Excited-State Properties

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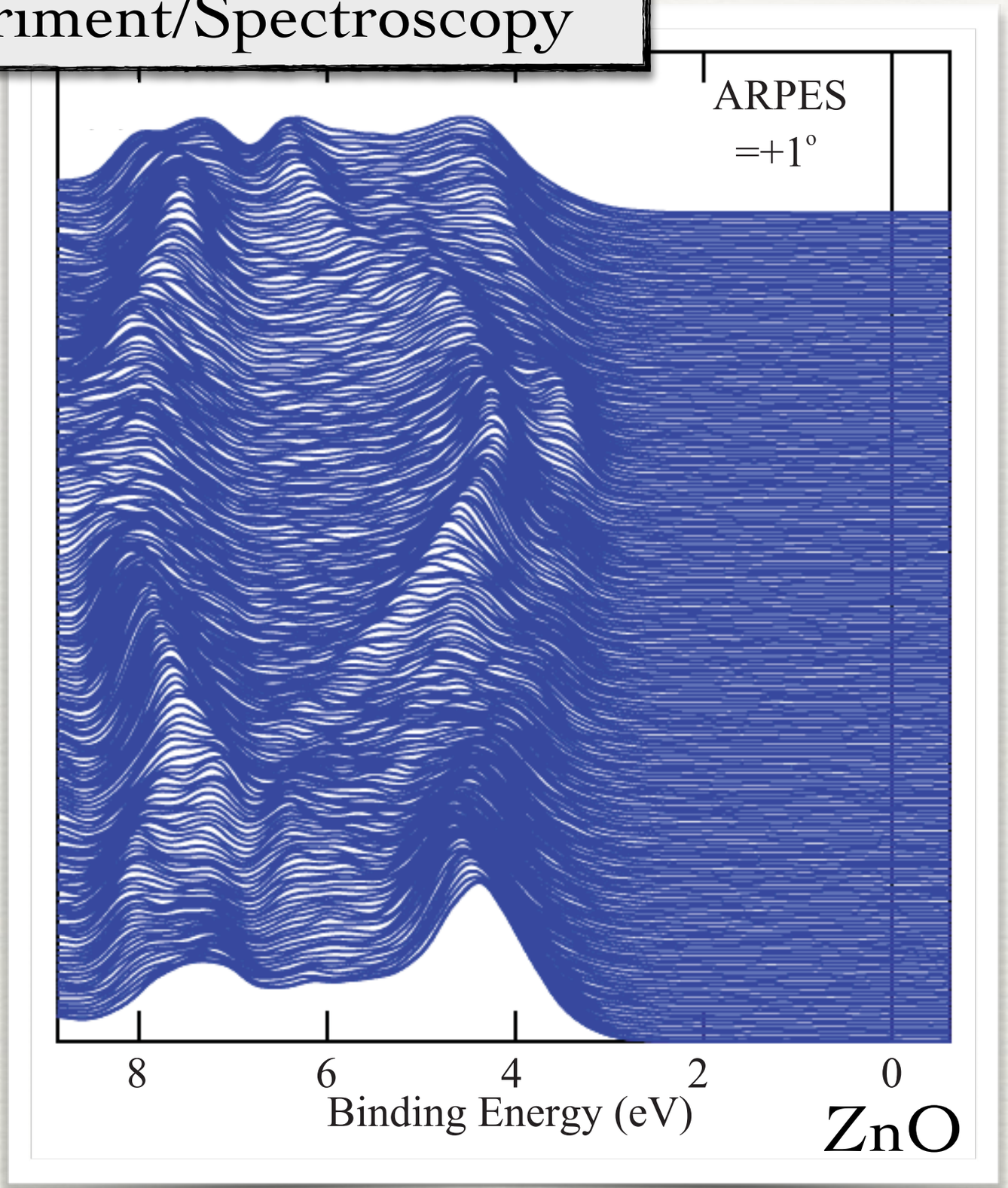
Excited states in material science are ubiquitous

Experiment/Spectroscopy



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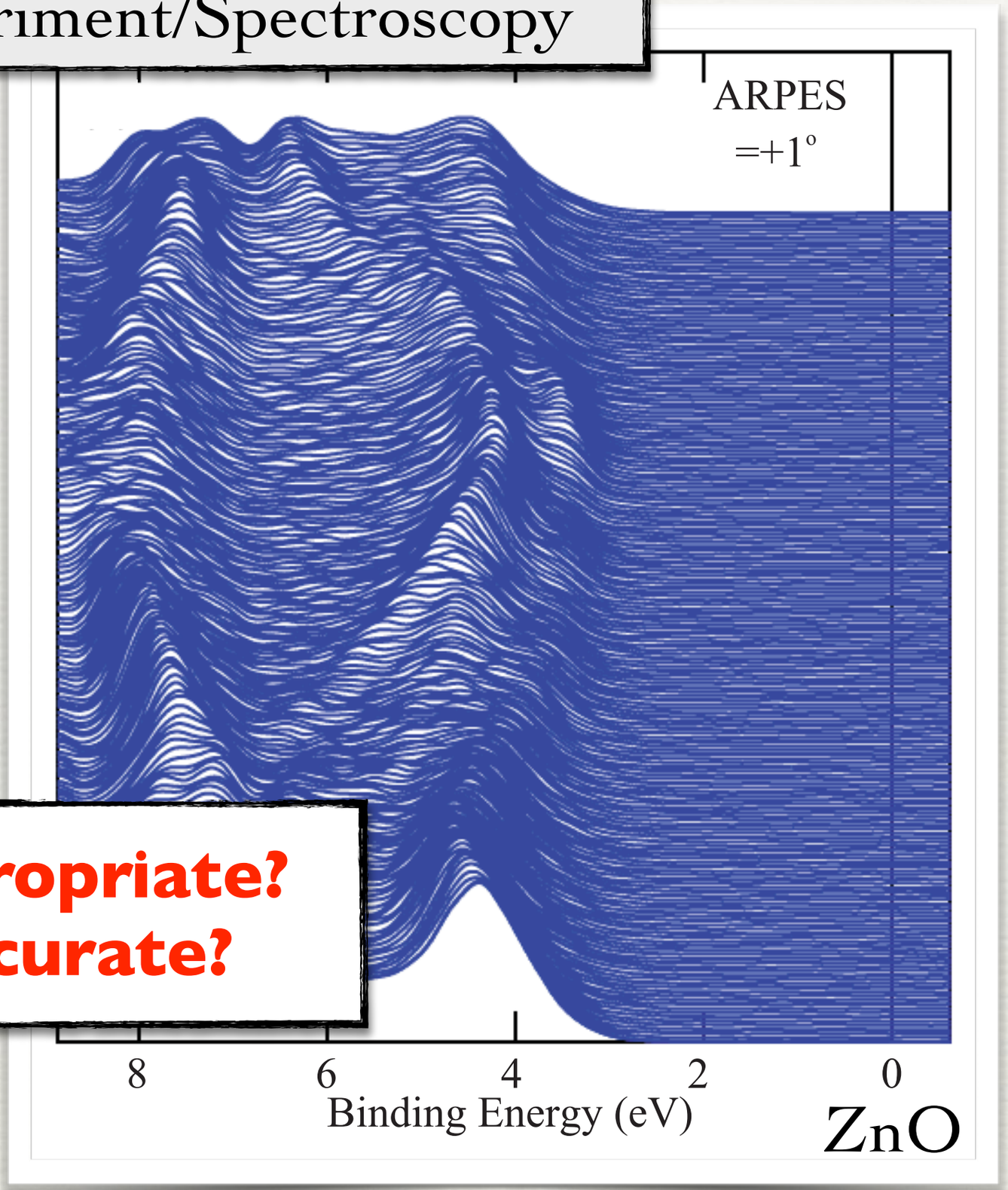
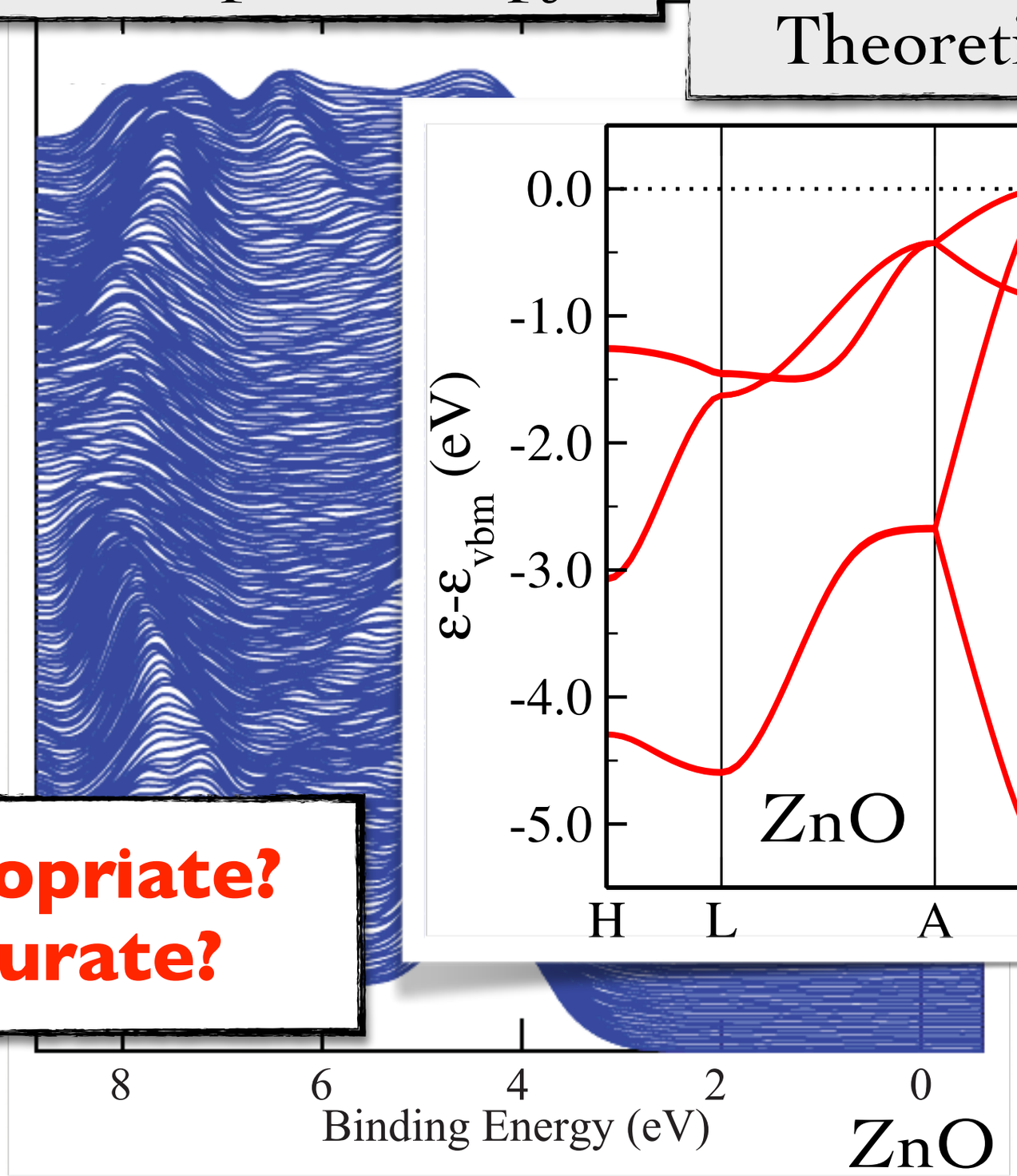


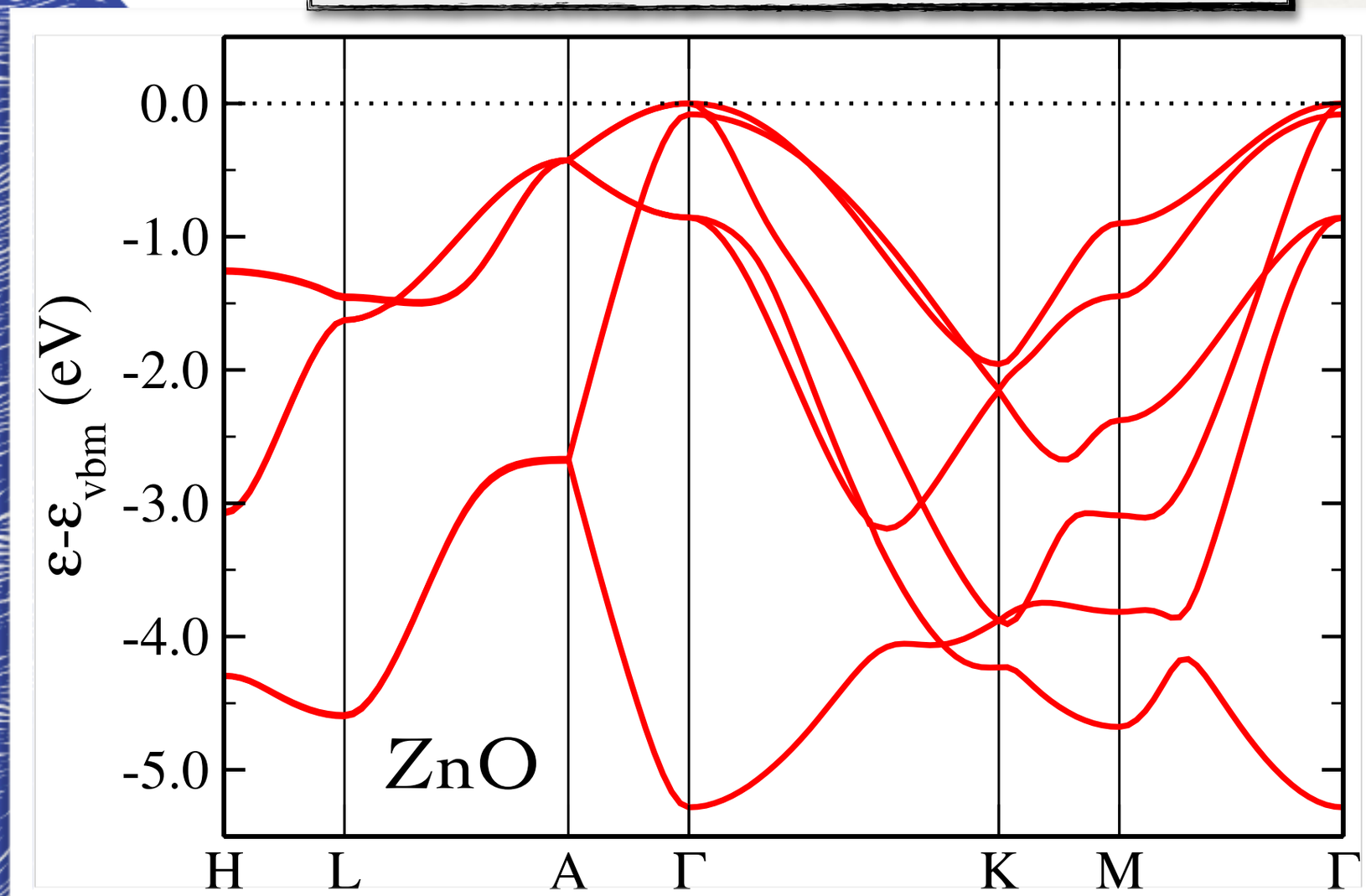
appropriate?
accurate?

Excited states in material science are ubiquitous

Experiment/Spectroscopy

Theoretical Spectroscopy





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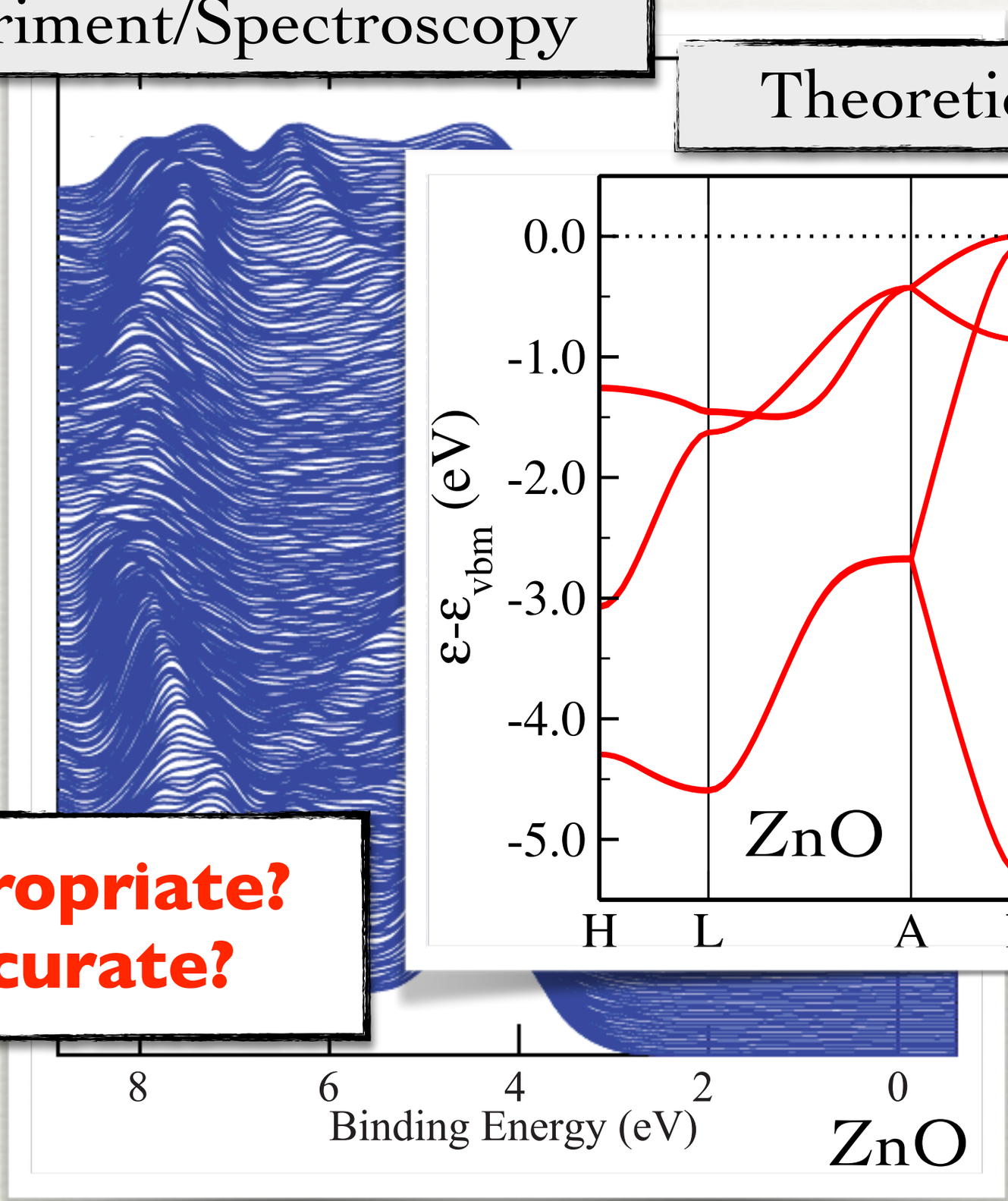
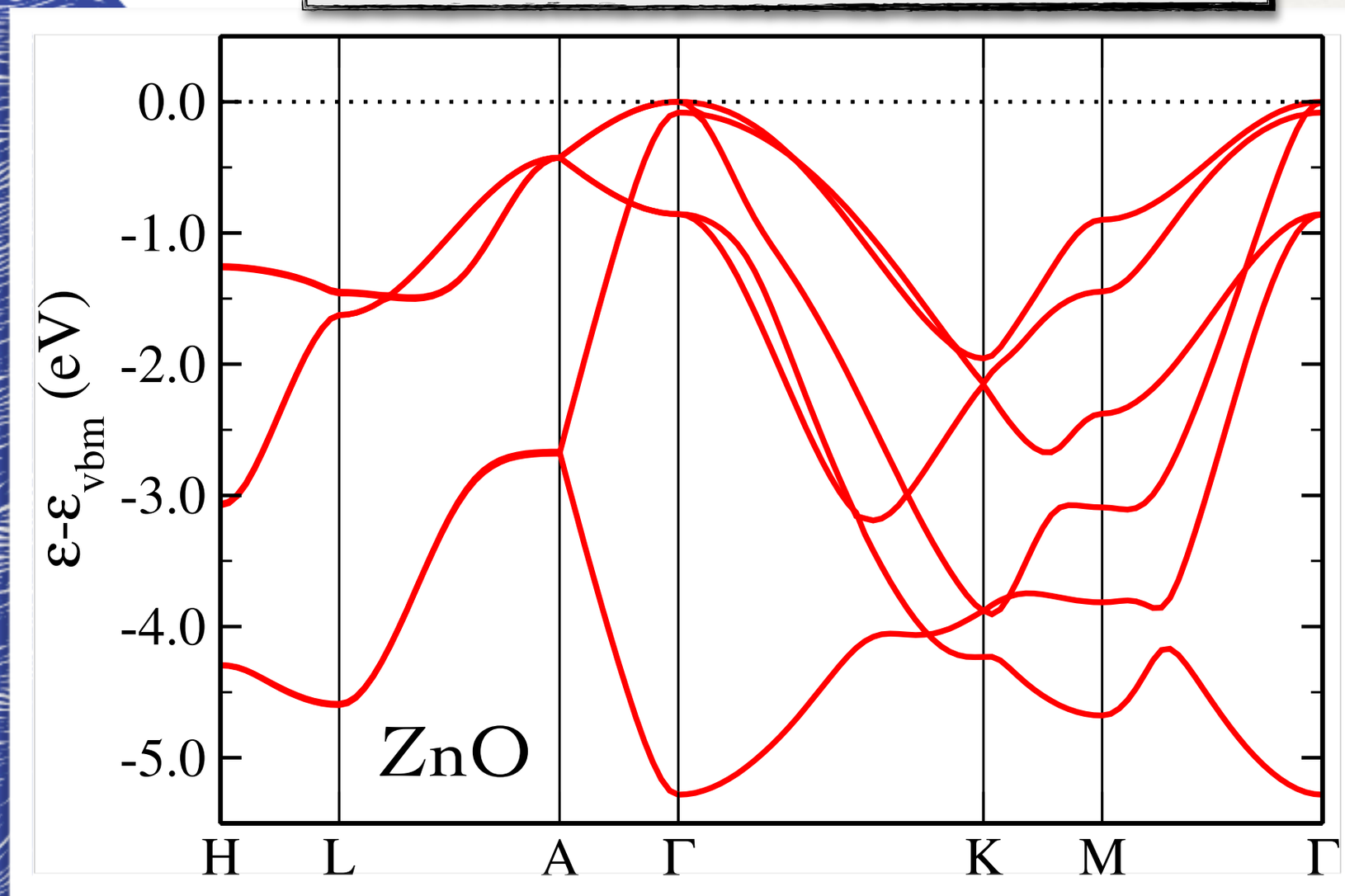
Experiment/Spectroscopy



Theoretical Spectroscopy



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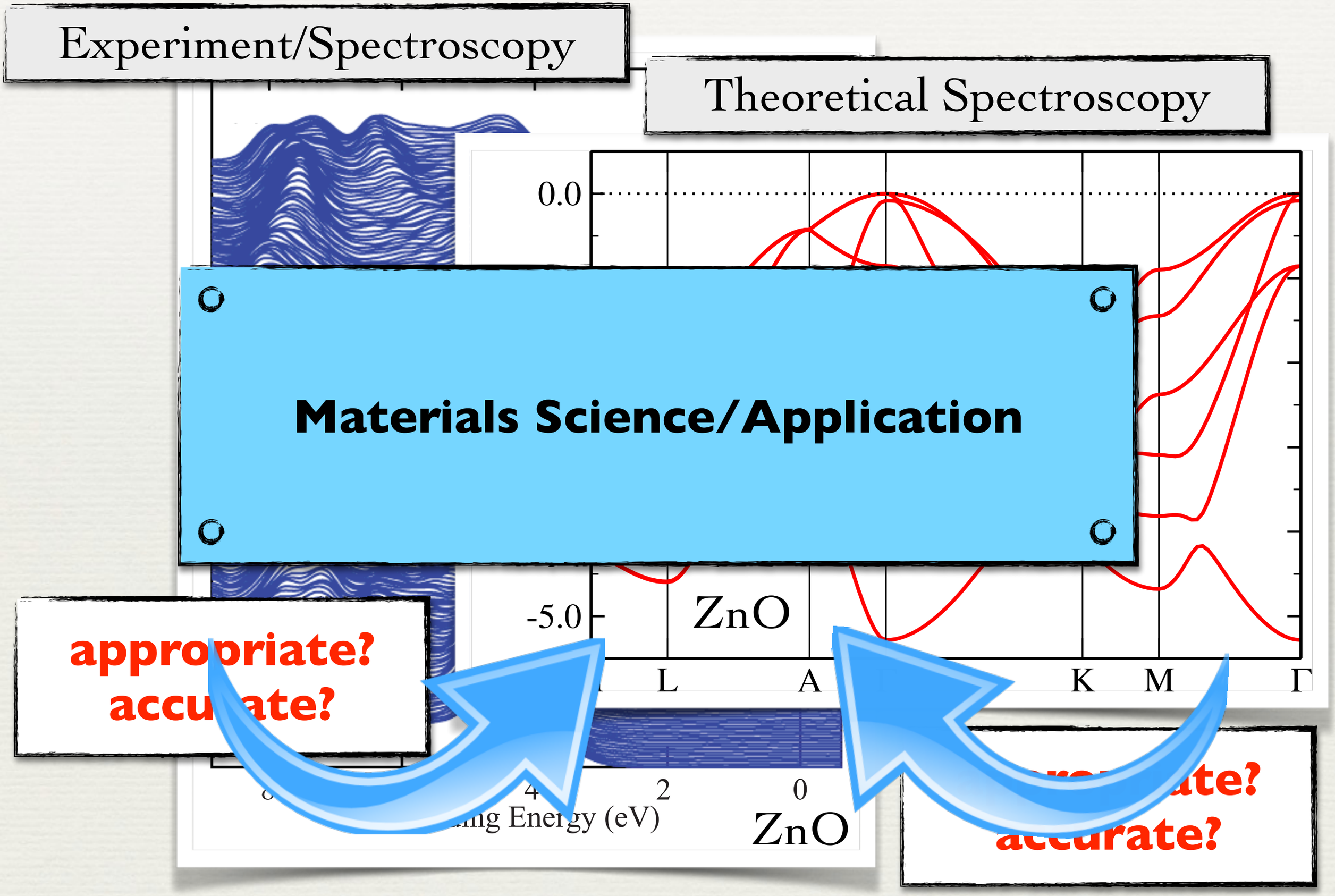
Excited states in material science are ubiquitous



Excited states in material science are ubiquitous

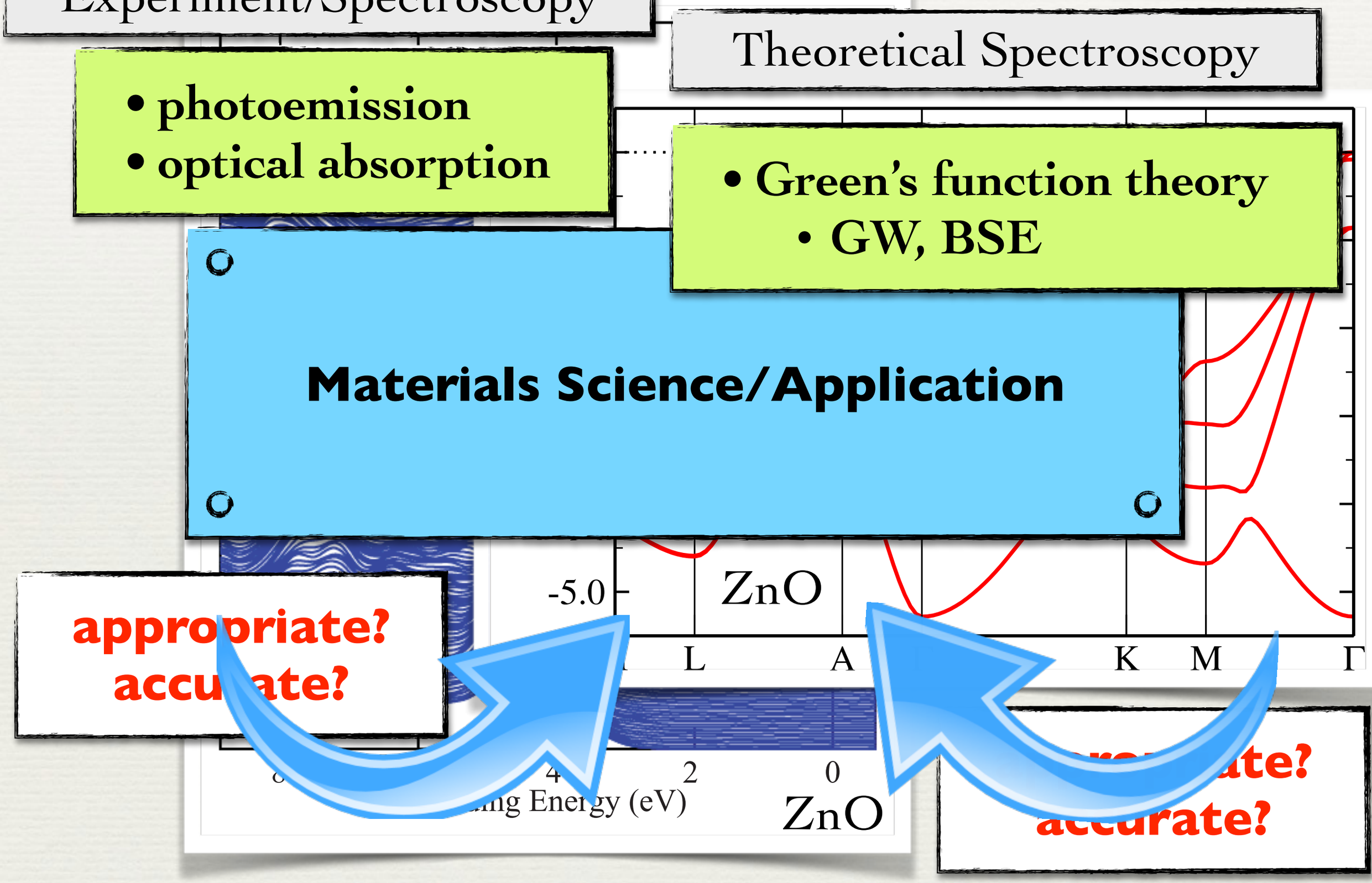
Experiment/Spectroscopy

- photoemission
- optical absorption

Theoretical Spectroscopy

- Green's function theory
  - GW, BSE

Materials Science/Application



appropriate?
accurate?

appropriate?
accurate?

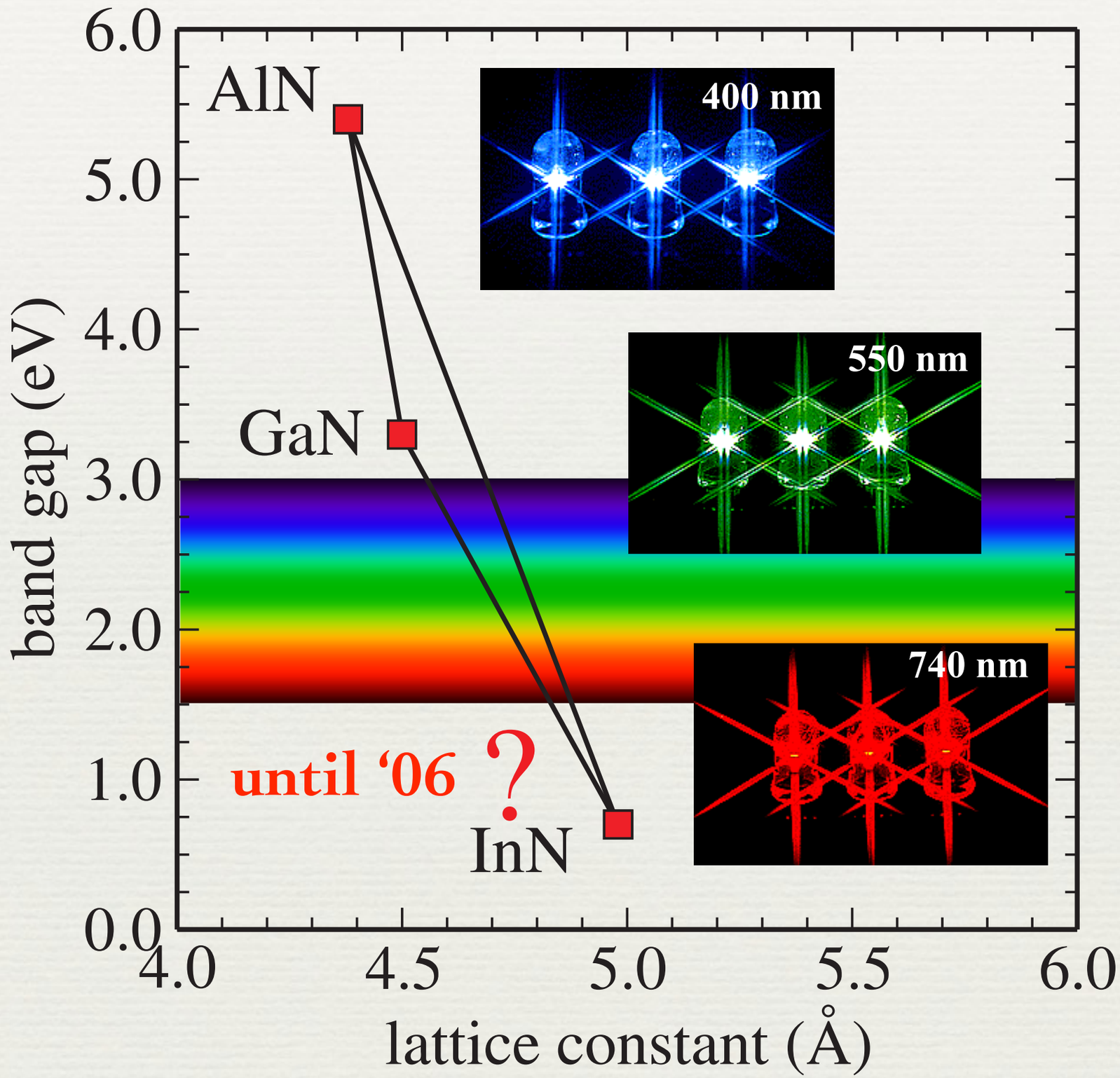
Nitride-based light emitters

- blue LED
- blue ray

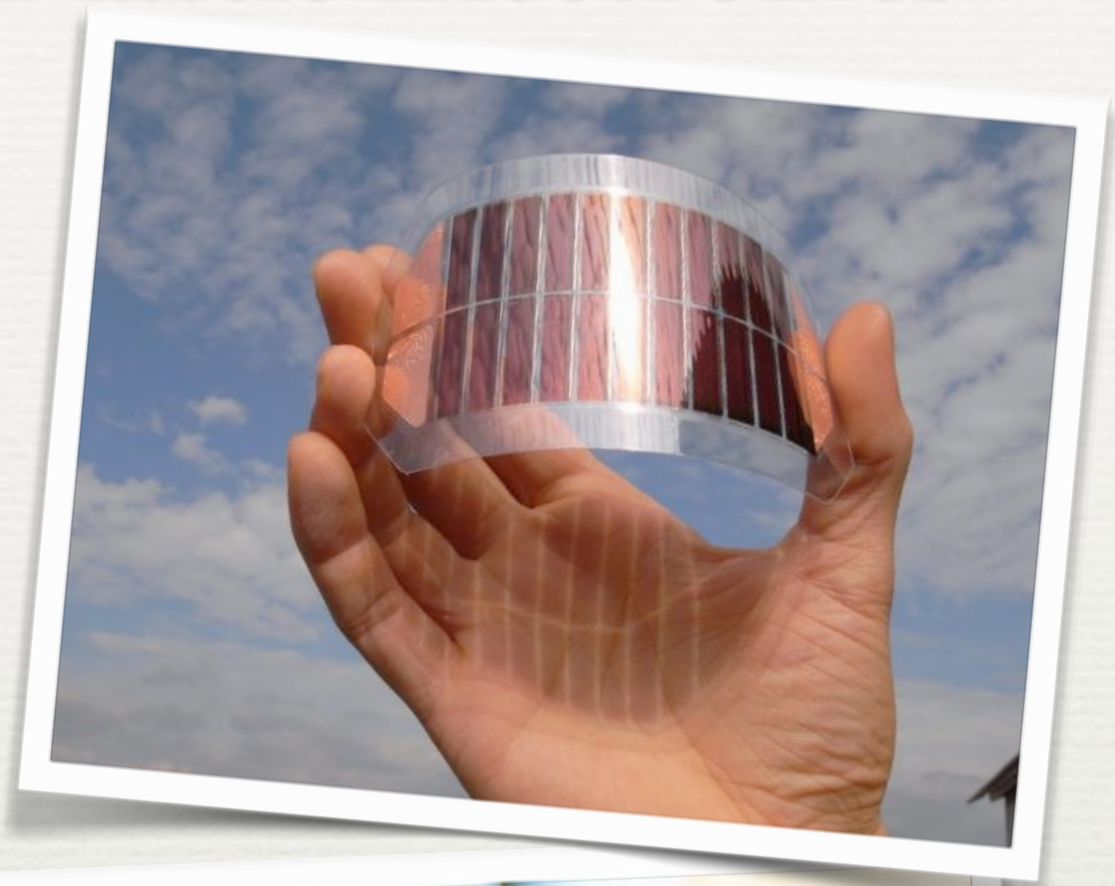
Challenges:

- solid state lighting
- RGP laser projectors

Do we know the band gap of InN?



