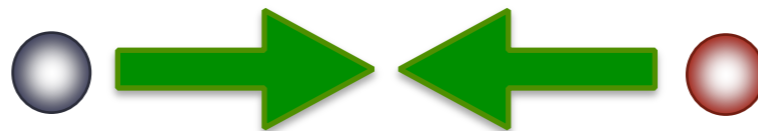
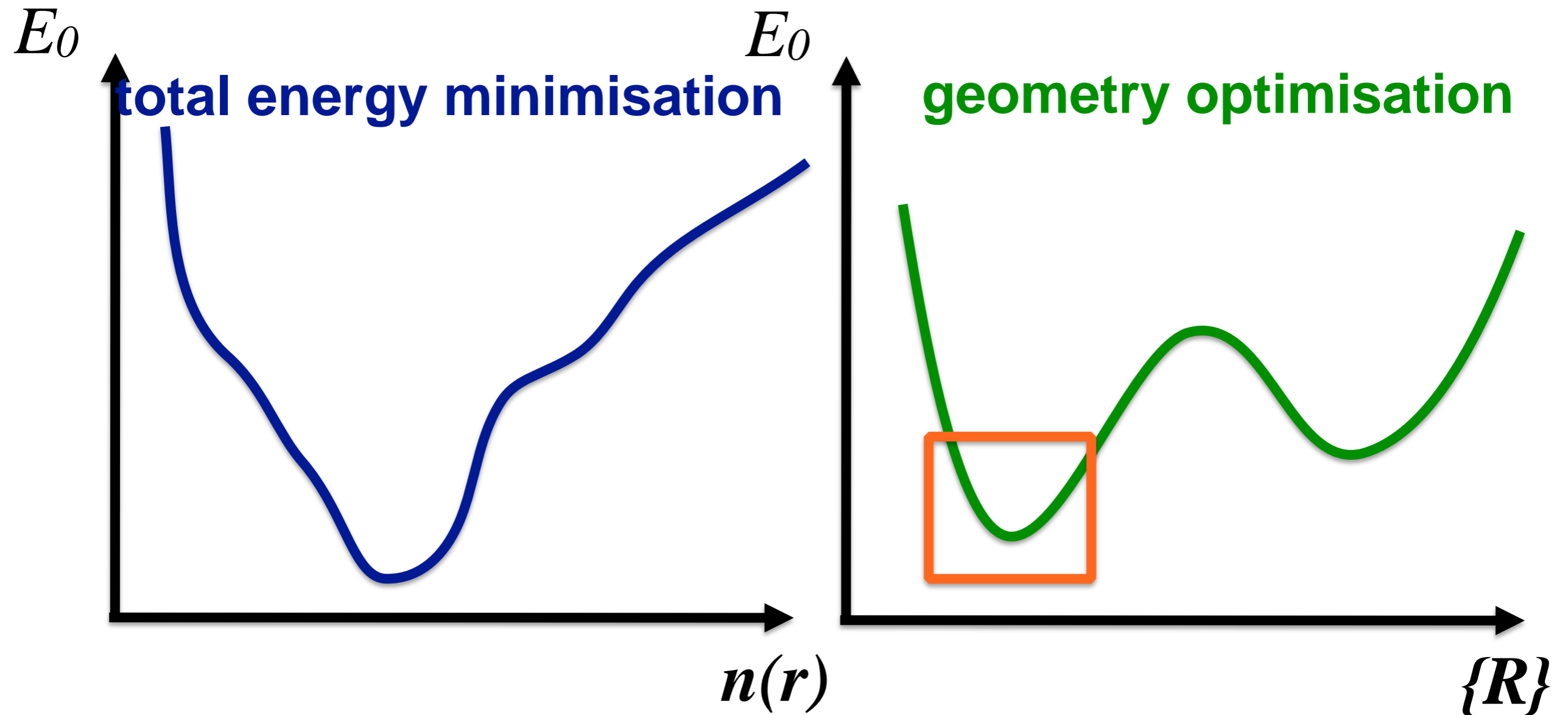


Density-Functional Theory for Practitioners - Tutorial 2

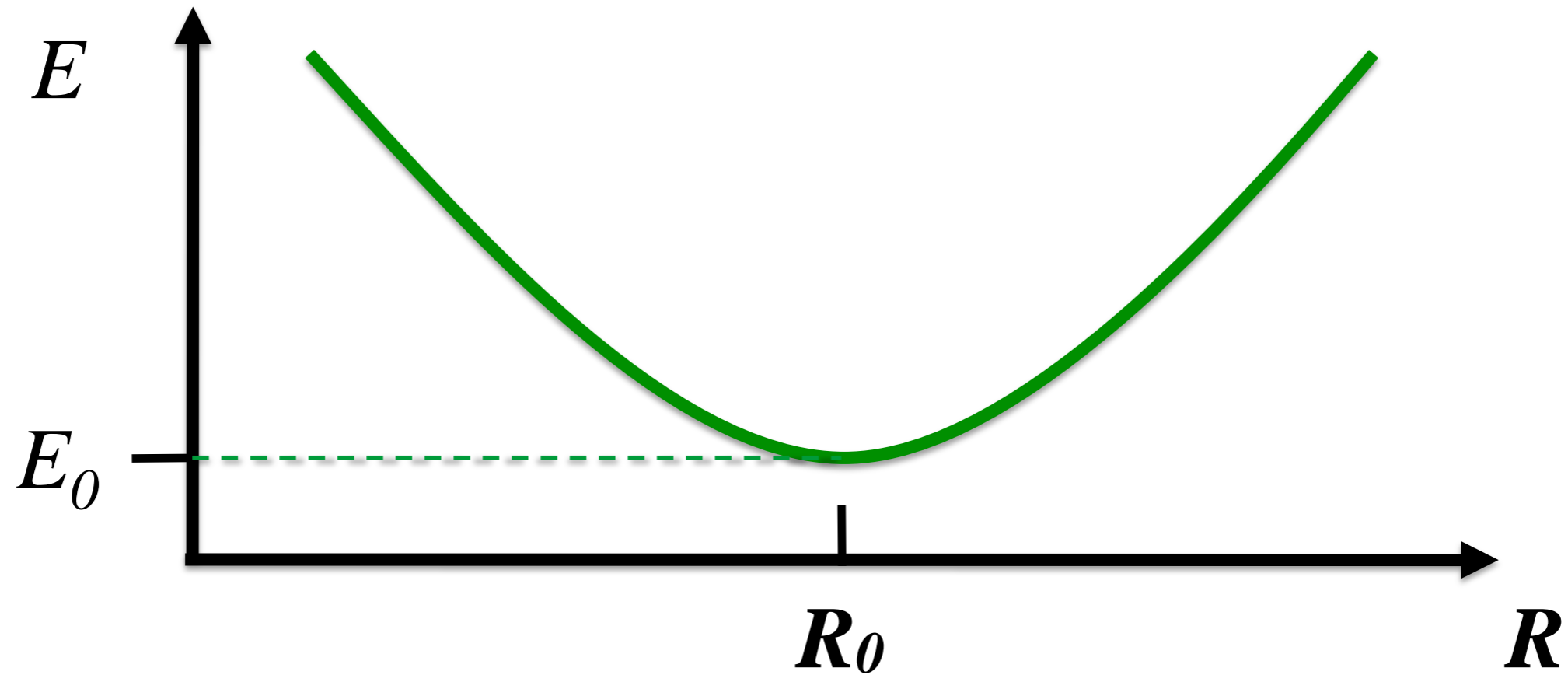
Orlando Silveira Júnior, Adolfo Otero Fumega
and Ondřej Krejčí,
(Developed by Patrick Rinke and Milica Todorović)

