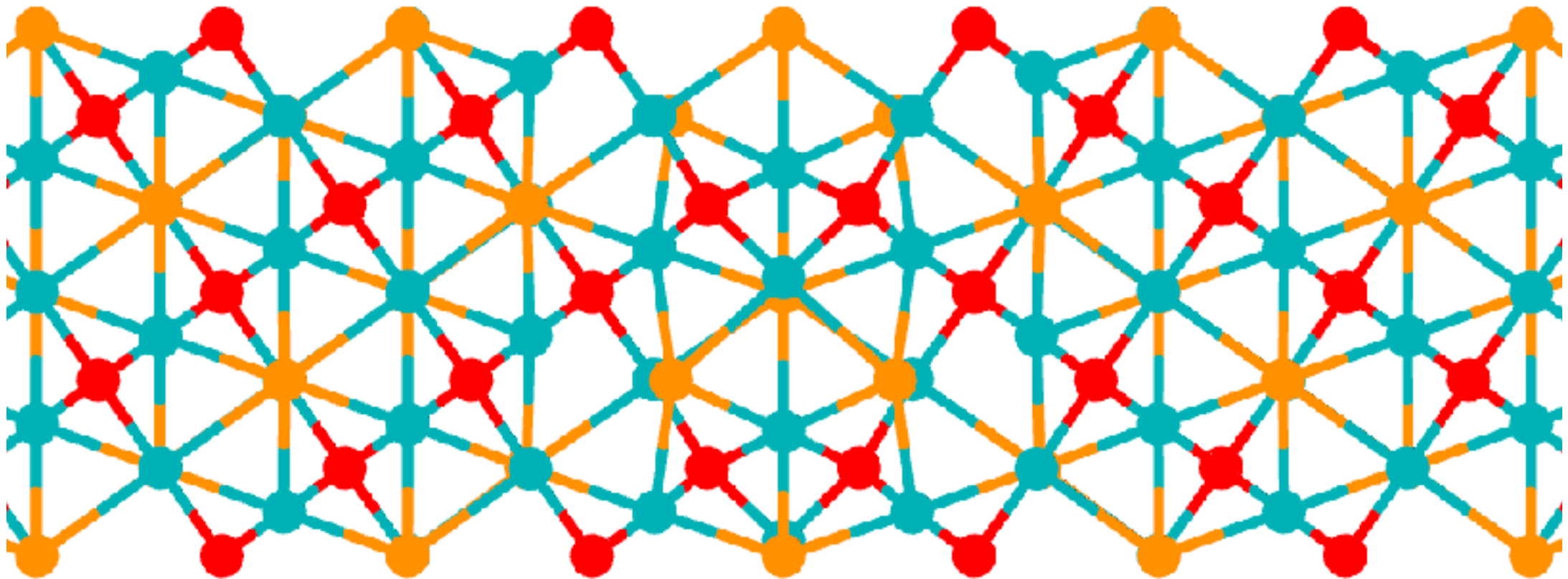
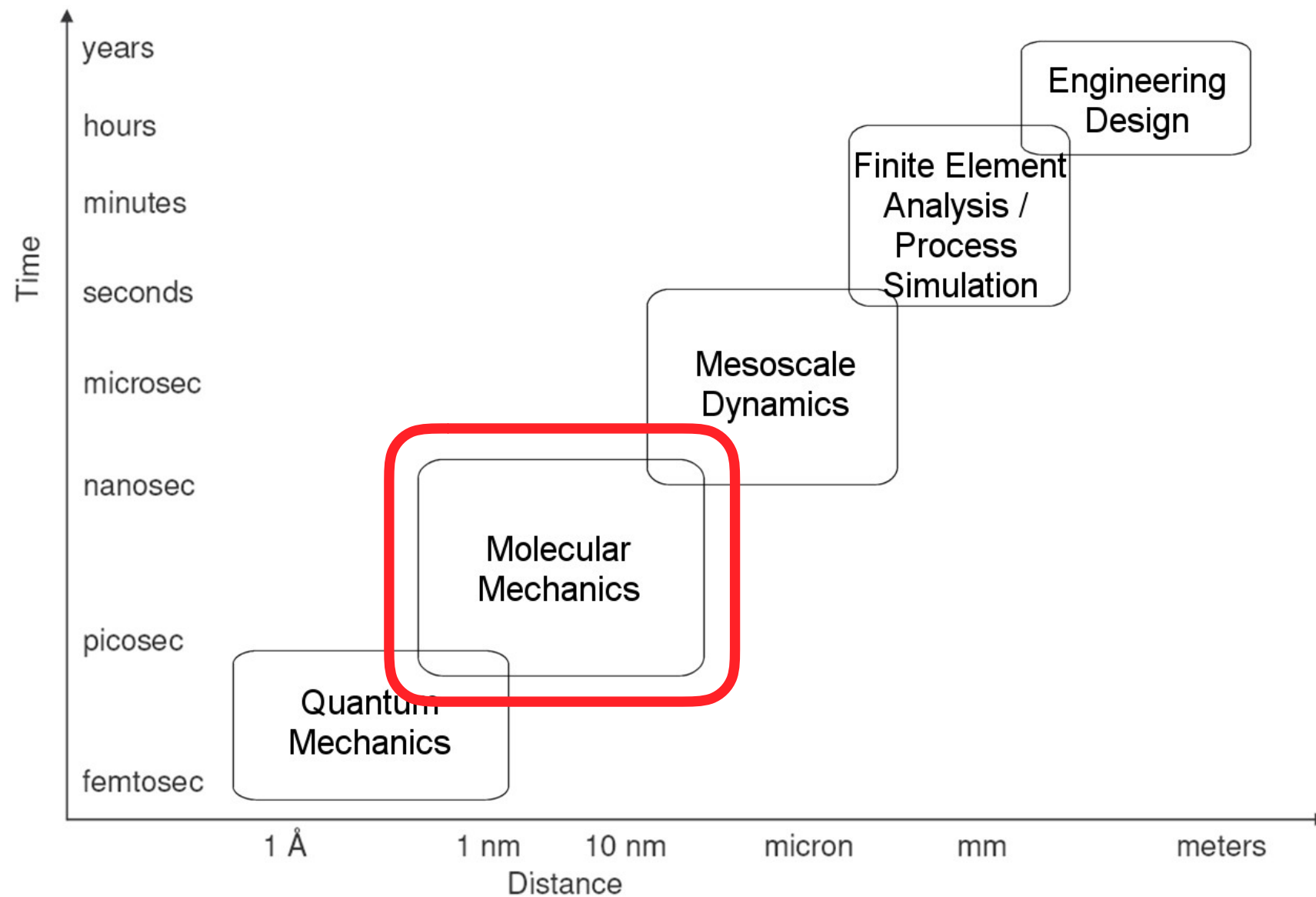


Interatomic Potentials & Defect Simulations



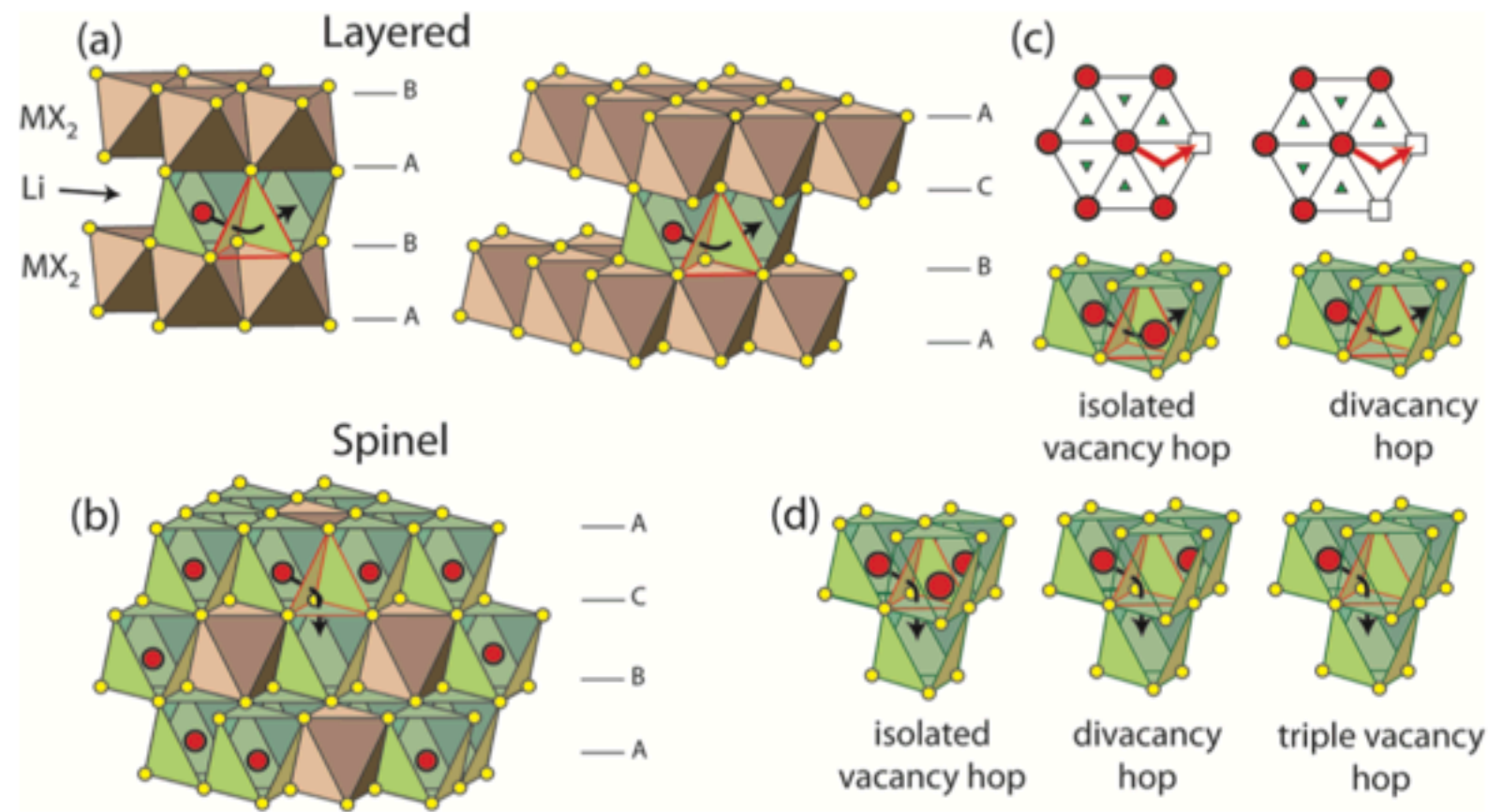
introduction to “atomistic” modelling

hierarchy of modelling techniques



why “atomistic” modelling?

