An accurate method to calculate band gaps

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This is a review of our papers, PRB 78, 125116 (2008) and PRB 79, 241312(R) (2009), and a report on further developments. Our method is based on Slater's transition state idea and Janak's theorem. With those tools we were able to define a self-energy, not the self-energy of GW but that of elementary Electrostatics, and find a way to calculate it for the electronic elementary excitations in a crystal. Our point of view is that the elementary excitations are in localized wavefunctions, not Bloch functions, and that is why they have sizable self-energies. The inclusion of the self-energy is made by means of a ``self-energy potential'' defined in the atoms of the crystal. Thus the procedure is very simple and fast. The new band gap results are as good as, or perhaps even better than, the published GW results. Originally we adapted our method to the codes VASP and SIESTA (for programs and instructions see www.gf1901.net). Lately we adapted the method to WIEN2k, with which we calculated CdTe, CdSe, MnO, and NiO. In the case of the last oxide, we diverged from Professor Blaha's paper [PRL 102, 226401 (2009)], with whom we would welcome a friendly discussion.

$$\frac{\partial E}{\partial f_\alpha} = e_\alpha(f_\alpha)$$

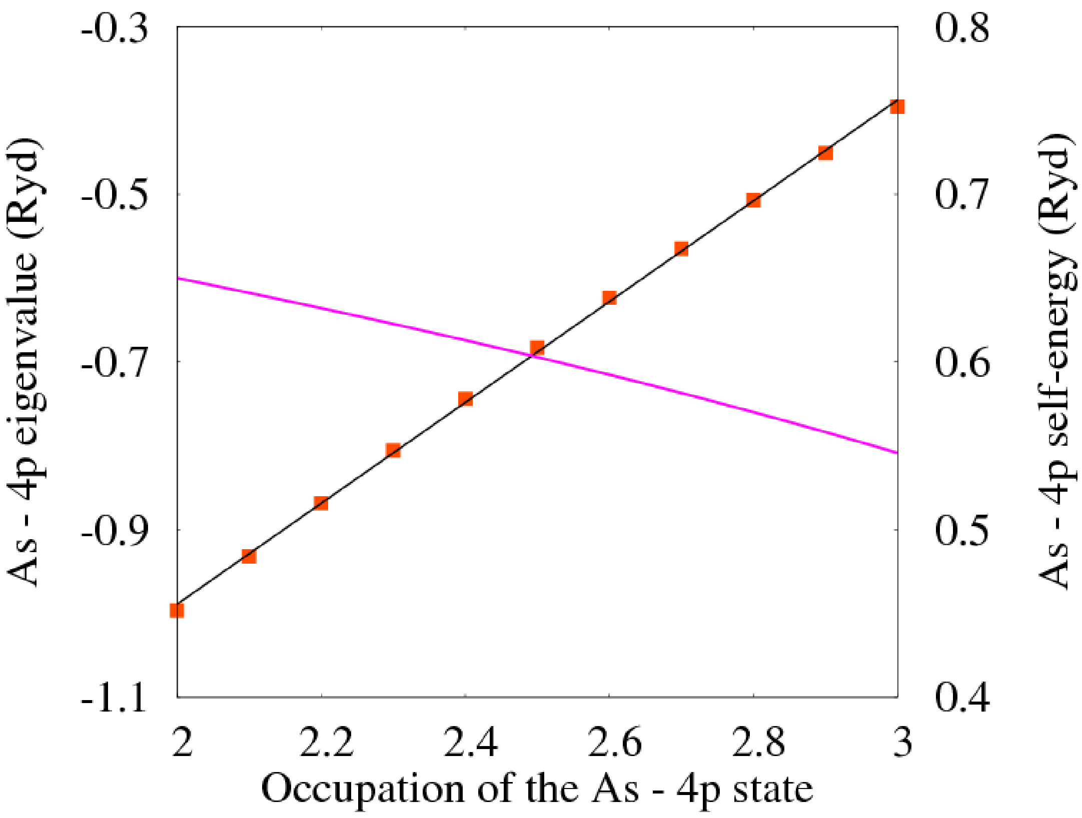
E = total energy

e = Kohn-Sham eigenvalue

f = occupation

α = KS one-particle state

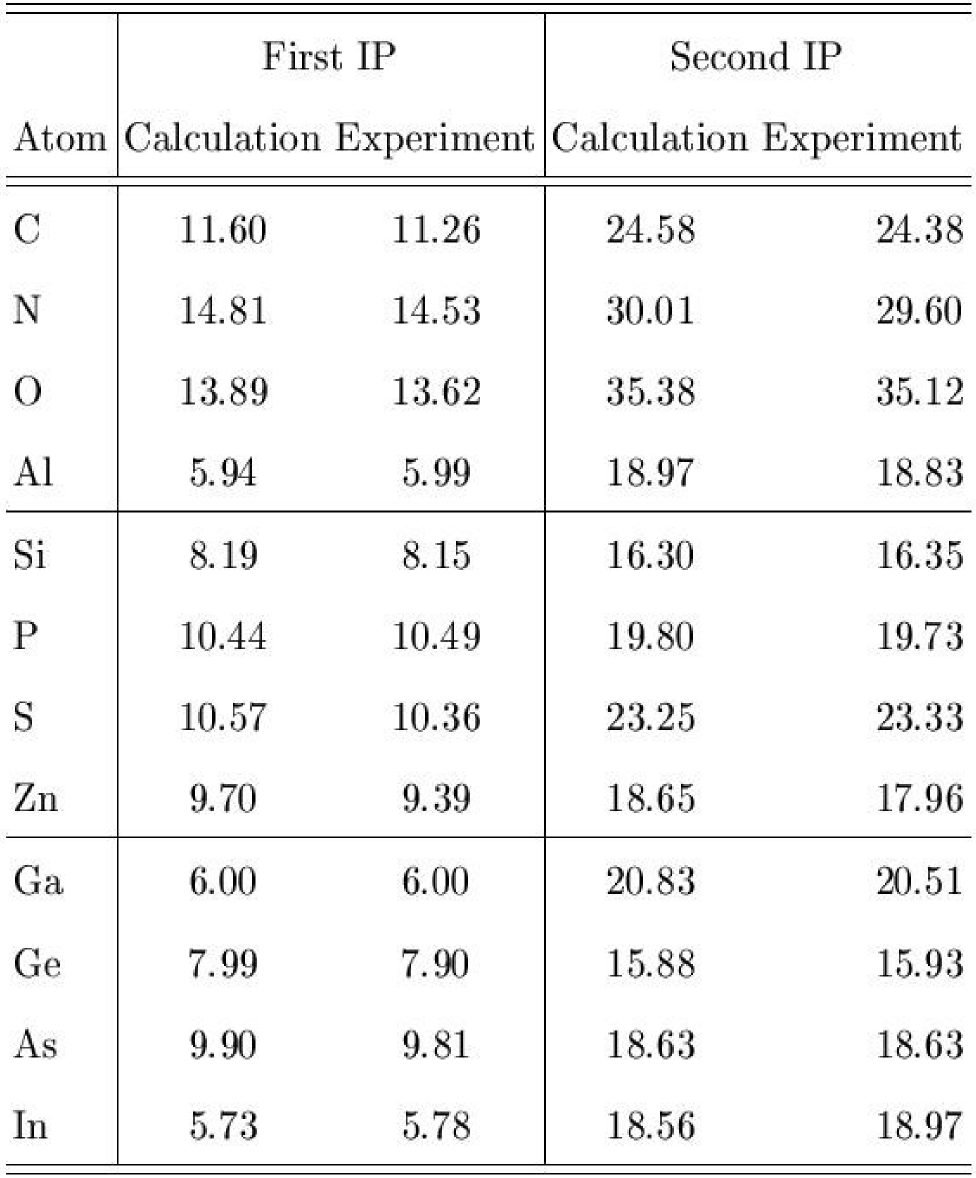
Janak, 1978



Leite and Ferreira, 1971

$E(0) - E(-1) = e_{\alpha}(-1/2) = -$ Ionization Potential

$E(0)$ = energy of atom $E(-1)$ = energy of ion



	First IP		Second IP	
Atom	Calculation	Experiment	Calculation	Experiment
C	11.60	11.26	24.58	24.38
N	14.81	14.53	30.01	29.60
O	13.89	13.62	35.38	35.12
Al	5.94	5.99	18.97	18.83
Si	8.19	8.15	16.30	16.35
P	10.44	10.49	19.80	19.73
S	10.57	10.36	23.25	23.33
Zn	9.70	9.39	18.65	17.96
Ga	6.00	6.00	20.83	20.51
Ge	7.99	7.90	15.88	15.93
As	9.90	9.81	18.63	18.63
In	5.73	5.78	18.56	18.97

