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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Functionals

A ***function*** maps *numbers* to *numbers*: $f(x_{1,} \ldots, x_N) = (y_{1,\ldots}, y_m)$

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:

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

Alternative notation:

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

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

Functionals

A *function* maps real numbers to real numbers: $f(x_{1,} \ldots, x_N) = (y_{1,\ldots}, y_m)$

A *functional* maps functions and numbers to functions.

Example for mapping a function to a number:

$$x = F[f] = \int_0^\infty f(\boldsymbol{s})\, d\boldsymbol{s}$$

$$x = F[f] = f(\boldsymbol{s_0})$$

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

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

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

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

Functional Derivatives

Definition:

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

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

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

Example: $\quad F[f] = \int f(\boldsymbol{s}) d\boldsymbol{s}$

$$\lim_{\epsilon \to 0} \frac{F[f+\epsilon g]-F[f]}{\epsilon} = \lim_{\epsilon \to 0} \frac{\int \left(f(\boldsymbol{s}) + \epsilon g(\boldsymbol{s}) \right) d\boldsymbol{s} - \int f(\boldsymbol{s}) d\boldsymbol{s}}{\epsilon}$$

$$= \int g(\boldsymbol{s}) d\boldsymbol{s}$$

so $\dfrac{\delta F[f]}{\delta f(\boldsymbol{r})} = 1$

Functional Derivatives

Definition:

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

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

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

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

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

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

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: $f(\boldsymbol{r}) \rightarrow (f_{1,} \ldots f_N)$ with $f_j \equiv f(x_j)$

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

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

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

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

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Ab initio

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

But: détermination de l'état fondamental d'un système d'électrons dans une champ exteriour.
Stratégie: calcul variationnel.

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

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

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

$$P_a\in S_N,\quad p_a=parity\,of\;P_a$$

Slater determinant:

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

Ab initio

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

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

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

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

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

$$\langle\hat{O}\rangle_G=\frac{1}{2}\sum_{1\le a<b\le N}\left(\langle\psi_a\psi_b|\hat{o}|\psi_a\psi_b\rangle-\langle\psi_a\psi_b|\hat{o}|\psi_b\psi_a\rangle\right)$$

$$=\frac{1}{2}\sum_{1\le a<b\le N}\left(\langle\psi_a(\boldsymbol{r}_1)\psi_b(\boldsymbol{r}_2)|\hat{o}(\boldsymbol{r}_1,\boldsymbol{r}_2)|\psi_a(\boldsymbol{r}_1)\psi_b(\boldsymbol{r}_2)\rangle-\underbrace{\langle\psi_a(\boldsymbol{r}_1)\psi_b(\boldsymbol{r}_2)|\hat{o}(\boldsymbol{r}_1,\boldsymbol{r}_2)|\psi_b(\boldsymbol{r}_1)\psi_{aj}(\boldsymbol{r}_2)\rangle}_{\text{exchange term}}\right)$$

Ab initio

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

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

Hamiltonienne:

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

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

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

Coordonnées des noyaux

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

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

Ab initio

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

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

Lagrangian:

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

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

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

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

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

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

Ab initio

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

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

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

"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

$$E_0^{HF}(N_e) - E_0^{HF}(N_e - 1) = \epsilon_m$$

"Koopman's theorem"

Ab initio: Vxc for uniform electron gas

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

$$\psi_a^{(pw)}(\boldsymbol{r}) = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}_a\cdot\boldsymbol{r}}$$ Spin states α,β

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

$$\hat{V}_{xc}\psi_a^{(pw)}(\boldsymbol{r}) = -\sum_{b=1}^{(occ)} \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}_b\cdot\boldsymbol{r}} \int \frac{1}{\sqrt{V}} e^{-i\boldsymbol{k}_b\cdot\boldsymbol{r}'} \frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|} \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}_a\cdot\boldsymbol{r}'} d\boldsymbol{r}'$$

$$= -\frac{1}{\sqrt{V}} e^{i\boldsymbol{k}_a\cdot\boldsymbol{r}} \sum_{b=1}^{(occ)} \int \frac{1}{V} e^{i(\boldsymbol{k}_b-\boldsymbol{k}_a)\cdot(\boldsymbol{r}-\boldsymbol{r}')} \frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}'$$

$$= -\psi_a^{(pw)}(\boldsymbol{r}) \sum_{k_b<k_F} \frac{4\pi e^2}{|\boldsymbol{k}_a-\boldsymbol{k}_b|}$$

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

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

Ab initio: Vxc for uniform electron gas

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

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

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

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

Thomas-Fermi Theory

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

Une electron dans un boit:

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

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

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

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

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

Thomas-Fermi Theory

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

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

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 $$\mu - e\Phi(\boldsymbol{r}) = \frac{p_F^2(\boldsymbol{r})}{2m}$$

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

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

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

Thomas-Fermi Theory

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

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

Condition à la limite : $V_{TF}(\boldsymbol{r}) \to_{r\to 0} -\frac{Ze^2}{r}$

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: $N_e = \int_0^{r_0} \rho(r)\, d\boldsymbol{r}$

Thomas-Fermi-Dirac Theory

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

L'idee Thomas-Fermi:

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

L'idee Thomas-Fermi-Dirac:

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

+l'equation Poisson

Thomas-Fermi-Dirac Theory

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

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

Derivation alternatif

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

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

Minimizer:

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

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

Thomas-Fermi-Dirac Theory

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

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

$$\Rightarrow a_0(3\rho/\pi)^{1/3}\equiv y=\frac{1}{\pi^2}\left(1+\sqrt{1-2\pi^2\frac{Va_0}{e^2}}\right),\quad a_0\equiv\frac{\hbar^2}{m e^2}$$

