EXCHANGE CORRELATION FUNCTIONALS

12TH SEPTEMBER 2019 I MATTHIAS REDIES

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INTRODUCTION

Total energy in solids

Many-body energy

$$E_H = \int d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$
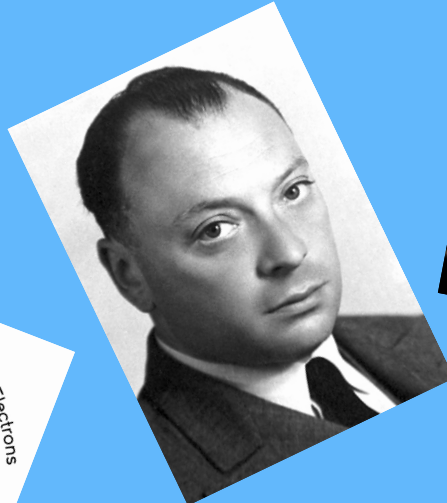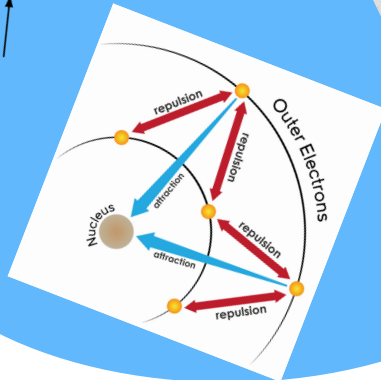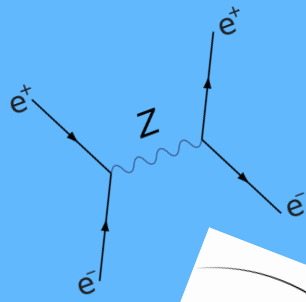
$$E[n] \approx T_s[n] + \int d\mathbf{r}v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + E_H[n]$$

Mean-field approach

INTRODUCTION

What's in E_{xc}

$$E[n] = T_s[n] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + E_H[n] + E_{\text{xc}}[n]$$

INTRODUCTION

Hartree approximation

$$E[n] = T_s[n] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + E_H[n] + E_{xc}[n]$$

$$E_H = \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

➡ $E_{xc}[n]$ includes a self-interaction correction

$E_{xc}[n]$ describes how electrons avoid each other

x: pauli exclusion principle

c: screening,
   self-interaction correction,
   "the rest"

Lot's of bonding happens here!

INTRODUCTION

Local Spin Density Approximation

$$v(\mathbf{r}) \to v_\uparrow(\mathbf{r}), v_\downarrow(\mathbf{r})$$

$$n(\mathbf{r}) \to n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})$$

In a system with $v(\mathbf{r}) = v_\uparrow(\mathbf{r}) = v_\downarrow(\mathbf{r})$ whose groundstate can be spin-polarized, LSDA will preform better than LDA
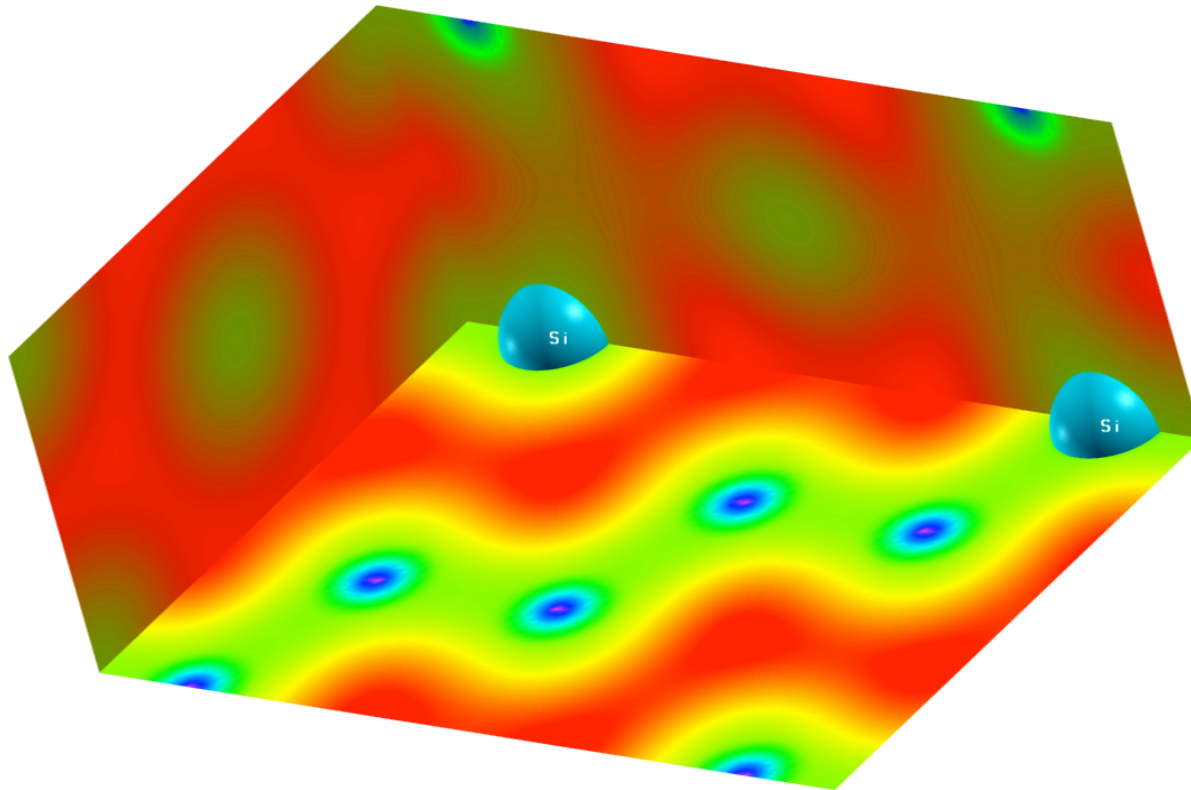
INTRODUCTION