Aalto University
School of Science
Department of Applied Physics

Recap - two minimisations in DFT structure search



Expansion around the equilibrium

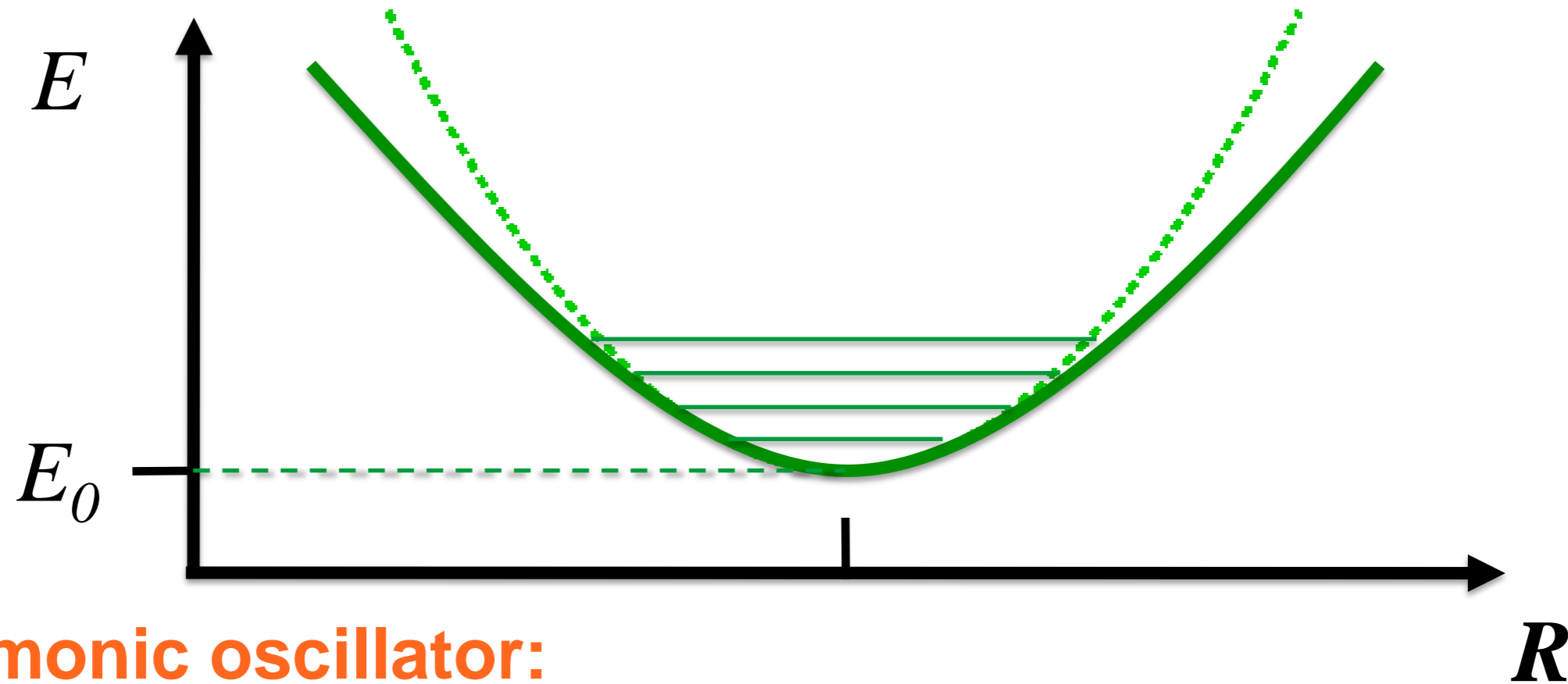


$$E_0(\mathbf{R}) = E_0(\mathbf{R}_0) + \frac{\partial E_0(\mathbf{R})}{\partial \mathbf{R}} \Big|_{\mathbf{R}_0} (\mathbf{R} - \mathbf{R}_0) + \frac{1}{2} \frac{\partial^2 E_0(\mathbf{R})}{\partial \mathbf{R}^2} \Big|_{\mathbf{R}_0} (\mathbf{R} - \mathbf{R}_0)^2 + \dots$$

equilibrium energy

forces are 0 in minimum

Harmonic approximation



harmonic oscillator:

$$E_0(\mathbf{R}) = E_0(\mathbf{R}_0) + \underbrace{\frac{1}{2} \frac{\partial^2 E_0(\mathbf{R})}{\partial \mathbf{R}^2} \Big|_{\mathbf{R}_0}}_k (\mathbf{R} - \mathbf{R}_0)^2$$

atomic mass \rightarrow

vibrational frequency \leftarrow

Vibrational frequencies

In general we have to solve a matrix equation:

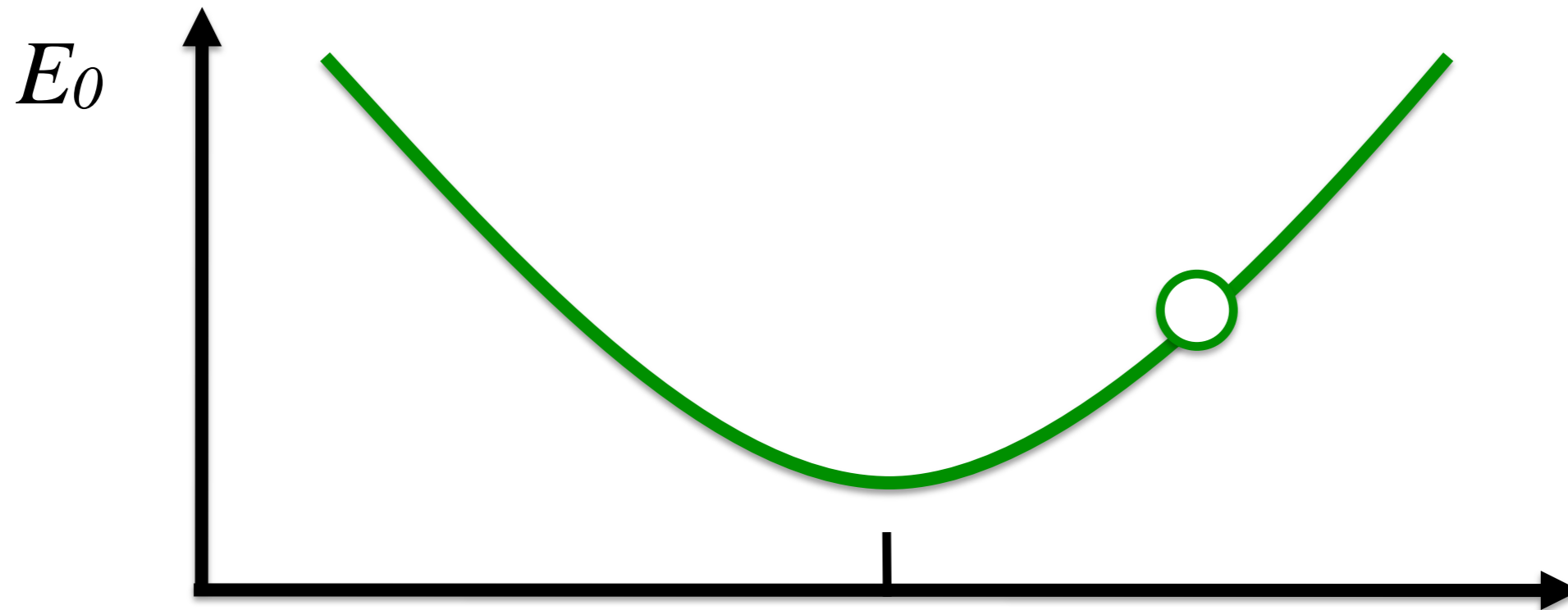
$$\det \left| \frac{1}{\sqrt{M_i M_j}} \sum_j \underbrace{\frac{\partial^2 E_0}{\partial \mathbf{R}_i \partial \mathbf{R}_j}}_{\text{Hessian matrix}} - \omega_i^2 \right| = 0$$