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

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

Definissez $x=r/b$ $\quad r\Psi=a_0 Z\Phi$ $\quad b=\frac{(3\pi)^{2/3}}{2^{7/3}}\frac{\hbar^2}{me^2}Z^{-1/3}=0.885\,a_0 Z^{-1/3}$

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

“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

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Hohenberg-Kohn théorème

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

N électrons dans un champ extérieur:

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

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

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

Densité (de nombre) électronique locale:

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

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

Hohenberg-Kohn théorème

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$$V_{ext} = \int \hat{n}(\boldsymbol{r}) v_{ext}(\boldsymbol{r}) d\boldsymbol{r}$$

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Hohenberg-Kohn théorème

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

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

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

Preuve:

Partie 1: la potentiel exterieur détermine la densite: trivial

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

Partie 2: la densité détermine la potentiel

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

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

Hohenberg-Kohn théorème

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

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

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

Preuve: Partie 2: la densité détermine la potentiel

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

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

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

Sommez:

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

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

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

Hohenberg-Kohn théorème

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

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

Preuve:

$$v_{ext}(\boldsymbol{r}) \Rightarrow n(\boldsymbol{r}) = n(\boldsymbol{r},[v_{ext}])$$
$$v_{ext}^{(a)}(\boldsymbol{r}) \neq v_{ext}^{(b)}(\boldsymbol{r}) \Rightarrow n^{(a)}(\boldsymbol{r}) \neq n^{(b)}(\boldsymbol{r})$$

SO

$$n^{(a)}(\boldsymbol{r}) \neq n^{(b)}(\boldsymbol{r}) \Rightarrow v_{ext}^{(a)}(\boldsymbol{r}) \neq v_{ext}^{(b)}(\boldsymbol{r})$$
$$v_{ext}^{(a)}(\boldsymbol{r}) \neq v_{ext}^{(b)}(\boldsymbol{r}) \Rightarrow n^{(a)}(\boldsymbol{r}) \neq n^{(b)}(\boldsymbol{r})$$

$\Rightarrow$ relation inversible

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

Conséquences:

$$\Psi_G = \Psi_G[v_{ext}] = \Psi_G[v_{ext}[n]] \Rightarrow \Psi_G[n]$$

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

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

Kohn-Sham equations

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

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

Developper le densite: $n(\boldsymbol{r}) = \sum_i \phi_i^*(\boldsymbol{r}) \phi_i(\boldsymbol{r})$

(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.)

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

Definnesez:

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

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

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

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

Kohn-Sham equations

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

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

Minimisez:

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

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

“Kohn-Sham equations”

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

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

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

Kohn-Sham equations

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

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

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

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

Empirical fit to simulations of uniform electron gas:

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

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

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).

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

$$V_{coul}(\boldsymbol{r};[\phi])\equiv\int\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}n(\boldsymbol{r}')\,d\boldsymbol{r}'$$

$$V_{xc}(\boldsymbol{r},[\phi])\equiv\frac{\delta E_{xc}[n]}{\delta n(\boldsymbol{r})}$$

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

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

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

Comparison

D'apres "Solid State Physics", G. Grosso & G. P. Parrravicini, 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.
Si_2 (D_{2h})	0.85	1.98	1.580(7)	1.61(4)
Si_3 (C_{3v})	1.12	2.92	2.374(8)	2.45(6)
Si_4 (D_{2h})	1.61	3.50	2.86(2)	3.01(6)
Si_6 (C_{2v})	1.82	4.00	3.26(1)	3.42(4)
Si_7 (D_{5h})	1.91	4.14	3.43(2)	3.60(4)
Si_9 (C_s)	1.74	4.06	3.28(2)	···
Si_9 (D_{h3})	1.77	4.14	3.39(2)	···
Si_{10} (T_d)	1.94	4.25	3.44(2)	···
Si_{10} (C_{3v})	1.89	4.32	3.48(2)	···
Si_{13} (I_h)	1.41	3.98	3.12(2)	···
Si_{13} (C_{3v})	1.80	4.28	3.41(1)	···
Si_{13}^- (C_{3v})	1.88	4.43	3.56(1)	···
Si_{20} (I_h)	1.61	4.10	3.23(3)	···
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 Si_n clusters (n ~ 20)*", Phys. Rev. Lett. **74**, 1323 (1995)

Comparison

Nonlocal (weighted density)

Generalized Gradient

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
ADA	527.322
WDA	528.957
GGA (B88LYP)	527.551
experiment	527.6

Table 1: Ground-state energy in atomic units (1 a.u. = 1 Hartree = 2 Rydberg = $27.21eV \hat{=} 627.5kcal/mol$) 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).

Density Functional Theory

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  - Thomas-Fermi-Dirac
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  - Théorème fondamental du DFT

Théorème fondamental du DFT: départ

N particule $\Gamma^{(N)}=(\boldsymbol{q}_1, \boldsymbol{p}_1 \ldots \boldsymbol{q}_N, \boldsymbol{p}_N)$

Hamiltonienne $H^{(N)}=\sum_{i=1}^{N} \frac{p_i^2}{2\mathrm{m}_i}+\sum_{1\le i<j\le N} U(q_{ij})+\sum_{i=1}^{N} \phi(\boldsymbol{q}_i)$

Grand-canonical equilibrium distribution

$$f_N(\Gamma;[\phi])=\frac{1}{\Xi[\phi]N!h^{ND}}\exp\left(-\beta\left(H^{(N)}-\mu N\right)\right)$$

$$\Xi[\phi]\equiv\exp(-\beta\Omega[\phi])=\sum_{N=0}^{\infty}\frac{1}{N!h^{ND}}\int\exp\left(-\beta\left(H^{(N)}-\mu N\right)\right)d\Gamma^{(N)}$$

Definissez la densite locale: $\hat{\rho}(\boldsymbol{r})=\sum_{i=1}^{N}\delta(\boldsymbol{r}-\boldsymbol{q}_i)$

Alors, $\frac{\delta\Omega[\phi]}{\delta\phi(\boldsymbol{r})}=-\langle\hat{\rho}(\boldsymbol{r})\rangle\equiv-\rho(\boldsymbol{r})$

"Ensemble-averaged density"

Lutsko, Adv. Chem. Phys. **144**, 1-91 (2010).

