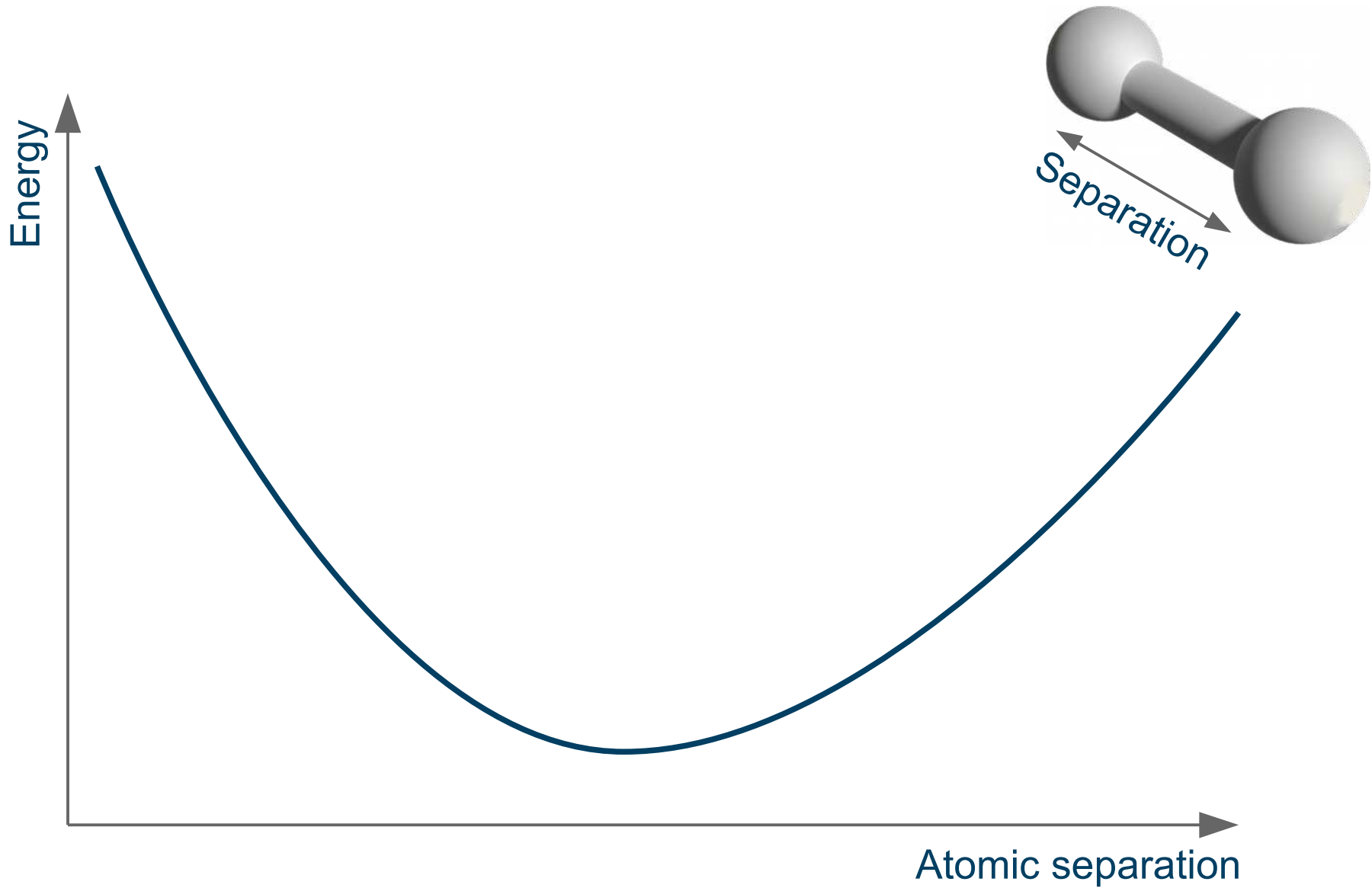


Vibrational modes, phonons, and atomic relaxation in diffusion Monte Carlo

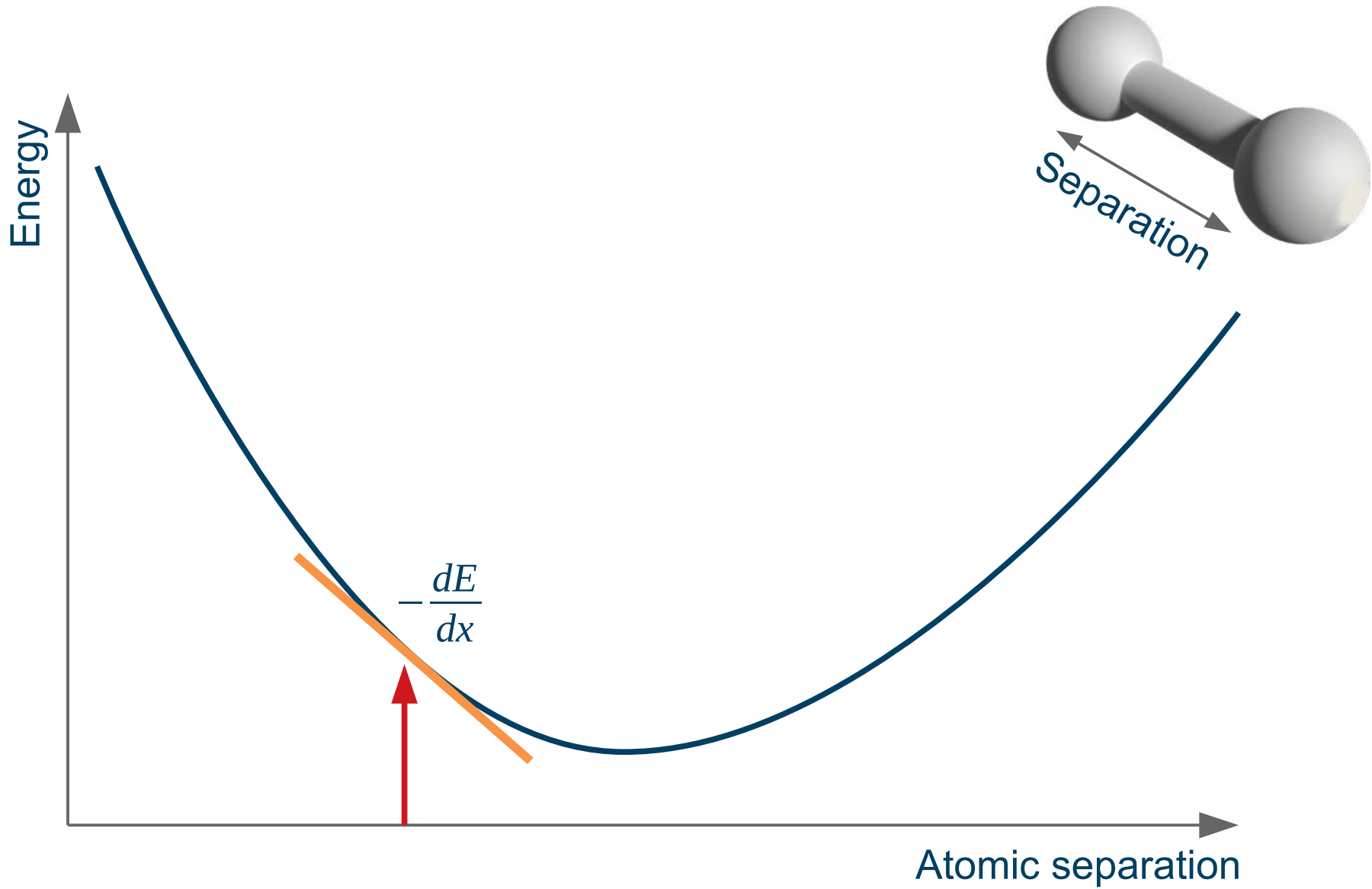
Yu Yang Liu, Bartholomew Andrews, Gareth Conduit

