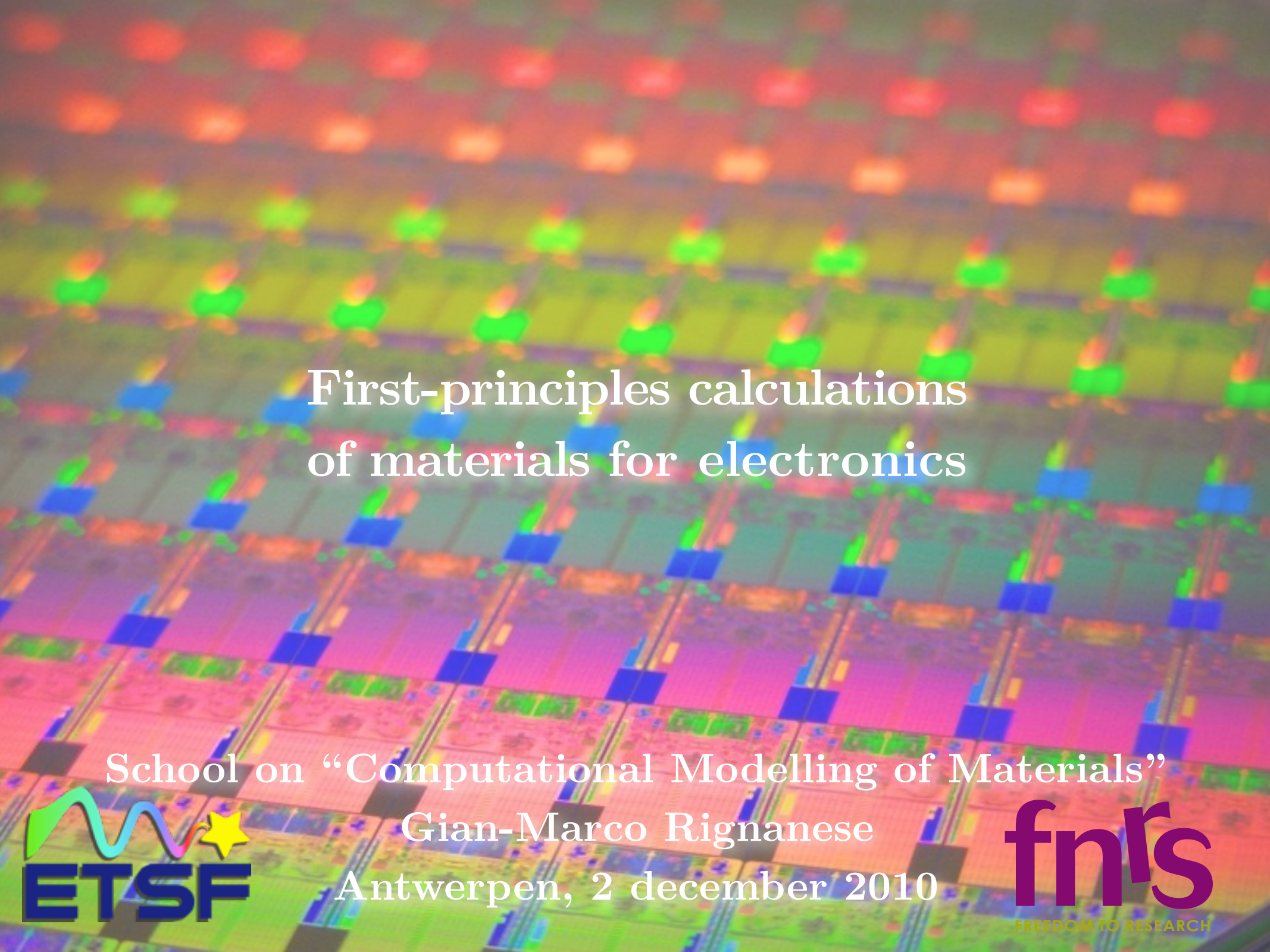


# First-principles calculations of materials for electronics

School on "Computational Modelling of Materials"

Gian-Marco Rignanese

Antwerpen, 2 december 2010

ETSF

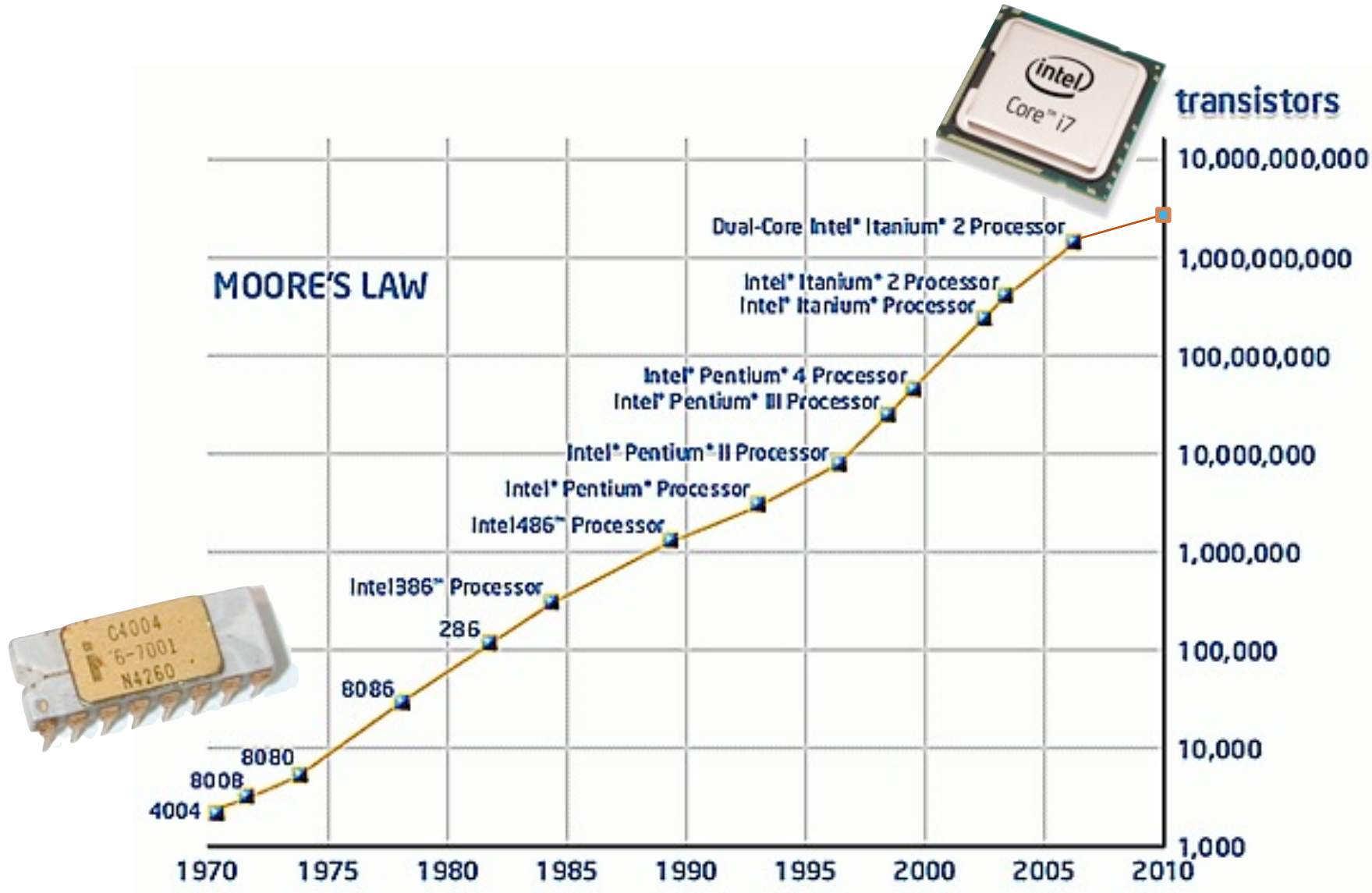
fnrs FREEDOM TO RESEARCH

# The general framework

- **Miniaturization** is the dominant trend in our every-day life:

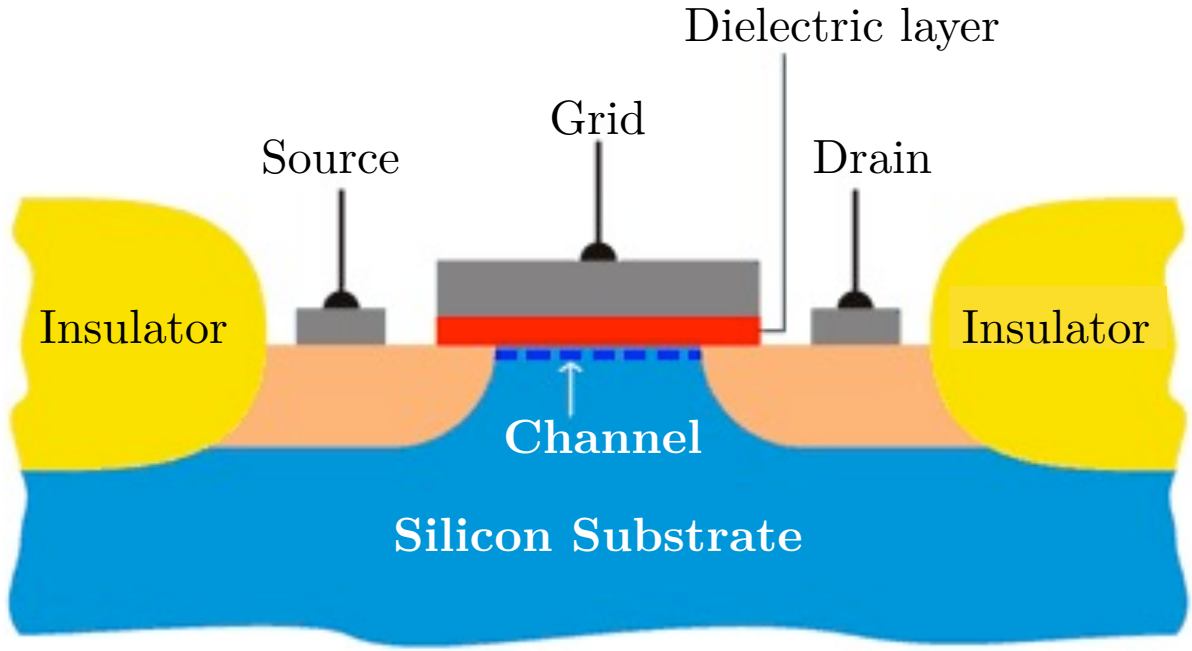
# The specific framework

- In electronics, this trend is translated into **Moore's law**:



# At the heart of electronics

- The MOS transistor :

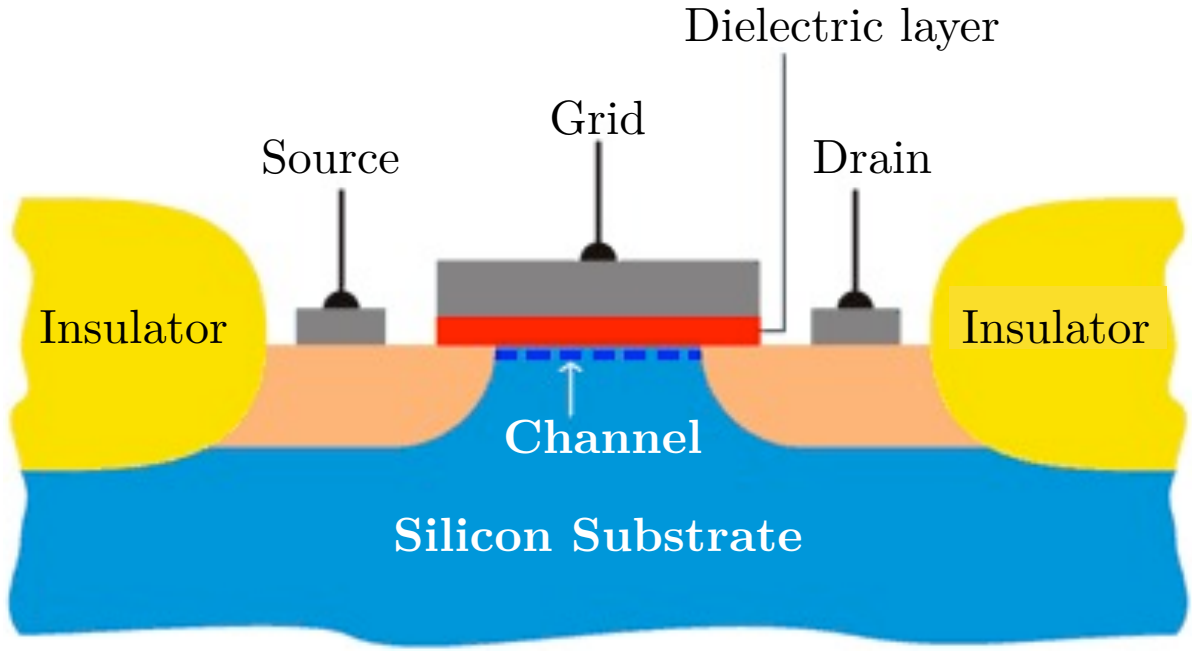



| | $L$ (nm) | $t$ (nm) |
|---|---|---|
| 2000 | 100-150 | 1.5-2.0 |
| 2008 | 45 | 1.0 |
| 2015 | 25 | 0.5 |

$L \approx$ 40-50 $t$

# The problem

- $SiO_2$ has now reached its limits:

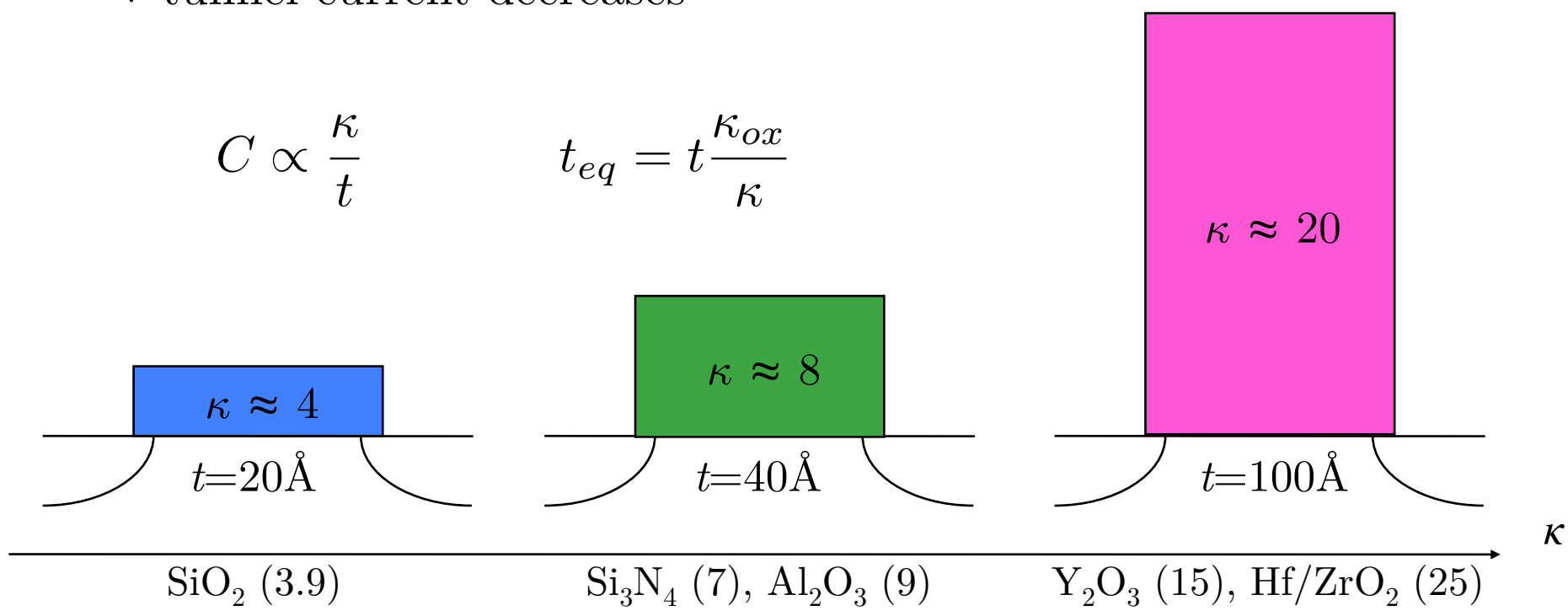



  - tunnel current through the grid oxide
  - degradation and rupture
  - penetration of dopants through the grid oxide
  - increased presence of defects