Théorème fondamental du DFT

N. D. Mermin, Phys. Rev. 137, A1441 (1965).

Definissez la fonctionale:
$$f_N(\Gamma;[\phi])=\frac{1}{\Xi[\phi]\,N!\,h^{ND}}\exp\left(-\beta\left(H^{(N)}-\mu N\right)\right)$$

$$\Lambda[\phi,\phi_0]\equiv k_B T\sum_{N=0}^{\infty}\int\left(\ln\left(f_N(\Gamma^{(N)};[\phi])/f_N(\Gamma^{(N)};[\phi_0])\right)-\ln\Xi[\phi_0]\right)f_N(\Gamma^{(N)};[\phi])\,d\Gamma^{(N)}$$

et notez que
$$\Lambda[\phi_0,\phi_0]=-k_B T\ln\Xi[\phi_0]=\Omega[\phi_0]$$

de sorte que
$$\Lambda[\phi,\phi_0]=\Lambda[\phi_0,\phi_0]+k_B T\sum_{N=0}^{\infty}\int f_N(\Gamma^{(N)};[\phi])\ln\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}\right)d\Gamma^{(N)}$$

En utilisant $x\ln x\geq x-1$ avec égalité si et seulement si $x=1$

$$\int_N f_N(\Gamma^{(N)};[\phi])\ln\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}\right)d\Gamma^{(N)}$$
$$=\int f_N(\Gamma^{(N)};[\phi_0])\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}\right)\ln\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}\right)d\Gamma^{(N)}$$
$$\geq\int f_N(\Gamma^{(N)};[\phi_0])\left(\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}\right)-1\right)d\Gamma^{(N)}=0$$

Théorème fondamental du DFT

N. D. Mermin, Phys. Rev. 137, A1441 (1965).

$$f_N(\Gamma;[\phi])=\frac{1}{\Xi[\phi]N!h^{ND}}\exp(-\beta(H^{(N)}-\mu N))$$

$$\Lambda[\phi,\phi_0]=\Lambda[\phi_0,\phi_0]+k_BT\sum_{N=0}^{\infty}\int f_N(\Gamma^{(N)};[\phi])\ln\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}\right)d\Gamma^{(N)}$$

Donc,

$$\int_N f_N(\Gamma^{(N)};[\phi])\ln\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}\right)d\Gamma^{(N)}\geq 0$$

$$\Rightarrow\Lambda[\phi,\phi_0]\geq\Lambda[\phi_0,\phi_0]$$

avec égalité si et seulement si $f_N(\Gamma^{(N)};[\phi])=f_N(\Gamma^{(N)};[\phi_0])$

ca veux dire $\phi(\boldsymbol{r})=\phi_0(\boldsymbol{r})+\text{constante}$

Mais, avec la forme explicite des distributions,

$$\Lambda[\phi,\phi_0]=\Lambda[\phi,\phi]+\int(\phi(\boldsymbol{r})-\phi_0(\boldsymbol{r}))\rho(\boldsymbol{r};[\phi])\,d\boldsymbol{r}$$

Donc, $\Lambda[\phi_0,\phi_0]\leq\Lambda[\phi,\phi]+\int(\phi(\boldsymbol{r})-\phi_0(\boldsymbol{r}))\rho(\boldsymbol{r};[\phi])\,d\boldsymbol{r}$

Théorème fondamental du DFT

N. D. Mermin, Phys. Rev. 137, A1441 (1965).

$$\Lambda[\phi_0,\phi_0]\leq\Lambda[\phi,\phi]+\int\left(\phi(\boldsymbol{r})-\phi_0(\boldsymbol{r})\right)\rho(\boldsymbol{r};[\phi])\,d\boldsymbol{r}$$

On peut répéter l'argument avec $\phi\Leftrightarrow\phi_0$

$$\Lambda[\phi,\phi]\leq\Lambda[\phi_0,\phi_0]+\int\left(\phi_0(\boldsymbol{r})-\phi(\boldsymbol{r})\right)\rho(\boldsymbol{r};[\phi_0])\,d\boldsymbol{r}$$

Donc, si $\rho(\boldsymbol{r};[\phi_0])=\rho(\boldsymbol{r};[\phi])$ on trouve que

$$\Lambda[\phi_0,\phi_0]-\Lambda[\phi,\phi]\leq\int\left(\phi(\boldsymbol{r})-\phi_0(\boldsymbol{r})\right)\rho(\boldsymbol{r};[\phi])\,d\boldsymbol{r}\leq\Lambda[\phi_0,\phi_0]-\Lambda[\phi,\phi]$$

Conclusion: $\phi\neq\phi_0\Rightarrow\rho(\boldsymbol{r};[\phi])\neq\rho(\boldsymbol{r};[\phi_0])$

Car il est claire que $\rho(\boldsymbol{r};[\phi])\neq\rho(\boldsymbol{r};[\phi_0])\Rightarrow\phi\neq\phi_0$ la relation est un a un.