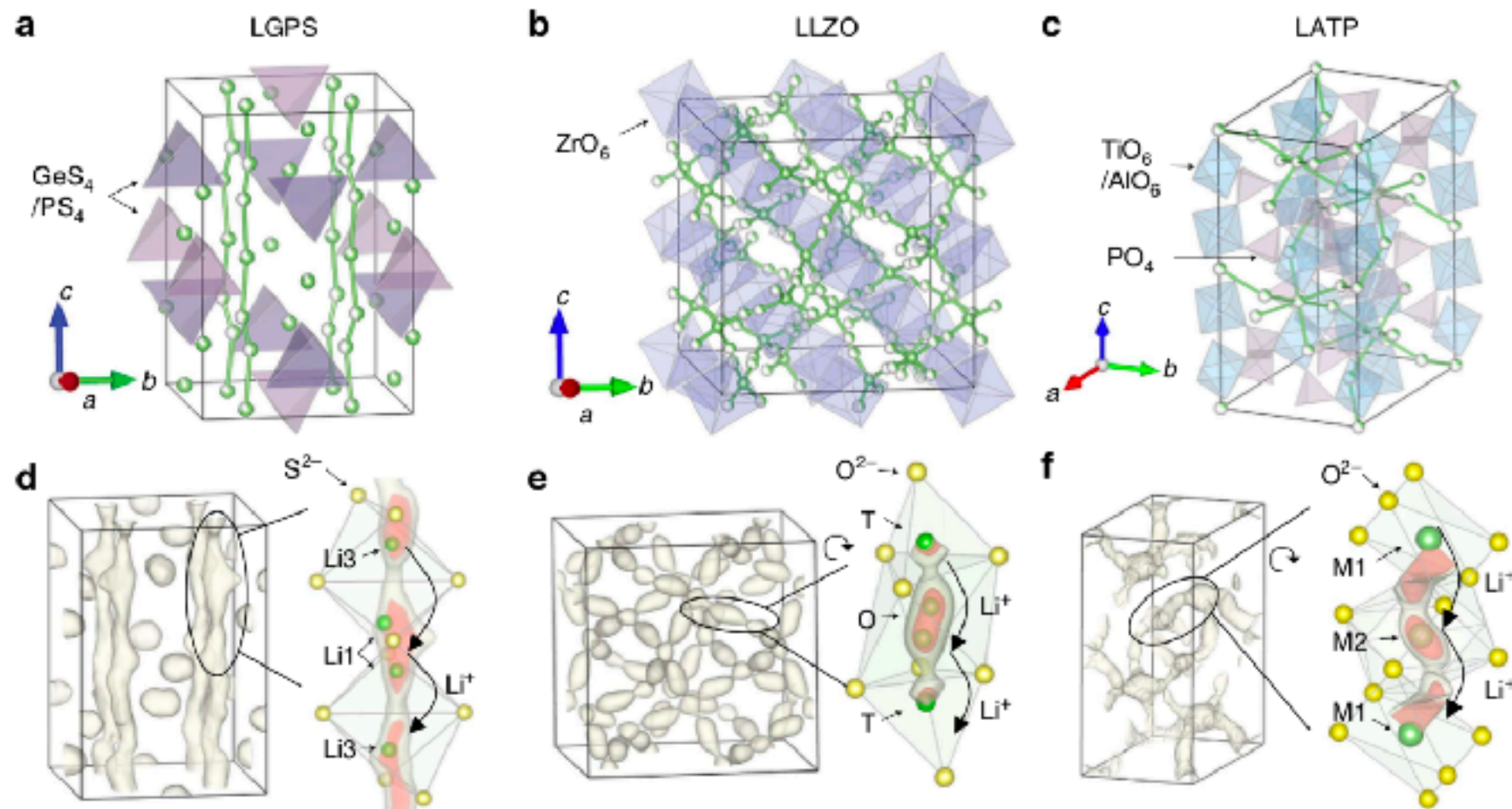
Typical questions at the atomic scale concern how the properties of a system depend on the arrangement & identities of atoms.



Li intercalation and diffusion in layered vs. spinel cathodes.

why “atomistic” modelling?

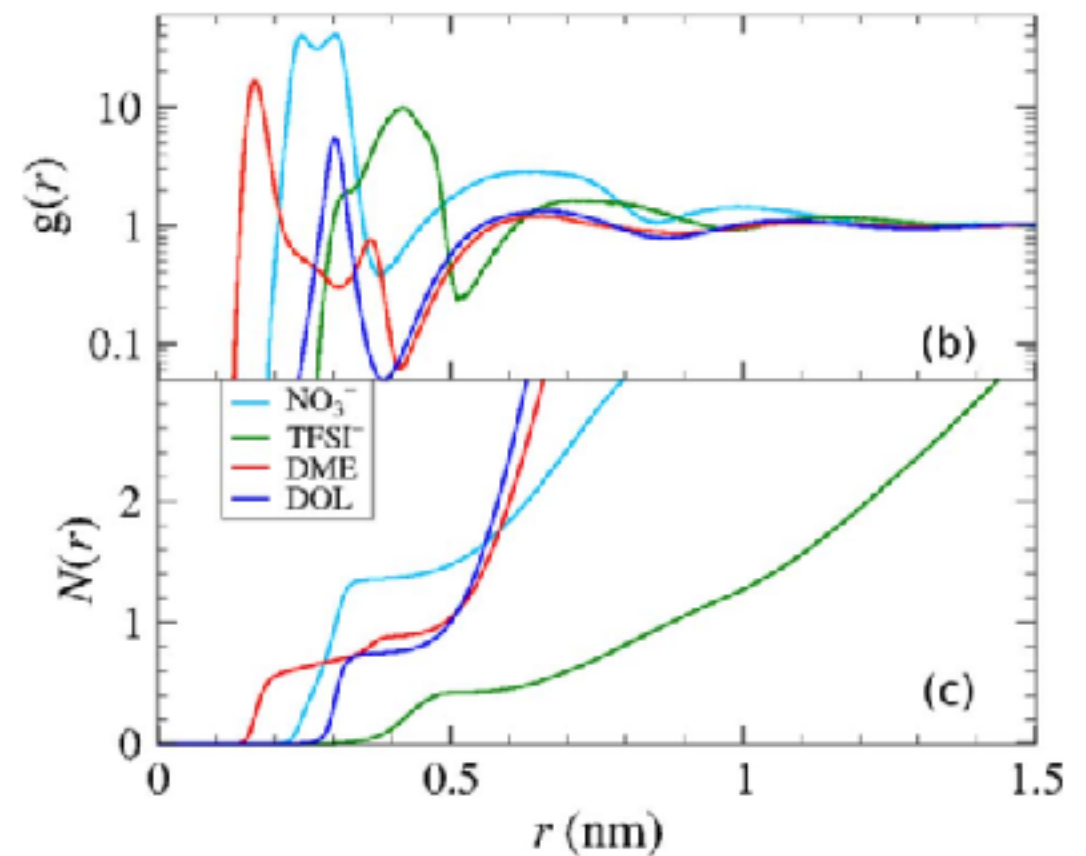
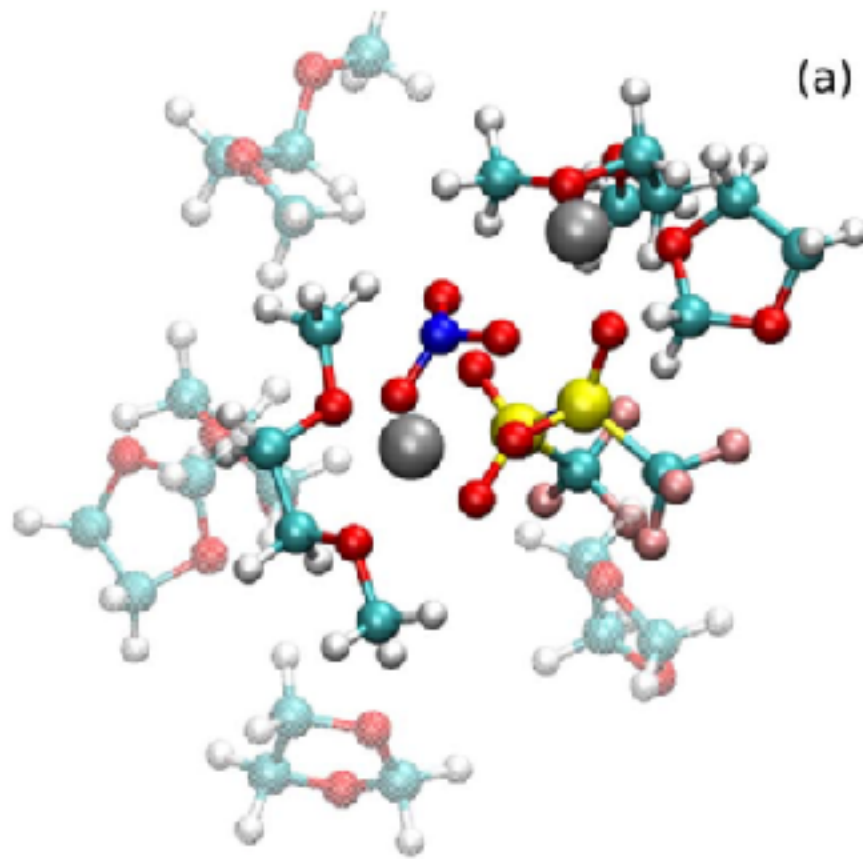
Typical questions at the atomic scale concern how the properties of a system depend on the arrangement & identities of atoms.



Li diffusion pathways in solid electrolytes

why “atomistic” modelling?

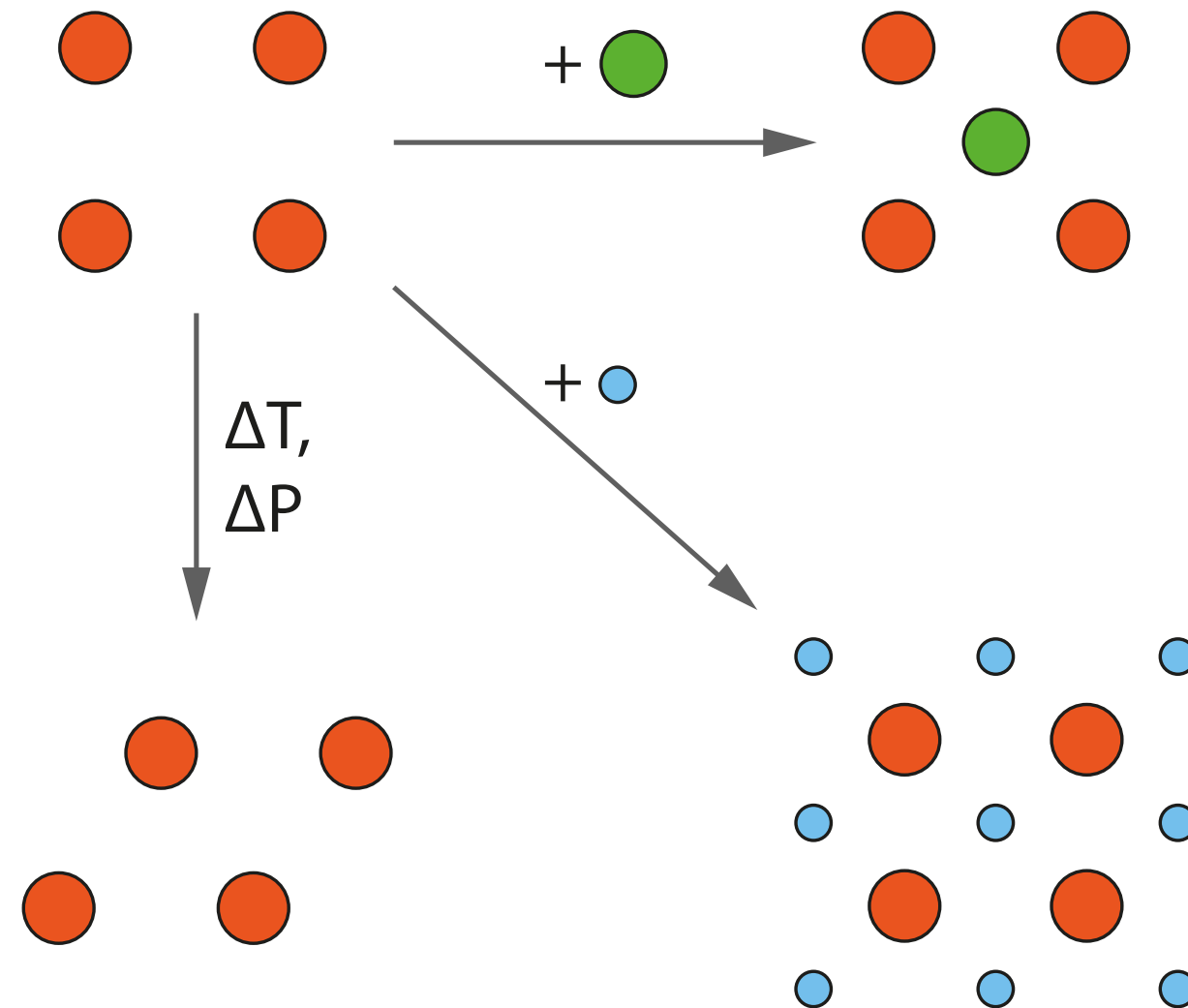
Typical questions at the atomic scale concern how the properties of a system depend on the arrangement & identities of atoms.



