Computing defect formation energies in GW

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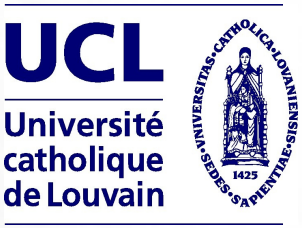
UCL/IMCN/NAPS

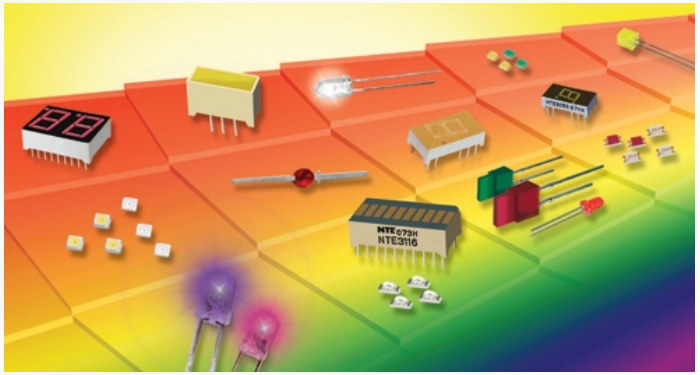


ABINIT Developper Workshop 2011
Han-sur-Lesse
13 April 2011

Amorphous silica

Structural,
Electronic and
Optical properties
=>
Many applications

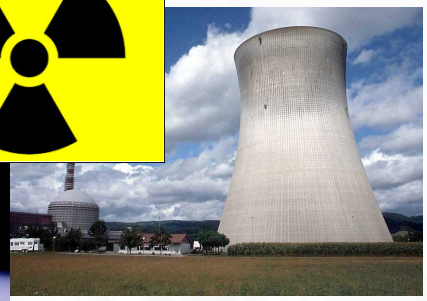
Optoelectronic devices



Optical
fibers

Radiations

Satellites



Nuclear plants

Defects,
Radiations and
Operating conditions
=>
Alteration of the properties !

Defects in bulk systems with DFT

=> Can have different charged states

=> Band-gap problem in DFT

=> Defect energy levels in the band gap

=> Poor description of defect formation energies

=> ...

Outline

- Defect formation energies in DFT
- Combining DFT and GW
- Application to hydrogen in a-SiO_2
- Shortcomings and possible workarounds
- Conclusion

Defect formation energies

$$E_f(X^q) = E_{tot}(X^q) - E_{tot}(bulk) - \sum_i n_i \mu_i + q(\epsilon_F + \epsilon_v + \Delta V)$$

n_i : number of atoms added (> 0) or removed (< 0) from the bulk to generate the defect

μ_i : chemical potential of the atoms added or removed

q : charge of the defect

ϵ_F : Fermi level of the system

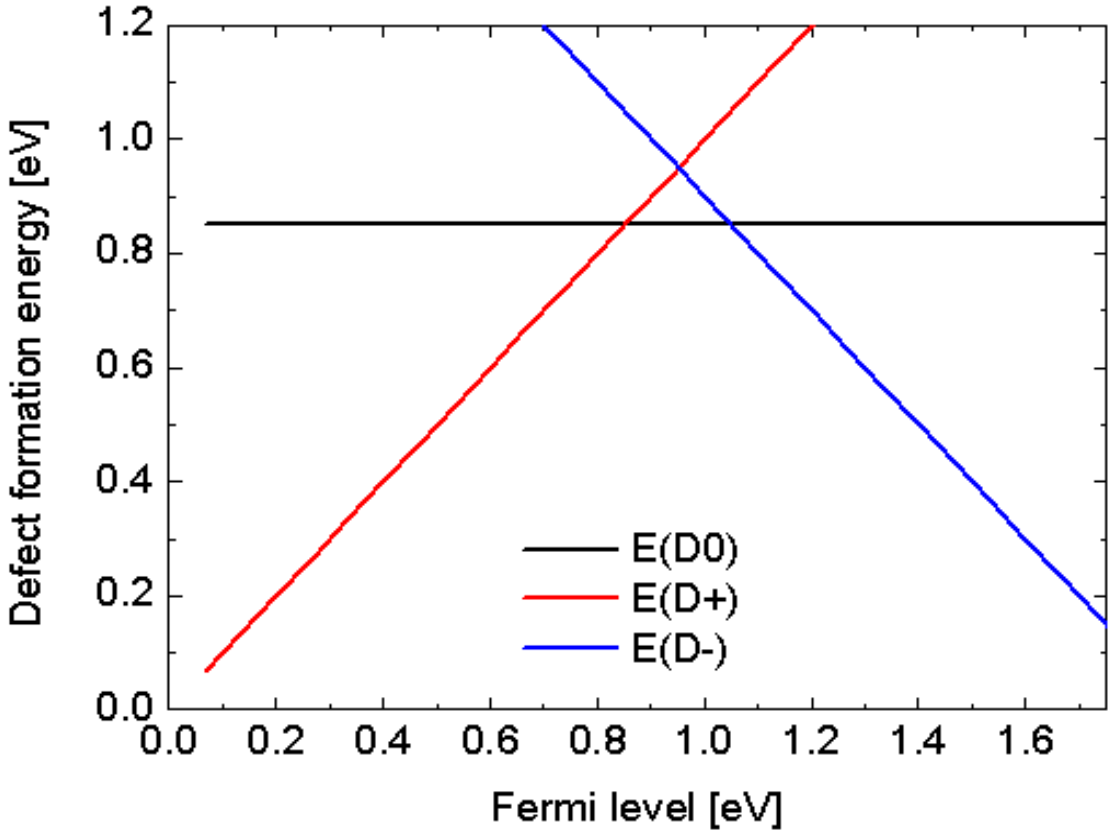
ϵ_v : valence band maximum

ΔV : alignment potential

Review article : C. G. Van de Walle & J. Neugebauer J. App. Phys., 2004, 95, 3851

Defect formation energies (2)

=> Charge transition levels



Defect formation energies (2)

