Exact-exchange approach in the KS formalism of DFT

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Collaborators & Support

- Collaborators:

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  - New comers: Matthias Wahn and Hazem Abu-Farsakh

- Support: from the Volkswagen Stiftung.

KS formalism

- Total energy separation

$$E_{tot} = T_o + E_H + E_{e-i} + E_X + E_C$$

- Single particle KS equations

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 + V_{ion} + V_H[\rho] + V_X[\rho] + V_C[\rho] \right\} \psi_i = \varepsilon_i \psi_i, \text{ with}$$

$$\rho(r) = \sum_i^{occ} |\psi_i(r)|^2 \quad ; \quad V_y = \frac{\delta E_y}{\delta \rho(\mathbf{r})} \quad (y = H, X \text{ and } C)$$

(1)

Approximations to $E_X + E_C$ (E_{XC})

- LDA: $E_{XC}^{LDA} = \int \varepsilon_{xc}^{\text{hom}}(\rho(\mathbf{r}))\rho(\mathbf{r})d\mathbf{r}$
- GGA: $E_{XC}^{GGA} = \int \rho(\mathbf{r}) f_{xc}(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \ldots)d\mathbf{r}$
- For the success and weaknesses of LDA and GGA, see the lecture notes of Martin Fuchs (L8).

The exact-exchange (EXX) approach

- In this approach E_X is exactly calculated ==> only E_C needs to be approximated

- Two views:
- E_{XC} is only a small portion of E_{tot}, and E_X is an order larger than E_C

  ⟶ EXX is a major step forward.

- LDA and GGA are good because of some cancellation of errors between E_X and E_C ==> treating one of them exactly may do more bad than good.

- Which view is more correct?

Outline:

- Introduction => Self-interaction and its correction
- Exact-exchange (EXX) scheme and its implementation in a pseudopotential-PW code
- Results

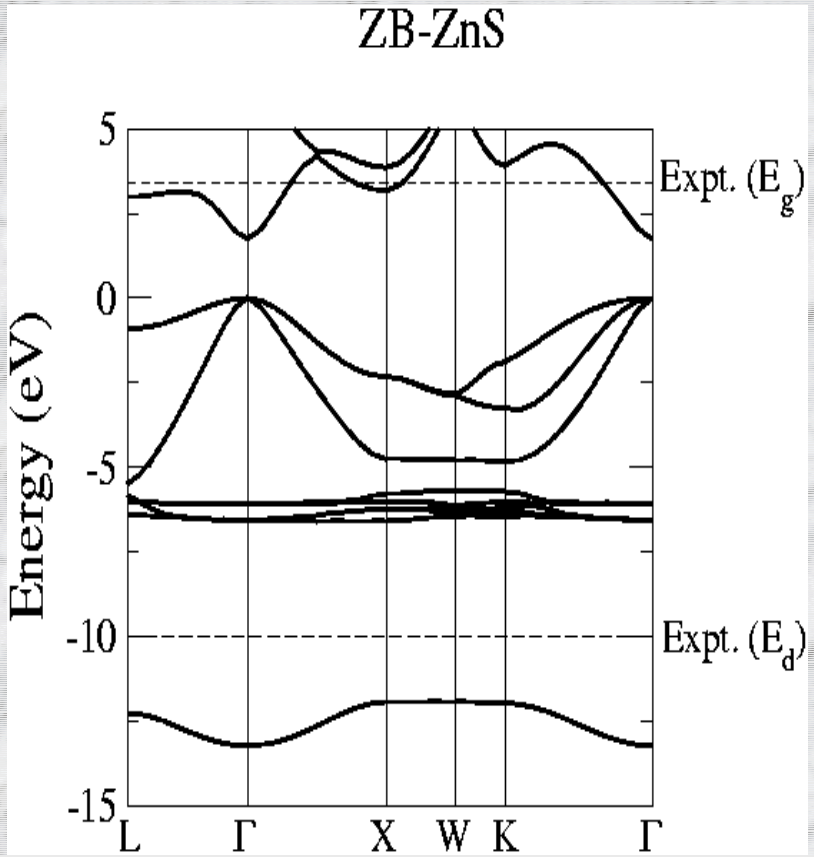
Part I: Introduction

Some serious drawbacks of LDA and GGA:

- Band-gap problem: E_g of semiconductors and insulators are underestimates by 50 to 100%.

- Binding energies of the *semicore* electrons are higher than experiment by 2 to 4 eV, in case of II-IV and group-III nitrides.

→ **Due to self-interaction (SI), Zhang, Wei and Zunger, PRB 52, 13975 (1995).**

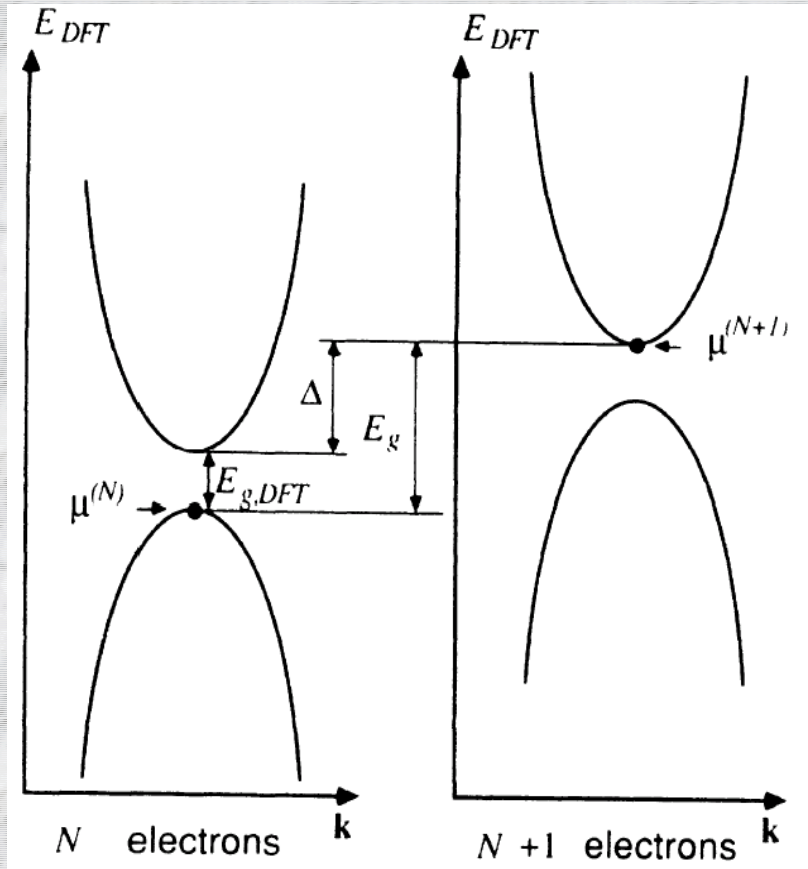


Reason for the Band-gap problem

- Discontinuity in V_{XC}

$$\Delta \equiv E_g - (E^{(N)}_{N+1,\mathrm{DFT}} - E^{(N)}_{N,\mathrm{DFT}})$$
$$= V^{(N+1)}_{\mathrm{xc}}(\mathbf{r}) - V^{(N)}_{\mathrm{xc}}(\mathbf{r})$$

- The magnitude of Δ is still an open problem



Godby Schlutter and Sham, PRB 37, 10 159 (88) ,

Main problem with LDA and GGA

- They allow for spurious **self-interaction** (SI).
- Exact DFT is SI free:

$$E_x = -\frac{e^2}{2}\sum_{\nu\nu'\mathbf{k}\mathbf{k}'}\iint \frac{\varphi^*_{\nu\mathbf{k}}(\mathbf{r})\varphi_{\nu\mathbf{k}}(\mathbf{r}')\varphi_{\nu'\mathbf{k}'}(\mathbf{r}')\varphi^*_{\nu'\mathbf{k}'}(\mathbf{r})}{|r-r'|}d\mathbf{r}d\mathbf{r}'$$

for $\nu\mathbf{k} = \nu'\mathbf{k}'$,

$$E_x^{self} = -\frac{e^2}{2}\iint \frac{\rho_{\nu\mathbf{k}}(\mathbf{r})\rho_{\nu\mathbf{k}}(\mathbf{r}')}{|r-r|}d\mathbf{r}d\mathbf{r}' = -E_H^{Self}$$

$\Rightarrow$ Exact cancelation between *self* V_H and V_X

$\Rightarrow$ This is not the case for LDA and GGA.

