Excited State Calculations with GW and GW+BSE

FHI-aims Tutorial Series 2021

Dorothea Golze

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Technische Universität Dresden

FHI-aims
The ab initio materials simulation package

Content

1. Theoretical photoemission & absorption spectroscopy
2. Limits of DFT-based methods
3. GW for photoemission
4. GW+BSE for absorption
5. Summary of functionality

What this lecture is about

Bit of GW theory

- basic idea and formalism
- for more: "DFT and beyond" summer schools (Feb. 2022 in Brazil)

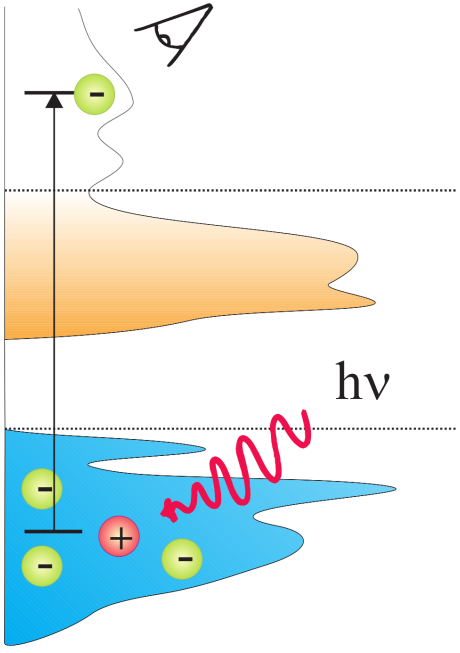
Mostly practicalities of GW and GW+BSE

- how to obtain well-converged GW results
- functionality in FHI-aims

Theoretical photoemission & absorption spectroscopy

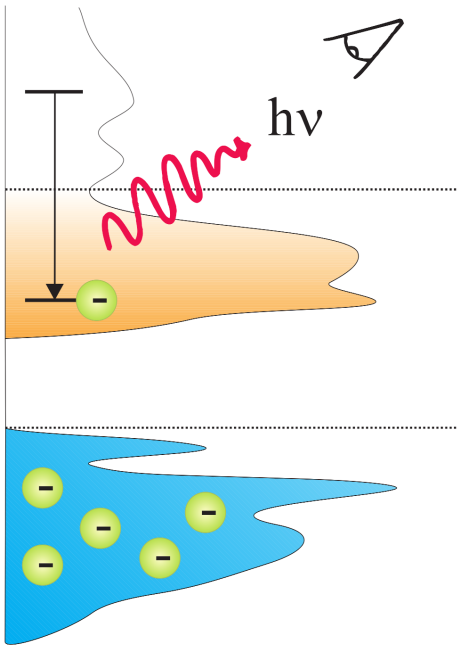
Spectroscopy types discussed here

Photoemission



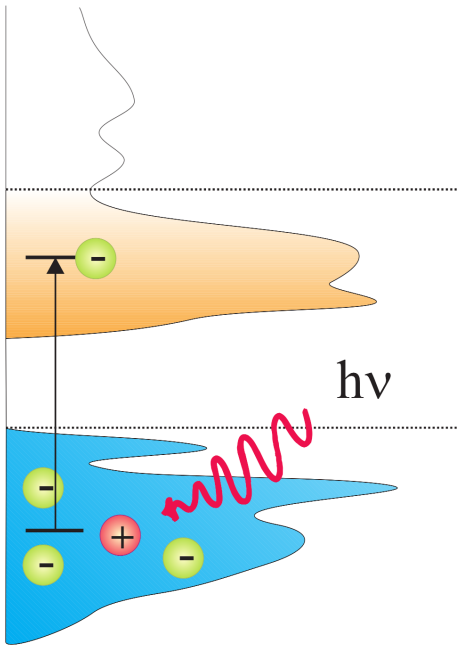
GW

Inverse photoemission



GW

Absorption



BSE
TDDFT

Photoemission spectroscopy

Ionization potential IP

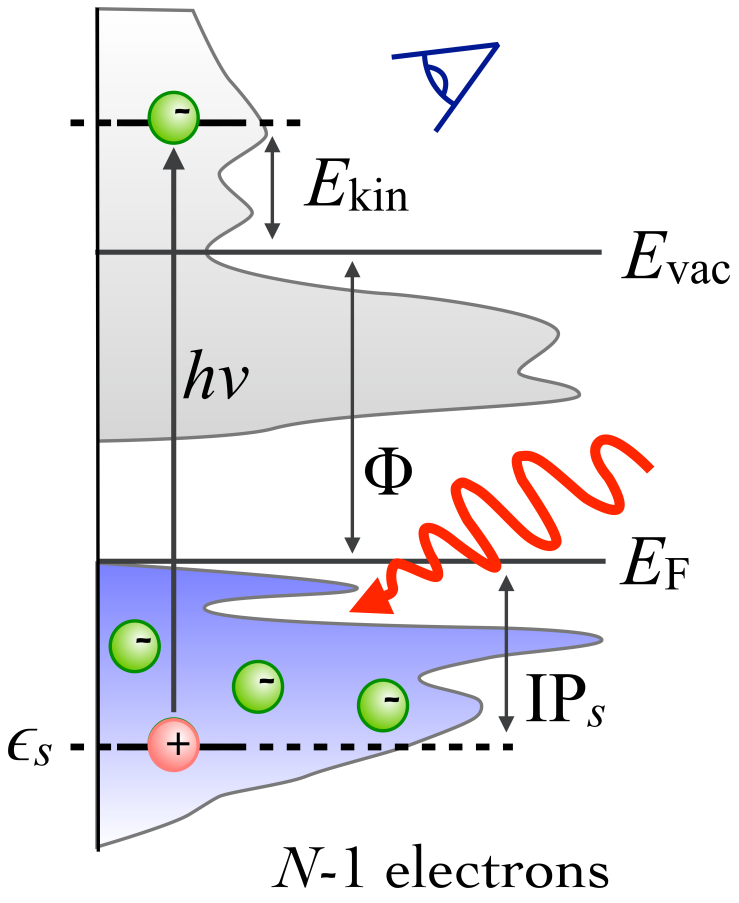
$$\mathrm{IP}_s = -\epsilon_s = h\nu - E_{\mathrm{kin}} - \Phi$$

Electron removal energies ϵ_s

$$\epsilon_s = E(N) - E(N-1, s)$$

Electron removal amplitude

$$\psi_s(\mathbf{r}) = \langle N-1, s|\hat{\psi}(\mathbf{r})|N\rangle$$



$|N\rangle$... manybody ground state

Inverse photoemission spectroscopy

Electron affinity EA

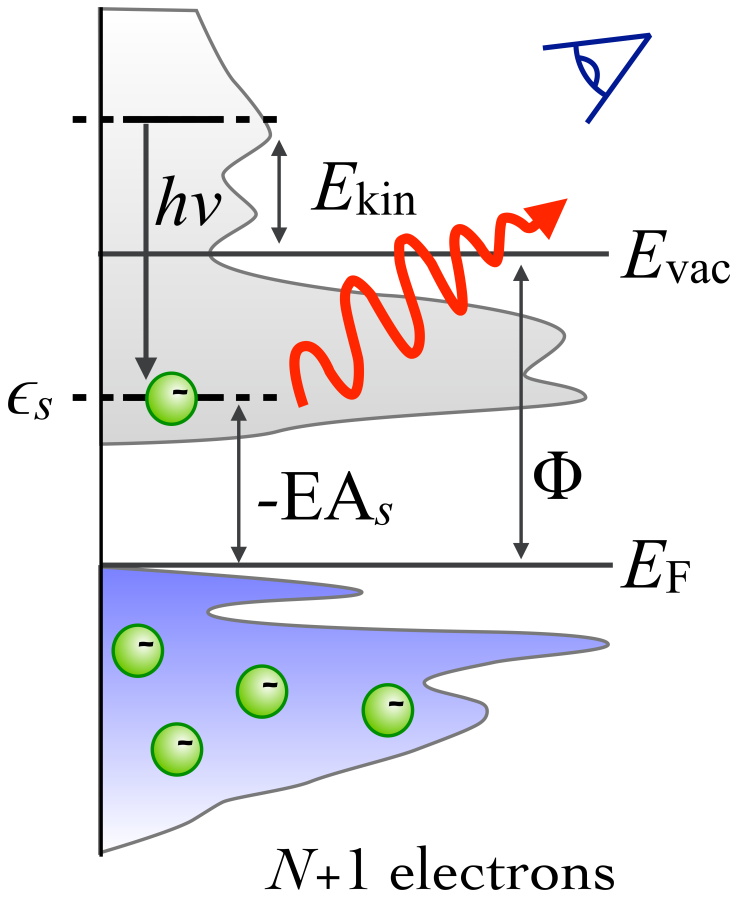
$$-\mathrm{EA}_s = \epsilon_s = E_{\mathrm{kin}} - h\nu + \Phi$$

Electron addition energies ϵ_s

$$\epsilon_s = E(N+1, s) - E(N)$$

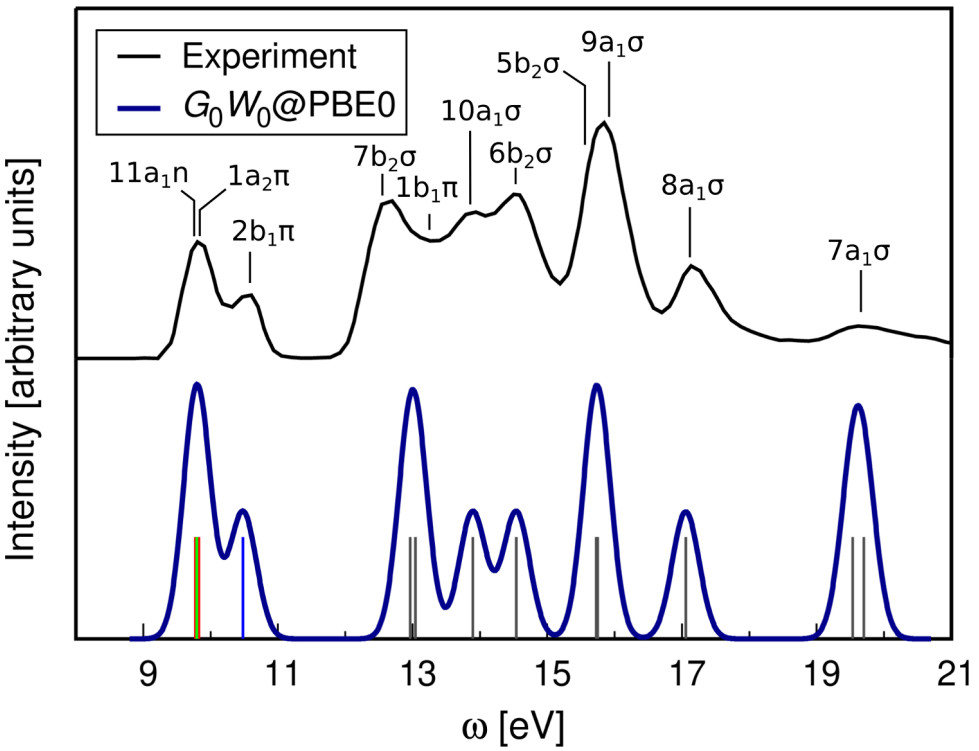
Electron addition amplitude

$$\psi_s(\mathbf{r}) = \langle N+1, s | \hat{\psi}^\dagger(\mathbf{r}) | N \rangle$$



