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Electronic Structure of Dye-Sensitized TiO$_2$ Clusters from Many-Body Perturbation Theory

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Abstract

The development of new types of solar cells is driven by the need for clean and sustainable energy. In this respect dye sensitized solar cells (DSC) are considered as a promising route for departing from the traditional solid state cells. The physical insight provided by computational modeling may help develop improved DSCs. To this end it is important to obtain an accurate description of the electronic structure, including the fundamental gaps and level alignment at the dye-TiO$_2$ interface. This requires a treatment beyond ground-state density functional theory (DFT). We present a many-body perturbation theory study, within the $G_0W_0$ approximation, of two of the crystalline phases of dye-sensitized TiO$_2$ clusters, reported by Benedict and Coppens [J Am Chem Soc 132 (9), 2938 (2010)]. We obtain geometries in good agreement with experiment by using DFT with the Tkatchenko-Scheffler van der Waals correction. We demonstrate that even when DFT gives a good description of the valence spectrum and a qualitatively correct picture of the electronic structure of the dye-TiO$_2$ interface, $G_0W_0$ calculations yield more valuable quantitative information regarding the fundamental gaps and level alignment. In addition, we systematically investigate the issues pertaining to $G_0W_0$ calculations, namely: (i) convergence with respect to the number of basis functions, (ii) dependence on the mean field starting point, and (iii) the validity of the assumption that the DFT wave-function is a good approximation to the quasi-particle wave-function. We show how these issues are manifested for dye molecules and for dye-sensitized TiO$_2$ clusters.
1. Introduction

The development of new types of solar cells is driven by the need for clean, sustainable energy. One promising route for departing from the traditional solid-state cells is a dye sensitized solar cell (DSC).\(^1,2\) In this type of cell, the light is harvested by a sensitizer, which may be a dye molecule or a semiconductor quantum dot,\(^3\) attached to a wide band gap semiconductor of mesoporous or nanocrystalline morphology, typically TiO\(_2\). Charge separation occurs via electron injection from the photoexcited sensitizer into the oxide.\(^1,2\) This can happen either indirectly, by electron transfer from the excited state of the dye to the conduction band of the oxide, or directly, through a charge-transfer excitation. The injected electrons subsequently migrate to the collector electrode and the dye is regenerated by electron donation from an organic hole-conductor or an electrolyte.

DSCs have achieved efficiencies exceeding 11%\(^4,1\) and are still far from their theoretical limit, as compared to the more technologically mature solid state cells.\(^5\) One actively pursued research avenue toward improving the performance and reducing the cost of DSCs is the synthesis of new dyes. Specifically, there is an interest in dyes with a smaller gap that can maximally utilize the solar spectrum and in fully organic dyes without expensive transition metals. The physical insight provided by computational modeling may help engineer new dyes and assess their performance.

Many electronic structure calculations have been done for various dye molecules (see, e.g. refs. 4,6), typically employing density functional theory (DFT) for the ground state properties and time-dependent DFT (TDDFT) for the absorption spectrum. However, the efficiency of electron injection depends not only on the dye molecule itself but also on its interface with the TiO\(_2\). The interaction between the dye and the TiO\(_2\) leads to changes in their relative energy level alignment and to hybridization of their molecular orbitals. To capture this, the combined dye+TiO\(_2\) system has to be treated as a whole. Such studies are scarce owing to the size and complexity of the combined system. The few studies reported thus far\(^7,8,9\) have employed TDDFT with conventional semi-local and hybrid functionals.

Like DFT, TDDFT is exact in principle,\(^10,11\) but still suffers from the deficiencies of commonly used approximations to the exchange-correlation (xc) functional, e.g., the incorrect derivative discontinuity and self-interaction errors (SIE).\(^12\) These affect the description of the ground state and of excited states. For example, SIE have been shown to lead to an unsatisfactory description of the ground state electronic structure of transition metal phthalocyanines,\(^13,14\) which are chemically similar to commonly used dyes. Indeed, TDDFT has been shown to provide an inconsistent description of the
absorption spectrum of porphyrins and large extended π-systems.\textsuperscript{15} Problems stemming from the xc-functional also lead to difficulties in the description of charge-transfer excitations when TDDFT is used with standard functionals, including conventional hybrids.\textsuperscript{16} Recently, a successful treatment of charge-transfer excitations in coumarine-based dyes has been achieved by using TDDFT with a range-separated hybrid functional, where the range separation parameter is tuned to a system-specific value.\textsuperscript{17} However, even this method is not guaranteed to succeed for dye-sensitized TiO\textsubscript{2} because, as is often the case for interfaces between dissimilar materials, the two sides of the interface may require different fractions of exact exchange (Exx) and different range-separation parameters.

An alternative route to calculating the optical absorption spectrum is through Green’s function based many-body perturbation theory.\textsuperscript{18,19} Within this approach quasiparticle (QP) excitation energies are obtained via the $GW$ approximation, where $G$ is the one-particle Green’s function and $W$ is the dynamically screened Coulomb potential. On the basis of $GW$, one may construct the two-particle Green’s function, which describes coupled electron-hole excitations, and then solve the Bethe-Salpeter equation (BSE)\textsuperscript{11,20} to obtain the optical spectrum. The $GW$+BSE approach has been applied successfully to obtain the optical spectra of several molecular systems\textsuperscript{21,22,23} and of TiO\textsubscript{2},\textsuperscript{24} therefore it is a promising method for treating dye-sensitized TiO\textsubscript{2}.