Self-interaction correction (SIC)

[Predew and Zunger, PRB 23, 5048 (1981)]

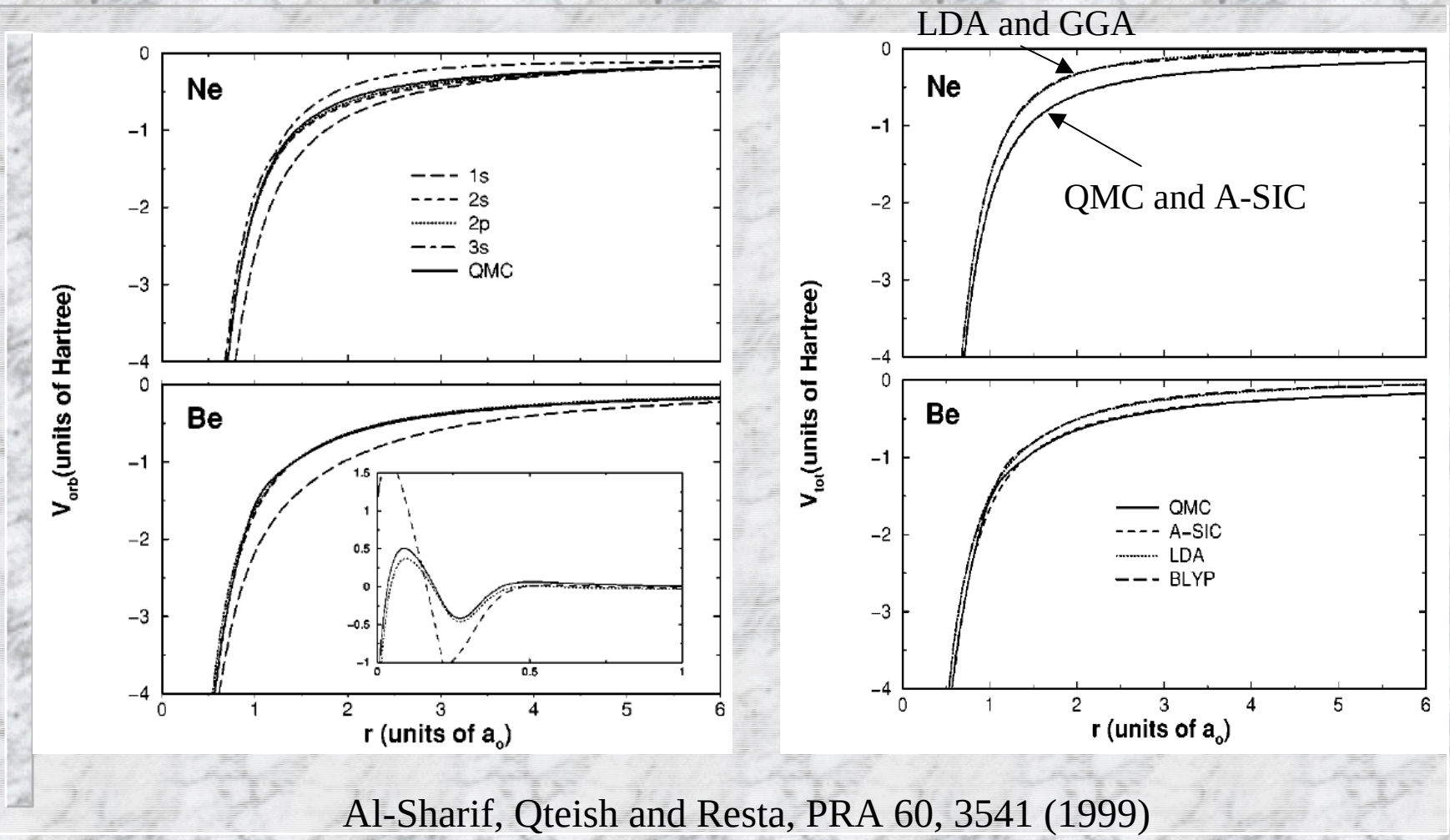
$$E_{tot}^{\text{SIC-LDA}} = T_o + E_{ext} + E_H[\rho] + E_{\text{XC}}^{\text{LDA}}[\rho] - \sum_i^{occ} \left[\frac{1}{2} \int V_H[\rho_i]\rho_i(\mathbf{r}) d\mathbf{r} + E_{\text{XC}}^{\text{LSD}}[\rho_{i\uparrow}, 0] \right]$$

And the single particle equations become (in atomic units)

$$(-\nabla^2/2 + V_{ext} + V_H[\rho] + V_{\text{XC}}^{\text{LDA}}[\rho] - V_H[\rho_i] - V_{\text{XC}}^{\text{LSD}}[\rho_{i\uparrow}, 0])\Psi_i^{\text{SIC}}(\mathbf{r}) = \varepsilon_i^{\text{SIC}}\Psi_i^{\text{SIC}}(\mathbf{r}),$$

→ *Orbital dependent effective (or KS) potential*

Comparison with Near-Exact KS potentials, obtained from QMC calculations



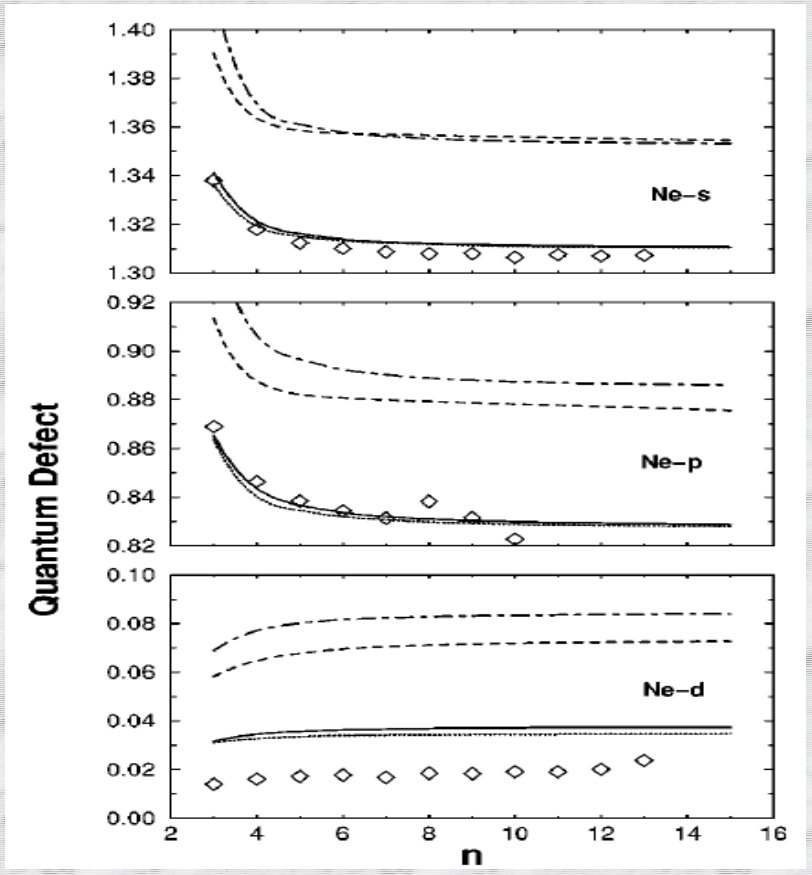
Al-Sharif, Qteish and Resta, PRA 60, 3541 (1999)

Physical reality of KS potentials

- Near-exact KS potentials are the ones which reproduce the near-exact ρ(r), obtain from QMC calculations.

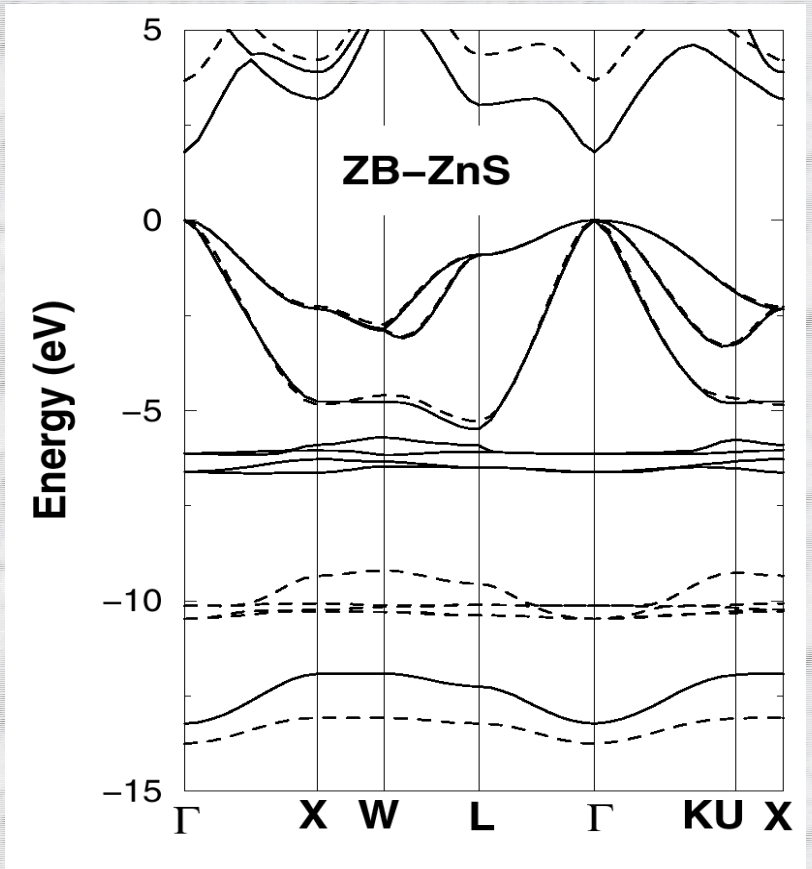
Relation between Quantum defects and eigenvalues

$$E_{nl} = -\frac{1}{2(n-\delta_{n,l})^2}$$



SIC pseudopotential method (Vogel, Kruger and Pollmann, 1996)

- SIC is introduced in a non-self-consistent manner, and taken to be that of the corresponding atomic valence orbitals.
- Incorporated as part of the pseudopotential.
- The band-gaps and positions of semi-core d-electrons are well reproduced.



