



Computational treatment of lanthanide dopants in oxides by DFT with Hubbard corrections

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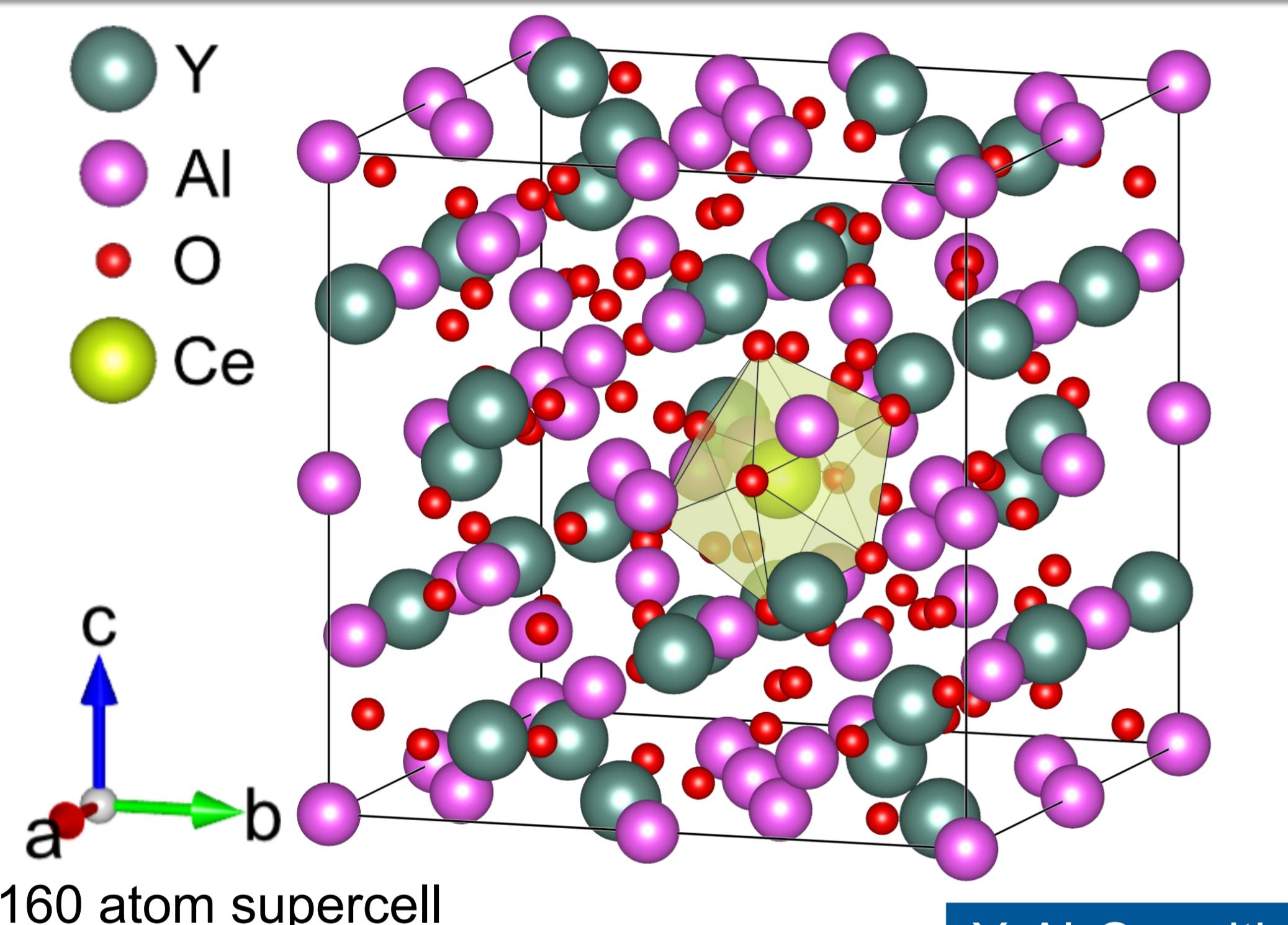
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Abstract

