Modeling excited states in $(TiO_2)_4$: TD-DFT and recombination times

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Abstract

The following manuscript describes the short project I conducted for the Excited States and Nonadiabatic Dynamics CyberTraining Workshop. It corresponds to a application of a Libra/CP2K workflow for analysing the excited states of 4-size titania (TiO_2) nanoparticles (NPs). Libra software was thoroughly detailed during the first two days of the workshop, putting special attention to its use interfaced with CP2K for obtaining TD-DFT excitations and conducting calculations of trajectory surface hoping (TSH) nonadiabatic Moleular Dynamics (NAMD). The reason behind studying titania lies in its use as photocatalyst for water splitting procedures, as detailed in the following section. I've been working with titania systems for more than two years now (during my PhD), designing new finite systems of stoichiometric NPs and exploring their structure and ground-state properties when interacting with water. The study of excited states with NAMD represents a very appealing and promising field of study that will take my research one step further into the design of future photocatalysts for water splitting.

Keywords titania, nanoparticle, photocatalysis, TD-DFT, NAMD, TSH

1 Introduction

Among the metal oxides, titanium dioxide (TiO_2) -or titania- has gained considerable attention over the last decades in the field of photocatalysis due to its unique electronic and optical properties.[1, 2, 3] Titania is abundant, chemically stable, non-toxic, and inexpensive, making it an attractive candidate for various environmental and energy applications like air[4] and water purification[5], organic pollutant degradation[6] or production of H_2 as green fuel.[7]

As a wide-bandgap semiconductor, titania can absorb ultraviolet (UV) light and generate electron-hole pairs that can be used for redox reactions on its surface. In this way, since the seminal discovery than titania can catalyse the splitting of water into hydrogen and oxygen when exposed to UV light[8], the combination of TiO_2 and water has been established as a reference system for investigating the fundamental principles that underlie a wide range of photocatalytic processes. A lot of attention has gone specially into titania anatase crystal polymorph, which, even if is not the most stable one among the titania polymorphism (rutile is[9]), it is the one most used as efficient photocatalyst for water splitting, due to its high surface area, high photoactivity, and favourable energy band structure.[8]

Light activates the photocatalyst promoting the generation of electrons and holes, charged species needed to the generation of H_2 and O_2, the main products resulting from the water splitting. One of the main limitations of this complex process resides in the short lifetime of such photogenerated species and somehow constitutes one of the rate-limiting steps in any photocatalyzed process. Therefore, understanding and working on charge carrier recombination dynamics is of key importance for tuning and enhancing the photocatalyst performance. To this end, nonadiabatic Molecular Dynamics (NAMD) computational implementation is commmonly trusted as suited technique to investigate the properties of excited states.

In this way, I perform here a short study with $(TiO_2)_4$ as test-study. I explore the use of either classical (force fields) or more expensive ab-initio (DFT) approaches for performing the Molecular Dynamics (MD) and getting the trajectories used to compute the system excitations. Speaking of which, I introduce here again two possibilities: using either a semilocal or a hybrid functional for describing said TD-DFT excitations. Thus, I have followed a total of four different methodologies before running nonadiabatic dynamics. I analyze the use of each of the methods in the different outputs generated through the workflow with the final goal of getting some insight into recombination dynamics of my small NP. However, since it is my first full completed workflow, some problems and strange results sprout out for some of the methods. My goal is to end up understanding all these results and be able to apply this methodology to larger titania NPs (with and without water) of different shapes and morphologies and be able to design future high-efficiency titania photocatalysts for watter splitting and sustanaible hydrogen production.

2 Computational Details and Methodology

Fig. 1 represents a general schematic view of the different steps comprising the Libra[10]/CP2K[11, 12] workflow, ending with the calculation of the decay (and recovery) times of the different excited states.

