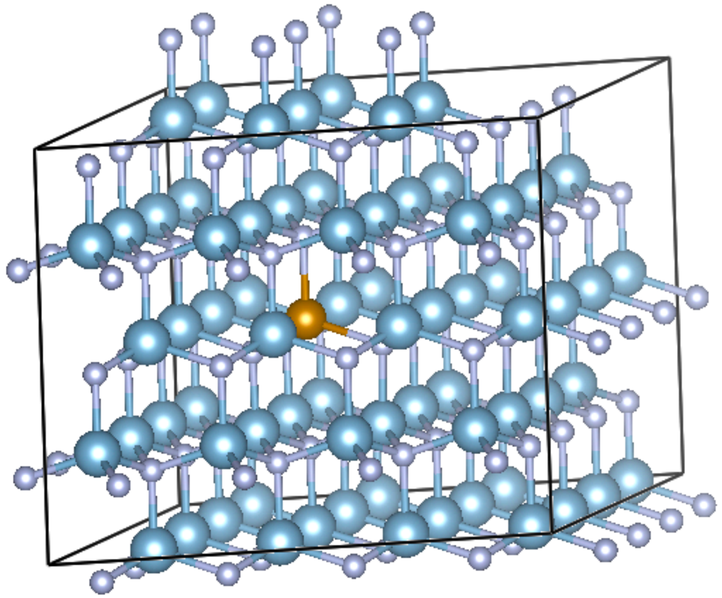
Downfolding interacting models in the constrained random phase approximation (cRPA)

Step-by-step demonstration with an Fe impurity in AlN using the VASP code



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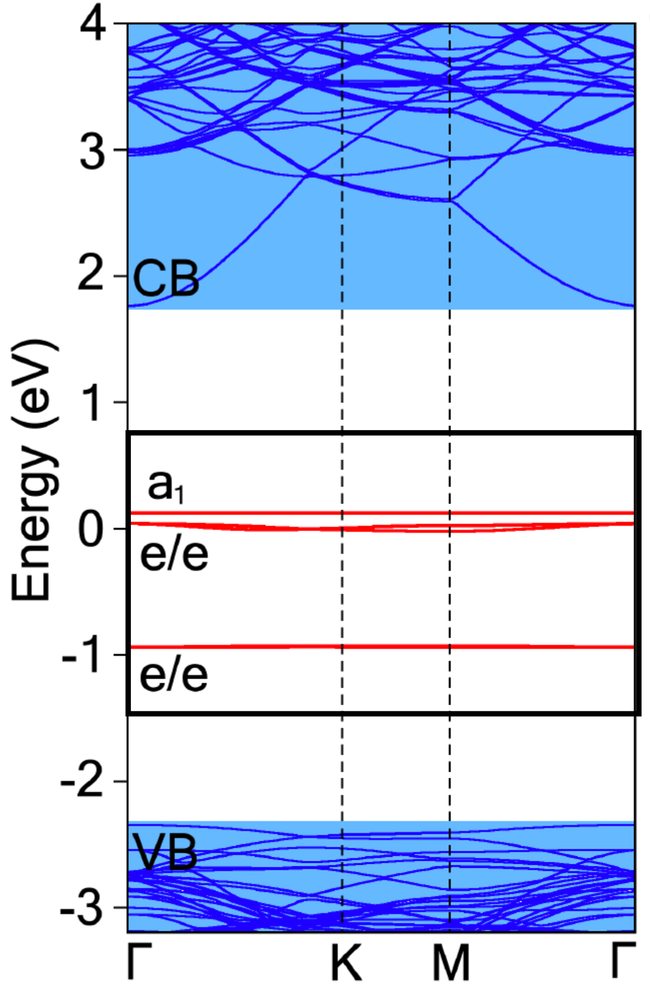
Downfolding School May 12, 2022

Applying the downfolding procedure for *Fe*-in-*AlN*

Despite the large system size, a beyond-DFT treatment should only be needed for the 3*d*-subspace



