Titania nanostructures electronic and optical response

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ABSTRACT

TiO$_2$ nanomaterials are object of strong research interest for their promising performances in photocatalysis, photovoltaics and gas sensing. Investigating the microscopic nature of their opto-electronic properties is a fundamental prerequisite for rationalizing experimental data and improving devices performances. First-principle excited states methods, based on Many-Body Perturbation Theory on top of Density Functional Theory calculations, provide a reliable tool to identify, explain and predict specific behavior related to the electronic and optical properties of nanostructures, that can be hidden in the experimental processes.

Examples of titania nanostructures (clusters, reconstructed surfaces, and nanosheets, also related to nanotubes and nanowires) are analyzed, and the relationship among structure and electro-optical behaviour is clearly highlighted. Strong excitonic effects, explaining photoexcited processes, are observed in all considered nanostructures.

I. INTRODUCTION

The importance of titanium dioxide in a range of technological applications from catalysis and photocatalysis to solar energy conversion and gas sensors is testified by the large and increasing number of publications on the subject. 1-5

Several lines of research are focused to improve the present devices performances, among others the study of the role of nanostructuring, the investigation of defects influence on the devices response, and of the extrinsic doping effect in improving transport and modifying the absorbance and other related characteristics with respect to the intrinsic material.

In particular in recent years nanostructured TiO$_2$-based materials, such as nanocrystallites, nanofibers, nanosheets, and nanotubes, are emerging as good candidates for devices realization, due to the enhancement of the available surface area and to the improvement of their photochemical and photophysical activities. 3, 6

Most of the applications involving titanium dioxide as photo-active nano-material are based on the creation of excitons and on the flow and collection of electrons and holes. In this perspective, the knowledge of the interaction of TiO$_2$ with an incoming electromagnetic wave and of the electronic excited states is of fundamental importance.

The numerous experimental investigations provide important information on the characteristics of excitations in TiO$_2$ based materials, useful for predicting the properties of newly designed (nano)devices. Nevertheless, very often the experimental efforts are dictated by a trial-error approach and the pursue of nanoscale optimization is solely justified by the observation of higher overall efficiencies of the photoreactions when scaling down the size of TiO$_2$ moieties, while a complete understanding of the microscopic related phenomena is far from being reached.

Clearly the ability to determine the exact atomic arrangements as well as the related electronic and optical properties is a crucial point for future progress in applications. From experimental point of view one of the most evident difficulties is to control, during the synthesis process, the crystal phase, the geometrical structure and other most complex aspects such as defects presence and intrinsic doping, and to relate these properties to a specific response of the system.

In this regards the theoretical investigation is playing a crucial role to enlarge the fundamental knowledge of TiO$_2$ microscopic properties related to photo-excited processes and consequent improvement of devices performances, and to guide the experimental studies towards a more optimized and focused research path.

As many of the measured results and devices performances depend on the synthesis conditions, presence of
defects, dopants and codopants, and size and shape of structures, unbiased calculations can provide a unique and very powerful instrument to control and design properties of these new nano-oxide materials.

In particular, regarding the structural characterization of nanostructures, several models based on Wulff and surface area constructions have been proposed,

while regarding the investigation of their electronic properties, models based on effective mass approximation for band transport, carriers density and mobility and quantum size confinement effects\textsuperscript{8,9} have been very often used, although their outcomes and applicability have been extensively debated for TiO\textsubscript{2} nanomaterials.

Only in the last years, increasing successful efforts started to model both structural and electronic properties of such complex materials by reliable first-principle methods, mainly based on the density functional theory (DFT)\textsuperscript{10} within the Kohn-Sham (KS) single-particle equations scheme\textsuperscript{11}.

In spite of the theoretical strictness and the unpaired ability to offer a pure first-principles approach when dealing with the ground state energetic and electronic properties of whichever polyatomic system, the DFT main shortcomings are essentially ascribable to the difference of the properties of a system when excited by an external applied field with respect to its ground state. DFT is a rigorous theory if ground state properties have to be addressed and indeed many TiO\textsubscript{2} properties have already been satisfactorily reproduced (i.e., lattice constants, crystal phase stability at the nanoscale, surfaces relative stabilities, atomic orbital decomposition of the electronic valence states).\textsuperscript{2,12-14}

On the other hand, as mentioned before, most of the properties that are relevant for TiO\textsubscript{2} opto-electronic applications are related to electronic excited states. This means that their analysis at the DFT level of theory can provide at most a qualitative understanding and only when many-body effects, related to the electron-electron interactions, are negligible.

