

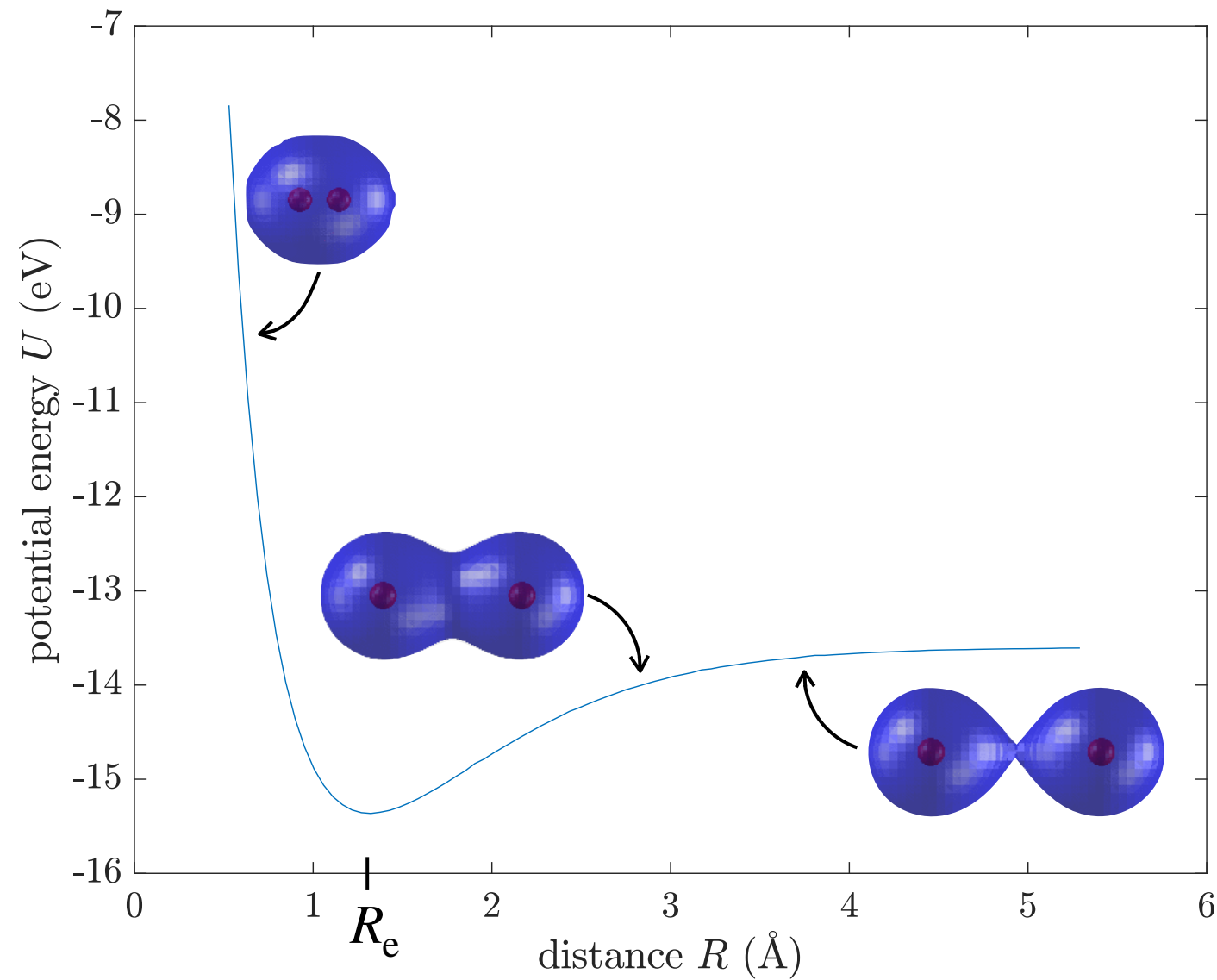
# Born-Oppenheimer

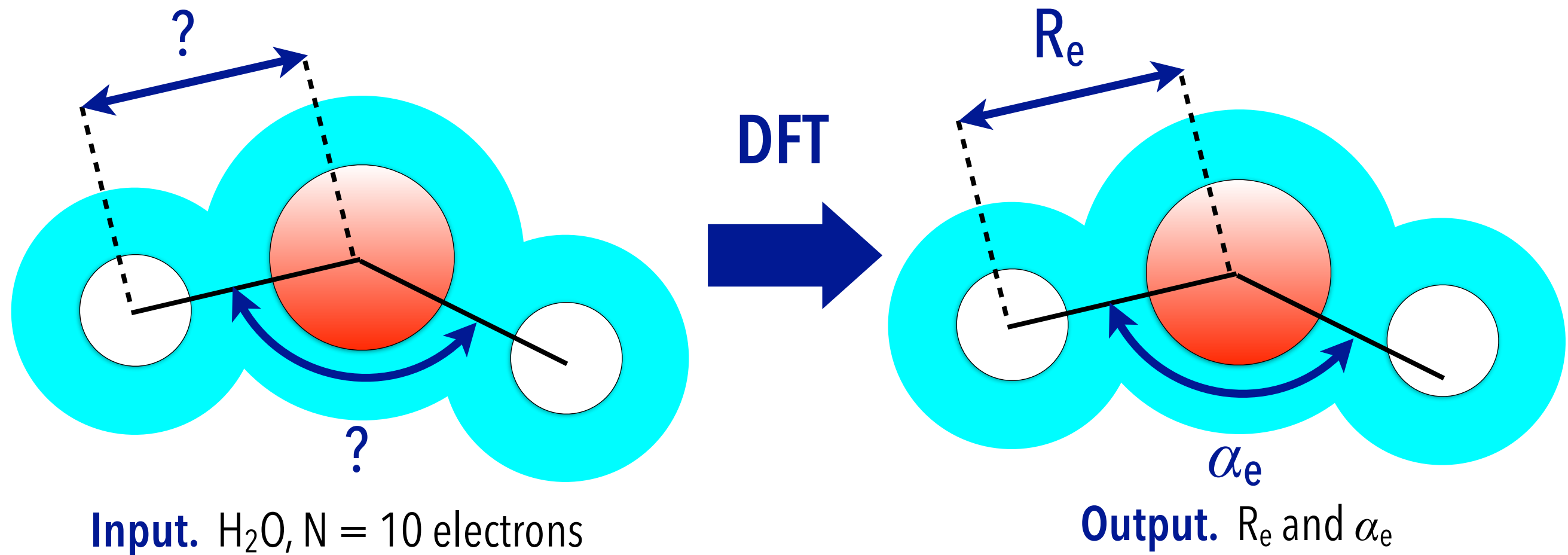


Max Born  
(1882–1970)



Julius Robert  
Oppenheimer  
(1904–1967)

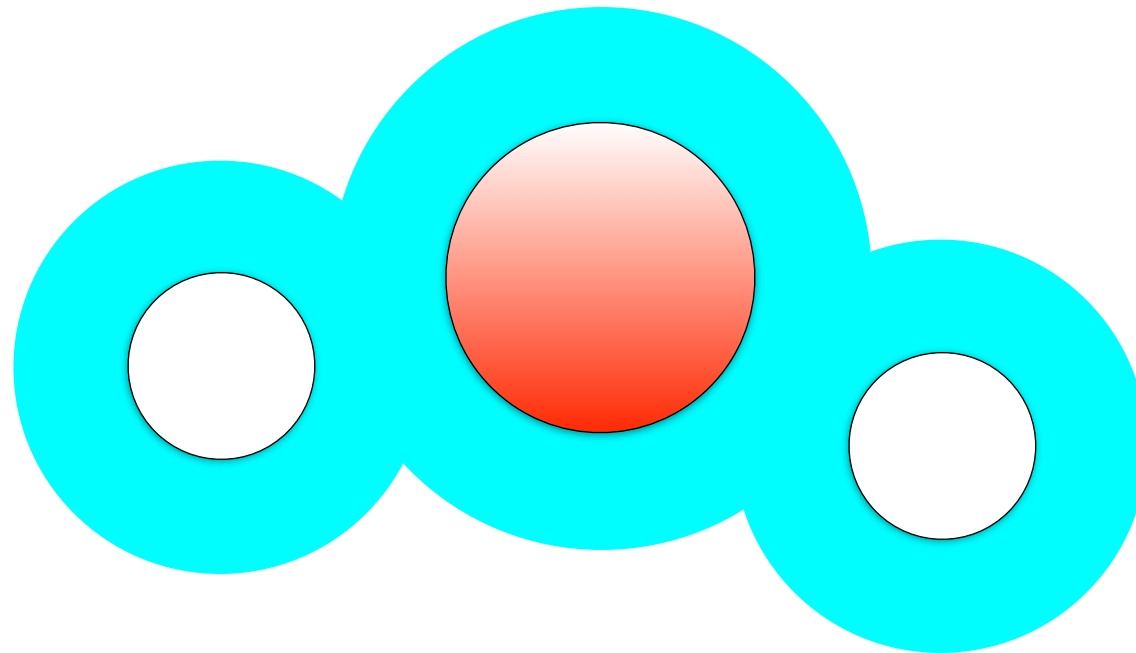




**Density-Functional Theory (DFT)** is a quantum method widely used in materials science and chemistry to calculate the properties of systems of atoms (energy, geometry, reactivity, phase stability) using limited experimental data.

# Density-functional theory

► Now, let's study the potential energy  $U$  of the molecule



Potential Energy  
of the Molecule

↘

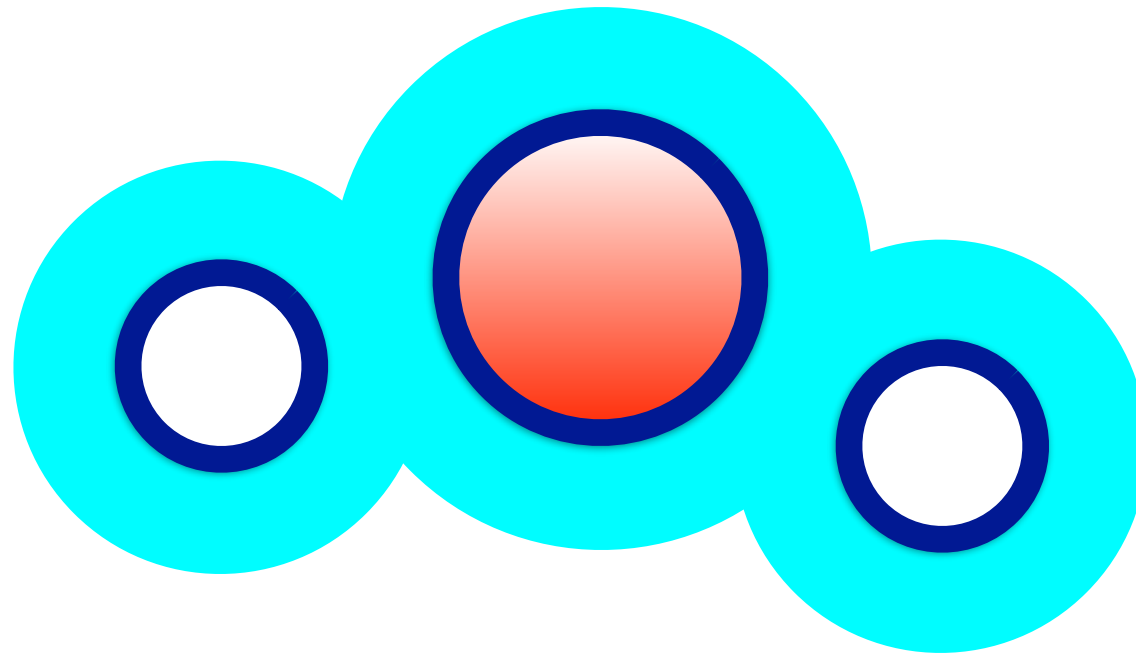
$$U = \mathcal{E} + \frac{1}{2} \sum_i \sum_j' \frac{Z_i Z_j e^2}{4\pi\epsilon_0 R_{ij}}$$

**Recall.** We have seen this equation.

It is the **Born-Oppenheimer Equation**.