Theory of Condensed Matter group

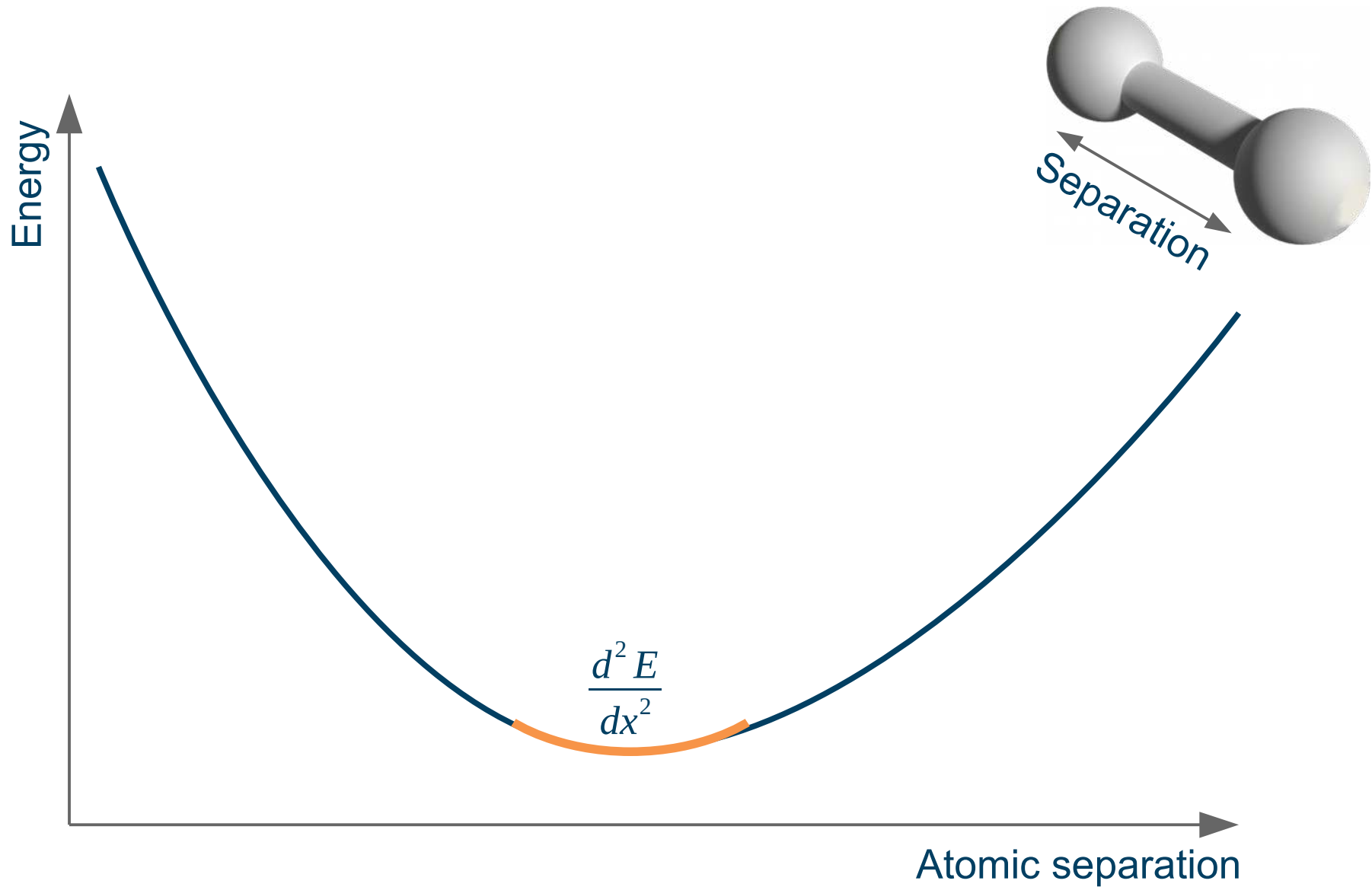
Energy landscape for a diatomic



Calculate the force



Calculating the matrix of force constants



Matrix of force constants

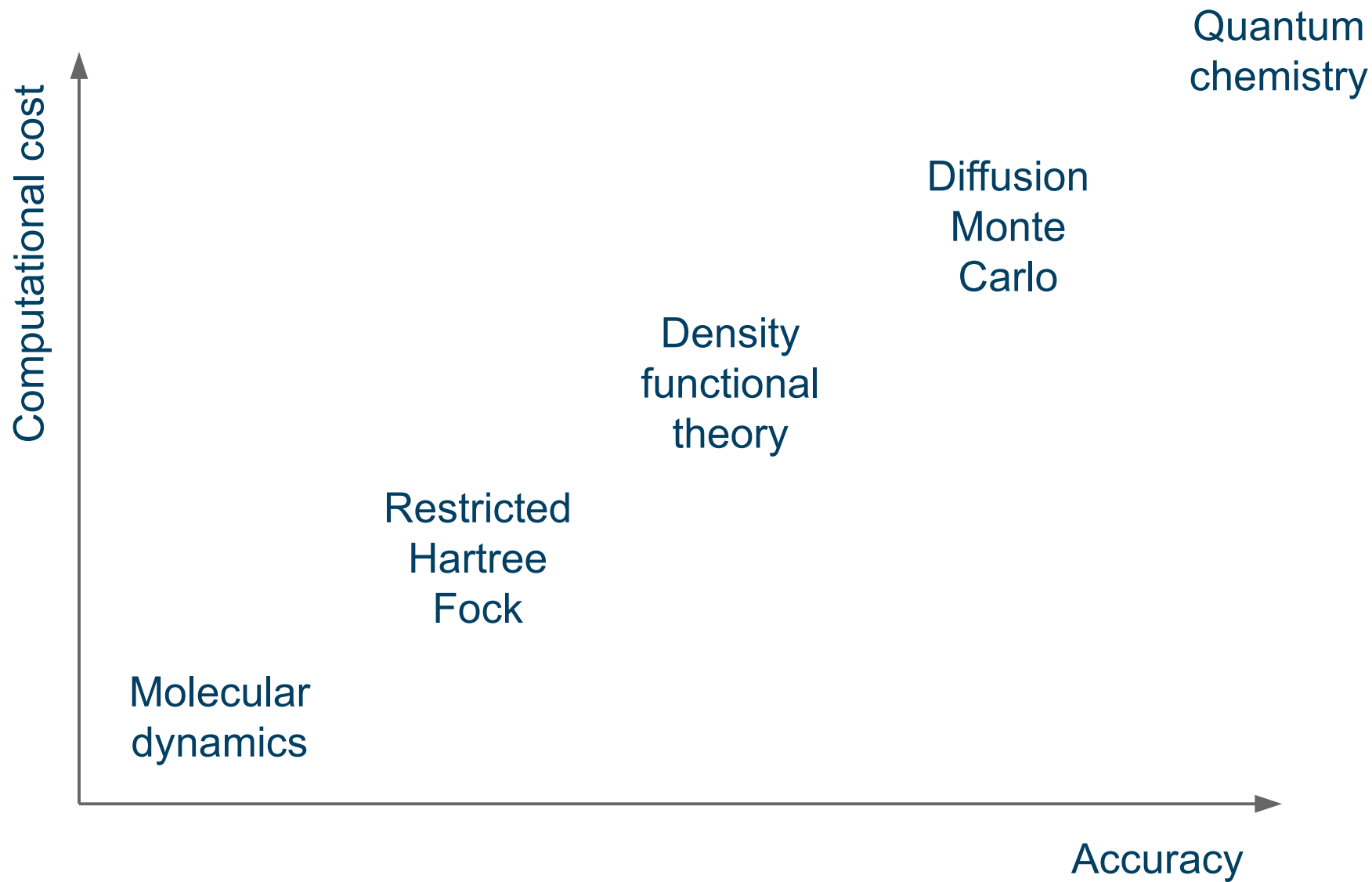
$$\begin{pmatrix} \frac{d^2 E}{dX_1 dX_1} & \frac{d^2 E}{dX_1 dX_2} & \dots & \frac{d^2 E}{dX_1 dX_N} \\ \frac{d^2 E}{dX_2 dX_1} & & & \frac{d^2 E}{dX_2 dX_N} \\ \vdots & & & \vdots \\ \frac{d^2 E}{dX_N dX_1} & \frac{d^2 E}{dX_N dX_2} & \dots & \frac{d^2 E}{dX_N dX_N} \end{pmatrix}$$

Relax atom positions

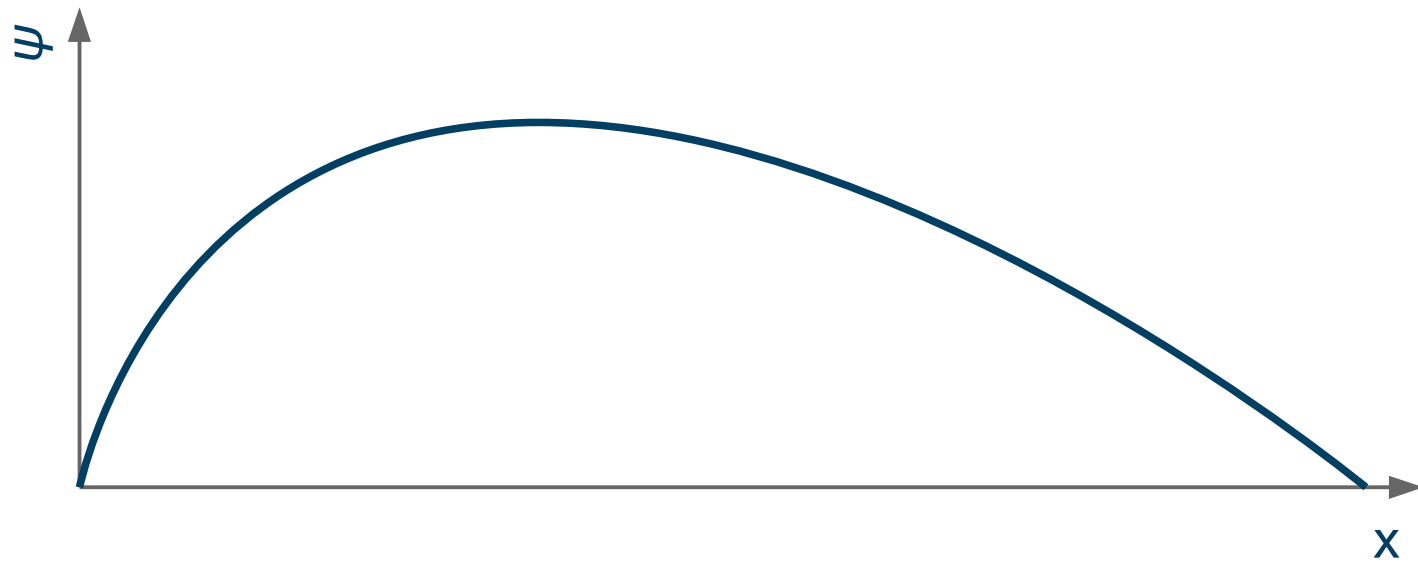
Study **vibrational modes** of molecules

