Structure, electronic, and optical properties of TiO₂ atomic clusters: An ab initio study

Letizia Chiodo, Martin Salazar, Aldo H. Romero, Savio Laricchia, Fabio Della Sala et al.

Citation: *J. Chem. Phys.* **135**, 244704 (2011); doi: 10.1063/1.3668085

View online: <http://dx.doi.org/10.1063/1.3668085>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v135/i24>

Published by the [American Institute of Physics](#).

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT

AIPAdvances

Special Topic Section:
PHYSICS OF CANCER

Why cancer? Why physics? [View Articles Now](#)

Structure, electronic, and optical properties of TiO₂ atomic clusters: An *ab initio* study

Letizia Chiodo,^{1,2,a)} Martin Salazar,³ Aldo H. Romero,³ Savio Laricchia,¹
Fabio Della Sala,^{1,4} and Angel Rubio²

¹Center for Biomolecular Nanotechnologies @Unile, Istituto Italiano di Tecnologia Via Barsanti,
I-73010 Arnesano (LE), Italy

²Nano-Bio Spectroscopy group and ETSF Scientific Development Centre, Dpto. Física de Materiales,
Universidad del País Vasco, Centro de Física de Materiales CSIC-UPV/EHU- MPC and
Donostia Int-Phys Center (DIPC), Av. Tolosa 72, E-20018 San Sebastián, Spain

³CINVESTAV, Unidad Querétaro, Libramiento Norponiente 2000, CP76230,
Real de Juriquilla, Querétaro, México

⁴National Nanotechnology Laboratory (NNL), Istituto Nanoscienze-CNR, Via per Arnesano 16,
I-73100 Lecce, Italy

(Received 30 June 2011; accepted 21 November 2011; published online 23 December 2011)

Atomic clusters of TiO₂ are modeled by means of state-of-the-art techniques to characterize their structural, electronic and optical properties. We combine *ab initio* molecular dynamics, static density functional theory, time-dependent density functional theory, and many body techniques, to provide a deep and comprehensive characterization of these systems. TiO₂ clusters can be considered as the starting seeds for the synthesis of larger nanostructures, which are of technological interest in photocatalysis and photovoltaics. In this work, we prove that clusters with anatase symmetry are energetically stable and can be considered as the starting seeds to growth much larger and complex nanostructures. 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, the use of various levels of theory demonstrates that charge transfer effects play an important role under photon absorption, and therefore the use of adiabatic functionals in time dependent density functional theory has to be carefully evaluated. © 2011 American Institute of Physics. [doi:10.1063/1.3668085]

I. INTRODUCTION

Titanium dioxide (TiO₂) is one of the materials most actively investigated in the recent years,^{1–4} due to its broad range of technological applications, such as in biocompatible materials, gas sensors, photocatalysis, photovoltaics, energy storage, and many others. A considerable number of experimental and theoretical works appeared in the recent literature, investigating physical and chemical properties of bulk phases,^{5–14} surfaces,^{15–23} and nanostructures.^{24–29} One of the appealing properties of TiO₂, especially in its anatase phase, is the strong catalytic and photocatalytic activity. Anatase is the most stable structure observed at the nanoscale, for particle sizes smaller than 14 nm,^{30,31} or at 0 K and ambient pressure.³²

Therefore, the use and optimization of anatase nanoclusters or nanowires is one of the main topics under investigation nowadays. However, a clear explanation of the improved performances of this phase is still missing. Possible cofactors include defects and doping, phonons role, or the different octahedra packing constituting the material in the various phases. As structural, electronic and optical response of the material are quite complex, an accurate control of nano-

and mesoscopic properties would be advisable, relying on a detailed and deep knowledge of the basic TiO₂ properties. Most of the work from the experimental side is actually devoted to the synthesis paths, to improve control over cluster size, shape at nano- and mesoscale and to optimize their technological performance. However, the experimental control of all the involved factors contributing to excitations and transport in the nanostructures is not at all straightforward.

As synthesis of systems with well defined structural, opto-electronic and transport properties, under full control, is difficult, the use of a computational approach can, in a step-by-step procedure, clarify the role played by, e.g., quantization, surfaces, defects, focusing on each of the different aspects at a time. On the other hand, the simulation of the material, via different computational approaches, presents important challenges. Concerning the bulk phases,¹⁴ including surfaces,³³ the standard density functional theory (DFT) (Refs. 34 and 35) can be successfully applied to describe structural and energetic properties of the material, also connected to catalysis.³⁶ 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 methods, such coupled cluster (CC) approaches^{37,38} or many body perturbation theory (MBPT)

^{a)} Author to whom correspondence should be addressed. Electronic mail: letizia.chiodo@iit.it.

techniques, such as G_0W_0 method,^{39–43} are used. Basically in these approaches correlation and excited states are explicitly taken into account. A proper optical description should also need, on the other side, the inclusion of interaction among excited electrons and holes. Such effects are embedded in time-dependent DFT (TDDFT) (Ref. 44), or in many body treatments as in the Bethe–Salpeter equation (BSE) solution.⁴³

Focusing here on 0D systems, we should distinguish between atomic clusters, more similar to inorganic molecules than to portions of crystal structures, and nanoclusters, which indeed present a well determined crystal structure, and expose precise crystal surfaces. Atomic clusters can be investigated via refined quantum-chemistry approaches,^{37,38} but the feasibility of such calculations rapidly decreases with the cluster dimension. Most recent calculations^{28,29} report on electronic properties of some highly symmetric clusters, used to study doping effects, and on optical response of similar clusters via TDDFT. Comparison of these cluster properties with our results is presented in following sections. For nanoclusters, with a number of atoms around 100, recent studies⁴⁵ have been performed with *ab initio* DFT methods to analyze structural stability and electronic properties of real-shaped clusters. On the other hand, bulk-cut clusters have often been used to model real clusters as well as their interaction with organic molecules within DFT and TDDFT.^{46–51}

The experimental and computational characterization of atomic clusters is usually⁵² quite complex due to the system dimensionality. Indeed, even the structural determination of such structures, by just experimental techniques, can be difficult, mainly due to the large variation in cluster size and structure in the experimental setup. In contrast to organic molecules, atomic clusters are found not to have a fixed size, structure, or composition in most synthesis paths. The structural determination also constitutes a difficult task for the theoretical approach. As it is not straightforward that atomic clusters will assume a bulk-like geometry, and the degrees of freedom increase with the number of atoms, the determination of the structure giving the global minimum can be complicated, much more when various geometries have similar energies and conduct to different energy ordering depending on the theoretical approximations.⁵³

A further complication arises from the fact that, for the smallest cluster, the TiO_2 molecule, even high level correlated methods fail in describing excited states,⁵⁴ and hybrid TDDFT results are in better agreement with experiments than CC. So, particular attention has to be paid when investigating this material, in the finite size systems limit, in relation with the theoretical approach used. The TiO_2 monomer has been optically characterized, by multireference configuration interaction,^{54,55} focusing on its low-lying excited states. In the first theoretical studies on small clusters of TiO_2 ,^{56,57} the $(\text{TiO}_2)_2$ unit was identified as a unitary building block for the growth of larger clusters. We reach similar conclusions within this work.