# Density-functional theory (cont'd)

► Now, let's study the potential energy  $U$  of the molecule

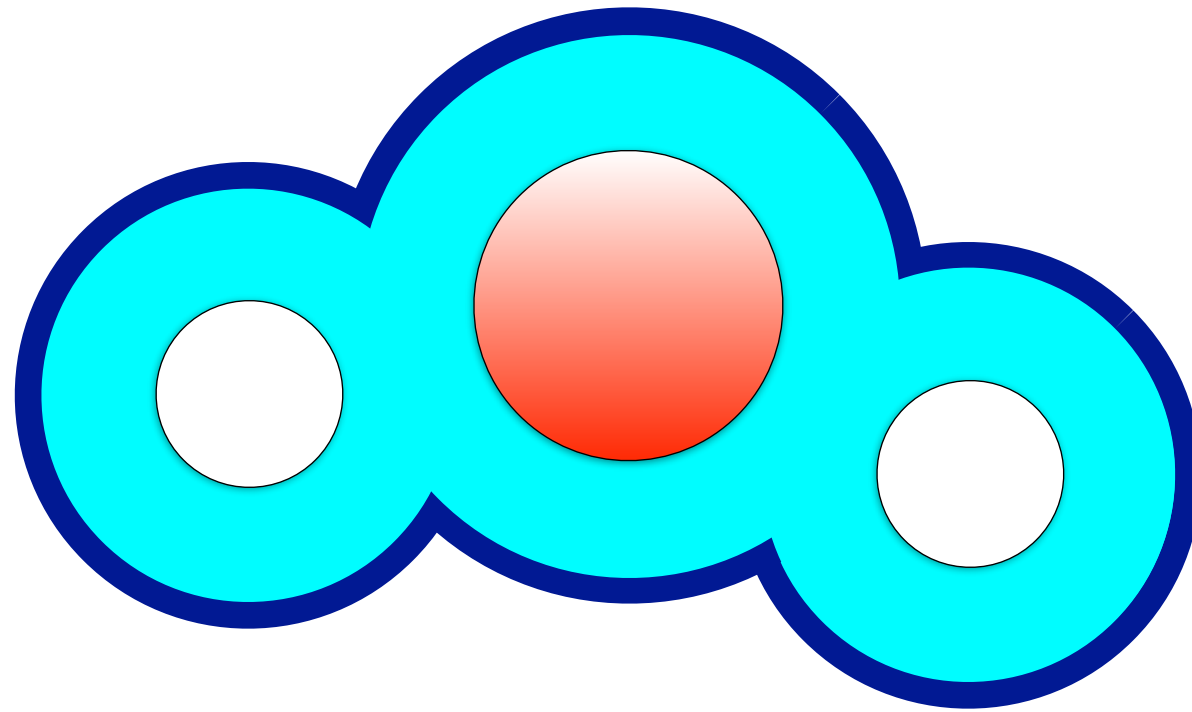


$$U = \mathcal{E} + \frac{1}{2} \sum_i \sum_j' \frac{Z_i Z_j e^2}{4\pi\epsilon_0 R_{ij}}$$

Energy of the 3 Nuclei

# Density-functional theory (cont'd)

► Now, let's study the potential energy  $U$  of the molecule

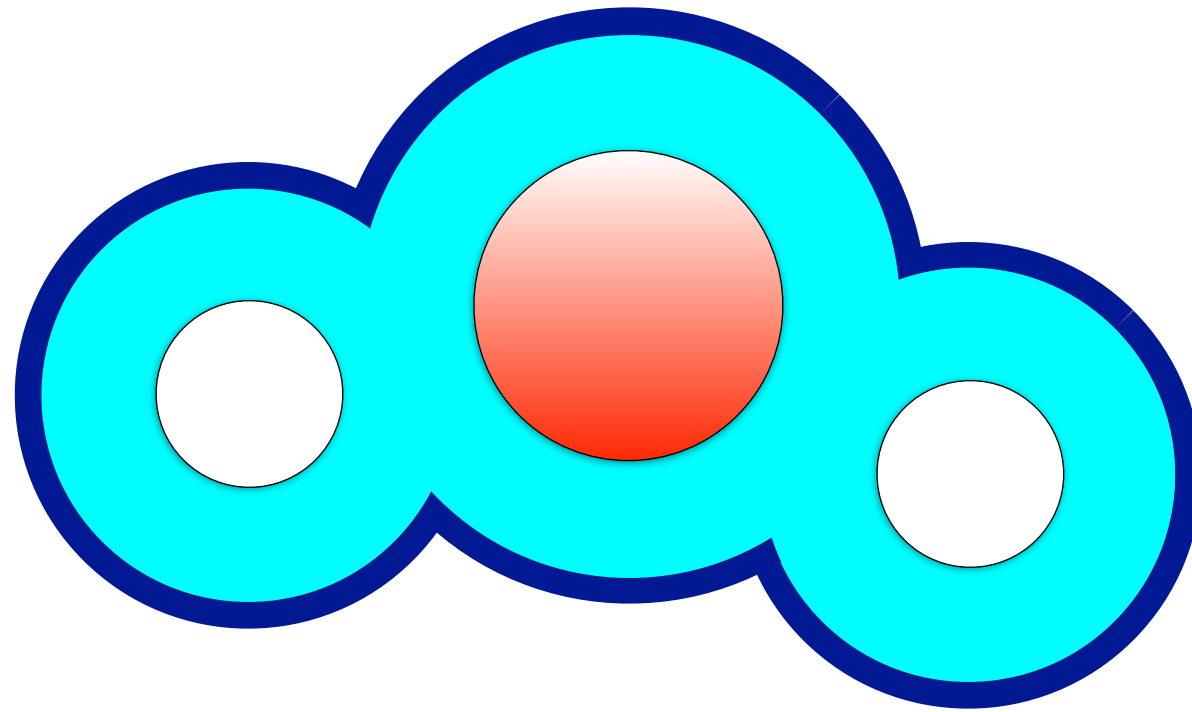


$$U = \boxed{\mathcal{E}} + \frac{1}{2} \sum_i \sum_j' \frac{Z_i Z_j e^2}{4\pi\epsilon_0 R_{ij}}$$

Energy of the 10 Electrons

# Density-functional theory (cont'd)

► Now, let's study the potential energy  $U$  of the molecule




$$U = \boxed{\mathcal{E}} + \frac{1}{2} \sum_i \sum_j' \frac{Z_i Z_j e^2}{4\pi\epsilon_0 R_{ij}}$$

► DFT provides a way to calculate  $\boxed{\mathcal{E}}$

# Density-functional theory (cont'd)

- Here is how the energy of the interacting electrons is written within DFT:

Energy of Interacting  
Electrons



$$\mathcal{E} = \sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r})$$
$$+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}(\rho)$$

# Density-functional theory (cont'd)

- Here is how the energy of the interacting electrons is written within DFT:

Energy of Interacting  
Electrons

Energy of Noninteracting  
Electrons


$$\mathcal{E} = \sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}(\rho)$$



# Density-functional theory (cont'd)

- Here is how the energy of the interacting electrons is written within DFT:

Energy of Interacting  
Electrons

Energy of Noninteracting  
Electrons

$$\mathcal{E} = \sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}(\rho)$$

Classical Interaction  
Energy of the Electrons

# Density-functional theory (cont'd)

- Here is how the energy of the interacting electrons is written within DFT:

Energy of Interacting  
Electrons

Energy of Noninteracting  
Electrons

$$\mathcal{E} = \sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + E_{xc}(\rho)$$

Classical Interaction  
Energy of the Electrons


Quantum Interaction Energy  
of the Electrons

# Density-functional theory (cont'd)

- Here is how the energy of the interacting electrons is written within DFT:

$$\mathcal{E} = \sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r}) \\ + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + E_{xc}(\rho)$$

Quantum Interaction Energy  
of the Electrons




- **Question 1.** Why is this method called density-functional theory?

# Density-functional theory (cont'd)

- Here is how the energy of the interacting electrons is written within DFT:

$$\mathcal{E} = \sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r}) \\ + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}(\rho)$$

Quantum Interaction Energy  
of the Electrons




- **Answer 1.** Because the quantum interaction energy  $E_{\text{xc}}$  is a function of the electron density  $\rho$ .

# Density-functional theory (cont'd)

- Here is how the energy of the interacting electrons is written within DFT:

$$\mathcal{E} = \sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r}) \\ + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}(\rho)$$

Quantum Interaction Energy  
of the Electrons




- **Question 2.** Do you remember the expression of the electron density  $\rho$ ?

# Density-functional theory (cont'd)

- Here is how the energy of the interacting electrons is written within DFT:

$$\mathcal{E} = \sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r}) \\ + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}(\rho)$$

Quantum Interaction Energy  
of the Electrons



- **Answer 2.** The electron density is  $\rho(\mathbf{r}) = \sum_{n=1}^N |\psi_n(\mathbf{r})|^2$

# Density-functional theory (cont'd)

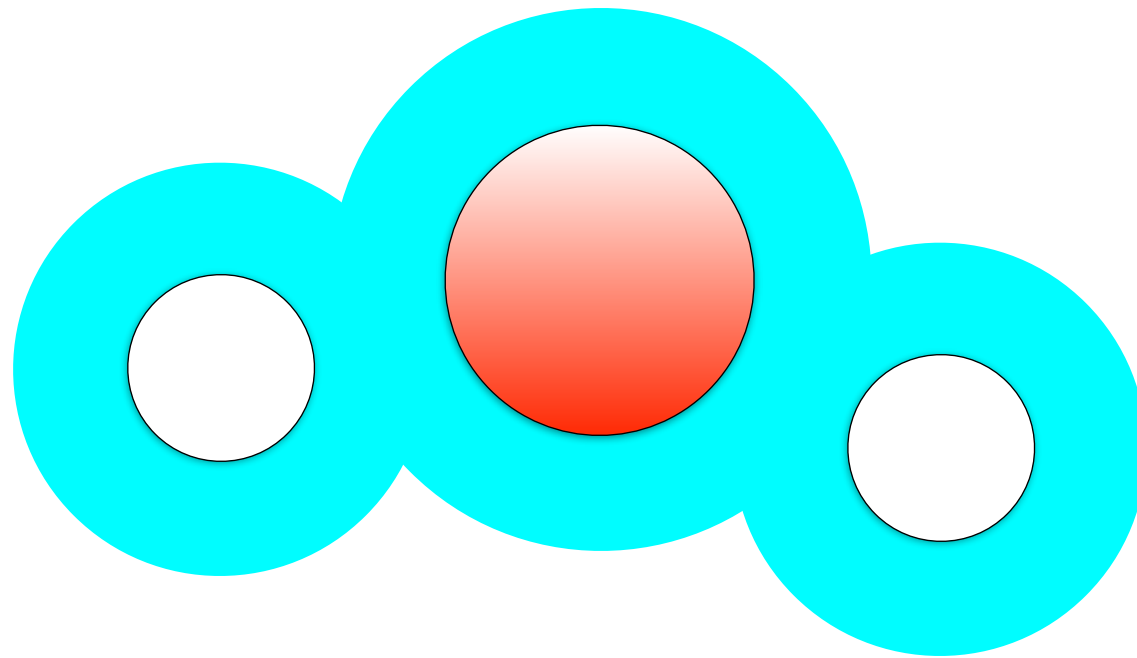
► Now, we define DFT.

► **Definition | Density-functional theory.** Density-functional theory is a method to calculate the energy of interacting electrons. Electron interactions include two contributions: a **classical** (electrostatic) contribution and a **quantum** (exchange-correlation) contribution that depends on the electron density  $\rho(\mathbf{r}) = \sum_{n=1}^N |\psi_n(\mathbf{r})|^2$ .

$$\mathcal{E} = \sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}(\rho)$$

# Density-functional theory (cont'd)

► This is the energy of the molecule:

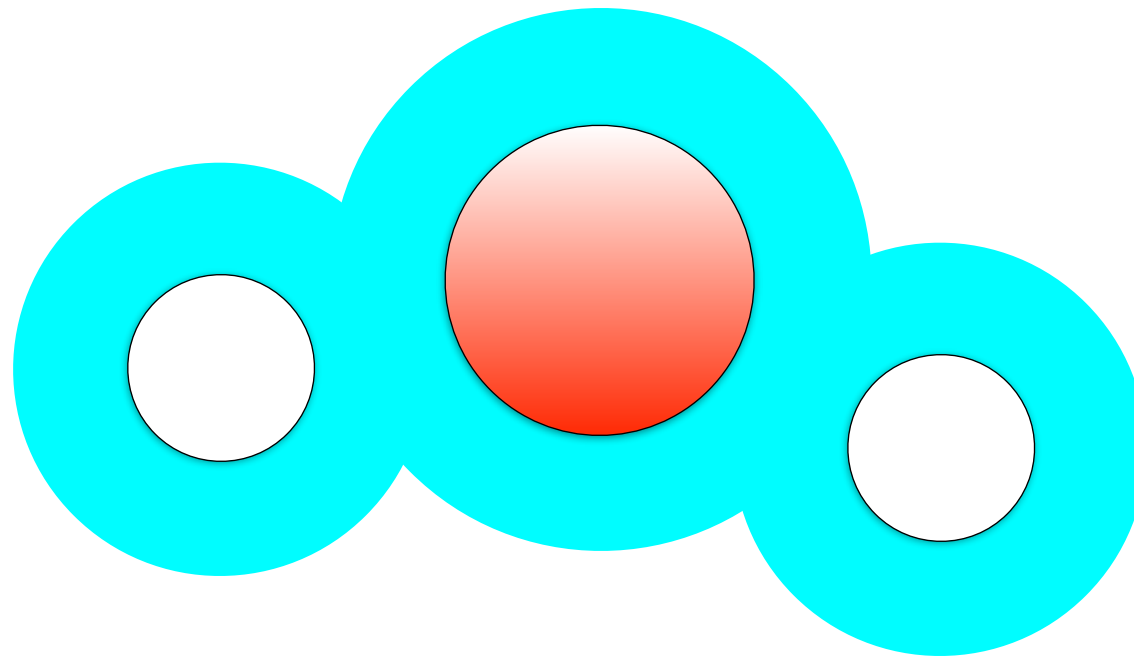


$$U = \mathcal{E} + \frac{1}{2} \sum_i \sum_j' \frac{Z_i Z_j e^2}{4\pi\epsilon_0 R_{ij}}$$



