Self-consistent *GW* in FHI-aims

Fabio Caruso

Fritz-Haber-Institut, Berlin

**FHI-aims Developers'
and Users' Meeting**

Berlin,
29 August 2012

Outline

- **The *GW* approximation (why self-consistency?)**

- **Implementation of sc-*GW* in FHI-aims**

- **Application to atoms, molecules and molecular interfaces**

The one-body Green function

$$G_{\sigma\sigma'}(\mathbf{r}t, \mathbf{r}'t') = -i\langle\Psi_0|\hat{T}[\psi_\sigma(\mathbf{r}t)\psi_{\sigma'}^\dagger(\mathbf{r}'t')]\|\Psi_0\rangle$$

Lehmann representation:

$$G_{\sigma\sigma'}^{R}(\mathbf{r}, \mathbf{r}', \omega) = \sum_s \frac{f_{s,\sigma}(\mathbf{r})f_{s,\sigma'}^*(\mathbf{r}')}{\omega - \varepsilon_s + i\eta}$$
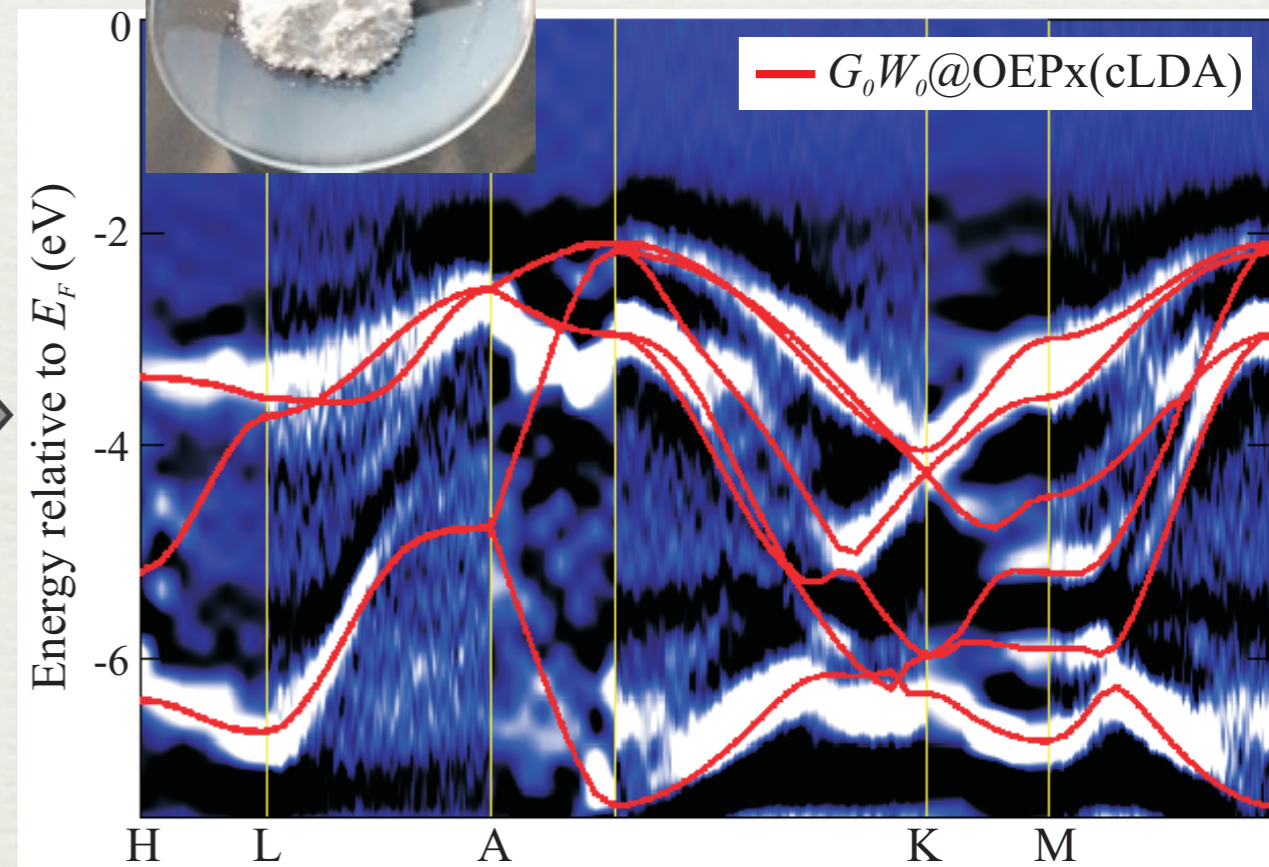
where $\quad \varepsilon_s \equiv E_s^{N+1} - E_0$

G: contains information on charged excitations

G: an ideal for calculating band-structures and photo-emission spectra

Solids: ZnO

Q. Yan, P. Rinke, *et al*. Semicond. Sci. Technol. **26,** 014037 (2011)

Green's function is solution to Hedin's equations

notation: $\quad 1 = (\mathbf{r}_1, \sigma_1, t_1)$

$$P(1,2) = -i \int G(2,3)G(4,2^+)\Gamma(3,4,1)d(3,4)$$

$$W(1,2) = v(1,2) + \int v(1,3)P(3,4)W(4,2)d(3,4)$$

$$\Sigma(1,2) = i \int G(1,4)W(1^+,3)\Gamma(4,2,3)d(3,4)$$

$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \int \frac{\delta\Sigma(1,2)}{\delta G(4,5)}G(4,6)G(7,5)\Gamma(6,7,3)d(4,5,6,7)$$

Dyson's equations

$$G^{-1}(1,2) = G_0^{-1}(1,2) - \Sigma(1,2)$$

- links non-interacting (G_0) with interacting (G) system

Green's function is solution to Hedin's equations

notation: $\quad 1 = (\mathbf{r}_1, \sigma_1, t_1)$

GW approx.

$$P(1,2) = -i \int G(2,3) G(4,2^+) \cancel{\Gamma(3,4,1)} d(3,4)$$

$$W(1,2) = v(1,2) + \int v(1,3) P(3,4) W(4,2) d(3,4)$$

$$\Sigma(1,2) = i \int G(1,4) W(1^+,3) \cancel{\Gamma(4,2,3)} d(3,4)$$

$$\cancel{\Gamma(1,2,3) = \delta(1,2)\delta(1,3) + \int \frac{\delta\Sigma(1,2)}{\delta G(4,5)} G(4,6) G(7,5) \Gamma(6,7,3) d(4,5,6,7)}$$

Dyson's equations

$$G^{-1}(1,2) = G_0^{-1}(1,2) - \Sigma(1,2)$$

- links non-interacting (G_0) with interacting (G) system
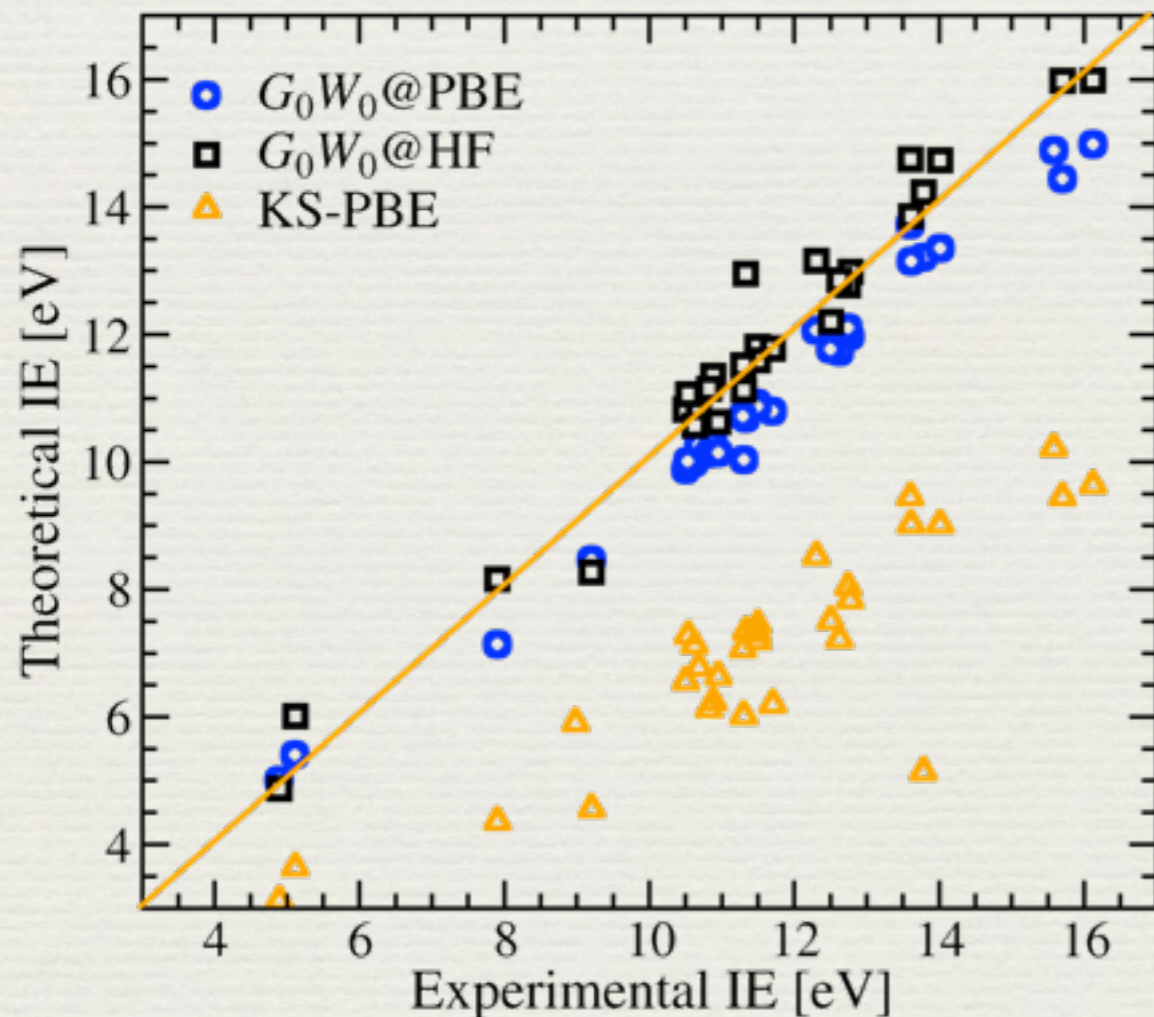
The *GW* approximation

