Excited States and *GW*/BSE

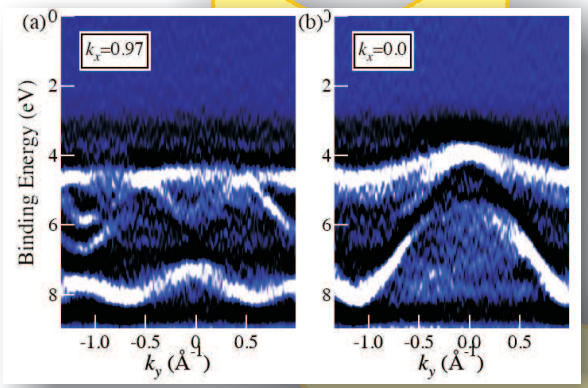
Patrick Rinke

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin - Germany

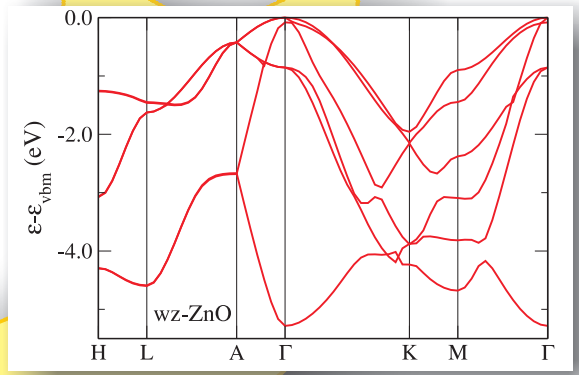
Hands-on Tutorial on *Ab Initio* Molecular Simulations: Toward a First-Principles Understanding of Materials Properties and Functions

Excited States in (Material) Science – Are Ubiquitous

Experiment/Spectroscopy



Theoretical Spectroscopy



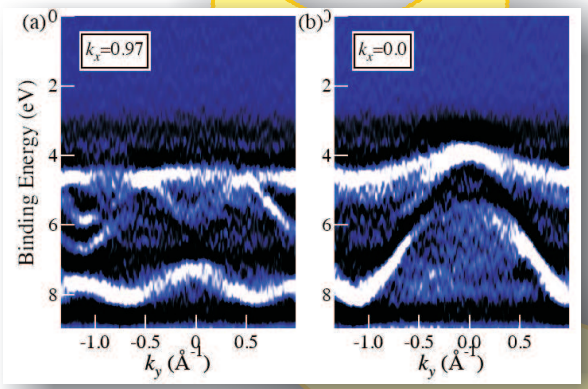
appropriate?
accurate?

appropriate?
accurate?

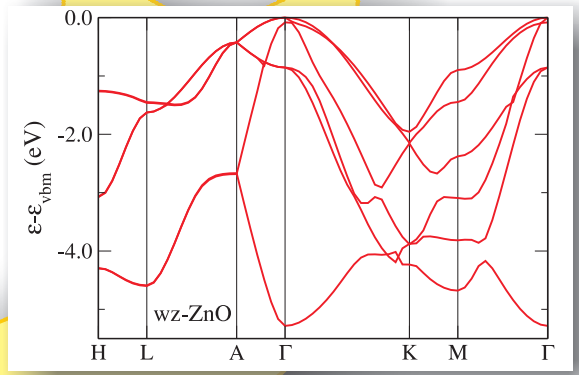
Material Properties + Applications

Excited States in (Material) Science – Are Ubiquitous

Experiment/Spectroscopy



Theoretical Spectroscopy



appropriate?
accurate?

appropriate?
accurate?

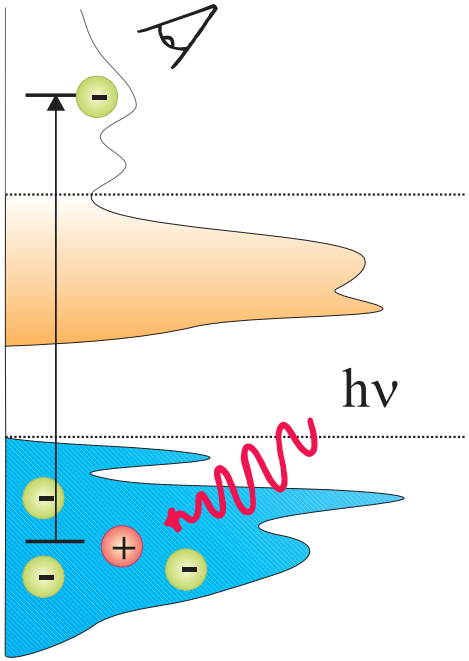
photoemission
optical absorption

DFT+G_0W_0
DFT+G_0W_0+BSE

Material Properties + Applications

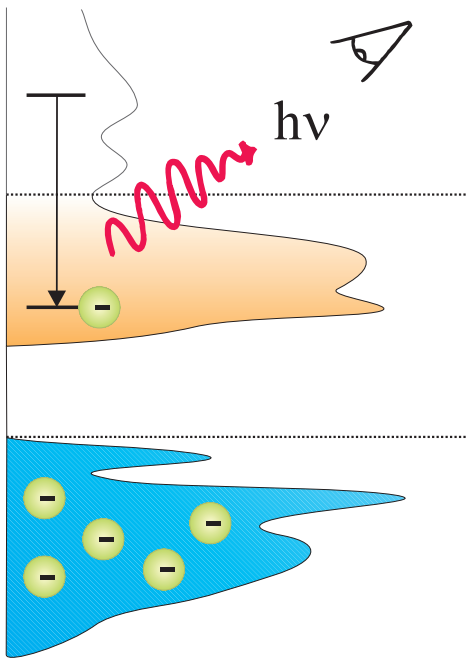
Band structures: photo-electron spectroscopy

Photoemission



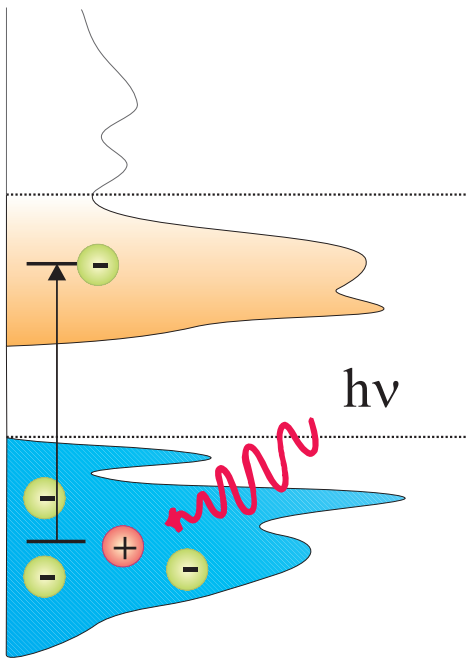
GW

Inverse Photoemission



GW

Absorption



BSE
TDDFT

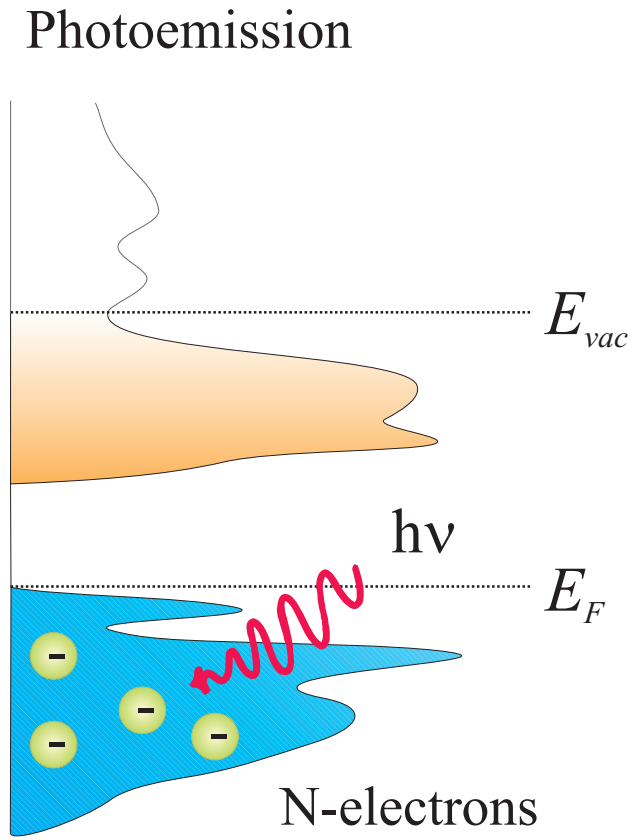
Photo-Electron Excitation Energies

- Photoemission
  - electron removal

$$|N\rangle$$

  - removal energy

$$E(N)$$



$\|N\rangle$	:	N-particle ground state
$E(N,s)$	:	total energy in state s

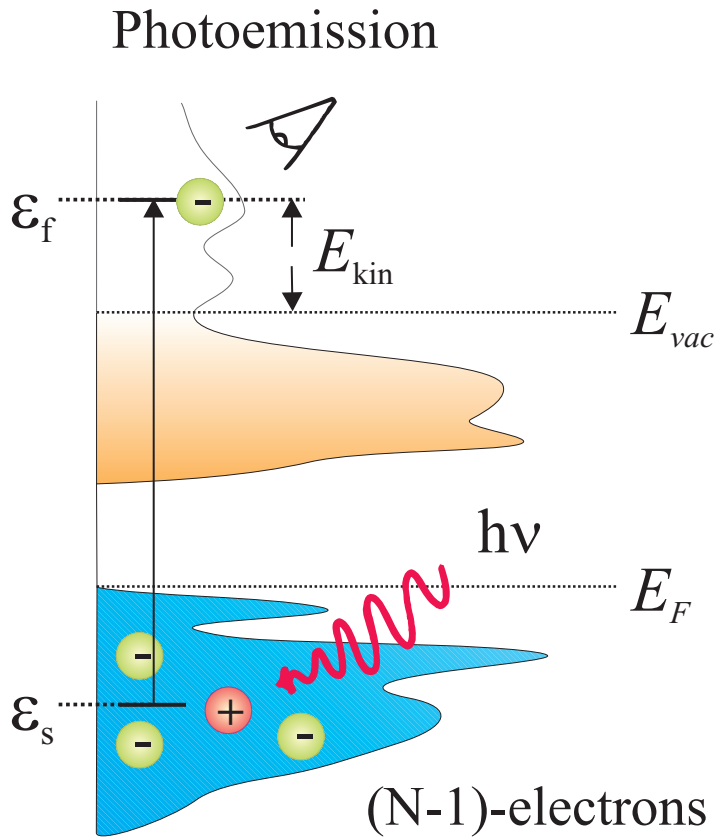
Photo-Electron Excitation Energies

- Photoemission
  - electron removal

$$\hat{\psi}(\mathbf{r})|N\rangle$$

  - removal energy

$$E(N)$$



$\|N\rangle$	:	N-particle ground state
$E(N,s)$	:	total energy in state s

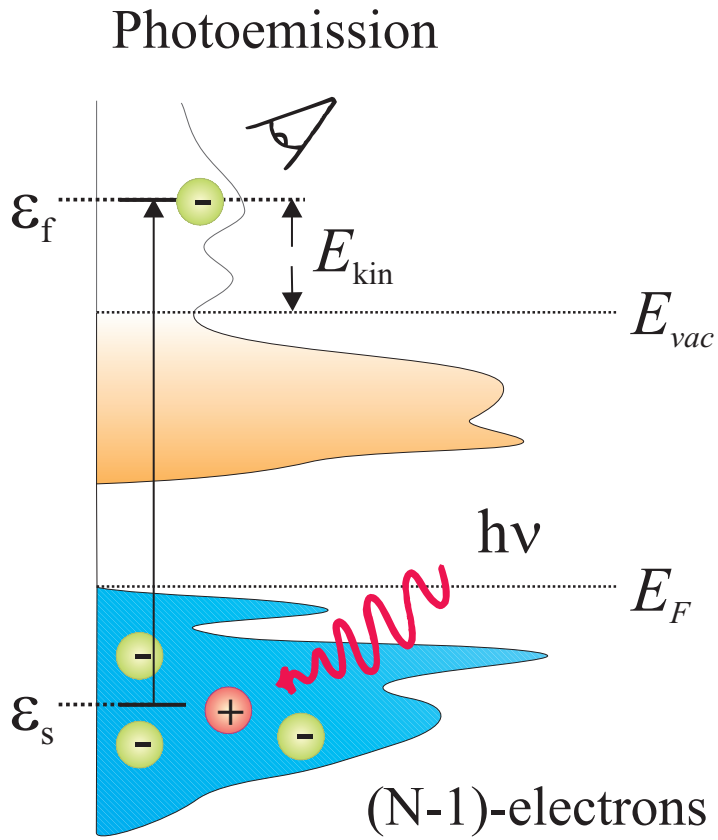
Photo-Electron Excitation Energies

- Photoemission
  - electron removal

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

  - removal energy

$$E(N) - E(N-1, s)$$



$\|N\rangle$	:	N-particle ground state
$\|N-1, s\rangle$	:	$(N-1)$-particle excited state s
$E(N, s)$	:	total energy in state s

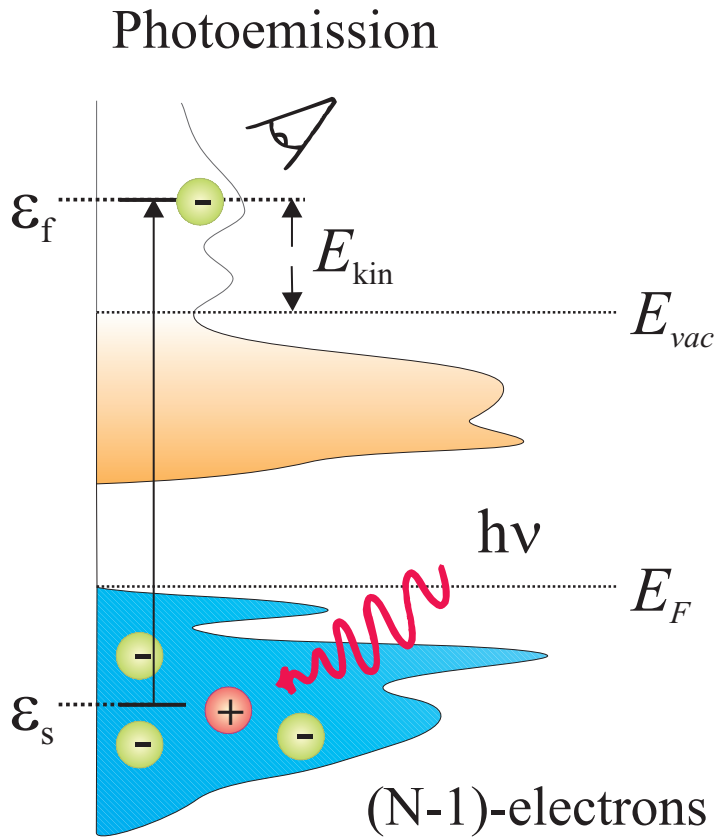
Photo-Electron Excitation Energies

- Photoemission
  - electron removal

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

  - removal energy

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



$\|N\rangle$	:	N-particle ground state
$\|N-1, s\rangle$	:	$(N-1)$-particle excited state s
$E(N, s)$	:	total energy in state s

Photo-Electron Excitation Energies

- Photoemission
  - electron removal

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

  - removal energy

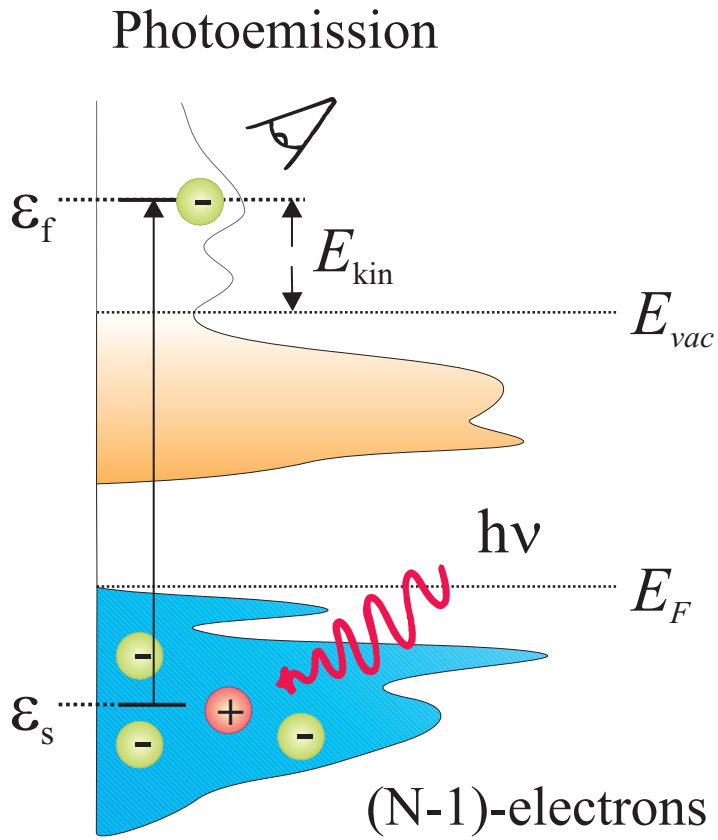
    $$\epsilon_s = E(N) - E(N-1, s)$$

- Inverse Photoemission
  - electron addition

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

  - addition energy

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



$\|N\rangle$	:	N-particle ground state
$\|N-1, s\rangle$	:	$(N-1)$-particle excited state s
$E(N, s)$	:	total energy in state s

Single Particle Green's Functions

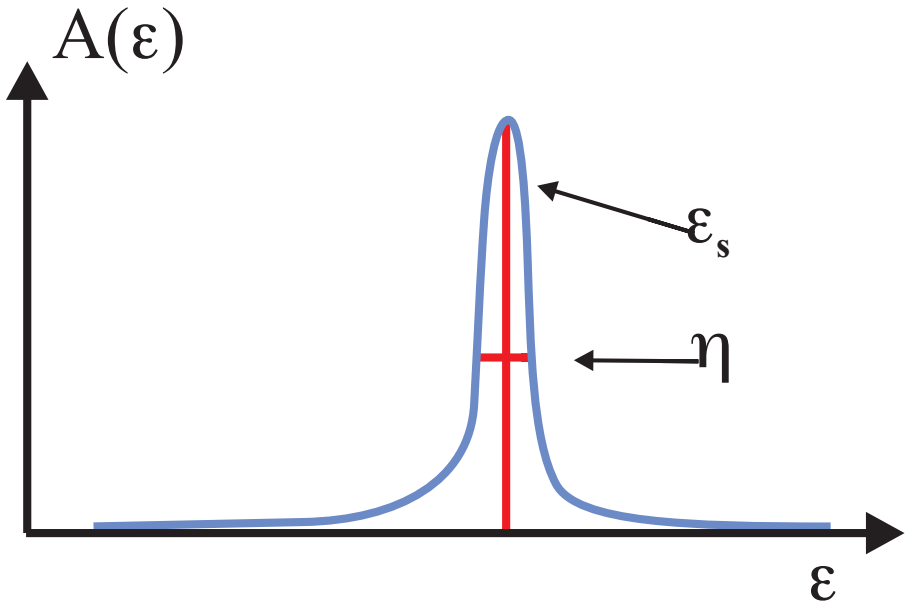
- Lehmann representation of single particle Green's function G:

$$G(\mathbf{r},\mathbf{r}';\epsilon) = \lim_{\eta\to 0^+} \sum_s \frac{\psi_s(\mathbf{r})\psi_s^*(\mathbf{r}')}{\epsilon - (\epsilon_s + i\eta\,\mathrm{sgn}(E_f - \epsilon_s))}$$

Excitation energies are poles of the Green's function!

