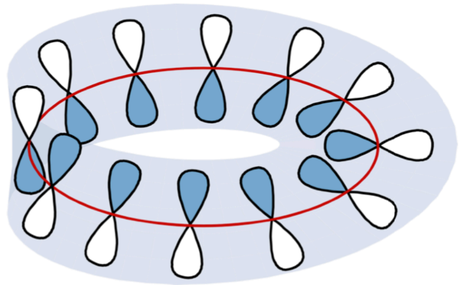
# Quantum embedding methods for correlated excited states of point defects

## Case studies and challenges

**Lukas Muechler**

**April 13th 2022**

PennState
Eberly College of Science



# The Muechler Lab

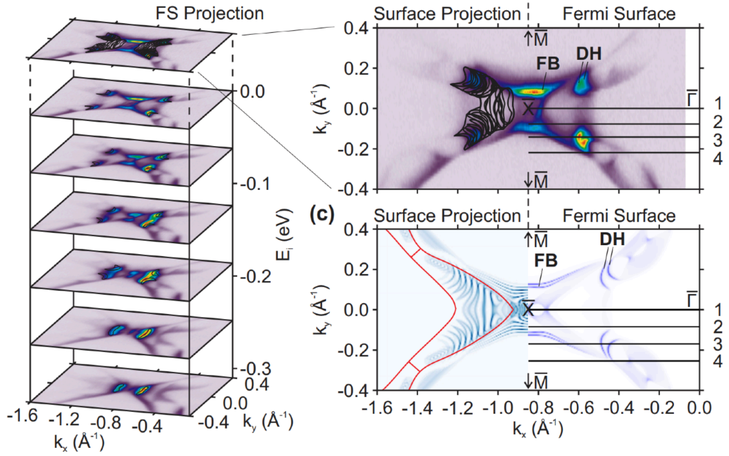
- www.muechlerlab.com


PennState Eberly College of Science

FLATIRON INSTITUTE
Center for Computational Quantum Physics

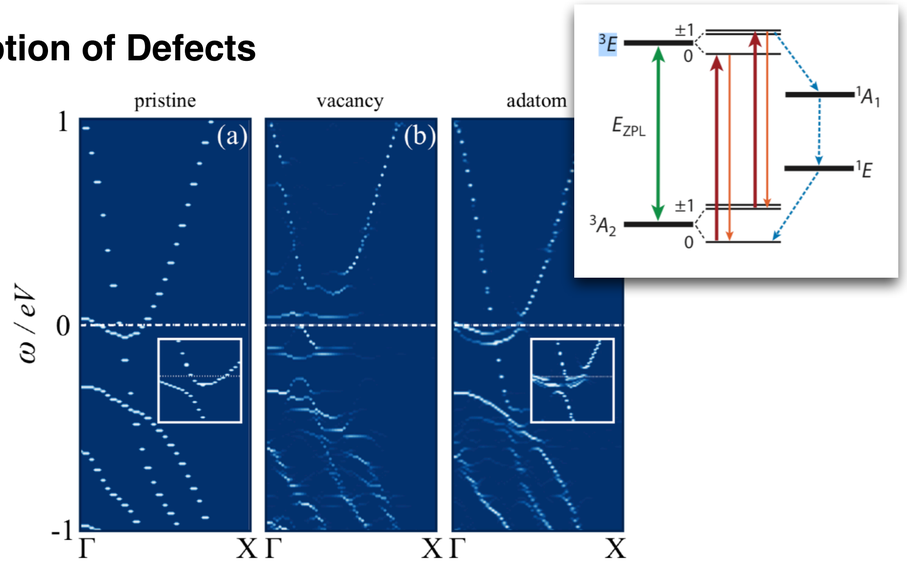
# Research Interests

## Topology in Real Materials



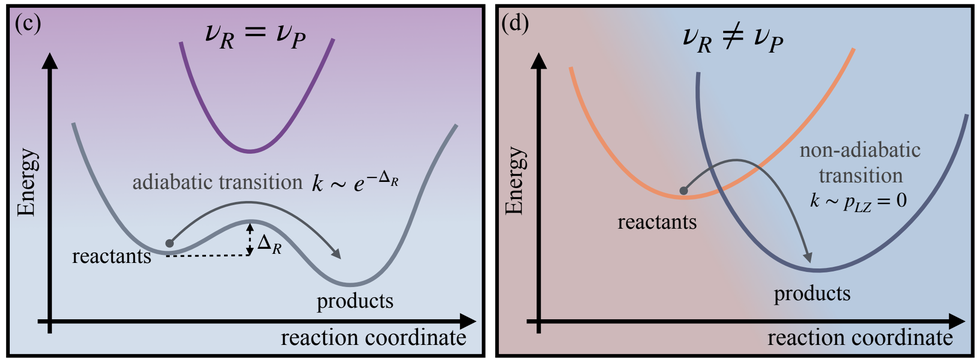

L Muechler, et. al.
PRX 10, 011026
(2020)

## *ab-initio* Description of Defects

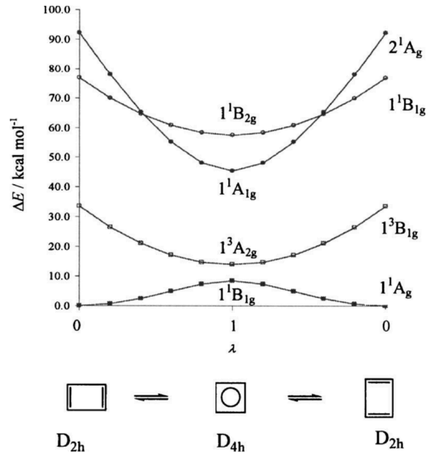


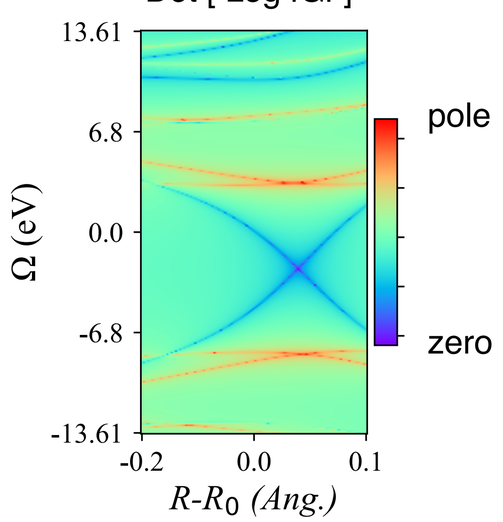

arXiv:2105.08705

## Topology and Strong Correlations in Molecules




L Muechler PRB 101 (4), 045123 (2020)



# Acknowledgements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CCQ

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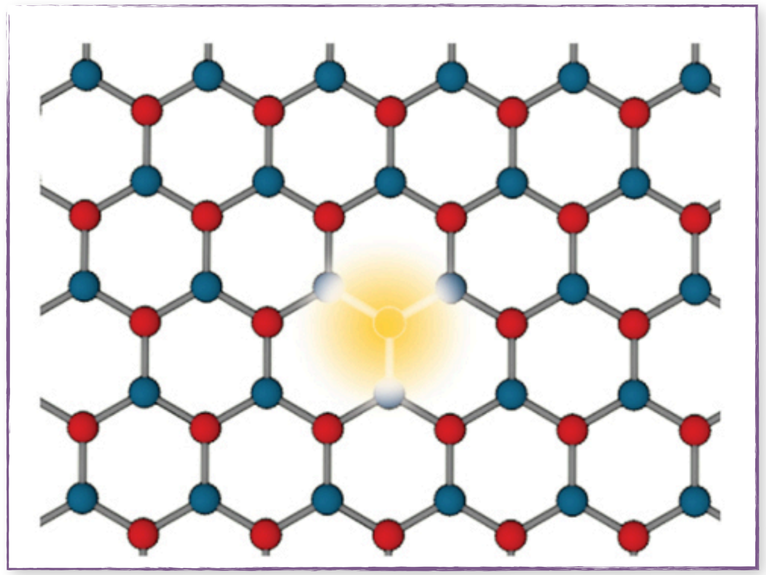
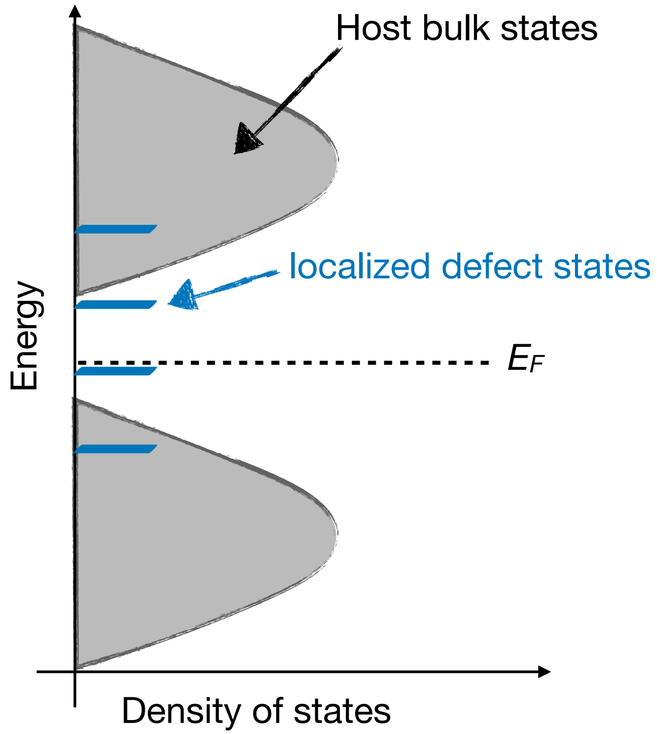
Radboud University