The self-energy

$$\Sigma = -iGW$$

First order perturbation theory:

$$\epsilon_i^{\mathrm{QP}} = \epsilon_i^{\mathrm{KS}} + \langle \phi_0 | \Sigma(\epsilon_i^{\mathrm{QP}}) - v_{\mathrm{xc}} | \phi_0 \rangle$$

molecules

Good correlation with experiments, but:

there are undesirable problems

- results depend on starting point
- ground-state is treated at the DFT/HF level
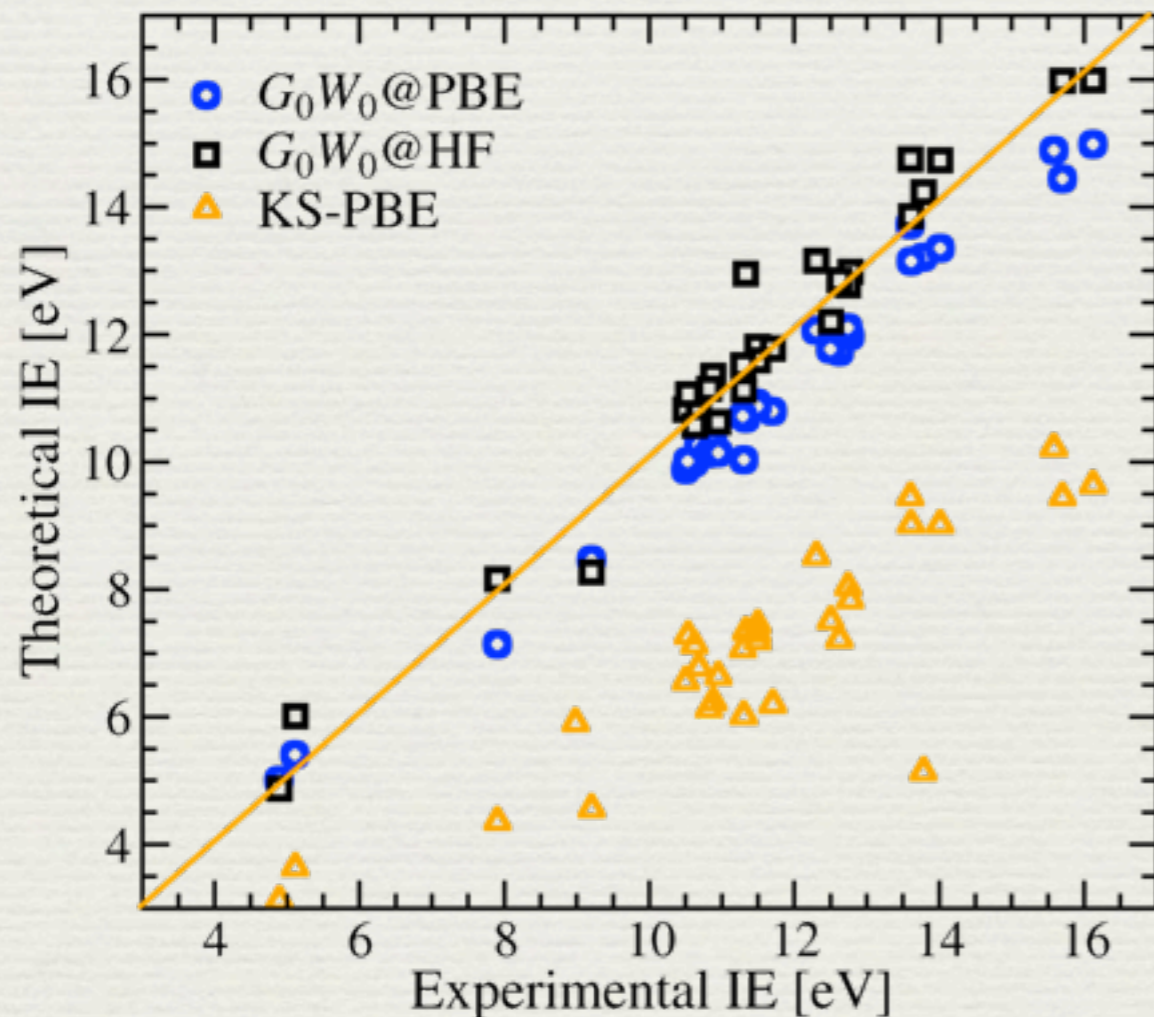- violation of conservation laws

The *GW* approximation

The self-energy

$$\Sigma = -iGW$$

First order perturbation theory:

$$\epsilon_i^{\text{QP}} = \epsilon_i^{\text{KS}} + \langle \phi_0 | \Sigma(\epsilon_i^{\text{QP}}) - v_{\text{xc}} | \phi_0 \rangle$$

molecules

Good correlation with experiments, but:

there are undesirable problems

- results depend on starting point
- ground-state is treated at the DFT/HF level
- violation of conservation laws

How to go beyond 1st order PT (within the *GW* approximation)?

- **Self-consistency in the eigenvalues**
  Hybertsen and Louie, Phys. Rev. B 34, 5390 (1986)

- **Optimization of the perturbed Hamiltonian (Quasi-particle self-consistent *GW*)**
  Faleev et al. , Phys. Rev. Lett. 93, 126406 (2004)

- **Iteration of Dyson equation with fixed *W***

- **Fully self-consistent *GW***
  Hedin, Phys. Rev. 139, A796 (1965)

Outline

- The *GW* approximation (why self-consistency?)

