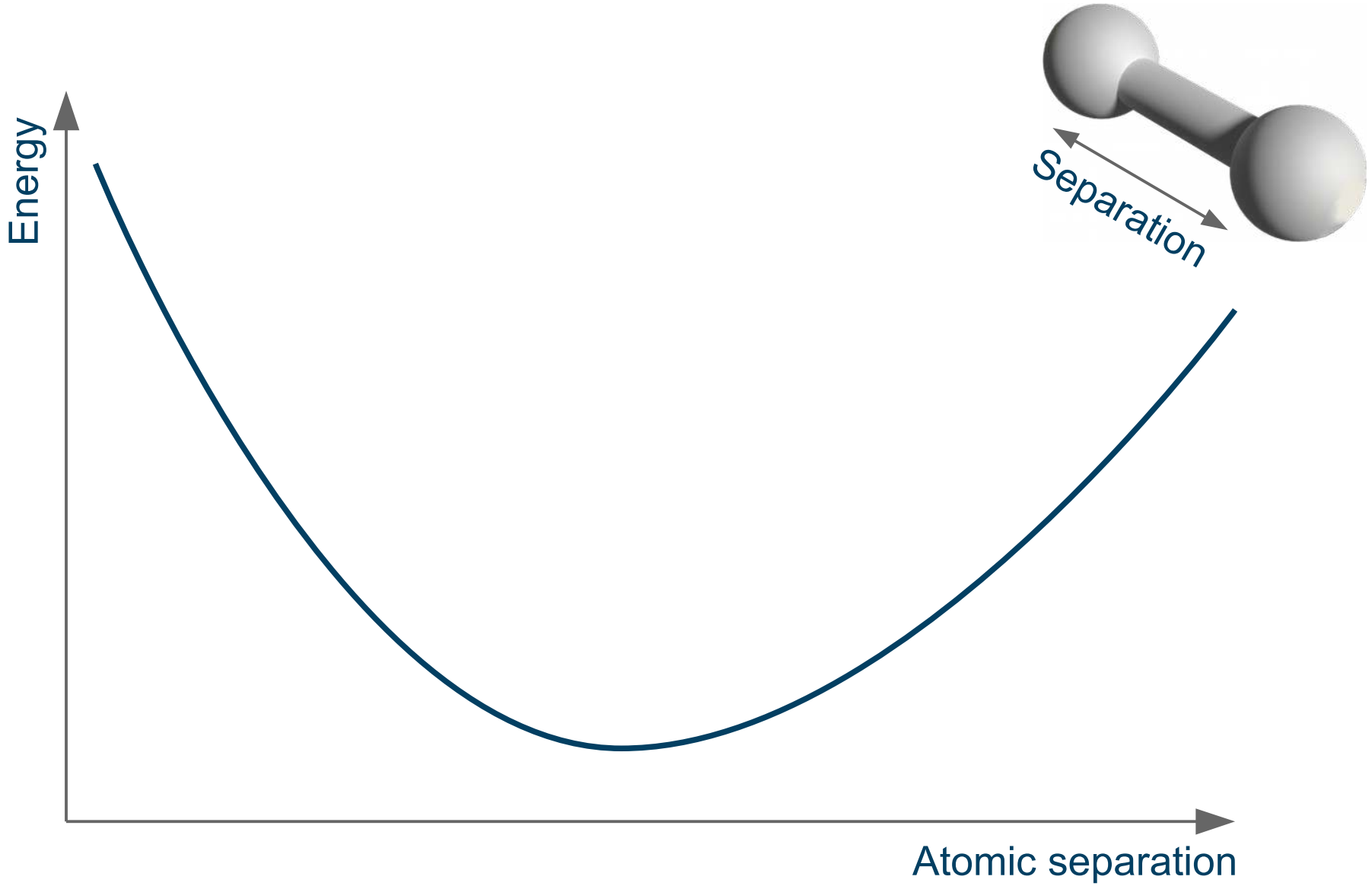
UNIVERSITY OF CAMBRIDGE

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

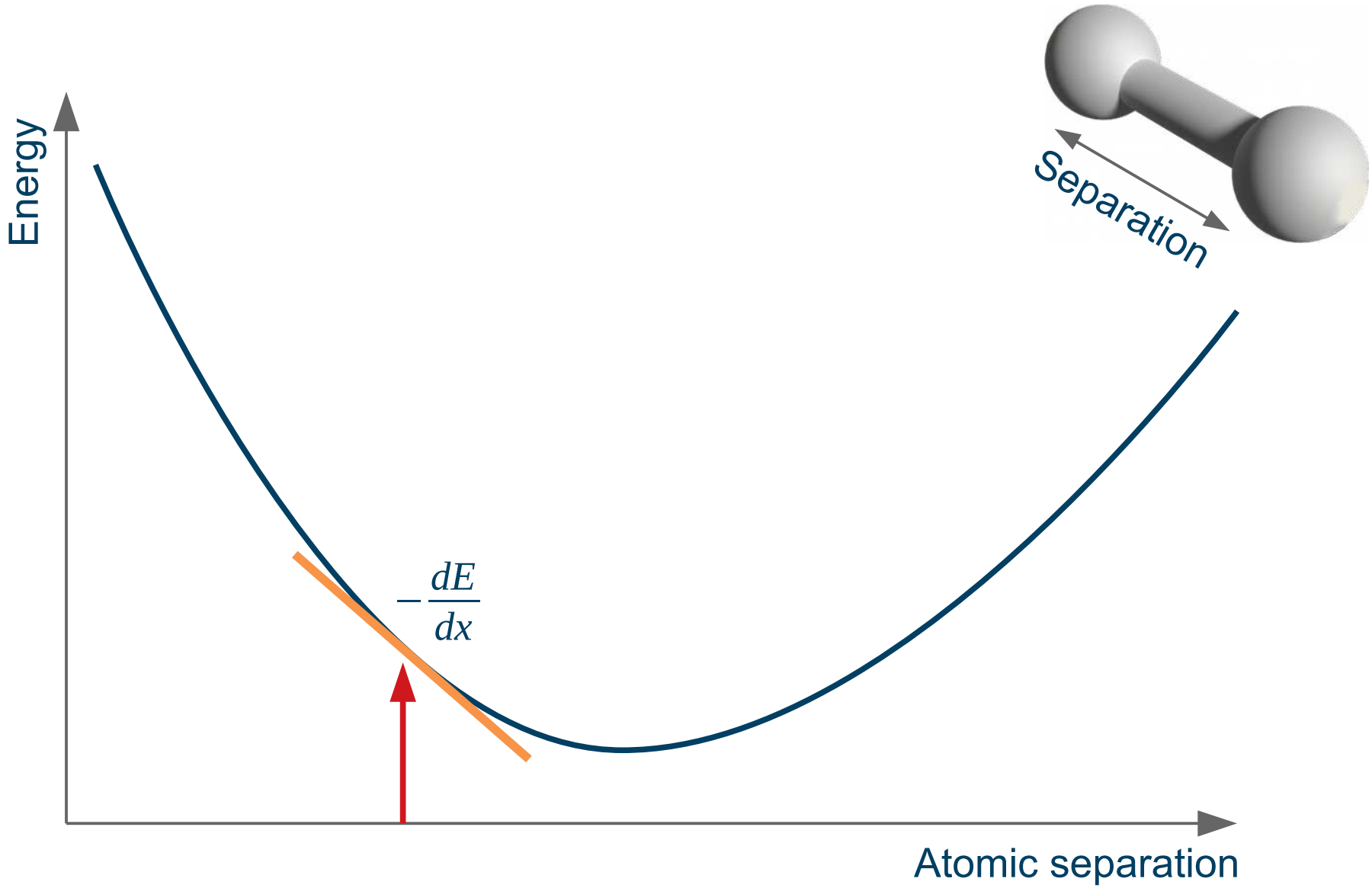
Yu Yang Liu, Bartholomew Andrews, Gareth Conduit

