

Advanced School on
QUANTUM MODELLING
of Materials with CRYSTAL



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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

$$E_{\text{xc}}^{\text{dHGA}}[n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau(\mathbf{r}), \varepsilon_{\text{EXX}}, \varepsilon_c^{\text{PT}}]$$

Hybrids

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

meta-GGA

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

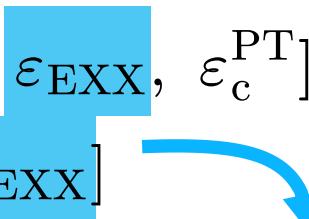
GGA

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

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

A. D. Becke, A new mixing of Hartree–Fock and local density-functional theories. *J. Chem. Phys.*, **1993**, *98*, 2, 1372–1377



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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

$$E^{\text{DFT}} = \tilde{T} + \int \hat{v}_{\text{ext}} n \, d\mathbf{r} + E_H[n] + E_{\text{xc}}[n]$$

$$\frac{1}{2} \sum_{i,j} \iint \frac{\vartheta_i^*(\mathbf{r}_1) \vartheta_i(\mathbf{r}_1) \vartheta_j^*(\mathbf{r}_2) \vartheta_j(\mathbf{r}_2)}{\mathbf{r}_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + E_{\text{xc}}[n]$$

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

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

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**

$$E_{xc} = E_c + E_x$$

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

- 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%

A. D. Becke, A new mixing of Hartree–Fock and local density-functional theories. *J. Chem. Phys.*, **1993**, *98*, 2, 1372–1377

The Range Separation

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

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

- 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!

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

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

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  20%

PBE0  25%

HSE06  25% - 0%

Easy and **Convenient**

Low Accuracy for “Limit” Cases:

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

The Choice for Alpha

Fixed α Parameter

Use the Functional **as is**

B3LYP \longrightarrow 20%

PBE0 \longrightarrow 25%

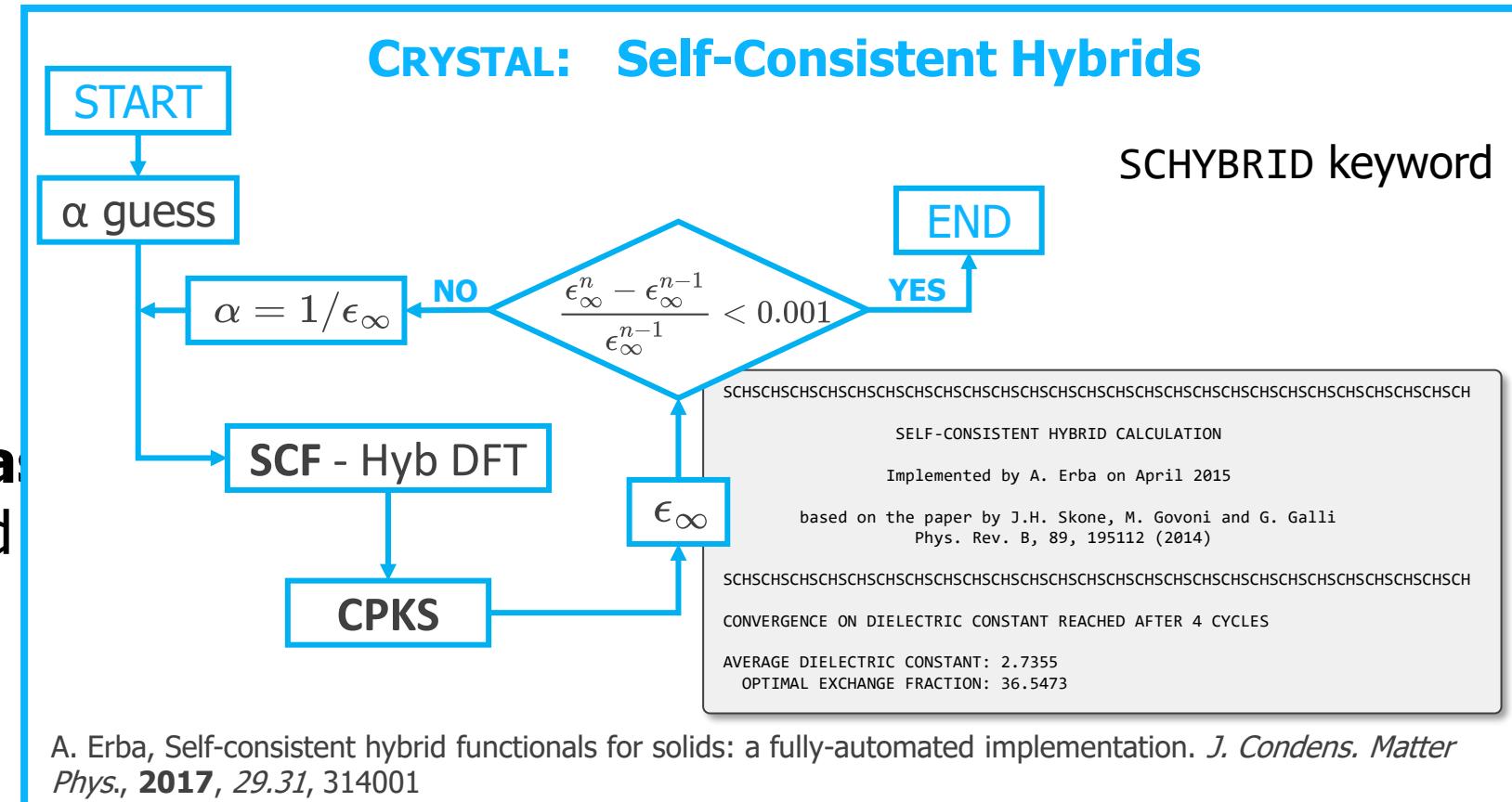
HSE06 \longrightarrow 25% - 0%

Easy and **Convenient**

Low Accuracy for “Limit” Cases

\longrightarrow *very-low or very-high band*

Material Specific α Parameter



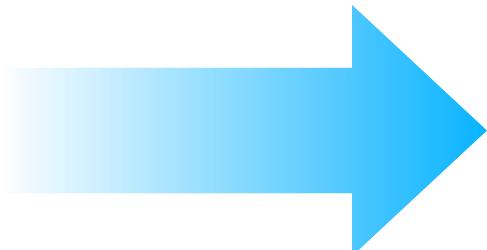
Hybrids in CRYSTAL Input

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)

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

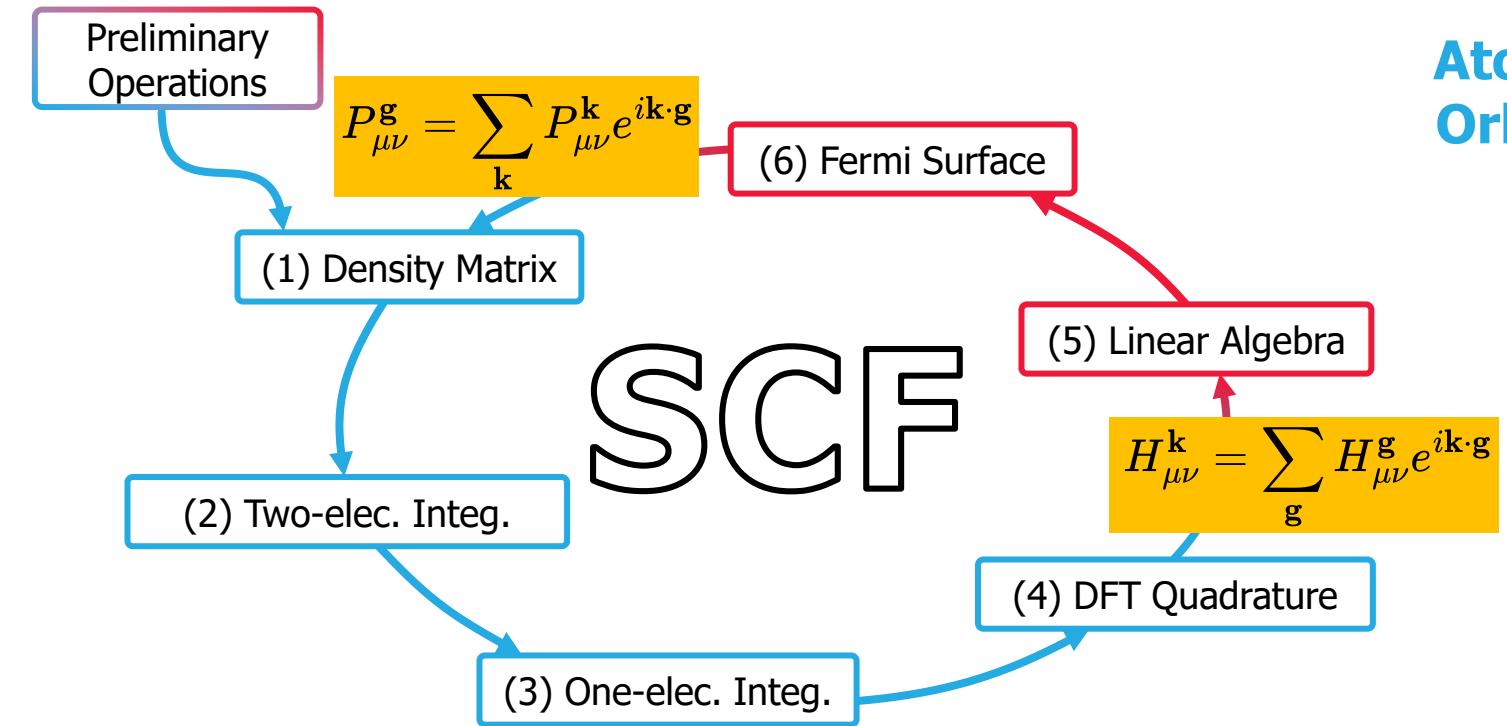
```
DFT
PBE
HYBRID
15
END
```



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

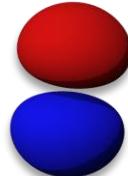
```
DFT
CAM-B3LYP
END
```

Why Hybrids are Efficient?