Calculate **phonon** frequencies

Hierarchy of methods



Trial wavefunction

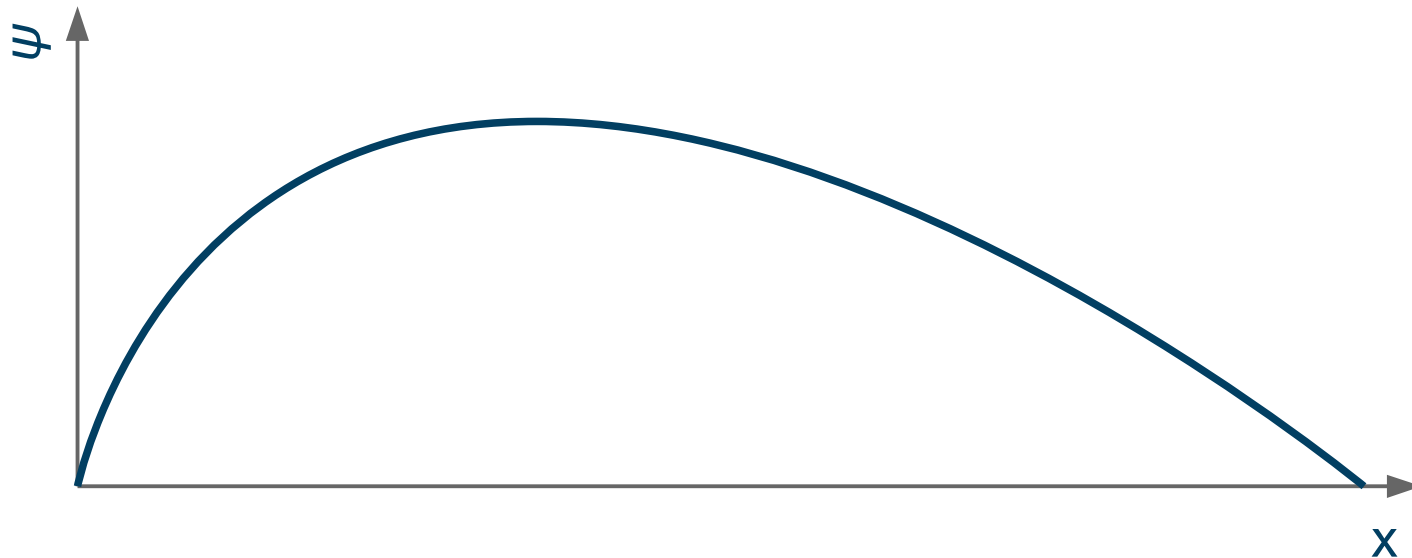


Diffusion Monte Carlo

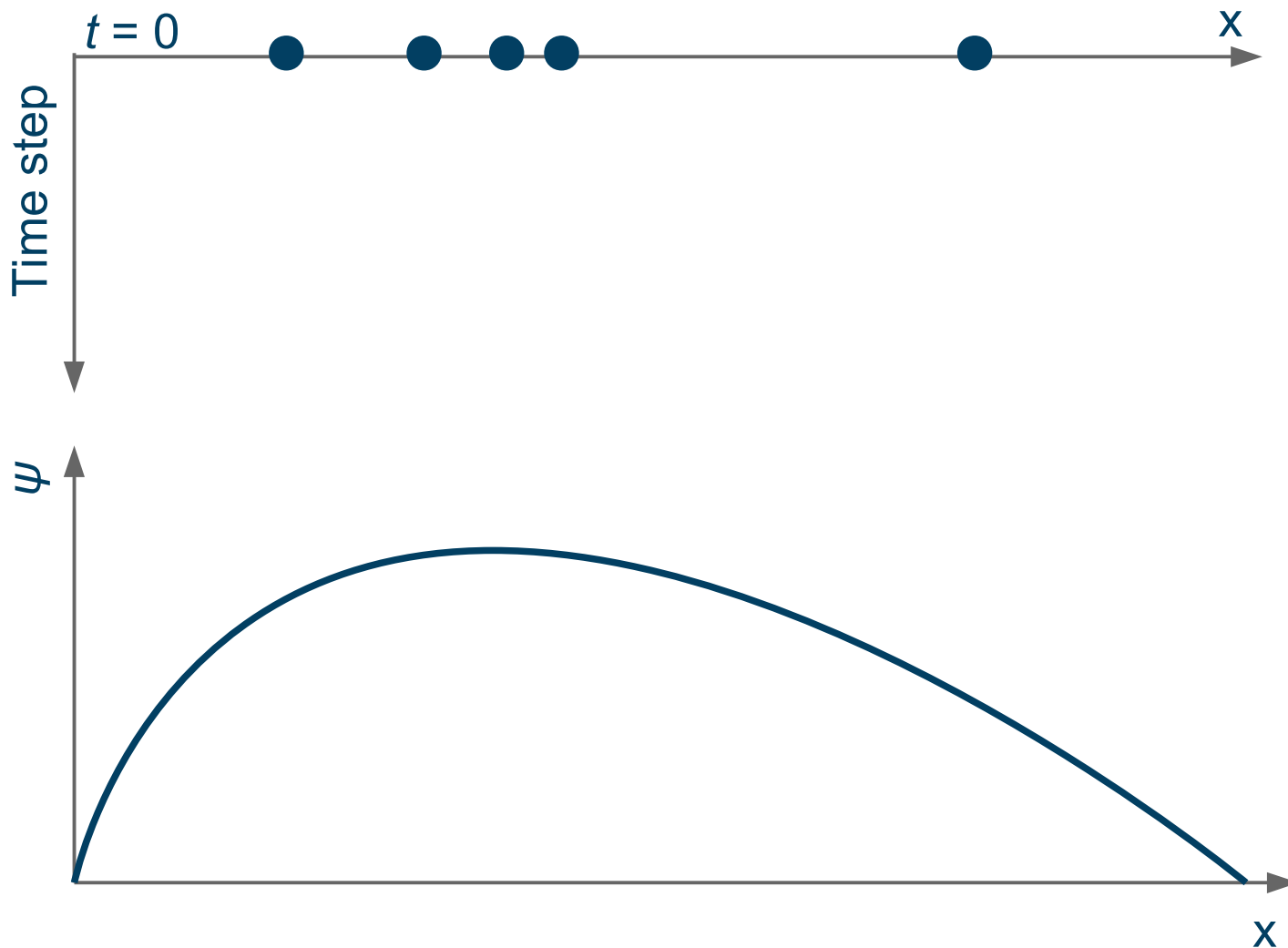
$$i \hbar \frac{d \psi}{d t} = H \psi$$

$$\frac{d \psi}{d \tau} = H \psi$$

$$\frac{d \psi}{d \tau} = - \frac{\nabla^2 \psi}{2 m}$$



$t=0$ configuration

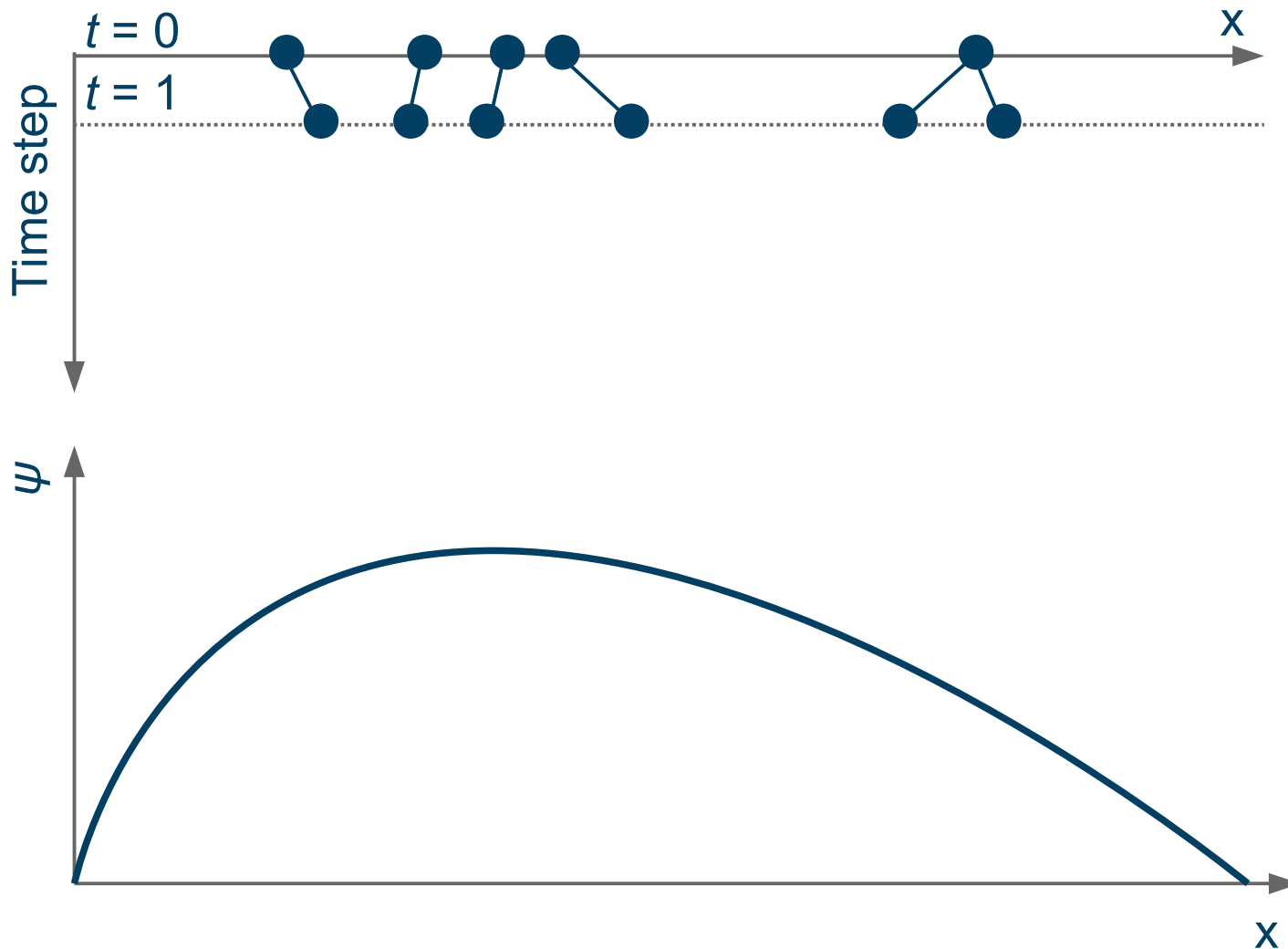


$$i \hbar \frac{d \psi}{d t} = H \psi$$

$$\frac{d \psi}{d \tau} = H \psi$$

$$\frac{d \psi}{d \tau} = -\frac{\nabla^2 \psi}{2 m}$$

Propagate forward in time

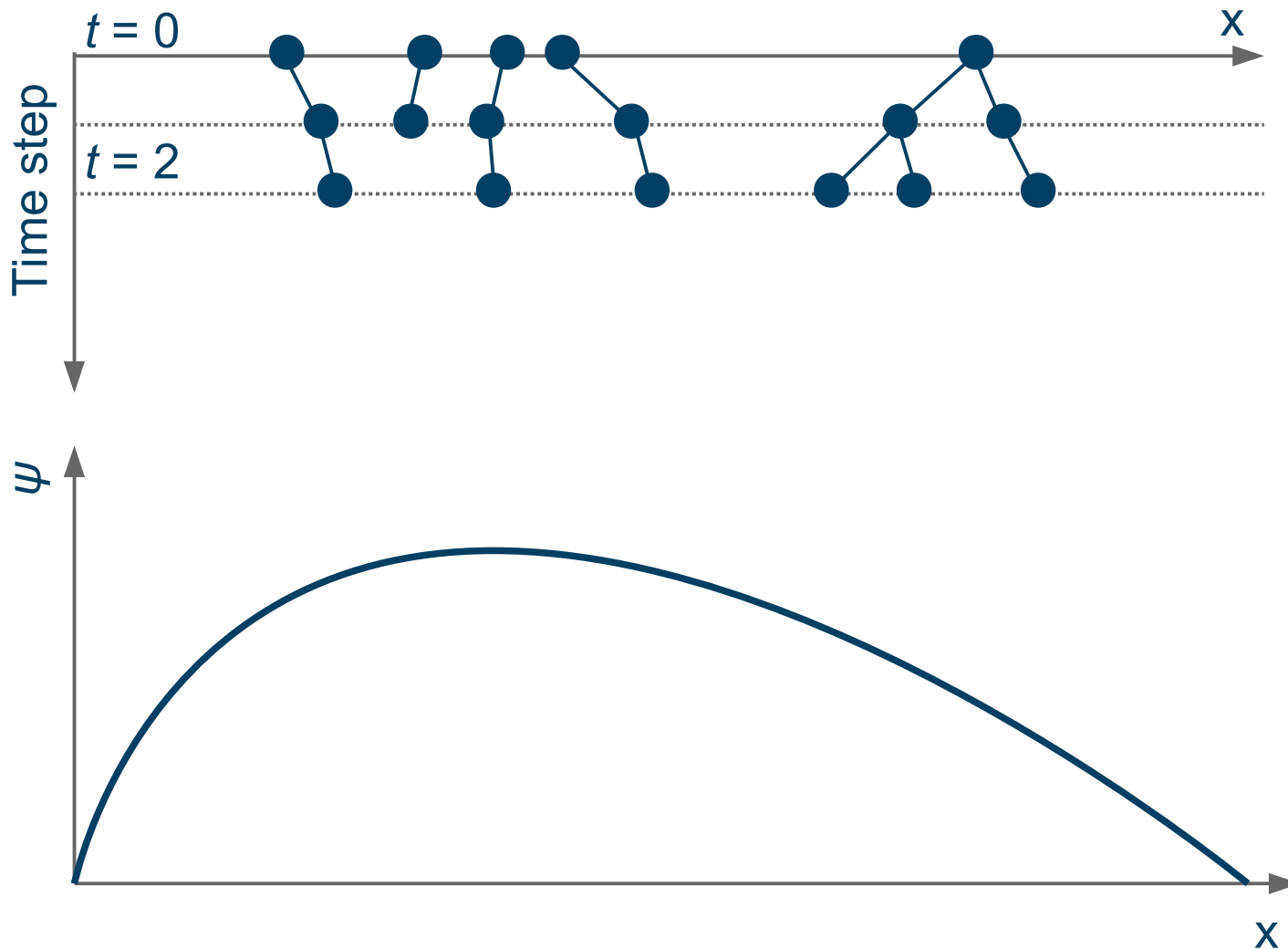


$$i \hbar \frac{d \psi}{d t} = H \psi$$

$$\frac{d \psi}{d \tau} = H \psi$$

$$\frac{d \psi}{d \tau} = -\frac{\nabla^2 \psi}{2 m}$$

Propagate forward in time

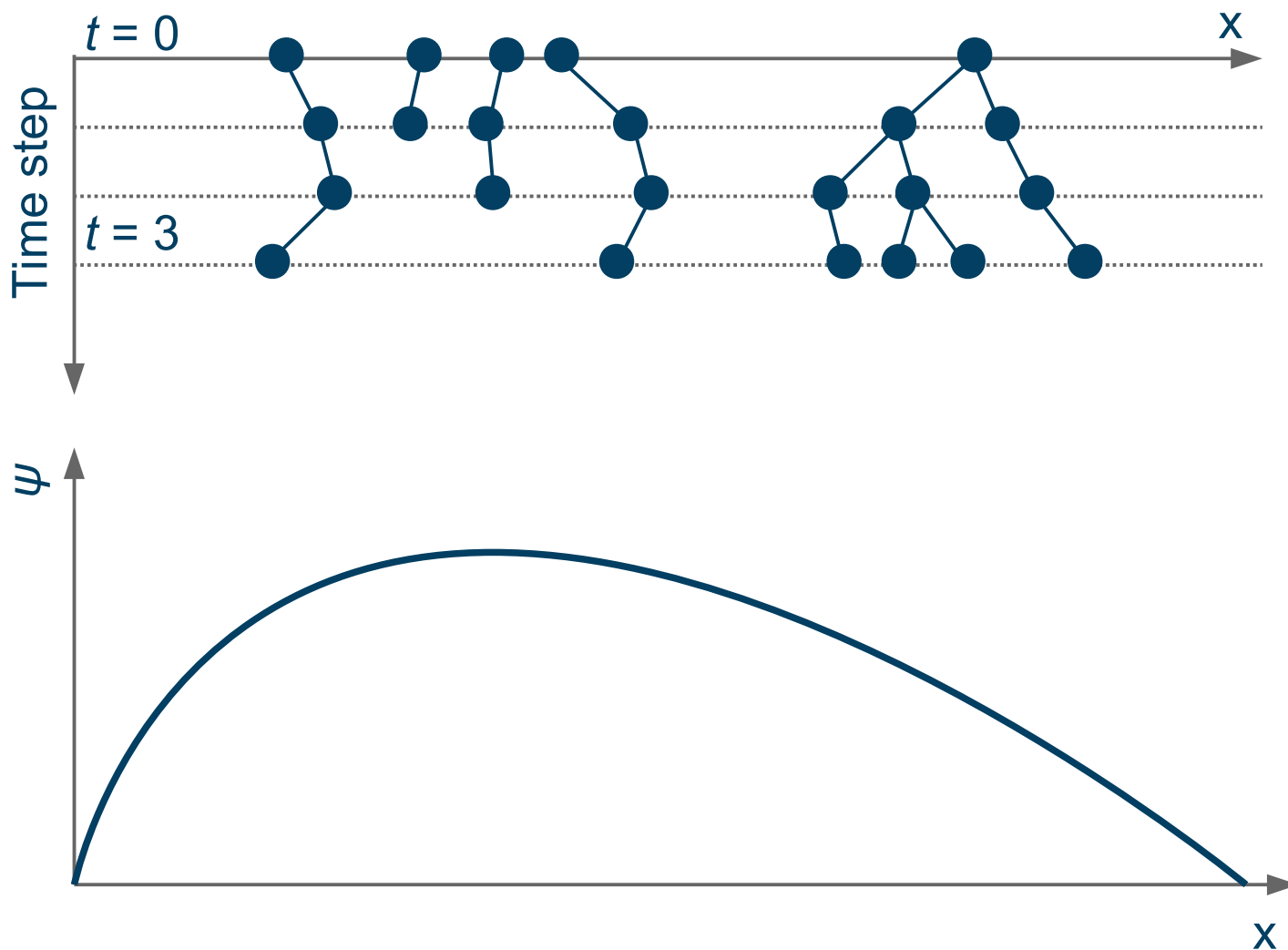


$$i \hbar \frac{d \psi}{d t} = H \psi$$

$$\frac{d \psi}{d \tau} = H \psi$$

$$\frac{d \psi}{d \tau} = -\frac{\nabla^2 \psi}{2 m}$$

