Density Functional Theory Analysis of Transition Metal Doped Thin Film Anatase for Photoelectrochemical Applications

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Density functional theory is implemented with GGA functional to calculate electronic properties of transition metal doped thin film anatase. Properties, such as density of states, optical absorption spectra, partial charge density distribution, molecular dynamics, and relaxation dynamics are all studied to find characteristics of promising materials for photoelectrochemical and photocatalytic applications. These characteristics include decreased band gap, absorption peaks in the visible range, surface centered charge distribution, opposite surface charge for electron/hole during relaxation, long relaxation rates, and varying electron/hole relaxation rates to extend charge separation as long as possible.

As the research as progressed, it is becoming more and more evident that spin unrestricted calculations are needed; that is, separating the spin up and spin down electrons. This process is especially important in materials involving transition metals as many take on high spin configurations. Due to this, one of our main research goals is to incorporate spin unrestricted relaxation dynamics into our research and eventually develop new methods which would calculate noncollinear spin orbit coupling.

Brief Example: Cobalt doped thin film anatase

Figure 1 shows the studied model. A Ti ion is replaced with a Co ion at the surface, which is functionalized with 4 water molecules on both top and bottom. Vacuum space is added along the Z axis and periodic boundary conditions apply in the X and Y directions (repeated units of what is shown).

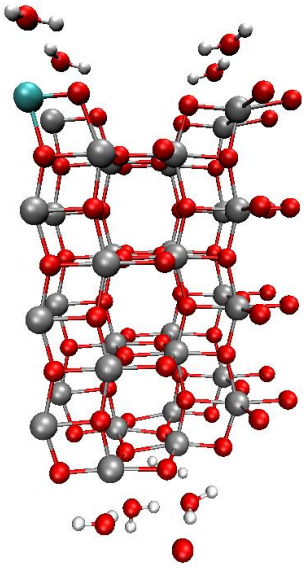


Figure 1: Cobalt Doped Anatase Models where a cobalt ion replaces a Ti ion on the surface in a distorted octahedral coordination. Grey = Titanium, Red = Oxygen, White = Hydrogen, Cyan = Cobalt, Blue = Nitrogen.

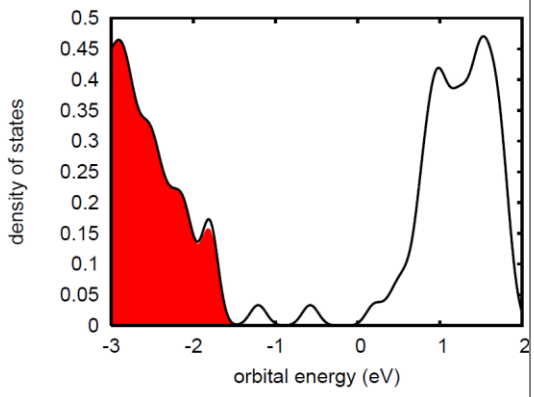
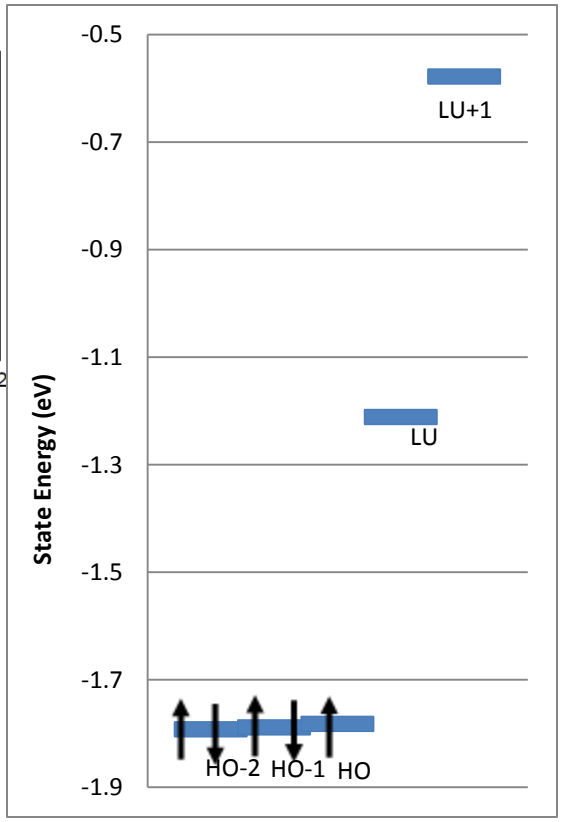


Figure 2: A) Density of States and B) Orbital Splitting of Cobalt States. A) DOS shows empty d cobalt states near the band gap and B shows clear distorted octahedral for Cobalt (IV) with 5 d electrons occupying five d-orbitals.



