Many-body and *GW*

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School of Science

What we will learn today

Basic principles of electron spectroscopy

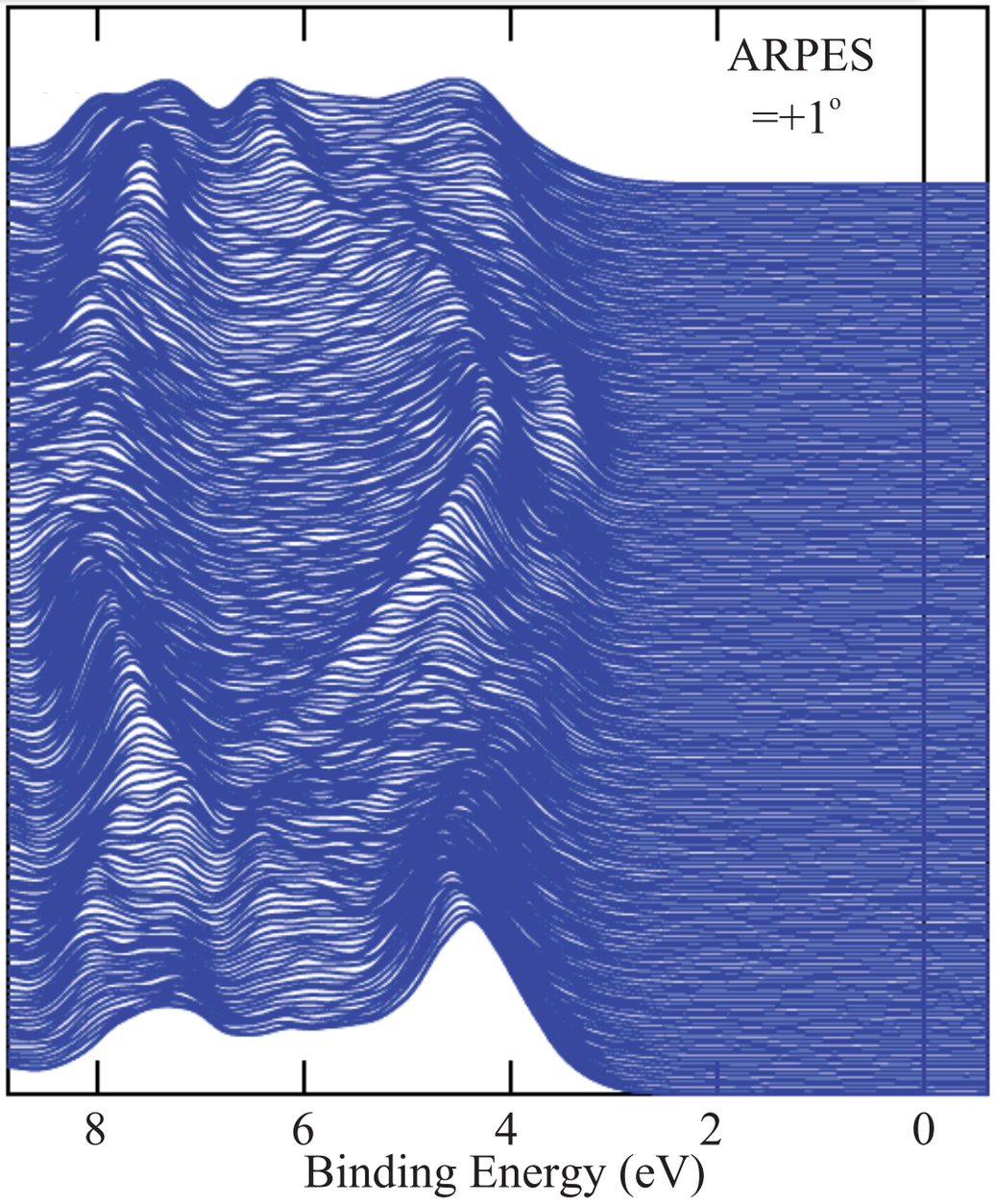
The Green's function and the self-energy

The *GW* approximation to the self-energy

Pros and cons of density-functional theory for electron spectroscopies

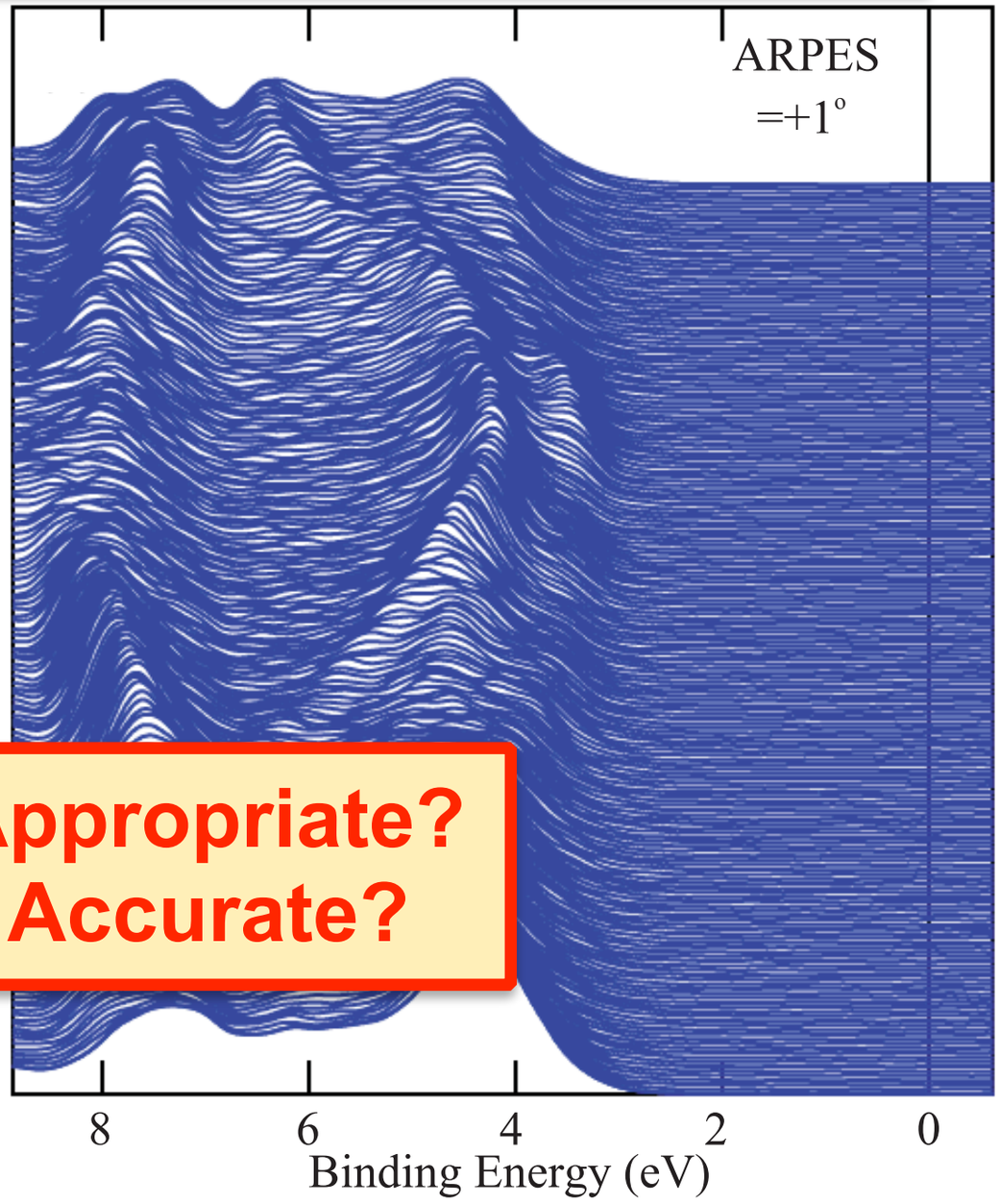
Spectroscopy and materials science

Experiment/Spectroscopy



Spectroscopy and materials science

Experiment/Spectroscopy

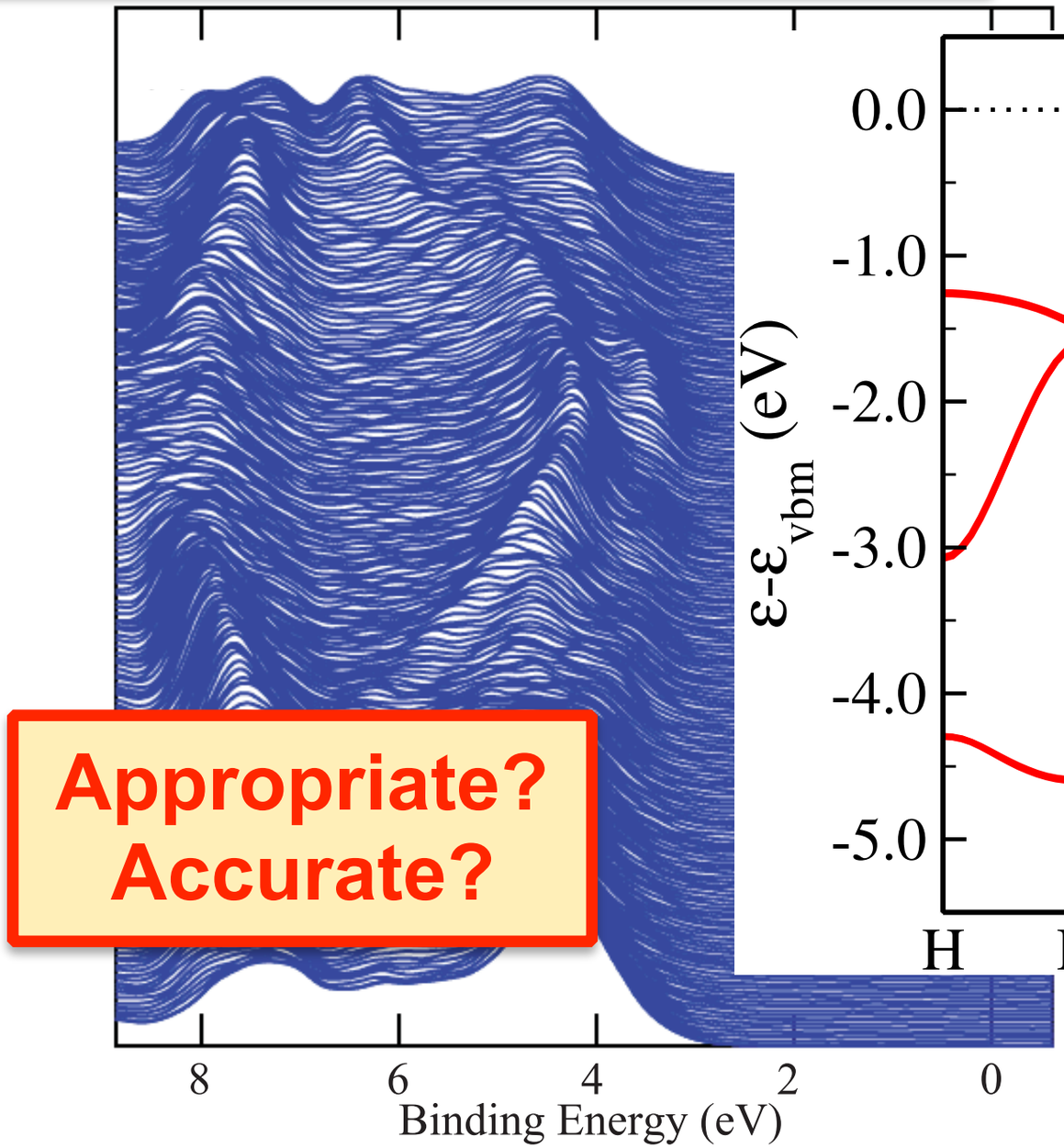


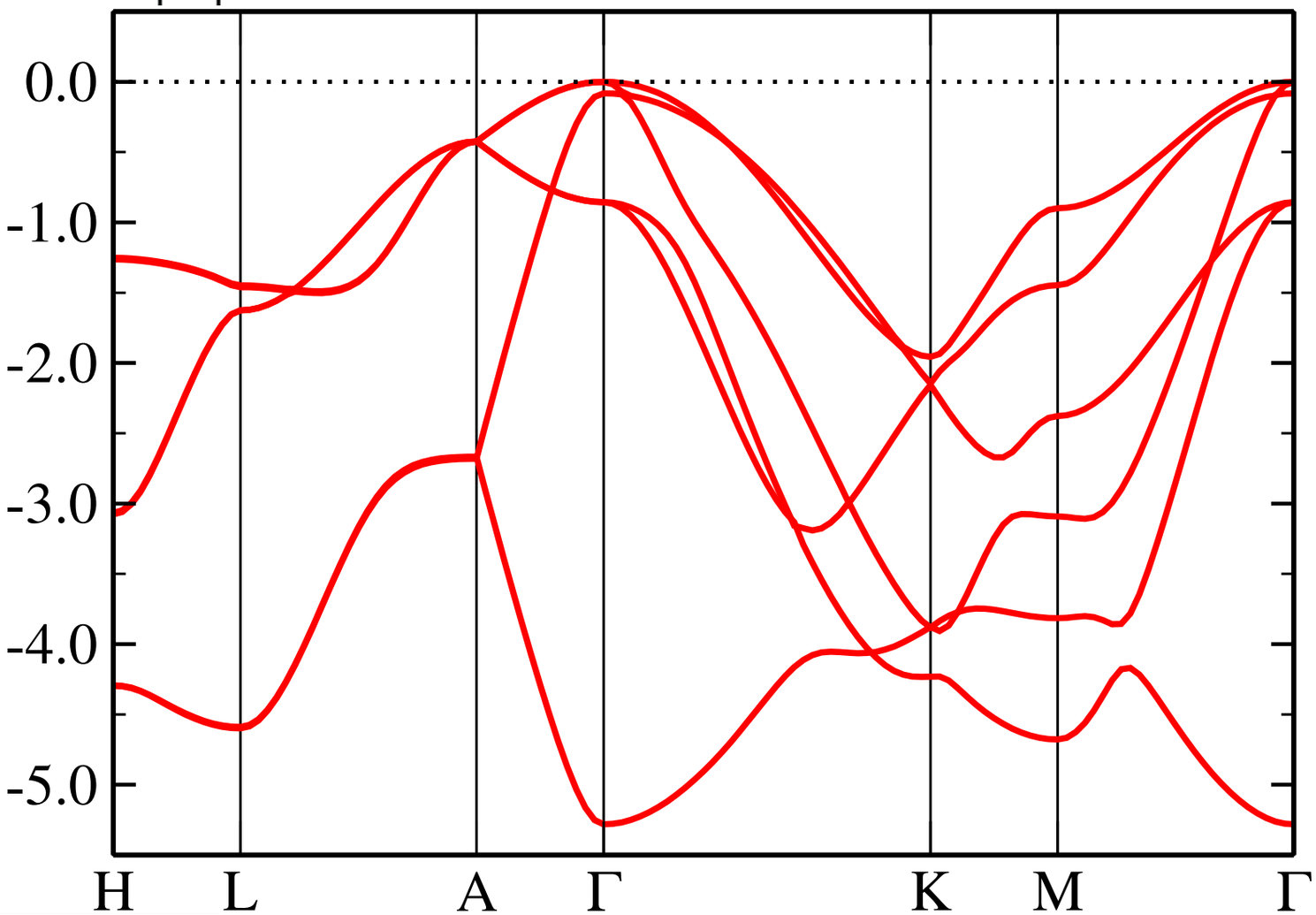
Appropriate?
Accurate?

Spectroscopy and materials science

Experiment/Spectroscopy

Theoretical Spectroscopy





Appropriate?
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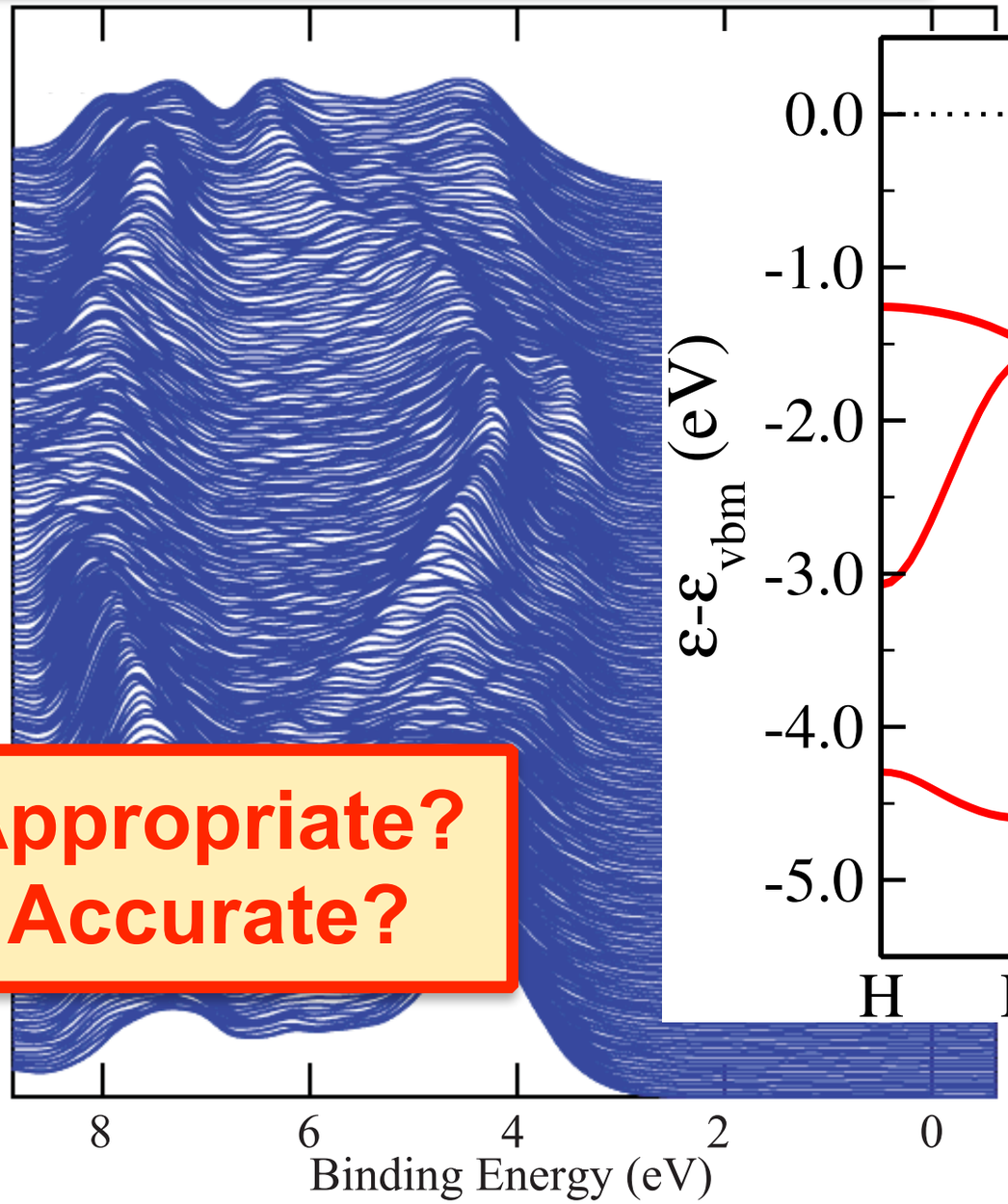
Spectroscopy and materials science

Experiment/Spectroscopy



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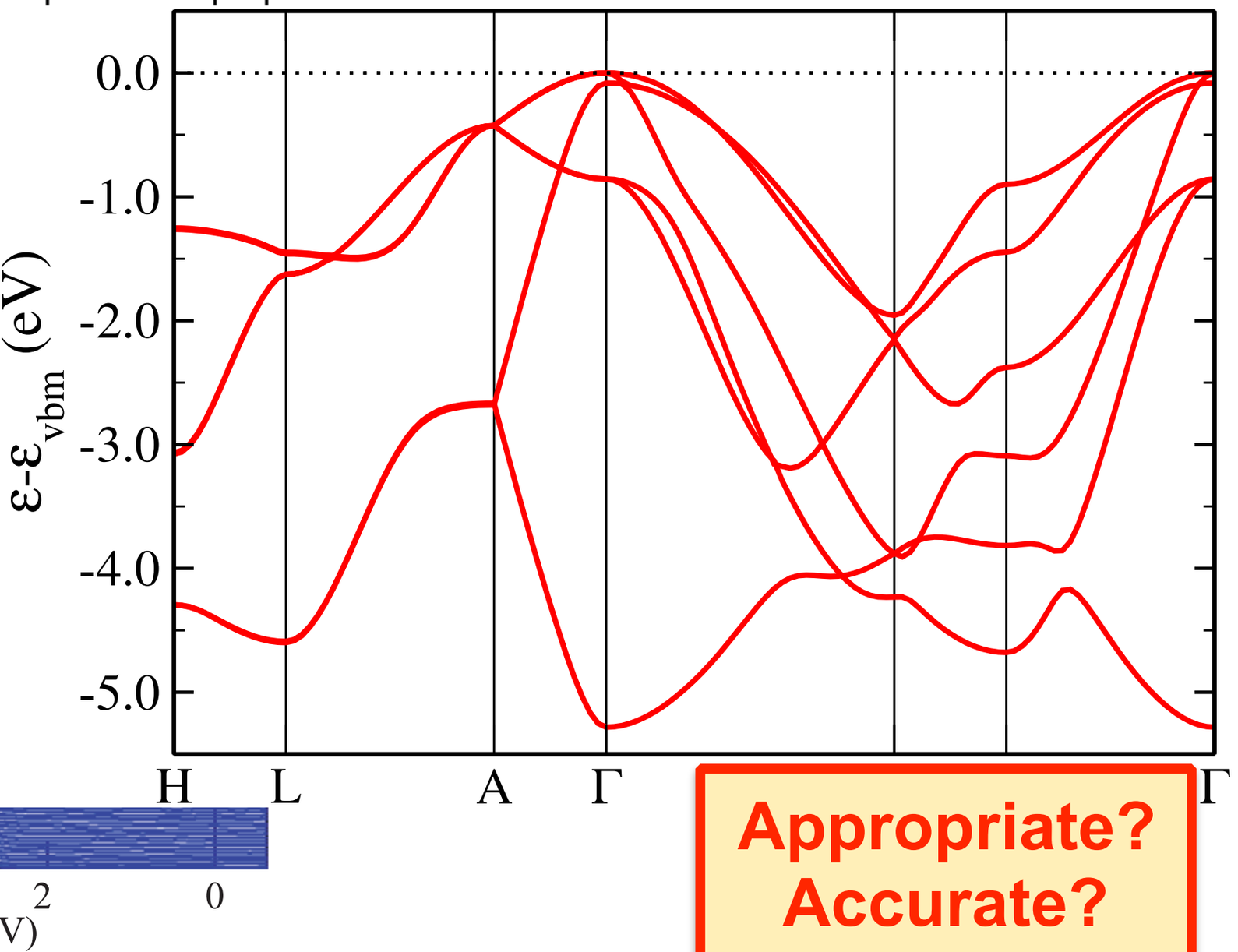
Theoretical Spectroscopy



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Accurate?

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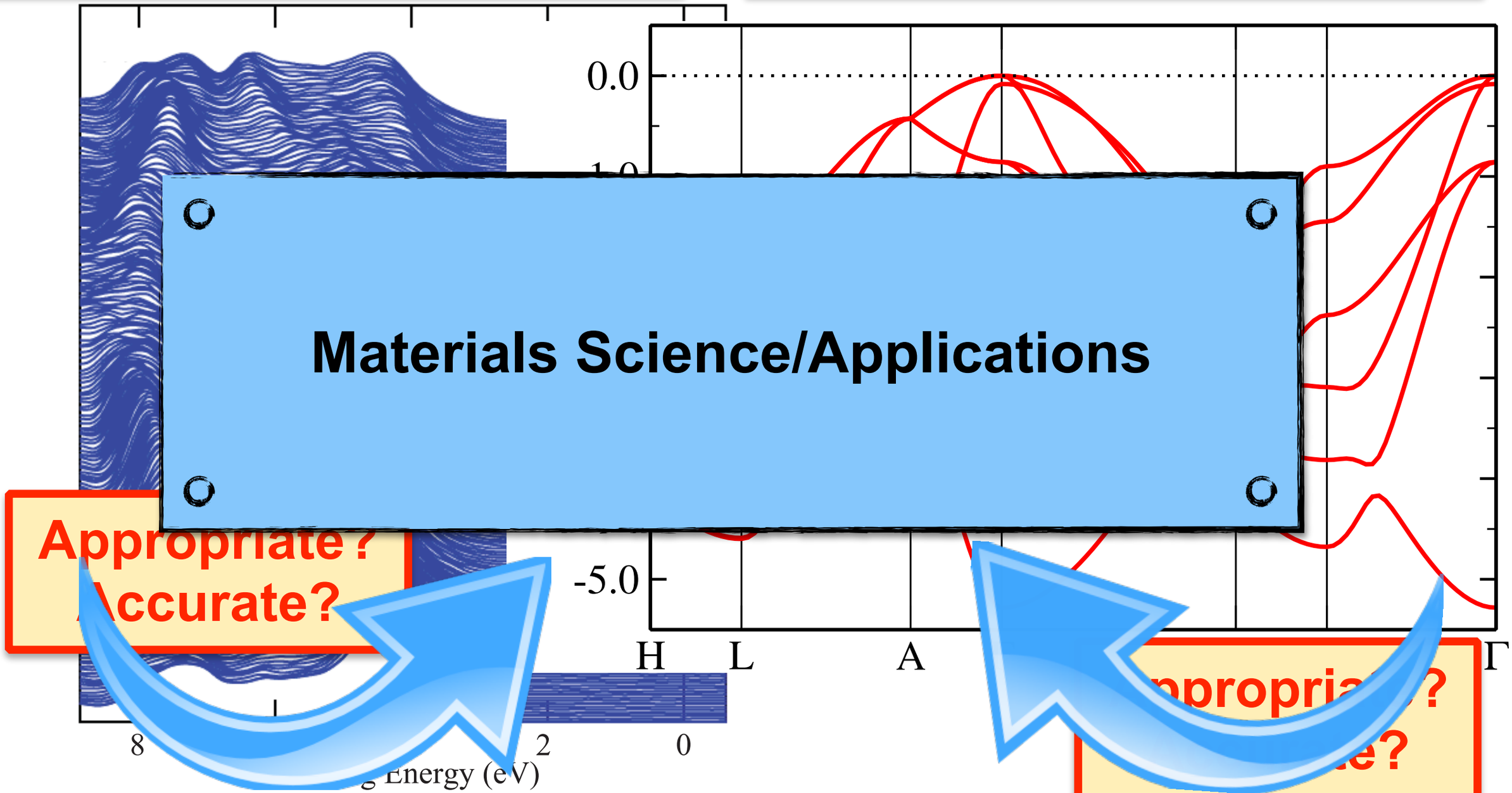
Spectroscopy and materials science

Experiment/Spectroscopy

Theoretical Spectroscopy



Materials Science/Applications

Appropriate?
Accurate?

Appropriate?
Accurate?

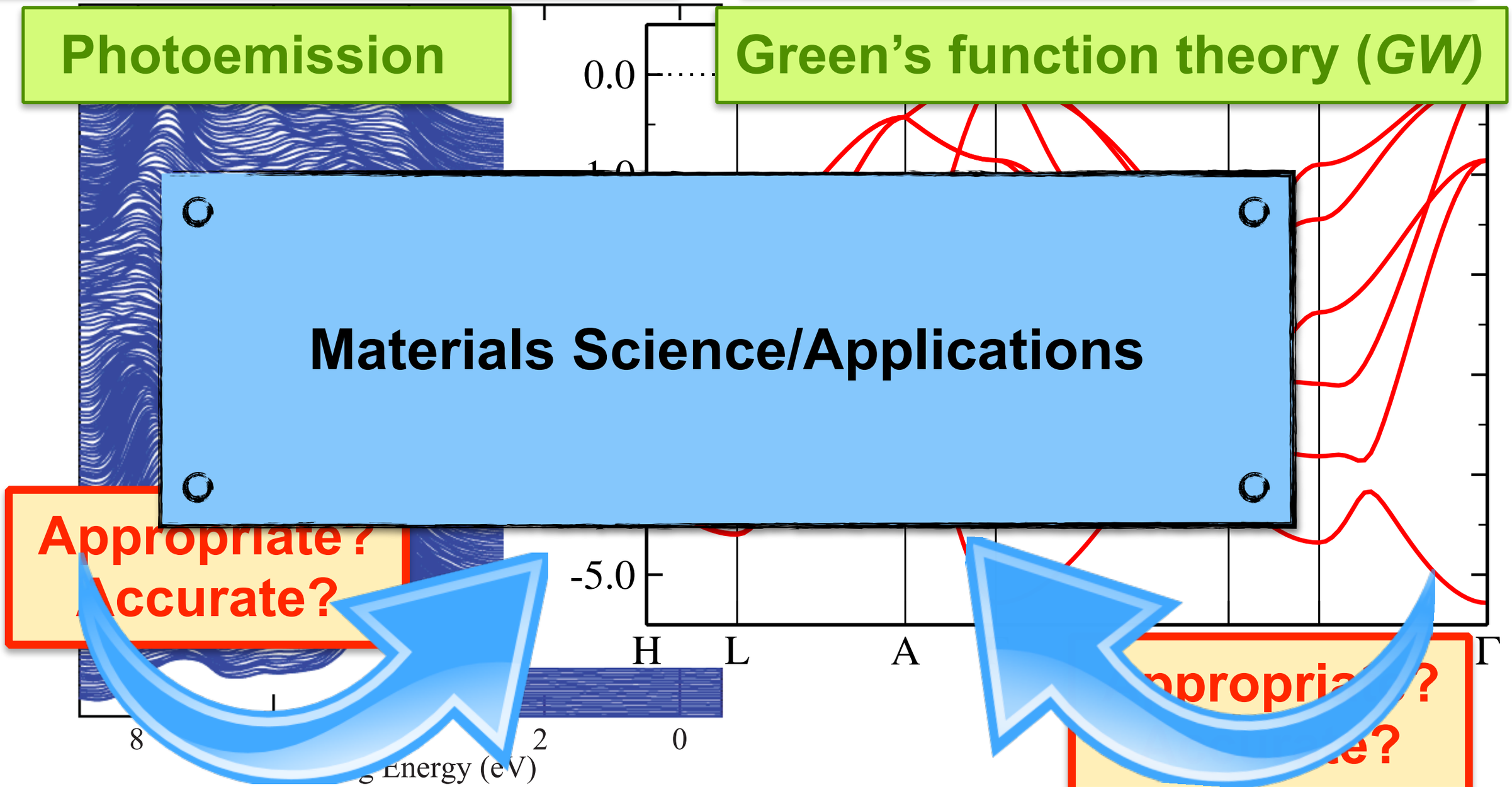
Spectroscopy and materials science

Experiment/Spectroscopy

Theoretical Spectroscopy

Photoemission

Green's function theory (*GW*)



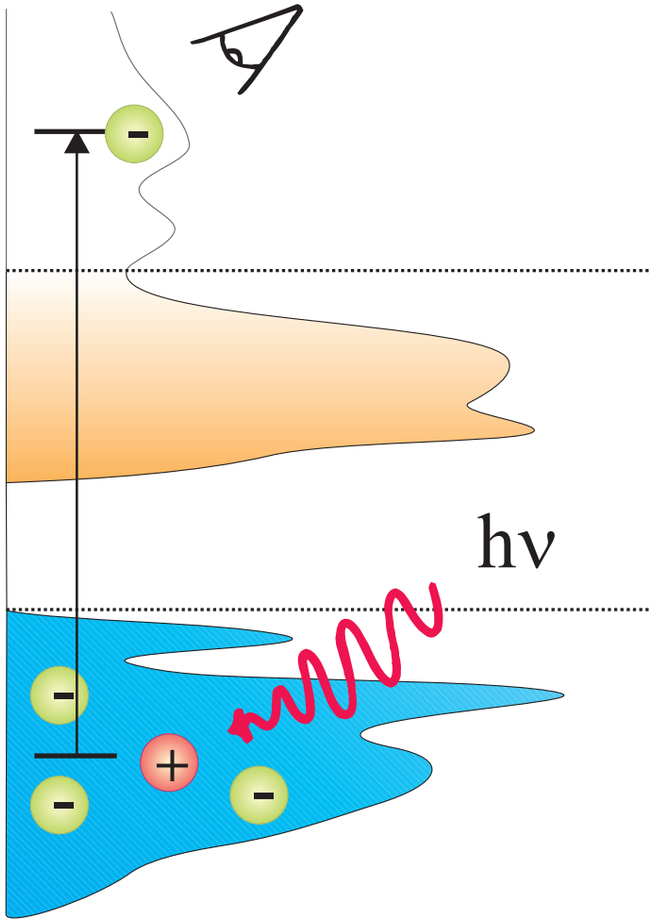
Materials Science/Applications

Appropriate?
Accurate?

Appropriate?
Accurate?

