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EXCHANGE-CORRELATION POTENTIALS

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OVERVIEW

- preliminaries
  - self-interaction (Hartree approximation)
  - exchange (Hartree-Fock approximation)
- density functional theory
  - local density approximation (LDA)
  - exchange-correlation hole
- beyond LDA
  - gradient expansions and GGA
  - some simple applications

MANYBODY WAVEFUNCTIONS

$$\mathcal{H} = -\frac{1}{2}\sum_i \nabla_i^2 + V(\vec{r}) + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\vec{r}_i - \vec{r}_j|}$$

Hartree: $\Psi = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\ldots\phi_N(\vec{r}_N)$

Hartree-Fock: $\Psi = \begin{vmatrix} \phi_1(\vec{r}_1) & \phi_2(\vec{r}_1) & \ldots & \phi_N(\vec{r}_1) \\ \phi_1(\vec{r}_2) & \phi_2(\vec{r}_2) & \ldots & \phi_N(\vec{r}_2) \\ \vdots & \vdots & & \vdots \\ \phi_1(\vec{r}_N) & \phi_2(\vec{r}_N) & \ldots & \phi_N(\vec{r}_N) \end{vmatrix} = |\phi_N(\vec{r}_N)|$

CI: $\Psi = c_1|\phi_N^{(1)}(\vec{r}_N)| + c_2|\phi_N^{(2)}(\vec{r}_N)| + \ldots$

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HARTREE APPROXIMATION

$$\sum_i \left(h_i + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|} \right) \Psi = \varepsilon \Psi \qquad \text{with} \qquad h_i = -\frac{1}{2} \nabla_i^2 + V_{\text{ext}}(\vec{r}_i)$$

Interacting electrons ($\Psi = \phi_1 \phi_2 \ldots \phi_N$):

$$(h_i + V_i(\vec{r}_i))\, \phi_i(\vec{r}_i) = (\varepsilon - \sum_{j \neq i} \epsilon_j) \phi_i(\vec{r}_i) \quad ; \quad V_i(\vec{r}_i) = \sum_{j \neq i} \left\langle \phi_j(\vec{r}_j) | \frac{1}{|\vec{r}_i - \vec{r}_j|} | \phi_j(\vec{r}_j) \right\rangle$$

Average V_i over all particles (introduce self-interaction):

$$V_{\text{H}}(\vec{r}) = \sum_j \left\langle \phi_j(\vec{r}_j) | \frac{1}{|\vec{r} - \vec{r}_j|} | \phi_j(\vec{r}_j) \right\rangle = \int \frac{n(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d\vec{r}\,'$$

Hartree-equation: $(h + V_{\text{H}}(\vec{r}))\, \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r})$

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HARTREE-FOCK APPROXIMATION

Incorporate antisymmetry condition for fermions:

$$\Psi_{\text{Slater}}(\vec{x}_1 \ldots \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{x}_1) & \ldots & \phi_1(\vec{x}_N) \\ \vdots & \ddots & \vdots \\ \phi_N(\vec{x}_1) & \ldots & \phi_N(\vec{x}_N) \end{vmatrix}$$

$$= \frac{1}{\sqrt{N!}} \sum_P (-1)^P P \left(\phi_1(\vec{x}_1) \ldots \phi_N(\vec{x}_N)\right).$$

Hartree-Fock equation ($\vec{x} = \{\vec{r}, \sigma\}$):

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\vec{r}) + V_{\text{H}}(\vec{r})\right)\phi_{i,\sigma}(\vec{r}) - \sum_{j,\sigma'} \int \frac{\phi^*_{j,\sigma'}(\vec{r}')\phi_{i,\sigma'}(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \phi_{j,\sigma}(\vec{r}) = \varepsilon_{i,\sigma}\phi_{i,\sigma}$$

Exchange term: antisymmetry + Coulomb-interaction

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EXCHANGE IN HF

$$\mathcal{H} = -\sum_i \left(\frac{1}{2}\nabla_i^2 + V_{\text{ext}}\right) + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\vec{r}_i - \vec{r}_j|} = \sum_i h_i + \sum_{i,j} g_{ij}$$

