



# Overview of Density-Functional Theory

12<sup>th</sup> Conference of African Materials Research Society  
Workshop: Introduction to Computational Materials Science

**UniPod** · College of Science & Technology  
University of Rwanda · December 14, 2024



**UniPod**

**Link to materials chemistry:  
How to compute the energy of a molecule**

# Objective: potential energy curves

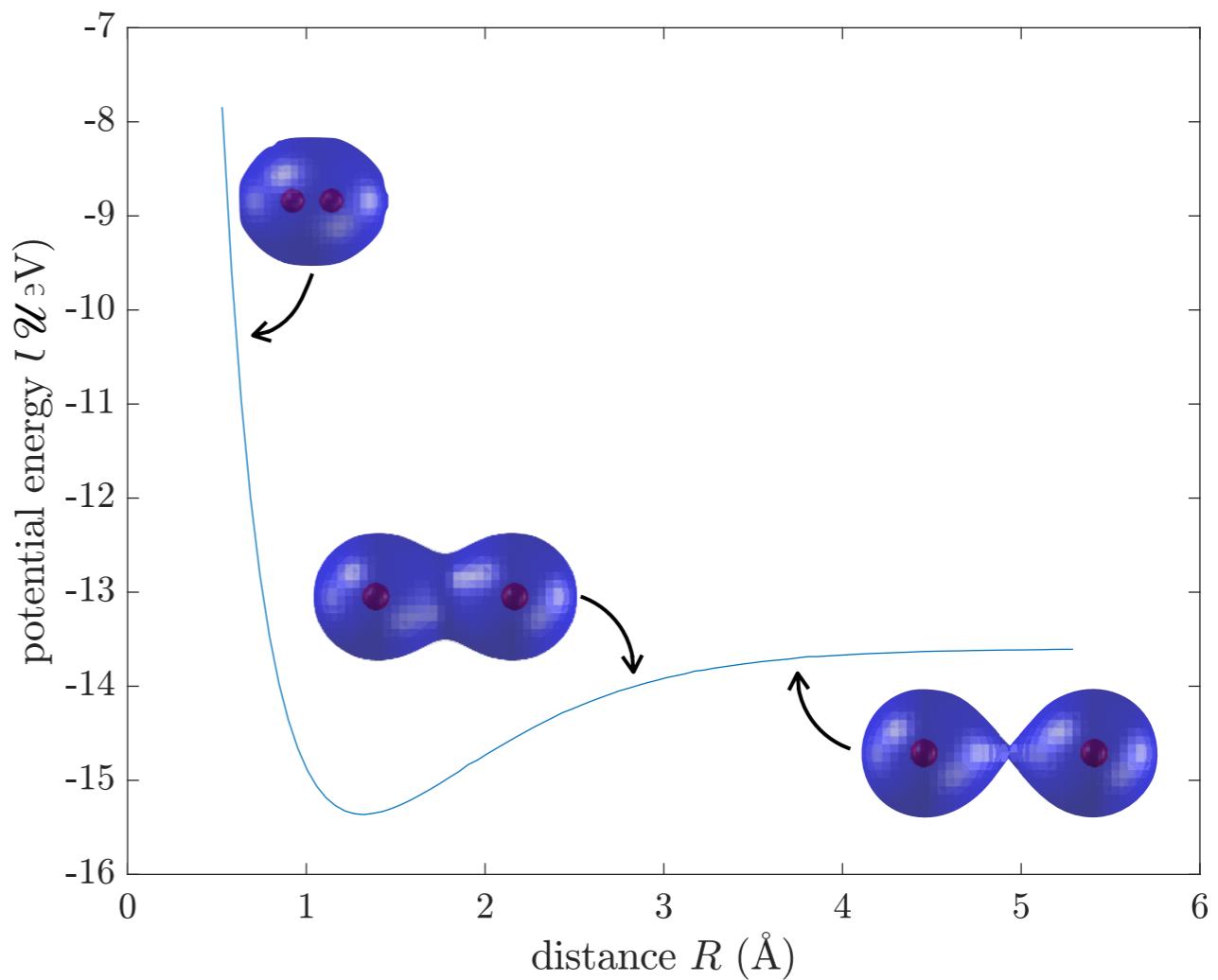
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- We have learned to compute the **total energy  $E$**  of an electron
- Now, we want to use this knowledge to compute the **potential energy  $\mathcal{U}$**  of molecule

# Objective: potential energy curves

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- Now, we want to use this knowledge to compute the **potential energy  $\mathcal{U}$**  of molecule
- **Example.** The simplest possible molecule is  $\text{H}_2^+$  (it consists of two proton nuclei and one electron).
- **Question.** How would you calculate the **potential energy  $\mathcal{U}$**  of  $\text{H}_2^+$  from the **total energy  $E$**  of its electron?



# Born-Oppenheimer approximation

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- ▶ **Answer.** To calculate the **potential energy**  $\mathcal{U}$  of  $\text{H}_2^+$ , we add the energy of the electron and the energy of the protons



Max Born  
(1882-1970)



Julius Robert  
Oppenheimer  
(1904-1967)

$$\mathcal{U} = E + \frac{e^2}{4\pi\epsilon_0 R}$$

# Born-Oppenheimer approximation

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## Definition | Born-Oppenheimer approximation

The Born-Oppenheimer approximation consists of treating electrons using quantum mechanics and nuclei using classical electrostatics

$$\mathcal{U} = E + \sum_i \sum_{j>i} \frac{Z_i Z_j e^2}{4\pi\epsilon_0 R_{ij}}$$

$R_{ij}$  is the distance between nuclei  $i$  and  $j$

$Z_i$  is the charge of the nucleus  $i$

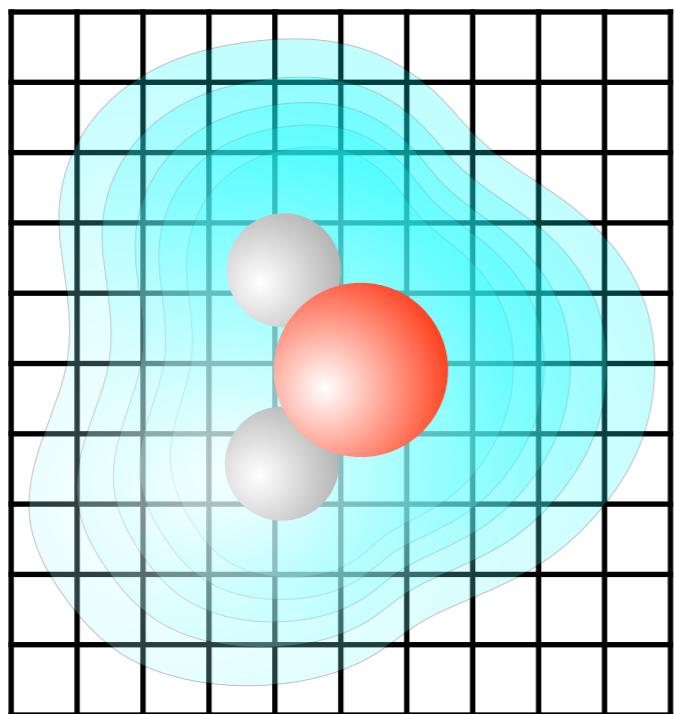
## **How to simulate many electrons: water as an example**

