

Recent developments in DFTB: bits and pieces

Thomas Niehaus
University of Regensburg



Electron Dynamics in Complex Systems

Cecam workshop: Development of next generation accurate
approximate DFTB methods

October 11th - 15th 2015

Bremen

- 1 Onsite corrections for ground and excited DFTB
- 2 Exciton couplings from TD-DFTB
- 3 LC-DFTB: Range-separated functionals in DFTB

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Onsite corrections for ground and excited DFTB



Adriel Dominguez Garcia



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Struktur und Dynamik der Materie

-  A. Dominguez, B. Aradi, T. Frauenheim, V. Lutsker, TAN – JCTC **9** 4901 (2013)
-  A. Dominguez, A., TAN, T. Frauenheim – JPC A **119** 3535 (2015)

Time dependent Density Functional Theory

... describes the density evolution of a many electron system subject to a time dependent external potential

The time-dependent density of the **interacting** system of interest can be calculated as density

$$\rho(\mathbf{r}, t) = \sum_{i=1}^N |\phi_i(\mathbf{r}, t)|^2$$

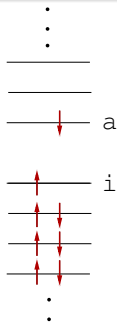
of an auxiliary **noninteracting (KS)** system

$$i \frac{\partial}{\partial t} \phi_i(\mathbf{r}, t) = \left[-\frac{1}{2} \nabla^2 + v_{\text{KS}}[\rho](\mathbf{r}, t) \right] \phi_i(\mathbf{r}, t)$$

with the **local** potential

$$v_{\text{KS}}[\rho](\mathbf{r}, t) = v(\mathbf{r}, t) + \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}[\rho](\mathbf{r}, t)$$

DFTB approximation of TDDFT = TD-DFTB



Equation to solve (Singlets):

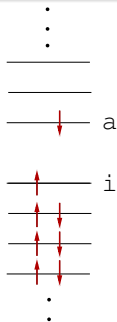
$$\sum_{jb} \left[\omega_{ia}^2 \delta_{ij} \delta_{ab} + 2\sqrt{\omega_{ia}} K_{ia,jb} \sqrt{\omega_{jb}} \right] F_{jb}^I = \omega_I^2 F_{ia}^I$$

Couplingmatrix K leads to correction of single-particle picture

$$\text{DFT: } K_{ia,jb} = 2 \iint \psi_i(\mathbf{r}) \psi_a(\mathbf{r}) \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}[\rho] \right) \psi_j(\mathbf{r}') \psi_b(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$



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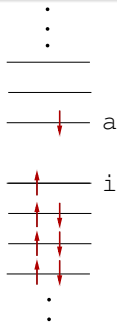
Get single particle energies $\{\epsilon_i\}$ from DFTB

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DFTB approximation of TDDFT = TD-DFTB



Mulliken approximation:

$$\phi_{\mu}(\mathbf{r})\phi_{\nu}(\mathbf{r}) \approx \frac{1}{2}S_{\mu\nu} \left(|\phi_{\mu}(\mathbf{r})|^2 + |\phi_{\nu}(\mathbf{r})|^2 \right)$$

Couplingmatrix **K** leads to correction of single-particle picture

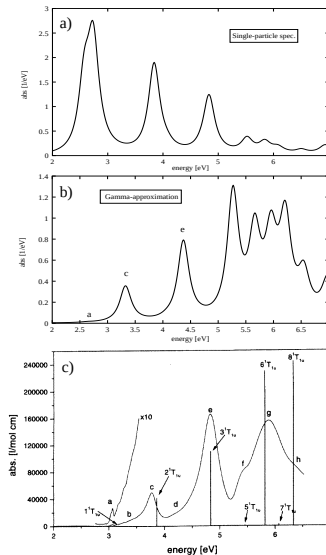
$$\text{DFT: } K_{ia,jb} = 2 \iint \psi_i(\mathbf{r}) \psi_a(\mathbf{r}) \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}[\rho] \right) \psi_j(\mathbf{r}') \psi_b(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

$$\text{DFTB: } K_{ia,jb} = 2 \sum_{AB} q_A^{ia} \gamma_{AB}(|\mathbf{R}_A - \mathbf{R}_B|, U_A, U_B) q_B^{jb}$$



TAN, Suhai, Della Salla, Lugli, Elstner, Seifert, Frauenheim – PRB **63** 085108 (2001)

TD-DFTB: Optical spectrum of C_{60}



TAN, Suhai, Della Salla, Lugli, Elstner, Seifert, Frauenheim – PRB **63** 085108 (2001)

TD-DFTB performance

Excitation energies (eV)