Hartree: $[h_i + \sum_j \langle\phi_j|g_{ij}|\phi_j\rangle - \langle\phi_i|g_{ij}|\phi_i\rangle]\phi_i = \varepsilon_i\phi_i$

HF: $[h_i + \sum_{j,\sigma'} \left\langle\phi_j^{\sigma'}|g_{ij}|\phi_j^{\sigma'}\right\rangle]\phi_i^\sigma - \underbrace{\sum_{j,\sigma'}\left\langle\phi_j^{\sigma'}|g_{ij}|\phi_i^{\sigma'}\right\rangle\phi_j^\sigma} = \varepsilon_i\phi_i^\sigma$

rewrite as: $\left[\frac{1}{\langle\phi_i^\sigma|\phi_i^\sigma\rangle}\sum_{j,\sigma'}\left\langle\phi_i^\sigma(\vec{r})\phi_j^{\sigma'}(\vec{r}')|g_{ij}|\phi_j^\sigma(\vec{r})\phi_i^{\sigma'}(\vec{r}')\right\rangle_{(\vec{r}')}\right]\phi_i^\sigma$

$$\left[h_i + \frac{1}{\langle\phi_i^\sigma|\phi_i^\sigma\rangle}\sum_{j,\sigma'}\left(\left\langle\phi_i^\sigma(\vec{r})\phi_j^{\sigma'}(\vec{r}')\quad|g_{ij}|\quad\phi_i^\sigma(\vec{r})\phi_j^{\sigma'}(\vec{r}')\right\rangle_{(\vec{r}')} - \left\langle\phi_i^\sigma(\vec{r})\phi_j^{\sigma'}(\vec{r}')\quad|g_{ij}|\quad\phi_j^\sigma(\vec{r})\phi_i^{\sigma'}(\vec{r}')\right\rangle_{(\vec{r}')}\right)\right]\phi_i^\sigma = \varepsilon_i\phi_i^\sigma$$

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EXCHANGE HOLE

$$V_{\mathrm{x}}^{\mathrm{HF}} = -\frac{1}{\langle \phi_i^\sigma | \phi_i^\sigma \rangle} \sum_{j,\sigma'} \left\langle \phi_i^\sigma(\vec{r}) \phi_j^{\sigma'}(\vec{r}') | g_{ij} | \phi_j^\sigma(\vec{r}) \phi_i^{\sigma'}(\vec{r}') \right\rangle_{(\vec{r}')}$$

is the potential produced by the exchange charge density:

$$n_{\mathrm{x}}^\sigma(\vec{r},\vec{r}') = -\sum_{j,\sigma'} \frac{\phi_i(\vec{r})^{\sigma *} \phi_j^{\sigma' *}(\vec{r}') \phi_j^\sigma(\vec{r}) \phi_i^{\sigma'}(\vec{r}')}{\phi_i(\vec{r})^* \phi_i(\vec{r})}$$

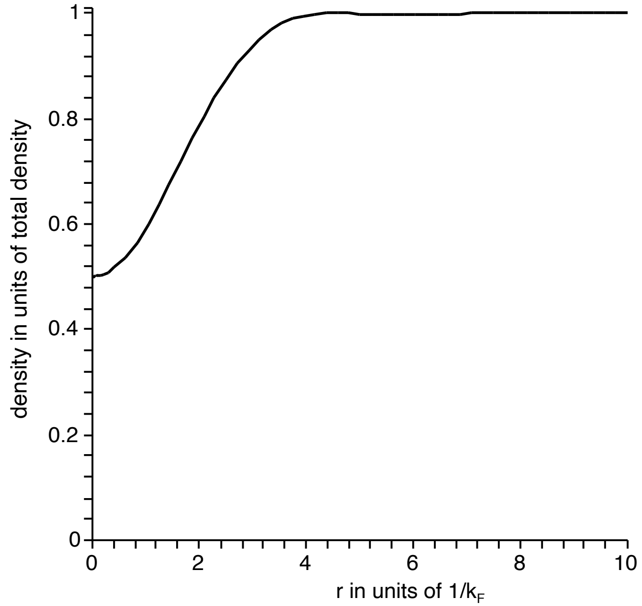
Properties of $n_{\mathrm{x}}^\sigma(\vec{r},\vec{r}')$:

Charge: $\int n_{\mathrm{x}}^\sigma(\vec{r},\vec{r}') d(\vec{r}') = -1$

Limit $(\vec{r}') \to (\vec{r})$:

$n_{\mathrm{x}}^\sigma(\vec{r},\vec{r}) = -\sum_j \phi_j^{\sigma *}(\vec{r}) \phi_j^\sigma(\vec{r})$

J.C.Slater, Physical Review **81**, 385 (1951)



correlation = everything beyond HF

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LOCAL DENSITY APPROXIMATION (LDA) TO DFT

HOHENBERG, KOHN & SHAM

- Hohenberg & Kohn (1964):

$$E[n(\vec{r})] = \int V_{\text{ext}}(\vec{r})n(\vec{r})d\vec{r} + \frac{1}{2}\int\int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}d\vec{r}' + G[n(\vec{r})]$$

  - Ψ and $V_{\text{ext}}(\vec{r})$ uniquely determined by $n(\vec{r})$
  - E stationary w.r.t. variations of $n(\vec{r})$
- Kohn & Sham (1965):
  - E_{kin} of non-interacting e: $T_0[n(\vec{r})] = -\frac{1}{2}\sum_i \langle\phi_i|\boldsymbol{\nabla}^2|\phi_i\rangle$
  - Exchange-correlation pot.: $E_{\text{xc}}[n(\vec{r})] = G[n(\vec{r})] - T_0[n(\vec{r})]$

$$\left[-\frac{1}{2}\boldsymbol{\nabla}^2 + V_{\text{ext}}(\vec{r}) + \int\frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}' + \frac{\delta E_{\text{xc}}}{\delta n(\vec{r})}\right]\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r})$$

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COMPARISON: DFT & HF

$$\mathcal{H} = -\frac{1}{2}\nabla^2 + V_{\text{ext}}(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}' + V_{\text{xc}}(\vec{r})$$

$$\mathcal{H} = -\sum_i \left(\frac{1}{2}\nabla_i^2 + V_{\text{ext}}\right) + \frac{1}{2}\sum_{i\neq j} \frac{1}{|\vec{r}_i-\vec{r}_j|} = \sum_i h_i + \sum_{i,j} g_{ij}$$

Hartree: $[h_i + \sum_j \langle\phi_j|g_{ij}|\phi_j\rangle - \langle\phi_i|g_{ij}|\phi_i\rangle]\phi_i = \varepsilon_i\phi_i$

HF: $[h_i + \sum_j \langle\phi_j|g_{ij}|\phi_j\rangle]\phi_i - \underbrace{\sum_j \langle\phi_j|g_{ij}|\phi_i\rangle\, \phi_j}_{} = \varepsilon_i\phi_i$

corresponds to $V_{\text{xc}}(\vec{r})$ in DFT

Local HF (Slater):

$$E_{\text{x}} = -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{\frac{1}{3}} \int [n(\vec{r})]^{\frac{4}{3}}\, d\vec{r} \quad ; \quad V_{\text{x}}(\vec{r}) = -3\left[\frac{3}{\pi}n(\vec{r})\right]^{\frac{1}{3}}$$

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XC-POTENTIAL IN LDA

"Modern" exchange-correlation (XC) hole:

$$n_{\text{xc}}(\vec{r},\vec{r}') = n(\vec{r}') \int_0^1 d\xi [g_n(\vec{r},\vec{r}',\xi) - 1] \equiv n(\vec{r}') h(\vec{r},\vec{r}')$$

and XC energy: $E_{\text{xc}}[n(\vec{r})] = \frac{1}{2} \int d\vec{r} n(\vec{r}) \int d\vec{r}' \frac{1}{|\vec{r}-\vec{r}'|} n_{\text{xc}}(\vec{r},\vec{r}')$

Local density approximation :

$$E_{\text{xc}}[n(\vec{r})] \rightarrow E_{\text{xc}}(n(\vec{r})) \quad ; \quad h(\vec{r},\vec{r}') \rightarrow h_0(|\vec{r}-\vec{r}'|, n(\vec{r}'))$$

(hole function h_0 for uniform electron gas with density n)