Local Density Approximation

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

➡ use quantum monte carlo to interpolate ε_{xc}^{HEG}

➡ lot's of parametrizations

➡ all equivalent
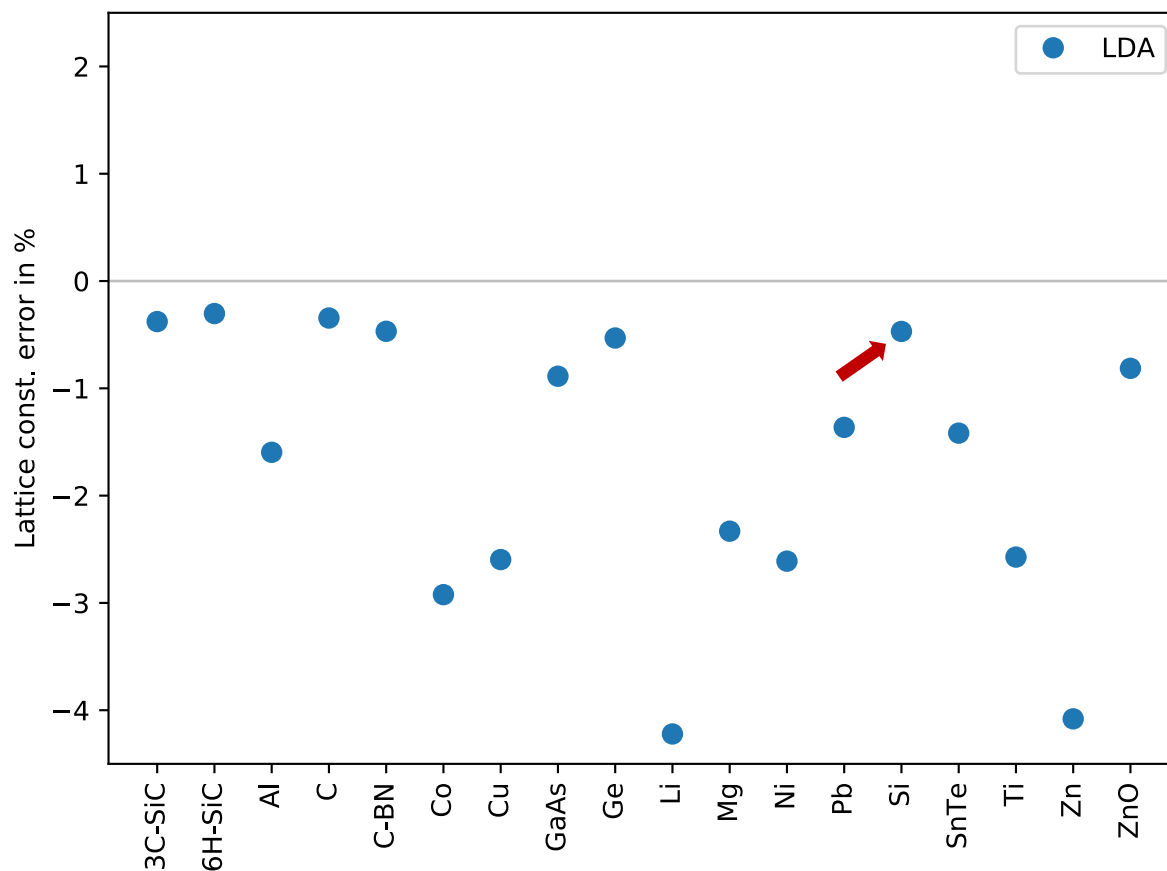
➡ Exact for any uniform density

INTRODUCTION

Density of silicone

PERFORMANCE OF LDA

Lattice parameters

Mean error: -6.1 pm

Mean abs. error: 6.1 pm

INTRODUCTION

Local Density Approximation: Why does it work?

$$E_{xc}[n] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

On the Constitution of Metallic Sodium

E. WIGNER AND F. SEITZ, *Department of Physics, Princeton University*
(Received March 18, 1933)

$n_{xc}(\mathbf{r}, \mathbf{r}')$: xc-hole density

$$n_{xc}(\mathbf{r}, \mathbf{r}') = n_x(\mathbf{r}, \mathbf{r}') + n_c(\mathbf{r}, \mathbf{r}')$$
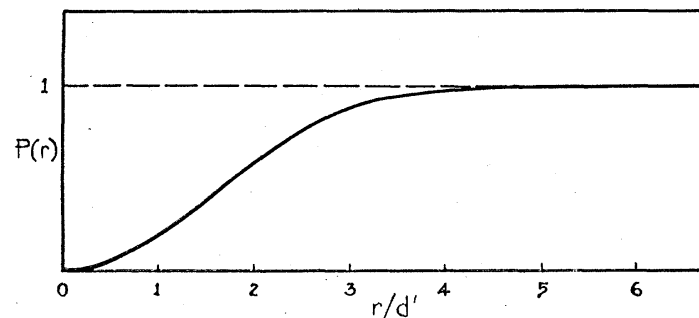
LDA fullfils these exact constraints:

$$n_x \leq 0$$

$$\int d\mathbf{r} \, n_x(\mathbf{r}, \mathbf{r}') = -1$$

$$\int d\mathbf{r} \, n_c(\mathbf{r}, \mathbf{r}') = 0$$

$n_{xc}^{LDA}(\mathbf{r}, \mathbf{r}')$ Fulfils these conditions, because it's based on a physical system!