# Many-electron molecular system

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- ▶ Solving the **many-electron problem** requires considerable computer memory and CPUs

Let us assume for example that we want to store the 10-electron wave function of our water molecule in the computer on a relatively coarse grid of  $10 \times 10 \times 10$  points

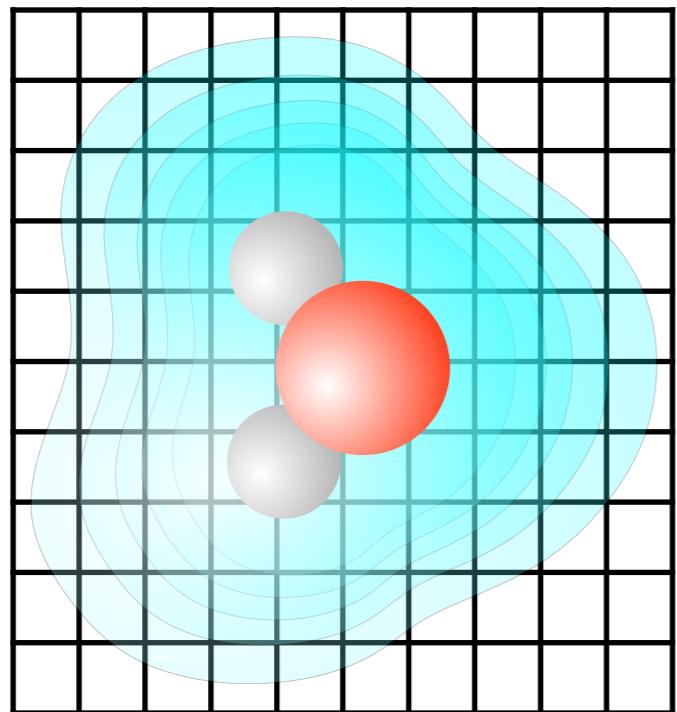


$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{10})$$

# Exponential bottleneck

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Let us assume for example that we want to store the 10-electron wave function of our water molecule in the computer on a relatively coarse grid of  $10 \times 10 \times 10$  points

$$\Psi(\underbrace{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{10}}_{10^3}, \underbrace{\mathbf{r}_{10}}_{10^3})$$

We would need to store  $10^{30}$  complex number. If each complex number is 8 bytes, we get  $\sim 10^{19}$  Tb, which exceed the memory of all computers in the world ( $\sim 100\text{-}1,000$  Eb =  $10^8\text{-}10^9$  Tb)

- ▶ This example illustrates why the many-electron problem **cannot be solved by brute force**

# **Density-functional theory**

# What is density-functional theory?

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- **Density-functional theory** provides an alternative to approximate the solution of the many-body problem by using the electron density as main variable:

$$E = \int \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \hat{H} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) d\mathbf{r}_1 \cdots d\mathbf{r}_N$$

$$E = \underbrace{F[\rho]}_{\text{A functional that does not depend on the system and embeds all the electron-electron interactions and electron kinetic energy}} + \underbrace{\int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}}_{\text{Interaction between the electrons and the electrostatic potential generated by the nuclei}}$$

A functional that does not depend on the system and embeds all the electron-electron interactions and electron kinetic energy

Interaction between the electrons and the electrostatic potential generated by the nuclei

- This substitution is enabled by the **Kohn-Hohenberg theorem**

# Hohenberg-Kohn theorem

## Property | Hohenberg-Kohn theorem

The ground-state energy  $E[\rho]$  of  $N$  electrons in the potential  $v$  can be found by solving

$$\min_{\rho} F[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$
$$\int \rho(\mathbf{r})d\mathbf{r} = N$$

where  $F[\rho] = E[\rho] - \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} = \int \Psi^*[\rho](T+W)\Psi[\rho]$



Pierre Hohenberg  
(1934-2017)



Walter Kohn  
(1923-2016)

**Notation.** We use [] to denote **functional** (which are functions of a function).

- $F$  is called the **universal functional**. It is often written in terms of the kinetic, electrostatic, and exchange-correlation contributions

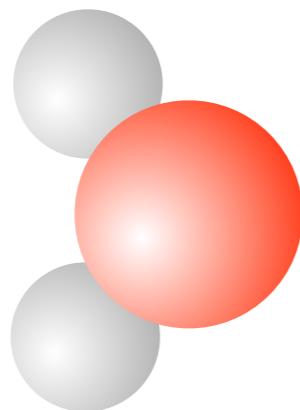
$$F[\rho] = K[\rho] + E_{xc}[\rho] + \int \int e^2 \rho(\mathbf{r})\rho(\mathbf{r}')/(8\pi\varepsilon_0|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}d\mathbf{r}'$$

# **The local density approximation**

# Local density approximation

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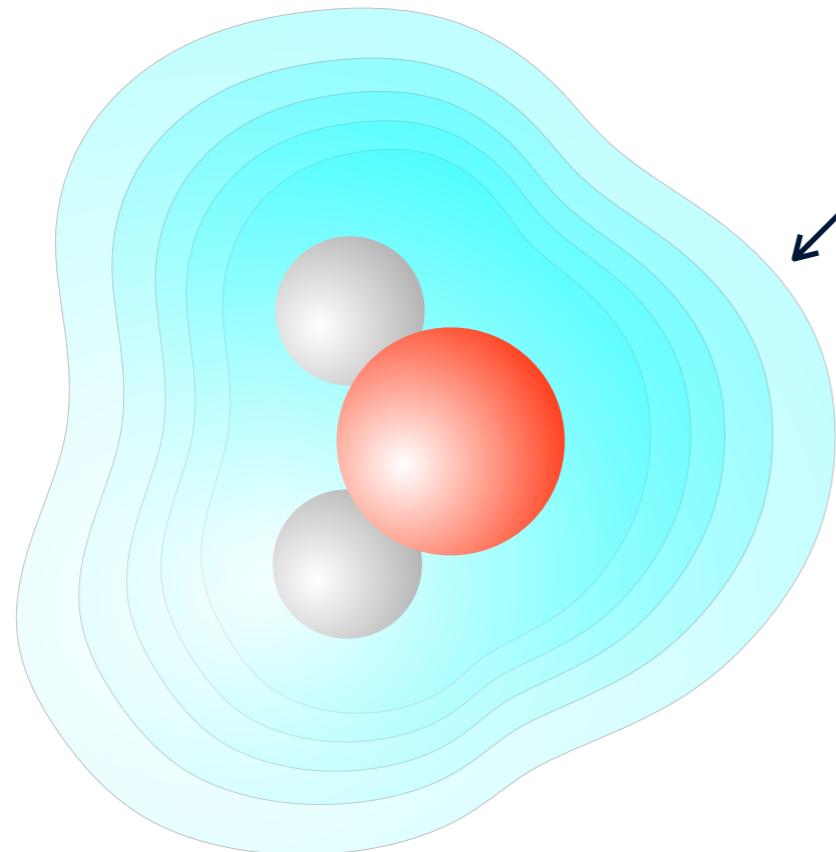
- Now, let's see how to approximate  $K[\rho]$  and  $E_{xc}[\rho]$ .



