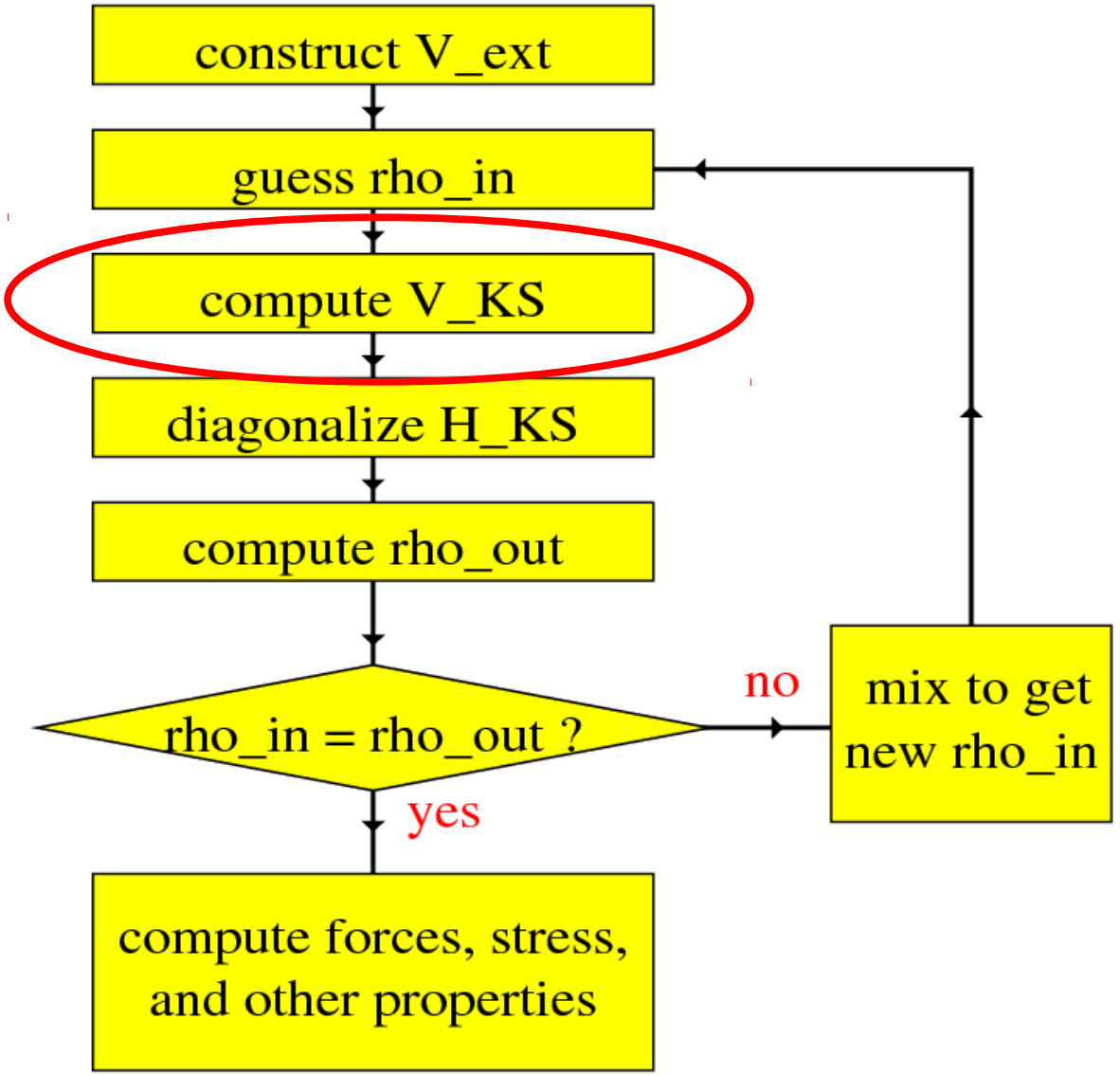
Electronic Structure: from BlackBoard to Source Code