# Point Defects as Quantum Embedding Problems



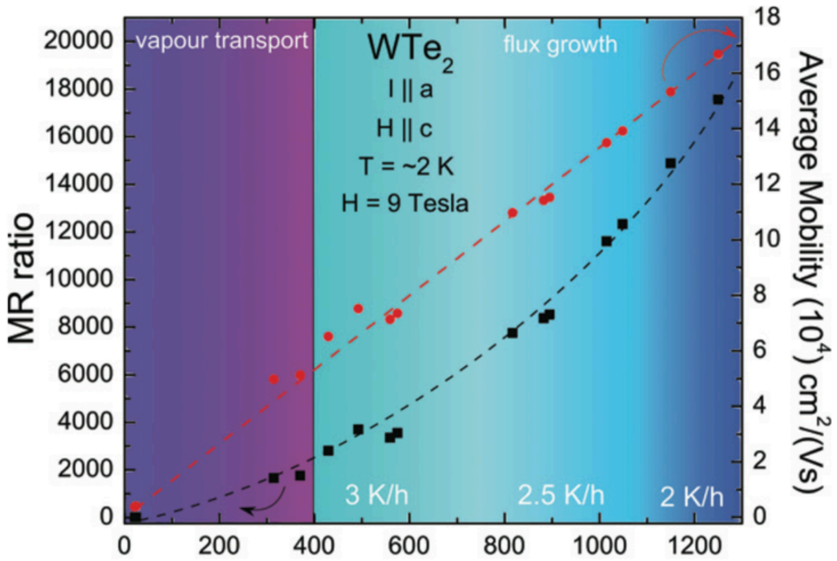
Aharonovich, I., Toth, M. *Science*, ***358*** 170-171 (2017)

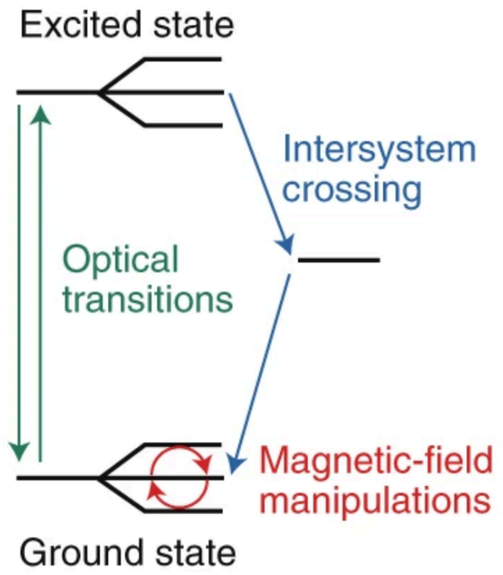



$$H = H_{host} + H_{defect} + H_{h-d}$$

# Defects make the material

- How will the defect affect material properties?
- How can we predict and identify defects and their properties?
- How will the material affect the defect?



# Defects as quantum materials

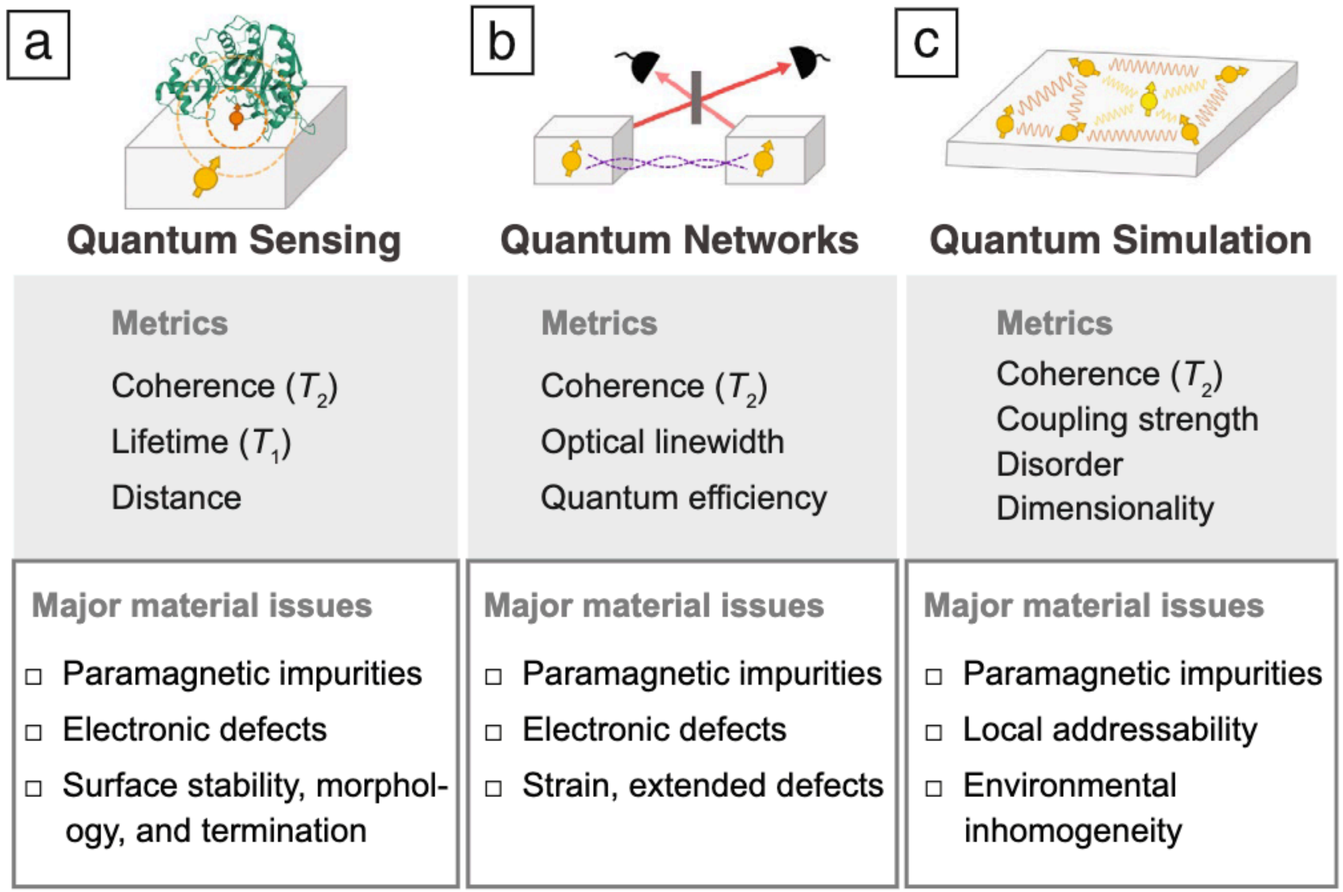
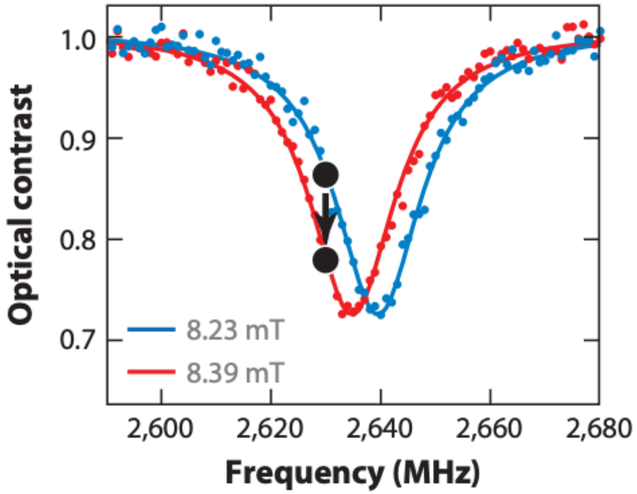


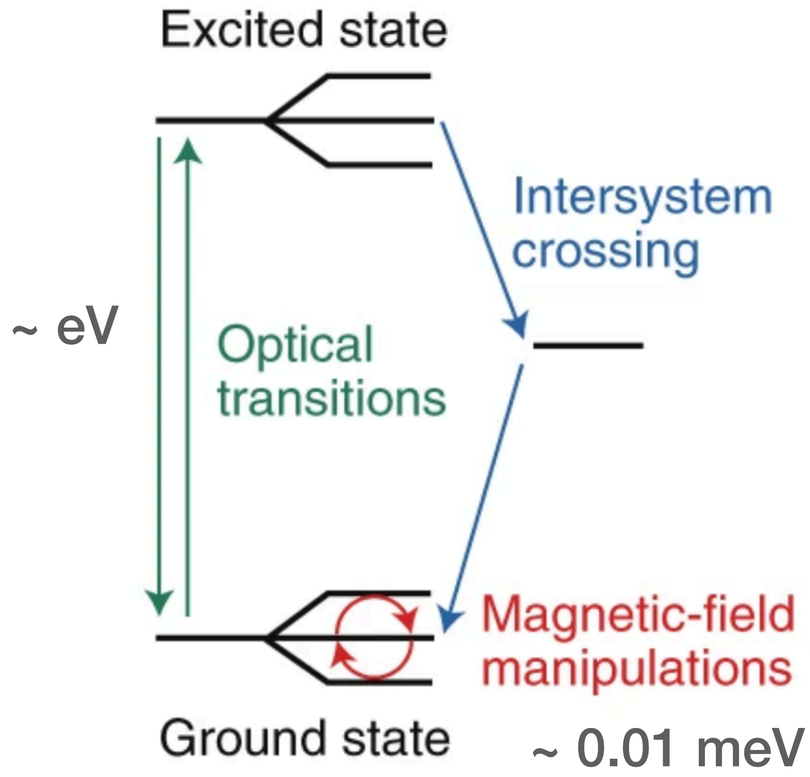

**Figure 2.** Cartoon illustrations and summaries of key metrics and corresponding material issues for quantum applications of diamond color centers.