Solvation structure in Li^+ liquid electrolytes

properties depend on structure

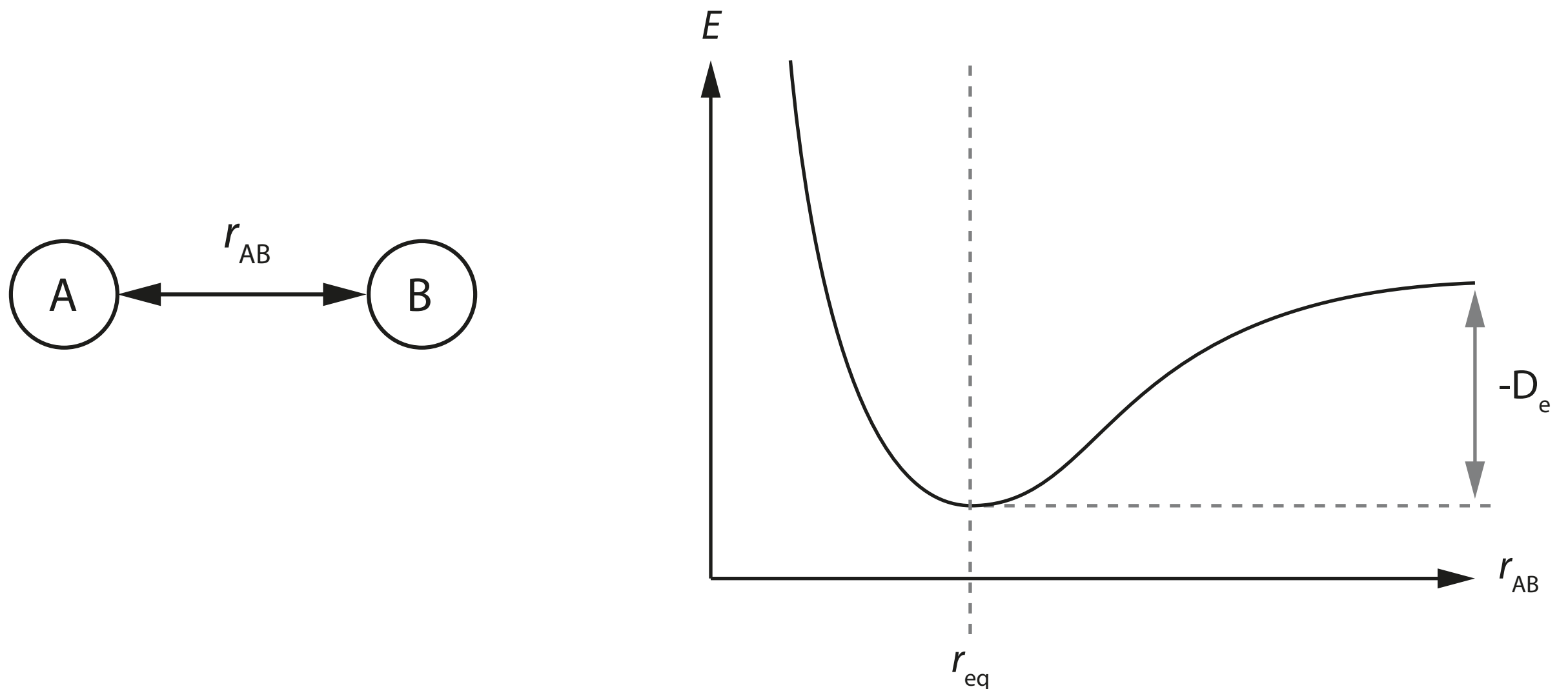
(but which structures are we interested in?)



most important property of a system is its energy

energy as a function of atomic coordinates → potential energy surface

The potential energy surface is, in general, a multidimensional complex function ($3N-6$ or $3N-5$ degrees of freedom).



what about electronic degrees of freedom?

Born-Oppenheimer approximation:

assume that motion of atomic nuclei and electrons can be separated.

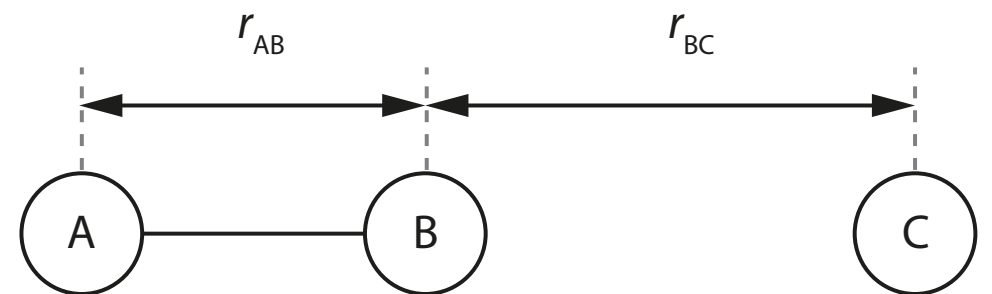
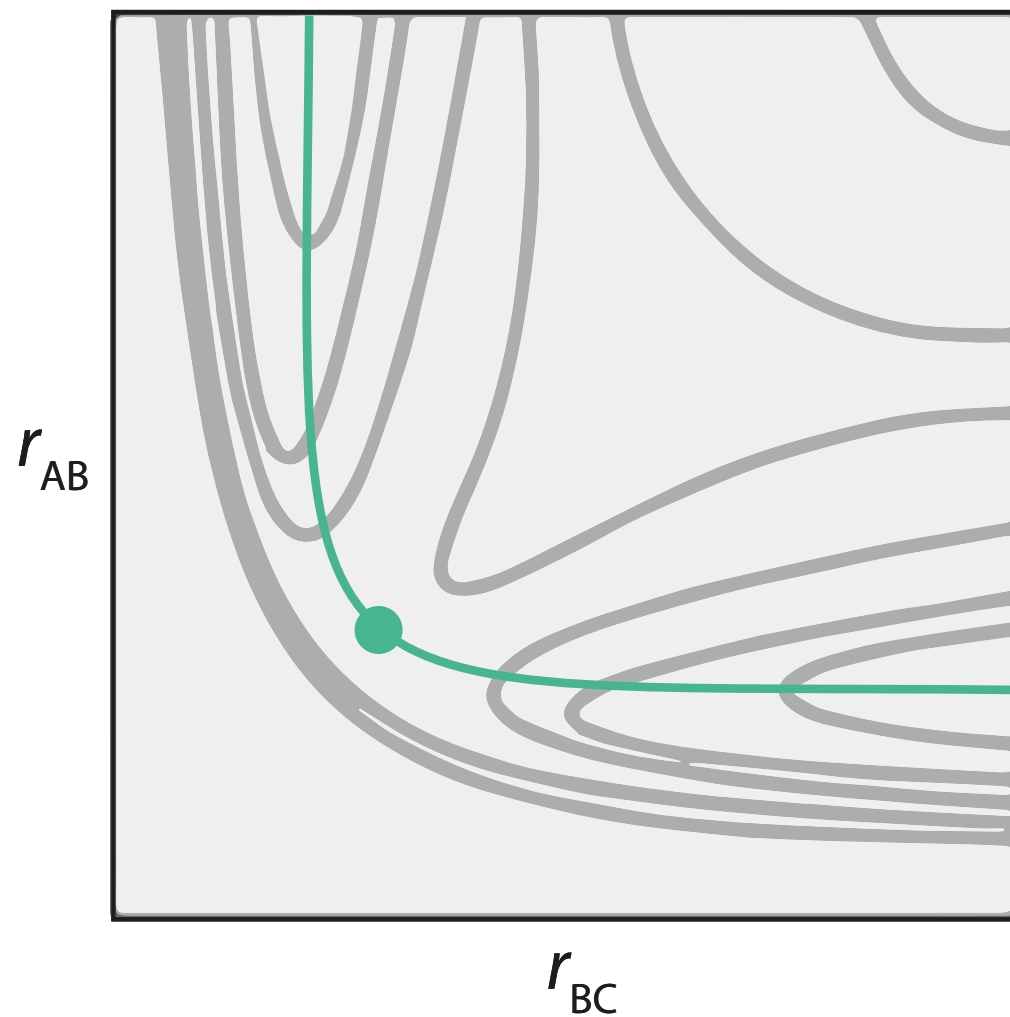
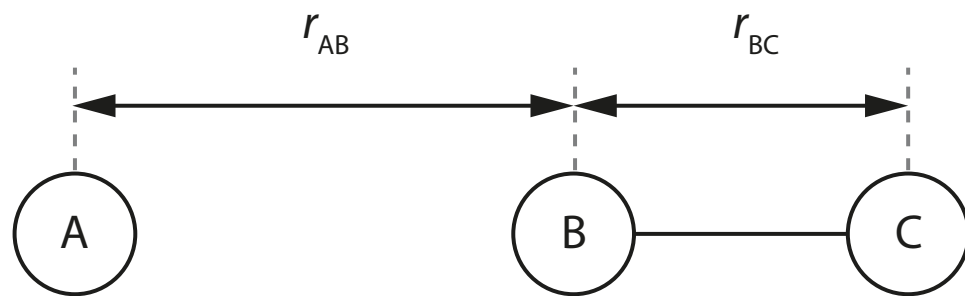
$$\Psi_{\text{total}} = \psi_{\text{electronic}} \otimes \psi_{\text{nuclear}}$$

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{nuclear}}$$

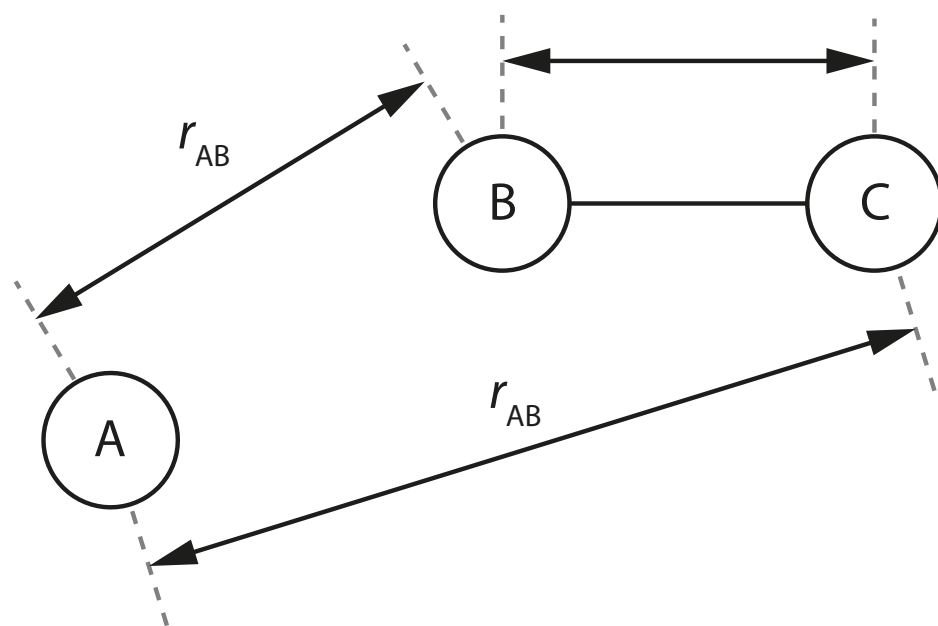
electrons are much lighter than nuclei

→ respond “instantaneously” to changes in nuclear coordinates

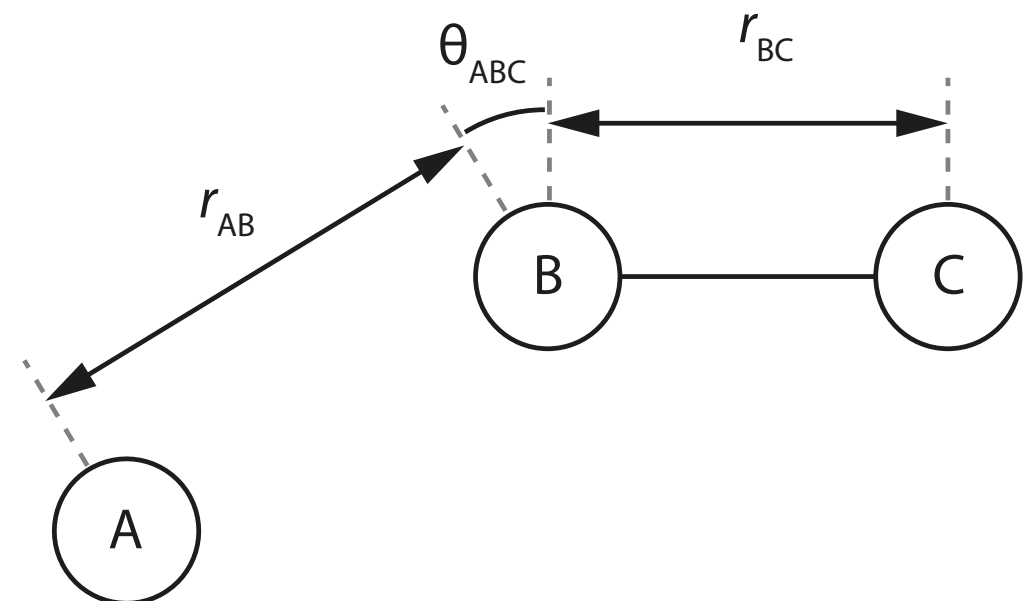
3 atoms collinear (2 DoF)



non-collinear case (3 DoF)



