

Electronic excitations, computational spectroscopy

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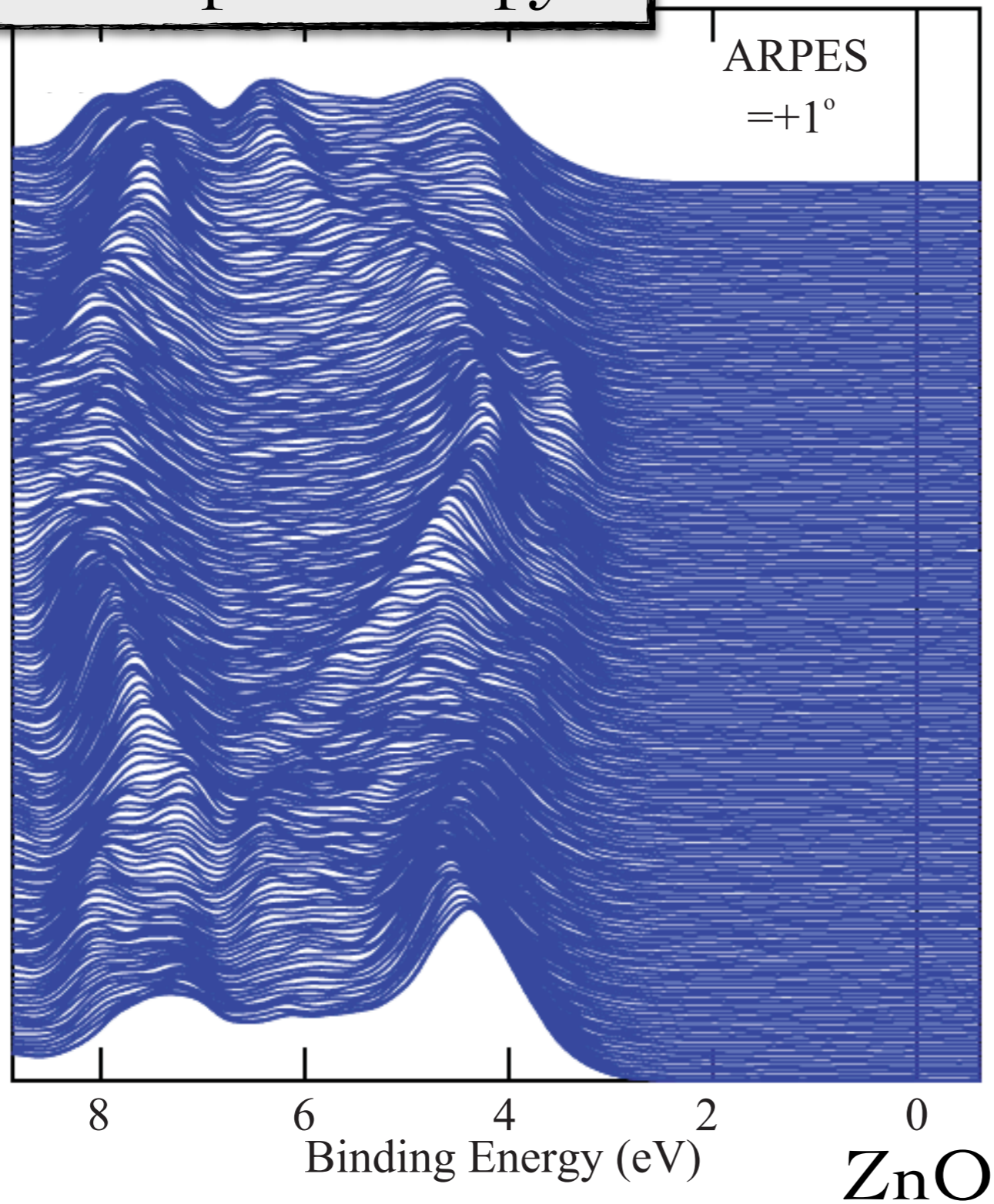


MAX-PLANCK-GESELLSCHAFT



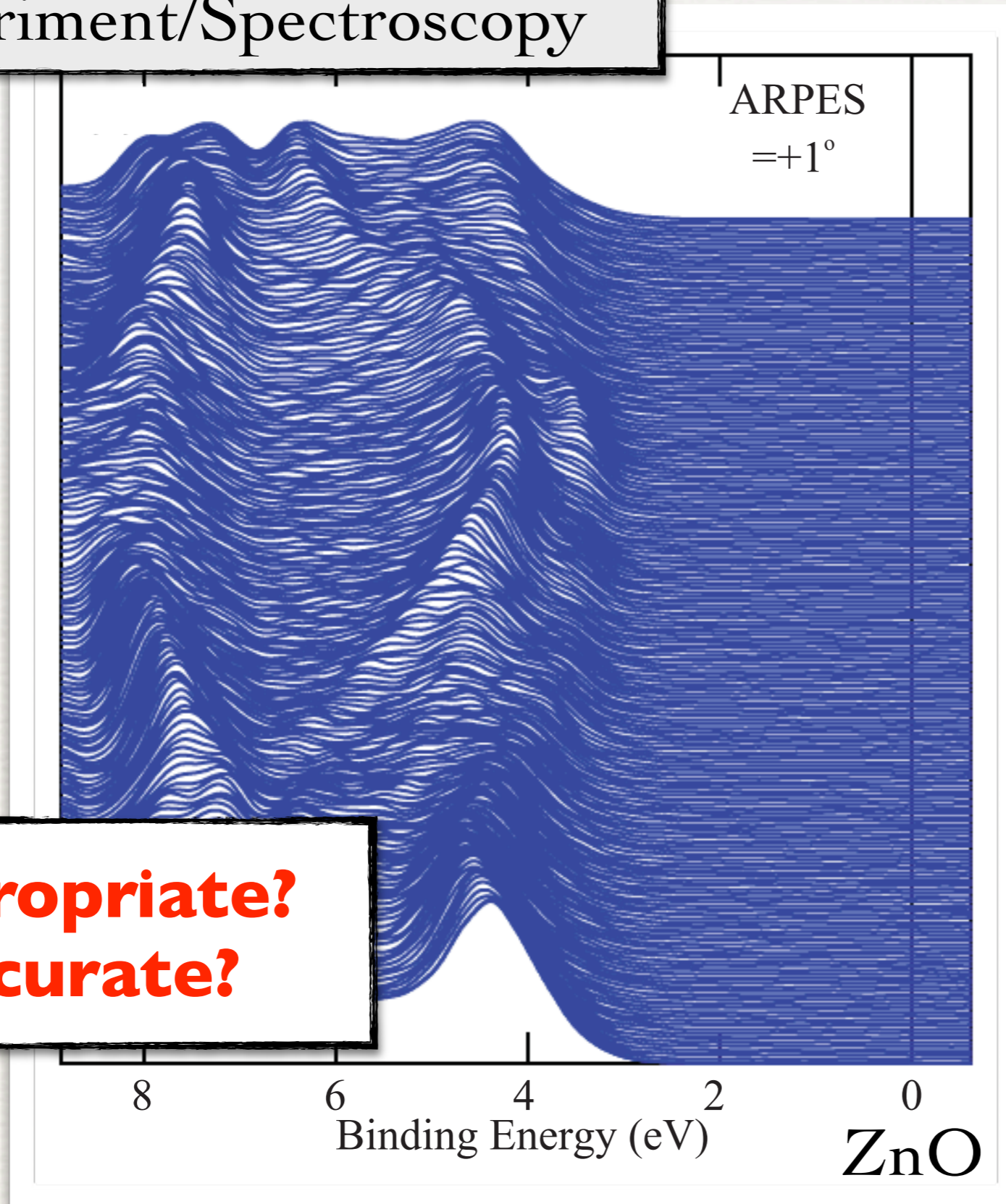
Excited states in material science are ubiquitous

Experiment/Spectroscopy



Excited states in material science are ubiquitous

Experiment/Spectroscopy

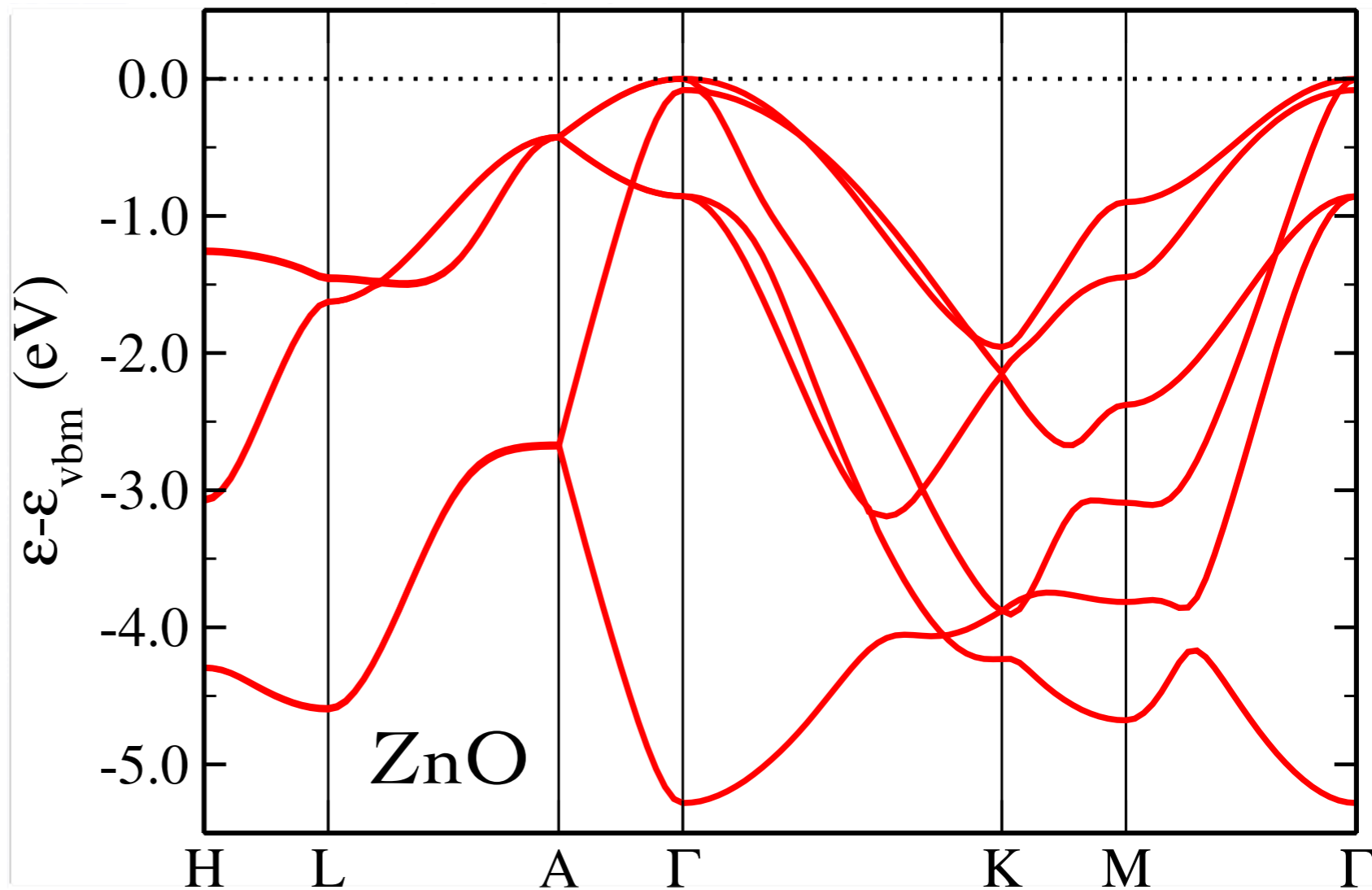
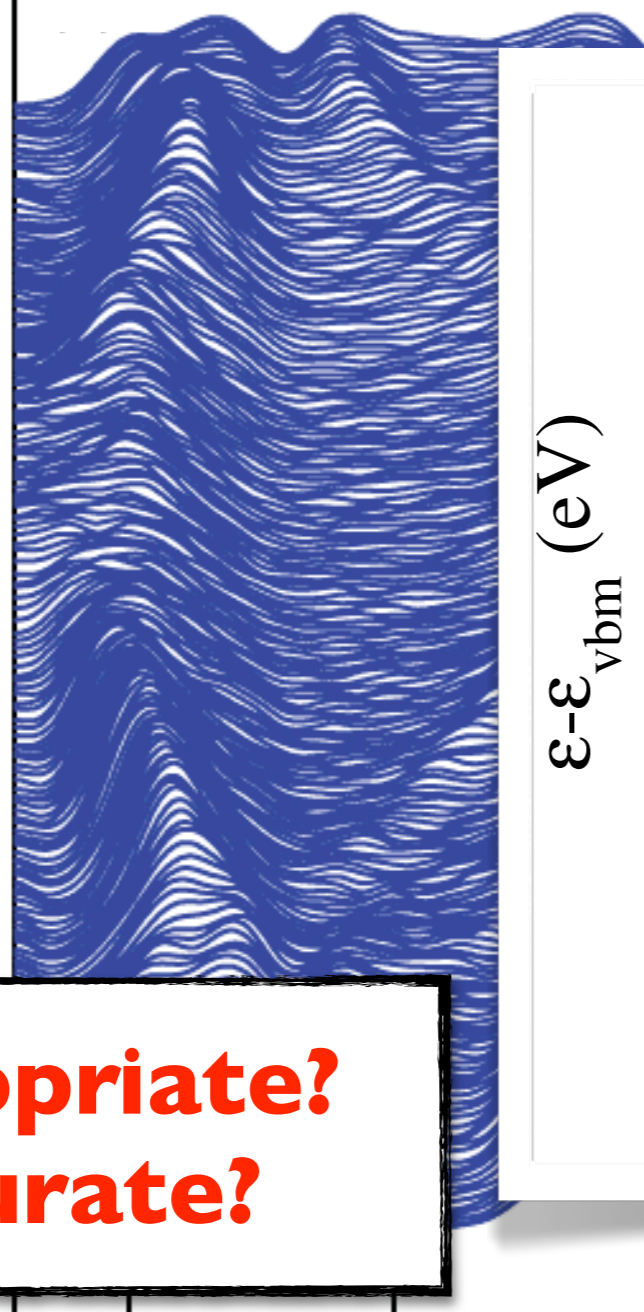


appropriate?
accurate?

Excited states in material science are ubiquitous

Experiment/Spectroscopy

Theoretical Spectroscopy



appropriate?
accurate?

8

6

4

2

0

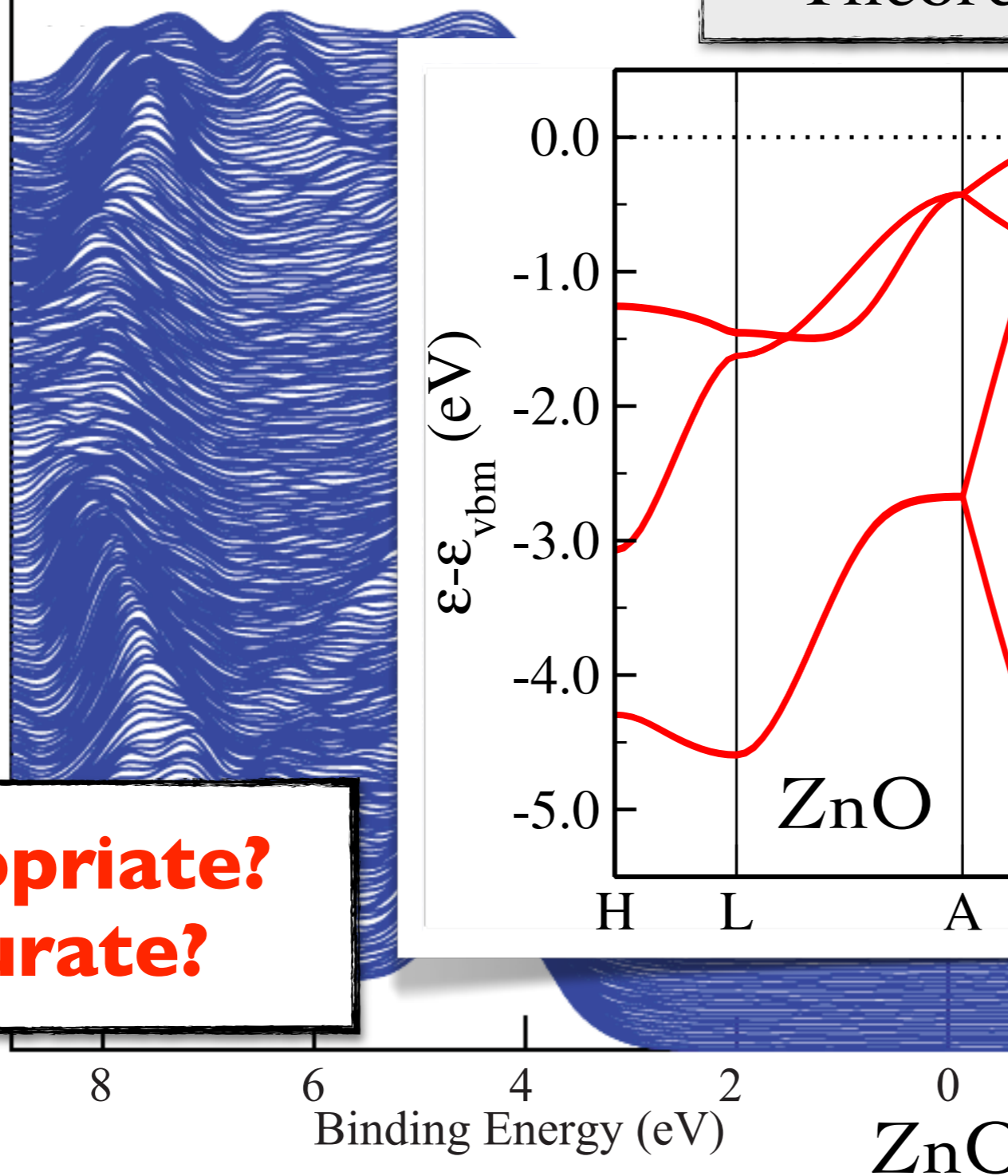
Binding Energy (eV)

ZnO

Excited states in material science are ubiquitous

Experiment/Spectroscopy

Theoretical Spectroscopy



appropriate?
accurate?

appropriate?
accurate?

Excited states in material science are ubiquitous

Experiment/Spectroscopy

Theoretical Spectroscopy

Materials Science/Application

**appropriate?
accurate?**

-5.0

ZnO

L

A

K

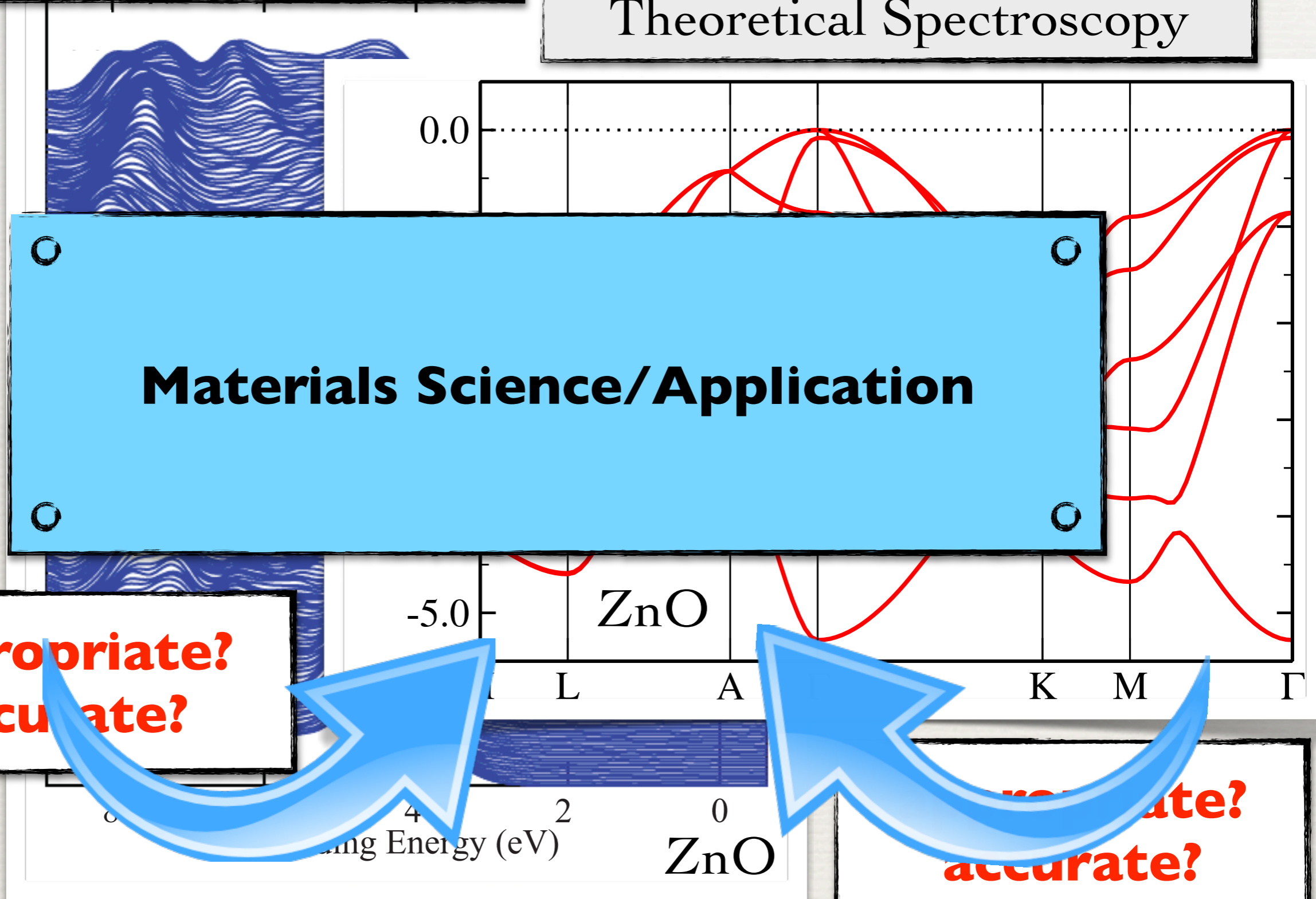
M

Γ

Binding Energy (eV)

ZnO

**appropriate?
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?**

-5.0

ZnO

L

A

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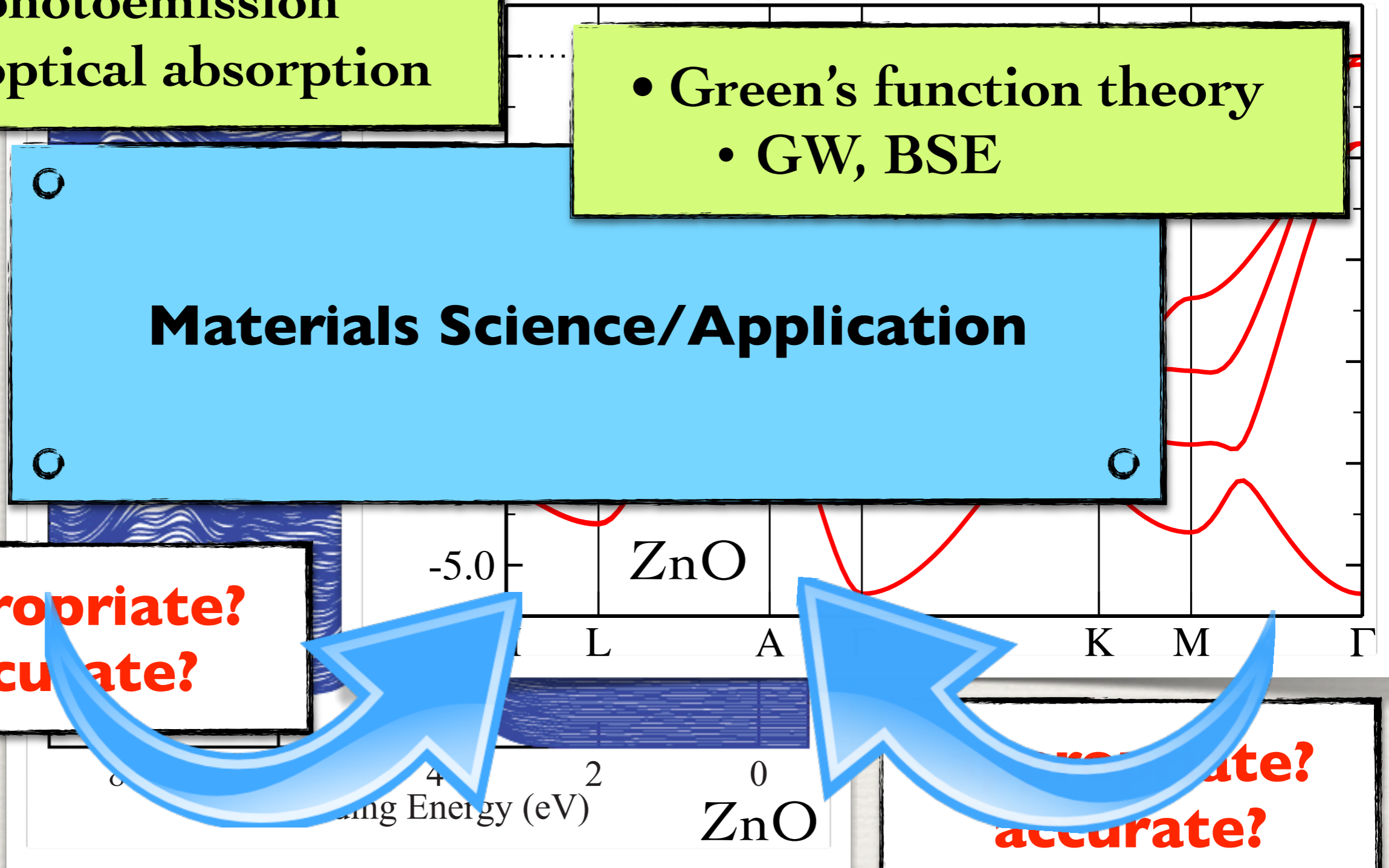
M

Γ

Binding Energy (eV)

ZnO

**appropriate?
accurate?**



Nitride-based light emitters

- blue LED
- blue ray

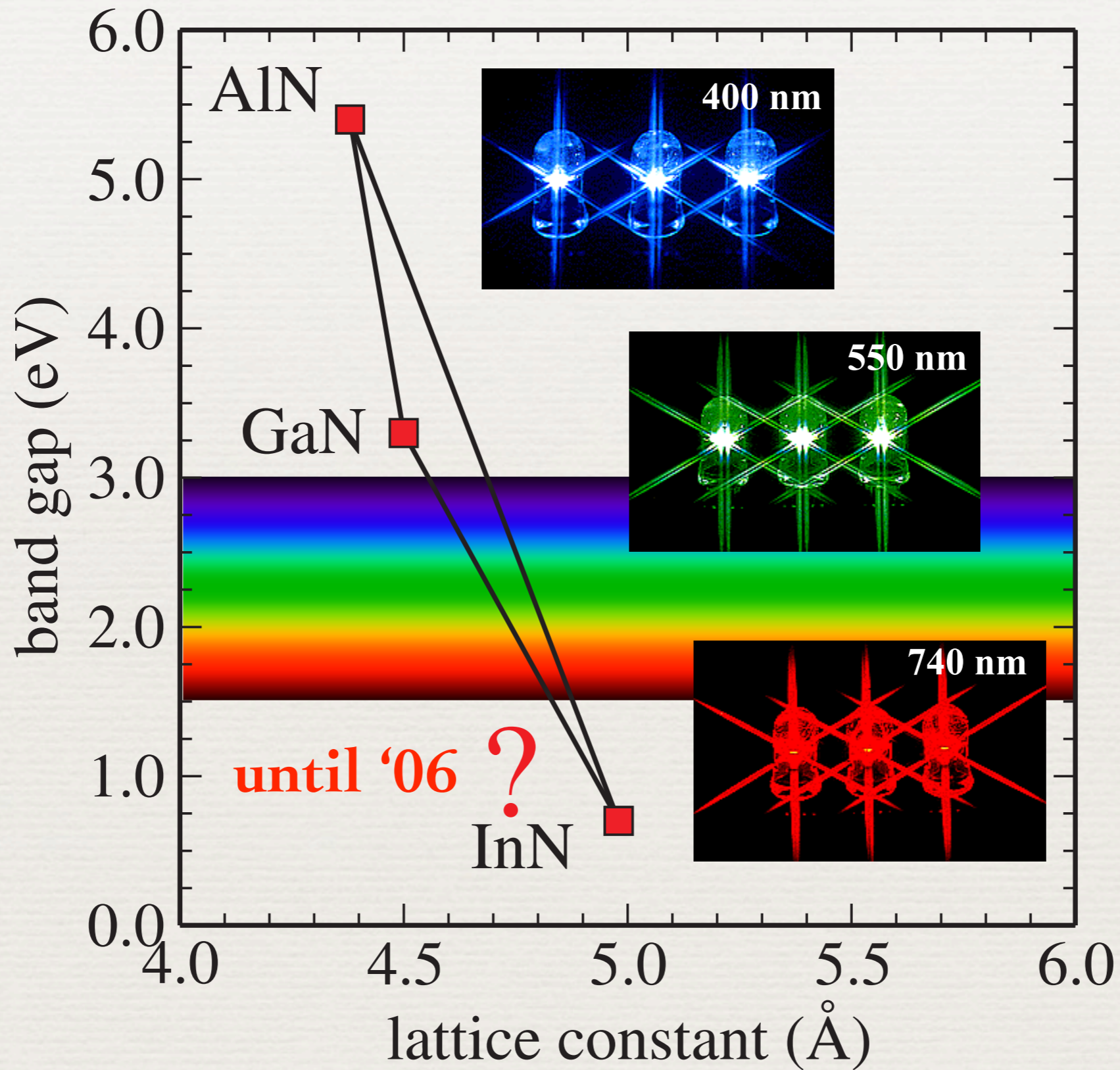


Challenges:

- solid state lighting
- RGP laser projectors

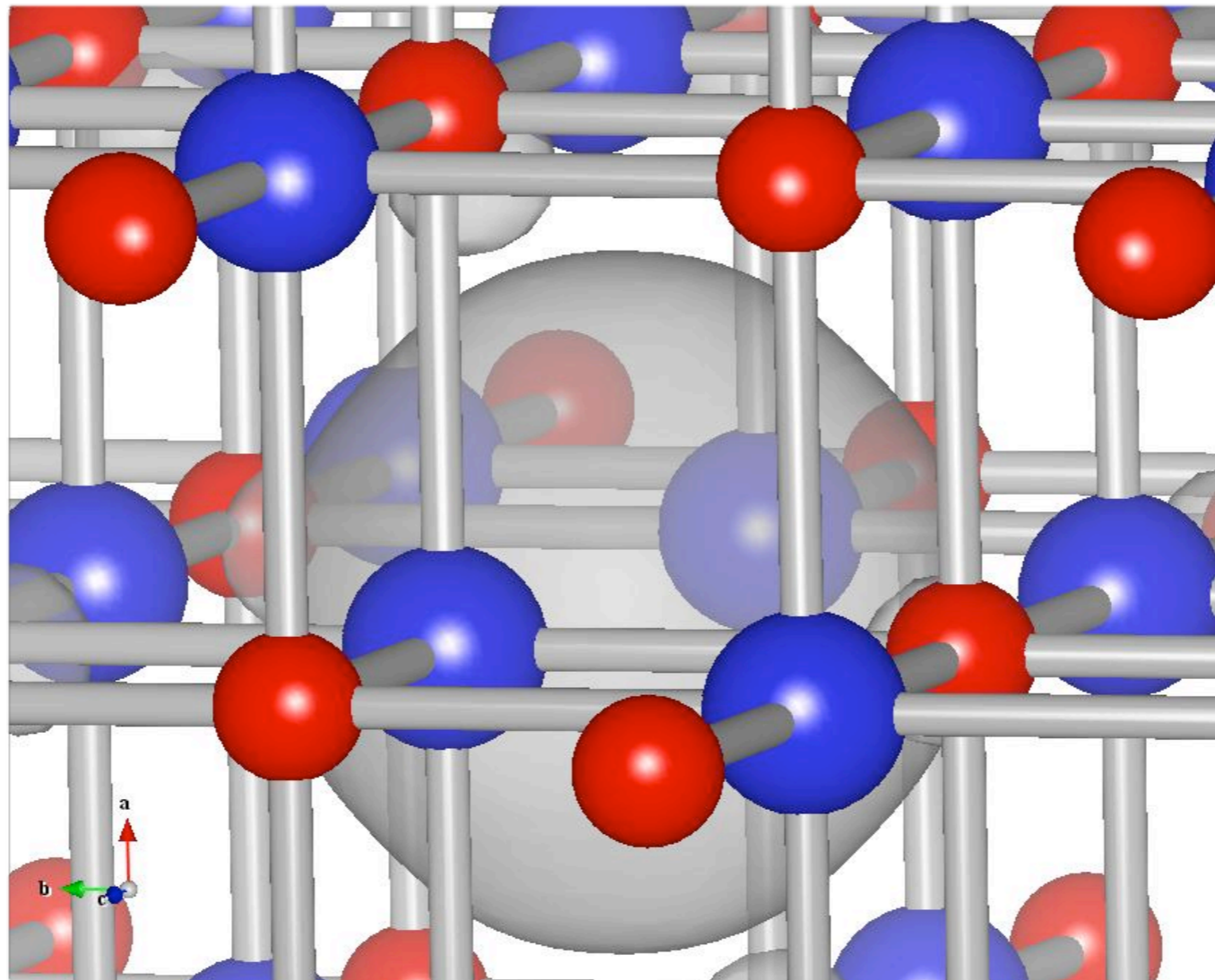


Do we know the band gap of InN?



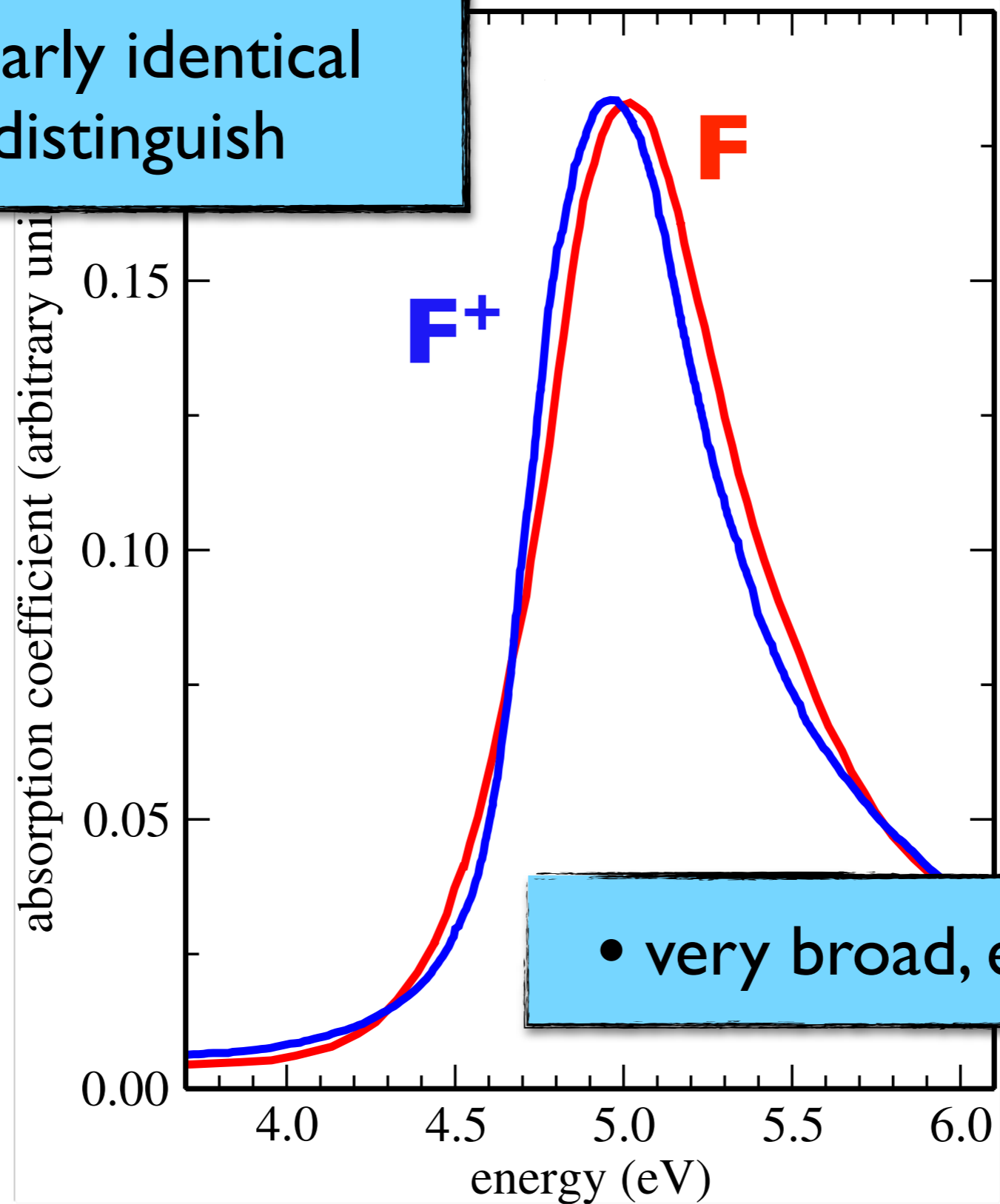
F-center: Oxygen vacancy in MgO

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



Experimental optical absorption spectra

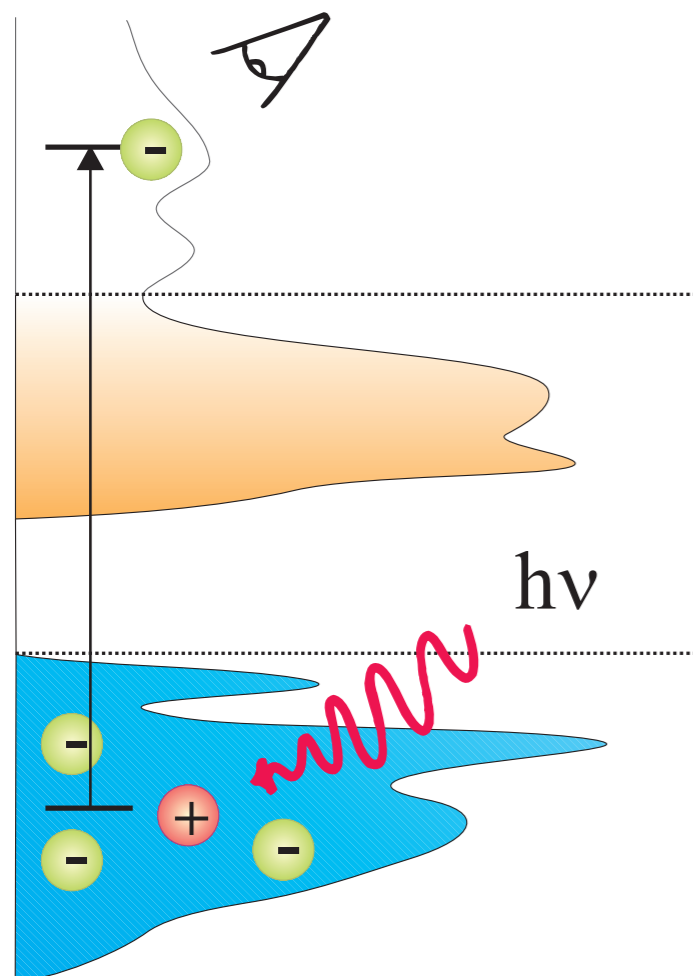
- F and F⁺ nearly identical
- difficult to distinguish



