Kohn–Sham density-functional theory

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Institut de Chimie de Strasbourg - Laboratoire de Chimie Quantique - Université de Strasbourg /CNRS
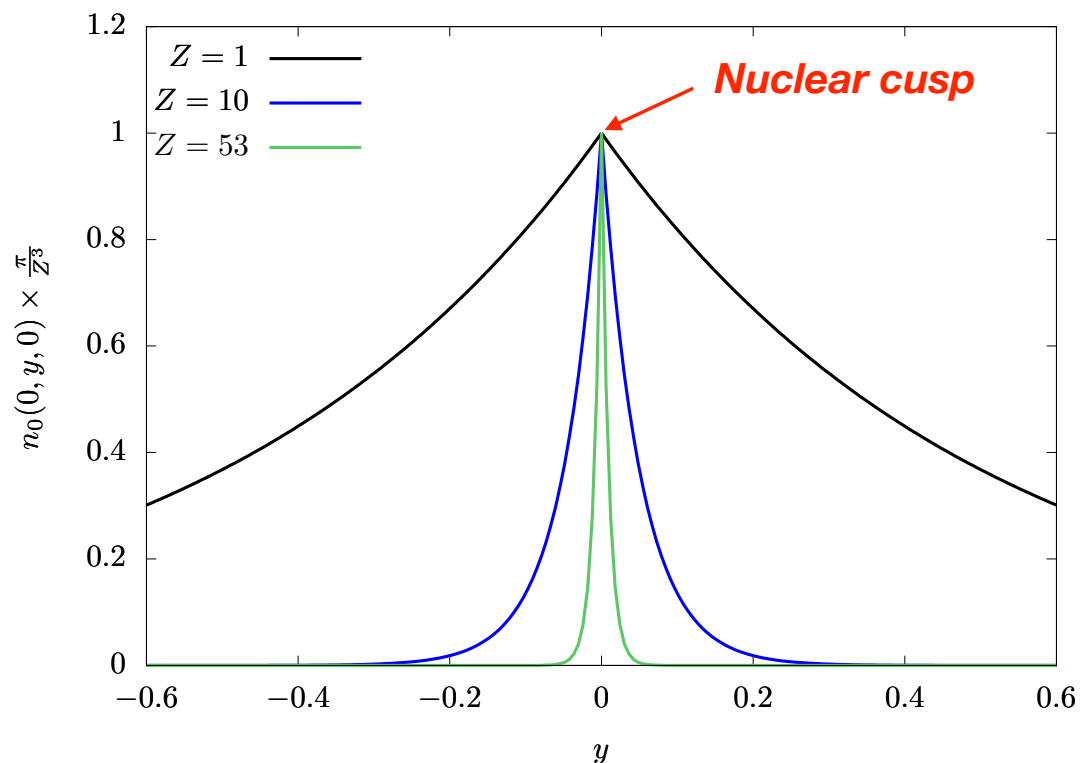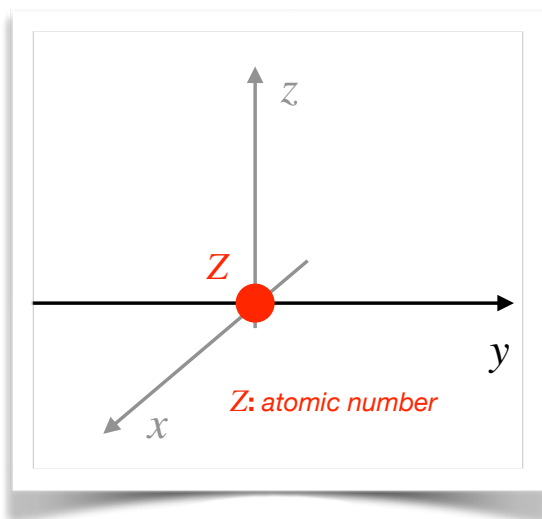
M1 course: Modelling 1

Ground-state densities of hydrogen-like atoms

One-electron ground-state wave function (1s orbital)

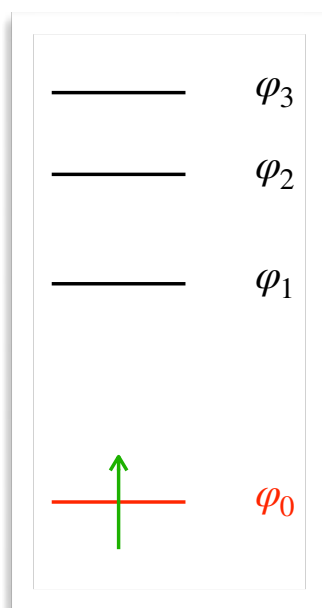$$\Psi_0(x, y, z) = \frac{Z^{3/2}}{\sqrt{\pi}} e^{-Z\sqrt{x^2 + y^2 + z^2}} \geq 0$$

Ground-state density

$$|\Psi_0(x, y, z)|^2 \overset{notation}{=} n_0(x, y, z) = \frac{Z^3}{\pi} e^{-2Z\sqrt{x^2 + y^2 + z^2}}$$

Z: atomic number

Nuclear cusp

Energy of non-interacting electrons: functional of the density?

One-electron case

$$E = \int d\mathbf{r} \, \varphi_0^*(\mathbf{r}) \times \underbrace{\left(-\frac{\nabla_{\mathbf{r}}^2}{2} + v(\mathbf{r}) \right) \varphi_0(\mathbf{r})}_{E \times \varphi_0(\mathbf{r})}$$
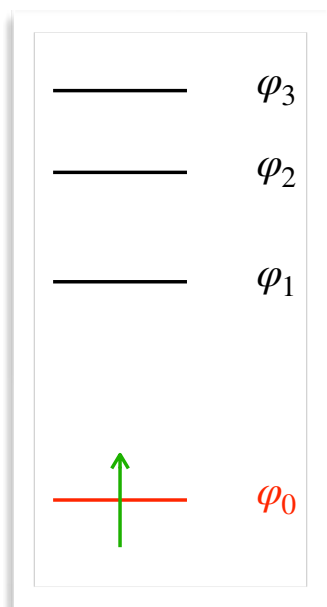
with

$$\int d\mathbf{r} \, \varphi_0^*(\mathbf{r}) \times \varphi_0(\mathbf{r}) = \int d\mathbf{r} \, \left| \varphi_0(\mathbf{r}) \right|^2 = 1$$

$$\nabla_{\mathbf{r}}^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

φ_3

φ_2

φ_1

φ_0

Energy of non-interacting electrons: functional of the density?

One-electron case *(and real algebra)*

φ_3

φ_2

φ_1

φ_0

$$E = -\frac{1}{2}\int d\mathbf{r}\,\varphi_0(\mathbf{r})\,\nabla_\mathbf{r}^2\varphi_0(\mathbf{r}) + \int d\mathbf{r}\,v(\mathbf{r})\varphi_0^2(\mathbf{r})$$

Kinetic energy   *Potential energy*

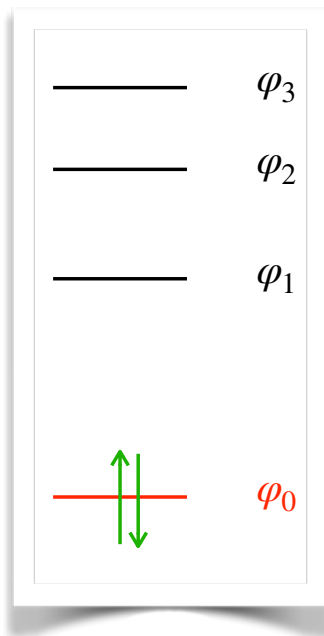$$n(\mathbf{r}) = \varphi_0^2(\mathbf{r}) \longrightarrow 0 \leq \varphi_0(\mathbf{r}) = \sqrt{n(\mathbf{r})}$$

$$E = -\frac{1}{2}\int d\mathbf{r}\,n^{1/2}(\mathbf{r})\,\nabla_\mathbf{r}^2\big(n^{1/2}(\mathbf{r})\big) + \int d\mathbf{r}\,v(\mathbf{r})n(\mathbf{r}) \equiv E[n]$$

$$\nabla_\mathbf{r}^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Energy of non-interacting electrons: functional of the density?

