NANOPHYSIQUE

INTRODUCTION PHYSIQUE AUX NANOSCIENCES

Ch6 . Density Functional Theory

James Lutsko

Lecture 8, 2022-2023

Density Functional Theory

- Prelude: Functionals and Functional Derivatives
- 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

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:

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

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

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

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

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

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

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:

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

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

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

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 $x \to x_j = j\Delta$

Then a functional of a function $f(x)$ becomes a vector: $f(\boldsymbol{r}) \to (f_{1,} \ldots f_N)$ with $f_j \equiv f(x_j)$

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

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

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

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

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

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

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

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

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

Slater determinant:

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

Ab initio

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

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

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

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

Espérance d'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:

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

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

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

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

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

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

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

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

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

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

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

donc, $\mu = E_F$

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

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

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 : $V_{TF}(\boldsymbol{r}) \rightarrow_{r\rightarrow 0} -\frac{Ze^2}{r}$

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

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: $$4\pi\rho=\nabla^2 V=\frac{e^2}{a_0}\nabla^2\frac{a_0}{e^2}V=-\frac{e^2}{a_0}\nabla^2\Psi$$

$\rho\rightarrow y$ and spherical symmetry $\Rightarrow$ $$\frac{d^2}{dr^2}(r\Psi)=\frac{2^{7/2}}{3a_0^2\pi}r\left(\sqrt{\Psi}+\frac{1}{\pi\sqrt{2}}\right)^3$$

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).