

Advanced School on
QUANTUM MODELLING
of Materials with CRYSTAL



UNIVERSITÀ
DI TORINO

Fock-Exchange in Solids with a Local Basis Set: Hybrid DFAs Made Efficient

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Outline

- **Hybrid Functionals**
 - Global Hybrid
 - Range separated
 - How to select a
- **The CRYSTAL Approach**
 - Infinite series truncation
 - Select the right tolerances
 - Bipolar expansion
- **Some Applications**

The Jacob's Ladder

One Further Step

In KS-DFT

$$E[n] = T_s[n] + E_{\text{ext}}[n] + E_H[n] + E_{\text{xc}}[n]$$

Only **unknown** term
Source of approximation

Chemical Heaven

Double-Hybrids

$$E_{\text{xc}}^{\text{dHGGGA}}[n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau(\mathbf{r}), \epsilon_{\text{EXX}}, \epsilon_{\text{c}}^{\text{PT}}]$$

Hybrids

$$E_{\text{xc}}^{\text{HGGGA}}[n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau(\mathbf{r}), \epsilon_{\text{EXX}}]$$

meta-GGA

$$E_{\text{xc}}^{\text{mGGA}}[n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau(\mathbf{r})]$$

GGA

$$E_{\text{xc}}^{\text{GGA}}[n(\mathbf{r}), \nabla n(\mathbf{r})]$$

LDA

$$E_{\text{xc}}^{\text{LDA}}[n(\mathbf{r})]$$

Hartree Hell



Fock Exchange or
Exact Exchange (EXX)

- **Nonlocal** quantity,
- Depends on **orbitals**, not just density

Why including EXX?

Generally, GGA functionals are **semi-local** (depends on density and its derivatives)

Problems related to them:

- **Self-interaction error** (SIE)
- **Over-delocalization** of electrons
- **Poor description** of
 - Band gaps
 - Charge transfer
 - Magnetic coupling

$$E^{\text{DFT}} = \tilde{T} + \int \hat{v}_{\text{ext}} n \, d\mathbf{r} + \underbrace{E_H[n]}_{\frac{1}{2} \sum_{i,j} \iint \frac{\vartheta_i^*(\mathbf{r}_1) \vartheta_i(\mathbf{r}_1) \vartheta_j^*(\mathbf{r}_2) \vartheta_j(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2} + E_{\text{xc}}[n]$$

For $i = j$ **non-zero contribution**
 E_{xc} fails to cancel them
 → **SIE**

Including **Exact exchange** can help

- Reduce self-interaction (for one-electron systems)
- Improves KS orbital energies
- Improves localization

$$-\frac{1}{2} \sum_{i,j} \iint \frac{\vartheta_i^*(\mathbf{r}_1) \vartheta_j(\mathbf{r}_1) \vartheta_j^*(\mathbf{r}_2) \vartheta_i(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

Global Hybrid Functionals

How to include EXX in E_{xc} ?

- Initially proposed by Becke in 1993
- Replace a **Fraction** " α " of DFT Exchange with **Exact Exchange**

$$E_{xc} = E_c + E_x$$
$$E_{xc} = E_c + \underbrace{(1 - \alpha)E_x + \alpha E_{EXX}}$$

- Any** E_{xc} **functional** can be used to construct the **global hybrid**
- α is usually a **Fixed parameter**

Functional	α
B3LYP	20%
PBE0	25%
B1WC	16%
mPW1K	42.8%

The Range Separation

Split exchange interaction into **short-range** (SR) and **long-range** (LR) parts, based on electron-electron distance (\mathbf{r}_{12})

$$E_{\text{EXX}} = -\frac{1}{2} \sum_{i,j} \iint \frac{\vartheta_i^*(\mathbf{r}_1) \vartheta_j(\mathbf{r}_1) \vartheta_j^*(\mathbf{r}_2) \vartheta_i(\mathbf{r}_2)}{\mathbf{r}_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

$\frac{1}{\mathbf{r}_{12}} = \underbrace{\frac{\text{erfc}(\omega \mathbf{r}_{12})}{\mathbf{r}_{12}}}_{\text{Short Range}} + \underbrace{\frac{\text{erf}(\omega \mathbf{r}_{12})}{\mathbf{r}_{12}}}_{\text{Long Range}}$

- ω is an adjustable **parameter** for the range separation
- EXX correctly describe **asymptotic behaviour** at long range
→ for $\mathbf{r}_{12} \rightarrow \infty$ the exchange goes to $-1/\mathbf{r}_{12}$
- In solids long range interaction are partially **screened** by the **surrounding electrons**
- Can be **computational efficient** to **neglect** EXX at **long range**
→ very important for PW calculations!

$$E_x = \underbrace{(1 - \alpha^{SR}) E_x^{SR} + \alpha^{SR} E_{\text{EXX}}^{SR}}_{\text{Short Range}} + \underbrace{(1 - \alpha^{LR}) E_x^{LR} + \alpha^{LR} E_{\text{EXX}}^{LR}}_{\text{Long Range}}$$

Functional	α^{SR}	α^{LR}
HSE06	25%	0%
wB97X	16.7%	100%
CAM-B3LYP	19%	65%

The Choice for Alpha

Fixed α Parameter

Use the Functional *as is*

B3LYP \longrightarrow 20%
PBE0 \longrightarrow 25%
HSE06 \longrightarrow 25% - 0%

Easy and **Convenient**

Low Accuracy for “**Limit**” Cases:
 \longrightarrow *very-low* or *very-high* band gaps

Material Specific α Parameter

Dielectric-Dependent, DD-DFT

$$\alpha = \frac{1}{\epsilon_{\infty}}$$

Uniform Accuracy in **Band Gap** Prediction
and other **Optical Properties**

	Global	Functional	α	
		DD-PBE0	$1/\epsilon_{\infty}$	
Range separated		Functional	α^{SR}	α^{LR}
		TF	25%	$1/\epsilon_{\infty}$
		DD-CAM	100%	$1/\epsilon_{\infty}$

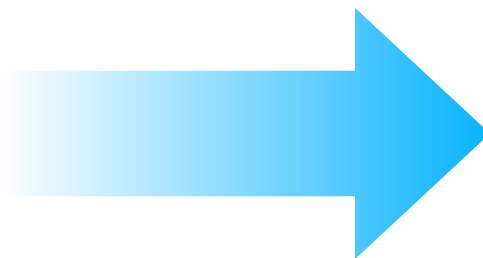
Hybrids in CRYSTAL Input

Global hybrids **can be created** from any functional using the keyword **HYBRID** in DFT block

Then, specify the percentage α of E_{EXX} (can be any real value)

$$E_{xc} = E_c + (1 - \alpha)E_x + \alpha E_{EXX}$$

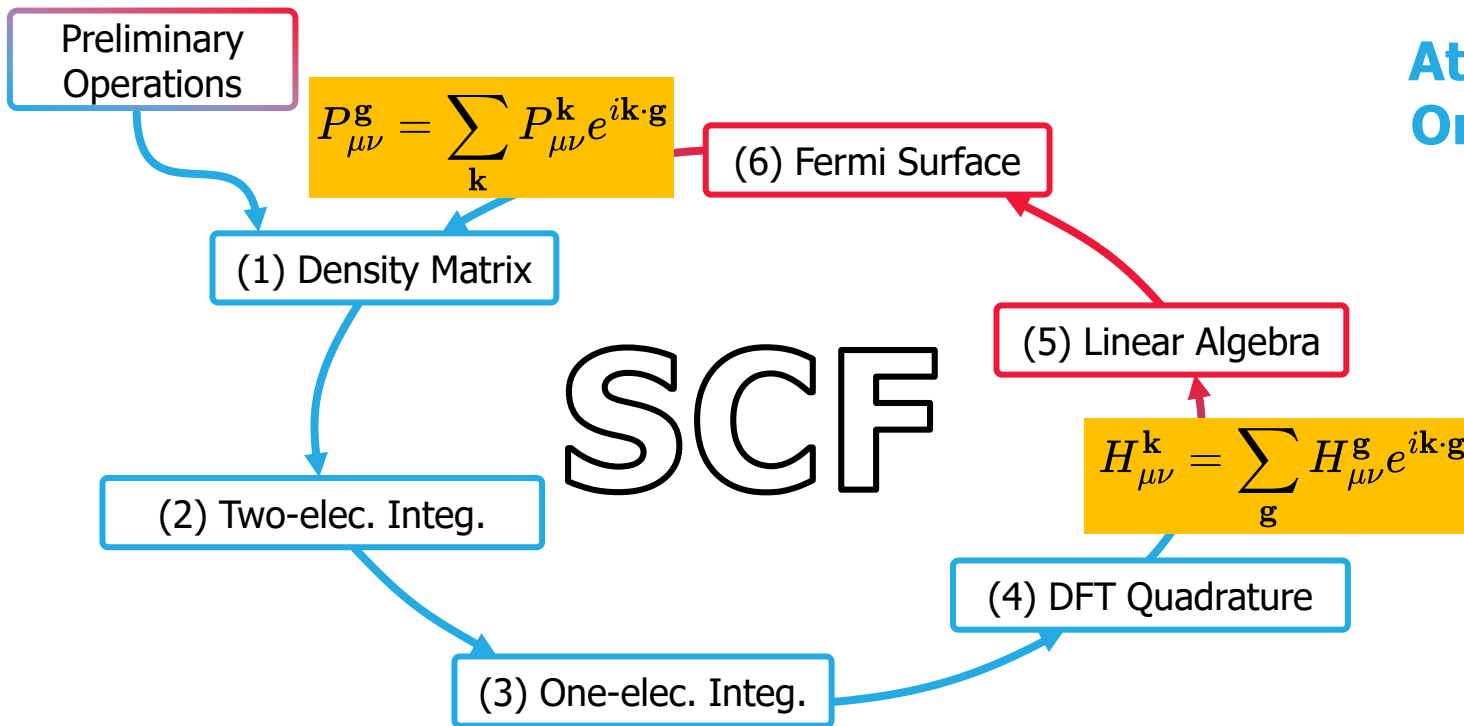
```
DFT
PBE
HYBRID
15
END
```



Many (hybrid) standard functionals are available as **standalone keywords**

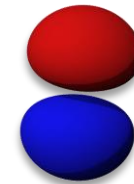
```
DFT
CAM-B3LYP
END
```

Why Hybrids are Efficient?