Organic Electronics - Plastic Electronics



sources (left to right): Organic Electronic Association, Eco Friend, Nature Publishing Group, Samsung

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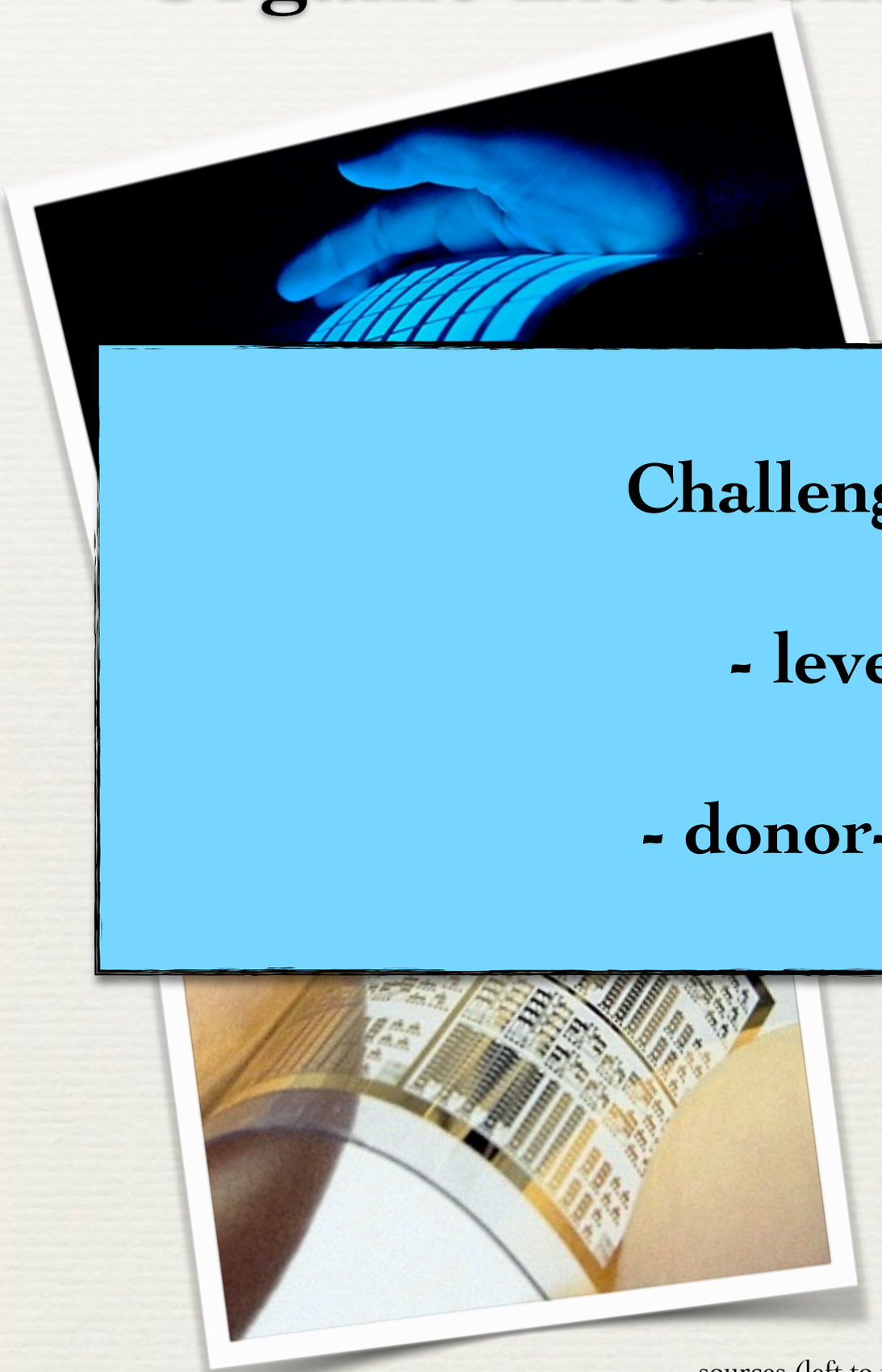


Challenges I'll address:

- level alignment

- donor-acceptor pairs

sources (left to right): Organic Electronic Association, Eco Friend, Nature Publishing Group, Samsung

Spectroscopies

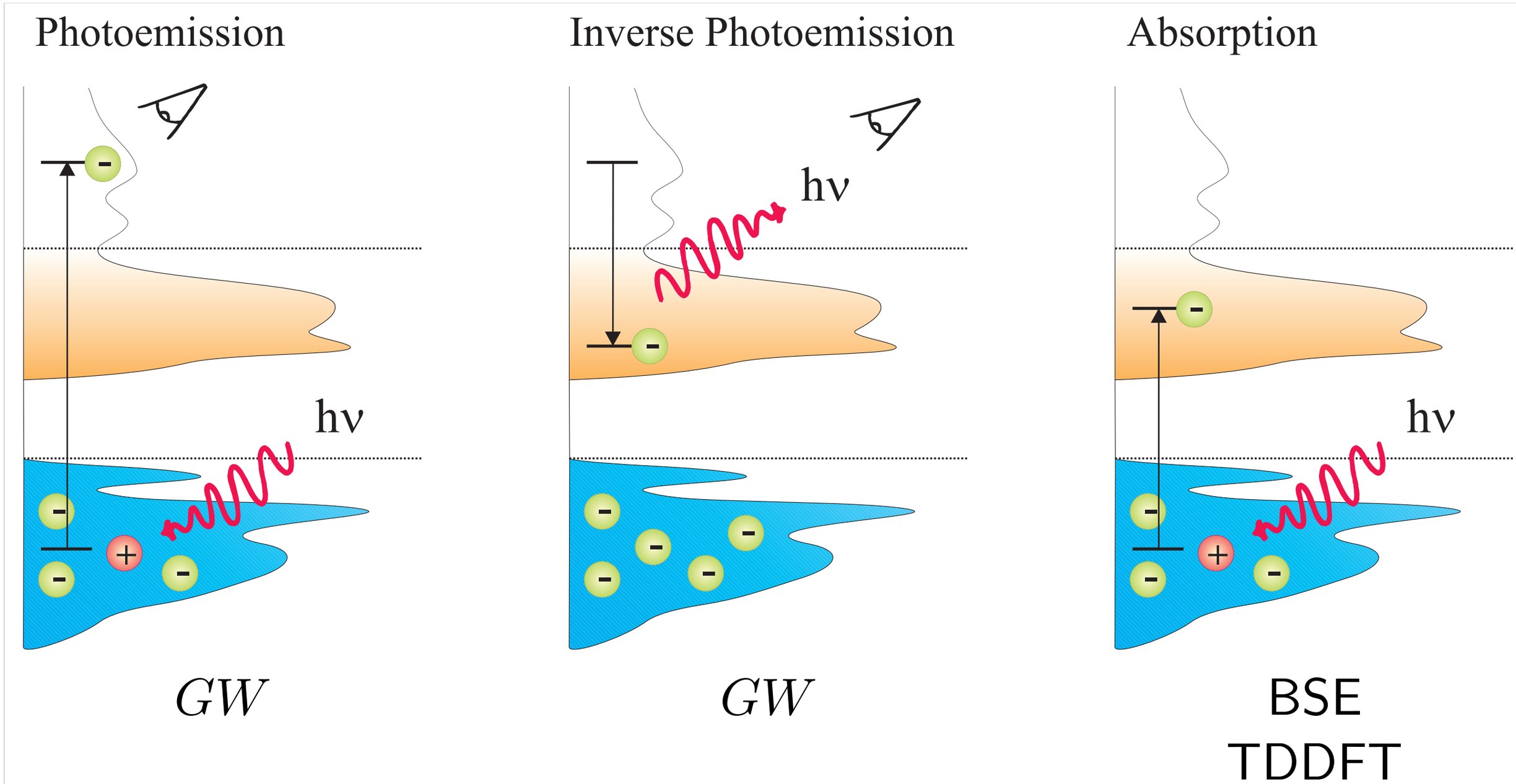


Photo-electron energies

Photoemission

- electron removal

ground state → $|N\rangle$

- removal energy

$E(N)$

ground state total energy

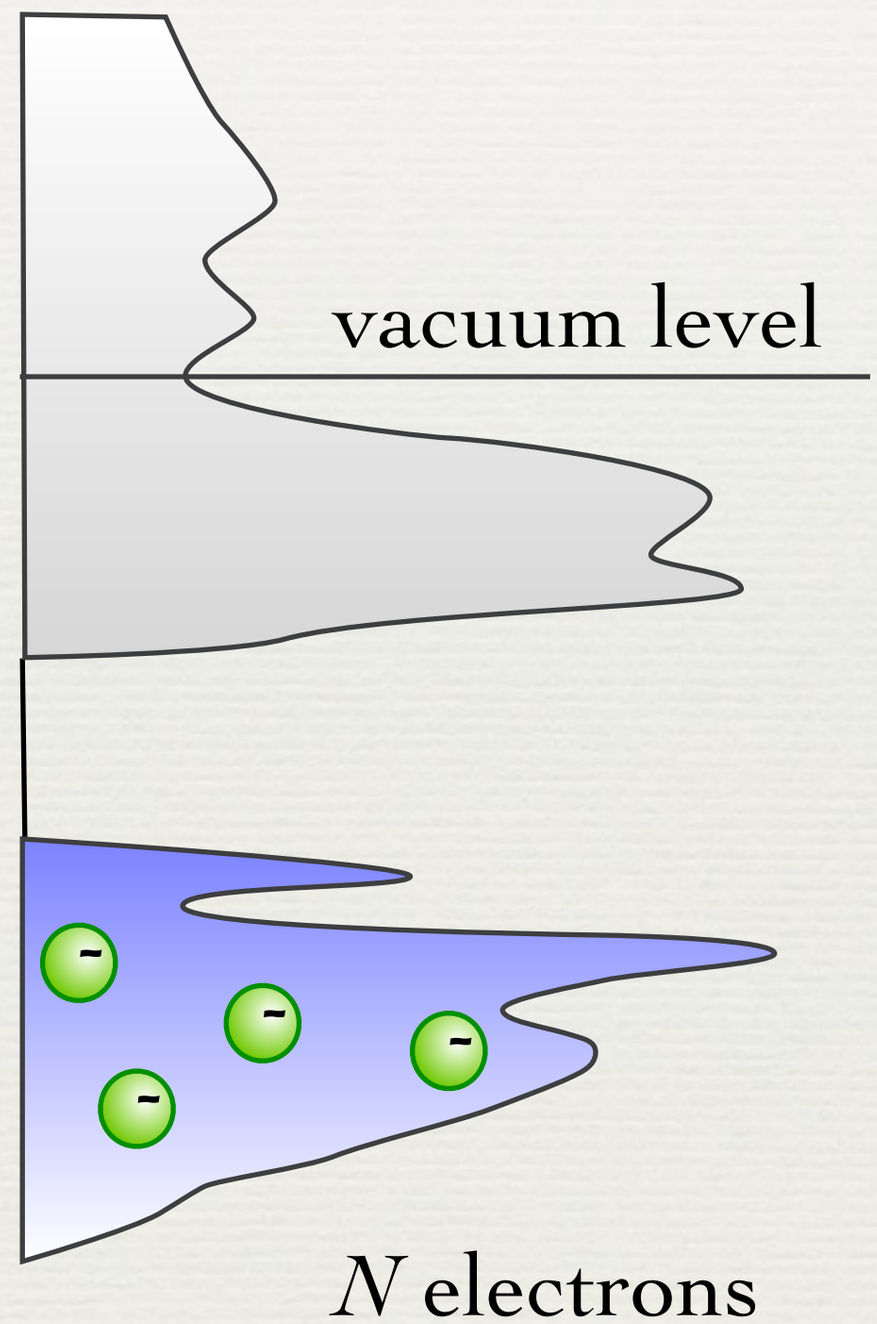


Photo-electron energies

Photoemission

- electron removal

annihilation operator

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

- removal energy

$$E(N)$$

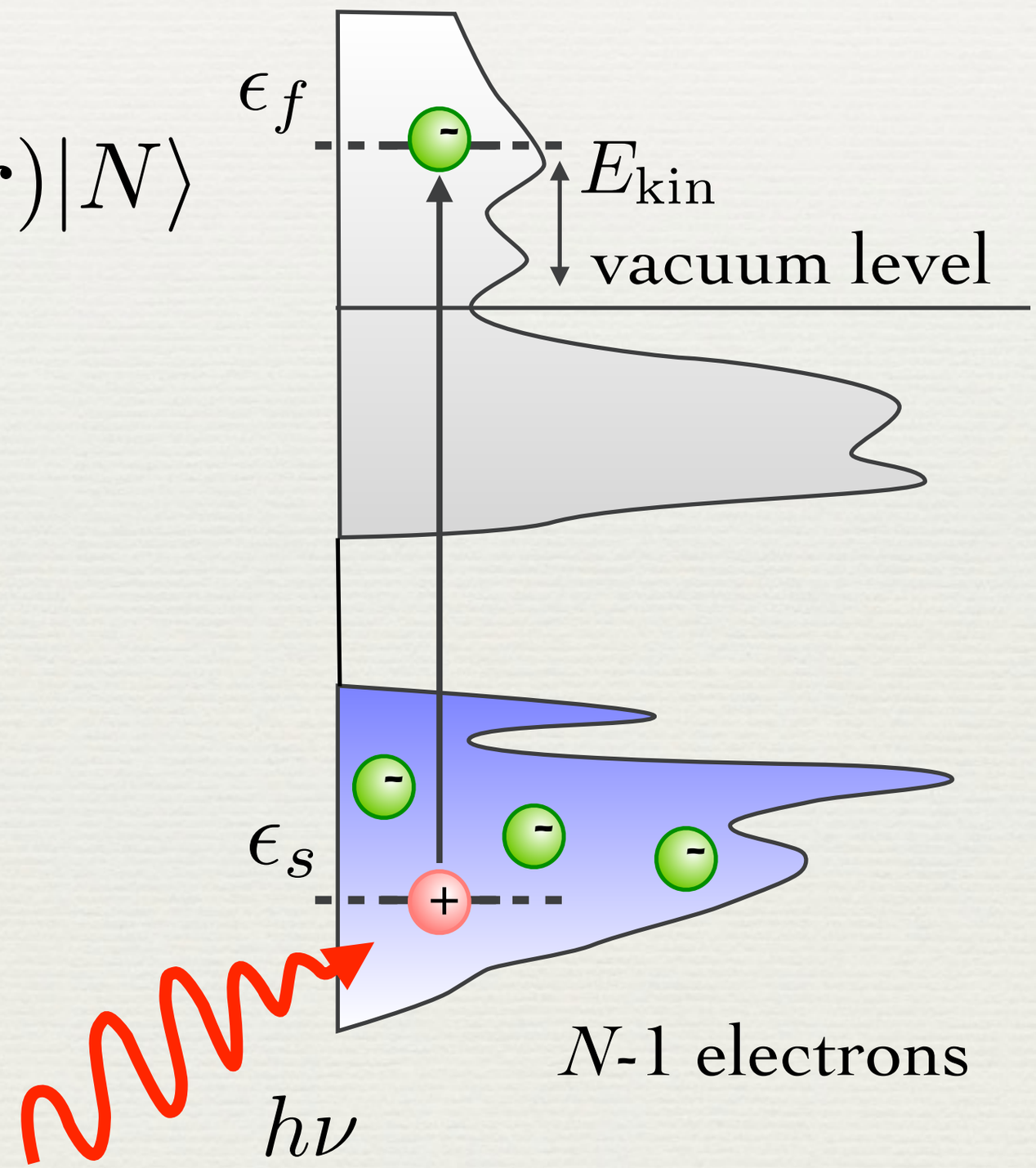


Photo-electron energies

Photoemission

- electron removal

sth excited state of N-1 electron system

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

- removal energy

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

total energy of sth excited state of N-1 electron system

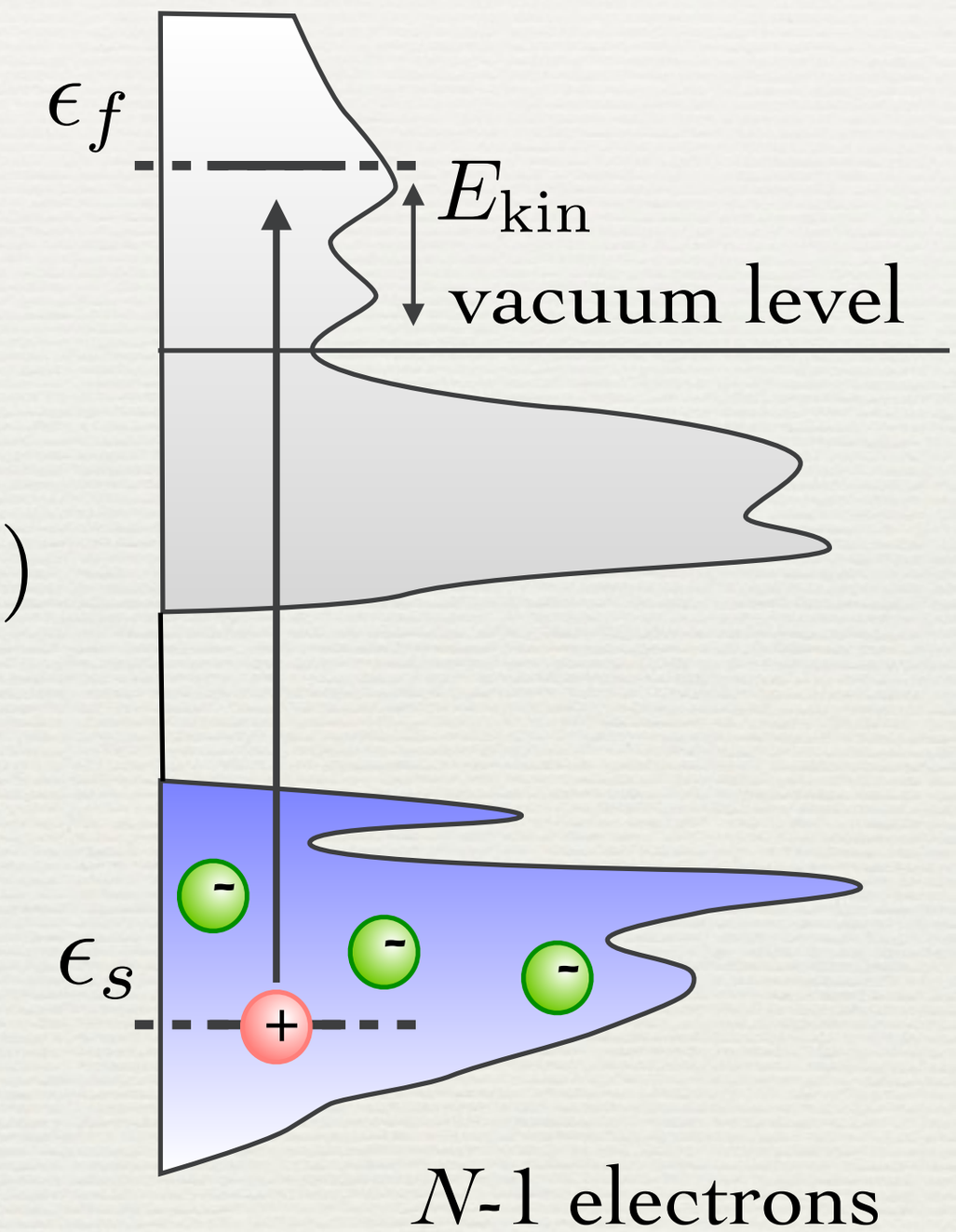


Photo-electron energies

Photoemission

- electron removal

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

- removal energy

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

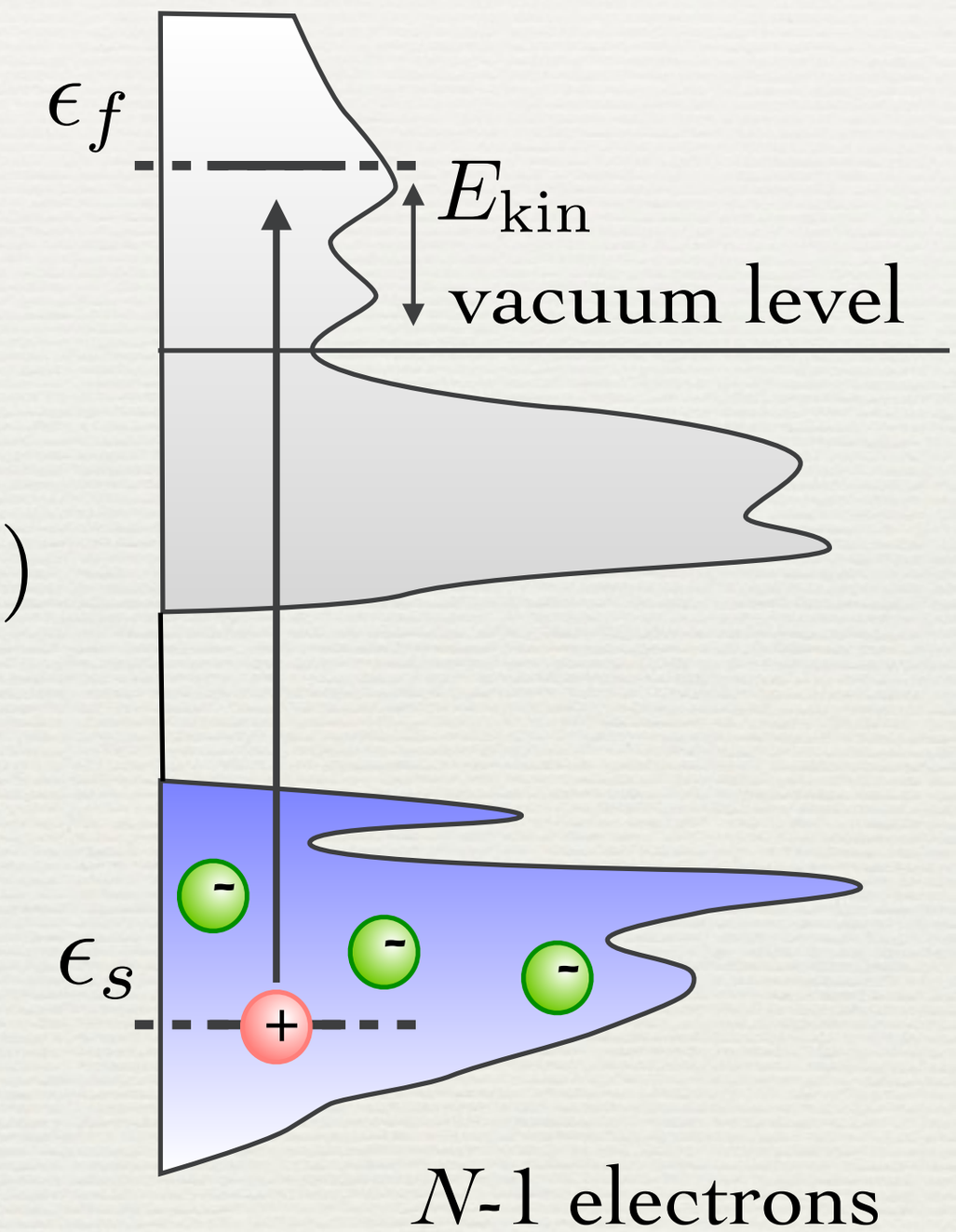


Photo-electron energies

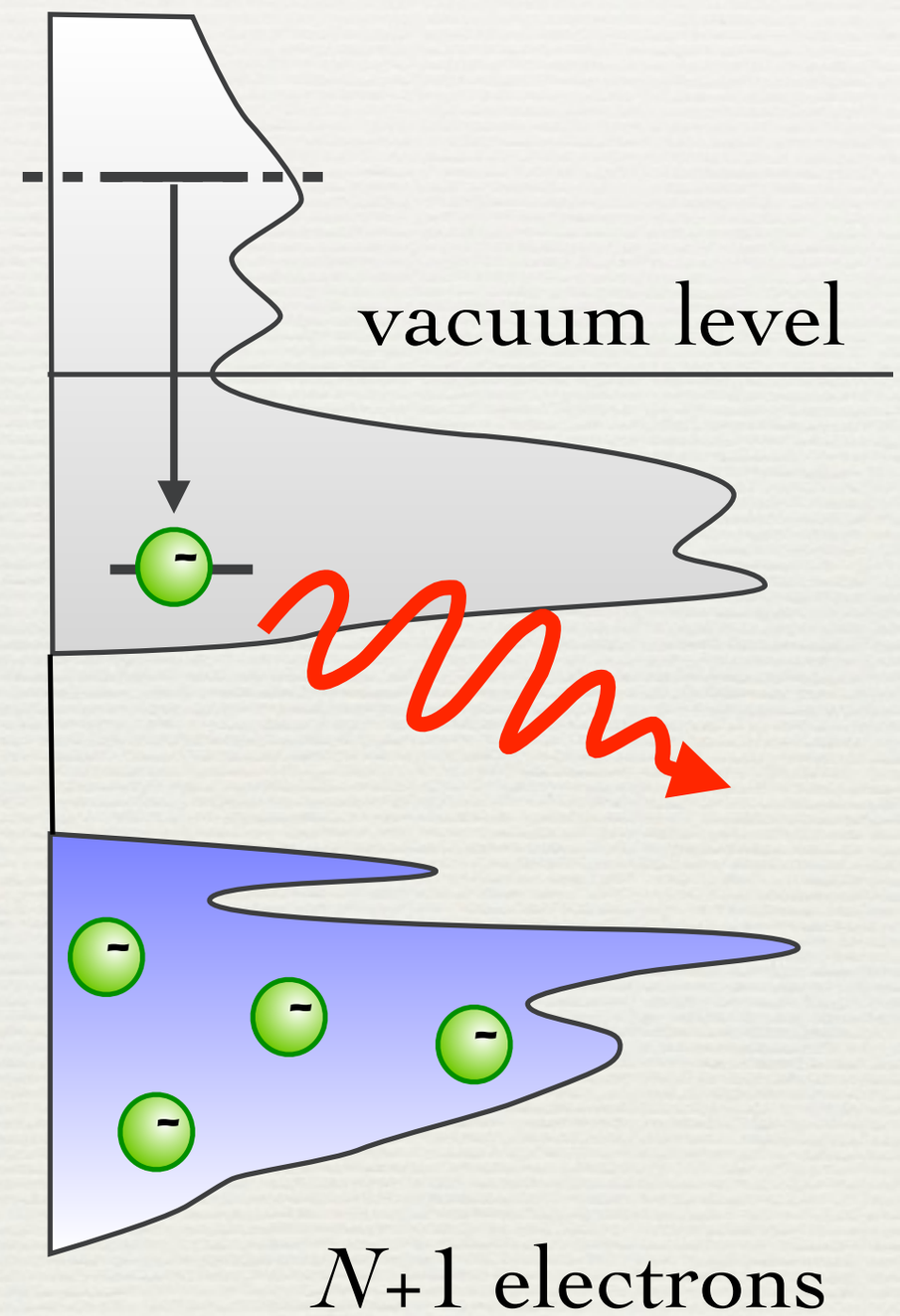
Inverse photoemission

- 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

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

Single-particle Green's function

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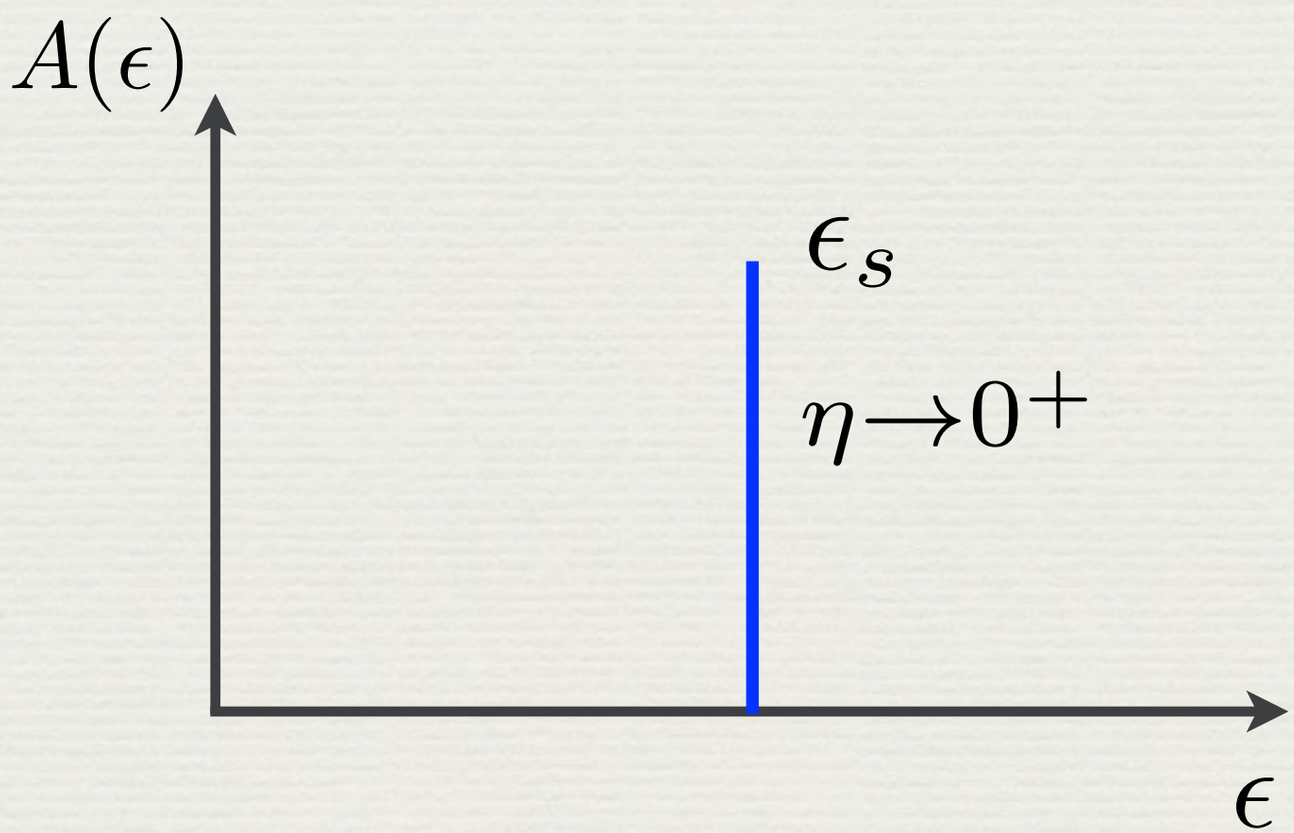
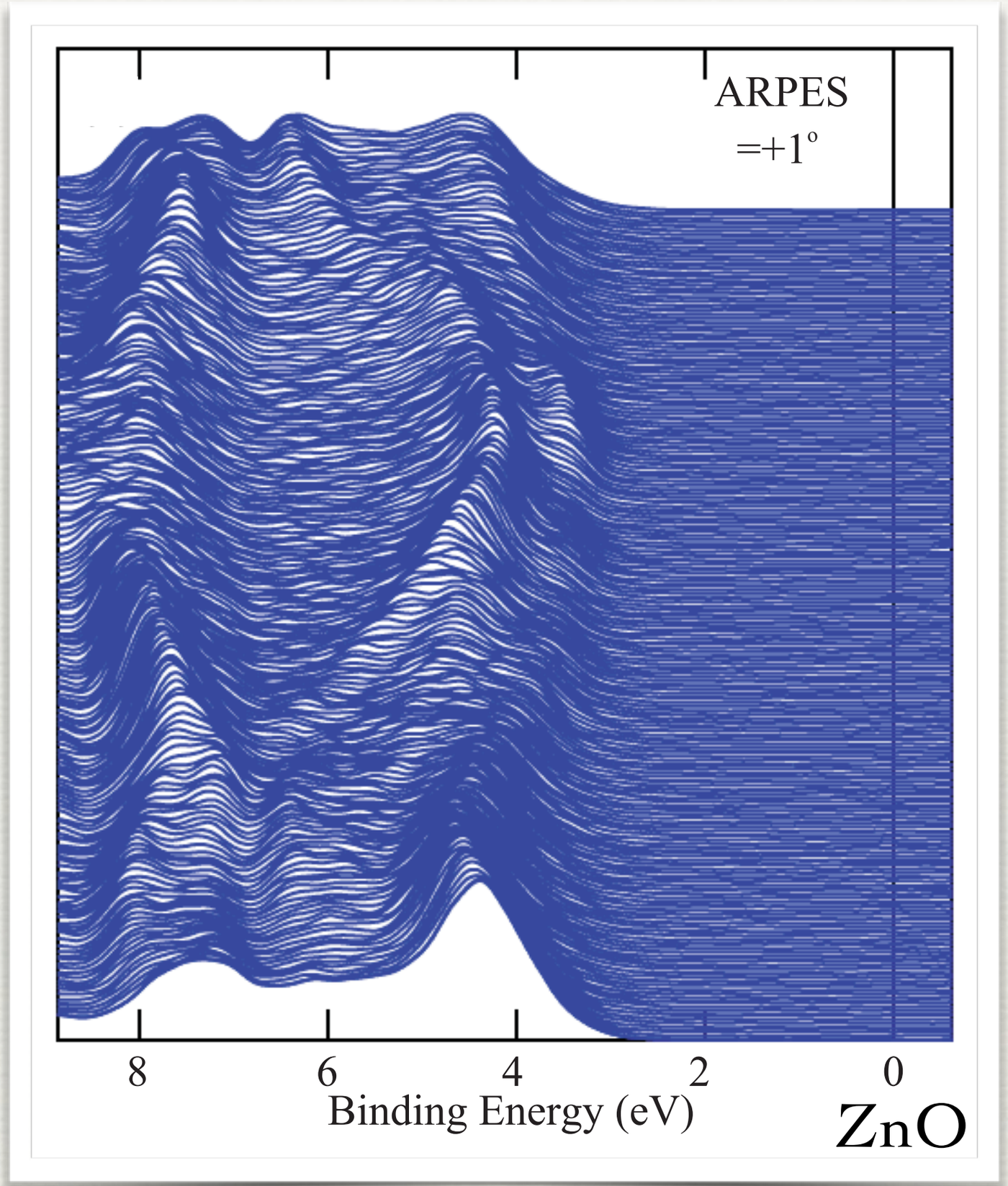
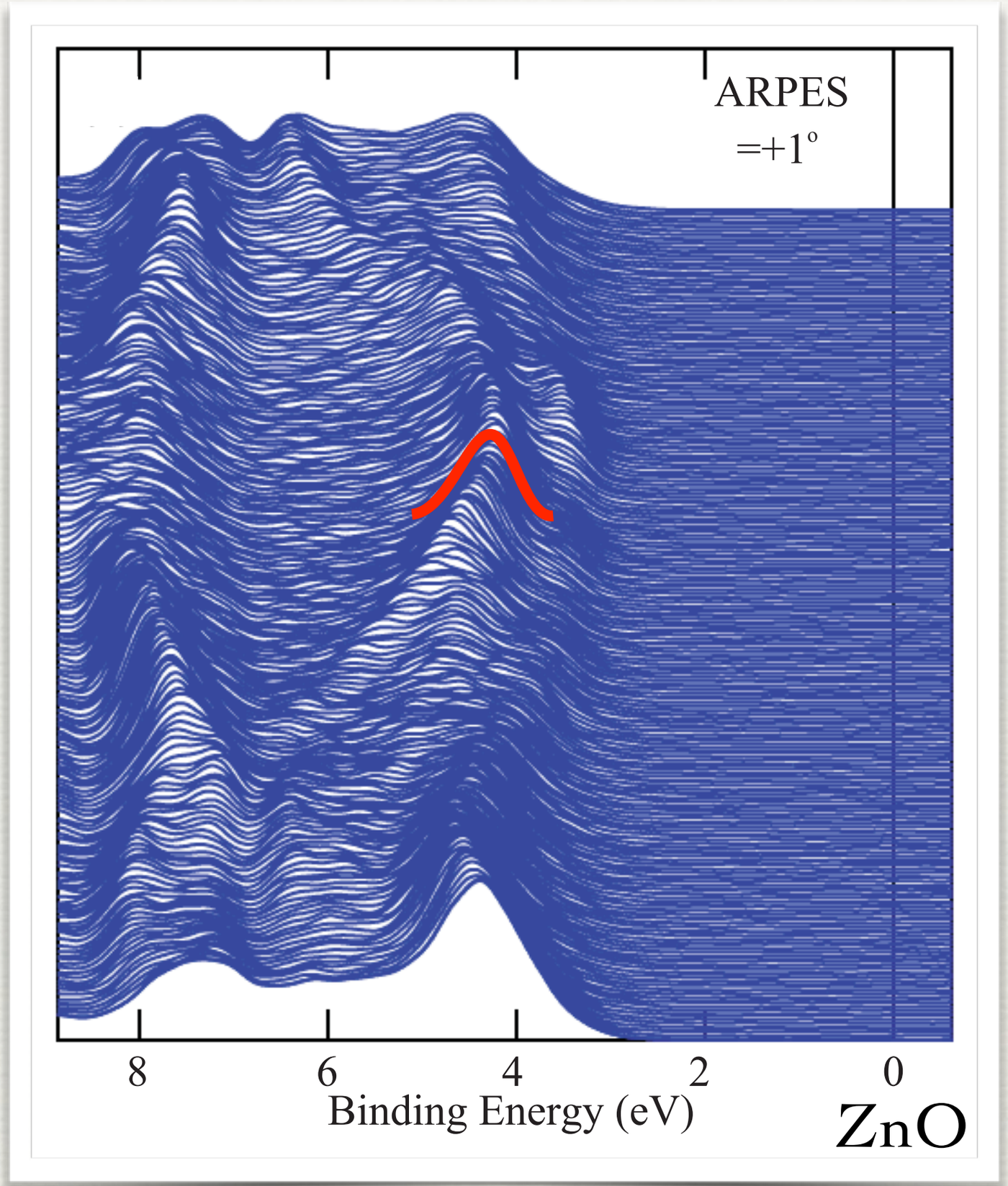


Angle-resolved photoemisson spectroscopy



Masaki Kobayashi,
PhD dissertation

Angle-resolved photoemisson spectroscopy



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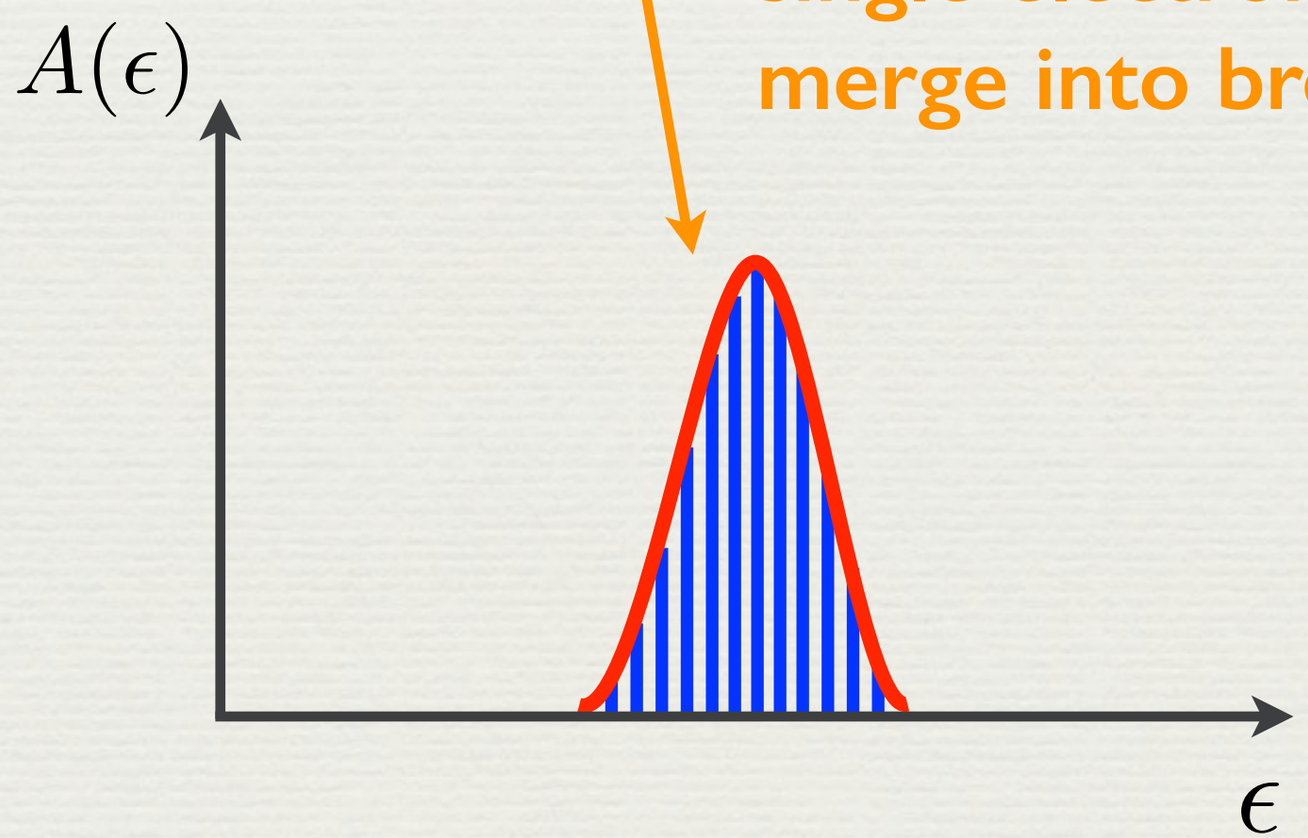
single electron excitations merge into broad peak