masses of
the atoms

Hessian matrix

vibrational
frequencies

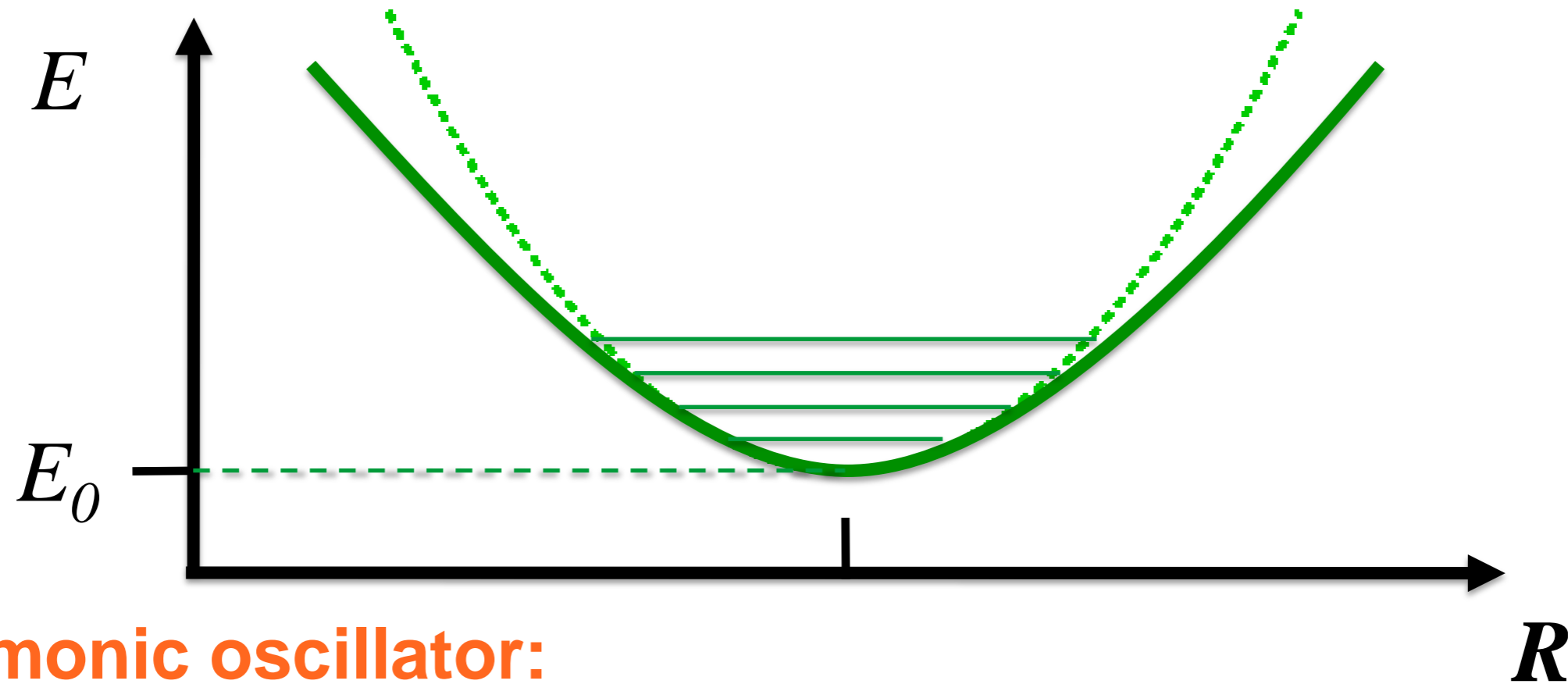
Negative frequencies



If we are not in the equilibrium structure, the 2nd derivative does not give us the vibrational frequency!

Imaginary (or negative) frequencies result!

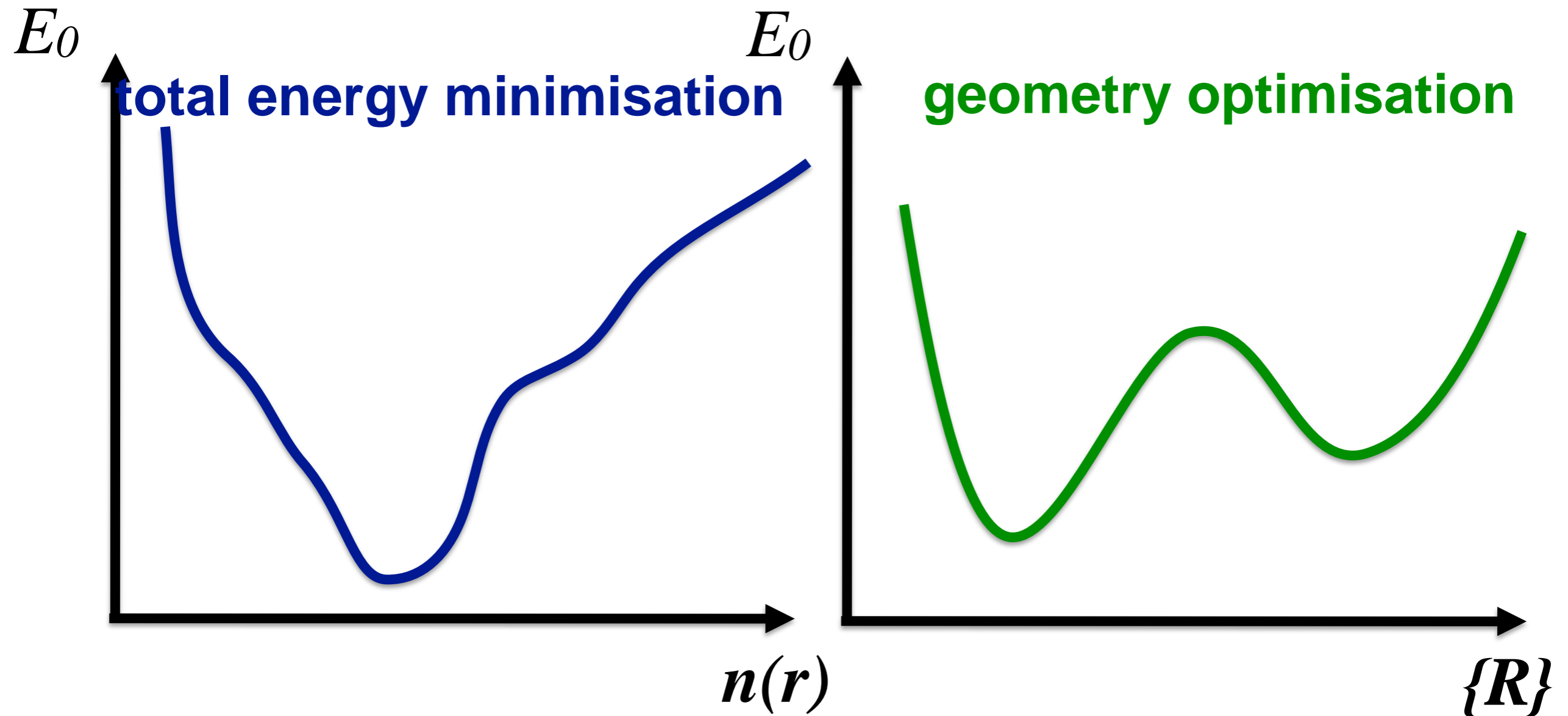
Questions on vibrations?