Rotation of $\hat{H}_{band}$ in the 3*d*-subspace

Coulomb interaction with static cRPA screening

Double counting correction

$$\hat{H}_{eff} = E_0 + \sum_{ij,\sigma} t_{ij,\sigma} \hat{c}^{\dagger}_{i,\sigma} \hat{c}_{j,\sigma} + \sum_{ijkl,\sigma\sigma'} U_{ijkl,\sigma\sigma'} \hat{c}^{\dagger}_{i,\sigma} \hat{c}^{\dagger}_{j,\sigma} \hat{c}_{k,\sigma'} \hat{c}_{l,\sigma'} - \hat{H}_{DC} + hc$$

$\hat{H}_{DC}$ removes DFT-treated interactions in the 3*d*-subspace

L. Muechler, et. al., arXiv:2105.08705 (2022).

Steps and approximations in the DFT+cRPA procedure

1. Compute the Kohn-Sham band structure

2. Determine the active space and $\hat{H}_{1-body}$

- Truncate the Hilbert space being described
- Take $\hat{H}_{band}$ as the non-interacting starting point

3. Determine the bare and screened interaction in the active space

- Calculate the screening to linear order in perturbation theory
- Truncate the sum for the bulk dielectric screening ϵ_{bulk}
- Take the static screening limit

4. Correct double counting of interactions in $\hat{H}_{1-body}$

- Approximate the interactions included through $\hat{V}_H$ and $\hat{V}_{xc}$

Step 1: Compute the Kohn-Sham band structure

Perform a spin-unpolarized SCF calculation in VASP set up as below

Parameters

```
SYSTEM = Fe_in_wz_AlN

ENCUT = 500
NBANDS = 300

ISMEAR = 0
SIGMA = 0.01

EDIFF = 1E-06
ALGO = All

NELM = 60
NELMIN = 5
```

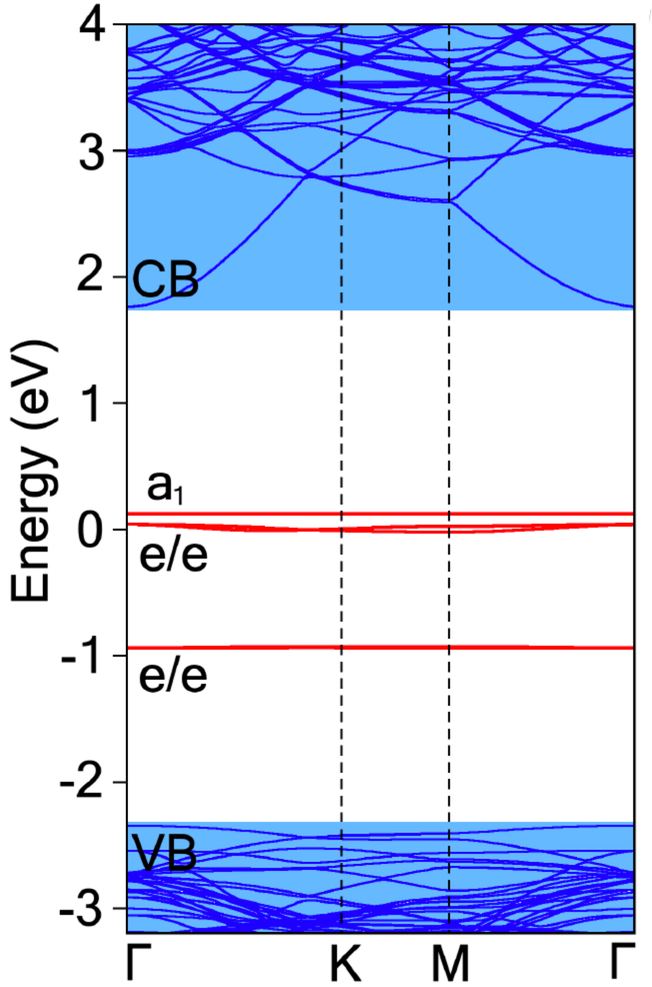
PAW PBE pseudopotentials for {Al, N, Fe}

k-mesh

```
Automatically generated mesh
0
Gamma
1 1 1
0 0 0
```

Plot the Kohn-Sham band structure

After converging SCF, we perform a non-self-consistent calculation along the high-symmetry k-path



This band structure is the <u>starting point</u> for downfolding

Step 2: Determine the active space and $\hat{H}_{1-body}$

I project the active space KS bands onto localized *Fe d*-orbitals with the WANNIER90 code

```
num_wann = 5
num_bands = 300

dis_froz_min = 7.0
dis_froz_max = 9.0

dis_win_min = 2.0
dis_win_max = 9.4

num_iter = 0
write_hr = T

begin projections
Fe:dz2,dxz,dyz,dx2-y2,dxy
end projections
```