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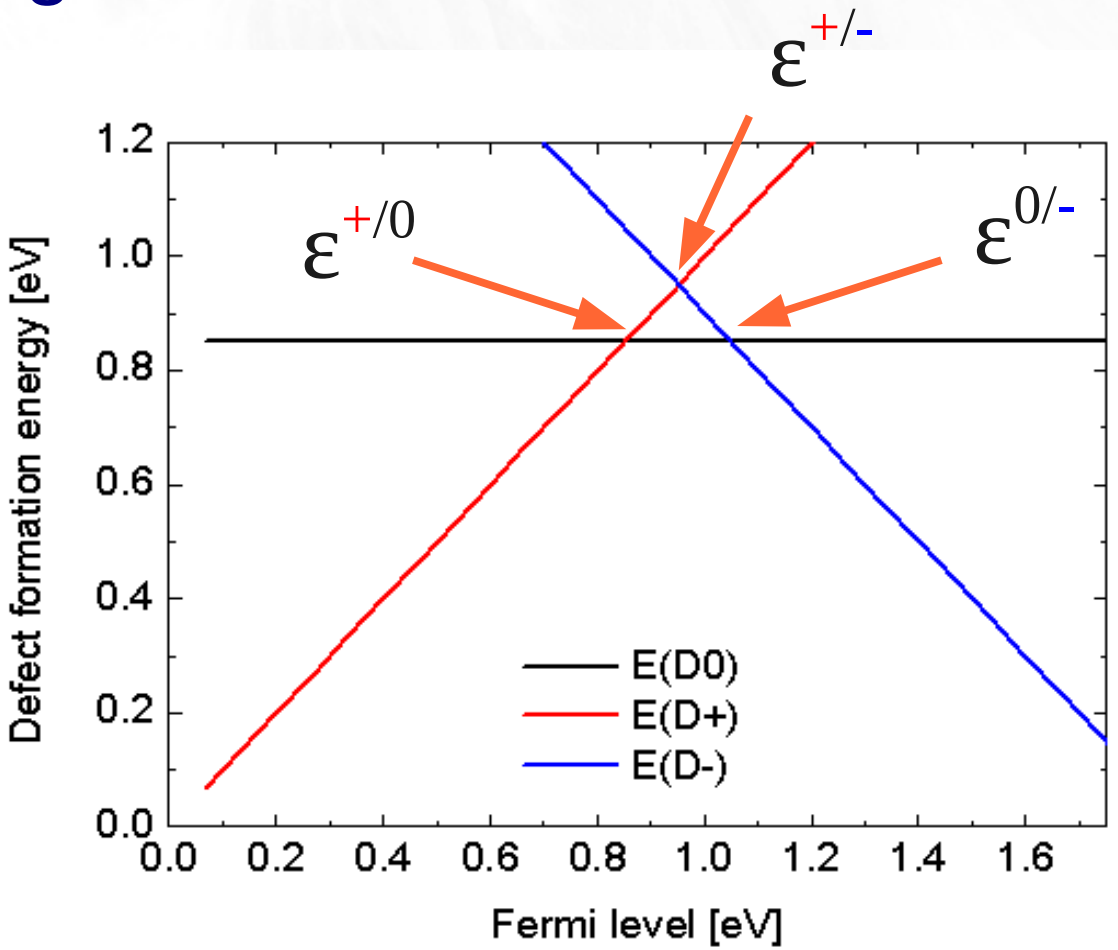
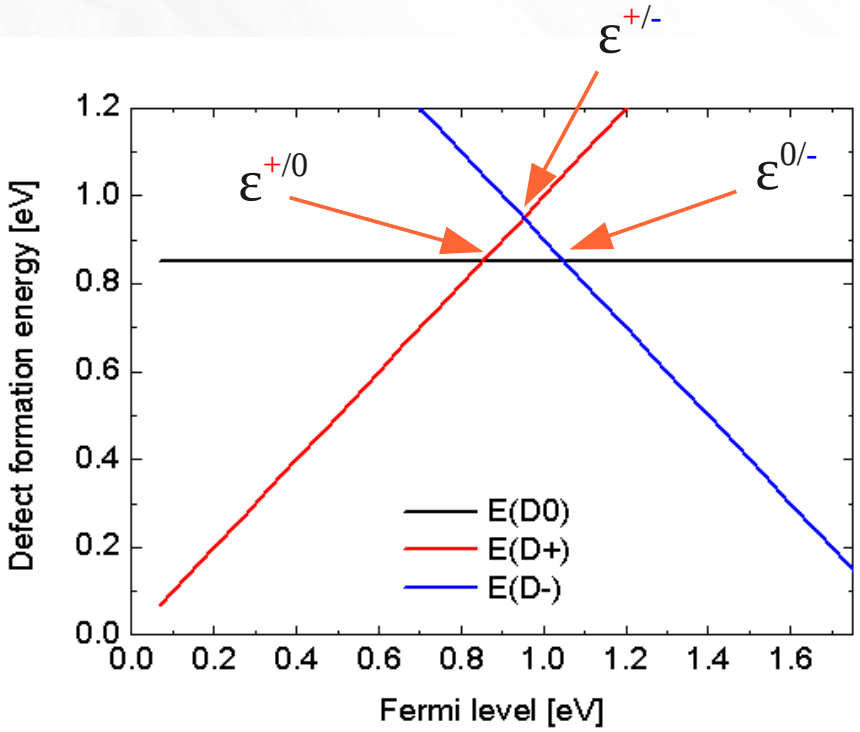


Defect formation energies (2)

=> Charge transition levels

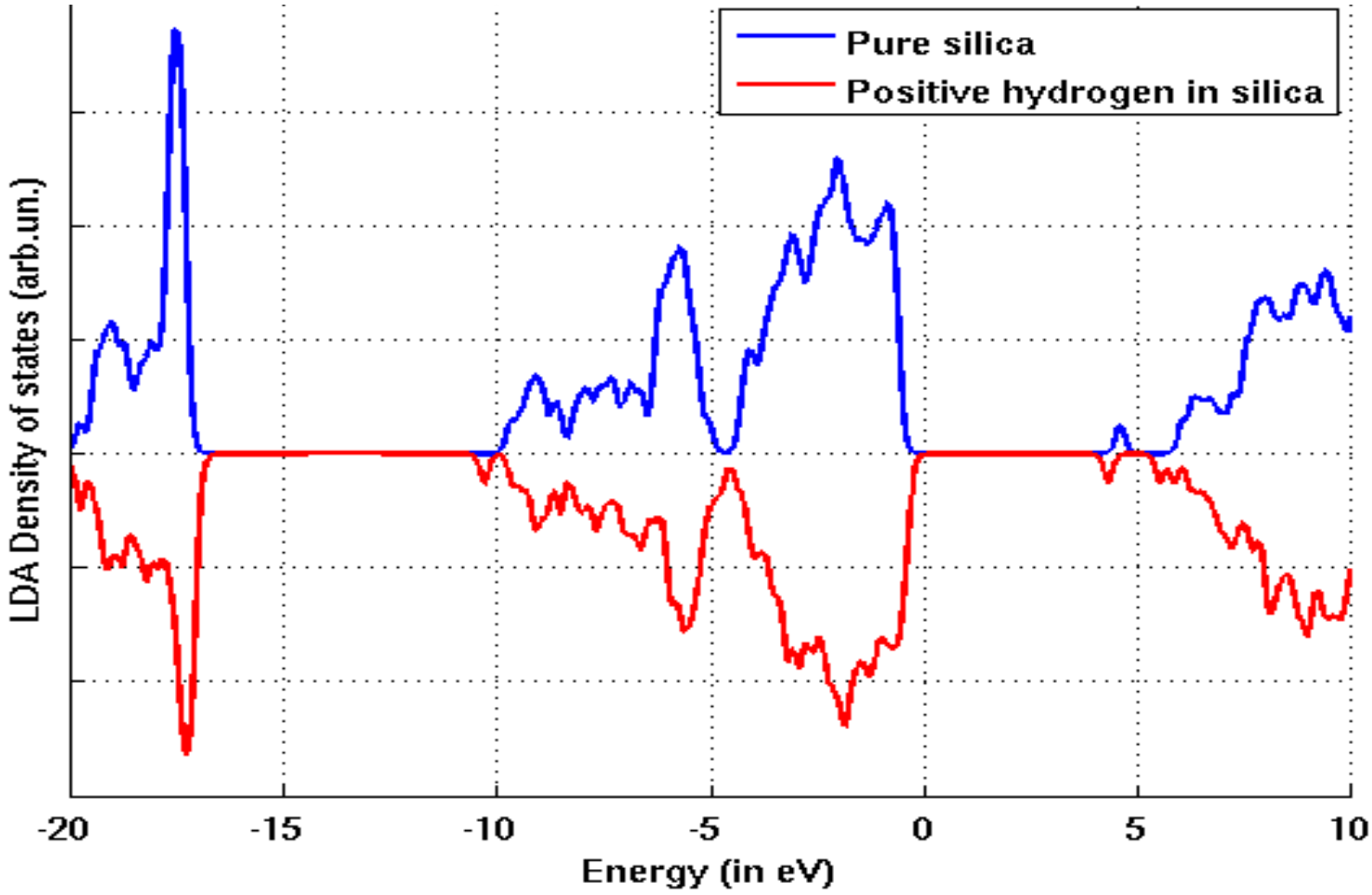
Hypothesis :

- Low defect concentration
- No complex conjugation with the dopants



Band alignment

$$E_f(X^q) = E_{tot}(X^q) - E_{tot}(bulk) - \sum_i n_i \mu_i + q(\epsilon_F + \epsilon_v + \Delta V)$$