Two-electron case

$$E = \textcolor{red}{2} \times \left(-\frac{1}{2} \int d\mathbf{r}\, \varphi_0(\mathbf{r})\, \nabla_\mathbf{r}^2 \varphi_0(\mathbf{r}) + \int d\mathbf{r}\, v(\mathbf{r})\varphi_0^2(\mathbf{r}) \right)$$

$$n(\mathbf{r}) = \textcolor{red}{2} \times \varphi_0^2(\mathbf{r}) \longrightarrow 0 \le \varphi_0(\mathbf{r}) = \sqrt{\frac{n(\mathbf{r})}{\textcolor{red}{2}}}$$

$$E = -\frac{1}{2} \int d\mathbf{r}\, n^{1/2}(\mathbf{r})\, \nabla_\mathbf{r}^2 \left(n^{1/2}(\mathbf{r}) \right) + \int d\mathbf{r}\, v(\mathbf{r})n(\mathbf{r}) \equiv \textcolor{red}{E[n]}$$
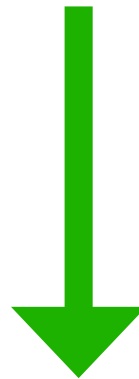
$$\nabla_\mathbf{r}^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Energy of non-interacting electrons: functional of the density?

Three-electron case

$$\underline{\qquad}\ \varphi_3$$

$$\underline{\qquad}\ \varphi_2$$

$$\underline{\uparrow\qquad}\ \varphi_1$$

$$\underline{\uparrow\downarrow\quad}\ \varphi_0$$

$$E = 2 \times \left(-\frac{1}{2} \int d\mathbf{r}\ \varphi_0(\mathbf{r})\, \nabla_{\mathbf{r}}^2 \varphi_0(\mathbf{r}) + \int d\mathbf{r}\ v(\mathbf{r})\varphi_0^2(\mathbf{r}) \right)$$

$$+ \left(-\frac{1}{2} \int d\mathbf{r}\ \varphi_1(\mathbf{r})\, \nabla_{\mathbf{r}}^2 \varphi_1(\mathbf{r}) + \int d\mathbf{r}\ v(\mathbf{r})\varphi_1^2(\mathbf{r}) \right)$$
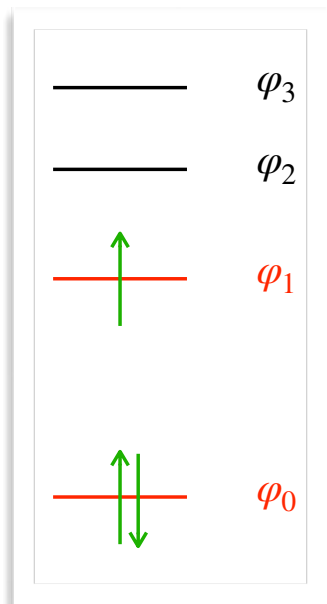
$$n(\mathbf{r}) = 2\varphi_0^2(\mathbf{r}) + \varphi_1^2(\mathbf{r})$$

$$\varphi_0(\mathbf{r}) = ?\quad \varphi_1(\mathbf{r}) = ?$$

$$\nabla_{\mathbf{r}}^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$E \overset{?}{\equiv} E[n]$$

Learning from another system: Thomas-Fermi (TF) model

Kinetic energy of non-interacting electrons in a *uniform* electron gas:

$$T_s^{\text{TF}}[n] = \frac{3}{10} \left(3\pi^2\right)^{\frac{2}{3}} \int d\mathbf{r} \left(n(\mathbf{r})\right)^{\frac{5}{3}}$$

$$n(\mathbf{r}) = \sum_{p}^{\text{occ. orbitals}} \varphi_p^2(\mathbf{r})$$

True non-uniform density

$$E \approx T_s^{\text{TF}}[n] + \int d\mathbf{r}\, v(\mathbf{r})n(\mathbf{r})$$

N-electron Schrödinger equation for the *ground* state

$$\hat{H}\Psi_0 = E_0\Psi_0$$

where $\quad \Psi_0 \equiv \Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N), \quad \mathbf{x}_i \equiv (\mathbf{r}_i, \sigma_i) \equiv (x_i, y_i, z_i, \sigma_i = \pm\tfrac{1}{2}) \quad$ for $\quad i = 1, 2, \ldots, N,$

and $\quad \hat{H} = \hat{T} + \hat{W}_{\text{ee}} + \hat{V}.$

$$\hat{T} \equiv -\frac{1}{2}\sum_{i=1}^{N}\nabla_{\mathbf{r}_i}^2 = -\frac{1}{2}\sum_{i=1}^{N}\left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right) \quad \longrightarrow \quad \textit{universal}\text{ kinetic energy operator}$$

$$\hat{W}_{\text{ee}} \equiv \sum_{i<j}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\times \quad \longrightarrow \quad \textit{universal}\text{ two-electron repulsion operator}$$

$$\hat{V} \equiv \sum_{i=1}^{N}v(\mathbf{r}_i)\times \quad \text{where} \quad v(\mathbf{r}) = -\sum_{A}^{\text{nuclei}}\frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} \quad \longrightarrow \quad \text{local }\textit{nuclear}\text{ potential operator}$$

(Fictitious) non-interacting electrons

- Solving the Schrödinger equation for non-interacting electrons is *easy*.

- You "just" have to solve the Schrödinger equation for a *single electron*.

$$\left(\hat{T} + \sum_{i=1}^{N} v(\mathbf{r}_i) \times \right)\Phi_0 = \mathcal{E}_0 \Phi_0 \quad \Leftrightarrow \quad \left[-\frac{1}{2}\nabla_{\mathbf{r}}^2 + v(\mathbf{r})\times\right]\varphi_i(\mathbf{x}) = \varepsilon_i \varphi_i(\mathbf{x}), \quad i = 1, 2, \ldots, N.$$

<u>Proof:</u>   a *simple solution* to the N-electron non-interacting Schrödinger equation is

$$\Phi_0 \equiv \varphi_1(\mathbf{x}_1) \times \varphi_2(\mathbf{x}_2) \times \ldots \times \varphi_N(\mathbf{x}_N) = \prod_{j=1}^{N} \varphi_j(\mathbf{x}_j) \qquad \leftarrow \text{Hartree product!}$$

since $\left(\hat{T} + \sum_{i=1}^{N} v(\mathbf{r}_i) \times \right)\Phi_0 = \sum_{i=1}^{N}\prod_{j\neq i}^{N}\varphi_j(\mathbf{x}_j) \times \left[-\frac{1}{2}\nabla_{\mathbf{r}_i}^2 + v(\mathbf{r}_i)\times\right]\varphi_i(\mathbf{x}_i) = \left(\sum_{i=1}^{N}\varepsilon_i\right)\Phi_0.$

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Proof: a *simple solution* to the N-electron non-interacting Schrödinger equation is

spin-orbitals (one-electron wave functions)

$$\Phi_0 \equiv \varphi_1(\mathbf{x}_1) \times \varphi_2(\mathbf{x}_2) \times \ldots \times \varphi_N(\mathbf{x}_N) = \prod_{j=1}^{N} \varphi_j(\mathbf{x}_j) \qquad \leftarrow \textit{Hartree product!}$$

since $$\left(\hat{T} + \sum_{i=1}^{N} v(\mathbf{r}_i) \times \right)\Phi_0 = \sum_{i=1}^{N}\prod_{j\neq i}^{N}\varphi_j(\mathbf{x}_j) \times \left[-\frac{1}{2}\nabla_{\mathbf{r}_i}^2 + v(\mathbf{r}_i)\times\right]\varphi_i(\mathbf{x}_i) = \left(\sum_{i=1}^{N}\varepsilon_i\right)\Phi_0.$$