Propagate forward in time

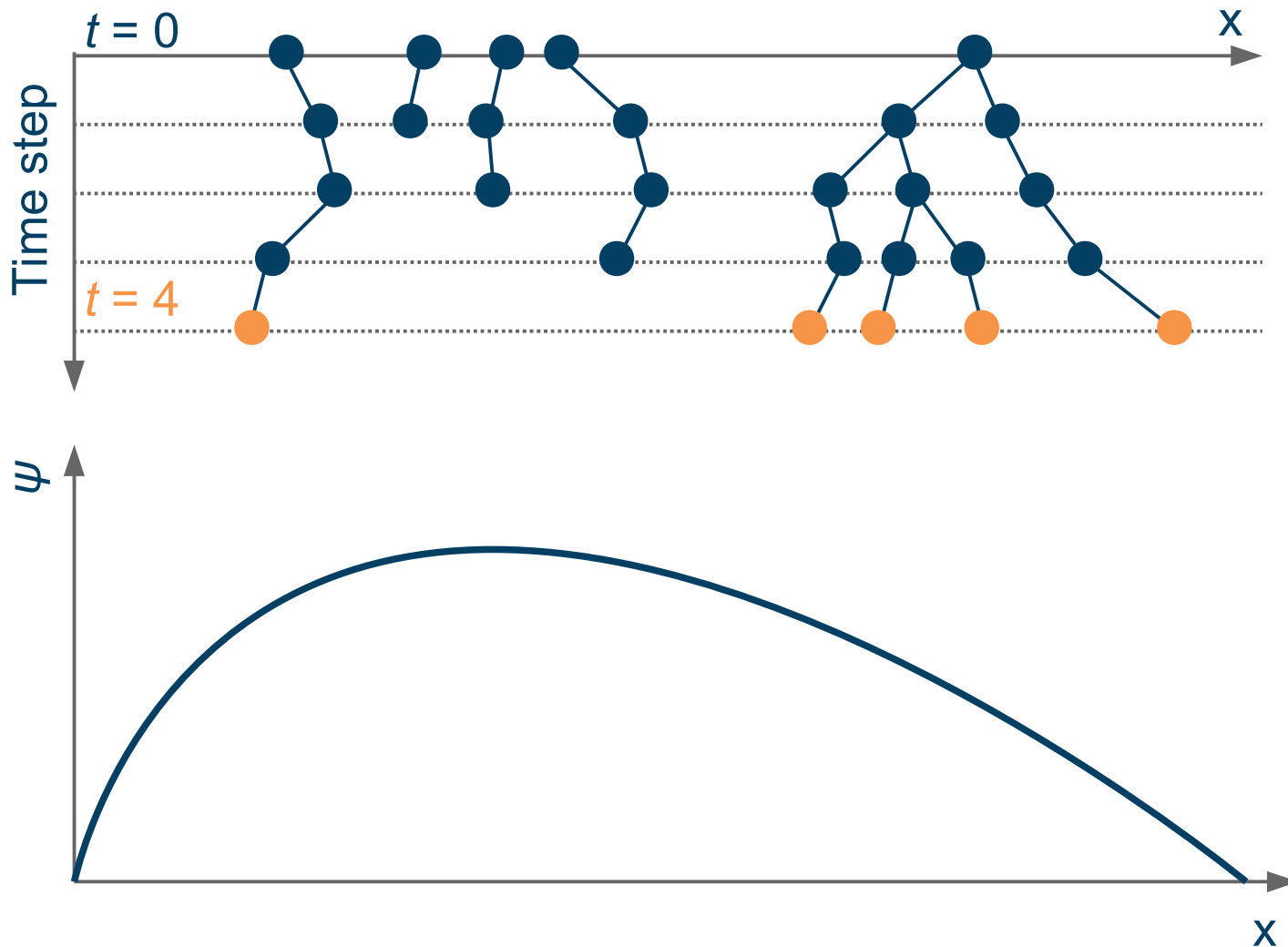


$$i \hbar \frac{d \psi}{d t} = H \psi$$

$$\frac{d \psi}{d \tau} = H \psi$$

$$\frac{d \psi}{d \tau} = -\frac{\nabla^2 \psi}{2 m}$$

Final time step

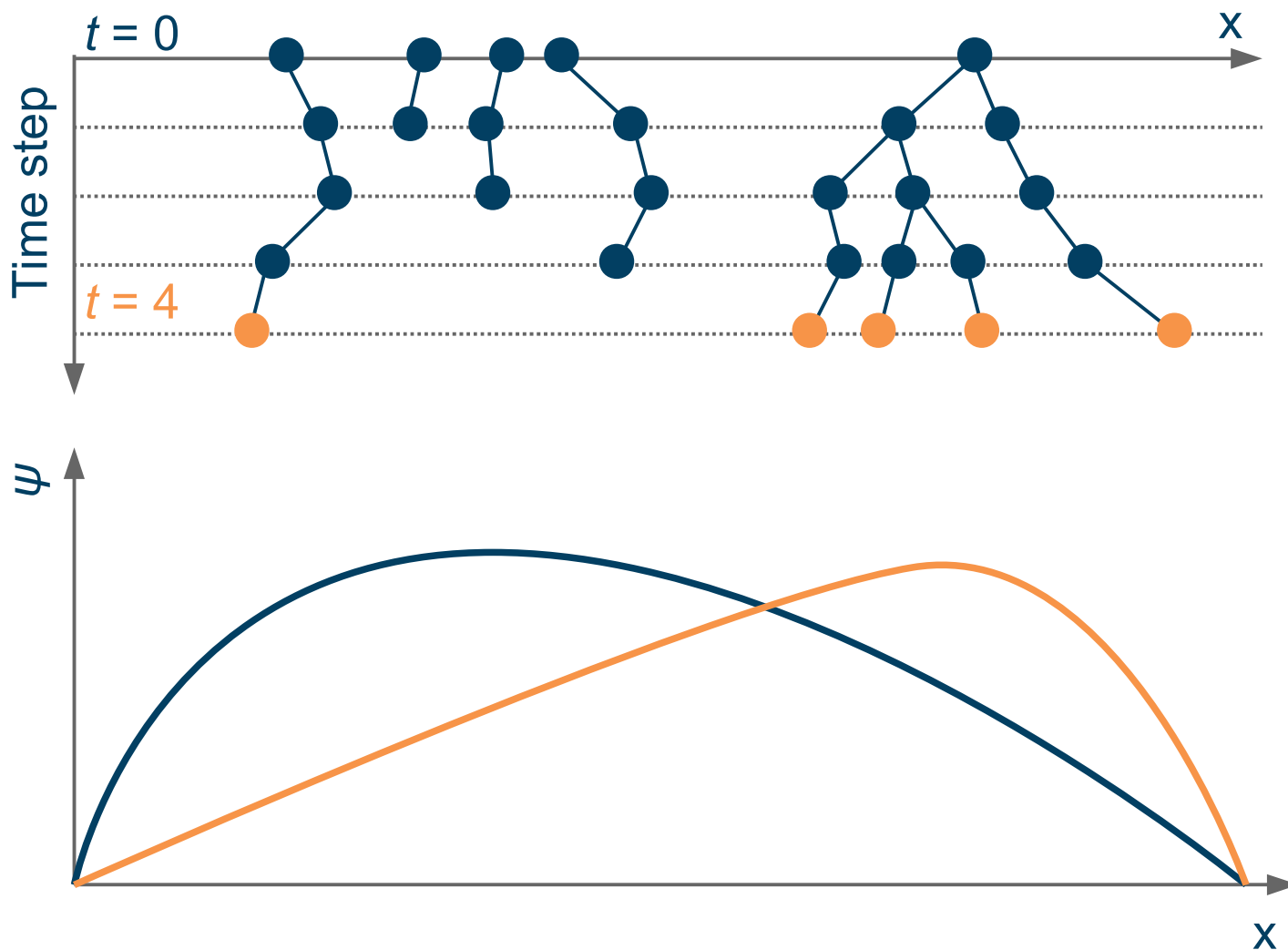


$$i \hbar \frac{d \psi}{d t} = H \psi$$

$$\frac{d \psi}{d \tau} = H \psi$$

$$\frac{d \psi}{d \tau} = -\frac{\nabla^2 \psi}{2 m}$$

Project out the ground state

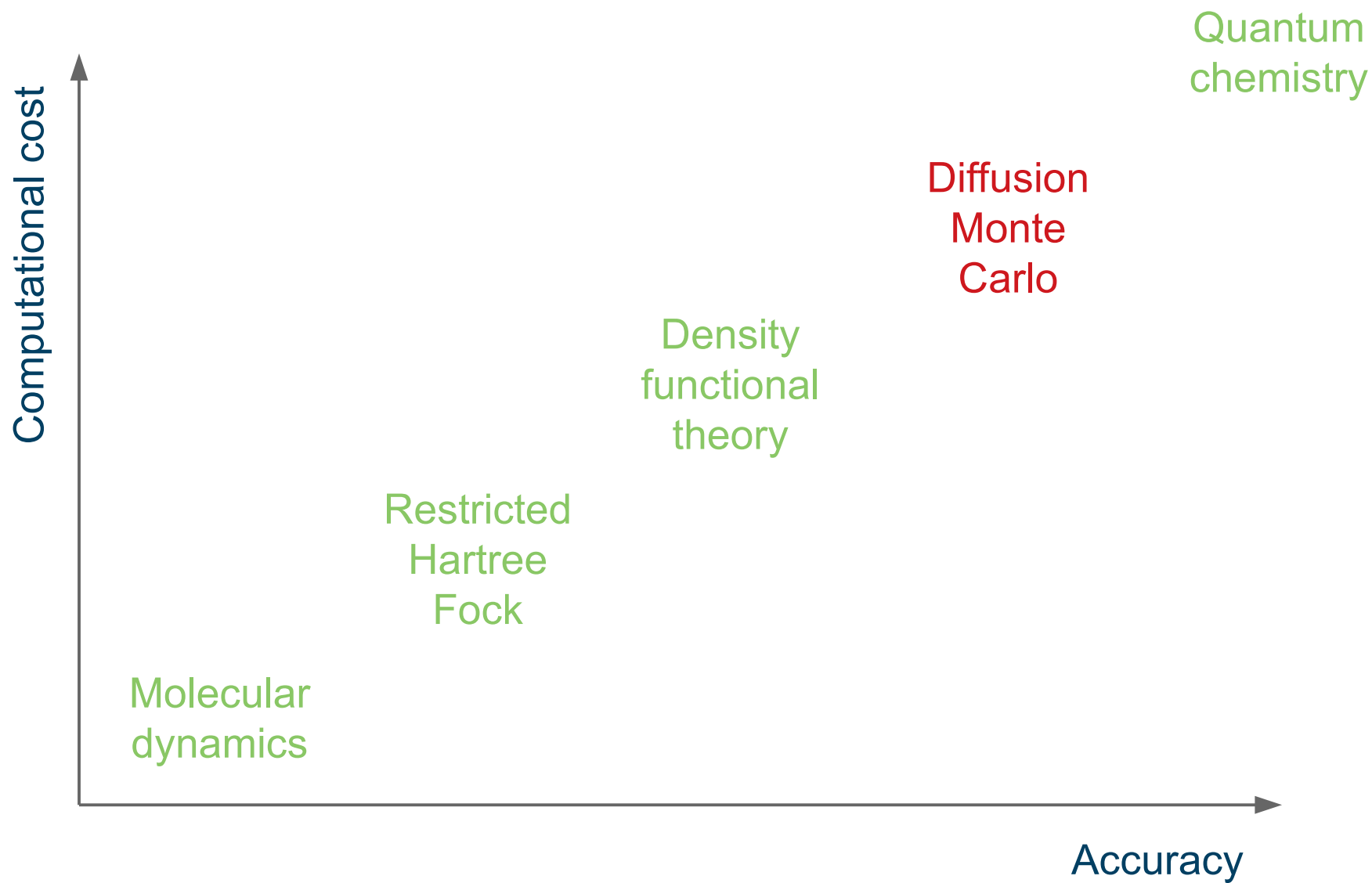


$$i \hbar \frac{d \psi}{d t} = H \psi$$

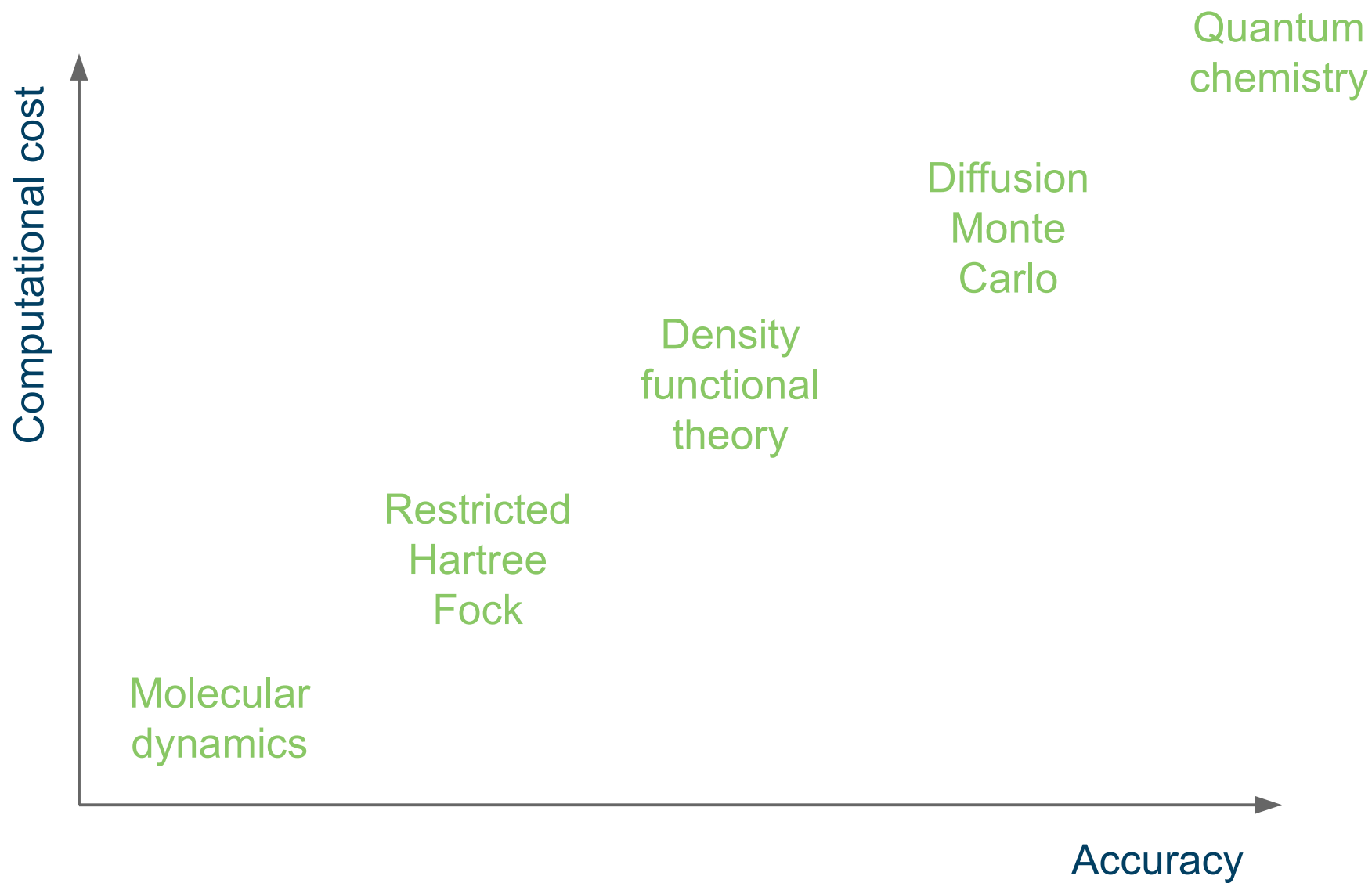
$$\frac{d \psi}{d \tau} = H \psi$$

$$\frac{d \psi}{d \tau} = -\frac{\nabla^2 \psi}{2 m}$$

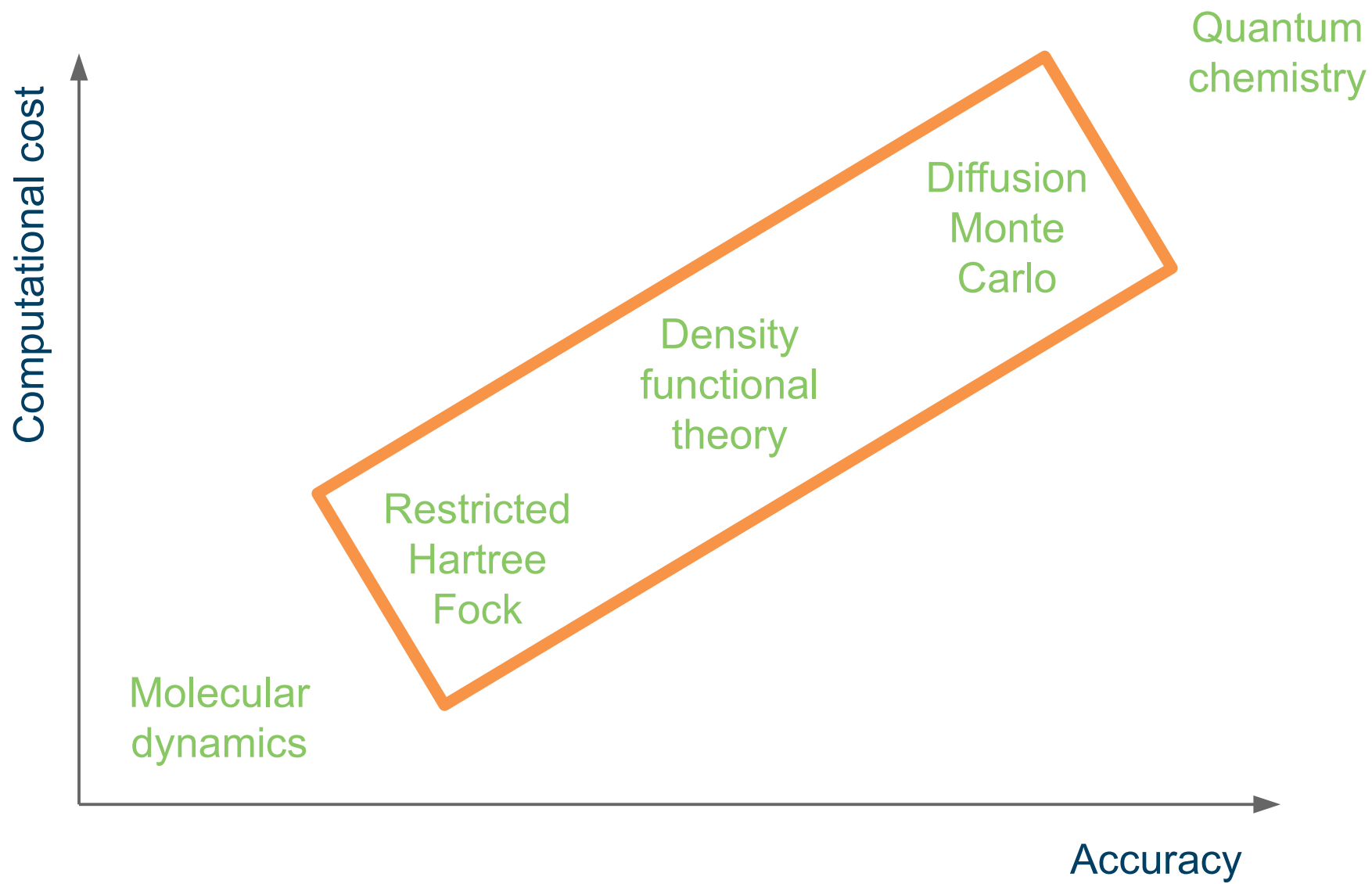
Hierarchy of methods



Hierarchy of methods



Hierarchy of methods



Diffusion Monte Carlo

$$E = \frac{\int \bar{\psi} H \psi d\mathbf{r}}{\int |\psi|^2 d\mathbf{r}}$$

Diffusion Monte Carlo

