Many body and *GW* (Computational spectroscopy)

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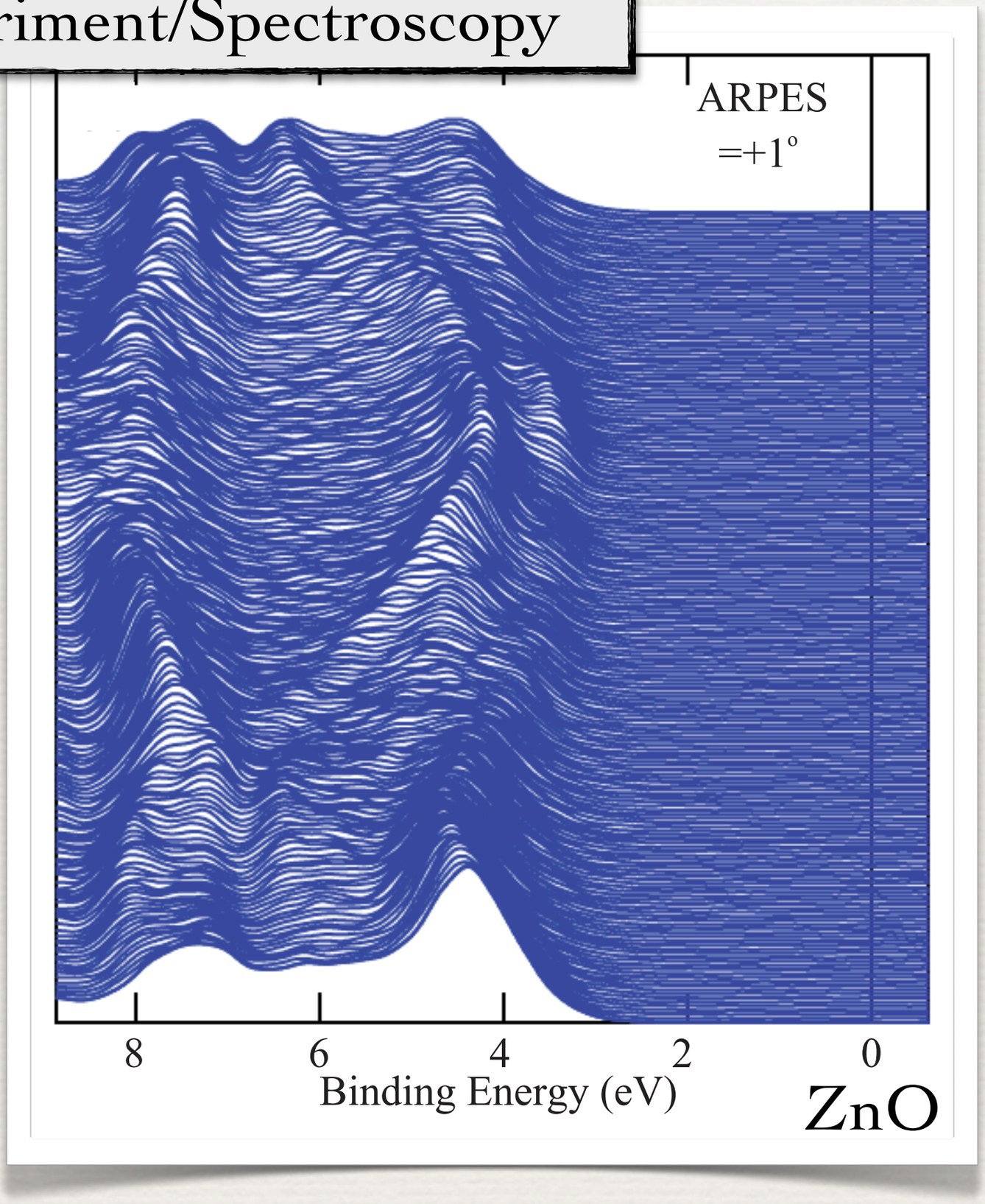
MAX-PLANCK-GESELLSCHAFT

TEXAS

ETSF

Excited states in material science are ubiquitous

Experiment/Spectroscopy



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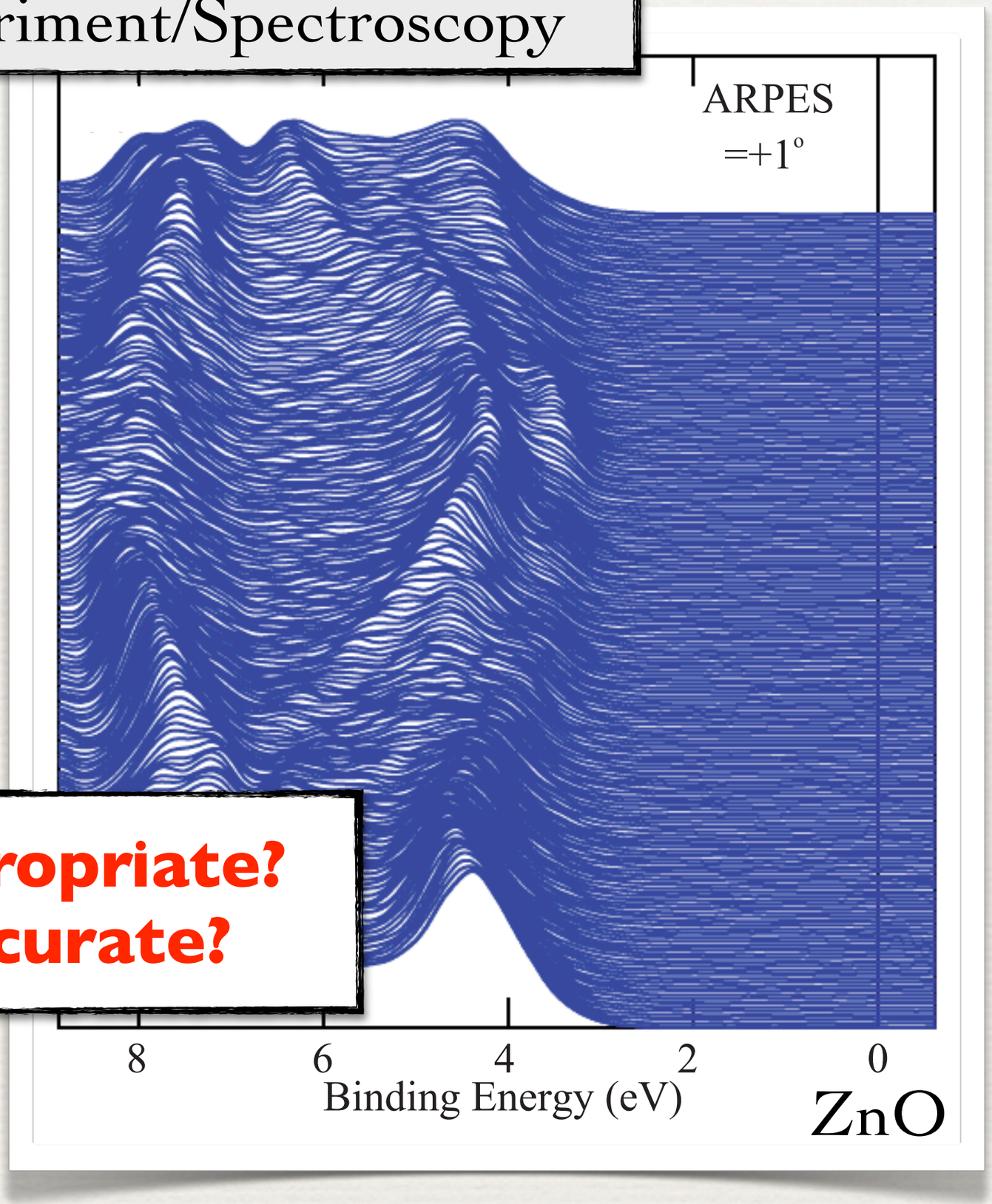
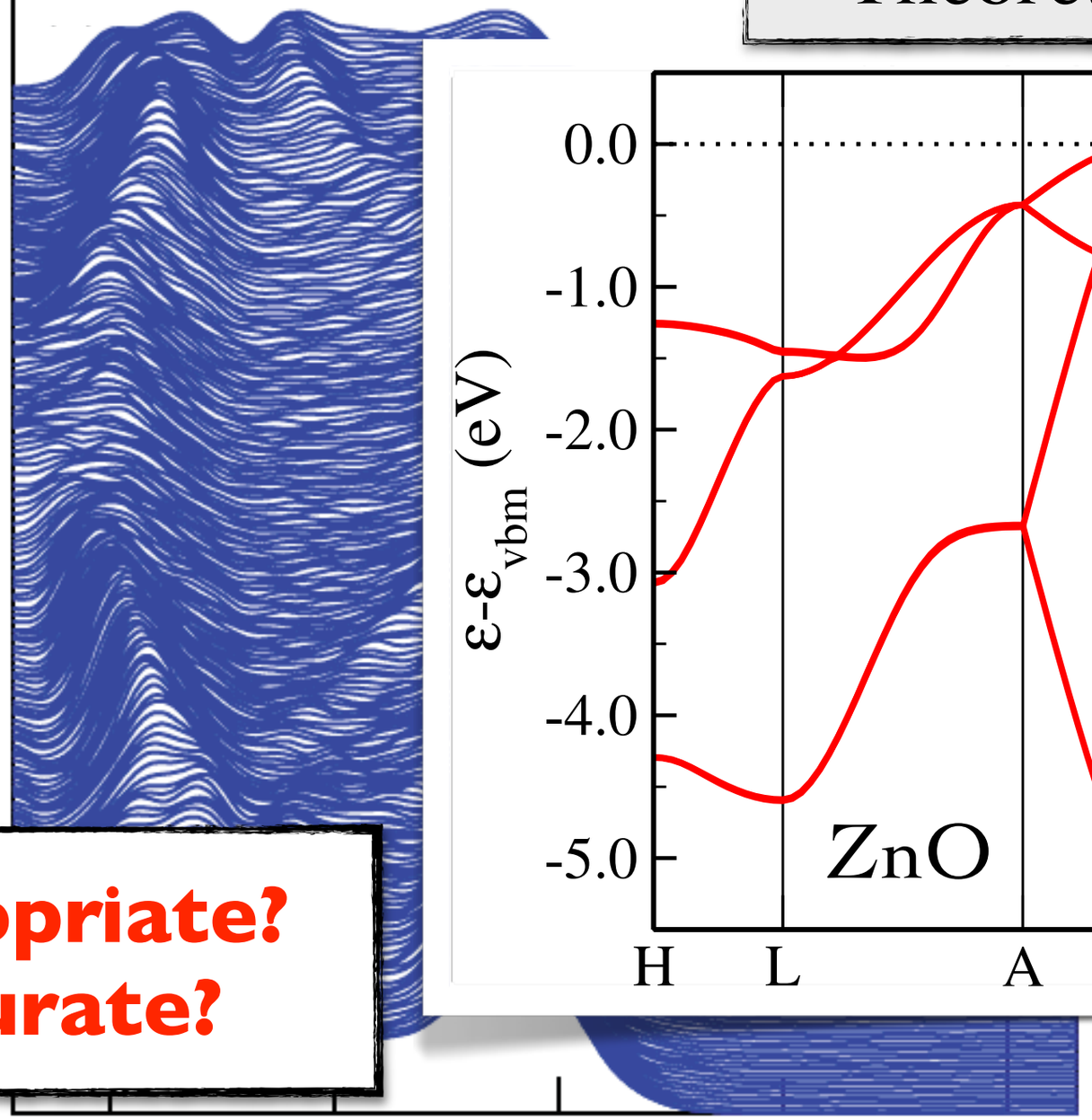


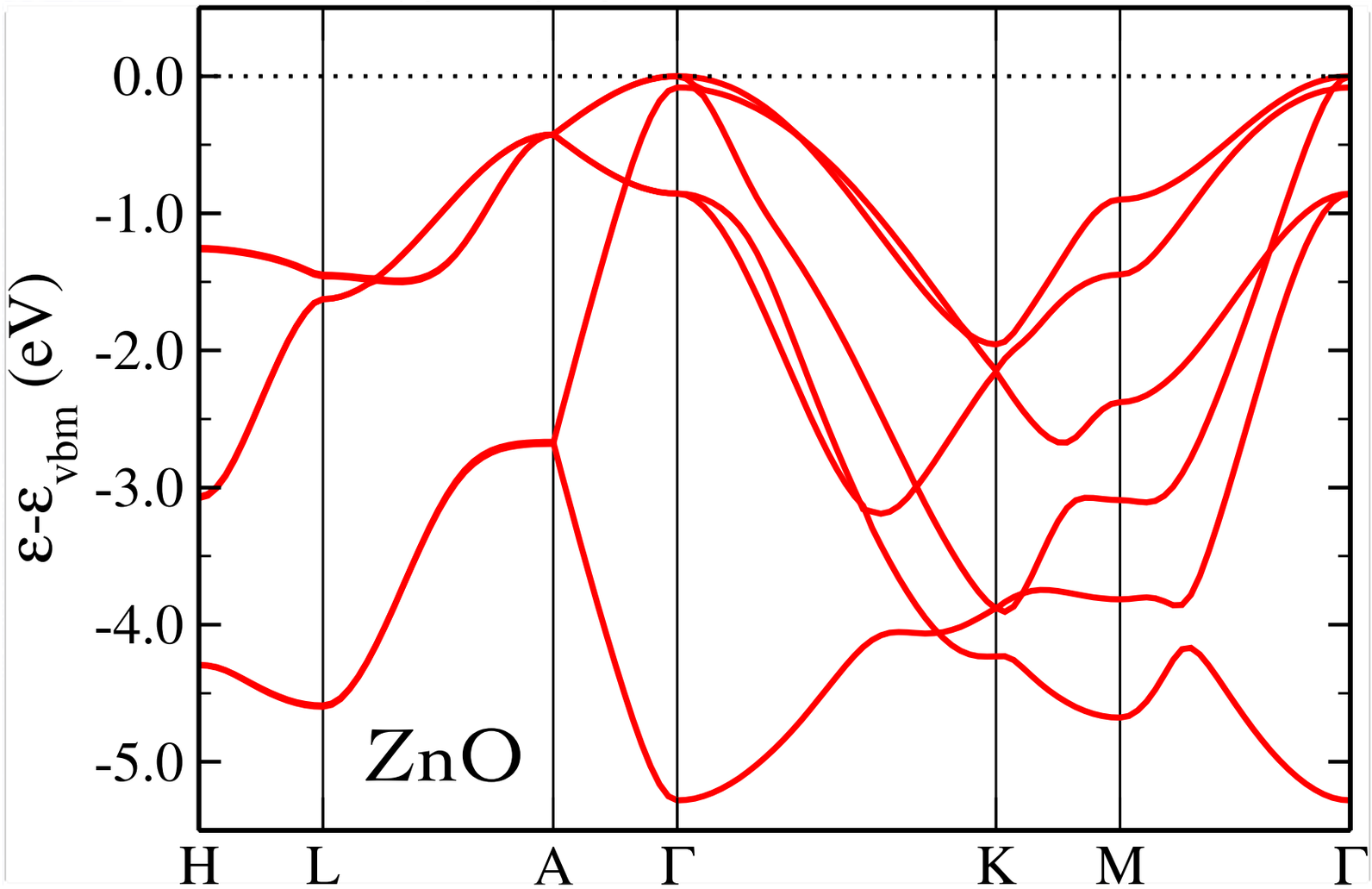
appropriate?
accurate?

Excited states in material science are ubiquitous

Experiment/Spectroscopy

Theoretical Spectroscopy





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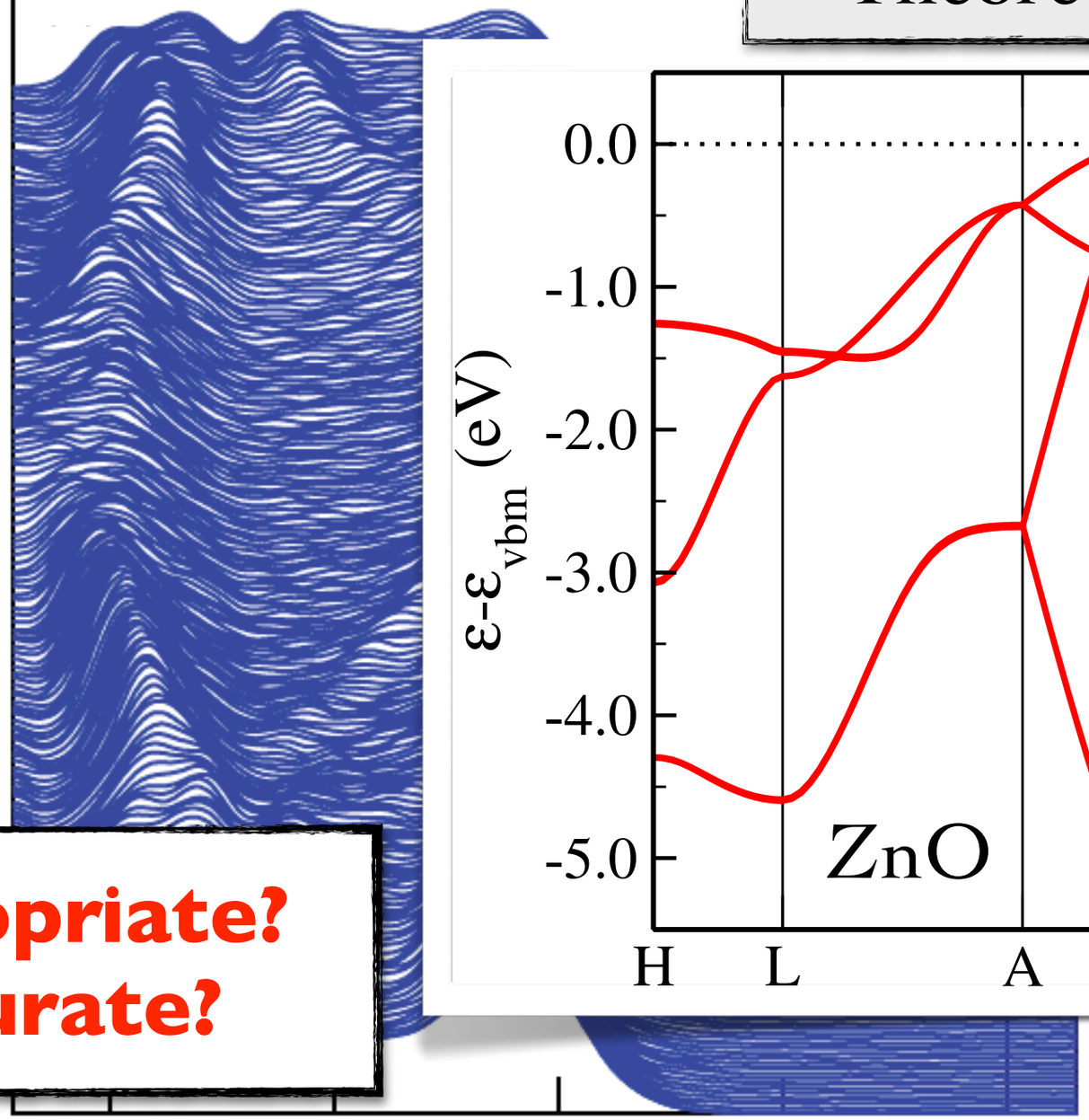
Experiment/Spectroscopy



appropriate?
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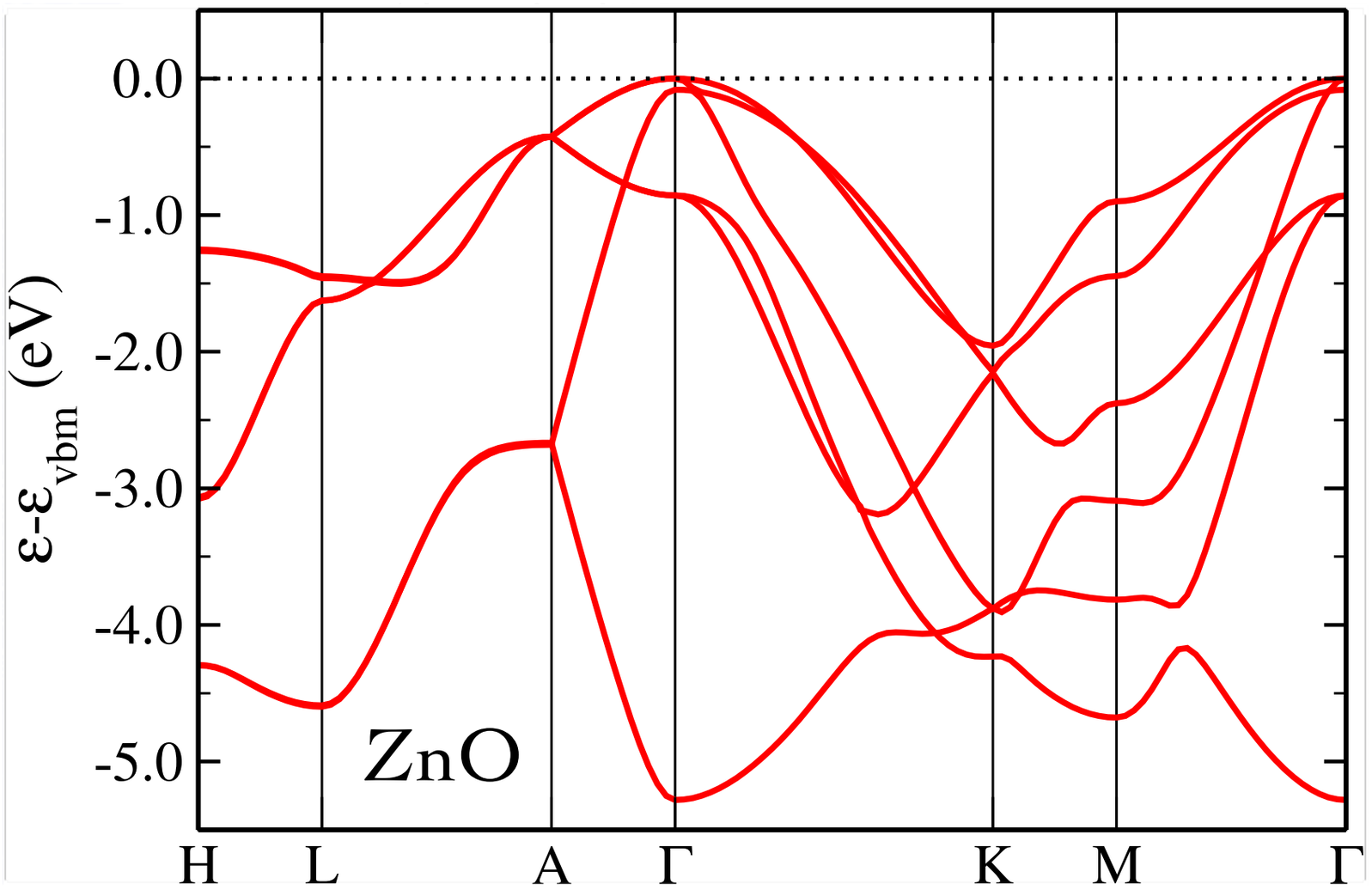
Theoretical Spectroscopy



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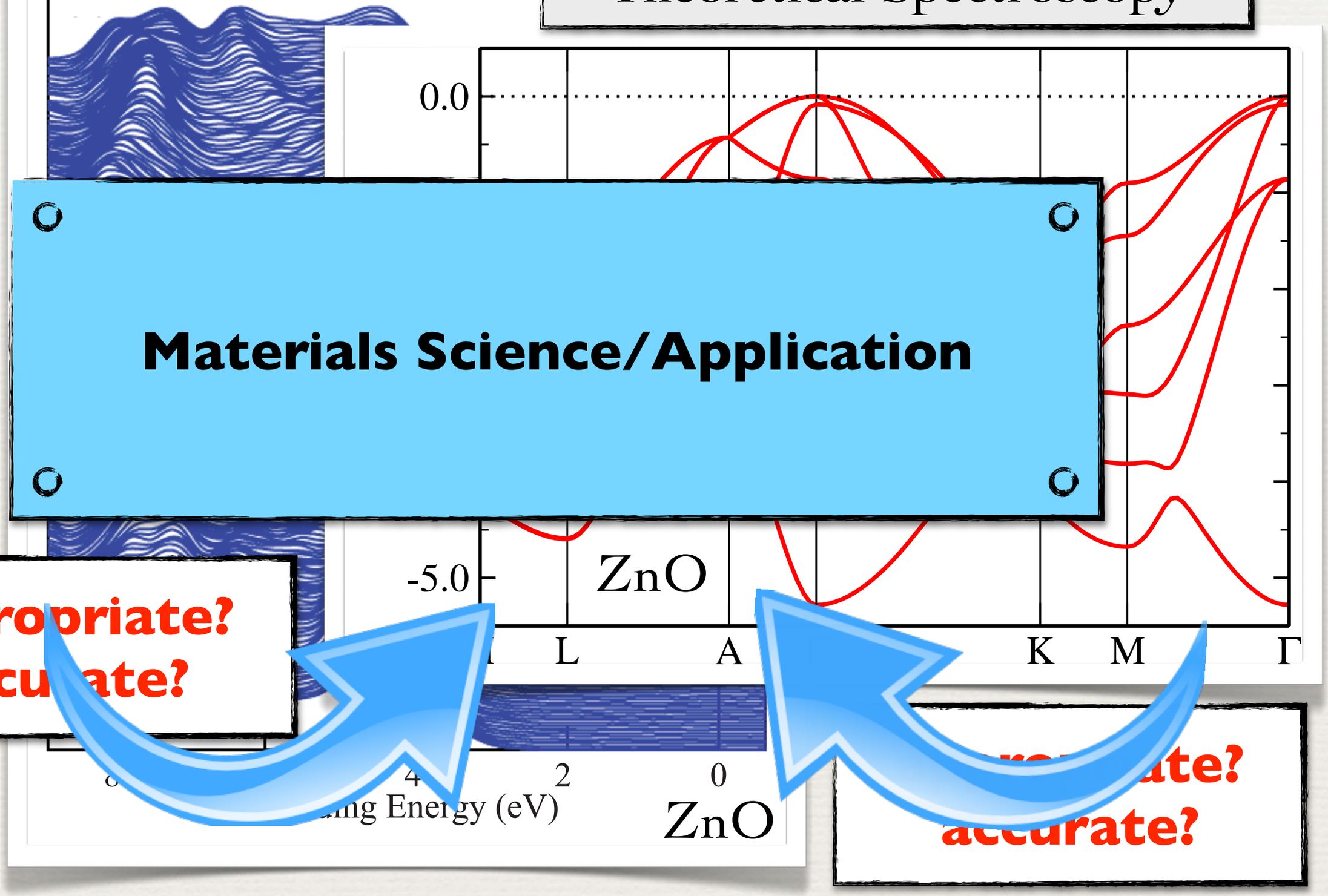
Excited states in material science are ubiquitous

Experiment/Spectroscopy

Theoretical Spectroscopy



Materials Science/Application

appropriate?
accurate?

accurate?

Excited states in material science are ubiquitous

Experiment/Spectroscopy

- **photoemission**
- **optical absorption**

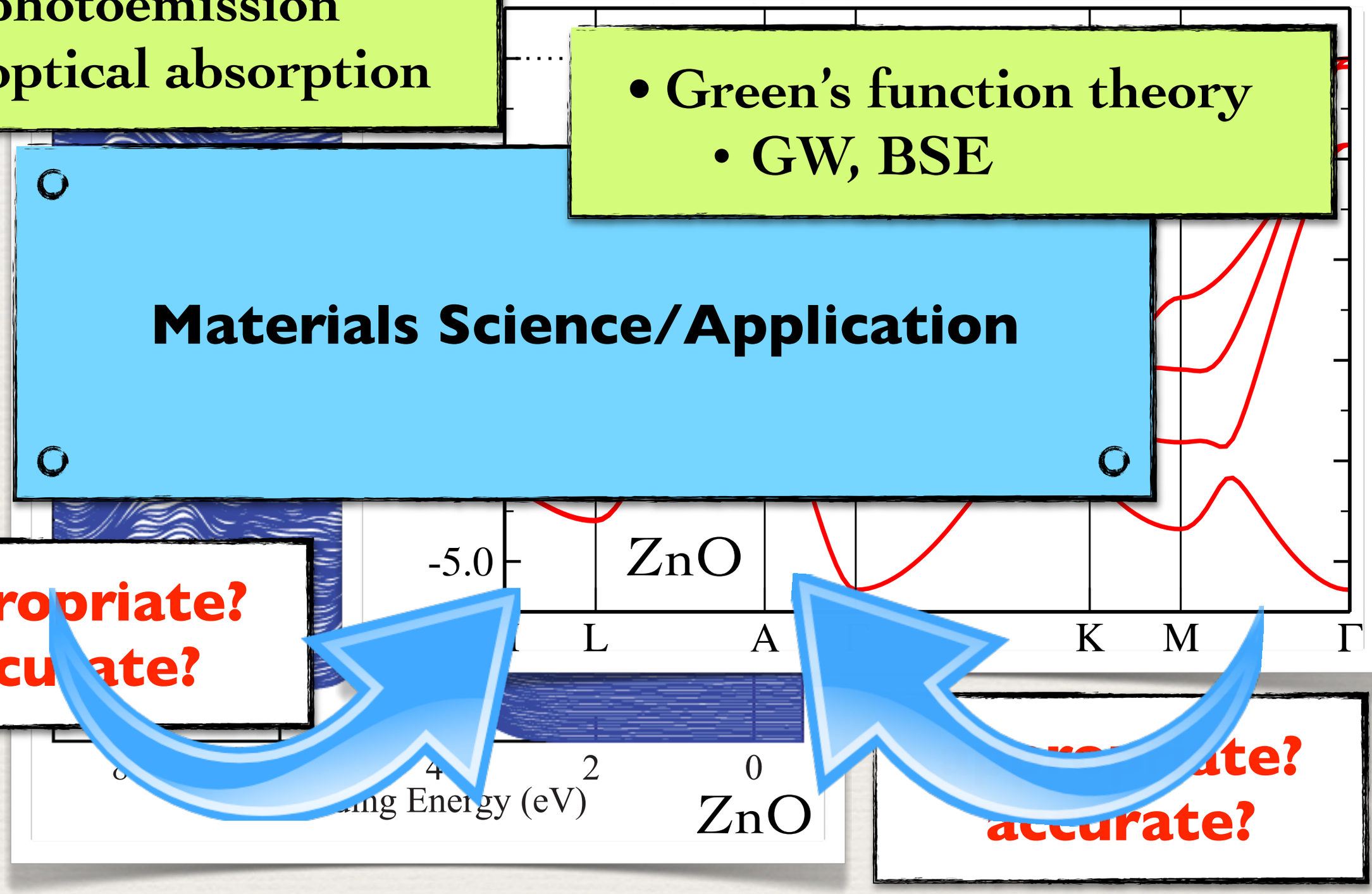
Theoretical Spectroscopy

- **Green's function theory**
  - **GW, BSE**

Materials Science/Application

appropriate?
accurate?

appropriate?
accurate?

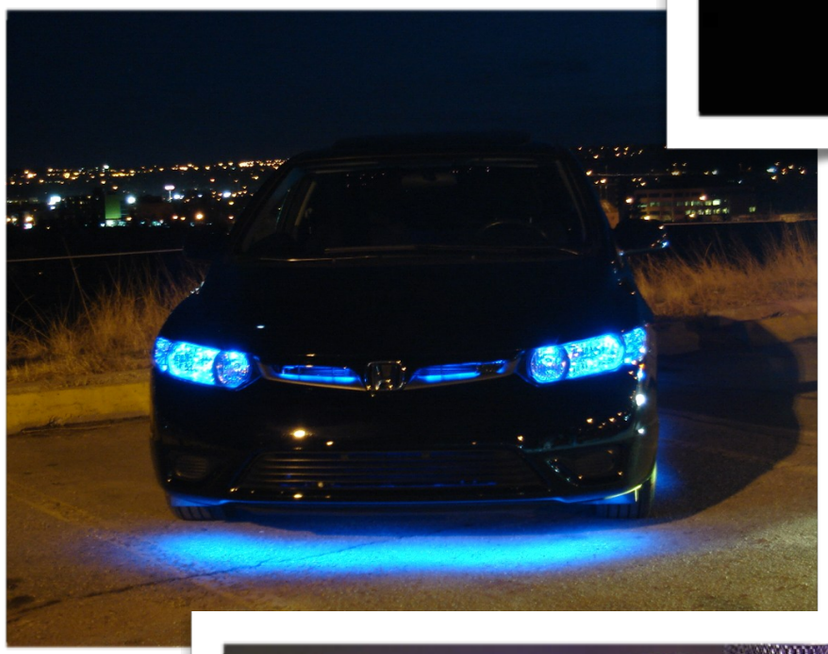


Nitride-based light emitters

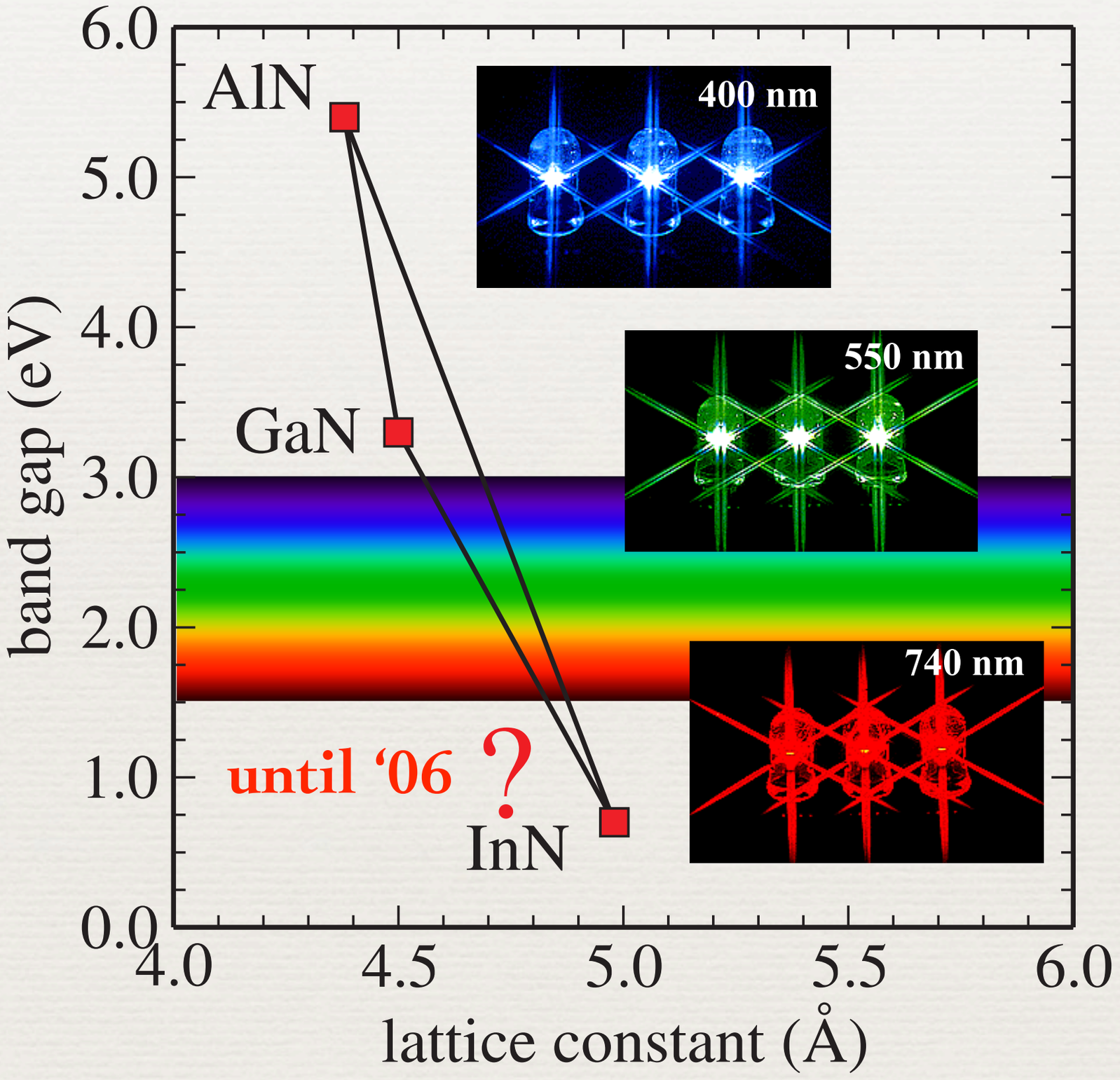
- blue LED
- blue ray

Challenges:

- solid state lighting
- RGP laser projectors

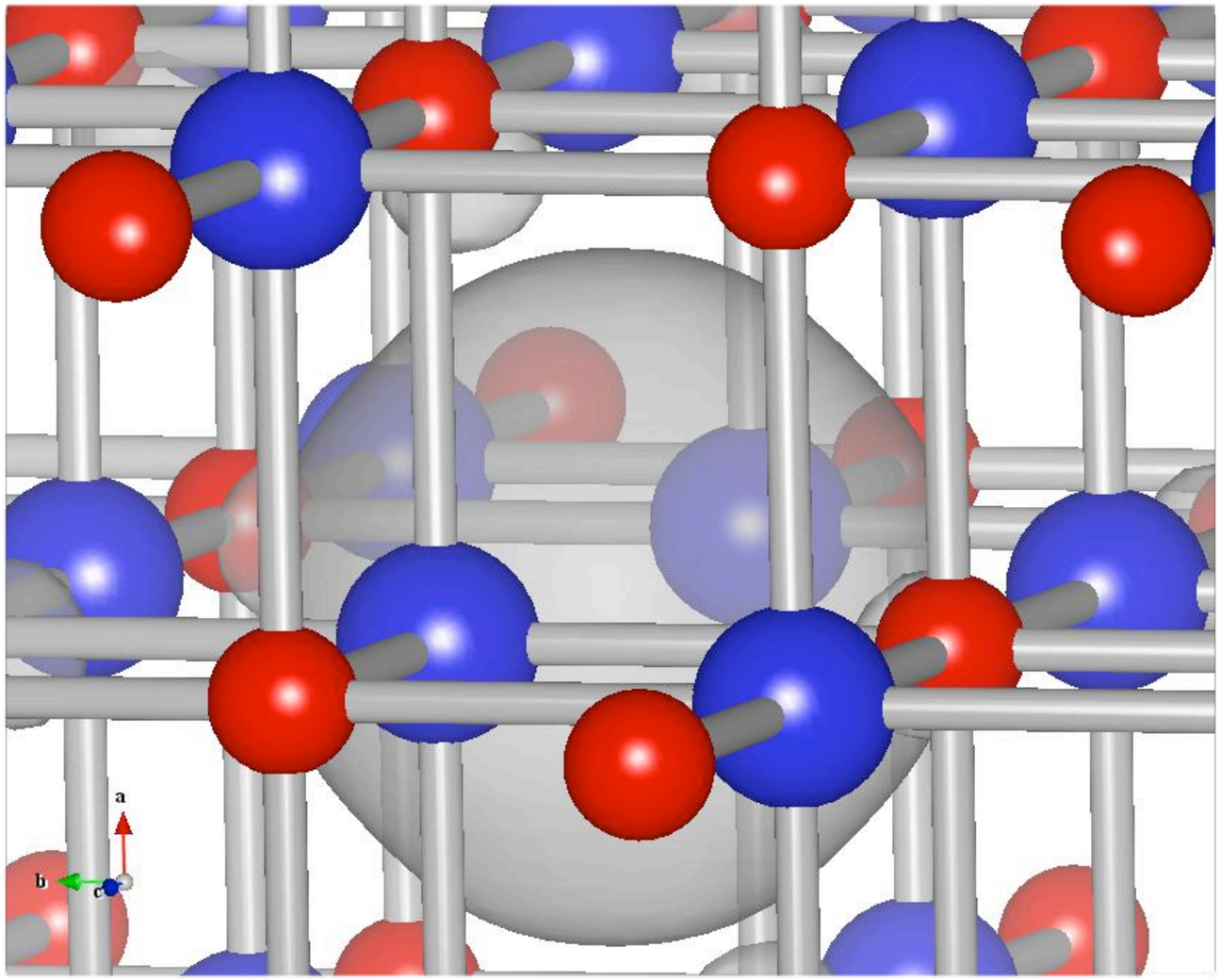


Do we know the band gap of InN?