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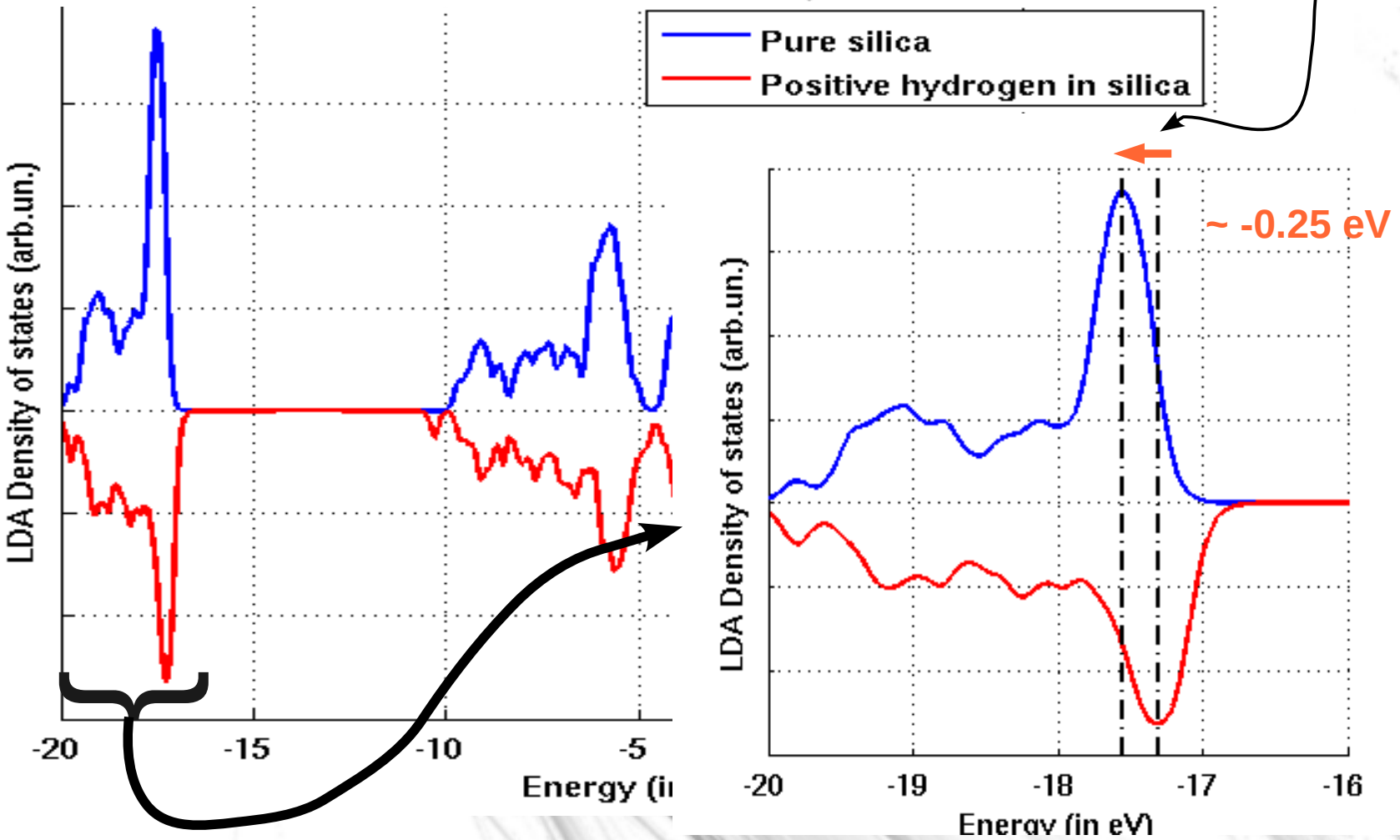


The band gap problem

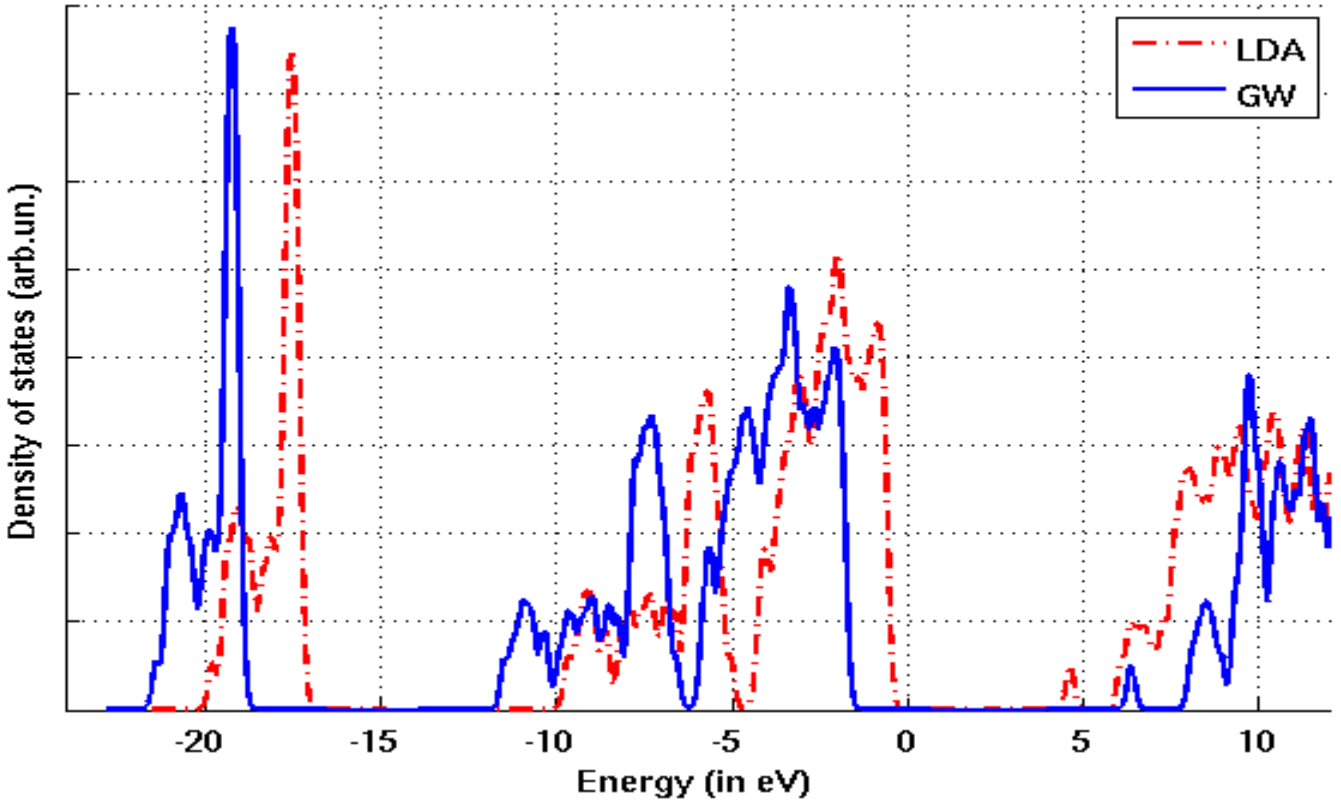
- Experimental gap of amorphous silica :

