Many electrons: Density functional theory Part I.

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V.

This class …

is devoted to the many-electron aspects of the solid state (computational) theory

• explores the many-electron features of the electronic structure of solids and solid surfaces

• discusses in some detail the jellium model

• explains in detail the original Kohn-Sham Density functional theory (DFT) and the local density approximation (LDA)

• outlines its various improvements and generalizations

General comments
on the many-electron problem

Basic formulation ("standard model")

1. DOGMA (simplest version) quantum treatment of the assembly

of electrons and nuclei solves all problems of atomic systems

2. Adiabatic approximation

Positions and charges of nuclei (ions) ... fixed parameters $\{\boldsymbol{R}_J, Z_J\}$

3. External field (for el.) • Coulomb field of nuclei • specifies the system

electron potential energy

$$\upsilon(\boldsymbol{r}) = -\sum_J \frac{e'^2 Z_J}{|\boldsymbol{r}-\boldsymbol{R}_J|}, \qquad e'^2 = \frac{e^2}{4\pi\varepsilon_0}$$

4. Total electron charge NEUTRALITY $N^{(e)} = \sum Z_J$ (or ... $\pm 1, \pm 2, ...$)

5. TASK OF THE EQUILIBRIUM THEORY

electron structure	I. Solve the SR ... electron ground state and energy $$\hat{H}|\Psi\rangle = \mathcal{E}|\Psi\rangle, \qquad \hat{H} = \hat{T} + \hat{U}_{ee} + \hat{V}$$
equilibr. energy geometry	II. Minimize the total energy w. resp. to $\boldsymbol{R}_J$ at fixed $N^{(e)}$ $$\nabla_J E_{\mathrm{TOT}}\big|_{N^{(e)}} = 0; \qquad E_{\mathrm{TOT}} = \mathcal{E}[\boldsymbol{R}_J, N^{(e)}] + \tfrac{1}{2}\sum_{J\neq K}\sum \frac{e'^2 Z_J Z_K}{|\boldsymbol{R}_J - \boldsymbol{R}_K|}$$

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Qualitative picture (~ for simple metals)

1. Quantum effects
   - classical elst. system ... unstable. Stabilized by Planck constant $\hbar$
     $$\Delta x \cdot \Delta p \gtrsim \hbar \quad \text{kinetic energy of quantum fluctuations}$$
   - at the surface leaking of electrons into vacuum

2. Pauli principle I.
   - Aufbau principle .... atoms
     Fermi sea .... solids
   - at the surface states from both continuous and discrete spectra

3. Hartree field $\upsilon_{\mathrm{H}}(\boldsymbol{r})$ ... (Coulomb) mean field of electron clouds

   - compensation of diverging fields and energies

   - screening -- suppresion of long range Coulomb fields

   - most of the Coulomb energy absorbed into the mean field part

   - at the surface electrostatic surface dipole, work function

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Qualitative picture (~ for simple metals) *cont'd*

4. Exchange (Pauli II.) and correlation

☐ kinematic (exchange/Pauli) and dynamical (Coulomb) correlation

☐ quantum fluctuations around the Hartree mean field

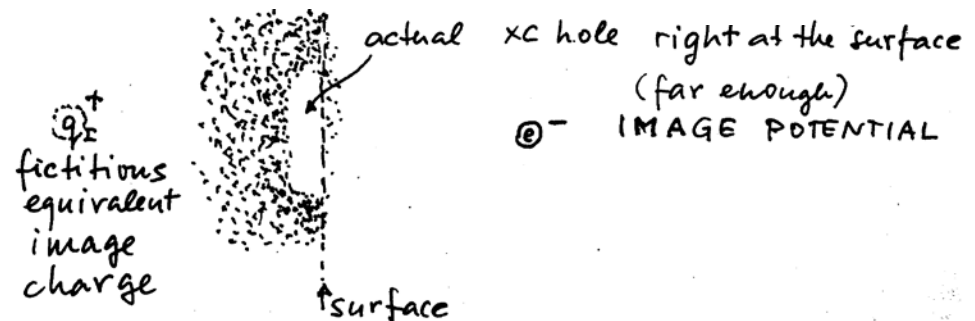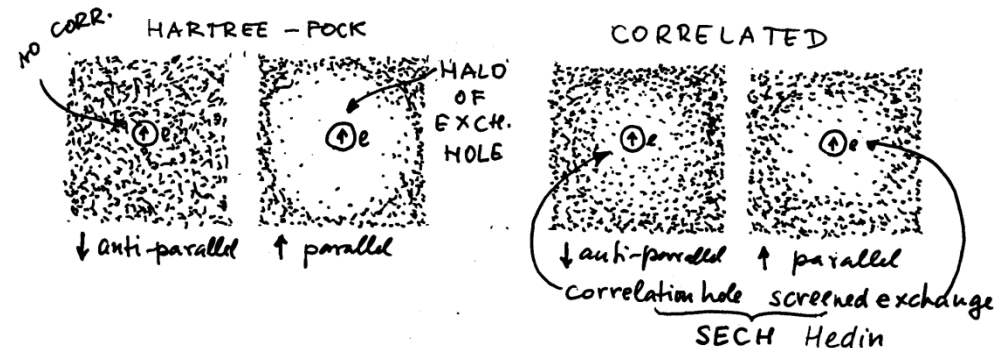☐ e**X**change and **C**orrelation
    hole (Hartree-Fock /exact)

☐ electron digs around itself
    a ditch (XC energy < 0) ...
    cohesion, chemical bond

☐ spin arrangement ... Hund's rules, magnetic ordering

☐ at the surface electron and
    its XC hole detached and
    spatially separated ...
    classical image potential

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A neat expression for the total electron energy

Hamiltonian $\quad \hat{H} = \hat{T} + \hat{U}_{ee} + \hat{V} \qquad \hat{T} = \sum_{i=1}^{N^{(e)}} \frac{1}{2m_e} \hat{\boldsymbol{p}}_i^2$

$$\hat{V} = \sum_i \upsilon(\boldsymbol{r}_i) = \int d^3\boldsymbol{r} \, \upsilon(\boldsymbol{r}) \underbrace{\sum \delta(\boldsymbol{r} - \boldsymbol{r}_i)} \equiv \int d^3\boldsymbol{r} \, \upsilon(\boldsymbol{r}) \boxed{\hat{n}(\boldsymbol{r})}$$

$$\hat{U}_{ee} = \frac{1}{2} \sum_{i \neq j} \sum \frac{e'^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} = \frac{1}{2} \int d^3\boldsymbol{r} \, d^3\boldsymbol{r}' \frac{e'^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \sum_{i \neq j} \sum \delta(\boldsymbol{r} - \boldsymbol{r}_i) \sum \delta(\boldsymbol{r}' - \boldsymbol{r}_j)$$

$$\hat{U}_{ee} = \frac{1}{2} \int d^3\boldsymbol{r} \, d^3\boldsymbol{r}' \frac{e'^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \sum_i \delta(\boldsymbol{r} - \boldsymbol{r}_i) \left\{ \sum_j \delta(\boldsymbol{r}' - \boldsymbol{r}_j) - \delta(\boldsymbol{r}' - \boldsymbol{r}) \right\}$$

$\delta(\boldsymbol{r}-\boldsymbol{r}_i)\delta(\boldsymbol{r}'-\boldsymbol{r}_i)$
$=\delta(\boldsymbol{r}-\boldsymbol{r}_i)\delta(\boldsymbol{r}'-\boldsymbol{r})$

Self-interaction avoided

Total energy $\quad \mathcal{E} = \langle \Psi \,|\, \hat{H} \,|\, \Psi \rangle \equiv \langle \hat{H} \rangle$