The molecular structure of larger clusters has been investigated through first principles, with main attention devoted to their stability and heats of formation $[(\text{TiO}_2)_n, n = 1–4$ (Ref. 38)] and to the dependence of the electronic properties on the cluster stability $[(\text{TiO}_2)_n$ with $n = 2–15$ (Refs. 53 and 58)].

For larger clusters, $(\text{TiO}_2)_n$ nanoparticles with $n = 10–16$, an interesting odd-even oscillation in the structural features and electronic properties of stable Ti=O defect-free has been observed.⁵⁹ The most recent works^{28,29} report electronic gaps, calculated from a many body approach, and optical absorption transitions for $(\text{TiO}_2)_n$ symmetric clusters up to $n = 13$. Concerning more complex structures, TiO_2 clusters rich in oxygen have been studied and characterized, as well as pristine clusters when deposited on surfaces.^{60,61} Additionally, the possibility of using titanium dioxide as remover of pollution has been analyzed⁶² by studying adsorption of ammonia and water molecules on anatase-like clusters. In most recent years, *ab initio* studies have been performed on catechol^{63–65} and water⁶³ molecules interacting with TiO_2 nanoparticles, such that molecular adsorption on favourable reaction sites is observed. Realistic shaped large nanocrystals⁴⁵ of anatase (up to 1.5 nm) have been recently investigated and also a new family of heterofullerenes⁶⁶ of TiO_2 nanostructures based on $(\text{TiO}_2)_2$ has been recently discovered and studied.

In this paper, we focus on atomic clusters with atomic sizes from 9 to 30 atoms, therefore, at the edge of calculations that can be afforded with quantum chemistry approaches (such as coupled-cluster methods^{37,38}), but accessible to DFT, TDDFT, and many body derived methods. We combine molecular dynamics and refined electronic and optical calculations to study structural and excited state properties as well as to clarify their basic properties, and connect them to experimental measurements performed by photoemission or optical absorption spectroscopies. Often the relative stability of inorganic molecules is subject to the different used approximations, in particular, the theory level such as HF, or post-HF, or DFT approach, which also relies on different approximations to the exchange-correlation potential. Therefore, the use of different levels of theory on the same ground, as well as the use of different observables, such as excited states, could help to disentangle the relation between different structures.

We considered the atomic cluster growth by studying four different small cluster seeds of titanium dioxide $(\text{TiO}_2)_n$ with n in the range $n = 2–10$: the four different starting geometries are a linear chain, a ring, a rutile-like, and an anatase-like. For the overall lowest energy configurations, namely, the anatase-like clusters, we investigated the electro-optical behavior calculated by DFT, TDDFT, and many body techniques with a threefold objective. We want indeed (i) to clarify the intrinsic properties of the material at the nanoscale, (ii) to understand by comparing with spectroscopic results, which structures are present in different synthesis conditions, and (iii) to establish reliability and applicability limits of the various theoretical tools for such oxide molecules. These clusters can be considered actually the core of nanoclusters of various crystalline phases.⁶⁷ Given the complexity in characterizing and calculating the electronic gaps of atomic clusters, we can rely on optical spectra as an important tool to understand the properties of such systems. To understand the behavior of these seed clusters, we calculated their response function to an optical excitation. The standard method of choice is TDDFT (Refs. 29, 46, and 47), which can be used in different implementations such as the real-time, real-space implementation,⁶⁸ or by solving the Casida equation.^{68,69} The advantages in using a real-time

real-space code are due to the large system dimension that can be investigated, and the wider energy spectrum which can be studied, not limited to few low energy transitions. For the largest systems considered here, with 30 atoms, the calculation within the linear response of TDDFT spectra in the frequency domain is quite computationally heavy, and rapidly becomes unaffordable for larger clusters. A further important aspect is treated in the last part of the paper: the appropriateness of TDDFT to investigate these inorganic clusters in comparison with many body techniques. For the four smallest anatase-like clusters, a detailed comparison among TDDFT and MBPT optical spectra and transitions is performed, and interesting conclusions are drawn.

II. COMPUTATIONAL METHODS AND DETAILS

We used a combination of *ab initio* theoretical and computational approaches to investigate the structural, electronic, and optical properties of TiO₂ atomic clusters. The equilibrium geometry of four different series of seed clusters is identified, and an electronic and optical analysis is then performed for the most energetically stable clusters.

A. Geometries and electronic properties based on DFT

Structural relaxations have been performed using the DMOL3 software^{70,71} with the PBE (Ref. 72) exchange-correlation functional. We selected a basis set composed of a double numerical basis (4*s* and 3*d*) with polarized function 4*p*. An all-electron calculation with relativistic effects has been considered for all the ground state results.^{73,74} The geometry convergence criterion was set to 10^{−3} eV/Å for the energy gradient and 5 × 10^{−3} Å for the atomic displacements. All clusters were fully optimized without spin restrictions and without imposing symmetry constraints, using an energy convergence tolerance up to 10^{−5} eV. For accurate calculations, we have chosen an octupole scheme for the multipolar expansion of the charge density and coulomb potential. In the generation of the numerical basis sets, a global orbital cutoff of 6.0 Å was used. For the class that has been identified as most stable, also the cationic and anionic geometries have been obtained.