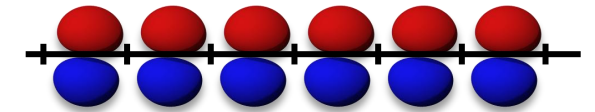


Atomic
Orbital

$$\chi_{\mu}^g(\mathbf{r})$$

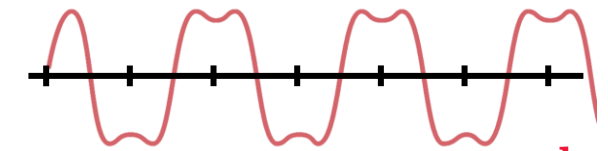


Translational Symmetry



FT

$$\phi_{\mu}^k(\mathbf{r}) = \sum_g \chi_{\mu}^g(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{g}}$$

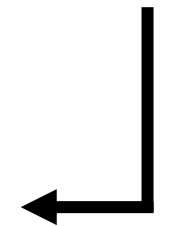


Bloch Function $\phi_{\mu}^k(\mathbf{r})$

Crystalline Orbitals

As Linear Combination of BFs

$$\vartheta_i^k(\mathbf{r}) = \sum_{\mu=1}^N a_{\mu i}^k \phi_{\mu}^k(\mathbf{k})$$



Each SCF iteration:

- Compute **integrals** in **direct space** (AO basis)
- Solve **Hamiltonian diagonalization** in **reciprocal space** (BF basis)

Exchange and Correlation Matrix

- Construct the full **Hamiltonian** matrix in **direct space** as sum of contributions

$$\mathbf{H}^g = \underbrace{\mathbf{T}^g + \mathbf{Z}^g}_{\text{One-electron}} + \underbrace{\mathbf{C}^g + \mathbf{V}_{\text{xc}}^g}_{\text{Two-electron}} \longrightarrow \text{Infinite Matrices}$$

- The **exchange and correlation** matrix is obtained as **partial derivative** (generalized Kohn-Sham) of the xc functional

$$[\mathbf{V}_{\text{xc}}^g]_{\mu\nu} = \frac{\partial E_{\text{xc}}[n, \{\vartheta_i^{\text{KS}}\}]}{\partial P_{\mu\nu}^g}$$

Exchange and Correlation Matrix

- Let's consider the general form of a **global hybrid functionals**:

$$E_{xc}[n, \{\vartheta_i^{KS}\}] = E_c[n] + (1 - \alpha)E_x[n] + \alpha E_{EXX}[\{\vartheta_i^{KS}\}]$$

- And the explicit form of the E_{EXX} :

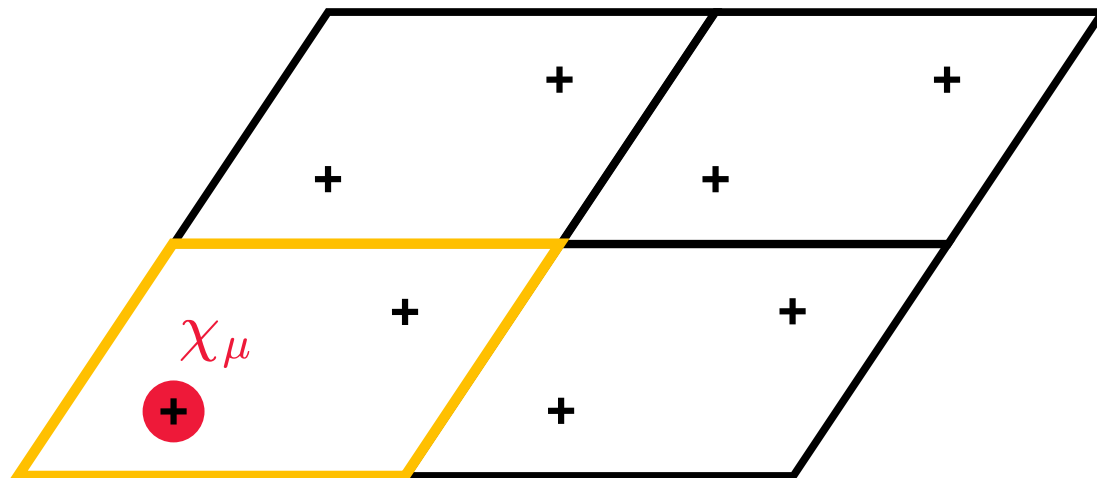
$$E_{EXX} = -\frac{1}{2} \sum_{\mu\nu} \sum_g P_{\mu\nu}^g \sum_{\sigma\rho} \sum_q P_{\sigma\rho}^q \sum_s (\chi_\mu^0 \chi_\sigma^s | \chi_\nu^g \chi_\rho^{s+q})$$

- The **EXX contribution** to the Hamiltonian matrix will be computed as:

$$[V_{EXX}^g]_{\mu\nu} = - \sum_{\sigma\rho} \sum_q P_{\sigma\rho}^q \sum_s (\chi_\mu^0 \chi_\sigma^s | \chi_\nu^g \chi_\rho^{s+q})$$

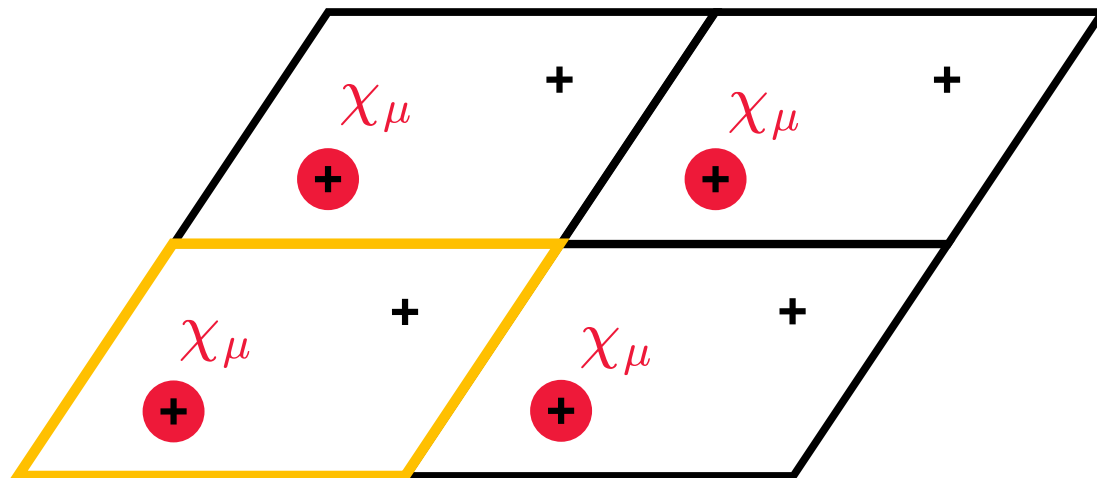
Infinite Matrices in CRYSTAL

- Elements of **direct space matrices** represent interactions between **two orbitals** μ ν $\longrightarrow [V_{\text{EXX}}^g]_{\mu\nu}$
- **BFs** χ_μ are defined for all atoms in the **reference cell**



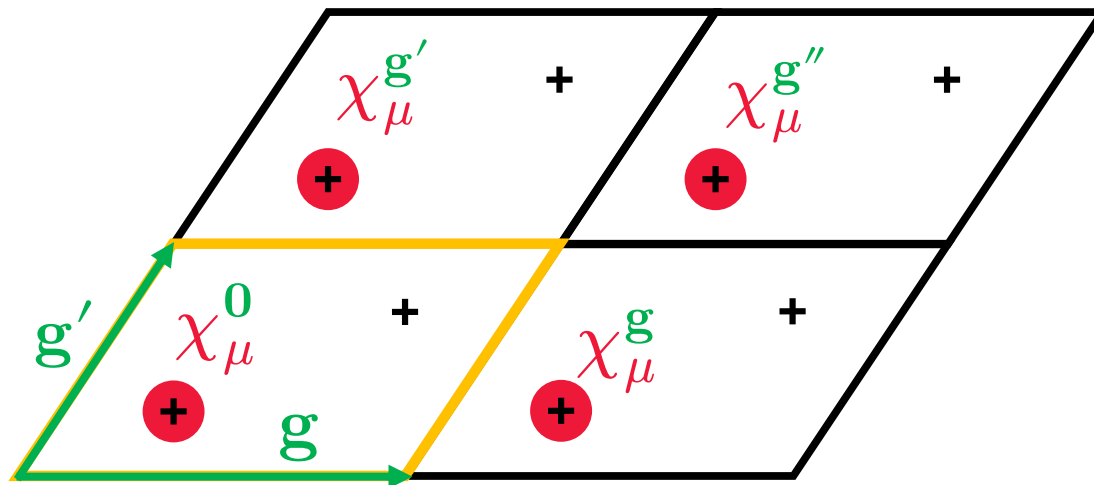
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- But they are **replicated** (infinitely) in all the other cells



Infinite Matrices in CRYSTAL

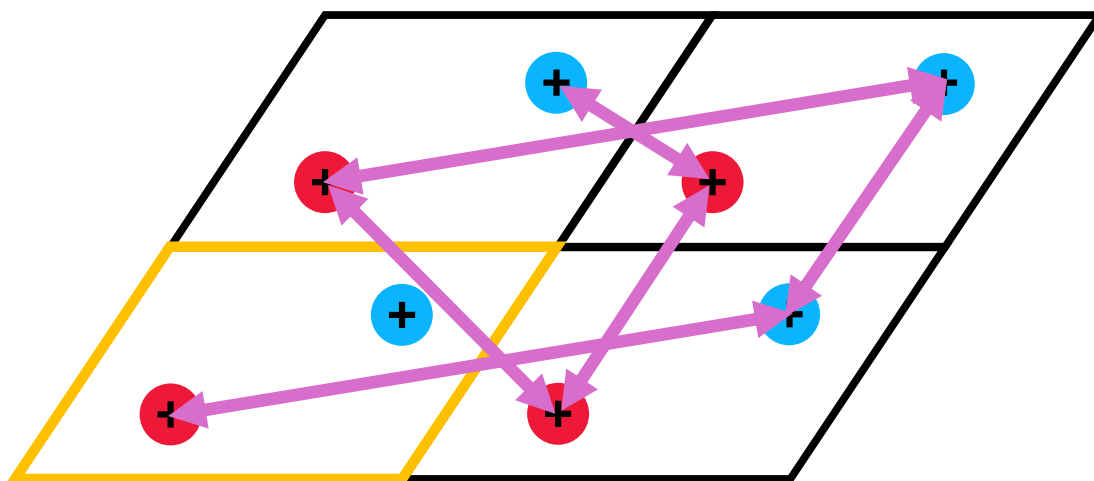
- Elements of **direct space matrices** represent interactions between **two orbitals** μ ν $\longrightarrow [V_{\text{EXX}}^g]_{\mu\nu}$
- **BFs** χ_μ are defined for all atoms in the **reference cell**
- But they are **replicated** (infinitely) in all the other cells
- We use **Bravais vectors** g to indicate specific cells



Infinite Matrices in CRYSTAL

- Any possible μ ν couple of BFs should be considered

$$\left\{ \begin{array}{l} \mu \\ \nu \end{array} \right. \quad \begin{array}{l} 1 \rightarrow \infty \\ 1 \rightarrow \infty \end{array}$$

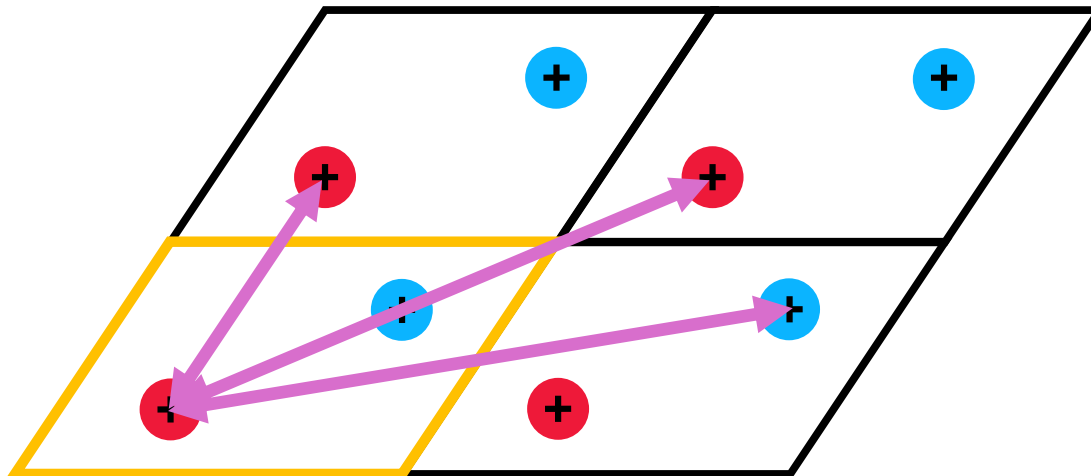


Infinite Matrices in CRYSTAL

- Any possible μ ν **couple of BFs** should be considered
- Due to **translational symmetry**, we can focus only on interactions originating from the **reference cell**

$$\begin{cases} \mu \\ \nu \end{cases} \begin{matrix} 1 \rightarrow \infty \\ 1 \rightarrow \infty \end{matrix}$$