Importantly, the success of a BSE calculation is contingent upon a reliable underlying $GW$ calculation. Owing to the exceedingly high computational cost of fully self-consistent $GW$\textsuperscript{25,26} a perturbative approach is often taken, where QP excitation energies are obtained as a first order correction to the DFT eigenvalues, based on the underlying single-electron DFT orbitals. This approach, which is also used here, is known as $G_0W_0$. The main issues pertaining to $G_0W_0$ calculations, further elaborated below, are: (i) convergence with respect to the number of basis functions, (ii) sensitivity to the mean field starting point, and (iii) the validity of the assumption that the DFT wave-function is a good approximation to the QP wave-function. Consequently, there is a need to examine the feasibility and performance of $G_0W_0$ for the valence spectrum, fundamental gaps, and level alignment of dye-sensitized TiO\textsubscript{2}.

In order to assess the performance of computational methods, a direct comparison to experiment is essential. Unfortunately, it is often the case that the structure of the dye+TiO\textsubscript{2} system is not known exactly owing to the difficulty in performing precise experimental measurements of the geometry of disordered interfaces. In such a situation it is difficult to determine whether discrepancies between theory and experiment arise from the
limitations of the computational methods used or simply from assuming an
incorrect geometry. Conversely, broadening of photoemission and adsorption
spectra may limit the ability to pin down meaningful differences between
theory and experiment. Therefore, we must carefully choose a test system
for the purpose of method validation.

Recently, Benedict and Coppens reported several crystalline phases of
dye-sensitized TiO$_2$ clusters.\textsuperscript{27} These systems have a well-defined structure,
characterized by x-ray diffraction (XRD). This, as well as the absence of
solvent and counter-ions, makes them an ideal test bed for theory because a
direct comparison to experiment is possible. For the purpose of this study,
we have chosen two of these systems, schematically depicted in Figure 1: (i)
Ti$_2$Cat$_2$, whose unit cell contains four units of C$_{30}$H$_{52}$O$_{10}$Ti$_2$ - a (TiO$_2$)$_2$ cluster
sensitized with two molecules of catechol (cat) and capped with six additional
molecules of isopropyl alcohol (IPA) - a total of 376 atoms, 94 in each
molecular unit; (ii) Ti$_3$INA$_3$, whose unit cell contains two units of
C$_{39}$H$_{61}$N$_3$O$_{14}$Ti$_3$ - a (TiO$_2$)$_3$ cluster sensitized with three molecules of
isonicotinic acid (INA) and capped with seven additional molecules of IPA – a
total of 240 atoms, 120 in each molecular unit.

Ti$_2$Cat$_2$ and Ti$_3$INA$_3$, though obviously much smaller than the dye molecules
and TiO$_2$ particles used in actual DSCs, contain all the essential physics of the
local interaction between the dye and the TiO$_2$ clusters, i.e. the level
alignment and the orbital hybridization between the two. Although the
fundamental gaps of the TiO$_2$ clusters modeled here are much wider than
those of the larger bulk-like nano-particles used in DSCs, the principles
demonstrated here, particularly with respect to method validation, will still
apply when it comes to the description of larger systems. Screening effects,
which are present in extended systems, are not accounted for here.

We present a benchmark $GW$ study of dye-sensitized TiO$_2$ clusters. We
demonstrate that even when DFT gives a good description of the valence
spectrum and a qualitatively correct picture of the electronic structure of the
dye-TiO$_2$ interface, $G_0W_0$ calculations yield more valuable quantitative
information regarding the fundamental gaps and level alignment. We then
discuss the level alignment of Ti$_2$Cat$_2$ and Ti$_3$INA$_3$, in the context of DSCs. In
addition, we systematically investigate the issues pertaining to $G_0W_0$
calculations, namely: (i) convergence with respect to the number of basis
functions, (ii) sensitivity to the mean field starting point, and (iii) the validity
of the assumption that the DFT wave-function is a good approximation to the
QP wave-function. We show how these issues are manifested for dye
molecules and for dye-sensitized TiO$_2$ clusters.

2. Methods
All calculations were performed using the all-electron numeric atom-centered orbital (NAO) code, FHI-aims.\textsuperscript{28,29} The NAO basis sets are grouped into a minimal basis, containing only basis functions for the core and valence electrons of the free atom, followed by four hierarchically constructed tiers of additional basis functions (tier 1-4). Geometry relaxations were carried out using the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE)\textsuperscript{30} with a tier 2 basis set, which has been demonstrated to approach the basis set limit for ground-state GGA calculations and be nearly free of basis set superposition errors (BSSE).\textsuperscript{28} The Tkatchenko-Scheffler (TS) van der Waals (vdW) correction\textsuperscript{31} was used to treat dispersion interactions. A detailed account is given in Appendix A.

The QP energy levels were computed using the \( G_0W_0 \) method. In this approach QP energies are obtained perturbatively as a first order correction to the Kohn-Sham (KS) DFT eigenvalues, employing the diagonal approximation to the self-energy. This amounts to assuming that the orbitals obtained from the DFT calculations mimic the quasi-particle wave-function sufficiently well, in which case only the orbital energies need to be corrected.\textsuperscript{18} Although this approximation is not universally valid (see, e.g., Ref. 22), it often yields excellent results. A complete account of the all-electron implementation of \( G_0W_0 \) in FHI-aims has been given elsewhere.\textsuperscript{32} Briefly, the implementation makes use of the resolution-of-identity (RI) technique, whereby a set of auxiliary basis functions is introduced to represent both the Coulomb potential and the non-interacting response function. This allows for efficient GW calculations with NAO basis functions. The RI accuracy and NAO basis set convergence have been benchmarked in Ref 32. The self-energy is first calculated on the imaginary frequency axis and then analytically continued to the real frequency axis using a two-pole fitting procedure.\textsuperscript{33} The NAO basis set convergence of \( G_0W_0 \) calculations is further examined below.