R. Schirhagl, et al., ARPC., **65**, 83 (2014)

## Excited state description of defects is essential

- Accurate description of optical, structural and dynamical properties of these defects is detrimental
- Proper modeling of excited states is particularly important
- Combination of very different energy scales ( defect, bath interaction, defect-defect)
- Often lack of experimental characterization (charge, chemical composition)



# Defects as quantum materials

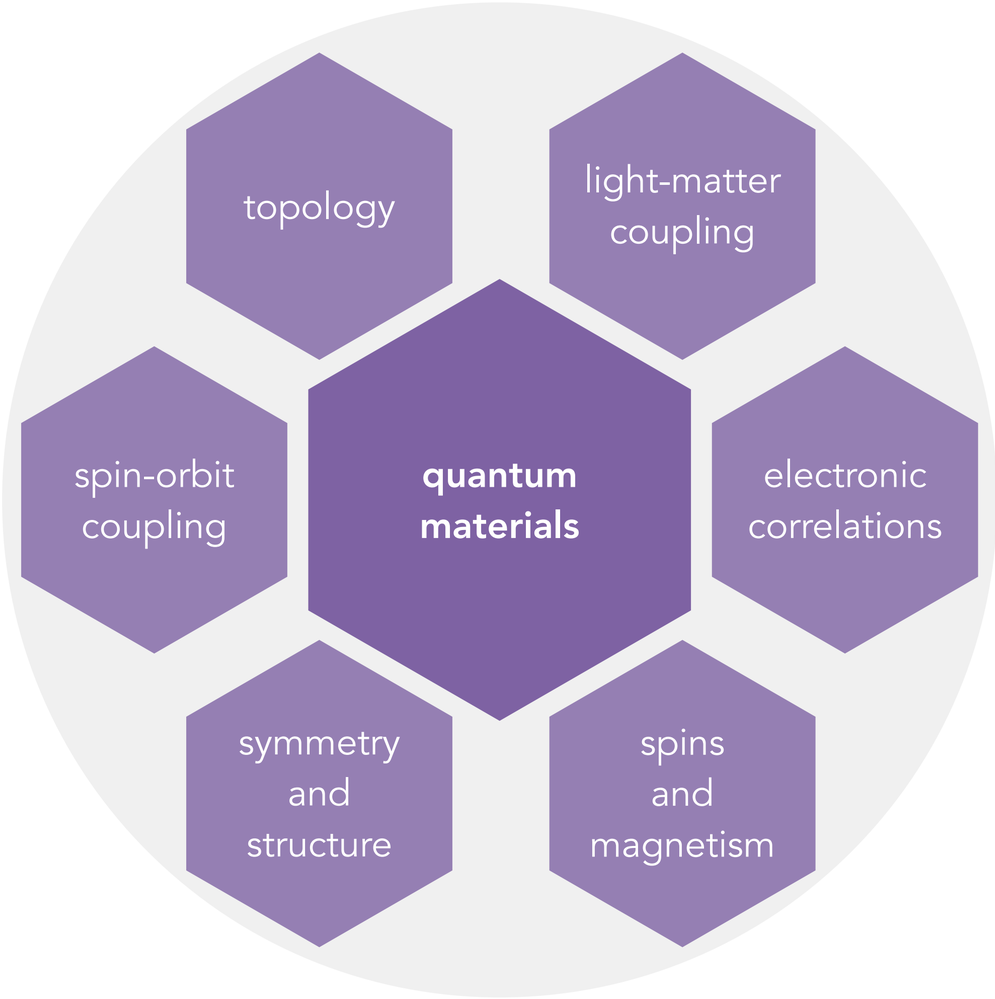
- Understanding and manipulating the electronic structure of point defects has become a focal point in the field of quantum materials

- Complicated interplay of many different quantum effects

  applications in quantum sensing, quantum computing, quantum communication

**Today**

*An overview over the challenges of modeling localized point defects in host materials and a possible route to overcome them through embedding approaches (arXiv:2105.08705)*



## Excited states require multi-reference methods

- Single particle Kramers partners

$$|n\rangle \text{ and } \mathcal{T}|n\rangle \equiv |\tilde{n}\rangle$$

- Spatial symmetry

$$\mathcal{R}^N = 1 \quad \mathcal{R}|n\rangle = \lambda_n |n\rangle$$
$$\lambda_n = e^{i2\pi\ell_n/N}, \quad \ell_n = 1, \ldots, N$$

- Eigenvalues of Kramers partners

$$\mathcal{R}|\tilde{n}\rangle = \mathcal{R}\mathcal{T}|n\rangle = \mathcal{T}\mathcal{R}|n\rangle$$
$$= \mathcal{T}\lambda_n |n\rangle = \lambda_n^* \mathcal{T}|n\rangle = \lambda_n^* |\tilde{n}\rangle$$

- Product state (Band insulator)

$$|\mathrm{BI}\rangle = \prod_{n,\tilde{n}\in\mathrm{occ}} c_n^\dagger c_{\tilde{n}}^\dagger |0\rangle$$

$$\mathcal{R}|\mathrm{BI}\rangle = \prod_{n,\tilde{n}\in\mathrm{occ}} \lambda_n \lambda_{\tilde{n}} |\mathrm{BI}\rangle = |\mathrm{BI}\rangle$$

A product state transforms trivially under point group transformations

If a state transforms non-trivially and is a singlet it *must* be *multi-reference (basis independant)*

$$\Lambda_{\mathrm{MR}} = \mathrm{Tr}(\boldsymbol{\rho} - \boldsymbol{\rho}^2)$$

## Embedding theories combine accuracy with low-cost

- **DFT and post DFT**

  scalable, but unable to describe strongly correlated states

- **finite sized clusters + quantum chemical methods**

  expensive and hard to converge finite size effects.

- **embedding (downfolding) approaches**

  treat small subsystem with highly accurate method and treat interaction with rest in terms of a lower level method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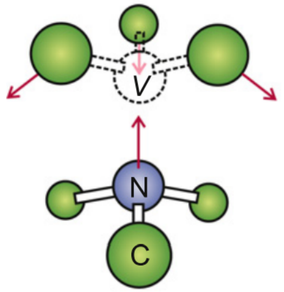
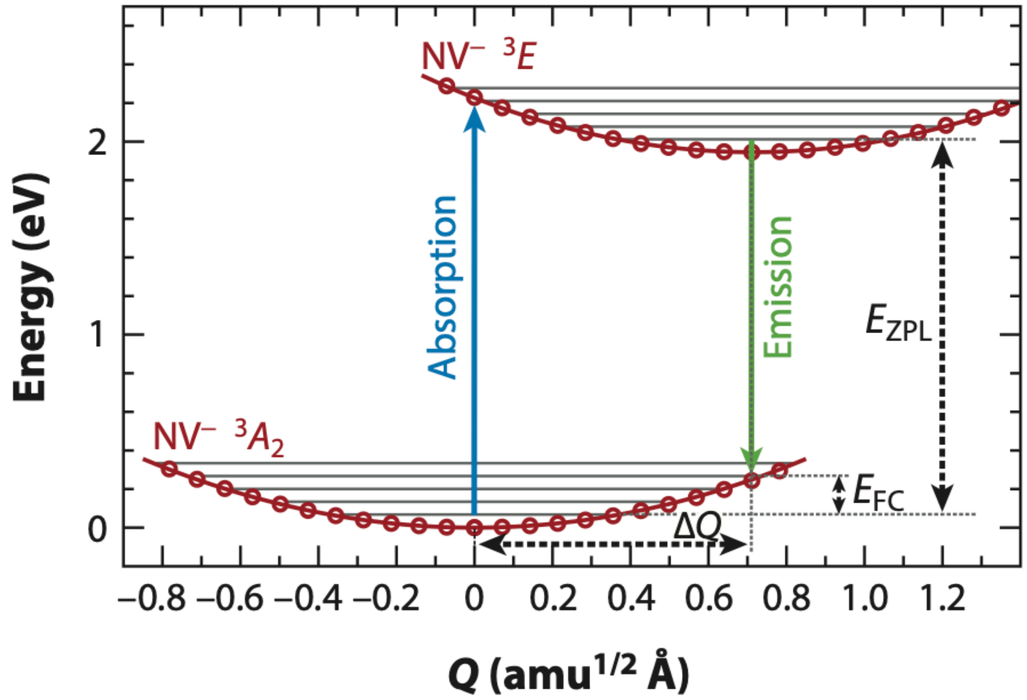
# NV- as a Benchmark