Unfortunately, it turns out not to be the case for TiO\textsubscript{2} that many body effects can be disregarded. The most striking example is given by the calculated electronic gaps and optical spectra of bulk TiO\textsubscript{2}\textsuperscript{12}, at different level of theoretical approximation in the ab-initio framework, and their comparison with available experimental data. Indeed the overall optical spectra of TiO\textsubscript{2} bulk crystals are not reproducible by application of the random phase approximation (RPA) on the single-particle transitions between ground state KS orbitals, but self-energy and excitonic effects, based on Many Body Perturbation Theory (MBPT)\textsuperscript{13} schemes, are mandatory in order to reproduce the experimental spectra.

In this chapter, we provide an overview of the state of the art of these ab-initio approaches applied to TiO\textsubscript{2} low-dimensional systems. The fundamental role of a treatment beyond the one-particle scheme based on DFT-KS equations for TiO\textsubscript{2} based materials is highlighted, focusing on the study of the electronic levels and of the optical absorption spectra, with a detailed analysis of electron-hole pairs components and their spatial distribution. The chapter is organized in an Introduction and a Methodology section, followed by three sections on Clusters, reconstructed Surfaces and 2-dimensional Nanosheets. Conclusions and perspectives section ends the chapter.

II. METHODOLOGY: AB INITIO METHODS FOR ELECTRO-OPTICAL CHARACTERIZATION OF NANOSTRUCTURES

The Density Functional Theory is probably at present the most widely used ab-initio method for the study of structural and electronic properties of bulk, surfaces, inorganic nanostructures and organic materials at the various flavours and levels of approximation related to exchange and correlation functionals (review functionals).

DFT is based on the Hohenberg and Kohn theorems\textsuperscript{10}, establishing that the ground state energy of a system of \( N \) interacting electrons in an external potential \( V_{\text{ext}}(r) \) is a unique functional of the electronic density \( \rho(r) \) and this functional is minimum at the the ground-state electronic density \( \rho(r) \).

The practical implementation of the DFT is mainly based on the Kohn-Sham\textsuperscript{11} (KS) formulation, which converts the minimization problem for density-based treatment to the self-consistent solution of single-particle KS equations where an effective mean-field Kohn-Sham potential \( V^{\text{KS eff}}[\rho(r)] \) appears. It results to be the sum of the external \( V_{\text{ext}}(r) \), the classical repulsive Hartree potential \( V_{\text{H}}[\rho(r)] \), and the exchange-correlation potential \( V_{\text{xc}}[\rho(r)] \) which embodies the many-body effects. Its exact form is still unknown and the approximation level of the exchange and correlation potential, determines the DFT results validity and accuracy. The most used and less computational expensive \( V_{\text{xc}} \) are expressed as local or semilocal functions of the electronic density (local density approximation, LDA,\textsuperscript{14,15} and generalized gradient approximation, GGA\textsuperscript{16}), but the study of organic molecules on one side, and of correlated materials on the other side,
induced the development of various families of exchange-correlation functionals. They are semi-empirical hybrid functionals (we cite the very popular PBE0, B3LYP and HSE06, but new ones are continuously introduced), that include a certain amount of exact exchange contribution; and meta-GGAs and hyper-GGAs functionals, which by introducing the dependence of the kinetic energy from the density, improve the correlation part description. Such improved functionals provide more refined results for material properties than LDA and GGAs, but at a computational cost that is comparable or even higher that the one associated to the methods based on MBPT, reported below. The results shown in the following sections are obtained at the GGA level of DFT, by using the PBE exchange-correlation functional.

One of the main drawbacks present in the KS implementation of the DFT is that the electronic KS eigenvalues do not formally correspond to the electronic addition or removal energies of the many electron system, apart from the HOMO, whose energy can be formally associated to the IP of the system when the exact exchange-correlation potential is used.

A main, striking result of the approximations hindered in the KS exchange and correlation potential is the underestimation of the electronic (and consequently optical) gap, for both extended and finite systems, an underestimation ranging from 20% to 100% depending on the material and on the system (Figure 1).

The underestimation itself can be partially solved by using hybrid functionals, but DFT remains a ground state theory, whose application to excited states description is not formally justified.

For finite systems such as molecules and nano clusters, a method for overcoming the gap underestimation, is the ΔSCF approach, which resides on the usage of the total energy of the system (calculated for N, N+1 and N-1 electrons), that is, in principle, a quantity exact in DFT, independently of the KS implementation, once that a good description of the density and of the exchange-correlation term is provided, without relating the electronic gaps to the single particle KS levels. This approach has been used for atomic clusters studied in the following.

Nevertheless for a more realistic description of excited states and for reliable predictive results, it is necessary to overcome the ground state DFT description. Two main approaches can be used, both of them based on DFT as starting point.