Definition of EA: energy to detach an electron from negatively charged species

Photoemission experiment: Molecules



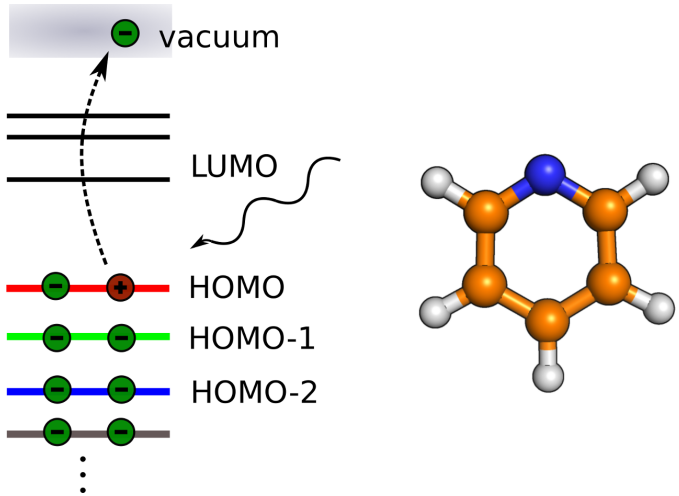


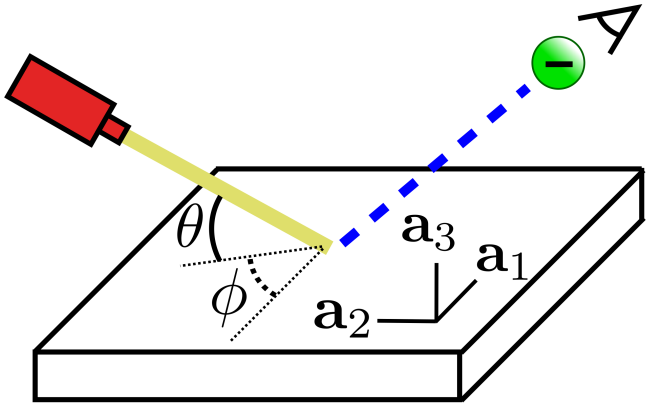
Fig. from GW *compendium*, Front. Chem., 7 (2019), 377

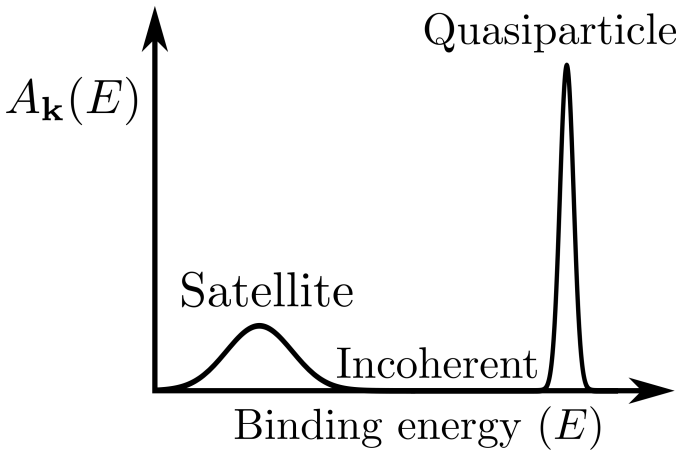
Properties

- Ionization potentials/ionization spectra
- electron affinity
- fundamental HOMO-LUMO gap: $\Delta_{\text{fgap}} = \text{IP}_{\text{HOMO}} - \text{EA}_{\text{LUMO}}$

Photoemission experiment: Solids

▷ **A**ngle **r**esolved **p**hotoemission **s**pectroscopy (ARPES)





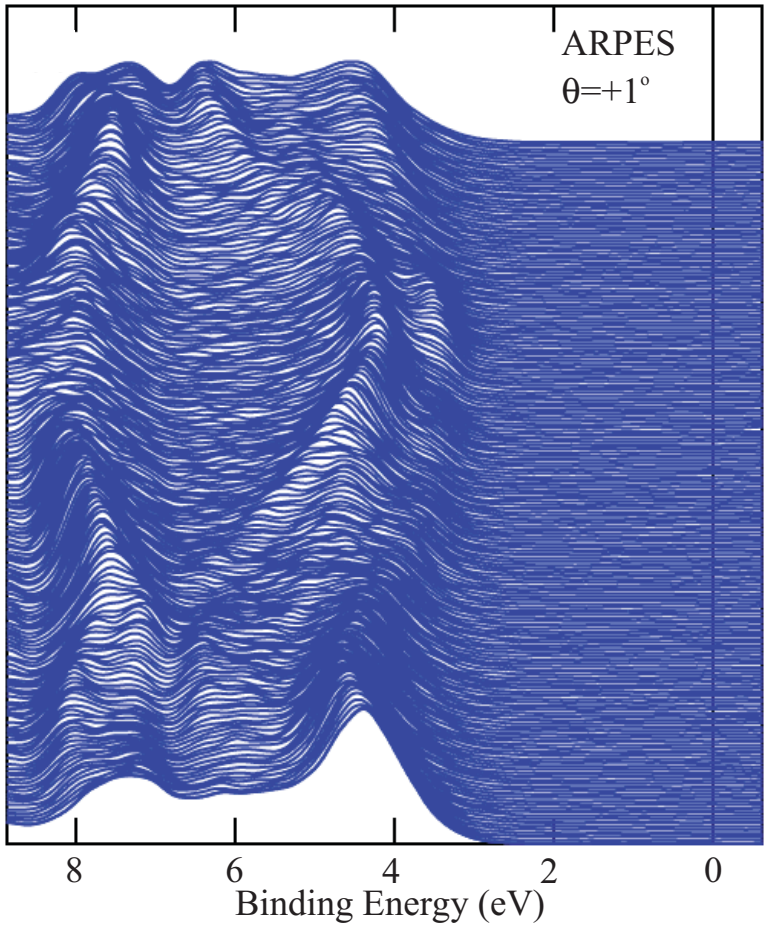
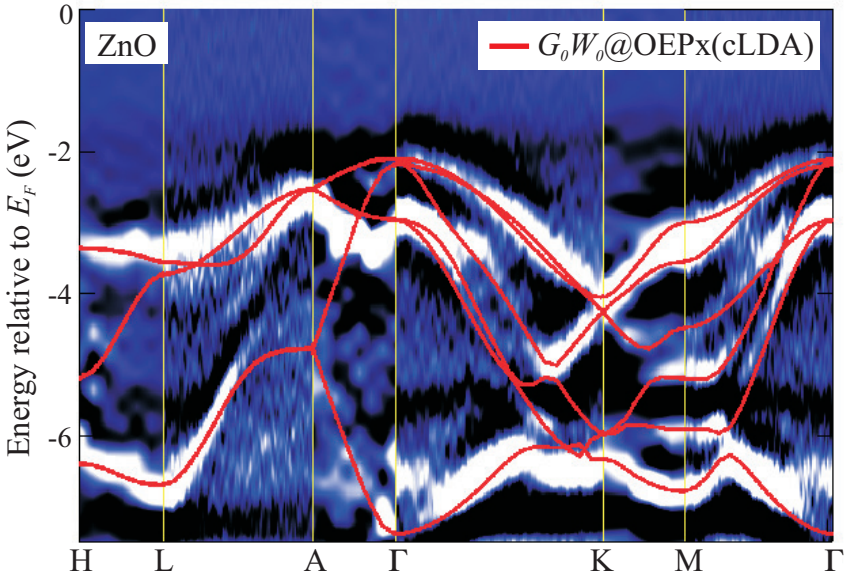


Fig.: ARPES of ZnO, source: PhD thesis of Masaki Kobayashi

Photoemission experiment: Solids

Example: ZnO band structure



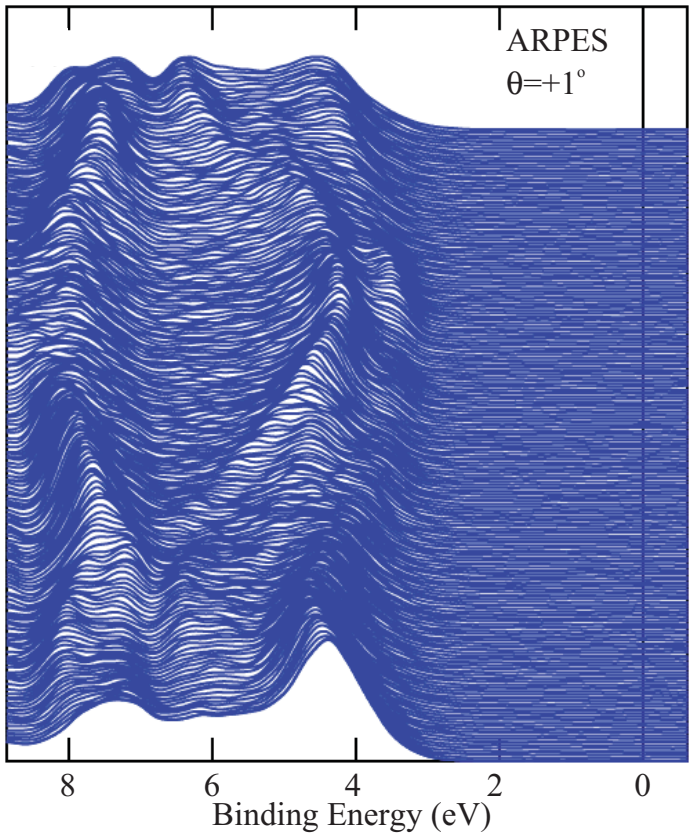
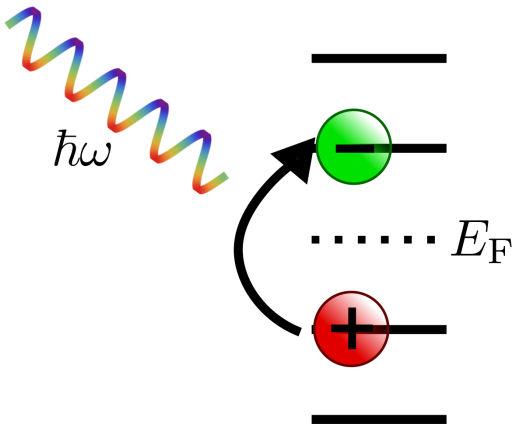


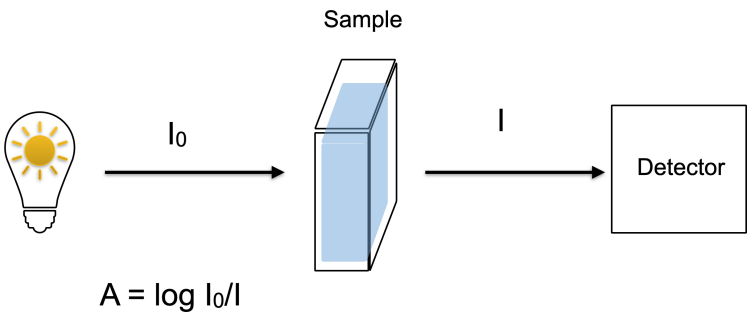
Fig.: Semicond. Sci. Technol., 26 (2011), 014037