3 distances

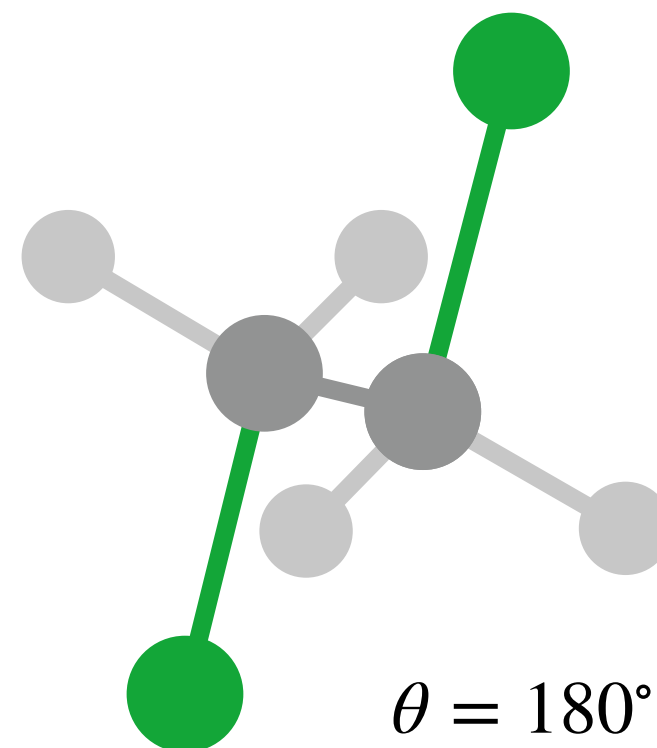
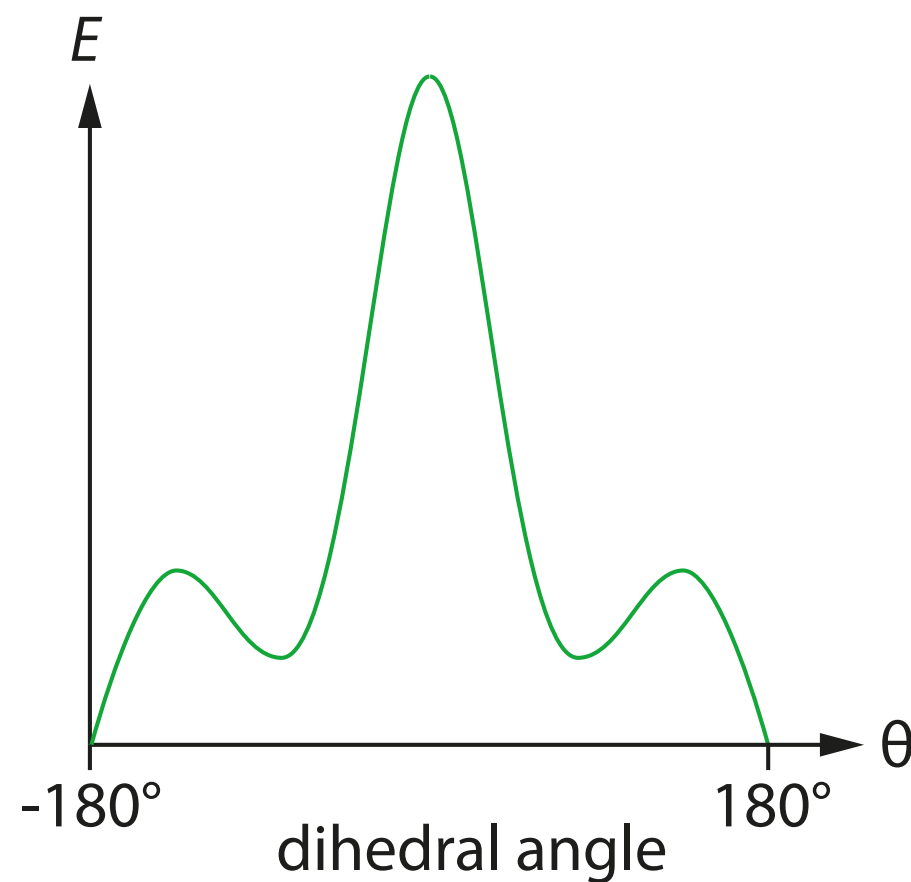


2 distances
+ 1 angle

parameters defining PES do not need to be interatomic distances
(choice of coordinate system / orthogonal basis)

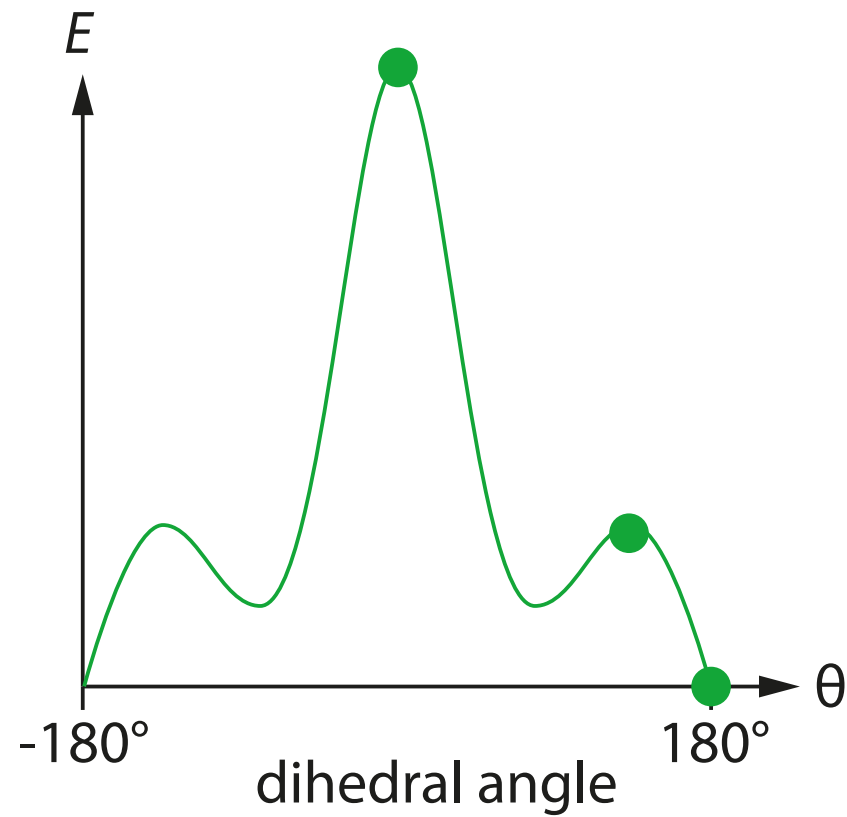
focus on “relevant” degrees of freedom
→ reduced PES