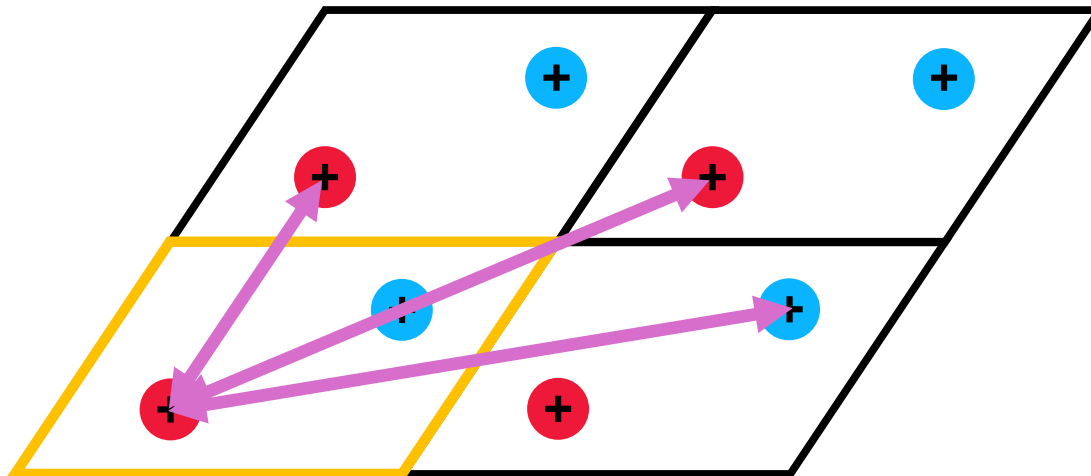
$$\begin{cases} \mu \\ \nu \end{cases} \begin{matrix} 1 \rightarrow N_{BS} \\ 1 \rightarrow \infty \end{matrix}$$



Infinite Matrices in CRYSTAL

- Any possible μ ν **couple of BFs** should be considered
- Due to **translational symmetry**, we can focus only on interactions originating from the **reference cell**
- With the notation $[\mathbf{V}_{\text{EXX}}^g]_{\mu\nu}$ we indicate the element of the matrix that correspond to the interaction between χ_{μ}^0 (in ref. cell) and χ_{ν}^g (in g cell)

$$\begin{cases} \mu & 1 \rightarrow \infty \\ \nu & 1 \rightarrow \infty \end{cases} \quad \begin{cases} \mu & 1 \rightarrow N_{BS} \\ \nu & 1 \rightarrow \infty \end{cases}$$



The only infinite index
is the **Bravais vector**

Computing EXX in CRYSTAL

$$[\mathbf{V}_{\text{EXX}}^{\mathbf{g}}]_{\mu\nu} = - \sum_{\sigma\rho} \sum_{\mathbf{q}} P_{\sigma\rho}^{\mathbf{q}} \sum_{\mathbf{s}} (\chi_{\mu}^0 \chi_{\sigma}^{\mathbf{s}} | \chi_{\nu}^{\mathbf{g}} \chi_{\rho}^{\mathbf{s}+\mathbf{q}})$$

Total of **7 indices**:

- $\mu \nu \sigma \rho$ are **orbitals** in the reference cell ($1 \rightarrow N_{BS}$)
- $\mathbf{g} \mathbf{q} \mathbf{s}$ are **Bravais vectors** ($1 \rightarrow \infty$)



Truncation

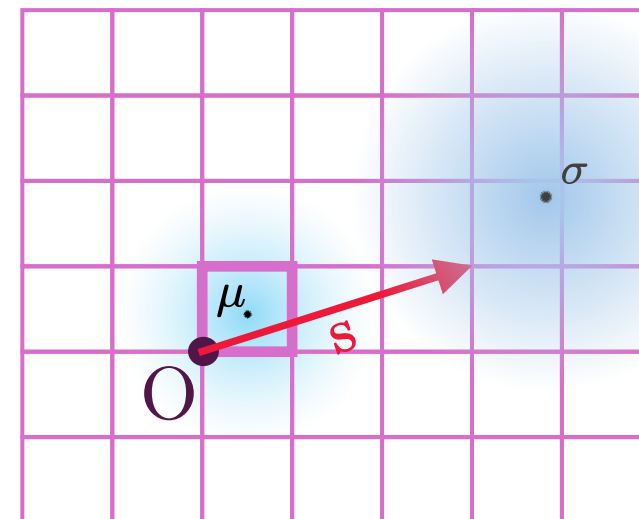
Based on Orbital Overlap

- This is the key point for the **efficiency** of the code in the treatment of integrals

The \mathbf{s} summation

$$[\mathbf{V}_{\text{EXX}}^{\mathbf{g}}]_{\mu\nu} = - \sum_{\sigma\rho} \sum_{\mathbf{q}} P_{\sigma\rho}^{\mathbf{q}} \sum_{\mathbf{s}} (\chi_{\mu}^0 \chi_{\sigma}^{\mathbf{s}} | \chi_{\nu}^{\mathbf{g}} \chi_{\rho}^{\mathbf{s}+\mathbf{q}})$$

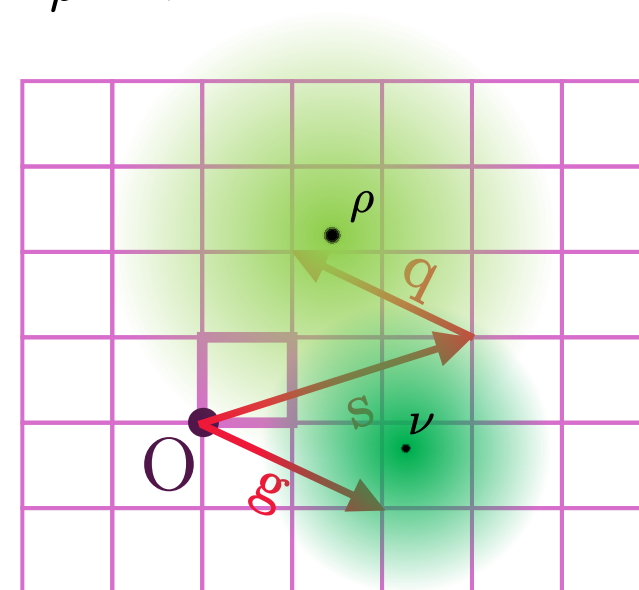
- Evaluate the overlap of $\chi_{\mu}^0 \chi_{\sigma}^{\mathbf{s}} < S_s$



The **s** summation

$$[\mathbf{V}_{\text{EXX}}^{\mathbf{g}}]_{\mu\nu} = - \sum_{\sigma\rho} \sum_{\mathbf{q}} P_{\sigma\rho}^{\mathbf{q}} \sum_{\mathbf{s}} (\chi_{\mu}^0 \chi_{\sigma}^{\mathbf{s}} | \chi_{\nu}^{\mathbf{g}} \chi_{\rho}^{\mathbf{s}+\mathbf{q}})$$

- Evaluate the overlap of $\chi_{\mu}^0 \chi_{\sigma}^{\mathbf{s}} < S_s$
- Evaluate the overlap of $\chi_{\nu}^{\mathbf{g}} \chi_{\rho}^{\mathbf{s}+\mathbf{q}} < S_s$



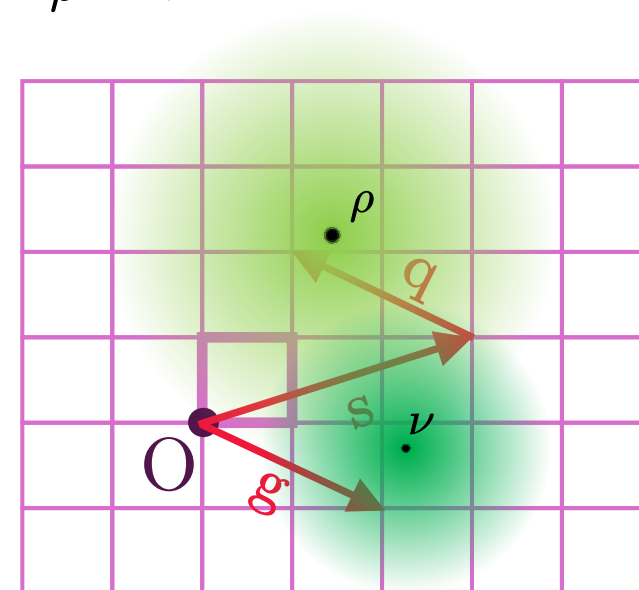
The s summation

$$[\mathbf{V}_{\text{EXX}}^{\mathbf{g}}]_{\mu\nu} = - \sum_{\sigma\rho} \sum_{\mathbf{q}} P_{\sigma\rho}^{\mathbf{q}} \sum_{\mathbf{s}} (\chi_{\mu}^0 \chi_{\sigma}^{\mathbf{s}} | \chi_{\nu}^{\mathbf{g}} \chi_{\rho}^{\mathbf{s}+\mathbf{q}})$$

- Evaluate the overlap of $\chi_{\mu}^0 \chi_{\sigma}^{\mathbf{s}} < S_s$
- Evaluate the overlap of $\chi_{\nu}^{\mathbf{g}} \chi_{\rho}^{\mathbf{s}+\mathbf{q}} < S_s$
- S_s is a **threshold** value from **input**

$$S_s = 10^{-7}$$

TOLINTEG
7 7 7 15 30



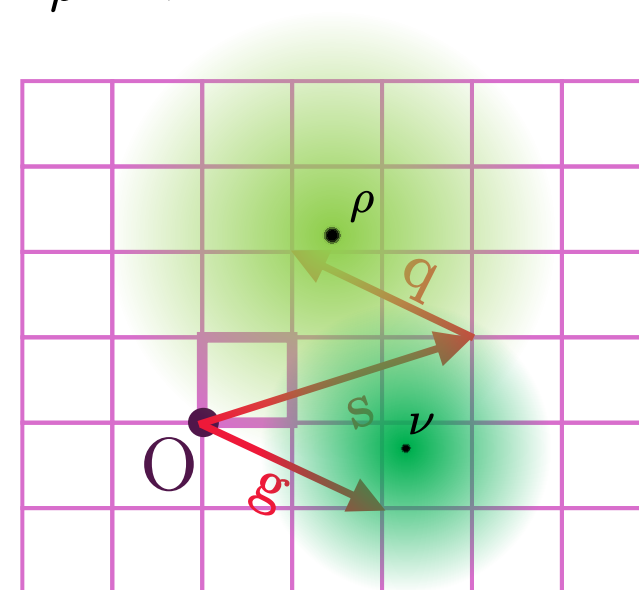
The **s** summation

$$[\mathbf{V}_{\text{EXX}}^{\mathbf{g}}]_{\mu\nu} = - \sum_{\sigma\rho} \sum_{\mathbf{q}} P_{\sigma\rho}^{\mathbf{q}} \sum_{\mathbf{s}} (\chi_{\mu}^0 \chi_{\sigma}^{\mathbf{s}} | \chi_{\nu}^{\mathbf{g}} \chi_{\rho}^{\mathbf{s}+\mathbf{q}})$$

- Evaluate the overlap of $\chi_{\mu}^0 \chi_{\sigma}^{\mathbf{s}} < S_s$
- Evaluate the overlap of $\chi_{\nu}^{\mathbf{g}} \chi_{\rho}^{\mathbf{s}+\mathbf{q}} < S_s$
- S_s is a **threshold** value from **input**

$$S_s = 10^{-7}$$

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- If either one of the two is below S_s the **s** summation is **truncated**

The **q** Summation

$$[\mathbf{V}_{\text{EXX}}^{\mathbf{g}}]_{\mu\nu} = - \sum_{\sigma\rho} \sum_{\mathbf{q}} P_{\sigma\rho}^{\mathbf{q}} \sum_{\mathbf{s}} (\chi_{\mu}^0 \chi_{\sigma}^{\mathbf{s}} | \chi_{\nu}^{\mathbf{g}} \chi_{\rho}^{\mathbf{s}+\mathbf{q}})$$