Theory of Condensed Matter group

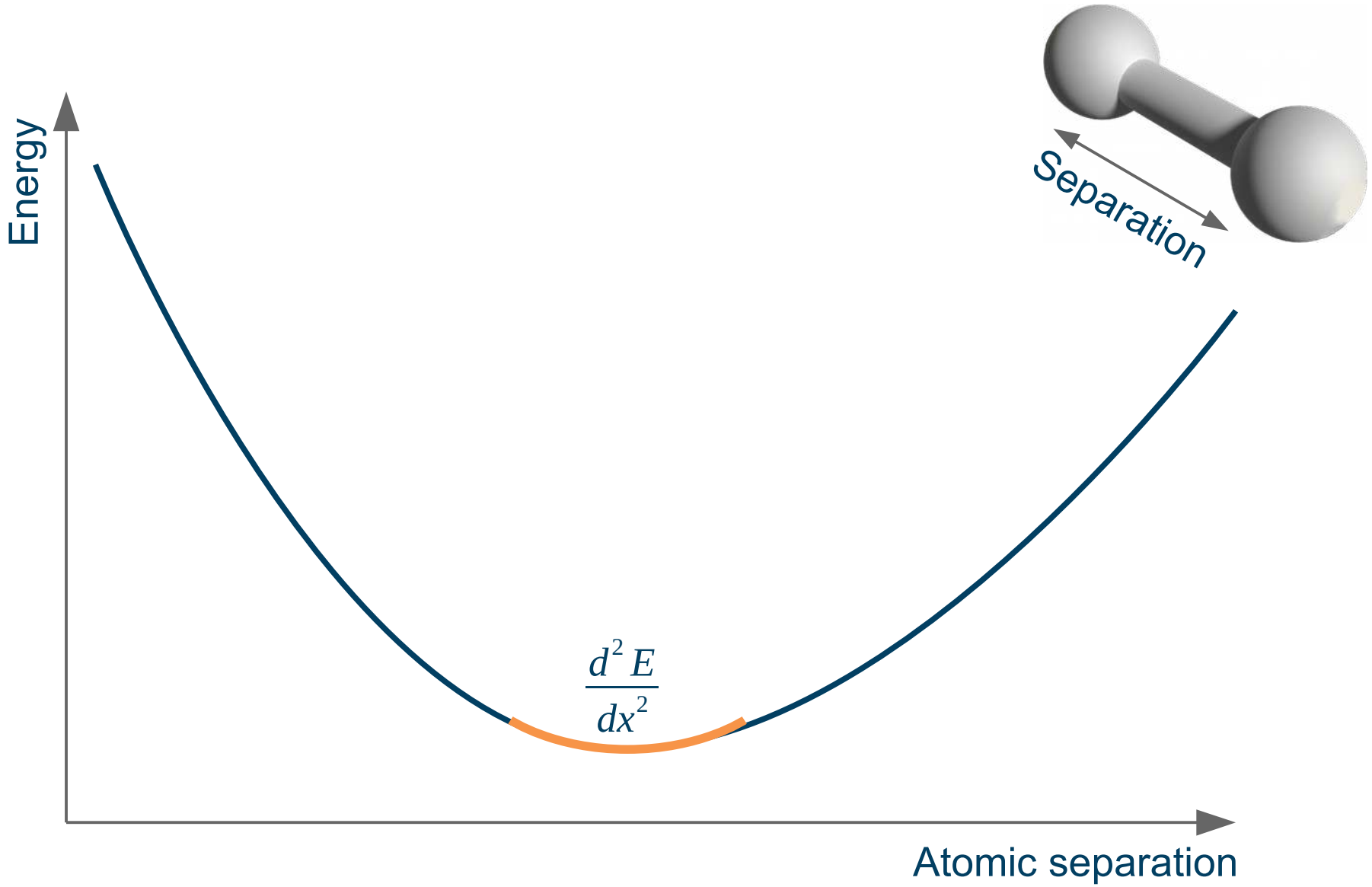
Energy landscape for a diatomic



Calculate the force



Calculating the matrix of force constants



Matrix of force constants

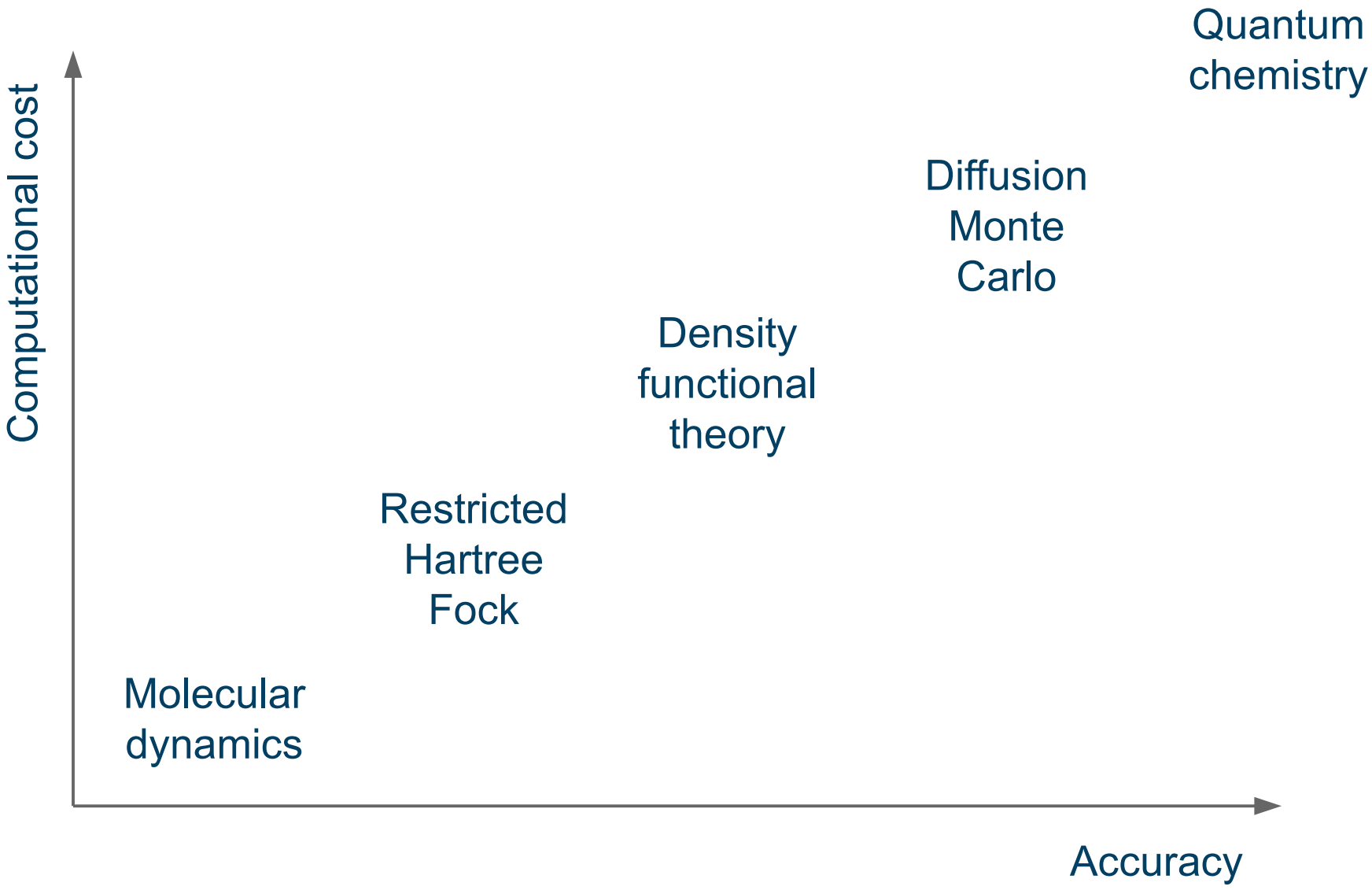
$$\begin{pmatrix} \frac{d^2E}{dX_1 dX_1} & \frac{d^2E}{dX_1 dX_2} & \cdots & \frac{d^2E}{dX_1 dX_N} \\ \frac{d^2E}{dX_2 dX_1} & & & \frac{d^2E}{dX_2 dX_N} \\ \vdots & & & \vdots \\ \frac{d^2E}{dX_N dX_1} & \frac{d^2E}{dX_N dX_2} & \cdots & \frac{d^2E}{dX_N dX_N} \end{pmatrix}$$