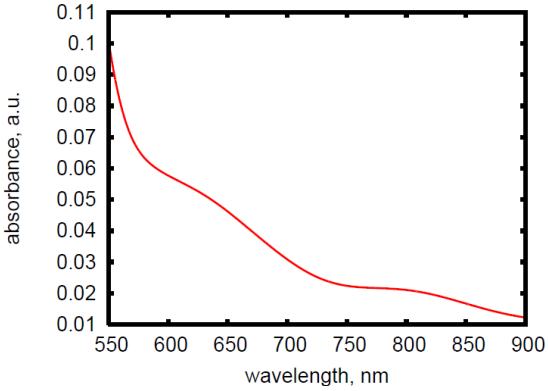


Figure 3: Optical Absorption Spectra shows 2 peaks in the range of 550-725 nm and 725-900 nm.

The density of states and octahedral orbital splitting (**figure 2**) shows cobalt states are empty near the band gap. This indicates that cobalt will most likely be an electron acceptor upon photoexcitation. It also shows the distorted octahedral orbital splitting of the cobalt dopant. The absorption spectra (**figure 3**) shows one shoulder and one peak in the low energy range (~650 and ~775 nm respectively). Molecular dynamics are run after heating the model to 300 K and shown in **figure 4**. The states around the band gap are attributed to cobalt d orbitals and have much larger amplitudes of energy fluctuation; this is most likely due to isolation of the cobalt ion as it is unable to transfer energy to other ions as oxygen and titanium do quite easily.

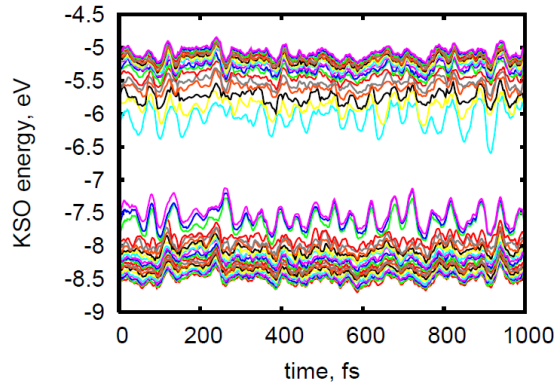
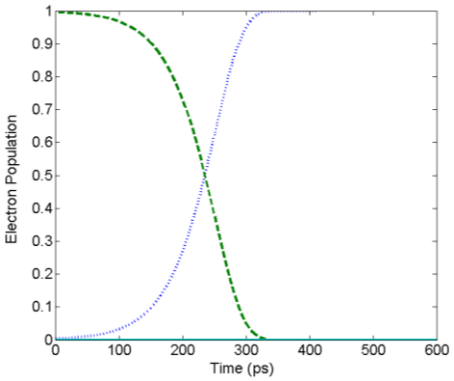


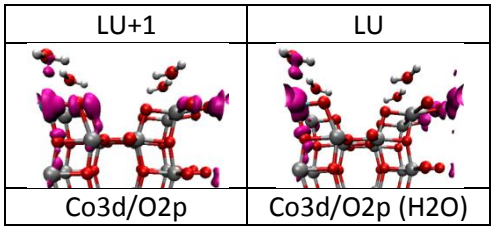
Figure 4: Time Evolution of Orbital Energy Monitored along Adiabatic Molecular Dynamics The c states due to cobalt have much higher amplitudes of fluctuation most likely due to the spatial isolation of the dopant ion.

Non adiabatic relaxation dynamics are shown in **figure 5**. The first typical transition for surface ingrained model, HO-15 → LU+1, occurs when an O2p electron is excited to an empty Co3d state. After excitation, the electron occupation only occurs in two states, LU+1 and LU, as shown in **figure 5A**. The hole occupation occupies many states (HO-15 to HO) and does not contain a trapping state but does spend considerable time in HO-4, HO-3, HO-2, and HO-1, as shown in **figure 5B** by large peaks right before the final orbital. The states are within 0.1 eV of the HO so they are not considered trapping states, but rather transitioning states when the hole travels from O2p in the thin film to Co 3d dopant states. A combined image of dynamics for electrons and holes as a distribution of energy is shown in **figure 5C** and shows a mixed state where the electron is located on both LU+1 and LU. The hole travels quickly from HO-15 to aforementioned transition states, but these states are indistinguishable due to the energy closeness of the states. A visual representation of the charge dynamics in space shows the hole is within the anatase thin film, the oxygen atoms, and the electron on the cobalt dopant; once the hole reaches the cobalt dopant, recombination is expected to occur. The electron excitation to a Co state provides charge separation with negative charge on the Co ion and disperses the positive charge with in the anatase thin film (**figure 5d**). This charge separation can be exploited to use the negative charge on the surface for catalysis applications.