Molecule	State	Exp.	TD-DFTB		TDDFT ¹	
			ω_I	ω_{ij}	ω_I	ω_{ij}
Ethylen	$^3B_{1u}(\pi \rightarrow \pi^*)$	4.40	5.47	6.30	4.16	5.66
	$^1B_{1u}(\pi \rightarrow \pi^*)$	7.65	7.81	6.30	7.44	5.66
Propynal	$^3A''(n \rightarrow \pi^*)$	2.99	4.04	4.04	2.74	3.15
	$^1A''(n \rightarrow \pi^*)$	3.56	4.04	4.04	3.37	3.15

[1] BPW91//6-311+G**

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Mean absolute error (eV)

	TD-DFTB	BPW91		INDO/S
		6-311+G**	STO-3G	
Sing. (16 Com.)	0.38	0.36	1.19	0.56
Trip. (13/11 Com.)	0.64	0.37	0.49	1.38



TAN, Suhai, Della Salla, Lugli, Elstner, Seifert, Frauenheim – PRB **63** 085108 (2001)

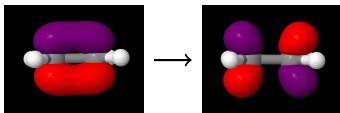
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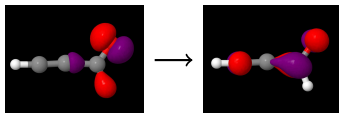
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Ethylen ($q_A^{ia} \neq 0$)



Propynal ($q_A^{ia} = 0$)



Beyond the Mulliken approximation: The onsite correction

Second order DFTB: $E = E^{(0)}[\rho_0] + E^{(2)}[\rho_0, \Delta\rho]$

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$$E^{(2)}[\rho_0, \Delta\rho] \approx \frac{1}{2} \sum_{\mu\nu} \tilde{P}_{\mu\mu} (\mu\mu||\nu\nu) \tilde{P}_{\nu\nu}$$

Beyond the Mulliken approximation: The onsite correction

Second order DFTB: $E = E^{(0)}[\rho_0] + E^{(2)}[\rho_0, \Delta\rho]$

Dual density matrix: $\tilde{P} = \frac{1}{2} (PS - SP)$

$$E^{(2)}[\rho_0, \Delta\rho] \approx \frac{1}{2} \sum_{\mu\nu} \tilde{P}_{\mu\mu} (\mu\mu||\nu\nu) \tilde{P}_{\nu\nu} \\ + \frac{1}{2} \sum_A \sum_{\mu, \nu \in A}^{\mu \neq \nu} \tilde{P}_{\mu\nu} (\mu\nu||\mu\nu) \tilde{P}_{\mu\nu}$$

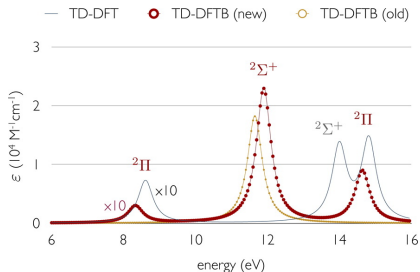
Same idea as in INDO

TD-DFTB performance (beyond Mulliken)

Excitation energies (eV)

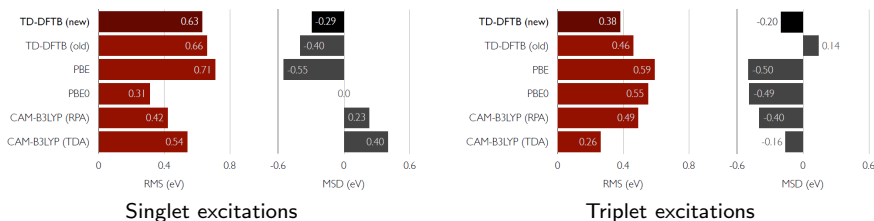
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[1] BPW91//6-311+G**



Absorption of nitric oxide (NO)

Thiel's benchmarks set: Comparison against best estimates

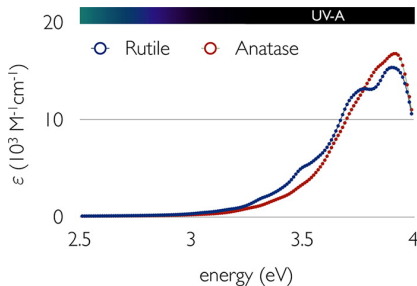


Qualitative improvement in general and also quantitative improvement for triplets

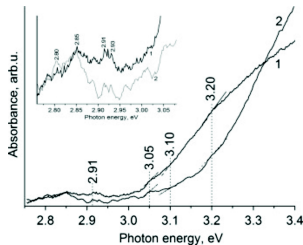


Dominguez, Aradi, Frauenheim, Lutsker, TAN – JCTC 9 4901 (2013)

