Complete basis limit with hybrid functionals using LAPW

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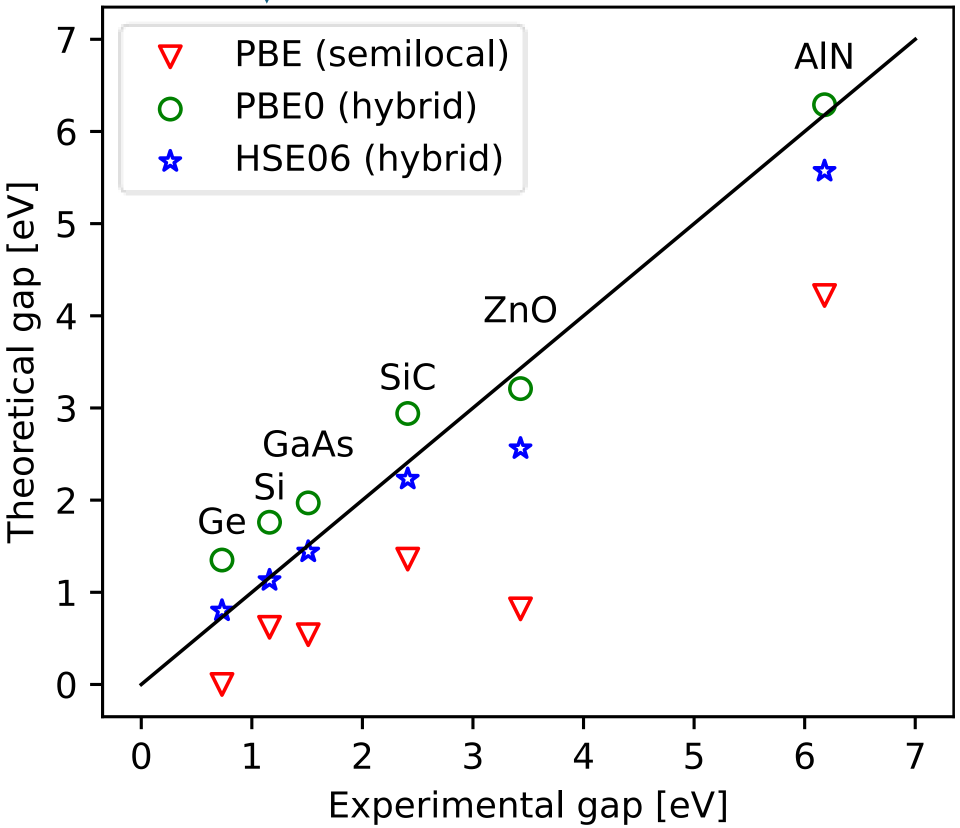
Motivation

Why are hybrids needed?

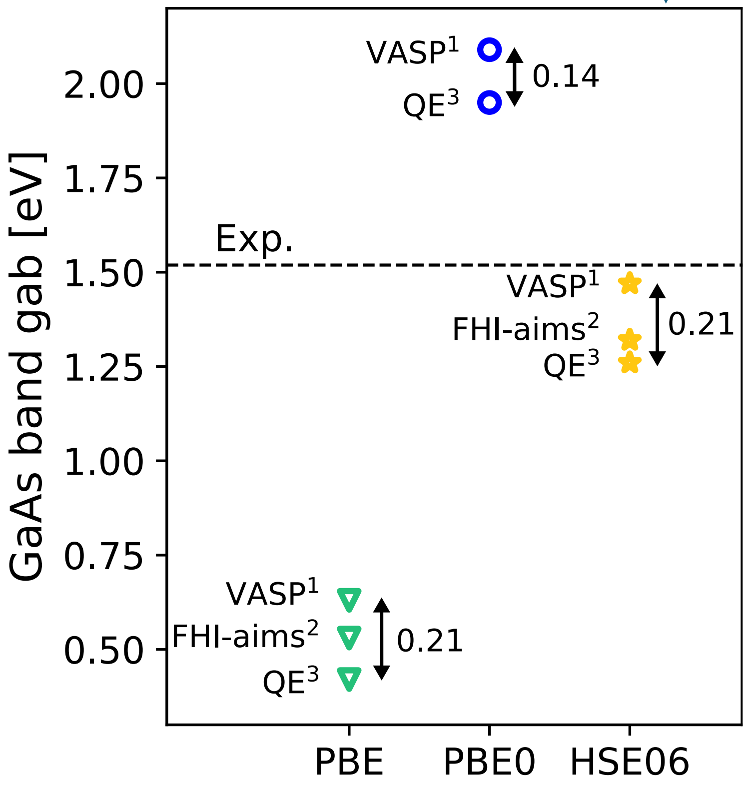
Why we need high precision methods?