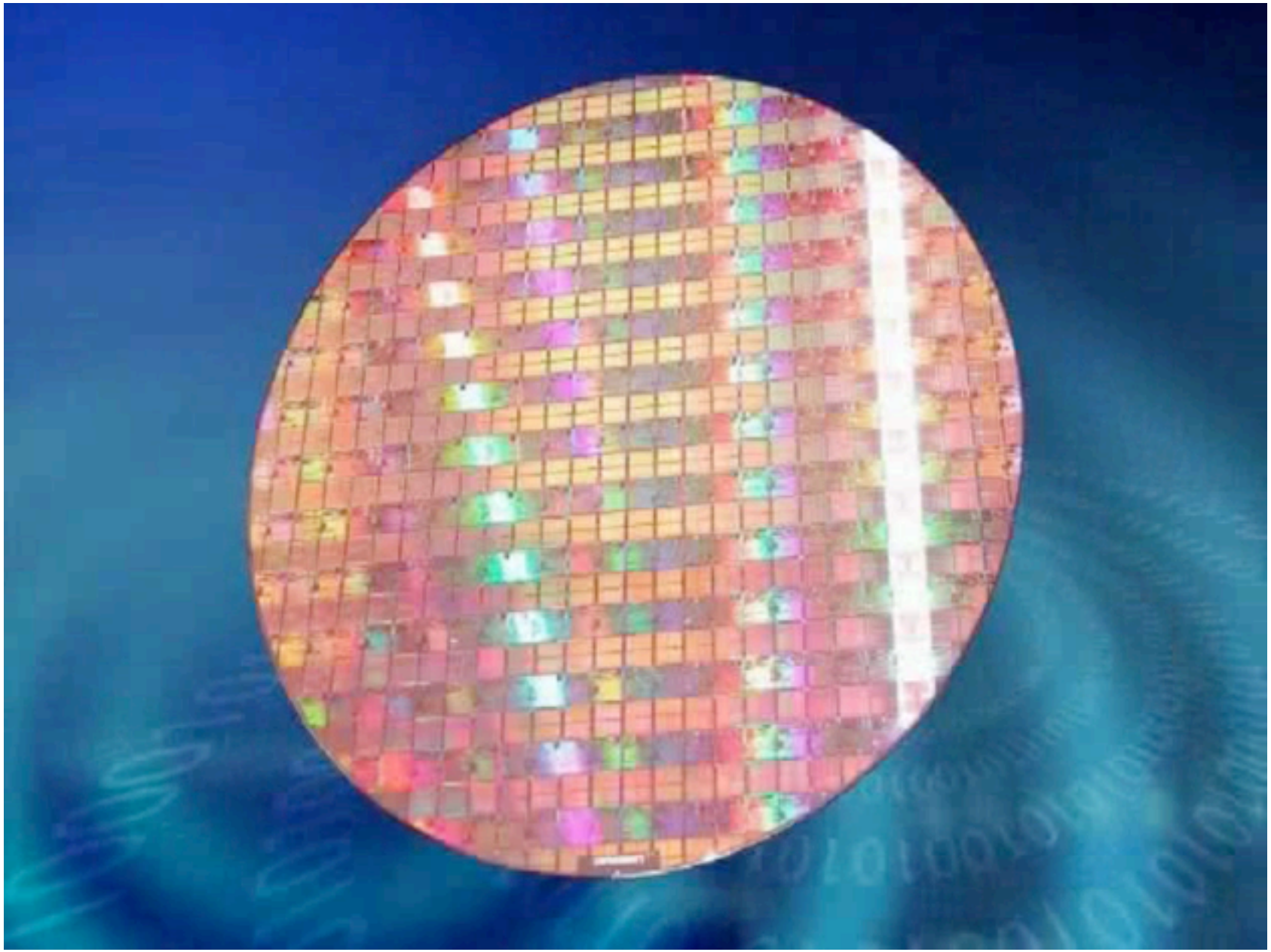
# The solution

- Dielectrics with high-permittivity (high-κ)
  - For the same **equivalent thickness** ($t_{eq}$), the **physical thickness** ($t$) can be increased when the permittivity ($\kappa$) is higher
    ⇒ tunnel current decreases

$$C \propto \frac{\kappa}{t} \qquad t_{eq} = t\frac{\kappa_{ox}}{\kappa}$$



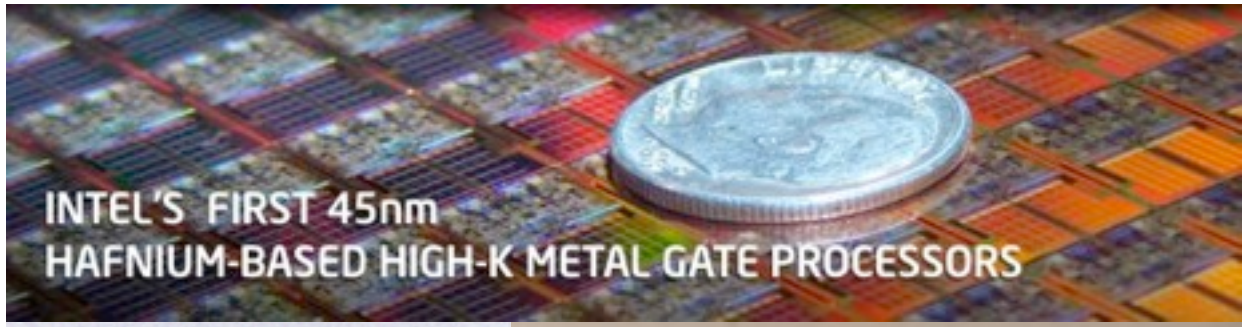
# Not such a simple change

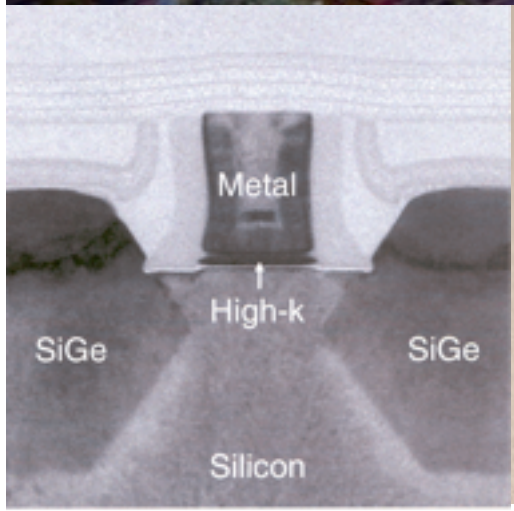


# The recent chips...

- 2008: Intel Core 2 Extreme

  "30 Million transistors fit on the head of a pin. Using an entirely new transistor formula, the processor incorporate 410 million transistors for each dual core chip, and 820 million for each quad core chip."



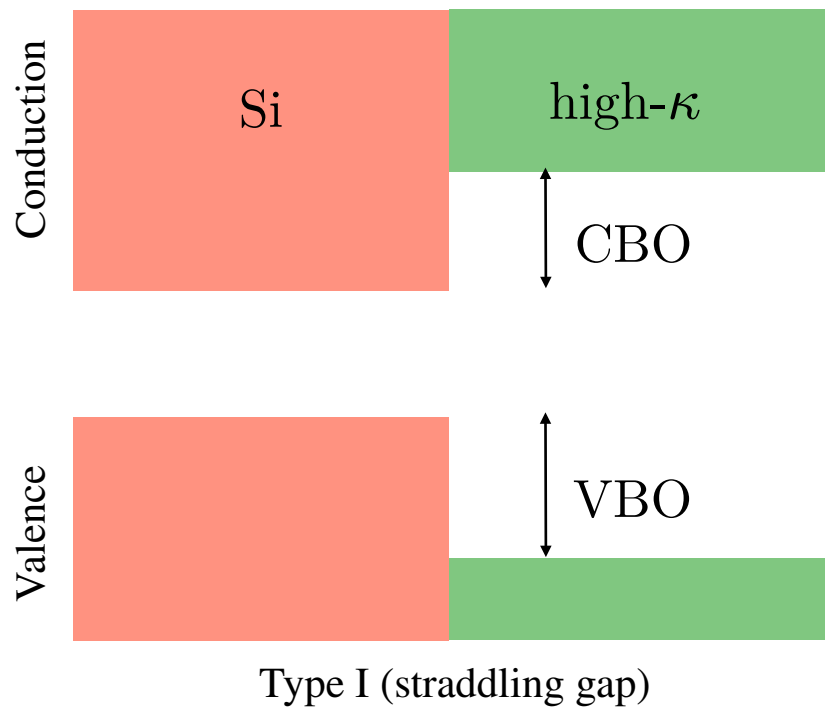



- 2010: Intel Core i7

  $L$=32 nm / six-core / 1170 million transistors

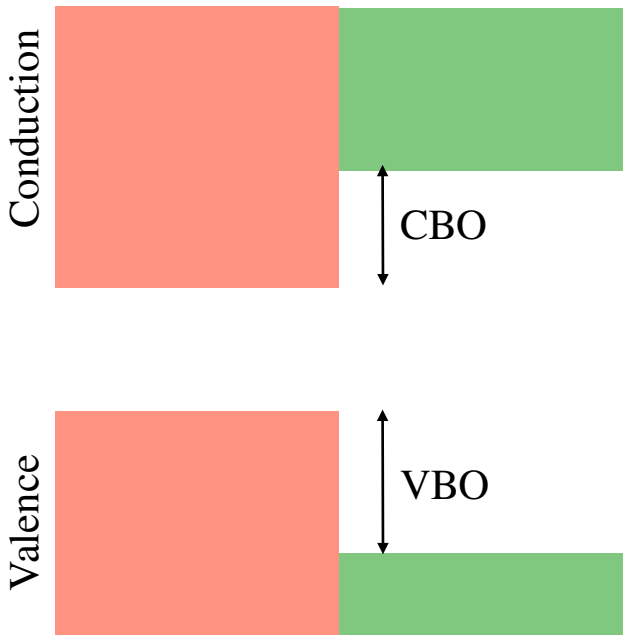
# Technical requirements

- At the interface of the high-$\kappa$ material with silicon, the valence (V) and conduction (C) **band-offsets** (BOs) should be larger than 1.0-1.5 eV to avoid $e^-$ or $h^+$ injection from Si to the high-$\kappa$.

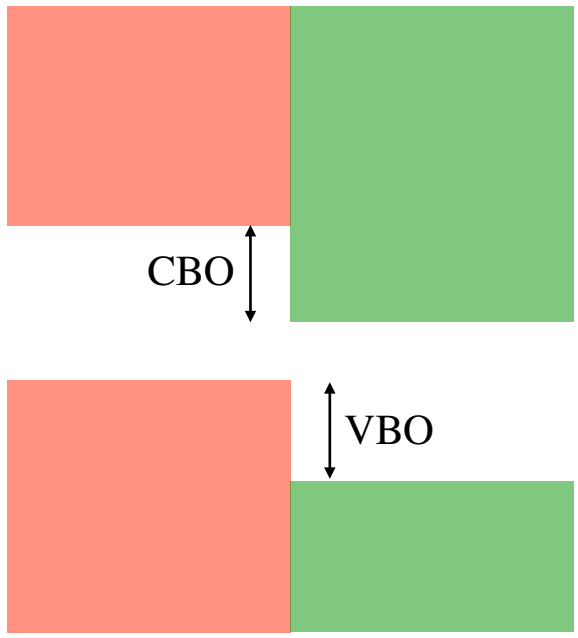


# Band offsets importance...

- Band offsets are among the most important properties of a heterostructure. Their precise knowledge is extremely important to engineer electronic and optoelectronic devices.



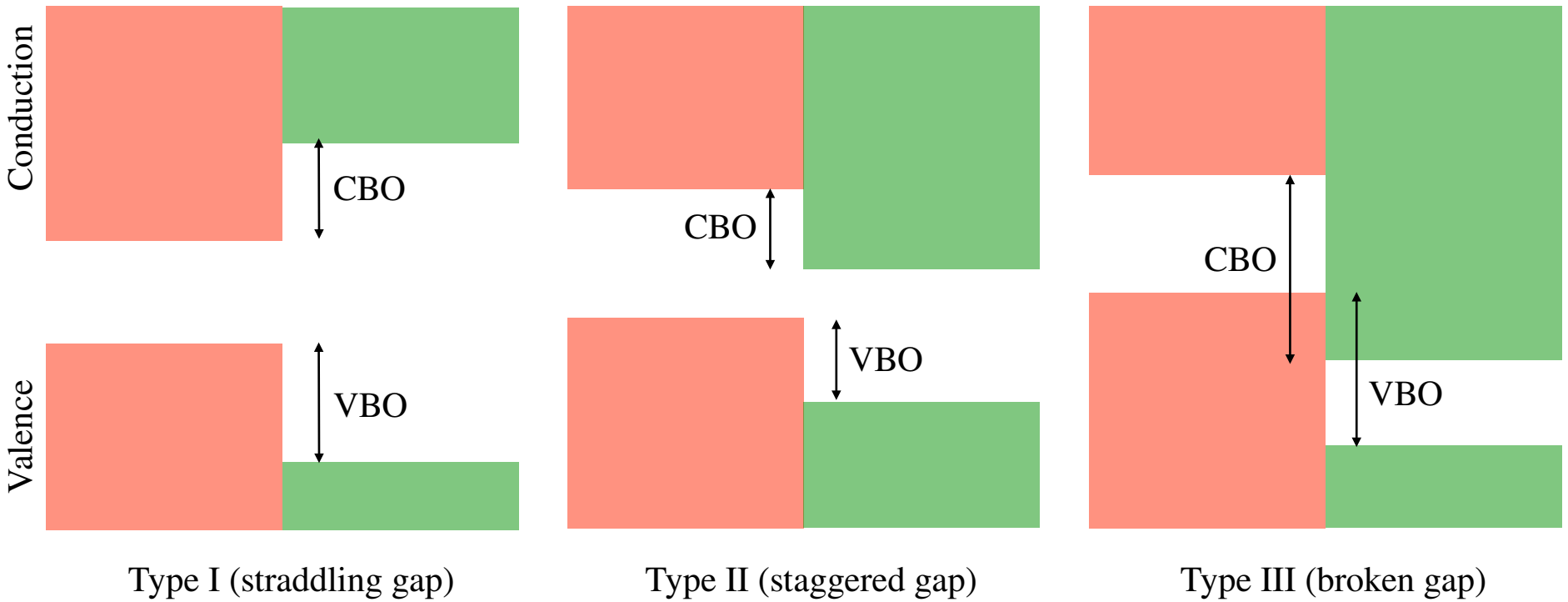

Type I (straddling gap)




Type II (staggered gap)

# Band offsets importance...

- Band offsets are among the most important properties of a heterostructure. Their precise knowledge is extremely important to engineer electronic and optoelectronic devices.



