Exchange-correlation approximations: Trying to get them accurate and efficient

T. Lebeda, M. Brütting, T. Aschebrock, J. Förster, I. Schelter, H. Bahmann

Stephan Kümmel
Department of Physics, University of Bayreuth, Germany

10th Time-Dependent Density-Functional Theory: Prospects and Applications

April 14, 2025

Outline

Part 1: One (personal view) example of DFT strengths and challenges

Part 2: Local range separation

Part 3: A new look at the gradient expansion and MGGAs

Part 1: DFT strengths and challenges

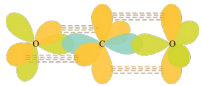
The energy and materials challenge

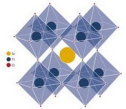
Sustainable energy supply: Light harvesting and converting light into other forms of energy is a key challenge

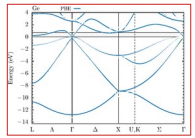
- New materials can have a significant positive impact
- Computer aided material design can play a major role
- Therefore, electronic structure methods are extremely relevant

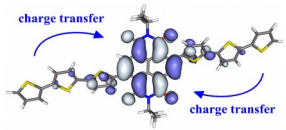
Theory must be able to predict:

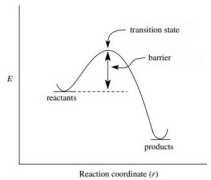
- bond energies
- structures
- band gaps
- electronic excitations
- reaction barrier heights

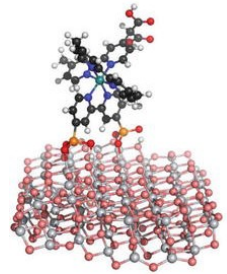












for large systems

Electronic structure and dynamics with good ratio of accuracy to computational effort
→ **Density Functional Theor**y (DFT)

Accuracy and efficiency of a DFT calculation depend on the choice of E_{xc}

$$E[n] = \sum_{i=1}^{N} \langle \varphi_i | \hat{t} | \varphi_i \rangle + \int n(\mathbf{r}) v_{\text{ext}}(\mathbf{r})\, d^3r + \frac{e^2}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d^3r d^3r' + E_{\text{xc}}[n]$$

DFT *can be first principles* and *can be efficient*...

... but how useful is *in practice for energy converting systems*?

Look at one example (personal choice) →

Strengths and challenges example: Understanding photosynthesis

Photosynthesis can convert sunlight very efficiently. Can we learn from it?

Heliobacterium modesticaldum: Simple natural light harvesting machinery

https://www.iflscience.com

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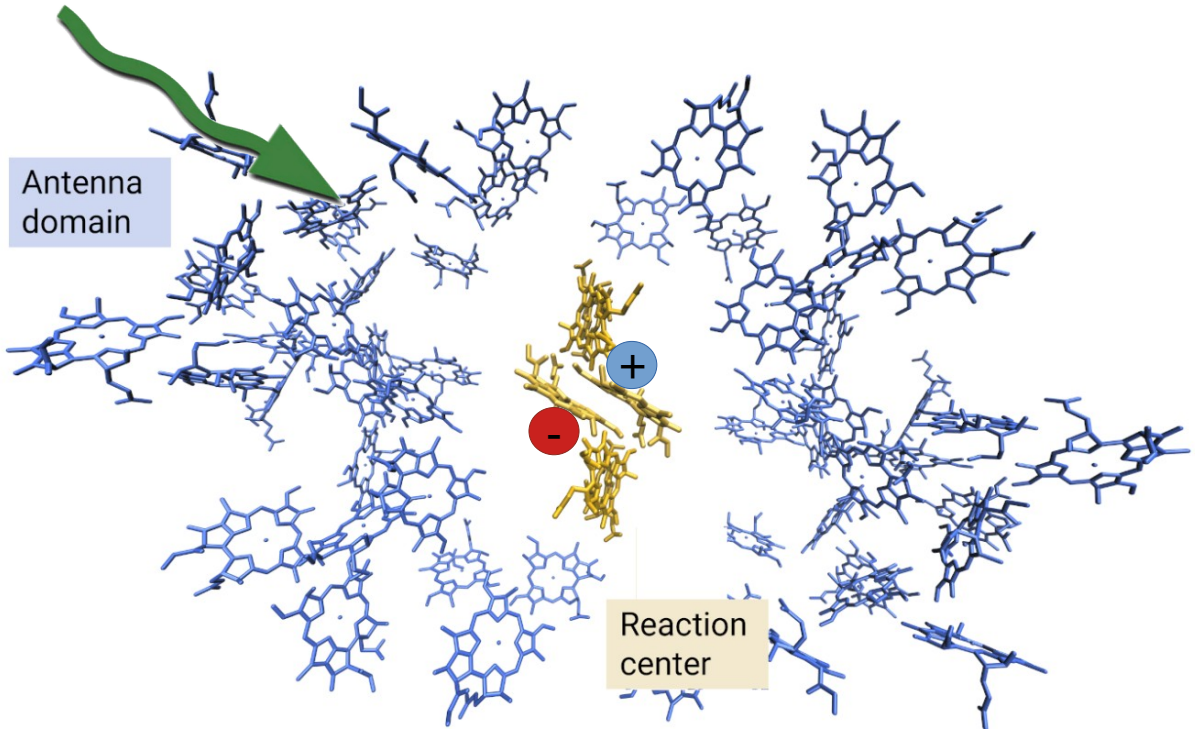
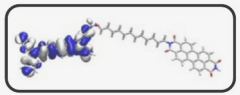
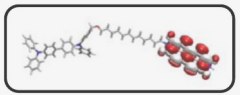


- Nature uses just one chromophore, bacteriochlorophyll
- Man-made devices use the donor-acceptor concept