- very broad, even at low T

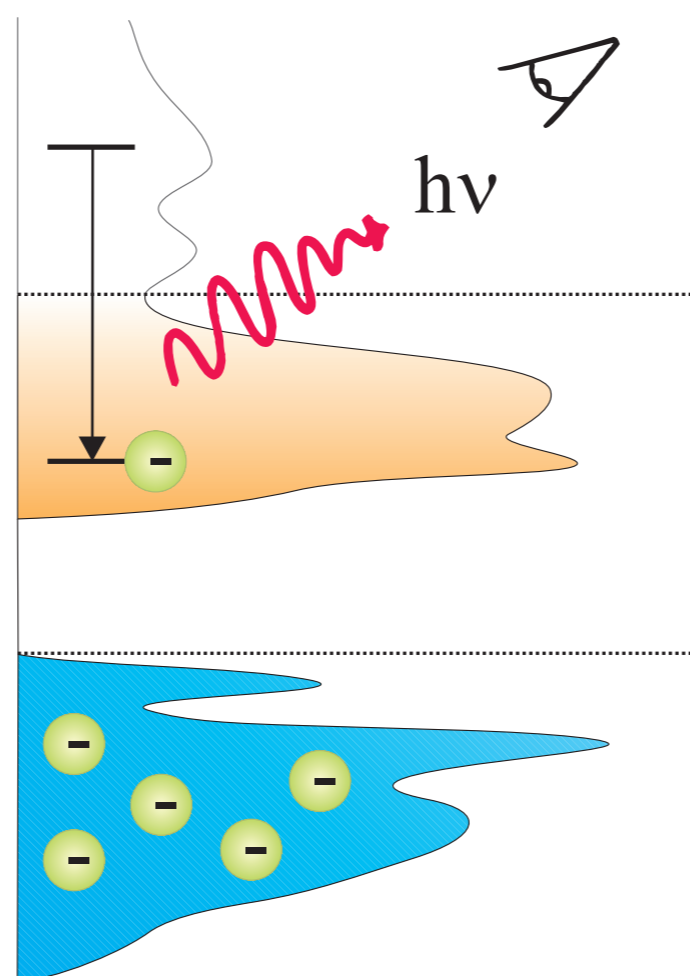
Spectroscopies

Photoemission



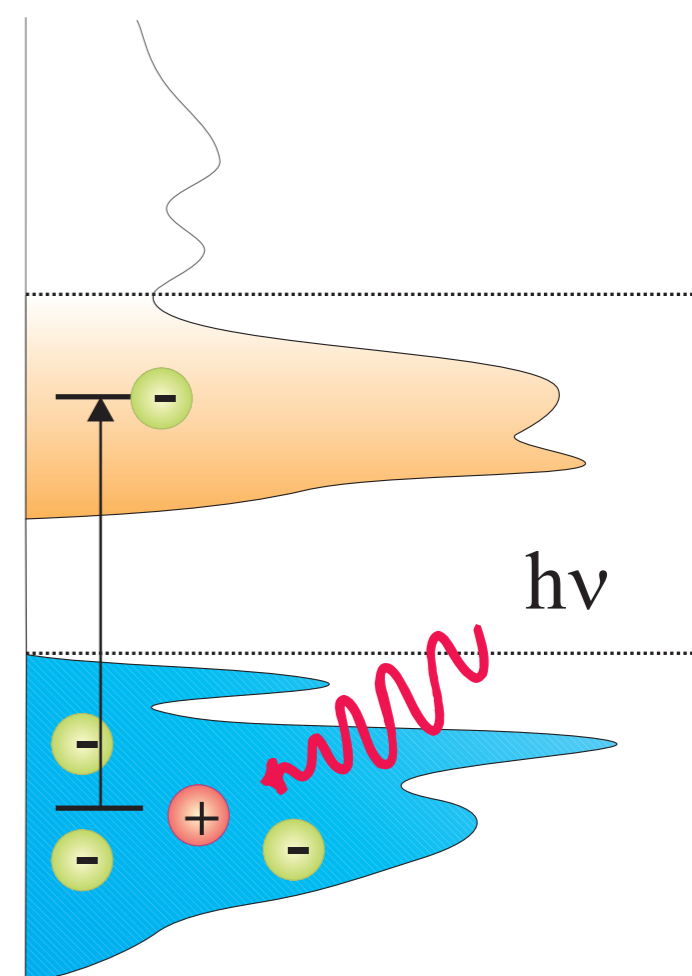
GW

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**

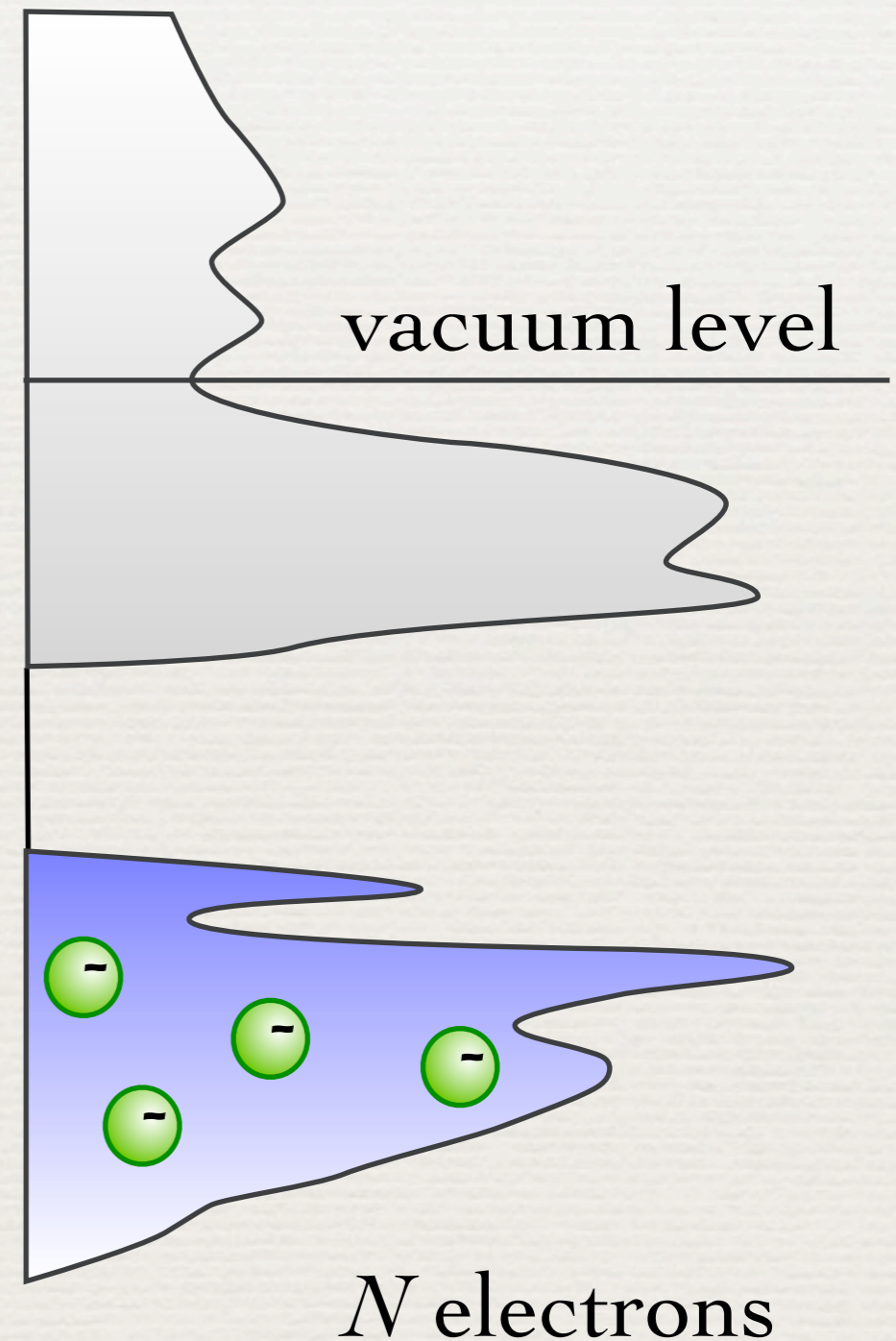


Photo-electron energies

Photoemission

annihilation operator

- electron removal

- removal energy

$$E(N)$$

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

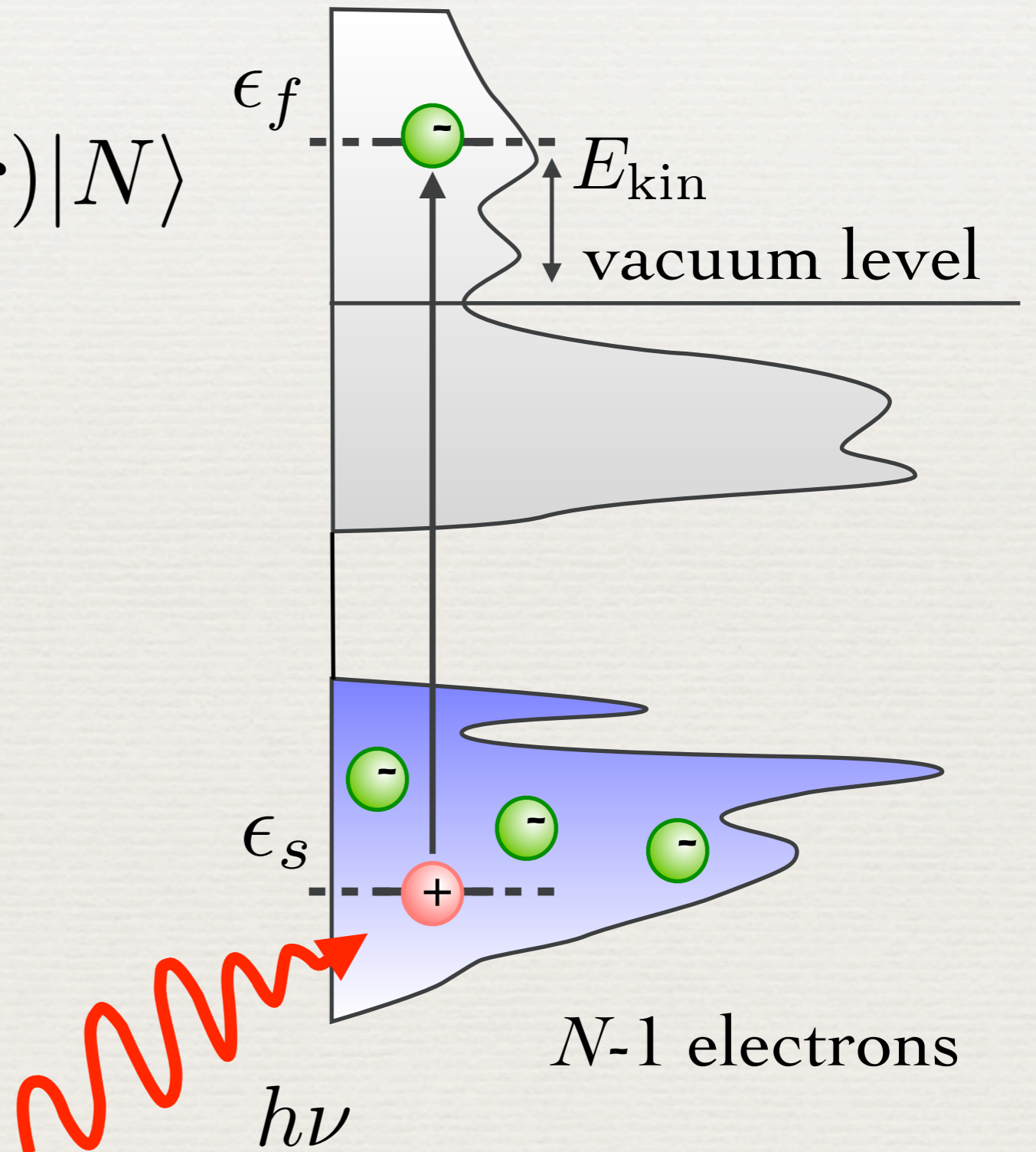


Photo-electron energies

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

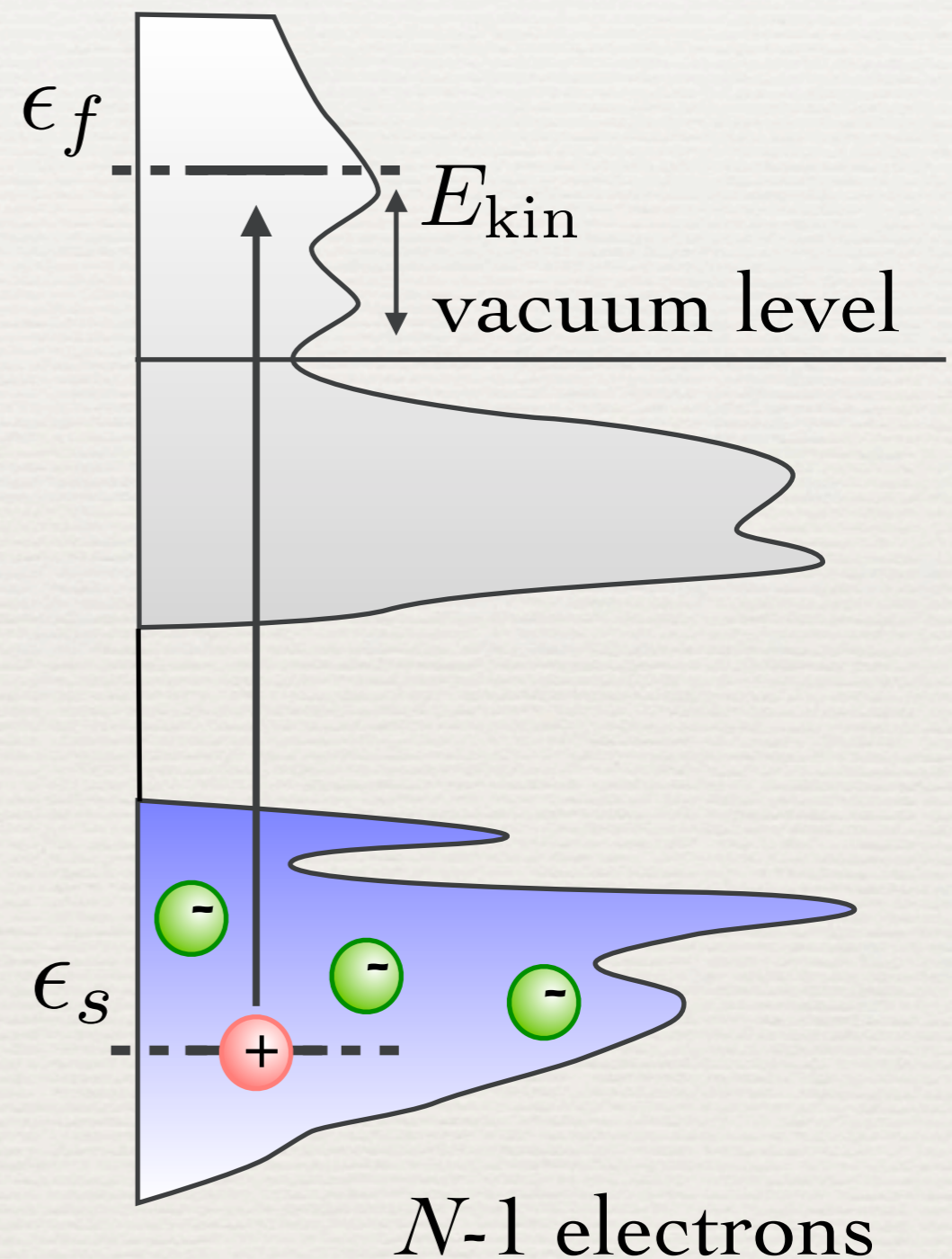


Photo-electron energies

Photoemission

- electron removal

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

- removal energy

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

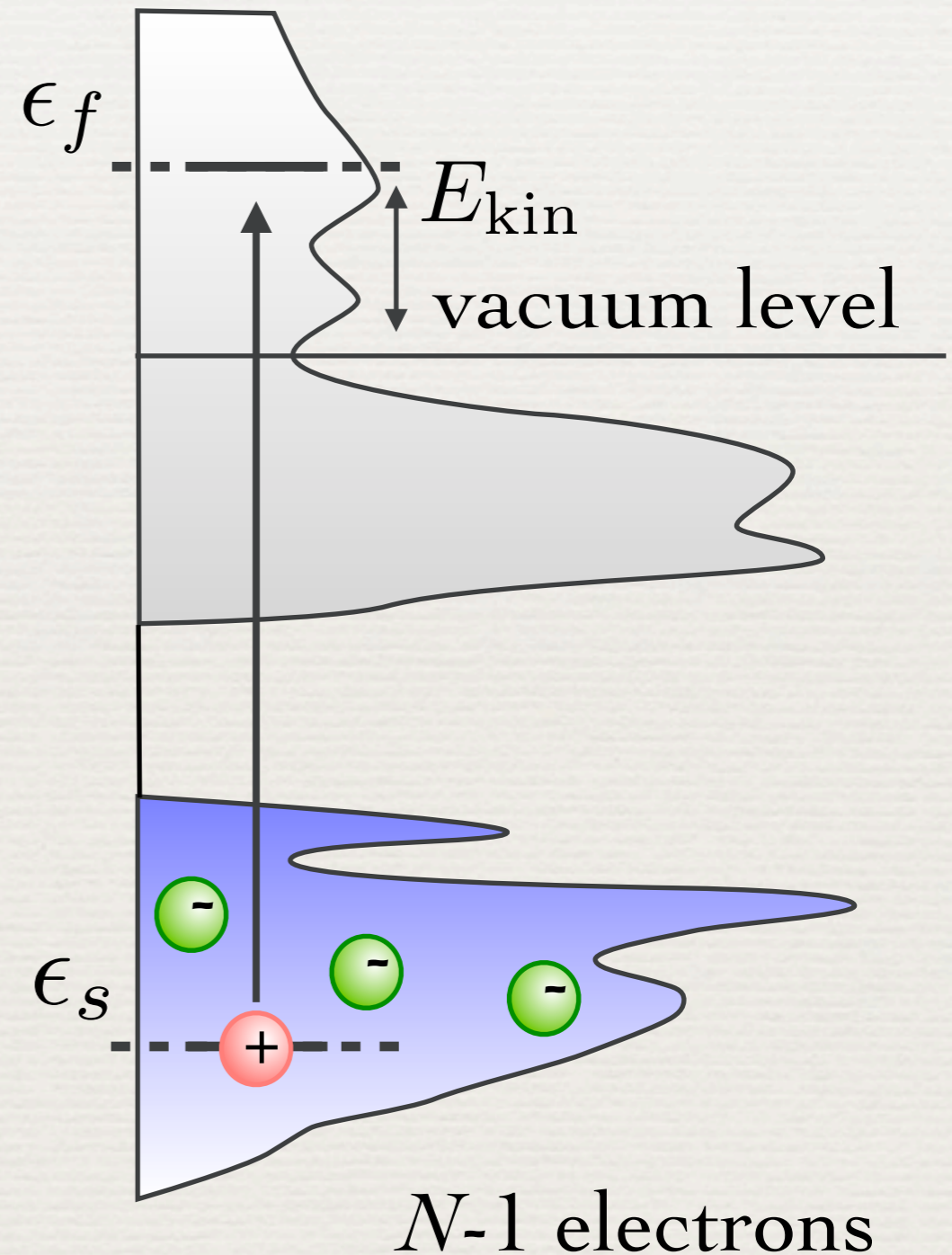


Photo-electron energies

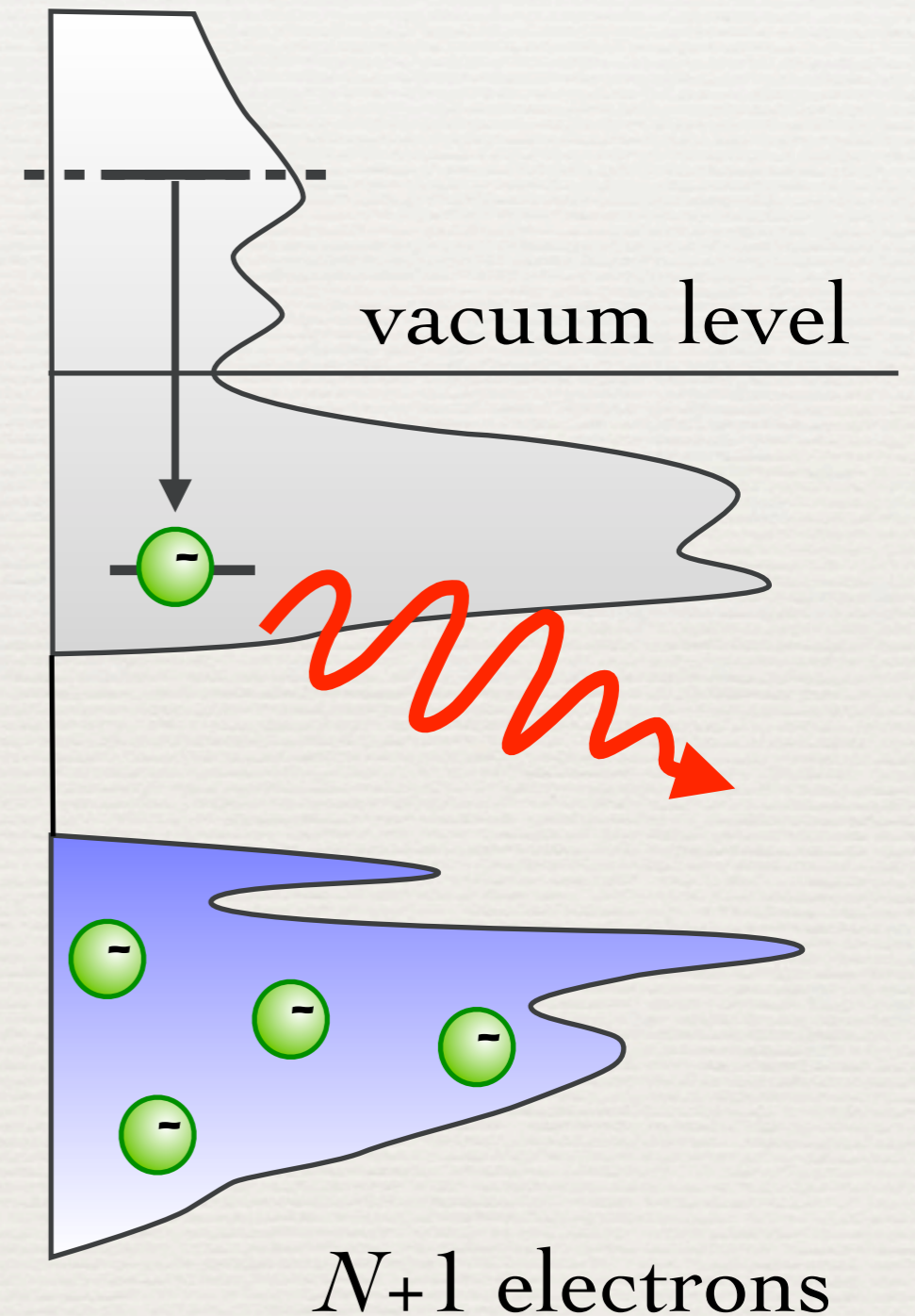
Inverse photoemission

- 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

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

**excitation energies are poles
of the Green's function**

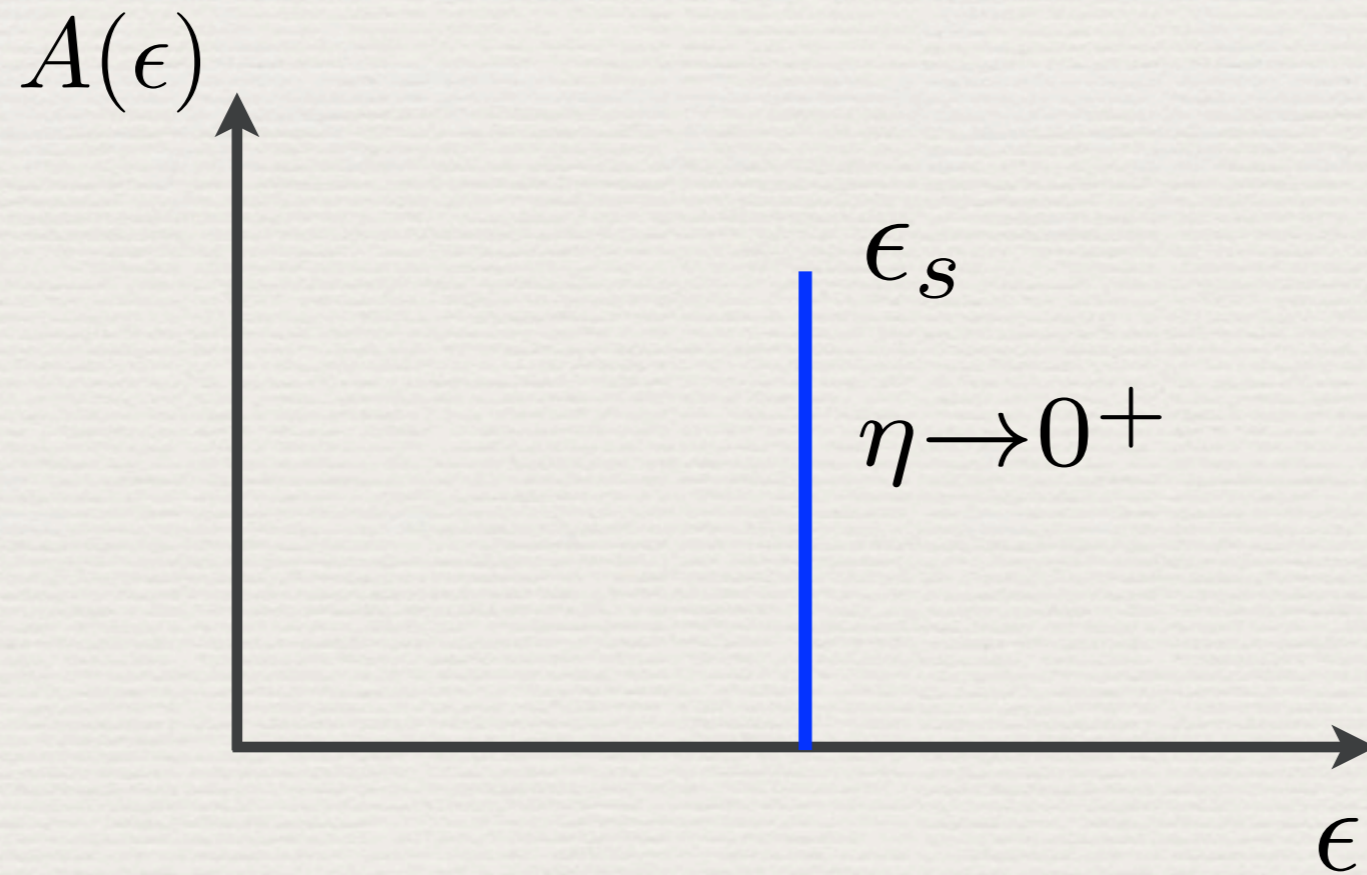
- spectroscopically relevant quantity: spectral function

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

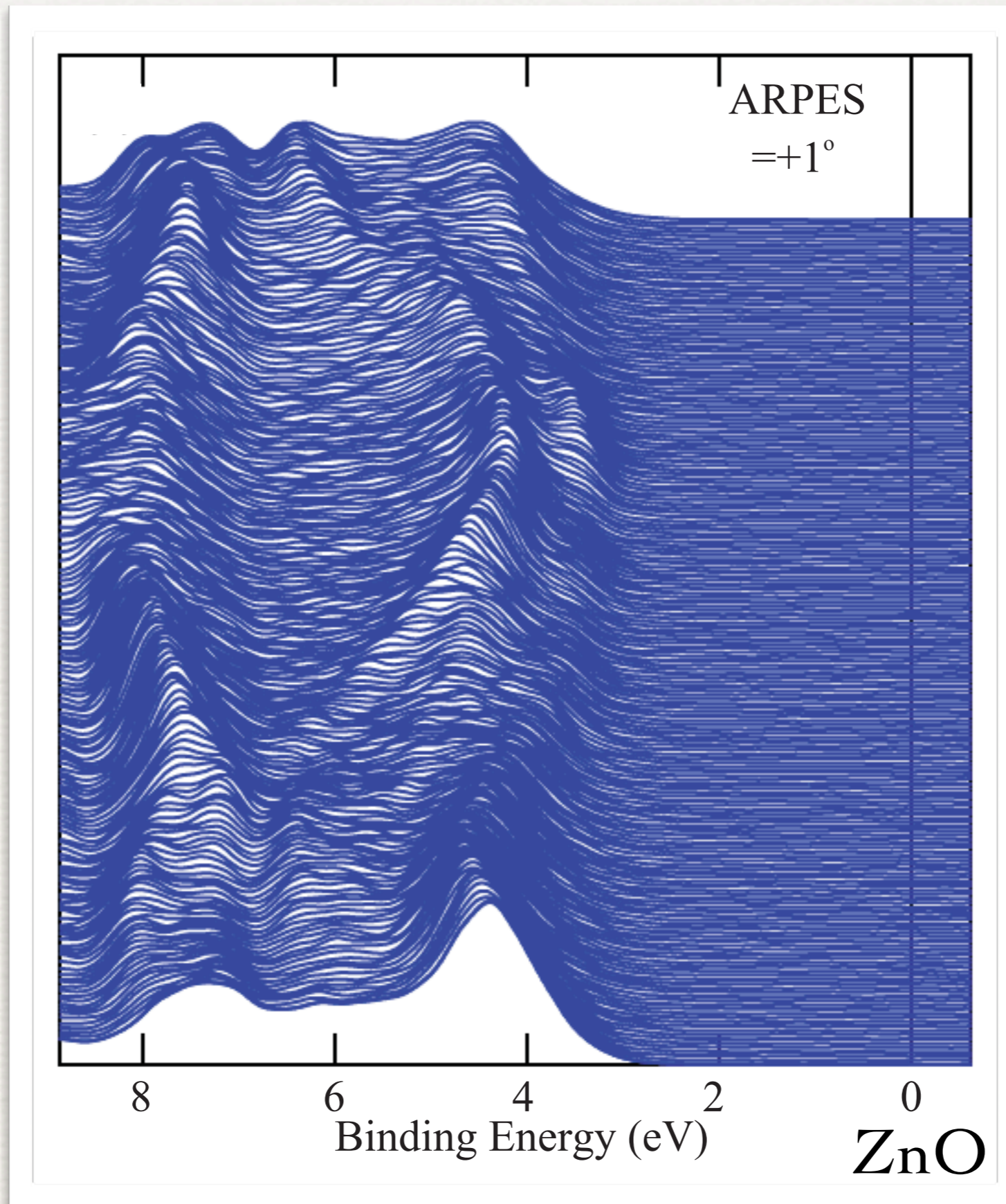
Single-particle Green's function

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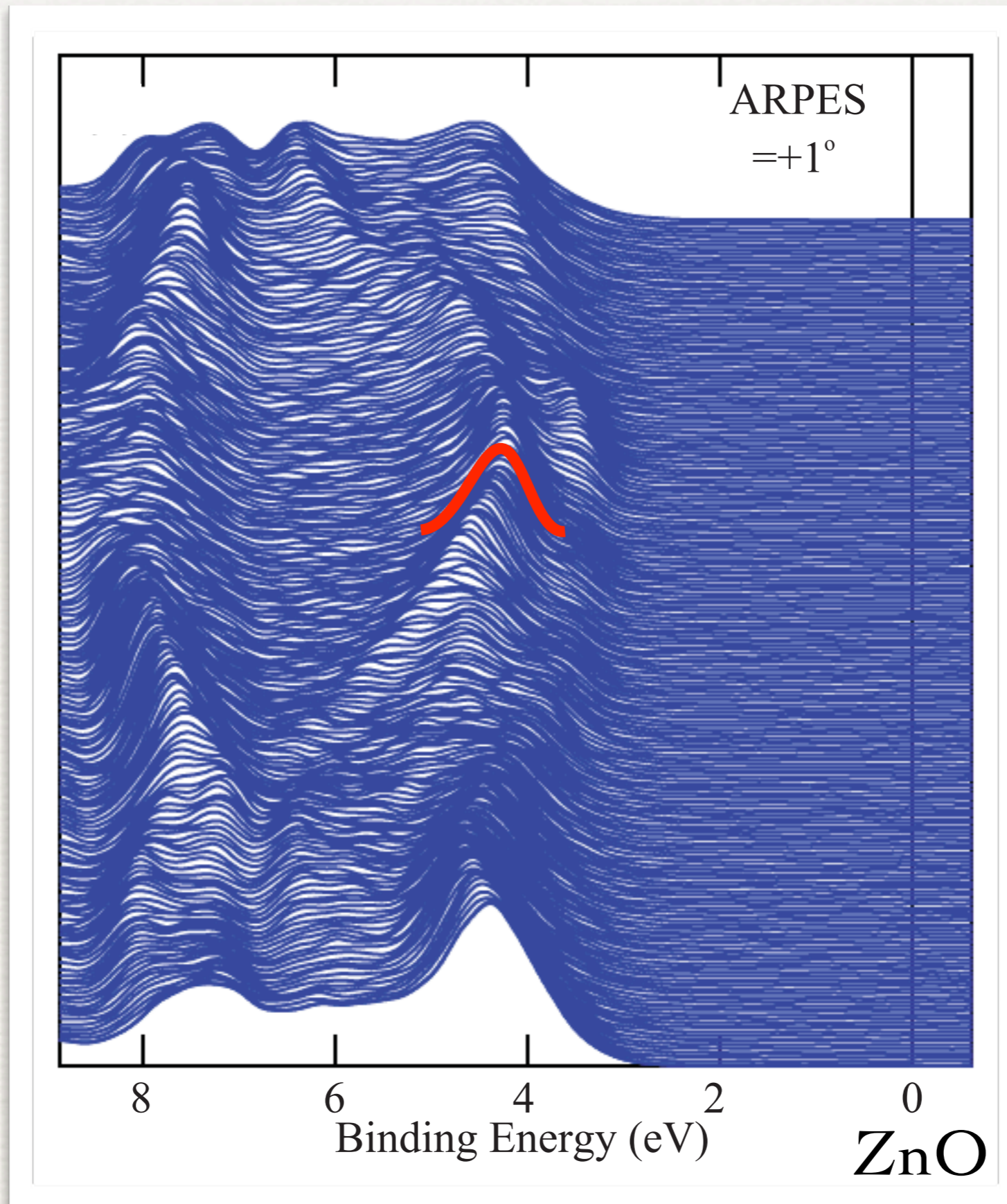


Angle-resolved photoemission spectroscopy



Masaki Kobayashi,
PhD dissertation

Angle-resolved photoemission spectroscopy



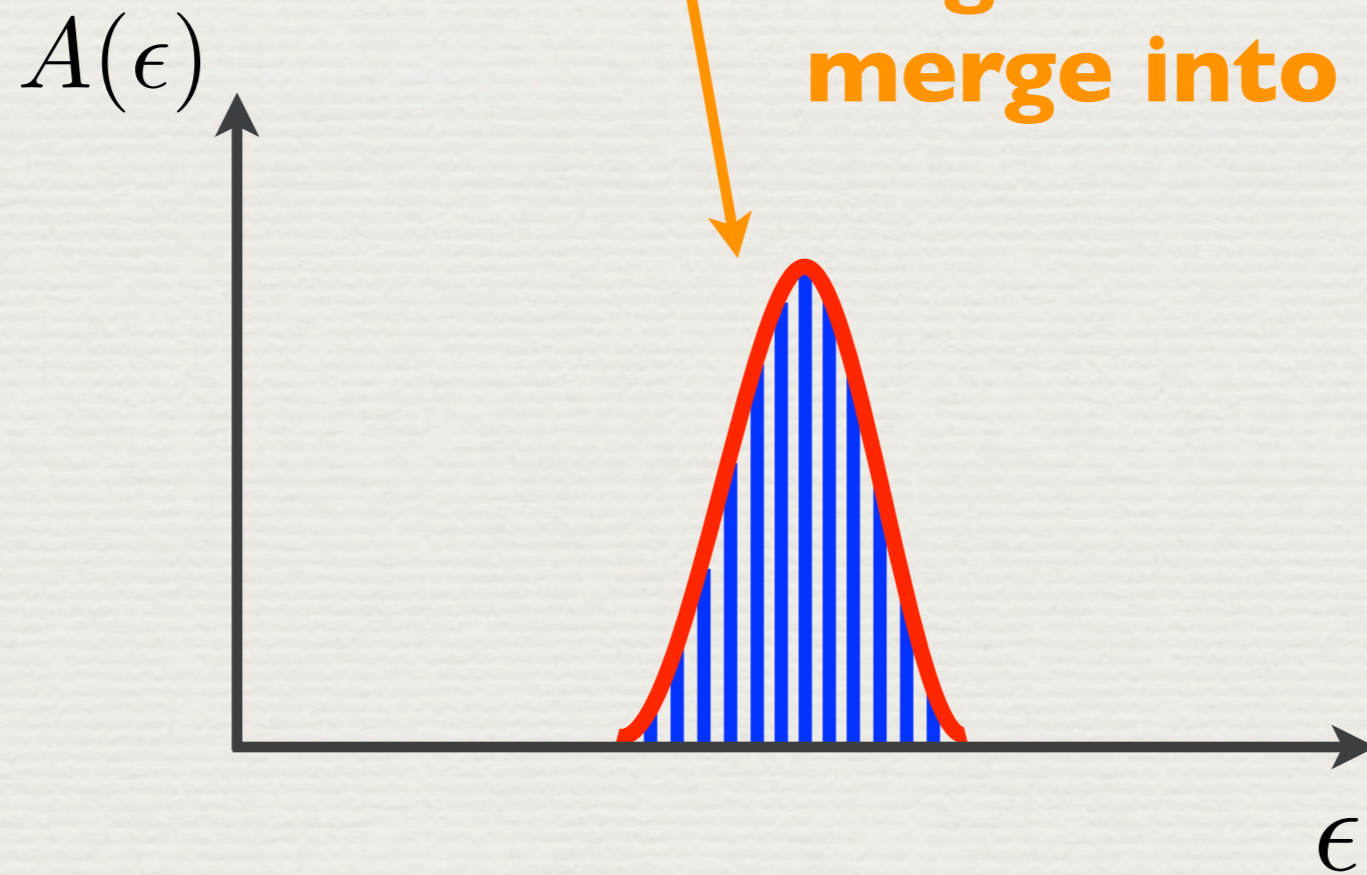
Masaki Kobayashi,
PhD dissertation

Single-particle Green's function

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

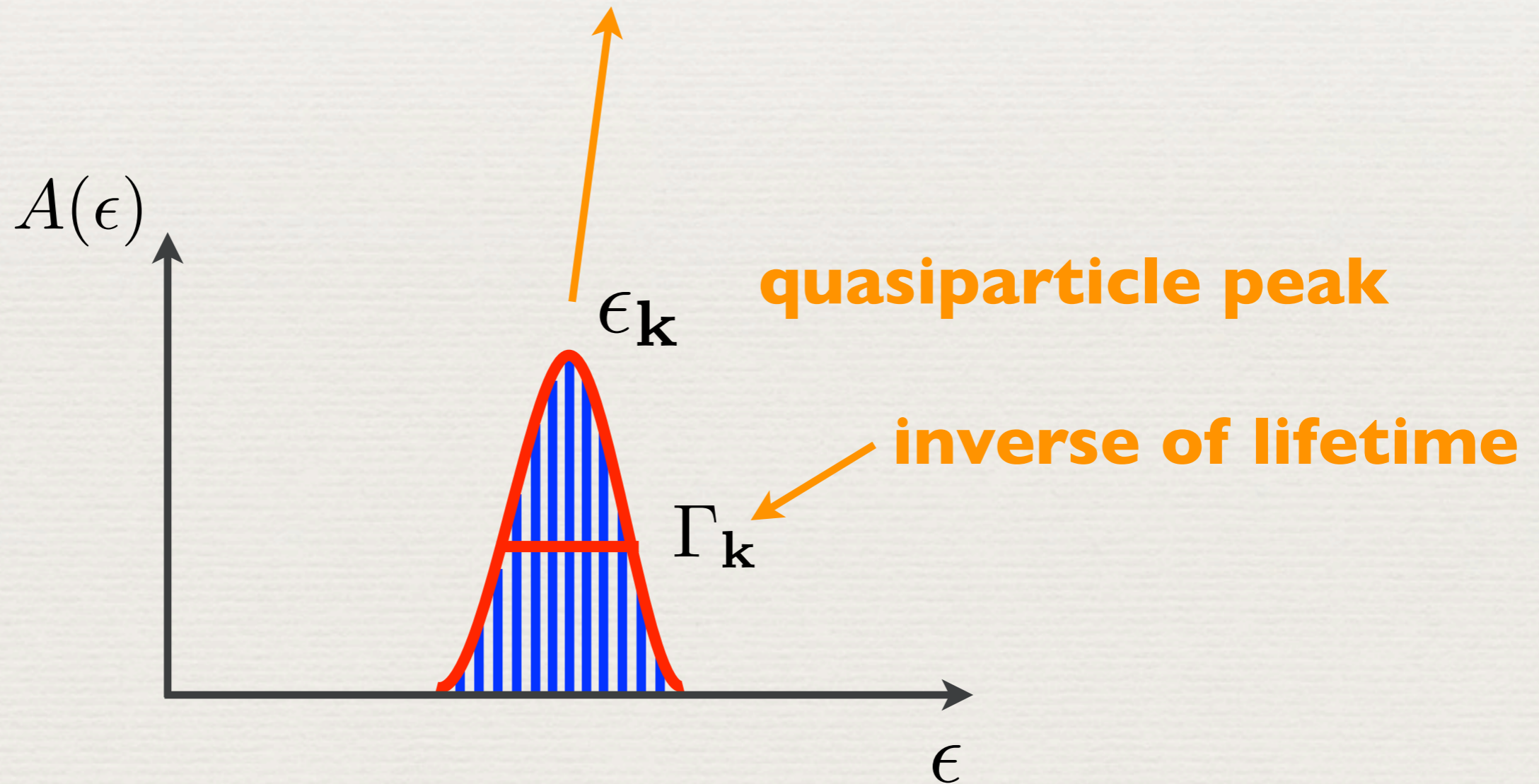
**single electron excitations
merge into broad peak**