$\boxed{n(\boldsymbol{r})}$ ←particle density

$$\langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{V} \rangle + \langle \hat{U}_{ee} \rangle = \langle \hat{T} \rangle + \int d^3\boldsymbol{r} \, \upsilon(\boldsymbol{r}) \langle \hat{n}(\boldsymbol{r}) \rangle +$$

$$+ \frac{1}{2} \int d^3\boldsymbol{r} \, d^3\boldsymbol{r}' \frac{e'^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \underbrace{\langle \hat{n}(\boldsymbol{r}) \{ \hat{n}(\boldsymbol{r}') - \delta(\boldsymbol{r}' - \boldsymbol{r}) \} \rangle}$$

$\boxed{n_2(\boldsymbol{r}, \boldsymbol{r}')}$ pair correlation function

A neat expression for the total electron energy 2

Final form of the total energy

external field ←potential energy→Hartree mean field

$$\langle \hat{H} \rangle = \langle \hat{T} \rangle + \int d^3 \boldsymbol{r}\ \upsilon(\boldsymbol{r}) n(\boldsymbol{r}) + \tfrac{1}{2} \int d^3 \boldsymbol{r}\, d^3 \boldsymbol{r}'\, \frac{e'^2}{|\boldsymbol{r} - \boldsymbol{r}'|} n(\boldsymbol{r}) n(\boldsymbol{r}')$$

exchange and correlation

$$+ \tfrac{1}{2} \int d^3 \boldsymbol{r}\, d^3 \boldsymbol{r}'\, \frac{e'^2}{|\boldsymbol{r} - \boldsymbol{r}'|} (n_2(\boldsymbol{r}, \boldsymbol{r}') - n(\boldsymbol{r}) n(\boldsymbol{r}'))$$

$$\tfrac{1}{2} \int d^3 \boldsymbol{r}\, d^3 \boldsymbol{r}'\, \frac{e'^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \langle\ (\hat{n}(\boldsymbol{r}) - n(\boldsymbol{r}))(\hat{n}(\boldsymbol{r}') - n(\boldsymbol{r}')) - \hat{n}(\boldsymbol{r}) \delta(\boldsymbol{r} - \boldsymbol{r}')\ \rangle$$

quant. fluct. about mean-field +   excl. SI

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A neat expression for the total electron energy 2

Final form of the total energy

external field ←potential energy→Hartree mean field

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exchange and correlation

$$+ \tfrac{1}{2}\int d^3\boldsymbol{r}\, d^3\boldsymbol{r}' \frac{e'^2}{|\boldsymbol{r}-\boldsymbol{r}'|} (n_2(\boldsymbol{r},\boldsymbol{r}') - n(\boldsymbol{r})n(\boldsymbol{r}'))$$

Instead of the unwieldy wave function Ψ it is enough to know

- particle density n dual to the external field
- pair correlation function n_2 dual to the Coulomb interaction

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Exchange and correlation hole

Suggestive transformation

$$\langle \hat{H} \rangle = \langle \hat{T} \rangle - \int d^3\boldsymbol{r}\, n(\boldsymbol{r}) \int d^3\boldsymbol{r}'\, \frac{e'^2}{|\boldsymbol{r}-\boldsymbol{r}'|} \overset{\sum Z_J \delta(\boldsymbol{r}'-\boldsymbol{R}_J)}{n^+(\boldsymbol{r}')}$$

$$+ \frac{1}{2} \int d^3\boldsymbol{r}\, n(\boldsymbol{r}) \int d^3\boldsymbol{r}'\, \frac{e'^2}{|\boldsymbol{r}-\boldsymbol{r}'|} n(\boldsymbol{r}')$$

XC hole

$$+ \int d^3\boldsymbol{r}\, n(\boldsymbol{r}) \int d^3\boldsymbol{r}'\, \frac{1}{2} \frac{e'^2}{|\boldsymbol{r}-\boldsymbol{r}'|} \underbrace{\left(\frac{n_2(\boldsymbol{r},\boldsymbol{r}')}{n(\boldsymbol{r})} - n(\boldsymbol{r}') \right)}_{h_{xc}(\boldsymbol{r},\boldsymbol{r}')}$$

$$\langle \hat{H} \rangle = \langle \hat{T} \rangle + \int d^3\boldsymbol{r}\, n(\boldsymbol{r}) \upsilon(\boldsymbol{r}) \qquad \text{external field}$$

$$+ \frac{1}{2} \int d^3\boldsymbol{r}\, n(\boldsymbol{r}) \upsilon_{\mathrm{H}}(\boldsymbol{r}) \qquad \text{Hartree mean field}$$

$$+ \int d^3\boldsymbol{r}\, n(\boldsymbol{r}) \varepsilon_{\mathrm{XC}}(\boldsymbol{r}) \qquad \text{XC energy per particle}$$

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Properties of the exchange and correlation hole

$$h_{xc}(\boldsymbol{r}, \boldsymbol{r}') = \frac{n_2(\boldsymbol{r}, \boldsymbol{r}')}{n(\boldsymbol{r})} - n(\boldsymbol{r}')$$

$$\varepsilon_{\mathrm{XC}}(\boldsymbol{r}) = \tfrac{1}{2} \int d^3 \boldsymbol{r}' \frac{e'^2}{|\boldsymbol{r} - \boldsymbol{r}'|} h_{xc}(\boldsymbol{r}, \boldsymbol{r}') \qquad \text{XC energy per particle}$$

Properties of the XC hole

◻ parametric dependence on the electron position

◻ for $|\boldsymbol{r} - \boldsymbol{r}'| \to \infty$, it holds $h_{xc}(\boldsymbol{r}, \boldsymbol{r}') \to \infty$ (decay of correlations)

◻ sum rule $\int d^3 \boldsymbol{r}' \, h_{xc}(\boldsymbol{r}, \boldsymbol{r}') = -1$

◻ that includes • elimination of SI • XC hole

◻ decay may be slow: *Friedel oscillations*

Any reasonable theory must contain these elements
and obey these rules

Jellium

Jellium: definition

Jellium

- model of extended electron systems
- pedigree: Sommerfeld model
- ... and its justification
- central problem of an interaction electron gas:

  Long range of Coulomb forces

Definition neutral crystal $\rightarrow$ ionic charge evenly spread

$$n^+ = \sum Z_J \delta(\boldsymbol{r} - \boldsymbol{R}_J) \rightarrow \qquad n^J = \frac{1}{\Omega} \int_\Omega d^3\boldsymbol{r}\, n^+(\boldsymbol{r})$$

Properties

- in equilibrium -- homogeneous and neutral

$$n_{\mathrm{TOT}} = n - n^+ = 0$$

- compensation:

$$\upsilon + \upsilon_{\mathrm{H}} = -\infty + \infty = 0$$

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Jellium: properties *cont'd*

 single parameter $n = n^+$
determines all equilibrium properties
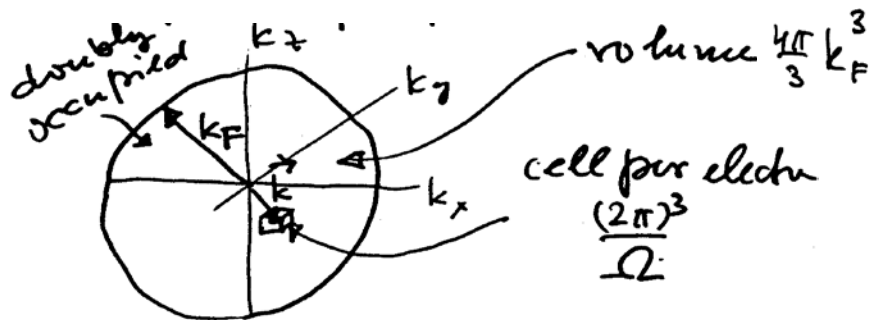
 WIGNER RADIUS volume per electron

$$\frac{1}{n} = \frac{4\pi}{3}\left(a_0 r_s\right)^3$$

Bohr radius   dimensionless parameter

$$\frac{n}{\text{m}^3} = 1.612 \times 10^{30}\, r_s^{-3}$$

simple metals $r_s = 2 \dots 6$

in k-space   FERMI SPHERE   one-el. distr. • diagonal in k
                                            • indep. of interaction

volume $\frac{4\pi}{3} k_F^3$

cell per electron $\frac{(2\pi)^3}{\Omega}$

$$N^{(e)} = n \cdot \Omega = 2 \cdot \frac{\frac{4\pi}{3} k_F^3}{\frac{(2\pi)^3}{\Omega}}$$

$$\boxed{\begin{array}{l} n = \dfrac{1}{3\pi^2} k_F^3 \\[2mm] k_F = \left(\dfrac{9\pi}{4}\right)^{1/3} \dfrac{1}{a_0 r_s} \end{array}}$$