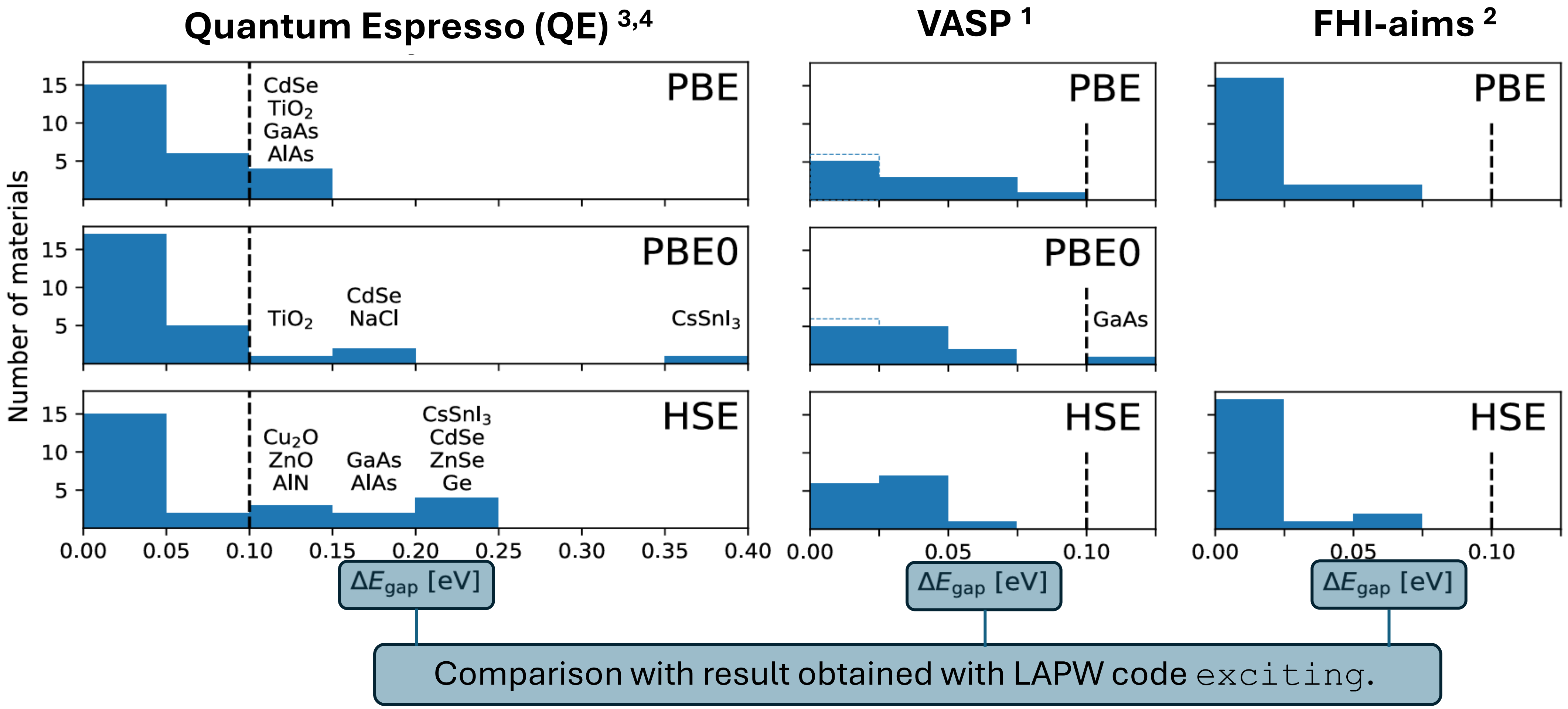
post-HF methods* rely on **HF calculation.**

*- RPA, MP2, MP3, CCSD., CCSD(T) etc.

[1] – Marques *et al.*, Phys.Rev.B 83, 035119 (2011).
[2] – Huhn *et al.*, Phys. Rev. Mater. 1, 033803 (2017).
[3] – Yang *et al.*, npj Comput. Mater. 9, 108 (2023).



Band gap survey for 26 materials



[1] – Marques *et al.*, Phys.Rev.B 83, 035119 (2011).

[2] – Huhn *et al.*, Phys. Rev. Mater. 1, 033803 (2017).

[3] - Chen *et al.*, Phys. Rev. Mater. 2, 073803 (2018)

[4] – Yang *et al.*, npj Comput. Mater. 9, 108 (2023).

Methods, functionality and precision

		LCAO (GTO, STO, NAO ..)	**PW** (PAW, pseudo-potentials)	**MRA**	**LAPW**
atoms	(semi)local	green	yellow	green	green
	hybrids	green	yellow	green	yellow
molecules	(semi)local	yellow	yellow	green	green
	hybrids	yellow	yellow	green	yellow
solids	(semi)local	yellow	yellow	red	green
	hybrids	yellow	yellow	red	yellow
		Gaussian NWChem FHI-aims …	QE VASP ABINIT …	MRChem MADNESS …	exciting WIEN2k FLEUR …

- green - supports (CBL*)
- yellow - supports (w/o CBL*)
- red - does not support

* - possible to converge the total energy up to few μHa precision.

