

# NANOPHYSIQUE

## INTRODUCTION PHYSIQUE AUX NANOSCIENCES

### *Ch6 . Density Functional Theory*

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# Density Functional Theory

- Prelude: Functionals and Functional Derivatives
- Introduction
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  - Thomas-Fermi
  - Thomas-Fermi-Dirac
- 0K DFT
  - Hohenberg-Kohn theoreme
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  - Approximations for the exchange term
- $T > 0$ 
  - Théorème fondamental du DFT

# Functionals

A **function** maps *numbers* to *numbers*:  $f(x_1, \dots, x_N) = (y_1, \dots, y_m)$

A **functional** maps *functions* and *numbers* to *functions*.

Notation for mapping a function to a number:  $F[f] = x$

Notation for mapping a function and a vector to a function:

$$F(\mathbf{r}; [f]) = g(\mathbf{r})$$

Alternative notation:

$$F(f(\cdot)) = x$$

$$F(\mathbf{r}; f(\cdot)) = g(\mathbf{r})$$

# Functionals

A *function* maps real numbers to real numbers:  $f(x_1, \dots, x_N) = (y_1, \dots, y_m)$

A *functional* maps functions and numbers to functions.

Example for mapping a function to a number:

$$x = F[f] = \int_0^\infty f(s) ds$$

$$x = F[f] = f(s_0)$$

Example for mapping a function and a vector to a function:

$$g(\mathbf{r}) = F(\mathbf{r}; [f]) = \sqrt{f(\mathbf{r})}$$

$$g(\mathbf{r}) = F(\mathbf{r}; [f]) = \frac{\partial f(\mathbf{r})}{\partial \mathbf{r}}$$

$$g(\mathbf{r}) = F(\mathbf{r}; [f]) = \int_0^\infty f(\mathbf{r}, s) ds$$

# Functional Derivatives

Definition:

For any 'reasonable' function  $g(\mathbf{r})$ , if

$$\lim_{\epsilon \rightarrow 0} \frac{F[f + \epsilon g] - F[f]}{\epsilon} = \int K(\mathbf{r}) g(\mathbf{r}) d\mathbf{r}$$

then  $K(\mathbf{r})$  is the functional derivative of  $F$  with respect to  $f$ :  $\frac{\delta F[f]}{\delta f(\mathbf{r})} \equiv K(\mathbf{r})$

Example:

$$F[f] = \int f(\mathbf{s}) d\mathbf{s}$$

$$\begin{aligned} \lim_{\epsilon \rightarrow 0} \frac{F[f + \epsilon g] - F[f]}{\epsilon} &= \lim_{\epsilon \rightarrow 0} \frac{\int (f(\mathbf{s}) + \epsilon g(\mathbf{s})) d\mathbf{s} - \int f(\mathbf{s}) d\mathbf{s}}{\epsilon} \\ &= \int g(\mathbf{s}) d\mathbf{s} \end{aligned}$$

$$\text{so } \frac{\delta F[f]}{\delta f(\mathbf{r})} = 1$$

# Functional Derivatives

Definition:

For any 'reasonable' function  $g(\mathbf{r})$ , if

$$\lim_{\epsilon \rightarrow 0} \frac{F[f + \epsilon g] - F[f]}{\epsilon} = \int K(\mathbf{r}) g(\mathbf{r}) d\mathbf{r}$$

then  $K(\mathbf{r})$  is the functional derivative of  $F$  with respect to  $f$ :  $\frac{\delta F[f]}{\delta f(\mathbf{r})} \equiv K(\mathbf{r})$

There are analogies to most of the simple rules of calculus:

Chain rule: 
$$\frac{\delta F[f]G[f]}{\delta f(\mathbf{r})} = \frac{\delta F[f]}{\delta f(\mathbf{r})} G[f] + F[f] \frac{\delta G[f]}{\delta f(\mathbf{r})}$$

Taylor expansion: 
$$F[f+g] = F[f] + \int \frac{\delta F[f]}{\delta f(\mathbf{r})} g(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{\delta^2 F[f]}{\delta f(\mathbf{r}_1) \delta f(\mathbf{r}_2)} g(\mathbf{r}_1) g(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 + \dots$$

# Functional Derivatives

Alternative “Definition” (not so rigorous):

Imagine that space is discretized so that  $x \rightarrow x_j = j \Delta$

Then a functional of a function  $f(x)$  becomes a vector:  $f(\mathbf{r}) \rightarrow (f_1, \dots, f_N)$  with  $f_j \equiv f(x_j)$

and a functional of  $f(x)$  becomes a function of that vector:  $F[f] \rightarrow F(f_1, \dots, f_N)$

The functional derivative is then: 
$$\frac{\delta F[f]}{\delta f(\mathbf{r})} \rightarrow \frac{1}{\Delta} \frac{\partial F(f_1, \dots, f_N)}{\partial f_N}$$

Example: 
$$F[f] = \int f(x) dx \rightarrow F(f_1, \dots, f_N) = \sum_{j=1}^N f_j \Delta$$

$$\frac{\delta F[f]}{\delta f(\mathbf{r})} \rightarrow \frac{1}{\Delta} \frac{\partial F(f_1, \dots, f_N)}{\partial f_l} = 1$$

# Density Functional Theory

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# Ab initio

D'apres "Solid State Physics", G. Grosso & G. P. Parravicini, Acad. Press, 2000

**But:** détermination de l'état fondamental d'un système d'électrons dans une champ extérieur.

**Stratégie:** calcul variationnel.

Devinez:  $\Psi(\mathbf{r}_1, \sigma_1, \dots, \mathbf{r}_N, \sigma_N) = \psi_a(\mathbf{r}_1, \sigma_1) \dots \psi_n(\mathbf{r}_N, \sigma_N), \quad \{\psi_\alpha(\mathbf{r}, \sigma)\}_{\alpha=a}^n$  orthonormaux