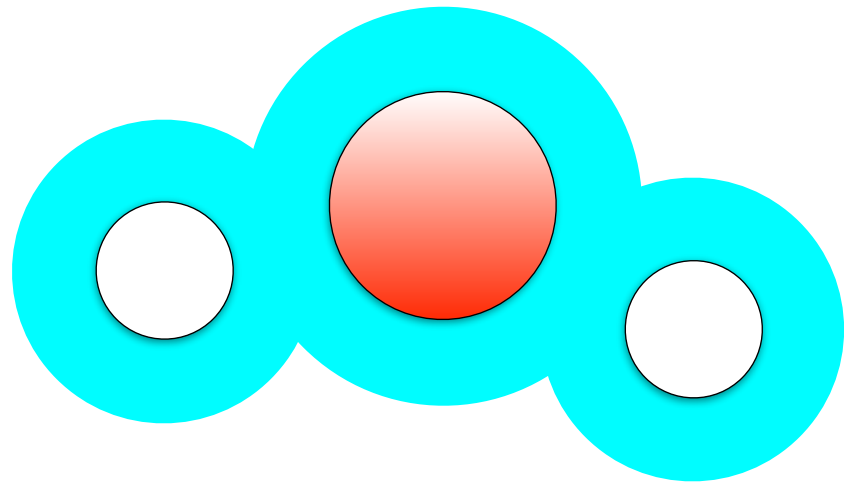
# Density-functional theory (cont'd)

► Substituting the DFT energy, we obtain:



$$\begin{aligned} U = & \sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r}) \\ & + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}(\rho) \\ & + \frac{1}{2} \sum_i \sum_j' \frac{Z_i Z_j e^2}{4\pi\epsilon R_{ij}} \end{aligned}$$

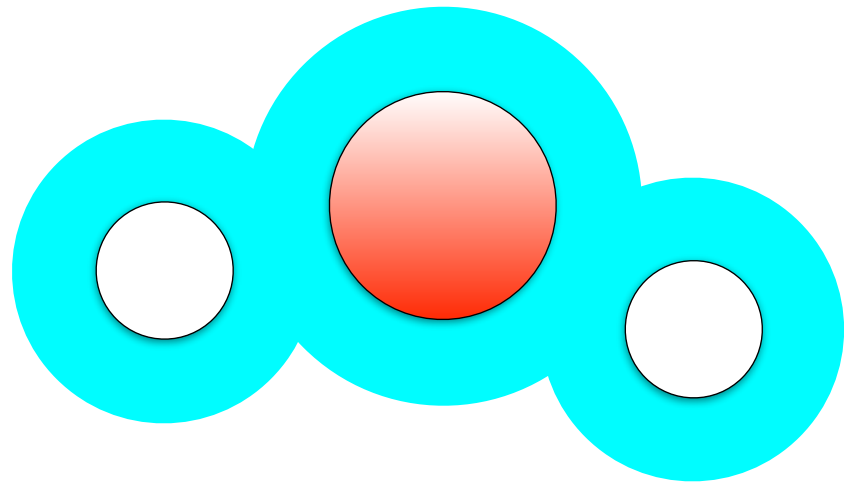
# Minimization



$$U = \sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r}) \\ + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}(\rho) \\ + \frac{1}{2} \sum_i \sum_j' \frac{Z_i Z_j e^2}{4\pi\epsilon R_{ij}}$$

- **Objective.** We must find the minimum of  $U$  to get the geometry.
- Let's break down this complexity.

# Minimization (cont'd)



$$U = \sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r})$$
$$+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + \cancel{E_{xc}(\rho)}$$
$$+ \frac{1}{2} \sum_i \sum_j' \frac{Z_i Z_j e^2}{4\pi\epsilon R_{ij}}$$

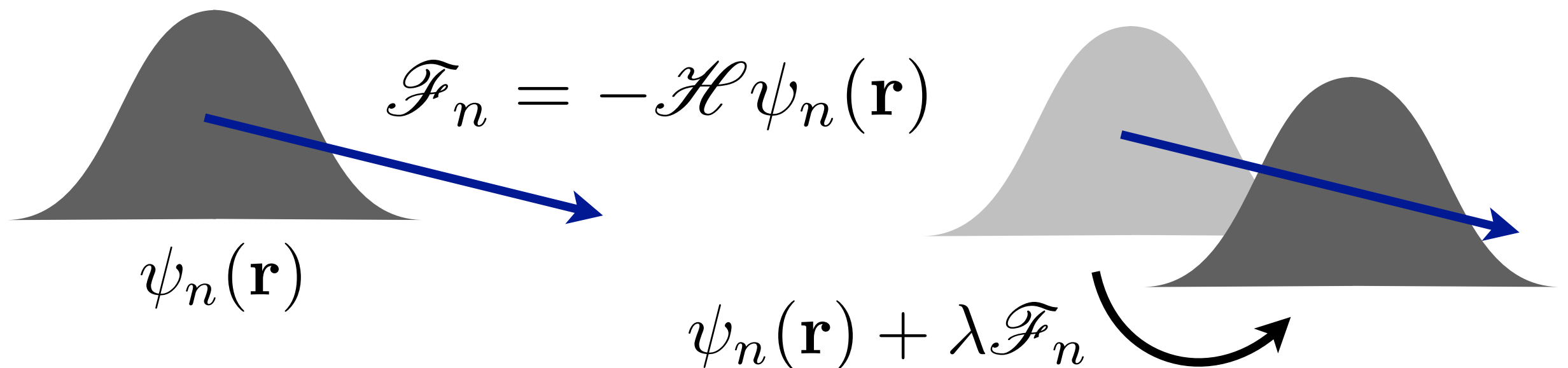
- **Objective.** We must find the minimum of  $U$  to get the geometry.
- Let's break down this complexity.
- **We ignore the last 3 terms (!).**

# Minimization (cont'd)

$$\sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r})$$

- We know how to minimize this expression.
- We can use **steepest descent**

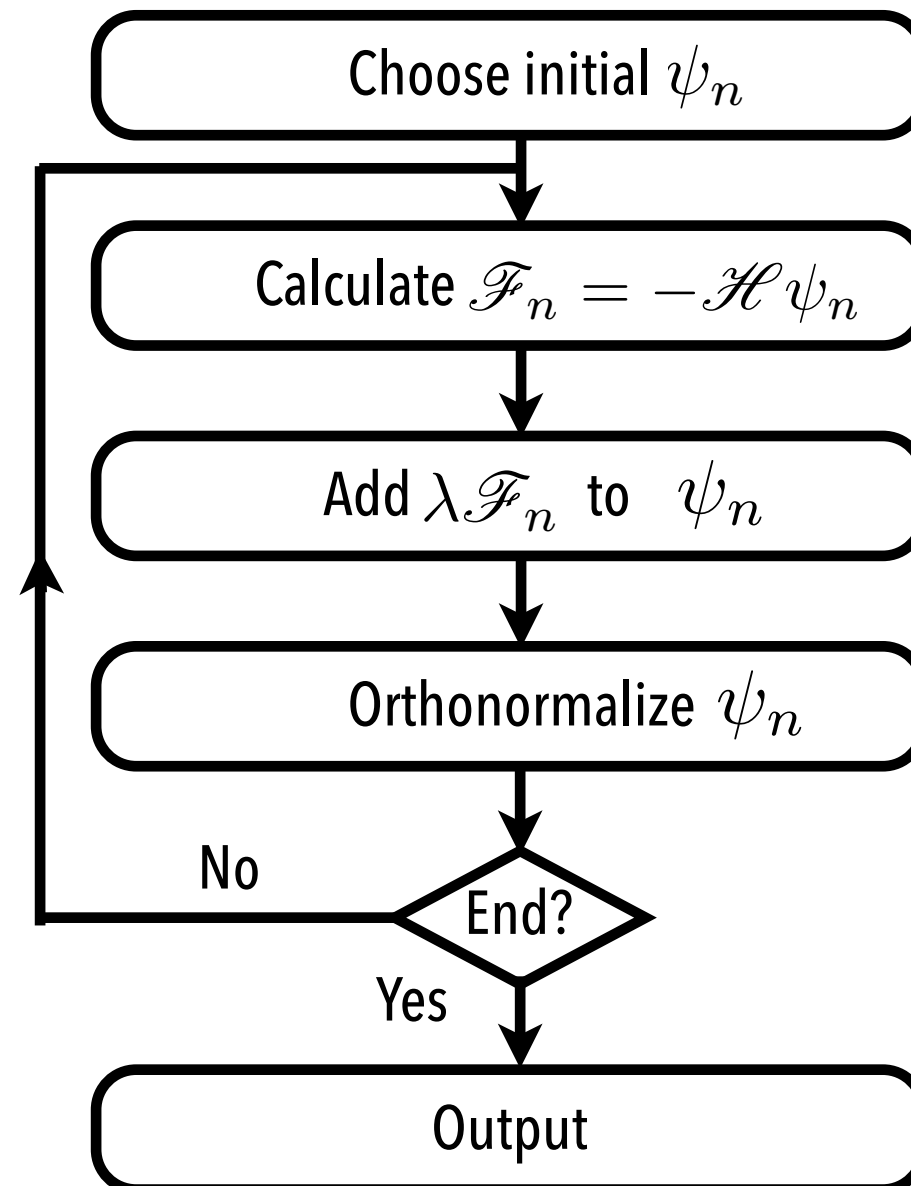
Steepest-Descent Method in Quantum Mechanics



# Minimization (cont'd)

$$\sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r})$$

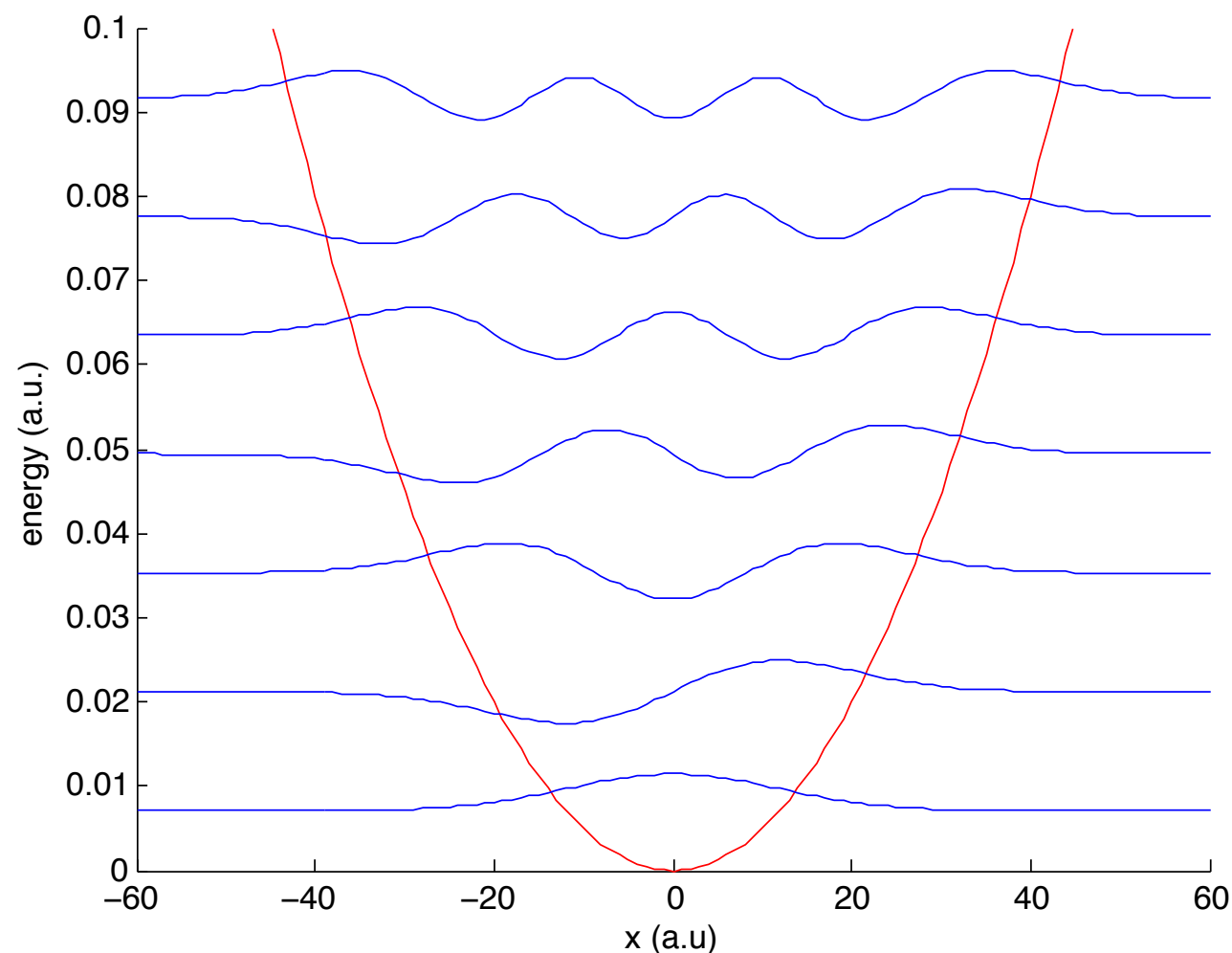
► **Steepest descent** runs as follows



# Simulation

► Let's test the steepest-descent algorithm

► We've already coded steepest descent:



We coded steepest descent to find electronic states in a harmonic well.