Methods, functionality and precision

		LCAO (GTO, STO, NAO ..)	**PW** (PAW, pseudo-potentials)	**MRA**	**LAPW** (before)	**LAPW** (after)
atoms	(semi)local	green	yellow	green	green	green
	hybrids	green	yellow	green	yellow	green
molecules	(semi)local	yellow	yellow	green	green	green
	hybrids	yellow	yellow	green	yellow	green
solids	(semi)local	yellow	yellow	red	green	green
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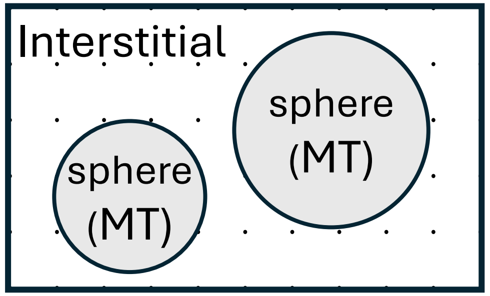
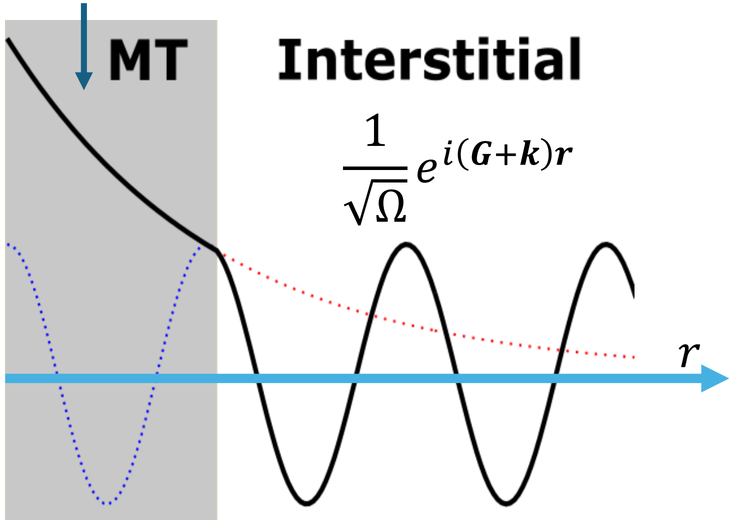
Linearized augmented plane wave (LAPW) basis



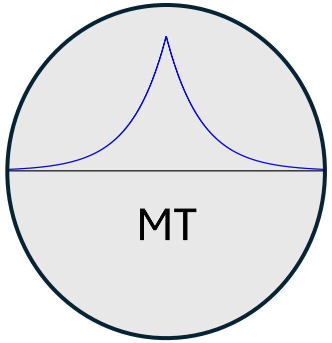
LAPW basis:

$$\sum_{\ell m} \left(A_{\ell m} u_\ell(r; \epsilon_\ell) + B_{\ell m} \dot{u}_\ell(r; \epsilon_\ell)\right) Y_{\ell m}(\hat{r})$$



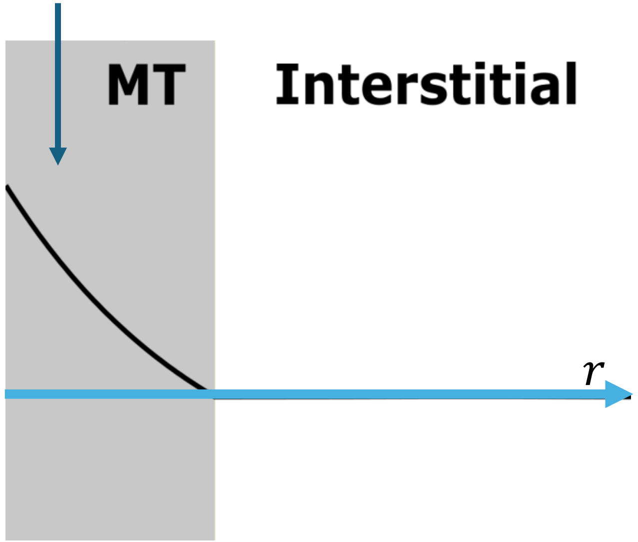
Core orbitals:

$u_{n\ell}(r) Y_{\ell m}(\hat{r})$

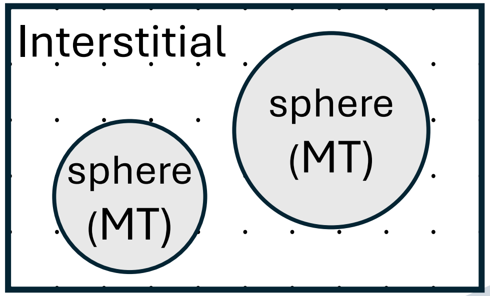


Local orbitals (LO):

$$\left(a_{\ell m} u_\ell(r; \epsilon_\ell) + b_{\ell m} \dot{u}_\ell(r; \epsilon_\ell)\right) Y_{\ell m}(\hat{r})$$



Linearized augmented plane wave (LAPW) basis



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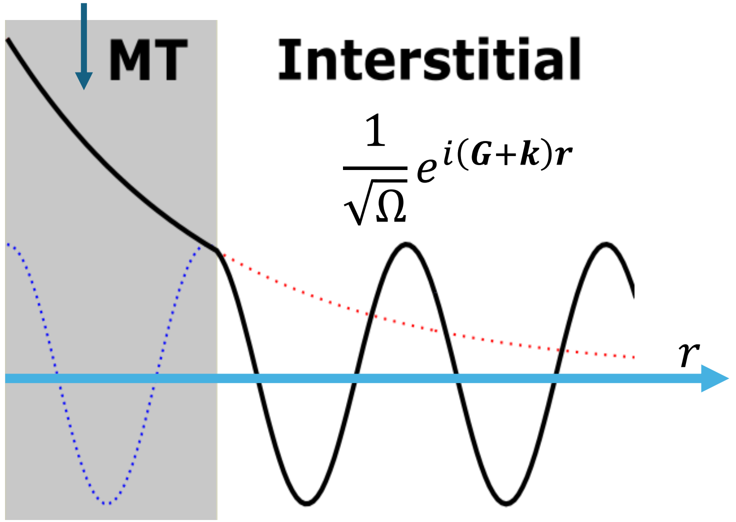