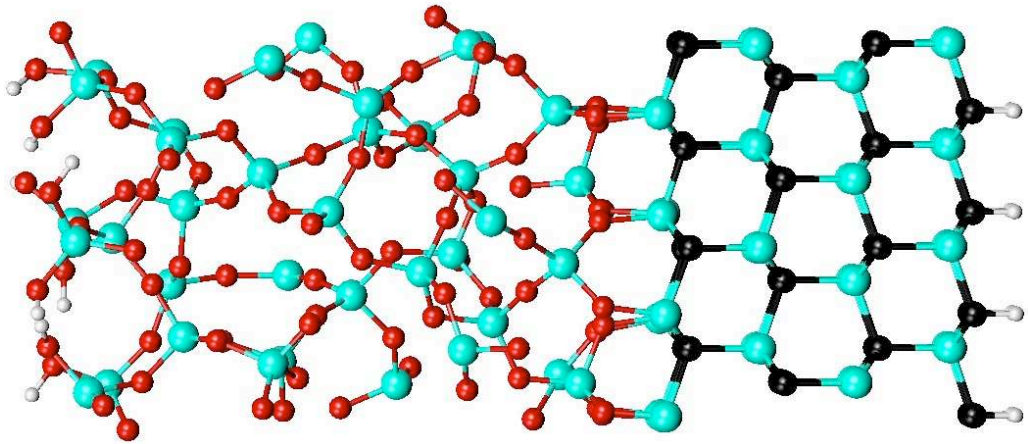
# Theoretical prediction of band offsets

- The BOs between two materials are controlled by the **charge transfer across the interface** and the resulting **interface dipoles**.
- Various semi-empirical methods have been used to estimate the BOs:
  - C. Tejedor and F. Flores, J. Phys. C 11, L19 (1977)
  - W.A. Harrison, Electronic Structure and the Properties of Solids (Freeman, San Francisco, 1980), p. 253
  - J. Tersoff, Phys. Rev. B 30, 4874 (1984)
  - J. Robertson, J. Vac. Sci. Technol. B 18, 1785 (2000)
  - P.W. Peacock and J. Robertson, J. Appl. Phys. 92, 4712 (2002)
- In contrast, density-functional theory (DFT) calculations allow one to study the variation of interface dipoles with the interface structure, **without resorting to experimental input**.

# Band offsets within DFT

- Two methods can be used to compute the band offsets within DFT.
- In the first method, the Kohn-Sham equation is solved for an interface model (supercell calculation):

$SiO_2$/SiC interface model*



(*) Taken from F. Devynck, Ph.D. Thesis, EPFL (2008), p. 42

$$\left[-\frac{1}{2}\nabla^2_{\mathbf{r}} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right]\phi_{n\mathbf{k}}(\mathbf{r}) = \epsilon_{n\mathbf{k}}\phi_{n\mathbf{k}}(\mathbf{r})$$

and the **local density of states** is computed:

$$\rho(\mathbf{r}, E) = \sum_{n\mathbf{k}} |\phi_{n\mathbf{k}}(\mathbf{r})|^2 \delta(\epsilon_{n\mathbf{k}} - E)$$

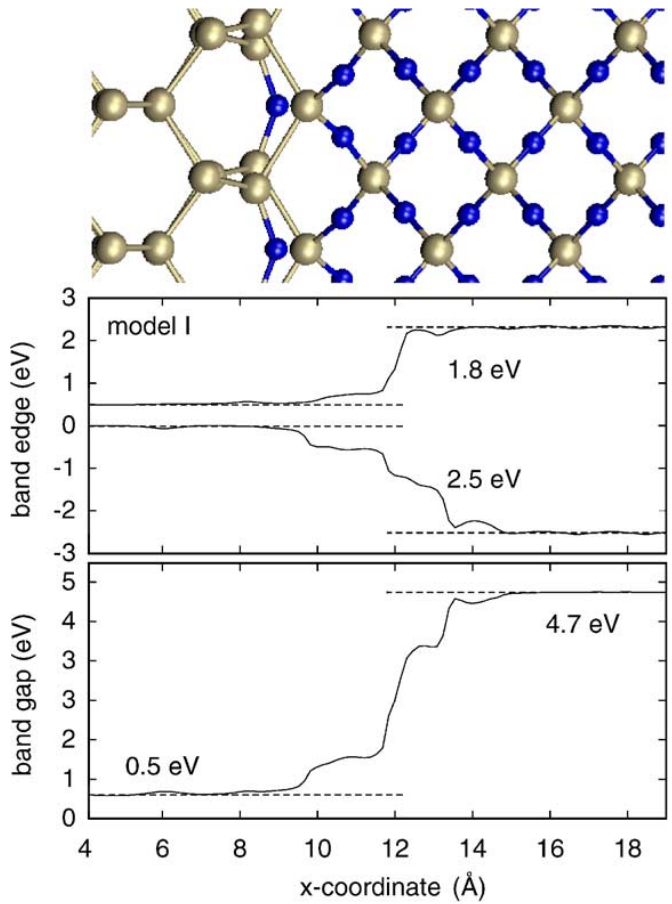
→ replace by Gaussian functions

need to check **k**-point sampling ← $n\mathbf{k}$

# Band offsets within DFT

- The local density of states is **planar averaged** by integrating the electronic density in planes parallel to the interface.

Si/$SiO_2$ interface model*

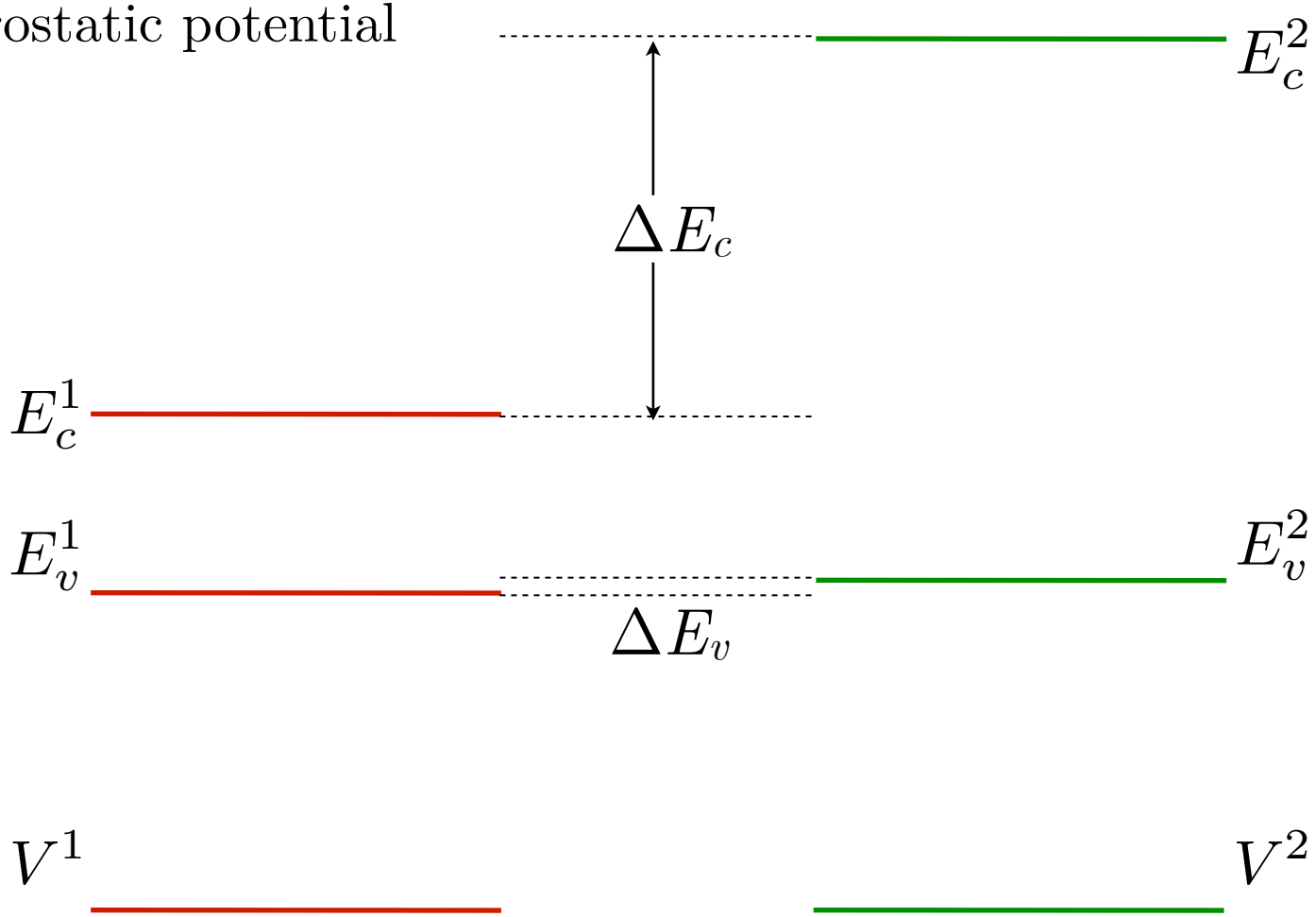



- The **local band edges** are determined by requiring that the number of states falling between the cell mid gap and the band edge equals a pre-defined threshold value.
  [T. Yamasaki *et al.*, Phys. Rev. B **63**, 115314 (2001)]
- Due to the quantum confinement, the band edges determined in this way are biased (the band gap is sightly overestimated depending on the size of the supercell).

(*) F. Giustino and A. Pasquarello, Surf. Sci. **586**, 183 (2005)

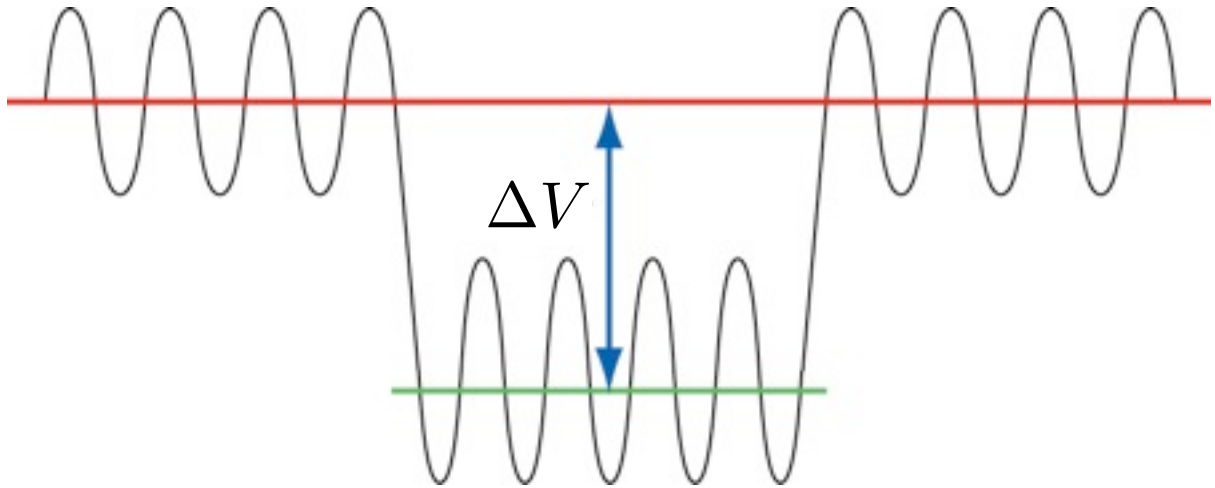
# Band offsets within DFT

- In the second method, the band offsets are divided in two terms:
  - the difference between the band edge energies in the two bulk materials $\Delta E_v$ and $\Delta E_c$, each edge being referred to the average bulk electrostatic potential

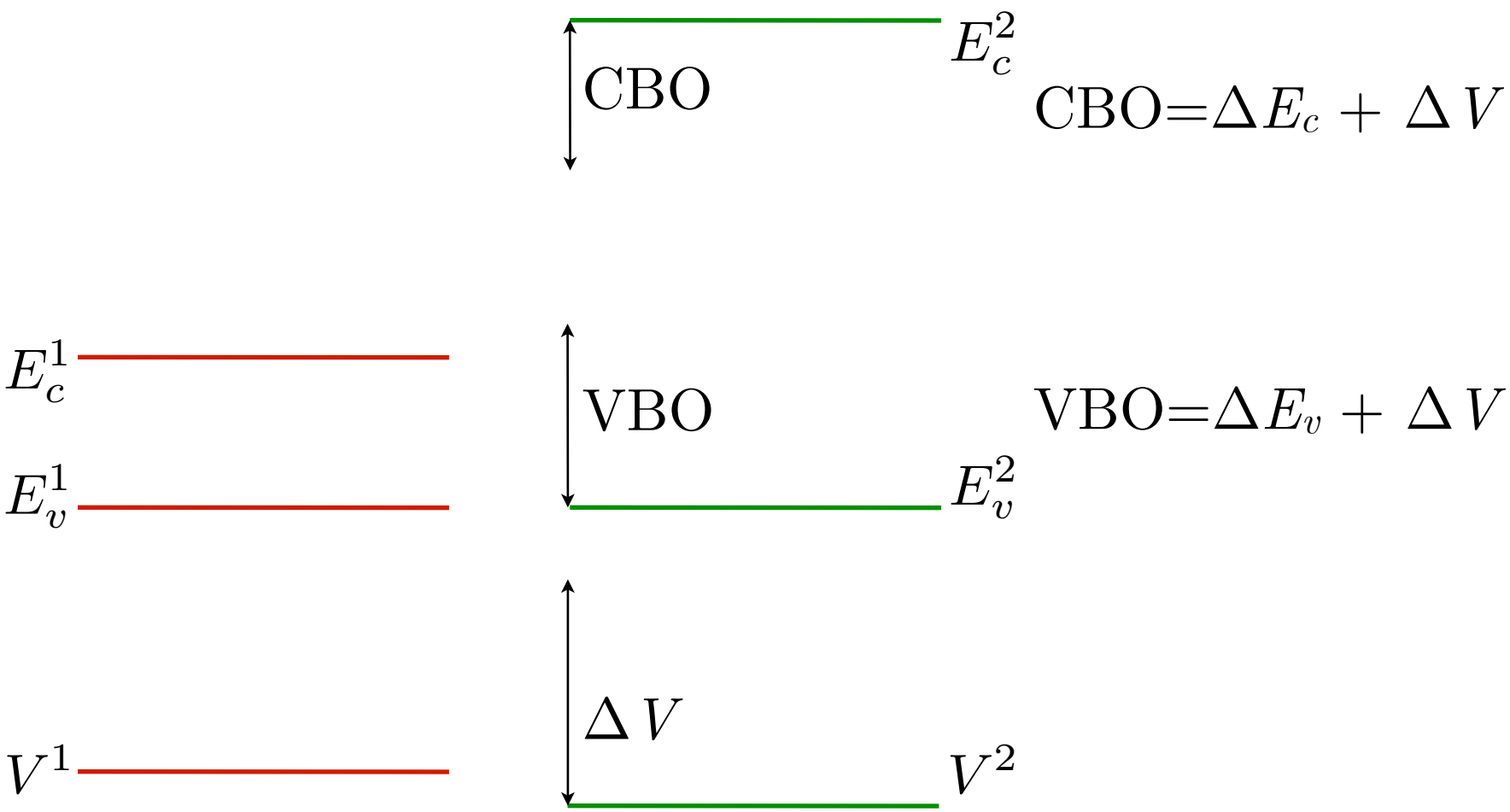


# Band offsets within DFT

- The band offsets are divided in two terms:
  - the difference between the band edge energies in the two bulk materials $\Delta E_v$ and $\Delta E_c$, each edge being referred to the average bulk electrostatic potential
  - the step $\Delta V$ in the macroscopic average of the electrostatic potential across the interface