- **Implementation of sc-*GW* in FHI-aims**

- Application to atoms, molecules and molecular interfaces

Self-Consistent *GW* in practice

DFT / HF

$\{\psi_n(r), \epsilon_n\}$

G_0^{KS}

Σ

W

G

χ
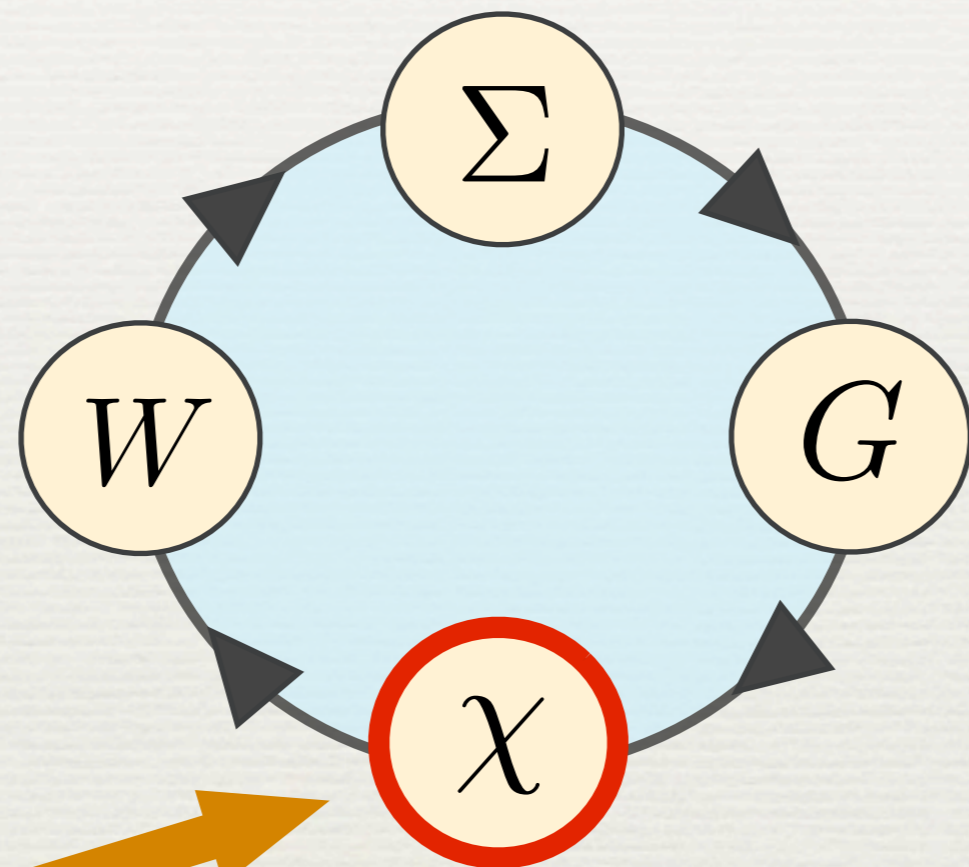
SCF loop

$\Gamma = 1$

$$\chi_0(i\tau) = -iG(i\tau)G(-i\tau)$$

Self-Consistent *GW* in practice

DFT / HF

$\{\psi_n(r), \epsilon_n\}$

G_0^{KS}

Σ

W

G

χ
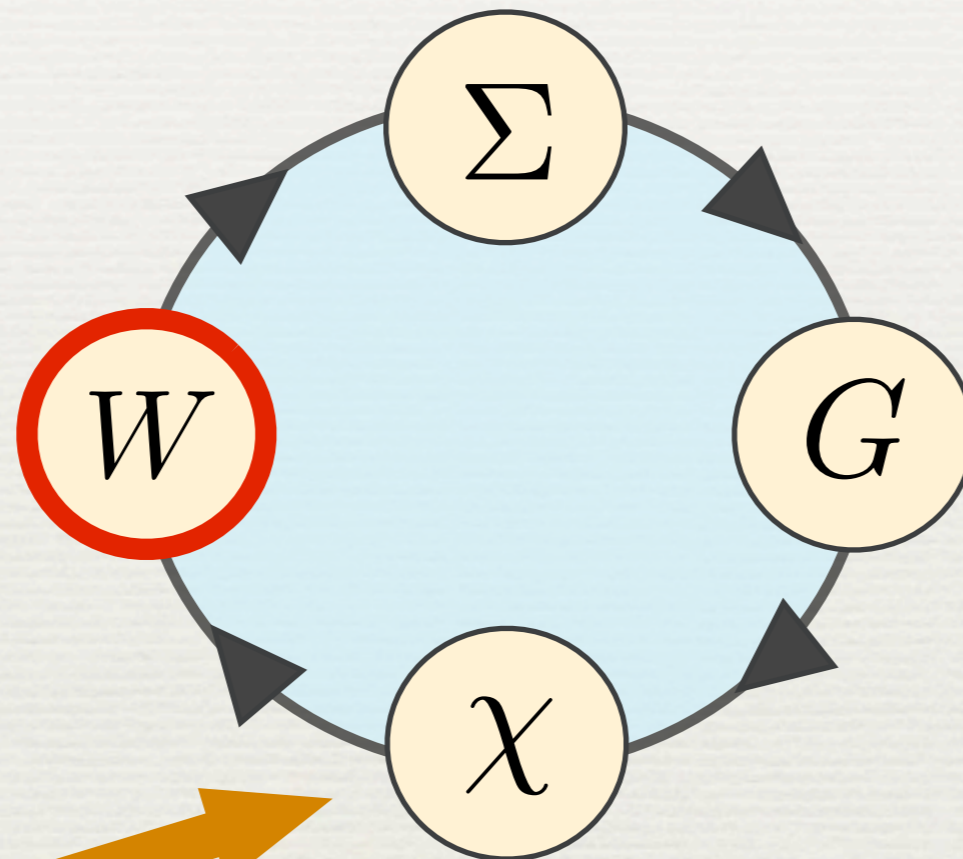
SCF loop

$\Gamma = 1$

$$W(i\omega) = \frac{v}{1 - v\chi_0(i\omega)}$$

Self-Consistent *GW* in practice
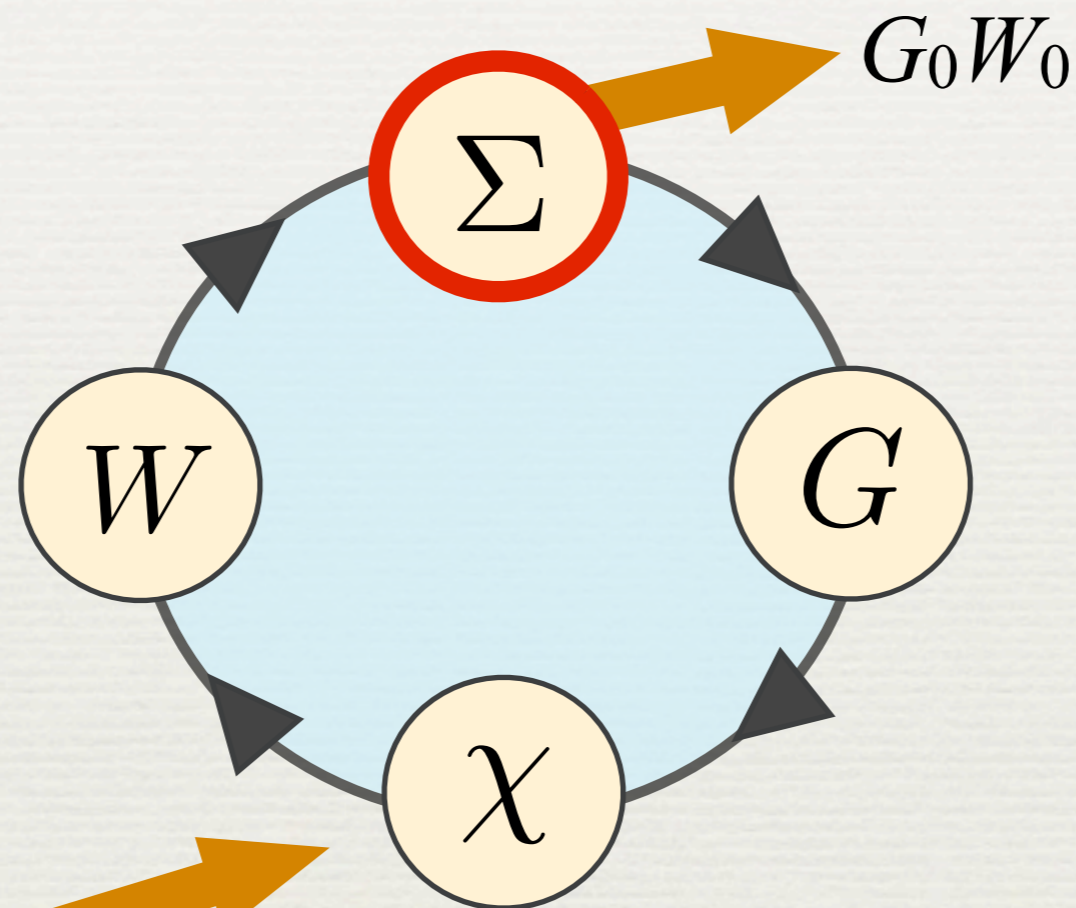
Self-Consistent *GW* in practice

DFT / HF

$\{\psi_n(r), \epsilon_n\}$

G_0^{KS}

Σ

W

G

χ
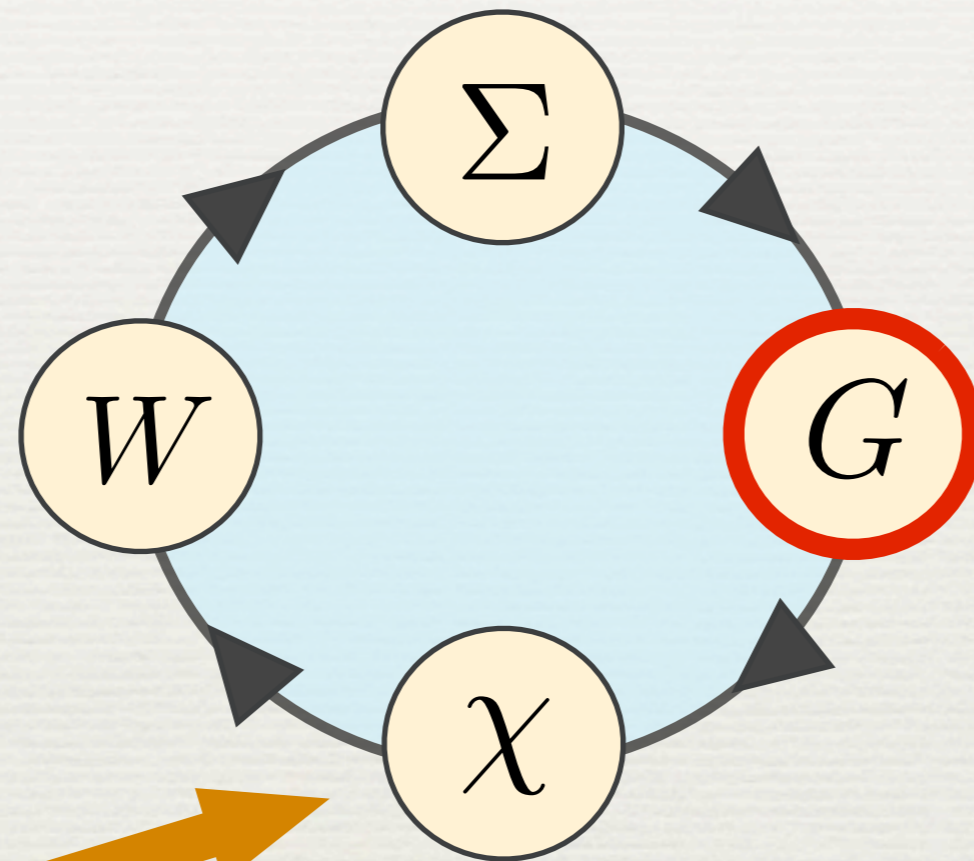
SCF loop
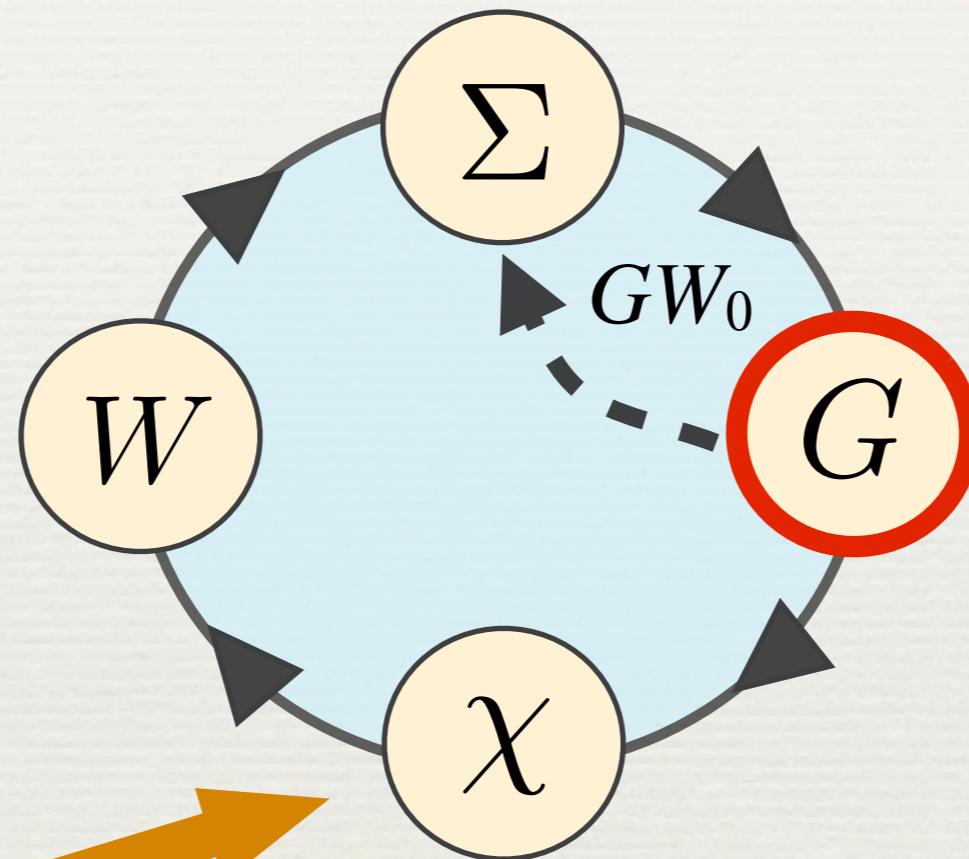
$\Gamma = 1$

