



Overview of Density-Functional Theory

12th Conference of African Materials Research Society
Workshop: Introduction to Computational Materials Science

UniPod · College of Science & Technology
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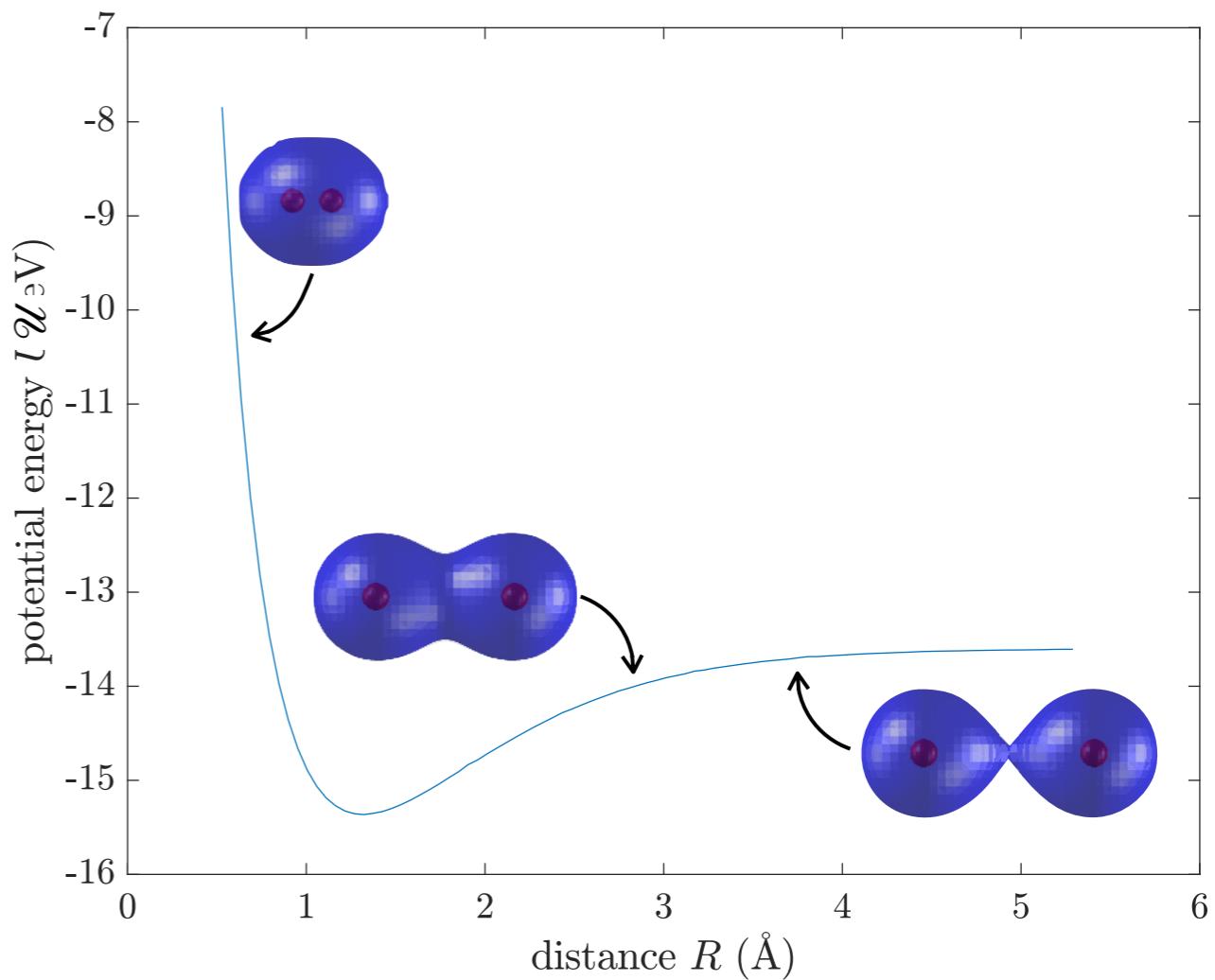
**Link to materials chemistry:
How to compute the energy of a molecule**

Objective: potential energy curves

- 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

- 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
- **Example.** The simplest possible molecule is H_2^+ (it consists of two proton nuclei and one electron).
- **Question.** How would you calculate the **potential energy \mathcal{U}** of H_2^+ from the **total energy E** of its electron?



Born-Oppenheimer approximation

- ▶ **Answer.** To calculate the **potential energy** \mathcal{U} of 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