# Local density approximation

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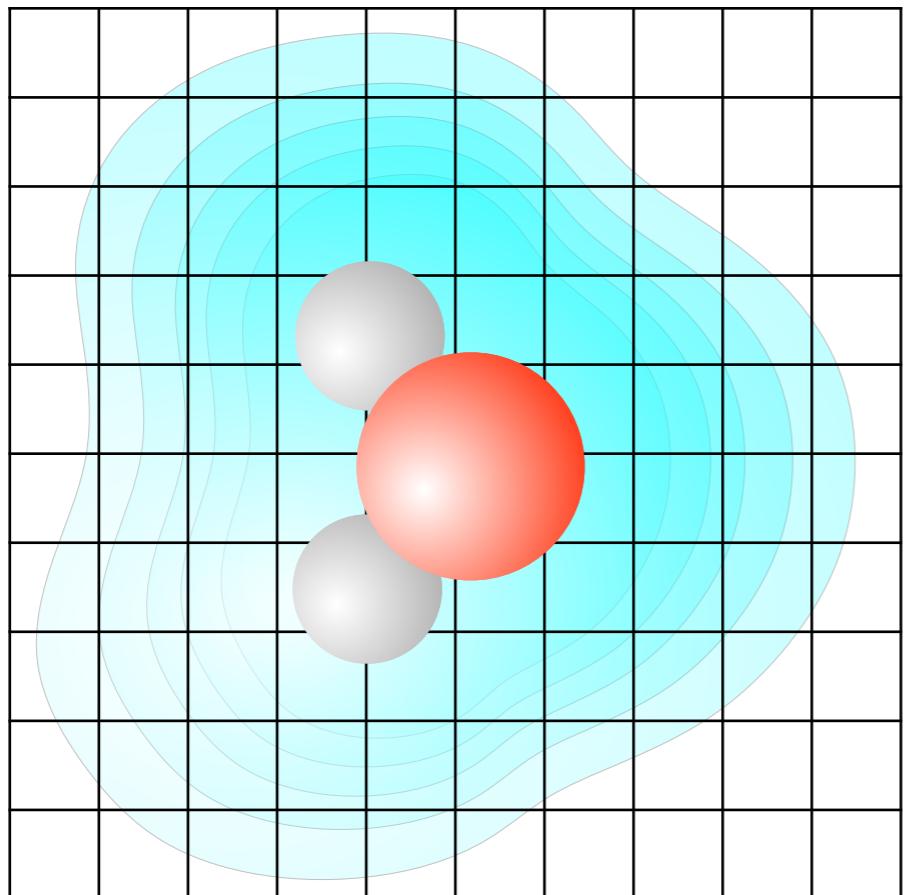
$$\rho(\mathbf{r}) = \sum_{n=1}^N |\phi_n(\mathbf{r})|^2$$

Start from the electronic density...

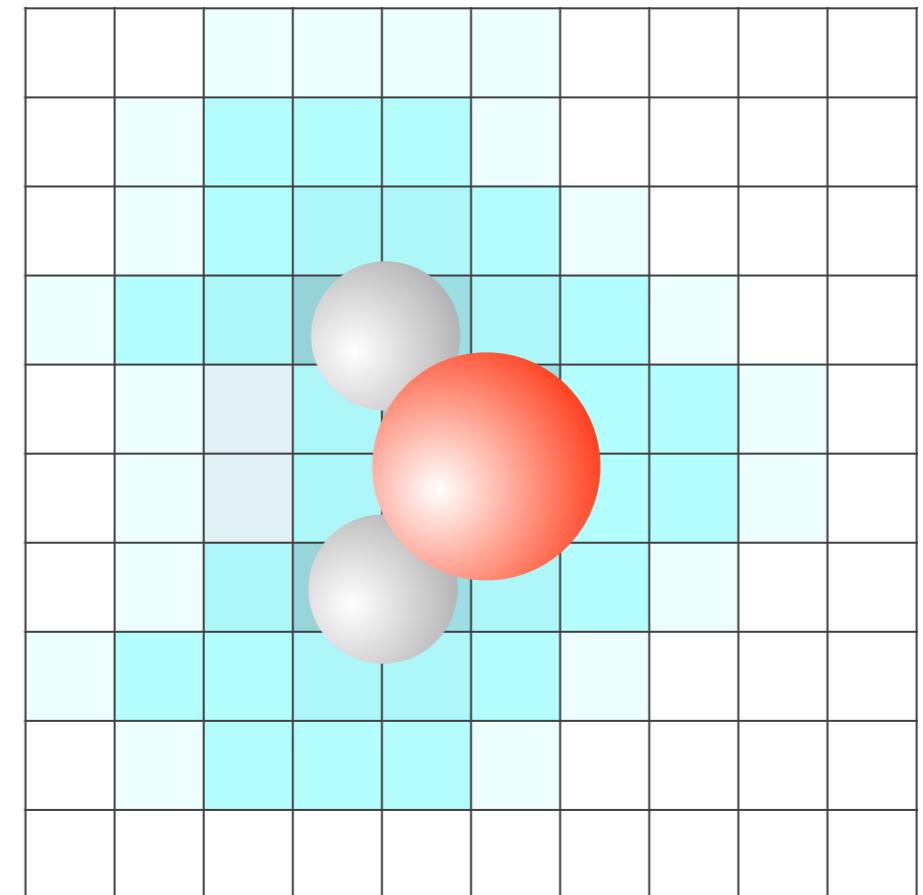
# Local density approximation (cont'd)

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- Now, let's see how to approximate  $K[\rho]$  and  $E_{xc}[\rho]$ .