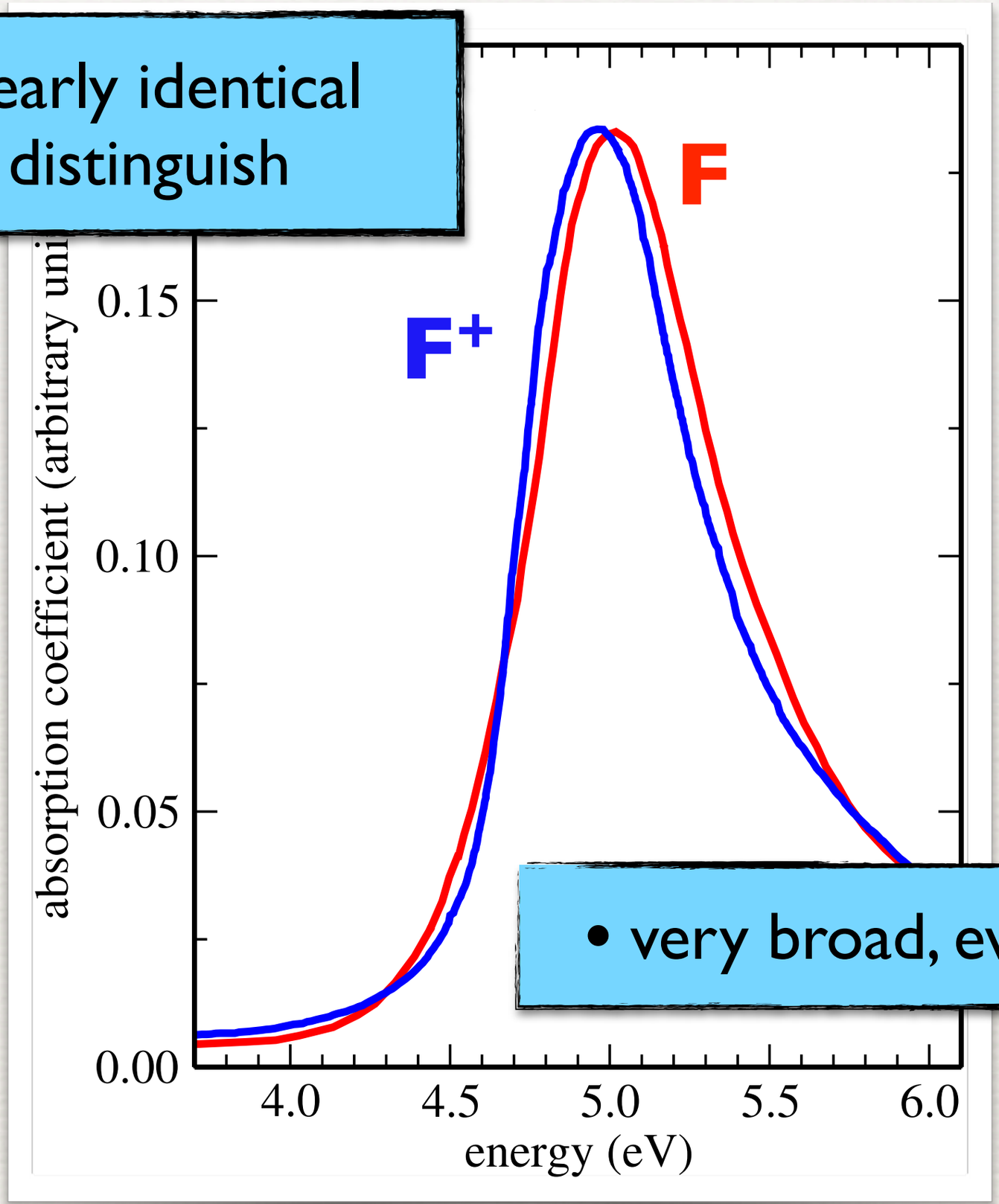
F-center: Oxygen vacancy in MgO

- *the* classic F-center
- also known as color center
- studied for > 5 decades
- still enigmatic



Experimental optical absorption spectra

- F and F^+ nearly identical
- difficult to distinguish

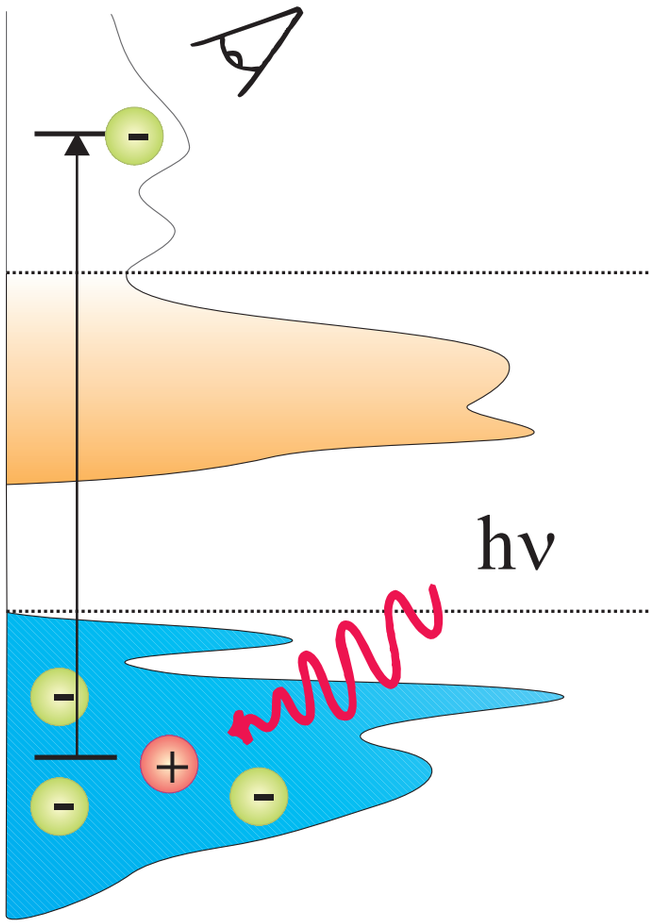


- very broad, even at low T

Kappers *et al.* PRB 1, 4151 (1970)

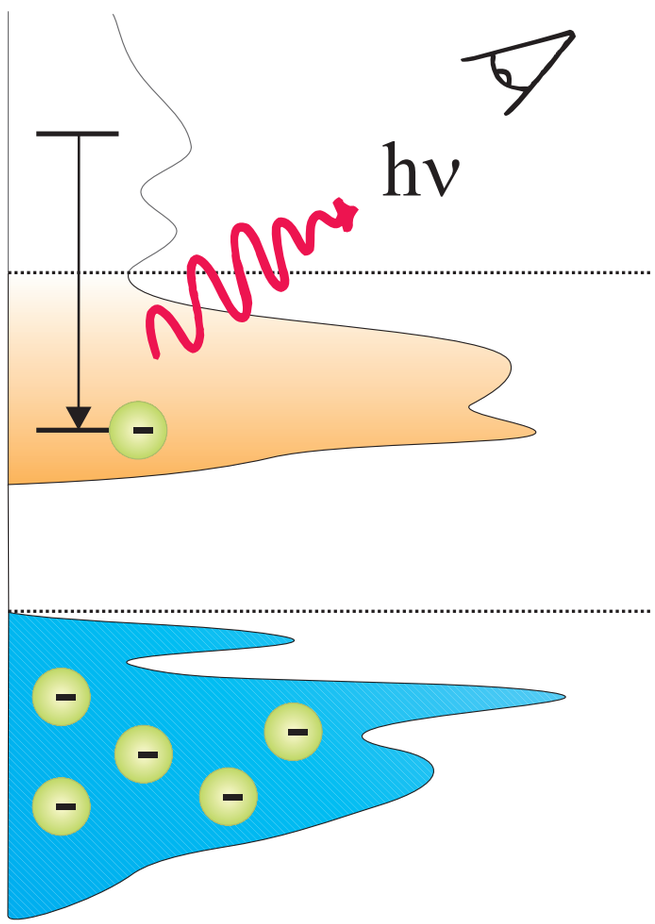
Spectroscopies

Photoemission



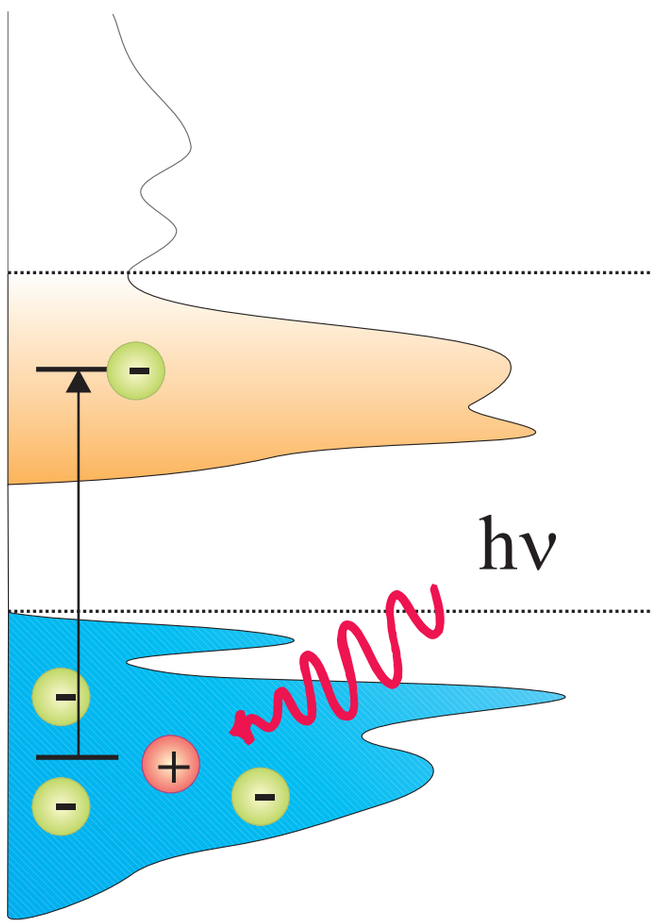
GW

Inverse Photoemission



GW

Absorption



BSE
TDDFT

Photo-electron energies

Photoemission

- electron removal

ground state $\longrightarrow$ $|N\rangle$

- removal energy

$E(N)$

ground state total energy

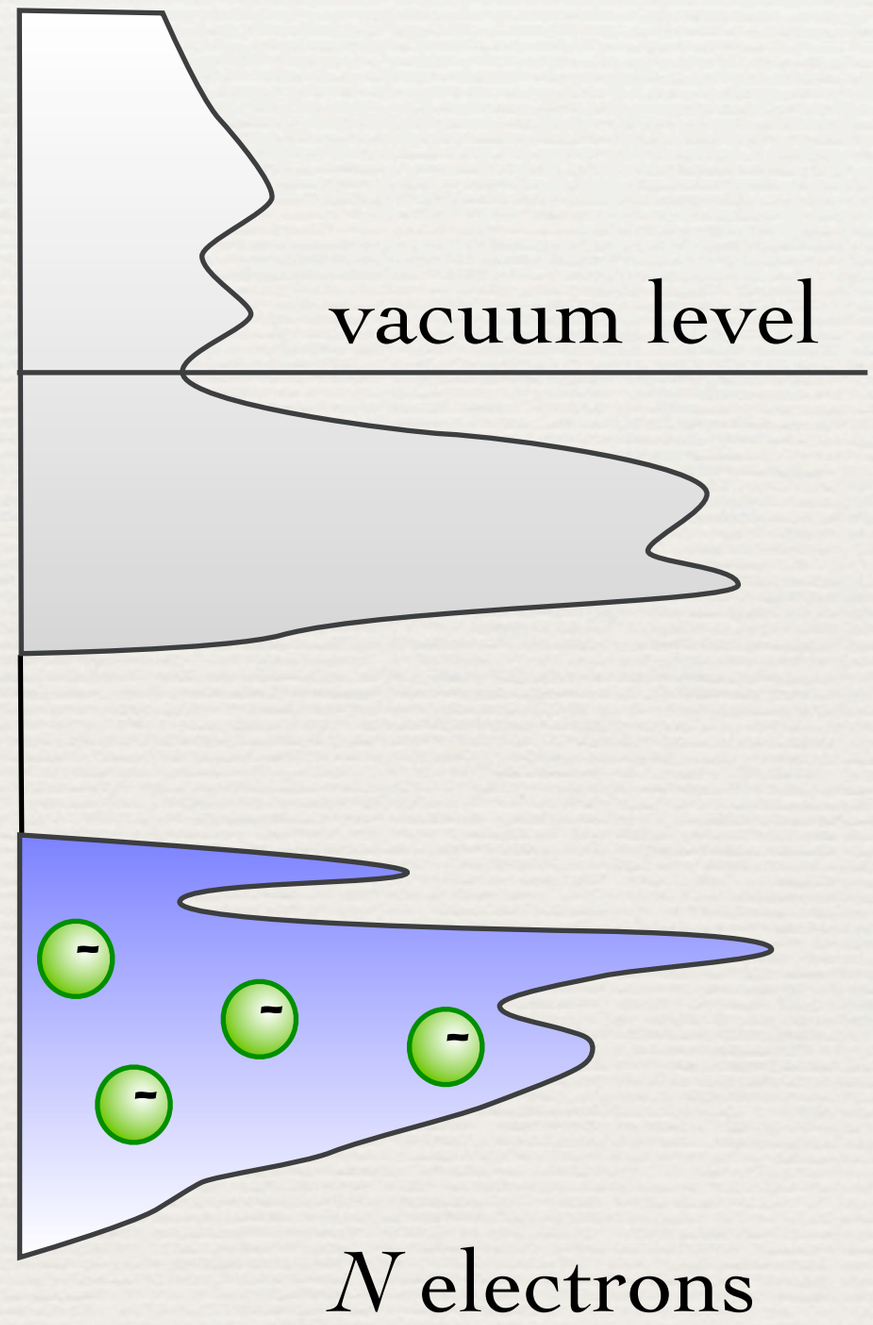


Photo-electron energies

Photoemission

- electron removal

annihilation operator

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

- removal energy

$$E(N)$$

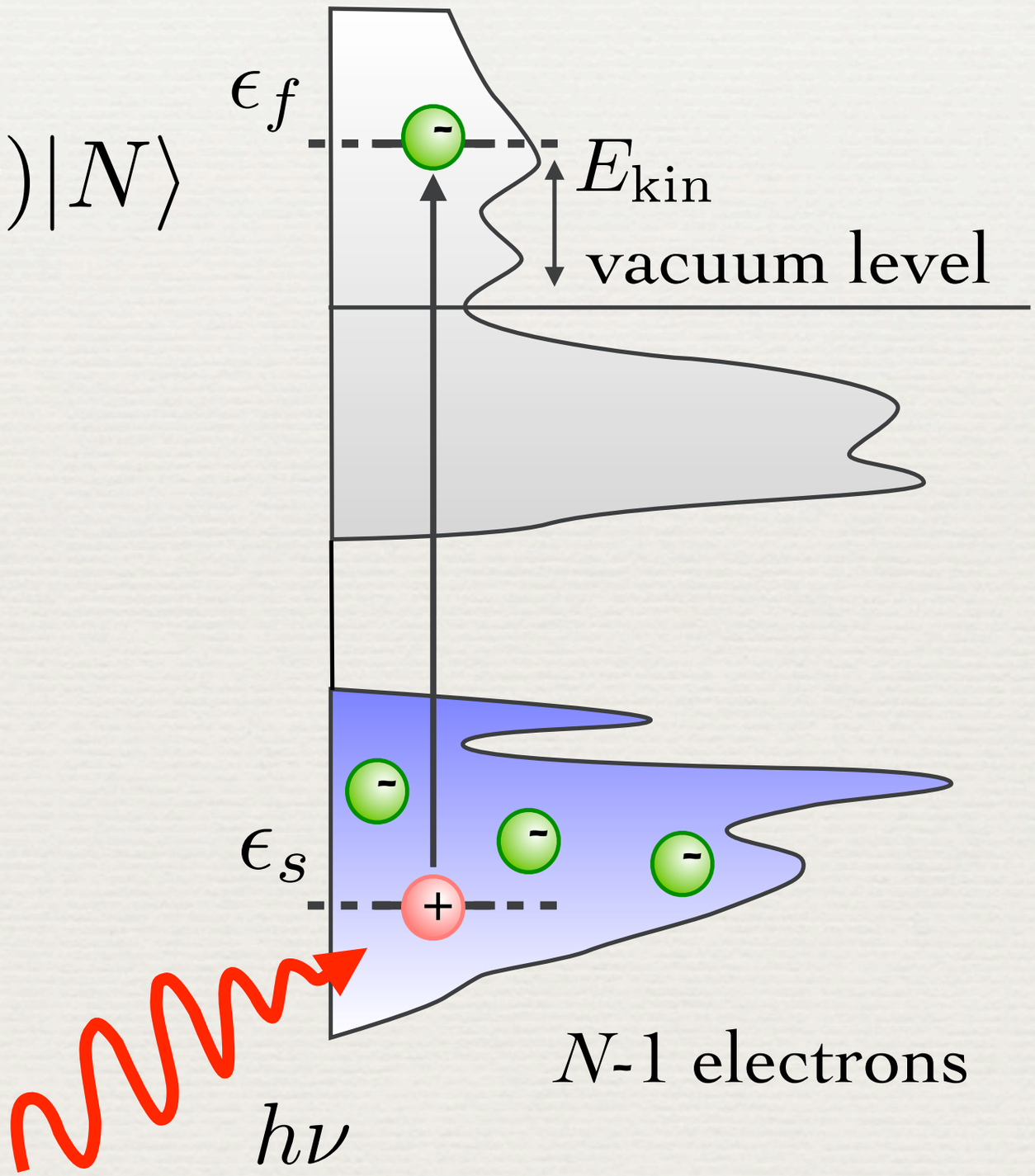


Photo-electron energies

Photoemission

s^{th} excited state of N-1 electron system

- electron removal

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

- removal energy

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

total energy of s^{th} excited state of N-1 electron system

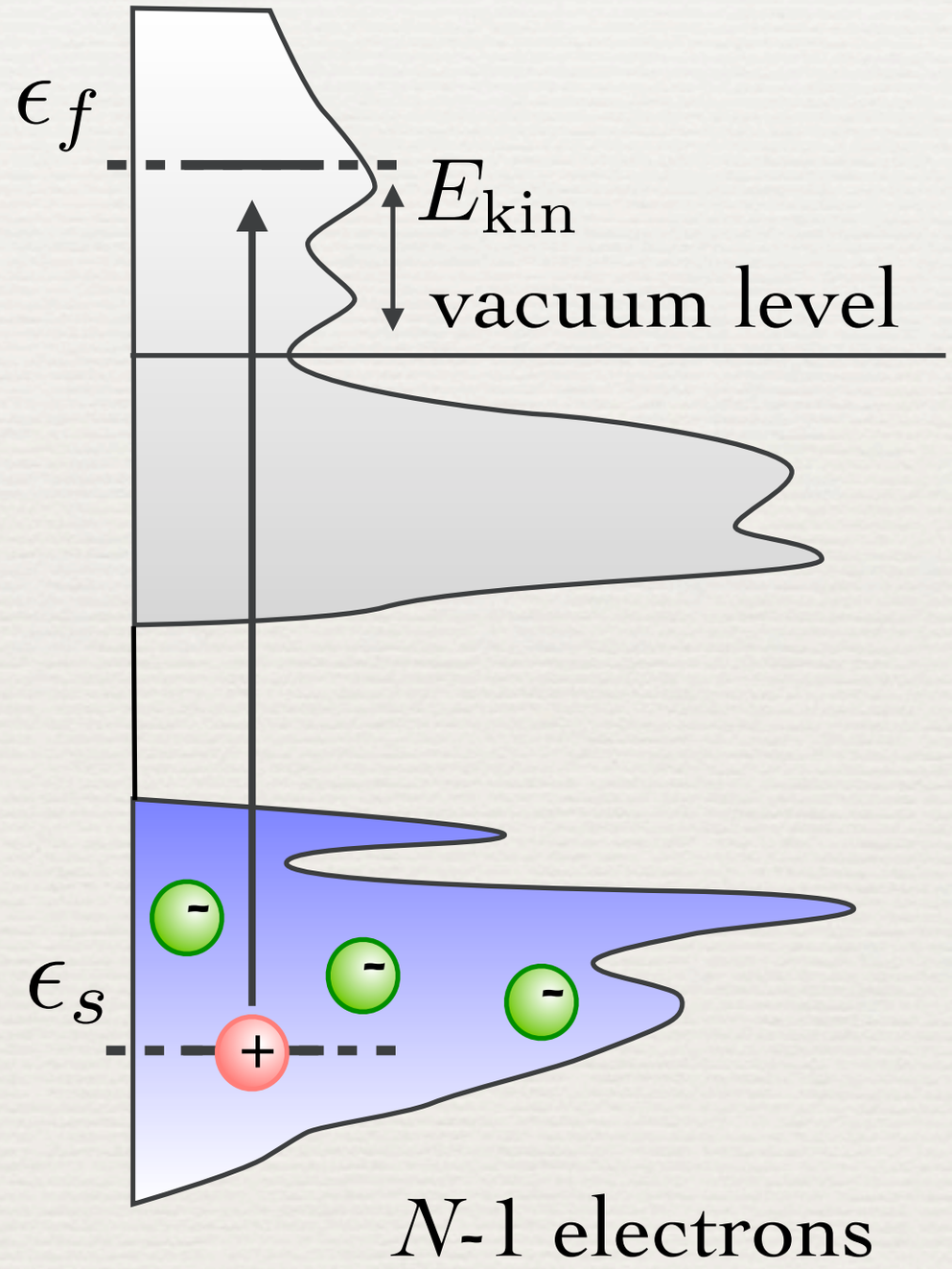


Photo-electron energies

Photoemission

- electron removal

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

- removal energy

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

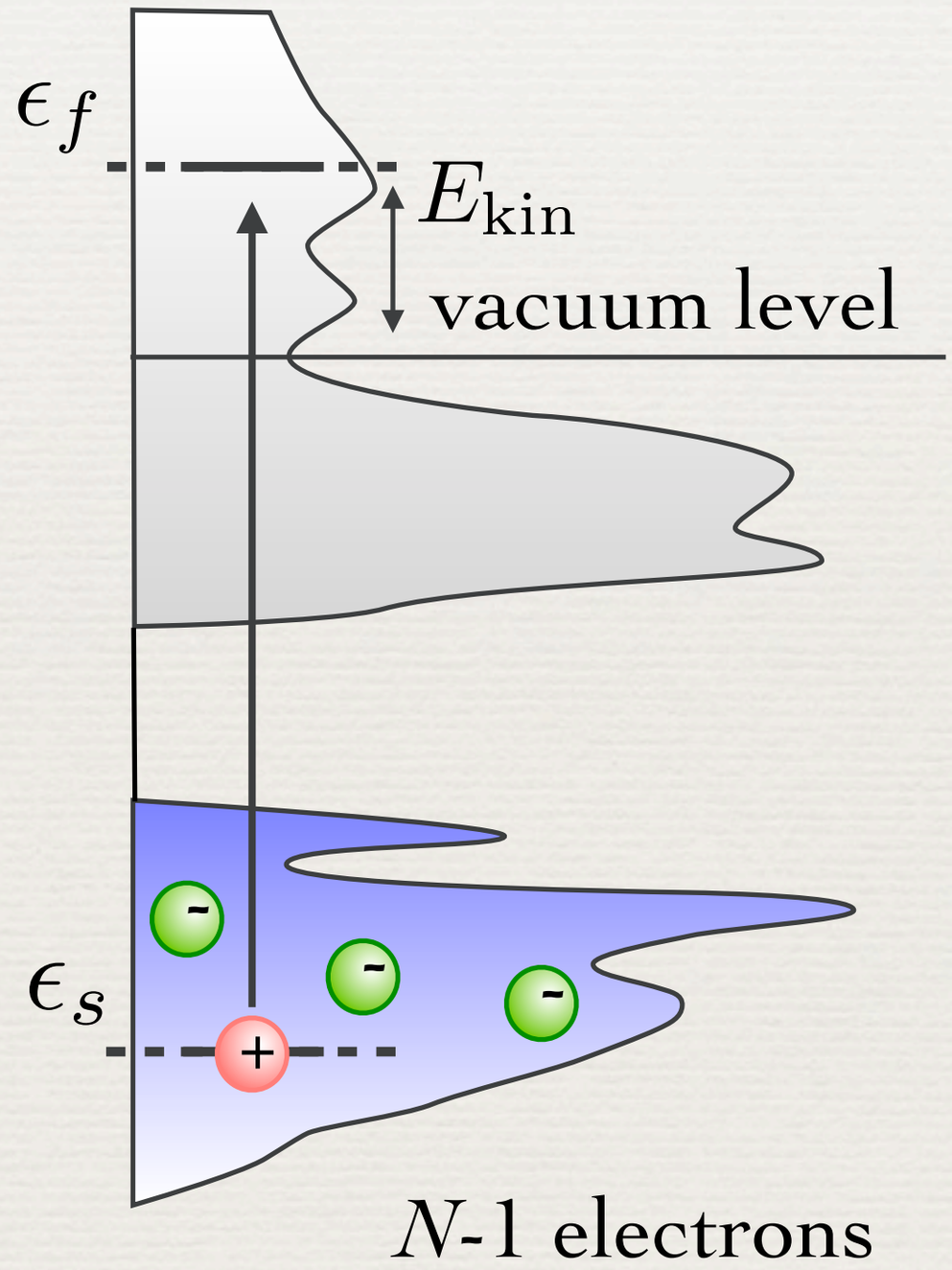


Photo-electron energies

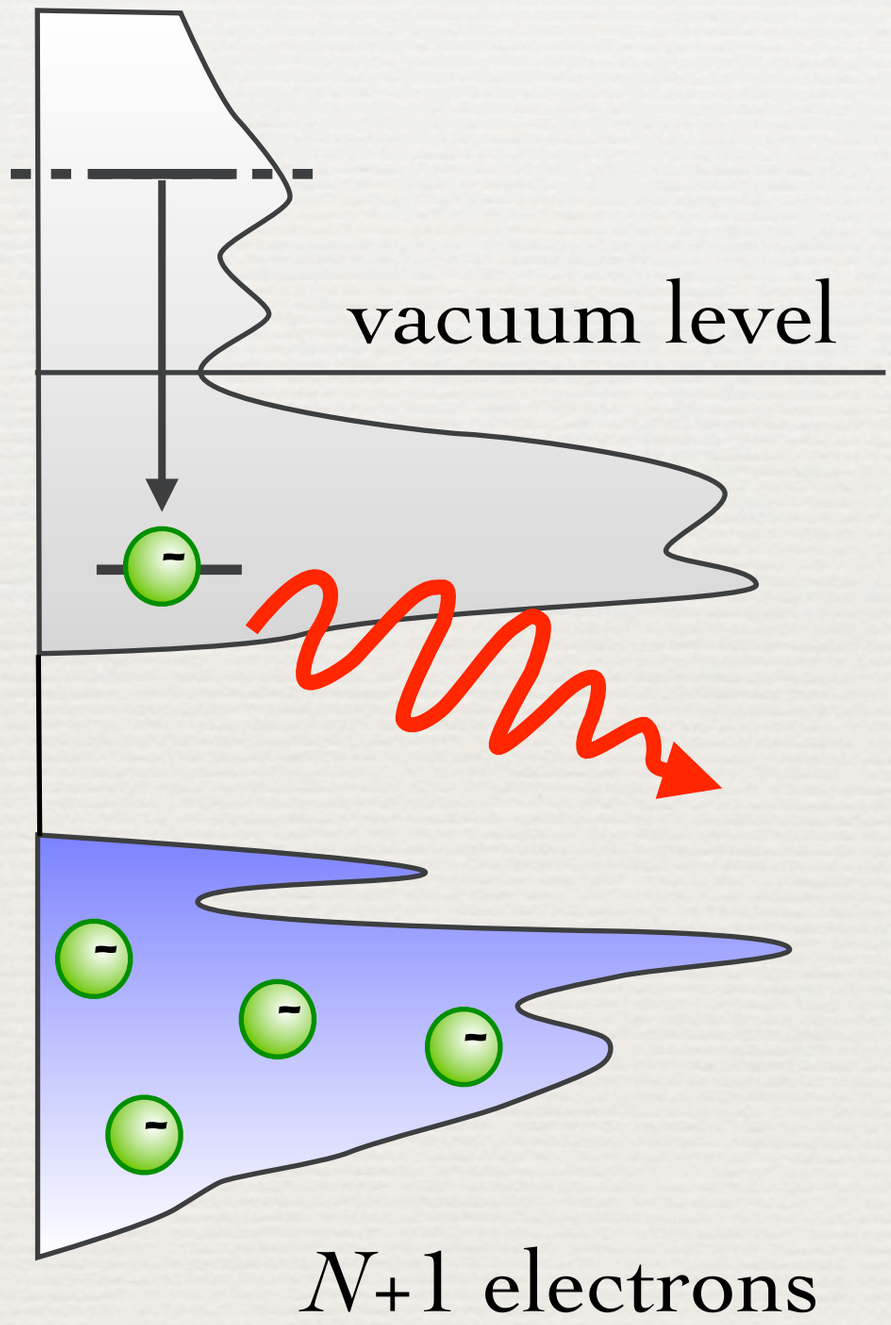
Inverse photoemission

- electron addition

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

- addition energy

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



Single-particle Green's function

- Lehmann representation of 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

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

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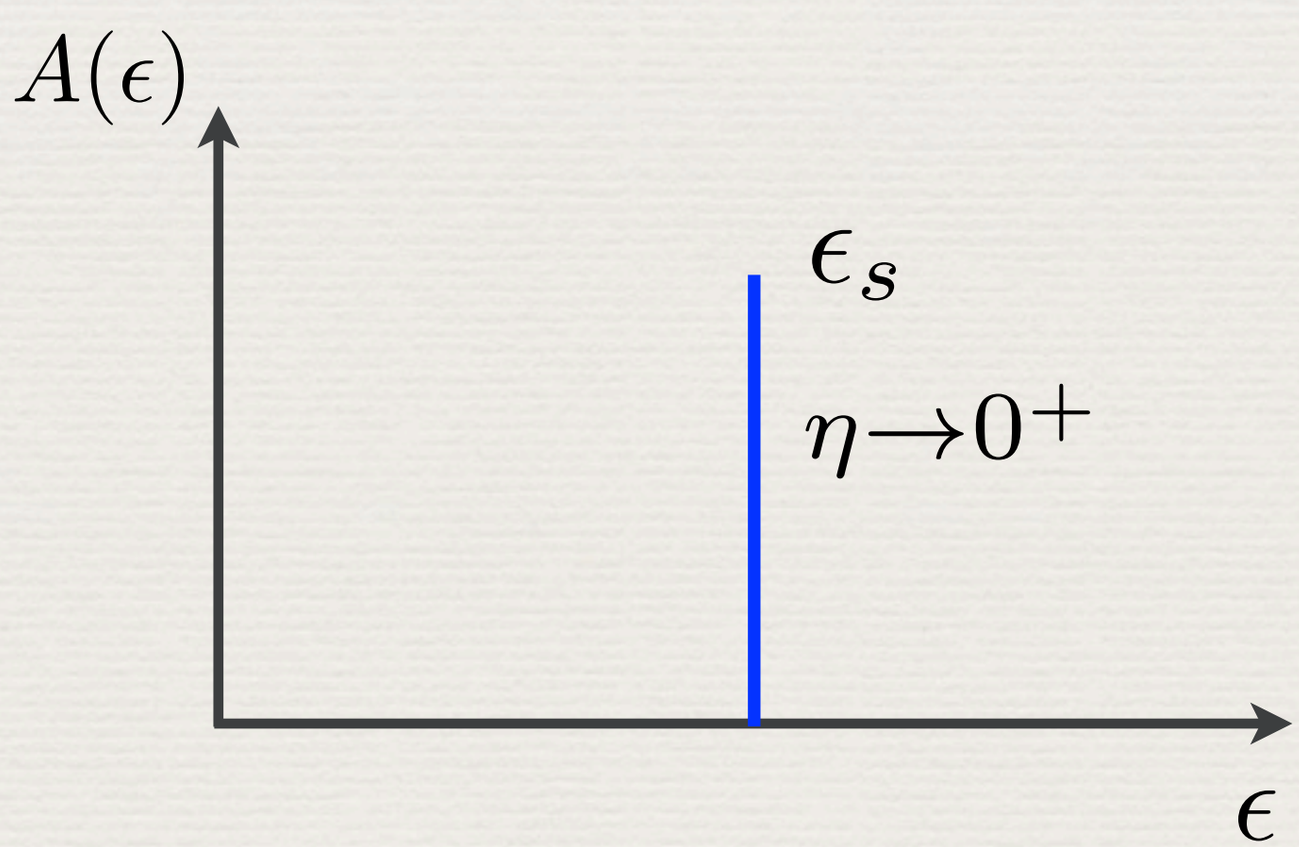
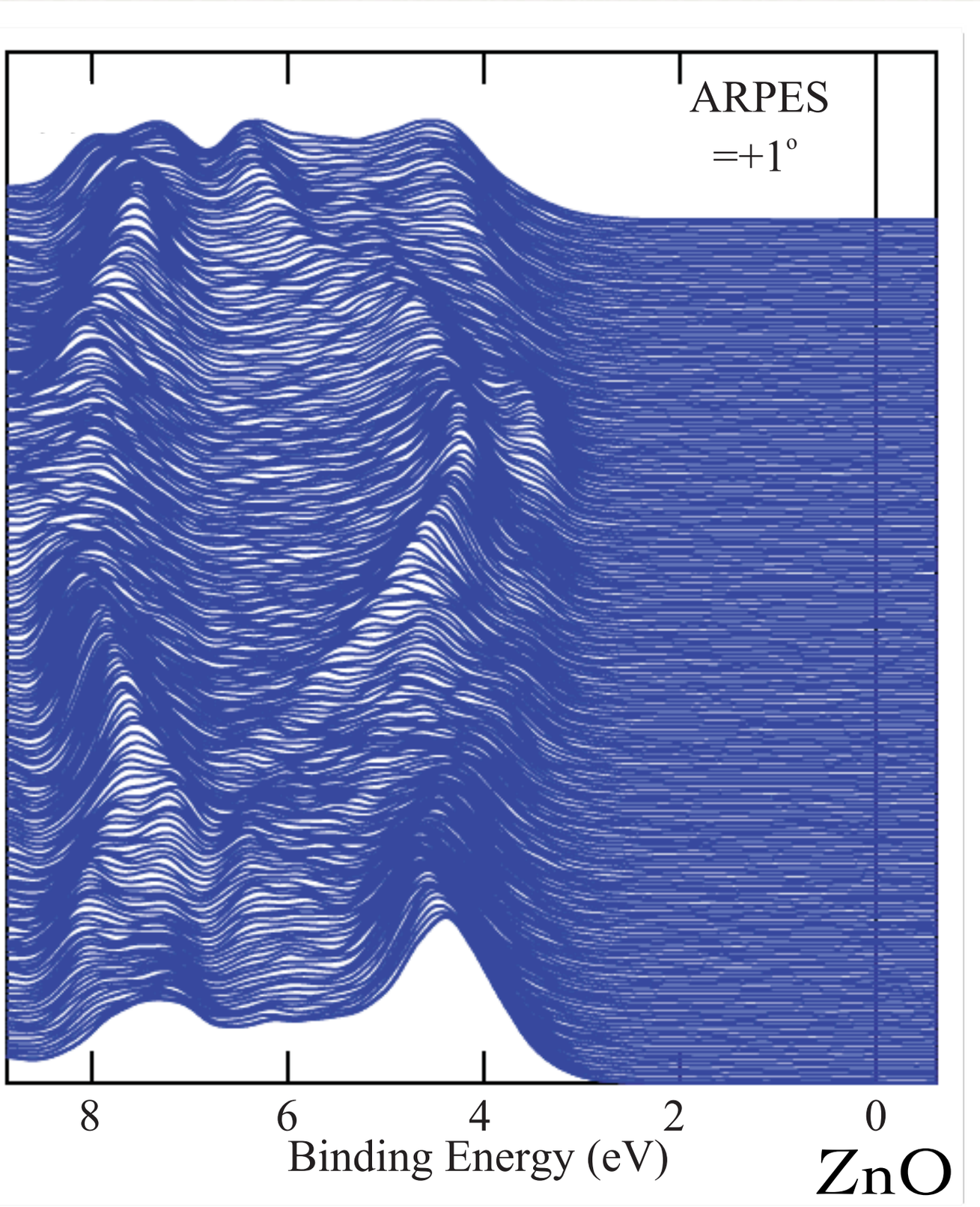
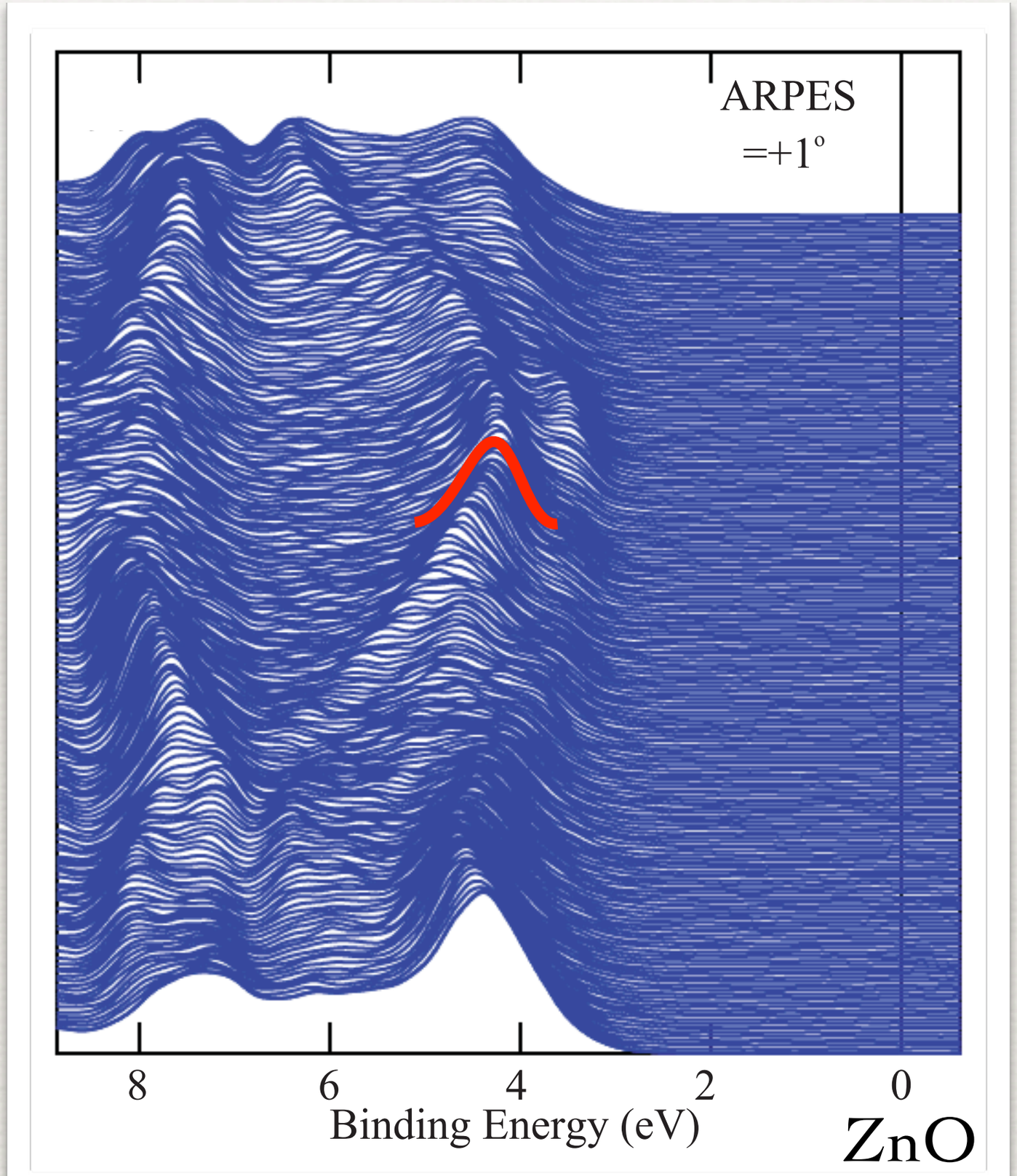


Angle-resolved photoemisson spectroscopy



Masaki Kobayashi,
PhD dissertation

Angle-resolved photoemisson spectroscopy



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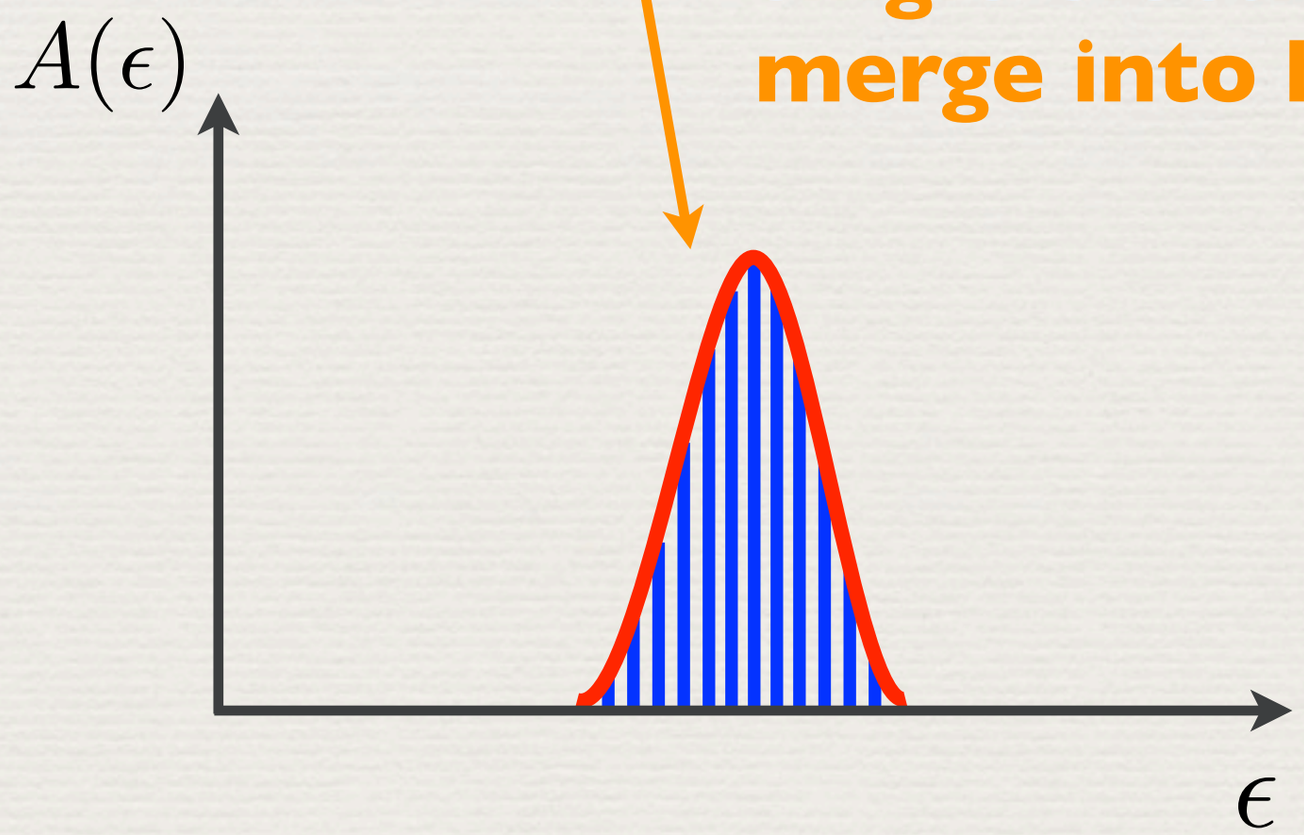
single electron excitations merge into broad peak