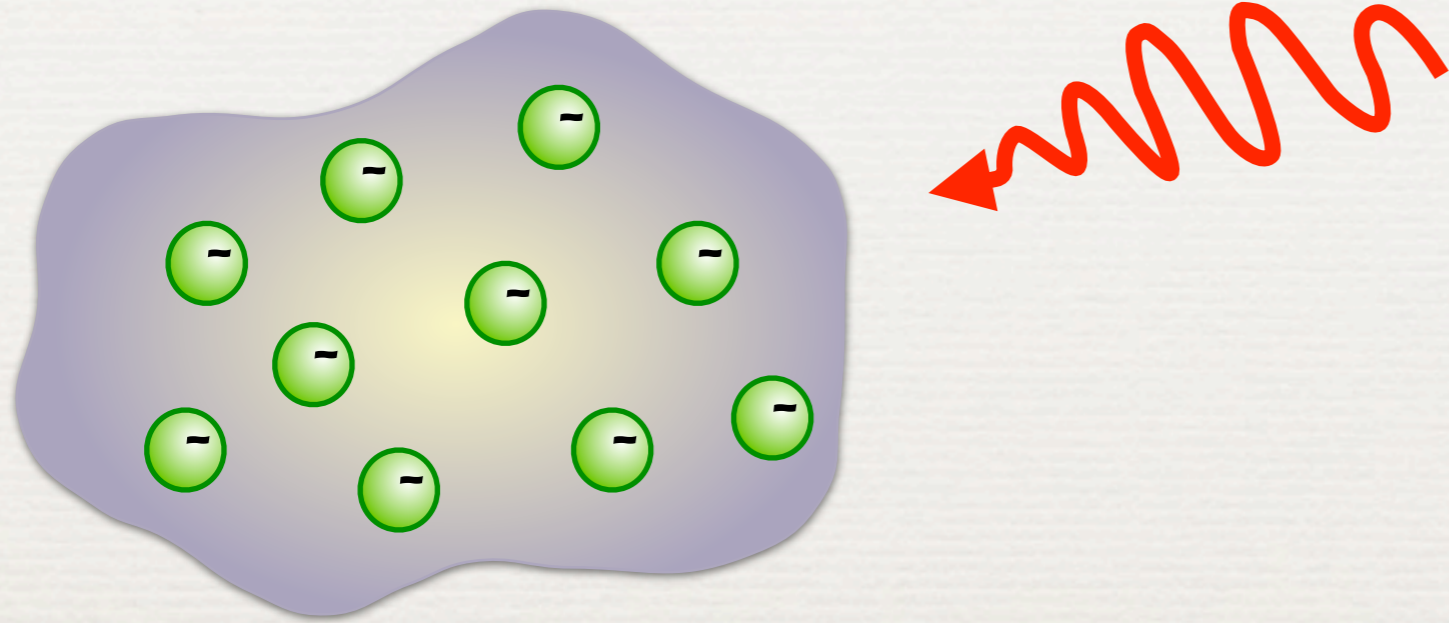
Single-particle Green's function

- single particle-like spectral function: **quasiparticle weight**

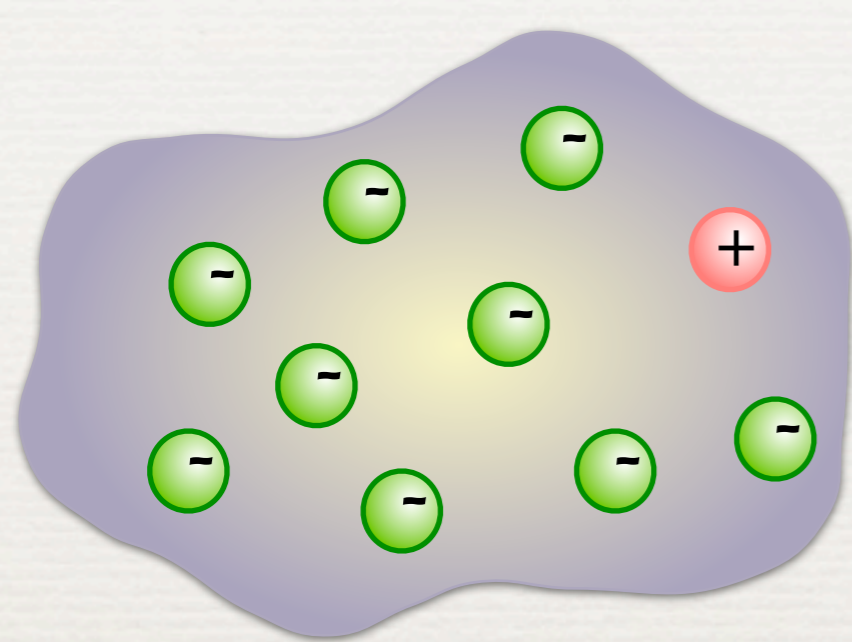
$$A_{\mathbf{k}}(\epsilon) = \text{Im}G_{\mathbf{k}}(\epsilon) \approx \frac{Z_{\mathbf{k}}}{\epsilon - (\epsilon_{\mathbf{k}} + i\Gamma_{\mathbf{k}})}$$



Another take on quasiparticles

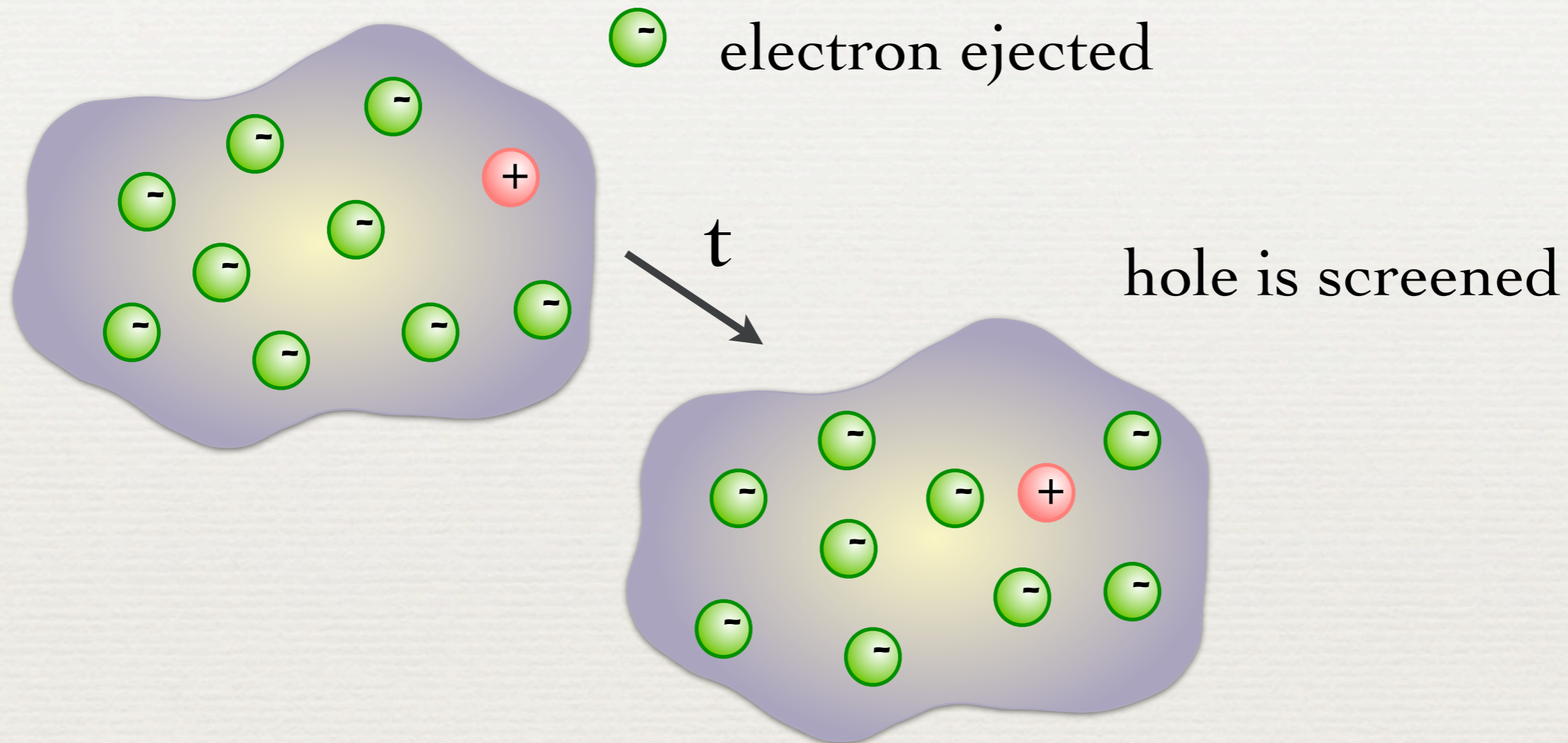


Another take on quasiparticles

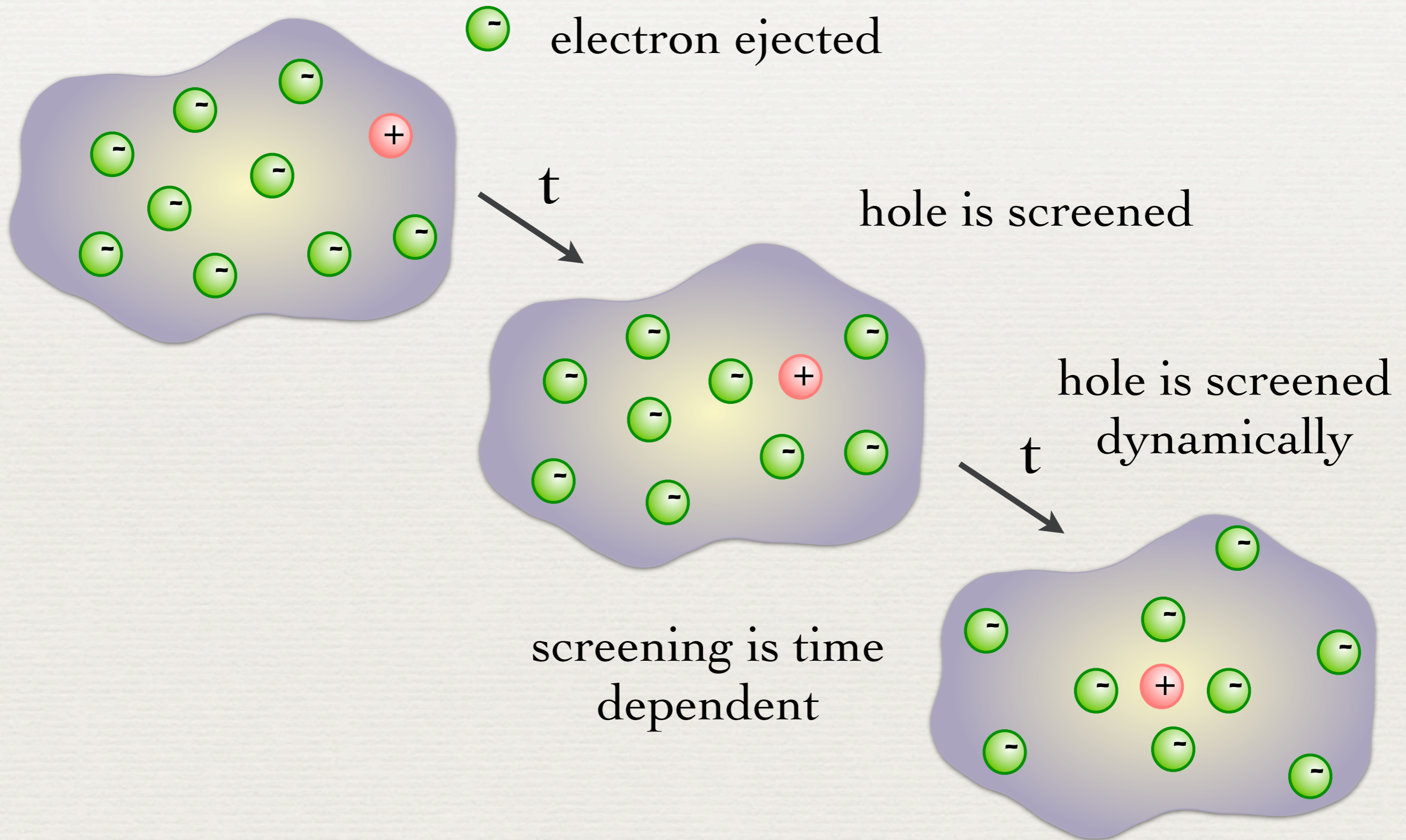


 electron ejected

Another take on quasiparticles



Another take on quasiparticles



The screened Coulomb interaction

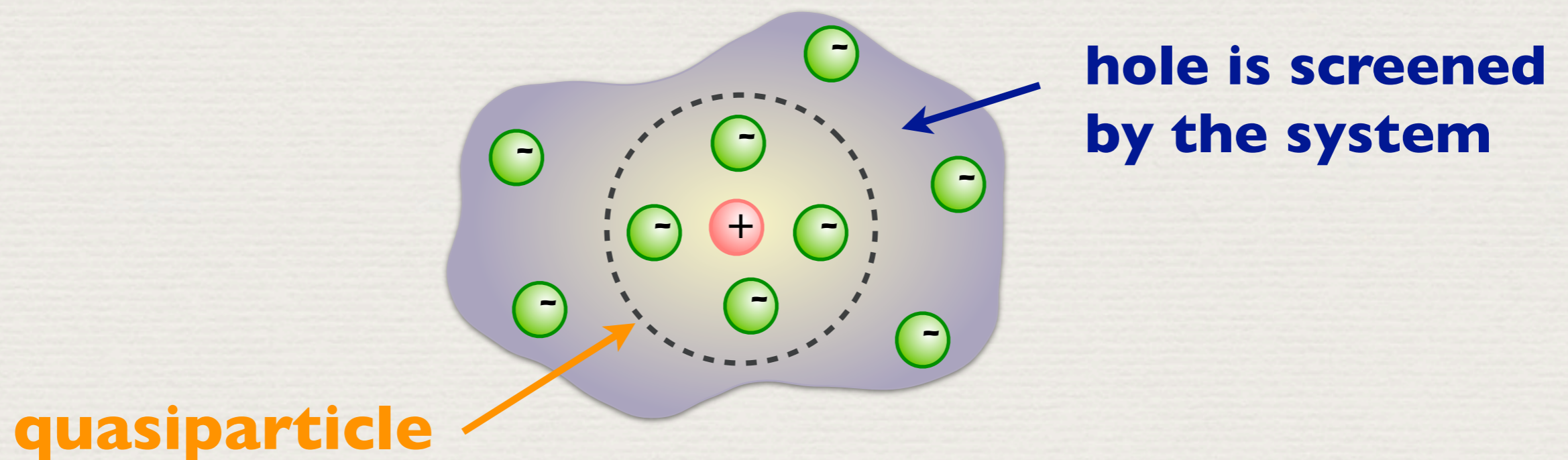
dielectric function

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

screened

bare

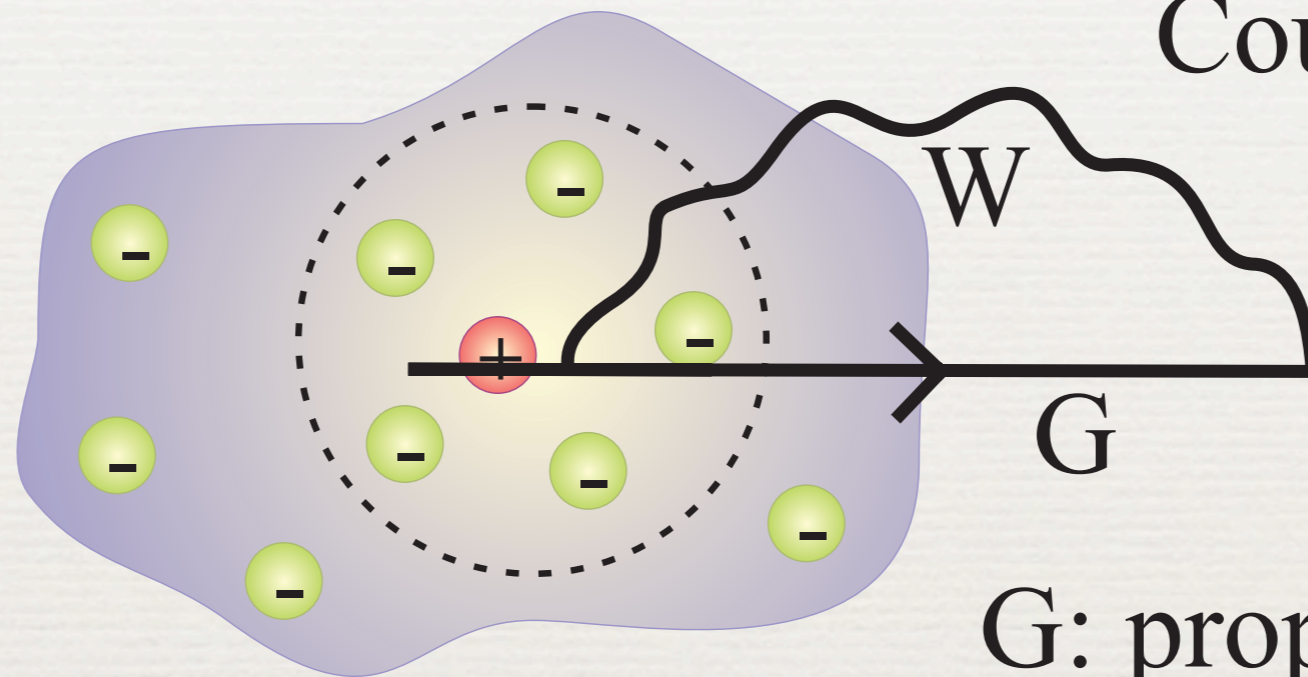
Coulomb interaction



GW approximation - screened electrons

$$\Sigma = iGW$$

W: screened
Coulomb



self-energy:

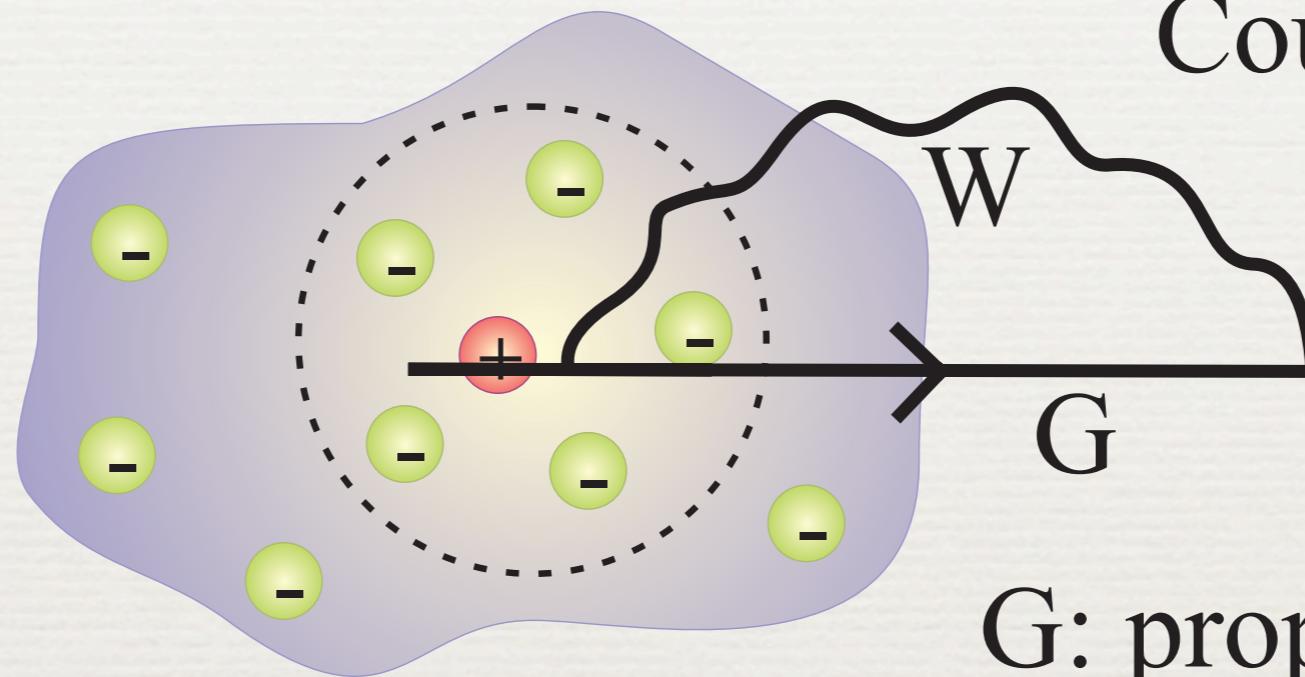
- energy that the quasiparticle feels due to its own presence

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

GW approximation - screened electrons

$$\Sigma = iGW$$

W: screened
Coulomb



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)

G is solution of Hedin's equations

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exact, therefore not tractable

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

G is solution of Hedin's equations

GW approximation

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

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

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

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

do not despair

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

GW in practice

Step 1:

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

GW in practice

Step 1:

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

Step 2:

- Set up Kohn-Sham Green's function:

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

GW in practice

Step 1:

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

Step 2:

- Set up Kohn-Sham Green's function:

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

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

Step 4:

- Dielectric function:

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

Step 5:

- Screened Coulomb interaction:

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

GW in practice

Step 4:

- Dielectric function:

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

Step 5:

- Screened Coulomb interaction:

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

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: $\psi_s(\mathbf{r}) = \phi_s^{\text{KS}}(\mathbf{r})$

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

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: $\psi_s(\mathbf{r}) = \phi_s^{\text{KS}}(\mathbf{r})$

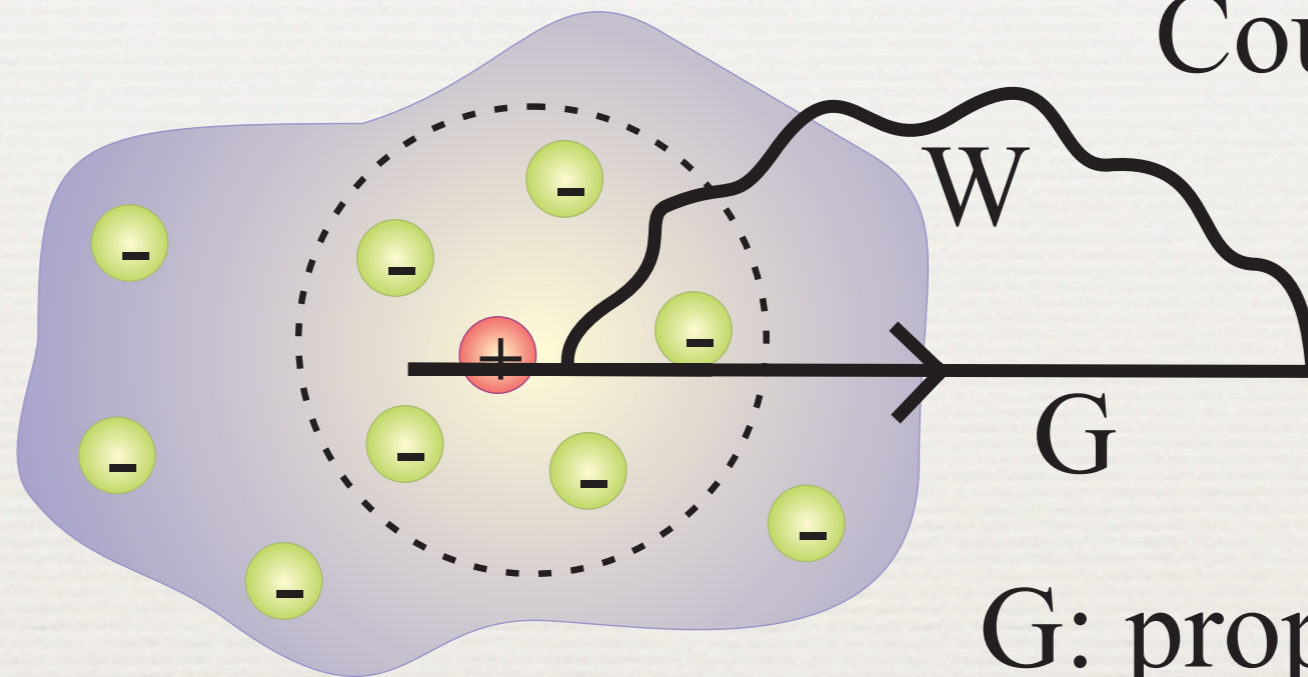
$$\epsilon_s^{qp} = \epsilon_s^{\text{KS}} + \langle s | \Sigma(\epsilon_s^{qp}) | s \rangle - \langle s | v_{xc} | s \rangle$$

GW formal scaling ~ system size⁴

GW approximation - screened electrons

$$\Sigma = iGW$$

W : screened
Coulomb



G : propagator

self-energy:

$$\Sigma = \Sigma_x + \Sigma_c$$

iGv

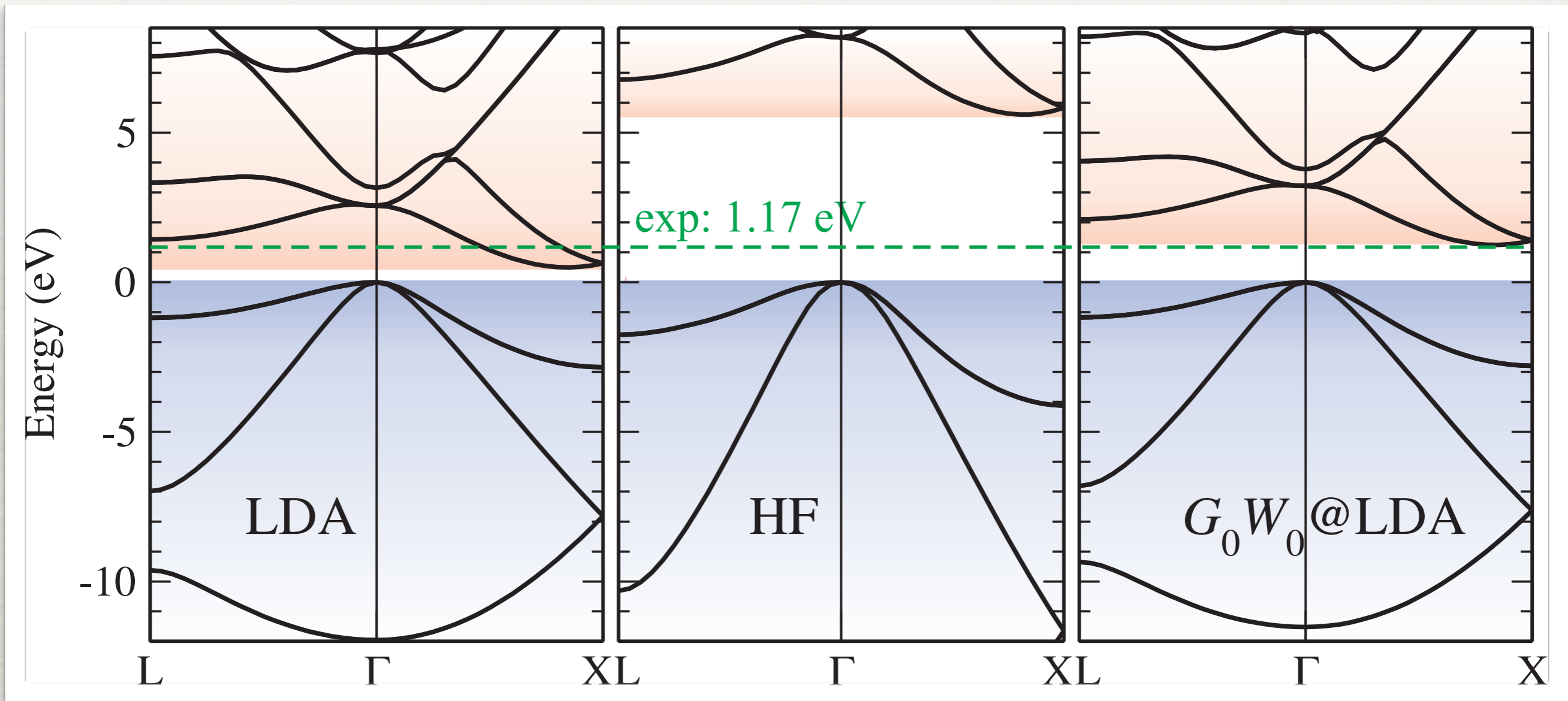
**exact exchange
(Hartree-Fock)**

$iG(W - v)$

**screening (due to
other electrons)**

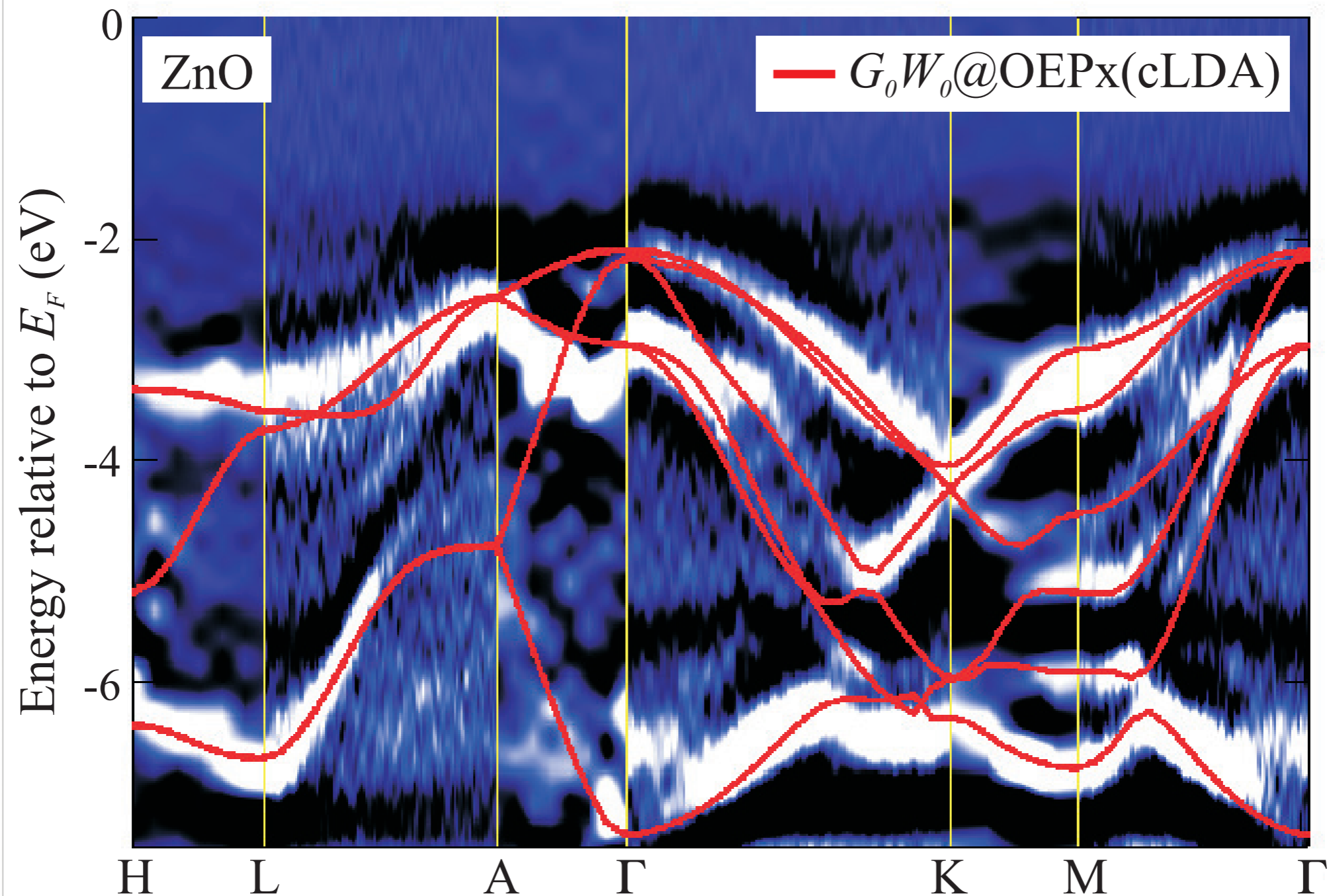
On the importance of screening

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



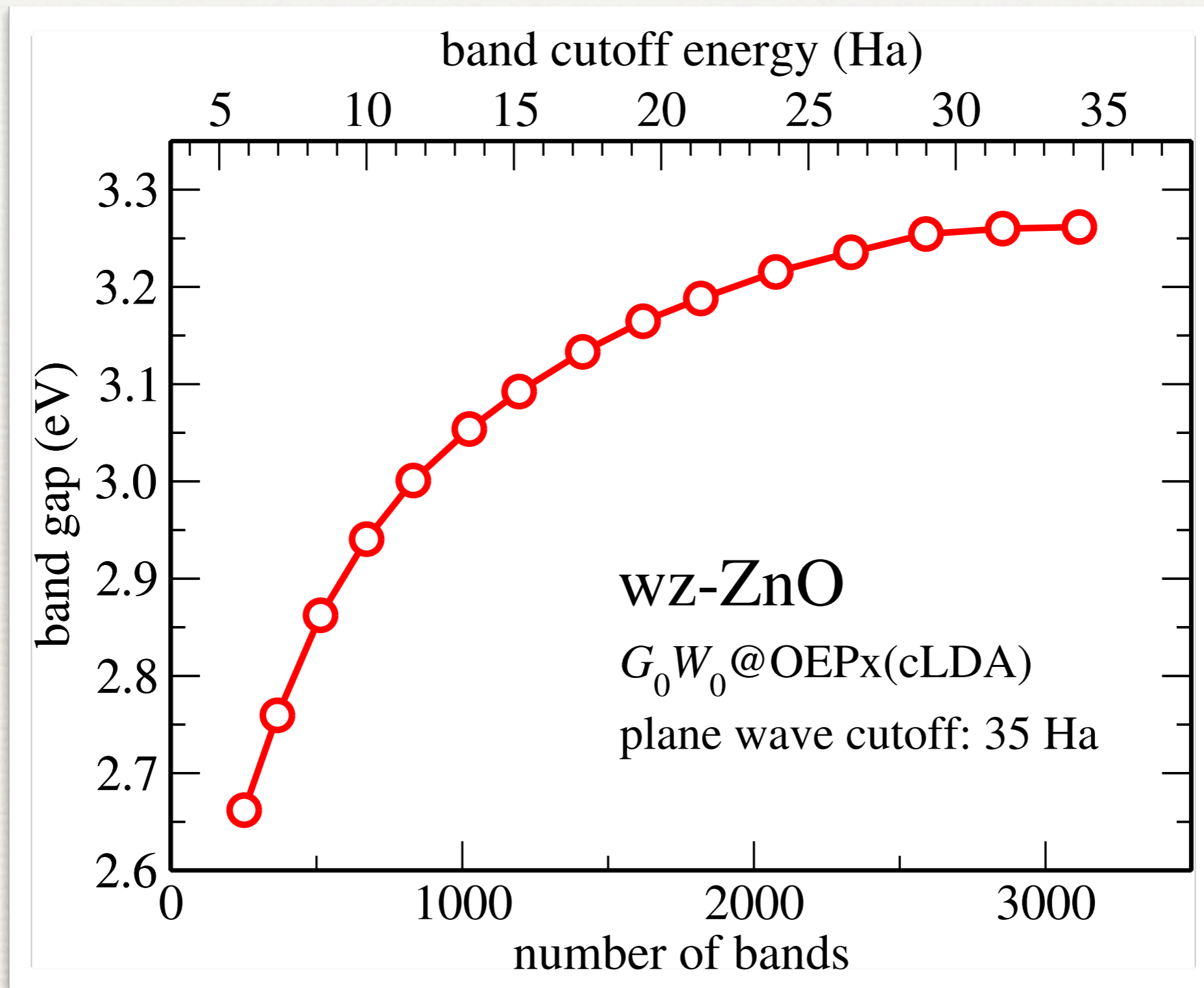
- Hartree-Fock (HF) exact exchange gap much too large
- W is essential for solids

Angle resolved photoemission - ZnO



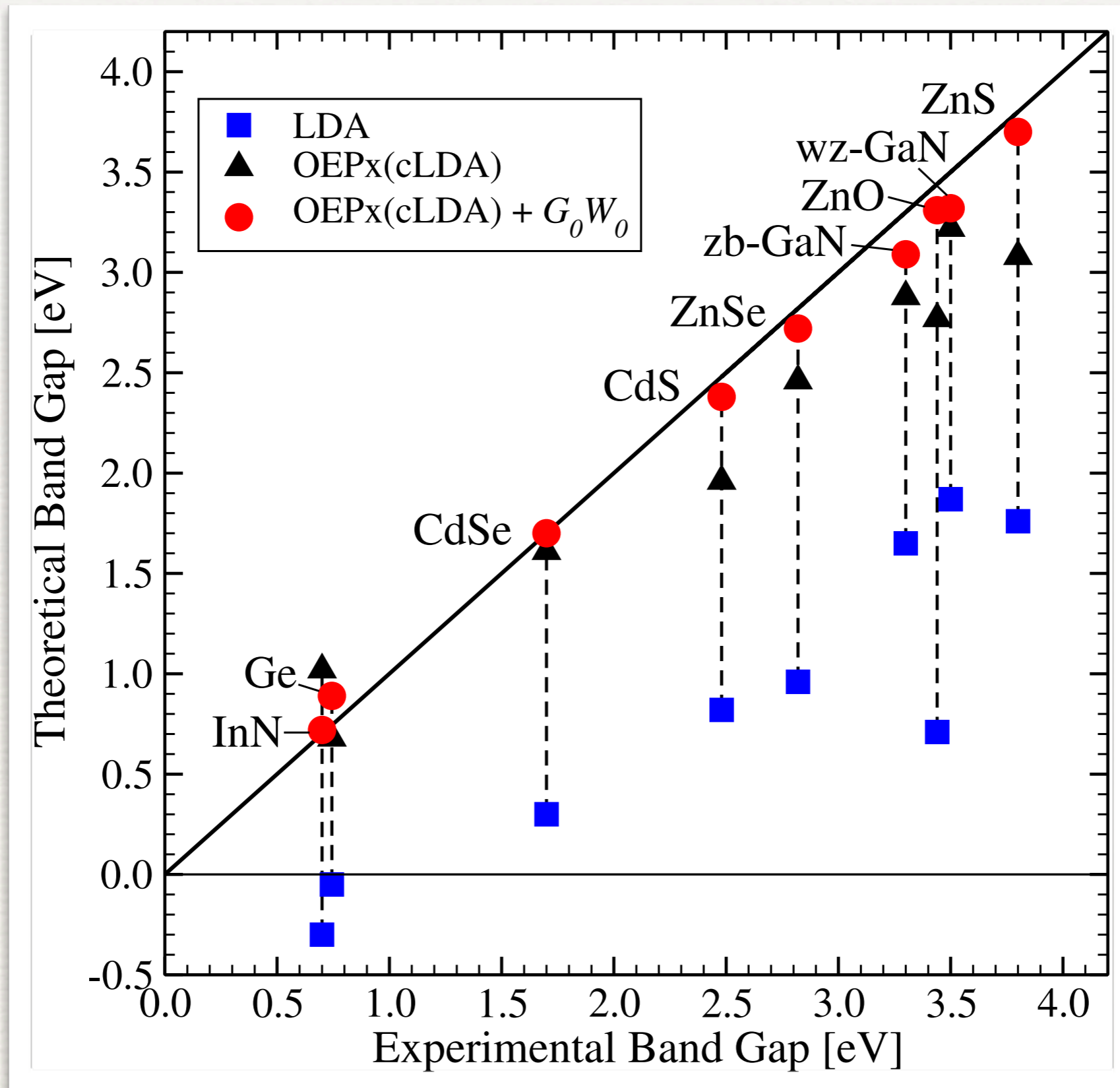
Q. Yan, P. Rinke, M. Winkelkemper, A. Qteish, D. Bimberg, M. Scheffler, C. G. Van de Walle, *Semicond. Sci. Technol.* 26, 014037 (2011)

Convergence of G_0W_0 for ZnO

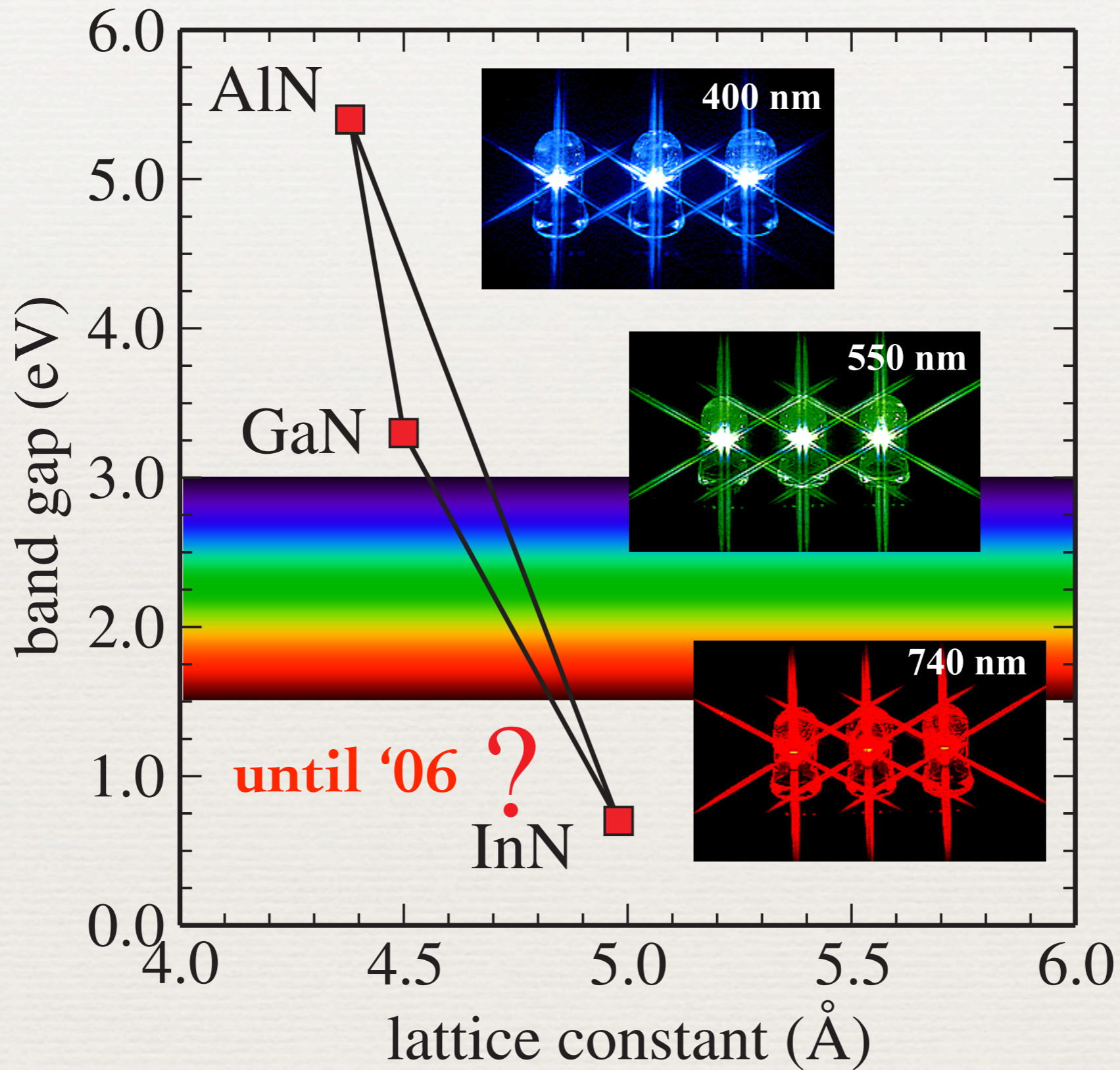


Yan, Rinke, Winkelkemper, Qteish, Bimberg, Scheffler, Van de Walle,
Semicond. Sci. Technol. 26, 014037 (2011)

Band gaps of solids



Do we know the band gap of InN?