- spectroscopically relevant quantity: spectral function A:

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



Single Particle Green's Functions

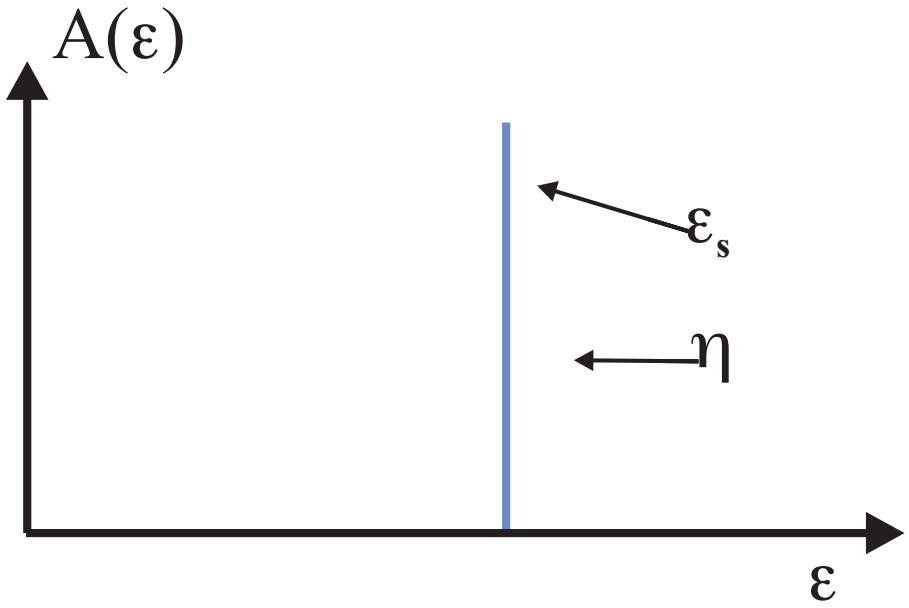
- Lehmann representation of single particle Green's function G:

$$G(\mathbf{r},\mathbf{r}';\epsilon) = \lim_{\eta\to 0^+} \sum_s \frac{\psi_s(\mathbf{r})\psi_s^*(\mathbf{r}')}{\epsilon - (\epsilon_s + i\eta\,\mathrm{sgn}(E_f - \epsilon_s))}$$

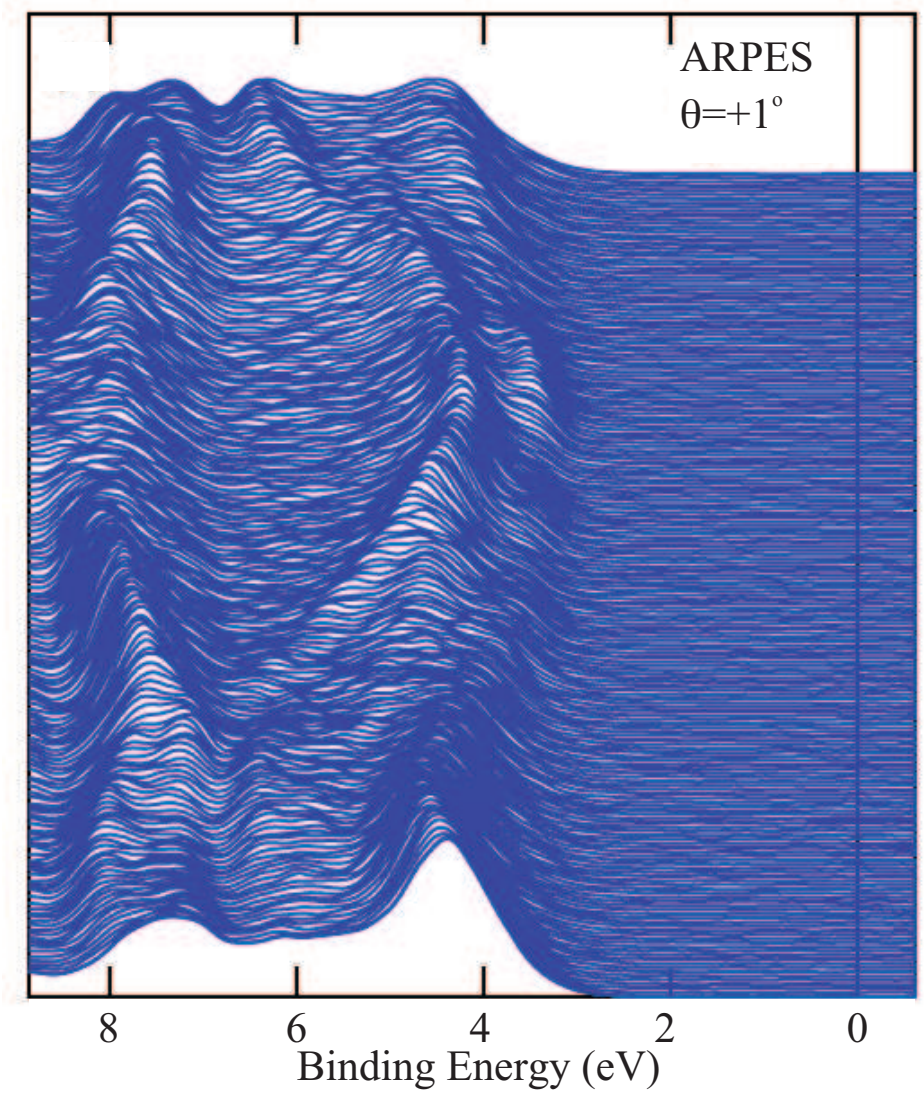
Excitation energies are poles of the Green's function!

- spectroscopically relevant quantity: spectral function A:

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

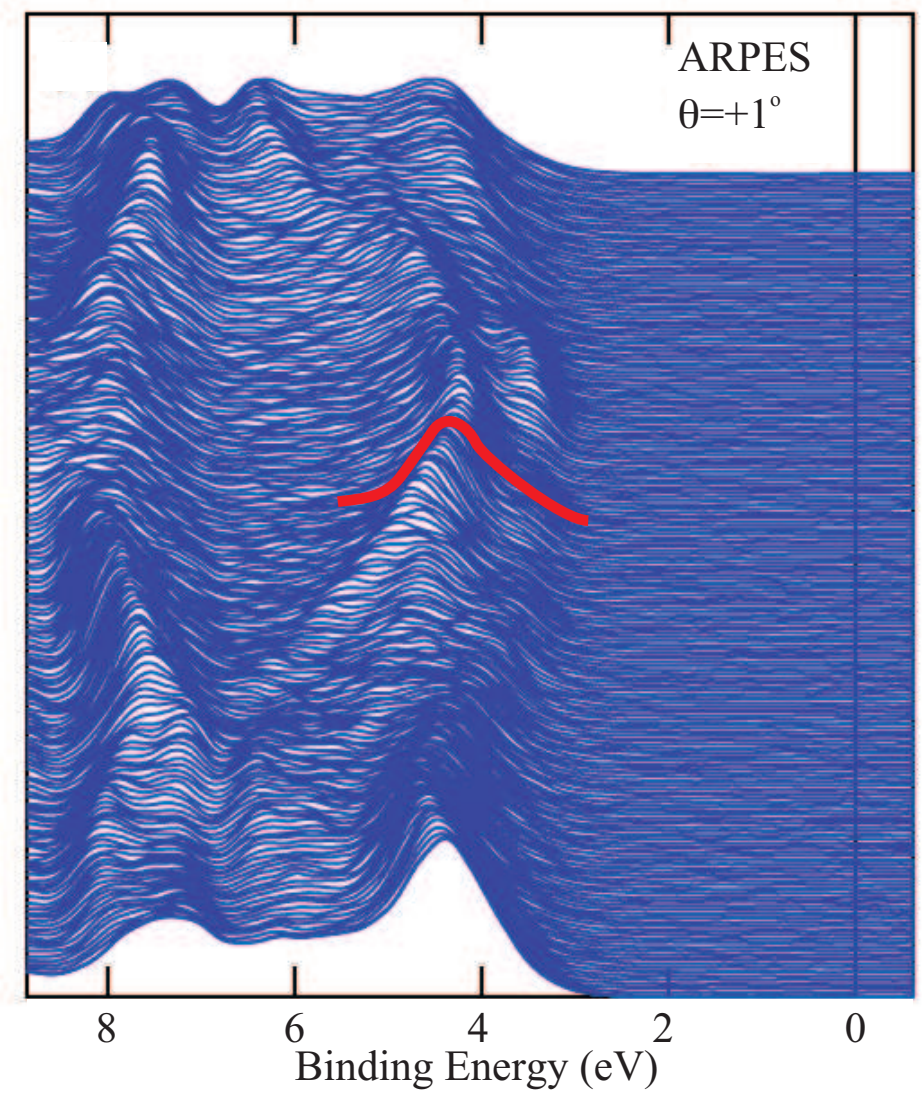


Experimental: angle-resolved photoemission spectroscopy



Masaki Kobayashi, PhD dissertation

Experimental: angle-resolved photoemission spectroscopy

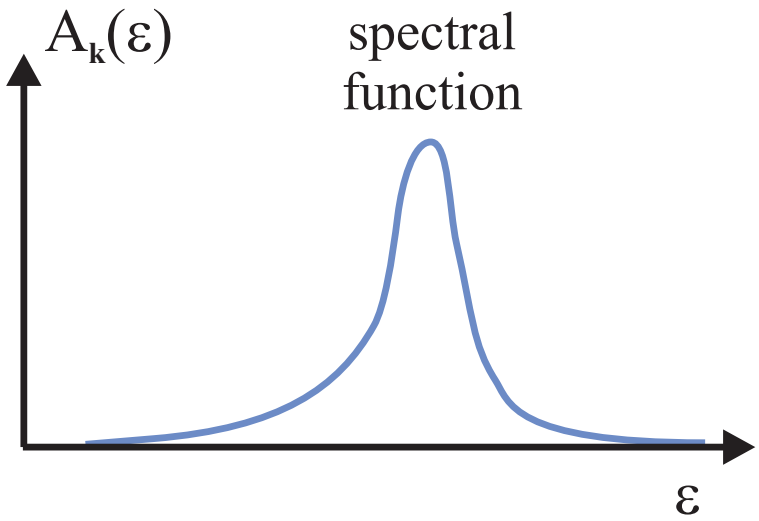


Masaki Kobayashi, PhD dissertation

ARPES vs GW: the quasiparticle concept

Quasiparticle:

- single-particle like excitation

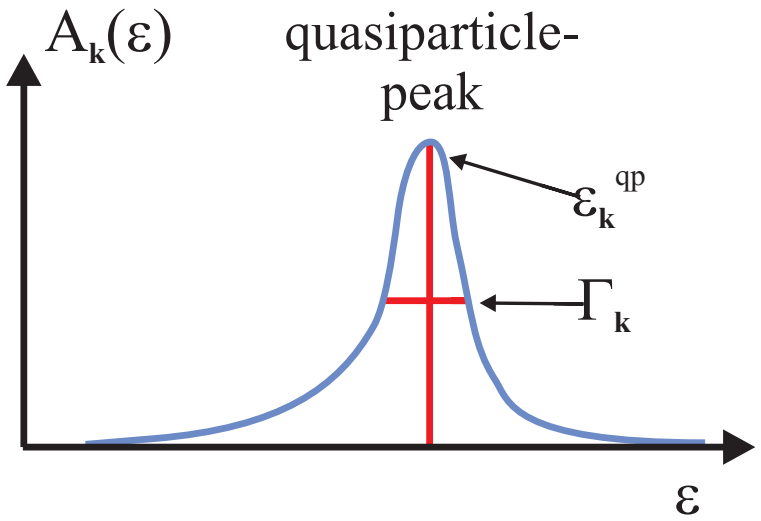


ARPES vs GW: the quasiparticle concept

Quasiparticle:

- single-particle like excitation
- $A_{\mathbf{k}}(\epsilon) = ImG_{\mathbf{k}}(\epsilon) \approx \dfrac{Z_{\mathbf{k}}}{\epsilon - (\epsilon_{\mathbf{k}} + i\Gamma_{\mathbf{k}})}$

$\epsilon_{\mathbf{k}}$: excitation energy
$\Gamma_{\mathbf{k}}$: lifetime
$Z_{\mathbf{k}}$: renormalisation

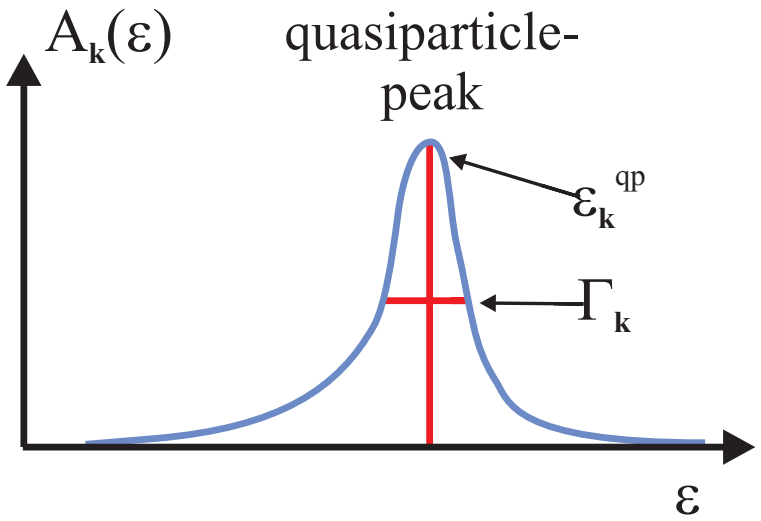


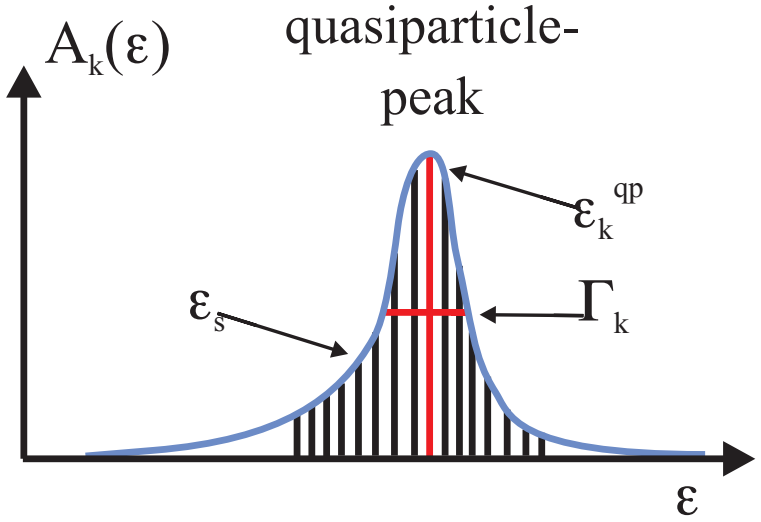
ARPES vs GW: the quasiparticle concept

Quasiparticle:

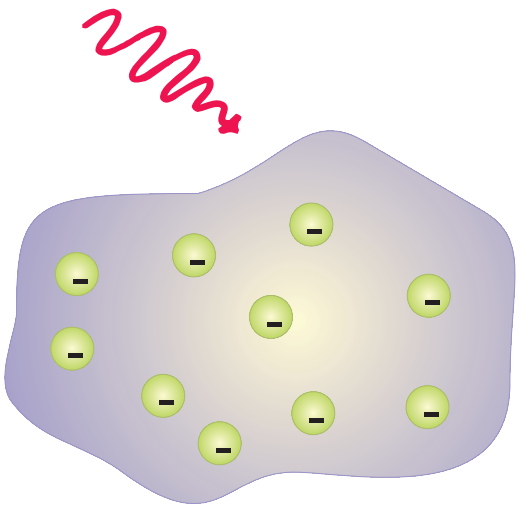
- single-particle like excitation
- $A_{\mathbf{k}}(\epsilon) = ImG_{\mathbf{k}}(\epsilon) \approx \dfrac{Z_{\mathbf{k}}}{\epsilon - (\epsilon_{\mathbf{k}} + i\Gamma_{\mathbf{k}})}$

$\epsilon_{\mathbf{k}}$: excitation energy
$\Gamma_{\mathbf{k}}$: lifetime
$Z_{\mathbf{k}}$: renormalisation