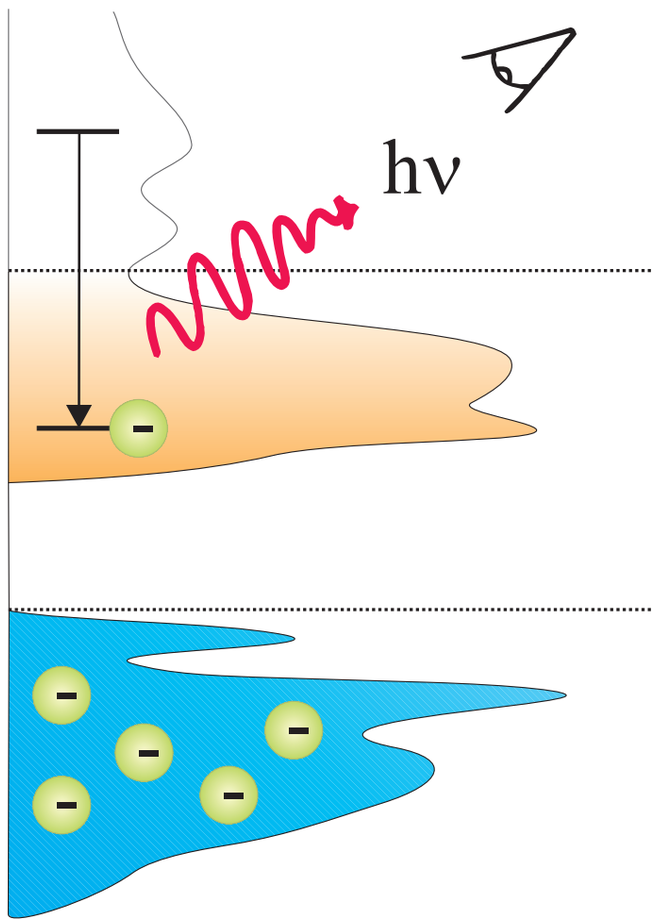
Spectroscopies

Photoemission



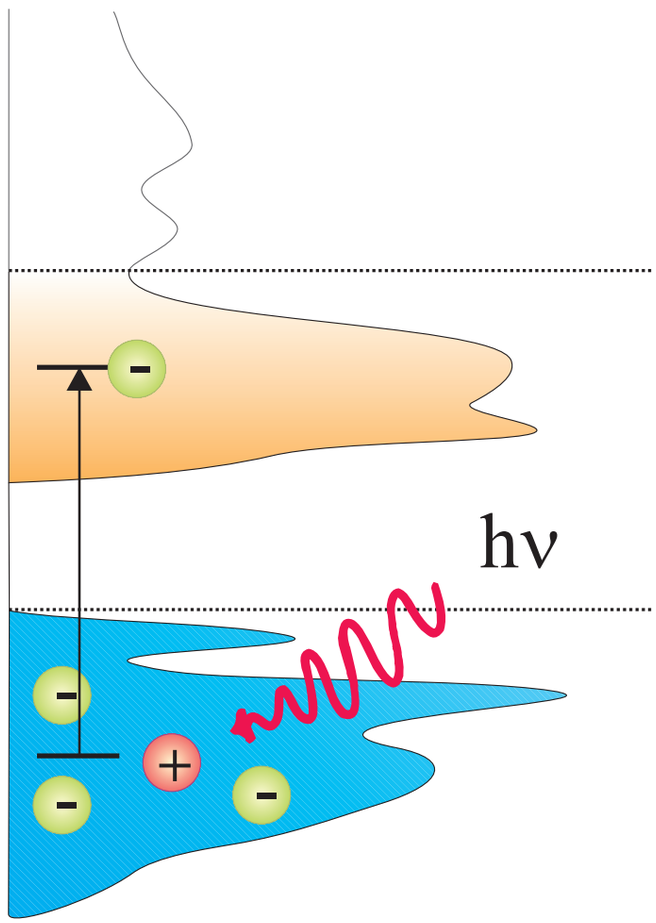
GW

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

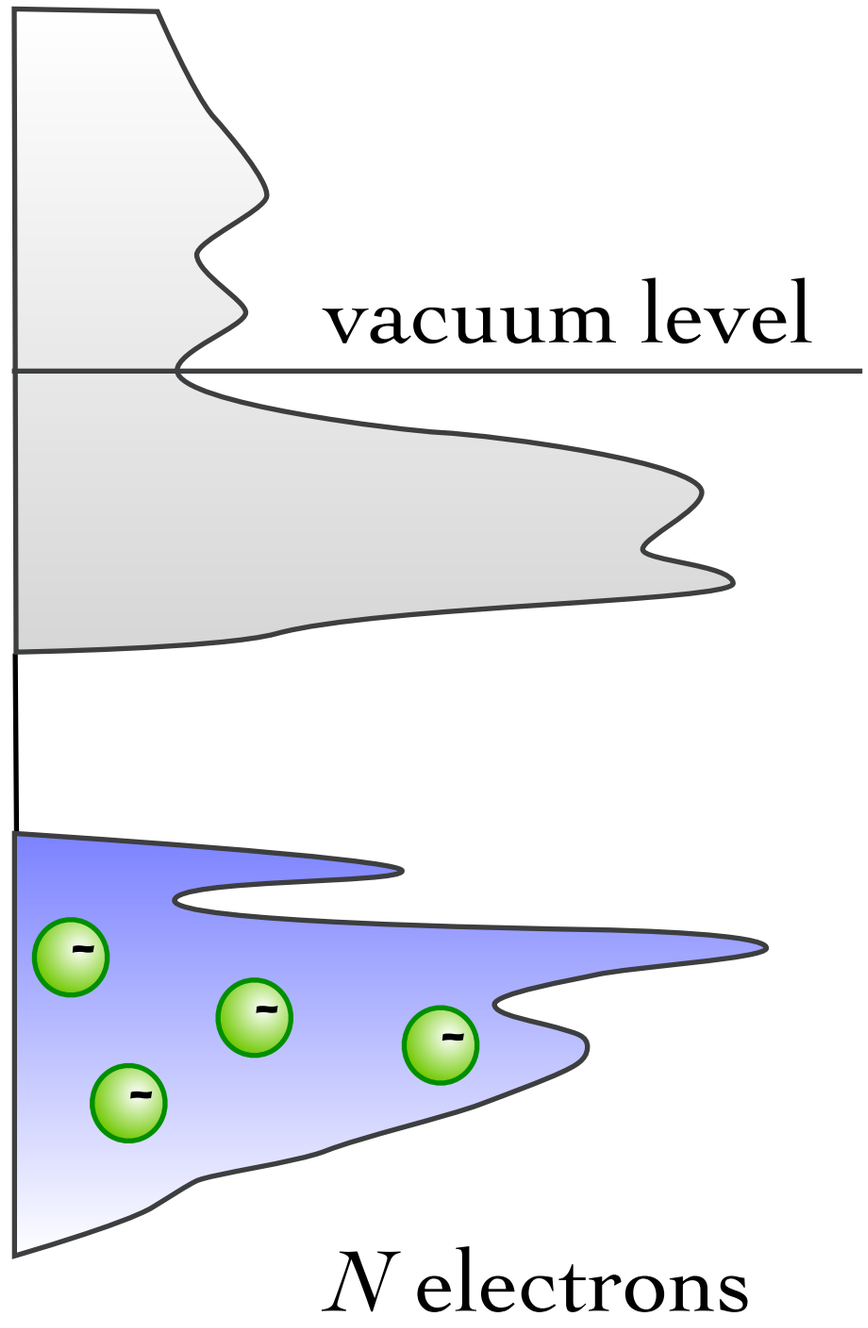


Photo-electron energies

Photoemission

annihilation operator

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

- electron removal

- removal energy

$$E(N)$$

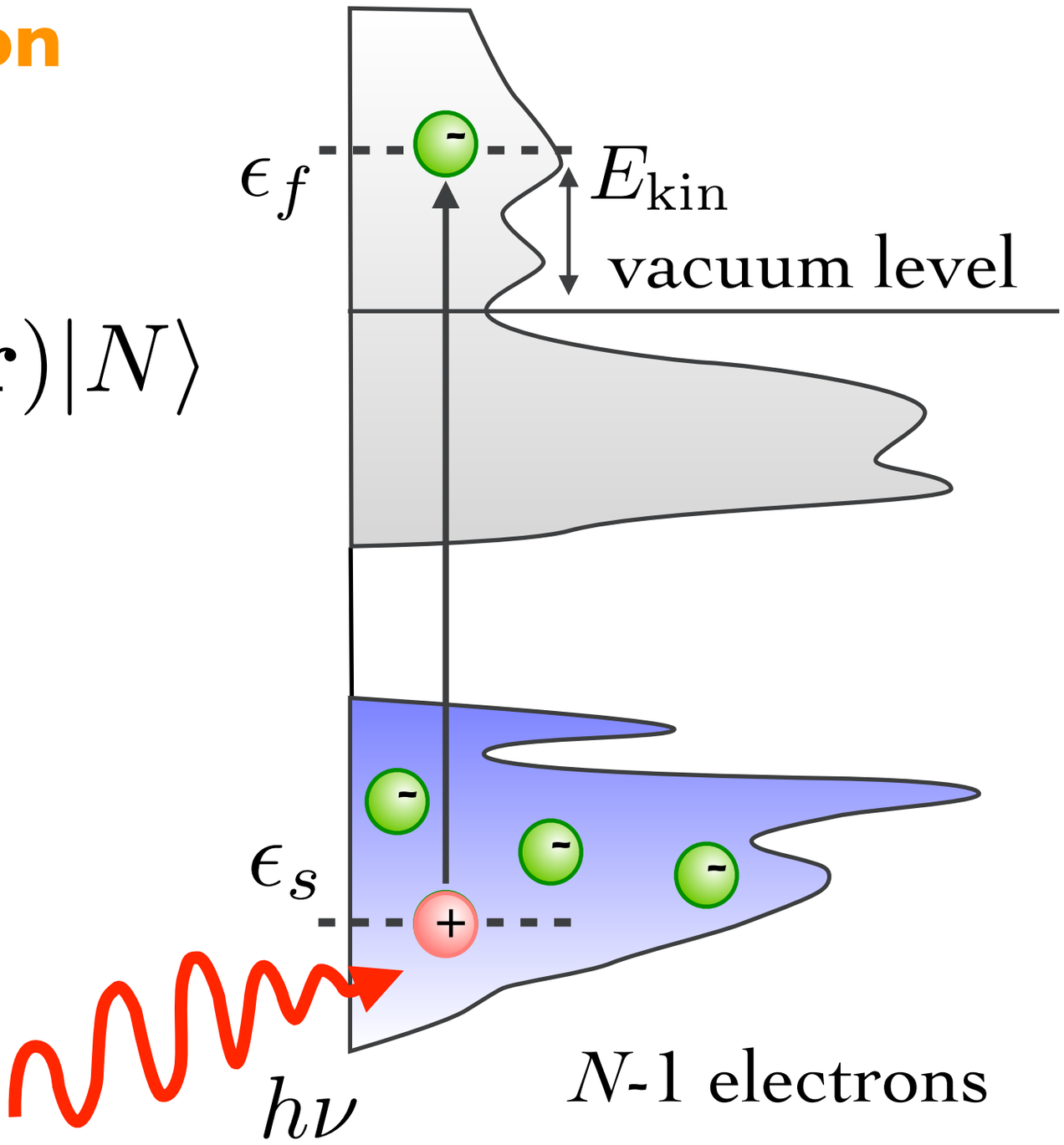


Photo-electron energies

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

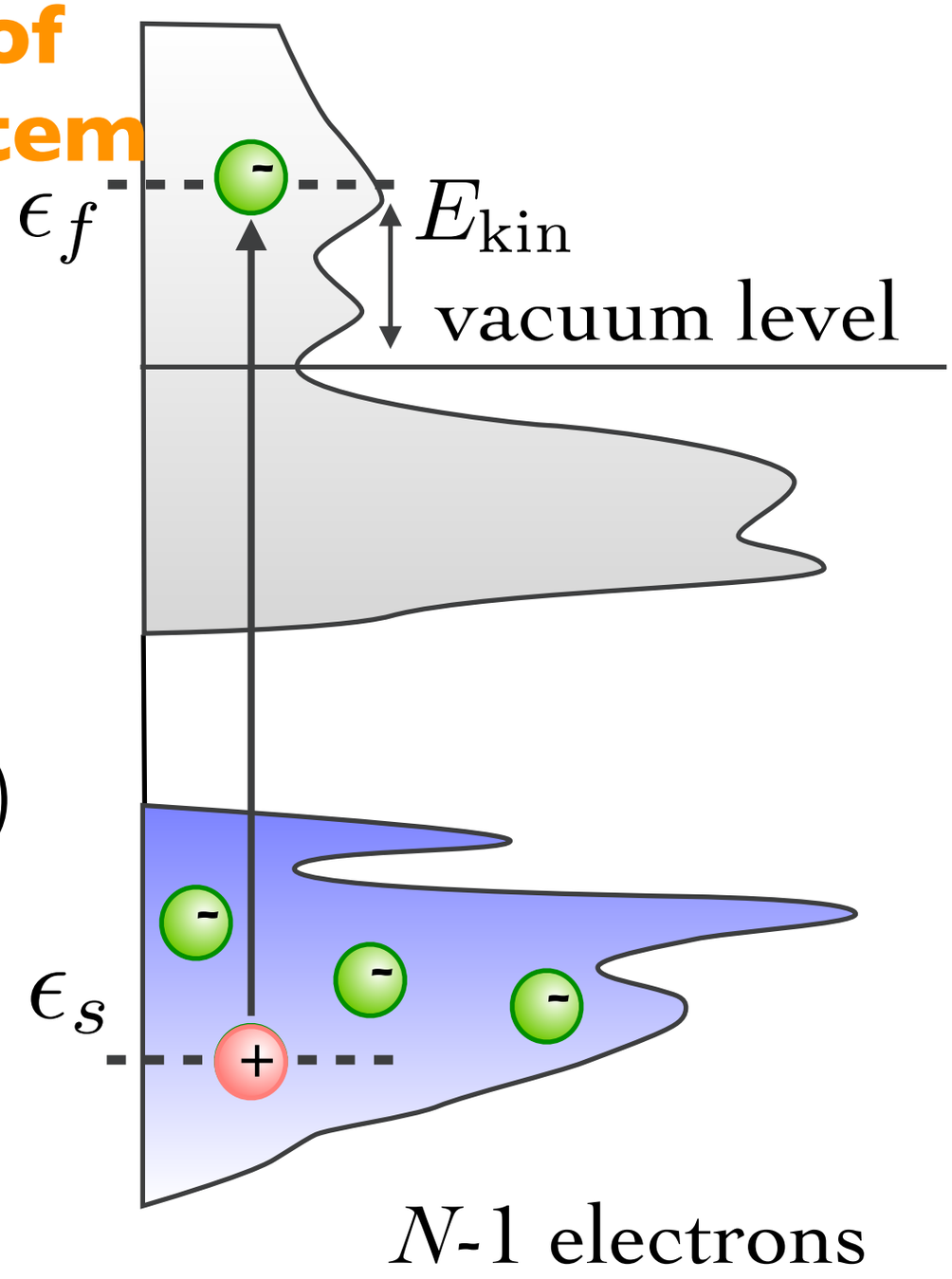


Photo-electron energies

Photoemission

- electron removal

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

- removal energy

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

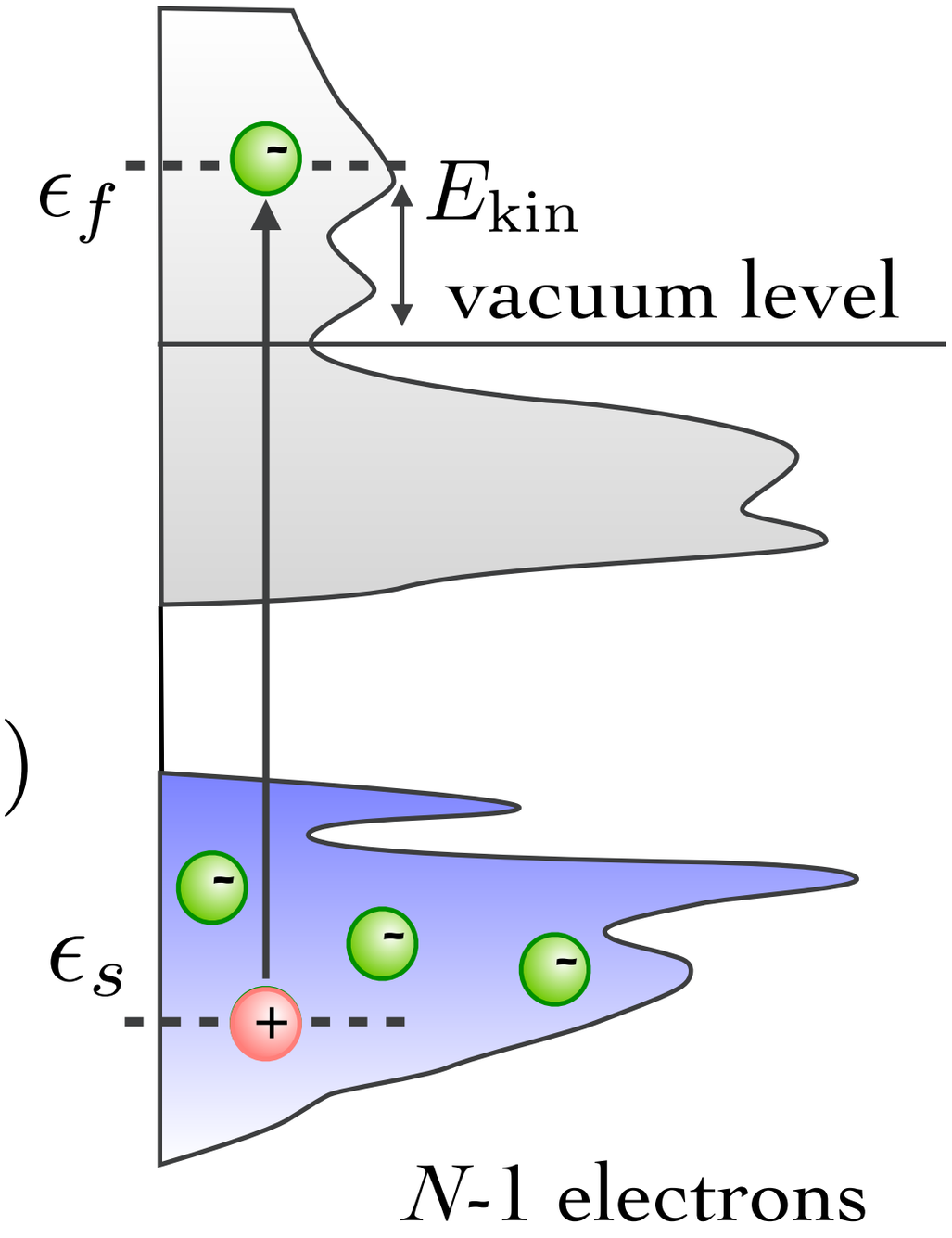


Photo-electron energies

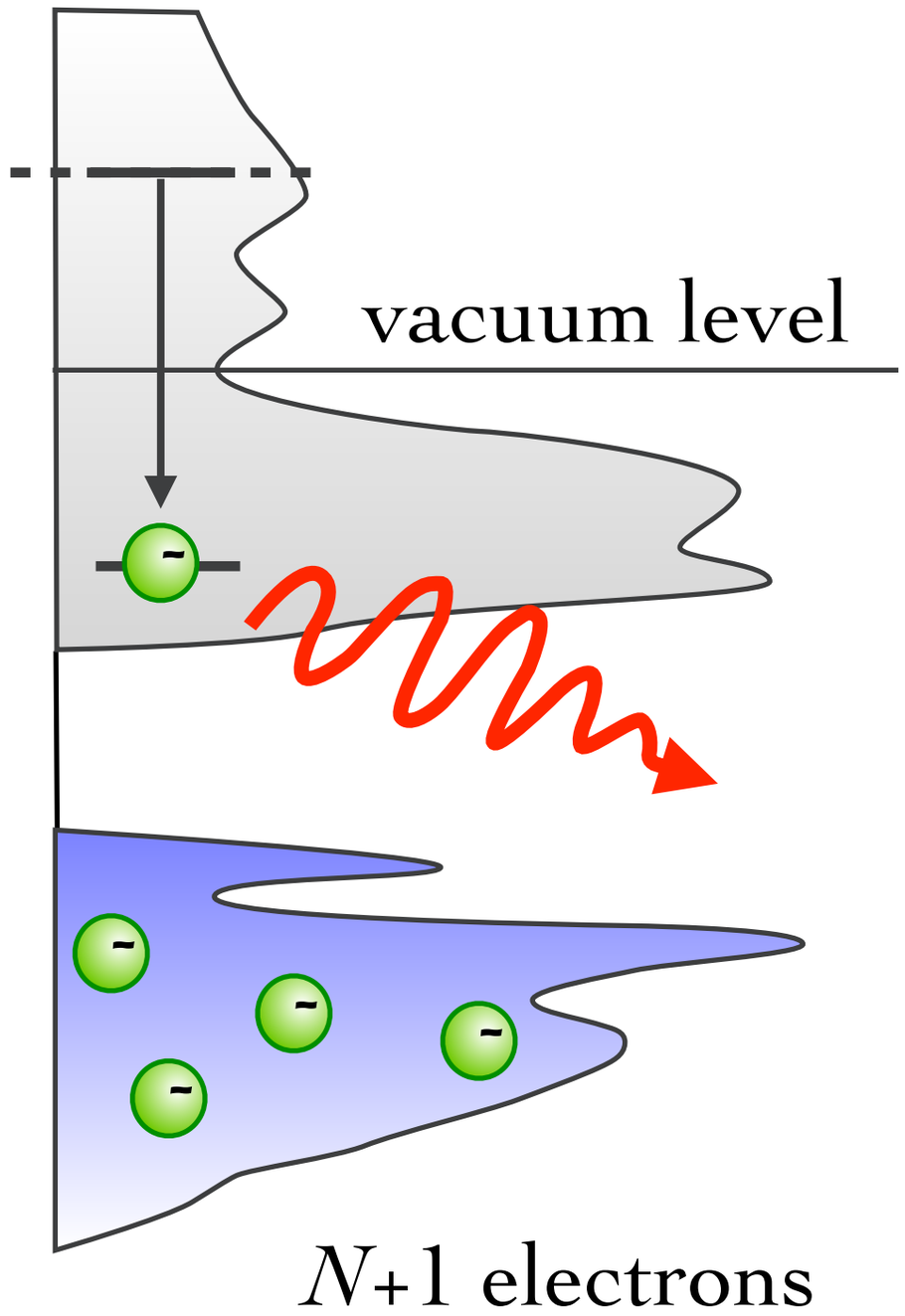
Inverse photoemission

- 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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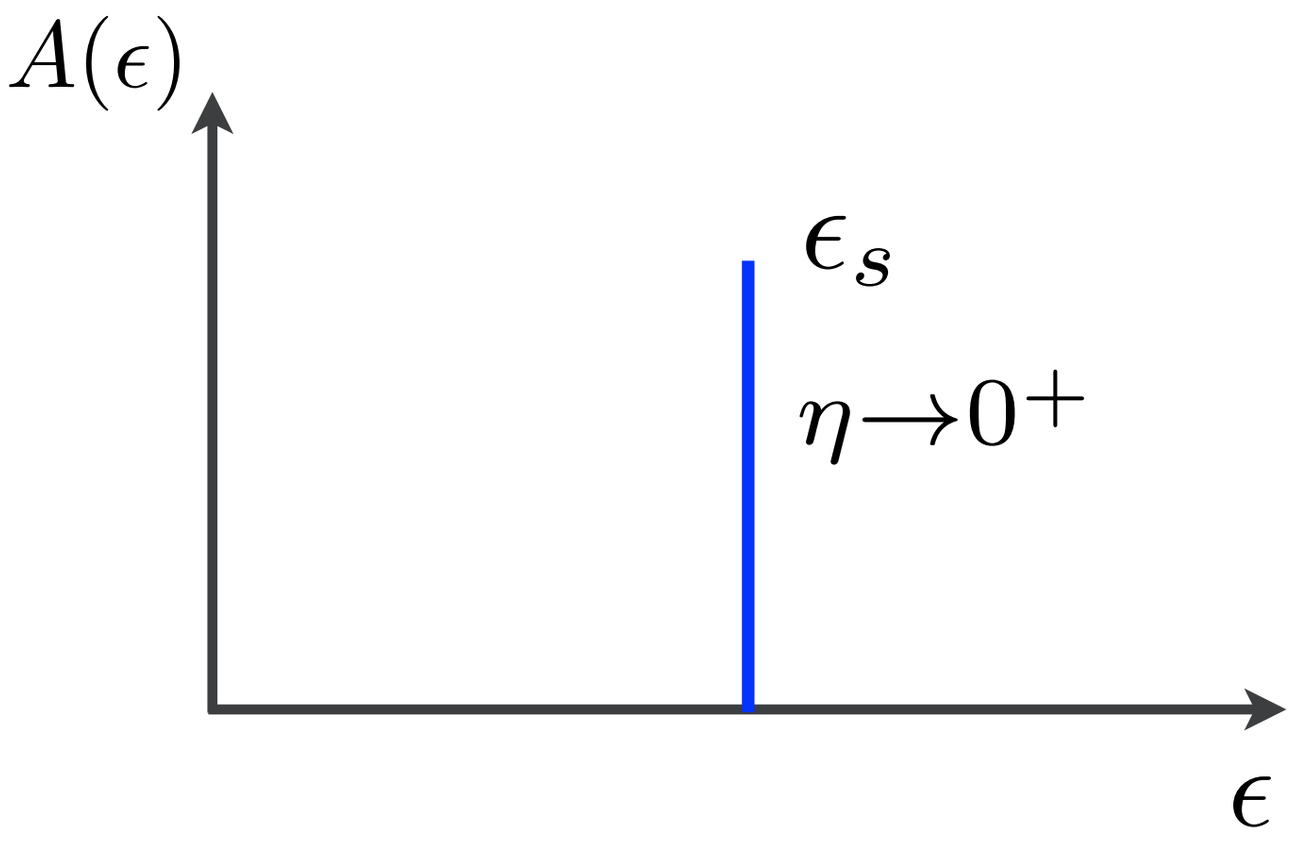
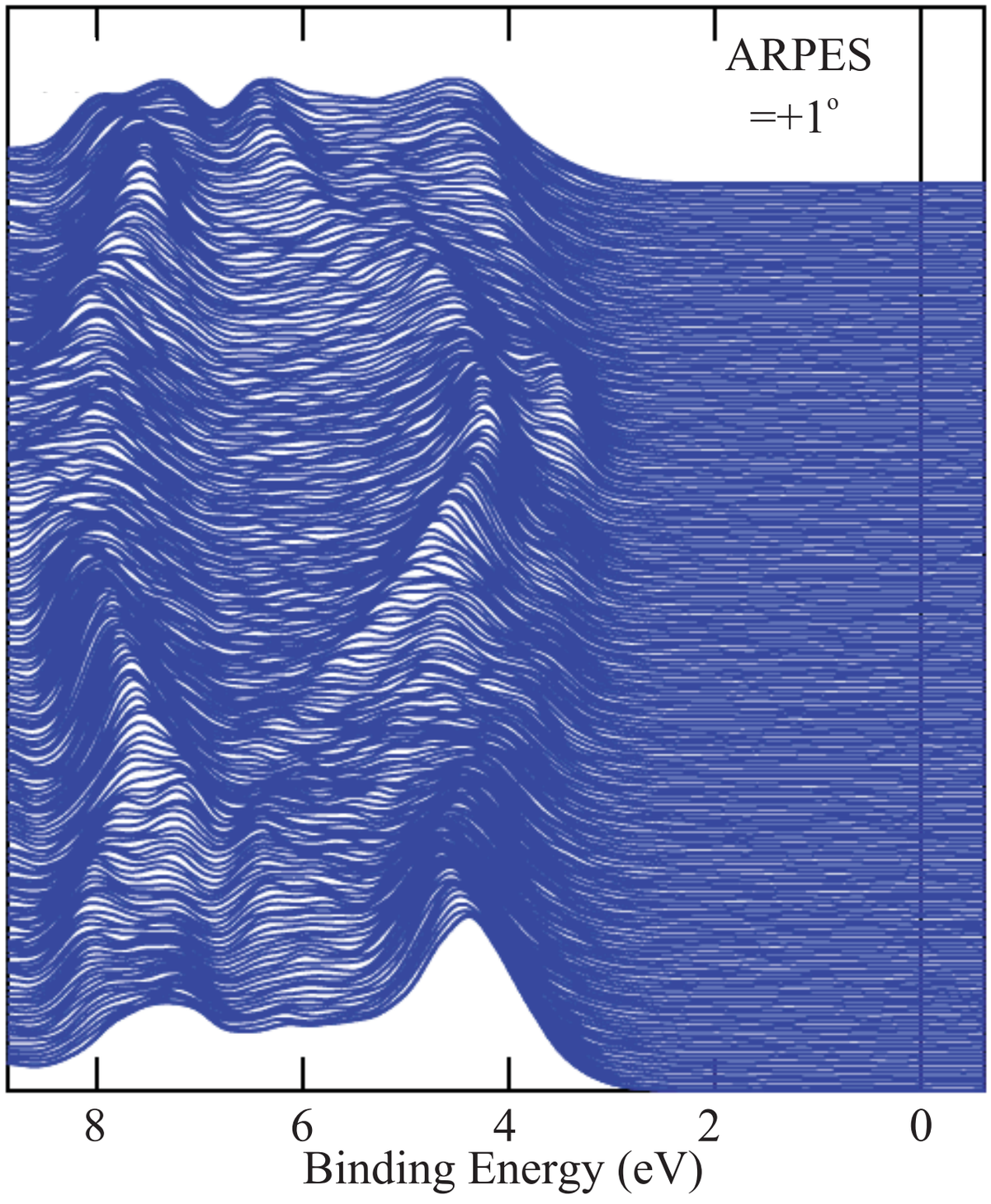


Angle-resolved photoemisson spectroscopy



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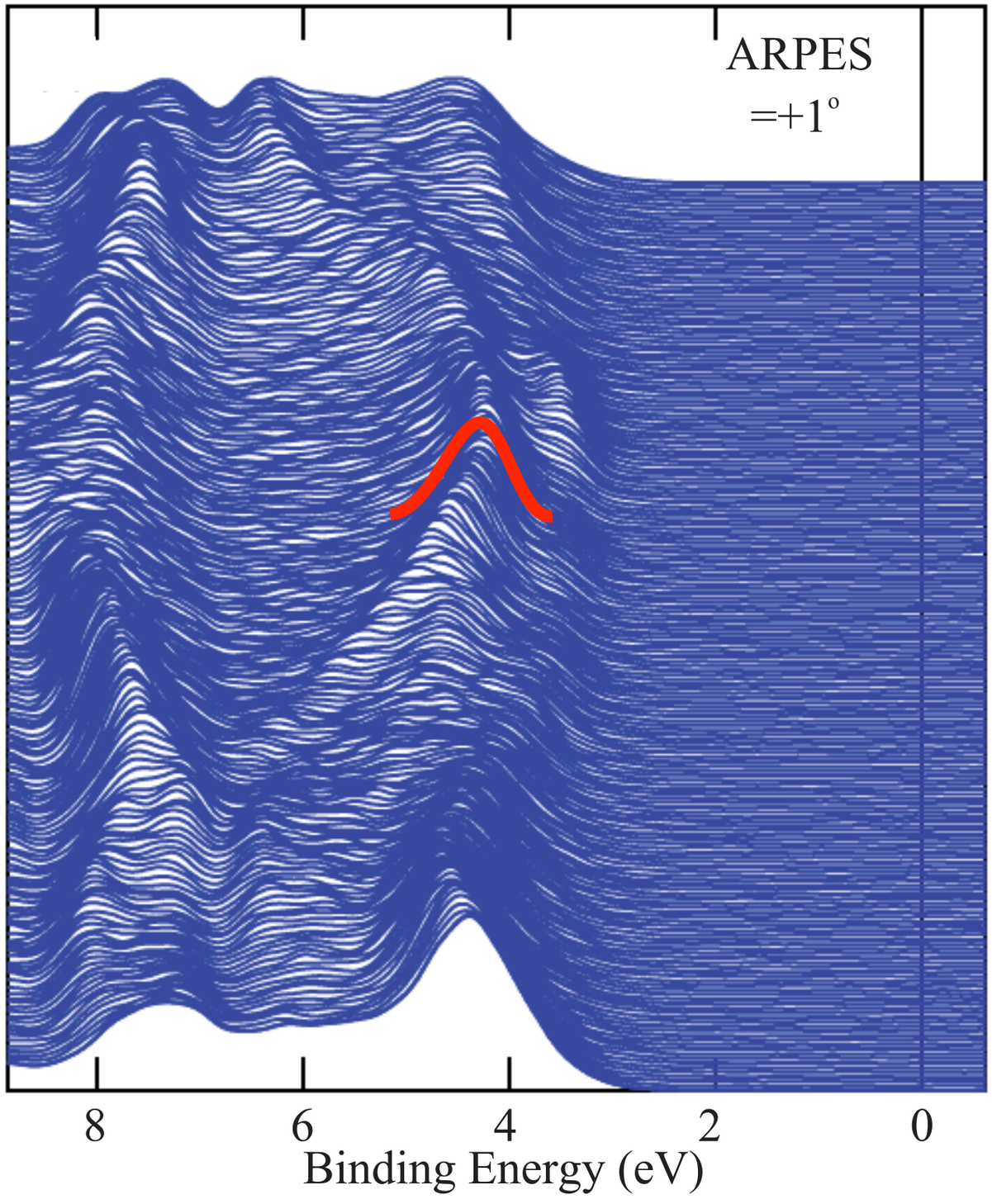
source: Masaki Kobayashi, PhD dissertation

Angle-resolved photoemisson spectroscopy



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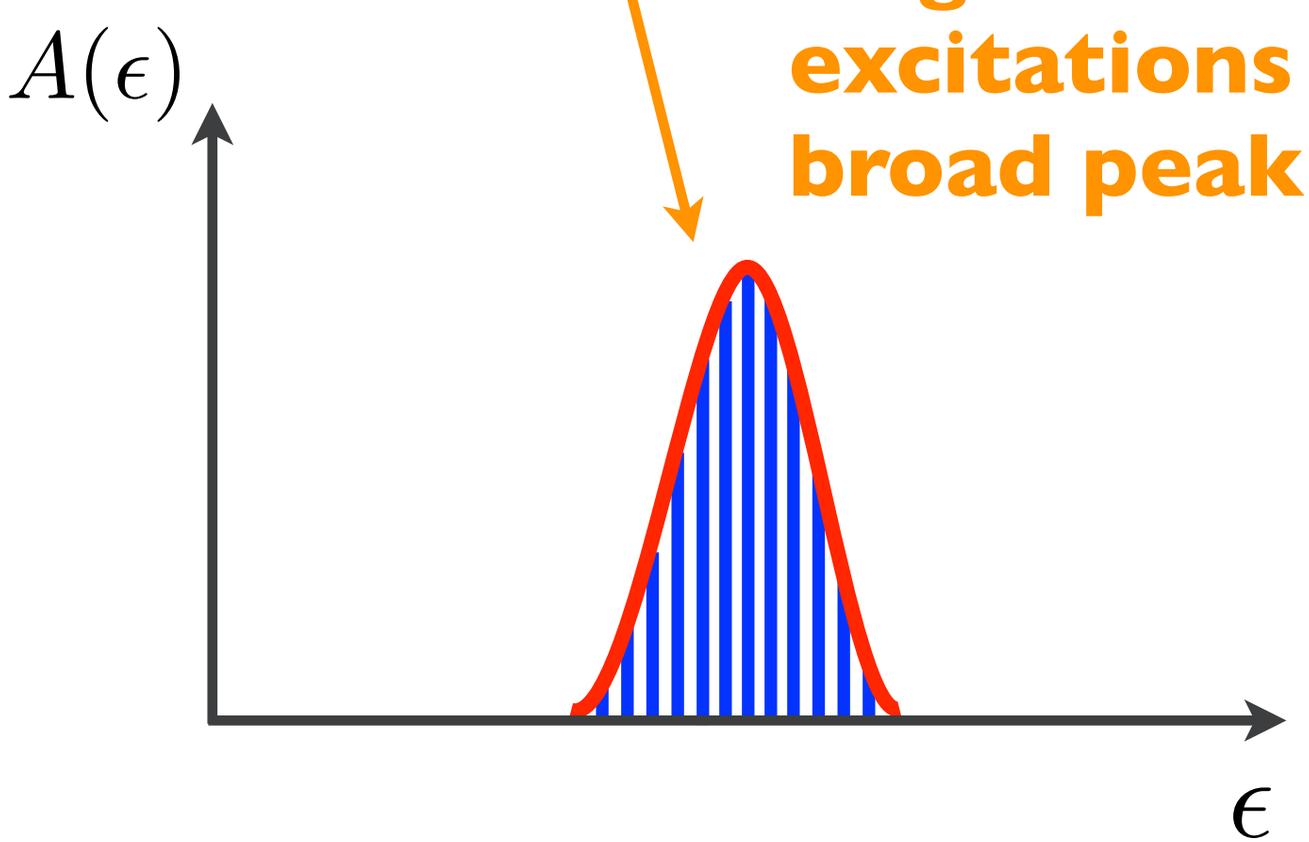
single electron excitations merge into broad peak