For the most stable identified structures, the electronic properties were calculated with two different implementations: plane waves (PWs) with the code Quantum Espresso,⁷⁵ and real space grid, with OCTOPUS.⁶⁸ Both codes were used at different stages of calculations of excited state properties. For the real-space code, details are reported in Sec. II C. Calculations in PWs are based on norm conserving pseudopotentials (PPs), with a cutoff of 170 Ry with semicore Ti states included. The clusters are treated as isolated systems in a cubic box of 40 bohr side to prevent image interaction. The Makov–Payne correction⁷⁶ is included, and a jellium background is inserted to remove divergences for the non neutral clusters. From DFT calculations, the Kohn–Sham gap E_{gap}^{KS} , the dipole moments, the ionization potential (IP) and electronic affinity (EA) are obtained. The electronic gap was evaluated from IP-

EA⁷⁷ as

$$E_{gap}^{DFT} = E_0(N + 1) + E_0(N - 1) - 2E_0(N) \quad (1)$$

with $E_0(N)$ ground-state energy for the system with N electrons. The approach relies indeed on DFT calculations, whose complication can just arise from the non-closed shell of the investigated charged systems. The quality of obtained results is eventually limited by the used approximation to the DFT exchange-correlation functional. In particular the anion calculations, involving the evaluation of an unoccupied state in the neutral configuration, could present some drawbacks⁷⁸ and affect the final result. The E_{gap}^{DFT} values can be compared with more refined, but computationally more demanding, techniques to assess the reliability of the description. E_{gap}^{DFT} corresponds indeed to the quantity calculated, in the many body theory, by the GW approach for the electronic gap.

B. Quasi-particle properties

The other method to calculate the electronic gap is based on many body theory, that is, the “standard” G_0W_0 evaluation for the self-energy. This approach provides the real electronic gap, as correlation is correctly described. Many-body calculations in the PW-PPs framework have been performed with the YAMBO code.⁷⁹ The code starts from DFT eigenvalues and eigenfunctions calculated from previous ground-state calculations obtained from Quantum Espresso. Due to the computational costs, just the smallest clusters ($n = 3$ –6) have been investigated, focusing on their electronic G_0W_0 gaps and optical absorption spectra. A cell of 40 a.u. side has been used, and to ensure convergence on vacuum a Coulomb cutoff has been applied.⁸⁰ The G_0W_0 values has been converged with respect to the number of PWs, empty bands, and dimension of dielectric matrix whose inverse is used in the W evaluation, and the screening is evaluated in the plasmon pole approximation.⁸¹ 20 Ry (3 Ry) are used for the exchange (correlation) part of the self-energy. The number of empty bands is more than 900, and all calculations are done at the Γ point. The optical spectra are calculated by solving the Bethe–Salpeter equation, using the same code, with a cutoff of 20 Ry and 3 Ry for local field effects, and by including the coupling term, as described in Ref. 82 for localized systems.

C. Optical properties with TDDFT

We used TDDFT methods to investigate the optical spectrum of neutral and charged clusters. For neutral clusters, the absorption spectrum at high energies with a real-space, real-time method, was calculated and compared to a linear-response method using a Gaussian basis set. Real-space real-time TDDFT calculations have been performed with the OCTOPUS code. The radius of the sphere associated to each atom is of 7.5 Å. The used grid spacing was of 0.10 Å, due to the presence of oxygen states, and of the strongly localized Titanium d electrons, with a time step of 0.00033 fs. The time evolution was extended up to a maximum of 16 fs. We used local density approximation (LDA) in the Perdew–Zunger parameterization, because we observed from

preliminary tests, that the main features in the spectra are not improved or changed by using generalized gradient approximation (GGA), while the LDA implementation is numerically more stable. The absorption spectra along the three polarization directions are obtained by Fourier transforming the time propagated dipole moment of the system.

Excitation energies, from the linear response Casida's equations, have been also computed with both OCTOPUS and TURBOMOLE.⁶⁹ We used the PBE (Ref. 72) and PBE0 (Ref. 83) functionals and the Gaussian basis set of triple zeta valence quality (def2-TZVP).⁸⁴ Excitation energies obtained at PBE level from the two codes match well, and are discussed in the results section. The use of different exchange-correlation functionals and the relative agreement between our observations confirm our surmise.

III. RESULTS: ELECTRONIC PROPERTIES

The results of structural optimization, cluster stability, and the Kohn–Sham derived electronic description of anatase-like clusters (density of states and HOMO, LUMO spatial shape) are reported in the supplementary material.⁸⁵ In this section we present the study of the electronic structure of the various anatase-derived clusters (see Fig. 5 in the supplementary material), at different levels of theory. Due to the dimensions of the studied atomic clusters (between 6 Å and 10 Å), it can be expected that the electronic properties of these clusters differ strongly from the bulk, due to finite-size quantization and shape-anisotropy.

A. Ionization potential and electron affinity

In Fig. 1, panels (a)–(d), the vertical and adiabatic ionization potential (IP_V and IP_A), electron affinity (EA), dipole moments, and Kohn–Sham gaps are reported for all the neutral anatase clusters. It has to be noted that experimental photoemission data are only available, to the best of our knowledge, for negatively charged clusters,⁸⁶ therefore not direct comparison with the results for neutral clusters is in principle due. In Fig. 1(b) we report calculations of adiabatic and vertical detachment energies (ADE and VDE, respectively), compared to the same quantities but measured on anionic systems.⁸⁶ The vertical electron affinity (VEA) is close to the experimental ADE, even included in the error bar, apart from the very symmetric $(TiO_2)_8$ and $(TiO_2)_{10}$ clusters. The adiabatic electron affinity (AEA) is within 1 eV to the experimental values, for $n = 3, 4, 6, 7, 8$, but quite different for $n = 5, 9, 10$. ADE and VDE are almost equivalent for $n = 3, 4, 6, 7, 8$, and strongly differ for $n = 5, 9, 10$, again. From 3 to 7 units, the calculated VDE are also in quite good agreement with experimental data,⁸⁶ while for $n = 8, 9, 10$ they are underestimated, and close to the experimental values for ADE.

The oscillations observed in calculated ADE and VDE are probably related to the clusters structure, as some of them present highly isotropic or anisotropic geometries and charge distribution. Similar oscillations are also reported for more symmetric clusters,^{28,29} and for larger clusters.⁵⁹ Comparison with experimental data is somewhat complicated by two

FIG. 1. Calculated electronic properties of $(TiO_2)_n$ clusters, within DFT-PBE theory. (a) Vertical and adiabatic ionization potential, for $(TiO_2)_n$, $n = 3$ –10. (b) Vertical electron affinity, adiabatic and vertical detachment energy, and corresponding experimental data,⁸⁶ for $(TiO_2)_n$, $n = 3$ –10. (c) Dipole moments for the same neutral systems. (d) Kohn–Sham HOMO–LUMO gap. All quantities are calculated via pseudopotential plane wave method.

cofactors: it is possible that the structural determination becomes less precise with growing cluster size, and it may be dependent on chosen functional. On the other side, the experimental samples can in principle include more isomers.