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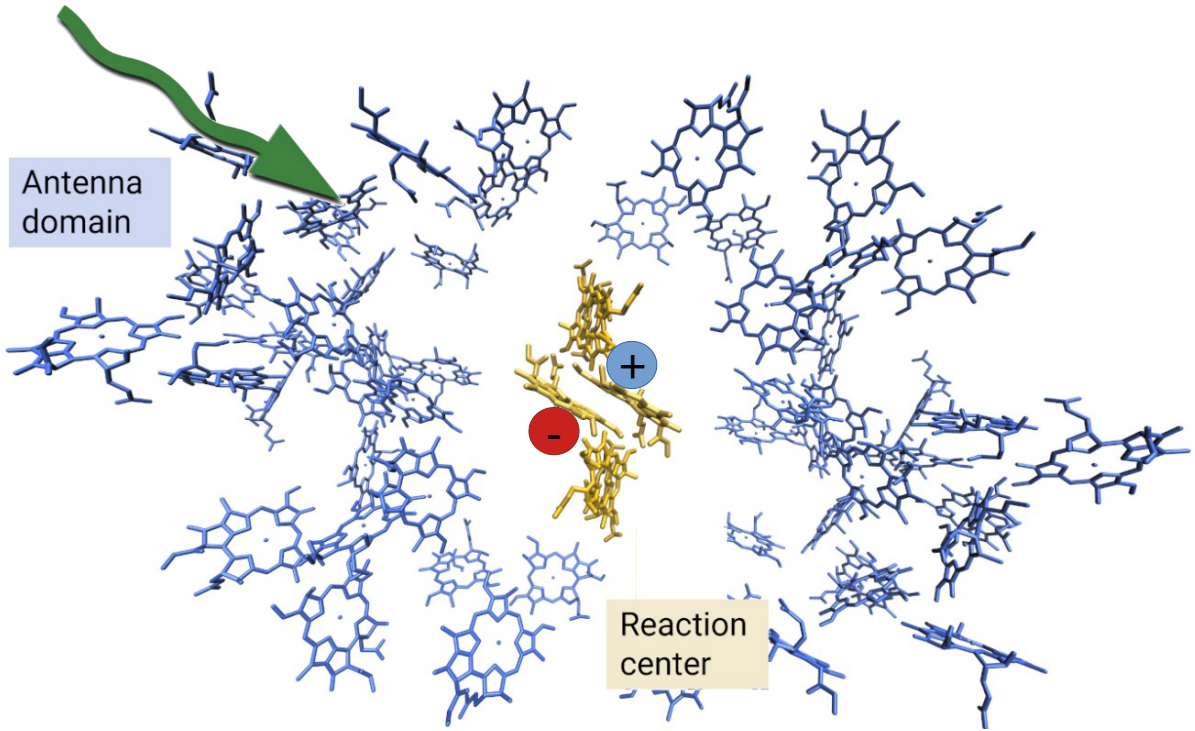
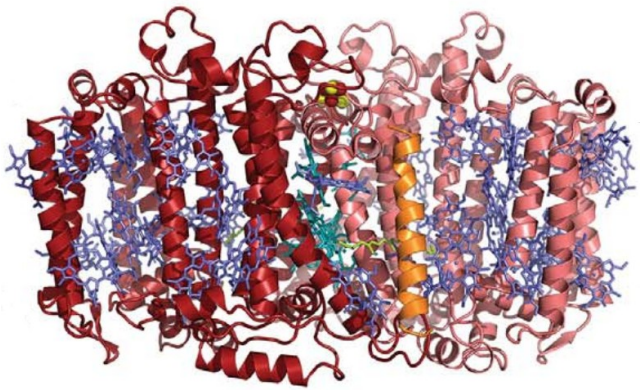




Gisriel et al., Science 357, 1021 (2017)

CT excitations: Range-separated hybrid functionals

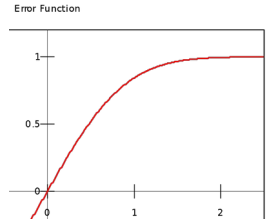
Range-separation in the Coulomb interaction:

$$\frac{1}{r} = \frac{\mathrm{erf}(\omega r)}{r} + \frac{1-\mathrm{erf}(\omega r)}{r}$$

long range *short range*

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2}\, dy$$

Leininger, Stoll, Werner, Savin, CPL 275, 151 (1997)
Iikura, Tsuneda, Yanai, Hirao, JCP 115, 3540 (2001)
Yanai, Tew, Handy, CPL 393, 51 (2004)
Baer, Neuhauser, PRL 94, 043002 (2005)
Vydrov, Scuseria, JCP 125, 234109 (2006)
...



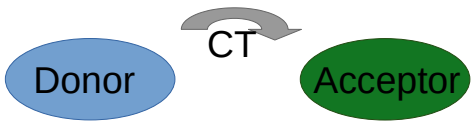
$$v_{\mathrm{x}} = \hat{v}_{\mathrm{x}}^{\mathrm{lr},\omega} + v_{\mathrm{x}}^{\mathrm{sr},\omega}$$

where

$$\hat{v}_{\mathrm{x}}^{\mathrm{lr},\omega}\varphi_i(\mathbf{r}) = -\sum_{j=1}^{N} \varphi_j(\mathbf{r}) \int \frac{\mathrm{erf}(\omega|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} \varphi_j^*(\mathbf{r}')\varphi_i(\mathbf{r}')$$

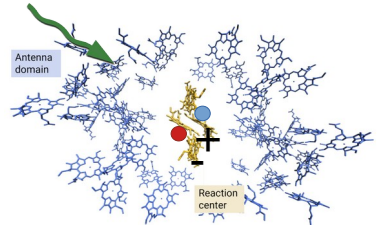
Decisive: range separation parameter ω

Non-empirical optimal tuning: choose ω such that $-\varepsilon_{\mathrm{H}} = E_N - E_{N-1}$ *Stein, Kronik, Baer, JACS 131, 2818 (2009); Kronik et al., JCTC8, 1515 (2012), ...*



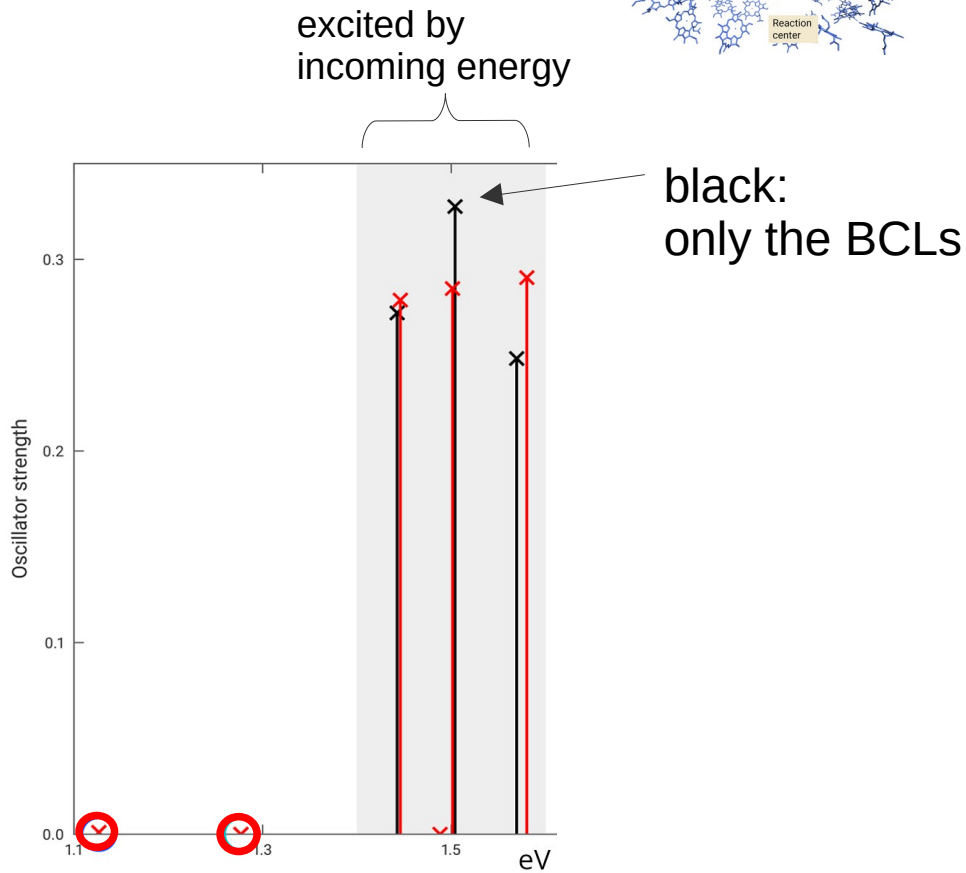
Prerequisite for tuning to work: same ω works for donor & acceptor