Total noninteracting
N-electron **energy**

The one-electron picture

$$\left[-\frac{\nabla_{\mathbf{r}}^2}{2} + v(\mathbf{r}) \right] \varphi_i(\mathbf{x}) = \varepsilon_i \varphi_i(\mathbf{x})$$

$i = N+2$

LUMO $i = N+1$

HOMO $i = N$

$i = N-1$

$i = N-2$

$i = 2$

$i = 1$
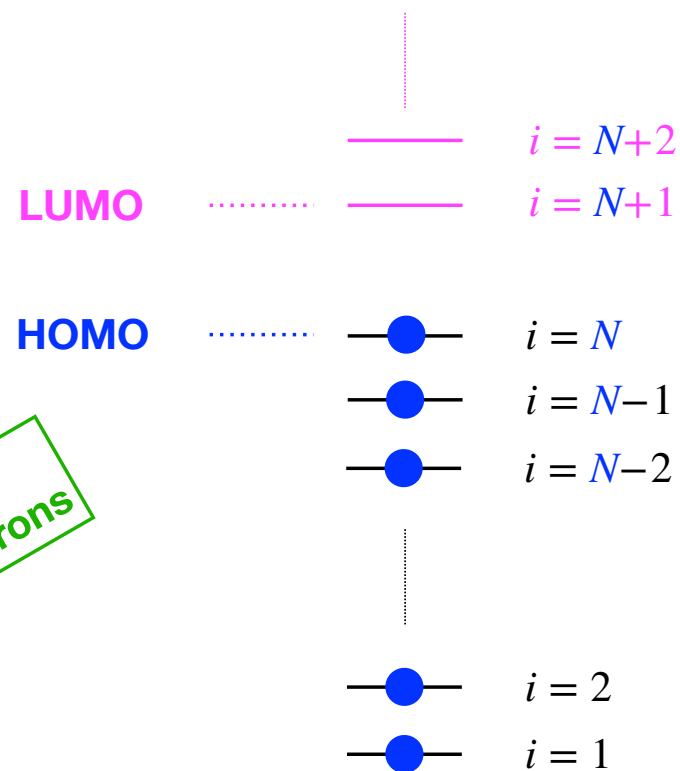
Exact for noninteracting electrons

(Real) interacting many-electron problem

- Before addressing the true (interacting) problem we should keep in mind that electrons are *fermions*.

- Consequently, they should be described by *Slater determinants* instead of Hartree products.

- Therefore, in the particular case of *two electrons*, we have

$$\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2) \quad \longrightarrow \quad \Phi_0 \equiv \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(\mathbf{x}_1) & \varphi_1(\mathbf{x}_2) \\ \varphi_2(\mathbf{x}_1) & \varphi_2(\mathbf{x}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \Big[\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2) - \varphi_1(\mathbf{x}_2)\varphi_2(\mathbf{x}_1) \Big].$$

Antisymmetric

$= 0$ *if* $\mathbf{x}_1 = \mathbf{x}_2$

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- When computing the two-electron repulsion energy $\left\langle \Phi_0 \middle| \hat{W}_{\text{ee}} \middle| \Phi_0 \right\rangle$ we describe the so-called *Hartree* (i.e. electrostatic) and *exchange* energies.

Two-electron repulsion energy of an N-electron Slater determinant

$$\langle \Phi_0 | \hat{W}_{\text{ee}} | \Phi_0 \rangle = \frac{1}{2} \int d\mathbf{x} \int d\mathbf{x}' \frac{\left(\sum_{i=1}^{N} |\varphi_i(\mathbf{x})|^2 \right) \left(\sum_{j=1}^{N} |\varphi_j(\mathbf{x}')|^2 \right)}{|\mathbf{r} - \mathbf{r}'|} + \dots$$

Two-electron repulsion energy of an N-electron Slater determinant

$$\langle \Phi_0 \,|\, \hat{W}_{\text{ee}} \,|\, \Phi_0 \rangle = \frac{1}{2} \int d\mathbf{x} \int d\mathbf{x}' \frac{\left(\sum_{i=1}^{N} |\varphi_i(\mathbf{x})|^2 \right) \left(\sum_{j=1}^{N} |\varphi_j(\mathbf{x}')|^2 \right)}{|\mathbf{r} - \mathbf{r}'|} + \dots$$

$\|$

**Electron density** (local)

$$\frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n_{\Phi_0}(\mathbf{r}) n_{\Phi_0}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Hartree (or Coulomb) energy

Two-electron repulsion energy of an N-electron Slater determinant

$$\langle \Phi_0 | \hat{W}_{ee} | \Phi_0 \rangle = \frac{1}{2} \int d\mathbf{x} \int d\mathbf{x}' \frac{\left(\sum_{i=1}^{N} |\varphi_i(\mathbf{x})|^2 \right) \left(\sum_{j=1}^{N} |\varphi_j(\mathbf{x}')|^2 \right)}{|\mathbf{r} - \mathbf{r}'|}$$

$$-\frac{1}{2} \int d\mathbf{x} \int d\mathbf{x}' \frac{\left(\sum_{i=1}^{N} \varphi_i^*(\mathbf{x})\varphi_i(\mathbf{x}') \right) \left(\sum_{j=1}^{N} \varphi_j(\mathbf{x})\varphi_j^*(\mathbf{x}') \right)}{|\mathbf{r} - \mathbf{r}'|}$$

Two-electron repulsion energy of an N-electron Slater determinant

$$\langle \Phi_0 \,|\, \hat{W}_{\text{ee}} \,|\, \Phi_0 \rangle = \frac{1}{2} \int d\mathbf{x} \int d\mathbf{x}' \frac{\left(\sum_{i=1}^{N} |\varphi_i(\mathbf{x})|^2 \right) \left(\sum_{j=1}^{N} |\varphi_j(\mathbf{x}')|^2 \right)}{|\mathbf{r} - \mathbf{r}'|}$$

$$-\frac{1}{2} \int d\mathbf{x} \int d\mathbf{x}' \frac{\left(\sum_{i=1}^{N} \varphi_i^*(\mathbf{x})\varphi_i(\mathbf{x}') \right) \left(\sum_{j=1}^{N} \varphi_j(\mathbf{x})\varphi_j^*(\mathbf{x}') \right)}{|\mathbf{r} - \mathbf{r}'|}$$

Exchange energy

Two-electron repulsion energy of an N-electron Slater determinant

local   local

$$\langle \Phi_0 \,|\, \hat{W}_{\mathrm{ee}} \,|\, \Phi_0 \rangle = \frac{1}{2} \int d\mathbf{x} \int d\mathbf{x}' \frac{\left(\sum_{i=1}^{N} |\varphi_i(\mathbf{x})|^2 \right) \left(\sum_{j=1}^{N} |\varphi_j(\mathbf{x}')|^2 \right)}{|\mathbf{r} - \mathbf{r}'|}$$

$$-\frac{1}{2} \int d\mathbf{x} \int d\mathbf{x}' \frac{\left(\sum_{i=1}^{N} \varphi_i^*(\mathbf{x}) \varphi_i(\mathbf{x}') \right) \left(\sum_{j=1}^{N} \varphi_j(\mathbf{x}) \varphi_j^*(\mathbf{x}') \right)}{|\mathbf{r} - \mathbf{r}'|}$$
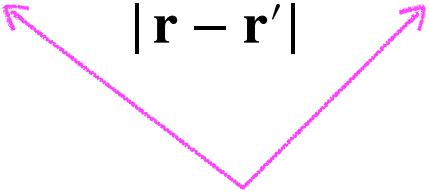
non-local

(Real) interacting many-electron problem

- Before addressing the true (interacting) problem we should keep in mind that electrons are *fermions*.