Absorption of TiO₂ polymorphs



TD-DFTB: UV-vis absorption spectrum for rutile and anatase TiO₂ clusters



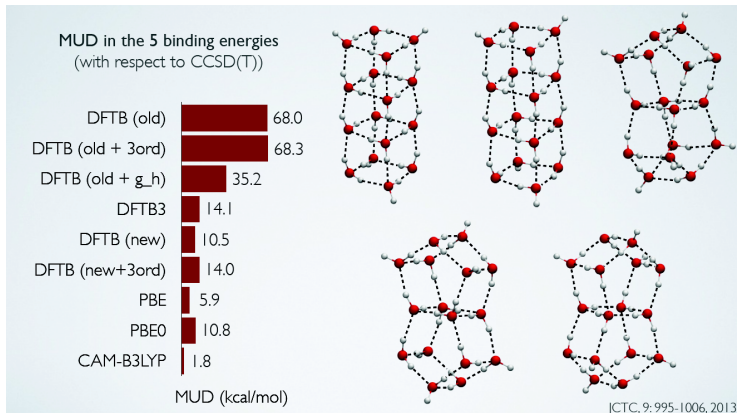
Experiment:

 J. Lumin **146** 199 (2014)

 J. Freitag, A. Dominguez, TAN, A. Huelsewig, R. Dillert, T. Frauenheim, D. Bahnemann – JPC C **119** 4488 (2015)

Onsite correction: Impact on ground state properties

Hydrogen bonding in water 16-mers:



Competitive with DFTB3, but free of empirical parameters



A. Dominguez, A., TAN, T. Frauenheim – JPC A **119** 3535 (2015)

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Exciton couplings from TD-DFTB

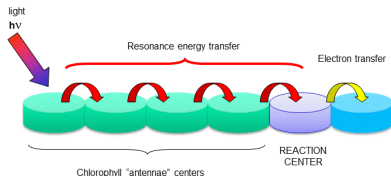


Oliver Kühn

Universität
Rostock



Traditio et Innovatio



Förster energy transfer

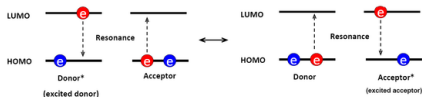


Figure 2
The schematic diagram of coulombic interaction.

UC Davis ChemWiki

$$k \propto |\langle \Psi_{\text{ex}}^D \Psi_{\text{gs}}^A | \hat{V}_{\text{coul}} | \Psi_{\text{gs}}^D \Psi_{\text{ex}}^A \rangle|^2$$



P.-A. Plötz, TAN, O. Kühn, JCP **140** 174101 (2014)

Required matrix element for Förster transfer:

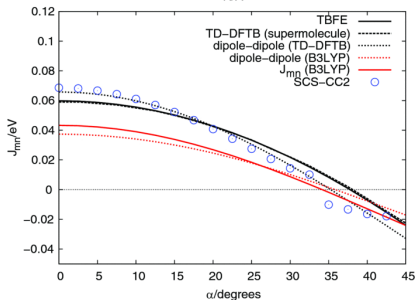
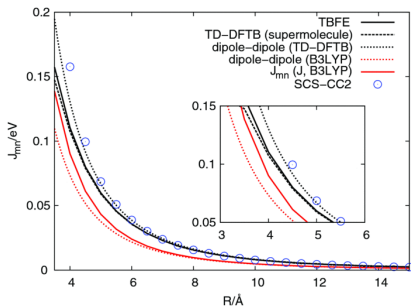
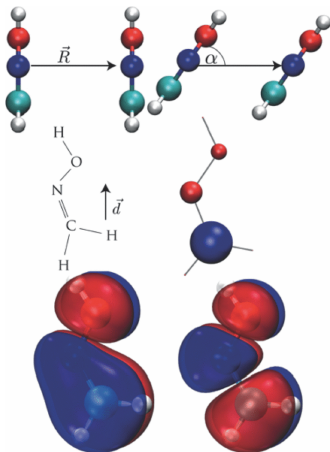
$$J_{mn} = \iint \frac{\langle \Psi_{\text{gs}}^m | \hat{n}(\mathbf{r}) | \Psi_{\text{ex}}^m \rangle \langle \Psi_{\text{ex}}^n | \hat{n}(\mathbf{r}') | \Psi_{\text{gs}}^n \rangle}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

Transition density known exactly in TD-DFT(B):