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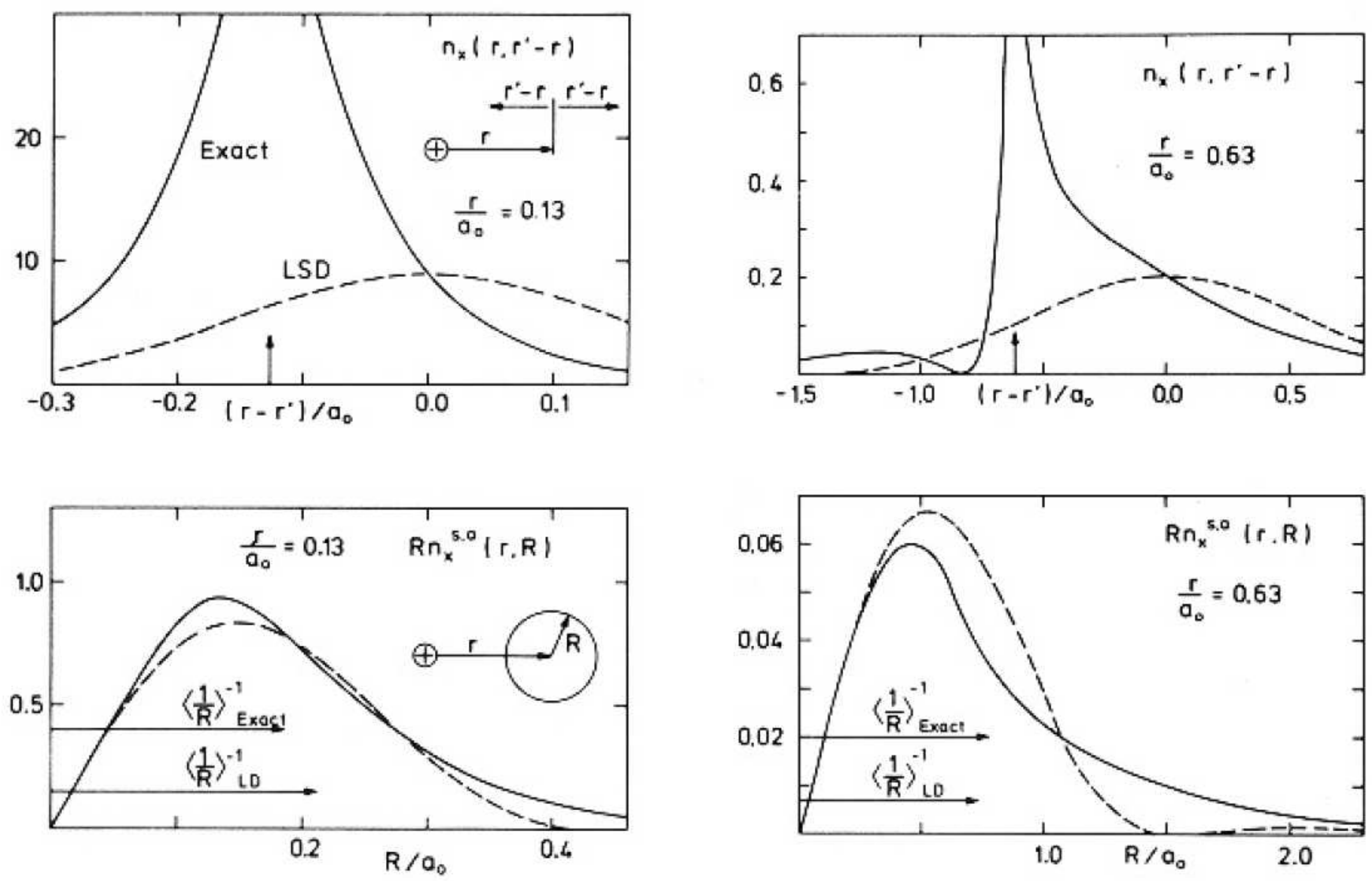
EXACT vs. LDA XC HOLE



- exact and LDA XC hole in a N atom (top) quite different
- spherical average around the electron agrees well (bottom)