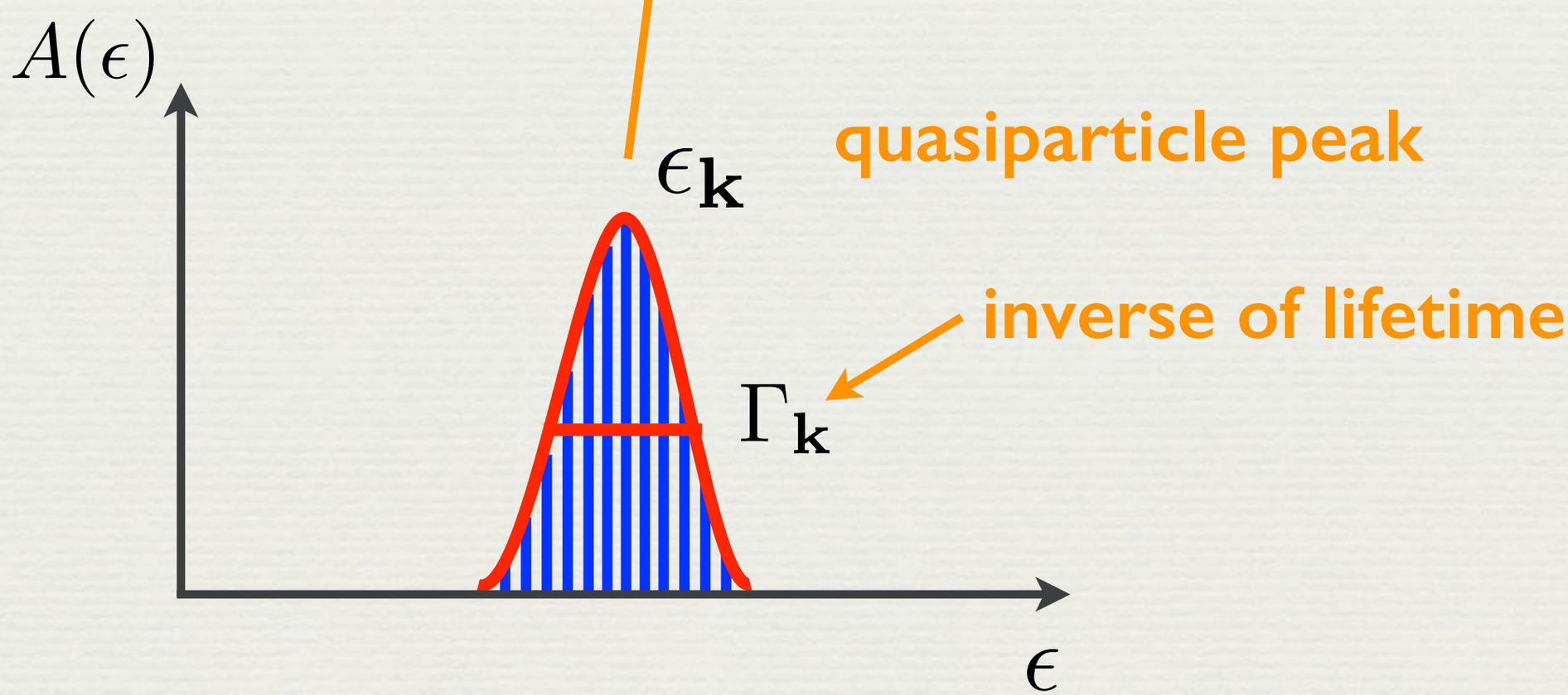


Single-particle Green's function

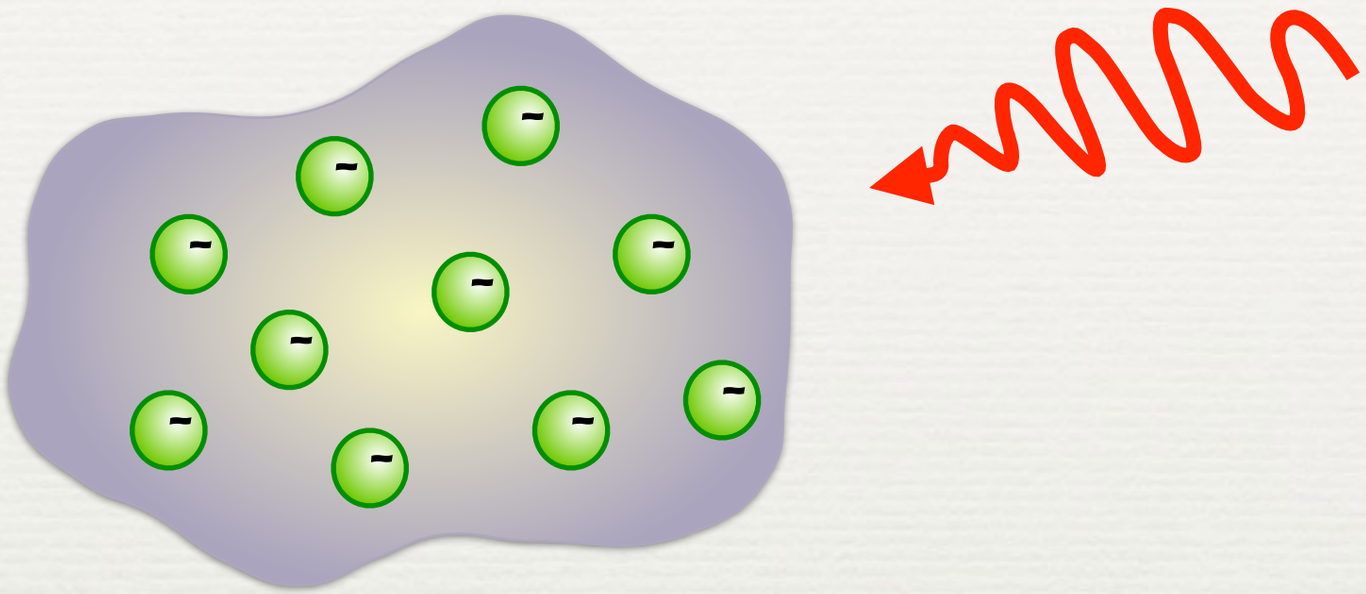
- single particle-like spectral function:

quasiparticle weight

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



Another take on quasiparticles



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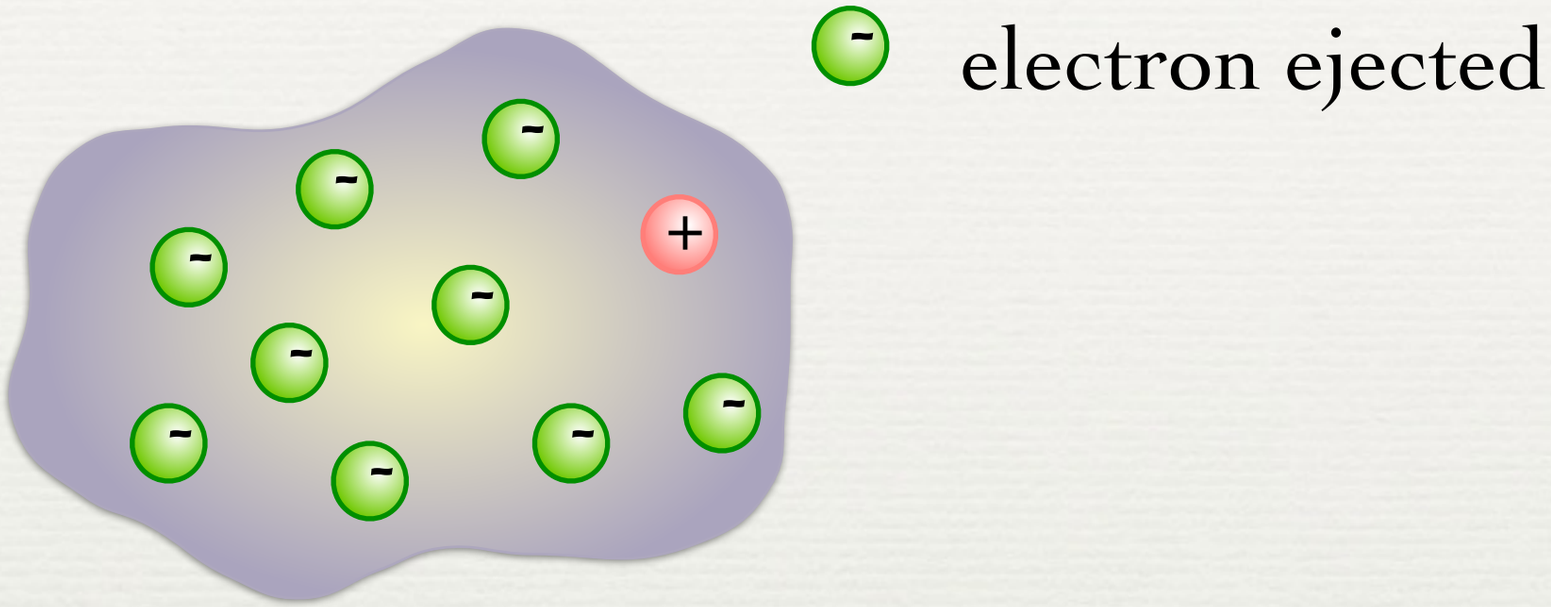

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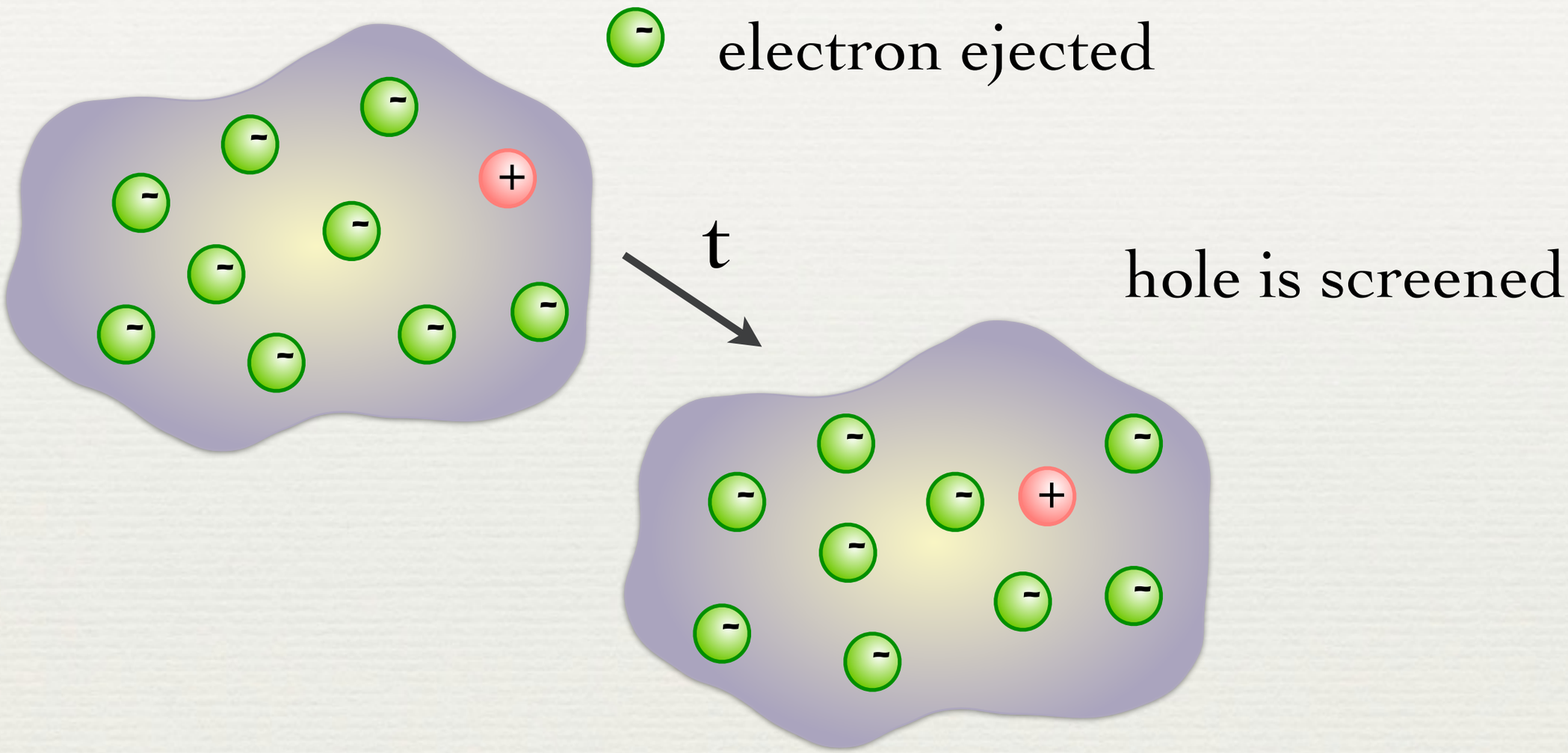

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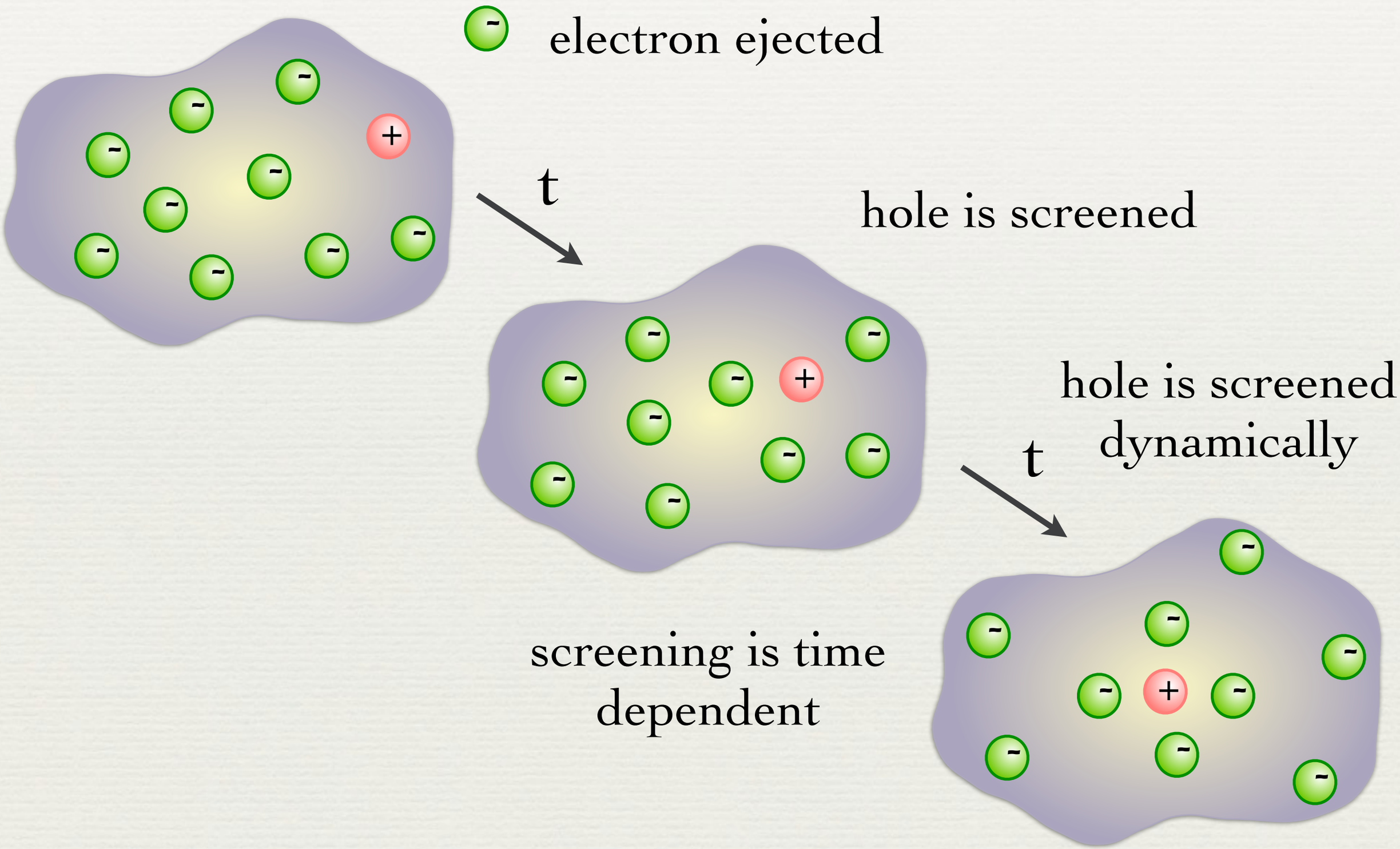

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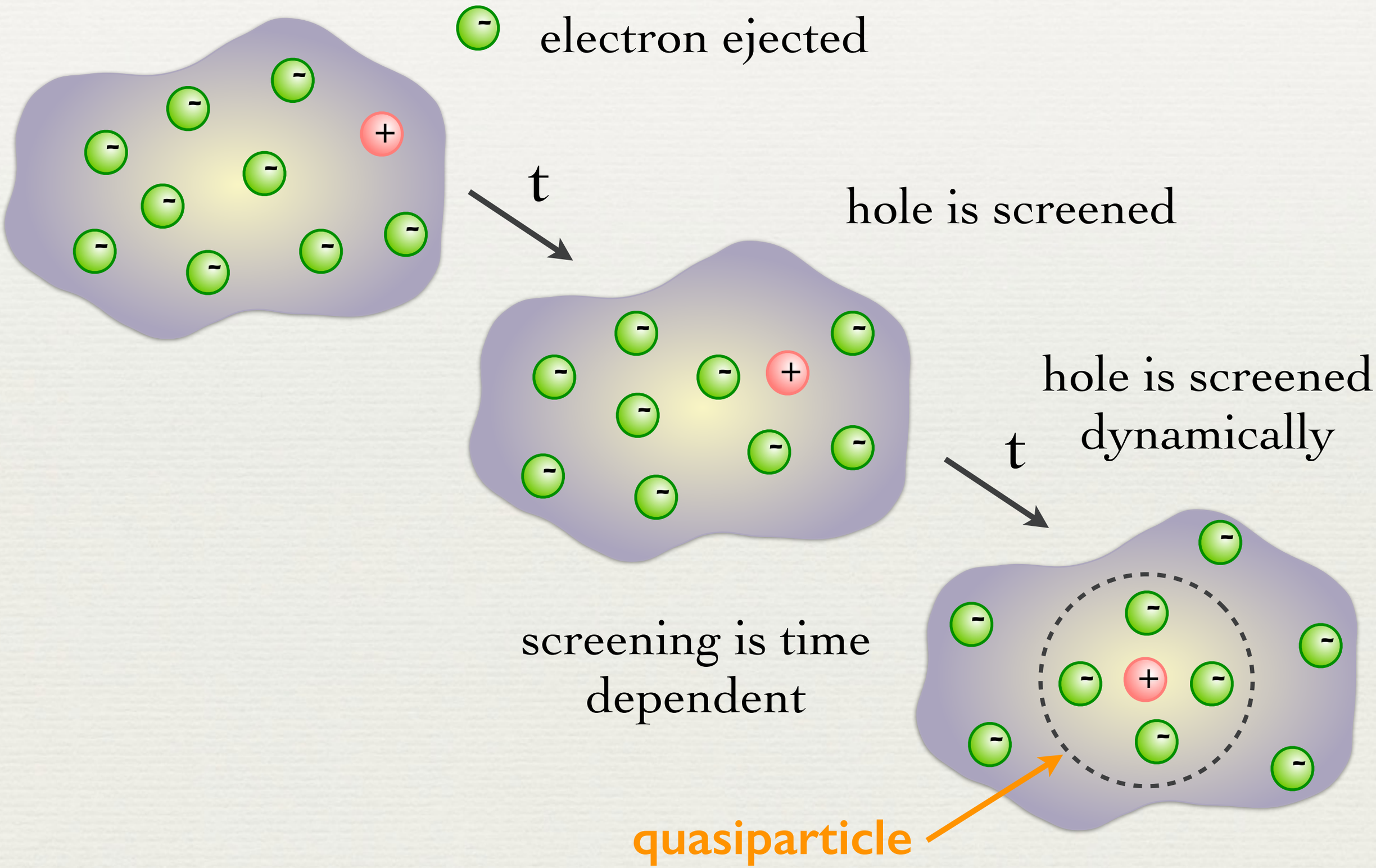


The screened Coulomb interaction

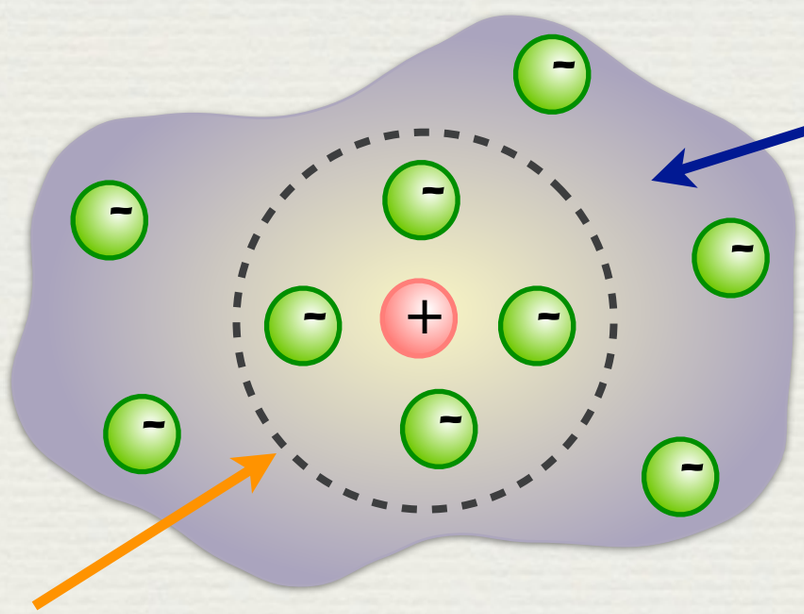
dielectric function

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

screened

bare

Coulomb interaction



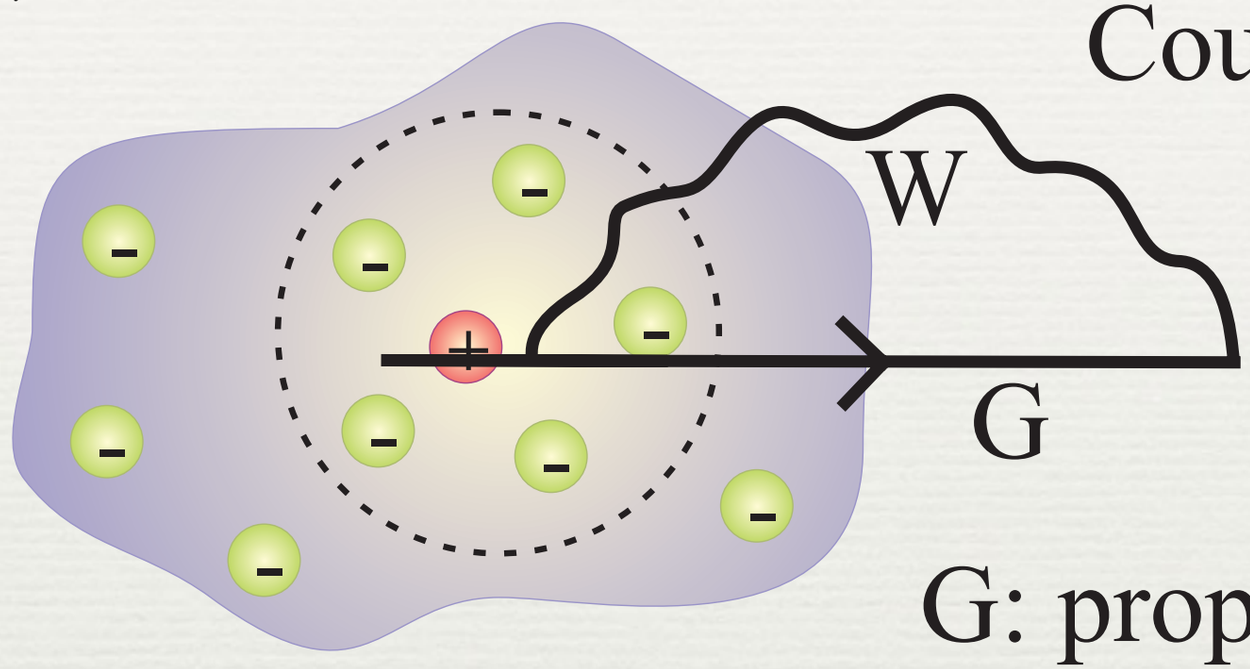
hole is screened by the system

quasiparticle

GW approximation - screened electrons

$$\Sigma = iGW$$

W: screened Coulomb



G: propagator

self-energy:

- energy that the quasiparticle feels due to its own presence

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

GW approximation - screened electrons

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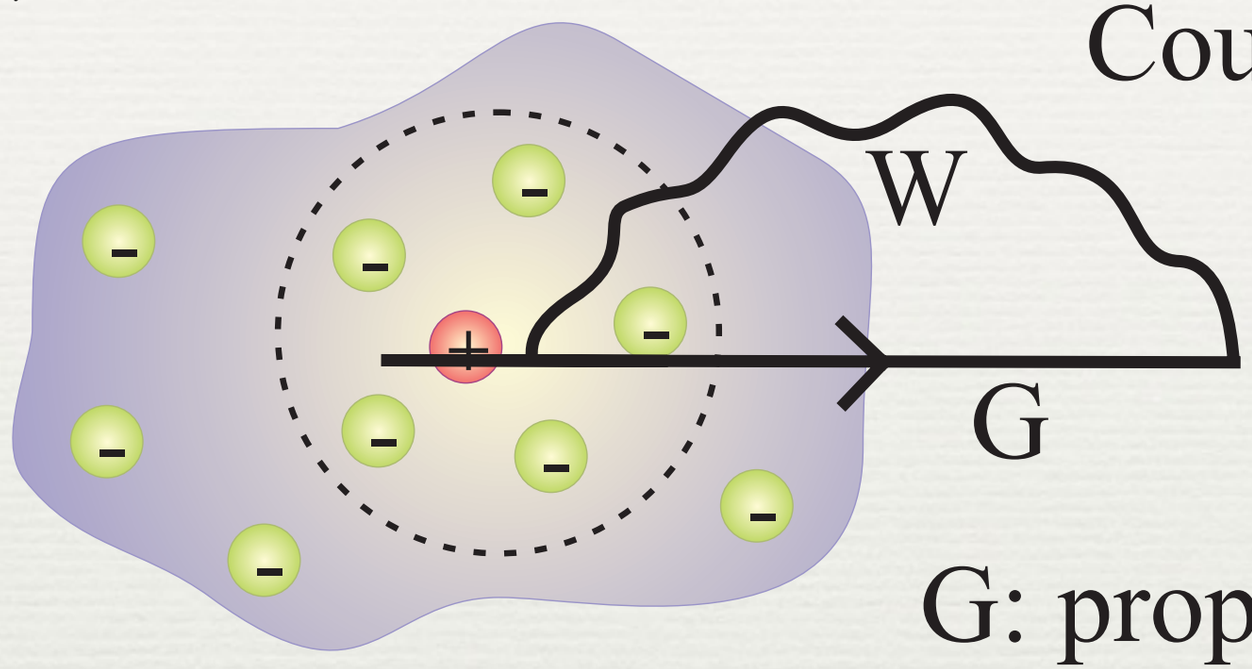

G: propagator

Dyson equation:

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

non-interacting Green's function

G is solution of Hedin's equations

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

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

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

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

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

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

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exact, therefore not tractable

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GW approximation

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do not despair

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

GW in practice

Step 1:

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

GW in practice

Step 1:

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

Step 2:

- Set up Kohn-Sham Green's function:

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

GW in practice

Step 1:

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Step 3:

- Construct polarizability:

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

GW in practice

Step 4:

- Dielectric function:

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

GW in practice

Step 4:

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

Step 5:

- Screened Coulomb interaction:

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

GW in practice

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Step 6:

- Self-energy:

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

GW in practice

Step 7:

- Solve quasiparticle equation:

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

Step 7b:

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

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

GW in practice

Step 7:

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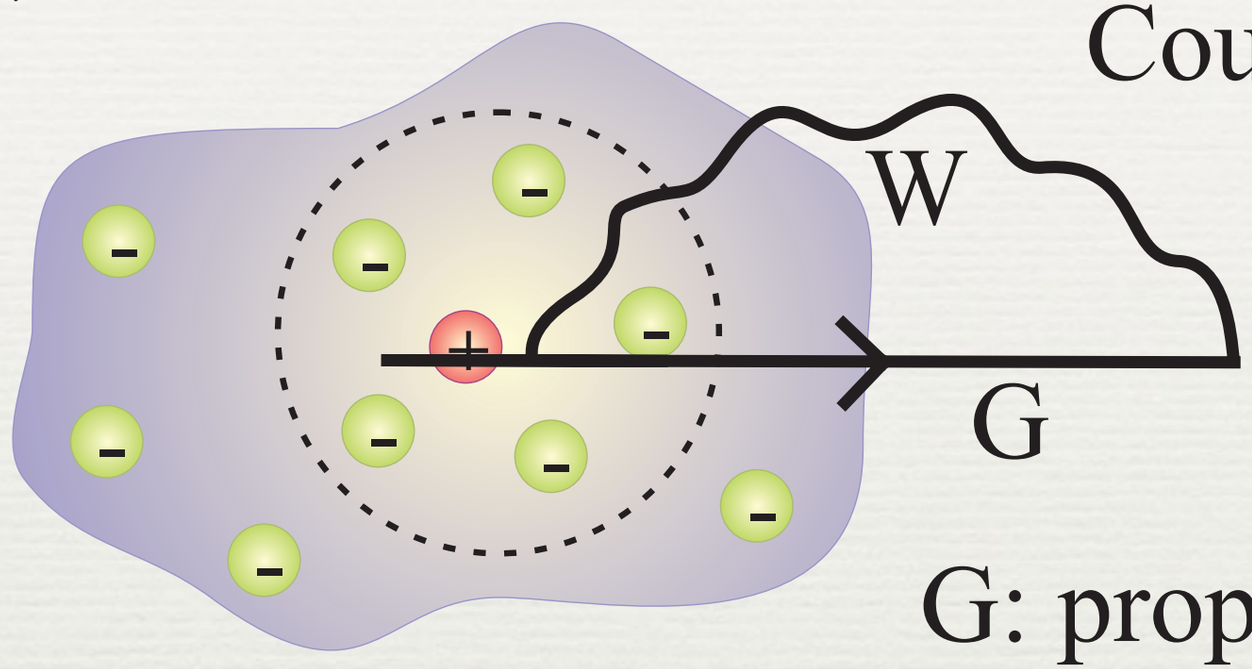
***GW* formal scaling ~ system size^4**

GW approximation - screened electrons

$$\Sigma = iGW$$

W: screened Coulomb



G: propagator

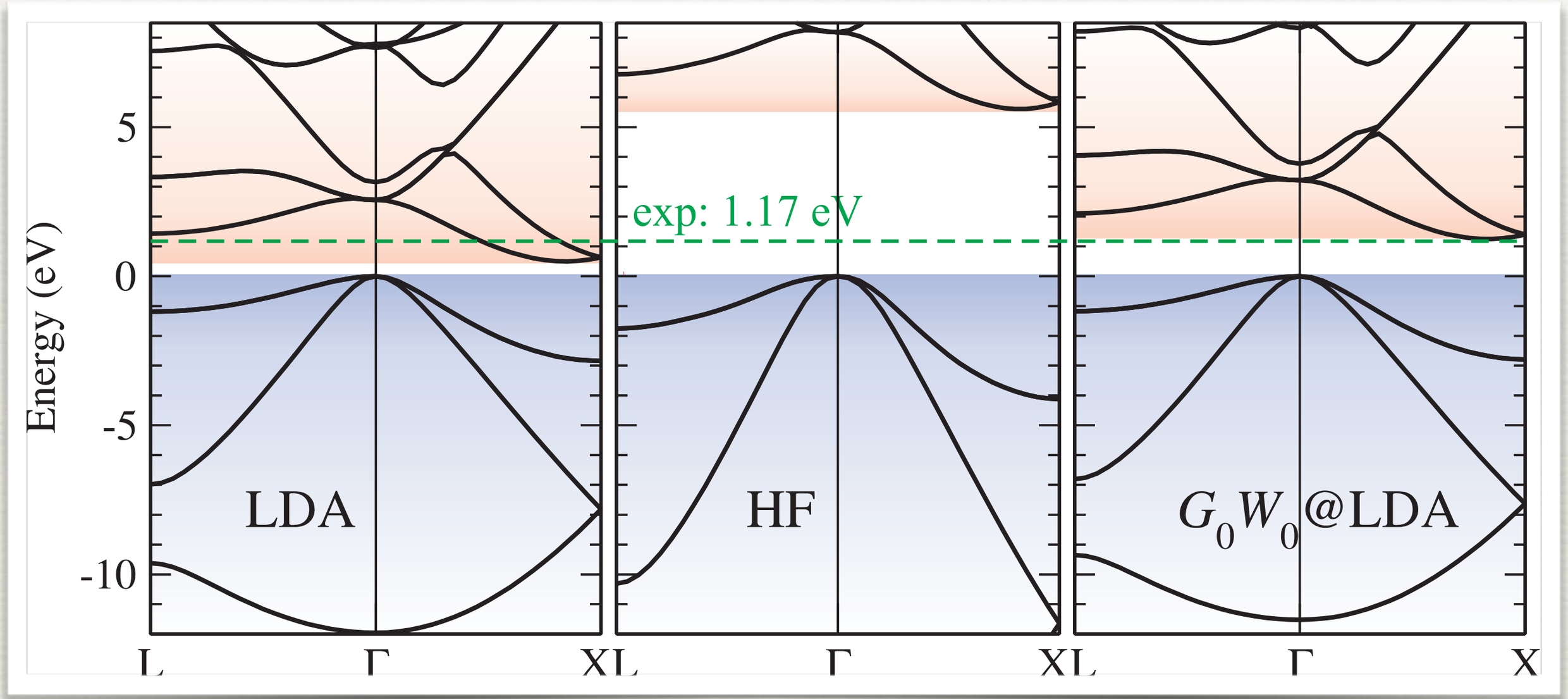
self-energy: $\Sigma = \Sigma_x + \Sigma_c$

iGv — exact exchange (Hartree-Fock)

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

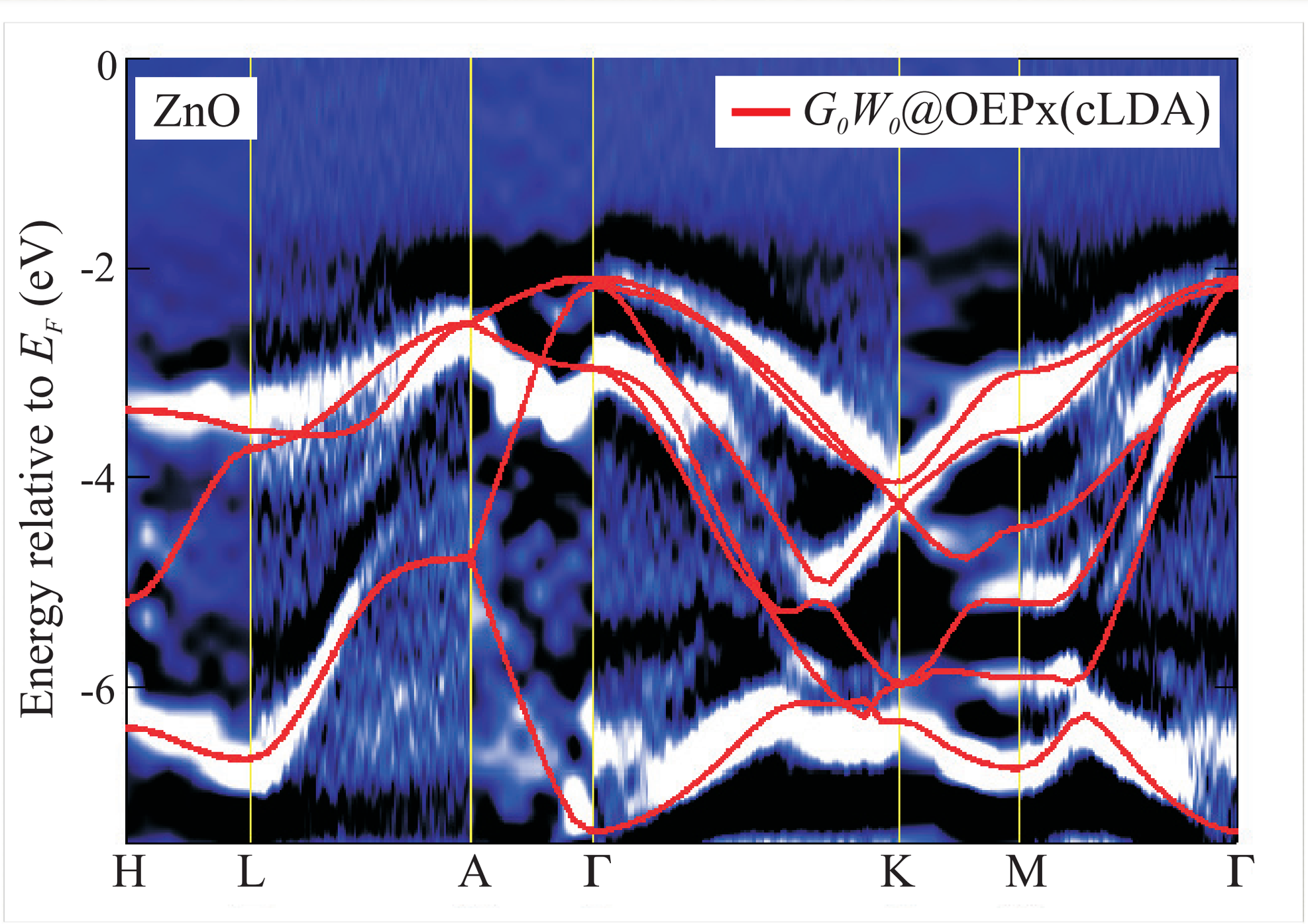
On the importance of screening

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



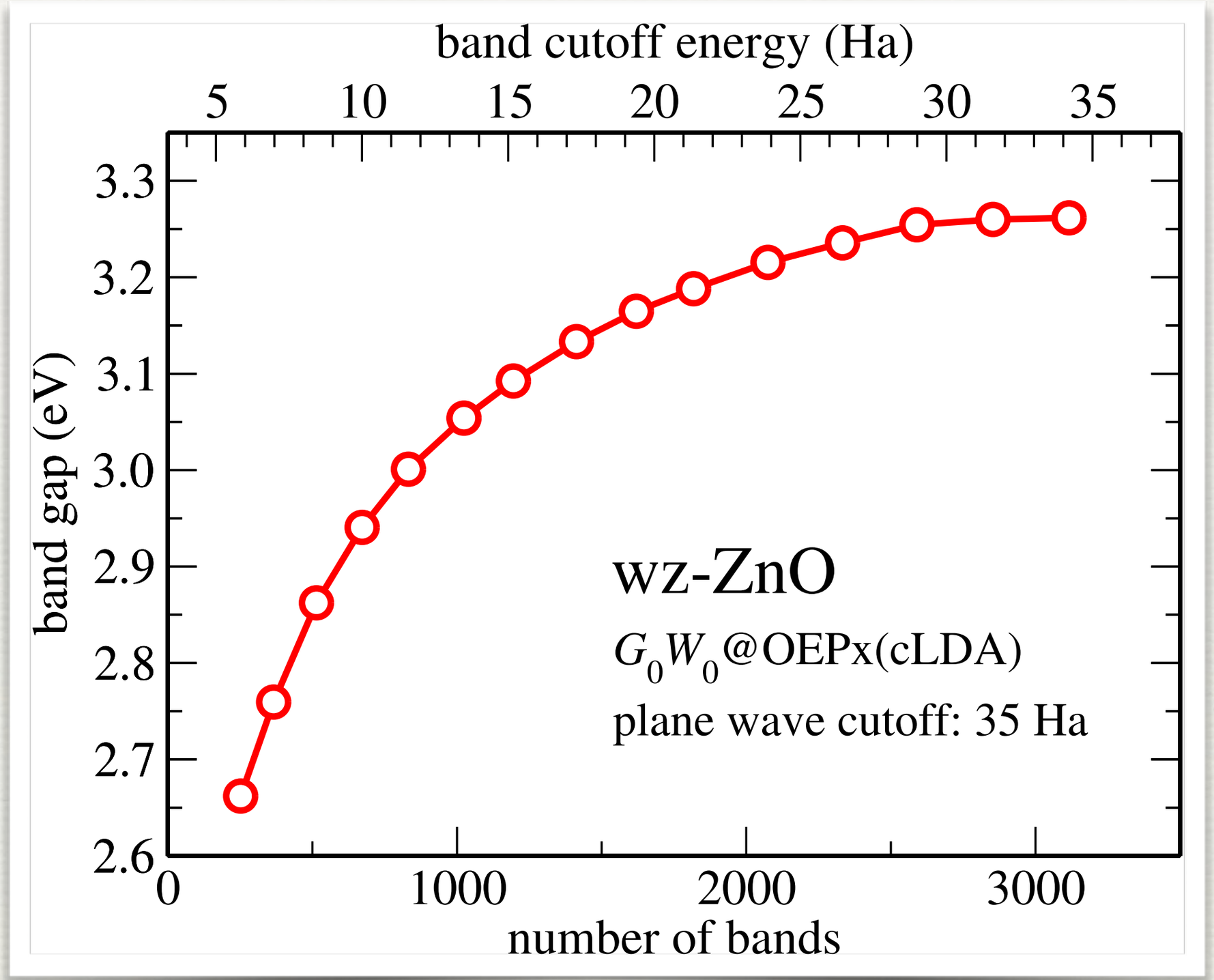
- Hartree-Fock (HF) exact exchange gap much too large
- *W* is essential for solids