On one side, the DFT itself has been developed in a time dependent theory (TDDFT) formulation, that is still based on the charge density as main variable, but charge is allowed to evolve in time, subject to a time-dependent potential. Therefore, the case of an external electromagnetic field perturbing the system is described and formally solved by the TDDFT.

Another rigorous method for describing electronic excitations is based on the Green’s functions approach. In the following, we refer to single-particle, charged excited states in relationship with electronic levels, and to two-particles, neutral excited states, when talking about optical excitations. Based on the Green’s functions formalism, is indeed possible to derive a description, based on quasi-particles (electrons and holes surrounded by their own screening cloud), of electronic and optical response of the systems, directly related to the experimental results coming from direct and inverse photoemission spectroscopy, and optical absorption measurements, in its different versions (transmittance, absorbance, anisotropy, etc).

Figure 1: A simplified scheme of the electronic energy levels of a generic system, from the ground state (DFT, only occupied states are properly described), to one-electron excited states (GW, one electron is removed from the system, one hole is left behind, and the gap between empty and occupied states increases), to two-particle excited states (BSE, one electron and one hole are present, coupled in an exciton, their interaction creates energy levels inside the electronic gap, so that the optical gap results smaller or at maximum equal to the electronic one).

To go a deeper in detail, when a bare particle, such as an electron or hole, enters an interacting system, it perturbs the particles in its vicinity. The particle becomes “dressed” by the polarization cloud of the
surrounding particles, and is called a quasi-particle. Using this concept, it is possible to describe the system through a set of quasi-particle equations by introducing a non-local, time-dependent, non-Hermitian operator, the self-energy $\Sigma$.

The most often used approximation to calculate the self-energy is the so-called GW method, derived as the first-step iterative solution of the Hedin integral equations. As a matter of fact, since the KS wavefunctions are often very similar to the GW ones, it is often sufficient to calculate the quasi-particle (QP) corrections within first-order perturbation theory ($G_0W_0$). Quasi-particle energies are calculated as corrections to Kohn-Sham eigenvalues, and the proper inclusion of exchange and correlation produces an electronic gap and empty levels energy in good agreement with photoemission experiments. This holds for a large number of materials, as the $G_0W_0$ approximation of $\Sigma$ works quite well at correcting the KS electronic gap from DFT, and it is also the case for the material and nanostructures analyzed in this chapter.

As pointed out in the introduction, most of the applicable realm of TiO$_2$ is based on the movement and collection of charges excited by light (e.g. photocatalysis and photovoltaics), therefore related to the excitations and de-excitations of electrons inside the material. While the study of photoluminescence via ab initio methods is at forefront of current research, the ab initio optical properties study is a challenging computational task, but relies on well established theory.

The physical quantity to be determined in order to obtain the absorption optical spectra, and related quantities as absorbance and optical conductivity, is the macroscopic dielectric function $\varepsilon_{\text{m}}(\omega)$. This may be calculated at different levels of accuracy within a theoretical ab initio approach. The calculation of the optical absorption spectrum as a sum over transitions of independent particles (RPA) gives in general an incorrect shape and intensity of the peaks, even if a quasi-particle picture is used to replace KS electrons. Indeed, when going from one-electron excited properties, such as the ones described by the electronic levels, to two-particles properties, like the absorption of light, a further step in the many body description is necessary, namely, to include the description of the interaction between the excited electron in the conduction band and the hole created in the valence band. The inclusion of many-body effects gives the proper optical gap, and a good description of the absorption spectrum and excitonic peaks, in a wide range of materials and systems, from bulk semiconductors, to nanostructures, to organic molecules.

To take into account the electron–hole interaction, the Bethe-Salpeter equation (BSE) describes the electron–hole pair dynamics, needs to be solved. The diagonalization of the excitonic Hamiltonian in the calculation of the optical response provides excitonic eigenvalues and excitonic eigenstates. Practically, the KS electronic levels are mixed to produce optical transitions, which are not anymore between pairs of independent particles, and the resulting eigenvalues describe the excitonic energies.

Calculations performed for insulators and semiconductors show that the inclusion of the electron–hole Coulomb interaction yields a near-quantitative agreement with experiment. This is not only true below the electronic gaps, where bound excitons are generally formed, but also above the continuum edge. The same results apply to the titania-based materials investigated here as shown in the following sections. The theoretical-computational scheme (see Figure 1) applied to the various TiO$_2$ based systems is the following: DFT (applied when needed on preliminary structures obtained via molecular dynamics calculations) is used to obtain the equilibrium structure and the ground state description of the nanostructures. The $G_0W_0$ calculations are performed to obtain the quasi-particle corrections to the energy levels, starting from the DFT eigenvalues and eigenfunctions. On top of $G_0W_0$ results, BSE is solved, obtaining the optical absorption spectra, to be compared, when available, with TDDFT results.