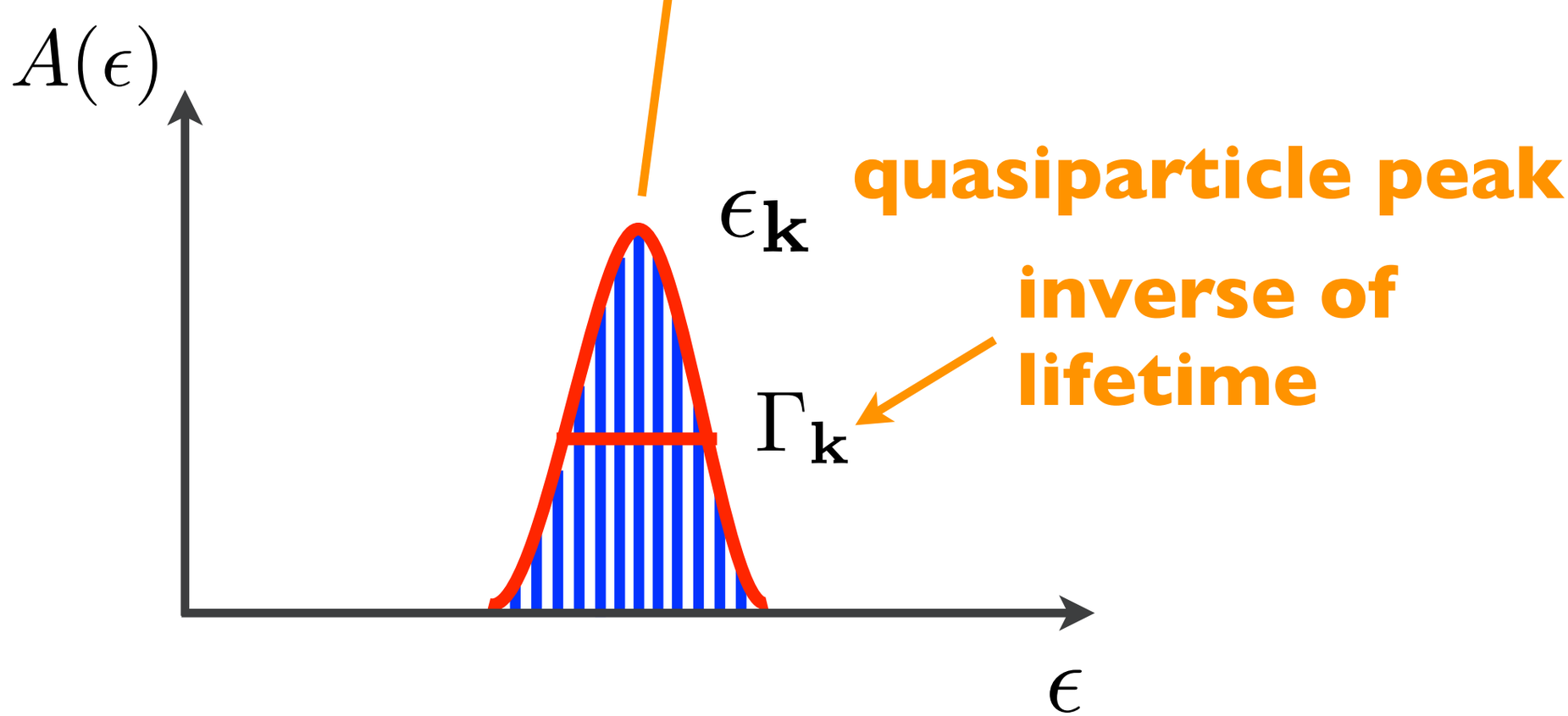


Single-particle Green's function

- single particle-like spectral function:

quasiparticle weight

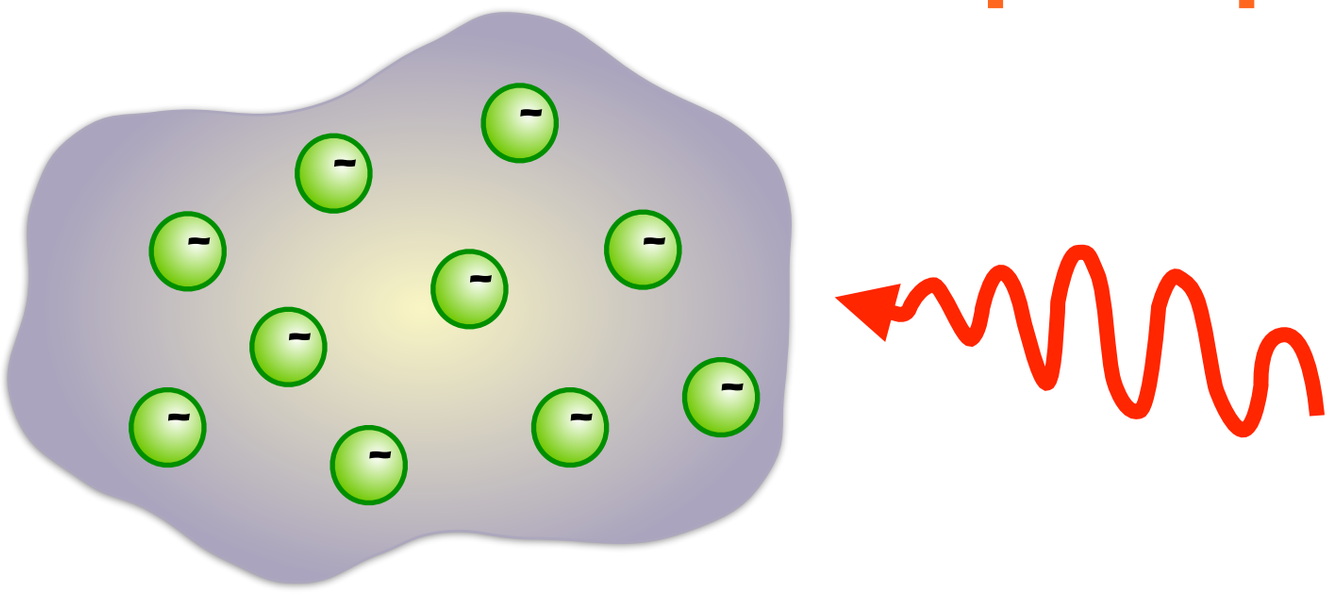
$$A_{\mathbf{k}}(\epsilon) = ImG_{\mathbf{k}}(\epsilon) \approx \frac{Z_{\mathbf{k}}}{\epsilon - (\epsilon_{\mathbf{k}} + i\Gamma_{\mathbf{k}})}$$



quasiparticle peak

inverse of lifetime

Another look at quasiparticles



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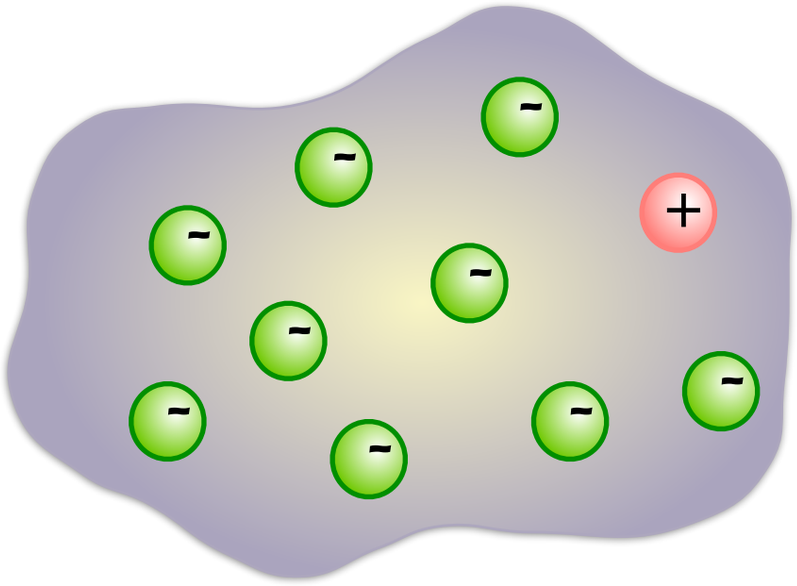
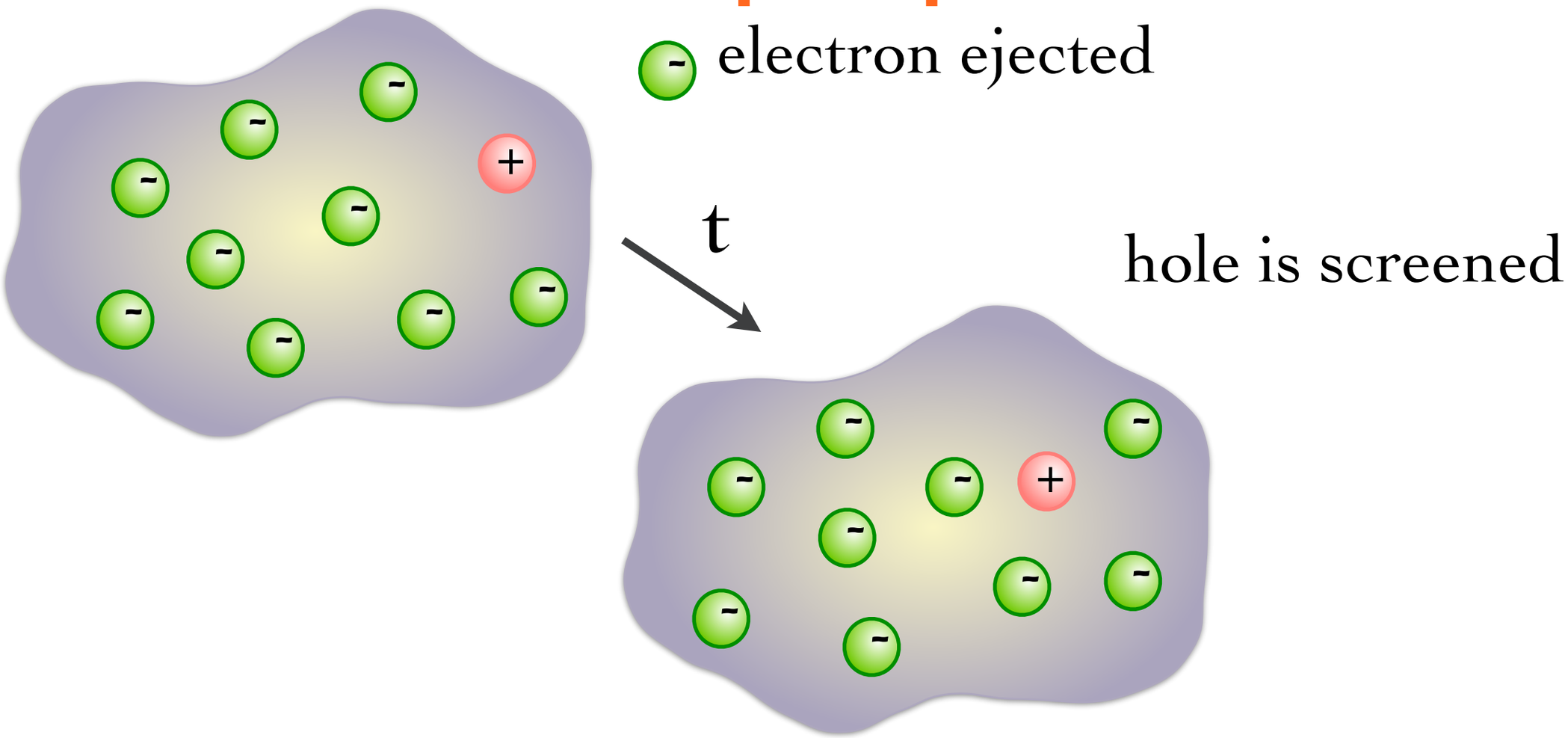


electron ejected

Another look at quasiparticles



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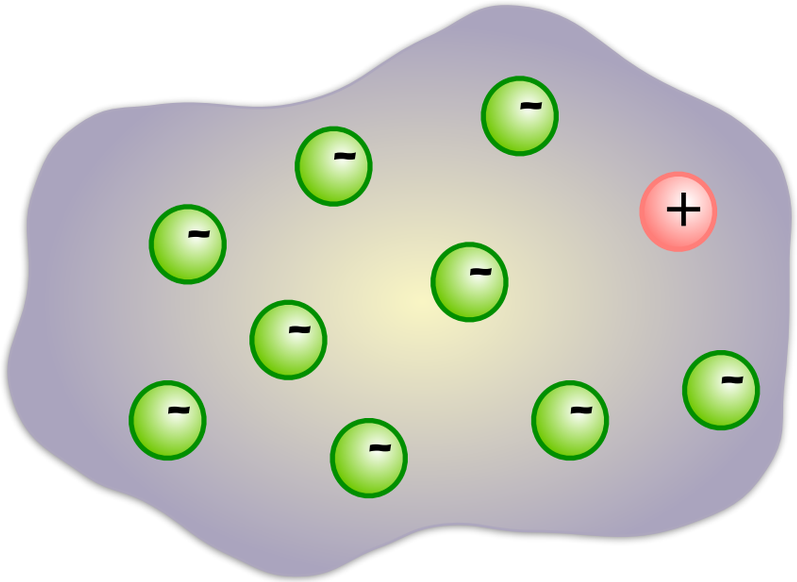
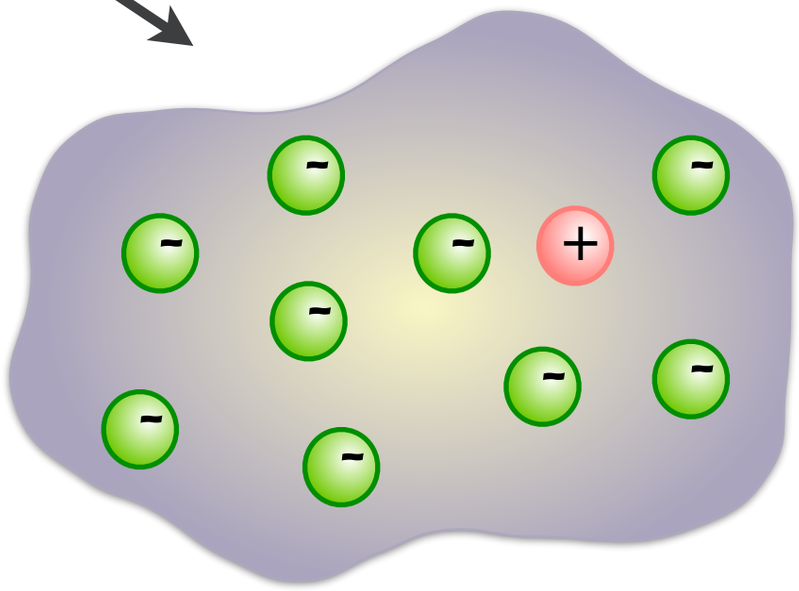


electron ejected

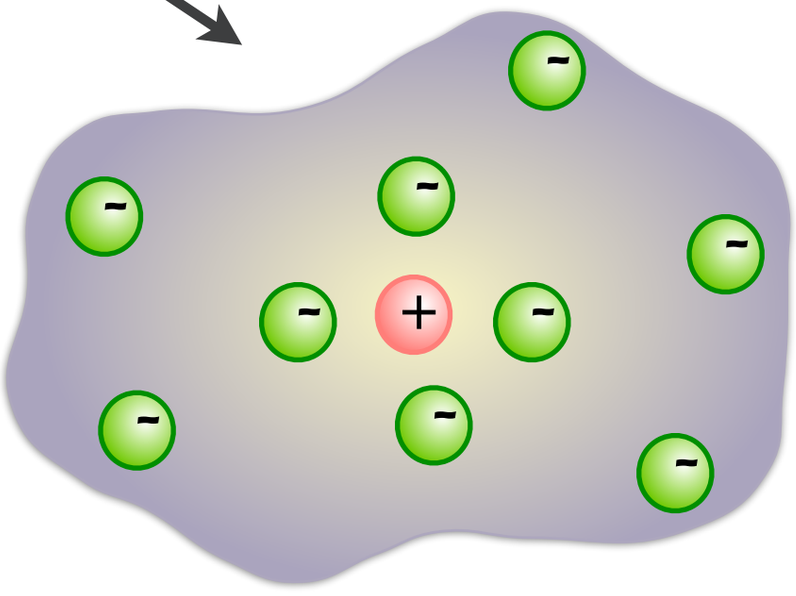
t

hole is screened



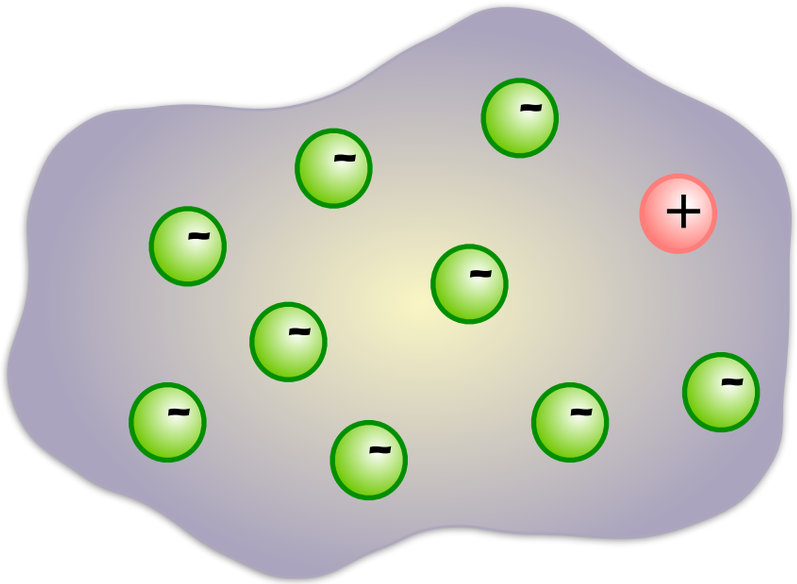
t

hole is screened dynamically



screening is time dependent

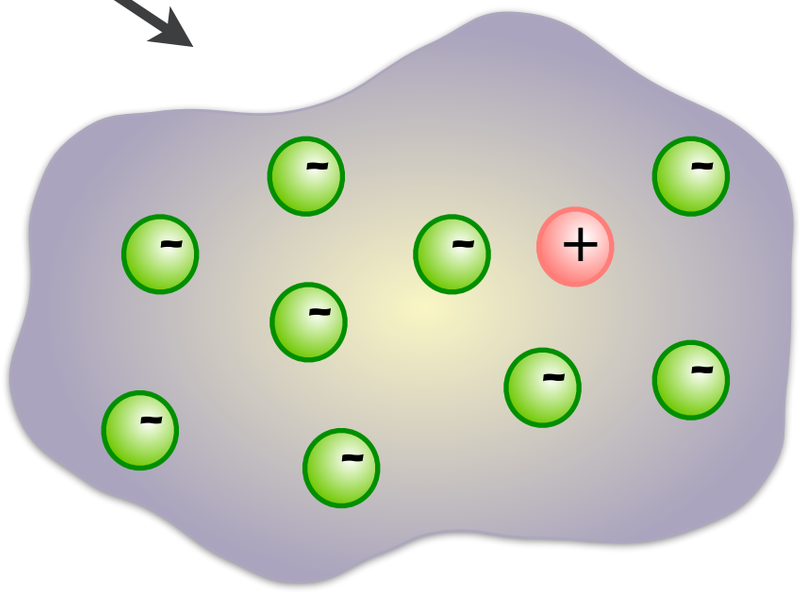
Another look at quasiparticles



electron ejected

t

hole is screened



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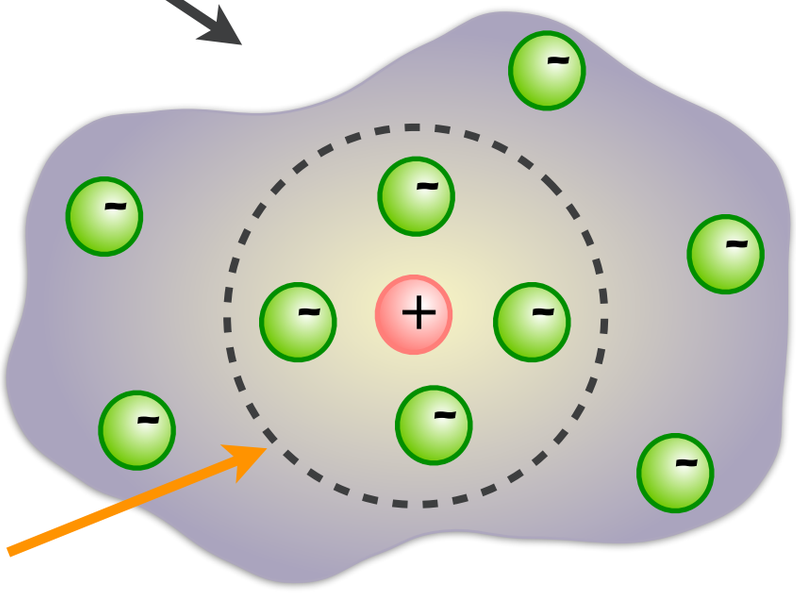


screening is time dependent

quasiparticle

The screened Coulomb interaction

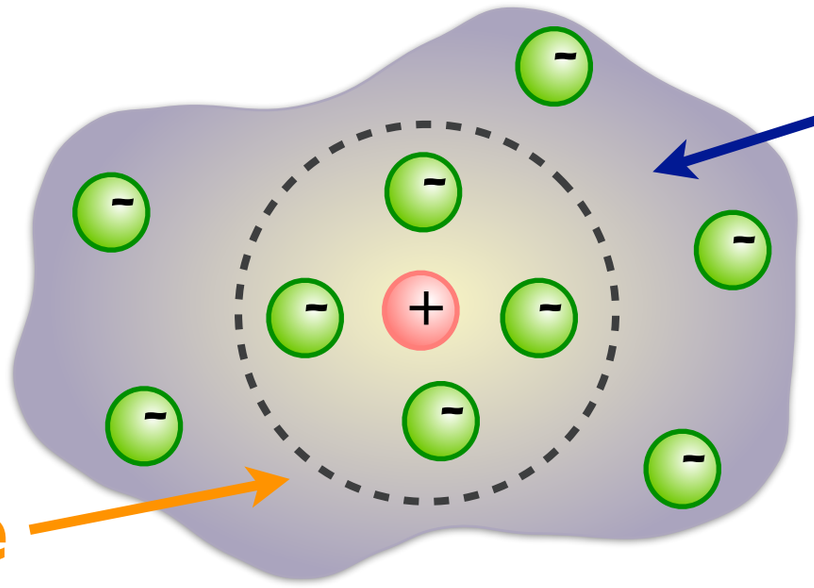
$$W(\mathbf{r},\mathbf{r}',t) = \int d\mathbf{r}'' \frac{\varepsilon^{-1}(\mathbf{r},\mathbf{r}'',t)}{|\mathbf{r}''-\mathbf{r}'|}$$

dielectric function

screened

Coulomb interaction

bare

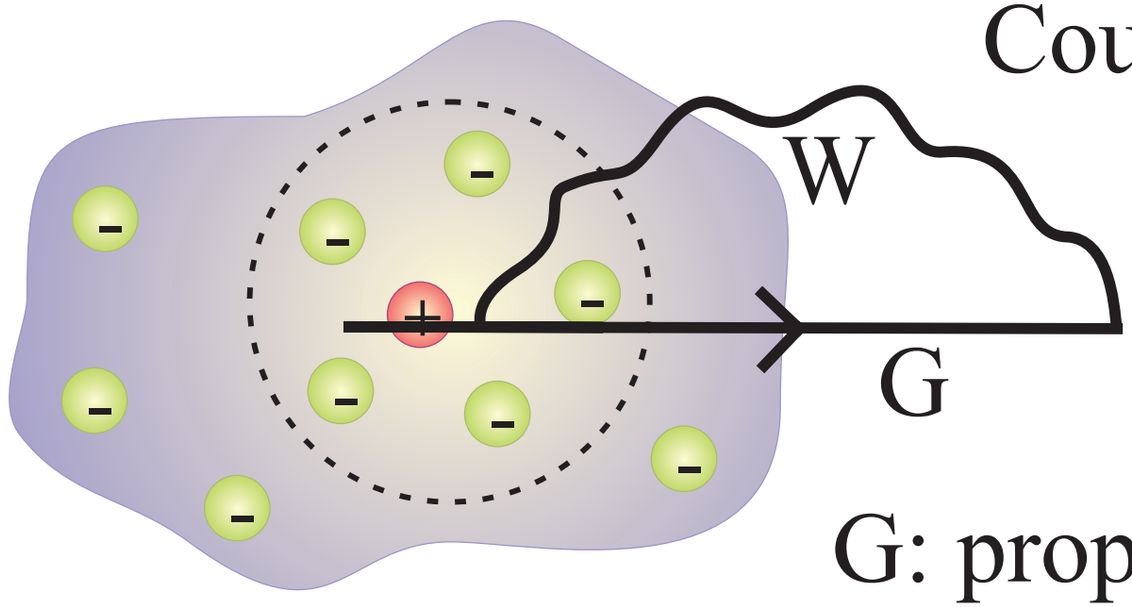


hole is screened by the system

quasiparticle

GW approximation - screened electrons

$$\Sigma = iGW$$



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

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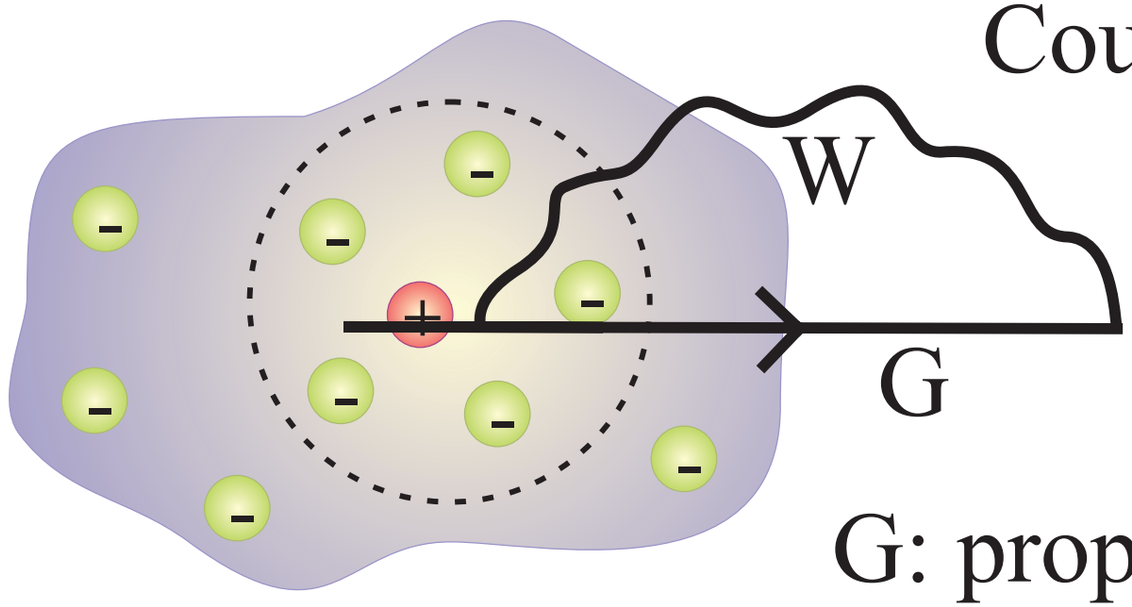

Dyson equation:

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

non-interacting Green's function

Exact solution - 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!

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Do not despair!

We will make an approximation!

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Hedin's *GW* approximation!

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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:

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

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Step 3:

- Construct polarizability:

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

GW in practice

Step 4:

- Dielectric function:

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

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 (G_0W_0):

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

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**

Let’s get (a little bit) more real

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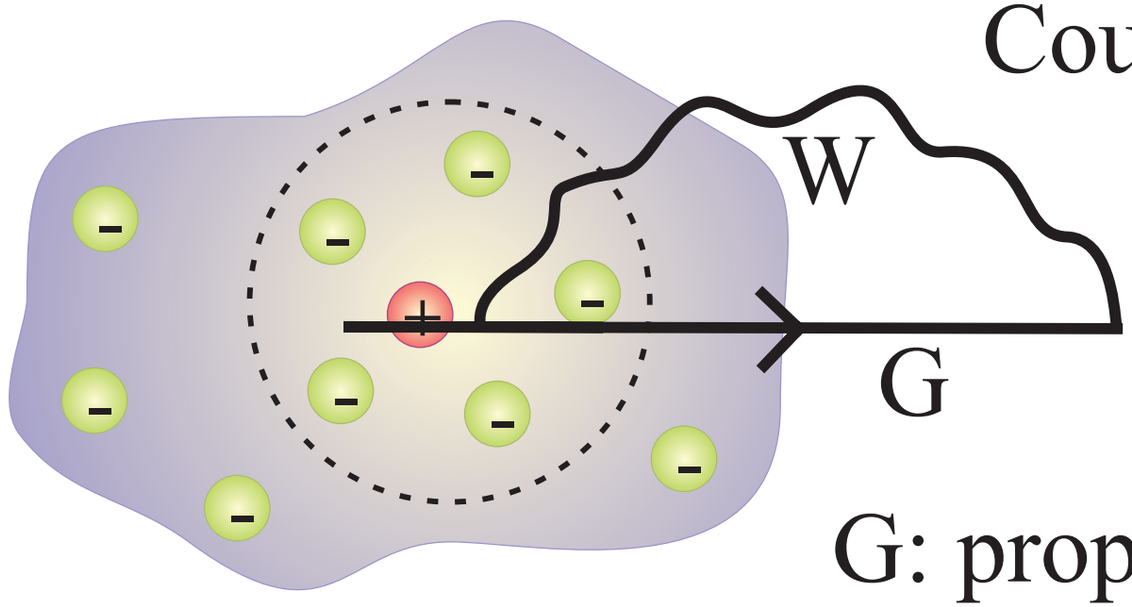
GW approximation - screened electrons

$$\Sigma = iGW$$



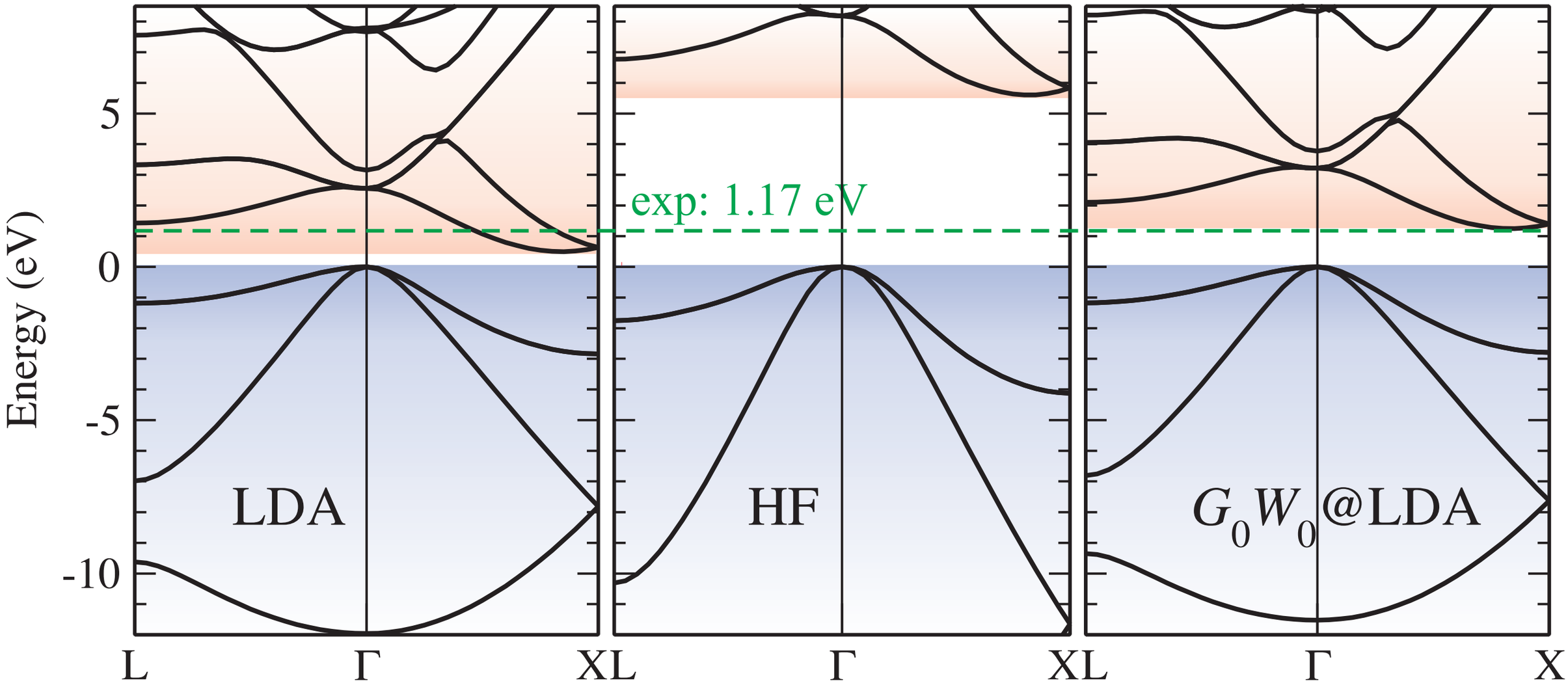
self-energy: $\Sigma = \Sigma_x + \Sigma_c$

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

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

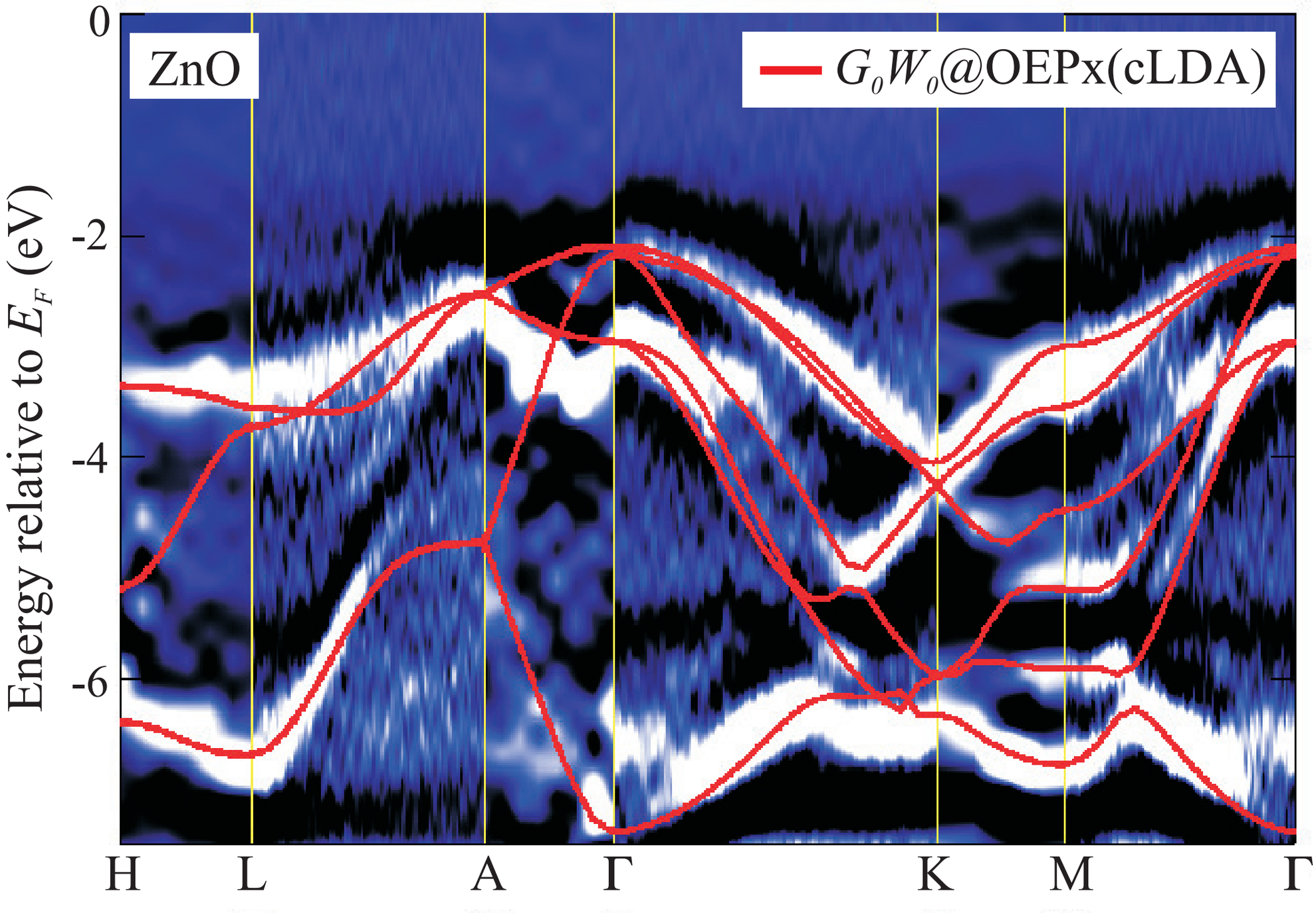
On the importance of screening

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



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

Angle resolved photoemission - ZnO



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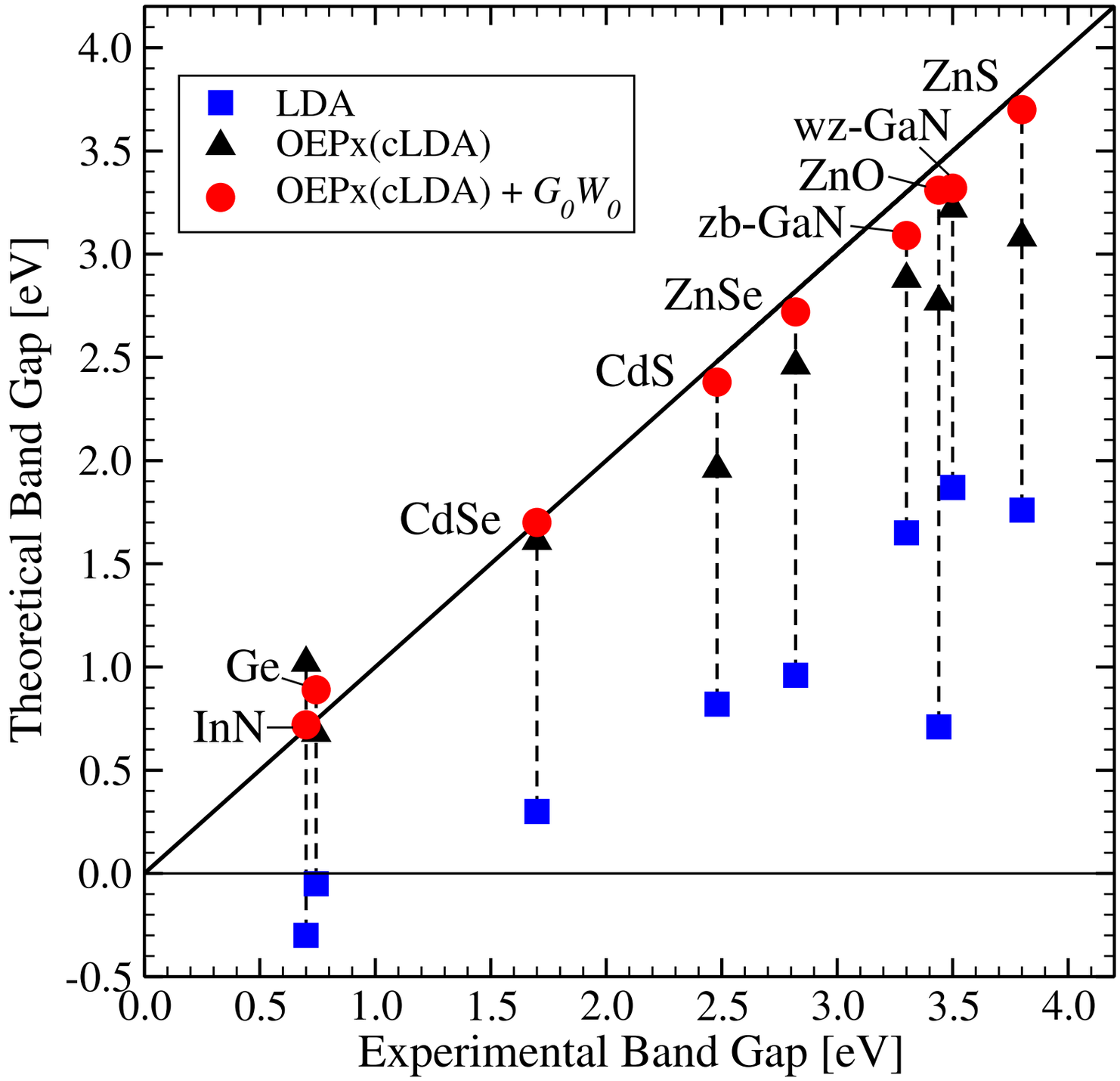
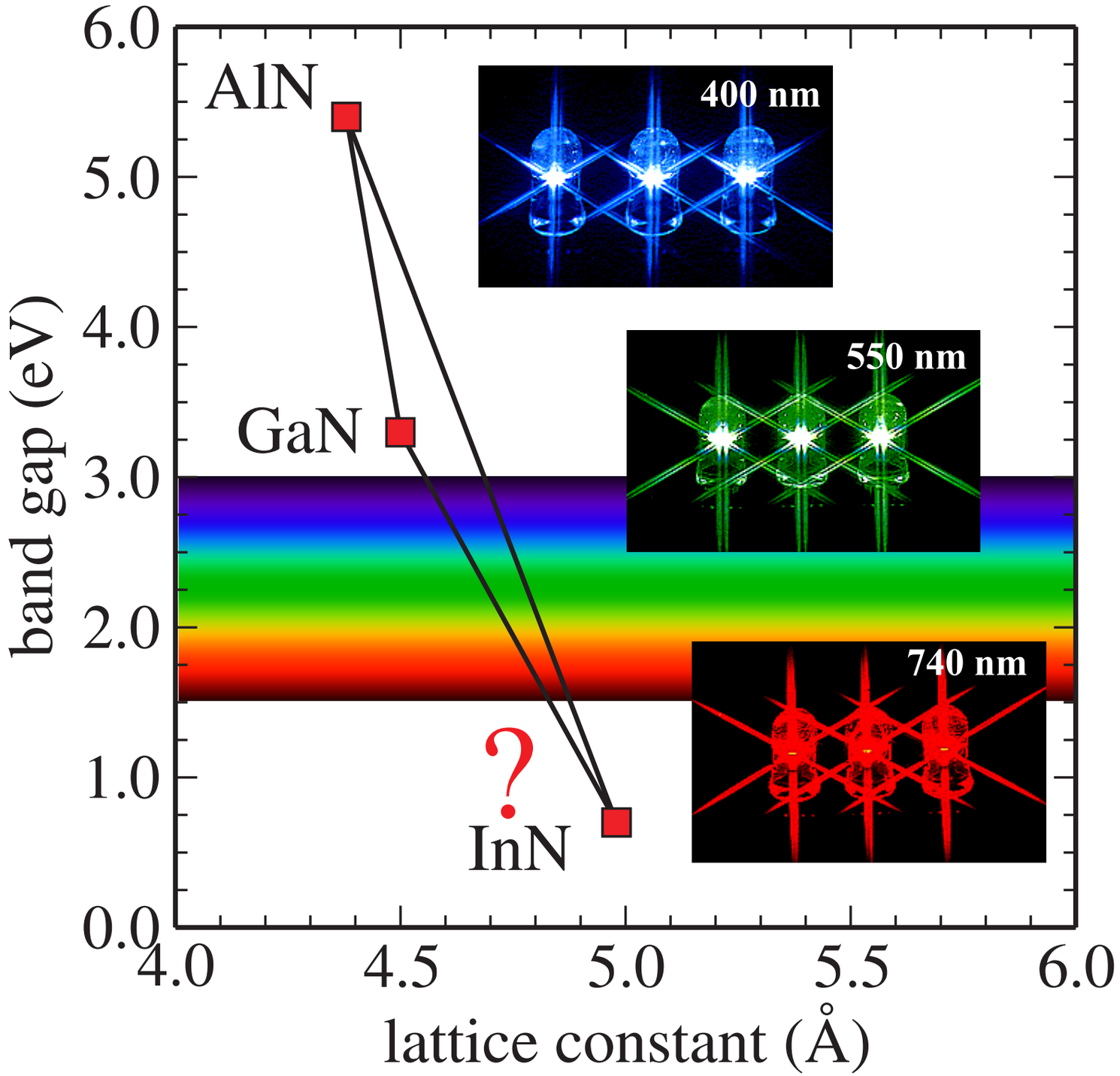
Q. Yan, P. Rinke, *et al.*, Semicond. Sci. Technol. 26, 014037 (2011)

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?