First of all, Molecular Dynamics (MD) simulations were performed to obtain a 2 ps trajectory at 300 K of our structure of bare $(TiO_2)_4$ NP. This structure (Fig. 2) was previously globally optimized in my research group. Two codes were employed for the subsequent MD simulation: GULP4.4[13, 14] package for running classical MD imple-
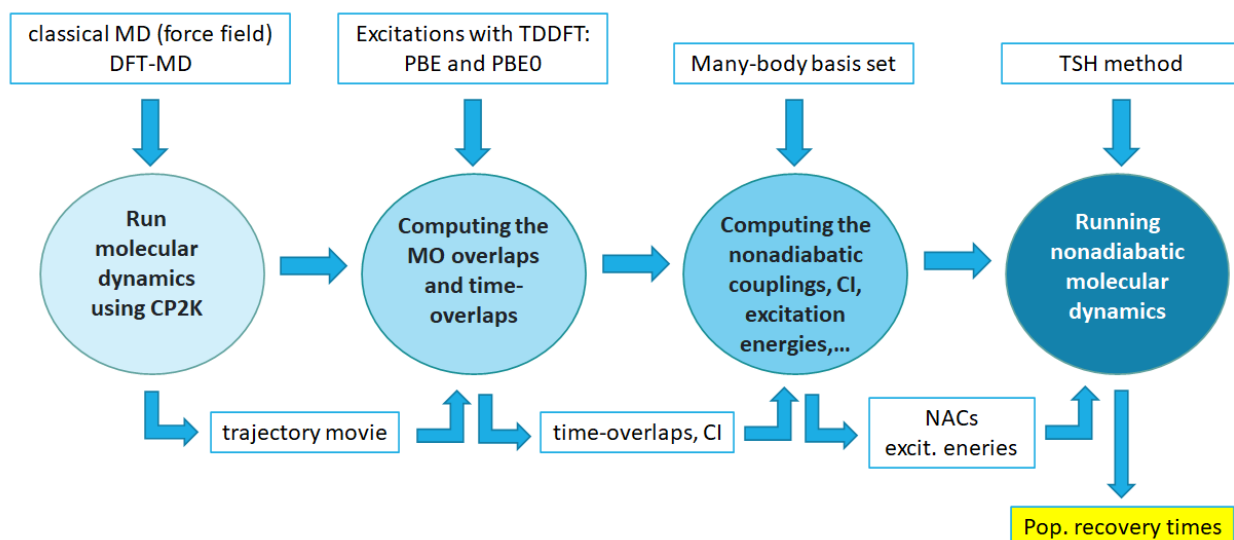
Figure 1: Schematic representation of the Libra/CP2K workflow

menting a NanoTiO interatomic potential (IP)[15]; and CP2K for performing ab-initio MD using DFT. In the latter case, the electronic exchange and correlation is treated using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation.[16] The valence electrons are described by the mix of the localized double-zeta-valence-polarized (DZVP) basis set[17] and the plane-wave basis selected with a charge density cutoff of 300 Ry. The core electrons for Ti and O are described using Goedecker-Teter-Hutter (GTH) pseudopotentials[18]
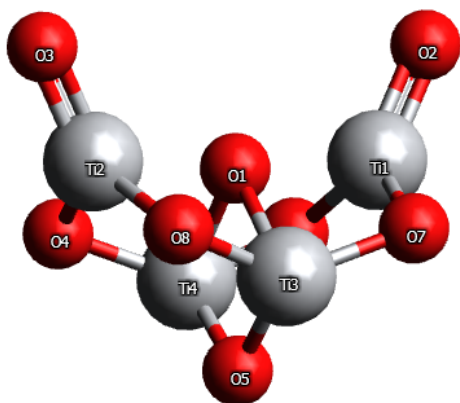

Figure 2: $(TiO_2)_4$ globally optimized structure

The MD trajectories obtained following these two procedures are then used to compute the MO overlaps and time-overlaps in the step 2 of the workflow, relying on the "Gaussian cube-file"-based approach[19] within CP2K. Linear-response TD-DFT calculations are trusted in order to perform our excited states analysis. We use semilocal PBE and hybrid PBE0 (that includes 25% of the exact exchange energy from Hartree-Fock theory) functionals in this step, exploring 10 different

excited states. I note here that we have conducted therefore 4 different methodologies leading to our excited states calculation: (i) classical IP MD + PBE TD-DFT; (ii) IP MD + PBE0 TD-DFT; (iii) ab-initio PBE MD + PBE TD-DFT; and (iv) PBE MD + PBE0 TD-DFT.

In step 3 of the workflow, we compute the nonadiabatic couplings (NACs) between different pairs of excited states. These states can be either Kohn-Sham states or single-particle or many-body excited states. We are working here at the Many-body level, as we will later justify.

Finally, in step 4 of our workflow we run nonadiabatic molecular dynamics using the computed nonadiabatic couplings (NACs) in the MB bases and the average excitation energy of the excited states over the MD trajectory. The Neglect-of-BackReaction Approximation (NBRA) is trusted[20, 21, 22] and NADruns are propagated through 1000 fs. For each nonadiabatic simulation, 40 realizations (each one with different initial conditions) of the stochastic TSH trajectories are used. We calculate properties of interest- in our case the population recovery times- based on an average of the total number of trajectories. As for the TSH algorithms, we consider the FSSH (Tully's fewest switches surface hoping).[23] We leave the introduction of decoherence for future research.