- extremely well characterized experimentally
  - zero-phonon line at 1.945 eV
  - $C_{3v}$ symmetry









## Wannierization and c-RPA

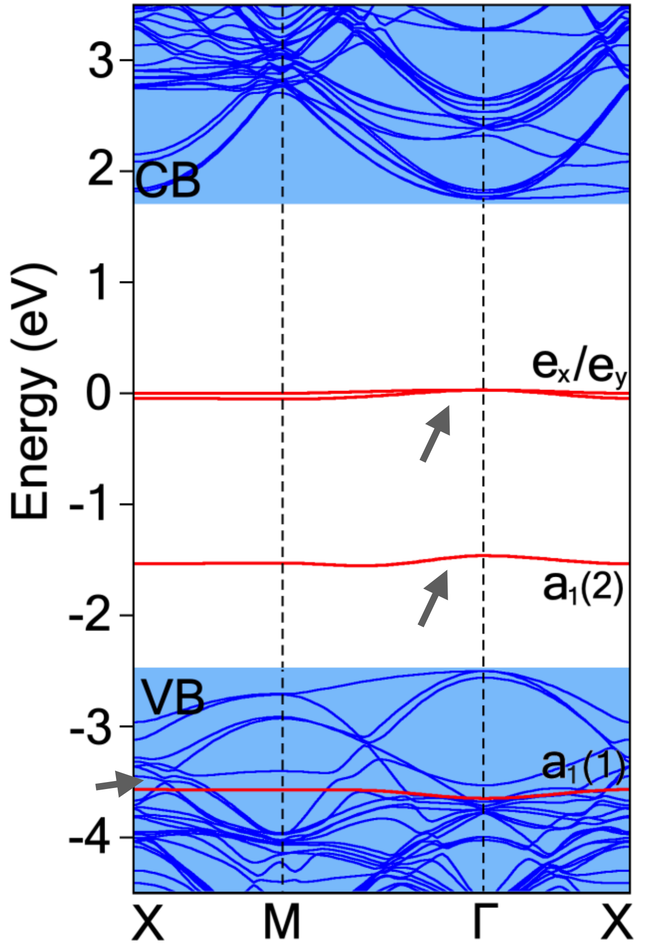
- DFT calculation of supercell with defect

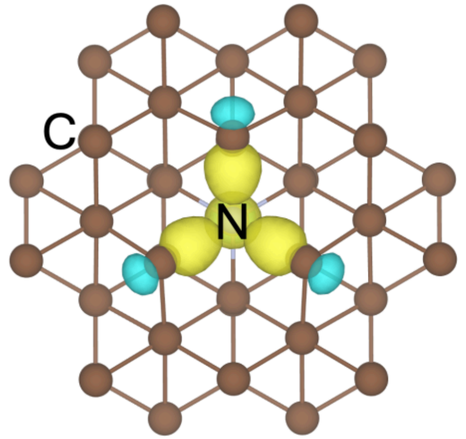
  geometry relaxation and selection of active space

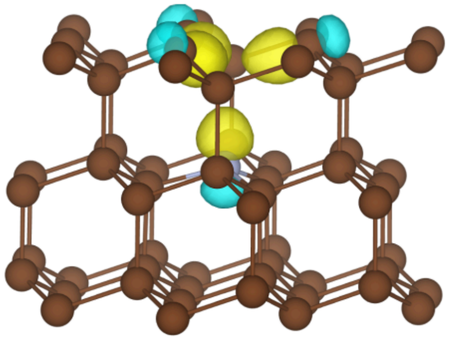
- Wannierzation of active space states and single particle hamiltonian (restricted DFT)

  yields localized, molecular like orbitals around defect and single particle hamiltonian

  incorporates effects of host material



## Wannierization and c-RPA

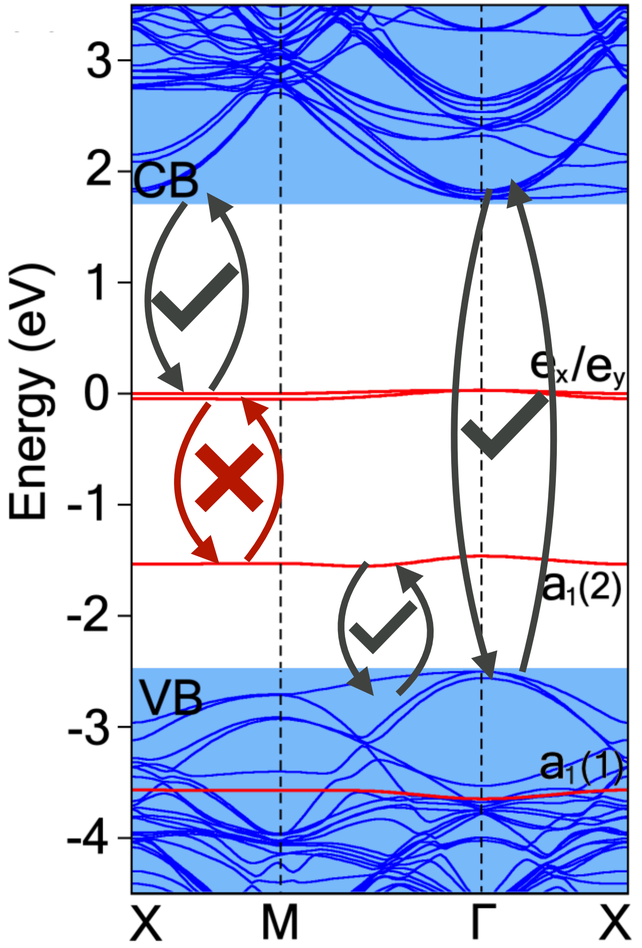
- Define correlated subspace problem

$$H = -\sum_{ij,\sigma}(t_{ij}c^{\dagger}_{i\sigma}c_{j\sigma} + \text{H.c.}) + \frac{1}{2}\sum_{ijkl,\sigma\sigma'} U_{ijkl}c^{\dagger}_{i\sigma}c^{\dagger}_{j\sigma'}c_{l\sigma'}c_{k\sigma} - H_{\text{DC}} - \mu\sum_{i,\sigma} c^{\dagger}_{i\sigma}c_{i\sigma},$$

- Calculate screened coulomb matrix elements with c-RPA

$$\hat{U} = \left[1 - \hat{v}\,\hat{\Pi}_{\text{cRPA}}(\omega = 0)\right]^{-1}\hat{v}$$

$$\hat{\Pi}_{\text{cRPA}} = \hat{\Pi}_{\text{full}} - \hat{\Pi}_{\text{defect}},$$