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Jellium: energetics

Energetics   for any kind of energy

$$E = \Omega \times \frac{E}{\Omega} = N \times \frac{E}{N}$$

thermodynamics $\rightarrow$ $\boxed{\dfrac{E}{\Omega} = n \times \varepsilon}$ $\leftarrow$ microscopic picture

$$\varepsilon_{TOT} = \underbrace{\overbrace{\varepsilon_K + \cancel{\upsilon_H}}^{} \overbrace{\varepsilon_{XC}}^{}}_{} = \underbrace{\varepsilon_H + \varepsilon_X}_{\varepsilon_{HF}} + \varepsilon_C$$

Fermi energy and average kinetic energy

$$E_F = \frac{h^2}{2m} k_F^2$$

$$\varepsilon_K = \frac{3}{5} E_F$$

Atomic units $E_F = \dfrac{h^2}{2ma_0^2}\left(a_0 k_F\right)^2 = \text{Ry} \times 3.68 \times \dfrac{1}{r_s^2}$

15   $\varepsilon_K = \dfrac{3}{5} E_F = \text{Ry} \times 2.21 \times \dfrac{1}{r_s^2}$

Jellium: some results
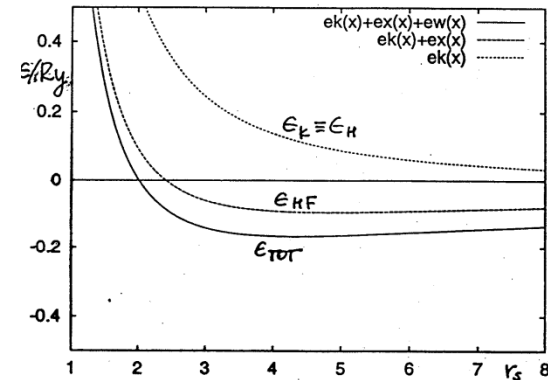
TOTAL ENERGY/ELECTRON atomic units

$$\varepsilon_{\text{TOT}} = \varepsilon_{\text{H}} + \varepsilon_{\text{X}} + \varepsilon_{\text{C}}$$

$$= \frac{2.21}{r_s^2} - \frac{0.916}{r_s} - \frac{0.88}{r_s + 8.7}$$

WIGNER FORMULA

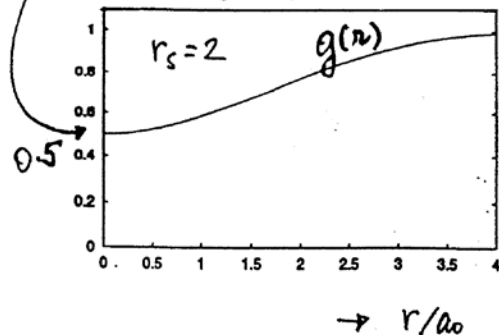Jellium is   stabilized by exchange

and further by the correlations
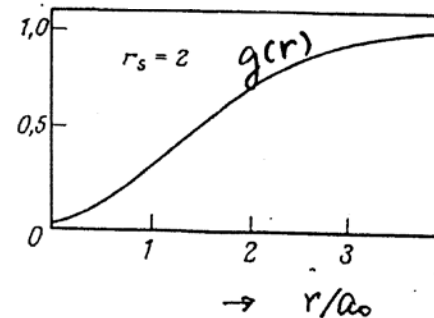
XC hole

$$g(r) \equiv \frac{n_2(r)}{n^2} = \frac{h_{xc}(\boldsymbol{r}, \boldsymbol{r}')}{n(\boldsymbol{r})} + 1$$

EXCHANGE HOLE

only kinematic (Pauli) correlation
.. opposite spins only at r=0
... anelyt. formula

$r_s = 2$ $g(r)$

FULL XC HOLE

additional Coulomb repulsion
... both spins affected
... numerical result

$r_s = 2$ $g(r)$

$\rightarrow r/a_0$

$\rightarrow r/a_0$

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Correlation energy in jellium -- crucial for LDA
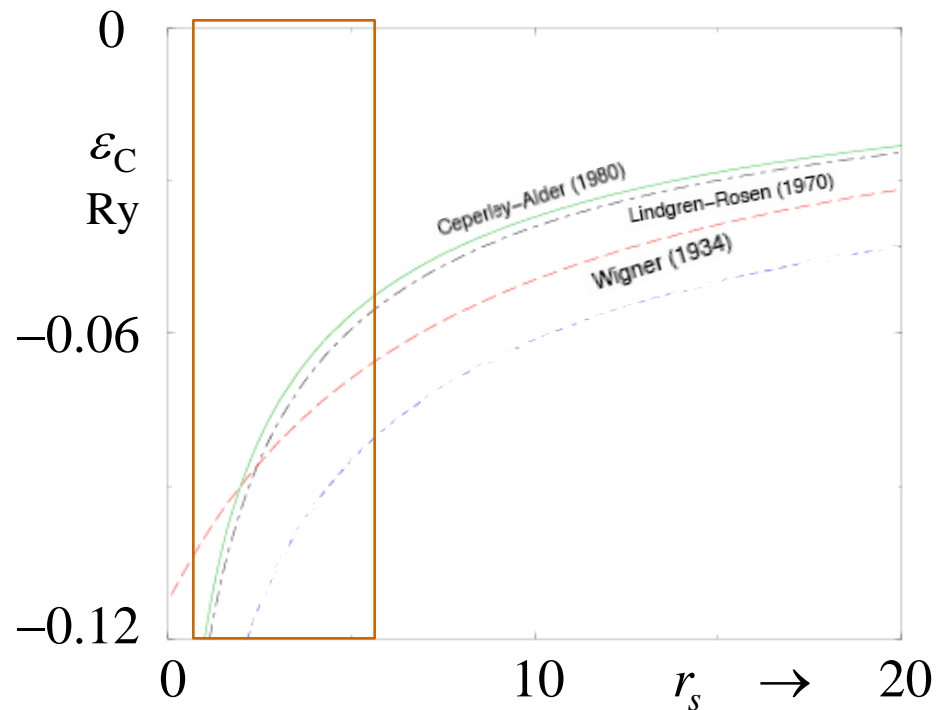
Correlation energy in jellium

- Wigner ... historical, approx.

- compared with QMC
  numerical, heavy computation

- in practice -- Perdew-Zunger
  fit by analytic expressions

- range of previous slide

Density functional theory (DFT)

Hohenberg - Kohn theorem

Density functional theory

☐ is an exact many-electron theory in principle

☐ true interacting electrons $\rightarrow$ effective problem of fictitious non-interacting eletrons

☐ yields: $n(\boldsymbol{r}), m(\boldsymbol{r})$, total energy $\mathcal{E}$ (+ other things, perhaps)

☐ repeatedly employs the variational principle for the ground state

$$\mathcal{E} = \langle \Psi | \hat{H} | \Psi \rangle < \langle \Psi' | \hat{H} | \Psi' \rangle \quad \text{iff} \quad \left| \langle \Psi | \Psi' \rangle \right| < 1$$

theorem Hohenberg - Kohn the total energy of a ground state of interacting electrons is a unique functional of the electron density

Valid chain $\quad \upsilon(\boldsymbol{r}) \rightarrow \hat{H} \rightarrow |\Psi\rangle, \mathcal{E} \rightarrow n(\boldsymbol{r})$

KH theorem claims that the correspondence is unique:

$$\upsilon(\boldsymbol{r}) \rightleftarrows n(\boldsymbol{r})$$

(details of the proof by variational principle - next slide)