Inorganics: Challenges

LEDs - solid state lighting

- to increase efficiency
  -> brightness
- to produce colour variability and stability

Laser diodes

- to produce a bright green laser diode

sources: Pixelligent

Do we know the band gap of InN?

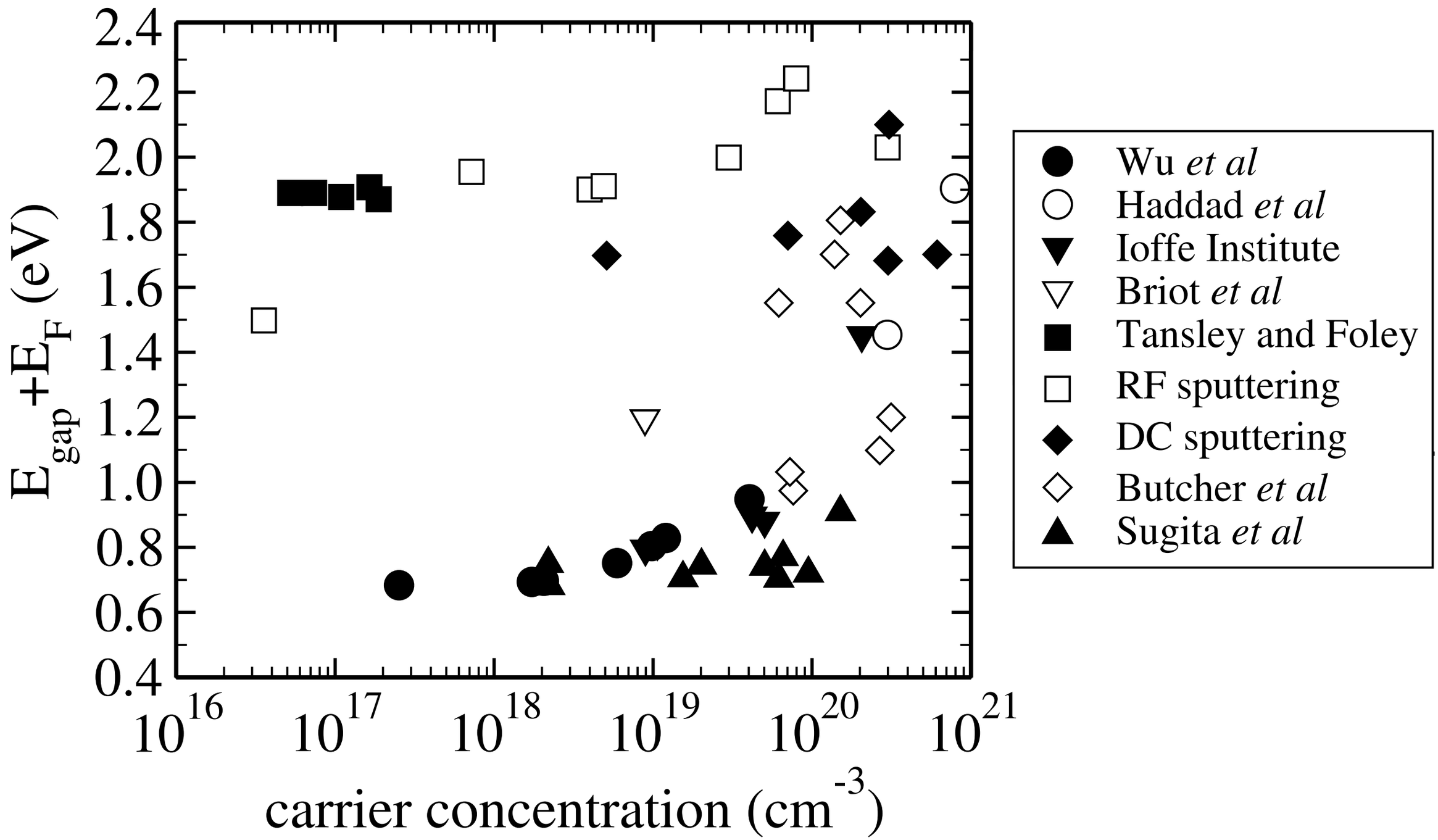
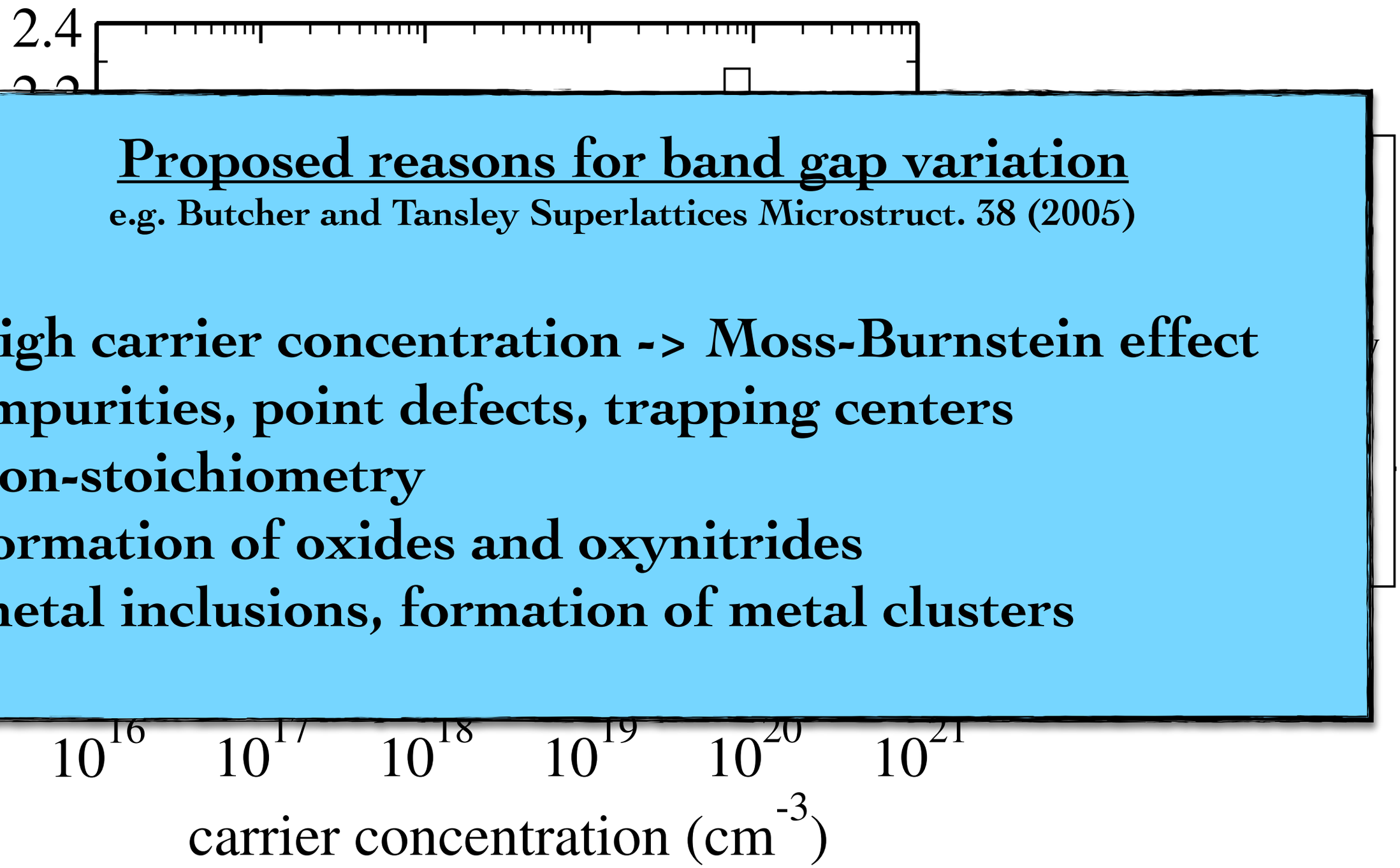


Figure adapted from Butcher and Tansley Superlattices Microstruct. 38, 1 (2005)

Do we know the band gap of InN?



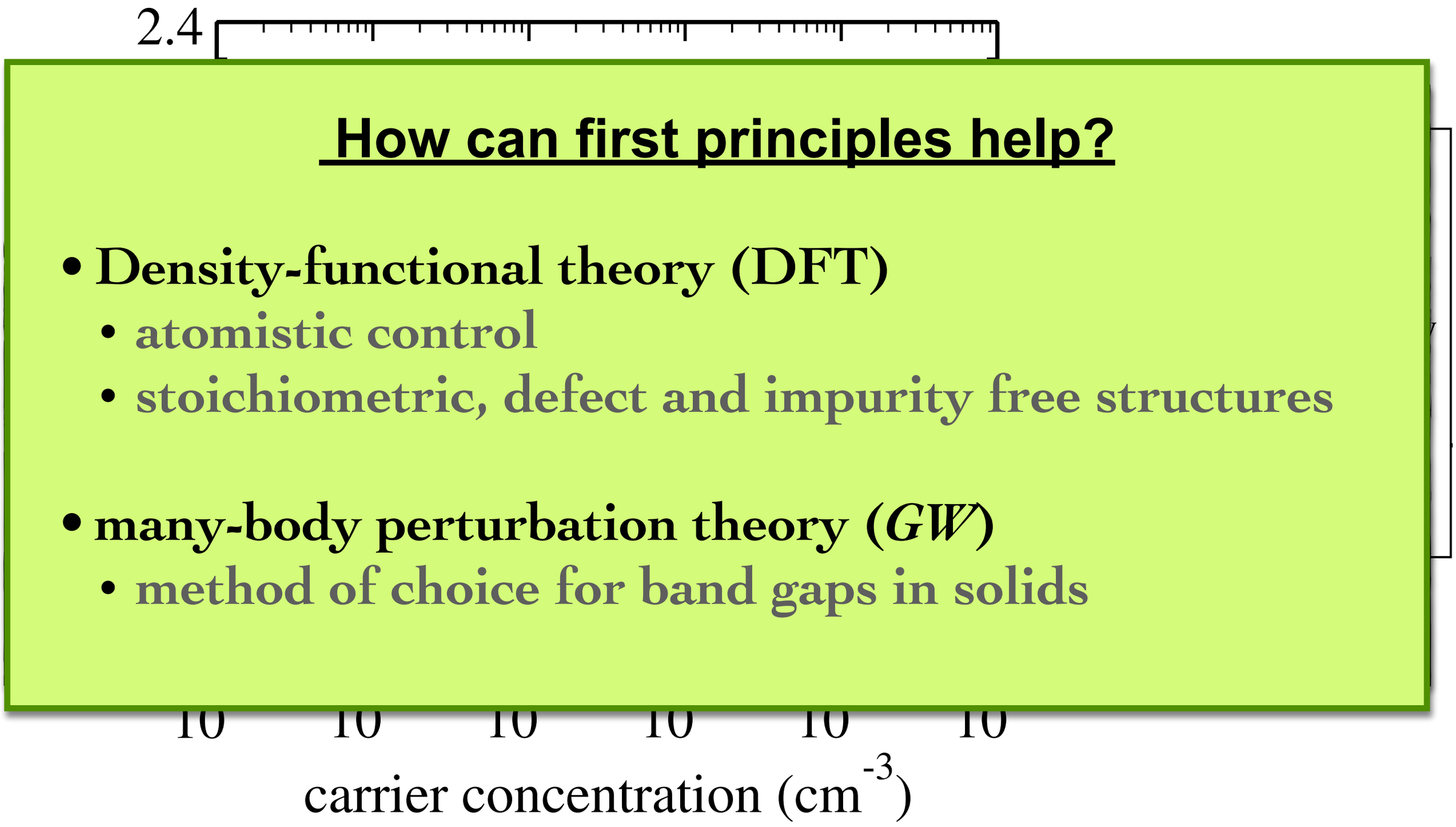
Proposed reasons for band gap variation

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

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

Do we know the band gap of InN?

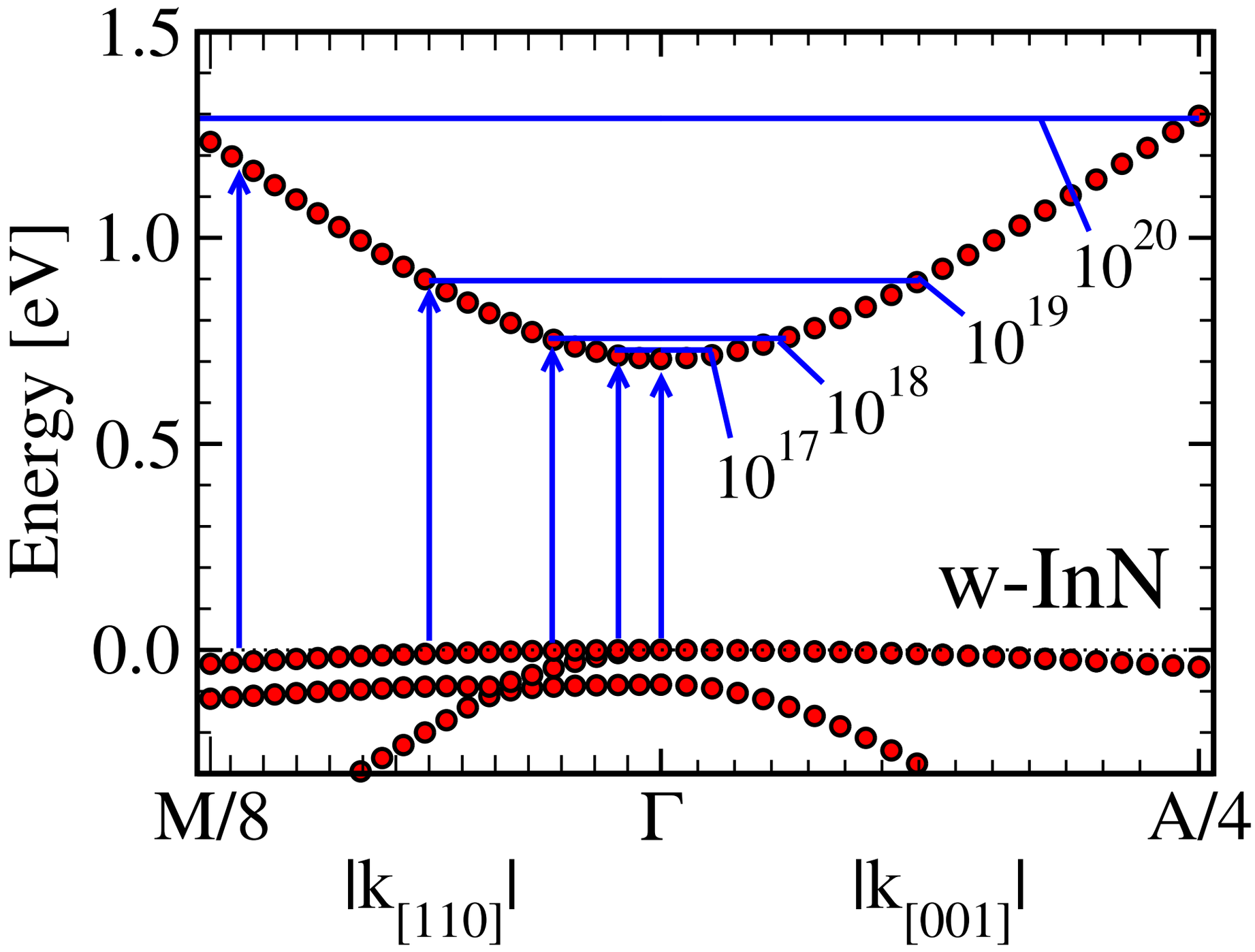


How can first principles help?

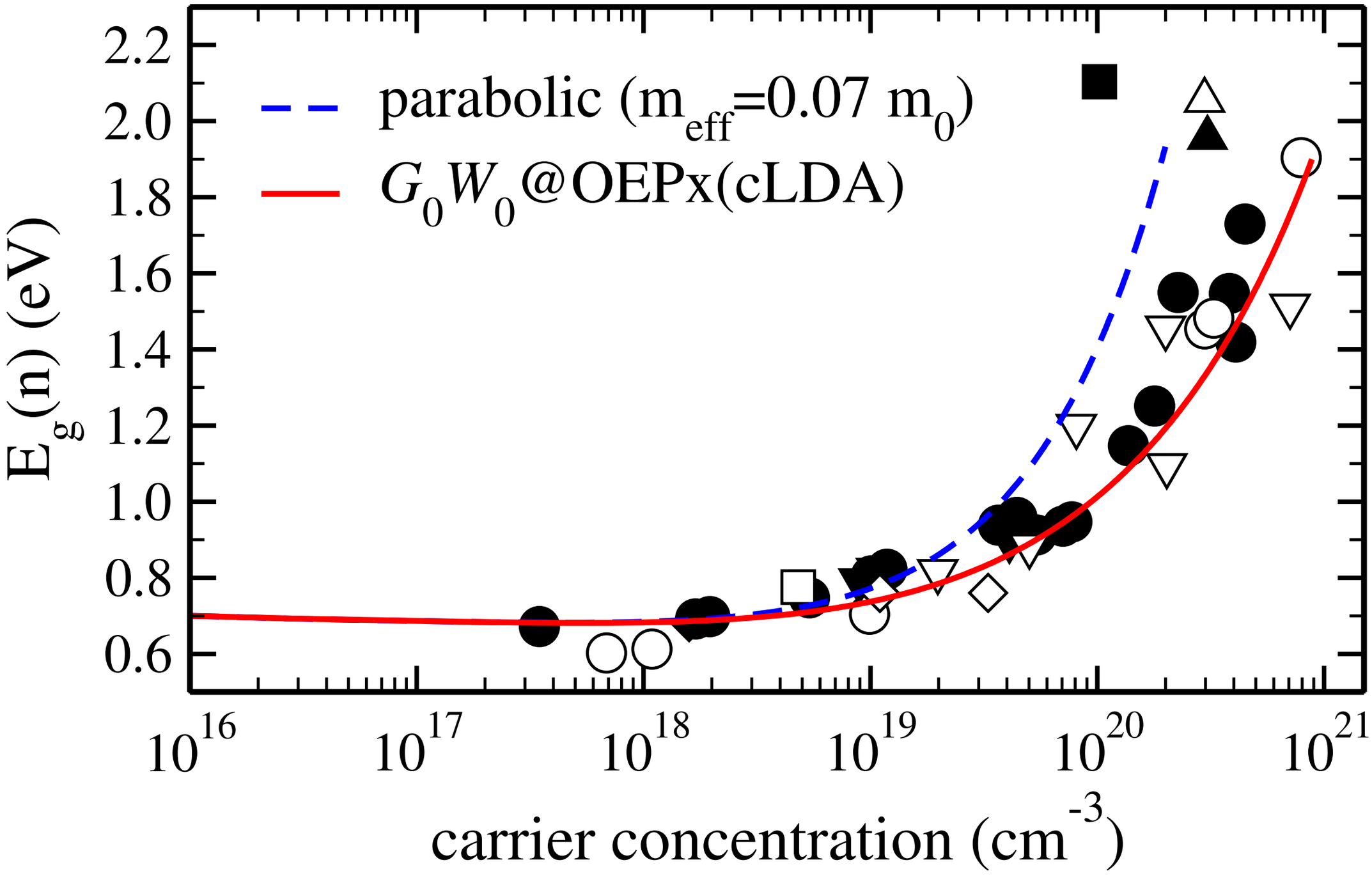
- **Density-functional theory (DFT)**
  - atomistic control
  - stoichiometric, defect and impurity free structures
- **many-body perturbation theory (*GW*)**
  - method of choice for band gaps in solids

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

InN - *GW* band structure and Moss-Burstein

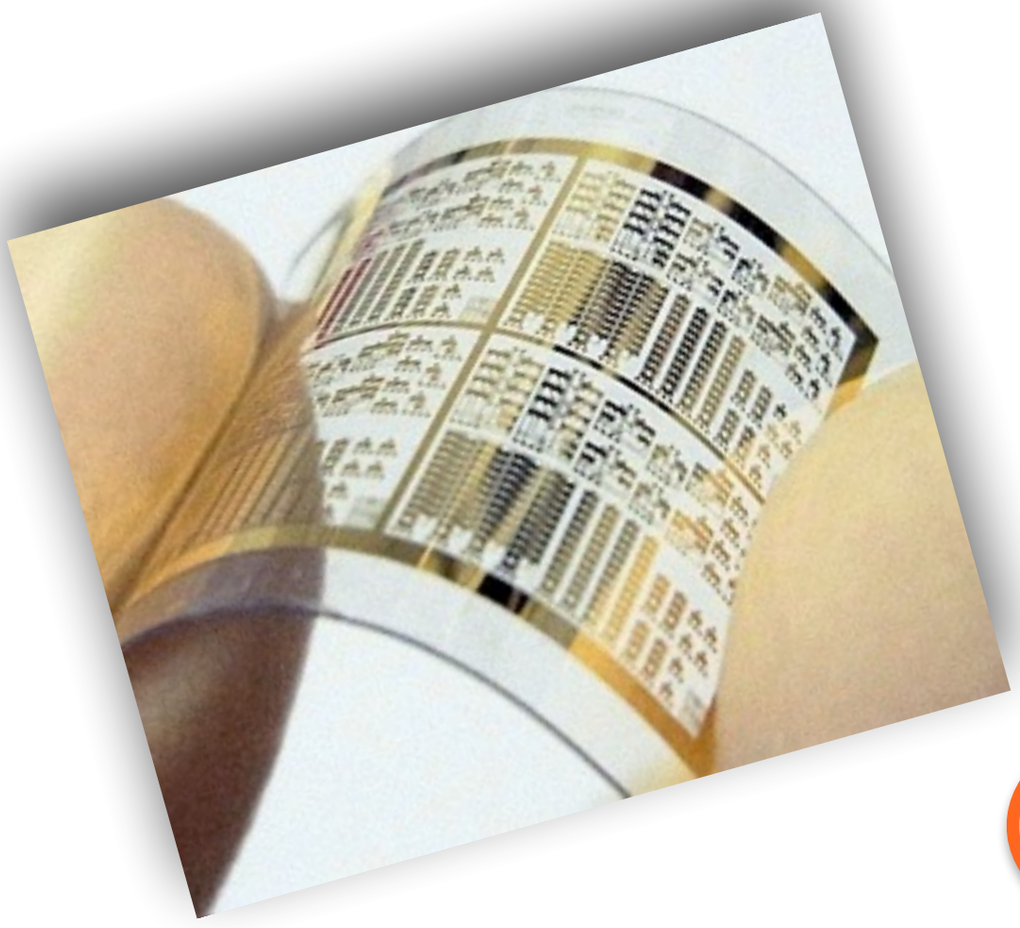


InN - *GW* band structure and Moss-Burstein



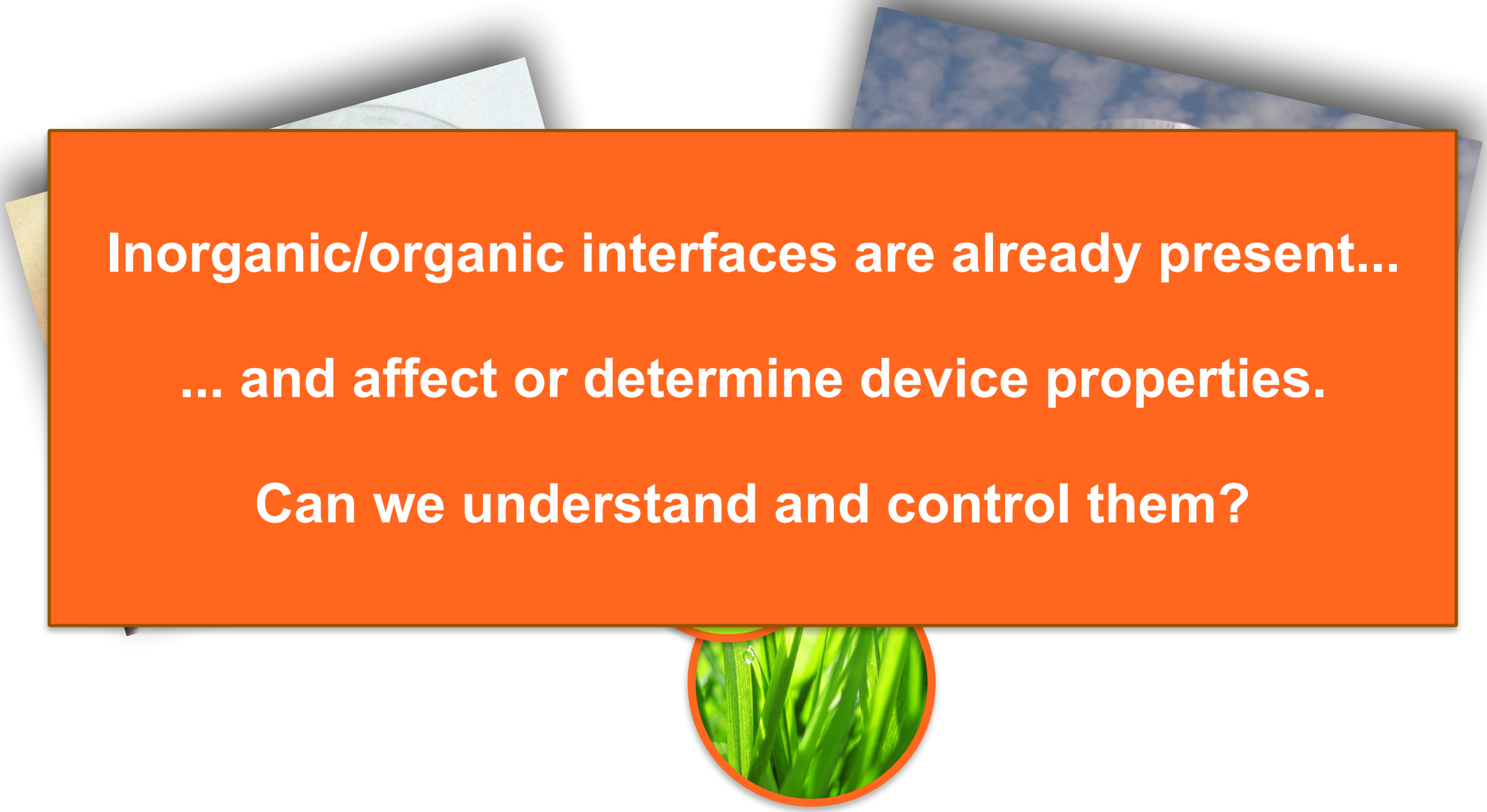
P. Rinke, et al., Appl. Phys. Lett. 89,161919 (2006)

Organic or plastic electronics



sources (left to right): Eco Friend, Nature Publishing Group

Organic or plastic electronics



Inorganic/organic interfaces are already present...

... and affect or determine device properties.

Can we understand and control them?

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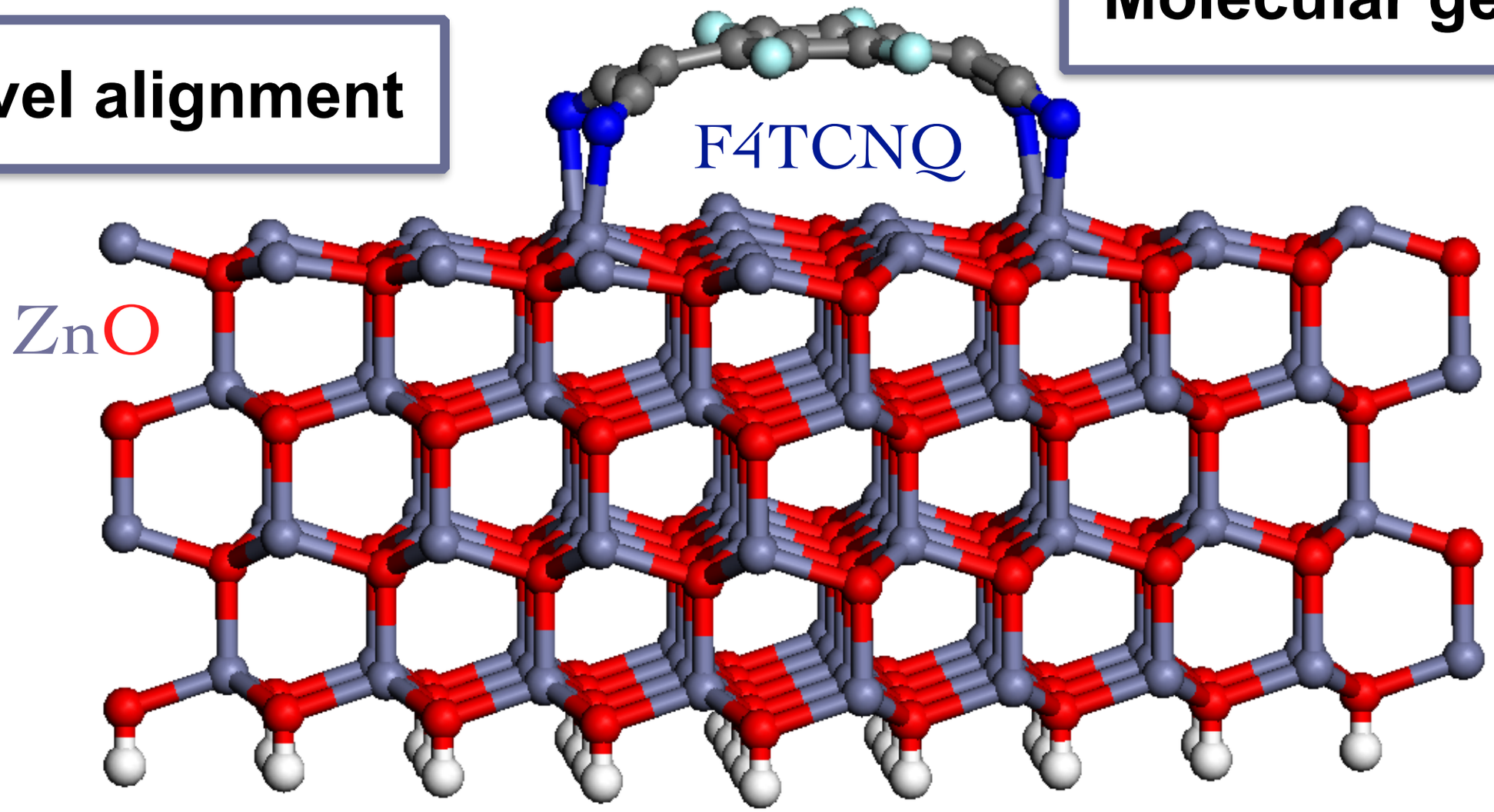
sources (left to right): Eco Friend, Nature Publishing Group

