# Predictive computational spectroscopy with BSE@GW



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# **Theoretical Spectroscopy**



- Common idea: System of non-interacting renormalised electrons (quasiparticles)
- Direct Photoemission:  $\left(\Psi_0^{(N)}, E_0^{(N)}\right) \rightarrow \left(\Psi_S^{(N-1)}, E^{(N-1)}\right), \quad E^{(N-1)} = E^{(N)} \epsilon_N$ 
  - Excited electron leaves the system
- Photoabsorption:  $\left(\Psi_0^{(N)}, E_0\right) \rightarrow \left(\Psi_S^{(N)}, E_S\right), \quad E_S = E_0 + \Omega_S$ 
  - Excited electron stays in the system
  - Excited electron is bound to other electron in system by Coulomb interactions

Onida, Reining, Rubio, Rev. Mod. Phys. (2002) 74 (2)



# Some details: TD-DFT vs. BSE

- Such processes are typically studied using response theory:
- Leads to the concept of Dyson equation (Dyson, PR, 1949, 75(11), 1736)
  - kernel : Correlation function<sup>(0)</sup>  $\mapsto$  Correlation function

### **Examples:**

- Green's function perturbation theory (Landau ~1957):
  - Solve Dyson equation for 2-particle Green's function  $G_2$

• 
$$K: G_2^{(0)} \mapsto G_2$$
  $K(1,2,3,4) = \frac{\delta \Sigma_{Hxc}(1,4)}{\delta n(3,2)}$ 

- Called Bethe-Salpeter equation (BSE) (~1950) (Salpeter, Bethe, 1951, 84(6), 1951)
- Time-dependent density-functional theory:
  - Solve Dyson equation for density-density response  $\chi$

• 
$$K: \chi^{(0)} \mapsto \chi$$
  $K(1,2) = \frac{\delta v_{Hxc}(1)}{\delta n(2)}$ 



# Some issues of DFT

- Wrong asymptotic behaviour of xc potential
- Incorrect description of Charge transfer states
- Underestimated fundamental gaps

### The GW approximation (and beyond)

- $\Sigma = \Sigma_H + iGW GWGWG + O(W^3)$  W = screened interaction
- $W = v_c + v_c PW$
- P = -iGG
- $G = G^{(0)} + G^{(0)} \Sigma G$

Self-consistency: In practice, we simplify the last equation



### Solving the Quasiparticle equations



3) *qsGW*: Iterate **eigenvalues and orbitals** until self-consistency:

- 1) Faleev, S.; van Schilfgaarde, M.; Kotani, T., PRL, 2004, 93, 126406
- 2) van Schilfgaarde, M.; Kotani, T.; Faleev, S., PRL, **2006**, 96, 226402
- 3) van Schilfgaarde, M.; Kotani, T.; Faleev, S., PRB, 2007, 76, 165106



# What can you calculate?

- QP energies (GW)
  - Ionization potentials, Electron affinities, HOMO-LUMO gaps
  - Redox potentials (Belić et al., PCCP (2022), 24, 197)
- Excited states (BSE@GW)
  - Excitation energies, Oscillator strength, Life times
  - Spectra
- Ground state energies
  - RPA, RPA+SOSEX etc.
- Additional functionality with quasi-particle self-consistent GW:
  - Population analysis, Mulliken population analysis,
  - Symmetry adapted fragment orbital analysis
- All supported at all levels of self-consistency:  $G_0W_0$ , evGW, qsGW
- 2-Component implementation available —> spin-orbit coupling (upcoming release)



### **QP** energies of Organic Acceptor Molecules

Comparison to experiment and CCSD(T) reference data<sup>1</sup> (all calculations complete basis set limit extrapolated)





1)

2)

