# Condensed Matter Physics 2018 - Toward Rational Design Of New Photocatalytic Materials For Solar Fuel Generation Using Density Functional Theory -Moussab Harb - King Abdullah University of Science and Technology.

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**Abstract**

The design of new materials with particular fundamental features in relation with solar light absorption, dissociation ability of photogenerated exciton, transport of charge carriers, and their ability to be driven for water redox reactions is of major importance for converting solar energy into clean hydrogen from water splitting.

Although the fabrication of highly crystalline material with a very minimal number of defects is essential, the design of a suitable photocatalyst for good solar-driven water splitting needs at least these four additional challenging fundamental parameters to be present:

(a) Specific band gap energy between 2.0 and 2.5 eV for the good solar photon absorption in the visible region;

(b) high macroscopic dielectric constant (greater than 10) together with low exciton binding energ y for the good dissociation of excitons to free holes and electrons at room temperature;

(c) small electron and hole effective masses along two different crystallographic directions for the good charge carrier transport throughout the crystal lattice together with the low possible electron/hole recombination rate on the surface;

(d) lower valence band maxima (VBM) energy position than the O2/H2O level and higher conduction band minima (CBM) than the H+ /H2 level for driving the generated holes and excited electrons for water oxidation and protons reduction, respectively.

In recent computational works reported on electronic structure features of three-dimensional transition-metal oxide-, oxynitride-, and nitride-based semiconductor materials, we have demonstrated that the use of DFT together with the range-separated hybrid Heyd−Scuseria−Ernzerhof (HSE06)21,22 exchange−correlation functional leads to much more accurate results than those obtained from the standard Perdew−Burke−Ernzerhof (PBE) functional in comparison with experiments.

Our theoretical results obtained in these studies motivated us to carry out a systematic DFT investigation [including the perturbation approach density functional perturbation theory (DFPT)] on essential fundamental parameters for solar energy conversion of a series of large, medium, and small band gap selected materials widely utilized in fuel cells, photocatalysis, optoelectronics, photovoltaics, and dye-sensitized solar devices such as BN, AlN, C, ZrO2, Na2Ta4O11, Bi4Ti3O12, ZnS, GaN, SrTiO3, TiO2, Bi12TiO20, SiC, WO3, TaON, ZnSe, BiVO4, CuNbO3, CdS, AlP, ZnTe, GaP, Cu2O, AlAs, Ta3N5, BP, CdSe, SnWO4, GaAs, CdTe, and Si.

In this paper, we first report the electronic band gaps of these materials by considering the spin−orbit-coupling (SOC) interaction to determine the influence of relativistic effects on the computed band gap of solids containing heavy elements using the standard PBE and the range-separated hybrid HSE06 functionals. Then, we report the VBM/CBM energy levels relative to water redox potentials, the macroscopic dielectric constants, the charge carrier effective masses, and the exciton binding energy of some relevant materials among them using both the PBE and HSE06 functionals. We systematically compared our calculated values with the available experimental data to define an accurate firstprinciple quantum approach to be followed for predicting new suitable materials for visible light-driven photochemical water splitting and helping the experimentalists with a rational design of promising candidates for solar energy conversion applications.

RESULTS AND DISCUSSION

1. Electronic Properties

The computed band gaps with the PBE and HSE06 functionals in comparison with available experimental data of a series of 30 selected semiconductors such as BN, AlN, C, ZrO2, Na2Ta4O11, Bi4Ti3O12, ZnS, GaN, SrTiO3, TiO2, Bi12TiO20, SiC, WO3, TaON, ZnSe, BiVO4, CuNbO3, CdS, AlP, ZnTe, GaP, Cu2O, AlAs, Ta3N5, BP, CdSe, SnWO4, GaAs, CdTe, and Si.

Our obtained values with HSE06 show an excellent agreement compared to experiments with small error percentages in the 0−7% range for large or small band gaps and the 3−6% range for medium band gaps, while those computed with PBE reveal strongly underestimated values by 18−40% for large band gaps, 32−72% for medium band gaps, and 33−47% for large band gaps with respect to the experimental ones.

2. Redox Properties

The computed VBM and CBM energy levels using HSE06 in comparison with available experimental data of eight selected semiconductors largely utilized in fuel cells, photocatalysis, optoelectronics, photovoltaics, and dye-sensitized solar devices, such as ZrO2, ZnS, TiO2, SiC, CdS, GaP, CdSe, and Si. Overall, our obtained values show a very good agreement compared to experiments with small error percentages in the 0.5−2.5% range for the VBM and 0.5−8% for the CBM. The lower accuracy for the CBM computed values with respect to the measured ones

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particularly in the cases of SiC and Si crystals comes from such discrepancy in the predicted band gap energy value, while the predicted VBM values were not affected that much by such a band gap difference.

3.Dielectric and Transport Properties

Obtaining suitable band gap and VBM/CBM energy levels for H+ reduction and water oxidation cannot guarantee whether such a photocatalyst is a good candidate for solar-driven water splitting. Also, it is reasonable to note that the band positions are not a direct evidence for water splitting and modeling catalysis is more direct.

## CONCLUSION

In the work presented here, we have investigated using DFT along with the two standard PBE and hybrid HSE06 exchange−correlation formalisms, essential fundamental parameters for solar energy conversion of a series of large, medium, and small selected (covalent, binary and ternary) materials widely utilized in fuel cells, photocatalysis, optoelectronics, photovoltaics, and dye-sensitized solar devices such as BN, AlN, C, ZrO2, Na2Ta4O11, Bi4Ti3O12, ZnS, GaN, SrTiO3, TiO2, Bi12TiO20, SiC, WO3, TaON, ZnSe, BiVO4, CuNbO3, CdS, AlP, ZnTe, GaP, Cu2O, AlAs, Ta3N5, BP, CdSe, SnWO4, GaAs, CdTe, and Si.

A systematic comparison between the computed values and the available experimental data was also highlighted to confirm the accuracy of these two computational methods.

In conclusion, we have clearly shown that the computational approach based on DFT along with the range-separated hybrid HSE06 reveals very good accuracy in predicting the optoelectronic and redox properties of semiconductors, thanks to precise electronic structure calculations. The use of this firstprinciple quantum methodology led us to provide a rational design of new suitable solid solution materials for visible lightdriven photochemical water splitting. This strategy will definitely be applied to predict and propose promising candidates to the experimentalists for solar-to-chemical energy conversion.

***Bottom Note:*** *This work is partly presented at 5th International Conference on Theoretical, Materials and Condensed Matter Physics on November 26-28, 2018 Los Angeles, USA*

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