Introduction to Kohn–Sham density-functional theory

Emmanuel Fromager

Institut de Chimie de Strasbourg - Laboratoire de Chimie Quantique -
Université de Strasbourg /CNRS

EUR: Theory of extended systems

N-electron Schrödinger equation for the *ground* state

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

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

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

$$\hat{T} \equiv -\frac{1}{2}\sum_{i=1}^{N} \nabla^2_{\mathbf{r}_i} = -\frac{1}{2}\sum_{i=1}^{N}\left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right)$$

⟶ *universal* kinetic energy operator

$$\hat{W}_{\text{ee}} \equiv \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\times$$

⟶ *universal* two-electron repulsion operator

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

⟶ local *nuclear* 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*.

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

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

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

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

(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

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

- When computing the two-electron repulsion energy $\left\langle \Phi_0 \middle| \hat{W}_{\mathrm{ee}} \middle| \Phi_0 \right\rangle$ 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 ($\hat{W}_{\rm ee} \neq 0$) 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 $\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$:

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

Proof : 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,

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

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 $\mathbf{r}_2 \rightarrow \mathbf{r}_1 = \mathbf{r}$, it comes $\forall\, \mathbf{r}, \quad E_0 + \dfrac{\nabla^2_{\mathbf{r}}\varphi(\mathbf{r})}{\varphi(\mathbf{r})} - 2v(\mathbf{r}) \rightarrow +\infty$ 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:

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

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**:

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

- Questions to be answered:

(1) If $v^{\rm KS}(\mathbf{r})$ 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

$$\begin{tikzcd}
\hat{H} \arrow[d] & n_0(\mathbf{r}) \arrow[d, equal] \\
\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \arrow[r] \arrow[d] & N \sum_{\sigma} \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N \, |\Psi_0(\mathbf{r}, \sigma, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2 \\
E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \arrow[d, equal] & \\
\int d\mathbf{x}_1 \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N \, \Psi_0^*(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \times \hat{H} \Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) &
\end{tikzcd}$$

Wave function theory **Density functional theory**

$$\begin{tikzcd}
\hat{H} \arrow[d] & & n_0(\mathbf{r}) \arrow[ll, "\text{Hohenberg-Kohn theorem}"'] \\
\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \arrow[d] & & \\
E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle & &
\end{tikzcd}$$