Ground state dipole moment oscillations (Fig. 1(c)) are quite large and give estimation of structural and electronic anisotropy. The smallest dipole value is for the cluster $(TiO_2)_8$, which is indeed the most symmetric among this family. Low dipole cluster is also obtained from $(TiO_2)_5$, while the maximum dipole is associated to the very asymmetric $(TiO_2)_6$, $(TiO_2)_7$, and $(TiO_2)_9$. In Fig. 1(d) also the Kohn–Sham HOMO–LUMO are reported for the neutral clusters. Between $n = 5$ and $n = 10$ the KS gap oscillate with larger values for even clusters. The largest gap (2.5–2.8 eV) is for the $(TiO_2)_8$ system. This is also the only cluster with a gap larger than the bulk anatase value obtained from DFT. The relative KS energy gap also resembles the dipole moment. Larger (smaller) dipole moment, originating from large (small) charge-separation, is in fact associated with a smaller (larger) gap.

B. Electronic energy gap

In Fig. 2 we report the E_{gap}^{DFT} electronic gap of all neutral clusters, obtained within Δ SCF calculations within the plane waves implementation. The overall trend of DFT gaps

FIG. 2. Calculated electronic gap, within different theoretical level of approximation, for clusters with $n = 3$ –10. Results from DFT method are compared to Kohn–Sham gaps. The difference between the two methods, ΔE , is also reported, together with the G_0W_0 gap of $(\text{TiO}_2)_n$.

is not much dissimilar from the $E_{\text{gap}}^{\text{KS}}$ behavior. The difference ΔE between $E_{\text{gap}}^{\text{DFT}}$ and $E_{\text{gap}}^{\text{KS}}$ decreases, almost monotonically, from $n = 3$ to $n = 10$. The $E_{\text{gap}}^{\text{DFT}}$ values are close to each other at around 6.5 eV, for $n = 3$ –6, on the contrary of what happens for $E_{\text{gap}}^{\text{KS}}$, which is much lower. For larger clusters oscillations appear, with differences of almost 2 eV between 8 and 9–10 units. Given the small cluster dimension and the structure complexity, as at this scale the addition of one TiO₂ unit can change the cluster symmetry, therefore, disentangling effects of quantum confinement and symmetry in these clusters is not easy. All $E_{\text{gap}}^{\text{DFT}}$ are however larger than the bulk value, 3.8 eV.^{14,87,88} Largest gaps are found in $(\text{TiO})_3$ and $(\text{TiO})_8$ while in $(\text{TiO})_9$ and $(\text{TiO})_{10}$ the gap decreases toward the value calculated via G_0W_0 for the anatase bulk.¹⁴ As a matter of comparison, a cluster of anatase-like TiO₂ with a diameter of 7.9 Å (Ref. 45) and containing 87 atoms, has an electronic gap, calculated via DFT total energy difference, of 4.83 eV. The difference between $E_{\text{gap}}^{\text{DFT}}$ and $E_{\text{gap}}^{G_0W_0}$ is of 0.2 eV for $(\text{TiO}_2)_3$, and larger than (0.75 eV) for $(\text{TiO}_2)_6$. Such difference can be ascribed to the difficulties in converging the screened interaction in G_0W_0 calculation for localized systems in a plane waves approach, that could give a large error on the electronic gap. Similar results have already been reported for $(\text{TiO}_2)_n$ clusters,²⁸ in particular $(\text{TiO}_2)_7$ gap variation is of more than 1 eV going from $E_{\text{gap}}^{\text{DFT}}$ to G_0W_0 .

The general result is that the electronic gap for the $(\text{TiO}_2)_n$ clusters is 4.0–5.5 eV larger than the Kohn–Sham gap.²⁸ As shown in the following, the electronic gap is larger than the optical gap by almost the same amount.

C. Comparison with previous data

At this point it is important to make a comparison with other theoretical data and experimental results. The main difficulty is actually the comparison with clusters with the same

structure, as many different isomers of the $(\text{TiO}_2)_n$ are present in literature.

As an example, we could identify the $(\text{TiO}_2)_3$ structure as the same predicted in Refs. 58 and 60, but in both cases it is not its most stable structure, therefore no electronic characterization has been performed in those papers. The B3LYP method applied to a different $(\text{TiO}_2)_3$ isomer gives indeed a larger gap, by 2.5 eV, than the ones obtained here in the LDA/GGA approach,⁶⁰ as to be expected from hybrid functionals. Theoretical structures similar to the herewith discussed as anatase-derived clusters are reported for clusters $(\text{TiO}_2)_n$ (with $n = 4, 5, 6, 7, 10$) in Refs. 28, 29, 38, and 58–60, while we could not find a direct comparison on the experimental side. The $(\text{TiO}_2)_4$ cluster with the same structure as the one found here has a KS gap of 1.5 eV with a RPBE functional²⁸ and of 3.0 eV with PBE0.²⁹ For larger clusters, the KS gap is in the range of 1.8–3.0 eV,²⁹ close to our E_{KS} results. In Fig. 1(b), a comparison between our calculated ADE and VDE with experimental reported ones is shown, even though, the experimental data correspond to anionic systems.⁸⁶ Some of the values are really close to the predicted ones, and the general shape with n increasing is somehow reproduced. However, our VEA is much closer to the experimental one than our theoretical ADE, and some clusters ($n = 5, 8, 9, 10$) have quite dissimilar electronic properties. Therefore, given the extreme variability of electronic properties (and of structure stabilities) by also considering the different methodologies, it is not straightforward to draw general conclusions.

What we feel confident to say is that: (1) IPs are in the range of values obtained for similar clusters,^{53,59} (2) the VDE is in good agreement with experiments, at least concerning the behavior with n , up to $n = 7$, (3) the VEA is close to the experimental ADE, apart for $n = 8, 10$ (which are the two most symmetric clusters), (4) electronic gaps calculated via both DFT and G_0W_0 have much larger values than the ones attributed in literature to optical gaps, as to be expected. As shown in the following, the optical gaps obtained via TDDFT are instead quite close to the corresponding Kohn–Sham gap values.