Théorème fondamental du DFT

N. D. Mermin, Phys. Rev. 137, A1441 (1965).

Conclusion: $\phi \neq \phi_0 \Rightarrow \rho(\boldsymbol{r};[\phi]) \neq \rho(\boldsymbol{r};[\phi_0])$

Car il est claire que $\rho(\boldsymbol{r};[\phi]) \neq \rho(\boldsymbol{r};[\phi_0]) \Rightarrow \phi \neq \phi_0$

1. La relation entre densité est champ est un a un.

2.La distribution est une fonctionnel de la densite

$$f_N(\Gamma;[\phi]) \rightarrow f_N(\Gamma;[\rho])$$

3. Il y a un fonctionnel $\Omega[\rho,\phi_0] \equiv \Lambda[\phi[\rho],\phi_0]$ et car $\Lambda[\phi,\phi_0] \geq \Lambda[\phi_0,\phi_0]$

$\Omega[\rho,\phi_0]$ est minimizée par $\rho = \rho_0 \equiv \rho[\phi_0]$

4. $\Omega[\rho_0,\phi_0] = \Omega[\phi_0]$

5. $\Omega[\rho,\phi_0] = F[\rho] + \int \phi_0(\boldsymbol{r})\rho(\boldsymbol{r})d\boldsymbol{r}$ où "F" est indépendant du champ.

Lutsko, Adv. Chem. Phys. **144**, 1-91 (2010).

Density Functional Theory

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  - Applications

Le début de la DFT

N particule $\Gamma^{(N)} = (\boldsymbol{q}_1, \boldsymbol{p}_1 \ldots \boldsymbol{q}_N, \boldsymbol{p}_N)$

Hamiltonienne $H^{(N)} = \sum_{i=1}^{N} \frac{p_i^2}{2\mathrm{m}_i} + \sum_{1 \le i < j \le N} U(q_{ij}) + \sum_{i=1}^{N} \phi(\boldsymbol{q}_i)$

Grand-canonical equilibrium distribution

$$\langle O(\boldsymbol{\Gamma}) \rangle = \sum_{N=1}^{\infty} \frac{Z_N}{\Xi[\phi]\, N!\, h^{ND}} \exp(\beta \mu N) \int f^{(N)}(\boldsymbol{\Gamma})\, O^{(N)}(\Gamma^{(N)})\, d\Gamma^{(N)}$$

$$f^{(N)}(\Gamma^{(N)}) = \frac{1}{Z_N\, N!\, h^{ND}} \exp(-\beta H^{(N)})$$

$$Z_N[\phi] \equiv \exp(-\beta F[\phi]) = \frac{1}{N!\, h^{ND}} \int \exp(-\beta H^{(N)})\, d\Gamma^{(N)}$$ Helmholtz energie libre

$$\Xi[\phi] \equiv \exp(-\beta \Omega[\phi]) = \sum_{N=0}^{\infty} \frac{1}{N!\, h^{ND}} \int \exp(-\beta (H^{(N)} - \mu N))\, d\Gamma^{(N)}$$

"Grand potential"

Le début de la DFT: Densité locale

$$\Xi[\phi]\equiv\exp(-\beta\Omega[\phi])=\sum_{N=0}^{\infty}\frac{1}{N!\,h^{ND}}\int\exp(-\beta(H^{(N)}-\mu N))\,d\Gamma^{(N)}$$

Definissez la densite locale: $\hat{\rho}(\boldsymbol{r})=\sum_{i=1}^{N}\delta(\boldsymbol{r}-\boldsymbol{q}_i)$

$$H^{(N)}=\sum_{i=1}^{N}\frac{p_i^2}{2\mathrm{m}_i}+\sum_{1\le i<j\le N}U(r_{ij})+\sum_{i=1}^{N}\phi(\boldsymbol{q}_i)=\sum_{i=1}^{N}\frac{p_i^2}{2\mathrm{m}_i}+\sum_{1\le i<j\le N}U(r_{ij})+\int\hat{\rho}(\boldsymbol{r})\phi(\boldsymbol{r})$$

Alors, $\dfrac{\delta\Omega[\phi]}{\delta\phi(\boldsymbol{r})}=\langle\hat{\rho}(\boldsymbol{r})\rangle\equiv\rho(\boldsymbol{r})$ "Ensemble-averaged density"

$$\frac{\delta^2\Omega[\phi]}{\delta\phi(\boldsymbol{r})\delta\phi(\boldsymbol{r}')}=\langle\hat{\rho}(\boldsymbol{r})\hat{\rho}(\boldsymbol{r}')\rangle-\langle\hat{\rho}(\boldsymbol{r})\rangle\langle\hat{\rho}(\boldsymbol{r}')\rangle$$

$$\frac{\delta\rho(\boldsymbol{r}|\phi)}{\delta\phi(\boldsymbol{r}')}=\langle\hat{\rho}(\boldsymbol{r})\hat{\rho}(\boldsymbol{r}')\rangle-\langle\hat{\rho}(\boldsymbol{r})\rangle\langle\hat{\rho}(\boldsymbol{r}')\rangle=\underbrace{\langle(\hat{\rho}(\boldsymbol{r})-\rho(\boldsymbol{r}))(\hat{\rho}(\boldsymbol{r}')-\rho(\boldsymbol{r}'))\rangle}_{\text{positive definite}}$$

Théorème fondamental du DFT

N. D. Mermin, Phys. Rev. 137, A1441 (1965).

Definissez la fonctionales:

$$f_N(\Gamma;[\phi]) = \frac{1}{\Xi[\phi] N! h^{ND}} \exp(-\beta(H^{(N)} - \mu N))$$

$$\Lambda[\phi, \phi_0] \equiv k_B T \sum_{N=0}^{\infty} \int \left(\ln\left(f_N(\Gamma^{(N)};[\phi]) / f_N(\Gamma^{(N)};[\phi_0]) \right) - \ln \Xi[\phi_0] \right) f_N(\Gamma^{(N)};[\phi]) \, d\Gamma^{(N)}$$

et notez que

$$\Lambda[\phi_0, \phi_0] = -k_B T \ln \Xi[\phi_0] = \Omega[\phi_0]$$

de sorte que

$$\Lambda[\phi, \phi_0] = \Lambda[\phi_0, \phi_0] + k_B T \sum_{N=0}^{\infty} \int f_N(\Gamma^{(N)};[\phi]) \ln\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])} \right) d\Gamma^{(N)}$$