Understanding the heliobacterial reaction center



- Optimally tuned RSH allows to calculate the excitation spectrum of the reaction center
- Reliable prediction of the charge-transfer states

Why just BChl sufficient, no donor-acceptor pairs needed?



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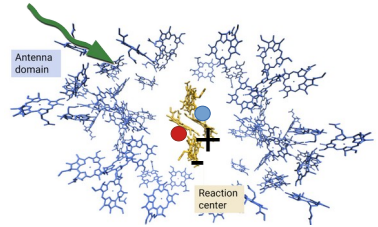

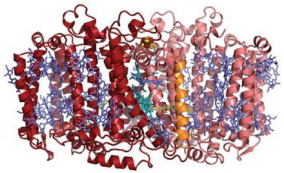

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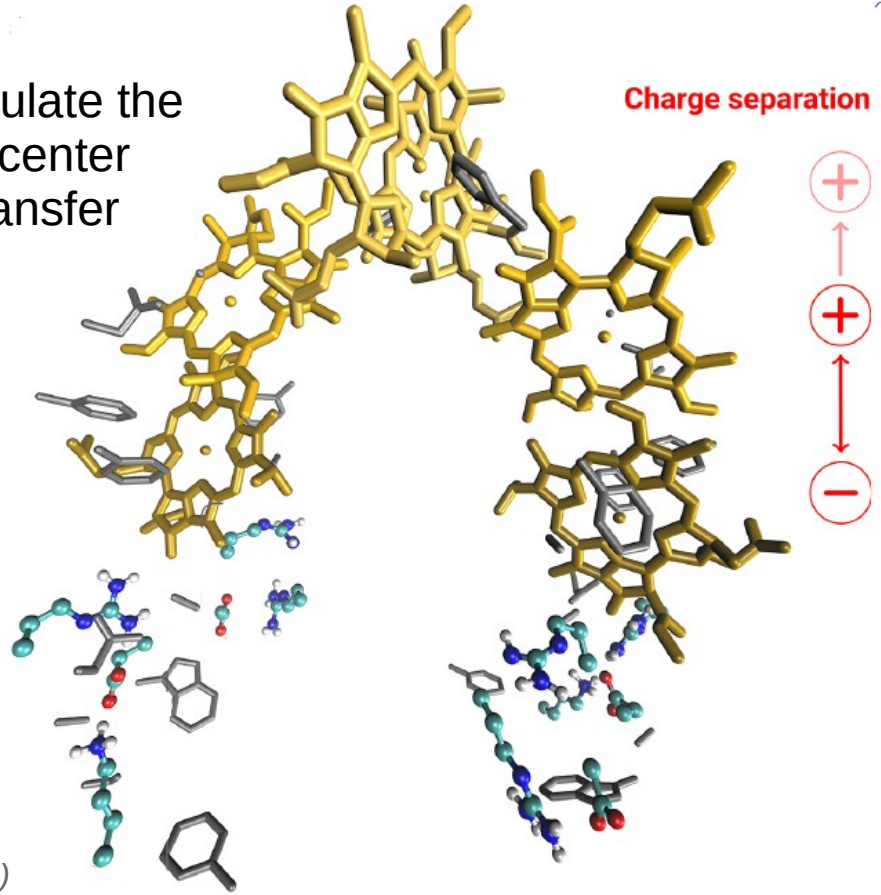
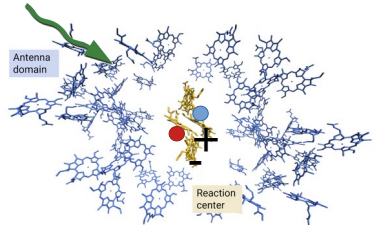


Brütting, Förster, SK, J. Phys. Chem. Lett. 14, 3092 (2023)

Understanding the heliobacterial reaction center



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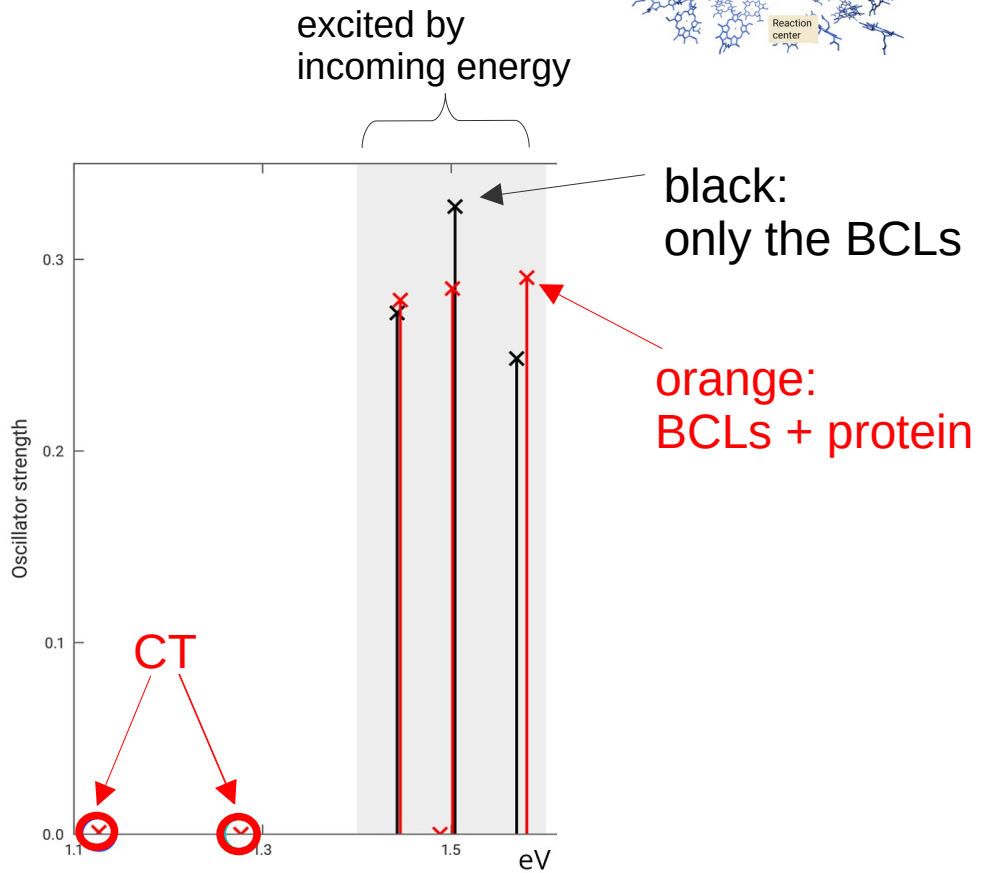
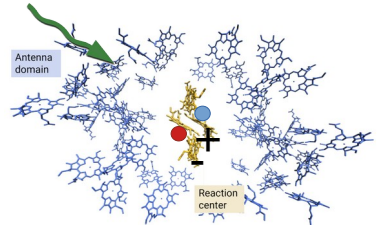


