

# Utilizing Density Functional Theory to Investigate Polaron Formation in Compositionally Complex Oxides

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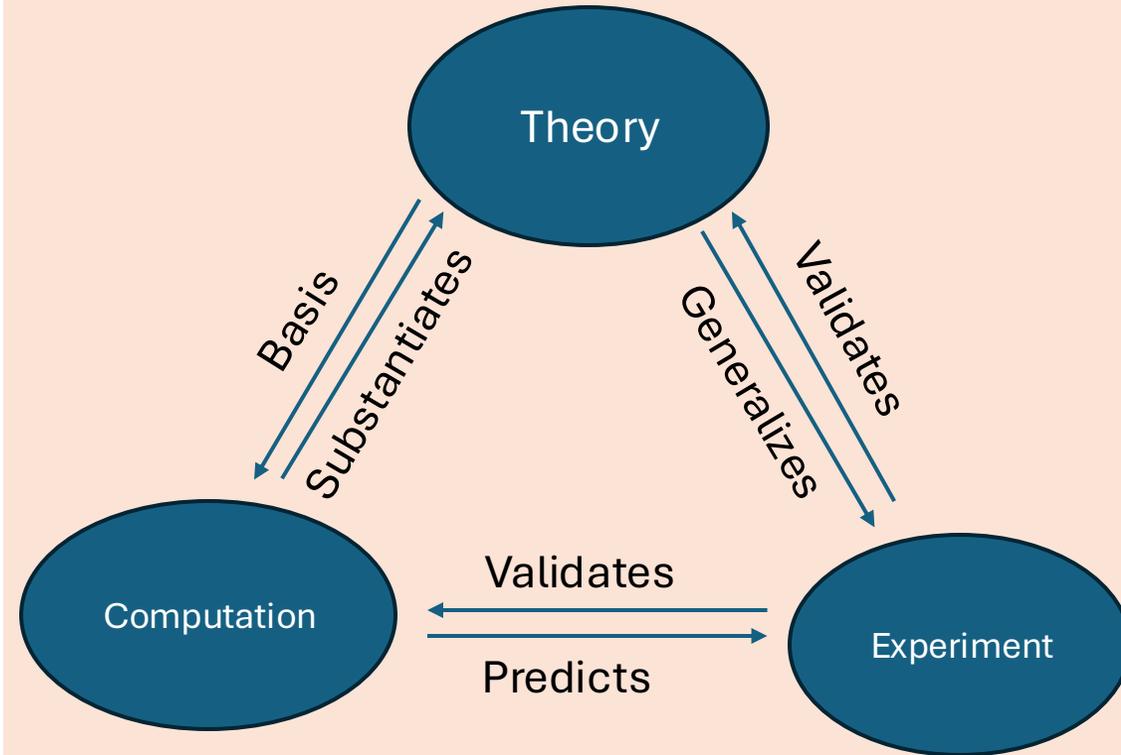
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# Outline

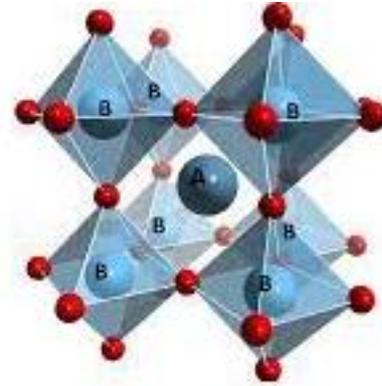
- Motivation
- Experimental Discrepancies
- Intro to Polarons
- Basics of Density Functional Theory
- Procedure
- Future Work
- Conclusion

## Complex Material Science Problems



# Motivation

- Multiferroic compositional complex oxides (CCOs)
  - $\text{Eu}(\text{Sc}_{0.2}\text{Al}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Ni}_{0.2})\text{O}_3$
  - $\text{Gd}(\text{Sc}_{0.2}\text{Al}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Ni}_{0.2})\text{O}_3$
  - $\text{Sm}(\text{Sc}_{0.2}\text{Al}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Ni}_{0.2})\text{O}_3$
- Potential applications
  - ultrasound devices
  - actuators
  - non-volatile memory storage



← Conventional  $\text{ABO}_3$  unit cell [1]



Figure 2: The synthesized CCOs are a variation of  $\text{A}^{2/3}\text{B}^{3/4}\text{O}_3^{2-}$  structure with rare earth metals at the A site and various elements at the B site.