- There is no direct relation to orbitals involved in the integral
- We use the **decay** of **density matrix elements** $P_{\sigma\rho}^{\mathbf{q}}$ used for the contraction
 → $P_{\sigma\rho}^{\mathbf{q}}$ tends to **zero** if χ_{σ}^0 is *far* from $\chi_{\rho}^{\mathbf{q}}$

Evaluate **overlap** of **corresponding orbitals**, against threshold $\chi_{\sigma}^0 \chi_{\rho}^{\mathbf{q}} < S_q$

- **Consistency** with other parameters
- Take account for **small/big shells**

$$S_q = 10^{-30}$$

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7 7 7 15 30

The **g** Index

$$[\mathbf{V}_{\text{EXX}}^{\mathbf{g}}]_{\mu\nu} = - \sum_{\sigma\rho} \sum_{\mathbf{q}} P_{\sigma\rho}^{\mathbf{q}} \sum_{\mathbf{s}} (\chi_{\mu}^0 \chi_{\sigma}^{\mathbf{s}} | \chi_{\nu}^{\mathbf{g}} \chi_{\rho}^{\mathbf{s}+\mathbf{q}})$$

- Same considerations as for the **q** summation apply
- The potential $V_{\mu\nu}^{\mathbf{g}}$ **decays** similarly with the distance of orbitals χ_{μ}^0 and $\chi_{\nu}^{\mathbf{g}}$
- We use another threshold value: $\chi_{\mu}^0 \chi_{\nu}^{\mathbf{g}} < S_g$

$$S_g = 10^{-15}$$

TOLINTEG				
7	7	7	15	30

About **g** and **q**

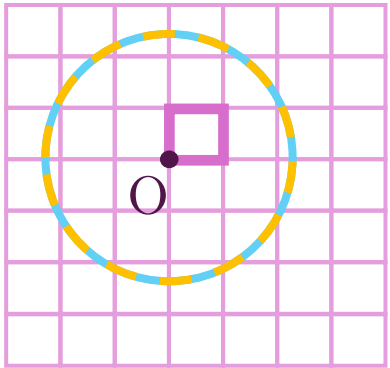
Warnings:

- Density matrix **evolves during SCF**
- Dependent from the **nature of the system**
 - **Insulators:** P elements decay **exponentially** with distance
→ as the orbital overlap
 - **Metals:** P elements decay **slower**
→ need to include **more elements**
Higher TOLINTEG required

Selection of Thresholds

Why different threshold for **g** and **q**?

- Let's consider the case of using the **same value for both**
- This will define one single *radius* around the origin of **included contributions**



$$S_g = S_q$$

$$\chi_{\mu}^0 \chi_{\nu}^g < S_g$$

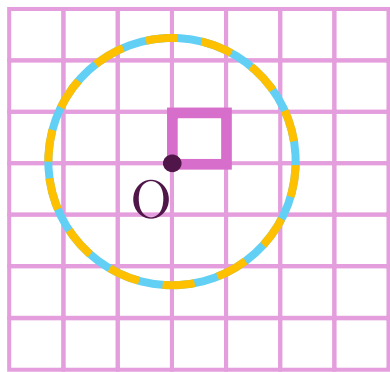
$$\chi_{\sigma}^0 \chi_{\rho}^q < S_q$$

TOLINTEG
7 7 7 15 15

Selection of Thresholds

Why different threshold for **g** and **q**?

- Let's consider the case of using the **same value for both**
- This will define one single **radius** around the origin of **included contributions**



$$S_g = S_q$$

$$\chi_\mu^0 \chi_\nu^g < S_g$$

$$\chi_\sigma^0 \chi_\rho^q < S_q$$

TOLINTEG

7 7 7 15 15

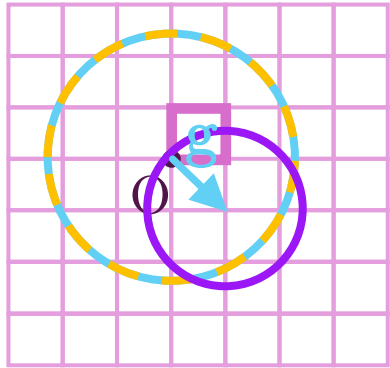
$$[\mathbf{V}_{\text{EXX}}^g]_{\mu\nu} = - \sum_{\sigma\rho} \sum_{\mathbf{q}} P_{\sigma\rho}^{\mathbf{q}} \sum_{\mathbf{s}} (\chi_\mu^0 \chi_\sigma^{\mathbf{s}} | \chi_\nu^g \chi_\rho^{\mathbf{s}+\mathbf{q}})$$

- Now let's consider the **maximum contribution** that we can have in the potential
→ This is obtained for $\sigma = \mu$, $\rho = \nu$, and $\mathbf{s} = \mathbf{0}$

Thus, the **maximum contribution** is $(\chi_\mu^0 \chi_\mu^0 | \chi_\nu^g \chi_\nu^q)$

Selection of Thresholds

- This means that given any **g** inside our initial radius, we can define a second radius centered in **g** of **non-zero contributions**



$$S_g = S_q$$

$$\chi_\mu^0 \chi_\nu^g < S_g$$

$$\chi_\sigma^0 \chi_\rho^q < S_q$$

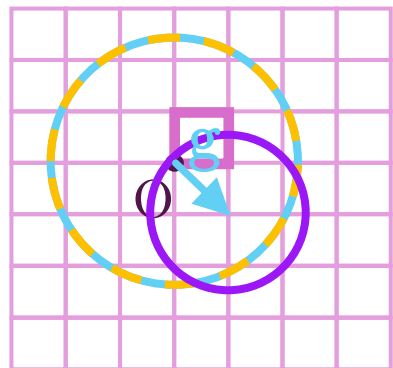
TOLINTEG				
7	7	7	15	15

$$(\chi_\mu^0 \chi_\mu^0 | \chi_\nu^g \chi_\nu^q)$$

- Clearly some of these contributions are **not inside** the initial radius **we are excluding them!**
 - The SCF will probably not converge

Selection of Thresholds

- This means that given any **g** inside our initial radius, we can define a second radius centered in **g** of **non-zero contributions**



$$S_g = S_q$$

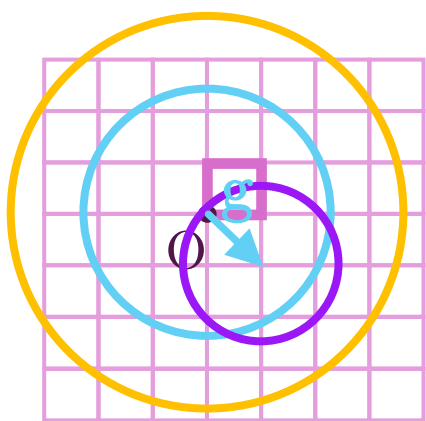
$$\chi_\mu^0 \chi_\nu^g < S_g$$

$$\chi_\sigma^0 \chi_\rho^q < S_q$$

TOLINTEG
7 7 7 15 15

$$(\chi_\mu^0 \chi_\mu^0 | \chi_\nu^g \chi_\nu^q)$$

- Clearly some of these contributions are **not inside** the initial radius
→ we are excluding them!



$$S_g > S_q$$

$$\chi_\mu^0 \chi_\nu^g < S_g$$

$$\chi_\sigma^0 \chi_\rho^q < S_q$$

TOLINTEG
7 7 7 15 30

Need to consider smaller **q** threshold to **Not Exclude** relevant contribution for large **g** vectors

Bipolar Expansion

Considering the **double spatial integral** we need to solve:

$$(\chi_\mu^0 \chi_\sigma^s | \chi_\nu^g \chi_\rho^{s+q}) = \iint \frac{\chi_\mu^0(\mathbf{r}_1) \chi_\sigma^s(\mathbf{r}_1) \chi_\nu^g(\mathbf{r}_2) \chi_\rho^{s+q}(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

- For **well-separated AO product distributions**, the integral can be simplified using **multipole expansions**:

$$\begin{cases} \rho_1(\mathbf{r}_1 - \mathbf{s}_1) = \chi_\mu^0(\mathbf{r}_1) \chi_\sigma^s(\mathbf{r}_1) \\ \rho_2(\mathbf{r}_2 - \mathbf{s}_2) = \chi_\nu^g(\mathbf{r}_2) \chi_\rho^{s+q}(\mathbf{r}_2) \end{cases}$$

$$\frac{1}{r_{12}} = \sum_{l_1, l_2=0}^{\infty} \frac{1}{R^{2l_1+2l_2+1}} \sum_{m_1, m_2=-l_1, -l_2}^{l_1, l_2} B(l_1, m_1, l_2, m_2) Y_{l_1+l_2}^{-m_1-m_2}(\mathbf{R}) Y_{l_1}^{m_1}(\mathbf{r}_1 - \mathbf{s}_1) Y_{l_2}^{m_2}(\mathbf{r}_2 - \mathbf{s}_2)$$

- Reducing the double integral in a **product of single integrals**

$$(\chi_\mu \chi_\sigma | \chi_\nu \chi_\rho) = \sum_{l_1, l_2=0}^{\infty} \frac{1}{R^{2l_1+2l_2+1}} \sum_{m_1, m_2=-l_1, -l_2}^{l_1, l_2} B(l_1, m_1, l_2, m_2) Y_{l_1+l_2}^{-m_1-m_2}(\mathbf{R}) \int d\mathbf{r}_1 \rho_1(\mathbf{r}_1) Y_{l_1}^{m_1}(\mathbf{r}_1) \int d\mathbf{r}_2 \rho_2(\mathbf{r}_2) Y_{l_2}^{m_2}(\mathbf{r}_2)$$

- Overlap based threshold** to select:
 - if integral is computed with Bipolar Approx
 - or computed Exactly

$$S_b = 10^{-14}$$



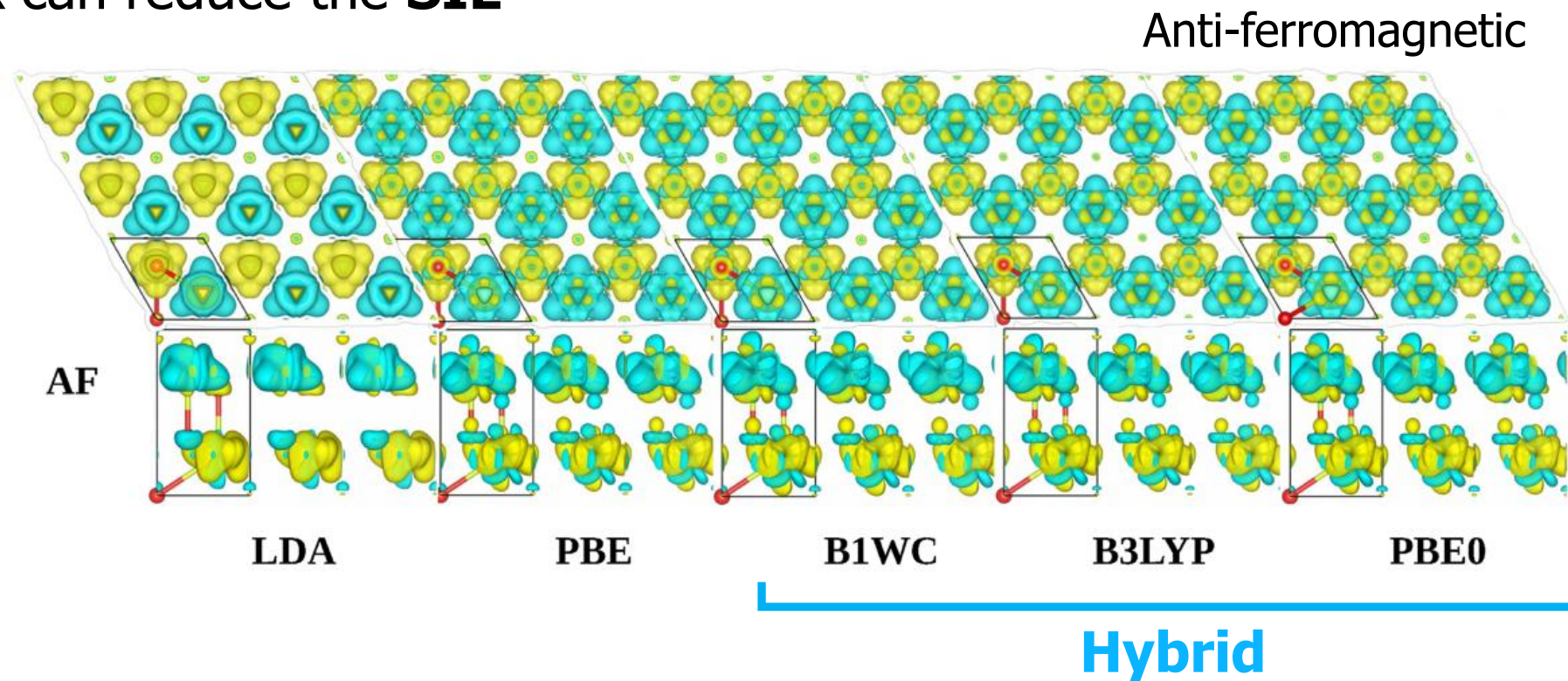
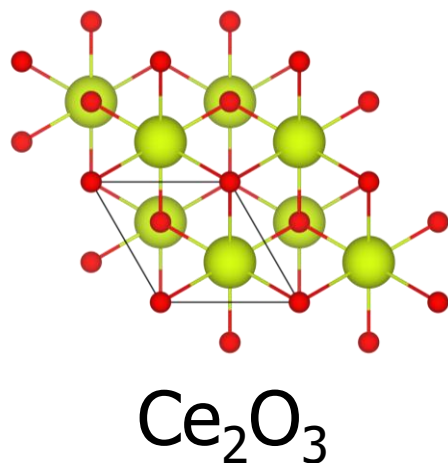
Applications