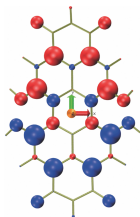
$$\rho^{\text{TD}}(\mathbf{r}) = \langle \Psi_{\text{gs}}^m | \hat{n}(\mathbf{r}) | \Psi_{\text{ex}}^m \rangle = \sum_{ia} \sqrt{\frac{2\omega_{ia}}{\Omega}} F_{ia} \psi_i(\mathbf{r}) \psi_a(\mathbf{r}')$$

$$\Rightarrow J_{mn} \approx \sum_{A \in m} \sum_{B \in n} Q_A^{\text{TD}} \gamma_{AB} Q_B^{\text{TD}}$$

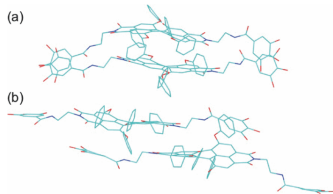
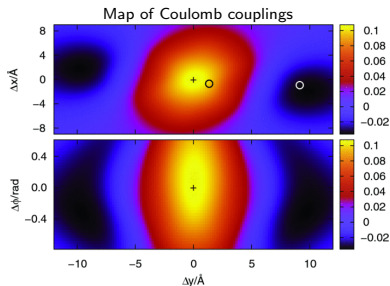
Proof of concept: The formaldehyde oxime dimer



A more complex case: PBI



TD-DFTB $S_0 \rightarrow S_1$ transition charges for PBI



H and J aggregates of PBI

Couplings J_{mn} [eV]

Configuration	TD-DFTB	TD-B3LYP
H	0.091	0.103
H + 1 Å	0.068	0.076
J	-0.030	-0.034
J + 1 Å	-0.019	-0.021

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Range-separated functionals in the DFTB method



Vitalij Lutsker



Bálint Aradi
(BCCMS)



Fabio della Sala
(NNL Lecce)



Julien Toulouse
(CNRS Paris)

 *Implementation and benchmark of a long-range corrected functional in the density functional based tight-binding method*

V. Lutsker, B. Aradi, T.A. Niehaus

arXiv:1504.00243

Some failures of local/semi-local functionals

- ▶ Incorrect dissociation of radical cations
 📖 A. J. Cohen et al. – Science **321** 792 (2008)
- ▶ Incorrect description of metal-organic interfaces
 📖 J. B. Neaton et al. – PRL **97** 216405 (2006)
- ▶ Instability of polaronic defects
 📖 T. A. Niehaus et al. – Org. Electron. **5** 167 (2004)
- ▶ Underestimation of charge-transfer excited states
 📖 A. Dreuw and M. Head-Gordon – JACS **126** 4007 (2004)
- ▶ Overestimation of conductances
 📖 S. H. Ke et al. JCP **126** 201102 (2007)
- ▶

Often due to self-interaction error

Hartree-Fock energy:

$$E_{\text{HF}} = \sum_i^N h_{ii}^0 + \frac{1}{2} \sum_{ij}^N (J_{ij} - K_{ij}) + E_{\text{nuc}}$$

Hartree-Fock energy: $J_{ii} = K_{ii} \Rightarrow$ self-interaction drops out

$$E_{\text{HF}} = \sum_i^N h_{ii}^0 + \frac{1}{2} \sum_{ij}^N (J_{ij} - K_{ij}) + E_{\text{nuc}}$$

Self-interaction in DFT

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In LDA/GGA exchange is approximated
 $\Rightarrow$ remaining self-interaction

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Hybrid functionals:

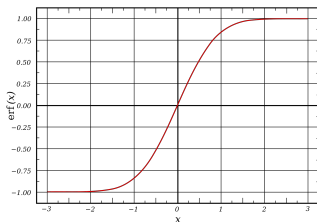
$$E_{\text{xc}} = a_0 E_{\text{x}}^{\text{HF}} + (1 - a_0) E_{\text{x}}^{\text{DFA}} + E_{\text{c}}^{\text{DFA}}$$

Either full SIE removal and low accuracy ($a_0 = 1$) or good accuracy for *many* systems and remaining SIE ($a_0 \neq 1$)

Range-separation

Idea: Separate e-e interaction into **short-range** and **long-range** parts

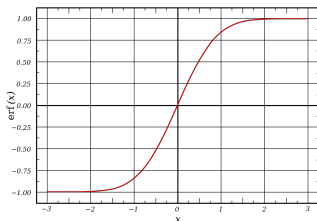
$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{1 - \operatorname{erf}(\omega|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} + \frac{\operatorname{erf}(\omega|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|}$$



