

Characterization of TiO₂ Atomic Crystals for Nanocomposite Materials Oriented to Optoelectronics

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Abstract—Atomic cluster (TiO₂)₃ is studied by means of state of the art techniques for structural, electronic and optical properties. We combine molecular dynamics, density functional theory, time dependent density functional theory and many body techniques, to provide a deep and comprehensive characterization of the system. Atomic clusters can be considered the starting seeds for the synthesis of larger nanostructures of technological interest. Also, given the complexity of the material itself, a clear theoretical description of its basic properties provides interesting results both from the solid state physics and chemistry point of view.

Keywords—component; *ab-initio* excited states; atomic clusters

I. INTRODUCTION

Titanium dioxide is one of the materials under most active investigation since many years, in its different crystalline phases and morphological nanostructured shapes. It is widely used for several technological applications, as in the fields of biocompatible materials, gas sensors, photocatalysis, photovoltaics and energy storage. A consistent number of experimental and theoretical works appeared up to now in the literature, contributing to important progresses in the knowledge of the physical and chemical properties of bulk phases, surfaces, and nanostructures. The modelization, via different computational approaches, of the material, presents however important drawbacks. Standard Density Functional Theory¹ (DFT) can be successfully applied to describe structural properties of the material, and energetic behaviours, also connected to catalysis², are well described by DFT. But, as soon as one moves to properties involving excited states, as in photocatalysis and photovoltaic applications, relying on DFT is not sufficient to correctly describe the electronic and optical

properties. The electronic description is definitely improved if more refined quantum chemistry or many body techniques, such as GoWo method³, are used, because in these approaches excited states are explicitly taken into account. A proper optical description should need, on the other side, the inclusion of interaction among excited electrons and holes. Such effects are embedded in Time Dependent DFT⁴ (TDDFT), or in many body treatments as BSE solution.³

II. COMPUTATIONAL APPROACH

A. Ground State Properties

On the most stable structure obtained with molecular dynamics, DFT electronic properties calculations were performed with the plane waves pseudopotentials code Quantum Espresso⁵. As shown in Fig.1, the HOMO wavefunction is mainly localized on Oxygen atoms, while the LUMO is given by Titanium atoms, on the opposite side of the

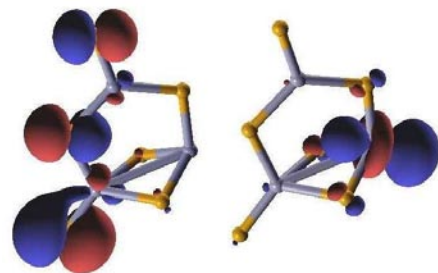


Figure 1. Geometry, HOMO and LUMO via DFT of (TiO₂)₃.

molecule.

B. Electronic and Optical properties.

Many-body calculations in the PW-PPs framework have been performed with the code Yambo.⁶ The code relies on DFT eigenvalues and eigenfunctions calculated from previous ground-state calculations with Quantum-Espresso. A cell of 40 a.u. side has been used, and to ensure convergence on vacuum, a Coulomb cutoff has been applied. The G_0W_0 value has been converged towards number of PWs, empty bands, and dimension of dielectric matrix which inverse is used in the W evaluation. A cutoff of 12 Ry, and 5000 PWs are used for screening matrix inversion. The number of empty bands is 300, and calculations are done at Gamma point. Optical calculation by solving the Bethe Salpeter equation is performed with a cutoff of 20 Ry, 3500 plane waves for local field effects, and by including the coupling term.⁷

III. RESULTS AND DISCUSSION

The G_0W_0 gap is of 7.07 eV, that is 5.65 eV larger than the Kohn-Sham gap, and more than 3 eV larger than the correct bulk value. This result has to be expected, due to the strong quantization effects acting on the molecule. The electronic gap is also definitely larger than the optical gap, reported in the following, due again to the strong electron-hole interaction acting in a localized system. Two methods have been used, BSE and TDDFT, to investigate the optical absorption spectrum. Usually, the optical gap is larger than the Kohn-Sham gap, but for inorganic clusters it has already been reported⁷ that the effect of TDDFT calculations can be not a shift of the absorption edge, but instead a redistribution of spectral weights, resulting in an overall energy blue-shift of the spectrum. This blue-shift is due to the localization induced on states by the molecular nature of these systems, which are actually closer, for dimension, to inorganic molecules than to

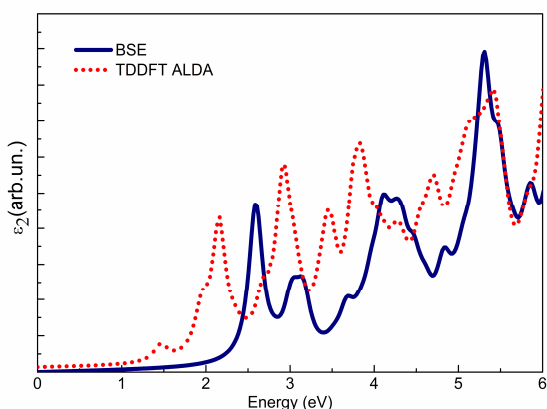


Figure 2. Optical absorption spectra of $(\text{TiO}_2)_3$, via BSE and TDDFT.

solid systems. Also, the presence of strong charge transfer effects, not described by TDDFT, can contribute to the observed behaviour. In the TDDFT spectrum, the first transition, with a low oscillator strength, is at 1.5 eV, and the first more intense optical transition is at 2.1 eV. On the other side, the BSE spectrum gives an allowed transition at 2.5 eV. So, in the two approaches, the transitions present different energy and different nature, being of different intensity.

IV. CONCLUSIONS

We show one example of application of many body techniques to inorganic molecules. The electronic gap, to be compared with photoemission data, is 7.07 eV, due to the strong quantum confinement of this atomic-size system. The optical gap, intended as the first optically allowed transition, is instead quite smaller than the electronic one, being in the range 2.1-2.5 eV. Well defined optical peaks can be identified. The inclusion of many body effects, explicitly treated in the Bethe Salpeter equation, on one side confirms the range of optical gap calculated with TDDFT, on the other side, introduces more refined description of charge transfer phenomena, which could affect excitonic distribution in such material.

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