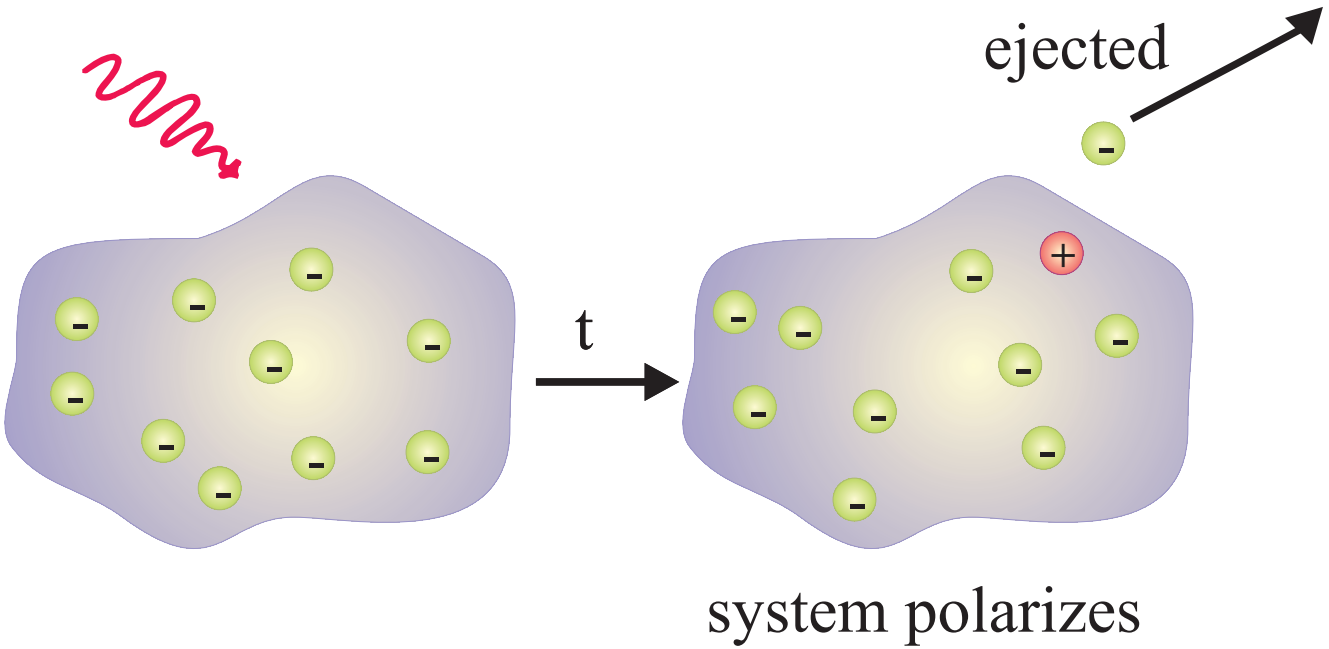




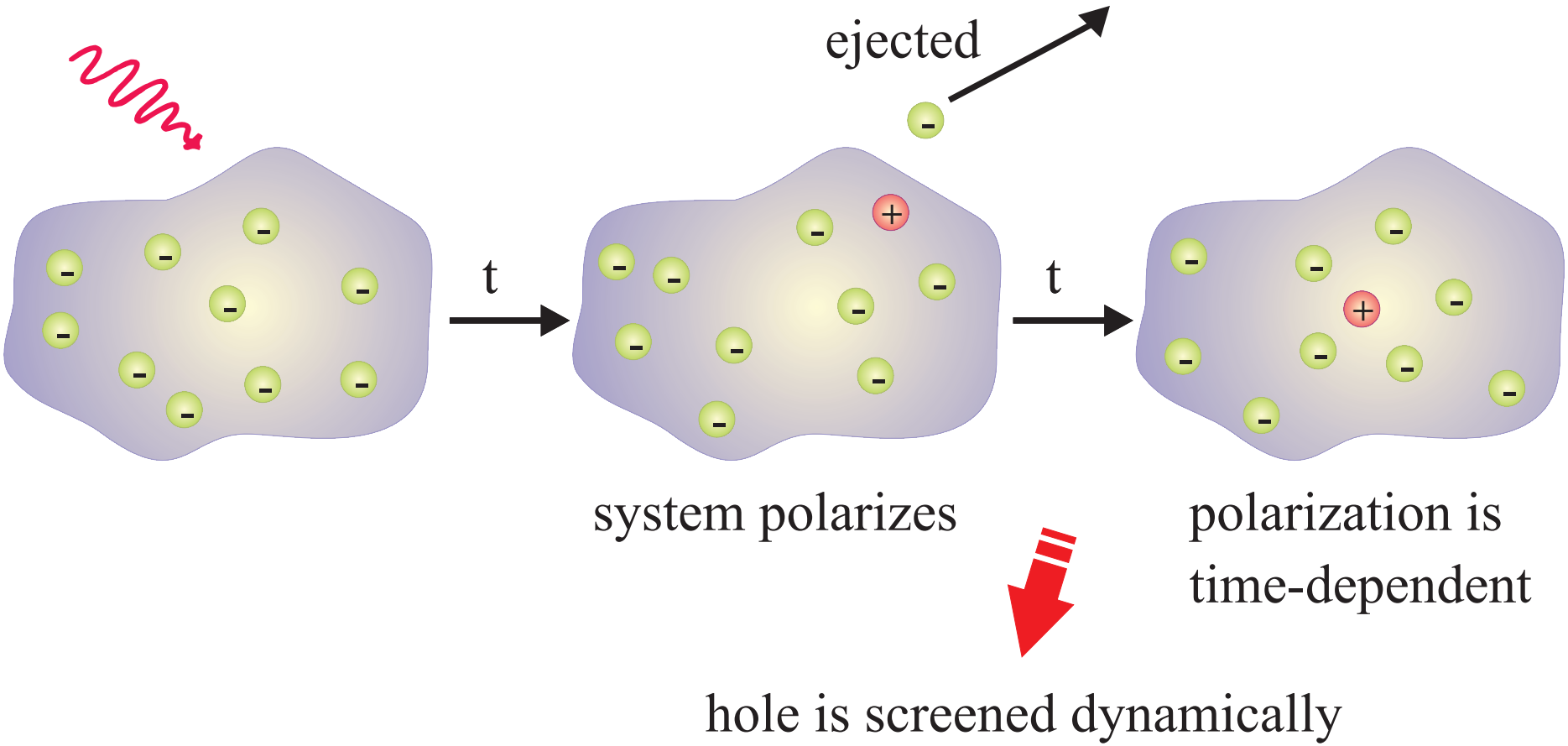
Green's function and screening



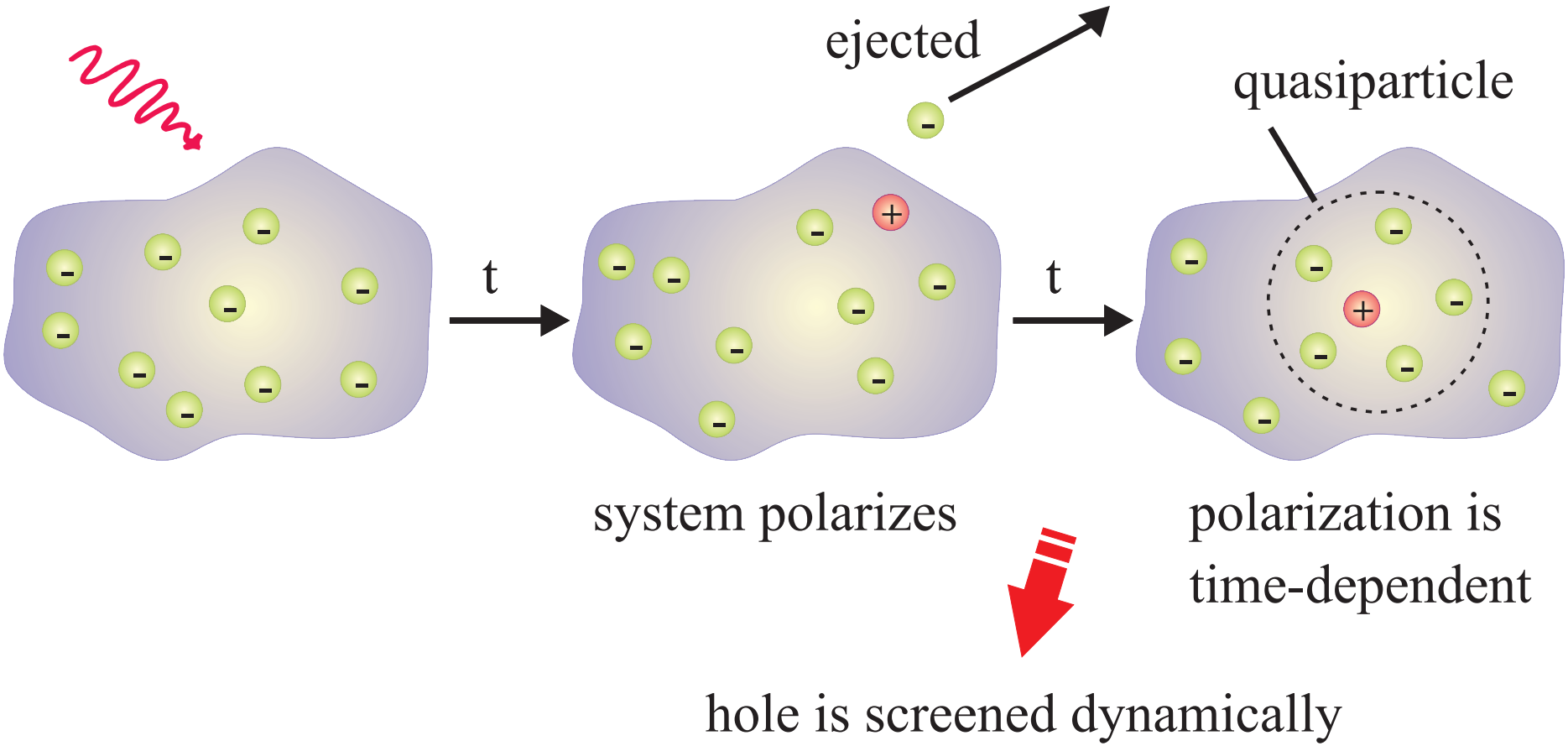
Green's function and screening



Green's function and screening

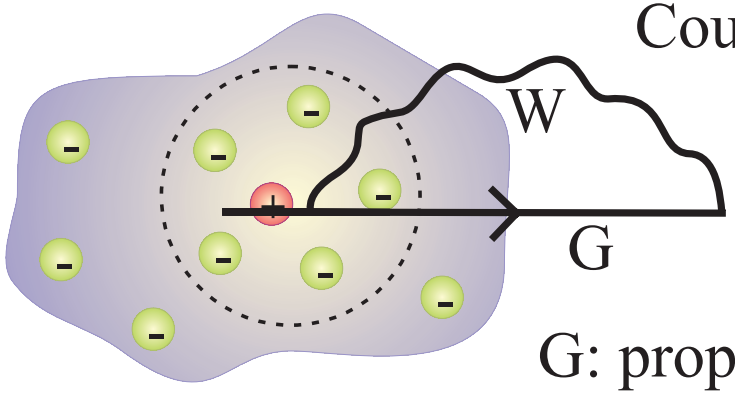


Green's function and screening



GW Approximation - Screened Electrons

Σ=GW :



Self-Energy

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

Green's function is solution to Hedin's equations

Hedin's equations - exact

L. Hedin, Phys. Rev. **139**, A796 (1965)

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

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

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

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

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

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

Hedin's equations - exact

L. Hedin, Phys. Rev. **139**, A796 (1965)

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

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

$$W(1,2) = v($$

$$\Sigma(1,2) = i$$

$$\Gamma(1,2,3) = \delta($$

$$3)d(4,5,6,7)$$

- exact : yes
- tractable: no

But, do not despair!

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

Hedin's GW equations

L. Hedin, Phys. Rev. **139**, A796 (1965)

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

$$\Gamma(1,2,3) = \delta(1,2)\delta(1,3)$$

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

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

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

G_0W_0 Approximation in Practise

1. start from Kohn-Sham calculation for ϵ_s^{KS} and $\phi_s^{\mathrm{KS}}(\mathbf{r})$
2. KS Green's function:

$$G_0(\mathbf{r},\mathbf{r}';\epsilon) = \lim_{\eta\to 0^+} \sum_s \frac{\phi_s^{\mathrm{KS}}(\mathbf{r})\phi_s^{\mathrm{KS}*}(\mathbf{r}')}{\epsilon - (\epsilon_s^{\mathrm{KS}} + i\eta\,\mathrm{sgn}(E_f - \epsilon_s^{\mathrm{KS}}))}$$

3. Polarisability:

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

4. Dielectric function:

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

G_0W_0 Approximation in Practise

5. Screened interaction:

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

6. G_0W_0 self-energy:

$$\Sigma(\mathbf{r},\mathbf{r}';\epsilon) = \frac{i}{2\pi}\int d\epsilon' e^{i\epsilon'\delta} G_0(\mathbf{r},\mathbf{r}';\epsilon+\epsilon') W_0(\mathbf{r},\mathbf{r}';\epsilon')$$

7. Quasiparticle equation:

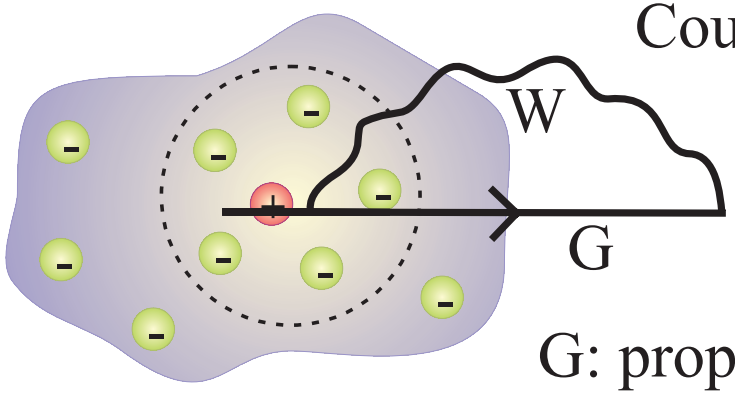
$$\hat{h}_0(\mathbf{r})\psi_s(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r},\mathbf{r}';\epsilon_s^{qp})\psi_s(\mathbf{r}') = \epsilon_s^{qp}\psi_s(\mathbf{r})$$

   - solve for quasiparticle energies ϵ_s^{qp} and wavefunctions $\psi_s(\mathbf{r})$
   - perturbation theory: $\psi_s(\mathbf{r}) = \phi_s^{\mathrm{KS}}(\mathbf{r})$

$$\Rightarrow \epsilon_s^{qp} = \epsilon_s^{\mathrm{KS}} + \langle s|\Sigma(\epsilon_s^{qp})|s\rangle - \langle s|v_{xc}|s\rangle$$

GW Approximation - Screened Electrons

Σ=GW :



W: screened Coulomb

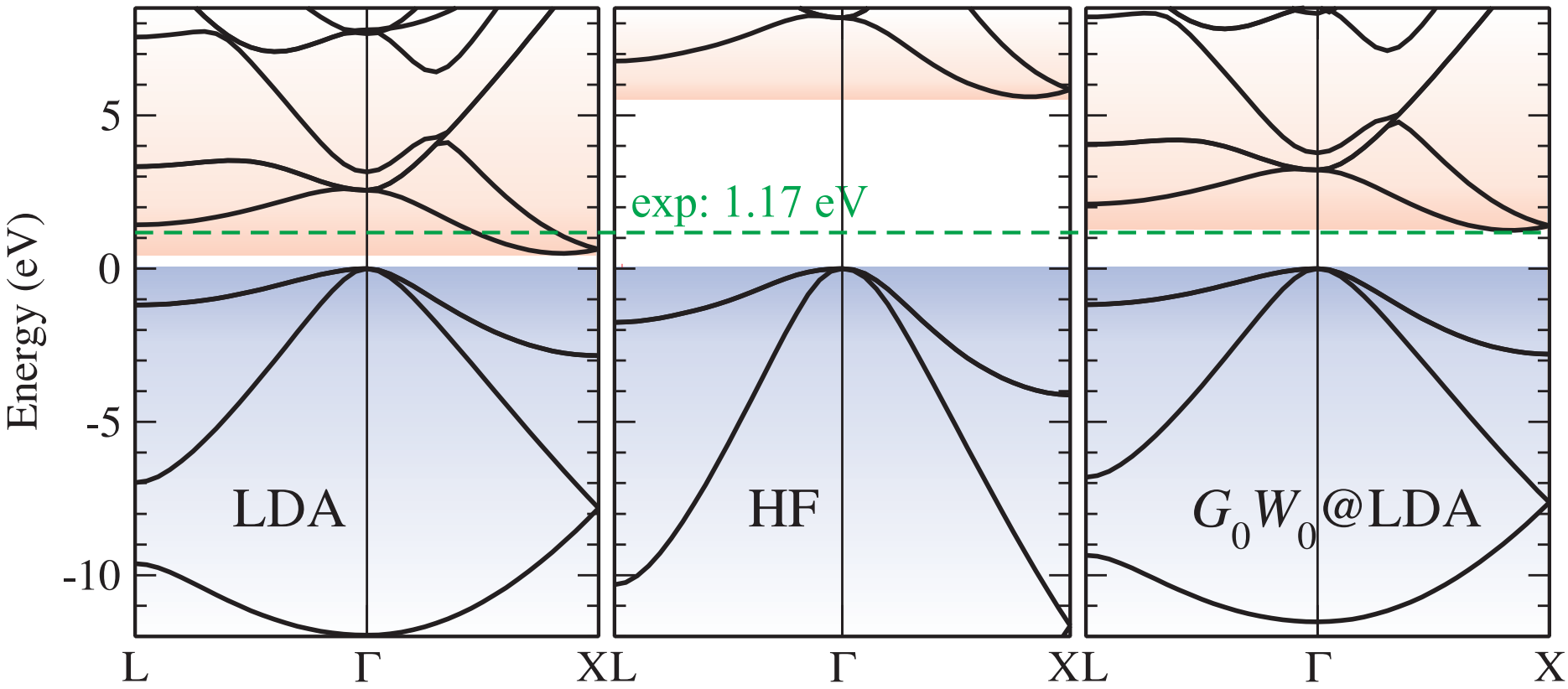
G: propagator

Self-Energy: $\Sigma = \Sigma_x + \Sigma_c$

- $\Sigma_x = iGv$:
  - exact (Hartree-Fock) exchange
- $\Sigma_c = iG(W - v)$:
  - correlation (screening due to other electrons)

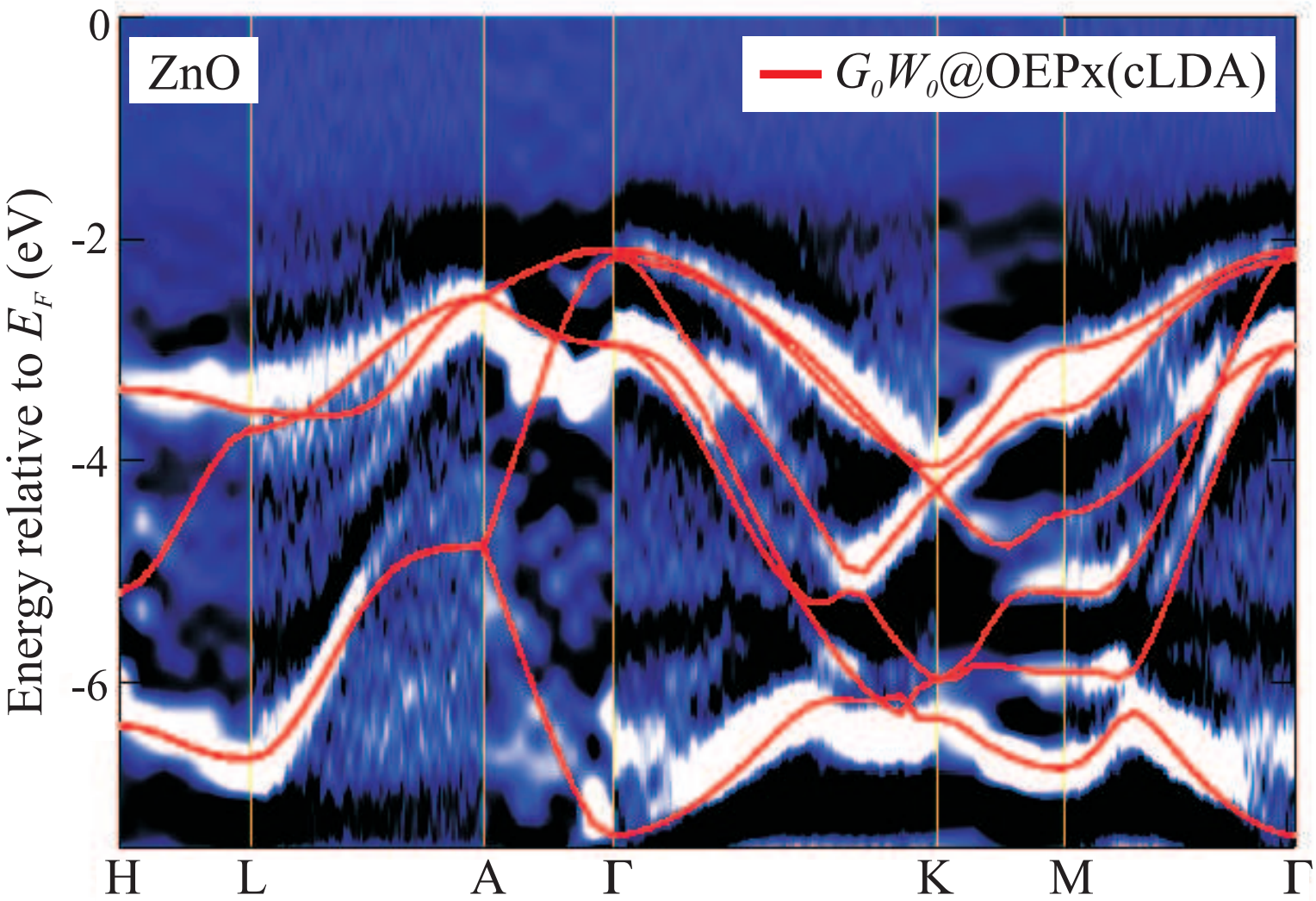
On the importance of screening – Silicon

$$\epsilon^{qp}_{n\mathbf{k}} = \epsilon^{LDA}_{n\mathbf{k}} + \langle \phi_{n\mathbf{k}} | \Sigma_x + \Sigma_c(\epsilon^{qp}_{n\mathbf{k}}) - v_{xc} | \phi_{n\mathbf{k}} \rangle$$



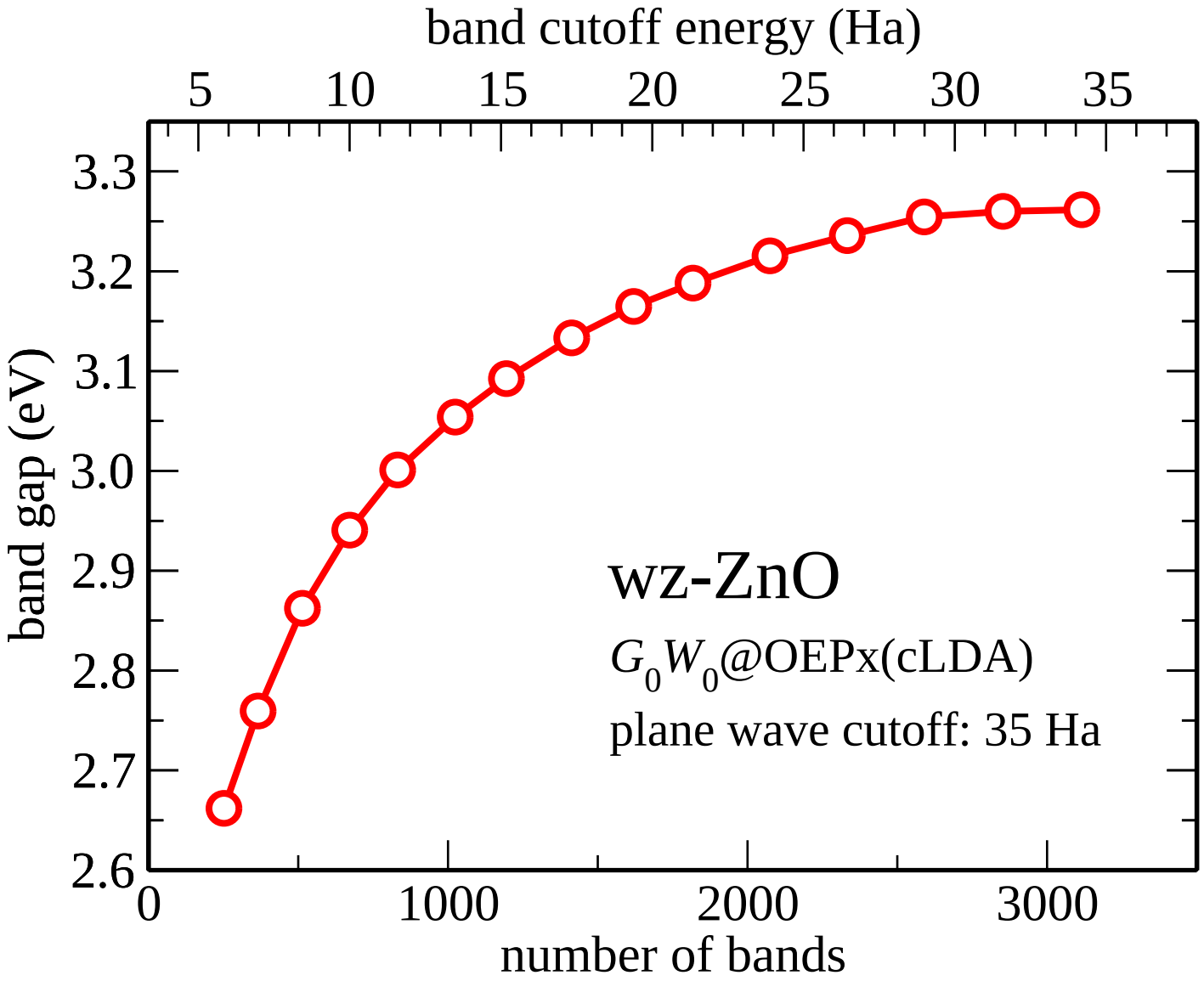
- Hartree-Fock (exchange-only) gap much too large
- Screening is very important in solids!