Performing \( GW \) calculations in an all-electron code has the advantage that no pseudo-potential errors are introduced.\textsuperscript{26,34} In addition, using NAO basis functions has been observed to lead to a more rapid convergence with the number of basis functions, as compared to plane-waves, because NAOs are inherently localized over regions of large electron density, in contrast to delocalized plane-waves. The fact that periodic boundary conditions are not imposed in FHI-aims is another advantage for \( GW \) calculations of molecular systems, as there is no need for large regions of vacuum to avoid artifacts from spurious interactions between periodic replicas.

In order to examine the starting point dependence of \( G_0W_0 \) and find an optimal starting point, \( G_0W_0 \) calculations were carried out from different mean-field starting points. These include PBE, the one-parameter PBE-based
hybrid functional (PBEh),\textsuperscript{35} PBE with a varying fraction of exact exchange (Exx), and Hartree-Fock (HF). The name “PBEh” is reserved for PBE with 25\% exact exchange. Functionals with a different fraction of exact exchange are denoted as, e.g., PBE+35\%Exx. $G_0W_0$ calculations are denoted as $GW@[\text{mean-field starting point}]$. For example, $GW@PBE$ denotes a $G_0W_0$ calculation on top of a PBE DFT calculation. The scaled zero-order regular approximation (ZORA) method\textsuperscript{36} was used to account for scalar relativistic effects in the single-point DFT calculations that served as starting points for $G_0W_0$.

3. Results and Discussion

3.1 Basis Set Convergence

We begin by verifying the basis set convergence of our $G_0W_0$ calculations. The standard implementation of the $G_0W_0$ self-energy contains an infinite sum over states, which in practice translates into a finite sum over a very large number of occupied and unoccupied states. This leads to a notoriously slow convergence of such calculations with respect to basis set size.\textsuperscript{37} Owing to the size of Ti$_2$cat$_2$ and Ti$_3$I\textsubscript{1}NA$_3$ the basis set convergence studies were conducted for smaller fragments of the full systems, shown in Figure 2: a TiO$_2$ molecule, catechol, and IPA. In Figure 3, the QP HOMO and LUMO levels, calculated based on PBE and PBEh with increasingly large basis sets are compared to experimental ionization potentials (IP) and electron affinities (EA), respectively. QP energies computed from equilibrium geometries should be compared to vertical IP and EA. However, for some of the systems studied here, only adiabatic experimental values are available. Often the addition or removal of an electron results in a minor structural relaxation such that the adiabatic values are not very far from the vertical values and can still provide a sense of whether a reasonable agreement with experiment is achieved.

$G_0W_0$ calculations have been shown to be adequately converged at the tier 4 level, as compared to reference calculations using larger basis sets augmented with Gaussian basis functions and to experimental vertical IPs for a set of small molecules.\textsuperscript{32} For TiO$_2$\textsuperscript{38,39} and IPA\textsuperscript{40} the $GW@PBEh$ HOMO and LUMO at the tier 4 level are within 0.1 eV of the experimental IP and EA. For catechol,\textsuperscript{41} the $GW@PBEh$ HOMO is very close to the adiabatic IP and about 0.4 eV above the vertical IP.\textsuperscript{42} The $GW@PBE$ HOMO and LUMO follow the same basis set convergence trends as those of $GW@PBEh$. However, they are generally not as close to the experimental IP and EA. This reflects the sensitivity of $G_0W_0$ calculations to the DFT starting point, elaborated below.
Our findings are consistent with those reported for other small organic molecules\textsuperscript{32} and for copper phthalocyanine (CuPc).\textsuperscript{43}

### 3.2 Starting Point Sensitivity

Because the $G_0W_0$ QP energies are calculated in a “one-shot” non-self-consistent manner, based on the DFT eigenvalues and orbitals, some dependence on the starting point is expected. The starting point dependence of $G_0W_0$ calculations may enter through the DFT orbitals, whose spatial distribution (e.g., the degree of localization/delocalization) and hybridization may vary, or through the DFT eigenvalues. The question of what is the appropriate starting point for $G_0W_0$ calculations has been raised before, mostly in the context of narrow-gap semiconductors, which semi-local functionals predict to be metallic, or in the context of wide-gap semiconductors whose band gaps are severely underestimated by semi-local functionals.\textsuperscript{44} It has also been shown that for CuPc there is a qualitative difference between the semi-local and hybrid DFT spectra, which stems from the SIE affecting highly localized metal-derived orbitals.\textsuperscript{13} This carries over to $G_0W_0$ calculations, leading to qualitative differences between $GW$@PBE and $GW$@PBEh in the ordering of the frontier orbitals.\textsuperscript{43} For this reason, we now examine the dependence of the QP energies of TiO$_2$, catechol, and INA on the fraction of exact exchange in the underlying DFT calculation.

Figure 4 shows the DFT and QP HOMO and LUMO energies of a TiO$_2$ molecule, IPA, and catechol, calculated with a tier 4 basis set, using PBE with an increasingly large fraction of exact exchange, as well as HF, and compared to experimental values of IP and EA. We note that the difference between the PBE+100% Exx and the HF starting points is the absence of correlation in the latter. The corresponding IP and EA obtained from total energy differences at the DFT level ($\Delta$SCF) with a tier 2 basis set are also shown for comparison.