Théorème fondamental du DFT

N. D. Mermin, Phys. Rev. 137, A1441 (1965).

$$\Lambda[\phi,\phi_0]=\Lambda[\phi_0,\phi_0]+k_B T\sum_{N=0}^{\infty}\int f_N(\Gamma^{(N)};[\phi])\ln\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}\right)d\Gamma^{(N)}$$

$$\Lambda[\phi_0,\phi_0]=-k_B T\ln\Xi[\phi_0]=\Omega[\phi_0]$$

En utilisant $x\ln x\geq x-1$ avec égalité si et seulement si $x=1$

$$\int_N f_N(\Gamma^{(N)};[\phi])\ln\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}\right)d\Gamma^{(N)}$$

$$=\int f_N(\Gamma^{(N)};[\phi_0])\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}\right)\ln\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}\right)d\Gamma^{(N)}$$

$$\geq\int f_N(\Gamma^{(N)};[\phi_0])\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}-1\right)d\Gamma^{(N)}=0$$

Théorème fondamental du DFT

N. D. Mermin, Phys. Rev. 137, A1441 (1965).

$$f_N(\Gamma;[\phi]) = \frac{1}{\Xi[\phi] N! h^{ND}} \exp(-\beta(H^{(N)} - \mu N))$$

$$\Lambda[\phi,\phi_0] = \Lambda[\phi_0,\phi_0] + k_B T \sum_{N=0}^{\infty} \int f_N(\Gamma^{(N)};[\phi]) \ln\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}\right) d\Gamma^{(N)}$$

Donc,

$$\int_N f_N(\Gamma^{(N)};[\phi]) \ln\left(\frac{f_N(\Gamma^{(N)};[\phi])}{f_N(\Gamma^{(N)};[\phi_0])}\right) d\Gamma^{(N)} \geq 0$$

$$\Rightarrow \Lambda[\phi,\phi_0] \geq \Lambda[\phi_0,\phi_0]$$

avec égalité si et seulement si $f_N(\Gamma^{(N)};[\phi]) = f_N(\Gamma^{(N)};[\phi_0])$

ca veux dire $\phi(\boldsymbol{r}) = \phi_0(\boldsymbol{r}) + \text{constante}$

Mais, avec la forme explicite des distributions,

$$\Lambda[\phi,\phi_0] = \Lambda[\phi,\phi] + \int (\phi(\boldsymbol{r}) - \phi_0(\boldsymbol{r}))\rho(\boldsymbol{r};[\phi])\, d\boldsymbol{r}$$

Donc, $\Lambda[\phi_0,\phi_0] \leq \Lambda[\phi,\phi] + \int (\phi(\boldsymbol{r}) - \phi_0(\boldsymbol{r}))\rho(\boldsymbol{r};[\phi])\, d\boldsymbol{r}$

Théorème fondamental du DFT

N. D. Mermin, Phys. Rev. 137, A1441 (1965).

$$\Lambda[\phi_0,\phi_0] \le \Lambda[\phi,\phi] + \int \left(\phi(\boldsymbol{r}) - \phi_0(\boldsymbol{r})\right)\rho(\boldsymbol{r};[\phi])\,d\boldsymbol{r}$$

On peut répéter l'argument avec $\phi \Leftrightarrow \phi_0$

$$\Lambda[\phi,\phi] \le \Lambda[\phi_0,\phi_0] + \int \left(\phi_0(\boldsymbol{r}) - \phi(\boldsymbol{r})\right)\rho(\boldsymbol{r};[\phi_0])\,d\boldsymbol{r}$$

Donc, si $\rho(\boldsymbol{r};[\phi_0]) = \rho(\boldsymbol{r};[\phi])$ on trouve que

$$\Lambda[\phi_0,\phi_0] - \Lambda[\phi,\phi] \le \int \left(\phi(\boldsymbol{r}) - \phi_0(\boldsymbol{r})\right)\rho(\boldsymbol{r};[\phi])\,d\boldsymbol{r} \le \Lambda[\phi_0,\phi_0] - \Lambda[\phi,\phi]$$

Conclusion: $\phi \ne \phi_0 \Rightarrow \rho(\boldsymbol{r};[\phi]) \ne \rho(\boldsymbol{r};[\phi_0])$

Théorème fondamental du DFT

N. D. Mermin, Phys. Rev. 137, A1441 (1965).

Conclusion: $\phi \neq \phi_0 \Rightarrow \rho(\boldsymbol{r};[\phi]) \neq \rho(\boldsymbol{r};[\phi_0])$

Car il est claire que $\rho(\boldsymbol{r};[\phi]) \neq \rho(\boldsymbol{r};[\phi_0]) \Rightarrow \phi \neq \phi_0$ il s'ensuite que:

1. La relation entre densité est champ est un a un et, donc, inversible:

$$\rho(\boldsymbol{r};[\phi]) \Leftrightarrow \phi(\boldsymbol{r};[\rho])$$

2.La distribution est une fonctionnel de la densite $f_N(\Gamma;[\phi]) \to f_N(\Gamma;[\rho])$

3. Il y a un fonctionnel $\Omega[\rho,\phi_0] \equiv \Lambda[\phi[\rho],\phi_0]$ et car $\Lambda[\phi,\phi_0] \geq \Lambda[\phi_0,\phi_0]$

$\Omega[\rho,\phi_0]$ est minimizée par $\rho = \rho_0 \equiv \rho[\phi_0]$

4. $\Omega[\rho_0,\phi_0] = \Omega[\phi_0]$

5. $\Omega[\rho,\phi_0] = F[\rho] + \int (\phi_0(\boldsymbol{r}) - \mu)\rho(\boldsymbol{r})\, d\boldsymbol{r}$ où "F" est indépendant du champ.