harmonic oscillator:

$$E_0(\mathbf{R}) = E_0(\mathbf{R}_0) + \underbrace{\frac{1}{2} \frac{\partial^2 E_0(\mathbf{R})}{\partial \mathbf{R}^2} \Big|_{\mathbf{R}_0}}_k (\mathbf{R} - \mathbf{R}_0)^2$$

Recap - two minimisations in DFT structure search



How do we actually minimise the total energy?

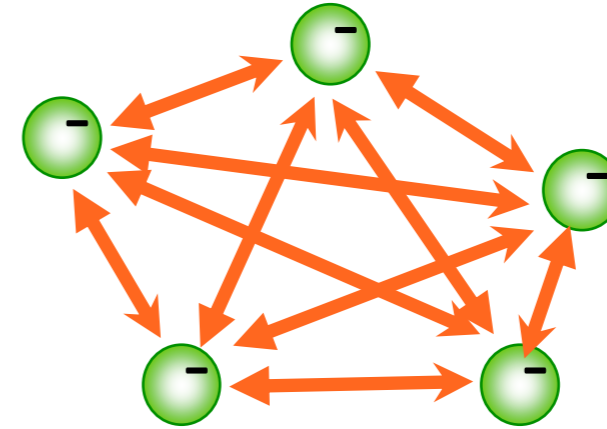
Let's go back to the full Hamiltonian

$$\begin{aligned}
 & H(\underbrace{\text{---}}_{T^e} \dots) \\
 & \mathcal{H}^e = \underbrace{-\sum_{i=1}^{N_e} \frac{\nabla_{\mathbf{r}_i}^2}{2}}_{T^e} + \underbrace{\sum_{i=1}^{N_e} v_{\text{ext}}(\mathbf{r}_i)}_{V^{ne}} + \underbrace{\sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{V^{ee}} \\
 & = \sum_{i=1}^{N_e} \left[\underbrace{-\frac{\nabla_{\mathbf{r}_i}^2}{2} + v_{\text{ext}}(\mathbf{r}_i)}_{\text{1 electron}} + \underbrace{\sum_{j>i}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\text{all electrons}} \right]
 \end{aligned}$$

Let's go back to the full Hamiltonian

$$H(\ominus \ominus \ominus \dots)$$

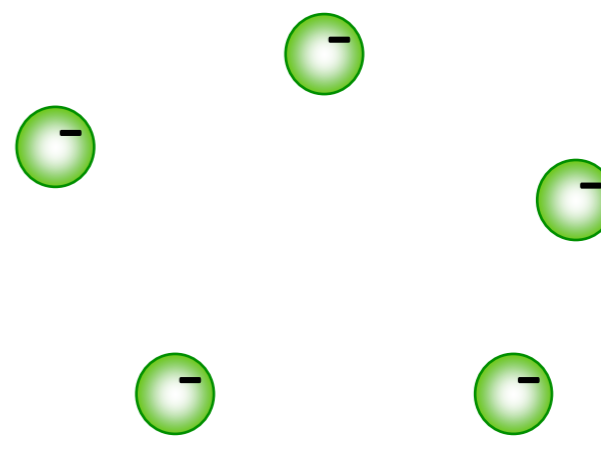
all electrons interact with each other \rightarrow intractable



$$\mathcal{H}^e = \sum_{i=1}^{N_e} \left[\underbrace{-\frac{\nabla_{\mathbf{r}_i}^2}{2} + v_{\text{ext}}(\mathbf{r}_i)}_{\text{1 electron}} + \underbrace{\sum_{j>i}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\text{all electrons}} \right]$$

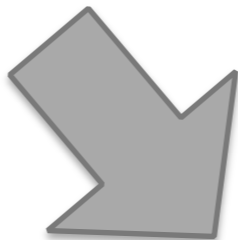
Non-interacting Hamiltonian

Let's assume we have a non-interacting system.

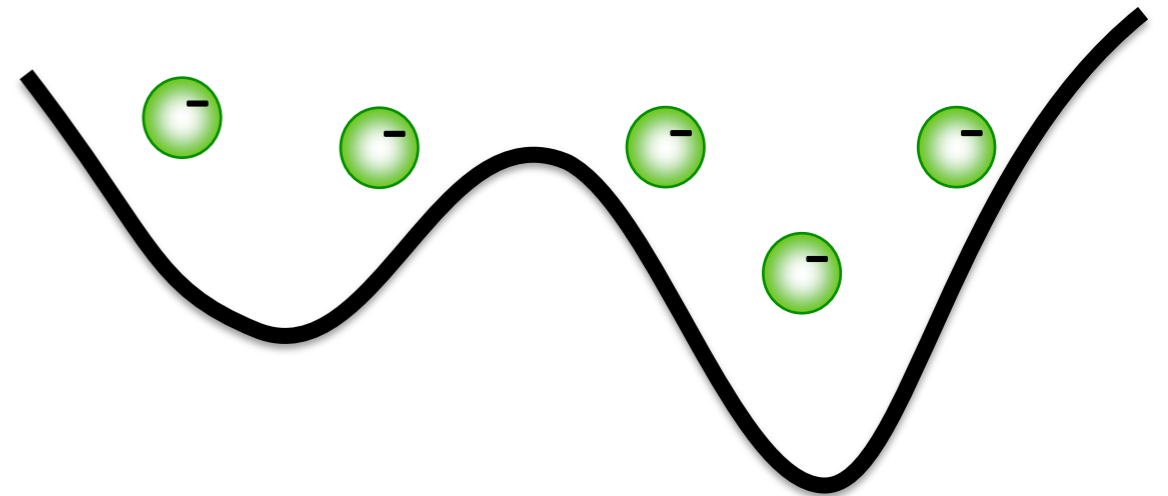
$$\mathcal{H}^e = \sum_{i=1}^{N_e} \left[-\frac{\nabla_{\mathbf{r}_i}^2}{2} + v_{\text{aux}}(\mathbf{r}_i) \right]$$
A diagram showing five green spheres, each with a minus sign inside, representing electrons. They are arranged in a scattered pattern: one at the top left, one at the top right, one at the middle right, one at the bottom left, and one at the bottom right.

Non-interacting Hamiltonian

Let's assume we have a non-interacting system.

$$\mathcal{H}^e = \sum_{i=1}^{N_e} \left[-\frac{\nabla_{\mathbf{r}_i}^2}{2} + v_{\text{aux}}(\mathbf{r}_i) \right]$$


Electrons move in an auxiliary potential that is the same for all electrons.