Mais, car les électrons sont fermions, il faut que la fonction d'onde est antisymétrique:

$$\Psi(\mathbf{r}_1, \sigma_1, \dots, \mathbf{r}_N, \sigma_N) = \frac{1}{\sqrt{N!}} \sum_{a=1}^{N!} (-1)^{p_a} P_a \psi_a(\mathbf{r}_1, \sigma_1) \dots \psi_n(\mathbf{r}_N, \sigma_N)$$

$$P_a \in S_N, \quad p_a = \text{parity of } P_a$$

Slater determinant:

$$\Psi(\mathbf{r}_1, \sigma_1, \dots, \mathbf{r}_N, \sigma_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(\mathbf{r}_1, \sigma_1) & \psi_a(\mathbf{r}_2, \sigma_2) & \dots & \psi_a(\mathbf{r}_N, \sigma_N) \\ \psi_b(\mathbf{r}_1, \sigma_1) & \psi_b(\mathbf{r}_2, \sigma_2) & \dots & \psi_b(\mathbf{r}_N, \sigma_N) \\ \vdots & \vdots & \dots & \vdots \\ \psi_n(\mathbf{r}_1, \sigma_1) & \psi_n(\mathbf{r}_2, \sigma_2) & \dots & \psi_n(\mathbf{r}_N, \sigma_N) \end{vmatrix} \equiv \det \{ \psi_a \dots \psi_n \}$$

# Ab initio

D'apres "Solid State Physics", G. Grosso & G. P. Parravicini, Acad. Press, 2000

$$\Psi(\mathbf{r}_1, \sigma_1, \dots, \mathbf{r}_N, \sigma_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(\mathbf{r}_1, \sigma_1) & \psi_a(\mathbf{r}_2, \sigma_2) & \dots & \psi_a(\mathbf{r}_N, \sigma_N) \\ \psi_b(\mathbf{r}_1, \sigma_1) & \psi_b(\mathbf{r}_2, \sigma_2) & \dots & \psi_b(\mathbf{r}_N, \sigma_N) \\ \vdots & \vdots & \dots & \vdots \\ \psi_n(\mathbf{r}_1, \sigma_1) & \psi_n(\mathbf{r}_2, \sigma_2) & \dots & \psi_n(\mathbf{r}_N, \sigma_N) \end{vmatrix} \equiv \det \{ \psi_a \dots \psi_n \}$$

Espérance d'opérateur 1-particule:  $\hat{O} = \sum_{j=1}^N \hat{O}_j = \sum_{j=1}^N \hat{o}(\mathbf{r}_j)$

$$\begin{aligned} \langle \hat{O} \rangle_G &= \sum_{j=1}^N \langle \hat{O}_j \rangle_G \\ &= \frac{1}{N!} \sum_{j=1}^N \langle \det \{ \psi_a \dots \psi_n \} | \hat{O}_j | \det \{ \psi_a \dots \psi_n \} \rangle \\ &= \sum_{j=1}^N \langle \psi_a \dots \psi_n | \hat{O}_j | \psi_a \dots \psi_n \rangle \\ &= \sum_{\alpha} \langle \psi_{\alpha} | \hat{o} | \psi_{\alpha} \rangle \end{aligned}$$

Espérance d'opérateur 2-particule:  $\hat{O} = \sum_{1 \leq i < j \leq N} \hat{O}_{ij} = \sum_{1 \leq i < j \leq N} \hat{o}(\mathbf{r}_i, \mathbf{r}_j)$

$$\begin{aligned} \langle \hat{O} \rangle_G &= \frac{1}{2} \sum_{1 \leq a < b \leq N} \left( \langle \psi_a \psi_b | \hat{o} | \psi_a \psi_b \rangle - \langle \psi_a \psi_b | \hat{o} | \psi_b \psi_a \rangle \right) \\ &= \frac{1}{2} \sum_{1 \leq a < b \leq N} \left( \langle \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) | \hat{o}(\mathbf{r}_1, \mathbf{r}_2) | \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) \rangle - \underbrace{\langle \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) | \hat{o}(\mathbf{r}_1, \mathbf{r}_2) | \psi_b(\mathbf{r}_1) \psi_a(\mathbf{r}_2) \rangle}_{\text{exchange term}} \right) \end{aligned}$$

# Ab initio

D'après "Solid State Physics", G. Grosso & G. P. Parravicini, Acad. Press, 2000

$$\Psi(\mathbf{r}_1, \sigma_1, \dots, \mathbf{r}_N, \sigma_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{a1}(\mathbf{r}_1, \sigma_1) & \psi_a(\mathbf{r}_2, \sigma_2) & \dots & \psi_a(\mathbf{r}_N, \sigma_N) \\ \psi_b(\mathbf{r}_1, \sigma_1) & \psi_b(\mathbf{r}_2, \sigma_2) & \dots & \psi_b(\mathbf{r}_N, \sigma_N) \\ \vdots & \vdots & \dots & \vdots \\ \psi_n(\mathbf{r}_1, \sigma_1) & \psi_n(\mathbf{r}_2, \sigma_2) & \dots & \psi_n(\mathbf{r}_N, \sigma_N) \end{vmatrix} \equiv \det \{ \psi_a \dots \psi_n \}$$