Euler-Lagrange equation: $$\boxed{0 = \frac{\delta \Omega[\rho,\phi_0]}{\delta \rho(\boldsymbol{r})} = \frac{\delta F[\rho]}{\delta \rho(\boldsymbol{r})} + \phi_0(\boldsymbol{r}) - \mu}$$

Lutsko, Adv. Chem. Phys. **144**, 1-91 (2010).

Density Functional Theory

- Introduction
- 0K DFT
- T > 0
  - Théorème fondamental du DFT
  - des quantities du mechanique statistique
  - Gaz parfait
  - Des modèles
  - Sphères Dures: FMT
  - Interactions de longue portée
  - Applications

Digression: des quantities du mechanique statistique

1. La distribution un particule est la densite locale:

$$f_N^{(N)}(\Gamma^{(N)};[\phi])=\frac{1}{Z[\phi]N!h^{ND}}\exp(-\beta H^{(N)})$$

$$f_{N-1}^{(N)}(\Gamma^{(N-1)}|\phi)=\int f_N(\Gamma|\phi)\,d\boldsymbol{x}_N, \quad d\boldsymbol{x}_N\equiv d\boldsymbol{q}_N\,d\boldsymbol{p}_N$$

$$f_{N-2}^{(N)}(\Gamma^{(N-1)}|\phi)=\int f_N(\Gamma|\phi)\,d\boldsymbol{x}_{N-1}\,d\boldsymbol{x}_N$$

$$\vdots$$

$$f_1^{(N)}(\boldsymbol{x}_1|\phi)=\int f_N(\Gamma|\phi)\,d\boldsymbol{x}_2\dots d\boldsymbol{x}_N$$

$$\left(\frac{N}{V}\right)^2 g_2^{(N)}(\boldsymbol{q}_1,\boldsymbol{q}_2|\phi)=\int f_2^{(N)}(\boldsymbol{x}_1,\boldsymbol{x}_2|\phi)\,d\boldsymbol{p}_1\,d\boldsymbol{p}_2$$

$$\frac{N}{V}g_1^{(N)}(\boldsymbol{q}_1|\phi)=\int f_1^{(N)}(\boldsymbol{x}_1|\phi)\,d\boldsymbol{p}_1$$

$$\hat{\rho}(\boldsymbol{r})=\sum_{i=1}^{N}\delta(\boldsymbol{r}-\boldsymbol{q}_i)$$

$$\rho(\boldsymbol{r})\equiv\langle\hat{\rho}(\boldsymbol{r})\rangle=\sum_{N=0}^{\infty}\frac{Z_N[\phi]}{\Xi[\phi]}\exp(\beta\mu)\frac{N}{V}g_1^{(N)}(\boldsymbol{r}) \xrightarrow[\text{canonique}]{} \rho(\boldsymbol{r})=\frac{N}{V}g_1^{(N)}(\boldsymbol{r})$$

La probabilité de trouver une particule à la position **r**

Digression: des quantities du mechanique statistique

2. La distribution deux particule (canonique):

$$\frac{N(N-1)}{V^2} g_2^{(N)}(\boldsymbol{q}_1, \boldsymbol{q}_2|\phi) = \frac{N(N-1)}{V^2} \int f_2^{(N)}(\boldsymbol{x}_1, \boldsymbol{x}_2|\phi)\, d\,\boldsymbol{p}_1\, d\,\boldsymbol{p}_2 \;= \langle \hat{\rho}(\boldsymbol{q}_1)\hat{\rho}(\boldsymbol{q}_2)\rangle - \langle \hat{\rho}(\boldsymbol{q}_1)\rangle \delta(\boldsymbol{q}_1 - \boldsymbol{q}_2)$$

4. Direct correlation function

$g_2^{(N)} - 1$

Definissez

$$\frac{\delta \rho(\boldsymbol{r}|\phi)}{\delta \beta \phi(\boldsymbol{r}')} = \langle \hat{\rho}(\boldsymbol{r})\hat{\rho}(\boldsymbol{r}')\rangle - \langle \hat{\rho}(\boldsymbol{r})\rangle\langle \hat{\rho}(\boldsymbol{r}')\rangle \equiv \langle \hat{\rho}(\boldsymbol{r})\rangle \delta(\boldsymbol{r} - \boldsymbol{r}') + \langle \hat{\rho}(\boldsymbol{r})\rangle\langle \hat{\rho}(\boldsymbol{r}')\rangle \underline{h(\boldsymbol{r}, \boldsymbol{r}'|\phi)}$$

$$\frac{\delta \beta \phi(\boldsymbol{r}|\rho)}{\delta \rho(\boldsymbol{r}')} \equiv -\frac{1}{\langle \hat{\rho}(\boldsymbol{r})\rangle} \delta(\boldsymbol{r} - \boldsymbol{r}') + \underline{\Gamma(\boldsymbol{r}, \boldsymbol{r}'|\rho)}$$

Digression: des quantities du mechanique statistique

2. La distribution deux particule (canonique):

$$\frac{N(N-1)}{V^2} g_2^{(N)}(\boldsymbol{q}_1,\boldsymbol{q}_2|\phi) = \frac{N(N-1)}{V^2}\int f_2^{(N)}(\boldsymbol{x}_1,\boldsymbol{x}_2|\phi)\, d\,\boldsymbol{p}_1\, d\,\boldsymbol{p}_2 \;= \langle\hat{\rho}(\boldsymbol{q}_1)\hat{\rho}(\boldsymbol{q}_2)\rangle - \langle\hat{\rho}(\boldsymbol{q}_1)\rangle\delta(\boldsymbol{q}_1-\boldsymbol{q}_2)$$