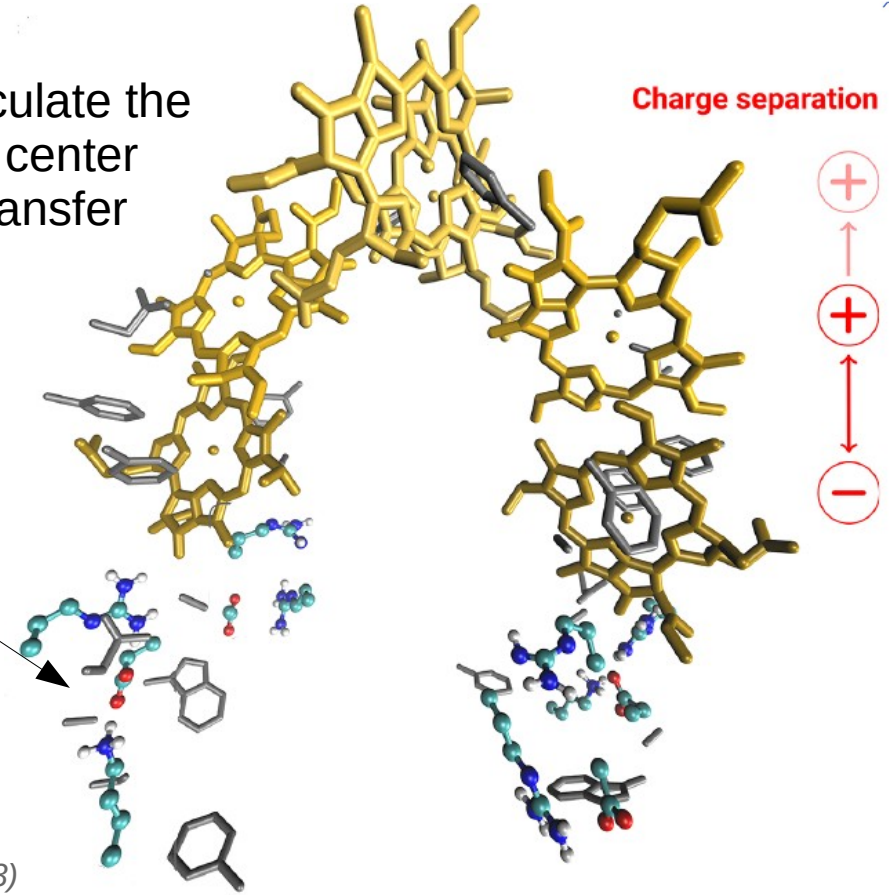
Understanding the heliobacterial reaction center



- Optimally tuned RSH allows to calculate the excitation spectrum of the reaction center
- Reliable prediction of the charge-transfer states

Why just BChl sufficient, no donor-acceptor pairs needed?

Charged amino acids in the surrounding protein structure build a potential gradient that drives the charge-separation:
“Smart matrix”



Brütting, Förster, SK, J. Phys. Chem. Lett. 14, 3092 (2023)

Lessons learned

- OT-RSH allows to predict (many) electronic excitations reliably
  - Choosing ω in a system specific way (“tuning”) is decisive for predictive power

⟹ ω is really a density functional, i.e., $\omega \overset{!}{=} \omega[n]$

Reaction center: protein “wants” a different ω than BCL. OT worked because of the large influence of the charges...

- Observable dilemma: All hybrid functionals (global, local, range-separated) suffer from a “parameter dilemma”: *Brütting, Bahmann, SK, JPC A 128, 5212 (2024)*

One value of the parameter yields reasonable binding energies, a different value is needed to yield reasonable CT excitations, band gaps, reaction barrier heights

$$E_{\mathrm{xc}}^{\mathrm{global-hyb}} = aE_{\mathrm{x}}^{\mathrm{ex}} + (1-a)E_{\mathrm{x}}^{\mathrm{sl}} + E_{\mathrm{c}}^{\mathrm{sl}}$$

bond energies: a ≈ 0.25
band gaps, reaction barriers: a ≈ 0.75

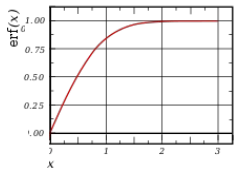
Part 2: Local range separation

Realizing ω[n]: local range separation

$$\mathrm{E}_{\mathrm{xc}}^{\mathrm{LRSH}} = E_{\mathrm{x,ex}}^{\mathrm{lr},\omega} + E_{\mathrm{x,LDA}}^{\mathrm{sr},\omega} + E_{\mathrm{c}}^{\mathrm{sl}}$$

range-separation in the Coulomb interaction:

$$\frac{1}{r} = \underbrace{\frac{\mathrm{erf}(\omega r)}{r}}_{\textit{long range}} + \underbrace{\frac{1-\mathrm{erf}(\omega r)}{r}}_{\textit{short range}}$$



$$v_{\mathrm{xc}} = \hat{v}_{\mathrm{x,ex}}^{\mathrm{lr},\omega} + v_{\mathrm{x,LDA}}^{\mathrm{sr},\omega} + v_{\mathrm{c}}^{\mathrm{sl}}$$ Generalized Kohn-Sham

where

$$\hat{v}_{\mathrm{x,ex}}^{\mathrm{lr},\omega}\varphi_i(\mathbf{r}) = -\sum_{j=1}^{N}\varphi_j(\mathbf{r})\int \frac{\mathrm{erf}(\omega(\mathbf{r})|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\varphi_j^*(\mathbf{r}')\varphi_i(\mathbf{r}')\,dr'$$

Realize $\omega \stackrel{!}{=} \omega[n]$ explicitly with local range separation $\omega([n],\mathbf{r})$

How to design the density functional $\omega([n],\mathbf{r})$?