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Proof of the Hohenberg - Kohn theorem

iff $\left| \langle \Psi | \Psi' \rangle \right| < 1$

$$\langle \Psi_1 | \hat{H}_2 | \Psi_1 \rangle = \langle \Psi_1 | \hat{T} + \hat{U} | \Psi_1 \rangle + \int dr\, v_2 n_1 = E_1 + \int dr\, (v_2 - v_1) n_1 > E_2$$

$$\langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle = \langle \Psi_2 | \hat{T} + \hat{U} | \Psi_2 \rangle + \int dr\, v_1 n_2 = E_2 + \int dr\, (v_1 - v_2) n_2 > E_1$$

so that: $\int dr\, (v_1 - v_2)(n_1 - n_2) < 0$

$$n_1(r) \neq n_2(r)$$

$$v_1(r) \neq v_2(r) + \text{con st}$$

$$\boxed{\underset{\text{ext. field}}{v + \text{const.}} \quad \neg \quad \underset{\text{ground state}}{\Psi} \quad \neg \quad \underset{\text{density}}{n} = \langle \Psi | \hat{n} | \Psi \rangle}$$

Objections

⬜ particle density is an excessively reduced quantity

⬜ is it clear that to given $n(r)$ a $v(r)$ exists?

Answers:

⬜ in the field of nuclei, $n(r)$ obeys the cusp conditions, which specify $v(r)$:

$$Z_\alpha = -\frac{1}{n_{Av}(0)} \frac{\partial n_{Av}(r_\alpha)}{\partial r_\alpha}\bigg|_{r_\alpha \to 0+} , \quad r_\alpha = |r - R_\alpha|$$

By this example (*E. B. Wilson*), the correspondence is *clare et distincte*

⬜ this problem of "v-representability" resolved by *M. Levy* and *E. Lieb*

Variational principle for the energy functional

HK theorem claims the unique correspondence

$$\upsilon(\boldsymbol{r}) \underset{\longleftarrow}{\longrightarrow} n(\boldsymbol{r})$$

Then $\qquad n(\boldsymbol{r}) \to |\Psi\rangle, \mathcal{E}$ functionals of $n(\boldsymbol{r})$

$$\langle \Psi | \hat{H} | \Psi \rangle = \underbrace{\langle \Psi | \hat{T} | \Psi \rangle + \langle \Psi | \hat{U}_{ee} | \Psi \rangle} + \langle \Psi | \hat{V} | \Psi \rangle$$

$$\mathcal{E}_\upsilon[n] = \qquad \mathcal{F}[n] \qquad + \int d\boldsymbol{r}^3 \upsilon(\boldsymbol{r}) n(\boldsymbol{r})$$

$\qquad\qquad$ universal functional $\qquad \upsilon(\boldsymbol{r})$ enters

Variational principle (K. - H.) $\quad N^{(e)} = \int d\boldsymbol{r}^3 n'(\boldsymbol{r})$ fixed

$$\mathcal{E}_\upsilon[n] = \langle \Psi | \hat{H} | \Psi \rangle < \langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{T} + \hat{U}_{ee} | \Psi' \rangle + \int d\boldsymbol{r}^3 \upsilon(\boldsymbol{r}) n'(\boldsymbol{r})$$

$$\mathcal{E}_\upsilon[n] = \mathrm{Min}\, \mathcal{E}_\upsilon[n']$$

$$\mathcal{E}_\upsilon[n'] = \mathcal{F}[n'] + \int d\boldsymbol{r}^3 \upsilon(\boldsymbol{r}) n'(\boldsymbol{r})$$

$$\mathcal{N}^{(e)}[n] = \mathcal{N}^{(e)}[n'] = N^{(e)}$$

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Orbital theory of Kohn and Sham

What is $\mathcal{F}[n]$

$$\mathcal{F}[n] = \mathcal{T}[n] + \mathcal{U}_{ee}[n] \quad \text{natural decomposition}$$

$$\mathcal{F}[n] = \mathcal{T}_s[n] + \underbrace{\{\mathcal{T} - \mathcal{T}_s + \mathcal{U}_{ee}\}}_{\mathcal{G}}[n] \quad \text{KS decomposition}$$

NEW

Tacit adiabatic postulate $\qquad \mathcal{T}_s$ kinetic energy of fictitious

$e'^2 \neq 0 \quad n \,\square \quad \upsilon \quad n \to \mathcal{T}$ $\qquad$ non-interacting electrons

$e'^2 = 0 \quad n \,\square \quad \upsilon_s \quad n \to \mathcal{T}_s$ $\qquad$ having the same n

We develop two cases in parallel, one is clear and serves as an aid for the other:

$e'^2 = 0$ non-interacting el 's $\qquad e'^2 \neq 0$ Kohn-Sham theory

$$\mathcal{E}_{0\upsilon_s}[n] = \mathcal{T}_s[n] + \int dr^3 \upsilon_s(\boldsymbol{r}) n(\boldsymbol{r}) \qquad \mathcal{E}_\upsilon[n] = \mathcal{T}_s[n] + \mathcal{G}[n] + \int dr^3 \upsilon(\boldsymbol{r}) n(\boldsymbol{r})$$

Orbital theory of Kohn and Sham

We develop two cases in parallel, one is clear and serves as an aid for the other:

$e'^2 = 0$ non-interacting el 's $e'^2 \neq 0$ Kohn-Sham theory

$$\mathcal{E}_0[n] = \mathcal{T}_s[n] + \int d\boldsymbol{r}^3 \upsilon_s(\boldsymbol{r})n(\boldsymbol{r}) \qquad \mathcal{E}[n] = \mathcal{T}_s[n] + \mathcal{G}[n] + \int d\boldsymbol{r}^3 \upsilon(\boldsymbol{r})n(\boldsymbol{r})$$

Employ the HK variational principle to find $n(\boldsymbol{r})$

$$\mathcal{E}_{0\upsilon}[n] = \text{Min}\,\mathcal{E}_{0\upsilon}[n'] \qquad \mathcal{E}_{0\upsilon}[n] = \text{Min}\,\mathcal{E}_{0\upsilon}[n']$$

$$\mathcal{N}^{(e)}[n] = \mathcal{N}^{(e)}[n'] = N^{(e)}$$

Exact Kohn - Sham equations

Write Euler-Lagrange equations

$e'^2 = 0$ non-interacting el 's

$E_0[n] = T_s[n] + \int d\mathbf{r}^3 \upsilon_s(\mathbf{r})n(\mathbf{r})$

$\delta E_0 - \mu \delta N^{(e)} = 0$

$\dfrac{\delta T_s}{\delta n(\mathbf{r})} + \upsilon_s(\mathbf{r}) - \mu = 0$

EQUATION FOR $n(\mathbf{r})$

$e'^2 \neq 0$ Kohn-Sham theory

$E[n] = T_s[n] + G[n] + \int d\mathbf{r}^3 \upsilon(\mathbf{r})n(\mathbf{r})$

$\delta E - \mu \delta N^{(e)} = 0$ μ Lagrange multiplier

$\dfrac{\delta T_s}{\delta n(\mathbf{r})} + \underbrace{\dfrac{\delta G}{\delta n(\mathbf{r})} + \upsilon(\mathbf{r})}_{\upsilon_{\text{eff}}(\mathbf{r})} - \mu = 0$

Here, the solution is known

$(-\dfrac{\hbar^2}{2m_e}\Delta + \upsilon_s(\mathbf{r}))\psi_\alpha = E_\alpha \psi_\alpha$

$n(\mathbf{r}) = \sum |\psi_\alpha(\mathbf{r})|^2$

$E_0 = T_s + \int d\mathbf{r}^3 \upsilon_s n$

$E_0 = \sum E_\alpha$

$\boxed{\mu = \dfrac{\delta E}{\delta N^{(e)}}}$

Use the eff. potential as a real one

$(-\dfrac{\hbar^2}{2m_e}\Delta + \upsilon_{\text{eff}}(\mathbf{r}))\psi_\alpha = E_\alpha \psi_\alpha$