## Benchmarking Assumptions and Challenges of method

- **dependence on DFT functional**

  quality of single-particle hamiltonian and active space

- **Choice of local orbitals and disentanglement**

  Wannier functions and cRPA

- **Double counting**

  Subtract correlation effects included in DFT

- **localized nature and interaction with host**

  size of active space, screening

*Requires careful benchmarking and comparison to experiments*

# Difference to quantum chemical approaches

- **Hilbert space of active orbitals is small**

  Allows to build simplified models and interpret results

- **Environment is taken into account through c-RPA**

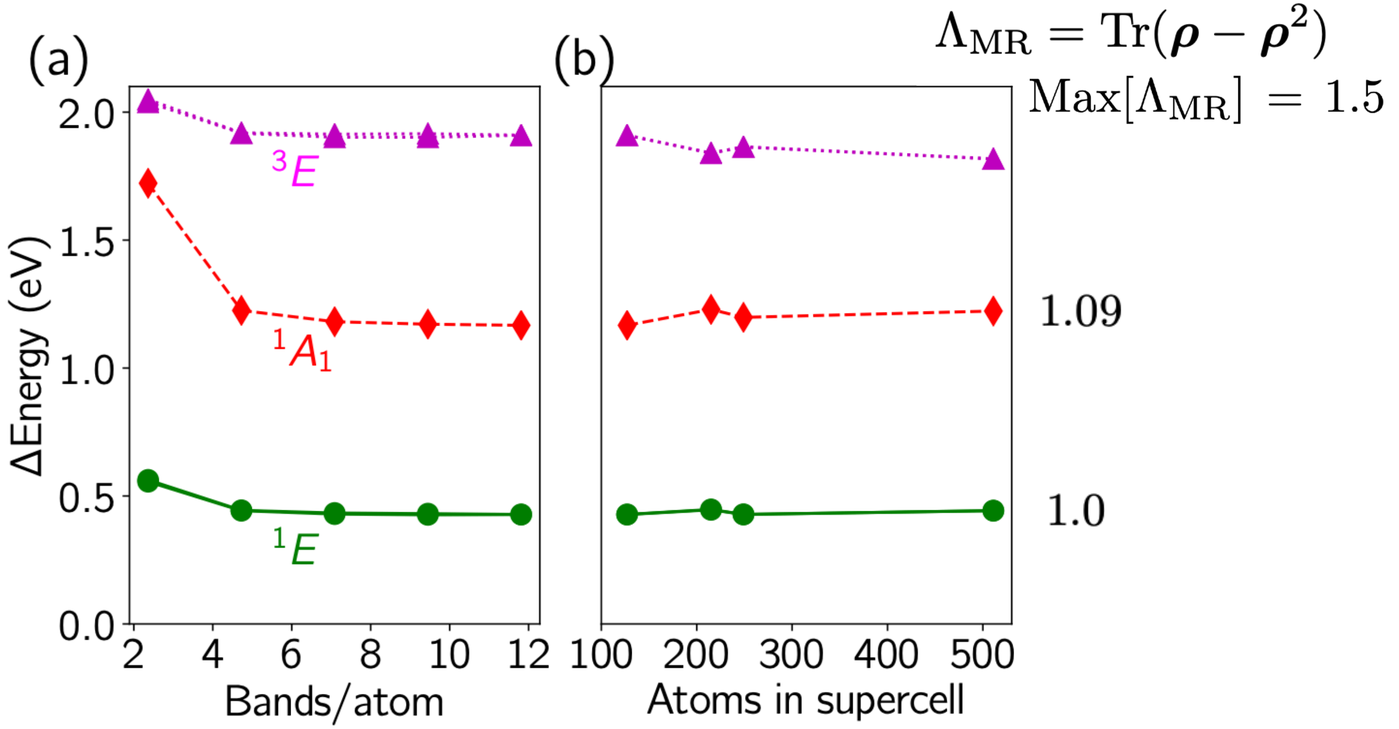
  Bottleneck of the method

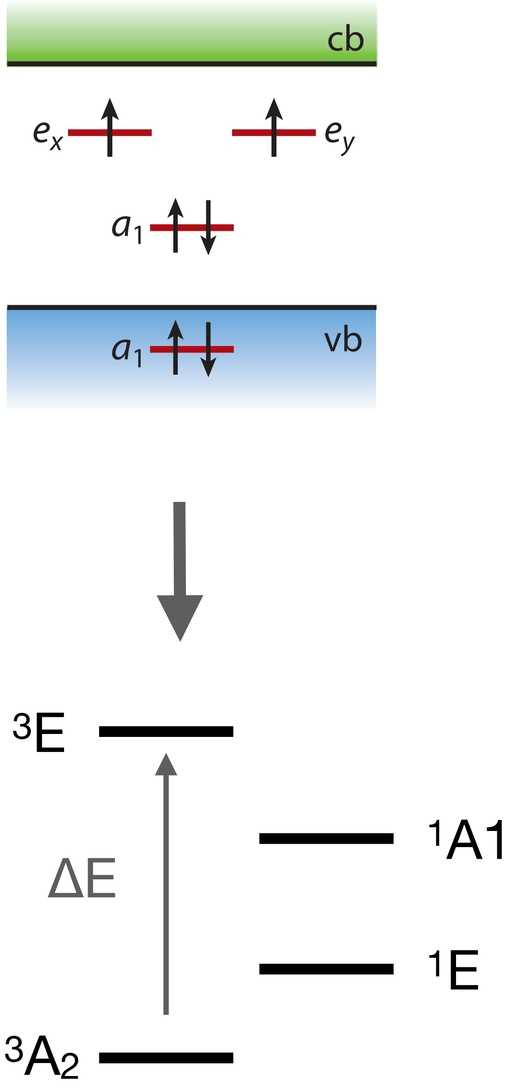
- **Qualitatively correct starting point (DFT vs HF)**

  make use of existing DFT methodology for defects

# NV- Level ordering

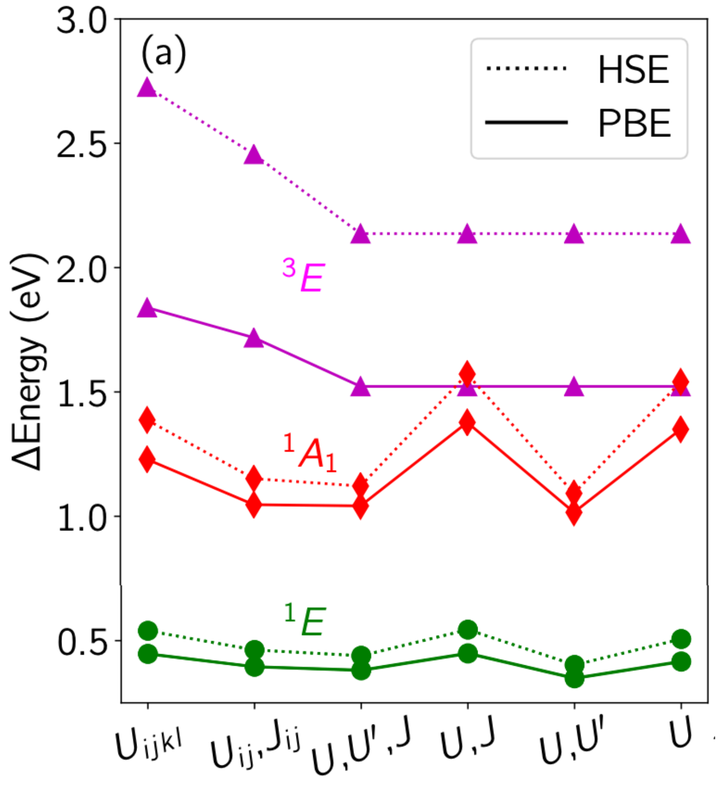
- Careful convergence of supercell size and unoccupied states (no DC)

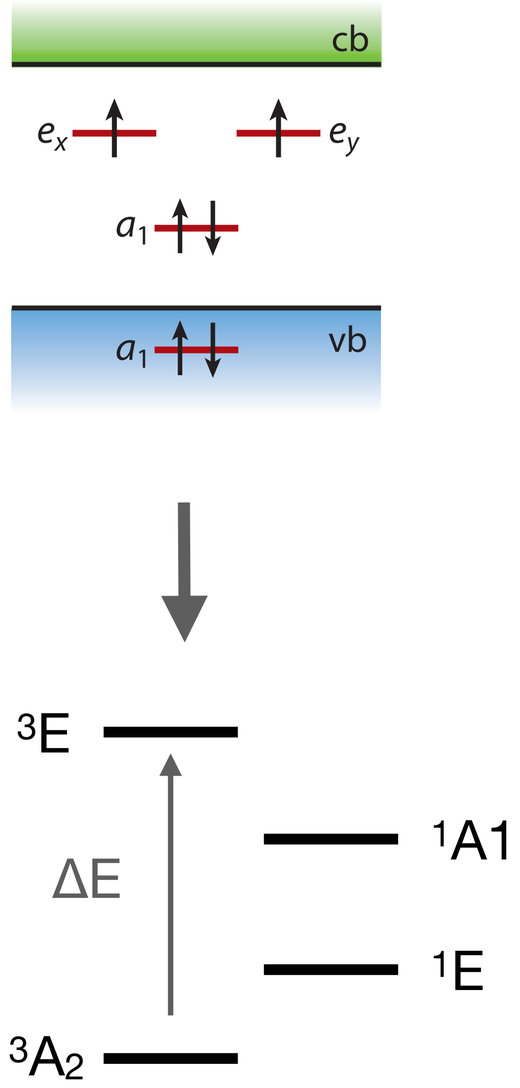


# NV- Level ordering

- Strong dependence on DFT functional and matrix elements (model building)