Properties

- band gaps
- band structures & density of states
- band parameters & life times

Absorption spectroscopy





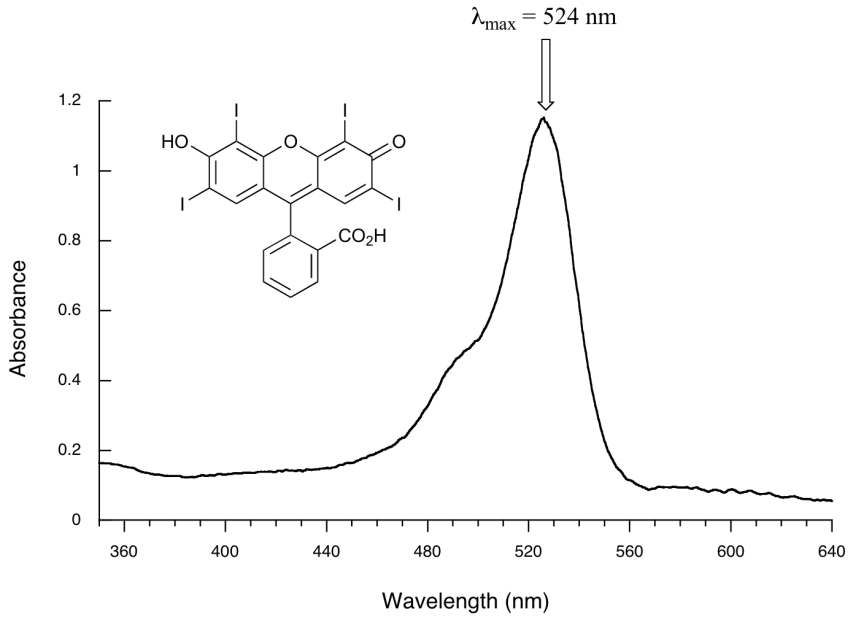


Fig. https://courses.lumenlearning.com/suny-mcc-organicchemistry/chapter/interpreting-uv-spectra/

Properties

- UV/Vis or X-ray absorption spectra
- optical gaps

Limits of DFT-based methods

IPs and EAs from Kohn-Sham DFT eigenvalues

- ionization potentials:
  $\mathrm{IP}_n = -\epsilon_n^{\mathrm{KS}}$
- deviation from experiment:
  - valence: 3 eV
  - deep core: 30 eV
- too small gaps

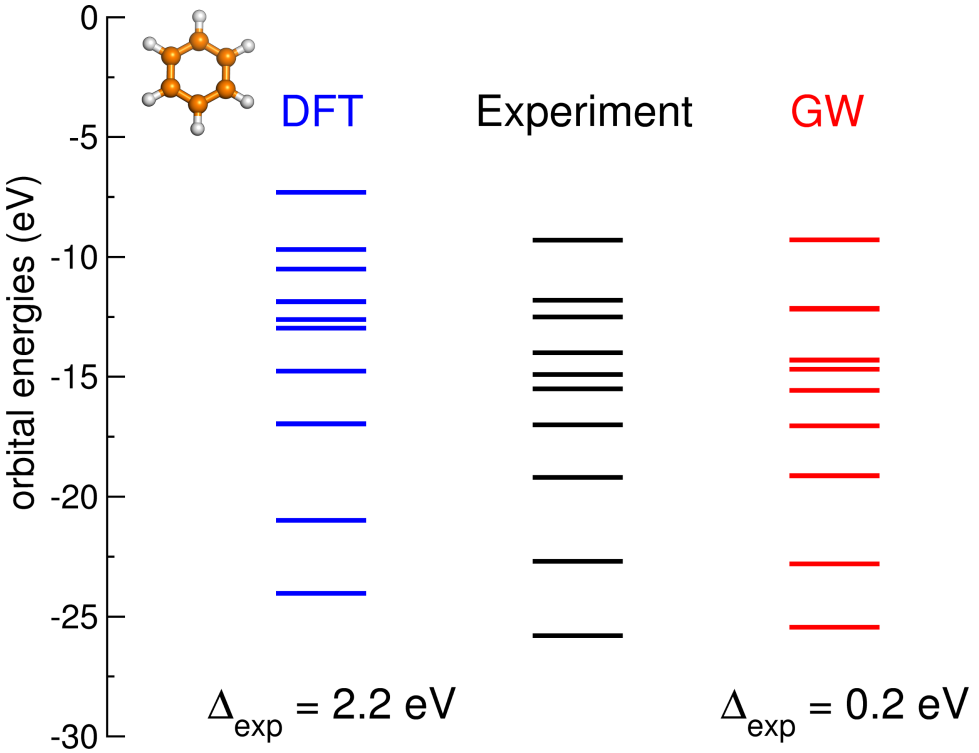
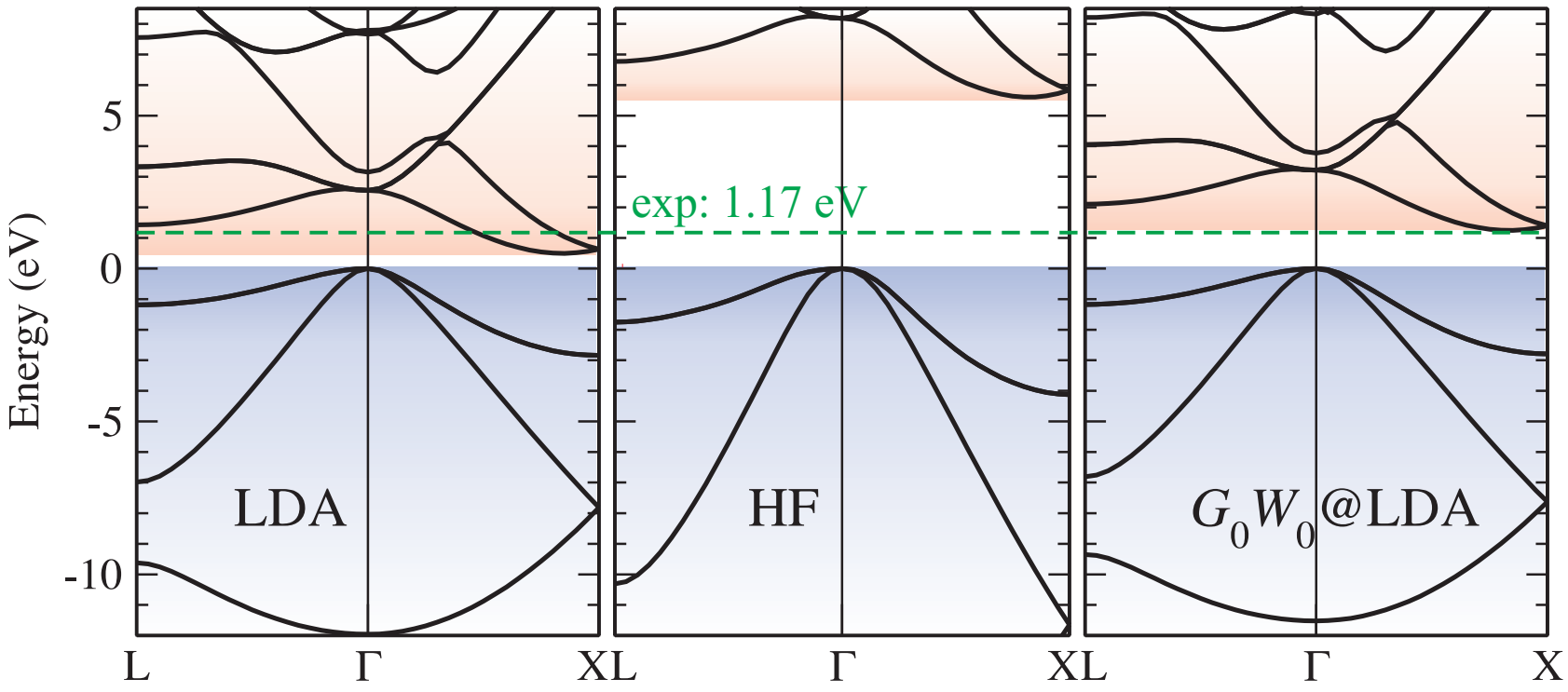


Fig. Occupied states and average deviation from experiment Δ_{exp}. Calculations performed with PBE0.

DFT/HF band structures

Example: silicon band structure



DFT bandgaps

Example: Band gaps of semiconductors and insulators

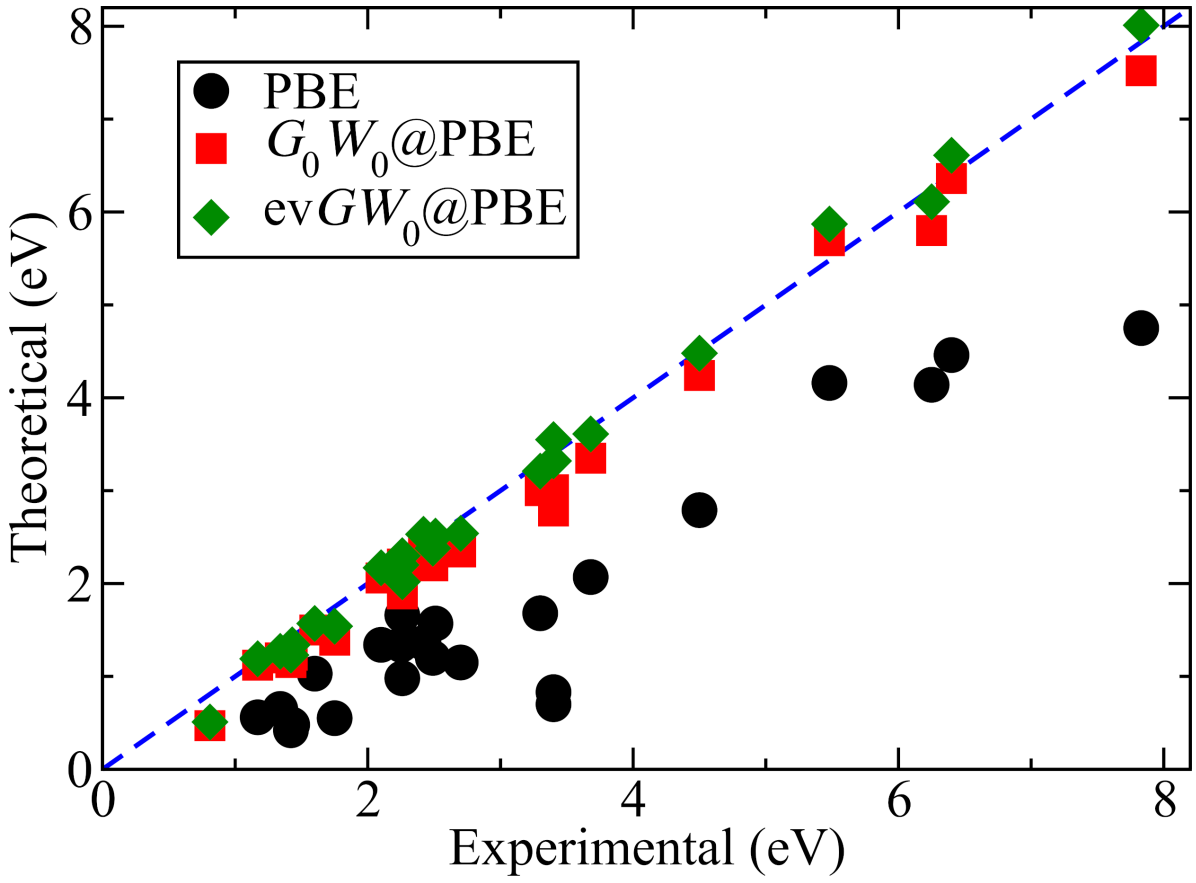


Fig.: PRB, 93 (2016), 115203

Delta Self-consistent Field (ΔSCF)