IV. RESULTS: OPTICAL PROPERTIES

A. Time-dependent DFT description

Figures 3 and 4 report the optical spectra for the neutral and the charged clusters, calculated via the real time approach. Spectra for neutral systems are in good agreement with the ones obtained via the linear response approach. As a general remark, the spectra show a high intensity with maximum at 10 eV, and smooth edge at 7.5 eV, as clearly visible in the left panel of Fig. 3. Those excitations are due to transitions from deep valence levels of the clusters to lower energy part of the empty states (LUMO and LUMO+1, LUMO+2, etc.).

In Fig. 4 we report the spectra, obtained from time propagation calculations, for the anionic and cationic clusters cases. Quite intense features can be observed already at the low energy regime. Cations have Kohn–Sham gaps always lower than 0.4 eV. Therefore, quite low energy transitions can be

FIG. 3. Calculated absorption cross sections for neutral clusters, from $n = 3$ to $n = 10$. The optical range, going from 200 nm to >800 nm, is reported in the right panel, and the black points denote the TDDFT gap, as obtained from linear response theory. The zero of each curve has been shifted along the y axis, by arbitrary quantities, with respect to the neighbouring curves, to make easier the comparison between absorption edges and peaks. In the left panel, the same spectra on a wider range of energies. Here a shift of $0.5 \text{ \AA}^2$ has been applied. As comparison, the absorption spectrum for anatase bulk has its maximum absorption intensity around 5 eV.

obtained, in particular for $n = 6, 8, 9, 10$. $(\text{TiO}_2)_8$ has a quite intense absorption structure at low energy. These spectra present smoother structures, while clusters with $n = 3, 4, 5, 7$ have some well defined peaks in the optical range. The optical spectra for anions have also, for few selected cases, well defined peaks (e.g., $n = 3, 8, 10$), but again smooth states are present.

The analysis of optical transitions for neutral clusters indicates that the optical TDDFT gaps, shown in Fig. 3, are quite close to the Kohn–Sham gap data, differing by around 0.1 eV. The same happens if a hybrid functional is used, that is, a PBE0 hybrid exchange–correlation functional. The PBE0, DFT, and TDDFT gaps are larger than the ones obtained at LDA or GGA level, as to be expected (see

FIG. 4. Calculated TDDFT absorption cross sections for cationic (left panel) and anionic (right panel) clusters, from $n = 3$ to $n = 10$, using the real time propagator scheme. The zero of each curve has been shifted along the y axis, by a variable amount, with respect to the neighboring curves, to make easier the comparison among absorption edges and peaks.

TABLE I. Optical transition energies for neutral clusters. Results are reported for calculations with Gaussian based method, PBE and PBE0 functionals. Values obtained with LDA and PBE functionals in the real space method are equivalent to PBE linear response results here shown and not reported.

Transition (eV)	(TiO ₂) ₃	(TiO ₂) ₄	(TiO ₂) ₅	(TiO ₂) ₆	(TiO ₂) ₇	(TiO ₂) ₈	(TiO ₂) ₉	(TiO ₂) ₁₀
$f \geq 10^{-6}$ (PBE)	1.46	1.40	1.56	1.68	0.80	2.69	0.40	0.82
$f \geq 10^{-6}$ (PBE0)	2.68	2.57	2.83	3.02	2.15	3.65	0.71	1.84
$f \geq 10^{-3}$ (PBE)	2.15	2.66	1.80	2.19	1.58	2.94	0.75	0.99
$f \geq 10^{-3}$ (PBE0)	3.00	3.17	2.88	3.12	2.78	3.75	1.12	2.07

Table I), but very close to each other. So, in both PBE and PBE0, the expected opening of the optical gap with respect to the KS one is missing. Usually, the optical gap is larger than the Kohn–Sham gap. Instead, for inorganic clusters, it has already been reported⁴⁴ that the effect of TDDFT might not lead to a shift of the absorption edge, but instead to a redistribution of spectral weights, resulting in an overall energy blueshift of the spectrum, as happens in solids.⁴³ This blueshift is due to the localization induced on states by the molecular nature of these systems, which are closer, for dimension, to inorganic molecules than to solid systems. Additionally, the presence of strong charge transfer effects, not described by TDDFT,^{44,89–94} can contribute to the observed behavior. We show in the following that this is exactly the case.

First allowed transitions ($f \geq 10^{-6}$) are characterized in Table I. For all neutral clusters apart $n = 4$, the first allowed optical transition is given by the HOMO–LUMO excitation. However, the relative intensities (oscillator strength) of such transitions can vary by three orders of magnitude among, e.g., the (TiO₂)₅, with very low intensity, and (TiO₂)₈. For clusters with $n = 4, 5, 10$, the HOMO–LUMO transition is indeed optically dark. To find optical transitions with the same strength ($f = 10^{-3}$) of the first transition from the (TiO₂)₈ system, we have to look at higher transitions, shown in rows 3–4 of Table I, and lower occupied states are involved in such excitations. However, a deeper analysis of PBE vs PBE0 results highlights that the number of states among the first optical transition, and the first transition with strength of at least $f = 10^{-3}$, decreases if PBE0 is used instead of PBE. This is a well known consequence of the use of PBE and PBE0 to describe charge transfer phenomena, as PBE0 can partially reduce the number of fictitious excitations given by TDDFT, but not completely remove them. We investigate therefore the (TiO₂)_{*n*}, $n = 3–6$, systems to clarify if a charge transfer exists in those clusters.

B. Bethe–Salpeter solution and charge transfer effects

The large variation observed among electronic gaps (via G_0W_0 and DFT) 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. We performed calculations for the smallest clusters at the many body level, including the electron-hole interaction (i.e., by solving the BSE equation⁴³), by using the calculated G_0W_0 corrections. On one side, the strong redshift from electronic gap to optical gap is confirmed in agreement with TDDFT re-

sults. On the other side, the BSE gap is larger than the PBE gap, and quite close to the PBE0 values.

Even more interesting information comes indeed from the transitions analysis. The optical transitions described by BSE are, for some of the considered systems, quite different from the ones provided by the two TDDFT flavours. As shown in Figs. 5–8, apart from the overall shift, the spectral shapes are quite different for $n = 3$, slightly different for $n = 5, 6$, while they result very similar for $n = 4$.