- Consequently, they should be described by *Slater determinants* instead of Hartree products.

- Therefore, in the particular case of *two electrons*, we have

$$
\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2) \;\longrightarrow\; \Phi_0 \equiv \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(\mathbf{x}_1) & \varphi_1(\mathbf{x}_2) \\ \varphi_2(\mathbf{x}_1) & \varphi_2(\mathbf{x}_2) \end{vmatrix} = \frac{1}{\sqrt{2}}\Big[\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2) - \varphi_1(\mathbf{x}_2)\varphi_2(\mathbf{x}_1)\Big].
$$

- When computing the two-electron repulsion energy $\left\langle \Phi_0 \middle| \hat{W}_{\text{ee}} \middle| \Phi_0 \right\rangle$ we describe the so-called *Hartree* (i.e. electrostatic) and *exchange* energies.

- Finally, Φ_0 *cannot* be the exact solution to the interacting Schrödinger equation [whatever choice is made for the spin-orbitals $\{\varphi_i(\mathbf{x})\}_{i=1,2,\ldots}$].

- The energy contribution that is missing is referred to as *correlation* energy.

(Real) interacting many-electron problem

- Describing interacting electrons ($\hat{W}_{\text{ee}} \neq 0$) is *not* straightforward. Indeed, the exact two-electron solution $\Psi_0(\mathbf{r}_1, \mathbf{r}_2)$ to the interacting Schrödinger equation cannot be written as $\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$:

$$\boxed{\Psi_0(\mathbf{r}_1, \mathbf{r}_2) \neq \varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2).}$$

<u>Proof</u> : Let us assume that we can find an orbital $\varphi(\mathbf{r})$ such that $\hat{H}\big(\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)\big) = E_0\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$ for any $\mathbf{r}_1$ and $\mathbf{r}_2$ values. Consequently,

$$\hat{W}_{\text{ee}}\big(\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)\big) = E_0\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2) - \big(\hat{T} + \hat{V}\big)\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2).$$

Using the definition of the operators and dividing by $\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$ leads to

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = E_0 + \frac{1}{2}\frac{\nabla^2_{\mathbf{r}_1}\varphi(\mathbf{r}_1)}{\varphi(\mathbf{r}_1)} + \frac{1}{2}\frac{\nabla^2_{\mathbf{r}_2}\varphi(\mathbf{r}_2)}{\varphi(\mathbf{r}_2)} - v(\mathbf{r}_1) - v(\mathbf{r}_2).$$

In the limit $\mathbf{r}_2 \to \mathbf{r}_1 = \mathbf{r}$,   it comes $\forall\,\mathbf{r},\quad E_0 + \dfrac{\nabla^2_{\mathbf{r}}\varphi(\mathbf{r})}{\varphi(\mathbf{r})} - 2v(\mathbf{r}) \to +\infty$ absurd!

Mapping the interacting problem onto a non-interacting one

- Is it possible to *extract* the exact (interacting) ground-state energy *from a non-interacting system*?

- If yes, then it would lead to a huge *simplification* of the problem.

- Nevertheless, the question sounds a bit weird since the two-electron repulsion is completely ignored in a non-interacting system.

- One way to establish a *connection* between interacting and non-interacting worlds is to use the *electron density* as basic variable (instead of the wavefunction).

- Electron density for a *non-interacting* system:
$$n_{\Phi_0}(\mathbf{r}) = \sum_{\sigma=\pm\frac{1}{2}} \sum_{i=1}^{N} |\varphi_i(\mathbf{r}, \sigma)|^2$$

- Electron density for an *interacting* system:

$$n_{\Psi_0}(\mathbf{r}) = N \sum_{\sigma=\pm\frac{1}{2}} \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N \, |\Psi_0(\mathbf{r}, \sigma, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2$$

Mapping the interacting problem onto a non-interacting one

- There is of course no reason to believe that these two densities are equal.

- However, we may assume that it is possible to *adjust* the local potential in the non-interacting system *such that the two densities become equal*.

- This "magical" potential is known as the *Kohn–Sham* (KS) potential.

- **In summary**:

$$
\begin{array}{rcl}
\text{interacting problem} & \rightarrow & \textit{non-interacting} \text{ KS problem} \\
\hat{W}_{\mathrm{ee}} & \rightarrow & 0 \\
v(\mathbf{r}) & \rightarrow & v^{\mathrm{KS}}(\mathbf{r}) \\
n_{\Psi_0}(\mathbf{r}) & = & n_{\Phi_0^{\mathrm{KS}}}(\mathbf{r})
\end{array}
$$

- Questions to be answered:

(1) If $v^{\mathrm{KS}}(\mathbf{r})$ exists, is it unique?   *yes!*

(2) Does the knowledge of $n_{\Psi_0}(\mathbf{r})$ gives access (in principle) to E_0?   *yes!*