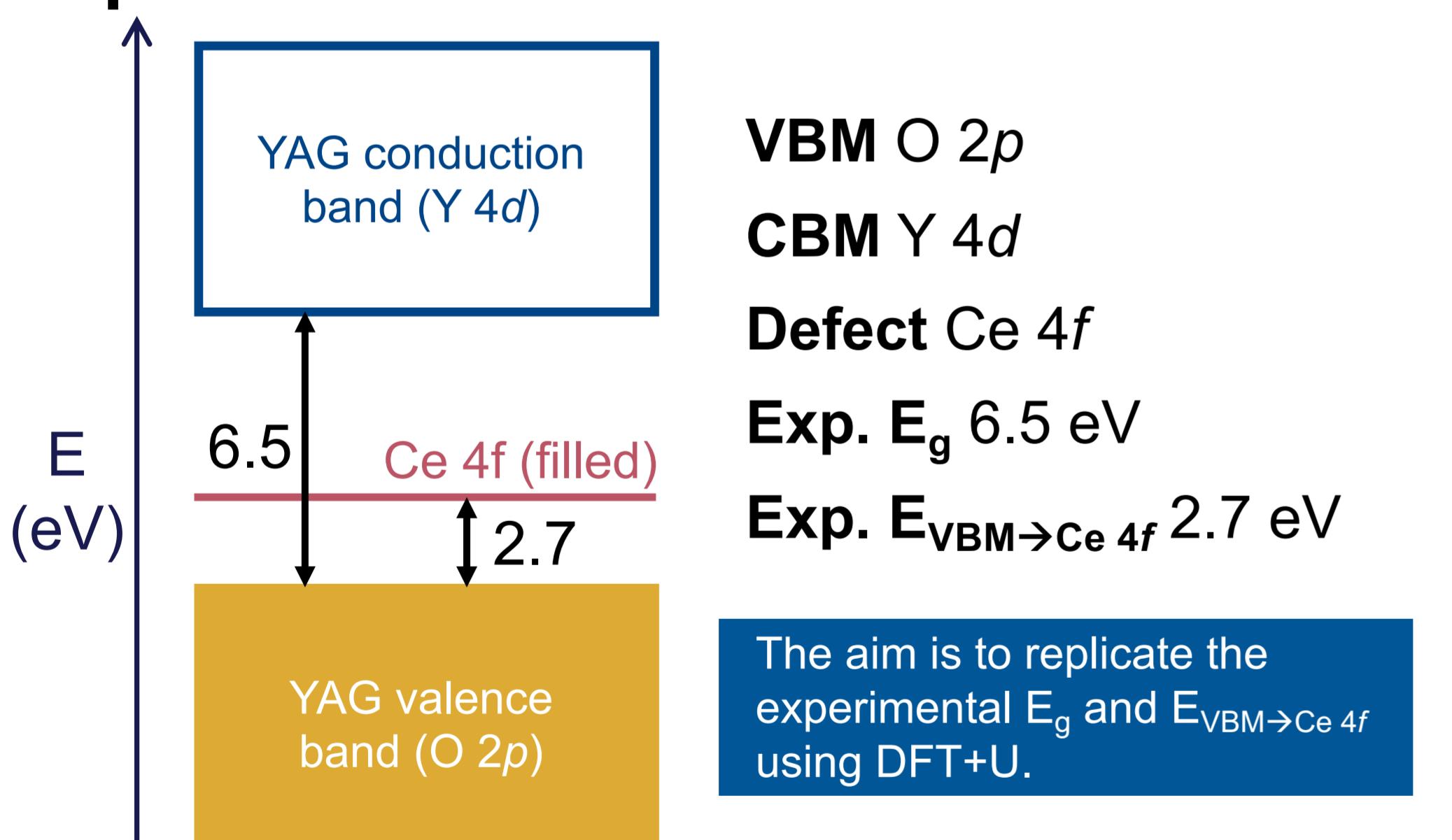
Density functional theory (DFT) is a computationally efficient choice for computing the quantum chemical properties of material systems. However, electron over-delocalization presents a problem in the DFT treatment of lanthanide elements as *d*- and *f*-electrons are highly localised.¹ One way to address this is with additive corrections to the DFT energy such as DFT+U²⁻⁴, in which a Hubbard U parameter is introduced to enforce localisation of a given subshell. This method has been highly successful for transition metals, and recent developments have also shown its applicability in the treatment of lanthanide compounds.^{5,6} Here, we investigate the use of these methods for lanthanide dopants in wide band gap oxides. Using cerium-doped yttrium aluminium garnet (YAG:Ce) as a model system, we compare the effect of DFT+U corrections on the electronic structure, and we show the limitations of self-consistent determination of U.⁷ Furthermore, we explore methods that address metastability issues introduced by DFT+U,⁸⁻¹⁰ which are particularly problematic for *f*-electron systems.¹⁰ We identify occupation matrix control⁸ as the preferred method to address metastability issues in YAG:Ce due to its ability to find the lowest energy electronic state compared to U-ramping.⁹ Successful implementation of such low-computational cost corrections would enable further theory-led innovations in lanthanide-doped oxides, with wide-ranging implications from lighting to quantum technologies.

