NANOPHYSIQUE

INTRODUCTION PHYSIQUE AUX NANOSCIENCES

Ch6 . Density Functional Theory

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Density Functional Theory

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- 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*: $f(x_{1,} \dots, x_N) = (y_{1,\dots}, y_m)$

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

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

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

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

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: $\quad \dfrac{\delta F[f] G[f]}{\delta f(\boldsymbol{r})} = \dfrac{\delta F[f]}{\delta f(\boldsymbol{r})} G[f] + F[f] \dfrac{\delta G[f]}{\delta f(\boldsymbol{r})}$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Ab initio

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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

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

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

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

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

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

Ab initio: Vxc for uniform electron gas

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

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

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