$$G^{-1} = G_0^{-1} - (\Sigma - v^{xc} + \delta v_H)$$

sc-*GW* vs *G₀W₀* implementations

Input from DFT/HF

$$\{\psi_n(r), \epsilon_n\} \quad \longrightarrow \quad G_0(r, r', i\omega) = \sum_i \frac{\psi_i(r)\psi_i(r')}{i\omega - (\epsilon_i - \mu)}$$

Perturbative *GW* (*G₀W₀*):

$$\chi_0(\mathbf{r}, \mathbf{r}', i\omega) = \sum_{n,m}^{\text{states}} \frac{\psi_n^* \psi_m \psi_m^* \psi_n}{i\omega - (\epsilon_n - \epsilon_m)}$$

$$W(i\omega) = \frac{v}{1 - v\chi_0(i\omega)}$$

$$\Sigma(\omega) = \int \frac{d\omega'}{2\pi} \sum_n^{states} \frac{\psi_n \psi_n^* W(\omega - \omega')}{i\omega' - \epsilon_n + \mu}$$

Linearized **quasi-particle equation:**

$$\epsilon_i^{\text{QP}} = \epsilon_i + \langle \psi_i | \Sigma(\epsilon_i^{QP}) - V_0^{xc} | \psi_i \rangle$$

Fully self-consistent *GW:*

$$\chi(i\tau) = -iG(i\tau)G(-i\tau)$$

$$W(i\omega) = \frac{v}{1 - v\chi_0(i\omega)}$$

$$\Sigma(i\tau) = -iG(i\tau)W(-i\tau)$$

SCF loop

Dyson's eq.

$$G(i\omega)^{-1} = G_0(i\omega)^{-1} - $$
$$- [\Sigma_{GW}(i\omega) - V_0^{xc} + \delta v_H]$$

FC, P. Rinke, X. Ren, M. Scheffler and A. Rubio, PRB, 2012

Resolution of the identity

$$(ij|kl) = \iint \frac{\varphi_i(\mathbf{r})\varphi_j(\mathbf{r})\varphi_k(\mathbf{r}')\varphi_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}\, d\mathbf{r}'$$

matrix elements of the Coulomb operator (or any 2-particle operator)

very demanding to compute and store (large number of NAO pairs)

The idea: $\quad \varphi_i(\mathbf{r})\varphi_j(\mathbf{r}) \approx \sum_\mu C_{ij}^\mu P_\mu(\mathbf{r}) \quad \blacktriangleright \quad V_{\mu v} = \int \frac{P_\mu(\mathbf{r}) P_v(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}\, d\mathbf{r}'$

How to determine the expansion coefficients?

Minimize the error of the expansion

RI-SVS $\quad \delta\rho_{ij}(\mathbf{r}) = \sum_\mu C_{ij}^\mu P_\mu(\mathbf{r}) - \varphi_i(\mathbf{r})\varphi_j(\mathbf{r})$

RI-V $\quad \delta I_{ij,kl} = (\tilde{\rho}_{ij}|\tilde{\rho}_{kl}) - (\rho_{ij}|\rho_{kl})$

Representation of the Green's function

Numerical FT avoided

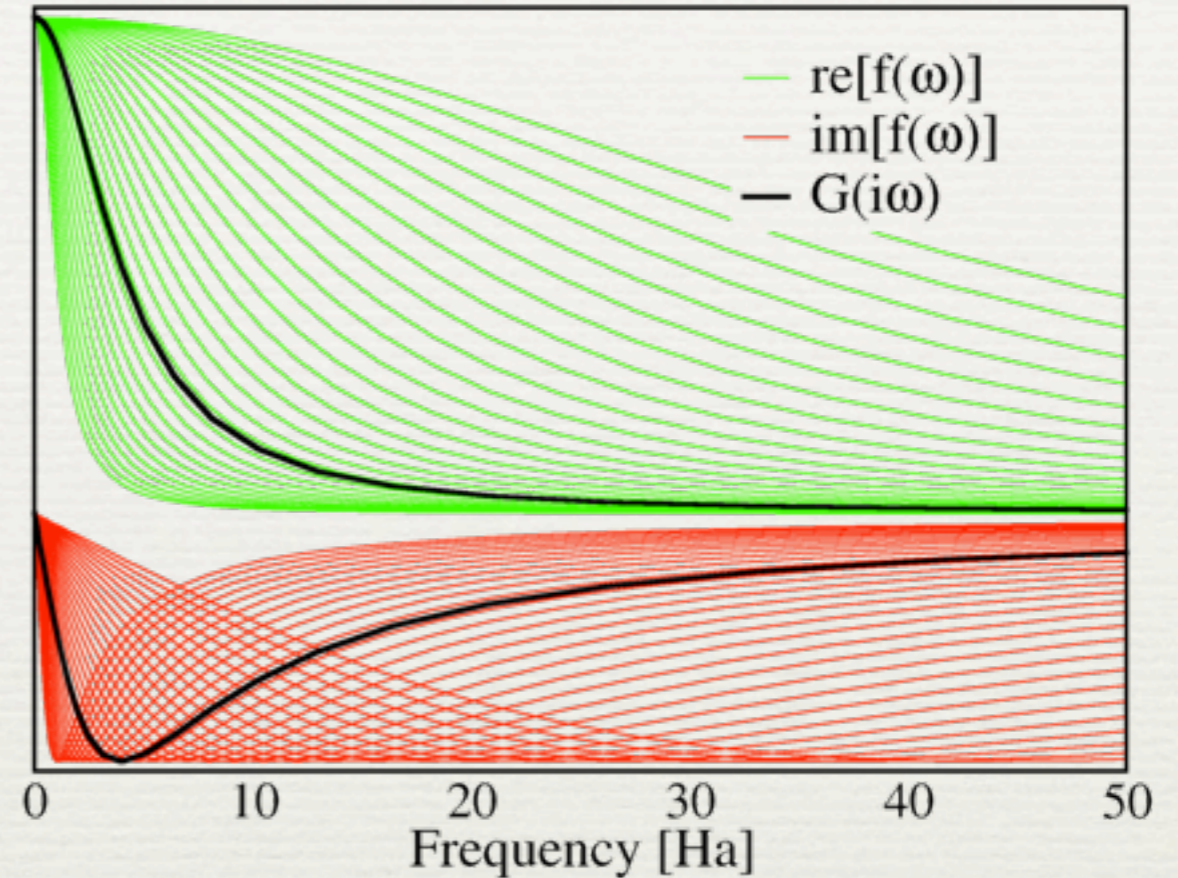**A basis for the frequency dependence of G**

$$G(i\omega) = \sum_{n=1}^{N_{poles}} \alpha_n f_n(i\omega)$$

$$\{f_n(i\omega)\} \qquad f_n(i\omega) = \frac{1}{b_n + i\omega}$$

The Fourier transform can be done analytically!
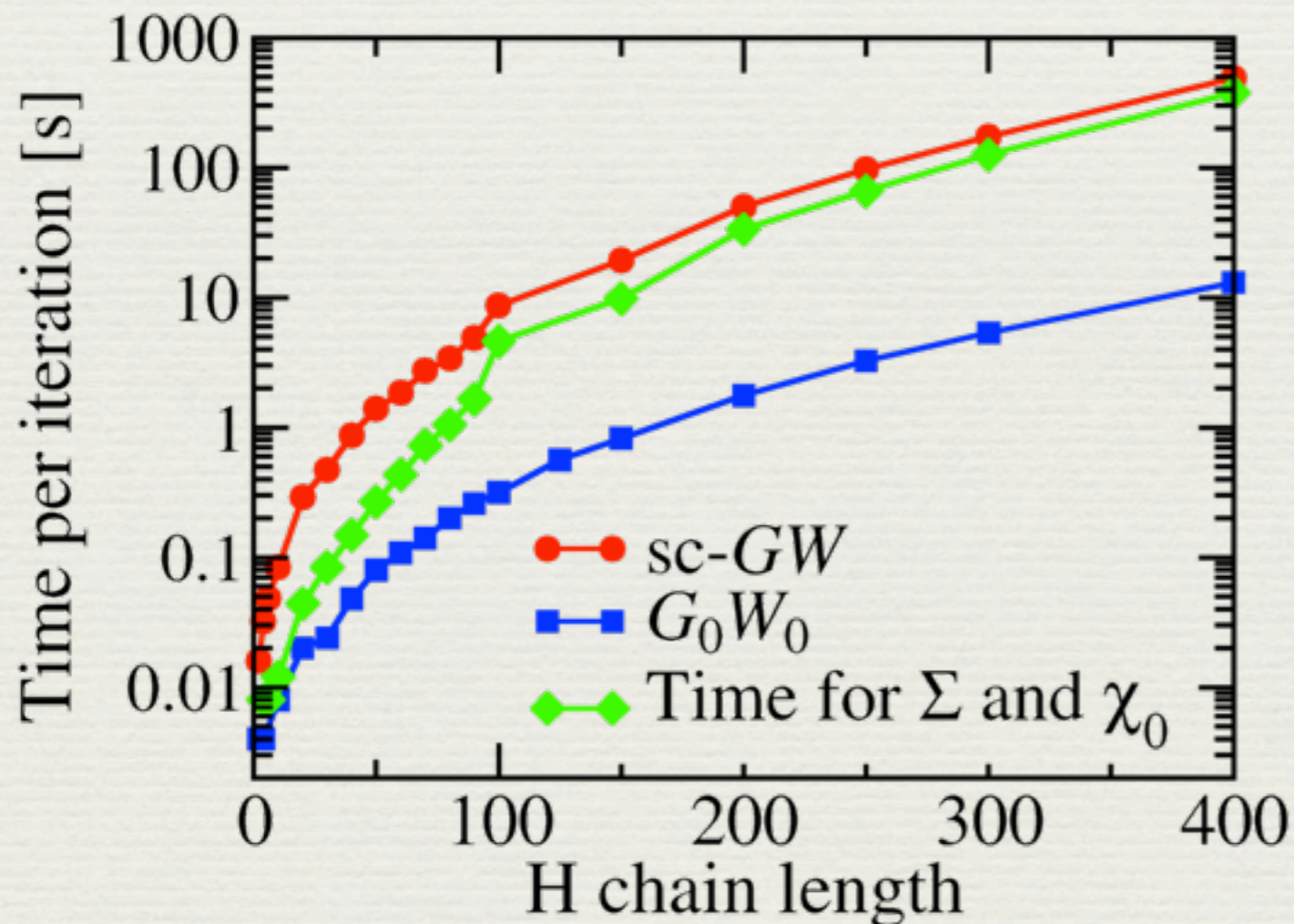
$$N_{poles} \sim 50$$