Angle resolved photoemission - ZnO



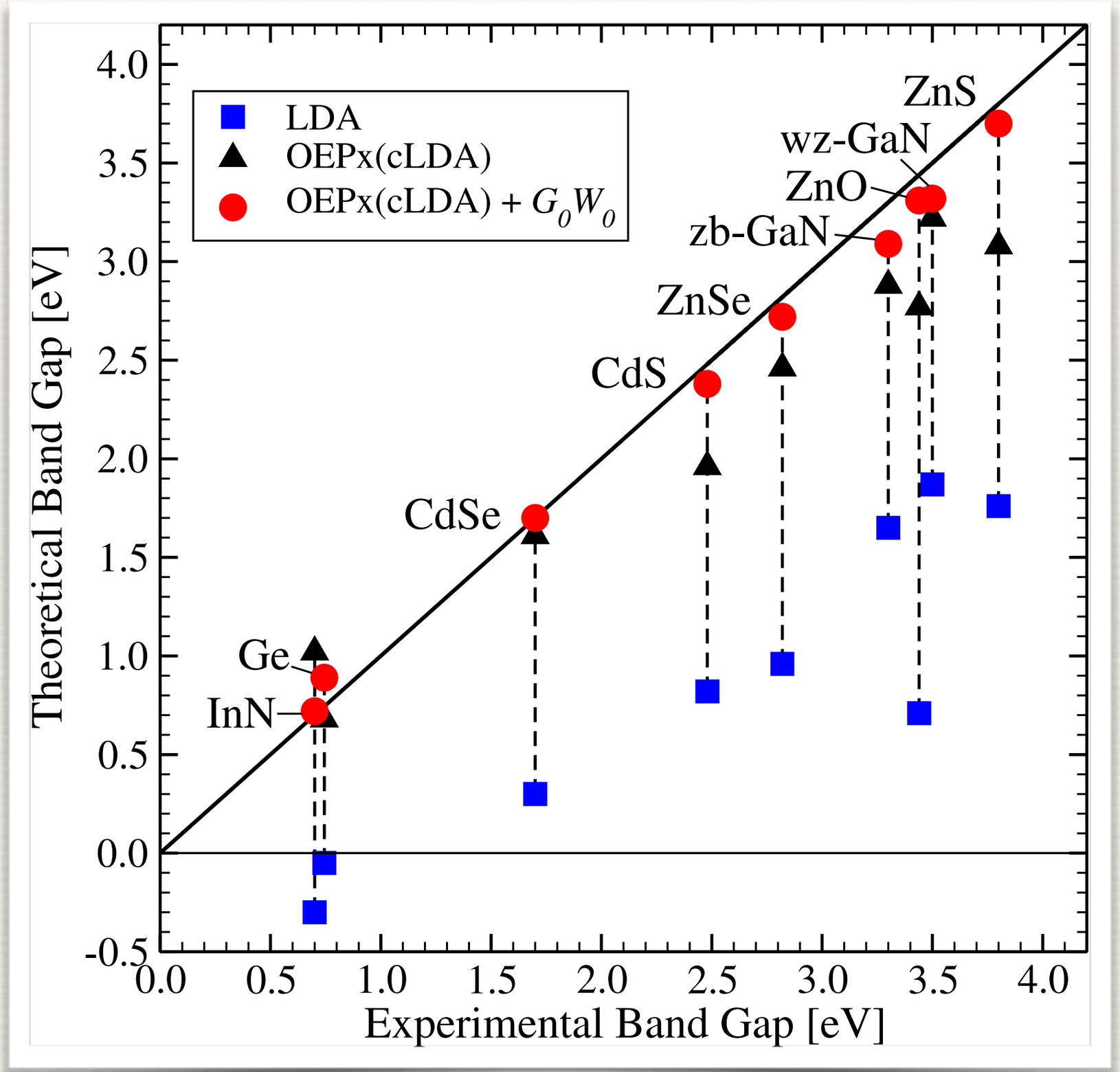
Q. Yan, P. Rinke, M. Winkelnkemper, A. Qteish, D. Bimberg, M. Scheffler, C. G. Van de Walle, Semicond. Sci. Technol. 26, 014037 (2011)

Convergence of G_0W_0 for ZnO



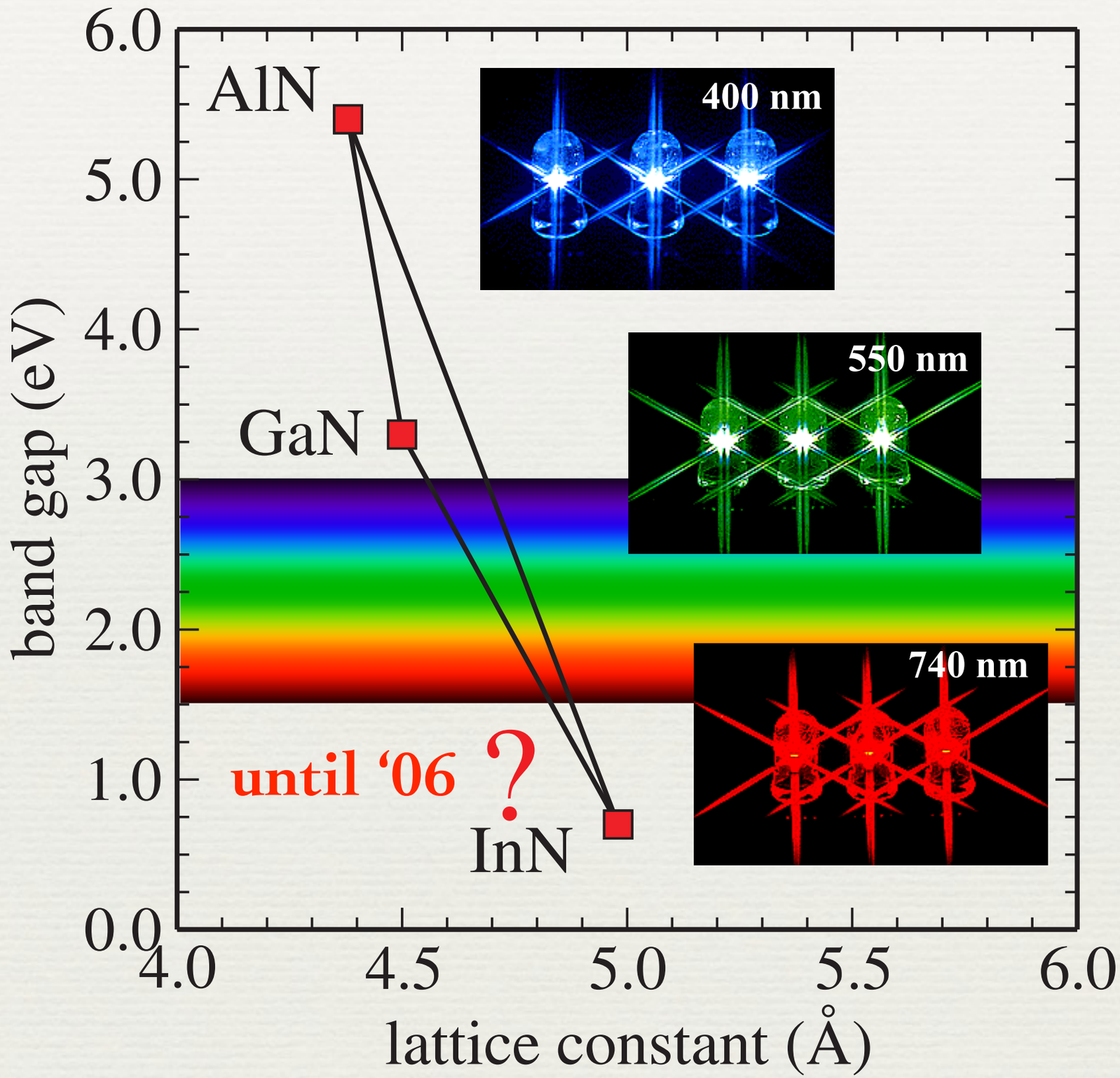
Yan, Rinke, Winkelnkemper, Qteish, Bimberg, Scheffler, Van de Walle, Semicond. Sci. Technol. 26, 014037 (2011)

Band gaps of solids



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

Do we know the band gap of InN?



Band gap of InN

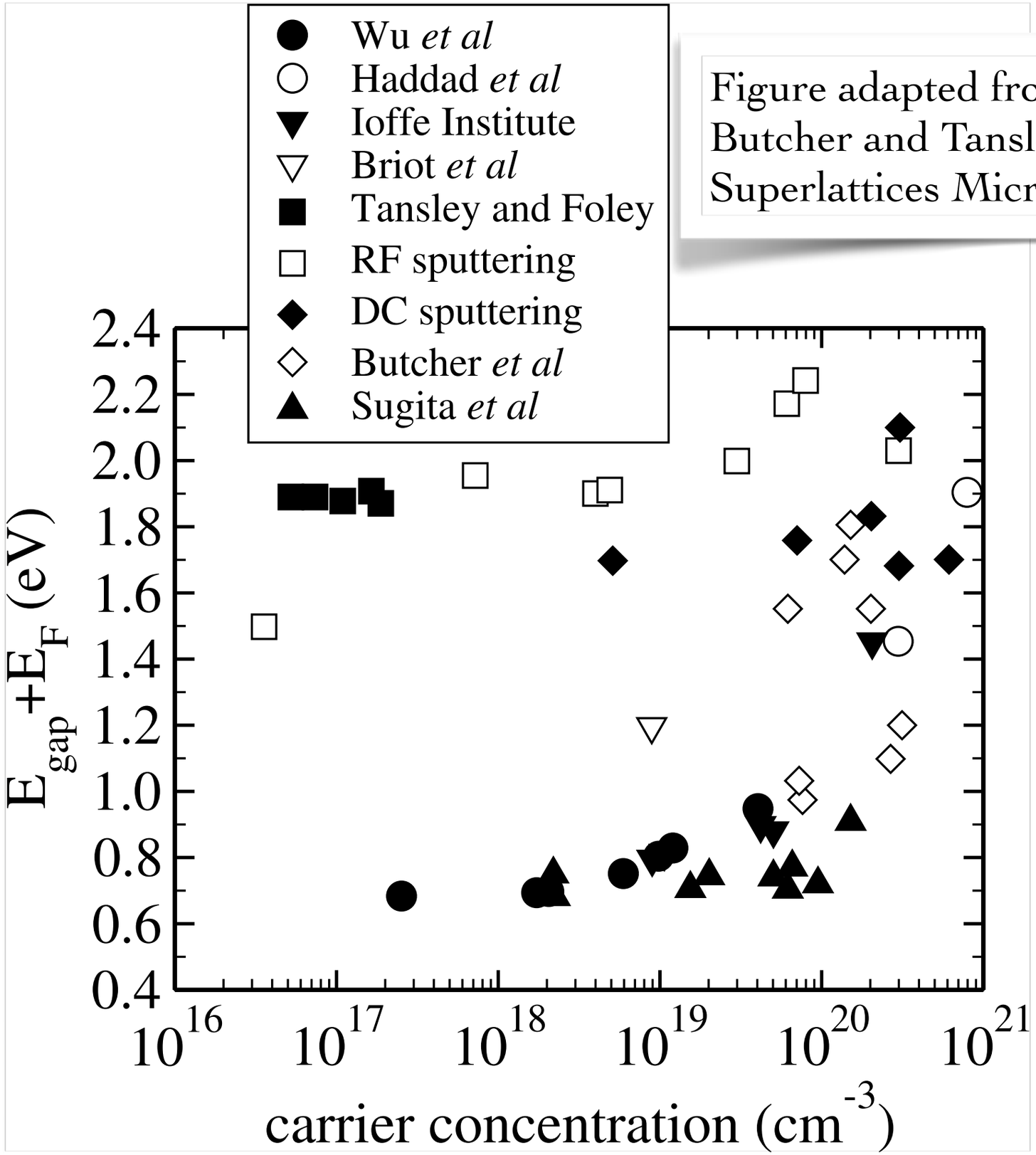


Figure adapted from
Butcher and Tansley
Superlattices Microstruct. **38**, 1 (2005)

Band gap of InN

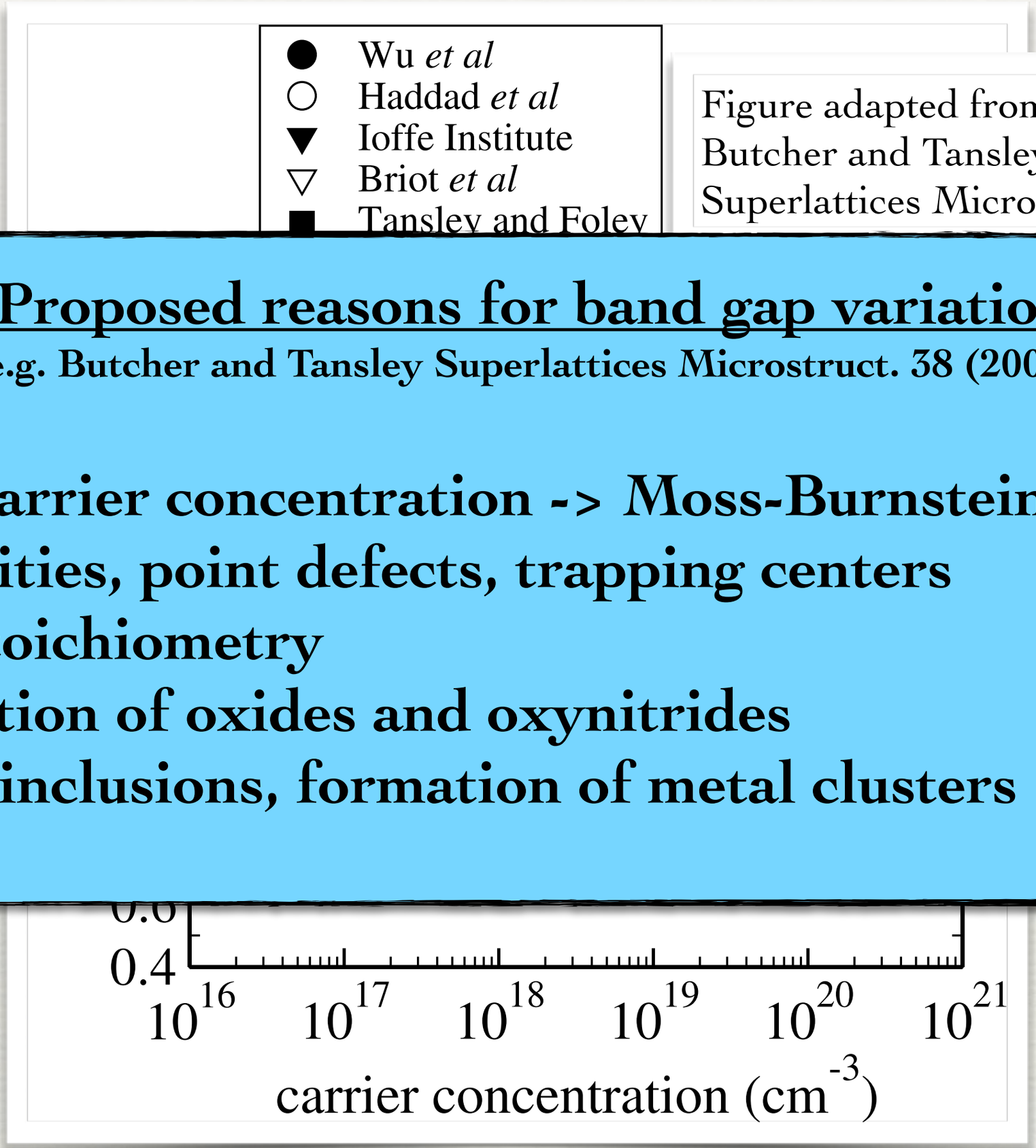


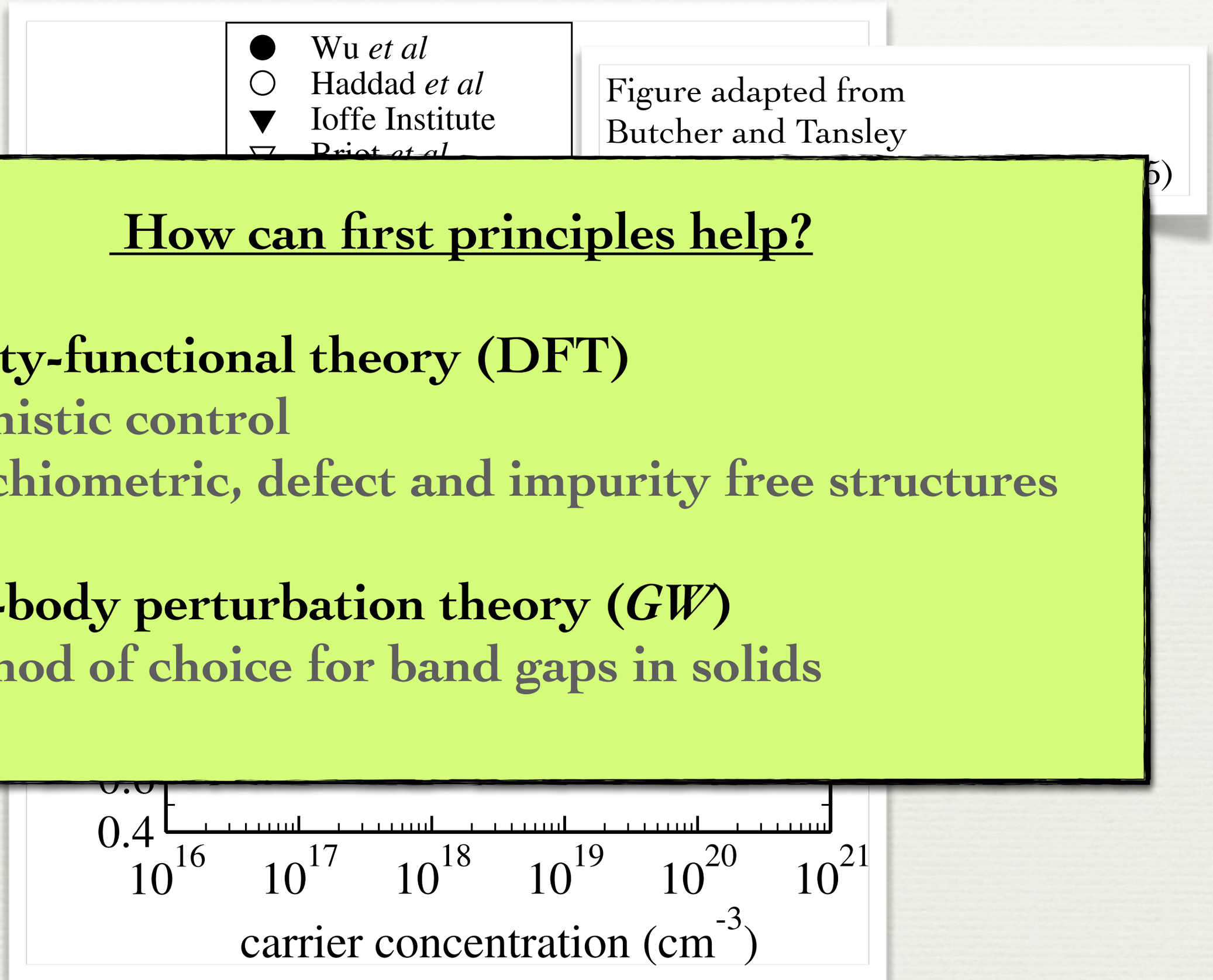
Figure adapted from
Butcher and Tansley
Superlattices Microstruct. **38**, 1 (2005)

Proposed reasons for band gap variation

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

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

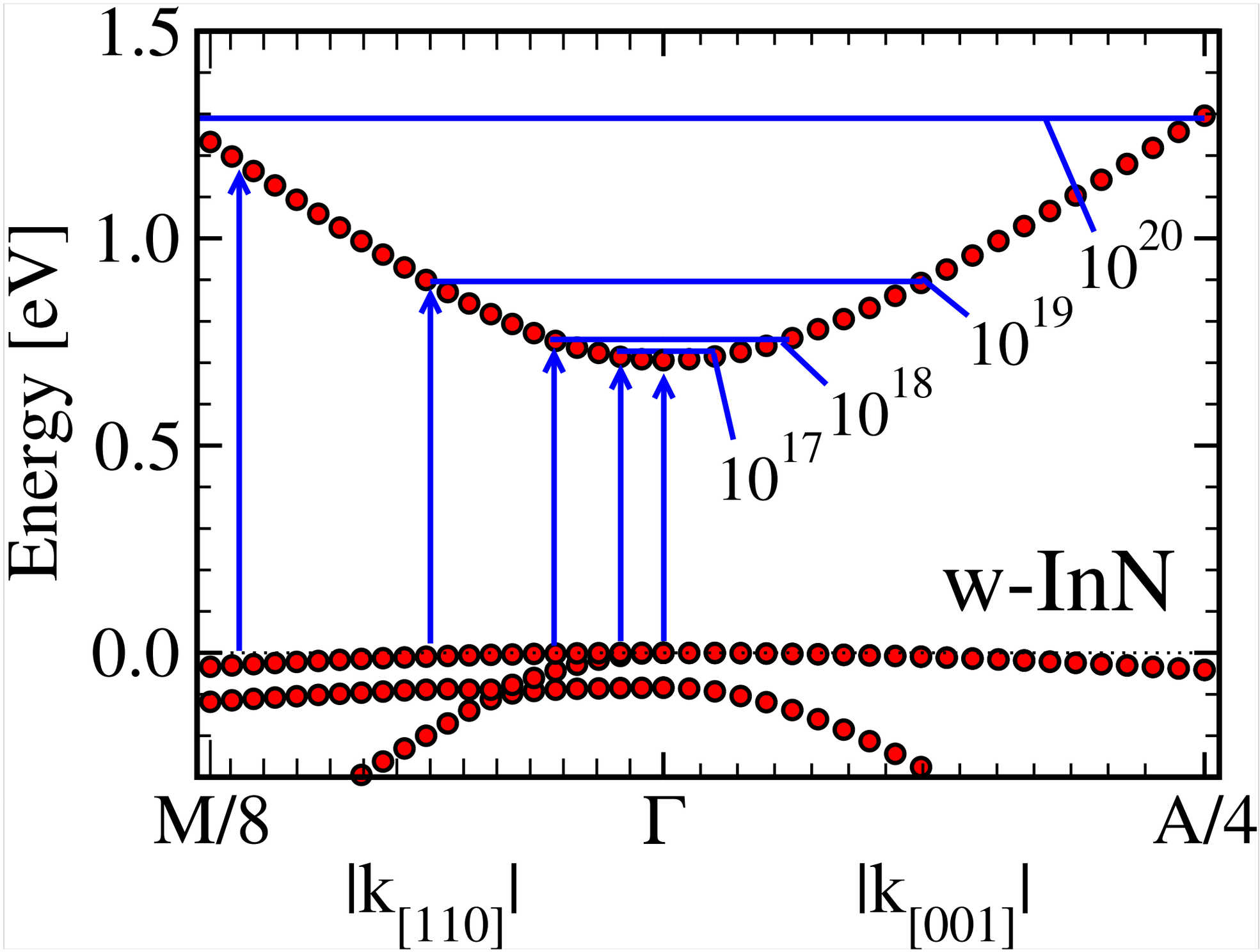
Band gap of InN



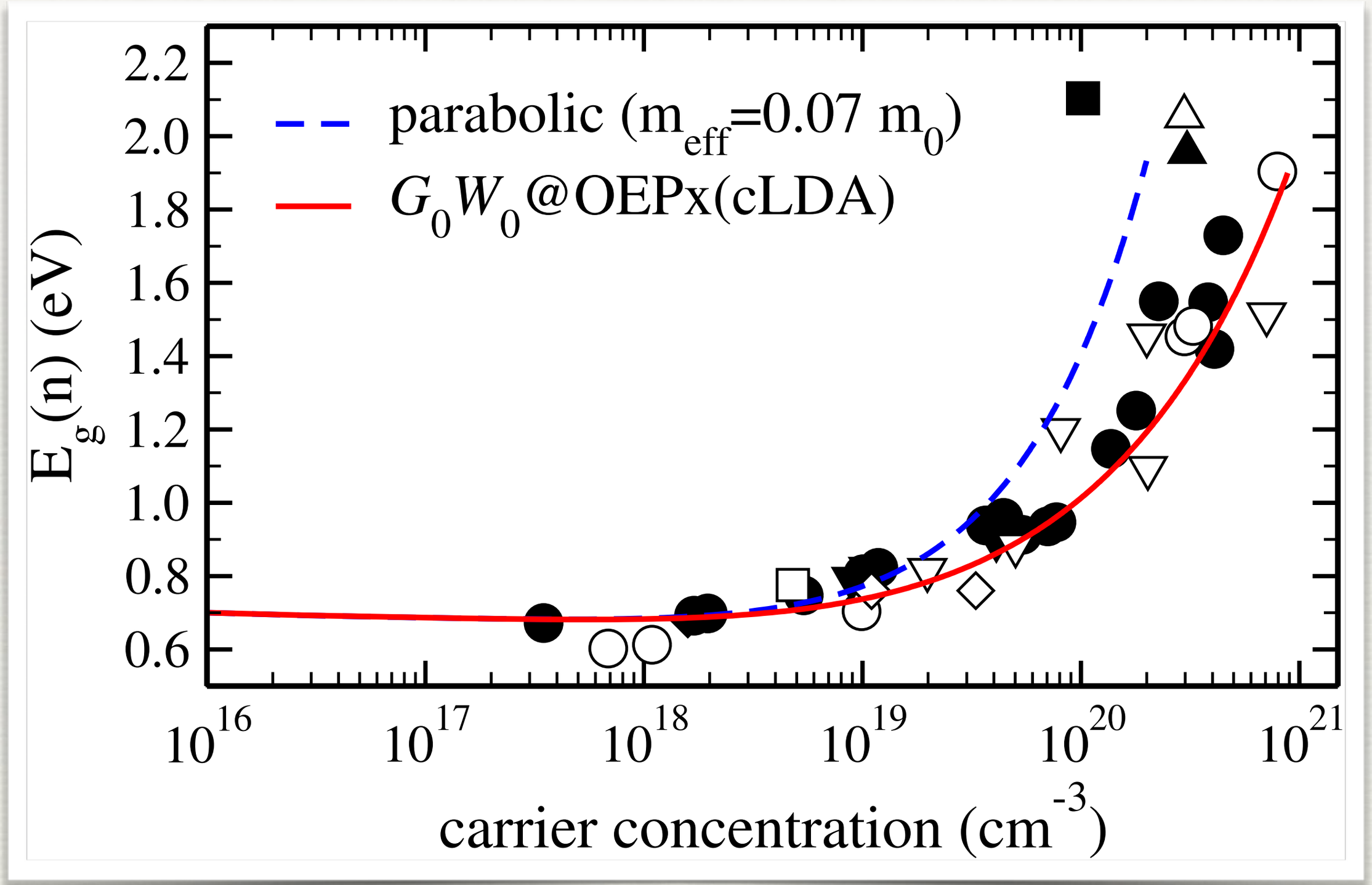
How can first principles help?

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

InN - *GW* band structure and Moss-Burstein

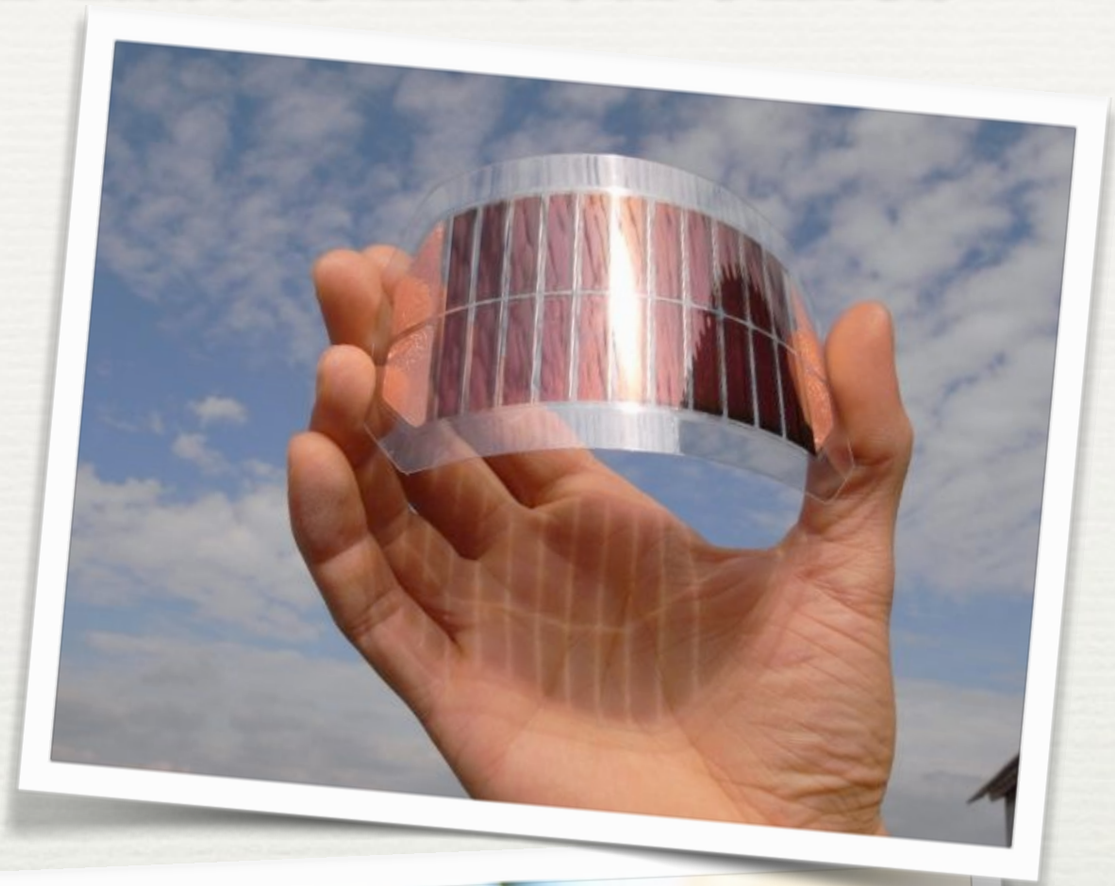


InN - *GW* band structure and Moss-Burstein



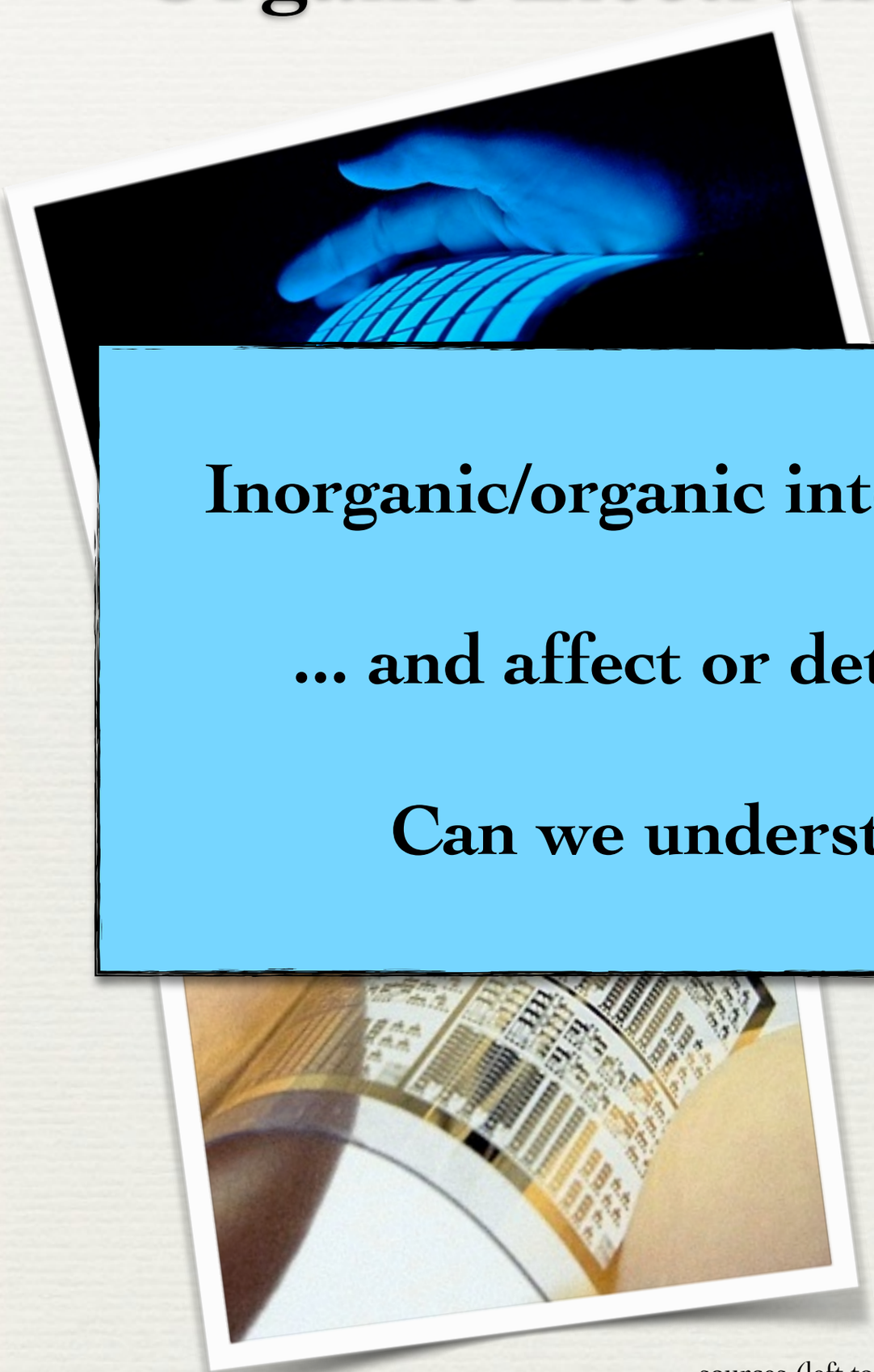
P. Rinke, et al., Appl. Phys. Lett. **89**, 161919 (2006)

Organic Electronics - Plastic Electronics



sources (left to right): Organic Electronic Association, Eco Friend, Nature Publishing Group, Samsung

Organic Electronics - Plastic Electronics



Inorganic/organic interfaces are already present...

... and affect or determine device properties.

Can we understand and control them?

sources (left to right): Organic Electronic Association, Eco Friend, Nature Publishing Group, Samsung