  ~ 8.7-9.2 eV

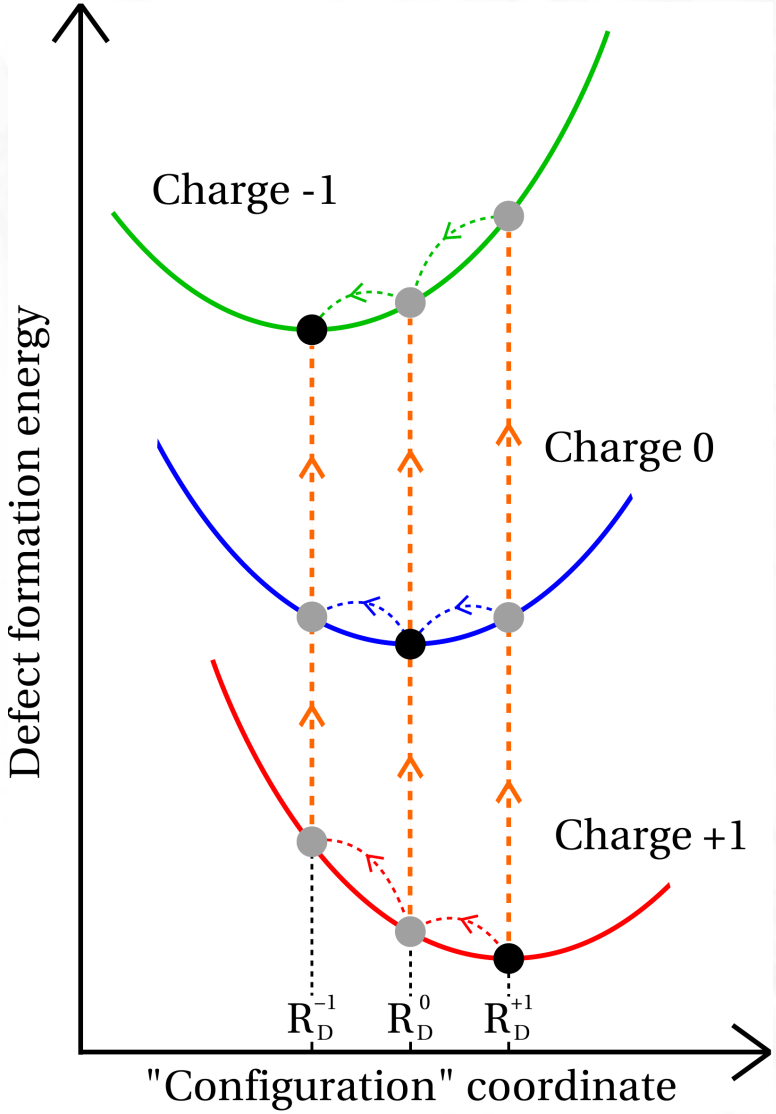
- LDA bandgap : 5.2 eV
- Poor description of defect energy levels in the band gap

The band gap problem

- GW band gap is better : ~8.3-8.4 eV



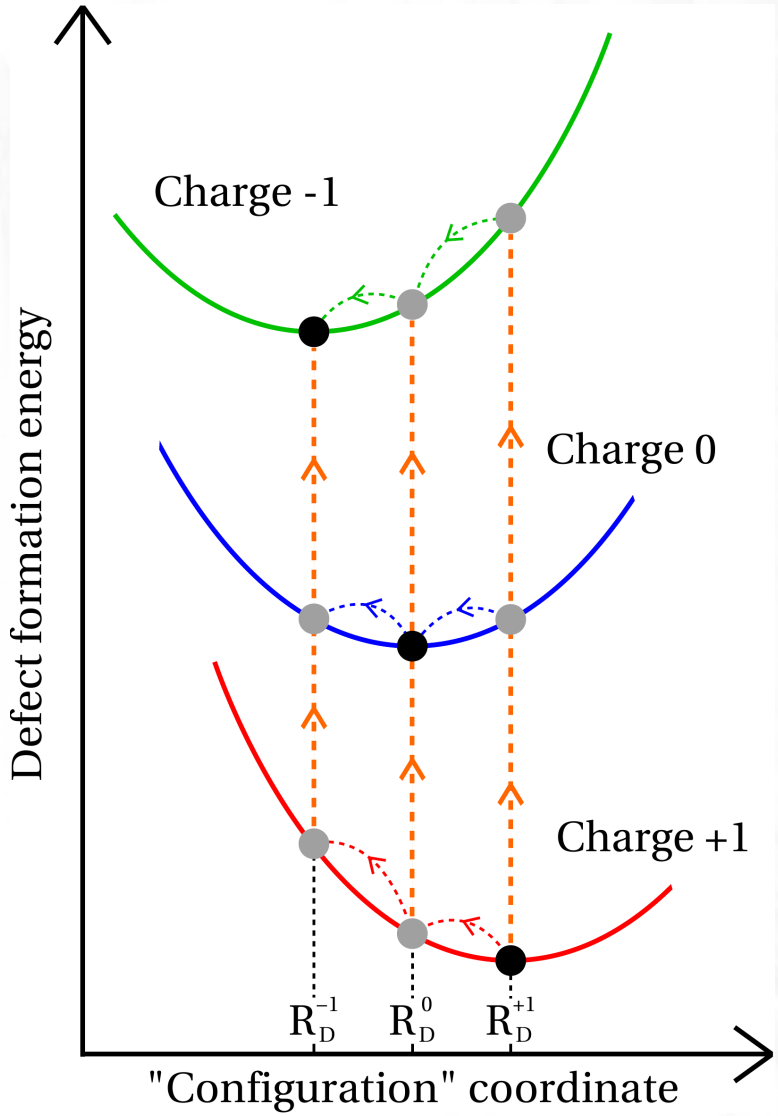
GW Defect formation energies



- Band gap problem in DFT
- Poor description of defect energy levels in DFT
- Affinity/Ionization of electrons : A(N-1) = I(N) not fulfilled

P. Rinke et al., PRL 102 (2009), 026402
F. Bruneval, PRL 103 (2009), 176403

GW Defect formation energies



- Band gap problem in DFT
- Poor description of defect energy levels in DFT
- Affinity/Ionization of electrons : A(N-1) = I(N) not fulfilled
- “Reference” formation energy
- Relaxation energies (horizontal) at fixed number of electrons computed in DFT
- Vertical transitions (electron addition or removal) computed in GW

P. Rinke et al., PRL 102 (2009), 026402
F. Bruneval, PRL 103 (2009), 176403

GW Defect formation energies (2)

H^0 : Start with the formation energy of H^+ (assumed to be well defined in LDA)

$$E_f(H^0) = E_f(H^+, \epsilon_F = 0) + E_{relax}^{H^+ \rightarrow H^0} + A(+/0)$$

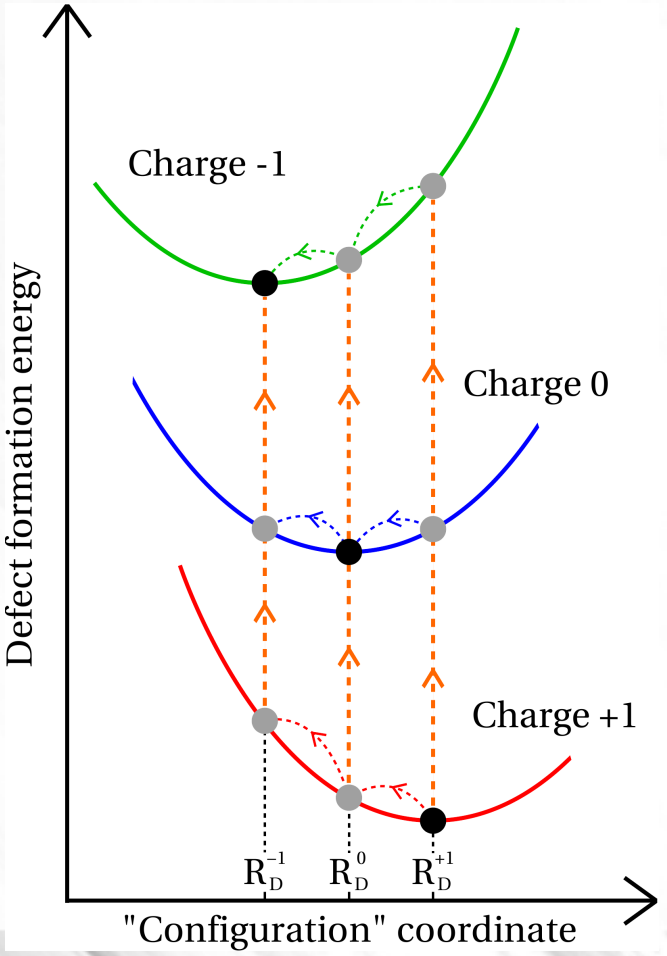
=> first relax,
then electron addition

=> first electron addition,
then relax

Electron addition :