$$\frac{\partial e_\alpha}{\partial f_\alpha} = 2S_\alpha$$

$$\begin{aligned}
S_\alpha = {}_{1/2}& \int\int d^3r\,d^3r'\,{}^{e}\frac{n_\alpha(\vec{r})n_\alpha(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}{}^{e} \\
&+ \frac{1}{2}\int\int d^3r\,d^3r'\,n_\alpha(\vec{r})\frac{\delta^2 E_{xc}}{\delta n(\vec{r})\delta n(\vec{r}\,')}n_\alpha(\vec{r}\,') \\
&+ \int\int d^3r\,d^3r'\,\frac{n_\alpha(\vec{r})}{|\vec{r}-\vec{r}\,'|}\sum_\beta f_\beta \frac{\partial n_\beta(\vec{r}\,')}{\partial f_\alpha} \\
&+ \frac{1}{2}\int\int d^3r\,d^3r'\,n_\alpha(\vec{r})\frac{\delta^2 E_{xc}}{\delta n(\vec{r})\delta n(\vec{r}\,')}\sum_\beta f_\beta \frac{\partial n_\beta(\vec{r}\,')}{\partial f_\alpha}
\end{aligned}$$

Self-energy !

Assuming linearity

$$E(0) = E(-1) + e_\alpha(0) - S_\alpha$$

The Eq. is telling us that, to restore the ground state, with total energy $E(0)$, from an ion with a hole at state α we add an electron whose energy is the eigenvalue $e_\alpha(0)$ minus the hole self-energy. The self-energy is large when the function is much localized as an atomic wavefunction, and is small and zero when it is much spread as a Bloch function. Since the energy of the restored ground state must be a minimum the hole self-energy must be a maximum. Thus the hole should be representable by a very localized wavefunction. *This is a demonstration of the hole localization*

$$S_\alpha = \int\int d^3r d^3r' \frac{n_\alpha(\vec{r})n_\alpha(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}$$

How to calculate the self-energy?

$$S_\alpha = \int d^3r\, n_\alpha(\vec{r}) V_S(\vec{r})$$

Self-energy potential

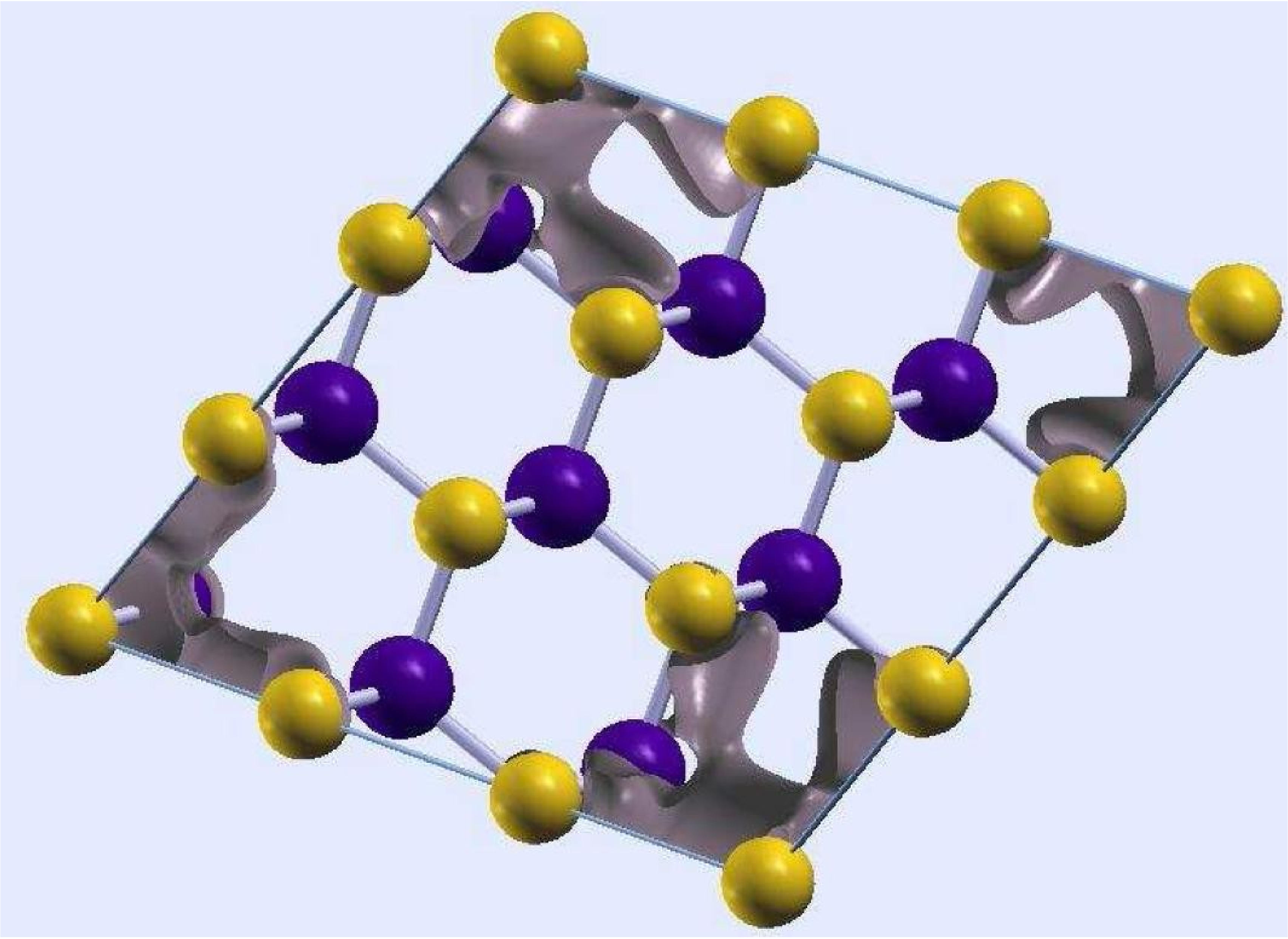
$$\begin{aligned} V_S(\vec{r}) \; = \; & \int d^3r\,' \frac{n_\alpha(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \\ & + \frac{1}{2}\int d^3r\,' \frac{\delta^2 E_{xc}}{\delta n(\vec{r})\delta n(\vec{r}\,')} n_\alpha(\vec{r}\,') \\ & + \int d^3r\,' \frac{\sum_\beta f_\beta \frac{\partial n_\beta(\vec{r}\,')}{\partial f_\alpha}}{|\vec{r}-\vec{r}\,'|} \\ & + \frac{1}{2}\int d^3r\,' \frac{\delta^2 E_{xc}}{\delta n(\vec{r})\delta n(\vec{r}\,')} \sum_\beta f_\beta \frac{\partial n_\beta(\vec{r}\,')}{\partial f_\alpha} \end{aligned}$$