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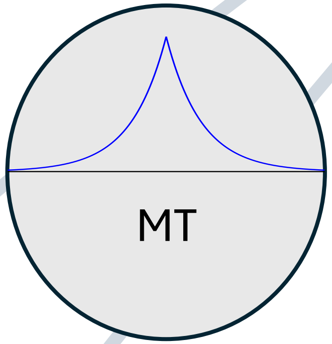

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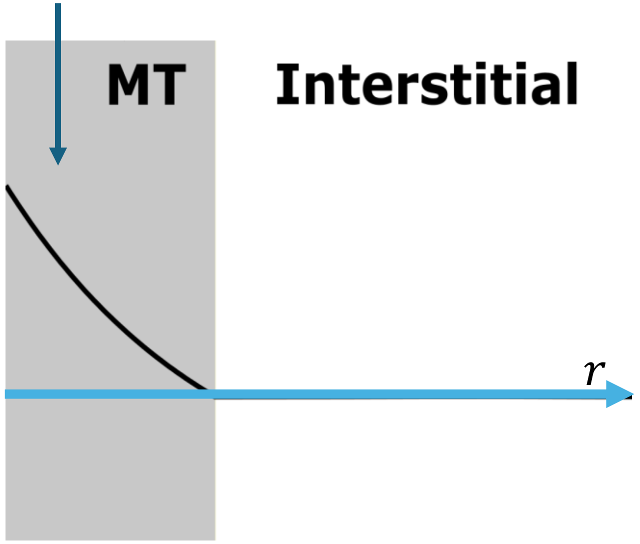


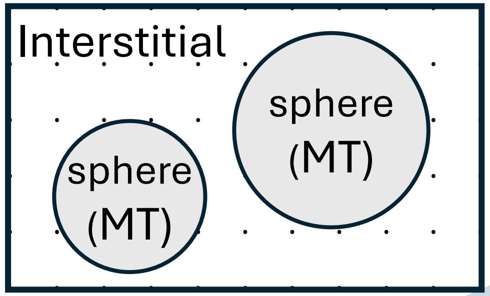
Solution of the radial SE.

Before:

Constructed with a **PBE** functional (does not comply with CBL*)

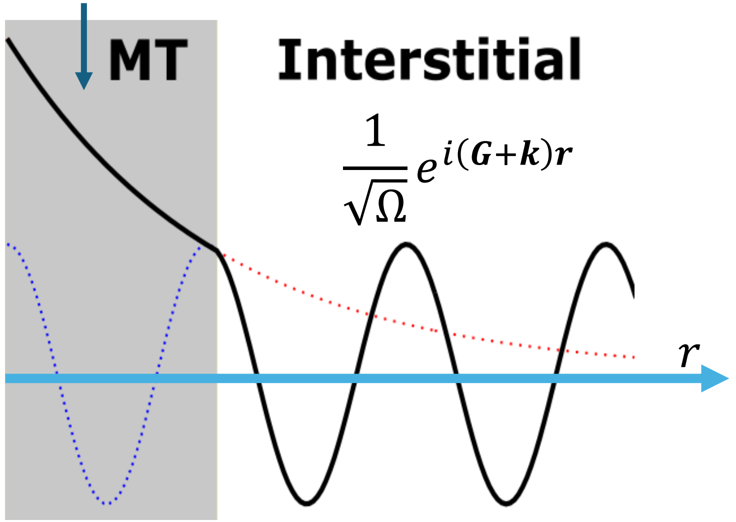
* - possible to converge the total energy up to few μHa precision.

Linearized augmented plane wave (LAPW) basis



LAPW basis:

$$\sum_{\ell m}\left(A_{\ell m} u_\ell(r;\epsilon_\ell) + B_{\ell m} \dot{u}_\ell(r;\epsilon_\ell)\right) Y_{\ell m}(\hat{r})$$



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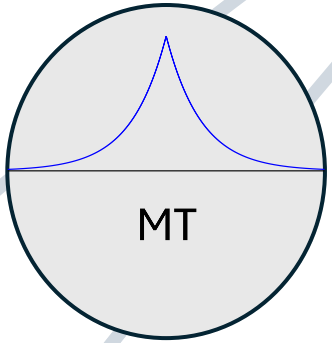

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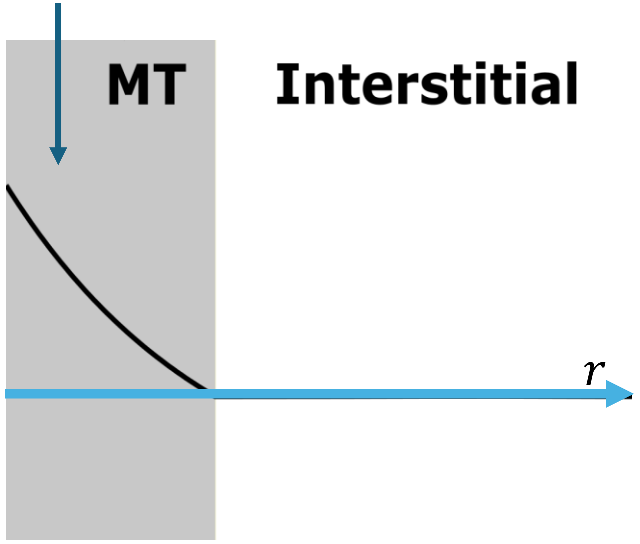


Solution of the radial SE.