=> system with charge +1

=> system with charge 0



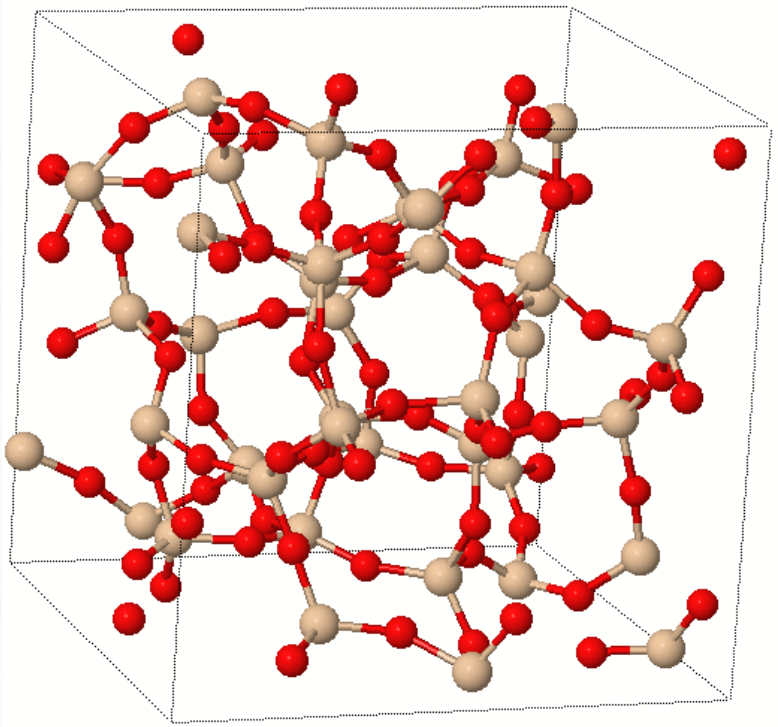
Application to hydrogen in a-SiO_2

- 20 different models with 72 atoms each

Structural properties :

Coordination numbers, bond lengths, angles, ...

No edge sharing tetrahedrons



Application to hydrogen in a-SiO_2

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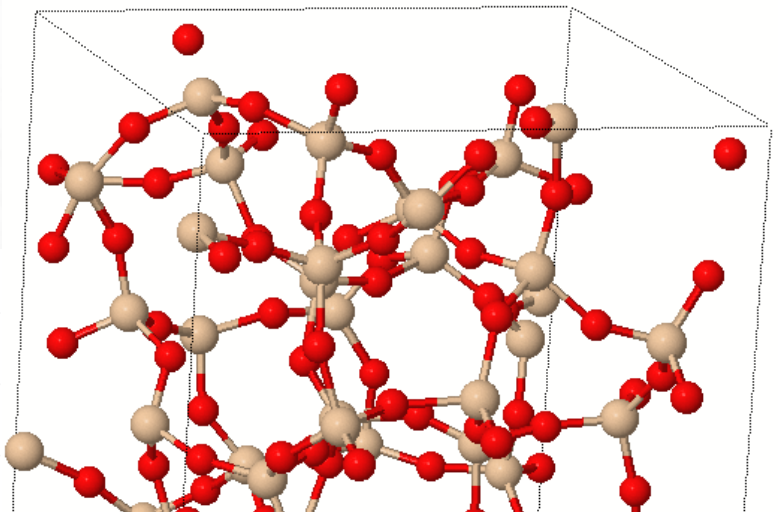
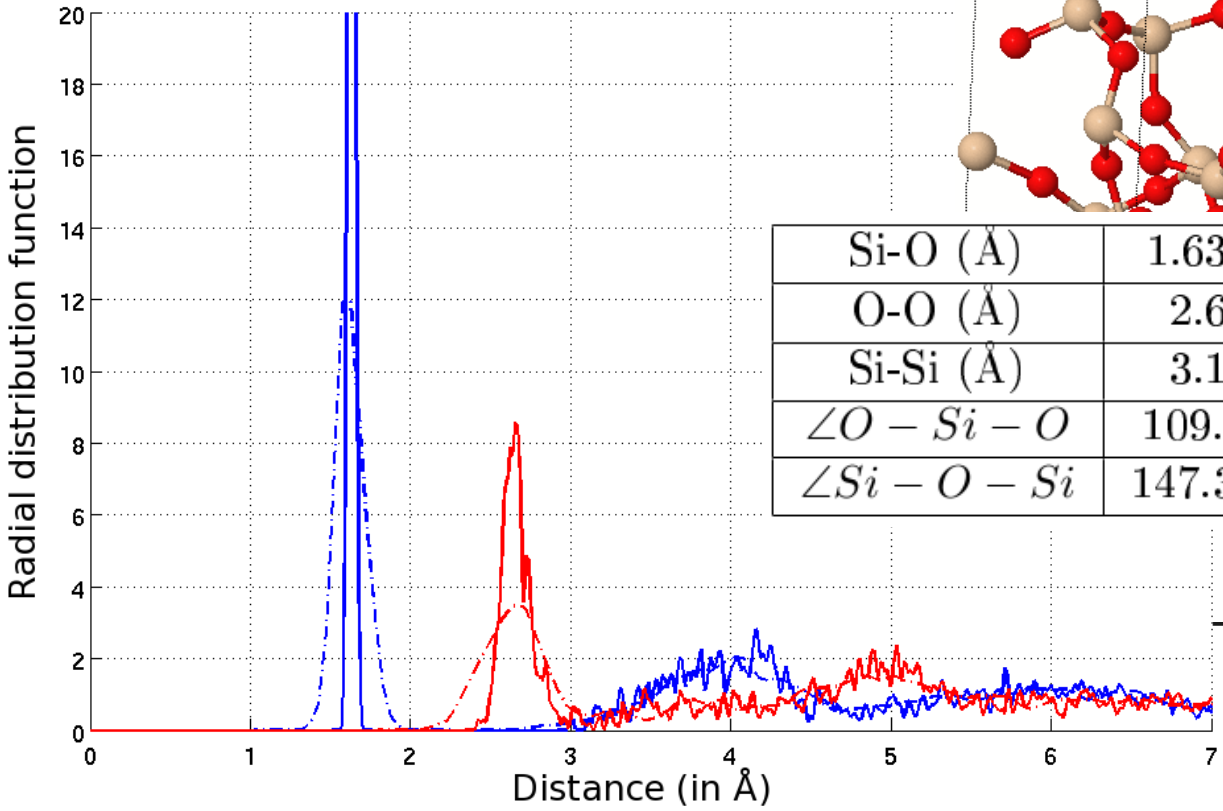




Si-O (Å)	1.630 (0.021)	1.62
O-O (Å)	2.67 (0.13)	2.65
Si-Si (Å)	3.10 (0.15)	3.12
$\angle O - Si - O$	109.5° (4.3°)	109.47°
$\angle Si - O - Si$	147.3° (13.1°)	148.3°