- **Electron density localization** in **Ce₂O₃**
→ Improvement of SIE
- **Optical properties** of **Fe₂O₃**
 - Band gap and band structure
 - Evolution with thresholds
 - Computational efficiency
- **Heavy metallic system: EuO**
 - Band structure and convergence with thresholds
 - Computational efficiency
- **Larger systems** and **symmetry** (MOF-5 and Faujasite)

Improvement on SIE

SIE is an *extra* e-e interaction

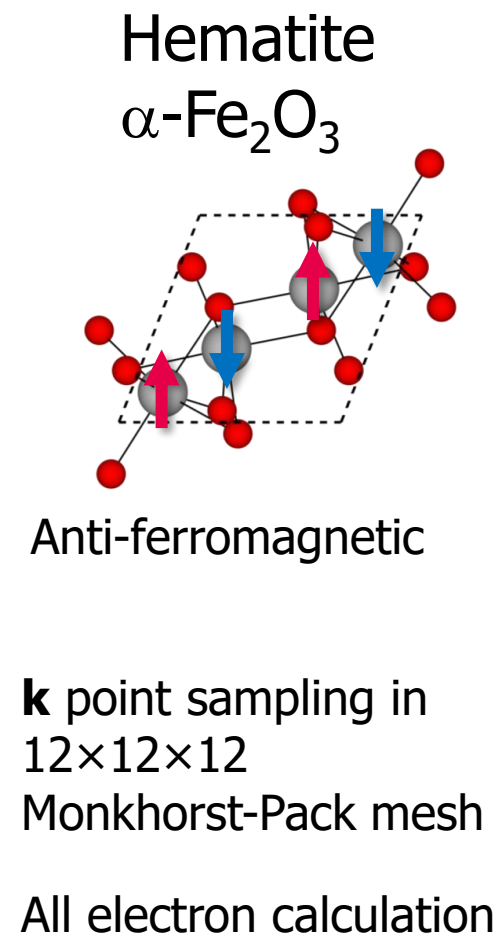
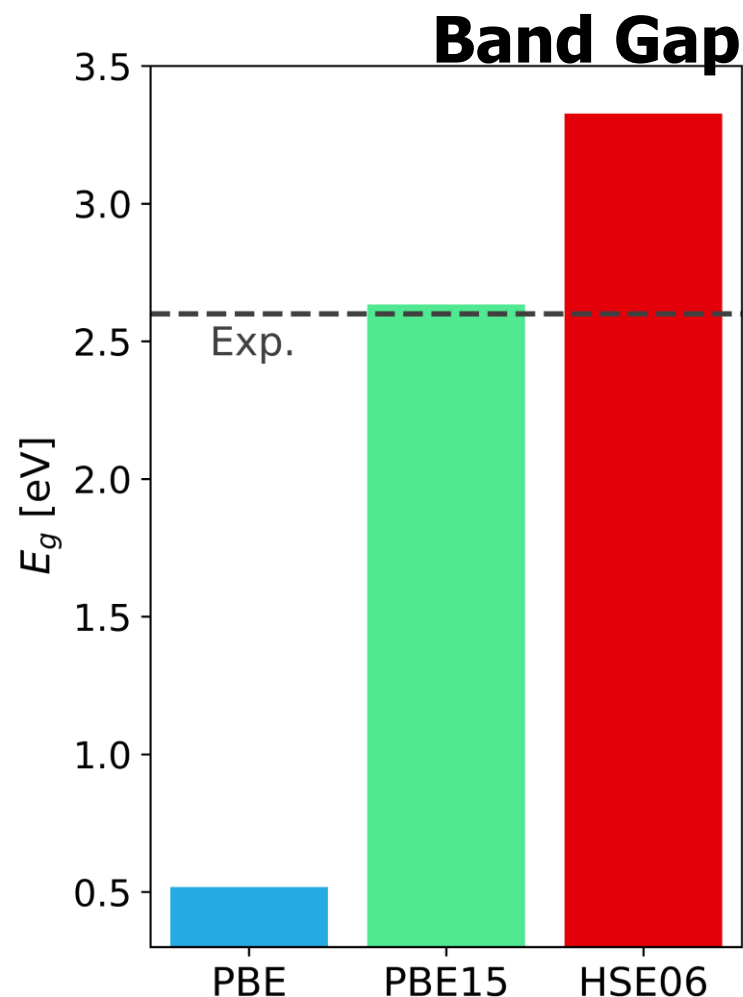
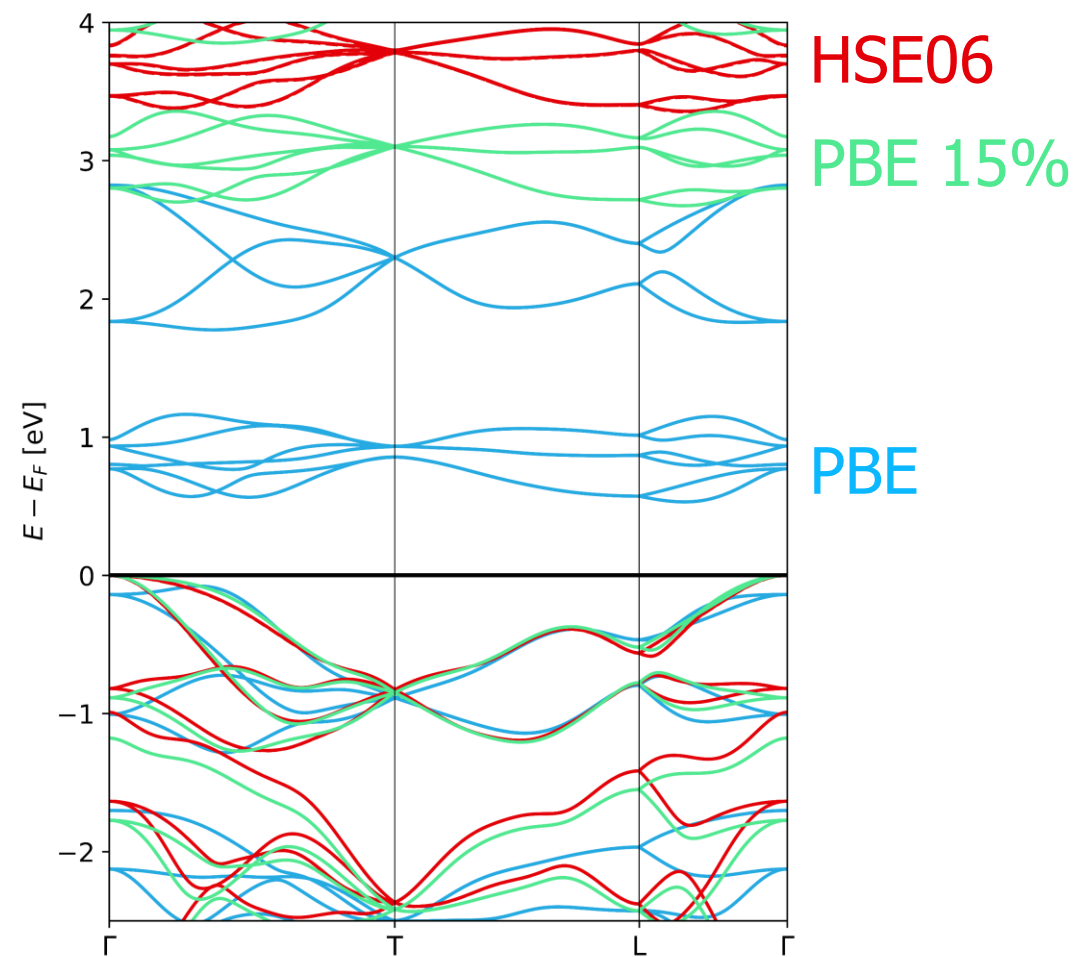
- It generate an over-delocalization of **electron density**
- Inclusion of **EXX** can reduce the **SIE**



K. E. El-Kelany, C. Ravoux, J. K. Desmarais, P. Cortona, Y. Pan, J. S. Tse, and A. Erba, Spin localization, magnetic ordering, and electronic properties of strongly correlated Ln_2O_3 sesquioxides (Ln=La, Ce, Pr, Nd), *Phys. Rev. B*, **2018**, 97.24, 245118.

