

— Supporting Information —

Evaluating transition-metal oxides within DFT-SCAN and SCAN+U frameworks for solar thermochemical applications

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Pressure-volume and zero-point energy contributions to theoretical enthalpy calculations

The zero-point energy (ZPE) of most solids are in the range of ~10-100 meV/f.u.^{1,2} Since we calculate the energy difference between solids both in formation (oxide and metal) and oxidation (reduced and oxidized metal oxides) enthalpies, the solid-phase ZPE contributions will mostly cancel and hence will not contribute significantly to theoretical determination of the enthalpy. A similar argument applies for pressure-volume contributions amongst solids.

In the case of oxygen, a combination of experimental measurements and theoretical modeling yield a ZPE of ~0.1 eV per O₂.^{3,4} Assuming oxygen is an ideal gas, the $P\Delta V$ contribution, from 0 K to 298 K, is equivalent to $R\Delta T \approx 0.025$ eV (R = gas constant). $P\Delta V$ +ZPE therefore yields ~0.125 eV per mole of O₂, which in turn should be added to $E_{O_2}^{SCAN}$. Although this number appears high in isolation, the $P\Delta V$ +ZPE contributions represent a constant shift, *i.e.*, more negative, in SCAN-enthalpy predictions of oxide formation energies (and oxidation enthalpies), which are on the scale of several eV per O₂.

While benchmarking formation energies of main group oxides (denoted as MO), any constant shift in predicted formation energies versus experiments can be attributed to an erroneous description of the O₂ ground state and therefore is added as a correction to the theory calculated with the O₂ energy. For example, if DFT-SCAN values were to display a constant shift in oxide formation energies, then $\Delta H_f^{t,corrected} =$

$$\frac{E_{MO}^{SCAN} - E_M^{SCAN} - \frac{1}{2}E_{O_2}^{SCAN,corrected}}{\frac{1}{2}}, \quad \text{where,} \quad E_{O_2}^{SCAN,corrected} = E_{O_2}^{SCAN} + P\Delta V + ZPE - E_{constant-shift}^{correction} \quad \text{If}$$

$P\Delta V$ +ZPE contributions cause a constant shift on formation energies, then they will simply be removed

using the correction term, *i.e.*, $E_{constant-shift}^{correction} = P\Delta V + ZPE + E_{other}^{correction}$. Adding in (or not) the $P\Delta V+ZPE$ contributions to O_2 gas therefore will not make a difference while benchmarking experimental and theoretical formation energies of main group oxides. Note that once $E_{constant-shift}^{correction}$ is determined, oxidation enthalpies (of transition-metal oxides) are also shifted by the same amount, hence cancelling any impact on $P\Delta V+ZPE$ on the identification of optimal U values.

However, we did include both $P\Delta V$ and ZPE contributions to accurately calculate the bond energy of the O_2 molecule.