### III. NANOCLUSTERS

As a first example of key importance in photo-related applications, we report ab-initio modelling results of atomic-size and nano-sized crystals. Nanostructures are the most common shape in which TiO$_2$ is synthesized, more easily obtained than nanowires and nanotubes. In nanocrystals, the most stable crystalline phase, among the various TiO$_2$ can assume, is anatase. Ab initio molecular dynamics calculations confirm, from atomic sized to nanometer-sized crystals, that clusters with anatase symmetry are energetically stable and can be considered as the starting seeds to growth much larger and complex nanostructures. Typical sizes of nanocrystals range from few nm to 20-50 nm, but here we focus on the smallest sizes, up to 2 nm of diameter. Atomic clusters of TiO$_2$ are a clear example of how heavily the description of electronic and optical properties is affected by the proper inclusion of many-body treatment. The electronic gap of these inorganic molecules is investigated, and shown to be larger than the optical gap by almost 4 eV.
Therefore, strong excitonic effects appear in these systems, much more than in the corresponding bulk phase. Moreover, charge transfer effects play an important role under photon absorption, and therefore it has to be carefully evaluated in TDDFT the use of standard functionals, which are based on the adiabatic approximation, and can not account for long range phenomena as charge transfer.

Figure 2: atomic clusters used to evaluate the effect of $G_0W_0$ and BSE treatment on TiO$_2$ nanostructures. From left top, to right bottom, (TiO$_2$)$_n$ with $n=3$-$10$. In each panel, the KS eigenfunction corresponding to the highest occupied molecular orbital (HOMO, top) and to the lower unoccupied molecular orbital (LUMO, bottom) are plotted. To be noted the different spatial localization of the two orbitals, the first one mainly located on O (red) atoms, the second one on Ti (grey) atoms. The most asymmetric clusters present a larger spatial separation of orbitals.

Figure 3: electronic gap of (TiO$_2$)$_n$ clusters, evaluated as KS gap (difference of the LUMO and HOMO eigenvalues), as DFT gap from $\Delta$SCF (Ionization Potential – Electron Affinity) and from $G_0W_0$ theory. Dashed lines indicate the values of KS and $G_0W_0$ gaps for the bulk phase anatase.
The first information, concerning electronic structure of NCs, is clearly extracted from Figure 3. The KS gap ranges from 1.0 to 2.5 eV, approximately, for clusters which dimension is 9-30 atoms. The calculation of the electronic gap, both via the ΔSCF method, and within the G_0W_0 scheme, allows to predict a much larger electronic gap, from 4.5 up to 7 eV. The larger correction, for the smallest cluster, is of 5.5 eV, and becomes around 4 eV at increasing dimensions. For larger nanostructures ((TiO_2)_29), corrections are of the same order of magnitude (IP-EA=7.4 eV), on top of a KS gap value of 2.5 eV. Slightly smaller correction (~3.0 eV) is obtained for a nanowire of similar dimensions (KS gap of ~ 1.0 eV). The importance of the correct determination of the electronic levels, apart its interest di per se, is related to most of the applications of titania, as it is usually interfaced with other inorganic materials, as in heterostructures for photovoltaic applications, or with organic molecules, as in photocatalysis and hybrid dye-sensitized solar cells. If the correct value of the IP-EA gap of the material is not determined (and the experimental determination of these quantities is usually quite challenging), it is not possible to assign the correct band bending at the interface with e.g. CdSe in heteronanostructures, or to know which organic molecules possesses the proper energy level spacings to fit in the TiO_2 gap, or to overcome it, depending on the technological needings.

Considering the optical properties, the first step to obtain any further photorelated process in a material is the light absorption. The evaluation of the optical gap, direct or indirect, and of the optical spectral shape, may even help in determining the structural and crystallographic details of the material, through the presence of specific features and transitions. Indeed, optical measurements are usually more feasible than electronic ones, and a comparison among experimental data and computed spectra for different phases or nanostructures may allow to confirm the presence of a certain specific structure.

Figure 4: Spectra for (TiO_2)_3,6 optical absorption within G_0W_0-BSE and TDDFT (PBE) methods.

For the atomic clusters, optical absorption could be evaluated at both levels of theory, TDDFT and MBPT. The direct optical gaps are in the range 1.0-3.0 eV, with variations depending on the size and on the used functionals in TDDFT, and with a substantial agreement of the optical gap value between TDDFT and BSE results. The large variation observed among electronic gaps (obtained via G_0W_0 and ΔSCF) and
optical gaps, which are almost 5 eV smaller, is not surprising, as in localized systems, the electron-hole interaction is strong and induces bound excitonic states, similarly to what happens in molecular systems. For larger nanostructures, the optical gaps are also reduced, to ~ 4.0 eV for a (TiO$_2$)$_{29}$ cluster, and to ~ 3.0 eV for the nanowire of same diameter.