## Double Counting strongly influences excited states

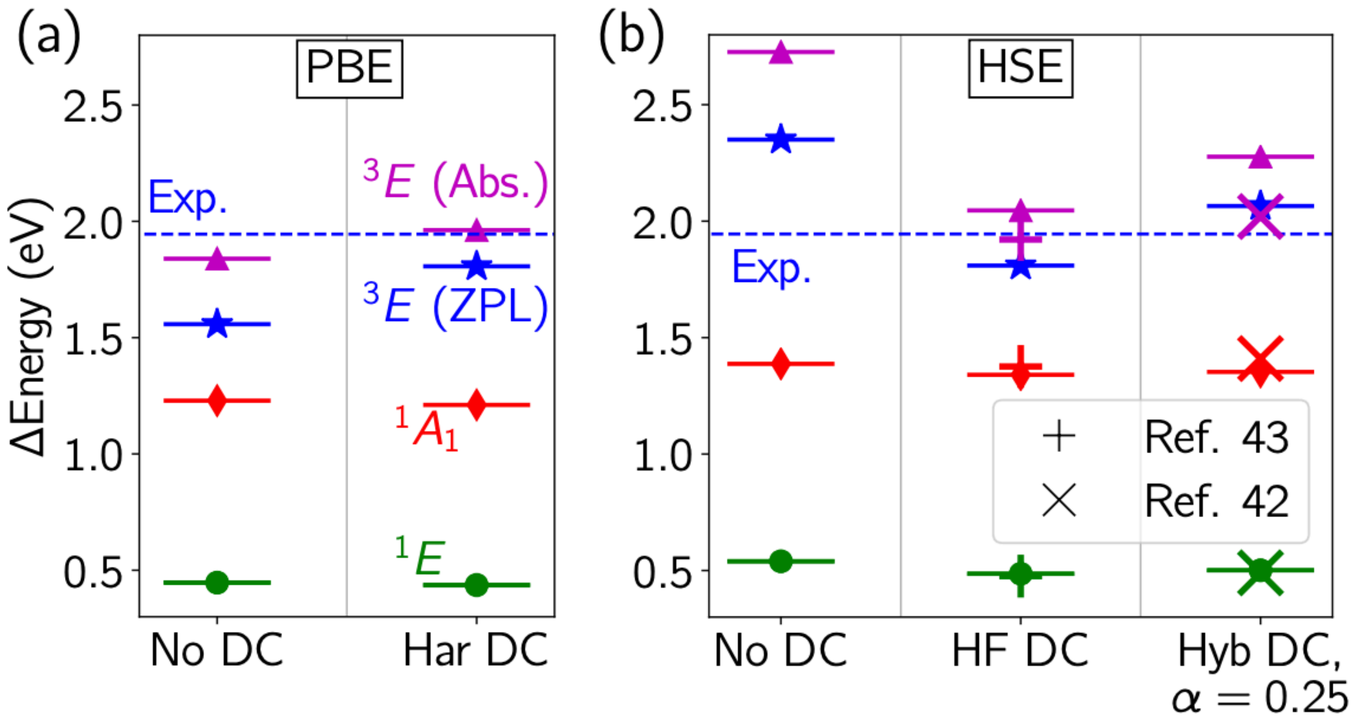
- Double counting corrections for HSE significantly affect excited state triplet (orbitally dependent)

Hartree double counting

$$H_{\mathrm{DC}}^{\mathrm{Har}} = \sum_{ij,\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} \sum_{kl} P_{kl} U_{iljk}$$

HSE-like double counting

$$H_{\mathrm{DC}} = \sum_{ij,\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} \sum_{kl} P_{kl} \left( U_{iljk} - \alpha U_{ilkj} \right)$$



## Carbon Dimer in hex. BN

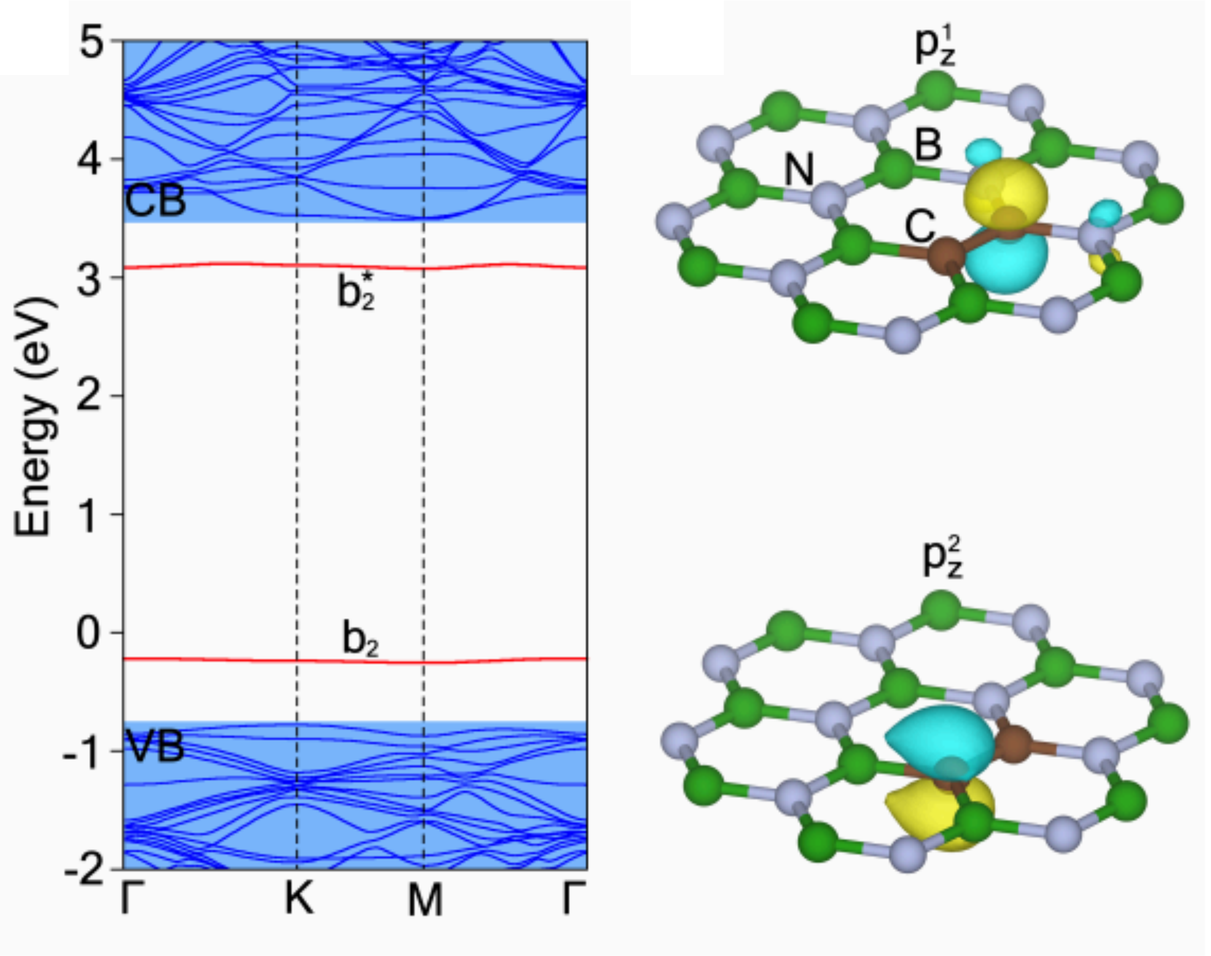
- neutral carbon-dimer ($C_nB_N$) in h-BN

  proposed to be origin of the 4.1 eV zero-phonon line in experiments

- Simple many-body problem

  Can be accurately modeled by two-site Hubbard model with known solution

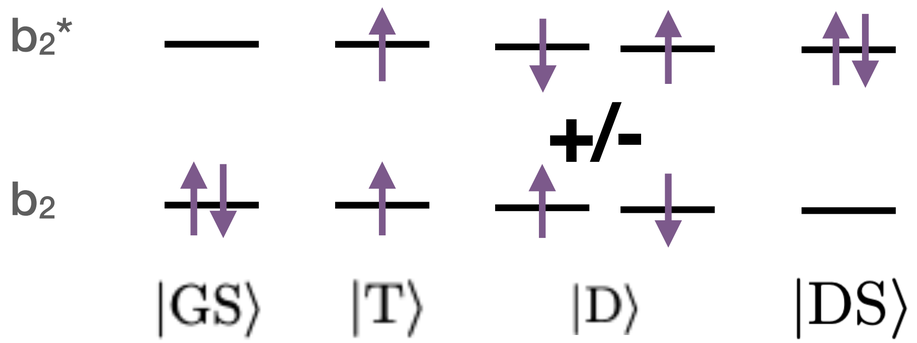
$$H_{\text{dimer}} = -\frac{U}{2}\left[(n_{p_z^1\uparrow} - n_{p_z^1\downarrow})^2 + (n_{p_z^2\uparrow} - n_{p_z^2\downarrow})^2\right] + t\sum_{\sigma}(c^{\dagger}_{p_z^1\sigma}c_{p_z^2\sigma} + \text{H.c.}),$$



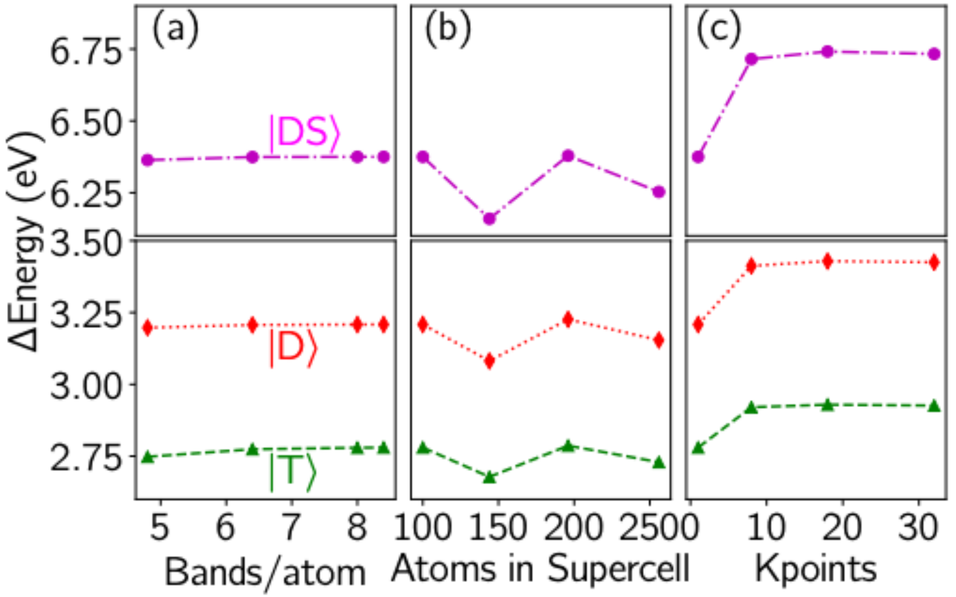

arXiv:2105.08705

# Carbon Dimer in hex. BN
# simple many Body structure

- Many-body states (simplified)