4. Direct correlation function

$g_2^{(N)}-1$

Definissez

$$\frac{\delta\rho(\boldsymbol{r}|\phi)}{\delta\beta\phi(\boldsymbol{r}')} = \langle\hat{\rho}(\boldsymbol{r})\hat{\rho}(\boldsymbol{r}')\rangle - \langle\hat{\rho}(\boldsymbol{r})\rangle\langle\hat{\rho}(\boldsymbol{r}')\rangle \equiv \langle\hat{\rho}(\boldsymbol{r})\rangle\delta(\boldsymbol{r}-\boldsymbol{r}') + \langle\hat{\rho}(\boldsymbol{r})\rangle\langle\hat{\rho}(\boldsymbol{r}')\rangle h(\boldsymbol{r},\boldsymbol{r}'|\phi)$$

$$\frac{\delta\beta\phi(\boldsymbol{r}|\rho)}{\delta\rho(\boldsymbol{r}')} \equiv -\frac{1}{\langle\hat{\rho}(\boldsymbol{r})\rangle}\delta(\boldsymbol{r}-\boldsymbol{r}') + \Gamma(\boldsymbol{r},\boldsymbol{r}'|\rho)$$

DFT: des quantities du mechanique statistique

4. Direct correlation function

$$\frac{\delta\rho(\boldsymbol{r}|\beta\phi)}{\delta\phi(\boldsymbol{r}')} \equiv \langle\hat{\rho}(\boldsymbol{r})\rangle\delta(\boldsymbol{r}-\boldsymbol{r}')+\langle\hat{\rho}(\boldsymbol{r})\rangle\langle\hat{\rho}(\boldsymbol{r}')\rangle h(\boldsymbol{r},\boldsymbol{r}'|\rho);$$

$$\frac{\delta\beta\phi(\boldsymbol{r}|\rho)}{\delta\rho(\boldsymbol{r}')} \equiv -\frac{1}{\langle\hat{\rho}(\boldsymbol{r})\rangle}\delta(\boldsymbol{r}-\boldsymbol{r}')+\Gamma(\boldsymbol{r},\boldsymbol{r}'|\rho)$$

$$\delta(\boldsymbol{r}-\boldsymbol{r}'')=\int\frac{\delta\rho(\boldsymbol{r}|\phi)}{\delta\phi(\boldsymbol{r}')}\frac{\delta\phi(\boldsymbol{r}'|\rho)}{\delta\rho(\boldsymbol{r}'')}d\boldsymbol{r}' \quad \Rightarrow h(\boldsymbol{r},\boldsymbol{r}'')=\Gamma(\boldsymbol{r},\boldsymbol{r}'')+\int h(\boldsymbol{r},\boldsymbol{r}')\rho(\boldsymbol{r}')\Gamma(\boldsymbol{r}',\boldsymbol{r}'')d\boldsymbol{r}'$$

"Ornstein-Zernike equation"

Euler-Lagrange:

$$0=\frac{\delta F[\rho]}{\delta\rho(\boldsymbol{r})}+\phi(\boldsymbol{r})-\mu \Rightarrow \phi(\boldsymbol{r}|\rho)=\mu-\frac{\delta F[\rho]}{\delta\rho(\boldsymbol{r})}$$

$$\Rightarrow\frac{\delta\beta\phi(\boldsymbol{r}|\rho)}{\delta\rho(\boldsymbol{r}')}=-\frac{\delta^2\beta F[\rho]}{\delta\rho(\boldsymbol{r})\delta\rho(\boldsymbol{r}')}$$

$$\Rightarrow\frac{\delta^2\beta F[\rho]}{\delta\rho(\boldsymbol{r})\delta\rho(\boldsymbol{r}')}=-\Gamma(\boldsymbol{r},\boldsymbol{r}'|\rho)+\frac{1}{\rho(\boldsymbol{r})}\delta(\boldsymbol{r}-\boldsymbol{r}')$$

DFT: lien entre la fonctionalle d'energie et la structure.

Direct correlation function

$$\frac{\delta^2 \beta F[\rho]}{\delta\rho(\boldsymbol{r})\delta\rho(\boldsymbol{r}')} = -\Gamma(\boldsymbol{r},\boldsymbol{r}'|\rho) + \frac{1}{\langle\hat{\rho}(\boldsymbol{r})\rangle}\delta(\boldsymbol{r}-\boldsymbol{r}')$$

En generale si $\frac{\delta\beta F[\rho]}{\delta\rho(\boldsymbol{r})} = c_1(\boldsymbol{r}|\rho)$ et si $\frac{\delta c_1(\boldsymbol{r}_1|\rho)}{\delta\rho(\boldsymbol{r}_2)} = \frac{\delta c_1(\boldsymbol{r}_2|\rho)}{\delta\rho(\boldsymbol{r}_1)}$

il s'ensuite que $\beta F[\rho_1] - \beta F[\rho_0] = \int_0^1 d\lambda \int d\boldsymbol{r} \frac{\partial\rho_\lambda(\boldsymbol{r})}{\partial\lambda} c_1(\boldsymbol{r}|\rho_\lambda)$

pour tout parametrization, e.g. $\rho_\lambda(\boldsymbol{r}) = \rho_0(\boldsymbol{r}) + \lambda(\rho_1(\boldsymbol{r}) - \rho_0(\boldsymbol{r}))$

Voire, e.g. T. Frankel, *The Geometry of Physics*, Cambridge University Press, Cambridge, UK, 1997.