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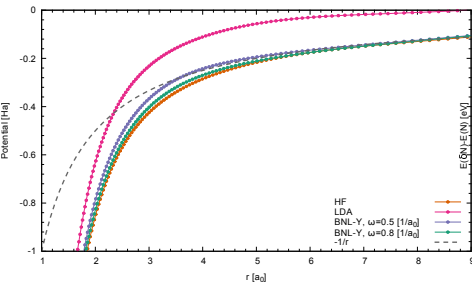
Short-range exchange treated by density functionals, **long-range** by Hartree-Fock

$$E_{\text{xc}} = E_{\text{x,sr}}^{\text{DFA}}(\omega) + E_{\text{x,lr}}^{\text{HF}}(\omega) + E_{\text{c}}^{\text{DFA}}$$

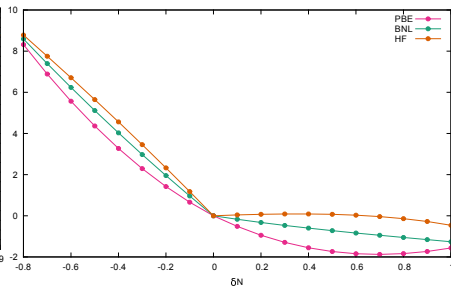
$E_{\text{x,sr}}^{\text{LDA}}$ is known, GGAs likewise  Savin & Flad – IJQC **56** 327 (1995)

Asymptotic behaviour

KS and average GKS potential tails for Argon



Total energy for fractional number of electrons



See for example

 Baer et al. – Annu. Rev. Phys. Chem. **61**, 85 (2010)

- ❶ DFTB is fundamentally a Kohn-Sham method and based on a density expansion
- ❷ Slater-Koster scheme possibly not applicable
- ❸ Typical approximations (2-center, crystal field) in DFTB are not guaranteed to work
- ❹ Method will be slower. Is the ratio $\frac{\text{accuracy}}{\text{cpu time}}$ still acceptable?

LC-DFTB: Derivation and implementation

 TAN & Della Sala – Phys. Status Solidi B, **249**, 237 (2012)

- Basis and atomic density matrix: $\{\phi_\mu, \epsilon_\mu\} \rightarrow \{\phi_\mu^\omega, \epsilon_\mu^\omega\}$

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- Basis and atomic density matrix: $\{\phi_\mu, \epsilon_\mu\} \rightarrow \{\phi_\mu^\omega, \epsilon_\mu^\omega\}$
- DFTB (Zeroth order):

$$H_{\mu\nu}^{(0)} \rightarrow H_{\mu\nu}^{(0),\omega} - \frac{1}{2} \sum_{\lambda\kappa} P_{\lambda\kappa}^0 (\mu\lambda|\kappa\nu)^{lr,\omega}$$

$$V_x \rightarrow V_x^{sr,\omega}$$

$$(\mu\lambda|\kappa\nu)^{lr,\omega} = \int \int \phi_\mu(\mathbf{r}_1) \phi_\lambda(\mathbf{r}_1) \frac{1 - \exp(-\omega r_{12})}{r_{12}} \phi_\kappa(\mathbf{r}_2) \phi_\nu(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

$\Rightarrow$ Evaluation of $(\mu\nu|\lambda\kappa)^{lr,\omega}$ done numerically

■ Becke & Dickson – J. Chem. Phys. **89**, 2993 (1988)

Slater-Koster tables?

$$v_{\mu\nu}^{x,lr}[\rho_0] = \sum_{Q=A,B} \sum_{\alpha\beta} P_{\alpha\beta}^{0,Q} \iint \phi_{\mu}^A(\mathbf{r}_2) \phi_{\alpha}^Q(\mathbf{r}_2) \frac{1 - \exp(-\omega r_{12})}{r_{12}} \phi_{\beta}^Q(\mathbf{r}_1) \phi_{\nu}^B(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2$$

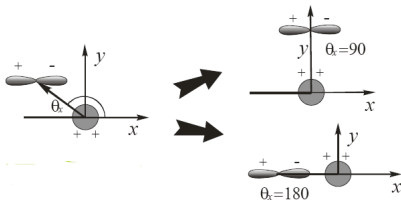
Reduction by symmetry

s	s	p _x	p _y	p _z	d _{xy}
p _x	p _x	p _z	p _y	p _x	d _{xy}
p _y	p _y	p _y	p _z	p _y	d _{xy}
p _z	p _z	p _z	p _z	p _z	d _{xy}
d _{xy}	d _{xy}	d _{xy}	d _{xy}	d _{xy}	d _{xy}
d _{xy}	d _{xy}	d _{xy}	d _{xy}	d _{xy}	d _{xy}

(Source: A. Krashennnikov, U Helsinki)

P^0 is diagonal $\Rightarrow$ Ok!

Rotation to molecular frame



(Source: A. Krashennnikov, U Helsinki)

No m -dependence $\Rightarrow$ Ok!