Band gap of InN

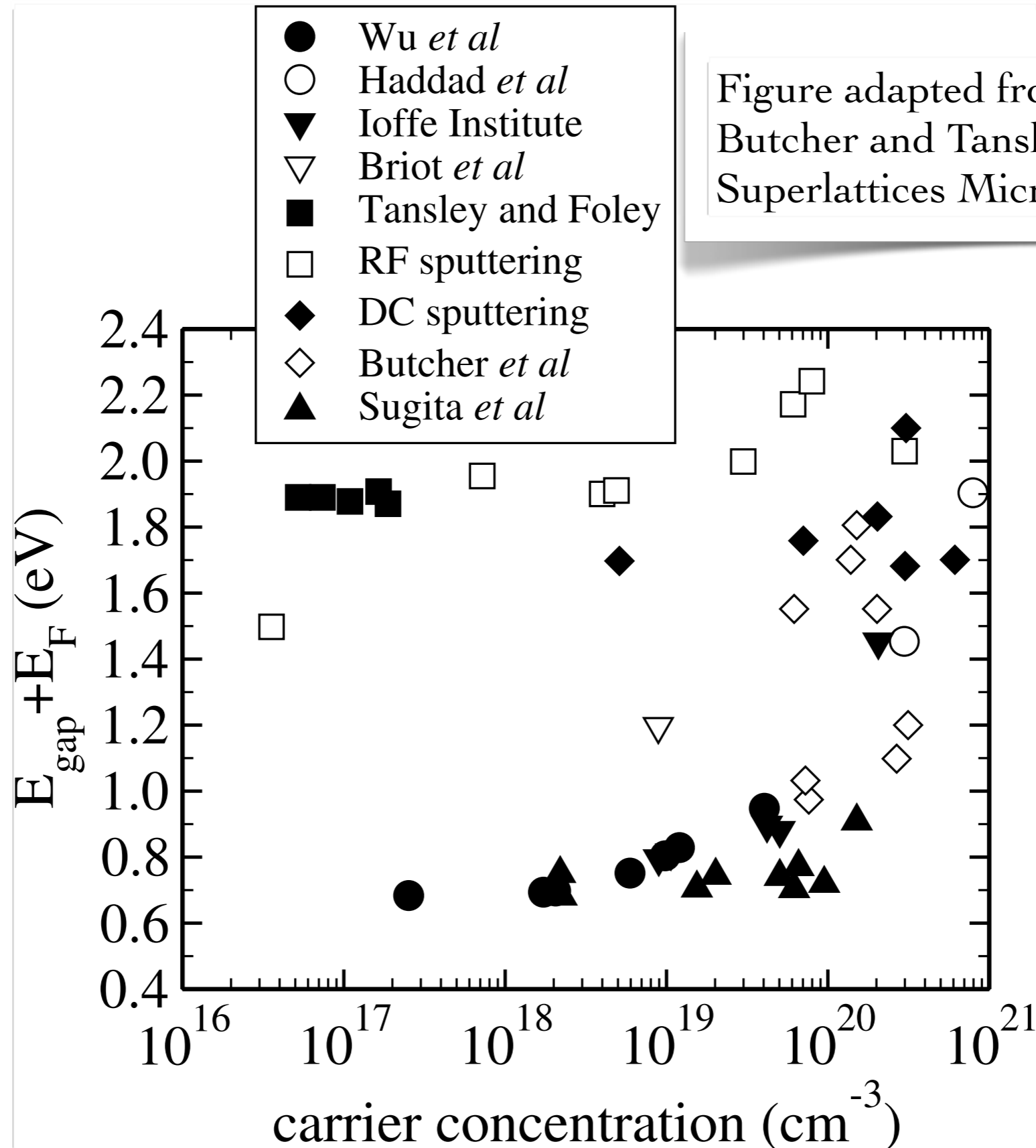


Figure adapted from
Butcher and Tansley
Superlattices Microstruct. **38**, 1 (2005)

Band gap of InN

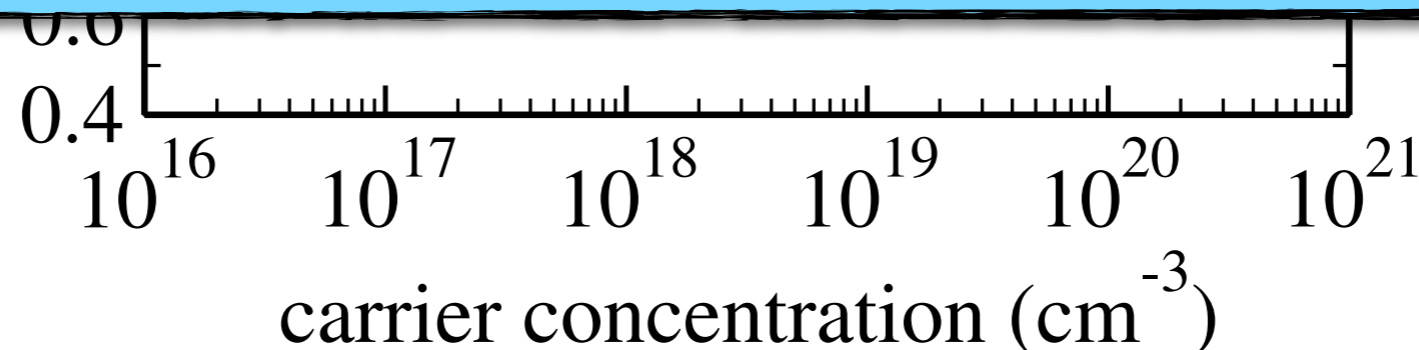
- Wu *et al*
- Haddad *et al*
- ▼ Ioffe Institute
- ▽ Briot *et al*
- Tansley and Foley

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

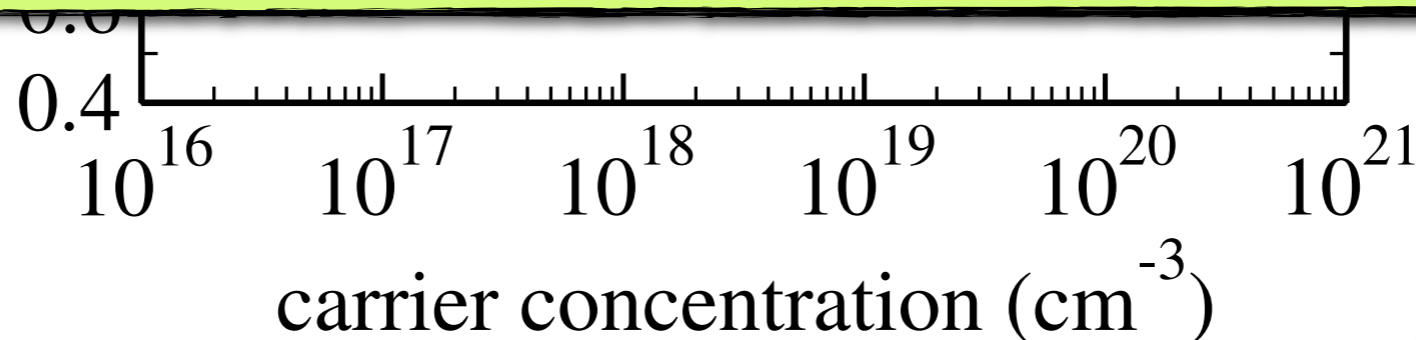
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Figure adapted from
Butcher and Tansley

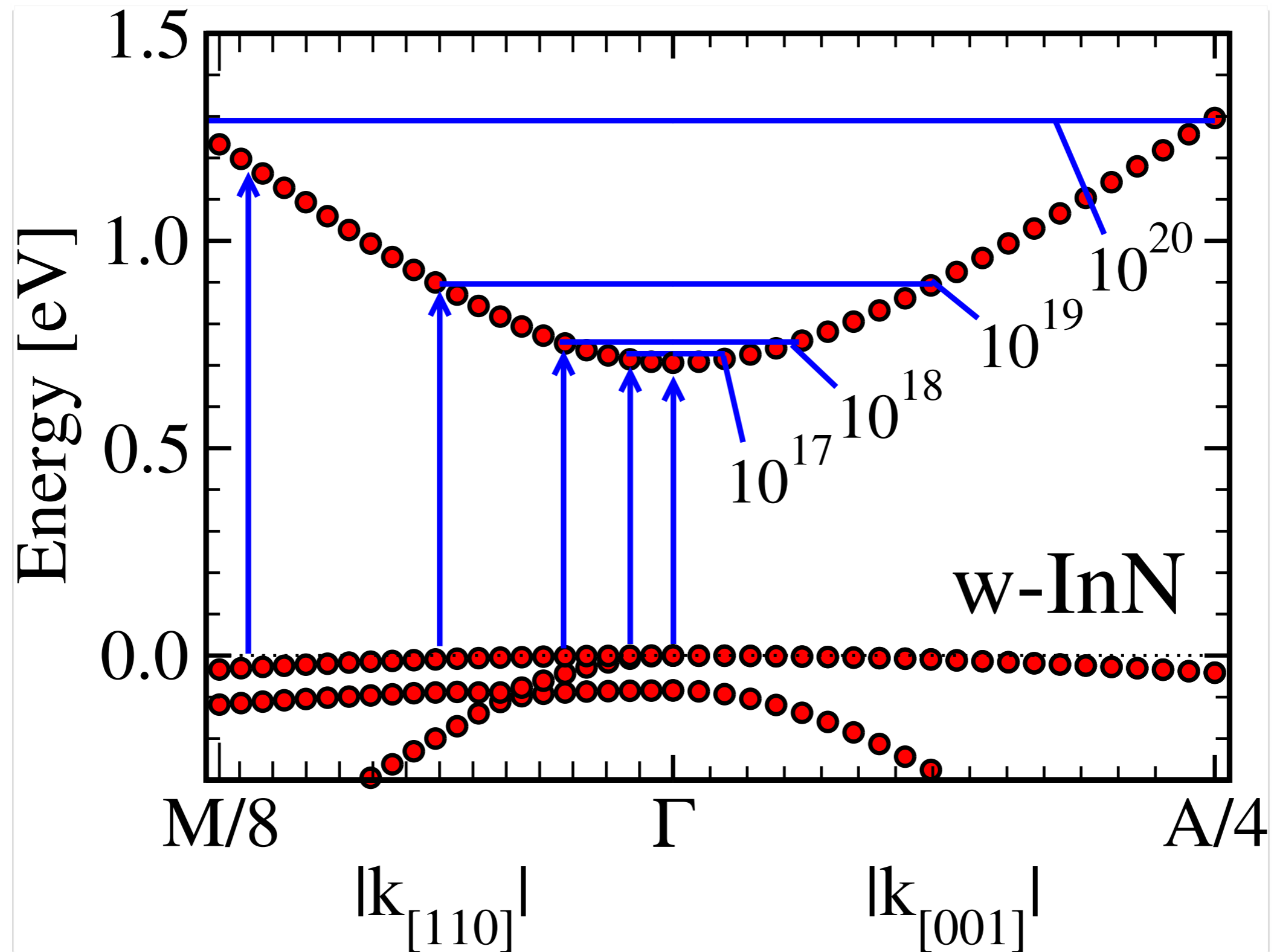
How can first principles help?

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

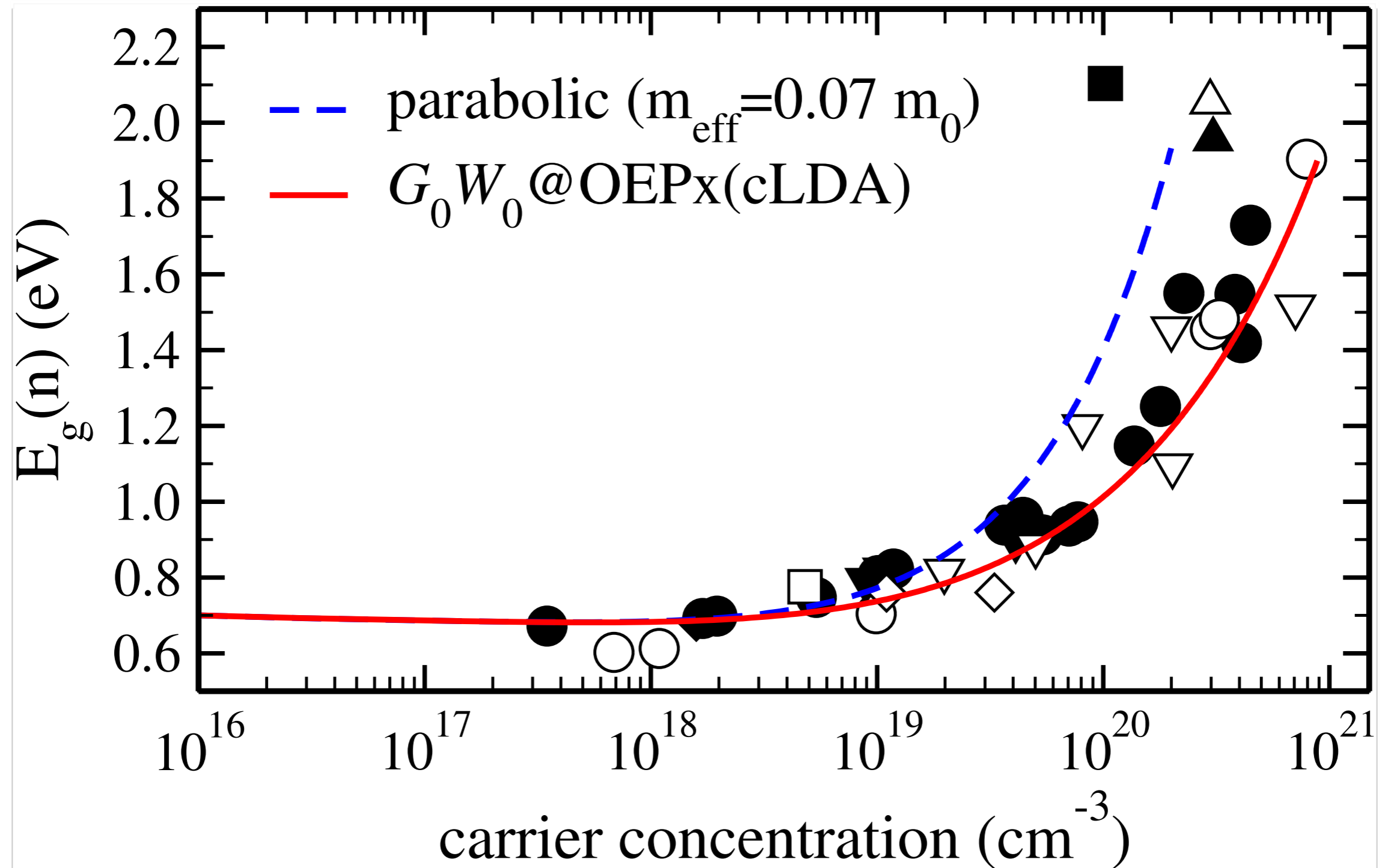
- **many-body perturbation theory (GW)**
 - method of choice for band gaps in solids



InN - *GW* band structure and Moss-Burstein



InN - *GW* band structure and Moss-Burstein



Atomistic understanding of molecules@surfaces

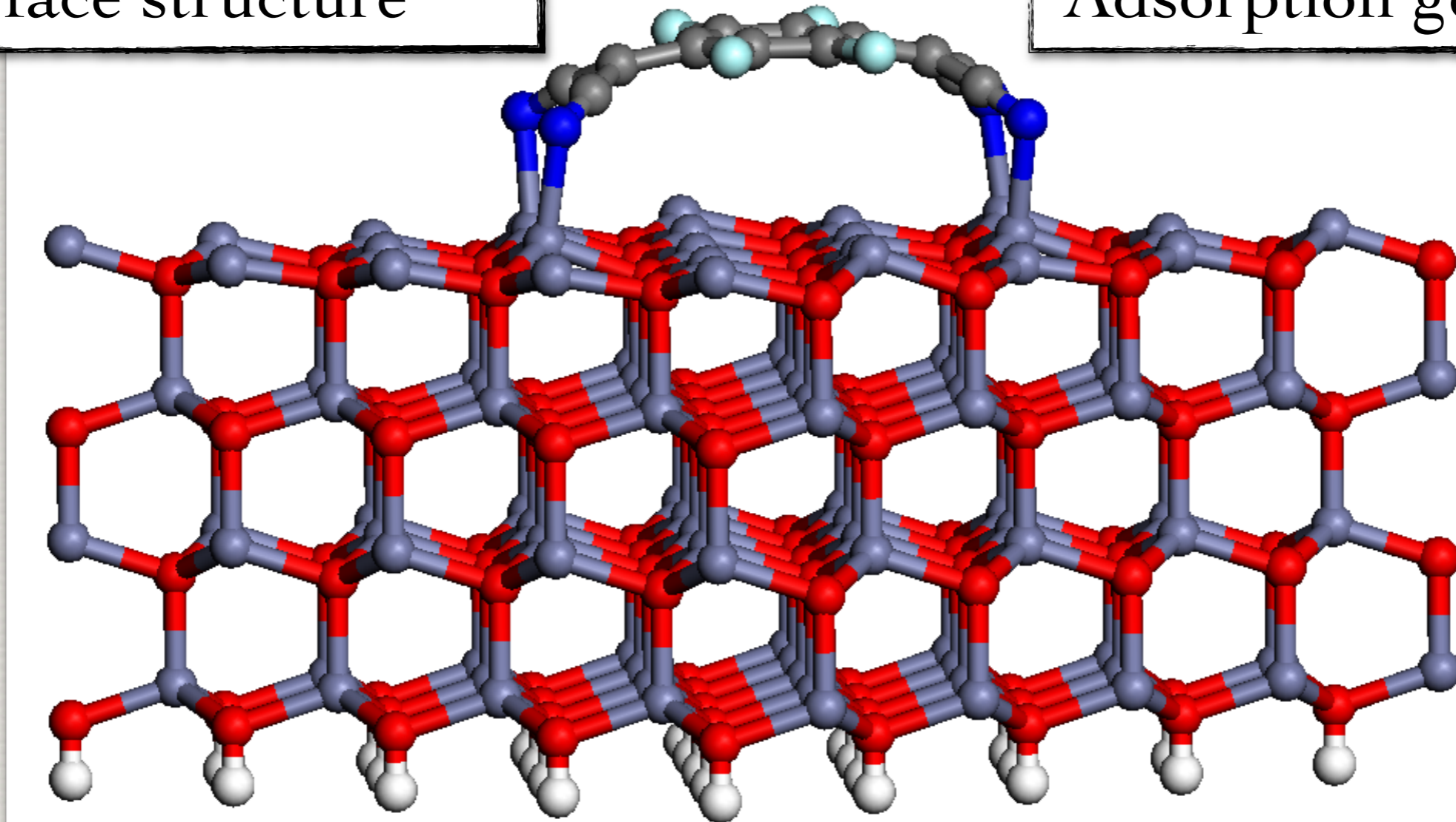
Charge transfer

Level alignment

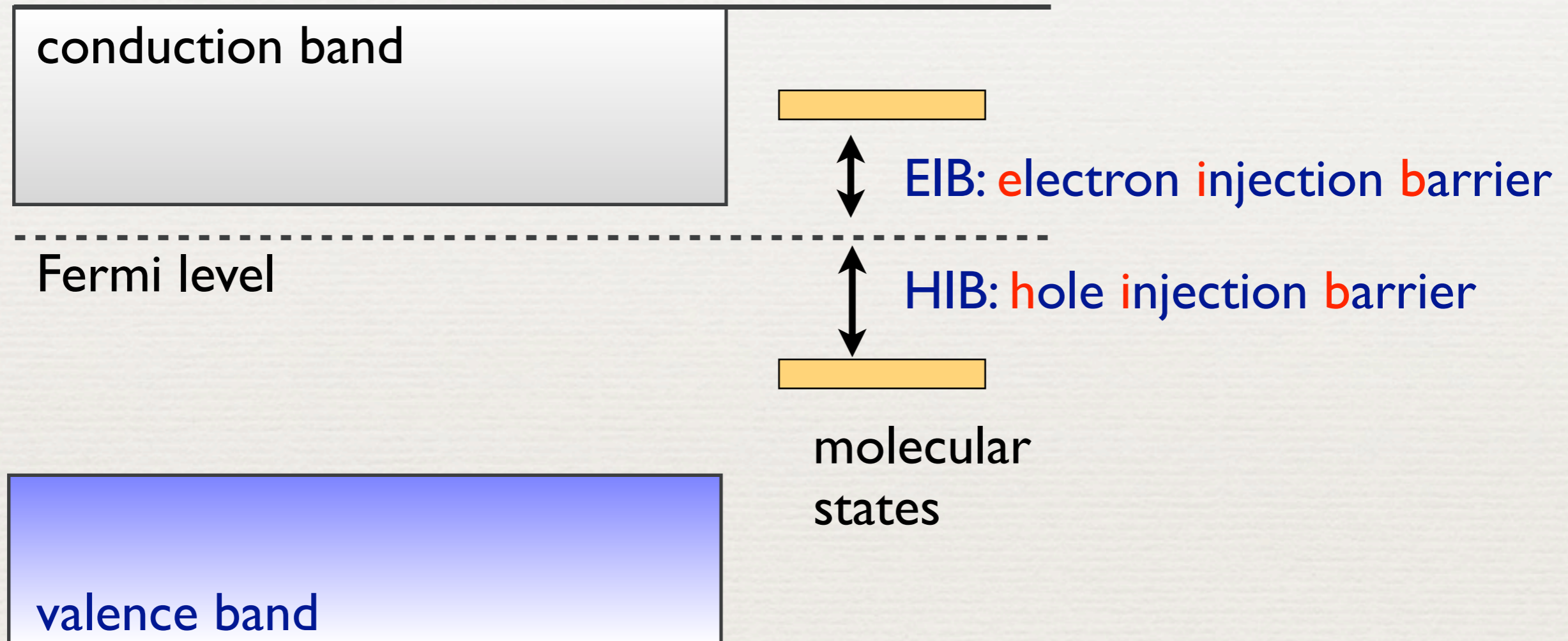
Van der Waals interaction

Surface structure

Adsorption geometry



Level alignment at interface



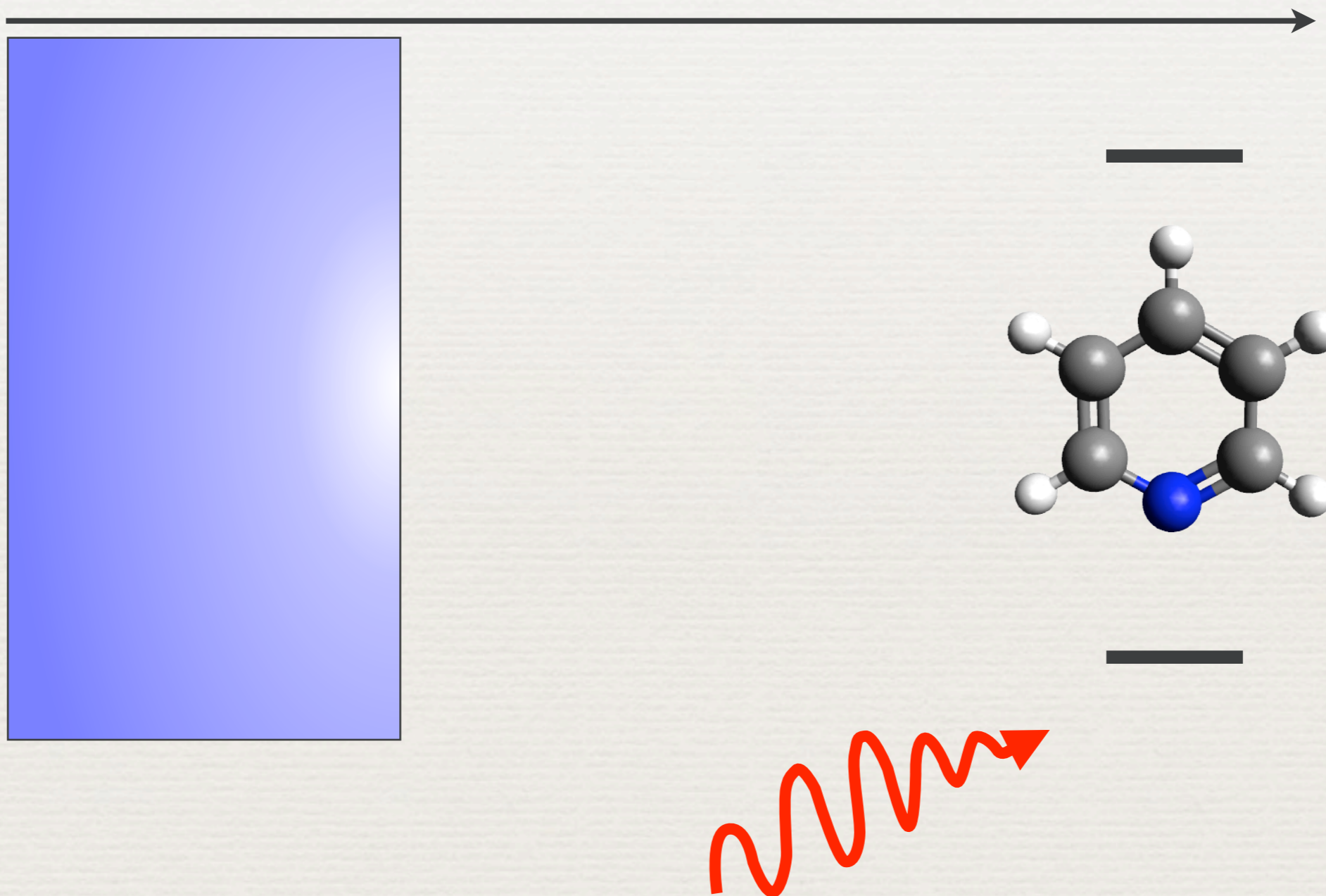
injection limited current:

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

Molecular levels at a surface

surface

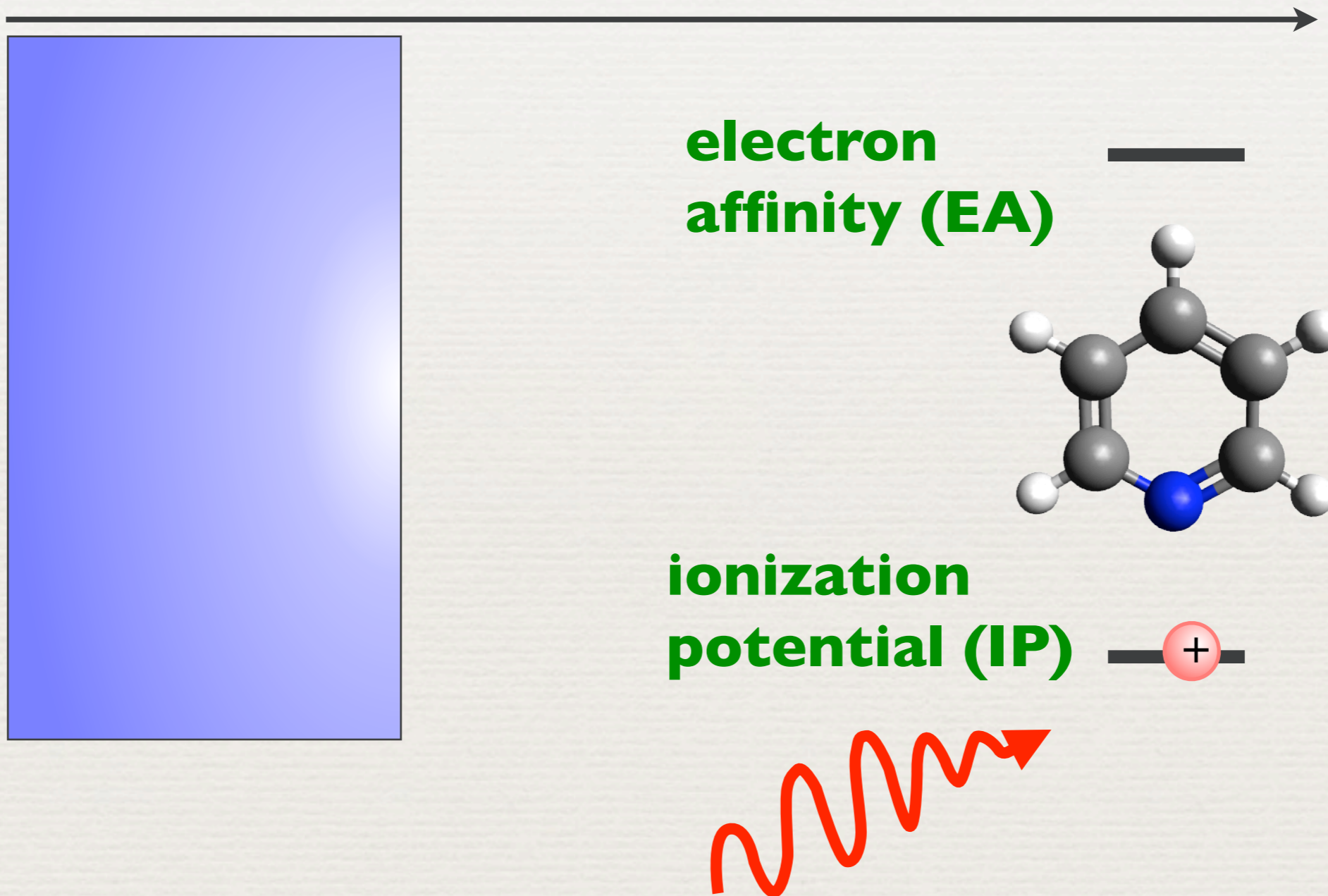
gas phase



Molecular levels at a surface

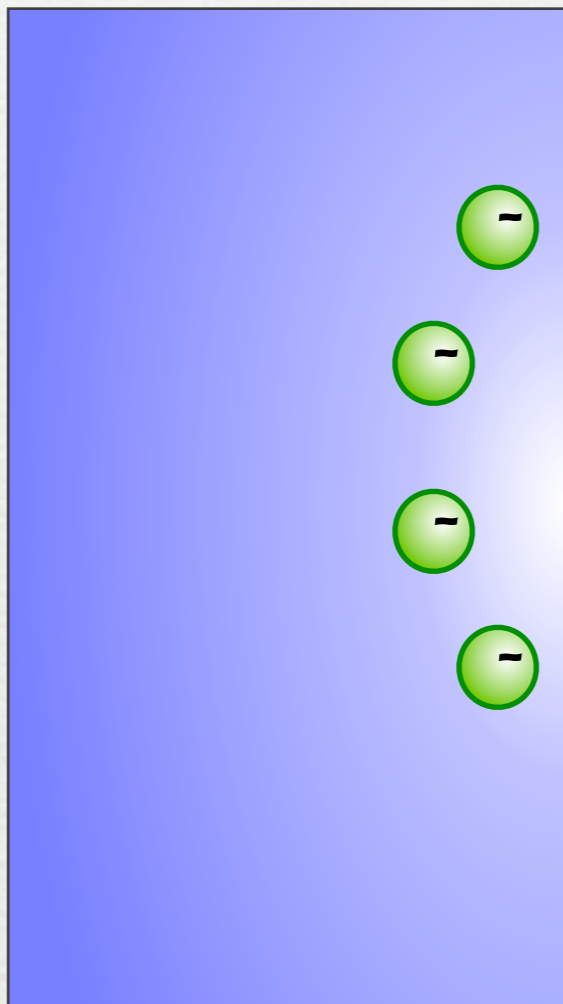
surface

gas phase



Molecular levels at a surface

surface



gas phase

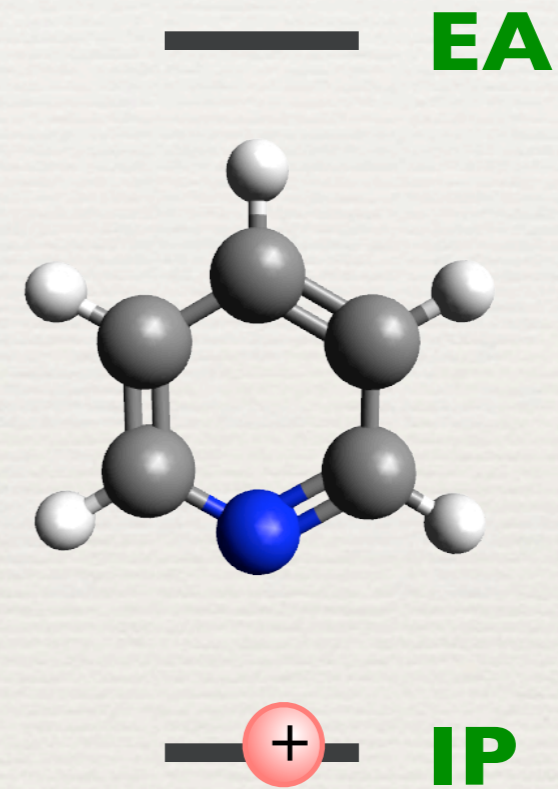


image effect

Molecular levels at a surface

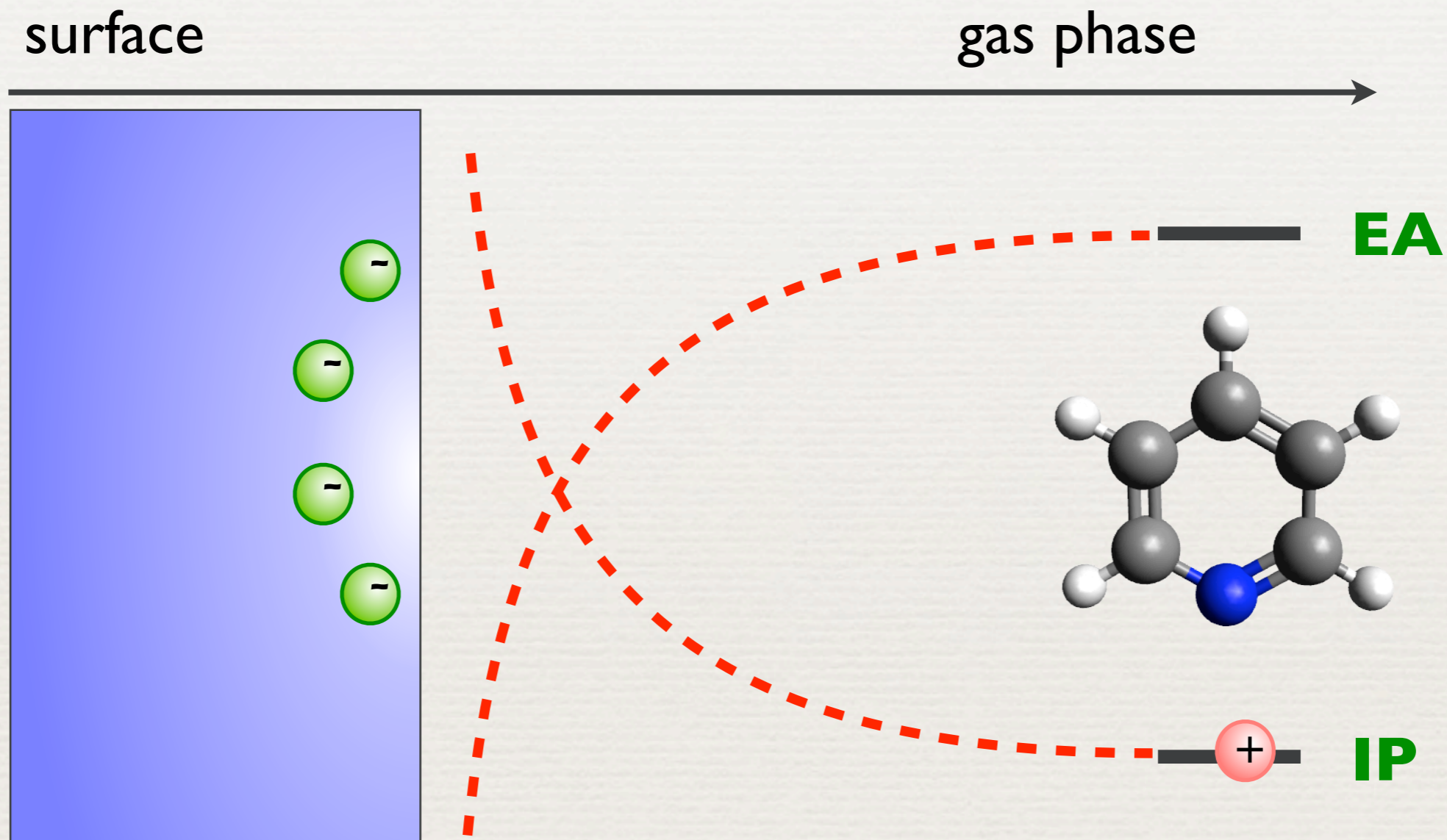


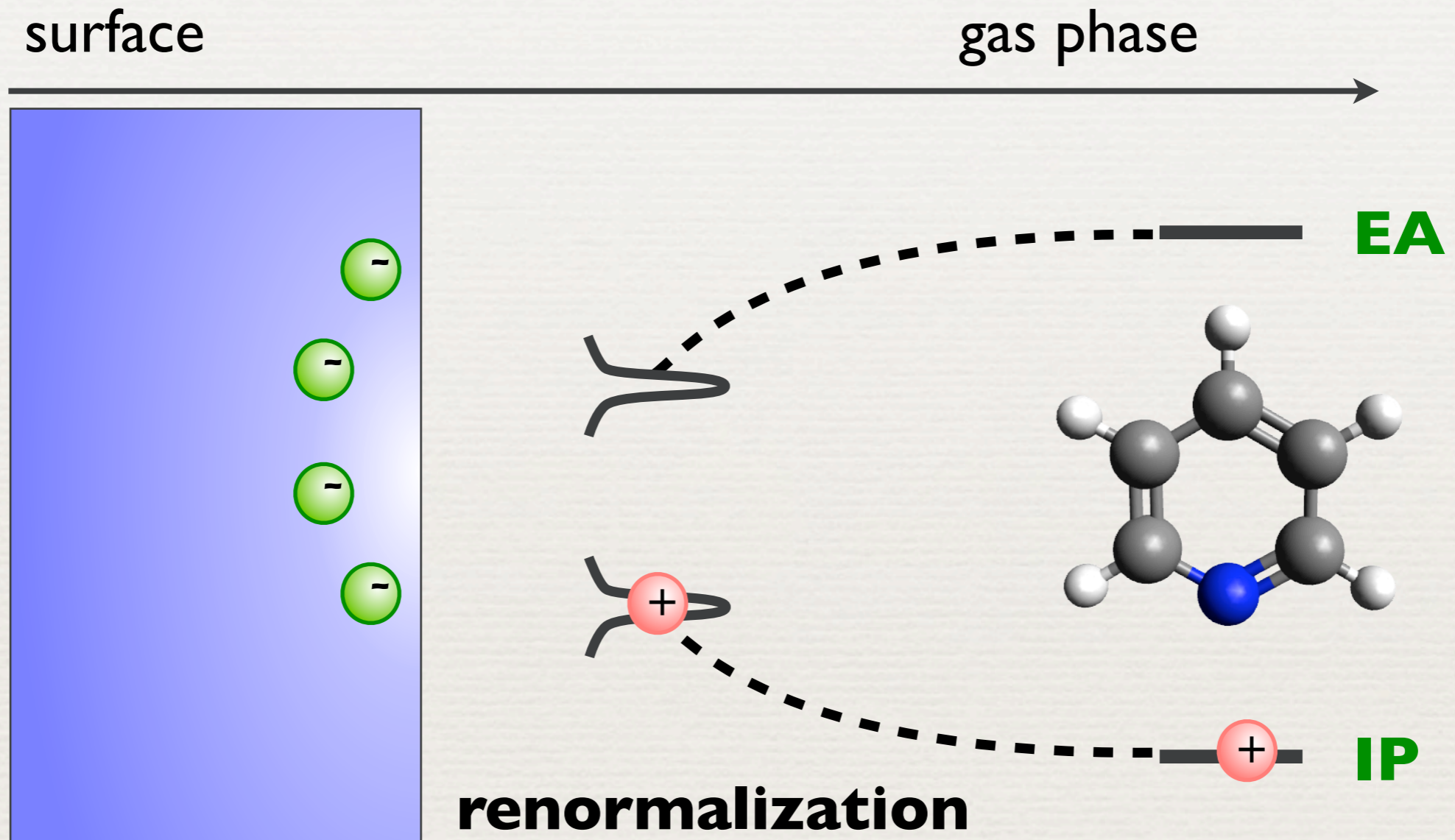
image potentials

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

semiconductor:
 ϵ dielectric constant

$$-\frac{(\epsilon - 1)}{4(\epsilon + 1)} \frac{1}{z}$$

Molecular levels at a surface

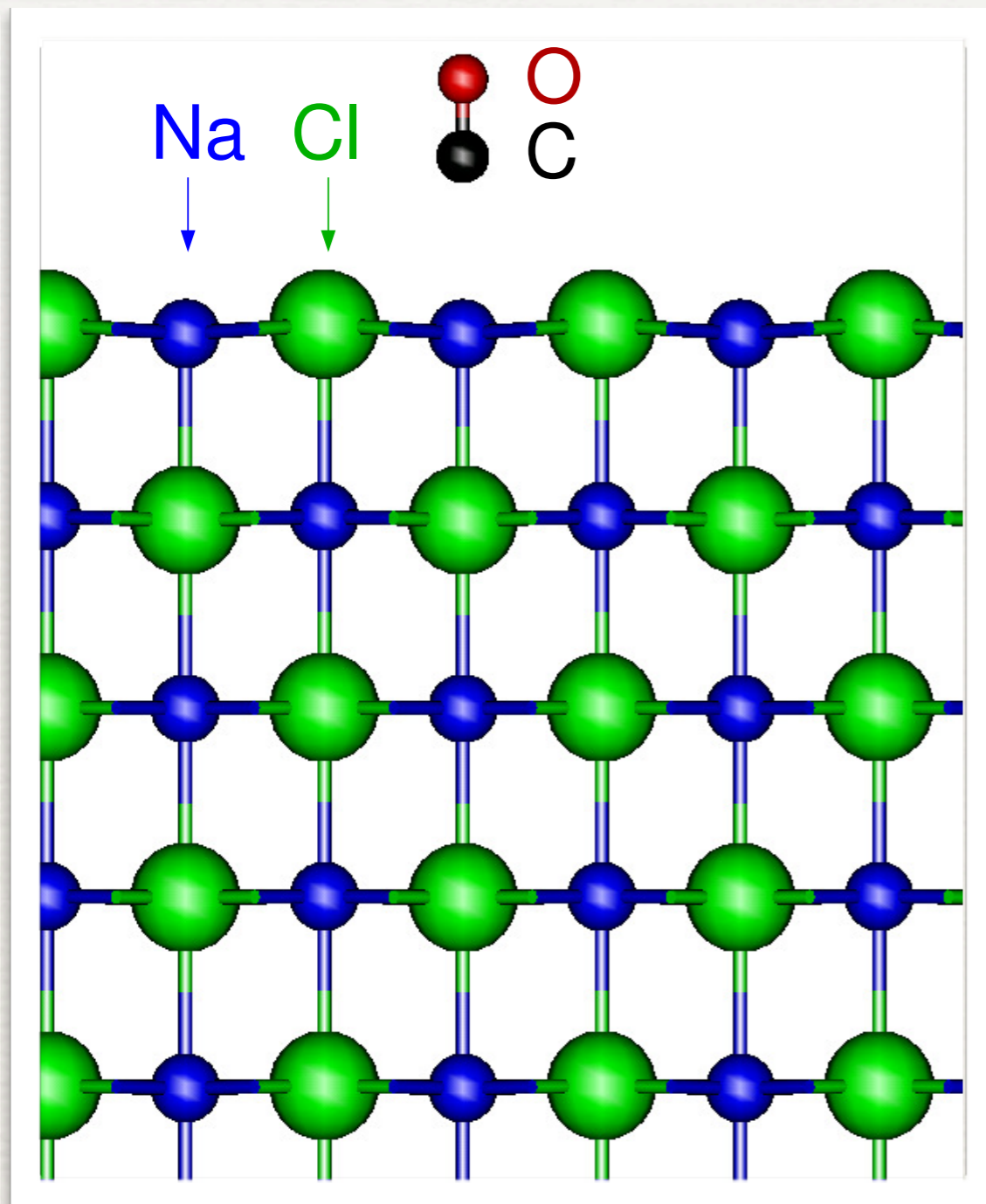


metal: $-\frac{1}{4z}$

semiconductor:
 ϵ dielectric constant

$$-\frac{(\epsilon - 1)}{4(\epsilon + 1)} \frac{1}{z}$$

Renormalization at insulator surfaces

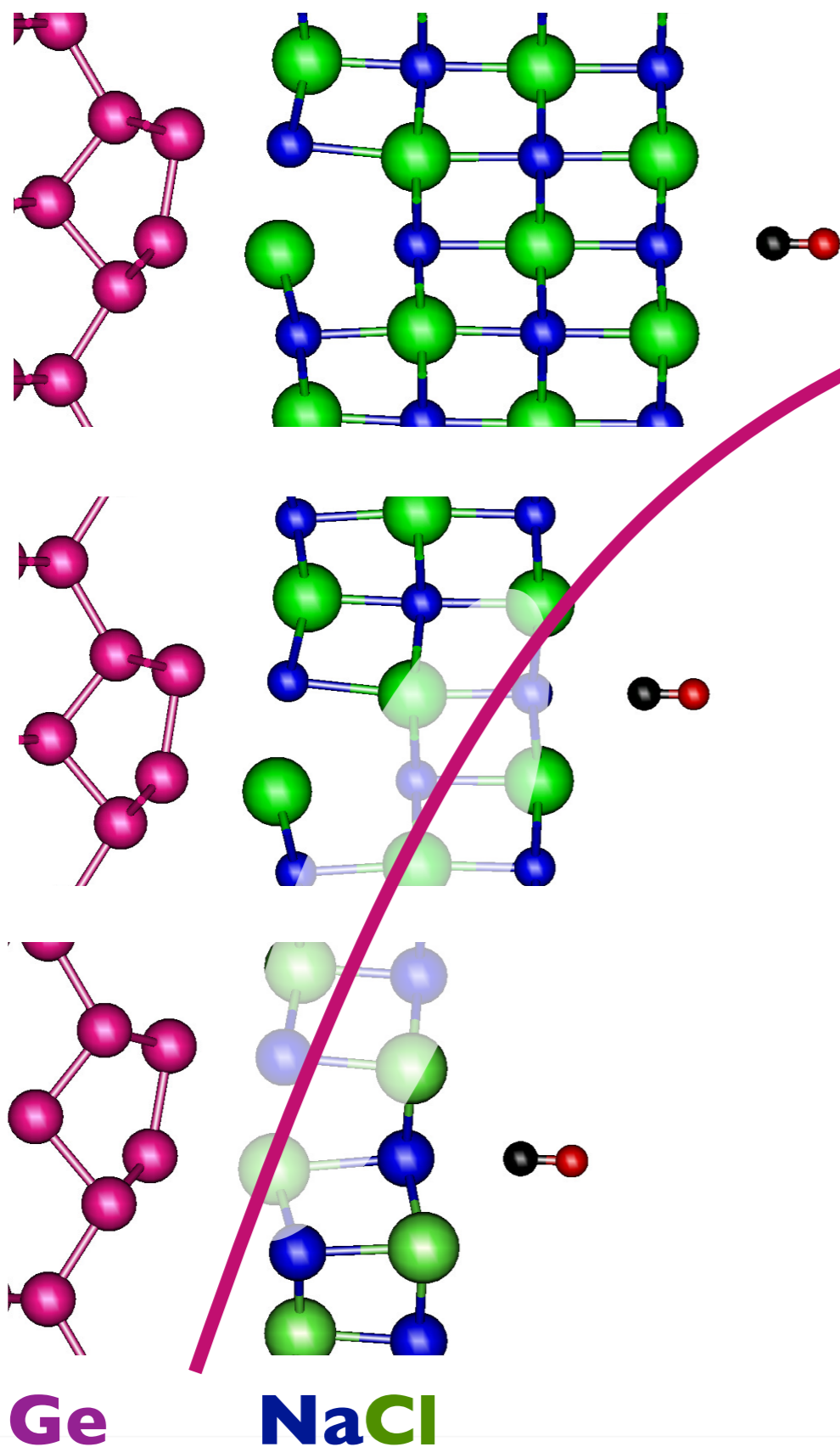


CO HOMO-LUMO gap

gap/eV	LDA	G ₀ W 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)

Make CO “ride the image potential”

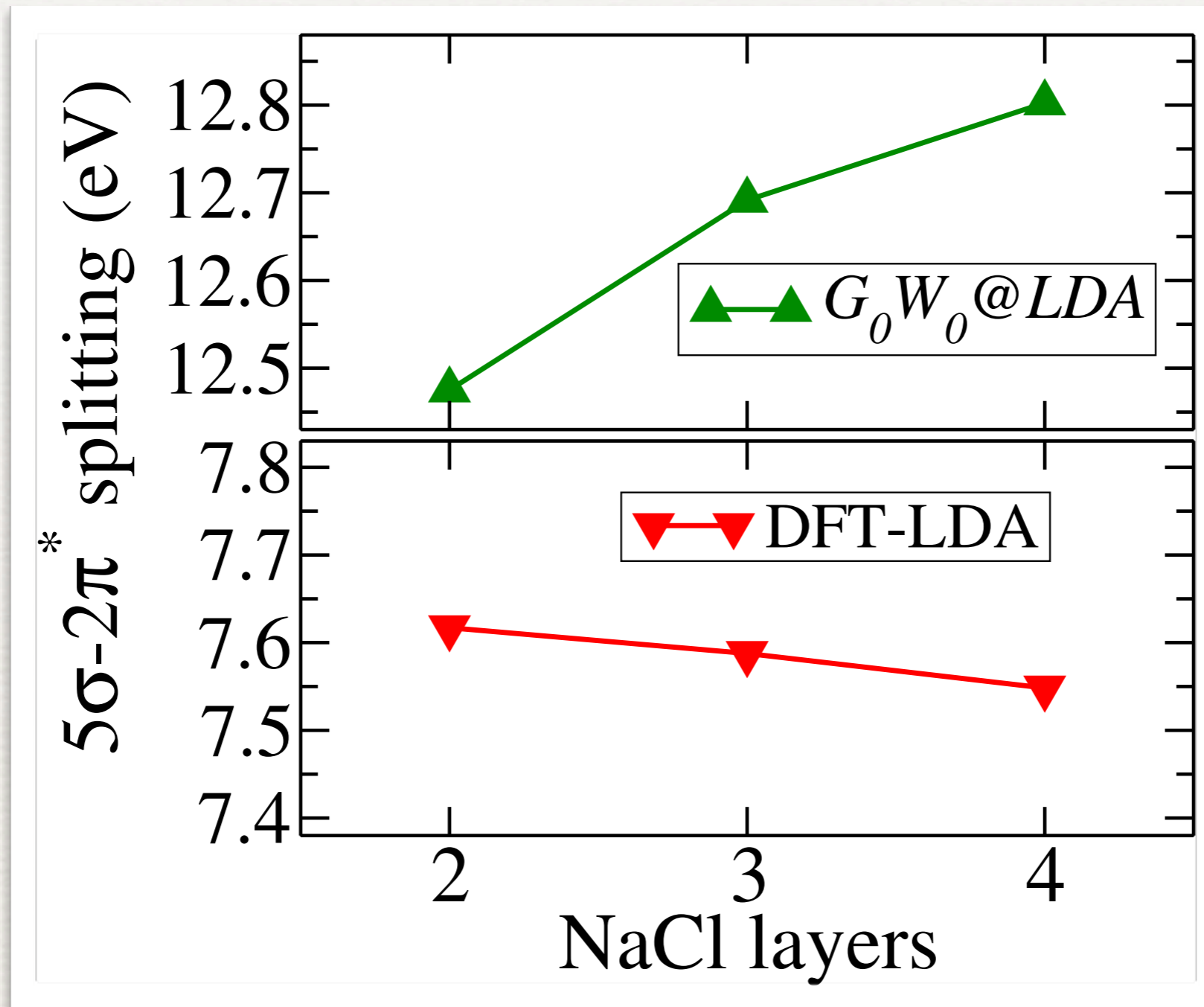


Ge image potential

- 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

Density-functional theory and excitations

exact DFT:

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

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

Density-functional theory and excitations

exact DFT:

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

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

otherwise:

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

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

rearranging and making mid-point 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 Δ SCF)

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

Ionization potential: *minimal energy to remove an electron*

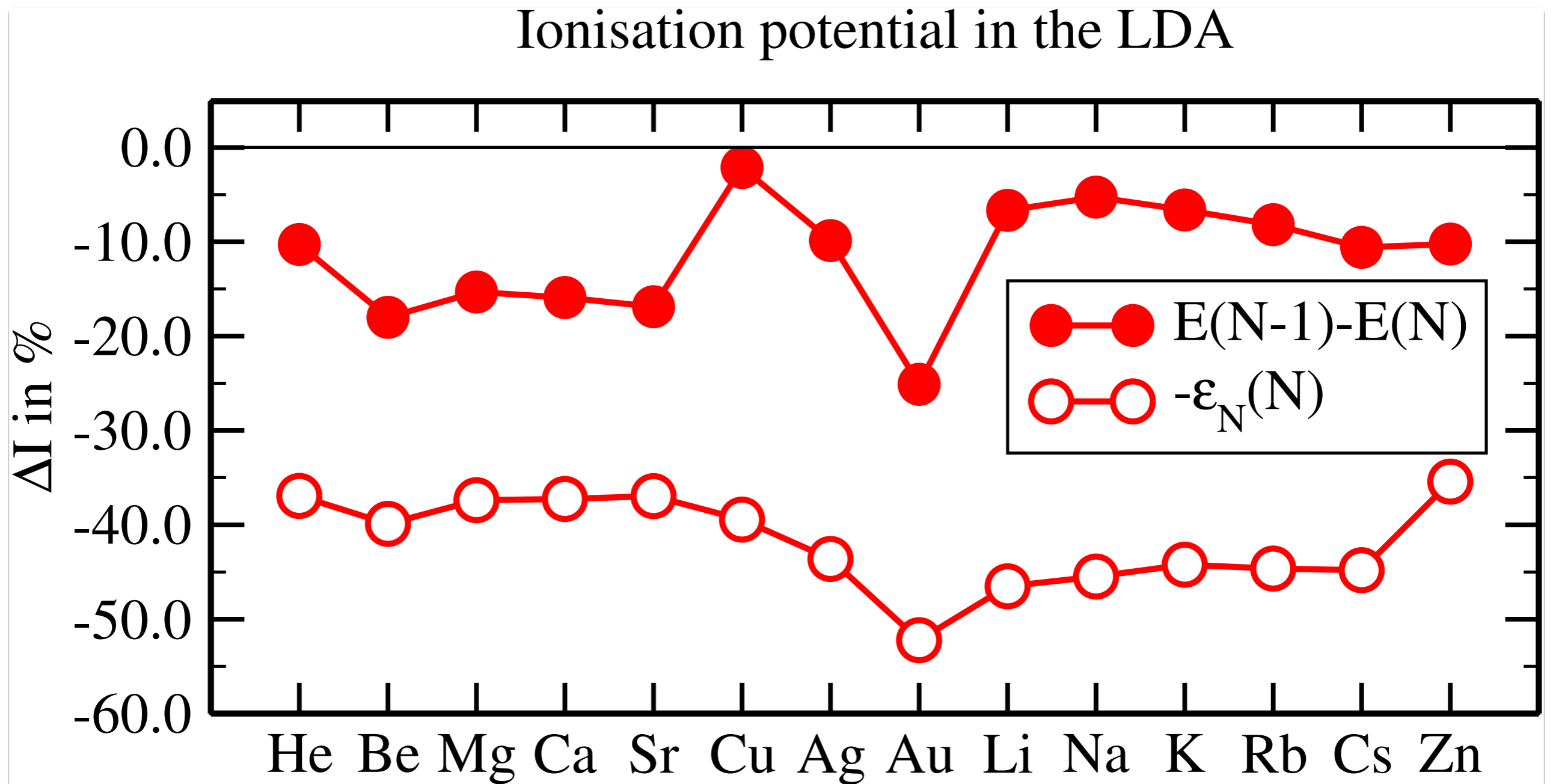
$$I = E(N - 1) - E(N)$$

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



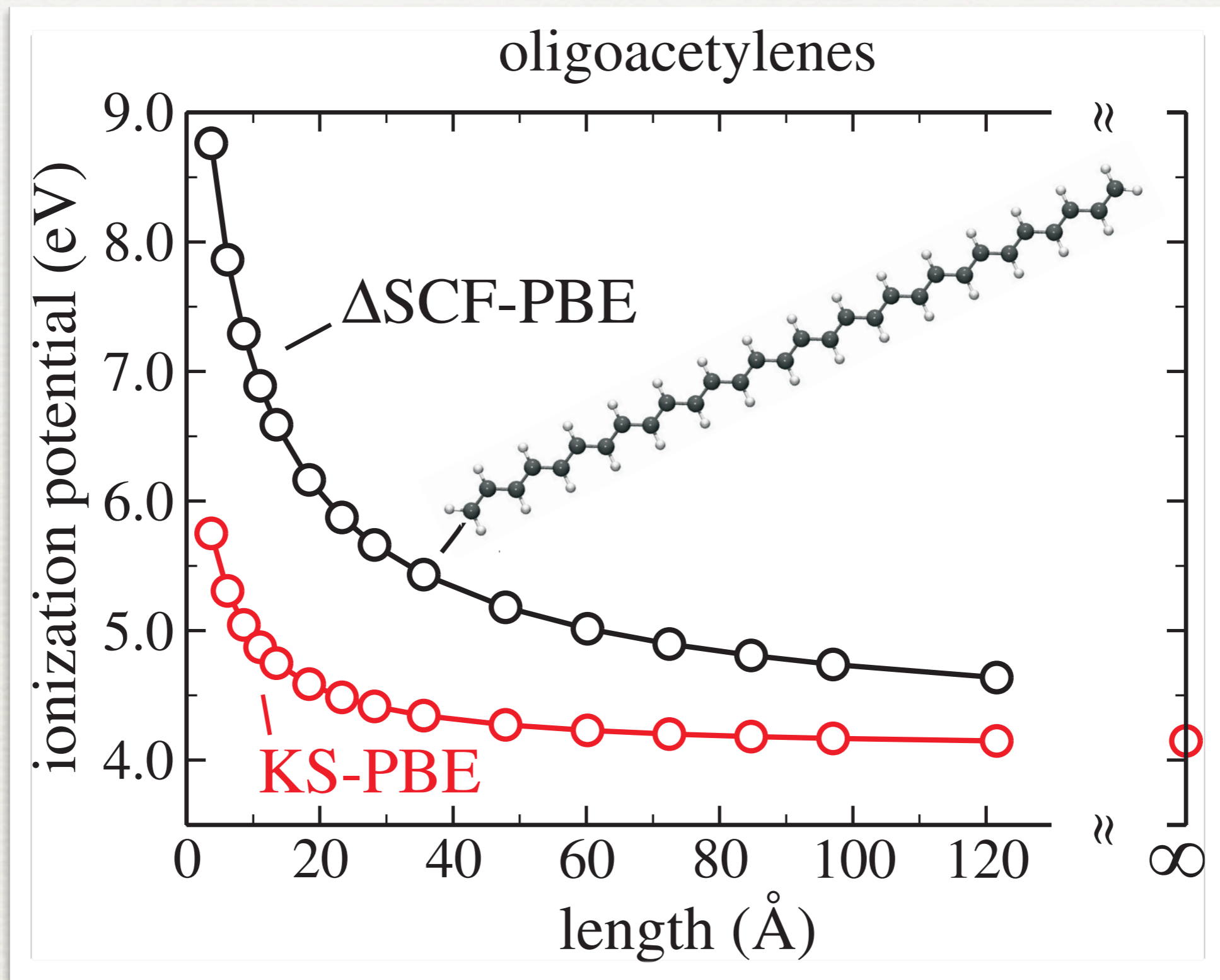
Reference: NIST -- Atomic reference data

Δ SCF 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

Δ SCF versus eigenvalues for finite systems



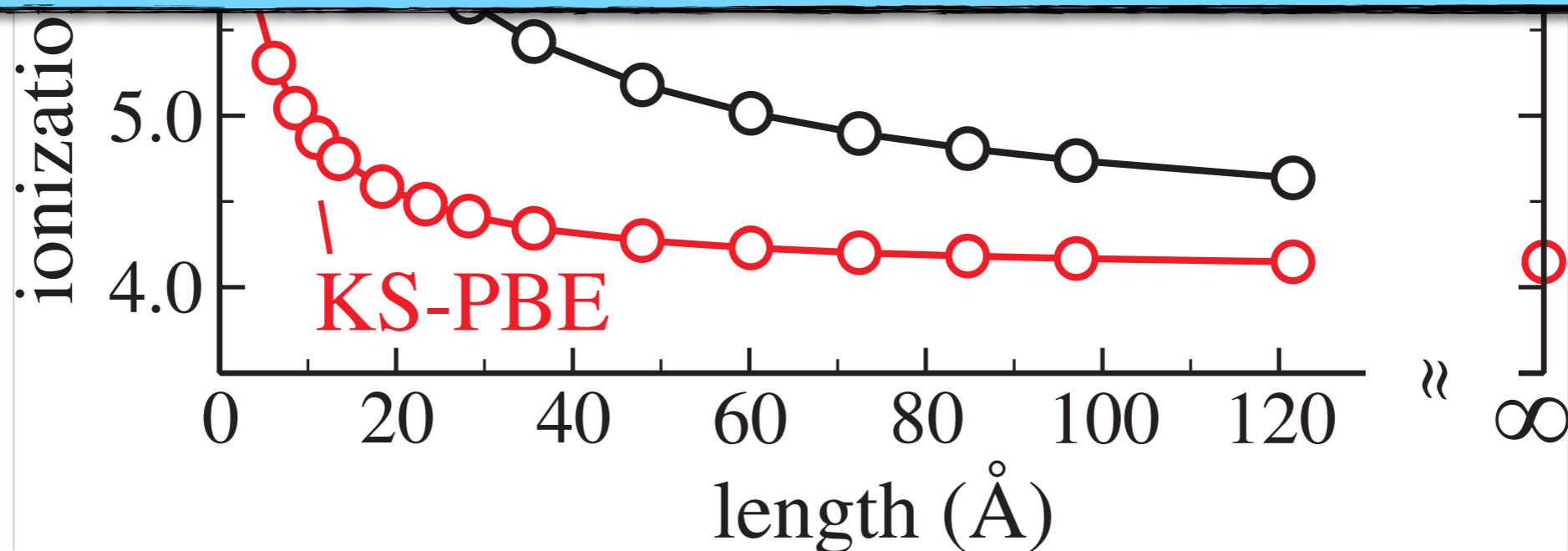
data courtesy of Max Pinheiro

Δ SCF versus eigenvalues for finite systems

oligoacetylenes

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

Δ SCF versus eigenvalues for finite systems

oligoacetylenes

90

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

length (Å)

data courtesy of Max Pinheiro

Band gaps of semiconductors and insulators

- DFT: highest Kohn-Sham state exact:

$$\begin{aligned} E_{gap} &= \epsilon_{N+1}^{\text{KS}}(N+1) - \epsilon_N^{\text{KS}}(N) \\ &= \underbrace{\epsilon_{N+1}^{\text{KS}}(N+1) - \epsilon_{N+1}^{\text{KS}}(N)}_{\Delta_{xc}} + \underbrace{\epsilon_{N+1}^{\text{KS}}(N) - \epsilon_N^{\text{KS}}(N)}_{E_{gap}^{\text{KS}}} \end{aligned}$$

Band gaps of semiconductors and insulators

- DFT: highest Kohn-Sham state exact:

$$\begin{aligned} E_{gap} &= \epsilon_{N+1}^{\text{KS}}(N+1) - \epsilon_N^{\text{KS}}(N) \\ &= \underbrace{\epsilon_{N+1}^{\text{KS}}(N+1) - \epsilon_{N+1}^{\text{KS}}(N)}_{\Delta_{xc}} + \underbrace{\epsilon_{N+1}^{\text{KS}}(N) - \epsilon_N^{\text{KS}}(N)}_{E_{gap}^{\text{KS}}} \end{aligned}$$

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

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

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

Band gaps of semiconductors and insulators

- DFT: highest Kohn-Sham state exact:

$$E_{gap} = \underbrace{\epsilon_{N+1}^{KS}(N+1) - \epsilon_N^{KS}(N)}_{E_{gap}^{KS}}$$

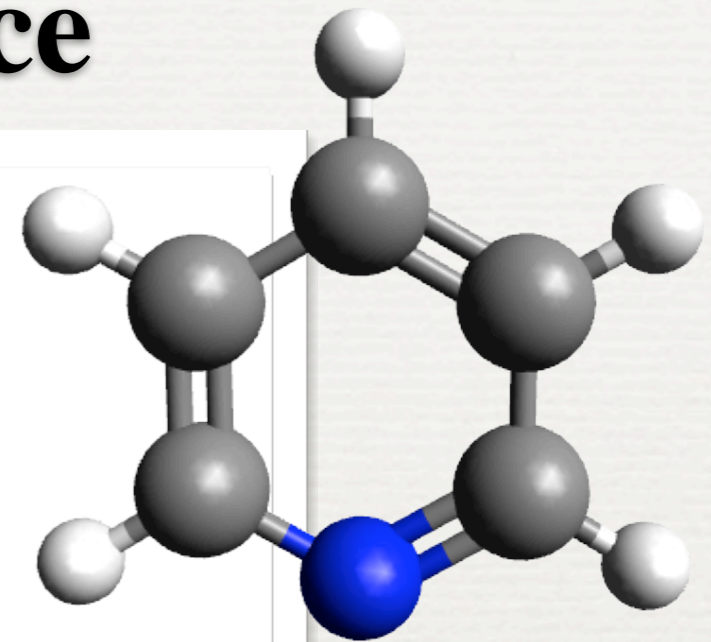
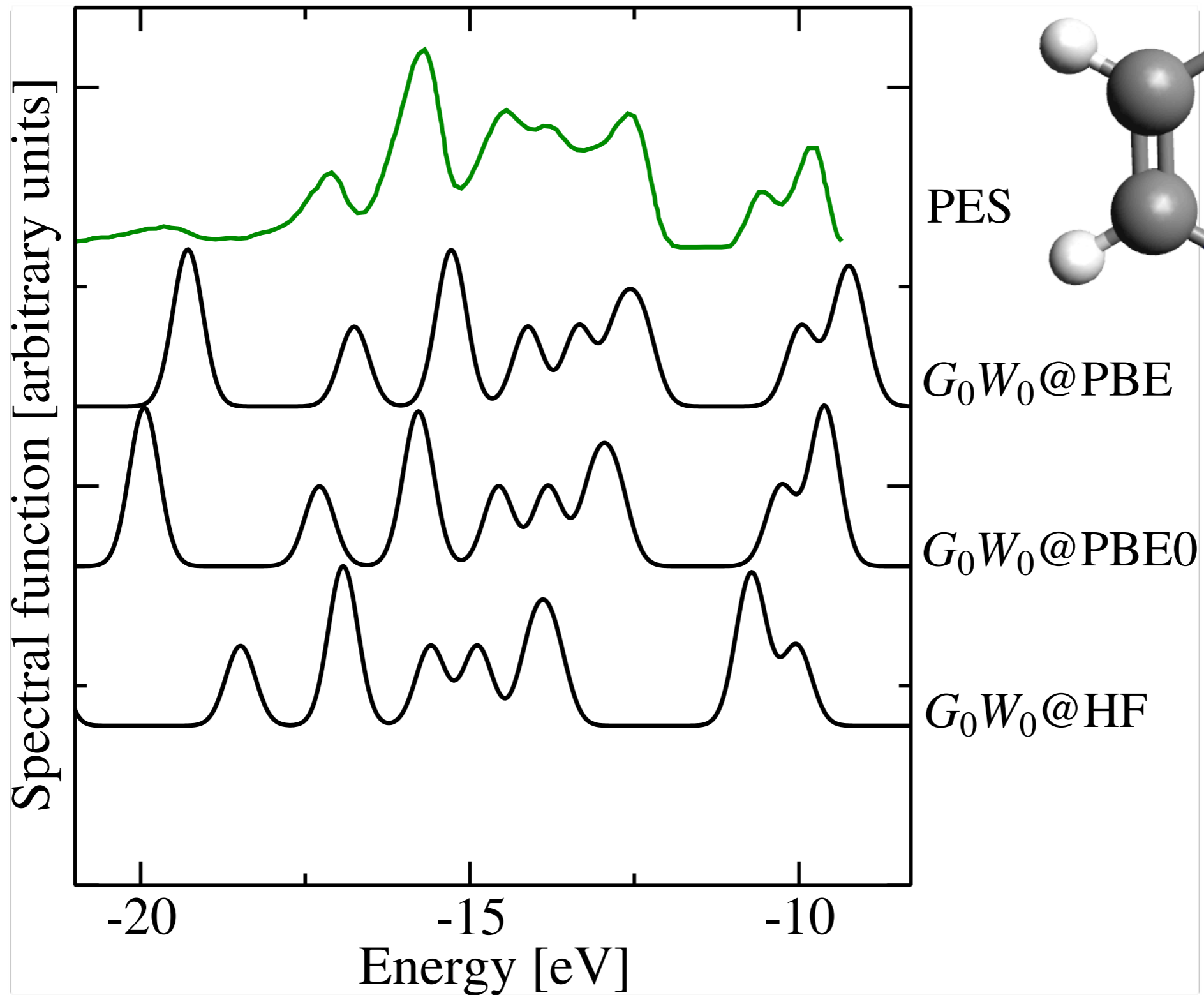
most DFT functionals do not contain this derivative discontinuity

- for so $\rightarrow N + 1$

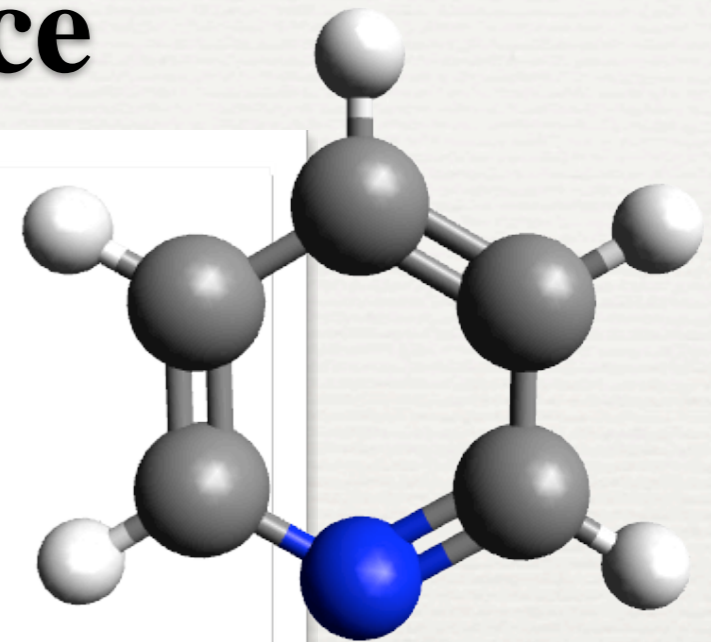
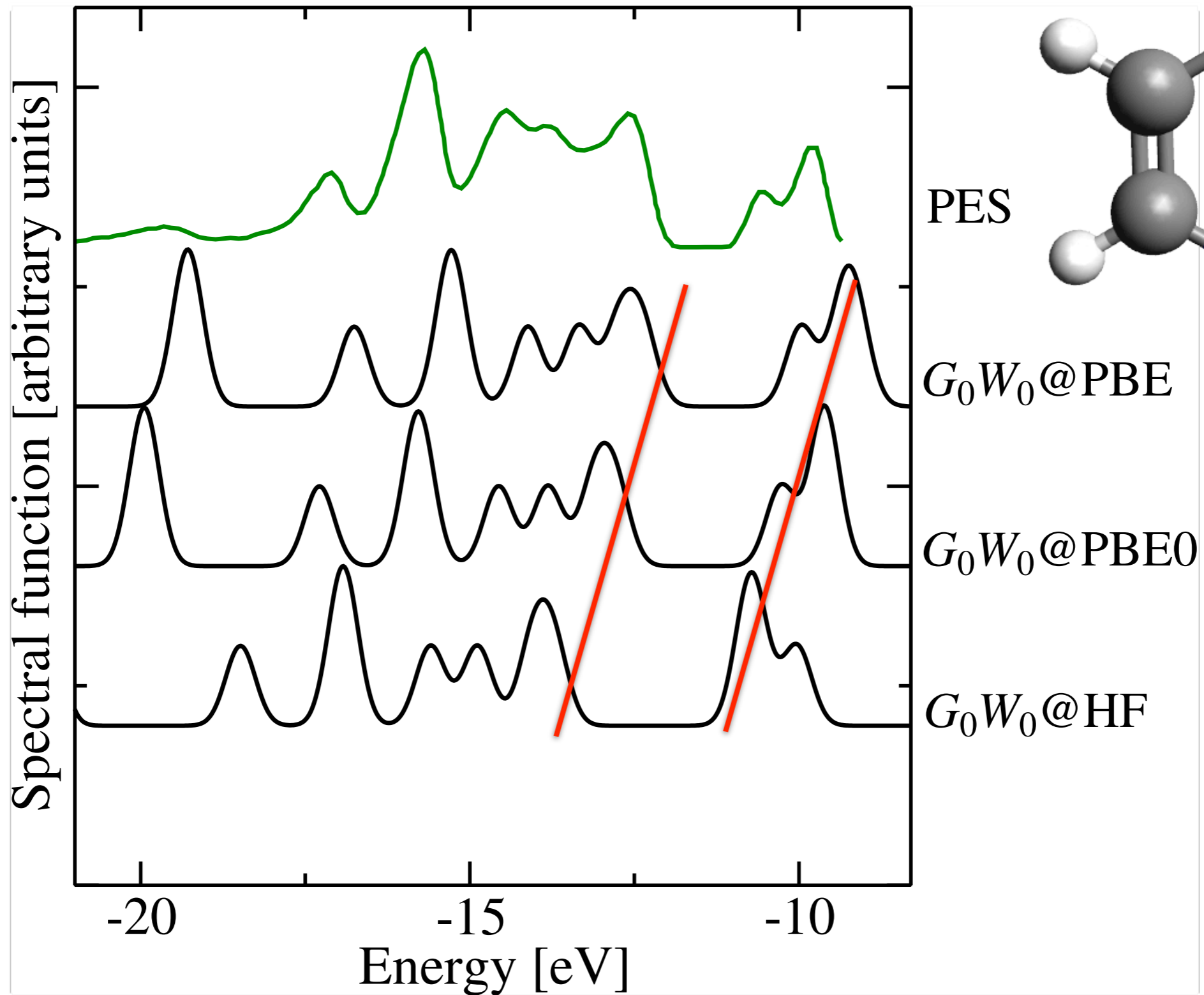
v_{xc} : discontinuity upon changing the particle number:

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

Starting point dependence



Starting point dependence



Self-consistent GW (scGW)

Hedin's GW equations:

$$G(1, 2) = G_0(1, 2) \quad 1 = (\mathbf{r}_1, \sigma_1, t_1)$$

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

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

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

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

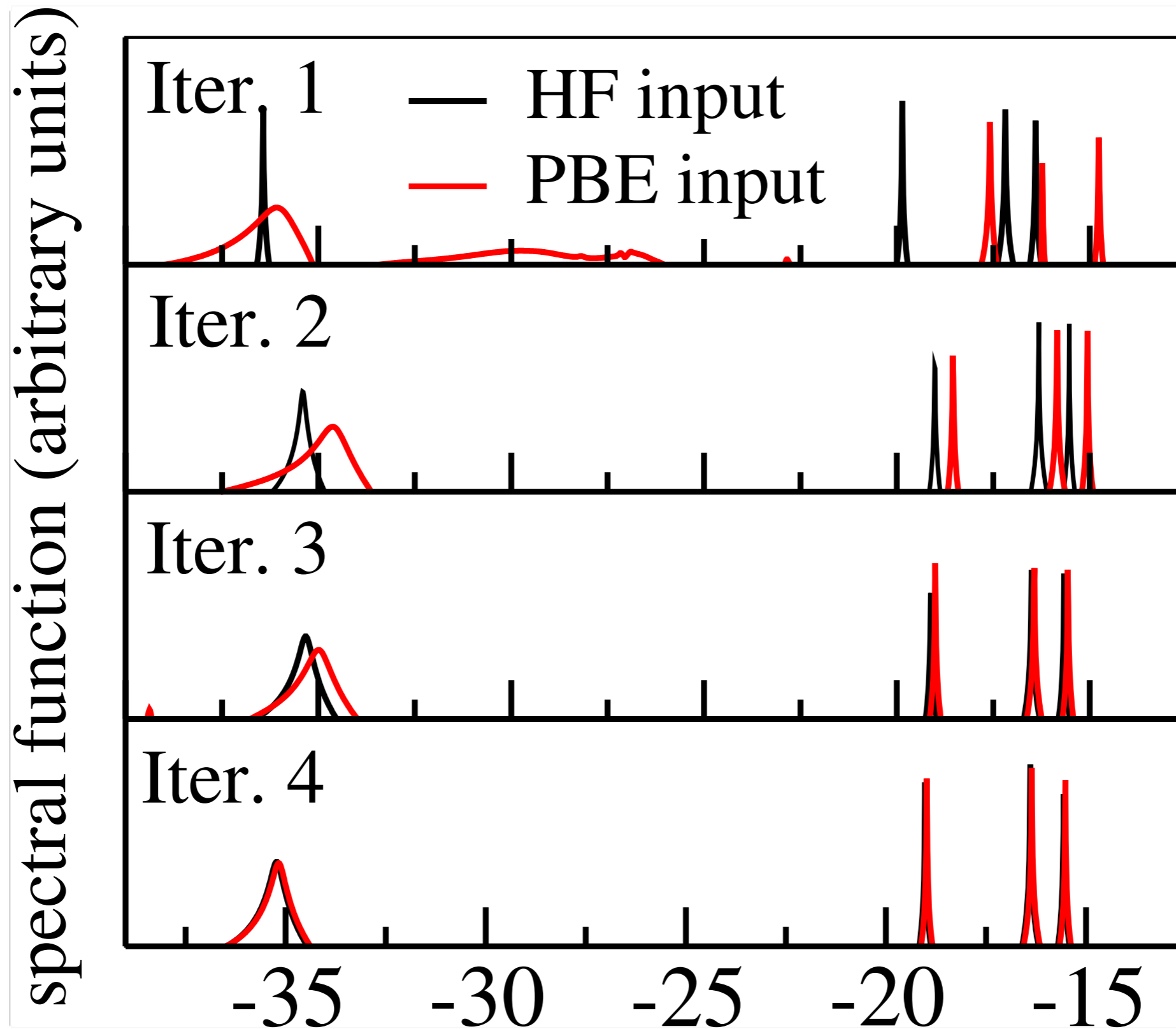
Dyson's equation:

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

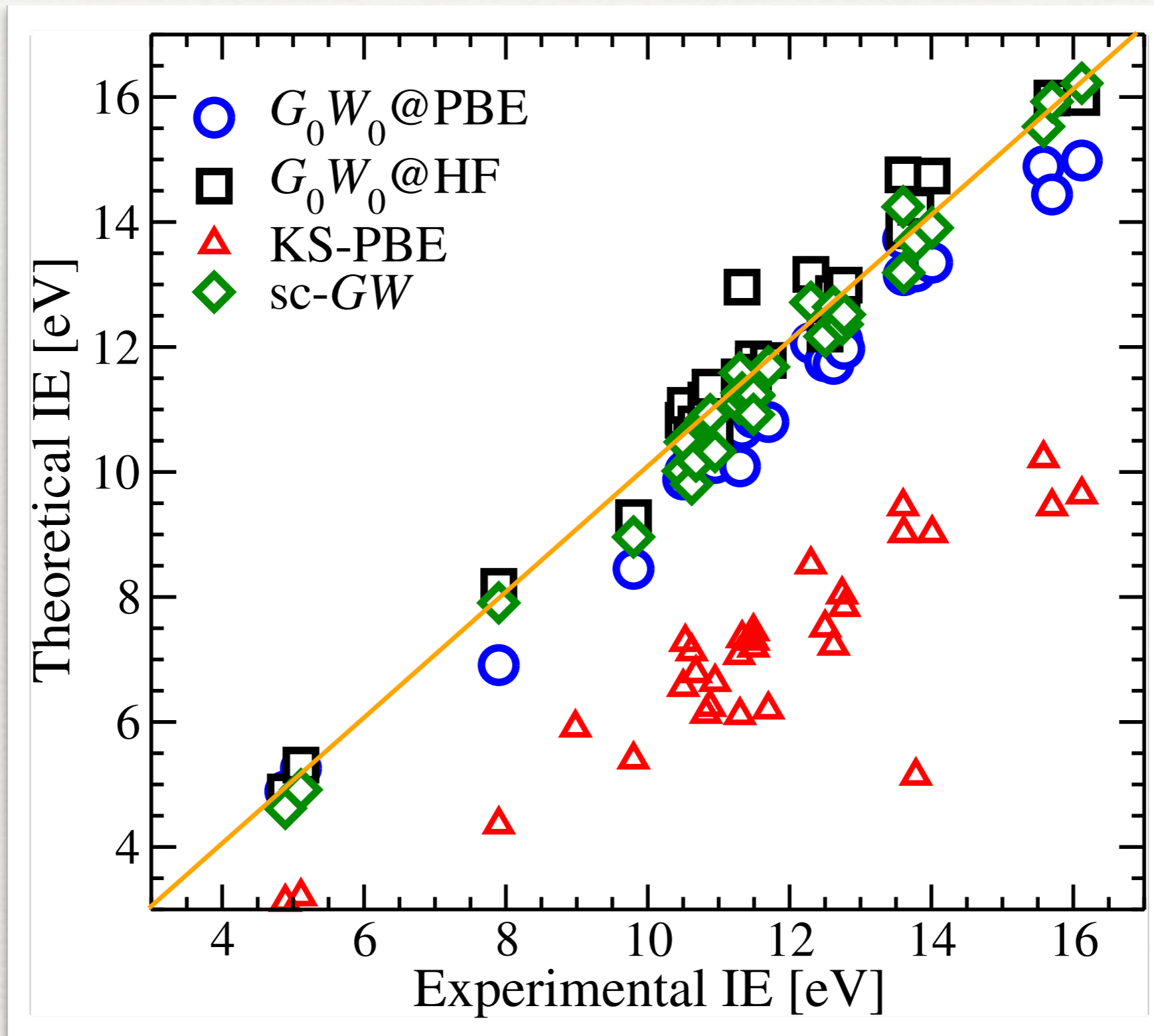
self-
consistency

self-
consistency

Unique solution in scGW - N₂

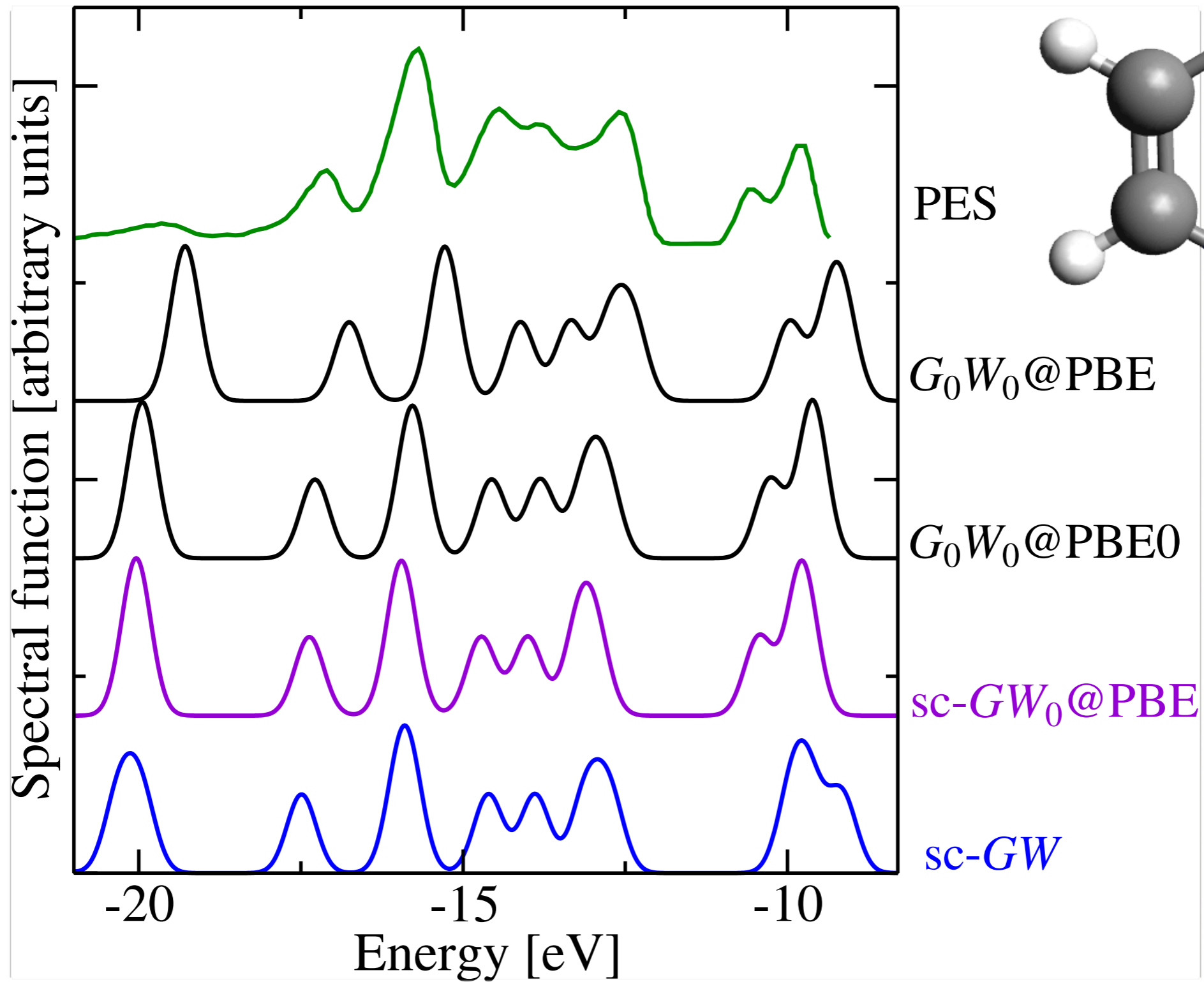


Ionization potentials in scGW

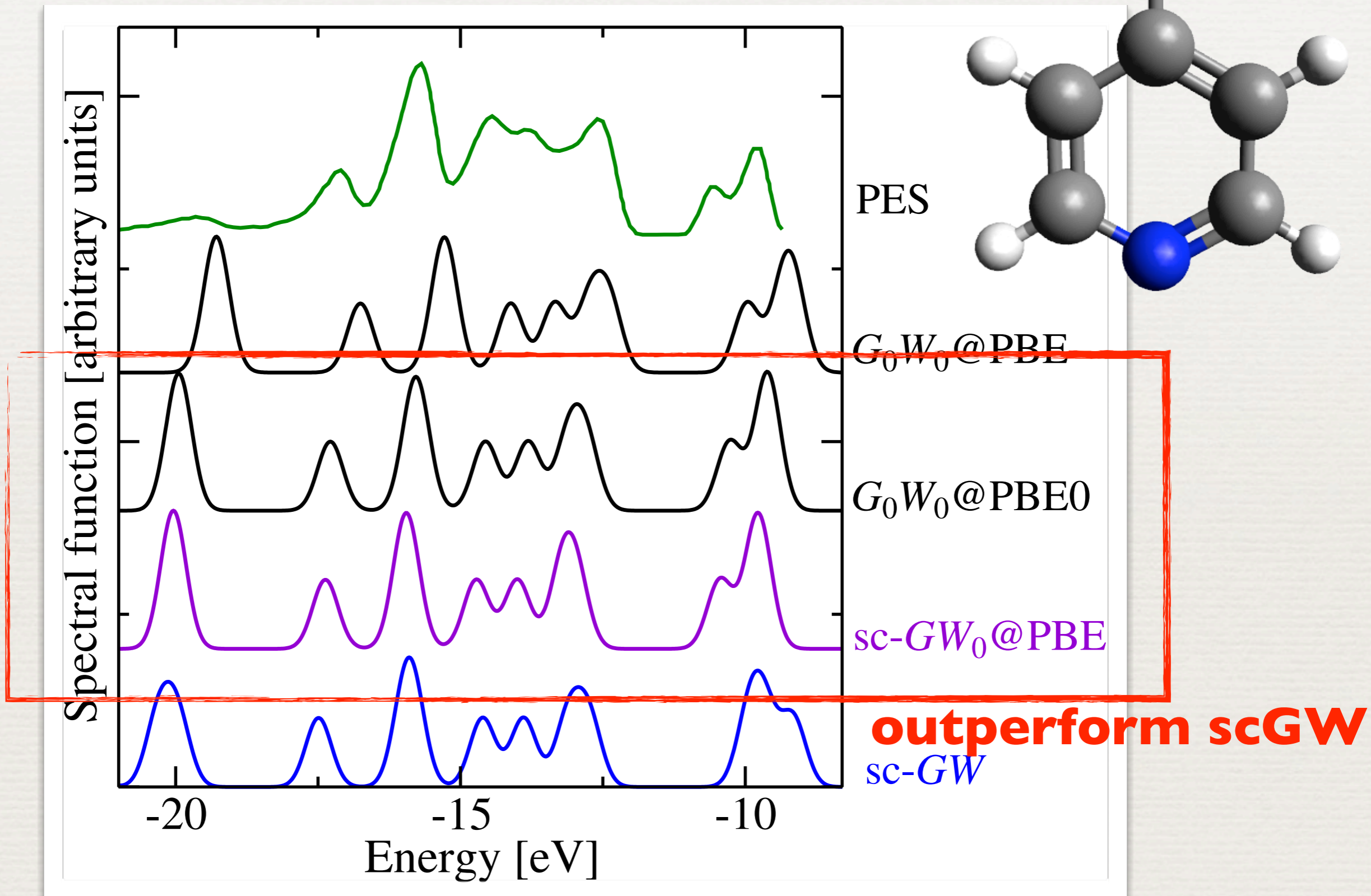


set taken from Rostgaard, Jacobsen, and Thygesen, PRB **81**, 085103, (2010)

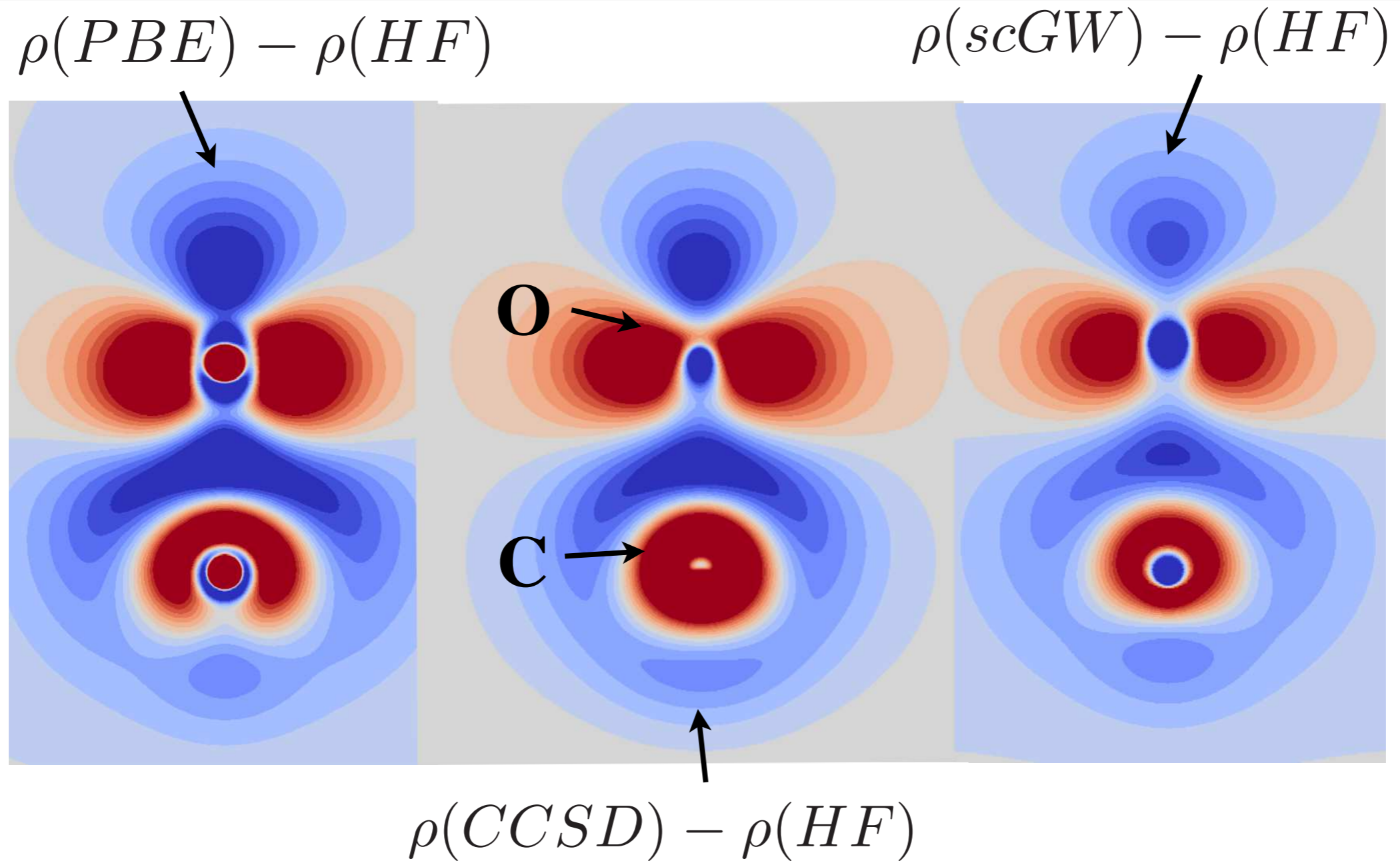
The loan pair in pyridine



The loan pair in pyridine



The *GW* density of CO



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

The GW density of CO

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

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

Dipole moment (in Debye):

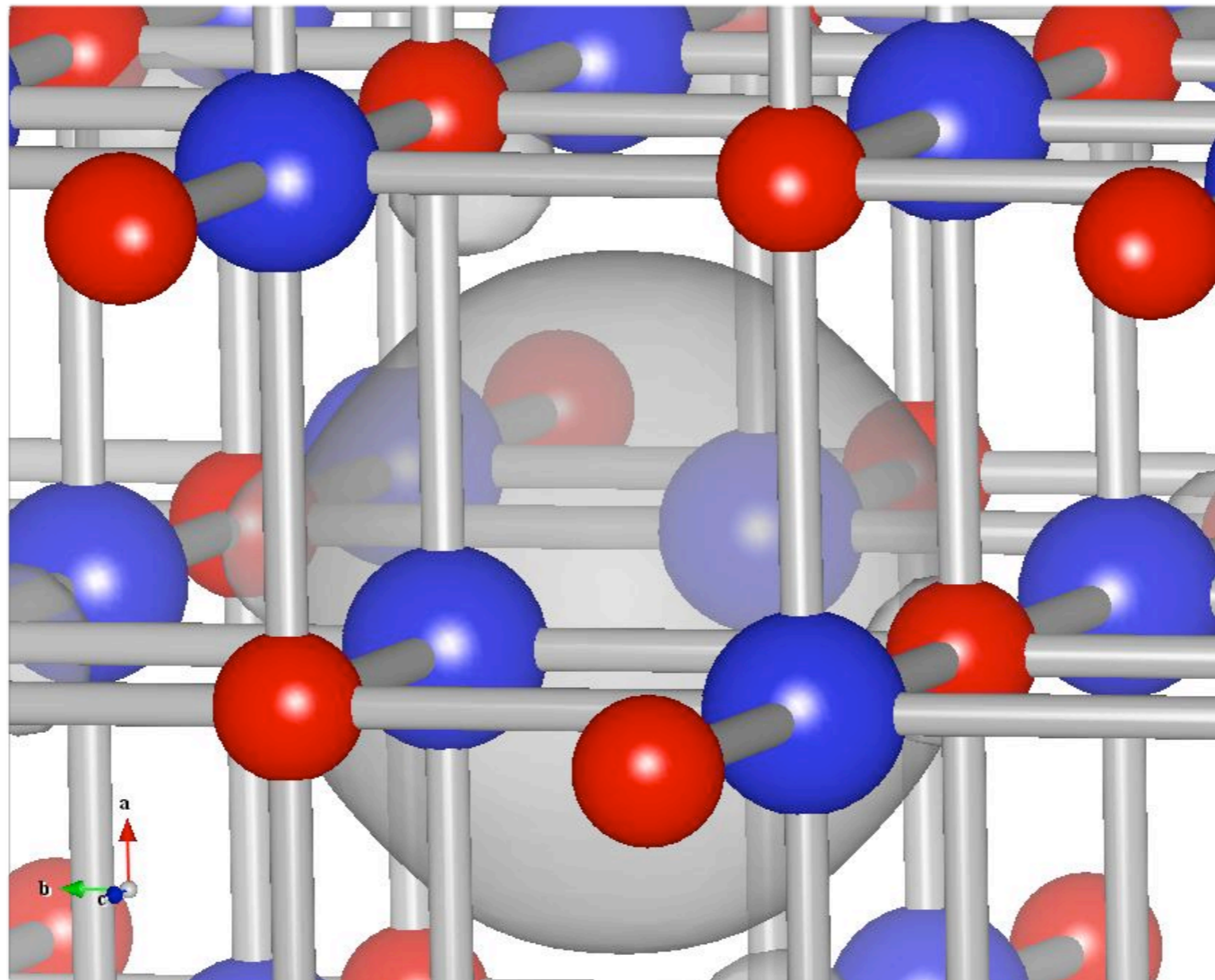
Exp.	scGW	CCSD	HF	PBE
0.11	0.07	0.06	-0.13	0.20

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

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

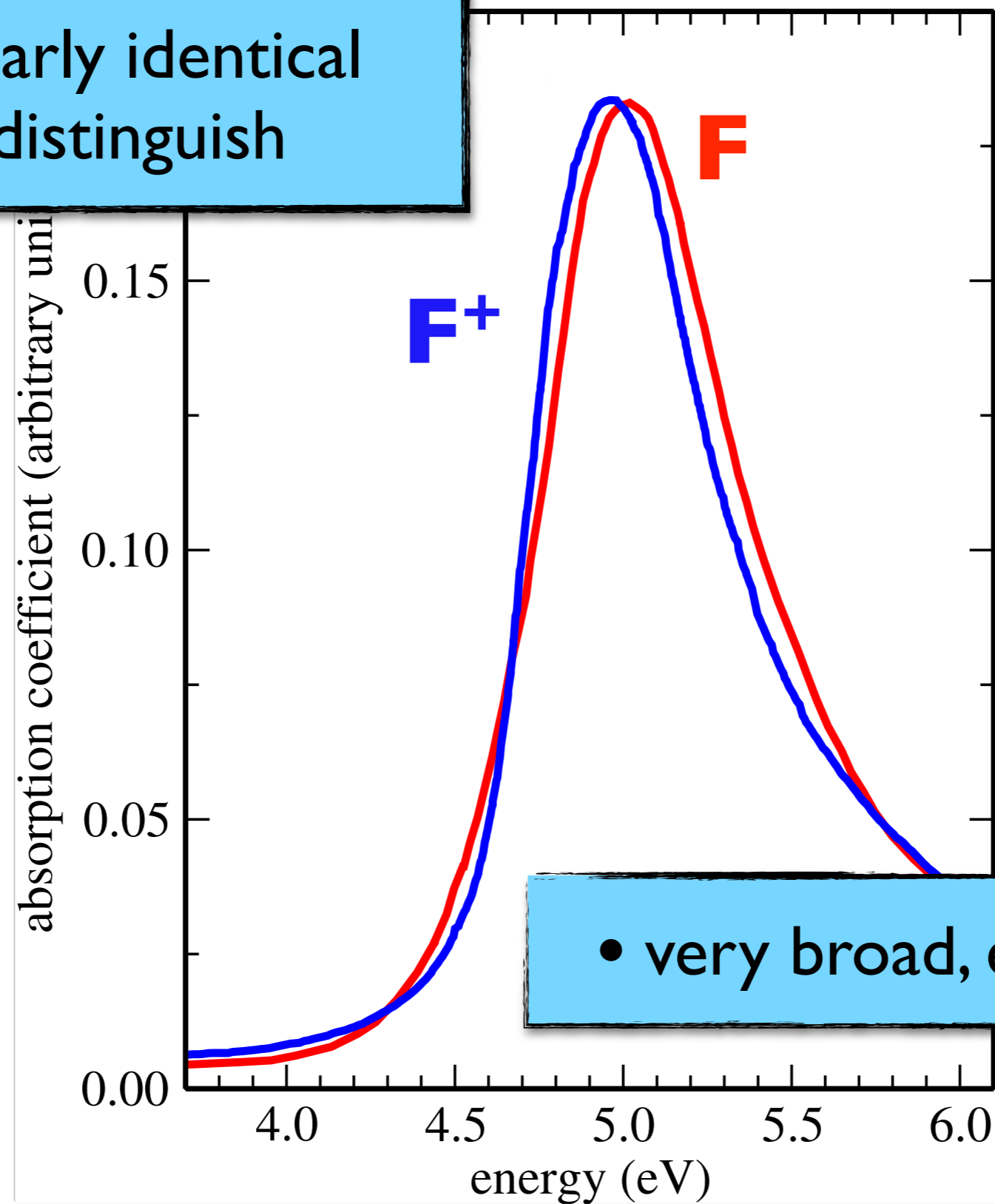
F-center: Oxygen vacancy in MgO

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



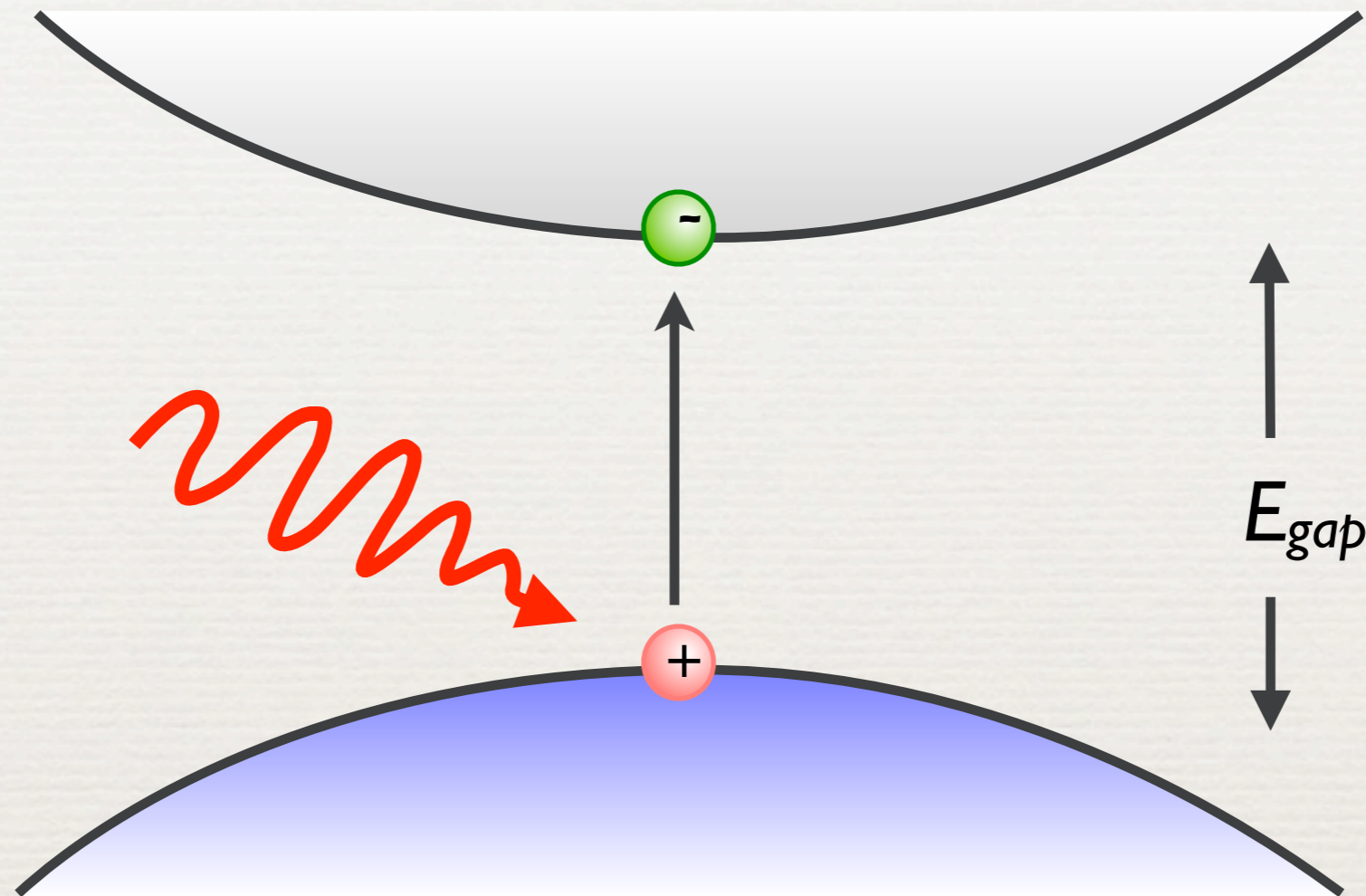
Experimental optical absorption spectra

- F and F⁺ nearly identical
- difficult to distinguish



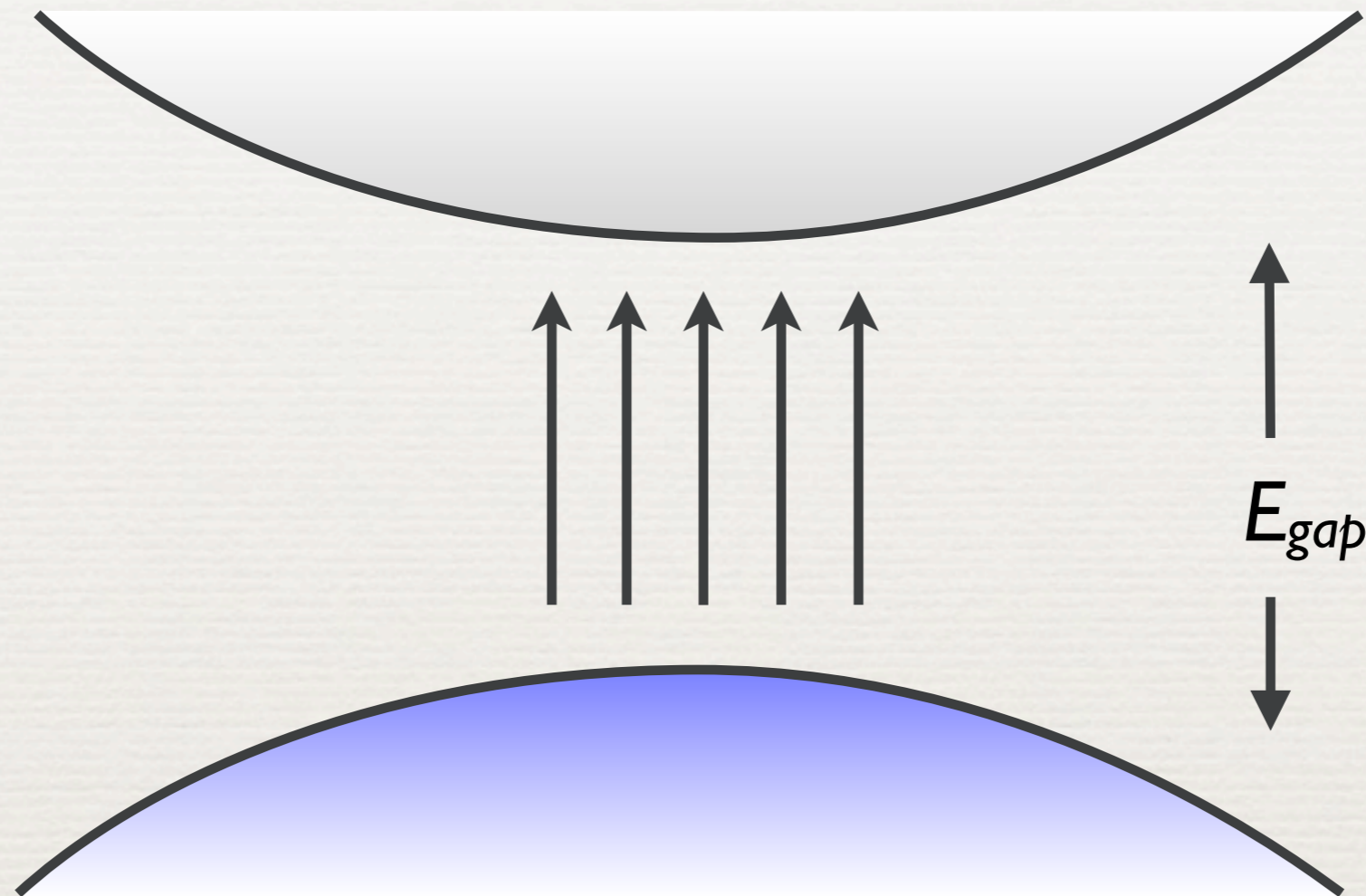
- very broad, even at low T

Absorption spectrum from first principles



Absorption spectrum = $\text{Im} \varepsilon_M(\omega)$ (macroscopic dielectric const.)

Absorption spectrum from first principles

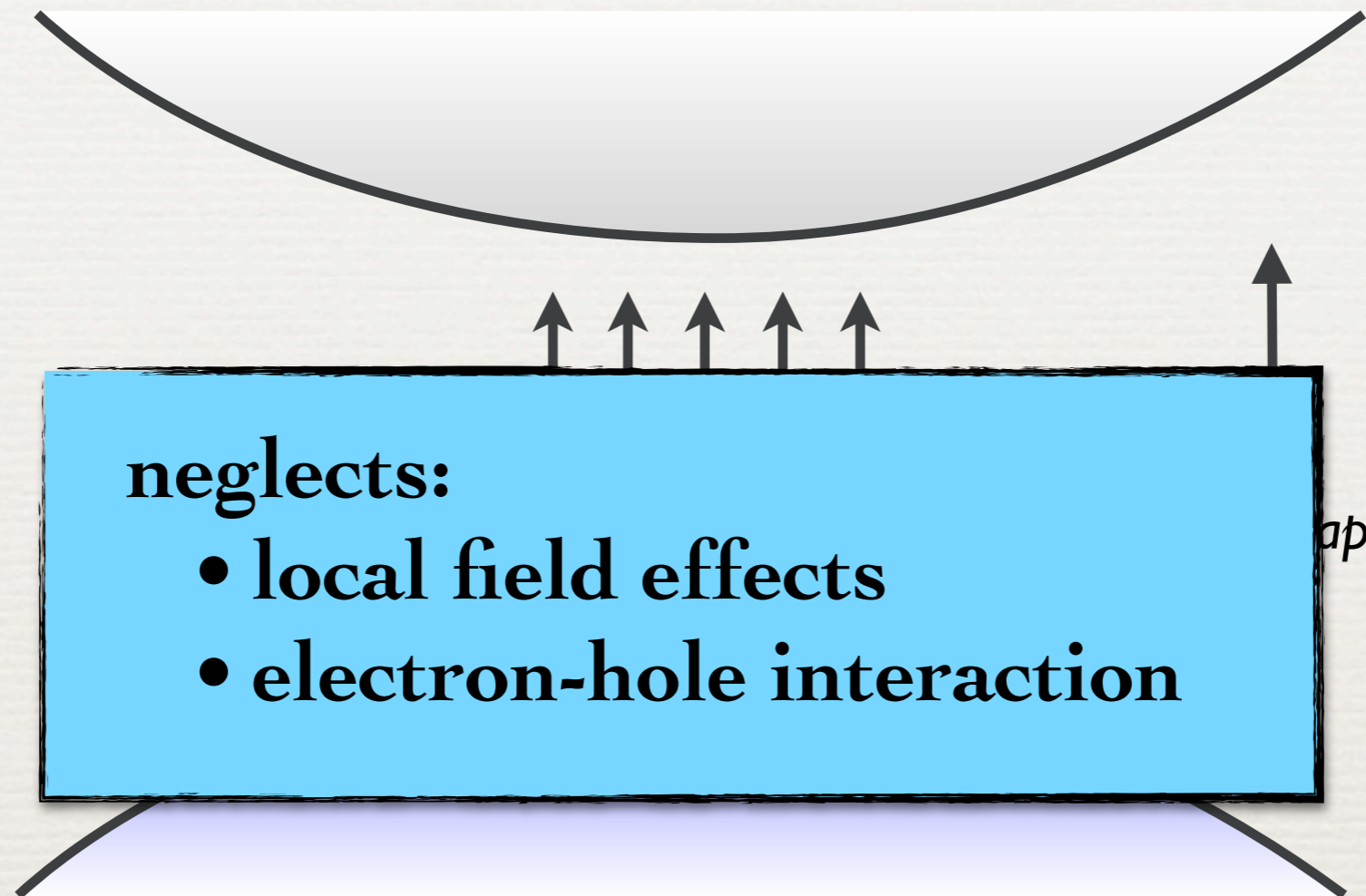


Fermi's golden rule:

$$Im \epsilon_M(\omega) = \frac{16\pi}{\omega^2} \sum_v^{occ} \sum_c^{unocc} |\langle \psi_v | \mathbf{v} | \psi_c \rangle|^2 \delta(\epsilon_c - \epsilon_v - \omega)$$

\mathbf{v} : velocity operator

Absorption spectrum from first principles



Fermi's golden rule:

$$\text{Im } \epsilon_M(\omega) = \frac{16\pi}{\omega^2} \sum_v^{\text{occ}} \sum_c^{\text{unocc}} |\langle \psi_v | \mathbf{v} | \psi_c \rangle|^2 \delta(\epsilon_c - \epsilon_v - \omega)$$

\mathbf{v} : velocity operator

Optical absorption - response function

Dielectric constant:

$$\text{Im } \varepsilon_M(\omega) = \lim_{\mathbf{q} \rightarrow 0} \frac{1}{\varepsilon_{\mathbf{G}=0, \mathbf{G}'=0}^{-1}(\mathbf{q}, \omega)}$$

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:

$$\text{Im } \varepsilon_M(\omega) = \lim_{\mathbf{q} \rightarrow 0} \frac{1}{\varepsilon_{\mathbf{G}=0, \mathbf{G}'=0}^{-1}(\mathbf{q}, \omega)}$$

Dielectric function:

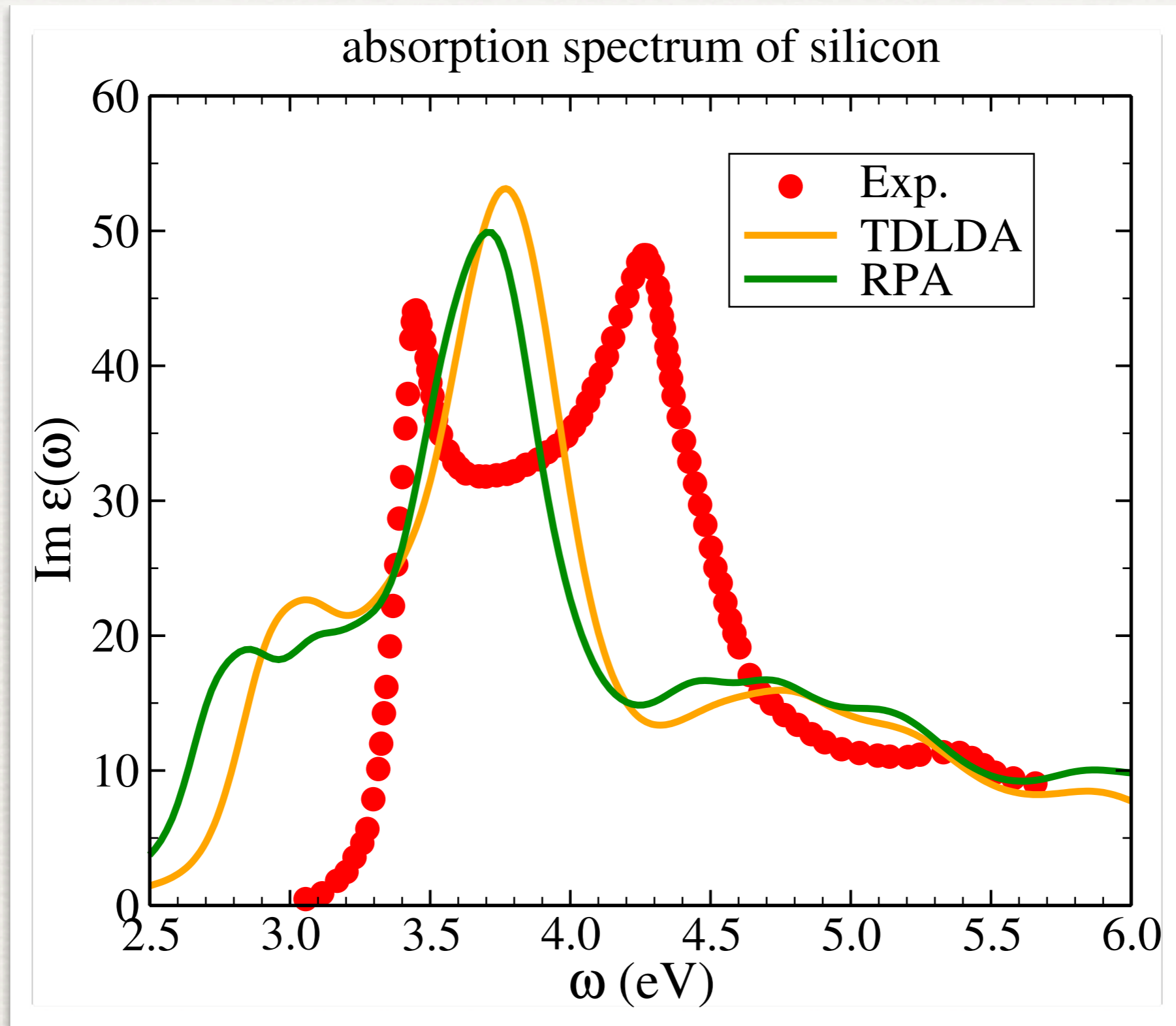
$$\varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r} - \mathbf{r}') - \int d\mathbf{r}'' v(\mathbf{r} - \mathbf{r}'') \chi(\mathbf{r}'', \mathbf{r}', \omega)$$

Response function in time dependent DFT (TDDFT):

$$\hat{\chi} = \hat{\chi}_0 + \hat{\chi}_0 \left[\hat{v} + \cancel{\hat{j}_c} \right] \hat{\chi}$$