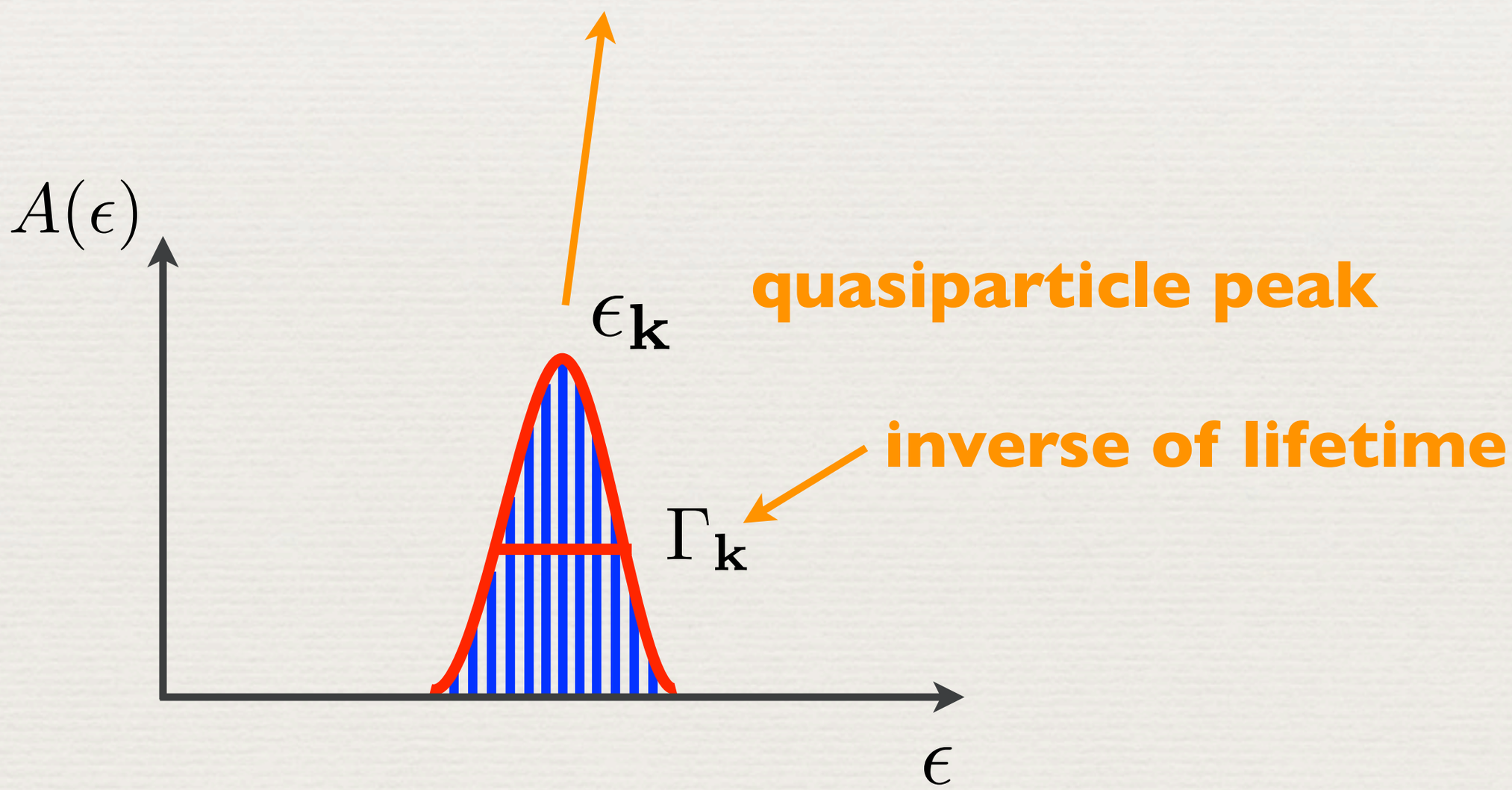


Single-particle Green's function

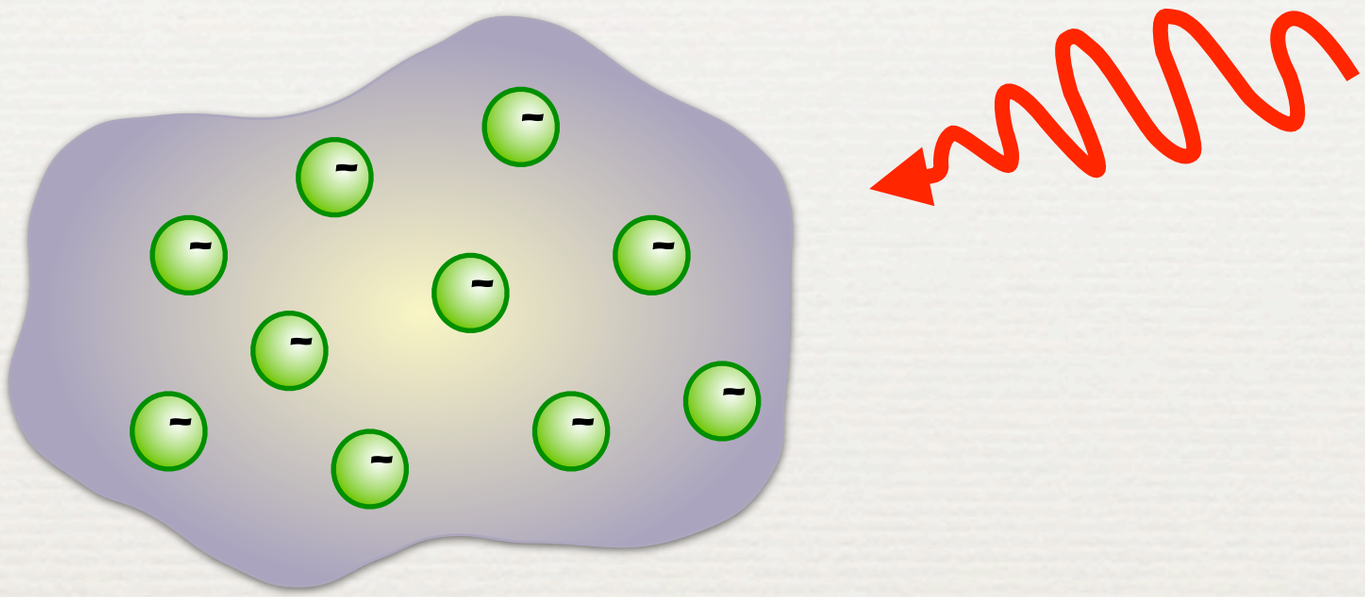
- single particle-like spectral function:

quasiparticle weight

$$A_{\mathbf{k}}(\epsilon) = ImG_{\mathbf{k}}(\epsilon) \approx \frac{Z_{\mathbf{k}}}{\epsilon - (\epsilon_{\mathbf{k}} + i\Gamma_{\mathbf{k}})}$$



Another take on quasiparticles



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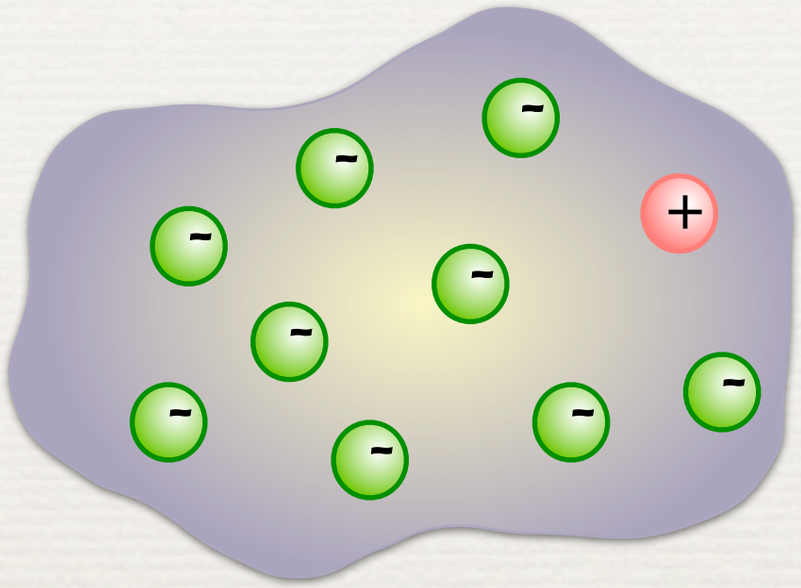
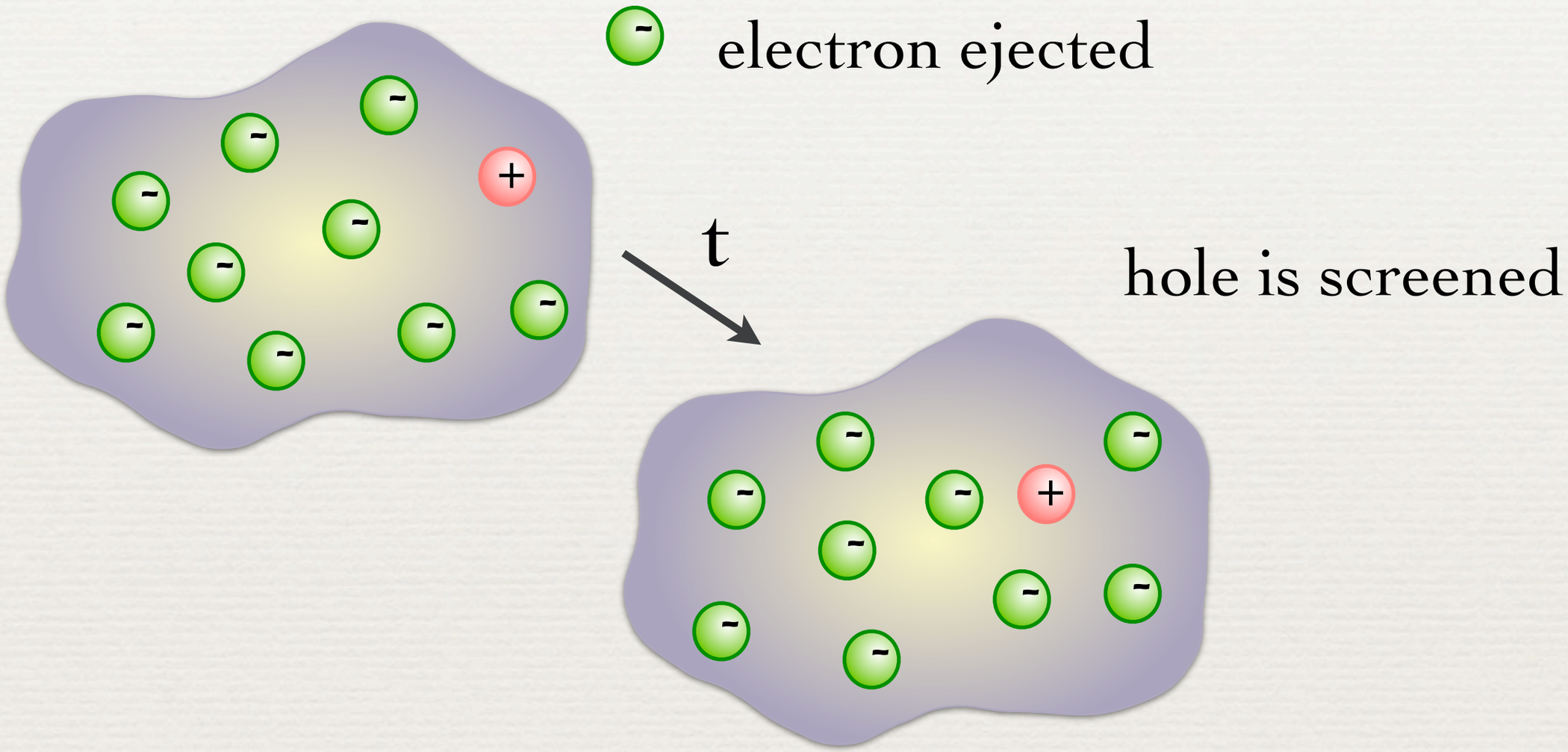


- electron ejected

Another take on quasiparticles



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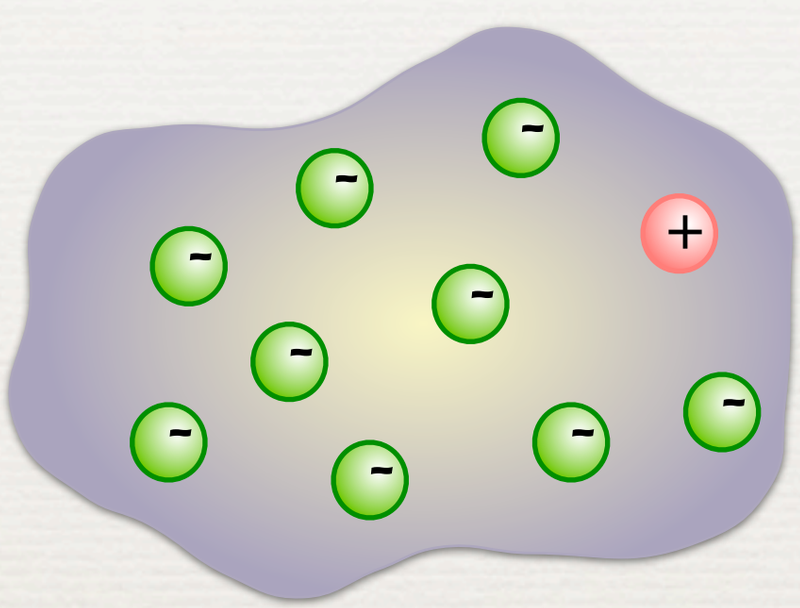
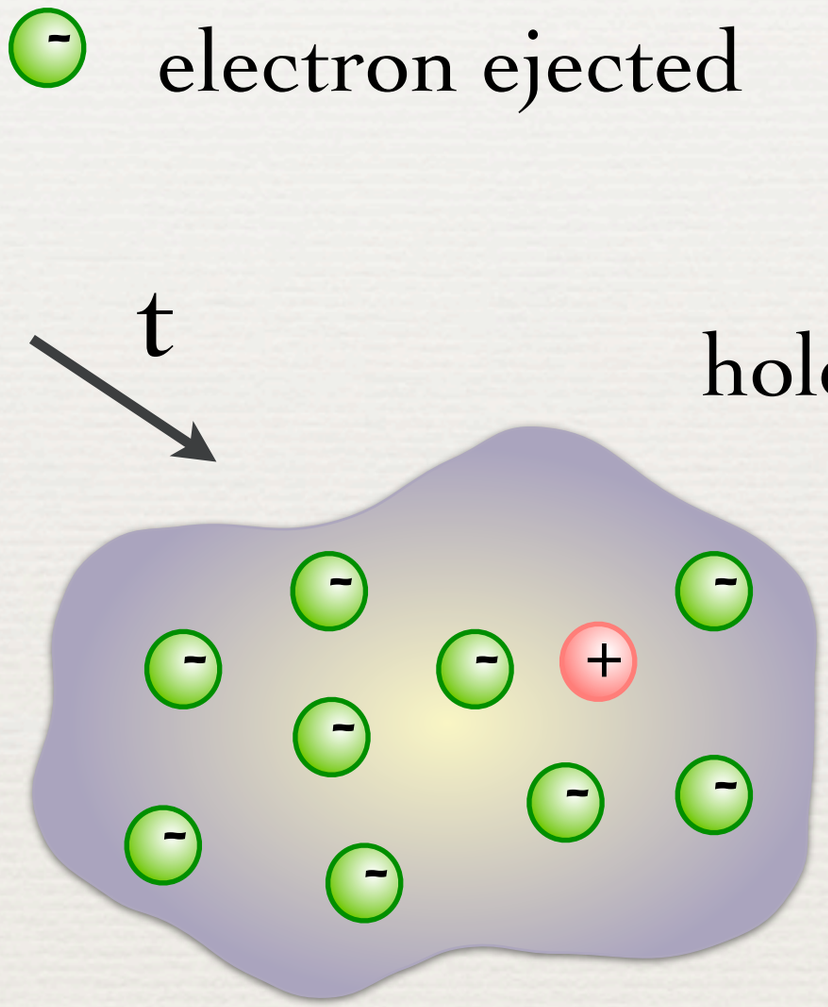
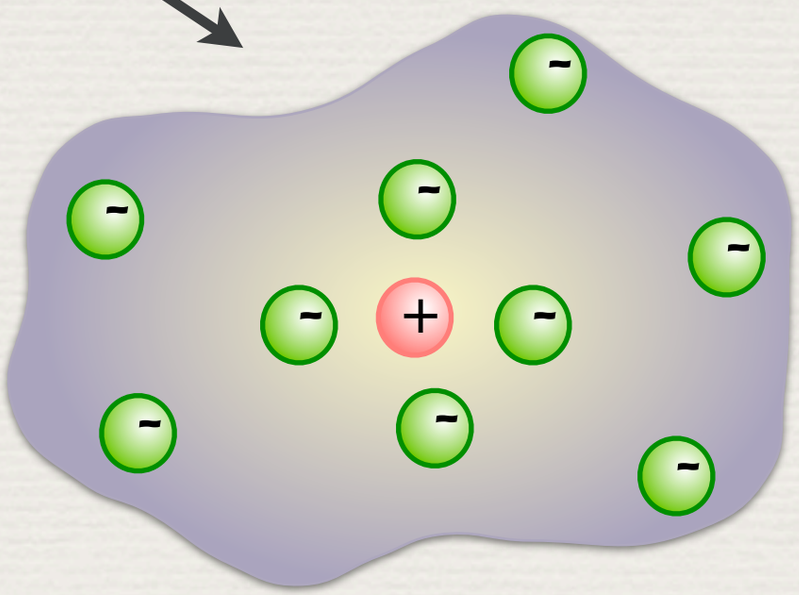






electron ejected

t

hole is screened

t

hole is screened dynamically

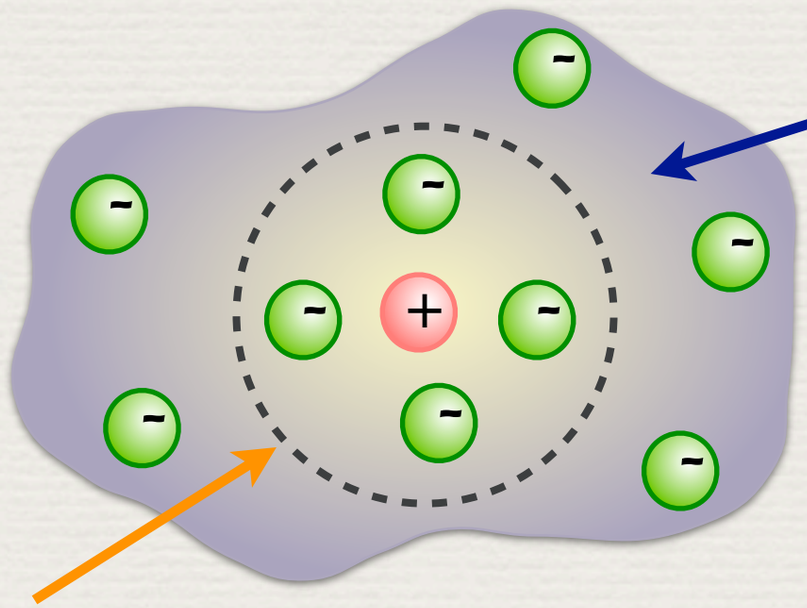
screening is time dependent

The screened Coulomb interaction

dielectric function

$$W(\mathbf{r},\mathbf{r}',t) = \int d\mathbf{r}'' \frac{\varepsilon^{-1}(\mathbf{r},\mathbf{r}'',t)}{|\mathbf{r}''-\mathbf{r}'|}$$

screened — **Coulomb interaction** — ***bare***



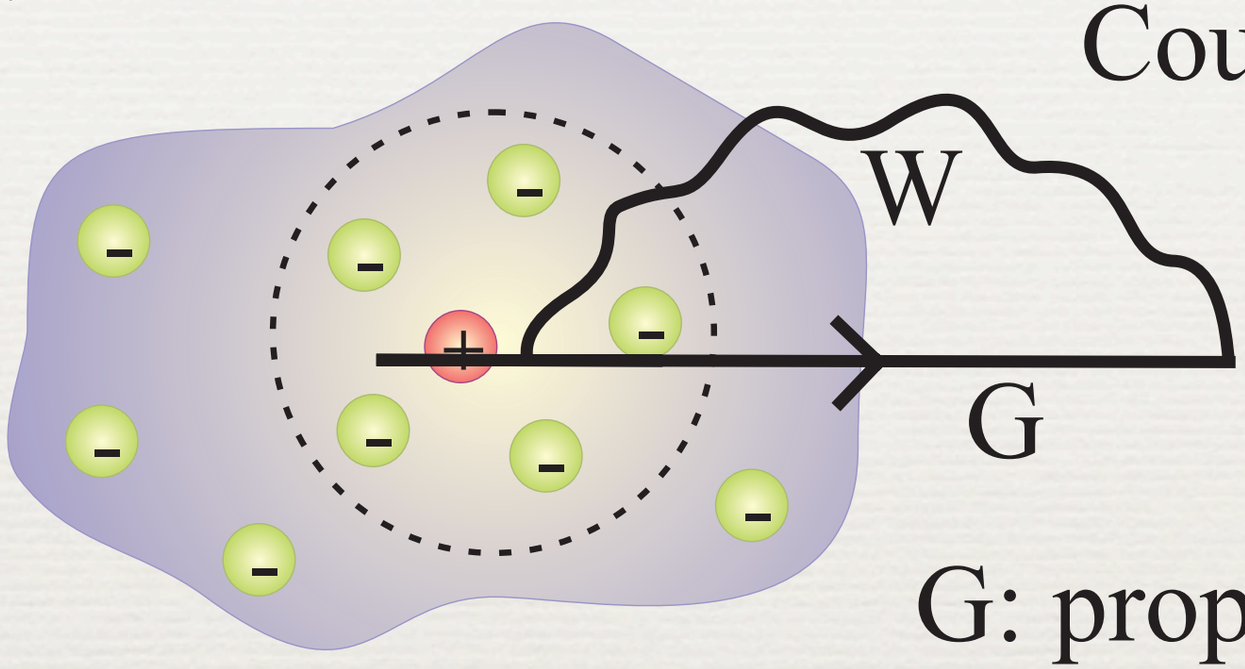
hole is screened by the system

quasiparticle

GW approximation - screened electrons

$$\Sigma = iGW$$

W: screened Coulomb



G: propagator

self-energy:

- energy that the quasiparticle feels due to its own presence

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

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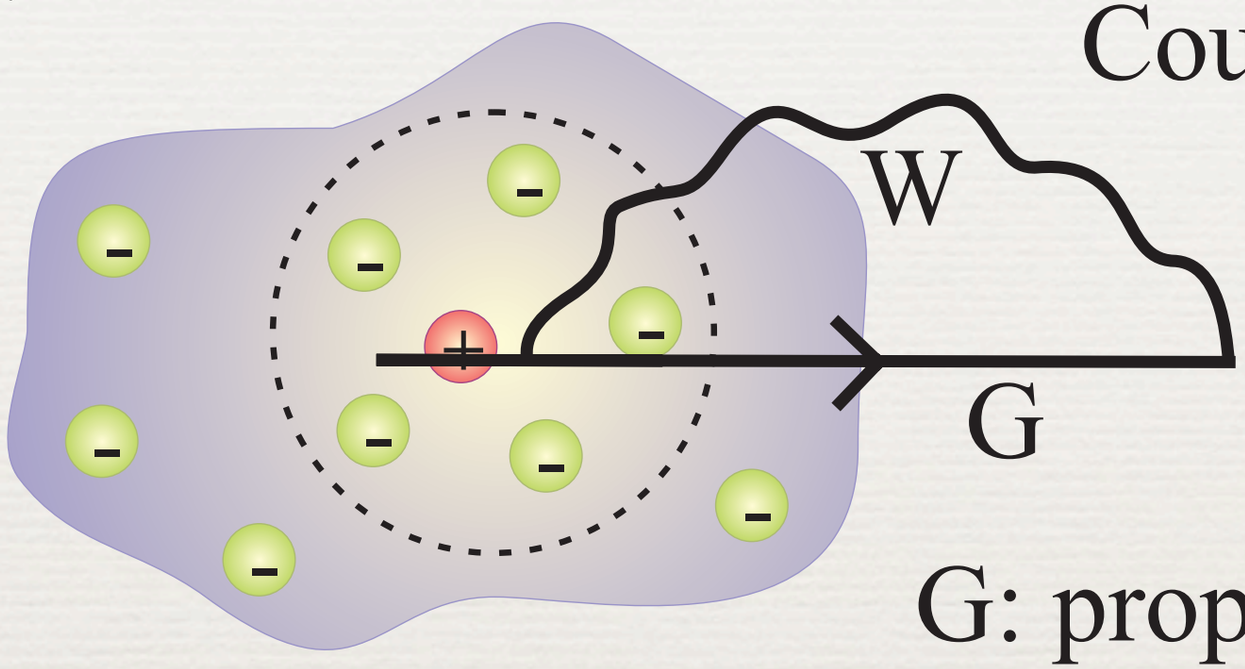

G: propagator

Dyson equation:

$$G^{-1} = G_0^{-1} - \Sigma$$

non-interacting Green's function

G is solution of Hedin's equations

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

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

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

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

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

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

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exact, therefore not tractable

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

G is solution of Hedin's equations

GW approximation

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do not despair

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

GW in practice

Step 1:

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

GW in practice

Step 1:

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

Step 2:

- Set up Kohn-Sham Green's function:

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

GW in practice

Step 1:

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Step 3:

- Construct polarizability:

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

GW in practice

Step 4:

- Dielectric function:

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

GW in practice

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Step 5:

- Screened Coulomb interaction:

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

GW in practice

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Step 6:

- Self-energy:

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

GW in practice

Step 7:

- Solve quasiparticle equation:

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

Step 7b:

- Perturbation theory: $\psi_s(\mathbf{r}) = \phi_s^{\mathrm{KS}}(\mathbf{r})$

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

GW in practice

Step 7:

- Solve quasiparticle equation:

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

Step 7b:

- Perturbation theory: $\psi_s(\mathbf{r}) = \phi_s^{\mathrm{KS}}(\mathbf{r})$

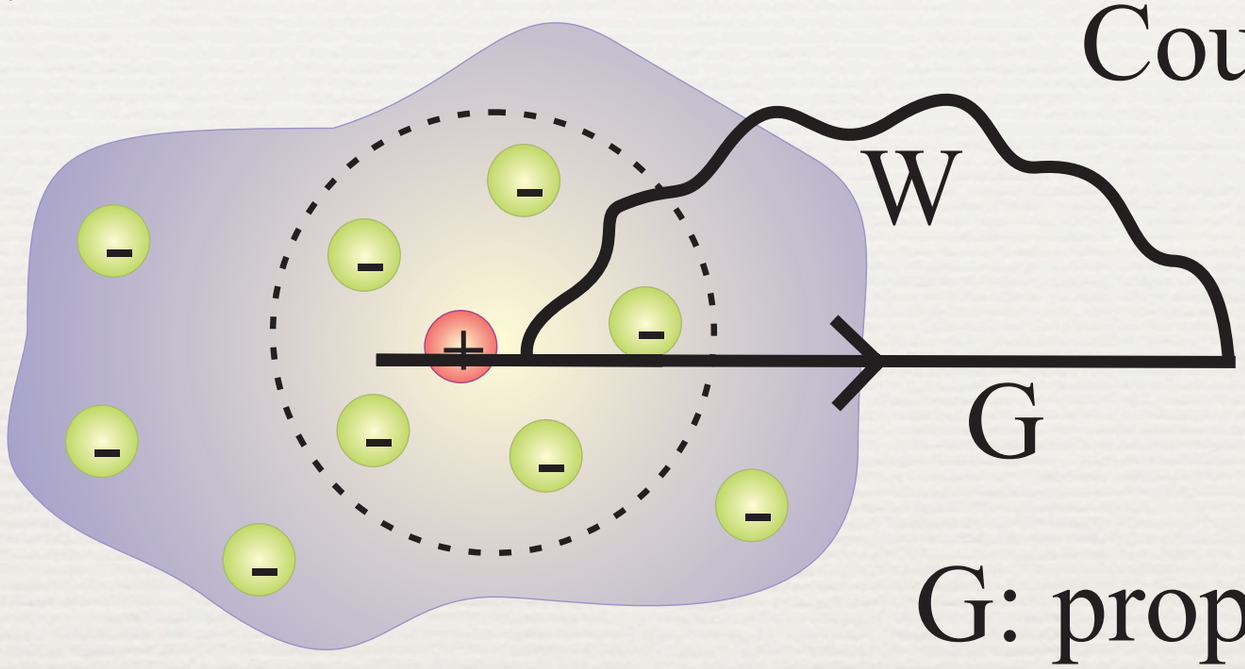
$$\epsilon_s^{qp} = \epsilon_s^{\mathrm{KS}} + \langle s|\Sigma(\epsilon_s^{qp})|s\rangle - \langle s|v_{xc}|s\rangle$$

_GW_ formal scaling ~ system size^4

GW approximation - screened electrons

$$\Sigma = iGW$$

W: screened Coulomb



G: propagator

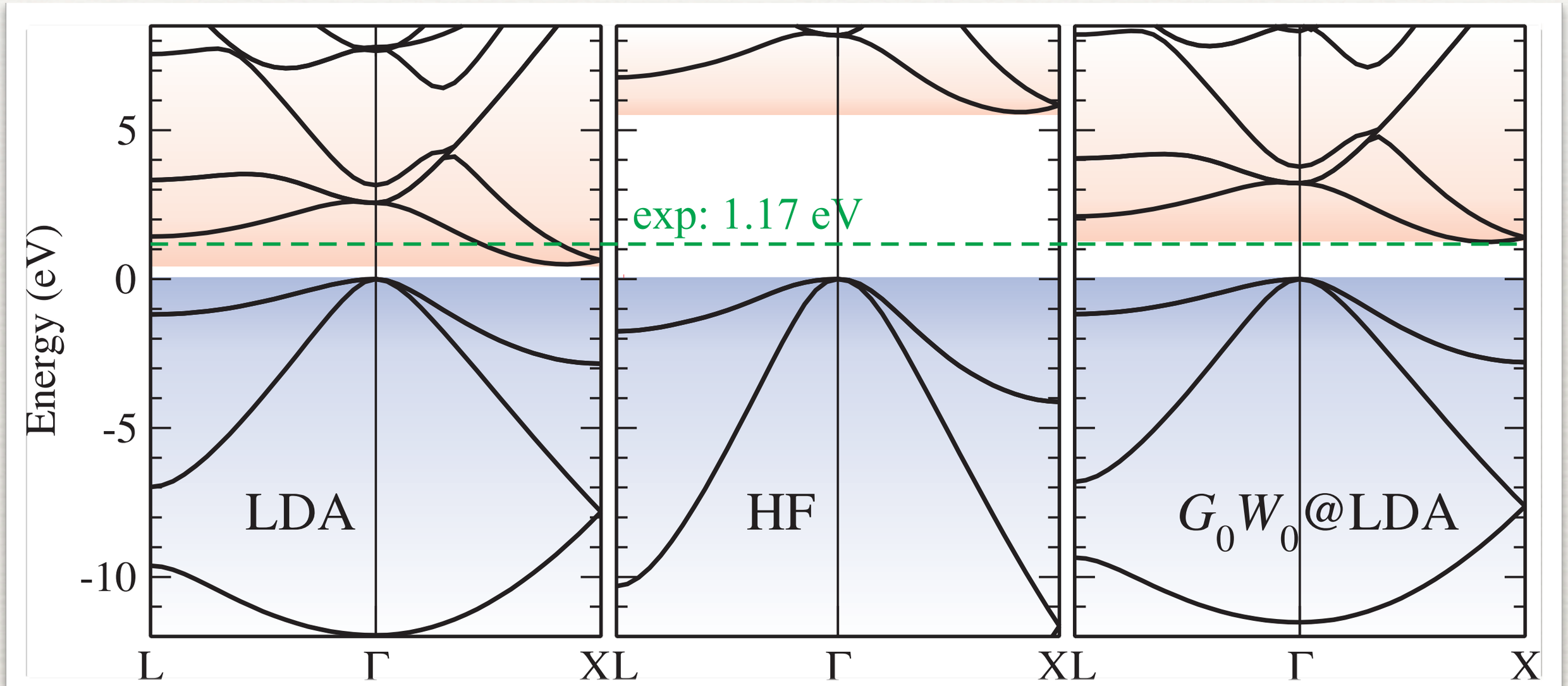
self-energy: $\Sigma = \Sigma_x + \Sigma_c$

iGv — **exact exchange (Hartree-Fock)**

$iG(W - v)$ — **screening (due to other electrons)**

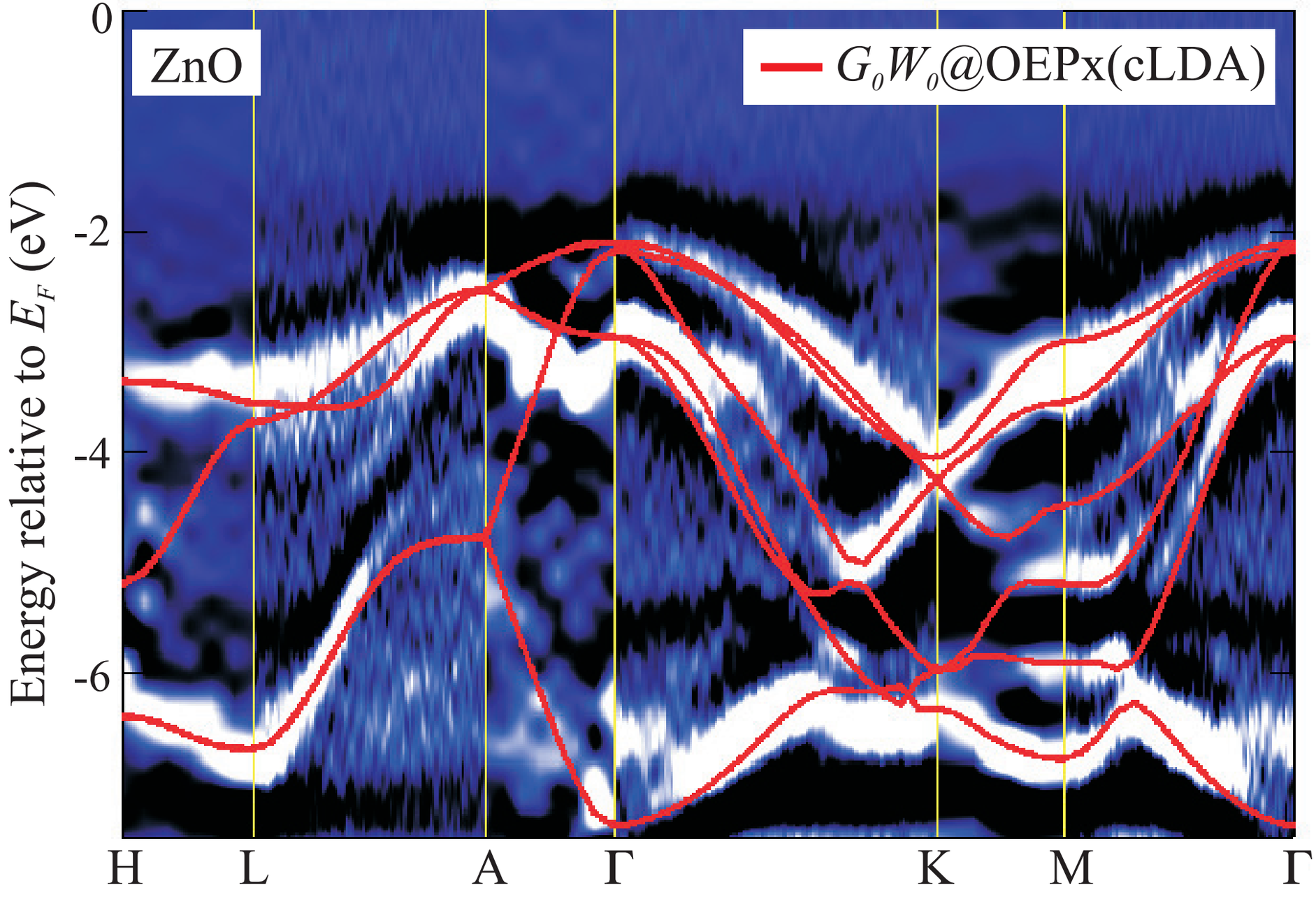
On the importance of screening

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



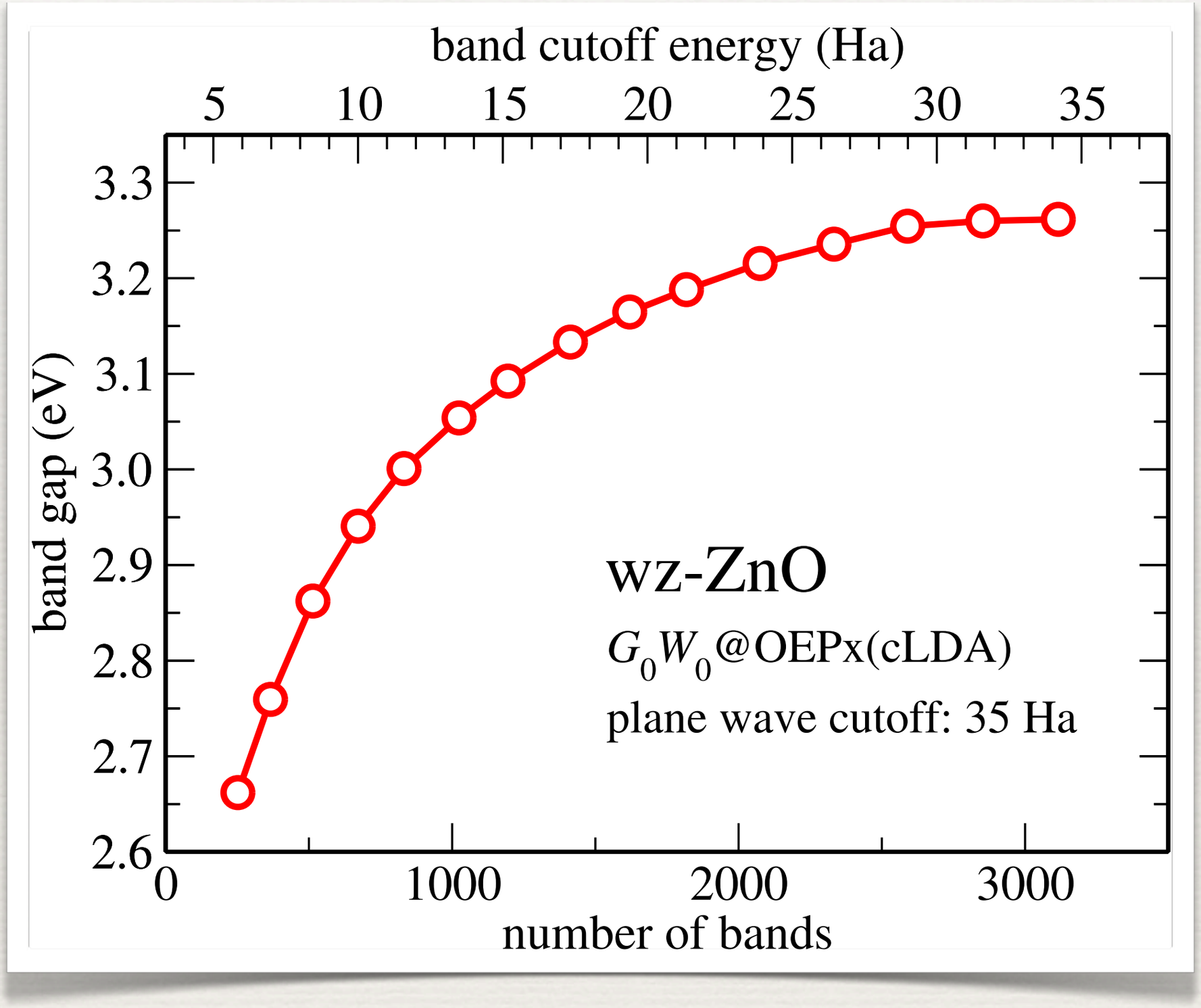
- Hartree-Fock (HF) exact exchange gap much too large
- *W* is essential for solids

Angle resolved photoemission - ZnO



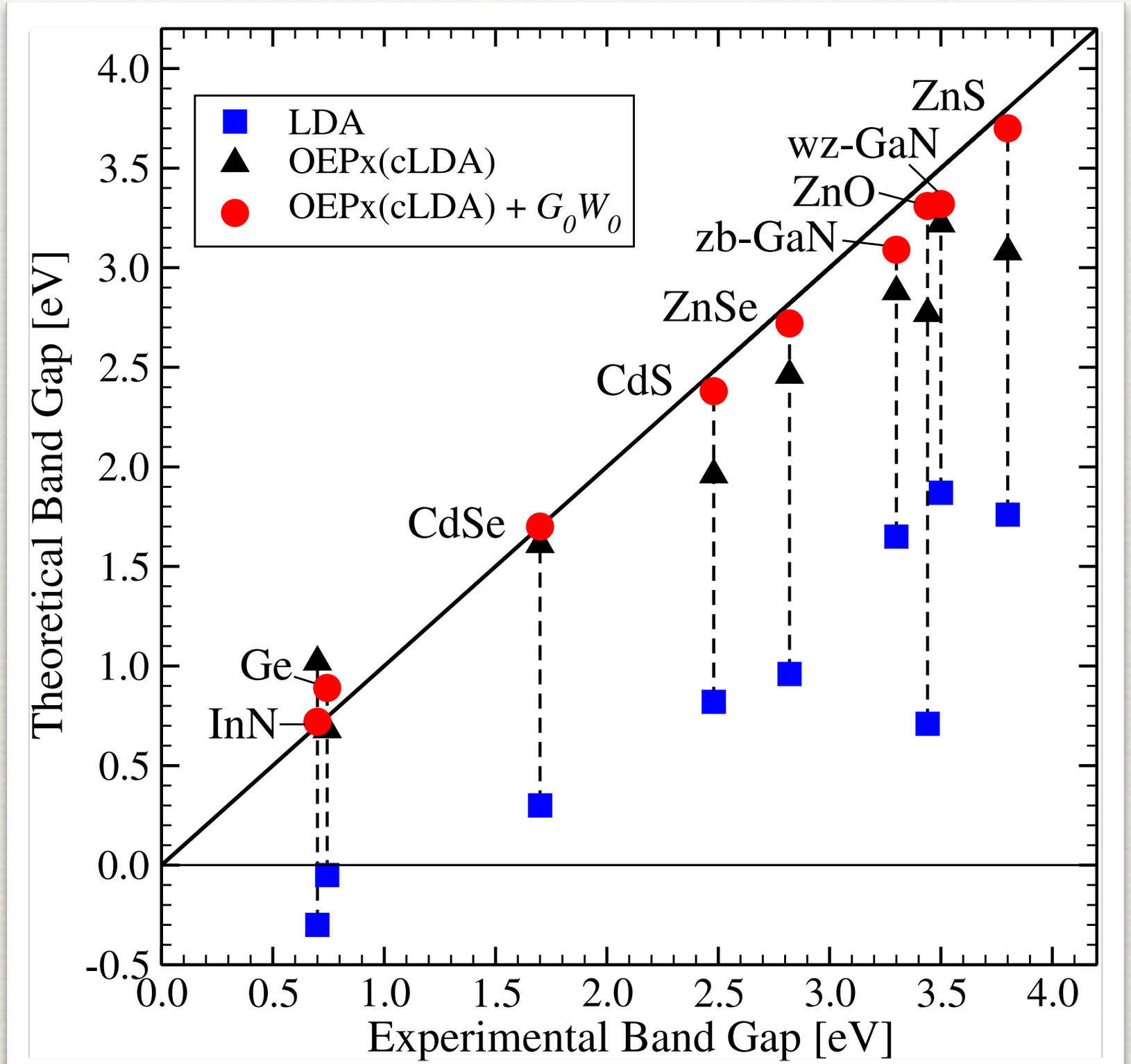
Q. Yan, P. Rinke, M. Winkelnkemper, A. Qteish, D. Bimberg, M. Scheffler, C. G. Van de Walle, Semicond. Sci. Technol. 26, 014037 (2011)

Convergence of G_0W_0 for ZnO



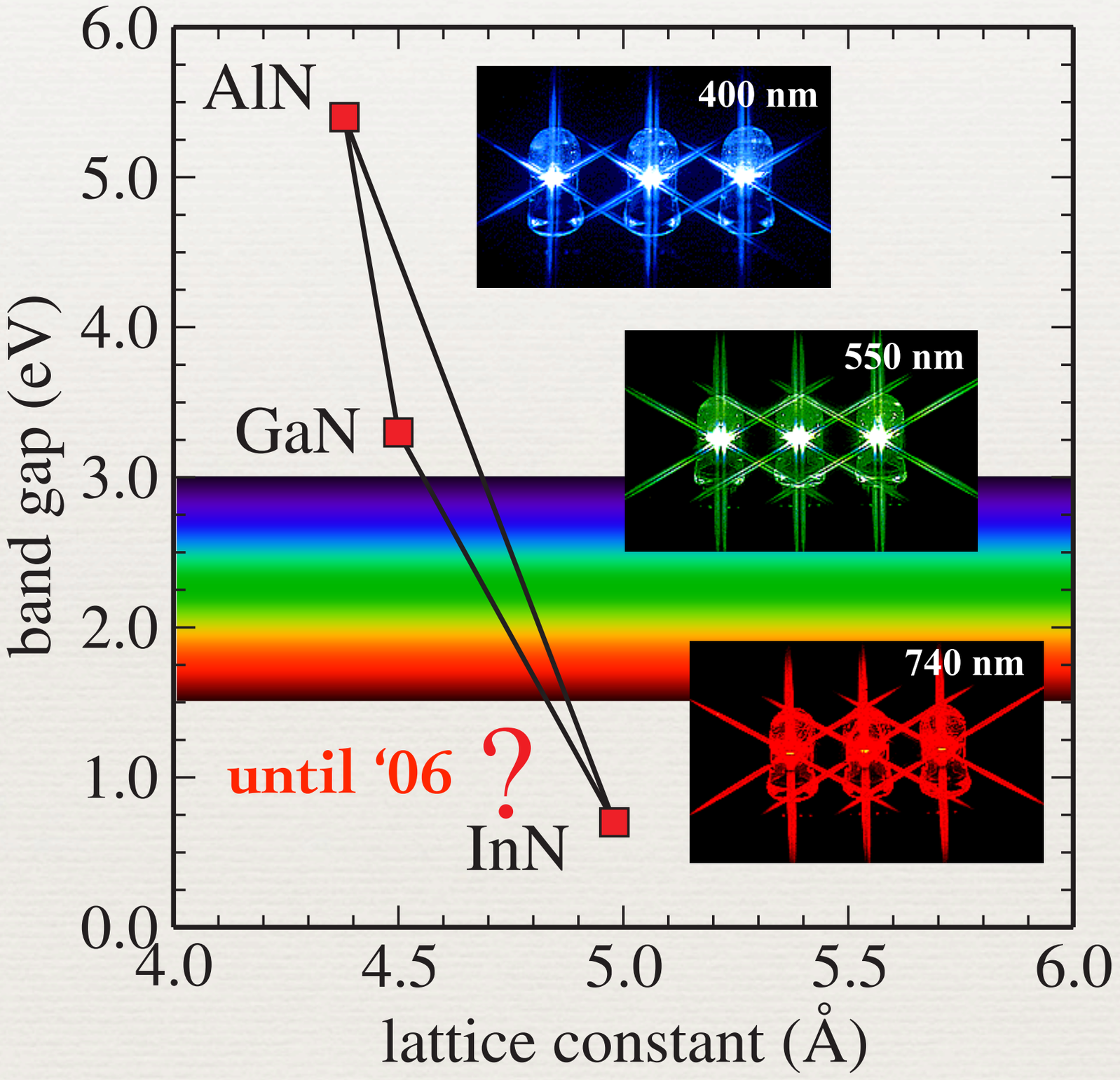
Yan, Rinke, Winkelnkemper, Qteish, Bimberg, Scheffler, Van de Walle, Semicond. Sci. Technol. 26, 014037 (2011)

Band gaps of solids



P. Rinke *et al.* New J. Phys. 7, 126 (2005), phys. stat. sol. (b) 245, 929 (2008)

Do we know the band gap of InN?