Atomistic organic/inorganic interface

Interface properties

Molecular geometry

Level alignment

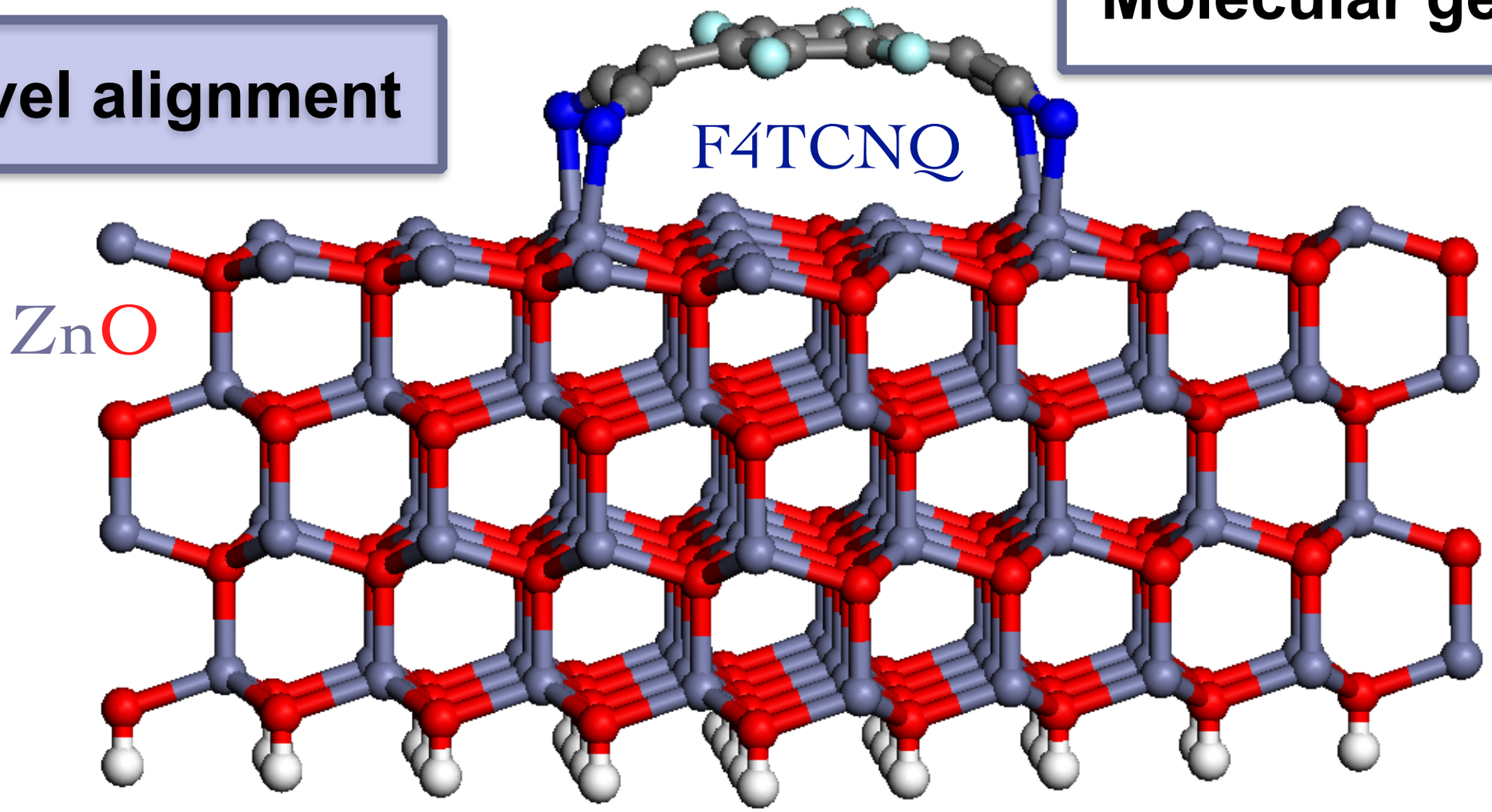


Atomistic organic/inorganic interface

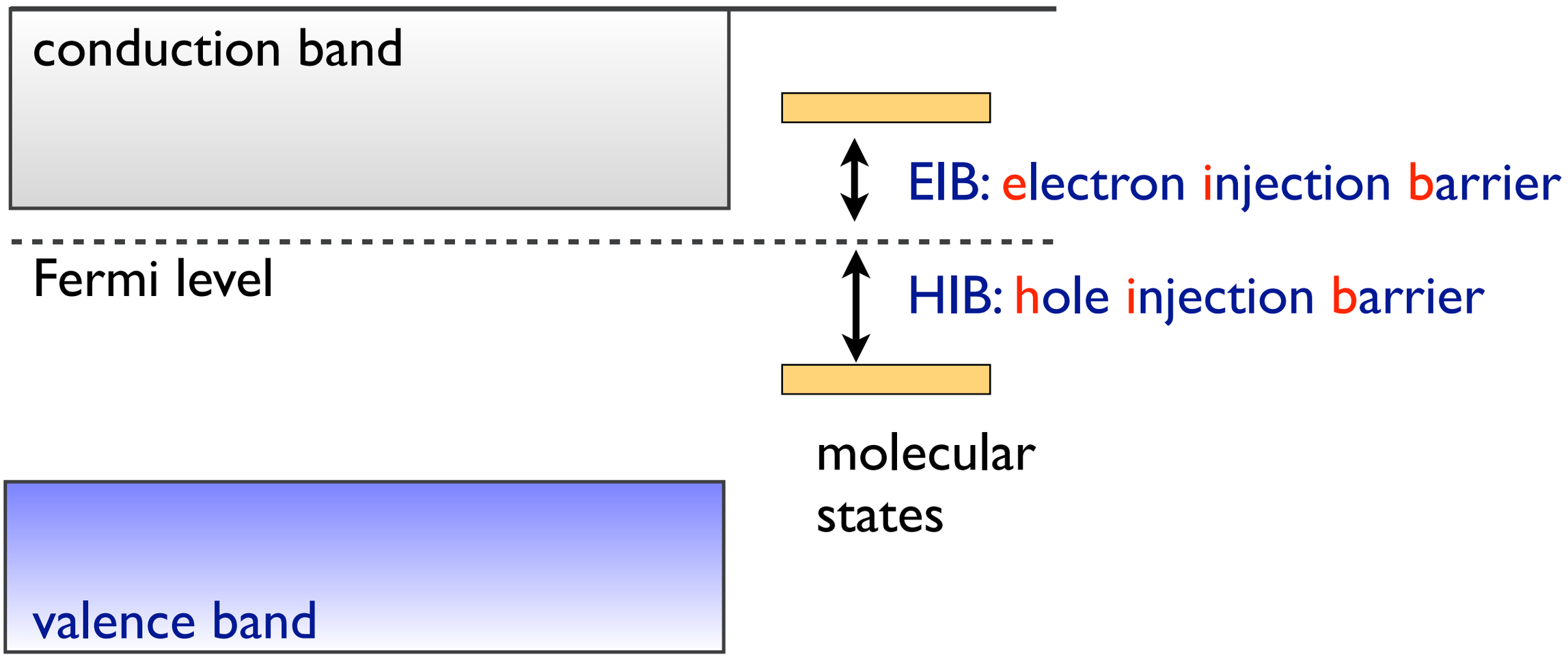
Interface properties

Molecular geometry

Level alignment



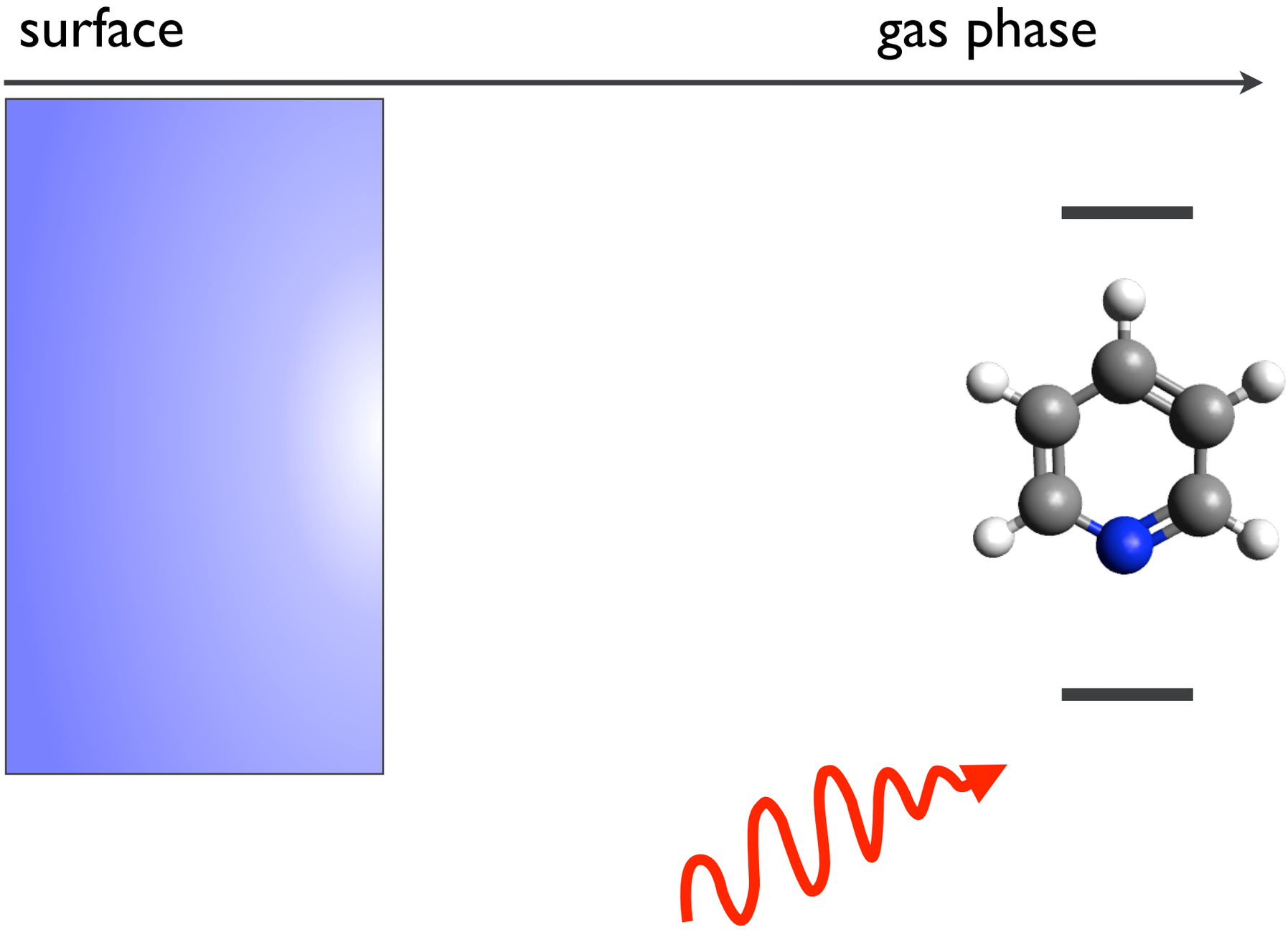
Level alignment at interface



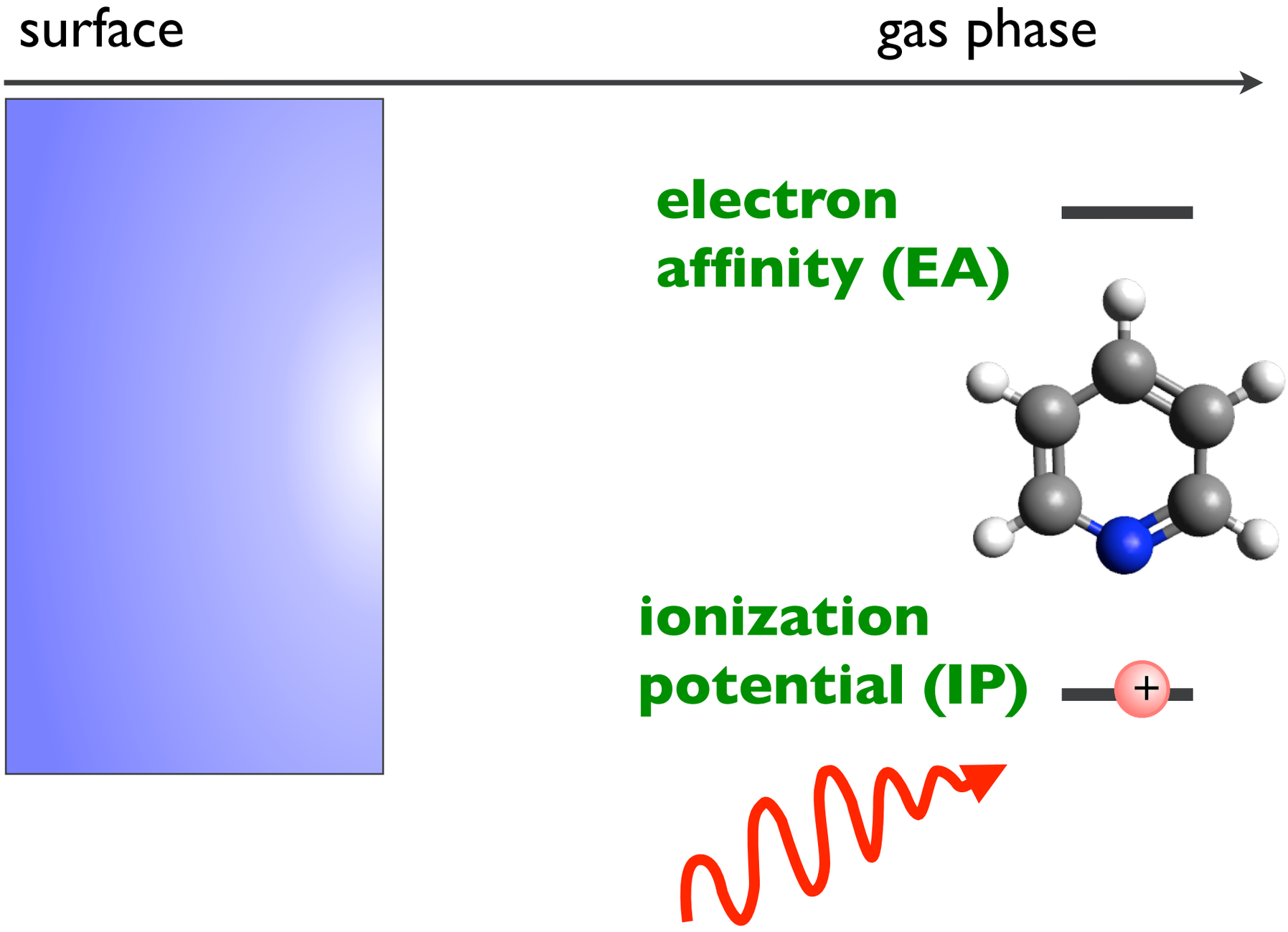
injection limited current:

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

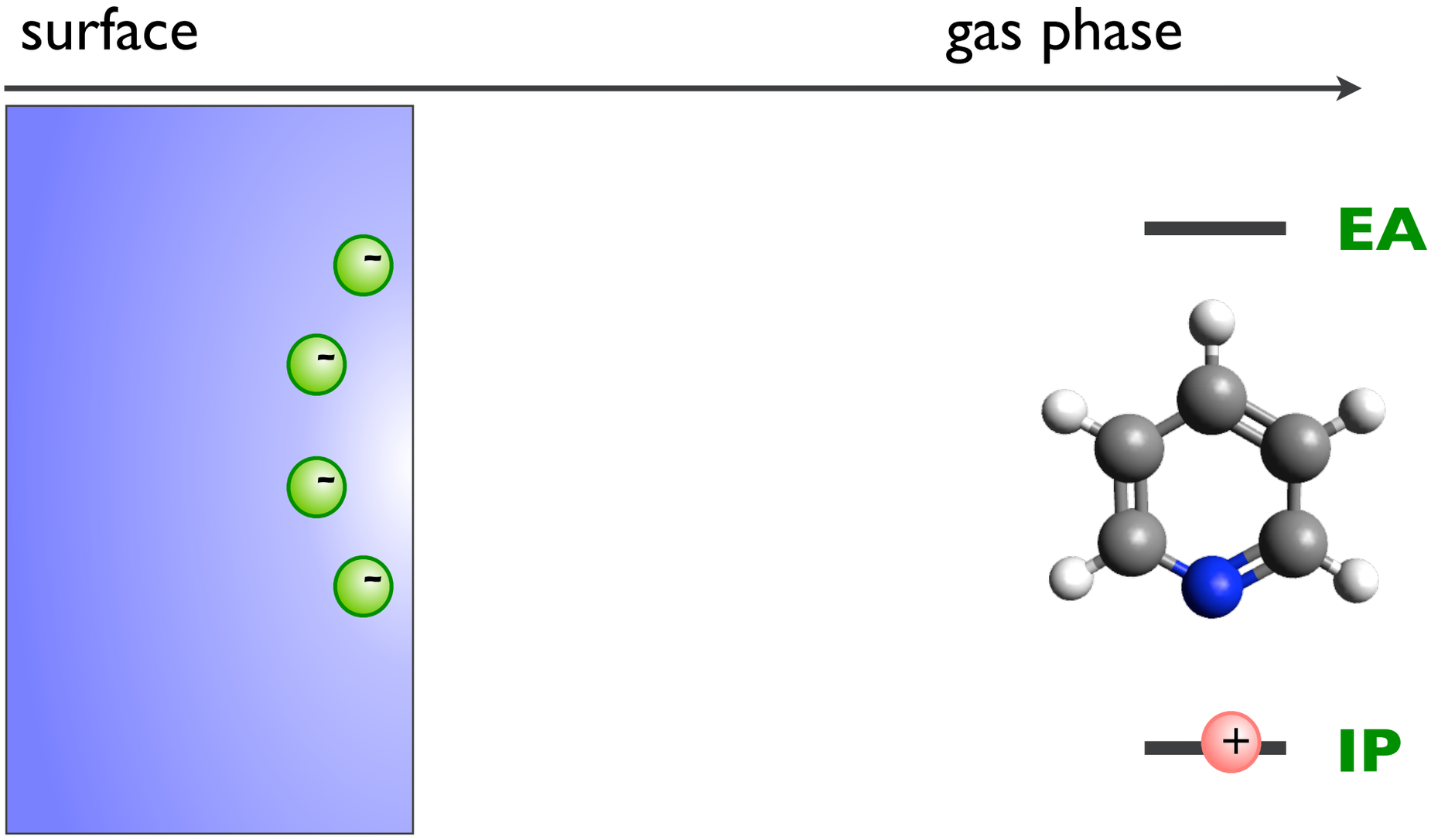
Molecular levels at surface



Molecular levels at surface



Molecular levels at surface



Molecular levels at surface

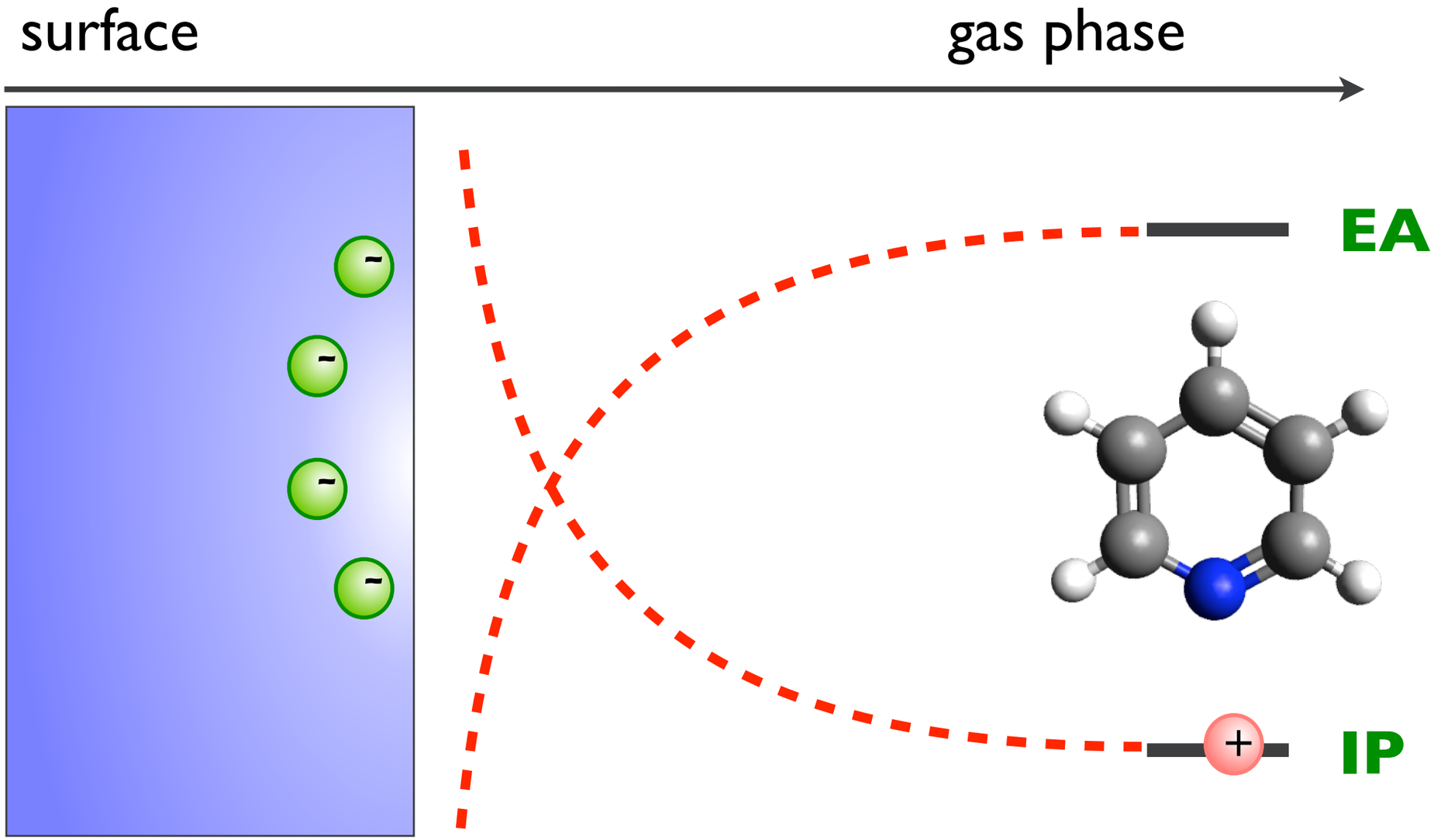
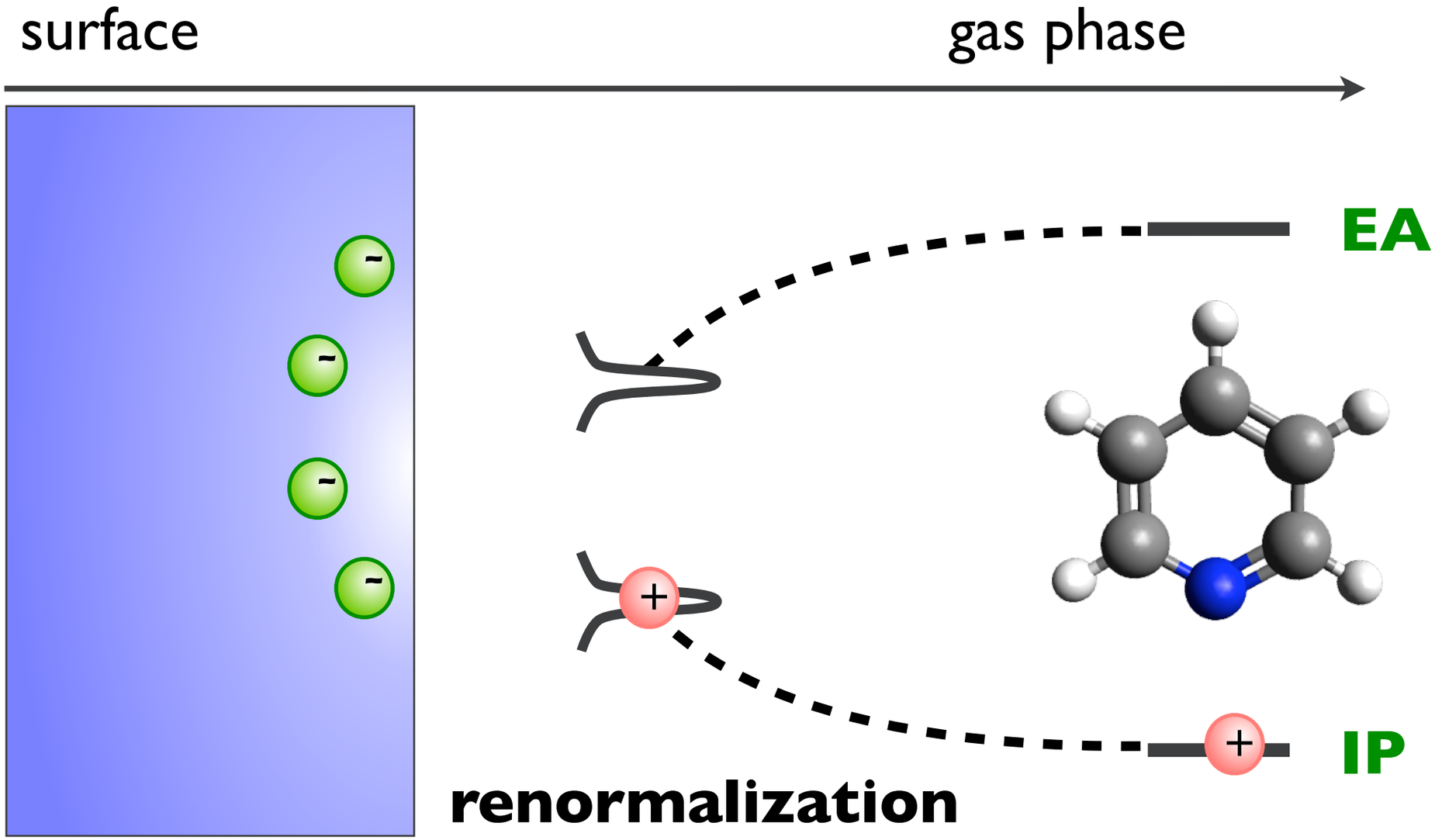


image potentials

Molecular levels at surface



Molecular levels at surface

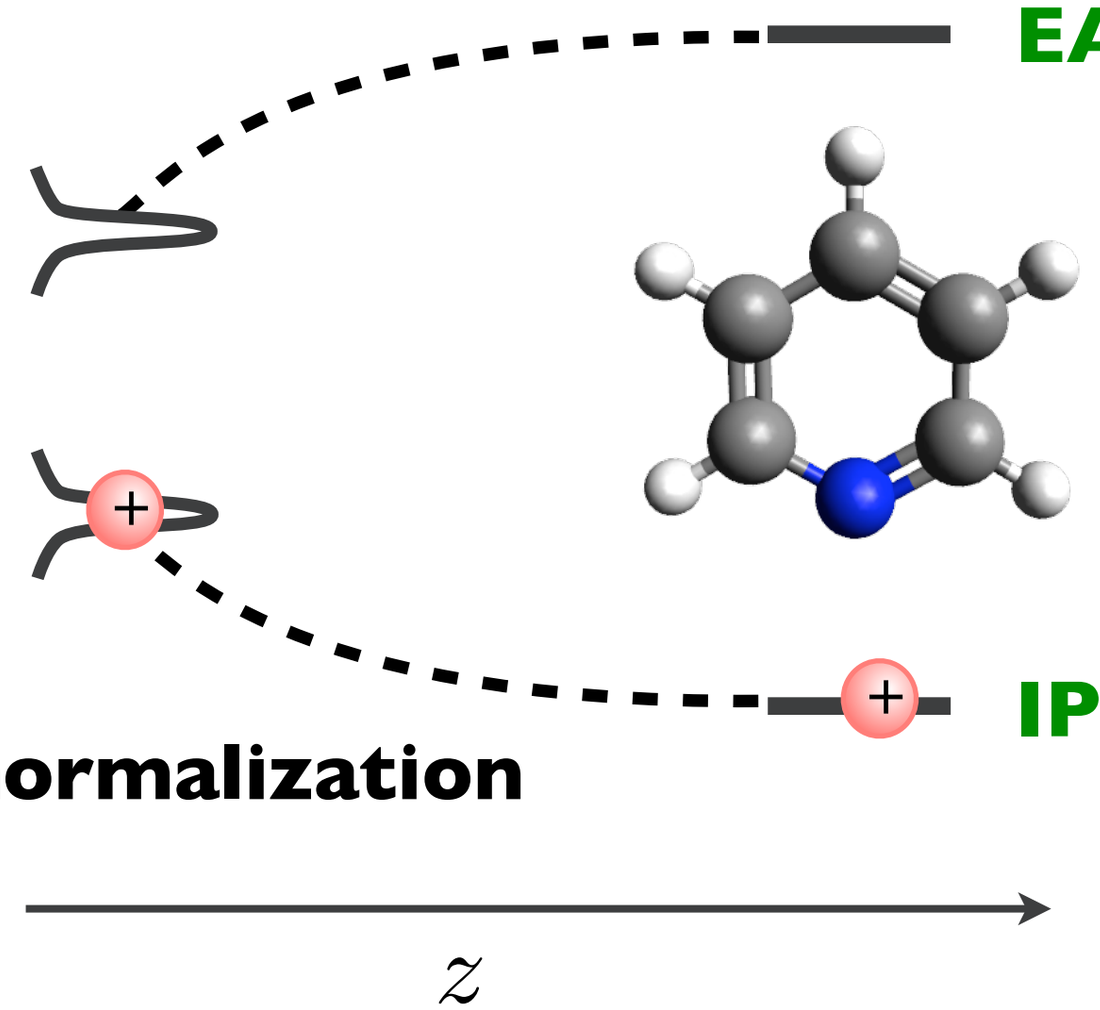
surface → gas phase

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

semiconductor:

ε dielectric constant

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



The screened Coulomb interaction

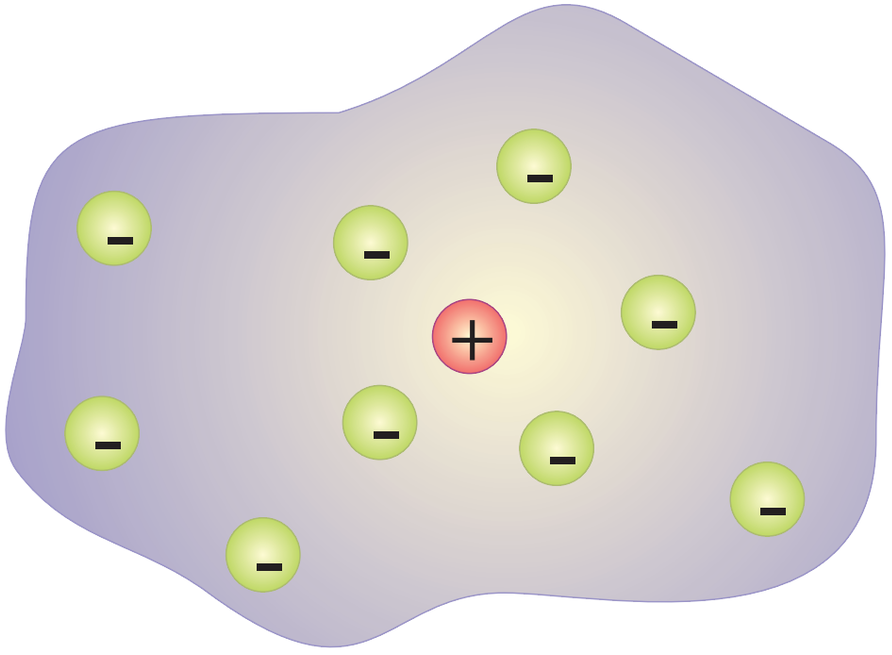
$$W(\mathbf{r},\mathbf{r}',t) = \int d\mathbf{r}'' \frac{\varepsilon^{-1}(\mathbf{r},\mathbf{r}'',t)}{|\mathbf{r}''-\mathbf{r}'|}$$

dielectric function

screened

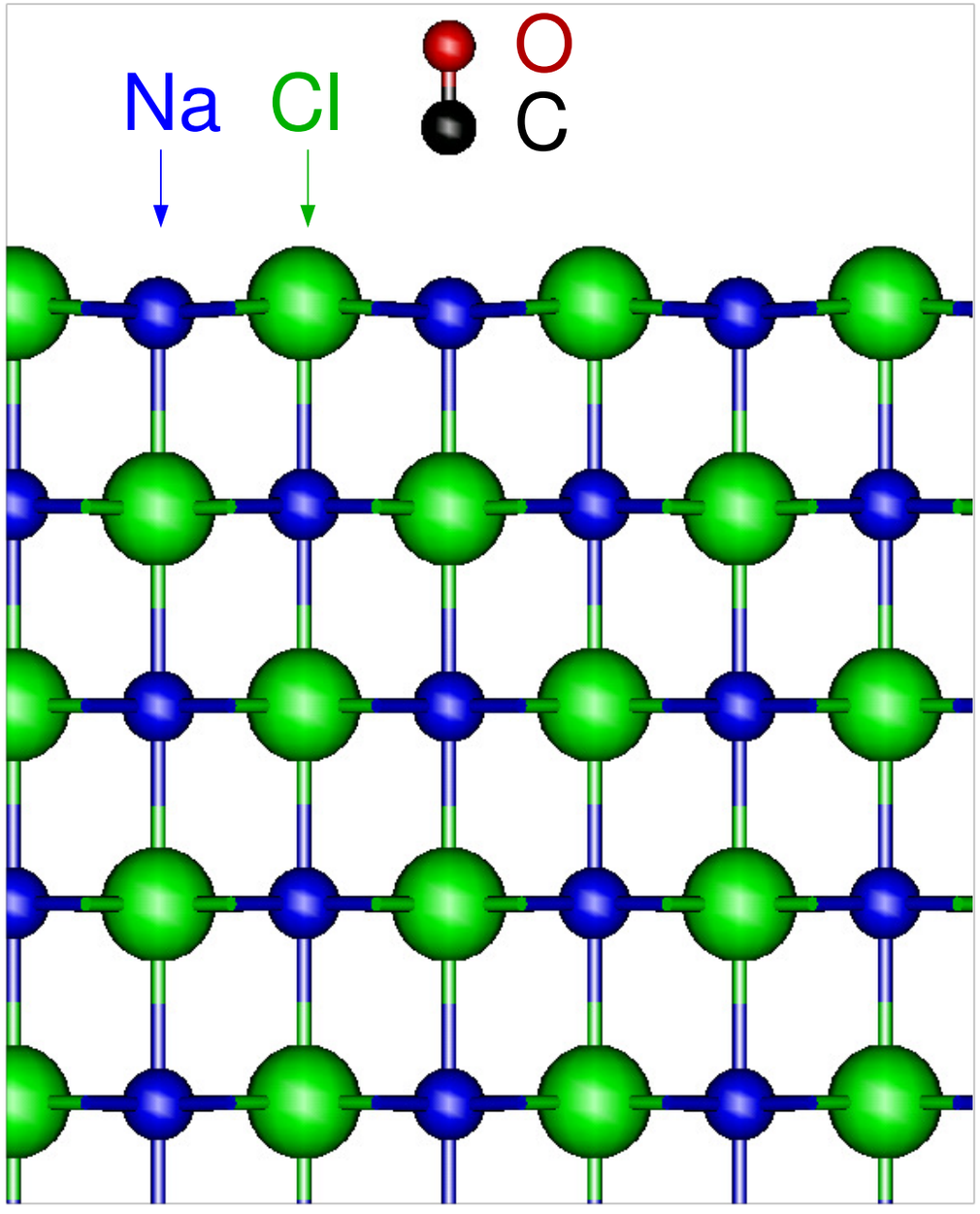
bare

Coulomb interaction



This is exactly what we are doing in *GW*!