# Band offsets within DFT



# Band offsets within DFT

PHYSICAL REVIEW B VOLUME 35, NUMBER 15 15 MAY 1987-II

## Theoretical study of band offsets at semiconductor interfaces

Chris G. Van de Walle*
*Stanford Electronics Laboratories, Stanford, California 94305*
*and Xerox Corporation, Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304*

Richard M. Martin
*Xerox Corporation, Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304*
(Received 11 August 1986)

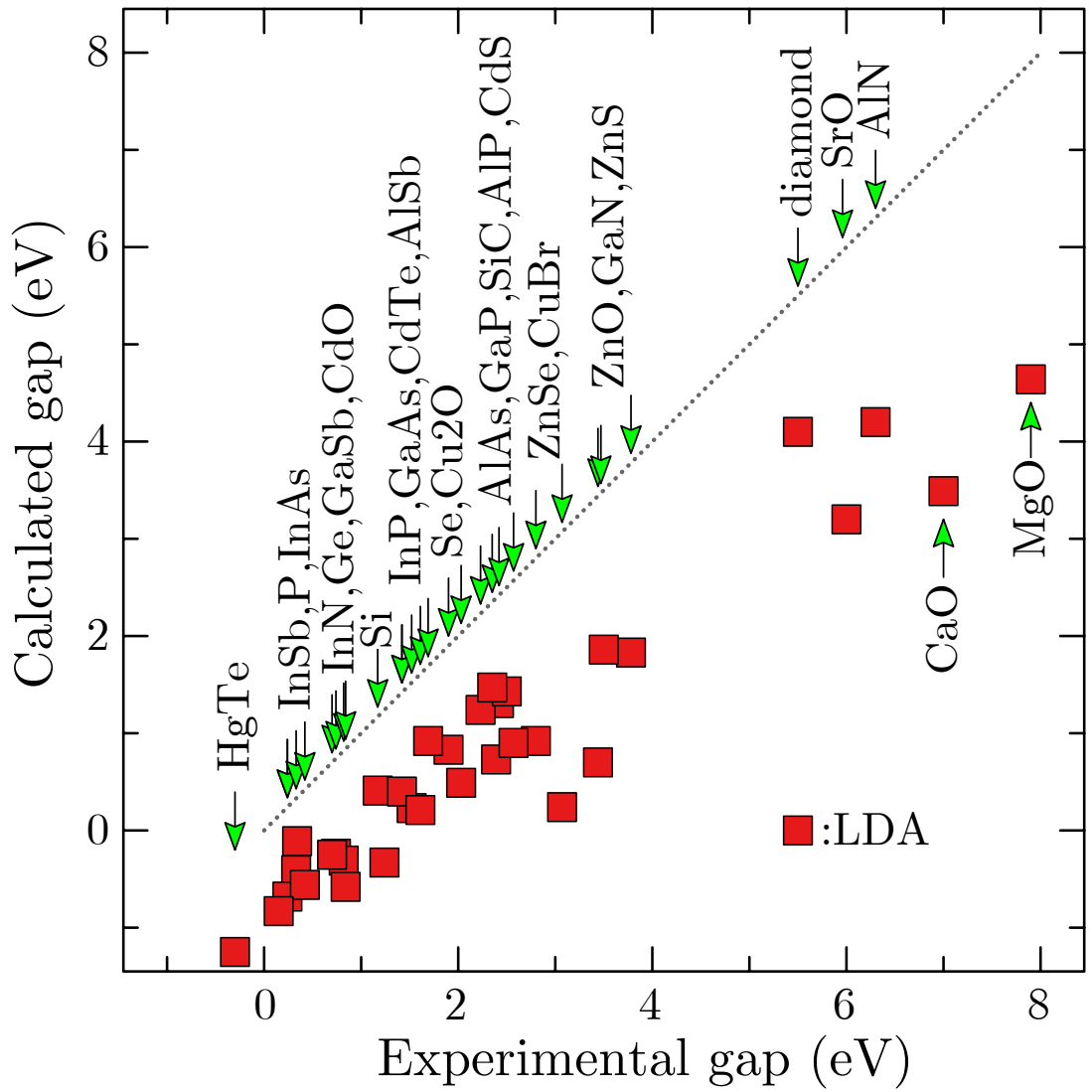
We present a first-principles approach to deriving the relative energies of valence and conduction bands at semiconductor interfaces, along with a model which permits a simple interpretation of these band offsets. Self-consistent density-functional calculations, using *ab initio* nonlocal pseudopotentials, allow us to derive the minimum-energy structure and band offsets for specific interfaces. Here we report results for a large number of lattice-matched interfaces, which are in reasonable agreement with reported experimental values.

| | $\Delta E_v$ (eV) | |
|---|---|---|
| Heterojunction | SCIC | Experiment |
| AlAs/Ge | 1.05 | 0.95[e] |
| GaAs/Ge | 0.63 | 0.56[f] |
| AlAs/GaAs | 0.37 | 0.55[g] |
| AlP/Si | 1.03 | |
| GaP/Si | 0.61 | 0.80[h] |
| AlP/GaP | 0.36 | |
| ZnSe/GaAs | 1.59 | 1.10[i] |
| ZnSe/Ge | 2.17 | 1.52[i] |
| InAs/GaSb | 0.38 | 0.51[j] |
| AlSb/GaSb | 0.38 | 0.45[k] |

It is not bad at all!!

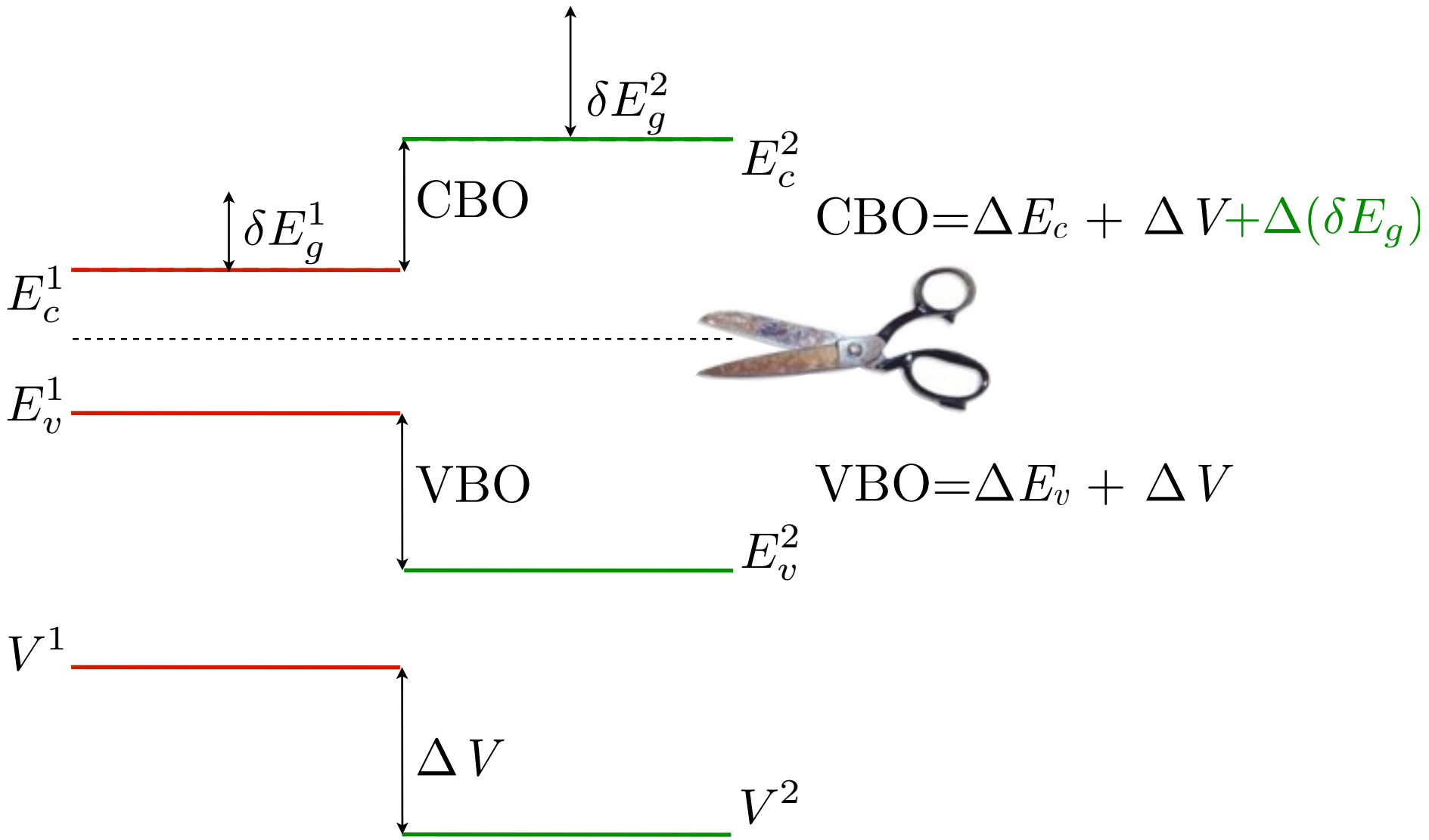
# The band-gap problem of DFT

- systematic underestimation




[adapted from van Schilfgaarde *et al.*, PRL **96**, 226402 (2006)]

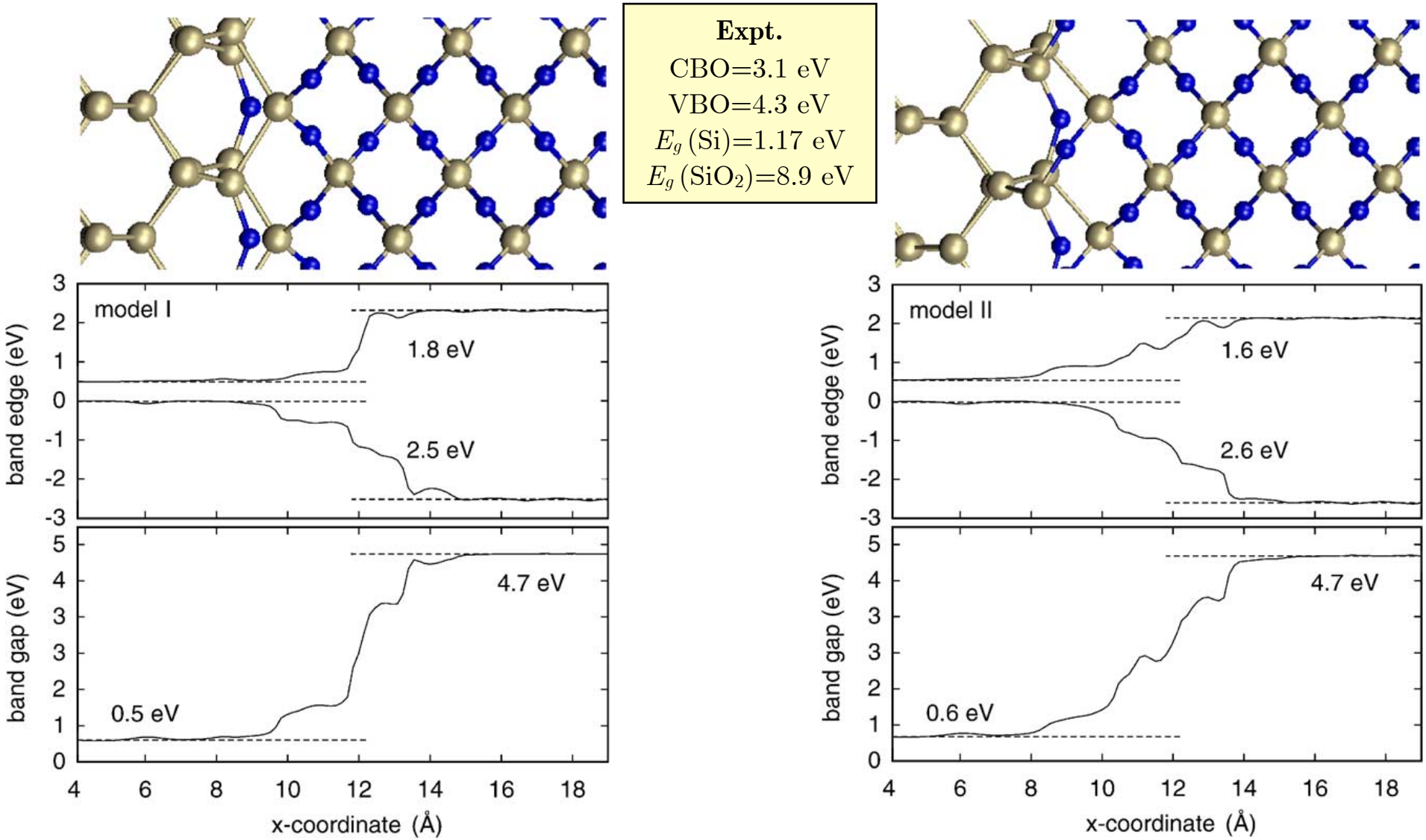
# Band offsets with a scissors-operator



# But does it really always work?

- $Si/SiO_2$ interface:

**Expt.**
CBO=3.1 eV
VBO=4.3 eV
$E_g$ (Si)=1.17 eV
$E_g$ ($SiO_2$)=8.9 eV




[Giustino & Pasquarello, Surf. Sci. **586**, 183 (2005)]

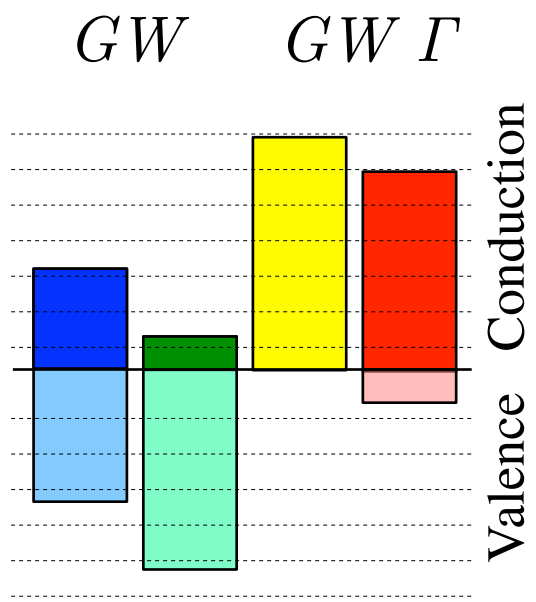
# Some justification to scissors-operator

- Till recently, $GW\Gamma$ had only been applied to Si:

  [1] Del Sole, Reining, & Godby, PRB **49**, 8024 (1994)