Atomistic understanding of molecules@surfaces

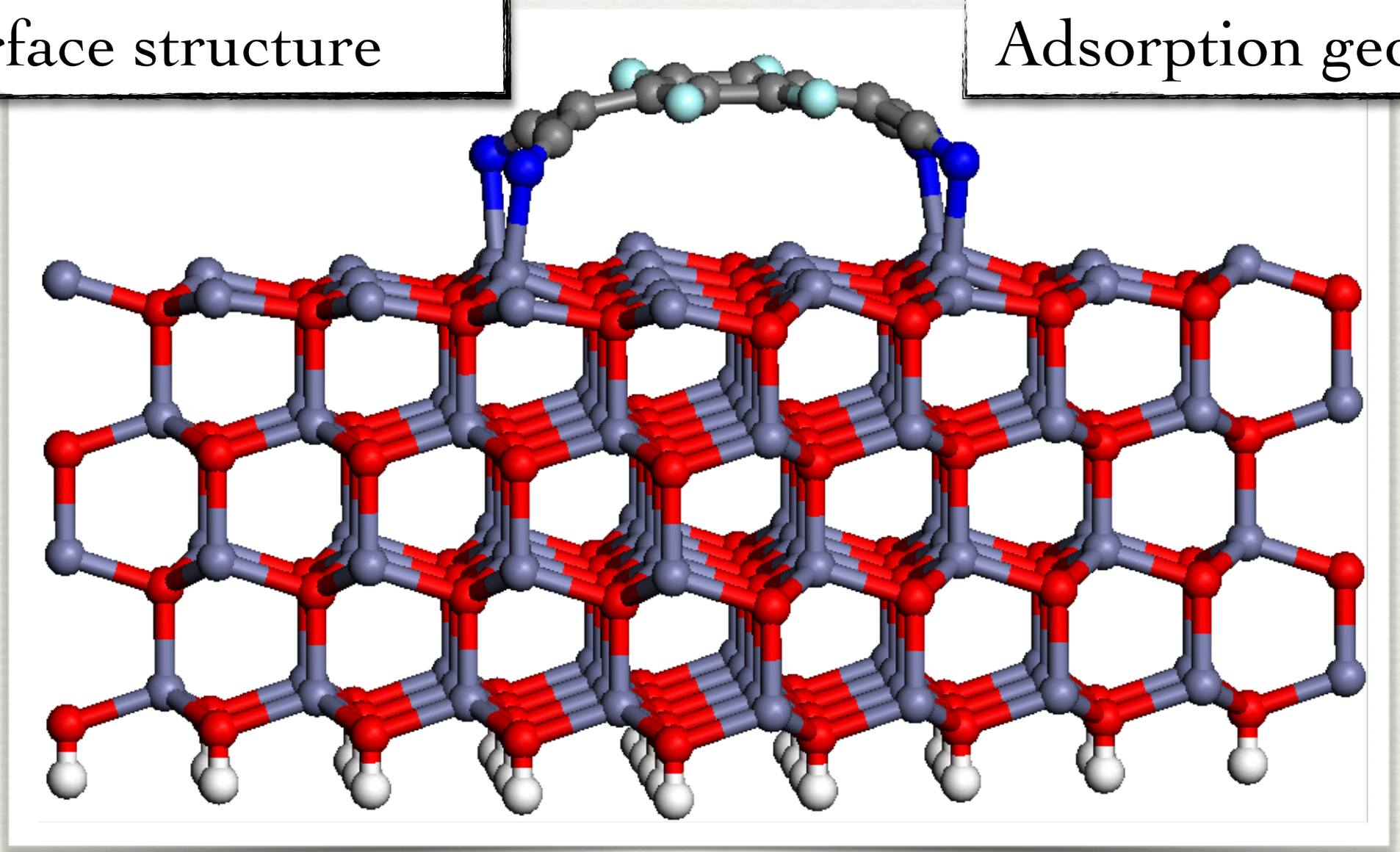
Charge transfer

Level alignment

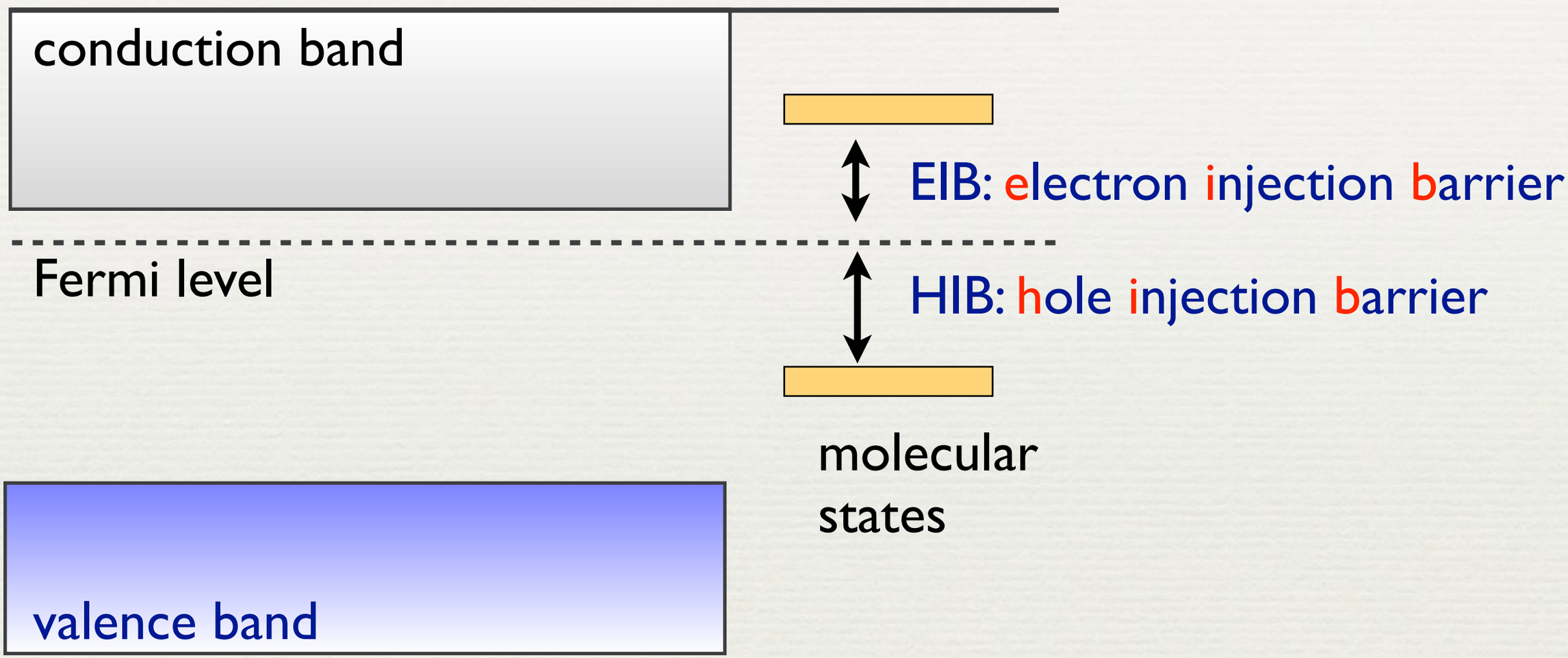
Van der Waals interaction

Surface structure

Adsorption geometry



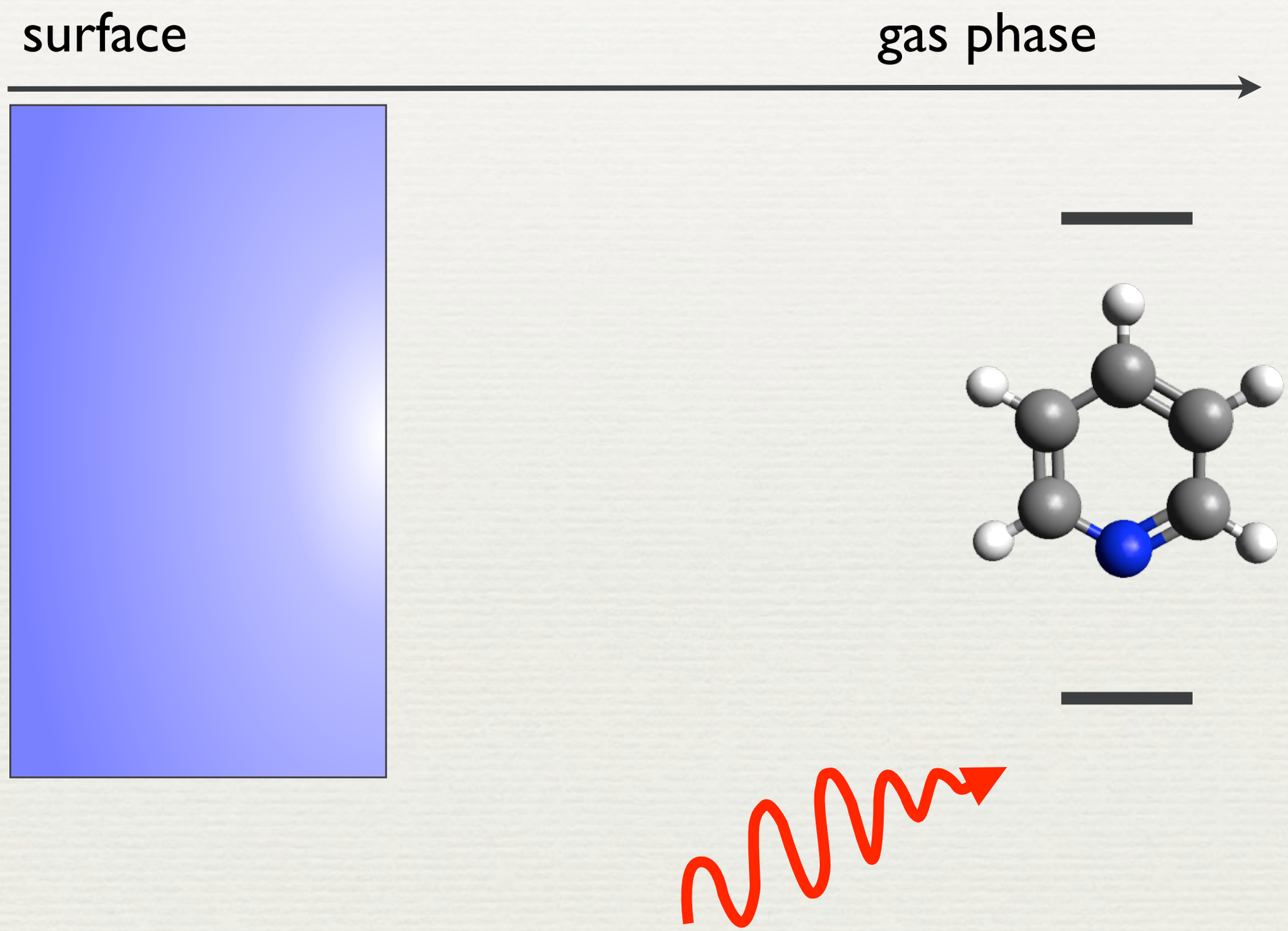
Level alignment at interface



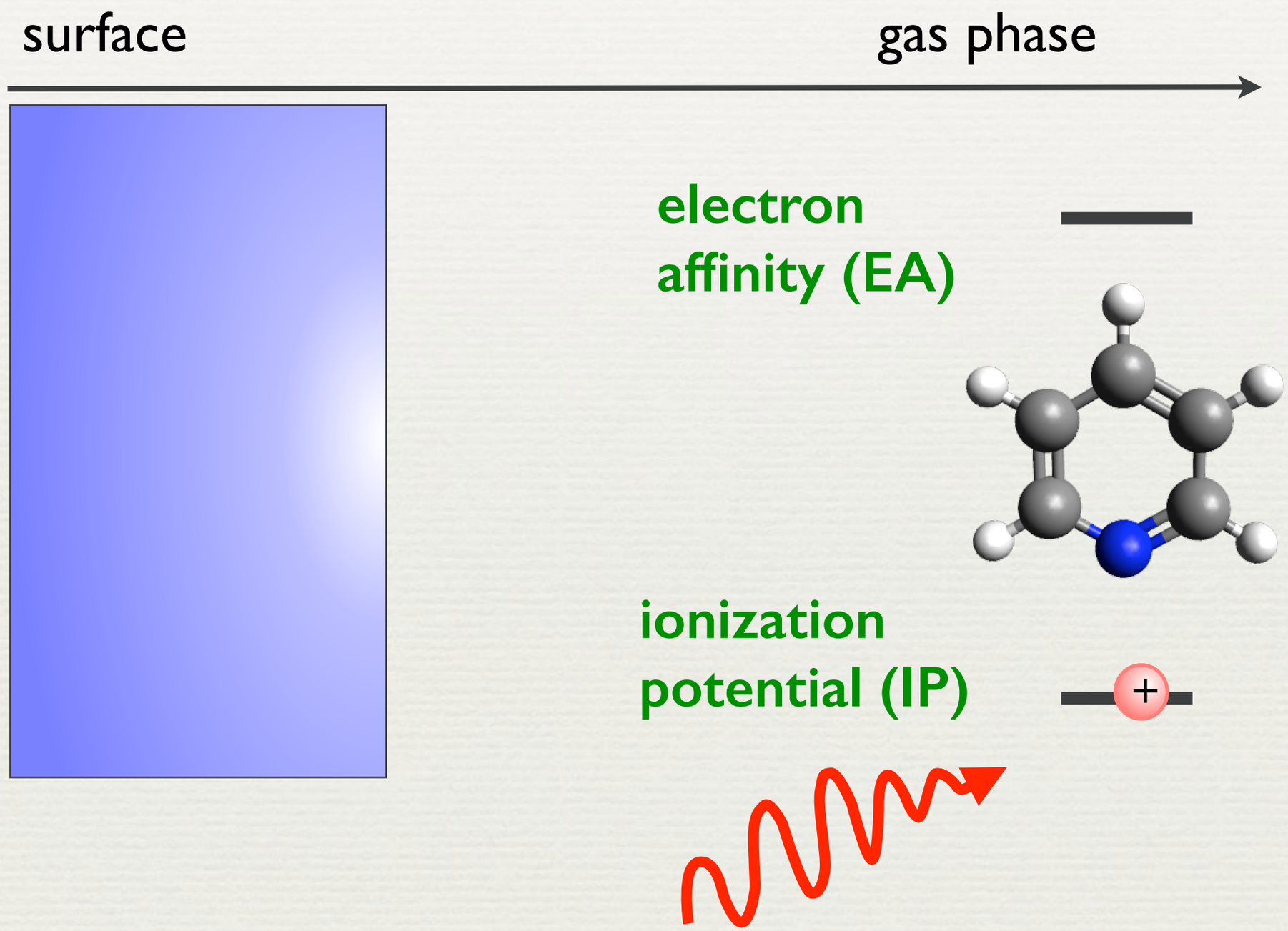
injection limited current:

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

Molecular levels at a surface



Molecular levels at a surface



Molecular levels at a surface

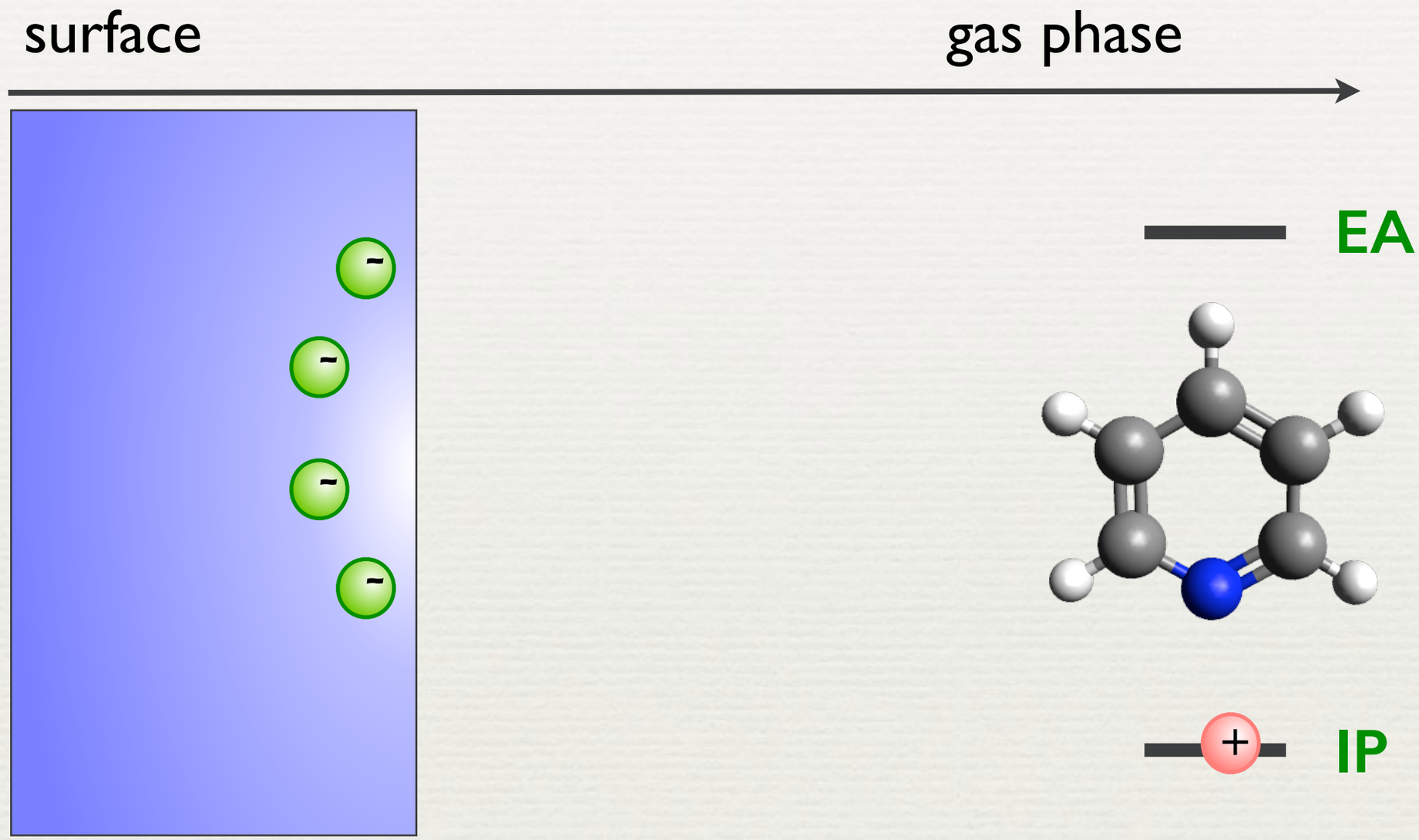


image effect

Molecular levels at a surface

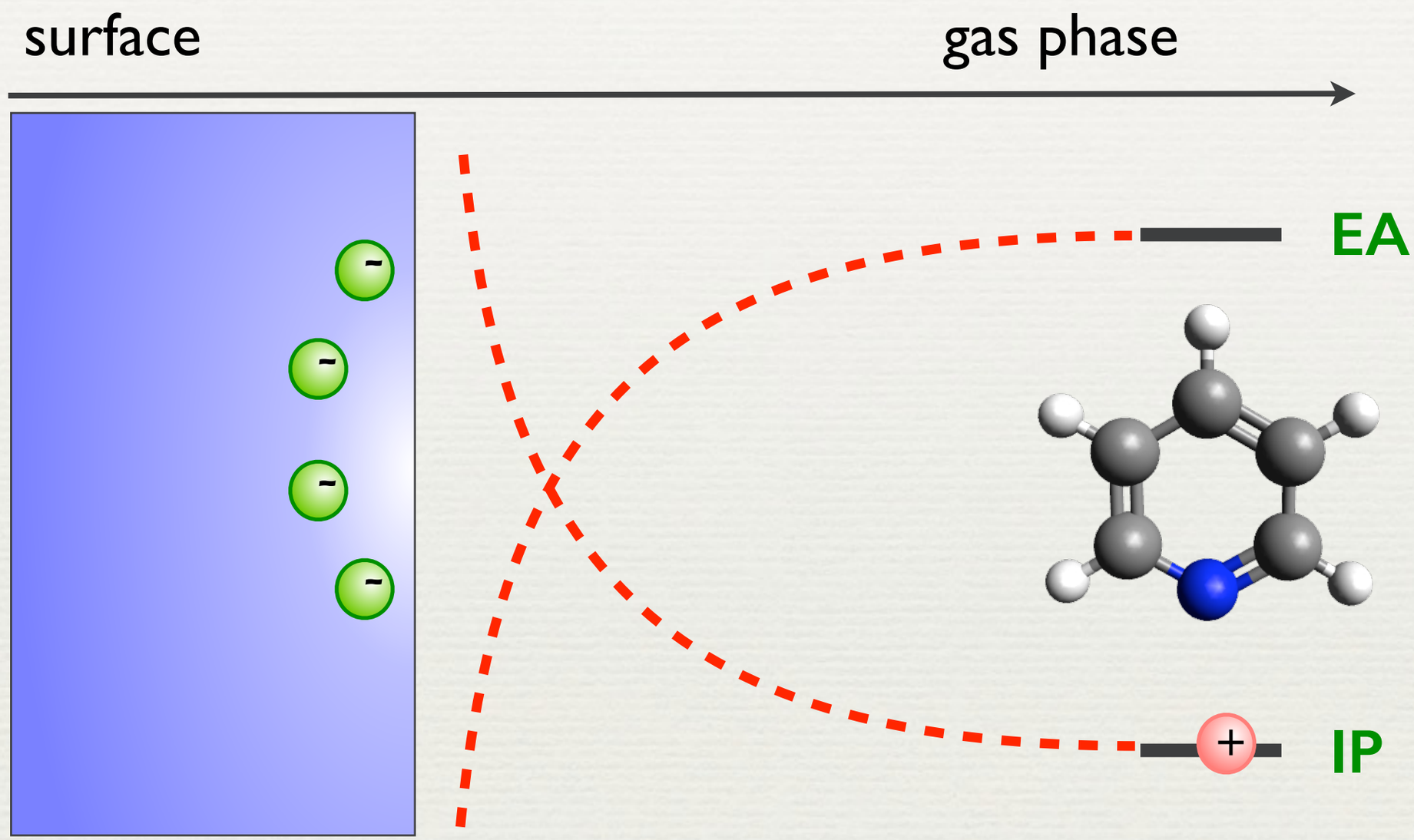


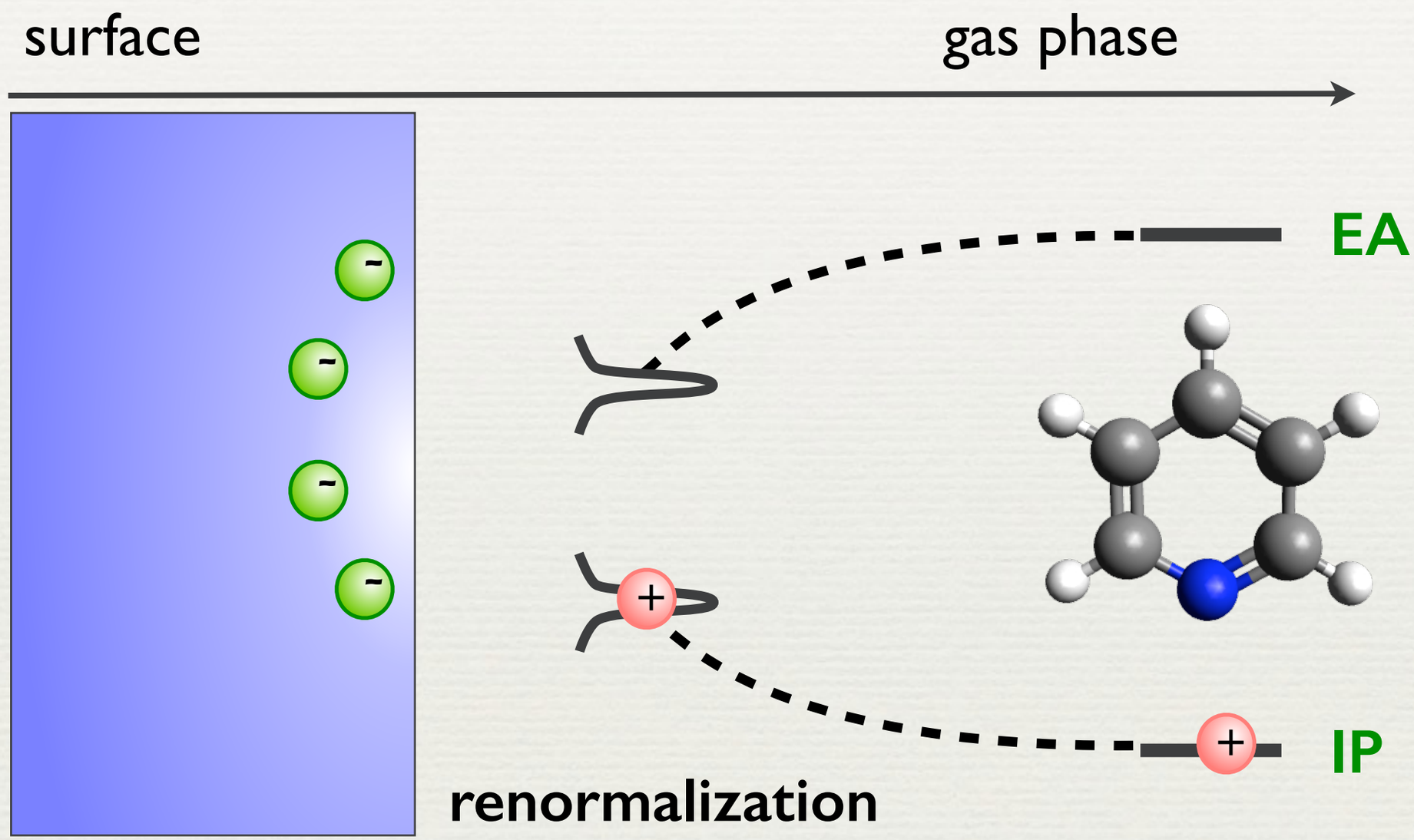
image potentials

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

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

ε dielectric constant

Molecular levels at a surface

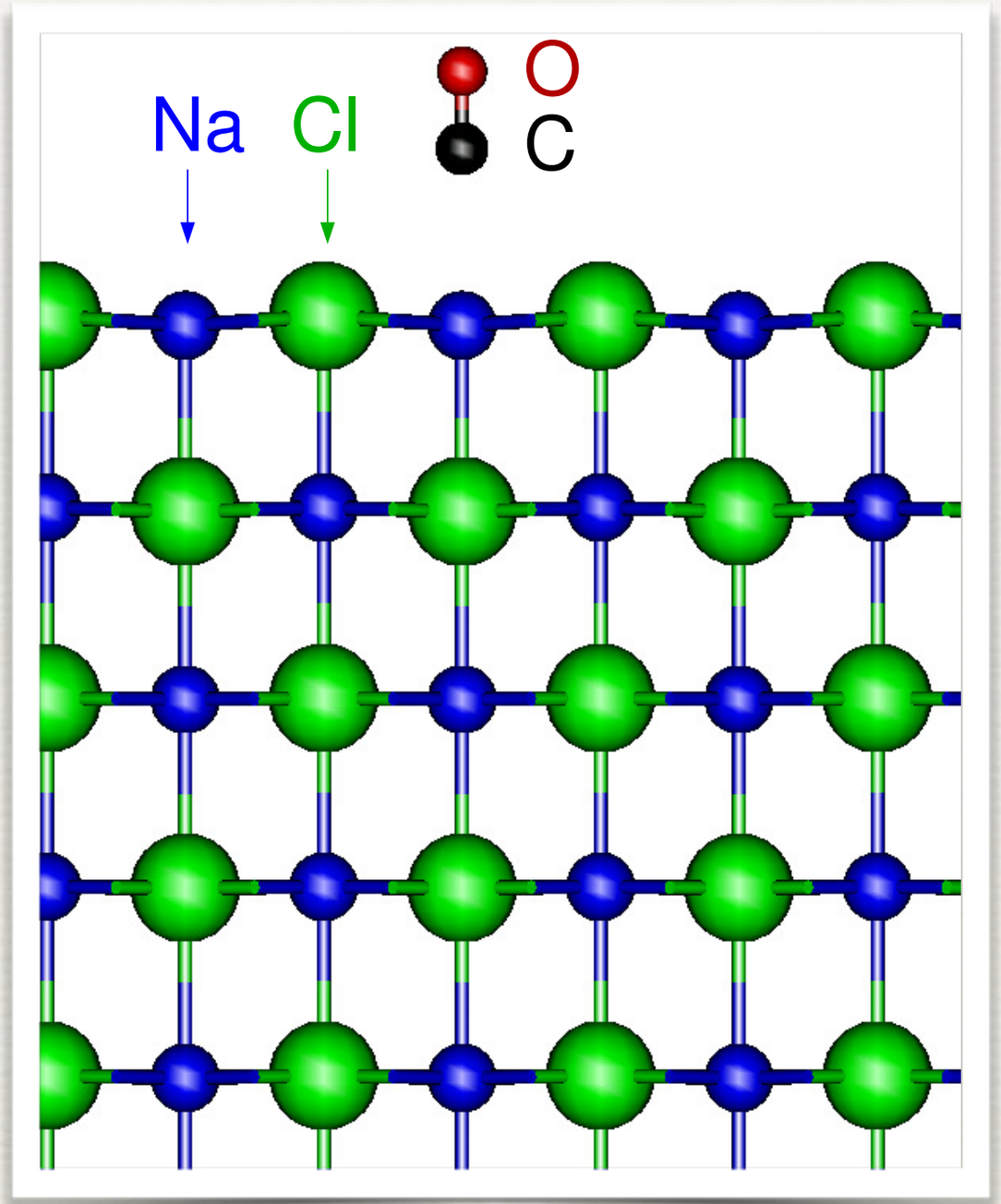


metal: $-\dfrac{1}{4z}$

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

ε dielectric constant

Renormalization at insulator surfaces



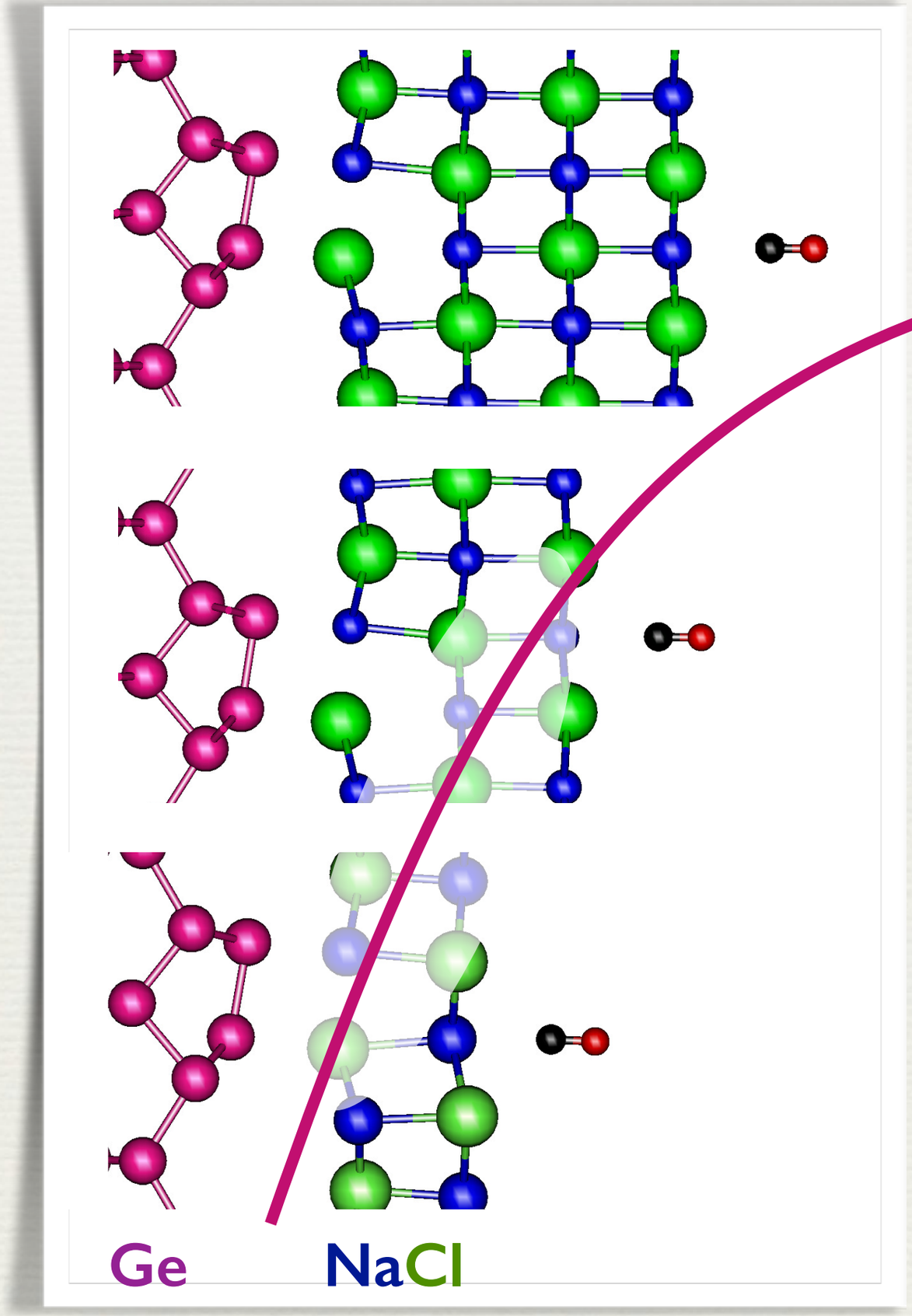
CO HOMO-LUMO gap

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

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

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

Make CO "ride the image potential"



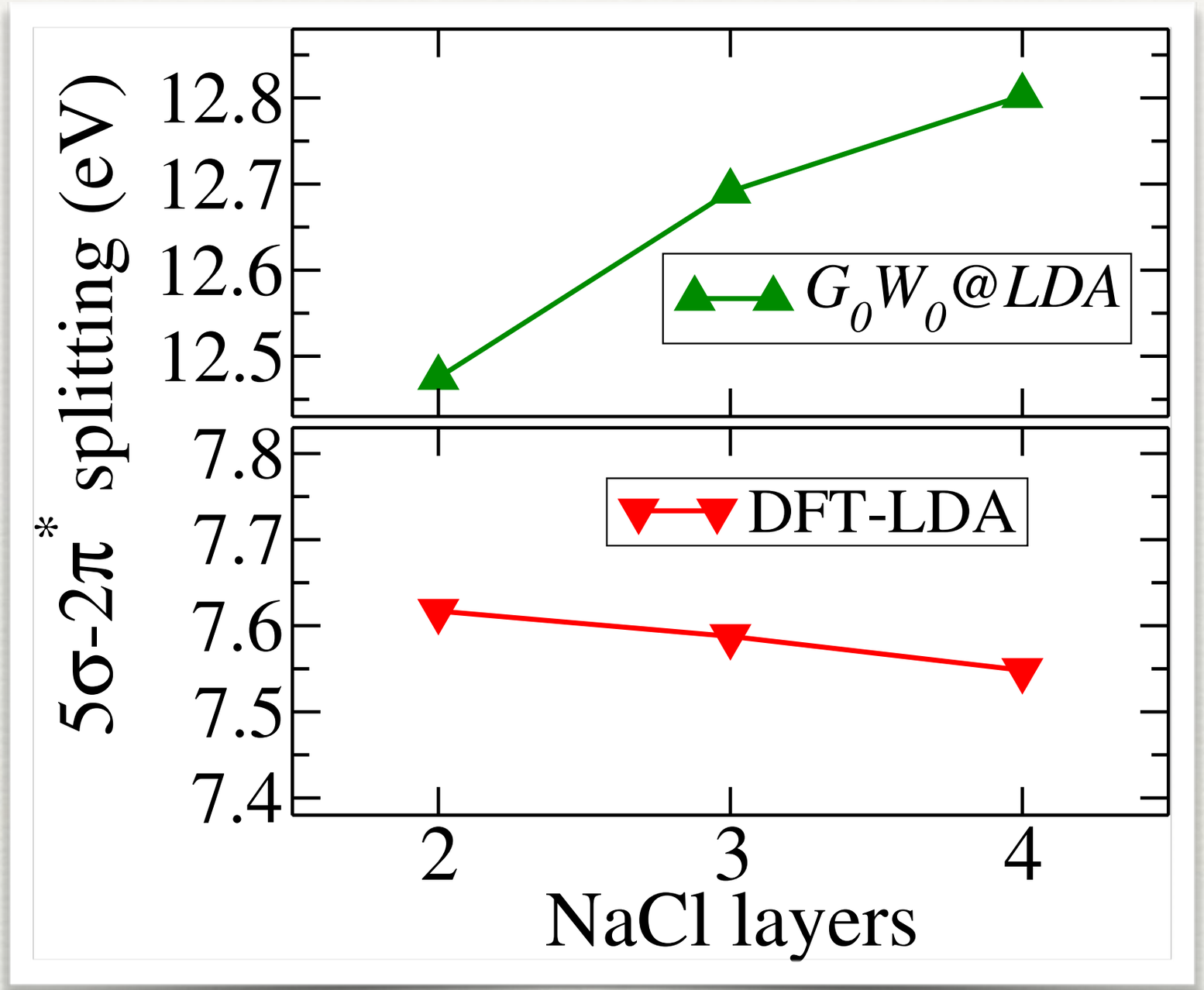
Ge image potential

- NaCl on Ge:
  - prototypical semiconductor/ insulator interface

- Will the CO gap depend on NaCl thickness?

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

CO on NaCl on Ge - layer dependent gap



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

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

Density-functional theory and excitations

exact DFT:

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

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

Density-functional theory and excitations

exact DFT:

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

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

otherwise:

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

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

rearranging and making mid-point approx.

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

Ionisation Potential, Affinity and (Band) Gaps

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

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

Ionization potential: *minimal energy to remove an electron*

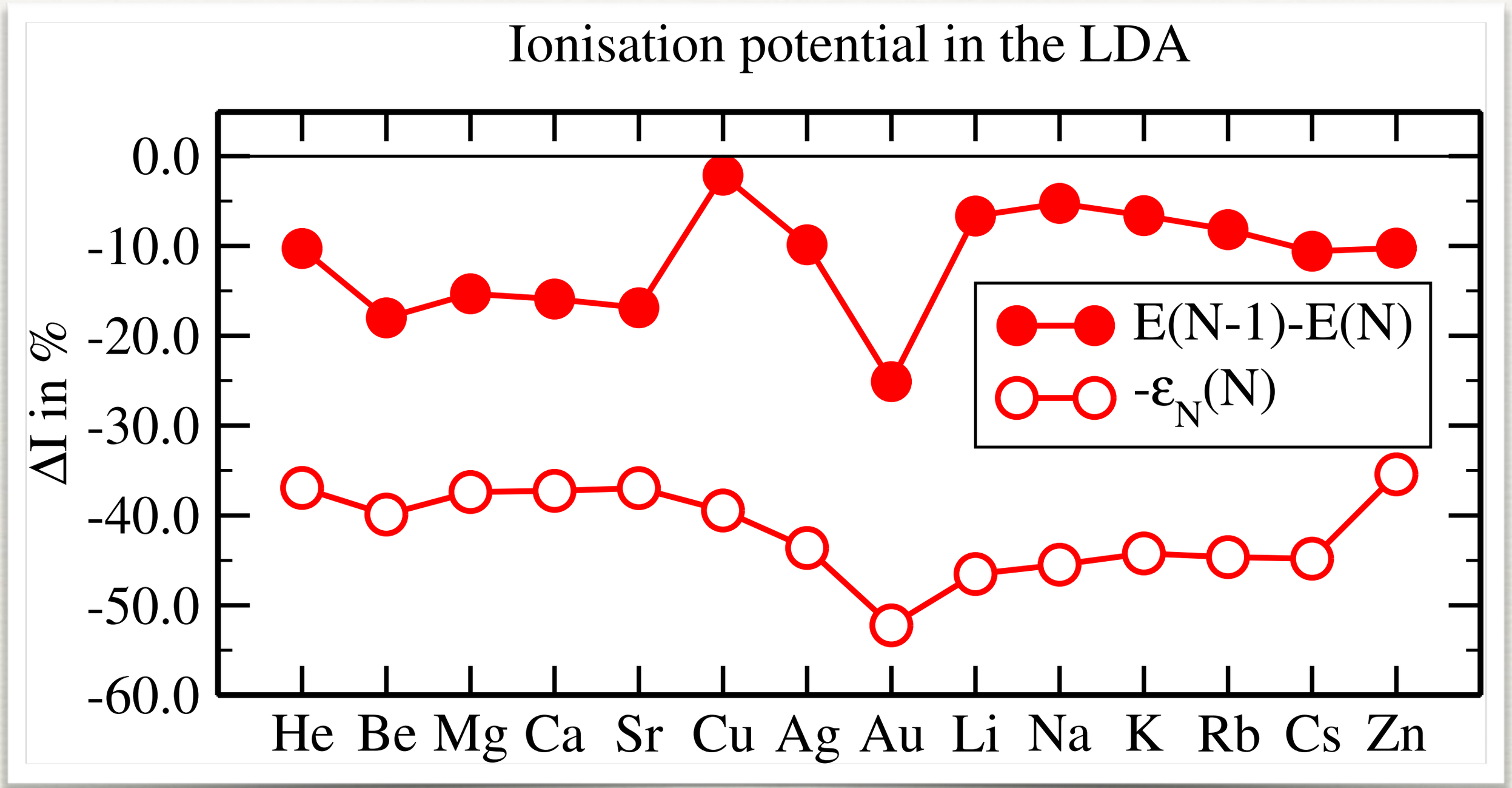
$$I = E(N-1) - E(N)$$

Electron affinity: *minimal energy to add an electron*

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

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

Ionisation Potential, Affinity and (Band) Gaps



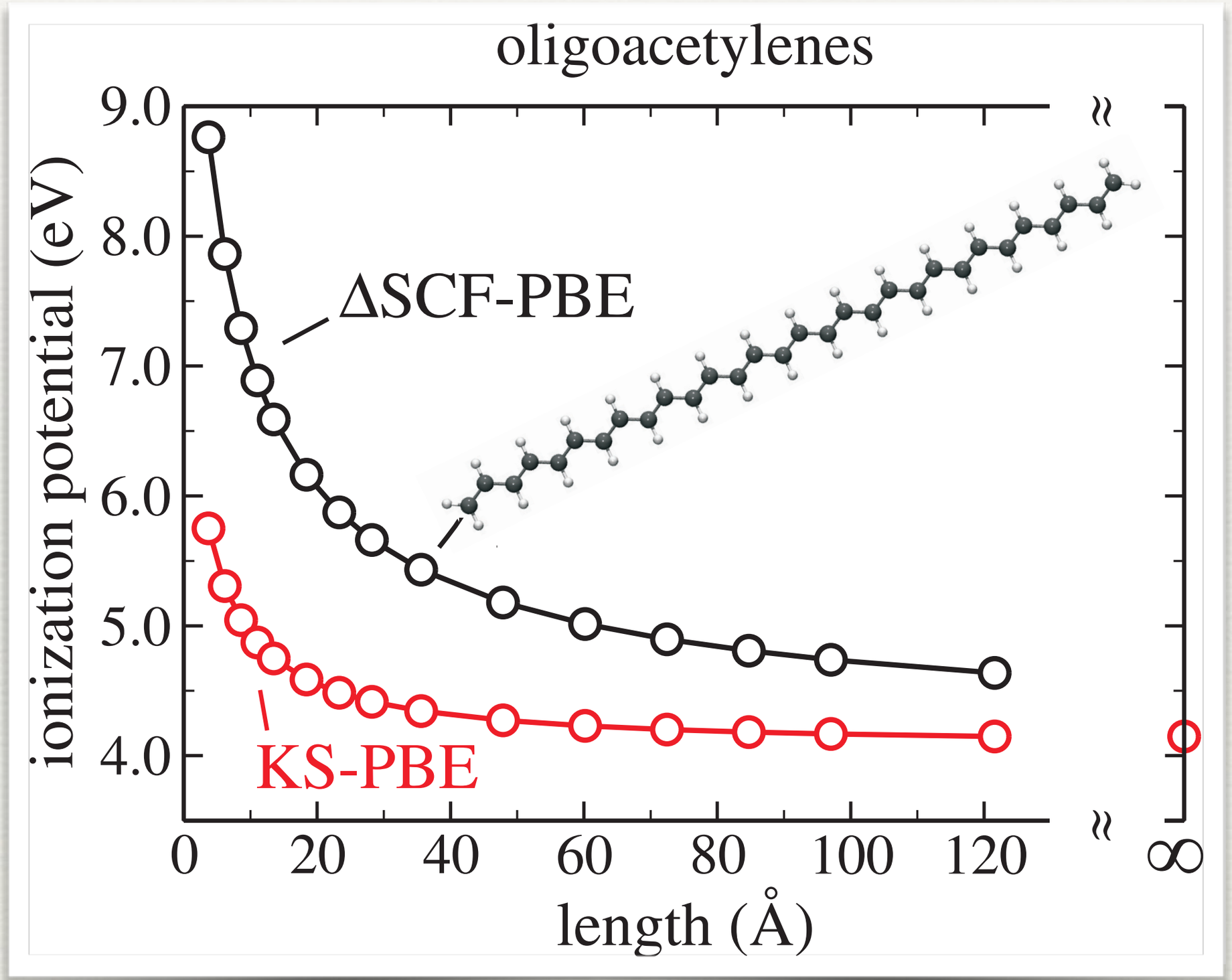
Reference: NIST -- Atomic reference data

ΔSCF better than eigenvalues for IPs!

but:

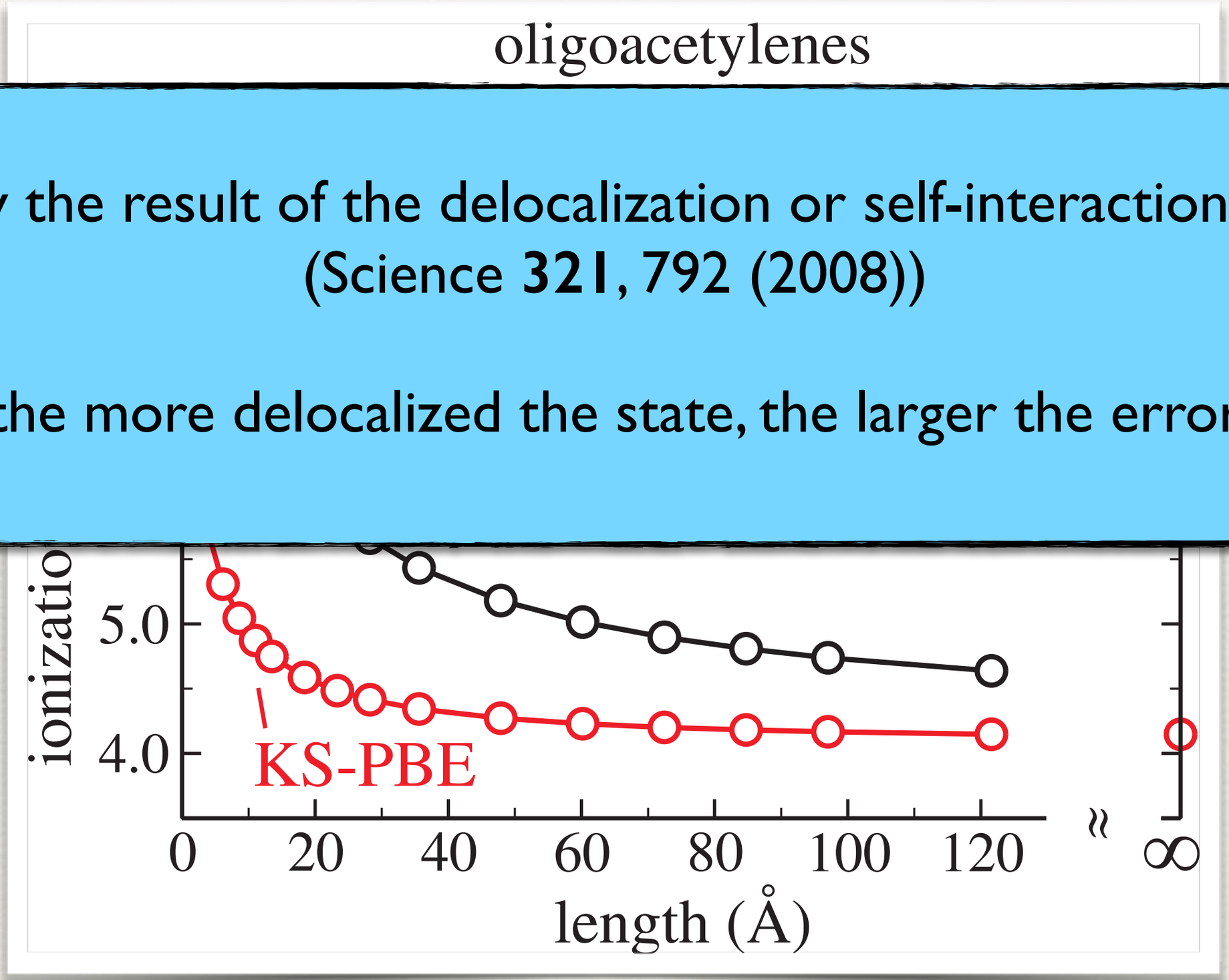
- **only justified for differences of ground states**
  - ionisation potential, electron affinity
  - excited states that are ground states of particular symmetry
- **difficult to find excited state density**
  - excited state density is not unique
- **separate calculation for every excitation needed**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