$n(\mathbf{r}) = \sum |\psi_\alpha(\mathbf{r})|^2$

$E = T_s + \int d\mathbf{r}^3 \upsilon n + G$

$E = \sum E_\alpha - \int d\mathbf{r}^3 (\upsilon_{\text{eff}} - \upsilon)n + G$

This is the complete set of equations
of the Kohn-Sham theory

Exchange and correlations in KS theory

Exact decomposition

$$\mathcal{G}[n] = \frac{1}{2}\int d^3\boldsymbol{r}\, n(\boldsymbol{r})\int d^3\boldsymbol{r}' \frac{e'^2}{|\boldsymbol{r}-\boldsymbol{r}'|} n(\boldsymbol{r}') + \frac{1}{2}\int d^3\boldsymbol{r}\, n(\boldsymbol{r})\int d^3\boldsymbol{r}' \frac{e'^2}{|\boldsymbol{r}-\boldsymbol{r}'|} h_{xc}^{\mathrm{KS}}(\boldsymbol{r},\boldsymbol{r}')$$

$$\equiv \mathcal{U}_{\mathrm{H}} + \mathcal{E}_{\mathrm{XC}} \quad \text{defines KS XC energy}$$

KS XC hole different from the true one, but similar properties

sum rule $\qquad \int d^3\boldsymbol{r}'\, h_{xc}^{\mathrm{KS}}(\boldsymbol{r},\boldsymbol{r}') = -1$

XC energy per particle $\quad \varepsilon_{\mathrm{XC}}^{\mathrm{KS}}(\boldsymbol{r},n) = \frac{1}{2}\int d^3\boldsymbol{r}' \frac{e'^2}{|\boldsymbol{r}-\boldsymbol{r}'|} h_{xc}^{\mathrm{KS}}(\boldsymbol{r},\boldsymbol{r}')$

Effective potential

$$\upsilon_{\mathrm{eff}}(\boldsymbol{r}) = \upsilon(\boldsymbol{r}) + \frac{\delta\mathcal{G}}{\delta n(\boldsymbol{r})} = \upsilon(\boldsymbol{r}) + \upsilon_{\mathrm{H}}(\boldsymbol{r}) + \frac{\delta\mathcal{E}_{\mathrm{XC}}}{\delta n(\boldsymbol{r})}$$

Final expression for the total energy

$$\mathcal{E} = \sum E_\alpha - \mathcal{U}_{\mathrm{H}} - \int d\boldsymbol{r}^3 \upsilon_{\mathrm{xc}} n + + \mathcal{E}_{\mathrm{XC}}$$

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Exchange and correlations in KS theory

Exact decomposition

$$\mathcal{G}[n] = \tfrac{1}{2}\int d^3\boldsymbol{r}\, n(\boldsymbol{r})\int d^3\boldsymbol{r}'\, \frac{e'^2}{|\boldsymbol{r}-\boldsymbol{r}'|} n(\boldsymbol{r}') + \tfrac{1}{2}\int d^3\boldsymbol{r}\, n(\boldsymbol{r})\int d^3\boldsymbol{r}'\, \frac{e'^2}{|\boldsymbol{r}-\boldsymbol{r}'|} h_{xc}^{KS}(\boldsymbol{r},\boldsymbol{r}')$$

$$\equiv \mathcal{U}_H + \mathcal{E}_{XC} \quad \text{defines KS XC energy}$$

KS XC hole different from the true one, but similar properties

sum rule $\quad \int d^3\boldsymbol{r}'\, h_{xc}^{KS}(\boldsymbol{r},\boldsymbol{r}') = -1$

XC energy per particle $\quad \varepsilon_{XC}^{KS}(\boldsymbol{r},n) = \tfrac{1}{2}\int d^3\boldsymbol{r}'\, \frac{e'^2}{|\boldsymbol{r}-\boldsymbol{r}'|} h_{xc}^{KS}(\boldsymbol{r},\boldsymbol{r}')$

Effective potential

$$\upsilon_{\text{eff}}(\boldsymbol{r}) = \upsilon(\boldsymbol{r}) + \frac{\delta \mathcal{G}}{\delta n(\boldsymbol{r})} = \upsilon(\boldsymbol{r}) + \upsilon_H(\boldsymbol{r}) + \frac{\delta \mathcal{E}_{XC}}{\delta n(\boldsymbol{r})}$$

Final expression for the total energy

$$\mathcal{E} = \sum E_\alpha - \mathcal{U}_H - \int d\boldsymbol{r}^3 \upsilon_{xc} n + + \mathcal{E}_{XC}$$

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The formidable $\mathcal{E}_{XC}$ functional is not known

. . . resort to approximations

Exact decomposition

$\mathcal{G}[n] = $ ⟨ ... ⟩ $^{s}(r, r')$

$\equiv \mathcal{U}_{H}$ ...

KS X... rties

sum r...

XC e...

Effec...

$\upsilon_{eff}(r$ ...

Final

$\mathcal{E} = \sum \mathcal{E}_{\alpha} - \mathcal{U}_{H} - \int dr \, \upsilon_{xc} n + + \mathcal{E}_{XC}$

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The formidable

$\mathcal{E}_{XC}$ functional

is not known

. . . resort to approximations

This seems to be a standard step, but ...

- DFT has no internal resources for systematically generating these approximations
- it has to use the results of other approaches
- it has to rely on physical intuition

LDA Local density approximation

For jellium, KS theory is exact

$$\varepsilon_{XC}^{KS}(\boldsymbol{r},n) = \varepsilon_{XC}^{J}(n)$$

CRUCIAL STEP LDA Ansatz

$$\varepsilon_{XC}^{KS}(\boldsymbol{r},[n]) = \varepsilon_{XC}^{J}(n(\boldsymbol{r}))$$ defines the LDA XC energy

$$\upsilon_{xc}^{LDA}(\boldsymbol{r}) = \frac{\delta \mathcal{E}_{XC}}{\delta n(\boldsymbol{r})} \rightarrow \frac{\partial}{\partial n}\left(n\varepsilon_{XC}^{J}(n(\boldsymbol{r}))\right)$$

LDA KS equations

$$(-\frac{\hbar^2}{2m_e}\Delta + \upsilon(\boldsymbol{r}) + \upsilon_H(\boldsymbol{r}) + \upsilon_{xc}^{LDA}(\boldsymbol{r}))\psi_\alpha = E_\alpha\psi_\alpha$$

(1) As easy to solve as Hartree or Slater equations

(2) Of course, by iteration in a self-consistent cycle

(3) LDA really works. Two questions • Why

28   • Could we do better

Why is LDA so good

General properties

LDA eqs. have the structure of the exact KS eqs.

Kinetic and Hartree parts are included in full, "only" v_{xc} is approximate

LDA is a parameter-free theory, no fitting, no adjustments

Numerically, LDA is comparatively undemanding, solutions fully converged

Altogether : a well structured AB - INITIO METHOD

Why is LDA so good $-$ qualitative criteria

1. exact in the limit of jellium and the high density limit

2. it has a variational principle

3. the LDA XC hole satisfies the sum rule $\int d^3 \bar{r} \, h_{xc} = -1$ and similar