# Experimental Characterization

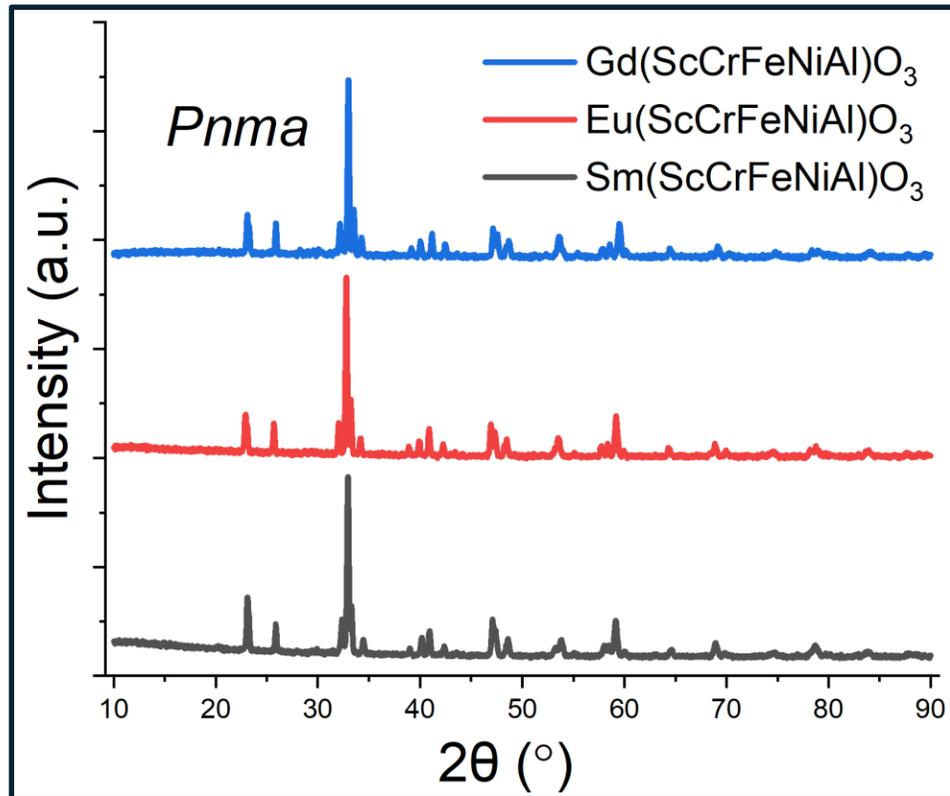


Figure 3: XRD illustrating the same crystal structure for each of the different CCOs

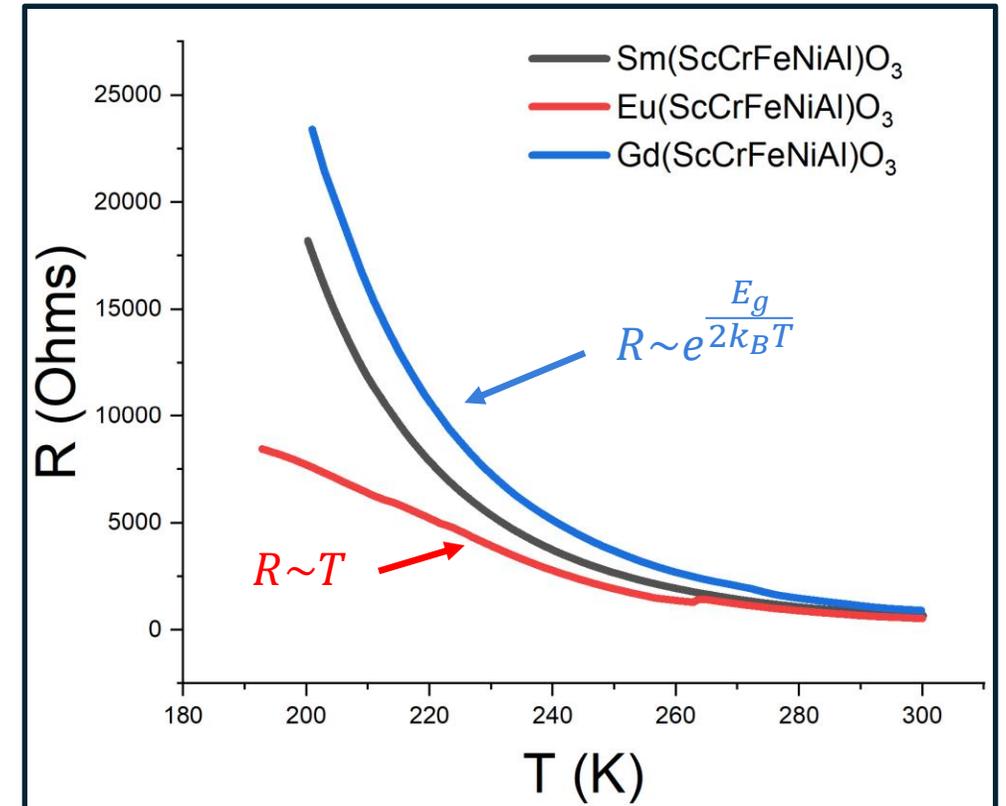
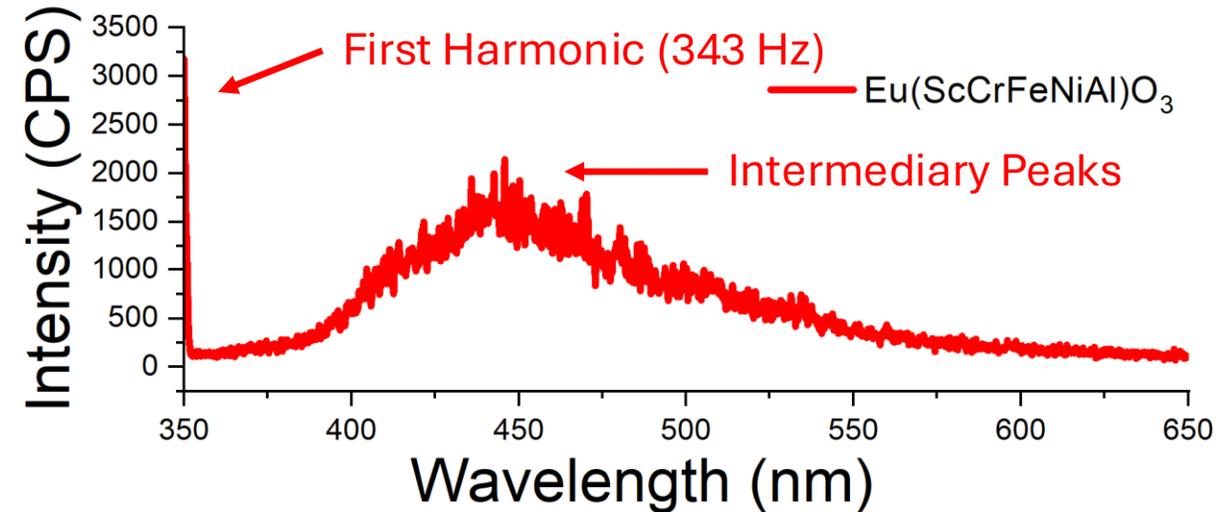
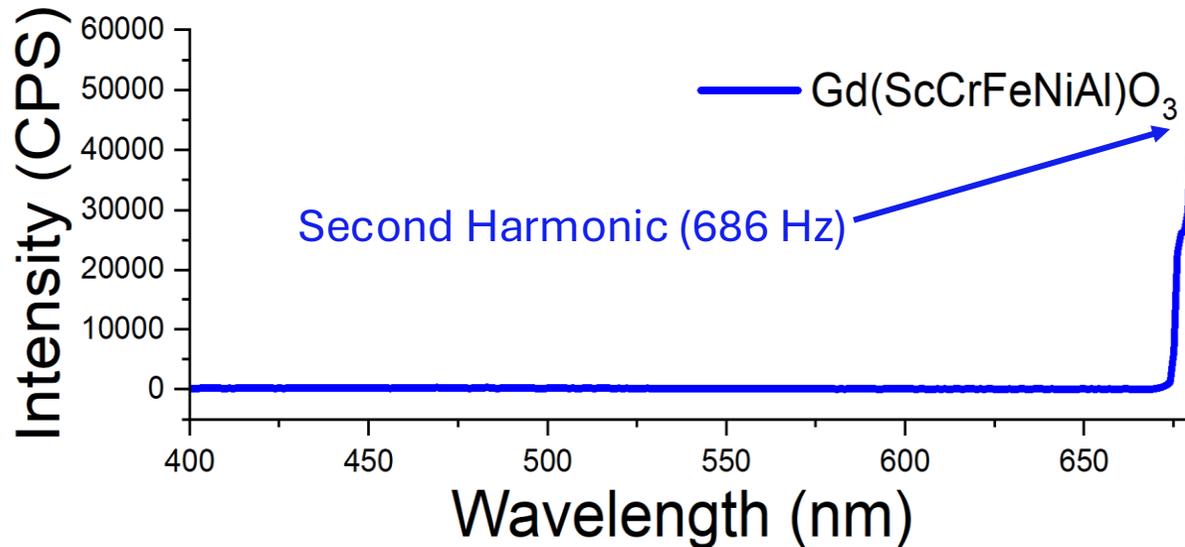