Stefano de Gironcoli
Scuola Internazionale Superiore di Studi Avanzati
Trieste-Italy

v_of_rho

Step 3 : compute V_H & V_{xc}



Hartree potential

Hartree potential is computed from the Poisson equation which is diagonal in reciprocal space.

$$V_H(G) = 4\pi e^2 \, \rho(G) / G^2$$

The divergent G=0 term cancels out (for neutral systems) with analogous terms present in the ion-ion and electron-ion interaction.

In charged systems a compensating uniform background is assumed.

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Periodic boundary conditions in *ab initio* calculations

G. Makov and M. C. Payne
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, United Kingdom
(Received 19 July 1994)

The convergence of the electrostatic energy in calculations using periodic boundary conditions is considered in the context of periodic solids and localized aperiodic systems in the gas and condensed phases. Conditions for the absolute convergence of the total energy in periodic boundary conditions are obtained, and their implications for calculations of the properties of polarized solids under the zero-field assumption are discussed. For aperiodic systems the exact electrostatic energy functional in periodic boundary conditions is obtained. The convergence in such systems is considered in the limit of large supercells, where, in the gas phase, the computational effort is proportional to the volume. It is shown that for neutral localized aperiodic systems in either the gas or condensed phases, the energy can always be made to converge as $O(L^{-5})$ where L is the linear dimension of the supercell. For charged systems, convergence at this rate can be achieved after adding correction terms to the energy to account for spurious interactions induced by the periodic boundary conditions. These terms are derived exactly for the gas phase and heuristically for the condensed phase.

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A reciprocal space based method for treating long range interactions in *ab initio* and force-field-based calculations in clusters

Glenn J. Martyna
Department of Chemistry, Indiana University, Bloomington, Indiana 47405-4001

Mark E. Tuckerman
Department of Chemistry and Courant Institute of Mathematical Sciences, New York University, New York, New York 10003

(Received 17 June 1998; accepted 3 November 1998)

A new reciprocal space based formalism for treating long range forces in clusters is presented. It will be shown how the new formalism can be incorporated into plane-wave based density function theory calculations, standard Ewald summation calculations, and smooth particle-mesh Ewald calculations to yield accurate and numerically efficient descriptions of long range interactions in cluster systems. © *1999 American Institute of Physics.* [S0021-9606(99)50806-4]

Exchange and Correlation in Density Functional Theory

in practice

Local Density Approximation

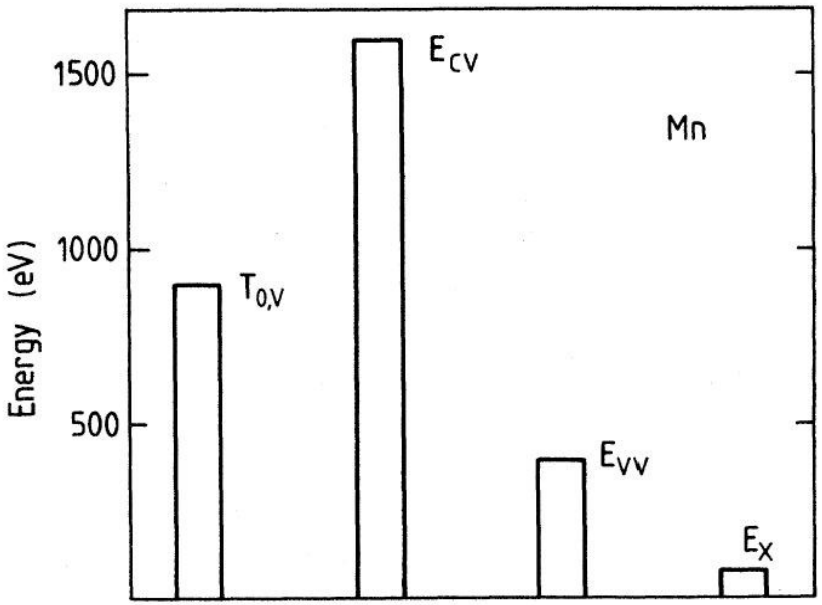
The simplest approximation is LDA that exploits nearsightedness of the electronic matter