→ guidance by exact constraints

Realizing ω[n]: constraints

Aschebrock, SK, JCP 151, 154108 (2019)
Brütting, Bahmann, SK, JCP 156, 104109 (2022)

- Homogeneous electron gas limit: $\omega_\sigma([n],\mathbf{r}) \to 0$, i.e., realize LDA limit
- Gradient expansion of the exchange energy density:

$$e_{\mathrm{x}\sigma}(r) = e_{\mathrm{x}\sigma}^{\mathrm{LDA}}(r)\left[1+\frac{10}{81}s_\sigma^2(r)+...\right]$$

On the other hand:

Maier, Ikabata, Nakai, JCP 154, 214101 (2021)

$$e_{\mathrm{x}\sigma}(r) = e_{\mathrm{x,ex},\sigma}^{\mathrm{lr},\omega}(r) + e_{\mathrm{x,LDA},\sigma}^{\mathrm{sr},\omega}(r)$$

Expand and equate ... $\Longrightarrow$ $\omega_\sigma(\mathbf{r}) = \frac{\sqrt{5}}{18}\frac{|\nabla n_\sigma(\mathbf{r})|}{n_\sigma(\mathbf{r})}$

- Uniform density scaling to the high-density limit $n(\mathbf{r}) \to n_\lambda(\mathbf{r}) = \lambda^3 n(\lambda\mathbf{r})$ with $\lambda \to \infty$:

$$\lim_{\lambda\to\infty}\frac{E_{\mathrm{xc}}[n_\lambda]}{E_{\mathrm{x}}^{\mathrm{ex}}[n_\lambda]} = 1$$

Full $E_{\mathrm{x}}^{\mathrm{ex}}$ reached in this limit with $\omega_\sigma([n_\lambda],\mathbf{r}) >> \lambda\omega_\sigma([n],\lambda\mathbf{r})$

Realizing ω[n]: constraints

Aschebrock, SK, JCP 151, 154108 (2019)
Brütting, Bahmann, SK, JCP 156, 104109 (2022)

- Eliminate one-electron self-interaction

$$E_{\mathrm{H}}[n_{j\sigma}] + E_{\mathrm{xc}}[n_{j\sigma}, 0] = 0 \qquad \text{where} \qquad n_{j\sigma} = |\varphi_{j\sigma}|^2$$

Can be achieved with
i) self-interaction free correlation functional $\mathrm{E_c^{LDA-SIC}} = \int e_{\mathrm{c}}^{\mathrm{LDA}}[1 - (\tau^W/\tau)\zeta^2]\, d^3r$ *and*

ii) $\omega_\sigma([n], \mathbf{r}) \to \infty$ for one-electron densities

Form that fulfills these constraints:

$$\omega_\sigma[n](\mathbf{r}) = \eta \frac{|\nabla n_\sigma(\mathbf{r})|}{n_\sigma(\mathbf{r})} \left[1 + \ln\left(1 + \gamma \frac{|\nabla n_\sigma(\mathbf{r})|}{n_\sigma(\mathbf{r})}\right)\right] \frac{1}{1 - \zeta^2(\mathbf{r})\tau_\sigma^{\mathrm{W}}(\mathbf{r})/\tau_\sigma(\mathbf{r})}$$

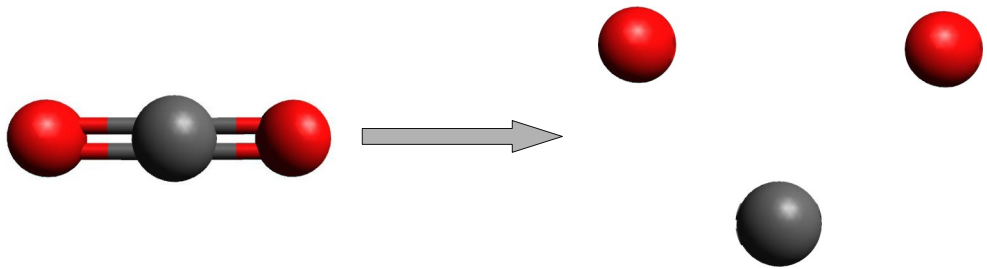
"ωBT21"

parameters: $\eta,\ \gamma$

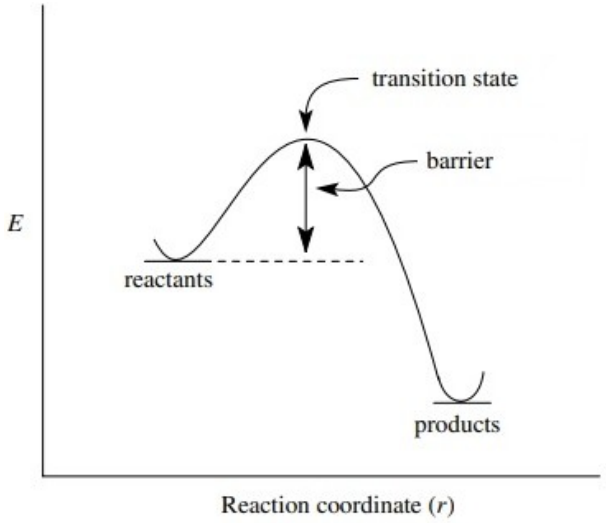
Systematic improvements from local range separation?

Observables:

Atomization energy (AE)



Reaction barrier height (BH)



“low amount of exact x needed”

“high amount of exact x needed”

Systematic improvements from local range separation?

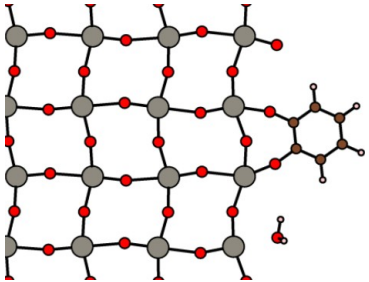
Brütting, Bahmann, SK, JCP 156, 104109 (2022)

Atomization energy (AE) **Reaction barrier height** (BH)

			mean absolute error		
Name	Parameter(s)	Type	AE6	BH6	kcal/mol
LDA	···	···	74.93	17.49	
PBE	···	GGA	14.27	9.22	
PBE0	···	Global hybrid	5.22	4.49	
ωPBE	$\omega = 0.4/a_0$	Global RSH	5.34	1.42	
BLYP	···	GGA	6.98	7.80	
B3LYP	···	Global hybrid	4.21	4.68	
CAM-B3LYP	···	Global RSH	1.95	3.75	
M11-L	···	meta-GGA	7.53	1.26	
MN15-L	·····	meta-GGA	4.00	1.45	
M11	···	Global RSH	3.14	1.41	
MN15	···	Global hybrid	**1.62**	**0.99**	58 parameters
ωBT21	$\eta = 0.115, \gamma = 0.202\ a_0$	Local RSH	**1.53**	**1.66**	2 parameters η_{nonemp}=0.124

Conclusions so far:

- Local range separation helps to achieve noteworthy “overall” improvement
- Conceptually promising for interface problems



Can we get rid of the empirical parameters?