Band gap of InN

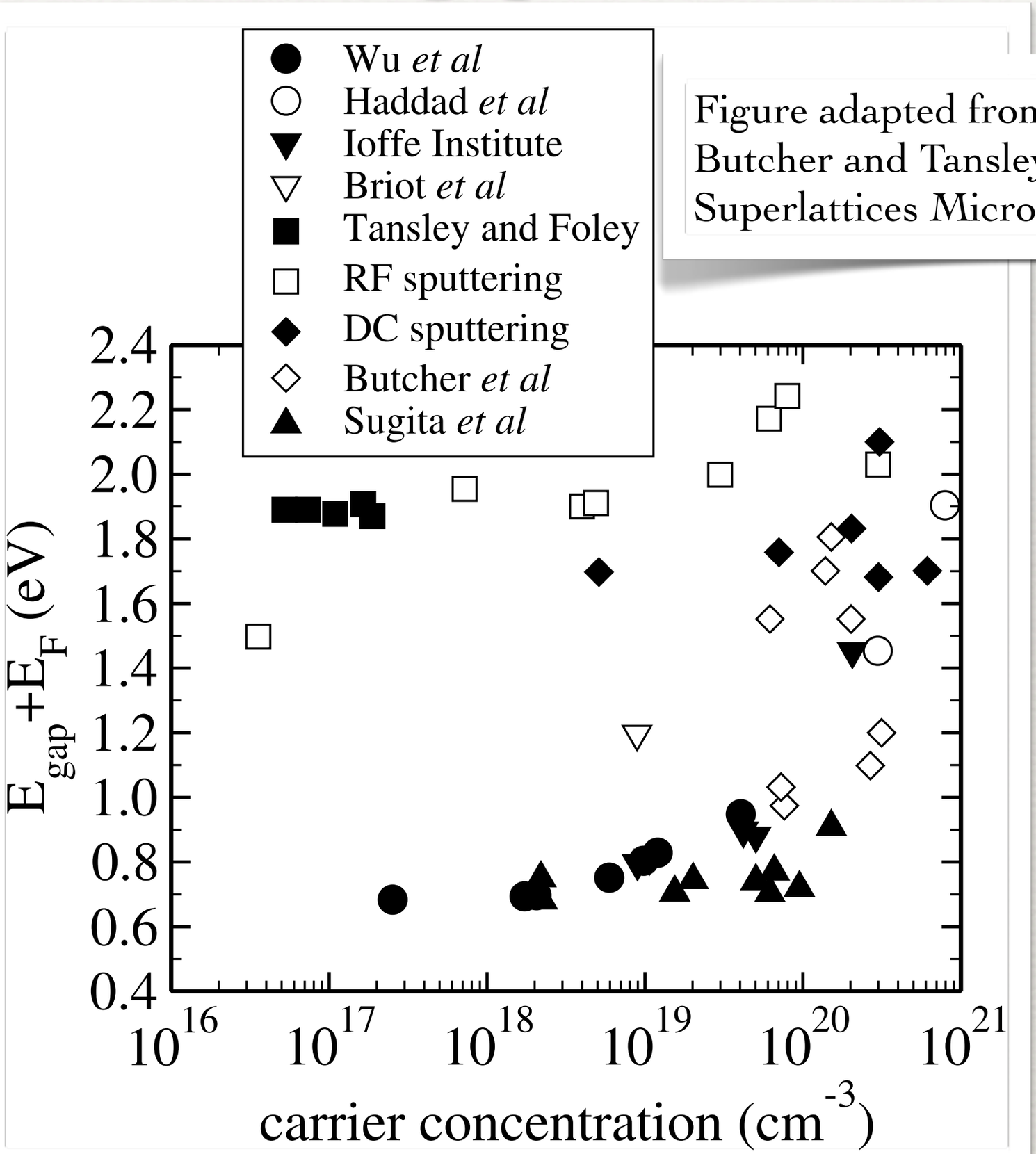


Figure adapted from
Butcher and Tansley
Superlattices Microstruct. **38**, 1 (2005)

Band gap of InN

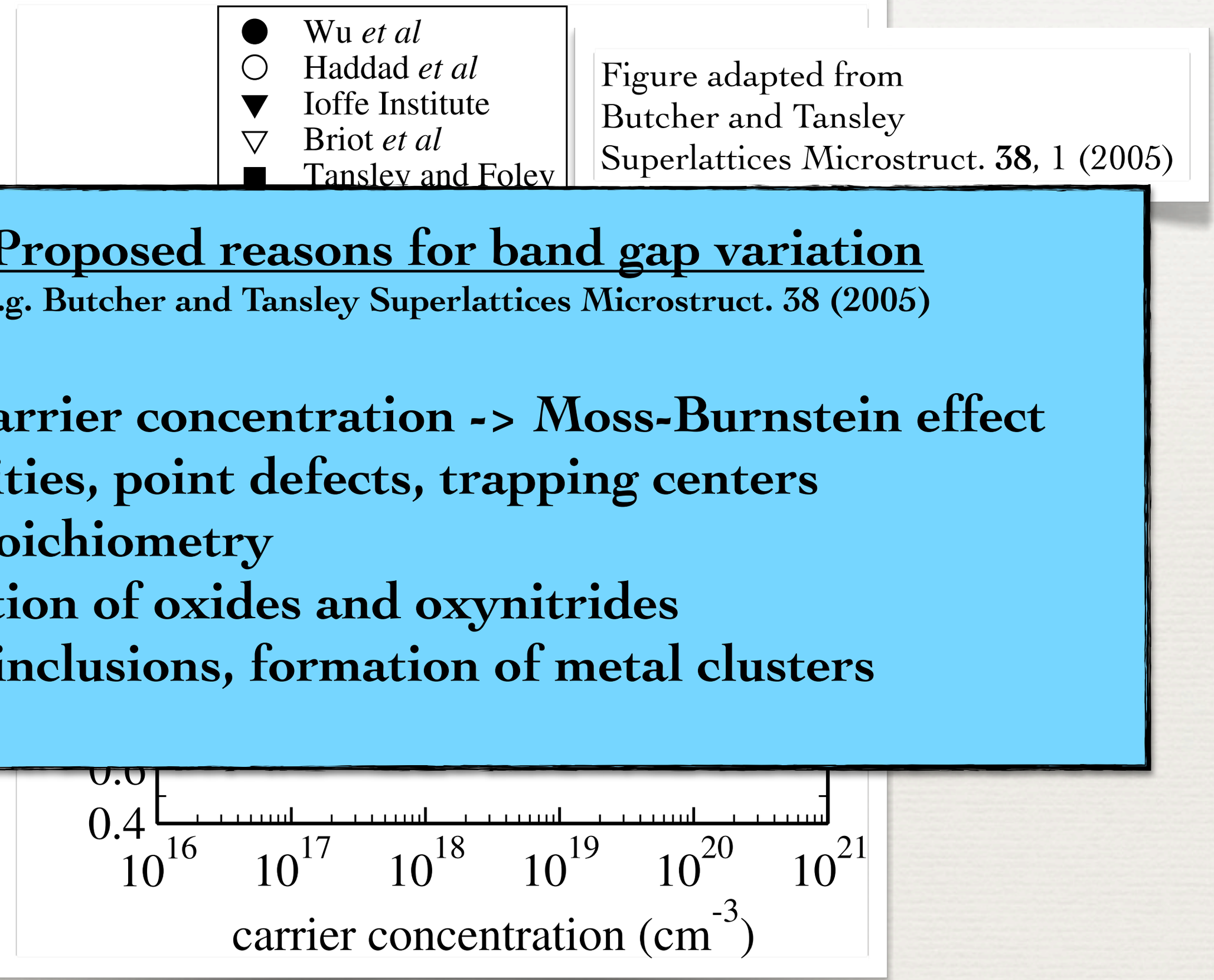


Figure adapted from
Butcher and Tansley
Superlattices Microstruct. **38**, 1 (2005)

Proposed reasons for band gap variation

e.g. Butcher and Tansley Superlattices Microstruct. 38 (2005)

- **high carrier concentration -> Moss-Burnstein effect**
- **impurities, point defects, trapping centers**
- **non-stoichiometry**
- **formation of oxides and oxynitrides**
- **metal inclusions, formation of metal clusters**

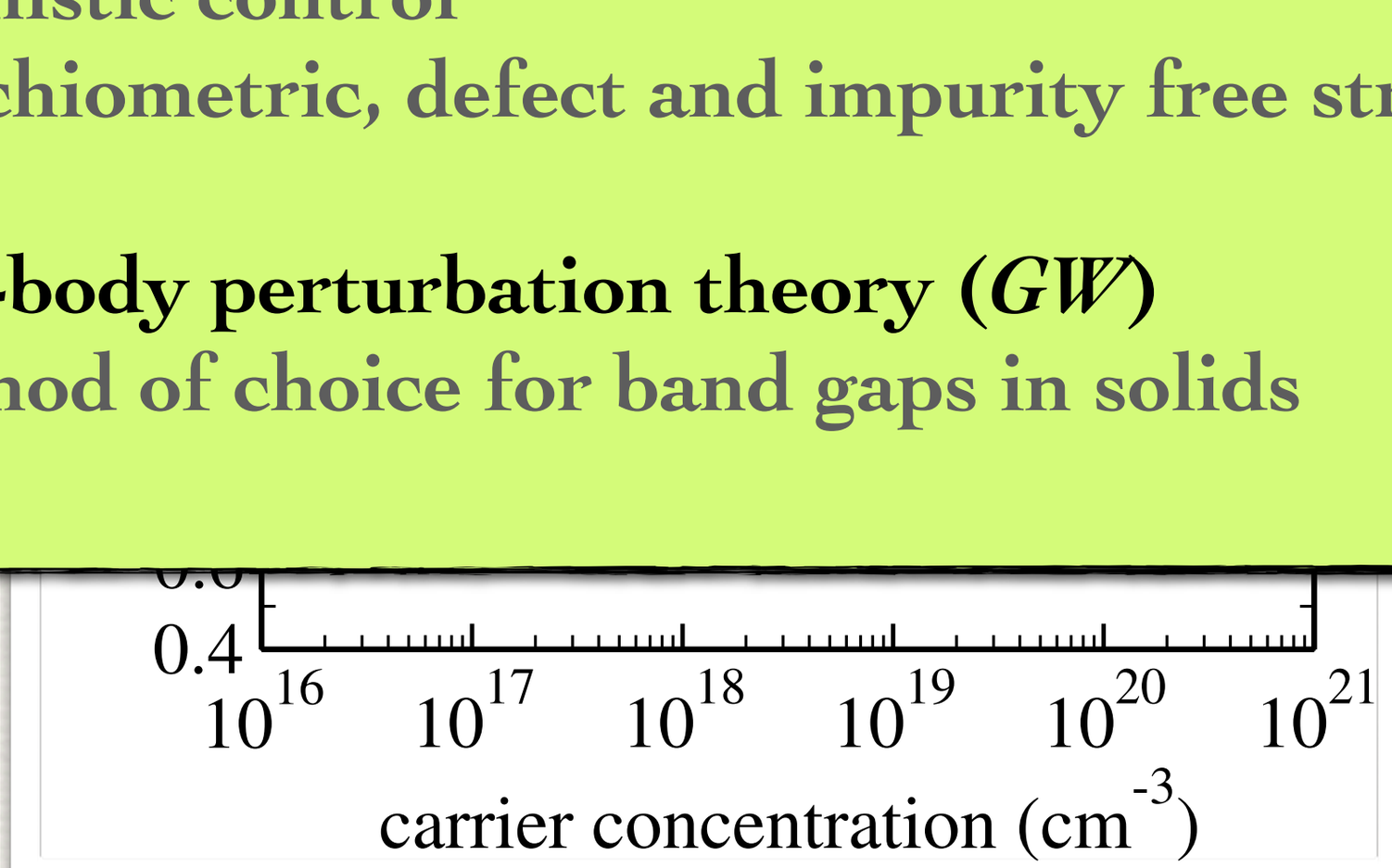
Band gap of InN

Figure adapted from
Butcher and Tansley

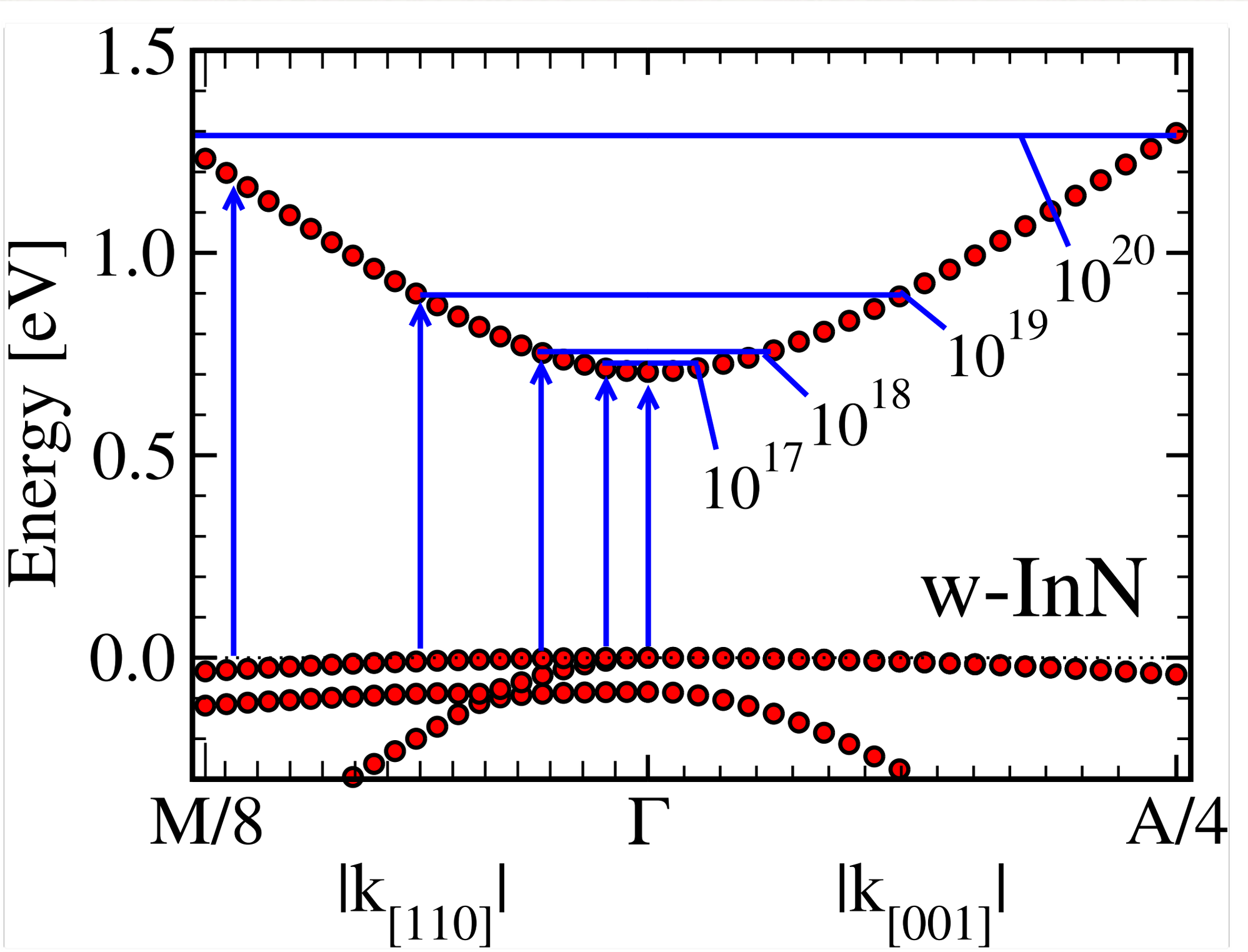
How can first principles help?

- **Density-functional theory (DFT)**
  - atomistic control
  - stoichiometric, defect and impurity free structures

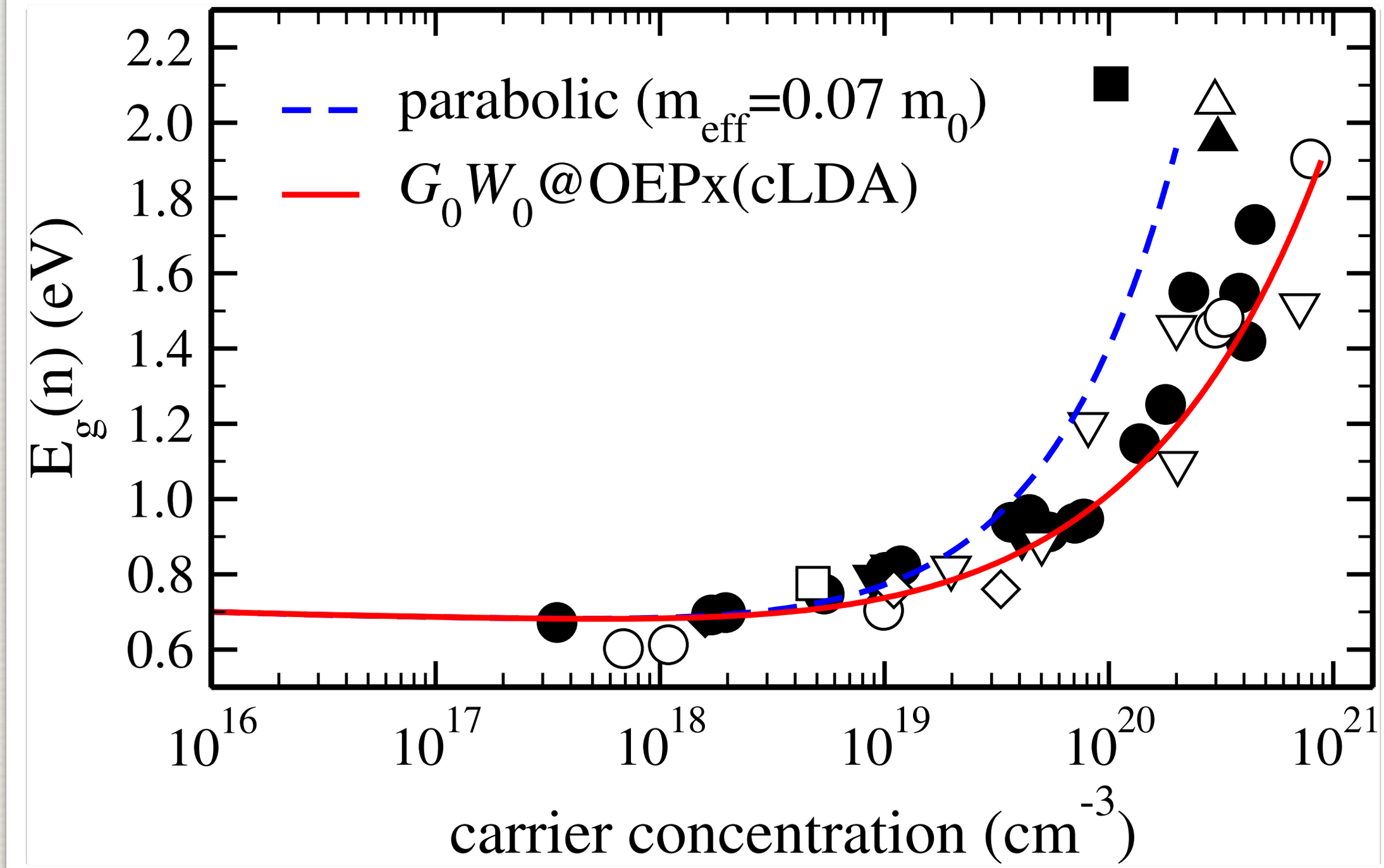
- **many-body perturbation theory (*GW*)**
  - method of choice for band gaps in solids



InN - *GW* band structure and Moss-Burstein



InN - *GW* band structure and Moss-Burstein



P. Rinke, et al., Appl. Phys. Lett. **89**, 161919 (2006)

Atomistic understanding of molecules@surfaces

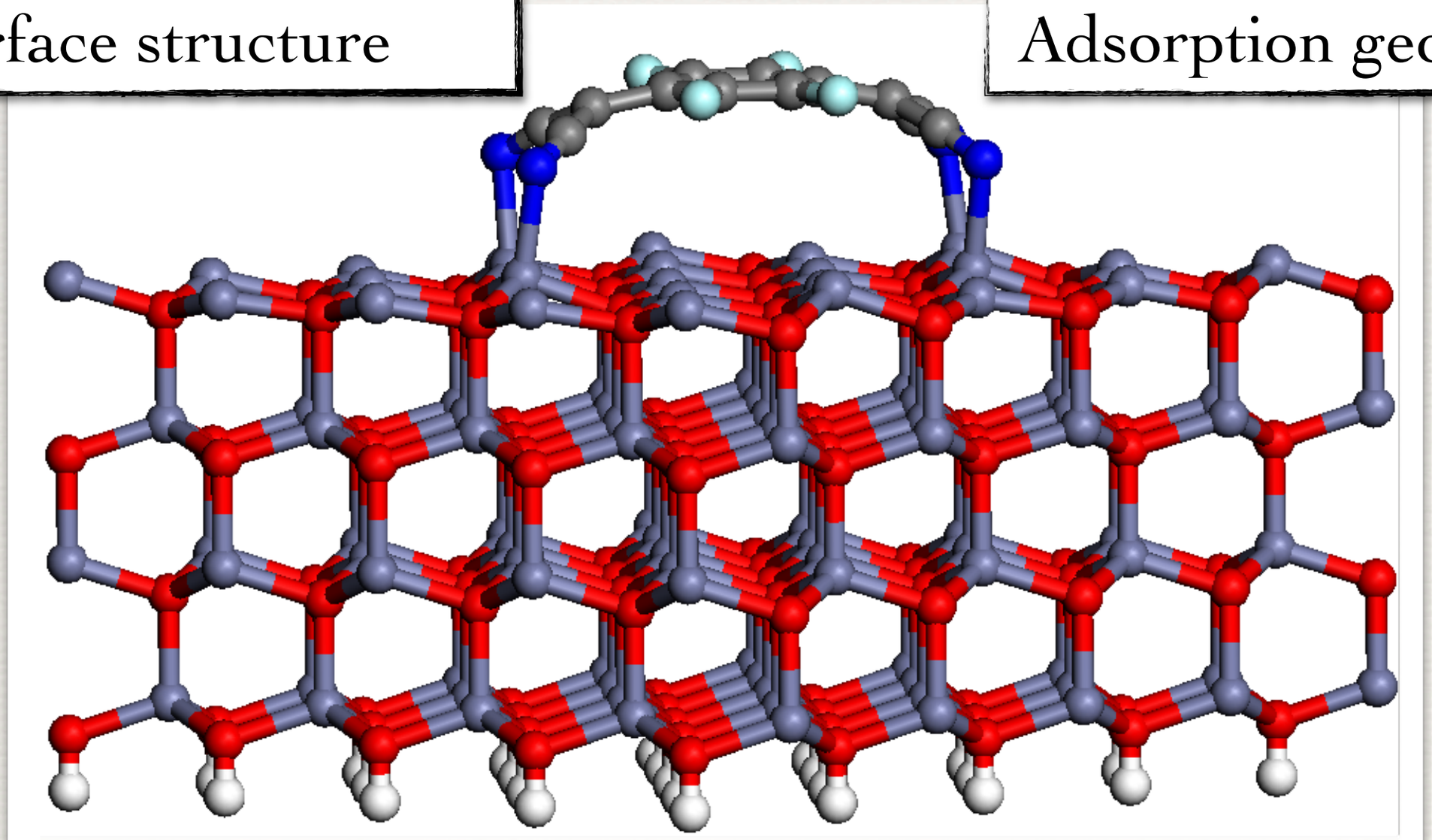
Charge transfer

Level alignment

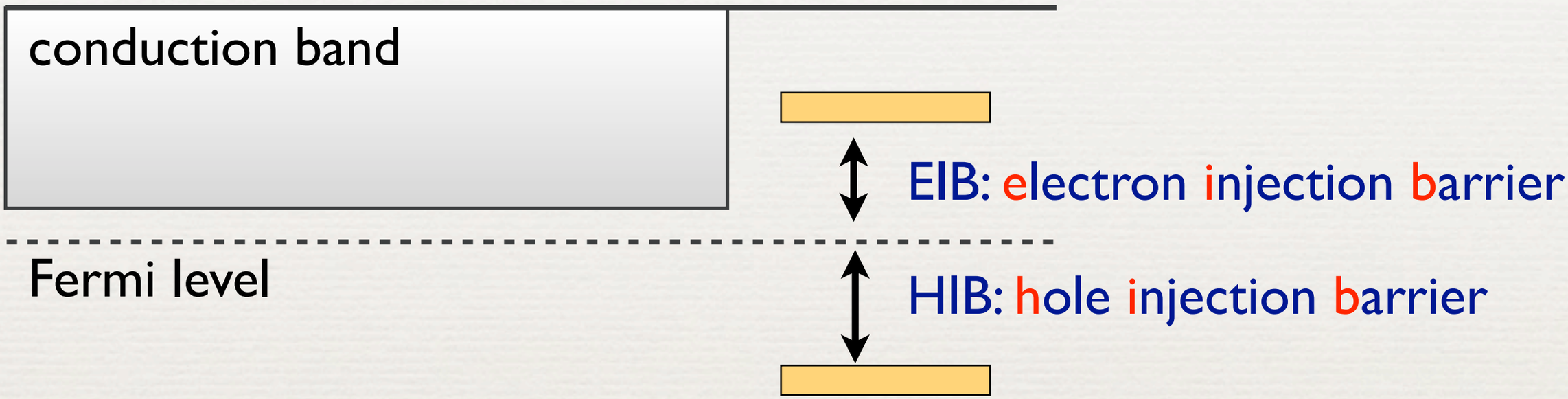
Van der Waals interaction

Surface structure

Adsorption geometry



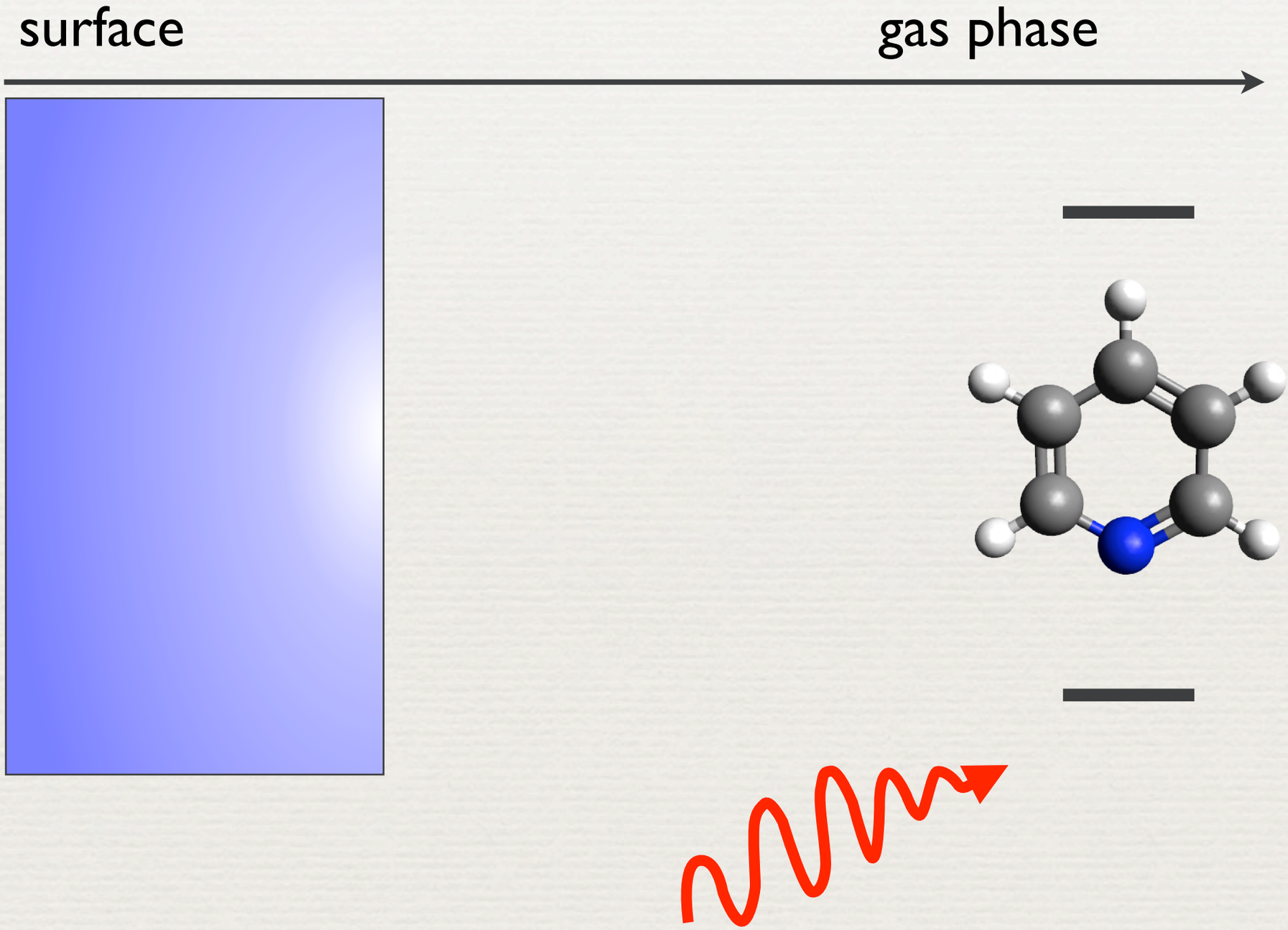
Level alignment at interface



injection limited current:

$$j \propto AT^2 \exp\left(-\frac{\text{charge injection barrier}}{k_B T}\right)$$

Molecular levels at a surface

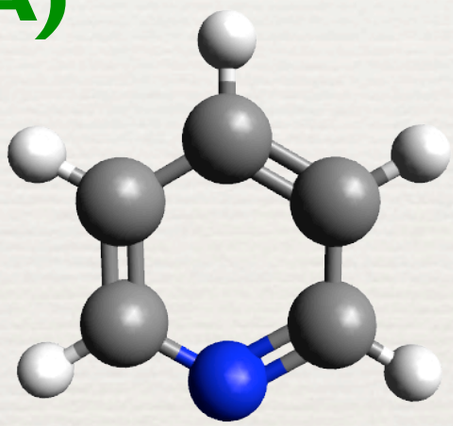


Molecular levels at a surface

surface

gas phase

electron affinity (EA)



ionization potential (IP)