→ Number of Wannier functions

→ Total number of KS bands

→ Energy window to reproduce KS spectrum

→ Energy window to disentangle desired bands from undesired ones

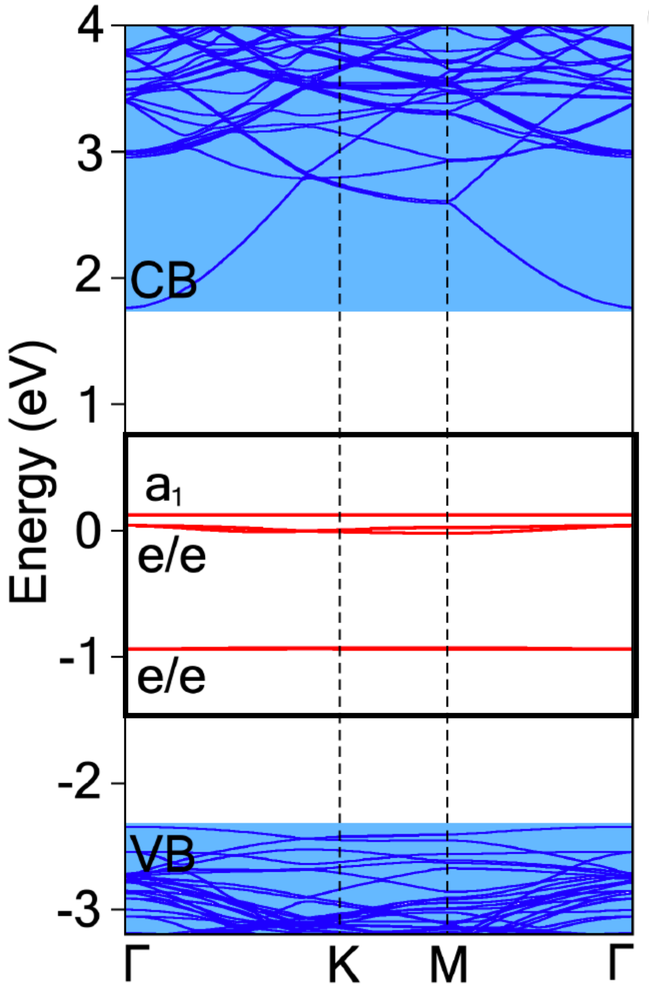
→ Number of localization steps

→ Write $\hat{H}_{1-body}$

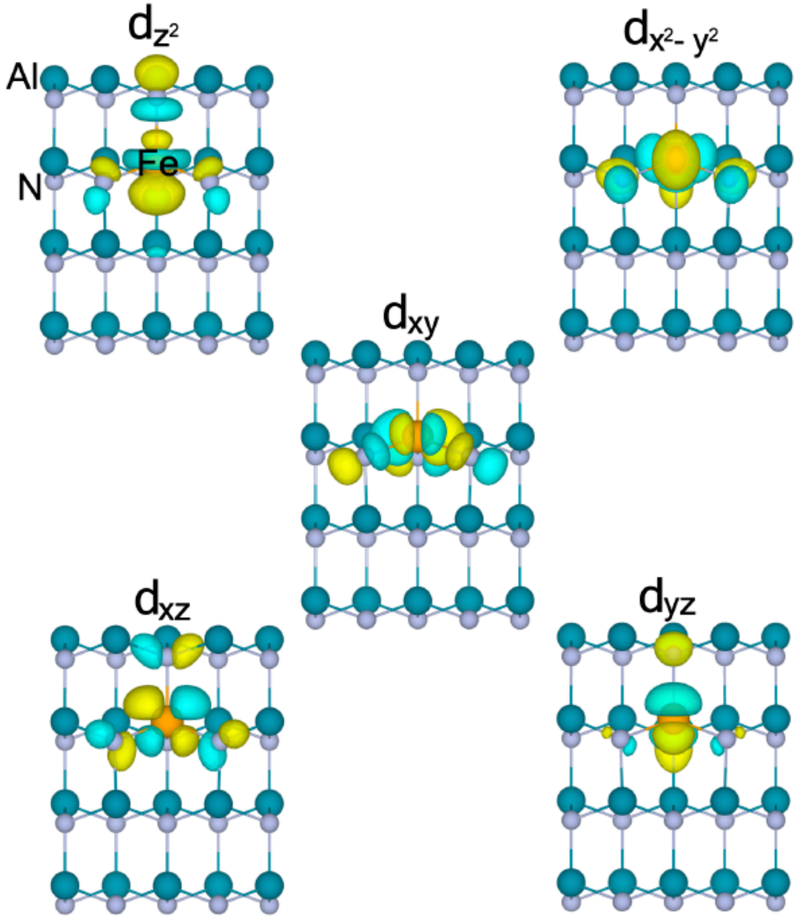
→ Initial AO projections for Wannier functions