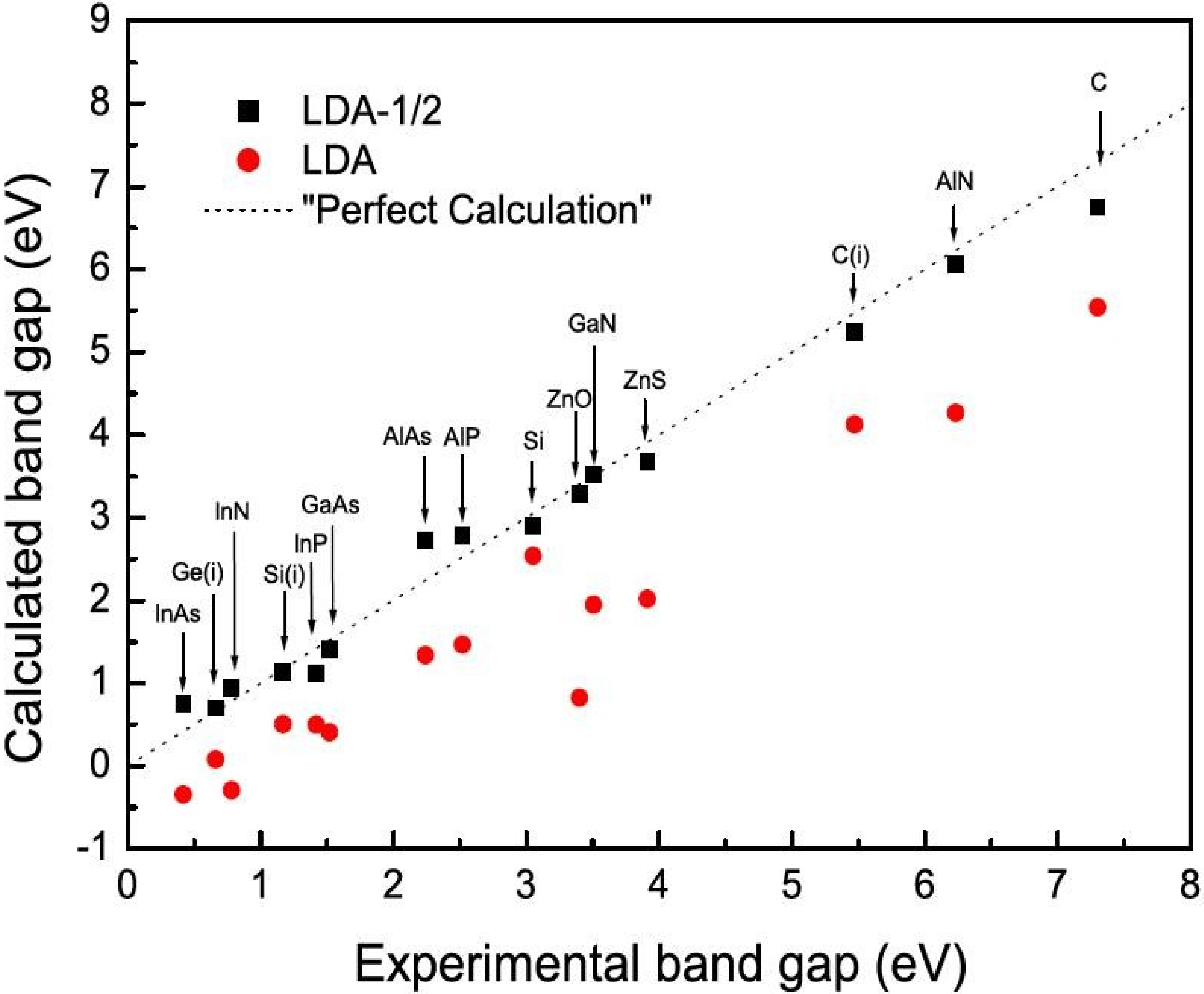
But we will never calculate this fantastic expression!

