Density-Functional Theory for Practitioners - Lecture 2

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Revision

At your table, reflect on last week's lecture and tutorial:

- What did we cover and what did you learn?
- Do you have any questions about the DFT calculations in the tutorial?
- Did the tutorial exercises help you to understand DFT better?

This lesson

Must know	Should know	Nice to know
DFT ground-state energies	Potential energy surfaces	Confomers and isomers
Energy derivatives (forces)	Structure relaxation	Hellman-Feynman theorem

Learning outcomes

After completion of this class you

- are familiar with the electronic ground state.
- know how to use the ground state to calculate certain materials properties.
- know how to determine the equilibrium structure of a molecule/material with DFT.

Recap - The three *principles* of DFT

1: DFT is in principle an exact ground state theory.

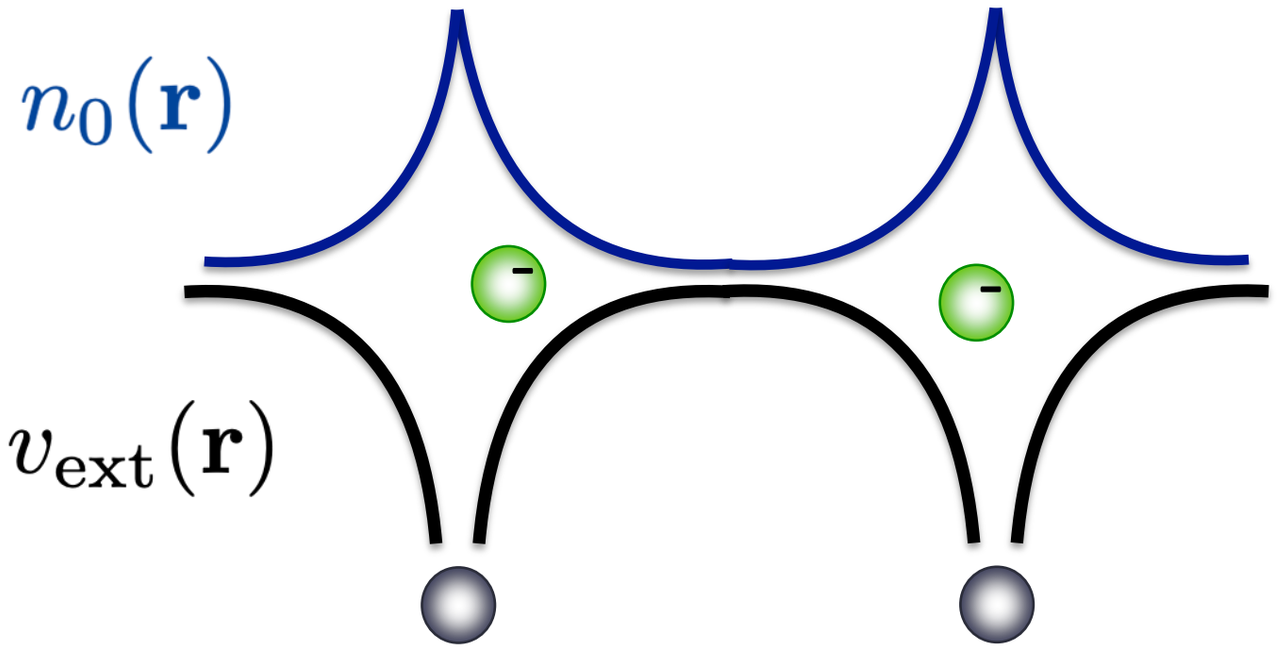
2: The energy is a functional of the density.
The ground state energy is attained at the ground state density.

3: The energy functional needs to be approximated in practice.

External potential and density

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

Note:
bold **r** means $\vec{r}$
small letters – -
large letters – +



e.g. H_2 molecule

The external potential

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

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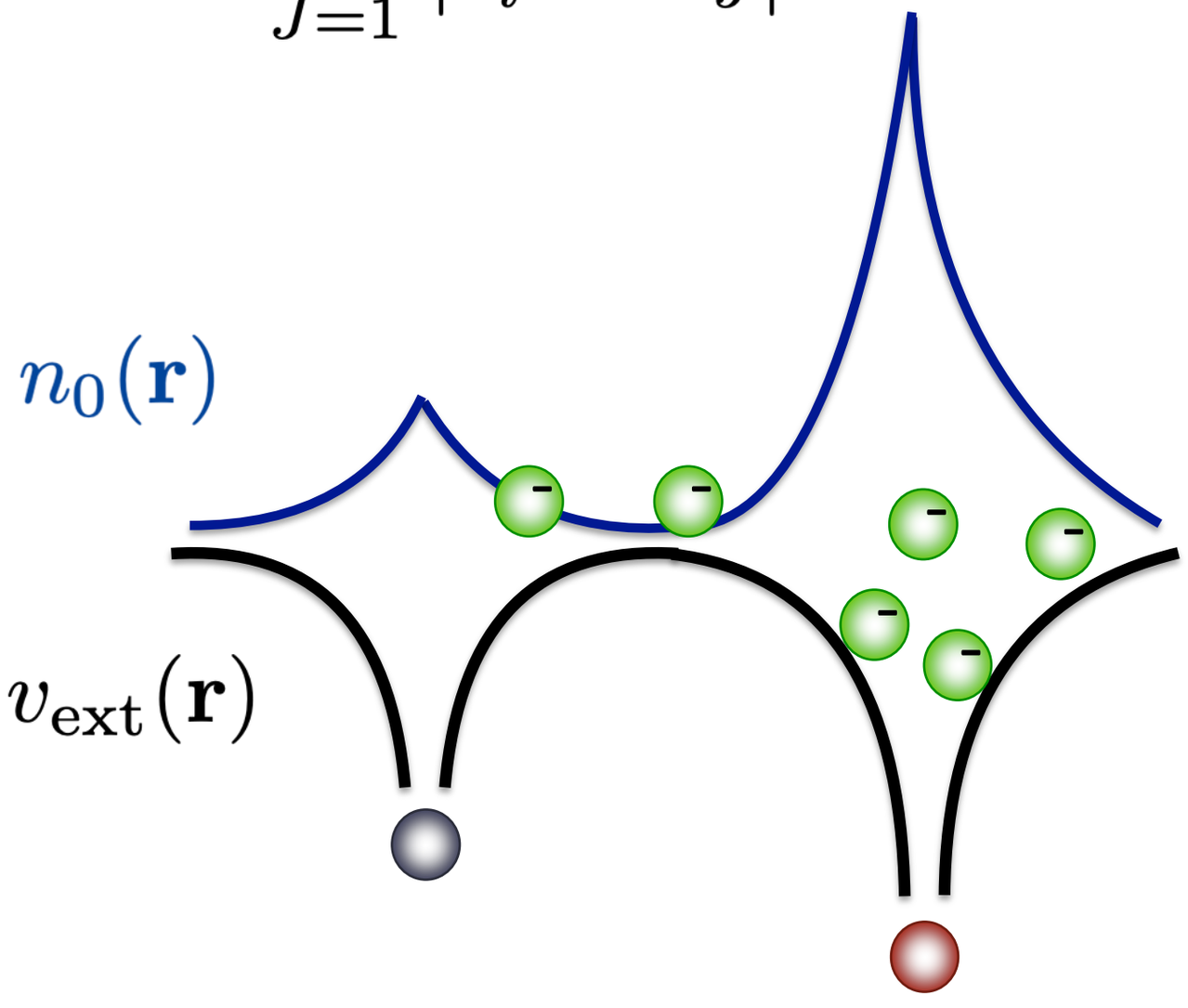
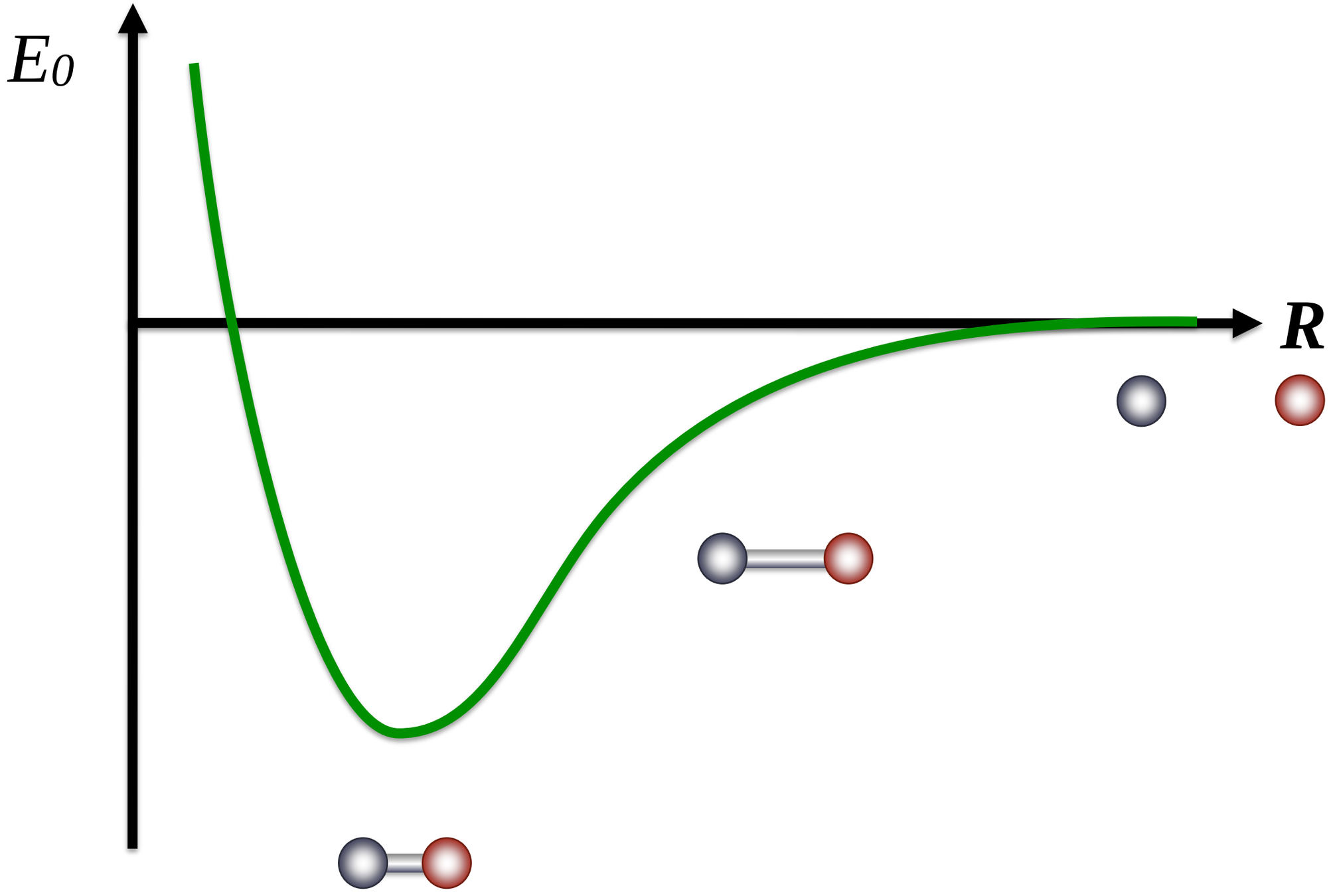


or HF molecule

Binding energy curve



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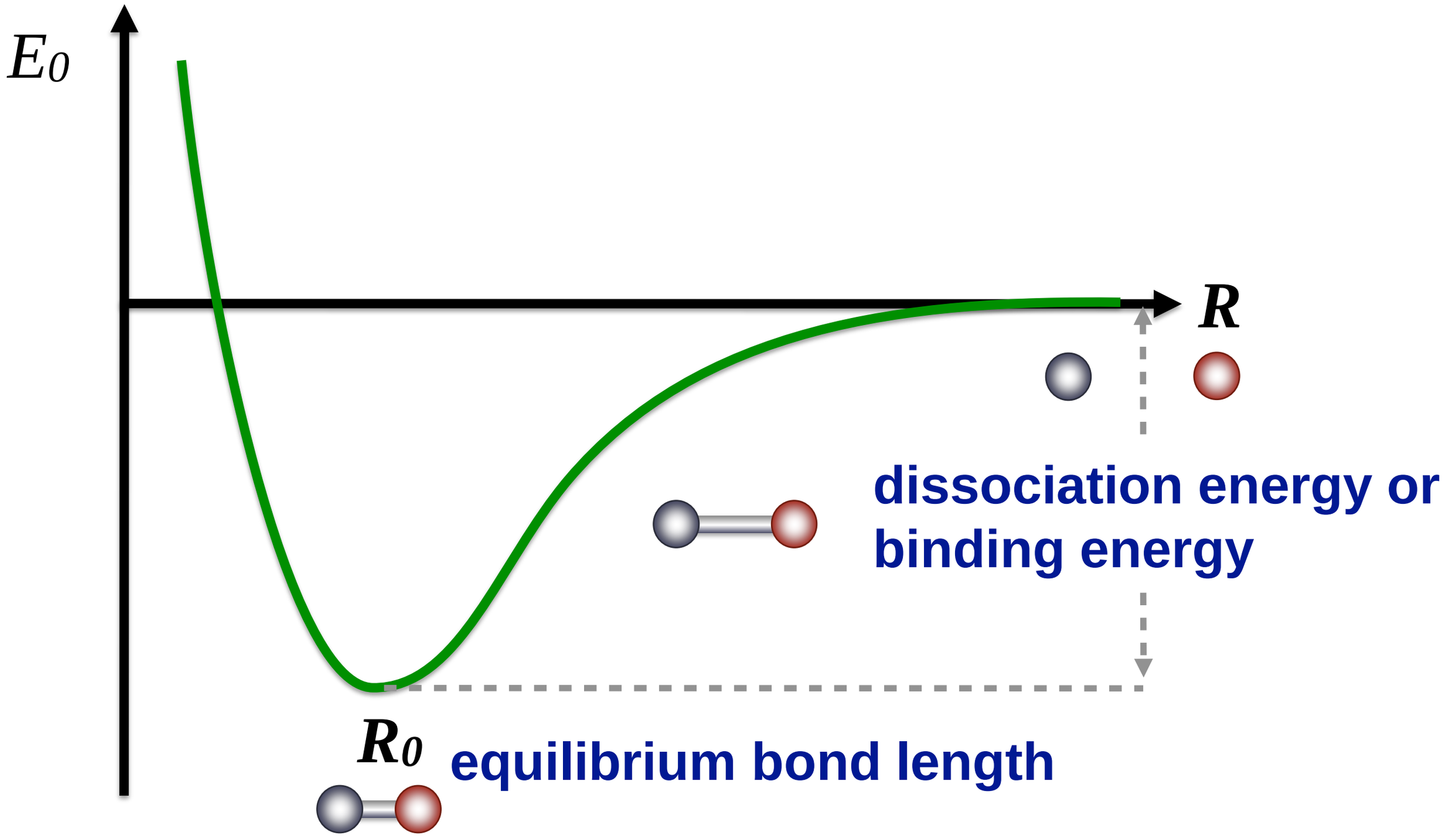