▷ better approach for band gaps, IP_{HOMO}, EA than DFT eigenvalues

IP_{HOMO} from ΔSCF :

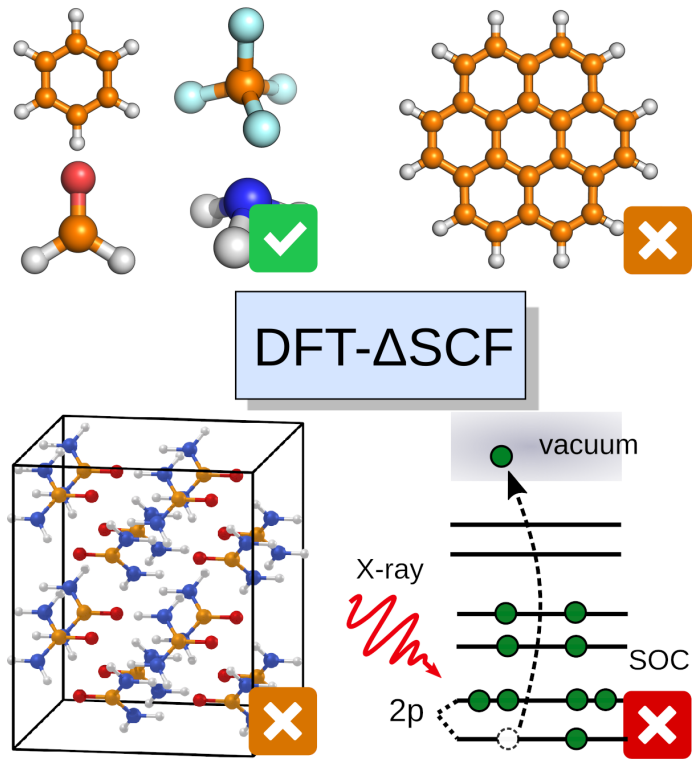
$$IP_{HOMO} = E_{tot}(N-1) - E_{tot}(N)$$

EA from ΔSCF :

$$EA = E_{tot}(N) - E_{tot}(N+1)$$

Approximation/limitations:

- for periodic systems
- large conjugated structures
- spin-orbit coupled states



GW for photoemission

GW review

frontiers in Chemistry | Theoretical and Computational Chemistry

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Density-Functional Theory and Beyond: Novel Materials Discovery fro
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REVIEW article

Front. Chem., 09 July 2019 | https://doi.org/10.3389/fchem.2019.00377

Check for updates

The *GW* Compendium: A Practical Guide to Theoretical Photoemission Spectroscopy

 Dorothea Golze*,  Marc Dvorak and  Patrick Rinke

Department of Applied Physics, Aalto University, School of Science, Espoo, Finland

Single-particle Green's function

Electron removal energies

$$\epsilon_s = E(N) - E(N-1, s)$$
$$\psi_s(\mathbf{r}) = \langle N-1, s|\hat{\psi}(\mathbf{r})|N\rangle$$

Electron addition energies

$$\epsilon_s = E(N+1, s) - E(N)$$
$$\psi_s(\mathbf{r}) = \langle N+1, s|\hat{\psi}^\dagger(\mathbf{r})|N\rangle$$

Definition of single-particle Green's function

$$G(\mathbf{r}, \sigma, t, \mathbf{r}', \sigma', t') = -i\langle N|\hat{T}\{\hat{\psi}(\mathbf{r}, \sigma, t)\hat{\psi}^\dagger(\mathbf{r}', \sigma', t')\}|N\rangle$$

- $\hat{T}$ ... time ordering operator
- $\hat{\psi}^\dagger$ ... creation operator
- $\hat{\psi}$ ... annihilation operator

Single-particle Green's function

Lehman's representation

$$G(\mathbf{r},\mathbf{r}',\omega) = \lim_{\eta\to 0^+} \sum_s \psi_s(\mathbf{r})\psi_s^*(\mathbf{r}') \times \left[\frac{\Theta(\epsilon_s - E_\mathrm{F})}{\omega - (\epsilon_s - i\eta)} + \frac{\Theta(E_\mathrm{F} - \epsilon_s)}{\omega - (\epsilon_s + i\eta)} \right]$$

▷ excitation energies ϵ_s are poles of G

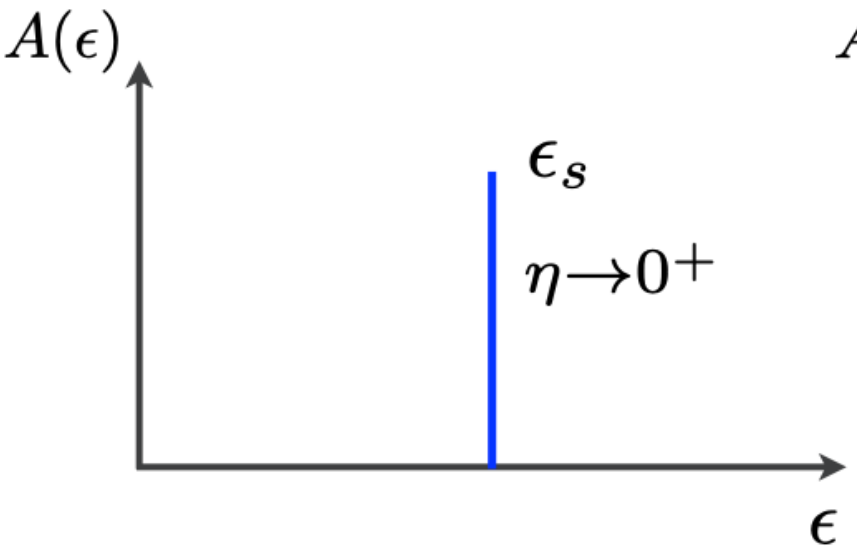
Spectroscopically relevant quantity: spectral function

$$A(\omega) = -\frac{1}{\pi} \int d\mathbf{r} \lim_{\mathbf{r}'\to\mathbf{r}} \mathrm{Im} G(\mathbf{r},\mathbf{r}',\omega)$$

Quasiparticle peak in spectral function

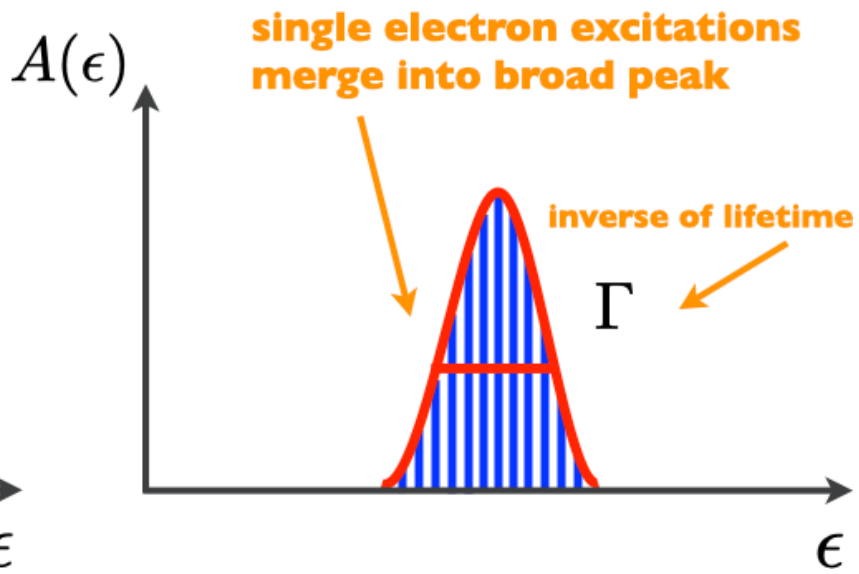
Non-interacting electrons

$$A_{ss'}(\epsilon) = \langle \psi_s | A(\epsilon) | \psi_{s'} \rangle = \delta_{ss'} \delta(\epsilon - \epsilon_s)$$

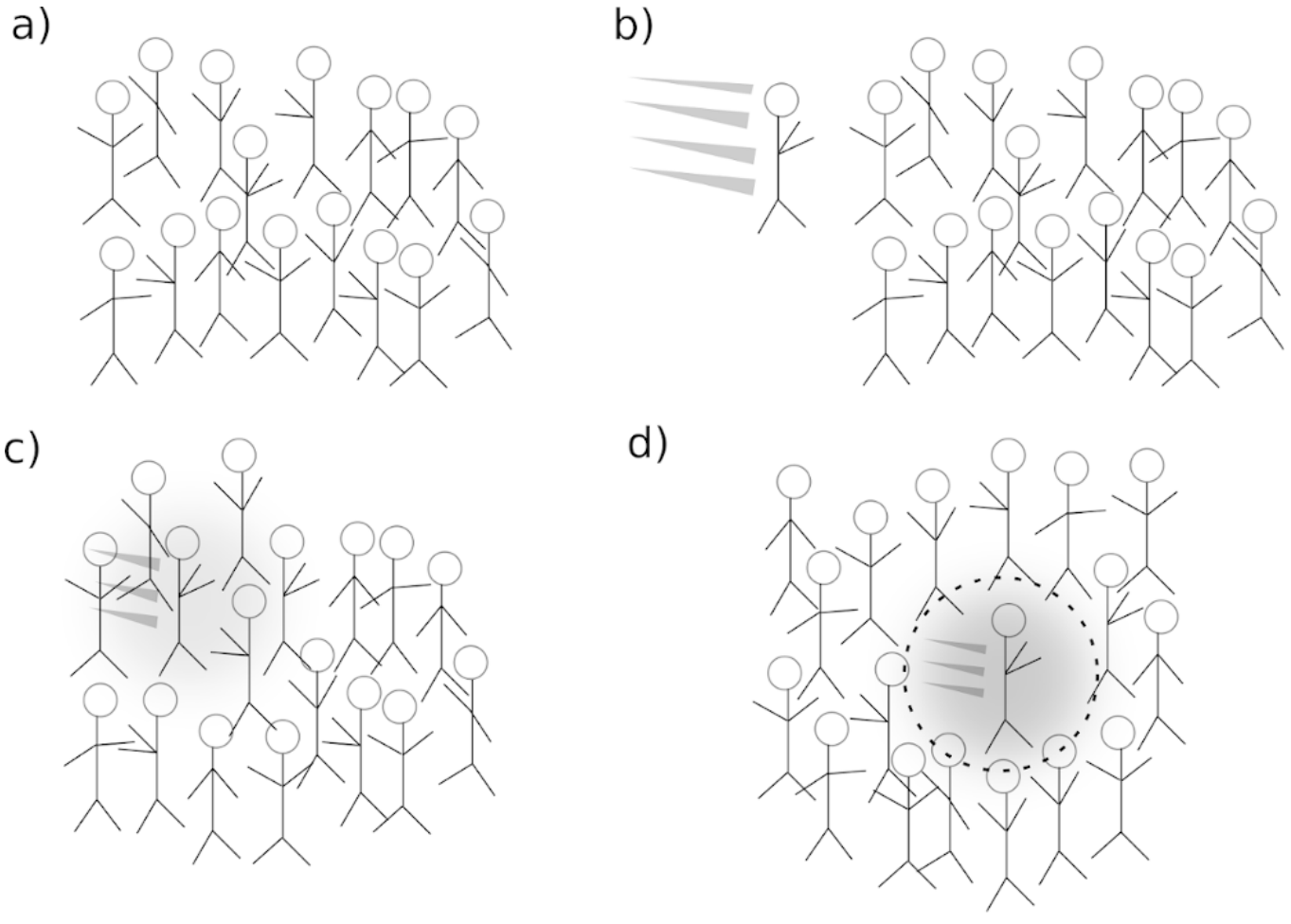


Interacting electrons

$$A_{ss}(\epsilon) \approx \frac{1}{\pi} \left| \frac{Z_s}{\epsilon - (\epsilon_s + i\Gamma)} \right|$$