► The code was [many\\_electrons.m](#)

## Simulation (cont'd)

- **Question.** How would you modify this code to show that the algorithm works (i.e., the energy goes down)?

$$\sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r})$$

- **Hint.** `H` and `psi` are already defined. We can compute the integral in the sum as

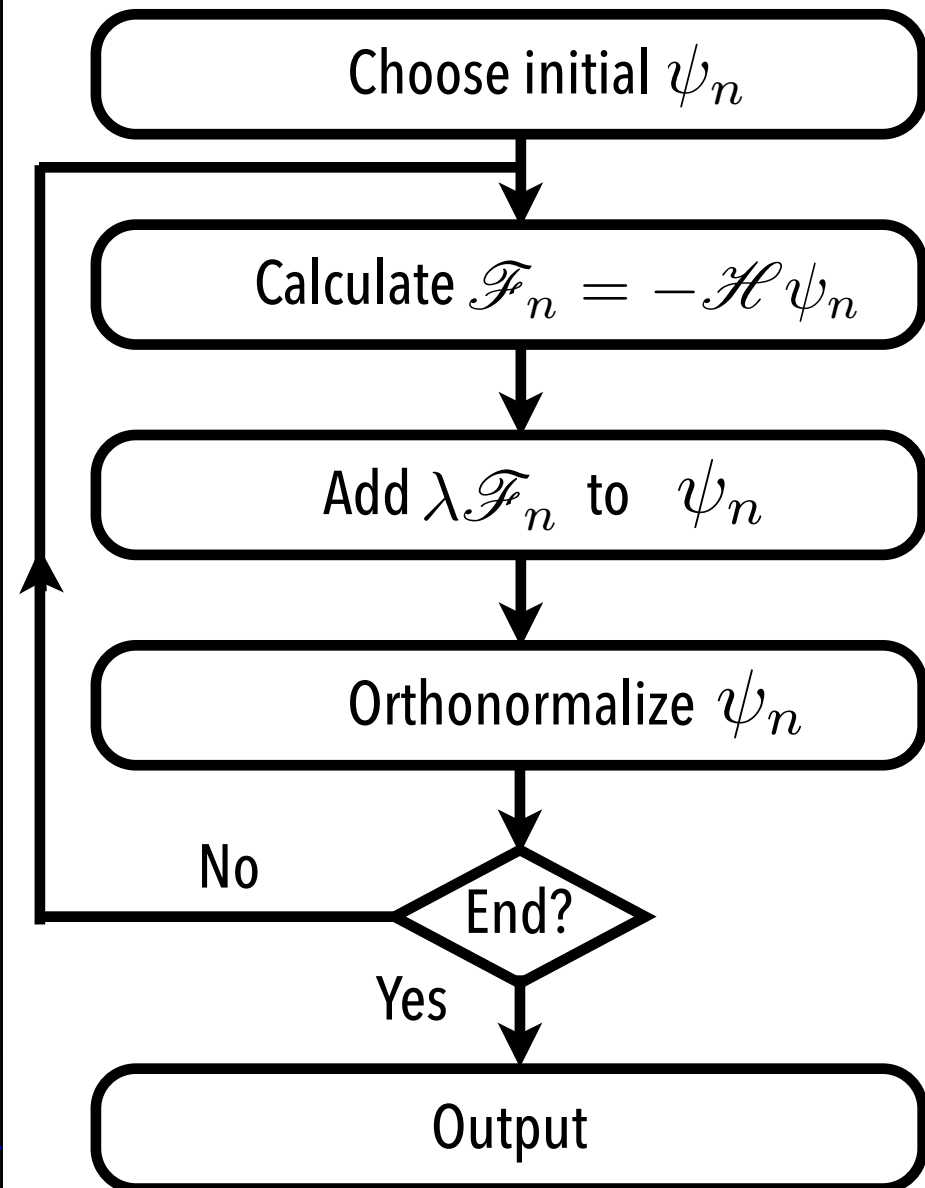
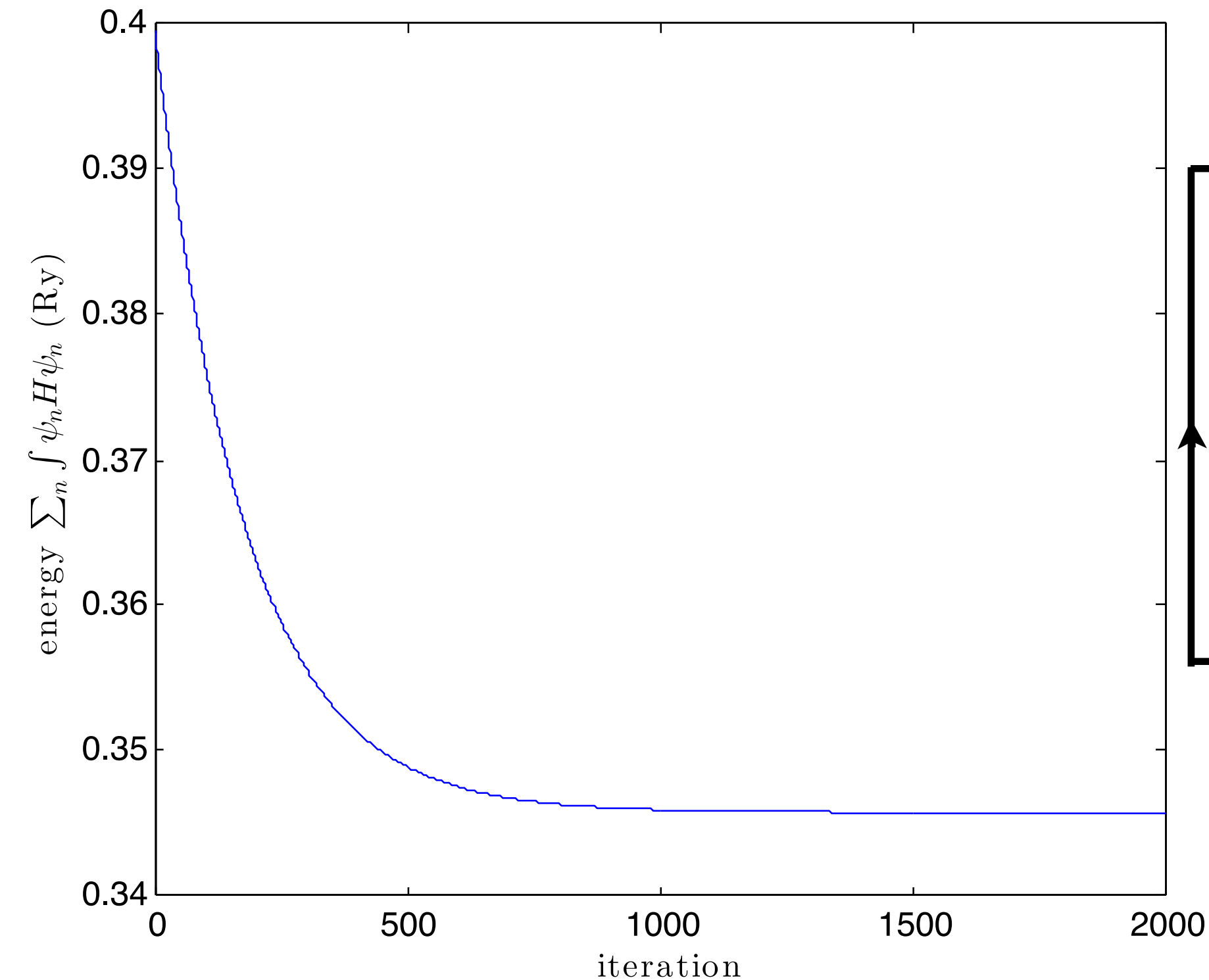
`sum(dx*conj(psi(:,n)).*(H*psi(:,n)))`

`n` : index of the wave function

`dx` : space step.

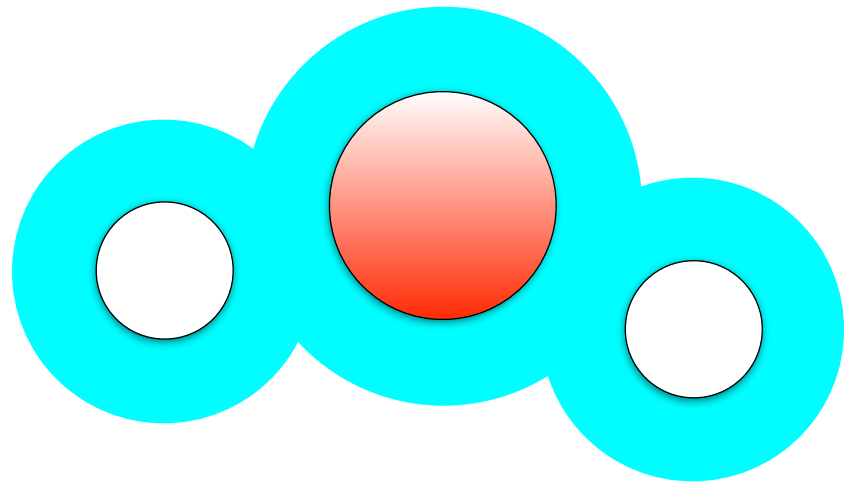
# Result

► The algorithm works (  $\sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r})$  goes down)





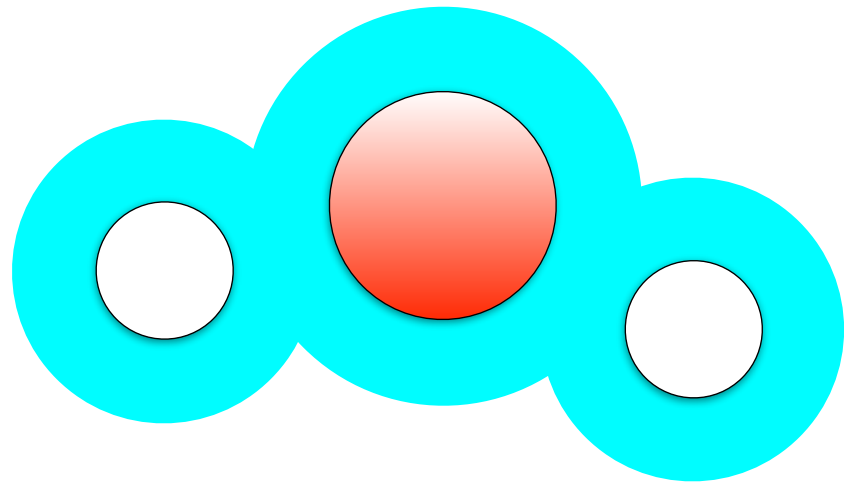
# Minimization



$$U = \sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r}) \quad \checkmark$$
$$+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + \cancel{E_{xc}(\rho)}$$
$$+ \frac{1}{2} \sum_i \sum_j' \frac{Z_i Z_j e^2}{4\pi\epsilon R_{ij}}$$

► So, we know how to handle the first term.

# Minimization (cont'd)



$$U = \sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r})$$
$$+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + \cancel{E_{xc}(\rho)}$$
$$+ \cancel{\frac{1}{2} \sum_i \sum_j' \frac{Z_i Z_j e^2}{4\pi\epsilon R_{ij}}}$$

► So, we know how to handle the first term.

► **Now, let's study the second term.**

# Electrostatic potential

$$\sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}$$

► We've an electrostatic term in the energy.

► Therefore, the force  $\mathcal{F}_n = -\mathcal{H} \psi_n(\mathbf{r})$

changes into

$$\mathcal{F}_n = -\mathcal{H} \psi_n(\mathbf{r}) - v_{\text{ele}}(\mathbf{r}) \psi_n(\mathbf{r})$$

This is the potential acting on the electrons  
due to the electrostatic interactions.