Active space and $\hat{H}_{1-body}$

Active space consisting of bands within the box



Real-space orbitals spanning the active space



$$\hat{H}_{eff} = \sum_{ij,\sigma}^{Active} t_{ij,\sigma} \hat{c}^{\dagger}_{i,\sigma} \hat{c}_{j,\sigma}$$

1	1	8.264876
2	1	0.000000
3	1	0.000001
4	1	-0.000001
5	1	-0.000001
1	2	0.000000
2	2	7.690532
3	2	0.000001
4	2	0.000001
5	2	0.322868
1	3	0.000001
2	3	0.000001
3	3	7.690530
4	3	0.322867
5	3	-0.000001
1	4	-0.000001
2	4	0.000001
3	4	0.322867
4	4	8.049096
5	4	-0.000001
1	5	-0.000001
2	5	0.322868
3	5	-0.000001
4	5	-0.000001
5	5	8.049094

At this stage, $\hat{H}_{eff}$ only describes the bands inside the box, not the entire band structure

Step 3: Determine the bare and screened interaction in the active space

I calculate $\langle ij|\hat{V}|kl\rangle$ and $\langle ij|\epsilon_{bulk}^{-1}\hat{V}|kl\rangle$ in the basis of 5 d-orbitals

```
SYSTEM = Fe_in_wz_AlN

ENCUT = 500
NBANDS = 1856

ISMEAR = 0
SIGMA = 0.01
EDIFF = 1E-06

LORBIT = 11

ALGO = CRPA
NTARGET_STATES = 1 2 3 4 5
NUM_WANN = 5

ENCUTGW = 333
ENCUTGWSOFT = 333
```

→ Include many unoccupied bands to converge ϵ_{bulk}

→ Perform a static-limit linear response calculation of ϵ_{bulk}

→ Exclude active space orbitals in ϵ_{bulk}

→ Truncate sum over G-vectors in ϵ_{bulk}

Output the all interaction terms in the 5-orbital basis

$$\hat{H}_{int} = \sum_{ijkl,\sigma\sigma'}^{Active} V_{ijkl,\sigma\sigma'} \hat{c}^{\dagger}_{i,\sigma} \hat{c}^{\dagger}_{j,\sigma} \hat{c}_{k,\sigma'} \hat{c}_{l,\sigma'}$$

```
# V_ijkl = [ij|kl] = < ik|jl>
#  I   J   K   L          RE(V_IJKL)
   1   1   1   1       14.2340625145
   2   1   1   1       -0.0000080131
   3   1   1   1        0.0000055804
   4   1   1   1        0.0000183761
   5   1   1   1       -0.0000231340
   1   2   1   1       -0.0000080131
   2   2   1   1       14.7038058563
```

⋮

$$\hat{H}_{int} = \sum_{ijkl,\sigma\sigma'}^{Active} [\epsilon^{-1}_{bulk} V]_{ijkl,\sigma\sigma'} \hat{c}^{\dagger}_{i,\sigma} \hat{c}^{\dagger}_{j,\sigma} \hat{c}_{k,\sigma'} \hat{c}_{l,\sigma'}$$

