NANOPHYSIQUE
INTRODUCTION PHYSIQUE AUX NANOSCIENCES

Ch6 . Density Functional Theory

James Lutsko

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Density Functional Theory

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  - Approximations for the exchange term
- T > 0
  - Théorème fondamental du DFT

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Thomas-Fermi Theory

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

Une electron dans un boit:

$$\psi_{n_x n_y n_z}(\boldsymbol{r}) = A \sin\left(\frac{2\pi n_x}{L} x\right) \sin\left(\frac{2\pi n_y}{L} y\right) \sin\left(\frac{2\pi n_z}{L} z\right) \qquad E_{n_x n_y n_z} = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2) \equiv \frac{\hbar^2}{2m} k^2_{n_x n_y n_z}$$

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

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

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

$$E_{Total} = \sum_{n_x, n_y, n_z = 0}^{N_{max}} E_{n_x n_y n_z} \approx \int_0^{k_{max}} \frac{\hbar^2 k^2}{2m} N(k) 4\pi k^2 dk = \int_0^{k_F(\rho)} \frac{\hbar^2 k^2}{2m} 2 \frac{V}{(2\pi)^3} 4\pi k^2 dk = V \frac{\hbar^2}{10 m \pi^2} k_F^5(\rho)$$

Thomas-Fermi Theory

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

Describe electrons by an average number density $\rho(\boldsymbol{r})$

Write total energy

$$E[\rho]=\int\left(\frac{1}{V}E_{kinetic}(\rho(\boldsymbol{r}))+(-e\,\rho(\boldsymbol{r})+e\,\rho_{ion}(\boldsymbol{r}))\Phi(\boldsymbol{r})+\frac{1}{2}(\nabla\Phi(\boldsymbol{r}))^2\right)d\boldsymbol{r}$$

$$\frac{1}{V}E_{kinetic}=\frac{\hbar^2}{10\,m\,\pi^2}k_F^5(\rho(\boldsymbol{r}))=\frac{\hbar^2}{10\,m}3^{5/3}\pi^{4/3}(\rho(\boldsymbol{r}))^{5/3}$$

$$0=\frac{\delta E}{\delta\rho(\boldsymbol{r})}=\frac{\hbar^2\pi^2}{2m}\left(\frac{3}{\pi}\rho(\boldsymbol{r})\right)^{2/3}-e\,\Phi(\boldsymbol{r}) \qquad 0=\frac{\delta E}{\delta\Phi(\boldsymbol{r})}=-e\,\rho(\boldsymbol{r})+e\,\rho_{ion}(\boldsymbol{r})-\nabla^2\Phi$$

$$\rho(\boldsymbol{r})=\frac{1}{3\,\hbar^3\,\pi^2}(2\,me\,\Phi(\boldsymbol{r}))^{3/2} \qquad \nabla^2\Phi=-\frac{e}{3\,\hbar^3\,\pi^2}(2\,m\,e\,\Phi(\boldsymbol{r}))^{3/2}+e\,\rho_{ion}(\boldsymbol{r})$$

Thomas-Fermi Theory

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

$$\rho(\boldsymbol{r}) = \frac{1}{3\hbar^3\pi^2}\left(2\,m\,e\,\Phi(\boldsymbol{r})\right)^{3/2} \qquad \nabla^2\Phi = -\frac{e}{3\hbar^3\pi^2}\left(2\,m\,e\,\Phi(\boldsymbol{r})\right)^{3/2} + e\,\rho_{ion}(\boldsymbol{r})$$

Atom: spherical symmetry and $\quad \rho_{ion}(\boldsymbol{r}) = Z\,\delta(\boldsymbol{r})$

$$\frac{1}{r}\frac{\partial^2}{\partial r^2}r\,\Phi(r) = -\frac{e}{3\hbar^3\pi^2}\left(2\,m\,e\,\Phi(r)\right)^{3/2}$$

Definissez

$$r\,\Phi = -Z\,e\,\Psi \qquad b = \frac{(3\pi^2)^{2/3}}{2}\frac{\hbar^2}{me^2}Z^{-1/3} = 4.8\,a_0\,Z^{-1/3} \qquad x = r/b$$

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

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

Thomas-Fermi-Dirac Theory

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

L'idee Thomas-Fermi:

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

L'idee Thomas-Fermi-Dirac:

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

+l'equation Poisson

$$E_{xc} = \int \left(-\frac{1}{2} \frac{3 e^2 (3 \pi^2 \rho(\boldsymbol{r}))^{1/3}}{2\pi} \rho(\boldsymbol{r}) \right) d\boldsymbol{r}$$

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

"Thomas-Fermi-Dirac equation"

Comparison

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

N électrons dans un champ extérieur:

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

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

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

Densité (de nombre) électronique locale:

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

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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Densité (de nombre) électronique locale:

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

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

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

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

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

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

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

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

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

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

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

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

relation inversible

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

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

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

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

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

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

Kohn-Sham equations

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

Minimisez:

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

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

"Kohn-Sham equations"

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

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

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

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

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

Empirical fit to simulations of uniform electron gas:

$$e_{xc}(n)=-\frac{0.4582}{r_s}+\begin{cases}-0.1423/(1+1.0529\sqrt{r_s}+0.3334r_s), & r_s\geq1 \\ -0.0480+0.0311\ln r_s-0.0116r_s+0.0020r_s\ln r_s, & r_s\leq1\end{cases}$$

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

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).

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

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

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

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

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

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)	$\cdots$
Si_9 (D_{h3})	1.77	4.14	3.39(2)	$\cdots$
Si_{10} (T_d)	1.94	4.25	3.44(2)	$\cdots$
Si_{10} (C_{3v})	1.89	4.32	3.48(2)	$\cdots$
Si_{13} (I_h)	1.41	3.98	3.12(2)	$\cdots$
Si_{13} (C_{3v})	1.80	4.28	3.41(1)	$\cdots$
Si_{13}^{-} (C_{3v})	1.88	4.43	3.56(1)	$\cdots$
Si_{20} (I_h)	1.61	4.10	3.23(3)	$\cdots$
Si_{20} (C_{3v})	1.55	4.28	3.43(3)	$\cdots$

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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

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

Nonlocal (weighted density)

Generalized Gradient

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

Density Functional Theory

Le début de la DFT

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

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

Grand-canonical equilibrium distribution

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

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

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

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

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

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

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

Definissez la fonctionales:

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

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

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

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

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

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

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

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

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

$$x=1\Rightarrow\phi(\boldsymbol{r})=\phi_0(\boldsymbol{r})+\text{constant}$$

Théorème fondamental du DFT

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

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

Donc,

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

$$\Rightarrow \phi(\boldsymbol{r}) = \phi_0(\boldsymbol{r}) + \text{constant} \ \ \text{ou} \ \ \Lambda[\phi,\phi_0] > \Lambda[\phi_0,\phi_0]$$

Mais, avec la forme explicite des distributions,

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

Donc,

$$\phi(\boldsymbol{r}) = \phi_0(\boldsymbol{r}) + \text{constant} \ \ \text{ou} \ \ \Lambda[\phi_0,\phi_0] < \Lambda[\phi,\phi] + \int\left(\phi(\boldsymbol{r})-\phi_0(\boldsymbol{r})\right)\rho(\boldsymbol{r};[\phi])\,d\boldsymbol{r}$$

Théorème fondamental du DFT
N. D. Mermin, Phys. Rev. 137, A1441 (1965).

$$\phi(\boldsymbol{r}) = \phi_0(\boldsymbol{r}) + \text{constant} \quad \text{ou} \quad \Lambda[\phi_0, \phi_0] < \Lambda[\phi, \phi] + \int \big(\phi(\boldsymbol{r}) - \phi_0(\boldsymbol{r})\big) \rho(\boldsymbol{r}; [\phi]) \, d\boldsymbol{r}$$

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

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

$$\phi(\boldsymbol{r}) = \phi_0(\boldsymbol{r}) + \text{constant} \quad \text{ou} \quad \int \big(\phi(\boldsymbol{r}) - \phi_0(\boldsymbol{r})\big) \rho(\boldsymbol{r}; [\phi_0]) \, d\boldsymbol{r} < \Lambda[\phi_0, \phi_0] - \Lambda[\phi, \phi]$$

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

soit $\phi(\boldsymbol{r}) = \phi_0(\boldsymbol{r}) + \text{constant}$ ou

soit $\Lambda[\phi_0, \phi_0] - \Lambda[\phi, \phi] < \int \big(\phi(\boldsymbol{r}) - \phi_0(\boldsymbol{r})\big) \rho(\boldsymbol{r}; [\phi]) \, d\boldsymbol{r} < \Lambda[\phi_0, \phi_0] - \Lambda[\phi, \phi]$

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

Théorème fondamental du DFT

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

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

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

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