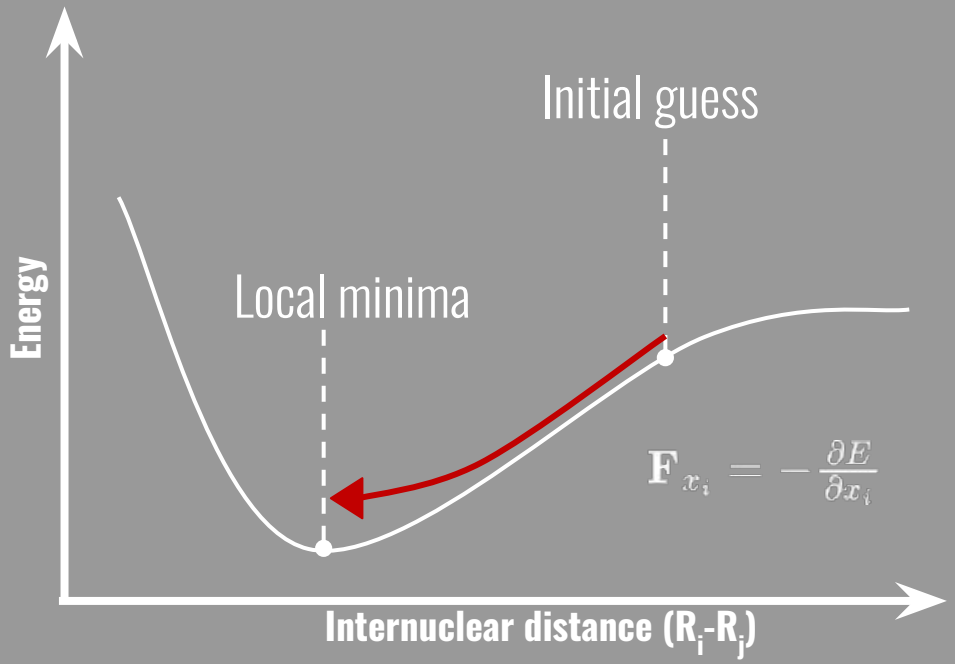


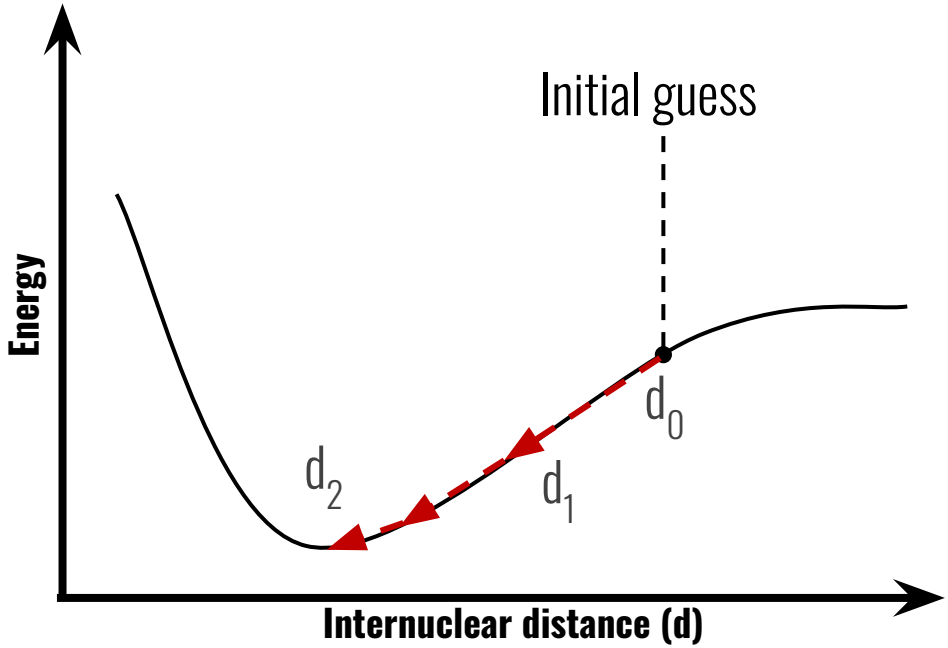
The bottom of the potential energy surface is the ground-state geometry. (Note: in more complex cases we may have multiple local minima on the potential energy surface).

The process of locating such minima given a first initial guess is called geometry optimization.

Q: How do we achieve the task indicated by the red arrow? Do you recall some standard tricks from your calculus?

Steepest descent (Gradient descent)

-An iterative search



- In a steepest descent search we "follow" the gradient towards the minima in a interactive process:

$$\mathbf{d}_{n+1} = \mathbf{d}_n - \gamma \nabla E(\mathbf{d}_n)$$

- The parameter γ controls the step-length.
- The slope is the negative of the force → we can execute a gradient descent if we have a means to compute forces e.g. using Hellmann-Feynman forces or an atomistic Force-Field.
- The iterations are carried out until the magnitude of the force(s) reach a predefined threshold (typical value 0.01 eV/Å).