PERFORMANCE OF LDA

Band gap
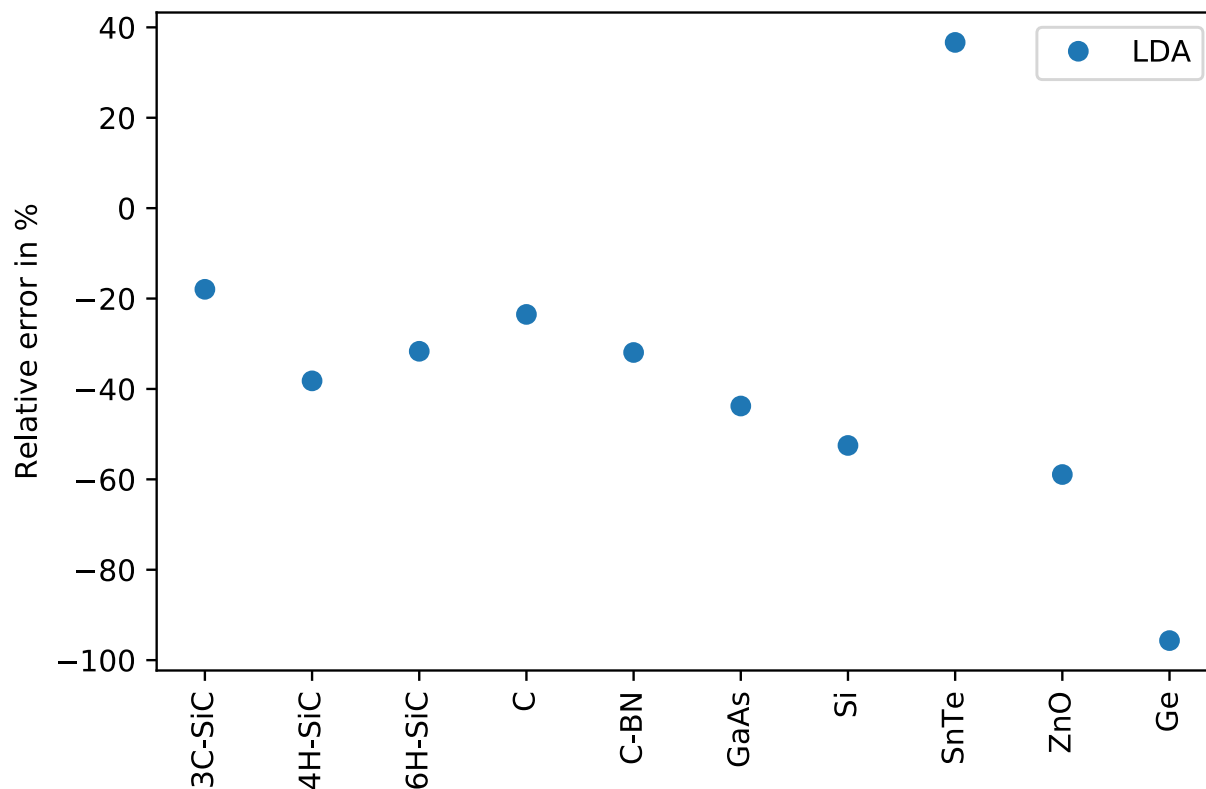
Mean Error:
-0.97 eV

Mean abs. Error:
0.984 eV

BEYOND LDA

Generalized Gradient Approximation

Idea:
Get more information about the density through a Taylor expansion

Include ∇n to

$$E_{\mathrm{xc}}[n, \nabla n] = \int d\mathbf{r}\, \varepsilon_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))$$

Unlike LDA, there are a lot of GGAs

Not strictly ab-initio anymore

Choice of GGA is a parameter

BEYOND LDA

GGAs in FLEUR

➡ FLEUR has 5 native GGAs:
pw91, pbe (1996),   rpbe(1998),   Rpbe(1998), wc(2006)

revises   revises

➡ LibXC has ~125 GGAs

PBEsol, EV93PW91 and everything else

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➡ *f*leur   has ~125 GGAs

GGAS IN FLEUR

LibXC

1.
```
redies@mb-redies ~
> $ FC=mpifort CC=gcc ./configure.sh -libxc true
```

2.
```
<xcFunctional name="pbe" relativisticCorrections="F"/>
```

⬇

```
<xcFunctional name="LibXC" relativisticCorrections="F">
   <LibXCName  exchange="gga_x_pbe_sol" correlation="gga_c_pbe_sol"/>
</xcFunctional>
```

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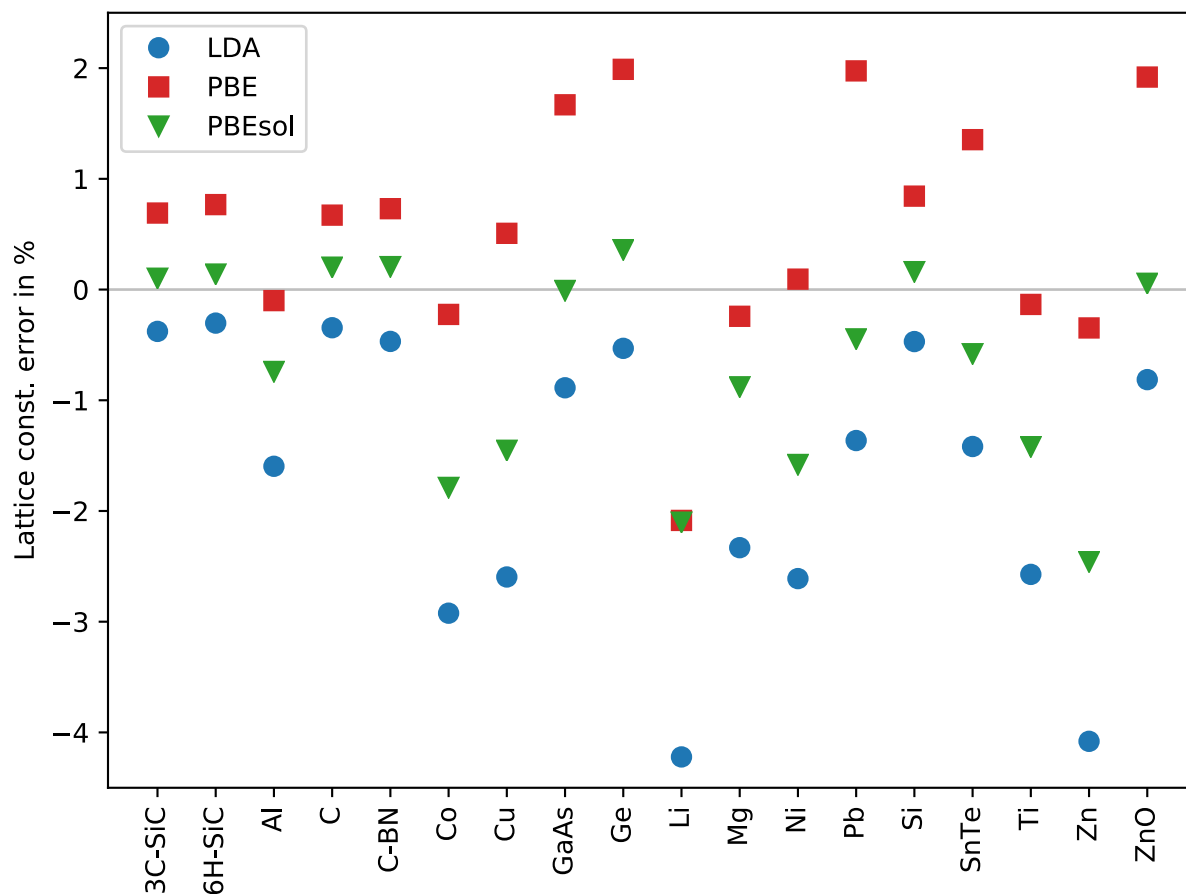
PERFORMANCE OF GGA