Hamiltonienne:

$$H = H_{ee} + V_{ext}$$

$$H_{ee} = T + V_{ee} = \sum_{j=1}^N \frac{\hbar^2}{2m} \nabla_j^2 + \frac{1}{2} \sum_{j \neq l} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_l|}$$

$$V_{ext} = \sum_{j=1}^N v_{ext}(\mathbf{r}_j), \quad v_{ext}(\mathbf{r}) = - \sum_I \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R}_I|}$$

Coordonnées des noyaux

$$\langle \Psi | H | \Psi \rangle = \sum_a^{(occ)} \langle \psi_a | \hat{h} | \psi_a \rangle + \frac{1}{2} \sum_{ab}^{(occ)} \left[ \langle \psi_a \psi_b | \frac{e^2}{r_{12}} | \psi_a \psi_b \rangle - \langle \psi_a \psi_b | \frac{e^2}{r_{12}} | \psi_b \psi_a \rangle \right]$$

$$\hat{h} = \sum_{j=1}^N \left( \frac{\hbar^2}{2m} \nabla_j^2 + v_{ext}(\mathbf{r}_j) \right)$$

# Ab initio

D'apres "Solid State Physics", G. Grosso & G. P. Parravicini, Acad. Press, 2000


Minimisez avec contraintes:  $\langle \psi_a | \psi_b \rangle = \delta_{ab}$

Lagrangian:

$$\langle \Psi | H | \Psi \rangle = \sum_a^{(occ)} \langle \psi_a | \hat{h} | \psi_a \rangle + \frac{1}{2} \sum_{ab}^{(occ)} \left[ \langle \psi_a \psi_b | \frac{e^2}{r_{12}} | \psi_a \psi_b \rangle - \langle \psi_a \psi_b | \frac{e^2}{r_{12}} | \psi_a \psi_b \rangle \right] - \sum_{ab}^{(occ)} \epsilon_{ab} (\langle \psi_a | \psi_b \rangle - \delta_{ab})$$

$\psi \in \mathbb{C} \Rightarrow \langle \delta \psi |$  et  $|\delta \psi \rangle$  independent

$$0 = \sum_i^{(occ)} \langle \delta \psi_a | \hat{h} | \psi_a \rangle + \sum_{ab}^{(occ)} \left[ \langle \delta \psi_a \psi_b | \frac{e^2}{r_{12}} | \psi_a \psi_b \rangle - \langle \delta \psi_a \psi_b | \frac{e^2}{r_{12}} | \psi_b \psi_a \rangle \right] - \sum_{ab}^{(occ)} \epsilon_{ab} \langle \delta \psi_a | \psi_b \rangle$$



$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V_{nuc}(\mathbf{r}) + V_{coul}(\mathbf{r}; [\{\psi\}]) + \hat{V}_{exch}(\mathbf{r}; [\{\psi\}]) \right) \psi_a(\mathbf{r}, \sigma) = \sum_b^{(occ)} \epsilon_{ab} \psi_b(\mathbf{r}, \sigma)$$

$$V_{coul} = \sum_b^{(occ)} \sum_{\sigma} \int \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_b^*(\mathbf{r}'; \sigma) \psi_b(\mathbf{r}'; \sigma) d\mathbf{r}'$$

$$\hat{V}_{exch} \psi_a(\mathbf{r}; \sigma) = - \sum_b^{(occ)} \psi_b(\mathbf{r}; \sigma) \sum_{\sigma'} \int \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi_a(\mathbf{r}'; \sigma') \psi_b^*(\mathbf{r}'; \sigma') d\mathbf{r}'$$

# Ab initio

D'apres “Solid State Physics”, G. Grosso & G. P. Parravicini, Acad. Press, 2000

Transformation unitaire:  $\epsilon_{ab} \rightarrow \epsilon_a \delta_{ab}$

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V_{nuc}(\mathbf{r}) + V_{coul}(\mathbf{r}; [\{\psi\}]) + \hat{V}_{exch}(\mathbf{r}; [\{\psi\}]) \right) \psi_a(\mathbf{r}, \sigma) = \epsilon_a \psi_a(\mathbf{r}, \sigma)$$

“Canonical Hartree-Fock equations”

## Points d'interpretation

L'energie d'état fondamental

$$E_0^{HF} = \sum_a^{(occ)} \epsilon_a - \frac{1}{2} \sum_{ab}^{(occ)} \left( \langle \psi_a \psi_b | \frac{e^2}{r_{12}} | \psi_a \psi_b \rangle - \langle \psi_a \psi_b | \frac{e^2}{r_{12}} | \psi_b \psi_a \rangle \right)$$

L'energie d'ionisation

$$E_0^{HF}(N_e) - E_0^{HF}(N_e - 1) = \epsilon_m \quad \text{“Koopman's theorem”}$$

# Ab initio: V<sub>xc</sub> for uniform electron gas

D'apres "Solid State Physics", G. Grosso & G. P. Parravicini, Acad. Press, 2000

$$\psi_a^{(pw)}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_a \cdot \mathbf{r}} \quad \text{Spin states} \quad \alpha, \beta$$

$$\Psi = \det \{ (\psi_1^{(pw)} \alpha) (\psi_1^{(pw)} \beta) (\psi_2^{(pw)} \alpha) (\psi_2^{(pw)} \beta) \dots (\psi_{N_e/2}^{(pw)} \alpha) (\psi_{N_e/2}^{(pw)} \beta) \}$$