e.g. dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$) internal rotation

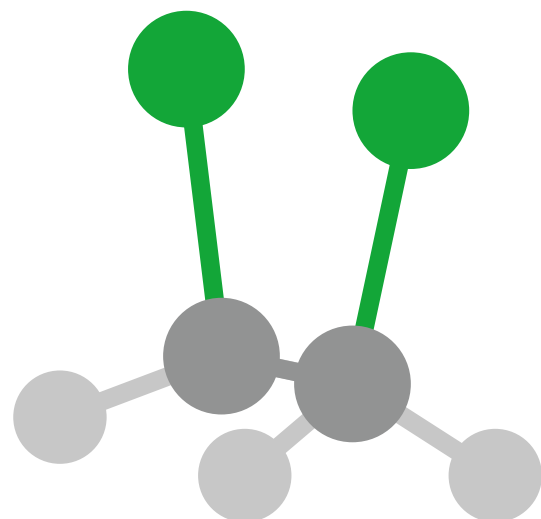


energy is lowest when chlorine atoms are oppositely oriented

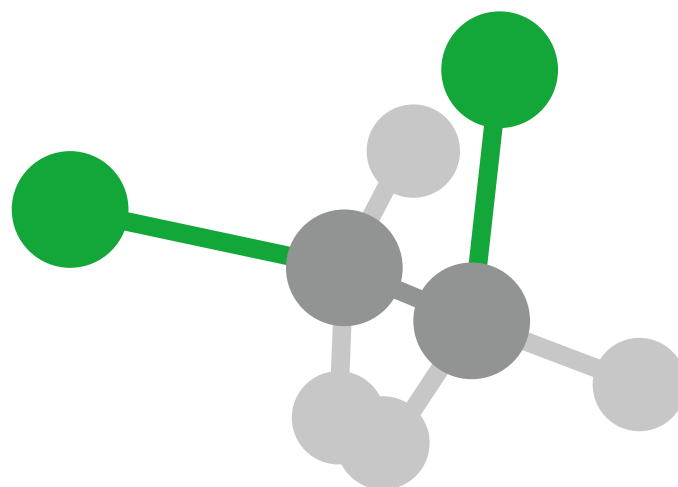
other important points on PES



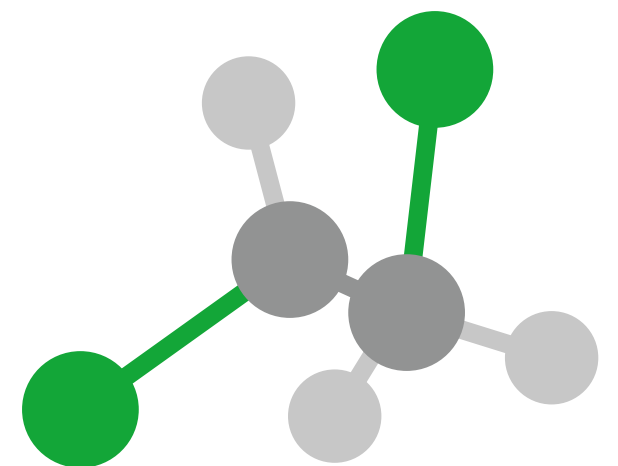
global maximum



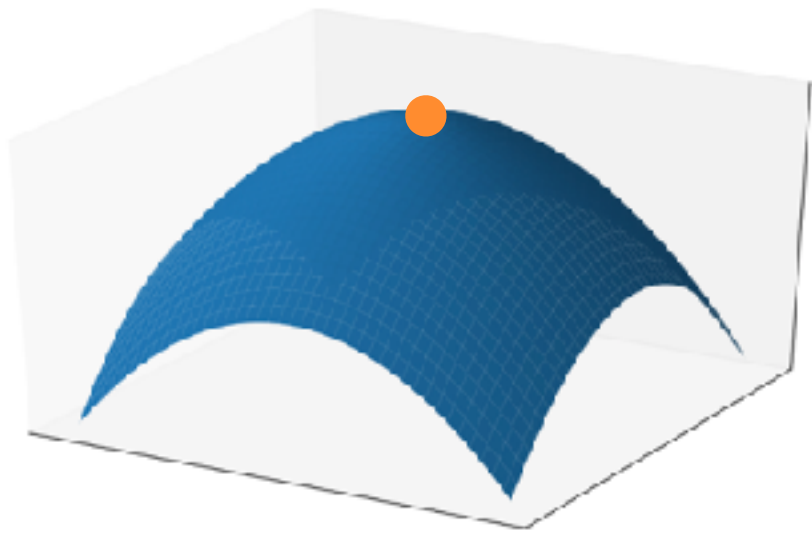
local minimum



local maximum



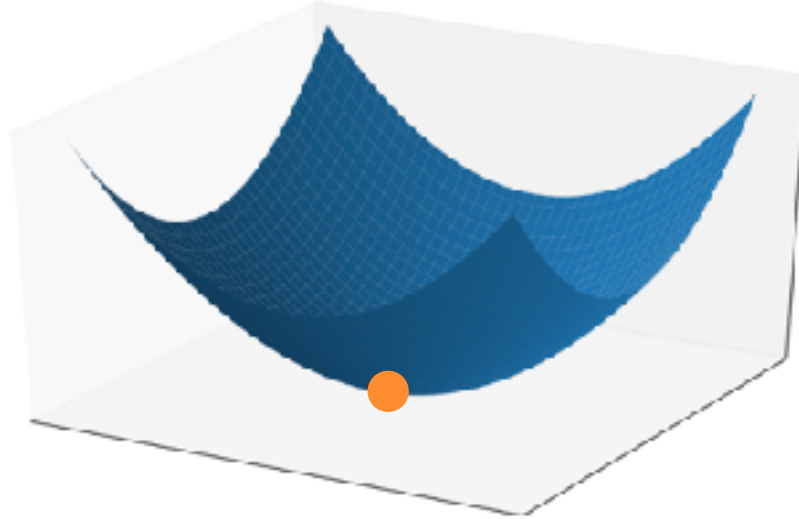
often interested in *stationary points* on the PES



local maximum

$$\frac{dE}{dx} = 0$$

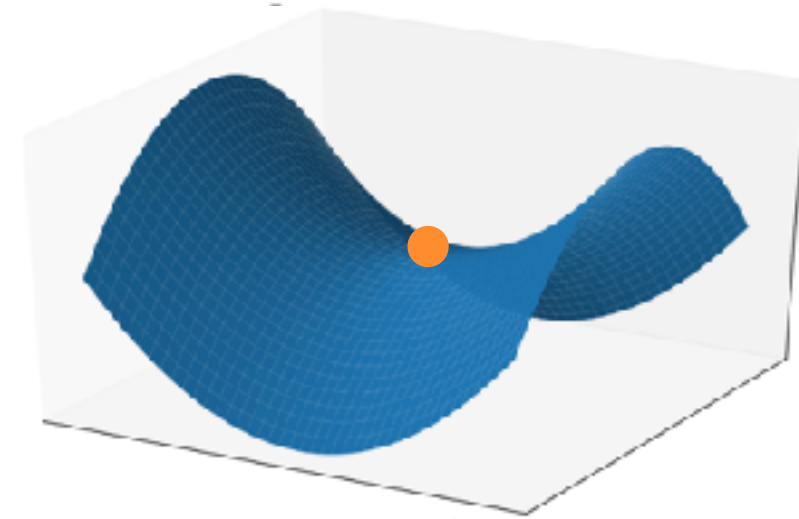
$$\frac{d^2E}{dx^2} < 0$$



local minimum

$$\frac{dE}{dx} = 0$$

$$\frac{d^2E}{dx^2} > 0$$



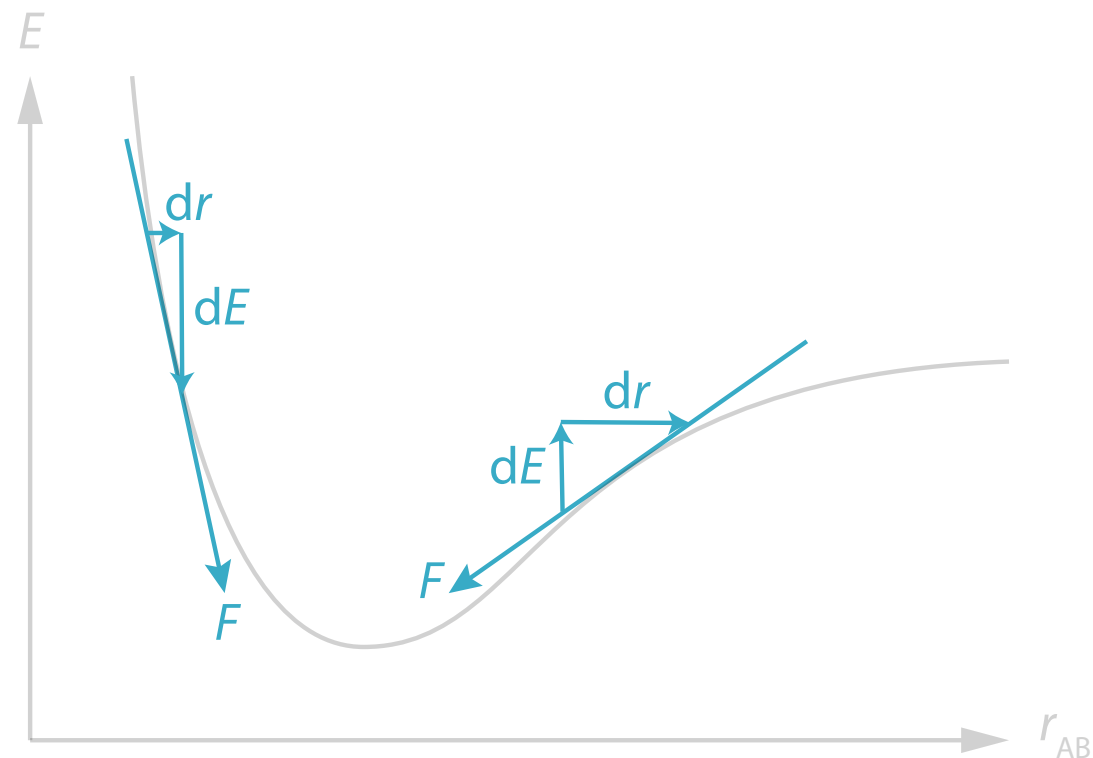
saddle point
(transition state)

$$\frac{dE}{dx} = 0$$

$$\frac{d^2E}{dx^2} > 0, \frac{d^2E}{dy^2} < 0$$

forces and second derivatives

gradient is first derivative with respect to position

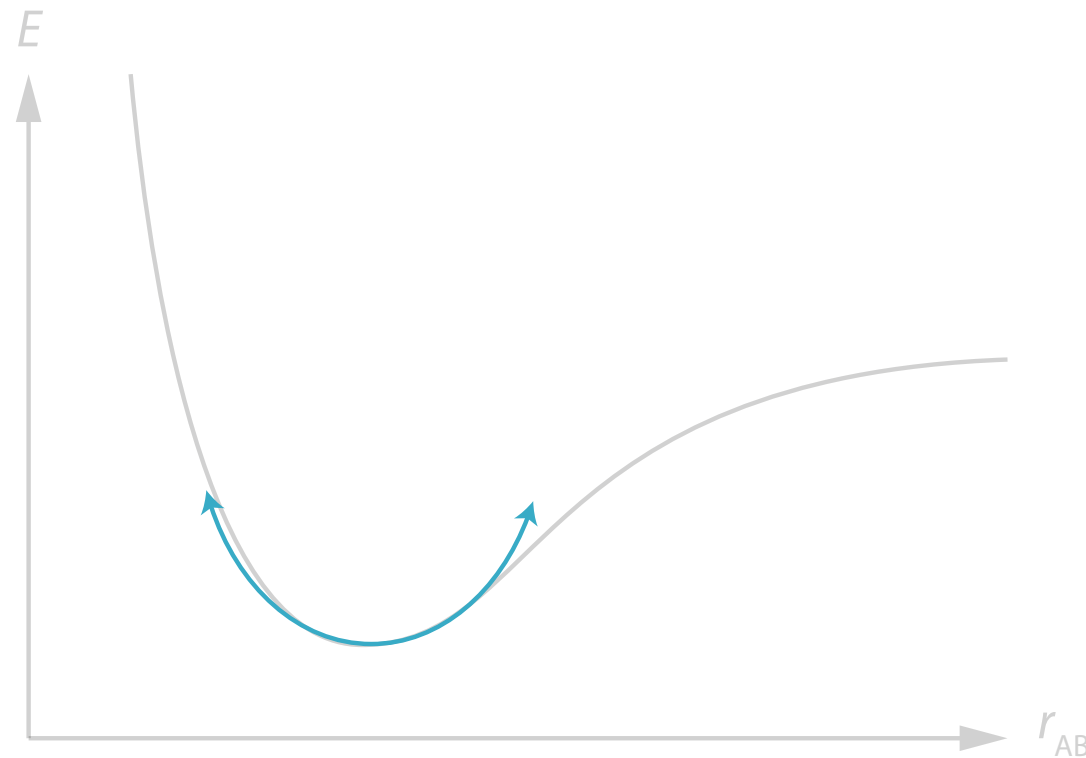


$$g = \frac{\partial E}{\partial x}$$

$$F = -g$$

forces and second derivatives

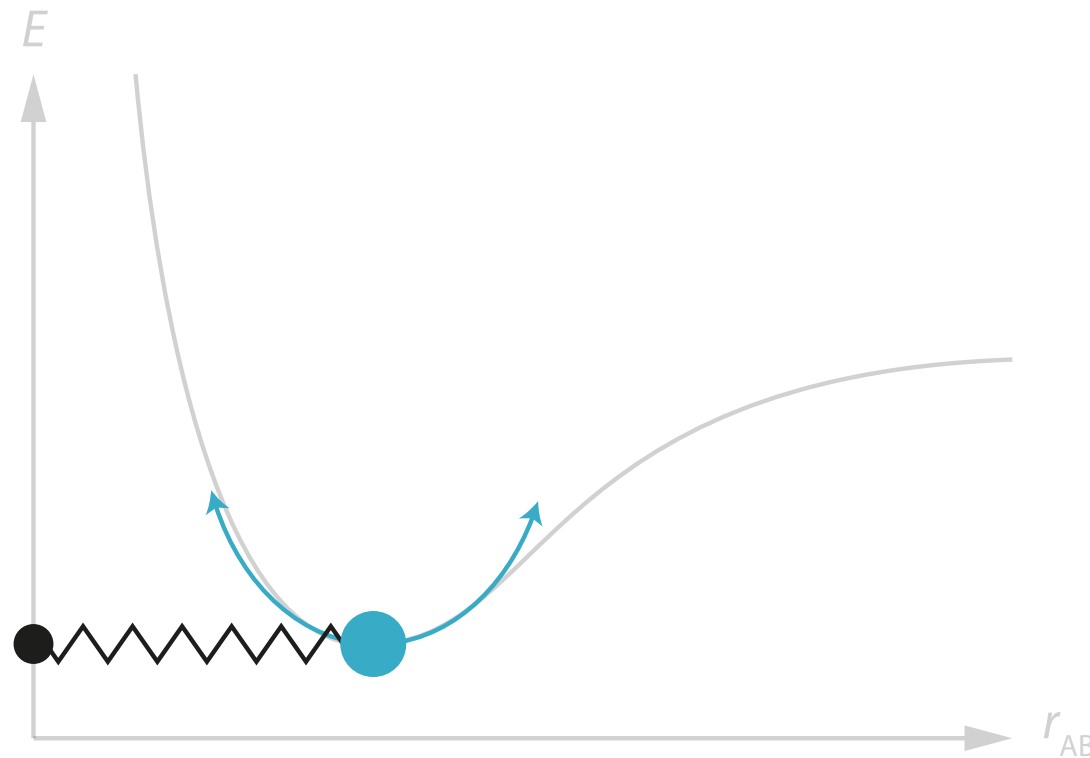
second derivative = local curvature
(how quickly does the slope change?)