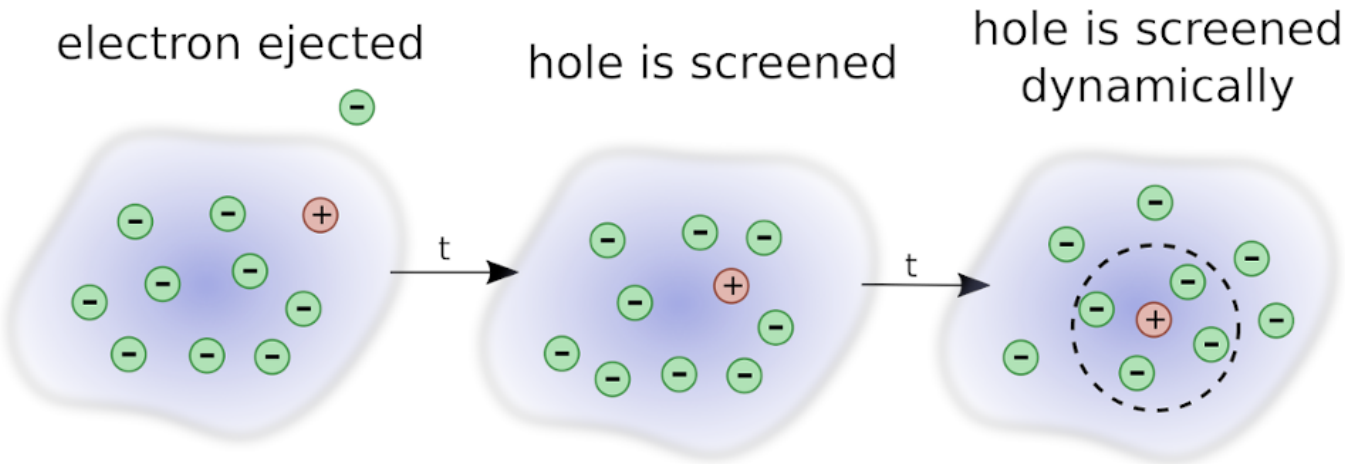
Quasiparticle (QP) concept



▷ person injected into crowd (= inverse photoemission)

Quasiparticle (QP) concept

Photoemission Process



- QP: composite object of electron interacting with its surrounding polarisation cloud
- QP properties: dispersion, life time, weight, satellite spectrum

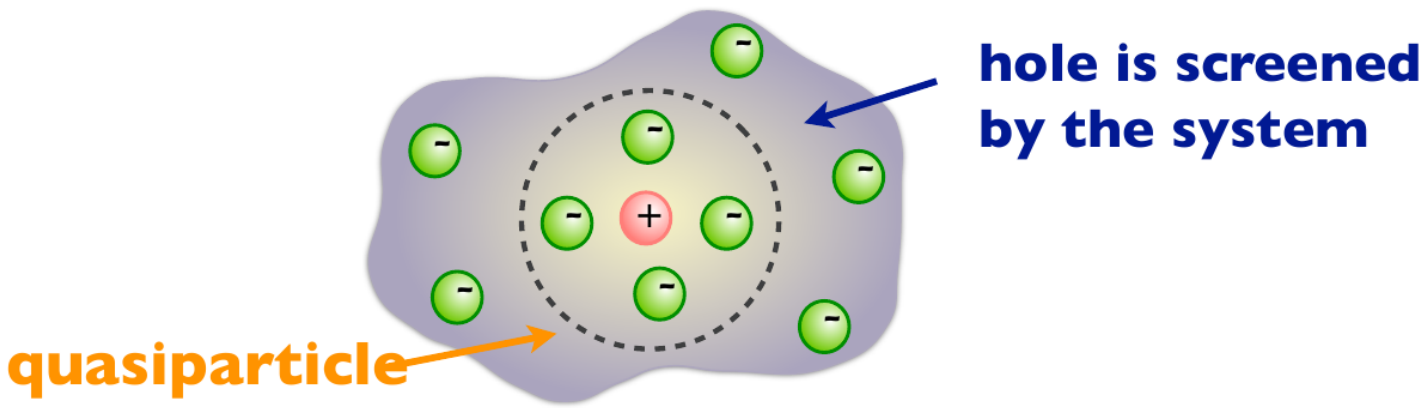
Quasiparticle energies from GW

Basic idea

- in analogy to DFT: replacement of XC potential by self-energy
- self-energy: energy QP feels due to its own presence

$$\Sigma(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{2\pi} \int d\omega' G(\mathbf{r}, \mathbf{r}', \omega + \omega') W(\mathbf{r}, \mathbf{r}', \omega') \, \mathrm{e}^{i\omega'\eta}$$

- G: Green's function; W: screened Coulomb interaction



GW in practice

Single-shot perturbation: G_0W_0

- most common GW flavor
- QP energies obtained as correction to KS-DFT orbital energies ϵ_n^{KS}

$$\epsilon_s^{G_0W_0} = \epsilon_s^{\text{KS}} + \langle \phi_s^{\text{KS}} | \Sigma(\epsilon_s^{G_0W_0}) - v_{xc} | \phi_s^{\text{KS}} \rangle$$

▷ this is what we call QP equation

GW in practice

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▷ this is what we call QP equation

Procedure in short:

1. run DFT calculation
2. calculate G_0 and W_0 from DFT orbital energies ϵ_s^{KS} and MOs $\{\phi_s^{\text{KS}}\}$
3. calculate self-energy from G_0 and W_0
4. solve quasi-particle equation

Procedure for G_0W_0 calculation

Step 1:

- Do a KS-DFT calculation: $\epsilon_s^{\mathsf{KS}}(\mathbf{r})$ and $\phi_s^{\mathsf{KS}}(\mathbf{r})$

Procedure for G_0W_0 calculation

Step 1:

- Do a KS-DFT calculation: $\epsilon_s^{\mathrm{KS}}(\mathbf{r})$ and $\phi_s^{\mathrm{KS}}(\mathbf{r})$

Step 2:

- Set up KS Green's function

$$G_0(\mathbf{r},\mathbf{r}',\omega) = \sum_m \frac{\phi_m^{\mathrm{KS}}(\mathbf{r})\phi_m^{\mathrm{KS}*}(\mathbf{r}')}{\omega - \epsilon_m^{\mathrm{KS}} - i\eta\,\mathrm{sgn}(E_{\mathrm{F}} - \epsilon_m^0)}.$$

Procedure for G_0W_0 calculation

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Step 3:

- Construct polarizability

$$\chi_0(\mathbf{r},\mathbf{r}',\omega) = -\frac{i}{2\pi}\int d\omega' G_0(\mathbf{r},\mathbf{r}',\omega+\omega')G_0(\mathbf{r}',\mathbf{r},\omega')$$

Procedure for G_0W_0 calculation

Step 4:

- Calculate dielectric function

$$\varepsilon(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r}, \mathbf{r}') - \int d\mathbf{r}'' v(\mathbf{r}, \mathbf{r}'') \chi_0(\mathbf{r}'', \mathbf{r}', \omega)$$

Procedure for G_0W_0 calculation

Step 4:

- Calculate dielectric function

$$\varepsilon(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r}, \mathbf{r}') - \int d\mathbf{r}'' v(\mathbf{r}, \mathbf{r}'') \chi_0(\mathbf{r}'', \mathbf{r}', \omega)$$

Step 5:

- Screened Coulomb interaction

$$W_0(\mathbf{r}, \mathbf{r}', \omega) = \int d\mathbf{r}'' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}'', \omega) v(\mathbf{r}'', \mathbf{r}'),$$

Procedure for G_0W_0 calculation

Step 4:

- Calculate dielectric function

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Step 5:

- Screened Coulomb interaction

$$W_0(\mathbf{r}, \mathbf{r}', \omega) = \int d\mathbf{r}'' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}'', \omega) v(\mathbf{r}'', \mathbf{r}'),$$

Step 6:

- Construct G_0W_0 self-energy

$$\Sigma^{G_0W_0}(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{2\pi} \int d\omega' G_0(\mathbf{r}, \mathbf{r}', \omega + \omega') W_0(\mathbf{r}, \mathbf{r}', \omega') \, \mathrm{e}^{i\omega'\eta}$$

Procedure for G_0W_0 calculation

Step 7:

- Solve QP equation

$$\hat{h}^{\mathrm{KS}}(\mathbf{r})\psi_s(\mathbf{r}) - \int d\mathbf{r}' v_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')\psi_s(\mathbf{r}') + \int d\mathbf{r}' \Sigma(\mathbf{r},\mathbf{r}',\epsilon_s)\psi_s(\mathbf{r}') = \epsilon_s \psi_s(\mathbf{r})$$

- Approximation: $\psi_s(\mathbf{r}) = \phi_s^{\mathsf{KS}}(\mathbf{r})$

$$\epsilon_s^{G_0W_0} = \epsilon_s^{\mathsf{KS}} + \langle \phi_s^{\mathsf{KS}} | \mathrm{Re}\Sigma^c(\epsilon_s^{G_0W_0}) + \Sigma^x - v_{xc} | \phi_s^{\mathsf{KS}} \rangle$$

