FHI Coffee Talk

Constraints for DFT Functional

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Reference

- J. P. Perdew and K. Schmidt,

  Jacob's ladder of density functional approximations for the exchange-correlation energy,

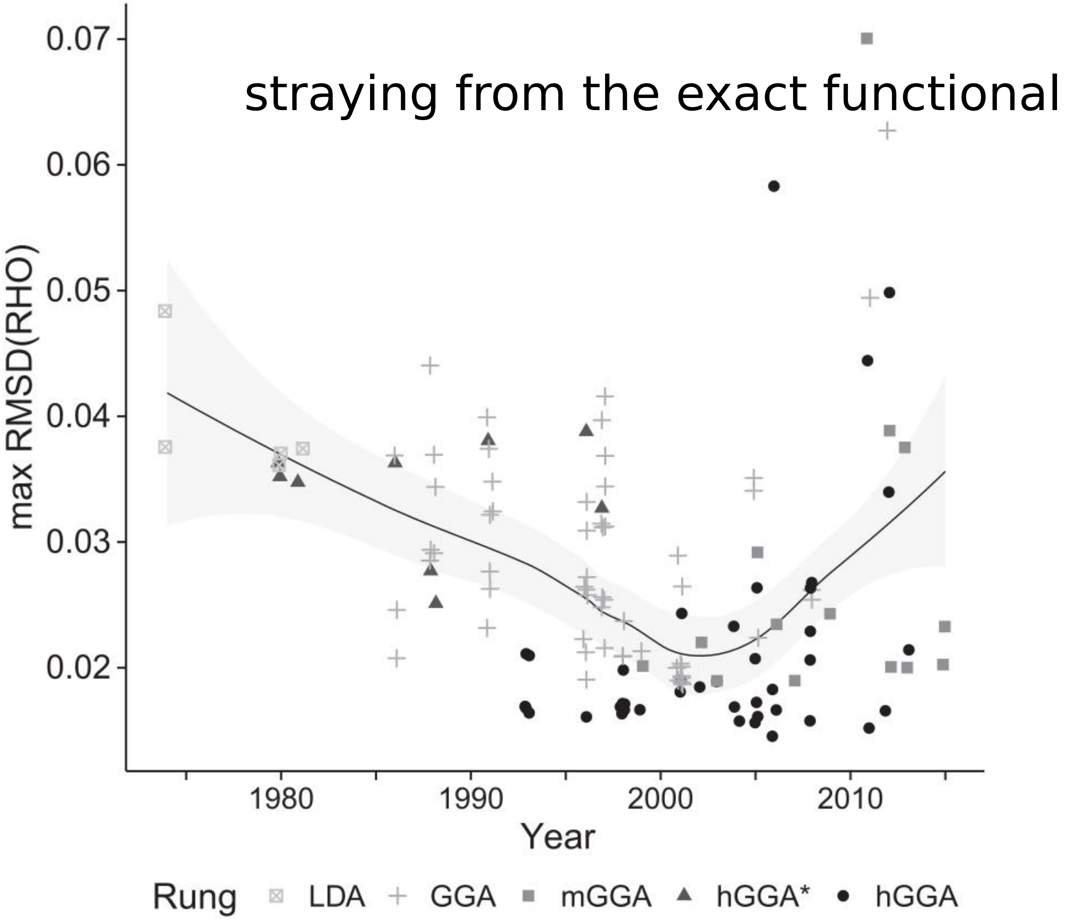
  AIP Conference Proceedings **577**, 1 (2001)

- J. P. Perdew, A. Ruzsinszky. J. Sun and K. Burke,

  Gedanken Densities and Exact Constraints in Density Functional Theory,

  The Journal of Chemical Physics **140**, 18A533 (2014)