Figure 4: Resistance data illustrating a linear trend for Eu CCOs but an exponential trend for Gd and Sm CCOs

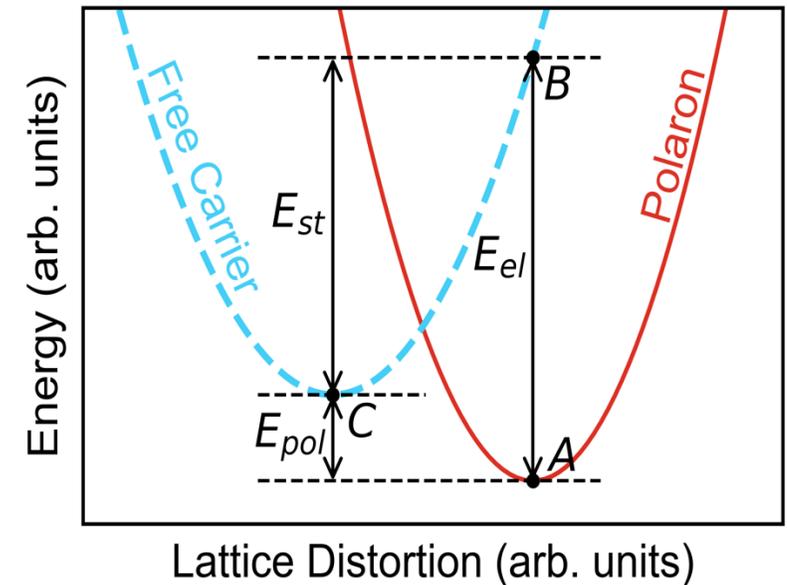
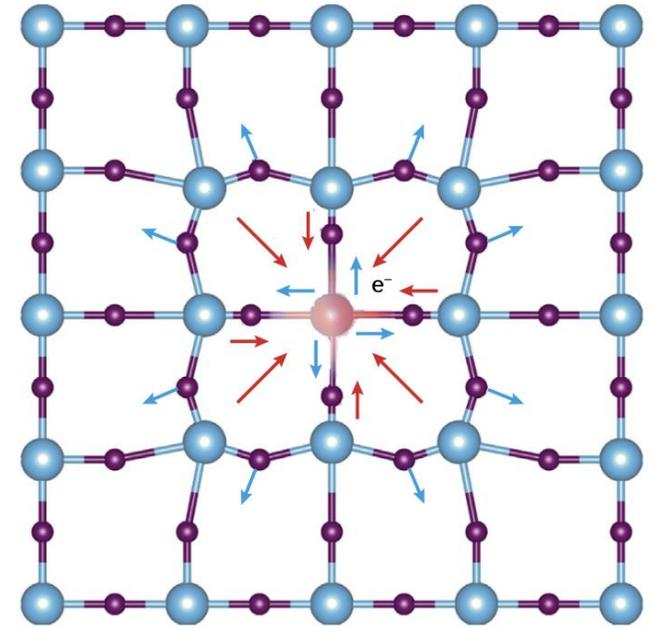
# Experimental Characterization