The most interesting information comes indeed from the optical transitions analysis of the atomic clusters. The optical transitions described by BSE are, for some of the considered systems, quite different from the ones provided by the TDDFT. As shown in Figure 4, apart from the overall shift, the spectral shapes are quite different for (TiO$_2$)$_3$, slightly different for (TiO$_2$)$_5$, (TiO$_2$)$_6$, but very similar for (TiO$_2$)$_4$.

In (TiO$_2$)$_3$, the very first excitonic transition is optically allowed, but much more intense than in the TDDFT spectrum, and involves more states than barely HOMO–LUMO transition (contributing only to a 6%). Namely the HOMO-2, HOMO-3, LUMO+2, LUMO+3 states are strongly involved. The resulting excitonic wave function is indeed localized on a Ti atom, different from the one on which the HOMO is located (Figure 5). (TiO$_2$)$_4$ presents, in both TDDFT and BSE spectra, the same optical transitions, giving spectra that are just rigidly shifted. The first transition, optically forbidden, is the HOMO–LUMO, followed by the HOMO-1 to LUMO transition. The first optically allowed, even if not very intense, transition, is at 2.9 eV, given by HOMO-2 to LUMO states. There is no admixture of states in this cluster to describe the electron-hole interaction, and the two theories, TDDFT and BSE, are equivalent for its study, apart an almost rigid energy shift.

The (TiO$_2$)$_3$ and (TiO$_2$)$_6$ clusters have a more complex behavior. Indeed the spectra from the two methods shown in Figure 4 are quite similar. However, a detailed analysis of transitions highlights that different states are involved, depending on the approach. For (TiO$_2$)$_3$, the first transition (at 3.02 eV) is given by both HOMO and HOMO-1 to LUMO. The following one (at 3.08 eV), more intense, is the HOMO-2 to LUMO, but the 5th and 7th transitions, at 3.38 and 3.55 eV, are given by HOMO-3, HOMO-4 to LUMO and HOMO, HOMO-1 to LUMO+1, respectively. Therefore an admixture of KS states contributes to some of the optical transitions. In (TiO$_2$)$_6$, the first transitions are less intense and the spectrum less sharp than in (TiO$_2$)$_3$, more similar to (TiO$_2$)$_5$ one. The first, optical allowed but really weak transition, at 2.08 eV, comes from HOMO, HOMO-1 to LUMO. The second one at 2.16 eV is two order of magnitude more intense and comes from a different mixture of the same states. Also the other transitions examined are produced by admixture of states.

The many body approach gives, therefore, a description of optical properties which includes effects not accounted for in TDDFT treatment, with absorption spectra that can differ slightly or in a more evident manner in the two methods, depending on the system. Among examined cases, the only one for which both methods give the same result is the (TiO$_2$)$_4$. The result should be ascribable to the high symmetry of the system, and to the consequent spatial overlapping of orbitals, which reduces charge transfer effects. For (TiO$_2$)$_3$, charge transfer effects, absent at the level of TDDFT approximations used here (although we recall that they should be in principle described by exact TDDFT), are instead predicted by BSE. If comparison

![Figure 5: representation of the excitonic wavefunction associated to the first peak in the BSE spectrum. The hole is represented by the green sphere, the wavefunction by the yellow isosurface. In the figure also the TDDFT performed with PBE0 functional is reported, and its spectral shape is similar to the TDDFT-PBE one, apart a rigid shift. Therefore, neither TDDFT-PBE0 catches the proper excitations described by the many body approach.](image-url)
with experimental data could be performed for these small clusters, it could be possible to clarify the reliability of the two methods, and the optical and electronic characterization of clusters with increasing dimensions could also provide relevant structural information on specific nanostructures.

IV. SURFACES

One of the most used approaches to model, within ab-initio (computational expensive) methods, large nanostructures properties, is based on the idea to enucleate and to study only the part of the nanostructure playing the key role in determining the characteristic behaviour of the system. In case of “large” (some tens of nanometers of diameters) nanotubes, nanoribbons, and nanoclusters, in the limit in which the evaluated properties can be considered “local”, the approach is to model as infinite surfaces the various crystal surfaces that constitute the facets of the nanostructure.