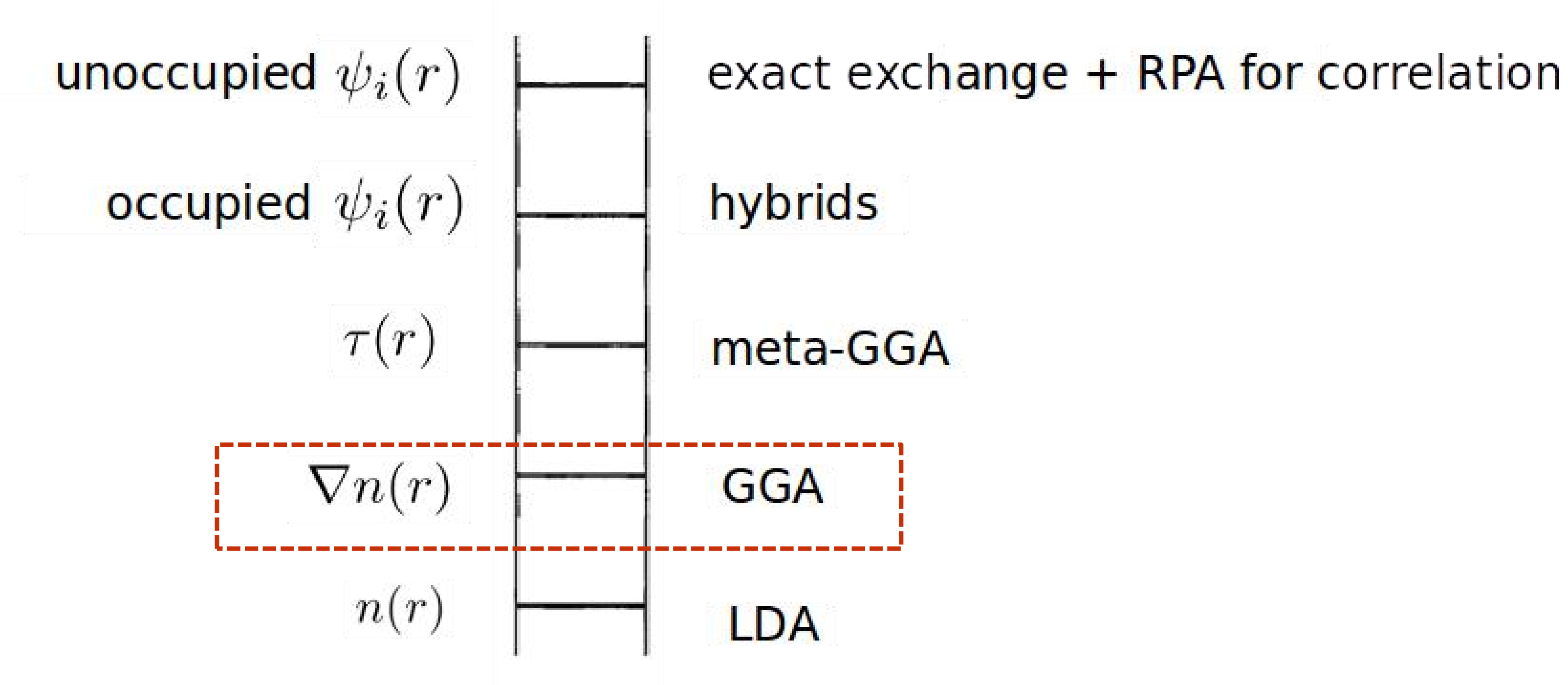
Dispute about DFT functional



very compact $1s^2$ and $1s^2 2s^2$ systems

- M. G. Medvedev, I. S. Bushmarinov, J. P. Perdew, and A. K. Lyssenko, Science **355**, 6320 (2017)
- Comment

Jacob's Ladder



- J. P. Perdew and K. Schmidt, AIP Conference Proceedings **577**, 1 (2001)

Second-Order Gradient Expansion Approximation (GE2)

Exchange :

$$E_x^{GE2}[n] = \int dr[n\epsilon_x^{unif}(n) + C_x \frac{|\nabla n|^2}{n^{4/3}}]$$

C_x is a negative constant

Second-Order Gradient Expansion Approximation (GE2)

Correlation :