STOP

Let us present some results

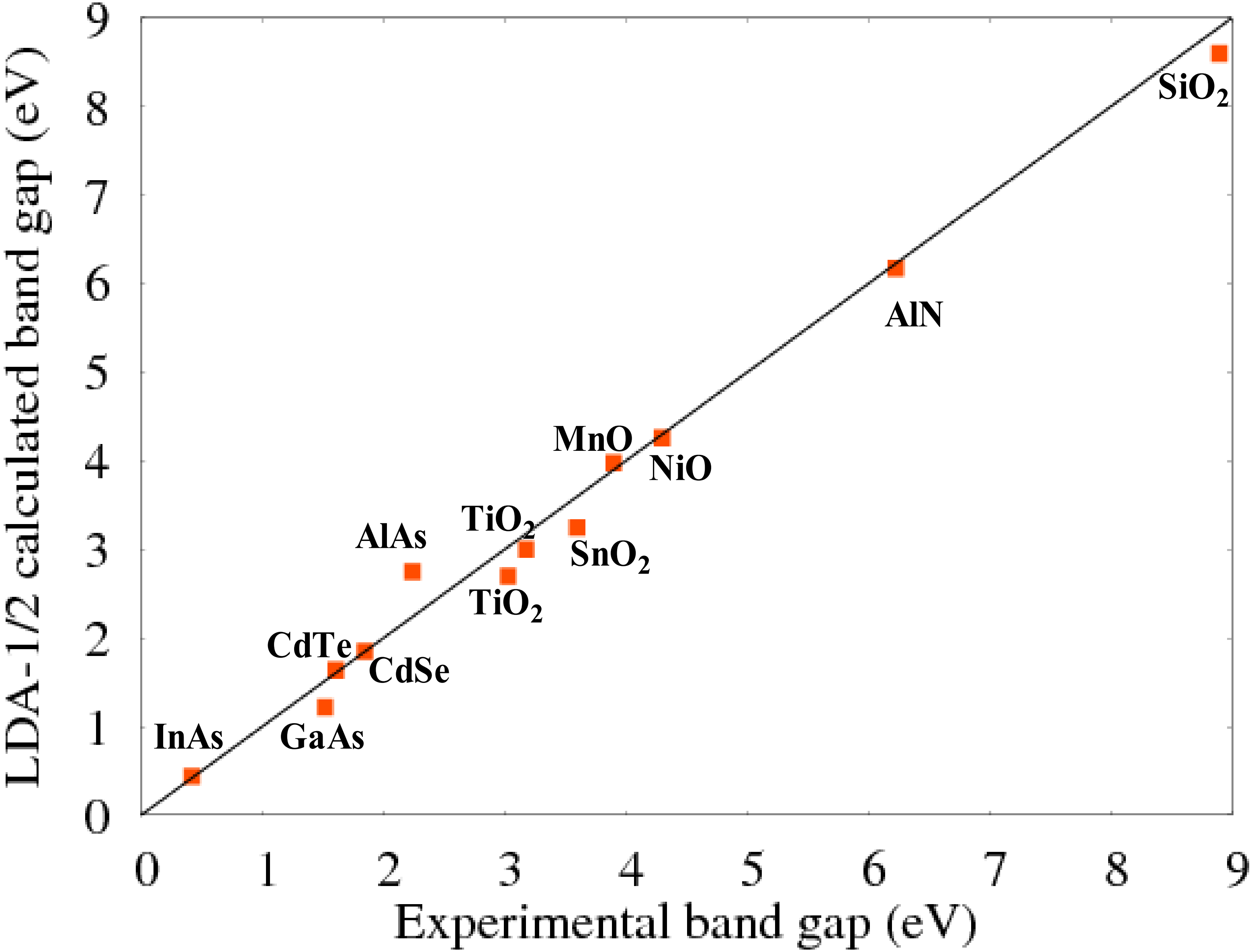
Later we return to theory



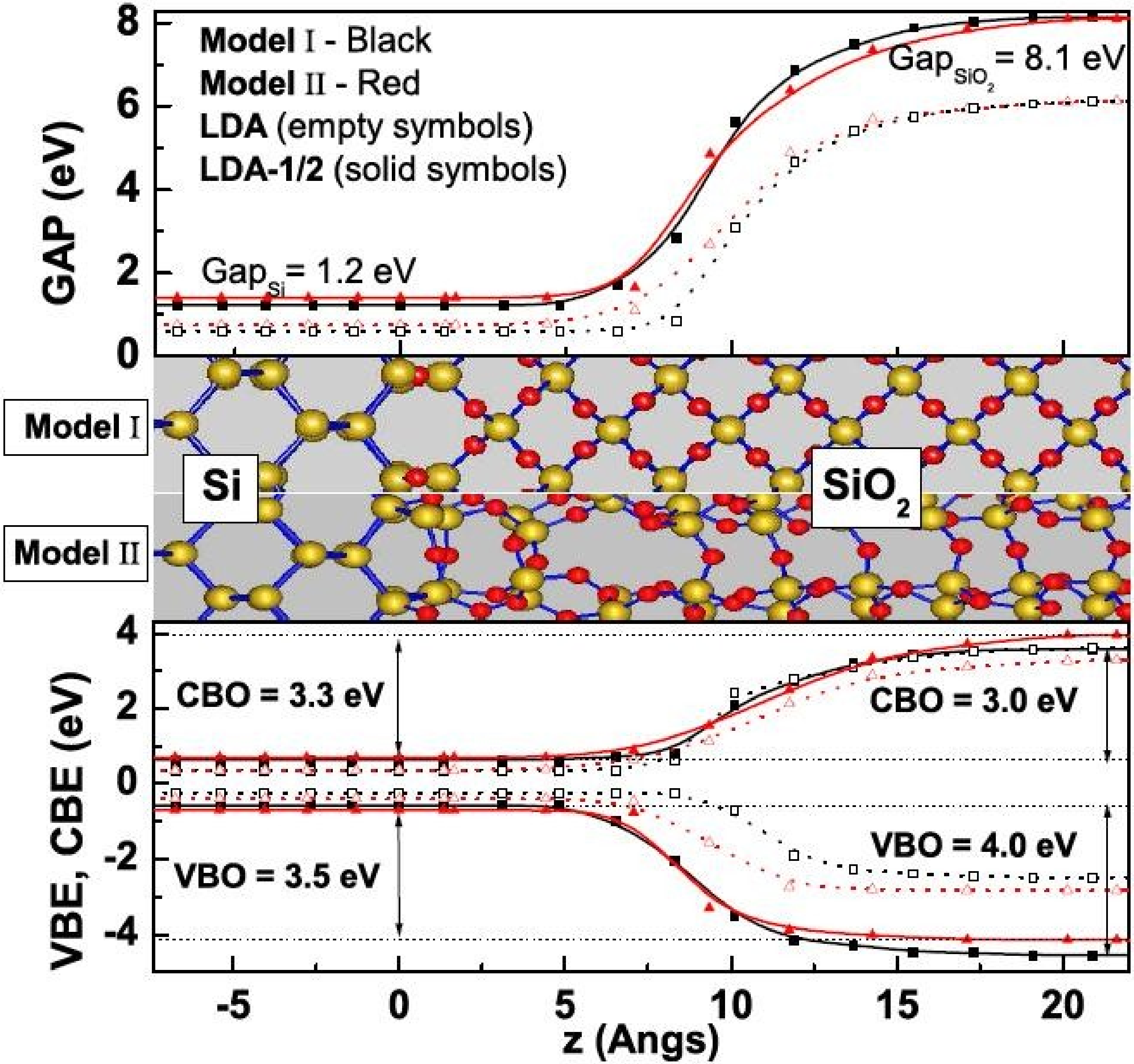

LDA-1/2
LDA
"Perfect Calculation"
Calculated band gap (eV)
Experimental band gap (eV)
9
8
7
6
5
4
3
2
1
0
-1
0
1
2
3
4
5
6
7
8
C
AlN
C(i)
GaN
ZnS
ZnO
AlAs
AlP
Si
GaAs
InN
InP
Si(i)
Ge(i)
InAs

Effective masses

	LDA-1/2	LDA	Exp.
AlN	0.38	0.30	-
GaN	0.30	0.17	0.18-0.29
InN	0.12	-	0.11-0.23
AlP	0.256	0.18	-
GaP	0.17	0.10	0.09-0.17
InP	0.088	0.04	0.077-0.081
AlAs	0.064	0.022	0.06-0.15
GaAs	0.064	0.026	0.065-0.07
InAs	0.047	0.033	0.023-0.03
ZnO	0.39	0.14	0.3-0.36[?]
ZnS	0.26	0.16	


LDA-1/2 calculated band gap (eV)
Experimental band gap (eV)
0
1
2
3
4
5
6
7
8
9
SiO$_2$
AlN
MnO
NiO
TiO$_2$
SnO$_2$
AlAs
TiO$_2$
CdTe
CdSe
InAs
GaAs

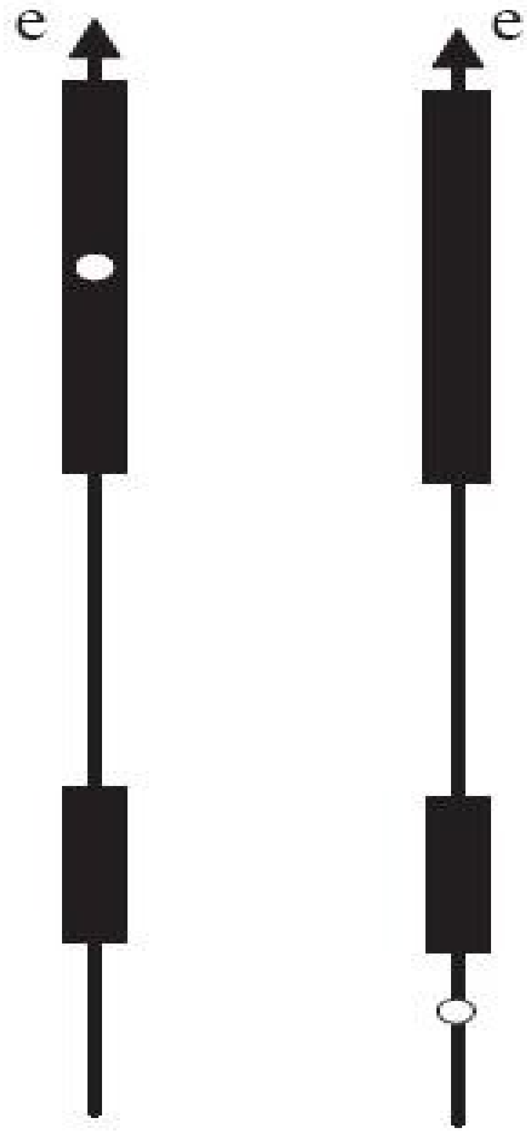
Si/SiO_2 Interface



Si/SiO$_2$ Band Offsets (eV)

	LDA	LDA-1/2	GW[b]	Exp.[a]
VBO (**I**)	2.2	4.0	4.1	4.5
VBO (**II**)	2.4	3.6		
CBO (**I**)	3.3	3.0	2.9	3.3
CBO (**II**)	3.0	3.3		

Conjecture



Returning to the theory

$$V(-1/2,r)\ -\ V(0,r) = \int_0^{-1/2} df_\alpha \frac{\partial}{\partial f_\alpha}\left\{-2\frac{Z}{r} + 2\int d^3r\,'\frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} + \frac{\delta E_{xc}}{\delta n(\vec{r})}\right\}$$

$$= \int_0^{-1/2} df_\alpha \left\{2\int d^3r\,'\frac{n_\alpha(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} + \int d^3r\,'\frac{\delta^2 E_{xc}}{\delta n(\vec{r})\delta n(\vec{r}\,')}n_\alpha(\vec{r}\,')\right\}$$

$$+ \int_0^{-1/2} df_\alpha \left\{2\int d^3r\,'\frac{\sum_\beta f_\beta \frac{\partial n_\beta(\vec{r}\,')}{\partial f_\alpha}}{|\vec{r}-\vec{r}\,'|} + \int d^3r\,'\frac{\delta^2 E_{xc}}{\delta n(\vec{r})\delta n(\vec{r}\,')}\sum_\beta f_\beta \frac{\partial n_\beta(\vec{r}\,')}{\partial f_\alpha}\right\}$$