$$\begin{aligned} \hat{V}_{xc} \psi_a^{(pw)}(\mathbf{r}) &= - \sum_{b=1}^{(occ)} \frac{1}{\sqrt{V}} e^{i\mathbf{k}_b \cdot \mathbf{r}} \int \frac{1}{\sqrt{V}} e^{-i\mathbf{k}_b \cdot \mathbf{r}'} \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \frac{1}{\sqrt{V}} e^{i\mathbf{k}_a \cdot \mathbf{r}'} d\mathbf{r}' \\ &= - \frac{1}{\sqrt{V}} e^{i\mathbf{k}_a \cdot \mathbf{r}} \sum_{b=1}^{(occ)} \int \frac{1}{V} e^{i(\mathbf{k}_b - \mathbf{k}_a) \cdot (\mathbf{r} - \mathbf{r}')} \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\ &= - \psi_a^{(pw)}(\mathbf{r}) \sum_{\mathbf{k}_b < \mathbf{k}_F} \frac{4\pi e^2}{|\mathbf{k}_a - \mathbf{k}_b|} \end{aligned}$$

$$\hat{V}_{xc} \psi_j^{(pw)}(\mathbf{r}) = - \frac{2e^2 k_F}{\pi} F\left(\frac{k_j}{k_F}\right) \psi_j^{(pw)}(\mathbf{r}), \quad F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right|$$

$$F(0)=1 \quad F(1)=\frac{1}{2} \Rightarrow F\left(\frac{k}{k_F}\right) \approx \frac{3}{4} \Rightarrow \hat{V}_{xc} \psi_j^{(pw)}(\mathbf{r}) \approx - \frac{3e^2 k_F}{2\pi} \psi_j^{(pw)}(\mathbf{r})$$

# Ab initio: $V_{xc}$ for uniform electron gas

D'apres "Solid State Physics", G. Grosso & G. P. Parravicini, Acad. Press, 2000

$$\hat{V}_{xc} \psi_a^{(pw)}(\mathbf{r}) \approx -\frac{3e^2 k_F}{2\pi} \psi_a^{(pw)}(\mathbf{r})$$

Slater:

$$\hat{V}_{xc} \psi_a(\mathbf{r}) \approx -\frac{3e^2 k_F(n(\mathbf{r}))}{2\pi} \psi_a(\mathbf{r})$$



$$\hat{V}_{xc} \rightarrow V_{xc}(\mathbf{r}) = -\frac{3e^2 (3\pi^2 n(\mathbf{r}))^{1/3}}{2\pi}$$

# Thomas-Fermi Theory

D'apres Hans Bethe et Roman Jackiw, "Intermediate Quantum Mechanics", 1982.

Une electron dans un boit:

$$\psi_{n_x n_y n_z}(\mathbf{r}) = A \sin\left(\frac{2\pi n_x}{L} x\right) \sin\left(\frac{2\pi n_y}{L} y\right) \sin\left(\frac{2\pi n_z}{L} z\right)$$

$$E_{n_x n_y n_z} = \frac{\hbar^2}{2m} \left(\frac{2\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2) \equiv \frac{\hbar^2}{2m} k_{n_x n_y n_z}^2$$

Nombre des etats avec vecteur de l'onde  $k$

$$N(k) dk \sim 2 \times 4\pi (n_x^2 + n_y^2 + n_z^2) = 2 \times 4\pi \left(\frac{L}{2\pi}\right)^2 k^2 \frac{dk}{\left(\frac{2\pi}{L}\right)} = 2 \frac{V}{(2\pi)^3} 4\pi k^2 dk$$

$$N_e \text{ electrons avec 2 electrons par etat: } N_e = 2 \sum_{n_x, n_y, n_z} \sim 2 \frac{4\pi}{3} n_{max}^3 \quad n_{max} \sim \left(\frac{3 N_e}{8\pi}\right)^{1/3}$$

$$E_F \sim \frac{\hbar^2}{2m} \left(\frac{2\pi}{L}\right)^2 n_{max}^2 \sim \frac{\hbar^2}{2m} \left(\frac{3 N_e}{8\pi}\right)^{2/3} \left(\frac{2\pi}{L}\right)^2 = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N_e}{L^3}\right)^{2/3} = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N_e}{V}\right)^{2/3}$$

$$k_F = \left(\frac{3\pi^2 N_e}{V}\right)^{1/3} \Leftrightarrow \frac{N_e}{V} \equiv \rho = \frac{1}{3\pi^2} k_F^3$$



# Thomas-Fermi Theory

D'apres Hans Bethe et Roman Jackiw, "Intermediate Quantum Mechanics", 1982.

$$E_F \sim \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N_e}{V} \right)^{2/3} \quad N(k) dk \sim 2 \frac{V}{(2\pi)^3} 4\pi k^2 dk \quad k_F = \left( \frac{3\pi^2 N_e}{V} \right)^{1/3} \Leftrightarrow \frac{N_e}{V} \equiv \rho = \frac{1}{3\pi^2} k_F^3$$

Fermi distribution: 
$$f(E) = \frac{1}{e^{-\beta(E-\mu)} + 1} \Rightarrow_{T \rightarrow 0} \begin{cases} 1, E < \mu \\ 0, E > \mu \end{cases}$$

donc,  $\mu = E_F$

Dans une champ extern 
$$\mu - e\Phi(\mathbf{r}) = \frac{p_F^2(\mathbf{r})}{2m}$$

$$\rho(\mathbf{r}) = \frac{1}{3\pi^2} k_F^3(\mathbf{r}) = \frac{1}{3\pi^2} \hbar^{-3} p_F^3(\mathbf{r}) = \frac{1}{3\pi^2} \hbar^{-3} (2m)^{3/2} (\mu - e\Phi(\mathbf{r}))^{3/2}$$