Lattice parameters

LDA
Mean error:
-6.1 pm
Mean abs. error:
6.1 pm

PBE:
Mean Error:
3.1 pm
Mean abs. Error:
4.3 pm

PBEsol:
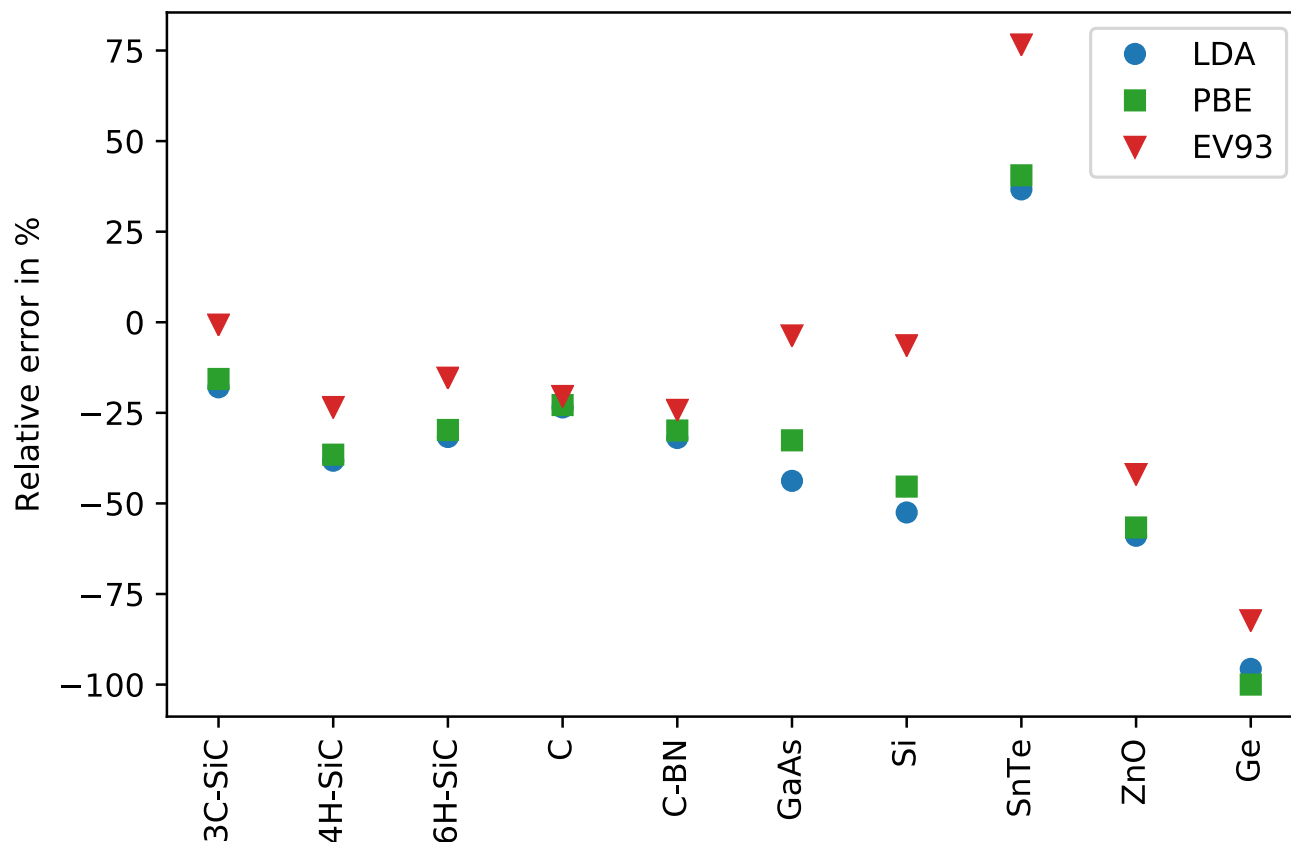Mean Error:
-2.2 pm
Mean abs. Error:
2.8 pm

PERFORMANCE OF GGA

Band gap

LDA:
Mean Error:
-0.97 eV
Mean abs. Error:
0.984 eV

PBE:
Mean Error:
-0.909 eV
Mean abs. Error:
0.923 eV

EV93PW91:
Mean Error:
-0.58 eV
Mean abs. Error:
0.6121 eV

VAN DER WAALS

PBE layer distance in Graphite
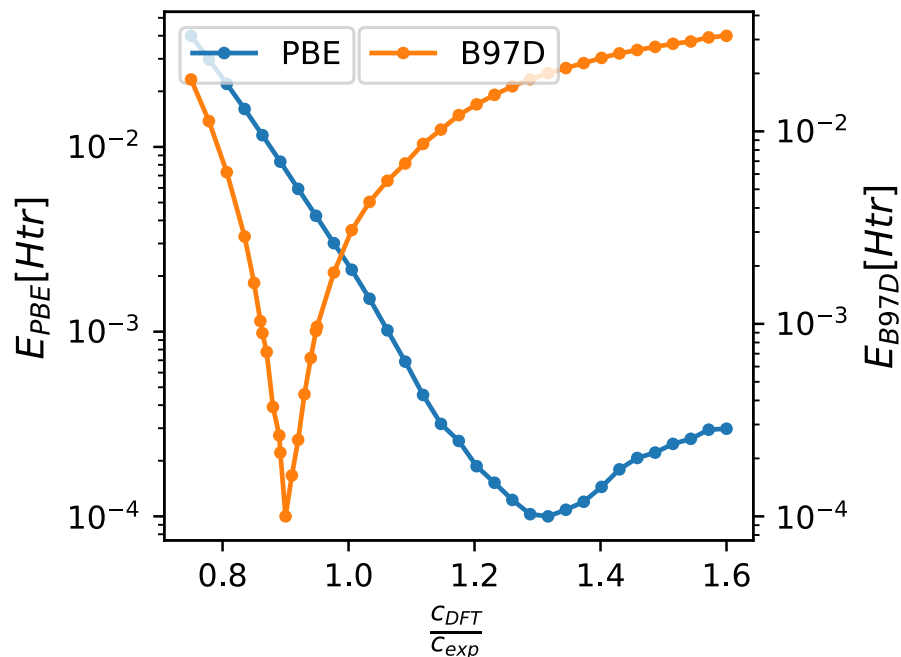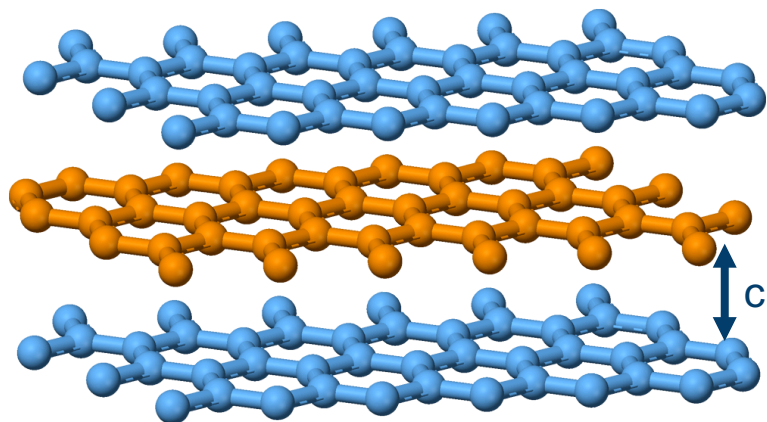
➡ Graphene layers are weakly van-der-Walls bonded

➡ GGAs and LDAs are bad with vdW materials

VAN DER WAALS

van-der-Waals functionals

$$E_{xc}[n] = E_x^{\mathrm{GGA}}[n] + E_c^{\mathrm{LDA}}[n] + E_c^{\mathrm{nl}}[n]$$

$$E[n] = \int d\mathbf{r}\, n(\mathbf{r})\varepsilon_{xc}(\mathbf{r})$$

$$E_c^{\mathrm{nl}} = \frac{1}{2}\int d^3r\, d^3r'\, n(\vec{r})\phi\left(\vec{r},\vec{r}'\right)n\left(\vec{r}'\right)$$

➡ Dispersion needs a non-local description

➡ Fleur has an undocumented van-der-Waals feature

➡ Contact us!