We observe that the $G_0W_0$ calculations are fairly insensitive to the choice of DFT functional. The QP HOMO and LUMO levels are remain within 1 eV of the experimental IP and EA while the corresponding DFT HOMO and LUMO vary by up to 7 eV. We note that the single-particle Kohn-Sham eigenvalues generated using popular DFT functionals are not expected to quantitatively agree with the IP and EA in practice, although in principle there is such a correspondence for the HOMO if the exact DFT functional is used.\textsuperscript{45} The $\Delta$SCF values are generally quite close to the $G_0W_0$ values and can be used in order
to shift DFT spectra for the purpose of comparison to photoelectron spectroscopy experiments, as done below.

Interestingly, it is evident from Figure 4 that the fraction of exact exchange required in order to achieve the best agreement with the experimental IP and EA may vary from one system to another. It has been shown that GW@PBEh gives smaller errors than GW@HF and GW@PBE with respect to the vertical IPs for a set of atoms and molecules. Moreover, in some cases the effect of using a PBEh starting point is more complex than a rigid shift of the QP energies. It is therefore desirable to develop guidelines for choosing the optimal starting point for a \( G_0 W_0 \) calculation. We attempt to do so by examining the effect of the DFT starting point on the valence QP spectra of (TiO\(_2\))^\text{−}, catechol, and INA.

Figure 5 shows the DFT and QP spectra of (TiO\(_2\))^\text{−}, broadened by a 0.25 eV Gaussian to simulate experimental resolution, compared to the gas phase ultraviolet photoemission spectrum (UPS). The DFT spectra are shifted to align the HOMO with the vertical electron detachment energies obtained by taking the total energy difference between the anion and the neutral in the anion geometry with the respective functional. QP energies are directly comparable to gas phase UPS, therefore they are not shifted. We also note that when comparing the calculated spectra to photoemission experiments we focus primarily on the peak positions because the peak intensity is also determined by cross-section effects, which our calculations do not include. The semi-local (PBE) and hybrid (PBEh) spectra of (TiO\(_2\))^\text{−} are qualitatively similar and a simple “stretch” of the semi-local spectrum will bring them into close agreement. The \( G_0 W_0 \) spectra obtained from these two starting points are also qualitatively similar. However, the GW@PBE spectrum is still too compressed while the GW@PBEh spectrum is in close agreement with experiment. GW@PBEh has also yielded excellent agreement with experiment for (TiO\(_2\))\(_2\) clusters.

Figure 6 shows DFT and QP spectra of catechol, broadened by a 0.35 eV Gaussian to simulate experimental resolution, compared to the gas phase UPS of catechol. The DFT spectra are shifted to align the HOMO with the vertical IP obtained by taking the total energy difference between the cation and the neutral in the neutral geometry with the respective functional. QP energies are directly comparable to gas phase UPS, therefore they are not shifted. As in the case of (TiO\(_2\))^\text{−}, the semi-local (PBE) and hybrid (PBEh) spectra of catechol are qualitatively similar and a simple “stretch” of the semi-local spectrum will bring them into close agreement. \( G_0 W_0 \) based on both starting points visibly improves the agreement with experiment. The \( G_0 W_0 \) spectra obtained from these two starting points are similar. However, the quantitative agreement of the GW@PBEh spectrum with experiment is
somewhat better than that of GW@PBE. A visualization of the molecular orbitals (obtained with PBEh) shows that there are no changes in orbital ordering from PBE to PBEh, and from DFT to $GW$.

Both (TiO$_2$)$_n$ and catechol are typical “well behaved” systems. In the absence of severe SIE effects $G_0W_0$ is fairly robust to the DFT starting point and a semi-local starting point is qualitatively adequate. Yet, as is evident from Figures 4-6, a hybrid starting point gives a better quantitative agreement with experimental electron removal energies.

The case of INA is more complicated. Figure 7a shows DFT and QP spectra of INA, broadened by a 0.5 eV Gaussian to simulate experimental resolution, compared to the UPS of a monolayer of INA on TiO$_2$(110). Single molecule QP energies can be directly and quantitatively compared to gas phase UPS. However, this is not the case for the comparison to an experiment performed on a monolayer because the screening from other surrounding molecules typically causes a uniform shift in the electron removal energies. In order to compensate for this, all the computed spectra are shifted to align the HOMO level with the first UPS peak for the purpose of comparison to experiment. A close-up of the first peak is shown in Figure 7b, the frontier orbitals of INA, obtained with PBEh, are visualized in Figure 7c.

Although the spectra (both DFT and $G_0W_0$) calculated with an increasingly large fraction of exact exchange may seem similar at first glance, especially after broadening, a closer look at the molecular orbitals reveals some qualitative differences. For INA, unlike the case of catechol, adding a fraction of exact exchange to PBE leads to changes in the ordering of the frontier orbitals: with PBE orbital b is the HOMO, orbital c is the HOMO-1, and orbital a in the HOMO-2; with PBEh orbital b is the HOMO, orbital a is the HOMO-1, and orbital c is the HOMO-2; and with PBE+35%Eex orbital a is the HOMO, orbital b is the HOMO-1, and orbital c is the HOMO-2. Adding a higher fraction of exact exchange does not lead to any further changes in the orbital ordering. Similarly to the case of CuPc, these differences persist in $G_0W_0$ calculations based on different starting points: with GW@PBE orbital b is the HOMO, orbital a is the HOMO-1, and orbital c is the HOMO-2; with GW@PBEh orbital a is the HOMO, but it is very close in energy to orbital b, which is the HOMO-1, and orbital c is the HOMO-2; and with GW@PBE+35%Eex orbital a is the HOMO, orbital b is the HOMO-1, and orbital c is the HOMO-2. It is worth noting that although the reordering of orbitals that are close in energy does not affect the shape of the broadened spectrum, it may affect, e.g., the nature of excitations in INA and the subsequent charge transfer to TiO$_2$, owing to differences in the symmetry and spatial distribution of these orbitals.
Table 1 shows the GW corrections to the DFT energies of orbitals a, b, and c for different fractions of exact exchange. The magnitude of the GW correction to the PBE energy of orbital a is significantly lower, by about 0.5 eV, than those of orbitals b and c. For GW@PBEh, the magnitude of the correction to the energy of orbital a is still lower by about 0.2 eV than those of orbitals b and c. When PBE+35%Exx is used as a starting point, the GW corrections to the DFT energies of all three orbitals are similar. The magnitude of the GW correction to the DFT eigenvalues is associated with SIE. This indicates that for PBE, orbitals b and c carry larger SIE than orbital a, resulting from the localization of the nitrogen lone pair. Consequently, their energies are shifted down more than that of orbital a in the G0W0 calculation. However, they are not shifted far enough to get the correct orbital ordering. Starting the G0W0 calculation from PBEh improves the situation to the point where the correct orbital ordering is obtained. However, GW@PBEh puts orbitals a and b almost on top of each other. When GW@PBE+35%Exx is used, the corrections for all three orbitals even out, giving not only the correct orbital ordering but also a bigger spacing between the energies of orbitals a and b. This indicates that GW@PBE+35%Exx is a good starting point for INA.