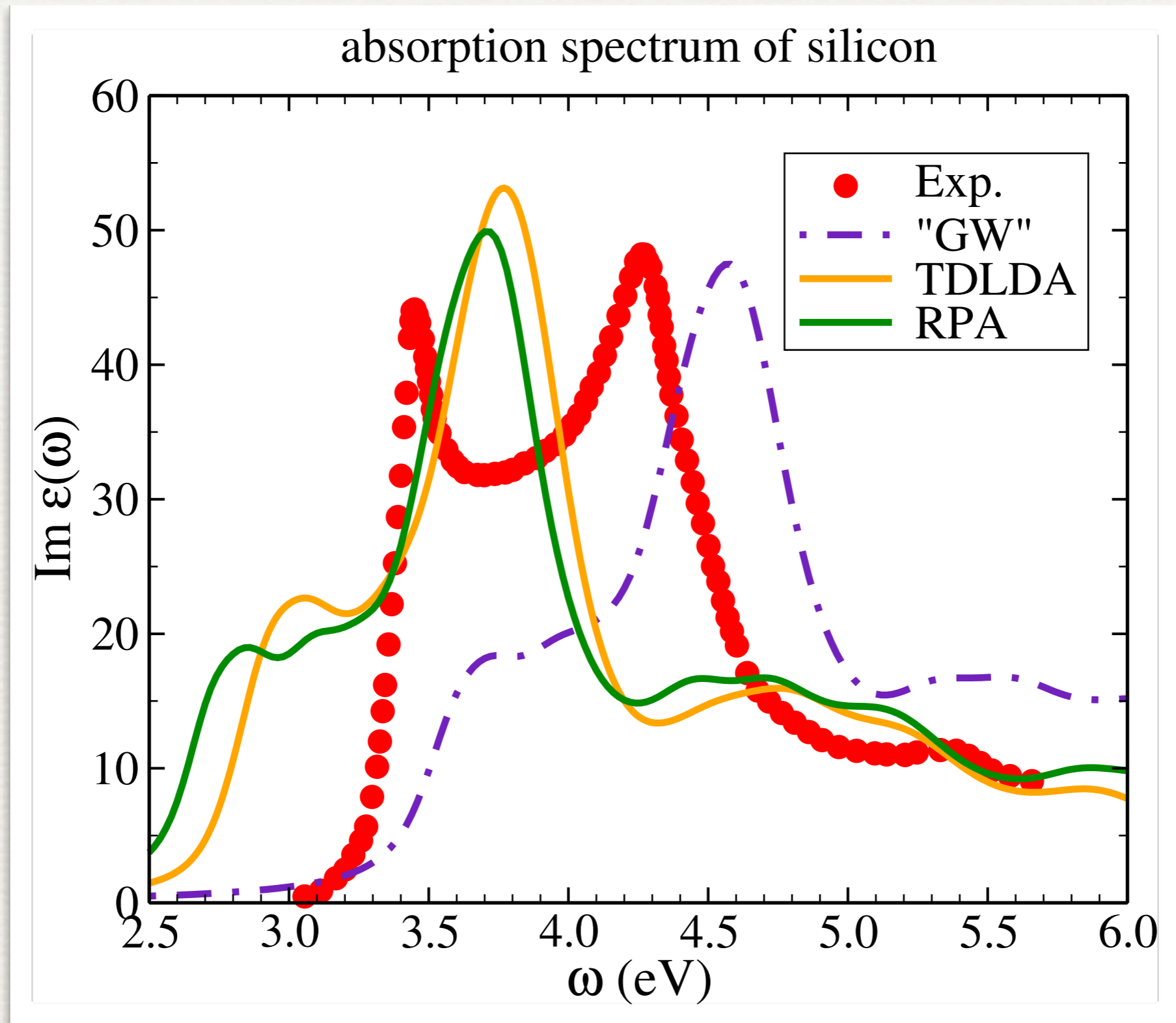
Random-phase approximation (RPA)

Optical absorption - response function



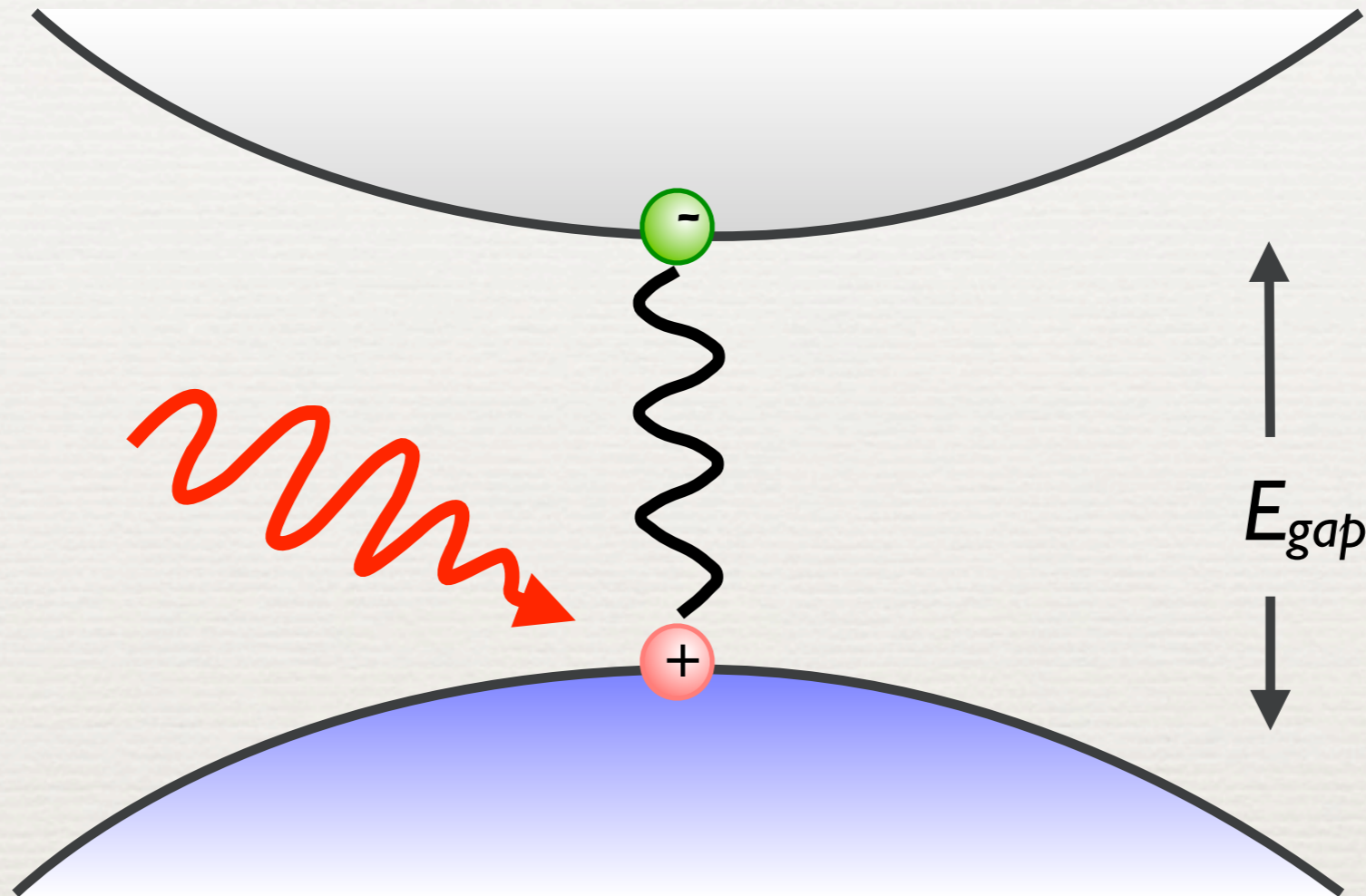
from Sottile, Olevano, and Reining, PRL 91, 056402 (2003)

Optical absorption - response function



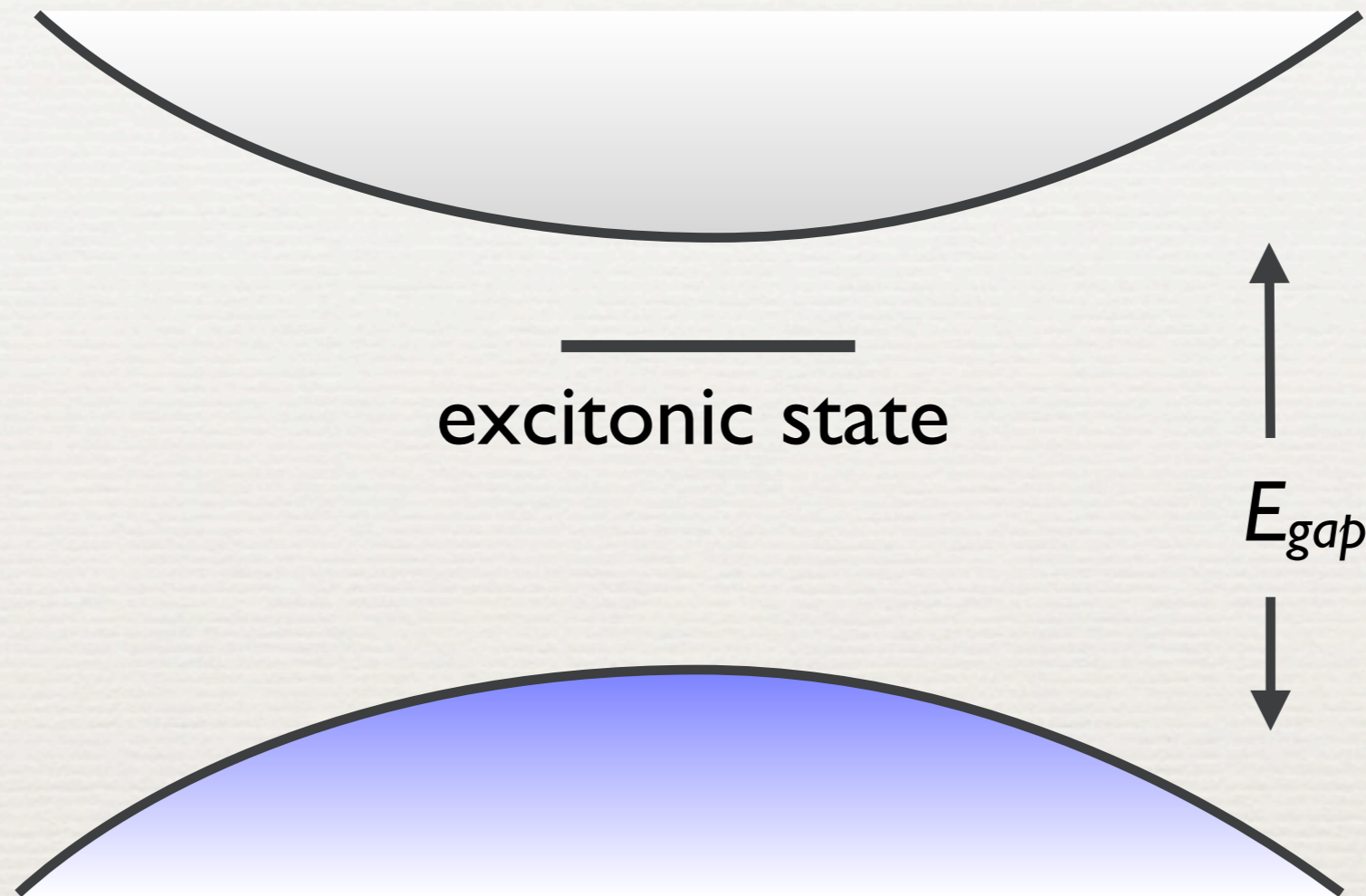
from Sottile, Olevano, and Reining, PRL 91, 056402 (2003)

Including electron-hole interaction



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

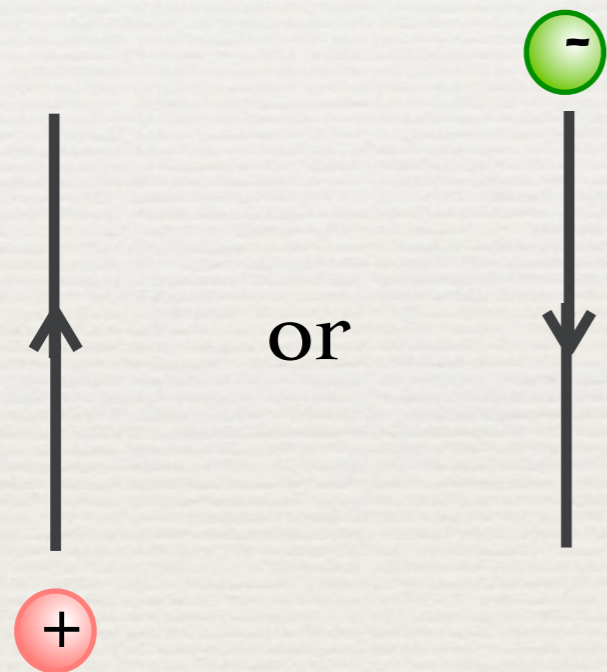
Including electron-hole interaction



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

Including electron-hole interaction

one particle
Green's function



$G(1, 2)$

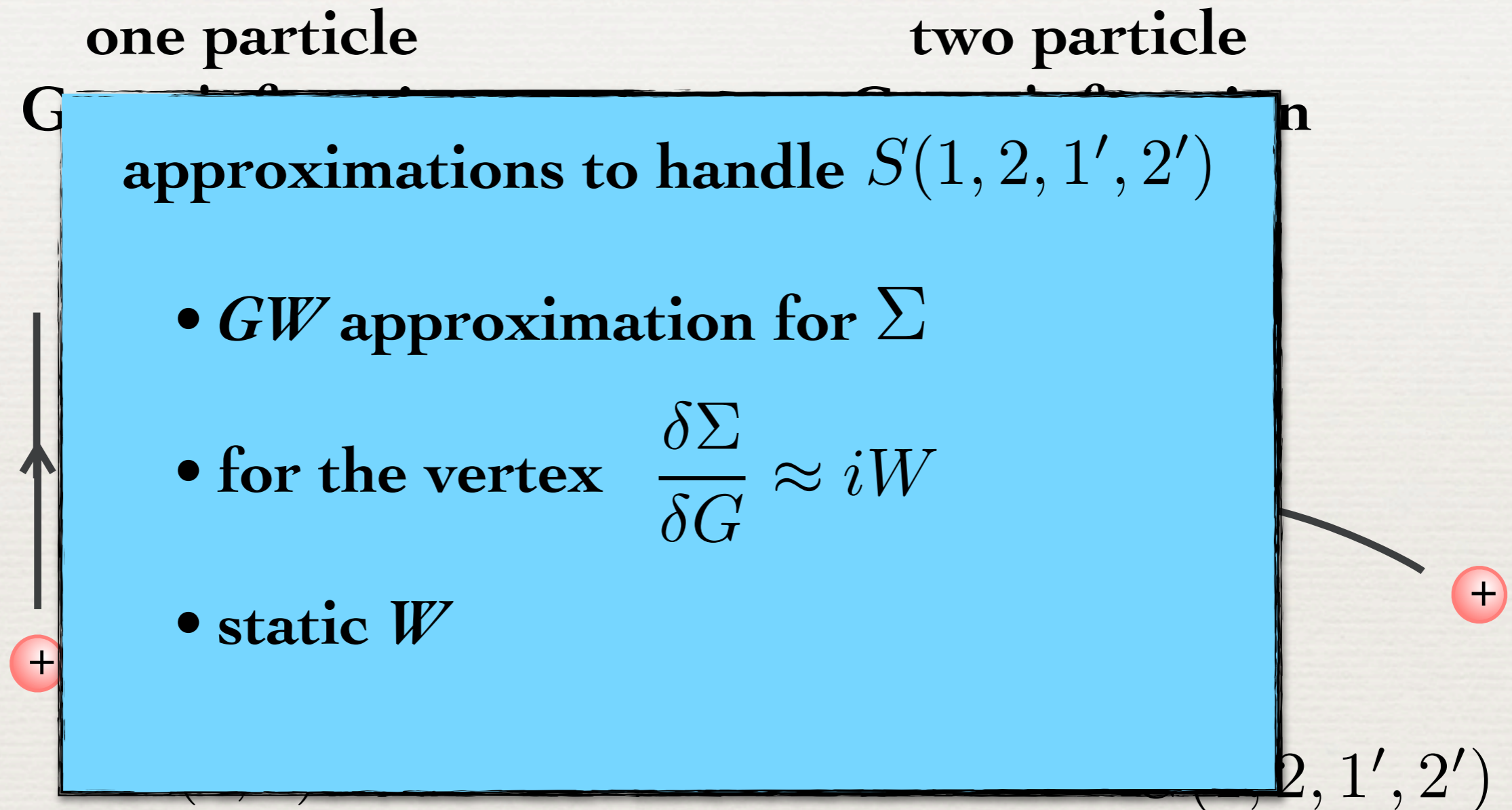
two particle
Green's function



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

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

Including electron-hole interaction



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

Absorption spectrum from first principles

Bethe-Salpeter equation

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

electron-hole pair

electron (GW)

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

hole (GW)

bare

Coulomb

screened

(RPA from GW)

Absorption spectrum from first principles

Bethe-Salpeter equation

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

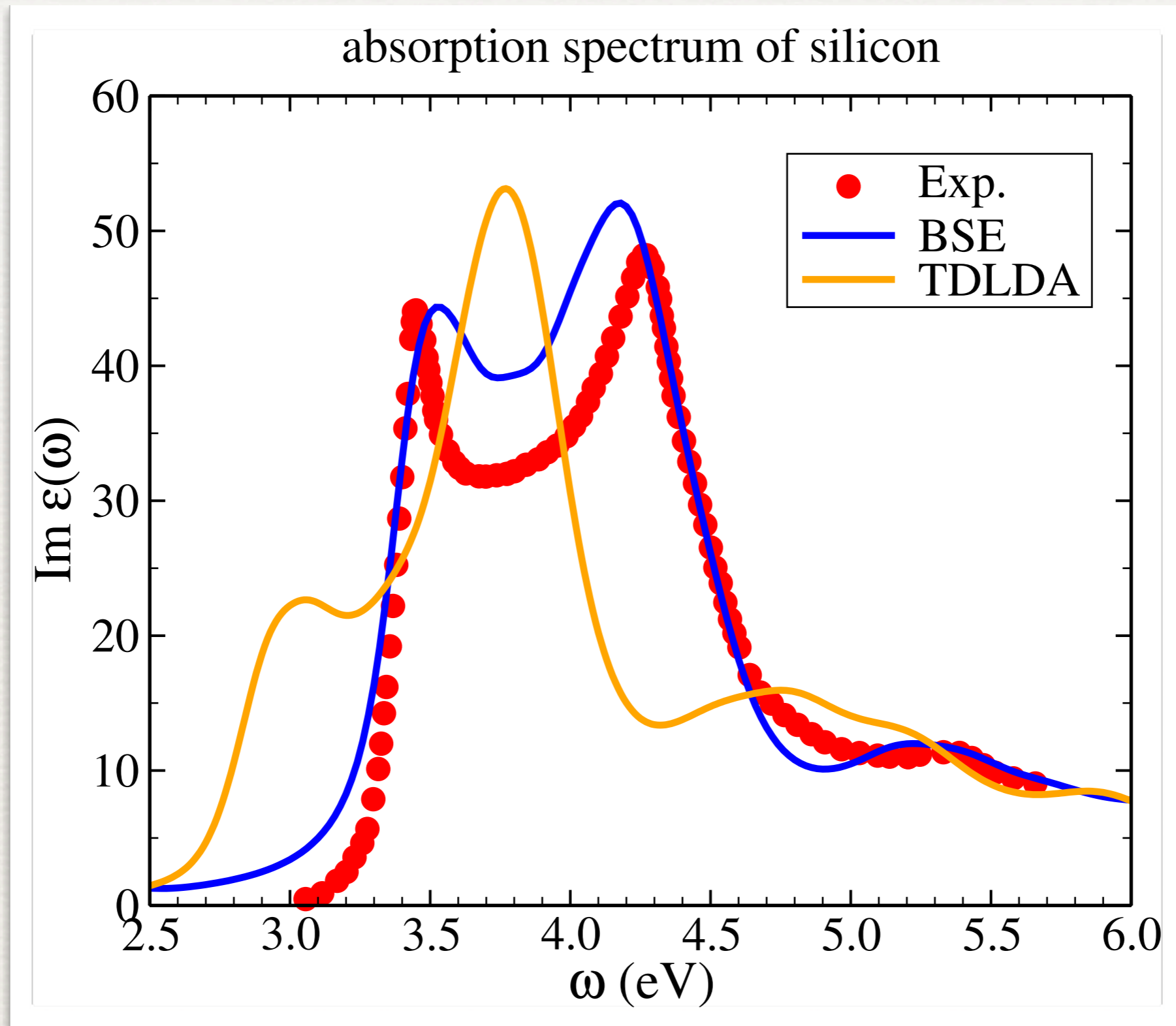
electron-hole pair

dielectric function:

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

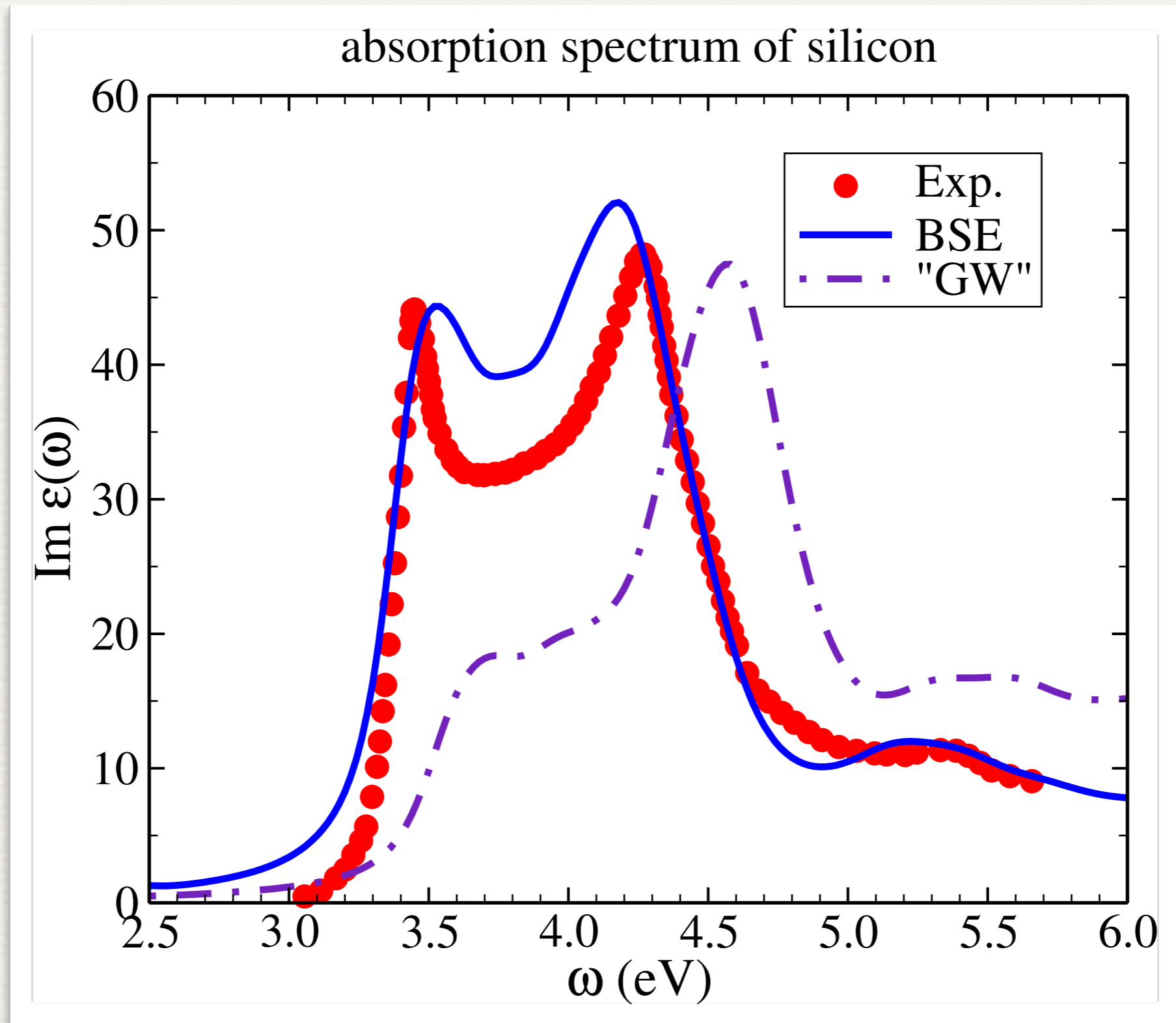
**wave function
coefficients**

Optical absorption - response function



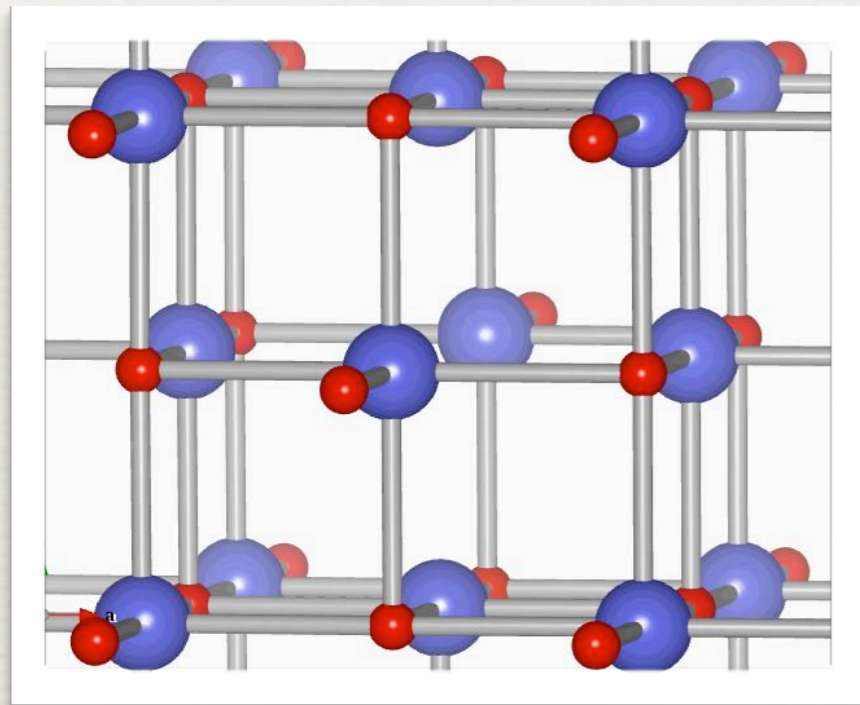
from Sottile, Olevano, and Reining, PRL 91, 056402 (2003)

Optical absorption - response function

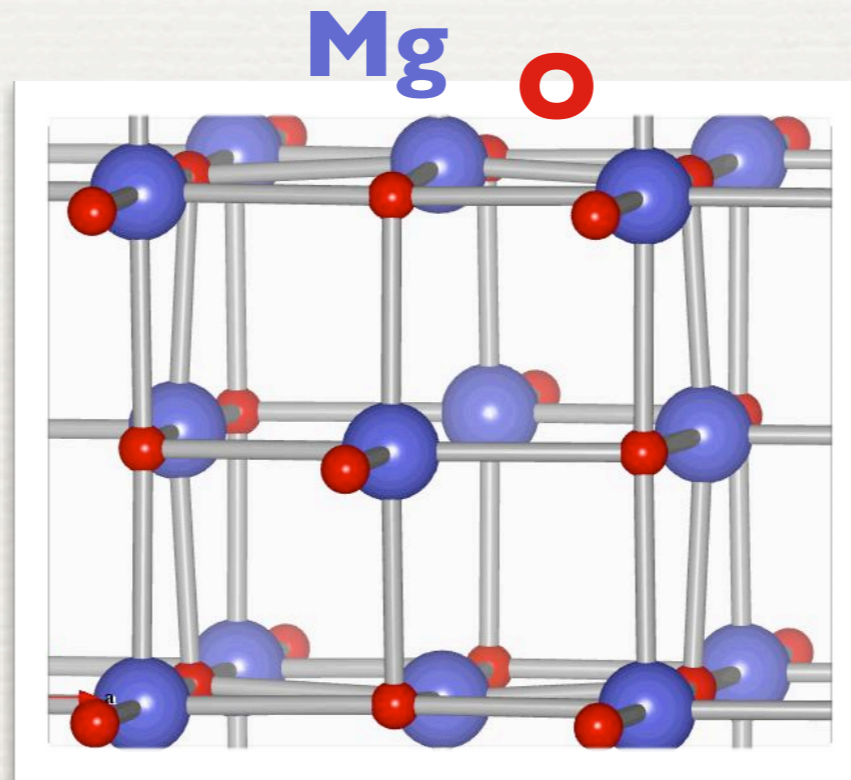


- BSE creates bound exciton and shifts spectral weight

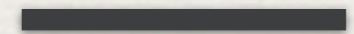
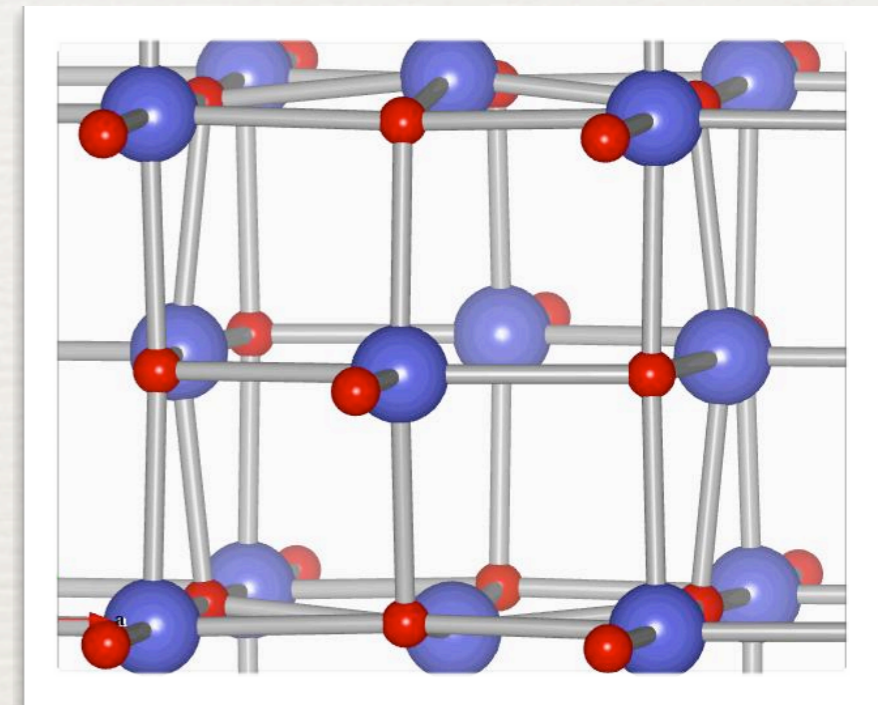
F-center: nomenclature



F-center

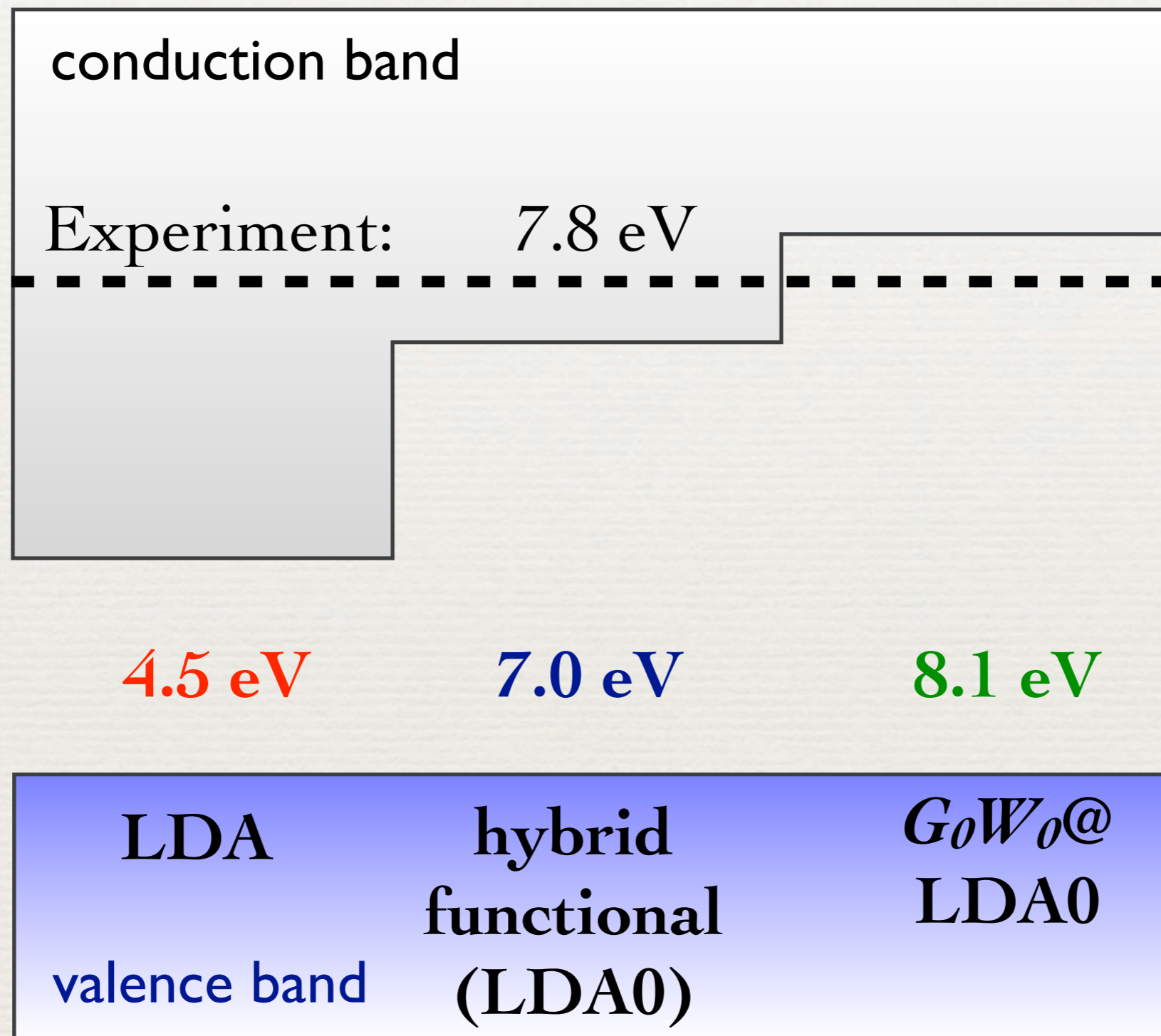


F⁺-center



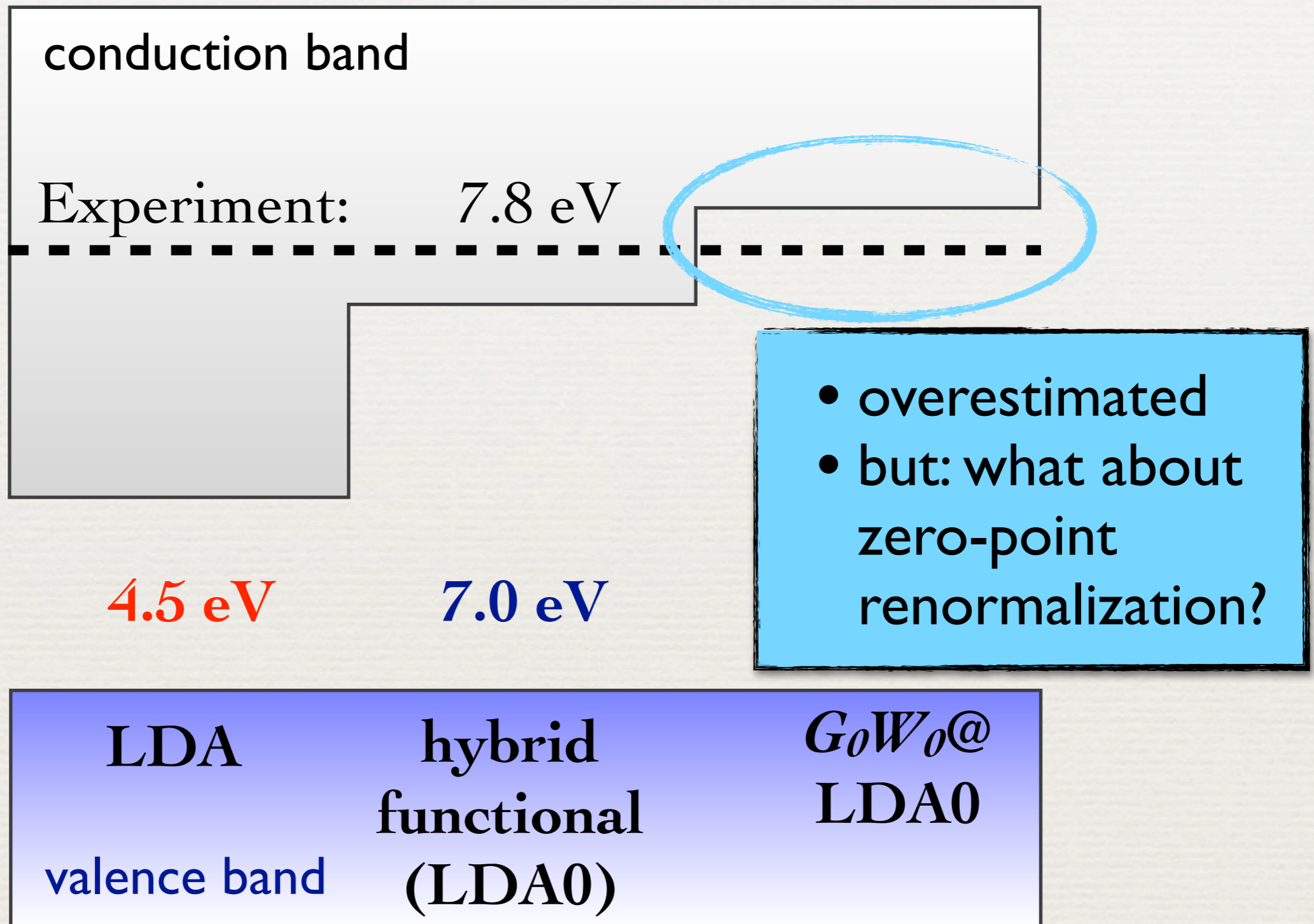
F²⁺-center

Getting the band gap of MgO right



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

Getting the band gap of MgO right

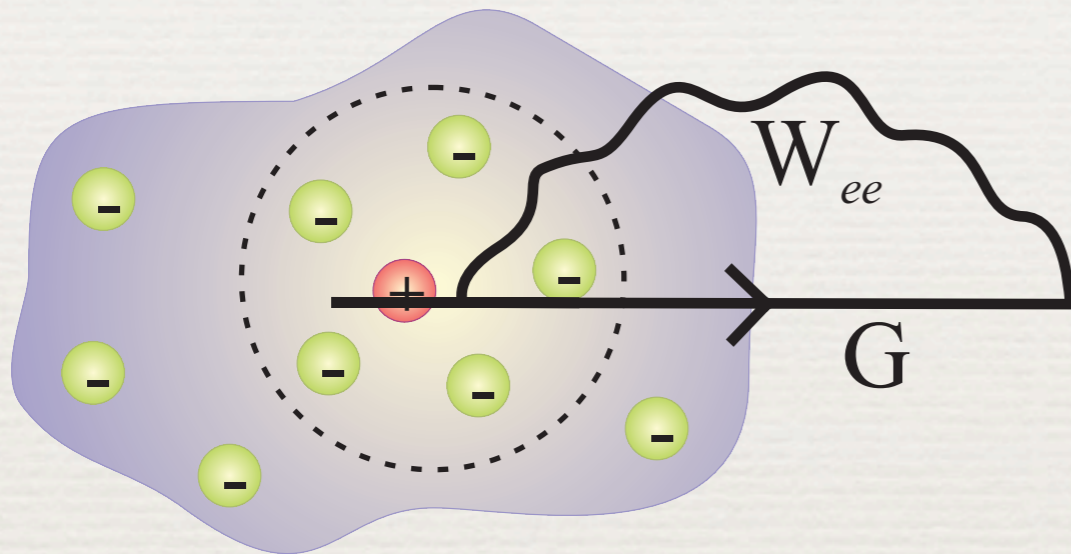


Exp.: R. C. Whited and W. C. Walker, Phys. Rev. Lett. 22, 1428 (1969)