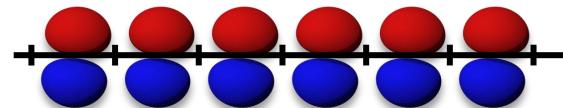


Atomic Orbital

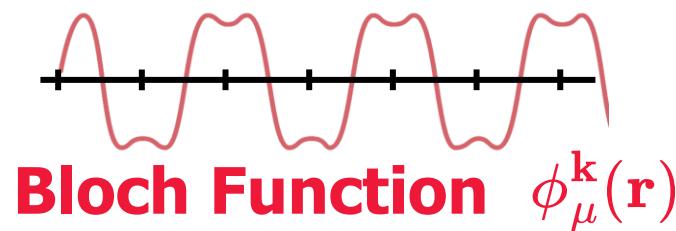
$$\chi_{\mu}^g(\mathbf{r})$$



Translational Symmetry



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



Crystalline Orbitals
As Linear Combination of BFs

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



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

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

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

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

Exchange and Correlation Matrix

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

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

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

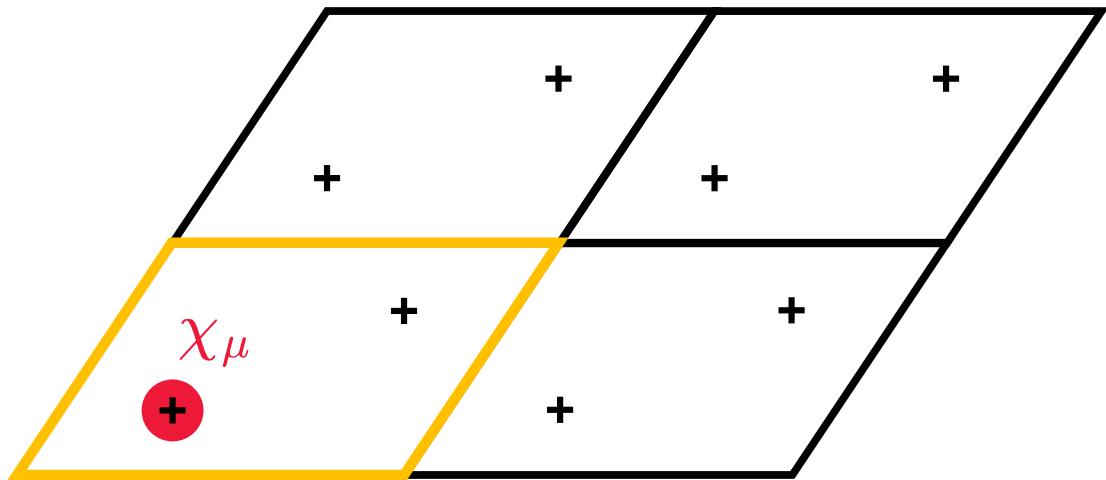
$$E_{\text{EXX}} = -\frac{1}{2} \sum_{\mu\nu} \sum_{\mathbf{g}} P_{\mu\nu}^{\mathbf{g}} \sum_{\sigma\rho} \sum_{\mathbf{q}} P_{\sigma\rho}^{\mathbf{q}} \sum_{\mathbf{s}} (\chi_{\mu}^0 \chi_{\sigma}^{\mathbf{s}} | \chi_{\nu}^{\mathbf{g}} \chi_{\rho}^{\mathbf{s+q}})$$

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

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

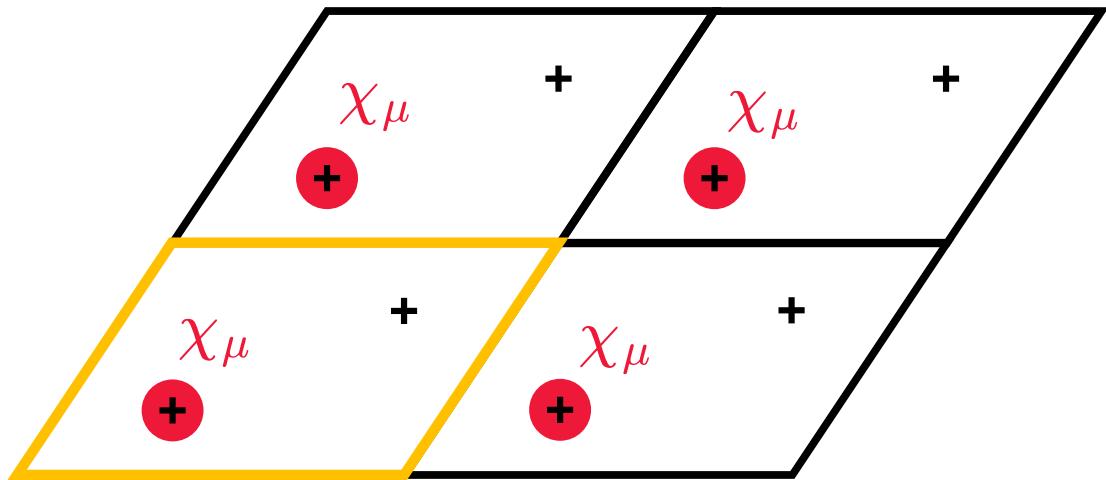
Infinite Matrices in CRYSTAL

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



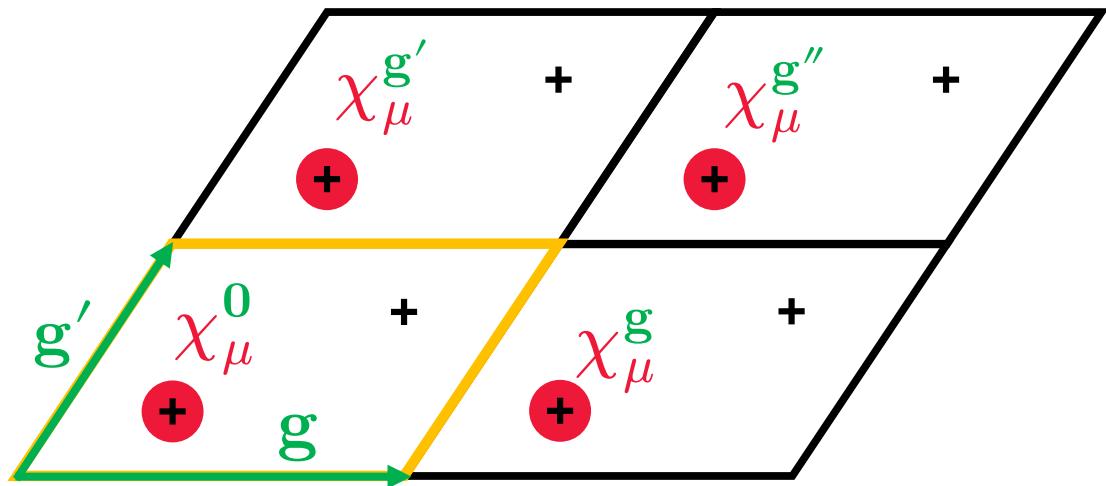
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- But they are **replicated** (infinitely) in all the other cells



Infinite Matrices in CRYSTAL

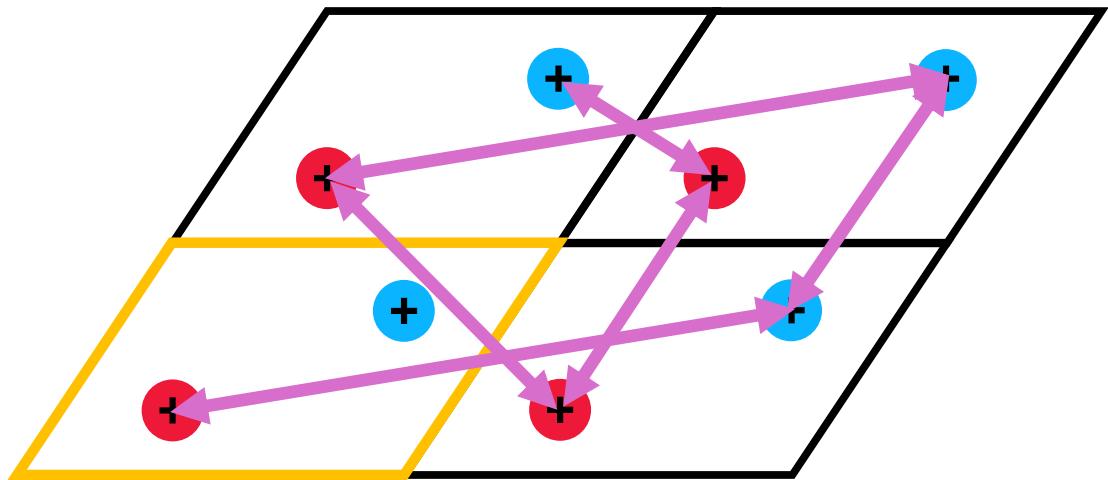
- Elements of **direct space matrices** represent interactions between **two orbitals** $\mu \nu$  $[V_{\text{EXX}}^g]_{\mu\nu}$
- BFs** χ_μ are defined for all atoms in the **reference cell**
- But they are **replicated** (infinitely) in all the other cells
- We use **Bravais vectors** g to indicate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