W. Kohn, PRL 76,3168 (1996)

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int \varepsilon_{xc}^{hom}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r}$$

Analogous to the Thomas Fermi approximation for the Kinetic Energy term but applied to the much smaller Exchange-Correlation term

In many cases it works very nicely



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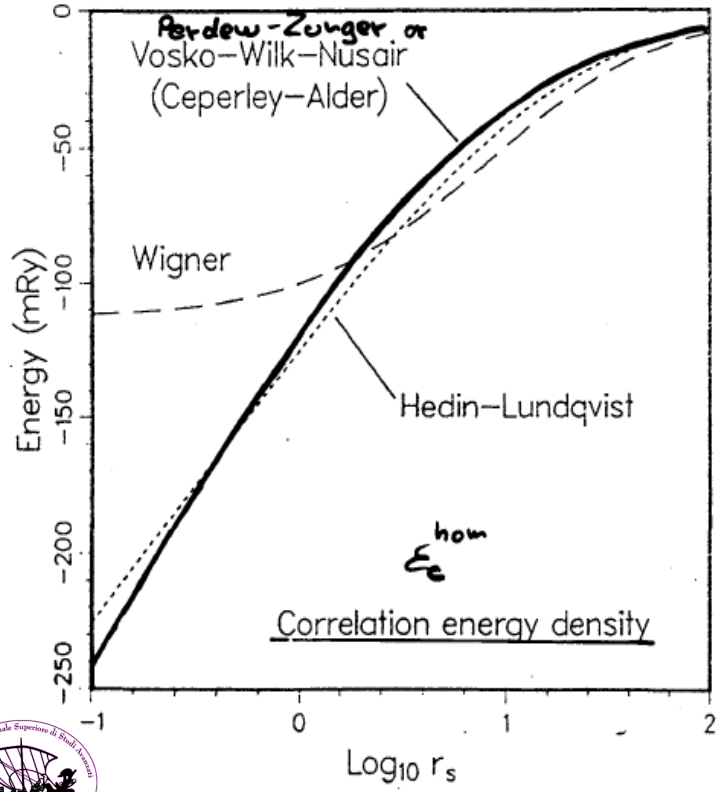


$$\varepsilon_{xc}^{hom}(n) = \varepsilon_x^{hom}(n) + \varepsilon_c^{hom}(n)$$

$$\varepsilon_x^{hom}(n) = -\frac{3}{4\pi}e^2\left(3\pi^2 n\right)^{\frac{1}{3}}$$

$\varepsilon_c^{hom}(n)$ From accurate DMC data
Ceperley-Alder PRL 45, 566 (1980)

$$n = \frac{1}{\frac{4}{3}\pi r_s^3}$$

Local Density Approximation

The simplest approximation is LDA that exploits nearsightedness of the electronic matter

W. Kohn, PRL 76,3168 (1996)

$$E_{xc}^{LDA}[\rho(\mathbf{r})] = \int \varepsilon_{xc}^{hom}(\rho(\mathbf{r}))\rho(\mathbf{r})d\mathbf{r}$$

$$v_{xc}^{LDA}(r) = \frac{\delta E_{xc}[\rho(r)]}{\delta\rho(r)} = \frac{d\varepsilon_{xc}^{hom}(\rho(r))}{d\rho(r)} + \varepsilon_{xc}^{hom}(\rho(r))$$

Technically: the integral is computed on the FFT grid and the potential is simply computed on each grid point in real space.