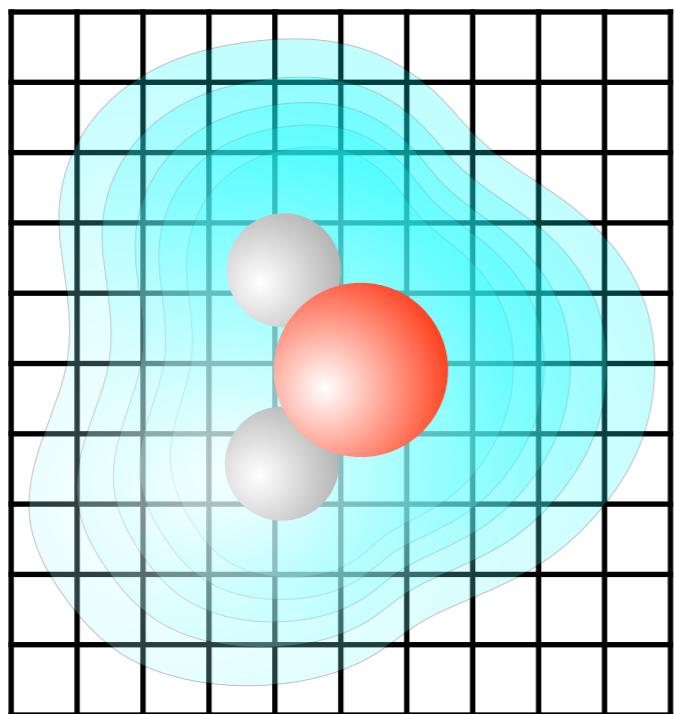
Z_i is the charge of the nucleus i

How to simulate many electrons: water as an example

Many-electron molecular system

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

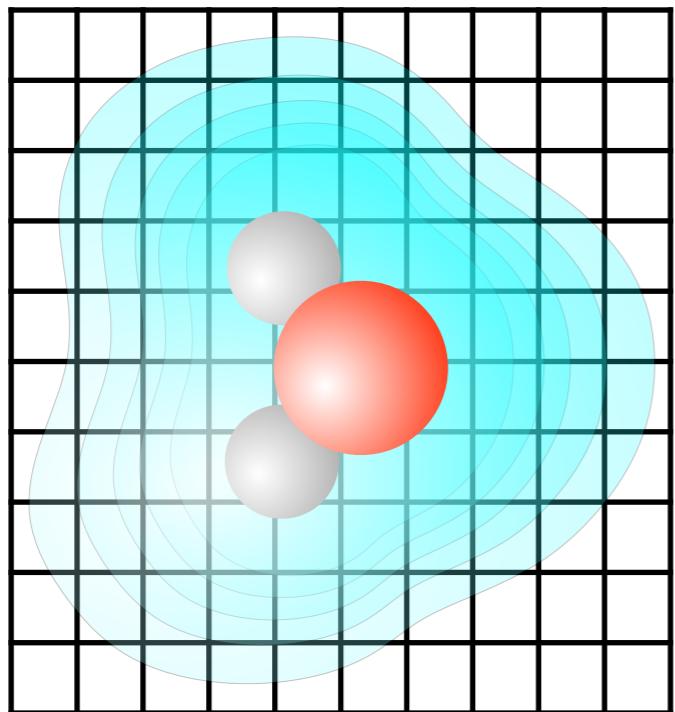
Let us assume for example that we want to store the 10-electron wave function of our water molecule in the computer on a relatively coarse grid of $10 \times 10 \times 10$ points



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

Exponential bottleneck

- ▶ 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

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

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?

- **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).

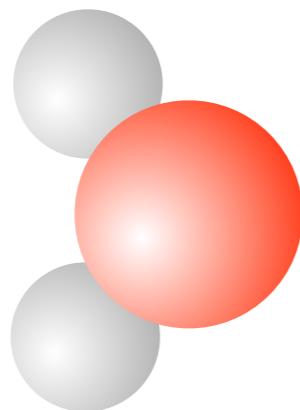
- F is called the **universal functional**. It is often written in terms of the kinetic, electrostatic, and exchange-correlation contributions

