

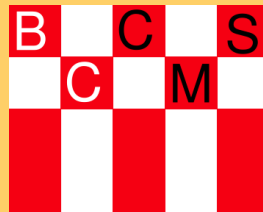
# Optical spectra from Tight-Binding methods

Time dependent DFT vs. Bethe-Salpether approaches

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# Optical spectra from DFT(B)

Static many body Hamiltonian  $H_{MB}$  yields spectrum directly

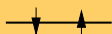
$$H_{MB}(r_1 \dots r_N) |\psi_I\rangle = \omega_I |\psi_I\rangle$$



Static DFT Hamiltonian yields only some single-particle spectrum



$$H_{DFT}(r) |\varphi_i\rangle = \epsilon_i |\varphi_i\rangle$$



State	DFTB $\omega_{ij}$	Experiment
Ethylene ${}^1B_{1u}$	6.30	7.65
Propene ${}^1A'$	5.94	7.19
Butadiene ${}^1B_u$	4.21	5.92

Observation: Differences  $\omega_{ij} = \epsilon_j - \epsilon_i$  underestimate optical excitation energies

# TDDFT

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

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

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

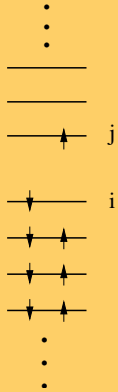
$$i \frac{\partial}{\partial t} \varphi_i(\mathbf{r}, t) = \left[ -\frac{1}{2} \nabla^2 + v_{\text{KS}}[\rho](\mathbf{r}) \right] \varphi_i(\mathbf{r}, t)$$

with the **local** potential

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

# Excitation energies from linear response

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Equation to solve (singlets):

$$\omega_{\text{I}}^2 F_{ij}^{\text{I}} = \sum_{kl} \left[ \omega_{ij}^2 \delta_{ik} \delta_{jl} + 2 \sqrt{\omega_{ij} K_{ij,kl}} \sqrt{\omega_{kl}} \right] F_{kl}^{\text{I}}$$

$$\omega_{\text{I}} \approx \omega_{ij} + K_{ij,ij}$$

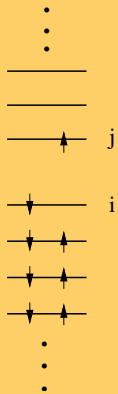
Coupling matrix  $\mathbf{K}$  leads to correction of single-particle picture

$$K_{ij,kl} = 2 \iint \psi_i(\mathbf{r}) \psi_j(\mathbf{r}) \left( \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{\text{xc}}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \right) \psi_k(\mathbf{r}') \psi_l(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

$\mathbf{K}$  is the derivative of the KS potential wrt the density

# DFTB approximation of TDDFT = TD-DFTB

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Equation to solve:

$$\sum_{kl} \left[ \omega_{ij}^2 \delta_{ik} \delta_{jl} + 2 \sqrt{\omega_{ij} \omega_{kl}} K_{ij,kl} \right] F_{kl}^I = \omega_I^2 F_{ij}^I$$

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

$$\text{DFT: } K_{ij,kl} = 2 \iint \psi_i(\mathbf{r}) \psi_j(\mathbf{r}) \left( \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{xc}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \right) \psi_k(\mathbf{r}') \psi_l(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

$$\text{DFTB: } K_{ij,kl} = 2 \sum_{\alpha\beta} q_{\alpha}^{ij} \gamma_{\alpha\beta}(|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|, U_{\alpha}, U_{\beta}) q_{\beta}^{kl}$$

## Excitation energies (eV)

Molecule	State	Exp.	TD-DFTB		TDDFT	
			$\omega_I$	$\omega_{ij}$	$\omega_I$	$\omega_{ij}$
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

## Mean error (eV)

	TD-DFTB	TDDFT	INDO/S
Singlets (16 Comp.)	0.38	0.36	0.56
Triplets (13/11 Comp.)	0.64	0.37	1.38

- Good description of  $\pi \rightarrow \pi^*$ -transitions
- Transferable error cancellation
- TD-DFTB works where TDDFT works, and fails ...