Before:

Constructed with a **PBE** functional (does not comply with CBL*)

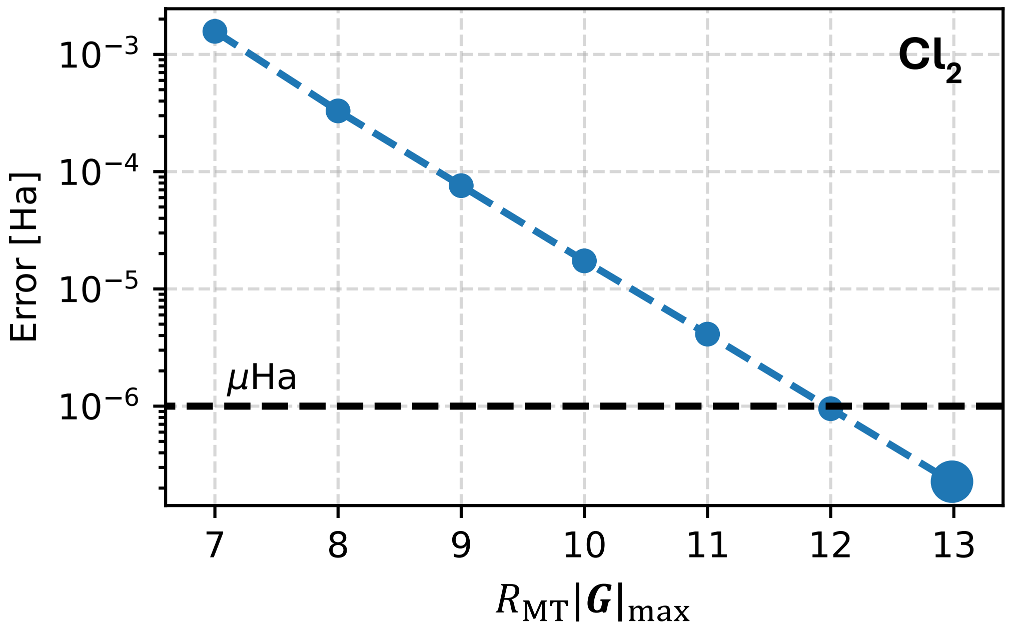
After:

Constructed with the **correct hybrid** functional (complies with CBL*)

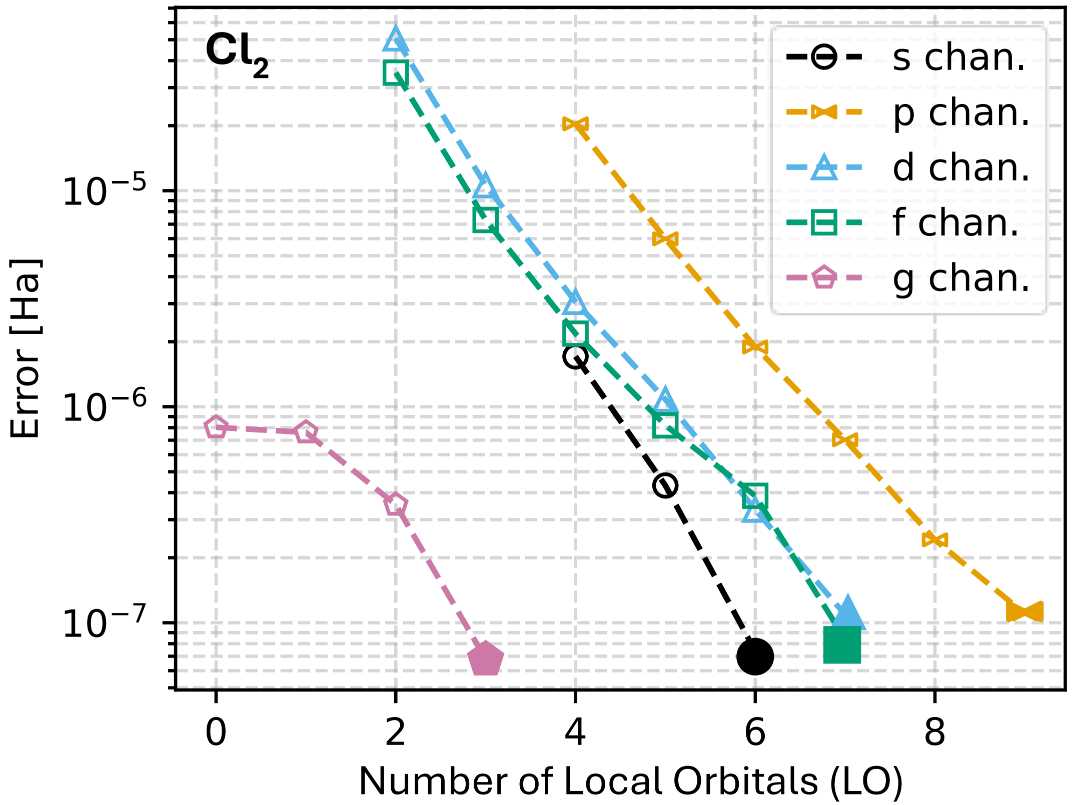
* - possible to converge the total energy up to few μHa precision.