Wave function theory
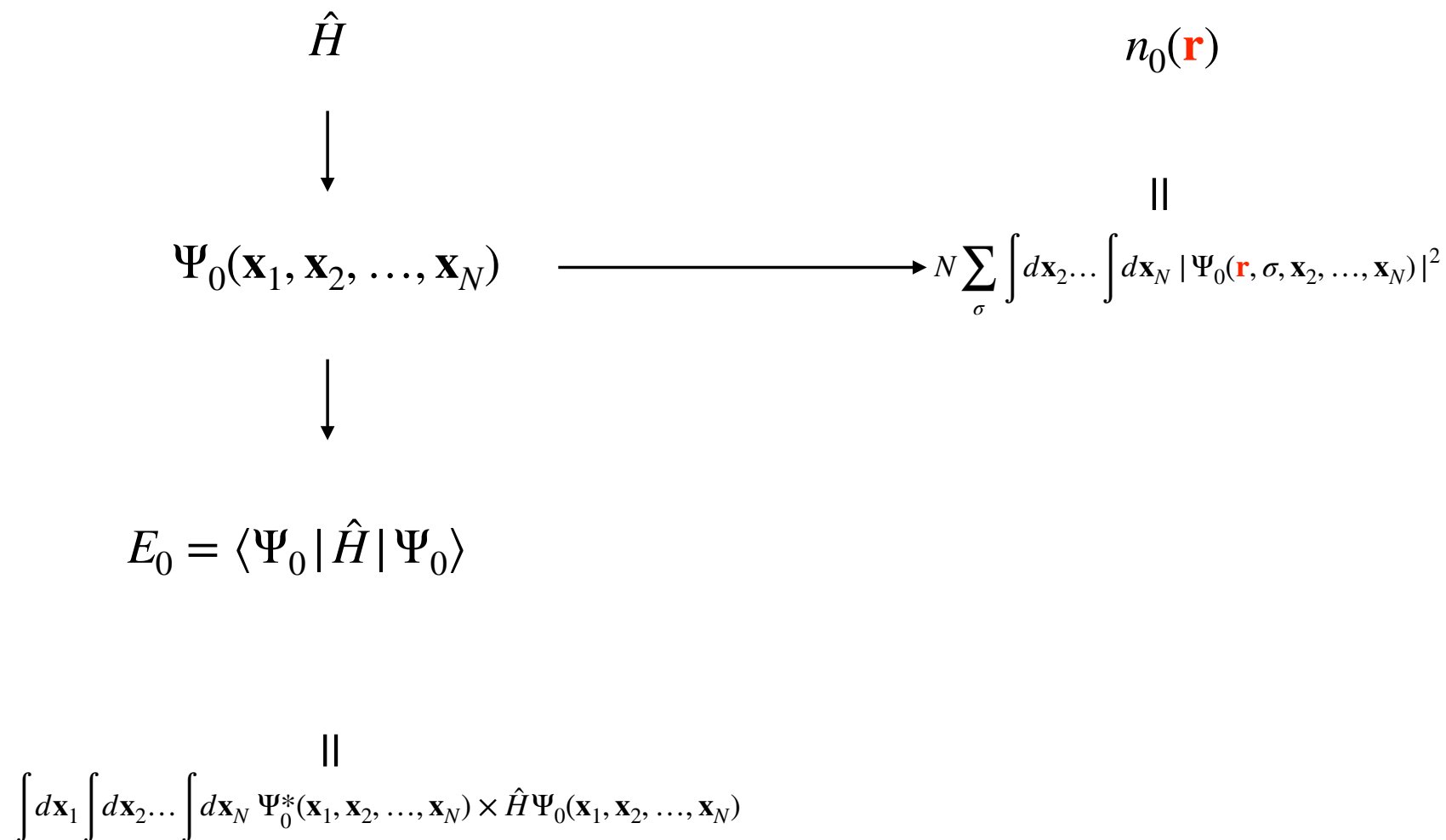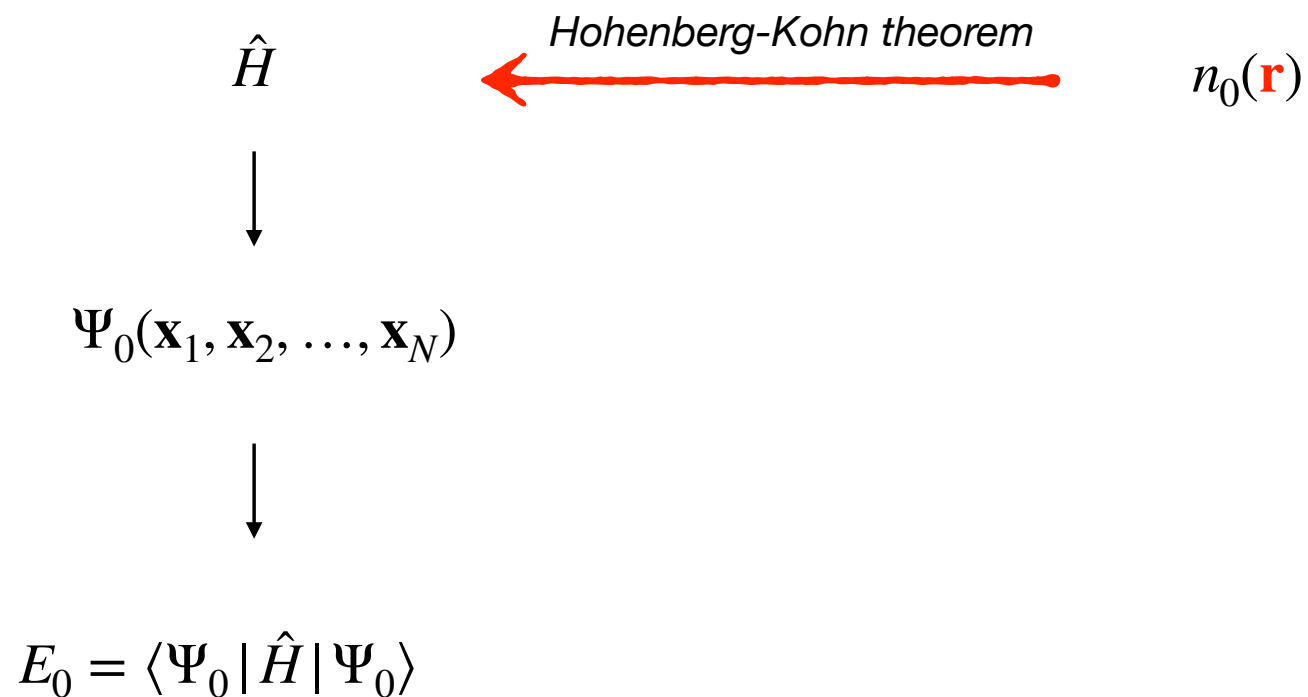
$$\hat{H} \qquad\qquad\qquad\qquad n_0(\textcolor{red}{\mathbf{r}})$$

$$\downarrow$$

$$\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \longrightarrow N \sum_\sigma \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N \, |\Psi_0(\textcolor{red}{\mathbf{r}}, \sigma, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2$$

$$\Vert$$

$$\downarrow$$

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$$

$$\Vert$$

$$\int d\mathbf{x}_1 \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N \, \Psi_0^*(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \times \hat{H} \Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$$

Wave function theory

Density functional theory

$$\hat{H}$$

Hohenberg-Kohn theorem

$$n_0(\mathbf{r})$$

$$\downarrow$$

$$\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$$

$$\downarrow$$

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$$

Wave function theory

Density functional theory

$\hat{H}$

$n_0(\mathbf{r})$

$\downarrow$

$\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$

$\downarrow$

$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$

Wave function theory

Density functional theory

$$\hat{H}$$

$$\downarrow$$

$$\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$$

$$n_0(\mathbf{r})$$

$$\downarrow$$

$$\parallel$$
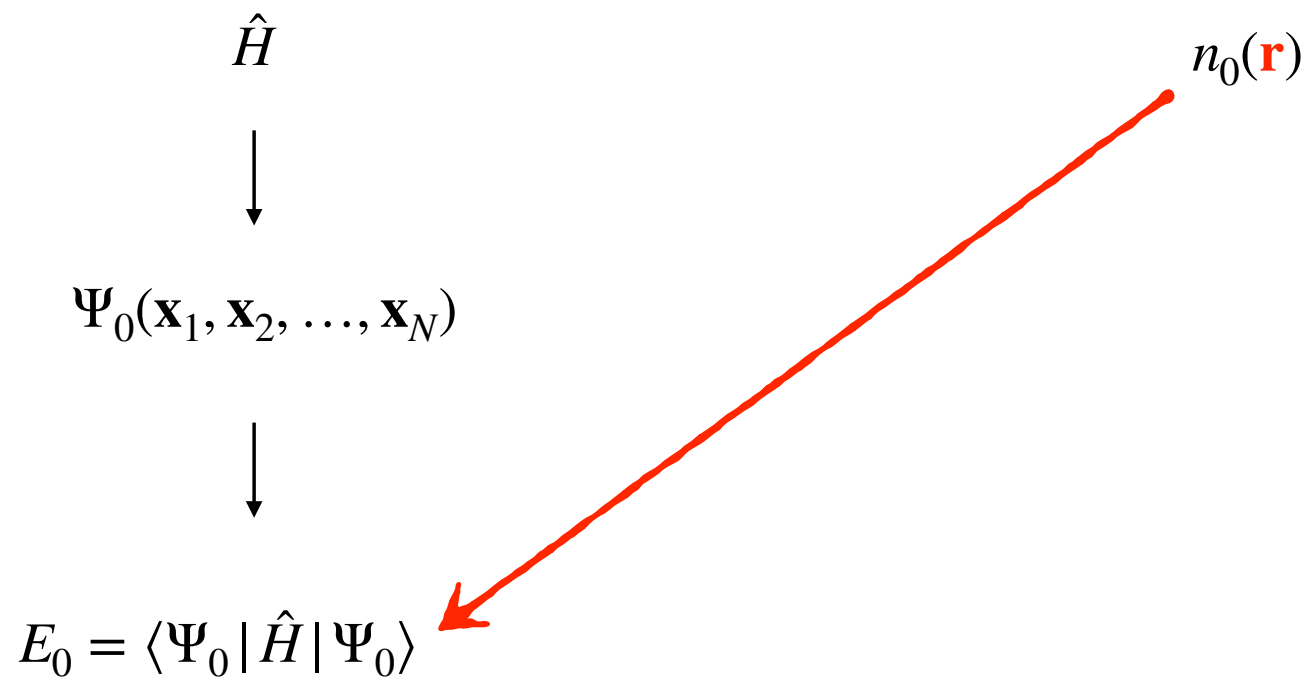
$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = E\left[\Phi_0^{\text{KS}}\right] \longleftarrow N \sum_\sigma \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N \, |\Phi_0^{\text{KS}}(\mathbf{r}, \sigma, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2$$