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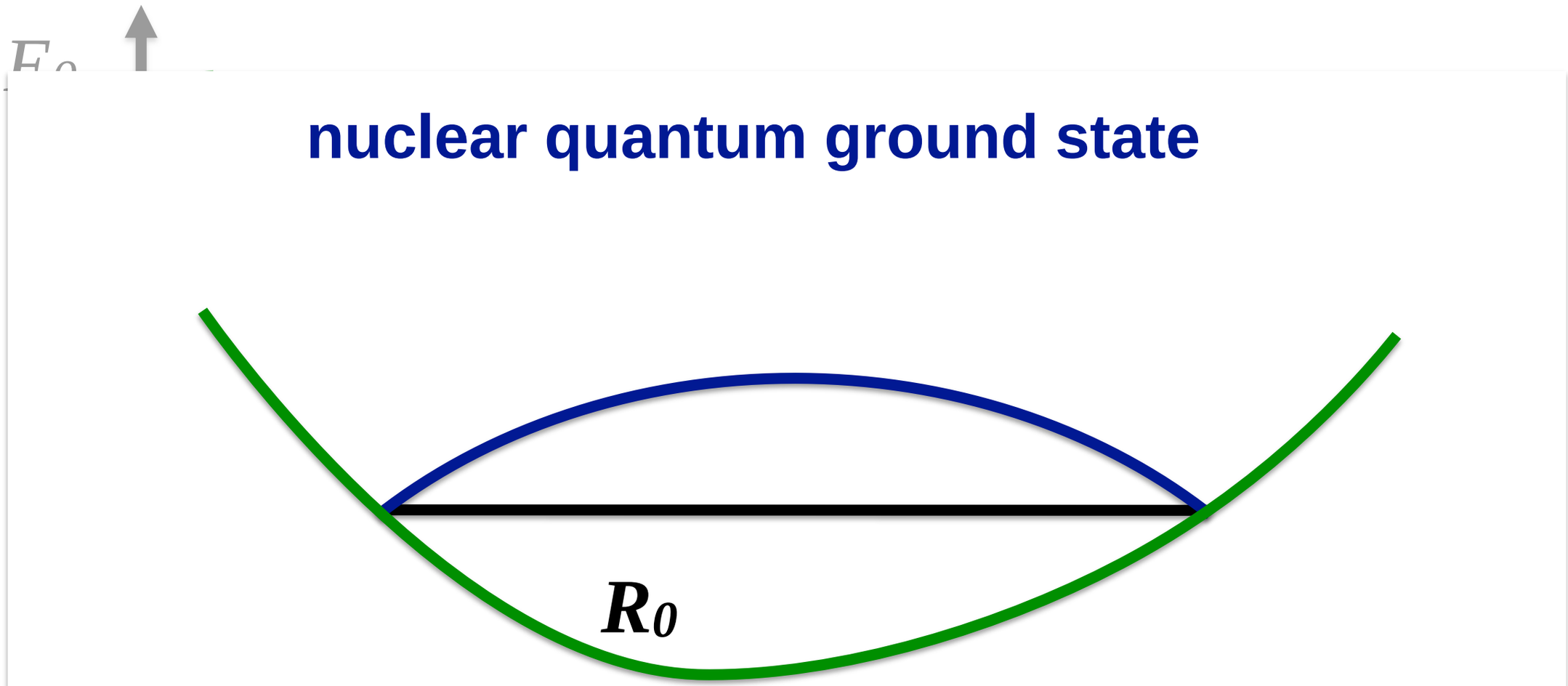
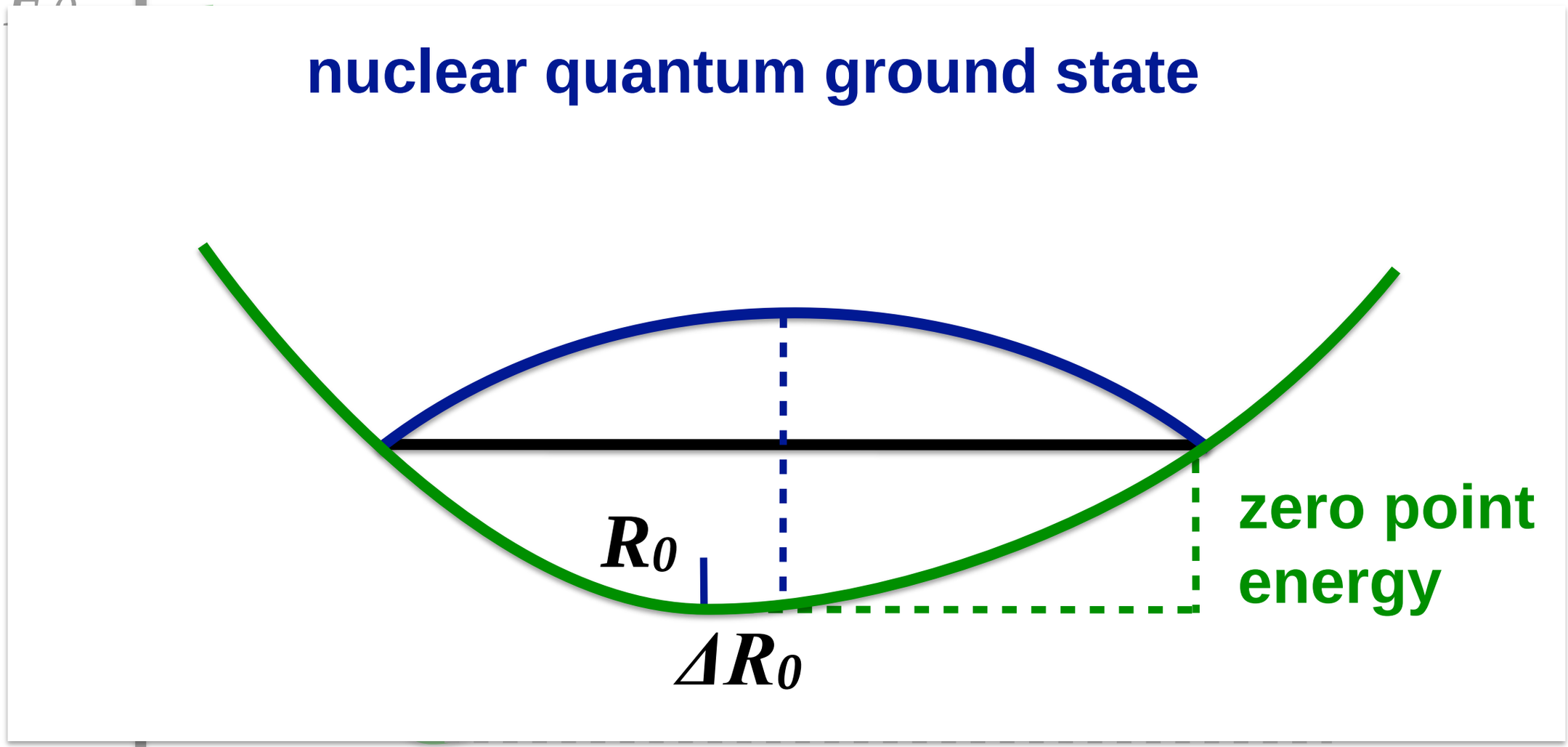


R_0 equilibrium bond length

Binding energy curve

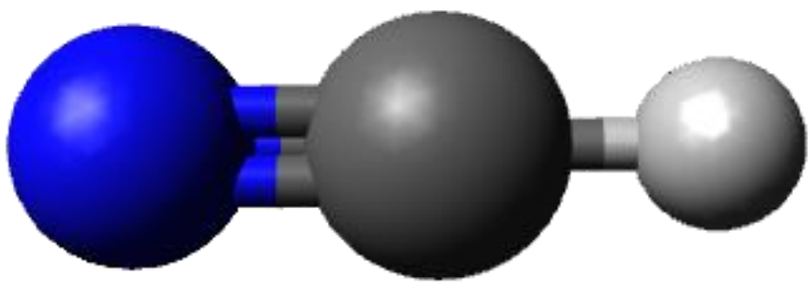


R_0 equilibrium bond length

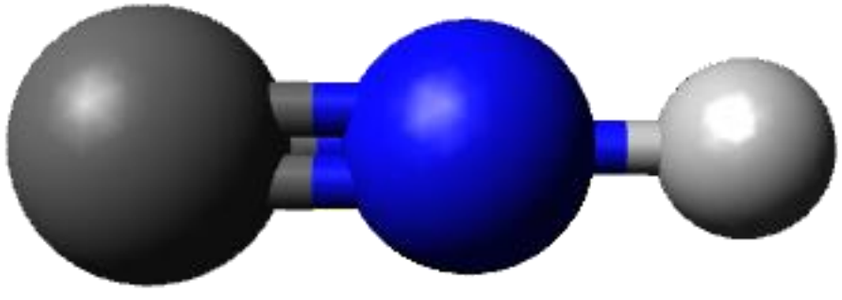
Potential energy of isomers

Isomer: molecules with the same chemical formula, but different atomic structure

Which one is more stable?
(and thus is usually more abundant)

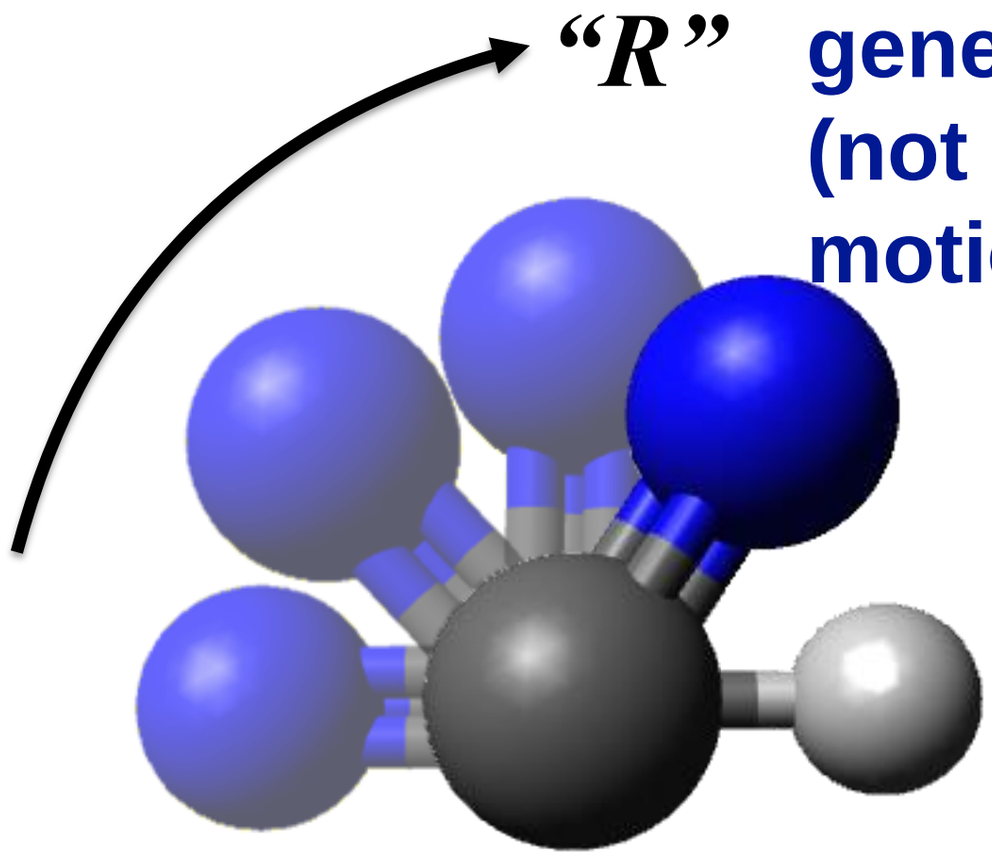


hydrogen cyanide (HCN)

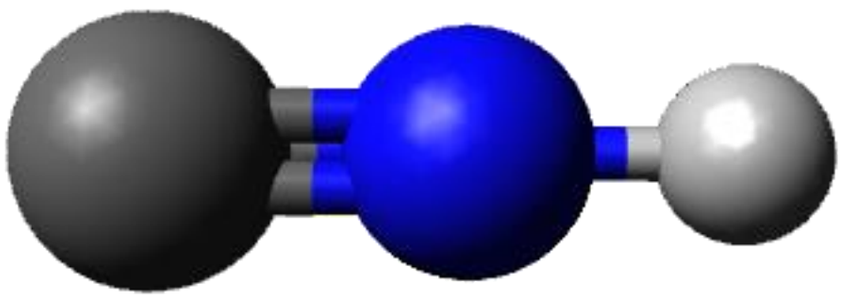


hydrogen isocyanide (HNC)

Potential energy of isomers



generalised coordinate (not necessarily just the motion of one atom)



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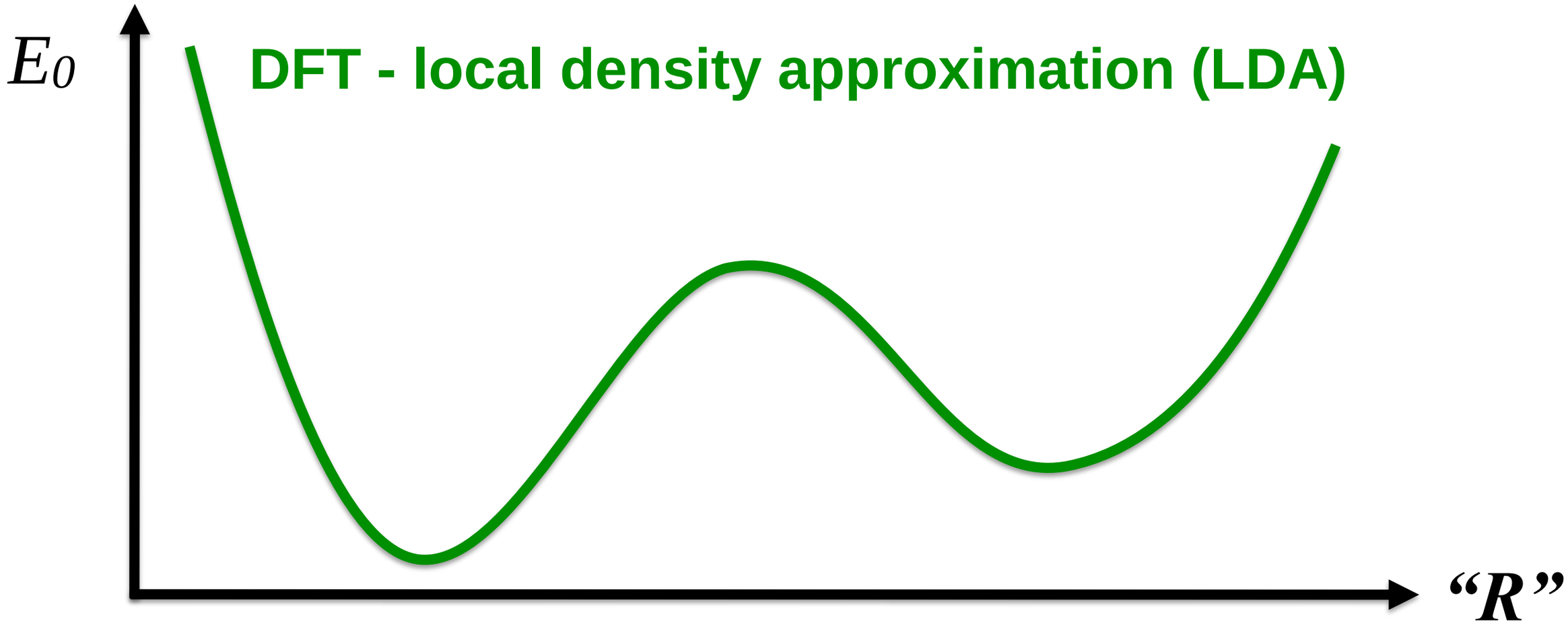
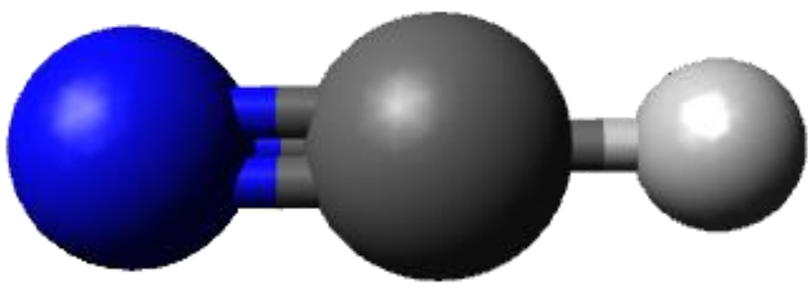
Potential energy of isomers