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$$H_{\mu\nu}^{(0)} \rightarrow H_{\mu\nu}^{(0),\omega} - \frac{1}{2} \sum_{\lambda\kappa} P_{\lambda\kappa}^0 (\mu\lambda|\kappa\nu)^{lr,\omega}$$

$$V_x \rightarrow V_x^{sr,\omega}$$

$$(\mu\lambda|\kappa\nu)^{lr,\omega} = \int \int \phi_\mu(\mathbf{r}_1) \phi_\lambda(\mathbf{r}_1) \frac{1 - e^{-\omega r_{12}}}{r_{12}} \phi_\kappa(\mathbf{r}_2) \phi_\nu(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

- ▶ SCC-DFTB (Second order):

$$H_{\mu\nu}^{(1)} = \Delta v_{\mu\nu}^{fr} + \Delta v_{\mu\nu}^{lr}$$

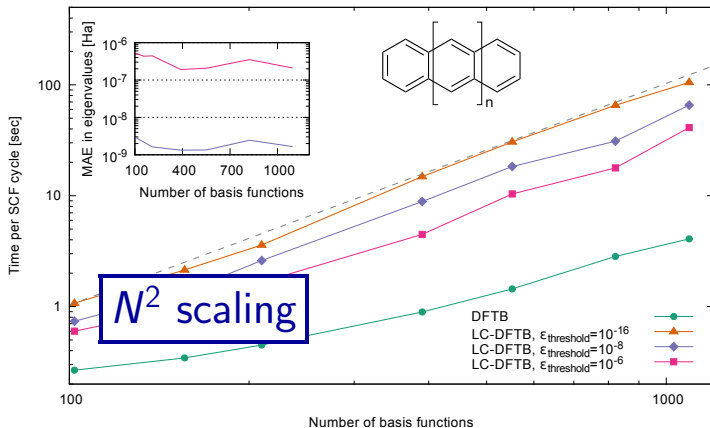
$$\Delta v_{\mu\nu}^{fr} = \frac{1}{2} S_{\mu\nu} \sum_C (\gamma_{AC}^{fr} + \gamma_{BC}^{fr}) \Delta q_C, \quad \mu \in A, \nu \in B$$

$$\Delta v_{\mu\nu}^{lr} = -\frac{1}{8} \sum_{\alpha\beta} S_{\mu\alpha} S_{\beta\nu} \Delta P_{\alpha\beta} \left(\gamma_{\mu\beta}^{lr} + \gamma_{\alpha\nu}^{lr} + \gamma_{\mu\nu}^{lr} + \gamma_{\alpha\beta}^{lr} \right)$$

Pre-screening and numerical performance

$$H_{\mu\nu}^{\text{lr}} = -\frac{1}{8} \sum_{\alpha\beta} \Delta P_{\alpha\beta} S_{\mu\alpha} S_{\beta\nu} (\gamma_{\mu\beta}^{\text{lr}} + \gamma_{\mu\nu}^{\text{lr}} + \gamma_{\alpha\beta}^{\text{lr}} + \gamma_{\alpha\nu}^{\text{lr}})$$

$$\overline{S}_{BD} \overline{S}_{AC} \overline{\Delta P^n} \leq \epsilon_{\text{threshold}}$$



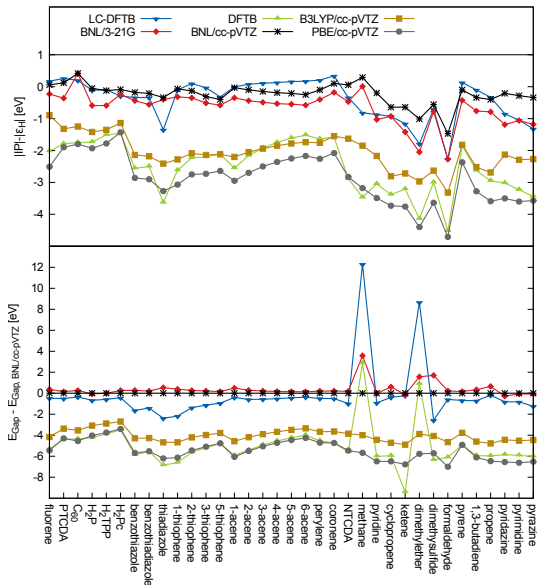
Pre-screening and numerical performance

Table : Wall time [s] of DFT calculations versus LC-DFTB
($\epsilon_{\text{thresh}} = 10^{-6}$). Asterisk denotes execution on 12 cores.