Magnetism needs to be explicitly accounted

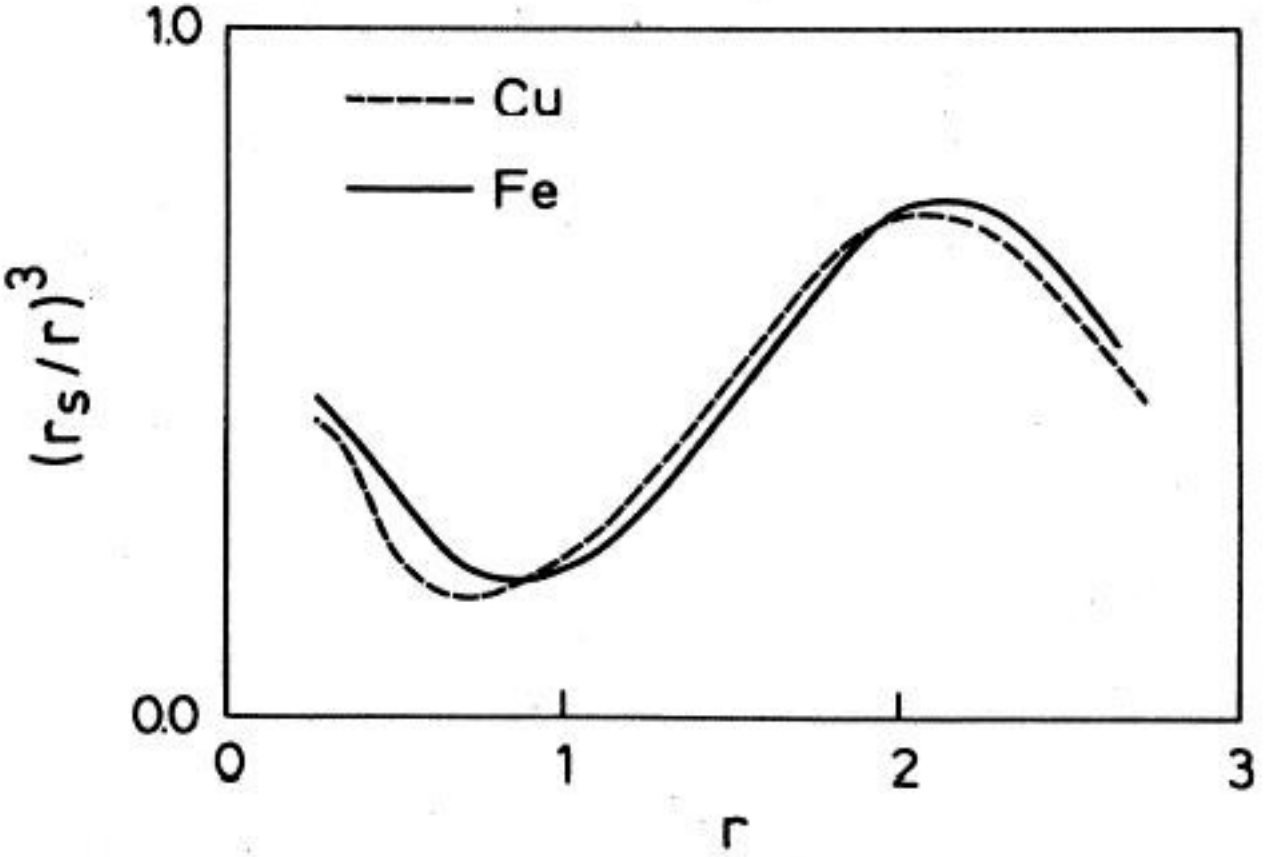


FIG. 6. Density of metallic Fe and Cu as a function of the radius r. The density n is expressed in terms of the parameter r_s, where $n = (4\pi r_s^3/3)^{-1}$.