Kohn-Sham DFT

Wave function theory

Density functional theory

$$\hat{H}$$

$$\downarrow$$

$$\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$$

$$n_0(\mathbf{r})$$

$$\downarrow$$

$$\parallel$$

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = E\left[\Phi_0^{\mathrm{KS}}\right] \longleftarrow \quad N \sum_\sigma \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N \, |\Phi_0^{\mathrm{KS}}(\mathbf{r}, \sigma, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2$$

Kohn-Sham DFT

Note that $E_0 \neq \langle \Phi_0^{\mathrm{KS}} | \hat{H} | \Phi_0^{\mathrm{KS}} \rangle$!

The Nobel Prize in Chemistry 1998
Walter Kohn - Facts

Walter Kohn

Born: 9 March 1923, Vienna, Austria

Died: 19 April 2016, Santa Barbara, CA, USA

Affiliation at the time of the award: University of California, Santa Barbara, CA, USA

Prize motivation: "for his development of the density-functional theory"

Field: theoretical chemistry

Prize share: 1/2

Three things to *remember* before we start ...

- The following expression for the expectation value of the *one-electron potential energy* in terms of the electron density will be used intensively in the rest of this lecture:

$$
\left\langle \Psi \middle| \sum_{i=1}^{N} v(\mathbf{r}_i) \times \middle| \Psi \right\rangle = \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\; v(\mathbf{r}) n_{\Psi}(\mathbf{r}) \overset{notation}{\equiv} (v|n_{\Psi})
$$

- Note that a *constant* shift $\quad v(\mathbf{r}) \to v(\mathbf{r}) - \mu \quad$ in the local potential does *not* affect the ground-state wavefunction (and therefore it does not affect the ground-state density):

$$
\left(\hat{T} + \hat{W}_{\mathrm{ee}} + \sum_{i=1}^{N} \left(v(\mathbf{r}_i) - \mu \right) \times \right) \Psi_0 = \left(\hat{H} \Psi_0 \right) - N\mu \times \Psi_0 = \left(E_0 - N\mu \right) \Psi_0.
$$

Three things to *remember* before we start ...

- **Rayleigh–Ritz variational principle**: the exact ground-state energy is a lower bound for the expectation value of the energy. The minimum is reached when the trial quantum state $|\Psi\rangle$ equals the ground state $|\Psi_0\rangle$:

$$E_0 = \min_{\Psi} \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\langle\Psi_0|\hat{H}|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle}.$$

  <u>Proof:</u> $\forall\,\Psi,\ |\Psi\rangle = \sum_{I\geq0} C_I|\Psi_I\rangle$ and $\langle\Psi|\hat{H}|\Psi\rangle - E_0\langle\Psi|\Psi\rangle = \sum_{I>0} |C_I|^2\Big(E_I - E_0\Big) \geq 0.$

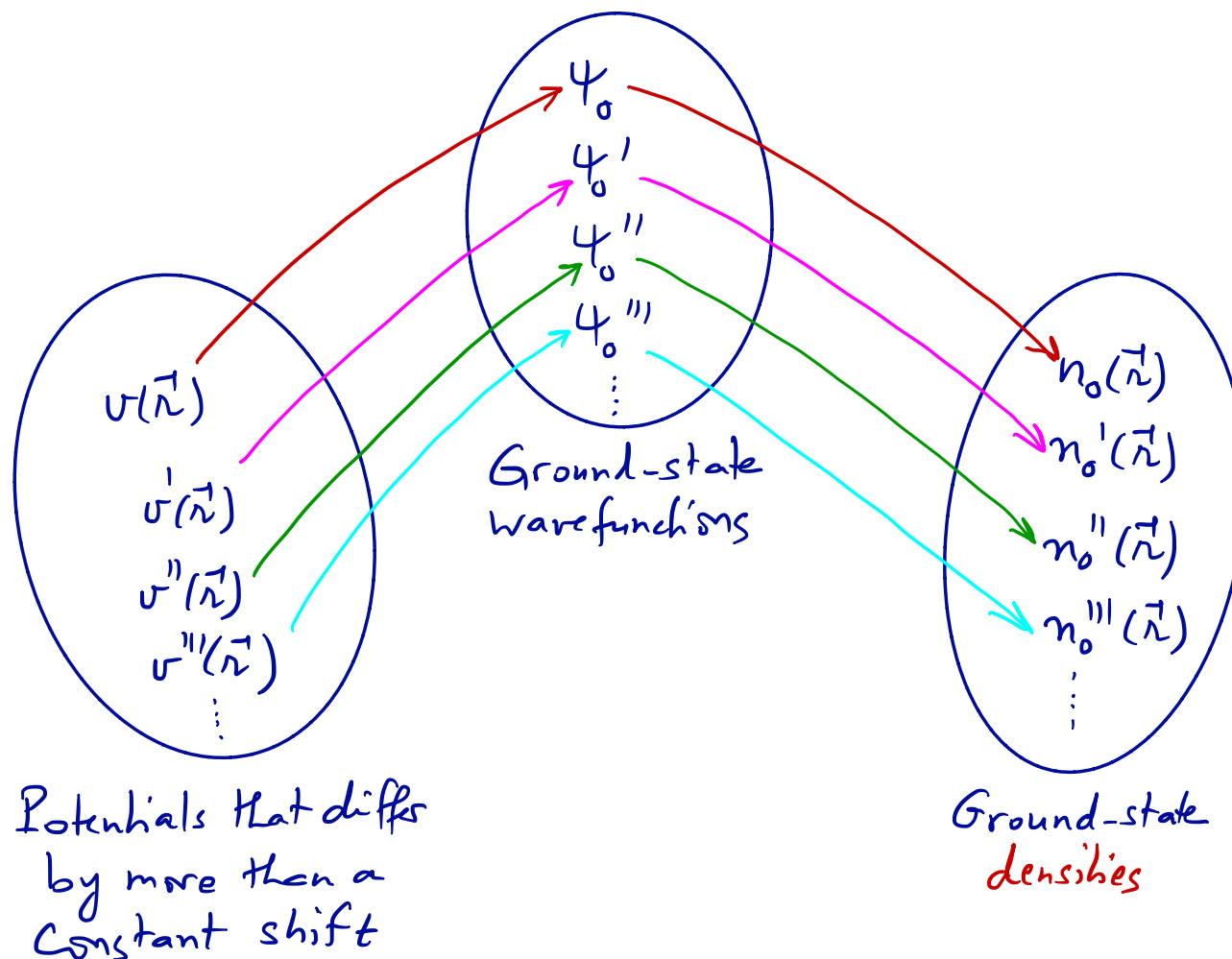- The ground state is usually normalized $\Big(\langle\Psi_0|\Psi_0\rangle = 1\Big)$ so that the variational principle can be rewritten as follows,

$$\boxed{E_0 = \min_{\Psi,\langle\Psi|\Psi\rangle=1} \langle\Psi|\hat{H}|\Psi\rangle = \langle\Psi_0|\hat{H}|\Psi_0\rangle}$$

- <u>Comment</u>: If $|\Psi_0\rangle$ is not degenerate, any normalized state $|\Psi\rangle$ that is not equal to $|\Psi_0\rangle$ is such that $\langle\Psi|\hat{H}|\Psi\rangle > E_0$.