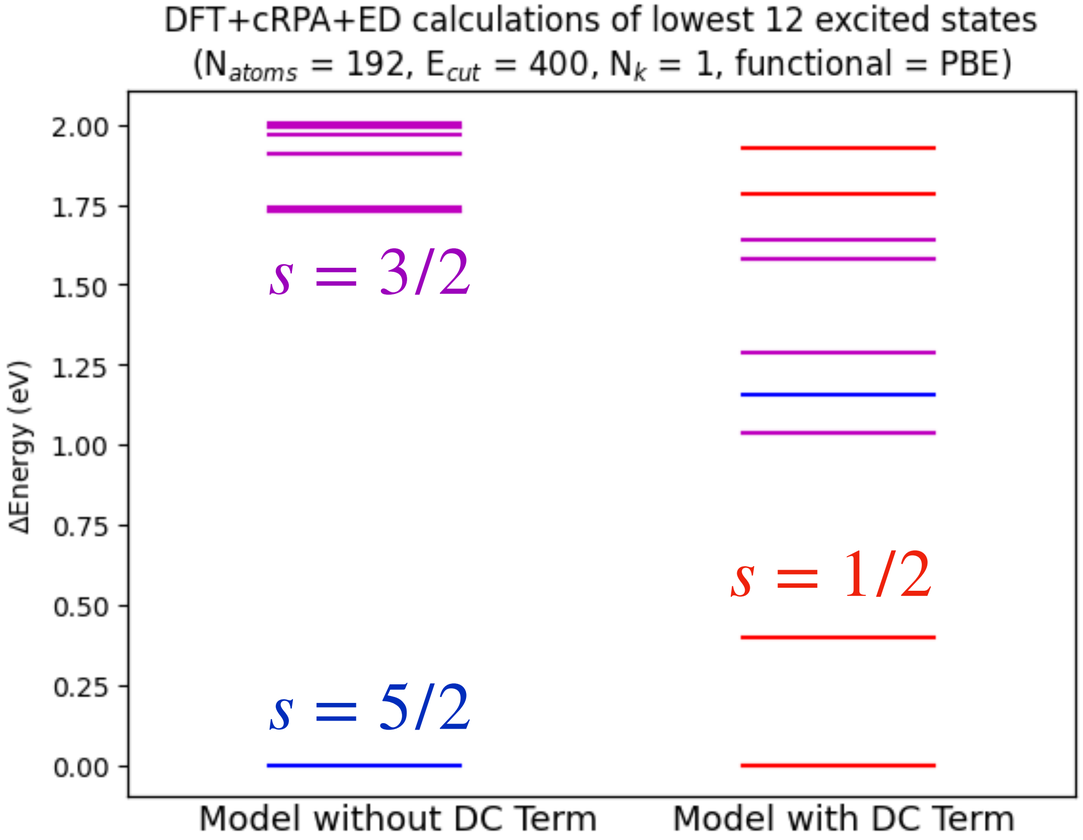
```
# W_ijkl = [ij|kl] = < ik|W(r1,r2)|jl>
# omega =       0.00000     0.00000
#  I   J   K   L          RE(W_IJKL)
   1   1   1   1        2.7929162736
   2   1   1   1       -0.0000037872
   3   1   1   1        0.0000010367
   4   1   1   1        0.0000036175
   5   1   1   1       -0.0000054342
   1   2   1   1       -0.0000037872
   2   2   1   1        2.3049725750
```

⋮

Our active space is small, so bulk screening significantly alters the interaction terms