Altogether : typical COMPREHENSIVE THEORY

BONUS: ε_c is not sensitive to the shape of the XC hole

interpolation scheme

Why II: ε_c is not sensitive to the shape of the XC hole

One reason for the success of LDA is that the correlation energy

depends only on gross features of the XC hole

$$\varepsilon_{XC}^{KS}(\boldsymbol{r},[n]) = \tfrac{1}{2}\int d^3\boldsymbol{r}' \underbrace{\frac{e'^2}{|\boldsymbol{r}'-\boldsymbol{r}|}} h_{xc}^{KS}(\boldsymbol{r},\boldsymbol{r}')$$

radial symmetry of the kernel

$$\varepsilon_{XC}^{KS}(\boldsymbol{r},[n]) = \tfrac{1}{2}\int d^3\boldsymbol{u}\,\frac{e'^2}{|\boldsymbol{u}|} h_{xc}^{KS}(\boldsymbol{r},\boldsymbol{r}+\boldsymbol{u})$$

$$= \tfrac{1}{2}\int e'^2 u\,du \underbrace{\iint \sin\vartheta\,d\vartheta\,d\varphi\, h_{xc}^{KS}(\boldsymbol{r},\boldsymbol{r}+\boldsymbol{u})}$$

spherical average $\widehat{h}_{xc}^{KS}(\boldsymbol{r},u)$

$$= \tfrac{1}{2}\int e'^2 u\,du\,\widehat{h}_{xc}^{KS}(\boldsymbol{r},u)$$

SUMMARY Correlation energy per particle of any kind (true, exact DFT, LDA)

is completely specified by a single global characteristic of the respective XC hole

obtained in two steps

(1) by the spherical average

(2) as the first moment of the resulting radial function
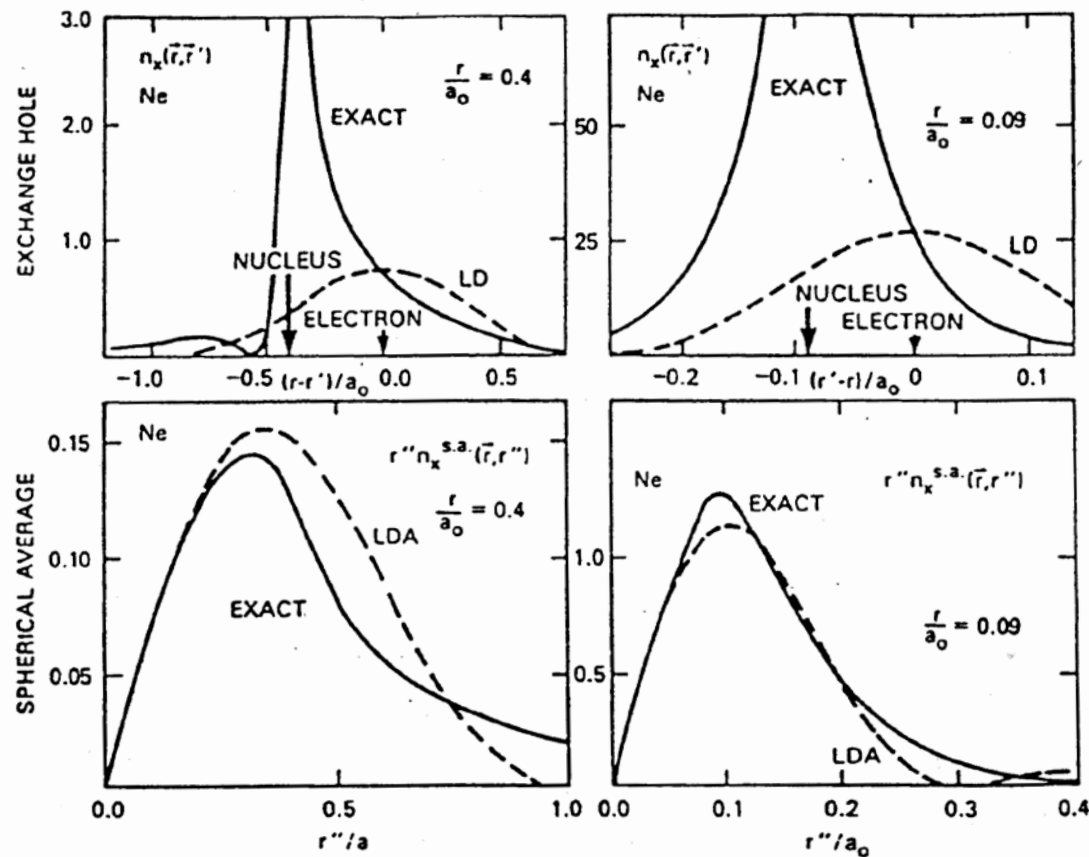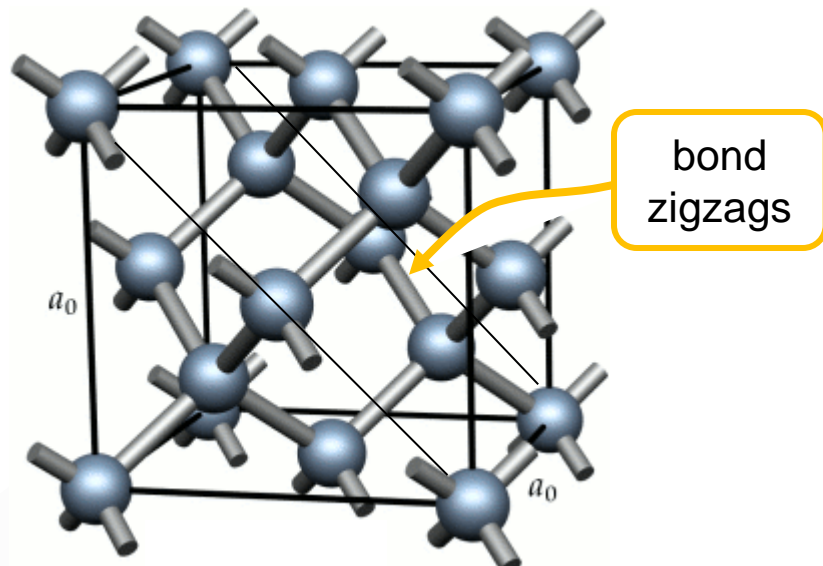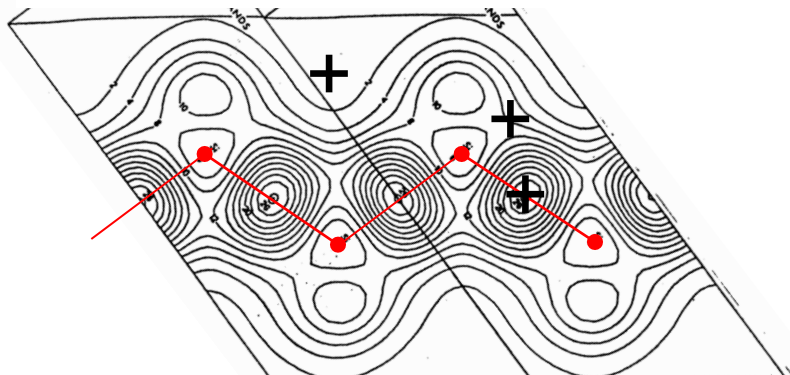
Exact and LDA XC hole in neon atom compared

FIGURE 2 Comparison of the exact exchange hole (solid lines) with exchange hole in LDA (dashed line) for Ne. The arrow marks the nuclear position. The actual exchange hole, on a line through the nucleus and through the position of the electron, is given in the upper panels while the spherical averages are shown in the lower panels. The left (resp.. right) panels correspond to the electron position at 0.4 a.u. (resp.. 0.09 a.u.) from the nucleus. Note that the spherical average is reasonable in LDA in spite of poor representation of the actual exchange hole. (After Gunnarsson. Jonson and Lundqvist. Ref. 16. with permission.)