Qteish, JPCM 12, 5639 (2000)

Energy differences within the SIC-PP method

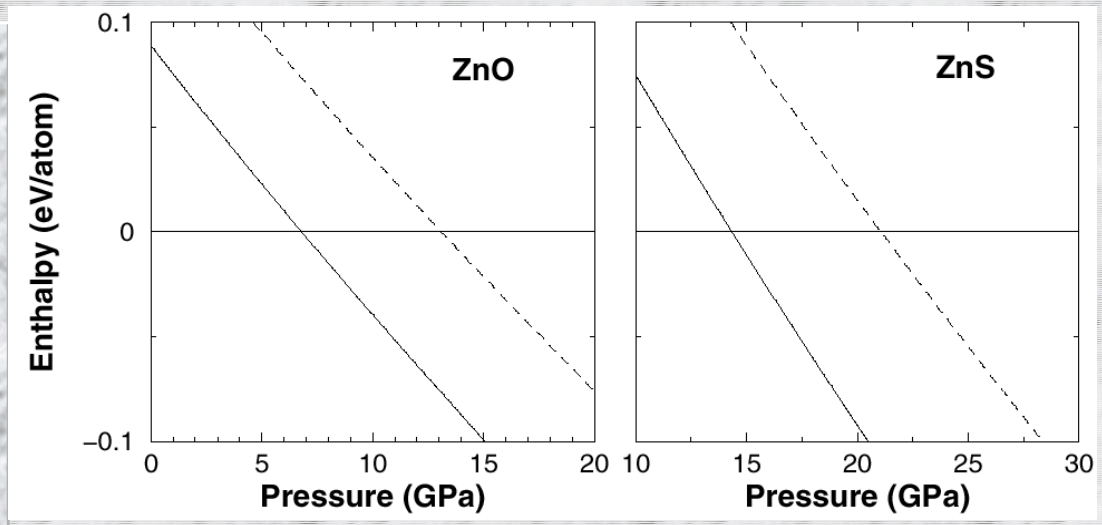


Table 3. Transition pressures (GPa) of the phase transitions of ZnO and ZnS studied.

		Present work		
System	Transition	LDA	SIC-PP	Experiment
ZnO	ZB → RS	6.6[a]	13.3[a], 13.4[b]	—
	W → RS	6.7[a]	—	2.0–8.7[c], 8.0[d], 9.0[e], 9.5[f]
ZnS	ZB → RS	14.35[a]	21.1[a]	14.7–15.4[g], 15.0–16.2[h], 12.0[i], 18.1[d]

→ Not good

Summary of part I:

- The spurious SI allowed by LDA and GGA is quite important, especially for highly localized states.
- SIC methods give very encouraging results.
- A SI free method within the KS formalism would highly desirable.

Part II: Theory and implementation of the EXX method

Theory of Exact-exchange (EXX)

[Stadele et al. PRB **59**, 10 031 (1999)]

- Total energy

$$E_{tot}[\rho] = T_o + E_{e-i} + \frac{e^2}{2}\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' -$$

$$\frac{e^2}{2}\sum_{vv'\mathbf{k}\mathbf{k}'}\iint \frac{\varphi^*_{v\mathbf{k}}(\mathbf{r})\varphi_{v\mathbf{k}}(\mathbf{r}')\varphi_{v'\mathbf{k}'}(\mathbf{r}')\varphi^*_{v'\mathbf{k}'}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_C[\rho]$$

- Single-particle equations

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V_{ion} + V_H[\rho] + V_X[\rho] + V_C[\rho]\right\}\psi_i = \varepsilon_i \psi_i, \text{ with}$$

$$V_X = \frac{\delta E_X}{\delta \rho(\mathbf{r})} = \sum_{vk}\iint \left[\frac{\delta E_X[\rho]}{\delta \varphi_{vk}(r')}\frac{\delta \varphi_{vk}(r')}{\delta V_{KS}(r'')} + c.c.\right]\frac{\delta V_{KS}(r'')}{\delta \rho(\mathbf{r})}$$

The derivatives appearing in above expression of V_x can be explicitly calculated

$$\frac{\delta E_x[\rho]}{\delta \varphi_{v\mathbf{k}}(\mathbf{r}')} = -e^2 \sum_{v'\mathbf{k}'} \int d\mathbf{r}_1 \frac{\varphi^*_{v'\mathbf{k}'}(\mathbf{r}')\varphi^*_{v\mathbf{k}}(\mathbf{r}_1)\varphi_{v'\mathbf{k}'}(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}'|}.$$

$$\frac{\delta \varphi_{v\mathbf{k}}(\mathbf{r}')}{\delta V_{KS}(\mathbf{r}'')} = \sum_{n'\mathbf{k}' \neq v\mathbf{k}} \varphi_{n'\mathbf{k}'}(\mathbf{r}') \frac{\varphi^*_{n'\mathbf{k}'}(\mathbf{r}'')\varphi_{v\mathbf{k}}(\mathbf{r}'')}{\varepsilon_{v\mathbf{k}} - \varepsilon_{n'\mathbf{k}'}}.$$

$$\frac{\delta \rho(\mathbf{r})}{\delta V_{KS}(\mathbf{r}')} = \chi_0(\mathbf{r},\mathbf{r}') \Rightarrow \frac{\delta V_{KS}(\mathbf{r}')}{\delta \rho(\mathbf{r})} = \chi_0^{-1}(\mathbf{r},\mathbf{r}')$$

So, V_x becomes,

$$V_x(\mathbf{r}) = \int d\mathbf{r}' \sum_{vc\mathbf{k}} \left[< \varphi_{v\mathbf{k}} | V_X^{NL} | \varphi_{c\mathbf{k}} > \frac{\varphi_{c\mathbf{k}}^*(\mathbf{r}')\varphi_{v\mathbf{k}}^*(\mathbf{r}')}{\varepsilon_{c\mathbf{k}} - \varepsilon_{v\mathbf{k}}} \right] \chi_0^{-1}(\mathbf{r}, \mathbf{r}')$$

with

$$V_X^{NL}(\mathbf{r}, \mathbf{r}') = -e^2 \sum_{v\mathbf{q}} \frac{\varphi_{v\mathbf{q}}(\mathbf{r})\varphi_{v\mathbf{q}}^*(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

The χ_0 is defined as

$$\chi_0(\mathbf{r}, \mathbf{r}') = 2 \sum_{vc\mathbf{k}} \frac{\varphi_{v\mathbf{k}}^*(\mathbf{r})\varphi_{c\mathbf{k}}(\mathbf{r})\varphi_{c\mathbf{k}}^*(\mathbf{r}')\varphi_{v\mathbf{k}}(\mathbf{r}') + \text{c.c.}}{\varepsilon_{v\mathbf{k}} - \varepsilon_{c\mathbf{k}}}.$$

In momentum space we have

$$V_x(\mathbf{G}) = \sum_{\mathbf{G}' \neq 0} [E(\mathbf{G}') + E^*(-\mathbf{G}')]\tilde{\chi}_0^{-1}(\mathbf{G},\mathbf{G}'),$$

$$E(\mathbf{G}) = \frac{2}{\Omega} \sum_{vc\mathbf{k}} \frac{\langle v\mathbf{k}|\hat{V}_x^{NL}|c\mathbf{k}\rangle\langle c\mathbf{k}|e^{-i\mathbf{G}\mathbf{r}}|v\mathbf{k}\rangle}{\varepsilon_{v\mathbf{k}} - \varepsilon_{c\mathbf{k}}}.$$

with

$$\chi_0(\mathbf{G},\mathbf{G}') = \frac{4}{\Omega} \sum_{vc\mathbf{k}} \frac{\langle v\mathbf{k}|e^{-i\mathbf{G}\mathbf{r}}|c\mathbf{k}\rangle\langle c\mathbf{k}|e^{i\mathbf{G}'\mathbf{r}}|v\mathbf{k}\rangle}{\varepsilon_{v\mathbf{k}} - \varepsilon_{c\mathbf{k}}}.$$

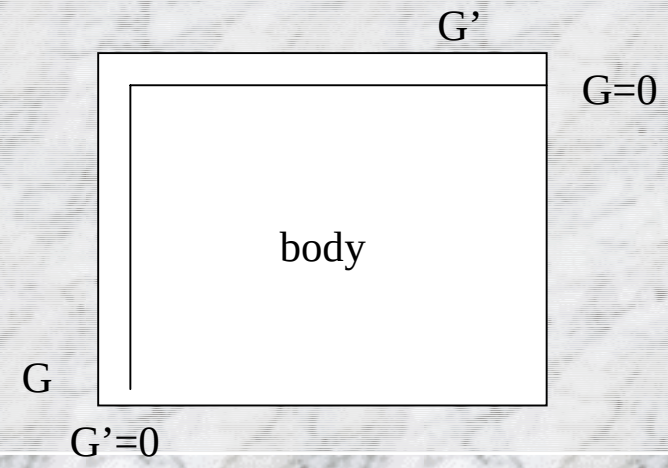
and

$$V_x^{NL}(\mathbf{k},\mathbf{G},\mathbf{G}') = -\frac{4\pi e^2}{\Omega} \sum_{v\mathbf{q}\mathbf{G}_1} \frac{C_{v\mathbf{q}}(\mathbf{G}+\mathbf{G}_1)C_{v\mathbf{q}}^*(\mathbf{G}'+\mathbf{G}_1)}{|\mathbf{q}-\mathbf{k}+\mathbf{G}_1|^2}$$

