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Band positions of Rutile surfaces and the possibility of water splitting

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ABSTRACT

It is well known that both the band gap and the band edge positions of oxide semiconductors are important for the photocatalytic water splitting. In this study, we show that different surface terminations of the same crystalline solid lead to considerable variations of the band gaps and band edges. As an example, we investigate the low-index surfaces of rutile TiO_2. A series of hybrid methods based on the PBE exchange-correlation functional, PBE0, HSE06 and HISS, are employed to study the effect of long-range exchange on the electronic properties. In aqueous solution, the oxide particles employed in photocatalysis are fully covered with water molecules.

We therefore study the influence of molecularly and dissociatively adsorbed water on the band positions. It is found that water adsorption leads to significant shifts of the band edge positions due to changes of the electrostatic potential at the surface atom positions.

1. Introduction

1.1. *Photocatalytical water splitting*

Water is the most important molecule for life on earth. It has also the power to solve the energy problem of the future. Water can be split into hydrogen and oxygen by sunlight on the surface of photoactive materials such as titanium dioxide [1]. The process of water splitting is complex with unsolved questions even after forty years of extensive research [2].

The electrochemical potential required for water splitting into hydrogen and oxygen is 1.23 V. The standard potential of H_2/H_2O is defined to 0 V at a pH-value of 0. Accordingly the potential of the H_2O/O_2 redox couple is $+1.23$ V. The reference is the so-called Standard Hydrogen Electrode (SHE) [3,4].

To compare these values with quantum-chemical calculations which are referring to the vacuum, the absolute potential of the SHE is required. The International Union of Pure and Applied Chemistry (IUPAC) defined its value at 298.15 K to -4.44 ± 0.02 eV relative to the vacuum reference [5,6]. In most experiments the Normal Hydrogen Electrode (NHE) is used as reference. In this work we used the SHE to refer but the deviation of the NHE to SHE is minimal (6 mV) [7].

In real electro- or photocatalytic systems the potential required for water splitting is higher than 1.23 V. Most of the systems have an overvoltage of $0.4-0.6$ V [8,9] and there are thermodynamic irreversibilities in the range of $0.3-0.4$ V [10]. Therefore the optimal bandgap for a photocatalyst is between 1.9 eV and 2.2 eV. The upper limit is due to the fact that an efficient photocatalyst should use a significant part of the sunlight spectrum [11].

In addition to the band gap the absolute position of the valence (VB) and conduction band (CB) relative to the H_2/H_2O- and H_2O/O_2-standard potential is important. The valence band maximum (VBM) resp. the highest occupied crystal orbital (HOCO) should be lower than -6 eV referred to the vacuum. Also the conduction band minimum (CBM) or the lowest unoccupied crystal orbital (LUCO) should be above -4 eV.

Due to the unknown $\mathbf{g} = \mathbf{0}$ constant in the Ewald sum it is not possible to calculate absolute band positions for solids with periodic models [12]. This is only possible for surfaces with two-dimensional periodicity. In plane-wave methods which are in principle three-dimensional periodic also in surface calculations, the averaged electrostatic potential in the center of the vacuum region between the slabs has to be taken as reference for the work function. In LCAO-based methods surface models have two-dimensional periodicity, and the crystal orbital energies directly refer to the vacuum reference.

A distinction must be made between the optical and fundamental band gap for solids and surfaces. The fundamental or electronic gap is the difference between the ionization energy (IE) and electron affinity (EA). The optical band gap corresponds to the energy of the lowest electronic excited states with nonzero oscillator strength. Experimentally the optical band gap is usually derived from extrapolation of measured intensities to zero, e.g. using the Kubelka-Munk function in diffuse reflectance spectroscopy [2].