Starting from (TiO₂)₃ (Fig. 5), we see that the first excitonic transition is optically allowed, but much more intense than in the TDDFT spectrum, and involves more states than HOMO–LUMO transition (contributing only 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.

(TiO₂)₄ has, in both TDDFT and BSE spectra, the same optical transitions, giving spectra that are rigidly shifted. As shown in the inset of Fig. 6, the first transitions in PBE0 and BSE have the same relative positions, and similar oscillator strengths. 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. We could not find admixture of states in this cluster, and the

FIG. 5. Spectra for (TiO₂)₃ optical absorption, within TDDFT (PBE and PBE0) and G_0W_0 -BSE methods. In the inset: comparison of energetic position and relative oscillator strengths among PBE0 and G_0W_0 -BSE spectra. The PBE0 transitions have been shifted to have the first transition coincide with the first G_0W_0 -BSE one, for the sake of clarity.

FIG. 6. Spectra for $(\text{TiO}_2)_4$ optical absorption within TDDFT (PBE and PBE0) and G_0W_0 -BSE methods. In the inset: comparison of energetic position and relative oscillator strengths among PBE0 and G_0W_0 -BSE spectra. The PBE0 transitions have been shifted to have the first transition coincide with the first G_0W_0 -BSE one, for the sake of clarity.

two theories, TDDFT and BSE, are equivalent for its study, apart an almost rigid energy shift.

The $(\text{TiO}_2)_5$ and $(\text{TiO}_2)_6$ clusters have a more complex behavior. Indeed the spectra from the two methods shown in Figs. 7 and 8 are quite similar. However, a detailed analysis of transitions highlights that different states are involved, depending on the approach. For $(\text{TiO}_2)_5$, 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 optical transitions.

In $(\text{TiO}_2)_6$, the first transitions are less intense and the spectrum less sharp than in $(\text{TiO}_2)_5$, more similar to $(\text{TiO}_2)_4$ one. The first, optical allowed but really weak ($f = 10^{-6}$)

FIG. 7. Spectra for $(\text{TiO}_2)_5$ optical absorption within TDDFT (PBE and PBE0) and G_0W_0 -BSE methods. In the inset: comparison of energetic position and relative oscillator strengths among PBE0 and G_0W_0 -BSE spectra. The PBE0 transitions have been shifted to have the first transition coincide with the first G_0W_0 -BSE one, for the sake of clarity.

FIG. 8. Spectra for $(\text{TiO}_2)_6$ optical absorption within TDDFT (PBE and PBE0) and G_0W_0 -BSE methods. In the inset: comparison of energetic position and relative oscillator strengths among PBE0 and G_0W_0 -BSE spectra. The PBE0 transitions have been shifted to have the first transition coincide with the first G_0W_0 -BSE one, for the sake of clarity.

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, depending on the system. Among examined cases, the only one for which both methods give the same result is the $(\text{TiO}_2)_4$, probably due to the high symmetry of the system. For $(\text{TiO}_2)_3$, 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 with experimental data could be performed, 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.

V. CONCLUSION

We identified the most stable class of atomic $(\text{TiO}_2)_n$ clusters among four different seed structures. For this anatase-like family, we investigated electronic and optical properties, observing a strong oscillating behavior for dipole moment, electronic gap, and optical gap. The electronic gap, to be compared with photoemission data for the neutral clusters, is in the range of 4.5–7.0 eV, due to the strong quantum confinement of these atomic-size systems.

The optical gap, intended as the first optically allowed transition, is instead quite smaller than the electronic one, ranging from 0.5 eV to <3.0 eV, depending on the method. In particular for some of the investigated clusters, both in their neutral and charged configurations, well defined optical peaks can be identified, and may provide a useful tool for

establishing the presence of well determined species in atomic clusters samples. As shown by the comparison among TDDFT and BSE spectra, the two methods provide results that can be different depending on the investigated system. Spectra from TDDFT and BSE can be in quite good quantitative agreement for some systems (TiO₂)₄, and in this case the usage of TDDFT is computationally more convenient. Or, spectra can be in good qualitative agreement but with differences in the details of the transitions, as for (TiO₂)_{5,6}, and in this case TDDFT can be used with some caution to identify for example the presence of an isomer from the existence of a peak in the spectrum. Finally, different spectral shapes (TiO₂)₃ can be produced by the two methods due to a different physical description, and those cases must be treated carefully.

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.

We think that, as for the case of less symmetric clusters here analyzed, the use of many body methods becomes more and more important when the symmetry of the system is lowered, and the effects of point defects or other asymmetries affect the electronic properties of the system. The present work is the first step to address the photoabsorption and photocatalytic activities of dye-functionalized TiO₂ nanostructures. Work along those lines is in progress.

ACKNOWLEDGMENTS

We acknowledge financial support from Spanish MEC (FIS2011-65702-C02-01), ACI-Promociona (ACI2009-1036), Grupos Consolidados UPV/EHU del Gobierno Vasco (IT-319-07), the European Research Council Advanced Grant DYNamo (ERC-2010-AdG -Proposal No. 267374) and the European Research Council Starting Grant DEDOM (Grant Agreement No. 207441). We acknowledge support by the Barcelona Supercomputing Center, “Red Espanola de Supercomputacion,” SGIker ARINA (UPV/EHU), Transnational Access Programme HPC-Europe++, CNS-Ipicyt, Mexico and CINECA. L.C. acknowledges funding from UPV/EHU through the “Ayudas de Especialización para Investigadores Doctores” program. A.H.R. has been supported by CONACyT Mexico under projects J-152153-F, and TAMU-CONACyT. L.C. and A.R. are grateful to Y. Pouillon for valuable technical support. We also thank M. Palummo for helpful discussions.

¹A. Heller, *Science* **223**, 1141 (1984).

²M. Grätzel, *Nature* **414**, 338 (2001).

³M. Grätzel, *J. Photochem. Photobiol. C* **4**, 145 (2003).

⁴D. V. Bavykin, J. M. Friedrich, and F. C. Walsh, *Adv. Mater.* **18**, 2807 (2006).

⁵K. M. Glassford and J. R. Chelikovsky, *Phys. Rev. B* **45**, 3874 (1992).

⁶K. M. Glassford and J. R. Chelikovsky, *Phys. Rev. B* **46**, 1284 (1992).