BEYOND LDA & GGA

Jacobs ladder

DFT Heaven

Computational Effort

GW, RPA	unoccupied $\psi_i(\mathbf{r'})$
Hybrid	occupied $\psi_i(\mathbf{r'})$
Meta-GGA	$\tau(\mathbf{r}) = \dfrac{1}{2}\sum_i |\nabla\psi_i(\mathbf{r})|^2$
Generalized gradient approx.	$\nabla n(\mathbf{r})$
Local density approximation	$n(\mathbf{r})$

GW, RPA
Hybrid
} non-local

⋮

Meta-GGA
Generalized gradient approx.
Local density approximation
} semi-local
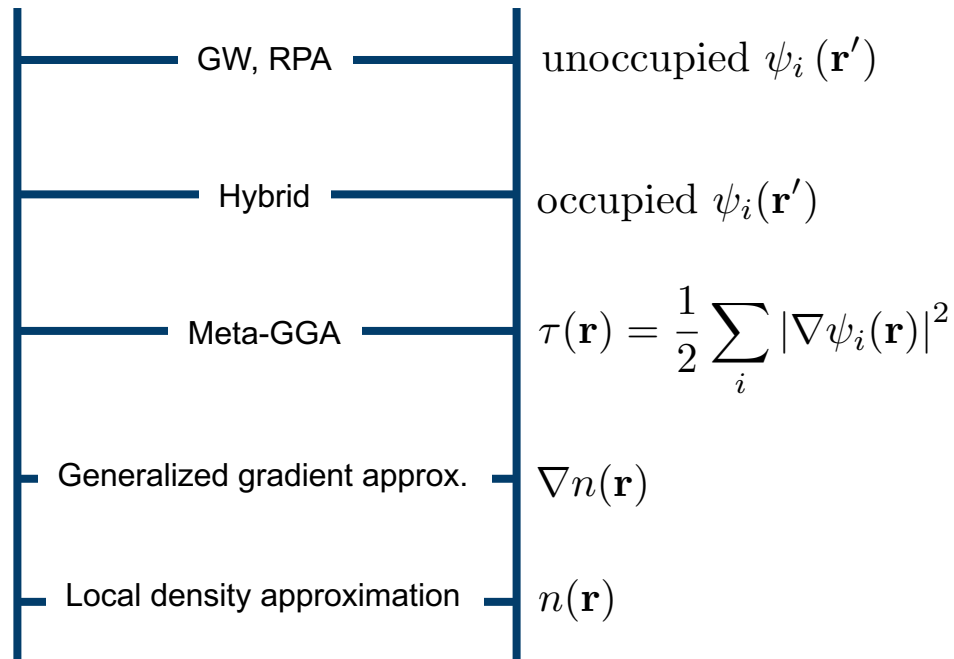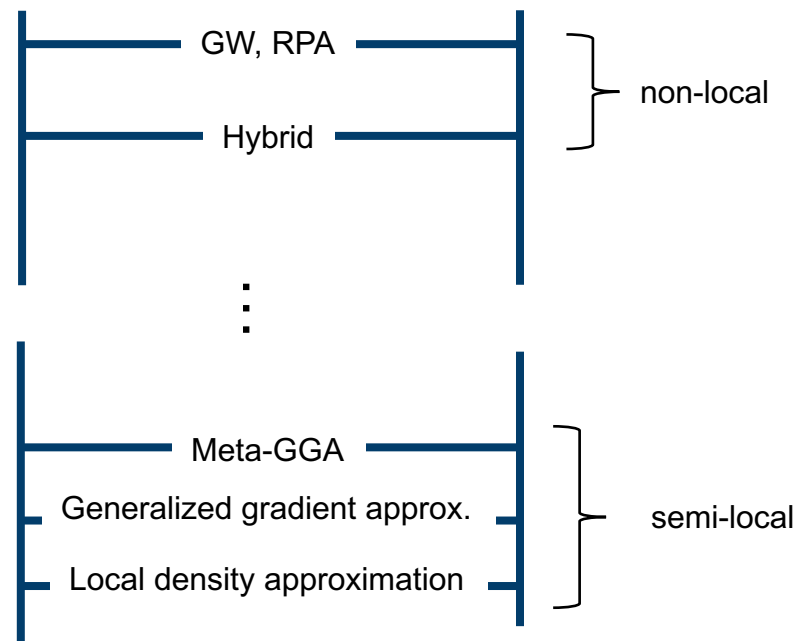
BEYOND LDA & GGA

TABLE I. Satisfaction (Yes/No) of selected exact constraints by approximate exchange–correlation functionals.

Constraint	LSDA	PBE	PKZB	TPSS
Global properties				
$E_x < 0$	Y	Y	Y	Y
$E_c \leq 0$	Y	Y	N	Y
$E_c = 0$ if $\int n(\mathbf{r})d^3r = 1$	N	N	Y	Y
$E_{xc} \geq -D\int n^{4/3}(\mathbf{r})d^3r$ [a]	Y	Y	YN[b]	Y
$E_{xc} = E_{xc}^{LSDA}$, $n_\uparrow, n_\downarrow = $ const	Y	Y	Y	Y
$E_x = -U[n]$ if $\int n(\mathbf{r})d^3r = 1$ [c]	N	N	N	YN[d]
Highest order in ∇ for E_x^{GEA} [e]	0	0	2[f]	4
Highest order in ∇ for E_c^{GEA} [e]	0	2	2	2
Spin and density scaling [g]				
$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2}\Sigma_{\sigma=\uparrow\downarrow}E_x[2n_\sigma]$ [h]	Y	Y	Y	Y
$E_x[n_\lambda] = \lambda E_x[n]$ [i]	Y	Y	Y	Y
$E_c[n_\lambda] > \lambda E_c[n]$, $\lambda > 1$ [i]	Y	Y	Y	Y
$\lim_{\lambda\to\infty} E_c[n_\lambda] > -\infty$ [j]	N	Y	Y	Y
$\lim_{\lambda\to 0}\lambda^{-1}E_c[n_\lambda] > -\infty$ [j]	Y	Y	Y	Y
$\lim_{\lambda\to\infty}E_x[n_\lambda^x] > -\infty$ [j]	N	N	N	N
$\lim_{\lambda\to 0}E_x[n_\lambda^x] > -\infty$ [j]	Y	Y	Y	Y
$\lim_{\lambda\to\infty}E_c[n_\lambda^x] > -\infty$ [j]	N	Y	Y	Y
Asymptotic behavior				
$v_x(\mathbf{r}) \to -1/r$, $r\to\infty$	N	N	N	N
$v_x(\mathbf{r})$ finite at the nucleus	Y	N	N	YN[k]
$v_c(\mathbf{r})$ finite at the nucleus	Y	N	YN[l]	YN[l]