A non-empirical local range-separated hybrid for spectroscopic observables

“More modest” aim: Not a universal functional for all observables, but a functional for spectroscopic observables such as band gaps, electronic excitations without fitting or tuning and respecting size consistency

Parameter-free, first principles local range-separation functional:

$$\omega_\sigma[n](\mathbf{r}) = c_{\mathrm{GE}} \frac{|\nabla n_\sigma(\mathbf{r})|}{n_\sigma(\mathbf{r})} \frac{1}{1 - \frac{1}{2}\left(\frac{\tau_\sigma^{\mathrm{W}}(\mathbf{r})}{\tau_\sigma(\mathbf{r})}\zeta^2 + \frac{\tau_\sigma^{\mathrm{W}}(\mathbf{r})}{\tau_\sigma(\mathbf{r})}\right)}$$

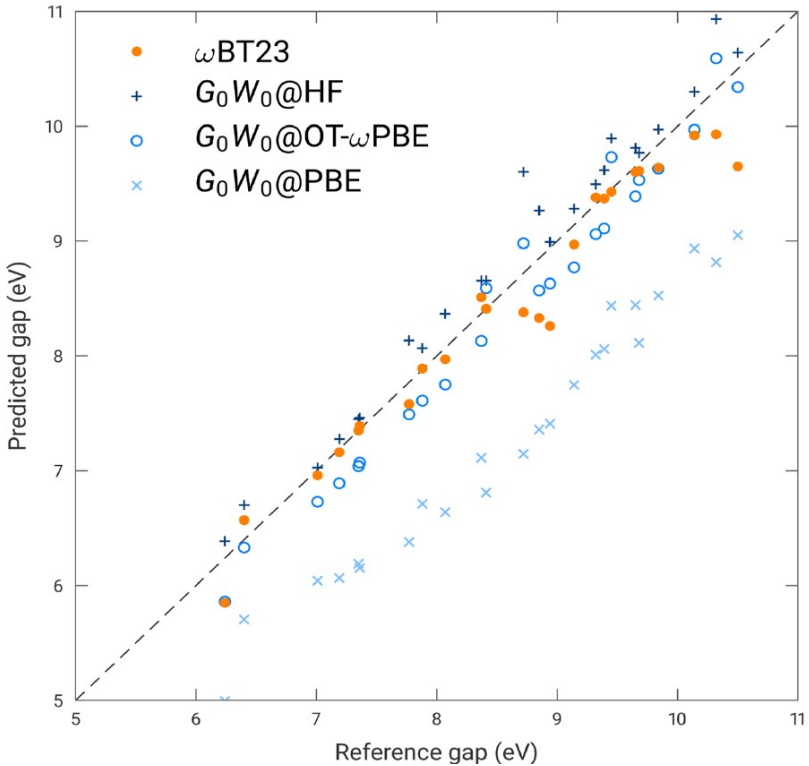
gradient expansion of the x energy density

one-electron SI free and straight line in E(N)

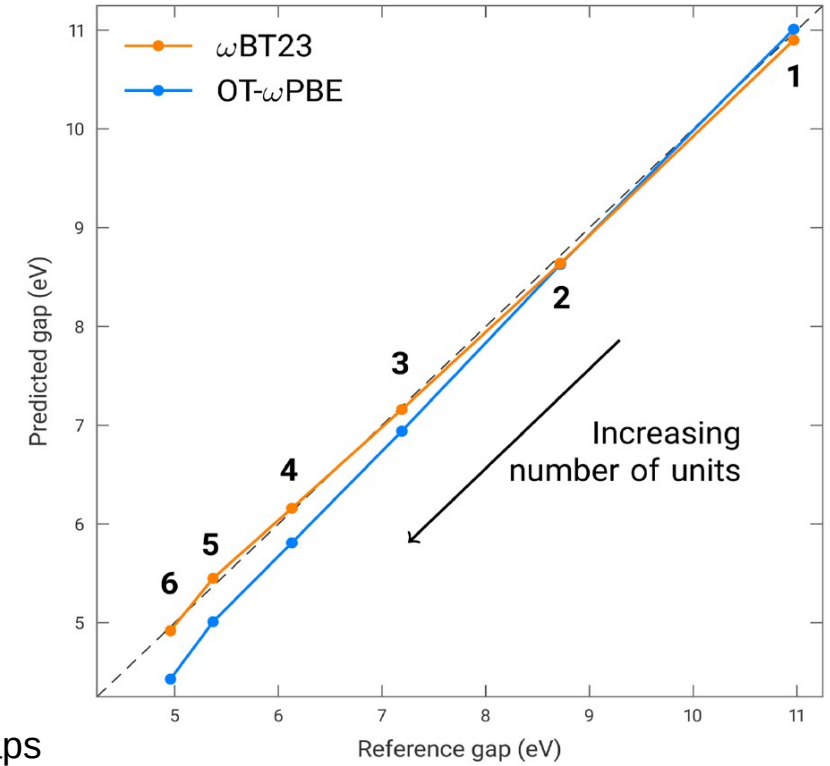
Brütting, Bahmann, SK, JCP Communication 160, 181101 (2024) “ωBT23”

Fulfills many formal constraints and has desired properties

- *Correct homogeneous electron gas limit*
- *Correct gradient expansion of the exchange energy*
- *Free from one-electron self-interaction,* $E_{\mathrm{H}}[n_1] + E_{\mathrm{xc}}[n_1] = 0$
- *No adjustable empirical parameters*



acceptor molecule gaps



oligoacene gaps

Brütting, Bahmann, SK, JCP Communication 160, 181101 (2024)

Summary on local range separation:

- local range separation excellent as a non-empirical functional for spectroscopy
- can complement optimal tuning as a DFT option for difficult cases

- local range separation in present functionals reduces the parameter dilemma, but does not yet eliminate it *Brütting, Bahmann, SK, JPC A 128, 5212 (2024)*
- computational cost of exact exchange plus some additional computational overhead

We need semilocal functionals with higher accuracy and more ultranonlocality

Part 3: A new look at the gradient expansion and MGGAs

Meta-GGAs

MGGA: $E_{\mathrm{x}}^{\mathrm{MGGA}} = A_{\mathrm{x}} \int n^{\frac{4}{3}} F_{\mathrm{x}}(s,\alpha)\, d^3r$ where $A_{\mathrm{x}} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}$