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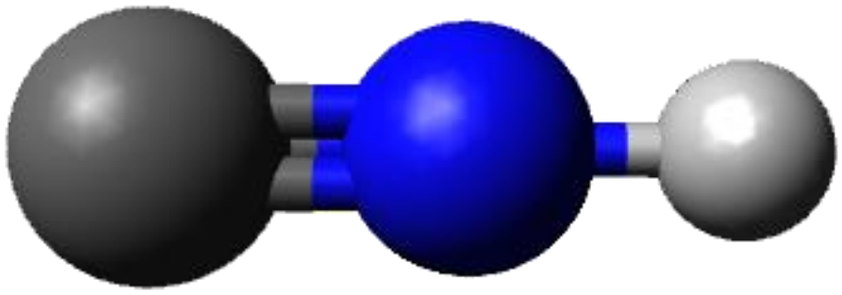
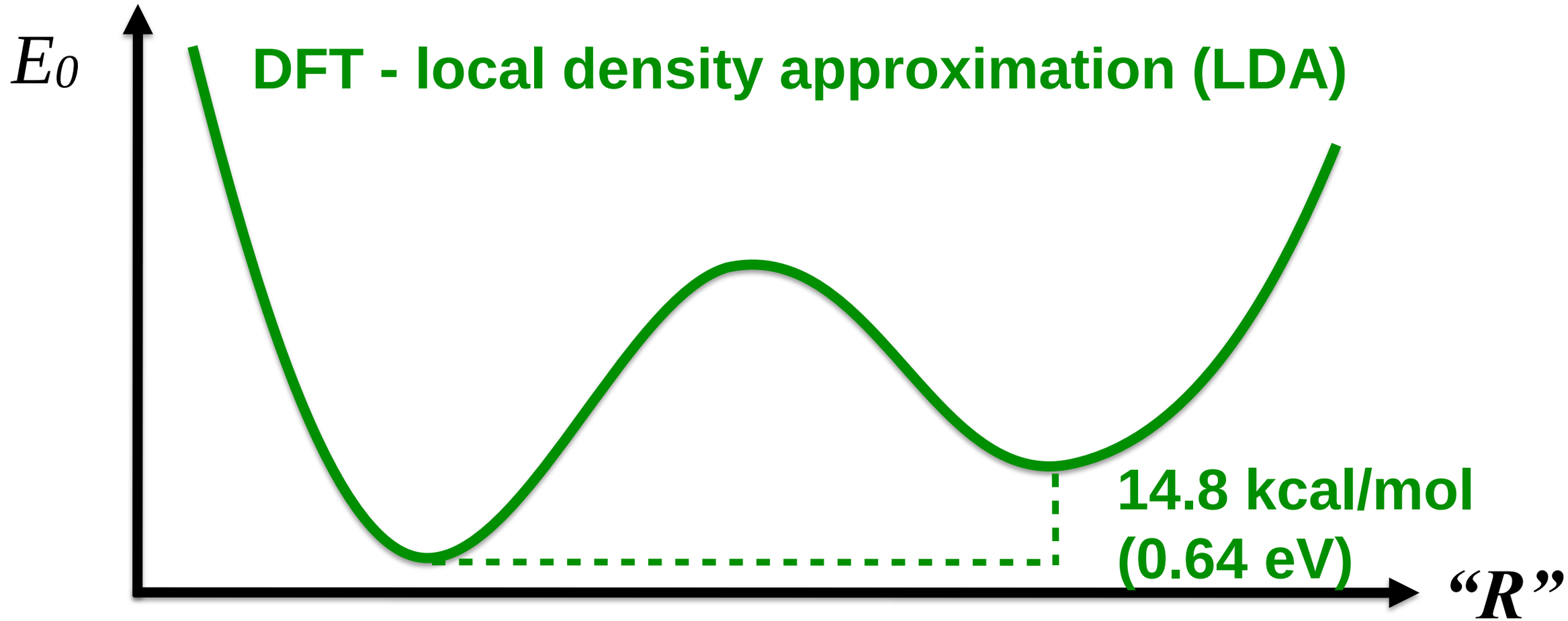
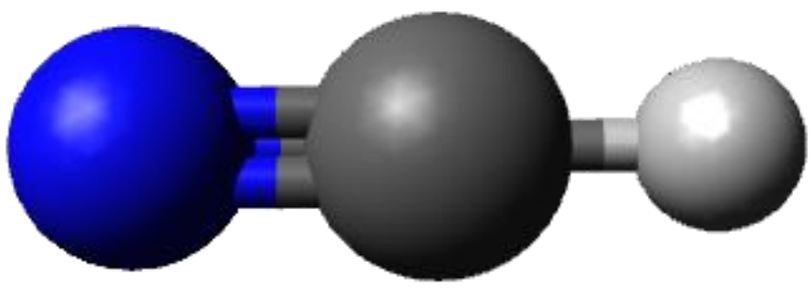


hydrogen isocyanide (HNC)

L. Deng and T. Ziegler, Int. J. Quantum Chem. 52, 731(1994)

Potential energy of isomers





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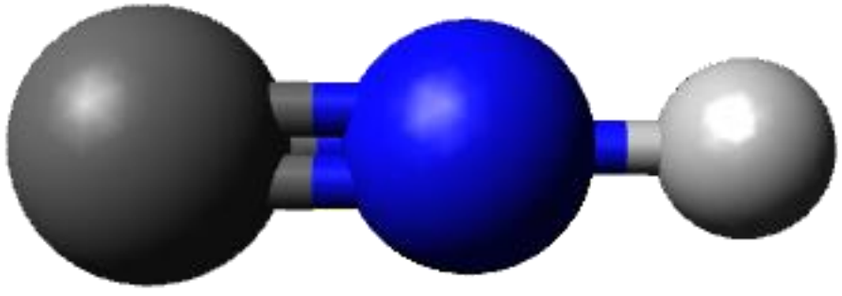

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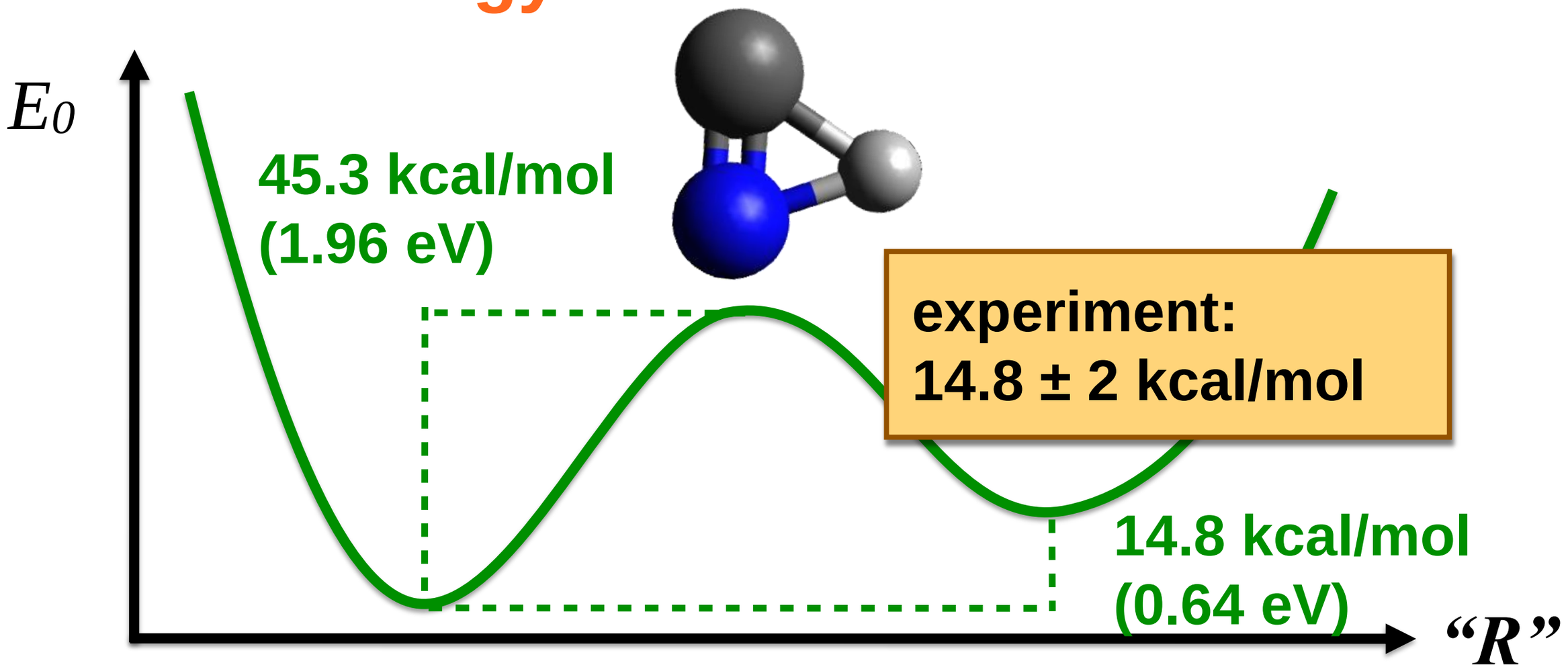

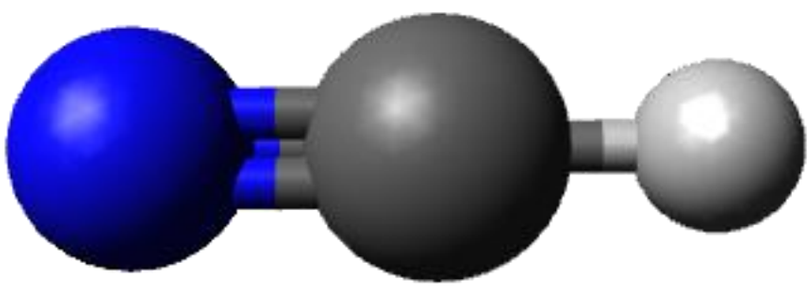

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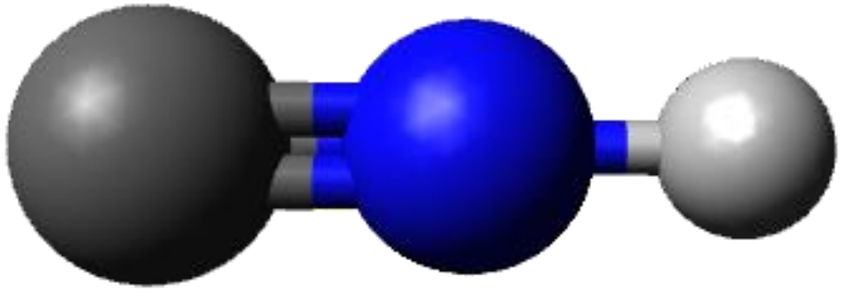

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Free energy

In principle: we should consider free energies!

Helmholtz free energy*:

$$F = E - TS$$

*In reaction, we have given number of particles and size. (NVT)

Free energy

In principle: we should consider free energies!

Helmholtz free energy:

temperature

$$F = E - TS$$

total energy

entropy:

- **vibrational**
- **configuration**
- **magnetic**

Free energy

In principle: we should consider free energies!

Helmholtz free energy:

$$F = E - TS$$

Gibbs free energy†:

$$G = E - TS + pV$$

volume

pressure

† In reaction, we have given number of particles and pressure. (NPT)

Free energy

In principle: we should consider free energies!

Helmholtz free energy:

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volume

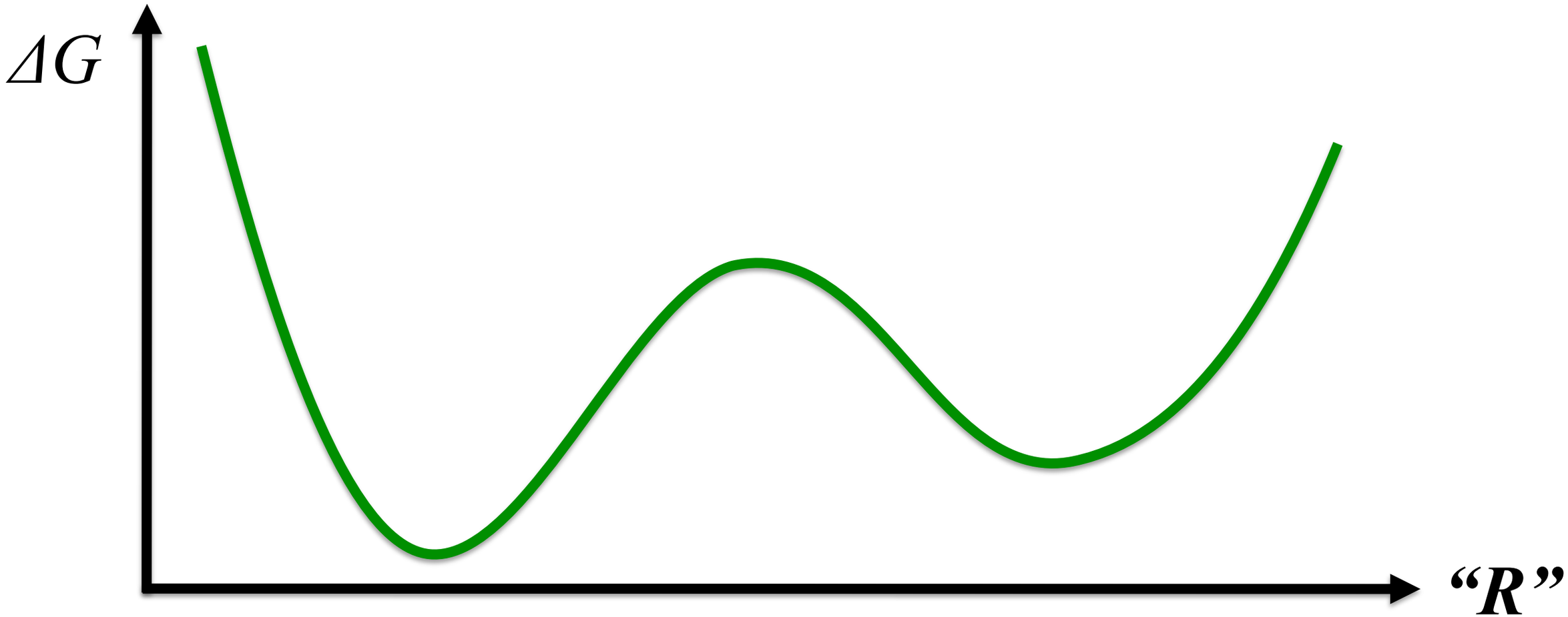
pressure

Enthalpy‡:

$$H = E + pV$$

‡ In reaction, we have given number of particles, pressure (1 bar) and standard temperature 298K for reactants and products = standard heat of reaction

Chemical reactions

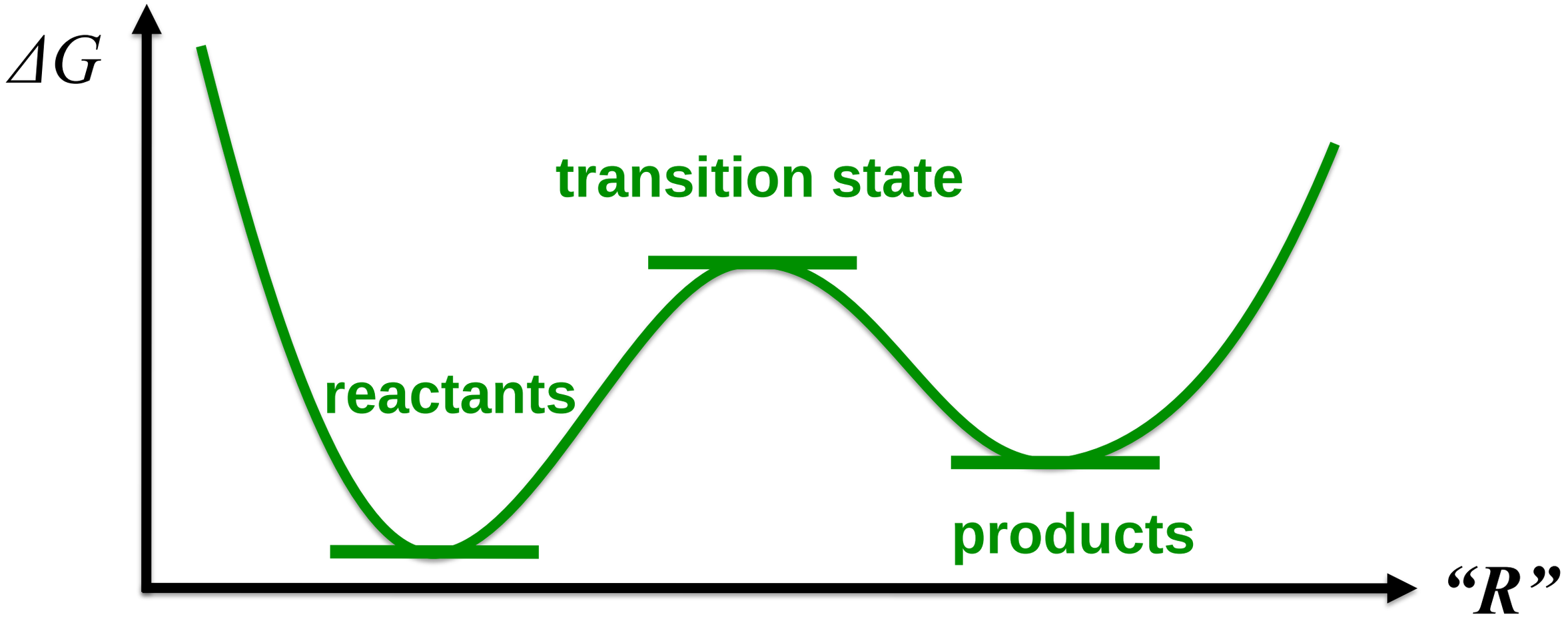


reactants: **products:**

$$A + B \longrightarrow C + D$$

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

Chemical reactions



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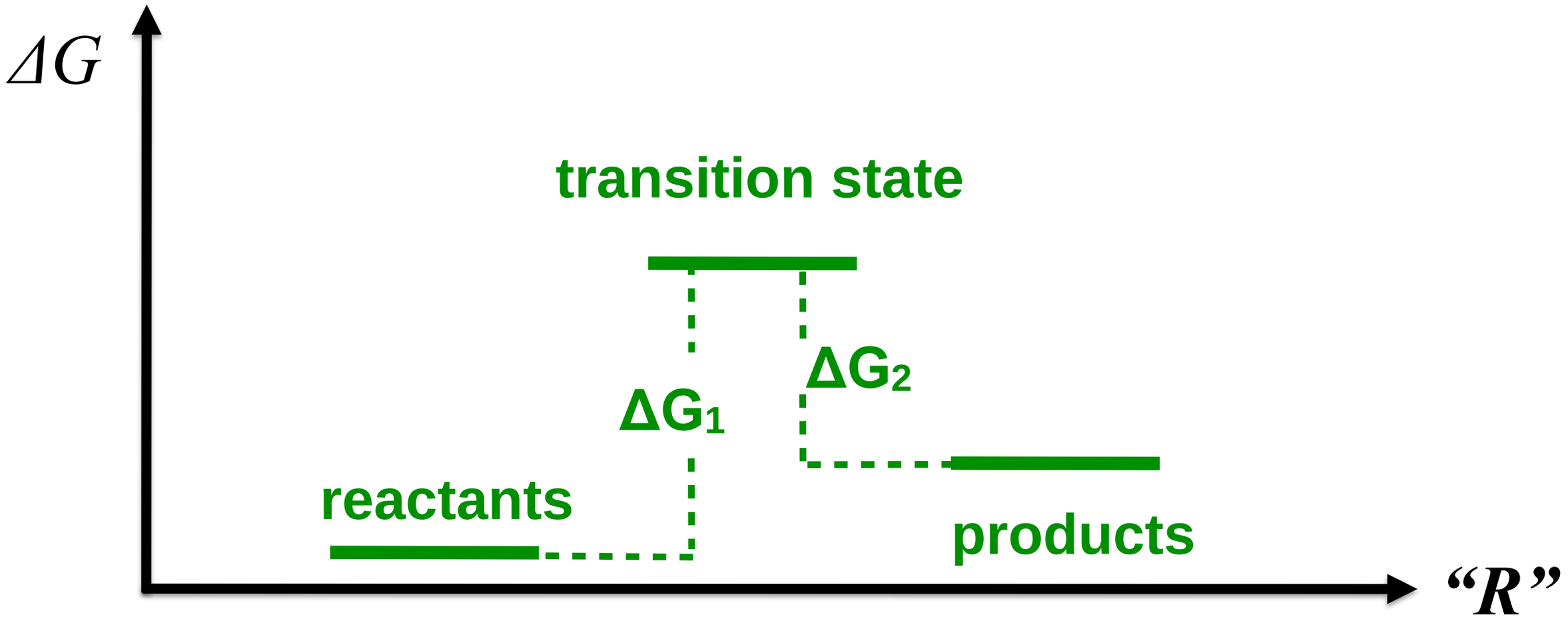