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

The local density approximation

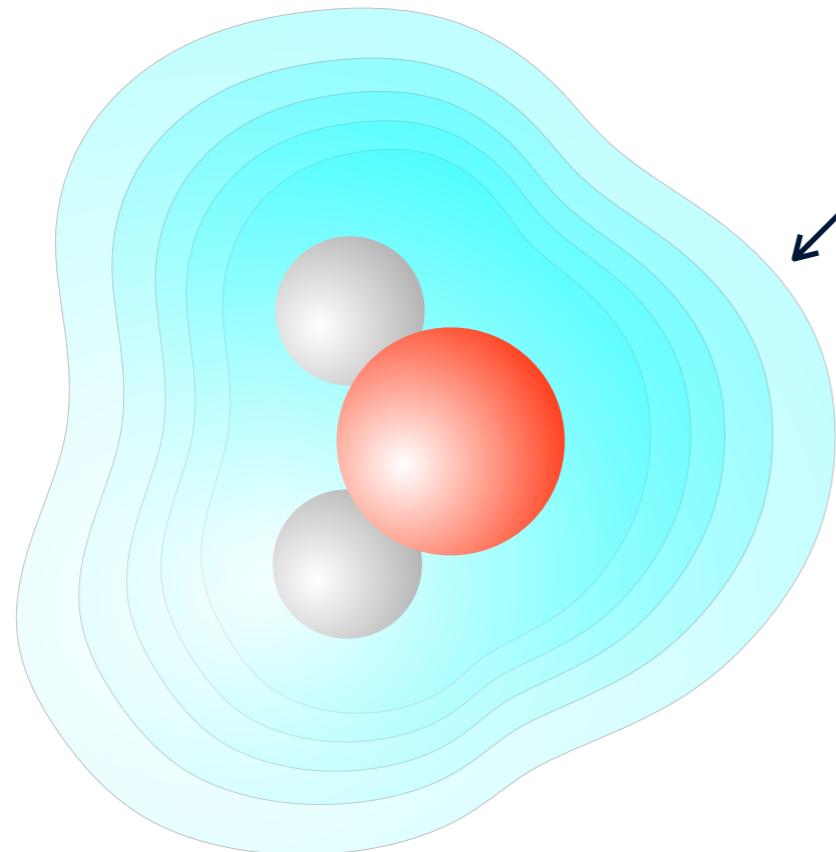
Local density approximation

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



Local density approximation

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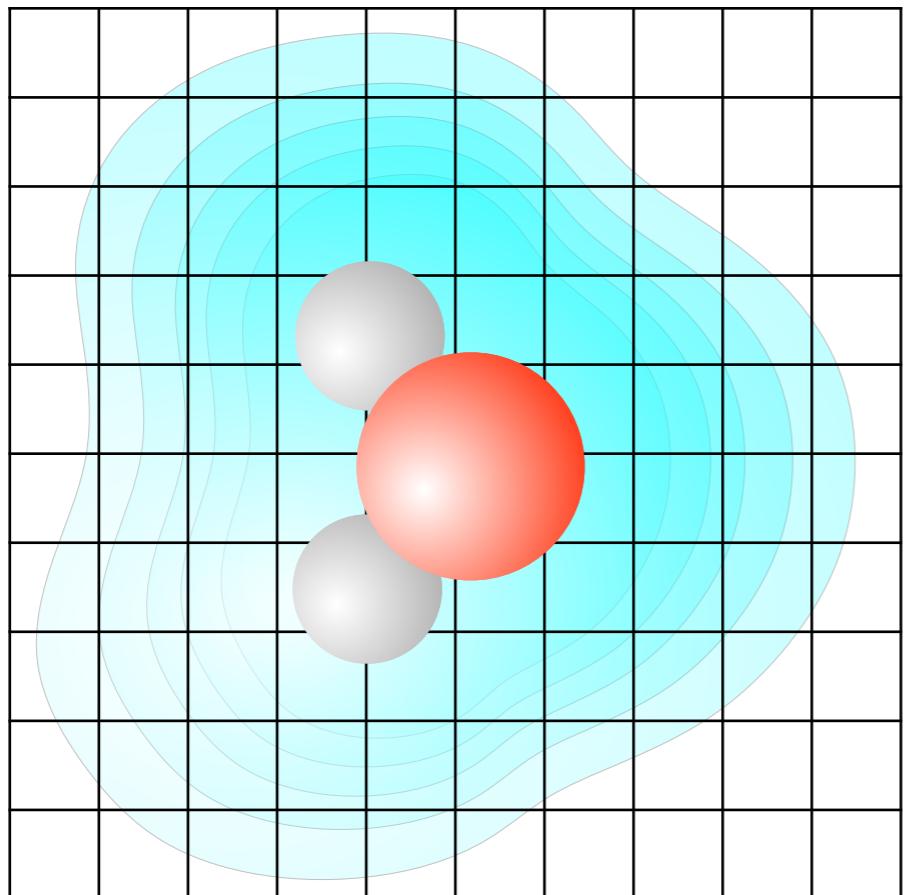


$$\rho(\mathbf{r}) = \sum_{n=1}^N |\phi_n(\mathbf{r})|^2$$

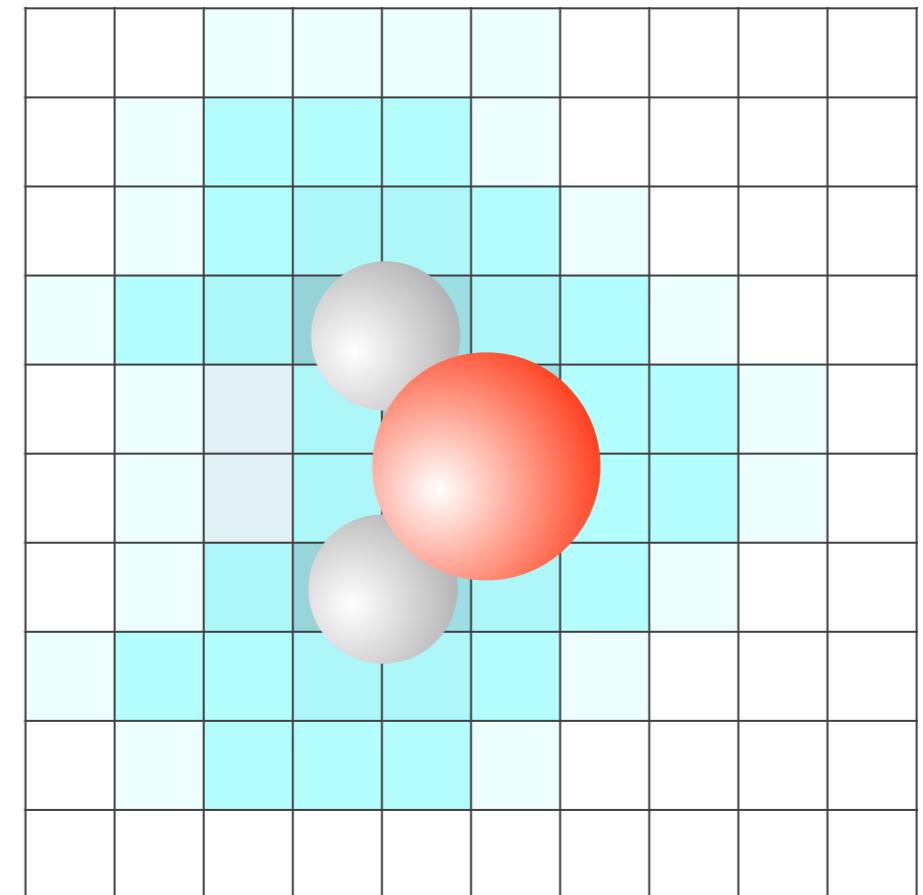
Start from the electronic density...

Local density approximation (cont'd)