- Many-body states (from embedding @PBE)




arXiv:2105.08705

# Model system:
# Carbon Dimer in h-BN

- Double counting corrections for zero-phonon line

Hartree-Fock double counting

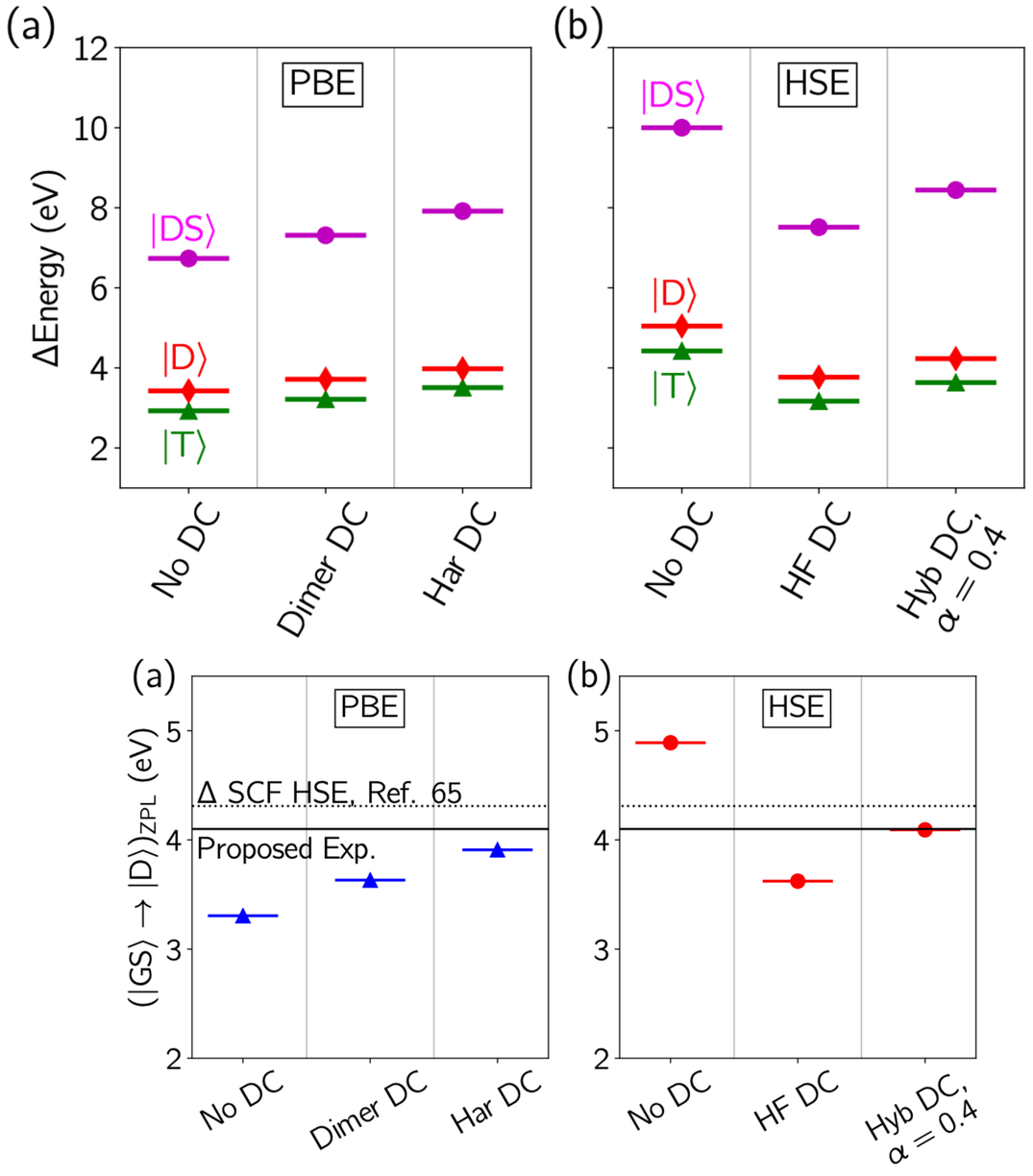
$$H_{\mathrm{DC}} = \sum_{ij,\sigma} c^{\dagger}_{i\sigma} c_{j\sigma} \sum_{kl} P_{kl} \left( U_{iljk} - \frac{1}{2} U_{ilkj} \right)$$

HSE-like double counting

$$H_{\mathrm{DC}} = \sum_{ij,\sigma} c^{\dagger}_{i\sigma} c_{j\sigma} \sum_{kl} P_{kl} \left( U_{iljk} - \alpha U_{ilkj} \right)$$