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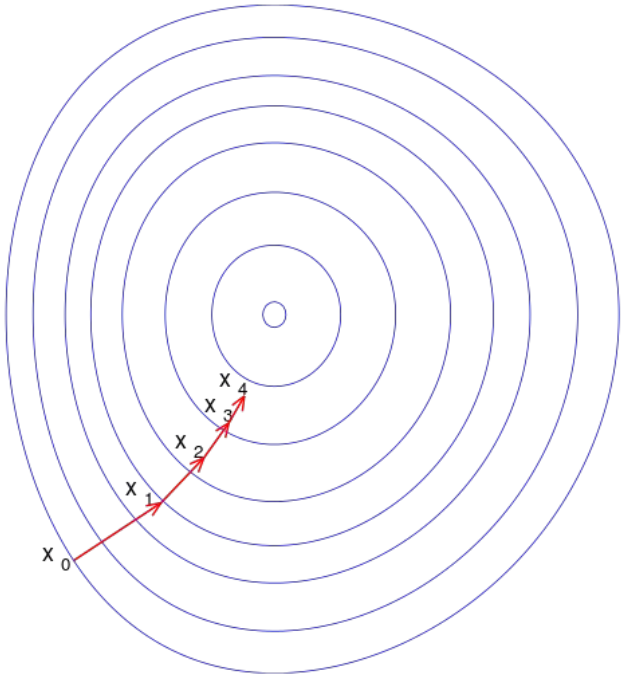
Steepest descent (Gradient descent)

-An iterative search



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- The slope is the negative of the force → we can execute a gradient descent if we have a means to compute forces e.g. the Hellmann-Feynman forces.
- In higher dimension the gradient is a vector. In the general case it has length 3N (3 for x,y,z and N for number of particles in our system).

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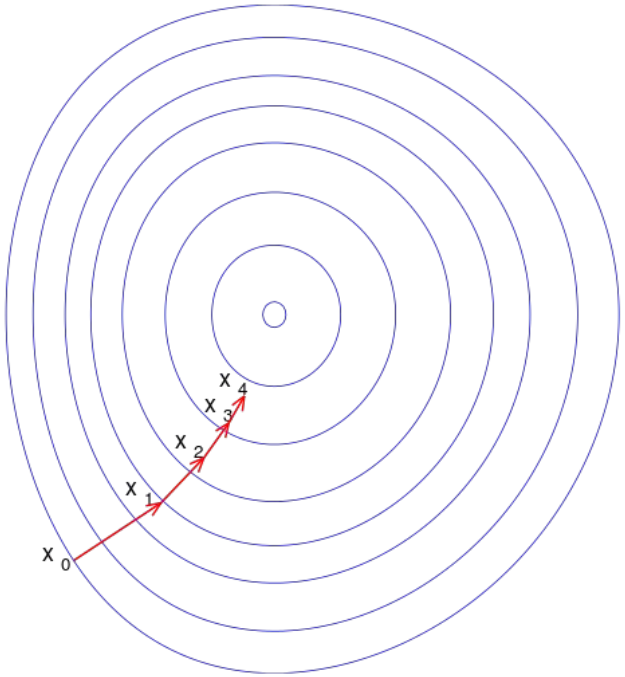
Image: Wikipedia

Gradient descent (Steepest descent)

-Pros & Cons



PROS

- Intuitive
- Easy to implement
- Robust

CONS

- Can be very slow, especially close to the minima.

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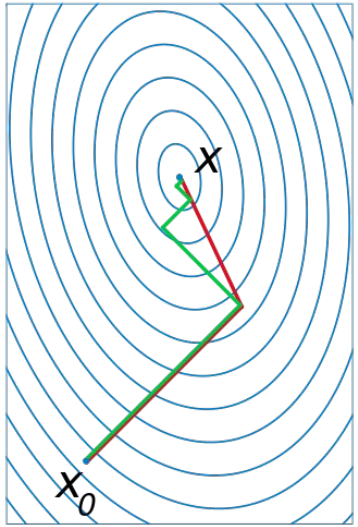
Image: Wikipedia

Conjugate gradient



Comparison of gradient descent (green) and conjugate gradient (red).

- Commonly attributed to Magnus Hestenes and Eduard Stiefel.
- Conjugate gradients method makes use of the gradient history to decide a better direction for the next step.