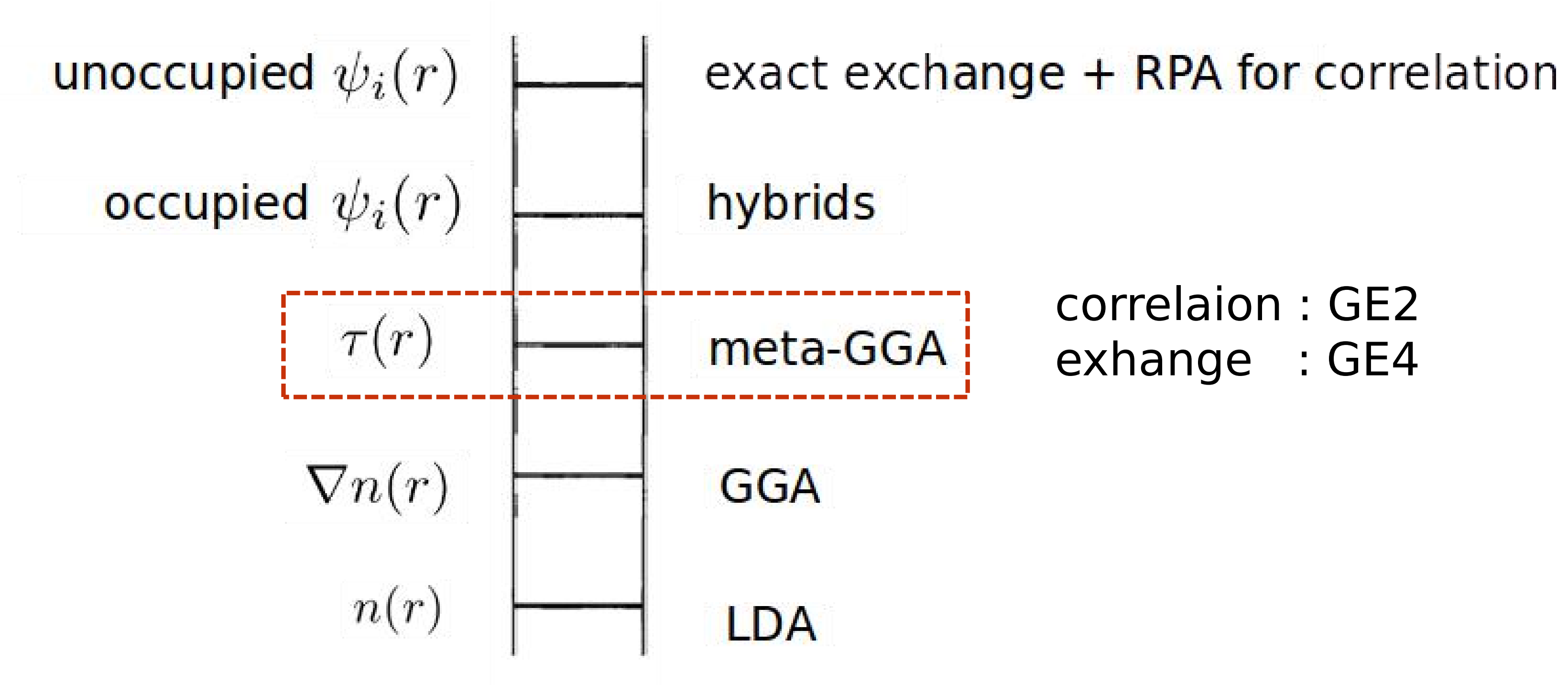
$$E_c^{GE2}[n_\uparrow, n_\downarrow] = \int dr[n\epsilon_x^{unif} + \phi(\zeta)C_c(n)\frac{|\nabla n|^2}{n^{4/3}}]$$

$$\zeta = (n_\uparrow - n_\downarrow)/n \qquad \phi(\zeta) = [(1+\zeta)^{2/3} + (1-\zeta)^{2/3}]/2$$

a weak function of density $C_c(n)$

$$C_c[\infty] \approx 4.235 \times 10^{-3}$$

Jacob's Ladder



correlaion : GE2
exhange : GE4

- J. P. Perdew and K. Schmidt, AIP Conference Proceedings **577**, 1 (2001)

Forth-Order
Gradient Expansion Approximation (GE4)

$$E_x^{GE4}[n] = \int dr[n\epsilon_x^{unif}(n) + C_x \frac{|\nabla n|^2}{n^{4/3}} + \alpha_x \frac{|\nabla^2 n|}{n^2} + \beta_x \frac{|\nabla n|^2 \nabla^2 n}{n^3} + \gamma_x \frac{|\nabla n|^4}{n^4}]$$

$$C_x = -2.382 \times 10^{-3} \quad \alpha_x = -3.633 \times 10^{-5} \quad \beta_x = 9.083 \times 10^{-5}$$

Forth-Order
Gradient Expansion Approximation (GE4)

$$E_x^{GE4}[n] = \int dr[n\epsilon_x^{unif}(n) + C_x \frac{|\nabla n|^2}{n^{4/3}} + \alpha_x \frac{|\nabla^2 n|}{n^2} + \beta_x \frac{|\nabla n|^2 \nabla^2 n}{n^3} + \gamma_x \frac{|\nabla n|^4}{n^4}]$$

$$C_x = -2.382 \times 10^{-3} \quad \alpha_x = -3.633 \times 10^{-5} \quad \beta_x = 9.083 \times 10^{-5}$$

fitting the atomization energies of 20 small molecules

- Size-Consistency

$$E_{xc}[n_A + n_B] = E_{xc}[n_A] + E_{xc}[n_B]$$

where $n_A(r)$ and $n_B(r)$ do not overlap.