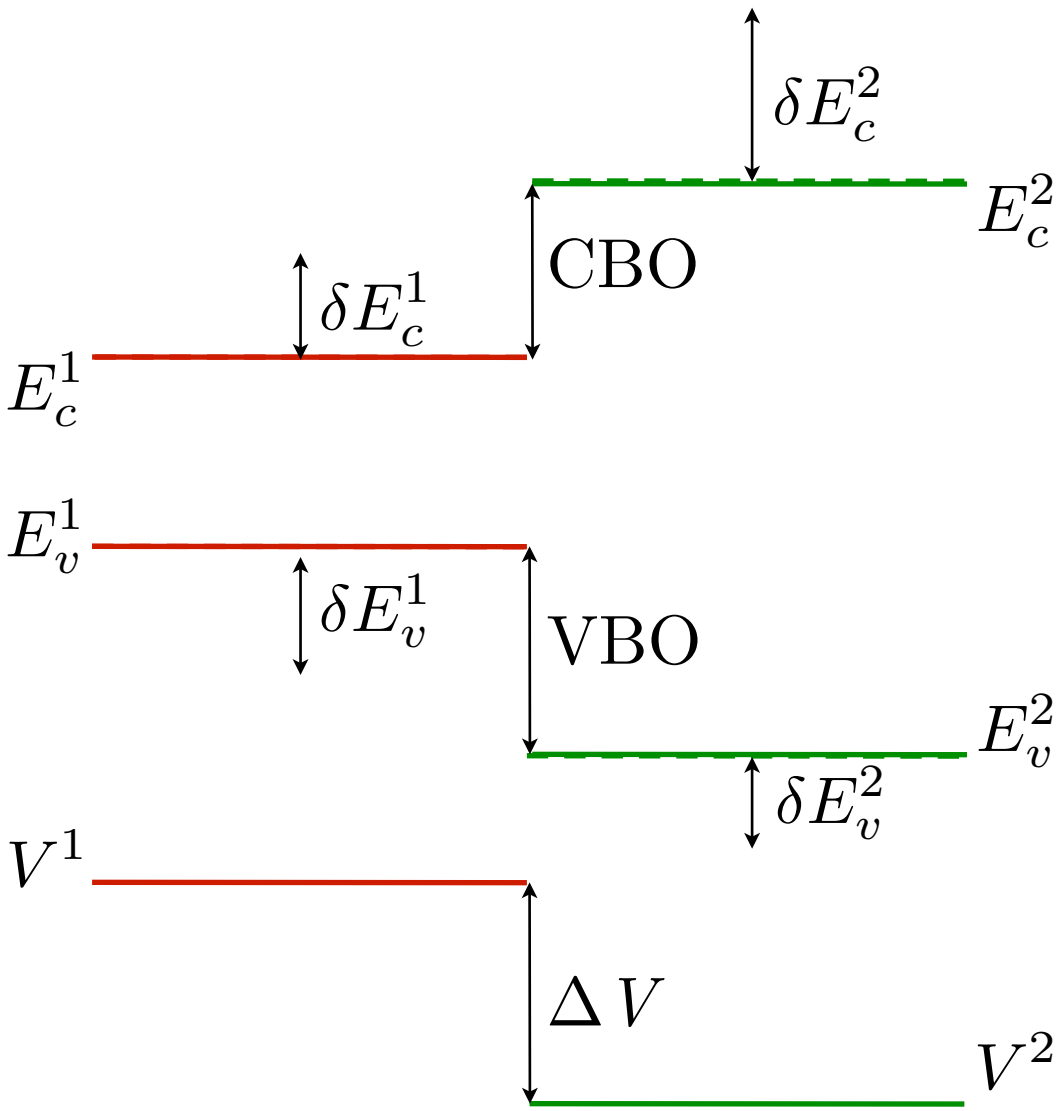
  [2] Fleszar & Hanke, PRB **56**, 10228 (1997)

| | $GW$ | | $GW\Gamma$ | |
|---|---|---|---|---|
| | Ref. [1] | Ref. [2] | Ref. [1] | Ref. [2] |
| $\delta E_v$ (eV) | −0.4 | −0.6 | +0.0 | -0.1 |
| $\delta E_c$ (eV) | +0.3 | +0.1 | +0.7 | +0.6 |
| $\delta E_g$ (eV) | +0.7 | +0.7 | +0.7 | +0.7 |




- The QP correction goes essentially on the conduction band giving credit to the "scissors-operator" approximation.

# Band offsets within MBPT




$$\mathrm{CBO}=\Delta E_c + \Delta V+\Delta(\delta E_c)$$

$$\mathrm{VBO}=\Delta E_v + \Delta V+\Delta(\delta E_v)$$

– QP corrections ($\delta E_v$ and $\delta E_c$) are accounted for based on bulk calculations

# Band offsets within MBPT

PHYSICAL REVIEW B VOLUME 43, NUMBER 17 15 JUNE 1991-I

## Quasiparticle band structure of thirteen semiconductors and insulators

Xuejun Zhu and Steven G. Louie
*Department of Physics, University of California, Berkeley, California 94720*
*and Materials Science Division, Lawrence Berkeley Laboratory, Berkeley, California 94720*
(Received 17 December 1990; revised manuscript received 21 March 1991)

| | LDA | Δ | QP | Expt. |
|---|---|---|---|---|
| AlAs-Ge | 1.05 | 0.20 | 1.25 | 0.95[a] |
| GaAs-Ge | 0.63 | 0.09 | 0.72 | 0.56[b] |
| AlAs-GaAs | 0.37 | 0.11 | 0.48 | 0.55[c] |
| AlP-Si | 1.03 | 0.17 | 1.20 | |
| GaP-Si | 0.61 | 0.07 | 0.68 | 0.80[d] |
| AlP-GaP | 0.36 | 0.10 | 0.46 | |
| InAs-GaSb | 0.38 | 0.11 | 0.49 | 0.51[e] |
| AlSb-GaSb | 0.38 | 0.09 | 0.47 | 0.45[f] |

The LDA has been found to be unable to give accurate band offsets for semiconductor interfaces.

Also, much attention needs to be paid to the accuracy of the experimental results because of the technical difficulties in measuring the valence-band offsets at semiconductor interfaces.

In general, the results with the many-body corrections for the valence-band offsets provide a better agreement with experiments.

# Frequency dependence of $W$

- Within $GW$, the frequency dependence of the dynamically screened Coulomb potential $W$ is most often approximated using various plasmon pole models (PPMs):

$$\text{Re } \epsilon^{-1}(\omega) = A\delta(\omega - \tilde{\omega}) \qquad \text{Im } \epsilon^{-1}(\omega) = 1 + \frac{\Omega^2}{\omega^2 - \tilde{\omega}^2}$$


[HL] M.S. Hybertsen and S.G. Louie, Phys. Rev. B **34**, 5390 (1986),

[vdLH] W. von der Linden and P. Horsch, Phys. Rev. B **37**, 8351 (1988),

[GN] R.W. Godby and R.J. Needs, Phys. Rev. Lett. **62**, 1169 (1989),

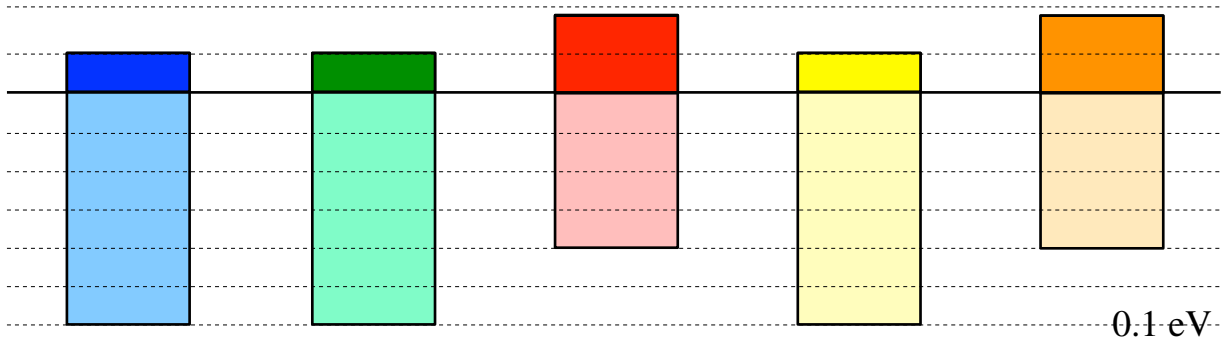
[EF] G.E. Engel and B. Farid, Phys. Rev. B **47**, 15931 (1993).


- The advantage is not only to reduce the computational load, but also to obtain an analytic expression for the self-energy.

# Frequency dependence of $W$

- However, we observed that $\delta E_v$ and $\delta E_c$ may vary from one PPM to another:

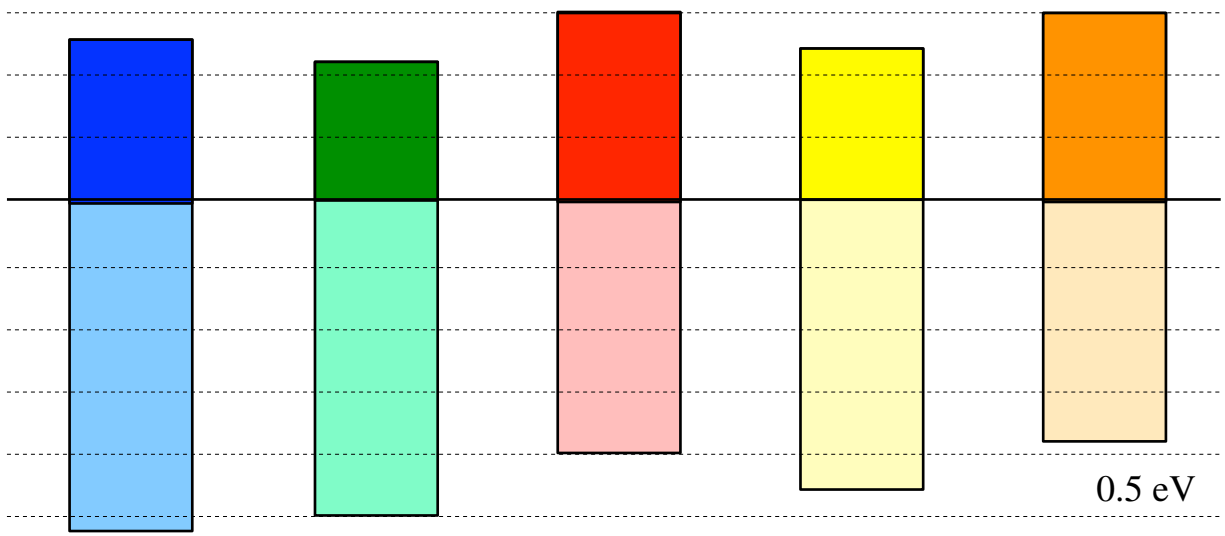
| | | HL | vdLH | GN | EF | no PPM |
|---|---|---|---|---|---|---|
| Si | $\delta E_v$ (eV) | −0.6 | −0.6 | −0.4 | −0.6 | −0.4 |
| | $\delta E_c$ (eV) | +0.1 | +0.1 | +0.2 | +0.1 | +0.2 |



# Frequency dependence of $W$

- However, we observed that $\delta E_v$ and $\delta E_c$ may vary from one PPM to another:

| | | HL | vdLH | GN | EF | no PPM |
|---|---|---|---|---|---|---|
| Si | $\delta E_v$ (eV) | −0.6 | −0.6 | −0.4 | −0.6 | −0.4 |
| | $\delta E_c$ (eV) | +0.1 | +0.1 | +0.2 | +0.1 | +0.2 |
| c-$SiO_2$ | $\delta E_v$ (eV) | −2.6 | −2.5 | −2.0 | −2.3 | −1.9 |
| | $\delta E_c$ (eV) | +1.3 | +1.1 | +1.5 | +1.2 | +1.5 |



# Frequency dependence of $W$

- However, we observed that $\delta E_v$ and $\delta E_c$ may vary from one PPM to another:

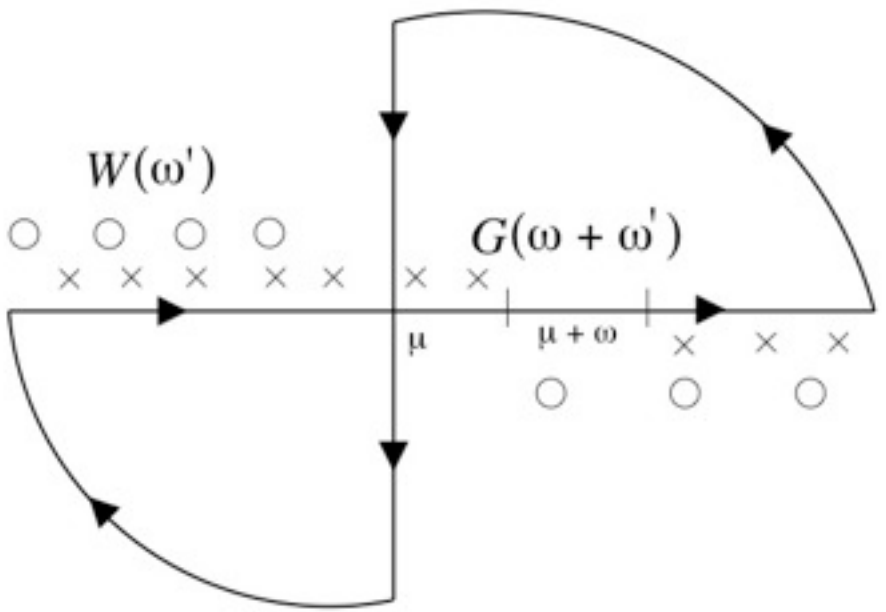
| | | HL | vdLH | GN | EF | no PPM |
|---|---|---|---|---|---|---|
| Si | $\delta E_v$ (eV) | −0.6 | −0.6 | −0.4 | −0.6 | −0.4 |
| | $\delta E_c$ (eV) | +0.1 | +0.1 | +0.2 | +0.1 | +0.2 |
| c-$SiO_2$ | $\delta E_v$ (eV) | −2.6 | −2.5 | −2.0 | −2.3 | −1.9 |
| | $\delta E_c$ (eV) | +1.3 | +1.1 | +1.5 | +1.2 | +1.5 |

- The frequency dependence of $W$ needs to be taken into account explicitly (contour deformation integration technique [S. Lebègue, B. Arnaud, M. Alouani and P.E. Bloechl, Phys. Rev. B **67**, 155208 (2003)]).

- Note that the Godby-Needs [GN] PPM leads to $\delta E_v$ and $\delta E_c$ in excellent agreement with the results without PPM.

# Frequency dependence of $W$

- We use the deformed contour integration technique [S. Lebègue, B. Arnaud, M. Alouani and P.E. Bloechl, Phys. Rev. B **67**, 155208 (2003)] to obtain the explicit frequency dependence.
- The integral along the real axis can be calculated from the integral over the contour depicted below: the integral along the imaginary axis requires less points ($\Sigma$ is smoother) and the sum of the poles of $\Sigma$ can be evaluated exactly.