3 Results and discussion

Excited sates of nanoscale systems and periodic solids are (nearly) always multiconfigurational so a single particle description -a single electron configuration- of our states would be inadequate most of the time. Therefore, excited states require a description based on a combination of different configurations, each representing a different arrangement of electrons in the MOs. These configurations contribute to the overall wavefunction of the excited state, and their combined effects give rise to the observed properties and behaviour of
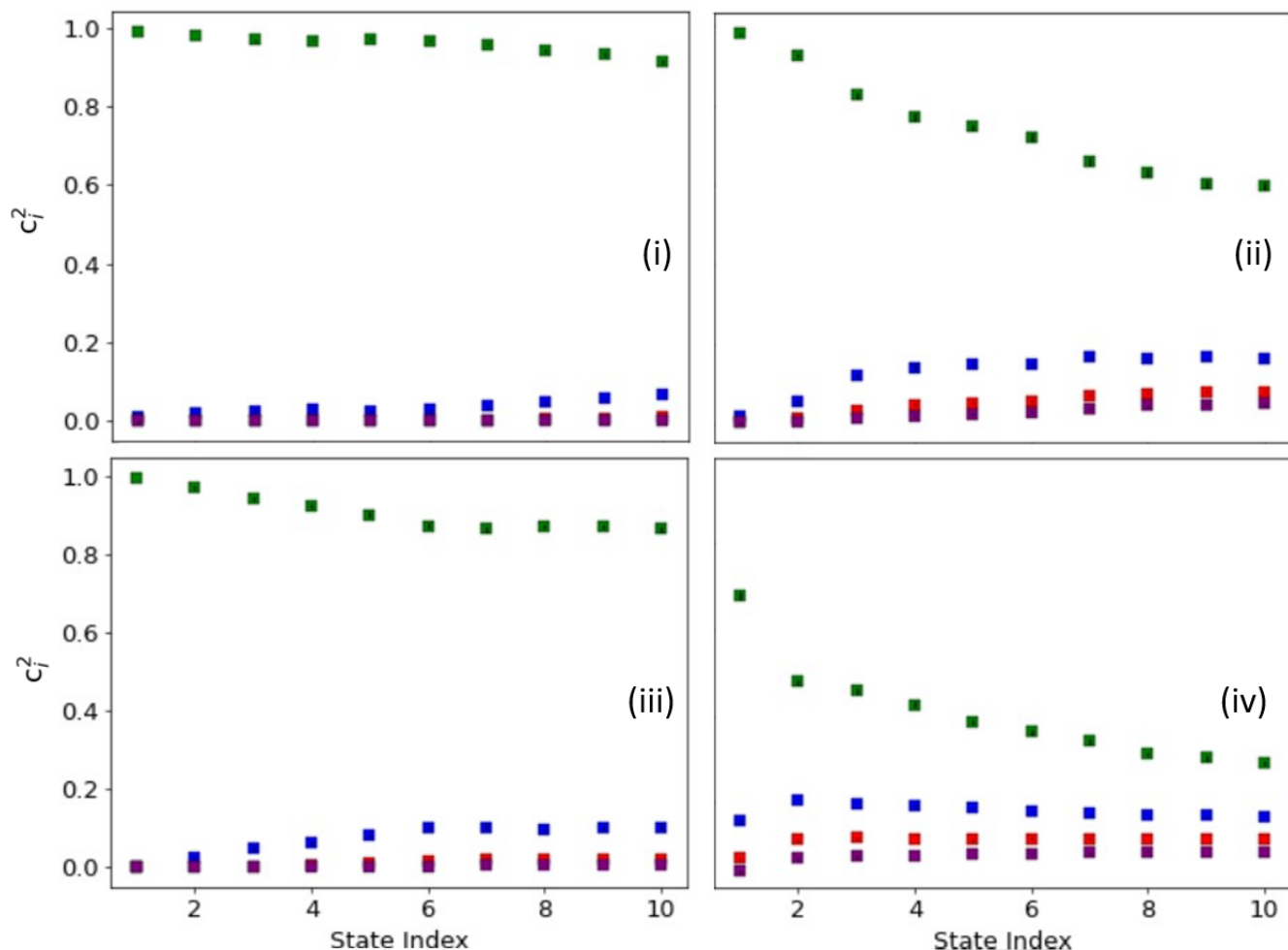
Figure 3: Squares of the four largest CI coefficients (green-blue-red-purple) for each of the considered 10 excited states and for the 4 ((i),(ii),(iii),(iv)) methodologies.

the system in that state. In this way, Many-body effects play an important role in quantum-confined systems, and it is key to account for these effects in nonadiabatic dynamics simulations, using thus many-body basis sets. In this MB representation, the composition of the excited states is quantified by the squares of the configuration interaction (CI) coefficients.