Relax atom positions

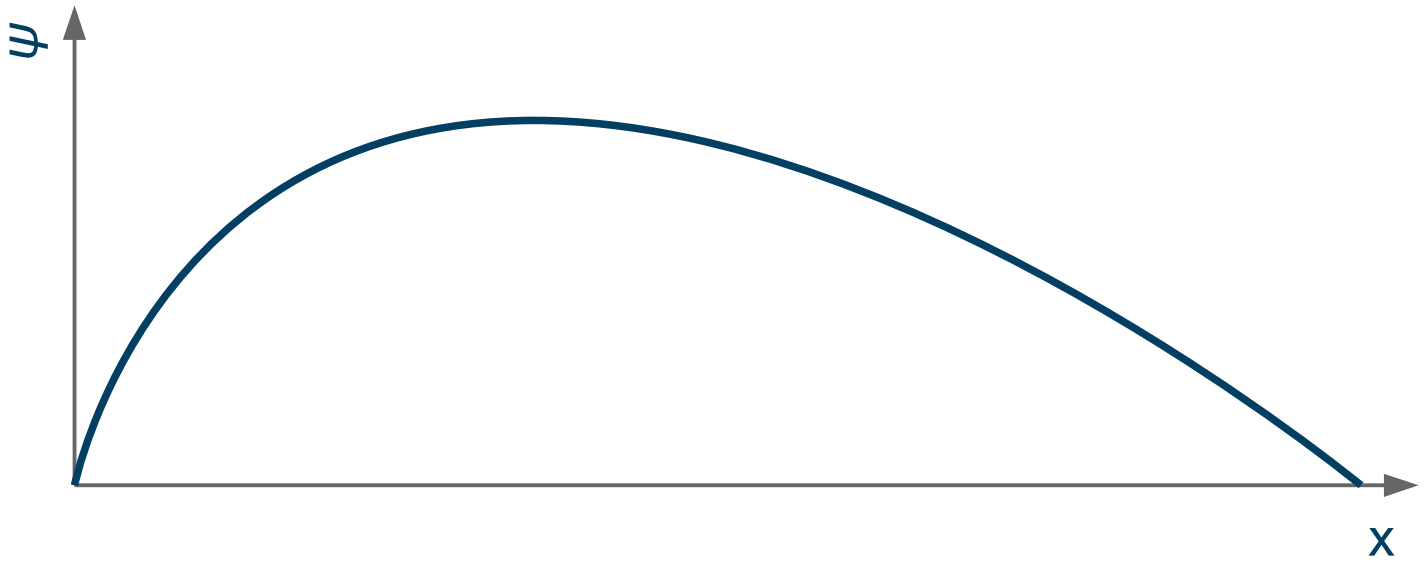
Study vibrational modes of molecules

Calculate phonon frequencies

Hierarchy of methods



Trial wavefunction

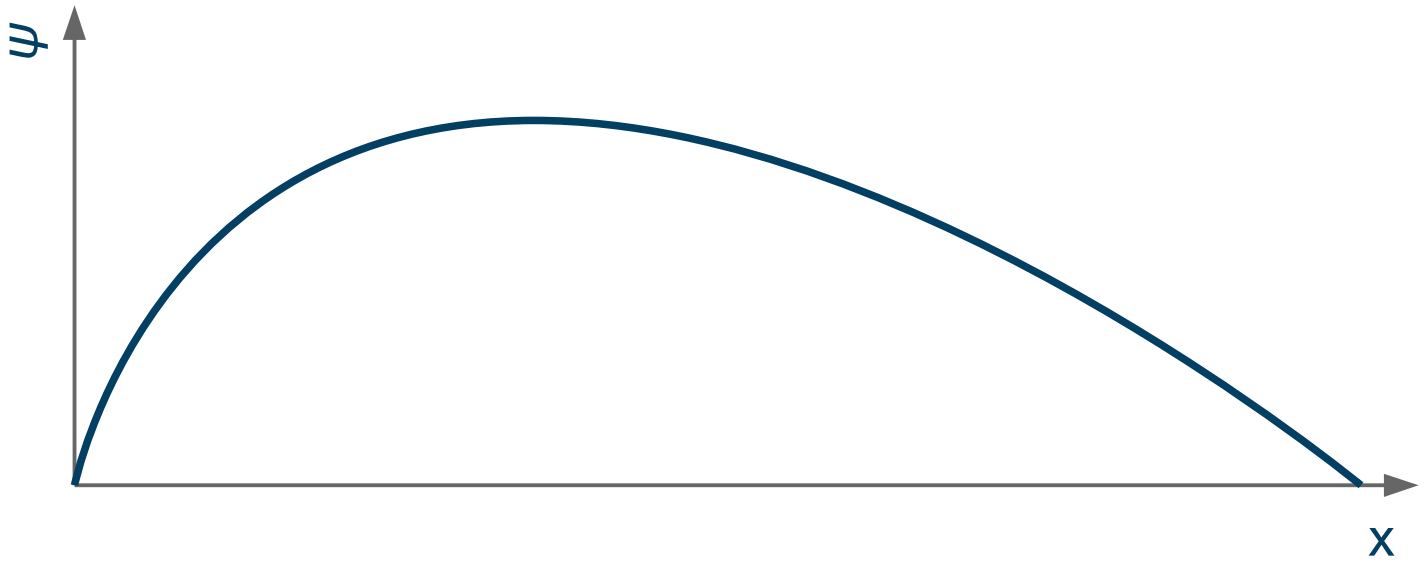


Diffusion Monte Carlo

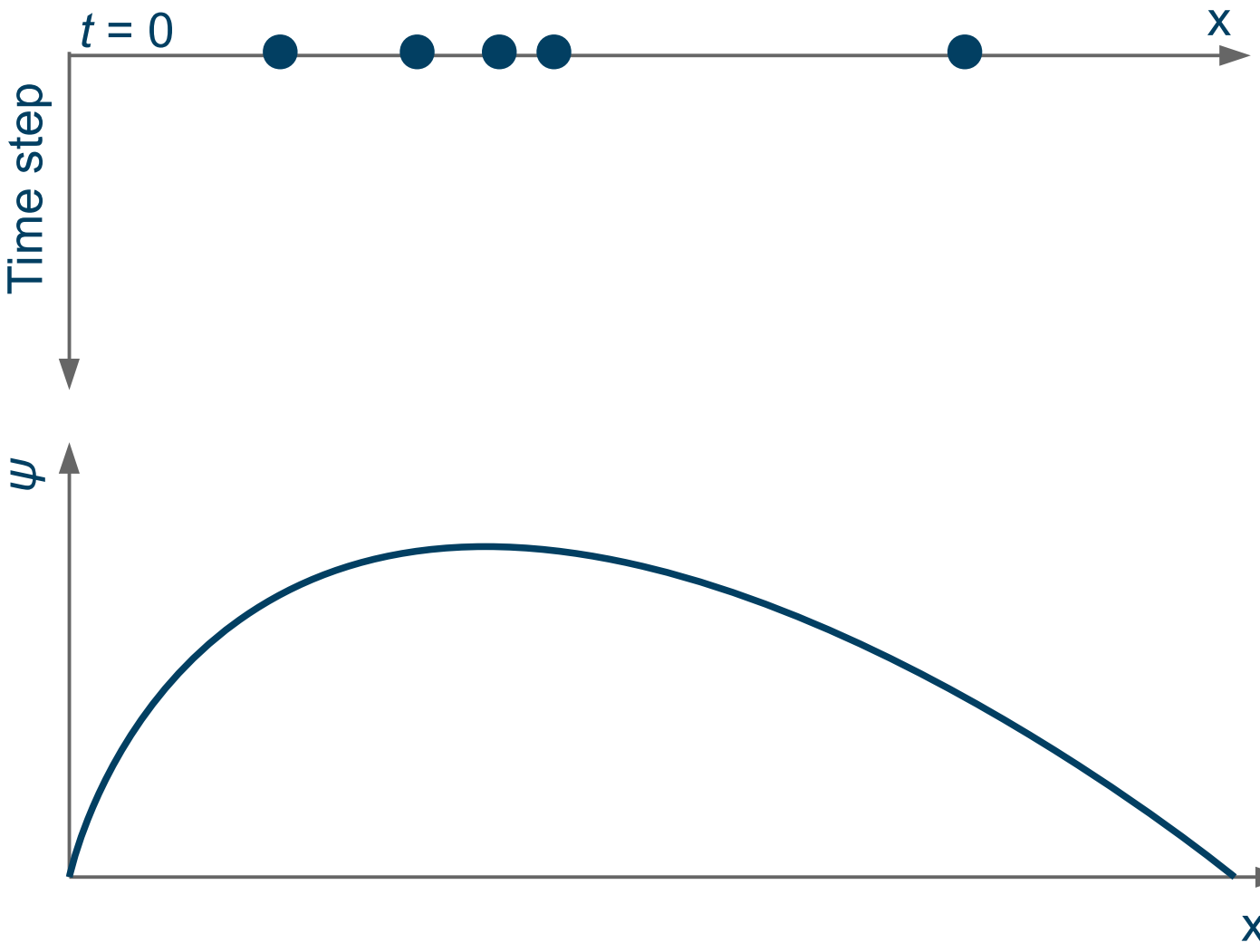
$$i\hbar \frac{d\psi}{dt} = H\psi$$

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

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



t=0 configuration

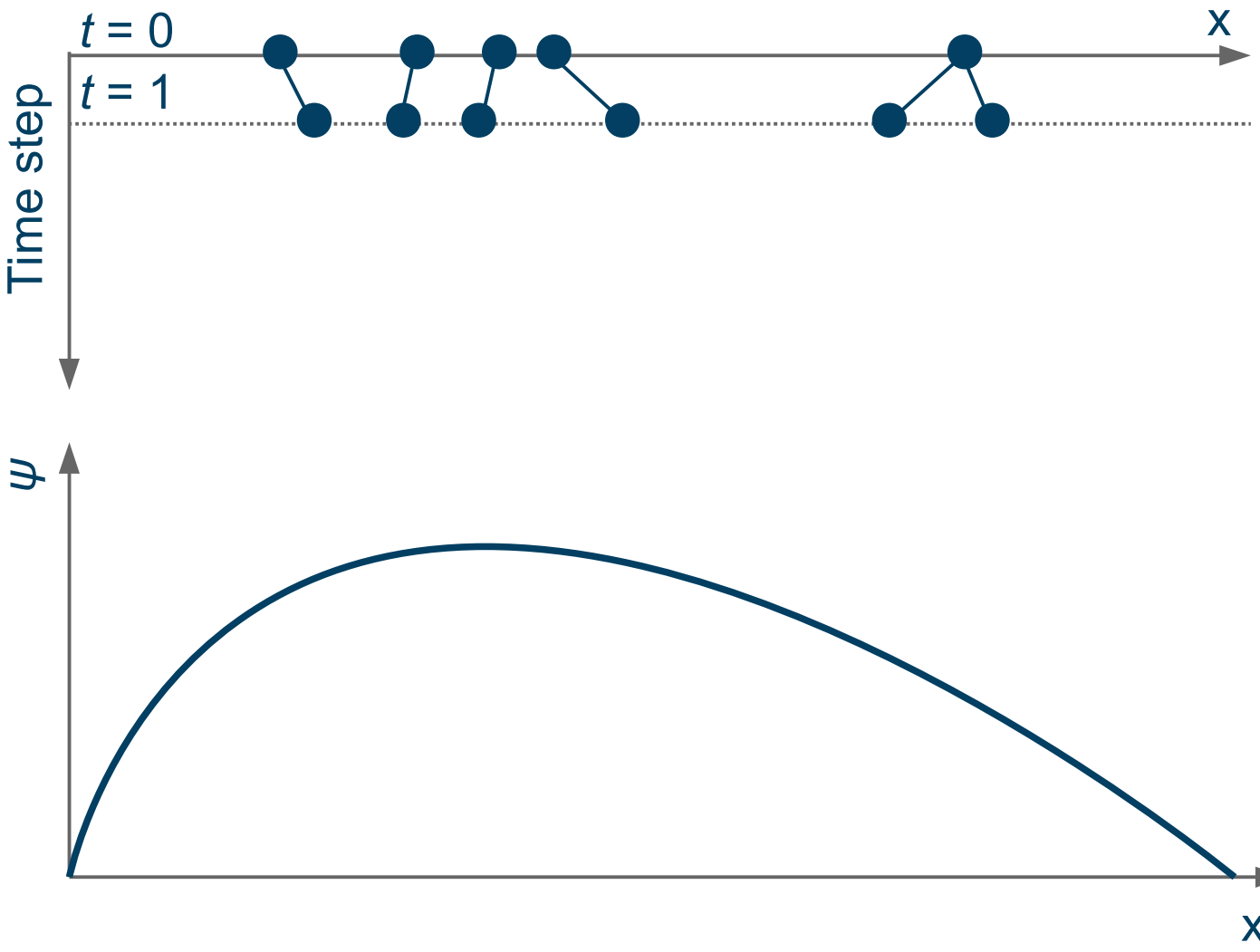


$$i\hbar \frac{d\psi}{dt} = H\psi$$

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

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

Propagate forward in time



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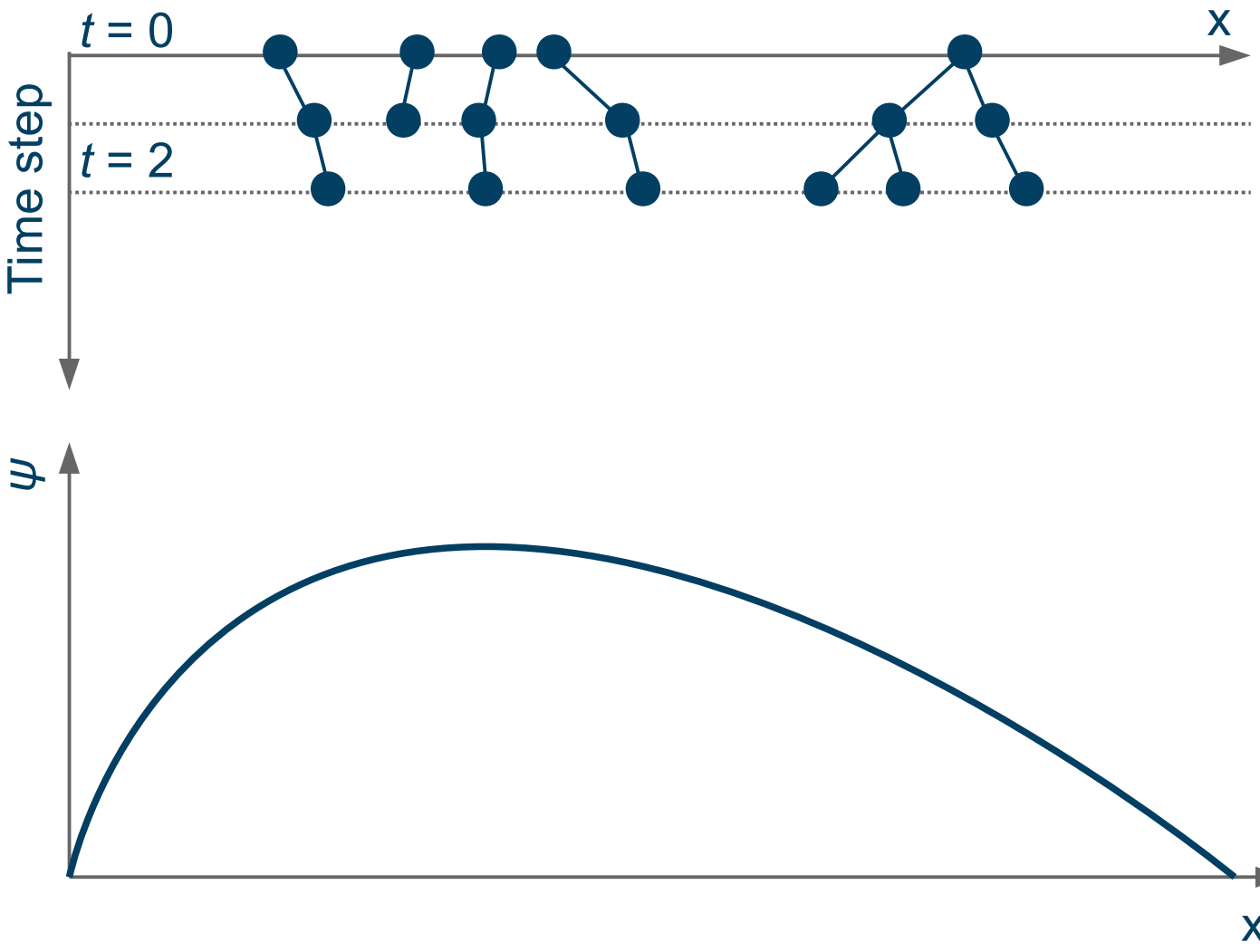
Propagate forward in time