Note: the no. of G-vectors included, here, is controlled in SFHIngX by: ChiEcut

Some Technical details:

- The singularities in V_x^{NL} **(k,G,G')** when **k**=**q**+$\mathbf{G_1}$, are removed as suggested by Gygi and Baldereschi [PRB **34**, 4405 (86)]
- The $\varphi_{c\mathbf{k}}$ and $\varepsilon_{c\mathbf{k}}$ needed for χ are obtained by direct diagonalization, and all conduction band states are included
- Only the body of χ is calculated and inverted:



- This is because we require that

$$\delta\rho(\mathbf{G}=0)=0 \quad , \text{ and}$$

$$\delta\rho(\mathbf{G})=0 \qquad \text{for} \qquad \delta V_{KS}=const.$$

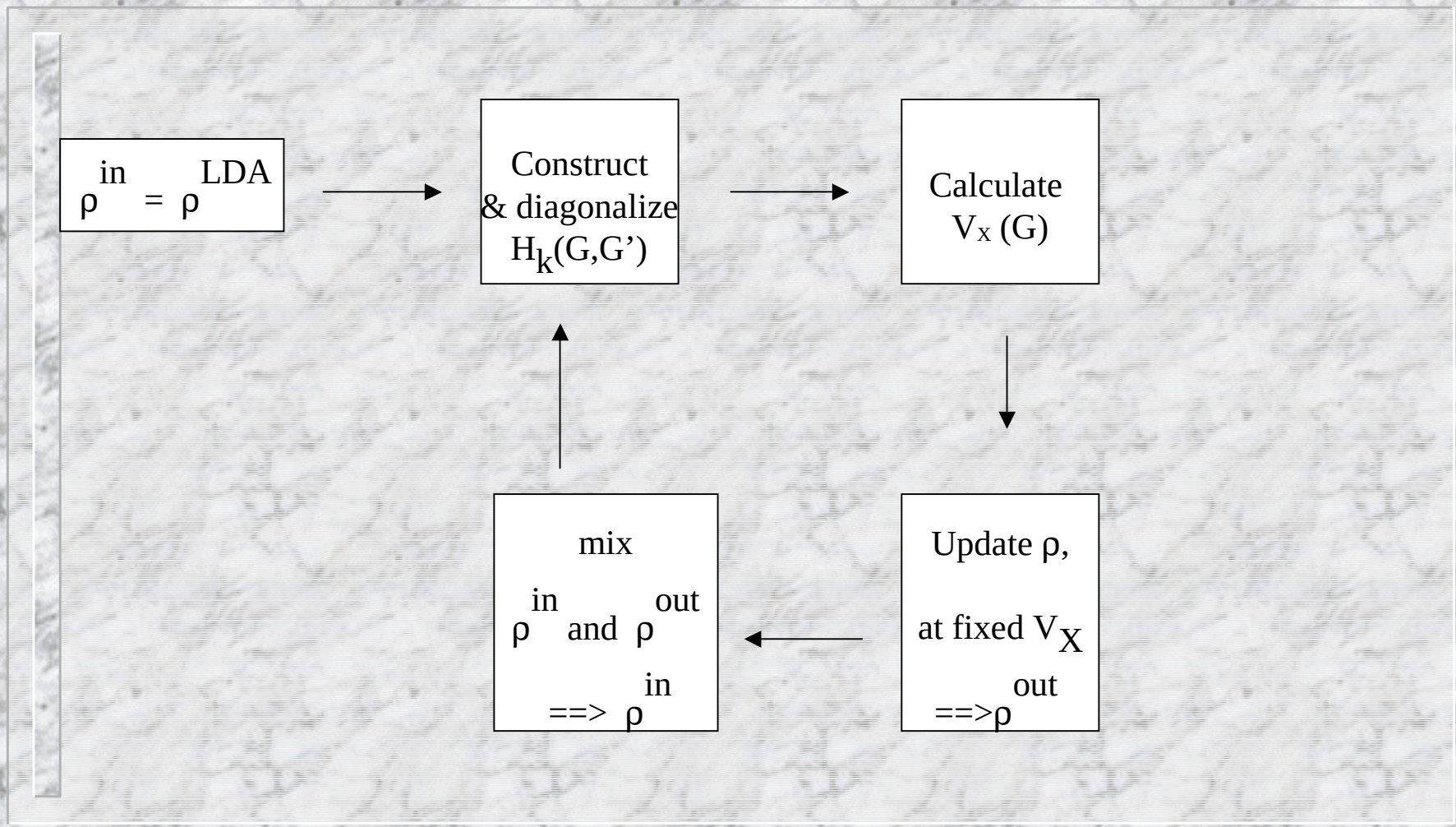
- Note that:

$$\delta\rho(\mathbf{G})=\sum_{G'}\chi_0(\mathbf{G},\mathbf{G}')\delta V_{KS}(\mathbf{G}')$$

- This leads to

$$V_X(\mathbf{G}=0)=0$$

EXX loop


$\rho^{in} = \rho^{LDA}$
Construct & diagonalize $H_k(G,G')$
Calculate $V_X(G)$
Update ρ, at fixed V_X ==>ρ^{out}
mix ρ^{in} and ρ^{out} ==> ρ^{in}

Summary of part II.

- The EXX approach is quite straightforward to implement in a PP-PW code.
- The EXX potential is local.
- It is highly demanding in terms of CPU time and memory.
- In its present implementation it works only for non-metallic systems.