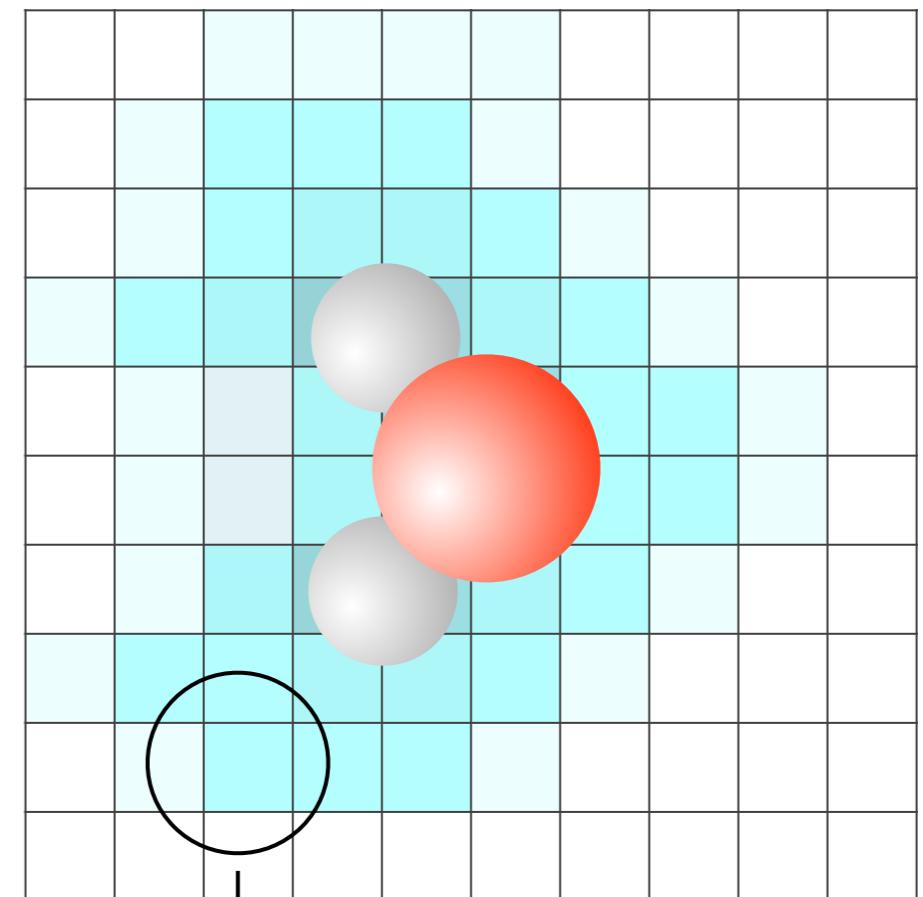
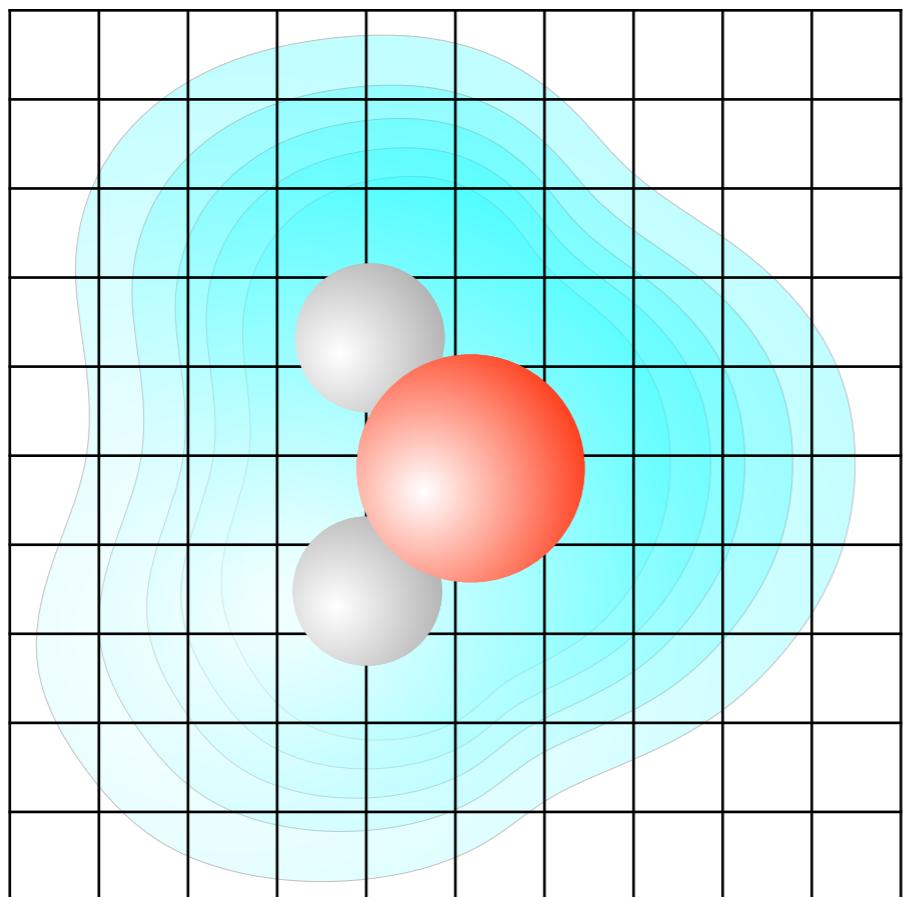
... Divide space into small volumes



... In each of these small volumes,  
approximate the density as uniform

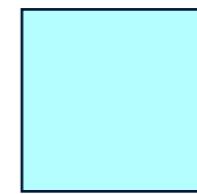
# Local density approximation (cont'd)

- Now, let's see how to approximate  $K[\rho]$  and  $E_{xc}[\rho]$ .



Kinetic energy per volume  
in uniform gas of density  $\rho$

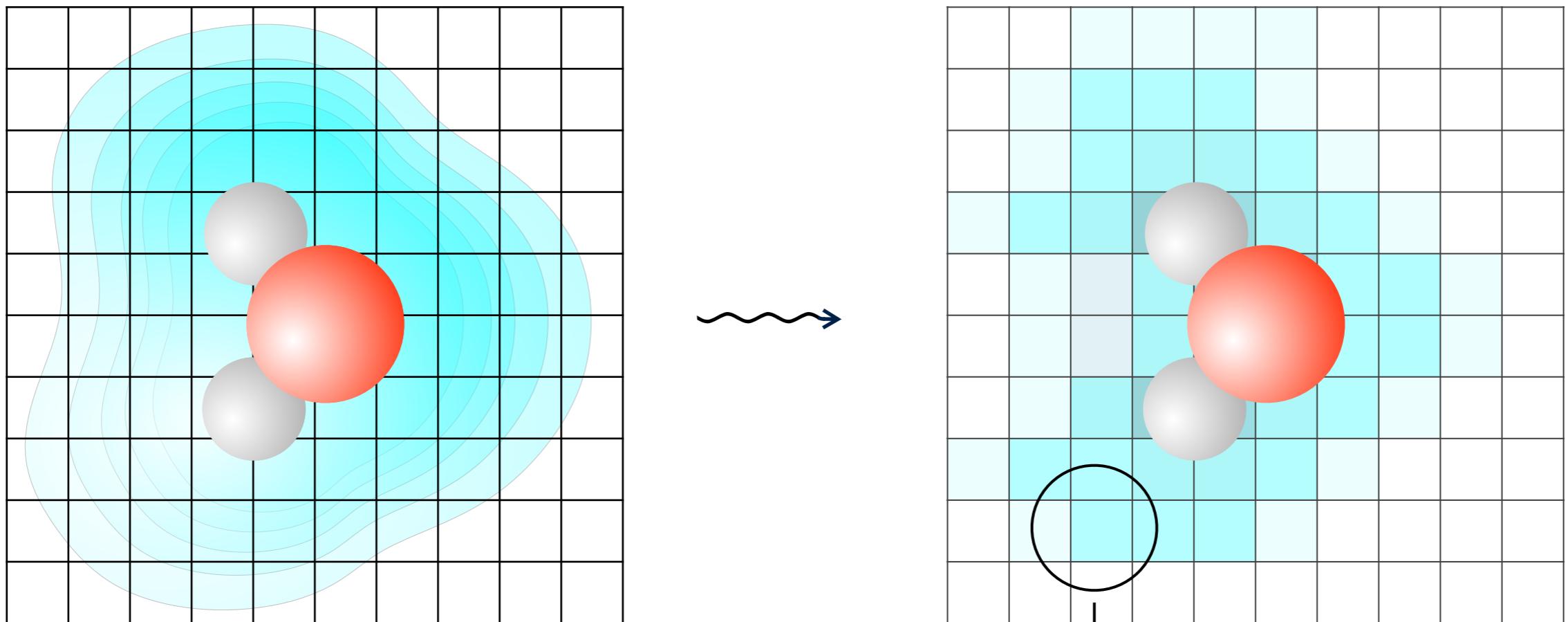
$$dK = \underbrace{k(\rho(r))}_{\text{Kinetic energy in } \square} dr$$



... Use uniform electron gas  
approximation to estimate  
 $T[\rho]$  in small volume

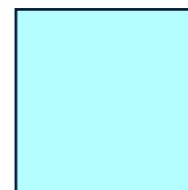
# Local density approximation (cont'd)

- Now, let's see how to approximate  $K[\rho]$  and  $E_{xc}[\rho]$ .