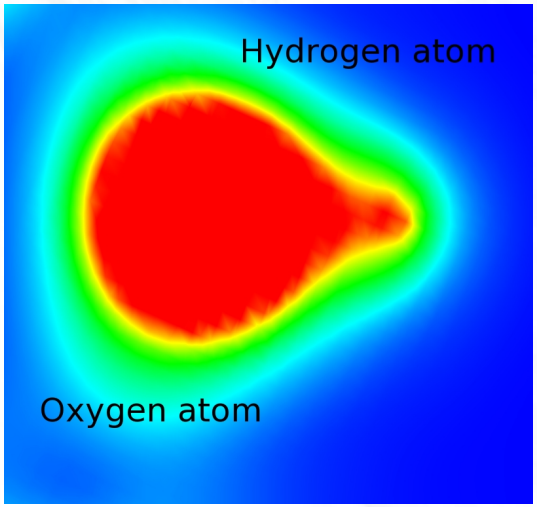
Theory

Experiment

Hydrogen containing silica

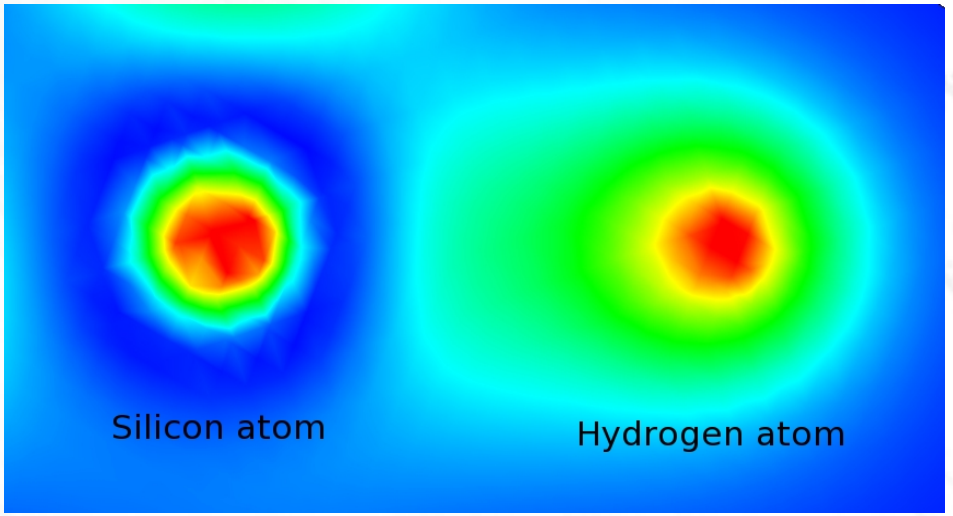
Different charged states of hydrogen :

Positive hydrogen



O-H distance : ~1 Å

Negative hydrogen



Si-H distance : ~1.5 Å

Neutral hydrogen : goes into the larger voids of the system

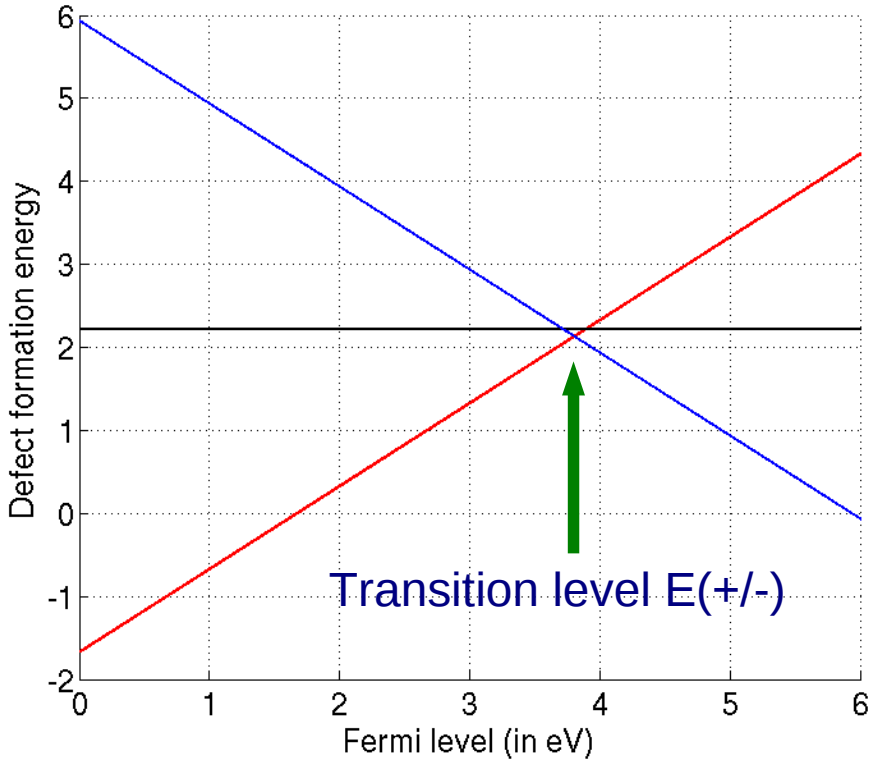
LDA Formation energies of $H^{+/0/-}$

$$E_f(X^q) = E_{tot}(X^q) - E_{tot}(bulk) - \sum_i n_i \mu_i + q(\epsilon_F + \epsilon_v + \Delta V)$$

Problem with charged states : self-interaction with the neighboring images of the net charge
=> Makov-Payne correction for positive and negative charged states :

$$E_{tot}(L) = E_{tot}(L \to \infty) - \frac{q^2 \alpha}{2\epsilon L}$$

=> + 0.47 eV



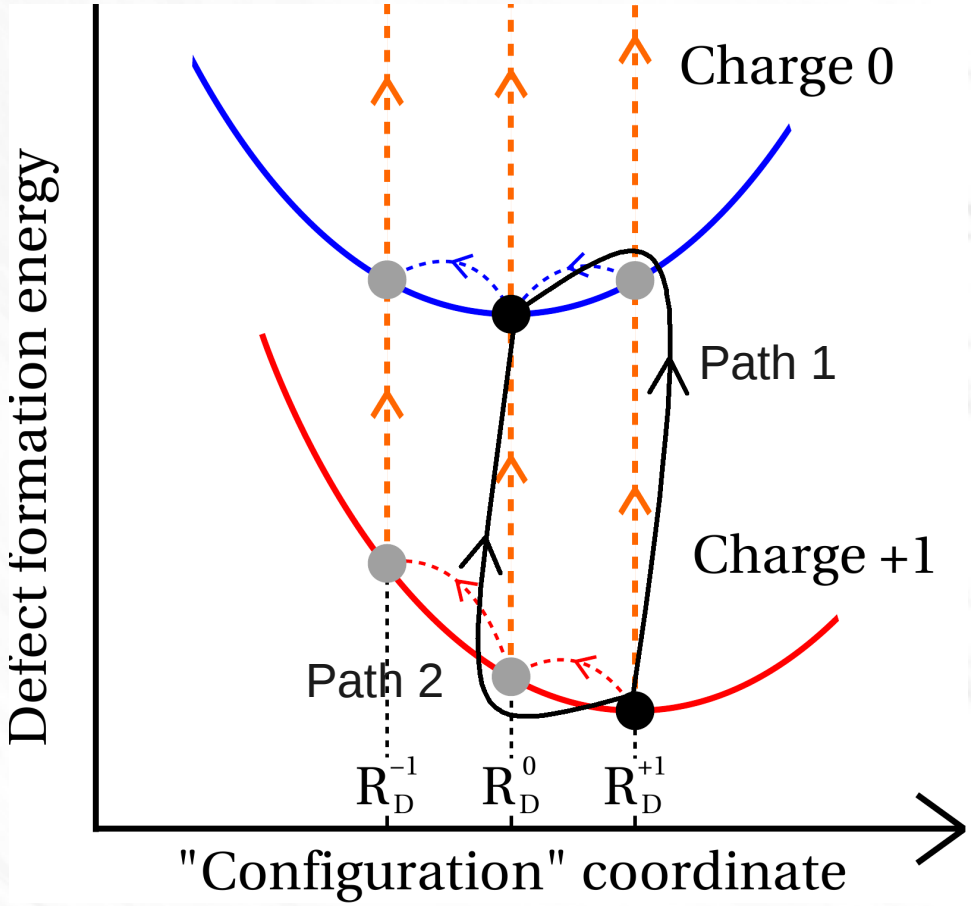
Formation energy of H^+ (ε_F=0) :

-1.67 eV (± 0.18 eV)

(Godet & Pasquarello : -1.28eV)