# Electrostatic potential (cont'd)

$$\sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}$$

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changes into

$$\mathcal{F}_n = -\mathcal{H} \psi_n(\mathbf{r}) - v_{\text{ele}}(\mathbf{r}) \psi_n(\mathbf{r})$$

**Question.** Can you guess the expression of the electrostatic potential  $v_{\text{ele}}$ ?

# Electrostatic potential (cont'd)

**Answer.** From classical electrostatics, we know that the electrostatic potential due to the charge density  $\rho(\mathbf{r})$  is

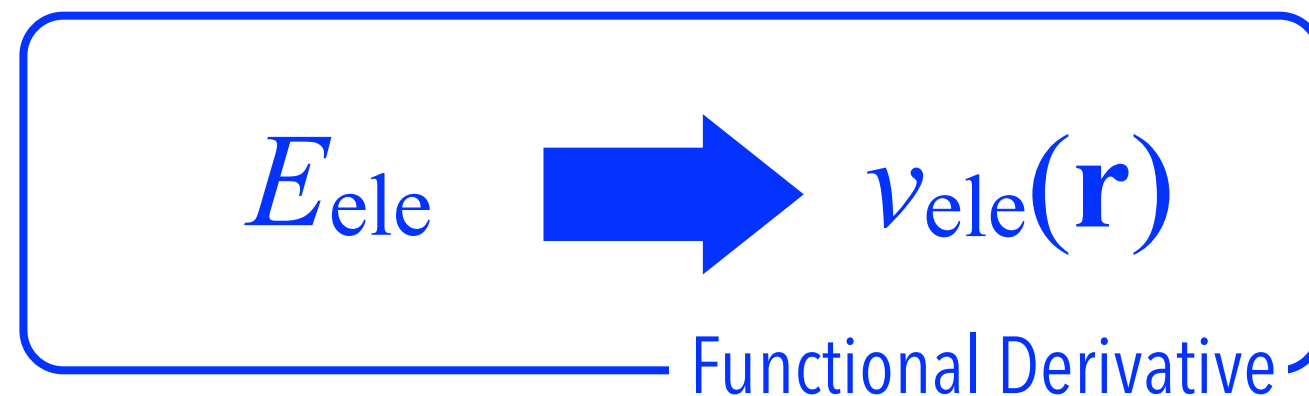
$$v_{\text{ele}}(\mathbf{r}) = \int d\mathbf{r}' \frac{e^2}{4\pi\epsilon_0} \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

# Electrostatic potential (cont'd)

**Answer.** From classical electrostatics, we know that the electrostatic potential due to the charge density  $\rho(\mathbf{r})$  is

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

**But let's assume** that you have forgotten this result. You could still recover it by applying a mathematical procedure called **functional derivative**.



This procedure is explained in the next slide.

# Electrostatic potential (cont'd)

**Computing the Functional Derivative of  $E_{\text{ele}}$ .** Consider the electrostatic energy

$$E_{\text{ele}}(\rho) = e^2/(8\pi\epsilon_0) \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|$$

Then expand this energy to first order to obtain an expression of the form

$$E_{\text{ele}}(\rho + \delta\rho) = E_{\text{ele}}(\rho) + \int d\mathbf{r} v_{\text{ele}}(\mathbf{r}) \delta\rho(\mathbf{r}) + \dots$$

The term  $v_{\text{ele}}(\mathbf{r})$  in front of  $\delta\rho(\mathbf{r})$  in the integral  
is called the functional derivative of  $E_{\text{ele}}$ .



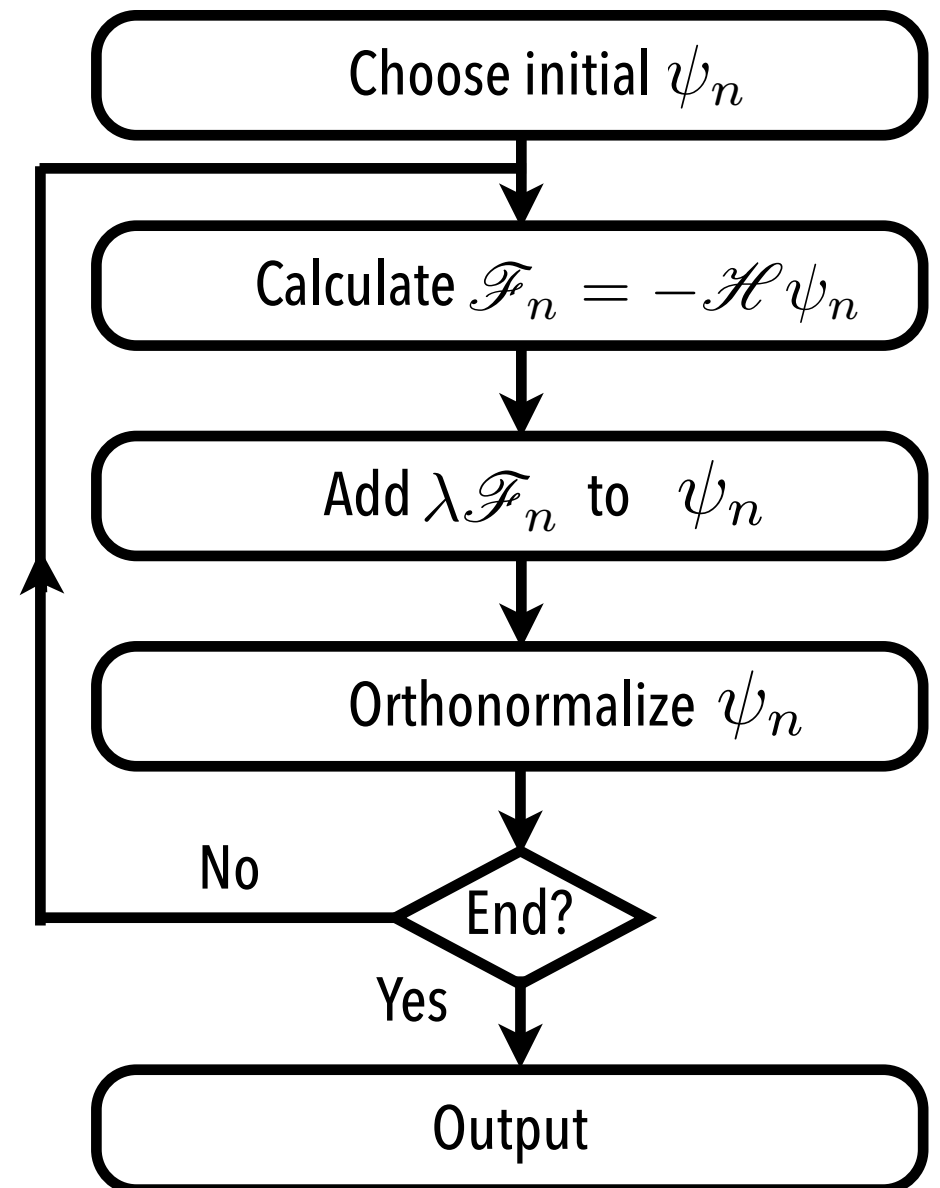
**Note.** If you are interested you can follow the derivation in the **Appendix**. You can also skip it if you are not so interested, but make sure that you understand the general idea.

# Minimization (cont'd)

► **Question.** Now, how would you change the algorithm?

$$\mathcal{F}_n = -\mathcal{H}\psi_n(\mathbf{r}) - \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}') \psi_n(\mathbf{r})}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}$$

We've the new term  $-v_{\text{ele}}(\mathbf{r})\psi_n(\mathbf{r})$  in the force.  
We need to change the algorithm accordingly.

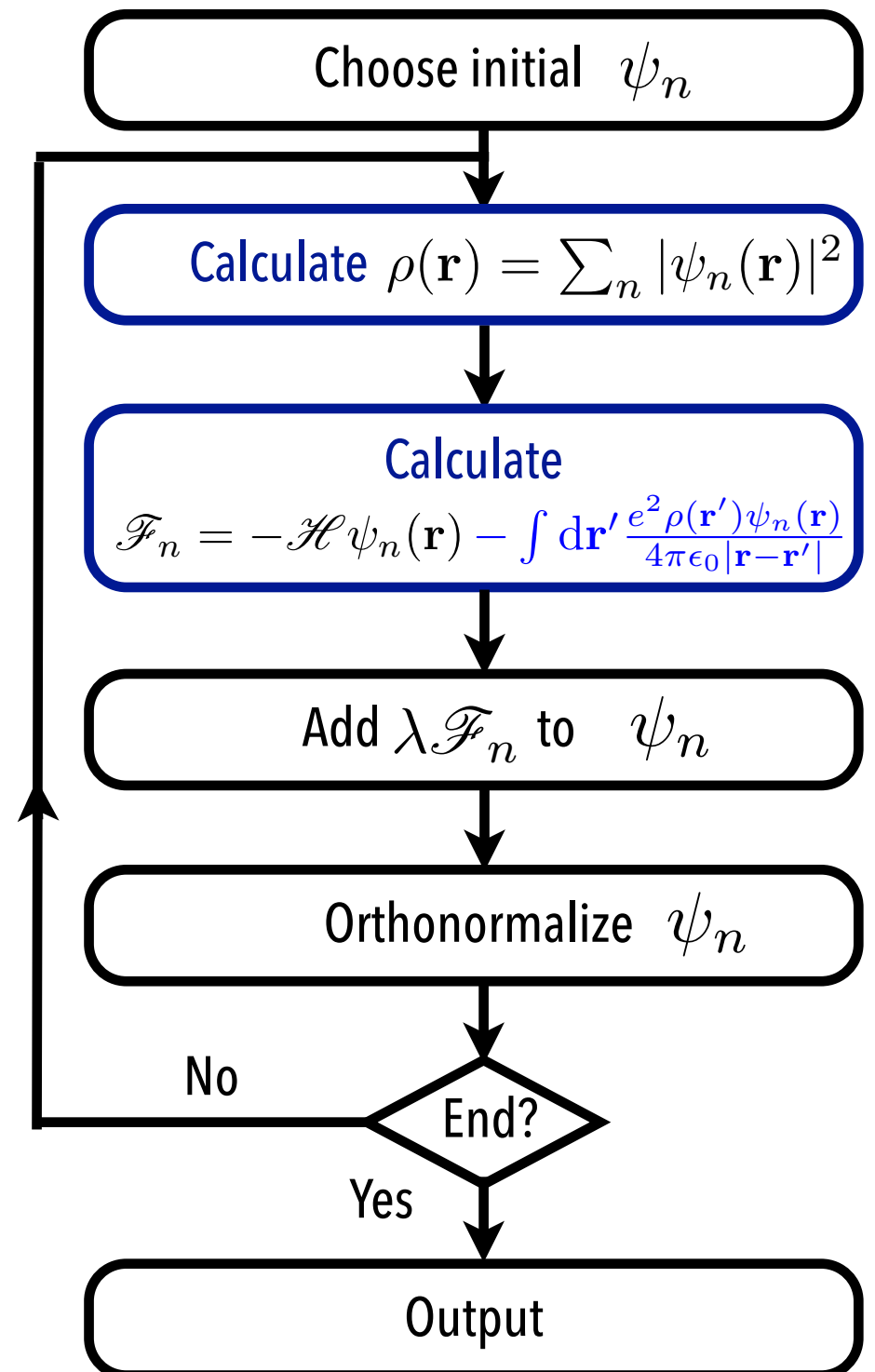




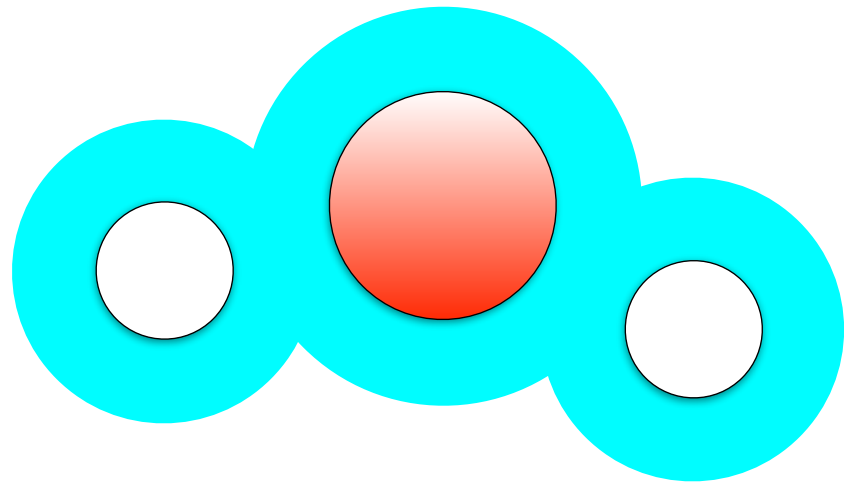
# Minimization (cont'd)

- **Answer.** We need to calculate the density  $\rho$  and the electrostatic potential  $v_{\text{ele}}$ .

$$\mathcal{F}_n = -\mathcal{H}\psi_n(\mathbf{r}) - \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}') \psi_n(\mathbf{r})}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}$$



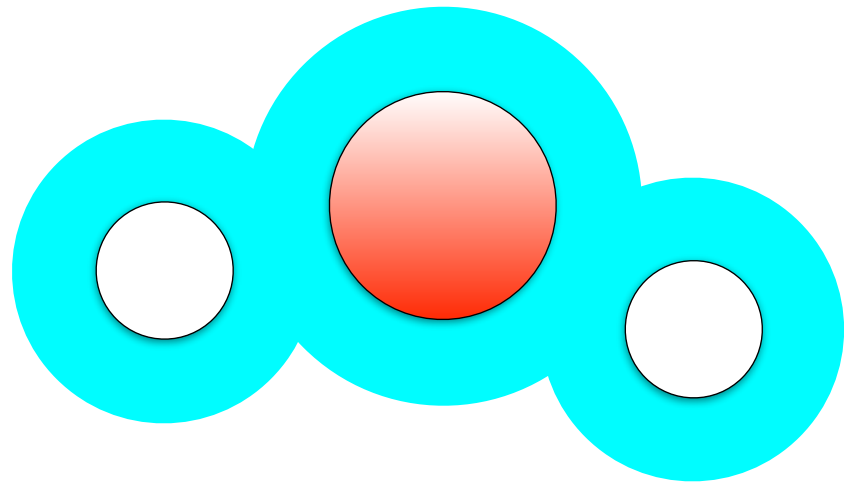
# Minimization (cont'd)



$$U = \sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r}) \quad \checkmark$$
$$+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + \cancel{E_{\text{xc}}(\rho)}$$
$$+ \frac{1}{2} \sum_i \sum_j' \frac{Z_i Z_j e^2}{4\pi\epsilon R_{ij}} \quad \checkmark$$

► So, we also know how to handle the second term.