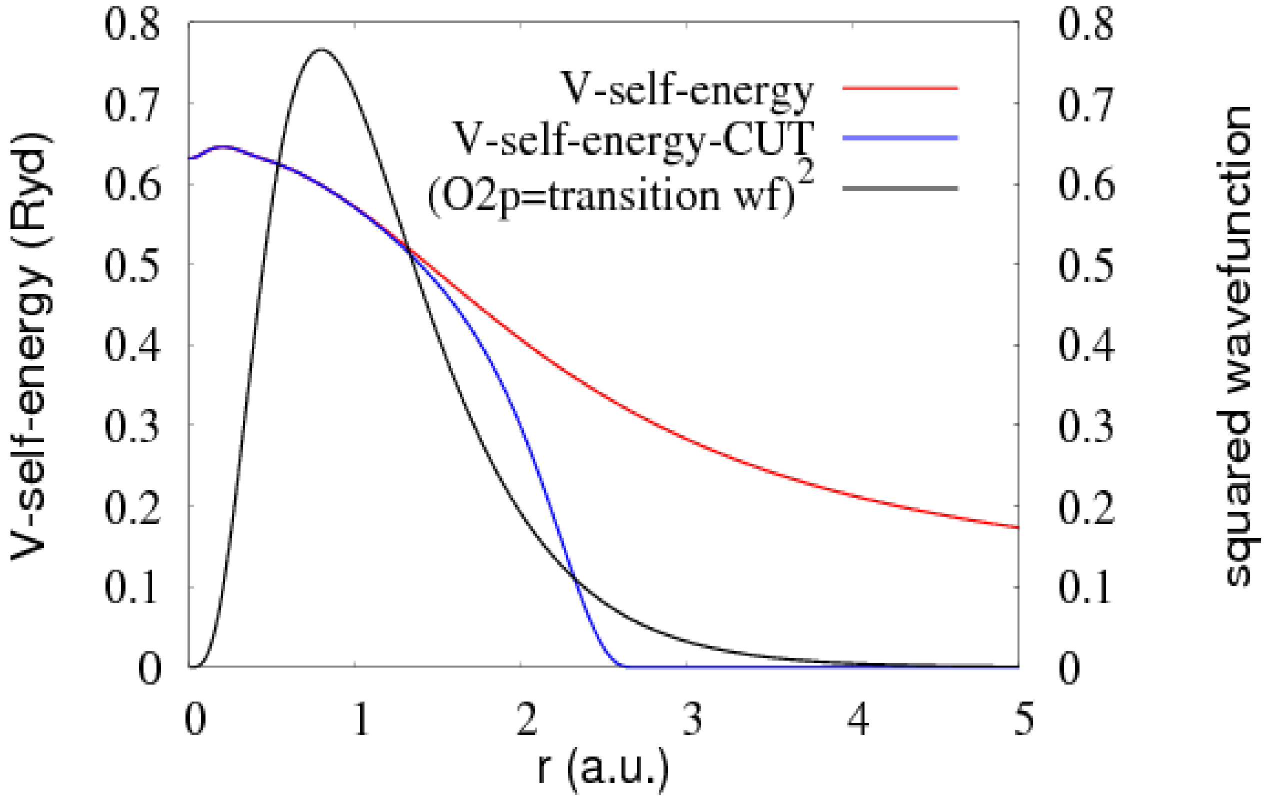
$$-V(-1/2,r)\ +\ V(0,r) =\ V_S(\vec{r})\ =$$

$$= \int d^3r\,'\frac{n_\alpha(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} + \frac{1}{2}\int d^3r\,'\frac{\delta^2 E_{xc}}{\delta n(\vec{r})\delta n(\vec{r}\,')}n_\alpha(\vec{r}\,')$$

$$+\ \int d^3r\,'\frac{\sum_\beta f_\beta \frac{\partial n_\beta(\vec{r}\,')}{\partial f_\alpha}}{|\vec{r}-\vec{r}\,'|} + \frac{1}{2}\int d^3r\,'\frac{\delta^2 E_{xc}}{\delta n(\vec{r})\delta n(\vec{r}\,')}\sum_\beta f_\beta \frac{\partial n_\beta(\vec{r}\,')}{\partial f_\alpha}$$

Add self-energy potentials to atoms of a crystal. Has to cut Coulomb tail of charge of +1/2.

$$\Theta(r) = \begin{cases} \left[1 - \left(\frac{r}{CUT}\right)^n\right]^3 & r \le CUT \\ 0 & r > CUT \end{cases}$$