GW Formation energies of H^0

$$E_f(H^0) = E_f(H^+, \epsilon_F = 0) + E_{relax}^{H^+ \rightarrow H^0} + A(+/0)$$



GW Formation energies of H^0

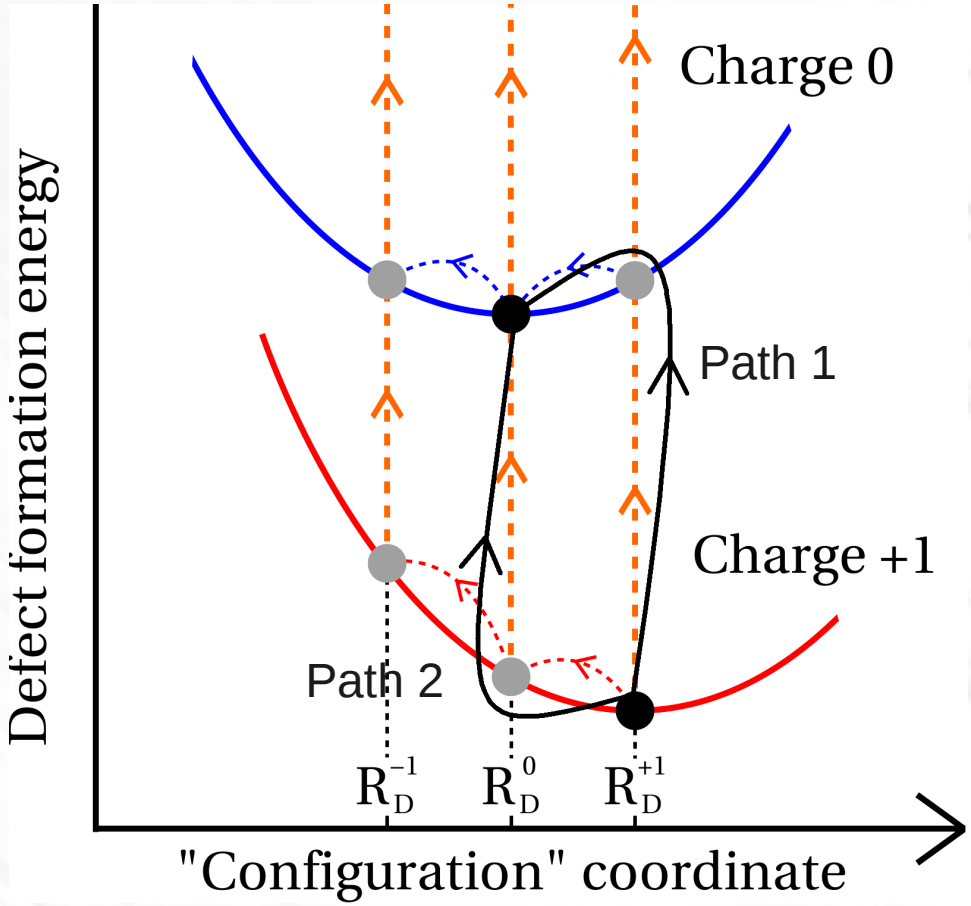
$$E_f(H^0) = E_f(H^+, \epsilon_F = 0) + E_{relax}^{H^+ \rightarrow H^0} + A(+/0)$$

$E^f(H^0)$	A(q-1/q)	I(q/q-1)
Path 1	5.02	3.93
Path 2	3.39	3.68

=> Large variations

- Depending on path
- Depending on the way the GW electron affinities are calculated

... anyway let's try to continue with H^-



GW Formation energies of H^-

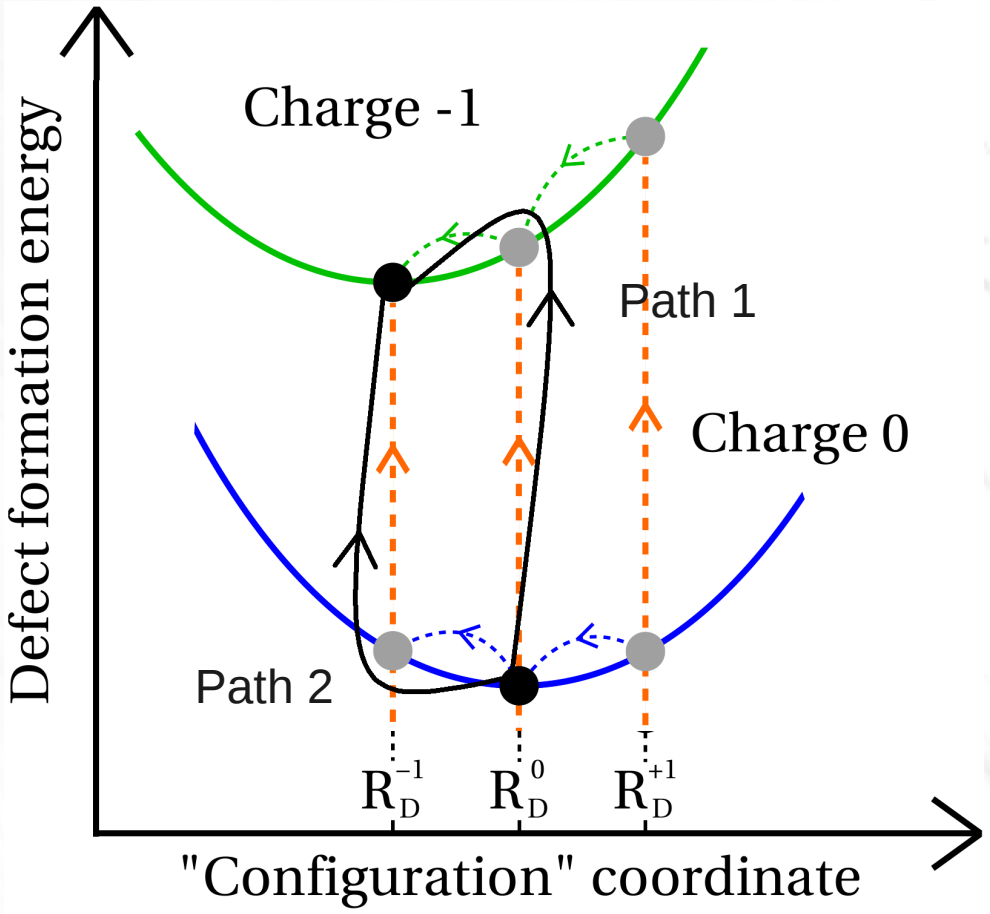
$$E_f(H^-) = E_f(H^0, \epsilon_F = 0) + E_{relax}^{H^0 \rightarrow H^-} + A(0/-)$$

$E^f(H^-)$	A(q-1/q)	I(q/q-1)
Path 1	8.88	8.1
Path 2	/	7.13

=> Large variations

What's wrong ?