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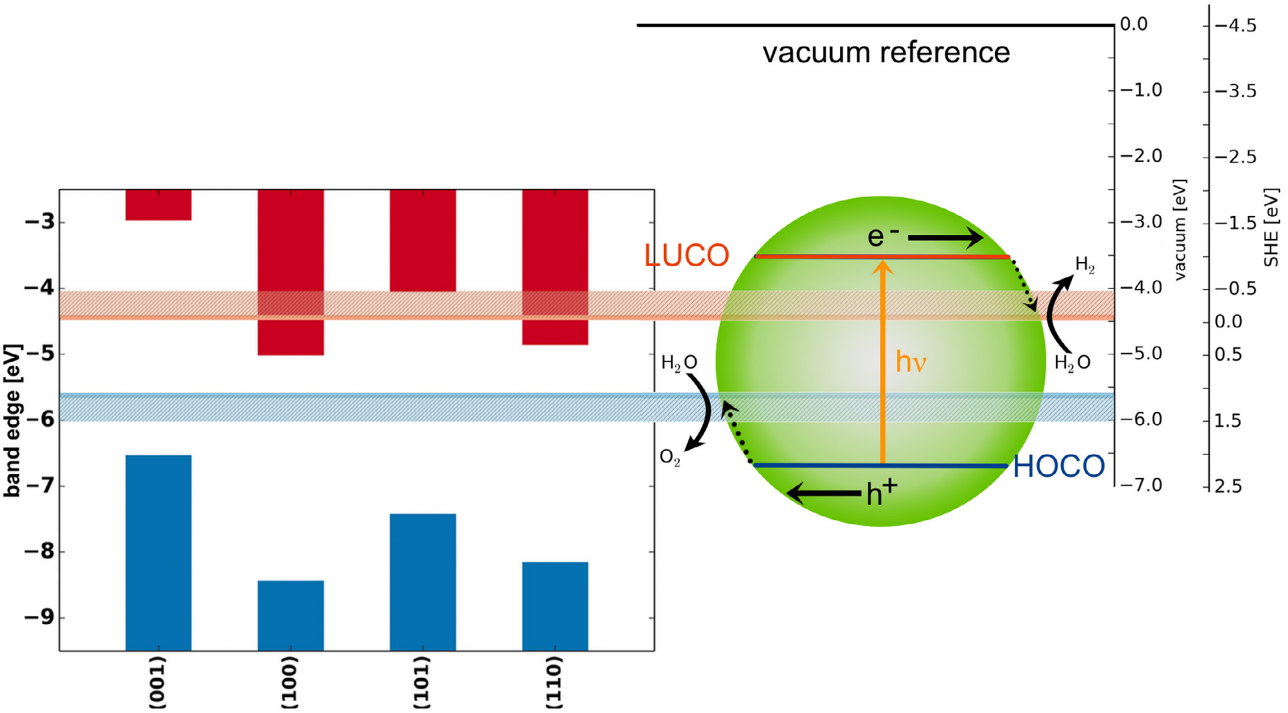

Fig. 1.

According to Baerends et al. the HOCO-LUCO-difference obtained from Kohn–Sham orbital energies in principle corresponds to the optical gap [13]. In practical calculations, however, experimental band gaps of solids and surfaces are often underestimated with the existing density functionals. This effect is more pronounced than for molecular systems. A reason is that nonlocal effects (exchange and correlation terms) have a larger influence for extended systems than for molecules [13]. Within Hartree–Fock (HF) theory on the other hand, IE and EA are approximated by the HOCO and LUCO energies according to the Koopmans theorem. The HF HOCO-LUCO gap therefore in principle corresponds to the electronic gap. In practical however the HF gaps are much larger than the experimental values due to the neglect of orbital relaxation and electron correlation. In order to remedy some of the problems with HF and Kohn–Sham theory, hybrid methods were introduced. The hybrid exchange is a linear combination of HF exchange and V_X^{GGA}. In many hybrid methods the coefficients are determined in a semi-empirical way. An exception is PBE0 [14] where they are obtained from perturbation theory.

A physically more correct method to determine electronic band gaps of solids and absolute band positions of surfaces is the Green-function method combined with screened Coulomb potential (GW). Kresse et al. recently demonstrated for a series of semiconductors and insulators that the self-consistent GW method with vertex corrections ($scGW^{\Gamma}$) gives highly accurate ionization energies [15]. However, this approach is computationally too demanding to be applied for titania surface models with the available computer resources. Therefore we employed DFT-HF hybrid methods for the present study. In a previous study by Carter et al. hybrid methods were used to calculate the band gap center of transition metal oxide surfaces [16]. The quasiparticle band gaps were calculated with the G_0W_0 method and used to determine absolute band edge positions.

In a comparative study of absolute band edge energies of rutile (110) Rubio et al. found that HSE06 provides similar results as scGW for the valence band maximum (VBM) but underestimates the conduction band maximum (CBM) [17].

In 2016 Deak et al. investigate also the clean and water-covered (110) surface of rutile [18].

The present study focuses on the relative band energies of different surfaces of the same material rutile. Thereby we assume that the trends are correctly reproduced with the computationally more efficient hybrid functionals. In order to give an account of the error range introduced by the particular form of the exchange-correlation functional we employed a series of hybrid and range-separated hybrid functionals based of the PBE0 functional.

In a recent study Selcuk and Selloni demonstrated that the (101) and (001) surface of anatase TiO_2 have a different behavior in terms of trapping and dynamics of excess electrons [19]. In the present study we investigate the electronic properties of surfaces of the rutile TiO_2 polymorph.

2. Results and discussion

2.1. Computational details

For all electronic structure calculations the crystalline-orbital program CRYSTAL14 [20] was used. We systematically investigated the effect of exchange contributions on calculated energetic and electronic properties by comparing PBE0 [14], HSE06 [21,22], and HISS [23]. We employed triple-zeta plus polarization basis sets (pob) [24] developed in our group. Surface geometry optimizations were carried out by fully relaxing all atoms of the slab within the symmetry restrictions of the cell, with fixed lattice parameters obtained for the rutile bulk. As it is known that the calculation of Hartree–Fock exchange requires a careful handling of integral thresholds, stricter tolerances were used compared to the standards of CRYSTAL14. The overlap thresholds for the pre-screening of the Coulomb and exchange integrals were set to 10^{-9} and 10^{-18}, respectively. Convergence of total energies with the density of the Monkhorst–Pack k point grid was tested in every case.

It must be noted that CRYSTAL uses a real 2D-system with symmetric and stoichiometric surfaces slabs for surface simulations. No dipole corrections or corrections to the vacuum reference are necessary.