L'equation de Poisson: 
$$\nabla^2 \Phi(\mathbf{r}) = \underbrace{-4\pi e \rho(\mathbf{r})}_{\text{electrons}} + \underbrace{4\pi Z e \delta(\mathbf{r})}_{\text{ions}}$$

$$\nabla^2 (e\Phi(\mathbf{r}) - \mu) \equiv \nabla^2 V_{TF}(\mathbf{r}) = -\frac{4e^2}{3\pi \hbar^3} (2m)^{3/2} (-V_{TF}(\mathbf{r}))^{3/2}$$

# Thomas-Fermi Theory

D'apres Hans Bethe et Roman Jackiw, "Intermediate Quantum Mechanics", 1982.

$$\nabla^2 (e\Phi(\mathbf{r}) - \mu) \equiv \nabla^2 V_{TF}(\mathbf{r}) = -\frac{4e^2}{3\pi\hbar^3} (2m)^{3/2} (-V_{TF}(\mathbf{r}))^{3/2}$$

Condition à la limite :  $V_{TF}(\mathbf{r}) \xrightarrow{r \rightarrow 0} -\frac{Ze^2}{r}$

Definissez  $b = \frac{(3\pi)^{2/3}}{2^{7/3}} \frac{\hbar^2}{me^2} Z^{-1/3} = 0.885 a_0 Z^{-1/3}$

$$x = r/b \qquad rV_{TF} = -Ze^2\Psi$$

L'equation Thomas-Fermi:  $\frac{d^2\Psi}{dx^2} = \frac{\Psi^{3/2}}{\sqrt{x}}, \quad \Psi(0)=1, \quad \Psi(r)>0$

Deuxieme condition à la limite:  $N_e = \int_0^{r_0} \rho(r) d\mathbf{r}$

# Thomas-Fermi-Dirac Theory

D'apres Hans Bethe et Roman Jackiw, "Intermediate Quantum Mechanics", 1982.

L'idee Thomas-Fermi:

$$E = \frac{p^2}{2m} + V(r) \Rightarrow E_{\max} = \mu = \frac{p_F^2}{2m} + V(r) \Rightarrow \rho(r) \Leftrightarrow V(r) \quad \text{+l'equation Poisson}$$

L'idee Thomas-Fermi-Dirac:

$$E = \frac{p^2}{2m} + V(r) + V_{xc}(r) \Rightarrow E_{\max} = \mu = \frac{p_F^2}{2m} + V(r) + V_{xc}(r) \Rightarrow \rho(r) \Leftrightarrow V(r) \quad \text{+l'equation Poisson}$$

# Thomas-Fermi-Dirac Theory

D'apres Hans Bethe et Roman Jackiw, "Intermediate Quantum Mechanics", 1982.

$$N(k) dk \sim 2 \frac{V}{(2\pi)^3} 4\pi k^2 dk \quad \rho = \frac{1}{3\pi^2} k_F^3$$

Derivation alternatif

$$E_K = \int d\mathbf{r} \left( \int_0^{k_F(\mathbf{r})} dk (N(k)/V) \frac{\hbar^2 k^2}{2m} \right) = \int d\mathbf{r} \frac{3}{5} \frac{\hbar^2 \pi^2}{2m} \left( \frac{3}{\pi} \rho(\mathbf{r}) \right)^{2/3} \rho(\mathbf{r})$$

$$E_V = \int d\mathbf{r} \left( -Z \frac{e^2}{r} \rho(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r}_2 \rho(\mathbf{r}) \rho(\mathbf{r}_2) \frac{e^2}{|\mathbf{r} - \mathbf{r}_2|} - \frac{1}{2} \frac{3e^2 (3\pi^2 \rho(\mathbf{r}))^{1/3}}{2\pi} \rho(\mathbf{r}) \right)$$

Minimizer:

$$0 = \frac{\delta E}{\delta \rho(\mathbf{r})} = \frac{\hbar^2 \pi^2}{2m} \left( \frac{3}{\pi} \rho(\mathbf{r}) \right)^{2/3} - Z \frac{e^2}{r} + \int d\mathbf{r}_2 \rho(\mathbf{r}_2) \frac{e^2}{|\mathbf{r} - \mathbf{r}_2|} - \frac{e^2 (3\pi^2 \rho(\mathbf{r}))^{1/3}}{\pi}$$

$$0 = \frac{\hbar^2 \pi^2}{2m} \left( \frac{3}{\pi} \rho(\mathbf{r}) \right)^{2/3} + V_{coul}(\mathbf{r}) - \frac{e^2 (3\pi^2 \rho(\mathbf{r}))^{1/3}}{\pi} \quad V_{coul}(\mathbf{r}) = -Z \frac{e^2}{r} + \int d\mathbf{r}_2 \rho(\mathbf{r}_2) \frac{e^2}{|\mathbf{r} - \mathbf{r}_2|}$$

# Thomas-Fermi-Dirac Theory

D'apres Hans Bethe et Roman Jackiw, "Intermediate Quantum Mechanics", 1982.

$$0 = \frac{\hbar^2 \pi^2}{2m} \left( \frac{3}{\pi} \rho(\mathbf{r}) \right)^{2/3} + V_{coul}(\mathbf{r}) - \frac{e^2 (3\pi^2 \rho(\mathbf{r}))^{1/3}}{\pi}$$

$$\Rightarrow a_0 (3\rho/\pi)^{1/3} \equiv y = \frac{1}{\pi^2} \left( 1 + \sqrt{1 - 2\pi^2 \frac{V a_0}{e^2}} \right), \quad a_0 \equiv \frac{\hbar^2}{m e^2}$$

$$\Rightarrow y = \frac{\sqrt{2}}{\pi} \left( \sqrt{\Psi} + \frac{1}{\pi \sqrt{2}} \right), \quad \Psi \equiv \frac{1}{2\pi^2} - \frac{a_0 V}{e^2}$$