Part III: Results

Lattice parameters

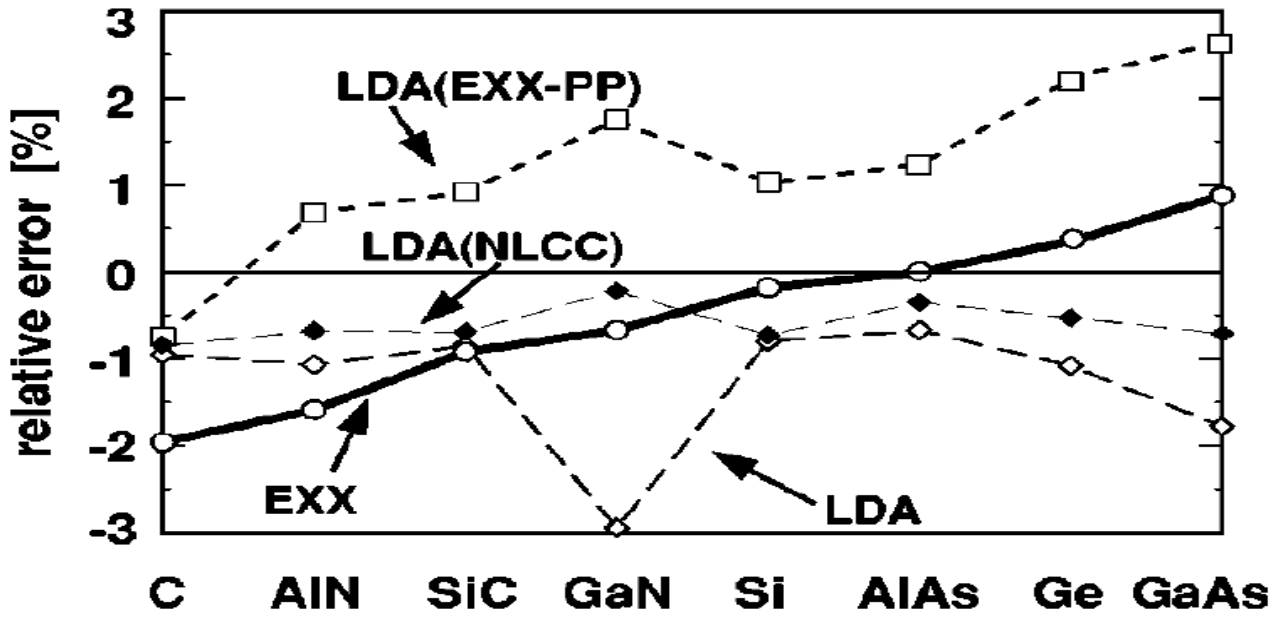
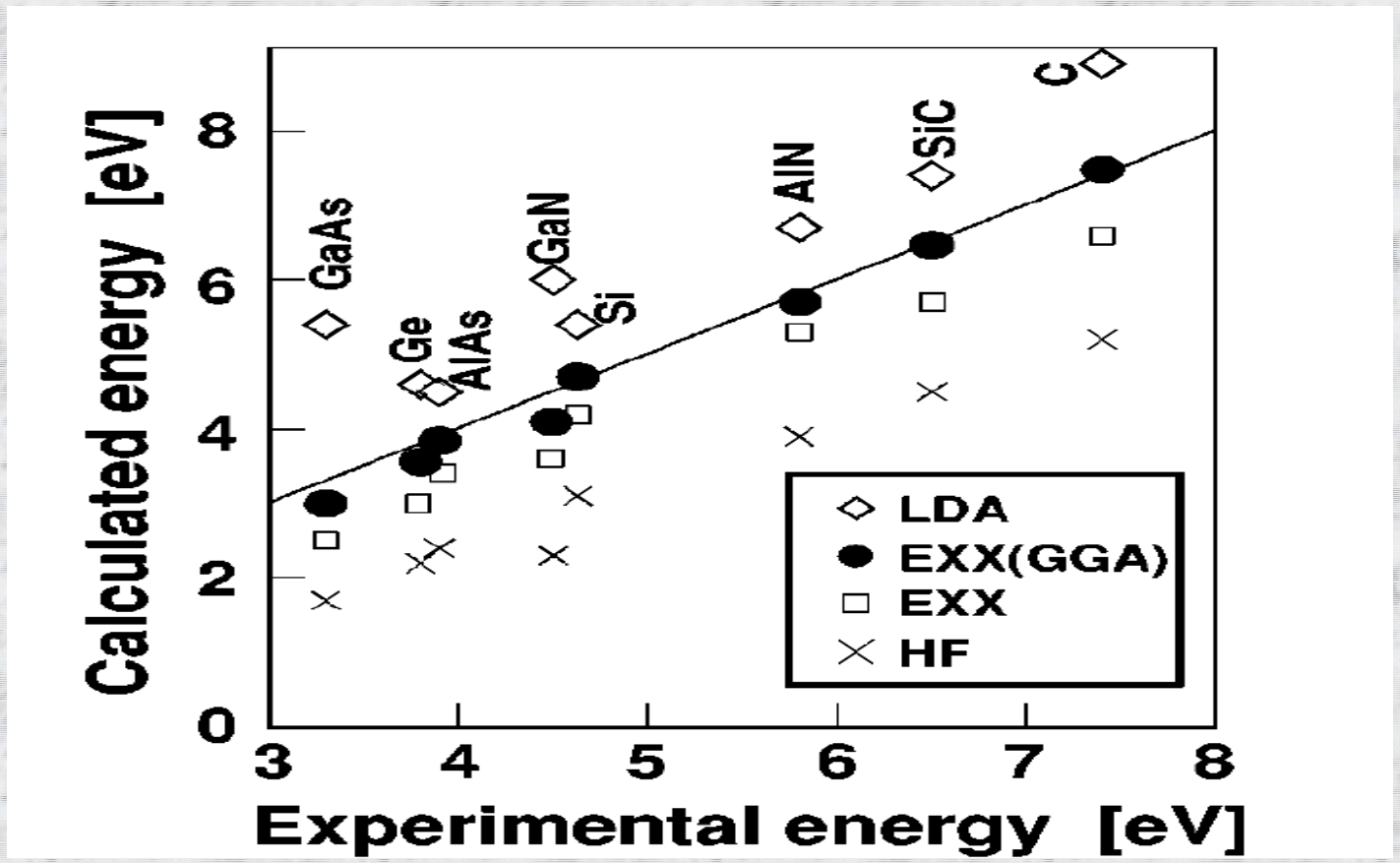


FIG. 1. Relative deviations (given in percent) of self-consistently calculated LDA and EXX lattice constants of various semiconductors from the experimental values that are taken from

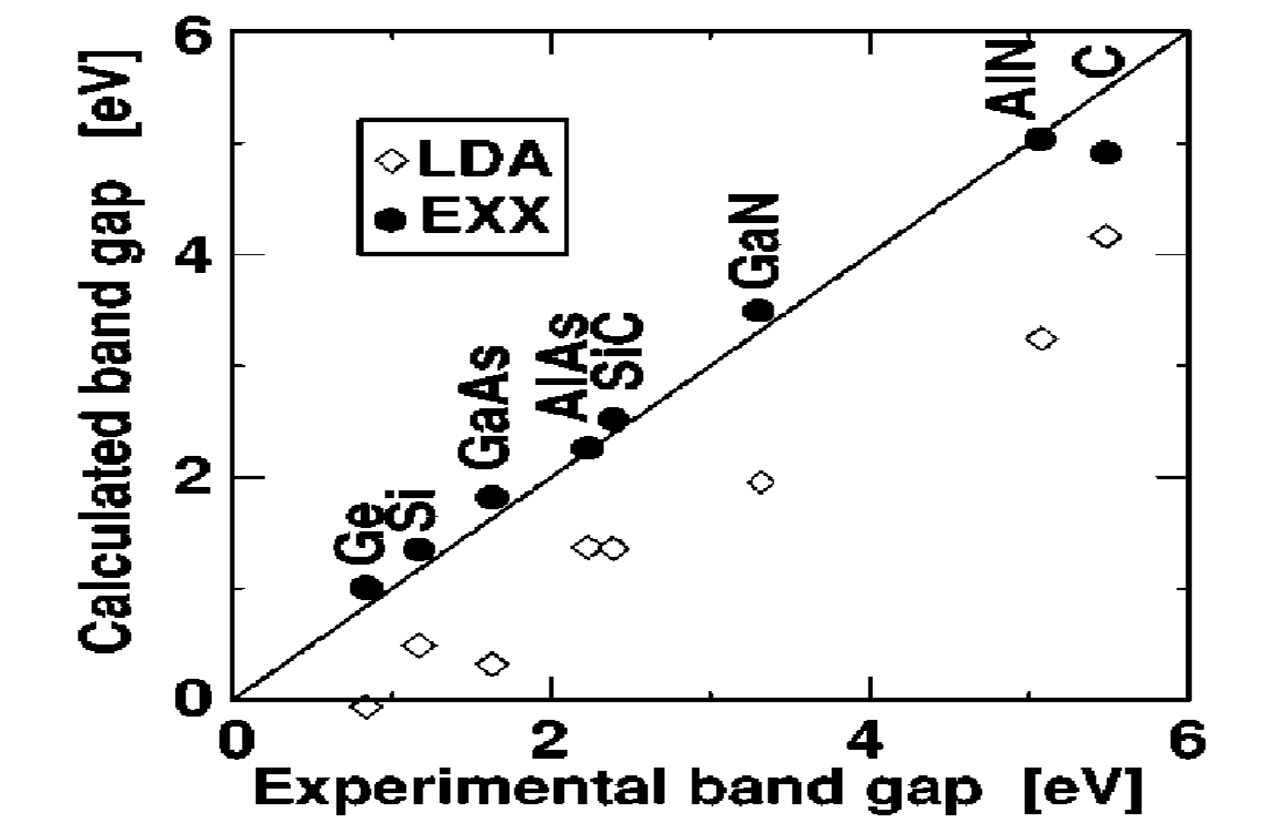
Stadele et al. PRB **59**, 10 031 (1999)

Cohesive energies



Stadele et al. PRB **59**, 10 031 (1999)

Band gaps



Stadele et al. PRB **59**, 10 031 (1999)

Effective masses [Stadele et al. PRB **59**, 10 031 (1999)]

		LDA	EXX	Expt.
Si	m_l^Δ	0.95	0.97	0.92
	m_t^Δ	0.19	0.22	0.19
Ge	m_l^L	1.71	1.70	1.57
	m_t^L	0.07	0.10	0.08
C	m_l^Δ	1.68	1.59	1.4
	m_t^Δ	0.29	0.29	0.36
GaAs	m_Γ	0.02	0.10	0.07
AlAs	m_l^X	0.84	0.95	1.0
	m_t^X	0.24	0.27	0.25
GaN	m_Γ	0.17	0.26	0.20
AlN	m_Γ	0.30	0.36	
SiC	m_l^X	0.68	0.67	0.68
	m_t^X	0.23	0.26	0.25