Relying on this idea, it is possible to study for example the electronic and optical response of large TiO$_2$ nanoclusters exposing some well determined facets. A particularly important role in the (photo)catalytic performances of TiO$_2$ is indeed played by the exposed surfaces: the (101) and (100)/(010) terminations are the dominant ones in anatase nanocrystals. However, the minority (001) facets seem to be more reactive and present a lower concentration of defects compared to other anatase orientations and rutile surfaces. Recent experiments succeeded in synthesizing anatase nanocrystals with up to 90% of the (001) exposed surface, which show improved photorelated performances with respect to nanostructures with lower percentages of (001) facets. Due to the key role of the (001) plane, it is clearly of interest to determine which is its most stable structure, and which are the related electronic and optical properties of the material. Two reconstructions, the (1 × 1) and the (1 × 4), are experimentally observed. While the (1 × 4) reconstruction appears after annealing under ultra-high vacuum conditions, the (1 × 1) periodicity can also be obtained, under specific experimental conditions. Moreover, under specific experimental conditions, anatase nanocrystals exposing up to 47% of (001)-(1×1) facets can be synthetized. Both (1 × 1) and (1 × 4) reconstructions have been investigate at the DFT level, to establish their equilibrium geometry and their relative stability. The (1 × 4) is more stable than the unreconstructed surface. The next step is the ab initio study, based on the application of Many-Body Perturbation Theory approaches on top of ground-state DFT calculations, to determine the optical behavior of the TiO$_2$ anatase (001) surface.

Figure 6: Macroscopic dielectric function $\varepsilon_2(\omega)$ for (1 × 1) (left) and (1 × 4)-(001) (right) case. (a) and (b) report spectra calculated including the e-hole coulomb attraction (BSE). The black curve is for light polarized along the [100] direction, the orange one for ([010] direction. The arrows indicate the main excitonic transitions.

The $G_0W_0$ gap correction for the (001)–(1 × 1) surface is 1.8 eV, close to the bulk correction of 1.66 eV. Results of BSE calculations for the two reconstructions are reported in Figure 6. Overall, a different optical
response for the two reconstructions is observed. Also, on both cases, optical anisotropy between the two high symmetry directions in the (001) plane is observed, that is not present in the bulk phase of anatase. 12
The (1 × 4) surface has an optical spectrum quite similar to the bulk anatase, while for the (1 × 1) surface new optical structures (S2 and S3) are present below the first bulk-related absorption peak B1. The physical origin of this different behavior is related to the different character of the highest valence band states in the two reconstructions. 54 The first direct exciton (S1 and S1', shoulders in the spectra), is at 3.2 eV and 3.5 eV, in (1 × 1) and (1 × 4), respectively. In both cases, it is built up by mixing vertical transitions at Γ', from the two highest occupied valence bands, with a clear surface character, to the two lowest unoccupied bands that are located mainly on the Ti atoms of the bulk. In the (1×1) reconstruction, the S2 and S3 peaks involve also the third unoccupied band. The peak B1 (which corresponds to the first structure, also called B1 in the inset, of the bulk spectrum for light polarized in the plane), receives contributions from more states, from seven valence states to five conduction states.
In both reconstructions, the surface termination induces an optical anisotropy in the (001) plane, absent in the bulk. This optical anisotropy, dependent on the surface reconstruction, is an interesting prediction that demands experimental proof using techniques sensitive to surface optical anisotropy.
Comparison of refined theoretical spectra with experiments requires in principle high resolution spectra, and well defined samples. However, both absorption and photoluminescence (PL) data are usually available for polycrystalline thin layers or nanostructures. Therefore, the measured optical properties often refer to a mixture of crystalline orientations, and various phases (mainly anatase and rutile) are present in the experimental samples. On one side, optical spectra of thin films have been reported55 to be very similar to bulk anatase spectra, suggesting presence of (1 × 4) reconstruction on the exposed (001) faces. On the other side, few reports of optical investigations56 57 on anatase thin films indicate absorption for energies around 3.2 eV, confirming the assignment. A quite recent experimental investigation 58 on absorption and photoluminescence from samples of nanotubes and nanorods, obtained under various and well controlled synthesis conditions, allows a good comparison of data. In particular, through a detailed analysis of excitonic peaks, it has been possible to establish a relationship between the (1 × 1) and nanotubes, while the (1 × 4) reconstruction has been related to nanorods. The distinct behavior in optical spectra, depending on the reconstruction has been used as a fingerprint to identify the presence of the most stable (1 × 4) or the most photoreactive (1 × 1) surface, in experimental samples of nanostructures.
The spatial analysis of excitonic wavefunctions related to the transitions S1-S3 and S1', by placing the hole on an Oxygen surface atom, indicates that the exciton is localized close to the surface plane in (1 × 1) geometry, while when the (1 × 4) reconstruction is present, a complete exciton delocalization in the subsurface and bulk phase is observed. For the (1 × 4) , it is therefore small the probability that both electron and hole are immediately available at surface sites and involved in subsequent chemical reactions), while the (1 × 1) fulfills two fundamental characteristics of photocatalytic processes: hole and electron are well spatially separated, but they both reside at the surface (this mainly holds for excitation energies <3.6 eV, where both the electron and hole are mainly located at the surface). The spatial distribution of the photoinduced e-hole pairs reveals that the (001) orientation, mainly its (1 × 1) unreconstructed shape, is photocatalytically efficient, given the high probability of having both carriers immediately available for oxidation-reduction processes at the surface.