Alternative ways to obtain the QP solution

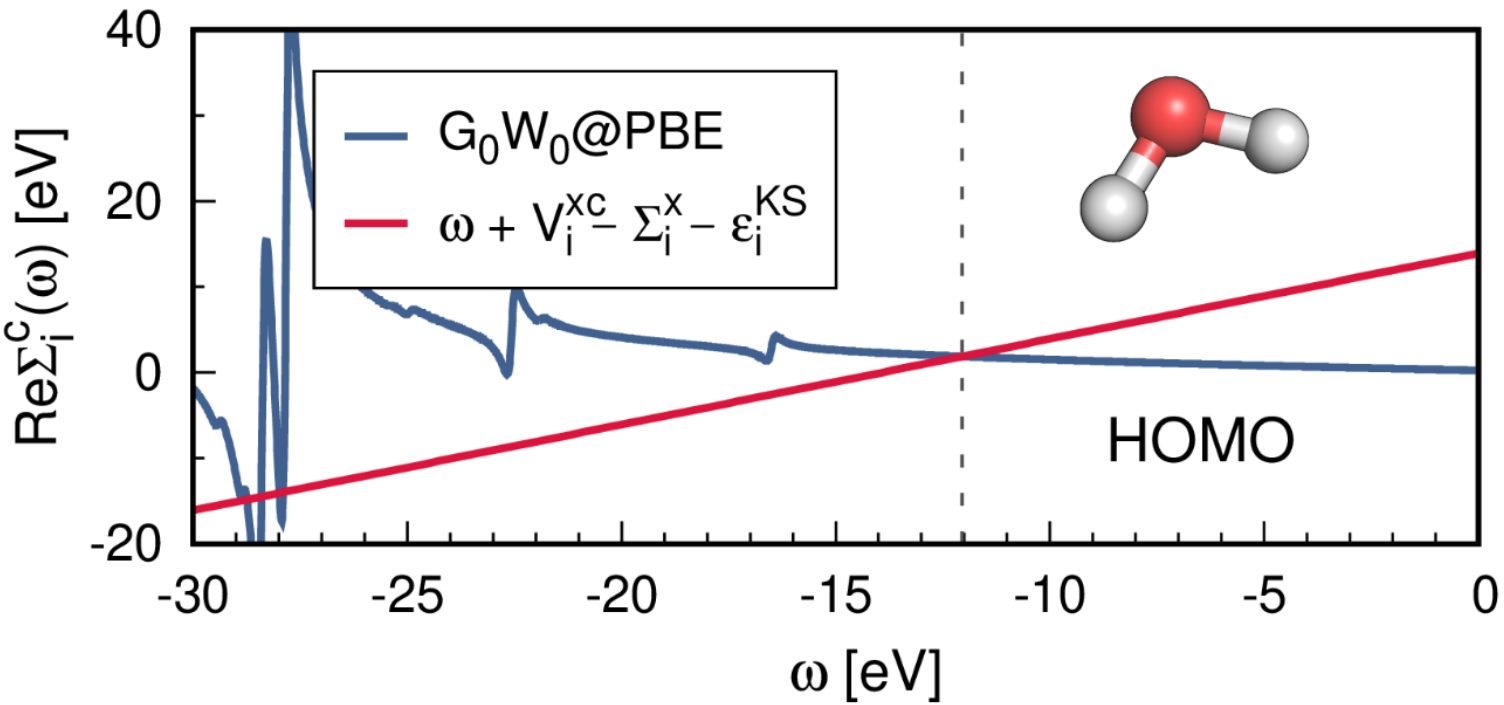
Methods to obtain QP solution

- iteration of QP equation $\rightarrow$ standard approach
- graphical solution of QP equation
- calculation of spectral function

Graphical solution

Procedure

1. calculate $\Sigma_s(\omega) = \langle \phi_s^{\mathrm{KS}} | \Sigma^c(\omega) + \Sigma^x | \phi_s^{\mathrm{KS}} \rangle$
2. plot Re $\Sigma_s^c(\omega)$
3. find intersections with $\omega + v_s^{xc} - \Sigma_s^x - \epsilon_s^{\mathrm{KS}}$



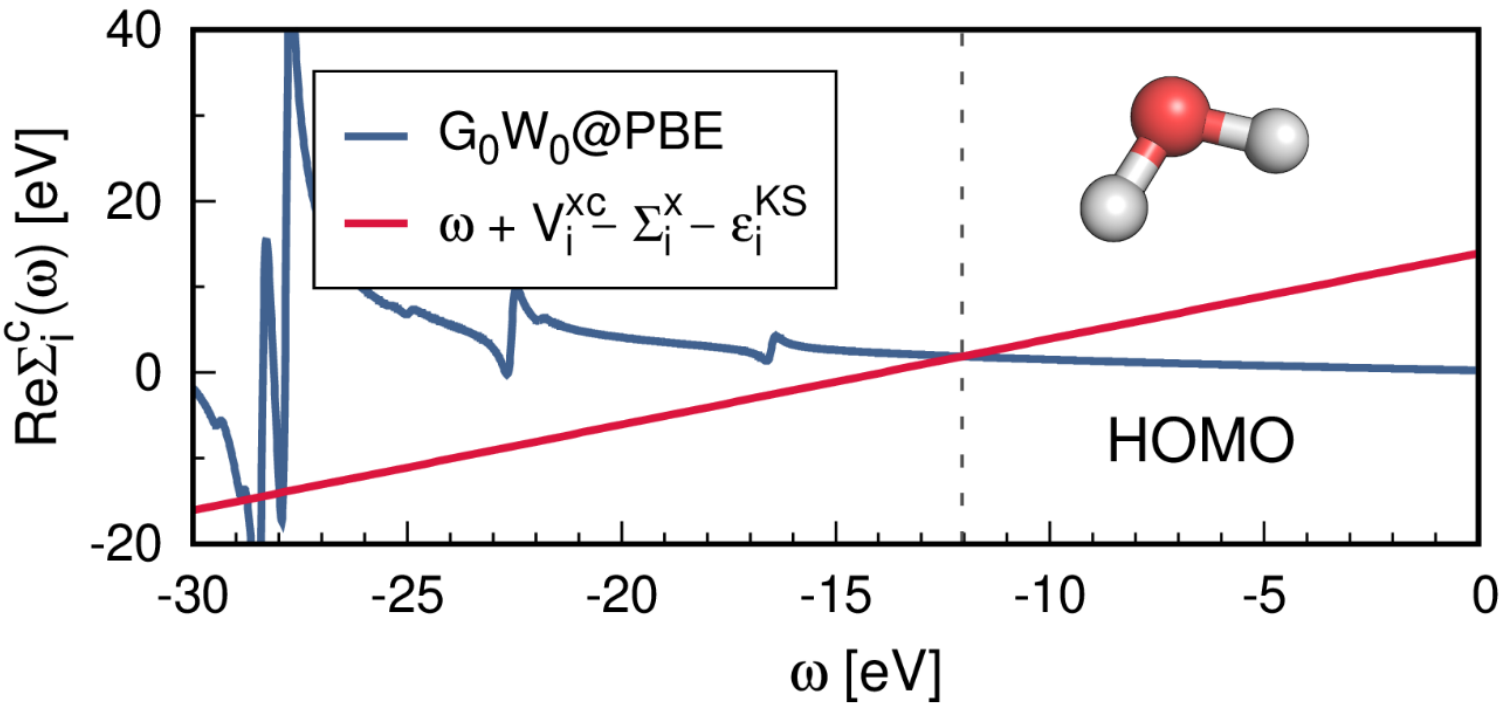
Graphical solution

Procedure

1. calculate $\Sigma_s(\omega) = \langle \phi_s^{\mathrm{KS}} | \Sigma^c(\omega) + \Sigma^x | \phi_s^{\mathrm{KS}} \rangle$
2. plot Re $\Sigma_s^c(\omega)$
3. find intersections with $\omega + v_s^{xc} - \Sigma_s^x - \epsilon_s^{\mathrm{KS}}$

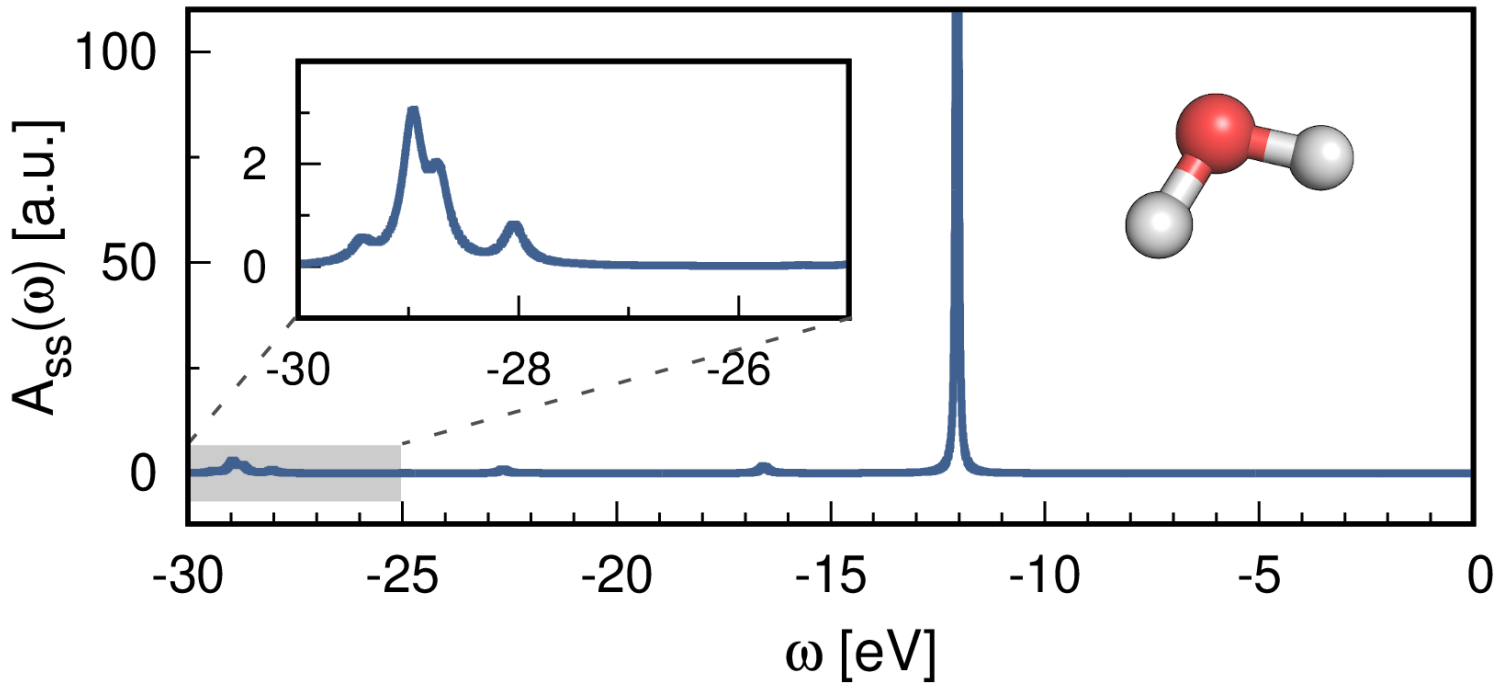
▷ renormalization factor

$$Z_s = \left[1 - \frac{d}{d\omega} \langle \phi_s^{\mathrm{KS}} | \mathrm{Re}\Sigma(\omega) | \phi_s^{\mathrm{KS}} \rangle_{\omega = \epsilon_s^{\mathrm{KS}}} \right]^{-1}$$