Exact and LDA XC hole in silicon crystal compared

[110]   plane in Si structure

bond zigzags

density contours of valence electrons

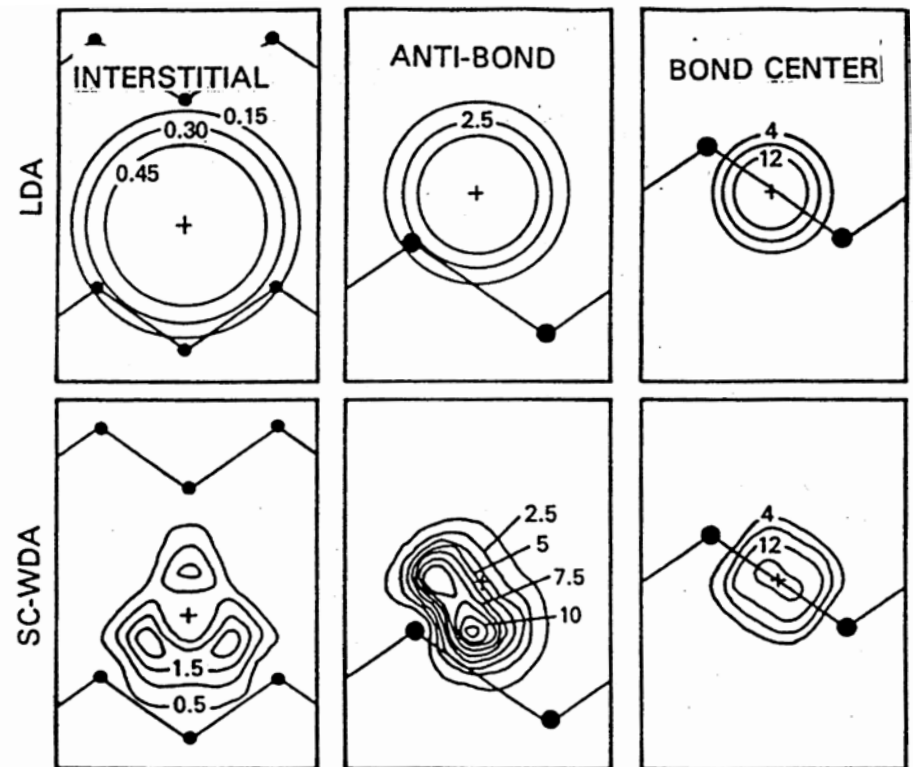|	INTERSTITIAL	ANTI-BOND	BOND CENTER
LDA	0.15 0.30 0.45	2.5	4 12
SC-WDA	2.5 5 7.5 10 1.5 0.5		4 12

FIGURE 4 Contour plots in the (110) plane of silicon of the XC hole in the LDA (upper panels) and in the semiconducting weighted density approximation (SC-WDA, lower panels). The XC holes are shown for three positions of the electron (denoted by crosses). Full circles denote atomic positions, with straight lines denoting the bonding chains. Note that the LDA is excellent in the bonding region but becomes increasingly worse in lower density regions. (After Hybertsen and Louie, Ref. 28, with permission.)

●—● Si nuclei and bond connecting lines

+ centers of XC holes in the main plot

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Why is LDA so good III

A mystic circumstance

It turns out that the errors in the exchange energy and the correlation energy,

individually quite significant,

tend to mutually compensate

Explanations have been forwarded

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LDA and beyond

Ways to go beyond LDA – present choice in green

Several forks
{
something entirely else: GW, QMC, DMFT

a non-system correction to LDA: LDA+U, LDA+DMFT

something within DFT
}

Within DFT
{
extensions
{
relativistic

with elmg fields

time dependent

finite temperatures
}

improvements within non-relativistic DFT
}

Ways to go beyond LDA – present choice in green

Several forks $\begin{cases}\text{something entirely else: GW, QMC, DMFT} \\ \text{a non-system correction to LDA: LDA+U, LDA+DMFT} \\ \text{something within DFT}\end{cases}$

Within DFT $\left\{\begin{array}{l}\text{extensions} \begin{cases}\text{relativistic} \\ \text{with elmg fields} \\ \text{time dependent} \\ \text{finite temperatures}\end{cases} \\ \text{improvements within non-relativistic DFT}\end{array}\right.$

$$\frac{1}{n}$$

L

D

A

$$\frac{a_0 |\nabla n|}{n}$$

LDA and beyond

Ways to go beyond LDA − present choice in green

Several forks
- something entirely else: GW, QMC, DMFT
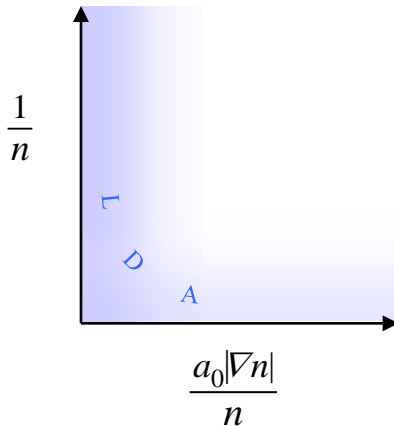- a non-system correction to LDA: LDA+U, LDA+DMFT
- something within DFT

Within DFT

extensions
- relativistic
- with elmg fields
- time dependent
- finite temperatures
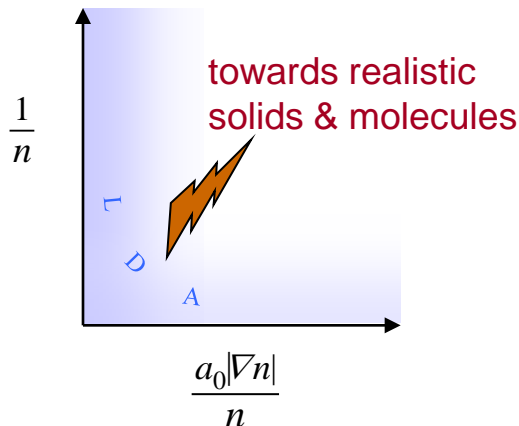
improvements within non-relativistic DFT

towards realistic
solids & molecules

$\dfrac{1}{n}$

L

D

A

$\dfrac{a_0 |\nabla n|}{n}$

Improving LDA within DFT

Classification according to John Perdew

Improving LDA -- Jacob' s ladder

orbital functionals
hyper-GGA
meta-GGA
GGA
L(S)DA

This is an oversimplified scheme of the vast list of approximations to DFT.
Try to look at
`http://sites.google.com/site/markcasida/dft`

Improving LDA within DFT

Classification according to John Perdew

Improving LDA -- Jacob' s ladder

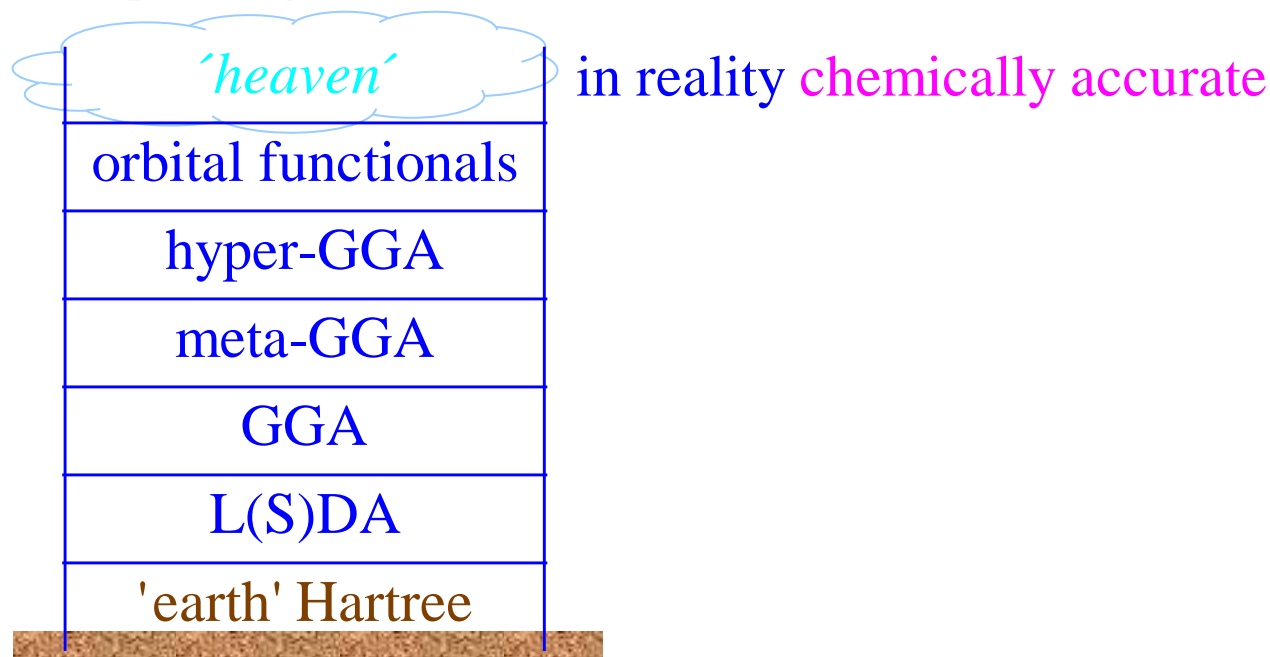|	
orbital functionals	*SI corrections; Third generation DFT*
hyper-GGA	hybrid functionals between DFT and HF
meta-GGA	Greek $\mu\varepsilon\tau\alpha -$ means 'beyond' or 'after' here
GGA	Generalized gradient approximation
L(S)DA	Local (spin)density approximation