Spins in Density Functional Theory

In principle Exc[rho] “knows” about this effect, but in practice it is poorly approximated since only the total charge is defined as a variable and this is similar for magnetic and non-magnetic systems

We need to help LDA to detect magnetism …

Solution: treat up and down densities separately

The Local Spin Density Approximation (LSDA)

- Electrons have spin +/- ½ bohr magneton

- Spin is treated as a scalar quantity (this is approximate)

- Two spin states often referred to as “up” ↑ and “down” ↓

- up-up interaction is different from up-down

Technically:

nspin =2 *k-points are doubled; half for spin_up and half for spin_dw*

rho(1:nrxx) → rho(1:nrxx,1:nspin) *is doubled*

Local Spin Density (LSD) = LDA with different charge densities for up and down electrons

The potential is also doubled

$$v^{\uparrow}_{eff}(r) = v_{ext}(r) + e^2 \int \frac{\rho(r')}{|r - r'|} dr' + \frac{\partial E_{xc}[\rho_{\uparrow}, \rho_{\downarrow}]}{\partial \rho_{\uparrow}(r)}$$

$$v^{\downarrow}_{eff}(r) = v_{ext}(r) + e^2 \int \frac{\rho(r')}{|r - r'|} dr' + \frac{\partial E_{xc}[\rho_{\uparrow}, \rho_{\downarrow}]}{\partial \rho_{\downarrow}(r)}$$

Up and down densities can be different
Similar to Restricted *vs* Unrestricted Hartree-Fock