- Photoluminescence experiment
  - excess peaks suggesting polaron formation in Eu CCO
- Intermediary peaks indicate excited electrons relaxed to higher energy orbitals in Eu CCOs compared to Gd CCOs.

# Polarons in Materials

- Polarons: trapped excess electrons coupled with lattice distortions
- Energetically favorable in materials with high lattice strain



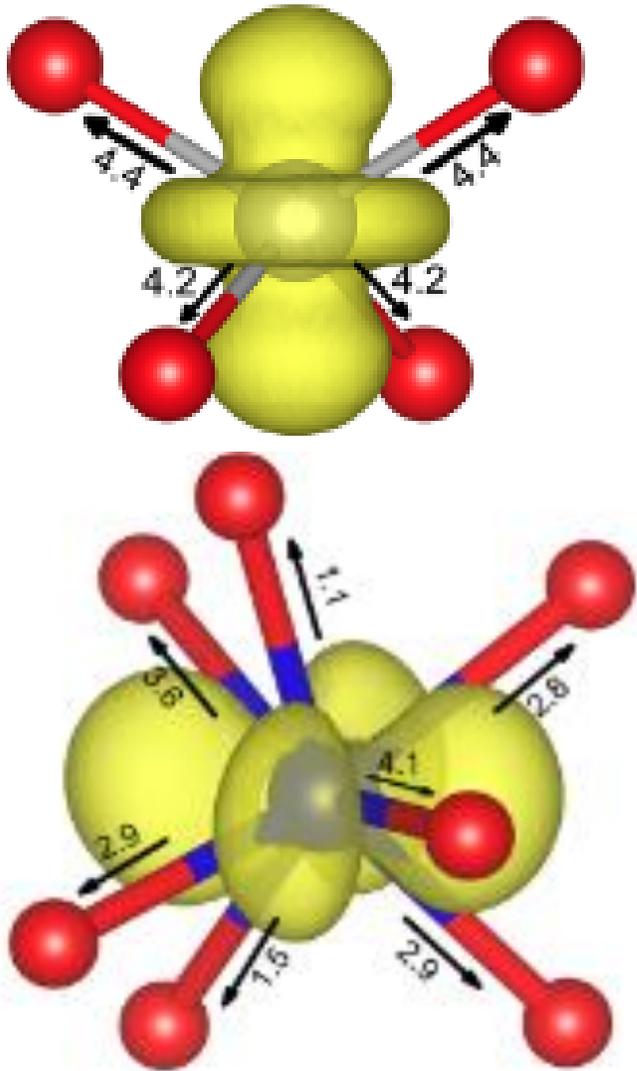


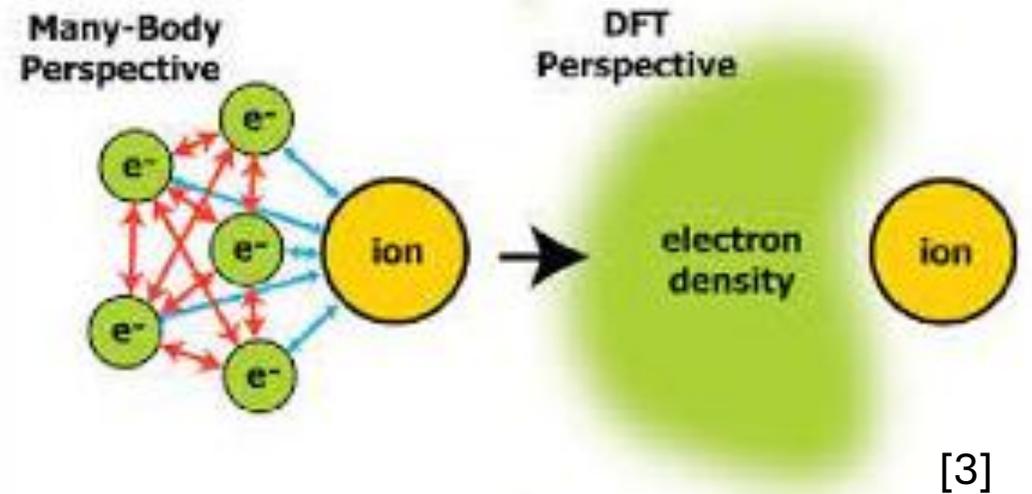
Figure 7: Increase in V-O bond lengths around in m-BiVO<sub>4</sub> (top) and Hf-O bond lengths in m-HfO<sub>2</sub> (bottom) due to polaron formation. [2]

# Polaron Formation Hypothesis

- Polaron formation may be the cause of experimental discrepancies.
- Experimental techniques are time consuming.
- How can Density Functional Theory be used to model the formation of polarons in CCOs?