This is an oversimplified scheme of the vast list of approximations to DFT.
Try to look at
`http://sites.google.com/site/markcasida/dft`

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Improving LDA within DFT

Classification according to John Perdew

Improving LDA -- Jacob' s ladder

´heaven´   in reality chemically accurate

orbital functionals
hyper-GGA
meta-GGA
GGA
L(S)DA
'earth' Hartree

I viděl ve snách, a *aj*, žebřík stál na zemi, jehožto vrch dosahal nebe; a aj, andělé Boží vstupovali a sstupovali po něm.
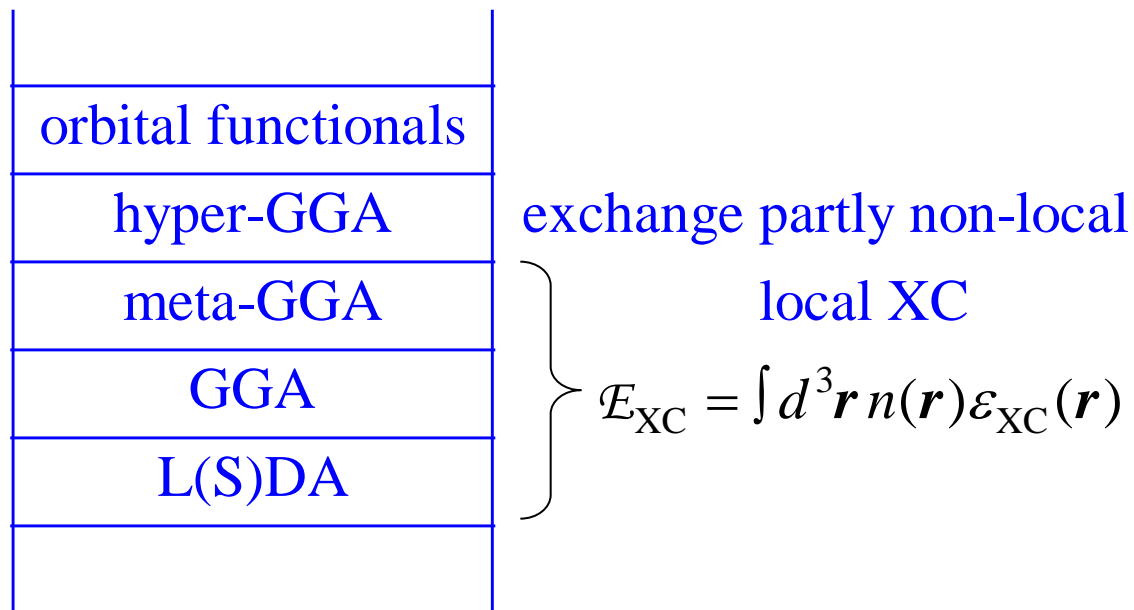
And he dreamed, and behold a ladder set up on the earth, and the top of it reached to heaven: and behold the angels of God ascending and descending on it.

Genesis 28:12

Improving LDA within DFT

Classification according to John Perdew

Improving LDA -- Jacob' s ladder

TWO RIVALS

orbital functionals

hyper-GGA   exchange partly non-local

meta-GGA   local XC

GGA $\mathcal{E}_{\mathrm{XC}} = \int d^3\boldsymbol{r}\, n(\boldsymbol{r}) \varepsilon_{\mathrm{XC}}(\boldsymbol{r})$

L(S)DA

semi-empirical parametrization

guided by general requirements: sum rule, ...

orthodox DFT no parameters

Improving LDA within DFT

Classification according to John Perdew

Improving LDA -- Jacob' s ladder

local kinetic energy

orbital functionals	
hyper-GGA	hybrid functionals -- admixture of non-local HF
meta-GGA	$\varepsilon_{XC}(\boldsymbol{r}) = \phi(n_\sigma, \nabla n_\sigma, \Delta n_\sigma, \tau_\sigma)$ $\quad \tau_\sigma = \sum |\nabla \psi_{\alpha\sigma}|^2$
GGA	$\varepsilon_{XC}(\boldsymbol{r}) = \phi(n_\sigma, \nabla n_\sigma)$
L(S)DA	$\varepsilon_{XC}(\boldsymbol{r}) = \phi(n), \quad \varepsilon_{XC}(\boldsymbol{r}) = \phi(n_\uparrow, n_\downarrow)$

Improving LDA within DFT

Classification according to John Perdew

Improving LDA -- Jacob' s ladder

local kinetic energy

orbital functionals
hyper-GGA
meta-GGA
GGA
L(S)DA

hybrid functionals -- admixture of non-local HF

$$\varepsilon_{XC}(\boldsymbol{r}) = \phi(n_\sigma, \nabla n_\sigma, \Delta n_\sigma, \tau_\sigma) \quad \tau_\sigma = \sum |\nabla \psi_{\alpha\sigma}|^2$$

$$\varepsilon_{XC}(\boldsymbol{r}) = \phi(n_\sigma, \nabla n_\sigma)$$

$$\varepsilon_{XC}^{\text{LDA}}(\boldsymbol{r}) = \phi(n), \quad \varepsilon_{XC}^{\text{LSDA}}(\boldsymbol{r}) = \phi(n_\uparrow, n_\downarrow)$$

all-important extension $\text{DFT} \rightarrow \text{SDFT}$

generalized HK theorem: in spin-polarized systems

$$\boxed{n_\uparrow, n_\downarrow \quad \square \quad |\Psi\rangle}$$

Approximations: LDA $\rightarrow$ LSDA similar to HF $\rightarrow$ unrestricted HF

Needed for: • magnetic field • magnetic order • odd electron number

Improving LDA within DFT

Classification according to John Perdew

Improving LDA -- Jacob's ladder

local kinetic energy

orbital functionals	
hyper-GGA	example B3LYP $-$ *see below*
meta-GGA	$\varepsilon_{XC}(\boldsymbol{r}) = \phi(n_\sigma, \nabla n_\sigma, \Delta n_\sigma, \tau_\sigma)$ $\tau_\sigma = \sum \mid \nabla \psi_{\alpha\sigma} \mid^2$
GGA	$\varepsilon_{XC}(\boldsymbol{r}) = \phi(n_\sigma, \nabla n_\sigma)$
L(S)DA	$\varepsilon_{XC}(\boldsymbol{r}) = \phi(n), \quad \varepsilon_{XC}(\boldsymbol{r}) = \phi(n_\uparrow, n_\downarrow)$

$$\mathcal{E}_{xc}^{B3LYP} = \mathcal{E}_{xc}^{LDA} + a_0(\mathcal{E}_{x}^{HF} - \mathcal{E}_{x}^{LDA}) + a_x(\mathcal{E}_{x}^{GGA} - \mathcal{E}_{x}^{LDA}) + a_c(\mathcal{E}_{c}^{GGA} - \mathcal{E}_{c}^{LDA})$$

$$a_0, a_x, a_c \quad \dots \text{ empirical parameters}$$

Epilogue

At surfaces, LDA works all too well, considering the fast drop of the electron density from the bulk value to zero

In the next class, we will have a look at truncated jellium.

The end