Renormalization at insulator surfaces



CO HOMO-LUMO gap

gap/eV	DFT (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)

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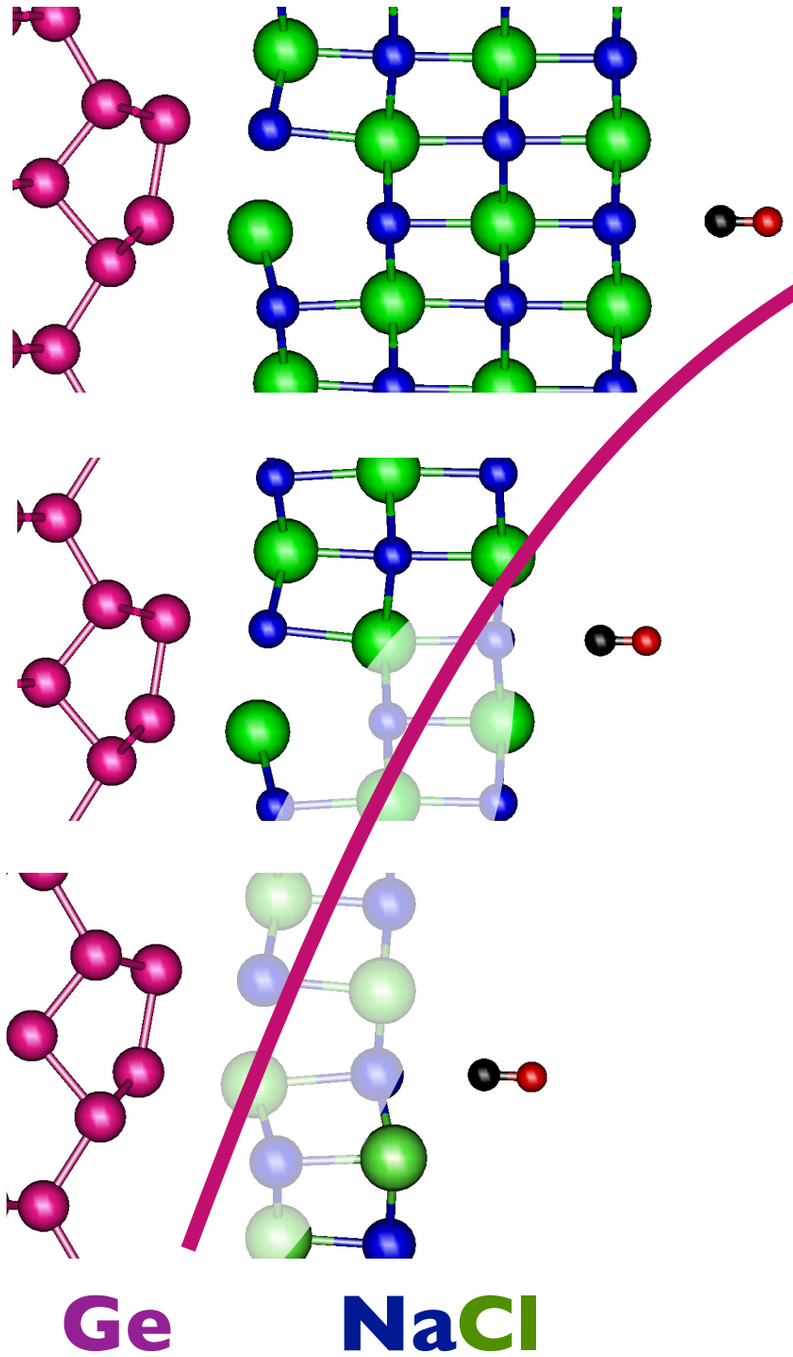
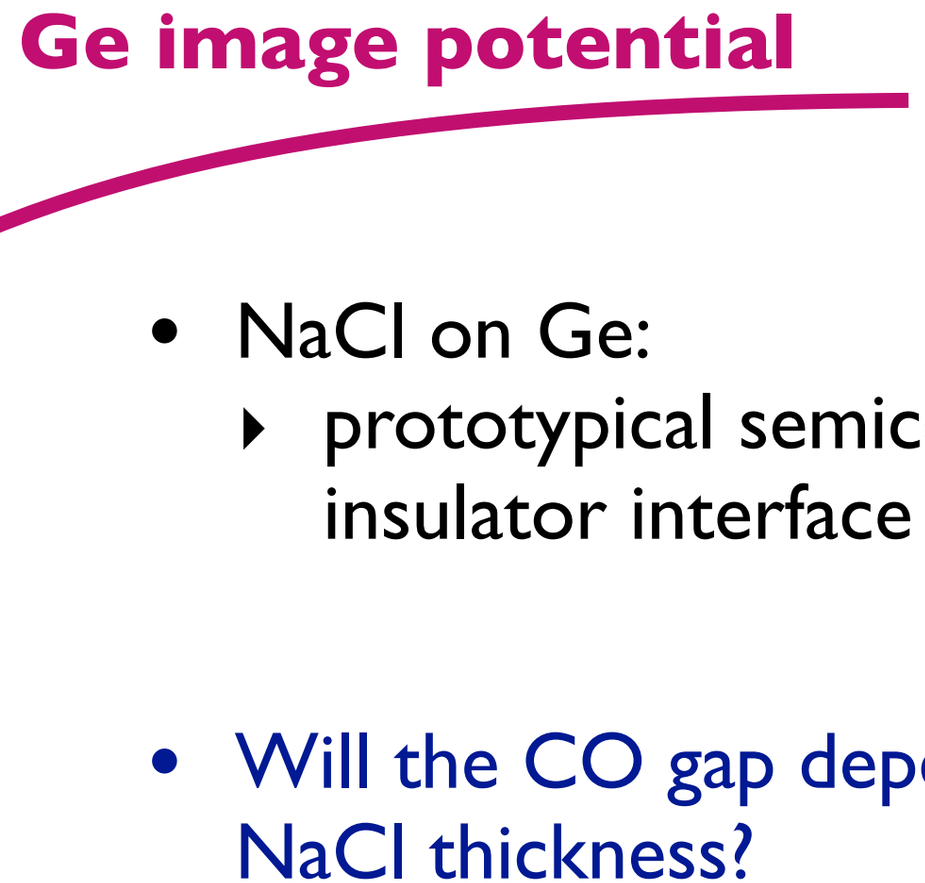
C. Freysoldt, P. Rinke, M. Scheffler, Phys. Rev. Lett. 103, 056803 (2009)

Make CO "ride the 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)

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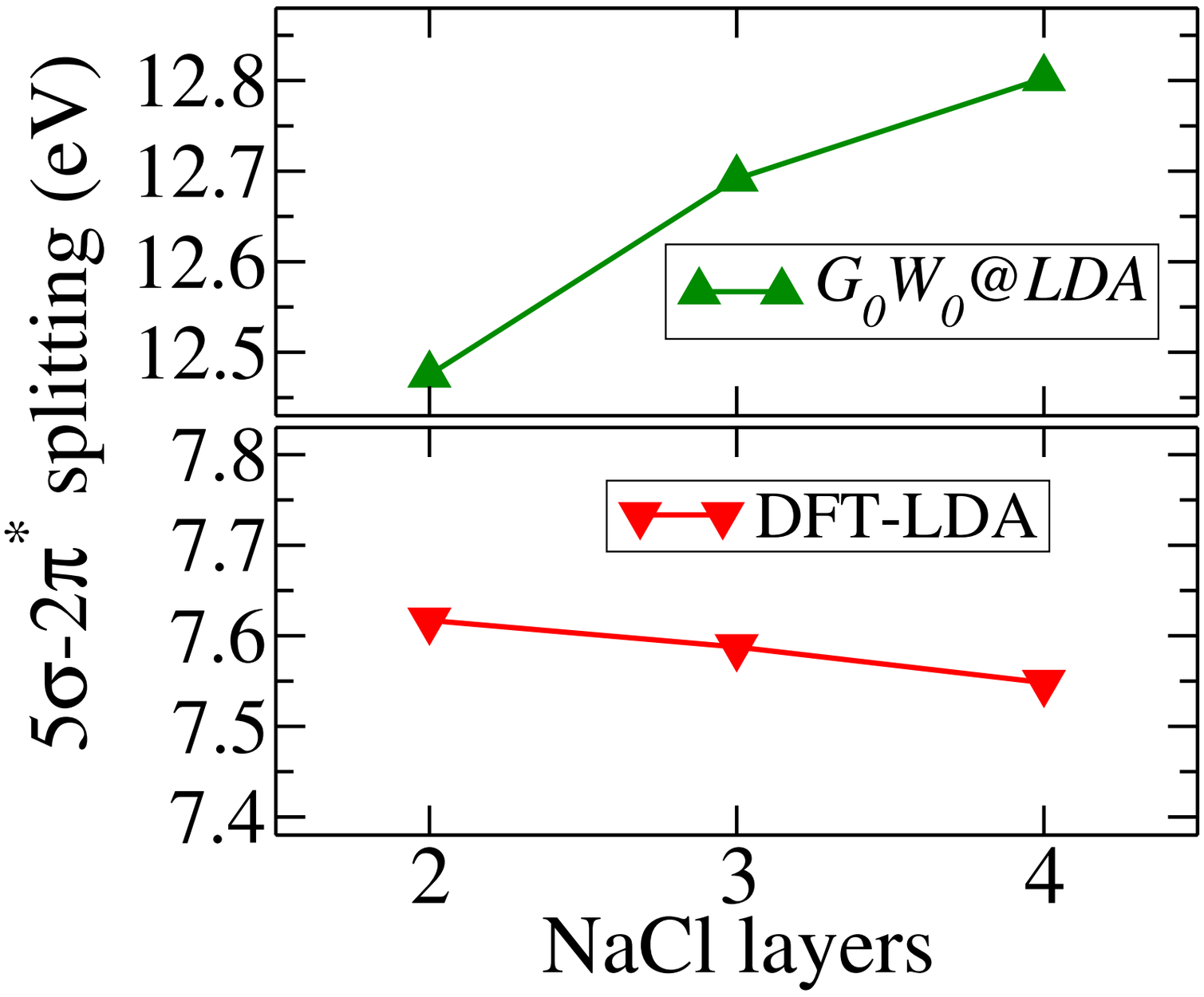
C. Freysoldt, P. Rinke, M. Scheffler, Phys. Rev. Lett. 103, 056803 (2009)

CO on NaCl on Ge - layer dependent gap



- molecular levels can be tuned by polarization engineering

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

Why bother with *GW*?

What's wrong with DFT?

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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*

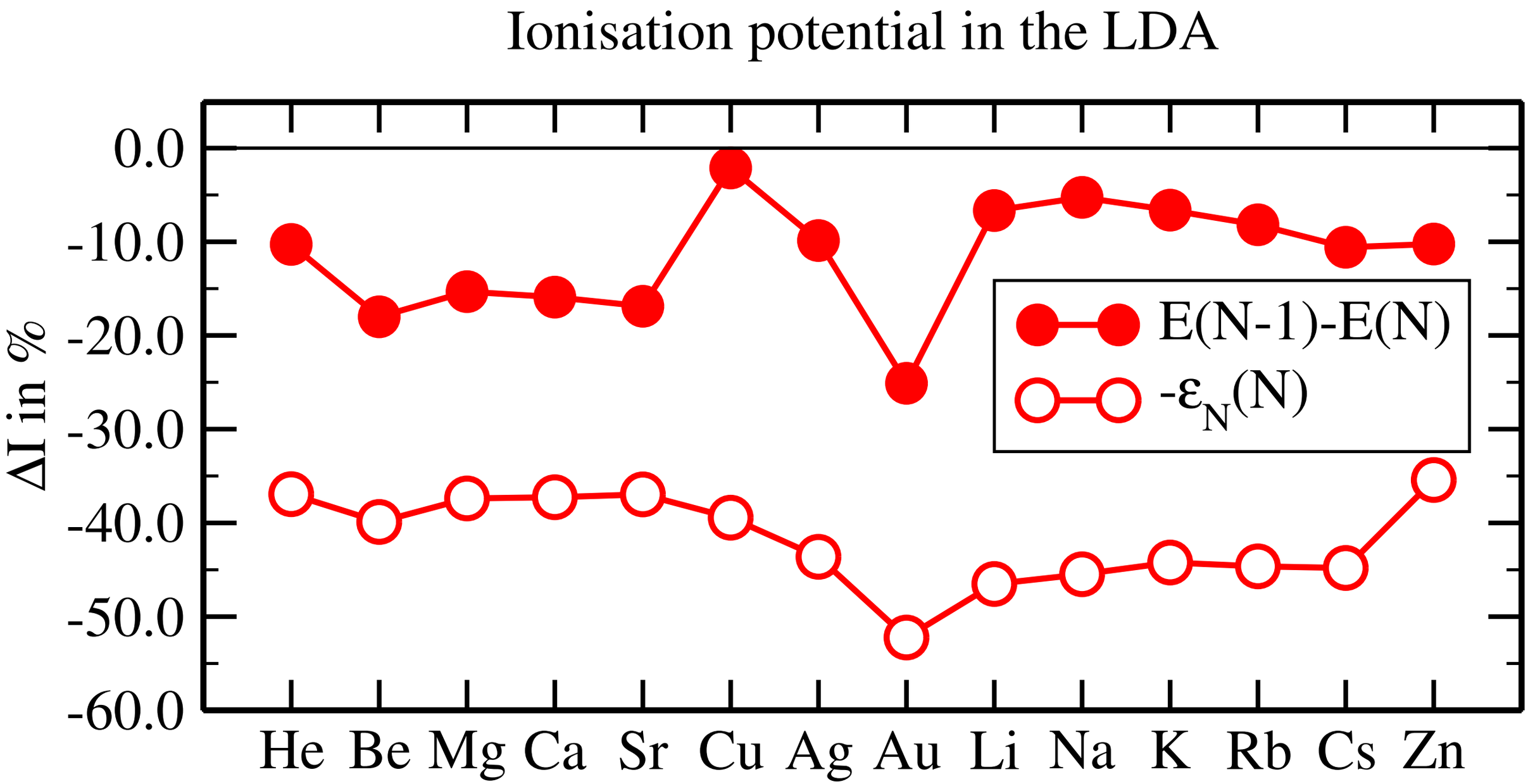
$$I = E(N-1) - E(N)$$

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



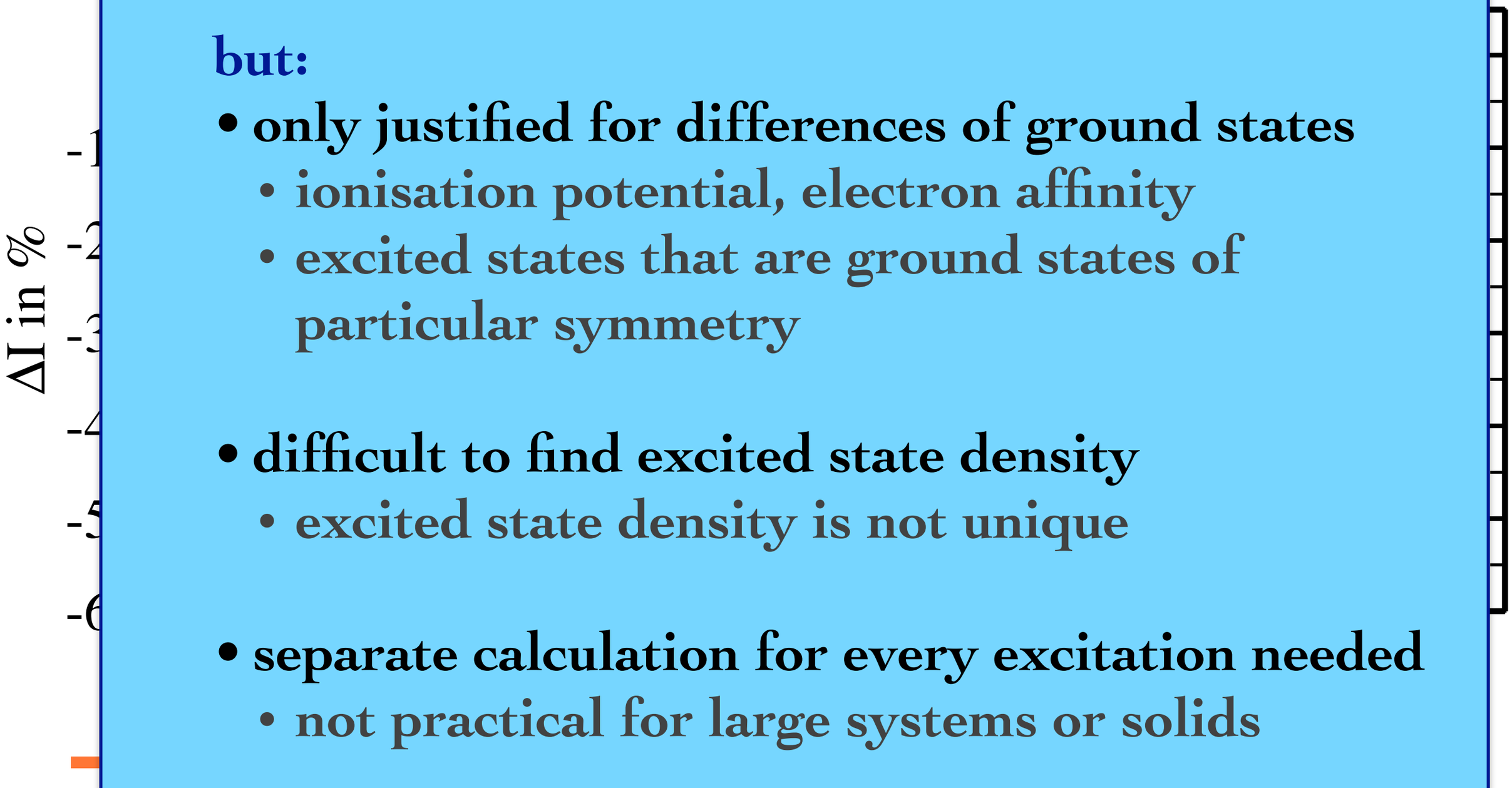
Reference: NIST -- Atomic reference data

Ionisation Potential, Affinity and (Band) Gaps

ΔSCF better than eigenvalues for IPs!

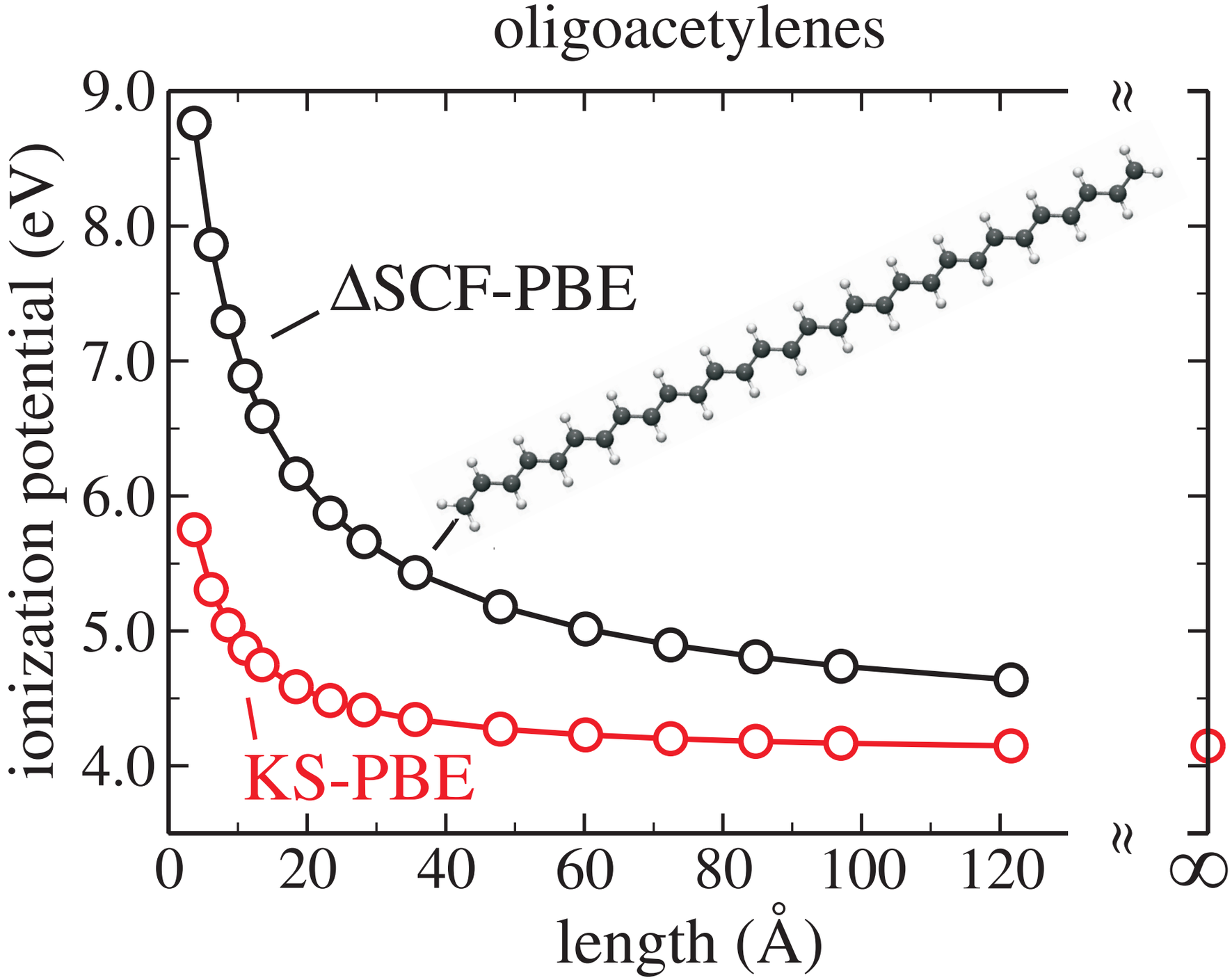
but:

- **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



Reference: NIST -- Atomic reference data

ΔSCF versus eigenvalues for finite systems



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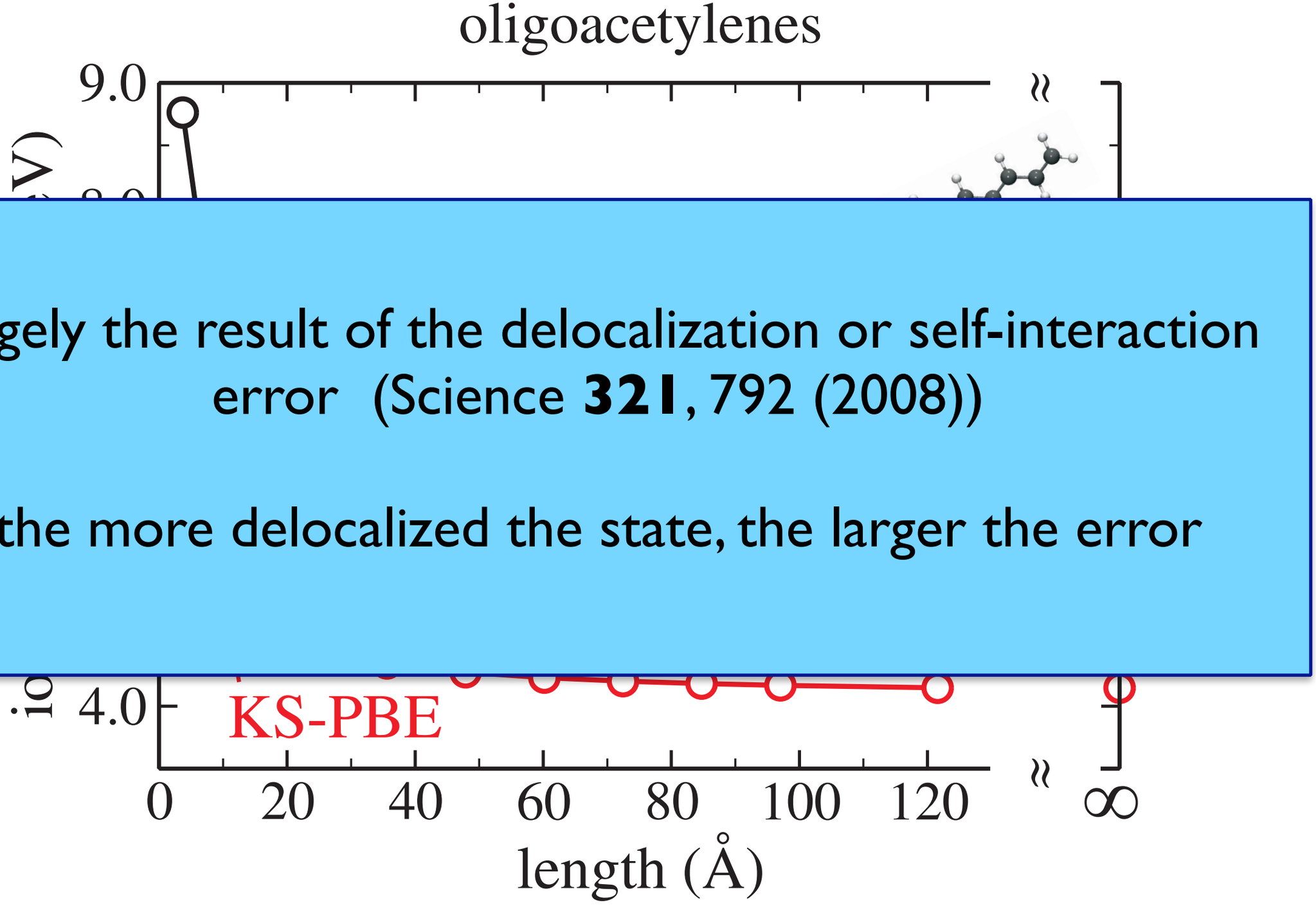
Pinheiro Jr, Caldas, Rinke, Blum, Scheffler
Phys. Rev. B, 92, 195134 (2015)

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

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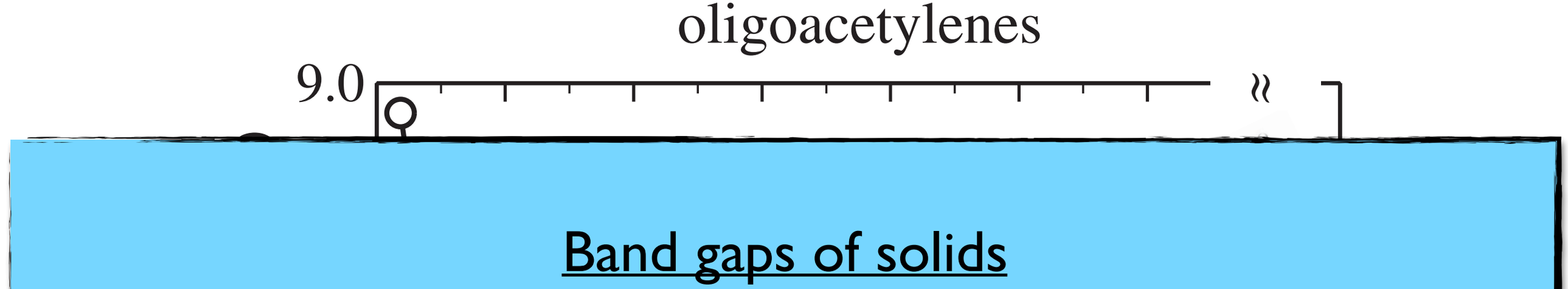
Pinheiro Jr, Caldas, Rinke, Blum, Scheffler
Phys. Rev. B, 92, 195134 (2015)

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:

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

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:

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

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

$$\underbrace{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}_{E^{\mathrm{KS}}_{gap}}$$

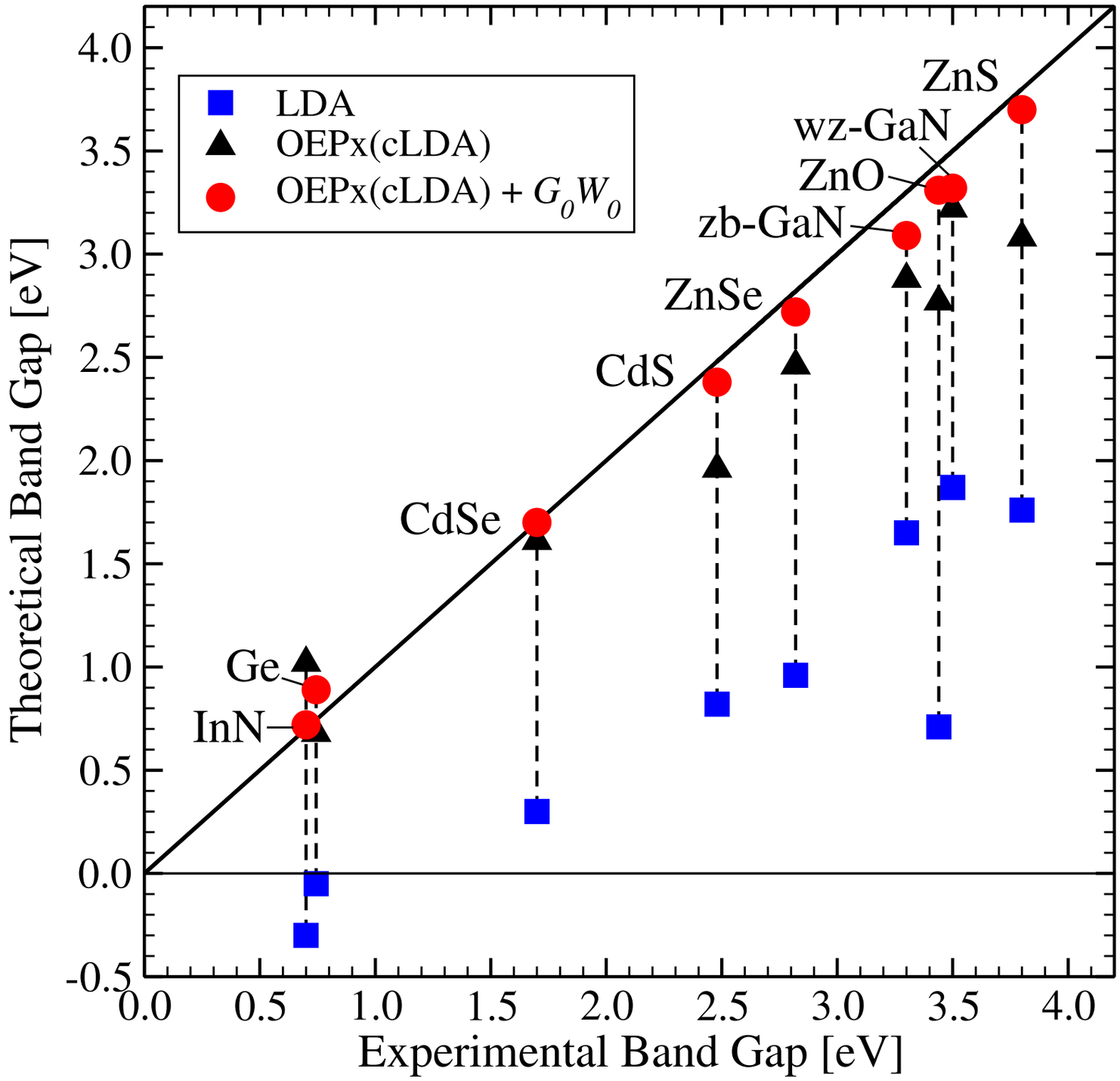
many DFT functionals do not capture this derivative discontinuity

- for so… $\to N+1$

v_{xc}: c… mber:

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

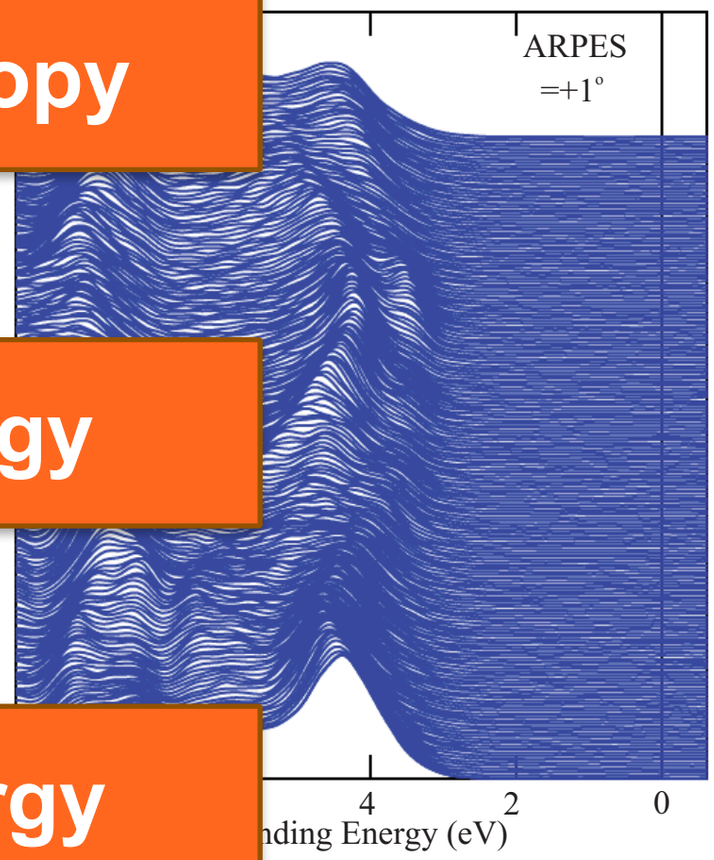
Band gaps of solids



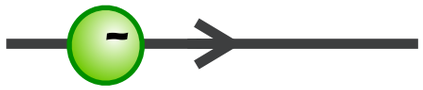
P. Rinke et al. New J. Phys. *7*, 126 (2005), phys. stat. sol. (b) 245, 929 (2008)

What we learned today

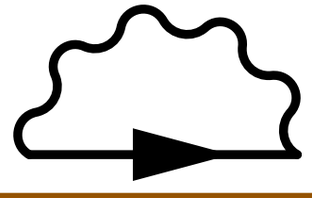
Basic principles of electron spectroscopy



The Green's function and the self-energy



The GW approximation to the self-energy

$$\Sigma^{GW} =$$ 

Pros and cons of density-functional theory for electron spectroscopies

Impact Factor 3.782 | CiteScore 3.51
More on impact ›

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REVIEW ARTICLE

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

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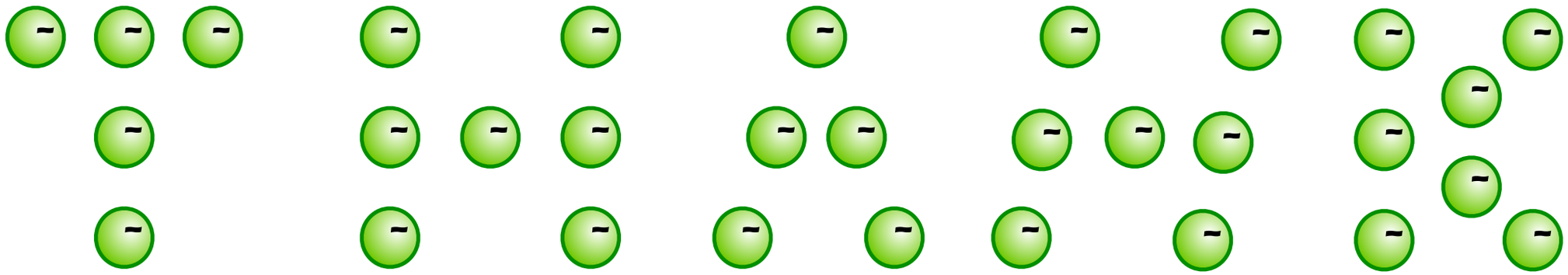
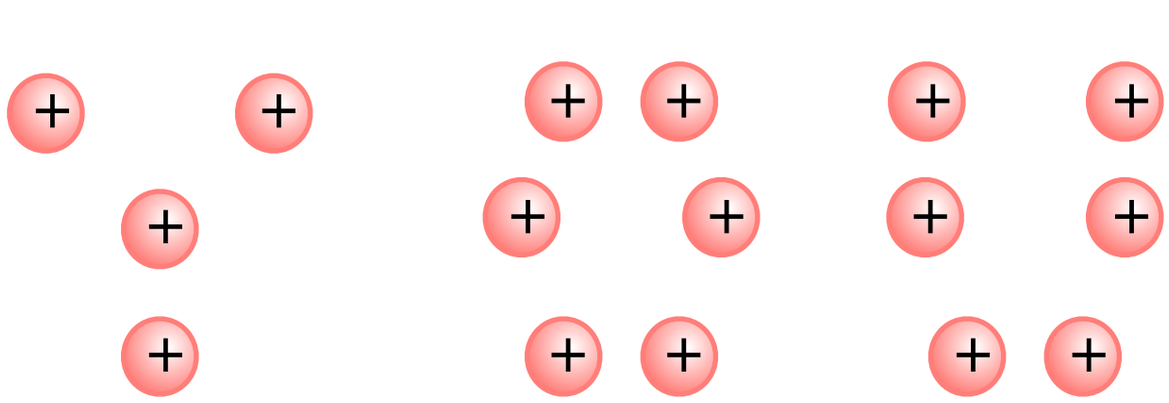
Aalto University
School of Science

I need your input!