Molecules – total HF energy

Interstitial region basis convergence.



MT region basis convergence.



Molecule	**exciting** [Ha]	FDM or FEM [Ha]	**ΔE [μHa]**
H_2	-1.133624	-1.133624*	**-0.3**
FH	-100.070801	-100.070803[1]	**1.4**
F_2	-198.773442	-198.773445[1]	**2.3**
ClF	-558.917625	-558.917626[1]	**0.9**
Cl_2	-919.008932	-919.008935[1]	**2.6**

* – calculated with HELFEM
[1] – Jensen, Theoretical Chemistry Accounts 113, 187–190 (2005)

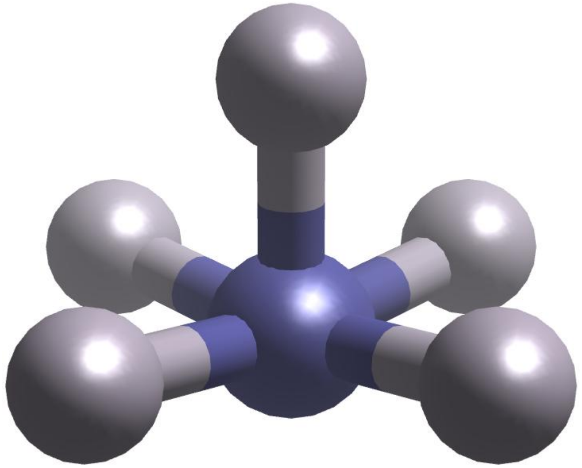
Molecules – HF reaction energy

exciting (LAPW)

			Reaction energy [kcal/mol]		
$R_{MT}G_{max}$	Core type	Basis type	FH*	ClF	ClF_5
13	HF	HF	-73.59	-16.59	-32.65

$$E_{\text{reaction}} = E_{\text{products}} - E_{\text{reactants}}$$

$$0.5\ Cl_2 + 2.5\ F_2 \rightarrow ClF_5$$



- corresponds to CBL (green)
- does not correspond to CBL (yellow)

* - hydrogen fluoride denoted as FH, to avoid confusion with Hartee-Fock.

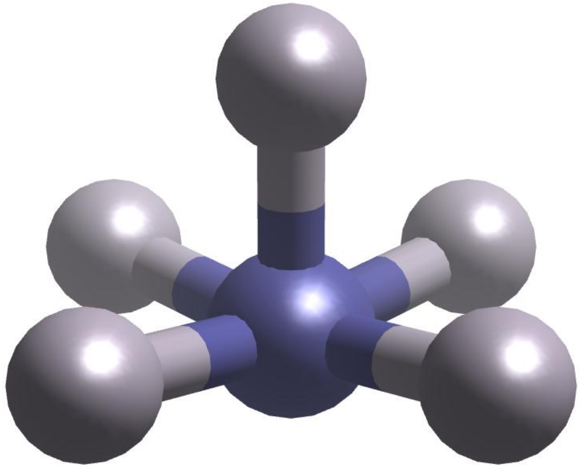
Molecules – HF reaction energy

exciting (LAPW)

			error [kcal/mol]		
$R_{MT}G_{max}$	Core type	Basis type	FH*	ClF	ClF_5
13	HF	HF	-	-	-
8	HF	HF	0.01	0.00	0.00
8	PBE	PBE	0.00	0.00	0.04

$$E_{\mathrm{reaction}} = E_{\mathrm{products}} - E_{\mathrm{reactants}}$$

$$0.5\ \mathrm{Cl_2} + 2.5\ \mathrm{F_2} \rightarrow \mathrm{ClF_5}$$



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Molecules – HF reaction energy

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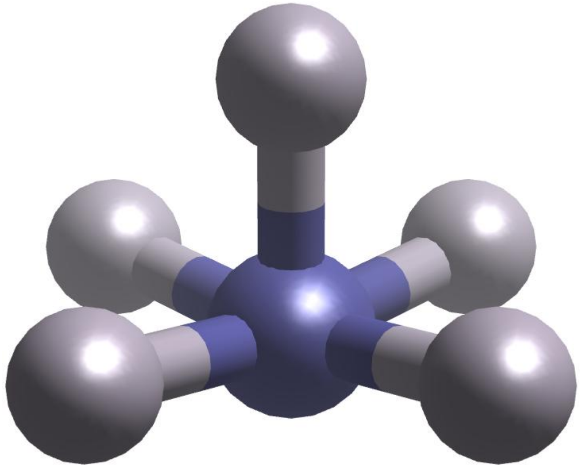
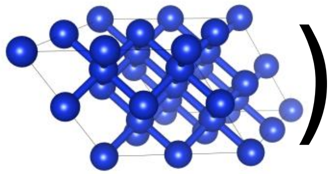
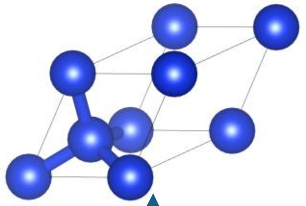


				error [kcal/mol]		
	$R_{MT}G_{max}$	Core type	Basis type	FH*	ClF	ClF_5
exciting (LAPW)	13	HF	HF	-	-	-
	8	HF	HF	0.01	0.00	0.00
	8	PBE	PBE	0.00	0.00	0.04
	Basis					
NWChem (LCAO)	aug-cc-pV6Z			0.00	0.03	0.60
	aug-cc-pV5Z			0.00	0.08	1.72
	aug-cc-pVQZ			-0.04	0.24	6.98
	aug-cc-pVTZ			0.06	0.74	13.10
	aug-cc-pVDZ			-1.51	-0.54	32.47