### Excited states of Chlorophyll monomers and dimers

	$Q_y$	$Q_x$	В	$\Delta_{Q_y - Q_x}$			
$\exp.$ (VEE)	1.99	2.30	3.12	0.31			
exp. (band max)	1.94	2.23	3.08	0.29			
CAM-B3LYP-D3(BJ)/def2-TZVP optimized structure							
DLPNO-STEOM-CCSD	1.75	2.24	3.17	0.49			
qsGW	1.97	2.29	3.15	0.32			
evGW@PBEH40	1.98	2.29	3.15	0.31			
evGW@LDA	1.94	2.20	3.01	0.26			
CAMY-B3LYP	1.94	2.23	3.08	0.29			
$\omega$ B97-X	2.10	2.71	3.57	0.61			



kernel	$\Omega_1$	$\Omega_2$	$\Omega_3$	$\Omega_4$	$\Omega_5$	$\Omega_6$		
exp. $(VEE)^{178}$	1.95 (estimated)							
exp. (band max) <sup>178</sup>	1.90							
CAM-B3LYP-D3(BJ)/TZP optimized structure <sup><math>c</math></sup>								
evGW@LDA	1.98	1.99	2.16	2.22	2.51	2.64		
evGW@PBEH40	1.97	2.02	2.24	2.27	2.58	2.67		
qsGW	1.94	1.98	2.25	2.28	2.56	2.68		
CAMY-B3LYP	2.12	2.16	2.38	2.43	2.51	2.61		
$\omega B97-X$	2.05	2.10	2.63	2.68	3.10	3.27		

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Förster and Visscher, JCTC, 2022, (in press)

# **BSE@GW: Performance**

 Calculation of Low-lying Excited states of six-chromophore model of photosystem II reaction centre (~ 2000 electrons/5 days on 1 node) Förster and Visscher, JCTC, 2022, (in press)



				Iterations		CPU time		
Method	Basis	$N_{\rm bas}$	$N_{\Omega}$	qsGW	BSE	GW	BSE	total
qsGW-BSE	TZ3P	11116	12	6	10	3401	3447	7283
	TZP	6256	24	6	8	1074	1729	2924
evGW-BSE	TZP	6256	24	5	8	826	1969	2917
$\omega B97-X$	TZP	6256	12	_	21	—	2675	2846



### Accurate Ground state energies - RPA and beyond

Different variants to RPA + second-order screened exchange MP2 like effort, but no divergences, higher accuracy



Förster A., JCTC (2022), 18(10), 5948

# Example: The singlet-triplet gap of Benzene





#### Exp. : **3.66** eV Adiabatic DLPNO-CCSD(T) + ZPE: **3.76** eV BSE@GW?

Bruno, et al., PCCP, 2022, 24, 14228-14241

### **Practical considerations**

### $G_0 W_0$ Choose the right starting point:

- Hybrid functional with 40-50 % of exact exchange, for instance BHandHLYP, PBE0(40%exx), or RSH
- PBE, LDA are **not** suitable

**Self-consistency** reduces this issue (6-8 iterations typically):

- qsGW: best method for high precision. Higher requirements on numerical settings
- evGW is a useful alternative

#### Large basis sets are required:

- Individual QP energies converge very slowly to the CBL
- Best is to use (T,Q) extrapolation scheme, T= Corr/TZ3P, Q = Corr/QZ6P
- BSE: less pronounced, TZ(2P,3P) is typically sufficient

### Use good or VeryGood numerical quality

• **BSE** converge best when only a subset of transitions is used (ModifyExcitations key)



# Example: The singlet-triplet gap of Benzene



- BSE@G<sub>0</sub>W<sub>0</sub>@PBE : 3.29 eV
- BSE@evGW@PBE: 3.45 eV
- BSE@qsGW@PBE0(40ex): 3.66 eV
- BSE@qsGW@PBE: 3.66 eV

# Implementation in AMS

- Space-time method: switch between time and frequency domains
- We work on the imaginary axes since quantities are smoother
- Analytical continuation to real frequency axis in the very end



Implemented with  $N^4$  scaling using global density fitting  $-> N^3 - N^2$  using local density fitting approximations

Caruso et al. *Phys. Rev. B*, **2013**, 88(7), 1-18
Wilhelm et al., *J. Phys. Chem. Let.* **2018**, 9, 306-312
Wilhelm et al., *J. Them. Theory. Comput.*, **2021**, 17, 1662-1677
Duchemin et al., *J. Them. Theory. Comput.*, **2021**, 17(4), 2383-2393

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Special in ADF: Full self-energy  $\Sigma(i\omega)$  is calculated in AO basis