TD-DFT has been used as a not-too-expensive-option to account for MB effects thanks to the introduction of a time-dependent exchange-correlation functional (PBE and PBE0 in our case). Fig. 3 shows the squares of the four largest CI coefficients for each of the considered 10 excited states and for the 4 ((i)-(iv)) methodologies. In the left-hand side plots -for which TD-DFT excitations were performed relying on the exchange-correlation PBE functional- we see similar evolution of the coefficients: a single SD excitation dominance that starts to slowly break down as we consider higher excited state indexes. We don't see major differences between using classical or AIMD for generating our trajectory files -which is always a good argument towards the use of classical MD. The use of PBE0 for computing the TDDFT excitations highlights the multiconfigurational nature of our excited states. In these two (right-hand side) cases the single particle approximation shouldn't be trusted to model the

excited states dynamics (even for lower excitation energies). This is specially prominent in the right bottom figure (trajectory enerated with AIMD), for which the most prominent single electron configuration contribution is no larger than 75%.

We can move on now to the excitation energy evolution of these 10 states. Fig. 4 shows a propagation of these energies in the first 500 fs of out simulation. The use of PBE0 functional clearly leads to higher energies, animprovement on the description when compared to semilocal functional such as PBE. GGA functionals tend to underestimate the highest occupied molecular orbital, and thus the the charge-transfer excited state energy. We also note a common upshift due to the use of AIMD for preparing our trajectories.

Lastly, we depict in Fig. 5 the population recovery of ground state for our methodologies (i) and (iii). Unfortunately, calculations involving PBE0 as TDDFT exchange-correlation functional yield strange results that need further exploration. Sticking to the two PBE-TDDFT methodologies we see a longer recovery time in the bottom figure associated to the use of AIMD for obtaining our structure.
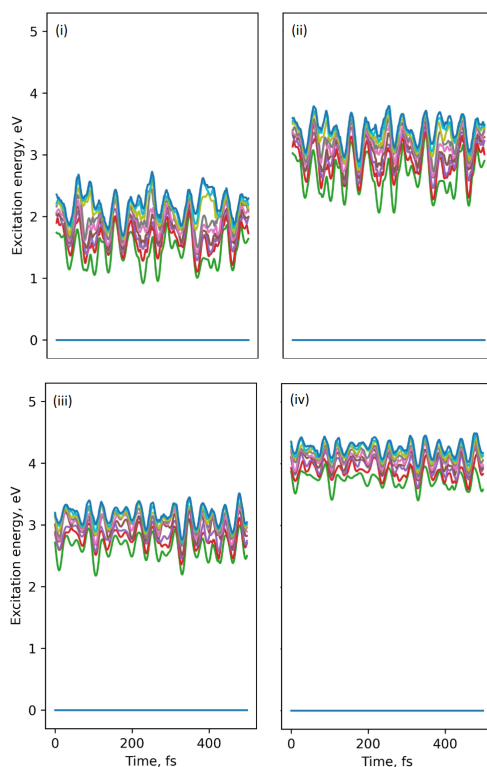
Figure 4: Calculated excitation energies evolution of the 10 considered excited states

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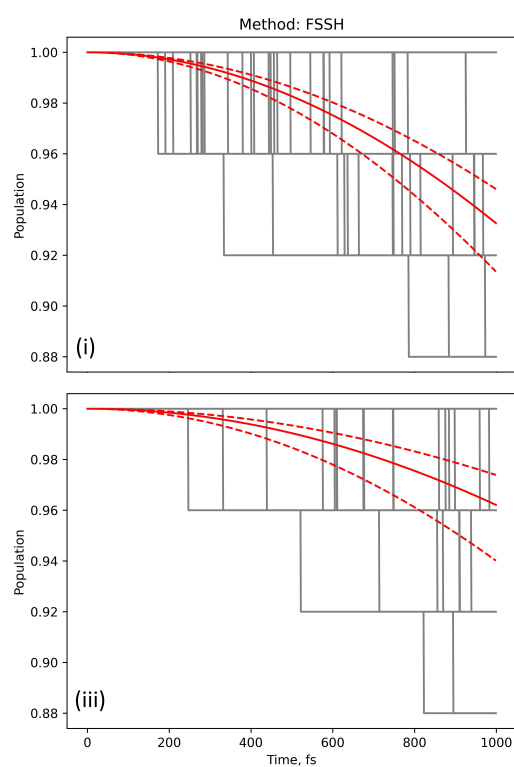
Figure 5: Decay of the total population of the excited states to the ground state