# Basics of Density Functional Theory

- Reformulates the many body Schrodinger equation to a single variable functional of the total electron density.



Stagnant nuclei-electron interactions

Electron-electron interactions

$$\left[ -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla^2 + \sum_{i=1}^N V_{n-e}(r_i) + \sum_{i=1}^N \sum_{j<i}^N V_{e-e}(r_j, r_i) \right] \Psi = E\Psi \rightarrow \left[ -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla^2 + \sum_{i=1}^N V_{n-e}(r_i) + \int \frac{\rho(r')}{|r-r'|} dr' + V_{xc}(r) \right] \varphi(r) \geq E_0\varphi$$

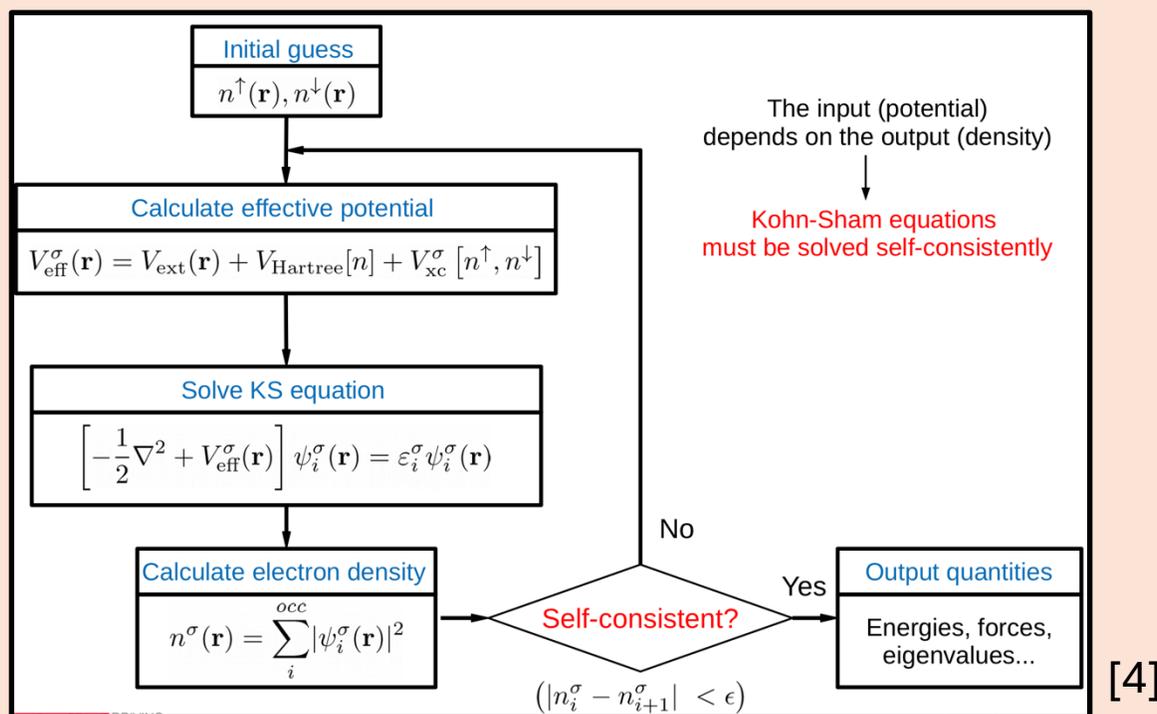
1. Ground state – 0K Approximation
2. Did not account for relativistic energy

Interactions with total electron density

Exchange-correlation potential

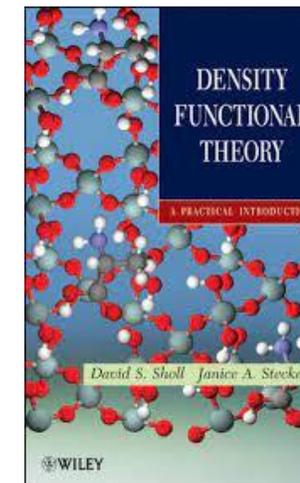
# Two Caveats of Density Functional Theory

1. No exact solution of the  $V_{xc}(\mathbf{r})$  term exists  $\rightarrow$  defines computational study.
2. A) To determine the Hamiltonian, we need the electron density.  
B) To determine the electron density, we need the Hamiltonian.



[4]

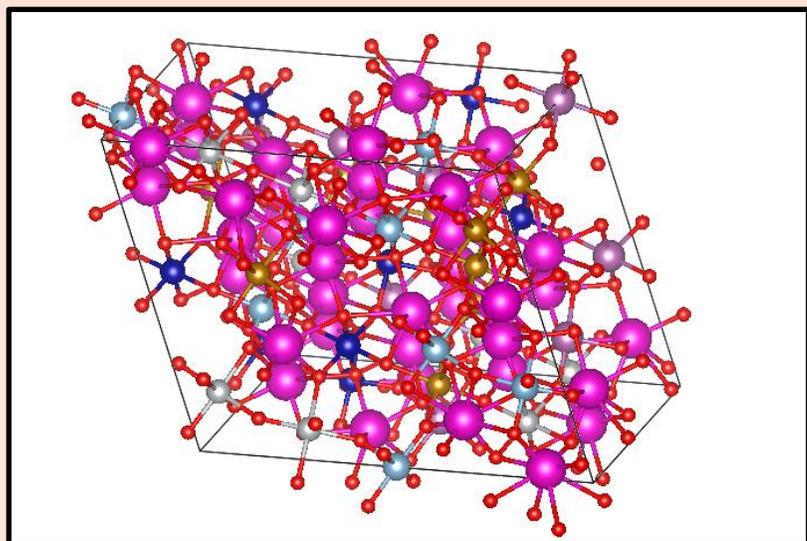
Further reading: Density Functional Theory: A Practical Introduction by Dr. David Sholl Director of UT-ORII