YAG:Ce – The Test System

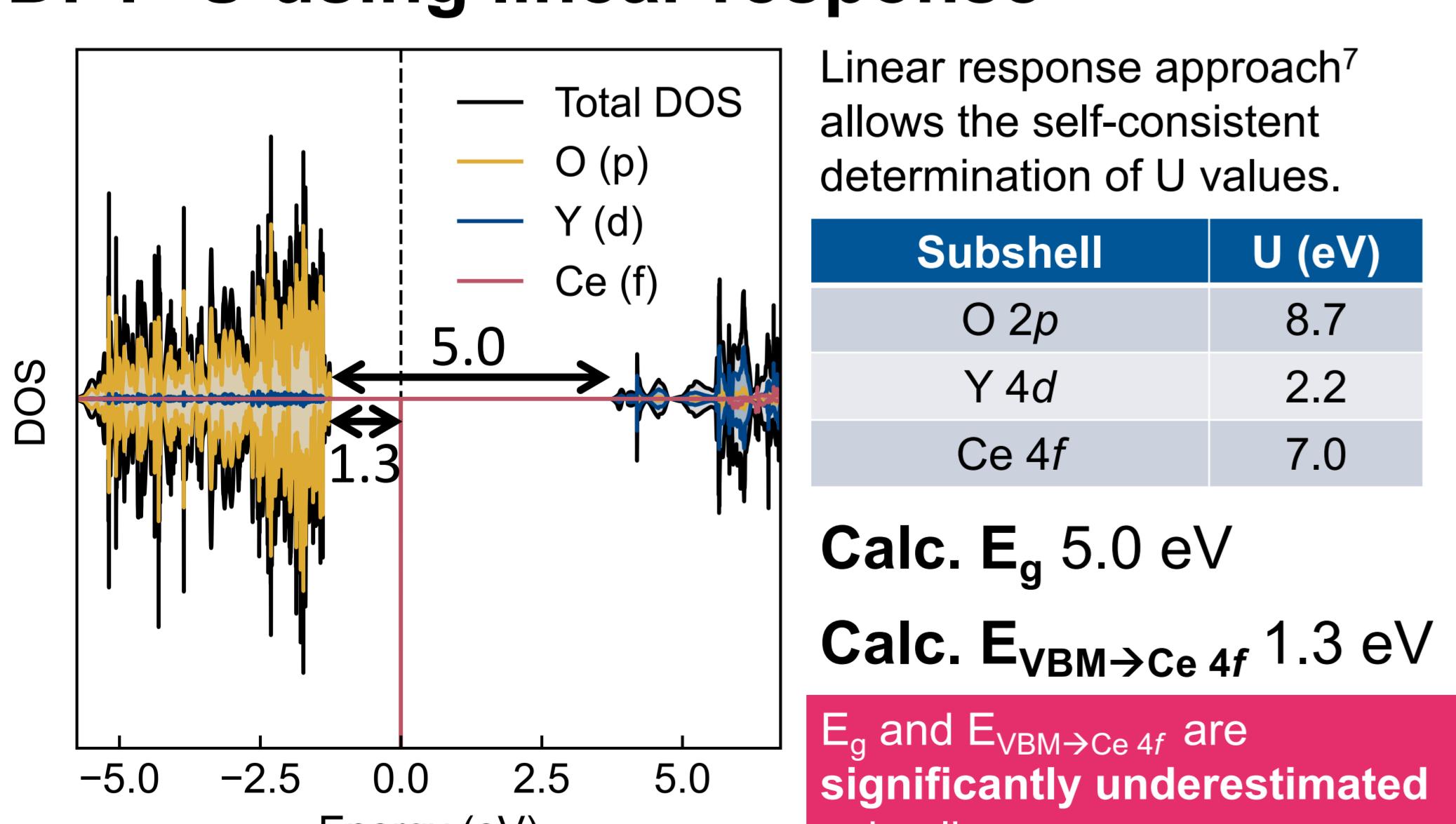


1. Linear Response

Experimental electronic structure



DFT+U using linear response