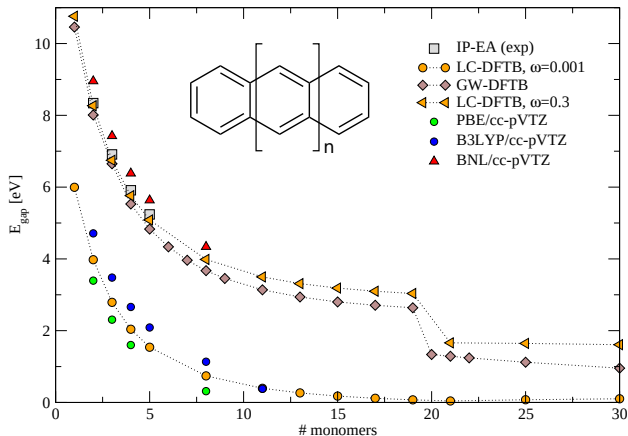
molecule	BNL/3-21G	BNL/cc-pVTZ	LC-DFTB	DFTB
5-acene	325	59701	6	1
perylene	541	113414	6	1
H ₂ P	932	23825*	8	1
coronene	2116	260677	6	1
6-acene	507	79993	8	2
5-thiophene	1303	144735	11	2
PTCDA	3748	521424	10	2
H ₂ Pc	3034	366838*	14	2
H ₂ TPP	5735	744967*	22	4
C ₆₀	7221	655789*	23	2

Speedup two orders of magnitude

Quasiparticle energies

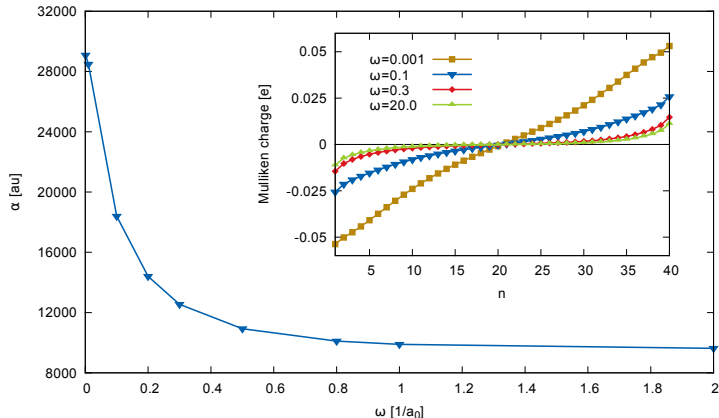


Polyacenes: Fundamental gap



Polarizability of polyacetylene chains

Figure : Long-axis linear polarizability of PA (40 units)



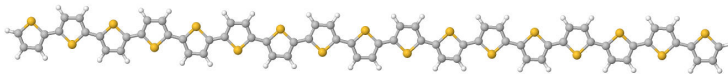
Counteracting electric field present in LC-DFTB

Test of LC-DFTB on polythiophene dications

Polaron

Localization of excess charge accompanied by a local lattice distortion

- ▶ Polaron is responsible for transport in charged polymer chains
- ▶ Thiophene nT^{2+} dication

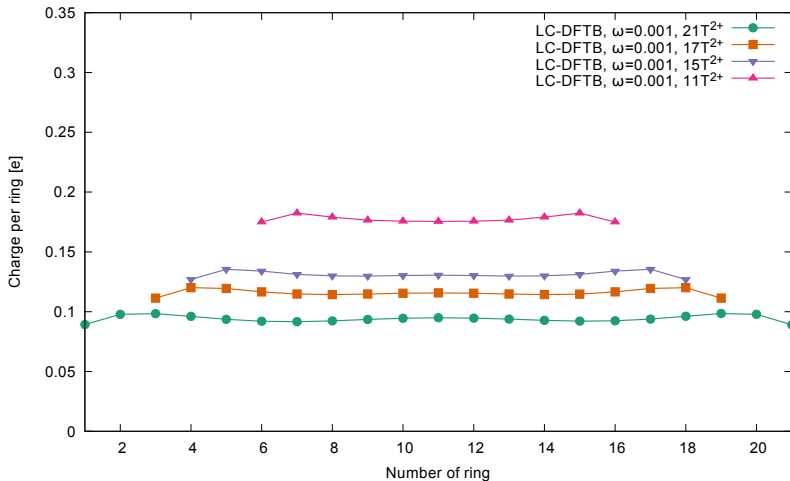
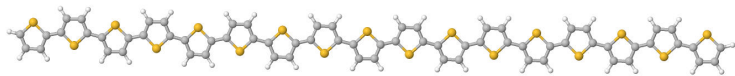


- ▶ local DFT(B) calculations predict delocalized charge
- ▶ (SIE-free) MP2, Hartree-Fock and SSH model predict charge localization