L'equation de Poisson:

$$\frac{d^2}{dr^2}(r \Psi) = \frac{2^{7/2}}{3 a_0^2 \pi} r \left( \sqrt{\Psi} + \frac{1}{\pi \sqrt{2}} \right)^2$$

Definissez

$$x = r/b$$

$$r \Psi = a_0 Z \Phi$$

$$b = \frac{(3\pi)^{2/3}}{2^{7/3}} \frac{\hbar^2}{m e^2} Z^{-1/3} = 0.885 a_0 Z^{-1/3}$$

$$\Phi'' = x \left( \sqrt{\frac{\Phi}{x}} + \beta \right)^3, \quad \beta \equiv \sqrt{\frac{b}{a_0 Z}} \frac{1}{\pi \sqrt{2}} = 0.2118 Z^{-2/3}$$

“Thomas-Fermi-Dirac equation”

# Comparison

D'apres Hans Bethe et Roman Jackiw, “Intermediate Quantum Mechanics”, 1982.

Level	HF	Thomas-Fermi-Dirac
1s	1828	1805
2s	270	263
2p	251	245
3d	29.8	29.2
4s	8.46	7.95

Comparison of energy levels of Ag (values in Ry). (Solution of Schrodinger equation with TFD potential. R. Latter, Phys. Rev. **99**, 510 (1955)).

# Density Functional Theory

- Introduction
  - Ab initio
  - Thomas-Fermi
  - Thomas-Fermi-Dirac
- 0K DFT
  - Hohenberg-Kohn theoreme
  - Kohn-Sham equations
  - Approximations for the exchange term
- $T > 0$ 
  - Théorème fondamental du DFT

# Hohenberg-Kohn théorème

P. Hohenberg et W. Kohn, Phys. Rev. B 136, 864 (1964).

N électrons dans un champ extérieur:

$$\begin{aligned} H &= H_{ee} + V_{ext} \\ H_{ee} &= T + V_{ee} = \sum_{j=1}^N \frac{\hbar^2}{2m} \nabla_j^2 + \frac{1}{2} \sum_{j \neq l} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_l|} \\ V_{ext} &= \sum_{j=1}^N v_{ext}(\mathbf{r}_j), \quad v_{ext}(\mathbf{r}) = - \sum_I \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R}_I|} \end{aligned}$$

Densité (de nombre) électronique locale:

$$n(\mathbf{r}) = \langle \hat{n}(\mathbf{r}) \rangle = \int \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_j) |\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_1 \dots d\mathbf{r}_N$$

**Hohenberg-Kohn théorème:** *il y a une relation un à un entre la densité de l'état fondamentale et le potentiel extérieur.*



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Densité (de nombre) électronique locale:

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# Hohenberg-Kohn théorème

P. Hohenberg et W. Kohn, Phys. Rev. B 136, 864 (1964).

$$n_G(\mathbf{r}) = \langle \hat{n}(\mathbf{r}) \rangle_G = \int \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_j) |\Psi_G(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_1 \dots d\mathbf{r}_N$$

**Hohenberg-Kohn théorème:** *il y a une relation un à un entre la densité de l'état fondamentale et le potentiel extérieur.*

## Preuve:

Partie 1: le potentiel extérieur détermine la densité: trivial

$$v_{\text{ext}}(\mathbf{r}) \Rightarrow \Psi_G[v_{\text{ext}}] \Rightarrow n(\mathbf{r})$$

Partie 2: la densité détermine le potentiel

Soit 
$$v_{\text{ext}}^{(a)}(\mathbf{r}) \neq v_{\text{ext}}^{(b)}(\mathbf{r}) \Rightarrow H^{(a)} = H_{\text{ee}} + V_{\text{ext}}^{(a)} \neq H^{(b)} = H_{\text{ee}} + V_{\text{ext}}^{(b)}$$

Avec les états fondamentaux

$$H^{(j)} \Psi_G^{(j)} = E_G^{(j)} \Psi_G^{(j)}, \quad j = a, b$$

# Hohenberg-Kohn théorème

P. Hohenberg et W. Kohn, Phys. Rev. B 136, 864 (1964).

$$n_G(\mathbf{r}) = \langle \hat{n}(\mathbf{r}) \rangle_G = \int \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_j) |\Psi_G(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_1 \dots d\mathbf{r}_N$$

**Hohenberg-Kohn théorème:** *il y a une relation un à un entre la densité de l'état fondamentale et le potentiel extérieur.*

**Preuve:**      Partie 2: la densité détermine le potentiel

$$H^{(j)} \Psi_G^{(j)} = E_G^{(j)} \Psi_G^{(j)}, \quad j = a, b$$

$$E_G^{(a)} < \langle H^{(a)} \rangle_{Gb} = \langle H^{(b)} + V_{\text{ext}}^{(a)} - V_{\text{ext}}^{(b)} \rangle_{Gb} = E_G^{(b)} + \int n_G^{(b)}(\mathbf{r}) \left( v_{\text{ext}}^{(a)}(\mathbf{r}) - v_{\text{ext}}^{(b)}(\mathbf{r}) \right) d\mathbf{r}$$

$$E_G^{(b)} < E_G^{(a)} + \int n_G^{(a)}(\mathbf{r}) \left( v_{\text{ext}}^{(b)}(\mathbf{r}) - v_{\text{ext}}^{(a)}(\mathbf{r}) \right) d\mathbf{r}$$