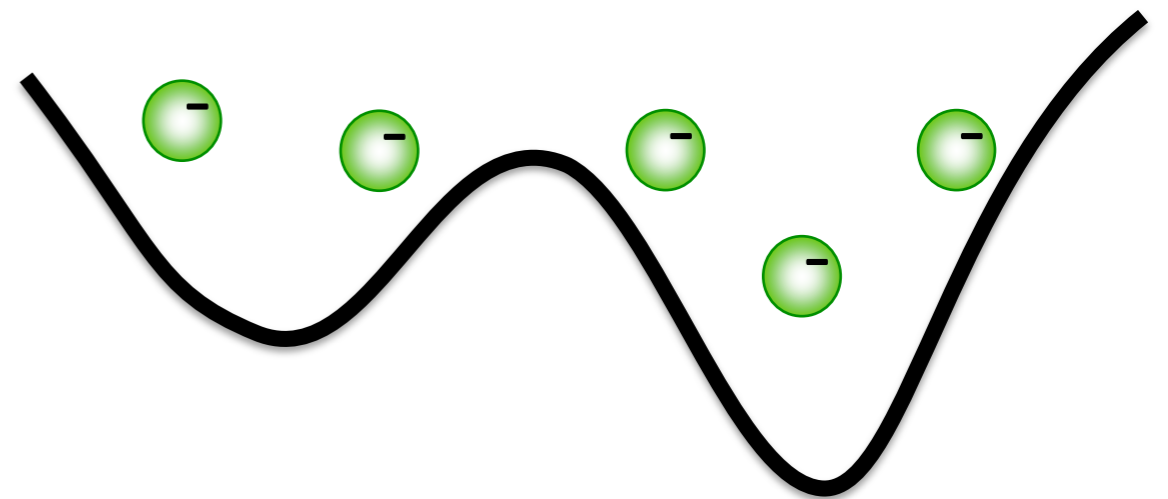


Non-interacting Hamiltonian

Let's assume we have a non-interacting system.

$$\mathcal{H}^e = \sum_{i=1}^{N_e} \left[\underbrace{-\frac{\nabla_{\mathbf{r}_i}^2}{2} + v_{\text{aux}}(\mathbf{r}_i)}_{h_{\text{aux}}(\mathbf{r}_i)} \right] = \sum_{i=1}^{N_e} h_{\text{aux}}(\mathbf{r}_i)$$

Electrons move in an auxiliary potential that is the same for all electrons.



Non-interacting Hamiltonian

$$\mathcal{H}^e = \sum_{i=1}^{N_e} h_{\text{aux}}(\mathbf{r}_i)$$

Now we have a mini Schrödinger equation.
The same for every electron.

$$h_{\text{aux}}(\mathbf{r})\phi(\mathbf{r}) = \epsilon\phi(\mathbf{r})$$

This is easy to solve, once we know h_{aux} .

The non-interacting wave function

Let's look at only two electrons.

$$\mathcal{H}^e(\mathbf{r}_1, \mathbf{r}_2) = h_{\text{aux}}(\mathbf{r}_1) + h_{\text{aux}}(\mathbf{r}_2)$$

The wave function becomes a simple product.

$$\Psi^e(\mathbf{r}_1, \mathbf{r}_2) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)$$

But there is a problem!

The non-interacting wave function

The wave function is not antisymmetric!

$$\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \neq -\phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)$$

Make the wave function antisymmetric!

$$\Psi^e(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)]$$

This is called a Slater determinant.

The non-interacting density

$$\Psi^e(\mathbf{r}, \mathbf{r}') = \frac{1}{\sqrt{2}} [\phi_1(\mathbf{r})\phi_2(\mathbf{r}') - \phi_1(\mathbf{r}')\phi_2(\mathbf{r})]$$

The density becomes very simple!

$$\begin{aligned} n(\mathbf{r}) &= 2 \iint d\mathbf{r}' |\Psi^e(\mathbf{r}, \mathbf{r}')|^2 \\ &= |\phi_1(\mathbf{r})|^2 + |\phi_2(\mathbf{r})|^2 \\ &= \sum_{i=1}^{N_e} |\phi_i(\mathbf{r})|^2 \end{aligned}$$

DFT - Hohenberg-Kohn theorems

$$v_{\text{ext}}(\mathbf{r}) \Leftrightarrow n_0(\mathbf{r})$$



Walter Kohn

Theorem 1:

The ground state density $n_0(r)$ uniquely determines the potential up to an arbitrary constant.



Pierre Hohenberg

DFT - Kohn-Sham system

$$v_{\text{ext}}(\mathbf{r}) \Leftrightarrow n_0(\mathbf{r}) = \sum_{i=1}^{N_e} |\phi_i(\mathbf{r})|^2$$



Walter Kohn

An auxiliary non-interacting system exists that gives the ground-state density.

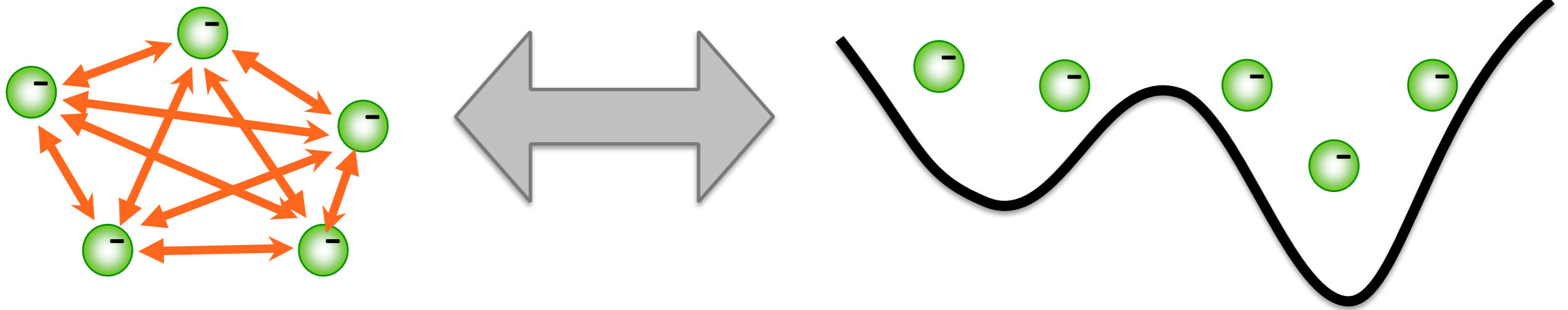
$$\mathcal{H}^e = \sum_{i=1}^{N_e} \left[\underbrace{-\frac{\nabla_{\mathbf{r}_i}^2}{2} + v_{\text{aux}}(\mathbf{r}_i)}_{h_{\text{aux}}(\mathbf{r}_i)} \right] = \sum_{i=1}^{N_e} h_{\text{aux}}(\mathbf{r}_i)$$