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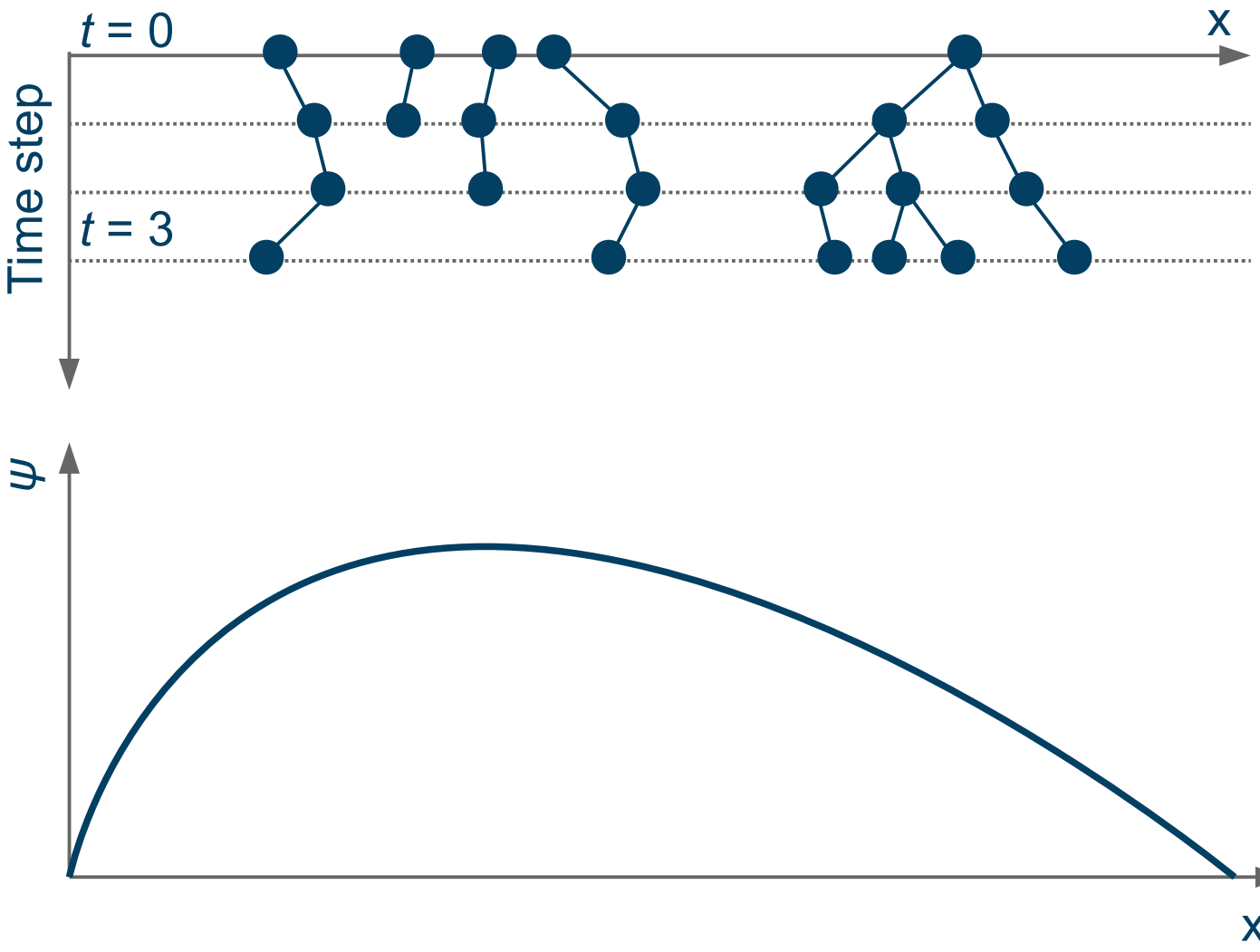
$$\frac{d\psi}{d\tau} = -\frac{\nabla^2 \psi}{2m}$$