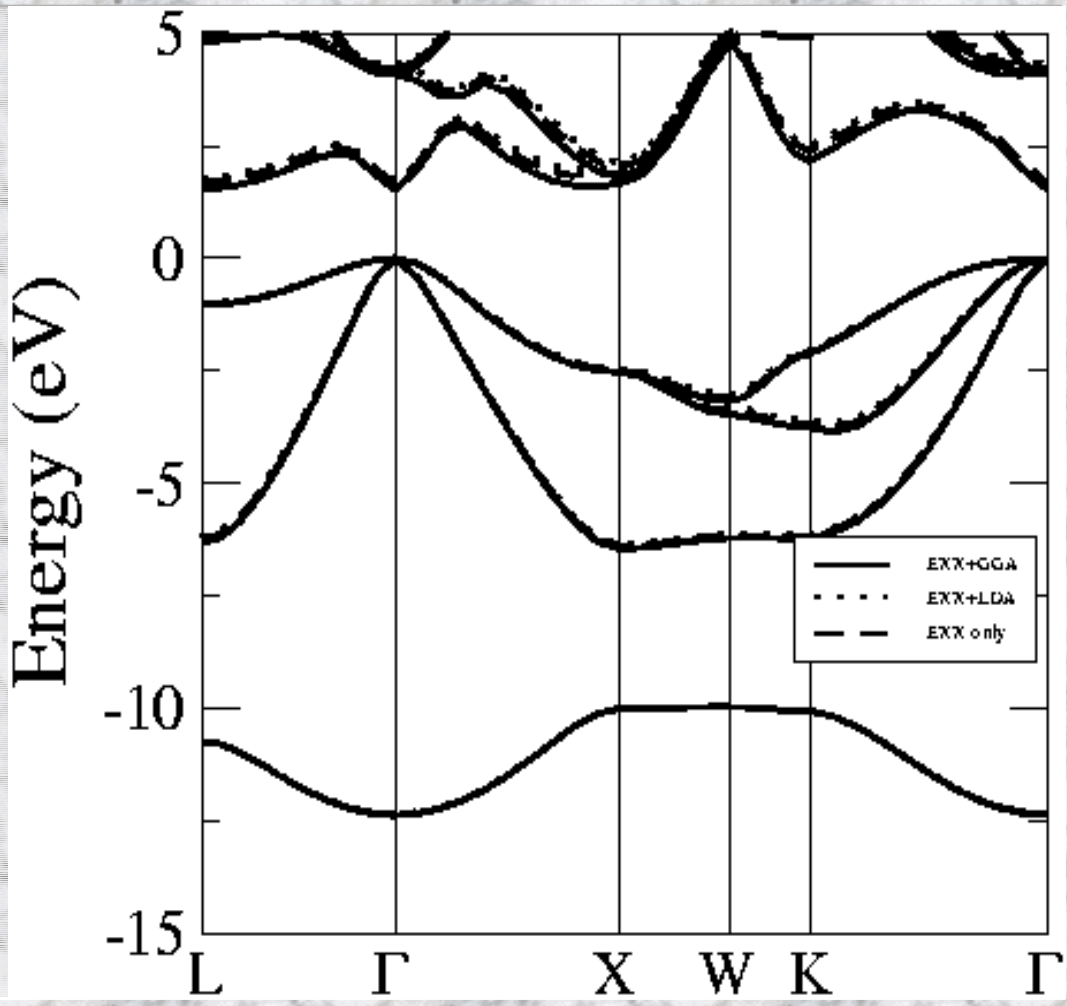
Correlation effects: I. On the band-gaps

Example == bulk GaAs

Band gap

Approach	Value (eV)
EXX+GGA Corr.	1.53
EXX+LDA Corr.	1.70
EXX (only)	1.68
Expt.	1.63

→ Similar results are also obtained by Stadele et al.



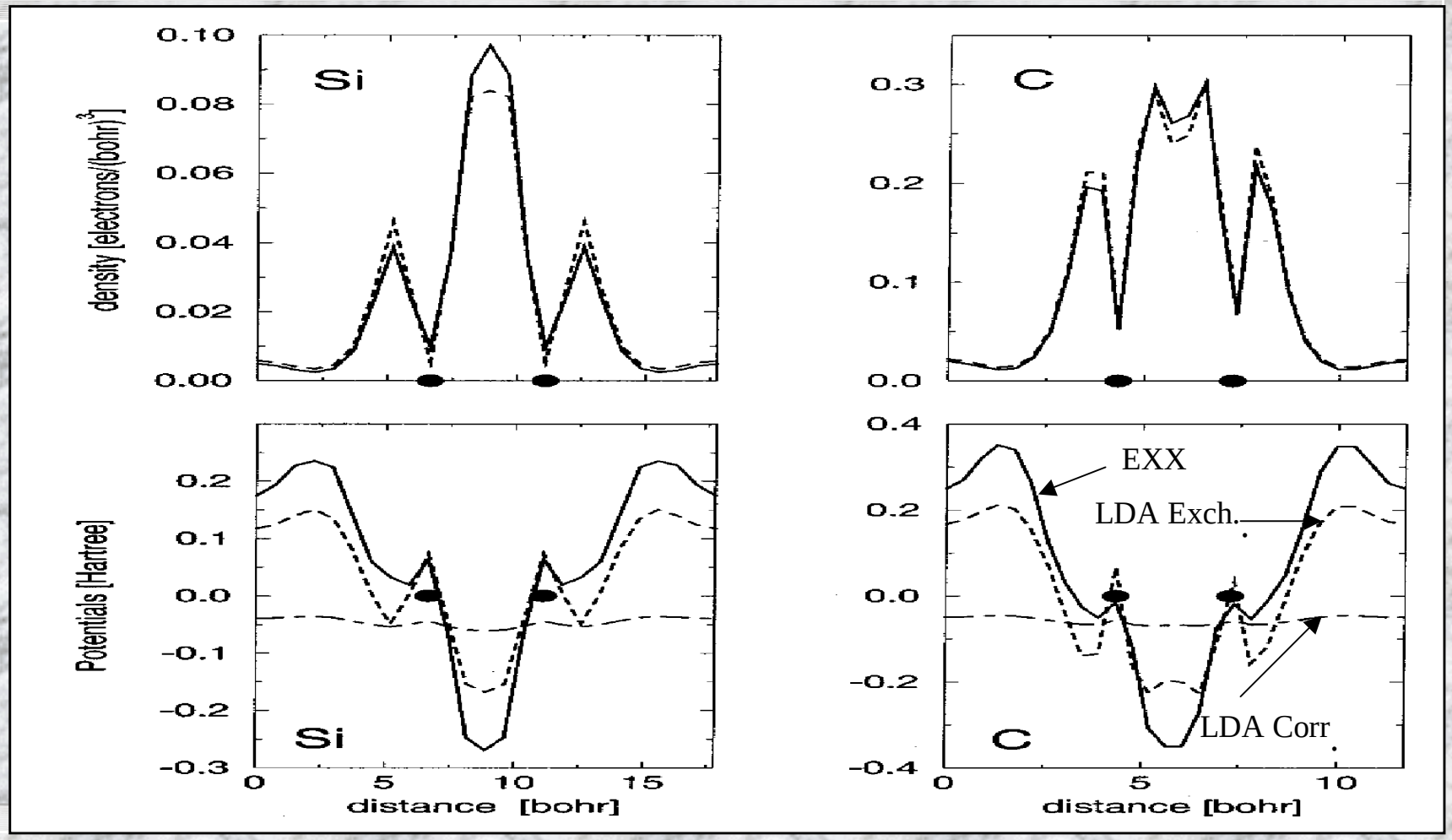
Correlation effects: II. On the structural properties

Example == bulk GaAs

	EXX+PBE_C	EXX+LDA_C	EXX(only)	LDA	Expt.
a_0(Bohr)	10.72	10.63	10.83	10.59	10.68
B_0 (Mbar)	0.76	0.88	0.78	0.74	0.77

→ Correlation effects are quite small for both structural and electronic structure properties of semiconductors.

Exchange vs correlation potentials



Band-gap problem revisited

[Stadele et al. PRB **59**, 10 031 (1999)]

$$E_{gap} = E(N+1) + E(N-1) - 2E(N)$$
$$= \varepsilon_{gap}^{KS} + \Delta_{xc} = \varepsilon_{gap}^{EXX(X)} + \varepsilon_{gap,c}^{KS} + \Delta_{xc}$$

The results shown imply that

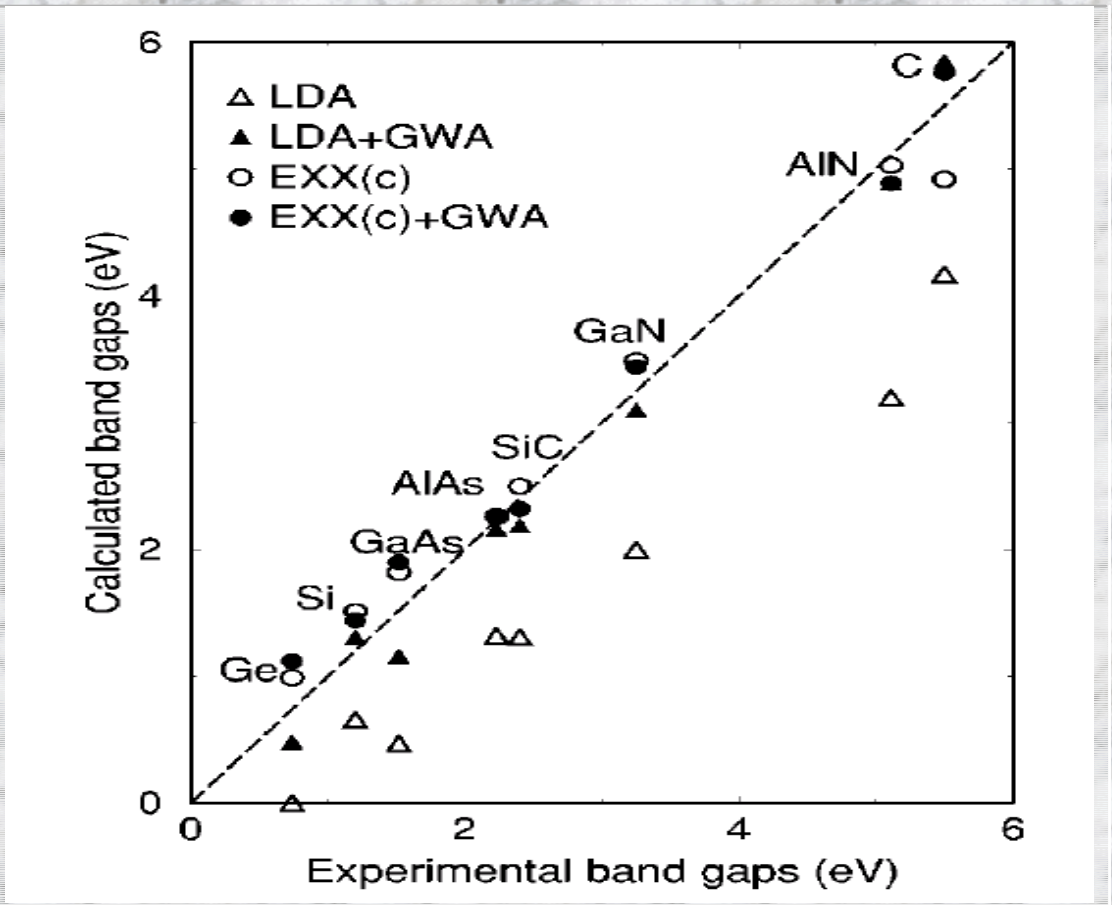
$$\Delta_{xc} \approx -\varepsilon_{gap,c}^{KS}$$