Improvement on Band Gap

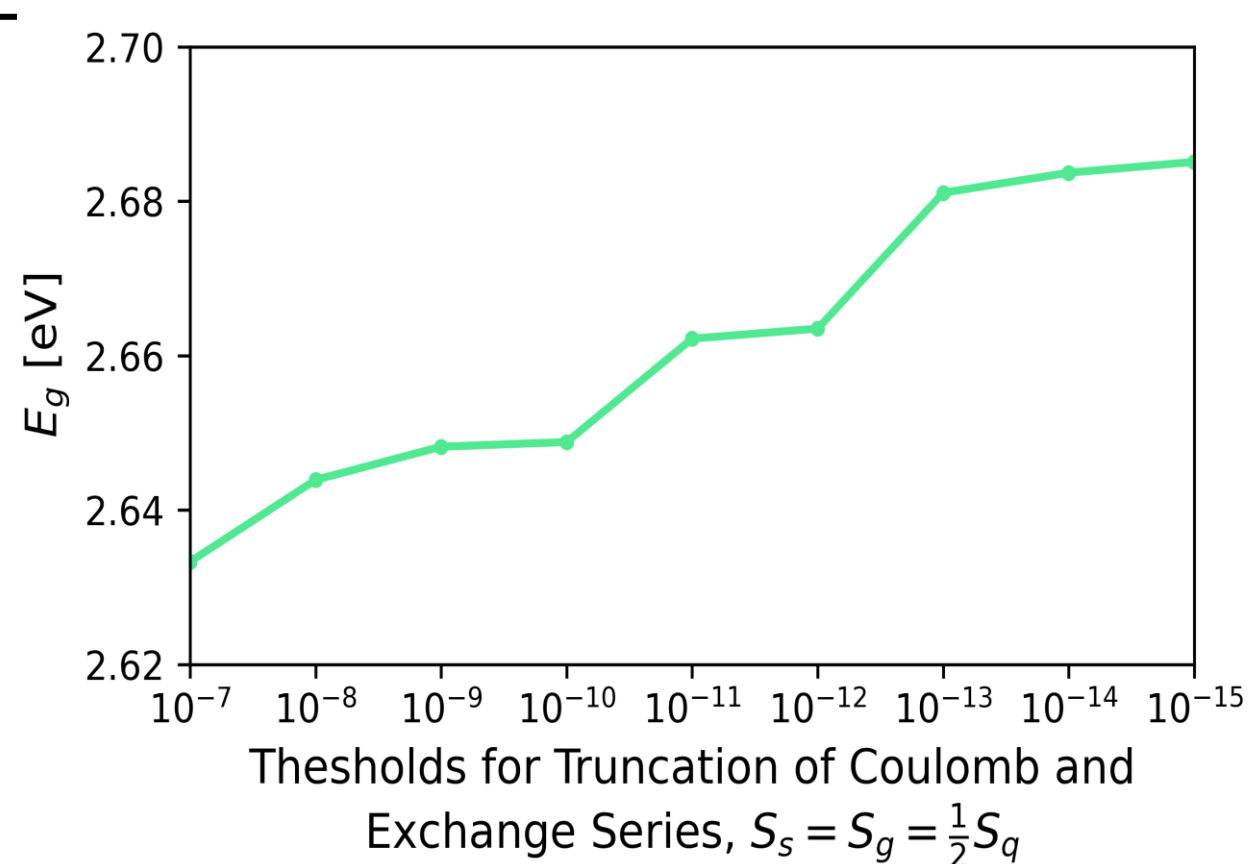
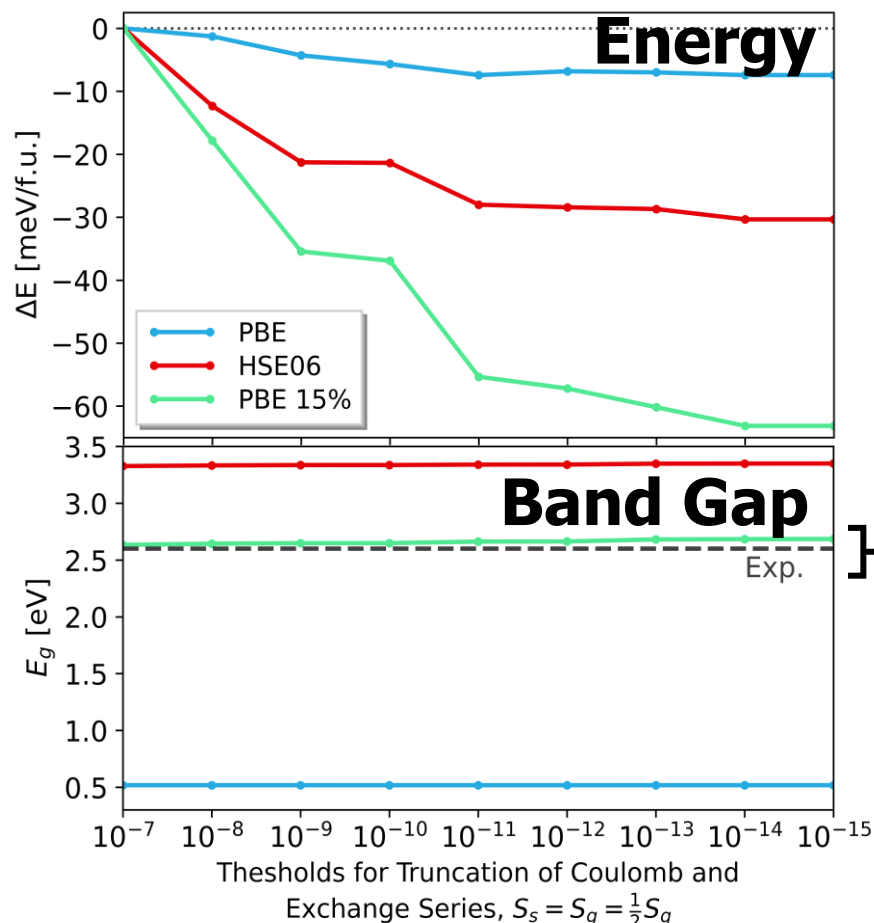
Bands structure of iron oxide can be greatly improved by **hybrid functionals**



Hematite: Convergence of EXX

Increasing TOLINTEG values, the energy and bandgap should **converge** to the *correct* solution

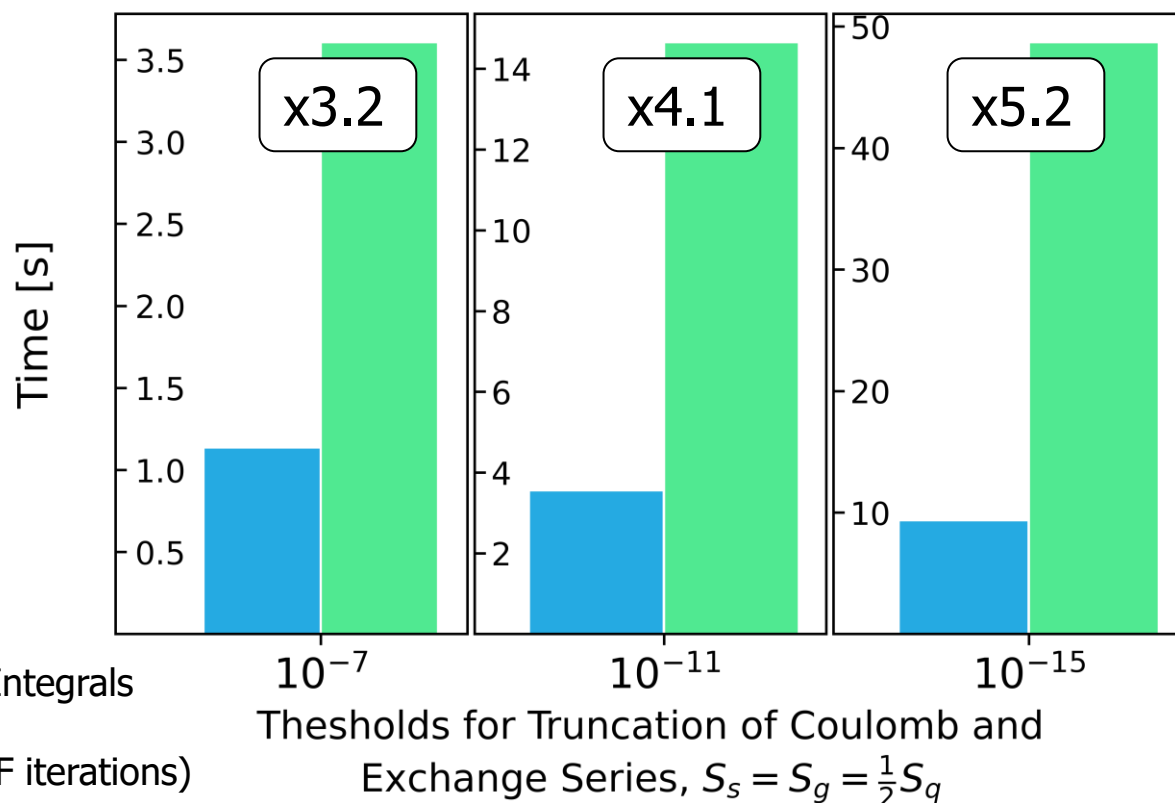
- Here we increase all TOLINTEG values similarly



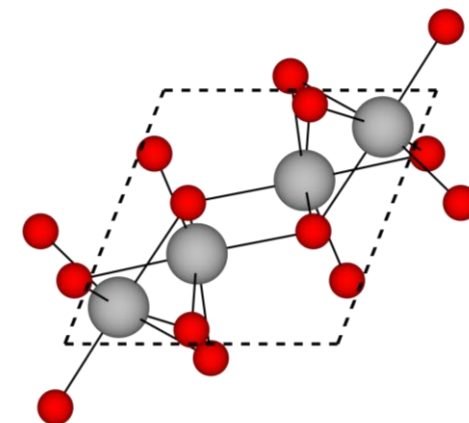
Hematite: Timings

Computing EXX on top of the standard GGA calculation **do not add** much **computational time**

- Increasing TOLINTG means computing more integrals (both Coulomb and EXX)



PBE
PBE+15%EXX



10 Atoms (two formula units)

186 AOs in Basis Set

1 Full Node of CPU Partition
of **Leonardo HPC**:

112 Cores (2x Intel Xeon 8480+)

EuO: Structure

A more challenging simulation as **stress-test** for our approach:

Under pressure phase of EuO (20 GPa)

- **7 unpaired electrons** in 4f orbital on each Eu

→ Highly localized electrons

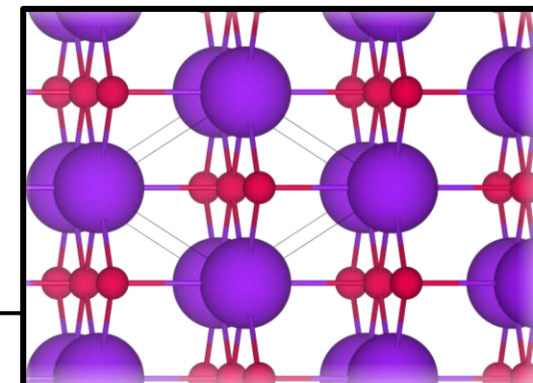
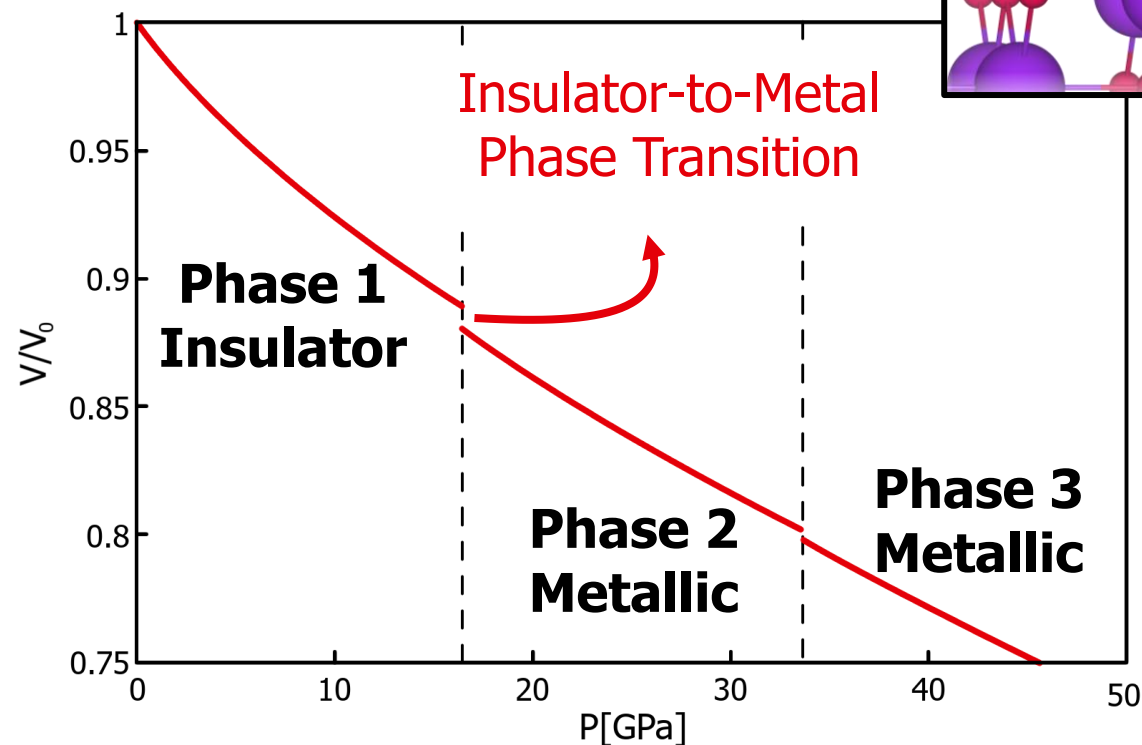
- **Metallic behaviour**