Step 4: Correct double counting of interactions in $\hat{H}_{1-body}$

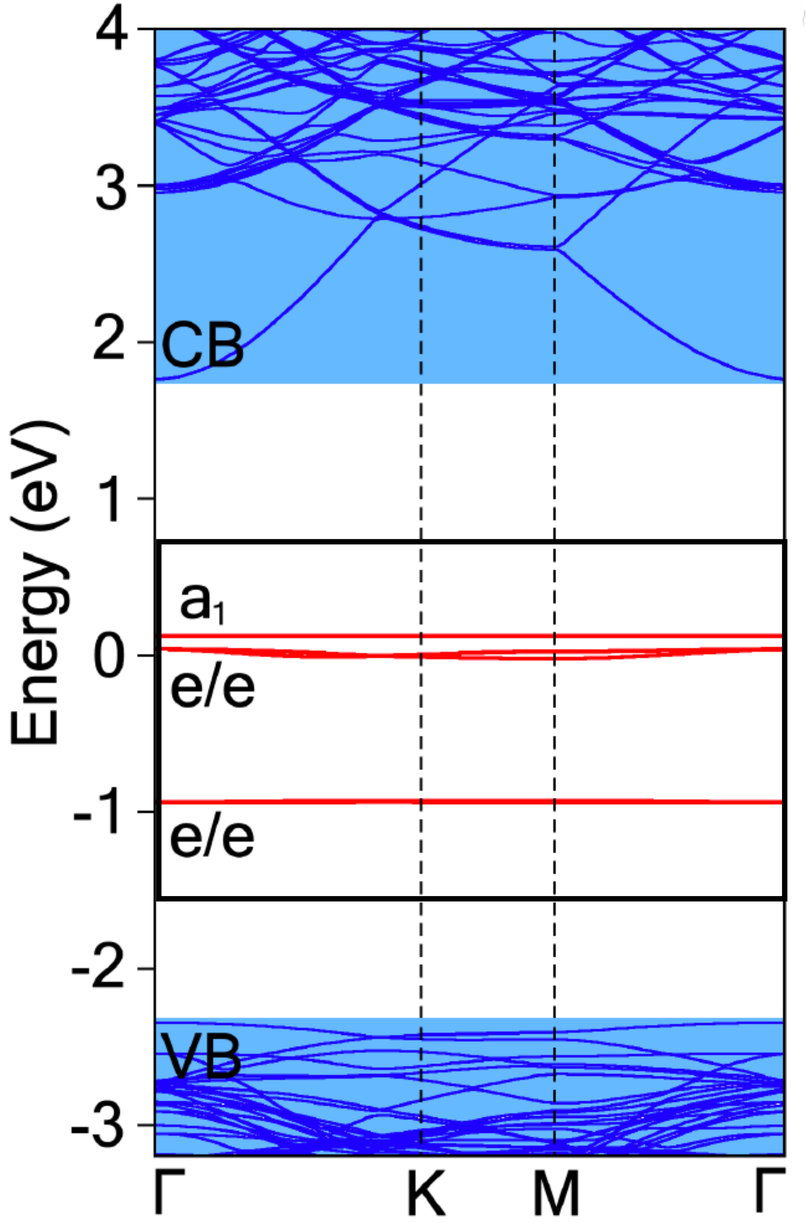
Apply the Hartree double counting correction* $\hat{H}_{DC} = \sum_{ij,\sigma}^{Active} \hat{c}^{\dagger}_{i,\sigma}\hat{c}_{j,\sigma} \sum_{kl,\sigma'} \rho_{kl,\sigma'} U_{iljk,\sigma'\sigma}$ then diagonalize $\hat{H}_{eff}$



Double counting is difficult to control: even the ground state symmetry depends on it

*H. Ma, et. al., J. Chem. Theory Comput. **17** 2116 (2021).

DFT+cRPA downfolding is promising, but far from perfect



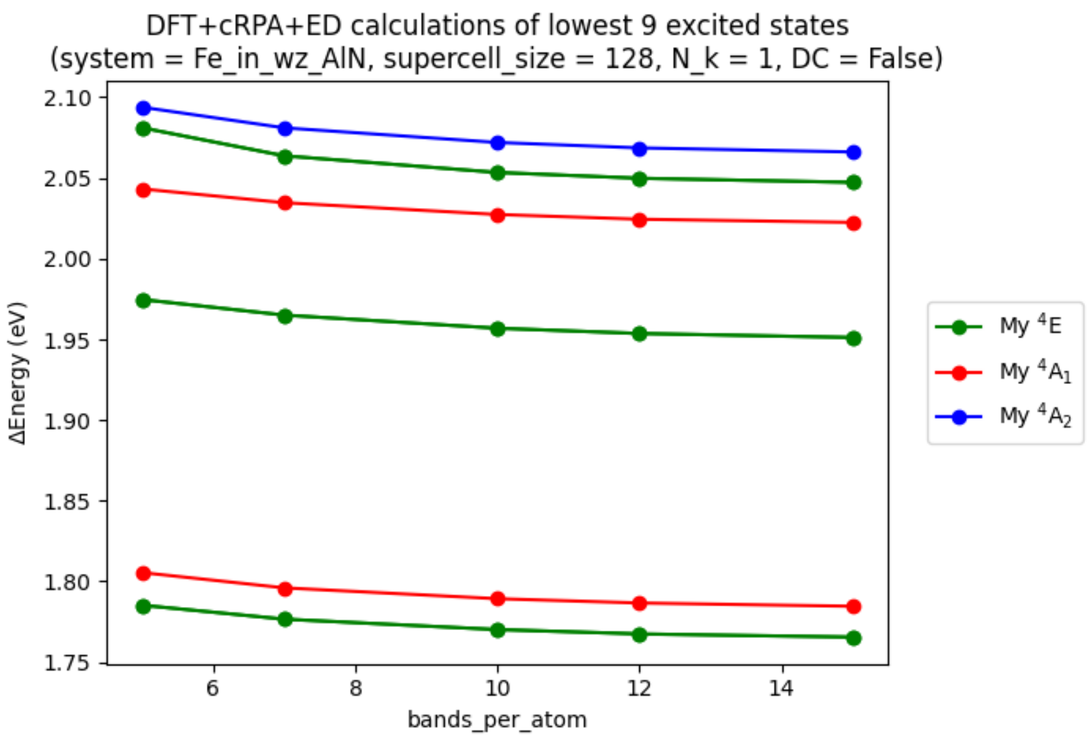
In the process of determining an active space and Hamiltonian