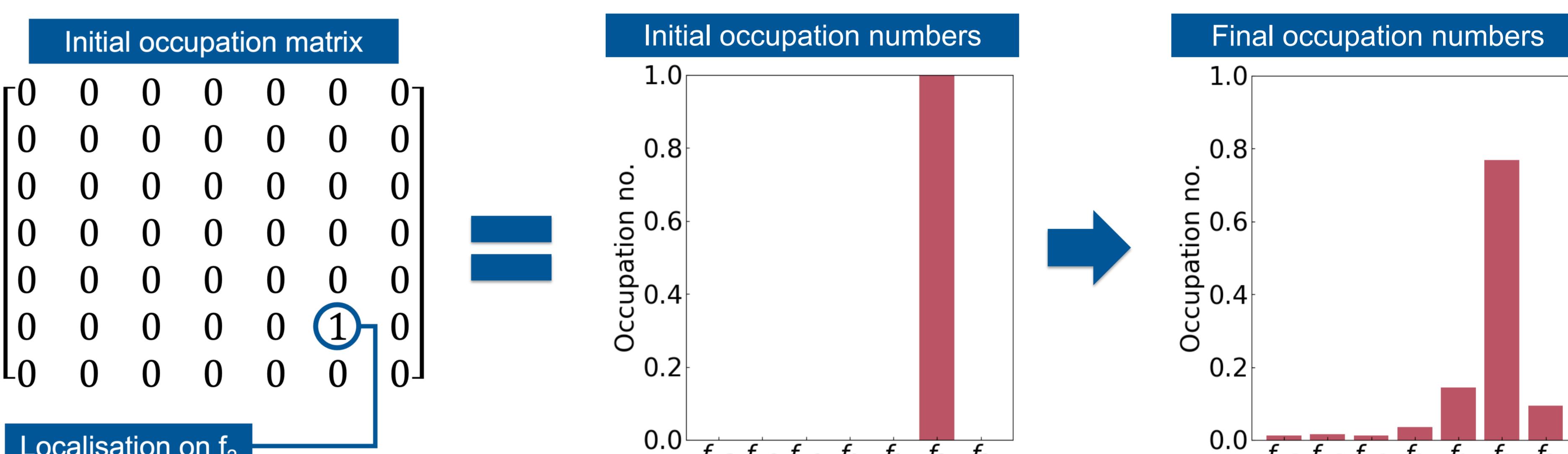
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2. Addressing DFT+U Metastability Issues