Lu Sham


DFT - Kohn-Sham system

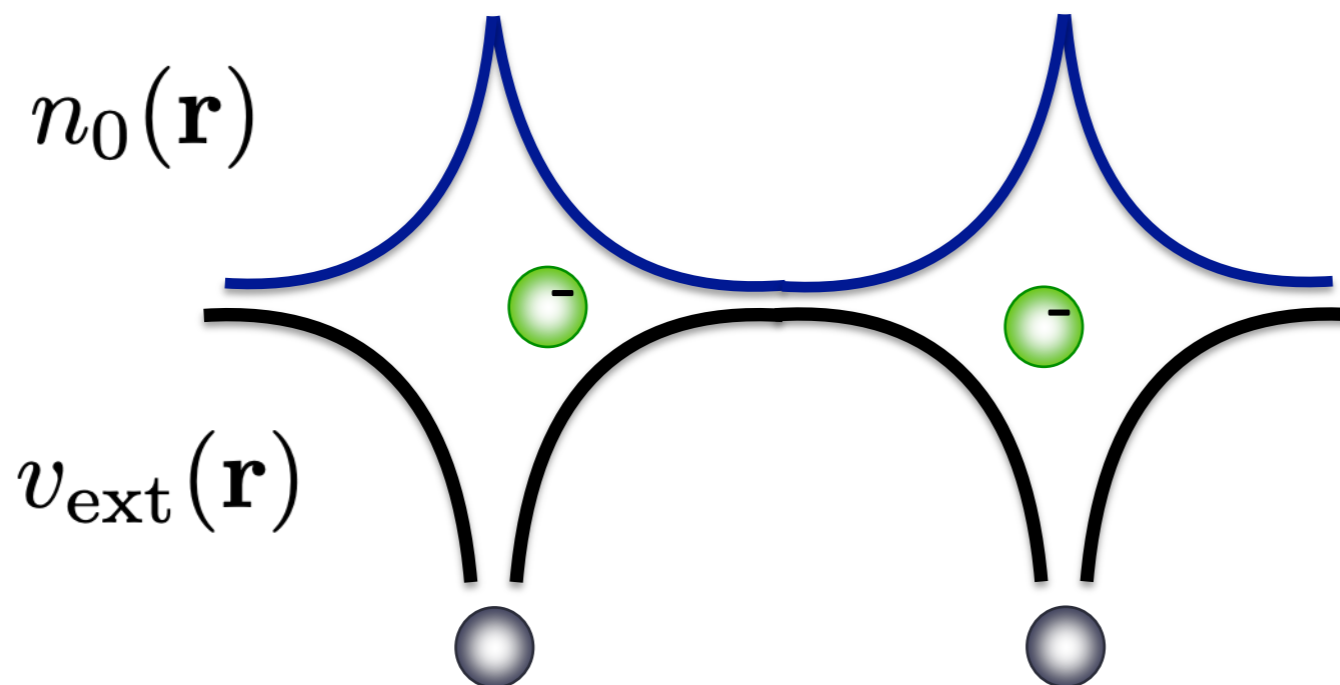
$$v_{\text{ext}}(\mathbf{r}) \Leftrightarrow n_0(\mathbf{r}) = \sum_{i=1}^{N_e} |\phi_i(\mathbf{r})|^2$$



But what is the auxiliary potential $v_{\text{aux}}(r)$?

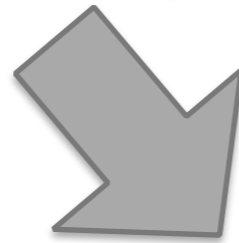
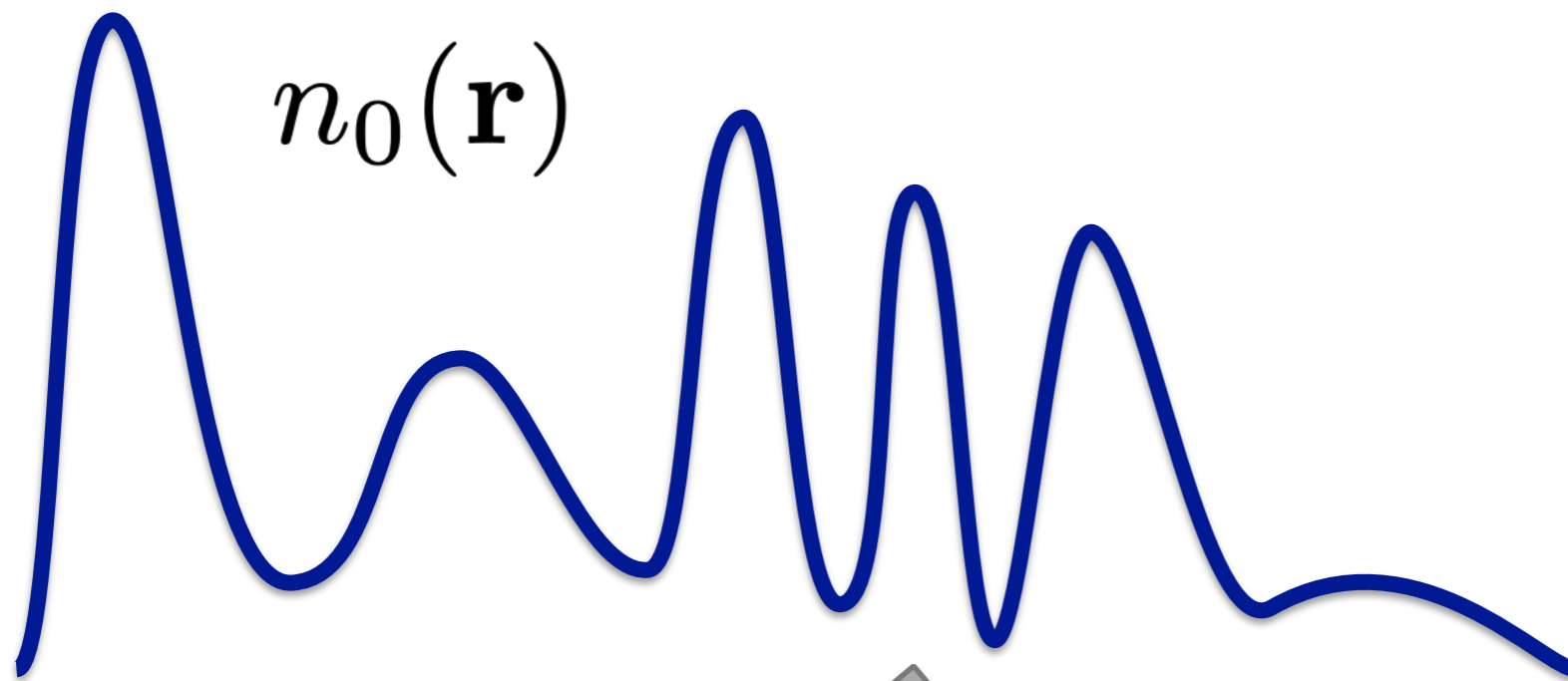
One part is the external potential

$$v_{\text{ext}}(\mathbf{r}) = \sum_{J=1}^{N_n} \frac{-Z_J}{|\mathbf{r}_i - \mathbf{R}_J|} \Leftrightarrow n_0(\mathbf{r})$$




e.g. H₂ molecule

Another the electrostatic potential



$$v_{\text{Hartree}}(\mathbf{r}) = \int d\mathbf{r}' \frac{n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Charge density creates electrostatic potential.