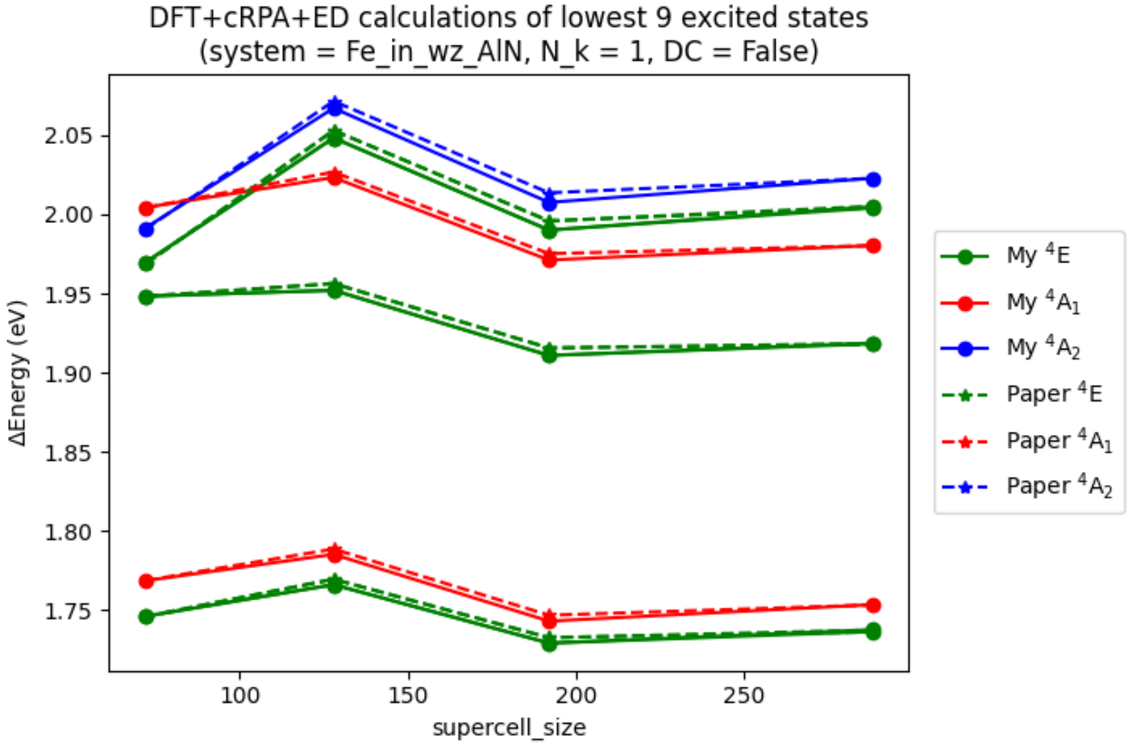
$$\hat{H}_{eff} = \sum_{ij,\sigma}^{Active} t_{ij,\sigma}\hat{c}^{\dagger}_{i,\sigma}\hat{c}_{j,\sigma} + \sum_{ijkl,\sigma\sigma'}^{Active} U_{ijkl,\sigma\sigma'}\hat{c}^{\dagger}_{i,\sigma}\hat{c}^{\dagger}_{j,\sigma}\hat{c}_{k,\sigma'}\hat{c}_{l,\sigma'} - \hat{H}_{DC} + hc,$$

this method makes several approximations affecting the accuracy

- Truncating the Hilbert space
- Taking $\hat{H}_{band}$ as the non-interacting starting point
- Determining $\hat{H}_{int}$ with first order perturbation theory
- Approximating double counting of interactions in $\hat{H}_{1-body}$

