Constructing an Improved Ce Pseudopotential in OPIUM Code
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Ce pseudopotential

- Ce: Electronic configuration is [Kr]4d^{10}5s^{2}5p^{2}4f^{1}5d^{1}6s^{2} with oxidation states 3+ and 4+.
- Pseudopotential (pseudopotential) of Ce (and other d- and f-block elements) is difficult to generate because d and f orbitals demonstrate high kinetic energy wave functions.

4f radial wave function of Ce: solid blue line is the all-electron wavefunction and the red line is the pseudized wavefunction.

Charge density of core (blue line) and valence (red line) states. The valence states include 5s, 5p, 6s, 6p, 5d, and 4f.

- For d- and f-orbitals, the overlap of the core and valence charge densities is reduced as the peak of the pseudized wavefunction is shifted outward. This reduced overlap can lead to a significant overestimation of exchange splitting.

Details of pseudopotential generation

- The Ce psp was generated using the Generalized Gradient Approximation (GGA) functional by the Optimized (RRKJ)[10] method in OPIUM (Open-source Pseudopotential Interface / Unification Module) Code Version 3.7 (http://opium.sourceforge.net/)
- Both semicore and partial core corrections have been applied.

✓ Semicore correction: inclusion of additional valence states to obtain an accurate description of the core states’ electronic structures. 1) Semicore is critical for Ce in order to depict the interaction between 4f states another core states that have significant spatial overlap with 4f. 2) In applying the psp to compounds, a small core region is preferred.

✓ Partial core correction (PCC)[11]: applied to obtain an accurate exchange-correlation functional, which is a non-linear function of charge density. PCC is particularly important for the elements in which the core region overlaps with valence states, and for magnetic systems in which there can be a large difference between spin-up and spin-down valence charge density. Both criteria are pertinent to Ce.

Applications to Ce-O systems

CeO₂ and Ce₂O₃

All DFT calculations were done using Quantum-ESPRESSO version 6.2.1

Density of States

CeO₂ reduction energy (U=0.0)

Defect formation energy (DFE) of an oxygen vacancy (V₀) in CeO₂

Ce₂O₃

Ce₂O₃ reduction energy (U=0.0)

Defect formation energy (DFE) of an oxygen vacancy (V₀) in Ce₂O₃

BaCe₁₋ₓPdₓO₃₋₃

Unit cell of cubic BaCe₁₋ₓPdₓO₃₋₃ (BCP) perovskite.

DFT of V₀ in bulk BCO and BCP (x = 0.03)

Without PCC, the DFE for sites adjacent to Pd is unphysical.
The improved psp yields the expected[10] result—Pd doping significantly increases the formation of V₀ in BCP—at all calculated values of U.

Oxygen migration kinetics for bulk BCP (x = 0.25)

- NEB calculation for O migration within the Pd octahedra.
- Using the Ce psp without PCC gives Eₐ higher than the entry value for all U with PCC.
- The lower value of Eₐ is more consistent with the existence of a bulk O diffusion mechanism in BCP[10].

Oxygen migration kinetics for Ce₂O₃

- The Nudged Elastic Band (NEB) method was employed to determine the activation energy (Eₐ) of O moving into an adjacent vacancy site. The theoretical agreement for U = 0 is shown.

Conclusions

- The partial core-corrected Ce psp significantly improves the electronic representation of 4f states for Ce-based oxides.
- The improved Ce psp adequately reproduces literature values for the reduction energy as well as the DFE of V₀ and the Eₐ for bulk O migration of Ce₂O₃.
- This psp is beginning to elucidate similar properties of BCP perovskite, a regenerative catalyst.

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