Wave function theory

Density functional theory

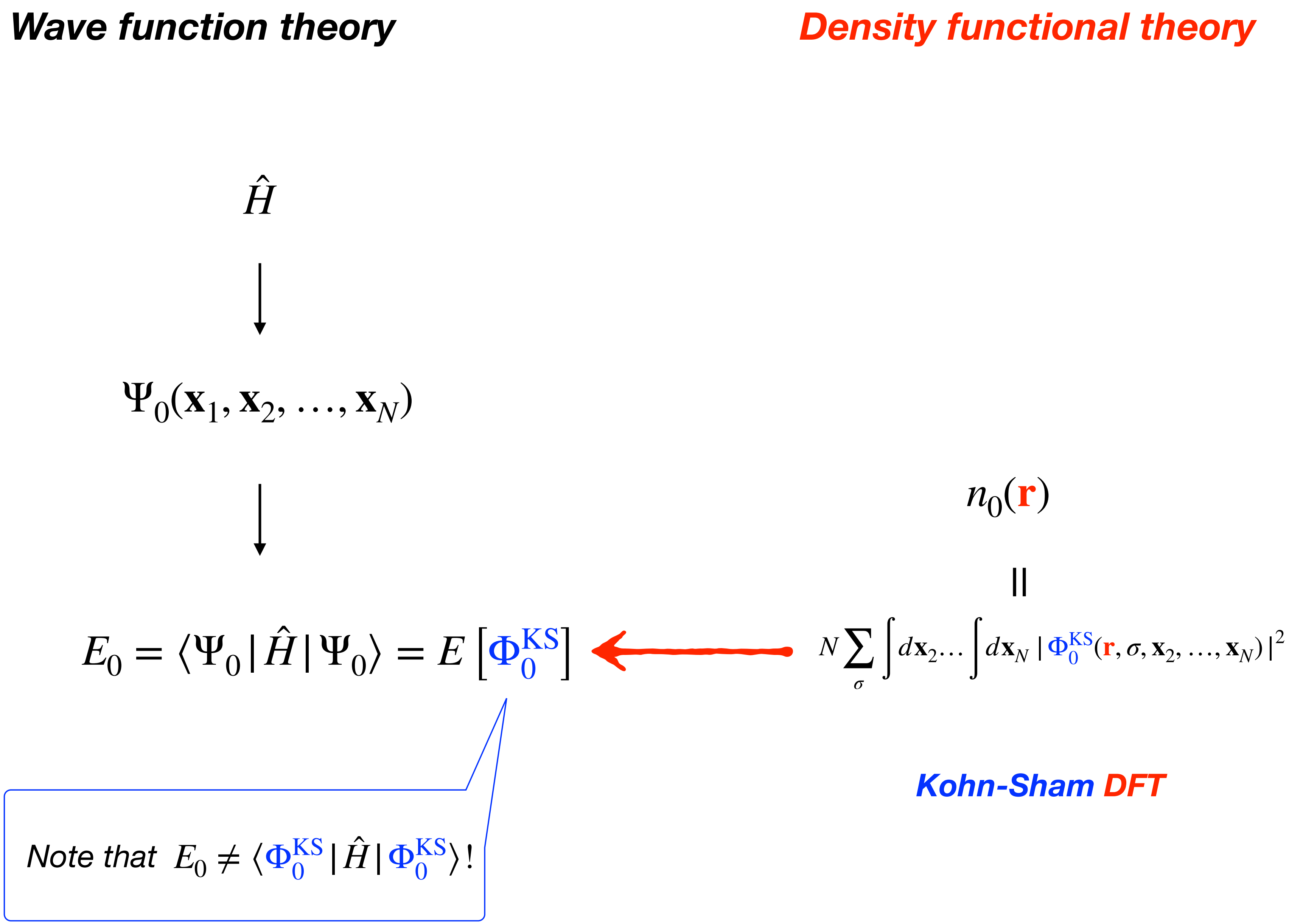
$$\begin{tikzcd}
\hat{H} \arrow[d] & & n_0(\mathbf{r}) \arrow[ddll] \\
\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \arrow[d] & & \\
E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle & &
\end{tikzcd}$$

Wave function theory

Density functional theory

$$\begin{tikzcd}
\hat{H} \arrow[d] & \\
\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \arrow[d] & n_0(\mathbf{r}) \arrow[d, equal] \\
E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = E\left[\Phi_0^{\mathrm{KS}}\right] & N \sum_{\sigma} \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N \, |\Phi_0^{\mathrm{KS}}(\mathbf{r}, \sigma, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2 \arrow[l]
\end{tikzcd}$$