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



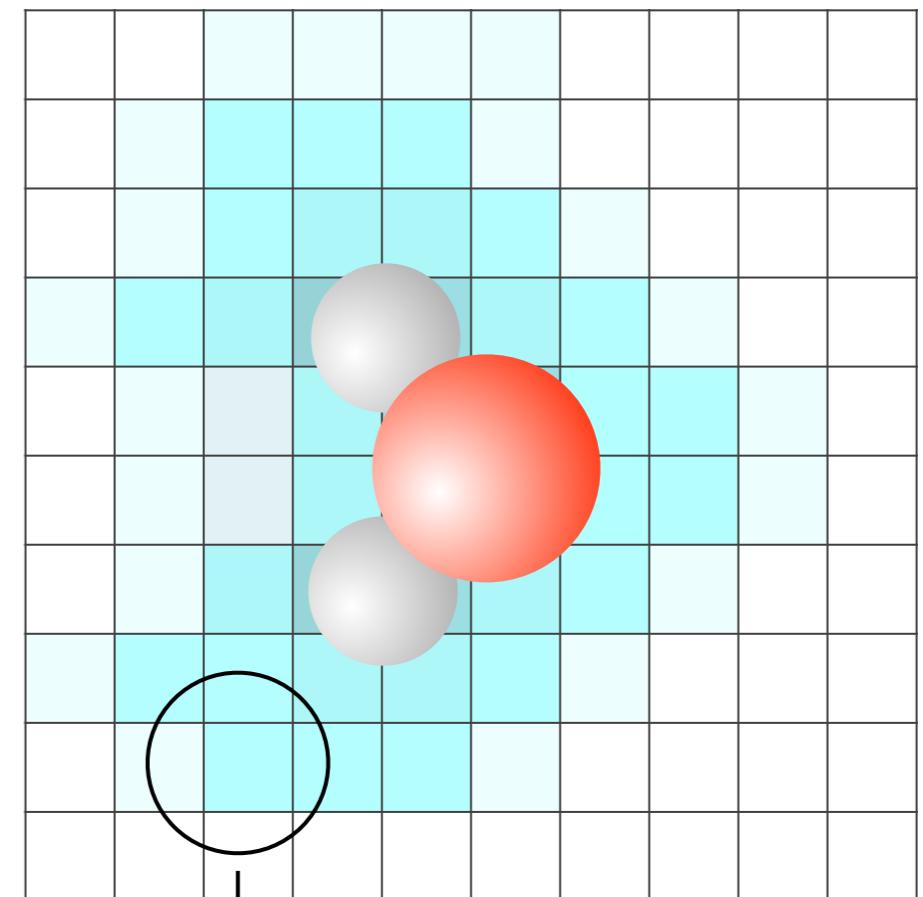
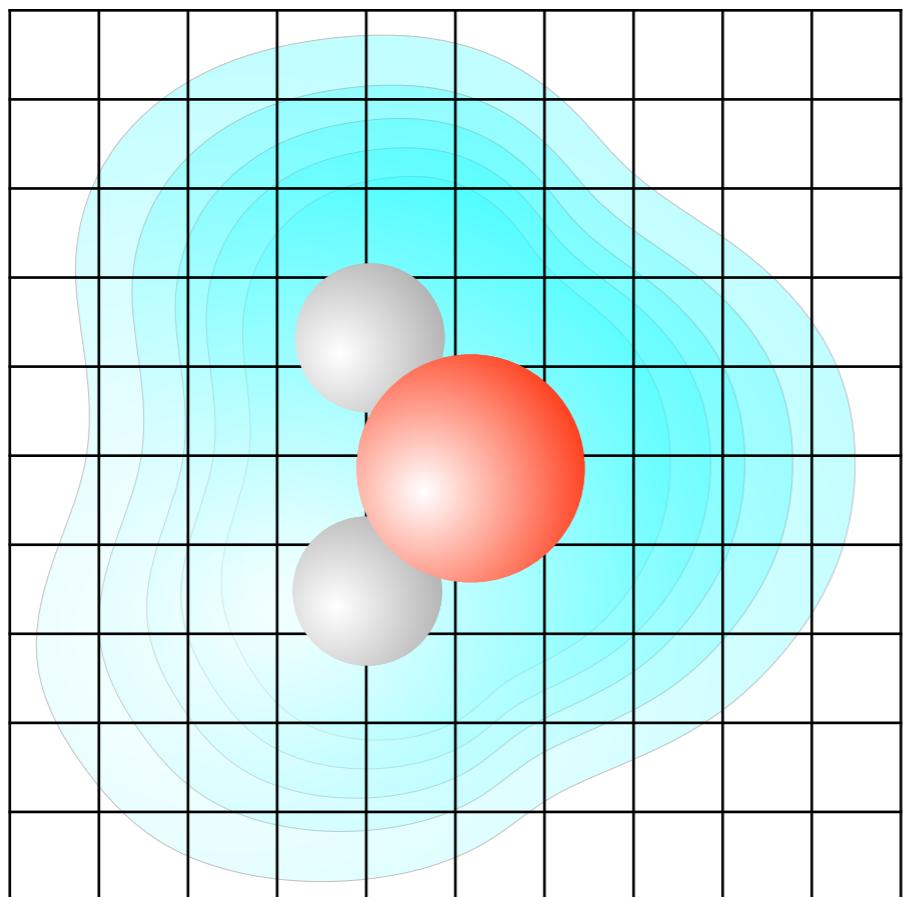
... Divide space into small volumes



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

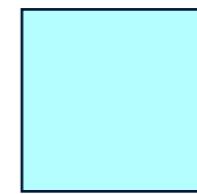
Local density approximation (cont'd)