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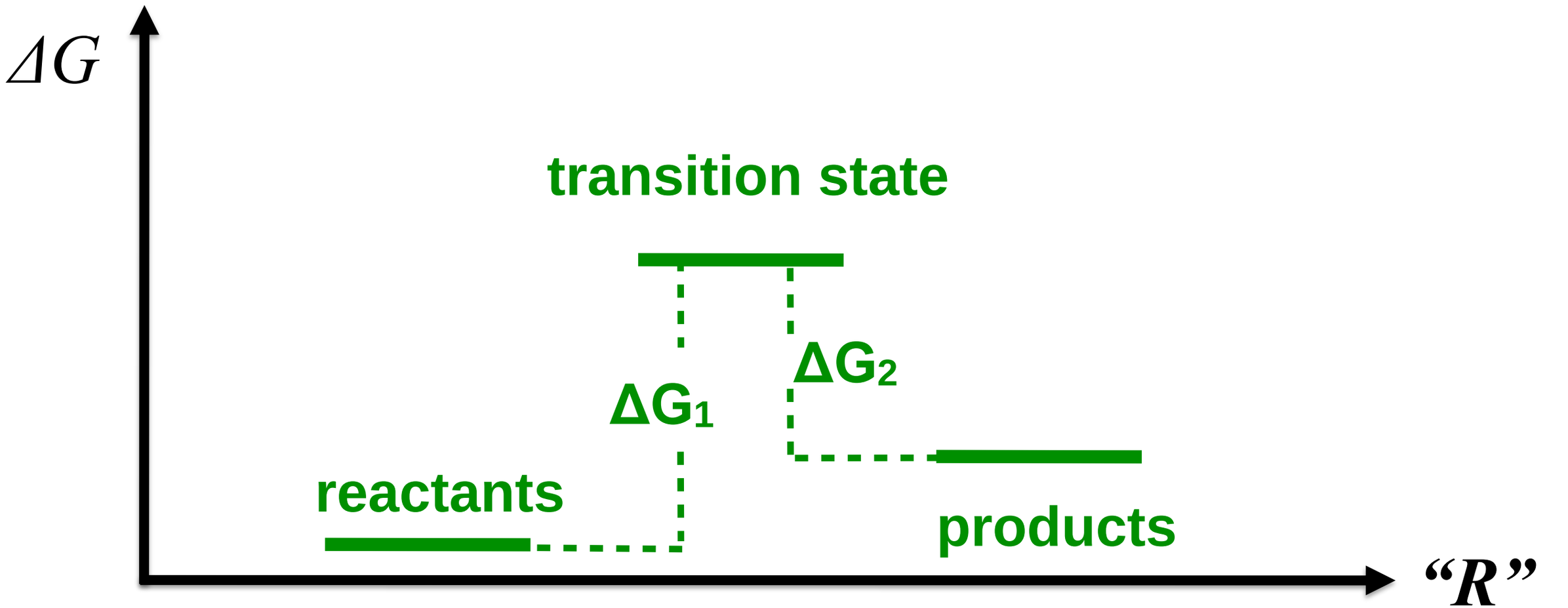


$$\Delta G = \Delta H - T\Delta S$$

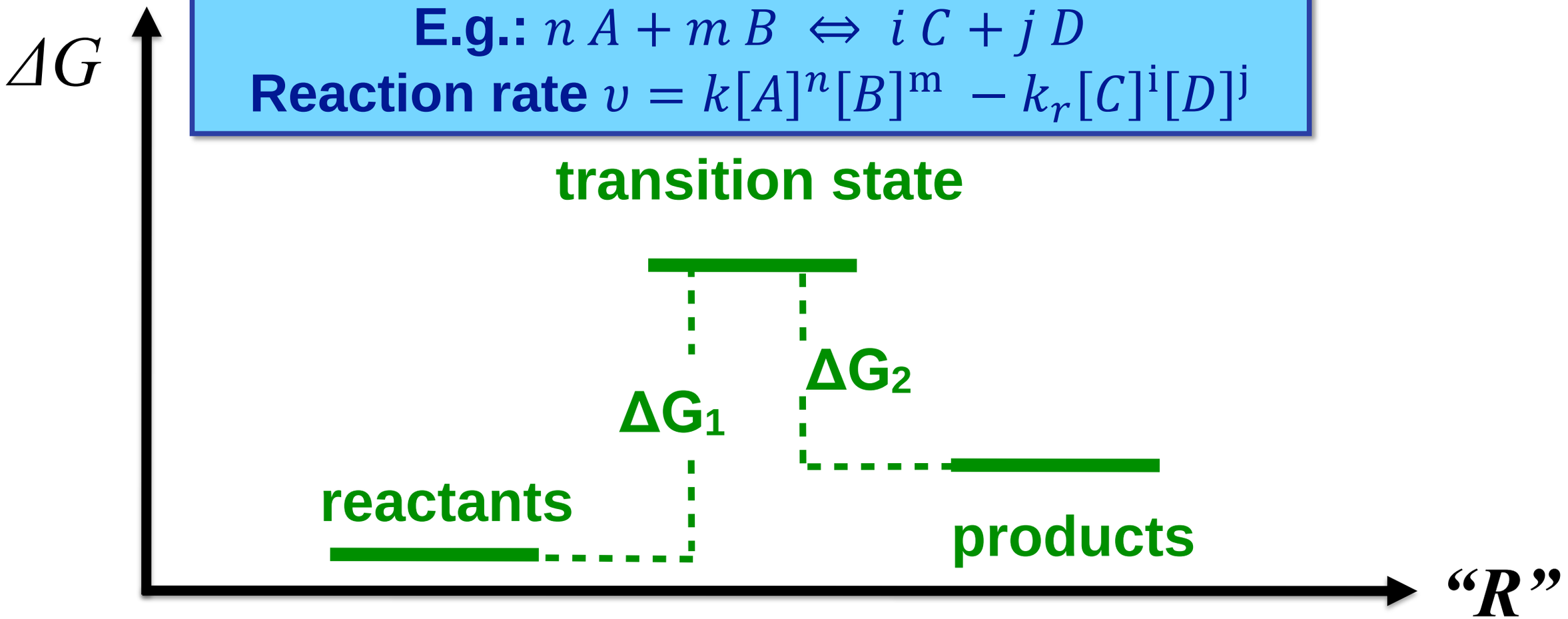
← change in entropy

change of enthalpy or
heat of reaction ← due to bond breaking or creation

Chemical reactions

E.g.: $n\,A + m\,B \;\Leftrightarrow\; i\,C + j\,D$

Reaction rate $v = k[A]^n[B]^{\mathrm{m}} - k_r[C]^{\mathrm{i}}[D]^{\mathrm{j}}$

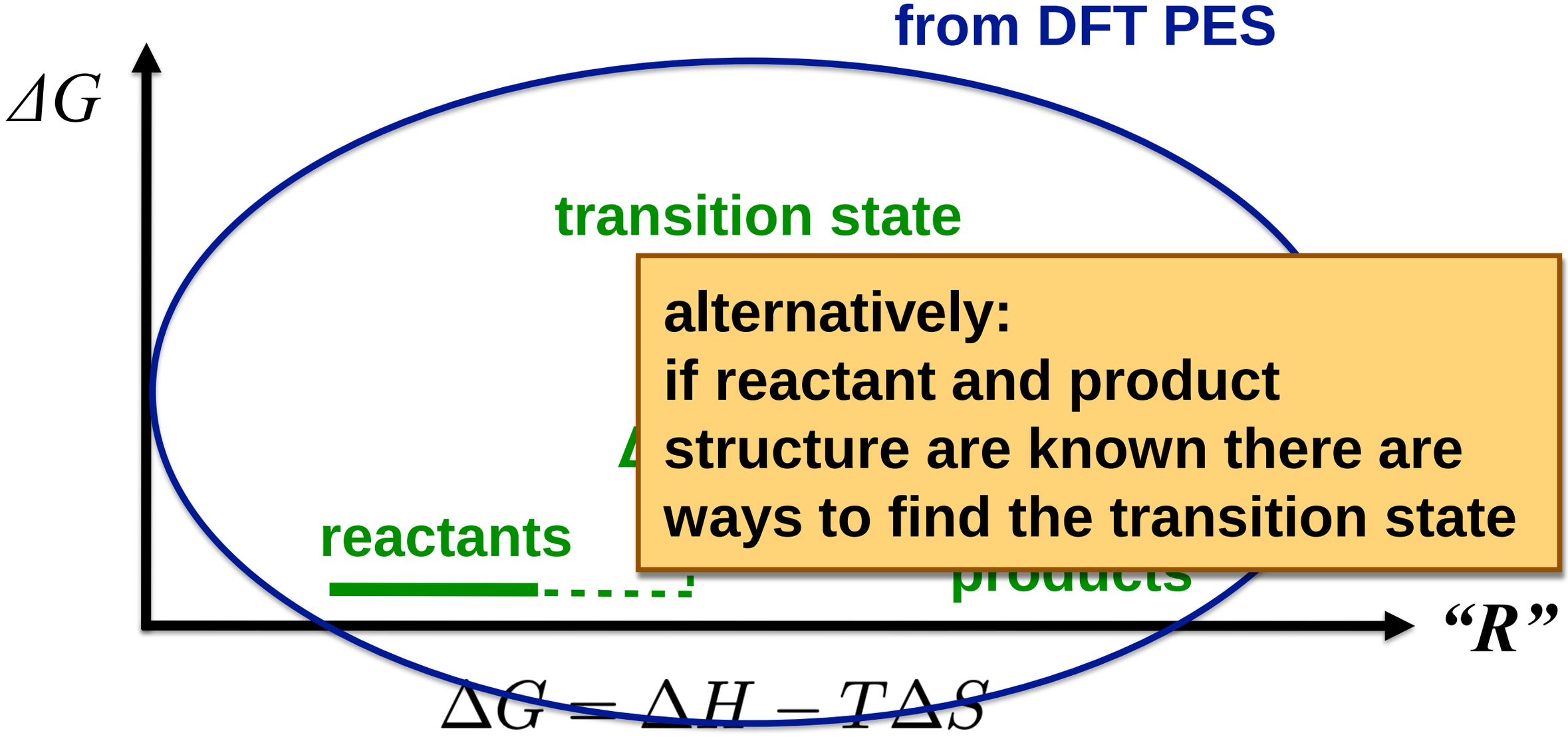


$$\Delta G = \Delta H - T\Delta S$$

$$k = \gamma(T) k_B T e^{\frac{\Delta G(T)}{k_B T}}$$

speed of the chemical process

Chemical reactions



alternatively:
if reactant and product structure are known there are ways to find the transition state

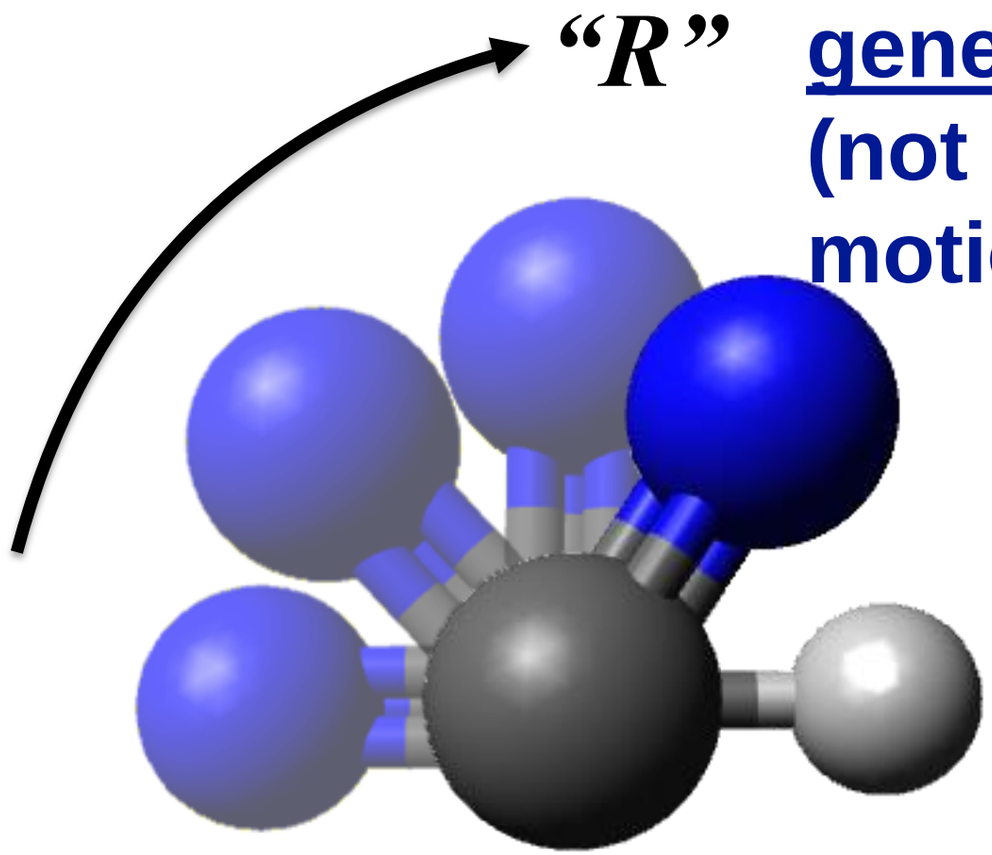
$$\Delta G = \Delta H - T\Delta S$$

$$\approx \Delta H$$

DFT

$$\approx \Delta E + p\Delta V$$

Back to the potential energy



generalised coordinate
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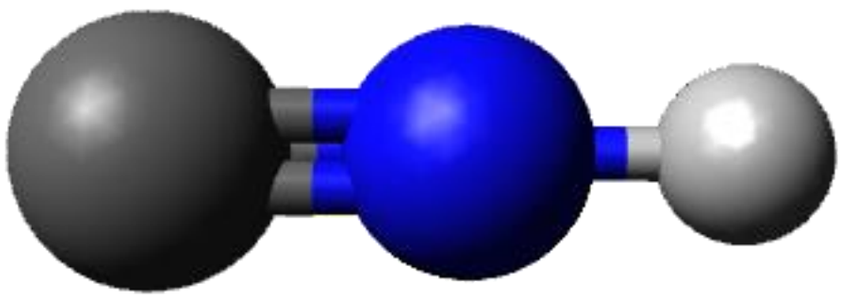
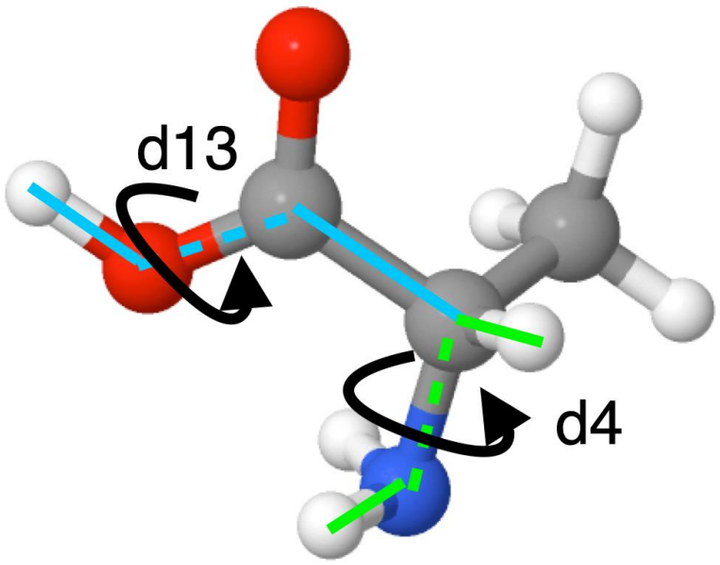