Kohn-Sham DFT



Wave function theory

Density functional theory

$$\hat{H}$$

$$\downarrow$$

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

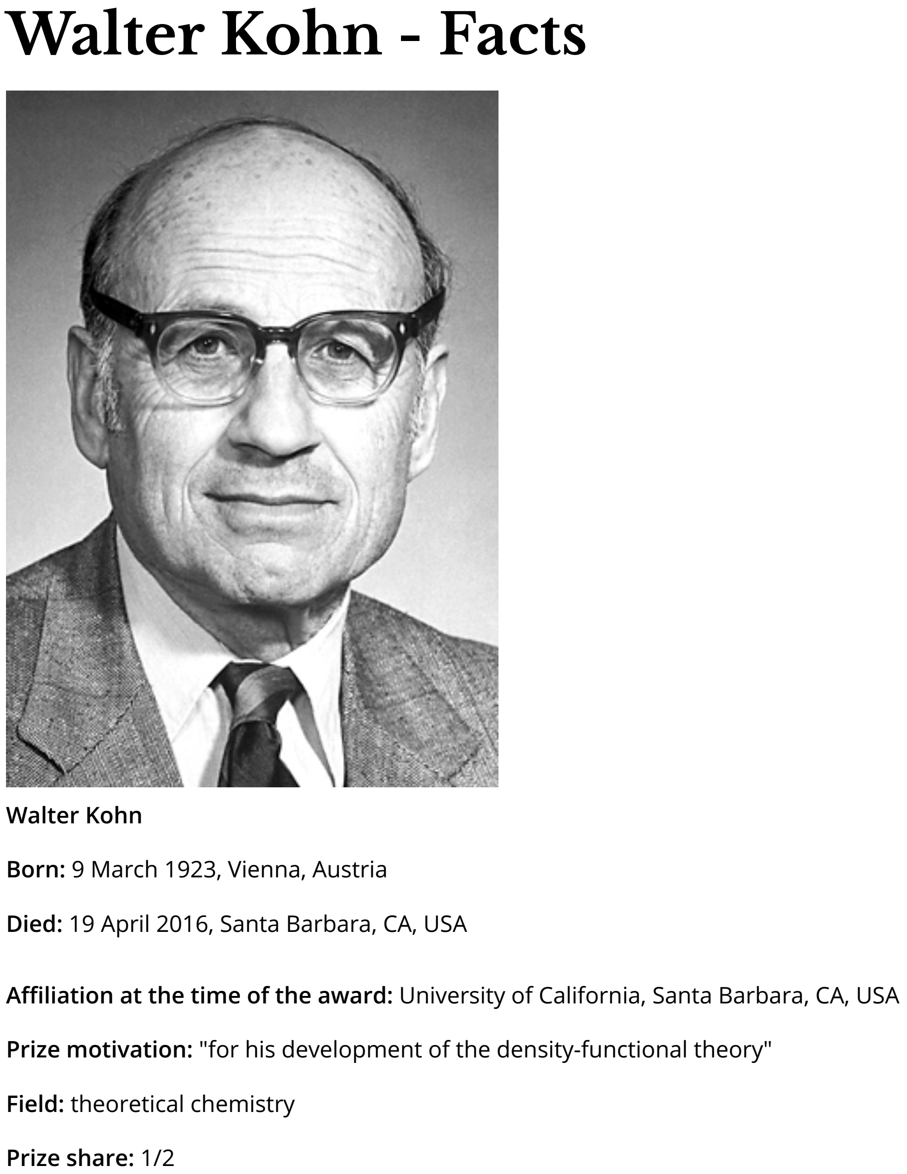
$$\downarrow$$

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = E\left[\Phi_0^{\mathrm{KS}}\right] \longleftarrow N \sum_\sigma \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N \, |\Phi_0^{\mathrm{KS}}(\mathbf{r}, \sigma, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2 = n_0(\mathbf{r})$$

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

Kohn-Sham DFT

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:

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

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

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

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 $|\Psi_0\rangle$:

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

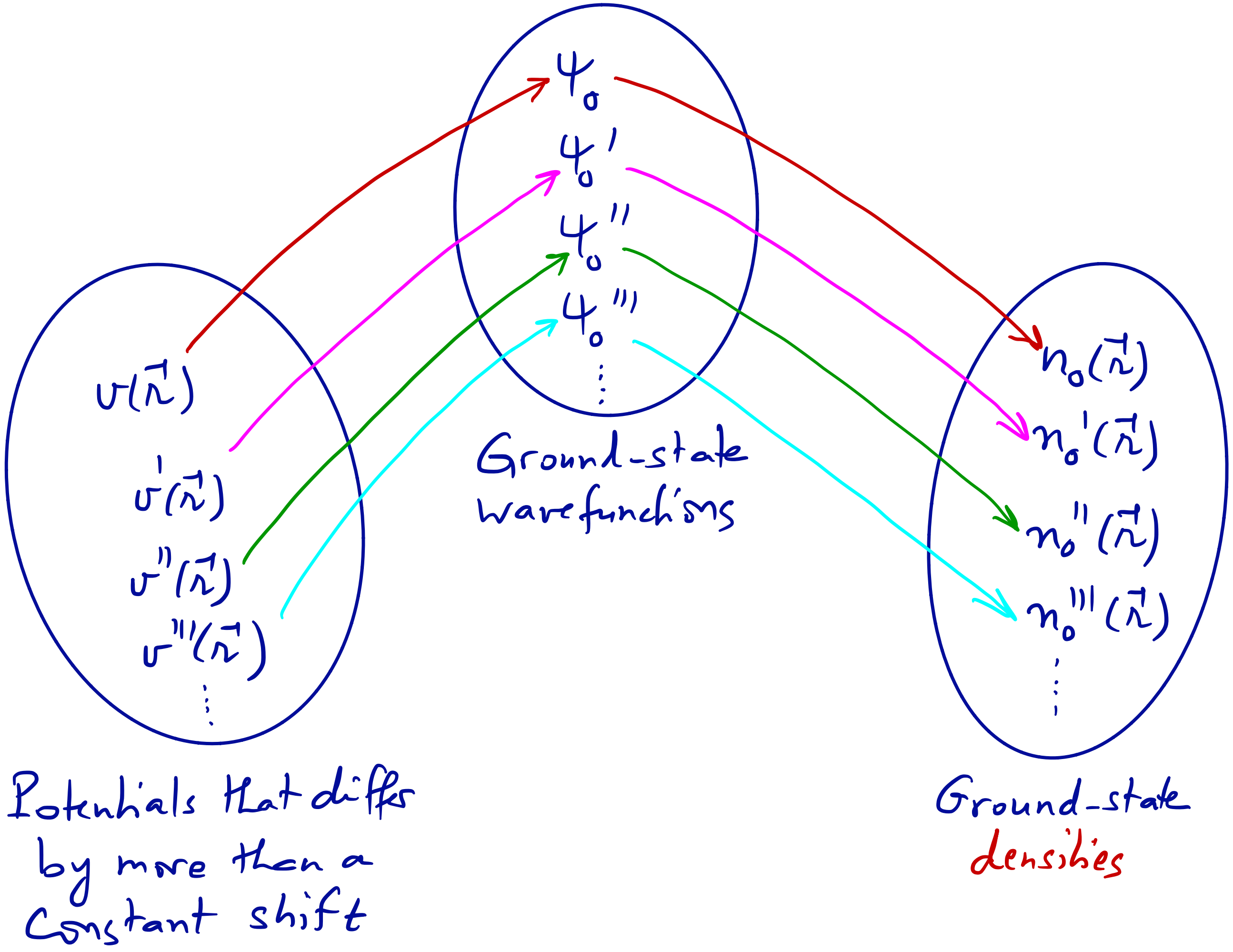
Proof: $\forall\,\Psi,\ |\Psi\rangle = \sum_{I\geq 0} C_I|\Psi_I\rangle \quad \text{and} \quad \langle\Psi|\hat{H}|\Psi\rangle - E_0\langle\Psi|\Psi\rangle = \sum_{I>0} |C_I|^2\Big(E_I - E_0\Big) \geq 0.$