ΔSCF versus eigenvalues for finite systems



data courtesy of Max Pinheiro

ΔSCF versus eigenvalues for finite systems

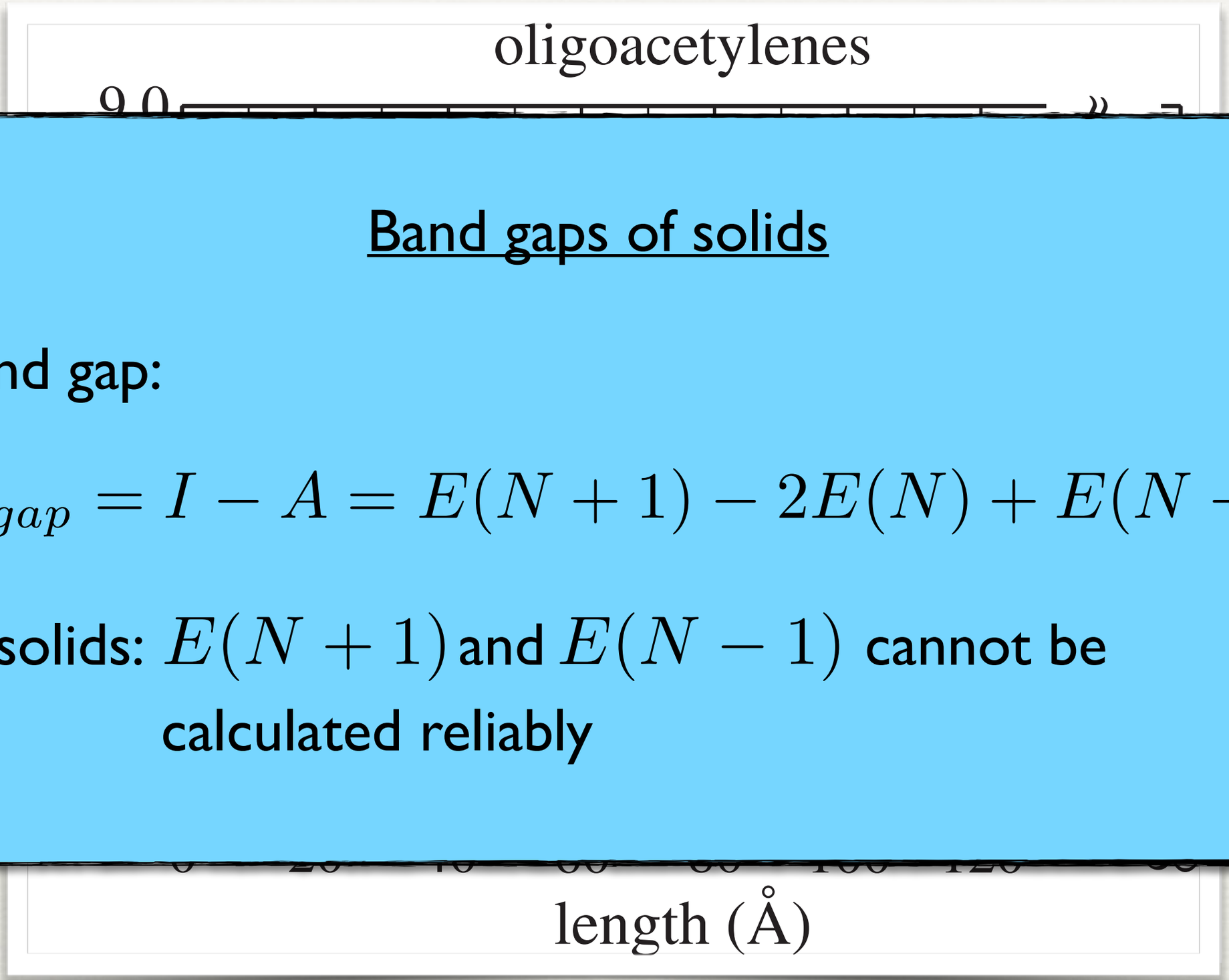


largely the result of the delocalization or self-interaction error (Science **321**, 792 (2008))

the more delocalized the state, the larger the error

data courtesy of Max Pinheiro

ΔSCF versus eigenvalues for finite systems



<u>Band gaps of solids</u>

- 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:

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

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

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

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

Band gaps of semiconductors and insulators

- DFT: highest Kohn-Sham state exact:

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

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

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

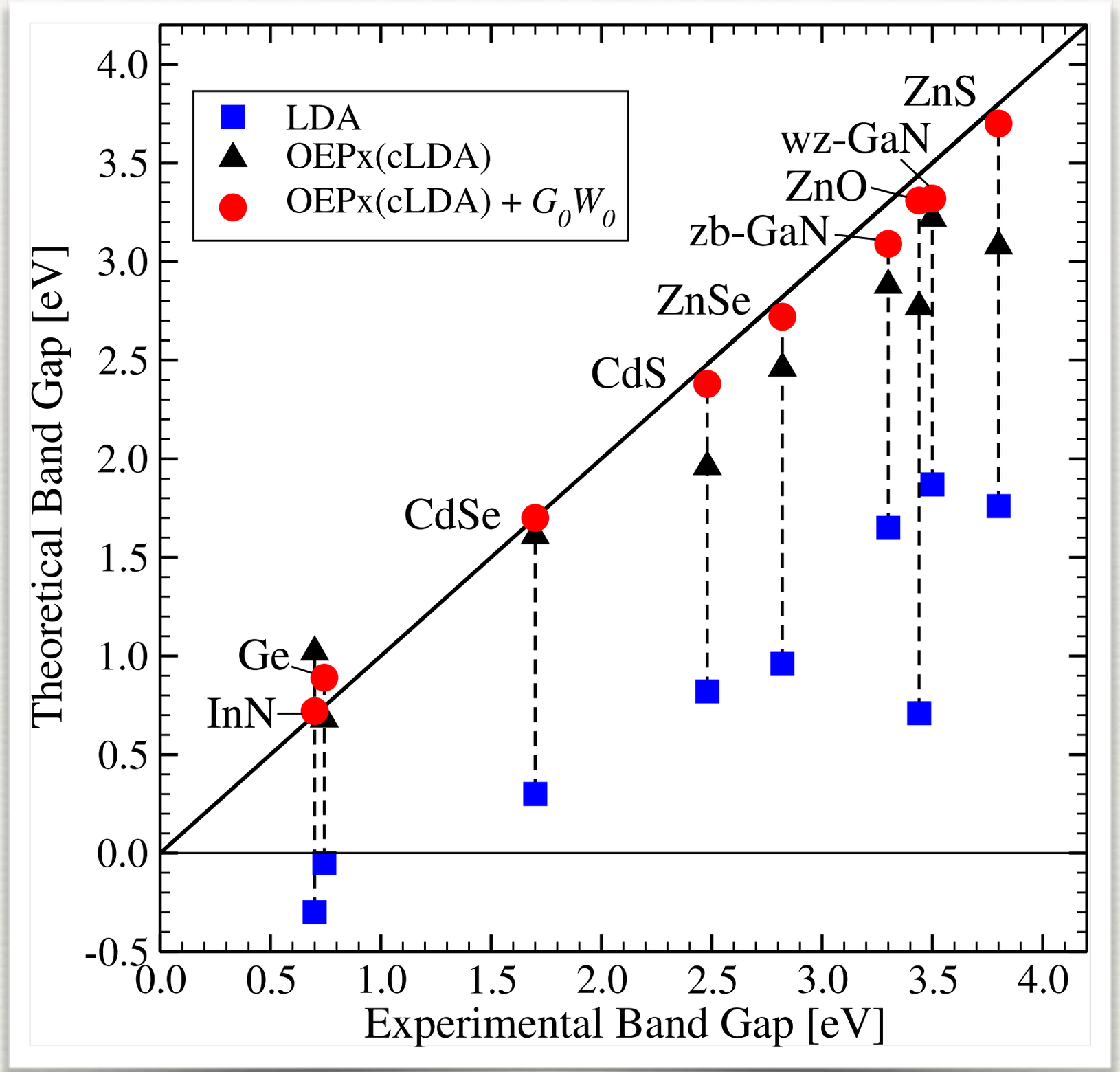
most DFT functionals do not capture this derivative discontinuity

- for sc $\rightarrow N+1$

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

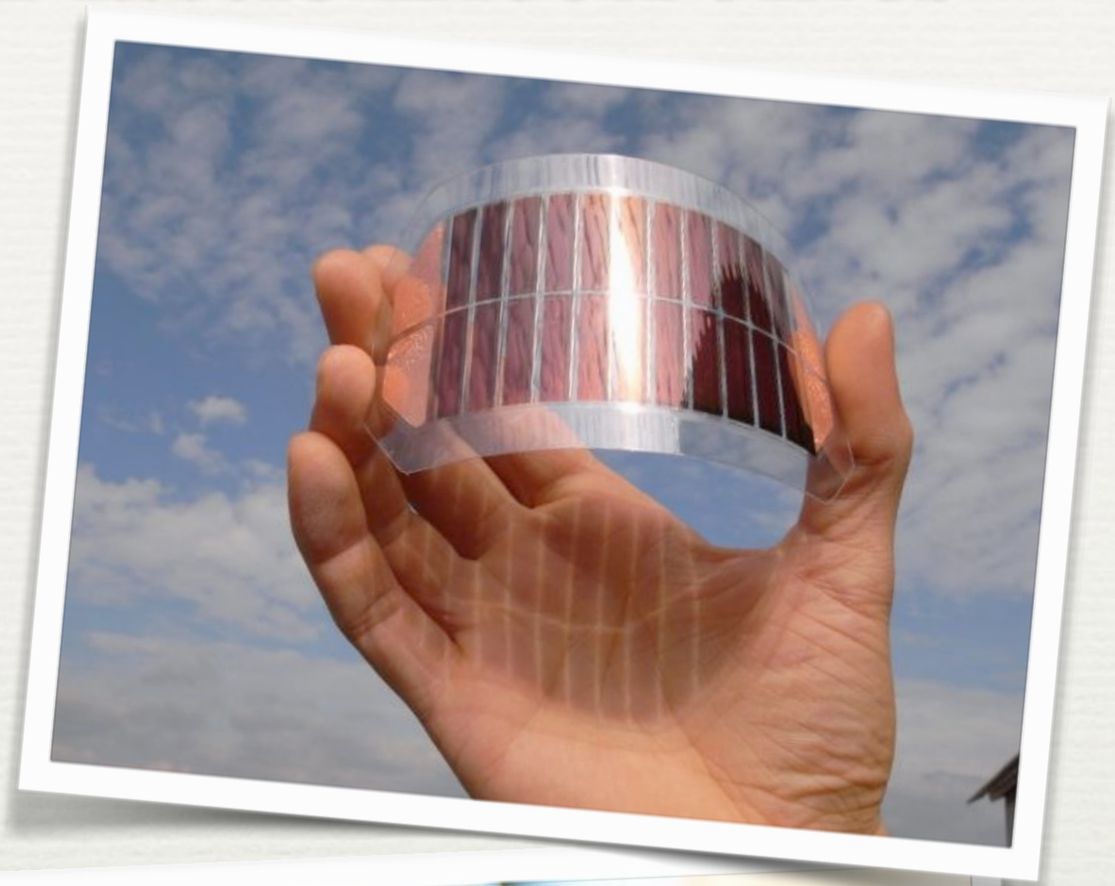
$$\Delta_{xc} = \left(\left.\frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}\right|_{N+1} - \left.\frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}\right|_{N} \right) + \mathcal{O}\left(\frac{1}{N}\right)$$

Band gaps of solids



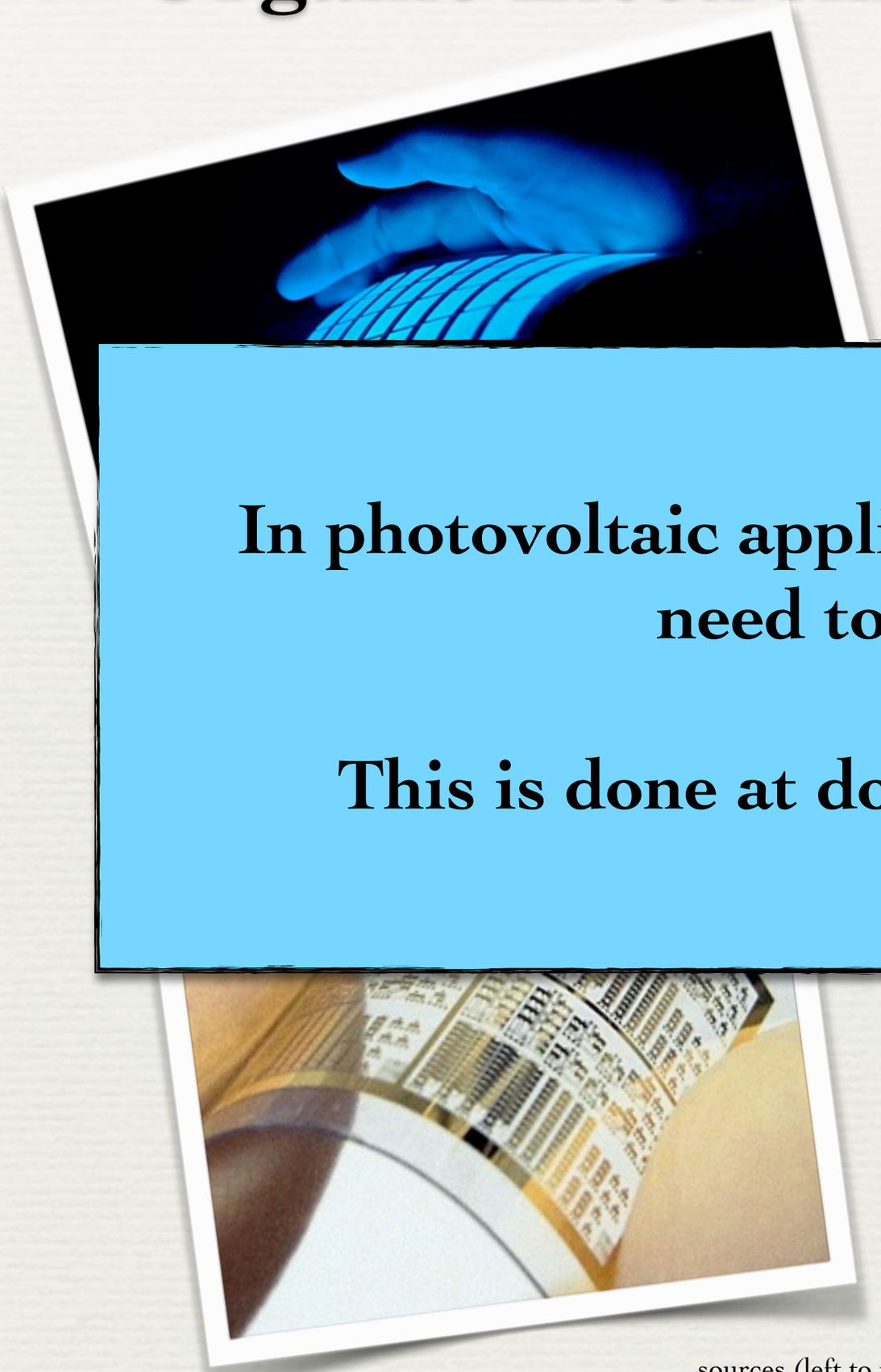
P. Rinke *et al.* New J. Phys. 7, 126 (2005), phys. stat. sol. (b) 245, 929 (2008)

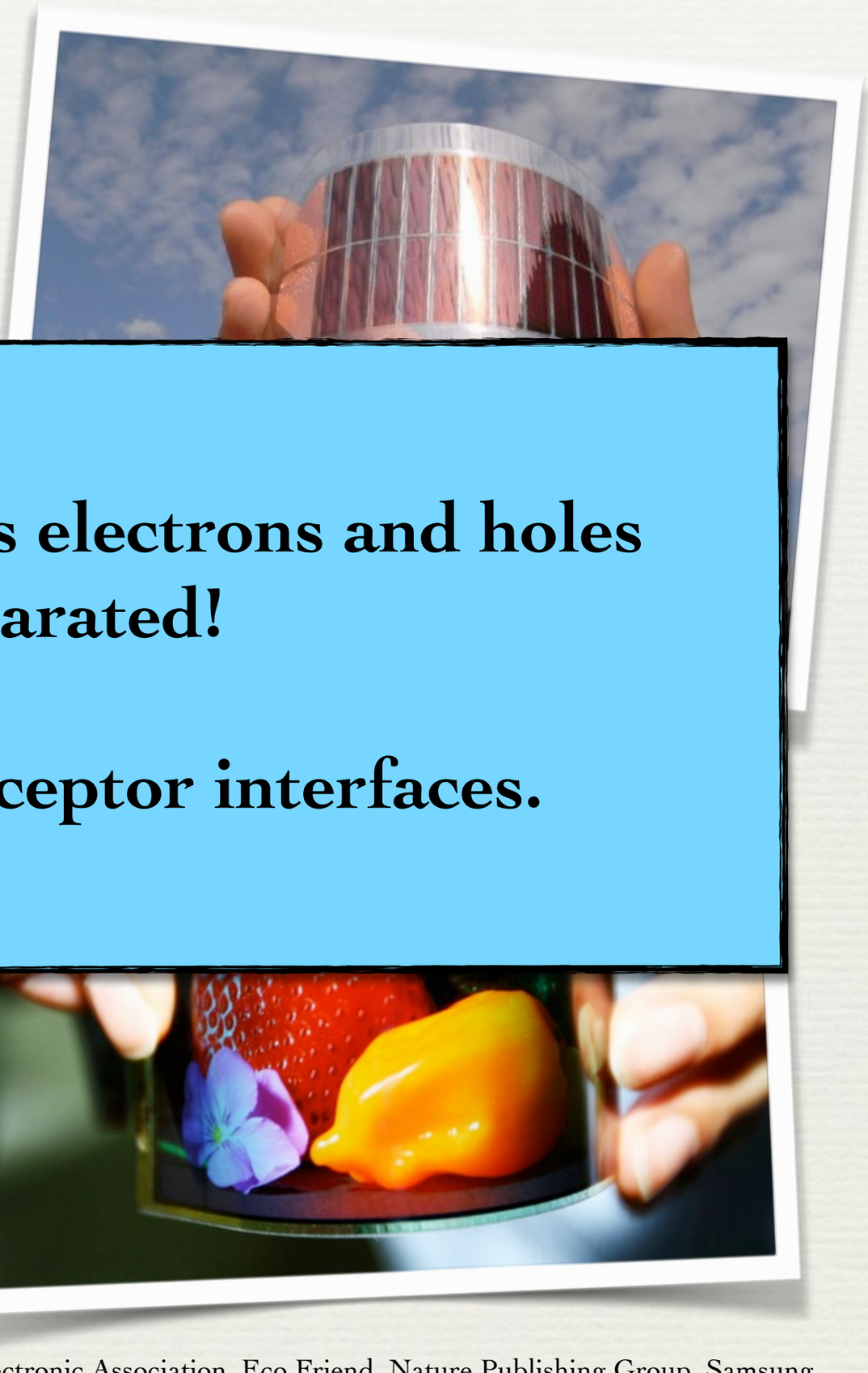
Organic Electronics - Plastic Electronics



sources (left to right): Organic Electronic Association, Eco Friend, Nature Publishing Group, Samsung

Organic Electronics - Plastic Electronics



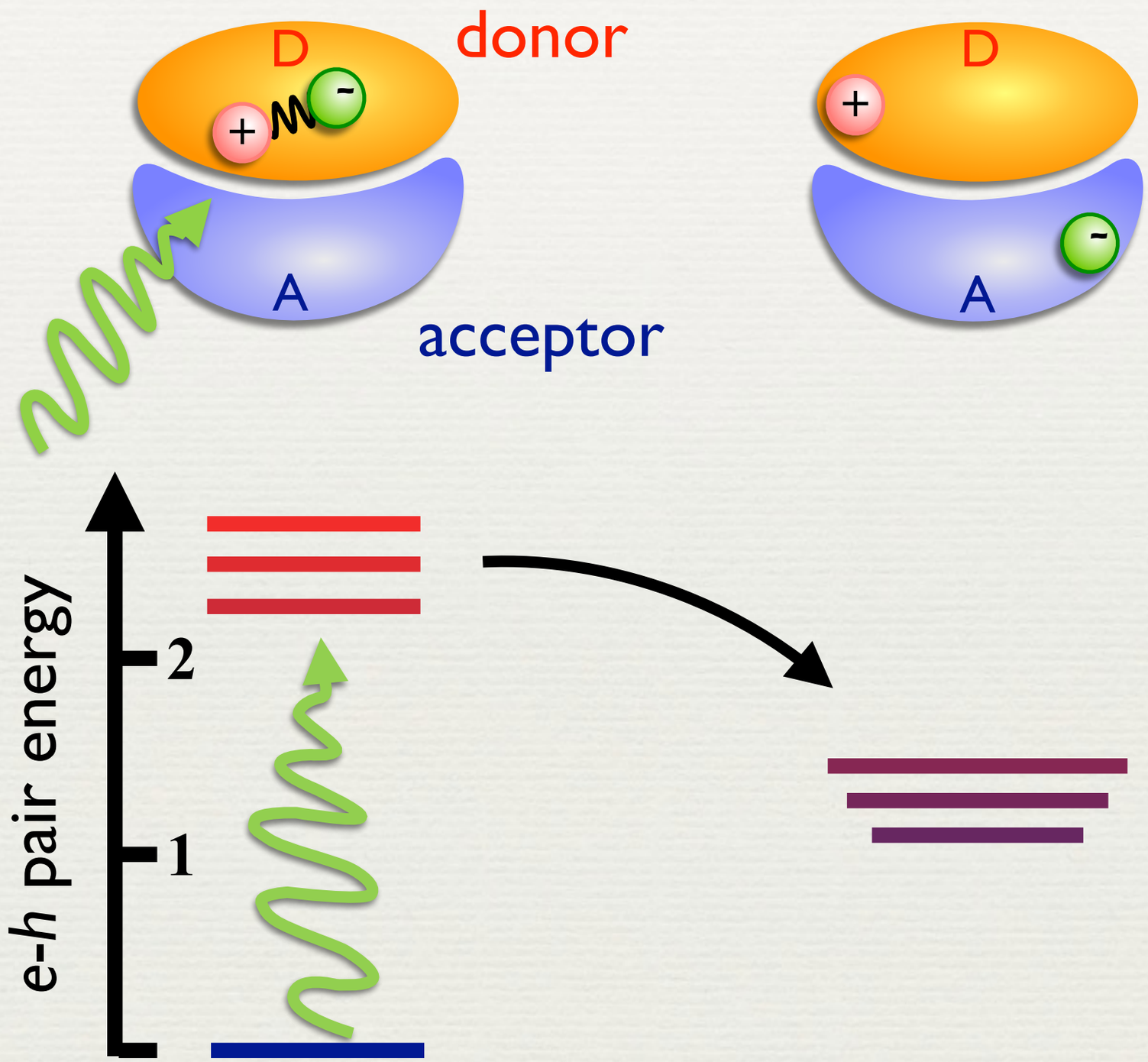


In photovoltaic applications electrons and holes need to be separated!

This is done at donor-acceptor interfaces.

sources (left to right): Organic Electronic Association, Eco Friend, Nature Publishing Group, Samsung

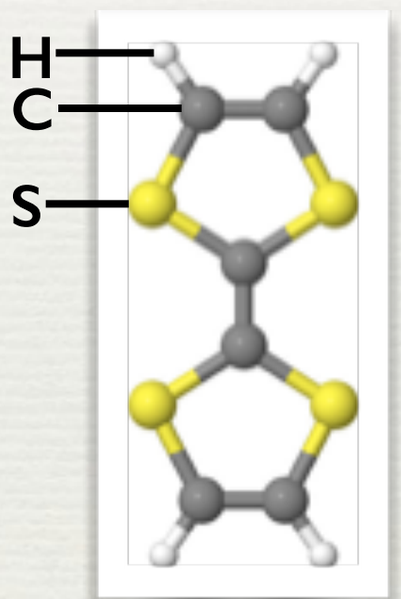
Charge separation at donor-acceptor pairs



