Correction to "Localized Electronic States from Surface Hydroxyls and Polarons in TiO$_2$(110)", "Defining the Role of Excess Electrons in the Surface Chemistry of TiO$_2$", and "Distribution of Ti^{3+} Surface Sites in Reduced TiO$_2$"

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We have became aware that in a series of papers[1−4] utilizing density functional theory (DFT) to model TiO$_2$ surfaces we reported erroneously the nature of the atomic basis set for Ti used in some of the calculations, a double-ζ basis set when in fact we used a single-ζ basis set when applying the DFT+U method.[5] The purpose of this erratum is to correct our error. We also report data that suggest that the conclusions stated in these papers hold true.

In refs 1 and 2 dealing with excess electron localization associated with defects (surface hydroxyls, charged polarons, and oxygen vacancies) we utilized DFT+U for the entire studies, and the calculations were performed with a single-ζ basis set on Ti. Double-ζ basis sets were used for other elements as well as for Ti when using conventional DFT (non DFT+U calculations). In ref 3 dealing with substrate-to-adsorbate charge transfer we used conventional DFT for the majority of calculations. Those were carried out with a double-ζ basis set for Ti. A few calculations used DFT+U, and those were carried out with a single-ζ basis set for Ti.

For our electron localization work[1,2] we predicted that electrons at Ti^{3+} centers preferentially localize at subsurface sites over surface sites. Use of both single-ζ and double-ζ basis sets leads to electron localization. The single-ζ basis set for Ti allowed control of the final location of the Ti^{3+} site. This was important as we were systematically comparing the stability of many Ti^{3+} centers (i.e., surface and subsurface sites). Localization of an excess electron to a designated Ti atom is possible with a double-ζ basis set but would have required many intricate attempts before converging to a wave function with the correct character. Ultimately we determined that a large number of states are nearly degenerate in energy, indicating that the electrons are in thermal equilibrium across an ensemble of electronic states at finite temperature and a large fraction of these states are subsurface. Similar conclusions were obtained by other authors[6−8] using planewave basis sets, as well as from experiment.[9−12] Our other work[3] examined how surface reduction affected surface adsorption and was largely based on DFT calculations with a double-ζ basis set for Ti. We used DFT+U and a single-ζ basis set for Ti to assess how increased electron localization (due to the U potential) affects electron transfer to adsorbates. Other work[13] examined surface reduction and adsorption over group 4 metal oxides and obtained similar conclusions using double-ζ basis sets with both DFT and DFT+U.

We have recently examined the effect of the Ti basis set on adsorption energies for several adsorbates using both single-ζ and double-ζ Ti basis sets (see Figure 1). For all of the
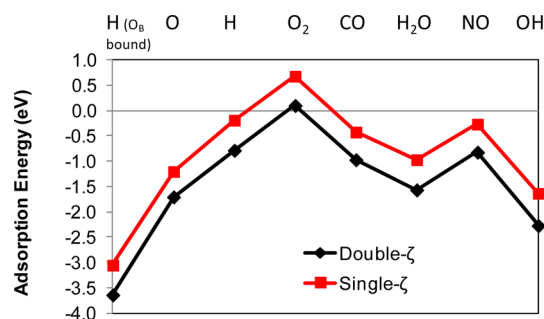

Figure 1. Comparison of adsorption energies for several adsorbates over the rutile (110) surface using single-ζ or double-ζ basis sets for Ti. All adsorbates are bound to a five-coordinated Ti atom, except for the one case of a H atom bound to a surface bridging O atom (O$_B$).

adsorbates, the difference in adsorption energy between the single-ζ and double-ζ Ti basis set calculations is ∼−0.5 eV, indicating that a double-ζ basis set binds molecules more strongly compared to a single-ζ basis set. The use of a single-ζ basis set introduces a systematic error (∼0.5 eV) in adsorption energies. This error, however, does not change the qualitative conclusions of our previous study.[3] Furthermore, in one of our papers[14] we compared the effect of basis set choice for Ti on the H diffusion from a surface of TiO$_2$ into bulk. We found the diffusion energies to be nearly identical when using single-ζ and double-ζ basis sets for Ti.

In summary we believe that the findings reported in our papers hold qualitatively true in spite of the use of a single-ζ basis for Ti in the DFT+U calculations.

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