$s = \frac{|\nabla n|}{2(3\pi^2)^{\frac{1}{3}} n^{\frac{4}{3}}}$ $\alpha = \frac{\tau - \tau^W}{\tau^{\mathrm{unif}}}$ and $\tau = \frac{\hbar^2}{2m}\sum_{i=1}^{N} |\nabla \varphi_i|^2$

$\tau^W = \frac{\hbar^2}{8m}\frac{|\nabla n|^2}{n}$

$\tau^{\mathrm{unif}} = \frac{3\hbar^2}{10m}(3\pi^2)^{\frac{2}{3}} n^{\frac{5}{3}}$

α=0: one electron systems
α=1: homogeneous electron gas

Meta-GGAs

MGGA: $E_{\mathrm{x}}^{\mathrm{MGGA}} = A_{\mathrm{x}} \int n^{\frac{4}{3}} F_{\mathrm{x}}(s,\alpha)\, d^3r$ where $A_{\mathrm{x}} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}$

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$\tau^W = \frac{\hbar^2}{8m}\frac{|\nabla n|^2}{n}$

$\tau^{\mathrm{unif}} = \frac{3\hbar^2}{10m}(3\pi^2)^{\frac{2}{3}} n^{\frac{5}{3}}$

$$E_{\mathrm{xc}}^{\mathrm{MGGA}} = \int n(\mathbf{r}) \epsilon_{\mathrm{xc}}^{\mathrm{MGGA}}(n, \nabla n, \tau)\, d^3r$$

MGGAs are a well known concept, why look at it again?

e.g.,
Van Voorhis, Scuseria, J. Chem. Phys. 109, 400 (1998)
Perdew, Kurth, Zupan, Blaha, Phys. Rev. Lett. 82, 2544 (1999)
Boese, Handy, J. Chem. Phys. 116, 9559 (2002)
Tao, Perdew, Staroverov, Scuseria, Phys. Rev. Lett. 91, 146401 (2003)
Zhao, Truhlar, J. Chem. Phys. 125, 194101 (2006)
Sun, Ruzsinszky, Perdew, Phys. Rev. Lett. 115, 036402 (2015)
...

Contrary to GGAs, MGGAs can have Δ_{xc} and (ultra)nonlocality

Why MGGAs are interesting

Meta-GGA: $E_{\mathrm{xc}}^{\mathrm{mGGA}} = \int n(\mathbf{r}) \epsilon_{\mathrm{xc}}^{\mathrm{mGGA}}(n, \nabla n, \tau)\, d^3r$ where $\tau(\mathbf{r}) = \frac{\hbar^2}{2m} \sum_{i=1}^{N} |\nabla \varphi_i(\mathbf{r})|^2$

- Have *implicit nonlocality* because of their explicit orbital dependence: Solving the KS equation is a nonlocal procedure, thus $\varphi(\mathbf{r}) = \varphi[n(\mathbf{r}')](\mathbf{r})$
- Can have a *large* Δ_{xc} due to their τ-dependence
- In terms of computational cost they are *semilocal*

→ **Hope for accuracy *and* efficiency**

Traditional Meta-GGAs showed little non-locality – why?

One can show that for a MGGA:

Aschebrock, SK, PRR 1, 033082 (2019)

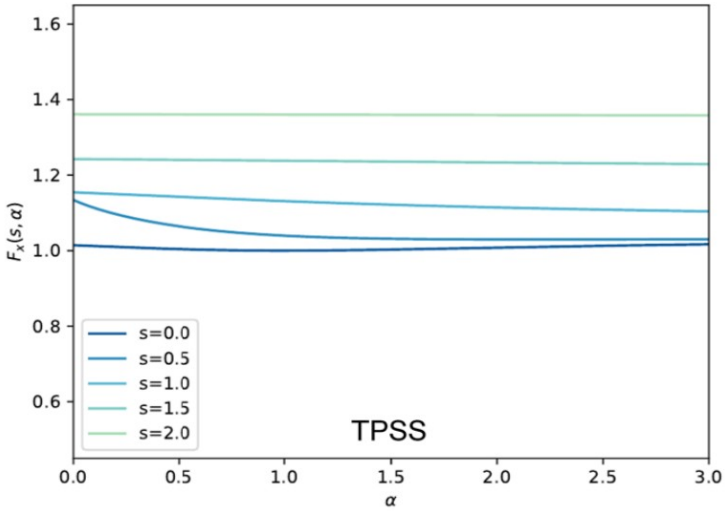
$$\frac{\partial F_\mathrm{x}}{\partial \alpha} < 0 \;\Rightarrow\; \Delta_\mathrm{x} > 0$$

and

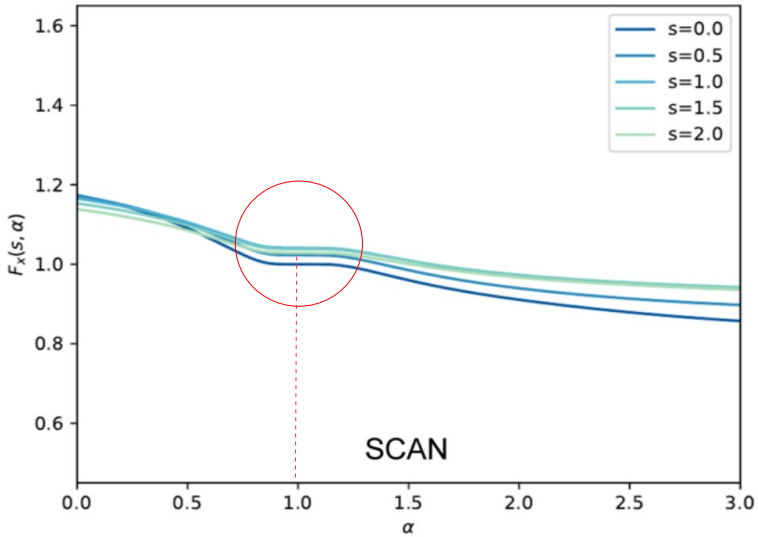
$$|\Delta_\mathrm{x}| \approx \text{proportional}\; \frac{\partial F_\mathrm{x}}{\partial \alpha}$$

plotting $F_x(s,\alpha)$ reveals size of Δ_x

Aschebrock, …, SK, JCP 159, 234107 (2023)



TPSS x



SCAN x

The missing slope in α around $\alpha = 1$ is a consequence of a particular way of ensuring the proper gradient expansion:

$$E_{\mathrm{x}}[n] = A_{\mathrm{x}} \int n^{\frac{4}{3}} (1 + \mu s^2 + ...)\, d^3 r$$

and

$$\alpha = 1 - \frac{40}{27} s^2 + ...$$

If you want to set μ directly via the gradient expansion, then you do not want a further contribution from α to the gradient expansion at $\alpha = 1$!