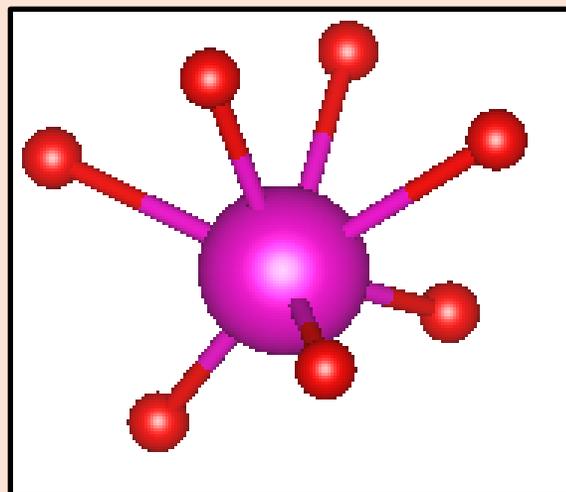
# Procedure

Due to the natural tendency of Eu to exist in states of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$ , Eu was selected as the site where the polaron is most likely to form.

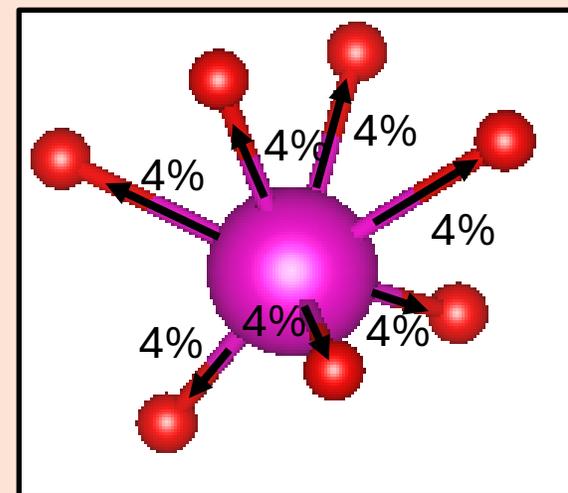
Bond Distortion Method:



Generate atomic positions using Special Quasi-random Structure code



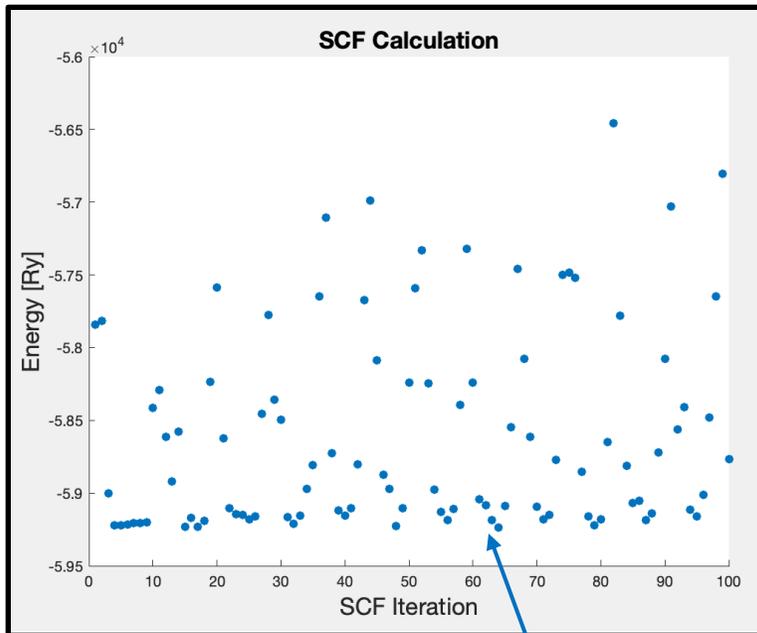
Isolate Eu atom closest to the center and its adjacent O atoms