Spectral function

$$A(\omega) = \frac{1}{\pi} \sum_m \frac{|\mathrm{Im}\Sigma_m(\omega)|}{\left[\omega - \epsilon_m^{\mathrm{KS}} - (\mathrm{Re}\Sigma_m(\omega) - v_m^{xc})\right]^2 + \left[\mathrm{Im}\Sigma_m(\omega)\right]^2}$$



Frequency integration

Self-energy

$$\Sigma(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{2\pi} \int d\omega' G(\mathbf{r}, \mathbf{r}', \omega + \omega') W(\mathbf{r}, \mathbf{r}', \omega') \, \mathrm{e}^{i\omega'\eta}$$

Frequency integration

Self-energy

$$\Sigma(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{2\pi} \int d\omega' G(\mathbf{r}, \mathbf{r}', \omega + \omega') W(\mathbf{r}, \mathbf{r}', \omega') \, \mathrm{e}^{i\omega'\eta}$$

Methods for self-energy evaluation in FHI-aims

▷ Analytic continuation (AC)

- suitable for valence states and gaps
- $O(N^4)$ scaling

▷ Contour deformation (CD)

- suitable for all states, including deep core
- $O(N^4)$ for valence, $O(N^5)$ for core levels
- much more accurate than AC, but more expensive

Analytic continuation

- integration for imaginary frequencies, then fit to model
- 2-pole model

$$\Sigma_s^c(i\omega) \approx \sum_{j=1}^{2} \frac{a_{s,j}}{i\omega + b_{s,j}} + a_{s,0}$$

- Padé model

$$\Sigma_s^c(i\omega) \approx \frac{a_0 + a_1(i\omega) + \cdots + a_{(N-1)/2}(i\omega)^{(N-1)/2}}{1 + b_1(i\omega) + \cdots + b_{N/2}(i\omega)^{N/2}}$$

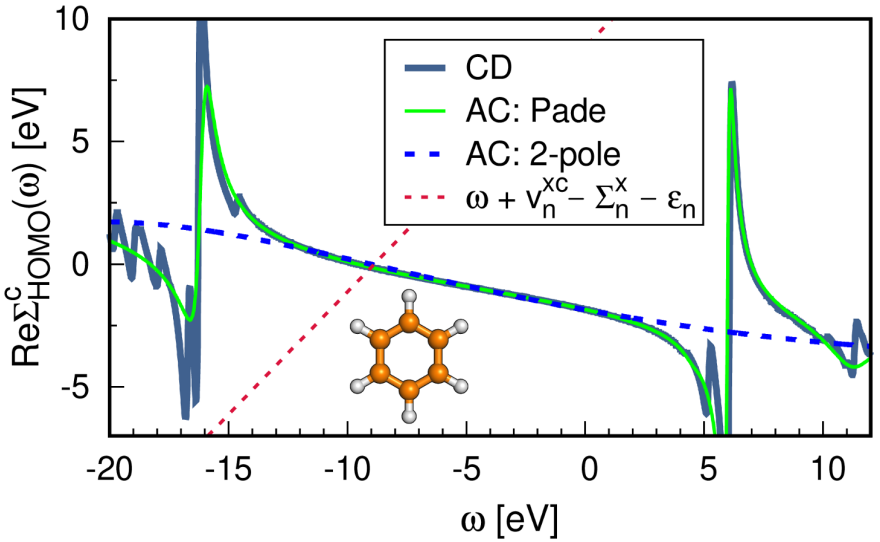


Fig. Front. Chem., 7 (2019), 377

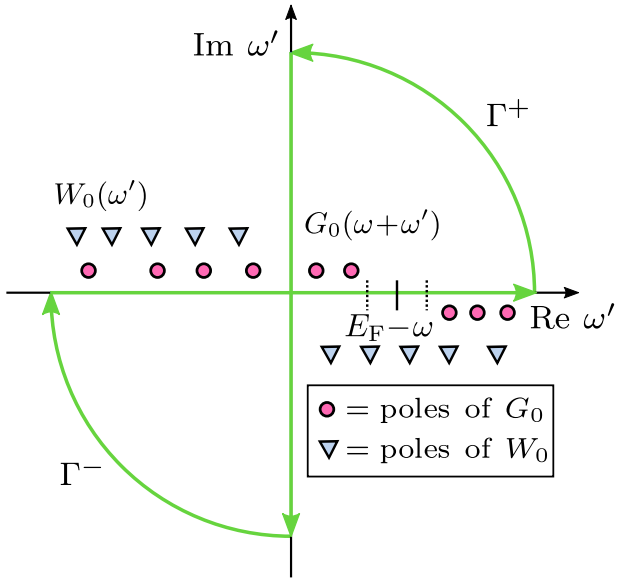
FHI-aims implementation paper

Ren *et al.*, New J. Phys., 14 (2012), 053020

Contour deformation

Contour integral

$$\frac{i}{2\pi}\oint d\omega' G_0(\omega+\omega')W_0(\omega')$$
$$= \int_{\mathrm{Re}} \cdots + \int_{\mathrm{Im}} \cdots + \int_{\mathrm{arc}\,\Gamma+} \cdots + \int_{\mathrm{arc}\,\Gamma-} \cdots$$



Self-energy expression

$$\Sigma(\mathbf{r},\mathbf{r}',\omega) = \frac{i}{2\pi}\oint d\omega' G_0(\mathbf{r},\mathbf{r}',\omega+\omega')W_0(\mathbf{r},\mathbf{r}',\omega')$$
$$-\frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega' G_0(\mathbf{r},\mathbf{r}',\omega+i\omega')W_0(\mathbf{r},\mathbf{r}',i\omega')$$

FHI-aims implementation paper

Golze *et al.*, JCTC, 14 (2018), 4856

Basis set convergence

- slow convergence
- extrapolation often required

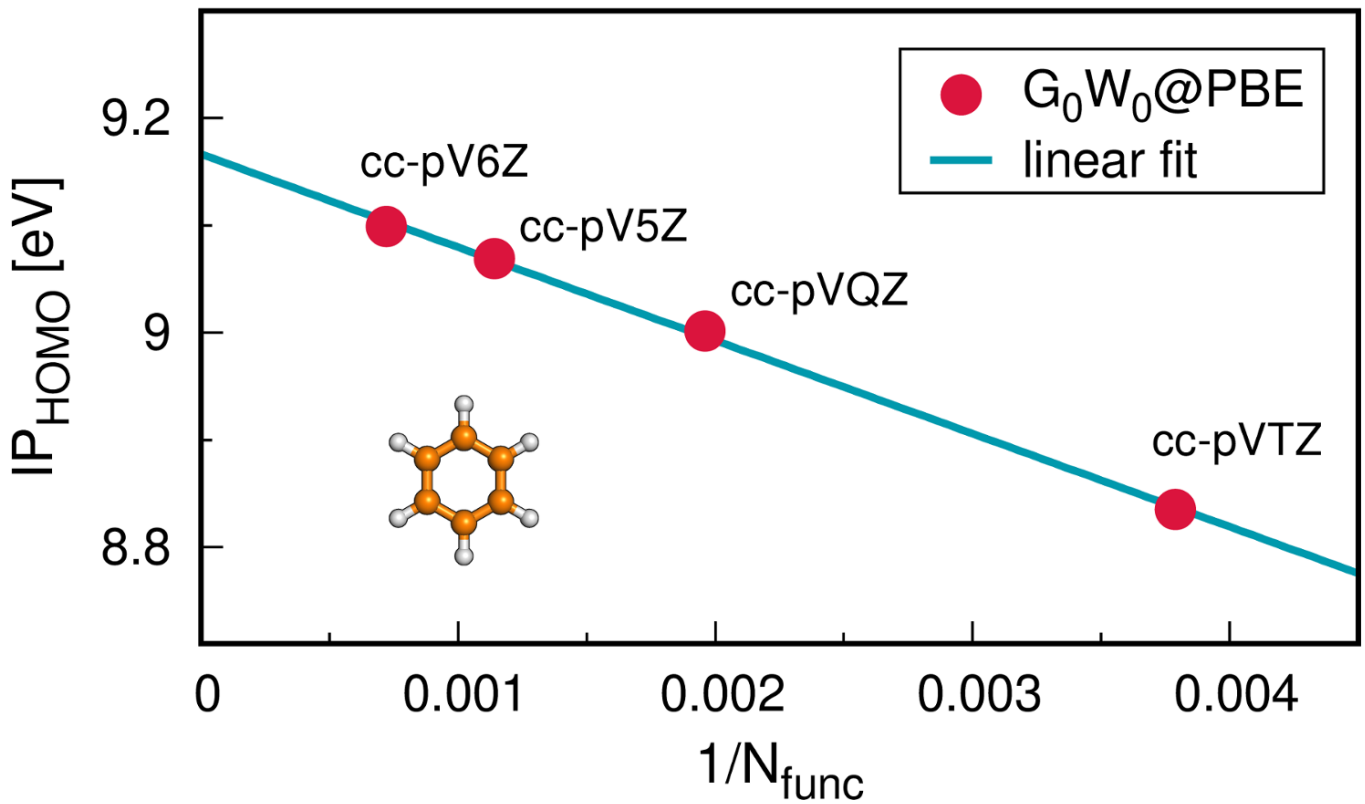


Fig. from GW *compendium*, Front. Chem., 7 (2019), 377

Starting point dependence

- G_0 and W_0 depend on DFT/HF eigenvalues
- tuning of exact exchange in functional necessary