PROS

- Require fewer steps than gradient descent

CONS

- Harder to implement
- Still a bit slow

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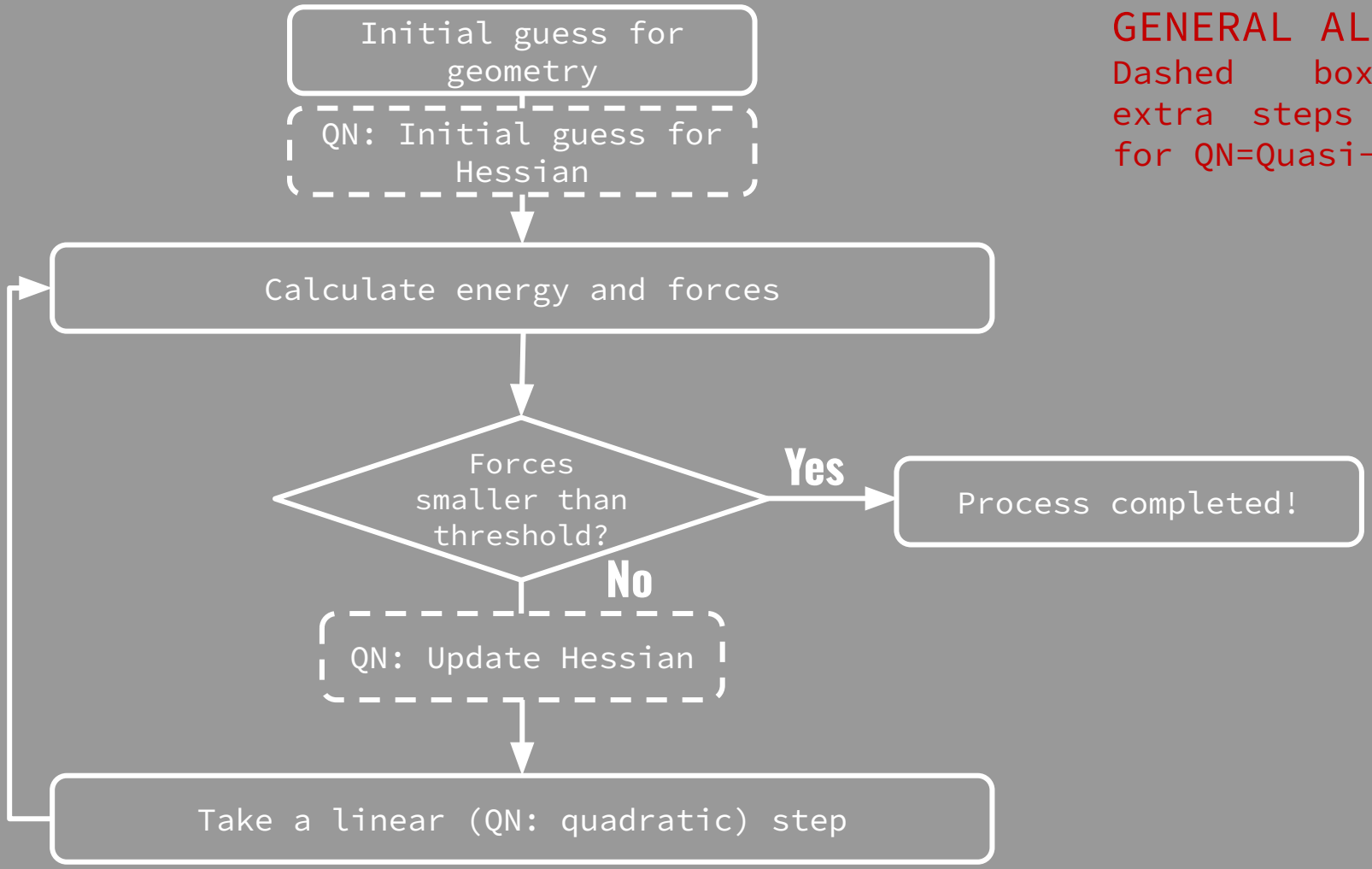
Image: Wikipedia

Quasi-Newton Methods

- These methods approximate the local curvature (Hessian: second derivative matrix) to more efficiently find the minima.
- Instead of a *linear step* along the gradient we can take a *quadratic step* using the approximated Hessian.
- They are more sophisticated but also much harder to implement.
- The most common algorithms are the:
  - BFGS (Broyden–Fletcher–Goldfarb–Shanno).
  - L-BFGS (Limited-memory BFGS) for memory efficiency in large-scale problems.

GENERAL ALGORITHM

Dashed boxes are extra steps required for QN=Quasi-Newton



Summary

- The *Born-Oppenheimer approximation* allow us to separate the motion of electrons and nuclei.
- The force acting on a nuclei is related to the negative of the gradient of the energy with respect to the position of nuclei.
- By following the direction of the forces we can locate the “optimal” geometry of the system.
- We use an iterative approach and a suitable algorithm where the most common choices are:
    - Steepest descent (Simple but requires many steps)
    - Conjugate gradient (Requires fewer steps but is less simple)
    - BFGS (Requires even fewer steps but is much more involved)