- corresponds to CBL (green)
- does not correspond to CBL (yellow)
- error above chemical accuracy (1 kcal/mol) (orange)

* - hydrogen fluoride denoted as FH, to avoid confusion with Hartee-Fock.

Si interstitial defects - HF formation energy

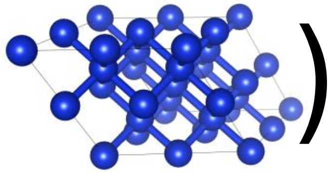
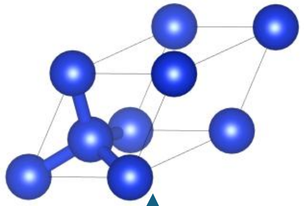
$E_{\text{form}} = E\,($  $) - \frac{17}{2}\,E\,($  $)$

17 atom supercell with self-interstitial defect.

bulk silicon

$R_{MT}G_{max}$	Core and basis type	Formation energy [kcal/mol]
13	HF	189.2

Si interstitial defects - HF formation energy

$$E_{\text{form}} = E\left(\right.$$  $$\left.\right) - \frac{17}{2} E\left(\right.$$  $$\left.\right)$$

17 atom supercell with self-interstitial defect.

bulk silicon

$R_{MT}G_{max}$	Core and basis type	Error [kcal/mol]
13	HF	-
8	PBE	0.1

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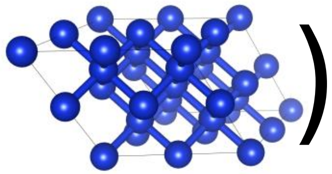
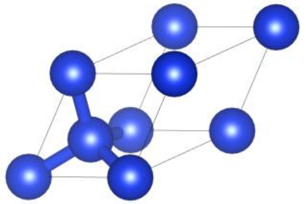
Si interstitial defects - HF formation energy

$$E_{\text{form}} = E\left(\right.$$  $$\left.\right) - \frac{17}{2}\, E\left(\right.$$  $$\left.\right)$$