The case of INA is reminiscent of other SIE-prone molecules, for which, at the DFT level, hybrid functionals offer a significant qualitative improvement over semi-local functionals. A similar issue has been reported recently for orbitals associated with the nitrogen lone pair of cytosine and uracil. Many dye molecules contain localizing sites, such as transition metal atoms, therefore they are likely to belong to this category. Errors in the ordering of the frontier orbitals of dyes, particularly in the identities of the HOMO and LUMO, may adversely affect the accuracy of the calculated spectra. In such cases it is particularly important to use an optimal starting point for G0W0 calculations and for subsequent BSE calculations. We suggest that the fraction of exact exchange at which there is no further reordering of frontier orbitals, if such a fraction exists, would be a good starting point for G0W0.

3.3 Ti2cat2 and Ti3INA3

Owing to the size of Ti2cat2 and Ti3INA3, G0W0 calculations were carried out for an isolated molecular unit rather than for the periodic crystal with multiple molecular units per unit cell. Because the units of Ti2cat2 and Ti3INA3 interact via weak dispersion forces, a periodic treatment is expected to have little consequence for the electronic structure at the dye-TiO2 interface. For molecular crystals screening effects result primarily in a rigid shift of the QP energies. The unit geometry was obtained via full unit cell relaxation using PBE+TS-vdW, as described in Appendix A. In order to isolate the contribution
of the dye from that of the IPA, which is not a typical component of a DSC, the calculations were performed with and without the IPA moieties. In order to preserve the Ti coordination the IPA oxygen was kept and passivated with hydrogen. The \( G_0W_0 \) calculations for the systems without IPA (40 atoms for Ti\(_2\)cat\(_2\) and 57 atoms for Ti\(_3\)INA\(_3\)) were performed with a tier 4 basis set. The larger calculations including the IPA (94 atoms for Ti\(_2\)cat\(_2\) and 120 atoms for Ti\(_3\)INA\(_3\)) were performed with a tier 2 basis set. The QP spectra obtained at the tier 2 level qualitatively resemble those obtained at the tier 4 level because the basis set truncation error is predominantly a uniform shift of 0.2-0.3 (see Refs 32,43 and Figure 3).

In the context of DSCs we are primarily interested in the level alignment of the dye with respect to the TiO\(_2\). We first discuss the Ti\(_2\)cat\(_2\) and Ti\(_3\)INA\(_3\) clusters without IPA. The level alignment of catechol with respect to Ti\(_2\)cat\(_2\) without IPA, obtained using DFT and \( G_0W_0 \), is shown in Figure 8. Visualization of the DFT orbitals, some of which are shown in Figure 9 (as obtained with PBEh), allows us to determine whether a particular orbital is associated with catechol or with TiO\(_2\), or has mixed contributions from both. Generally, we observe the following: (i) The HOMO, HOMO-1 and HOMO-2, HOMO-3 orbitals of the combined system, associated with the HOMO and HOMO-1 orbitals of catechol (shown in Figure 6), lie inside the gap of the TiO\(_2\) cluster (note that here we refer to the fundamental gap, not the optical gap); (ii) The LUMO – LUMO+9 orbitals of the combined system are associated with the TiO\(_2\) cluster; (iii) The LUMO+10 and LUMO+11 orbitals, associated with the catechol LUMO (shown in Figure 6), lie deep within the unoccupied states of the TiO\(_2\) cluster, and are strongly hybridized with TiO\(_2\) states. This is the desired level alignment for a DSC, such that an electron may be photoexcited from the catechol HOMO to the catechol LUMO and transferred from there to the TiO\(_2\).

Although the qualitative picture described above is maintained throughout, from PBE to PBEh and from both to \( GW \), the quantitative details of the level alignment change. One obvious difference is that adding exact exchange widens the gap and using \( GW \) widens it further. The position of the catechol HOMO level in the TiO\(_2\) gap also changes. PBE puts the orbital associated with the catechol HOMO in the middle of the TiO\(_2\) gap- 2.0 eV above the level associated with the TiO\(_2\) HOMO and 2.1 eV below the TiO\(_2\) LUMO. PBEh puts the catechol HOMO 2.6 eV above the TiO\(_2\) HOMO and 3.9 eV below the TiO\(_2\) LUMO. Here, the \( G_0W_0 \) calculations exhibit slight starting point sensitivity as \( GW@PBE \) puts the catechol HOMO 2.5 eV above the TiO\(_2\) HOMO and 5.8 eV below the TiO\(_2\) LUMO, while \( GW@PBEh \) puts the catechol HOMO 2.8 eV above the TiO\(_2\) HOMO and 6.2 eV below the TiO\(_2\) LUMO. Another difference is the absolute position of the catechol LUMO, which is bound in DFT but
above the vacuum level in $GW$, giving a qualitatively different picture. Accounting for electron-hole interactions should effectively rebind the LUMO level, similarly to benzene.\textsuperscript{23} This may be examined in future BSE calculations.