The diagram illustrates the ground state energy equation, $E = \frac{\int \bar{\psi} H \psi d\mathbf{r}}{\int |\psi|^2 d\mathbf{r}}$, with labels and arrows pointing to its components:

- Total energy**: Points to the energy E in the numerator.
- Hamiltonian**: Points to the operator H in the numerator.
- Vector of all electron positions**: Points to the integration variable $d\mathbf{r}$ in the numerator.
- Electron wavefunction**: Points to the wavefunction ψ in the denominator.

$$E = \frac{\int \bar{\psi} H \psi d\mathbf{r}}{\int |\psi|^2 d\mathbf{r}}$$

Calculation of force

$$\frac{dE}{d\mathbf{R}_I} = \frac{\int \bar{\psi} \frac{dH}{d\mathbf{R}_I} \psi d\mathbf{r}}{\int |\psi|^2 d\mathbf{r}} - \frac{2 \int \bar{\psi} (H - E) \frac{d\psi}{d\mathbf{R}_I} d\mathbf{r}}{\int |\psi|^2 d\mathbf{r}}$$

Calculation of force

Total energy

Displacement of I^{th} nucleus

Hamiltonian

Vector of all electron positions

Electron wavefunction

$$\frac{dE}{d\mathbf{R}_I} = \frac{\int \bar{\psi} \frac{dH}{d\mathbf{R}_I} \psi d\mathbf{r}}{\int |\psi|^2 d\mathbf{r}} - \frac{2 \int \bar{\psi} (H - E) \frac{d\psi}{d\mathbf{R}_I} d\mathbf{r}}{\int |\psi|^2 d\mathbf{r}}$$

Matrix of force constants

$$\begin{aligned} \frac{d^2 E}{d \mathbf{R}_I d \mathbf{R}_J} = & \frac{\int \bar{\psi} \frac{d^2 H}{d \mathbf{R}_I d \mathbf{R}_J} \psi d \mathbf{r}}{\int |\psi|^2 d \mathbf{r}} + \frac{\int \bar{\psi} \left[\frac{d \psi}{d \mathbf{R}_I} \left(\psi^{-1} \frac{d H}{d \mathbf{R}_J} \psi - \frac{d E}{d \mathbf{R}_J} \right) + (I \leftrightarrow J) \right] d \mathbf{r}}{2 \int |\psi|^2 d \mathbf{r}} + c.c. \\ & + \frac{1}{\int |\psi|^2 d \mathbf{r}} \frac{d}{d \mathbf{R}_I} \left[\int \frac{d \bar{\psi}}{d \mathbf{R}_J} (H - E) \psi d \mathbf{r} + (I \leftrightarrow J) \right] + c.c. \end{aligned}$$

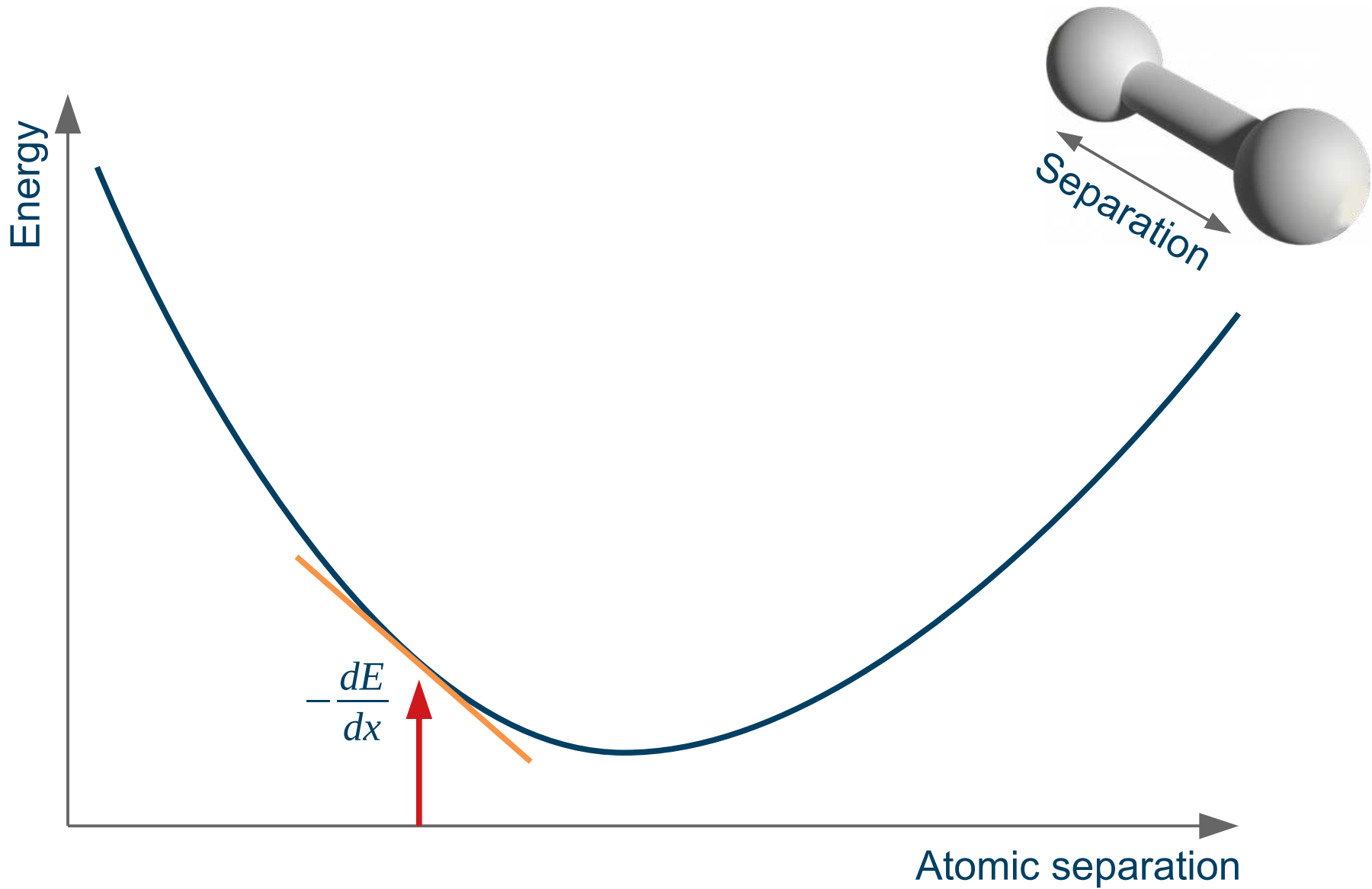
Matrix of force constants from numerical derivatives