Sommez:

$$E_G^{(a)} + E_G^{(b)} < E_G^{(a)} + E_G^{(b)} + \int \left( n_G^{(a)}(\mathbf{r}) - n_G^{(b)}(\mathbf{r}) \right) \left( v_{\text{ext}}^{(b)}(\mathbf{r}) - v_{\text{ext}}^{(a)}(\mathbf{r}) \right) d\mathbf{r}$$

$$0 < \int \left( n_G^{(a)}(\mathbf{r}) - n_G^{(b)}(\mathbf{r}) \right) \left( v_{\text{ext}}^{(b)}(\mathbf{r}) - v_{\text{ext}}^{(a)}(\mathbf{r}) \right) d\mathbf{r}$$

$$\Rightarrow n_G^{(a)}(\mathbf{r}) \neq n_G^{(b)}(\mathbf{r})$$

# Hohenberg-Kohn théorème

P. Hohenberg et W. Kohn, Phys. Rev. B 136, 864 (1964).

**Hohenberg-Kohn théorème:** *il y a une relation un à un entre la densité de l'état fondamental et le potentiel extérieur.*

**Preuve:**  $v_{\text{ext}}(\mathbf{r}) \Rightarrow n(\mathbf{r}) = n(\mathbf{r}, [v_{\text{ext}}])$       SO       $n^{(a)}(\mathbf{r}) \neq n^{(b)}(\mathbf{r}) \Rightarrow v_{\text{ext}}^{(a)}(\mathbf{r}) \neq v_{\text{ext}}^{(b)}(\mathbf{r})$   
 $v_{\text{ext}}^{(a)}(\mathbf{r}) \neq v_{\text{ext}}^{(b)}(\mathbf{r}) \Rightarrow n^{(a)}(\mathbf{r}) \neq n^{(b)}(\mathbf{r})$        $v_{\text{ext}}^{(a)}(\mathbf{r}) \neq v_{\text{ext}}^{(b)}(\mathbf{r}) \Rightarrow n^{(a)}(\mathbf{r}) \neq n^{(b)}(\mathbf{r})$



relation inversible

$$n(\mathbf{r}, [v_{\text{ext}}]) \Leftrightarrow v(\mathbf{r}, [n_{\text{ext}}])$$

**Conséquences:**  $\Psi_G = \Psi_G[v_{\text{ext}}] = \Psi_G[v_{\text{ext}}[n]] \Rightarrow \Psi_G[n]$

$$E[\Psi_G] \Rightarrow E[n]$$

$$E_G \equiv E[\Psi_G] = \min_{\Psi} E[\Psi] \Rightarrow E_G = \min_{n(\mathbf{r})} E[n]$$

# Kohn-Sham equations

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

D'après "Solid State Physics", G. Grosso & G. P. Parravicini, Acad. Press, 2000

Developper le densite:

$$n(\mathbf{r}) = \sum_i \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r})$$

(C'est la densité pour un système des électrons qui n'interact pas. C'est une conséquence de la HKT que pour toutes densité donnée, il y a un potentiel extérieur qui donne la meme densité pour un système sans interaction.)

Definnesez:

$$T_0[n] \equiv \sum_i \langle \phi_i | \left( -\frac{\hbar^2}{2m} \nabla^2 \right) | \phi_i \rangle$$

$$T_0 = \langle \Psi_0 | \Psi_0 \rangle, \quad \Psi_0 = \det \phi$$

$$V_H[n] \equiv \int n(\mathbf{r}) \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

$$E^{KS}[n; v_{ext}] = T_0[n] + V_H[n] + \int n(\mathbf{r}) v_{ext}(\mathbf{r}) d\mathbf{r} + E_{xc}[n]$$

$$E_{xc}[n] = T[n] - T_0[n] + V_{ee}[n] - V_H[n]$$

# Kohn-Sham equations

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

D'apres "Solid State Physics", G. Grosso & G. P. Parravicini, Acad. Press, 2000

Minimisez:

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + V_{\text{coul}}(\mathbf{r}; [\phi]) + V_{\text{xc}}(\mathbf{r}; [\phi]) \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$$V_{\text{coul}}(\mathbf{r}; [\phi]) \equiv \int \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}') d\mathbf{r}' \qquad V_{\text{xc}}(\mathbf{r}, [\phi]) \equiv \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}$$

"Kohn-Sham equations"

"Local density approximation" : pour un gaz d'electrons avec constante densite  $n$  l'energie d'exchange est un fonction de  $n$

$$E_{\text{XC}}[n] \rightarrow_{n(\mathbf{r})=n} e_{\text{XC}}(n) N_e = \int e_{\text{XC}}(n) n d\mathbf{r}$$

$$\text{LDA: } E_{\text{xc}}^{(\text{LDA})}[n] \approx \int e_{\text{xc}}(n(\mathbf{r})) n(\mathbf{r}) d\mathbf{r} \Rightarrow V_{\text{xc}}^{(\text{LDA})} = e_{\text{xc}}(n(\mathbf{r})) + \frac{\partial e_{\text{xc}}(n(\mathbf{r}))}{\partial n(\mathbf{r})} n(\mathbf{r})$$

# Kohn-Sham equations

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

D'apres "Solid State Physics", G. Grosso & G. P. Parravicini, Acad. Press, 2000

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + V_{\text{coul}}(\mathbf{r}; [\phi]) + V_{\text{xc}}(\mathbf{r}; [\phi]) \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$$V_{\text{coul}}(\mathbf{r}; [\phi]) \equiv \int \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}') d\mathbf{r}' \qquad V_{\text{xc}}^{(\text{LDA})} = e_{\text{xc}}(n(\mathbf{r})) + \frac{\partial e_{\text{xc}}(n(\mathbf{r}))}{\partial n(\mathbf{r})} n(\mathbf{r})$$