The level alignment of catechol and IPA with respect to Ti$_2$cat is also shown in Figure 8. We note that because the calculations for Ti$_2$cat were conducted with a tier 2 basis set, an upward shift of the QP energies by about 0.2 eV on average is expected (see Figure 3 and Refs 32,43). Using a larger basis set will not change the picture regarding the effect of IPA. At the DFT level, the IPA HOMO lies deep below the catechol HOMO and the IPA LUMO lies high above the catechol LUMO. $G_0W_0$ pushes the IPA HOMO even further down. In this case, the addition of IPA does not change the picture described above and thus has no implication for the photoexcitation of catechol and the subsequent charge transfer to the TiO$_2$.

Figure 10 shows DFT and QP spectra of Ti$_2$cat, with and without IPA, broadened by a 0.5 eV Gaussian to simulate experimental resolution, compared to the UPS of a monolayer of catechol on TiO$_2$(110), taken at two polarizations.\textsuperscript{53} The computed spectra are shifted to align the HOMO level with experiment. Similarly to the catechol molecule, whose signature is the dominant component of this spectrum, the $GW@PBE$ spectrum of the system without IPA is in very good agreement with experiment, offering a slight improvement over PBE, which is also in good agreement with experiment, at least at the presently available resolution. The addition of IPA changes the shape of the spectrum although the signature of catechol is still clearly visible. The spectrum of Ti$_2$cat may be compared directly to a UPS experiment for that system when such data become available.

In the case of Ti$_3$INA$_3$, as expected based on our findings for INA, there is a greater starting point sensitivity, not only in the level alignment, shown in Figure 11, but also in the nature of the frontier orbitals, shown in Figure 12 (as obtained with PBE and PBE+35%Exx). The predictions of PBE, PBE+35%Exx, $GW@PBE$ and $GW@PBE+35%Exx$ are qualitatively different. We begin by discussing the Ti$_3$INA$_3$ cluster without IPA. PBE places the orbital associated with the INA HOMO 0.8 eV above the orbital associated with the TiO$_2$ HOMO and 2.3 eV below the LUMO. Visualization of the frontier orbitals shows that the HOMO—HOMO-2 orbitals of the combined system are associated with orbital b of INA (Figure 12 b) and the HOMO-3 — HOMO-5 orbitals of the combined system are associated with orbital a of INA (Figure 12a). The HOMO-6 orbital of the combined system, shown in Figure 12c, has mixed contributions from orbitals a and c of INA and from the TiO$_2$ cluster. $GW@PBE$ gives the same orbital ordering but places the orbital associated with the INA HOMO 0.3 eV above the orbital associated with the TiO$_2$ HOMO and 6.8 eV below the LUMO.
PBE+35%Exx places the orbital associated with the INA HOMO 0.7 eV above the orbital associated with the TiO$_2$ HOMO and 5.7 eV below the LUMO. Visualization of the frontier orbitals shows that the HOMO—HOMO-2 orbitals of the combined system are associated with orbital a of INA (Figure 12a) and the HOMO-3—HOMO-5 orbitals of the combined system are associated with orbital b of INA (Figure 12b). The HOMO-6 (Figure 12d) and HOMO-7 orbitals of the combined system are associated with the HOMO-3 orbital from the PBE+35%Exx. The HOMO-8 orbital has mixed contributions from orbital c of INA and from the TiO$_2$ cluster. GW@PBE+35%Exx gives the same orbital ordering but places the orbital associated with the INA HOMO 0.6 eV above the orbital associated with the TiO$_2$ HOMO and 7.5 eV below the LUMO.

In all calculations the LUMO of the combined system, shown in Figure 12e, is associated with the TiO$_2$ cluster. The INA LUMO is highly hybridized with the TiO$_2$ orbitals and has contributions to orbitals as low as LUMO+1 and as high as LUMO+10. The orbitals with the strongest contributions from the INA LUMO (such an orbital is shown in Figure 12f) are the LUMO+8 and LUMO+9 for PBE and the LUMO+7 for PBE+35%Exx. These orbitals are found 1.0 eV above the LUMO with PBE and PBE+35%Exx and 1.2 eV and 1.4 eV above the LUMO with GW@PBE and GW@PBE+35%Exx respectively. As it pertains to DSCs, the level alignment of Ti$_3$INA$_3$ is somewhat less ideal than that of Ti$_2$cat$_2$. The INA HOMO is very close to the TiO$_2$ HOMO so there is little to gain by photoexciting the INA rather than the TiO$_2$. The INA LUMO and TiO$_2$ LUMO are too close to reasonably speculate on relative energies of photoexcited states on INA and charge transfer with the TiO$_2$ cluster without explicitly accounting for excitonic effects.