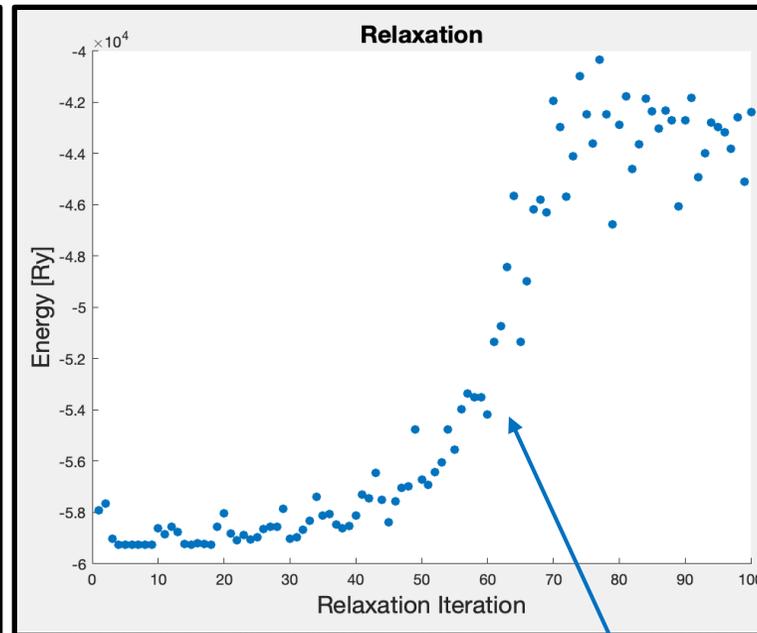
Increase the distance between Eu-O by an amount similar to expected distortions

# Results

Calculations ran in Quantum Espresso (open source)

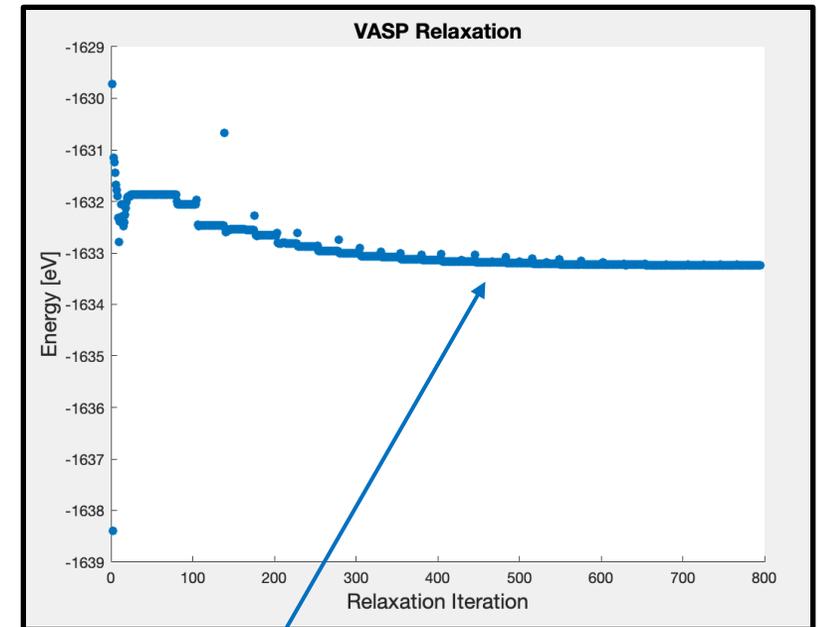


“Random scattering” = oscillations on the order  $0.2 \times 10^3$  Ry (bad)



Increasing towards a non convergent value (very bad)

Calculations ran in VASP (licensed software)

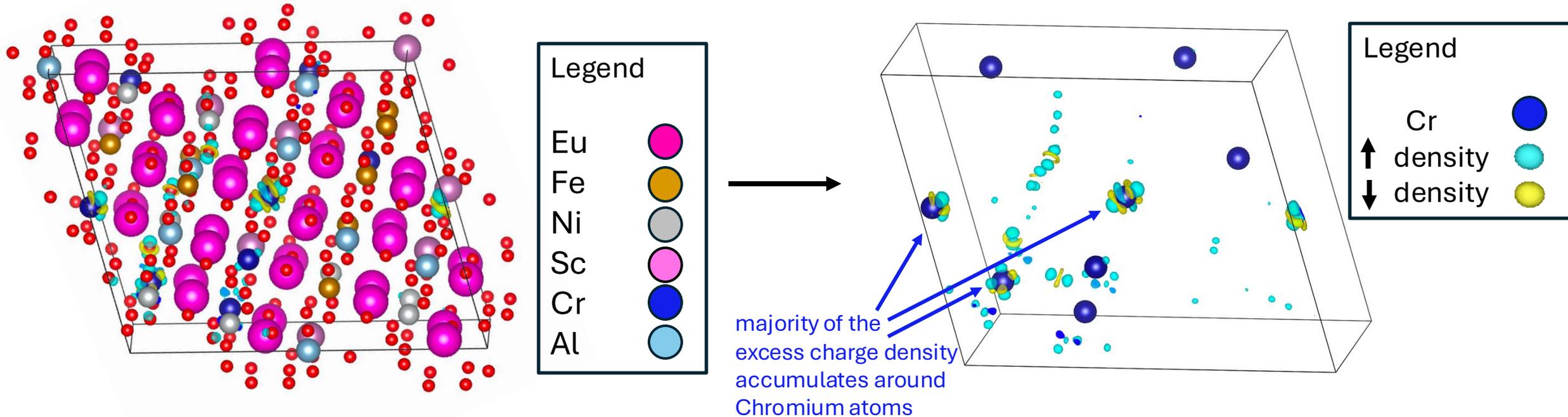


Decreasing towards a constant value (excellent)

- Non-convergence in QE calcs are due to computational techniques used to initialize the electron density

# Results

Subtracting the electron density of the neutral cell from the electron density of the unit cell with the extra electron, we found that the extra electron did not localize on Eu but instead localized on many different atoms:



These observations informed our next calculations where we sought to localize an electron around the center Chromium atom. However, current calculations have yet to converge.