Potential-density maps

Interacting map: $\hat{H} \equiv \hat{T} + \hat{W}_{\text{ee}} + \sum_{i=1}^{N} v(\mathbf{r}_i) \times$ or   *Non-interacting (KS) map:* $\hat{H} \equiv \hat{T} + \sum_{i=1}^{N} v(\mathbf{r}_i) \times$

Ground-state wavefunctions

Potentials that differ by more than a constant shift

Ground-state densities

First Hohenberg–Kohn theorem

- Note that $\quad v \to \Psi_0 \to E_0$

$$\to n_0 = n_{\Psi_0}$$

- **HK1:** Hohenberg and Kohn* have shown that, in fact, the ground-state electron density fully determines (up to a constant) the local potential v. Therefore

$$n_0 \to v \to \Psi_0 \to E_0$$

- In other words, the ground-state energy is a *functional* of the ground-state density: $E_0 = E[n_0]$.

<u>Proof</u> (part 1):

Let us consider two potentials v and v' that differ by more than a constant, which means that $v(\mathbf{r}) - v'(\mathbf{r})$ varies with $\mathbf{r}$. In the following, we denote Ψ_0 and Ψ_0' the associated ground-state wavefunctions with energies E_0 and E_0', respectively.

*P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

First Hohenberg–Kohn theorem

If $\Psi_0 = \Psi_0'$ then

$$
\begin{aligned}
\sum_{i=1}^{N} \Big(v(\mathbf{r}_i) - v'(\mathbf{r}_i) \Big) \times \Psi_0 \;&=\; \sum_{i=1}^{N} v(\mathbf{r}_i) \times \Psi_0 - v'(\mathbf{r}_i) \times \Psi_0' \\[2ex]
&=\; \left(\hat{T} + \hat{W}_{\text{ee}} + \sum_{i=1}^{N} v(\mathbf{r}_i) \times \right) \Psi_0 - \left(\hat{T} + \hat{W}_{\text{ee}} + \sum_{i=1}^{N} v'(\mathbf{r}_i) \times \right) \Psi_0' \\[2ex]
&=\; E_0 \Psi_0 - E_0' \Psi_0' \\[3ex]
&=\; \big(E_0 - E_0' \big) \times \Psi_0
\end{aligned}
$$

so that, in the particular case $\quad \mathbf{r}_1 = \mathbf{r}_2 = \ldots = \mathbf{r}_N = \mathbf{r}$, we obtain

$$
v(\mathbf{r}) - v'(\mathbf{r}) = \big(E_0 - E_0' \big)/N \qquad \longrightarrow \qquad \text{constant (absurd!)}
$$

Therefore Ψ_0 and Ψ_0' cannot be equal.

First Hohenberg–Kohn theorem

<u>Proof</u> (part 2): Let us now assume that Ψ_0 and Ψ_0' have the same electron density n_0.

According to the Rayleigh–Ritz variational principle

$$E_0 < \underbrace{\left\langle \Psi_0' \left| \hat{T} + \hat{W}_{ee} + \sum_{i=1}^{N} v(\mathbf{r}_i) \times \right| \Psi_0' \right\rangle}_{E_0' + (v - v'|n_0)} \quad \text{and} \quad E_0' < \underbrace{\left\langle \Psi_0 \left| \hat{T} + \hat{W}_{ee} + \sum_{i=1}^{N} v'(\mathbf{r}_i) \times \right| \Psi_0 \right\rangle}_{E_0 - (v - v'|n_0)}$$

thus leading to

$$0 < E_0 - E_0' - (v - v'|n_0) < 0 \qquad \text{absurd!}$$

[*]P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

Second Hohenberg–Kohn theorem

HK2: The exact ground-state density $n_0(\mathbf{r})$ of the electronic Hamiltonian

$$\hat{H}[v_{\mathrm{ne}}] \equiv \hat{T} + \hat{W}_{\mathrm{ee}} + \sum_{i=1}^{N} v_{\mathrm{ne}}(\mathbf{r}_i) \times$$

minimizes the energy density functional $E[n] = F[n] + \int_{\mathbb{R}^3} d\mathbf{r}\, v_{\mathrm{ne}}(\mathbf{r}) n(\mathbf{r}),$

where the Hohenberg–Kohn universal functional $F[n]$ is defined as

$$F[n] = \langle \Psi[n] | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi[n] \rangle,$$

and the minimum equals the exact ground-state energy E_0:

$$\boxed{\min_{n} E[n] = E[n_0] = E_0}$$

<u>Comment</u>: we know from **HK1** that $n(\mathbf{r}) \;\rightarrow\; v[n](\mathbf{r}) \;\rightarrow\; \underbrace{\Psi[v[n]] = \Psi[n]}$

<div align="right">ground-state wavefunction with density n.</div>

Second Hohenberg and Kohn theorem

Proof:

- for any density $n(\mathbf{r})$, $\Psi[n]$ is well defined according to **HK1** and

$$\langle\Psi[n]|\hat{H}[v_{\mathrm{ne}}]|\Psi[n]\rangle \geq E_0$$

$$\underbrace{\langle\Psi[n]|\hat{T}+\hat{W}_{\mathrm{ee}}|\Psi[n]\rangle}_{F[n]} + \int_{\mathbb{R}^3} d\mathbf{r}\; v_{\mathrm{ne}}(\mathbf{r})\,\underbrace{n_{\Psi[n]}(\mathbf{r})}_{n(\mathbf{r})} \geq E_0$$

thus leading to $\boxed{E[n] \geq E_0}$

- When $n(\mathbf{r})$ equals the exact ground-state density $n_0(\mathbf{r})$:

$$n_0(\mathbf{r}) \;\to\; v_{\mathrm{ne}}(\mathbf{r}) \;\to\; \Psi[n_0] = \Psi[v_{\mathrm{ne}}] = \Psi_0$$

$$E[n_0] = \langle\Psi_0|\hat{T}+\hat{W}_{\mathrm{ee}}|\Psi_0\rangle + \int_{\mathbb{R}^3} d\mathbf{r}\; v_{\mathrm{ne}}(\mathbf{r})n_0(\mathbf{r}) = \langle\Psi_0|\hat{T}+\hat{W}_{\mathrm{ee}}+\hat{V}_{\mathrm{ne}}|\Psi_0\rangle = E_0$$

Kohn–Sham DFT (KS-DFT)

- The HK theorems apply to non-interacting electrons:

$$\text{interacting problem} \quad \rightarrow \quad \textit{non-interacting } \text{KS problem}$$

$$\hat{W}_{\text{ee}} \quad \rightarrow \quad 0$$

$$v[n](\mathbf{r}) \quad \rightarrow \quad v^{\text{KS}}[n](\mathbf{r})$$

$$\Psi[n] \quad \rightarrow \quad \Phi^{\text{KS}}[n]$$

$$F[n] \quad \rightarrow \quad T_{\text{s}}[n] = \left\langle \Phi^{\text{KS}}[n] \middle| \hat{T} \middle| \Phi^{\text{KS}}[n] \right\rangle$$

$$n_{\Psi[n]}(\mathbf{r}) \quad = \quad n_{\Phi^{\text{KS}}[n]}(\mathbf{r}) \quad = \quad n(\mathbf{r})$$

- *KS decomposition* of the universal HK functional:

$$\boxed{F[n] = T_{\text{s}}[n] + E_{\text{Hxc}}[n]} \qquad \text{with} \qquad E_{\text{Hxc}}[n] = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{\text{xc}}[n].$$

W. Kohn and L. J. Sham, Phys. Rev. A **140**, 1133 (1965).

How can we determine the KS potential?