Convergence of total energy

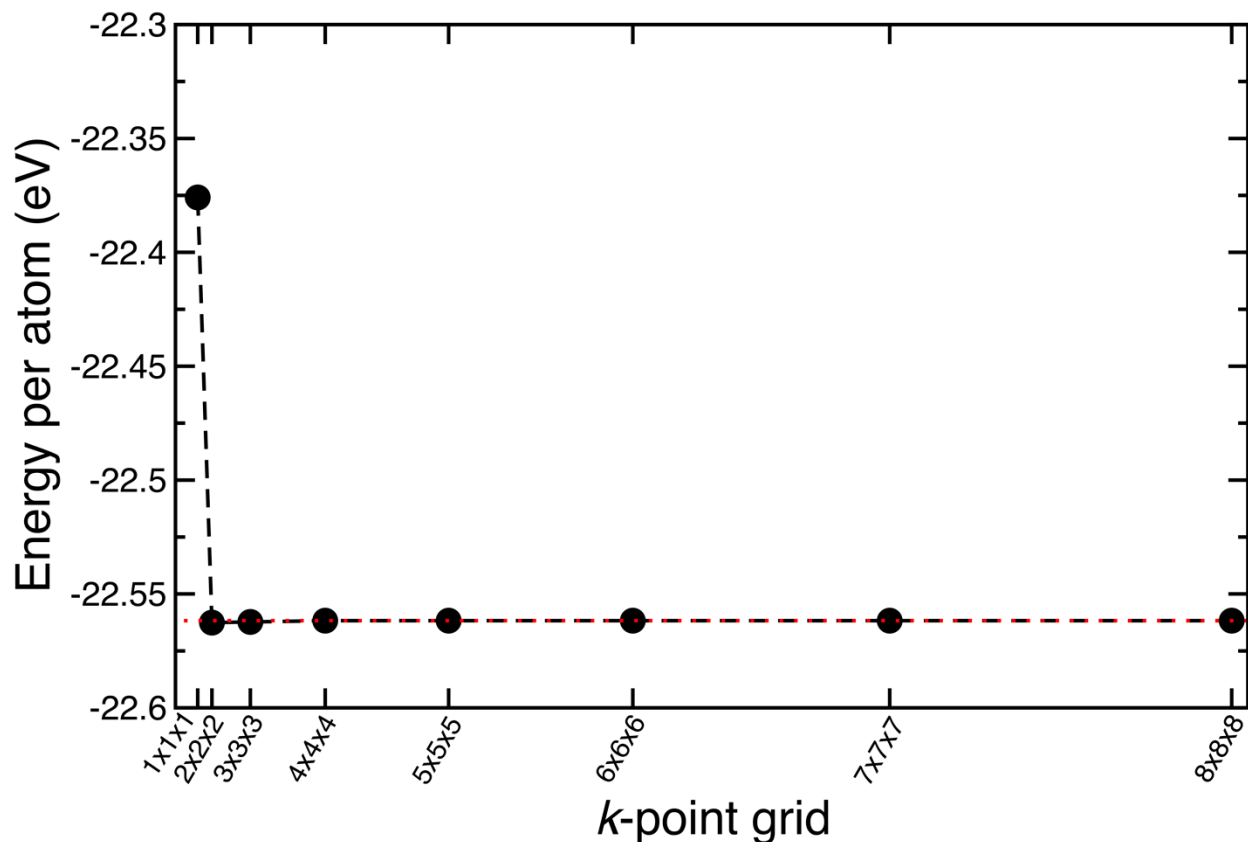


Figure S1: Convergence of total energy (in eV per atom) with increasing k -point grid size in CeO_2 . Total energies correspond to SCAN+ U calculations with $U_{Ce} = 2$ eV. A k -point grid with a spacing of 0.03 \AA^{-1} in CeO_2 corresponds to $6 \times 6 \times 6$ in the plot.

Density of states in rutile-MnO₂

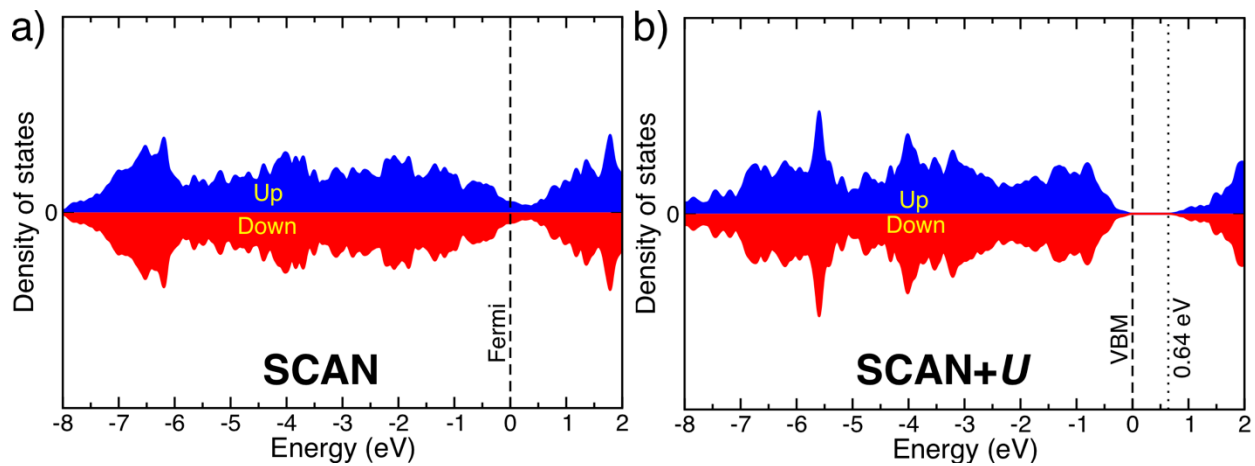


Figure S2: Total DOS in antiferromagnetic rutile-MnO₂, as calculated by DFT-SCAN (panel a) and SCAN+*U* (panel b), where $U_{\text{Mn}} = 2.7$ eV. Shaded blue (red) regions correspond to up (down) electronic spin states. Dashed lines in both panels indicates the zero on the energy scale, which is set to the Fermi level in panel a and to the VBM in panel b. The dotted line in panel b indicates the CBM, which is situated across a ~ 0.64 eV band gap.