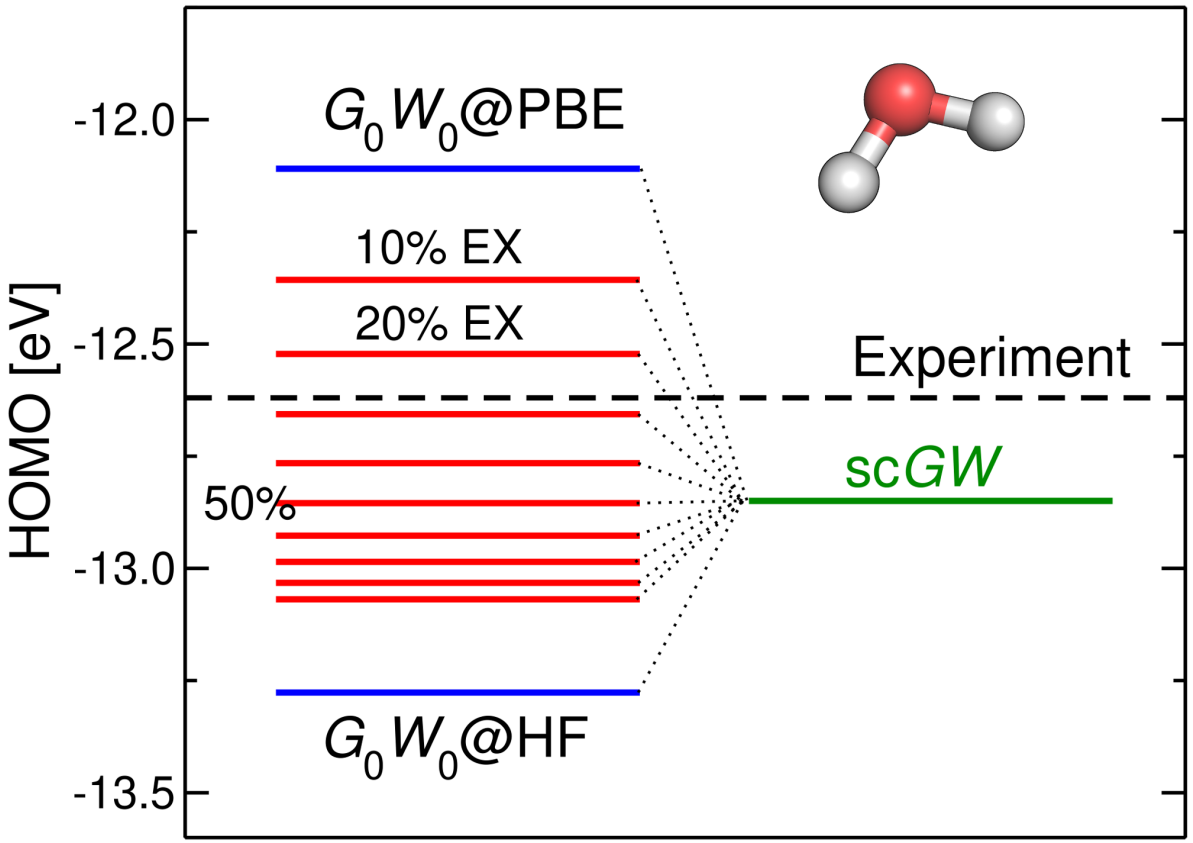
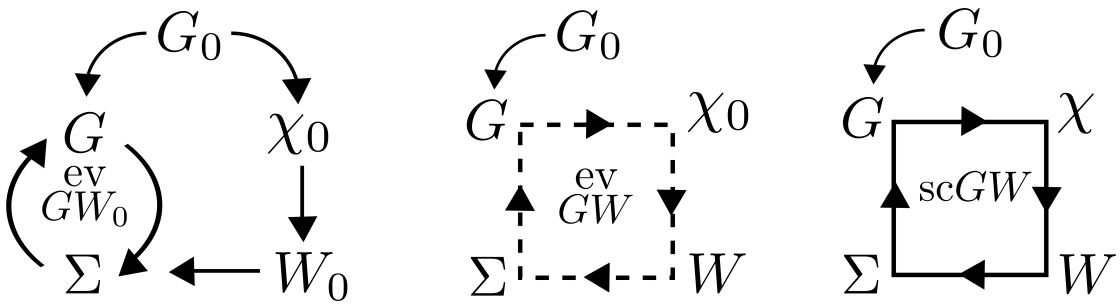


Fig. from GW *compendium*, Front. Chem., 7 (2019), 377

Self-consistent GW schemes

▷ reduction/removal of starting point dependence



Self-consistent schemes in FHI-aims

▷ eigenvalue-selfconsistent GW

- evGW_0: iteration of eigenvalues in G
- evGW: iteration of eigenvalues in G and W

▷ scGW: fully self-consistent GW, solve Dyson equation: $G = G_0 + G_0 \Sigma G$

FHI-aims implementation paper of scGW

Caruso *et al.*, PRB, 88 (2013), 075105

Practical guidelines

The following points should be considered

1. Frequency integration technique (AC, CD)
2. Basis set choice and convergence
3. Starting point choice/self-consistent scheme
4. Convergence of technical parameters, e.g., frequency points

GW calculations of molecular valence states

Some recommendations:

- Analytic continuation works usually well
  - use Padé model if numerical stable
  - check convergence with respect to frequency points
- PBE0 starting point (you might also try evGW_0@PBE)
- Dunning basis sets (cc-pVnZ) usually extrapolate well

GW calculations of molecular core states

Set-up for core states

- contour deformation
- G_0W_0@PBEh($\alpha = 0.45$) or evGW_0@PBE
- relativistic corrections
- basis set extrapolation required, cc-pVnZ works well

Tab.: Absolute BEs

	MAE [eV]
evGW_0@PBE	0.30
G_0W_0@PBEh	0.33

▷ results for CORE65 benchmark set

▷ MAE with respect to experiment

Relevant references

Golze *et al.*, JCTC, 14 (2018), 4856 → technical challenges/implementation

Golze *et al.*, JPCL, 11 (2020), 1840 → starting point optimization

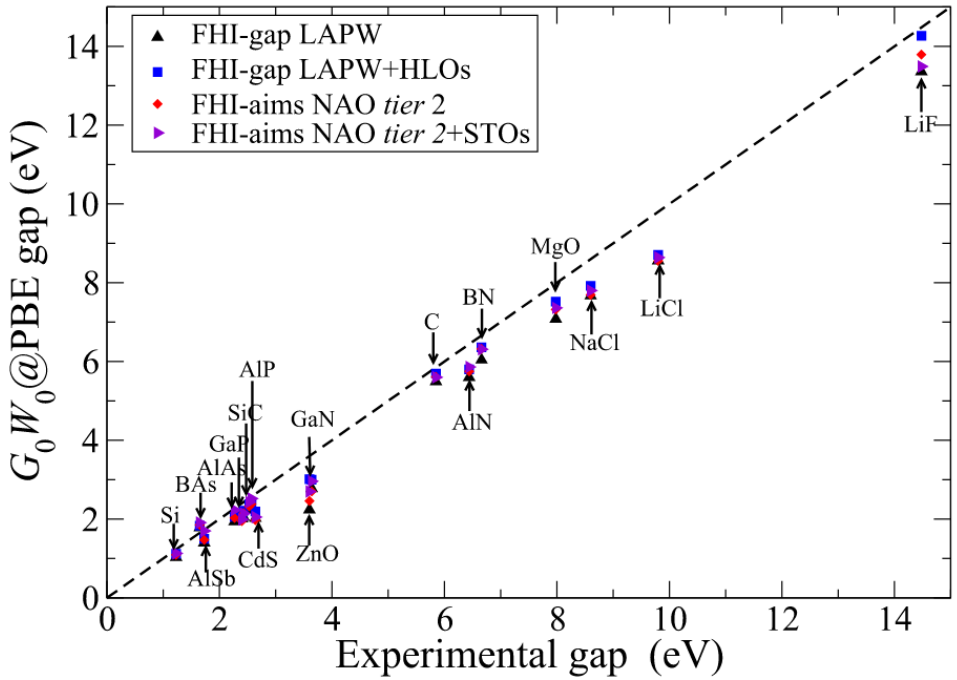
Keller *et al.* JCP, 153 (2020), 114110 → relativistic effects

GW calculations for periodic solids

▷ implementation with analytic continuation

Convergence parameters

- frequency points
- basis set
- k points



FHI-aims implementation/benchmark paper

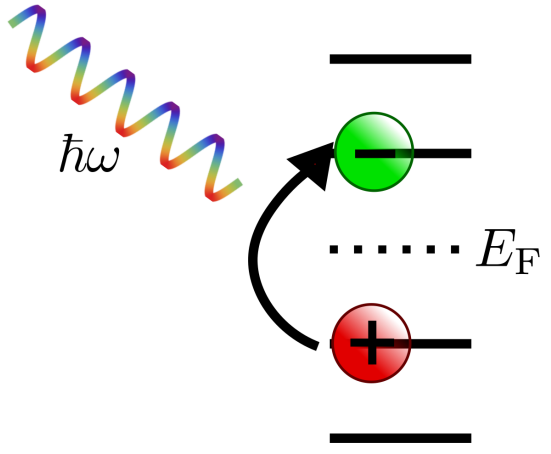
Ren *et al.*, PRB, 5 (2021), 013807

GW+BSE for absorption

Charge neutral excitations

GW + Bethe-Salpeter equation (BSE)

- alternative for TDDFT
- preceding GW calculation



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The Bethe–Salpeter equation in chemistry: relations with TD-DFT, applications and challenges

Xavier Blase,[a] Ivan Duchemin[b] and Denis Jacquemin[c]

BSE formalism

BSE in practical implementations

$$\begin{bmatrix} A & B \\ -B^\dagger & -A^\dagger \end{bmatrix} \begin{bmatrix} X_s \\ Y_s \end{bmatrix} = E_s \begin{bmatrix} X_s \\ Y_s \end{bmatrix}$$

Tamm-Dancoff approximation (TDA)

$$\mathbf{A}\mathbf{X}_s = E_s \mathbf{X}_s$$

$$A_{ij}^{ab} = (\epsilon_a^{GW} - \epsilon_i^{GW})\delta_{ij}\delta_{ab} - \alpha \langle \phi_i \phi_a | v | \phi_j \phi_b \rangle + \langle \phi_i \phi_j | W_0(\omega = 0) | \phi_a \phi_b \rangle$$

FHI-aims implementation/benchmark paper

Liu *et al.*, JCP, 152 (2020), 044105

BSE with FHI-aims

Properties

- singlet transitions
- triplet transitions
- oscillator strengths

Technical setup

- TDA typically sufficient
- basis set: augmentation functions important
- hybrid starting point

Summary of functionality

GW methods in FHI-aims

Single-shot G_0W_0

- molecular valence states
- molecular core states
- periodic systems

GW+BSE

- molecules only
- on-top of G_0W_0, evGW_0 and evGW

Eigenvalue-selfconsistent GW

- molecular valence states
- molecular core states

Fully-selfconsistent GW

- molecular valence states

Literature summary

▷ FHI-aims implementation and benchmark paper

GW for molecular valence states (analytic continuation)

Ren *et al.*, New J. Phys., 14 (2012), 053020

Setten *et al.*, JCTC, 11 (2015), 5665

GW for molecular core levels (contour deformation)

Golze *et al.*, JCTC, 14 (2018), 4856

Golze *et al.*, JPCL, 11 (2020), 1840

Keller *et al.* JCP, 153 (2020), 114110

Fully-selfconsistent GW

Caruso *et al.*, PRB, 88 (2013), 075105

Caruso *et al.*, JCTC, 12 (2016), 5076

Periodic G_0W_0 for solid-state materials

Ren *et al.*, PRB, 5 (2021), 013807

BSE@GW

Liu *et al.*, JCP, 152 (2020), 044105

Happy computing!

How to solve the QP equation

QP equation

$$\epsilon_s^{G_0W_0} = \epsilon_s^{\mathsf{KS}} + \langle \phi_s^{\mathsf{KS}} | \mathrm{Re}\Sigma^c(\epsilon_s^{G_0W_0}) + \Sigma^x - v_{xc} | \phi_s^{\mathsf{KS}} \rangle$$

1. Solve iteratively $\rightarrow$ **RECOMMENDED**
2. Linearize QP equation (Taylor expansion around ϵ_s^{KS}) $\rightarrow$ **AVOID**

$$\epsilon_s^{G_0W_0} = \epsilon_s^{\mathsf{KS}} + Z_s \langle \phi_s^{\mathsf{KS}} | \mathrm{Re}\Sigma(\epsilon_s^{\mathsf{KS}}) - v_{\mathrm{xc}} | \phi_s^{\mathsf{KS}} \rangle$$

$$Z_s = \left[1 - \frac{d}{d\omega} \langle \phi_s^{\mathsf{KS}} | \mathrm{Re}\Sigma(\omega) | \phi_s^{\mathsf{KS}} \rangle_{\omega = \epsilon_s^{\mathsf{KS}}} \right]^{-1}$$

$\rightarrow$ common, but leads to (unnecessary) linearization errors