# Minimization (cont'd)



$$U = \sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + E_{xc}(\rho) + \cancel{\frac{1}{2} \sum_i \sum_j' \frac{Z_i Z_j e^2}{4\pi\epsilon R_{ij}}}$$

- So, we also know how to handle the second term.
- **Now, let's study the third term.**

# Hohenberg-Kohn theorem

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## Property | Hohenberg-Kohn theorem

There exists a one-to-one correspondence between the ground-state wave function  $\Psi$  and charge density  $\rho$  of a (nondegenerate) system of  $N$  electrons in a potential  $v$ .

In other words, it is impossible for two ground-state wave functions  $\Psi_1$  and  $\Psi_2$  corresponding to two potentials  $v_1$  and  $v_2$  to have the same density  $\rho_1 = \rho_2$ .



Pierre Hohenberg  
(1934-2017)



Walter Kohn  
(1923-2016)

# Hohenberg-Kohn theorem (cont'd)

## Property | Hohenberg-Kohn theorem

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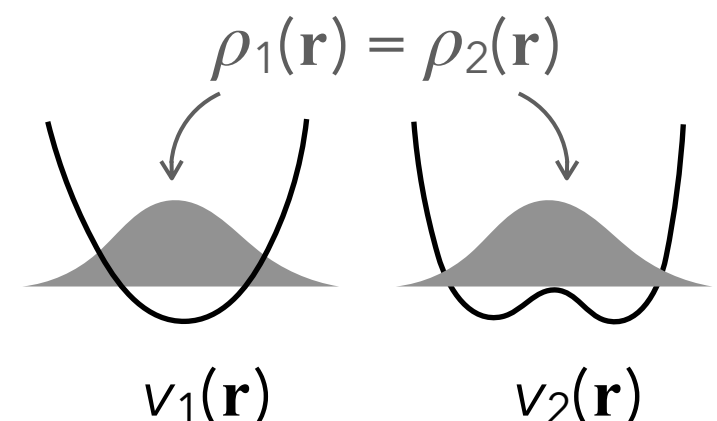


Pierre Hohenberg  
(1934-2017)



Walter Kohn  
(1923-2016)

- **Proof (optional).** To prove this theorem, take two potentials  $v_1$  and  $v_2$  and write the energy  $E_i[\Psi_j]$  of  $\Psi_j$  in  $v_i$  as  $E_i[\Psi_j] = \int \Psi_j^* (T+W) \Psi_j + \int v_i \rho_j$ , where  $T = -\sum_i (\hbar^2/2m) \nabla_i^2$  and  $W = 1/2 \sum_i \sum_{j \neq i} e^2 / (4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|)$ . Show that if the ground-state wave functions  $\Psi_1$  and  $\Psi_2$  are not degenerate, the equality  $\rho_1 = \rho_2$  gives a contradiction.



# Hohenberg-Kohn theorem (cont'd)

## Property | Hohenberg-Kohn theorem (cont'd)

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

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

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

In other words, instead of solving for the ground-state wave function, one can solve for the ground-state electron density.



Pierre Hohenberg  
(1934-2017)



Walter Kohn  
(1923-2016)

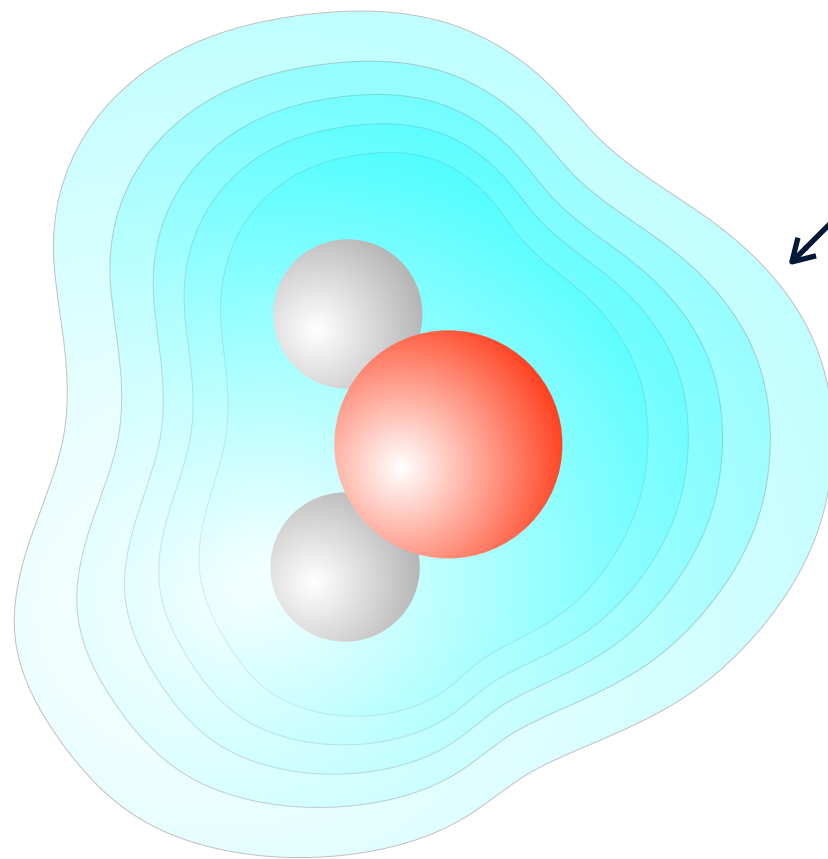
- $F$  is called the **universal functional**. It is often written in terms of the kinetic, electrostatic, and exchange-correlation contributions

$$F[\rho] = T[\rho] + \iint e^2 \rho(\mathbf{r})\rho(\mathbf{r}')/(8\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}d\mathbf{r}' + E_x[\rho] + E_c[\rho]$$

# Uniform electron gas

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- Now, let's see how to approximate  $T[\rho]$ ,  $E_x[\rho]$ , and  $E_c[\rho]$  using a **uniform electron gas** as a model:

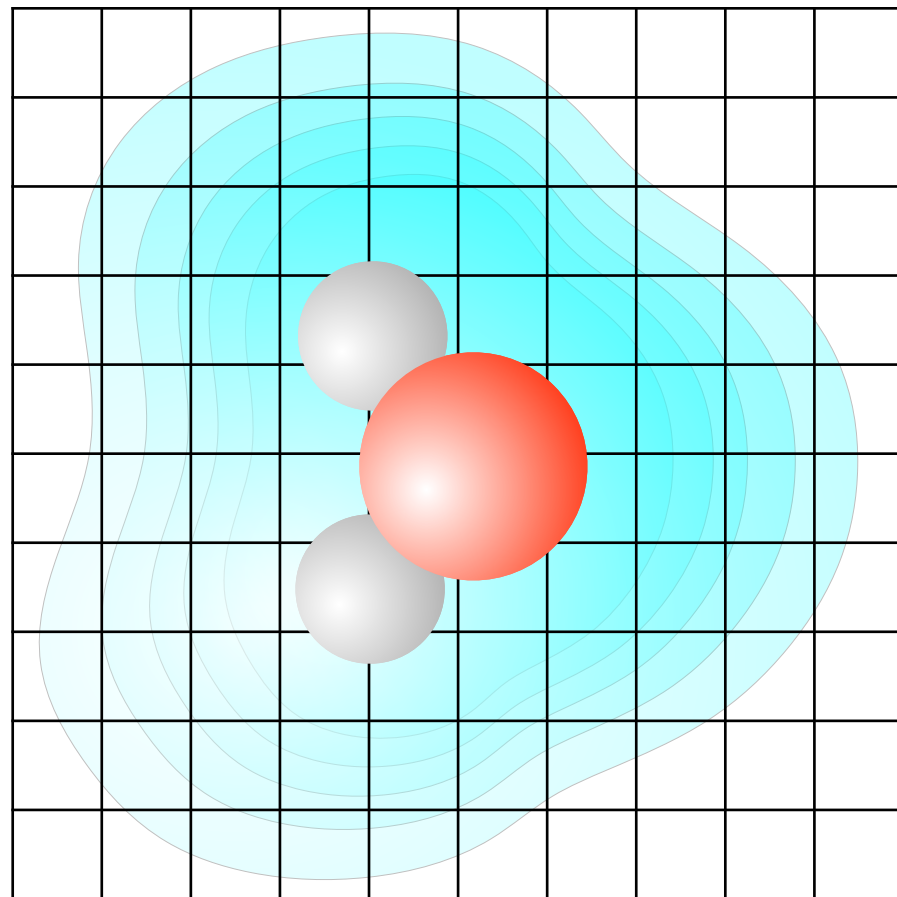


$$\rho(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \sum_{n=1}^N |\phi_{n\sigma}(\mathbf{r})|^2$$

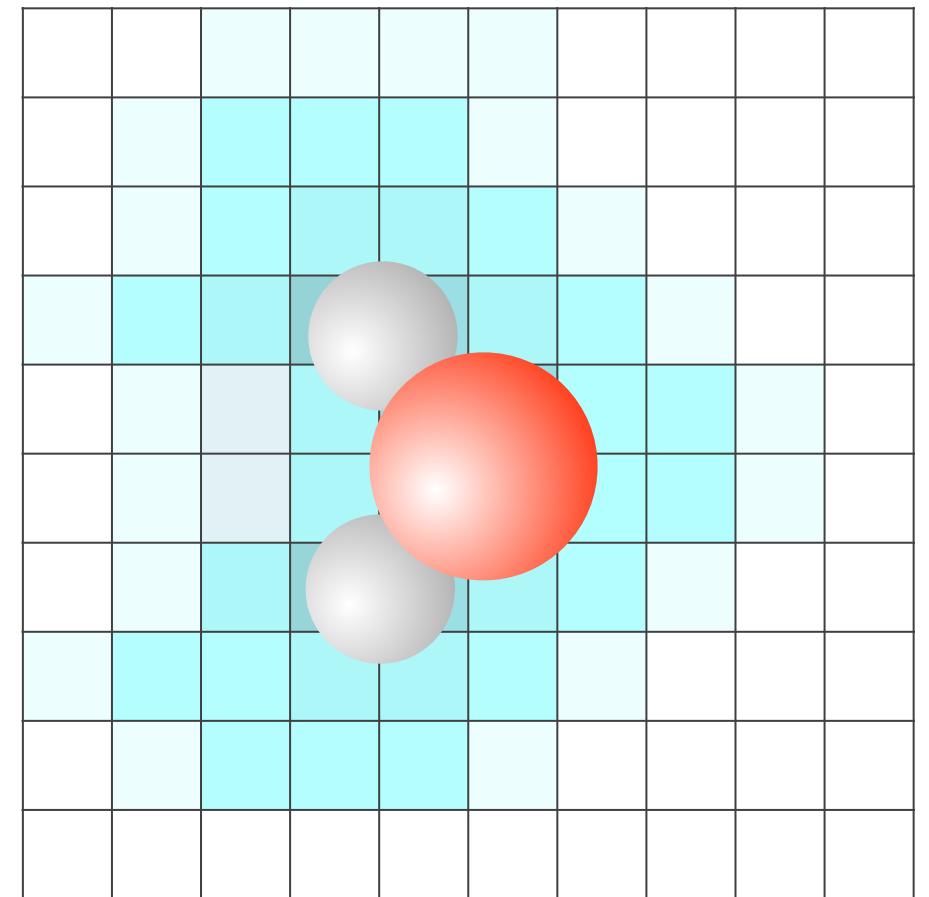
Start from the electronic density...