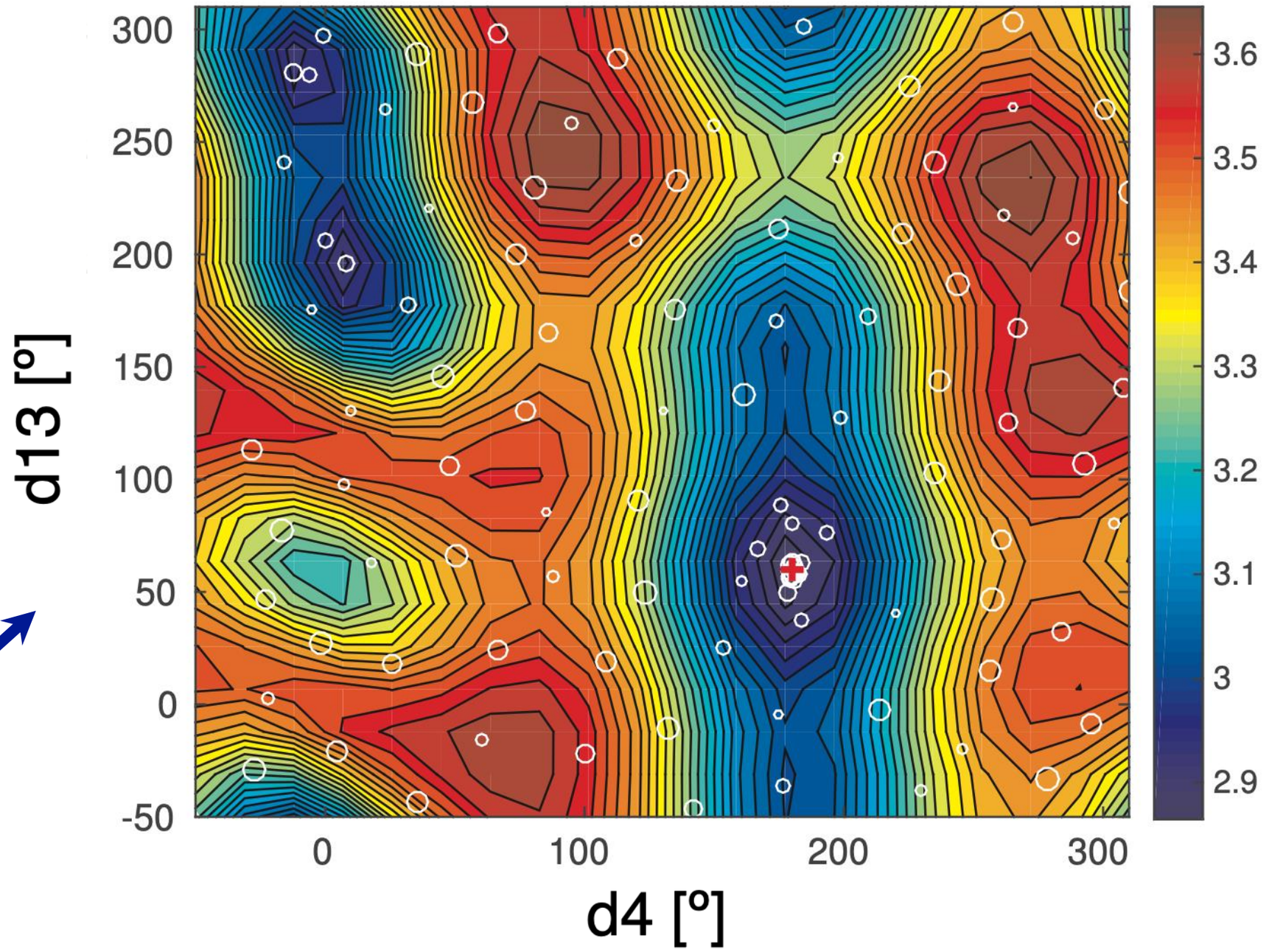
hydrogen cyanide (HCN)

hydrogen isocyanide (HNC)

Alanine - an amino acid



potential energy surface



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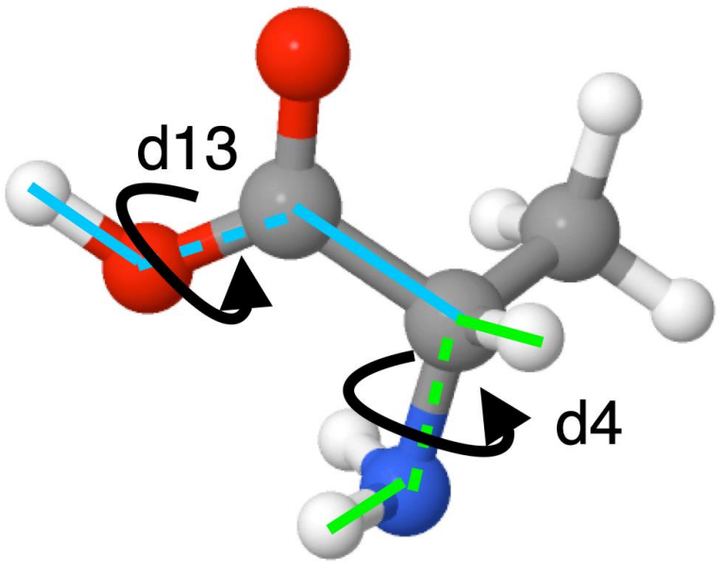


$$v_{\mathrm{ext}}(\mathbf{r}, \bullet\bullet\bullet \quad \ldots \quad \bullet\bullet)$$

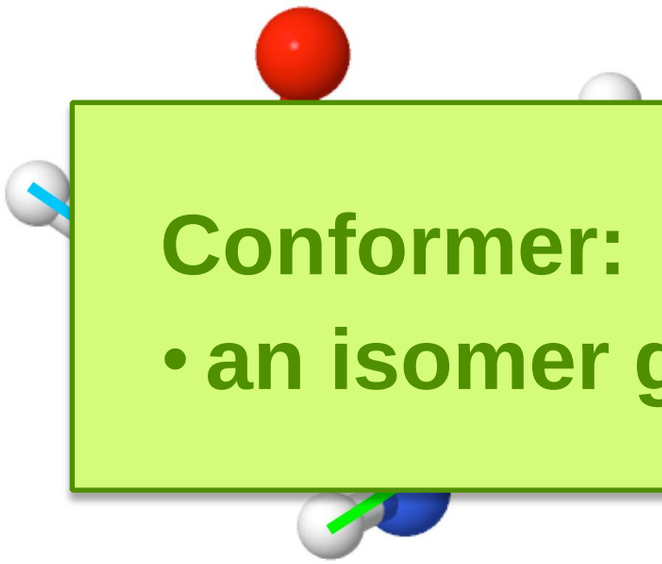
$\Downarrow$ **density-functional theory**

$$E_{\mathrm{tot}}(\bullet\bullet\bullet \quad \ldots \quad \bullet\bullet)$$

Potential energy surface (PES):

- **total energy in terms of the atomic positions**
- **the minima are the stable conformers/isomers**

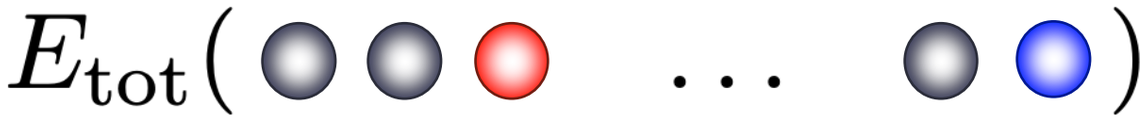
Potential energy surface



Conformer:

- **an isomer generated exclusively by rotations**

density functional theory



Potential energy surface (PES):

- **total energy in terms of the atomic positions**
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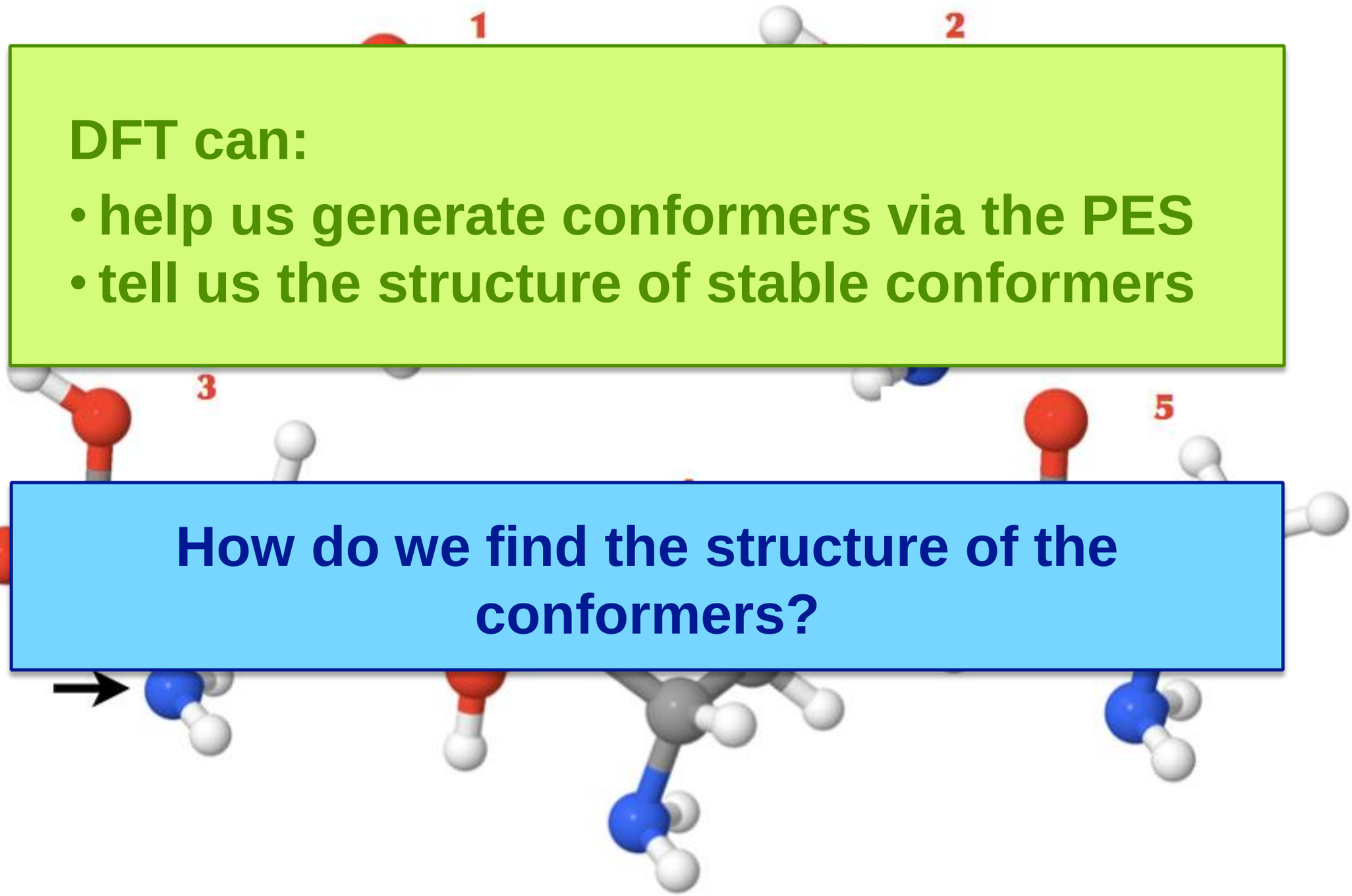
Conformers of alanine

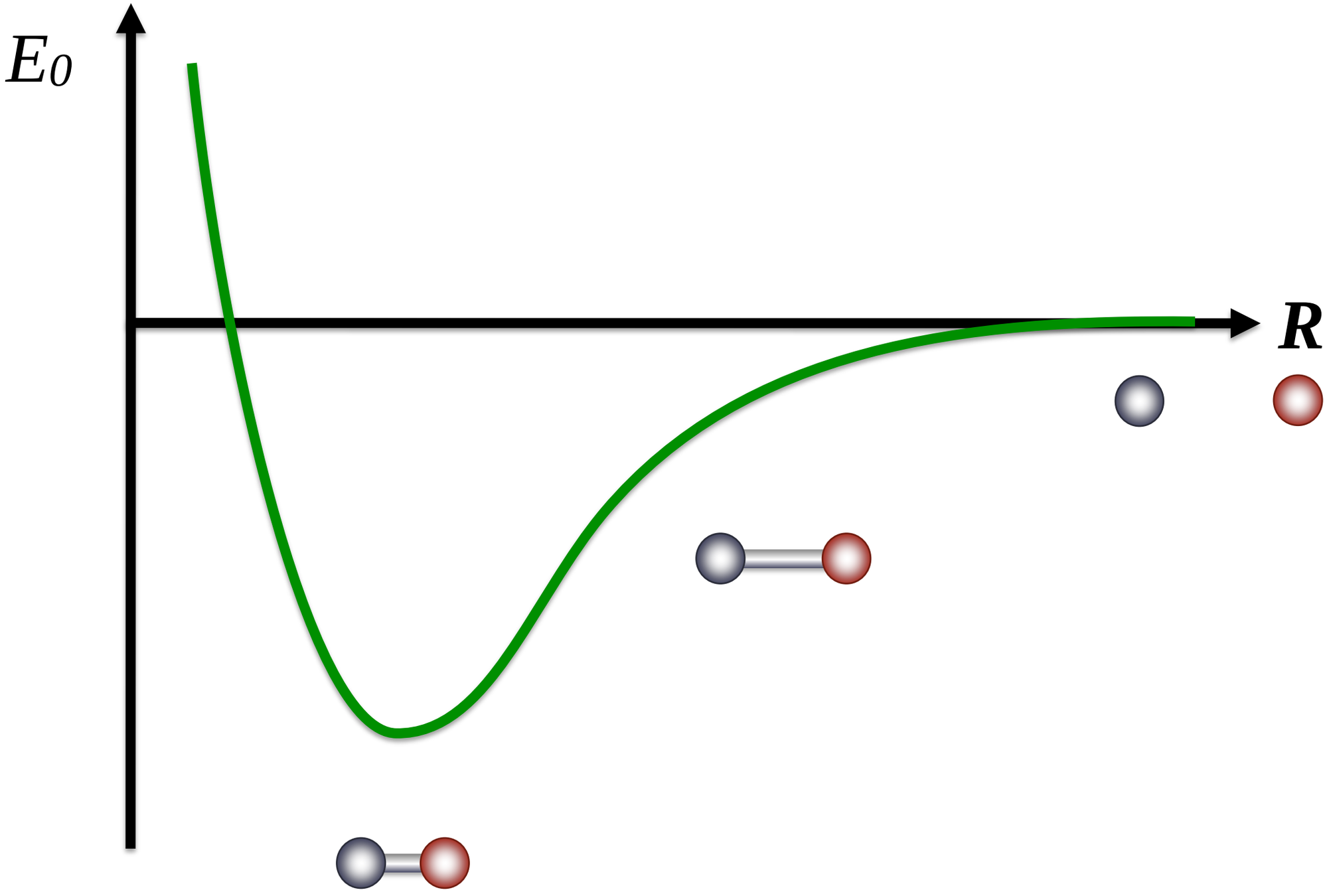


DFT can:

- **help us generate conformers via the PES**
- **tell us the structure of stable conformers**

How do we find the structure of the conformers?