⁷R. Asahi, Y. Taga, W. Mannstadt, and A. J. Freeman, *Phys. Rev. B* **61**, 7459 (2000).

⁸M. Mikami, S. Nakamura, O. Kitao, H. Arakawa, and X. Gonze, *Jpn. J. Appl. Phys.* **39**, L847 (2000).

⁹N. Hosaka, T. Sekiya, C. Satoko, and S. Kurita, *J. Phys. Soc. Jpn* **66**, 877 (1997).

¹⁰L. K. Dash, F. Bruneval, V. Trinité, N. Vast, and L. Reining, *Comput. Mater. Sci.* **38**, 482 (2007).

¹¹S.-D. Mo and W. Y. Ching, *Phys. Rev. B* **51**, 13023 (1995).

¹²H. Tang, F. Levy, H. Berger, and P. E. Schmid, *Phys. Rev. B* **52**, 7771 (1995).

¹³N. Hosaka, T. Sekiya, and S. Kurita, *J. Lumin.* **72**, 874 (1997).

¹⁴L. Chiodo, J. M. García-Lastra, A. Iacomino, S. Ossicini, J. Zhao, H. Petek, and A. Rubio, *Phys. Rev. B* **82**, 045207 (2010).

¹⁵U. Diebold, *Surf. Sci. Rep.* **48**, 53 (2003).

¹⁶R. A. Evarestov and A. V. Bandura, *Int. J. Quantum Chem.* **96**, 282 (2004).

¹⁷M. Ramamoorthy, D. Vanderbilt, and R. D. King-Smith, *Phys. Rev. B* **49**, 16721 (1994).

¹⁸R. A. Evarestov and A. V. Bandura, *Surf. Sci.* **603**, L117 (2009).

¹⁹H. Perron, C. Domain, J. Roques, R. Drot, E. Simoni, and H. Catalette, *Theor. Chem. Acc.* **117**, 565 (2007).

²⁰G. S. Herman, Z. Dohnálek, N. Ruzyski, and U. Diebold, *J. Phys. Chem. B* **107**, 2788 (2003).

²¹D. Vogtenhuber, R. Podloucky, A. Neckel, S. G. Steinemann, and A. J. Freeman, *Phys. Rev. B* **49**, 2099 (1994).

²²M. Lazzeri, A. Vittadini, and A. Selloni, *Phys. Rev. B* **63**, 155409 (2001).

²³Y. Liang, S. Gan, S. A. Chambers, and E. I. Altman, *Phys. Rev. B* **63**, 235402 (2001).

²⁴A. S. Barnard, S. Erdin, Y. Lin, P. Zapol, and J. W. Halley, *Phys. Rev. B* **73**, 205405 (2006).

²⁵A. S. Barnard and P. Zapol, *J. Phys. Chem. B* **108**, 18435 (2004).

²⁶L. Chiodo, J. M. García-Lastra, D. J. Mowbray, A. Iacomino, and A. Rubio, “Tailoring electronic and optical properties of TiO₂: nanostructuring, doping and molecular-oxide interactions,” in *Computational Studies of New Materials: From Nanostructures to Bulk Energy Conversion Materials*, edited by T. F. George, D. Jelski, R. R. Letfullin, and G. Zhang (World Scientific, Singapore, 2011).

²⁷M. R. Ranade, A. Navrotsky, H. Z. Zhang, J. F. Banfield, S. H. Elder, A. Zaban, P. H. Borse, S. K. Kulkarni, G. S. Doran, and H. J. Whitfield, *Proc. Natl. Acad. Sci. U.S.A.* **99**, 6476 (2002).

²⁸D. J. Mowbray, J. I. Martinez, J. M. García-Lastra, K. S. Thygesen, and K. W. Jacobsen, *J. Phys. Chem. C* **113**, 12301 (2009).

²⁹S. A. Shevlin and S. M. Woodley, *J. Phys. Chem. C* **114**, 17333 (2010).

³⁰A. A. Gribb and J. F. Banfield, *Am. Mineral.* **82**, 717 (1997).

³¹H. Zhang and J. F. Banfield, *J. Mater. Chem.* **8**, 2073 (1998).

³²J. Muscat, V. Swamy, and N. Harrison, *Phys. Rev. B* **65**, 224112 (2002).

³³G. Giorgi, M. Palummo, L. Chiodo, and K. Yamashita, *Phys. Rev. B* **84**, 073404 (2011).

³⁴P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).

³⁵W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133, (1965).

³⁶A. Selloni, *Nature Mater.* **7**, 613 (2008).

³⁷T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic-Structure Theory* (Wiley, England, 2000).

³⁸S. Li and D. A. Dixon, *J. Phys. Chem. A* **112**, 6646 (2008).

³⁹L. Hedin, *Phys. Rev.* **139**, A976 (1965).

⁴⁰M. S. Hybertsen and S. G. Louie, *Phys. Rev. B* **34**, 5390 (1986).

⁴¹R. W. Godby, M. Schlüter, and L. J. Sham, *Phys. Rev. B* **37**, 10159 (1988).

⁴²F. Aryasetiawan and O. Gunnarsson, *Rep. Prog. Phys.* **61**, 237 (1998).

⁴³G. Onida, L. Reining, and A. Rubio, *Rev. Mod. Phys.* **74**, 601 (2002).

⁴⁴*Time-Dependent Density Functional Theory*, edited by M. A. L. Marques, C. Ullrich, F. Nogueira, A. Rubio, K. Burke, and E. K. U. Gross (Springer, Berlin, 2006), Vol. 706.

⁴⁵A. Iacomino, G. Cantele, D. Ninno, I. Marri, and S. Ossicini, *Phys. Rev. B* **78**, 075405 (2008).

⁴⁶F. De Angelis, A. Tilotta, and A. Selloni, *J. Am. Chem. Soc.* **126**, 15024 (2004).

⁴⁷F. De Angelis, S. Fantacci, and A. Selloni, *Nanotechnology* **19**, 424002 (2008).

⁴⁸W. R. Duncan and O. V. Prezhdo, *Annu. Rev. Phys. Chem.* **58**, 143 (2007).

⁴⁹W. R. Duncan, C. F. Craig, and O. V. Prezhdo, *J. Am. Chem. Soc.* **129**, 8528 (2007).