- 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,

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

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

First Hohenberg–Kohn theorem



First Hohenberg–Kohn theorem

- Note that $v \rightarrow \Psi_0 \rightarrow E_0$

  $\rightarrow n_0 = n_{\Psi_0}$

- **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

$$n_0 \rightarrow v \rightarrow \Psi_0 \rightarrow E_0$$

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

Proof (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

$$\begin{aligned}
\sum_{i=1}^{N}\Big(v(\mathbf{r}_i) - v'(\mathbf{r}_i)\Big) \times \Psi_0 &= \sum_{i=1}^{N} v(\mathbf{r}_i) \times \Psi_0 - v'(\mathbf{r}_i) \times \Psi_0' \\
&= \left(\hat{T} + \hat{W}_{\mathrm{ee}} + \sum_{i=1}^{N} v(\mathbf{r}_i)\times\right)\Psi_0 - \left(\hat{T} + \hat{W}_{\mathrm{ee}} + \sum_{i=1}^{N} v'(\mathbf{r}_i)\times\right)\Psi_0' \\
&= E_0\Psi_0 - E_0'\Psi_0' \\
&= \Big(E_0 - E_0'\Big) \times \Psi_0
\end{aligned}$$

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

Proof (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

$$E_0 < \underbrace{\left\langle \Psi'_0 \middle| \hat{T} + \hat{W}_{\rm ee} + \sum_{i=1}^{N} v(\mathbf{r}_i)\times \middle| \Psi'_0 \right\rangle}_{E'_0 + (v - v'|n_0)} \quad \text{and} \quad E'_0 < \underbrace{\left\langle \Psi_0 \middle| \hat{T} + \hat{W}_{\rm ee} + \sum_{i=1}^{N} v'(\mathbf{r}_i)\times \middle| \Psi_0 \right\rangle}_{E_0 - (v - v'|n_0)}$$

thus leading to

$$0 < E_0 - E'_0 - (v - v'|n_0) < 0 \qquad \text{absurd !}$$

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* 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:

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

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

ground-state wavefunction with density n.

Second Hohenberg and Kohn theorem

Proof:

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

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

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

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

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

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

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

Kohn–Sham DFT (KS-DFT)

- The HK theorems apply to non-interacting electrons:

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

$$\begin{aligned} \hat{W}_{\mathrm{ee}} &\rightarrow 0 \\ v[n](\mathbf{r}) &\rightarrow v^{\mathrm{KS}}[n](\mathbf{r}) \\ \Psi[n] &\rightarrow \Phi^{\mathrm{KS}}[n] \\ F[n] &\rightarrow T_{\mathrm{s}}[n] = \left\langle \Phi^{\mathrm{KS}}[n] \middle| \hat{T} \middle| \Phi^{\mathrm{KS}}[n] \right\rangle \end{aligned}$$

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

- *KS decomposition* of the universal HK functional:

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

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

Mathematical interlude: 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)

$$f(x_0 + \delta x) = f(x_0) + \left.\frac{\mathrm{d}f}{\mathrm{d}x}\right|_{x=x_0} \times \delta x + \frac{1}{2}\left.\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}\right|_{x=x_0} \times \delta x^2 + \ldots$$

- 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 $\dfrac{\delta S}{\delta n(\mathbf{r})}[n_0]$. The latter is obtained from the Taylor expansion ($\delta n(\mathbf{r})$ is a small variation of the density around n_0):

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

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

Lieb maximization

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

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

  where $0 \leq \lambda \leq 1$ and $\Psi^{\lambda}[n]$ is the ground-state wavefunction of $\hat{T} + \lambda \hat{W}_{\rm ee} + \sum_{i=1}^{N} v^{\lambda}[n](\mathbf{r}_i)\times$ **with density** n, i.e. $\boxed{n_{\Psi^{\lambda}[n]}(\mathbf{r}) = n(\mathbf{r})}$.

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

- 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 $\mathbf{r}$): $F^{\lambda}(n) = \max_{v}\left\{\mathcal{F}^{\lambda}(v,n)\right\} = \mathcal{F}^{\lambda}\Big(v^{\lambda}(n), n\Big)$
  where $\mathcal{F}^{\lambda}(v,n) = E^{\lambda}(v) - vn.$

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

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

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

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

Self-consistent KS equations

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

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

Important conclusion: if we know the *xc functional* $E_{\rm xc}[n]$, 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

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

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