Molecular levels at a surface

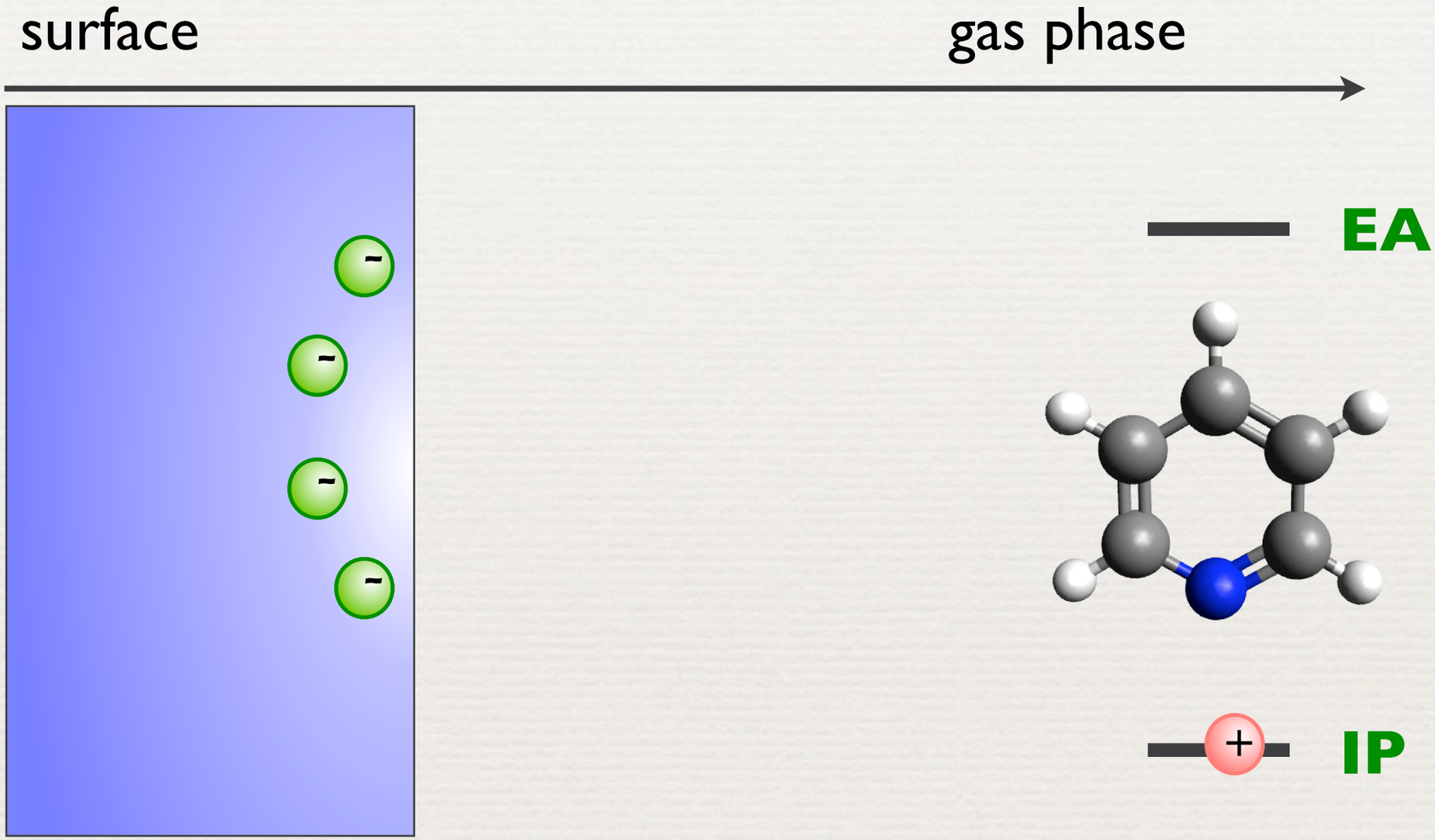


image effect

Molecular levels at a surface

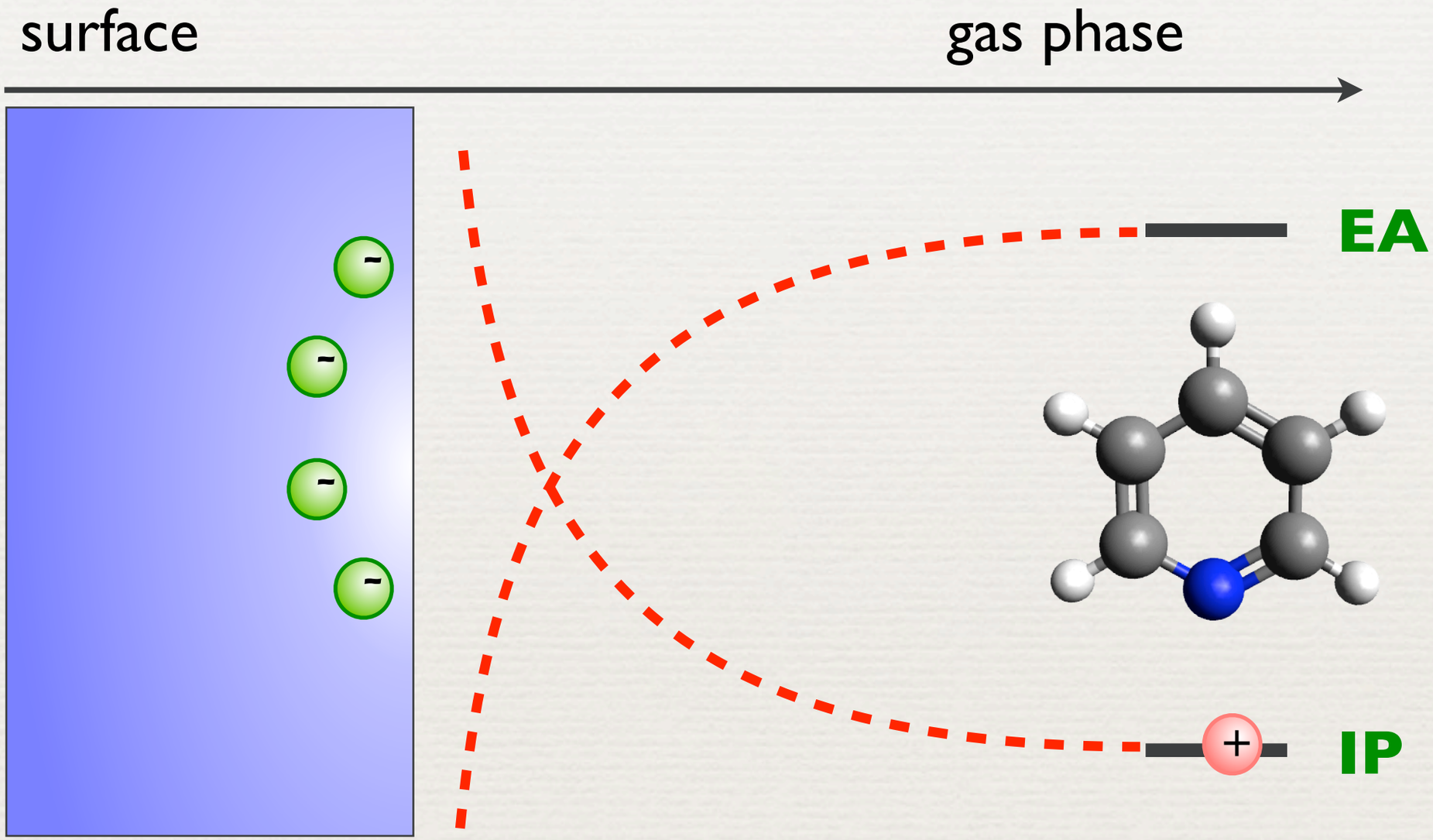


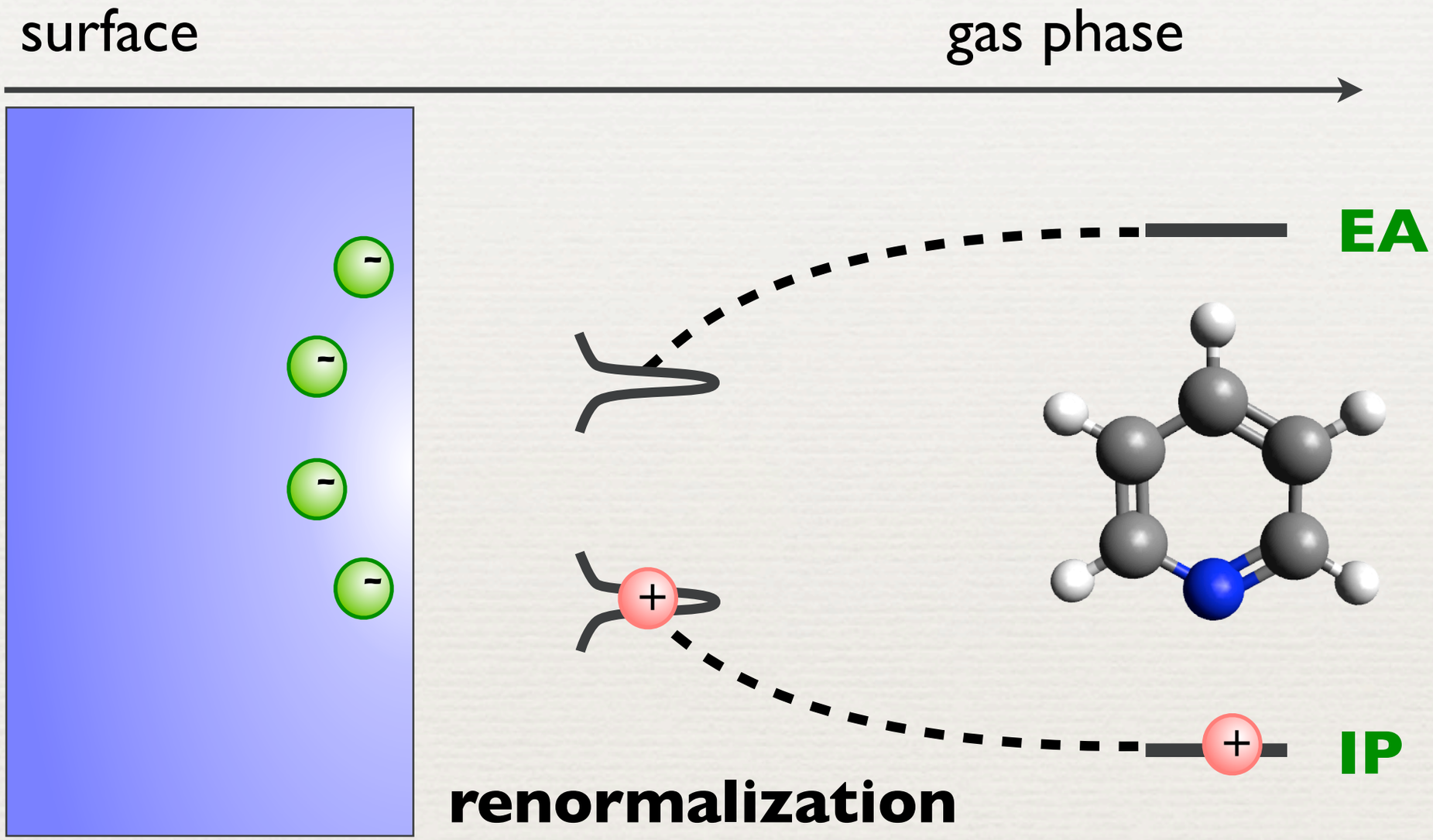
image potentials

metal: $-\frac{1}{4z}$

semiconductor: $-\frac{(\varepsilon-1)}{4(\varepsilon+1)}\frac{1}{z}$

ε dielectric constant

Molecular levels at a surface

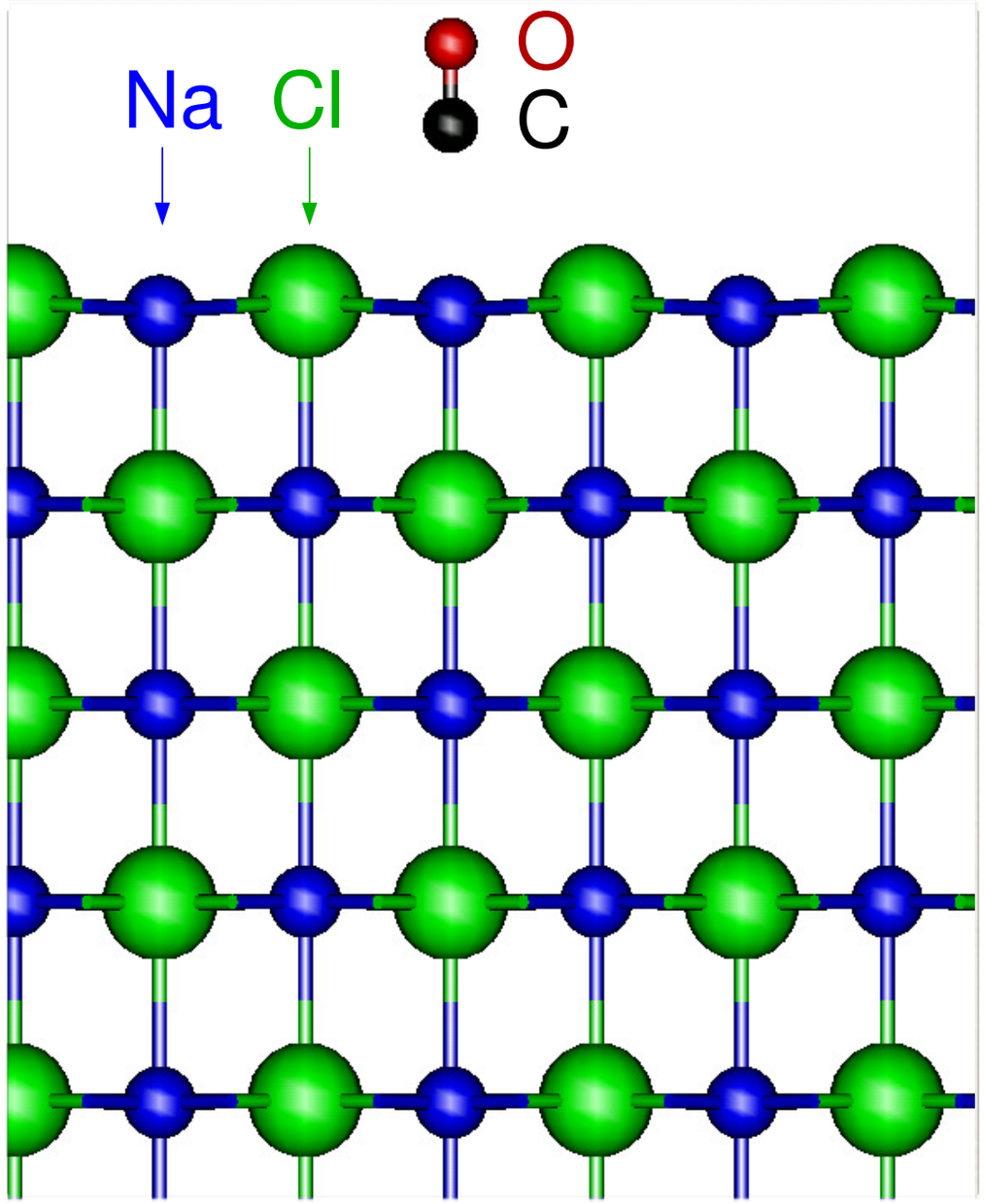


metal: $-\frac{1}{4z}$

semiconductor: $-\frac{(\varepsilon-1)}{4(\varepsilon+1)}\frac{1}{z}$

ε dielectric constant

Renormalization at insulator surfaces



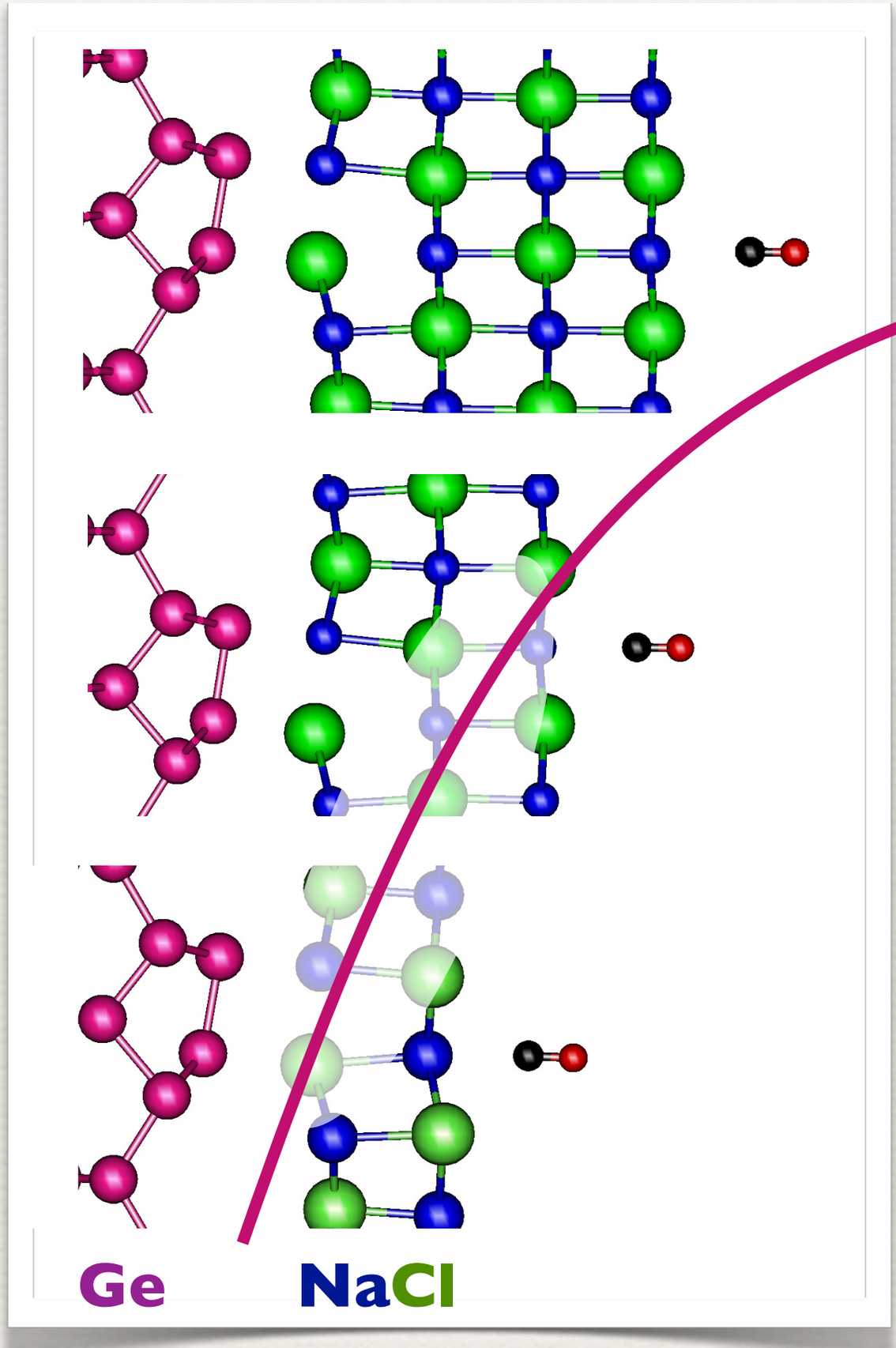
CO HOMO-LUMO gap

gap/eV	LDA	G_0W_0@ LDA	Exp.*
free CO	6.9	15.1	15.8
CO@NaCl	7.4	13.1	

* Constants of Diatomic Molecules (1979), Phys. Rev. Lett. 22, 1034 (1969)

C. Freysoldt, P. Rinke, M. Scheffler, Phys. Rev. Lett. 103, 056803 (2009)

Make CO "ride the image potential"



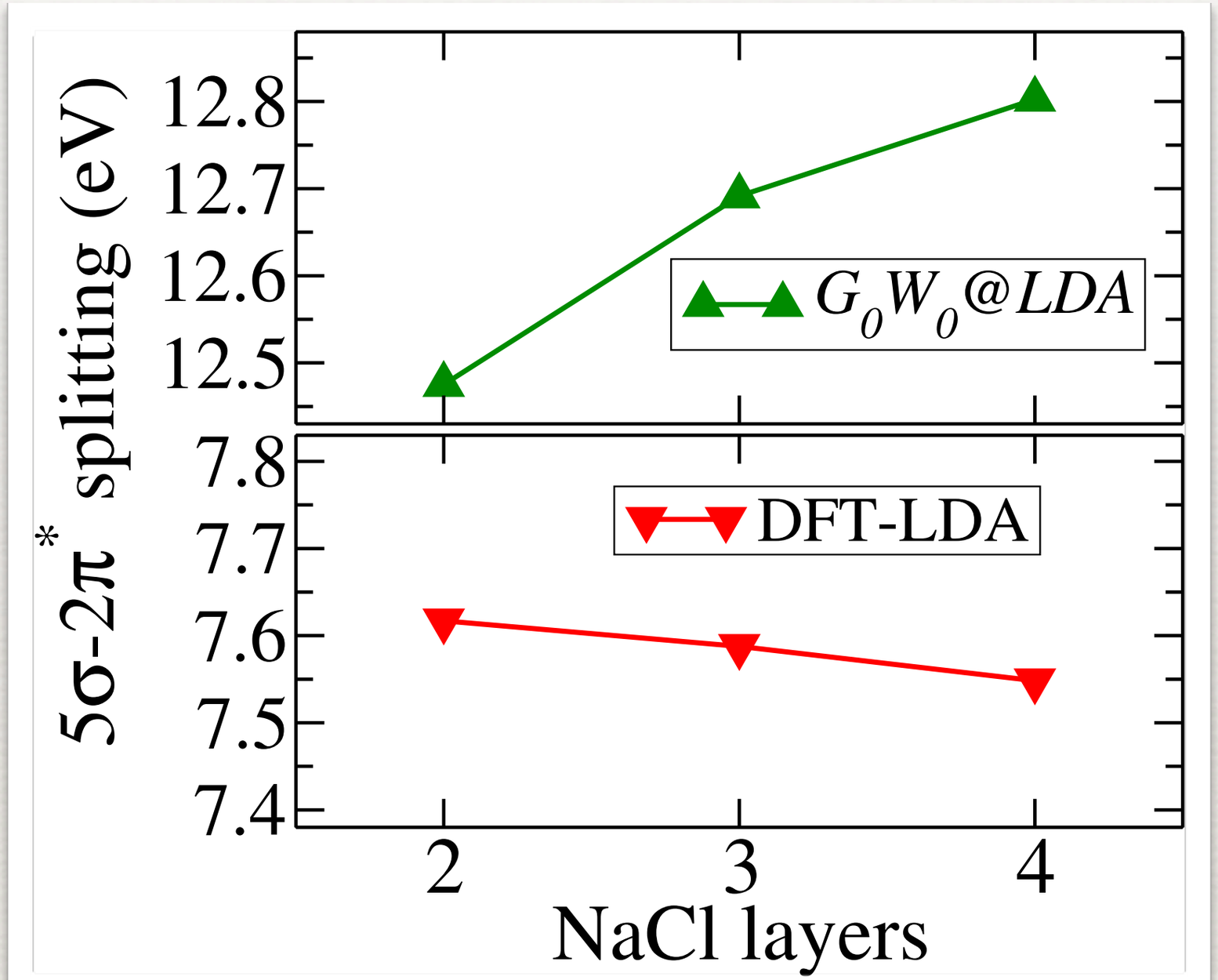
Ge image potential

- NaCl on Ge:
  - prototypical semiconductor/ insulator interface

- Will the CO gap depend on NaCl thickness?

Supported ultrathin films are novel nano-systems in their own rights:
C. Freysoldt, P. Rinke, M. Scheffler, Phys. Rev. Lett. 99, 086101 (2007)

CO on NaCl on Ge - layer dependent gap



- layer-dependent CO gap due to polarization
- molecular levels can be tuned by polarization engineering

C. Freysoldt, P. Rinke, M. Scheffler, Phys. Rev. Lett. 103, 056803 (2009)

Density-functional theory and excitations

exact DFT:

- *ionization potential given by Kohn-Sham eigenvalue of highest occupied state*

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

Density-functional theory and excitations

exact DFT:

- *ionization potential given by Kohn-Sham eigenvalue of highest occupied state*

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

otherwise:

- Janak's theorm (PRA 18, 7165 (1978))

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

rearranging and making mid-point approx.

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

Ionisation Potential, Affinity and (Band) Gaps

- Could use total energy method to compute (also known as ΔSCF)

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

Ionization potential: *minimal energy to remove an electron*

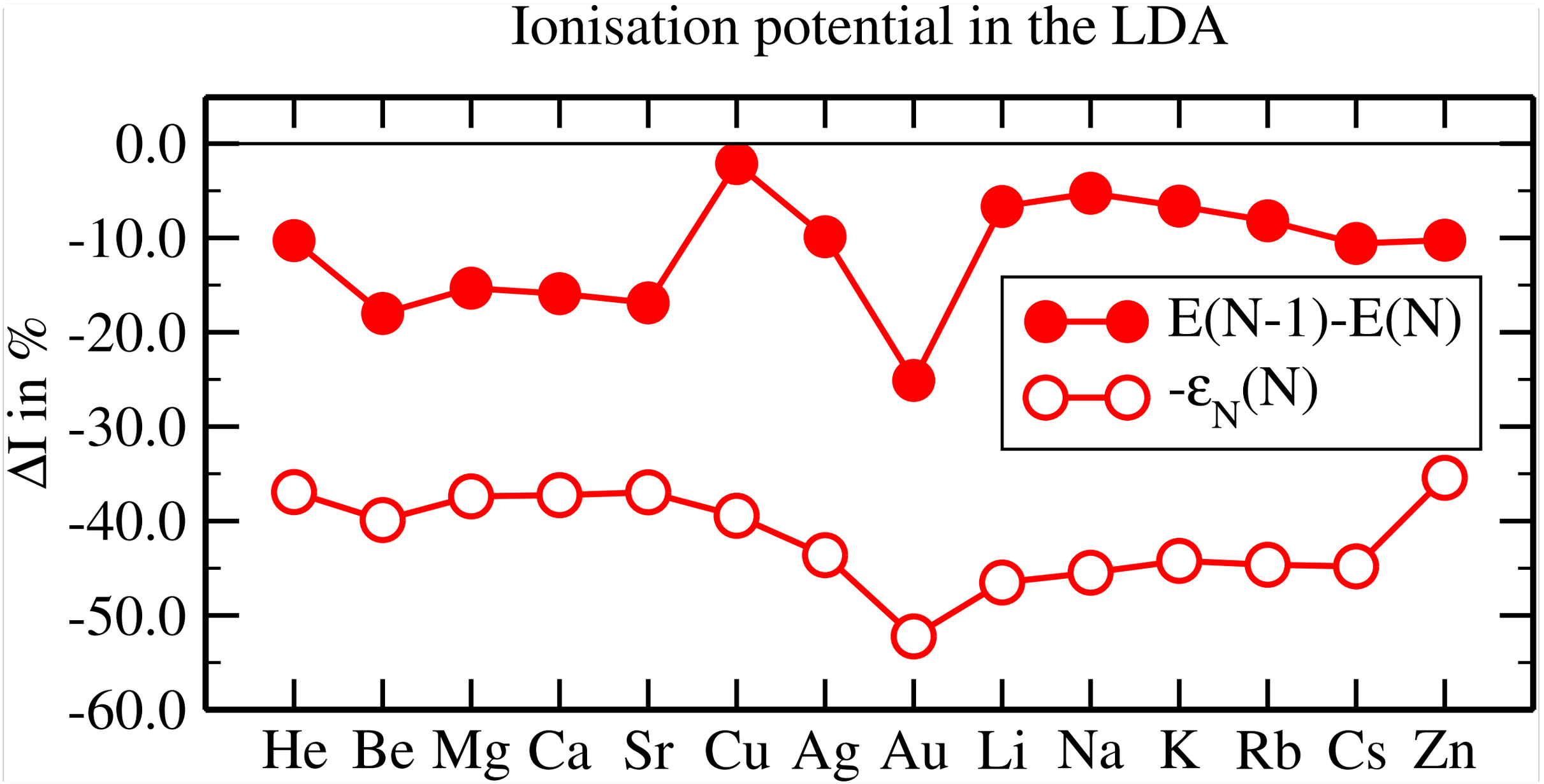
$$I = E(N-1) - E(N)$$

Electron affinity: *minimal energy to add an electron*

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

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

Ionisation Potential, Affinity and (Band) Gaps



Reference: NIST -- Atomic reference data

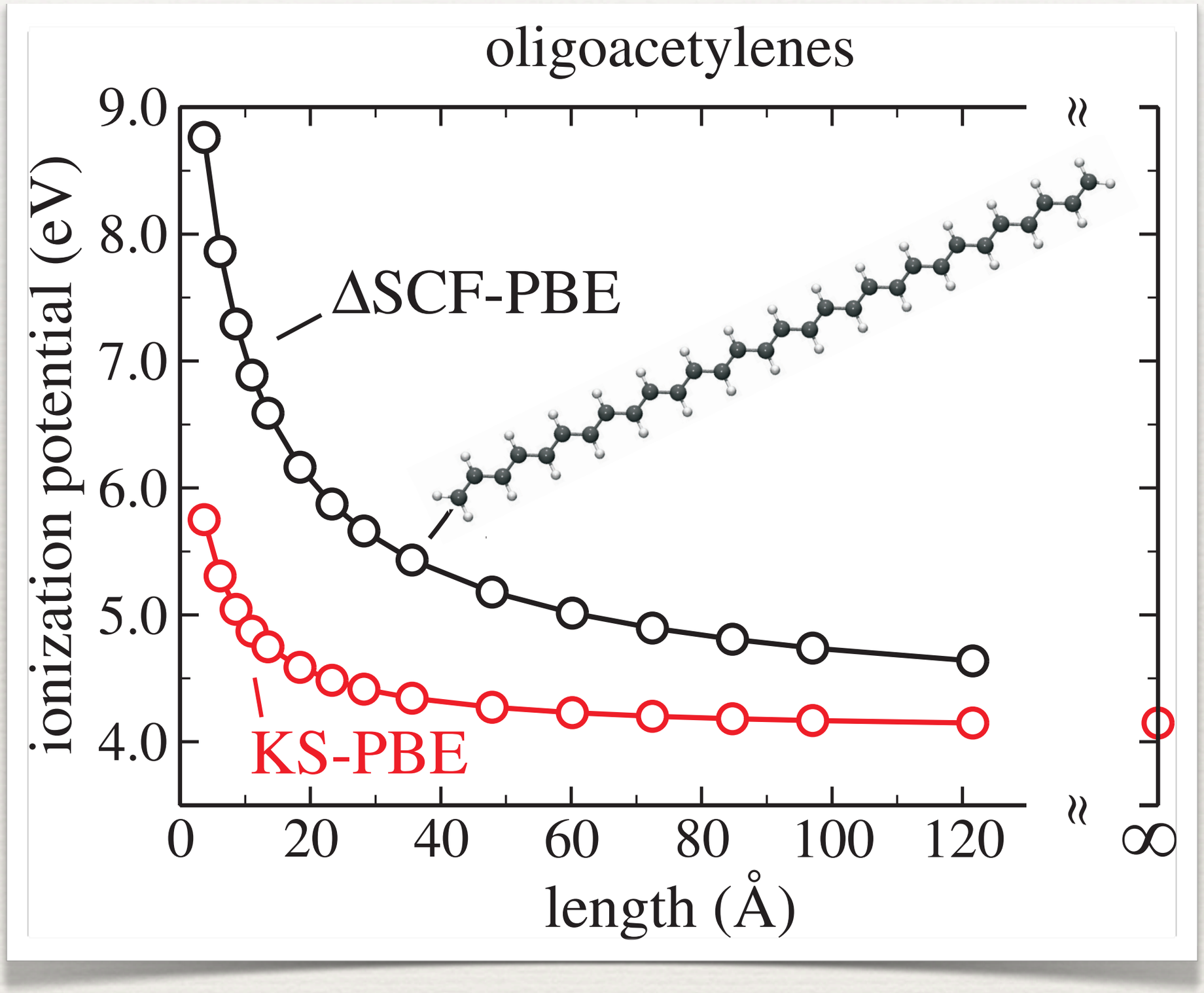
Ionisation Potential, Affinity and (Band) Gaps

ΔSCF better than eigenvalues for IPs!

but:

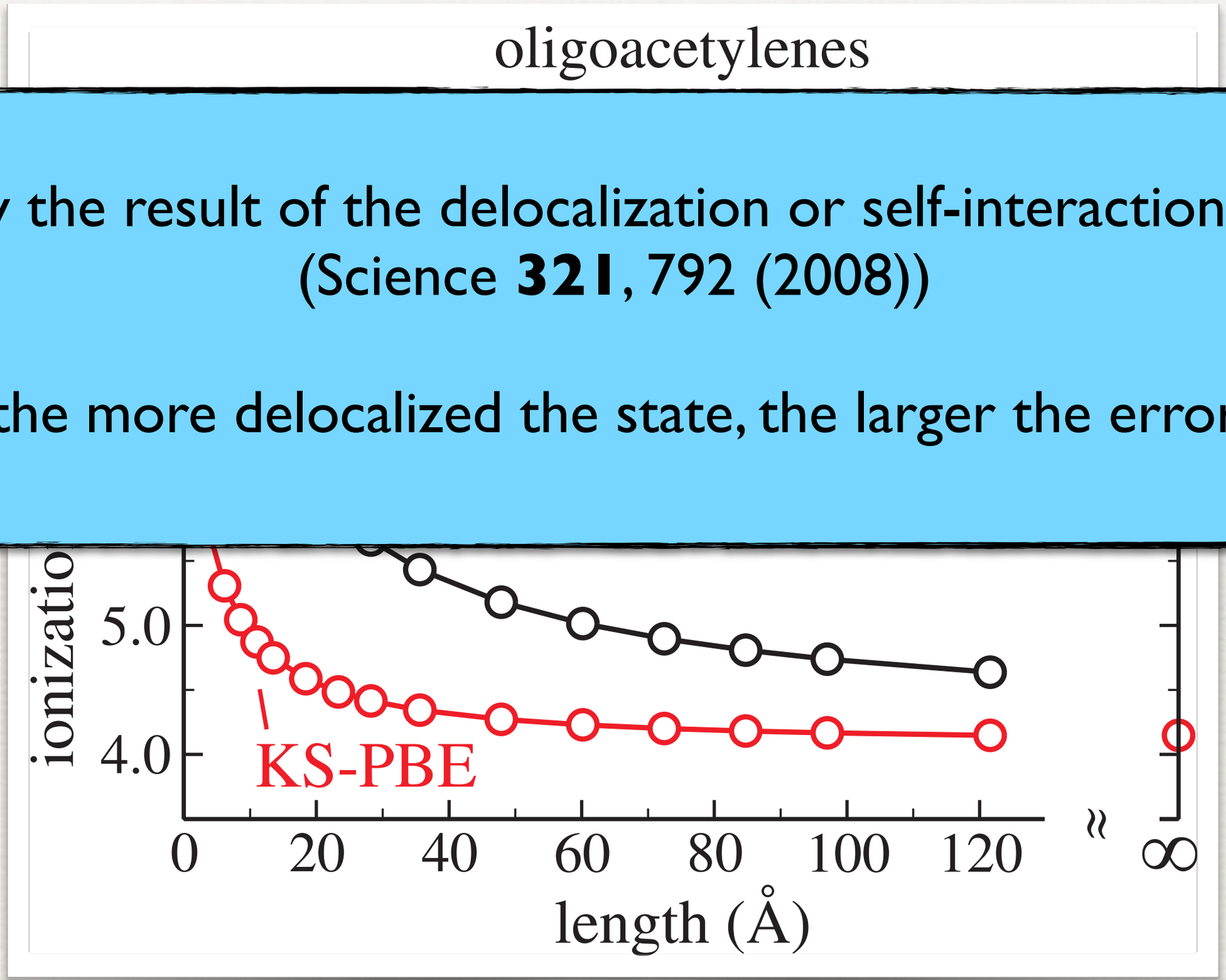
- **only justified for differences of ground states**
  - ionisation potential, electron affinity
  - excited states that are ground states of particular symmetry
- **difficult to find excited state density**
  - excited state density is not unique
- **separate calculation for every excitation needed**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

ΔSCF versus eigenvalues for finite systems



data courtesy of Max Pinheiro

ΔSCF versus eigenvalues for finite systems

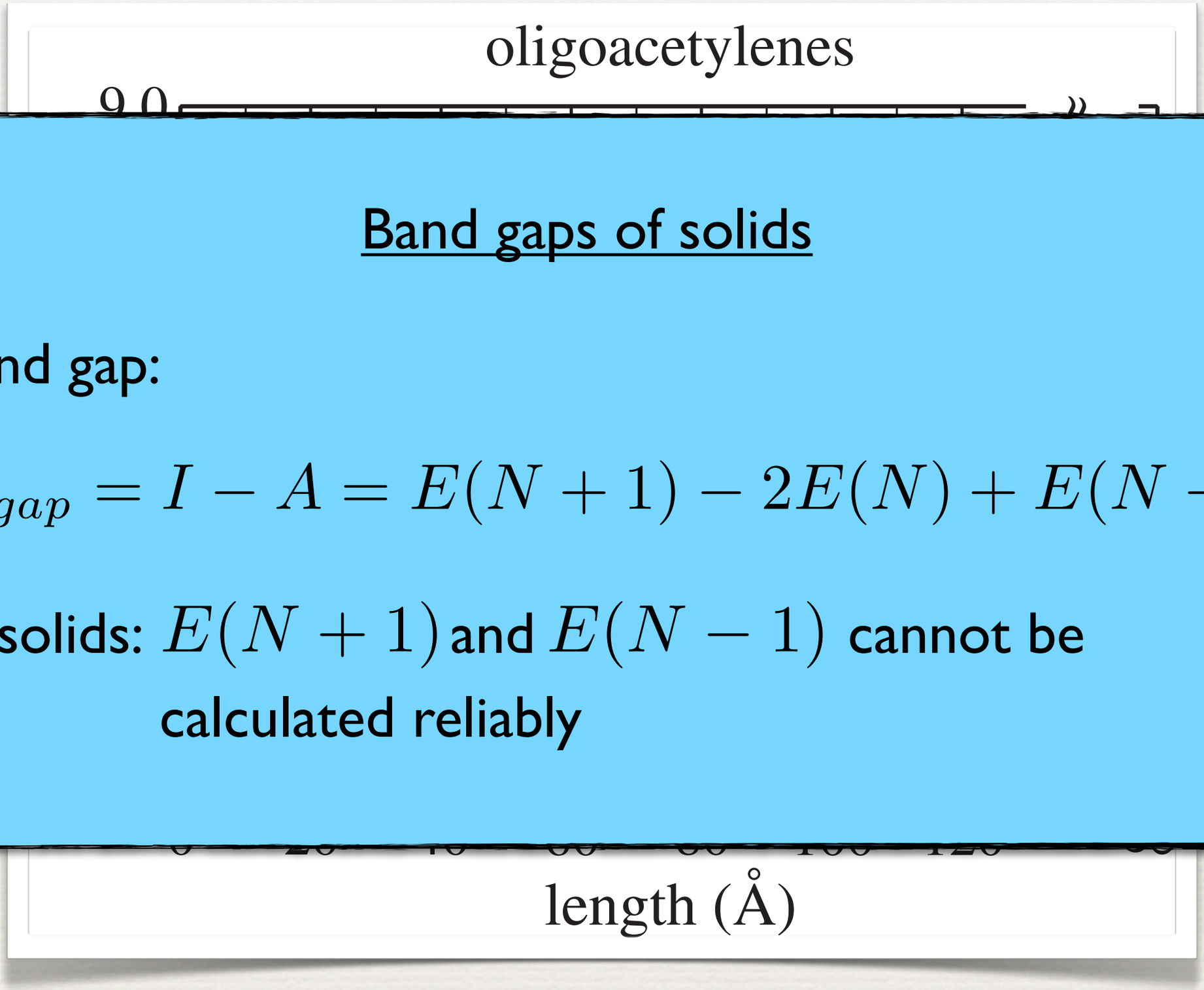


largely the result of the delocalization or self-interaction error
(Science **321**, 792 (2008))

the more delocalized the state, the larger the error

data courtesy of Max Pinheiro

ΔSCF versus eigenvalues for finite systems



Band gaps of solids

- band gap:

$$E_{gap} = I - A = E(N+1) - 2E(N) + E(N-1)$$

- in solids: $E(N+1)$ and $E(N-1)$ cannot be calculated reliably

data courtesy of Max Pinheiro

Band gaps of semiconductors and insulators

- DFT: highest Kohn-Sham state exact:

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

Band gaps of semiconductors and insulators

- DFT: highest Kohn-Sham state exact:

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

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

v_{xc} : discontinuity upon changing the particle number:

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

Band gaps of semiconductors and insulators

- DFT: highest Kohn-Sham state exact:

$$E_{gap} = \epsilon^{\mathrm{KS}}_{N+1}(N+1) - \epsilon^{\mathrm{KS}}_{N}(N)$$

$$= \epsilon^{\mathrm{KS}}_{N+1}(N+1) - \epsilon^{\mathrm{KS}}_{N}(N) + \epsilon^{\mathrm{KS}}_{N}(N) - \epsilon^{\mathrm{KS}}_{N}(N)$$

$$= E^{\mathrm{KS}}_{gap}$$

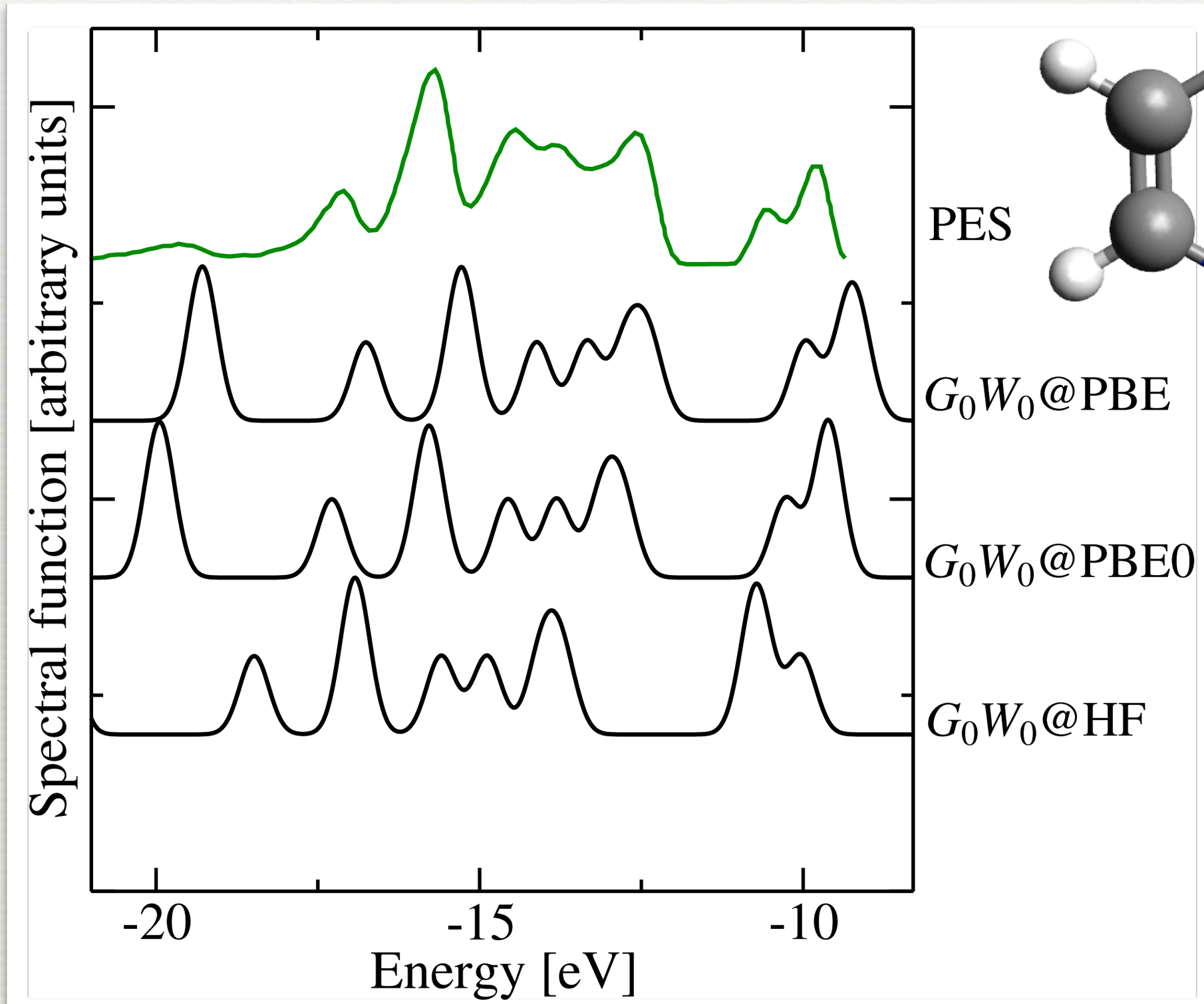
most DFT functionals do not contain this derivative discontinuity

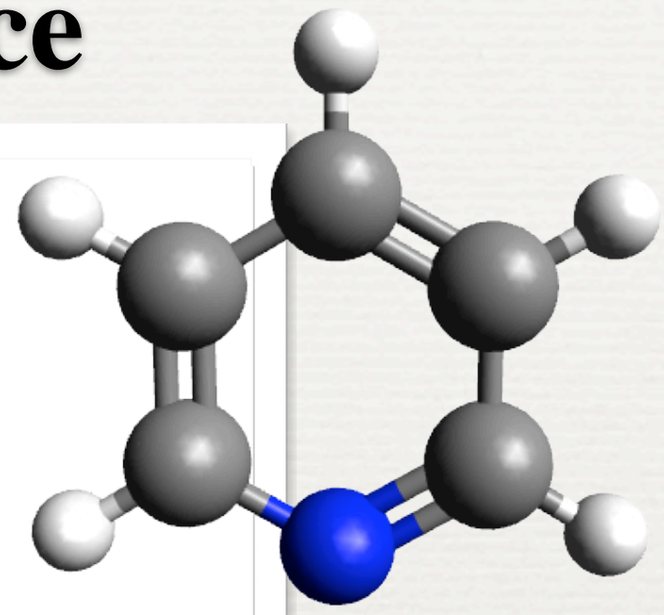
- for sc $\rightarrow N+1$

v_{xc} : discontinuity upon changing the particle number:

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

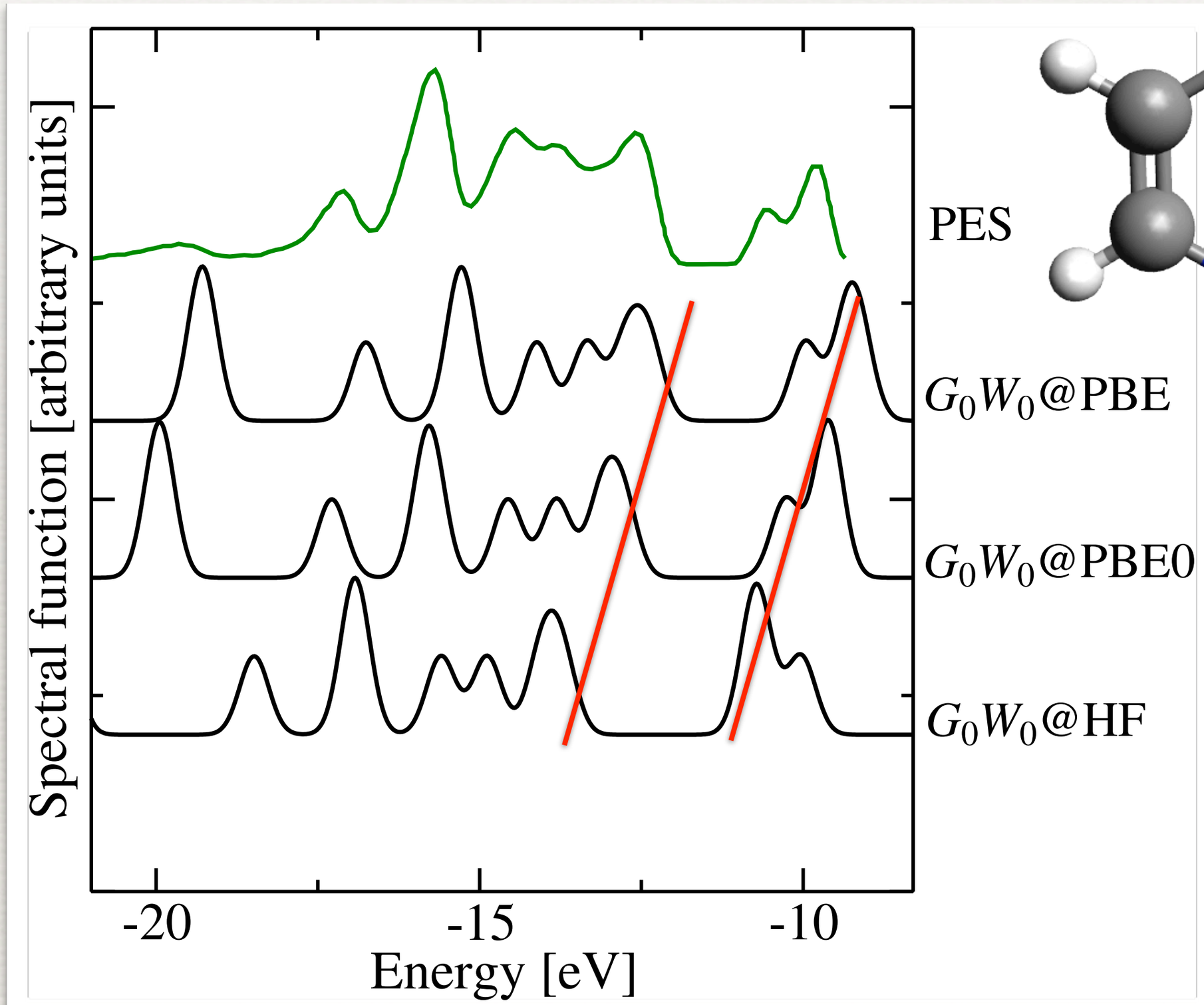
Starting point dependence

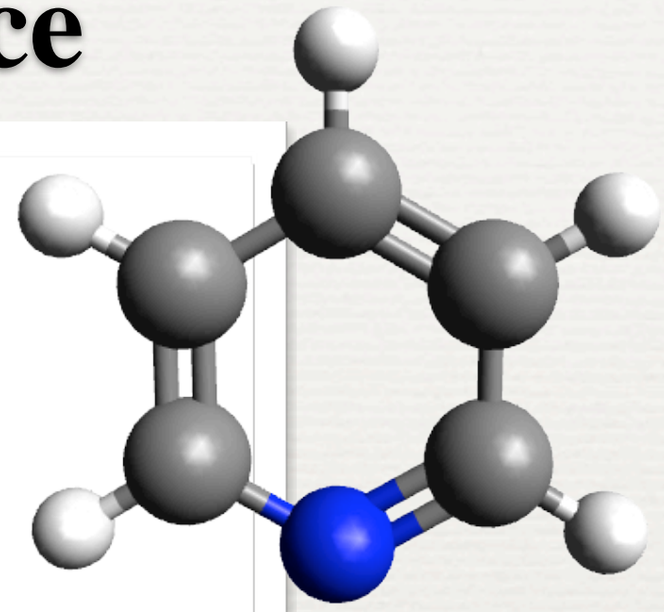




N. Marom *et al.* Phys. Rev. B 86, 245127 (2012)

Starting point dependence





N. Marom *et al.* Phys. Rev. B 86, 245127 (2012)

Self-consistent GW (scGW)