BEYOND LDA: GRADIENT EXPANSIONS

Gradient Expansion Approx. (GEA)

$$E_{xc}[n] = E_{xc}^{LDA}(n) + \int d\mathbf{r} f\left(n, \boldsymbol{\nabla} n, \nabla^2 n\right)$$

const. density n_0 + perturbation $\delta n(\mathbf{r})$ $\rightarrow$ $n(\mathbf{r}) = n_0 + \delta n(\mathbf{r})$

$$\int d\mathbf{r}\, n(\mathbf{r}) = N \quad \rightarrow \quad \int d\mathbf{r}\, \delta n(\mathbf{r}) = 0$$

$$E_{xc}[n+\delta n] = E_{xc}[n_0] + \int d\mathbf{r} \frac{\delta E_{xc}}{\delta n(\mathbf{r})}|_{n_0} \delta n(\mathbf{r}) + \frac{1}{2} \int\int d\mathbf{r} d\mathbf{r}' \frac{\delta^2 E_{xc}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')}|_{n_0} \delta n(\mathbf{r}) \delta n(\mathbf{r}')$$

only second order terms survive!

2ND ORDER TERMS IN GEA

$$\frac{\delta^2 E_{\mathrm{xc}}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}|_{n_0} = K_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')|_{n_0} \quad \overset{\text{HEG}}{=} K_{\mathrm{xc}}(|\mathbf{r}-\mathbf{r}'|, n_0)$$

local approx. $\frac{\partial V}{\partial n}|_{n_0} = \int d\mathbf{r} K_{\mathrm{xc}}(|\mathbf{r}|, n_0) = \tilde{K}_{\mathrm{xc}}(\mathbf{k}=0, n_0)$

known for HEG; expand:

$$\tilde{K}_{\mathrm{xc}}(\mathbf{k}, n_0) = \tilde{K}_{\mathrm{xc}}(\mathbf{k}=0, n_0) + \alpha(n_0)k^2 + \beta(n_0)k^4 + \ldots$$

$$E_{\mathrm{xc}}[n] = E_{\mathrm{xc}}^{\mathrm{LDA}}(n) + \frac{1}{2}\int d\mathbf{r}\alpha(n(\mathbf{r}))(\boldsymbol{\nabla} n(\mathbf{r}))^2 + \frac{1}{2}\int d\mathbf{r}\beta(n(\mathbf{r}))(\boldsymbol{\nabla}^2 n(\mathbf{r}))^2 + \ldots$$

good for small | r - r’ |, worse than LDA for large | r – r’ |

overall rather poor…

Generalized Gradient Approx. (GGA)
Design Principles

- no strict expansion in orders of δn
- chose $f\left[n, \boldsymbol{\nabla} n, \nabla^2 n\right]$ to fulfill exact properties
- or fit $f\left[n, \boldsymbol{\nabla} n, \nabla^2 n\right]$ to reproduce xc-energies of known systems

ideally:

- ✓ non-empirical
- ✓ universal
- ✓ simple
- ✓ accurate

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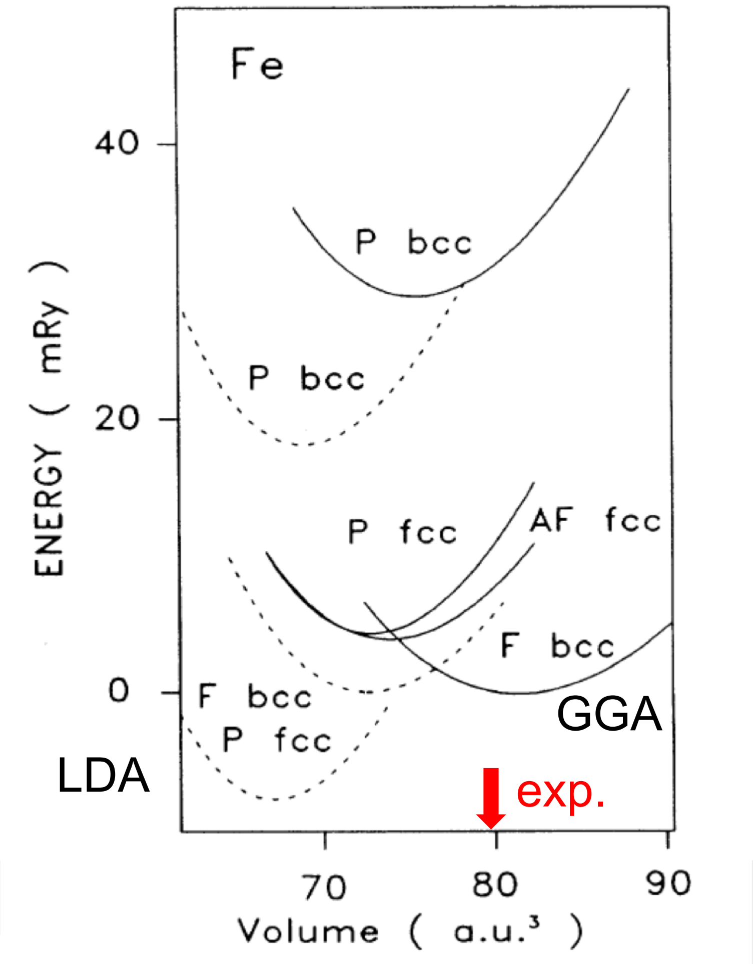
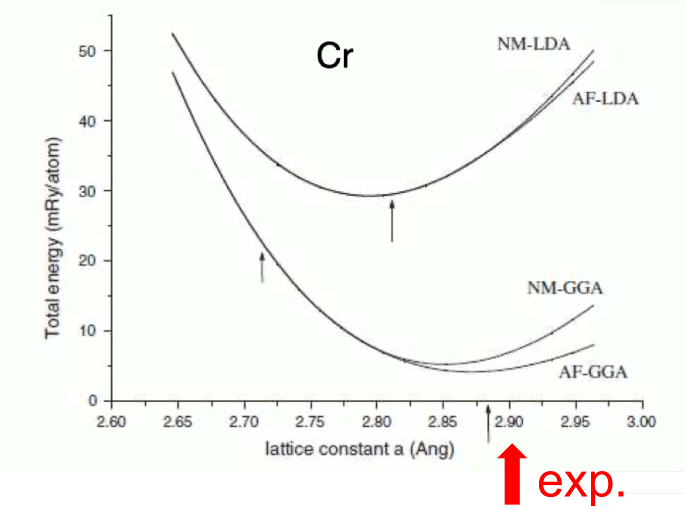
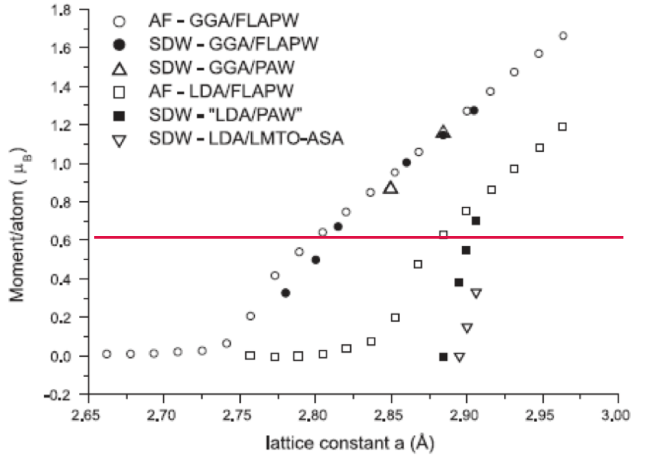
LDA vs. GGA: Fe and Cr







GGA gives better structure, not necessarily better magnetic properties

EVOLUTION OF XC POTENTIALS

full orbital based DFT (e.g. c-RPA)

hyper-GGA (+exact exchange energy)

meta-GGA (+kinetic energy density)

GGA (+gradients)

LDA (density)

$$E_{\mathrm{xc}}[n(\mathbf{r})] = E_{\mathrm{xc}}\left(n(\mathbf{r}), \boldsymbol{\nabla} n(\mathbf{r}), \tau(\mathbf{r}), \phi_i(\mathbf{r}) \ldots\right)$$

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SUMMARY:

Evolution of exchange-correlation potentials

- ”local Hartree-Fock” type
- better description of exchange-correlation holes
- parametrization of QMC data
- fitting to databases
- inclusion of data beyond the density

Thank you for your attention !