GGA { PBE, PKZB } MGGA { PKZB, TPSS }

Staroverov, Viktor N., et al *PRB*, 69

⟶ SCAN fulfils all 17 known constraints

Sun, Jianwei, et at *PRL* 115

Functional	Mean Error (a_0)	Mean abs. Error(a_0)
LDA	-0.071	0.071
PBE	0.056	0.061
SCAN	0.018	0.030

From F. Tran, et al Journal of Chemical Physics

⟶ SCAN is a significant improvement on PBE

⟶ Ask if you are interested

POTENTIALS IN METAGGAS

$$v_{xc}^{LDA}(\mathbf{r}) = \frac{\delta E[n]}{\delta n(\mathbf{r})}$$

$$v_{xc}^{GGA}(\mathbf{r}) = \frac{\delta E[n, \nabla n]}{\delta n(\mathbf{r})} + \frac{\delta E[n, \nabla n]}{\delta \nabla n(\mathbf{r})}$$

$$v_{xc}^{MGGA}(\mathbf{r}) = \frac{\delta E[n, \nabla n, \tau]}{\delta n(\mathbf{r})} + \frac{\delta E[n, \nabla n, \tau]}{\delta \nabla n(\mathbf{r})} + \frac{\delta E[n, \nabla n, \tau]}{\delta \tau}$$

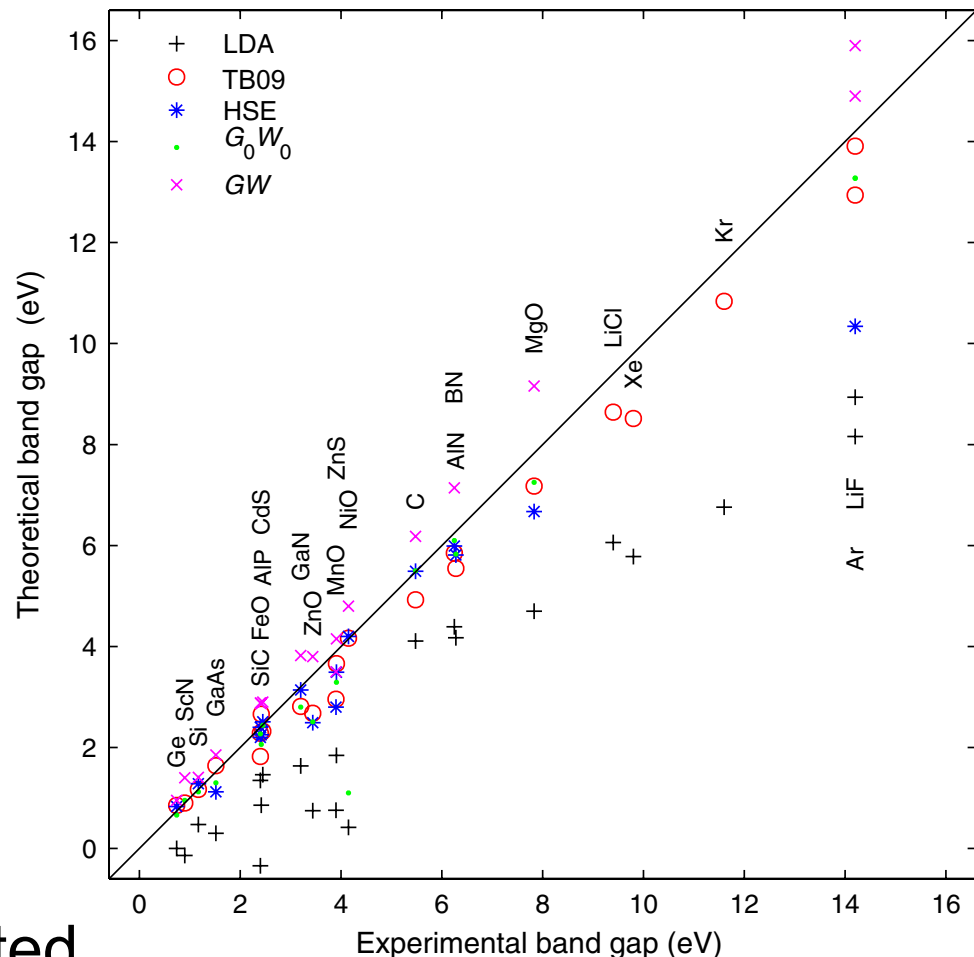Since τ depends on the orbitals, rather than the density this isn't straight-forward

$$\tau = \frac{1}{2} \sum_i |\nabla \psi_i|^2$$

→ In FLEUR:

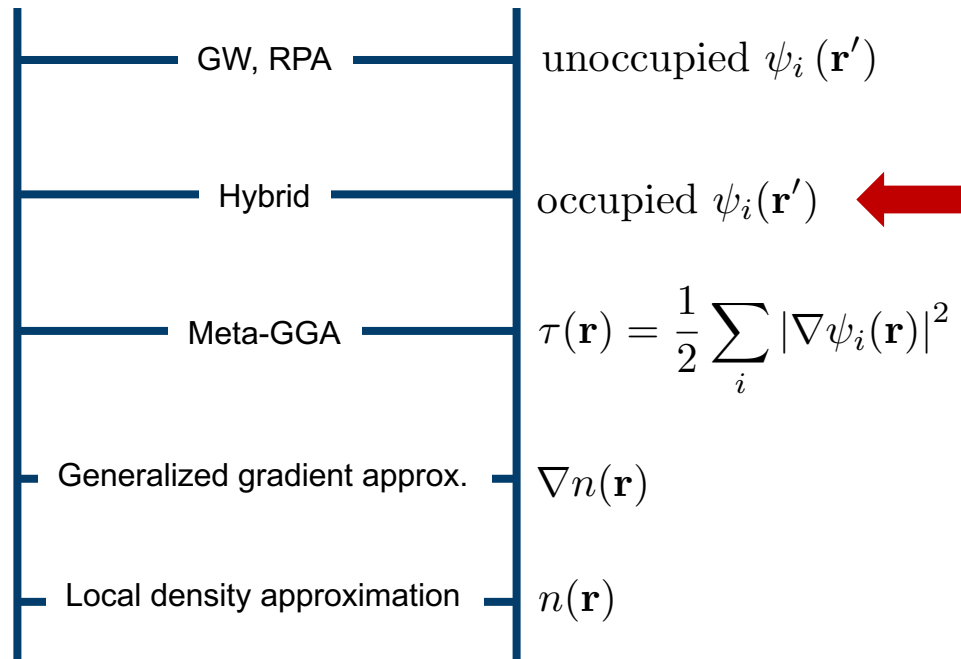calculate E_{xc} in SCAN and v_{xc} in PBE