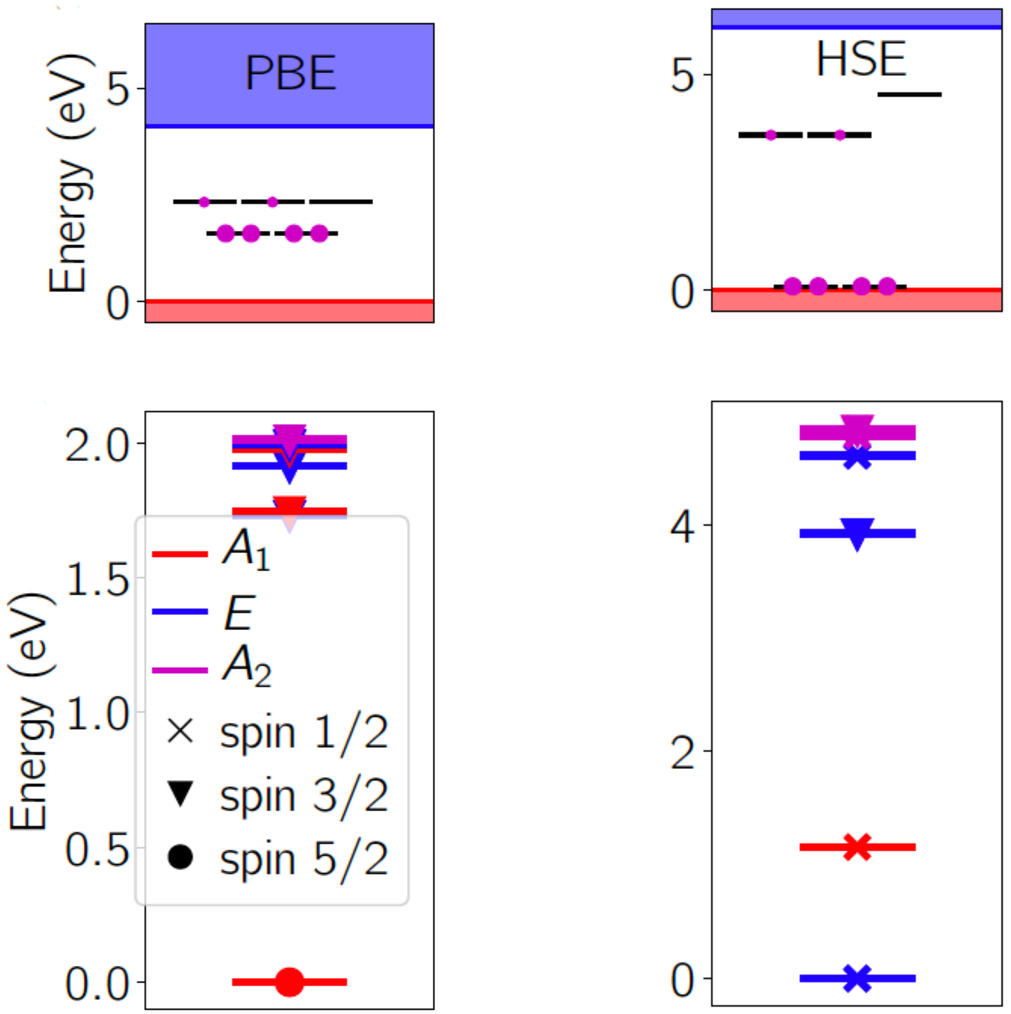
Backup: converging the dielectric screening and system size





We control these two sources of error in the DFT+cRPA method

Backup: different “non-interacting” starting points



Final states depend on the choice of functional, an uncontrolled approximation

L. Muechler, et. al., arXiv:2105.08705 (2022).