# Limitations of TDDFT/TD-DFTB

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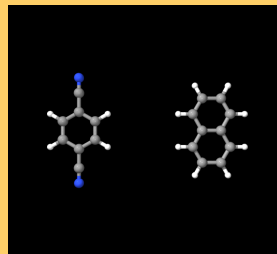
- High lying excitations
- Double excitations
- Solids
- Charge transfer systems

# Charge transfer excitations

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Exact excitation energy:

$$\omega_{CT} = IP_D - EA_A - \frac{1}{R}$$



In TDDFT:

$$\omega_{CT} = \epsilon_L - \epsilon_H + K$$
$$K = 2 \iint \psi_H(\mathbf{r}) \psi_L(\mathbf{r}) \left( \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{xc}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \right) \psi_H(\mathbf{r}') \psi_L(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

$-\epsilon_H \approx IP_D$ , but  $-\epsilon_L$  never =  $EA_A$  and  $K \approx 0$  for conv. functionals

# Beyond DFT: The GW approximation + Bethe-Salpeter equation

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- Solid state approach, now also applied to finite systems
- Systematic many body perturbation theory
- Two step approach
  - GW approx.: find physical single particle levels
  - BS equation: include electron-hole interaction

# First step: The GW approximation

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$$\left( H_{\text{Hartree}} + \Sigma(\epsilon_i^{\text{QP}}) \right) |\psi_i^{\text{QP}}\rangle = \epsilon_i^{\text{QP}} |\psi_i^{\text{QP}}\rangle$$

- Nonlocal Selfenergy  $\Sigma = iGW$   
describes exchange and correlation effects
- $W(\mathbf{r}, \mathbf{r}', \omega) = \int \epsilon^{-1}(\mathbf{r}, \mathbf{r}'', \omega) v(\mathbf{r}'', \mathbf{r}') d\mathbf{r}''$   
is screened Coulomb interaction  
 $\Leftrightarrow$  correlation hole reduces e-e interaction
- $\epsilon^{\text{QP}}$  are quasiparticle energies,  
i.e. ionization potentials and electron affinities.

# An approximate GW approach: DFTB-GW

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$$\epsilon_i^{\text{QP}} = \epsilon_i^{\text{DFTB}} + Z_i \langle \psi_i | \Sigma(\epsilon_i^{\text{DFTB}}) - v_{\text{xc}} | \psi_i \rangle$$

- $W, \epsilon$  expressed in minimal basis of atomic orbitals
- 2e-integrals approximated by interpolation functions
- $v_{\text{xc}}$  matrix elements in two-center approximation, precalculated and tabulated

Anthracene QP spectrum:

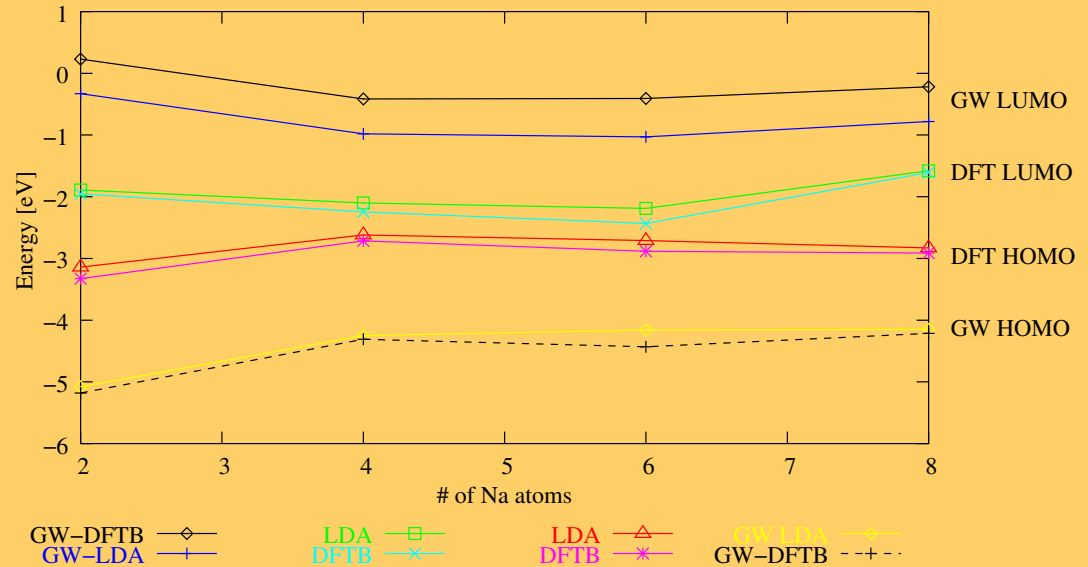
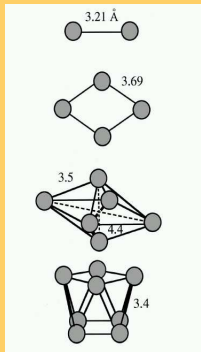
*ab initio* 170 min, DFTB-GW < 1s