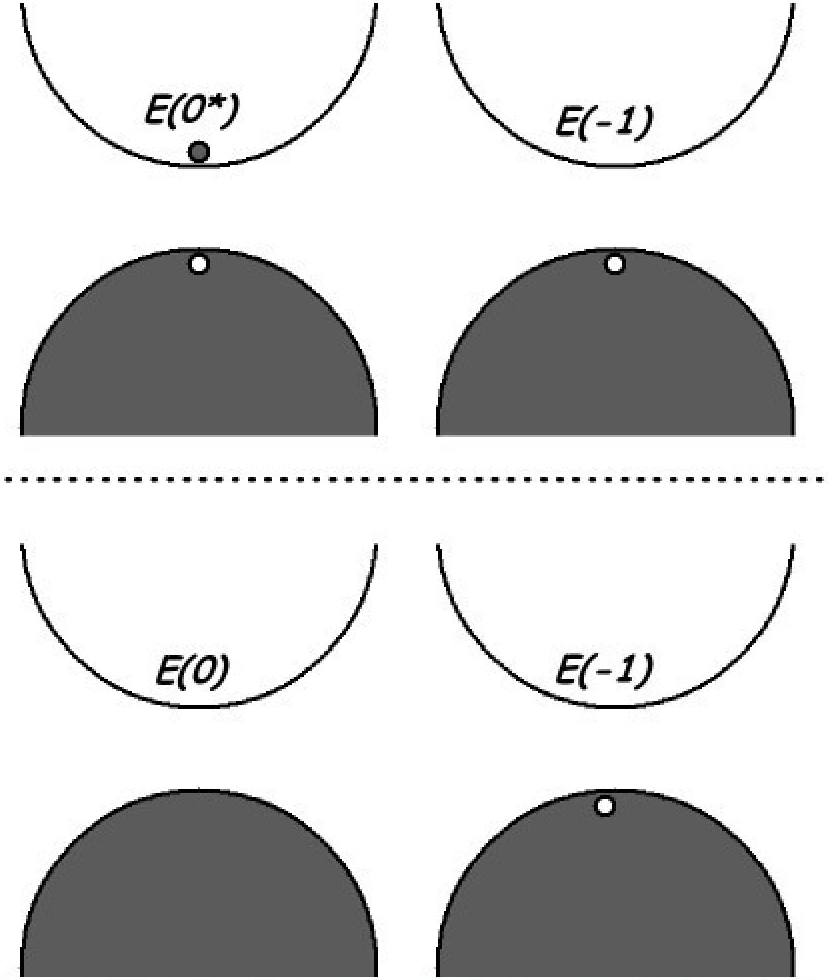


Determination of the Band Gap

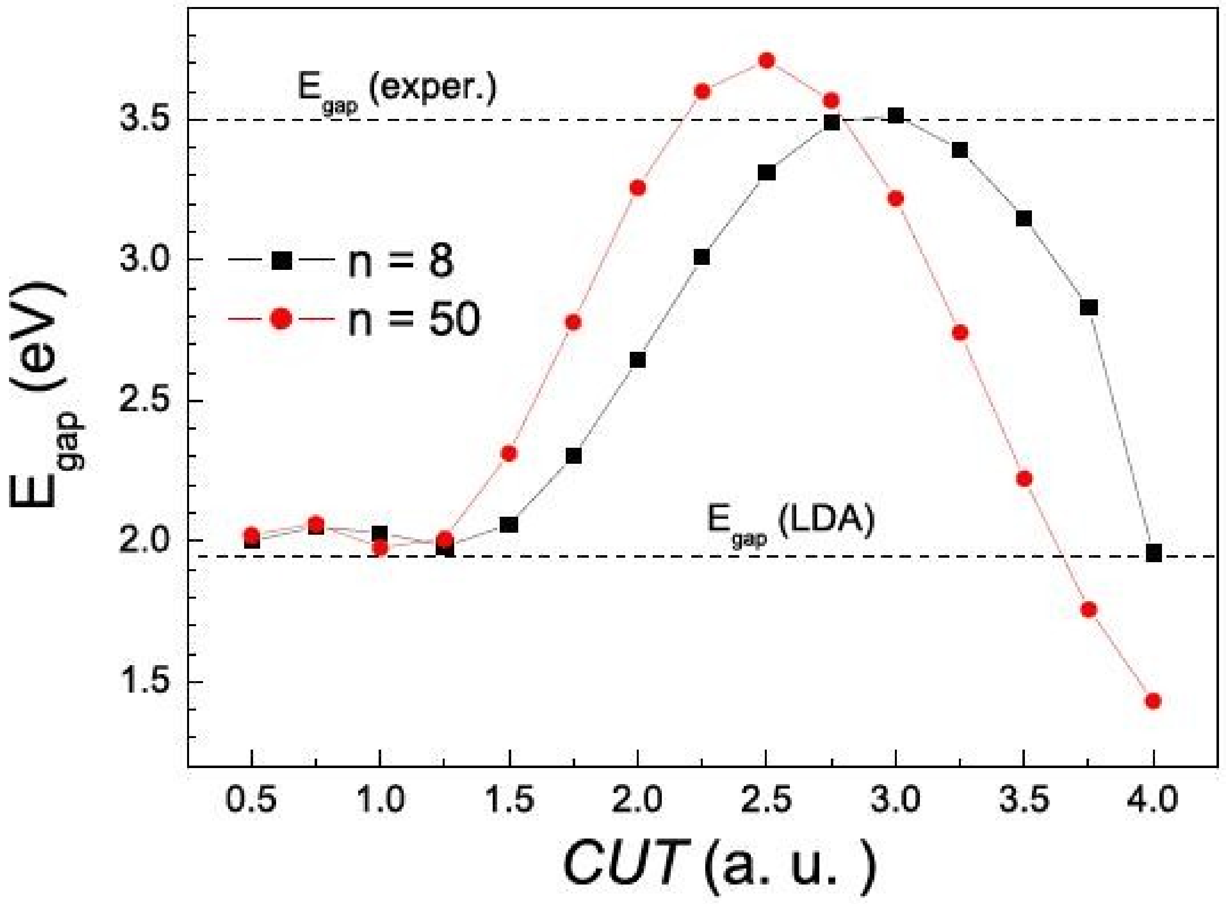
$$E(0^*) - E(0) = E(-1) + e_\beta(0^*) - S_\beta - E(-1) - e_\alpha(0) + S_\alpha$$

$$E(0^*) - E(0) = Gap \qquad e_\beta(0^*) - e_\alpha(0) = KS\ Gap$$

$$Gap = KS\ Gap + S(valence) - S(conduction)$$



The self-energy of conduction is usually unimportant and its potential does not differ much from that of the valence.



Choose

extremum

Then, the method consists of the following steps:

1 – Calculate the atoms and their -1/2 ions

2 – Take the differences between their KS potentials to define the “self-energy atomic potentials”.

3 – Multiply the self-energy atomic potentials by the cutting function so as to cut the Coulomb tails. This process defines the “self-energy crystalline potentials”.

4 – Add the self-energy crystalline potentials to all atoms of the crystal and make the band calculation.

5 – Repeat the band calculation for other values of the parameter CUT and choose the value leading to an extreme gap.

Note a – Usually only the self-energy of the anion is important (valence band).

Note b - The good parameter CUT is the same for all compounds of that atom with the same bonding type.

An energy functional

$$E[n,v,\rho] \;=\; K[n] - \int V[p]\rho + \frac{1}{2}\int V[\rho]\rho - \int V_S\rho + \int v(n-\rho) + E_{xc}[\rho]$$

$$V[\rho(\vec{r})] = 2\int \frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d^3r'$$

Ferreira et al, IJQC (1979), PRB (1979); Harris, IJQC (1979)

1. $\delta E/\delta v = 0$ leads to $\rho = n$

2. $\delta E/\delta\rho = 0$ leads to $\quad v = -V[p] + V[\rho] - V_S + \delta E_{xc}/\delta\rho$

3. $\delta E/\delta n \;=\; 0$ leads to

$$\left[-\nabla^2 - 2\sum_I \frac{Z_I}{|\vec{r}-\vec{r}_I|} + 2\int \frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d^3r\,' + \frac{\delta E_{xc}}{\delta\rho(\vec{r})} - V_S(\vec{r})\right]\psi_\alpha(\vec{r}) = e_\alpha\psi_\alpha(\vec{r})$$

Ground State; $\rho = n_0 \longrightarrow$

$$E_0 = \sum_\beta f_{\beta,0} e_\beta - \frac{1}{2}\int V[\rho]\rho + E_{xc}[\rho] - \int \rho \frac{\delta E_{xc}}{\delta\rho}$$

Excited State; $\rho = n_0$ still, and the same $v \longrightarrow$

$$E_1 = \sum_\beta f_{\beta,1} e_\beta - \frac{1}{2}\int V[\rho]\rho + E_{xc}[\rho] - \int \rho \frac{\delta E_{xc}}{\delta\rho}$$