Hedin's GW equations:

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

$$G(1,2) = G_0(1,2)$$

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

$$P(1,2) = -iG(1,2)G(2,1^+)$$

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

$$\Sigma(1,2) = iG(1,2)W(2,1)$$

self-consistency

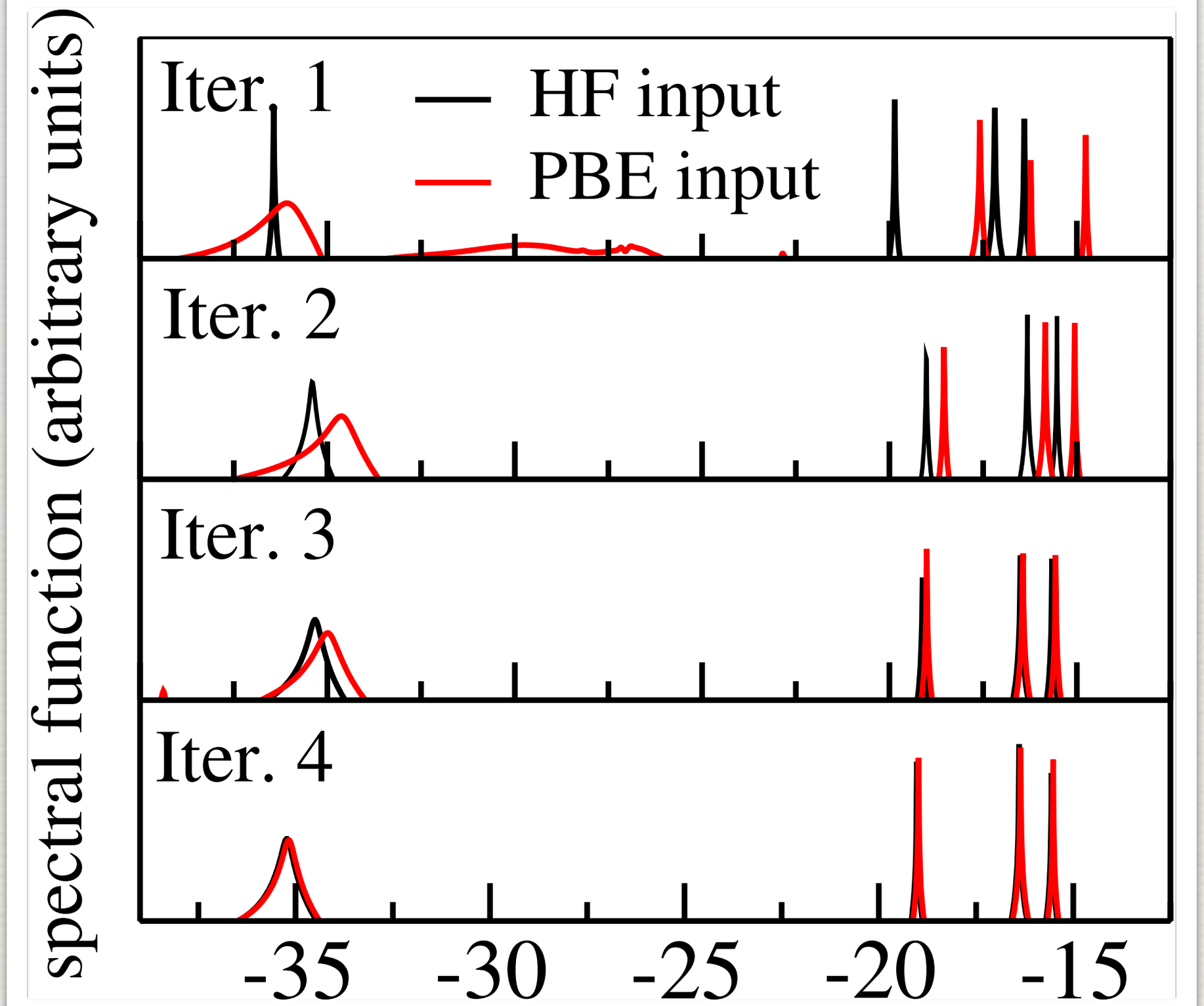
self-consistency

Dyson's equation:

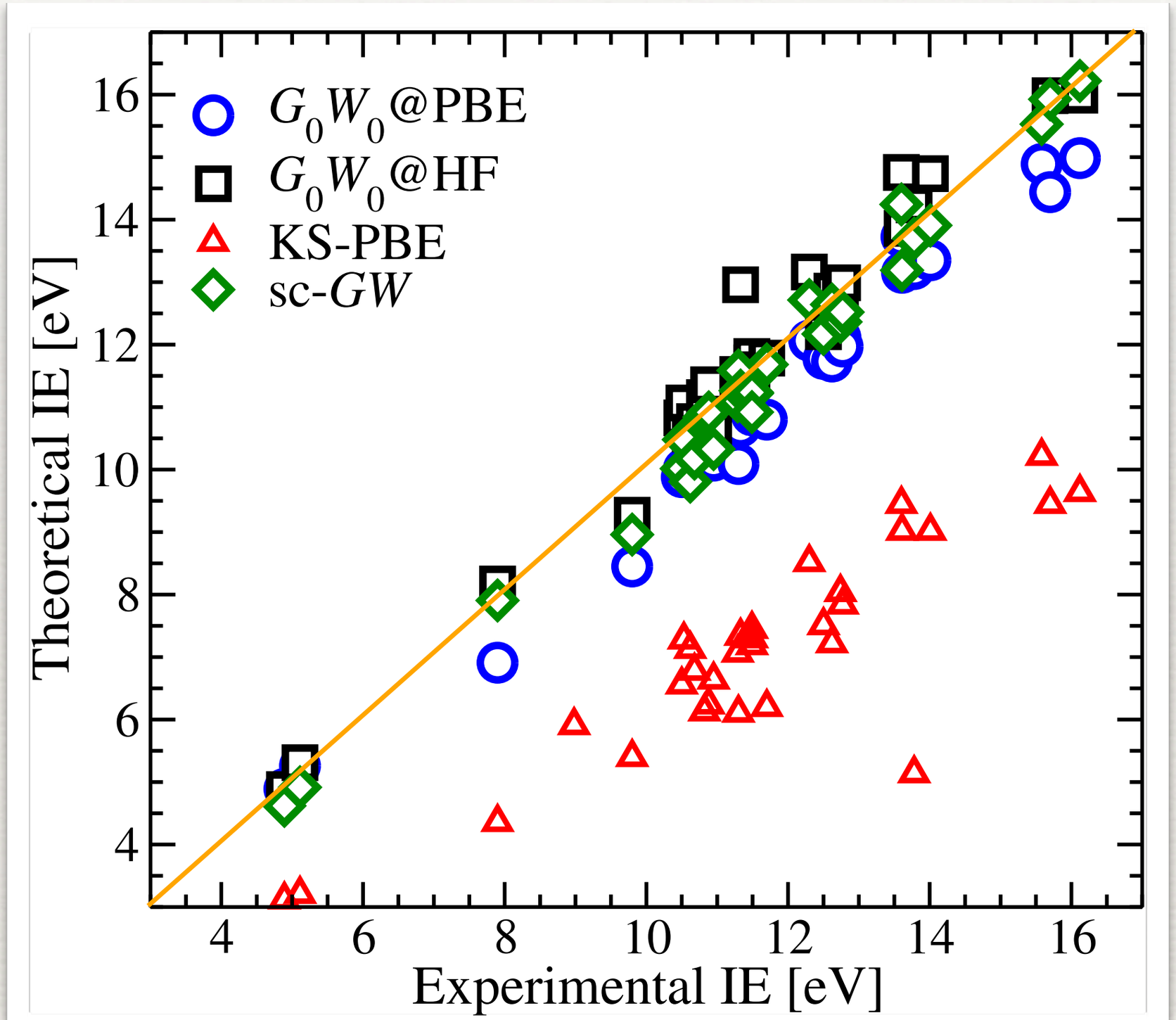
$$G^{-1}(1,2) = G_0^{-1}(1,2) - \Sigma(1,2)$$

implemented in FHI-aims: F. Caruso *et al. Phys. Rev. B* **86**, 081102(R) (2012)

Unique solution in scGW - N_2

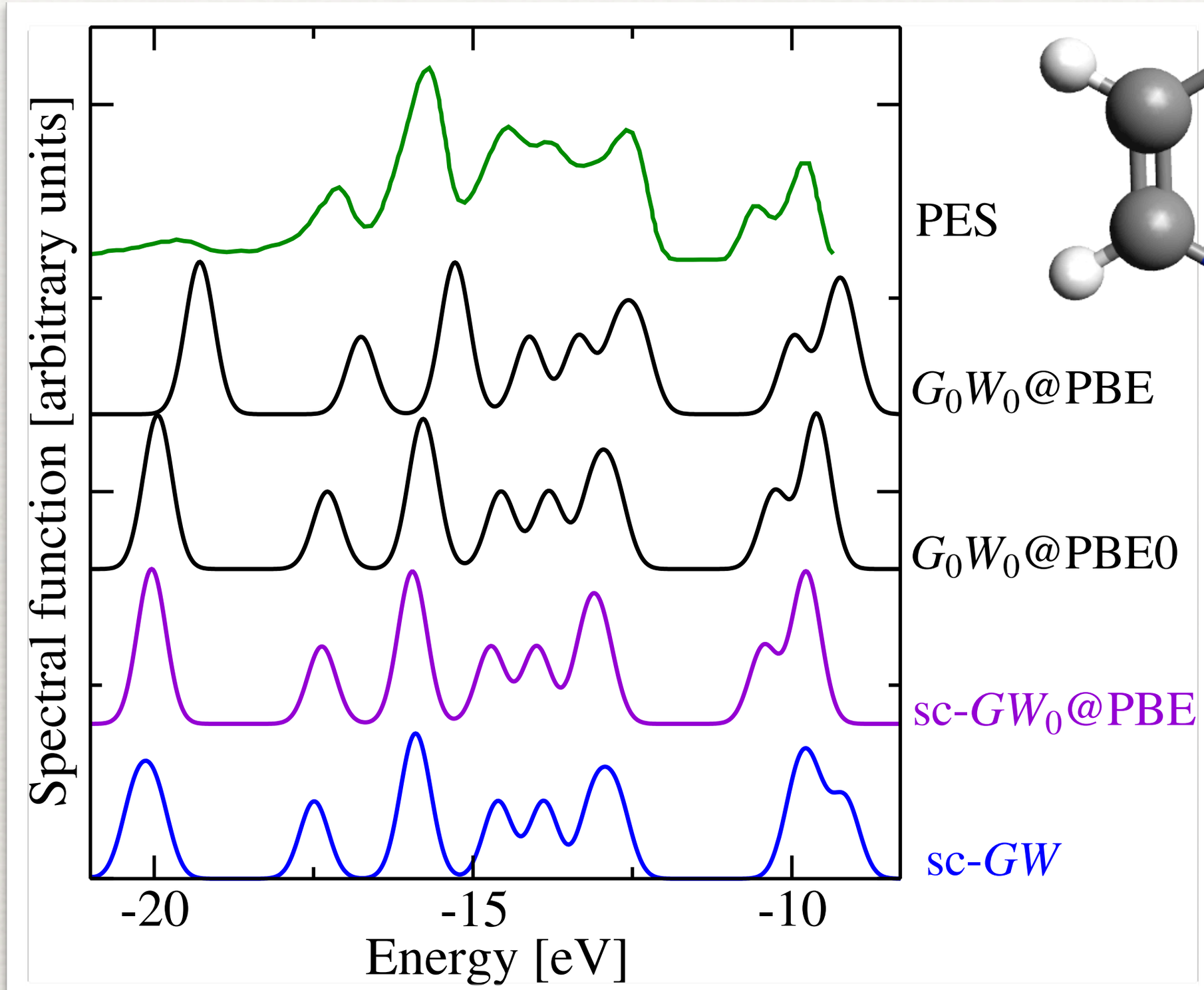


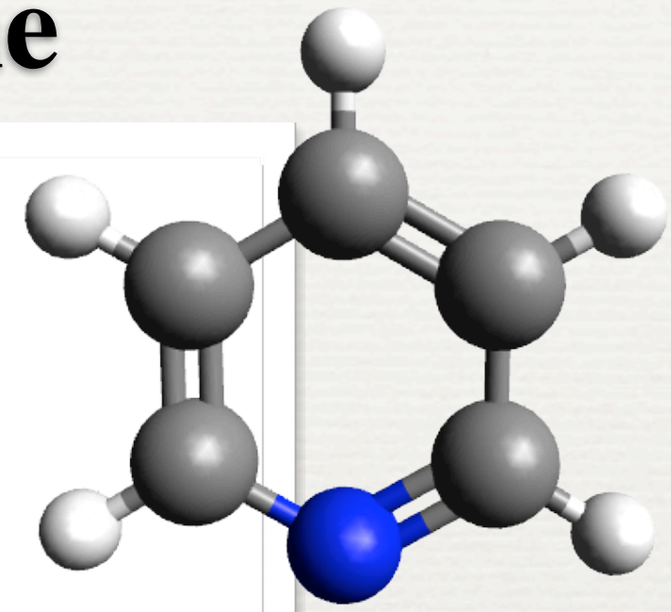
Ionization potentials in scGW



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

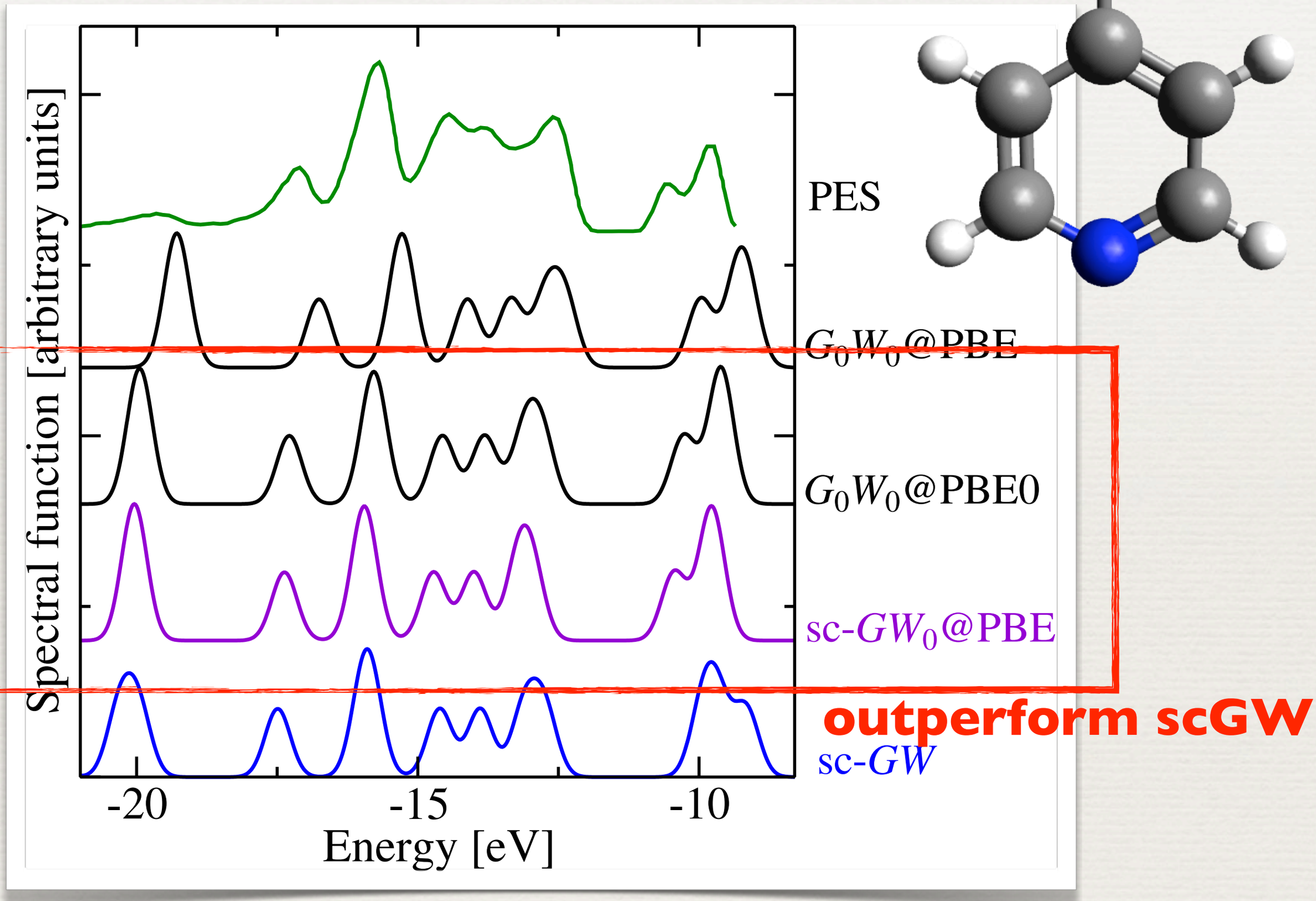
The loan pair in pyridine





N. Marom *et al.* Phys. Rev. B 86, 245127 (2012)

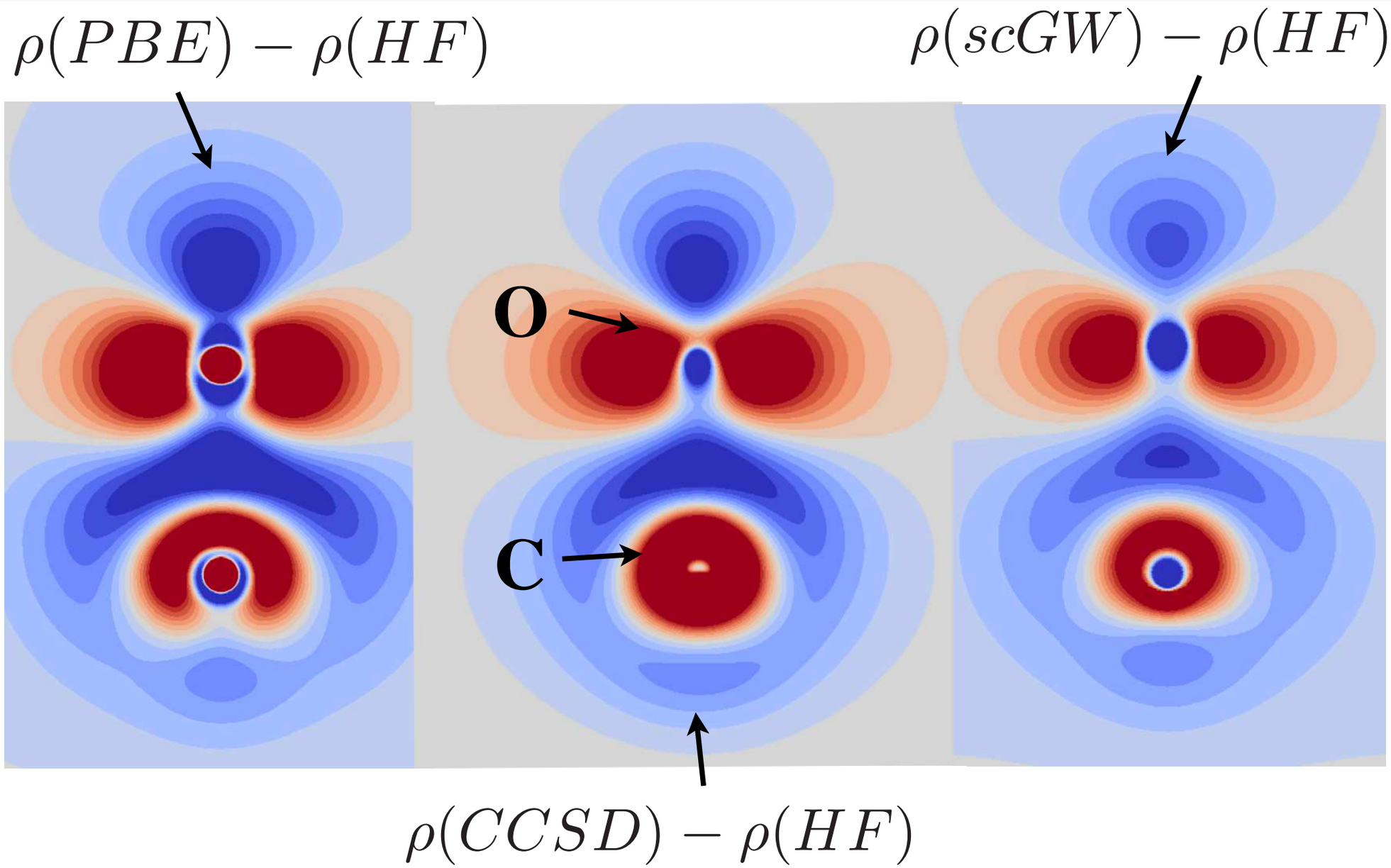
The loan pair in pyridine



outperform scGW

N. Marom *et al.* Phys. Rev. B 86, 245127 (2012)

The *GW* density of CO



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

Caruso, Ren, Rinke, Rubio, Scheffler, Phys. Rev. B 86, 081102(R) (2012)

The *GW* density of CO

$\rho(PBE) - \rho(HF)$

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

Dipole moment (in Debye):

Exp.	scGW	CCSD	HF	PBE
0.11	0.07	0.06	-0.13	0.20

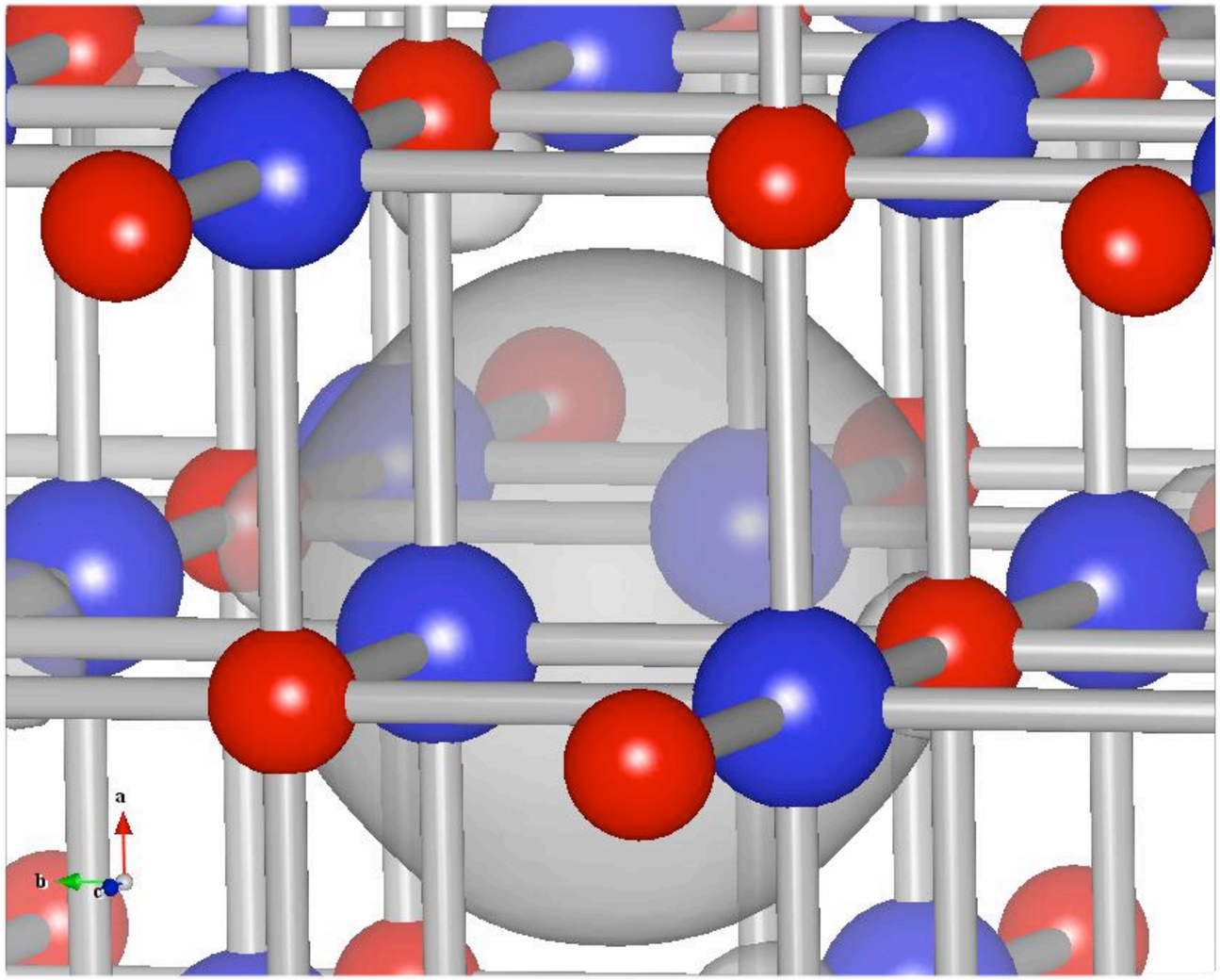
$\rho(CCSD) - \rho(HF)$

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

Caruso, Ren, Rinke, Rubio, Scheffler, Phys. Rev. B 86, 081102(R) (2012)

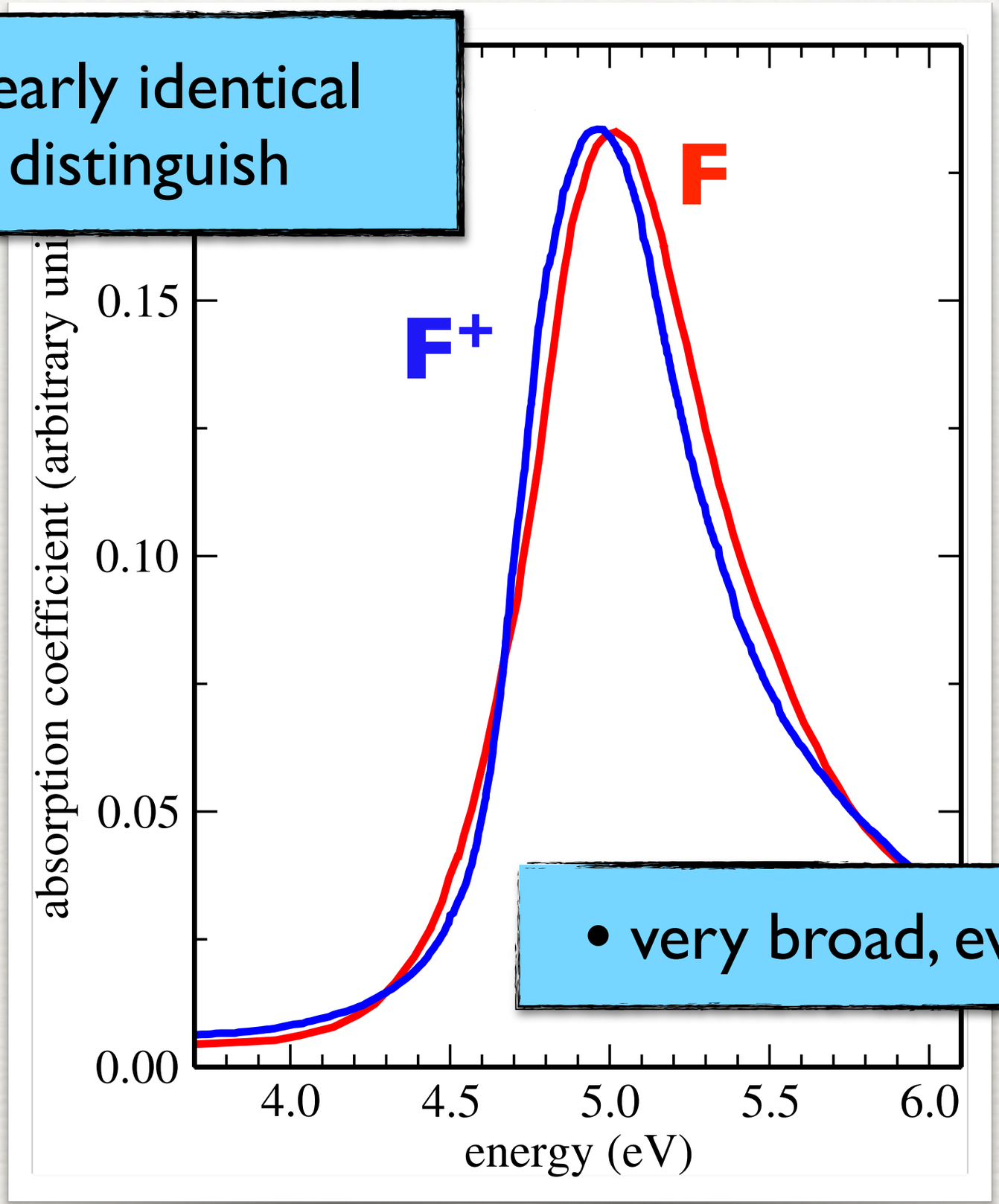
F-center: Oxygen vacancy in MgO

- *the* classic F-center
- also known as color center
- studied for > 5 decades
- still enigmatic



Experimental optical absorption spectra

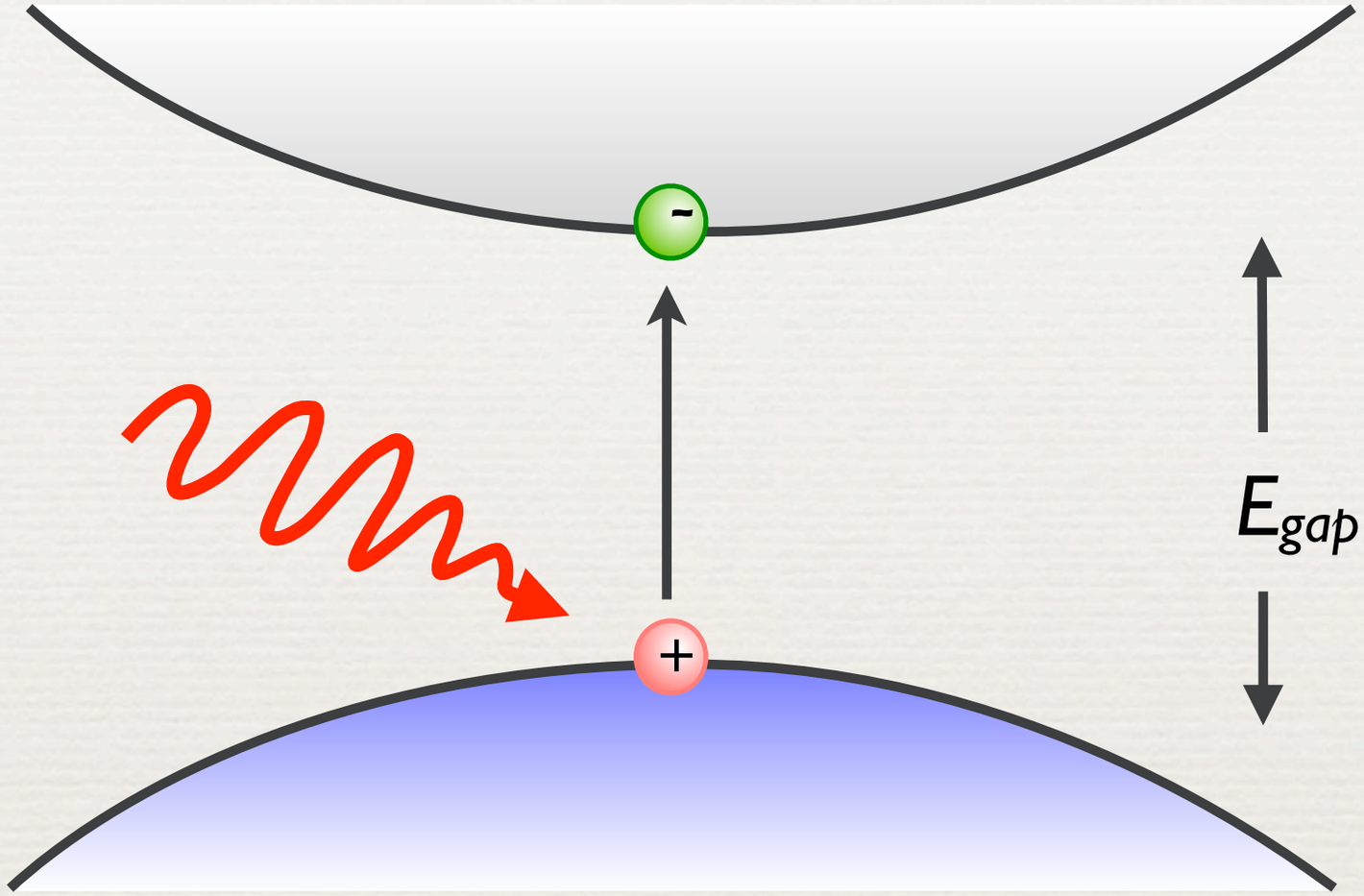
- F and F^+ nearly identical
- difficult to distinguish



- very broad, even at low T

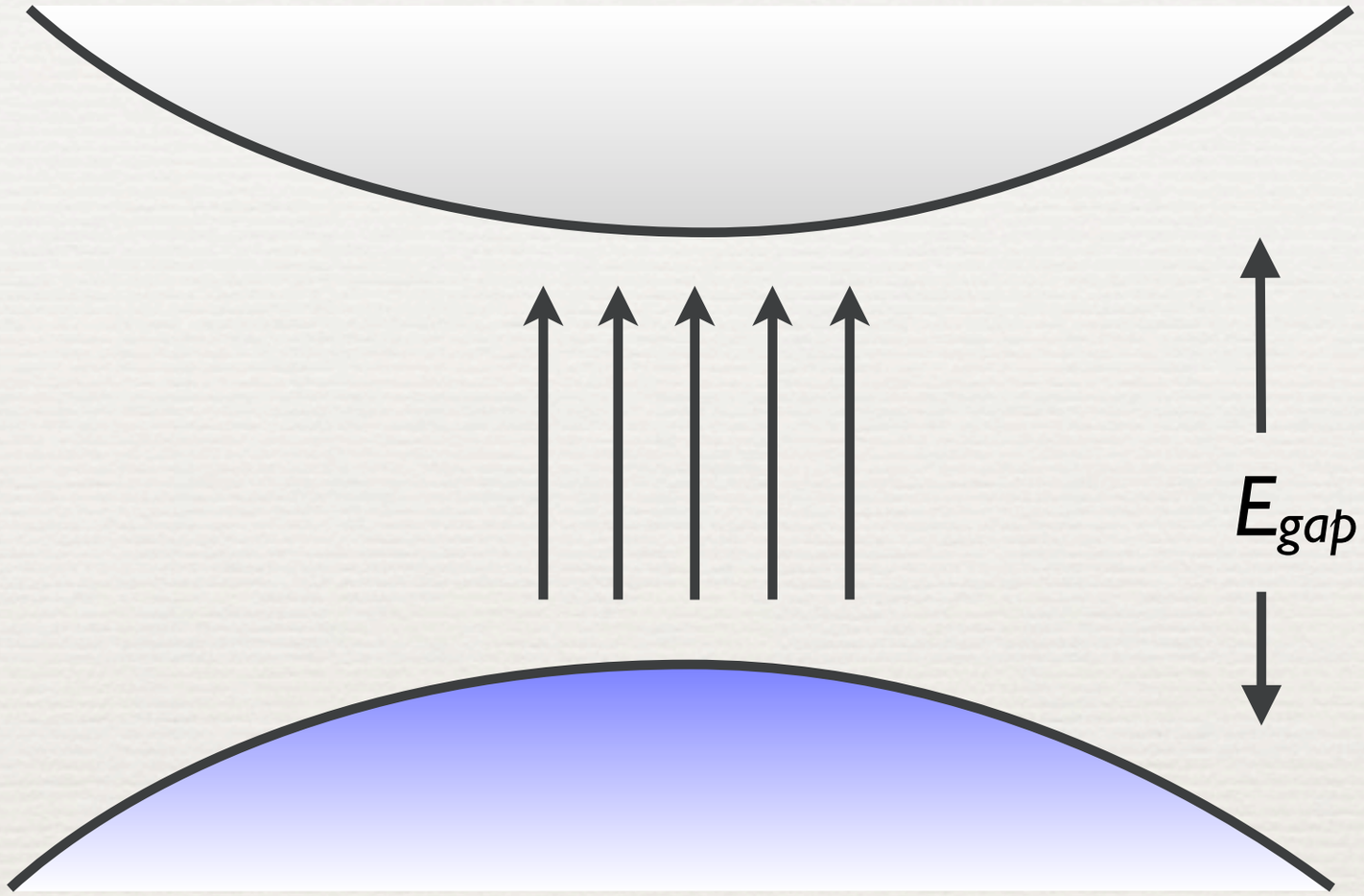
Kappers *et al.* PRB 1, 4151 (1970)

Absorption spectrum from first principles



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

Absorption spectrum from first principles

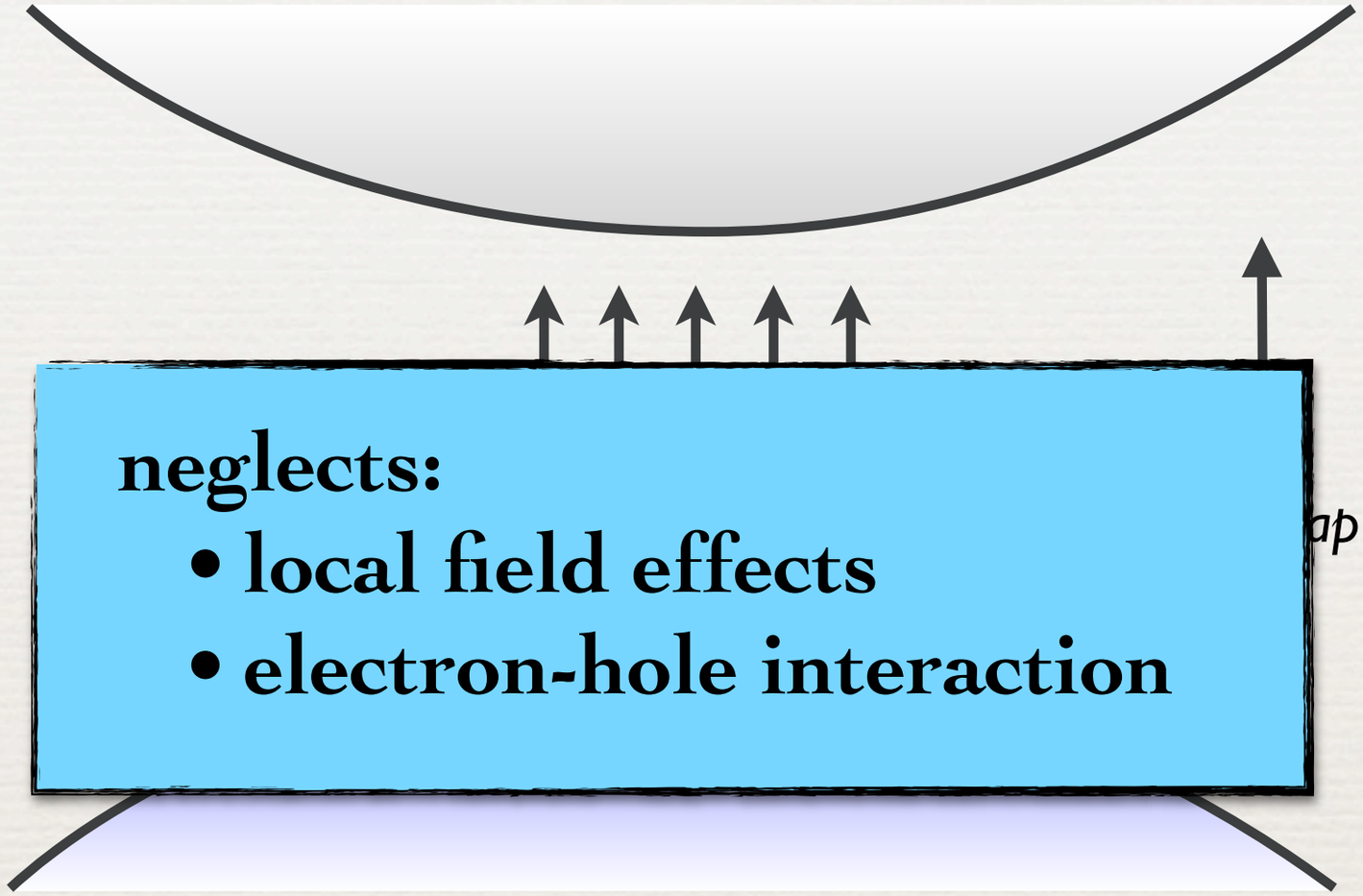


Fermi's golden rule:

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

$\mathbf{v}$: velocity operator

Absorption spectrum from first principles



Fermi's golden rule:

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$\mathbf{v}$: 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 time dependent DFT (TDDFT):

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

2nd derivative of E_{xc}

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:

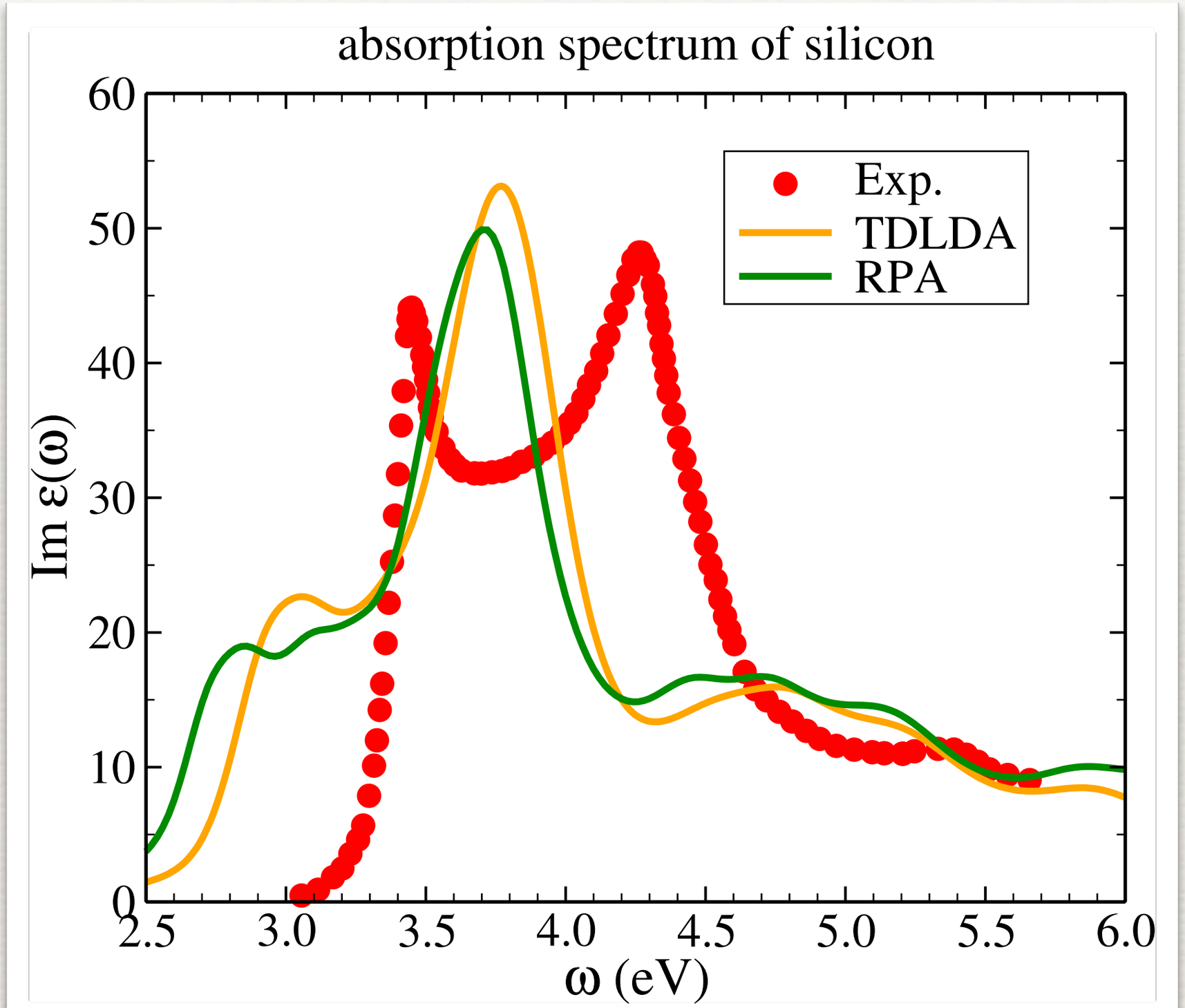
$$\varepsilon^{-1}(\mathbf{r},\mathbf{r}',\omega) = \delta(\mathbf{r}-\mathbf{r}') - \int d\mathbf{r}'' v(\mathbf{r}-\mathbf{r}'')\chi(\mathbf{r}'',\mathbf{r}',\omega)$$

Response function in time dependent DFT (TDDFT):

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

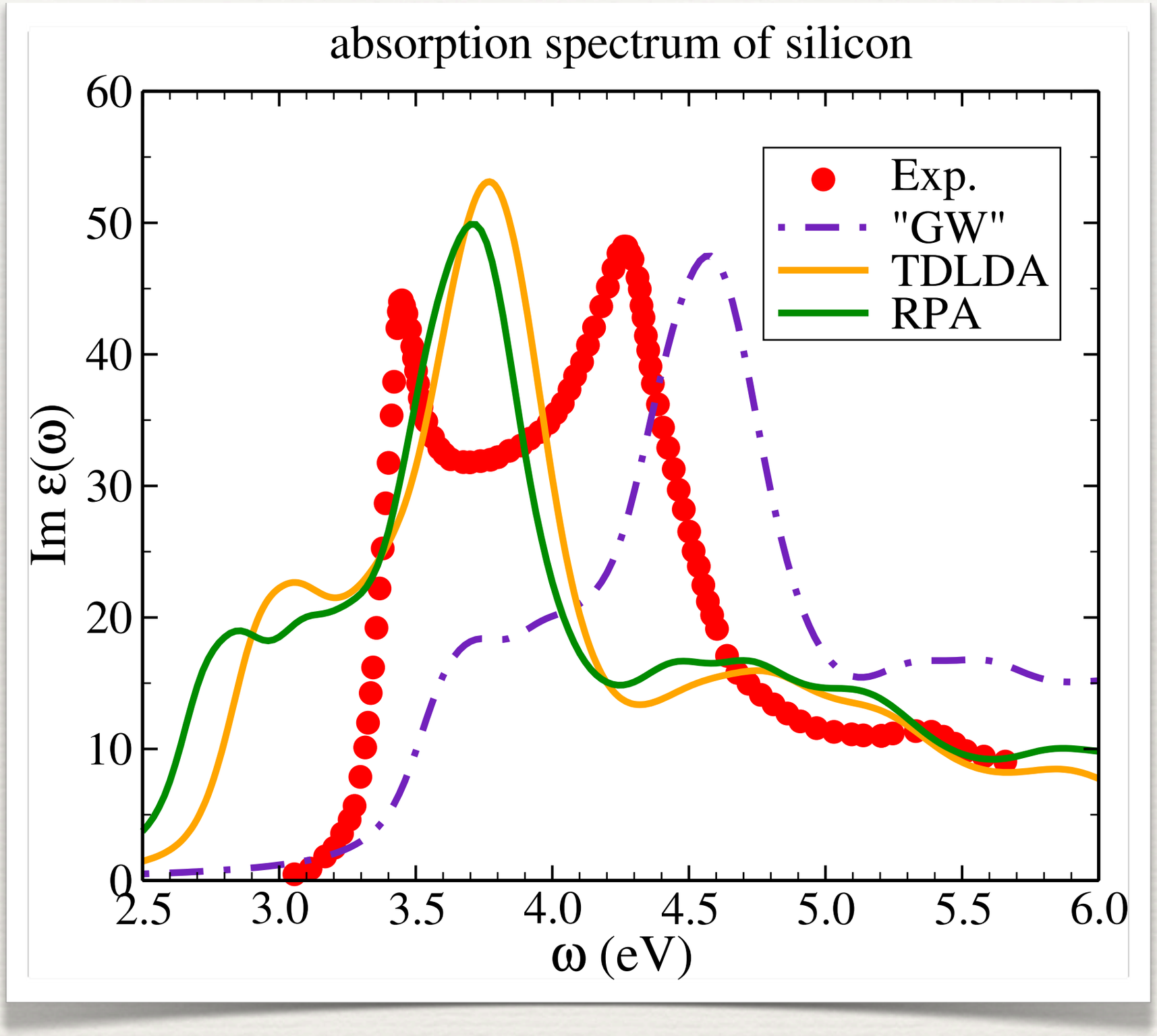
Random-phase approximation (RPA)

Optical absorption - response function



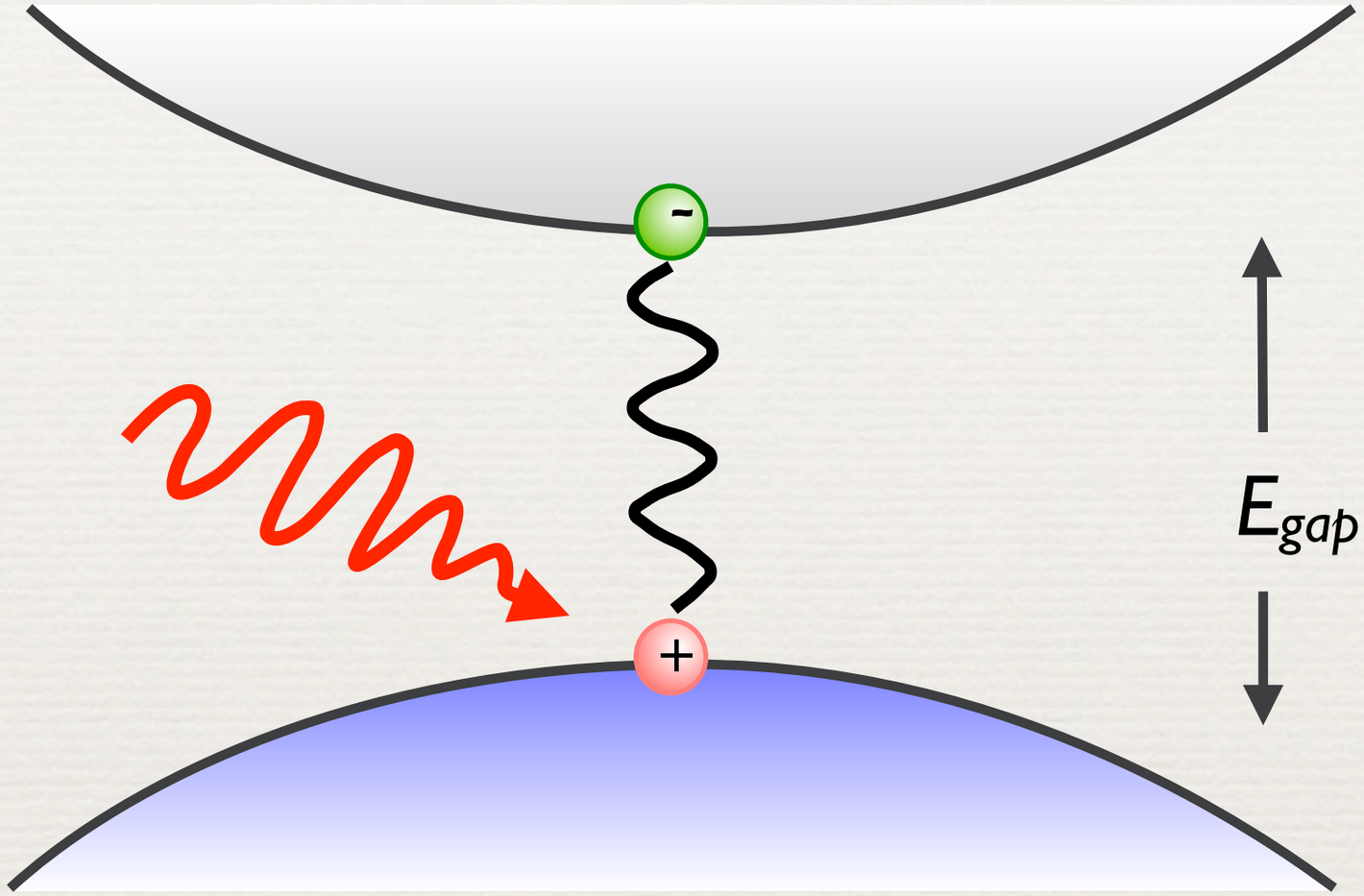
from Sottile, Olevano, and Reining, PRL **91**, 056402 (2003)

Optical absorption - response function



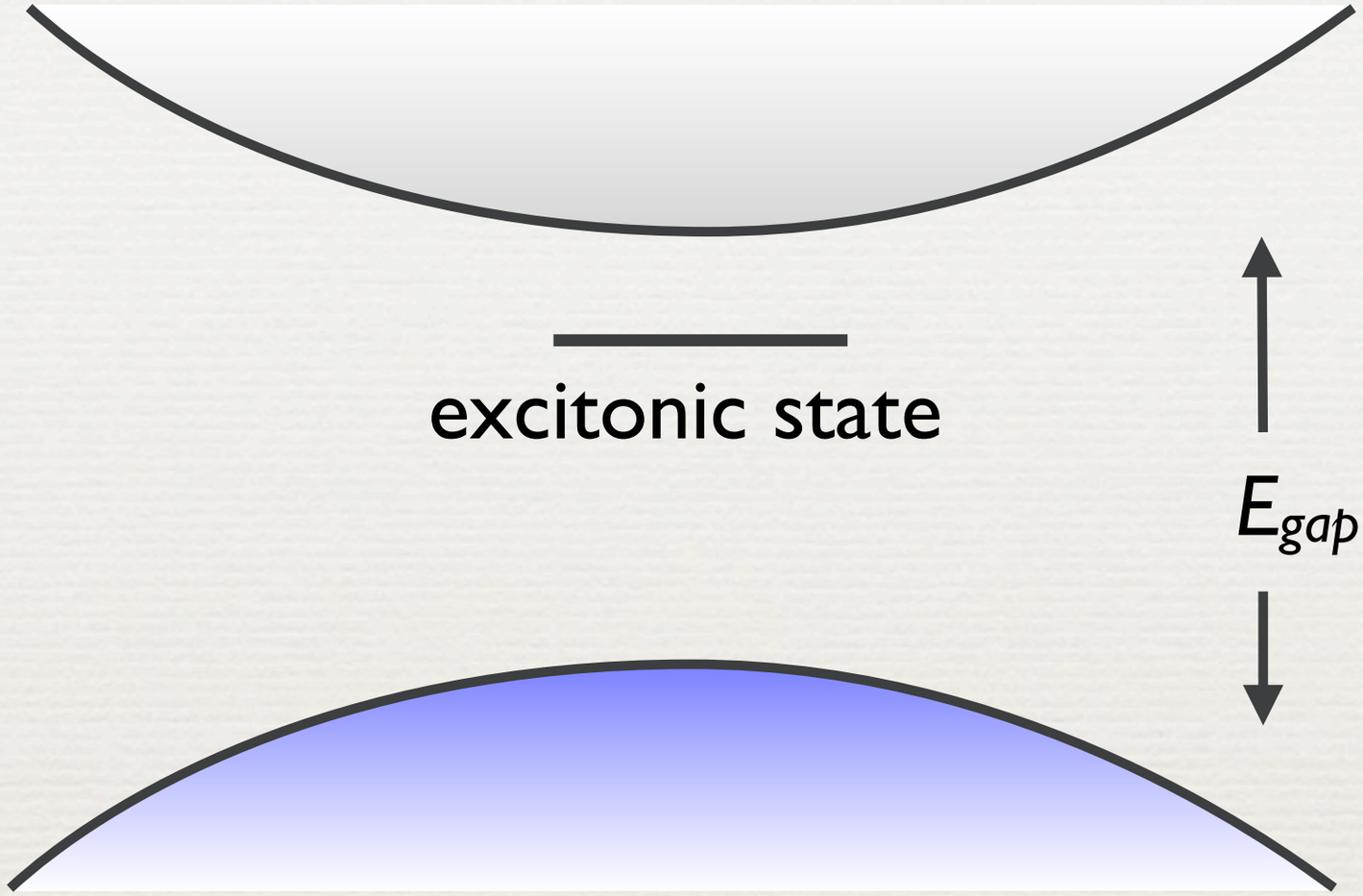
from Sottile, Olevano, and Reining, PRL **91**, 056402 (2003)

Including electron-hole interaction



- electron-hole interaction lowers the energy
- electron-hole pairs (excitons) form

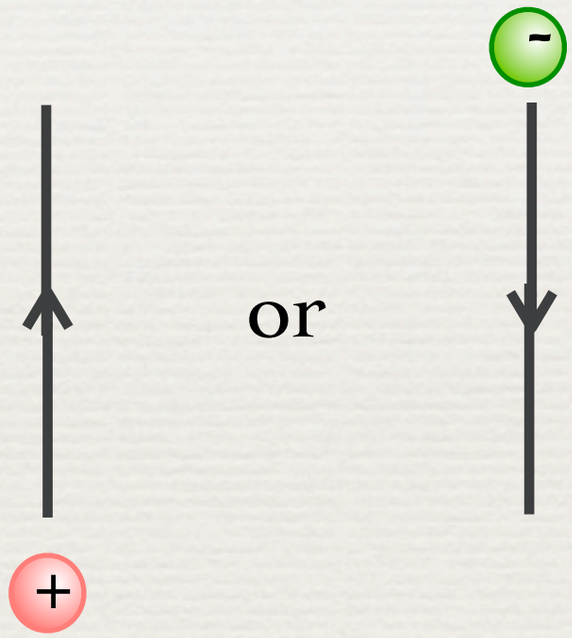
Including electron-hole interaction



- electron-hole interaction lowers the energy
- electron-hole pairs (excitons) form

Including electron-hole interaction

one particle
Green's function



$G(1,2)$

two particle
Green's function

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

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

Including electron-hole interaction

one particle

two particle

approximations to handle $S(1,2,1',2')$

- ***GW*** **approximation for** Σ
- **for the vertex** $\dfrac{\delta\Sigma}{\delta G} \approx iW$
- **static *W***

$2,1',2')$

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

Absorption spectrum from first principles

Bethe-Salpeter equation

$$H^{eff}\Psi_n^{e-h} = \underbrace{E_n^{e-h}\Psi_n^{e-h}}_{\text{electron-hole pair}}$$

$$H^{eff}_{hh'ee'} = (\epsilon_e - \epsilon_h)\delta_{hh'}\delta_{ee'} + \underbrace{\langle he|\bar{v}|h'e'\rangle}_{\text{bare Coulomb}} - \underbrace{\langle hh'|W|ee'\rangle}_{\text{screened (RPA from GW)}}$$

electron (GW)

hole (GW)

Absorption spectrum from first principles

Bethe-Salpeter equation

$$H^{eff}\Psi_n^{e-h} = \underbrace{E_n^{e-h}\Psi_n^{e-h}}$$

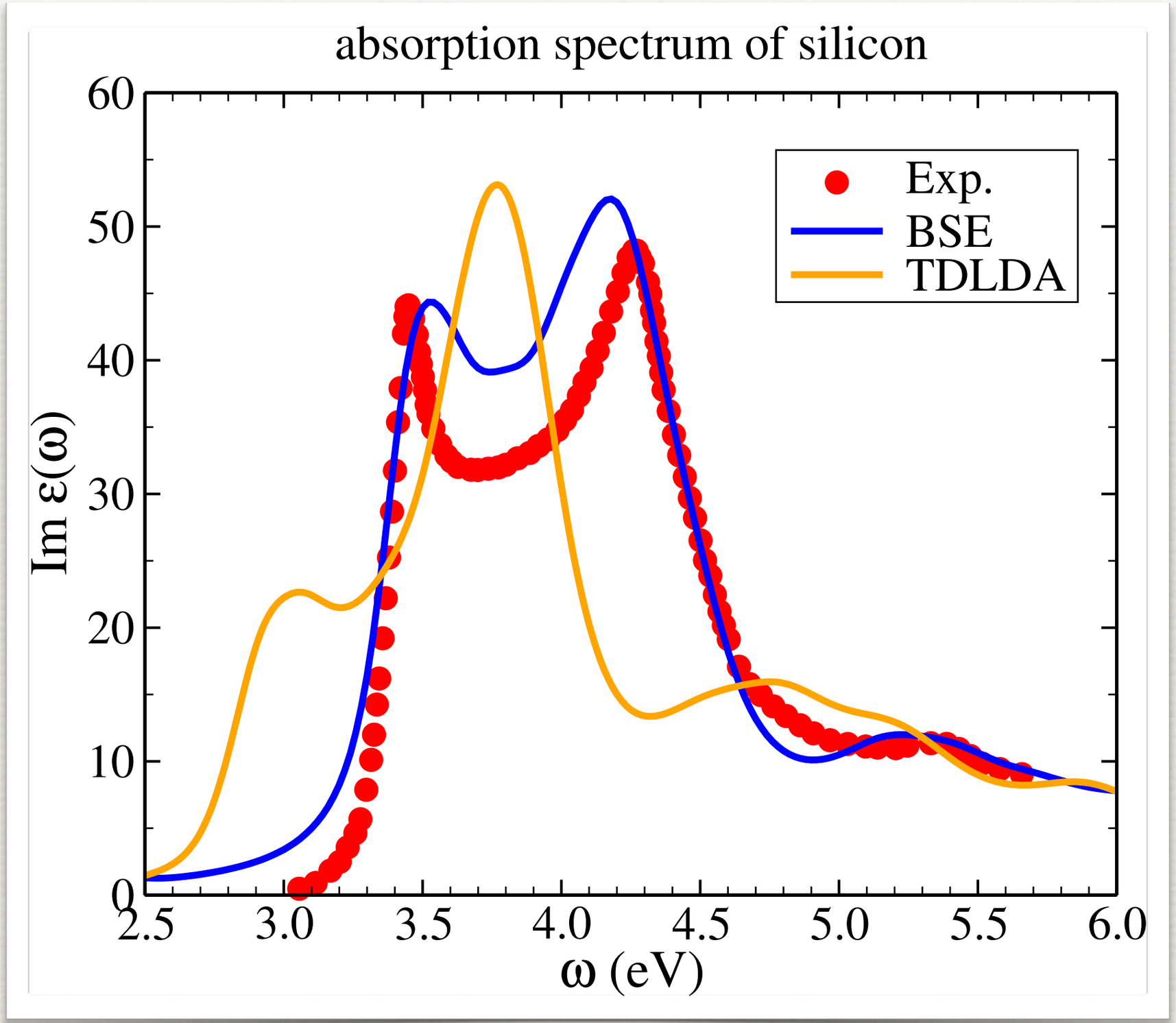
electron-hole pair

dielectric function:

$$Im\,\varepsilon_M(\omega) = \frac{8\pi^2}{V}\sum_n \left|\sum_v^{occ}\sum_c^{unocc} A_{vc}^n \frac{\langle v|\mathbf{p}|c\rangle}{\epsilon_c - \epsilon_v}\right|^2 \delta(\omega - E_n)$$

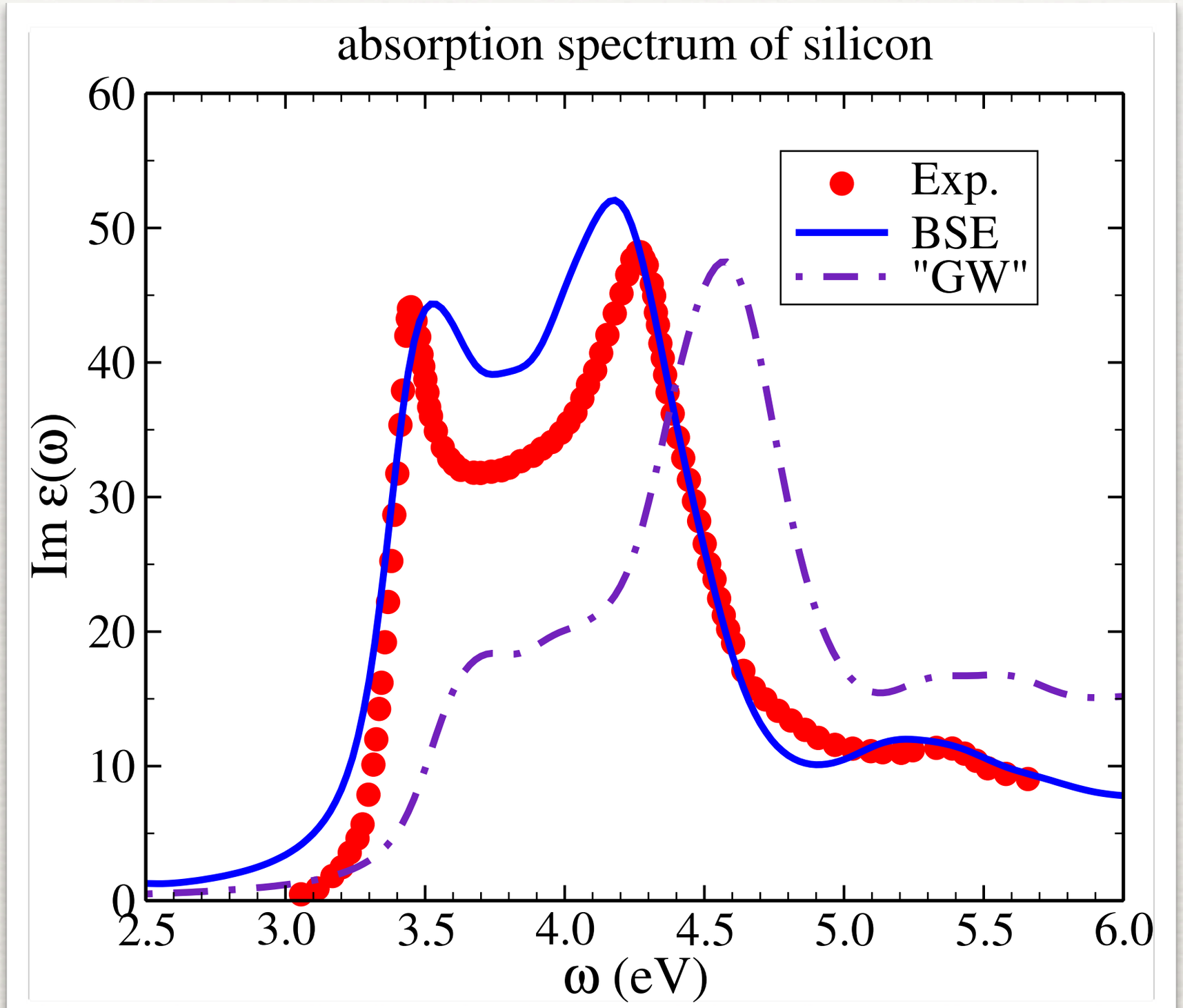
wave function coefficients

Optical absorption - response function



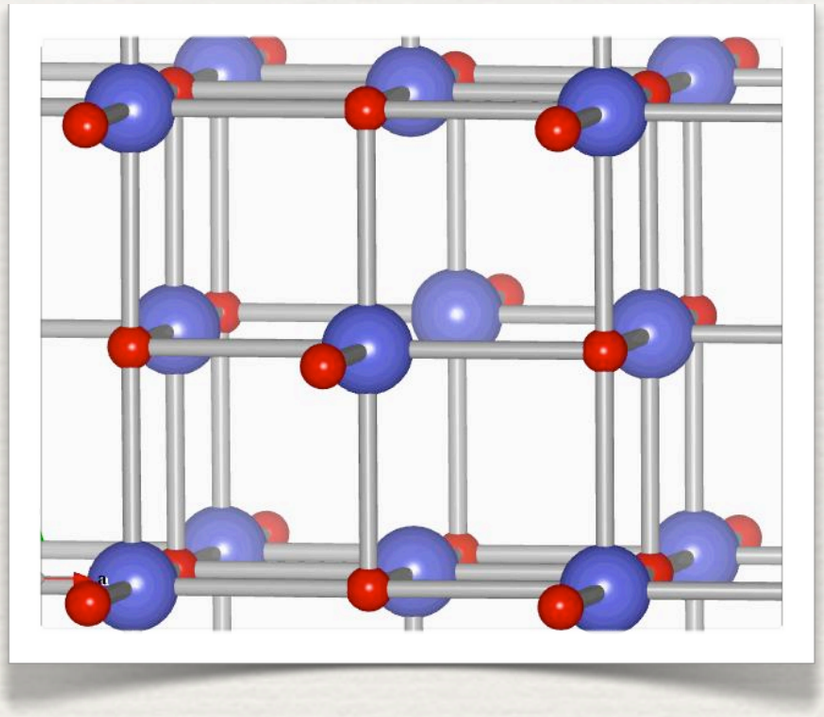
from Sottile, Olevano, and Reining, PRL **91**, 056402 (2003)

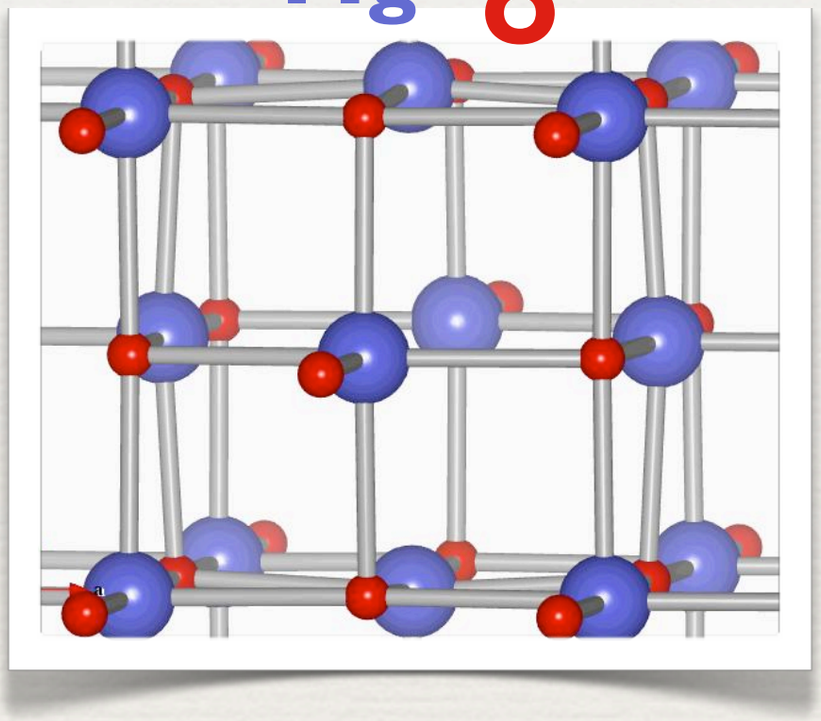
Optical absorption - response function

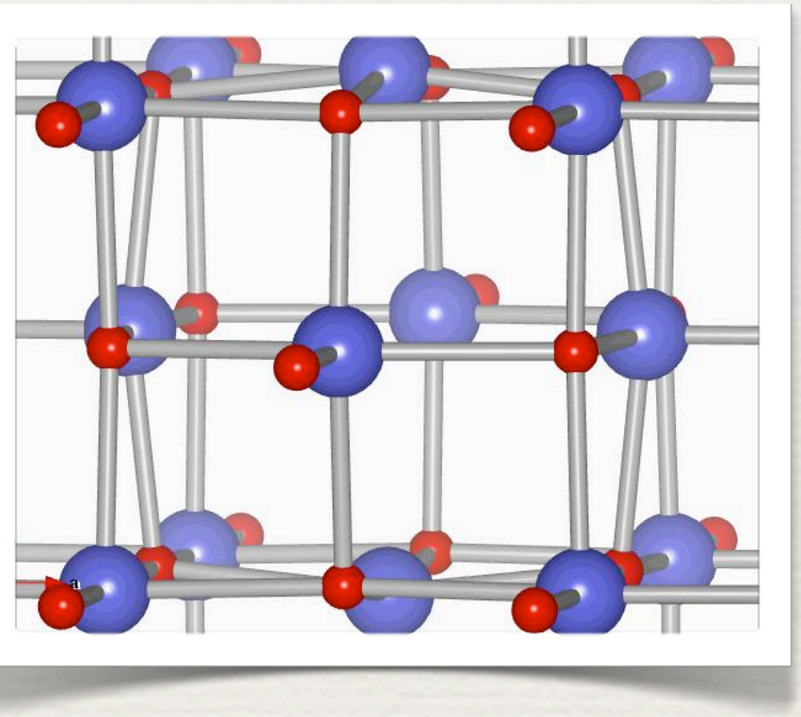


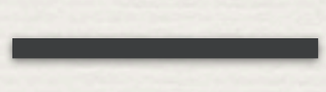
- BSE creates bound exciton and shifts spectral weight

F-center: nomenclature



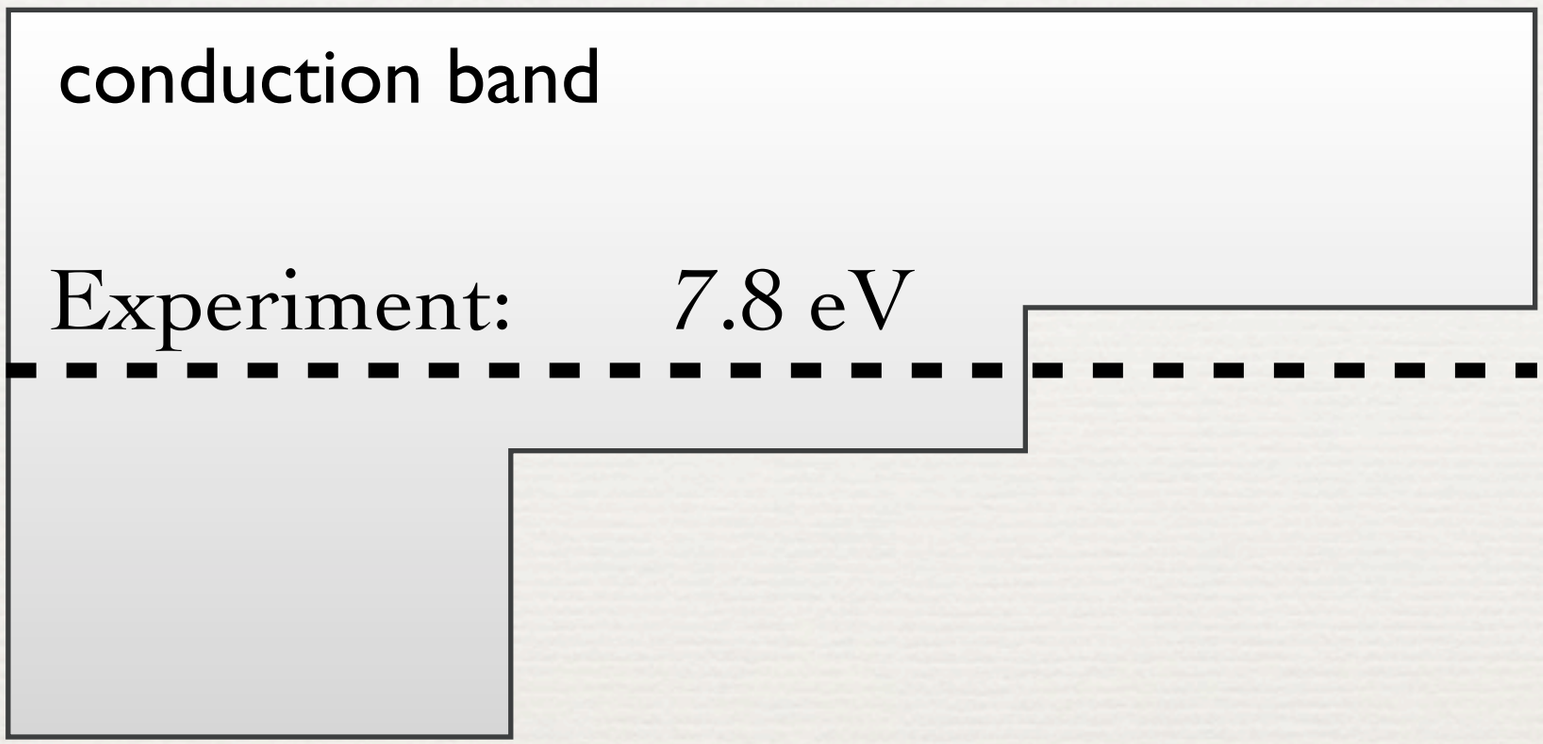






F-center **F^{+}-center** **F^{2+}-center**

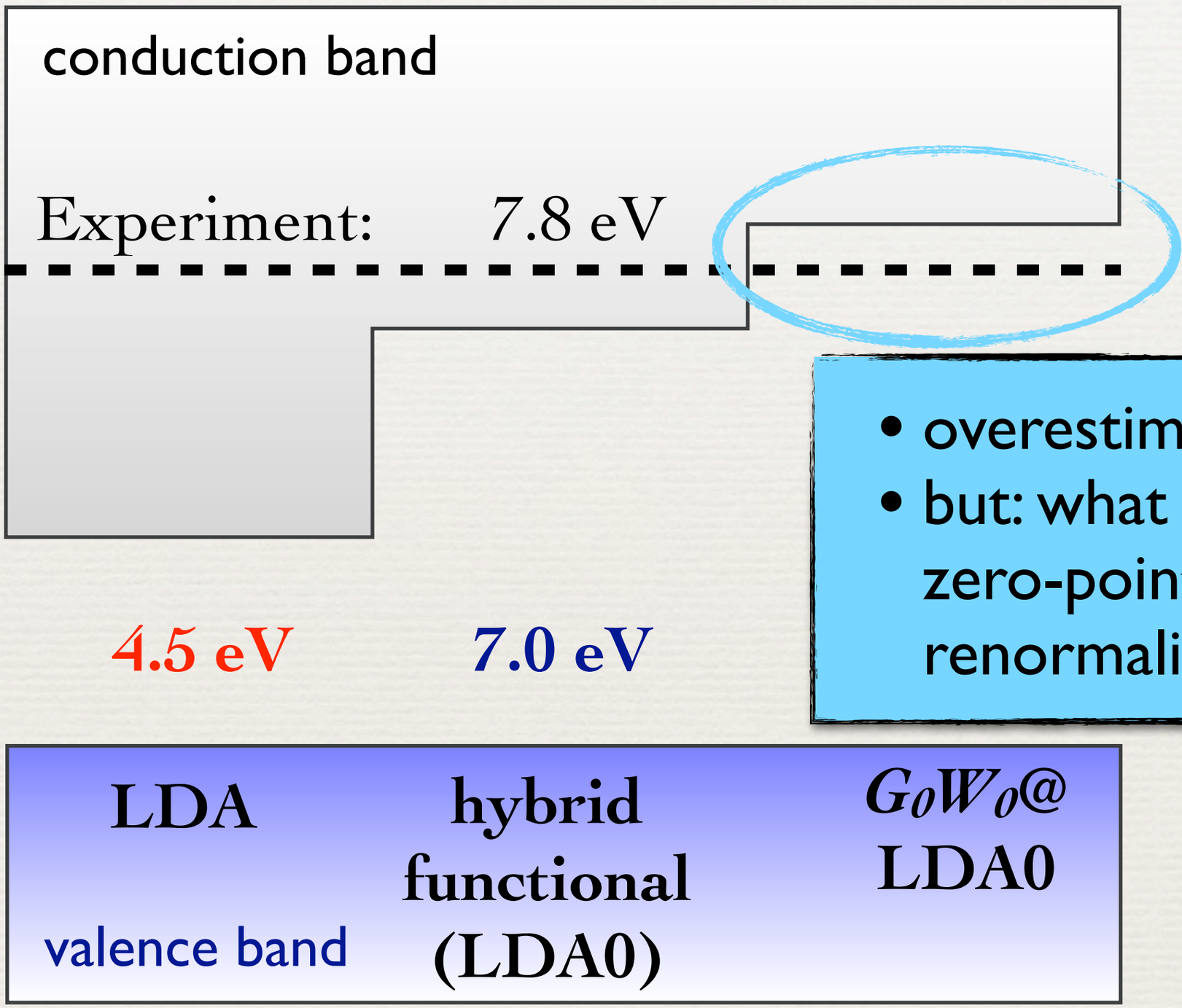
Getting the band gap of MgO right



LDA	hybrid functional (LDA0)	G_0W_0@ LDA0
4.5 eV	7.0 eV	8.1 eV
valence band		

Exp.: R. C. Whited and W. C. Walker, Phys. Rev. Lett. 22, 1428 (1969)

Getting the band gap of MgO right



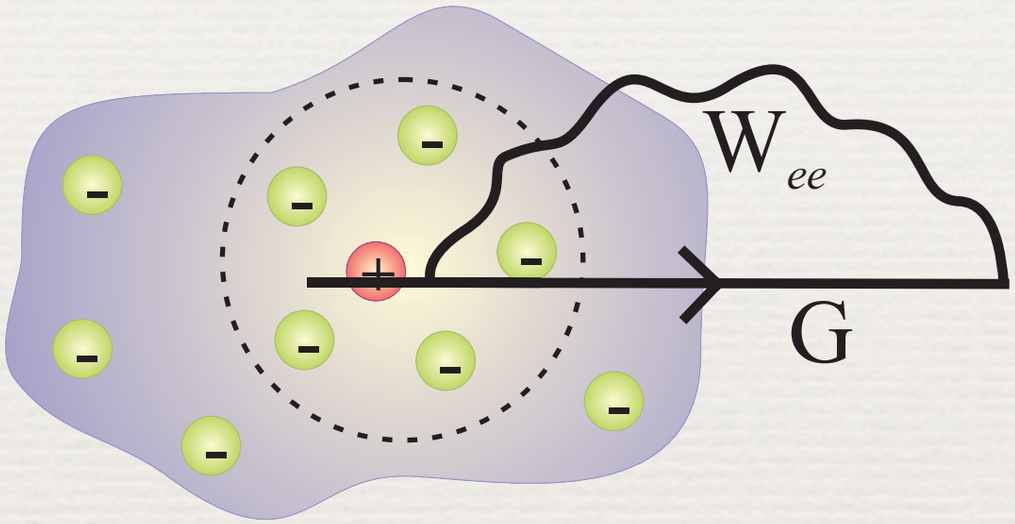
- overestimated
- but: what about zero-point renormalization?

Exp.: R. C. Whited and W. C. Walker, Phys. Rev. Lett. 22, 1428 (1969)

Electron-phonon interaction

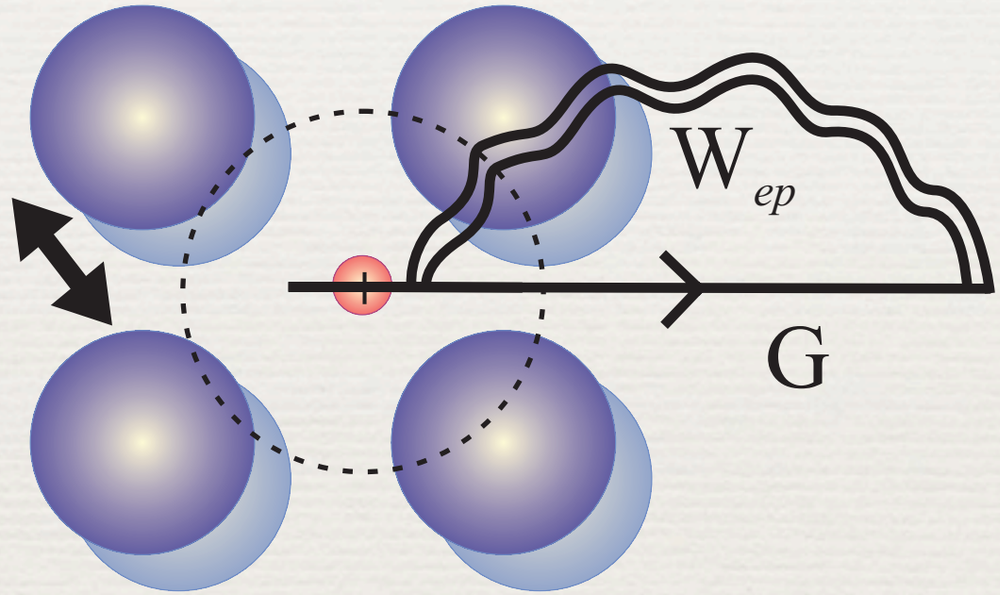
electron-electron

$$\Sigma_{ee} = GW_{ee} \quad :$$



electron-phonon

$$\Sigma_{ep} = GW_{ep} \quad :$$



Renormalizes electron/hole states!
Also at zero temperature.