- Exchange Energy is negative
- Correlation Energy is nonpositive

Spin-Scaling Relation

The exchange energy is

$$-\frac{1}{2}\sum_{\sigma}\sum_{\substack{i,j\\occ}}\int d^3r\int d^3r'\,\frac{\phi^*_{i\sigma}(\mathbf{r})\phi^*_{j\sigma}(\mathbf{r}')\phi_{i\sigma}(\mathbf{r}')\phi_{j\sigma}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$

$$\begin{aligned}E_x[n_\uparrow, n_\downarrow] &= E_x[n_\uparrow, 0] + E_x[0, n_\downarrow]\\ &= \frac{1}{2}E_x[n_\uparrow, n_\uparrow] + \frac{1}{2}E_x[n_\downarrow, n_\downarrow]\end{aligned}$$

The Lieb-Oxford inequality

$$\langle V_{ee} \rangle - U_H \geq B \int d^3r n_x^{unif}(n)$$

$$B \sim 1.67$$

The Lieb-Oxford Bound

$$\boxed{E_{xc}[n] \geq \langle V_{ee} \rangle - U_H} \geq B \int d^3r n_x^{unif}(n)$$

$$B \sim 1.67$$

The Lieb-Oxford Bound

$$E_{xc}[n] \geq \langle V_{ee} \rangle - U_H \geq B \int d^3 r\, n_x^{unif}(n)$$

$$B \sim 1.67$$

For two-electron densities

$$E_x \geq 1.174 \int d^3 r\, n_x^{unif}(n)$$

satisfied by LDA, but not by PBE or TPSS

One-Electron System

$$E_c[n, 0] = 0$$

$$\int d^3 r n(r) = 1$$

Uniform Density Scaling

$$n_\gamma(r) = \gamma^3 n(\gamma r)$$

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Uniform Density Scaling

$$n_\gamma(r) = \gamma^3 n(\gamma r)$$

For exchange : $E_x[n_\gamma] = \gamma E_x[n]$

$$E_x^{LDA}[n] = \int d^3r A n(r)^{4/3} \qquad A = -(3/4\pi)(3\pi^2)^{1/3}$$

$$E_x^{LDA}[n_\gamma] = \int d^3r A \gamma^4 n(\gamma r)^{4/3}$$

$$= \gamma \int d^3(\gamma r) A n(\gamma r)^{4/3}$$

$$= \gamma E_x^{LDA}[n]$$

Uniform Density Scaling

For correlation,

- in the low-density limit

$$\lim_{\gamma \to 0} E_c[n_\gamma] = \gamma E_c[n]$$

- in the high-density limit

$$\lim_{\gamma \to \infty} E_c[n_\gamma] \to const$$

Uniform Density Scaling

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$$\lim_{\gamma\to\infty} E_c^{LDA}[n_\gamma] \to const + \ln\gamma$$

Linear Response of Uniform Electron Gas

the exchange-correlation factor

$$f_{xc}(q) = f_{xc}(|r-r'|) = [\frac{\delta^2 E_{xc}[n]}{\delta n(r)\delta n(r')}]_{n_0}$$

$$f_{xc}(q) = -4\pi e^2/q^2 \boxed{G(q)}$$ local field factor

- S. Moroni, D. M. Ceperley, and G. Senatore, Phys. Rev. Lett. **75**, 689 (1995)

Linear Response of Uniform Electron Gas

response function $\chi(q) \longleftrightarrow$ local field factor $G(q)$

$\downarrow$

the exchange-correlation factor $f_{xc}(q) = -4\pi e^2/q^2 G(q)$

- S. Moroni, D. M. Ceperley, and G. Senatore, Phys. Rev. Lett. **75**, 689 (1995)

Non-Uniform Density Scaling

$$s = |\nabla n| / [2(3\pi^2)^{1/3} n^{4/3}]$$

$$\lim_{s \to \infty} E_x = \int d^3 r n \epsilon^{unif} O(s^{-1/2})$$

$$\lim_{s \to \infty} E_{xc} < \int d^3 r n \epsilon^{unif} O(s^{-1/2})$$

Strongly Constrained and Appropriately Normed Semilocal Density Functional (SCAN)

- All listed constraints
- rare-gas atoms and nonbonded interactions

- J. Sun, A. Ruzsinszky, and J. P. Perdew, Phys. Rev. Lett. **115**, 036402 (2015)