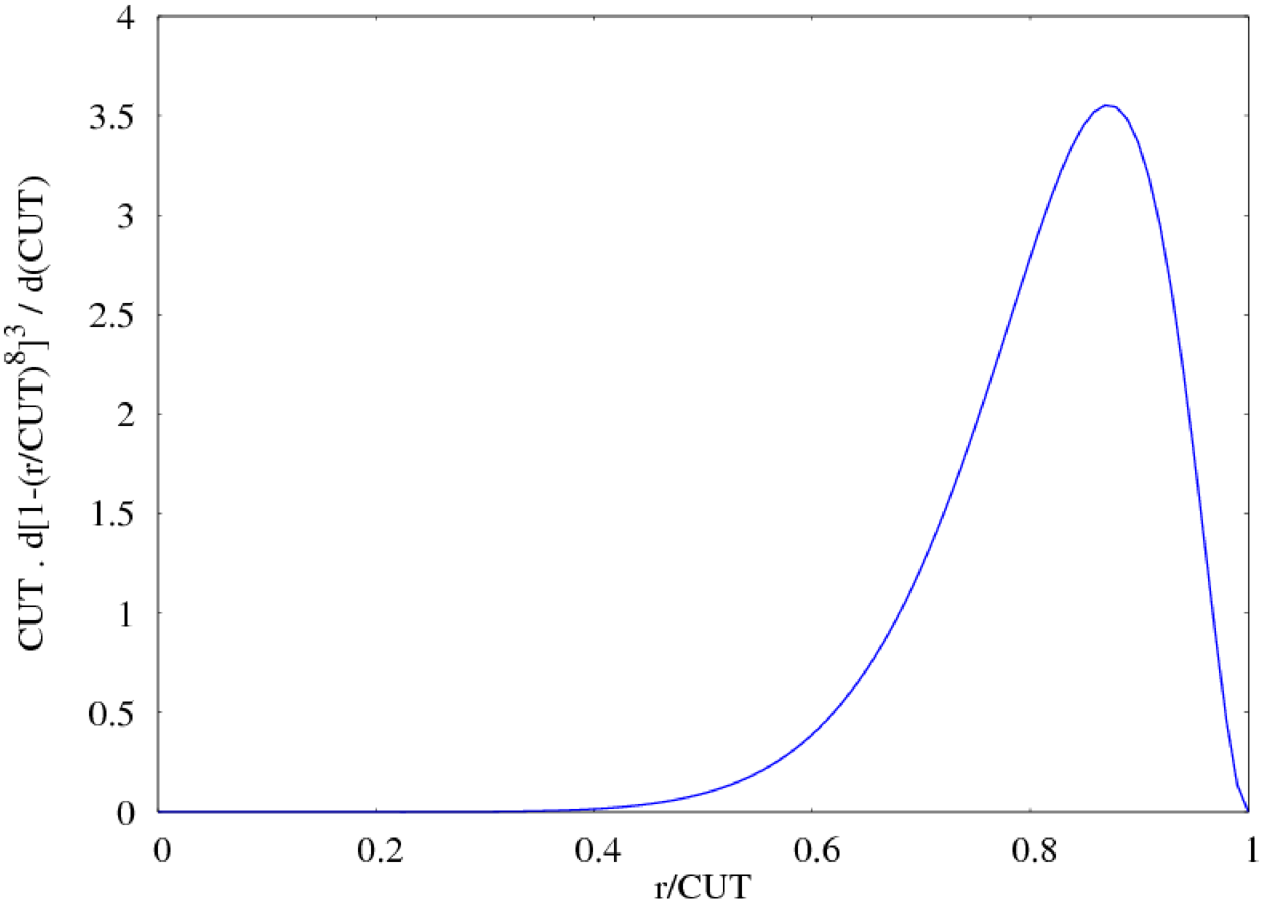
Same v implies the same wavefunctions, but different occupation numbers.

Excitation $\alpha \longrightarrow \gamma$

$$E_1 - E_0 = e_\gamma - e_\alpha$$

$$0 = \frac{d(E_1 - E_0)}{dCUT} = \frac{d(e_\gamma - e_\alpha)}{dCUT} = \int \frac{\partial v}{\partial CUT}(n_\gamma - n_\alpha)$$

Extremum always exists and probably at CUT near the atomic radius.



So far, only the one-particle excitations.

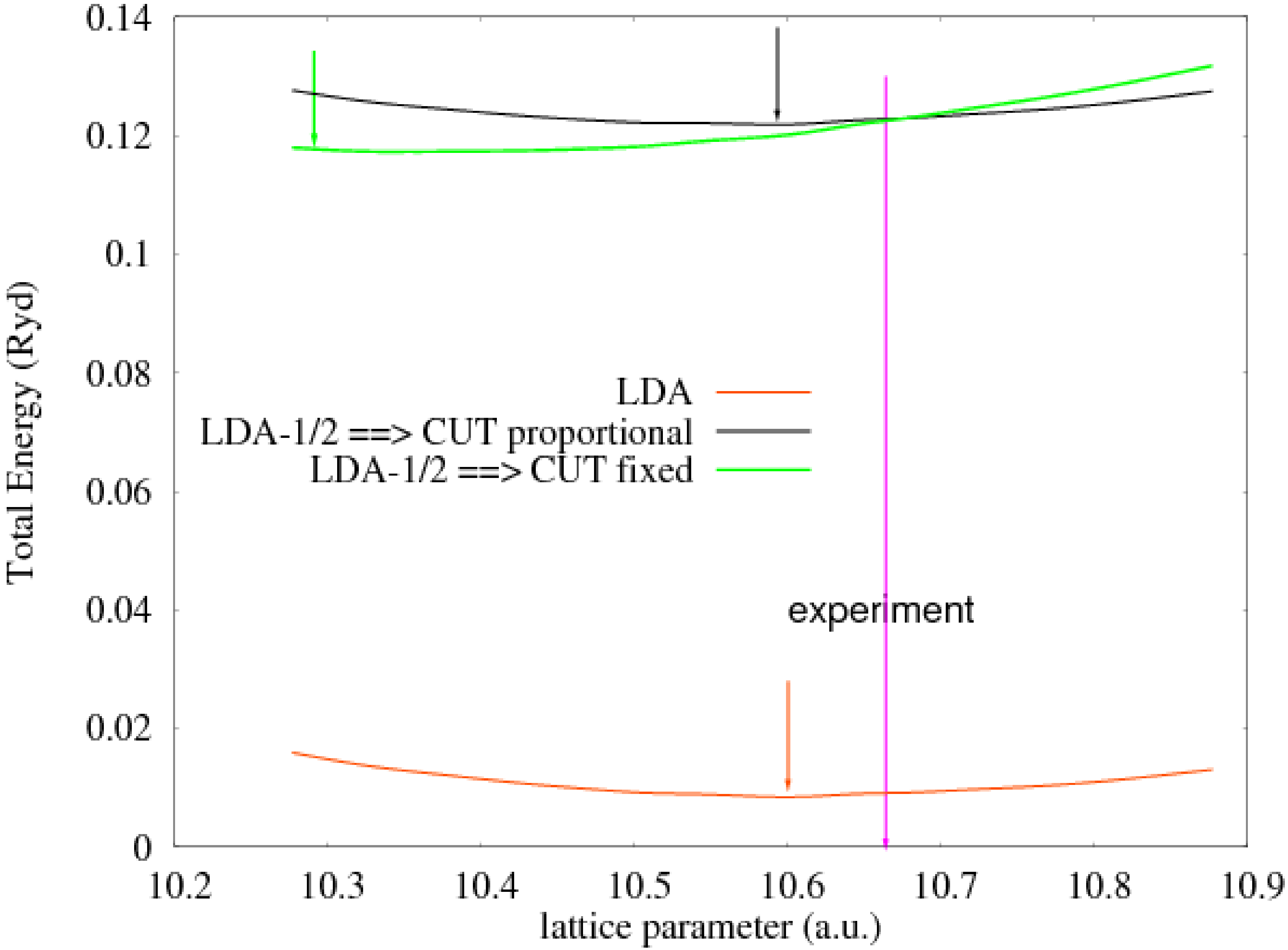
What about the ground state properties? Geometry, Bulk Modulus... ?

HK and KS never gave permission to subtract terms from the total energy.

What was subtracted must now be added

$$E_0 = \sum_{\beta} f_{\beta,0} e_{\beta} - \frac{1}{2} \int V[\rho]\rho + E_{xc}[\rho] - \int \rho \frac{\delta E_{xc}}{\delta \rho} + \int V_S \rho$$

GaAs


0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
Total Energy (Ryd)
10.2
10.3
10.4
10.5
10.6
10.7
10.8
10.9
lattice parameter (a.u.)
LDA
LDA-1/2 ==> CUT proportional
LDA-1/2 ==> CUT fixed
experiment