Propagate forward in time

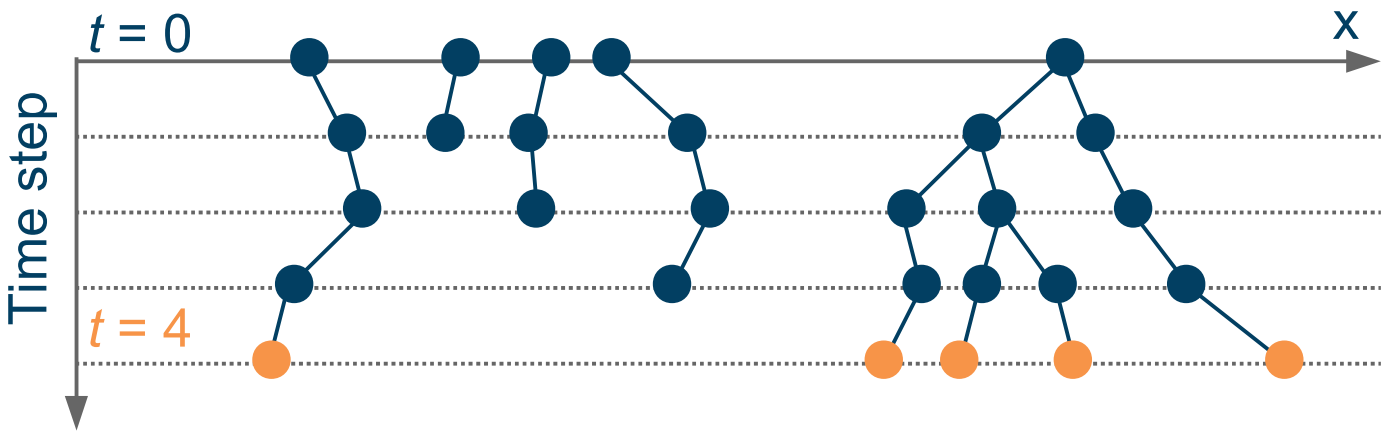


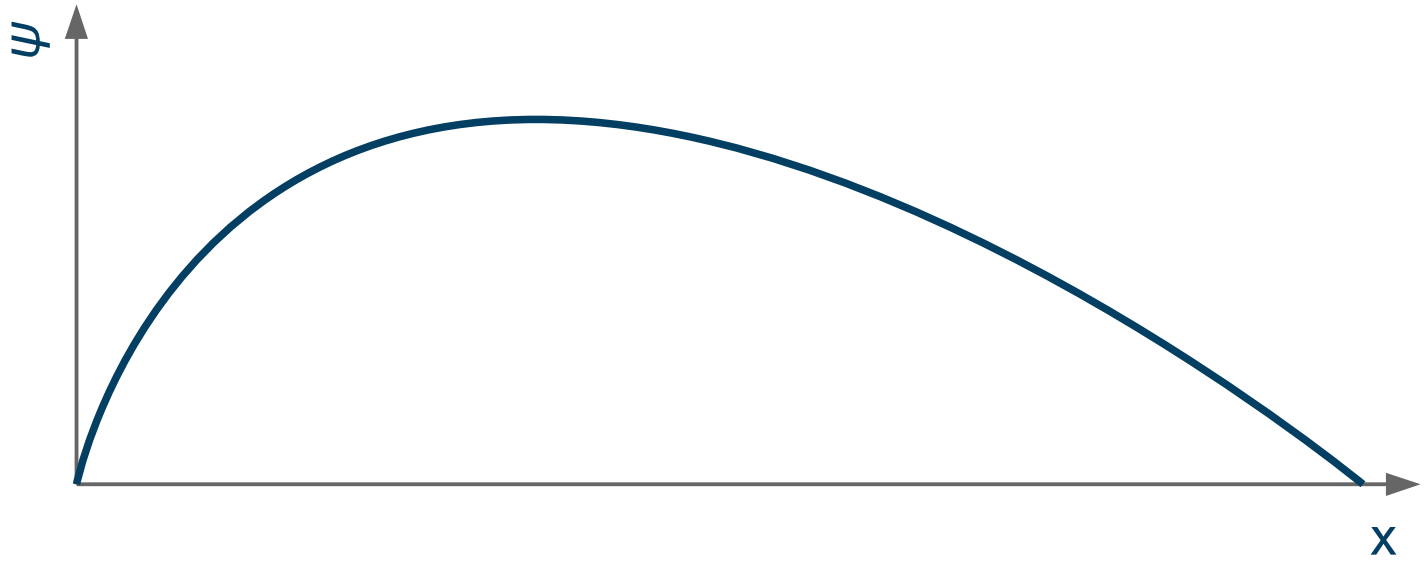
$$i\hbar \frac{d\psi}{dt} = H\psi$$

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

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

Final time step



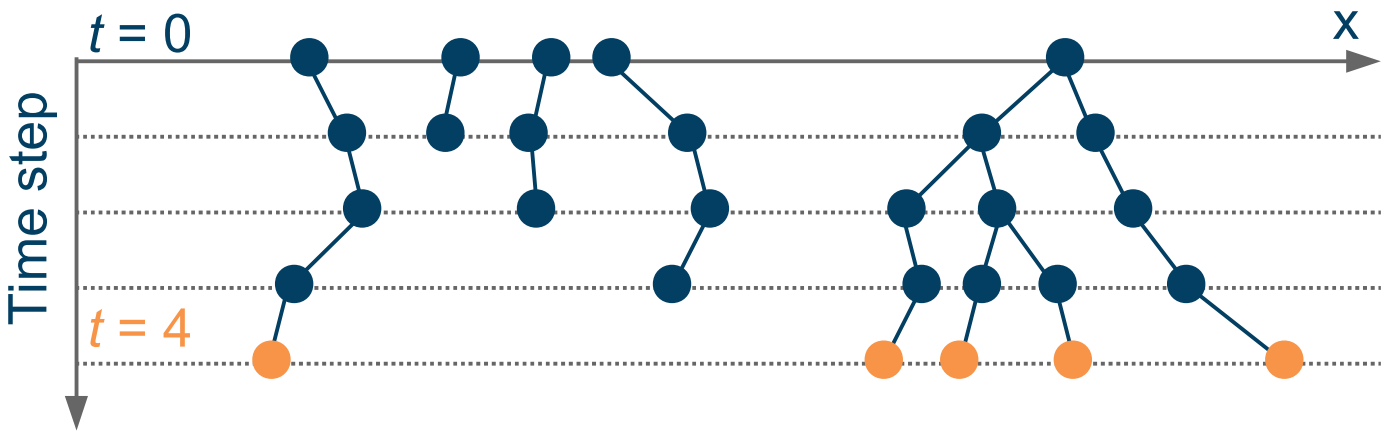


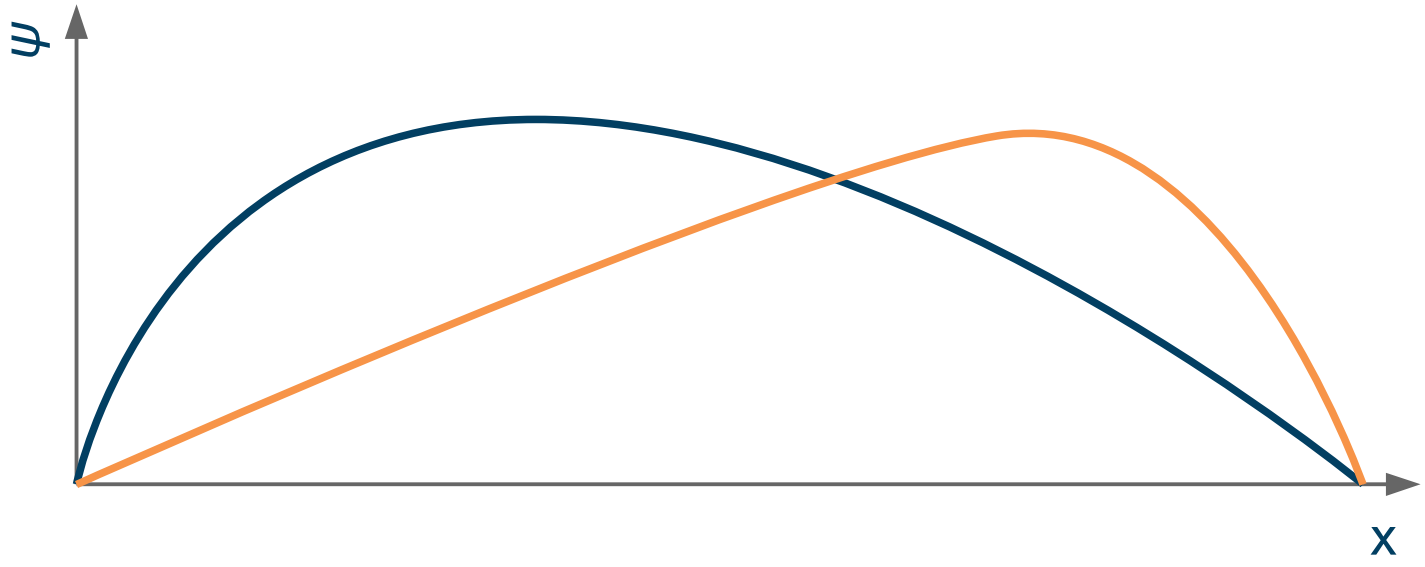
$$i\hbar \frac{d\psi}{dt} = H\psi$$

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

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

Project out the ground state





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

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

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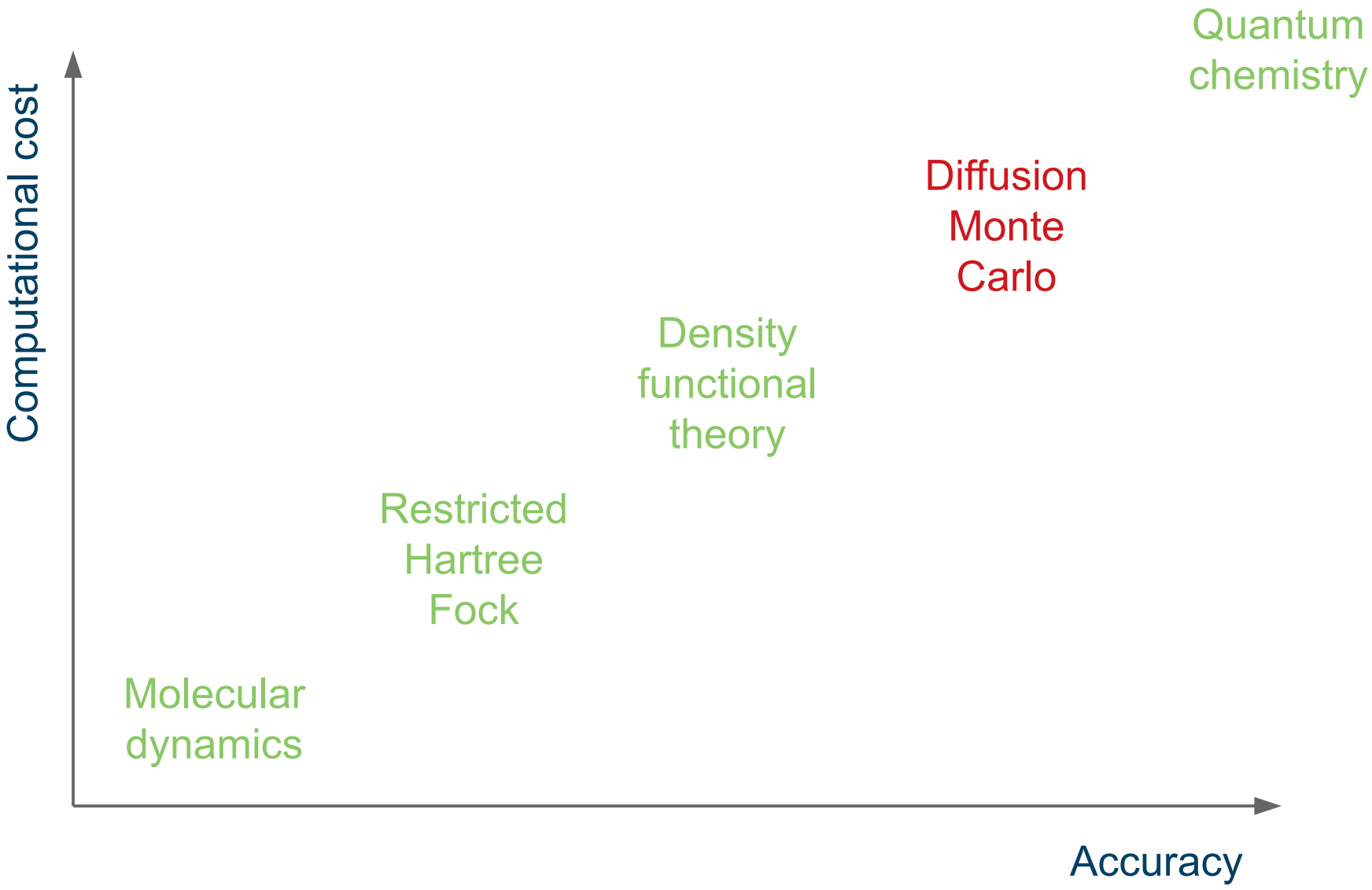
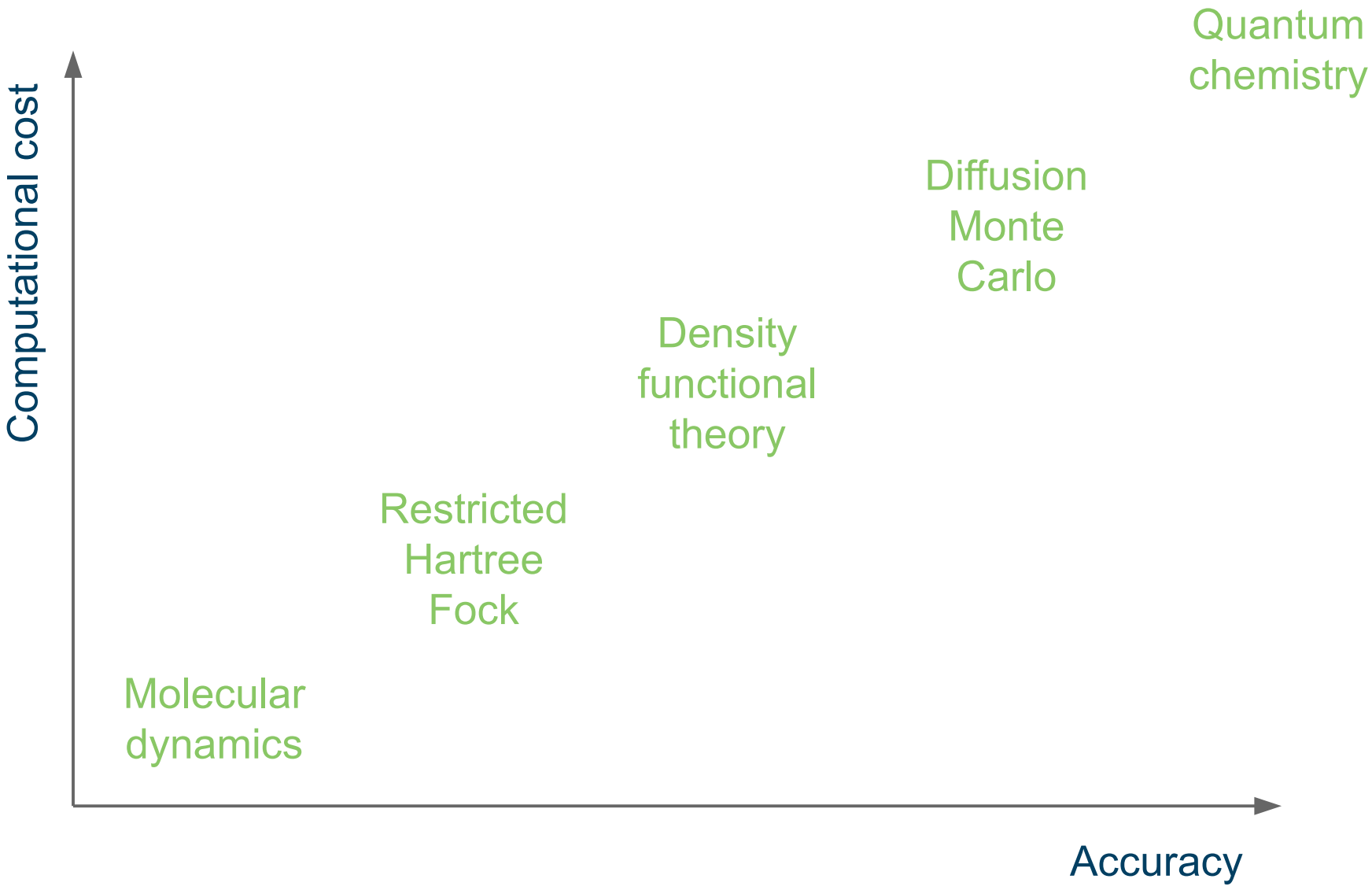
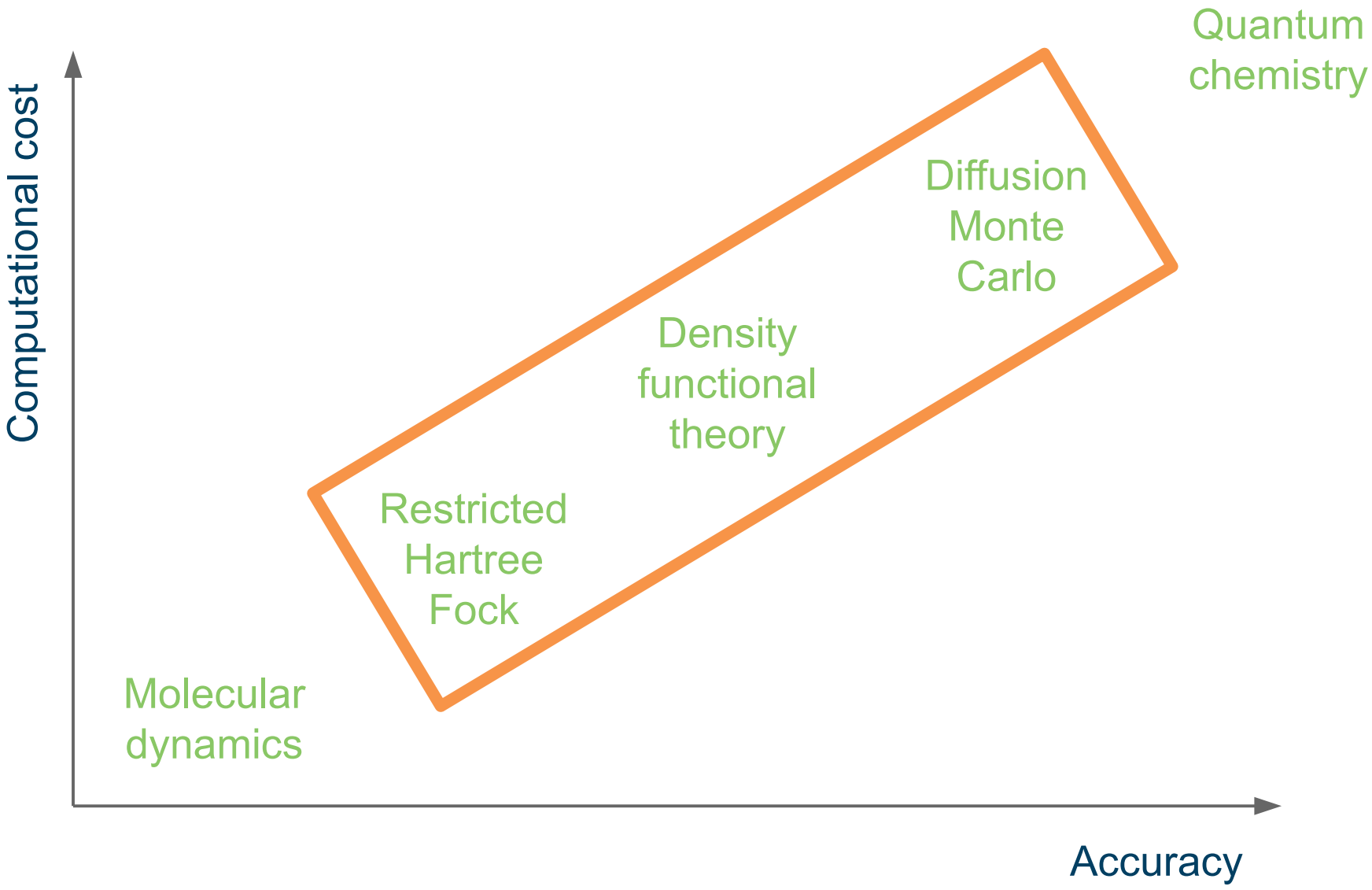
Hierarchy of methods