ARPES – GW: wurtzite ZnO



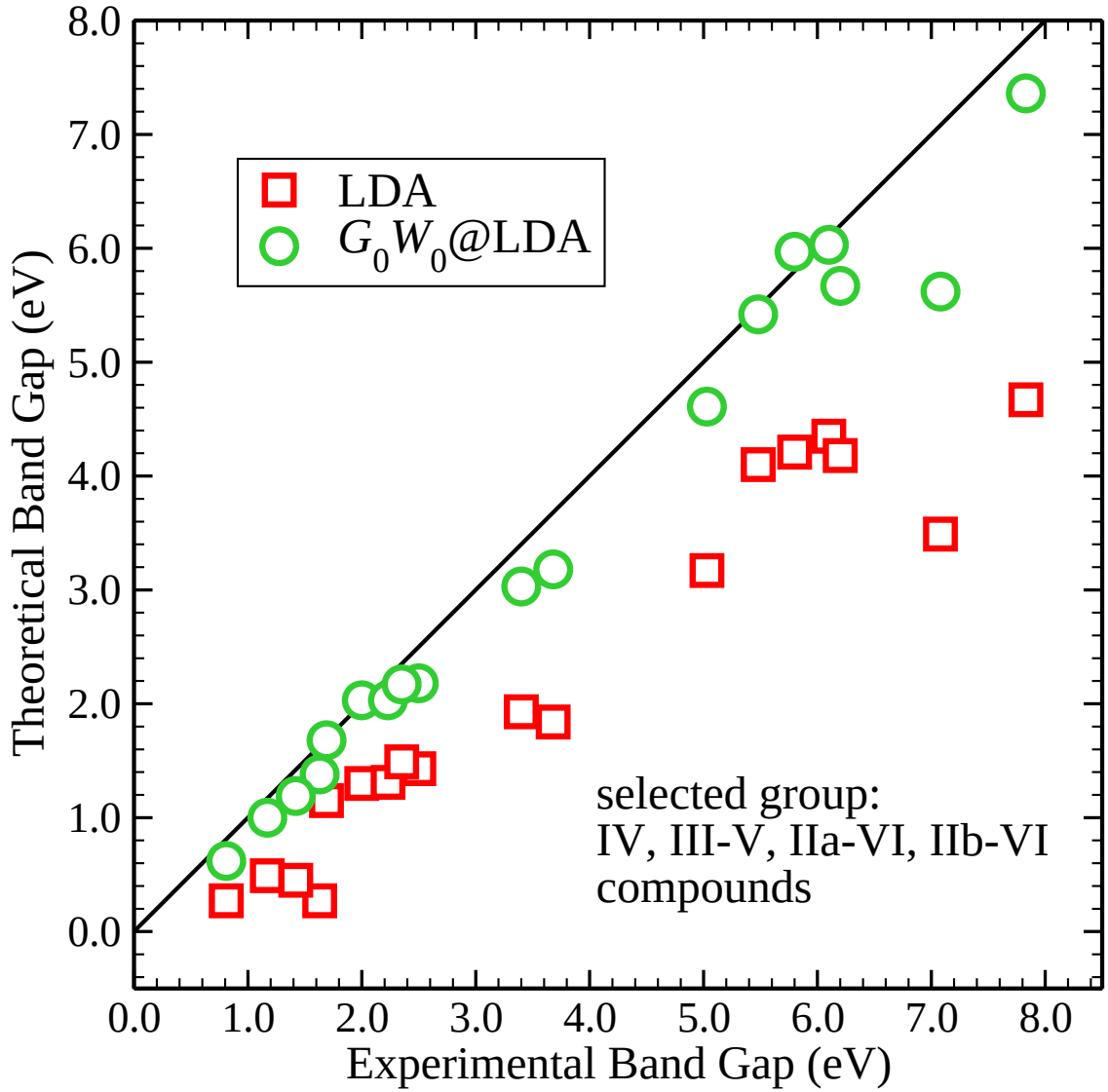
Yan, Rinke, Winkelnkemper, Qteish, Bimberg, Scheffler, Van de Walle, Semicond. Sci. Technol. **26**, 014037 (2011)

wurtzite ZnO – convergence of G_0W_0



see also related work by Shih, Xue, Zhang, Cohen and Louie, PRL **105**, 146401 (2010)

LDA and G_0W_0 – the band gap question



courtesy of Ricardo Gómez-Abal

DFT eigenvalues and excitation energies

Density-functional theory:

- in exact DFT: *ionization potential given by Kohn-Sham eigenvalue of highest occupied state*

$$I_{\mathrm{KS}} = -\epsilon_N(N)$$

- otherwise Janak's theorem: (PRA 18, 7165 (1978)))

$$\frac{\partial E}{\partial n_s} = \epsilon_s$$

rearranging and making mid point approximation:

$$E(N+1,s) - E(N) = \int_0^1 dn\, \epsilon_s(n) \approx \epsilon_s(0.5)$$

Ionisation Potential, Electron Affinity and (Band) Gaps

Could use total energy method to compute

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

Ionisation potential: *minimal energy to remove an electron*

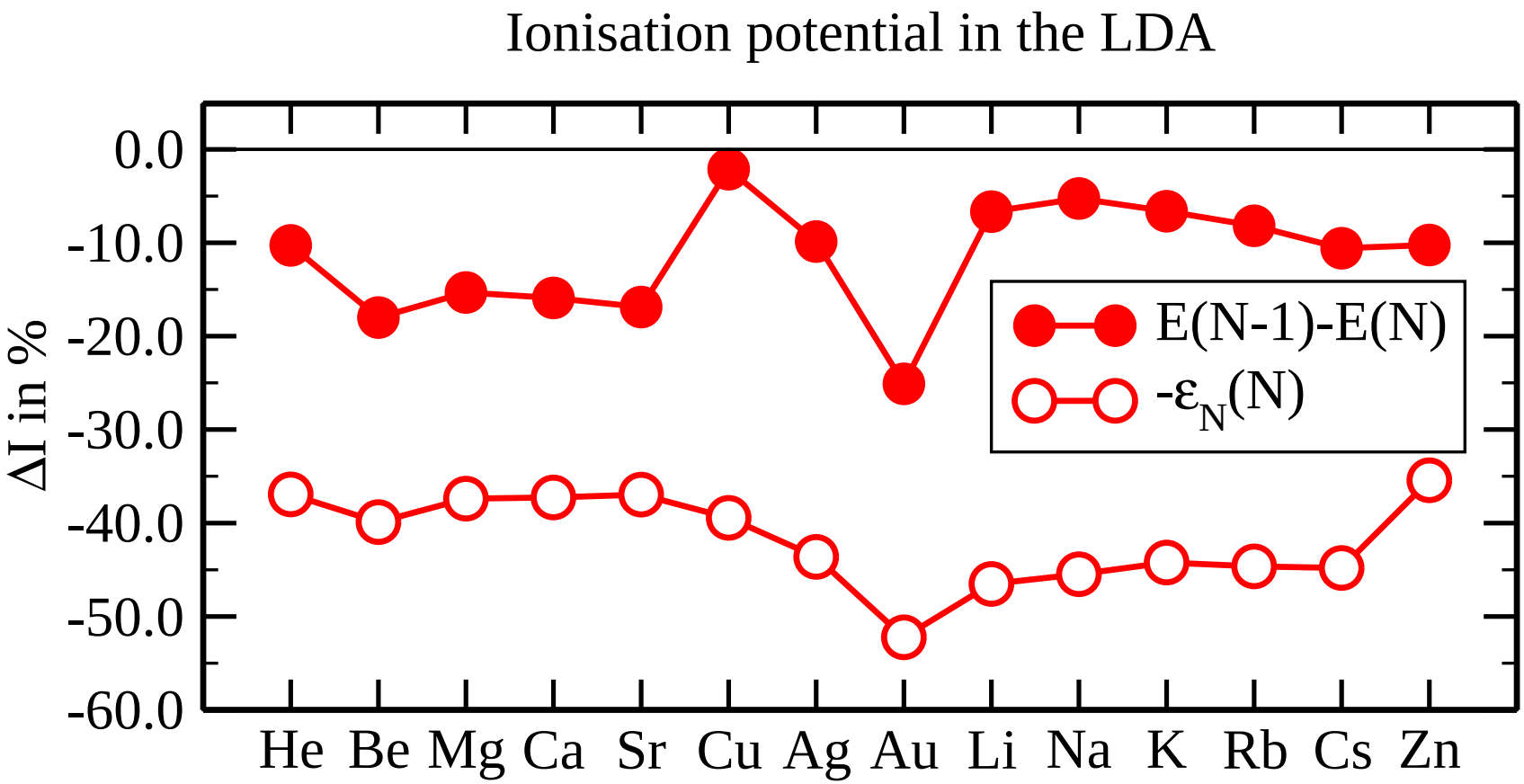
$$I = E(N-1) - E(N)$$

Electron affinity: *minimal energy to add an electron*

$$A = E(N) - E(N+1)$$

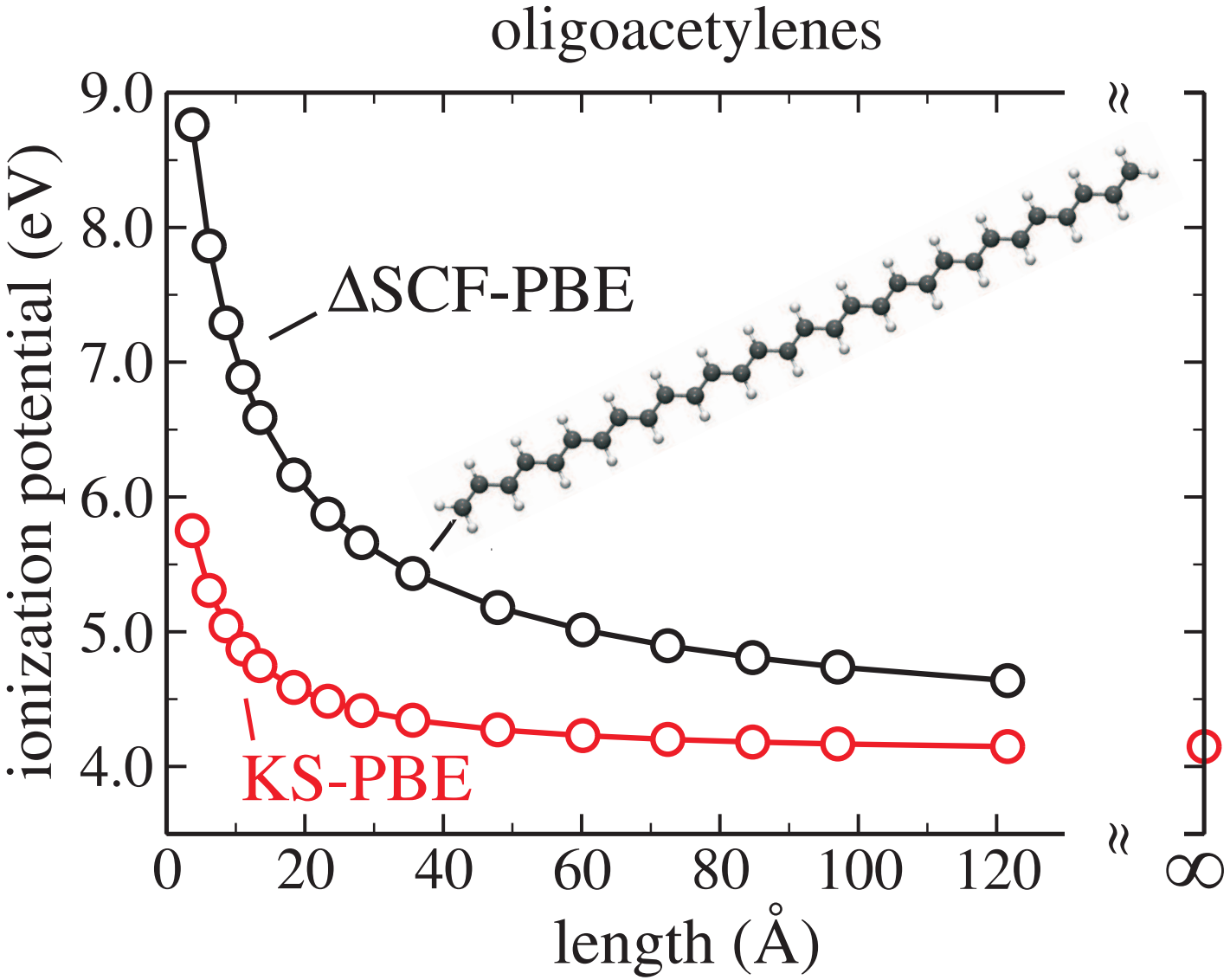
(Band) gap: $E_{gap} = I - A$

Ionisation Potential, Electron Affinity and Band Gap



Reference: NIST – Atomic reference data

ΔSCF versus eigenvalues for finite systems



data courtesy of Max Pinheiro

Band Gap of Semiconductors

- Band gap: $E_{gap} = I - A = E(N+1) - 2E(N) + E(N-1)$
- For solids $E(N+1)$ and $E(N-1)$ cannot be reliable computed
- In Kohn-Sham the highest occupied state is exact

$\Rightarrow$

$$\begin{aligned} E_{gap} &= \epsilon^{\mathrm{KS}}_{N+1}(N+1) - \epsilon^{\mathrm{KS}}_{N}(N) \\ &= \underbrace{\epsilon^{\mathrm{KS}}_{N+1}(N+1) - \epsilon^{\mathrm{KS}}_{N+1}(N)}_{\Delta_{xc}} + \underbrace{\epsilon^{\mathrm{KS}}_{N+1}(N) - \epsilon^{\mathrm{KS}}_{N}(N)}_{E^{\mathrm{KS}}_{gap}} \end{aligned}$$

- For solids: $N \gg 1 \quad \Rightarrow \quad \Delta n(\mathbf{r}) \to 0$ for $N \to N+1$

$\Rightarrow$ discontinuity in v_{xc} upon changing the particle number

$$\Delta_{xc} = \left(\left. \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \right|_{N+1} - \left. \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \right|_{N} \right) + \mathcal{O}\left(\frac{1}{N}\right)$$

Ionisation Potential, Electron Affinity and Band Gap

so what about ΔSCF for excitations?

ΔSCF: $\epsilon_s = E_{\mathrm{DFT}}(N) - E_{\mathrm{DFT}}(N \pm 1, s)$

- reasonably good for I and A of small finite systems

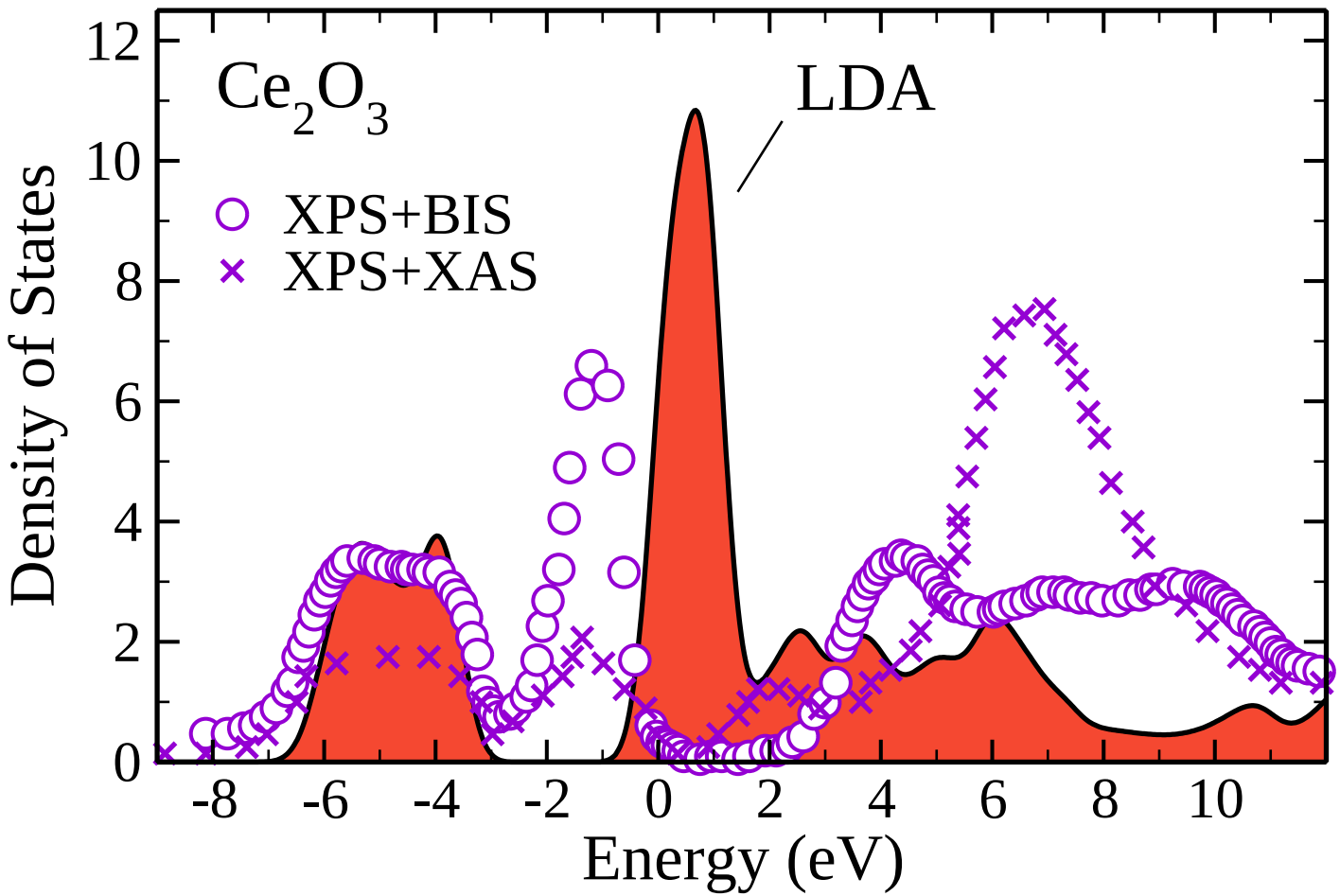
but:

- most functionals suffer from delocalization or self-interaction error (Science **321**, 792 (2008))

$\Rightarrow$ the more delocalized the state, the larger the error

- only truely justified for differences of ground states
  - ionisation potential, electron affinity
  - excited states that are ground states of particular symmetry
- difficult to find excited state wavefunction (density)
- excited state density is not unique
- separate calculation for every excitation needed
  - not practical for large systems or solids

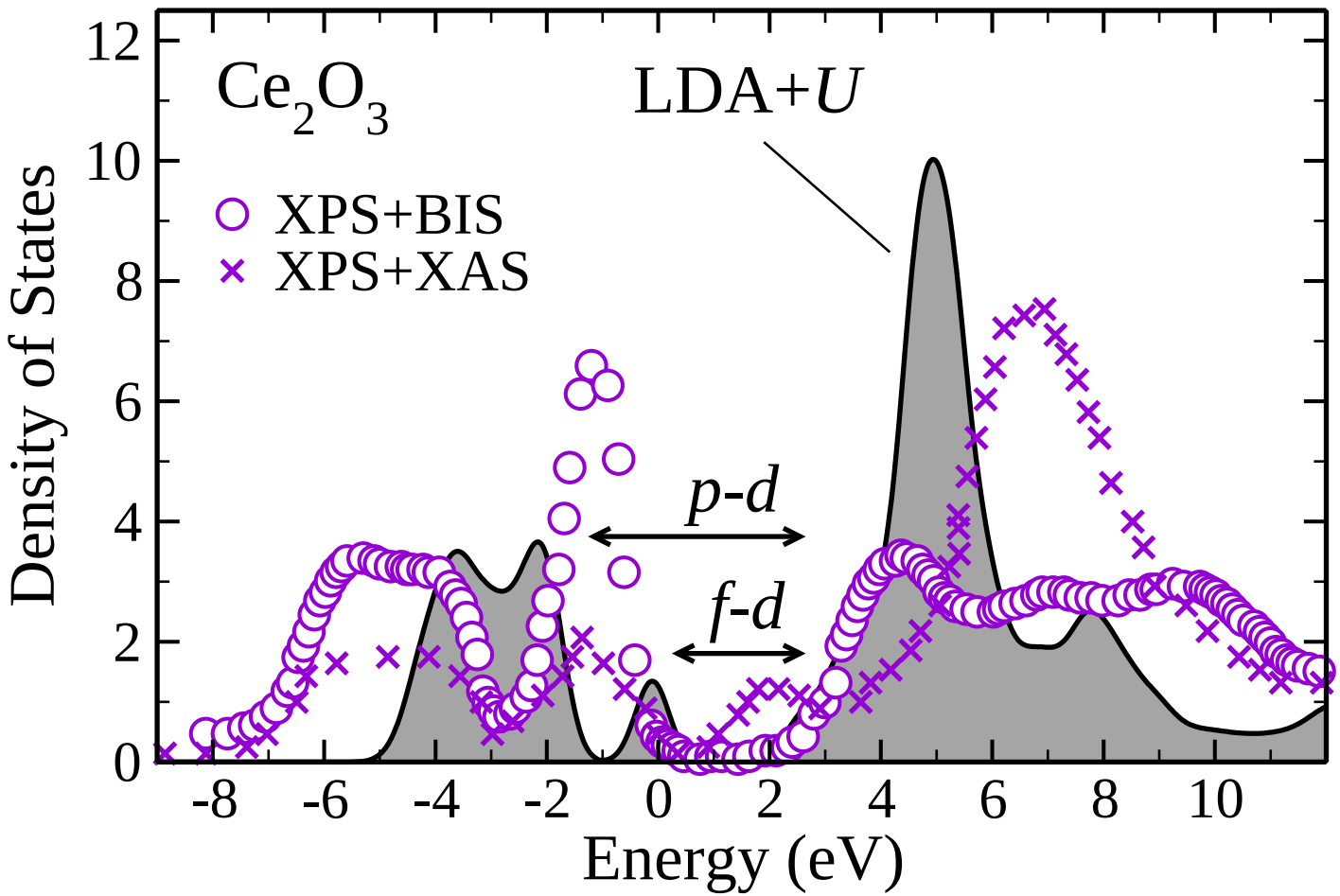
Can we also describe localized d- or f-electrons?