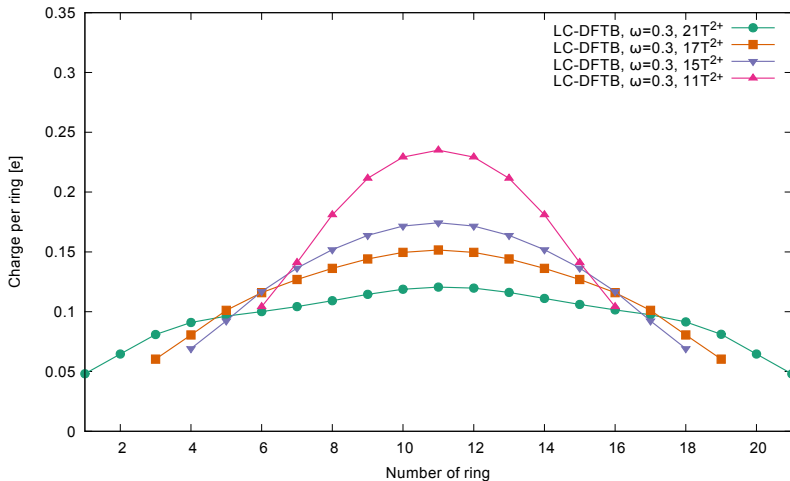
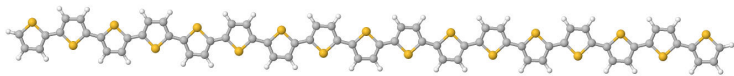
■ TAN et al. – Organic Electronics **5**, 167 (2004)

■ Ehrendorfer & Karpfen – J. Phys. Chem. **98**, 7492 (1994)

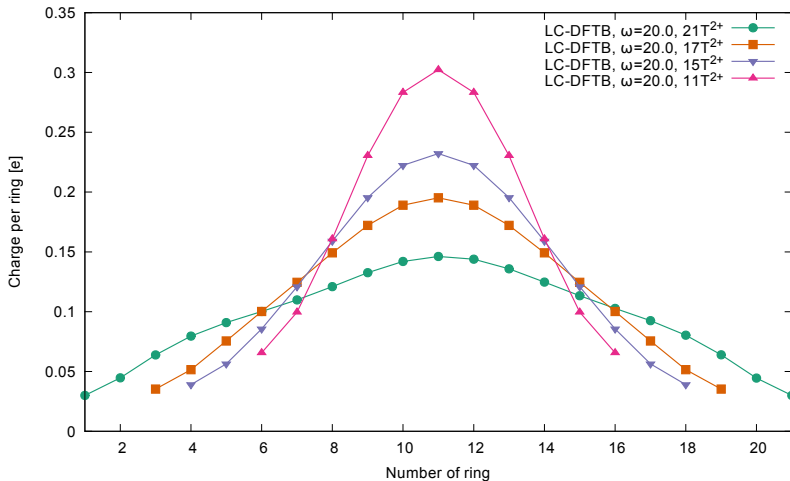
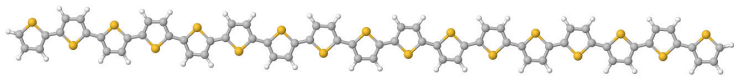
Charge distribution, $\omega = 0.001 \text{ a}_0^{-1}$ (local DFT limit)



Charge distribution, $\omega = 0.3 \text{ a}_0^{-1}$

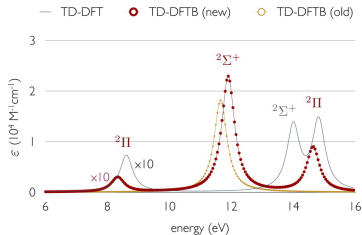


Charge distribution, $\omega = 20.0 \text{ a}_0^{-1}$ (HF+C limit)

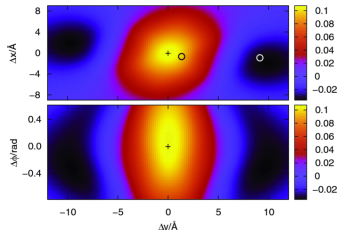


Summary - recent developments in DFTB

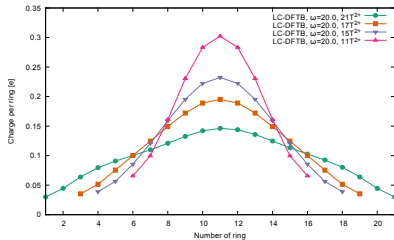
Onsite correction



Exciton couplings



New class of functionals



To-Do list LC-DFTB

- ▶ Optimized repulsive potentials
- ▶ Spin-unrestricted formalism
- ▶ Periodic boundary conditions
⇒ HSE functional
- ▶ TD-DFTB with LC