Hierarchy of methods



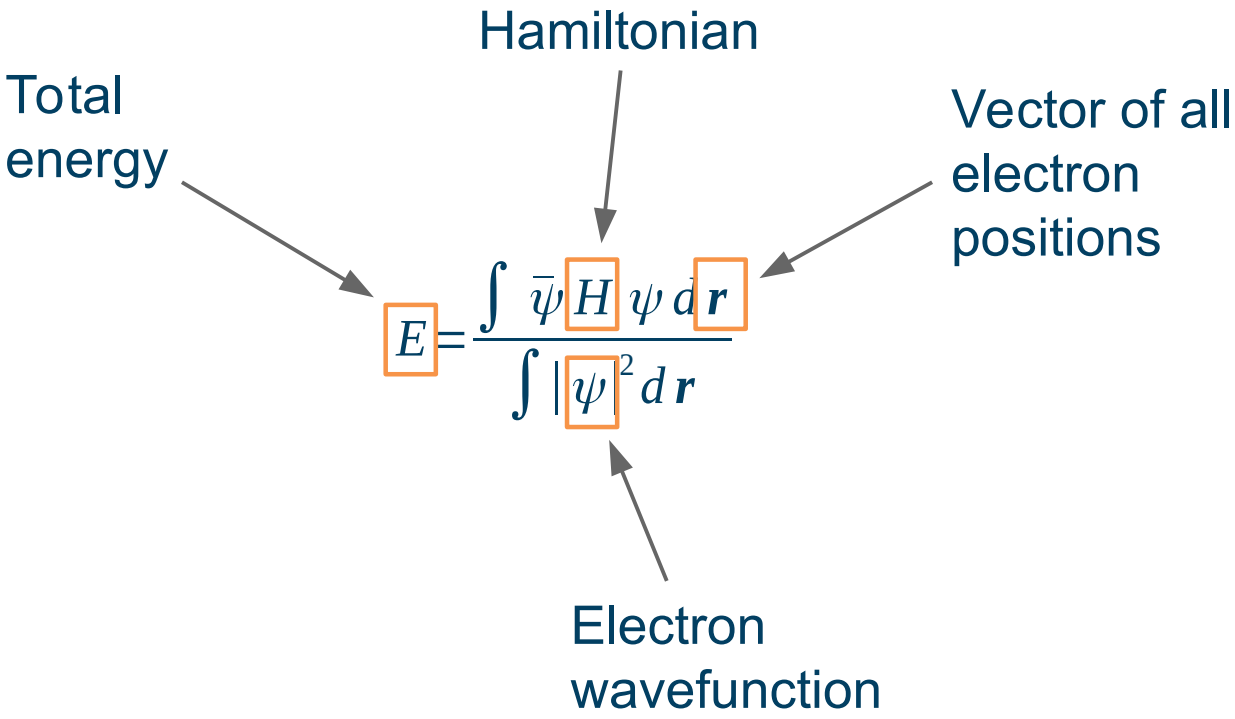
Hierarchy of methods



Diffusion Monte Carlo

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

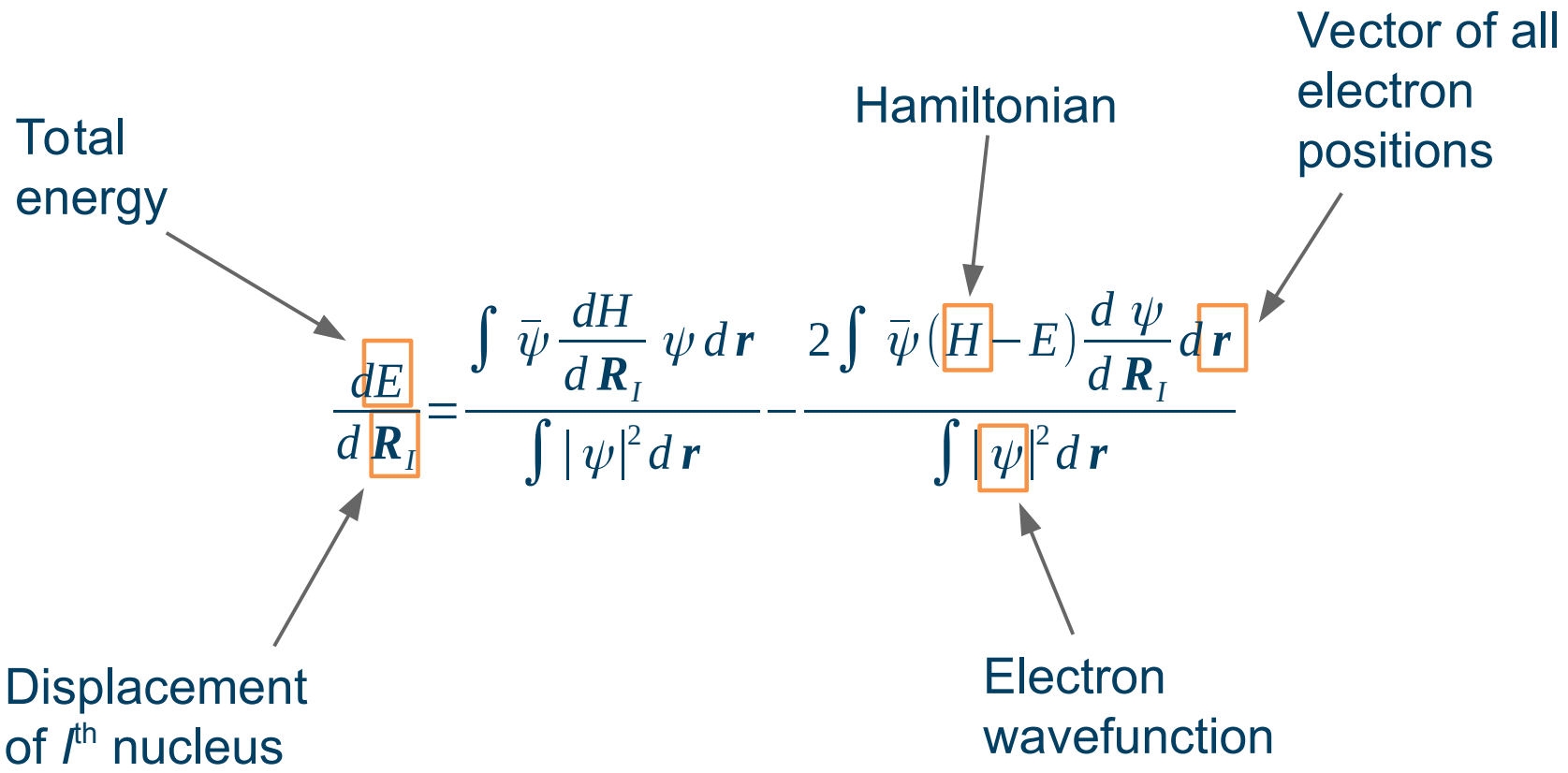
Diffusion Monte Carlo



Calculation of force

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

Calculation of force



Matrix of force constants

$$\frac{d^2 E}{d\boldsymbol{R}_I \boldsymbol{R}_J} = \frac{\int \bar{\psi} \frac{d^2 H}{d\boldsymbol{R}_I \boldsymbol{R}_J} \psi \, d\boldsymbol{r}}{\int |\psi|^2 d\boldsymbol{r}} + \frac{\int \bar{\psi} \left[\frac{d\psi}{d\boldsymbol{R}_I} \left(\psi^{-1} \frac{dH}{d\boldsymbol{R}_J} \psi - \frac{dE}{d\boldsymbol{R}_J} \right) + (I \Leftrightarrow J) \right] d\boldsymbol{r}}{2 \int |\psi|^2 d\boldsymbol{r}} + \text{c.c.}$$

$$+ \frac{1}{\int |\psi|^2 d\boldsymbol{r}} \frac{d}{d\boldsymbol{R}_I} \left[\int \frac{d\bar{\psi}}{d\boldsymbol{R}_J} (H - E) \psi \, d\boldsymbol{r} + (I \Leftrightarrow J) \right] + \text{c.c.}$$