- DFT-LDA erroneously predicts metallic state

Exp: J. W. Allen, J. Magn. Magn. Mater. (1985), D. R. Mullins *et al.*, Surf. Sci. (1998)

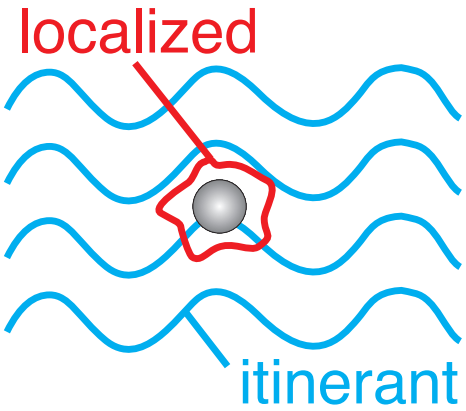
Ce_2O_3 in LDA+U



- LDA+U splits f-peaks and opens gap

f-Electron Systems – Lanthanide Oxides

f-Electrons



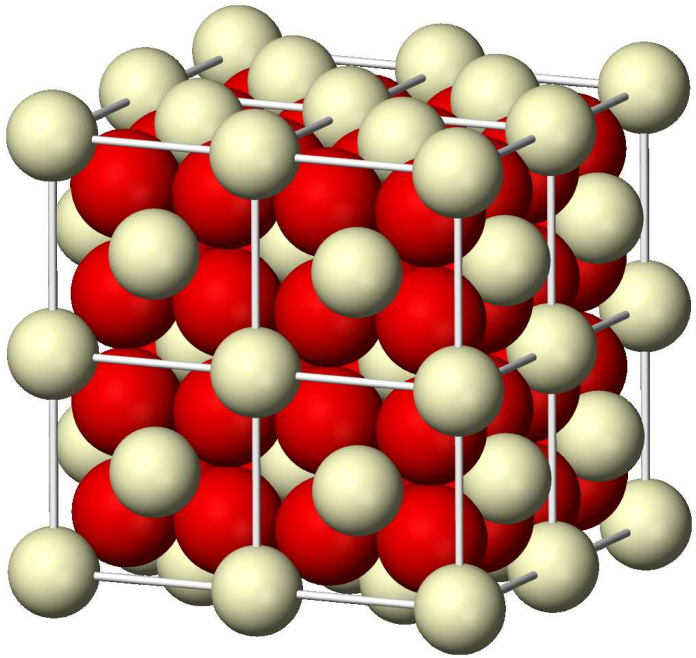
- localized and itinerant electrons

$\Rightarrow$ rich physics and chemistry

- LDA/GGA often not adequate
- often termed *strongly correlated*

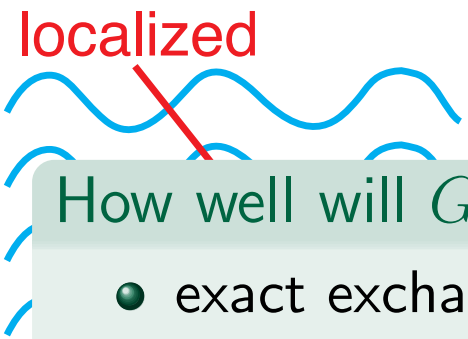
Lanthanide Oxides

- Ln_2O_3 (Ln=lanthanide series)
- technologically important materials e.g. catalysis



f-Electron Systems – Lanthanide Oxides

f-Electrons



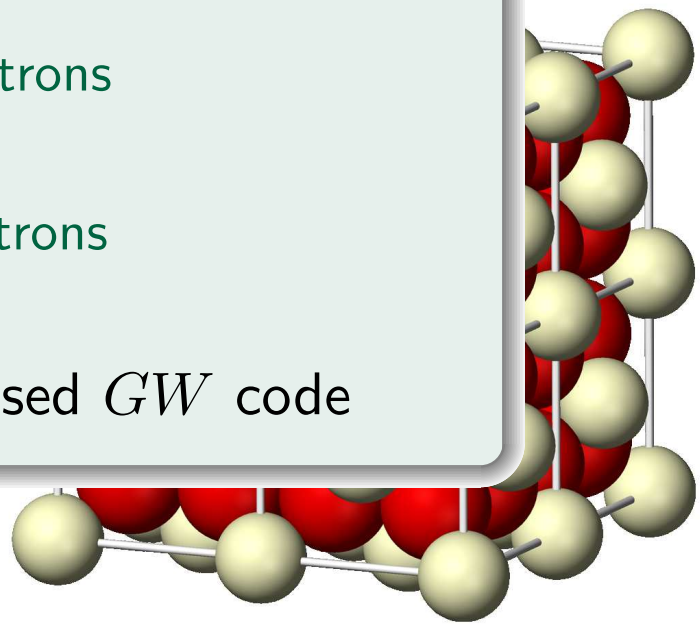
- localiz
- $\Rightarrow$ rich p
- LDA/
- often termed *strongly correlated*

Lanthanide Oxides

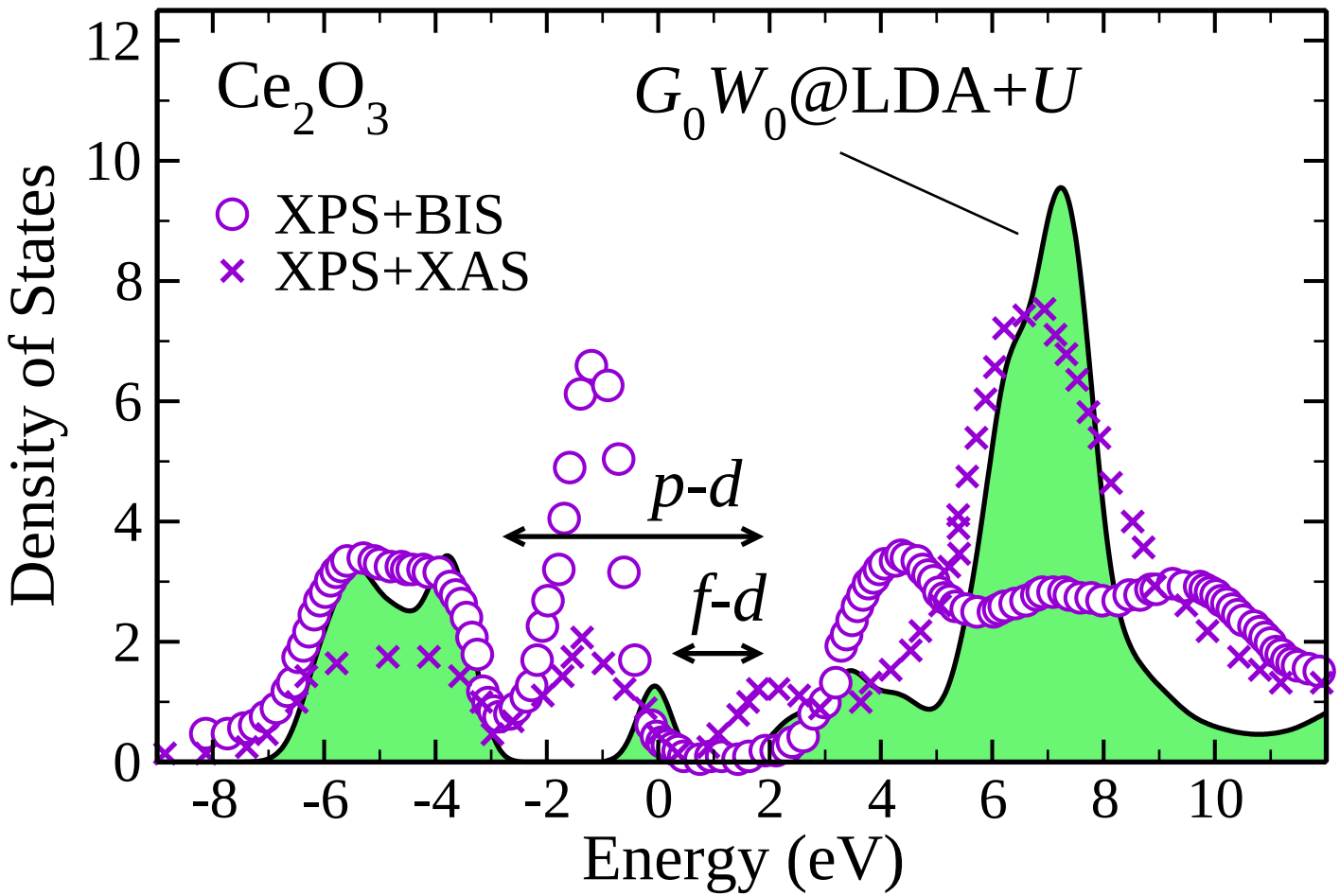
- Ln_2O_3 (Ln=lanthanide series)
- technologically important

How well will GW perform?

- exact exchange
  - essential for localized electrons
- screening
  - essential for itinerant electrons
- answers from new LAPW-based GW code



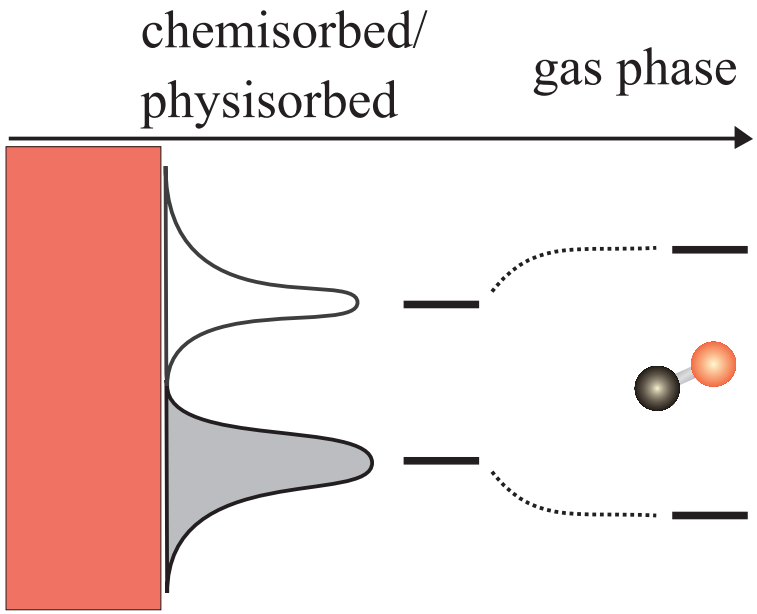
Ce_2O_3 in G_0W_0@LDA+U



- G_0W_0@LDA+U reproduces main peaks and gaps

H. Jiang, R. Gomez-Abal, P. Rinke and M. Scheffler, Phys. Rev. Lett. **102**, 126403 (2009)

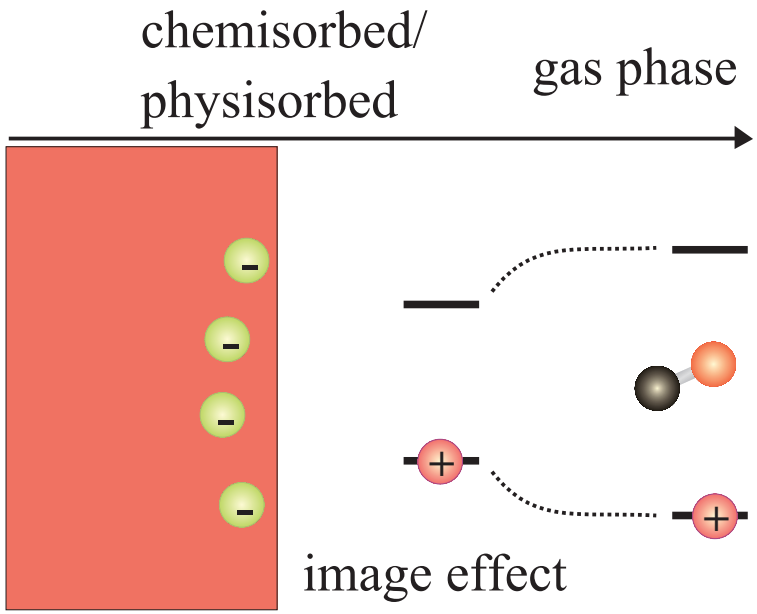
GW for surfaces – CO on NaCl



- change upon absorption:
  - chemical bonding
  - polarization of surface
  - polarization of molecule

PRL **103**, 056803 (2009), PRL **102**, 046802 (2009), PRL **97** 216405 (2006)

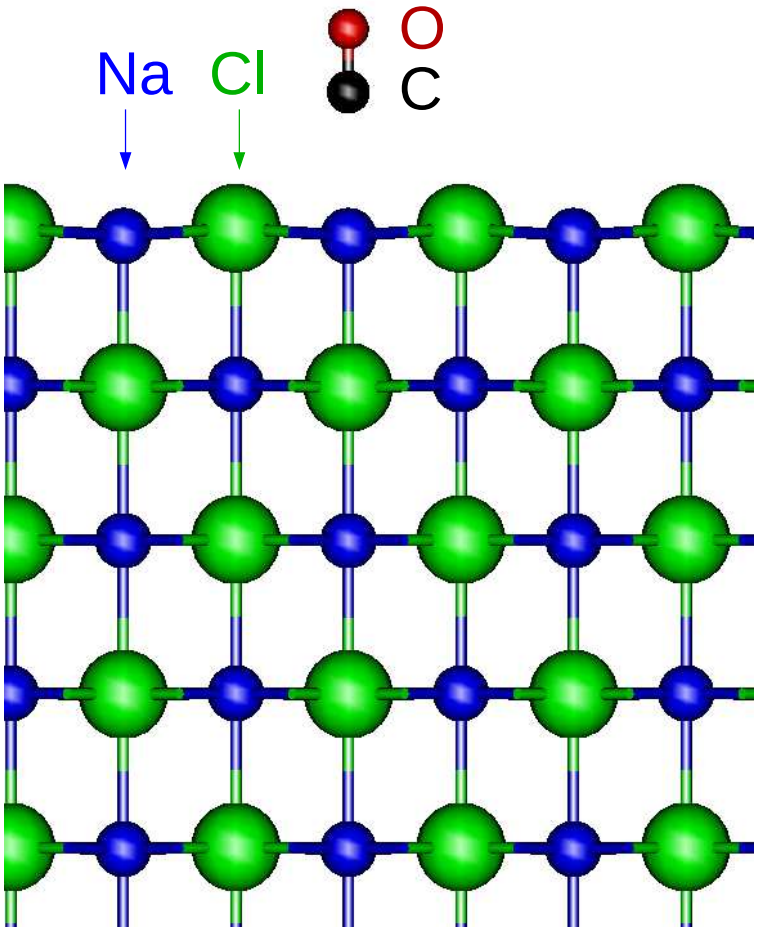
GW for surfaces – CO on NaCl



- change upon absorption:
  - chemical bonding
  - polarization of surface
  - polarization of molecule

PRL **103**, 056803 (2009), PRL **102**, 046802 (2009), PRL **97** 216405 (2006)

GW for surfaces – CO on NaCl



- change upon absorption:
  - chemical bonding
  - polarization of surface
  - polarization of molecule

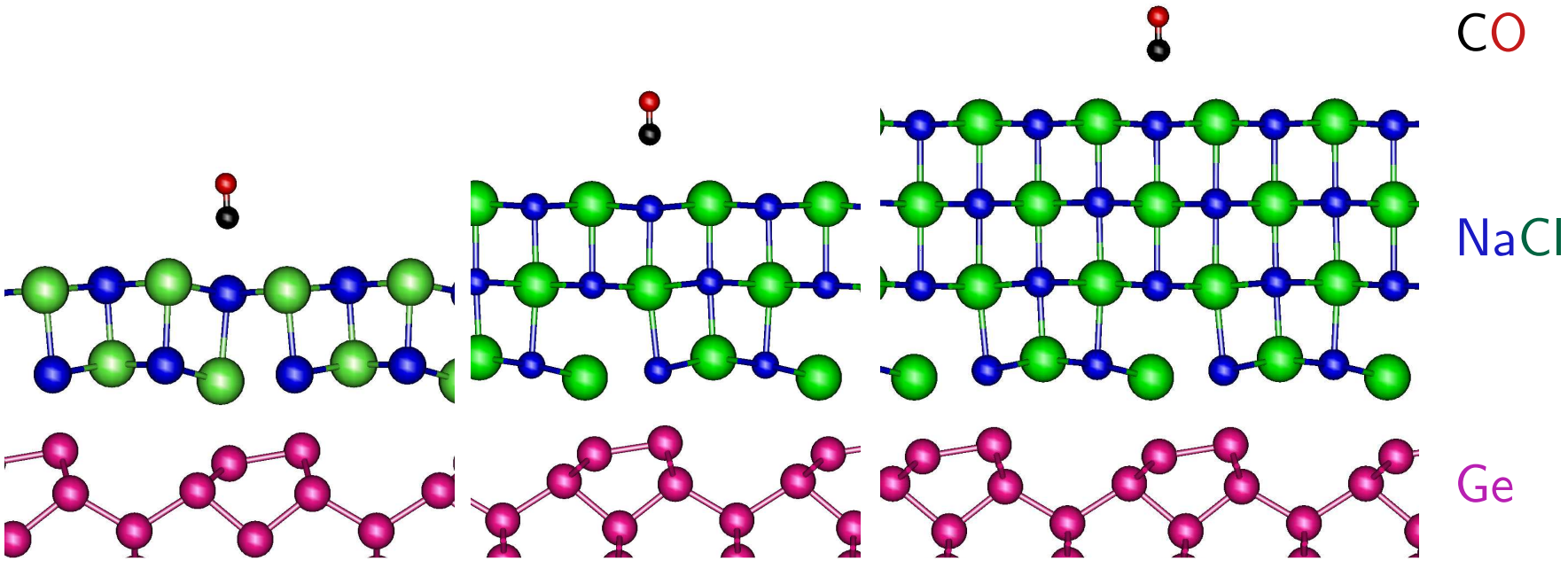
- HOMO-LUMO gap of CO:

gap/eV	LDA	G_0W_0@LDA
free CO :	6.9	15.1
CO@NaCl:	7.4	13.1

- surface polarization significant here

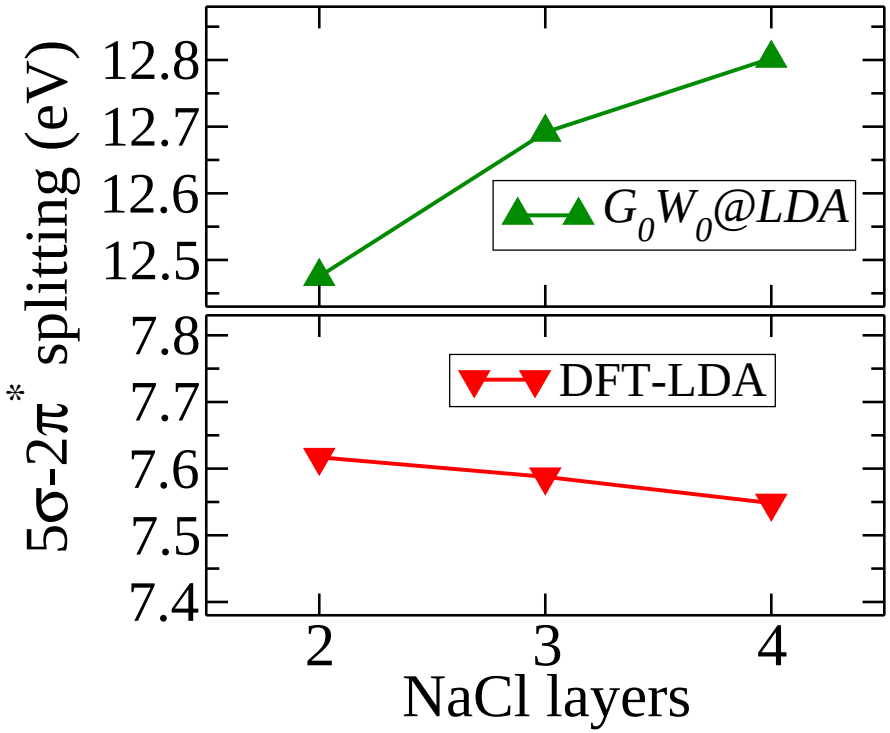
PRL **103**, 056803 (2009), PRL **102**, 046802 (2009), PRL **97** 216405 (2006)