H.Y. Fan, Phys. Rev. 82, 900 (1951)

Renormalizing electronic states

band gap renormalization

0.3 eV

- **with Fröhlich model for e-p coupling**

for comparison: experiment

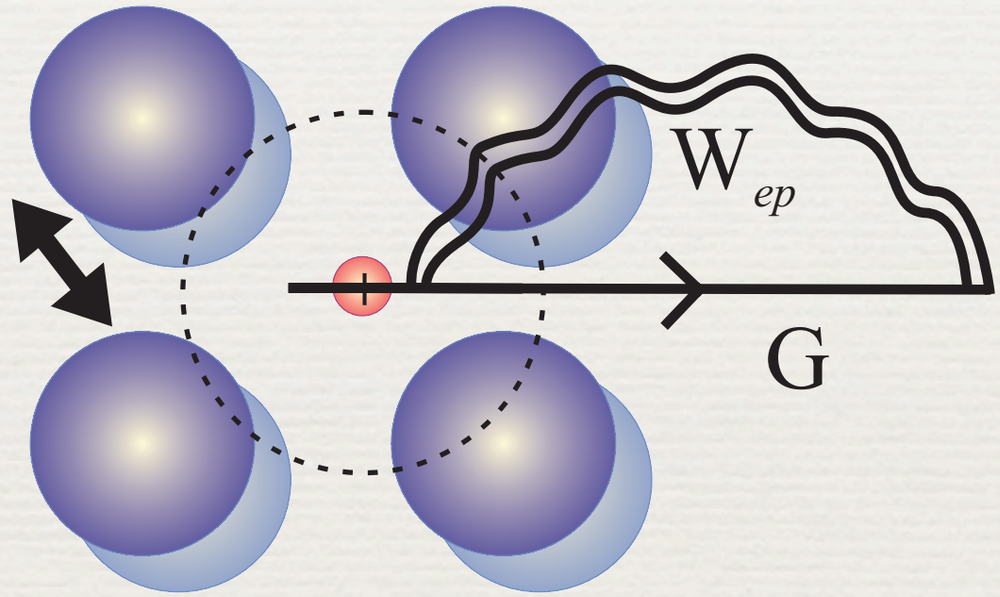
diamond: **0.37 eV**

silicon: **0.06 eV**

M. Cardona and M. L. W. Thewalt
Rev. Mod. Phys. 77, 001173 (2005)

electron-phonon

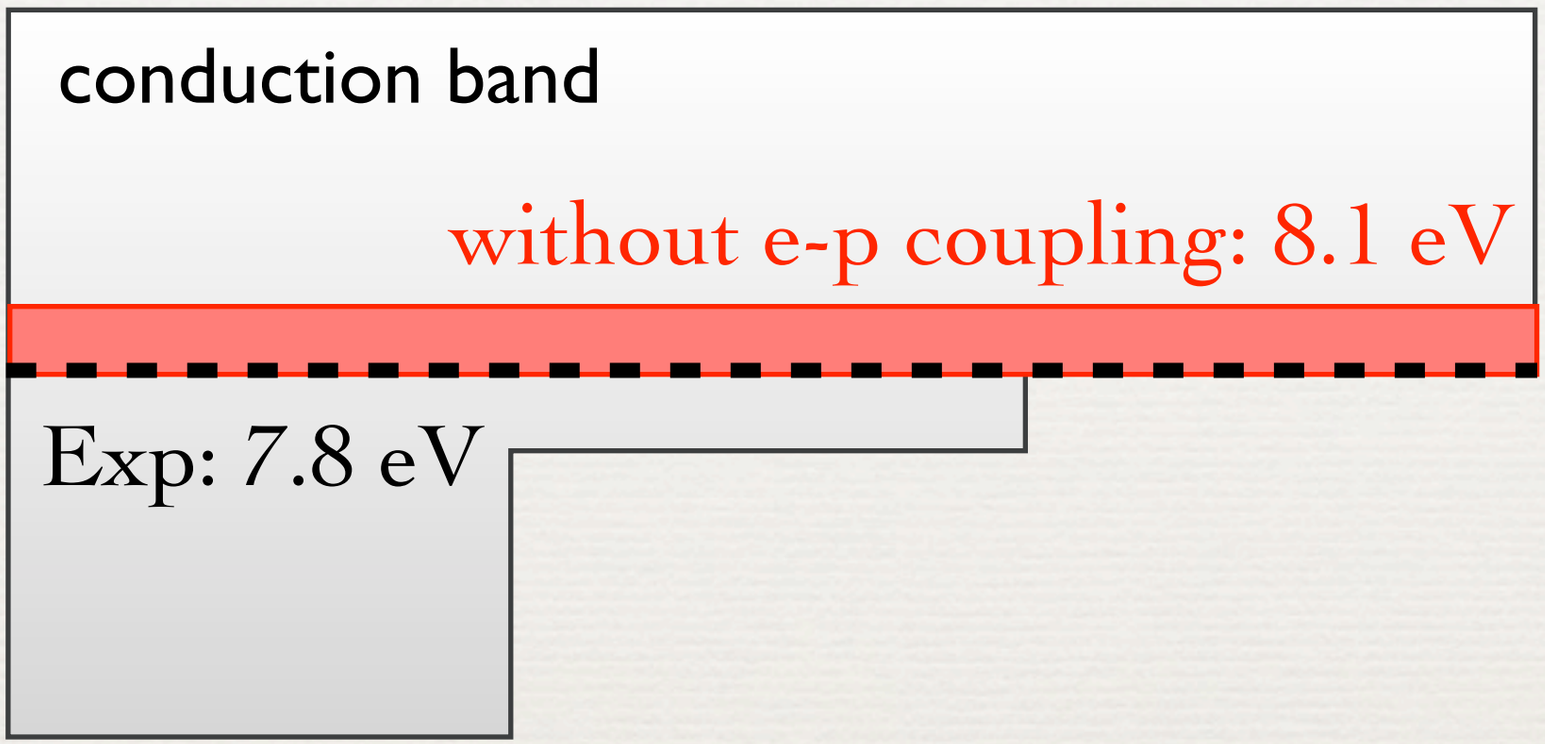
$\Sigma_{ep} = GW_{ep}$:



Band gap renormalization!
Also at zero temperature.

P. Rinke, A. Schleife, E. Kioupakis, A. Janotti, C. Rödl, F. Bechstedt, M. Scheffler, C. G. Van de Walle, Phys. Rev. Lett. 108, 126404 (2012)

Getting the band gap of MgO right



4.5 eV **7.0 eV** **8.1 eV**

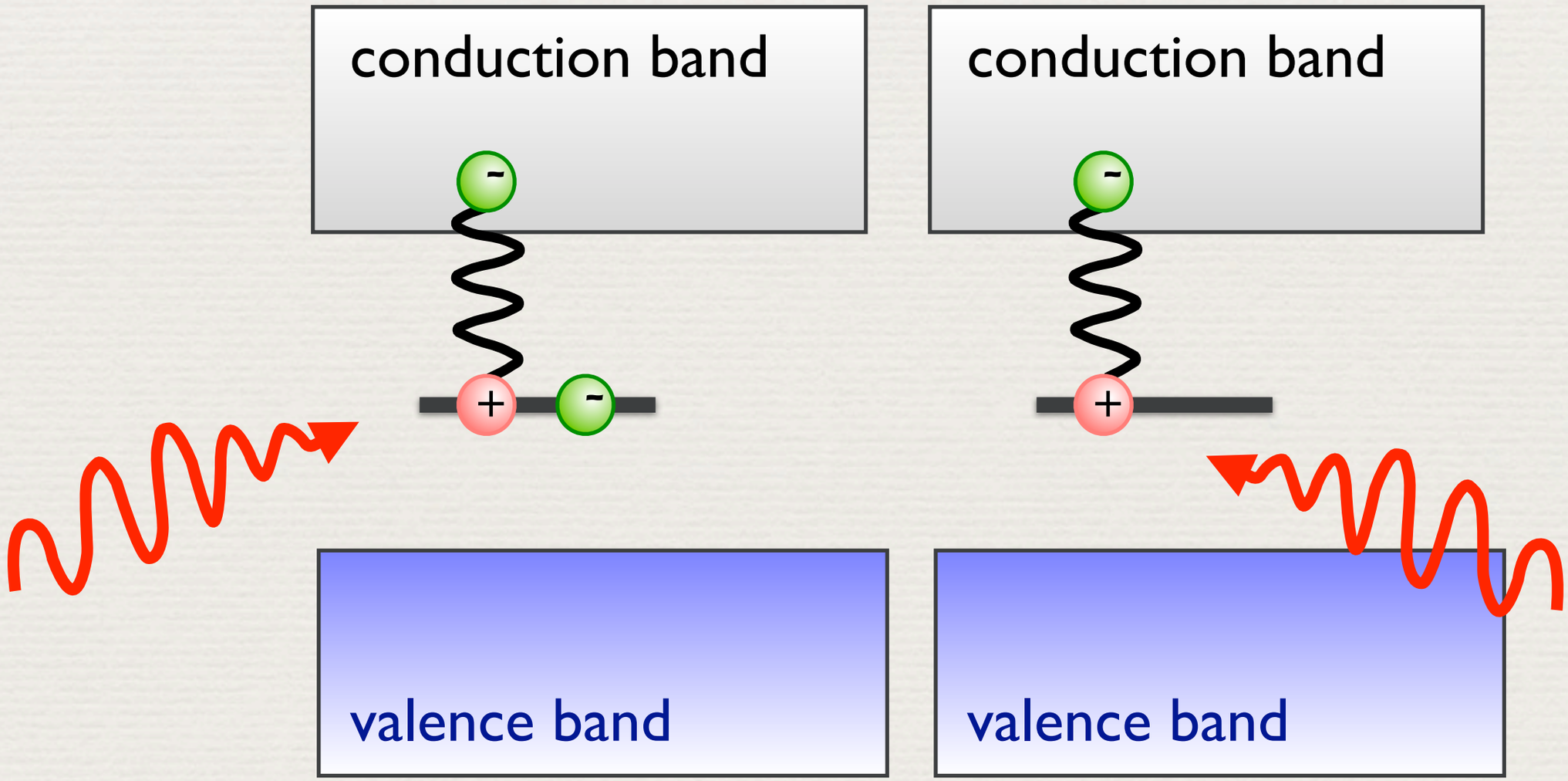
LDA **LDA0** ***G₀W₀@ LDA0***

valence band

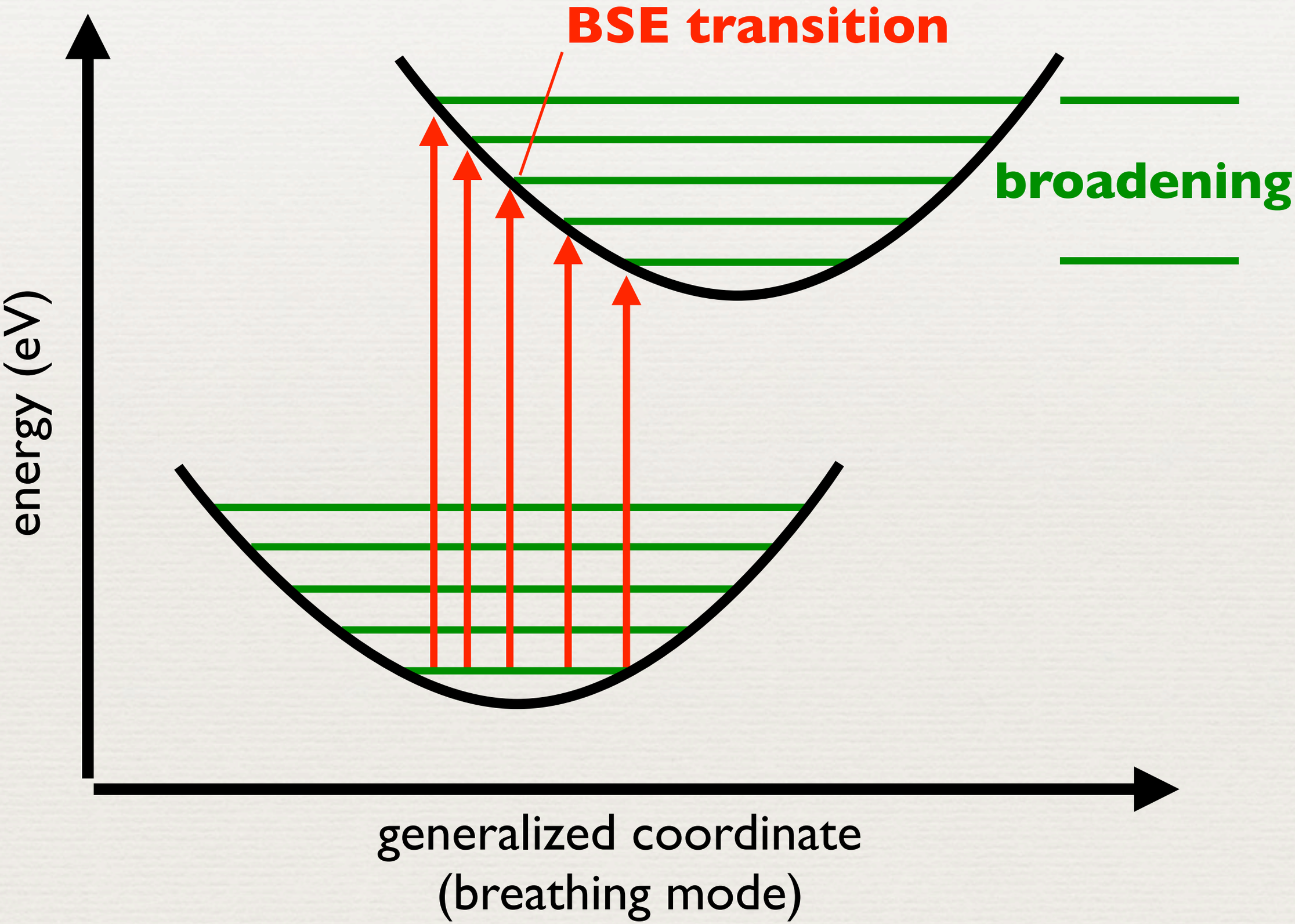
P. Rinke, A. Schleife, E. Kioupakis, A. Janotti, C. Rödl, F. Bechstedt, M. Scheffler, C. G. Van de Walle, Phys. Rev. Lett. 108, 126404 (2012)

F-center: Absorption energies

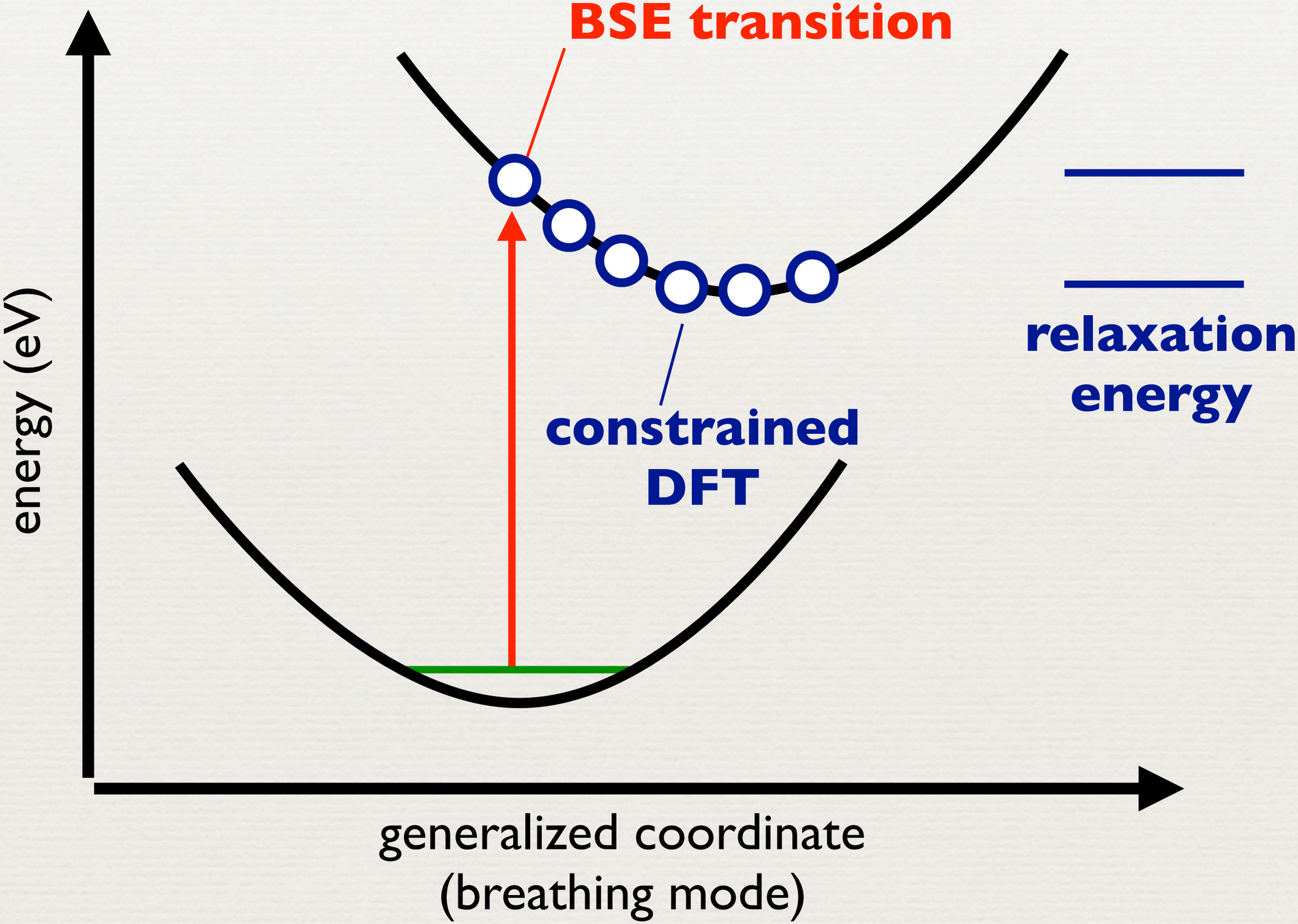
	F-center	F^+-center
G_0W_0@LDA0:	5.40 eV	5.48 eV
BSE binding energy:	0.45 eV	0.56 eV
GW-BSE:	4.96 eV	4.92 eV
Experiment:	5.00 eV	4.95 eV



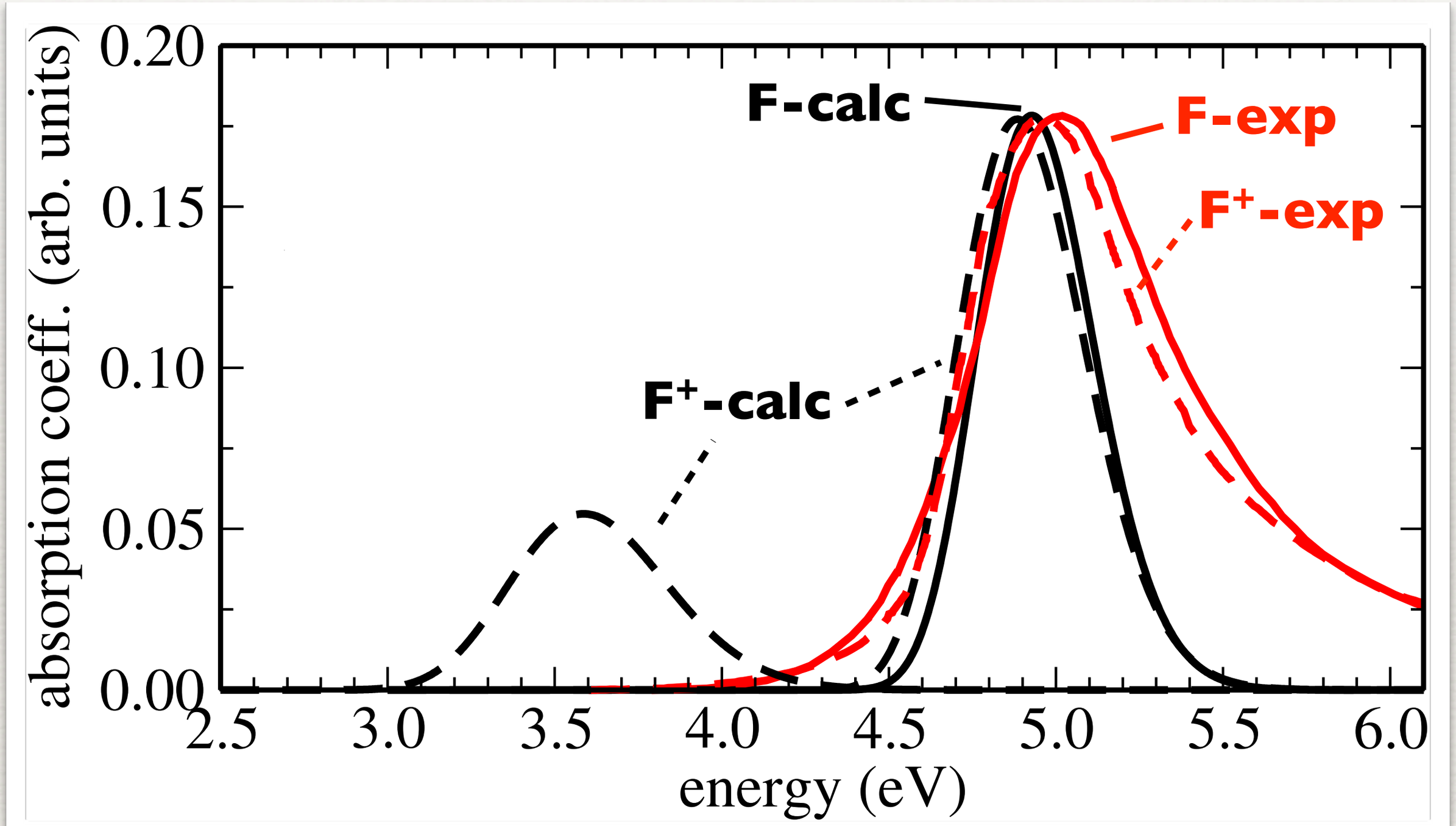
F-center: Peak broadening



F-center: Peak broadening



F-center: Optical absorption spectra



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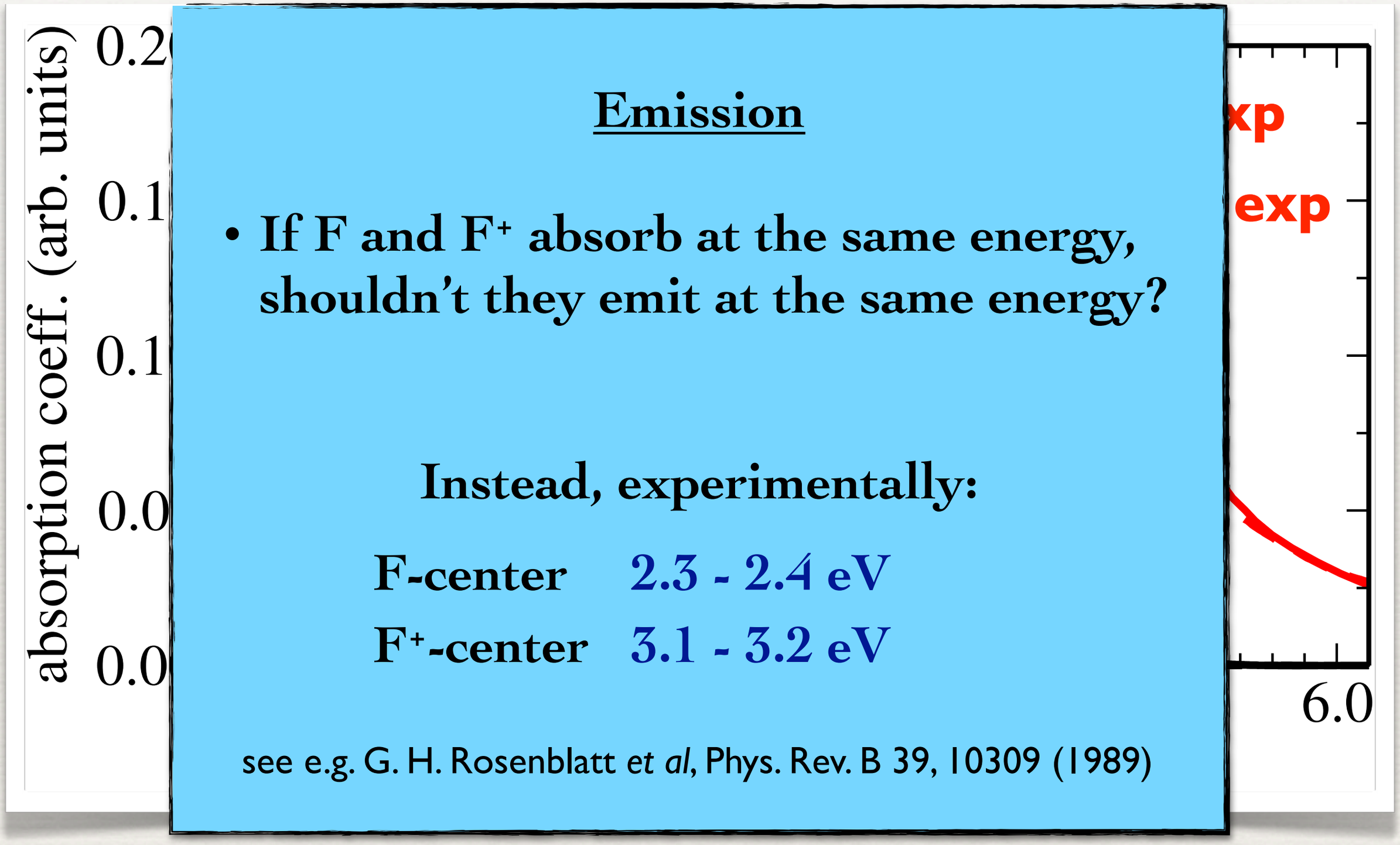


Emission

- **If F and F^+ absorb at the same energy, shouldn't they emit at the same energy?**

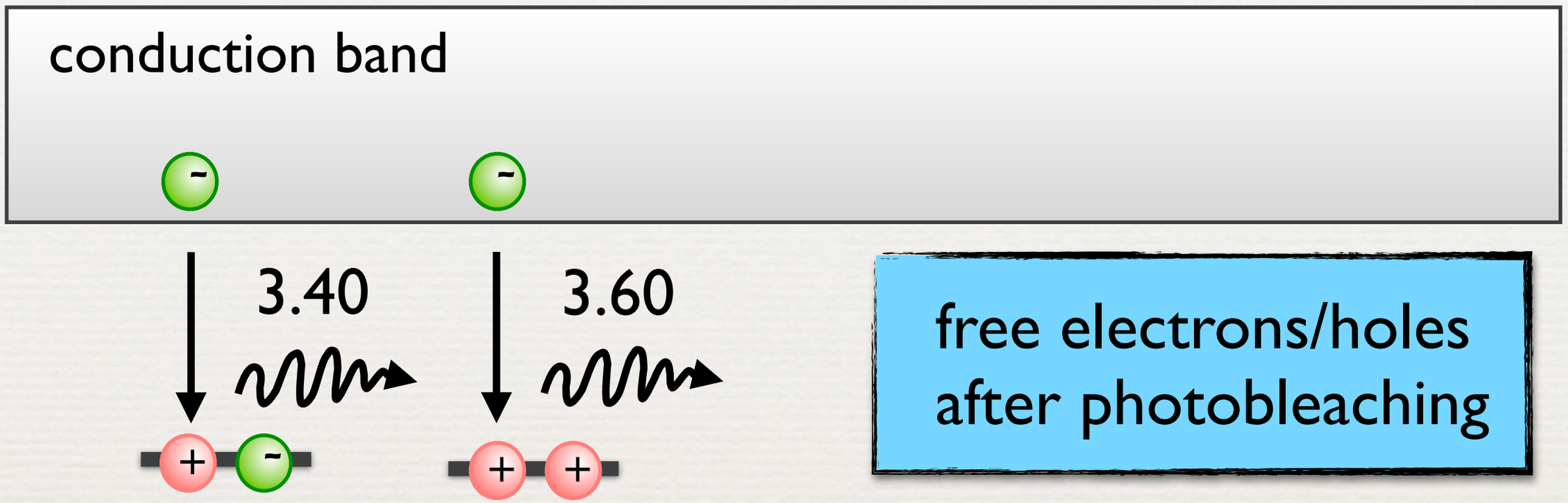
Instead, experimentally:

F-center **2.3 - 2.4 eV**

F^+-center **3.1 - 3.2 eV**

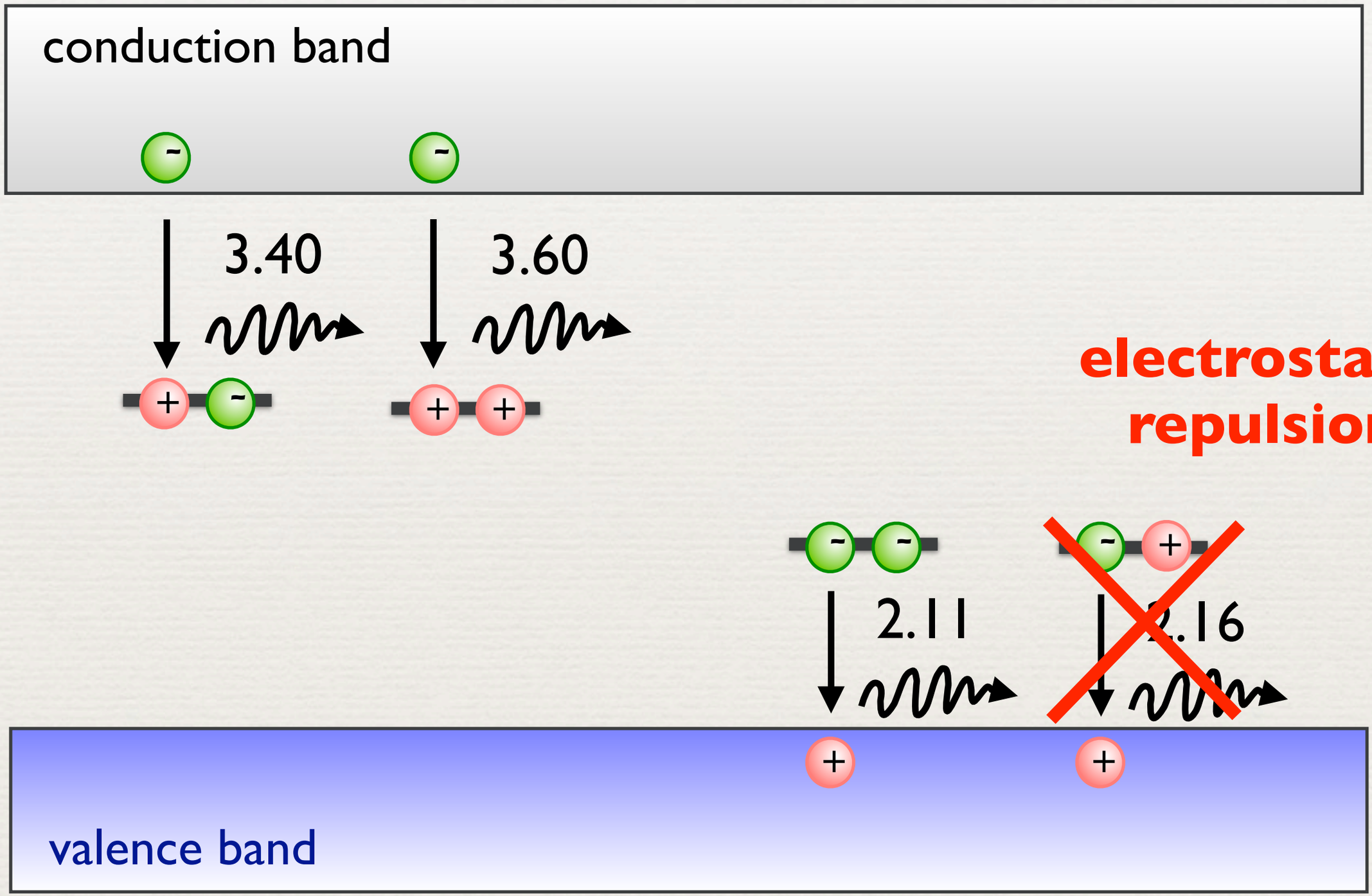
see e.g. G. H. Rosenblatt *et al*, Phys. Rev. B 39, 10309 (1989)

F-center: Emission



P. Rinke, A. Schleife, E. Kioupakis, A. Janotti, C. Rödl, F. Bechstedt, M. Scheffler, C. G. Van de Walle, Phys. Rev. Lett. 108, 126404 (2012)

Reinterpretation of F-center emission



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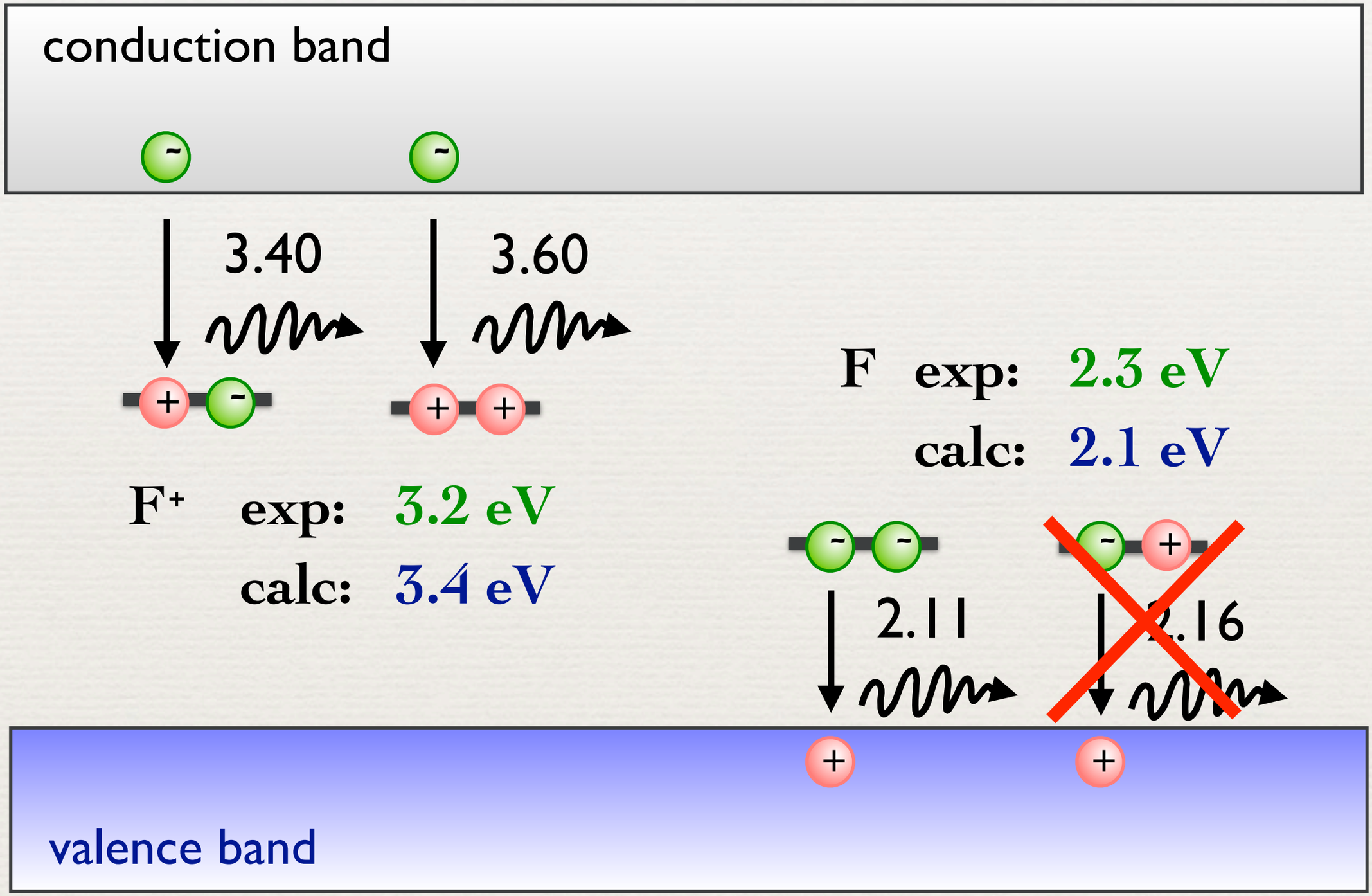
Reinterpretation of F-center emission



F exp: 2.3 eV

calc: 2.1 eV

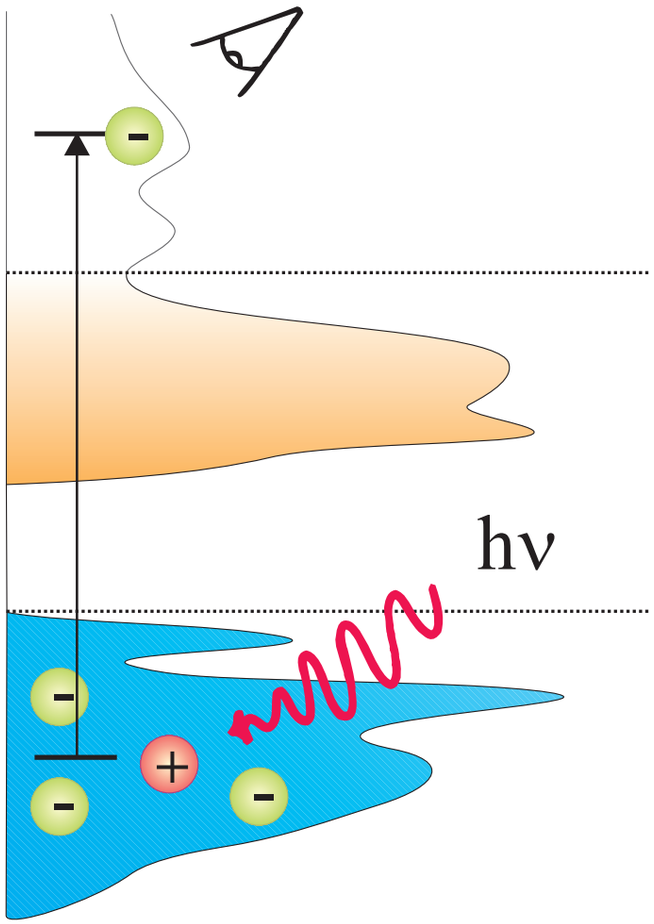
F^+ exp: 3.2 eV

calc: 3.4 eV

P. Rinke, A. Schleife, E. Kioupakis, A. Janotti, C. Rödl, F. Bechstedt, M. Scheffler, C. G. Van de Walle, Phys. Rev. Lett. 108, 126404 (2012)

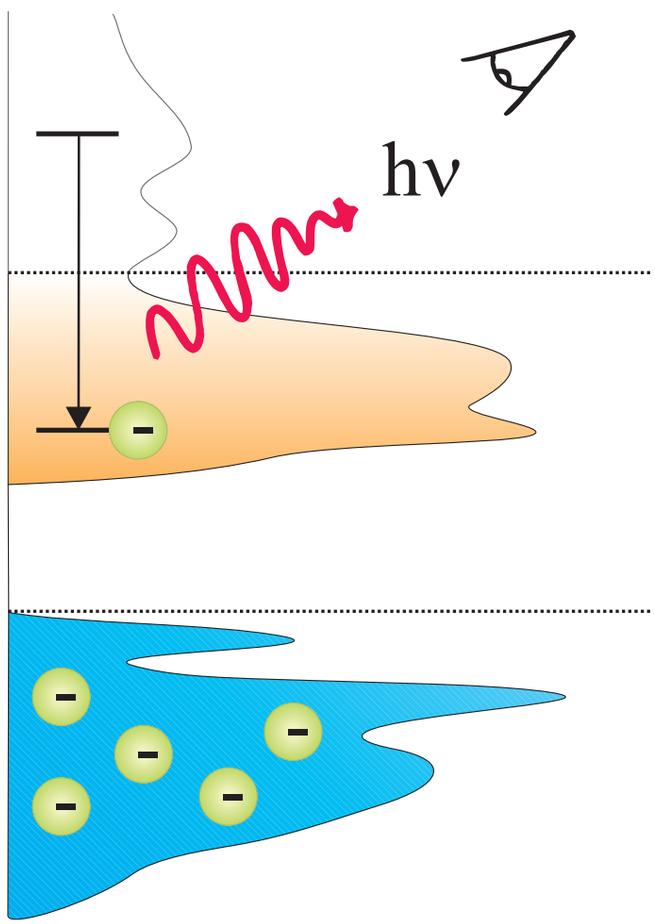
Summary

Photoemission



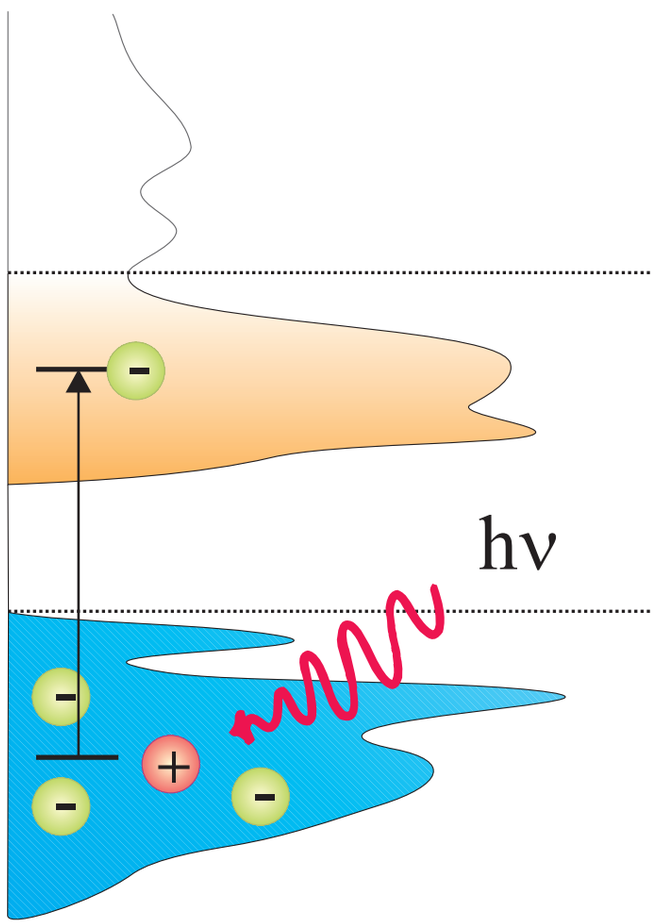
GW

Inverse Photoemission



GW

Absorption



BSE
TDDFT

Electron-phonon coupling

electron-phonon self-energy in Migdal approximation:

(Park *et al.* PRL **99**, 086804 (2007), Hedin and Lundqvist, Solid State Physics **23**, 1 (1969))

$$\Sigma_{n\mathbf{k}}(E,T) = \sum_{m,\nu} \int \frac{d\mathbf{q}}{\Omega_{\mathrm{BZ}}} |g_{mn,\nu}(\mathbf{k},\mathbf{q})|^2 \times \left[\frac{n_{\mathbf{q}\nu} + 1 - f_{m\mathbf{k}+\mathbf{q}}}{E - \epsilon_{m\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}\nu} - i\delta} + \frac{n_{\mathbf{q}\nu} + f_{m\mathbf{k}+\mathbf{q}}}{E - \epsilon_{m\mathbf{k}+\mathbf{q}} + \hbar\omega_{\mathbf{q}\nu} - i\delta} \right]$$

$n_{\mathbf{q}\nu}$	:	electron/hole occupation factors
$\epsilon_{m\mathbf{k}+\mathbf{q}}$	:	band structure energies
$f_{m\mathbf{k}+\mathbf{q}}$	:	phonon occupation factors
$\hbar\omega_{\mathbf{q}\nu}$	:	phonon energies
$g_{mn,\nu}$	:	electron-phonon coupling matrix elements