... And the same procedure can be applied to  $E_x[\rho]$  and  $E_c[\rho]$

$$dK = k(\rho(r)) dr$$
$$dE_{xc} = e_{xc}(\rho(r)) dr$$



# **The Kohn-Sham method**

# The Kohn-Sham method

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- A simple way to appreciate the difference between the **Hohenberg-Kohn** and **Kohn-Sham** methods is to put them side by side

$$E = K[\rho] + E_{\text{xc}}[\rho] + \iint \frac{e^2}{8\pi\epsilon_0} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$



Walter Kohn  
(1923-2016)



Pierre Hohenberg  
(1934-2017)

$$\left| \begin{array}{l} E = \sum_{n=1}^N \int \phi_n^*(\mathbf{r}) \left( -\frac{\hbar^2}{2m_e} \nabla^2 \phi_n(\mathbf{r}) \right) d\mathbf{r} + E_{\text{xc}}[\rho] + \iint \frac{e^2}{8\pi\epsilon_0} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \\ \\ \rho(\mathbf{r}) = \sum_{n=1}^N |\phi_n(\mathbf{r})|^2 \end{array} \right.$$

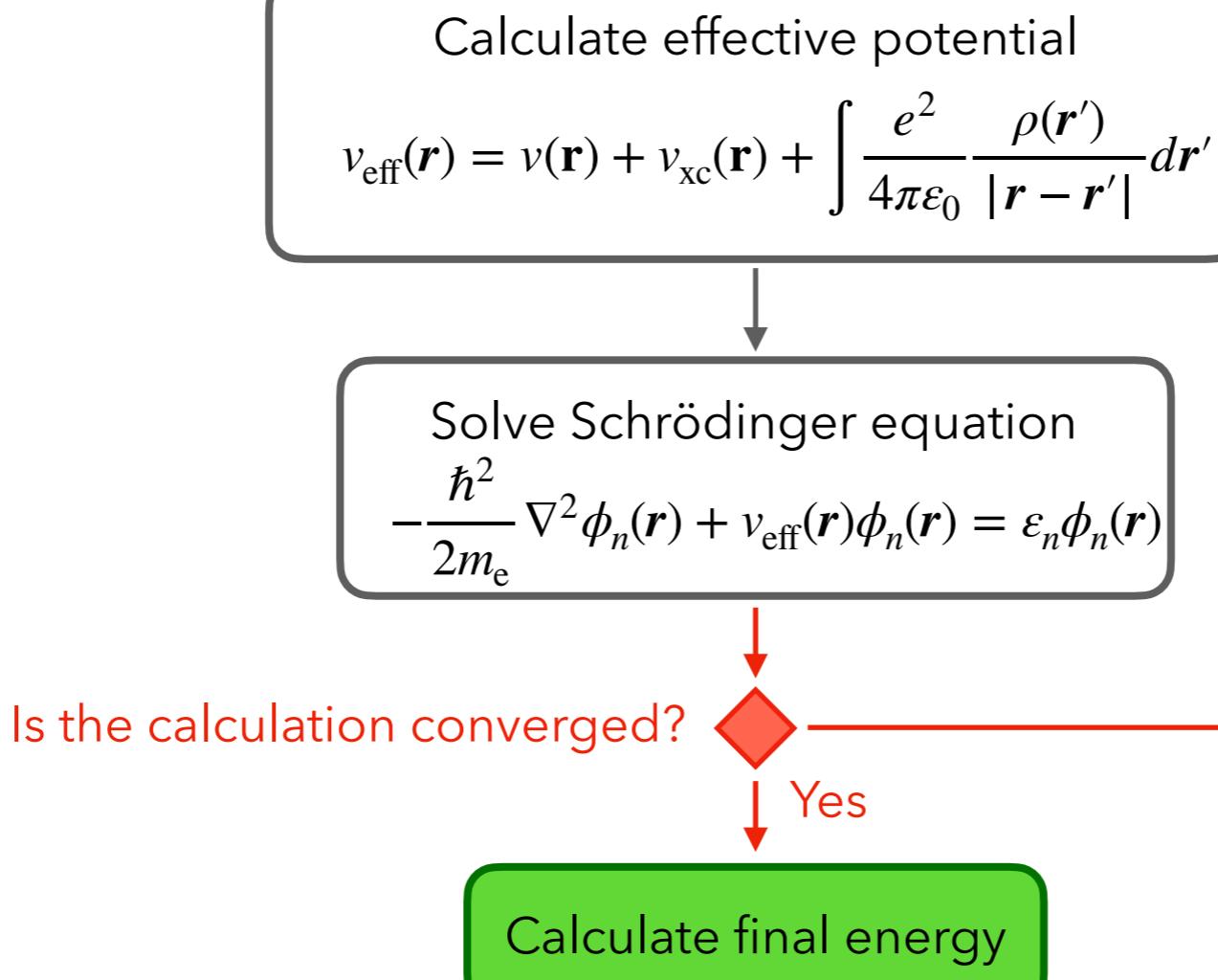


Walter Kohn  
(1923-2016)    Lu Sham  
(born 1938)

- **Takeaway.** The **Kohn-Sham** method avoids calculating the kinetic energy from the density (a very difficult, open problem).

# Kohn-Sham self-consistent-field (SCF) cycle

The **Kohn-Sham problem** can be solved by finding the equilibrium states of the electrons in an effective potential that depends on the density...



Walter Kohn  
(1923-2016)

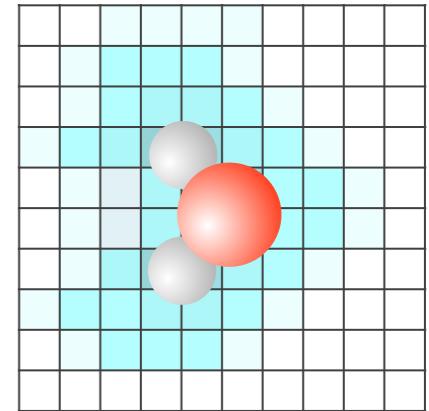
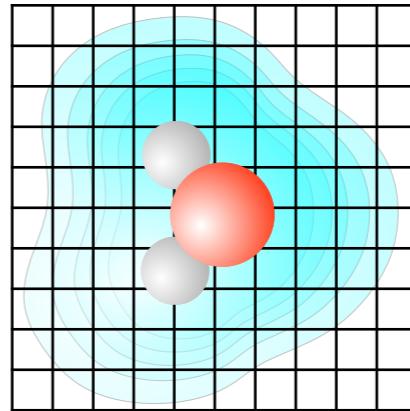