# Uniform electron gas (cont'd)

- Now, let's see how to approximate  $T[\rho]$ ,  $E_x[\rho]$ , and  $E_c[\rho]$  using a **uniform electron gas** as a model:



... Divide space into small volumes

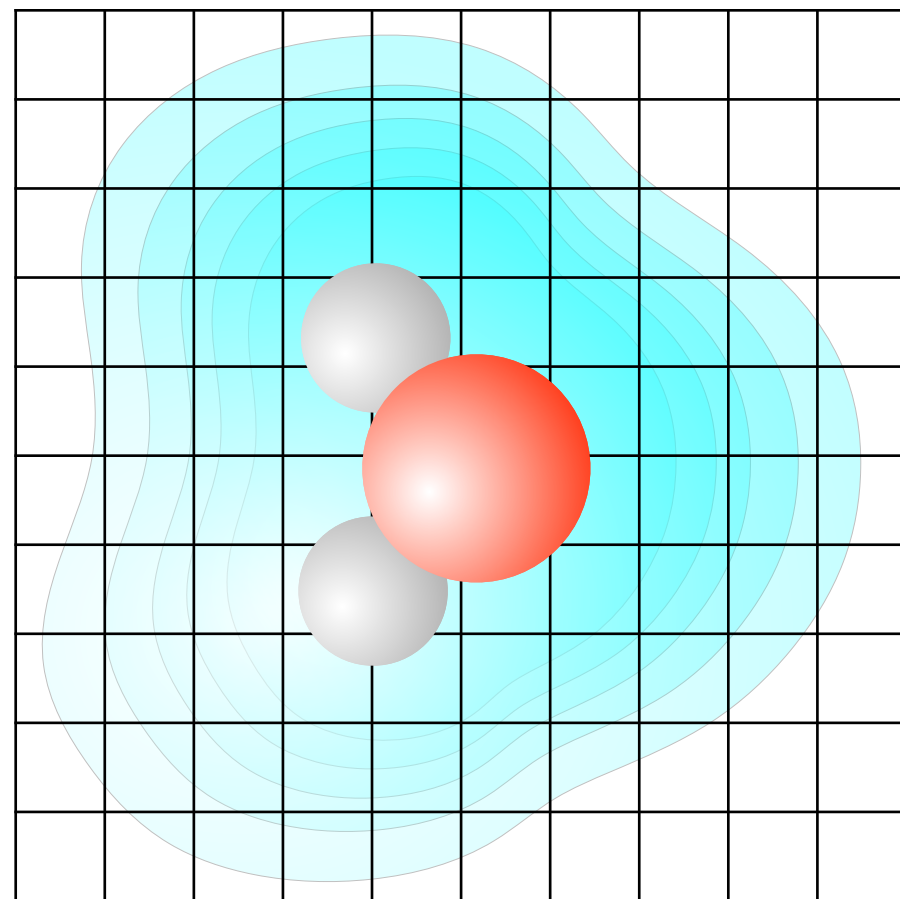


... In each of these small volumes,  
approximate the density as uniform




# Uniform electron gas (cont'd)

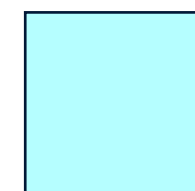
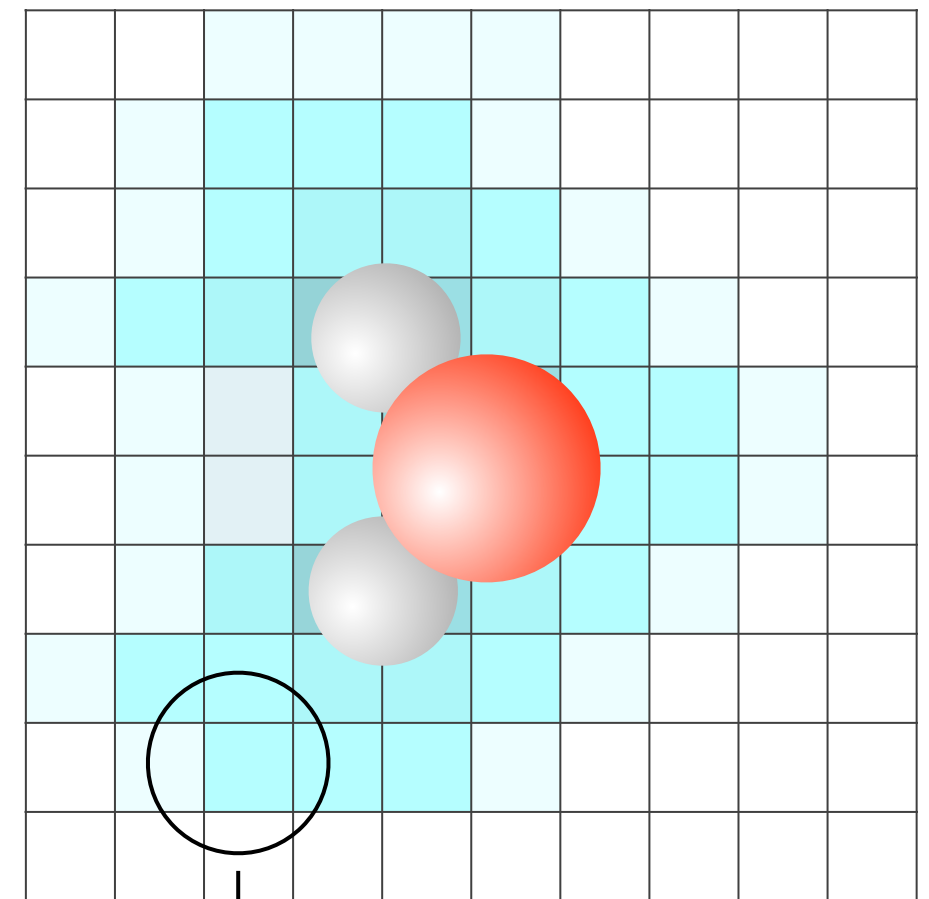
- Now, let's see how to approximate  $T[\rho]$ ,  $E_x[\rho]$ , and  $E_c[\rho]$  using a **uniform electron gas** as a model:



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

$$\underbrace{dT}_{\text{Kinetic energy contribution from the small volume}} = \overbrace{t(\rho(\mathbf{r}))}^{\text{Kinetic energy per volume in uniform gas of density } \rho} d\mathbf{r}$$

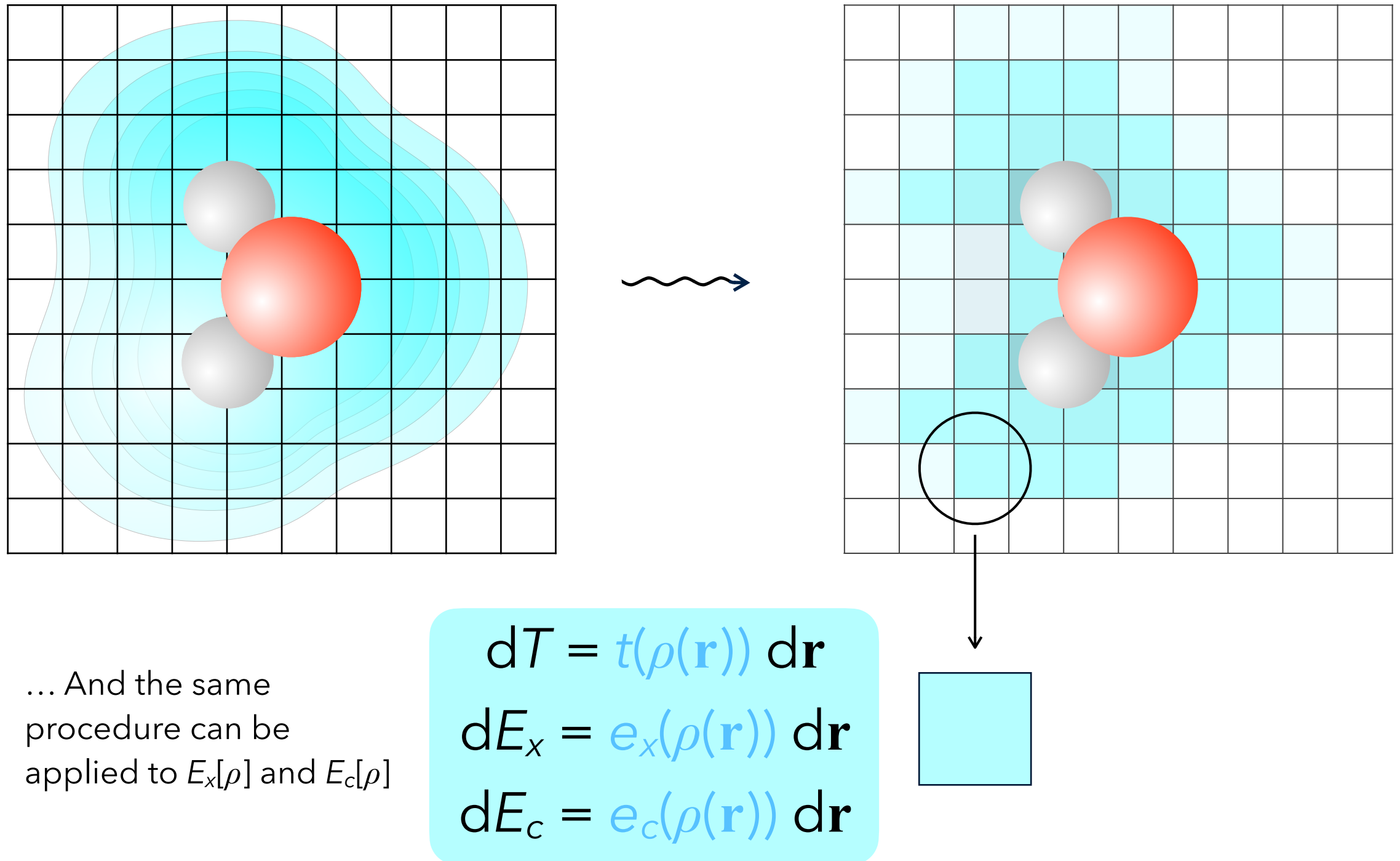
Kinetic energy contribution  
from the small volume 



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

# Uniform electron gas (cont'd)

- Now, let's see how to approximate  $T[\rho]$ ,  $E_x[\rho]$ , and  $E_c[\rho]$  using a **uniform electron gas** as a model:



# Minimization (cont'd)

$$\begin{aligned} &= \sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r}) \\ &\quad + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}(\rho) \end{aligned}$$

► The red term changes the force.

► The new force is

$$\mathcal{F}_n = -\mathcal{H} \psi_n(\mathbf{r}) - \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}') \psi_n(\mathbf{r})}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} - v_{\text{xc}}(\mathbf{r}) \psi_n(\mathbf{r})$$

►  $v_{\text{xc}}$  is called the exchange-correlation potential.

# Exchange-correlation potential (cont'd)

**Computing the Functional Derivative of  $E_{xc}$ .** Slater proposed the following expression for the XC energy

$$E_{xc}(\rho) = -C_\alpha \int d\mathbf{r} \rho^{4/3}(\mathbf{r})$$



John C. Slater  
(1900–1976)

By applying a functional derivative (see previous slides), we get

$$E_{xc}(\rho + \delta\rho) = E_{xc}(\rho) + \int d\mathbf{r} \left[ -\frac{4C_\alpha}{3} \rho^{1/3}(\mathbf{r}) \right] \delta\rho(\mathbf{r}) + \dots$$

As a result,

Slater's Exchange-Correlation Potential

$$v_{xc}(\mathbf{r}) = -\frac{4C_\alpha}{3} \rho^{1/3}(\mathbf{r})$$

**Note.** This is just one example. There exist many other types of XC energies.

# Exchange-correlation approximations

- ▶ Two popular families of XC energies are LDA and GGA:
- ▶ **Definition | Local density approximation (LDA) and generalized-gradient approximation (GGA).** LDA and GGA are two families of approximations to describe quantum electron interactions within DFT.