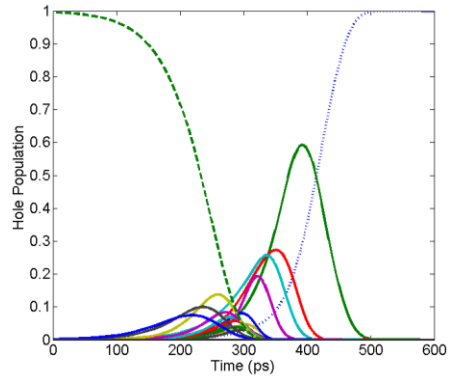
Initial ground state calculations of the density of states indicates the model is most likely to act as an electron acceptor. It is found transitions for the low energy peaks of the optical absorption spectra are p→d transitions. After heating the model to 300K, nonadiabatic molecular dynamics show the spatial isolation of the dopant ion has larger amplitudes of fluctuation. Nonadiabatic relaxation dynamics confirms that the dopant acts mainly as an electron acceptor. This information is useful as a negative charge can be focused at the surface of the model upon photoexcitation at the wavelengths shown in the optical absorption spectra peaks, and henceforth be used for photocatalysis.

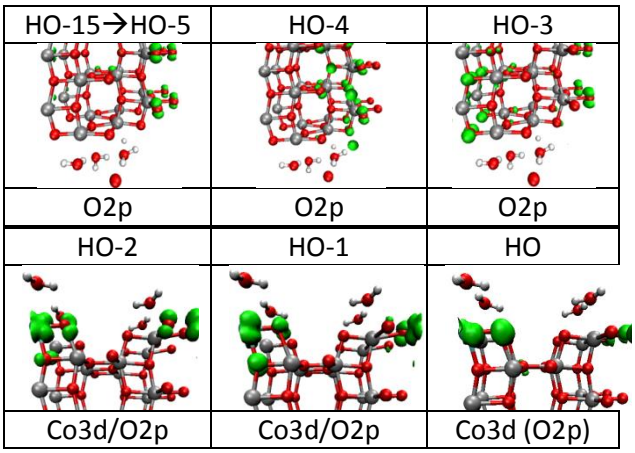
A) Electron Population vs. Time



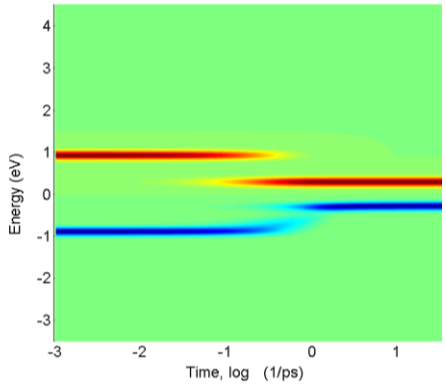


B) Hole Population vs. Time





A) Change in Energy vs. Time of Electron/Hole



B) Charge Distribution along the Z axis vs. Time

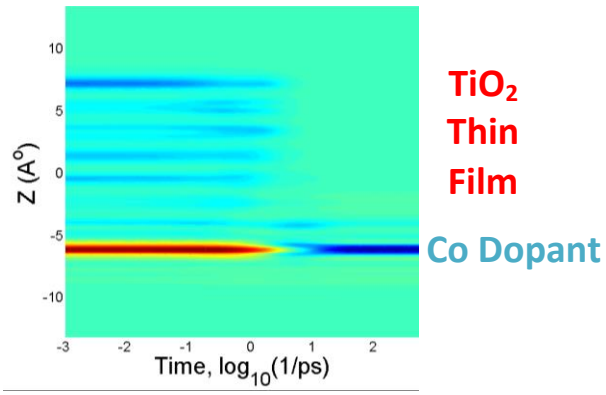


Figure 5: Relaxation Dynamics for Surface Ingrained Model for HO-15 → LU+1 Transition (Co as electron acceptor)
A shows the change of electron population vs. time (where the dashed line is the initial occupied orbital and the dotted the final as well as partial charge density images of involved states. **B** shows the same information as **A**, but with hole population. **C** shows how the electron/hole change in energy vs. time, while **D** shows change of charge along the z axis with time. The excitation occurs when an O2p electron is excited to an empty Co3d state. Both electron and hole relax to states of the cobalt dopant ion, which is why **D** shows the cobalt dopant having negative then positive charge; the hole takes longer to get to HO than the electron to LU as seen in **A** & **B**. Color code is interpreted as Green = No Charge, Blue = positive charge (hole), Red = negative charge (electron)