Exchange-correlation functional challenges in modeling chalcogenides

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Background

Solar power is a crucial component of any plan to mitigate climate change. Kesterite solar cells, based on Cu₂ZnSnS₄ (CZTS), are cheap to produce, nontoxic, abundant, and stable but their efficiencies are limited by defect-induced band-gap fluctuations and carrier recombination.

Research Question

How well does DFT predict the key thermodynamic (bulk and defect formation energies) and electronic properties of kesterite solar cells?

Methods

We calculate bulk/defect formation energies and band gaps using DFT and the following exchange-correlation (XC) frameworks:

• Perdew–Burke–Ernzerhof (PBE)¹
• Strongly constrained and appropriately normed (SCAN)² meta-GGA
• Heyd–Scuseria–Ernzerhof (HSE)³ hybrid functional
• Hubbard U⁴ and vdw⁵ corrections

Results

• Formation energies of charge-imbalanced defects are more sensitive to the choice of the XC functional than those of charge-balanced defects
• Can be explained by the differences in the extent of penalization of defect-generated delocalized electrons/holes by PBE, PBE+U, SCAN, and SCAN+U
• SCAN systematically underbinds Ge-containing compounds, thus highlighting the need for even further improvement of XC functionals

Conclusions

• Current DFT approximations can answer questions such as, “Does ion substitution promote/suppress defect formation?”, but not, “By how much?”
• Possible route to avoid ad hoc Ge corrections → generate SCAN PAW data sets
• Revisit bulk and attempt defect formation enthalpy measurements
• Why does SCAN predict smaller band gaps than PBE?

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References