# Final results: benzene

State	Sym.	$\epsilon^i$		$v_{XC}^i$		$\Sigma_X^i$	
		a.i.	DFTB	a.i.	DFTB	a.i.	DFTB
$A_{2u}$	$\pi$	-9.37	-8.95	-12.82	-12.39	-17.15	-16.35
$E_{2g}$	$\sigma$	-8.34	-7.71	-15.05	-12.25	-19.49	-15.62
$E_{1g}$	$\pi$	-6.59	-6.64	-13.03	-12.30	-15.61	-14.98
$E_{2u}$	$\pi^*$	-1.30	-1.32	-12.64	-11.72	-7.58	-7.41
$B_{2g}$	$\pi^*$	0.92	2.29	-6.96	-11.19	-2.89	-6.33

State	Sym.	$\Sigma_C^i$		$\epsilon_{QP}^i$	
		a.i.	DFTB	a.i.	DFTB
$A_{2u}$	$\pi$	2.03	2.47	-11.67	-10.45
$E_{2g}$	$\sigma$	1.86	1.41	-10.92	-9.67
$E_{1g}$	$\pi$	0.59	0.87	-8.58	-8.46
$E_{2u}$	$\pi^*$	-1.74	-0.99	2.01	2.00
$B_{2g}$	$\pi^*$	-2.31	-2.84	2.67	4.31

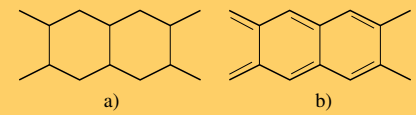
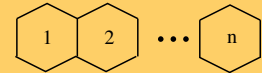
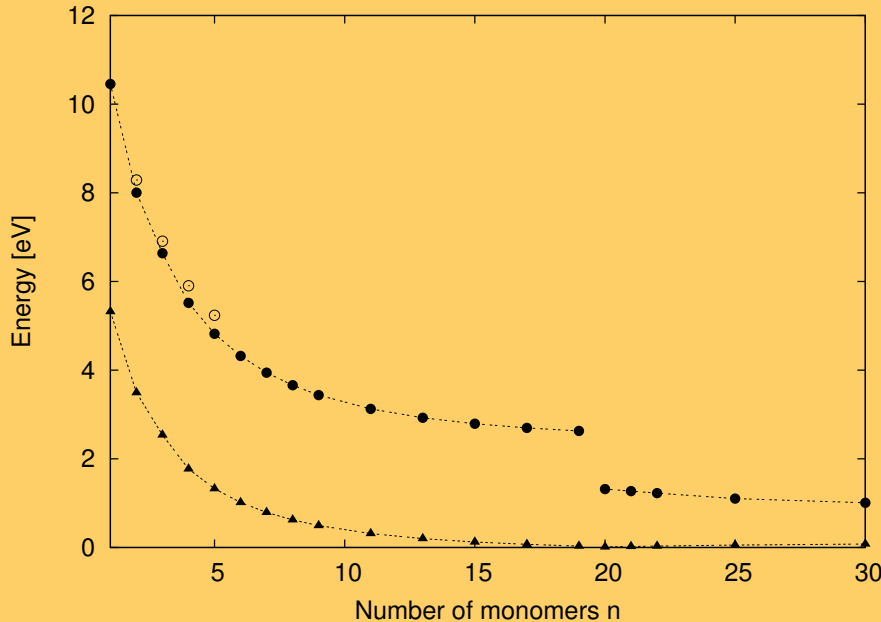
# Sodium cluster