Donc,

$$\beta F[\rho_1] - \beta F[\rho_0] = \int_0^1 d\lambda \int d\boldsymbol{r} \frac{\partial\rho_\lambda(\boldsymbol{r})}{\partial\lambda} c_1(\boldsymbol{r}|\rho_\lambda)$$
$$- \int_0^1 d\lambda \int_0^\lambda d\lambda' \int d\boldsymbol{r}\, d\boldsymbol{r}' \frac{\partial\rho_\lambda(\boldsymbol{r})}{\partial\lambda} \frac{\partial\rho_{\lambda'}(\boldsymbol{r}')}{\partial\lambda'} \left(\Gamma(\boldsymbol{r},\boldsymbol{r}'|\rho_{\lambda'}) - \frac{1}{\rho_{\lambda'}(\boldsymbol{r})}\delta(\boldsymbol{r}-\boldsymbol{r}')\right)$$

Lutsko, Adv. Chem. Phys. **144**, 1-91 (2010).

Digression: dans une fluide avec pair-interactions et symetrie spherique

1. Dans l'etat fluide (liquide ou gaz) et sans champ exteriour $\rho(\boldsymbol{r}) \equiv \bar{\rho} = \frac{N}{V}$

(exercise)

2. Pair correlation function

$$g_2^{(N)}(\boldsymbol{q}_1, \boldsymbol{q}_2 | \phi) \rightarrow g_2^{(N)}(|\boldsymbol{r}_1 - \boldsymbol{r}_2|; \bar{\rho}) = 1 + h_2^{(N)}(|\boldsymbol{r}_1 - \boldsymbol{r}_2|; \bar{\rho})$$

"pair correlation function" "structure function"

3. Ornstein-Zernike equation $h(r_{12}; \bar{\rho}) = c(r_{12}; \bar{\rho}) + \bar{\rho} \int h(r_{13}; \bar{\rho}) c(r_{32}; \bar{\rho}) \, d\boldsymbol{r}_3$

"direct correlation function"

4. Liquid-state theory: $c(r) = (1 - e^{\beta U(r)}) g(r)$, Percus-Yevik

$c(r) = g(r) - 1 - \ln g(r) - \beta U(r)$, Hypernetted-chain equation

(Diagramatic resummations of cluster expansion.)

Les spheres dure: résoudre (PY)

Percus-Yevik: $c_{PY}=\begin{cases} a_0+a_1 r+a_3 r^3, & r<d \\ 0, & r>d \end{cases}$

$g_{HS}(r<d)=0$

$$a_0=-\frac{(1+2\eta)^2}{(1-\eta)^4}, a_1=\frac{3\eta}{2}\frac{(2+\eta)^2}{(1-\eta)^4}, \quad a_3=\frac{\eta}{2}a_0$$

$$y(r)=e^{\beta U(r)}g(r)$$

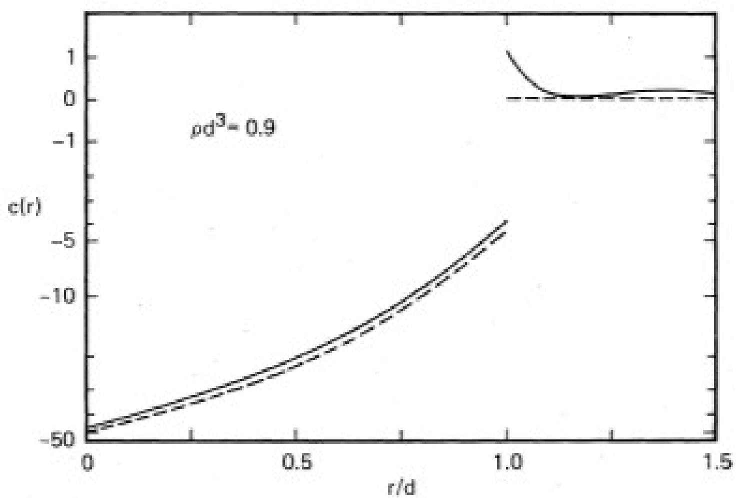

FIG. 18. Direct correlation function of hard spheres at $\rho d^3=0.9$. The solid curve gives the semiempirical results of Grundke and Henderson (1972) and the broken curve gives the PY results. The curve is plotted on a $\sinh^{-1}$ scale. This pseudologarithmic scale combines the advantages of a logarithmic scale with the ability to display zero and negative quantities.

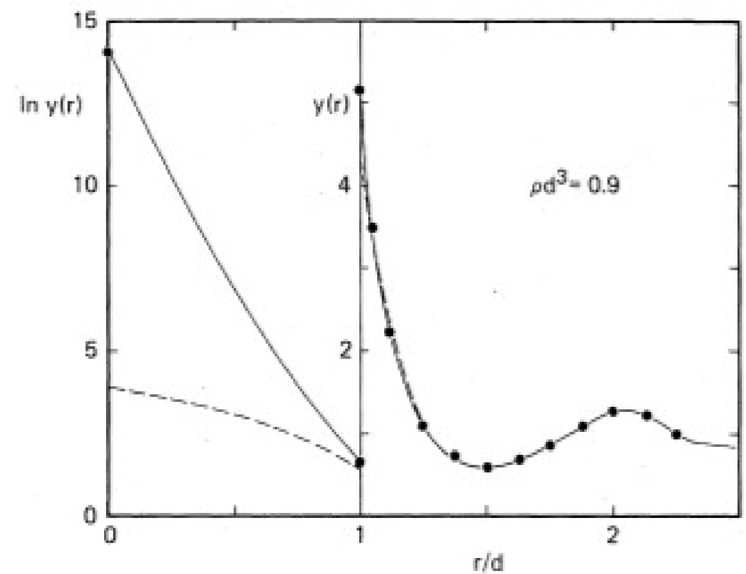

FIG. 17. $y(r)$ of hard spheres at $\rho d^3=0.9$. The points give the simulation results of Barker and Henderson (1971a, 1972) and the solid line gives the semiempirical results of Verlet and Weis (1972a) and Grundke and Henderson (1972) and the broken curve gives the PY results.

J.A. Barker and D. Henderson, “What is liquid?”, Rev. Mod. Phys. 48, 587 (1976)