Infinite Matrices in CRYSTAL

- Any possible $\mu \nu$ couple of BFs should be considered

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

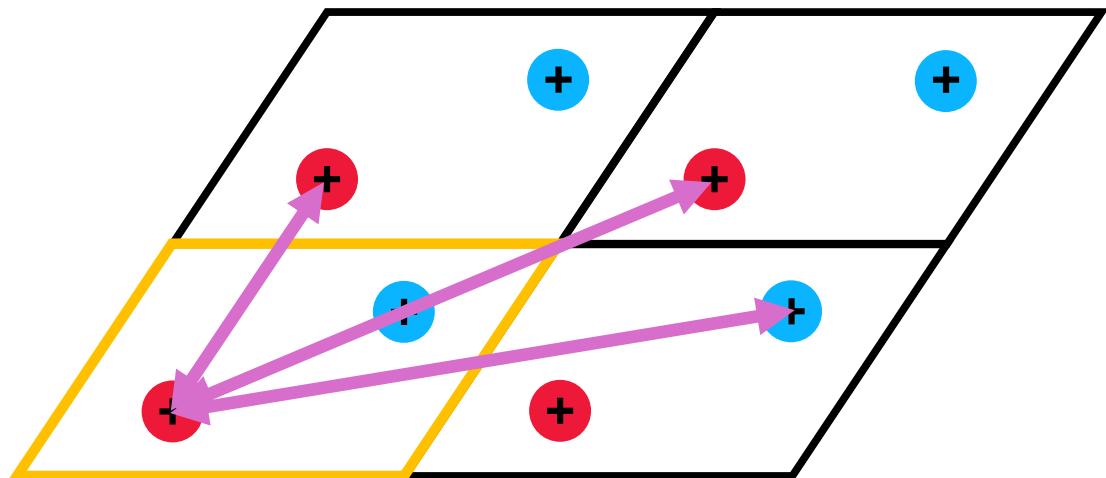


Infinite Matrices in CRYSTAL

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

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

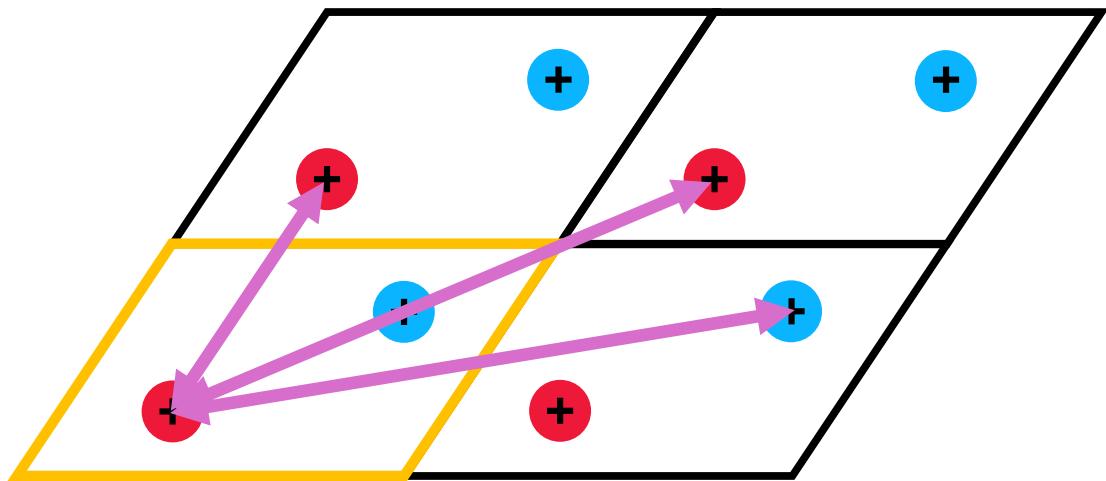
$$\left\{ \begin{array}{l} \mu \\ \nu \end{array} \right. \begin{array}{l} 1 \rightarrow N_{BS} \\ 1 \rightarrow \infty \end{array}$$



Infinite Matrices in CRYSTAL

- Any possible $\mu \nu$ couple of BFs should be considered
- Due to **translational symmetry**, we can focus only on interactions originating from the **reference cell**
- With the notation $[V_{\text{EXX}}^g]_{\mu\nu}$ 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

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

Total of **7 indices**:

- μ ν σ ρ are **orbitals** in the reference cell ($1 \rightarrow N_{BS}$)
- \mathbf{g} \mathbf{q} \mathbf{s} are **Bravais vectors** ($1 \rightarrow \infty$)



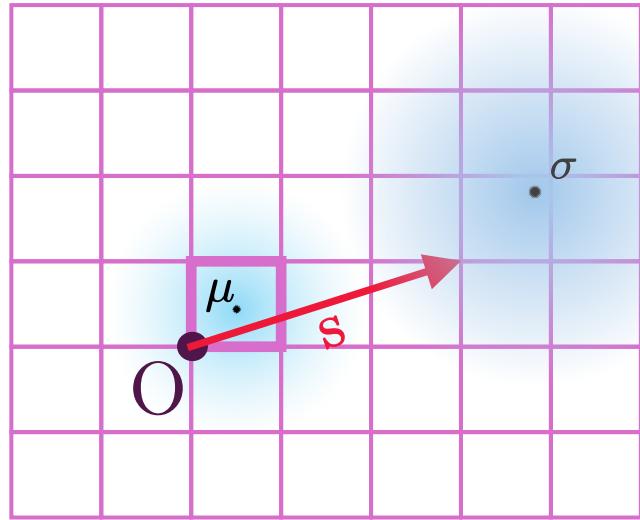
Truncation
Based on Orbital Overlap

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

The **s** summation

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

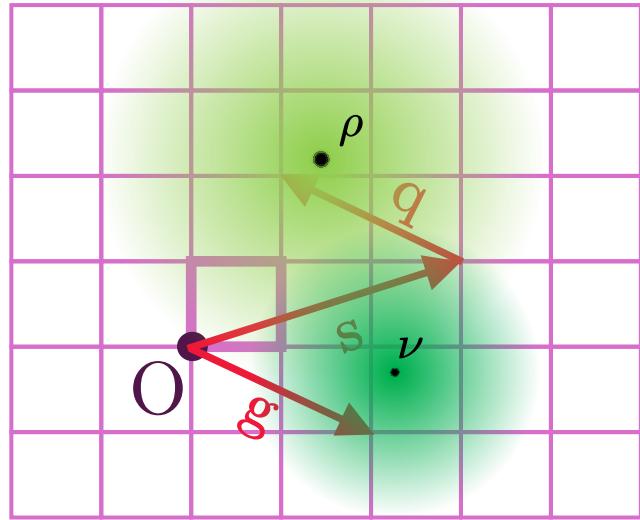
- Evaluate the overlap of $\chi_{\mu}^0 \chi_{\sigma}^s < S_s$



The **s** summation

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

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

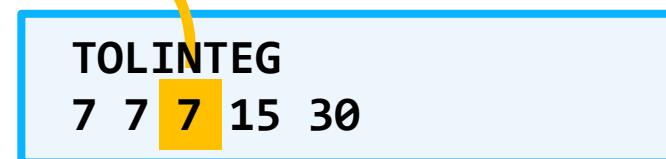


The **s** summation

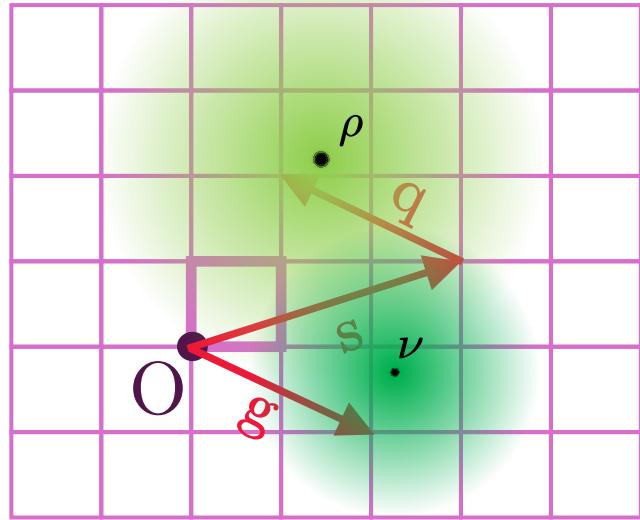
$$[V_{\text{EXX}}^g]_{\mu\nu} = - \sum_{\sigma\rho} \sum_{\mathbf{q}} P_{\sigma\rho}^{\mathbf{q}} \sum_s (\chi_{\mu}^0 \chi_{\sigma}^s | \chi_{\nu}^g \chi_{\rho}^{s+g})$$

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

$S_s = 10^{-7}$



TOLINTEG				
7	7	7	15	30

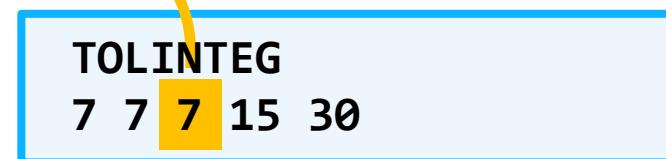


The **s** summation

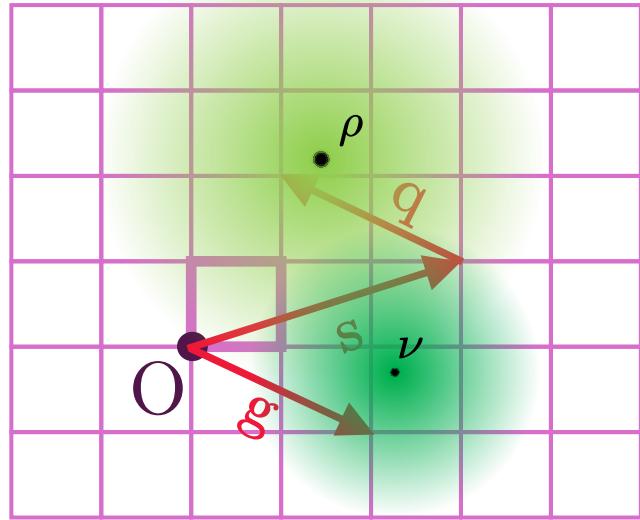
$$[V_{\text{EXX}}^g]_{\mu\nu} = - \sum_{\sigma\rho} \sum_{\mathbf{q}} P_{\sigma\rho}^{\mathbf{q}} \sum_{\mathbf{s}} (\chi_{\mu}^0 \chi_{\sigma}^{\mathbf{s}} | \chi_{\nu}^g \chi_{\rho}^{\mathbf{s}+\mathbf{q}})$$

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

$S_s = 10^{-7}$



TOLINTEG				
7	7	7	15	30



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

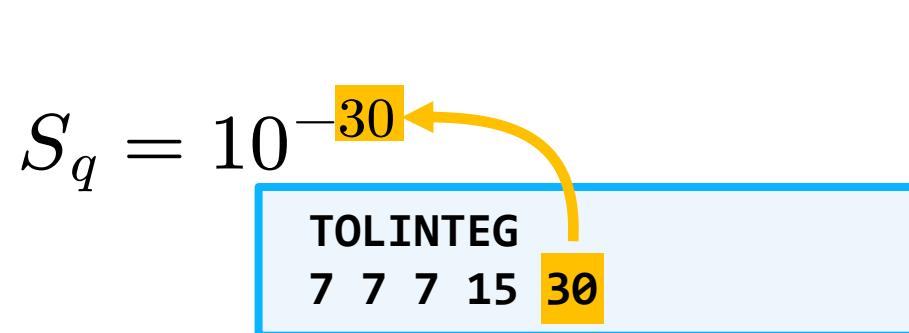
The \mathbf{q} Summation

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

- 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**



The g Index

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

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

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

TOLINTEG
 7 7 7 15 30

About g and q

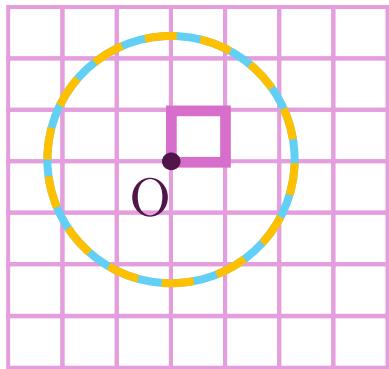
Warnings:

- 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**



$$S_g = S_q$$

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

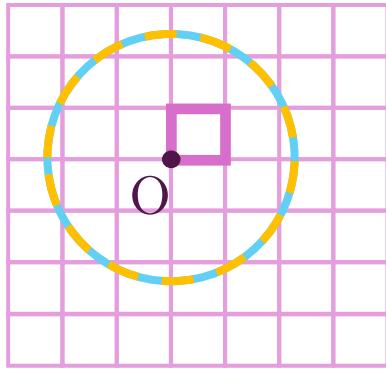
$$\chi_{\sigma}^{\mathbf{0}} \chi_{\rho}^{\mathbf{q}} < S_q$$

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

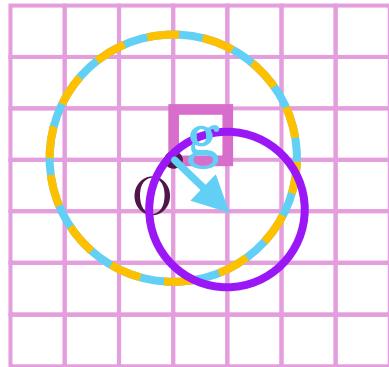
$$[V_{EXX}^g]_{\mu\nu} = - \sum_{\sigma\rho} \sum_{\mathbf{q}} P_{\sigma\rho}^{\mathbf{q}} \sum_s (\chi_{\mu}^0 \chi_{\sigma}^s | \chi_{\nu}^g \chi_{\rho}^{s+q})$$

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

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 \mathbf{g} inside our initial radius, we can define a second radius centered in \mathbf{g} of **non-zero contributions**



$$S_g = S_q$$

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

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

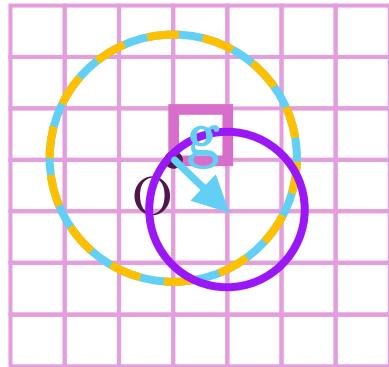
TOLINTEG
7 7 7 15 15

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

- 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 \mathbf{g} inside our initial radius, we can define a second radius centered in \mathbf{g} of **non-zero contributions**



$$S_g = S_q$$

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

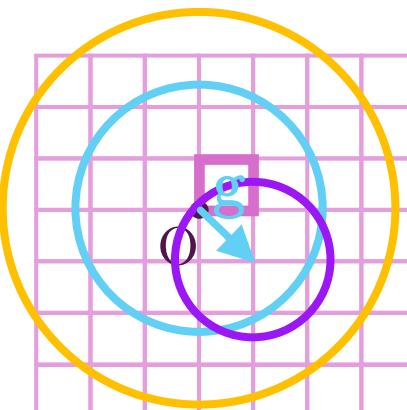
$$\chi_{\sigma}^0 \chi_{\rho}^{\mathbf{q}} < S_q$$

TOLINTEG
7 7 7 15 15

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

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

- The SCF will probably not converge



$$S_g > S_q$$

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

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

TOLINTEG
7 7 7 15 30

Need to consider smaller \mathbf{q} threshold to **Not Exclude** relevant contribution for large \mathbf{g} vectors

Bipolar Expansion

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

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

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

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

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

- 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

$S_b = 10^{-14}$

BIPOLAR
 18 14

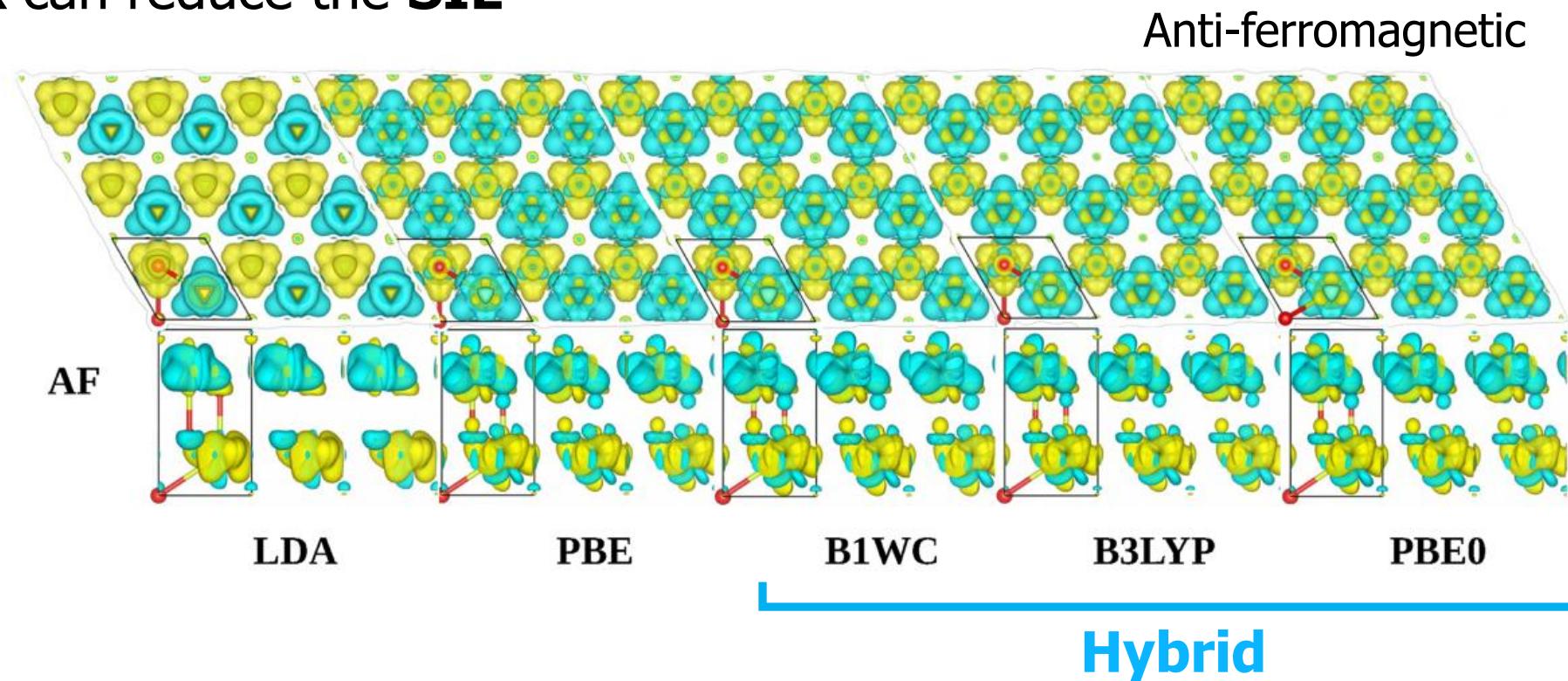
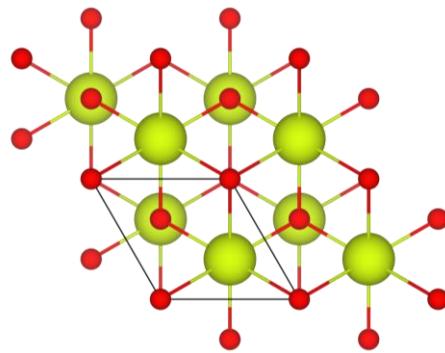
Applications

- **Electron density localization** in Ce_2O_3
→ Improvement of SIE
- **Optical properties** of Fe_2O_3
 - 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*