They can be written as:

$$E_{\text{xc}}^{\text{LDA}}(\rho) = \int \epsilon_{\text{xc}}(\rho(\mathbf{r})) d\mathbf{r}$$
$$E_{\text{xc}}^{\text{GGA}}(\rho) = \int \epsilon_{\text{xc}}(\rho(\mathbf{r}), \nabla \rho(\mathbf{r})) d\mathbf{r}$$

# Exchange-correlation approximations (cont'd)

- **Question 1.** To which family does the Slater's exchange-correlation energy belong?

$$E_{xc}(\rho) = -C_{\alpha} \int d\mathbf{r} \rho^{4/3}(\mathbf{r}) \begin{cases} ? \\ \rightarrow E_{xc}^{\text{LDA}}(\rho) = \int d\mathbf{r} \varepsilon_{xc}(\rho(\mathbf{r})) \\ \rightarrow E_{xc}^{\text{GGA}}(\rho) = \int d\mathbf{r} \varepsilon_{xc}(\rho(\mathbf{r}), \nabla \rho(\mathbf{r})) \end{cases}$$

- **Question 2.** Which one of the two families is more accurate in your opinion?

$$\text{Most Accurate} \begin{cases} ? \\ \rightarrow E_{xc}^{\text{LDA}}(\rho) = \int d\mathbf{r} \varepsilon_{xc}(\rho(\mathbf{r})) \\ \rightarrow E_{xc}^{\text{GGA}}(\rho) = \int d\mathbf{r} \varepsilon_{xc}(\rho(\mathbf{r}), \nabla \rho(\mathbf{r})) \end{cases}$$

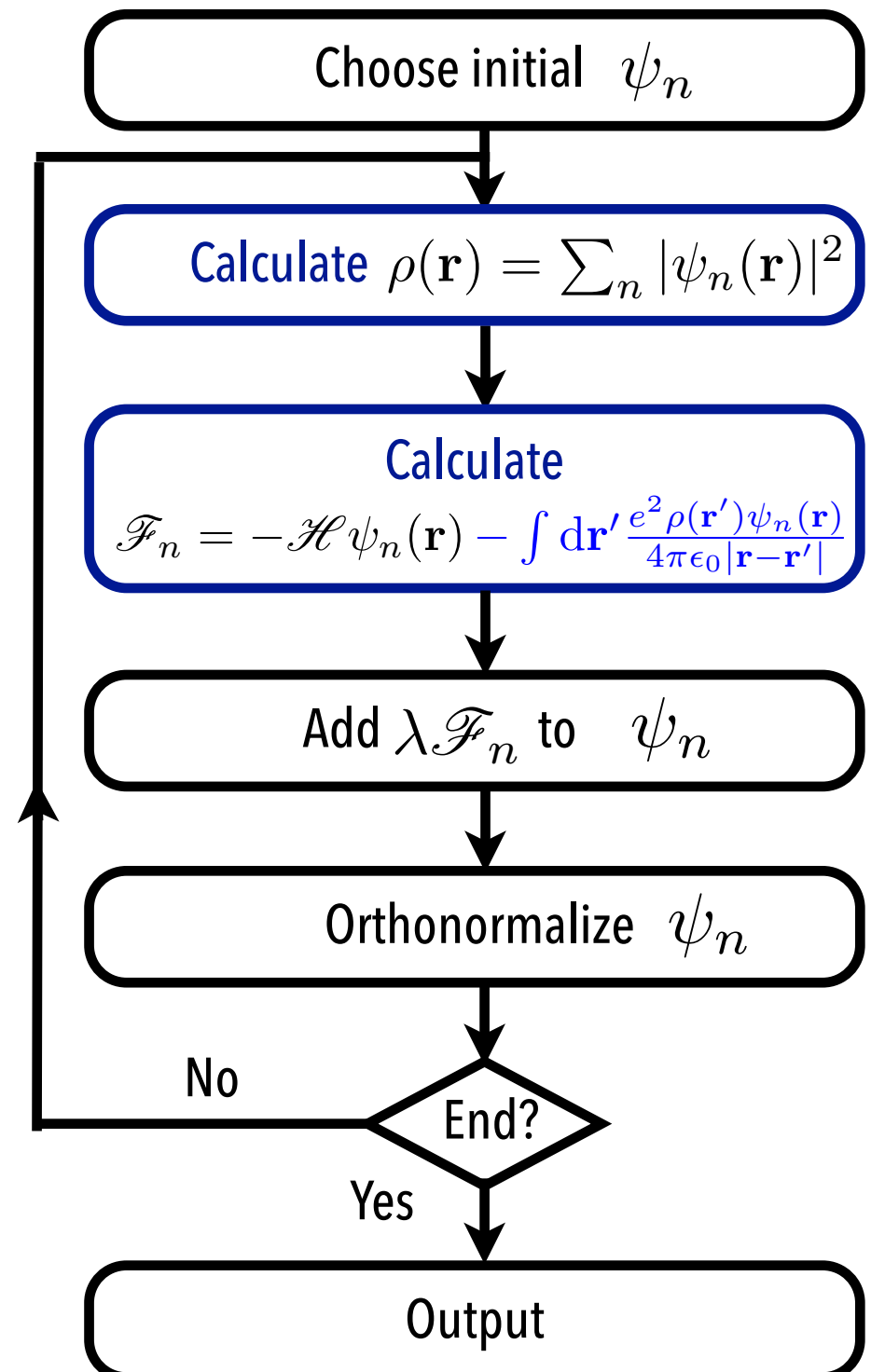
# Minimization

► **Question.** How would you change the algorithm?

$$\mathcal{F}_n = -\mathcal{H}\psi_n(\mathbf{r}) - \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}') \psi_n(\mathbf{r})}{4\pi\epsilon_0 |\mathbf{r}-\mathbf{r}'|} - v_{\text{xc}}(\mathbf{r}) \psi_n(\mathbf{r})$$

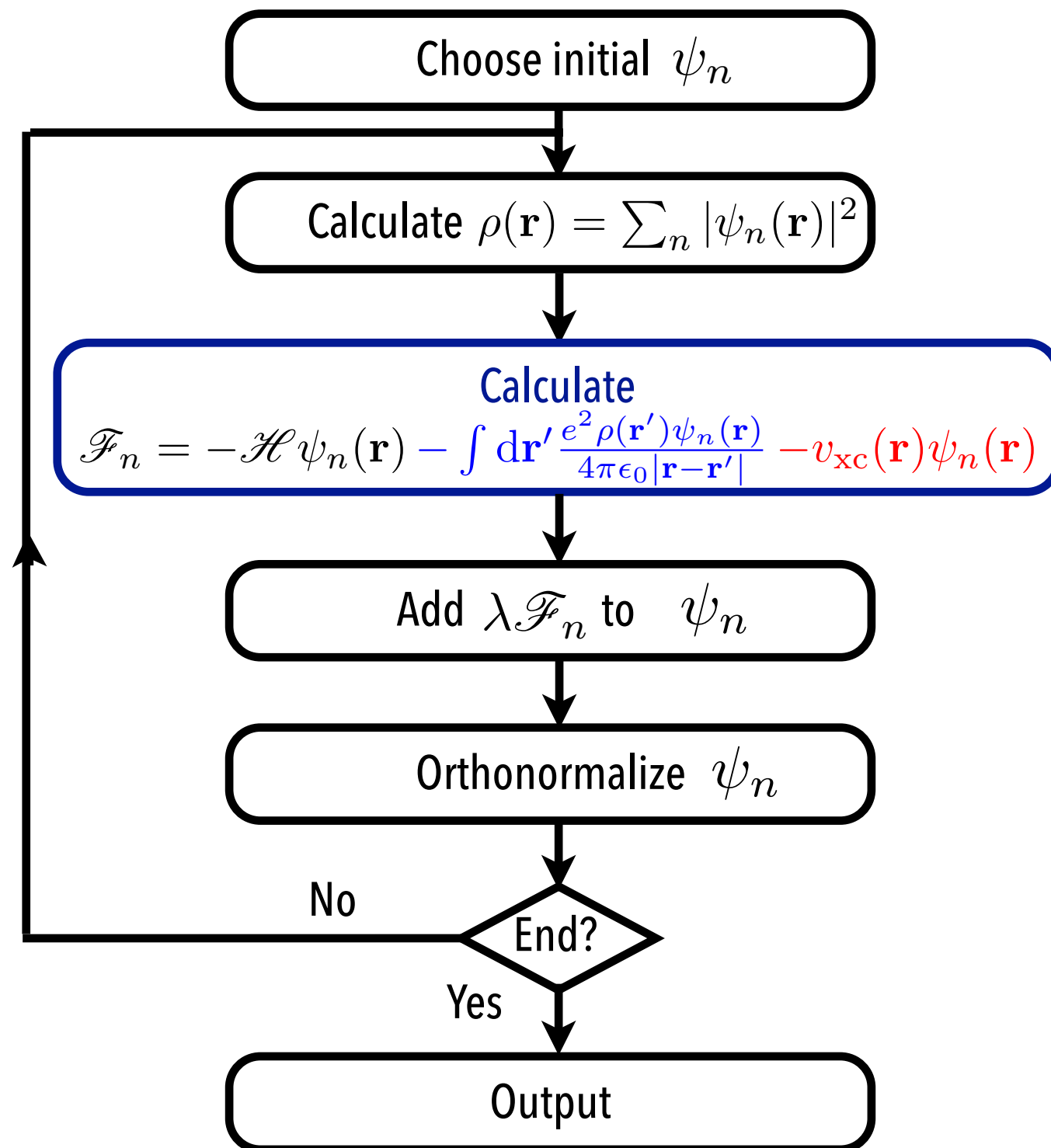
We've now 3 contributions:

- (1) Noninteracting Electronic Contribution;
- (2) Classical Interaction Contribution;
- (3) Quantum Interaction Contribution.



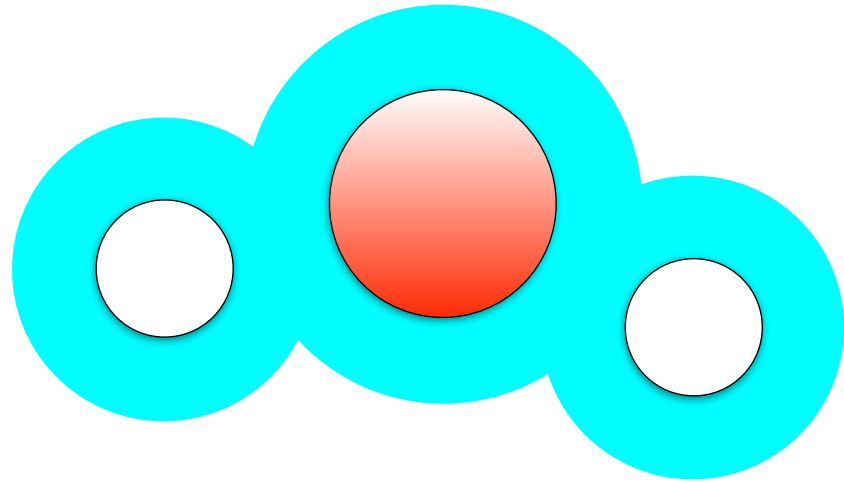
# Minimization (cont'd)

► **Answer.** Add the new contribution to the force.





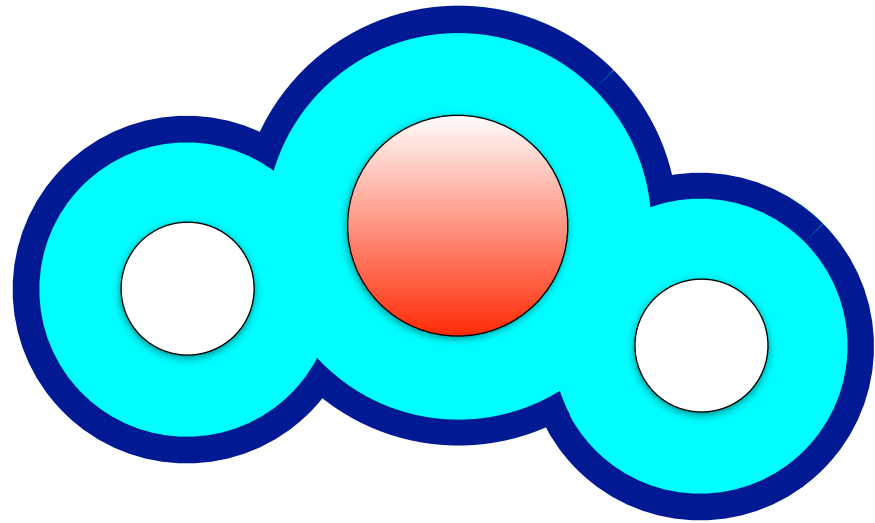
# Minimization (cont'd)



$$U = \sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r}) \quad \checkmark$$
$$+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}(\rho) \quad \checkmark$$
$$+ \frac{1}{2} \sum_i \sum_j' \frac{Z_i Z_j e^2}{4\pi\epsilon R_{ij}} \quad \checkmark$$

► We're done with the third term.

# Minimization (cont'd)



By minimizing these 3 terms (the only ones that depend on  $\psi_n$  and  $\rho$ ), we've found the electronic ground state.

$$U = \sum_n \int d\mathbf{r} \psi_n^*(\mathbf{r}) \cdot \mathcal{H} \psi_n(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{e^2 \rho(\mathbf{r}) \rho(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}(\rho) + \cancel{\frac{1}{2} \sum_i \sum_j' \frac{Z_i Z_j e^2}{4\pi\epsilon R_{ij}}}$$

► We're done with the third term.

► This means we've found the electronic ground state.