First-principles calc.:

S. Ishii, K. Ohno, Y. Kawazoe, and S.G. Louie, Phys. Rev. B **63**, 155104, (2001).

# The polyacene series: QP versus DFT gap



● QP gap      ▲ DFT gap      ○ Experiment

# Second step: Bethe-Salpeter equation

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$$\sum_{kl} \left[ (\epsilon_j^{\text{QP}} - \epsilon_i^{\text{QP}}) \delta_{ik} \delta_{jl} + K_{ij,kl}^{\text{X}} - K_{ij,kl}^{\text{D}} \right] F_{kl}^{\text{I}} = \omega_{\text{I}} F_{ij}^{\text{I}}$$

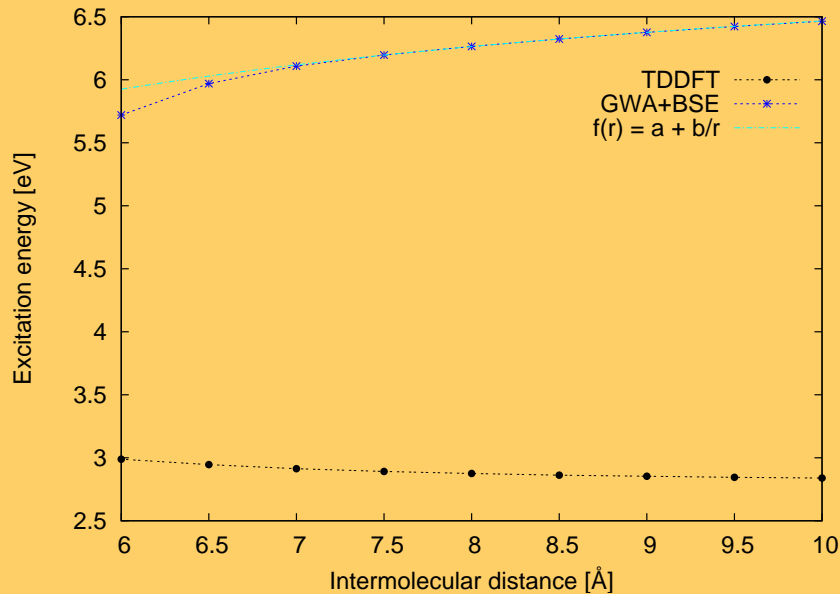
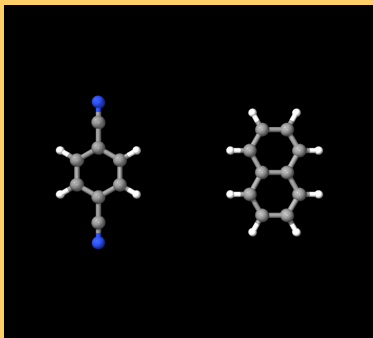
$$K_{ij,kl}^{\text{X}} = 2 \iint \frac{\psi_i(\mathbf{r}) \psi_j(\mathbf{r}) \psi_k(\mathbf{r}') \psi_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

$$K_{ij,kl}^{\text{D}} = \iint \psi_i(\mathbf{r}) \psi_k(\mathbf{r}) W(\mathbf{r}, \mathbf{r}') \psi_j(\mathbf{r}') \psi_l(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