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



Kinetic energy per volume
in uniform gas of density ρ

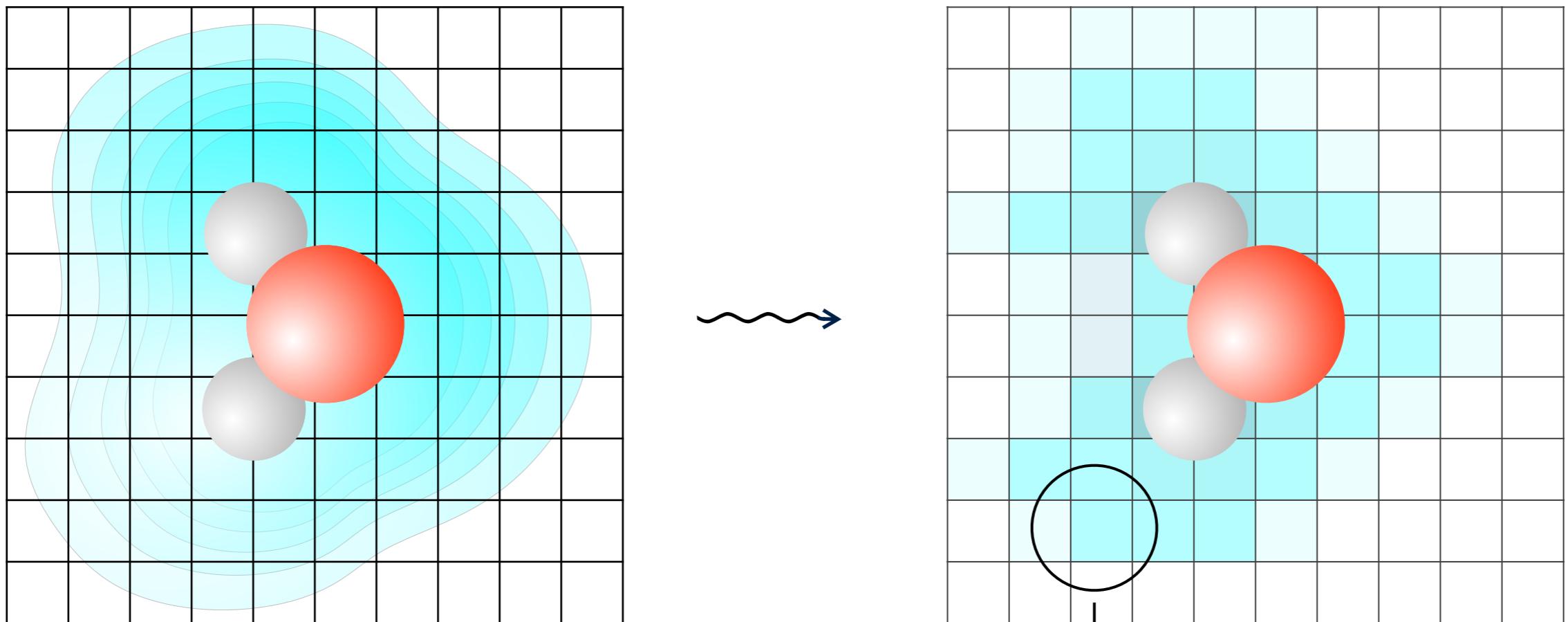
$$dK = \underbrace{k(\rho(r))}_{\text{Kinetic energy in } \square} dr$$



... 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

- 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)



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



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...

Is the calculation converged?



Yes

Calculate final energy

Set initial orbitals $\{\phi_{n\sigma}\}$

Calculate density

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

Calculate effective potential

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) + \int \frac{e^2}{4\pi\epsilon_0} \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

Solve Schrödinger equation

$$-\frac{\hbar^2}{2m_e} \nabla^2 \phi_n(\mathbf{r}) + v(\mathbf{r}) \phi_n(\mathbf{r}) = \epsilon_n \phi_n(\mathbf{r})$$



Walter Kohn
(1923-2016)

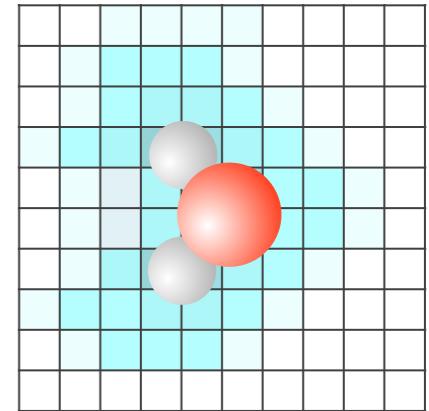
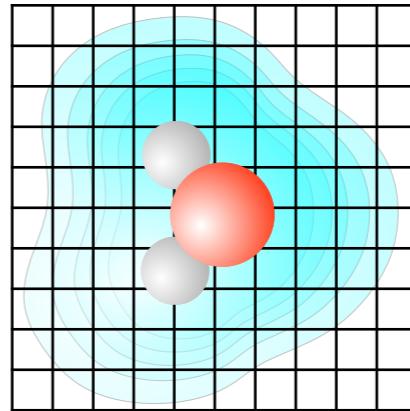


Lu Sham
(born 1938)

No

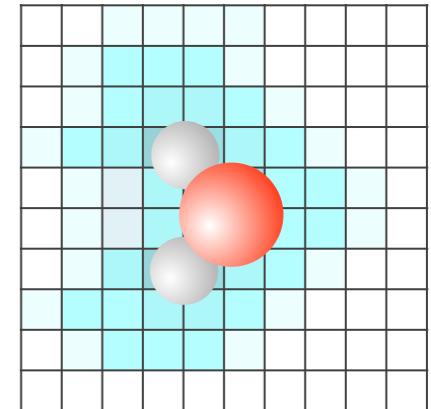
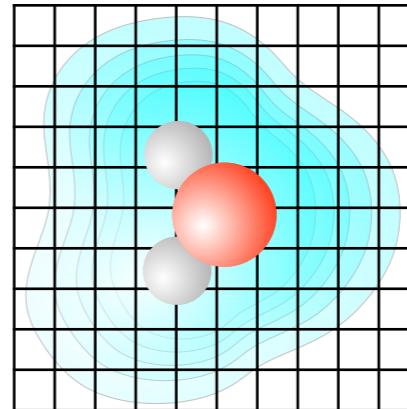
Summary

- ▶ **Density-functional theory** is an effective simplification of the many-electron problem using the density ρ as variable instead of the complicated many-electron wave function Ψ .
- ▶ 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.