donor-acceptor pair: TTF and TCNQ

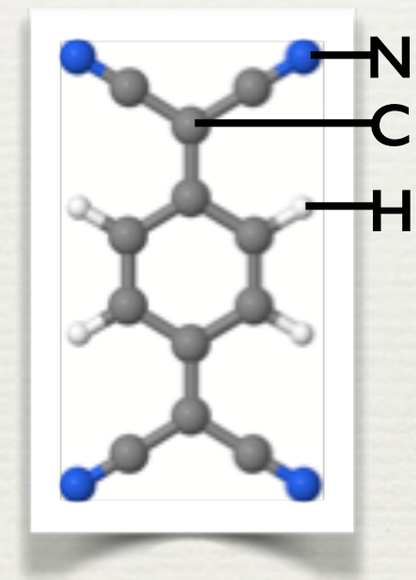
all values in eV

TTF

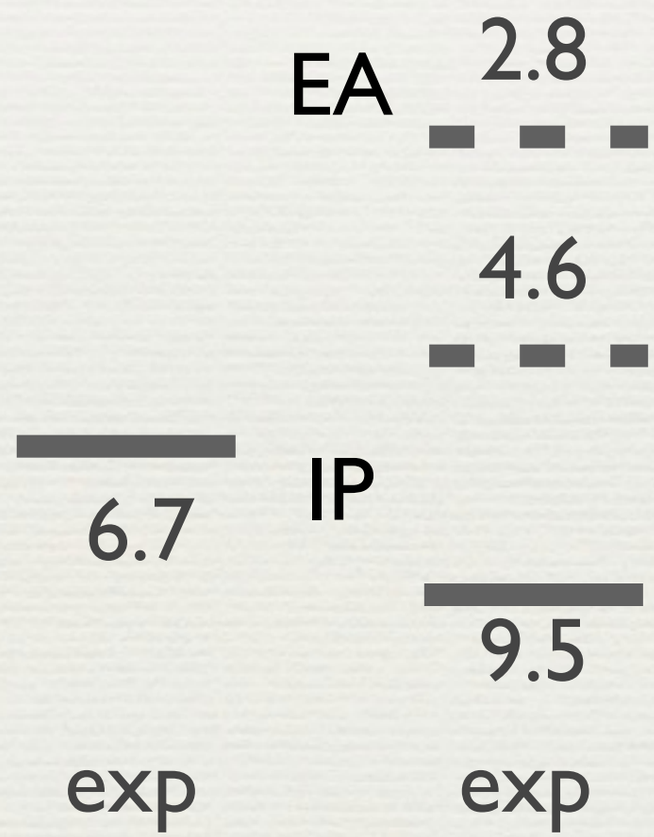


$C_6H_4S_4$

TCNQ



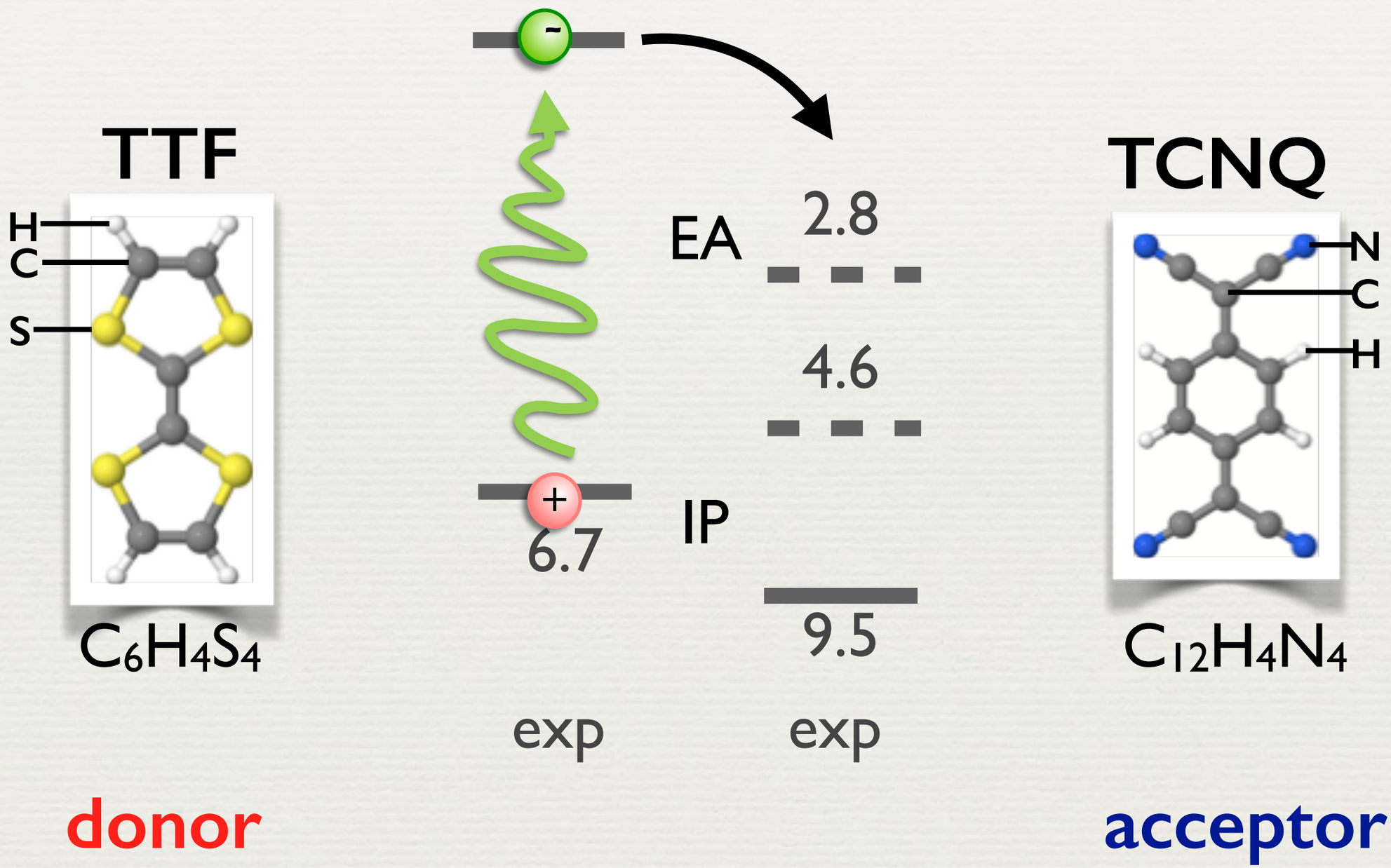
$C_{12}H_4N_4$



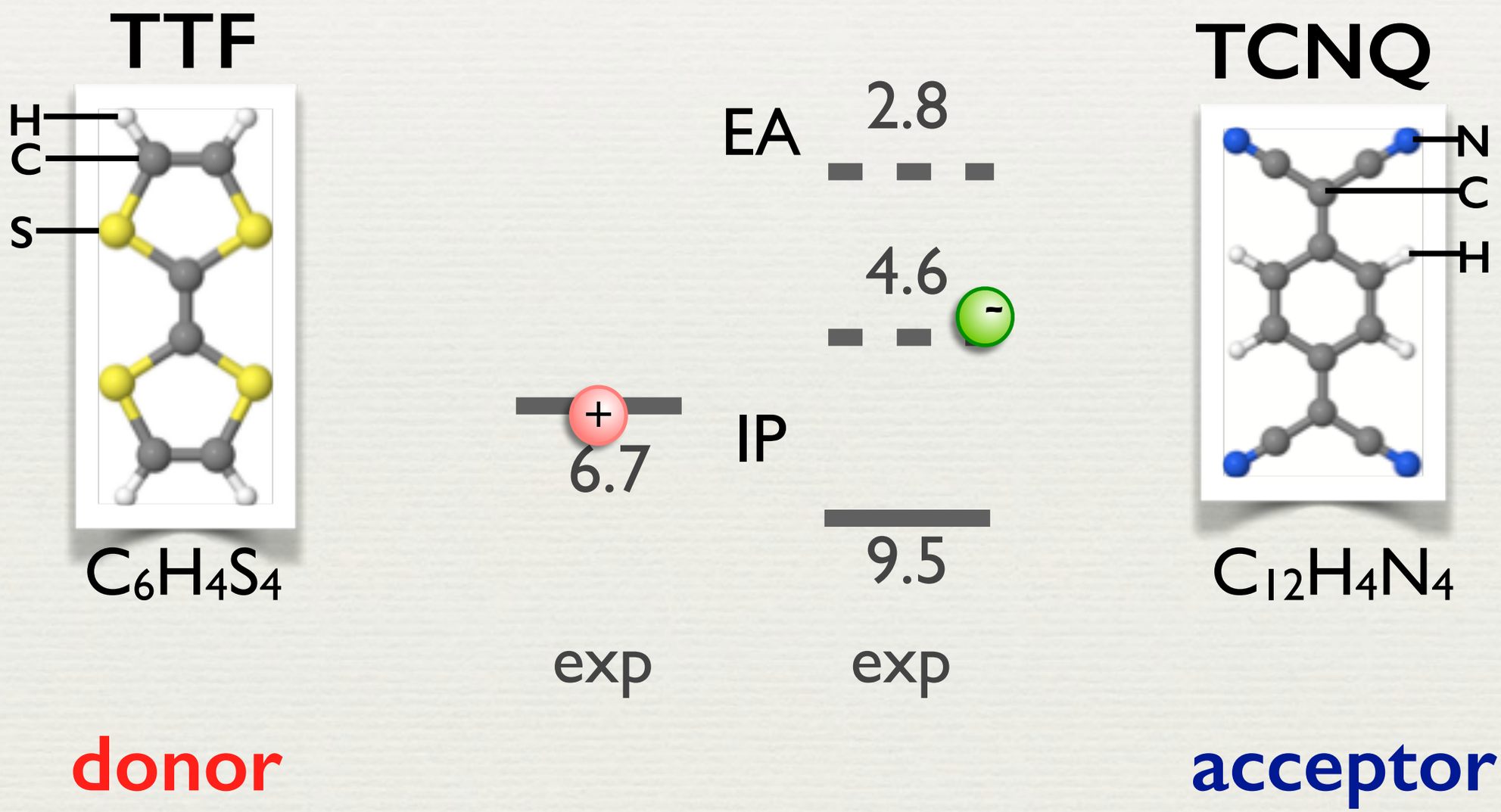
donor

acceptor

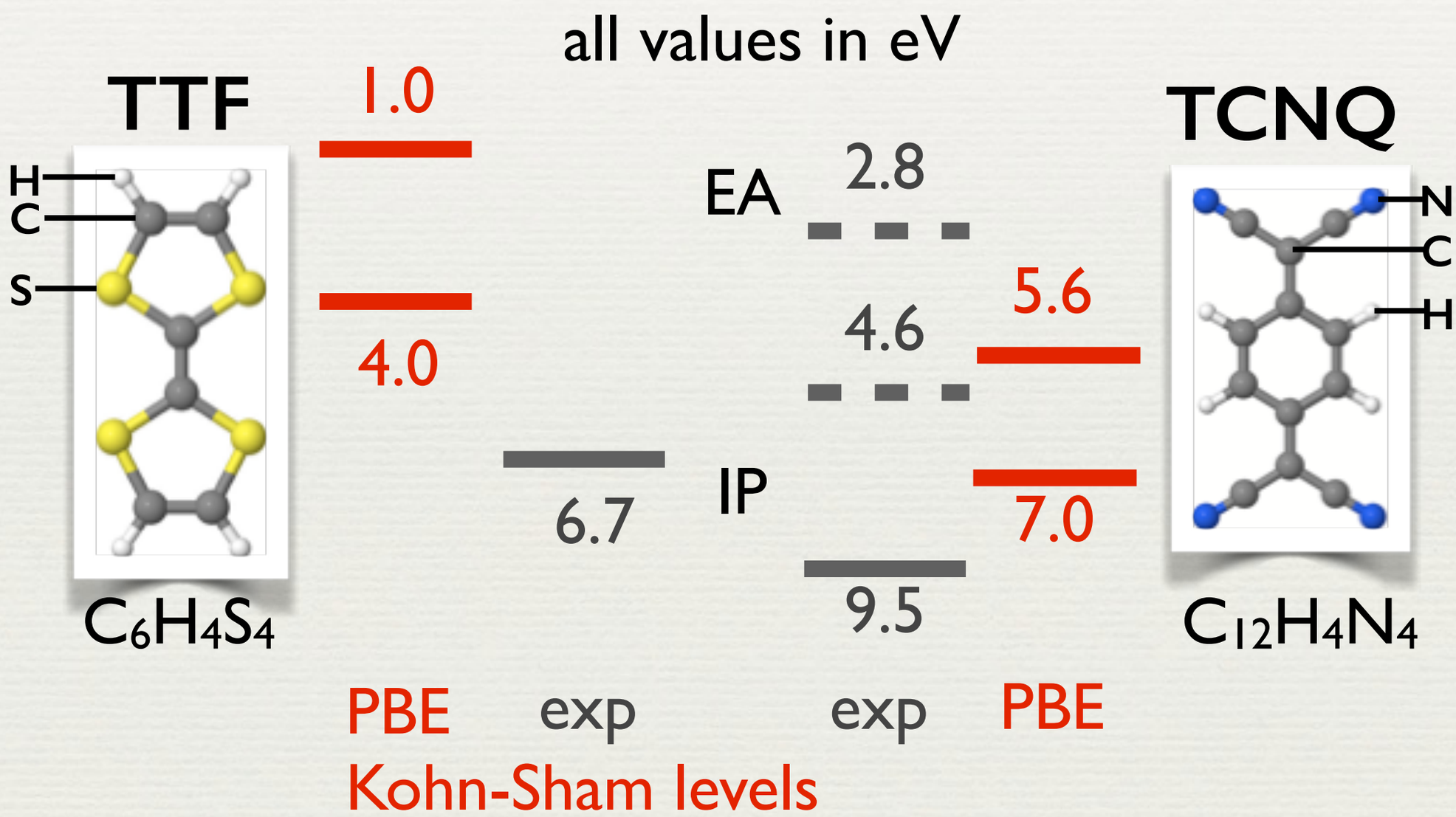
donor-acceptor pair: TTF and TCNQ



donor-acceptor pair: TTF and TCNQ

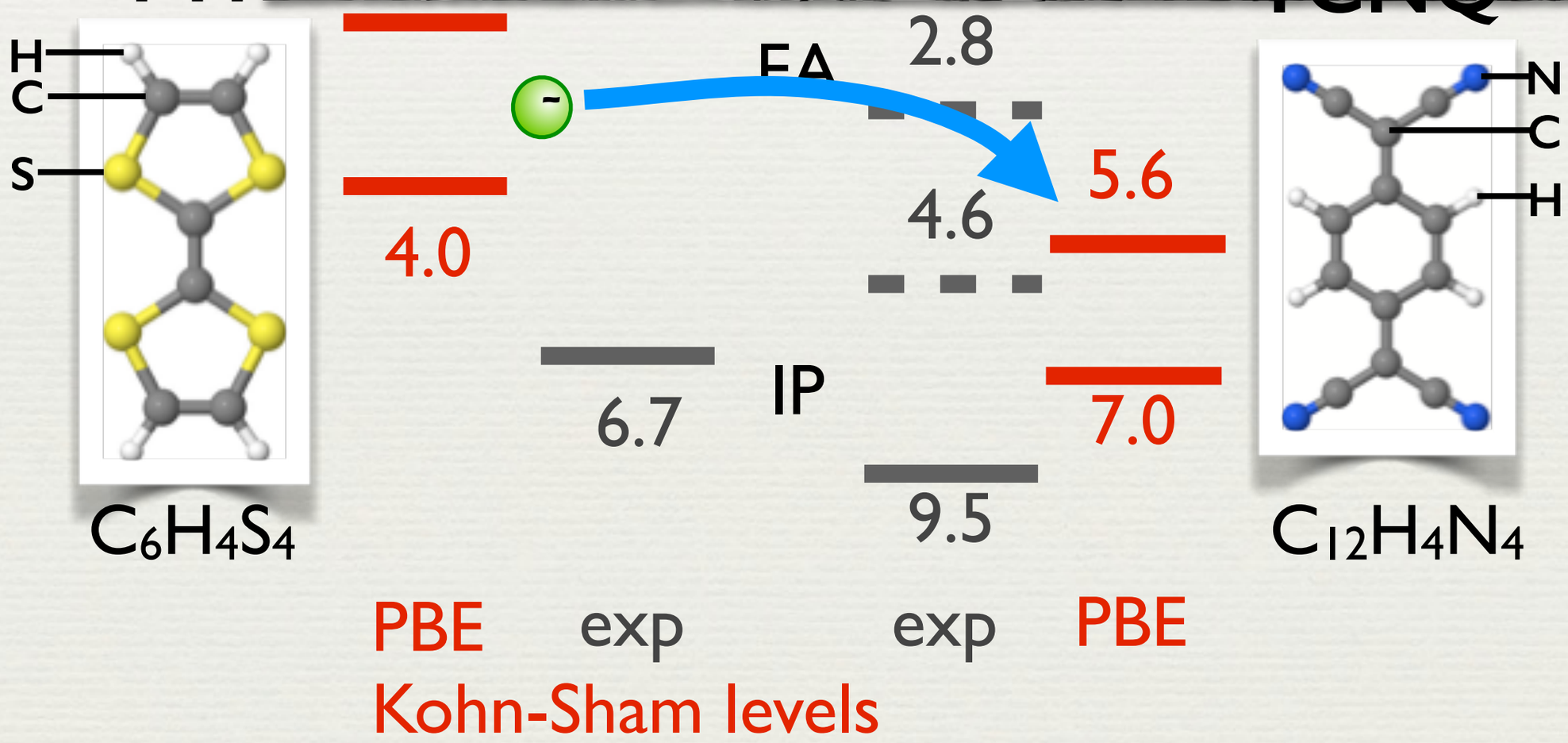


TTF and TCNQ in PBE

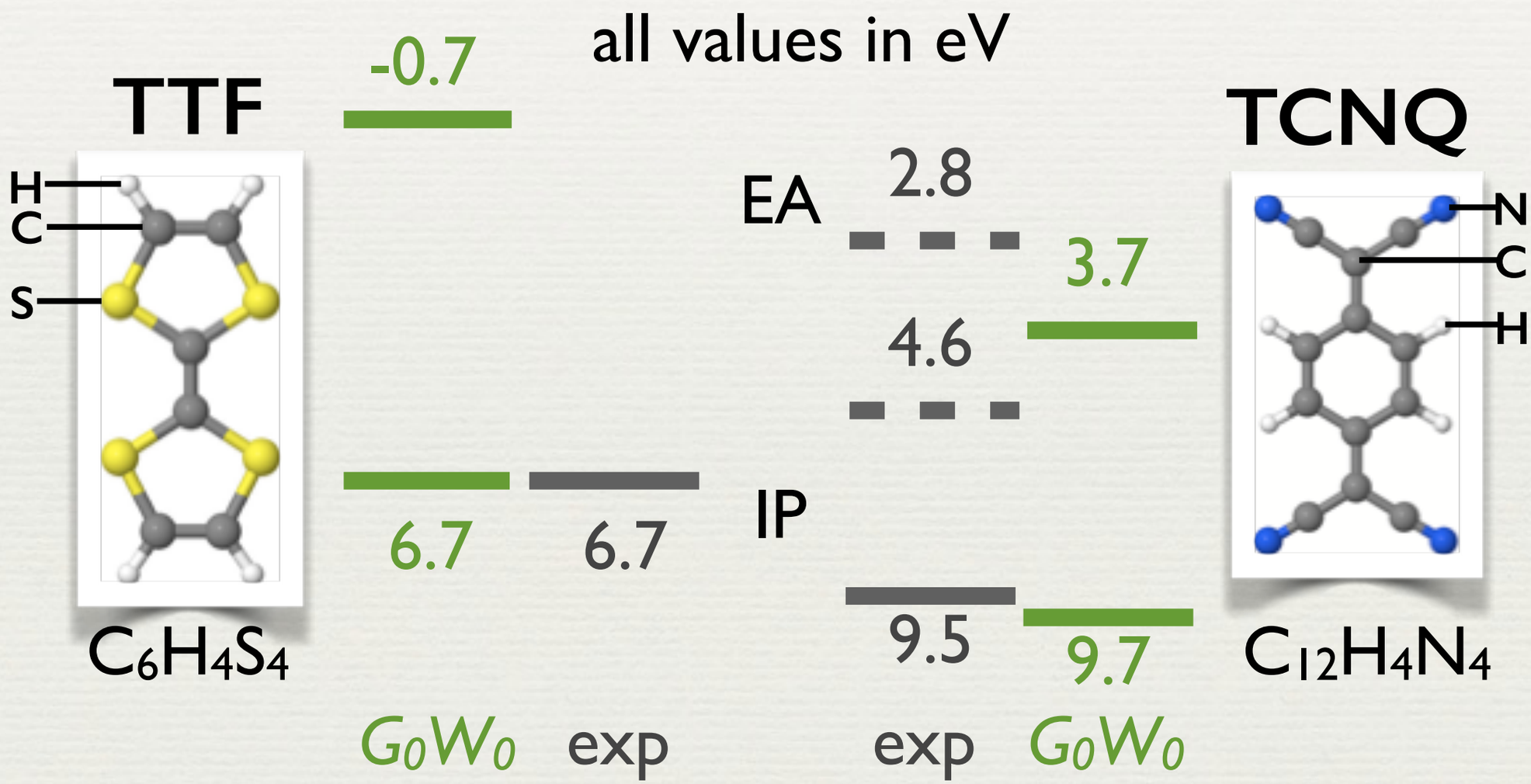


TTF and TCNQ in PBE

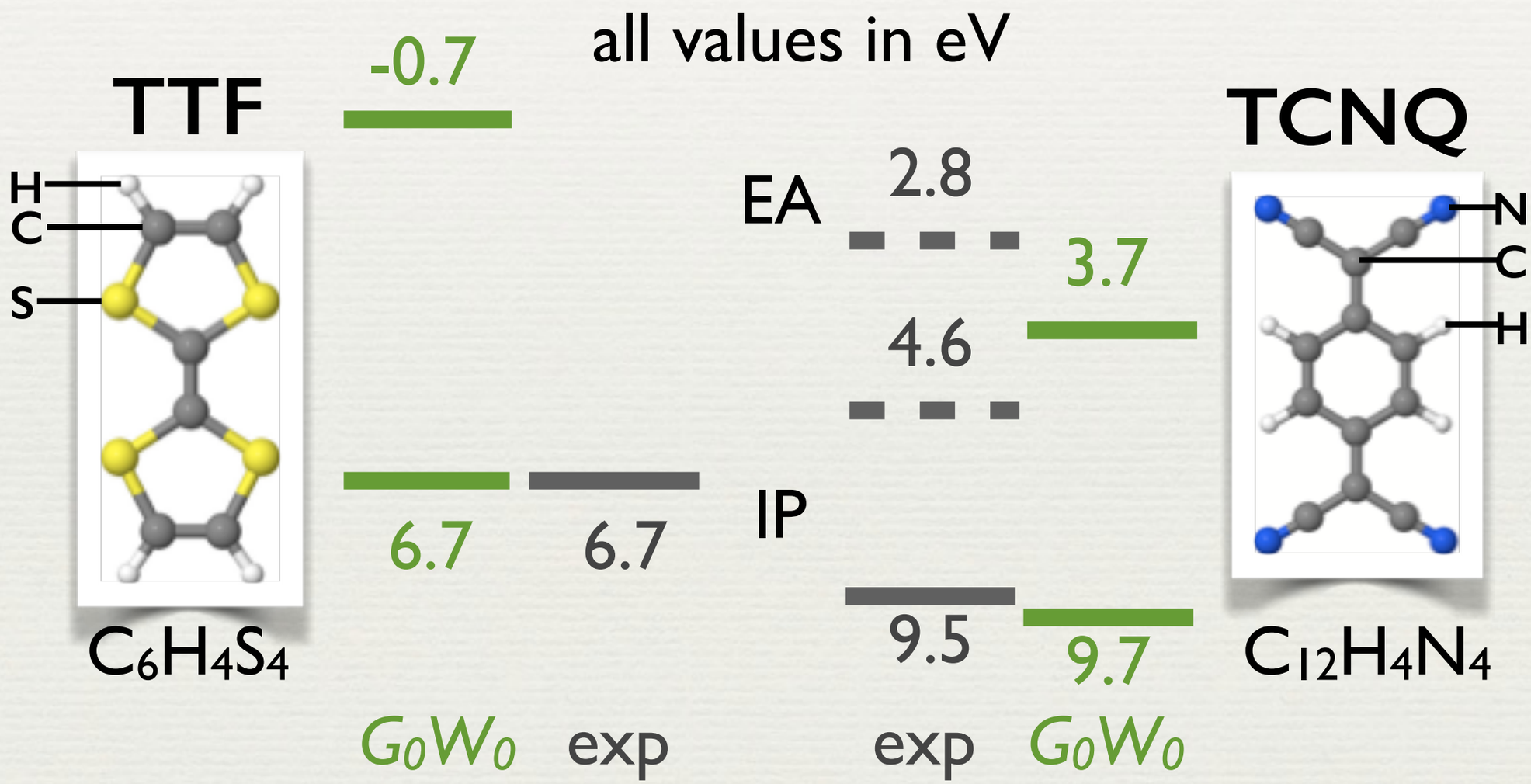
erroneous charge transfer in ground state!!!



TTF and TCNQ in G_0W_0

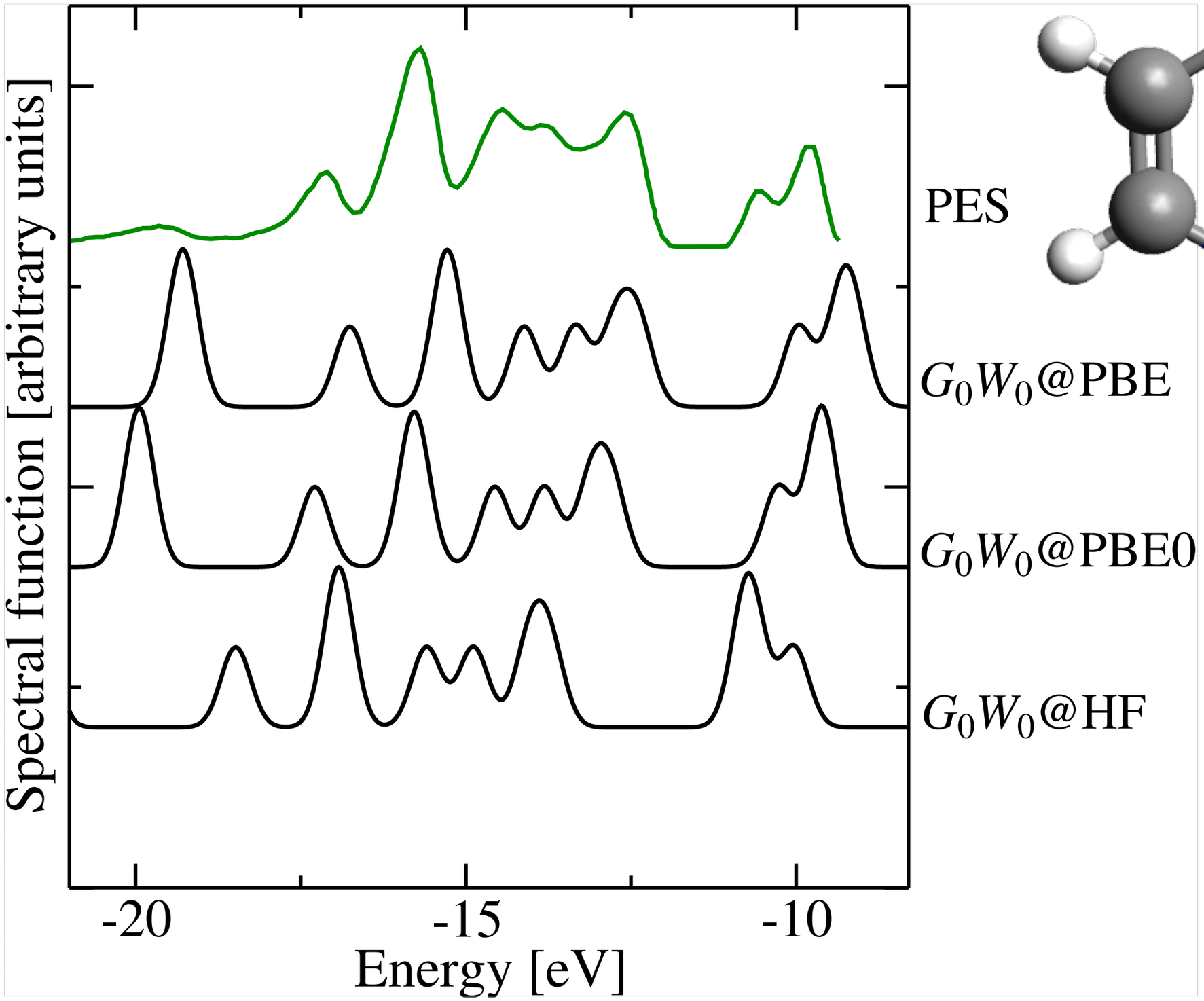


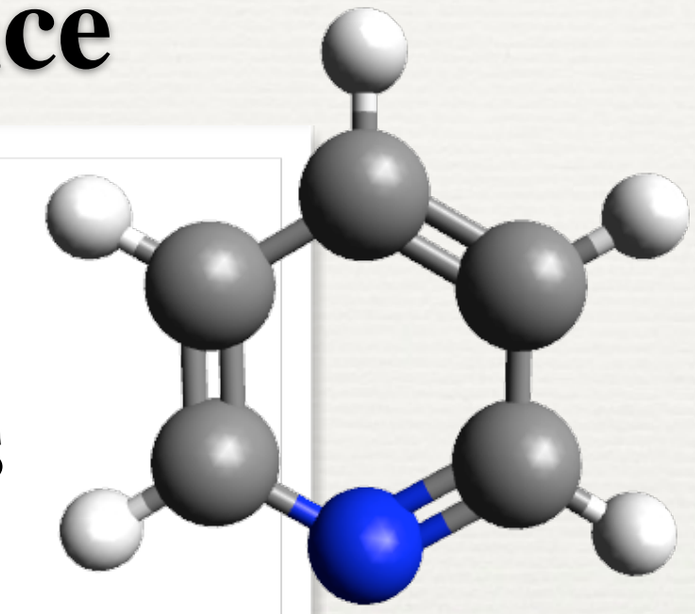
TTF and TCNQ in G_0W_0



Correct level order, but how to get back to ground state?
⇒ self-consistency

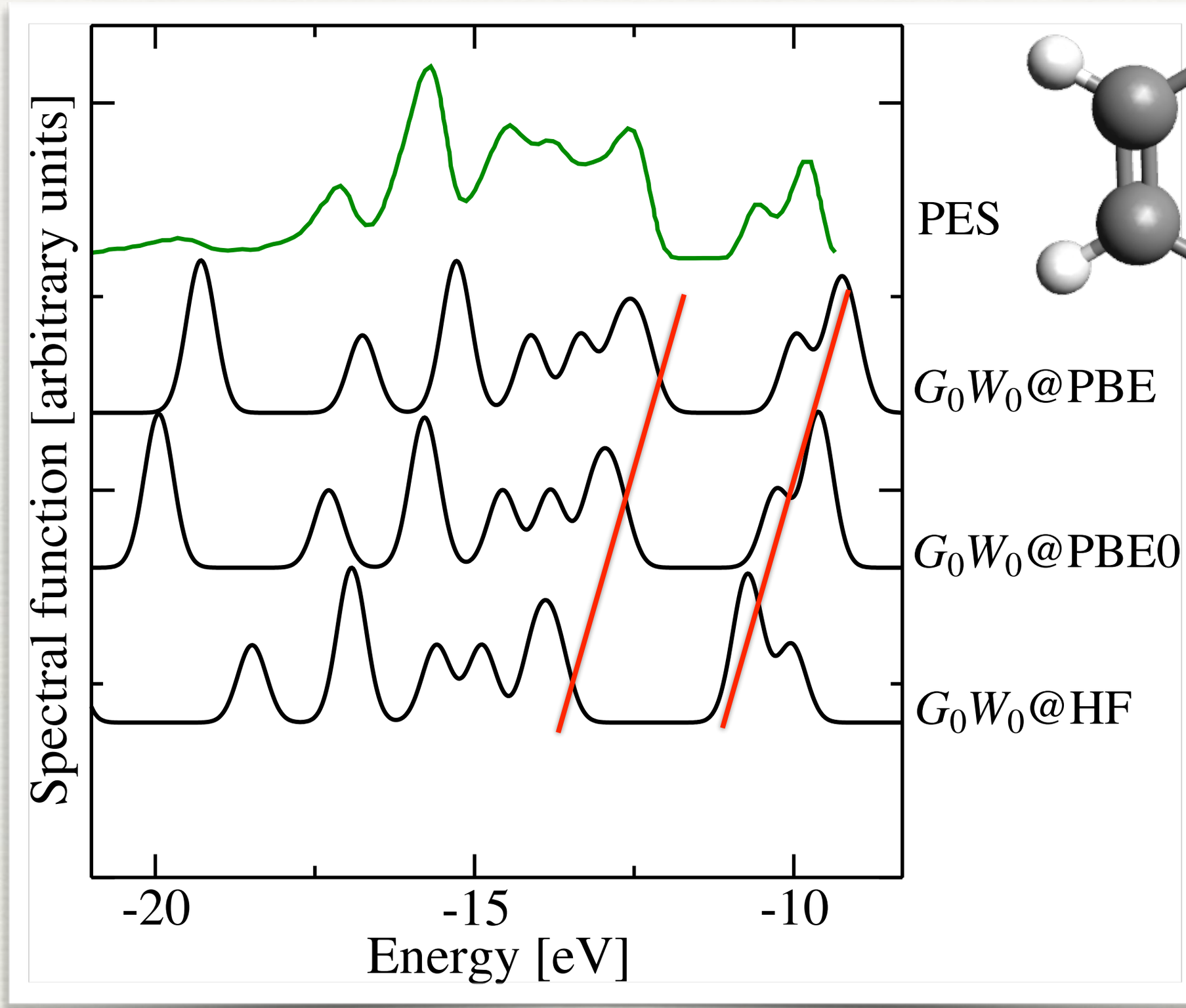
Starting point dependence

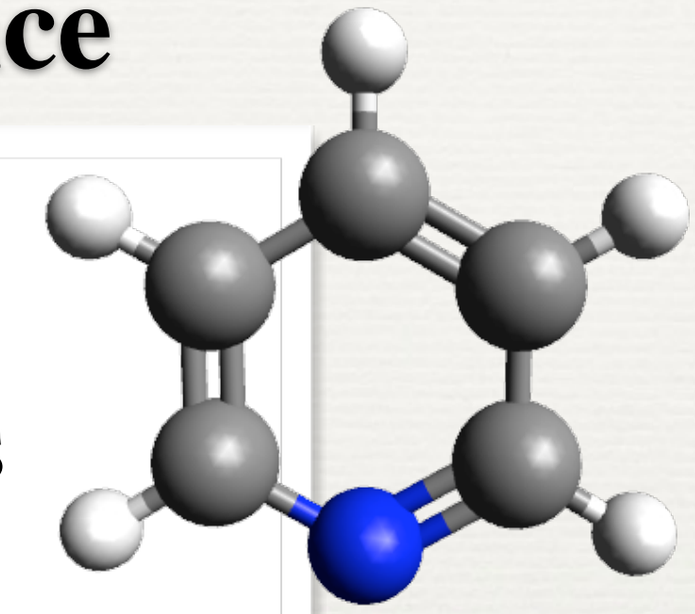




N. Marom *et al.* Phys. Rev. B 86, 245127 (2012)

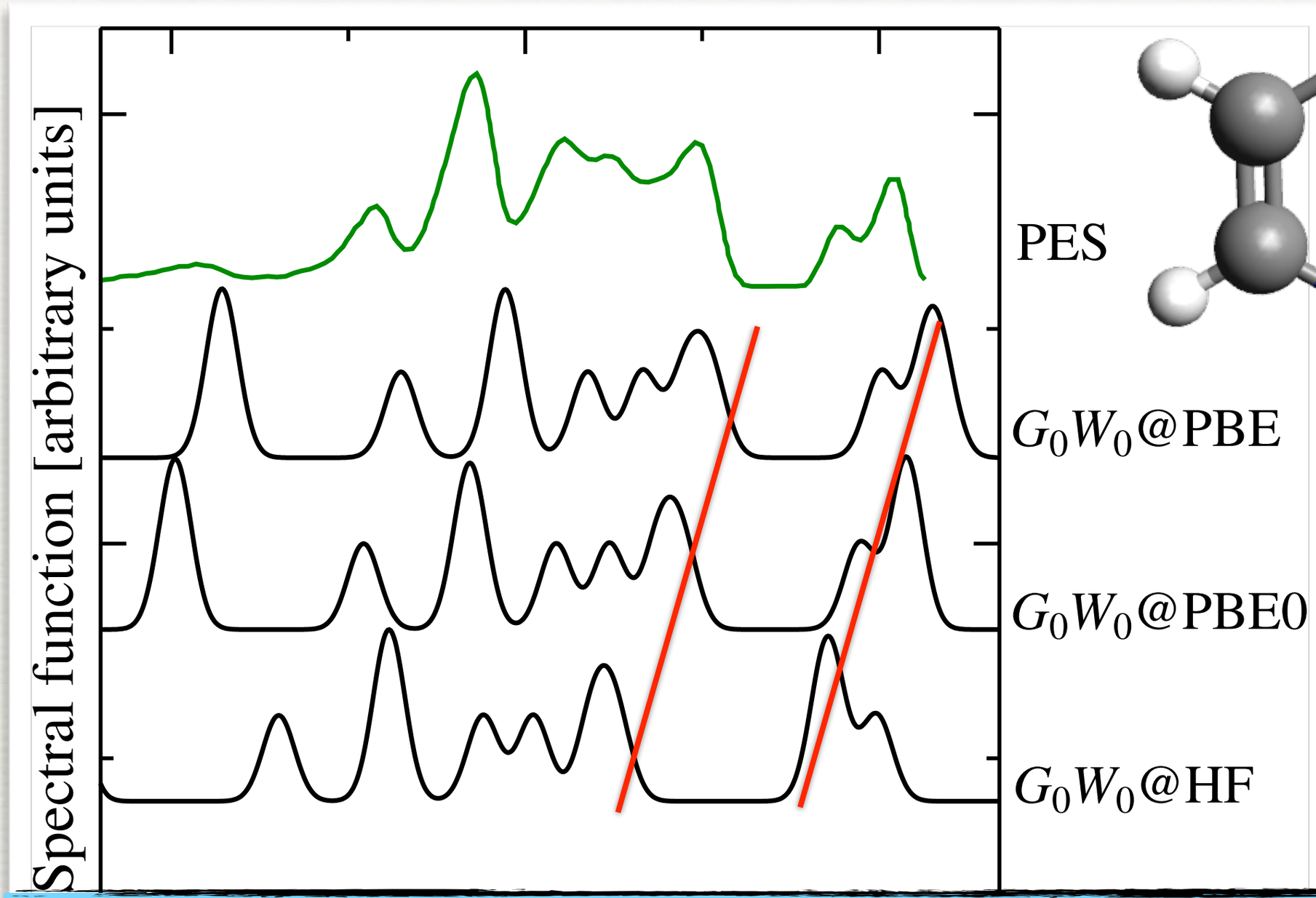
Starting point dependence

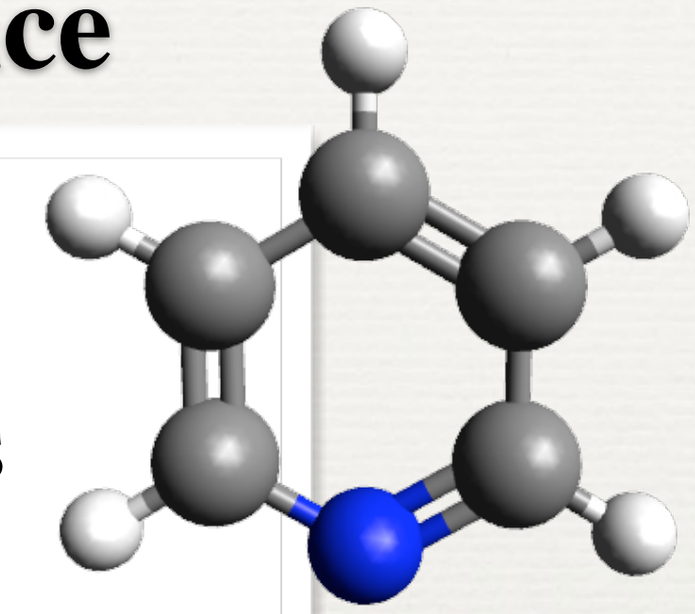




N. Marom *et al.* Phys. Rev. B 86, 245127 (2012)

Starting point dependence





Find optimal starting point or remove starting point dependence!
⇒ self-consistency

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

Self-consistent GW (scGW)

Hedin's GW equations:

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

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

self-consistency

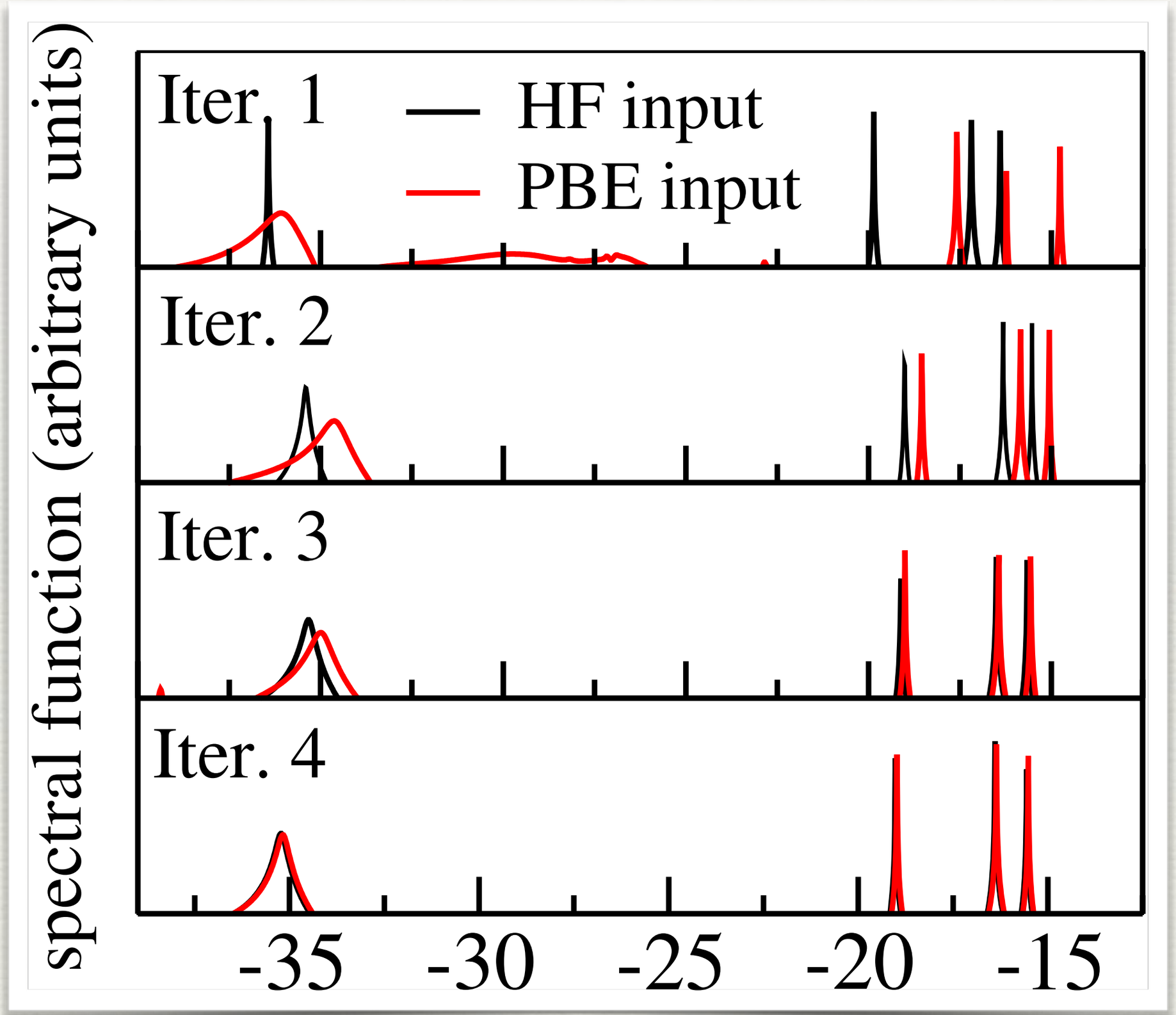
Dyson's equation:

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

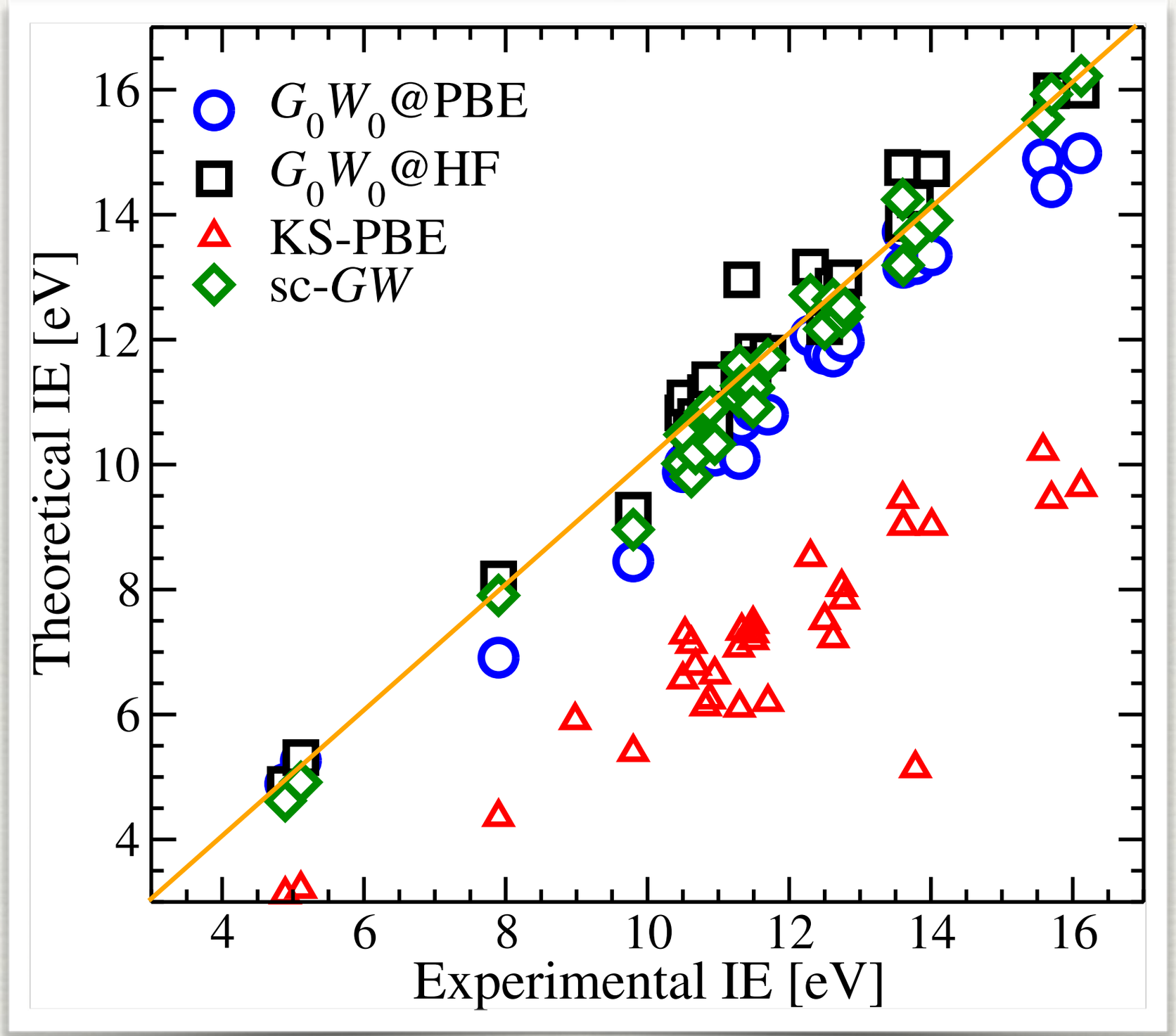
self-consistency

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

Unique solution in scGW - N_2

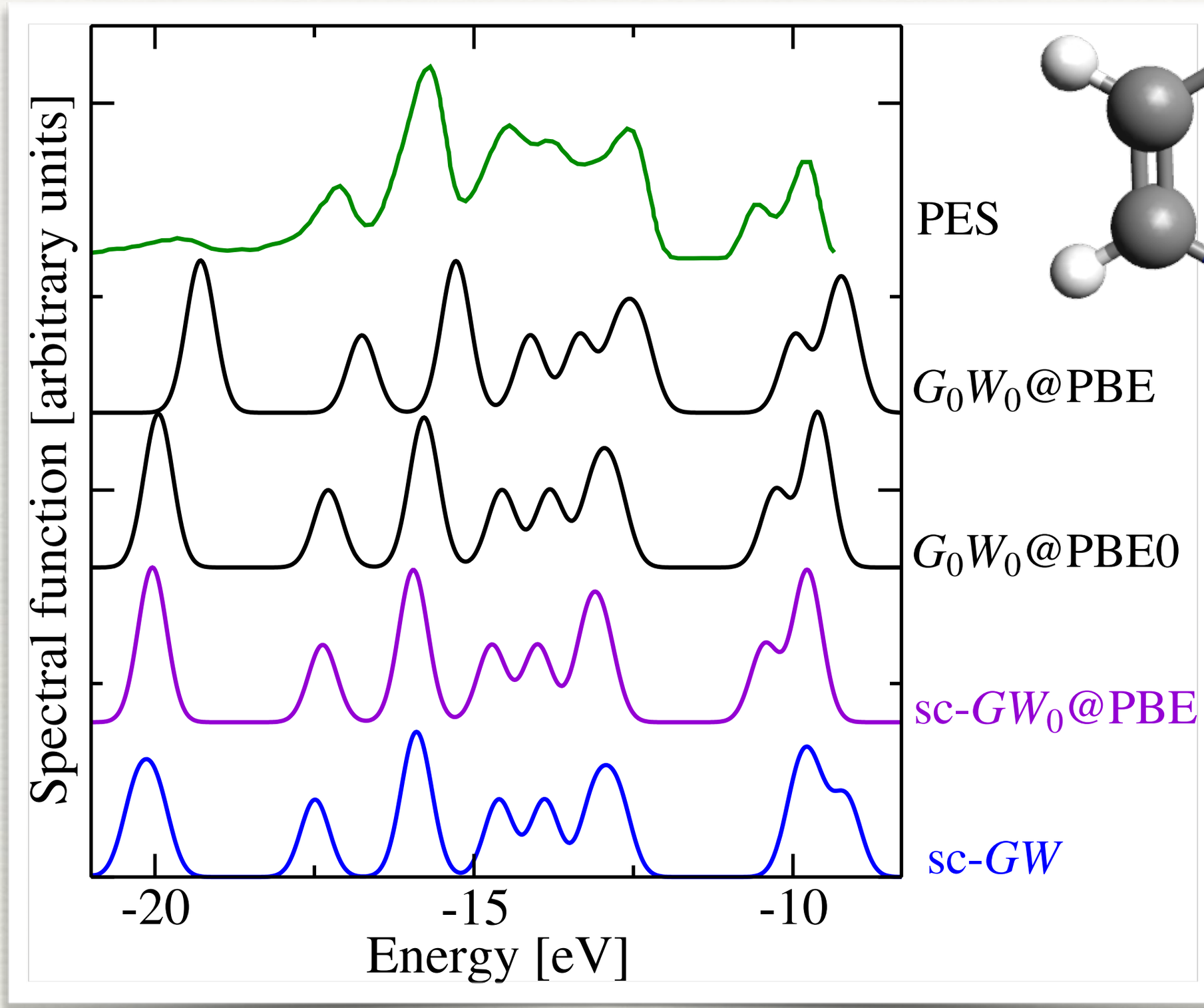


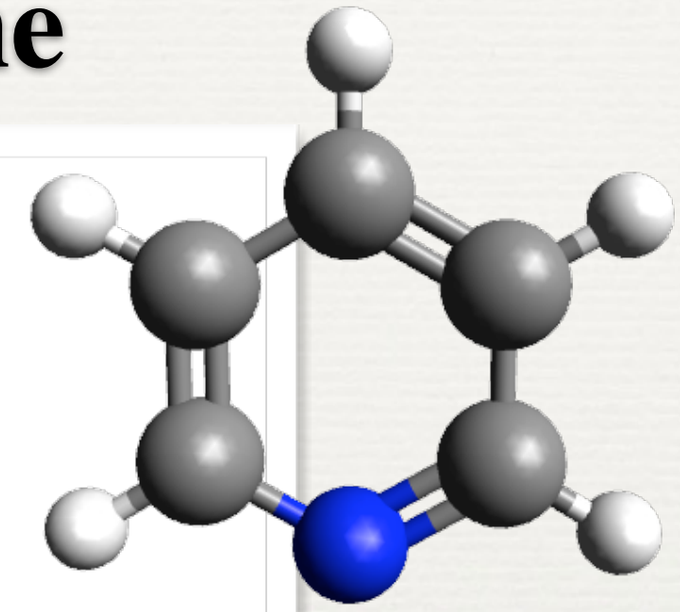
Ionization potentials in scGW



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

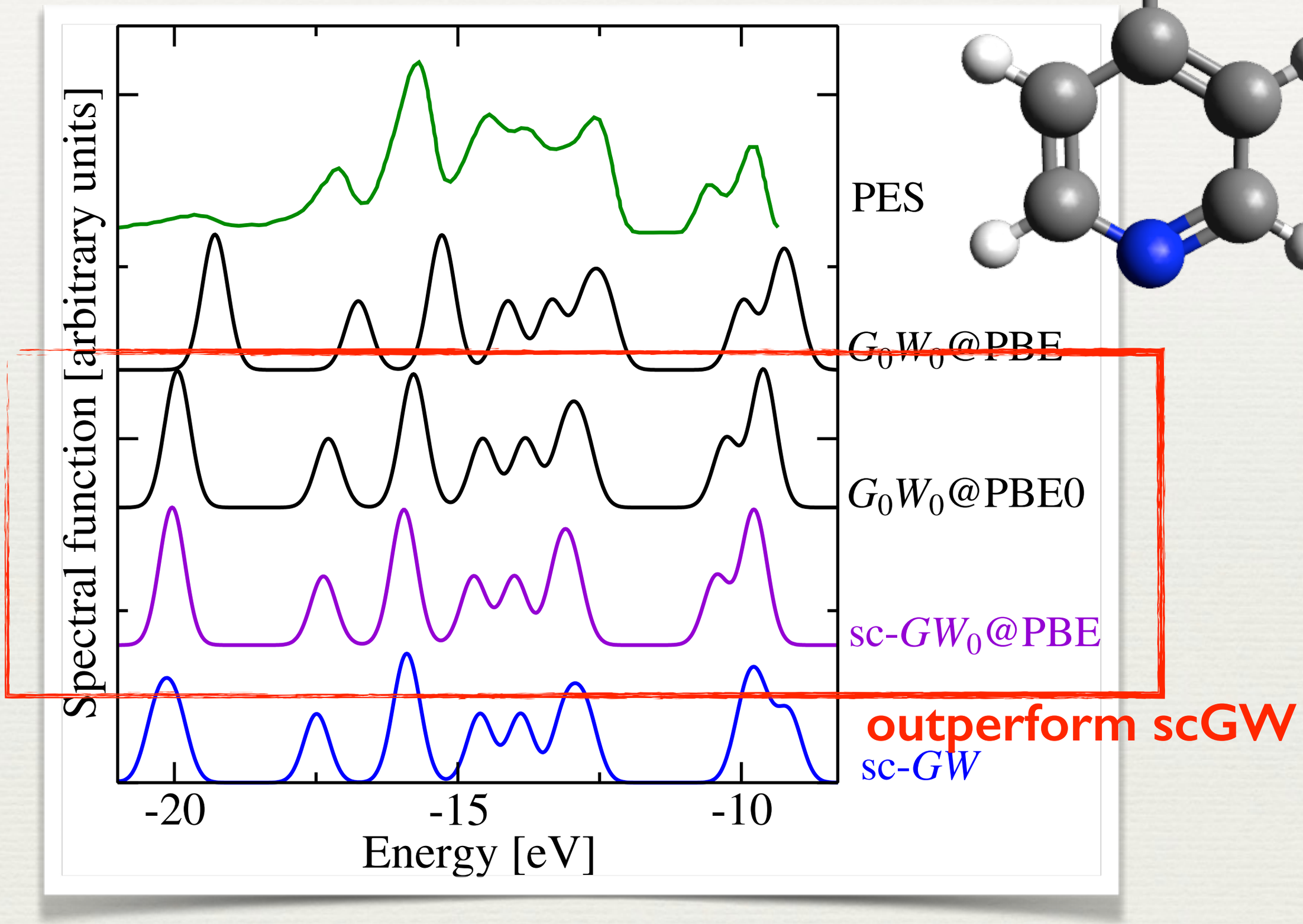
The loan pair in pyridine





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

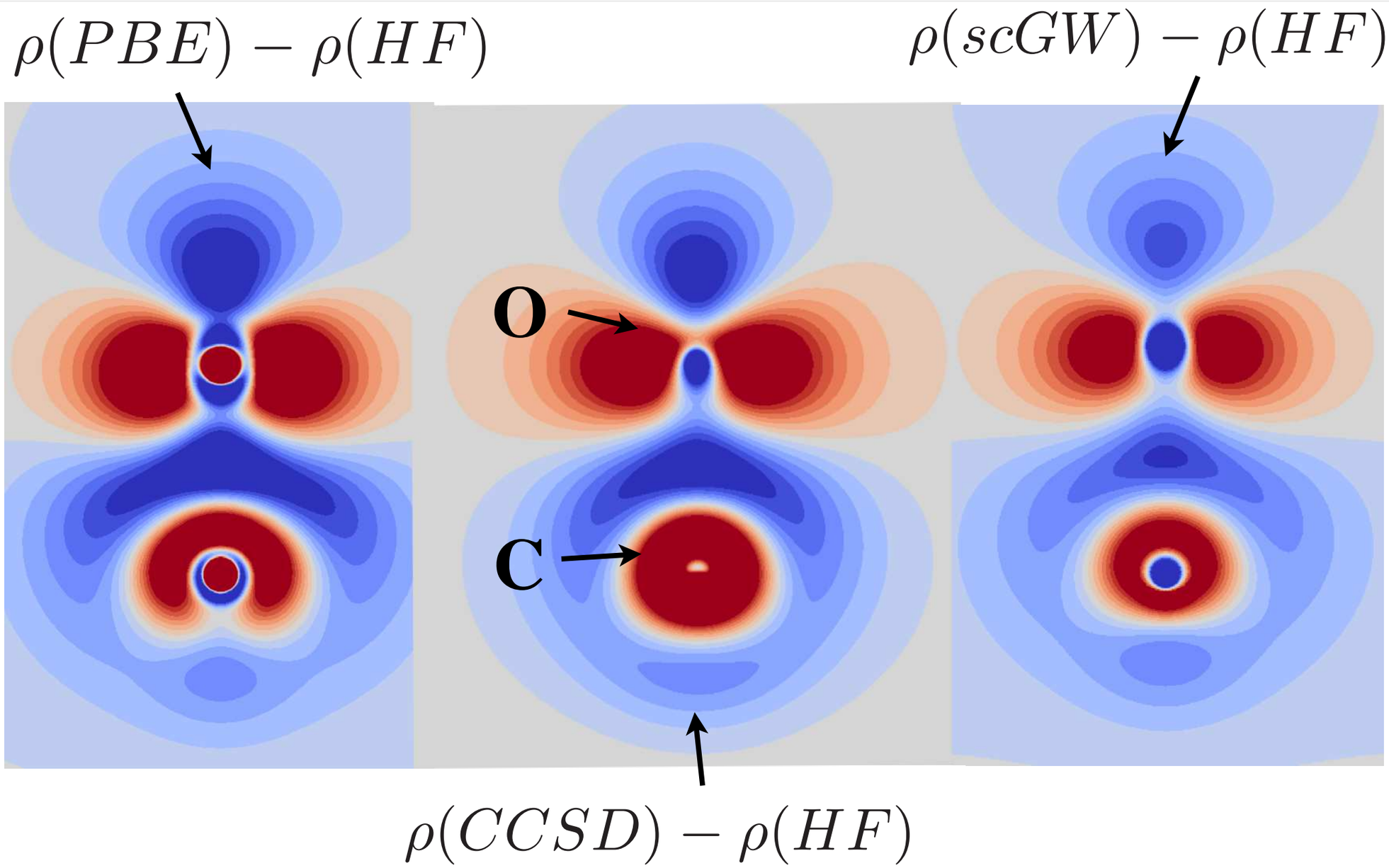
The loan pair in pyridine



outperform scGW

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

The *GW* density of CO



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

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

The *GW* density of CO

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

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

Dipole moment (in Debye):