- Electron-hole interaction is given by  $K^{\text{D}}$ :  
 $\psi_i(\mathbf{r}) \psi_j(\mathbf{r}) \rightarrow 0 \Rightarrow K_{ij,ij}^{\text{D}} \rightarrow 1/R !$
- GW+BS has correct asymptotic limit for CT excitations:  
 $\omega_{\text{CT}}^{\text{GW+BS}} \approx \text{IP}^{\text{D}} - \text{EA}^{\text{A}} - 1/R.$

# Case study: BDCN + Naphtalene

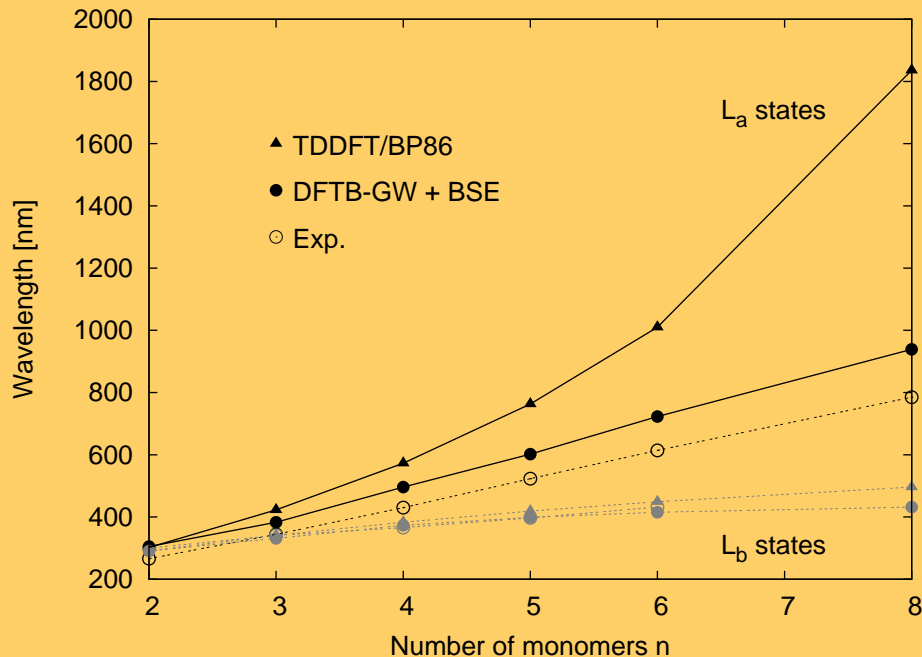
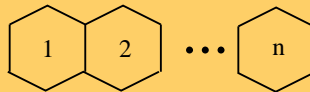
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Experiment ( $R \rightarrow \infty$ ): 7.05 eV

DFTB-GW+BSE: 7.28 eV

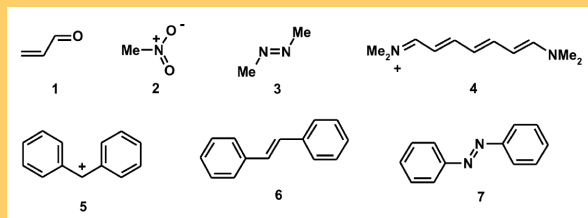
# Polyacenes



Wrong asymptotic behaviour of TDDFT for L<sub>a</sub> (ionic) states

Grimme and Parac, CPC 4 292 (2003)

# DFTB Bethe-Salpeter performance



Mol.	Type	$\Delta_{\text{DFT}}$		$\Delta_{\text{QP}}$		$\omega_{\text{I}}$		
		DFTB	a.i.#1	DFTB GW	a.i.#2	DFTB GW+BS	TDDFT#3	Exp.
1	$n \rightarrow \pi^*$	3.14	2.78	10.62	9.61	3.71	3.43	3.69
2	$n \rightarrow \pi^*$	4.66	3.70	11.26	11.32	3.40	4.06	4.44
4	$\pi \rightarrow \pi^*$	2.25	2.28	5.93	6.66	2.60	3.73	3.50
5	$\pi \rightarrow \pi^*$	2.02	2.21	5.64	6.51	2.37	3.33	2.80
6	$\pi \rightarrow \pi^*$	3.07	2.79	7.08	6.82	3.93	3.85	4.19
7	$n \rightarrow \pi^*$	2.02	1.96	8.03	7.47	3.59	2.57	2.76