Lu Sham  
(born 1938)

# Summary

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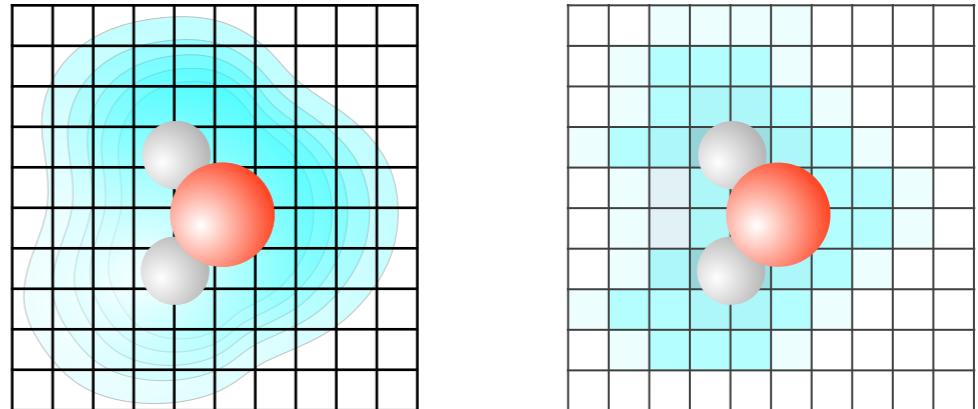
- ▶ **Density-functional theory** is an effective simplification of the many-electron problem using the density  $\rho$  as variable instead of the complicated many-electron wave function  $\Psi$ .
- ▶ The **local density approximation (LDA)** consists of pixelizing space and approximating the density as having a **constant value** in one.
- ▶ The **generalized gradient approximation (GGA)** consists of pixelizing space and approximating the density as having a **constant gradient** in each pixel.
- ▶ The **meta-generalized gradient approximation (meta-GGA)** consists of pixelizing space and approximating the density as having a **constant curvature** in each pixel.



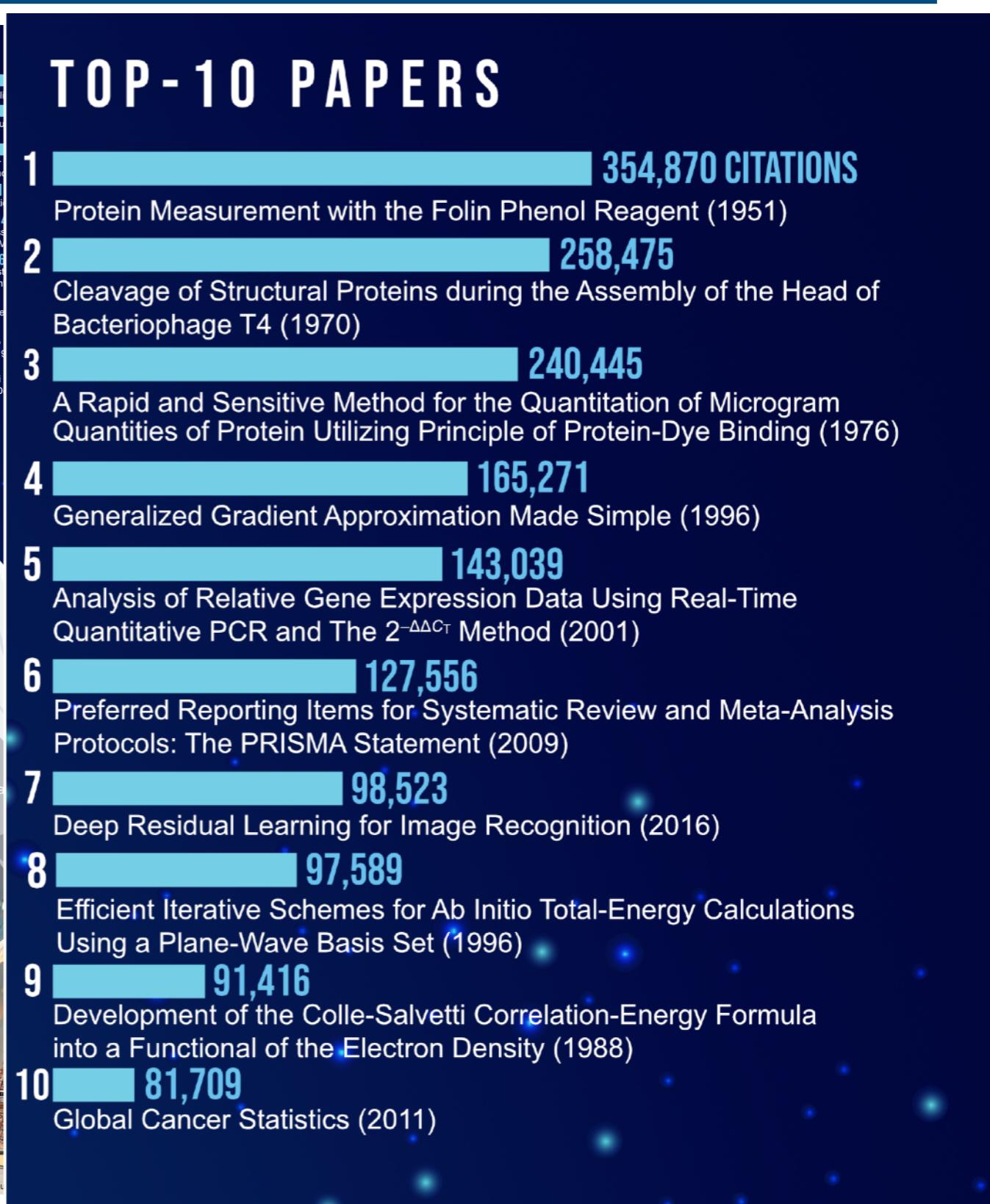
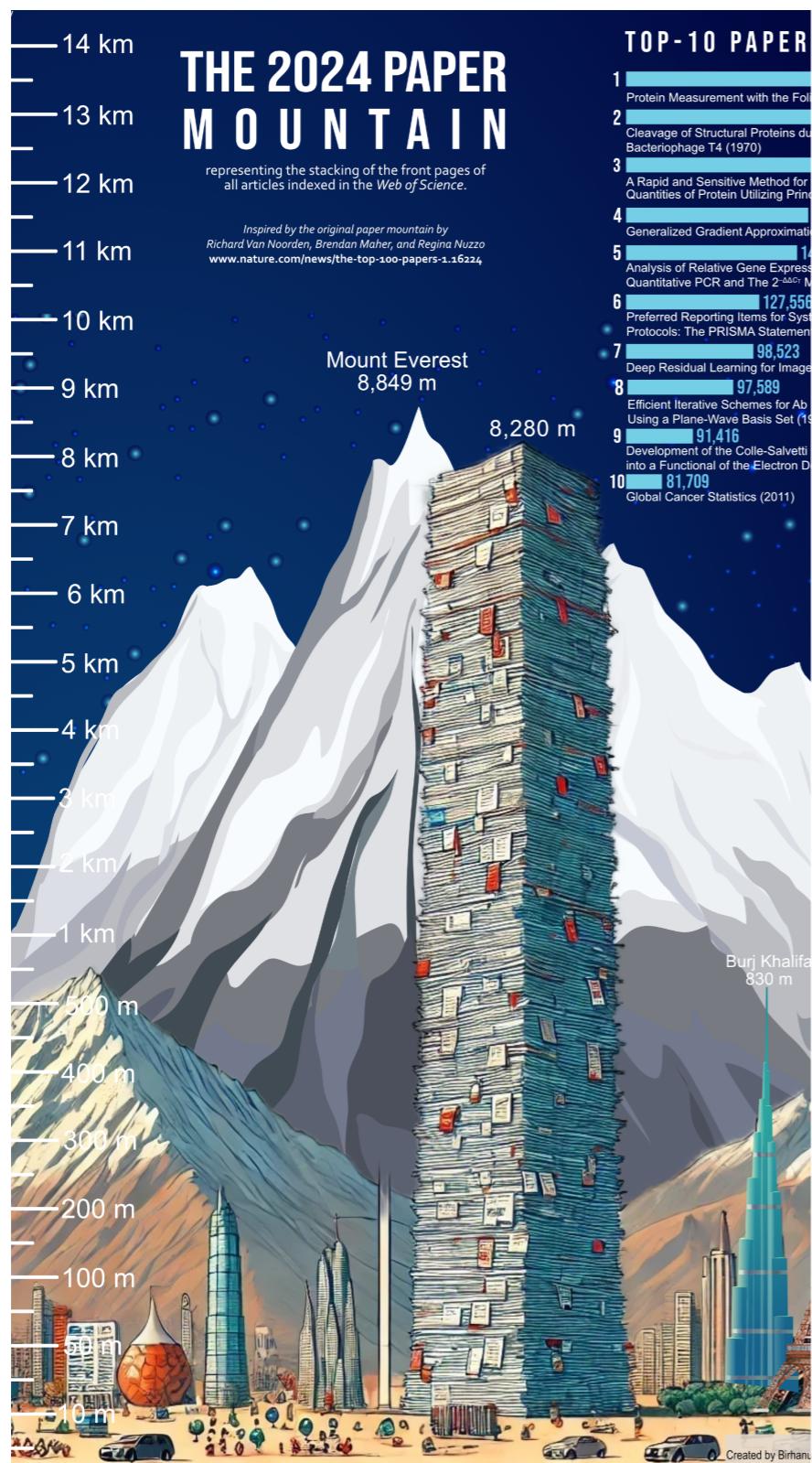
# Summary