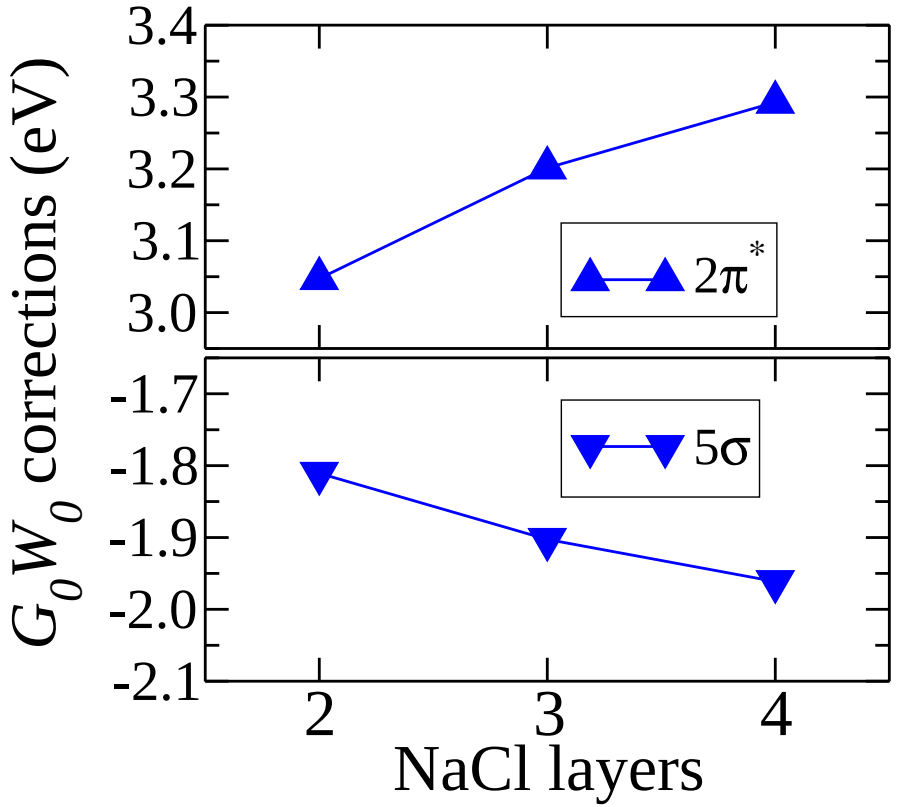
GW for surfaces – CO on Ultrathin NaCl on Ge



- Supported ultrathin films are novel nano-systems with unexpected features (PRL **99**, 086101 (2007))
- Additional electrons/holes on CO see two interfaces
- Will the CO gap depend on NaCl thickness?

GW for surfaces – CO on Ultrathin NaCl on Ge





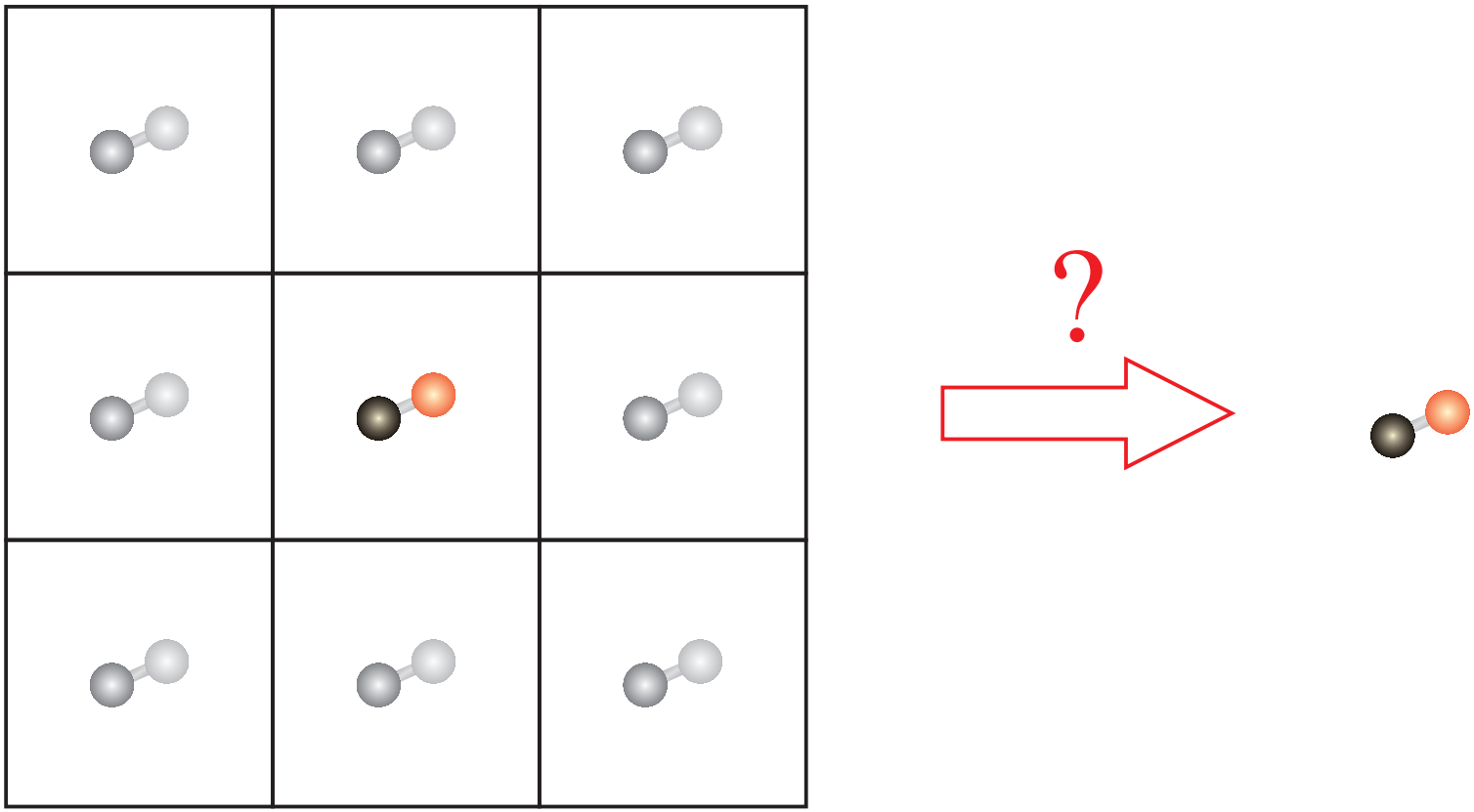
- Polarization at NaCl/Ge interface gives layer-dependent CO gap

$\Rightarrow$ molecular levels can be tuned by polarization engineering:

  - interesting for molecular electronics and quantum transport

C. Freysoldt, P. Rinke, and M. Scheffler, PRL **103**, 056803 (2009)

Can we Eliminate Periodic Boundary Conditions in GW for Finite Systems?



FHI-*aims* – FHI *ab initio molecular simulations* package

Local atom-centered basis

$$\varphi_{i[lm]}(\mathbf{r}) = \frac{u_i(r)}{r} Y_{lm}(\Omega)$$

Standard DFT (LDA, GGA)

- all-electron
- periodic, cluster systems on equal footing
- favorable scaling (system size and CPUs)

Beyond DFT (only for finite systems)

- Hartree-Fock, hybrid functionals, MP2, RPA
- quasiparticle self-energies: GW, MBPT2

V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, and M. Scheffler, Comp. Phys. Comm. **180**, 2175 (2009).

CO revisited – Comparison of FHI-aims and GWST

G_0W_0@LDA HOMO-LUMO gap of gas phase CO:

GWST†	:	15.10 eV
FHI-aims	:	15.05 eV
experiment*	:	15.80 eV

†GWST: GW space-time code (real-space/plane-waves)

(Steinbeck, Godby *et al.* CPC **117** (1999), CPC **125** (2000))

* *Constants of Diatomic Molecules* (1979), PRL **22**, 1034 (1969)

CO revisited – G_0W_0 with Different Starting Points

CO/eV	ϵ_{HOMO}	ϵ_{LUMO}
LDA	-9.12	-2.25
PBE	-9.04	-2.00
PBE0	-10.75	-0.75
G_0W_0@LDA	-13.31	1.74
G_0W_0@PBE	-13.17	1.84
G_0W_0@PBE0	-13.76	2.02
experiment*	-14.00	1.80

- PBE0 improves over LDA and PBE here
- G_0W_0@PBE0 gives the best performance

  (X. Ren, P. Rinke, and M. Scheffler, Phys. Rev. B **80**, 045402 (2009))

* *Constants of Diatomic Molecules* (1979), PRL **22**, 1034 (1969)

GW – The Issue of Self-Consistency

Hedin's GW equations:

$$
\begin{aligned}
G(1,2) &= G_0(1,2) \qquad \text{notation:} \quad 1 = (\mathbf{r}_1, \sigma_1, t_1) \\
\Gamma(1,2,3) &= \delta(1,2)\delta(1,3) \\
P(1,2) &= -iG(1,2)G(2,1^+) \\
W(1,2) &= v(1,2) + \int v(1,3)P(3,4)W(4,2)d(3,4) \\
\Sigma(1,2) &= iG(1,2)W(2,1)
\end{aligned}
$$

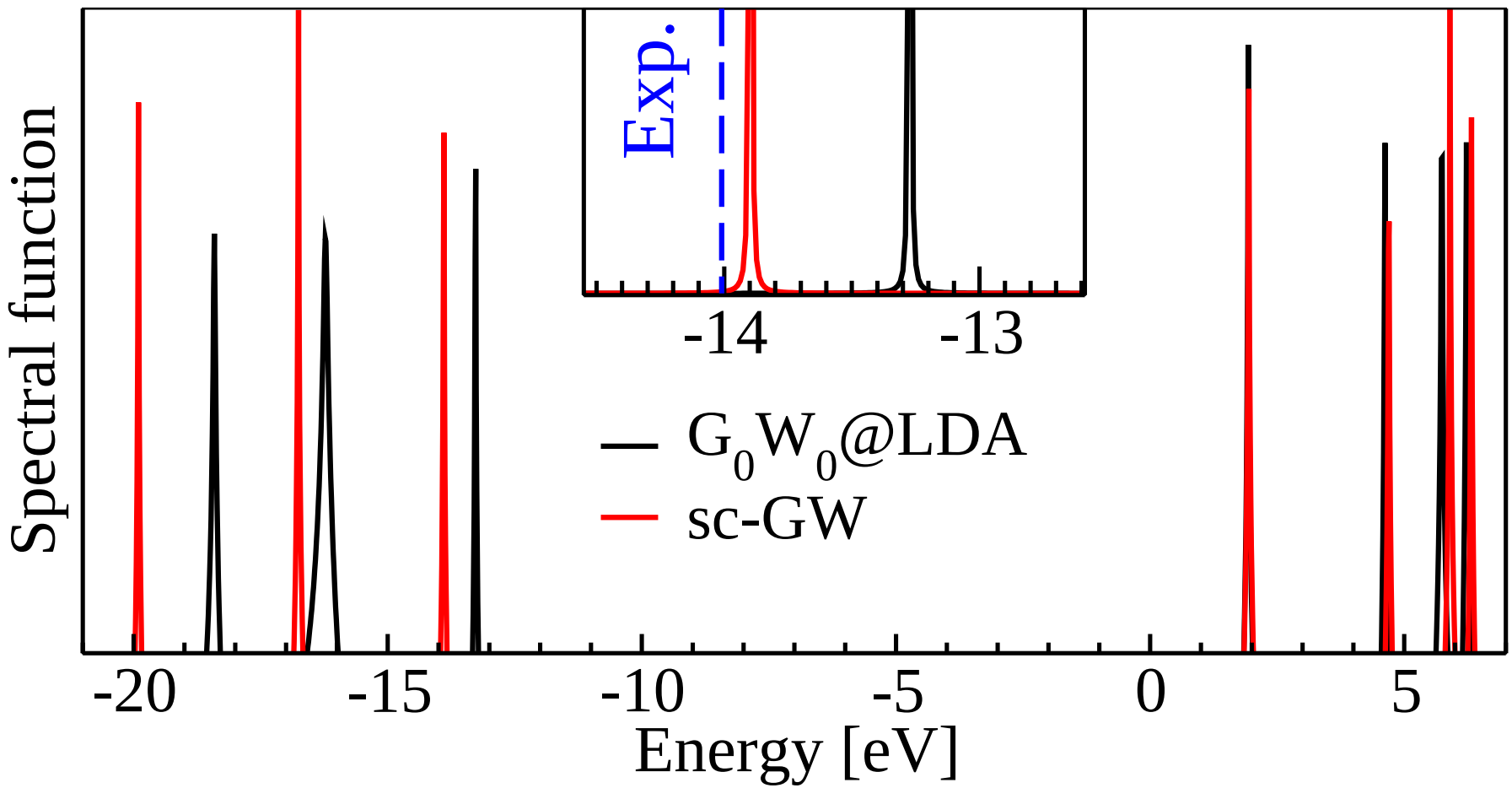
self-consistency

self-consistency

Dyson's equation:

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

CO – self-consistent GW



CO revisited – self-consistent GW

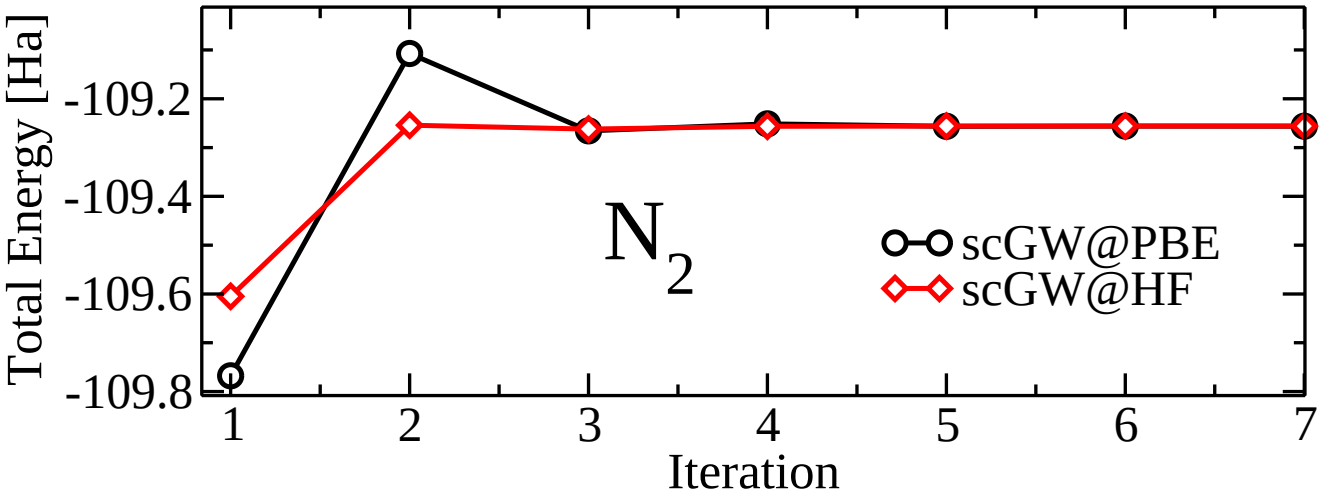
CO/eV	ϵ_{HOMO}	ϵ_{LUMO}
G_0W_0@LDA	-13.31	1.74
G_0W_0@PBE	-13.17	1.84
G_0W_0@PBE0	-13.76	2.02
$scGW$	-13.63	2.16
experiment*	-14.00	1.80

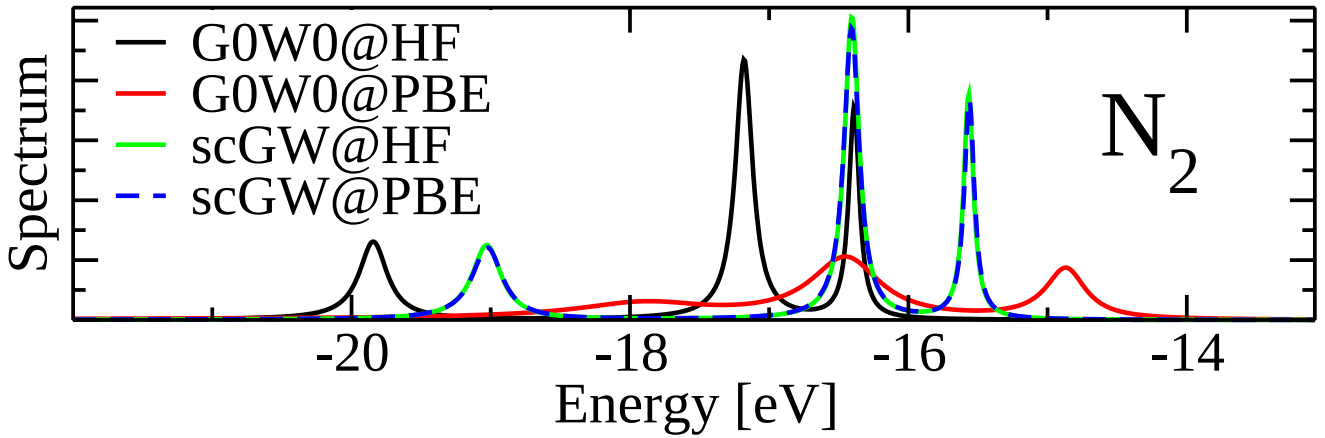
- $scGW$ independent of starting point
- G_0W_0@PBE0 outperforms $scGW$ in this case

** Constants of Diatomic Molecules* (1979), PRL **22**, 1034 (1969)

Dependence on the starting point: N_2

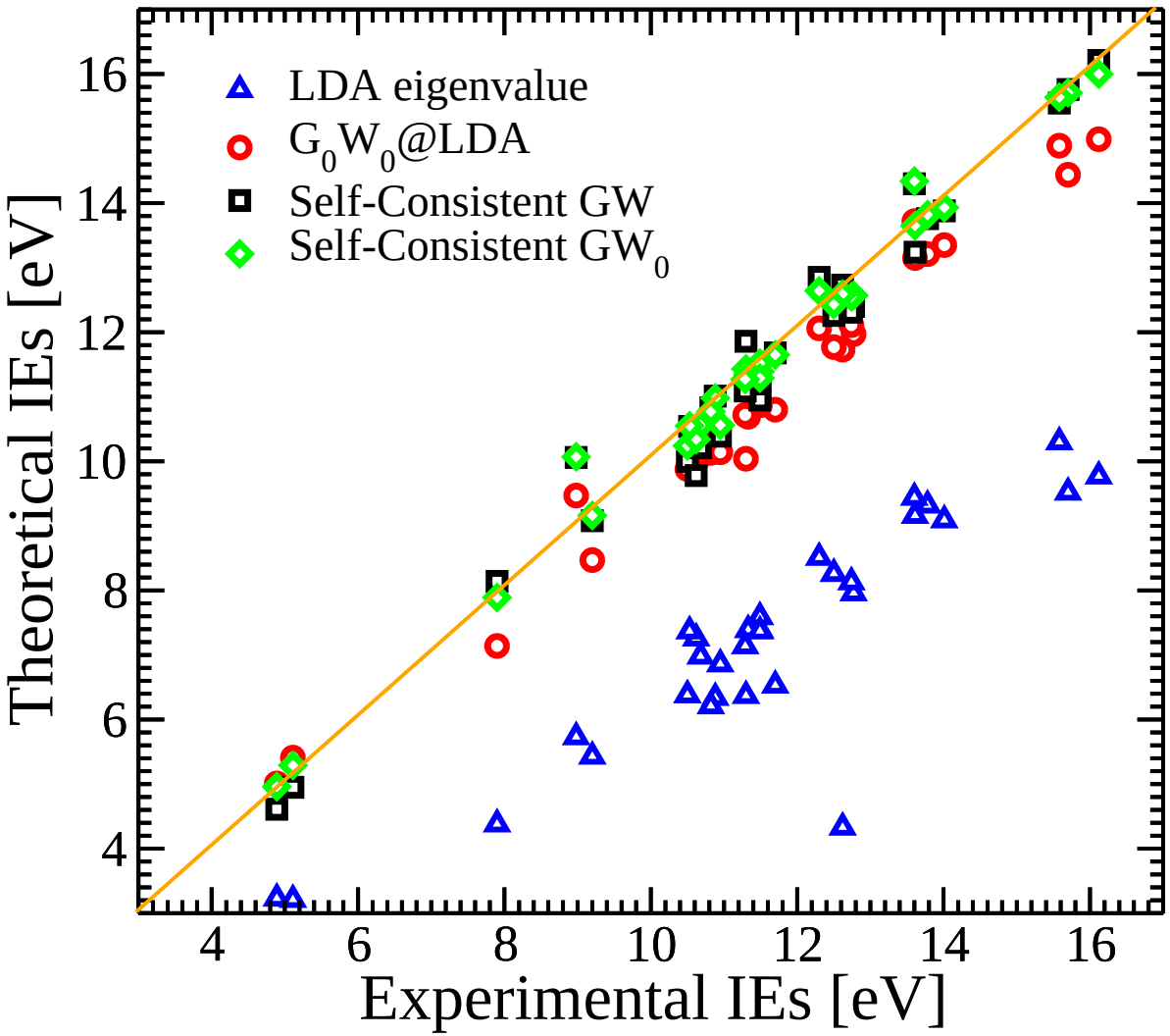
Galitskii-Migdal formula: $E_{\text{tot}} = -\frac{i}{2}\int Tr\left[(\omega + h_0)G(\omega)\right]\frac{d\omega}{2\pi}$





At self-consistency no dependence on input Green's function!