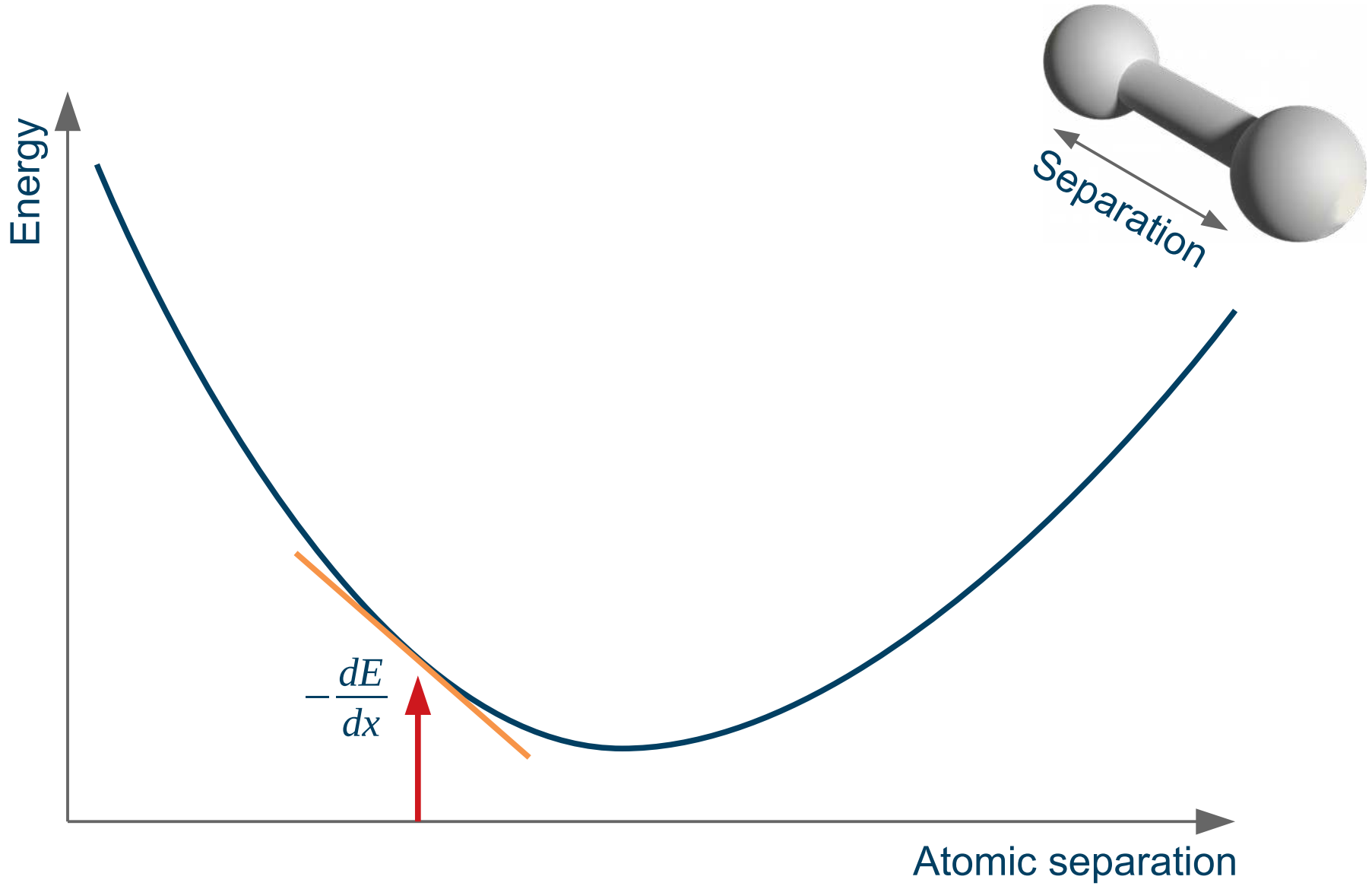
Matrix of force constants from numerical derivatives

Finite difference method leads to loss of accuracy

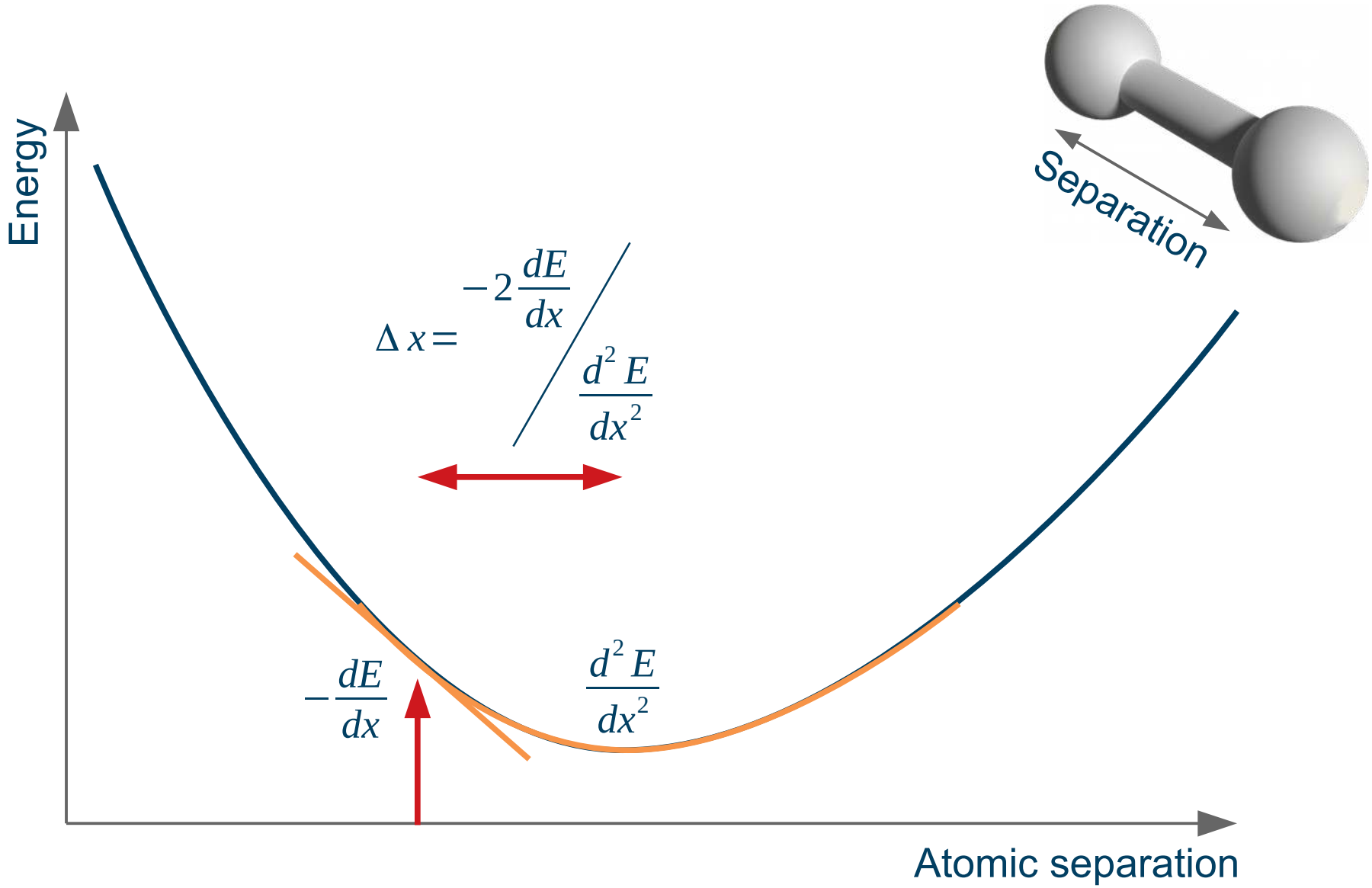
N atoms requires $9N^2$ calculations

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

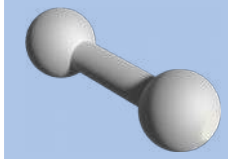
Relax atomic positions



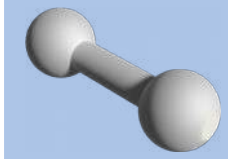
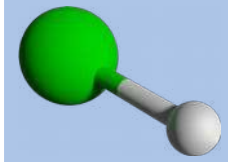
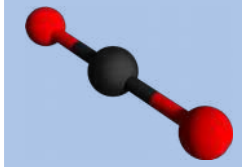
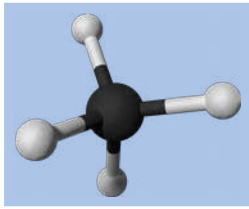
Relax atomic positions



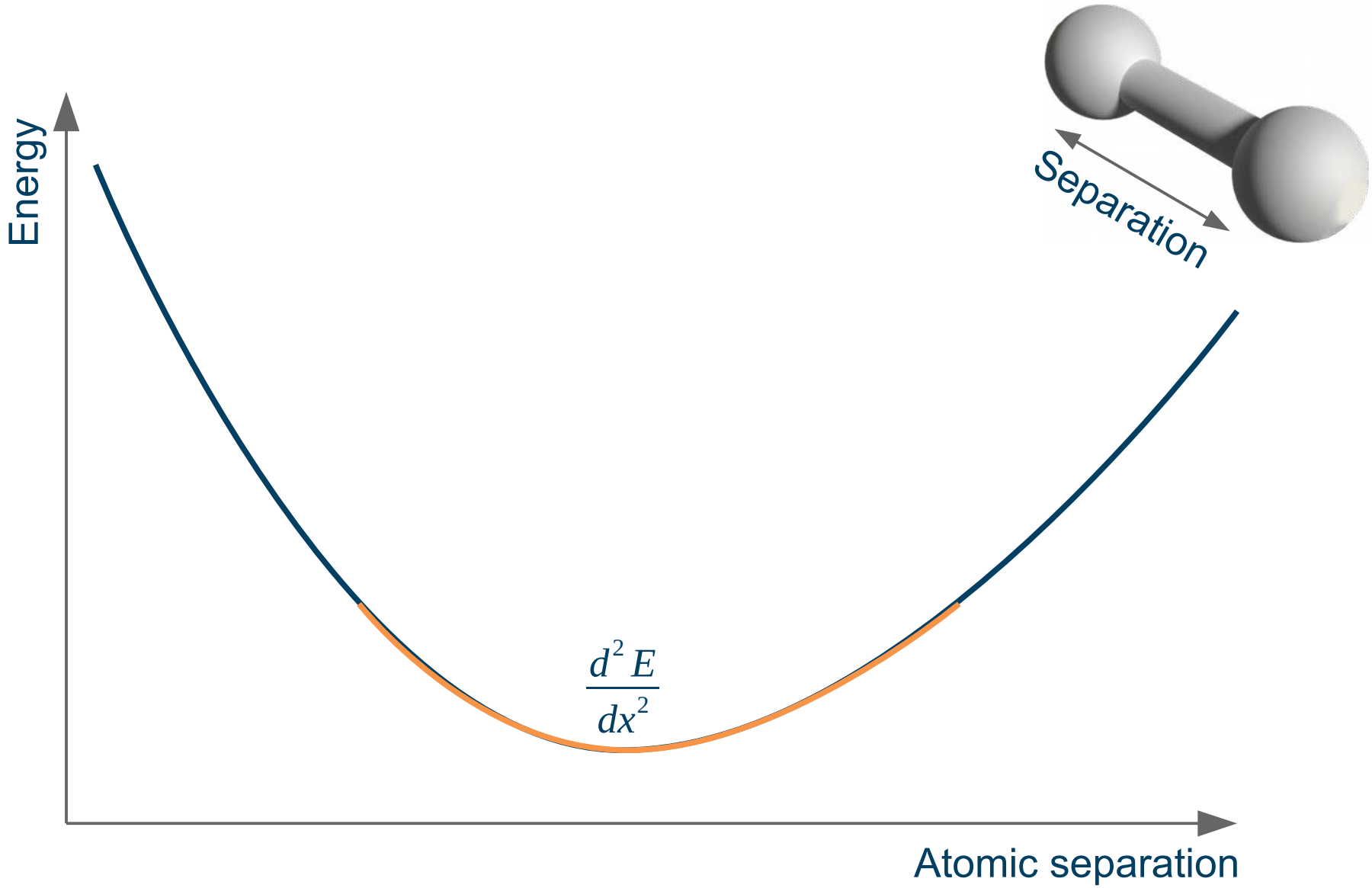
Bond length

Molecule	x_{RHF} / Å	x_{DFT} / Å	x_{DMC} / Å	x_{exp} / Å
 H_2	0.736	0.753	0.74±0.01	0.74130