And Δ_{xc} to be rather small --- of order of 0.1 eV

EXX vs GW band gaps

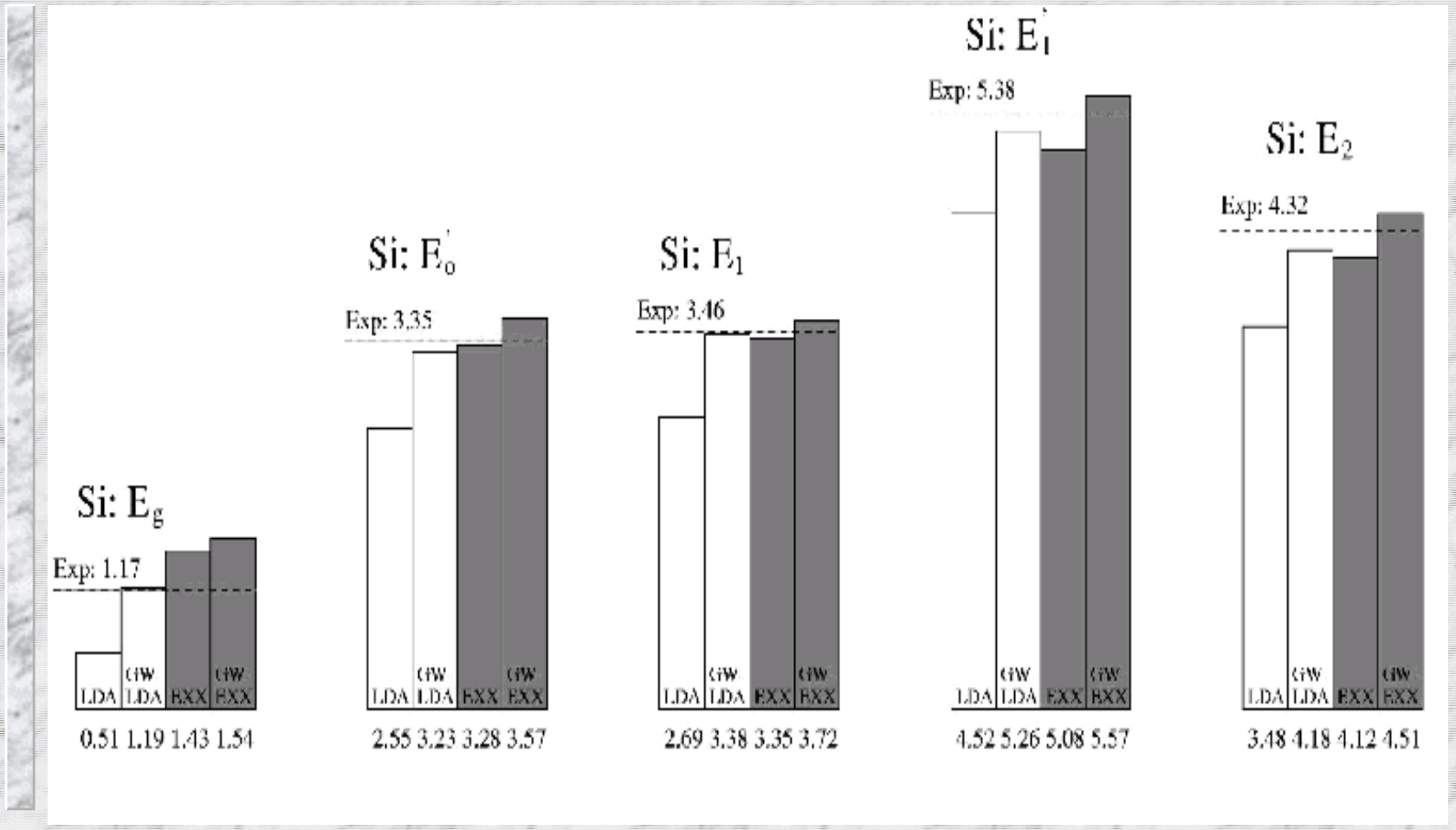
* LDA + GWA == GW calculations base on LDA results

* EXX + GWA == GW calculations base on EXX results

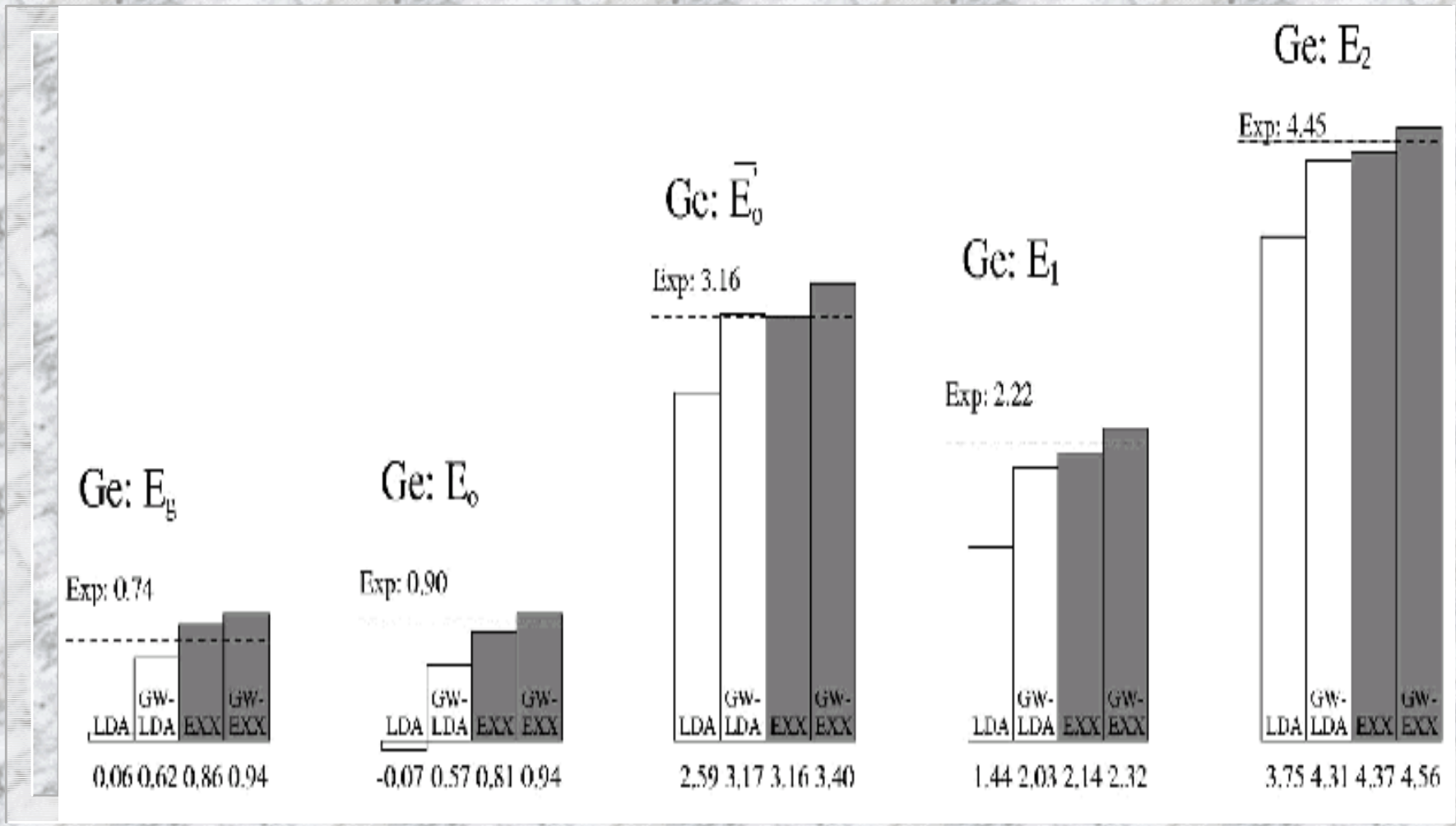


Aulbur et al. PRB **62**, 7121 (2000)