V. NANO SHEETS

Thanks to rapid progresses in the synthesis methods, large quantities of two-dimensional (2D) nanosheets (NSs) can be produced and used for further assembling of new nanostructured materials with different morphologies and functionalities, as nanotubes of various diameters and curvatures.59 Investigating the microscopic nature of NSs’ opto-electronic properties is a fundamental prerequisite for rationalizing experimental data and improving devices performances. As shown by the comparison with experimental data reported in the following, it is possible to determine the composition and the crystalline structure of samples, obtained via different synthetic routes, even when the optical spectra have a low resolution, by the analysis of specific features of the spectra.
We can deduce, from what said in the section dedicated to surfaces, that anatase NSs oriented along the (001) direction (Figure 7) are of main interest for technologies related to photoexcitations. However, when going down to lower dimensional nanostructures, as thin layers here considered, TiO$_2$ arranges in more complex structures than anatase, rutile and brookite observed in extended samples and in nanocrystals. For undoped NSs, the two main phases are anatase and lepidocrocite, which show a close structural relationship. In particular, it has been demonstrated that the transition from a bilayer (001)-oriented anatase film to a lepidocrocite phase occurs through a barrierless pathway, due to tensile stress reduction. The structures used to model possible nanosheets are represented in Figure 7.

Figure 7: structure of the modeled nanosheets, Ti (O) atoms are represented as yellow (blue) balls. (a) Anatase-S (symmetric), (b) anatase-AS1 (asymmetric 1), (c) anatase-AS2 (asymmetric 2, obtained by fully relaxing the cell), (100) side view. (d) Lepidocrocite-I sheet: top (bottom) view along the (100) ((010)) direction. (e) Lepidocrocite-I-SC sheet (double sheet, interlayer distance of 0.37nm), (010) orientation.

As expected, also for these 2D structures the electronic band gap evaluated at the G$_0$W$_0$ level is larger, by 2.5-3.0 eV, than the KS gaps (ranging in turn from 2.0 to 3.0 eV). A further critical aspect to be taken into account when evaluating the optical response of these nanostructures is related to the direct or indirect nature of the electronic gap, which, apart absorption, clearly affects also the photoluminescence behaviour. Ab-initio calculations reveal a change from indirect to direct band gap when moving from anatase-S to lepidocrocite-I structure. As a whole, there is a red-shift going from the symmetric anatase to the lepidocrocite. The optical (BSE) gaps result more than 1.5 eV smaller than the corresponding electronic gaps, for all the NSs structures. This gap narrowing is related to the nanosheet reduced dimensionality, which induces a strong attractive electron–hole interaction. As a consequence, the optical spectra presented in Figure 8 have a clear excitonic nature in the vis–UV region, presenting at the lower absorption edge more peaks than obtained in the independent particle treatment. In general, it is observed a strong oscillator strenghts redistribution, indicating that, when the excitonic description is used, not only the energy associated to the transitions is changing, but also the nature itself of states involved in the optical absorption.

Figure 8 also shows that it is possible to establish a unambiguous relation between atomic structure and optical properties of TiO$_2$-based NSs, by comparison with experimental absorption data available from literature. A substantial blue-shift with respect to the optical absorption of anatase bulk is clear in all the experimental curves, and a well defined difference in the spectrum shape exists between lepidocrocite and anatase films. The same blue shift is obtained in theoretical data, but compensated by a stronger red shift for anatase-S, which decreases going towards the lepidocrocite phase. The lepidocrocite single sheet offers a particular good agreement between experimental and ab initio data. In both, the onsed is around 4 eV, there is a main peak at 4.6 eV, and a second structure around 5.7 eV. This is therefore a crossed confirmation, that the model for the lepidocrocite phase is correct, and that the sample really contained lepidocrocite thin layers.
Figure 8: Comparison among BSE absorption spectra of the four isolated nanosheet models and some experimental absorption spectra reported in the inset: curve (a), absorption data of a single layer lepidocrocite; (b) same as (a) after annealing at 900 °C inducing a transition to anatase (001)-oriented nanosheet; (c) (001) anatase sheet produced through processing of titania nanotubes under neutral pH condition.