× poles of $G$

○ poles of $W$

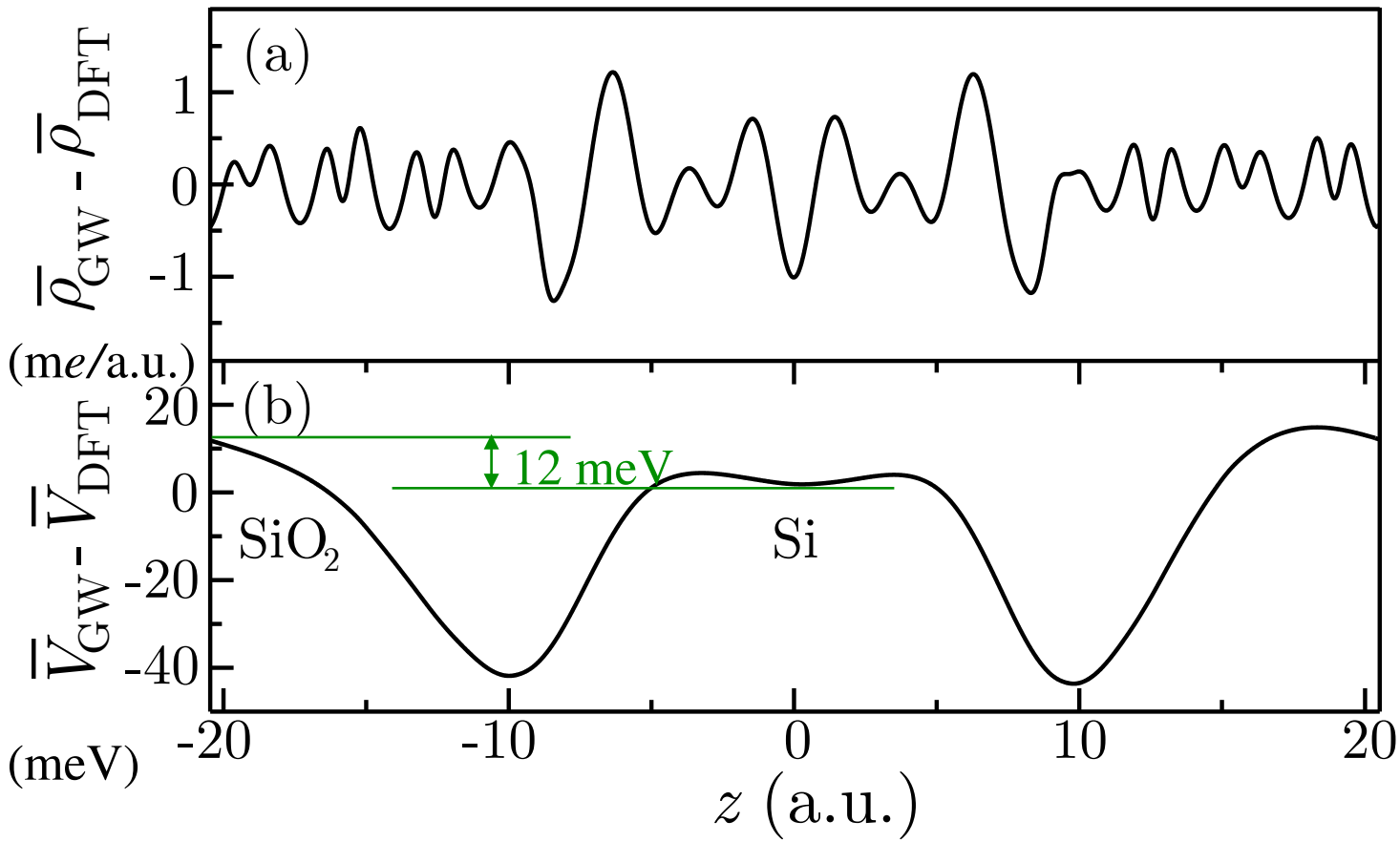
# $Si/SiO_2$ interface

| | Si | | | c-$SiO_2$ | | | s-$SiO_2$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | *GW* | *GW*Γ | QS*GW* | *GW* | *GW*Γ | QS*GW* | *GW* | *GW*Γ | QS*GW* |
| $\delta E_v$ (eV) | −0.4 | +0.1 | −0.6 | −1.9 | −1.3 | −2.8 | −1.9 | −1.3 | −2.8 |
| $\delta E_c$ (eV) | +0.2 | +0.7 | +0.2 | +1.5 | +1.8 | +1.3 | +1.4 | +1.8 | +1.1 |
| $\delta E_g$ (eV) | +0.6 | +0.6 | +0.8 | +3.4 | +3.1 | +4.1 | +3.3 | +3.1 | +3.9 |

- Compared to $GW$, the vertex Γ reduces (increases) the correction of the valence (conduction) band. But, the QP corrections can **not** be accounted for by **a simple scissors-operator**!
- The DFT band gap for $SiO_2$ is 5.4 eV. Hence, the QP corrections lead to $E_g = 8.5$ eV($GW\Gamma$)-8.9 eV ($GW$) in very good agreement with the experimental value $E_g = 8.9$ eV. QSGW overestimates the gap!

# $Si/SiO_2$ interface

- What about $\Delta V$? Is the DFT description enough?
- We performed a QSGW calculation on an interface model and checked the change in the density and the electrostatic potential.



# $Si/SiO_2$ interface

| | unstrained | | | | strained | | | |
|---|---|---|---|---|---|---|---|---|
| | DFT | *GW* | *GW* $\Gamma$ | QS*G* | *GW* | *GW* $\Gamma$ | QS*G* | *Expt.* |
| VBO (eV) | 2.5 | 4.0 | 3.9 | 4.7 | 4.0 | 3.9 | 4.7 | 4.3 |
| CBO (eV) | 1.8 | 3.1 | 2.9 | 2.9 | 3.1 | 2.9 | 2.7 | 3.1 |

- The agreement with experiment is very good.
- Compared to $GW$, the vertex $\Gamma$ seems not to affect the offsets: the effects on the two sides of the interface cancel.
  It is still an open question whether this is always true.
- The QS$GW$ results present a larger deviation from experiments.

Publication



# Band Offsets at the $Si/SiO_2$ Interface from Many-Body Perturbation Theory

R. Shaltaf,[1] G.-M. Rignanese,[1] X. Gonze,[1] Feliciano Giustino,[2,3,*] and Alfredo Pasquarello[2,3]

[1]*European Theoretical Spectroscopy Facility (ETSF) and Unité Physico-Chimie et de Physique des Matériaux (PCPM), Université Catholique de Louvain, 1 Place Croix du Sud, B-1348 Louvain-la-Neuve Belgique*

[2]*Ecole Polytechnique Fédérale de Lausanne (EPFL), Institute of Theoretical Physics, CH-1015 Lausanne, Switzerland*

[3]*Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), CH-1015 Lausanne, Switzerland*

(Received 5 July 2007; published 5 May 2008)

We use many-body perturbation theory, the state-of-the-art method for band-gap calculations, to compute the band offsets at the $Si/SiO_2$ interface. We examine the adequacy of the usual approximations in this context. We show that (i) the separate treatment of band structure and potential lineup contributions, the latter being evaluated within density-functional theory, is justified, (ii) most plasmon-pole models lead to inaccuracies in the absolute quasiparticle corrections, (iii) vertex corrections can be neglected, and (iv) eigenenergy self-consistency is adequate. Our theoretical offsets agree with the experimental ones within 0.3 eV.

DOI: 10.1103/PhysRevLett.100.186401 PACS numbers: 71.10.−w, 73.40.Ty, 85.40.−e, 85.60.−q

# $Si/ZrO_2$ and $Si/HfO_2$ interfaces

- Many DFT studies exist:


[1] V. Fiorentini and G. Gulleri, Phys. Rev. Lett. **89**, 266101 (2002)

[2] Y. F. Dong *et al.*, Phys. Rev. B **72**, 045327 (2005)

[3] R. Puthenkovilakam, E. A. Carter, and J. P. Chang, Phys. Rev. B **69**, 155329 (2004)

[4] R. Puthenkovilakam and J. P. Chang, J. Appl. Phys. **96**, 2701 (2004)

[5] P. W. Peacock and J. Robertson, Phys. Rev. Lett. **92**, 057601 (2004)

[6] P. W. Peacock, K. Xiong, K. Tse, and J. Robertson, Phys. Rev. B **73**, 075328 (2006)


- VBO $\approx$ 2.5-3.9 eV surprisingly good agreement with expts. (2.9-3.7 eV)
  CBO $\approx$ 1.5-2.0 eV (using a scissors-operator)

- In Ref. [1], $GW$ corrections have been added taken from:


[7] X. Zhu and S. G. Louie, Phys. Rev. B **43**, 14 142 (1991) $\rightarrow$ for Si

[8] B. Kralik, E. K. Chang, and S. G. Louie, Phys. Rev. B **57**, 7027 (1998) $\rightarrow$ for $ZrO_2$


  $\delta$VBO=+1.1 eV leading to VBO $\approx$ 3.7-4.7 eV and CBO $\approx$ 0.1-1.1 eV

# $Si/ZrO_2$ and $Si/HfO_2$ interfaces

- $GW_0$ corrections for the bulk materials:

| | Si | t-$ZrO_2$ | s-$ZrO_2$ | t-$HfO_2$ | s-$HfO_2$ |
|---|---|---|---|---|---|
| $\delta E_v$ (eV) | −0.4 | −0.4 | −0.3 | −0.4 | −0.4 |
| $\delta E_c$ (eV) | +0.2 | +1.4 | +1.5 | +1.5 | +1.6 |
| $\delta E_g$ (eV) | +0.6 | +1.8 | +1.8 | +1.9 | +2.0 |

- $GW_0$ corrections to the band offsets:

| | unstrained | | strained | |
|---|---|---|---|---|
| | $Si/ZrO_2$ | $Si/HfO_2$ | $Si/ZrO_2$ | $Si/HfO_2$ |
| $\delta$VBO (eV) | +0.0 | +0.1 | +0.0 | +0.0 |
| $\delta$CBO (eV) | +1.2 | +1.3 | +1.3 | +1.4 |

- The corrections to the valence band are similar on both sides of the interface. This explains the agreement of DFT VBO with experiments and justifies the use of a scissors-operator.

# $Si/ZrO_2$ and $Si/HfO_2$ interfaces

- $GW_0$ corrections to the band offsets:

| | unstrained $Si/ZrO_2$ | |
|---|---|---|
| | This work | Ref. [1] |
| $\delta$VBO (eV) | +0.0 | +1.1 |
| $\delta$CBO (eV) | +1.2 | +0.4 |

- $GW_0$ corrections for the bulk materials:

| | Si | | t-$ZrO_2$ | |
|---|---|---|---|---|
| | This work | Ref. [1] | This work | Ref. [1] |
| $\delta E_v$ (eV) | −0.4 | -0.2 | −0.4 | −1.3 |
| $\delta E_c$ (eV) | +0.2 | +0.4 | +1.4 | +0.8 |
| $\delta E_g$ (eV) | +0.6 | +0.6 | +1.8 | +2.1 |

- The differences in the $GW_0$ corrections are due to the use of different plasmon poles.

# Publication

PHYSICAL REVIEW B **81**, 035330 (2010)

# Quasiparticle calculations of the electronic properties of $ZrO_2$ and $HfO_2$ polymorphs and their interface with Si

Myrta Grüning,* Riad Shaltaf,† and Gian-Marco Rignanese
*European Theoretical Spectroscopy Facility (ETSF) and Unité PCPM, Université Catholique de Louvain, Place Croix du Sud 1, 1348 Louvain-la-Neuve, Belgium*

(Received 24 September 2009; revised manuscript received 9 December 2009; published 21 January 2010)

Quasiparticle calculations are performed to investigate the electronic band structures of various polymorphs of Hf and Zr oxides. The corrections with respect to density-functional-theory results are found to depend only weakly on the crystal structure. Based on these bulk calculations as well as those for bulk Si, the effect of quasiparticle corrections is also investigated for the band offsets at the interface between these oxides and Si assuming that the lineup of the potential at the interface is reproduced correctly within density-functional theory. On the one hand, the valence-band offsets are practically unchanged with a correction of a few tenths of electron volts. On the other hand, conduction-band offsets are raised by 1.3–1.5 eV. When applied to existing calculations for the offsets at the density-functional-theory level, our quasiparticle corrections provide results in good agreement with the experiment.

DOI: 10.1103/PhysRevB.81.035330 PACS number(s): 73.40.Ty, 73.40.Lq, 71.10.−w, 85.40.−e

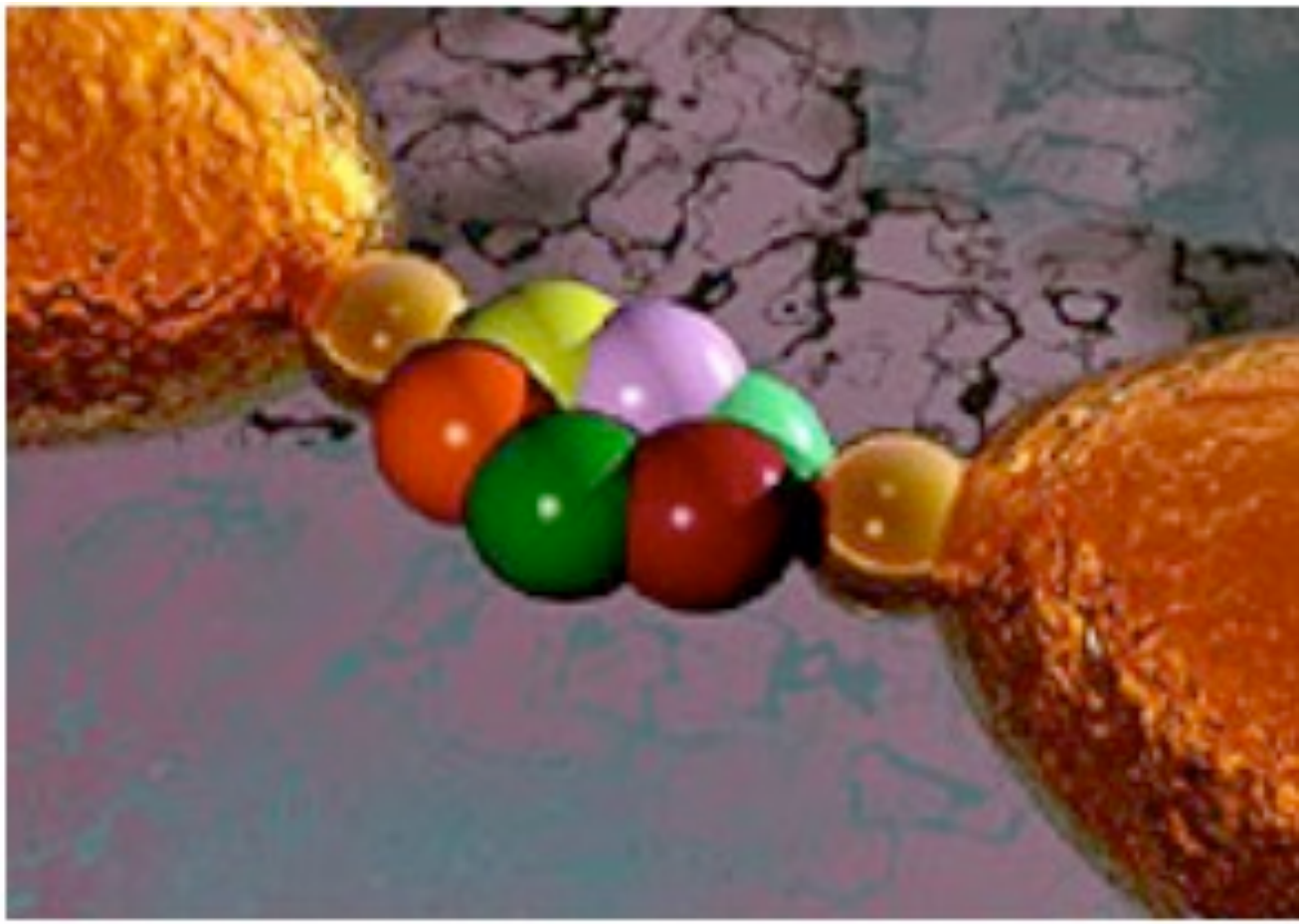
# Conclusions

- Accurate band offsets can be obtained using MBPT
  - band-structure and potential lineup contributions can be treated separately:
    - the **potential lineup** evaluated **within DFT** is reasonable
    - **quasiparticle corrections for the bulk materials** are the only additional ingredients that are required when DFT calculations of the VBO and CBO already exist
  - **WARNING:**
    most PPMs lead to inaccuracies in the absolute quasiparticle corrections
  - vertex corrections can be neglected (to be confirmed)
  - eigenenergy self-consistency is adequate