Finite difference method leads to loss of accuracy

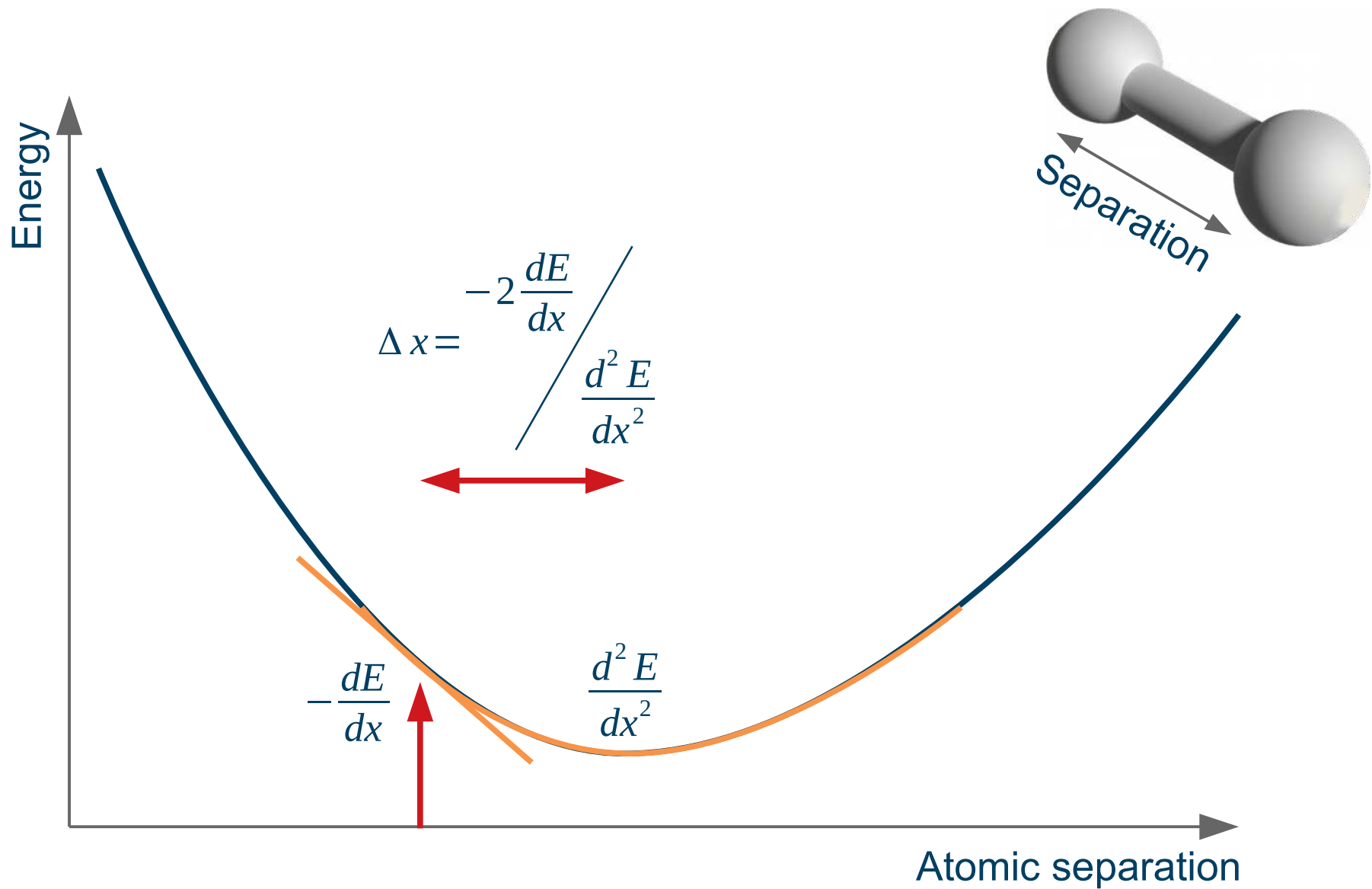
N atoms requires $9N^2$ calculations

$$\begin{pmatrix} \frac{d^2 E}{dX_1 dX_1} & \frac{d^2 E}{dX_1 dX_2} & \dots & \frac{d^2 E}{dX_1 dX_N} \\ \frac{d^2 E}{dX_2 dX_1} & & & \frac{d^2 E}{dX_2 dX_N} \\ \vdots & & & \vdots \\ \frac{d^2 E}{dX_N dX_1} & \frac{d^2 E}{dX_N dX_2} & \dots & \frac{d^2 E}{dX_N dX_N} \end{pmatrix}$$

Relax atomic positions




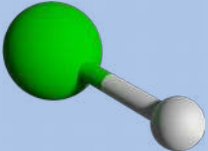
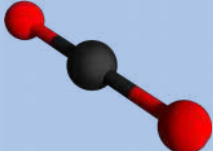
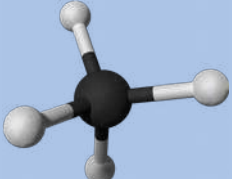
Relax atomic positions



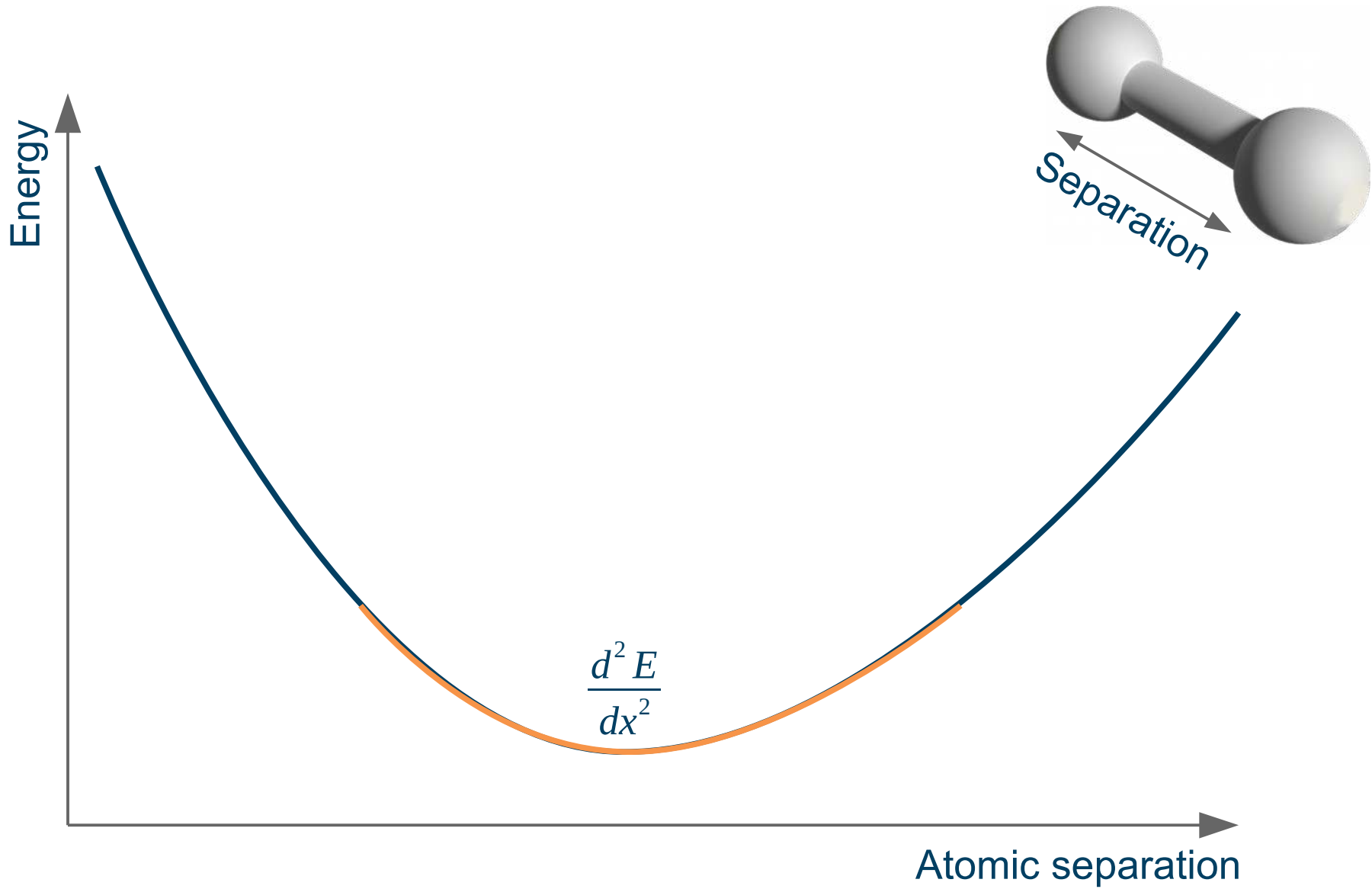
Bond length

Molecule	$x_{\text{RHF}} / \text{\AA}$	$x_{\text{DFT}} / \text{\AA}$	$x_{\text{DMC}} / \text{\AA}$	$x_{\text{exp}} / \text{\AA}$
 H ₂	0.736	0.753	0.74±0.01	0.74130

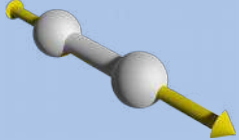
Bond lengths

Molecule	$x_{\text{RHF}} / \text{\AA}$	$x_{\text{DFT}} / \text{\AA}$	$x_{\text{DMC}} / \text{\AA}$	$x_{\text{exp}} / \text{\AA}$
 H ₂	0.736	0.753	0.74±0.01	0.74130
 HCl	1.260	1.286	1.27±0.05	1.275
 CO ₂	1.145	1.182	1.16±0.02	1.1598
 CH ₄	1.089	1.104	1.10±0.01	1.093