Jacob's ladder of Density Functional Theory

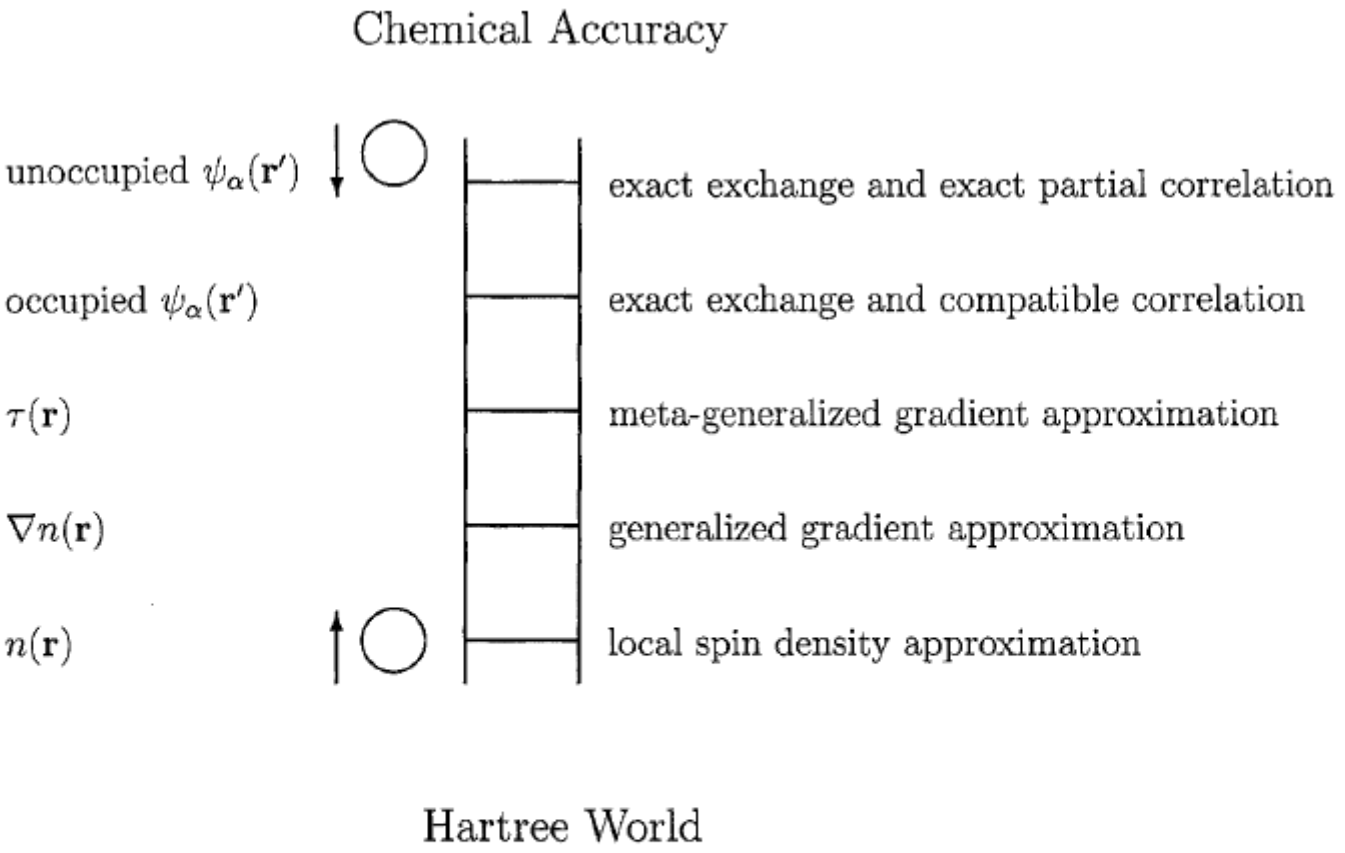


FIGURE 1. Jacob's ladder of density functional approximations. Any resemblance to the Tower of Babel is purely coincidental. Also shown are angels in the spherical approximation, ascending and descending. Users are free to choose the rungs appropriate to their accuracy requirements and computational resources. However, at present their safety can be guaranteed only on the two lowest rungs.

From L(S)DA

$$E_{xc}^{LSD}[\rho_\uparrow, \rho_\downarrow] = \int \rho(r)\varepsilon_{xc}^{hom}(\rho_\uparrow, \rho_\downarrow)dr$$

to GGA

$$E_{xc}^{GGA}[\rho_\uparrow, \rho_\downarrow] = \int F_{xc}^{GGA}(\rho_\uparrow, \rho_\downarrow, |\nabla\rho_\uparrow|, |\nabla\rho_\downarrow|)dr$$

... not a unique recipe

A lot of work went in proposing and comparing new functionals

A few functionals are widely used today

PW91, PBE, revPBE, RPBE ...
BLYP

For each functional (or combination thereof) there is a routine than computes the relevant function and its derivatives

Exchange-Correlation potential for a GGA functional

$$E_{xc}^{GGA}[\rho_\uparrow, \rho_\downarrow] = \int F_{xc}^{GGA}(\rho_\uparrow, \rho_\downarrow, |\nabla\rho_\uparrow|, |\nabla\rho_\downarrow|)dr$$

$$v_{xc}^{\sigma}(r) = \frac{\partial F_{xc}^{GGA}}{\partial \rho_\sigma} - \sum_\alpha \partial_\alpha \left(\frac{\partial F_{xc}^{GGA}}{\partial |\nabla\rho_\sigma|} \frac{\partial_\alpha \rho_\sigma}{|\nabla\rho_\sigma|} \right)$$

Technically the gradients of rho are computed by rho(R) → rho(G) FFT, iG rho(G), and then G → R FFT

The function Fxc and its derivatives are computed on each grid point and the result stored in a vector h(3, nrxx)

The divergence term is again computed by h(3,R) → h(3,G) FFT, sum_ia iG_ia h(ia,G), then G → R FFT