However, you can also ensure the correct gradient expansion with contributions from both s^2 and α !

A new non-empirical MGGA construction strategy yielding good atomization energies and good band gaps

- α itself has a gradient expansion → there are many ways to have the proper gradient expansion for E_{xc}: They differ in their relative contributions from *s* and *α.* For x and c:

$$E_{\mathrm{xc}}^{\mathrm{GE2}}[n] = A_{\mathrm{x}} \int n^{4/3} C_{\mu_\alpha}(r_s)[\mu_s s^2 + \mu_\alpha(\alpha - 1)] d^3 r$$

constraints

- Interpolate between *α=0* (one electron systems) and *α=1* (homogeneous electron gas)

- x: Gradient expansion to fourth order, strongly tightened bound, $F_x>0$, hydrogen atom energy

norm

construction principles:

- $$\frac{\partial F_{\mathrm{x}}}{\partial \alpha} \begin{cases} < 0, & \text{everywhere} \\ \text{roughly constant} & \text{for } 0.2 \lesssim \alpha \lesssim 1.5 \end{cases}$$

  ensures sizeable Δ_x

- $$\left.\frac{\partial F_{\mathrm{xc}}}{\partial s}\right|_{\alpha=1} \begin{cases} > 0 & \text{for } 0.5 \lesssim s \lesssim 1.2 \\ < 0 & \text{for } s \gtrsim 1.2 \end{cases}$$

  ensures non-covalent binding

A MGGA with good gaps and good atomization energies

- new realization of gradient expansion
- non-empirical
- for *x and c*
- self-correlation free
- same constraints as SCAN & TASK

	main group atomization energies	non-covalent interactions	main group bond lengths	solid lattice constants	semi-conductor band gaps
	MGAE109 (kcal/ mol)	S22 (kcal/ mol)	MGBL20 (Å)	LC20 (Å)	SCBG15 (eV)
PBE	13.9	2.42	0.009	0.055	0.91
SCAN	3.8	0.82	0.005	0.015	0.59
LAK	3.5	0.56	0.003	0.054	0.18
HSE06	4.0	2.19	0.006	0.032	0.17

Lebeda, Aschebrock, SK, PRL 133, 136402 (2024)

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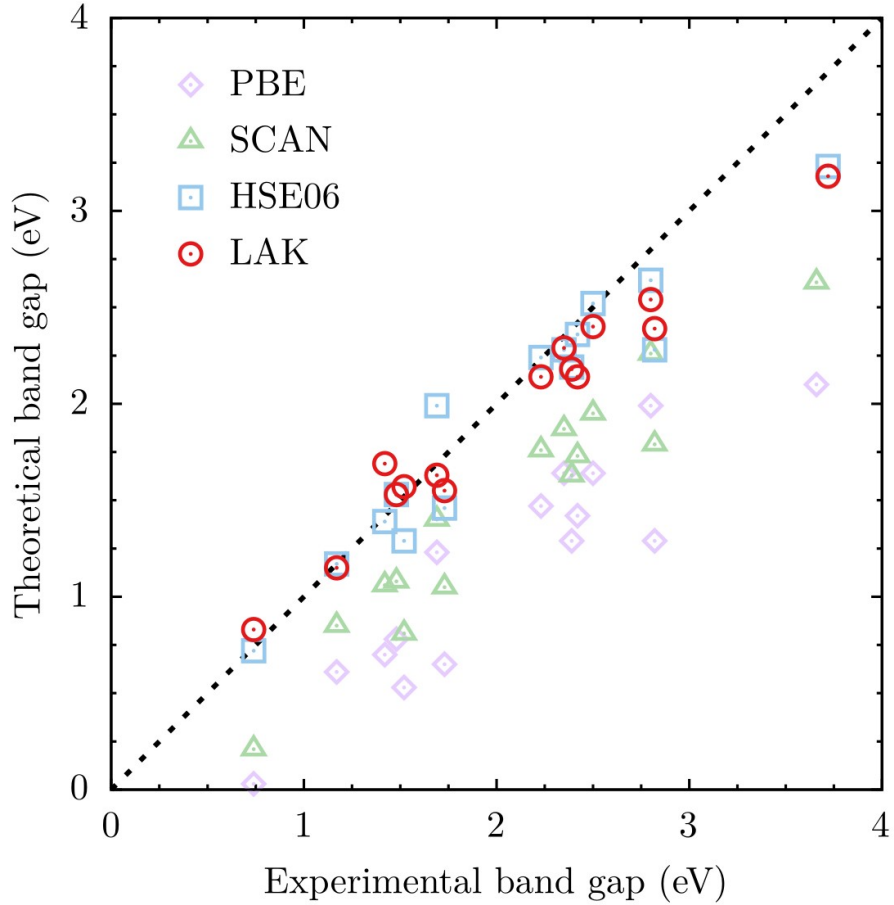

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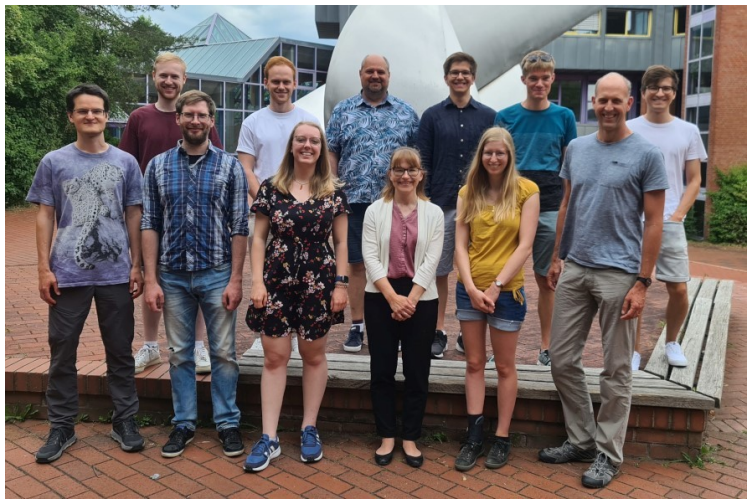
Conclusion

- Present-day DFT is not yet perfect for predicting the properties of energy-relevant materials, but helpful...
- … new xc approximations are very promising, in particular for the observables that are relevant for energy converting materials
- Still a lot to learn from “old concepts”, e.g., many ways of doing the gradient expansion correctly

Thank you for your attention!



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Normalverfahren

Biological Physics

Solar Technologies go Hybrid

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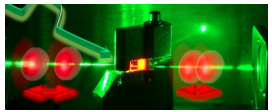

DFG SFB MultiTrans