Empirical fit to simulations of uniform electron gas:

$$e_{\text{xc}}(n) = -\frac{0.4582}{r_s} + \begin{cases} -0.1423 / (1 + 1.0529 \sqrt{r_s} + 0.3334 r_s), & r_s \geq 1 \\ -0.0480 + 0.0311 \ln r_s - 0.0116 r_s + 0.0020 r_s \ln r_s, & r_s \leq 1 \end{cases}$$

$$\frac{4\pi}{3} (r_s a_B)^3 = \frac{1}{n}, \quad [e_{\text{xc}}] = \text{Hartrees}$$

J. P. Perdew and A. Zunger, Phys. Rev. B23, 5048 (1981).

# Kohn-Sham equations

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

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + V_{\text{coul}}(\mathbf{r}; [\phi]) + V_{\text{xc}}(\mathbf{r}; [\phi]) \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

$$V_{\text{coul}}(\mathbf{r}; [\phi]) \equiv \int \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}') d\mathbf{r}' \qquad V_{\text{xc}}(\mathbf{r}, [\phi]) \equiv \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}$$

$$E_{\text{xc}}^{(\text{LDA})}[n] \approx \int e_{\text{ex}}(n(\mathbf{r})) n(\mathbf{r}) d\mathbf{r}$$

$$E_{\text{xc}}^{(\text{WDA})}[n] \approx \int e_{\text{ex}}(\bar{n}(\mathbf{r})) n(\mathbf{r}) d\mathbf{r}, \quad \bar{n}(\mathbf{r}) = \int w(|\mathbf{r} - \mathbf{r}'|) n(\mathbf{r}') d\mathbf{r}'$$

$$E_{\text{xc}}^{(\text{GGA})}[n] \approx \int e_{\text{ex}}(n(\mathbf{r}); \nabla n(\mathbf{r})) n(\mathbf{r}) d\mathbf{r},$$



# Comparison

D'apres “Solid State Physics”, G. Grosso & G. P. Parravicini, Acad. Press, 2000

TABLE I. Binding energies (eV/atom) calculated by the HF, LDA, and DMC methods compared with the available experimental data. HF and DMC valence atomic energies are  $-99.773$  and  $-102.121(3)$  eV, respectively.

	HF	LDA	DMC	Expt.
$\text{Si}_2$ ( $D_{2h}$ )	0.85	1.98	1.580(7)	1.61(4)
$\text{Si}_3$ ( $C_{3v}$ )	1.12	2.92	2.374(8)	2.45(6)
$\text{Si}_4$ ( $D_{2h}$ )	1.61	3.50	2.86(2)	3.01(6)
$\text{Si}_6$ ( $C_{2v}$ )	1.82	4.00	3.26(1)	3.42(4)
$\text{Si}_7$ ( $D_{3h}$ )	1.91	4.14	3.43(2)	3.60(4)
$\text{Si}_9$ ( $C_s$ )	1.74	4.06	3.28(2)	...
$\text{Si}_9$ ( $D_{3h}$ )	1.77	4.14	3.39(2)	...
$\text{Si}_{10}$ ( $T_d$ )	1.94	4.25	3.44(2)	...
$\text{Si}_{10}$ ( $C_{3v}$ )	1.89	4.32	3.48(2)	...
$\text{Si}_{13}$ ( $I_h$ )	1.41	3.98	3.12(2)	...
$\text{Si}_{13}$ ( $C_{3v}$ )	1.80	4.28	3.41(1)	...
$\text{Si}_{13}^-$ ( $C_{3v}$ )	1.88	4.43	3.56(1)	...
$\text{Si}_{20}$ ( $I_h$ )	1.61	4.10	3.23(3)	...
$\text{Si}_{20}$ ( $C_{3v}$ )	1.55	4.28	3.43(3)	...

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Jeffrey C. Grossman and Lubos Mitas, “*Quantum Monte Carlo Determination of Electronic and Structural Properties of  $\text{Si}_n$  clusters ( $n \sim 20$ )*”, Phys. Rev. Lett. **74**, 1323 (1995)

# Comparison

	method	-E/a.u.
	Thomas-Fermi	625.7
	Hartree-Fock	526.818
	OEP (exchange only)	526.812
	LDA (exchange only)	524.517
	LDA (VWN)	525.946
	LDA (PW92)	525.940
	LDA-SIC(PZ)	528.393
Nonlocal (weighted density)	ADA	527.322
	WDA	528.957
Generalized Gradient	GGA (B88LYP)	527.551
	experiment	527.6

Table 1: Ground-state energy in atomic units ( $1 \text{ a.u.} = 1 \text{ Hartree} = 2 \text{ Rydberg} = 27.21 \text{ eV} \hat{=} 627.5 \text{ kcal/mol}$ ) of the *Ar* atom ( $Z = 18$ ), obtained with some representative density functionals and related methods. The Hartree-Fock and OEP(exchange only) values are from Krieger et al. (third of Ref. [120]), ADA and WDA values are from Gunnarsson et al., Ref. [129], as reported in Ref. [5], and the LDA-SIC(PZ) value is from Perdew and Zunger, Ref. [93]. The experimental value is based on Veillard and Clementi, J. Chem. Phys. **49**, 2415 (1968), and given to less significant digits than the calculated values, because of relativistic and quantum electrodynamical effects (Lamb shift) that are automatically included in the experimental result but not in the calculated values.

Klaus Capelle, “A *bird's eye view of density functional theory*”, <http://arxiv.org/abs/cond-mat/0211443> (2006).