Revisit the binding energy curve



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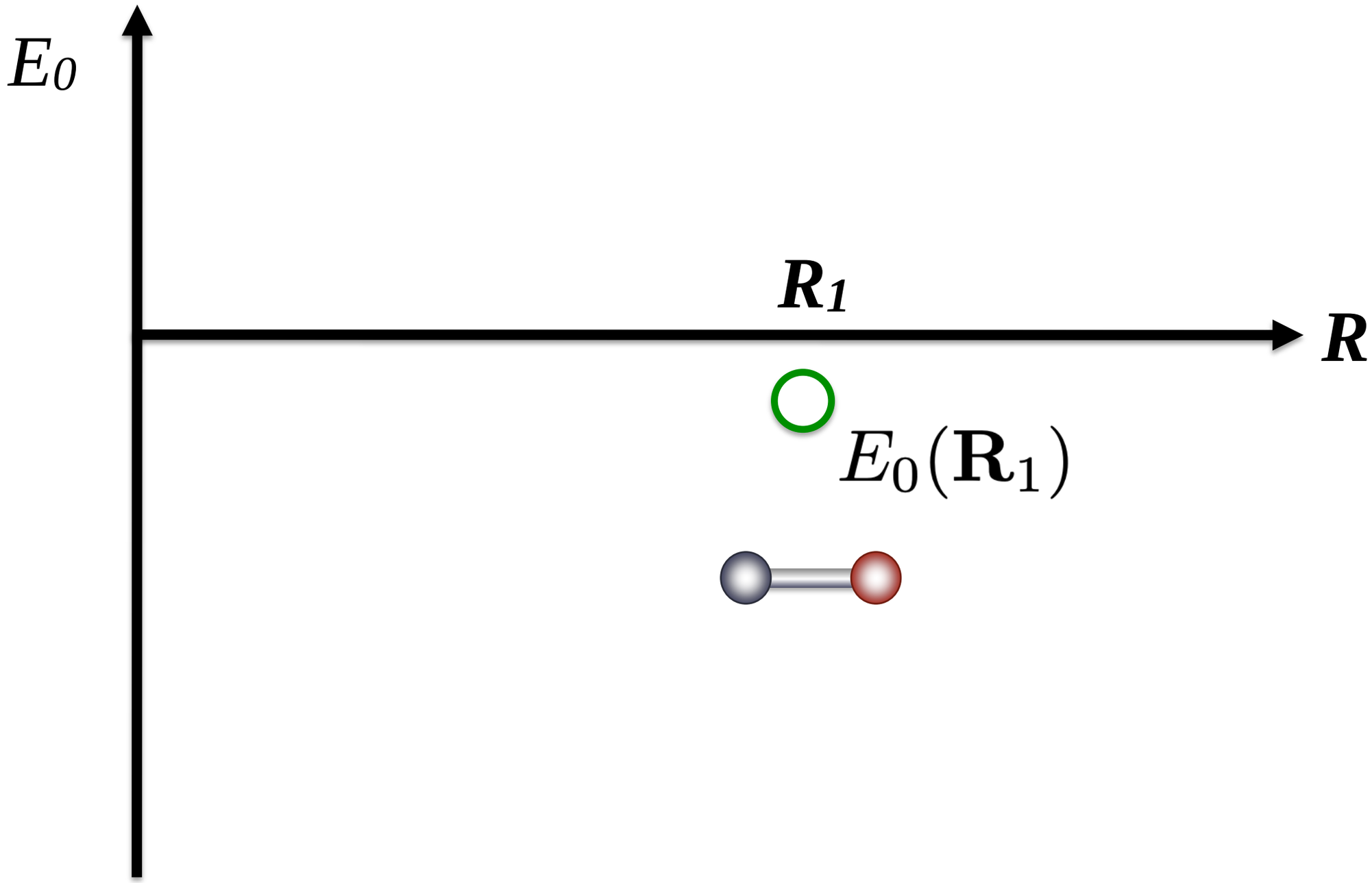

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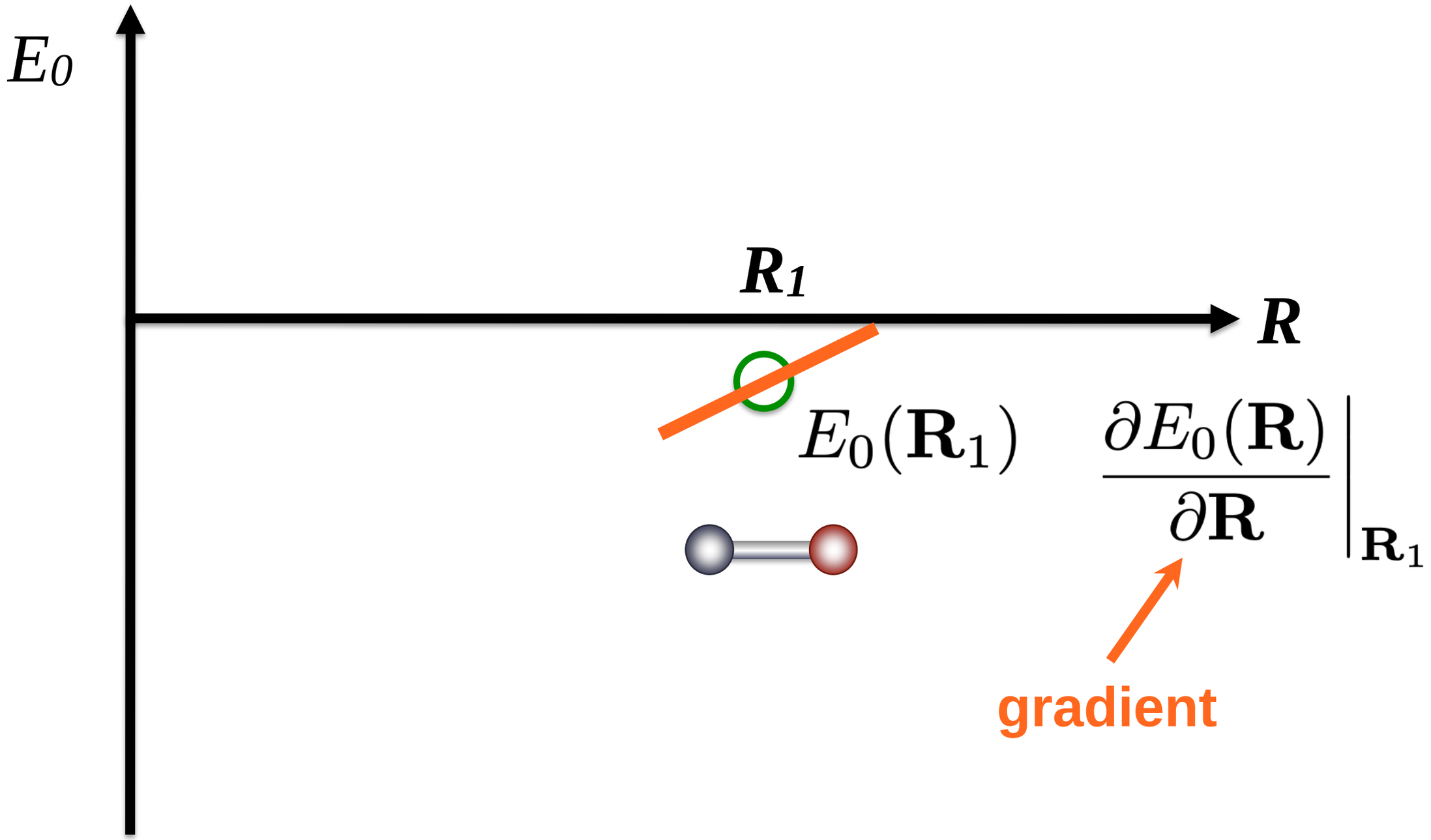

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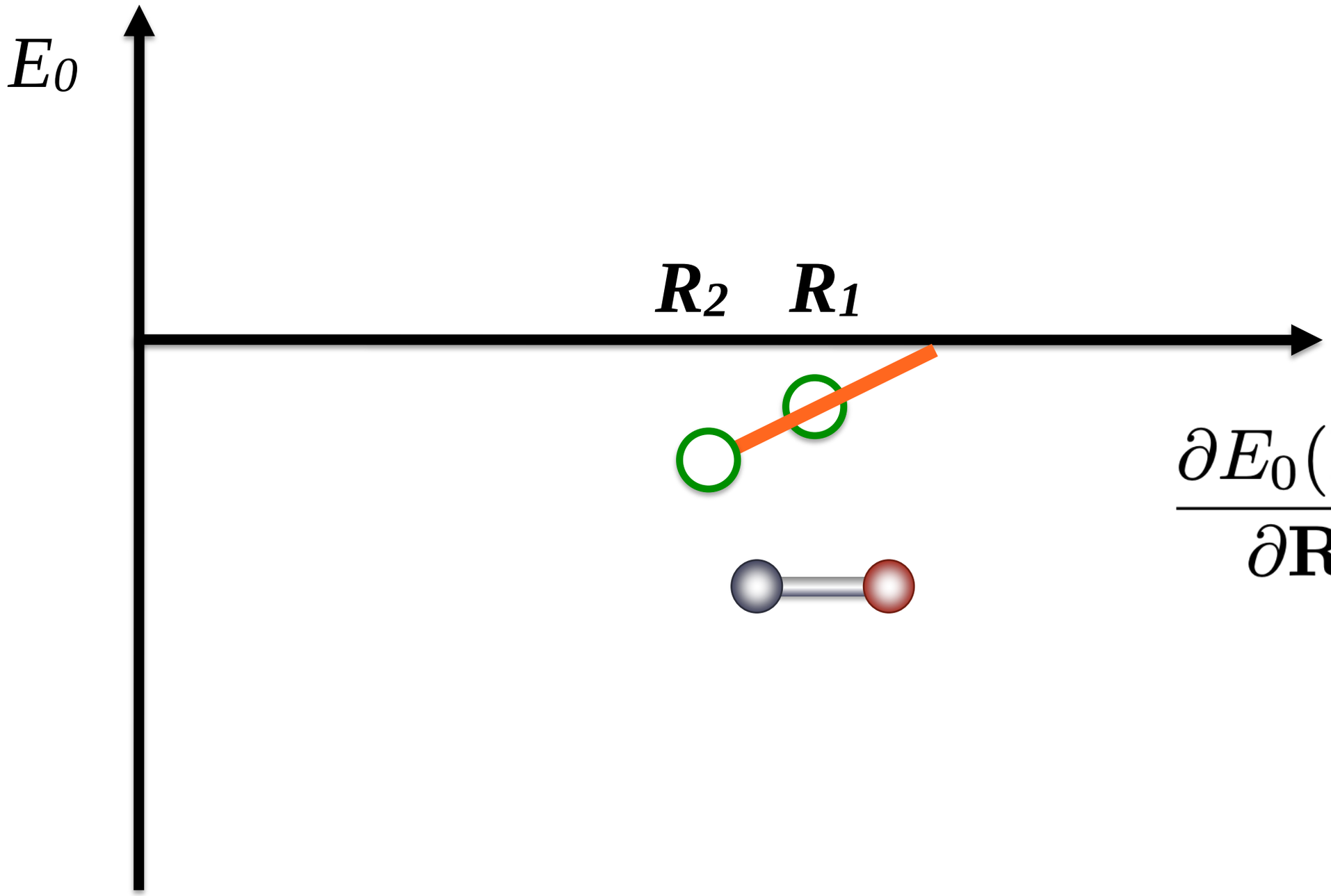

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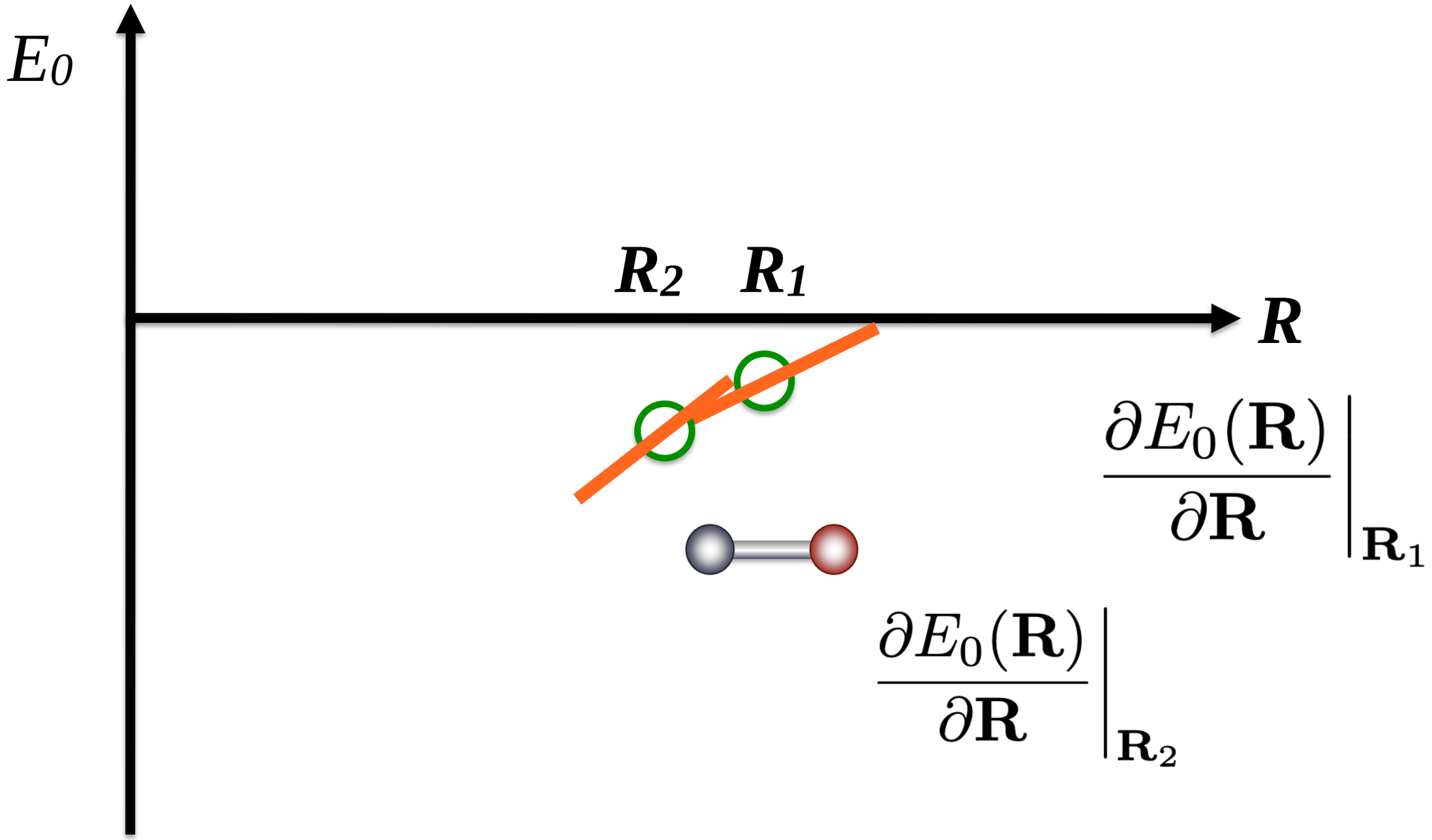

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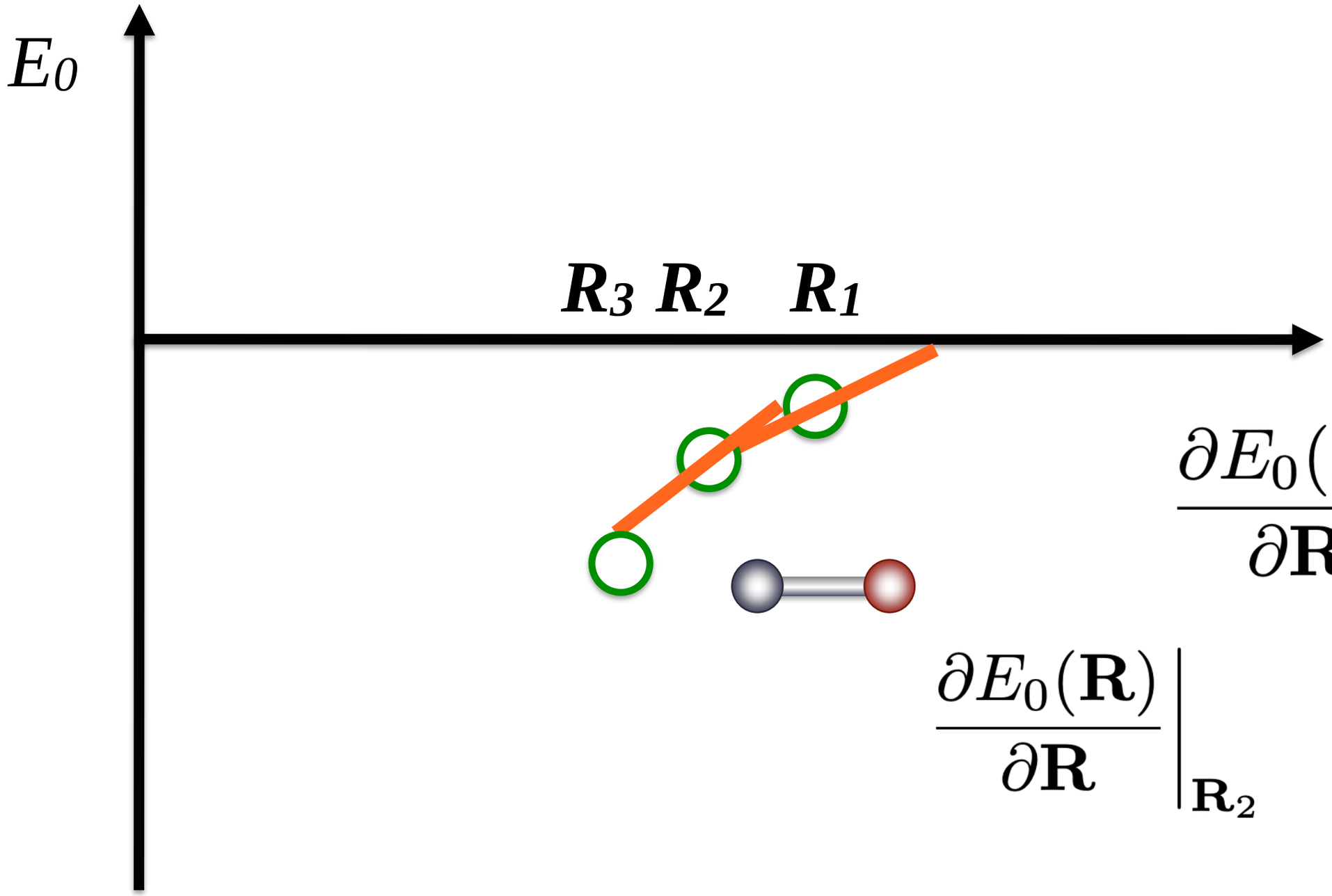