- Large structural changes
- PPM G_0W_0 is not enough



GW formation energies with transition paths

First method :

$$E_f^{GW}[D^0] \quad = \quad E_f^{LDA}[D^{+1}, \epsilon_F = 0] + \Delta[+1, R_D^0, R_D^{+1}] + A[+1, R_D^0]$$

Second method :

$$\begin{aligned} E_f[H^0] = & [E_{tot}(SC[R_{H^0}], q = 0) - E_{tot}(SC[R_T], q = 0)] \\ & [E_{tot}(SC[R_T], q = +1) - E_{tot}(SC[R_{H^+}], q = +1)] \\ & \left[E_{tot}(SC[R_{H^+}], q = +1) - E_{ref} - \frac{1}{2}E_{tot}(H_2)\right] \\ & [E_{tot}(SC[R_T], q = 0) - E_{tot}(SC[R_T], q = +1)] \end{aligned}$$

Choice for R_T ? $E_{tot}(SC[R_T], q = 0) = E_{tot}(SC[R_T], q = +1)$

=>

$$\begin{aligned} E_f[H^0] = & E_{tot}(SC[R_{H^0}], q = 0) - E_{tot}(SC[R_{H^+}], q = +1) \\ & + E_f(H^+, \epsilon_F = 0) + A(SC[R_T], q = +1) \end{aligned}$$

GW formation energies with transition paths

First method :

$$E_f^{GW}[D^0] \quad = \quad E_f^{LDA}[D^{+1}, \epsilon_F = 0] + \Delta[+1, R_D^0, R_D^{+1}] + A[+1, R_D^0]$$

Second method :

$$E_f[H^0] = [E_{tot}(SC[.$$
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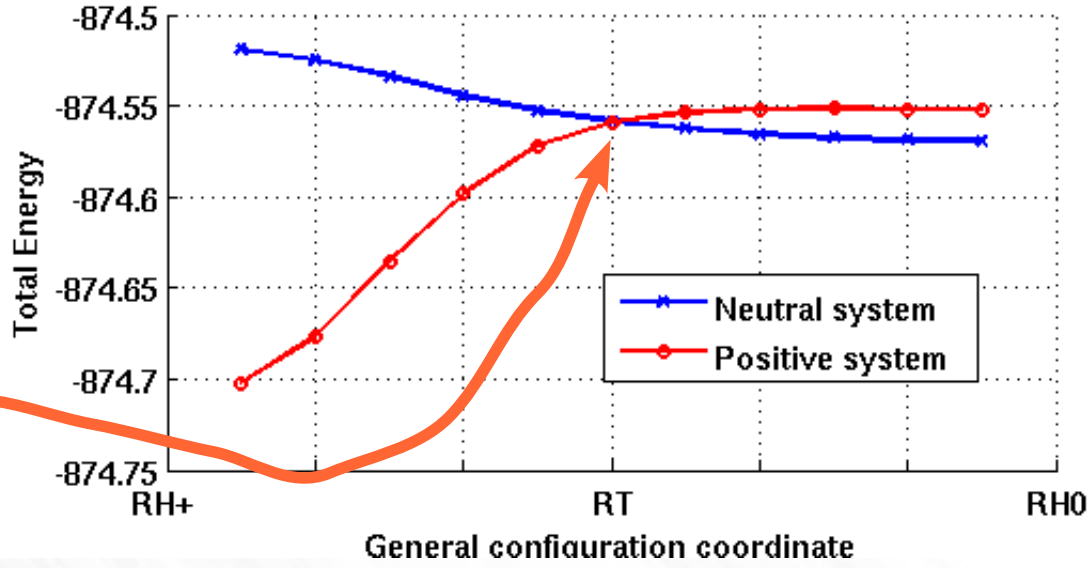


Choice for R_T ?

=>

$$E_f[H^0] = E_{tot}(SC[R_{H^0}], q = 0) - E_{tot}(SC[R_{H^+}], q = +1)$$
$$+ E_f(H^+, \epsilon_F = 0) + A(SC[R_T], q = +1)$$

GW formation energies with transition paths

$E^f(H^0)$	A(q-1/q)	I(q/q-1)
Path 1	5.02	3.93
Path 2	3.39	3.68

=> Defect formation energy of H^0
with transition path : 3.16 eV (or 3.6 eV)

... we are still not happy ...

Possible error from G_0W_0

=> Plasmon pole model ?

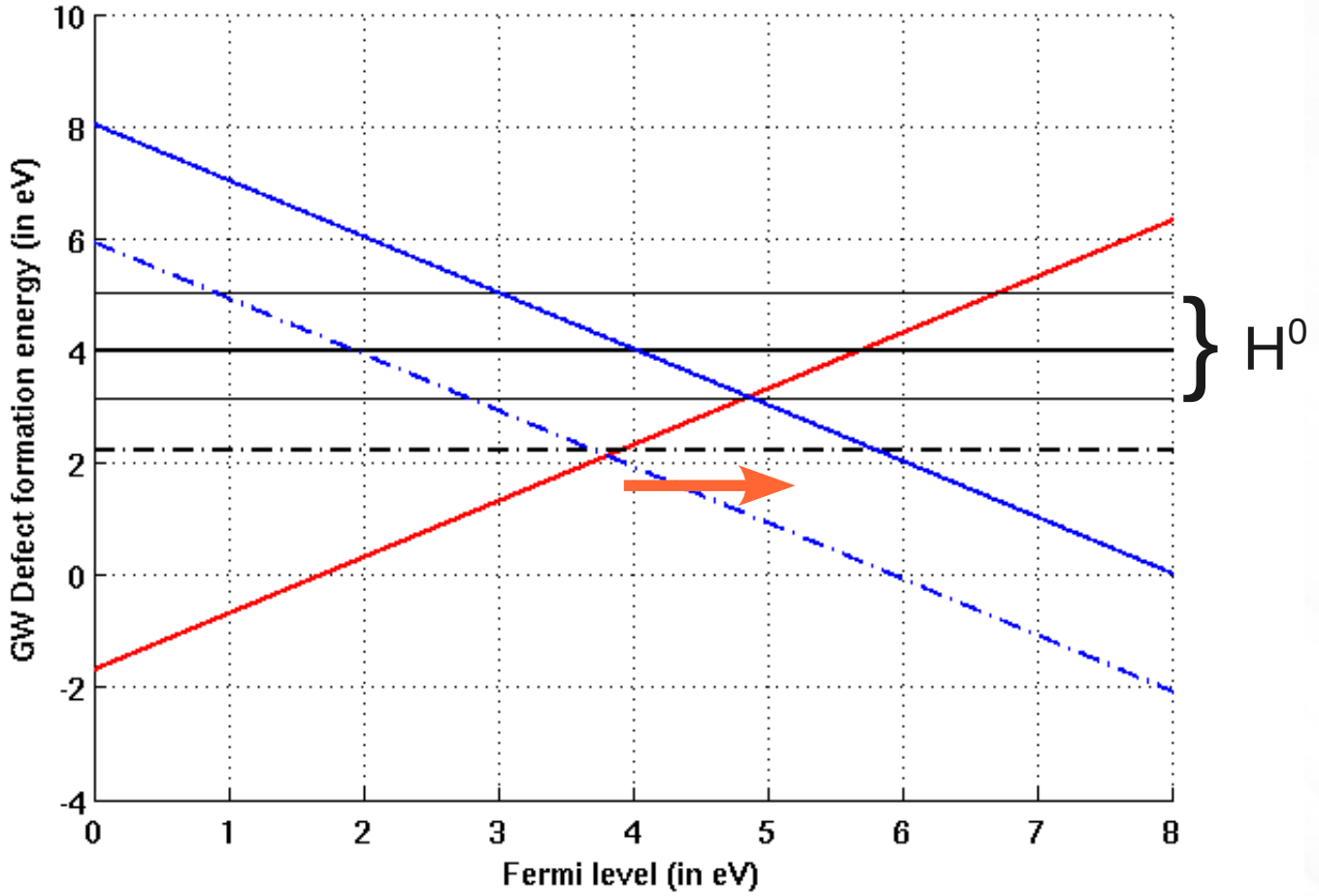
=> Self-consistency ?

=> Vertex corrections ?

=> Better starting point ?

Start from a DFT calculation with the meta-GGA functional of Tran and Blaha
Currently under testing (see poster)

“Qualitative” change in charge transition levels



=> The transition level E(+/-) is shifted to a higher Fermi energy

Conclusions

- Defect formation energies
  - in DFT-LDA
  - with a combined DFT/GW scheme
- Hydrogen formation energies still under debate
- Qualitative results
- There are still some problems to define an accurate formation energy within the GW formalism.

Acknowledgments

- Prof. X. Gonze
- Prof. G.-M. Rignanese
- Dr. M. Stankovski
- Dr. M. Giantomassi

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Thank you for your attention

GW density of states

1) Positive hydrogen

2) Addition of one electron

2) Relaxation to neutral configuration