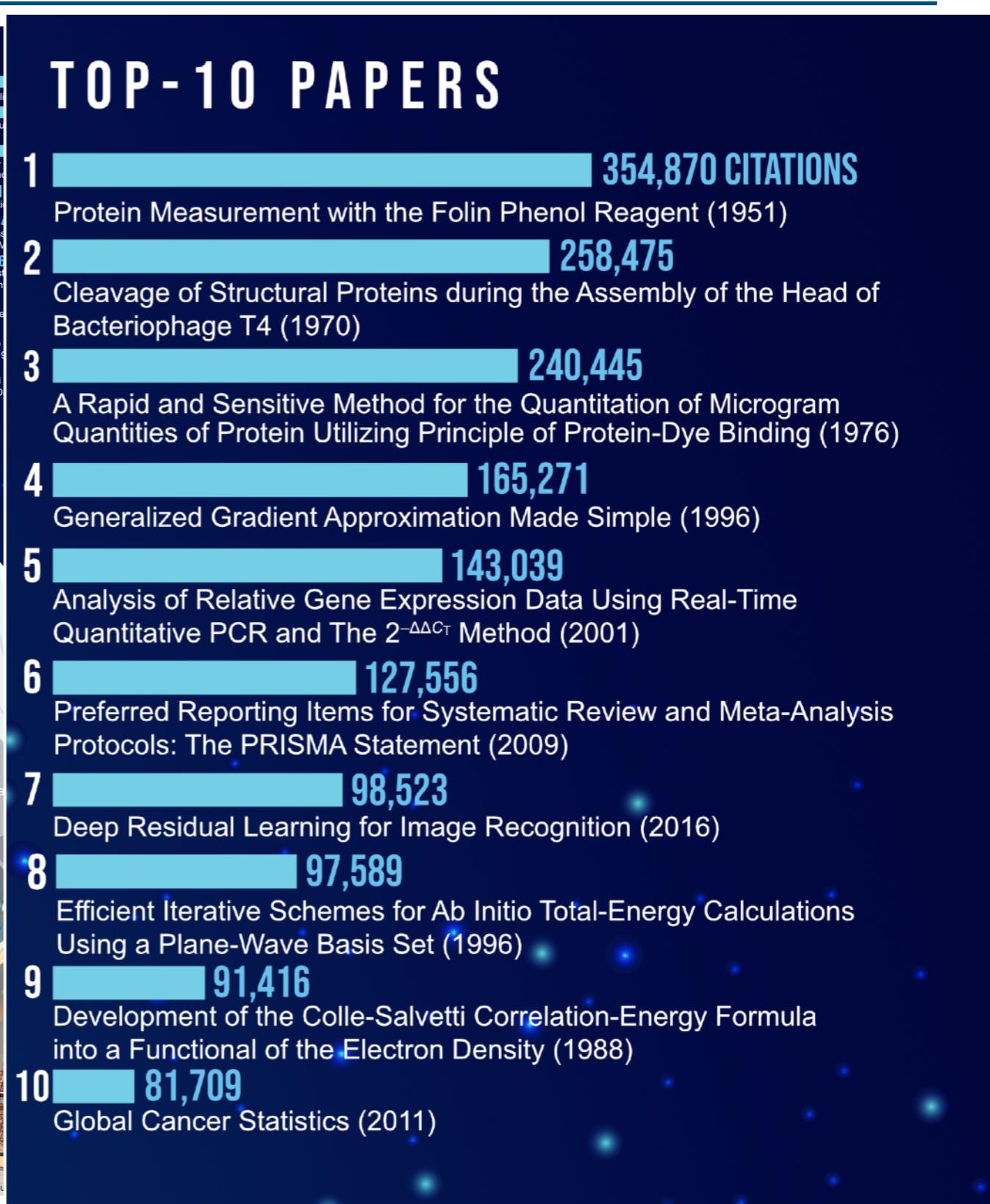
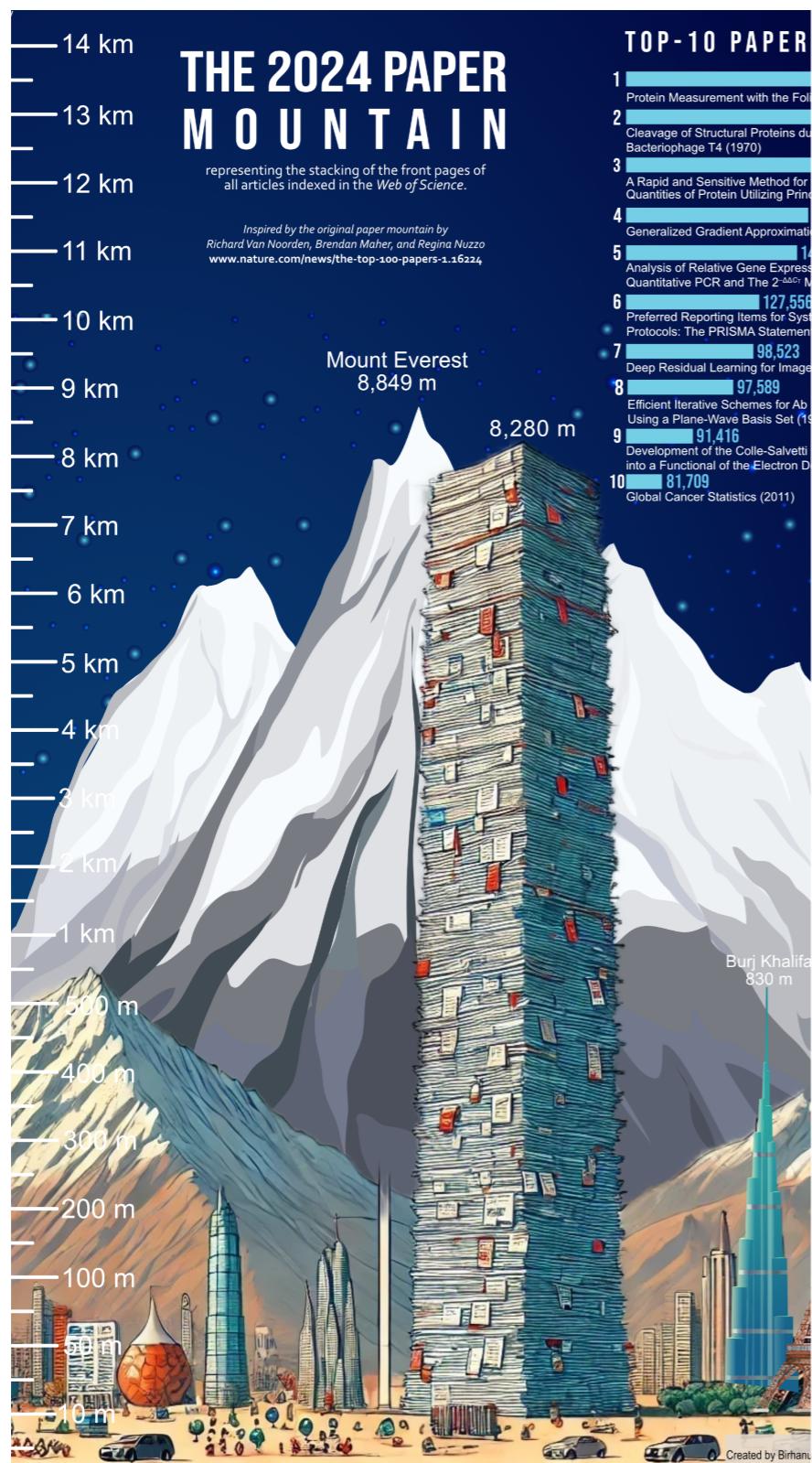