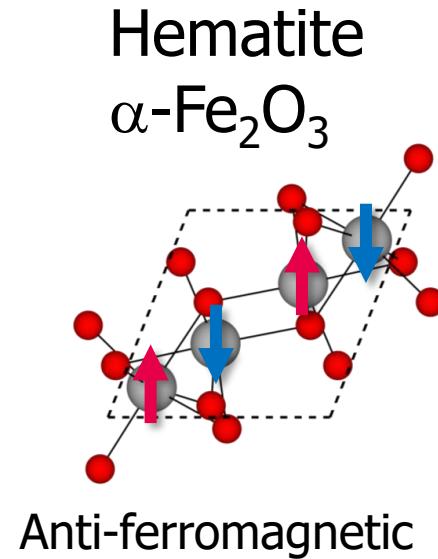
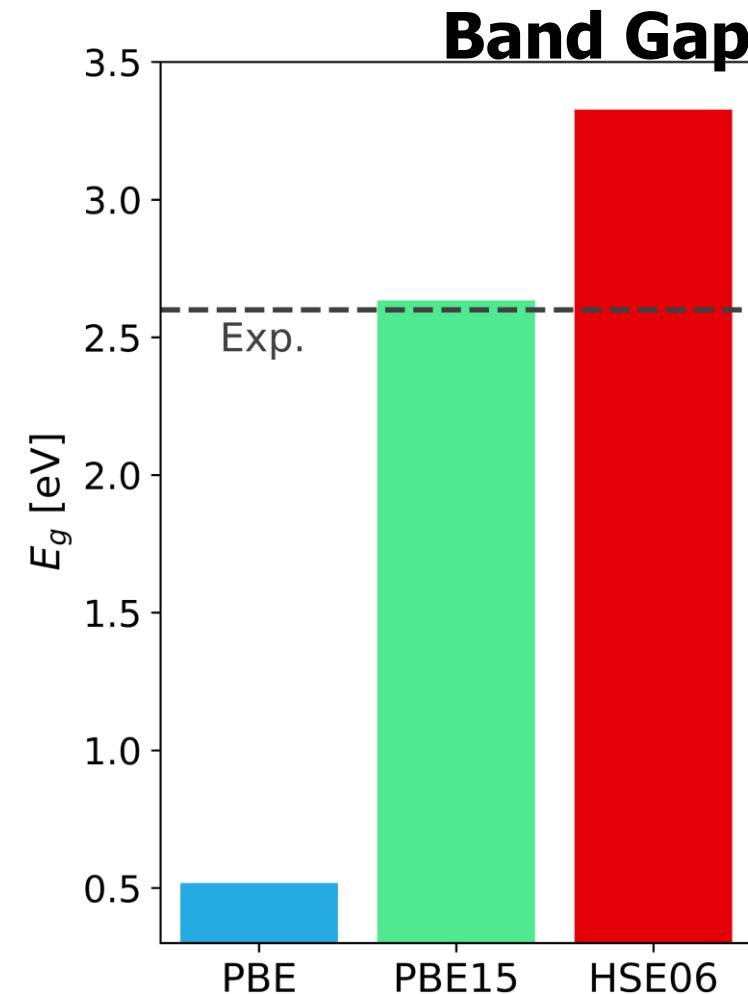
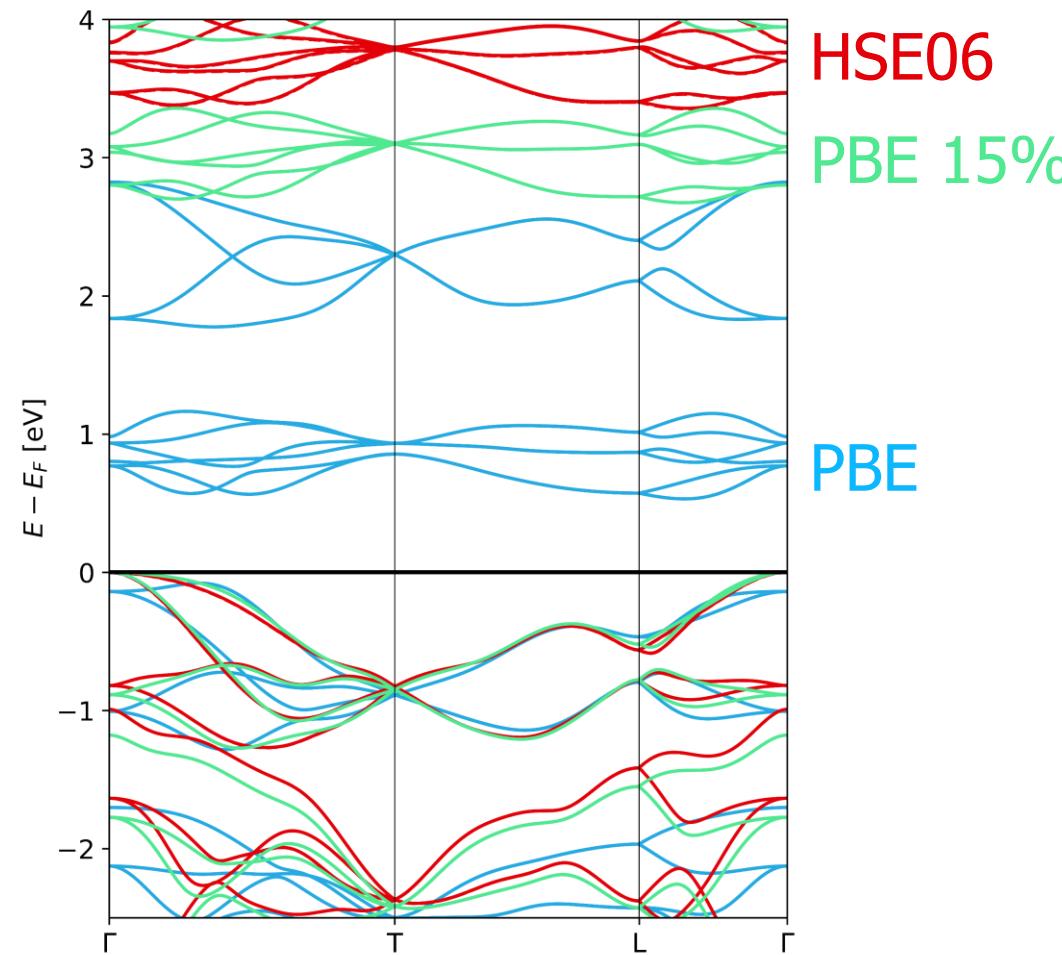
- It generate an over-delocalization of **electron density**
- Inclusion of **EXX** can reduce the **SIE**



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 ($\text{Ln}=\text{La}, \text{Ce}, \text{Pr}, \text{Nd}$), *Phys. Rev. B*, **2018**, 97.24, 245118.

Improvement on Band Gap

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

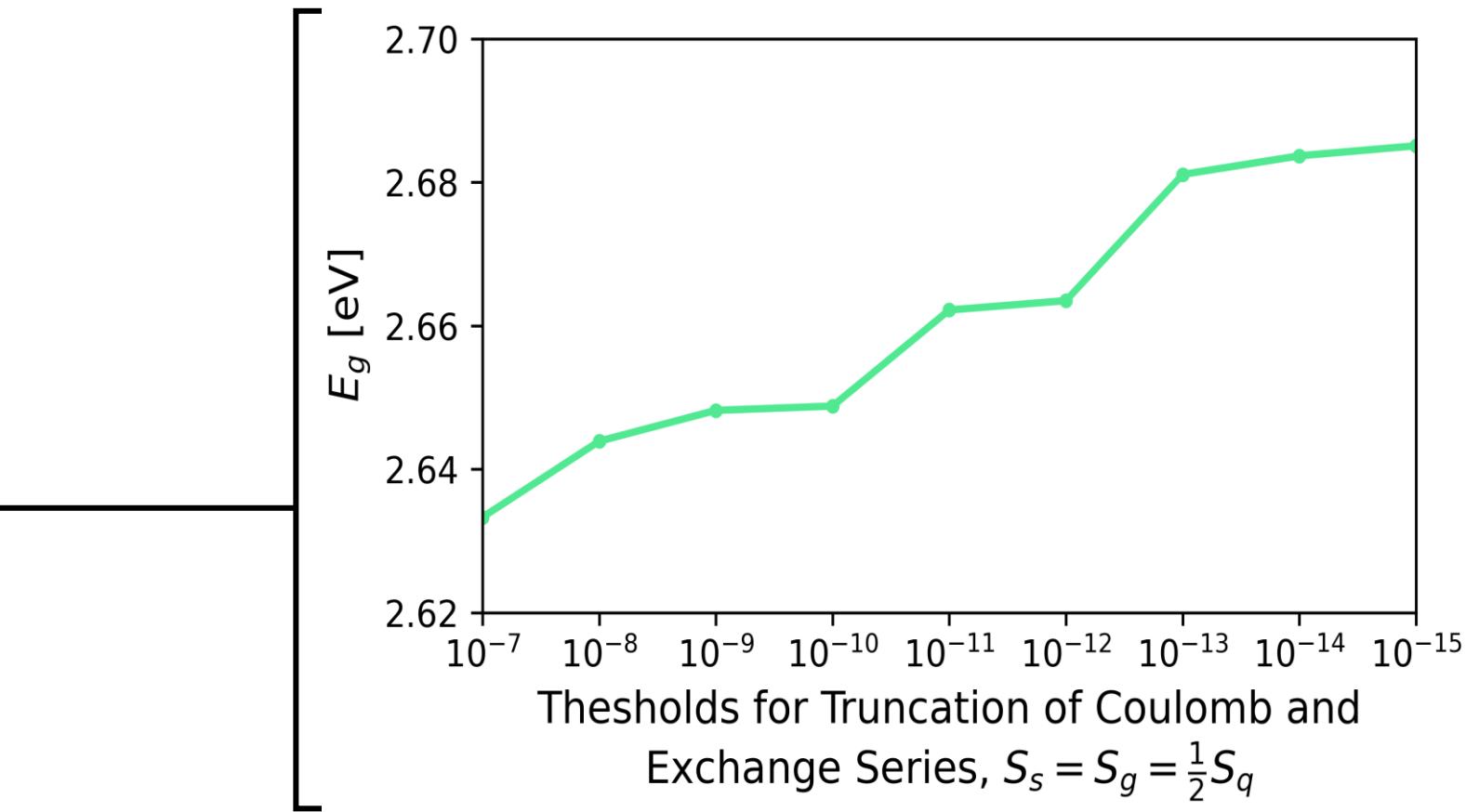
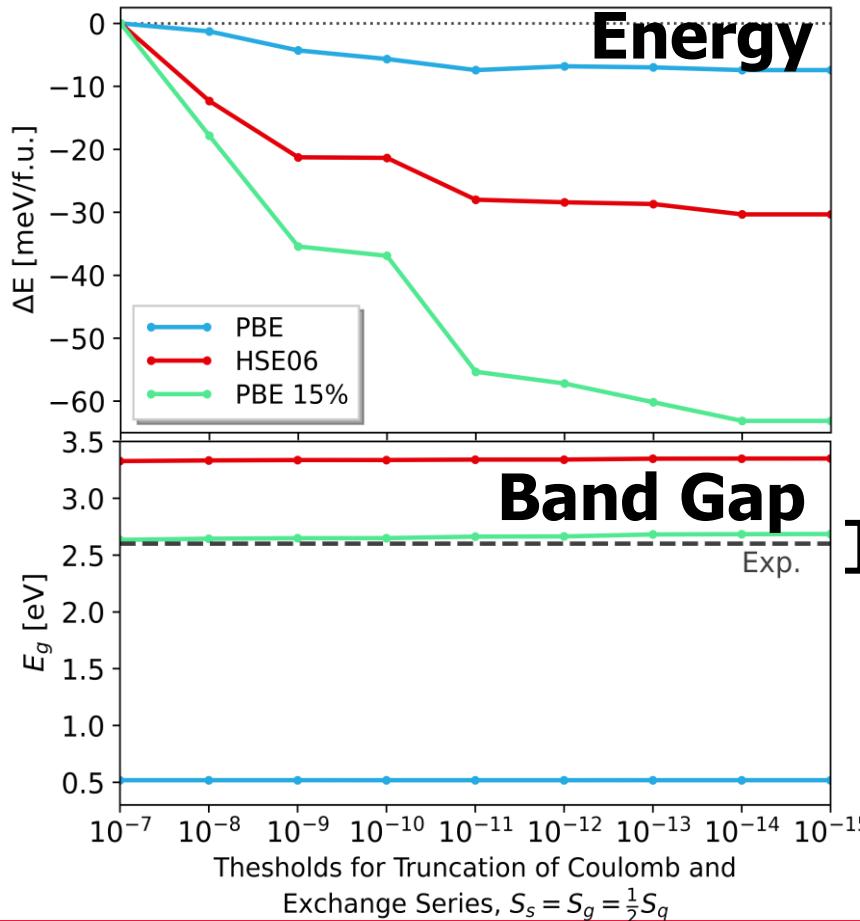