$$W = \frac{d^2E}{dx^2}$$

forces and second derivatives

second derivatives give vibrational frequencies
(harmonic approximation)



$$V(x) = V(x_0) + \left. \frac{dV(x)}{dx} \right|_{x_0} (x - x_0) + \frac{1}{2!} \left. \frac{d^2V(x)}{dx^2} \right|_{x_0} (x - x_0)^2 + \dots$$

$$V(x) = -k(x - x_0)^2$$

$$k = -W$$

forces and second derivatives

in general working with vector coordinates /
forces / second derivatives (e.g. 3N cartesian
coordinates)

$$g = \frac{\partial E}{\partial x}$$

$$w = \frac{\partial^2 E}{\partial x \partial y}$$

second derivatives are $3N \times 3N$ matrix:

- diagonalise to get independent directions
- eigenvectors = new coordinate basis
- eigenvalues = second derivatives in this basis

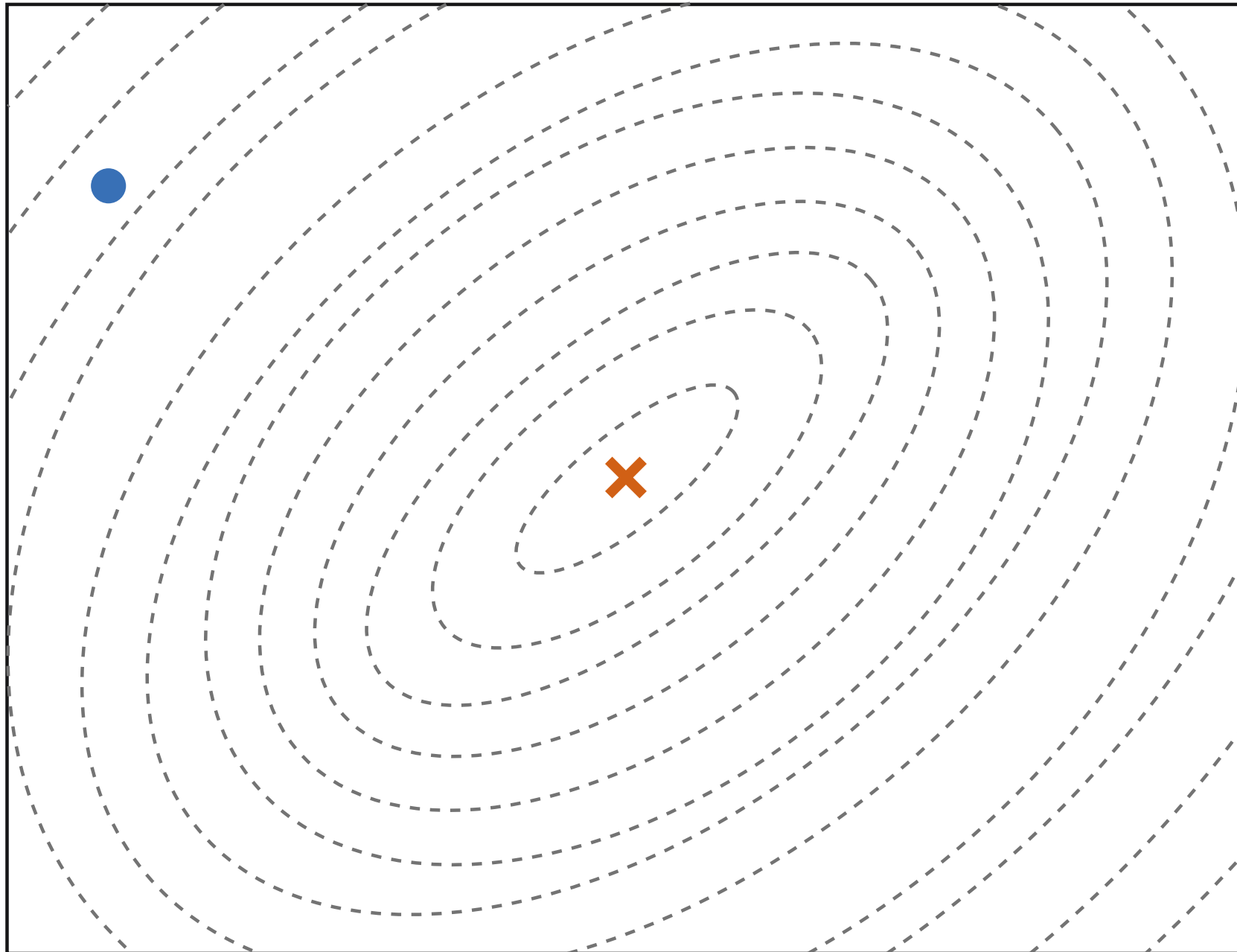
dynamical matrix \rightarrow mass weighted second derivatives

diagonalise \rightarrow

- eigenvectors = normal modes
- sqrt of eigenvalues = vibrational frequencies

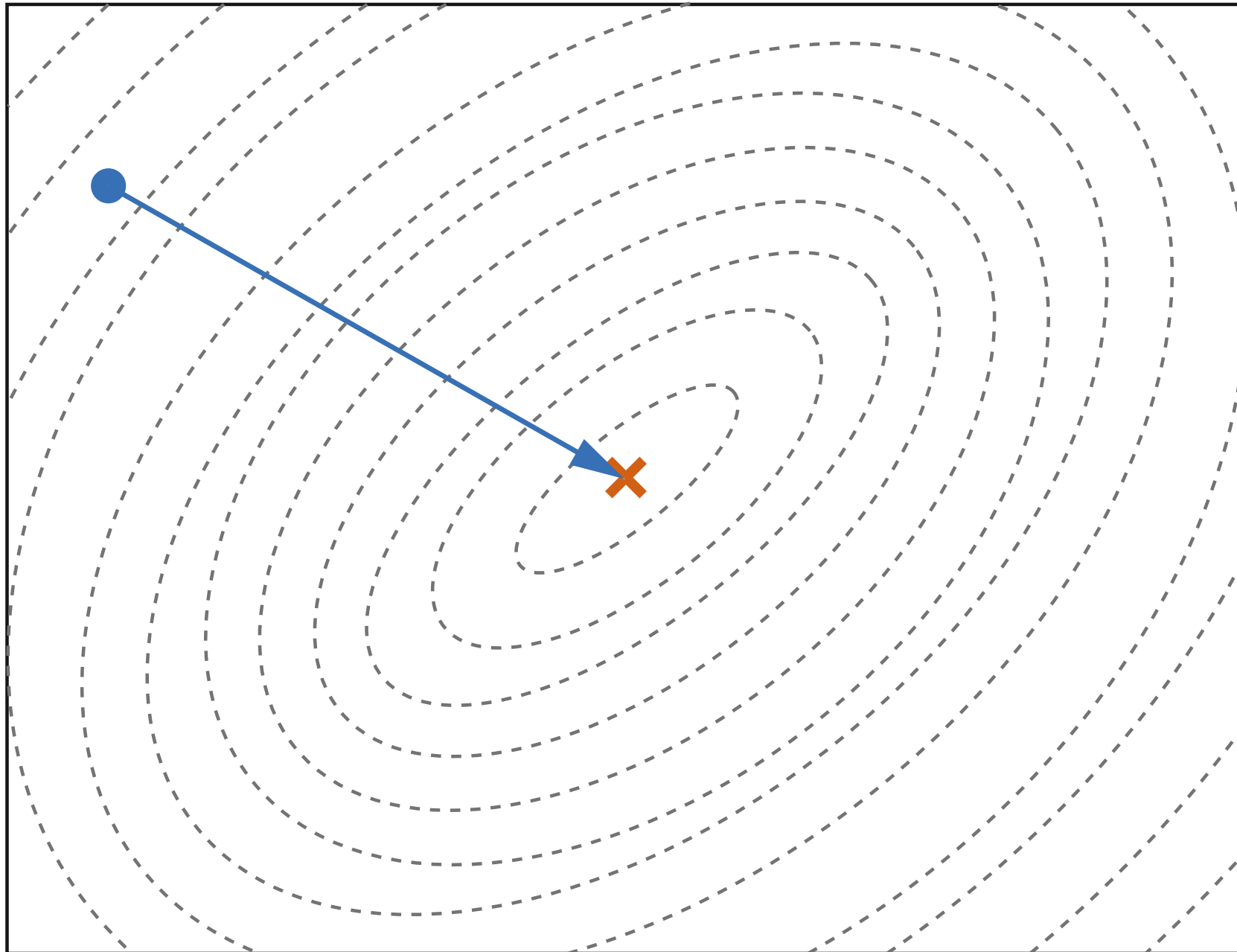
$$D = \frac{1}{\sqrt{m_x m_y}} \left(\frac{\partial^2 E}{\partial x \partial y} \right)$$

how to find (local) minima?



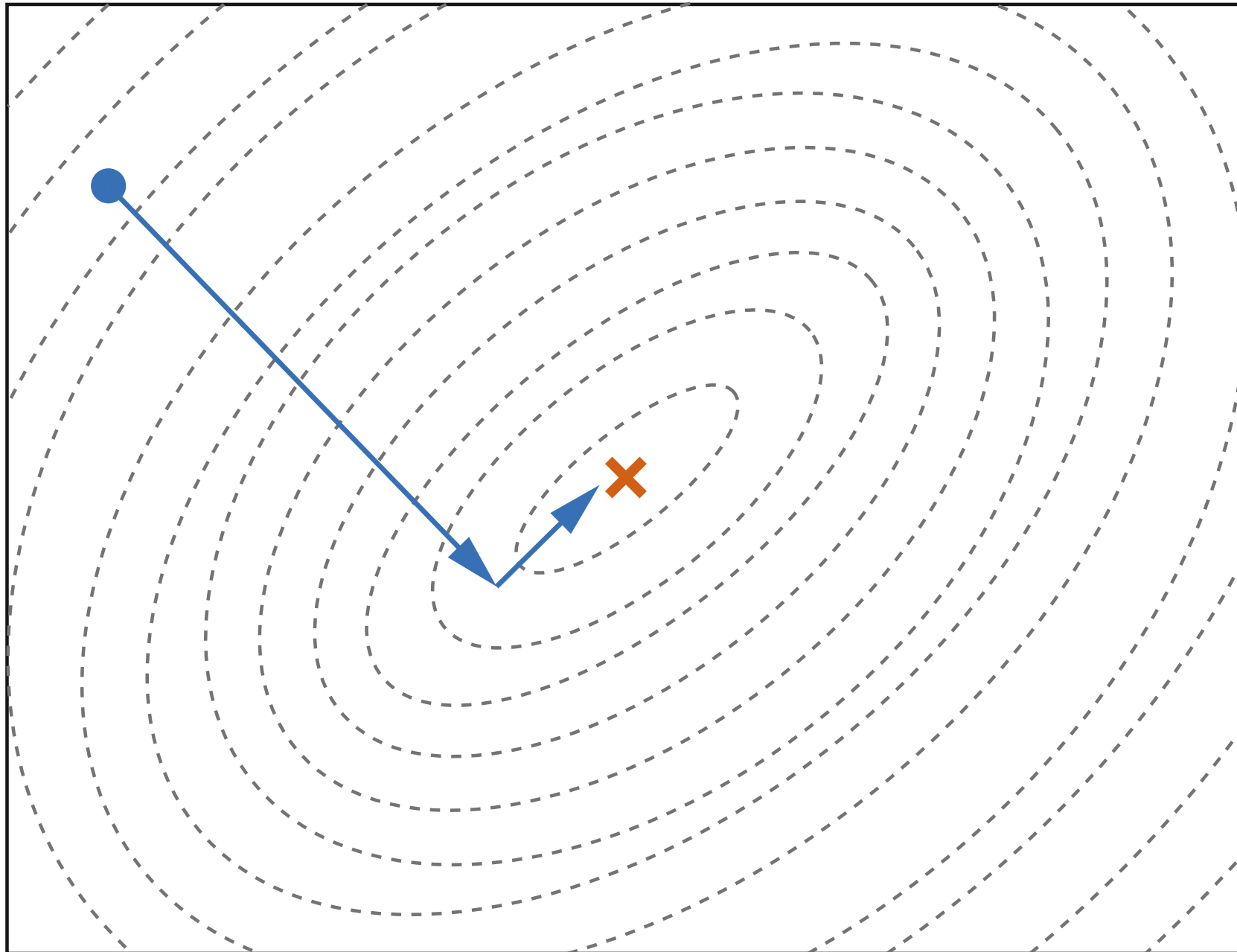
(hopefully) have a reasonable first guess

how to find (local) minima?