⁵⁰O. V. Prezhdo, W. R. Duncan, and V. V. Prezhdo, *Acc. Chem. Res.* **41**, 339 (2008).

⁵¹W. R. Duncan and O. V. Prezhdo, *J. Am. Chem. Soc.* **130**, 9756 (2008).

⁵²F. Balleto and R. Ferrando, *Rev. Mod. Phys.* **77**, 371 (2005).

⁵³Z.-W. Qu and G.-J. Kroes, *J. Phys. Chem. B* **110**, 8998 (2006).

⁵⁴D. J. Taylor and M. J. Paterson, *J. Chem. Phys.* **133**, 204302 (2010).

⁵⁵F. Grein, *J. Chem. Phys.* **126**, 034313 (2007).

- ⁵⁶A. Hagfeldt, R. Bergström, H. O. G. Siegbahn, and S. Lunell, *J. Phys. Chem.* **97**, 12725 (1993).
- ⁵⁷A. C. Tsipis and C. A. Tsipis, *Phys. Chem. Chem. Phys.* **1**, 4453 (1999).
- ⁵⁸S. Lago, J. A. Mejías, S. Hamad, C. R. A. Catlow, and S. M. Woodley, *J. Phys. Chem. B* **109**, 15741 (2005).
- ⁵⁹Z.-W. Qu and G.-J. Kroes, *J. Phys. Chem. C* **111**, 16808 (2007).
- ⁶⁰T. Albaret, F. Finocchi, and C. Noguera, *J. Chem. Phys.* **113**, 2238 (2000).
- ⁶¹T. Albaret, F. Finocchi, and C. Noguera, *Faraday Discuss.* **114**, 285 (1999).
- ⁶²I. Onal, S. Soyler, and S. Senkan, *Surf. Sci.* **600**, 2457 (2006).
- ⁶³P. C. Redfern, P. Zapol, L. A. Curtiss, T. Rajh, and M. C. Thurnauer, *J. Phys. Chem. B* **107**, 11419 (2003).
- ⁶⁴Z. Guo, W. Z. Liang, Y. Zhao, and G. H. Chen, *J. Phys. Chem. C* **112**, 16655 (2008).
- ⁶⁵R. Sánchez-de-Armas, M. A. San-Miguel, J. Oviedo, A. Márquez, and J. F. Sanz, *Phys. Chem. Chem. Phys.* **13**, 1506 (2011).
- ⁶⁶D. Zhang, H. Sun, J. Liu, and C. Liu, *J. Phys. Chem. C* **113**, 21 (2009).
- ⁶⁷H. Zhang, B. Chen, J. F. Banfield, and G. A. Waychunas, *Phys. Rev. B* **78**, 214106 (2008).
- ⁶⁸A. Castro, H. Appel, M. Oliveira, C. A. Rozzi, X. Andrade, F. Lorenzen, M. A. L. Marques, E. K. U. Gross, and A. Rubio, *Phys. Status Solidi B* **243**, 2465 (2006).
- ⁶⁹See <http://www.turbomole.com> for TURBOMOLE V6, 2009, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007.
- ⁷⁰B. Delley, *J. Chem. Phys.* **92**, 508 (1990).
- ⁷¹B. Delley, *J. Chem. Phys.* **94**, 7245 (1991).
- ⁷²J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ⁷³D. D. Koelling and B. N. Harmon, *J. Phys. C* **10**, 3107 (1977).
- ⁷⁴P. Pykkö, *Chem. Rev.* **88**, 563 (1988).
- ⁷⁵P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. Fabris, G. Fratesi, S. de Gironcoli, R. Gebauer, U. Gerstmann, C. Gougousis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazurek, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, *J. Phys. Condens. Matter* **21**, 395502 (2009).
- ⁷⁶G. Makov and M. C. Payne, *Phys. Rev. B* **51**, 4014 (1995).
- ⁷⁷K. Schonhammer and O. Gunnarsson, *J. Phys. C* **20**, 3675 (1987).
- ⁷⁸J. Simons and K. D. Jordan, *Chem. Rev.* **87**, 535 (1987).
- ⁷⁹A. Marini, C. Hogan, M. Grüning, and D. Varsano, *Comput. Phys. Commun.* **180**, 1392 (2009).
- ⁸⁰C. A. Rozzi, D. Varsano, A. Marini, E. K. U. Gross, and A. Rubio, *Phys. Rev. B* **73**, 205119 (2006).
- ⁸¹B. I. Lundqvist, *Phys. Kondens. Mater.* **6**, 193 (1967); *ibid.* **6**, 206 (1967); A. W. Overhauser, *Phys. Rev. B* **3**, 1888 (1971).
- ⁸²M. Palummo, C. Hogan, F. Sottile, P. Bagala, and A. Rubio, *J. Chem. Phys.* **131**, 084102 (2009).
- ⁸³C. Adamo and V. Barone, *J. Chem. Phys.* **110**, 6158 (1999).
- ⁸⁴F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* **7**, 3297 (2005).
- ⁸⁵See supplementary material at <http://dx.doi.org/10.1063/1.3668085> for structures of chain-like, ring-like, rutile-like and anatase-like clusters and for ground state electronic properties of anatase-like clusters.
- ⁸⁶H.-J. Zhai and L.-S. Wang, *J. Am. Chem. Soc.* **129**, 3022 (2007).
- ⁸⁷L. Thulin and J. Guerra, *Phys. Rev. B* **77**, 195112 (2008).
- ⁸⁸W. Kang and M. S. Hybertsen, *Phys. Rev. B* **82**, 085203 (2010).
- ⁸⁹M. E. Casida, F. Gutierrez, J. Guan, F.-X. Gadea, D. Salahub, and J.-P. Daudey, *J. Chem. Phys.* **113**, 7062 (2000).
- ⁹⁰Z.-L. Cai, K. Sendt, and J. R. Reimers, *J. Chem. Phys.* **117**, 5543 (2002).
- ⁹¹A. Dreuw, J. L. Weisman, and M. Head-Gordon, *J. Chem. Phys.* **119**, 2943 (2003).
- ⁹²D. J. Tozer, *J. Chem. Phys.* **119**, 12697 (2003).
- ⁹³S. Grimme and M. Parac, *ChemPhysChem* **4**, 292 (2003).
- ⁹⁴A. Dreuw and M. Head-Gordon, *J. Am. Chem. Soc.* **126**, 4007 (2004).