- Double counting shifts ZPL over 1.5 eV

DC shifts single particle levels significantly



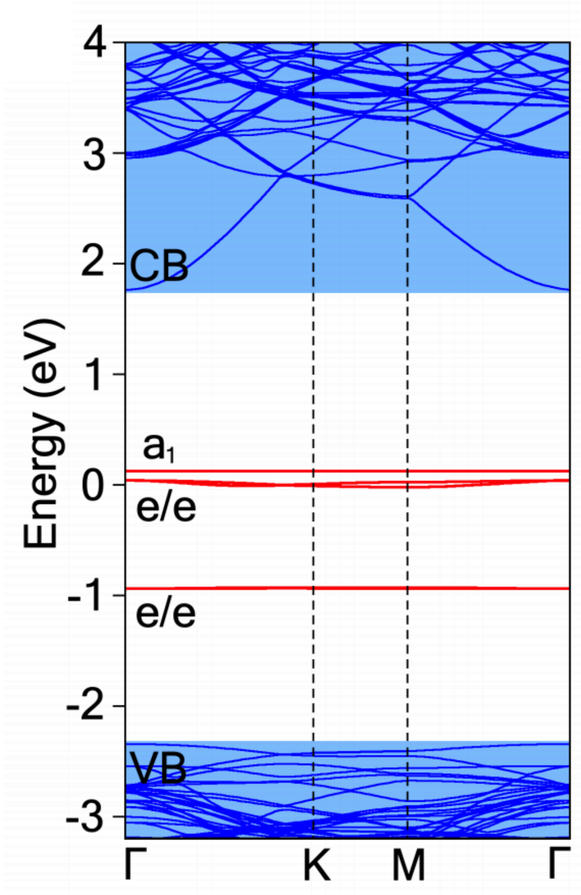
# d-electron defects as a challenge

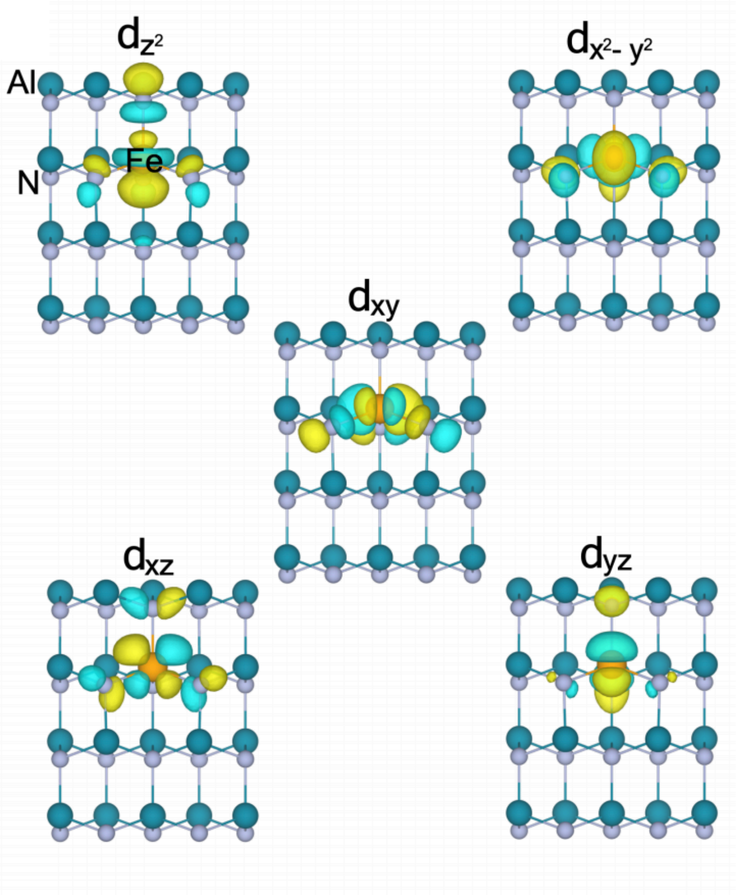
- $Fe_{Al}$ defect in AlN

  Multiplet structure of Fe as a challenge for the method

  d-electrons within band gap

  comparison to crystal field theory




arXiv:2105.08705

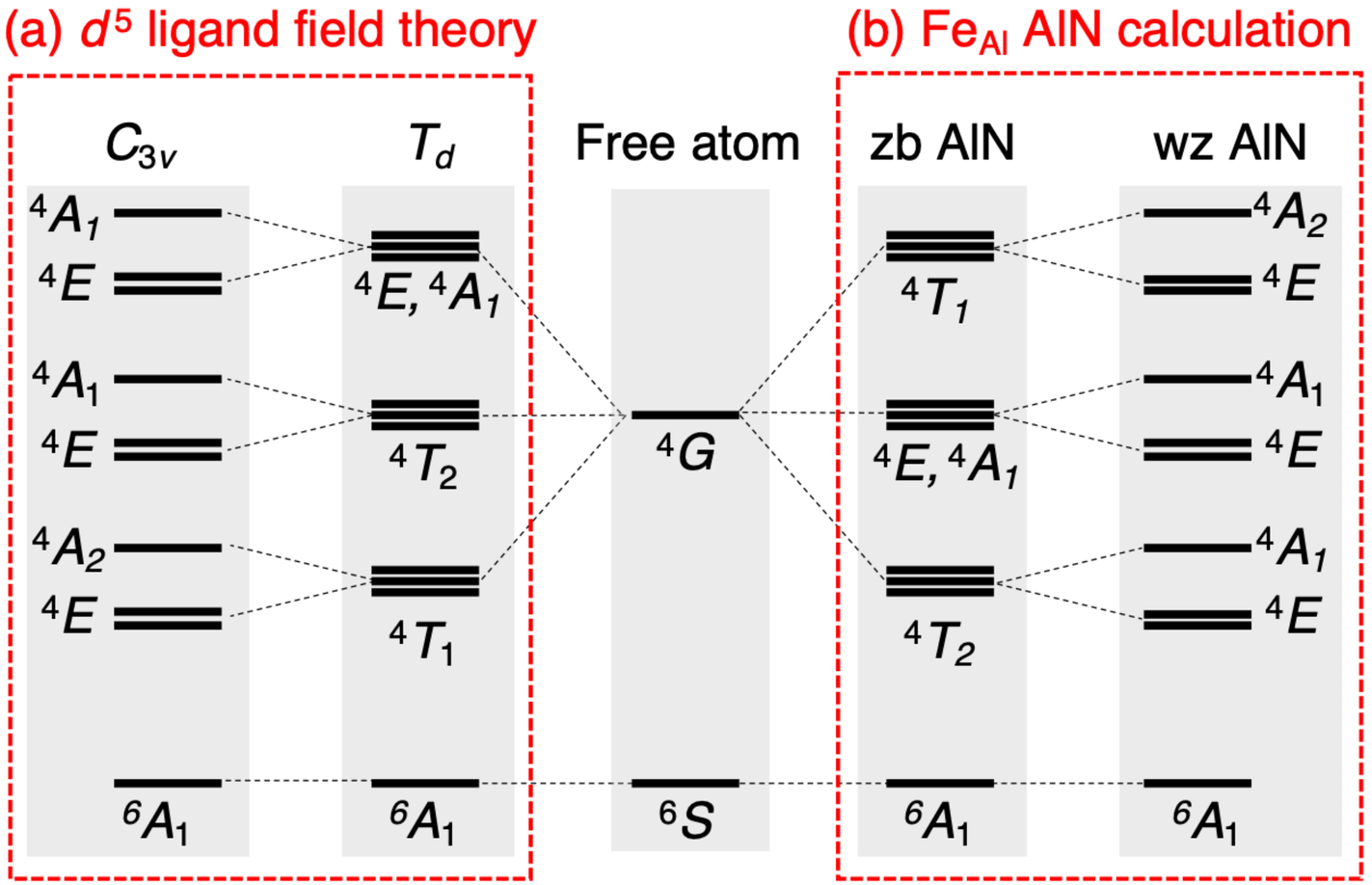
# d-electron defects as a challenge

- Many-body states labeled by irreps of point group
- Labeling of irreps

  decomposition in orbital and spin

  $$\boldsymbol{D}(R) = \boldsymbol{D}_{\text{spin}}(R) \otimes \boldsymbol{D}_{\text{orb}}(R)$$
- Prediction: Mutliplet structure differ from Tanabe-Sugano diagram prediction

  Full-Coulomb tensor needed to reproduce our ordering




arXiv:2105.08705

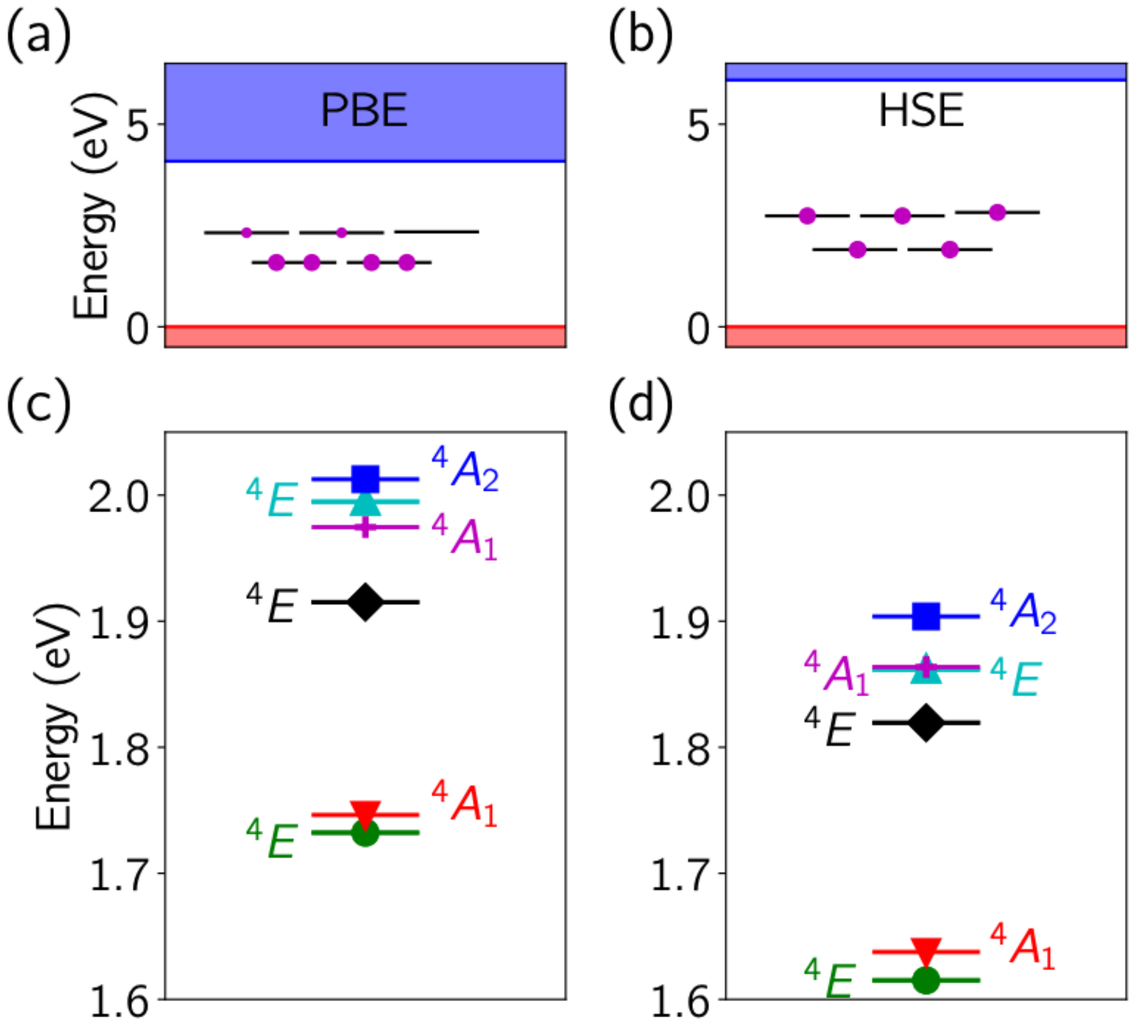
# d-electron defects as a challenge

- **Caveat: Extreme dependence on DFT functional and DFT ground state**

  HSE calculations only give qualitatively correct ordering if initial state configuration is as in (b)

- **Restricted HSE is not always the best starting point**

  HSE provides better description of bulk AlN, but not for the correlated subspace




arXiv:2105.08705

# Outlook

- Methodology can describe localized defects with considerable accuracy and comparably low computational cost
- Possibility to extend methodology for structural and dynamical properties due to low-cost
- Double counting and dependence on DFT functional are the biggest challenges for predictive modeling