The level alignment of INA and IPA with respect to Ti$_3$INA$_3$ is also shown in Figure 11. We note that because the calculations for Ti$_3$INA$_3$ were conducted with a tier 2 basis set the QP energies are shifted upward by about 0.2 eV on average (see Figure 3 and Refs 32,43). Using a larger basis set will not change the picture regarding the effect of IPA. In the case of Ti$_3$INA$_3$ the addition of IPA complicates the picture. As isolated molecules, the level alignment between INA and IPA is such that DFT places the IPA HOMO above the INA HOMO, while $G_0W_0$ places the IPA HOMO below the INA HOMO. In addition, the IPA HOMO is close to the TiO$_2$ HOMO. In the combined system, this leads to the formation of hybridized orbitals with mixed contributions from the frontier orbitals of two or more components. The addition of exact exchange changes the orbital alignment of the three components, resulting in different orbital hybridizations. This causes significant changes in the nature of the orbitals, not just in their ordering.
Figure 13 shows the ordering of the frontier orbitals of Ti₃INA₃ with DFT and GW, as well as visualizations of some of these orbitals, obtained with PBE and with PBE+35%Exx. With PBE, as for the system without the IPA, the HOMO—HOMO-2 orbitals of Ti₃INA₃ are associated with INA orbital b. The HOMO-3—HOMO-10 orbitals are associated mainly with the IPA HOMO. The HOMO-11, HOMO-12, and HOMO-14 orbitals are associated with INA orbital a. With PBE+35%Exx, as for the system without the IPA, the HOMO—HOMO-2 orbitals of the combined system are associated with INA orbital a. The HOMO-3—HOMO-12 orbitals are mainly hybridized orbitals comprising contributions from the IPA HOMO mixed with INA orbital b, except for the HOMO-7, which is associated only with INA orbital b.

Contrary to what one would expect based on the level alignment of free INA and IPA molecules, G₀W₀ shifts the orbitals associated with the IPA HOMO to higher energies than those associated with the INA HOMO. With GW@PBE, the HOMO-3—HOMO-7 orbitals rise above the PBE HOMO, and the HOMO-8—HOMO-9 orbitals rise above the PBE HOMO-1. At the same time, the HOMO-11, HOMO-12, and HOMO-13 orbitals, associated with INA orbital a, remain in their relative position below the orbitals associated with INA orbital b. With GW@PBE+35% the HOMO-3, HOMO-4, and HOMO-8 orbitals rise above the PBE+35%Exx HOMO, while the HOMO-5, HOMO-9, and HOMO-10 orbitals rise above the HOMO-1. Owing to the mixing between IPA and INA orbitals, these orbitals, associated with the IPA HOMO, drag along fragments of INA orbital b to higher energies, making it the HOMO of the combined system. At the same time, the HOMO-7 orbital, associated only with INA orbital b, without contributions from IPA, is not shifted to a higher energy and remains below the orbitals associated with INA orbital a and also below those associated with the IPA HOMO.

This indicates that there is a “conflict of interests” for orbitals with mixed contributions from INA orbital b and the IPA HOMO. The G₀W₀ corrections to the energies of orbitals associated with INA orbital b are more negative than the G₀W₀ corrections to the energies of orbitals associated with the IPA HOMO. However, because there is no self-consistency in the wave-functions, these orbitals cannot re-hybridize. In this case, the results of G₀W₀ calculations are unreliable. We find that the addition of any amount of exact exchange, up to HF, reshuffles the orbitals and leads to a different mixing of the frontier orbitals of INA, IPA, and TiO₂. Performing G₀W₀ on top of any starting point results in shifting of the orbitals associated with the IPA HOMO to higher energies. If these orbitals have mixed contributions from other components of the system, these are dragged along with the IPA HOMO. This demonstrates a failure of the assumption that the DFT wave-functions are good approximations to the QP wave-functions. When hybridization cannot
be properly treated by a DFT functional, some level of $GW$ self-consistency is required. This issue will be examined in future work. Barring some uncertainty regarding the orbital ordering, the fact that orbitals associated with IPA lie above orbitals associated with INA indicates that some contributions to the absorption spectrum of Ti$_3$INA$_3$ may actually come from IPA rather than INA.

Figure 14 shows the DFT and QP spectra of Ti$_3$INA$_3$, with and without IPA, broadened by a 0.5 eV Gaussian to simulate experimental resolution, compared to the UPS of a monolayer of INA on TiO$_2$(110). The computed spectra are shifted to align the HOMO level with experiment. Similarly to the INA molecule, whose signature is the dominant component of this spectrum, the $GW@PBE+35\%Exx$ spectrum of the system without IPA is in good agreement with experiment, offering a slight improvement over PBE+35\%Exx, which is also in good agreement with experiment, at least at the presently available resolution. The addition of IPA changes the shape of the spectrum although the signature of INA is still clearly visible. The changes in the ordering of the frontier orbitals of Ti$_3$INA$_3$ are in a dense part of the spectrum, making them impossible to discern at the presently available resolution. The spectrum of Ti$_3$INA$_3$ may be compared directly to a UPS experiment for that system, when such data become available.

4. Conclusion

We have conducted a $G_0W_0$ study of two systems of dye-sensitized TiO$_2$ clusters, Ti$_2$cat$_2$ and Ti$_3$INA$_3$. We have demonstrated the following:

(i) Accounting for van der Waals interactions is essential for obtaining geometries in good agreement with experiment.

(ii) The results of hybrid-based $G_0W_0$ calculations are in good agreement with the positions of resolvable peaks in presently available UPS data.

(iii) Even in cases where DFT gives the correct qualitative picture, $G_0W_0$ yields valuable quantitative information on the fundamental gaps and level alignment of the dye molecule and the TiO$_2$ cluster.