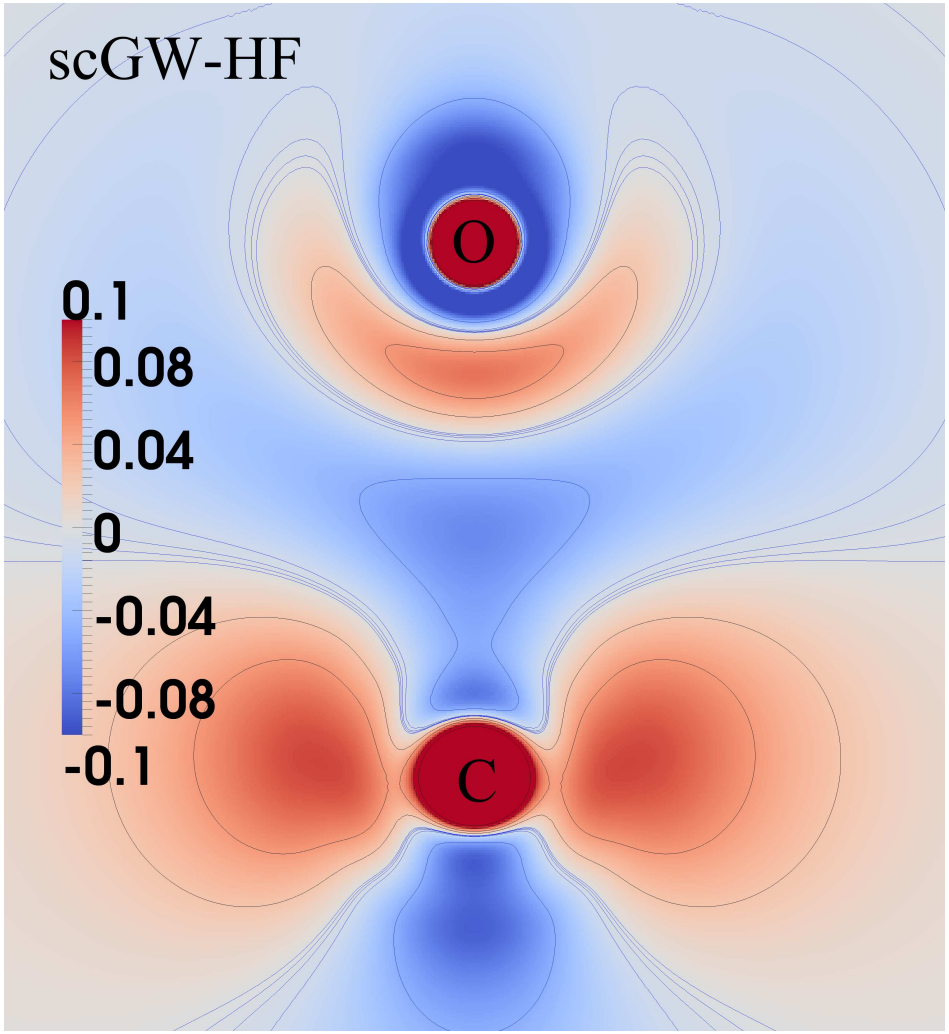
scGW and ionization potentials



deviation from exp.	
LDA	40.0%
G_0W_0@LDA	5.6%
scGW	2.9%
GW_0@LDA	1.5%

set taken from Rostgaard, Jacobsen, and Thygesen, PRB **81**, 085103, (2010)

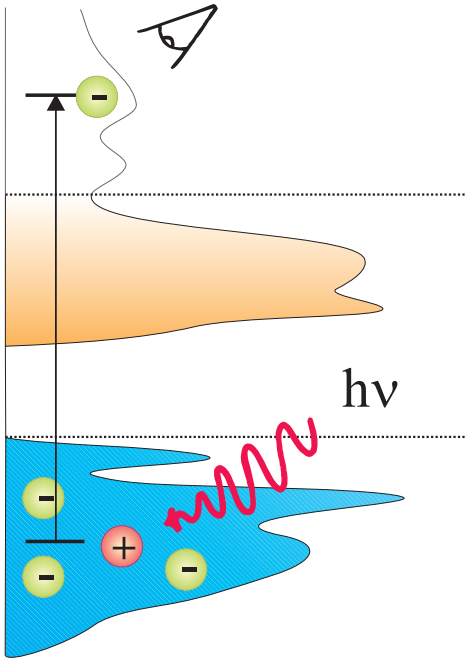
The scGW density



- density from Green's function: $\rho(\mathbf{r}) = -i \sum_\sigma G_{\sigma\sigma}(\mathbf{r}, \mathbf{r}, \tau = 0^+)$

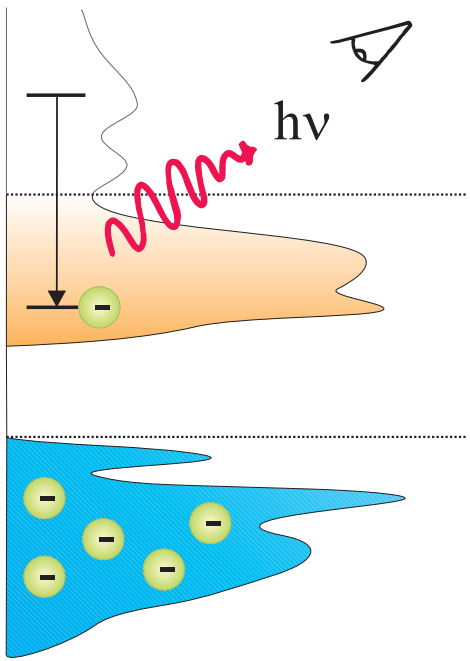
Band structures: photo-electron spectroscopy

Photoemission



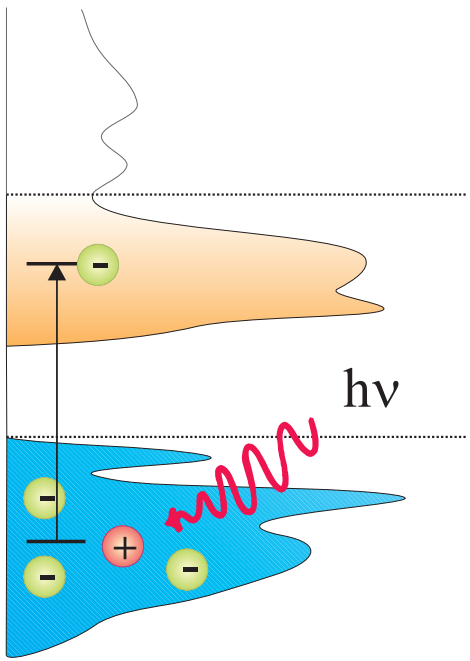
GW

Inverse Photoemission



GW

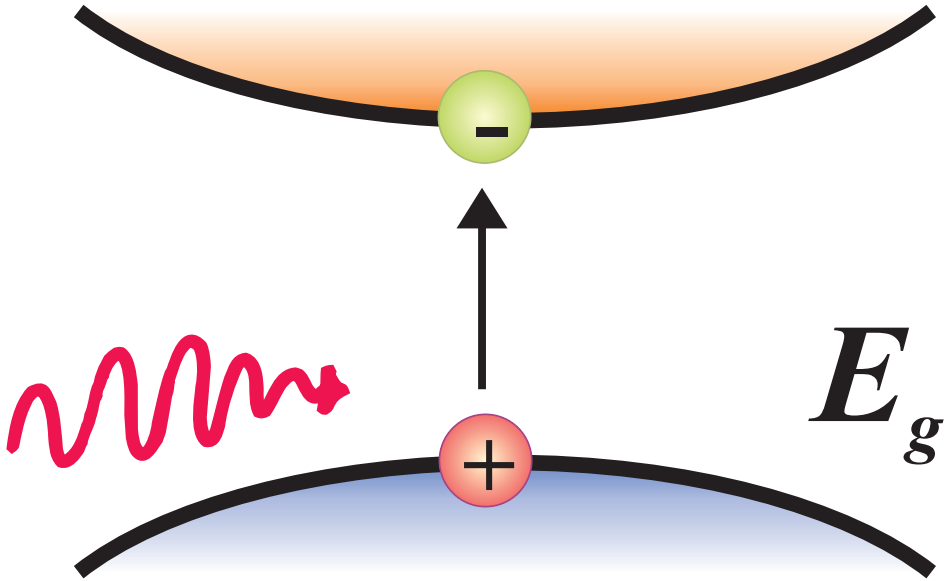
Absorption



BSE
TDDFT

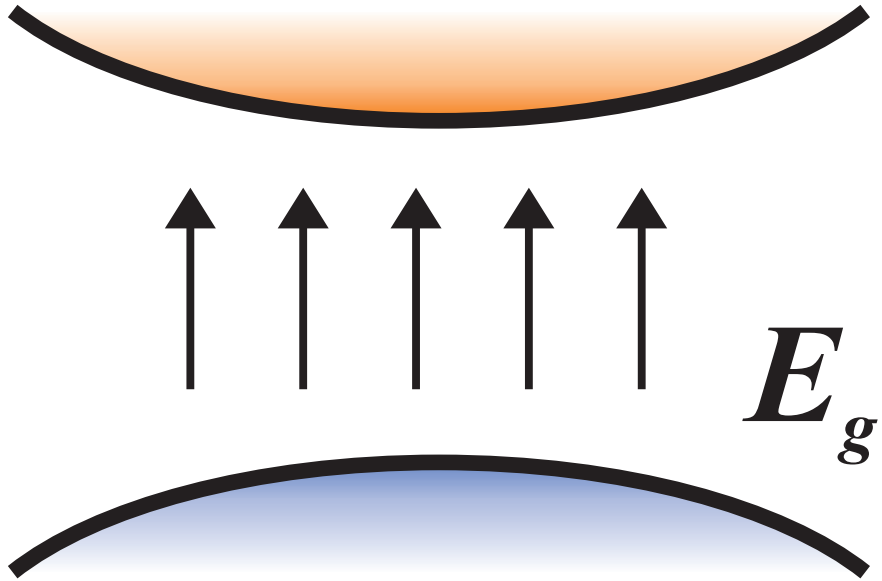
Optical absorption – independent particles

Absorption spectrum $= Im\, \varepsilon_M(\omega)$ (macroscopic dielectric constant)



Optical absorption – independent particles

Absorption spectrum $= Im\,\varepsilon_M(\omega)$ (macroscopic dielectric constant)



- Fermi's Golden rule:

$$Im\,\varepsilon_M(\omega) = \frac{16\pi}{\omega^2} \sum_{v}^{occ} \sum_{c}^{unocc} |\langle \psi_v | \mathbf{v} | \psi_c \rangle|^2 \, \delta(\epsilon_c - \epsilon_v - \omega)$$

$\mathbf{v}$: velocity operator

Optical absorption – response function

- Dielectric constant:

$$Im\,\varepsilon_M(\omega) = \lim_{\mathbf{q}\to 0} \frac{1}{\varepsilon^{-1}_{\mathbf{G}=0,\mathbf{G}'=0}(\mathbf{q},\omega)}$$

- Dielectric function:

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

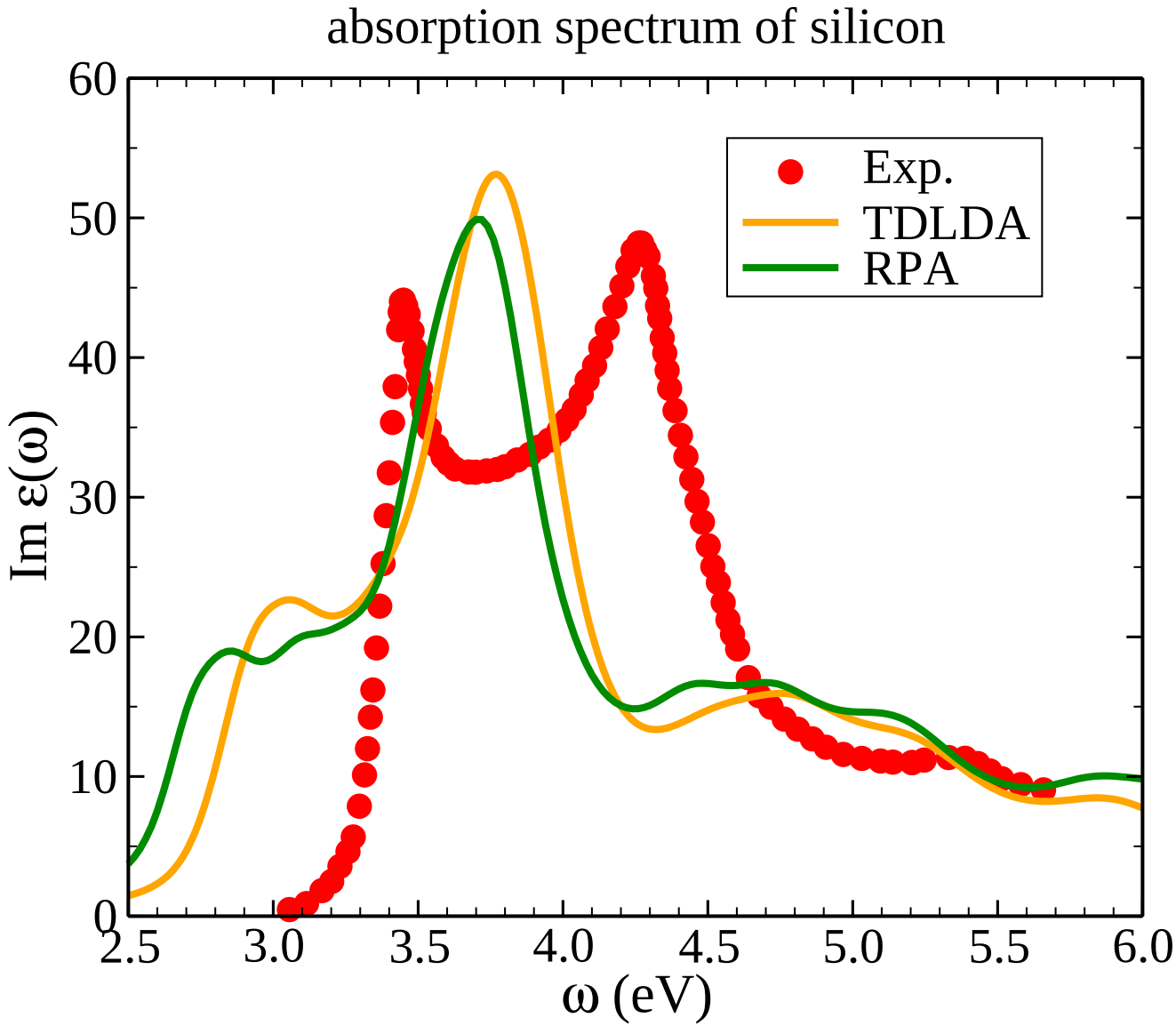
- Response function (in TDDFT):

$$\hat{\chi} = \hat{\chi_0} + \hat{\chi_0}\left[\hat{v} + \hat{f_{xc}}\right]\hat{\chi}$$

- Response function (in RPA):

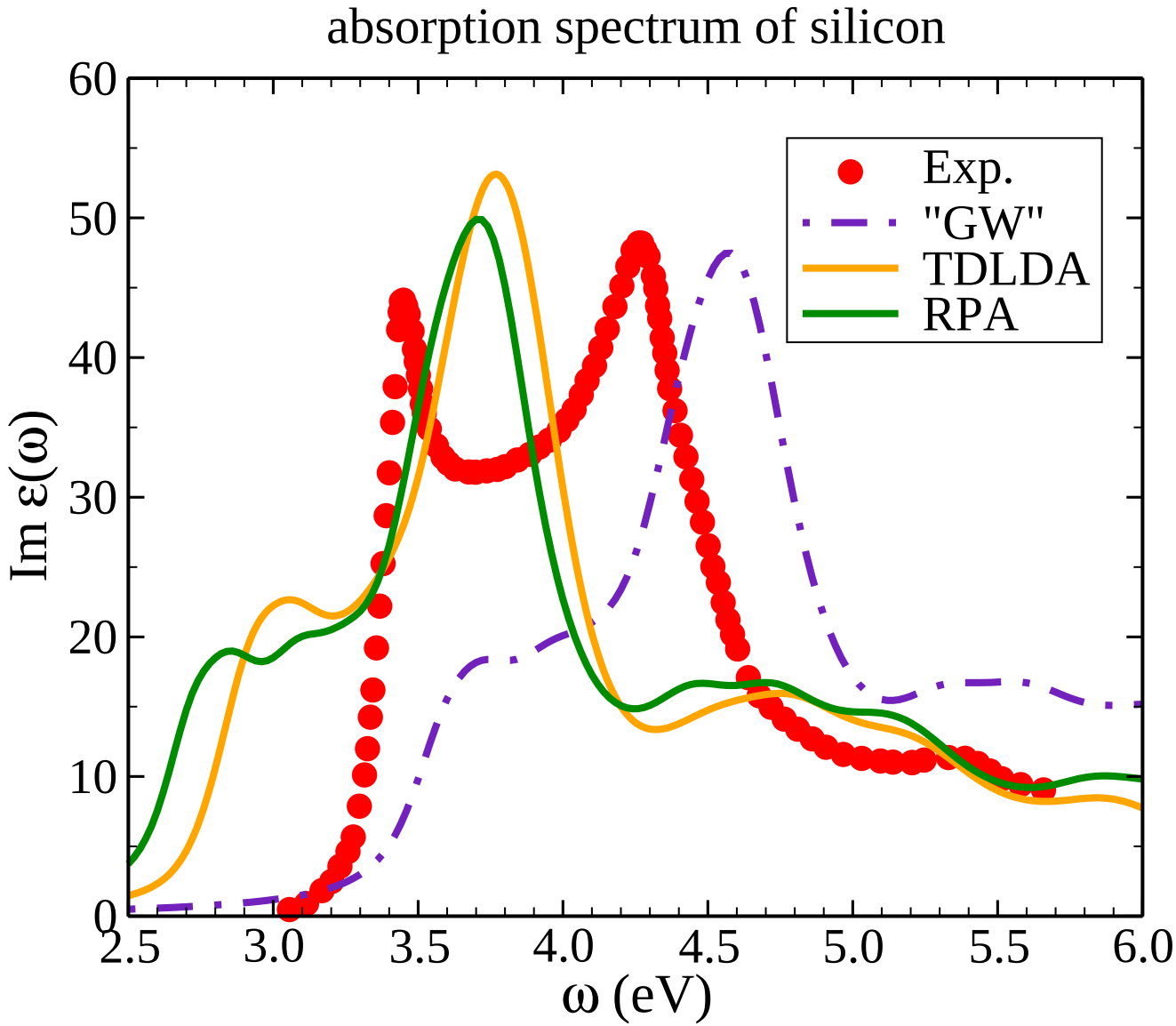
$$\hat{\chi} = \hat{\chi_0} + \hat{\chi_0}\left[\hat{v} + \cancel{\hat{f_{xc}}}\right]\hat{\chi}$$