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Summary: closing the loop

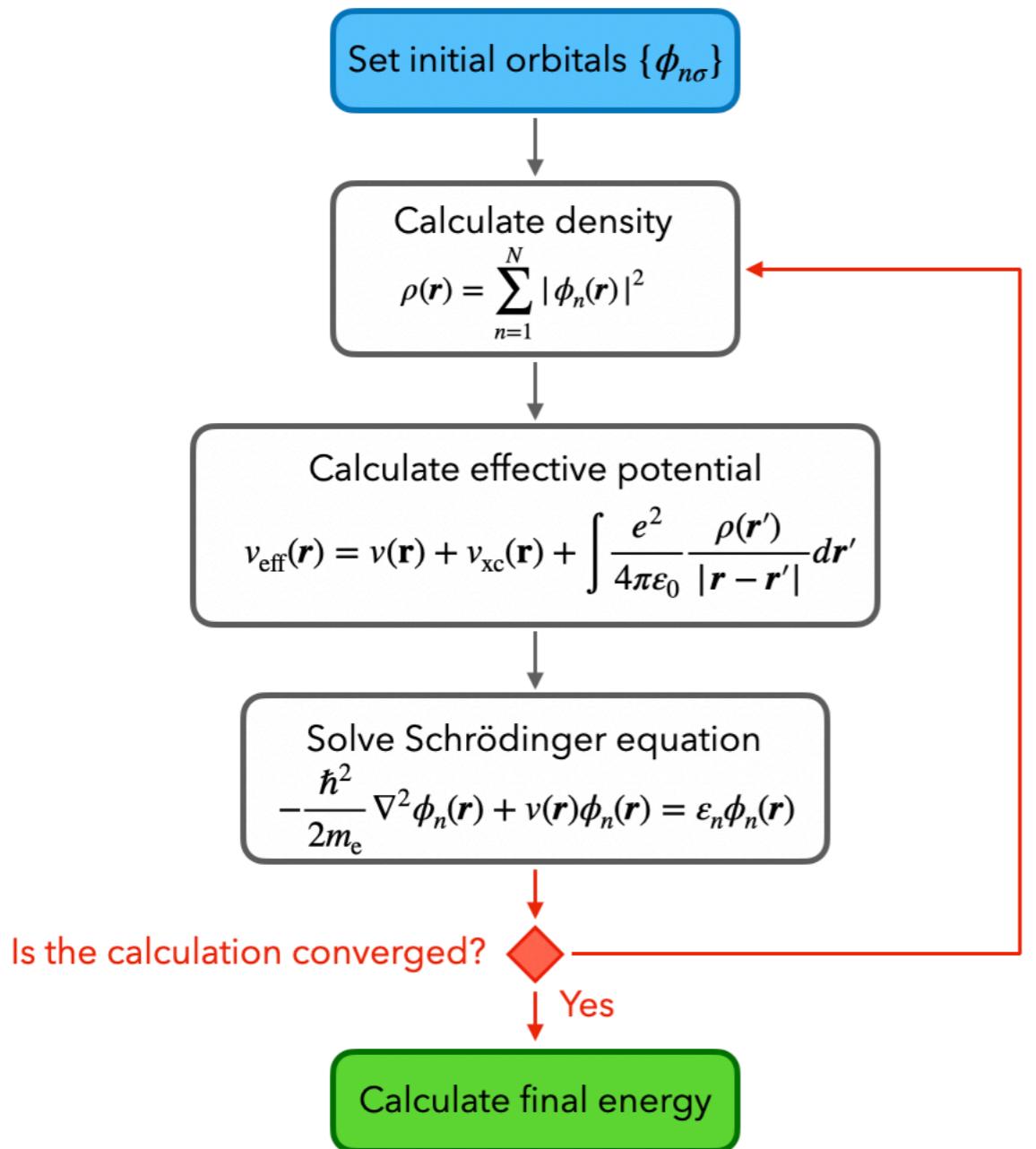


Hands-On:

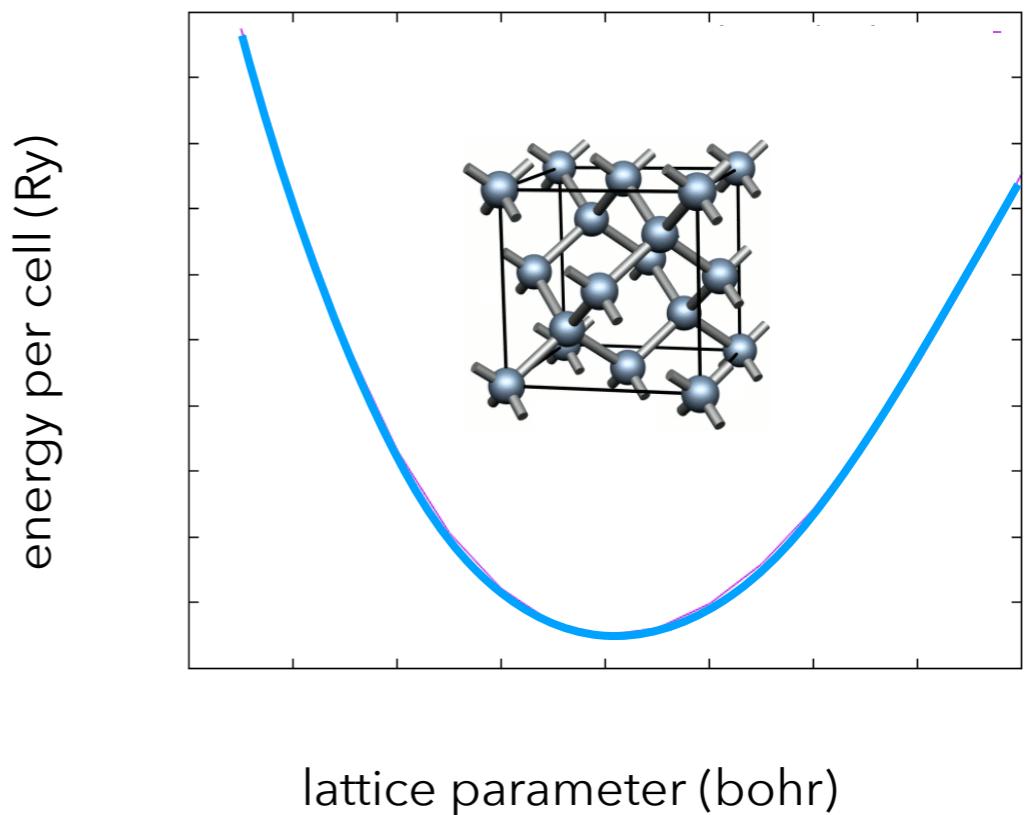
Convergence of Self-Consistent-Field Calculations

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      Number of k-points
Si 0.25 0.25 0.25      to sample the Brillouin zone
KPOINTS automatic
  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

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

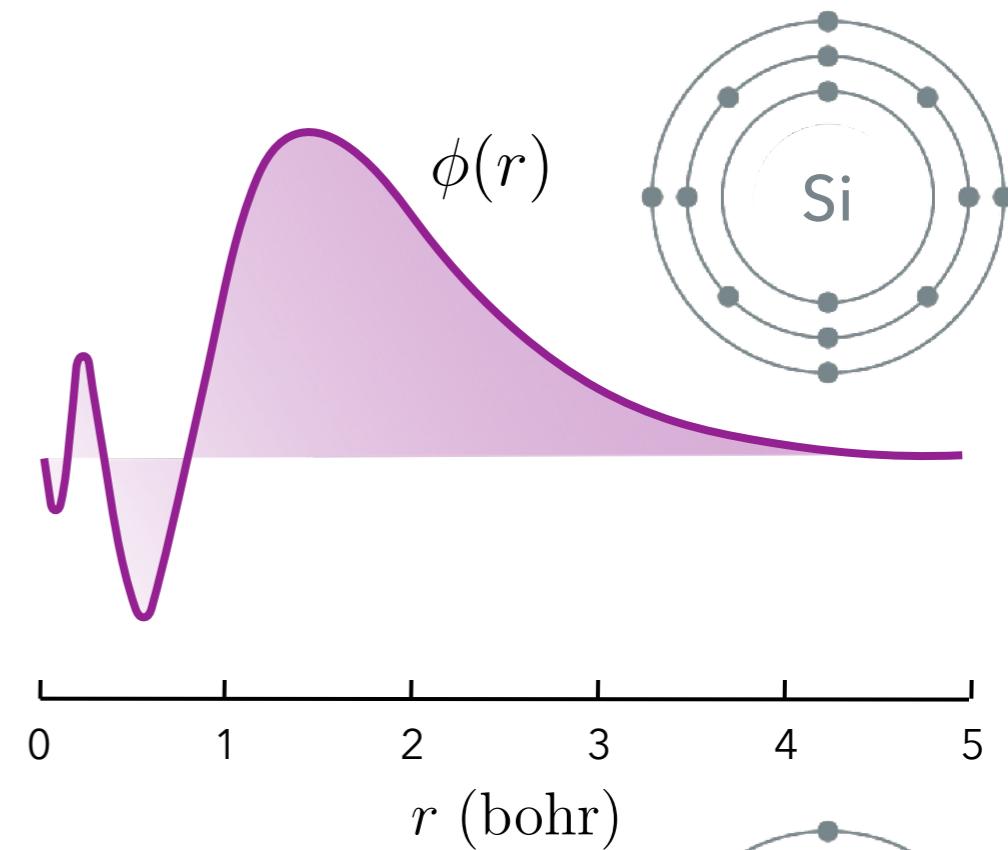
- To manage this infinite sum computationally, only the vectors of magnitude $|\mathbf{G}|$ below a chosen threshold are included
- This threshold is defined in terms of a **cutoff kinetic energy**

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

Important terminology: pseudopotentials

Strong oscillations

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



Pseudization

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