$$N_\omega < 100$$

Representation of the Green's function

Numerical FT avoided

A basis for the frequency dependence of G

$$G(i\omega) = \sum_{n=1}^{N_{poles}} \alpha_n f_n(i\omega)$$

$$\{f_n(i\omega)\} \qquad f_n(i\omega) = \frac{1}{b_n + i\omega}$$

The Fourier transform can be done analytically!

$$N_{poles} \sim 50$$

$$N_\omega < 100$$

Outline

- The *GW* approximation (why self-consistency?)

- Implementation of sc-*GW* in FHI-aims

- **Application to atoms, molecules and molecular interfaces**

Spectral function from *scGW*

Spectral function: $\quad A(\omega) = -\dfrac{1}{\pi} \displaystyle\int \mathbf{dr} \lim_{\mathbf{r'} \to \mathbf{r}} ImG(\mathbf{r}, \mathbf{r'}, \omega)$
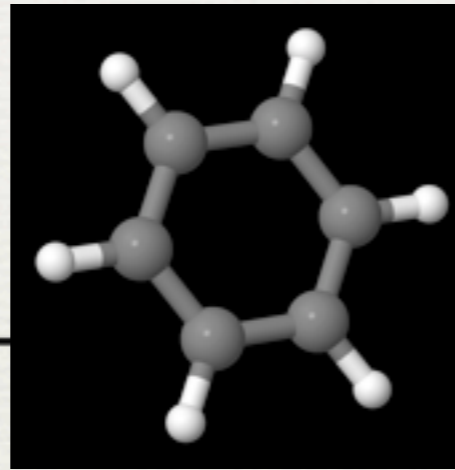
Benzene
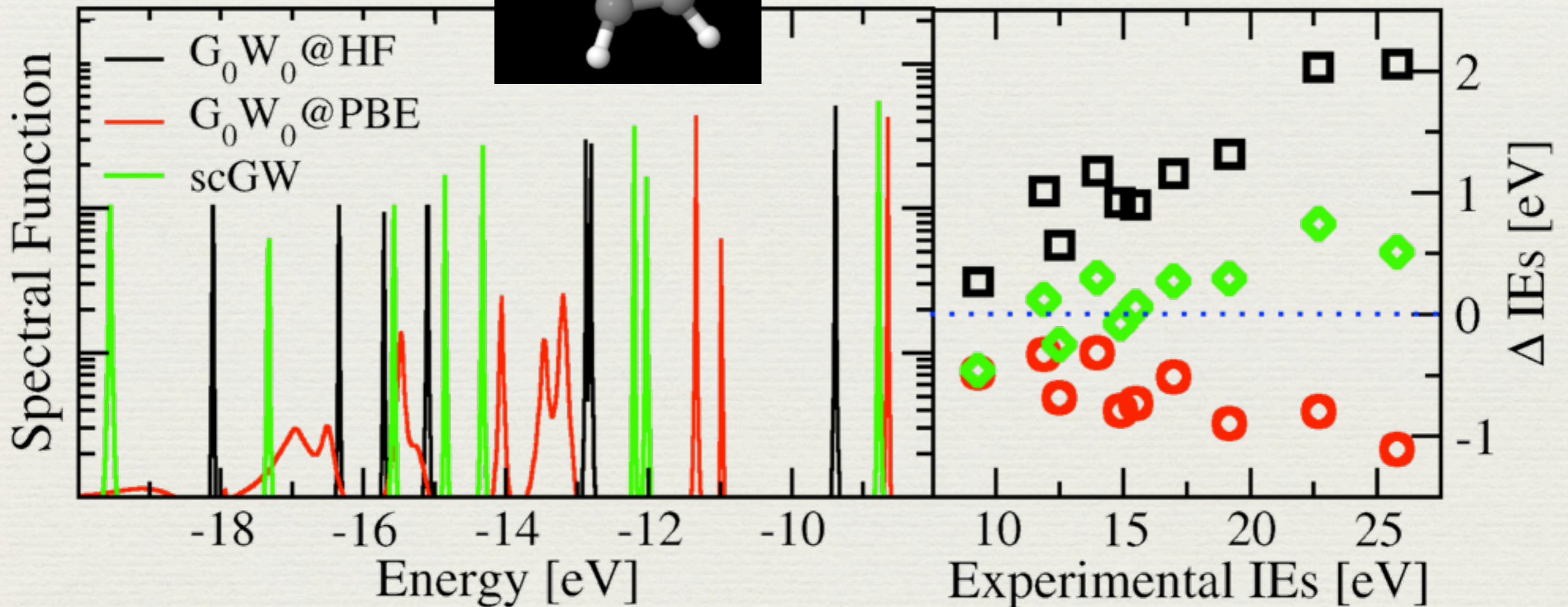
Comparison of several self-consistent approaches
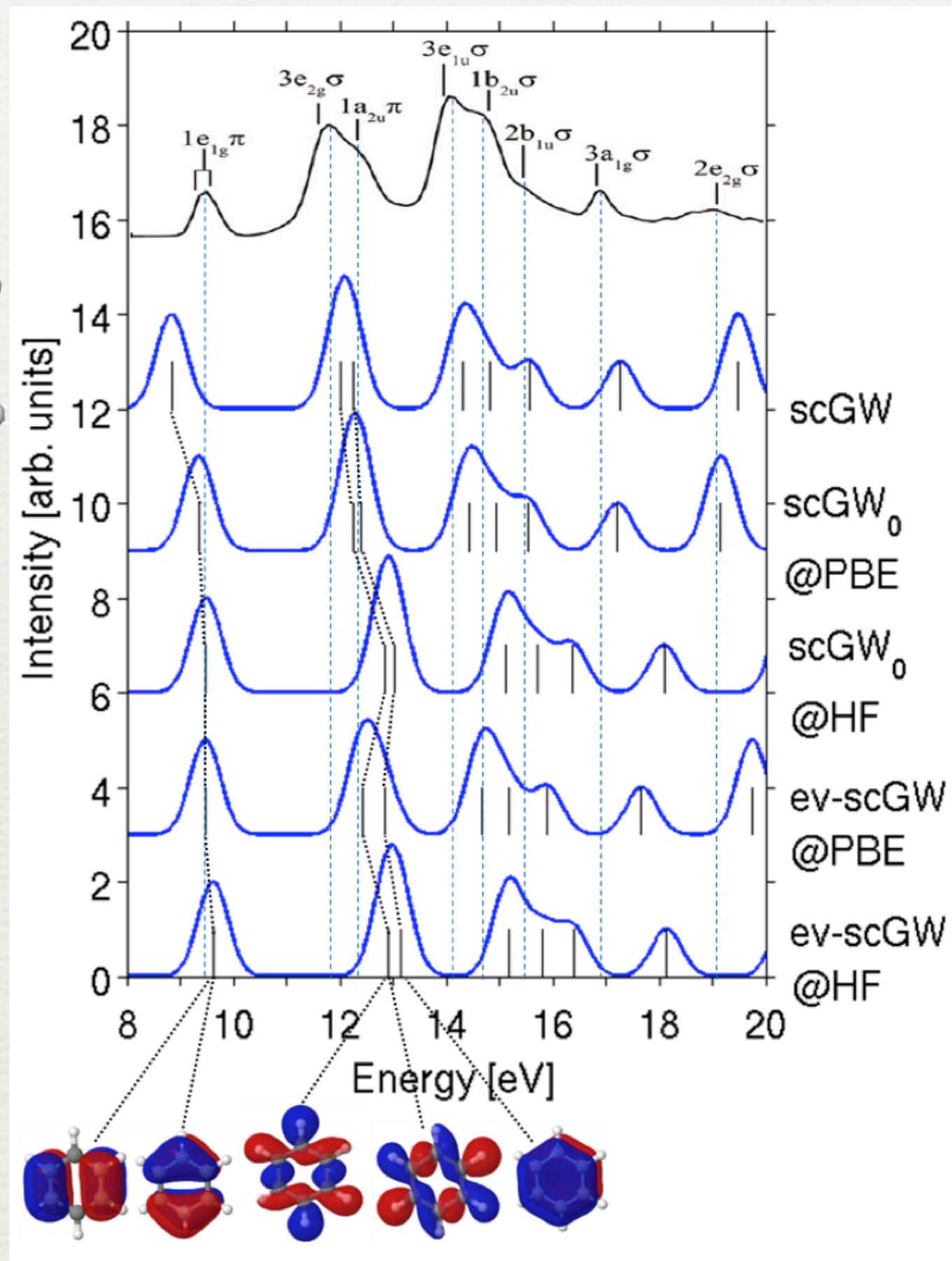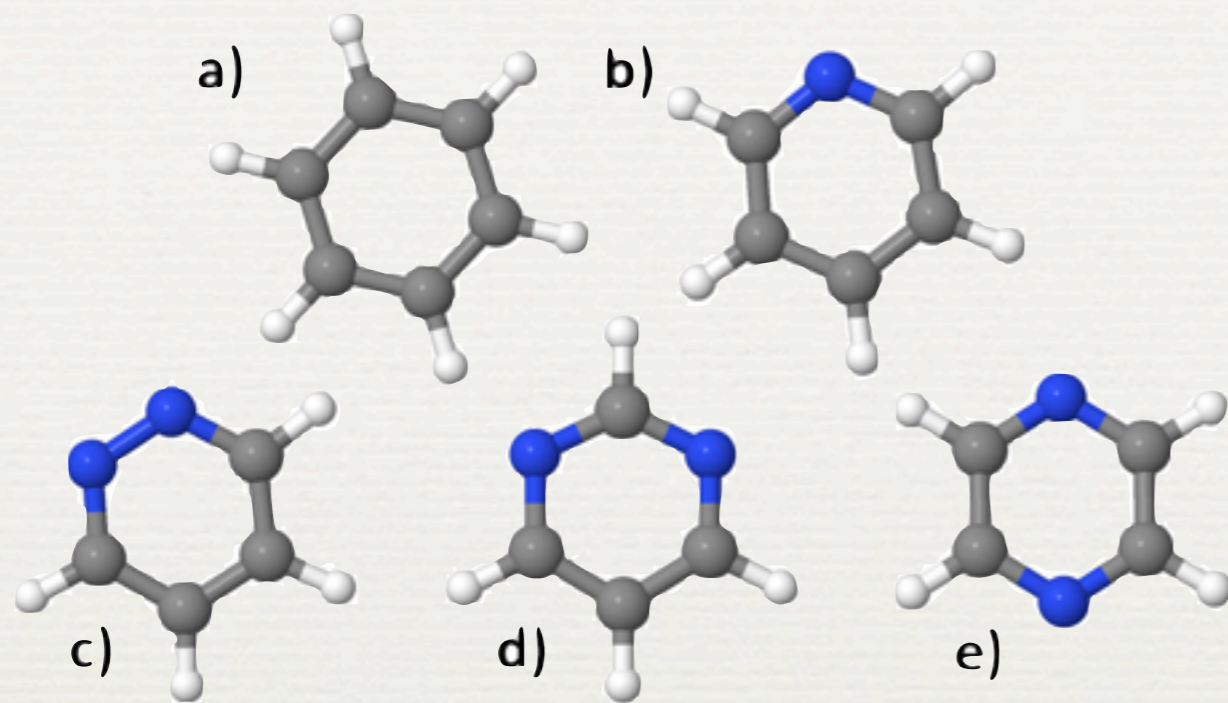
Comparison of several self-consistent approaches
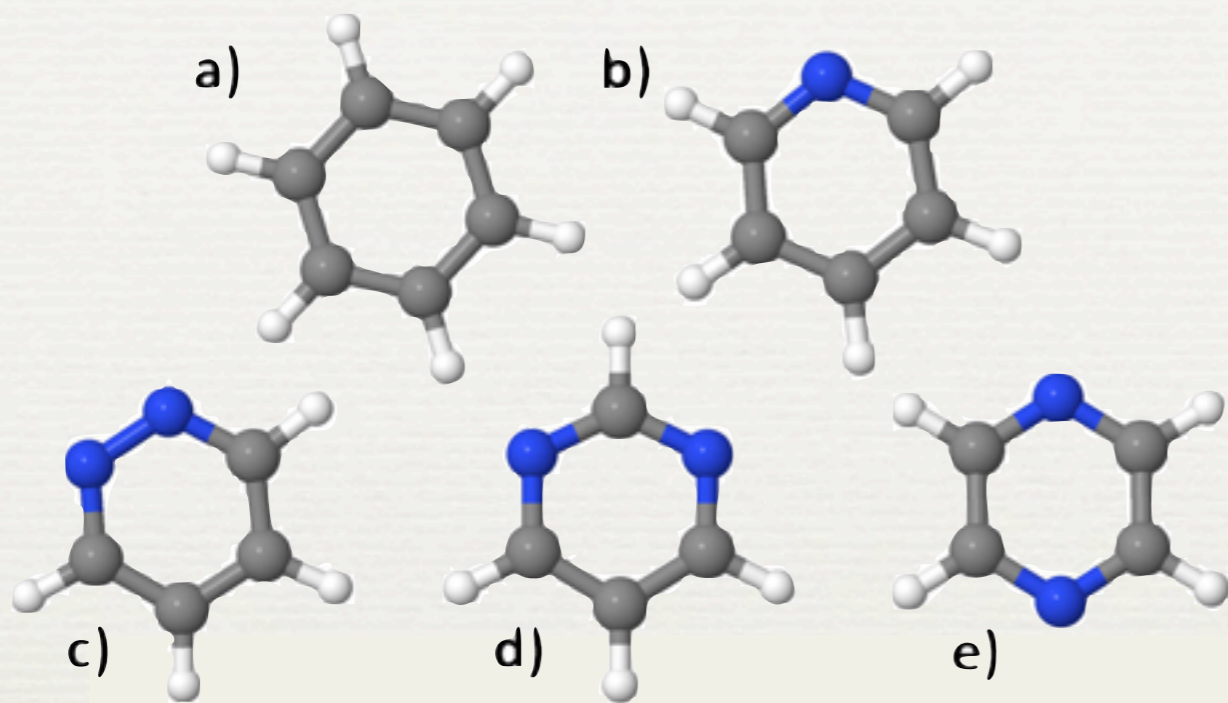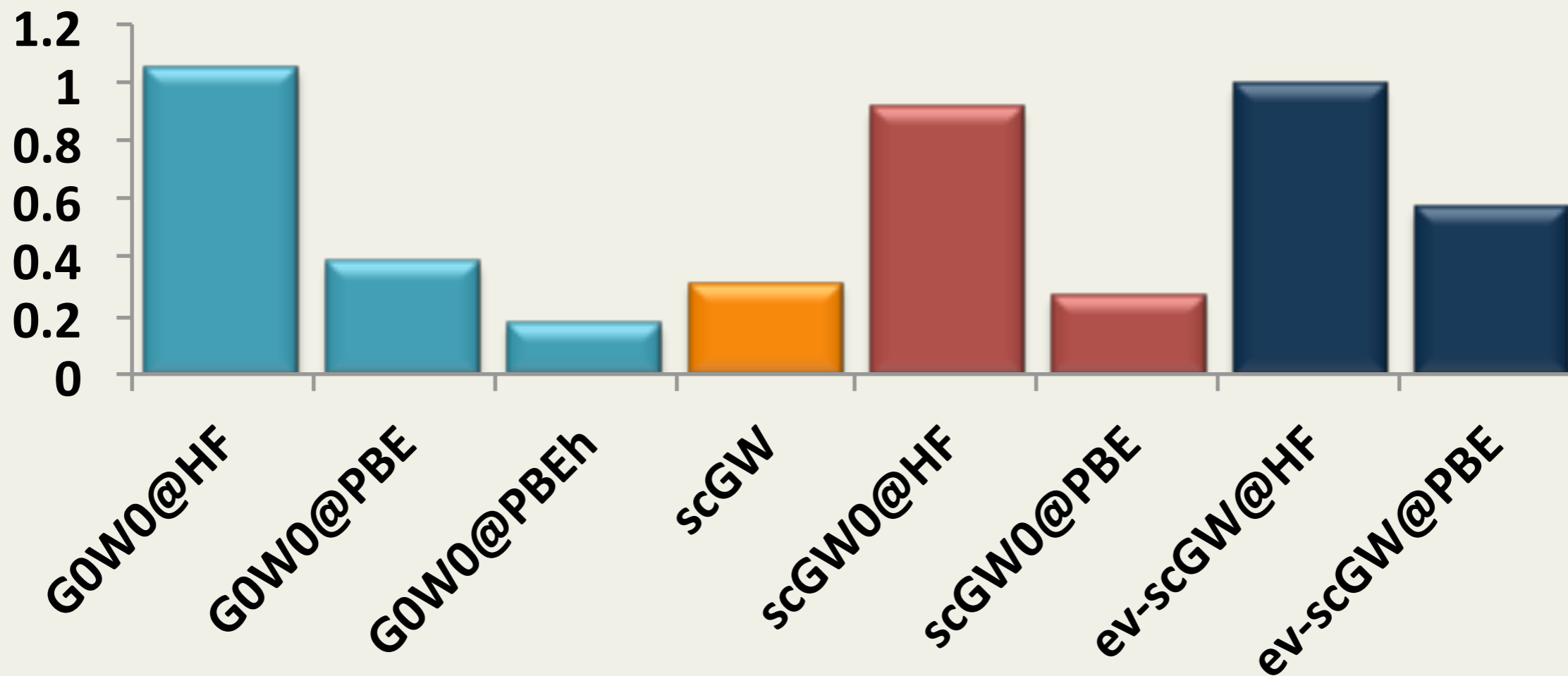
Ground-state properties from sc-*GW*

$$G^{-1} = G_0^{-1} - \Sigma \quad \text{from the self-consistent Green function}$$