# Future Work (a lot)

- Parameter optimization in QE and VASP to achieve convergence
- Comparison of polaron formation in various configurations of  $\text{Eu}(\text{Sc}_{0.2}\text{Al}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Ni}_{0.2})\text{O}_3$
- Demonstrate that the procedure does not form polarons in  $\text{Gd}(\text{Sc}_{0.2}\text{Al}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Ni}_{0.2})\text{O}_3$  and  $\text{Sm}(\text{Sc}_{0.2}\text{Al}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Ni}_{0.2})\text{O}_3$

# Conclusion

- Research project: The exact site of polaron formation is still not well understood and current DFT calculations contradict experimental expectations.
- Personally: I got to understand the practical extent of fundamental quantum mechanic computations which was something I was curious about ever since taking a quantum mechanics class.

# Works Cited

- [1] Lutfullin, Marat. “What Are Perovskite Materials? - Articles & Publications - Blog: Quantum Solutions.” *Articles & Publications - Blog | Quantum Solutions*, 6 June 2022, [quantum-solutions.com/blog/what-are-perovskite-materials/](https://quantum-solutions.com/blog/what-are-perovskite-materials/).
- [2] Pham, T., et al. American Chemical Society, 2020. p. 5266-5270
- [3] Lusk, Mark & Mattsson, Ann. (2011). High-performance computing for materials design to advance energy science. *MRS Bulletin*. 36. 10.1557/mrs.2011.30.
- [4] “The Self-Consistent-Field Cycle¶.” *Siesta Documentation*, [docs.siesta-project.org/projects/siesta/en/latest/tutorials/basic/scf-convergence/index.html](https://docs.siesta-project.org/projects/siesta/en/latest/tutorials/basic/scf-convergence/index.html). Accessed 15 July 2024.
- [5] Sholl, David S., and Janice A. Steckel. *Density Functional Theory: A Practical Introduction*. John Wiley & Sons, Inc, 2023.
- [6] Granhed, Erik Jedvik, et al. “Band vs. Polaron: Vibrational Motion and Chemical Expansion of Hydride Ions as Signatures for the Electronic Character in Oxyhydride Barium Titanate.” *Journal of Materials Chemistry A*, The Royal Society of Chemistry, 18 June 2019, [pubs.rsc.org/en/content/articlelanding/2019/ta/c9ta00086k](https://pubs.rsc.org/en/content/articlelanding/2019/ta/c9ta00086k).

# Backup slides

- Polarons in the electronic band structure and density of states

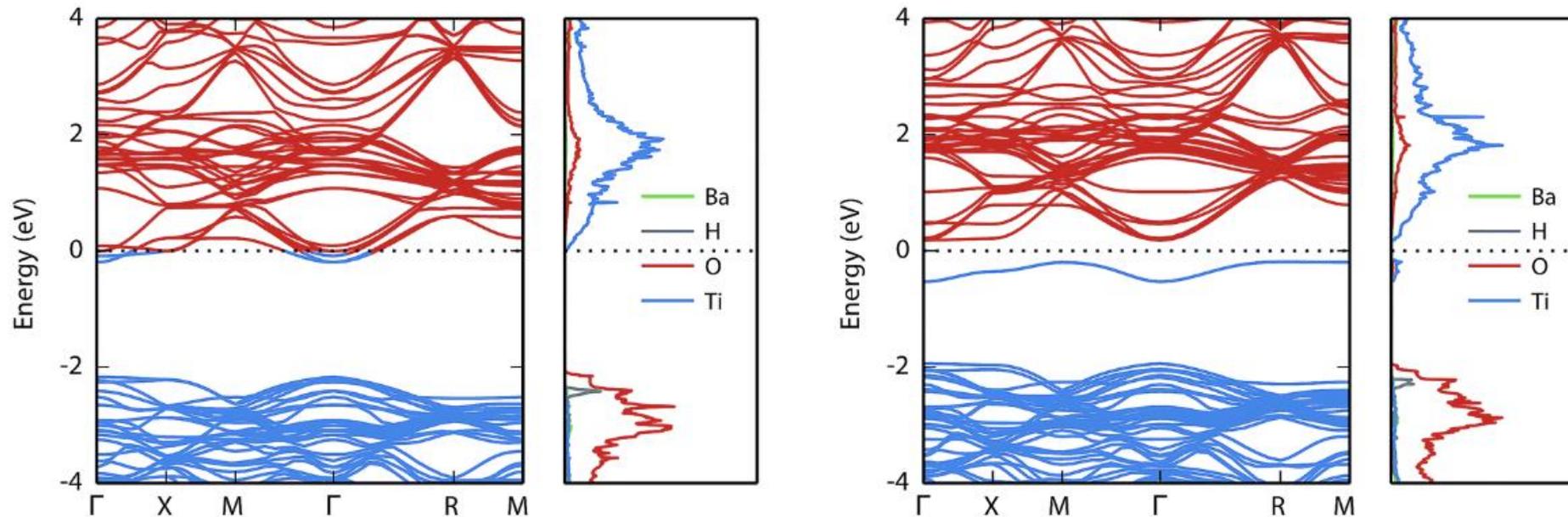


Figure 13: (Right) Band structure without a polaron compared to (left) band structure with a polaron. The addition of a polaron reduces the energy of one of the conduction bands making the transition energy from an excited to a relaxed state smaller. [6]