Band gaps of Si [Flezar, PRB **64**, 245204 (2001)]



Band gaps of Ge [Flezar, PRB **64**, 245204 (2001)]



Band Structure of group-III nitrides:

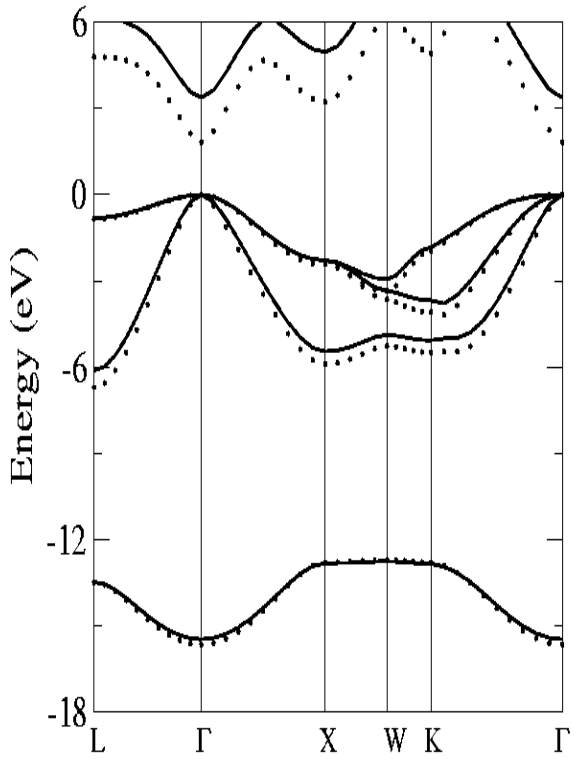
I. Treating the semicore d-electrons as core states

- Energy-gaps (eV)

	LDA	EXX (LDA Corr.)	Expt.
ZB-AlN	4.27	5.74	~6.0*
ZB-GaN	2.09	3.38	3.2-3.3
ZB-InN	0.17	1.49	0.7 * or 1.7 *

*Obtained by subtracting 0.2 eV from the band-gap of the corresponding wurtzite phase.

ZB-GaN



····· LDA ——— EXX

II. EXX and LDA calculations, using EEX-PP and treating the semicore d-electrons as core states

Energy-gaps (eV)

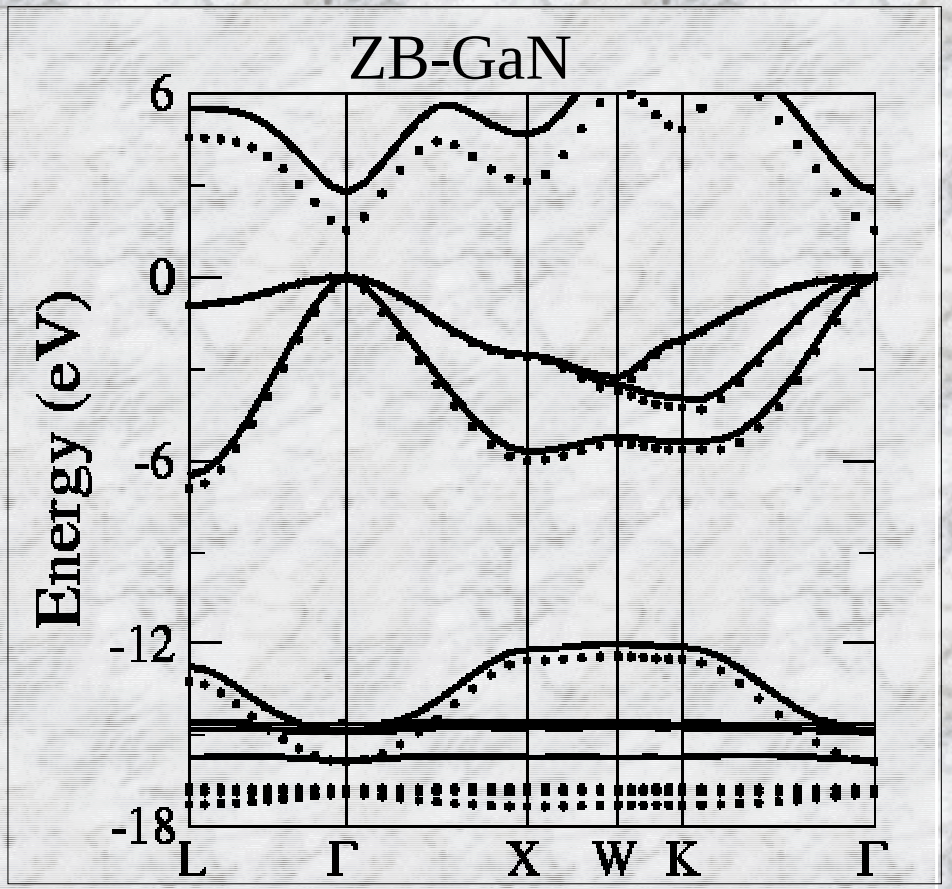
	LDA	EXX	Expt.
ZB-GaN	1.49[a],1.53[b]	2.76	3.2-3.3
ZB-InN	-0.49[a],-0.4[b]	0.81	0.7, 1.7[*]!!

[*]Obtained by subtracting 0.2 eV from the band-gap of the corresponding wurtzite phase.

Position of Occ. d-bands[*] (eV)

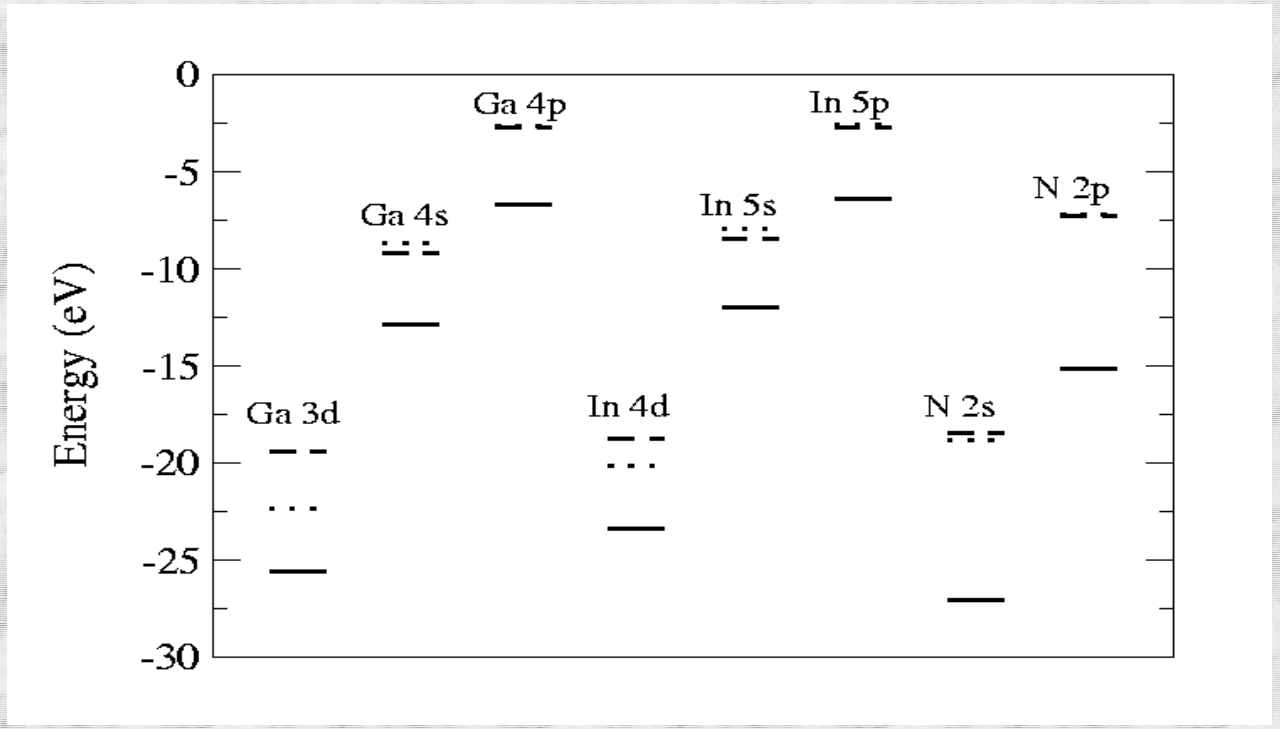
	LDA	EXX	Expt.
ZB-GaN	13.9[a],16.8[b]	14.7[b]	17.1
ZB-InN	13.6[a],14.9[b]	13.5[b]	14.9

[*]Below the valence band maximum
[a]Using LDA-PP.
[b]Using EXX-PP.



Explanation of the upward shift of the d-bands

Eigenvalues of the pseudo-atoms



Conclusions

- The EXX approach is really a major step forward.
- The EXX method gives band-gaps which are very close to those of GW.
- It is highly desirable to make it more efficient.