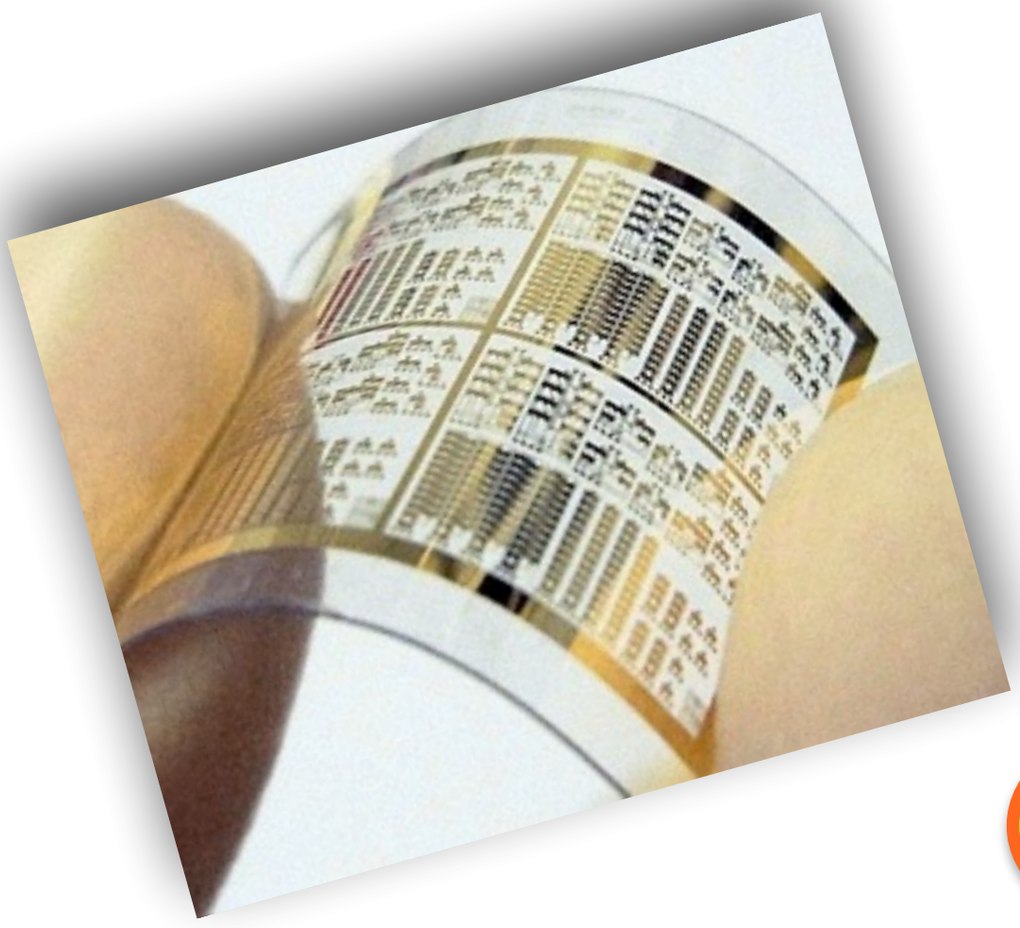
Take out your mobile phone (or laptop) and go to:

https://presemo.aalto.fi/barcelona2019gw



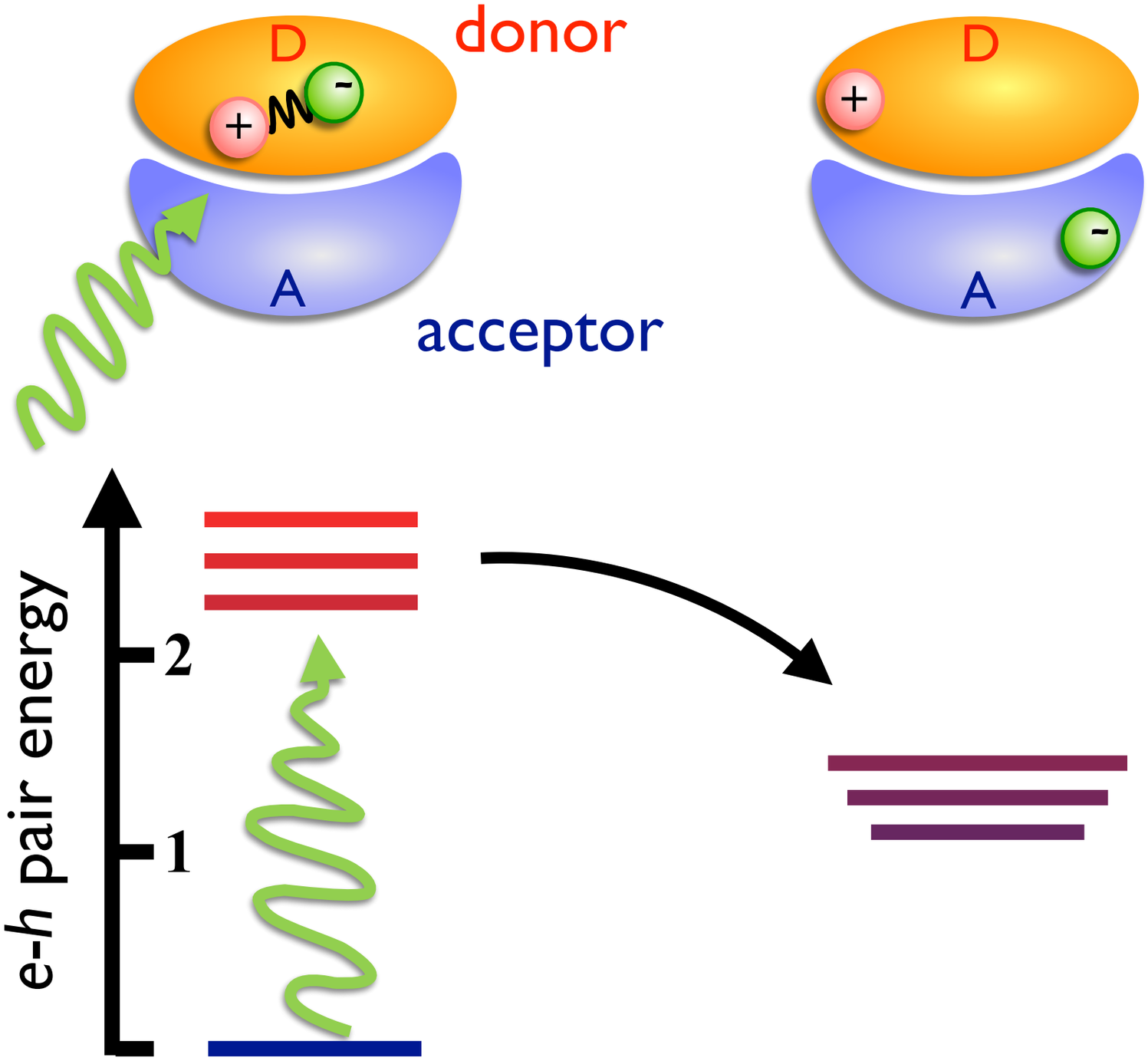


Organic or plastic electronics



sources (left to right): Eco Friend, Nature Publishing Group

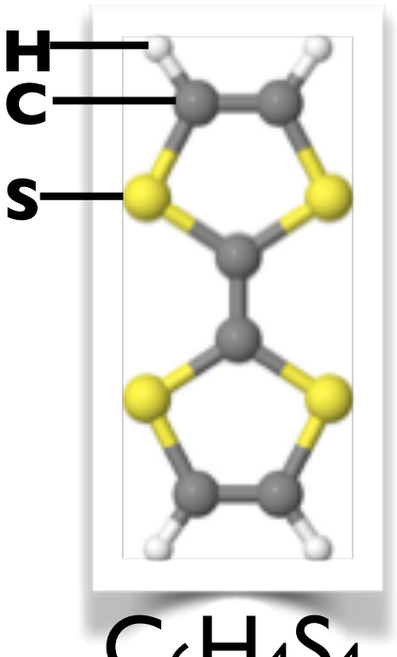
Charge separation at donor-acceptor pairs



Donor-acceptor pair: TTF and TCNQ

all values in eV

TTF



$C_6H_4S_4$

donor

EA

3.3

6.7

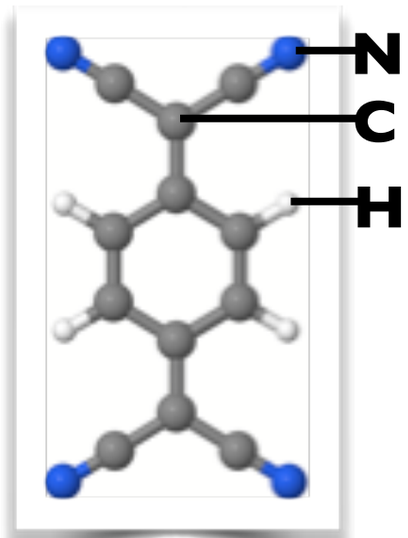
IP

9.5

exp

exp

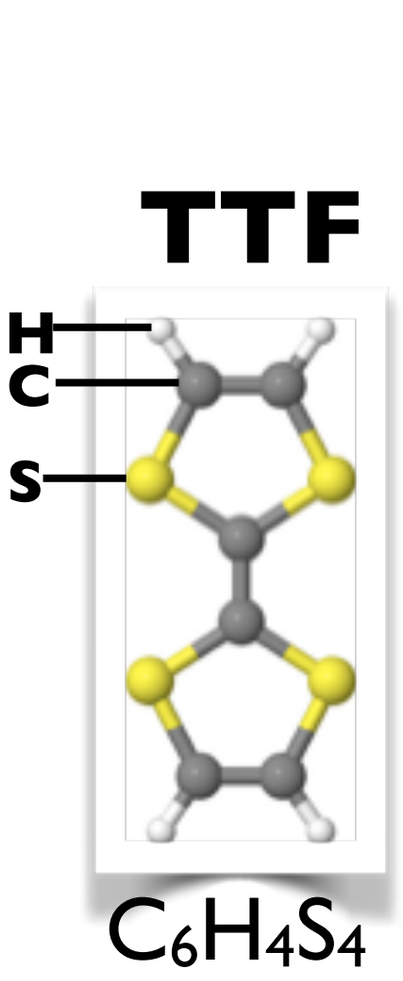
TCNQ



$C_{12}H_4N_4$

acceptor

Donor-acceptor pair: TTF and TCNQ



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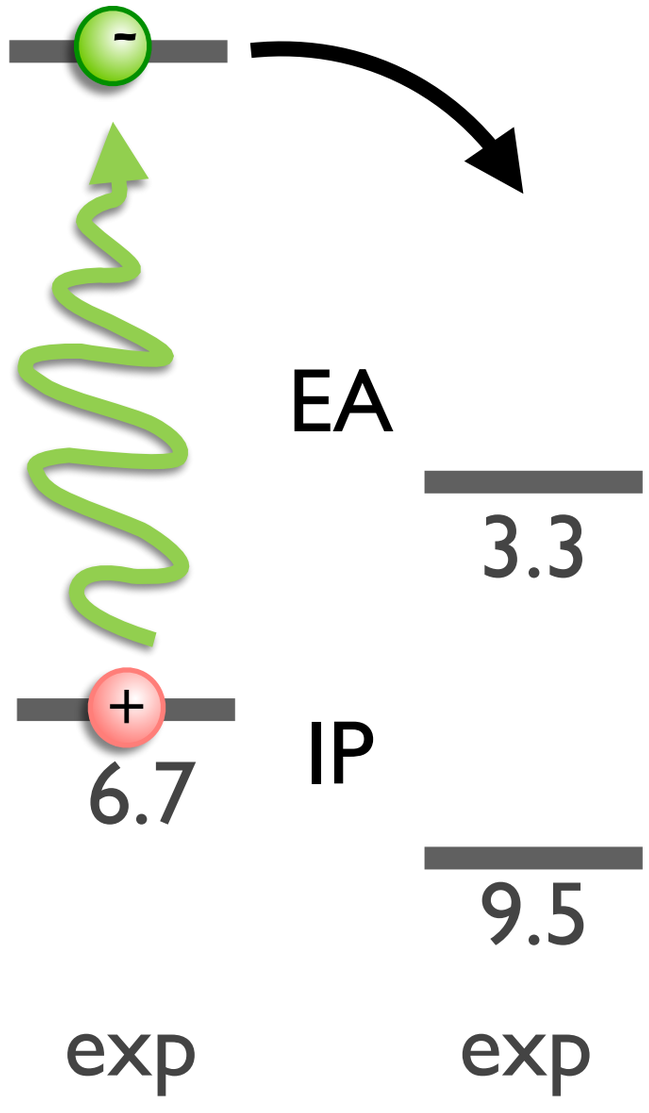
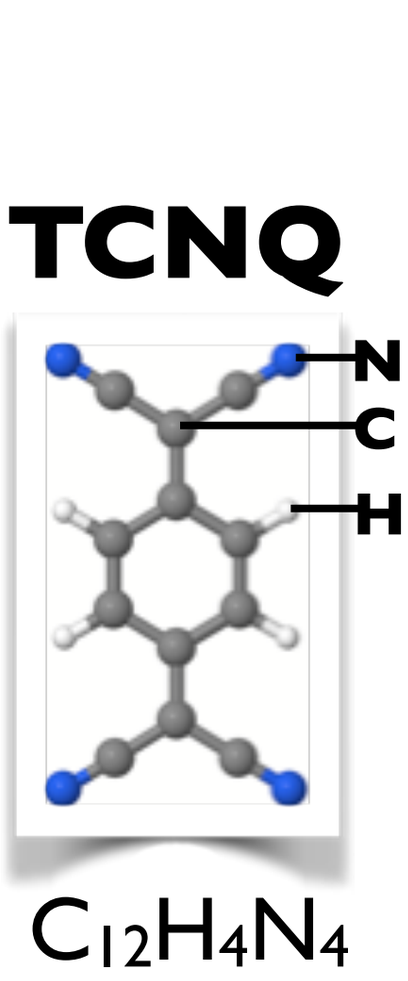




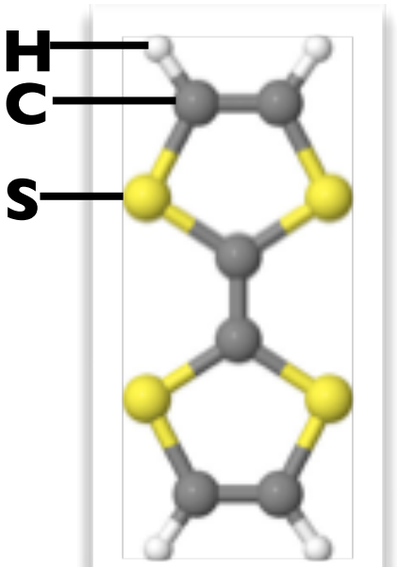
$C_{12}H_4N_4$

donor

acceptor

Donor-acceptor pair: TTF and TCNQ

TTF



$C_6H_4S_4$

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3.3

6.7

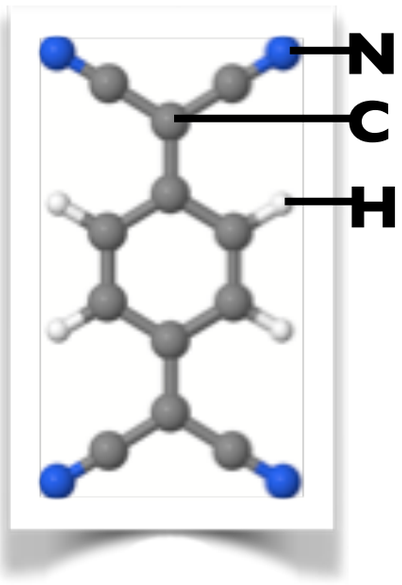
IP

9.5

exp

exp

TCNQ



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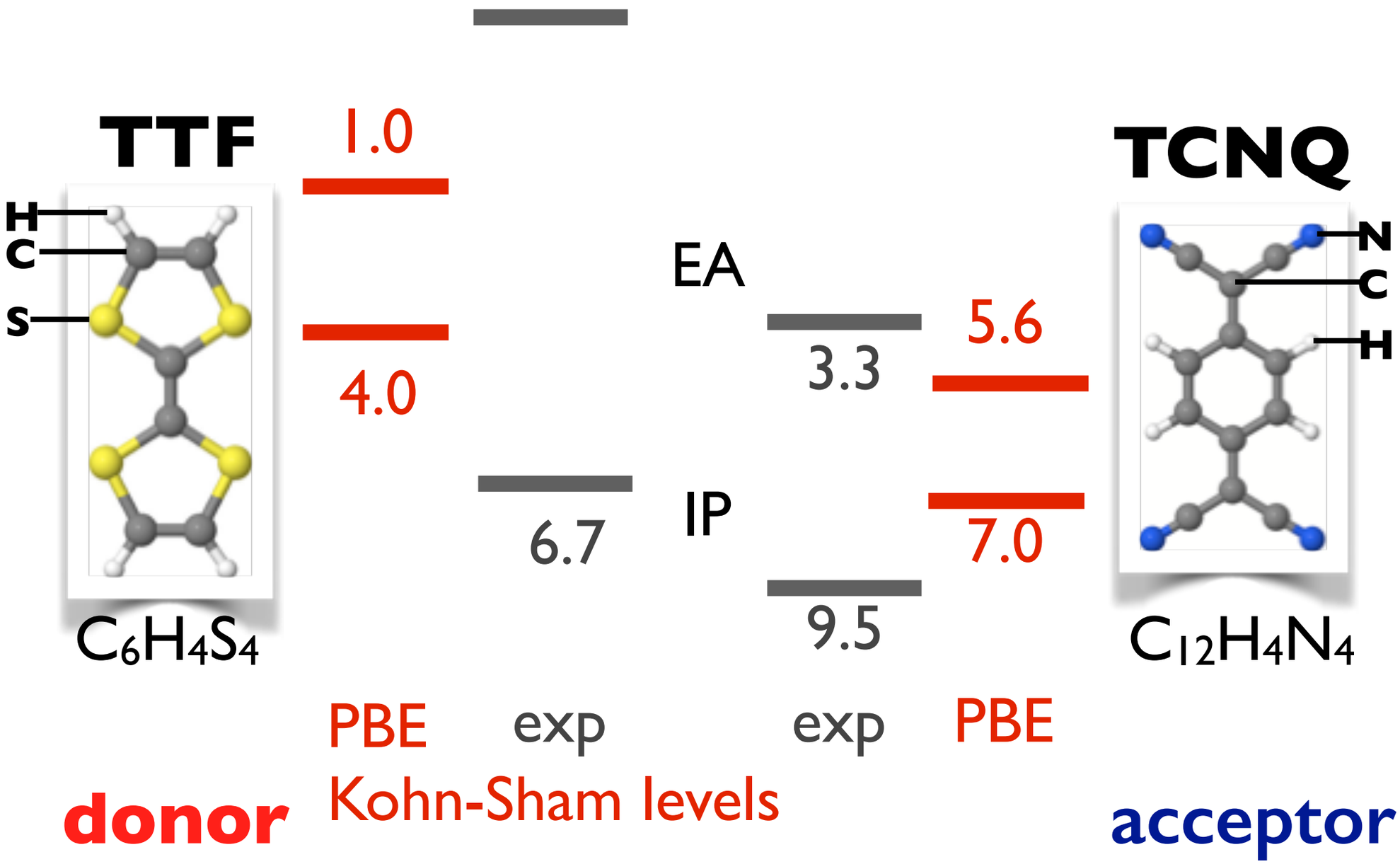

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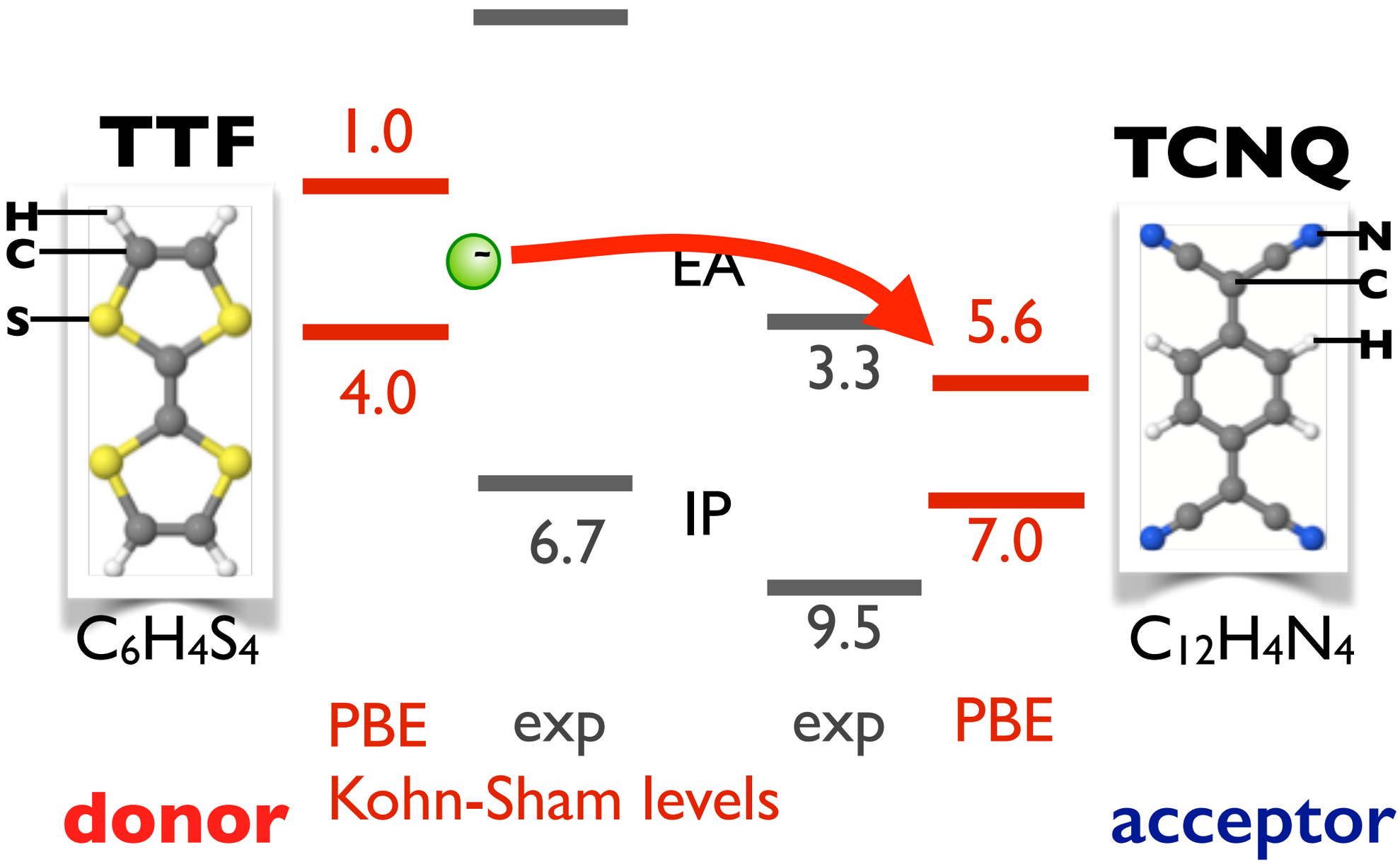
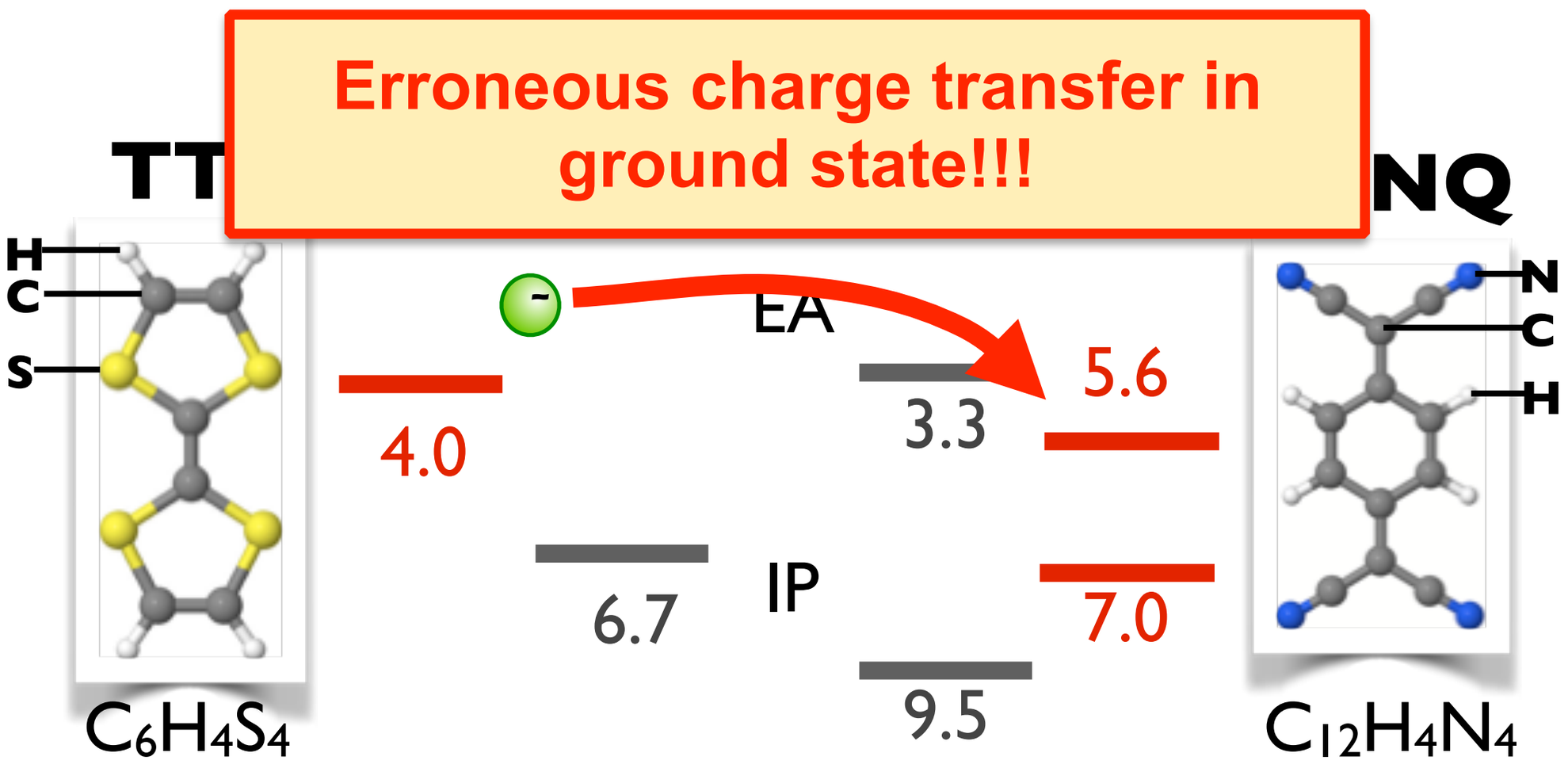


Donor-acceptor pair: TTF and TCNQ

Erroneous charge transfer in ground state!!!



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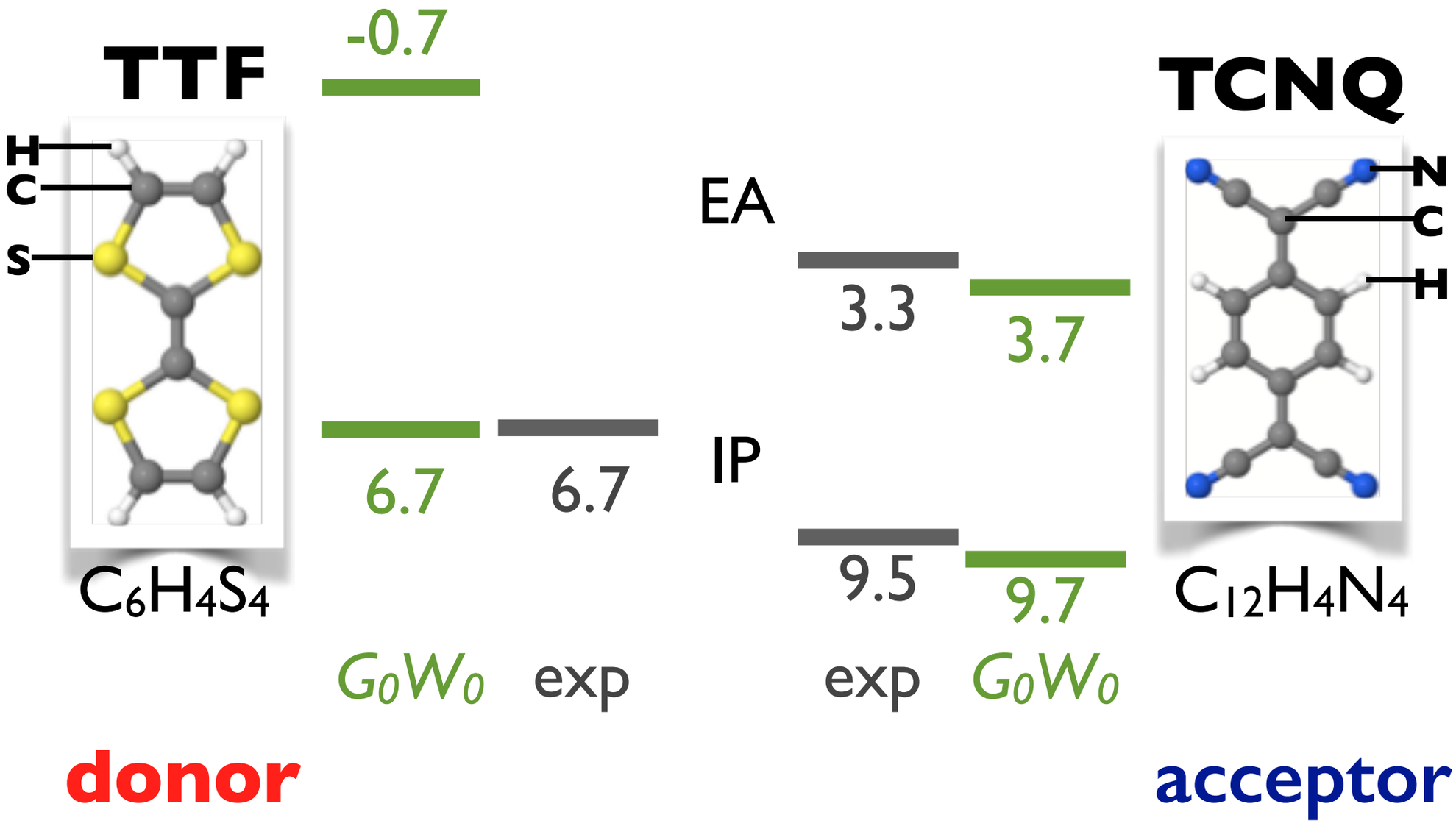

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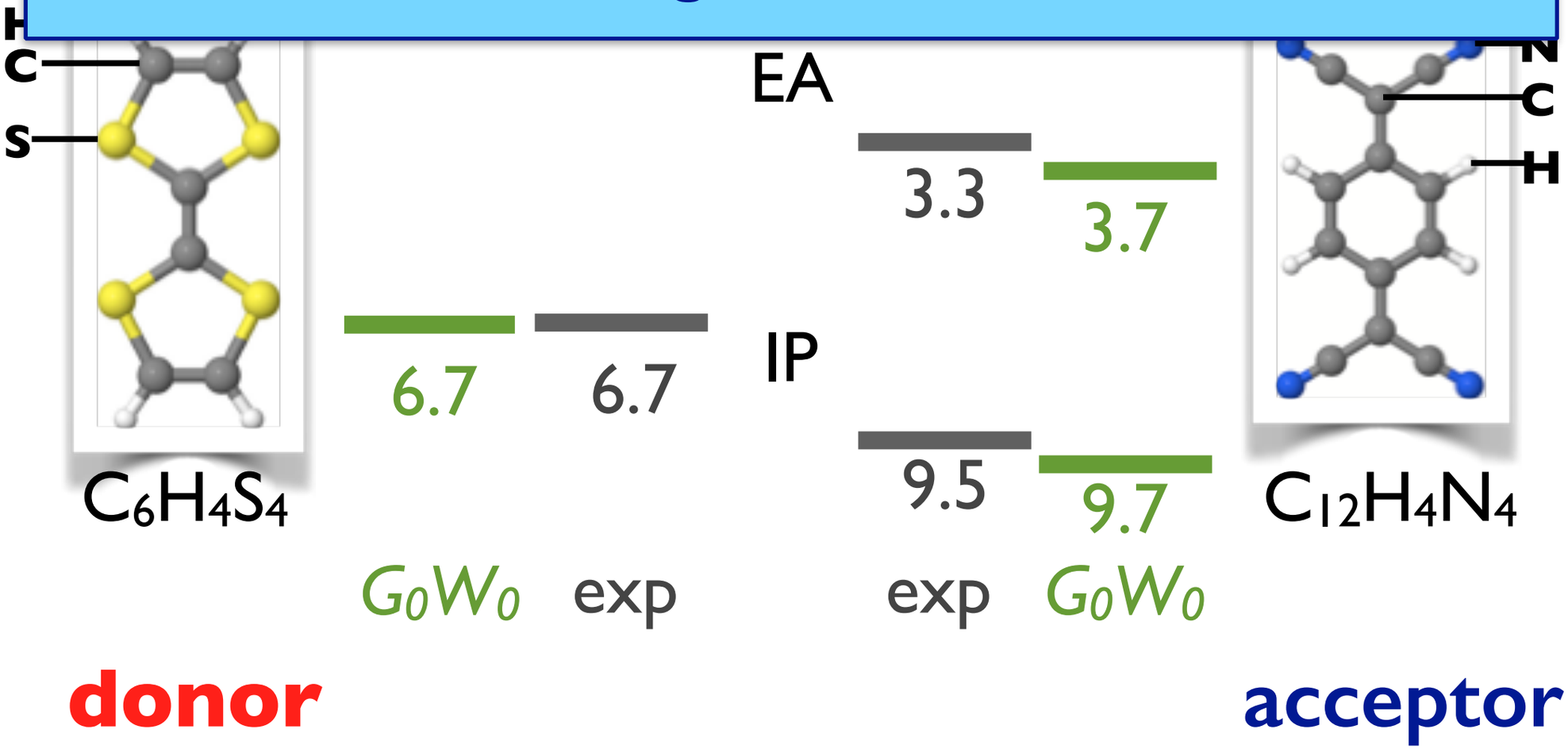
V. Atalla, M. Yoon, F. Caruso, P. Rinke, and M. Scheffler, Phys. Rev. B 88, 165122 (2013)

Donor-acceptor pair: TTF and TCNQ

Correct level ordering, but how to get back to the ground state?



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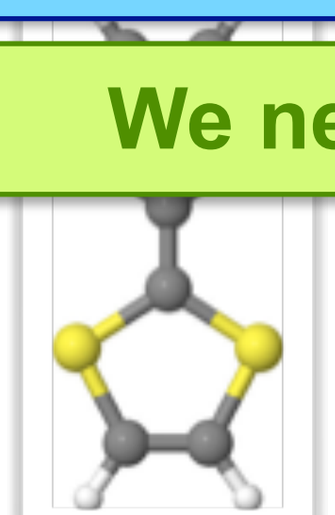
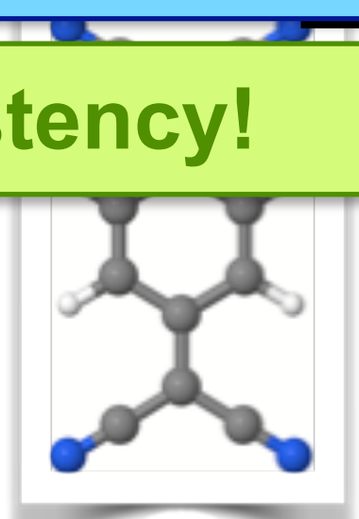
Donor-acceptor pair: TTF and TCNQ

Correct level ordering, but how to get back to the ground state?

We need some form of self-consistency!