Electron-phonon interaction

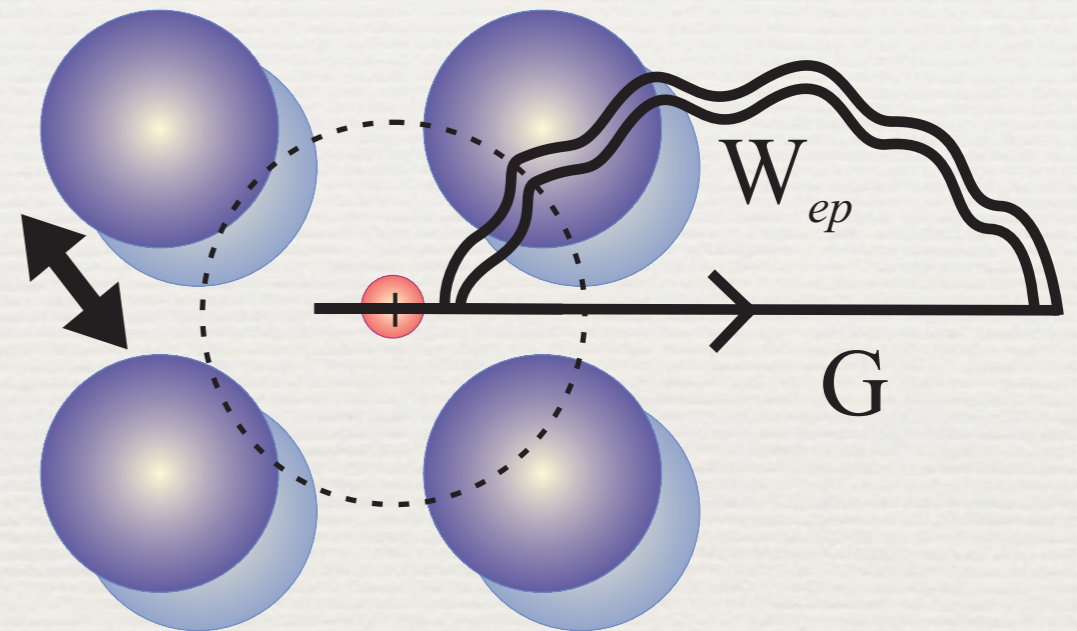
electron-electron

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



electron-phonon

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



**Renormalizes electron/hole states!
Also at zero temperature.**

Renormalizing electronic states

band gap renormalization

0.3 eV

- with Fröhlich model for e-p coupling

for comparison: experiment

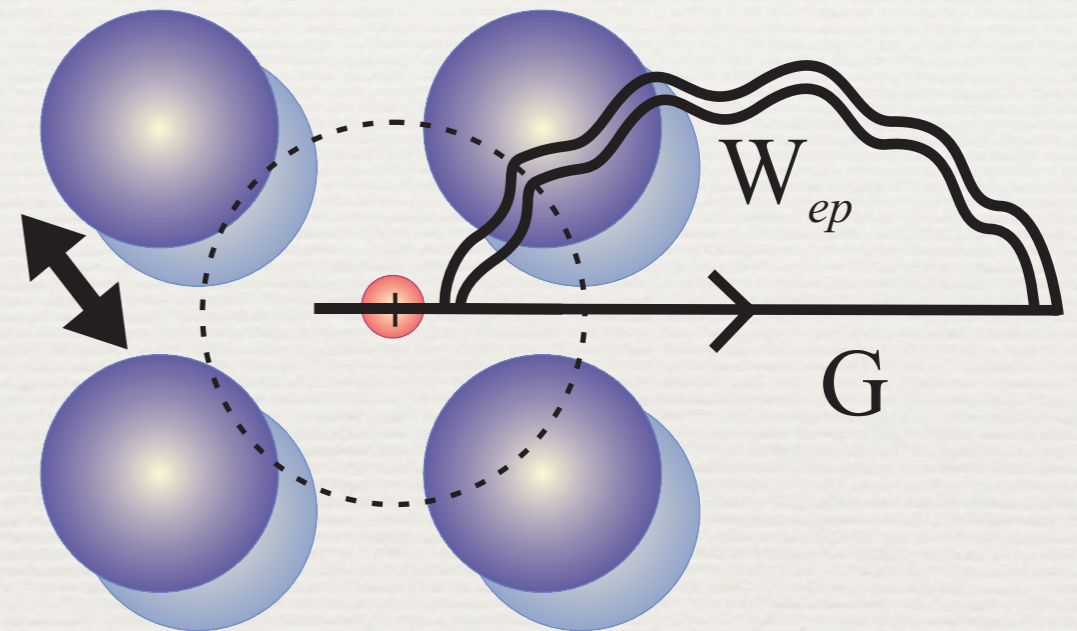
diamond: **0.37 eV**

silicon: **0.06 eV**

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

electron-phonon

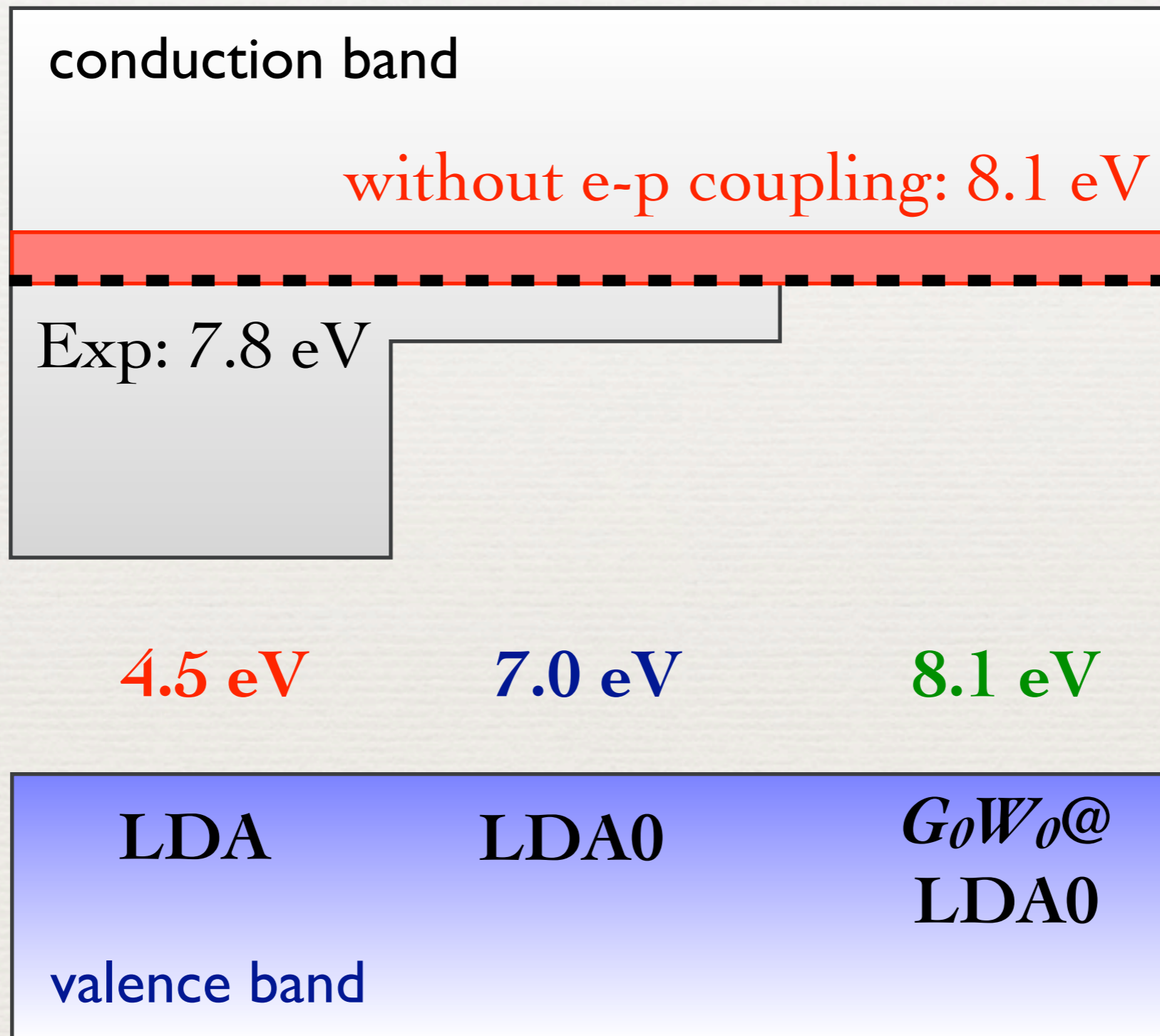
$$\Sigma_{ep} = GW_{ep} :$$



**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



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

G₀W₀@LDA0:

5.40 eV

5.48 eV

BSE binding energy:

0.45 eV

0.56 eV

GW-BSE:

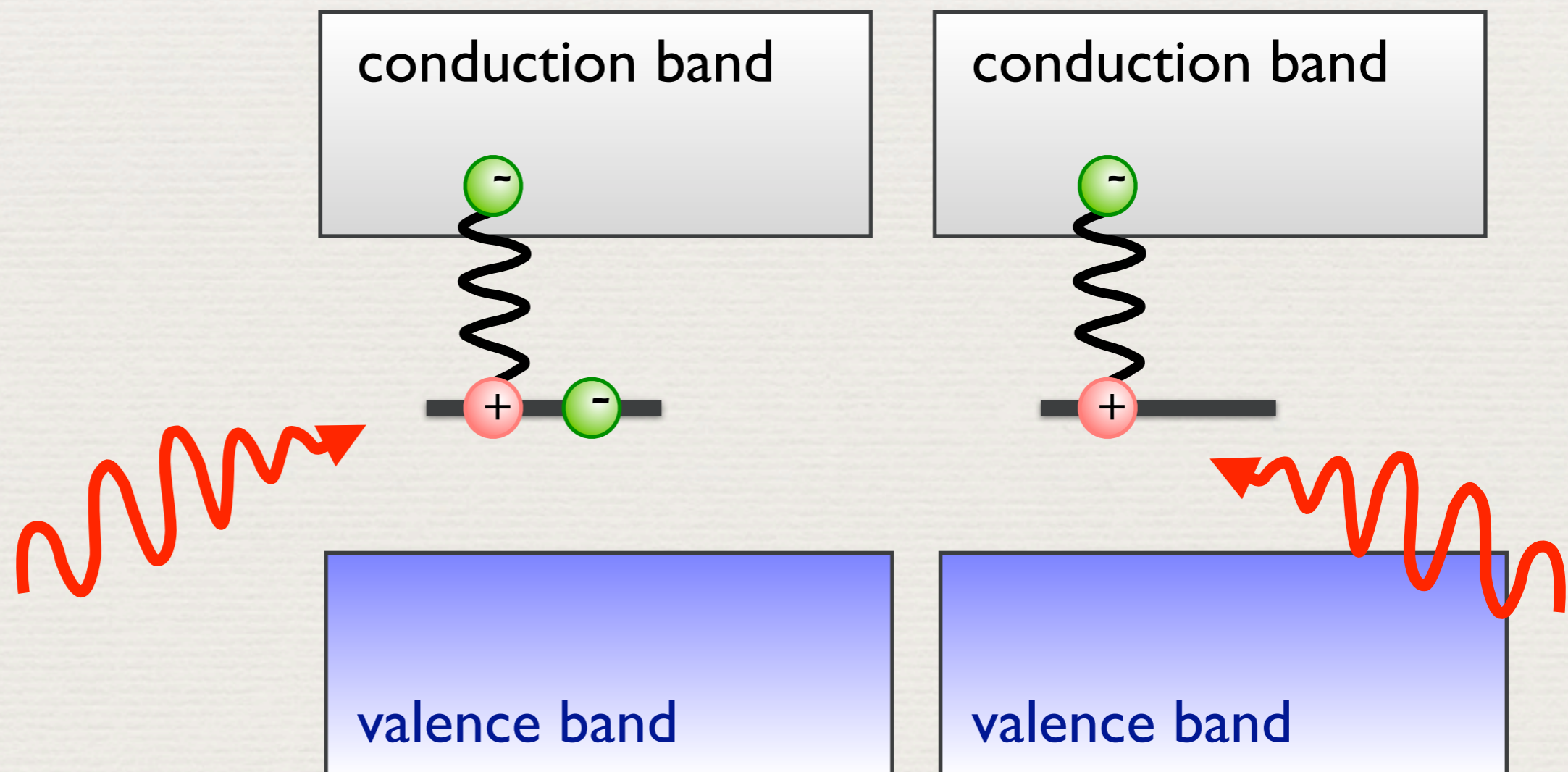
4.96 eV

4.92 eV

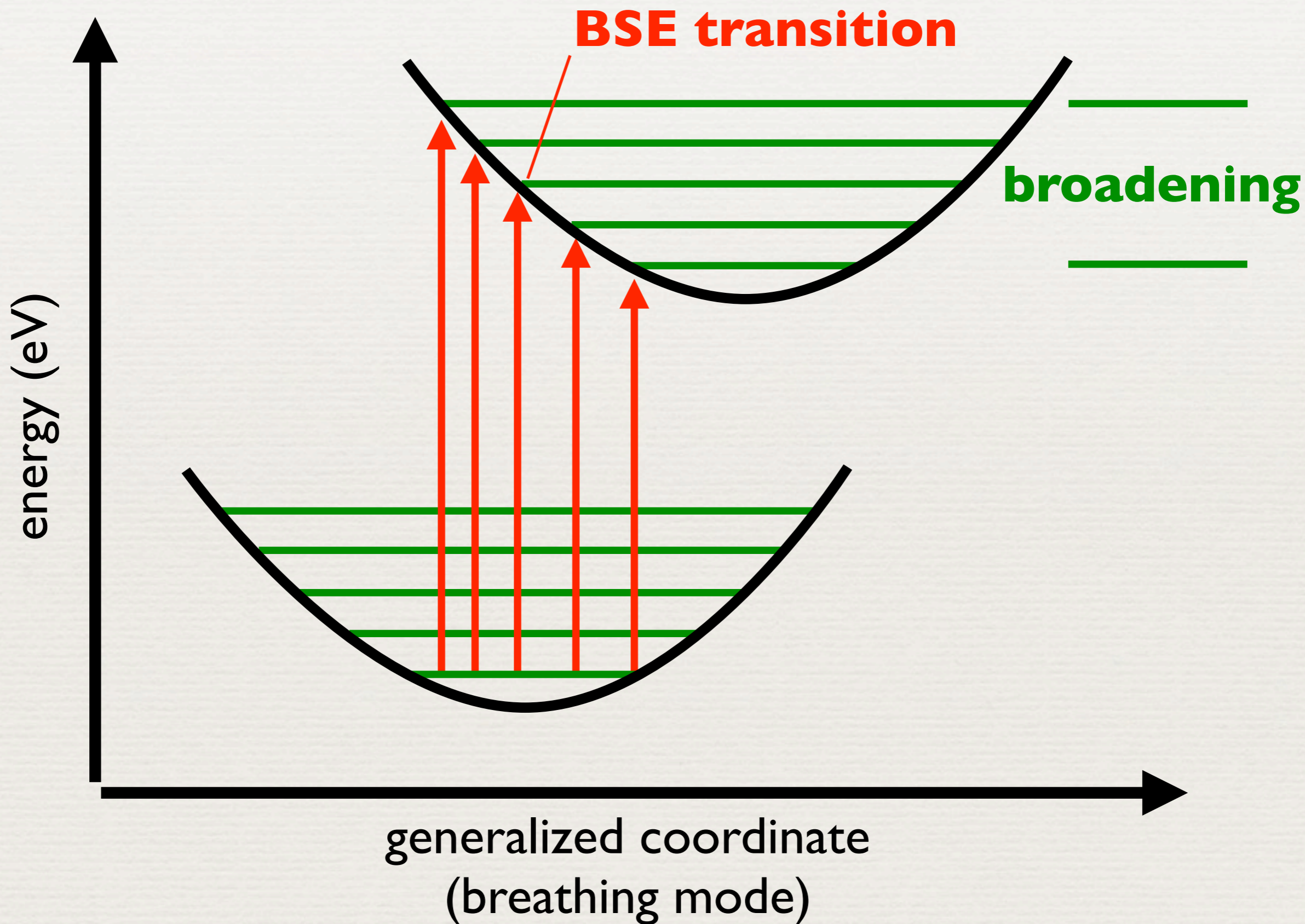
Experiment:

5.00 eV

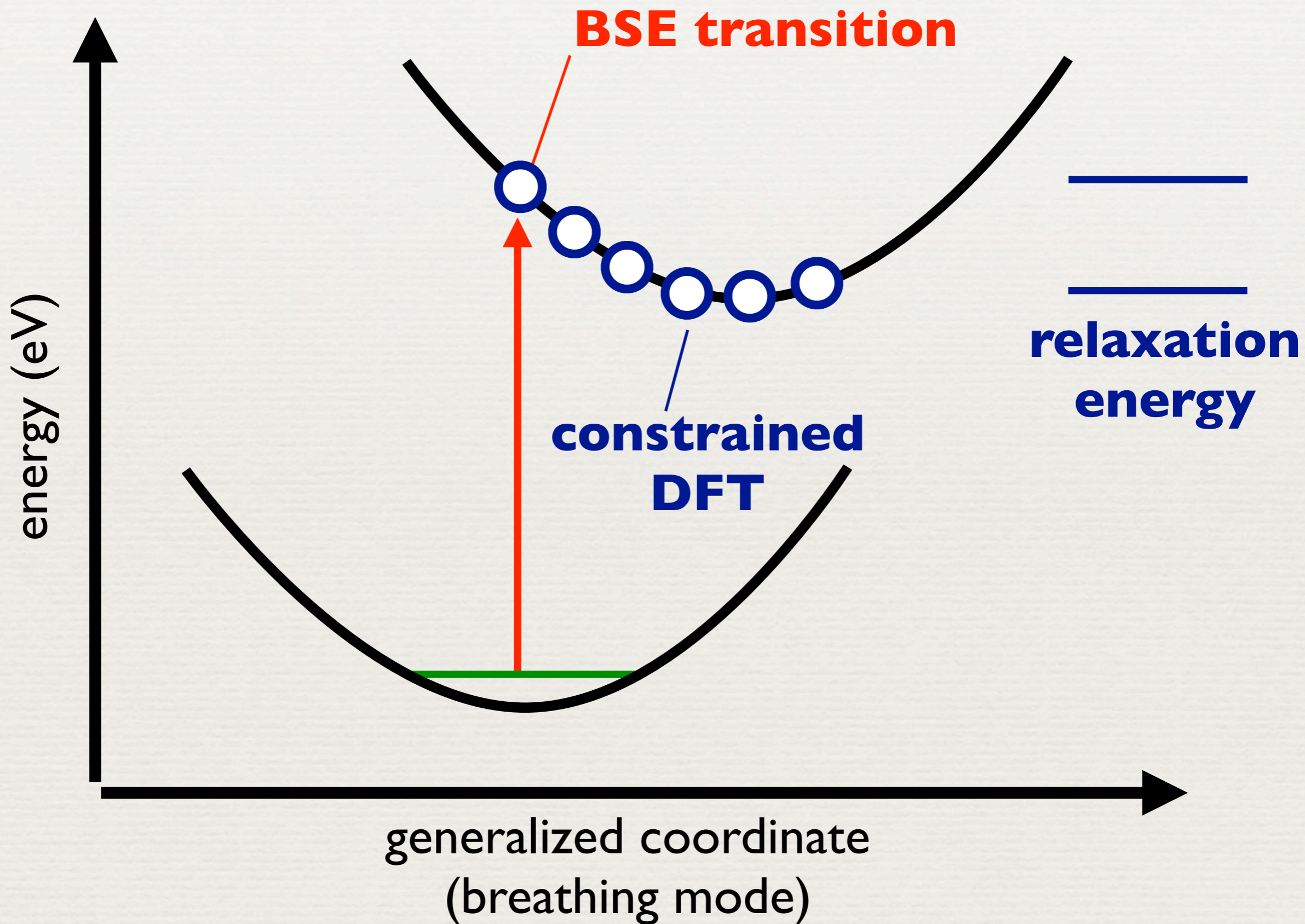
4.95 eV



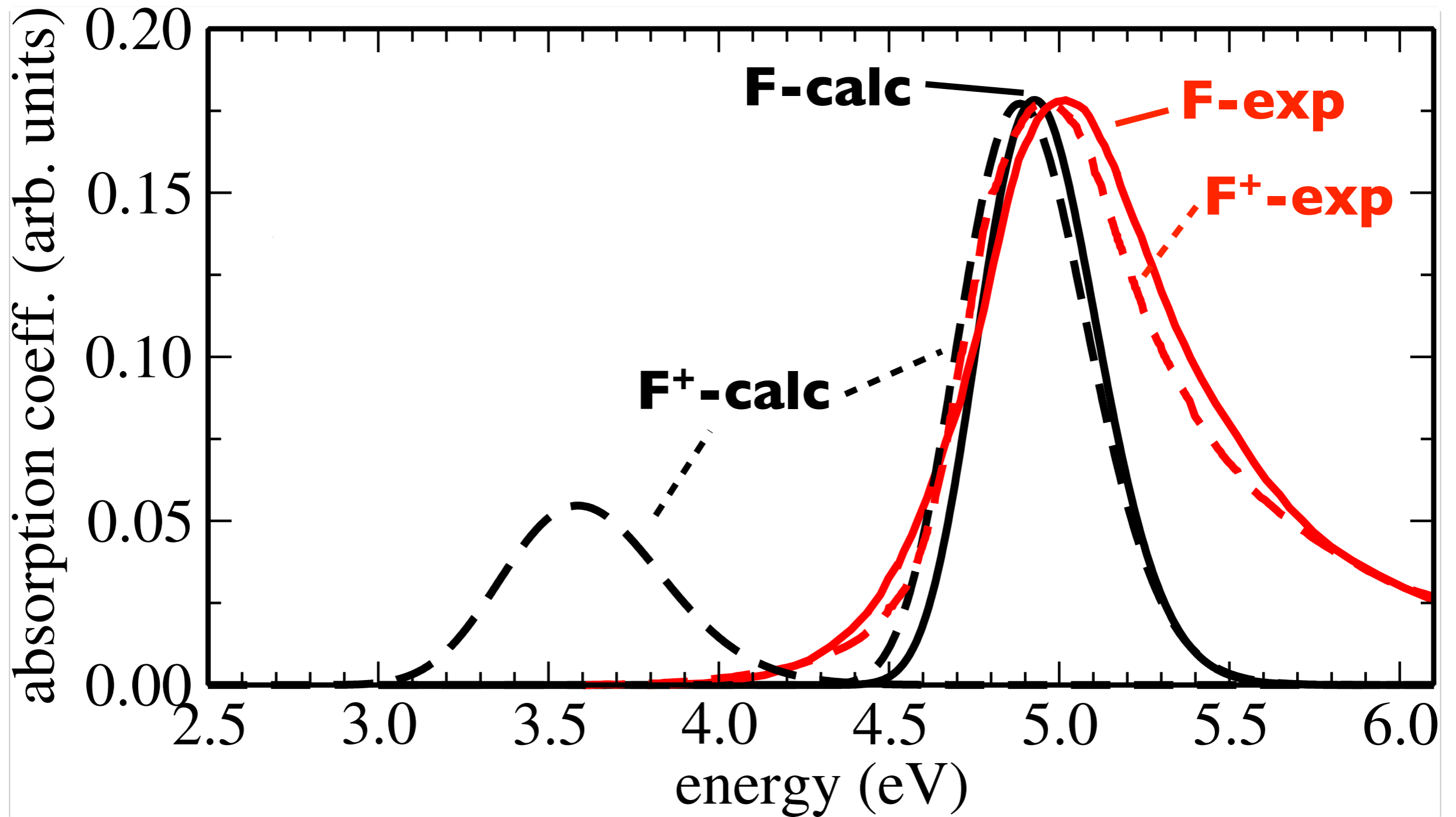
F-center: Peak broadening



F-center: Peak broadening



F-center: Optical absorption spectra



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: Optical absorption spectra

Emission

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

Instead, experimentally:

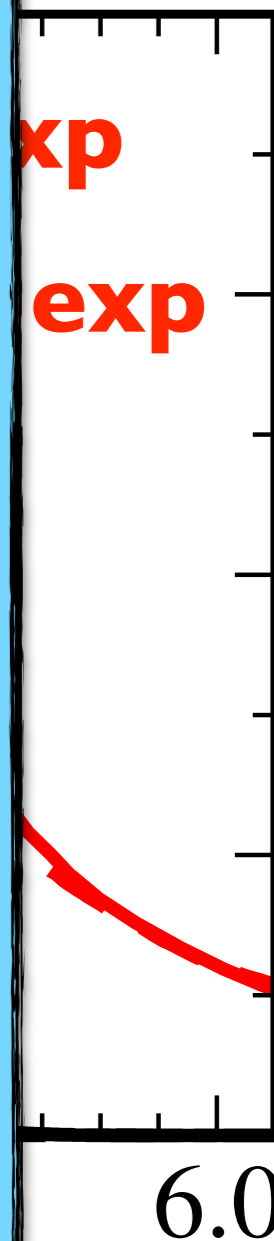
F-center 2.3 - 2.4 eV

F⁺-center 3.1 - 3.2 eV

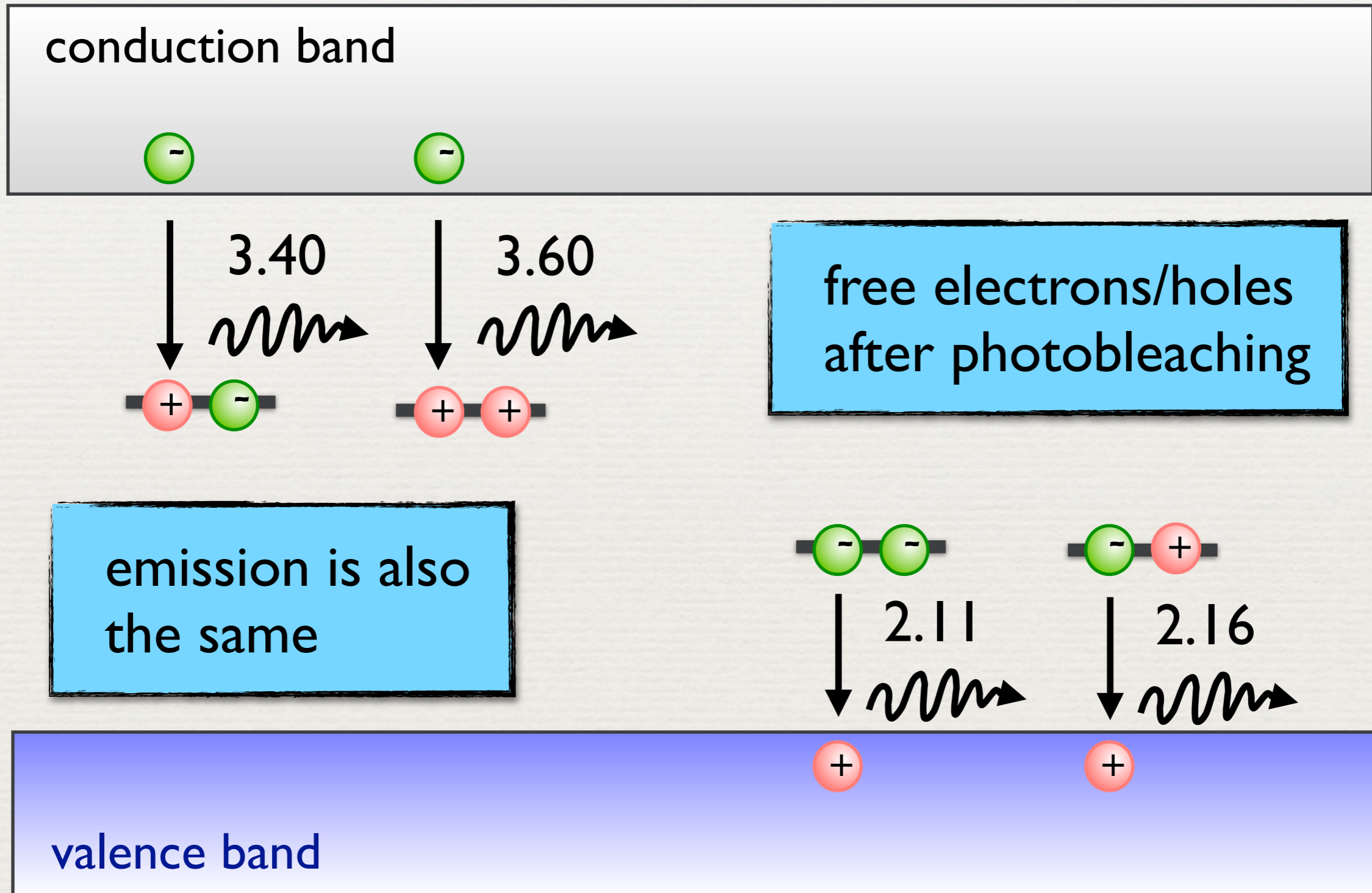
see e.g. G. H. Rosenblatt *et al*, Phys. Rev. B 39, 10309 (1989)

absorption coeff. (arb. units)

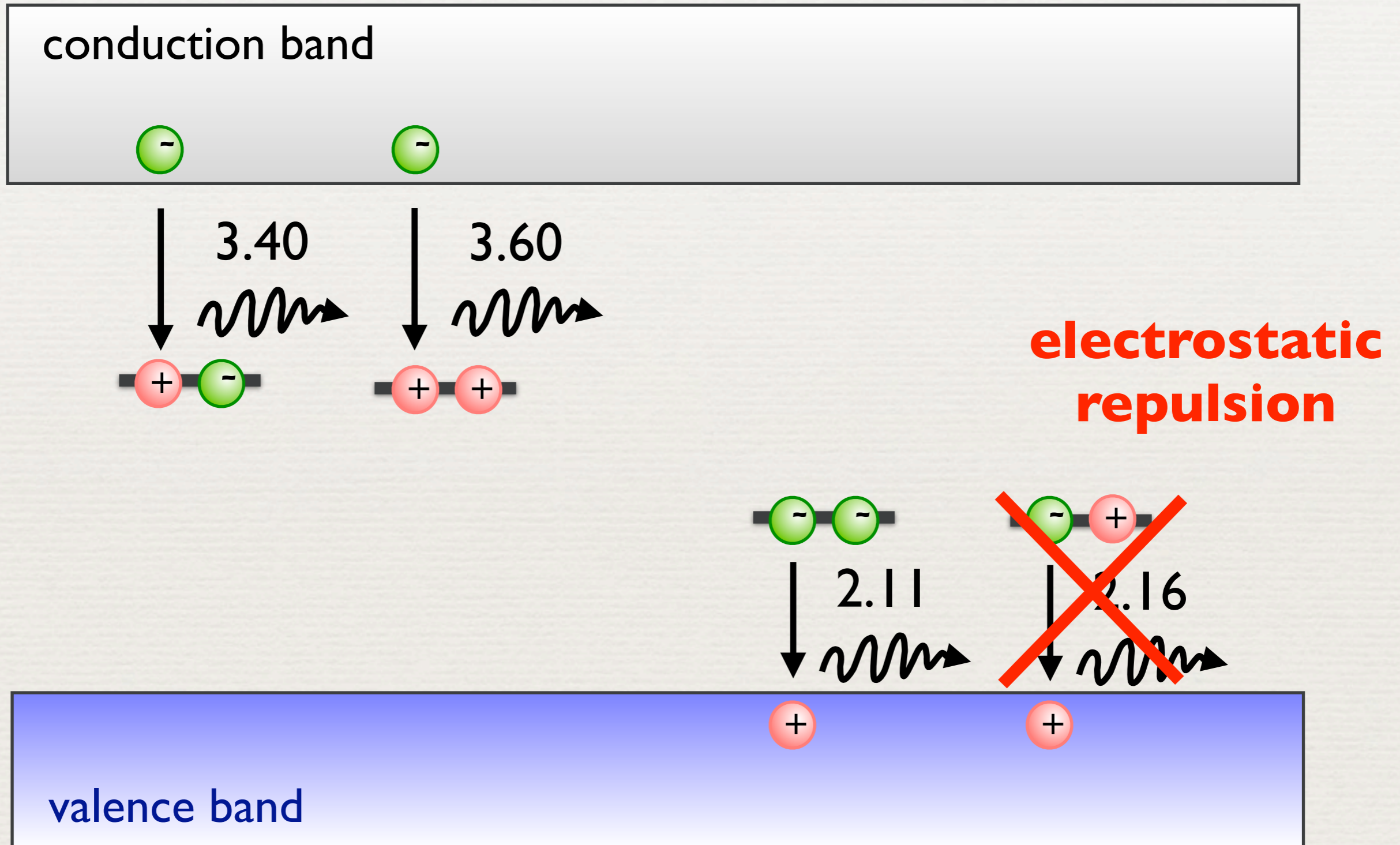
0.2
0.1
0.1
0.0
0.0



F-center: Emission

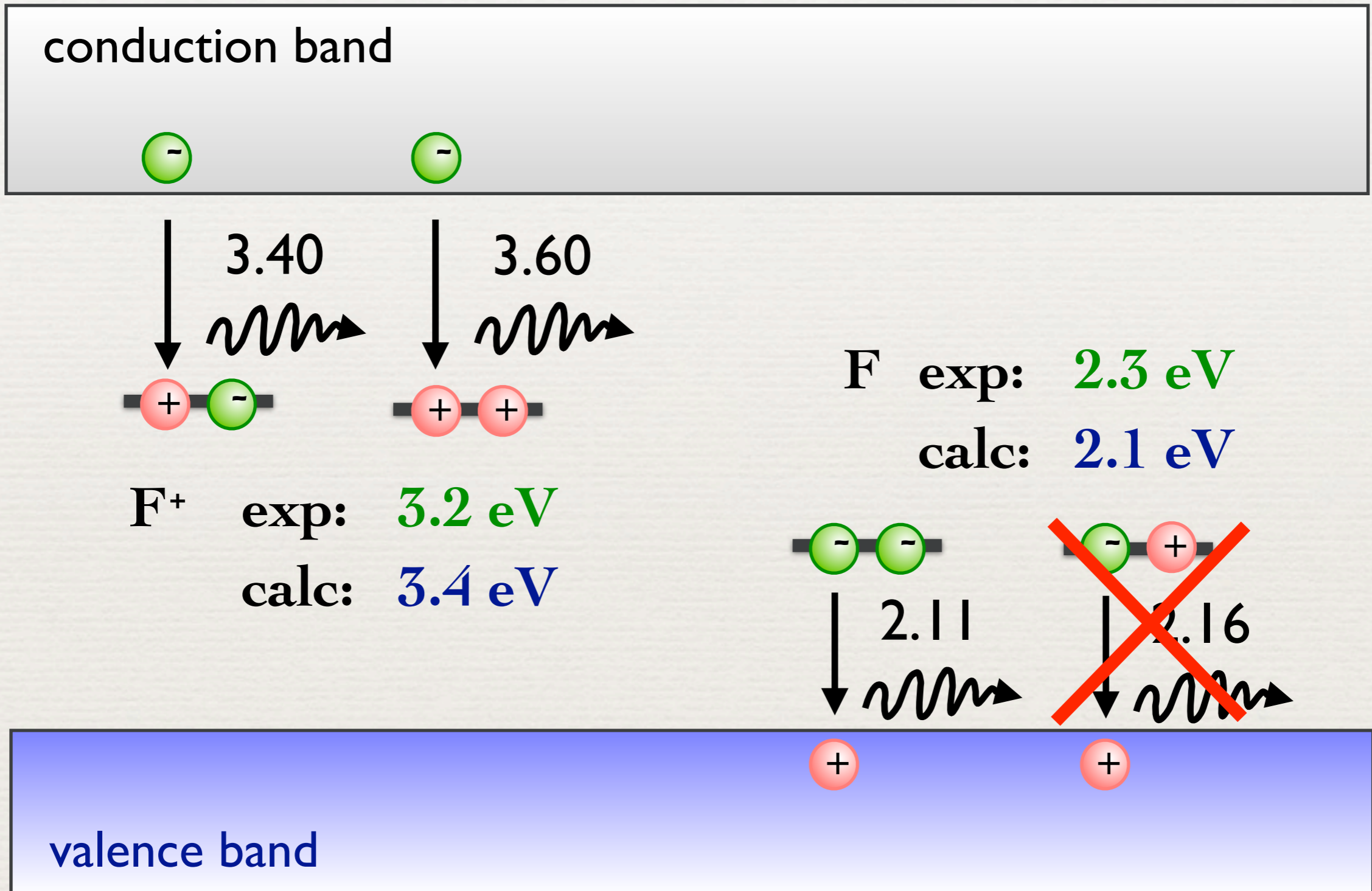


Reinterpretation of F-center emission



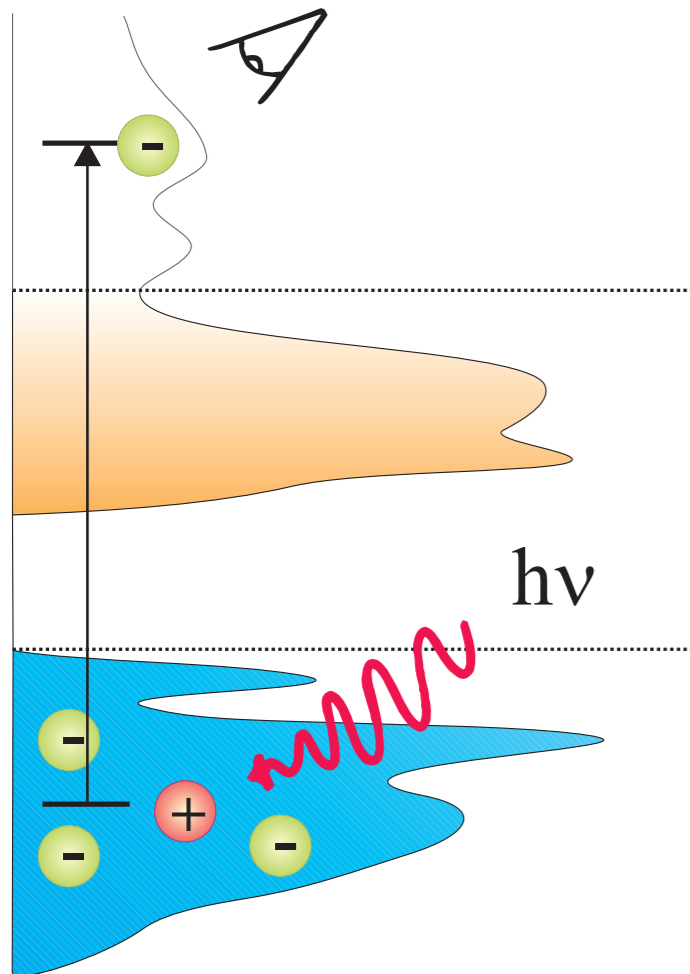
P. Rinke, A. Schleife, E. Kioupakis, A. Janotti, C. Rödl, F. Bechstedt, M. Scheffler, C. G. Van de Walle, Phys. Rev. Lett. 108, 126404 (2012)

Reinterpretation of F-center emission



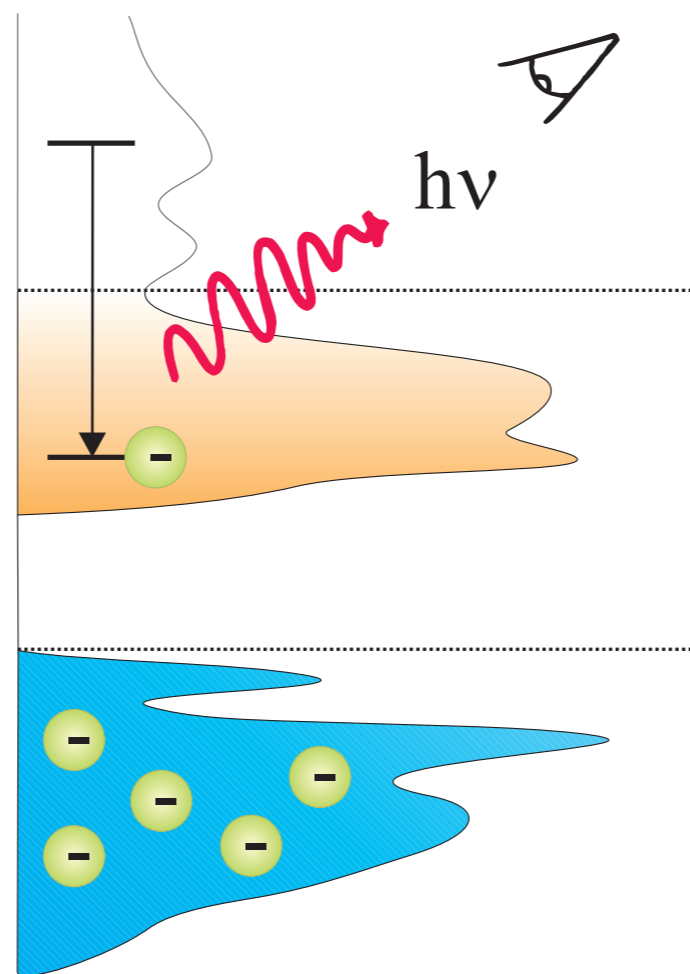
Summary

Photoemission



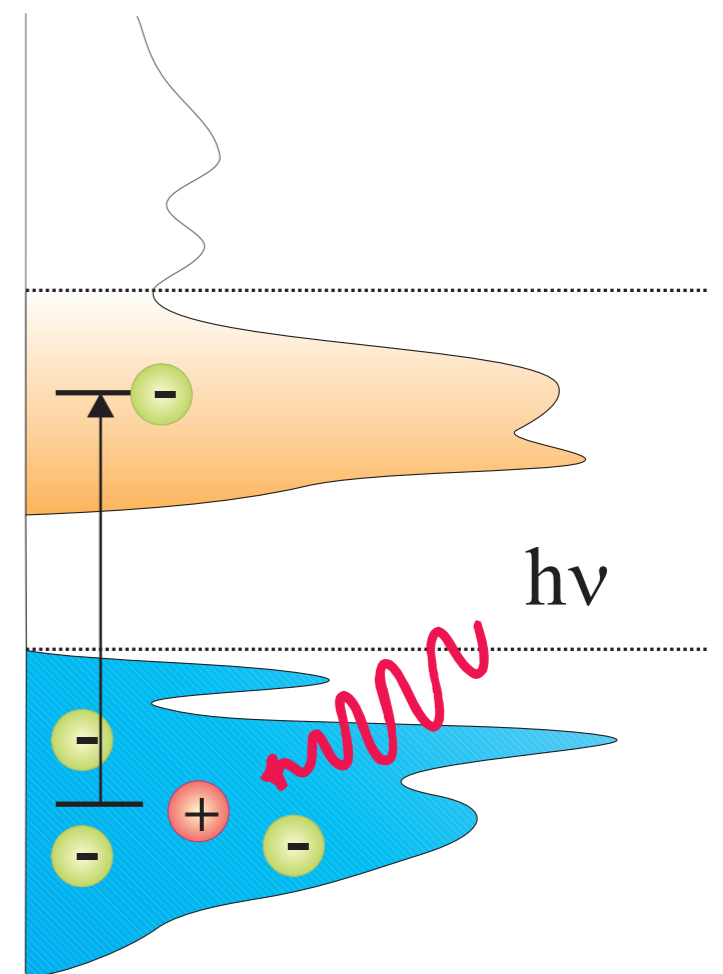
GW

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))

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

$n_{\mathbf{q}\nu}$: 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