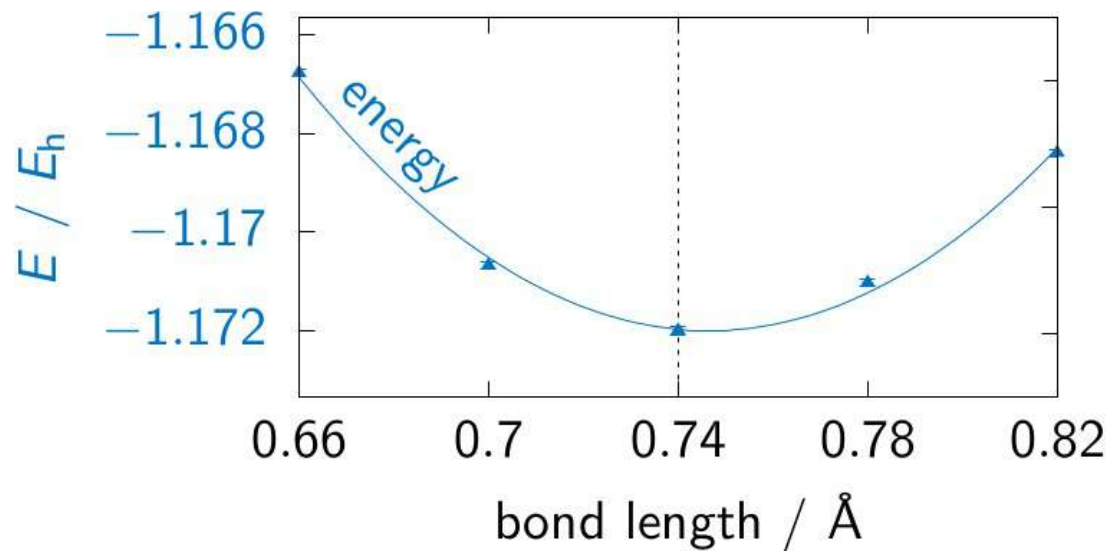
Relax atomic positions



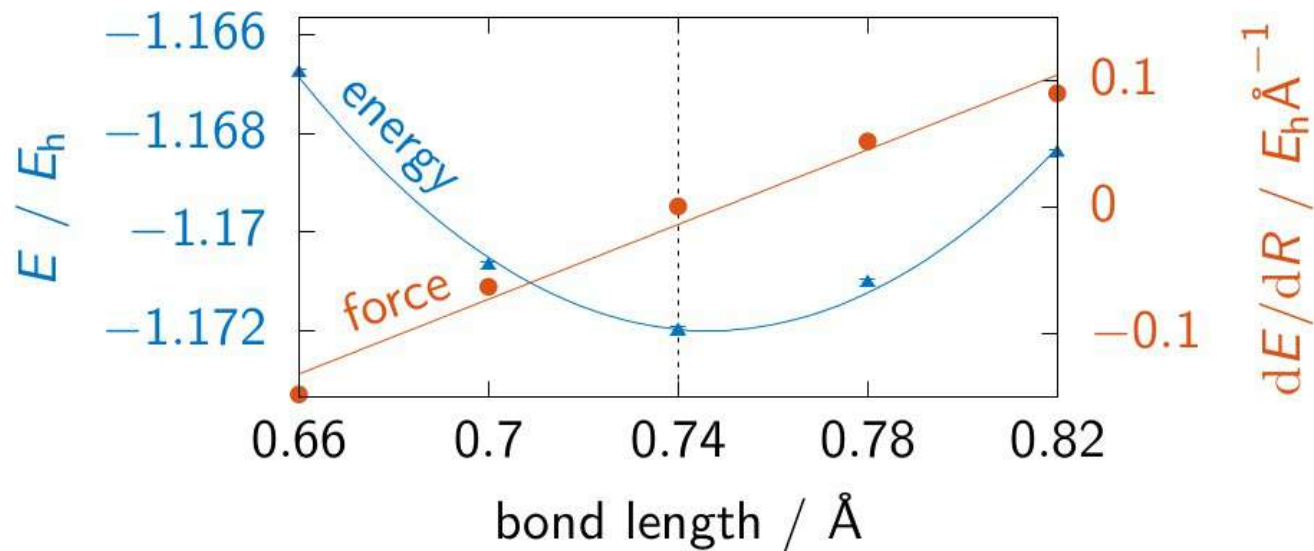
Diatomics

Molecule	$\omega_{\text{RHF}} / \text{cm}^{-1}$	$\omega_{\text{DFT}} / \text{cm}^{-1}$	$\omega_{\text{DMC}} / \text{cm}^{-1}$	$\omega_{\text{exp}} / \text{cm}^{-1}$
 H ₂	4379	4116	4170 ± 4	4161.1663 ± 0.0002

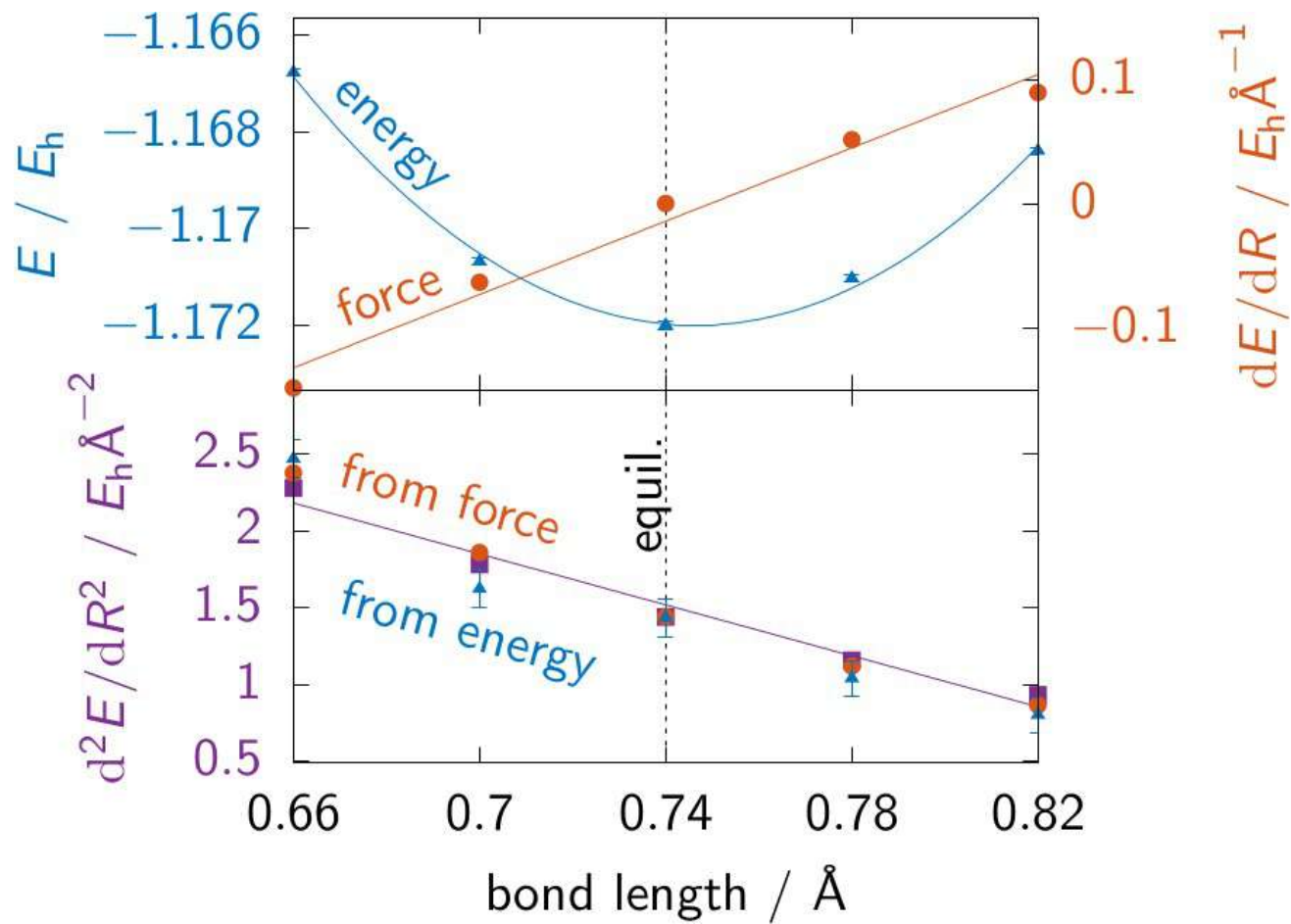
Hydrogen energy



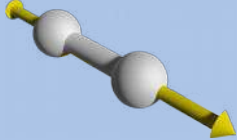
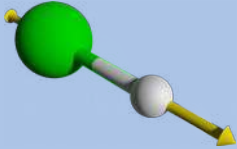
Hydrogen energy and force



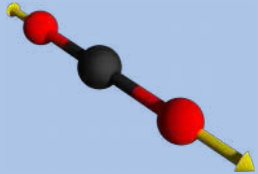
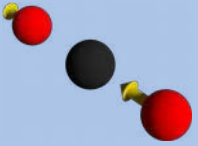
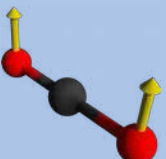
Hydrogen force constant



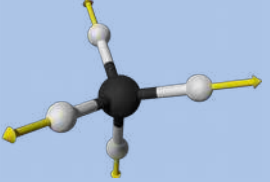
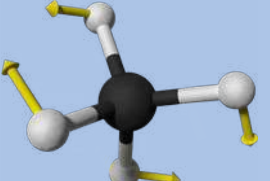
Diatomics

Molecule	$\omega_{\text{RHF}} / \text{cm}^{-1}$	$\omega_{\text{DFT}} / \text{cm}^{-1}$	$\omega_{\text{DMC}} / \text{cm}^{-1}$	$\omega_{\text{exp}} / \text{cm}^{-1}$
 H ₂	4379	4116	4170 ± 4	4161.1663 ± 0.0002
 HCl	3116	2894	3000 ± 8	2990.946 ± 0.003

Carbon dioxide

Mode	$\omega_{\text{RHF}} / \text{cm}^{-1}$	$\omega_{\text{DFT}} / \text{cm}^{-1}$	$\omega_{\text{DMC}} / \text{cm}^{-1}$	$\omega_{\text{exp}} / \text{cm}^{-1}$
	1468	1284	1350 ± 5	1333 ± 6
	2480	2297	2310 ± 6	2349 ± 1
	766	634	660 ± 2	667 ± 1

Methane

Mode	$\omega_{\text{RHF}} / \text{cm}^{-1}$	$\omega_{\text{DFT}} / \text{cm}^{-1}$	$\omega_{\text{DMC}} / \text{cm}^{-1}$	$\omega_{\text{exp}} / \text{cm}^{-1}$
	3101	3034	2890 ± 8	2917 ± 1
	1655	1496	1530 ± 9	1534 ± 1

Summary

Determine matrix of **force constants** from Diffusion Monte Carlo

Relax atomic **positions**

Calculate **vibrational modes** of molecules to better accuracy than density functional theory

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