finding the minimum using local information?

how to find (local) minima?



several numerical methods that try to solve this...

example: Newton-Raphson method

We want to find $f(x) = 0$:

Taylor expansion of $y = f(x)$ around x_0 :

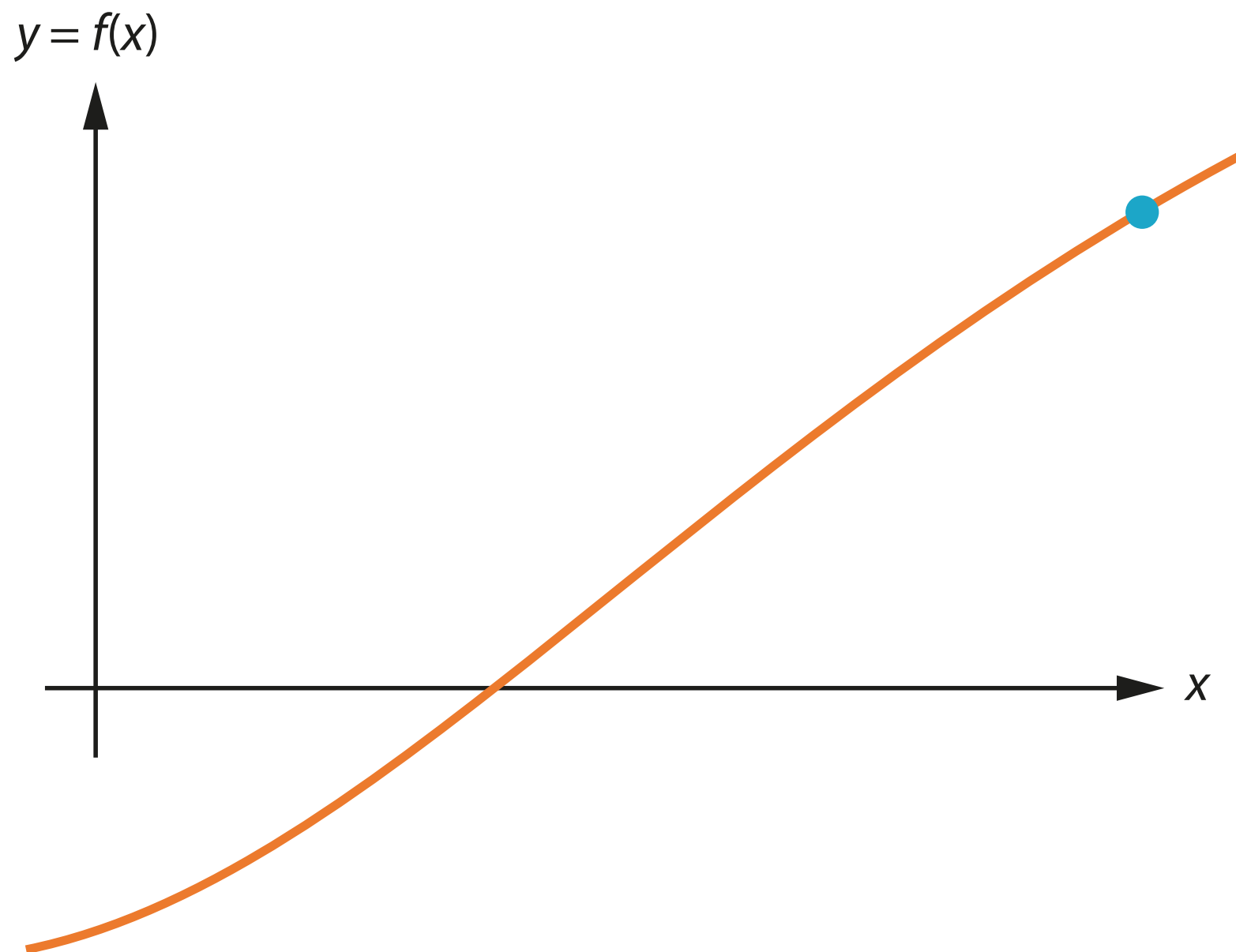
$$y = f(x_0) + f'(x_0)(x - x_0) + \dots$$

If we are close to the solution:

$$0 = f(x_n) + f'(x_n)(x_{n+1} - x_n)$$

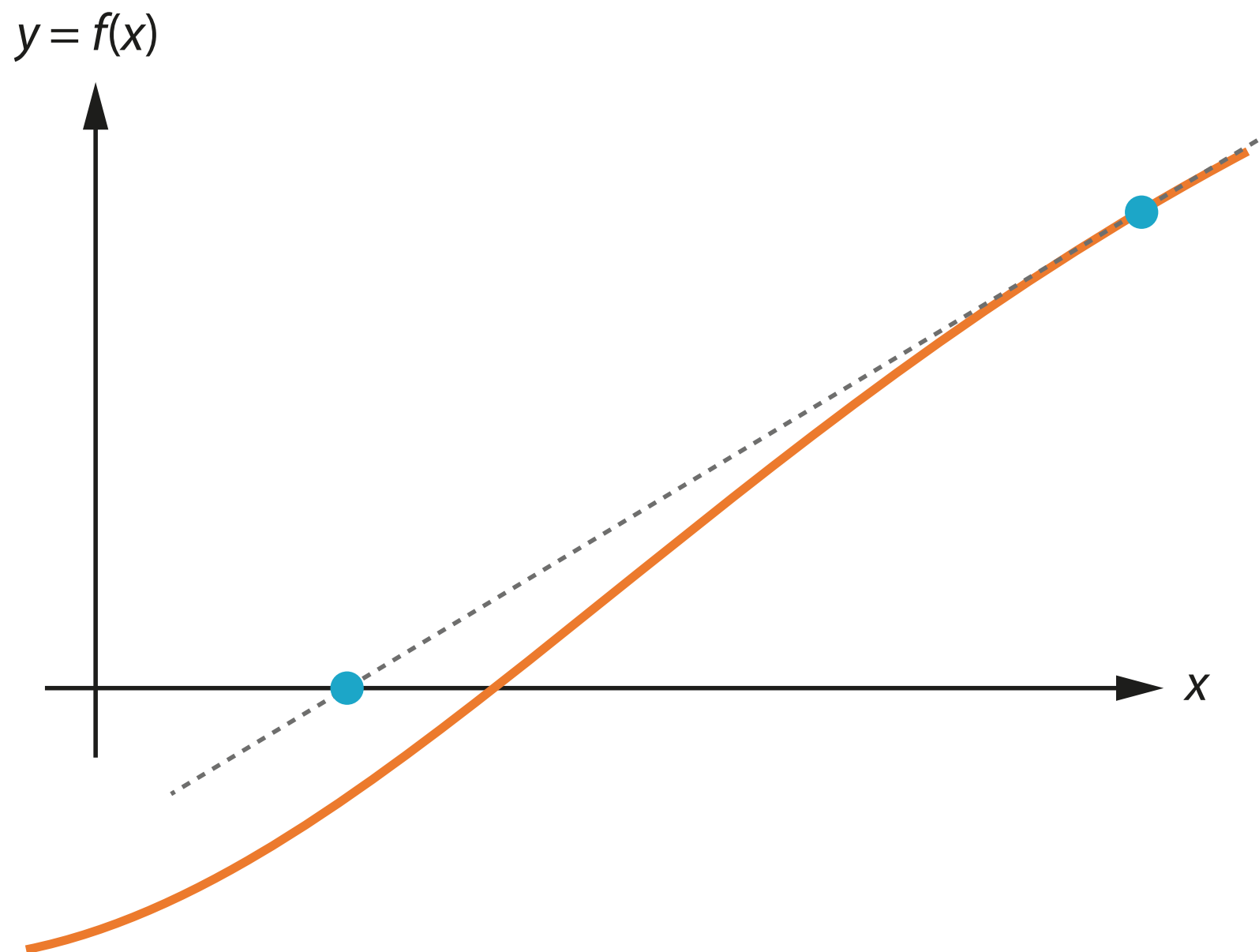
$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}$$