Example of quantities we can calculate:

Total energy $\quad E_{\mathrm{GM}} = -i \int \frac{d\omega}{2\pi} Tr\left\{ [\omega + h_0]\, G(\omega) \right\}$

→ **structural prop., binding energies, vibrations**

Density matrix $\quad n(\mathbf{r}, \mathbf{r}') = -2iG(\mathbf{r}, \mathbf{r}', \tau = 0^-)$

→ **natural orbitals, natural occupation**

Density $\quad n(\mathbf{r}) = -2iG(\mathbf{r}, \mathbf{r}, \tau = 0^-)$

→ **dipole moment**

Total energy of atoms

The Galitskii-Migdal formula: $E_{\mathrm{GM}} = -i \int \frac{d\omega}{2\pi} Tr\left\{[\omega + h_0] G(\omega)\right\}$
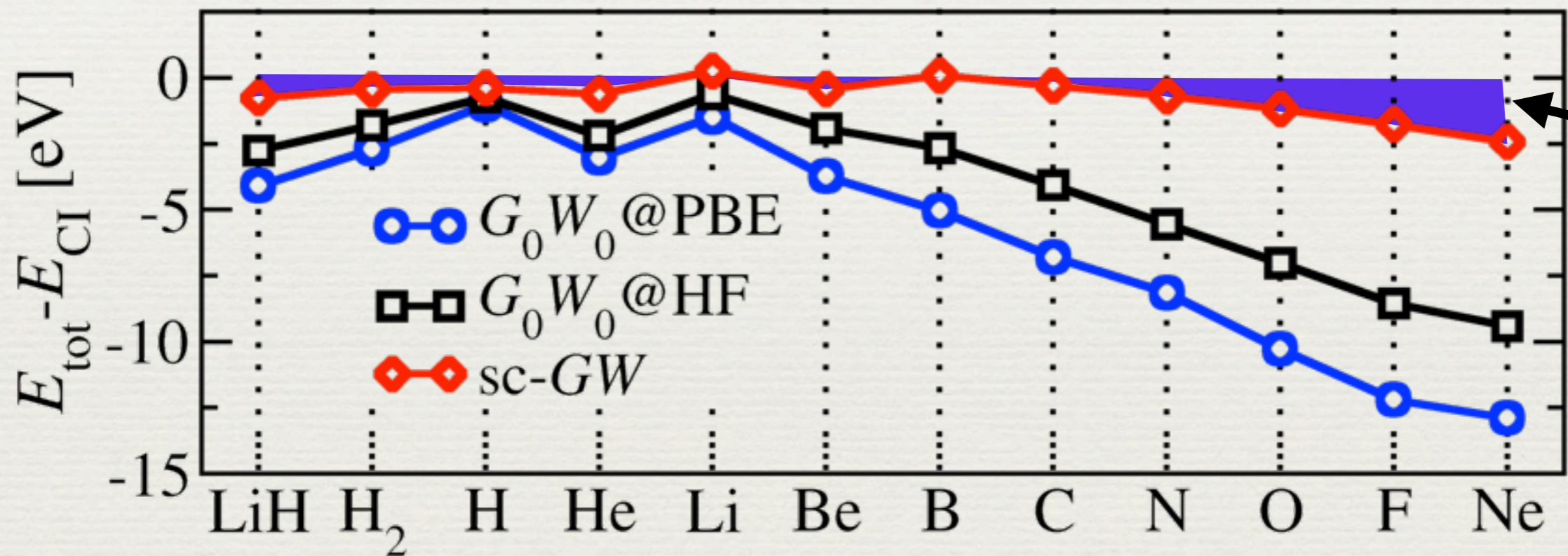
vertex Γ

full configuration interaction from:
Chakravorty et *al*., Phys. Rev. A 47, 3649 (1993).

Density from sc-*GW*: the CO dimer

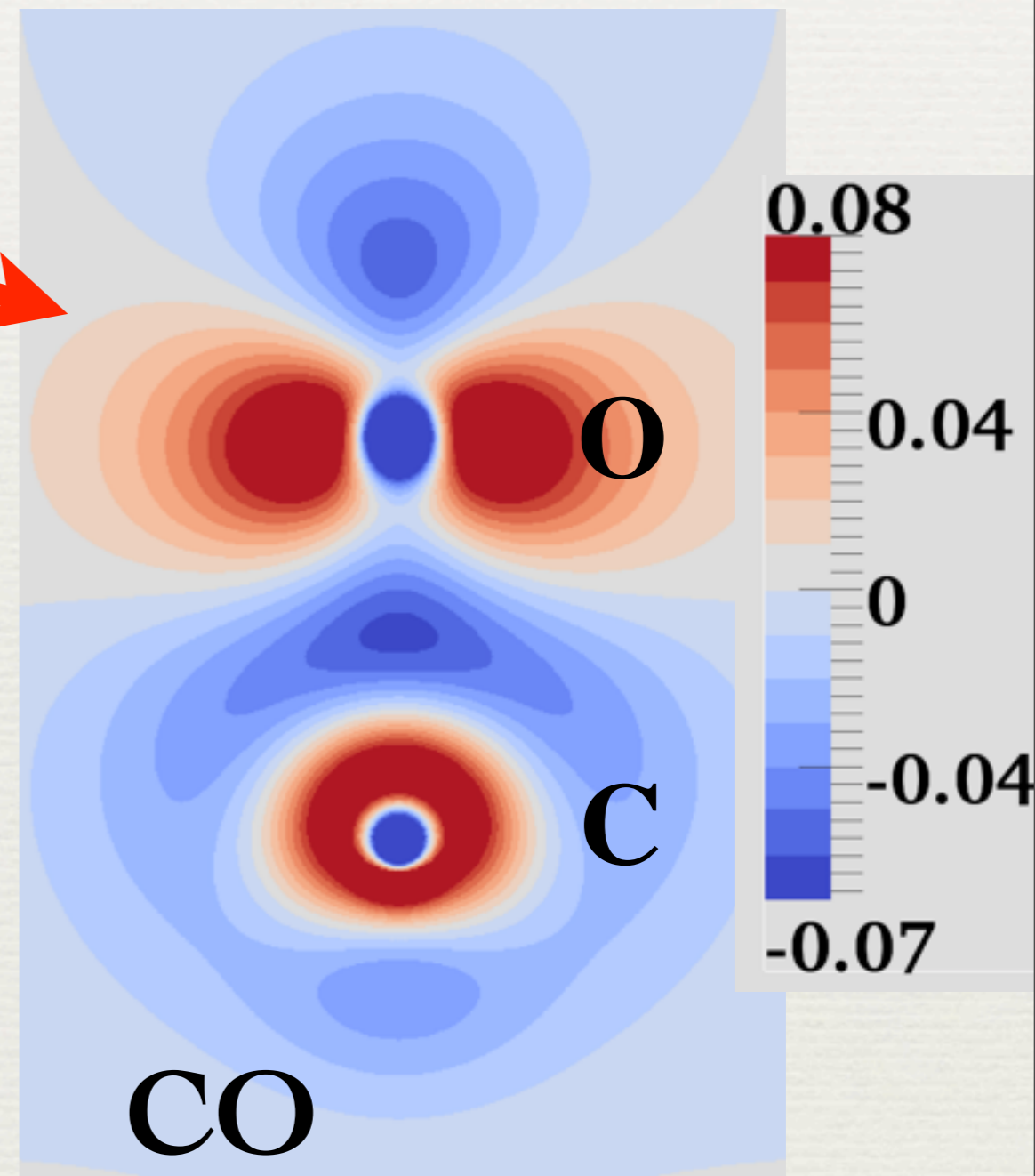$$\rho(\mathbf{r}) = -2iG(\mathbf{r}, \mathbf{r}, \tau = 0^-)$$

$$\rho(scGW) - \rho(HF)$$

Changes in the density reflect the effect of *GW* correlation

Improvement in the dipole moment:

Debye	Exp.	sc-*GW*	HF
μ	0.11	0.07	-0.13

sc-*GW* provides a new electronic structure

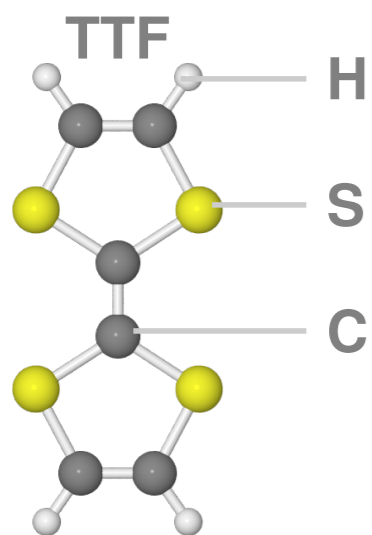# sc-*GW* for charge transfer: donor-acceptor compounds