PAW potentials used in calculations

We employed the “potPAW.52” set of PAW potentials designed for the PBE functional, which is available with VASP. Note that the potPAW.52 set contains information on the kinetic energy of the core electrons, which is required in SCAN calculations.

Table S1: Elements and their corresponding PAW potentials used in our calculations. The quoted text in the PAW potential column indicates the specific potential file that is available with VASP. For example, “Al” indicates “POTCAR.Al.gz”. The number in brackets indicates the number of valence electrons that is excluded from the core.

Element	PAW potential (valence electrons)
Aluminum	“Al” (3)
Beryllium	“Be” (4)
Calcium	“Ca_sv” (10)
Cerium	“Ce” (12)
Iron	“Fe_pv” (14)
Potassium	“K_sv” (9)
Lithium	“Li” (1)
Magnesium	“Mg_pv” (8)
Manganese	“Mn_pv” (13)
Sodium	“Na_pv” (7)
Oxygen	“O” (6)
Silicon	“Si” (4)

Sample input files for SCAN calculations

The following are sample input files (INCAR files) for VASP calculations involving the SCAN functional for CeO₂ and MnO.

CeO₂

```
#INCAR for CeO2 structure relaxation
ALGO = Normal
EDIFF = 1E-5
EDIFFG = -0.03
ENCUT = 520
IBRION = 2
ICHARG = 2
ISIF = 3
ISYM = 0
ISPIN = 2
ISMEAR = 0
SIGMA = 0.05
LREAL = Auto
NELMIN = 6
NELM = 100
NSW = 99
PREC = Accurate
```

```
#Assuming order of atoms in POSCAR: Ce, O
MAGMOM = 4*0.6 8*0.6
```

```
#SCAN-keywords
METAGGA = SCAN
LASPH = True
```

```
#+U keywords: please remove if only SCAN calculations are needed
LDAU = True
LDAUTYPE = 2
LMAXMIX = 6
#Following +U keywords assume order of atoms in POSCAR: Ce,O
LDAUL = 3 -1
LDAUU = 2.0 0.0
LDAUJ = 0.0 0.0
```

MnO

```
#INCAR for MnO structure relaxation
ALGO = Normal
EDIFF = 1E-5
EDIFFG = -0.03
ENCUT = 520
IBRION = 2
ICHARG = 2
```

```
ISIF = 3
ISYM = 0
ISPIN = 2
ISM EAR = 0
SIGMA = 0.05
LREAL = Auto
NELMIN = 6
NELM = 100
NSW = 99
PREC = Accurate
```

```
#Assuming order in POSCAR: Mn (up), Mn (down), O
MAGMOM = 4*5 4*-5 8*0.6
```

```
#SCAN-keywords
METAGGA = SCAN
LASPH = True
```

```
#+U keywords: please remove if only SCAN calculations are needed
```

```
LDAU = True
LDAUTYPE = 2
LMAXMIX = 4
#Following +U keywords assume order of atoms in POSCAR: Mn,O
LDAUL = 2 -1
LDAUU = 2.7 0.0
LDAUJ = 0.0 0.0
```

References

- ¹ K. Yu and E.A. Carter, *Chem. Mater.* **27**, 2920 (2015).
- ² W. Sun, S.T. Dacek, S.P. Ong, G. Hautier, A. Jain, W.D. Richards, A.C. Gamst, K.A. Persson, and G. Ceder, *Sci. Adv.* **2**, e1600225 (2016).
- ³ R.S. Grev, C.L. Janssen, and H.F. Schaefer, *J. Chem. Phys.* **95**, 5128 (1991).
- ⁴ B. Hammer, L.B. Hansen, and J.K. Nørskov, *Phys. Rev. B* **59**, 7413 (1999).