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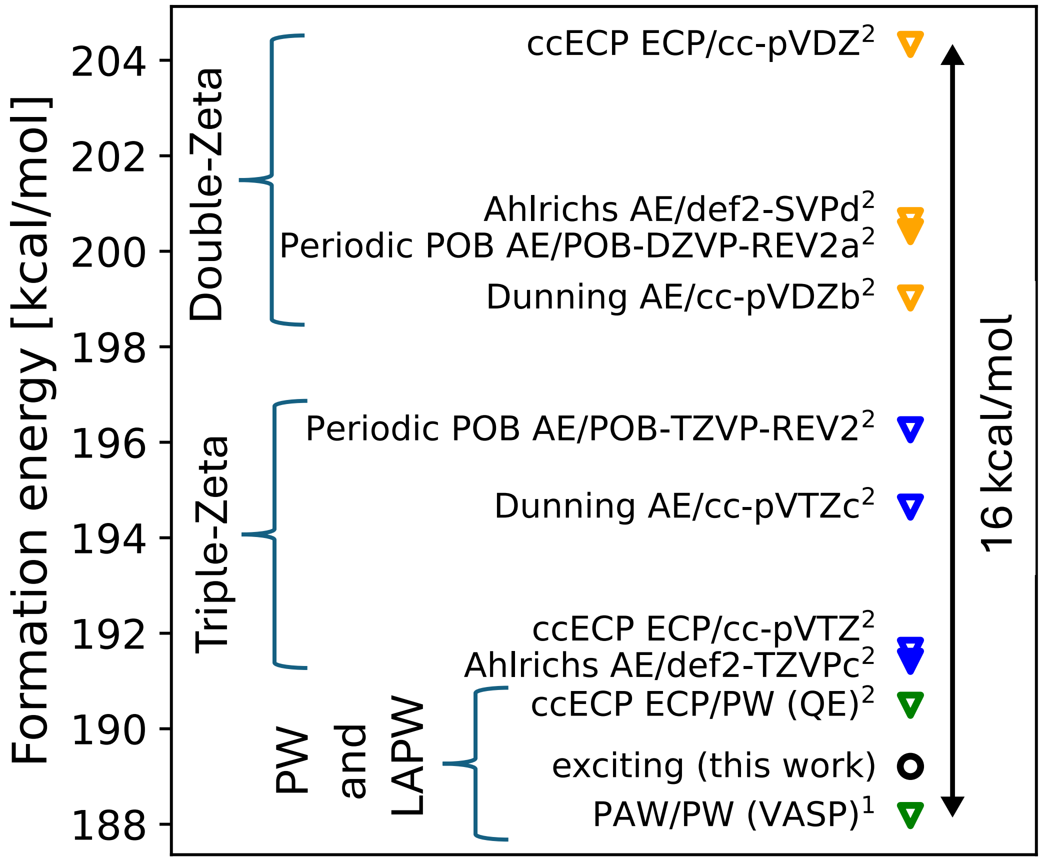
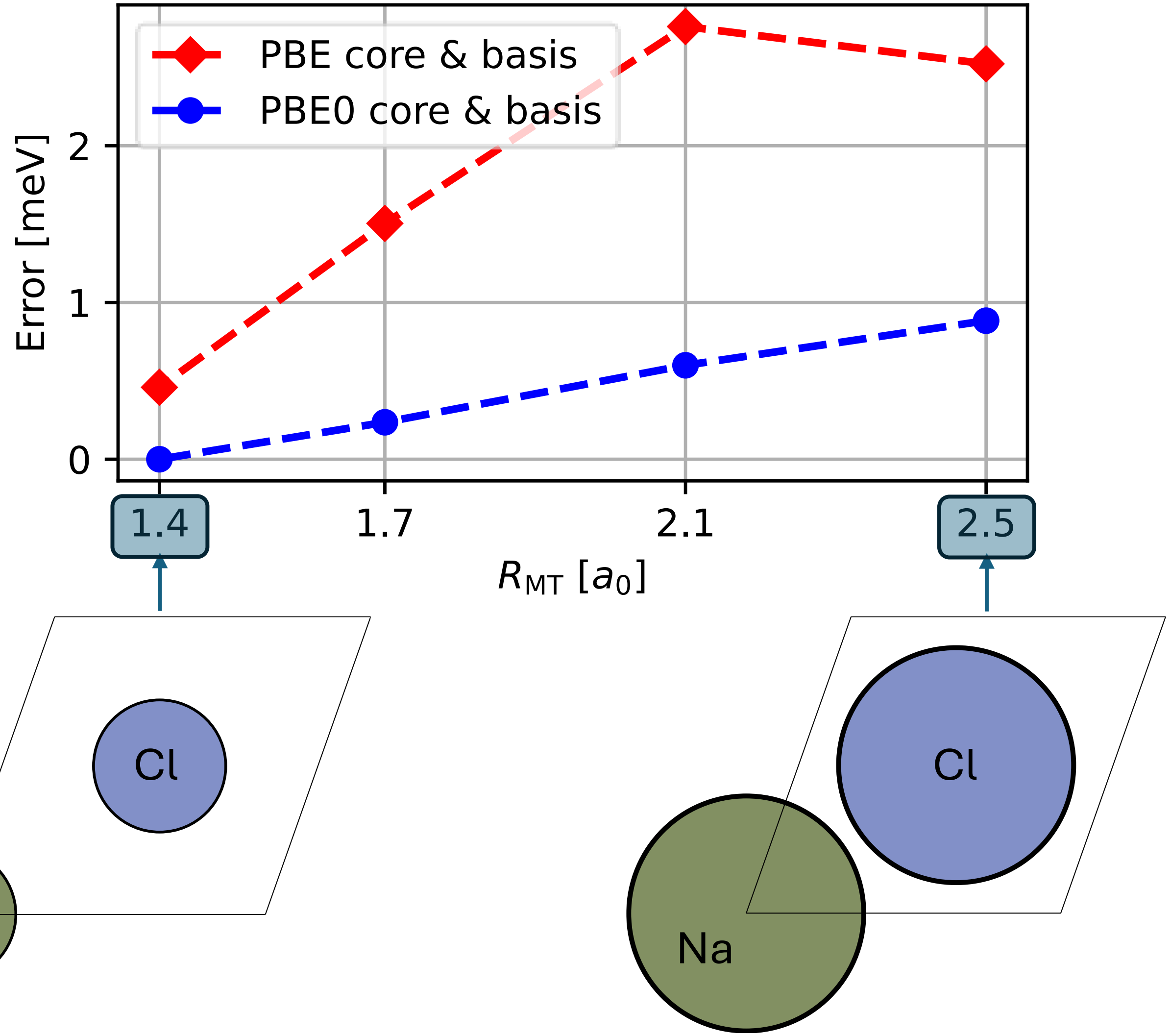


[1] - F. Salihbegović *et al.*, Phys. Rev. B 108, 115125 (2023)
[2] - K. Simula *et al.*, arXiv:2512.08276 (2025)

Band gap NaCl with PBE0

Core and basis type	Error [eV]
PBE0	< 0.001
PBE	< 0.003



Acknowledgments

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FLPP
FUNDAMENTAL AND APPLIED RESEARCH PROJECTS

Co-funded by the European Union

2027 National Development Plan

Summary

- By generating radial core and basis functions with a consistent Hamiltonian (instead of a PBE) it is possible to achieve **total energy precision of a few μHa**.

- In hybrid calculation the **choice of the core and basis function type** (standard PBE or new Hamiltonian consistent hybrid) **introduces an unsignificant error**:
  - Molecule reaction energies: max. error **0.04 kcal/mol** (ClF_5)
  - Si interstitial defect formation energy: max. error **0.1 kcal/mol**
  - Band gaps: max. error **< 10 meV**

- The correct **core state eigenvalues** allows to use hybrid calculations **in a core electron spectroscopy**.