→ Highly delocalized electrons

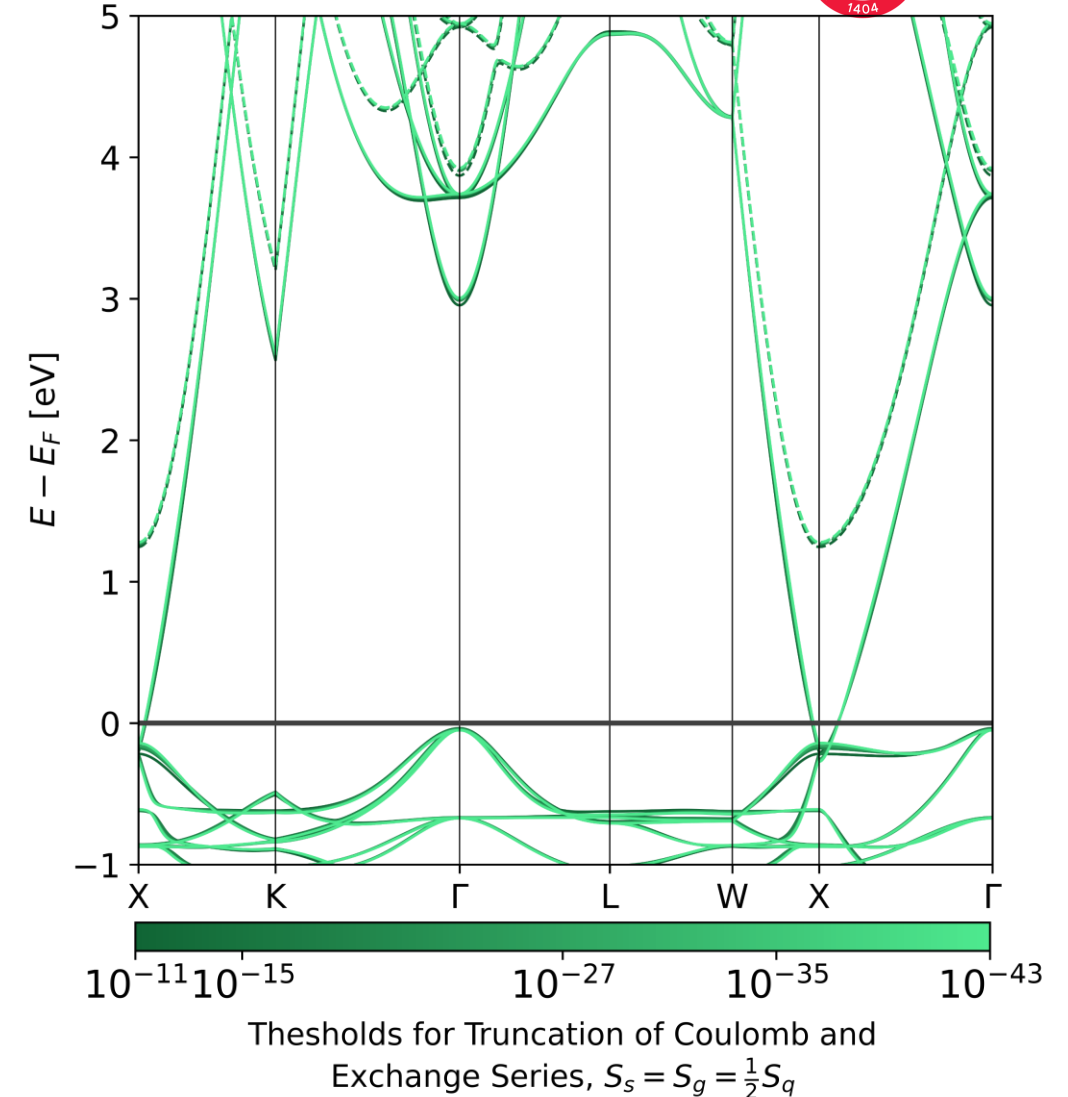
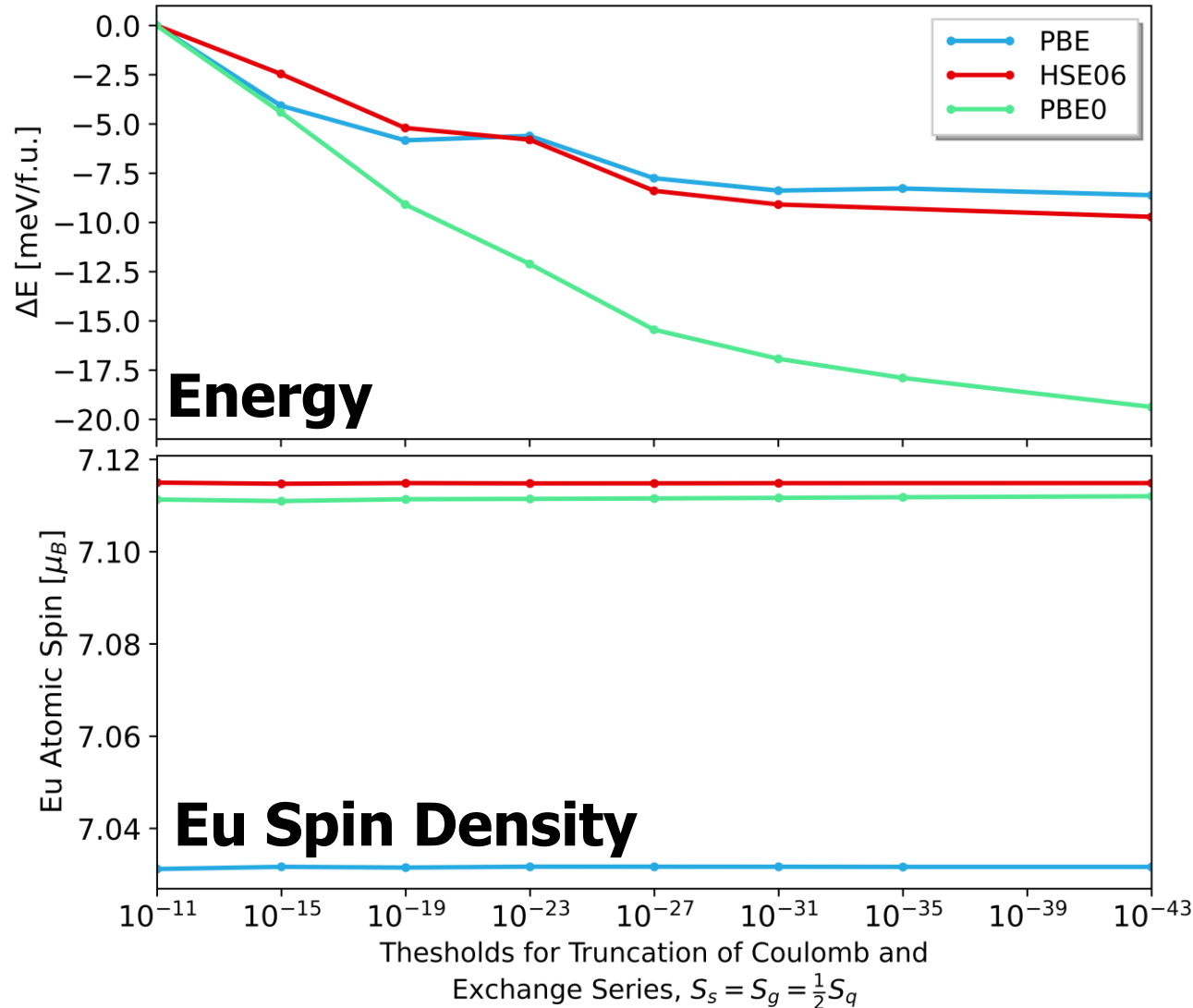
- **High density** due to pressure

- **Heavy Atoms**

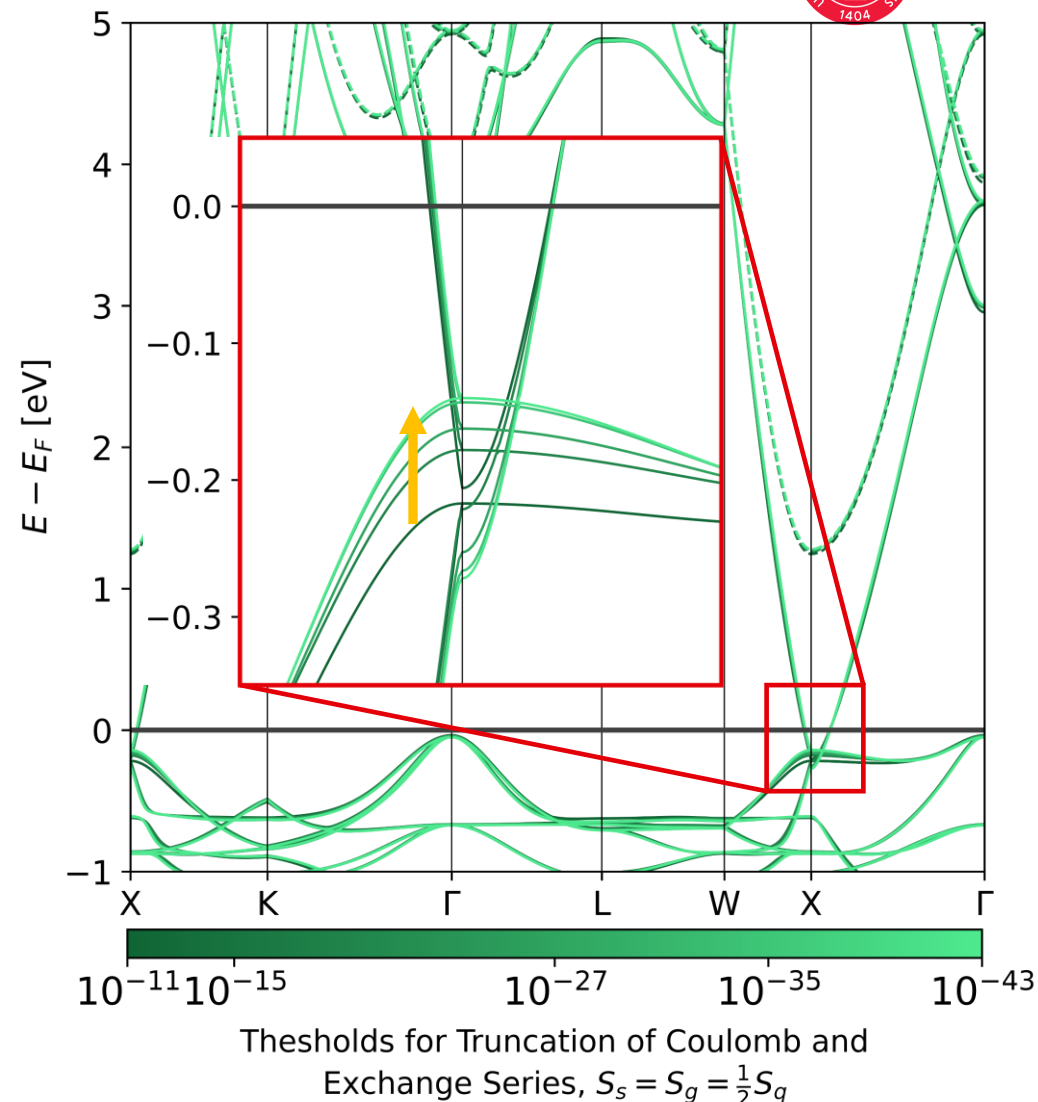
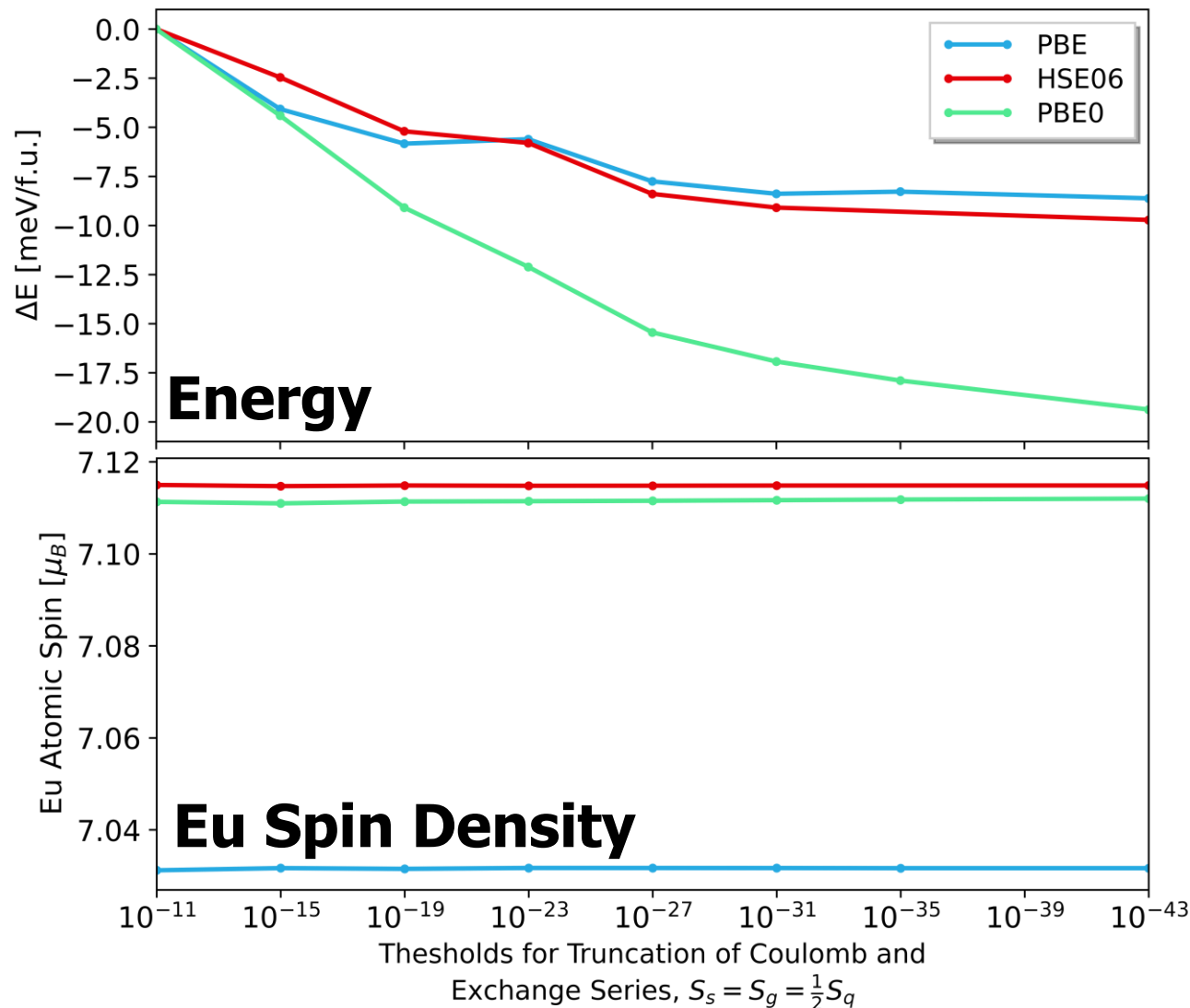
→ High number of integrals