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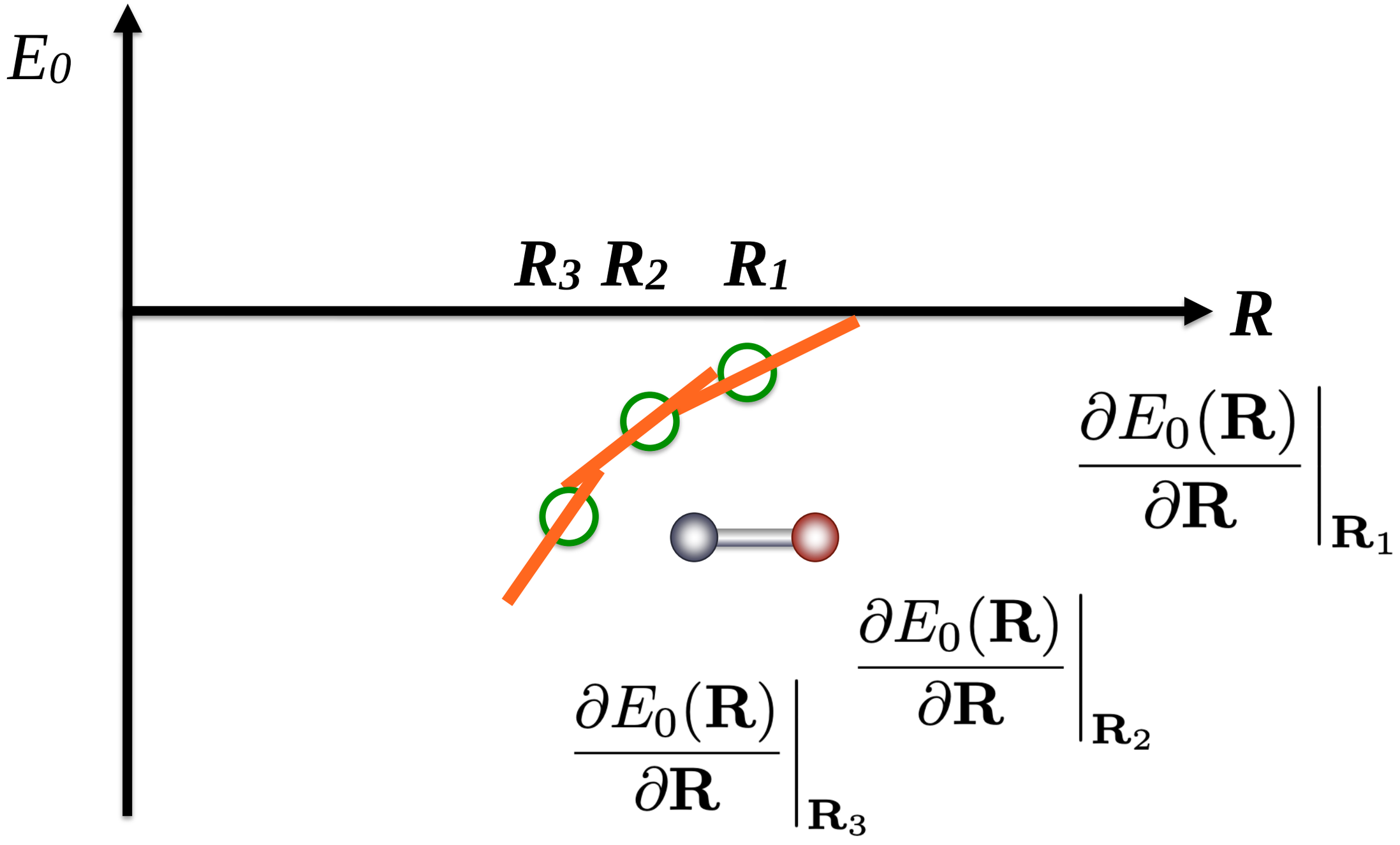

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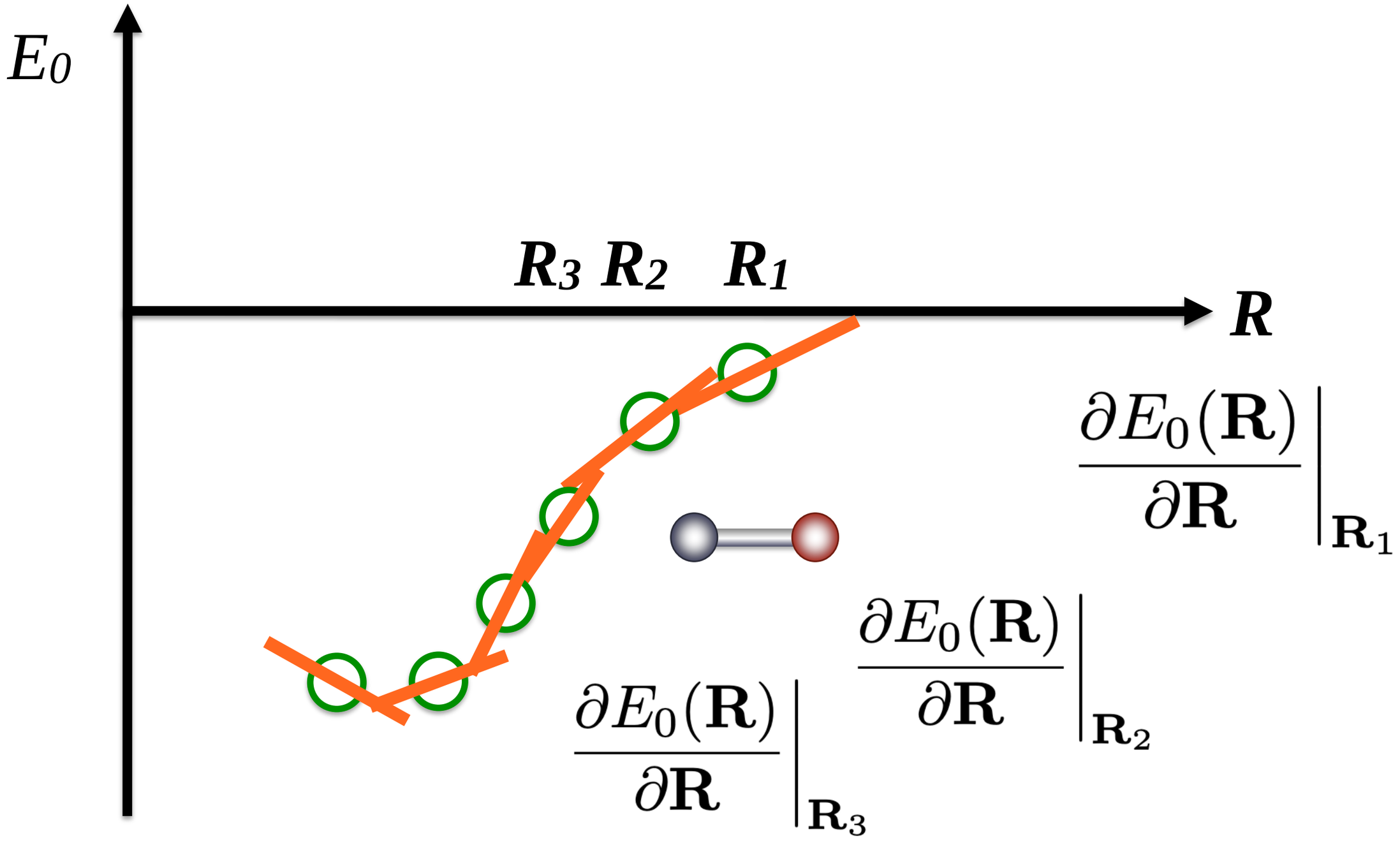

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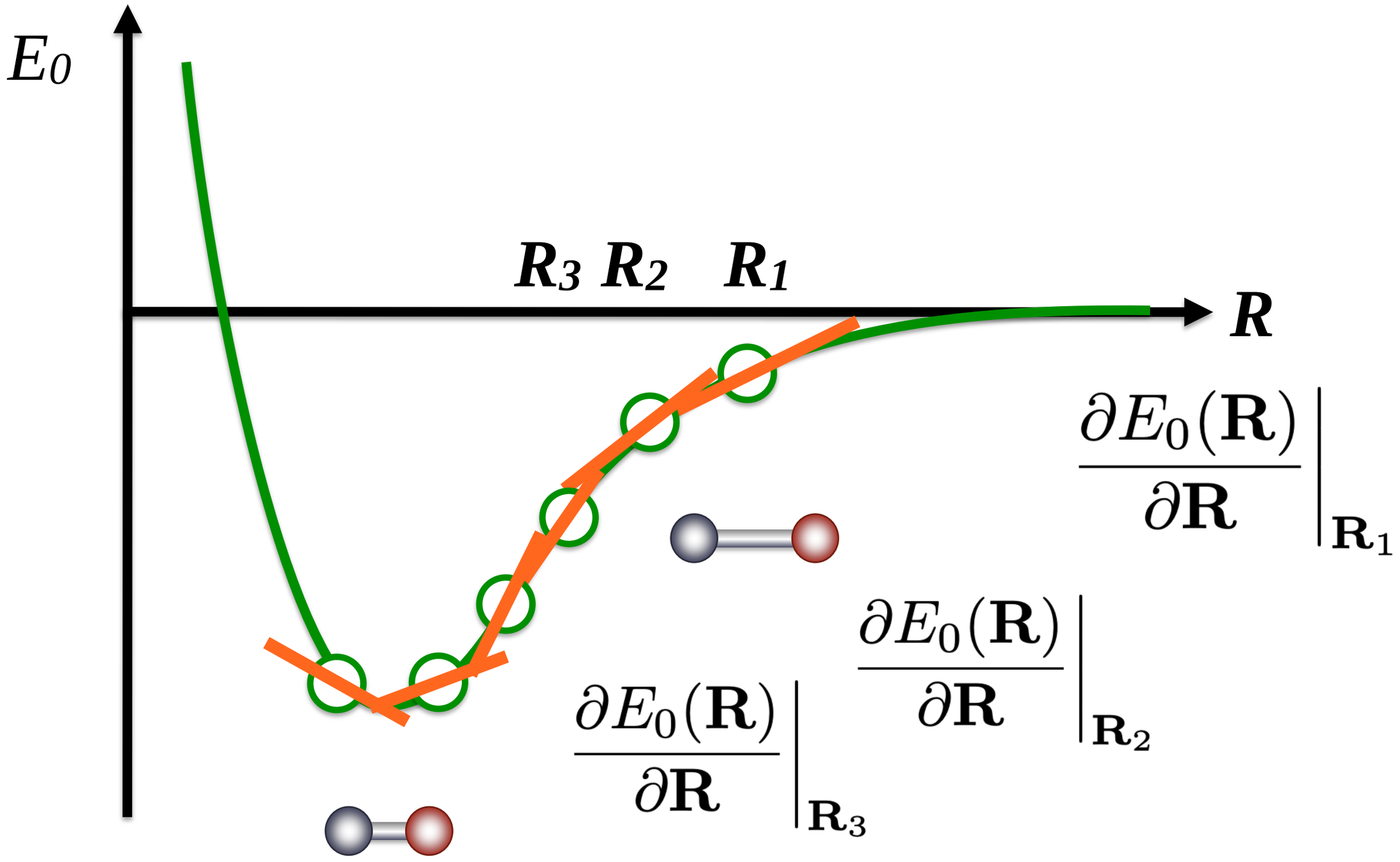


Revisit the binding energy curve

Forces in DFT :

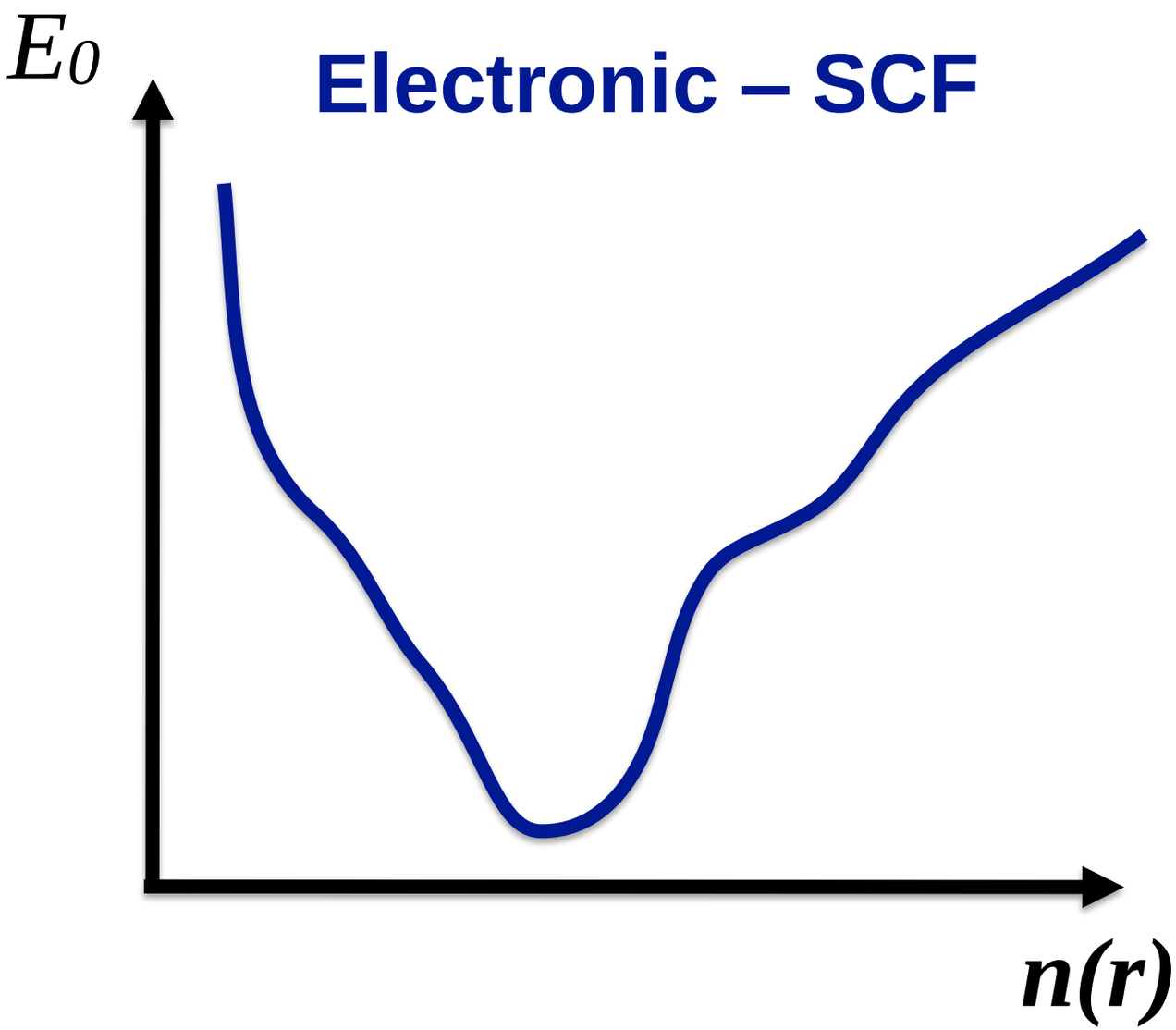
$$\mathbf{F}_I = -\frac{\partial}{\partial \mathbf{R}_I} E_0$$

$$\frac{\partial}{\partial \mathbf{R}_I} E_0 = \frac{\partial}{\partial \mathbf{R}_I} E_0^e + \frac{\partial}{\partial \mathbf{R}_I} \sum_{I=1}^{N_n} \sum_{J>I}^{N_n} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R'}_J|}$$