Two mathematical interludes

Mathematical interlude 1: functional derivative

- Let $f : x \longmapsto f(x)$ be a function of x. The derivative of f at $x = x_0$ is obtained from the Taylor expansion [δx is a small variation of x around x_0]

$$f(x_0 + \delta x) = f(x_0) + \delta x \left. \frac{\mathrm{d}f(x)}{\mathrm{d}x} \right|_{x=x_0} + \frac{(\delta x)^2}{2} \left. \frac{\mathrm{d}^2 f(x)}{\mathrm{d}x^2} \right|_{x=x_0} + \dots$$

- Let $S : n \longmapsto S[n]$ be a functional of the density n. The *functional derivative* of S at $n = n_0$ is by definition a *function of* $\mathbf{r}$ that is denoted $\boxed{\dfrac{\delta S[n_0]}{\delta n(\mathbf{r})} \equiv \left. \dfrac{\delta S[n]}{\delta n(\mathbf{r})} \right|_{n=n_0}}$. The latter is obtained from the following Taylor expansion [$\delta n(\mathbf{r})$ is a small deviation from $n_0(\mathbf{r})$ of the density at the position $\mathbf{r}$]:

$$S[n_0 + \delta n] = S[n_0] + \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r} \, \frac{\delta S[n_0]}{\delta n(\mathbf{r})} \times \delta n(\mathbf{r}) + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \, \frac{\delta^2 S[n_0]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} \times \delta n(\mathbf{r})\delta n(\mathbf{r}') + \dots$$

- <u>Example:</u> $S[n] = \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r} \, n^2(\mathbf{r}) \longrightarrow \dfrac{\delta S[n_0]}{\delta n(\mathbf{r})} = 2n_0(\mathbf{r})$

Mathematical interlude 2: Lieb maximization

- Let us introduce the *partially-interacting* universal HK functional:

$$F^\lambda[n] = \left\langle \Psi^\lambda[n] \middle| \hat{T} + \lambda \hat{W}_{\text{ee}} \middle| \Psi^\lambda[n] \right\rangle,$$

where $0 \leq \lambda \leq 1$ and $\Psi^\lambda[n]$ is the ground-state wavefunction of $\hat{T} + \lambda \hat{W}_{\text{ee}} + \sum_{i=1}^{N} v^\lambda[n](\mathbf{r}_i) \times$

with density n, i.e. $\boxed{n_{\Psi^\lambda[n]}(\mathbf{r}) = n(\mathbf{r})}$.

- Note that $F^{\lambda=1}[n] = F[n]$ and $F^{\lambda=0}[n] = T_{\text{s}}[n]$.

- Introducing $F^\lambda[n]$ is convenient for treating both interacting $\lambda = 1$ and non-interacting $\lambda = 0$ problems simultaneously (and for *connecting* them ...).

Lieb maximization

- Variational HK theorem for a partially-interacting system with *any* local potential v and ground-state energy $E^\lambda[v]$:

$$\boxed{\forall v, \quad E^\lambda[v] = \min_n \left\{ F^\lambda[n] + \int d\mathbf{r}\, v(\mathbf{r})n(\mathbf{r}) \right\}} \quad \Leftrightarrow \quad \forall v, \forall n, \quad E^\lambda[v] \leq F^\lambda[n] + \int d\mathbf{r}\, v(\mathbf{r})n(\mathbf{r})$$

$$\Leftrightarrow \quad \forall v, \forall n, \quad F^\lambda[n] \geq E^\lambda[v] - \int d\mathbf{r}\, v(\mathbf{r})n(\mathbf{r})$$

$$\Leftrightarrow \quad \boxed{\forall n, \quad F^\lambda[n] = \max_v \left\{ E^\lambda[v] - \int d\mathbf{r}\, v(\mathbf{r})n(\mathbf{r}) \right\}}$$

- The *maximizing potential* is $v^\lambda[n]$!

- If v and n were just numbers (not functions of $\mathbf{r}$): $\quad F^\lambda(n) = \max_v \left\{ \mathcal{F}^\lambda(v,n) \right\} = \mathcal{F}^\lambda\left(v^\lambda(n), n\right)$
  where $\quad \mathcal{F}^\lambda(v,n) = E^\lambda(v) - vn$.

- Stationarity condition: $\quad \left.\dfrac{\partial \mathcal{F}^\lambda(v,n)}{\partial v}\right|_{v=v^\lambda(n)} = 0 \quad \Rightarrow \quad \dfrac{\partial F^\lambda(n)}{\partial n} = -v^\lambda(n).$

- We deduce from the stationarity condition of the *maximizing* potential $v^\lambda[n]$ that

$$\frac{\delta F^\lambda[n]}{\delta n(\mathbf{r})} = -v^\lambda[n](\mathbf{r}).$$

- Let us return to the real system we are interested in with nuclear potential v_{ne} and ground-state density n_0.

- Since $v_{\text{ne}} = v^{\lambda=1}[n_0]$, the KS potential we are looking for is

$$
\begin{aligned}
v^{\text{KS}}[n_0](\mathbf{r}) &= v^{\lambda=0}[n_0](\mathbf{r}) \\
&= v^{\lambda=1}[n_0](\mathbf{r}) + \left(v^{\lambda=0}[n_0](\mathbf{r}) - v^{\lambda=1}[n_0](\mathbf{r}) \right) \\
&= v_{\text{ne}}(\mathbf{r}) + \left(\frac{\delta F^{\lambda=1}[n_0]}{\delta n(\mathbf{r})} - \frac{\delta F^{\lambda=0}[n_0]}{\delta n(\mathbf{r})} \right) \\
&= v_{\text{ne}}(\mathbf{r}) + \left(\frac{\delta F[n_0]}{\delta n(\mathbf{r})} - \frac{\delta T_{\text{s}}[n_0]}{\delta n(\mathbf{r})} \right)
\end{aligned}
$$

$$\boxed{v^{\text{KS}}[n_0](\mathbf{r}) = v_{\text{ne}}(\mathbf{r}) + \frac{\delta E_{\text{Hxc}}[n_0]}{\delta n(\mathbf{r})}}$$

Self-consistent KS equations

$$\left(-\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_{\mathrm{ne}}(\mathbf{r}) + \frac{\delta E_{\mathrm{Hxc}}[n_0]}{\delta n(\mathbf{r})} \right) \varphi_i^{\mathrm{KS}}(\mathbf{x}) = \varepsilon_i^{\mathrm{KS}} \varphi_i^{\mathrm{KS}}(\mathbf{x})$$

where

$$n_0(\mathbf{r}) = \sum_{\sigma=\pm\frac{1}{2}} \sum_{i=1}^{N} \left| \varphi_i^{\mathrm{KS}}(\mathbf{r},\sigma) \right|^2.$$

Important conclusion: if we know the *xc functional $E_{\mathrm{xc}}[n]$*, we can determine the ground-state density *self-consistently* (and therefore the ground-state energy), in principle *exactly*.

In KS-DFT, the physical ground-state *energy* reads

$$E_0 = T_{\mathrm{s}}[n_0] + E_{\mathrm{Hxc}}[n_0] + \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, v_{\mathrm{ne}}(\mathbf{r})n_0(\mathbf{r}),$$

where $T_{\mathrm{s}}[n_0] = \left\langle \Phi_0^{\mathrm{KS}} \middle| \hat{T} \middle| \Phi_0^{\mathrm{KS}} \right\rangle = -\frac{1}{2} \sum_{i=1}^{N} \int \mathrm{d}\mathbf{x}\, \varphi_i^*(\mathbf{x})\nabla_{\mathbf{r}}^2 \varphi_i(\mathbf{x}).$