\mathbf{k} point sampling in
 $12 \times 12 \times 12$
Monkhorst-Pack mesh
All electron calculation

Hematite: Convergence of EXX

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

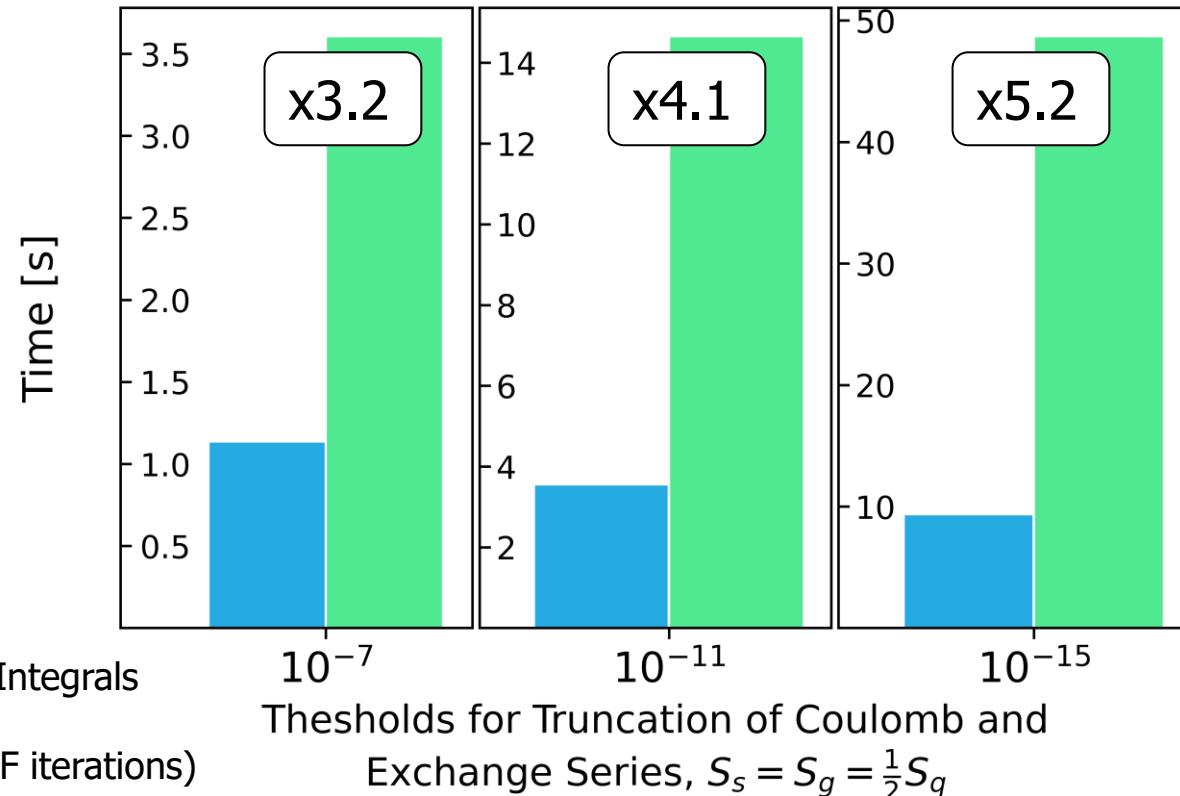
- Here we increase all TOLINTEG values similarly



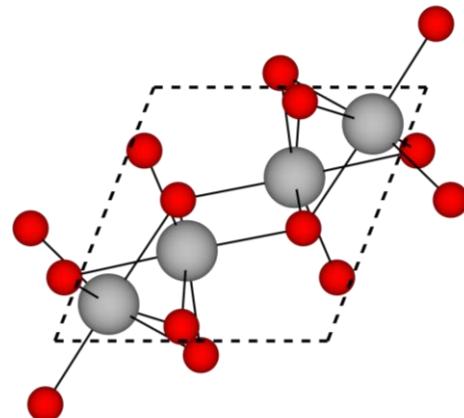
Hematite: Timings

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

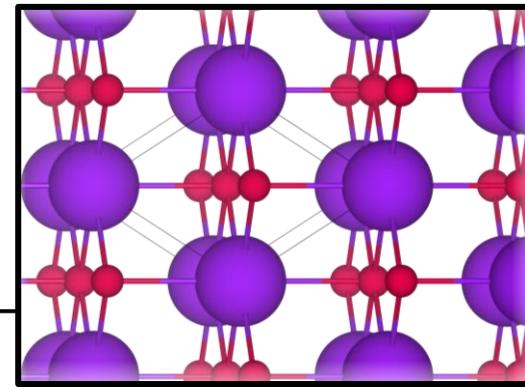
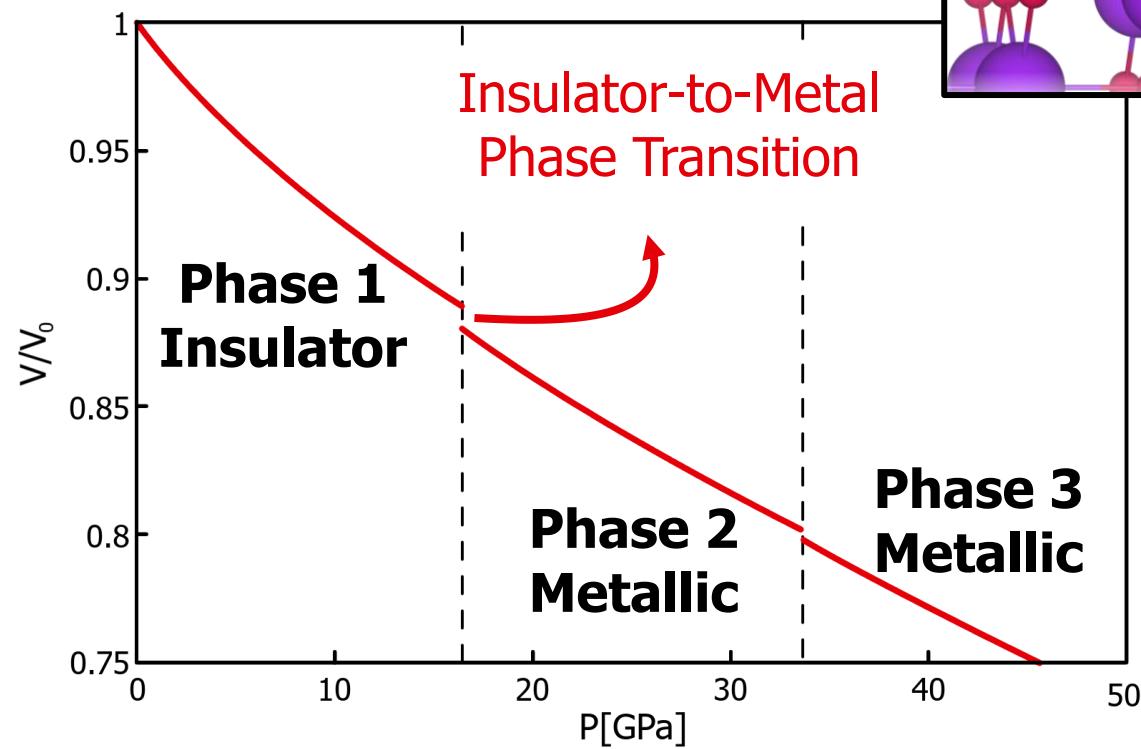
1 Full Node of CPU Partition of **Leonardo HPC**:
112 Cores (2x Intel Xeon 8480+)