$C_6H_4S_4$



$C_{12}H_4N_4$

donor				acceptor	
3.3					3.7
	6.7	6.7	IP		
				9.5	9.7
	G_0W_0	exp		exp	G_0W_0

donor **acceptor**

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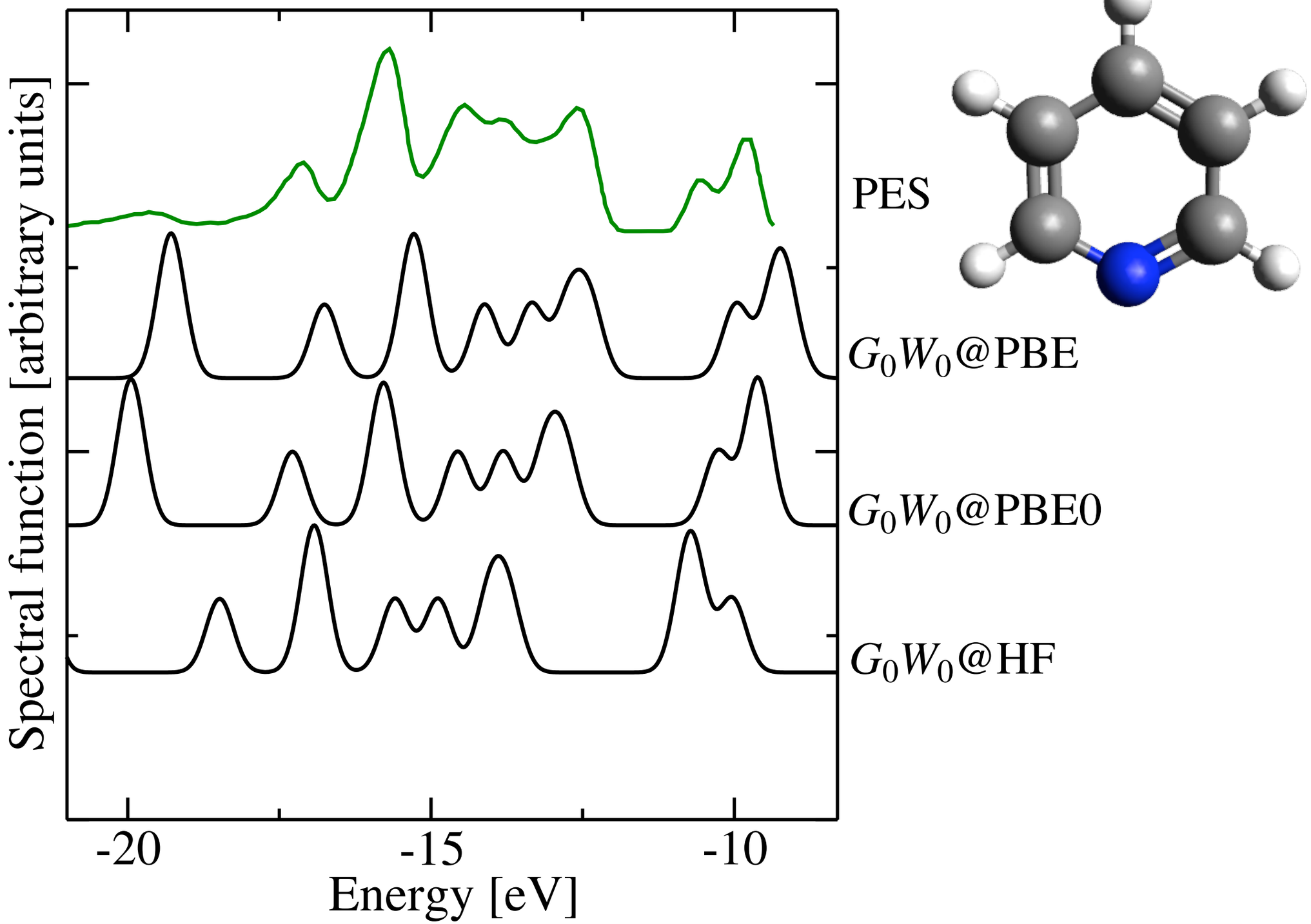
V. Atalla, M. Yoon, F. Caruso, P. Rinke, and M. Scheffler, Phys. Rev. B 88, 165122 (2013)

Another problem: starting-point dependence



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

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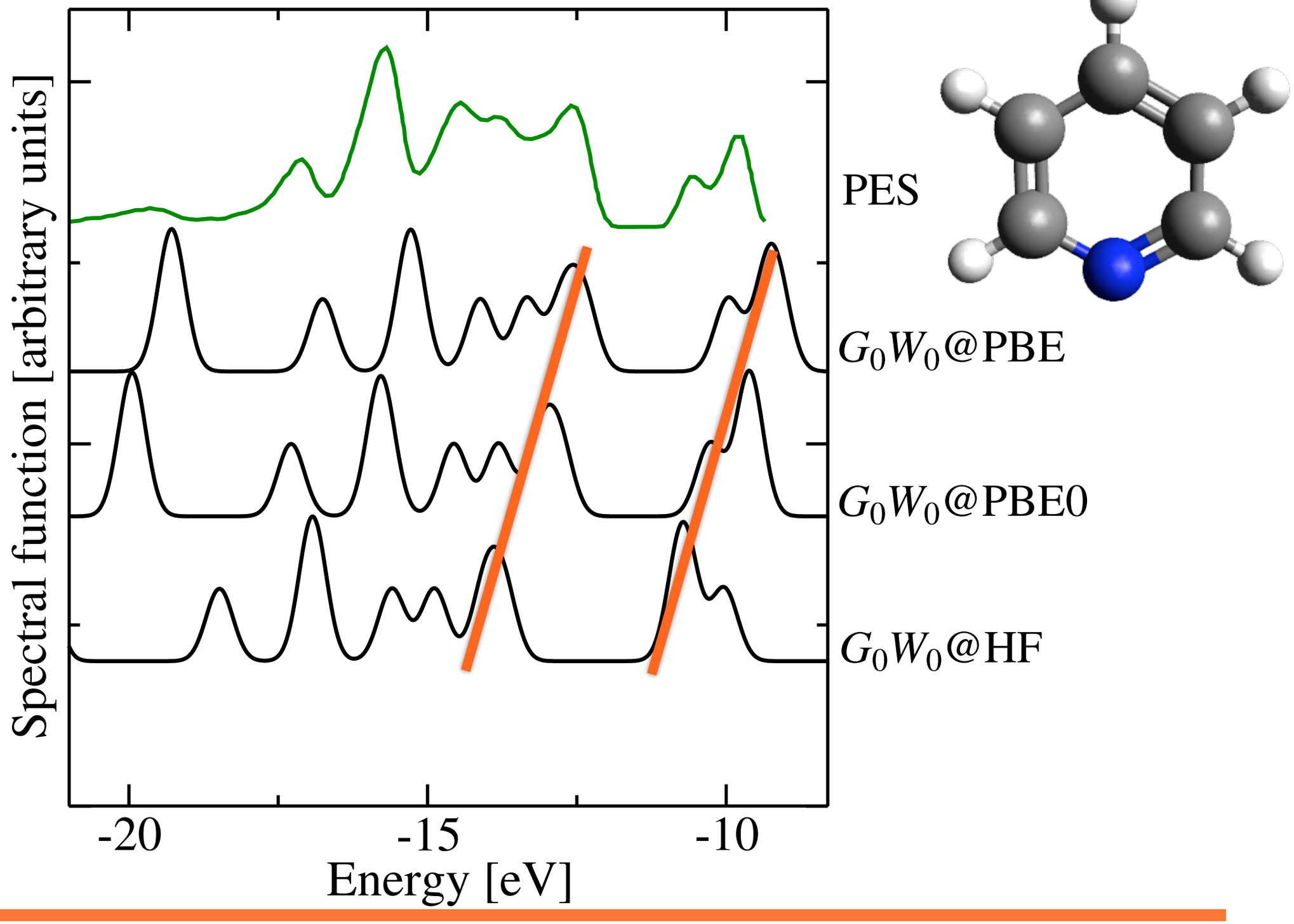

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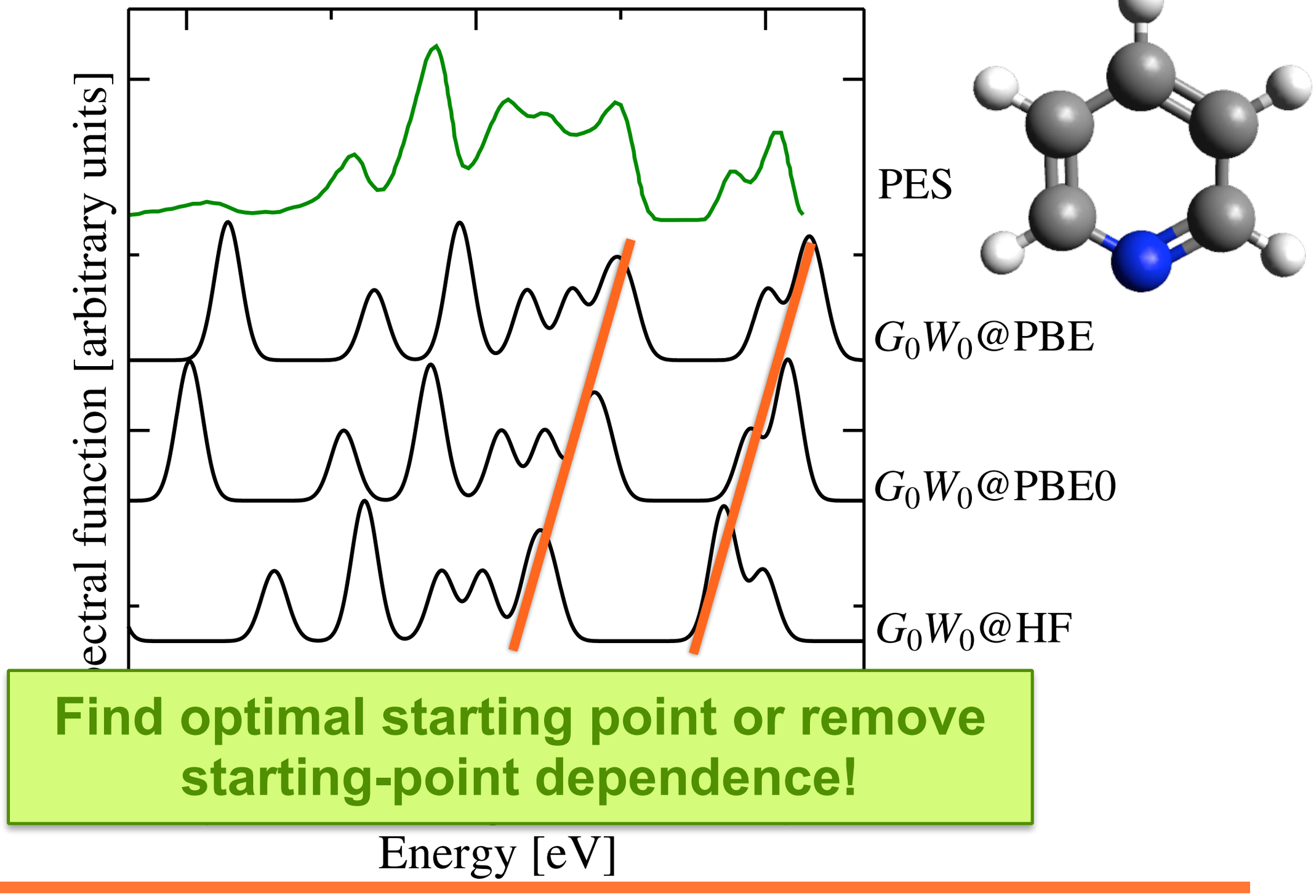

Find optimal starting point or remove starting-point dependence!

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

Self-consistent *GW* (scGW)

Hedin's GW equations:

$$
\begin{aligned}
G(1,2) &= G_0(1,2) \\
\Gamma(1,2,3) &= \delta(1,2)\delta(1,3) \\
P(1,2) &= -iG(1,2)G(2,1^+) \\
W(1,2) &= v(1,2) + \int v(1,3)P(3,4)W(4,2)d(3,4) \\
\Sigma(1,2) &= iG(1,2)W(2,1)
\end{aligned}
$$

self-consistency

Dyson's equation:

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

self-consistency

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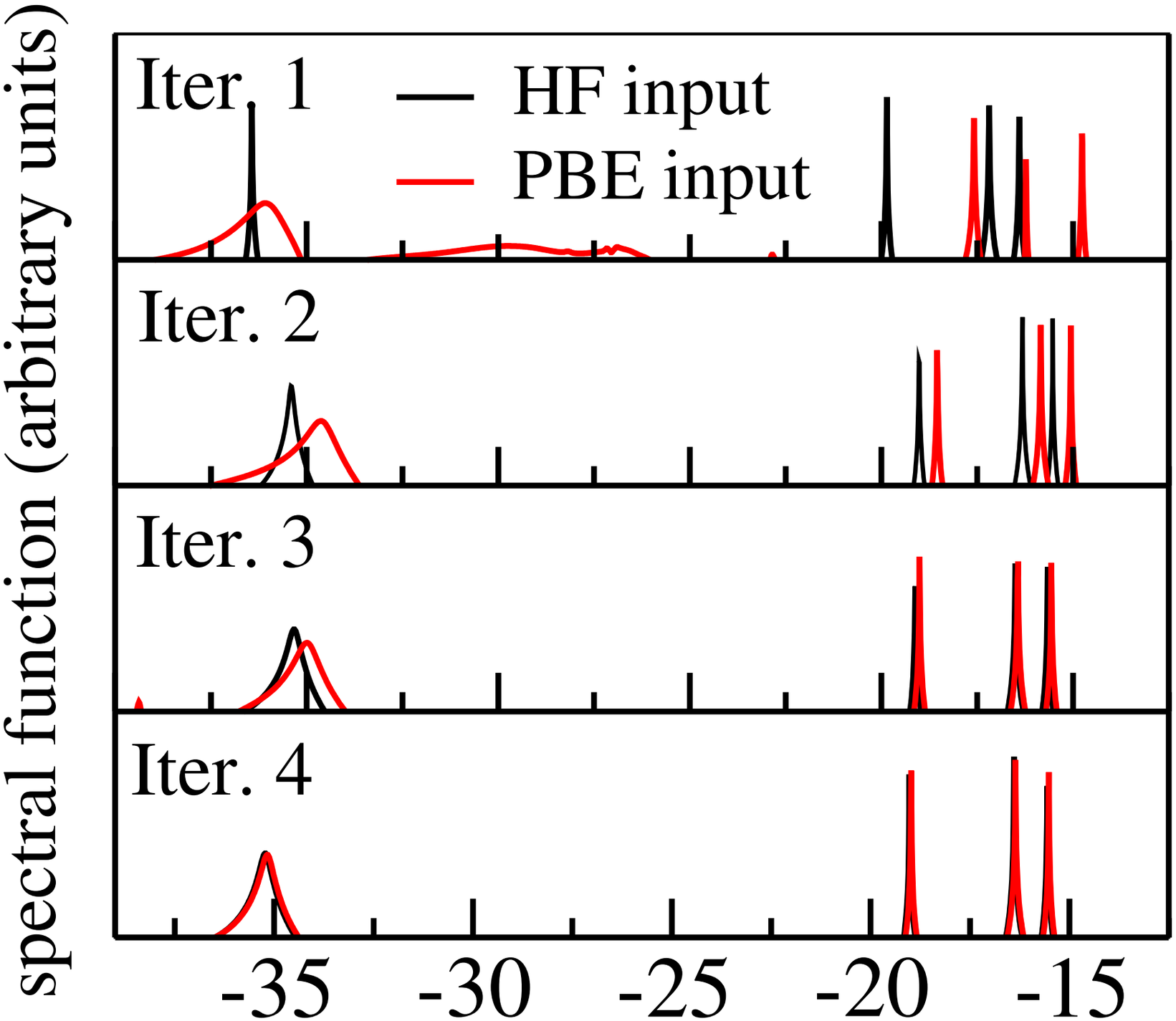
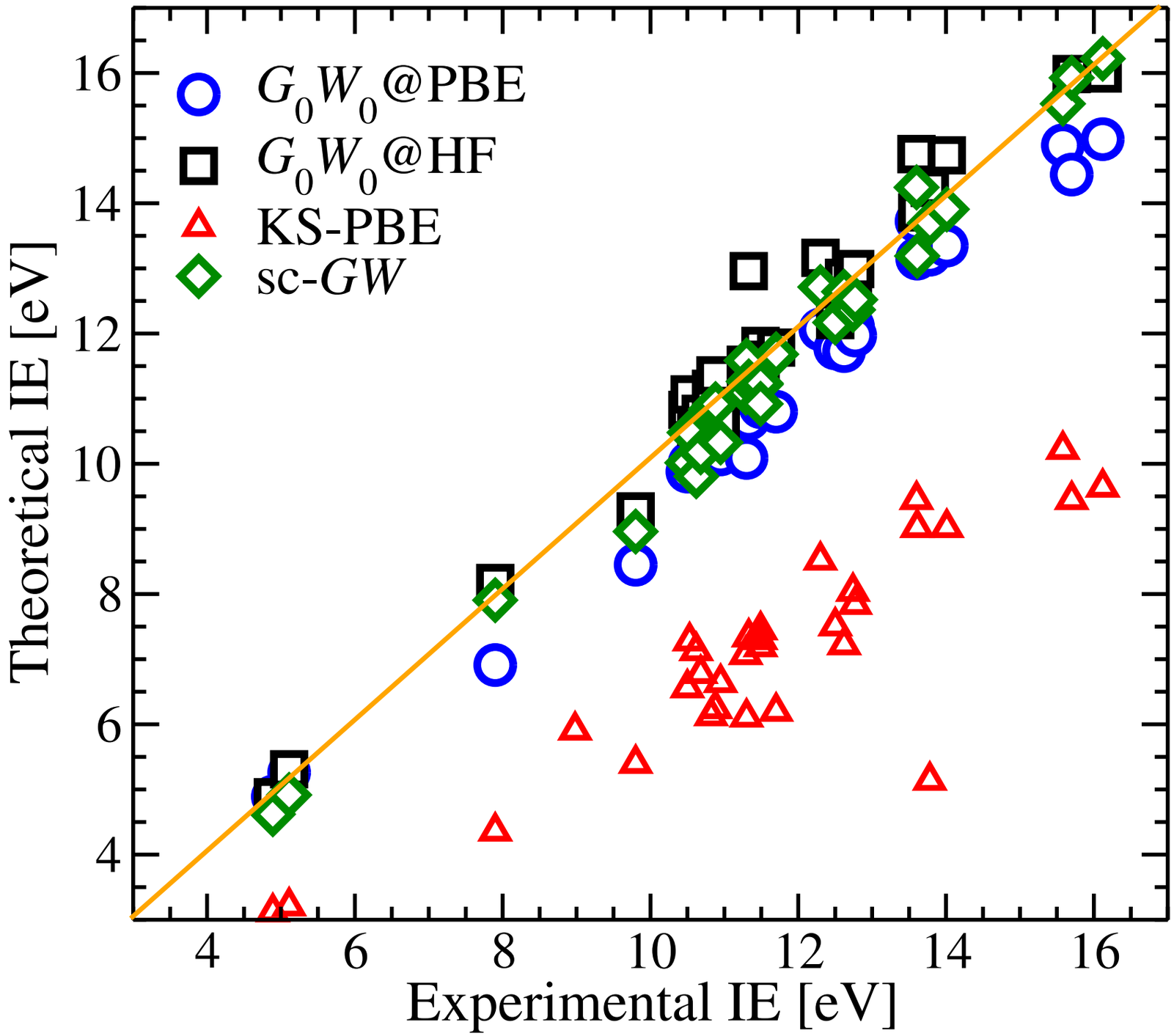
implemented in FHI-aims:
F. Caruso, P. Rinke et al. Phys. Rev. B 86, 081102(R) (2012)
Phys. Rev. B 88, 075105 (2013)

Unique solution in scGW - N_2



F. Caruso, P. Rinke et al. Phys. Rev. B 86, 081102(R) (2012)
Phys. Rev. B 88, 075105 (2013)

Ionization potentials in scGW



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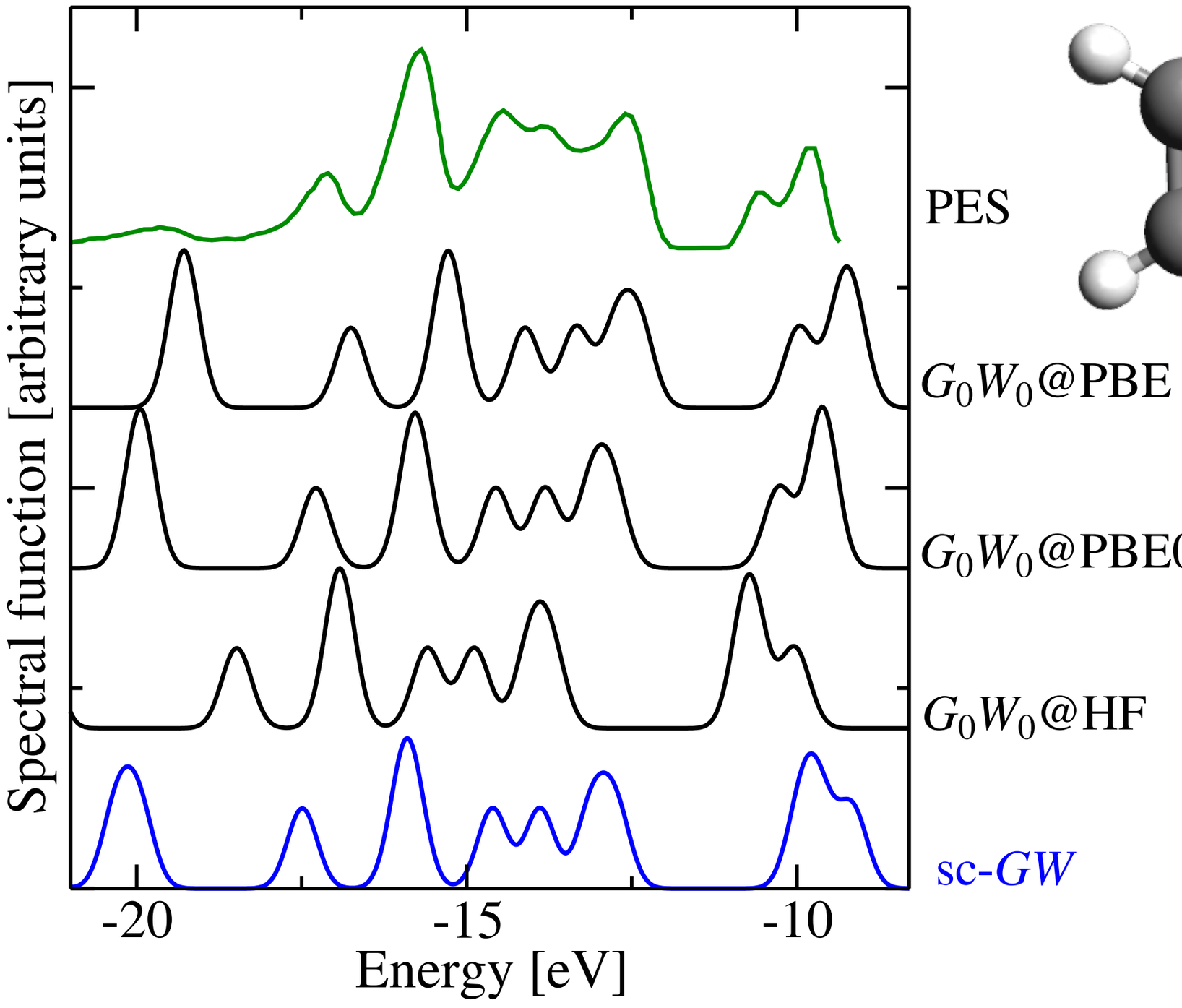
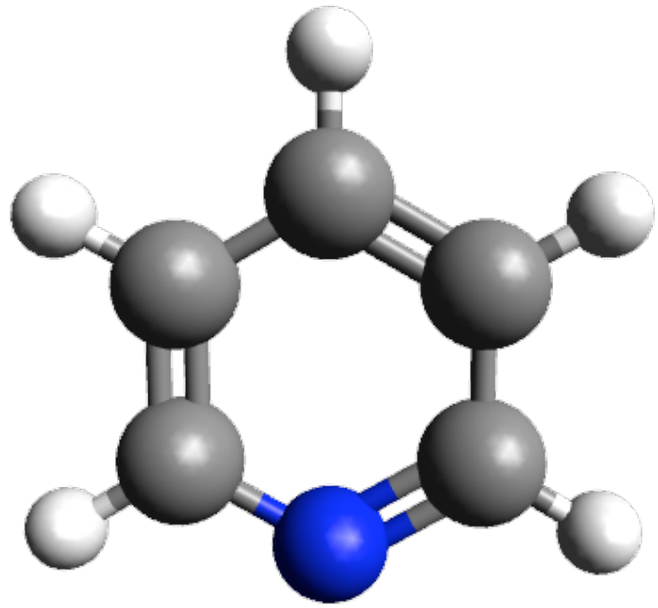
F. Caruso, P. Rinke et al. Phys. Rev. B 86, 081102(R) (2012)

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

The loan pair in pyridine





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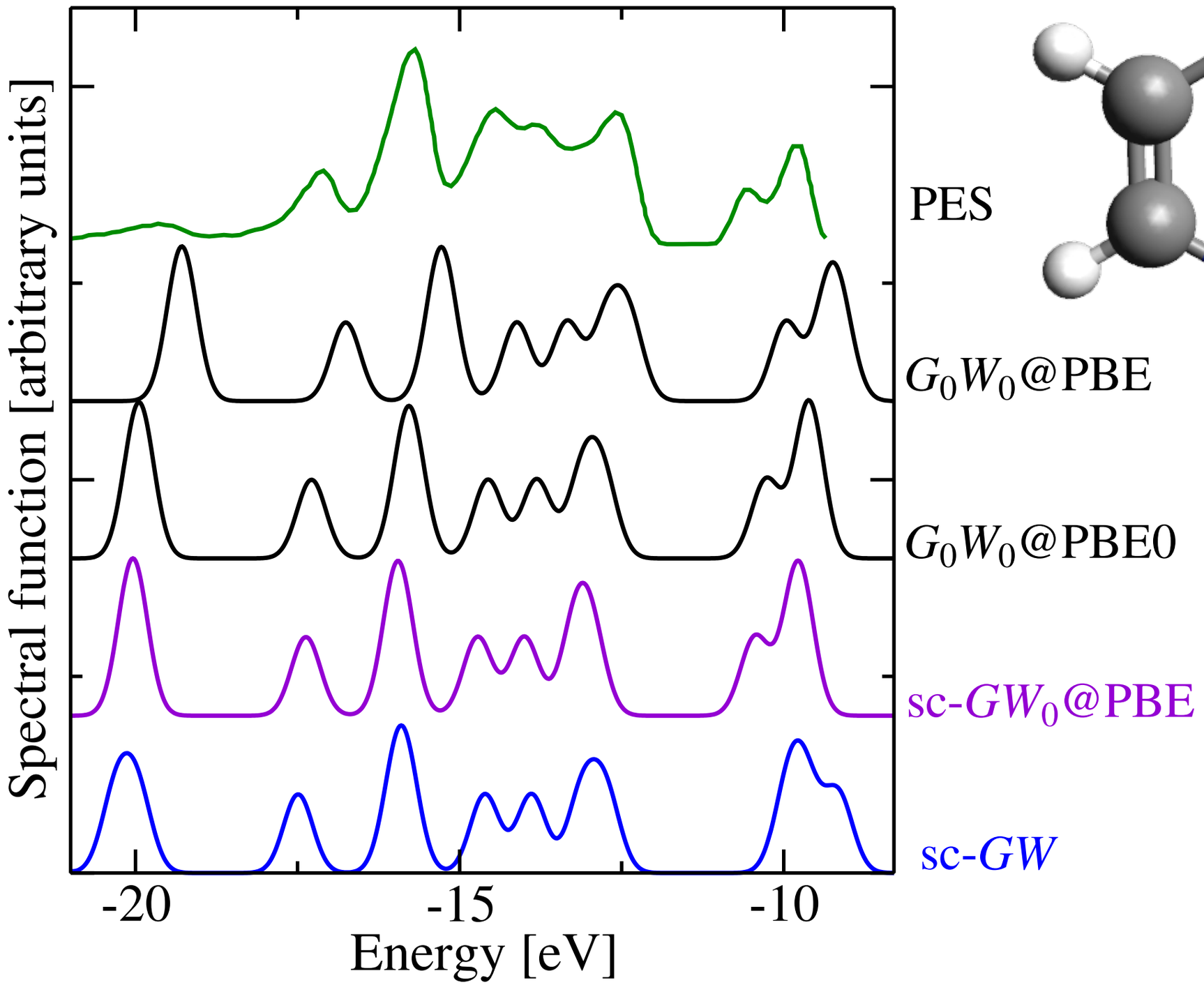
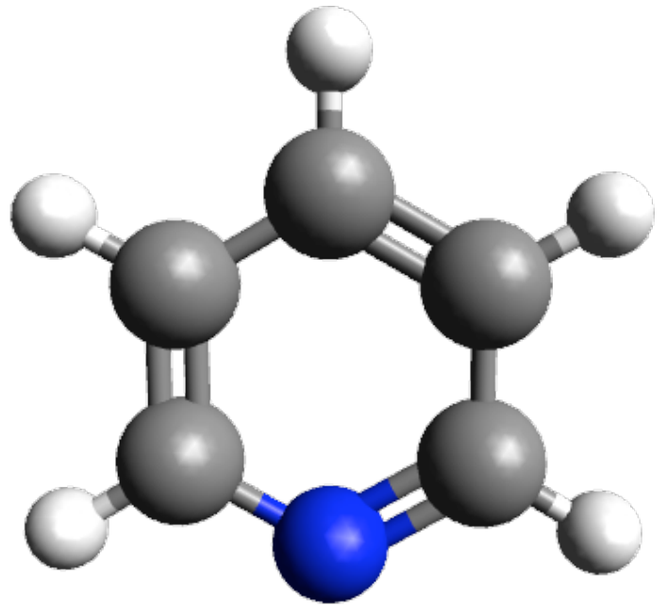
The loan pair in pyridine





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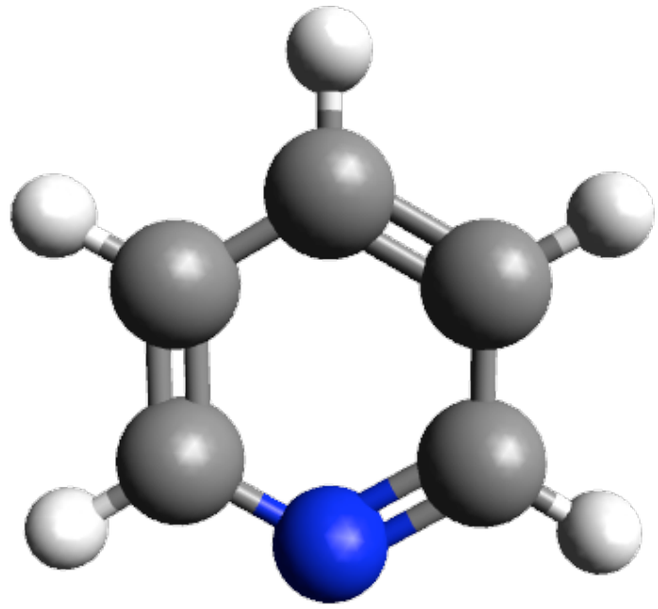
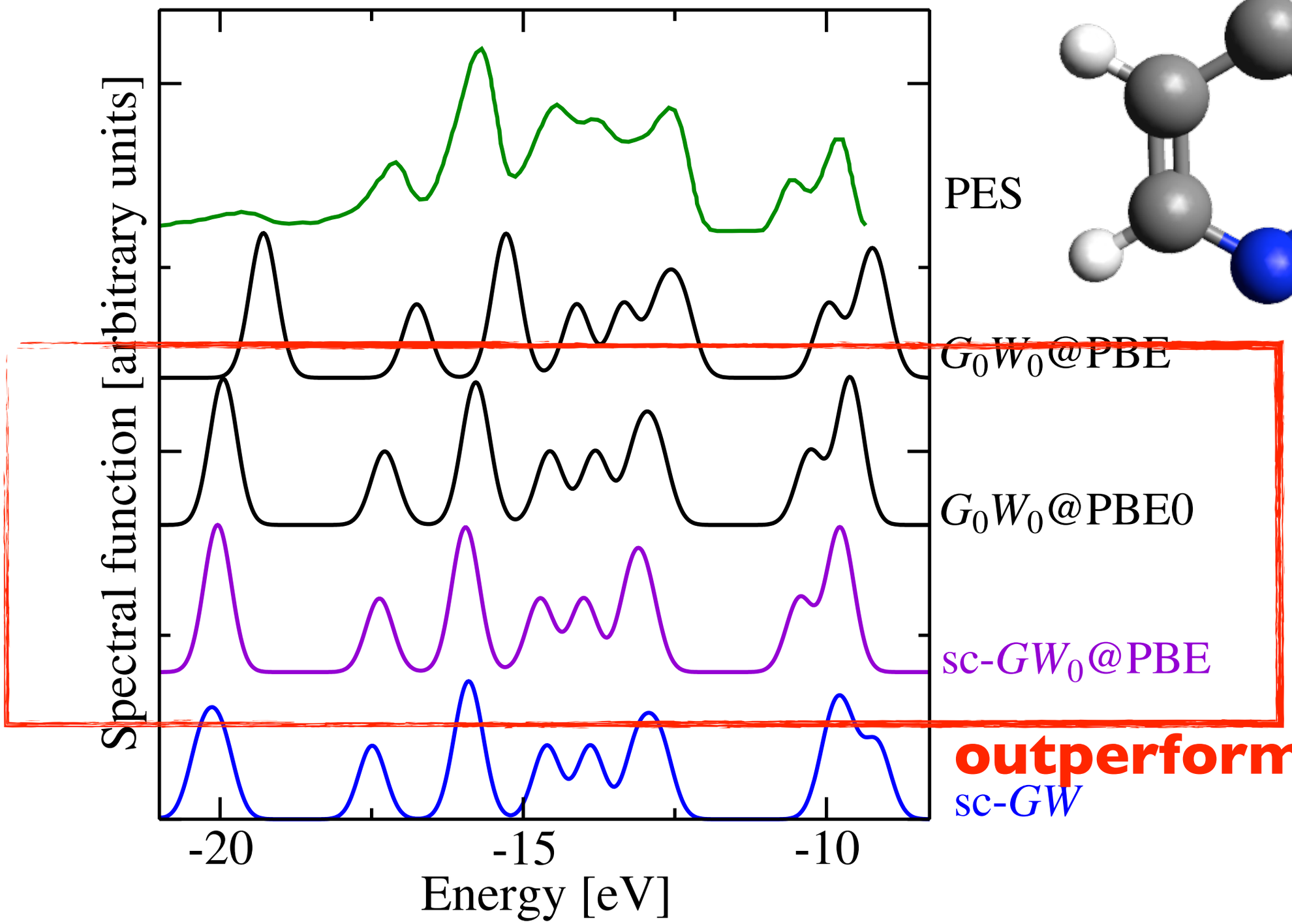
The loan pair in pyridine





outperform scGW

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

What the Green's function gives us

Spectral function:

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

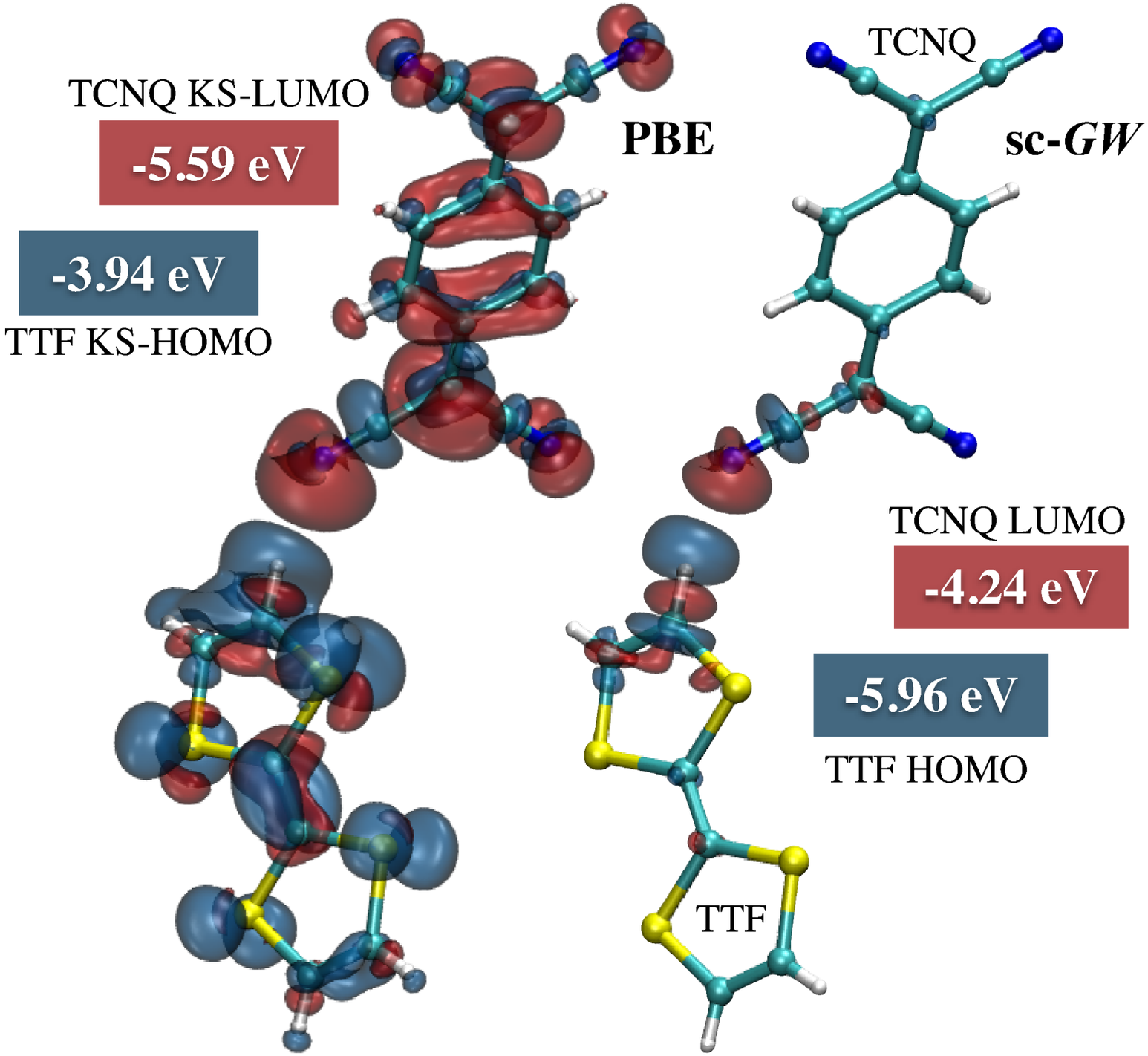
Density:

$$\rho(\mathbf{r}) = -i\sum\nolimits_{\sigma} G_{\sigma\sigma}(\mathbf{r},\mathbf{r},\tau=0^{+})$$

Total energy:

$$E_{\mathrm{GM}} = -i\sum_{\sigma}\int d\mathbf{r}\, dt \lim_{\substack{\mathbf{r}'\to\mathbf{r}\\ t'\to t^{+}}} \left[i\frac{\partial}{\partial t} - \frac{\nabla^{2}_{\mathbf{r}}}{2} + v_{\mathrm{ext}}(\mathbf{r})\right] G^{\sigma}(\mathbf{r}t,\mathbf{r}'t')$$

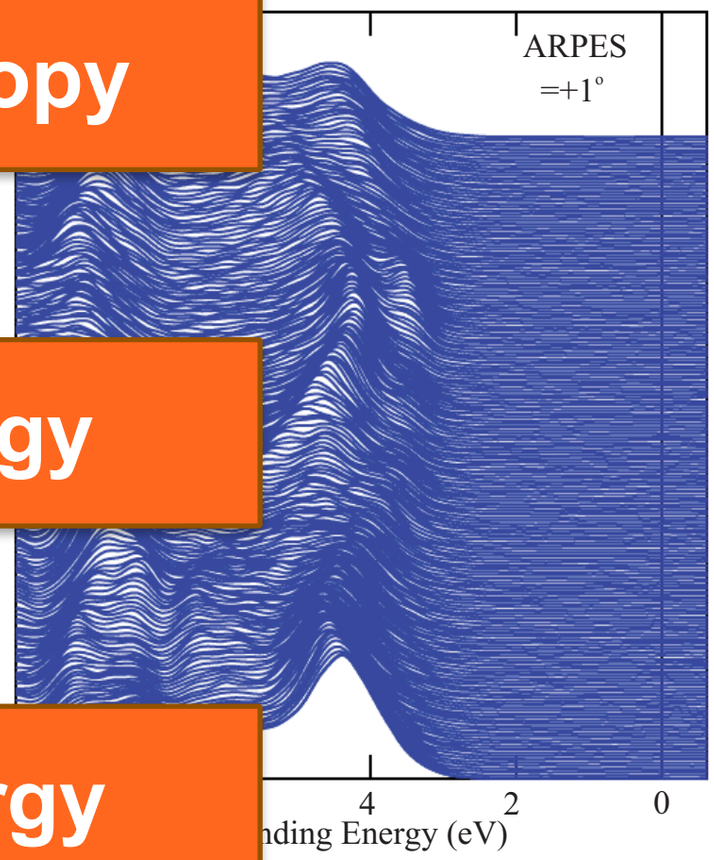
Return to the TTF/TCNQ dimer



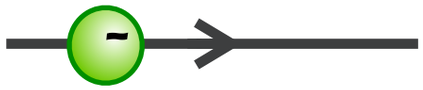
F. Caruso, P. Rinke, *et al.* Phys. Rev. B 90, 085141 (2014)

What we learned today

Basic principles of electron spectroscopy



The Green's function and the self-energy



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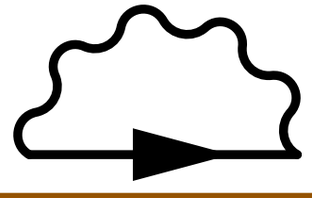
$$\Sigma^{GW} =$$ 

Pros and cons of density-functional theory for electron spectroscopies