POTENTIALS IN METAGGAS

➤ Special class of MetaGGAs provides v_{xc} directly

➤ Optimized for specific material properties

➤ TB09 provides an accurate Band gap prediction

➤ Ask if you are interested

F. Tran PRL102,226401 (2009)

EXACT EXCHANGE

DFT Heaven

GW, RPA — unoccupied $\psi_i(\mathbf{r}')$

Hybrid — occupied $\psi_i(\mathbf{r}')$ ⬅

Meta-GGA — $\tau(\mathbf{r}) = \dfrac{1}{2}\sum_i |\nabla \psi_i(\mathbf{r})|^2$

Generalized gradient approx. — $\nabla n(\mathbf{r})$

Local density approximation — $n(\mathbf{r})$

EXACT EXCHANGE

DFT Heaven

GW, RPA	unoccupied $\psi_i(\mathbf{r}')$ ⬅
Hybrid	occupied $\psi_i(\mathbf{r}')$
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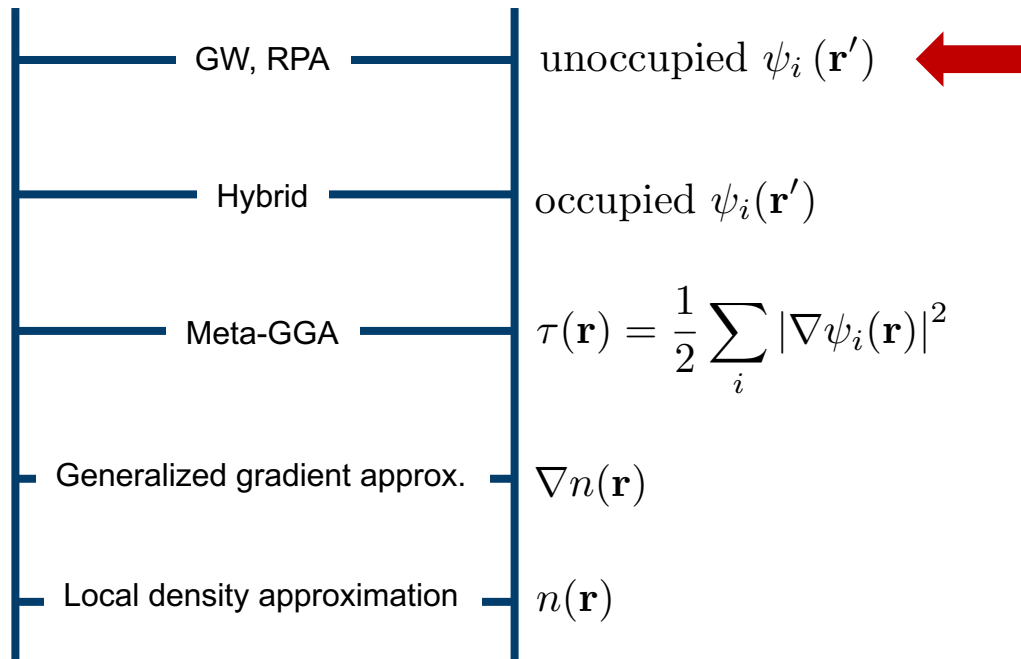
EXACT EXCHANGE

Hartree

$$\psi\left(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots \mathbf{r}_p\right) = \psi_\alpha\left(\mathbf{r}_1\right) \psi_\beta\left(\mathbf{r}_2\right) \psi_\gamma\left(\mathbf{r}_3\right) \ldots \psi_\pi\left(\mathbf{r}_p\right)$$

Fermions
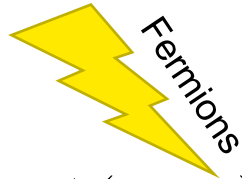
$$\psi\left(\mathbf{r}_1, \mathbf{r}_2\right) = -\psi\left(\mathbf{r}_2, \mathbf{r}_1\right)$$

Hartree-Fock

$$\psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \cdots & \psi_1(\mathbf{r}_n) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_n) & \cdots & \psi_2(\mathbf{r}_n) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_n(\mathbf{r}_2) & \psi_n(\mathbf{r}_2) & \cdots & \psi_n(\mathbf{r}_n) \end{vmatrix}$$

➡ By design: Exact exchange

$$E_\mathrm{x}^\mathrm{exx} = -\frac{1}{2} \sum_{i,j} \iint \psi_i^*\left(\mathbf{r}_1\right) \psi_j^*\left(\mathbf{r}_2\right) \frac{1}{r_{12}} \psi_j\left(\mathbf{r}_1\right) \psi_i\left(\mathbf{r}_2\right) d\mathbf{r}_1 d\mathbf{r}_2$$

6D-Integral

EXACT EXCHANGE

Hartree-Fock Problems

$$\psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \cdots & \psi_1(\mathbf{r}_n) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_n) & \cdots & \psi_2(\mathbf{r}_n) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_n(\mathbf{r}_2) & \psi_n(\mathbf{r}_2) & \cdots & \psi_n(\mathbf{r}_n) \end{vmatrix}$$

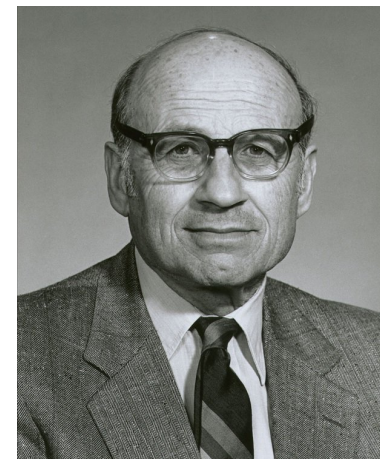➡ $n(\mathbf{r}_a, \mathbf{r}_b) \sim n(\mathbf{r}_a)\, n(\mathbf{r}_b)$
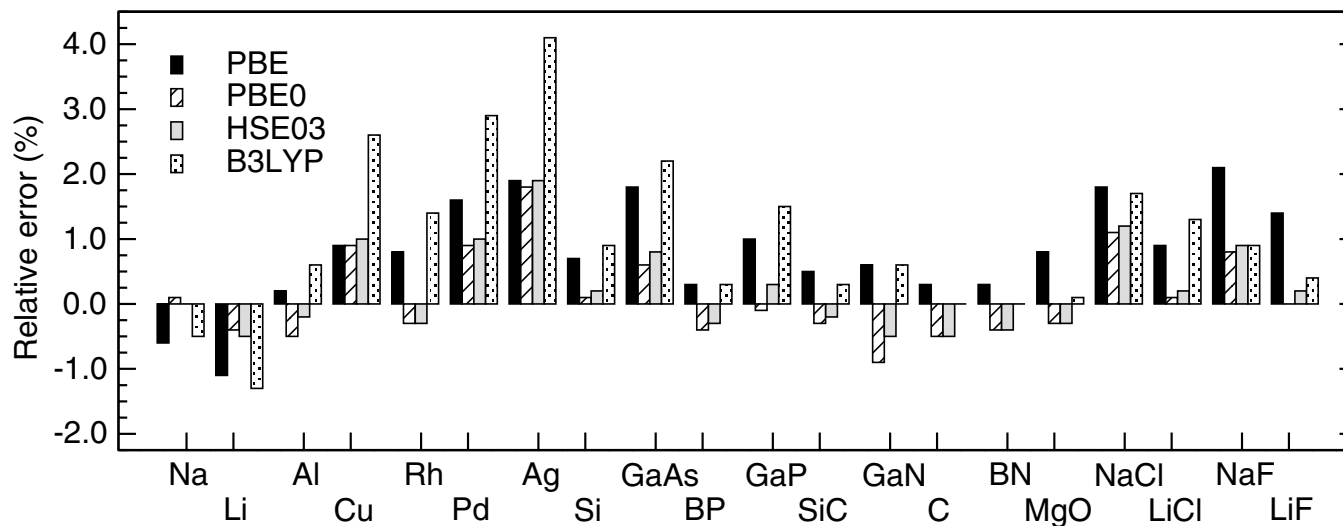