EuO: Structure

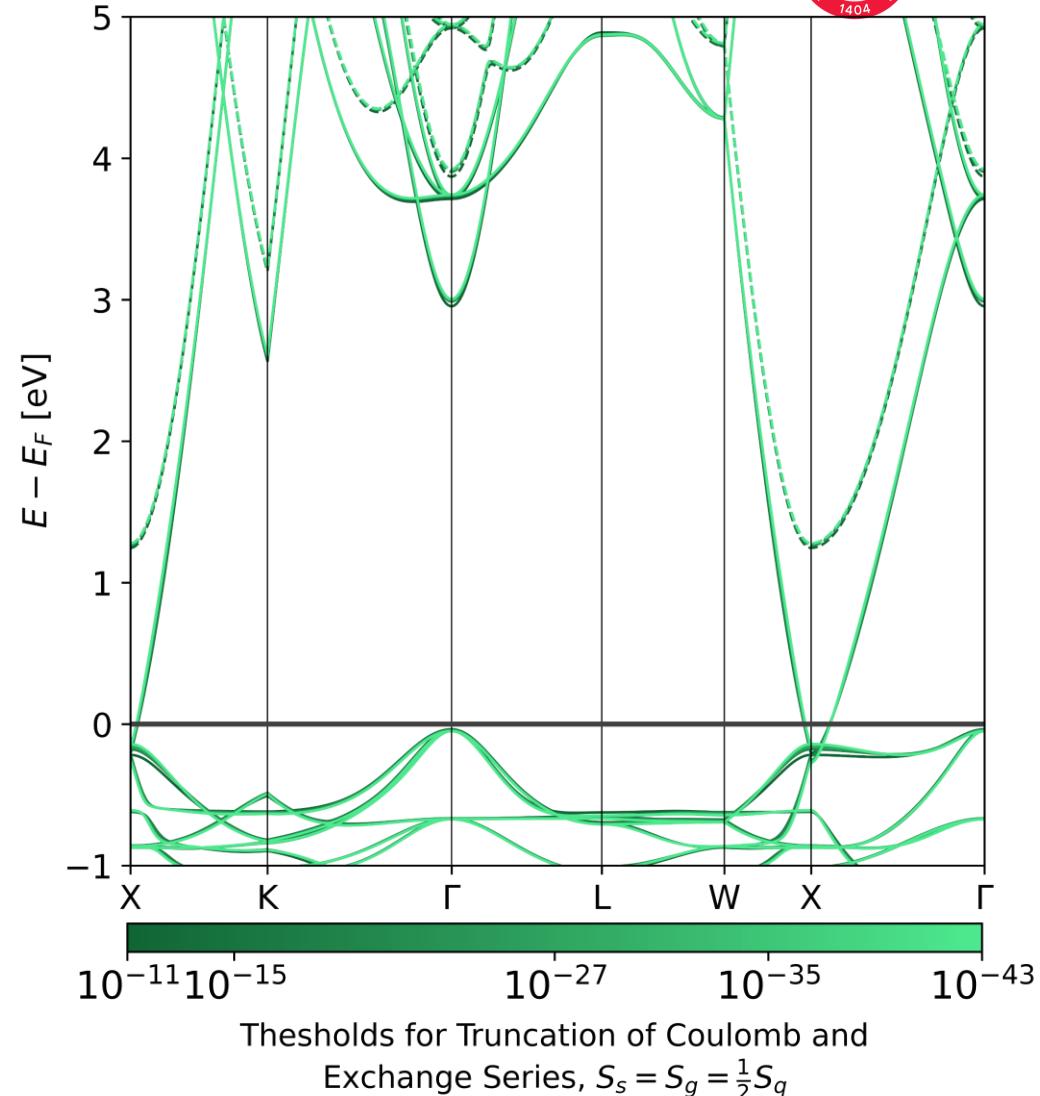
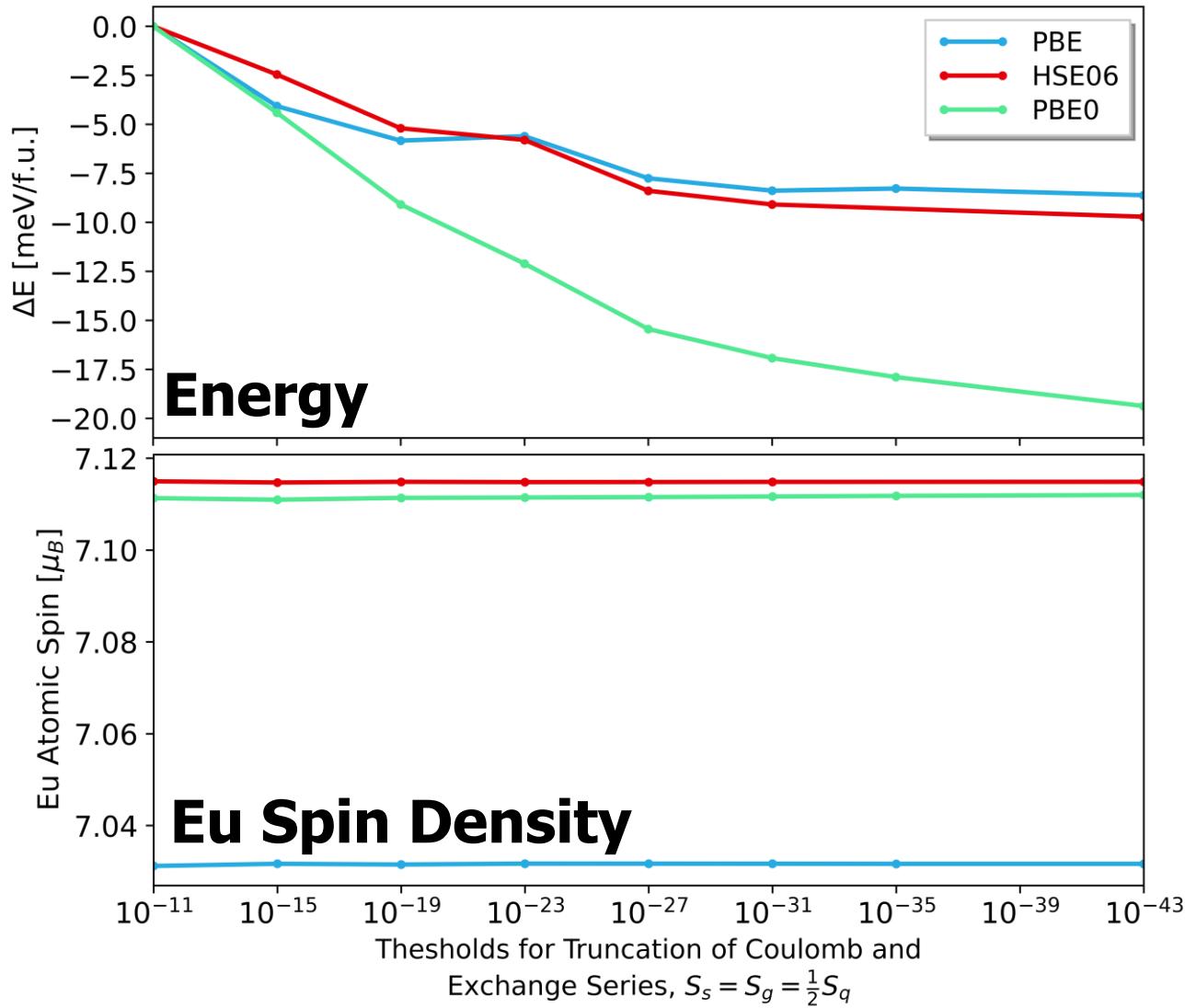
A more challenging simulation as **stress-test** for our approach:

Under pressure phase of EuO (20 GPa)

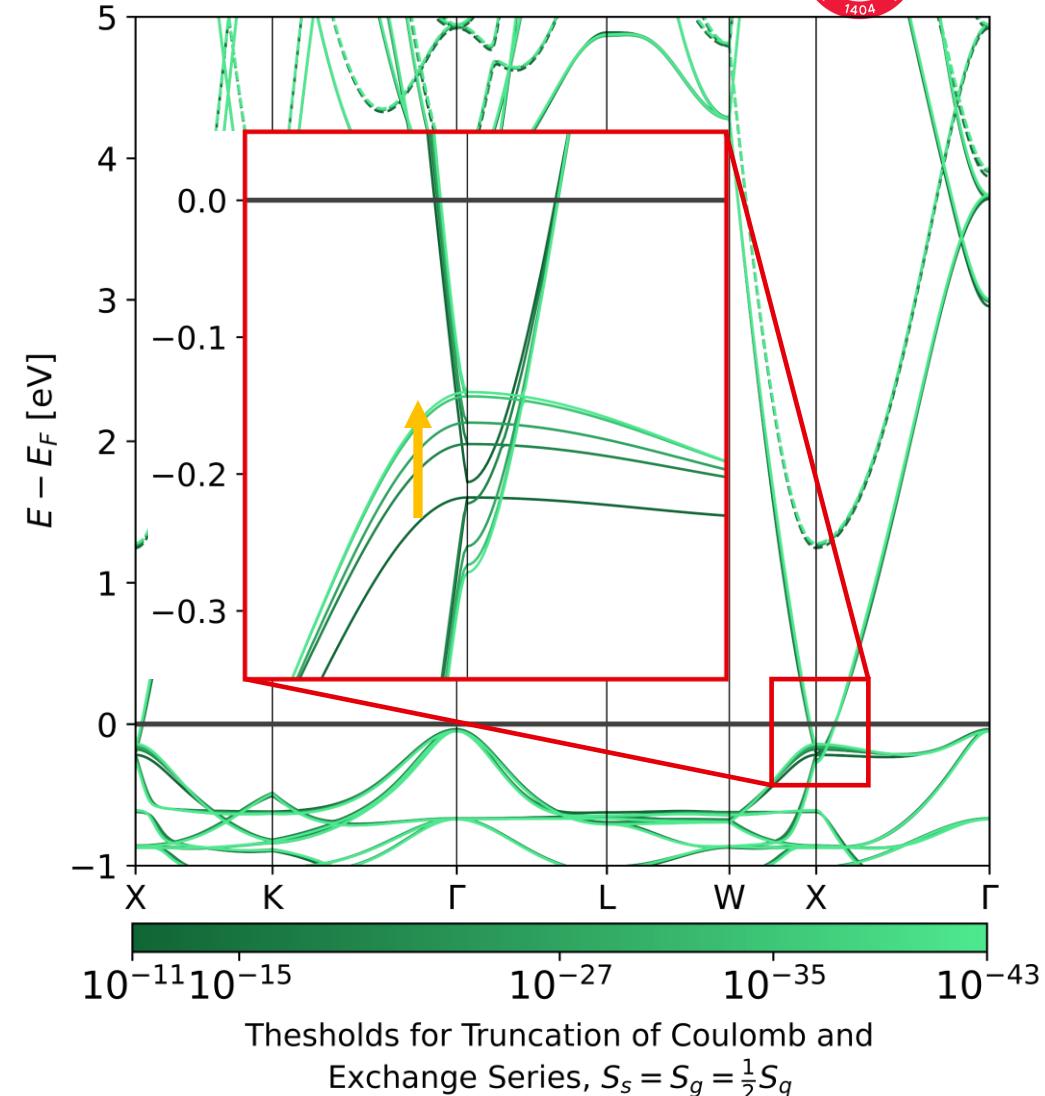
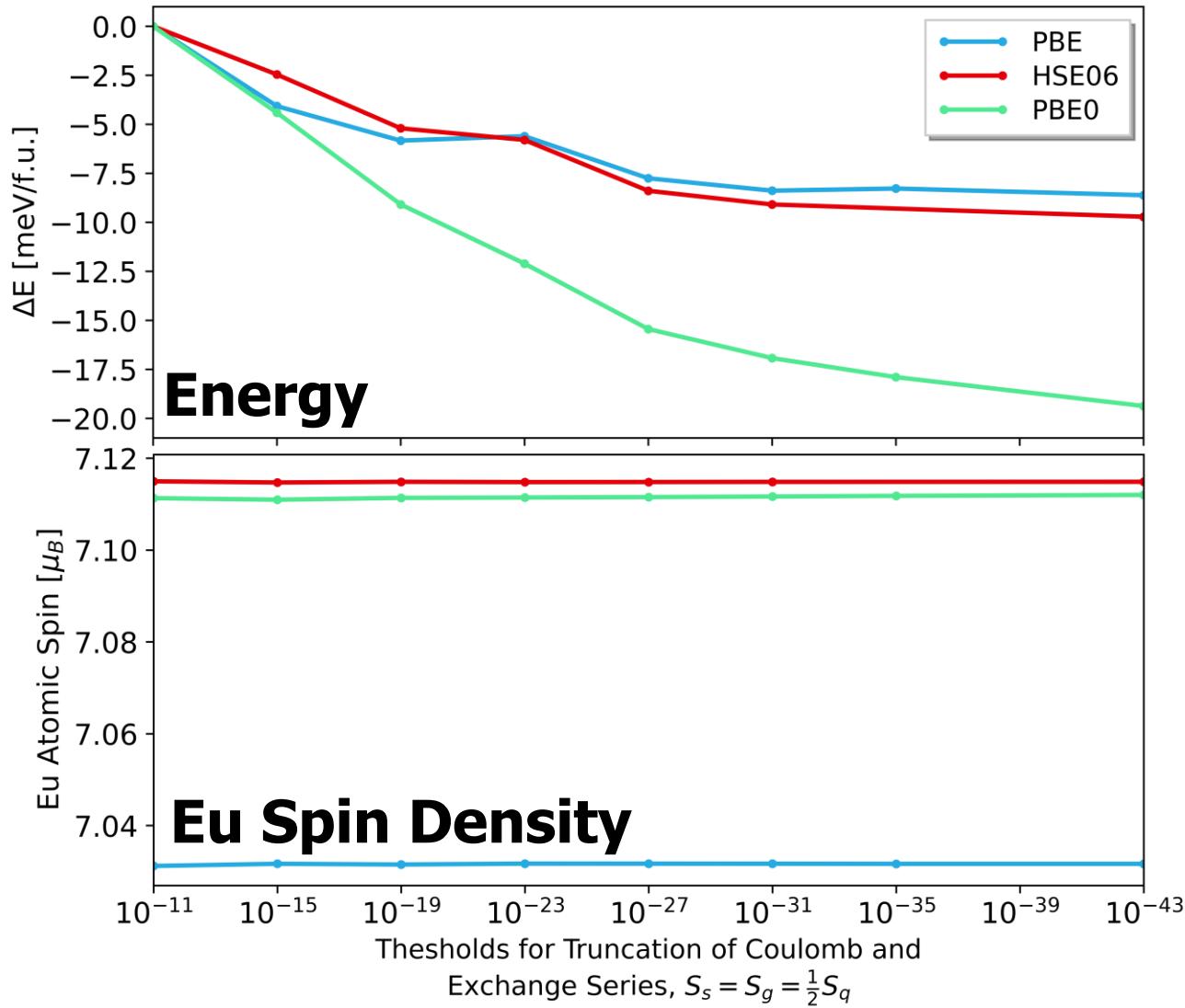
- **7 unpaired electrons** in 4f orbital on each Eu
→ Highly localized electrons
- **Metallic behaviour**
→ Highly delocalized electrons
- **High density** due to pressure
- **Heavy Atoms**
→ High number of integrals