# Single molecule junctions...

# the transistors of the future?

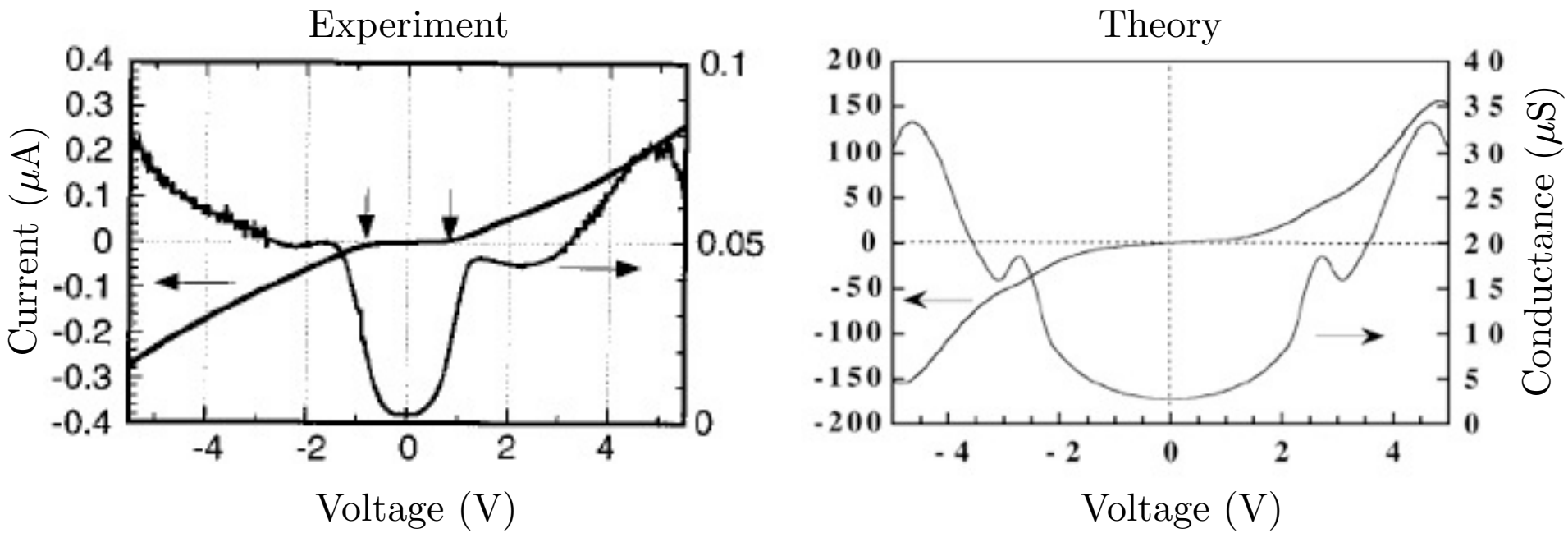
- Can we predict the $I$-$V$ curves from theoretical calculations?



http://www.eng.yale.edu/reedlab/

# Motivation

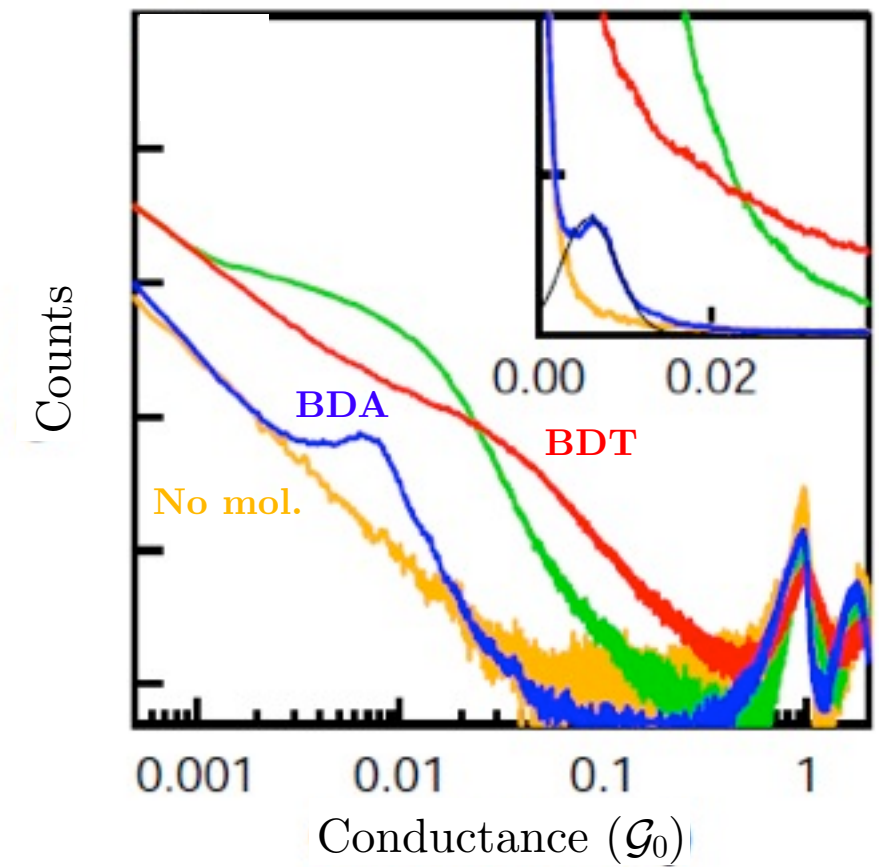
- The DFT theoretical conductance of single molecules attached to metallic leads often differs from the experimental one by 2 orders of magnitude.
- Is it due to the accuracy of the experiment, to the uncertainty about the geometry, or to many-body effects?




[Experiment from M.A. Reed *et al.*, Science **278**, 252 (1997)
Theory from M. Di Ventra, Phys. Rev. Lett. **84**, 979 (2000)]

# Accuracy of the experiments

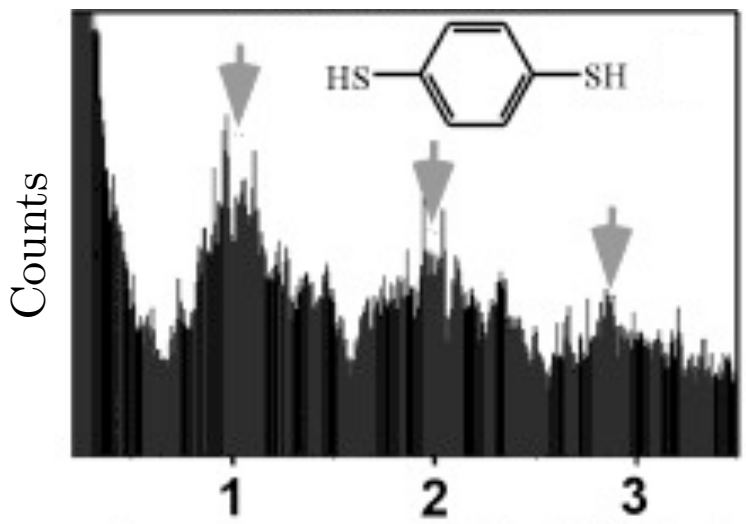
- BDA has a well defined conductance
- BDT not well defined.



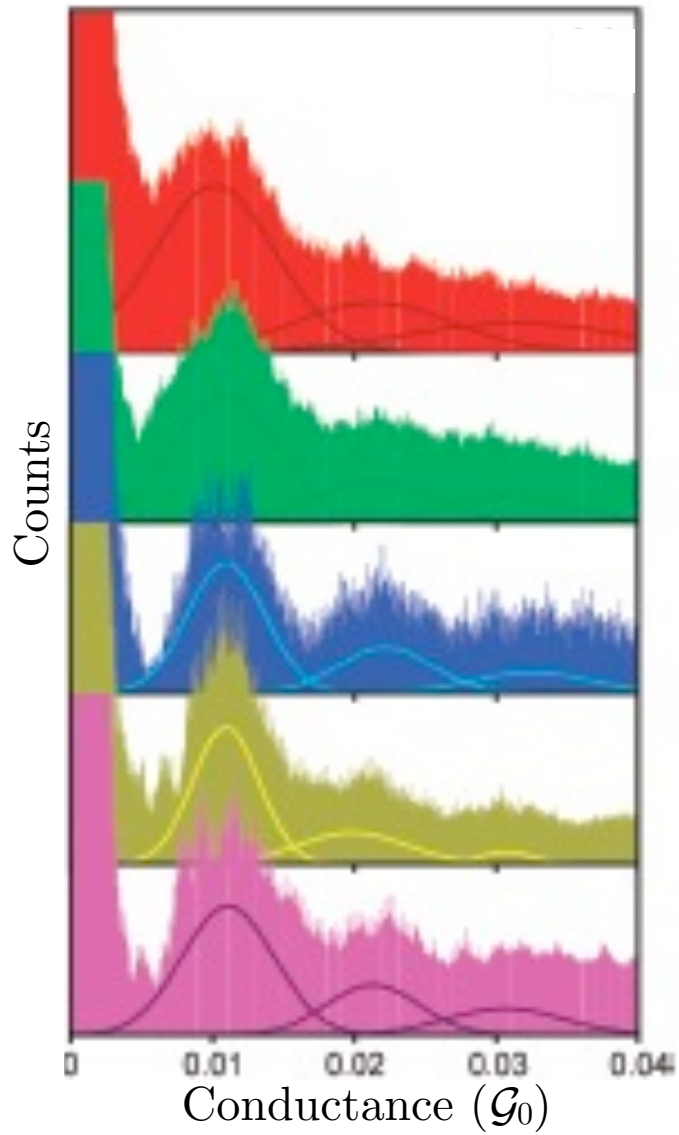

[L. Venkataraman *et al.*, Nano Lett. **6**, 458 (2006)]

# Accuracy of the experiments

- Consensus of stable BDT conductance at 0.01 G0.



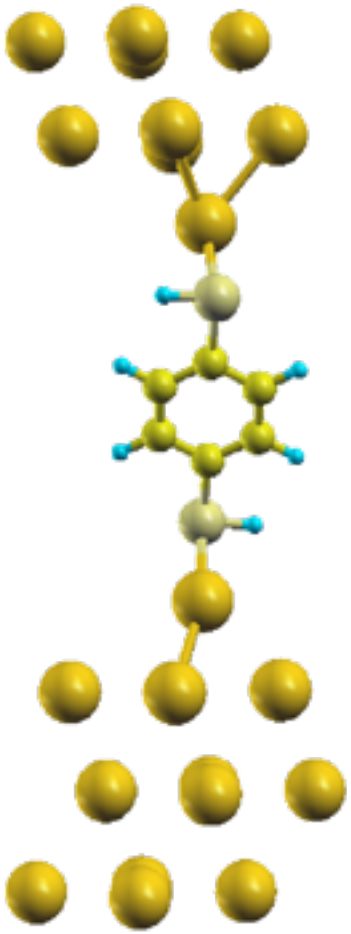

[X. Xiao, Nano Lett. **4**, 267 (2004)]




[M. Tsutsui, Nano Lett. **9**, 2433 (2009)]

# Uncertainty about the geometry

- The actual geometry of the BDT junction is still under debate.
- It is not clear whether H atoms desorb in the Au-thiol contact.



PRL 97, 045505 (2006) PHYSICAL REVIEW LETTERS week ending 28 JULY 2006

**Do Methanethiol Adsorbates on the Au(111) Surface Dissociate?**

Jian-Ge Zhou and Frank Hagelberg

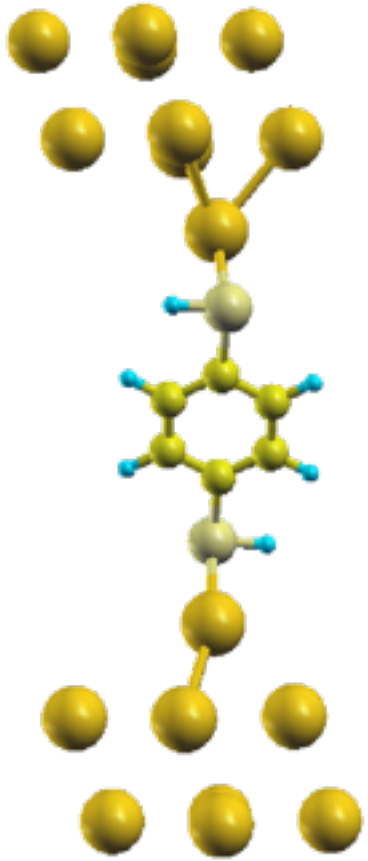
*Computational Center for Molecular Structure and Interactions, Department of Physics, Atmospheric Sciences, and General Science, Jackson State University, Jackson, Mississippi 39217, USA*

(Received 24 February 2006; published 28 July 2006)

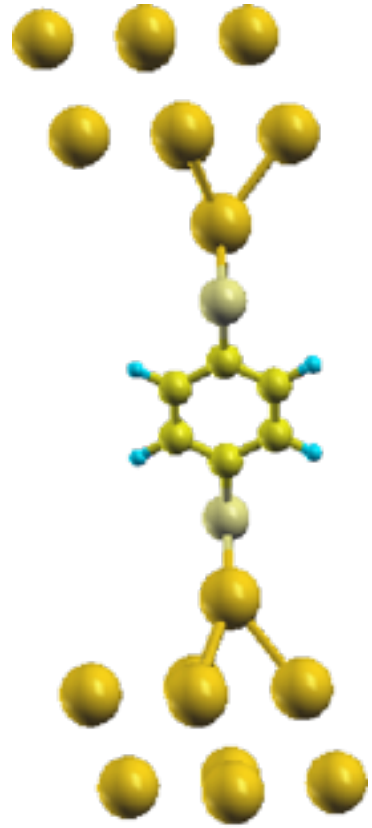
The interaction of methanethiol molecules $CH_3SH$ with the Au(111) surface is investigated, and it is found for the first time that the S-H bond remains intact when the methanethiol molecules are adsorbed on the regular Au(111) surface. However, it breaks if defects are present in the Au(111) surface. At low coverage, the fcc region is favored for S atom adsorption, but at saturated coverage the adsorption energies at various sites are almost isoenergetic. The presented calculations show that a methanethiol layer on the regular Au(111) surface does not dimerize.

# Uncertainty about the geometry

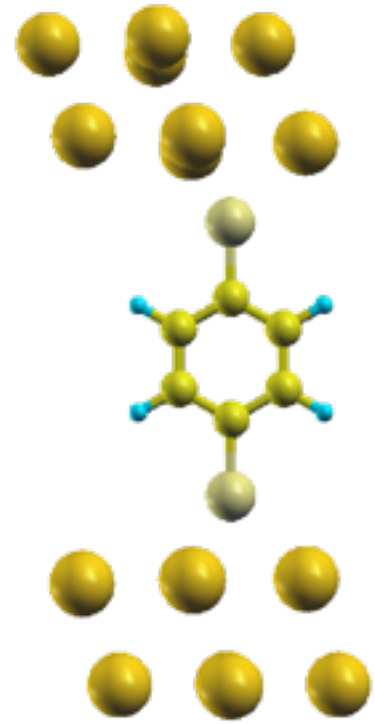
- Three different geometries are considered:



BDT-H
(H not desorbed)



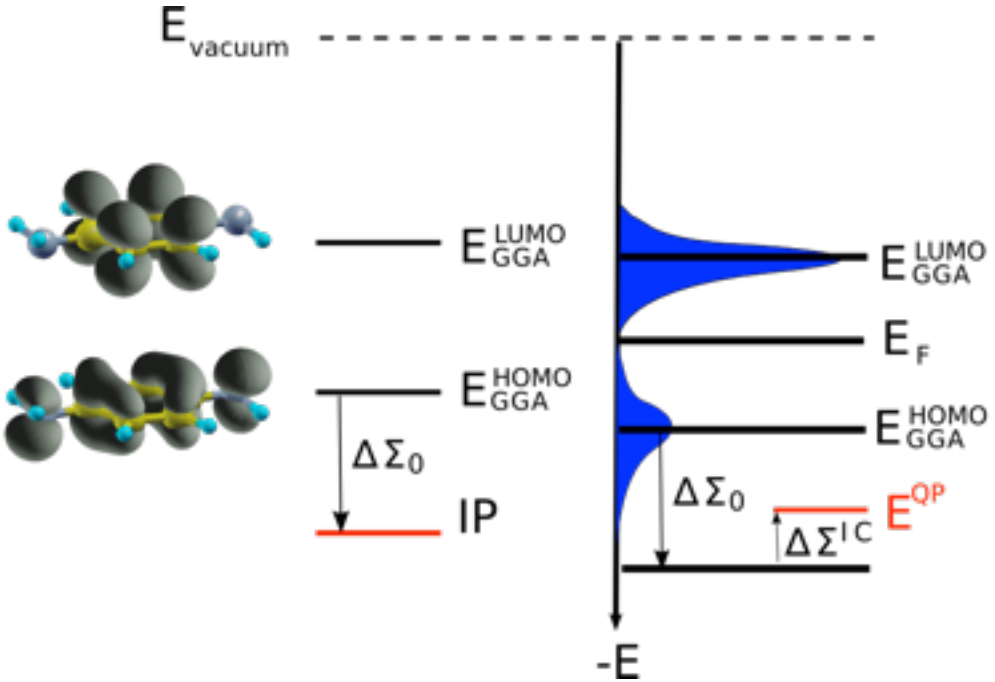
BDT-p
(pyramid-site)



BDT-h
(hollow-site)

# Many-body effects on the conductance

- Given the computational cost of MBPT calculations, a simple model has recently been proposed in which the position of the HOMO level is corrected by a simple scissors-operator, which we will refer to as molecular-projectors model (MPM).