NB: this is the exact functional derivarive of the discretized integral

LDA and LSDA

GGA : PW91, PBE, revPBE, RPBE, BLYP

~~META-GGA: PKZB, TPSS,~~

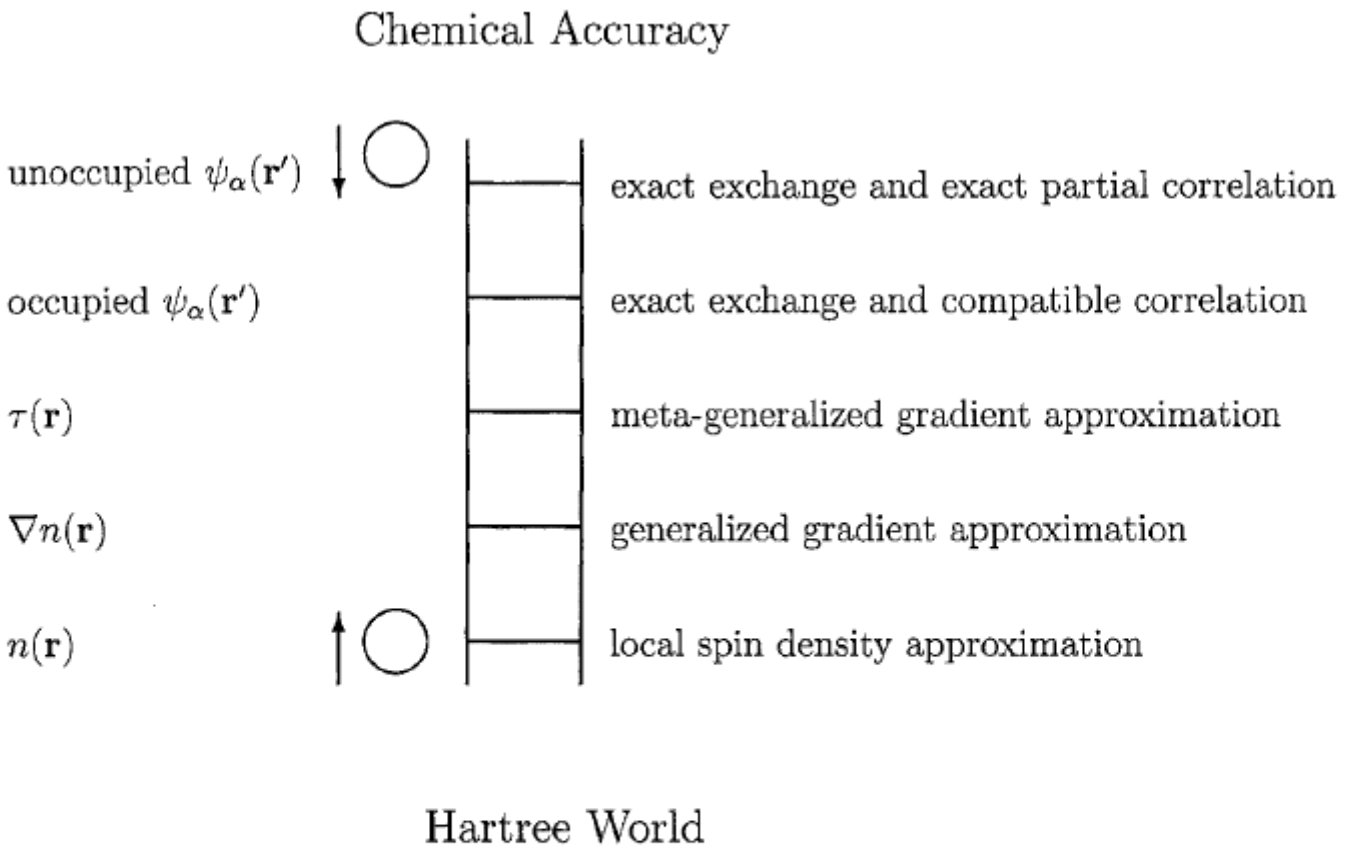
~~SIC, DFT+U,~~ hybrids

Van der Waals functionals

...

exact DFT

Jacob's ladder of Density Functional Theory



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... to be continued