Exp.	scGW	CCSD	HF	PBE
0.11	0.07	0.06	-0.13	0.2

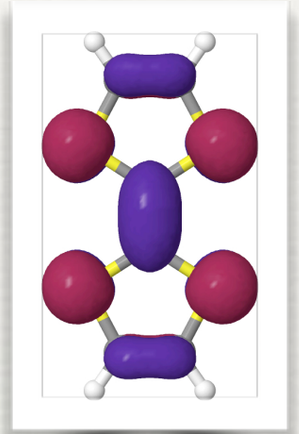
$\rho(CCSD) - \rho(HF)$

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

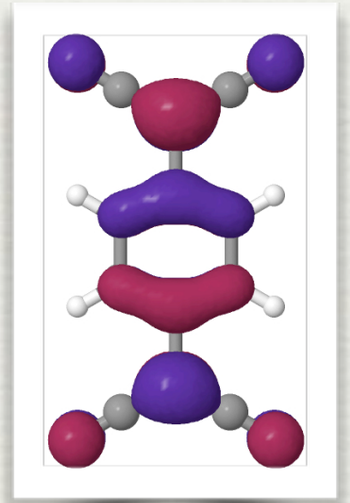
Caruso, Ren, Rinke, Rubio, Scheffler, Phys. Rev. B 86, 081102(R) (2012)

Back to the TTF/TCNQ dimer

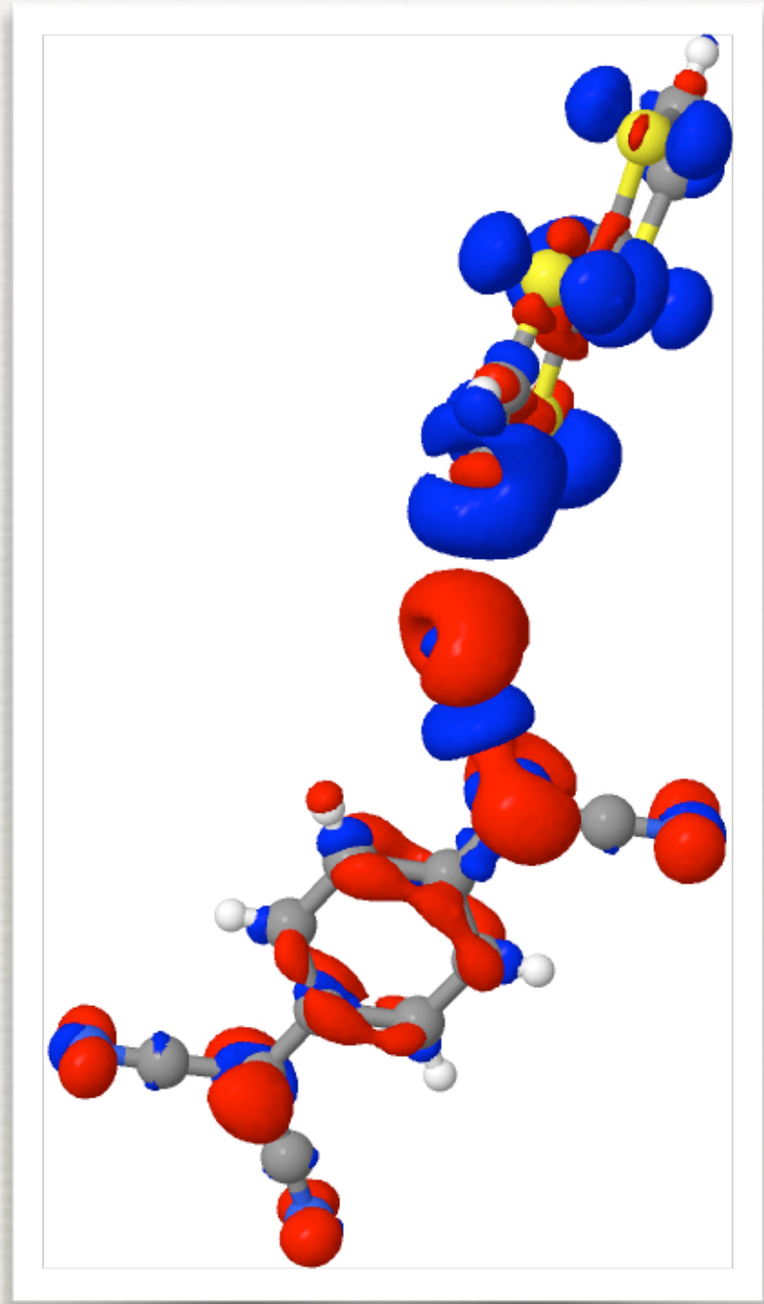
electron density difference



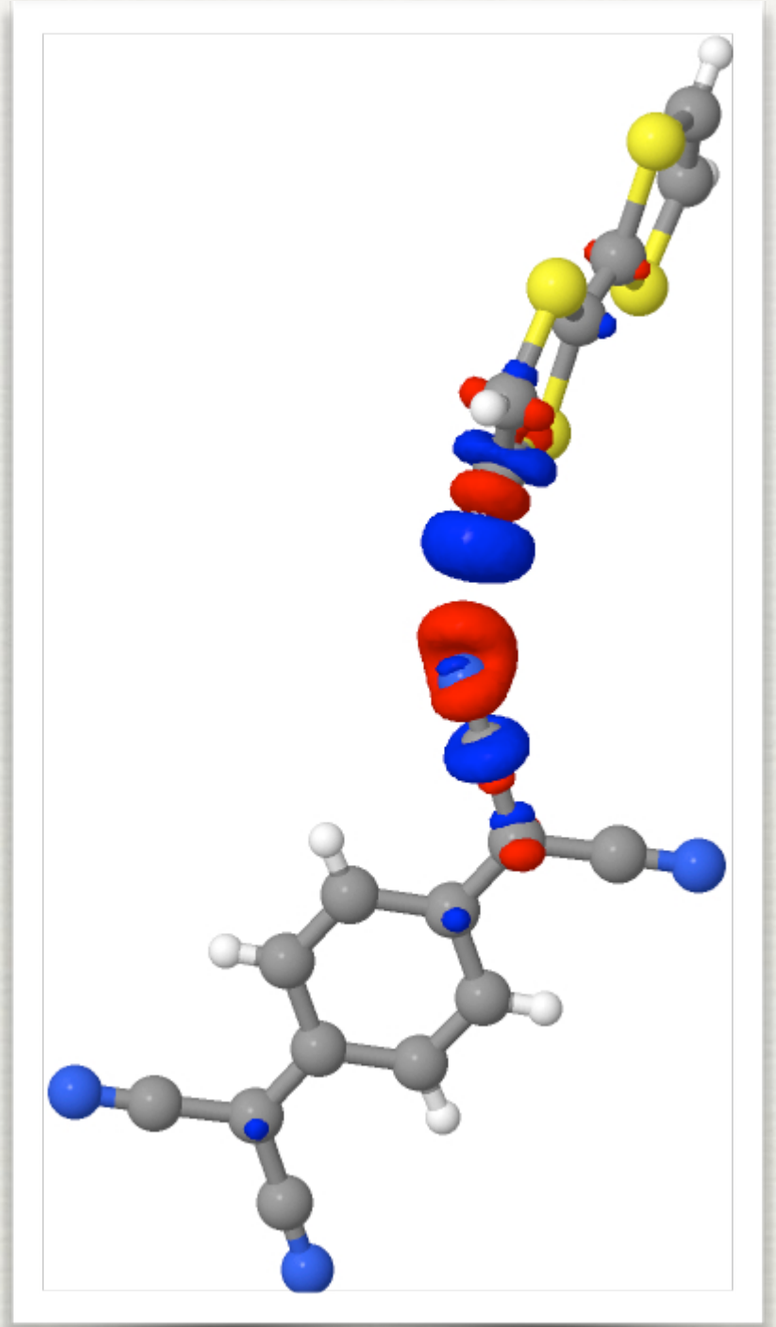
HOMO



LUMO



PBE



scGW

The *GW* total energy

Galitskii-Migdal equation (V. Galitskii and A. Migdal, Sov. Phys. JETP 7, 96 (1958)):

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

The *GW* total energy

Galitskii-Migdal equation (V. Galitskii and A. Migdal, Sov. Phys. JETP 7, 96 (1958)):

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

Use equation of motion to transform expression:

$$\left[i \frac{\partial}{\partial t} + \frac{\nabla^2_{\mathbf{r}}}{2} - v_{\mathrm{H}}(\mathbf{r}) - v_{\mathrm{ext}}(\mathbf{r}) \right] G^{\sigma}(\mathbf{r}t, \mathbf{r}'t') -$$

$$- \int d\mathbf{r}'' dt'' \Sigma^{\sigma}(\mathbf{r}t, \mathbf{r}''t'') G^{\sigma}(\mathbf{r}''t'', \mathbf{r}'t') = \delta(\mathbf{r} - \mathbf{r}')\delta(t - t')$$

The *GW* total energy

Galitskii-Migdal equation (V. Galitskii and A. Migdal, Sov. Phys. JETP 7, 96 (1958)):

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More convenient form:

$$\begin{aligned} E_{\mathrm{GM}} &= -i \sum_{ij} \left[2t_{ij} + 2v^{\mathrm{ext}}_{ij} + v^{H}_{ij} + \Sigma^{x}_{ij} \right] G_{ij}(t = 0^-) \\ &\quad -i \sum_{ij} \int \frac{d\omega}{2\pi} \Sigma^{c}_{ij}(\omega) G_{ij}(\omega) e^{i\omega\eta} \\ &= T + E_{\mathrm{ext}} + E_H + E_x + E_c^{GW} \end{aligned}$$

The *GW* total energy

Galitskii-Migdal equation (V. Galitskii and A. Migdal, Sov. Phys. JETP 7, 96 (1958)):

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

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interacting kinetic energy **Coulomb correlation**

The *GW* total energy

Galitsk 958)):

E_{GM} , $\mathbf{r}'t')$

More c

E_{GM}

$$= \boxed{T} + E_{\mathrm{ext}} + E_H + E_x + \boxed{E_c^{GW}}$$

interacting kinetic energy

Coulomb correlation

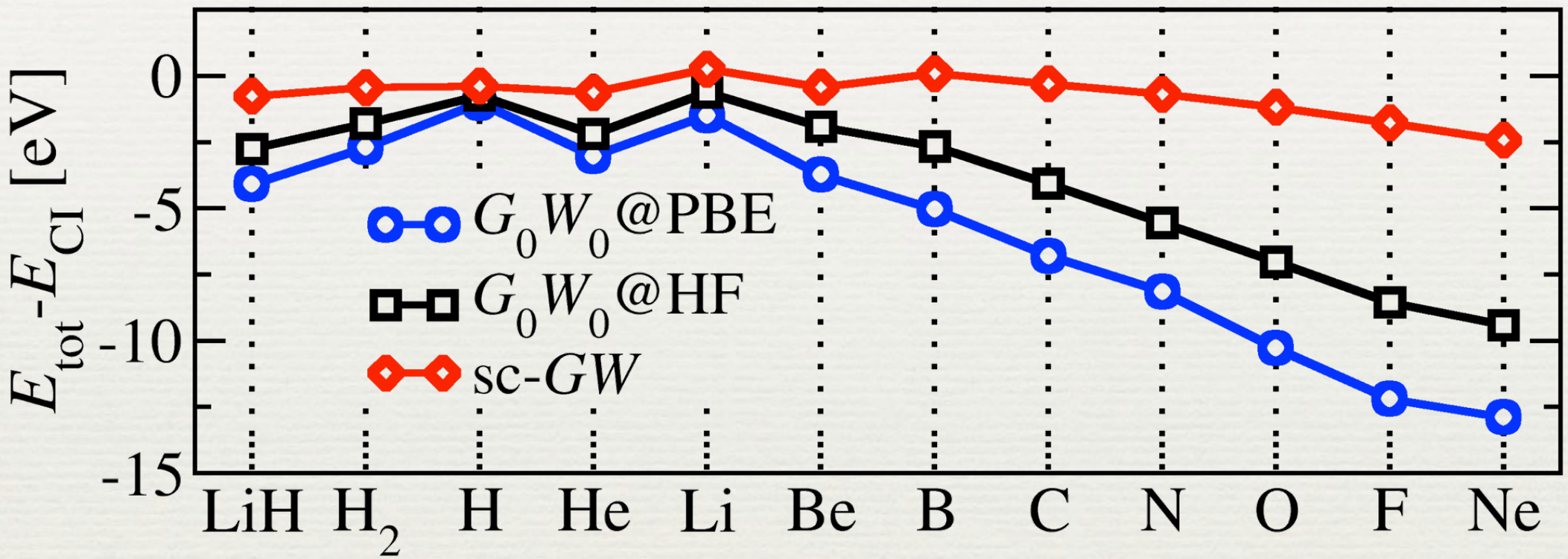
Our old friend, the homogenous electron gas

correlation energy per electron:

r	scGW	QMC
2.0	-0.0897 Ry	-0.0897 Ry
4.0	-0.0638 Ry	-0.0638 Ry

B. Holm, Phys. Rev. Lett. 83, 788 (1999)

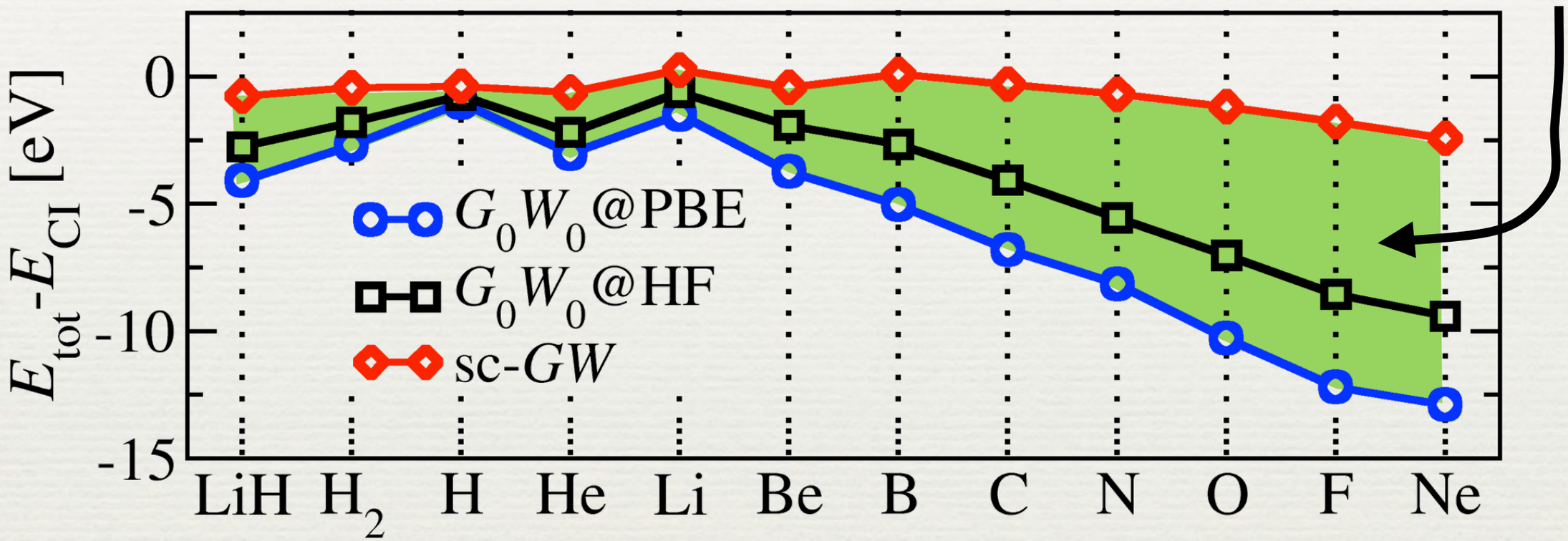
GW total energy of atoms



F. Caruso, P. Rinke, X. Ren, A. Rubio, and M. Scheffler, Phys. Rev. B 86, 081102(R) (2012)

GW total energy of atoms

(mostly) kinetic correlation



F. Caruso, P. Rinke, X. Ren, A. Rubio, and M. Scheffler, Phys. Rev. B 86, 081102(R) (2012)

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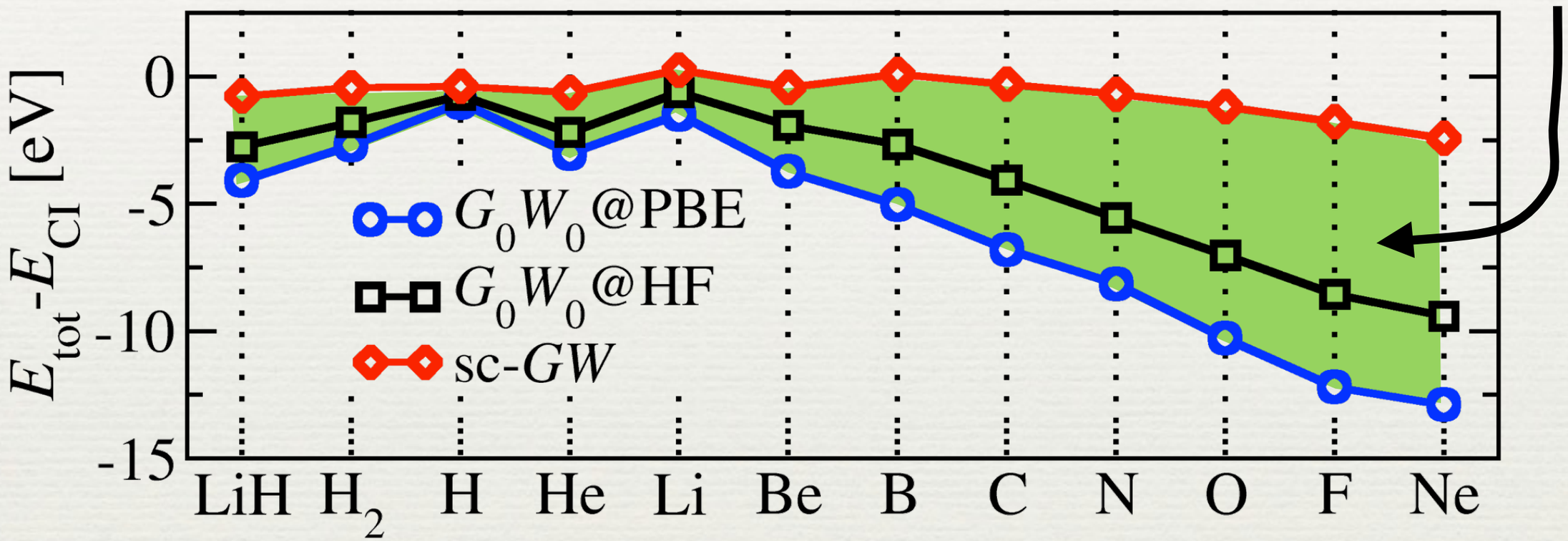
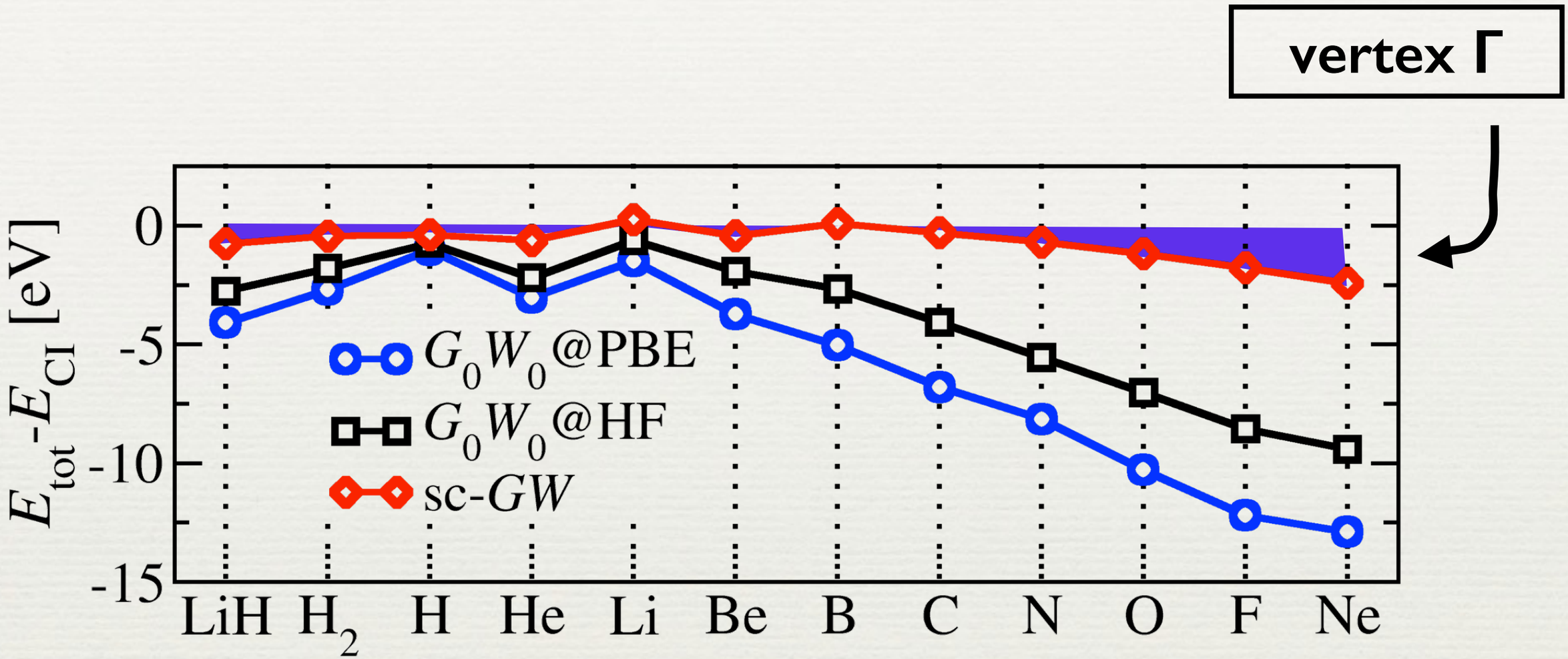


G_0W_0: $E_{\mathrm{tot}}\left[G_0\right] = T_{\mathrm{s}}\left[G_0\right] + E_{\mathrm{ext}} + E_{\mathrm{H}} + E_{\mathrm{x}}^{\mathrm{exact}} + E_{\mathrm{c}}\left[G_0W_0\right]$

scGW: $E_{\mathrm{tot}}\left[G\right] = T\left[G\right] + E_{\mathrm{ext}} + E_{\mathrm{H}} + E_{\mathrm{x}}^{\mathrm{exact}} + E_{\mathrm{c}}\left[GW\right]$

F. Caruso, P. Rinke, X. Ren, A. Rubio, and M. Scheffler, Phys. Rev. B 86, 081102(R) (2012)

GW total energy of atoms

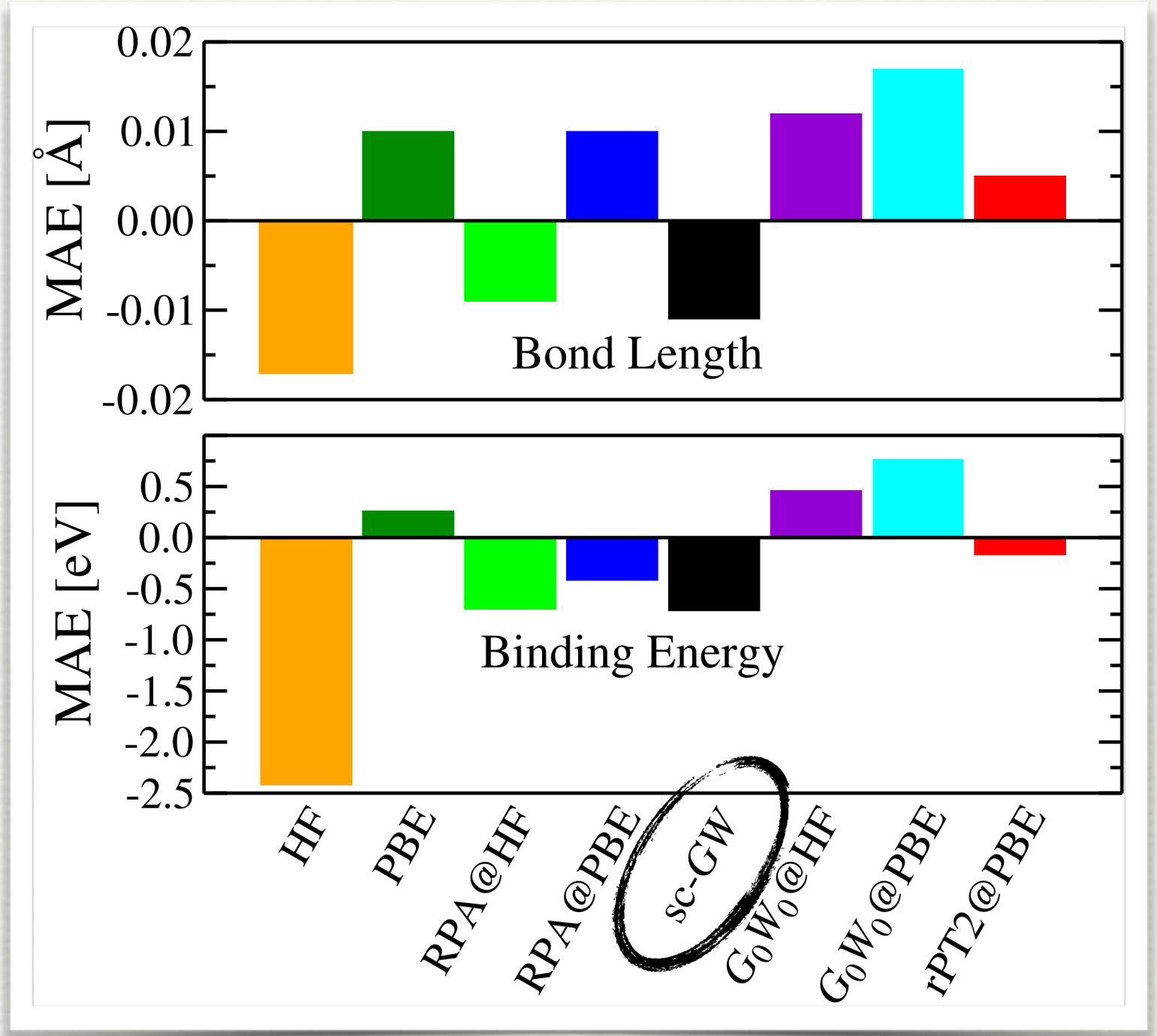


$$\Sigma(1,2) = i \int G(1,4) W(1^+,3) \Gamma(4,2,3) d(3,4)$$

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

F. Caruso, P. Rinke, X. Ren, A. Rubio, and M. Scheffler, Phys. Rev. B 86, 081102(R) (2012)

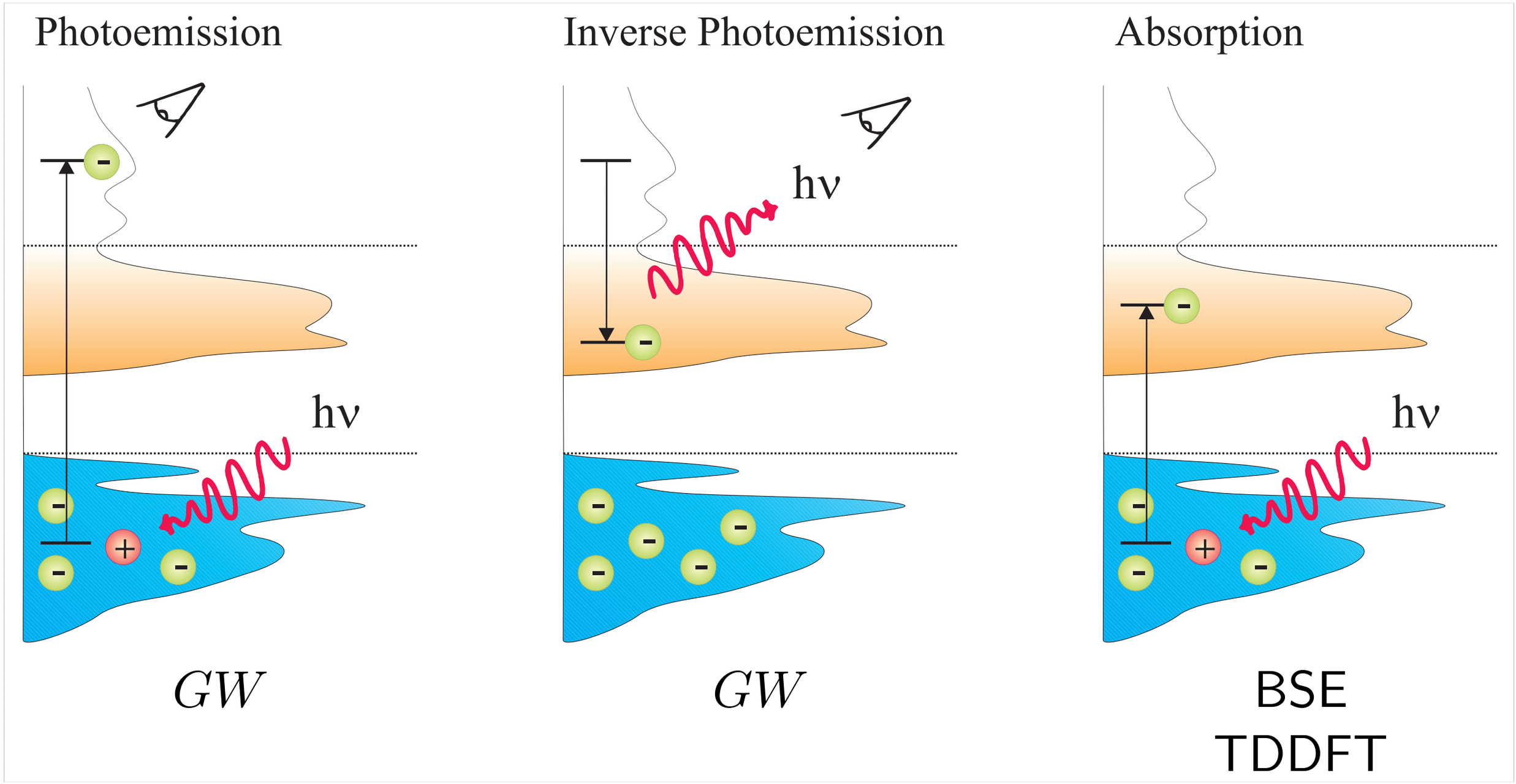
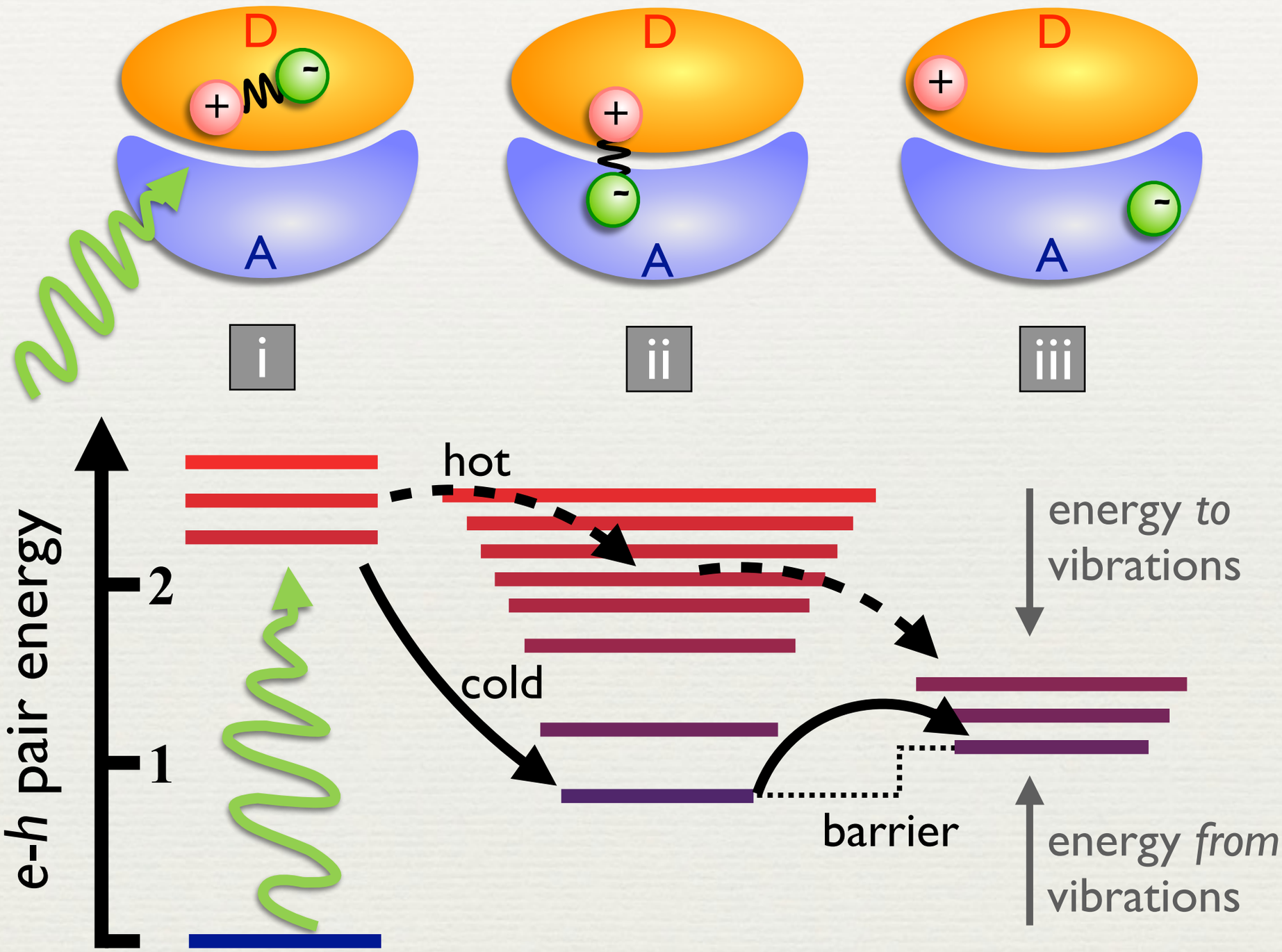
Further *GW* total energy assessment



- set of 6 dimers: LiH, LiF, HF, CO, H_2 and N_2

F. Caruso, P. Rinke, X. Ren, A. Rubio, and M. Scheffler, Phys. Rev. B 86, 081102(R) (2012)

Summary


Photoemission
hν
GW
Inverse Photoemission
hν
GW
Absorption
hν
BSE
TDDFT

Charge separation at donor-acceptor complex