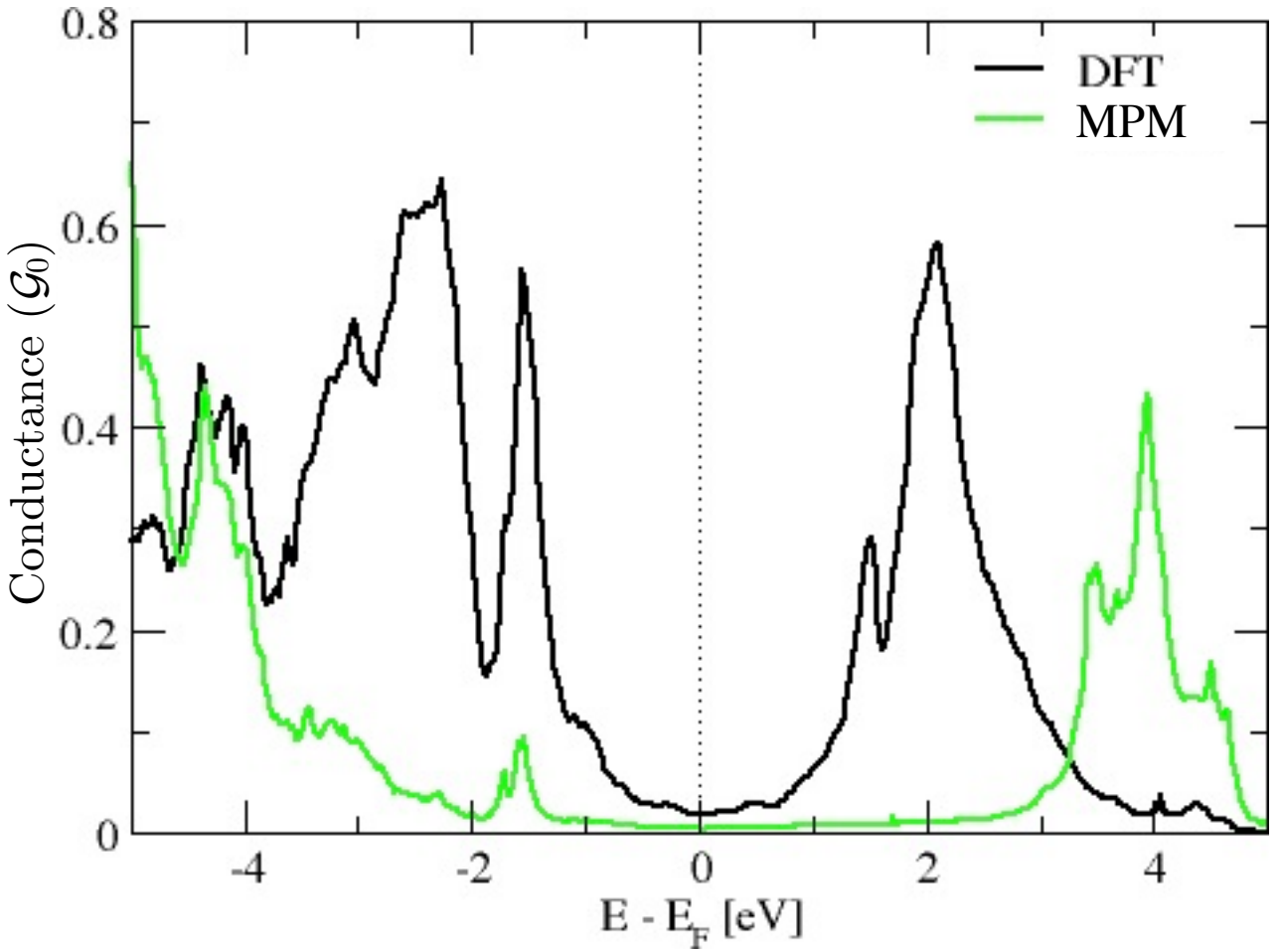

[Neaton *et al.*, Phys. Rev. Lett. **97**, 216405 (2006); Quek *et al.*, Nano Lett. **7**, 3472 (2007); Mowbray *et al.*, J. Chem. Phys. **128**, 11103 (2008)]

$$\Delta\Sigma = \sum_{i}^{\text{mol.}} |\phi_i\rangle \, \Delta_i \, \langle\phi_i|$$

- The value of $\Delta_i$ is obtained as the value of the correction to the HOMO-LUMO gap of the molecule in the gas phase ($\Delta\Sigma_0$) screened using a classical image-charge model ($\Delta\Sigma^{\text{IC}}$).

# Many-body effects on the conductance

- Using this model, the conductance for the Au-BDA-Au junction is indeed reduced towards the experimental value.

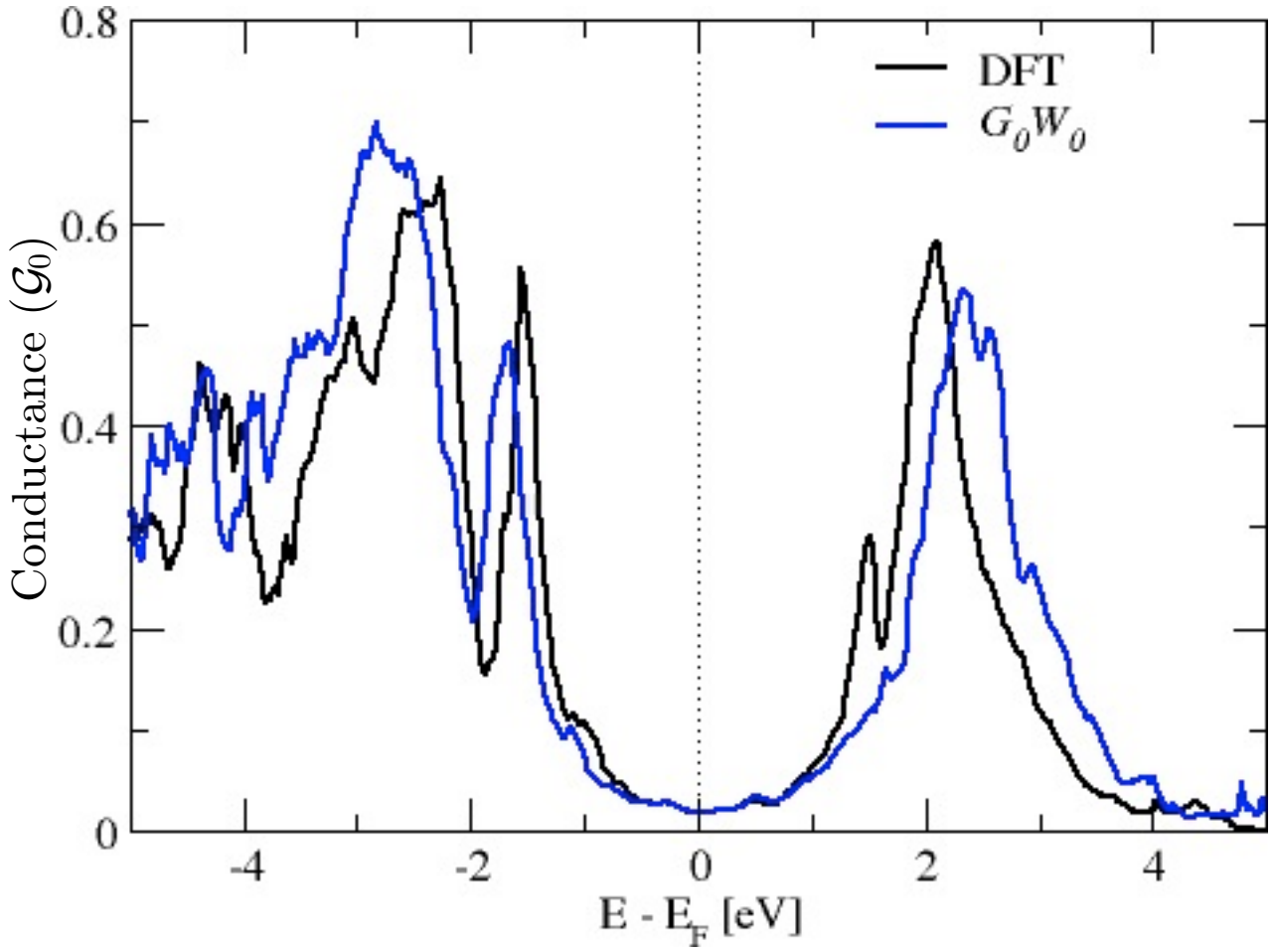



| Zero-bias Cond. [$\mathcal{G}_0$] | |
|---|---|
| DFT | 0.018 |
| MPM | 0.004 |
| Exp. | 0.007 |

- Can we validate this model by MBPT calculations on the junction?

# Many-body effects on the conductance

- Using $G_0W_0$, the HOMO-LUMO gap for the Au-BDA-Au junction is also modified, but the zero-bias conductance negligibly changed.




| Zero-bias Cond. [$\mathcal{G}_0$] | |
|---|---|
| DFT | 0.018 |
| $G_0W_0$ | 0.018 |
| Exp. | 0.007 |

- Is it also true for the other systems?

# Many-body effects

- Indeed, we find similar results for all the junctions using $G_0W_0$.

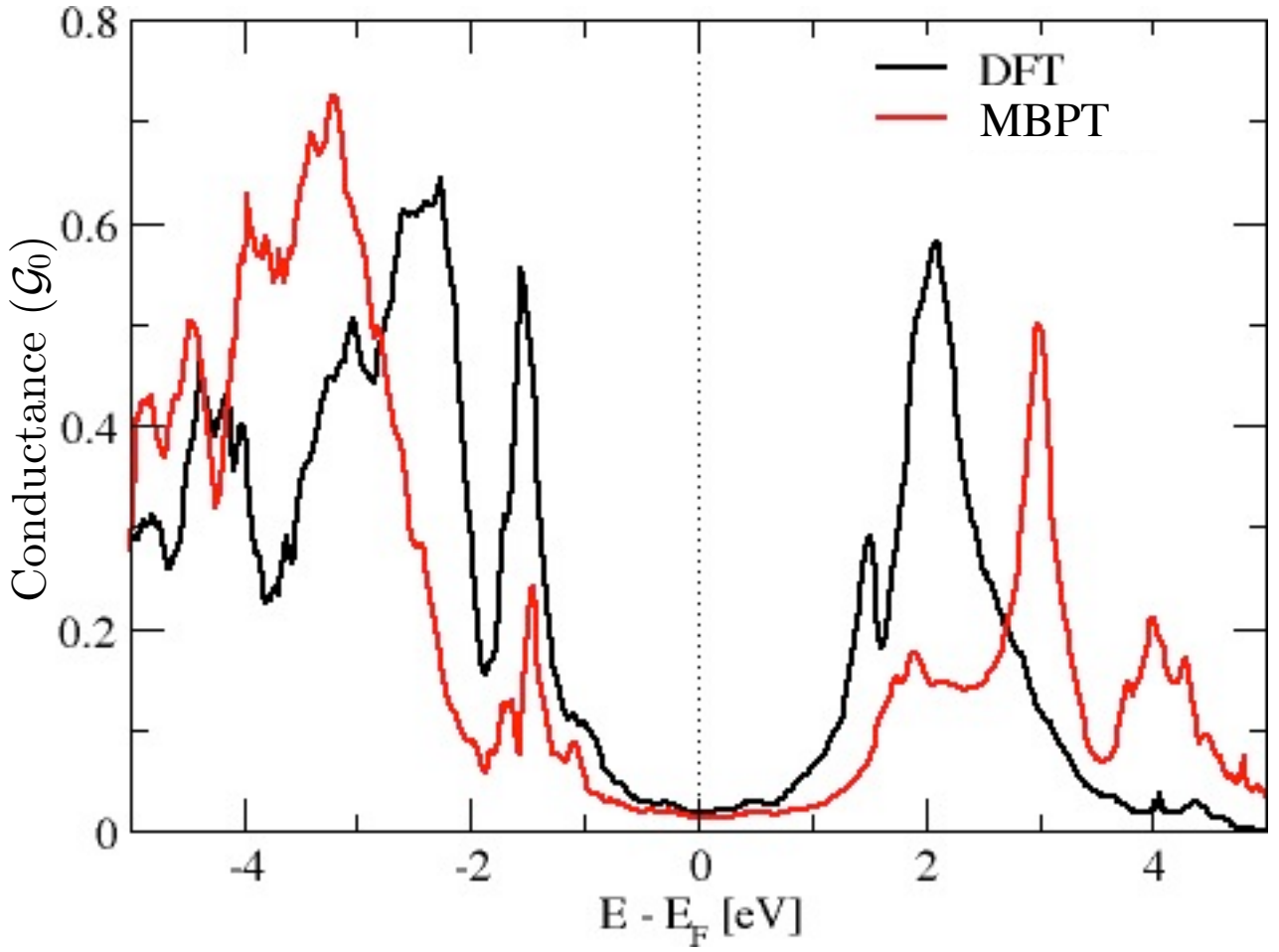
| | BDA | BDT-H | BDT-h | BDT-p |
|---|---|---|---|---|
| DFT | 0.018 | 0.034 | 0.28 | 0.37 |
| $G_0W_0$ | 0.018 | 0.037 | 0.28 | 0.40 |
| Exp. | 0.007[a] | 0.010[b] | | |
| | | 0.010[c] | | |
| | | 0.013[d] | | |

[(a) Venkataraman, Nano Lett 6, 458 (2006);
(b) Xiao et al, Nano Lett 4, 267 (2004);
(c) Tsutsui et al, Nano Lett 9, 2433 (2009);
(d) Song et al, Nature 462, 1039 (2009)]

- Why is it so?

# Many-body effects on the conductance

- Including self-consistency, both the HOMO-LUMO gap and the zero-bias conductance are modified for the Au-BDA-Au junction.




| Zero-bias Cond. [$\mathcal{G}_0$] | |
|---|---|
| DFT | 0.018 |
| MBPT | 0.013 |
| Exp. | 0.007 |

- Further investigations are still required...

# Conclusions

- Many-body effects are important to predict the zero-bias conductance.
- However, $G_0 W_0$ (which only renormalizes the eigenvalues) is not enough to change the initial DFT conductance.
- Self-consistency needs to be included to reach better results.