Equilibrium structure:

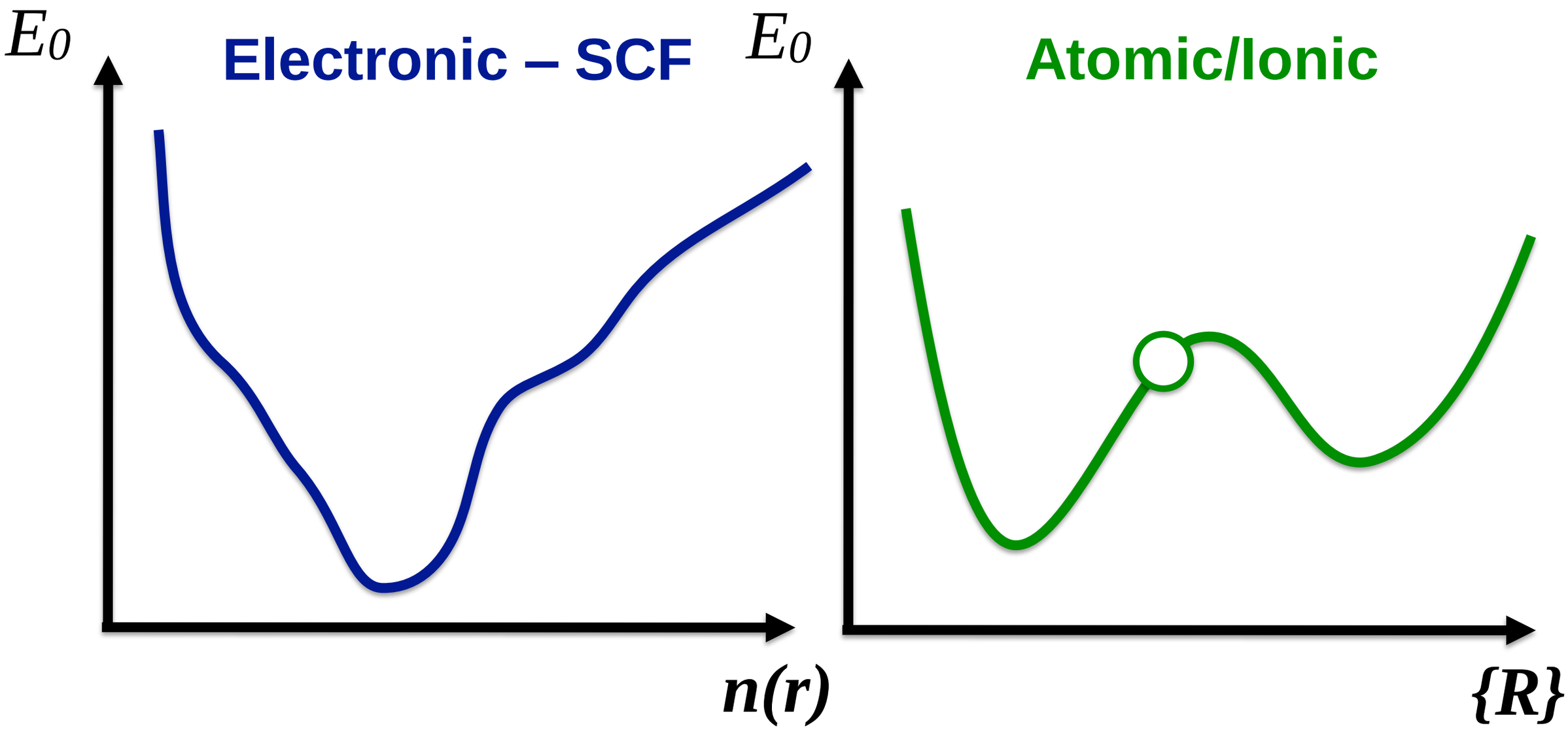
- **obtained when forces are zero**
- **find it by moving atoms according to forces**

Two minimisations in DFT structure search



1. take input atomic positions *{R}*
2. minimise electronic total energy

Two minimisations in DFT structure search



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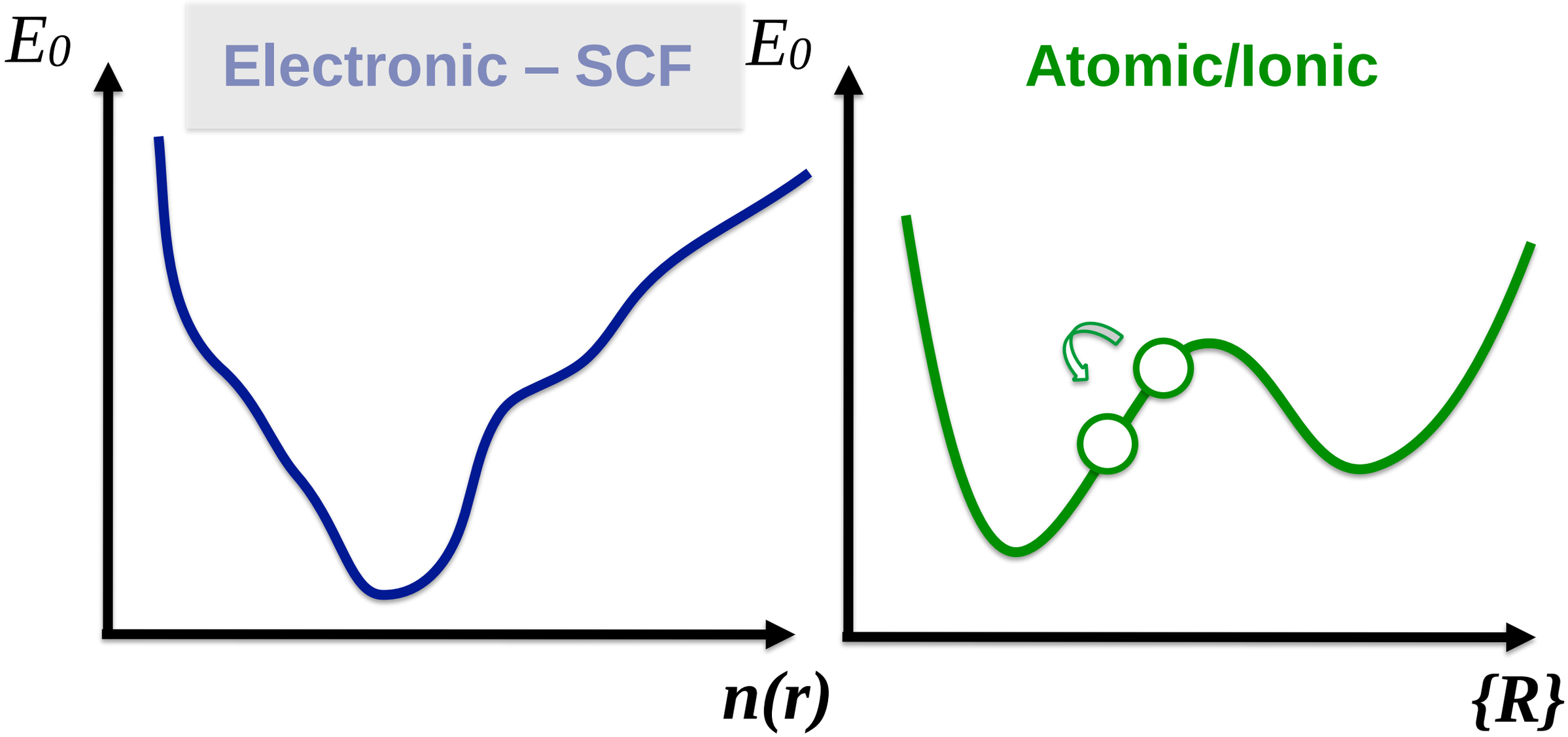
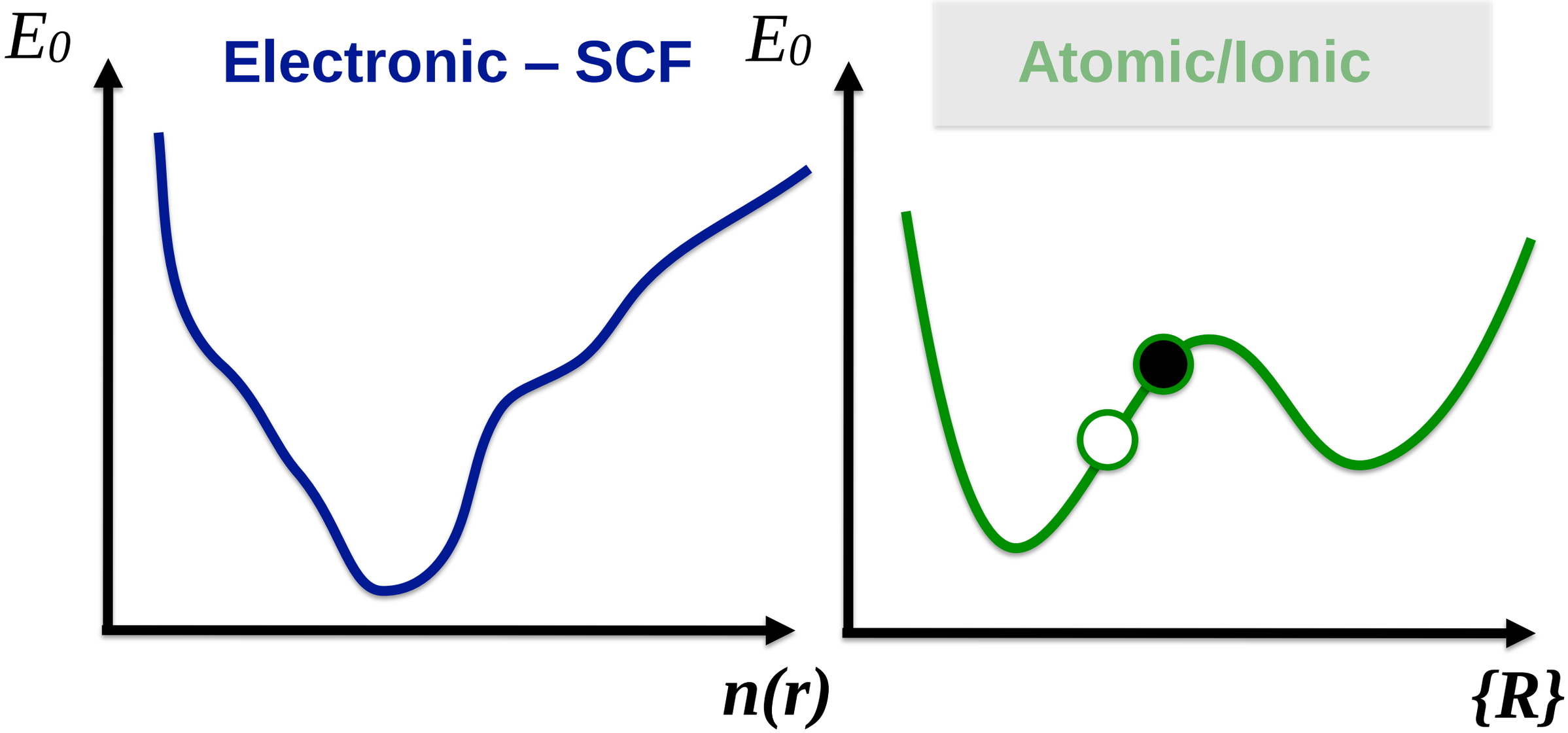


3. calculate forces

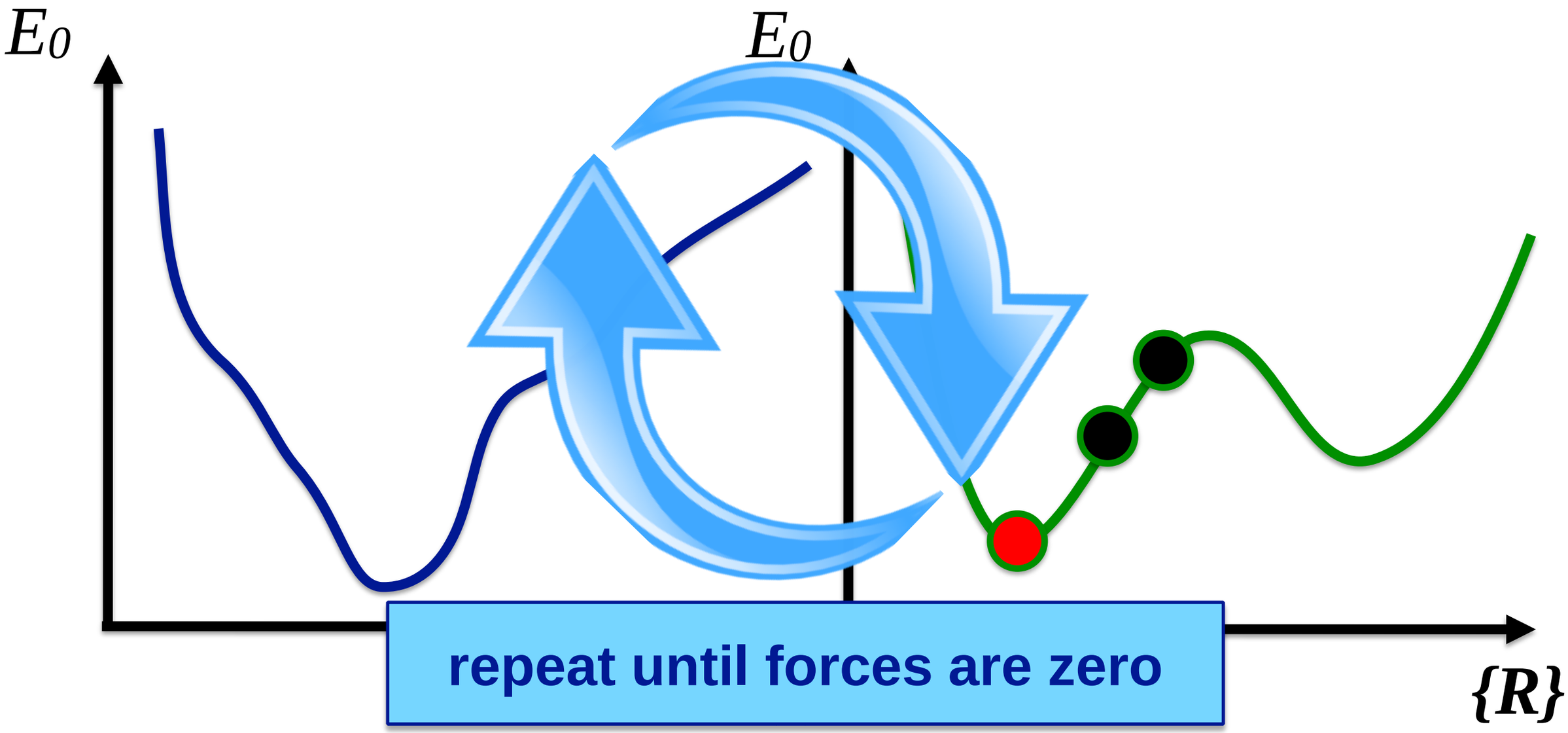
4. move atoms

Two minimisations in DFT structure search



5. new input atomic positions *{R}*
6. minimise electronic total energy

Two minimisations in DFT structure search



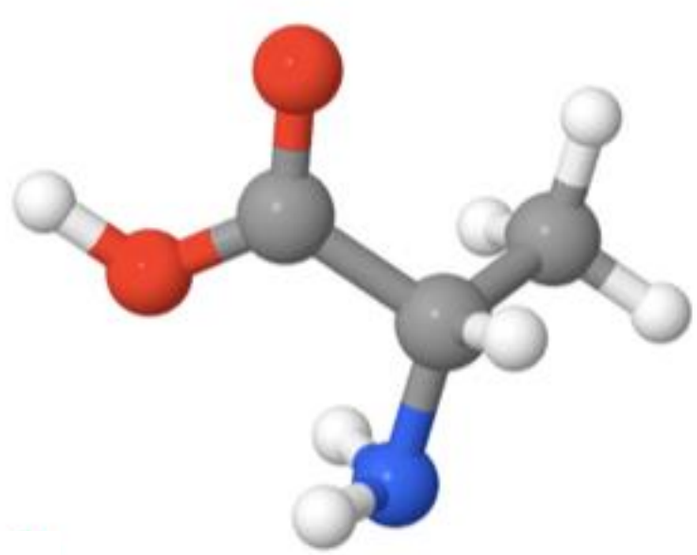
5. new input atomic positions *{R}*
6. minimise electronic total energy

Questions, comments, ideas?

- Chat: https://presemo.aalto.fi/dftpractitioner2022

- Some material about different types of geometry optimization methods – absolutely voluntary:
  - Atomic Simulation Environment: https://wiki.fysik.dtu.dk/ase/ase/optimize.html

Molecular foundry - build your own alanine



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