example: Newton-Raphson method



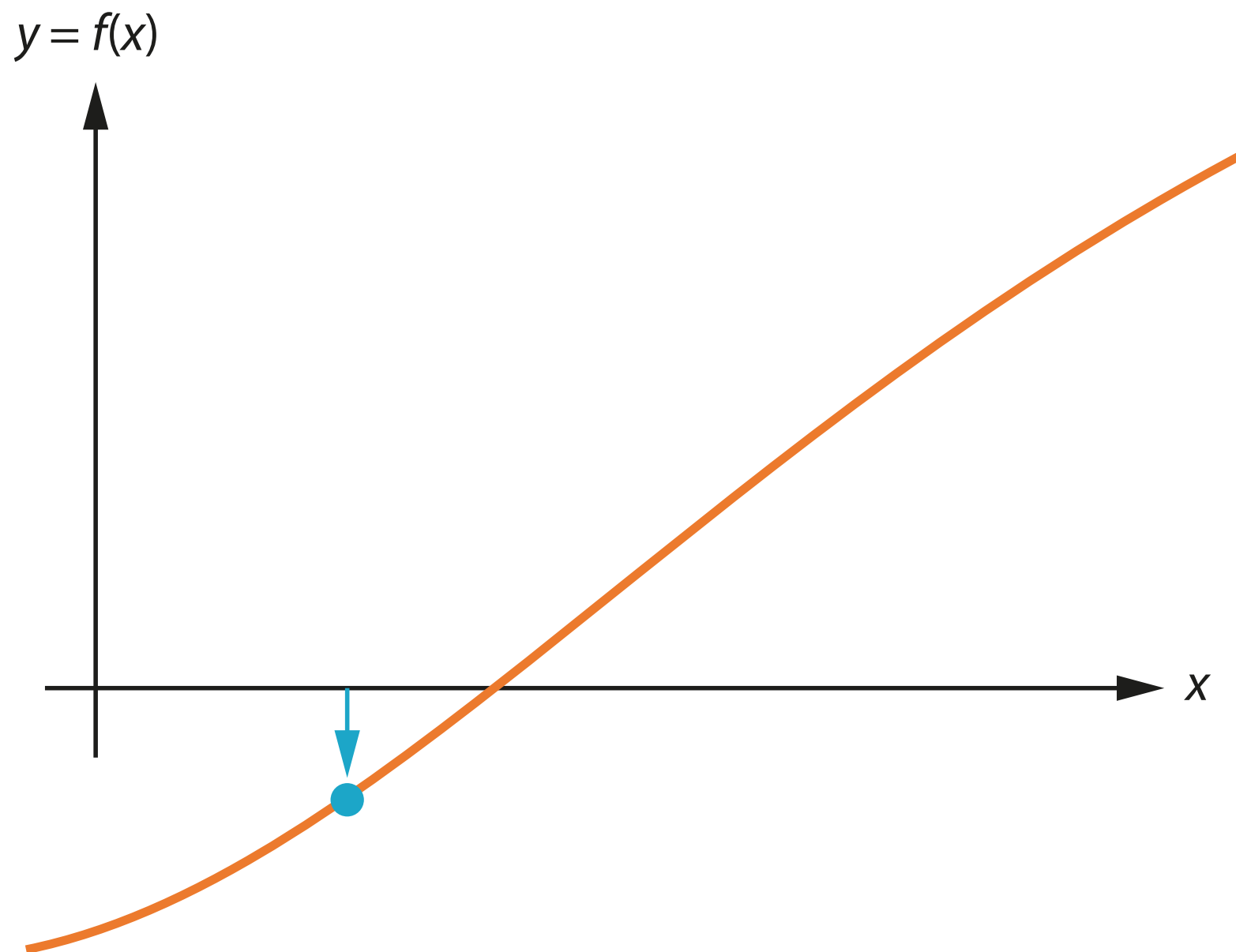
calculate $f(x_0)$ and $f'(x_0)$

example: Newton-Raphson method



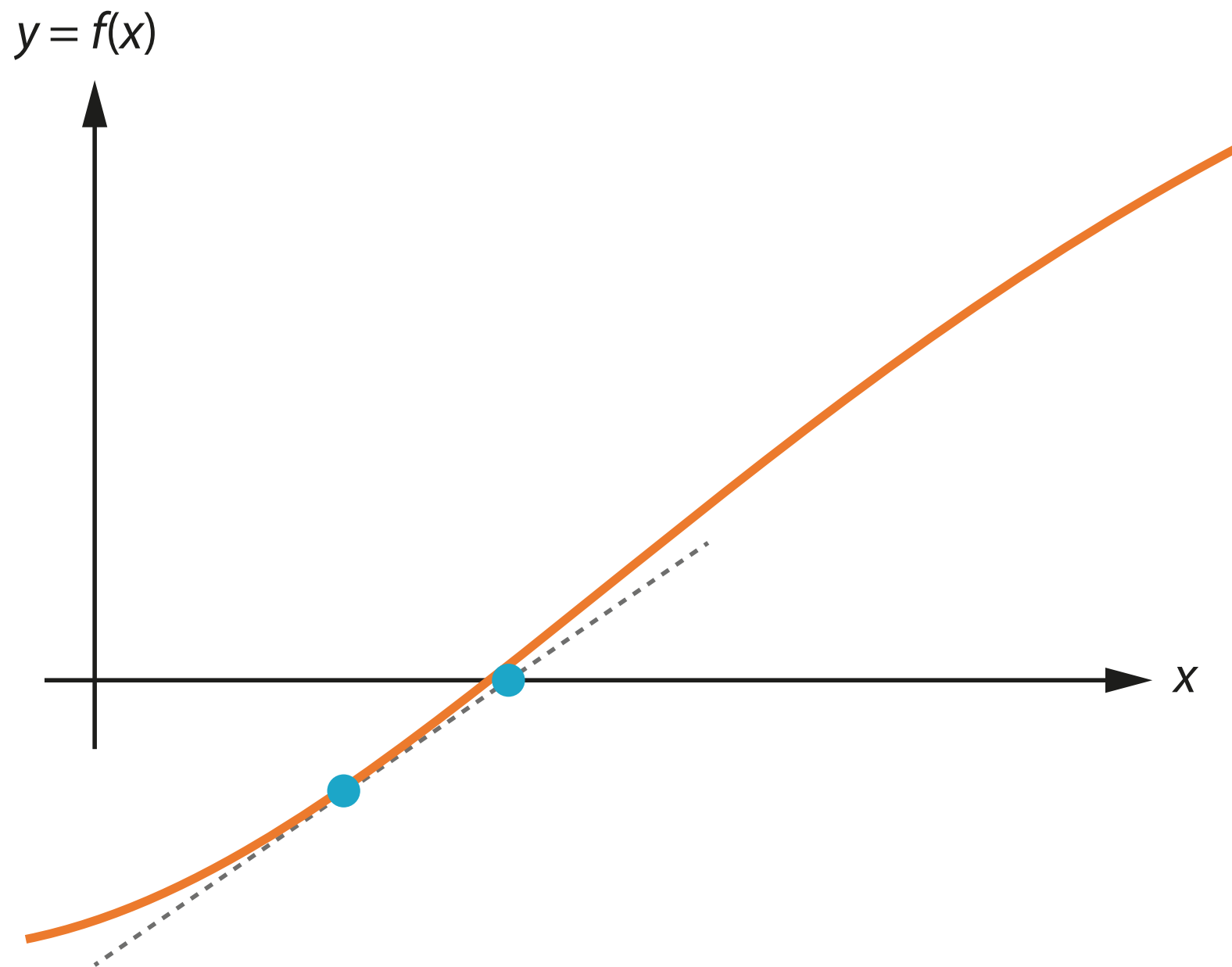
predict x_1 (assuming local linearity)

example: Newton-Raphson method



calculate $f(x_1)$

example: Newton-Raphson method



$$x_2 = x_1 - f(x_1)/f'(x_1)$$

Newton-Raphson geometry optimisation

We want to find points of zero force.

$$F = -g \qquad g = \frac{\partial E}{\partial x} = 0$$

\therefore work with 1st and 2nd derivatives of PES:

$$x_{n+1} = x_n - \frac{f'(x_n)}{f''(x_n)}$$

In multiple dimensions:

$$g_i = W_{ij}(\partial x_j) \qquad W_{ij} = \left(\frac{\partial^2 E}{\partial x_i \partial x_j} \right)$$

$$x_{n+1} = x_n - (W_{ij,n})^{-1} g_{i,n}$$

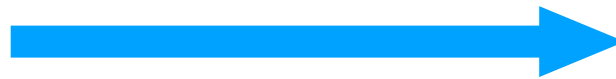
how to calculate $E(r)$ (and derivatives)?

“atomistic” modelling hierarchy

more degrees of freedom

shorter timescales / lengthscales

higher computational cost

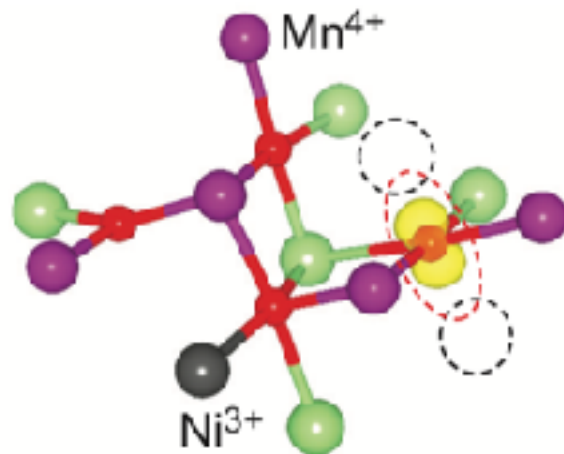


fewer degrees of freedom

longer timescales / lengthscales

lower computational cost

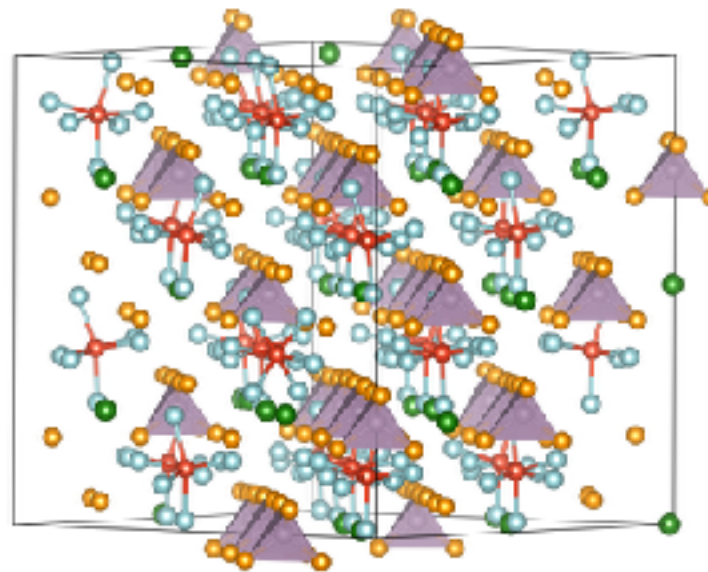
“ab initio”
electronic structure



$$E = \langle \psi | \hat{H} | \psi \rangle$$

DFT

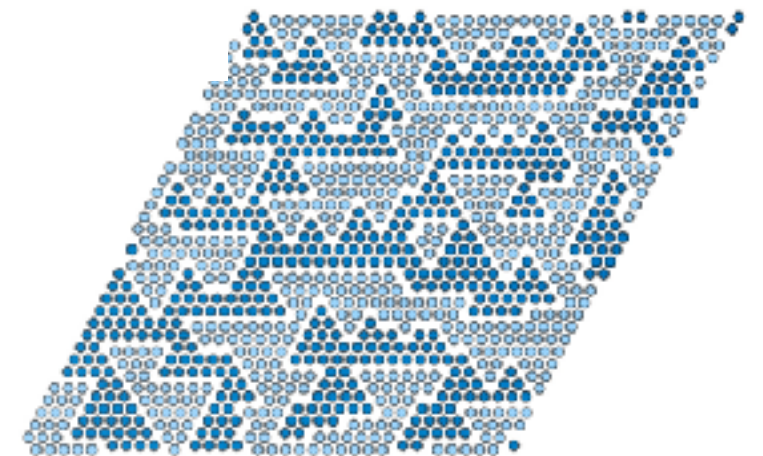
classical



$$E = F \left(\left\{ r_{ij} \right\} \right)$$

molecular mechanics /
interatomic potentials

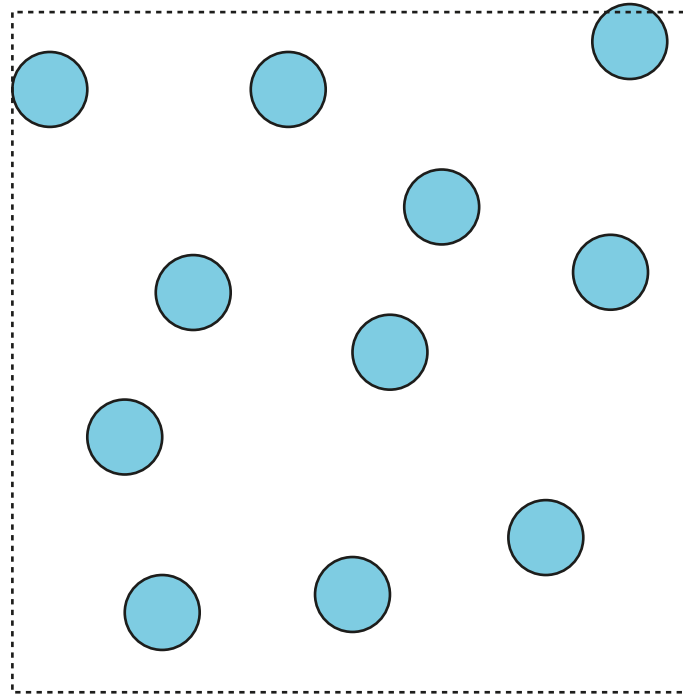
effective Hamiltonian
(e.g. lattice models)



$$E = F \left(\left\{ \sigma_i \right\} \right)$$

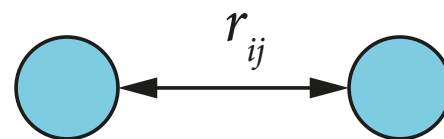
cluster expansion

“classical models”



analytical expression used to calculate the energy

e.g. simple “pairwise” model



$$U_{\text{total}} = \sum_{ij} F(r_{ij})$$

example 1: Lennard-Jones potential

$$U_{\text{LJ}} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