Kohn-Sham potential

$$v_{\text{aux}}[n](\mathbf{r}) = \underbrace{v_{\text{ext}}(\mathbf{r}) + v_{\text{Hartree}}[n](\mathbf{r})}_{\text{known}} + \underbrace{v_{\text{xc}}[n](\mathbf{r})}_{\text{unknown}}$$

$$\mathcal{H}^e = \sum_{i=1}^{N_e} \left[\underbrace{-\frac{\nabla_{\mathbf{r}_i}^2}{2} + v_{\text{aux}}(\mathbf{r}_i)}_{h_{\text{aux}}(\mathbf{r}_i)} \right] = \sum_{i=1}^{N_e} h_{\text{aux}}(\mathbf{r}_i)$$

Kohn-Sham potential

$$v_{\text{aux}}[n](\mathbf{r}) = \underbrace{v_{\text{ext}}(\mathbf{r}) + v_{\text{Hartree}}[n](\mathbf{r})}_{\text{known}} + \underbrace{v_{\text{xc}}[n](\mathbf{r})}_{\text{unknown}}$$

known

unknown

Now we can solve the Kohn-Sham equations:

$$\left[-\frac{\nabla_{\mathbf{r}}^2}{2} + v_{\text{aux}}[n](\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i^{N_e} |\phi_i(\mathbf{r})|^2$$

Kohn-Sham potential $v_{aux}(r)$

$$v_{aux}[n](\mathbf{r}) = v_{ext}(\mathbf{r}) + v_{H}[n](\mathbf{r}) + v_{xc}[n](\mathbf{r})$$

In practice:

1. start with trial density
2. iterate to self-consistency

The Kohn-Sham potential depends on the density.

$$\left[-\frac{\nabla_{\mathbf{r}}^2}{2} + v_{aux}[n](\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i^{N_e} |\phi_i(\mathbf{r})|^2$$

Kohn-Sham potential $v_{aux}(r)$

FHI-aims technical detail:

FHI-aims offers 3 convergence criteria for the self-consistency cycle:

sc_accuracy_rho : tolerance for the density

o

sc_accuracy_et : tolerance for the total energy

of

sc_accuracy_ee : tolerance for the sum of eigenvalues

v

sc_iter_limit : maximum number of self-consistences steps

$$n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$$

Kohn-Sham energy

$$E[n] = \underbrace{T[n] + E_{\text{ext}}[n] + E_{\text{Hartree}}[n]}_{\text{known}} + \underbrace{E_{\text{xc}}[n]}_{\text{unknown}}$$

$$E[n] = - \sum_i^{N_e} \int d\mathbf{r} \phi_i^*(\mathbf{r}) \frac{\nabla_{\mathbf{r}}^2}{2} \phi_i(\mathbf{r}) + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \\ + \frac{1}{2} \int d\mathbf{r} v_{\text{Hartree}}(\mathbf{r}) n(\mathbf{r}) + E_{\text{xc}}[n]$$

Kohn-Sham energy

$$E[n] = \underbrace{T[n] + E_{\text{ext}}[n] + E_{\text{Hartree}}[n]}_{\text{known}} + \underbrace{E_{\text{xc}}[n]}_{\text{unknown}}$$

- All energies are a functional of the density.
- The exchange-correlation (xc) functional:
 - encompasses all electron-electron interactions beyond Hartree
 - includes the difference between the non-interacting and the interacting kinetic energy

Questions on Kohn-Sham energy and scheme?

$$E[n] = \underbrace{T[n] + E_{\text{ext}}[n] + E_{\text{Hartree}}[n]}_{\text{known}} + \underbrace{E_{\text{xc}}[n]}_{\text{unknown}}$$

- All energies are a functional of the density.
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Kohn-Sham energy

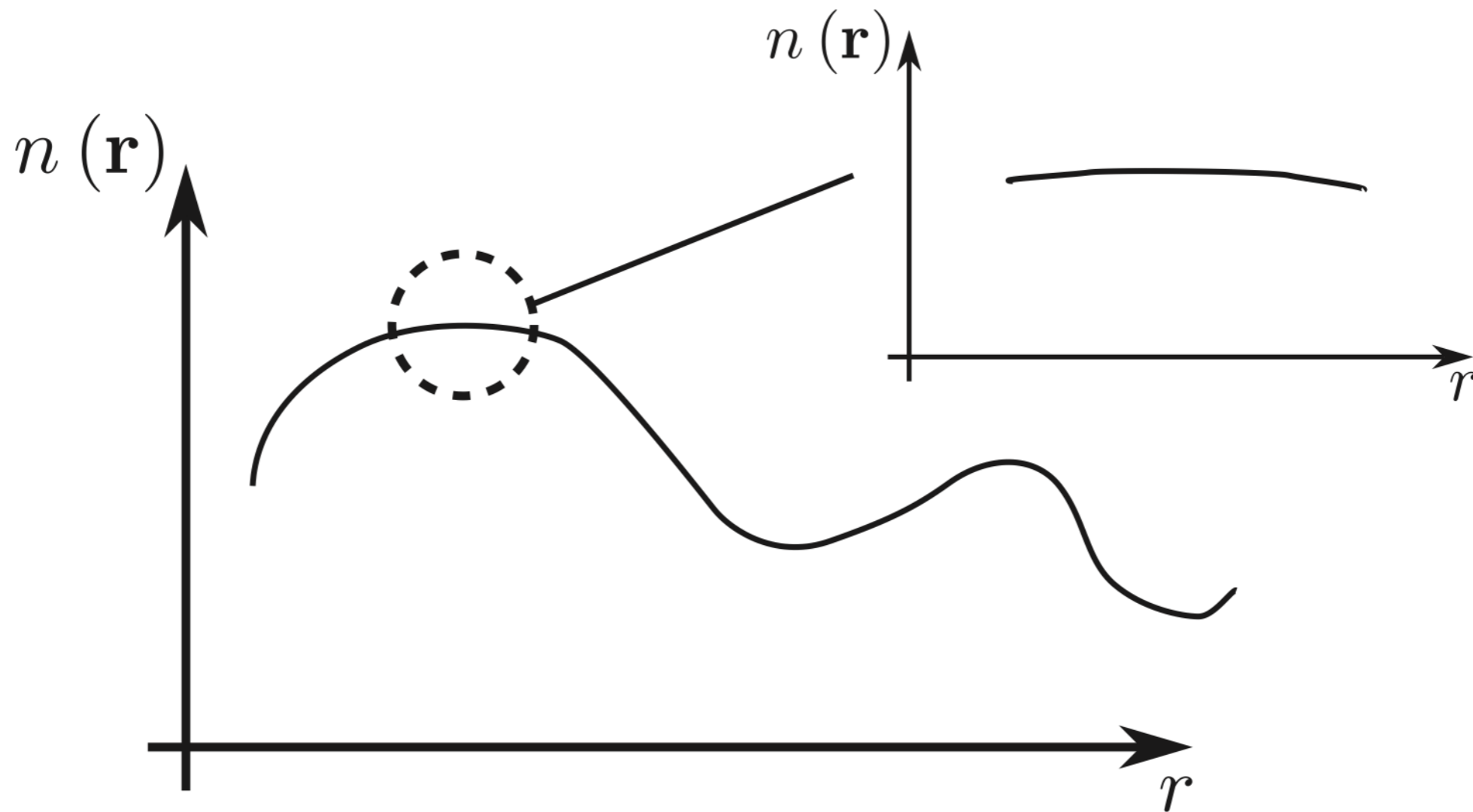
$$E[n] = \underbrace{T[n] + E_{\text{ext}}[n] + E_{\text{Hartree}}[n]} + \underbrace{E_{\text{xc}}[n]}$$

What is this “threatening” E_{xc} ?

- The exchange-correlation (xc) functional encompasses:
 - all electron-electron interactions beyond Hartree
 - the difference between the non-interacting and the interacting kinetic energy

The local density approximation (LDA)

If we zoom in enough, charge density \approx constant.