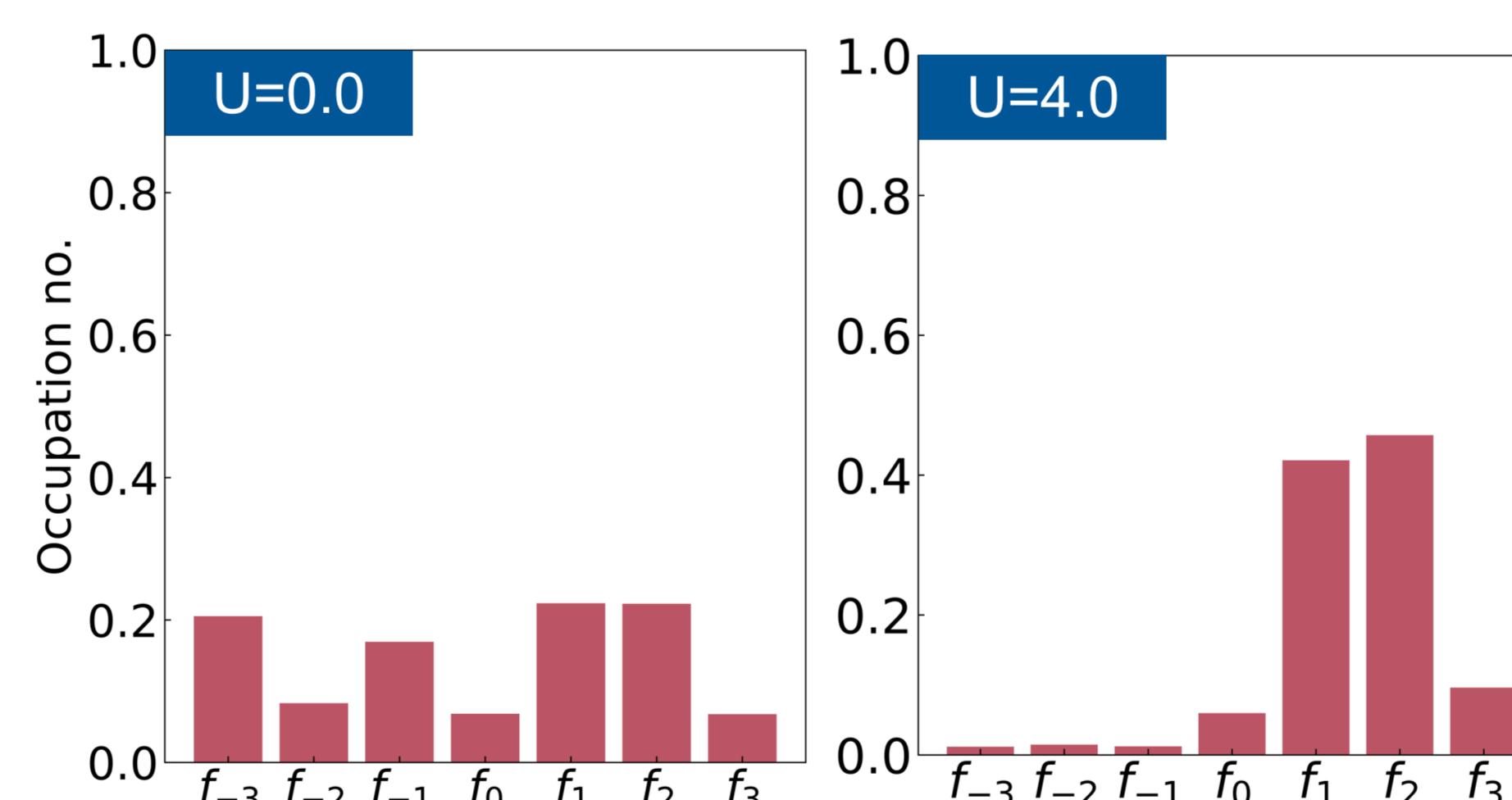
Problem: DFT+U introduces additional self-consistent solutions, making convergence to the ground state difficult.