Optical absorption – response function



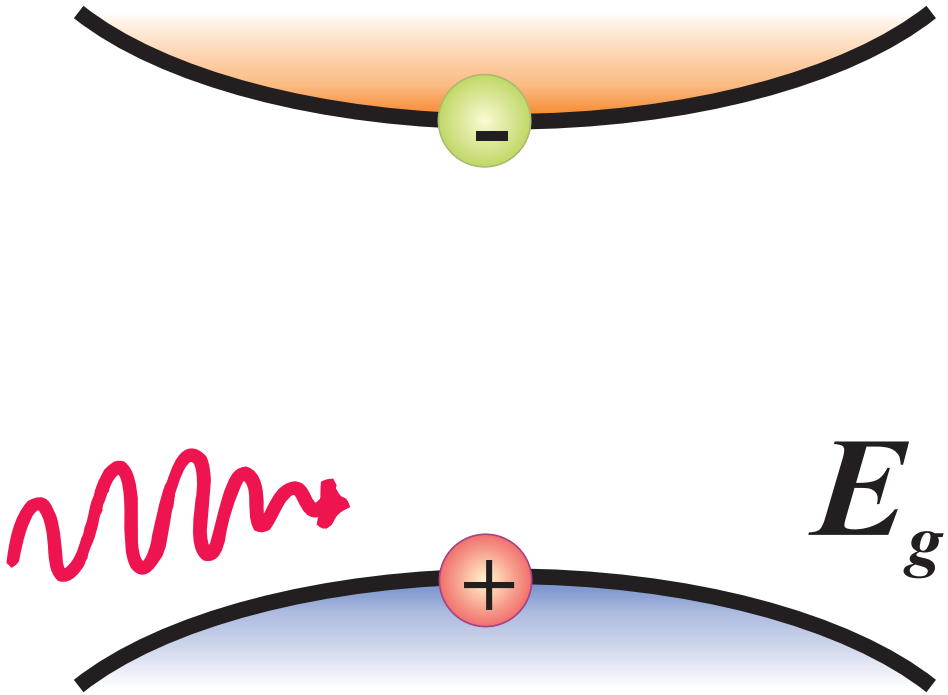
from Sottile, Olevano, and Reining, PRL **91**, 056402 (2003)

Optical absorption – response function

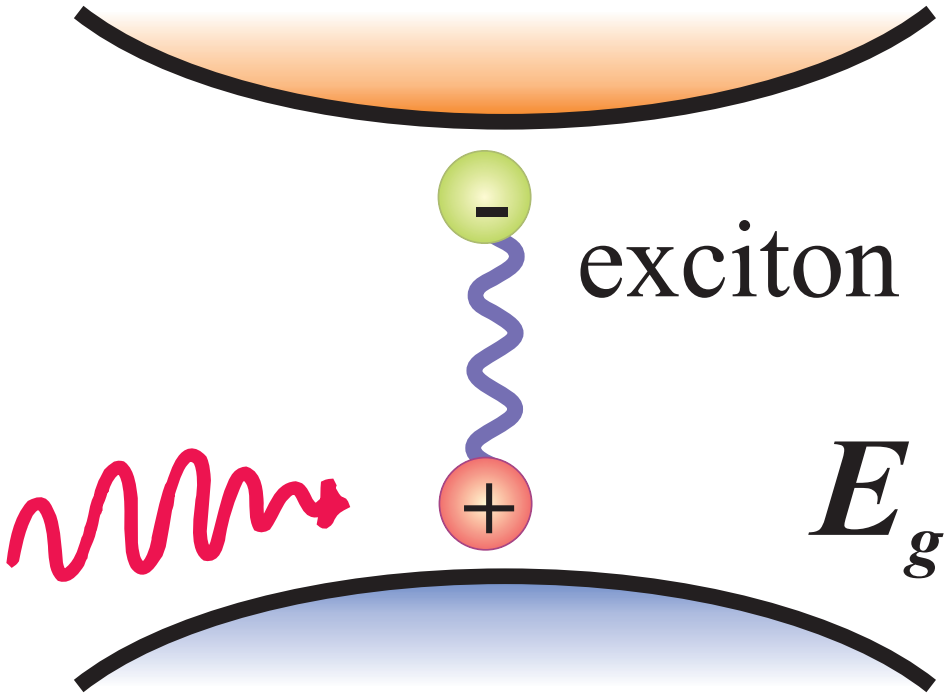


from Sottile, Olevano, and Reining, PRL **91**, 056402 (2003)

Optical absorption – concept of excitons

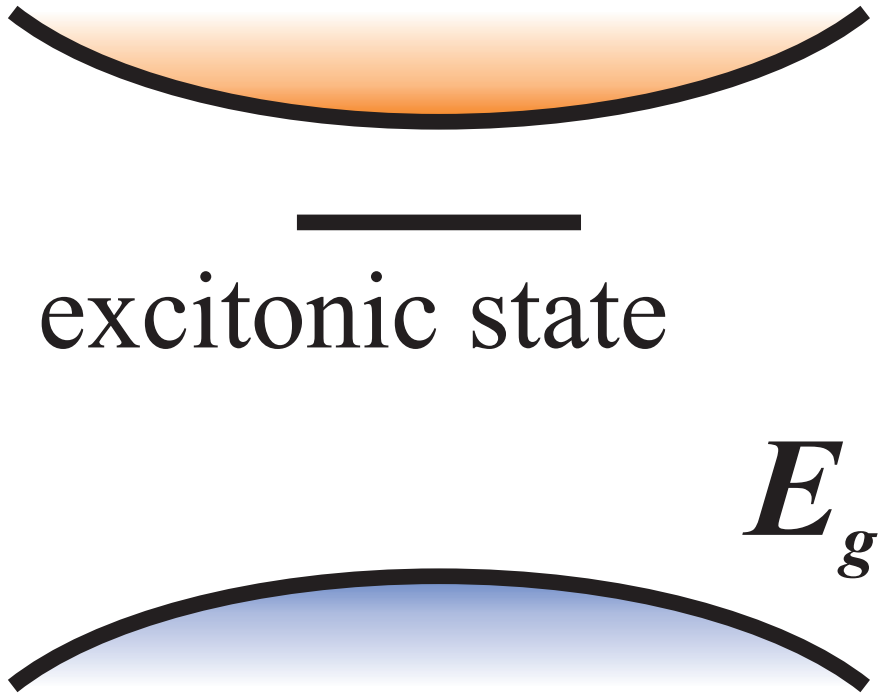


Optical absorption – concept of excitons



- electron-hole interaction lowers the energy
- electron-hole pair (exciton) forms

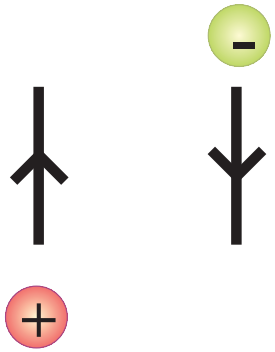
Optical absorption – concept of excitons



- electron-hole interaction lowers the energy
- electron-hole pair (exciton) forms

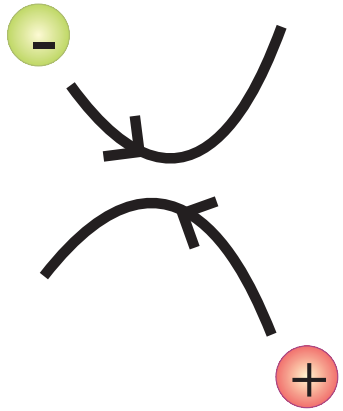
Optical absorption – concept of excitons

one particle Green's function



G(1,2)

two particle Green's function



G(1,2,1',2')

related quantity: two particle response function $S(1, 2, 1', 2')$

Optical absorption – Bethe-Salpeter equation

Approximations for $G(1,2,1',2')$ (or $S(1,2,1',2')$)

- GW approximation for Σ
- approximate $\frac{\delta\Sigma}{\delta G}$ by iW
- take W to be static

$\Rightarrow$ effective eigenvalue problem in electron-hole basis (like Casida's equation)

$$H^{eff} A^{\lambda} = E^{\lambda} A^{\lambda}$$

Optical absorption – Bethe-Salpeter equation

- Bethe-Salpeter equation (BSE):

$$H^{eff} A^{\lambda} = E^{\lambda} A^{\lambda}$$

$$H^{eff}_{vv'cc'} = (\epsilon_c - \epsilon_v)\delta_{vv'}\delta_{cc'} + \langle vc|\bar{v}|v'c'\rangle - \langle vc|W|v'c'\rangle$$

  - $\bar{v} \equiv$ Coulomb potential without the long-range part
  - $\epsilon_{v,c}$ are G_0W_0 quasiparticle energies

- macroscopic dielectric constant

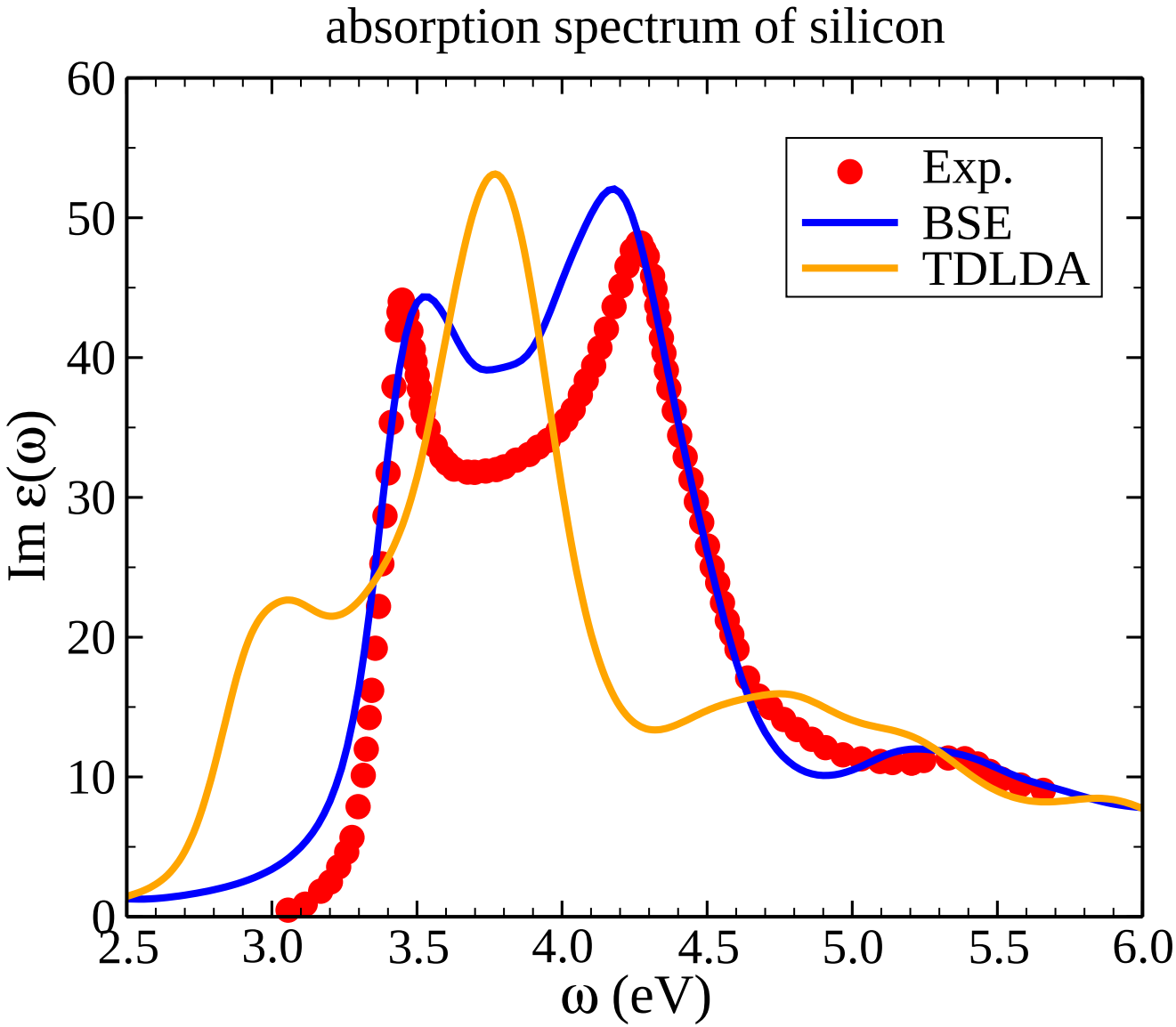
$$Im\,\varepsilon_M(\omega) = \frac{8\pi^2}{V} \sum_{\lambda} \left| \sum_{v}^{occ} \sum_{c}^{unocc} A^{\lambda}_{vc} \frac{\langle v|\mathbf{p}|c\rangle}{\epsilon_c - \epsilon_v} \right|^2 \delta(\omega - E^{\lambda})$$

  - $\mathbf{p} \equiv$ dipole operator

Optical absorption – Recipe for BSE

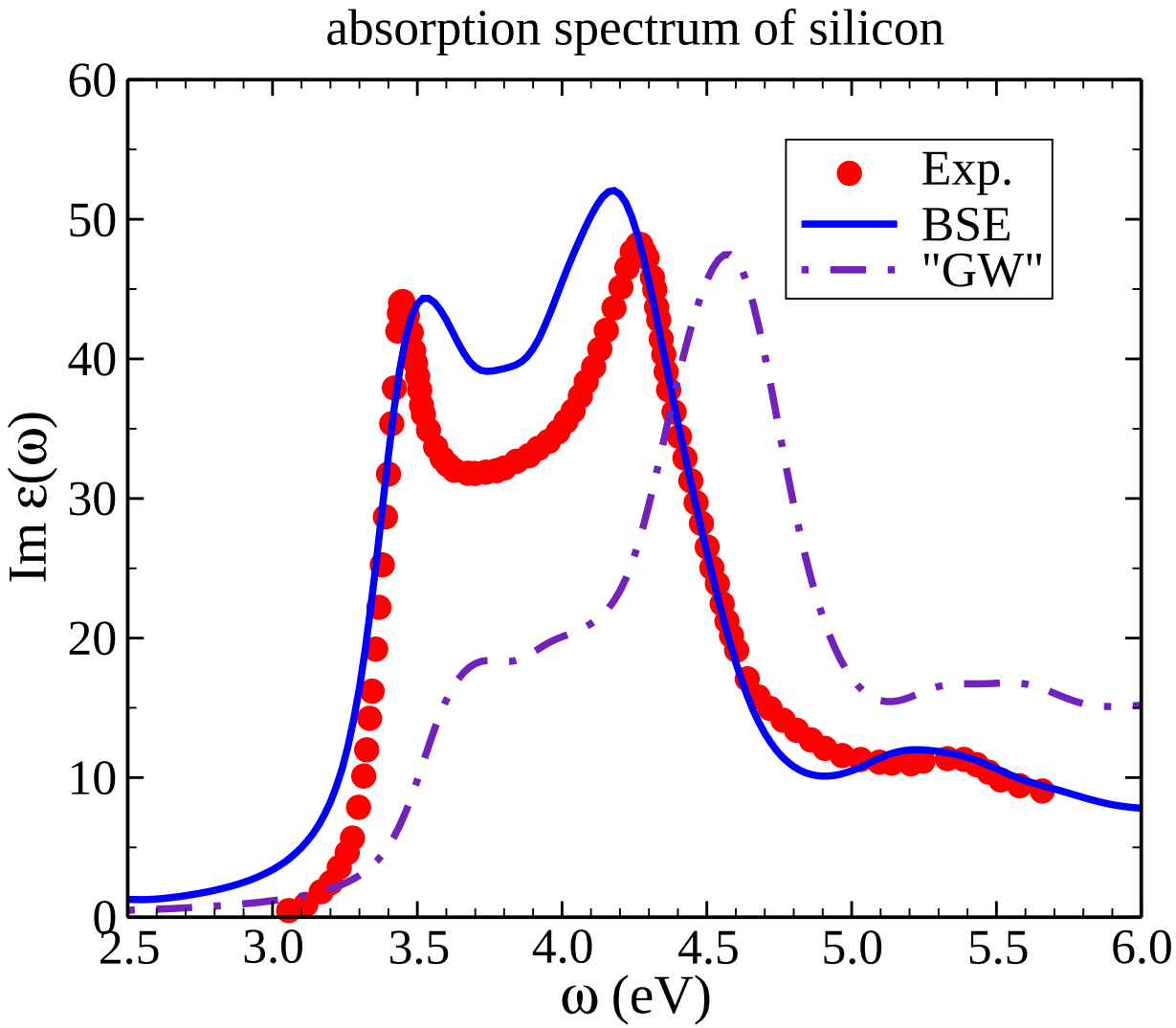
1. perform a DFT calculation
2. perform a G_0W_0 calculation
3. calculate $\langle vc|\bar{v}|v'c'\rangle$ and $\langle vc|W|v'c'\rangle$
4. solve $H^{eff}A^{\lambda} = E^{\lambda}A^{\lambda}$
5. calculate $Im\,\varepsilon_M(\omega)$

Optical absorption – response function



from Sottile, Olevano, and Reining, PRL **91**, 056402 (2003)

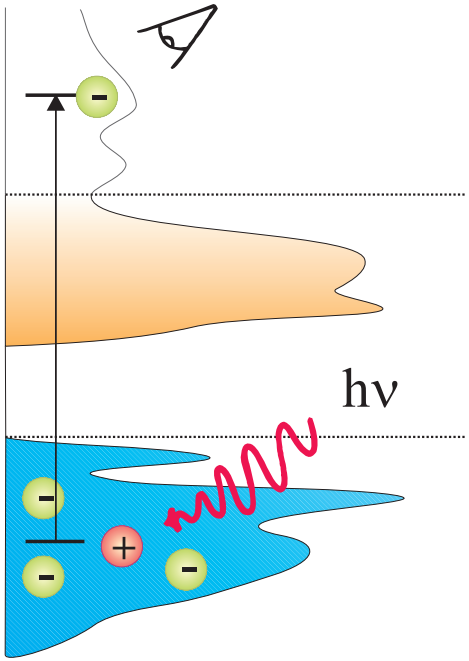
Optical absorption – response function



- BSE creates bound exciton
- BSE shifts spectral weight

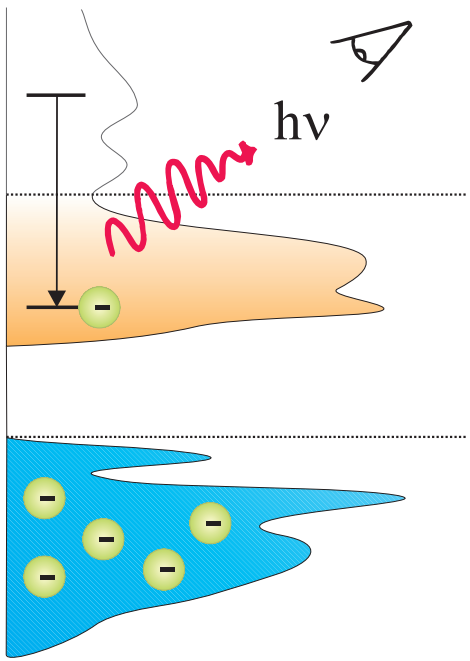
Band structures: photo-electron spectroscopy

Photoemission



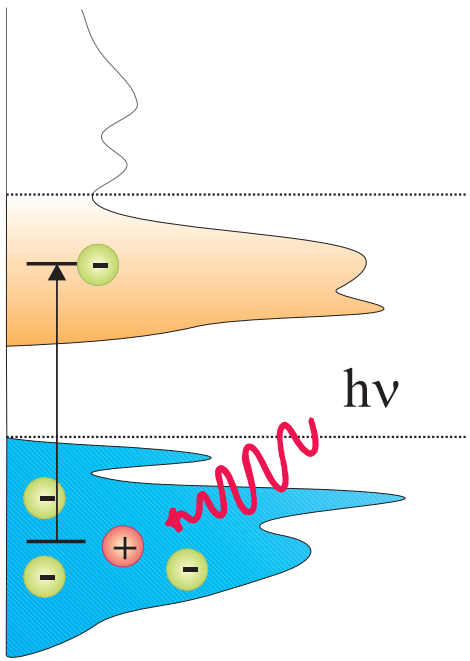
GW

Inverse Photoemission



GW

Absorption



BSE
TDDFT

Acknowledgements

GW surface calculations

Christoph Freysoldt

GW for f-electrons

Hong Jiang
Ricardo Gomez-Abal

G_0W_0 in FHI-*aims*

Xinguo Ren

scGW in FHI-*aims*

Fabio Caruso
Angel Rubio

Support and Ideas

Matthias Scheffler

`gwst`

Rex Goby

FHI-*aims*

Volker Blum
the whole FHI-*aims* developer team