All energies in eV

#1: DFT/PBE/6-311+G(2d,2p)

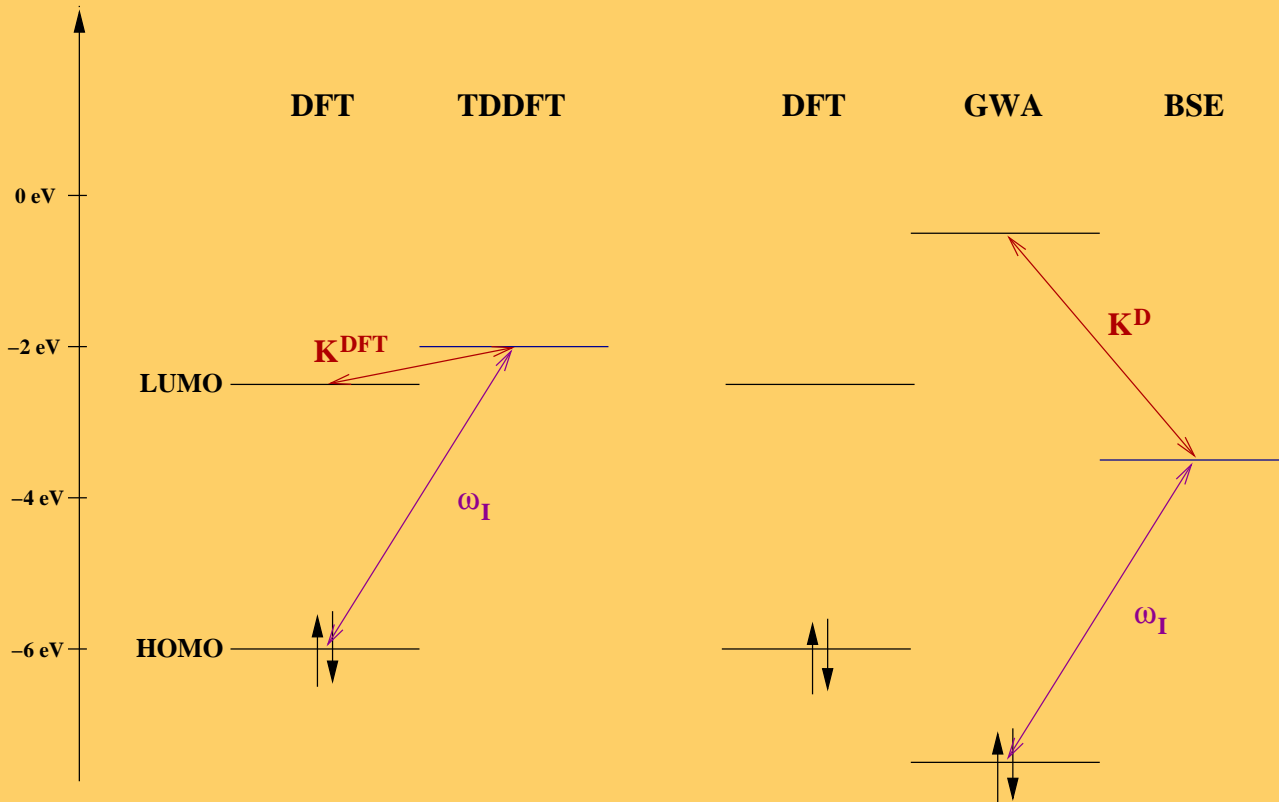
#2: From DFT/PBE/6-311+G(2d,2p) N and N $\pm$ 1 calc.

#3: B3LYP/6-31+G\* from Fabian et al., THEOCHEM 594 41 (2002).

Not a general purpose method!

# Summary: TDDFT vs. Bethe-Salpeter

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# Thanks ∞

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- ∞ Michael Rohlfing    *University of Osnabrück*
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