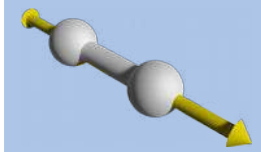
Bond lengths

Molecule	x_{RHF} / Å	x_{DFT} / Å	x_{DMC} / Å	x_{exp} / Å
 H_2	0.736	0.753	0.74±0.01	0.74130
 HCl	1.260	1.286	1.27±0.05	1.275
 $C0_2$	1.145	1.182	1.16±0.02	1.1598
 CH_4	1.089	1.104	1.10±0.01	1.093

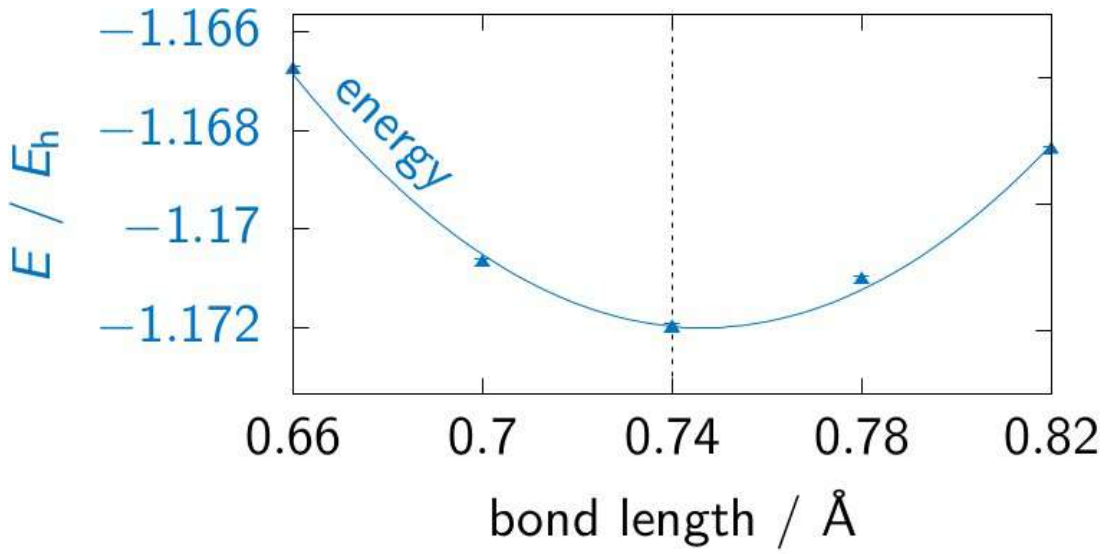
Relax atomic positions



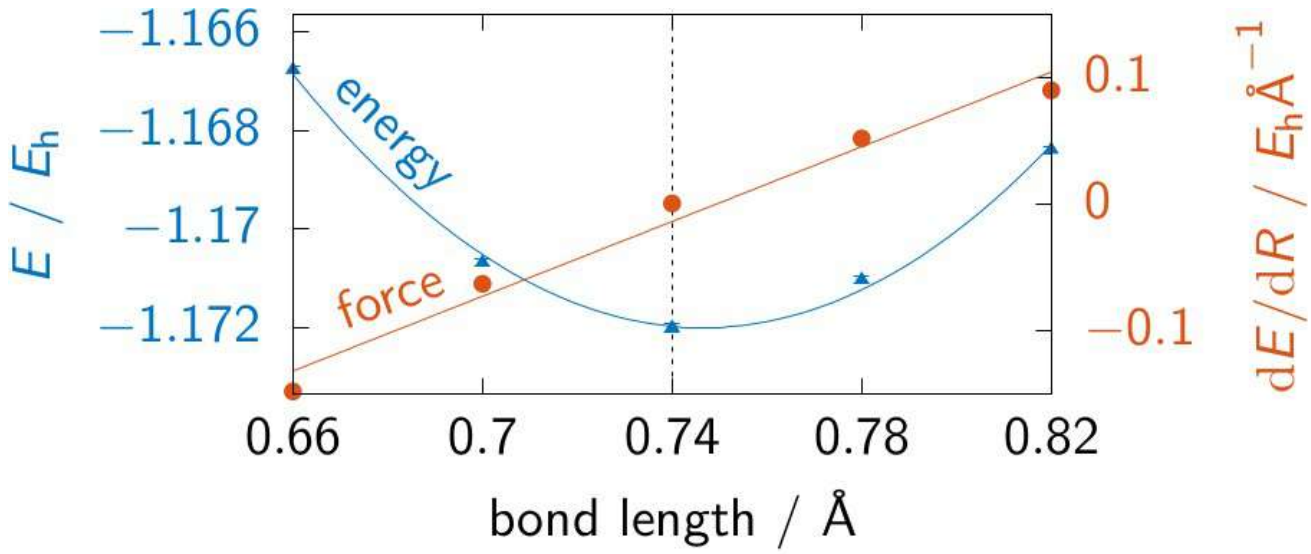
Diatomics

Molecule	ω_{RHF} / cm^{-1}	ω_{DFT} / cm^{-1}	ω_{DMC} / cm^{-1}	ω_{exp} / cm^{-1}
 H_2	4379	4116	4170 ± 4	4161.1663 ± 0.0002

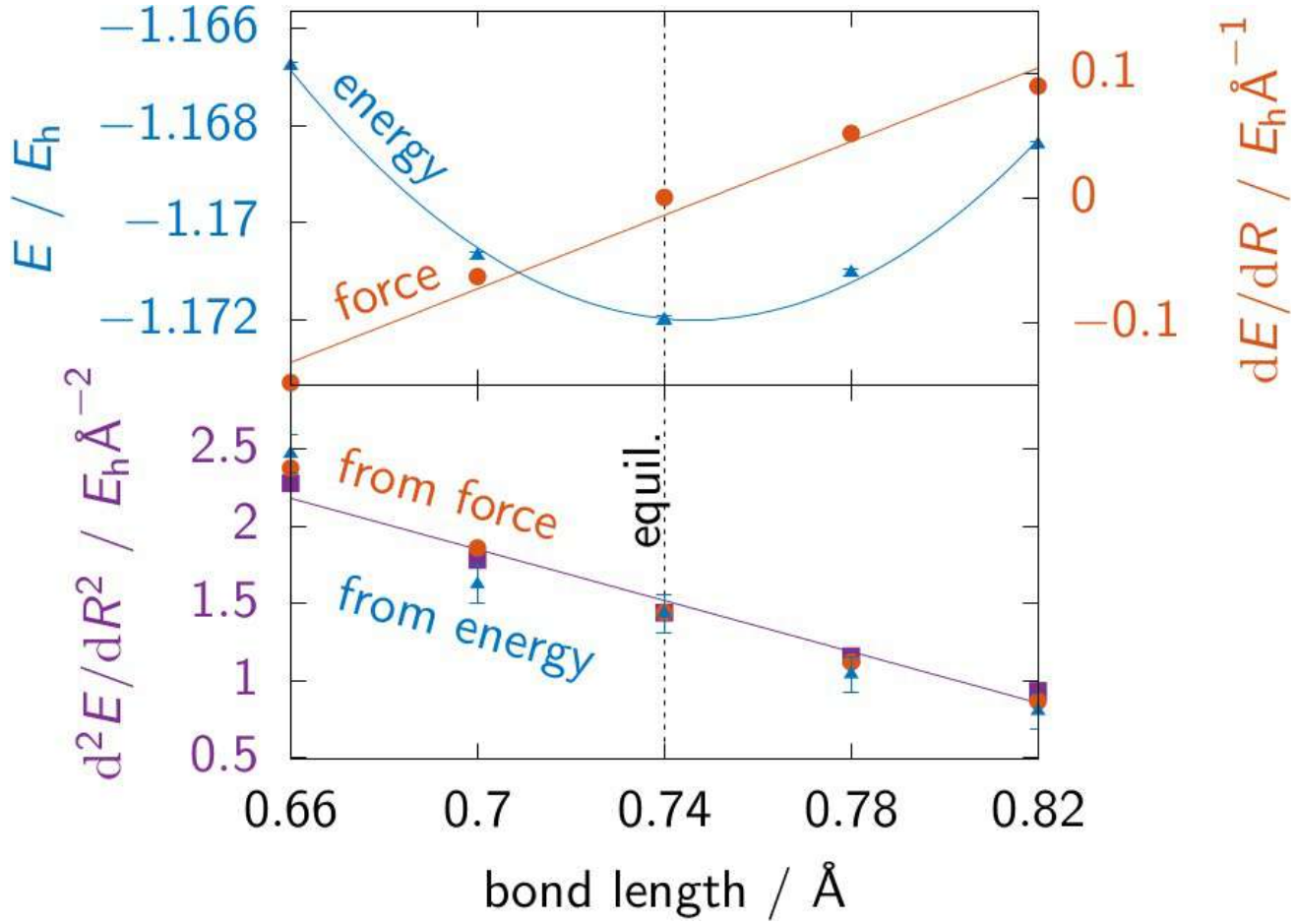
Hydrogen energy



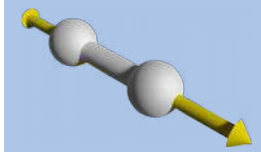
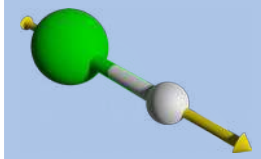
Hydrogen energy and force



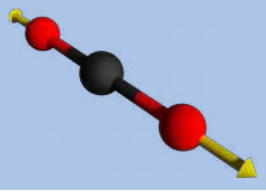
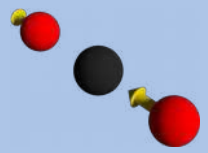
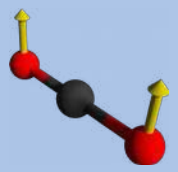
Hydrogen force constant



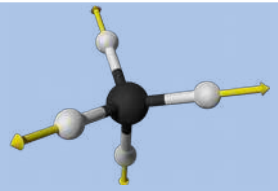
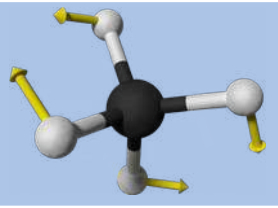
Diatomics

Molecule	ω_{RHF} / cm^{-1}	ω_{DFT} / cm^{-1}	ω_{DMC} / cm^{-1}	ω_{exp} / cm^{-1}
 H_2	4379	4116	4170 ± 4	4161.1663 ± 0.0002
 HCl	3116	2894	3000 ± 8	2990.946 ± 0.003

Carbon dioxide

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

Methane

Mode	ω_{RHF} / cm^{-1}	ω_{DFT} / cm^{-1}	ω_{DMC} / cm^{-1}	ω_{exp} / 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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