The local density approximation (LDA)

Constant $n(\mathbf{r})$ = homogenous electron gas (HEG)

Let's make a local approximation:

$$E_{xc}[n] = \int n(\mathbf{r}) \epsilon_{xc}(n(\mathbf{r})) \, d\mathbf{r}$$

exchange-correlation
energy density of HEG

The local density approximation (LDA)

HEG exchange energy density known analytically

$$E_x[n]^{\text{LDA}} = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int d\mathbf{r} n(\mathbf{r})^{4/3}$$

HEG correlation energy density known very accurately from Quantum Monte Carlo simulations

$$E_c[n]^{\text{LDA}} = \text{parameterised efficiently}$$



The local density approximation (LDA)

LDA exchange-correlation potential

$$v_x(\mathbf{r}) = \left(\frac{3}{\pi} \right)^{\frac{1}{3}} n(\mathbf{r})^{\frac{1}{3}}$$

$$v_c(\mathbf{r}) = \text{parameterised efficiently}$$



Beyond the local density approximation

We can incorporate also density-gradients in E_{xc} .

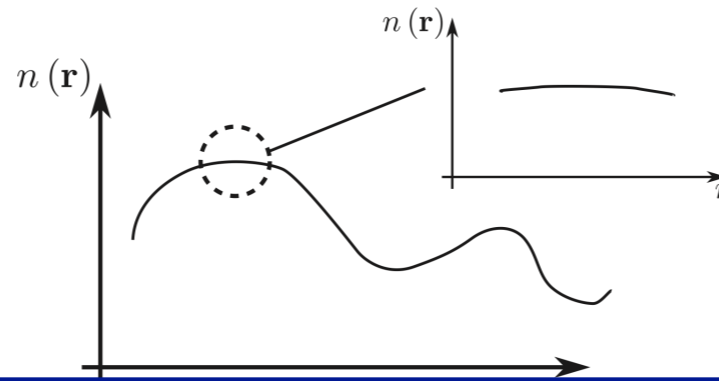
LDA and PBE are very efficient xc-functionals.

Applicable to ~100-1000 atoms.

The PBE xc-functional is such a generalised gradient approximation (GGA).

Questions on LDA?

We can incorporate also density-gradients in E_{xc} .



LDA and PBE are very efficient xc-functionals.
Applicable to ~100-1000 atoms.

The PBE xc-functional is such a generalised gradient approximation (GGA).

Basis functions

Let's expand Kohn-Sham states in a basis.

$$\phi_j(\mathbf{r}) = \sum_i c_{ij} \varphi_i(\mathbf{r})$$

Many basis choices:

- plane waves or real space
- linear augmented plane waves (LAPW)
- projector augmented plane waves (PAW)
- local orbitals (Linear Combination of Atomic Orbitals)
 - Gaussian orbitals
 - numeric atom centered orbitals (NAOs)

Basis functions

In FHI-aims: flexible basis function choice

$$\varphi_{i[lm]}(\mathbf{r}) = \frac{u_i(r)}{r} Y_{lm}(\Omega)$$

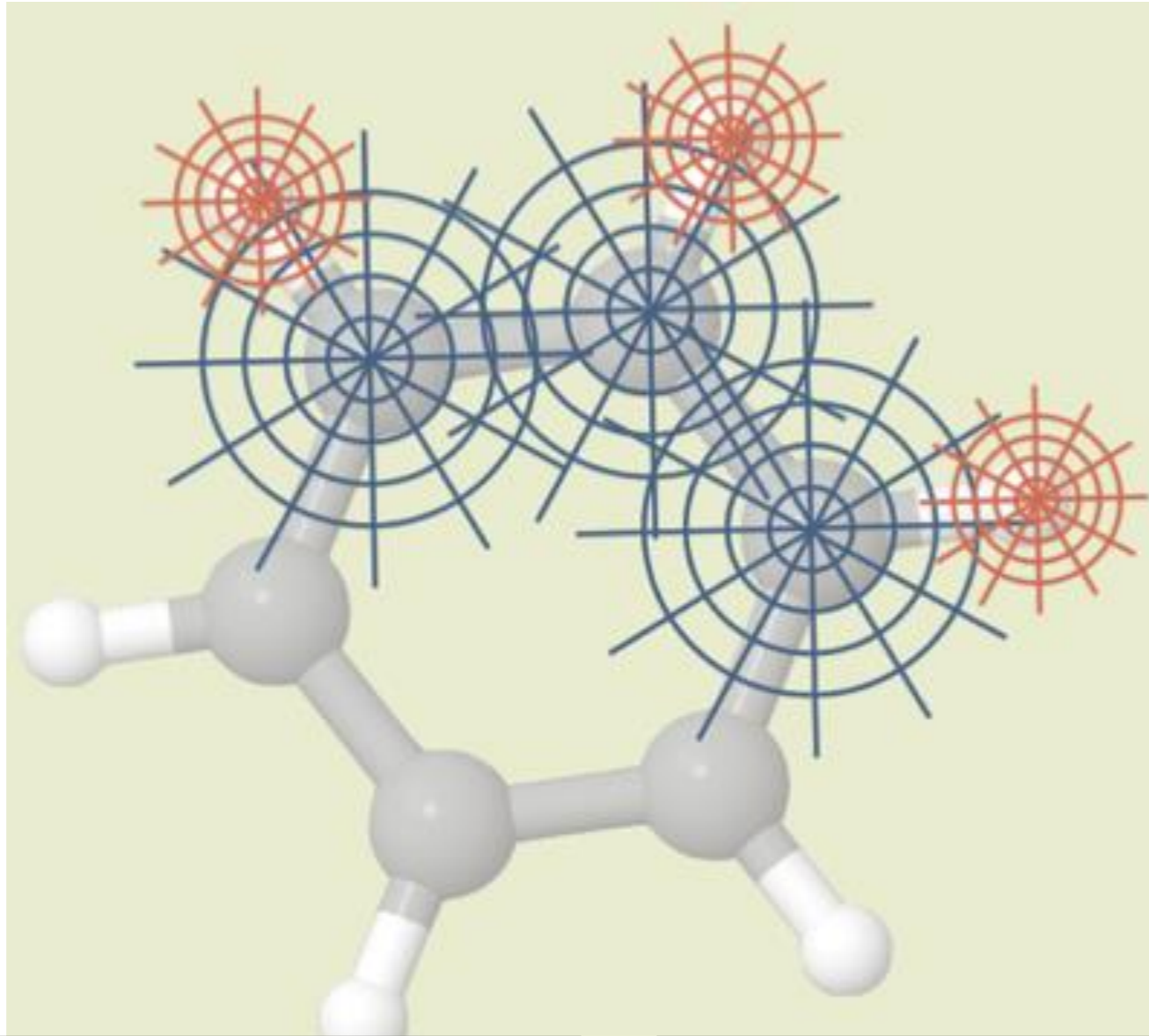
radial function

spherical harmonic

solution of a radial Schrödinger equation:

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + v_i(r) + v_{\text{cut}} \right] u_i(r) = \epsilon_i u_i(r)$$

Real-space grid for basis functions in FHI-aims



1: grid parameters
(light, tight, really tight)

2: number basis functions
(Tiers)



Questions?

Or start to work on the tutorials ...

Download the tutorial instructions and data from:

- MyCourses -> Hands-on tutorials
- `/work/courses/unix/PHYS/E0546/TUTORIALS`
- ask for printout version

Those who were not here the last week – let us know so we can help you with the setup.