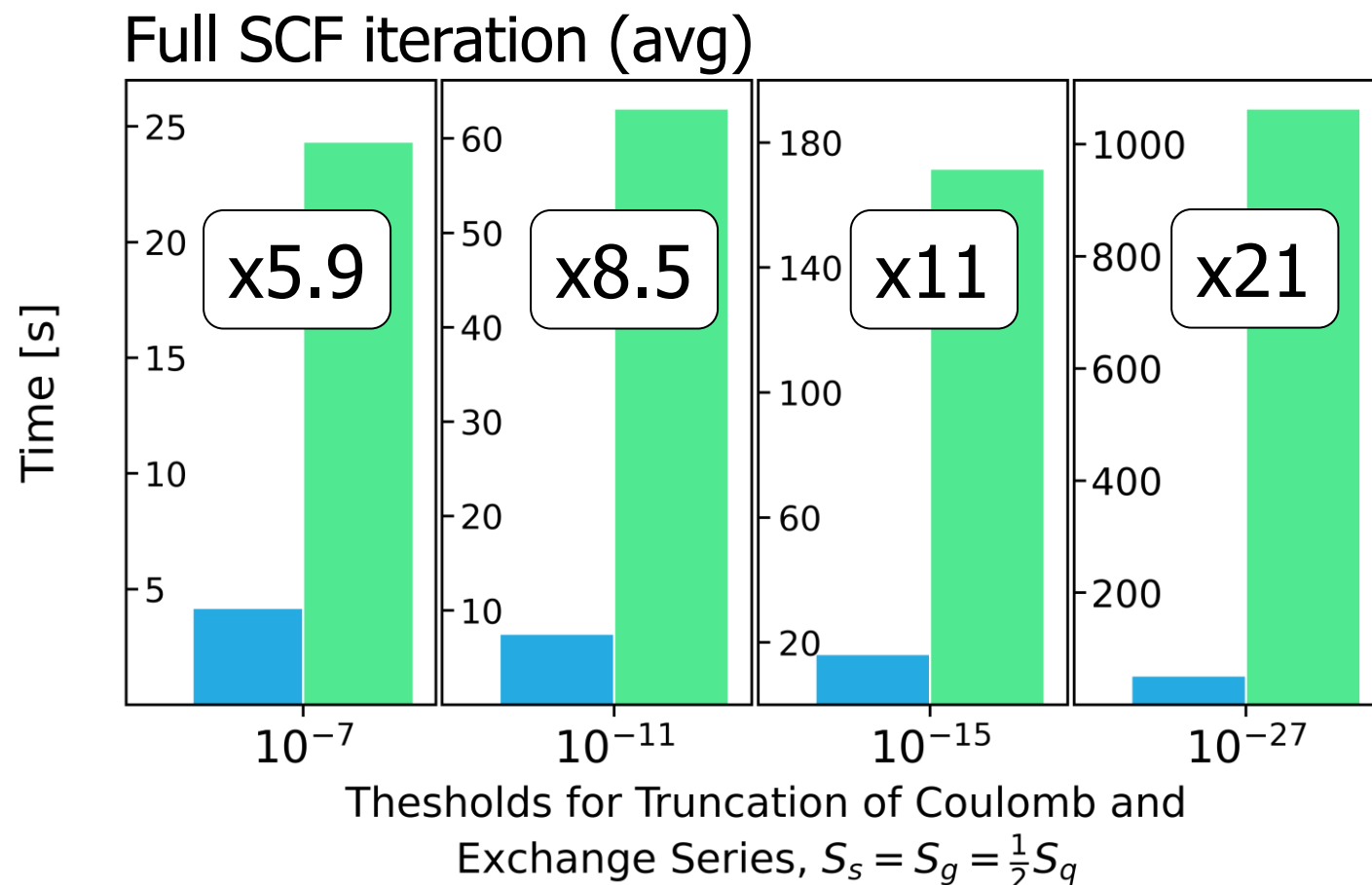
EuO: Electronic Structure



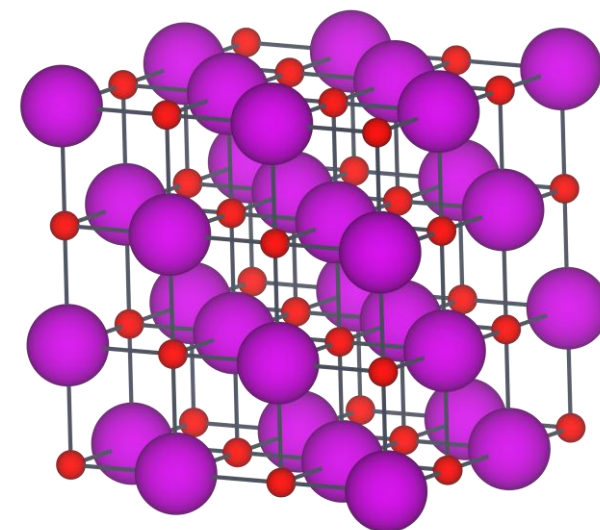
EuO: Electronic Structure



EuO: Timings



PBE **PBE 15%**



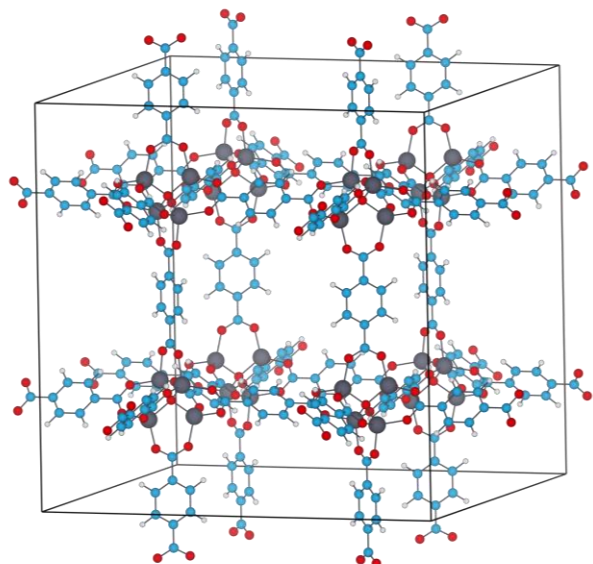
2 Atoms

147 AOs in Basis Set
(+ Pseudopotential for Eu)

1 Full Node of CPU Partition
of **Leonardo HPC**:

112 Cores (2x Intel Xeon 8480+)

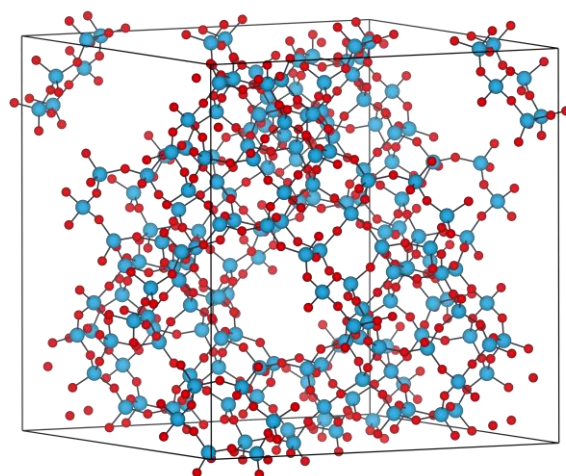
Additional Test Cases



MOF-5

424 Atoms, 7184 AOs

TIME [s]	PBE	B3LYP	
Two-elec. Integrals	1.84	4.39	x2.4
SCF Iteration	3.80	6.32	x1.66
Total	63.2	107.5	x1.7



FAUJASITE

576 Atoms, 11136 AOs

TIME [s]	PBE	B3LYP	
Two-elec. Integrals	24.36	39.72	x1.6
SCF Iteration	30.71	46.59	x1.5
Total	383.2	532.8	x1.4

**Exploitation of
Symmetry**

3 Nodes
60 CPU Cores
Intel Xeon
E5-2630

$$S_s = S_g = 7$$

$$S_q = 15$$

Final Remarks

- **Hybrid functionals** can **improve** the **description** of your system
→ Especially **optical properties** and **electron localization**
- Need to compute another *ingredient* for the functional: **EXX**
→ It can be **expensive**, especially in PW
- Computing EXX with **localized basis set** can be efficient:
 - **Direct space** approach
 - TOLINTEG **truncation techniques** for infinite summations
 - **Bipolar expansion**