EuO: Electronic Structure

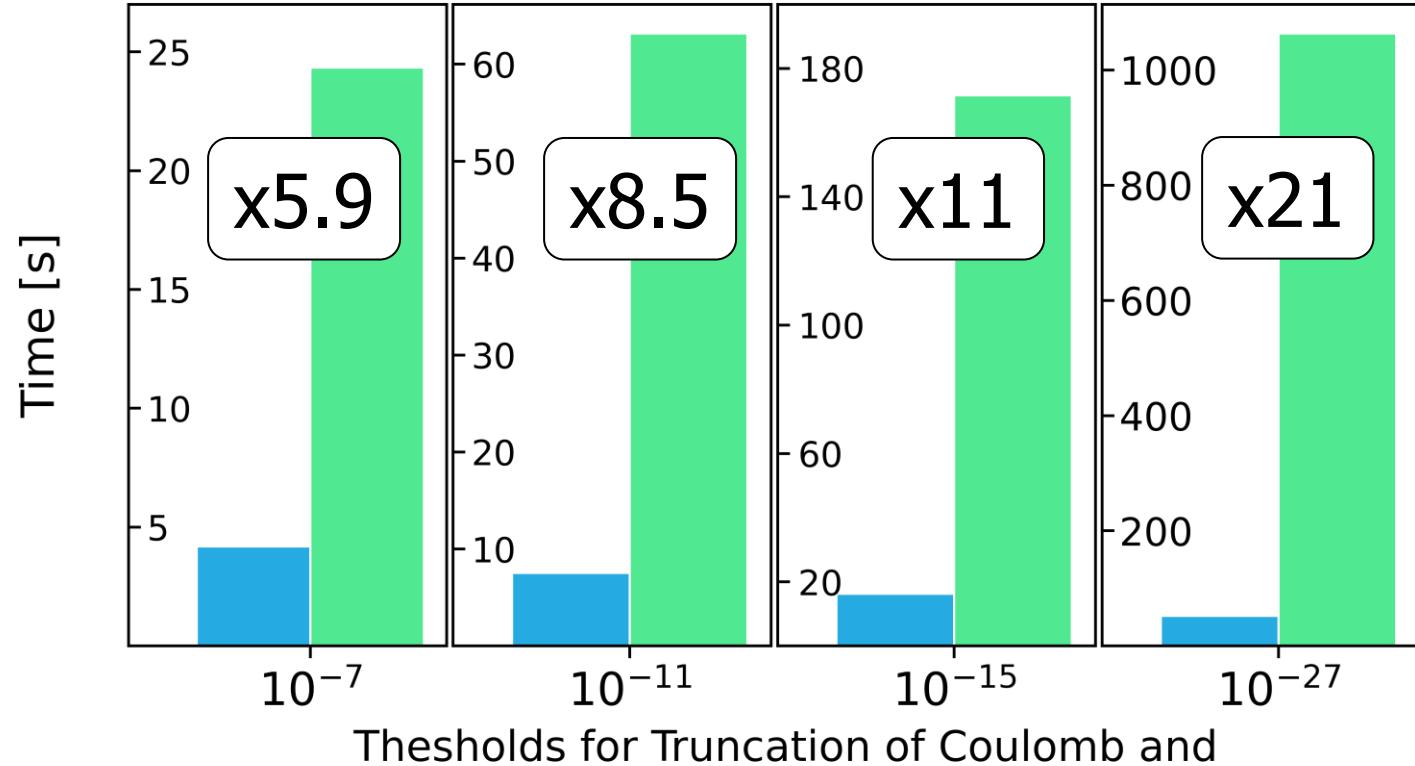


EuO: Electronic Structure

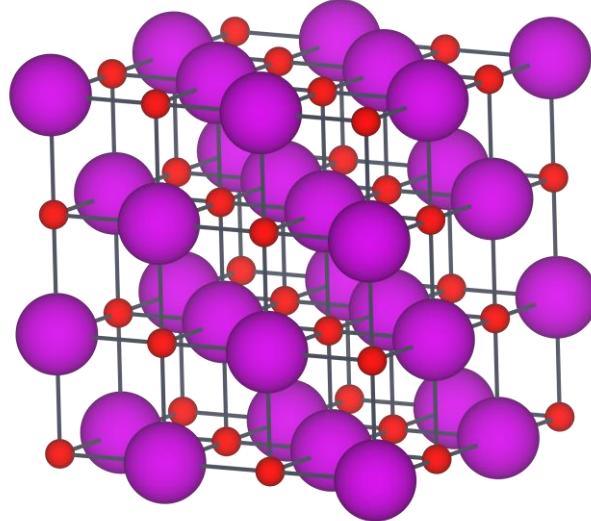


EuO: Timings

Full SCF iteration (avg)

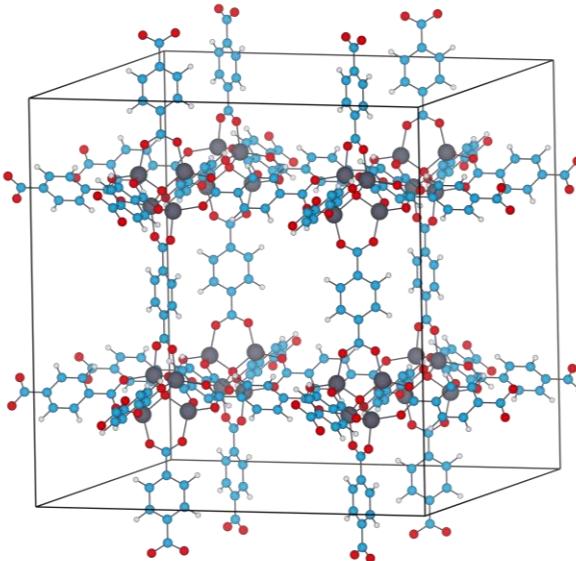


PBE PBE 15%



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

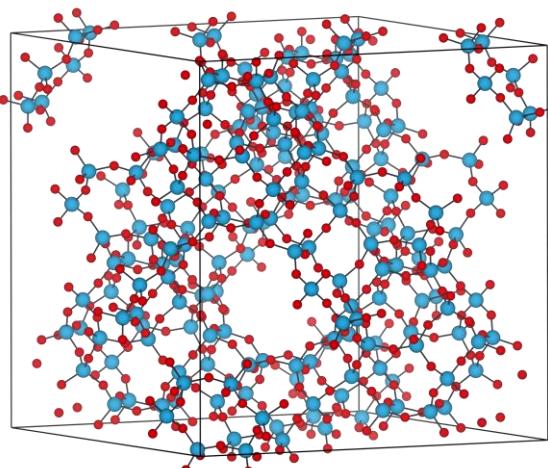


MOF-5

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

Exploitation of Symmetry



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

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**