No correlation

Good correlation

Exact exchange

No exact exchange

$$E_{\mathrm{xc}}^{\mathrm{hyb}} = b E_x^{\mathrm{exx}} + (1-b) E_x^{\mathrm{KS}} + E_c^{\mathrm{KS}}$$

$$E_{\mathrm{xc}}^{\mathrm{hyb}} = E_{\mathrm{xc}}^{\mathrm{LSDA}} + a_0 \left(E_x^{\mathrm{exact}} - E_x^{\mathrm{LSDA}} \right) + a_x \Delta E_x^{\mathrm{GGA}} + a_c \Delta E_c^{\mathrm{GGA}}$$

HYBRID FUNCTIONALS

Lattice constant performance

	PBE	PBE0	HSE03	B3LYP
		All solids		
ME	0.038	0.006	0.012	0.046
MAE	0.044	0.022	0.024	0.053
MRE (%)	0.8	0.1	0.2	1.0
MARE (%)	1.0	0.5	0.5	1.2

Marsman, M., et al, *J. o. Physics: Condensed Matter*, vol. 20, no. 6, 2008

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HYBRID FUNCTIONALS

Band gap performance
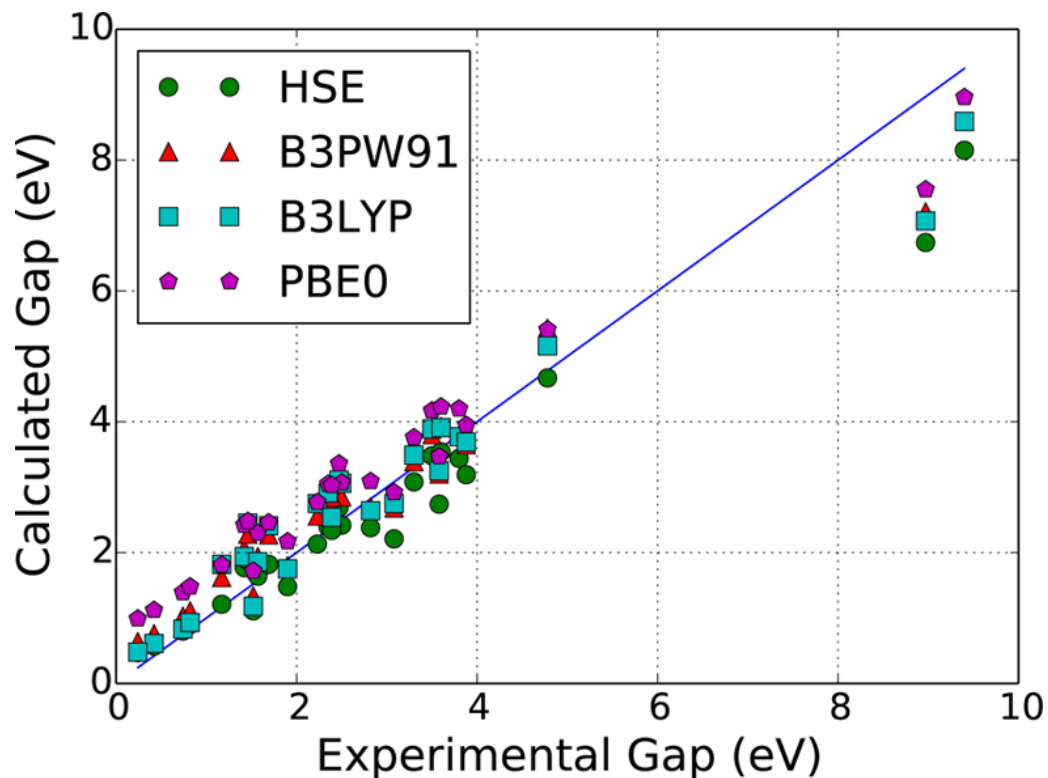
HSE:
Mean Error: -0.24 eV
Mean abs. Error: 0.37 eV (16%)

PBE0:
Mean Error: 0.43 eV
Mean abs. Error: 0.59 eV (45%)

B3LYP:
Mean Error: 0.16 eV
Mean abs. Error: 0.47 eV (25%)

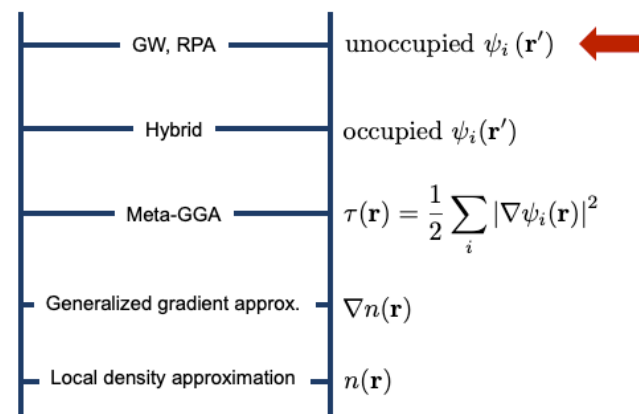Garza, Alejandro J. et al, *J. o. Physical Chemistry Letters*, vol. 7, no. (2016)

➡ HSE & PBE0 are implemented in FLEUR (Ask us)

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SUMMARY

- Confusing amount of functionals

- Some properties are described well
  with semi-local methods

  - Lattice constant

  - Bulk modulus

- For some properties semi-local functionals fail:

  - Band gap

- Use hybrid for improved accuracy

Next talk:

DFT Heaven

GW, RPA	unoccupied $\psi_i(\mathbf{r}')$
Hybrid	occupied $\psi_i(\mathbf{r}')$
Meta-GGA	$\tau(\mathbf{r}) = \frac{1}{2} \sum_i |\nabla \psi_i(\mathbf{r})|^2$
Generalized gradient approx.	$\nabla n(\mathbf{r})$
Local density approximation	$n(\mathbf{r})$

Right results for the right reasons