The experimental spectra for anatase sheets are, compared lepidocrocite data, much more smooth, with an onset around or below 4, and a broad structure, probably including various peaks that are not experimentally resolved, ranging from 4 to 6 eV. For anatase films, the theoretical analysis allows one to say that an admixture of anatase-AS2 and anatase-AS1 domains could reasonably explain the experimental data, giving, as a whole, optical transitions in the 4−6 eV range. Instead, the presence of large anatase-S reconstructions seems likely to be excluded, due to the presence in the theoretical spectrum of two intense and defined structures below 4 eV, not visible in the absorption experiments.

With respect to the analysis of specific transitions, the lowest energy exciton is a bright one in isolated nanosheets, both in anatase and in lepidocrocite geometries. The first bright exciton is spatially localized, with the hole placed on an Oxygen atom, the excitonic wavefunctions is localized on the first-neighbor Ti atoms (Figure 9). The extremely localized nature of the excitons observed here is consistent with experimental absorption and luminescence measurements done on TiO$_2$-based nanotubes, as the electron–hole couple, due to its high spatial localization, feels the curvature only in nanotubes with a very small diameter.

Therefore, ab-initio description of radiative transitions in the vis–UV spectral range in TiO$_2$-based NSs for the two phases pristine (001)-anatase and lepidocrocite reveals its basic excitonic nature and allows to relate them to experimentally obtained structures. The inclusion of many-body effects plays a fundamental role for a correct interpretation of the experimental data regarding photoexcited processes in low-dimensional titanium dioxide materials. Furthermore, these calculations on flat sheets can be useful for the analysis of large TiO$_2$-based nanotubes, for whom the curvatures and interatomic interactions between walls are negligible, and that can be considered as 2D (almost flat with respect to the atomic and excitonic lengthscale) layers.
Figure 9: Exciton in a titania sheet. The hole is denoted by the green sphere, the excitonic wavefunction by the red isosurface. The localized nature of the exciton is clearly visible.

VI. CONCLUSIONS

In this chapter we have presented an overview of the state of the art of ab initio many body perturbation theory methods for excited state properties applied to TiO$_2$ based nanostructures. The nature of the electronic excitations in titanium dioxide (TiO$_2$) nanostructures is described from a comprehensive point of view, including electronic levels alignment, optical absorption properties, and analysis of the spatial distribution of the electron-hole pairs mixed in the exciton creation. The quality of many-body results is summarized by the values of the gaps in Tab.1 for the various systems considered through the chapter. The KS gaps are strongly underestimated with respect to experimental data, as shown in columns 2 and 3. The inclusion of many body interactions, in particular the two-particles treatment of the electron-hole interaction in the optical transitions, properly describes the optical gaps at quantitative level (column 4), and this holds for both finite and extended systems. Ab initio results have a strong predictive ability when extended to new complex systems, where the interplay between excitations and other degrees of freedom (surface/interface charge transfer, surface functionalization, defects, and so on) plays a major role. The predictive strenght of the computational approach is demonstrated by the comparison among measured properties for various nanostructures (nanowires, nanotubes, and layers of titania realized under various synthesis recipes), and theoretical spectra of the modeled structures (surfaces and thin layers of anatase and lepidocrocite phases). The efficiency in the optical absorption and in the electron-hole spatial separation is a key issue in fundamental applications of TiO$_2$ nanostructures, as active elements in devices such as new generation solar cells. Most of themological applications of TiO$_2$ are based on the excitation dynamics within the bulk, at the surface, and interfaces. The modeling of optical response can definitely help in the design of new and more efficient TiO$_2$ nanodevices. On one side it helps in the selection of most efficient synthesis method by clarifying the presence of specific nanostructures in the samples depending on their optical spectra. On the other side, modeling can directly predict the basic characteristics of nanostructures as absorption offsets, exciton bindings, exciton localization, absorption maxima depending on the incident wavelength, all properties that in turn will affect the overall device performances.
<table>
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<th>$E_d^{\text{PBE}}$(eV)</th>
<th>$E_i^{\text{PBE}}$(eV)</th>
<th>$E_d^{\text{BSE}}$<a href="eV">@G$_0$W$_0$</a></th>
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Table 1: Schematic recap of the fundamental results coming out of DFT ground state electronic gaps (single particle approximation), namely PBE (direct/indirect gaps); many-body optical spectra onsets (direct transitions), obtained via BSE calculations on top of G$_0$W$_0$ results; and experimental optical onsets.

REFERENCES

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