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# Summary: closing the loop

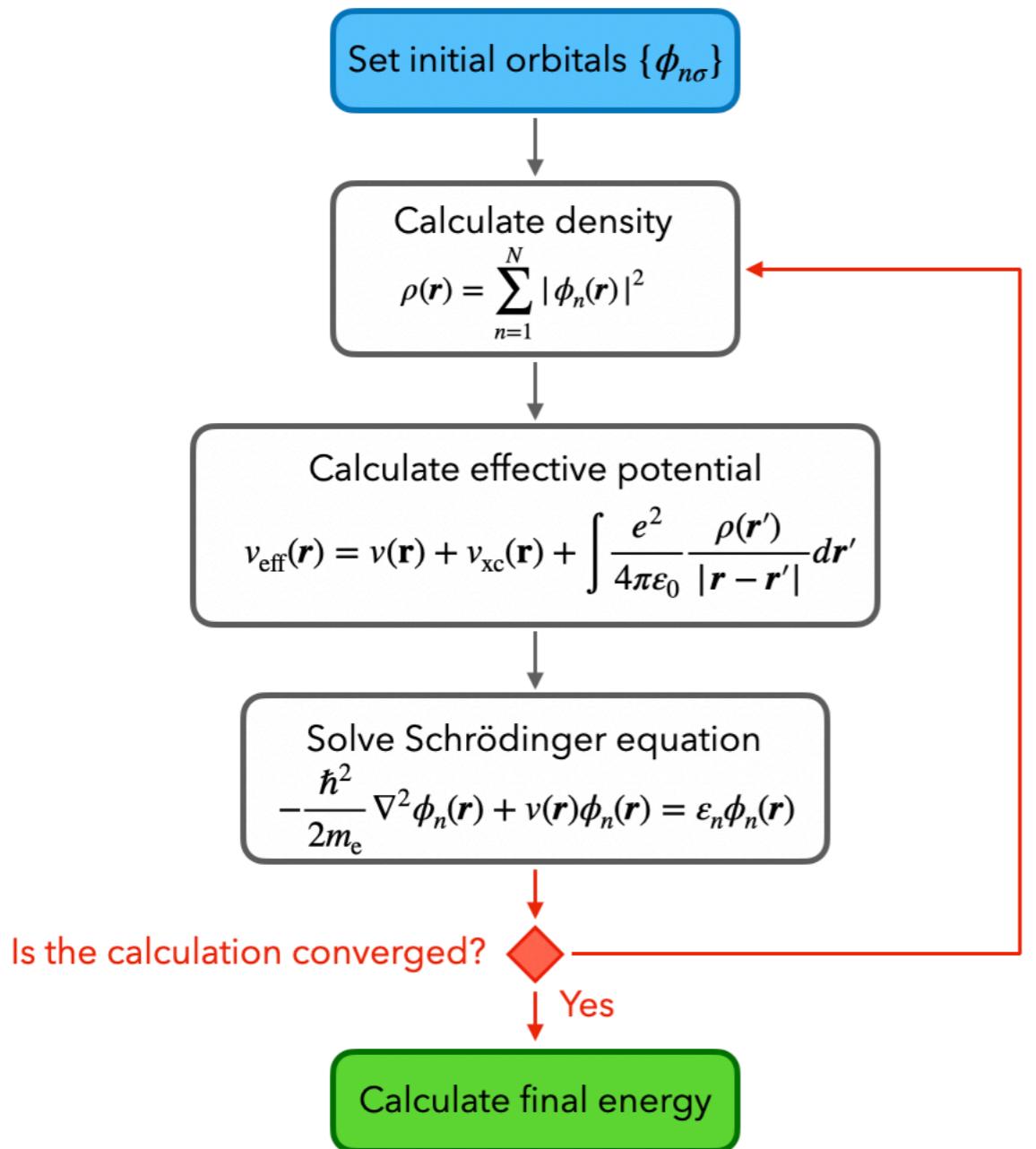


**Hands-On:**

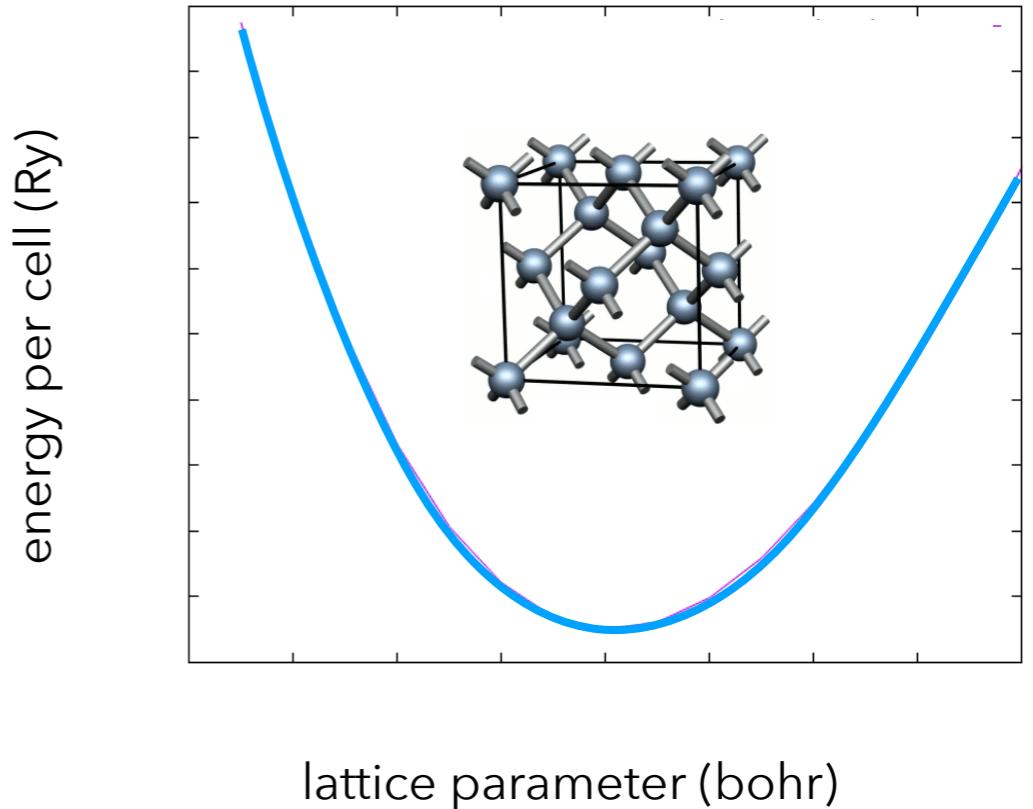
**Convergence of Self-Consistent-Field Calculations**

# Hands-On

- Let's learn how to predict the properties of molecules (water) and materials (silicon) using **Quantum-Espresso**



We will learn how to perform Kohn-Sham calculations using a software called **Quantum-Espresso**. There exist many other software ABINIT, VASP, CASTEP. They are all based on similar algorithms and input files. (**Quantum-Espresso** is open source and free)



# Numerical accuracy

- Importantly, we will need to tune two parameters of numerical accuracy, namely, the **cutoff kinetic energy** and the **number of Bloch wave vectors**.

Input cards '&... /' for a **Quantum-Espresso** simulation

```
&system
  ibrav = 2,
  celldm(1) = 10.2,
  nat = 2,           Plane-wave cutoff
  ntyp = 1,          ↘ kinetic energy
  ecutwfc = 30.0
/
&electrons
/
ATOMIC_SPECIES
Si 28.086 Si.pz-vbc.UPF
ATOMIC_POSITIONS alat
Si 0.00 0.00 0.00
Si 0.25 0.25 0.25
KPOINTS automatic    ↙ Number of k-points
                      to sample the Brillouin zone
                      4 4 4 1 1 1
```