The case of NiO

1 - Antiferromagnetic

2 – Rock Salt

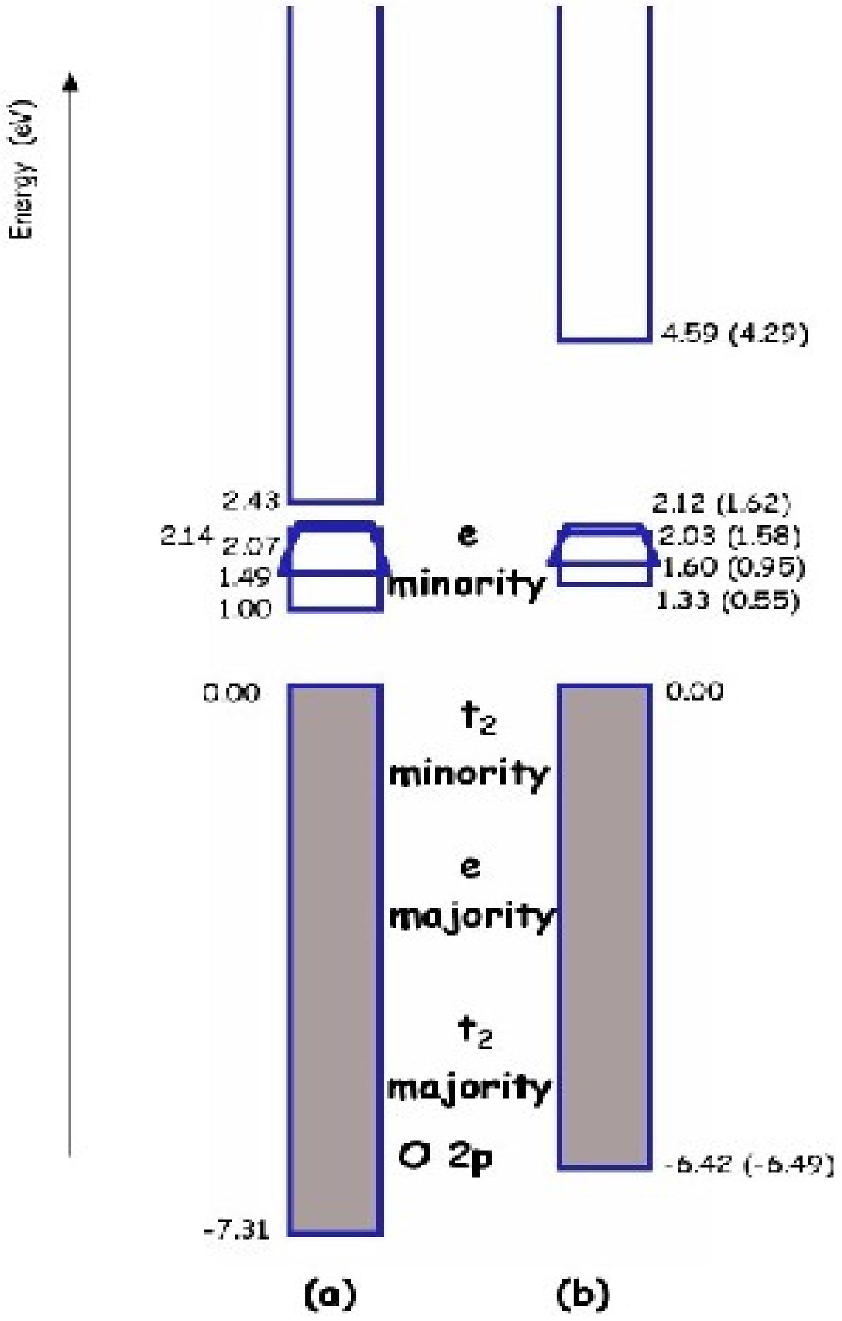
3 – Spin up and spin down planes alternating along the body diagonal

4 – Simple description

$$NiO = Ni^{++}[(t_2\uparrow)^3(e\uparrow)^2(t2\downarrow)^3]\;\; O^{--}[p^6]$$

5 – Alternation of Ni planes

$$Ni^{++}[\uparrow^5\downarrow^3]\;\; Ni^{++}[\uparrow^3\downarrow^5]\;\; Ni^{++}[\uparrow^5\downarrow^3]\;\; \ldots$$

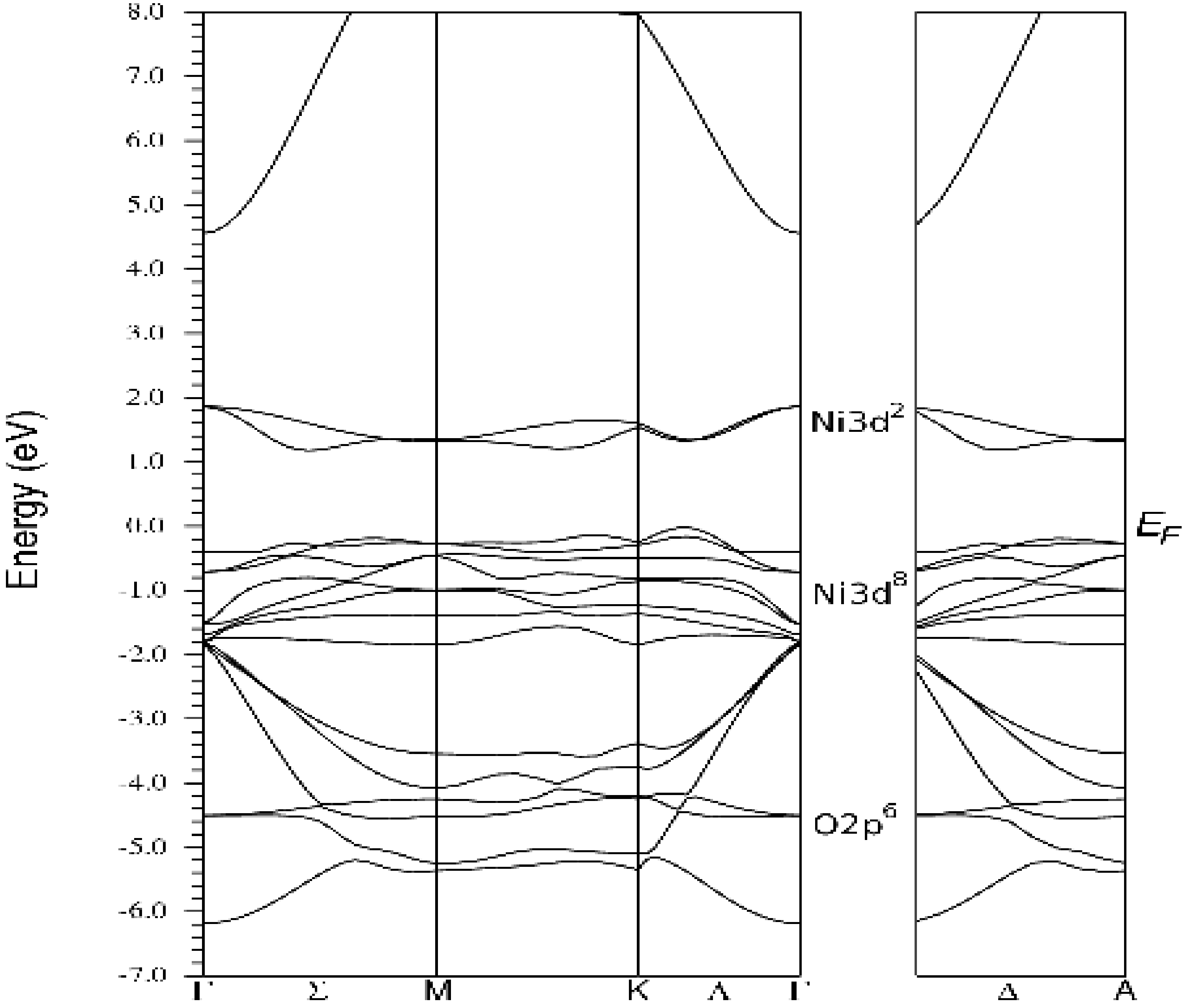


Parity and spin inhibit transition to first empty bands

Evidence for these bands:

1 – Electron-energy loss, Müller and Hüfner, PRB 2008.

2 – Inelastic x-ray, Huotari et al, PRB(R) 2008.


Energy (eV)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
Γ
Σ
M
K
Λ
Γ
Δ
A
$Ni3d^2$
E_F
$Ni3d^8$
$O2p^6$