Method I: Occupation Matrix Control



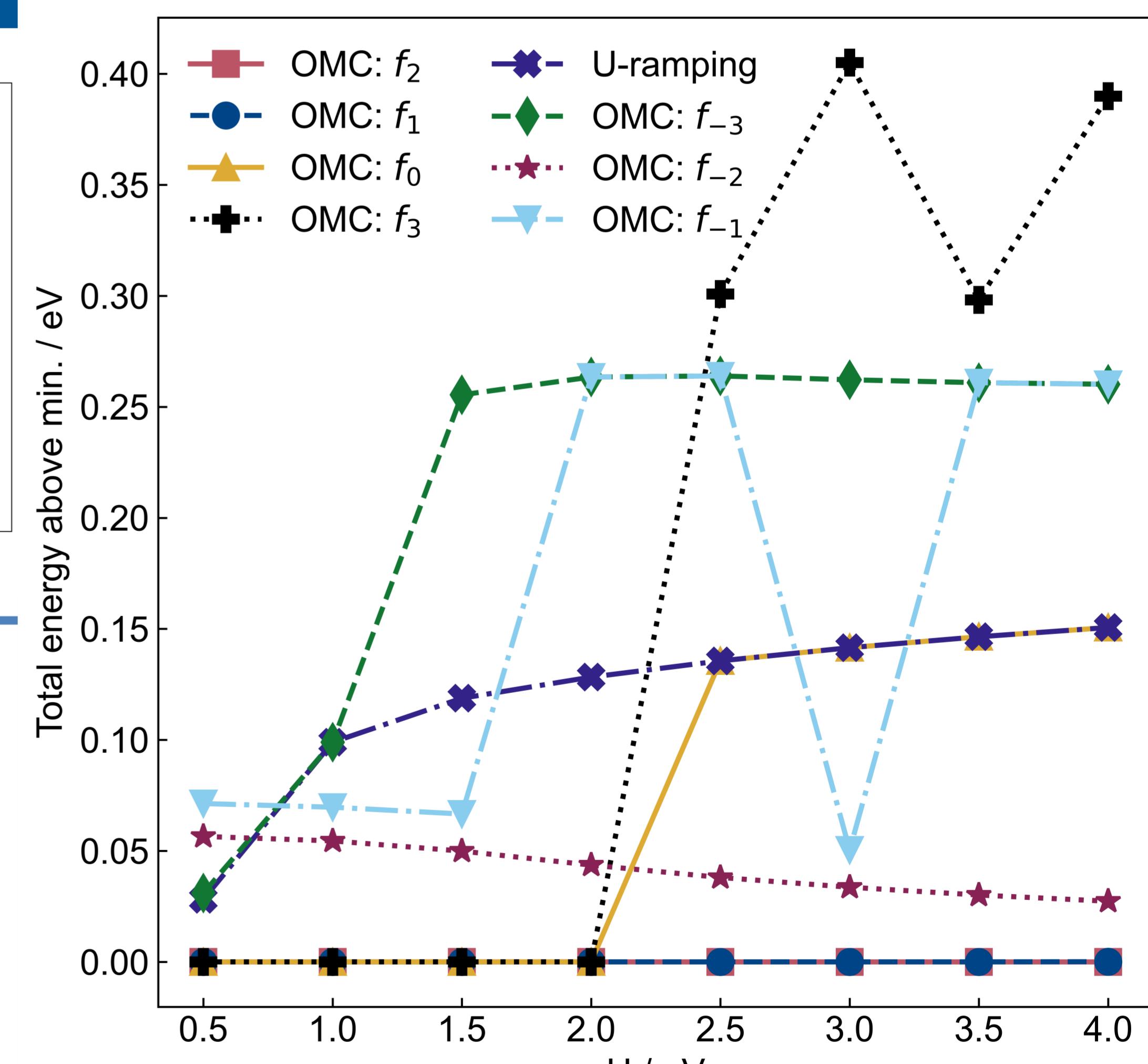
Method II: U-ramping

Approach: Ramp up U from 0 eV to target value in small steps (0.1 eV), passing occupation matrices between steps.



Comparison of methods

Occupation matrix control gives rise to the lowest energy state (initial OMC: f₂) for all U values, whereas U-ramping finds a metastable state.



Methodology

A YAG:Ce supercell was obtained using pymatgen¹¹ from undoped YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$), which was then doped with Ce. DFT calculations with the PBEsol+U functional were performed with the Dudarev (U_{eff}) DFT+U implementation.^{4,12} The linear response approach was applied to the Ce 4f, O 2p, and Y 4d subshells to acquire U_{eff} values, which were subsequently applied to their respective subshells. The U-ramping and occupation matrix control methods were compared to determine which method is able to find the lowest energy state for YAG:Ce.

Conclusions

- The linear response approach to acquire U values for DFT+U does not replicate experimental energy gaps in YAG:Ce.
- Occupation matrix control gives rise to a lower energy state than U-ramping in YAG:Ce for all tested U values and is thus the preferred method to address metastability caused by DFT+U.