TTF

H
S
C

TCNQ

N
H
C

PBE

0.24 e
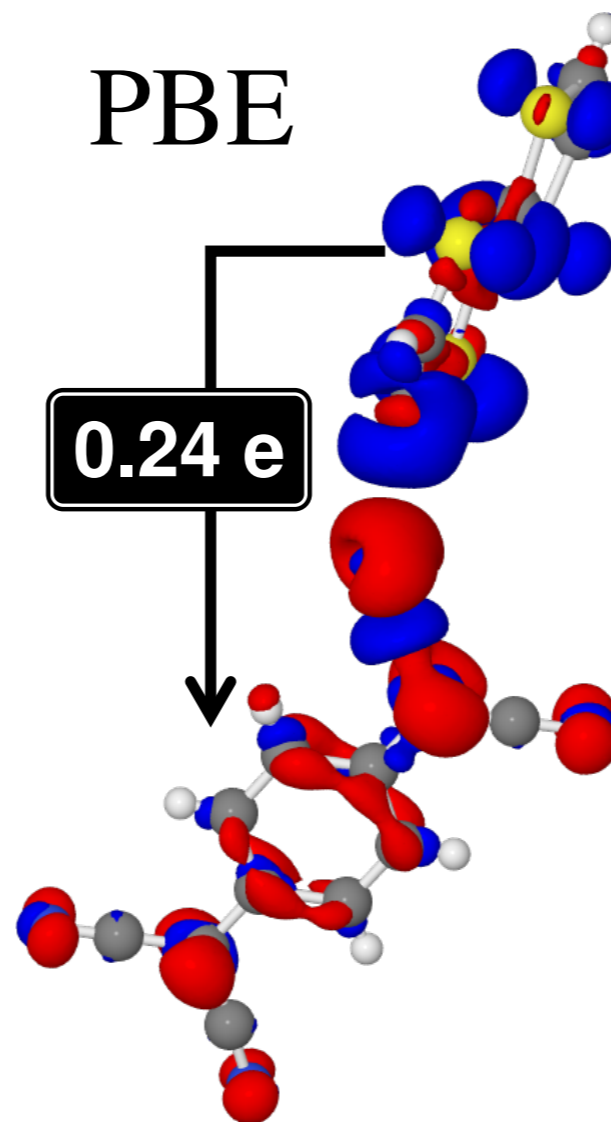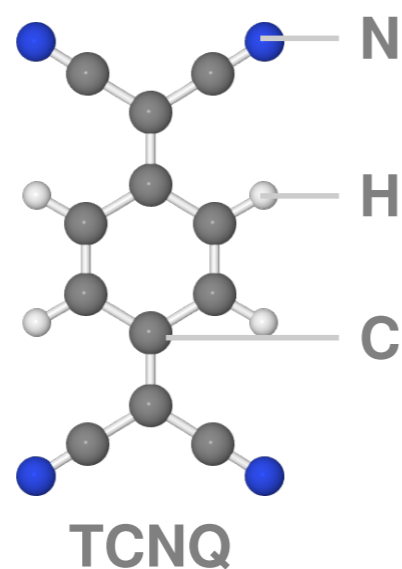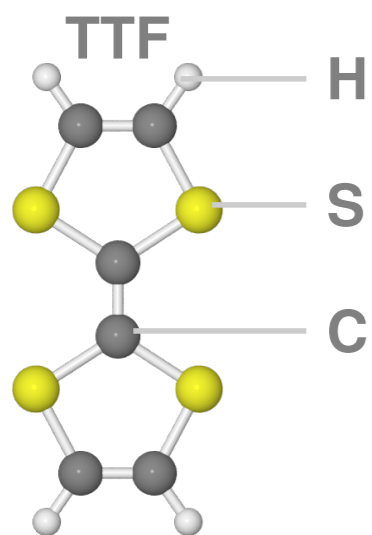
empty

occ.

empty

occ.

Viktor Atalla et al., submitted

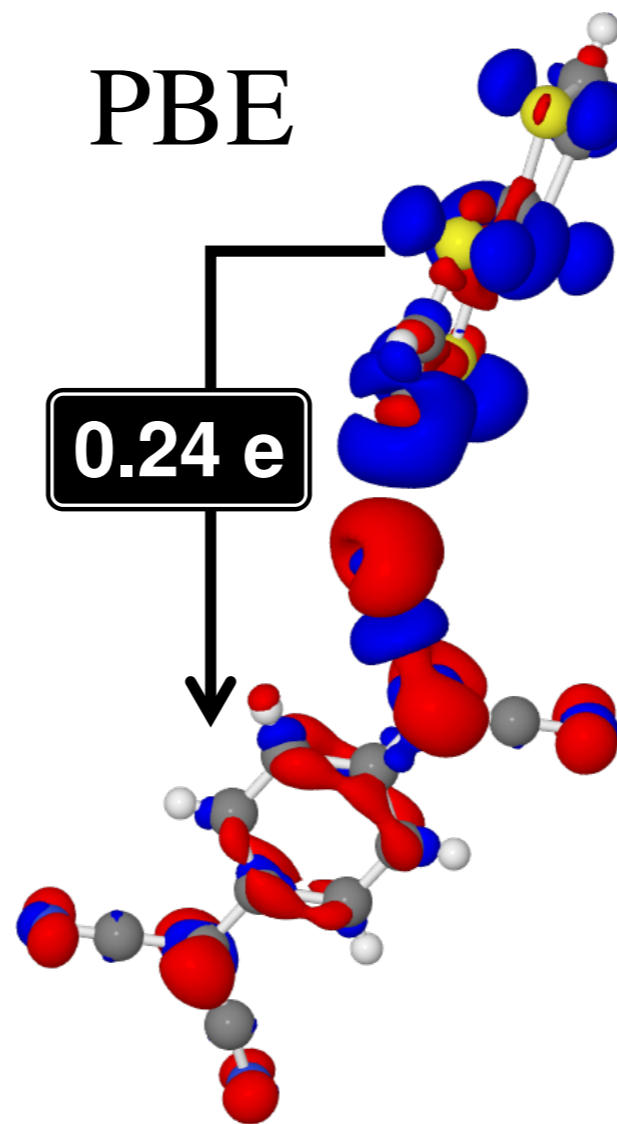# sc-*GW* for charge transfer: donor-acceptor compounds

TTF

H
S
C

TCNQ

N
H
C

PBE

0.24 e

sc-*GW*

empty

empty

occ.

occ.
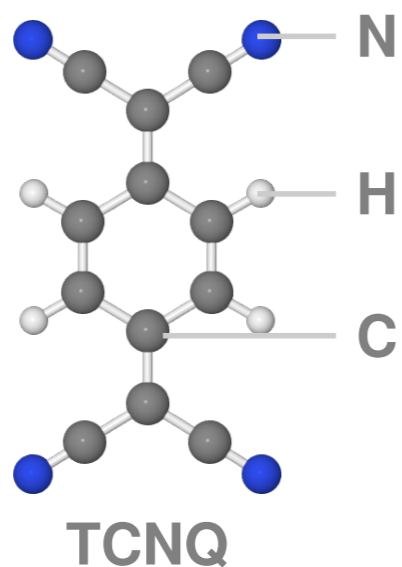
Small charge rearrangement in sc-*GW*!

Viktor Atalla et al., submitted

Summary

- **Implementation based on NAO and RI**

- **Poles expansion of G, for an efficient and accurate evaluation of Fourier integrals**

- **sc-*GW* is independent of the starting point and incorporate many-body effects in the ground-state**

- **Accurate excitation spectrum for molecules**

- **A promising framework for describing change-transfer at (molecular) interfaces**
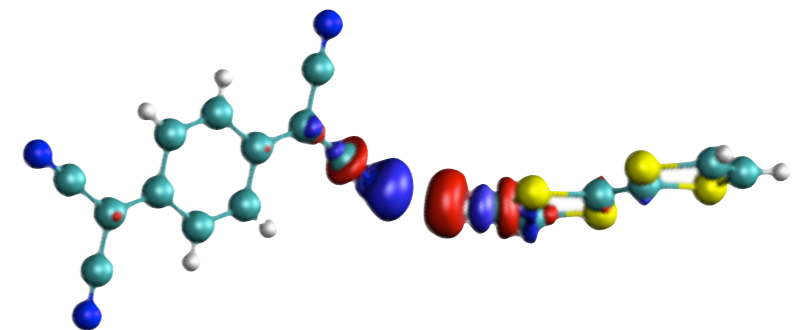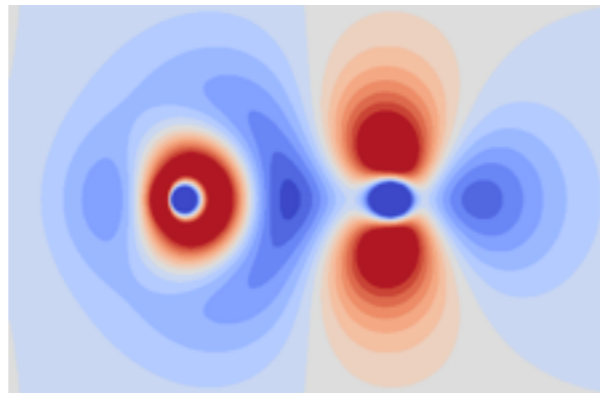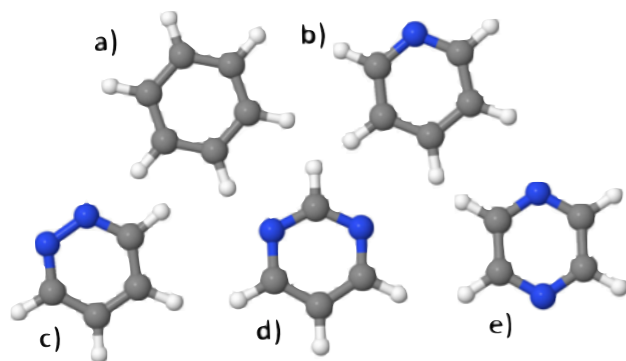
Acknowledgements

Fritz-Haber-Institute, Berlin
    Patrick Rinke
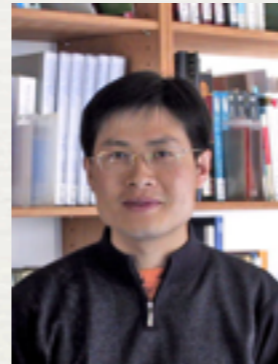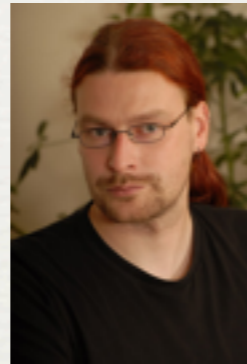   Xinguo Ren
    Angel Rubio
    Matthias Scheffler
    Viktor Atalla

University of Texas Austin
    Noa Marom

Thank you!