$$\phi_{n\mathbf{k}}(\mathbf{r}) = \sum_{|\mathbf{G}| < G_{\text{cutoff}}} c_{n\mathbf{k},\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}}$$

$$\rho(\mathbf{r}) = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} \sum_n |\phi_{n\mathbf{k}}(\mathbf{r})|^2$$

# Numerical accuracy

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## Plane-wave cutoff

- The orbitals of periodic systems can be written as a superposition of plane waves (Bloch's theorem)

$$\phi_{n\mathbf{k}}(\mathbf{r}) = \sum_{|\mathbf{G}| < G_{\text{cutoff}}} c_{n\mathbf{k},\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}}$$

Bloch vector in the Brillouin zone

Vector of the reciprocal lattice

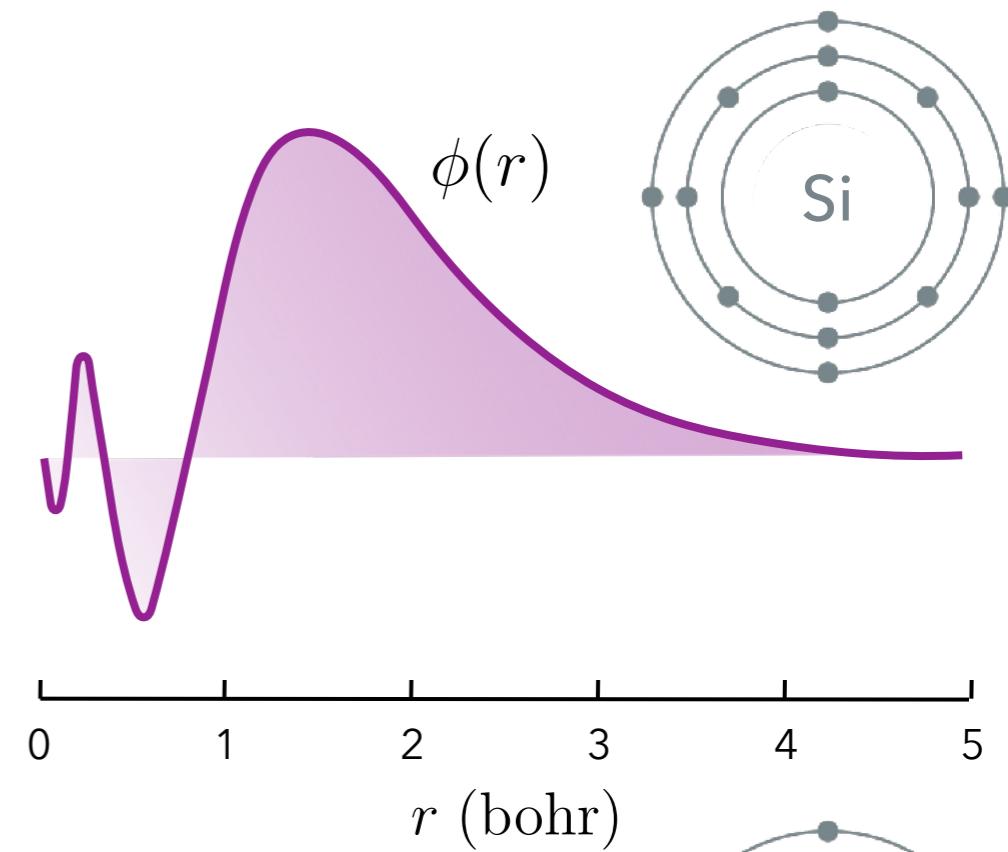
- To manage this infinite sum computationally, only the vectors of magnitude  $|\mathbf{G}|$  below a chosen threshold are included
- This threshold is defined in terms of a **cutoff kinetic energy**

$$\frac{\hbar^2}{2m} |\mathbf{G}|^2 < E_{\text{cutoff}}$$

# Important terminology: pseudopotentials

## Strong oscillations

- Near atomic cores, the orbitals exhibit strong oscillations
- Capturing these oscillations require a very high  $E_{\text{cutoff}}$



## Pseudization

- The pseudization consists of cancelling out oscillations by smoothing the nuclear potential
- The resulting pseudopotential does not include the core electrons