(iv) For Ti$_2$cat$_2$, the fundamental level alignment is such that the catechol HOMO lies deep in the TiO$_2$ gap, almost 3 eV above the TiO$_2$ HOMO, and the catechol LUMO lies about 2 eV above the TiO$_2$ LUMO. In principle, such a level alignment is desired for a DSC. The addition of IPA does not change this picture because the IPA HOMO is deep below the catechol HOMO and the IPA LUMO is high above the catechol LUMO.
(v) For Ti$_3$INA$_3$, the fundamental level alignment is less ideal because the INA HOMO is only ~0.5 eV above the TiO$_2$ HOMO and, although the main contribution from the INA LUMO is to an orbital ~1 eV above the TiO$_2$ LUMO, there are also contributions to much lower orbitals. Accounting for exciton binding energy will be necessary to establish even qualitatively the physics of photoexcitation in this system.

(vi) Care must be taken when choosing the mean field starting point for $G_0W_0$ calculations, particularly for systems with localizing groups, which are prone to SIE. As different systems require different fractions of exact exchange, we suggest that the fraction of exact exchange that minimizes the reordering of the molecular orbitals is a good starting point for $G_0W_0$.

(vii) Care must also be taken in $G_0W_0$ calculations of multicomponent systems, as orbitals with mixed contributions from different parts of the system, whose energies possess significantly different QP corrections, may need to rehybridize. In such cases, the assumption that the mean-field wave-function is a good approximation to the QP wave-function breaks down and self-consistency in the wave function may be required.

We may now proceed to GW/BSE calculations of the absorption spectra of such systems. Based on the calculations we have presented here, for systems with over a hundred atoms, we expect many-body perturbation theory to become a viable tool for obtaining highly accurate quantitative predictions for realistic systems with relevance to solar cell technology.

**Acknowledgements**

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Appendix A: Geometry Relaxation Using vdW-Corrected DFT

As discussed above, it is often the case that the geometry of dye-TiO₂ interfaces is not known exactly. Therefore, computational studies have typically relied on plausible suggested binding geometries whose structure was subsequently optimized using DFT with standard semi-local or hybrid functionals.⁷,⁸ A problematic aspect of this procedure is that conventional DFT functionals, based on semi-local correlation, lack dispersion, which is a long-range electron correlation effect. Dispersion corrections have been shown to be essential for obtaining realistic binding geometries of molecules on metal surfaces,⁵⁴ as well as on TiO₂.⁵⁵ Although van der Waals (vdW) interactions are not expected to affect the covalent bonds between the dye and the TiO₂, they may affect the orientation of the dye with respect to the TiO₂ and stabilize certain binding configurations with respect to others. This is particularly important because the electronic structure of the dye-TiO₂ system has been shown to be sensitive to the binding configuration.⁸,⁵³ We employ the Tkatchenko-Scheffler scheme³¹ in order to account for dispersion in the geometry optimization of Ti₂cat₂ and Ti₃INA₃.

In this correction scheme the leading order of the dispersion energy, $C_6/R^6$, is added in a pair-wise manner to the internuclear energy term. The dispersion coefficients, $C_6$, are determined from Hirshfeld partitioning of the DFT electron density. The Hirshfeld partitioning procedure underestimates ionic charges. This is particularly critical for metal cations, where this leads to significant overestimation of the ionic radii and of the dispersion coefficients. In order to solve this problem iterative Hirshfeld partitioning⁵⁶ has been implemented in FHI-aims. This procedure yields a charge of +1.2 e on Ti in Ti₃INA₃ and Ti₂cat₂, which corresponds to an estimated $C_6$ of 220 Hartree-Bohr⁶, considerably lower than that of 1440 Hartree-Bohr⁶ for neutral Ti.

In order to assess the effect of dispersive interactions with neighboring units on the geometry of the Ti₂cat₂ and Ti₃INA₃ units, geometry relaxation was carried out both for the isolated clusters (with 94 and 120 atoms respectively) and for the full unit cells (with 376 and 240 atoms respectively). The latter was performed by relaxing the internal coordinates at the experimental cell parameters of a= 14.142 Å, b= 13.474 Å, c= 19.913 Å, α= 90⁰, β= 115⁰, γ=90⁰ for Ti₂cat₂ and a= 11.739 Å, b= 12.886 Å, c= 18.312 Å, α= 94.758⁰, β= 90.202⁰, γ= 116.344⁰.²⁷ Figure A1 shows the cluster geometry obtained in isolation and in crystalline form superimposed on the experimental structure. For both clusters better agreement with experiment is obtained from a fully periodic treatment. This is consistent with the previously reported dependence of the geometry of the repeat unit of β-hematin on weak interactions with adjacent units.⁵⁷ In this case, the differences are somewhat less significant than in β-hematin. The geometry of the core TiO₂ clusters is almost
unaffected by weak interactions with neighboring units and the main differences are in the binding geometries of the side groups, particularly the IPA groups, to the TiO$_2$. For Ti$_2$cat$_2$, the periodic treatment results in an excellent agreement with experiment. For Ti$_3$INA$_3$ the agreement in the positions of the IPA groups is not as good. This is consistent with the experimentally observed disorder.$^{27}$

In order to demonstrate the importance of the TS-vdW correction for obtaining the correct structure of Ti$_2$cat$_2$ and Ti$_3$INA$_3$, binding energy curves were calculated along the crystal axes with and without the correction. This was done without relaxing the internal coordinates. The binding energies are given with respect to those of relaxed isolated units. The TS-vdW correction was performed both with the standard TS scheme and with the lower C$_6$ of 220 Hartree-Bohr$^6$, obtained for Ti using the iterative Hirshfeld method. The results are shown in Figures A2 and A3, respectively. Clearly, attempting to relax the geometry of such systems without accounting for dispersion would result in structures bearing little resemblance to reality. For Ti$_2$cat$_2$, bound only by weak vdW interactions between the catechol and IPA groups of different units, uncorrected PBE gives very shallow minima along all crystal axes and significantly overestimates the lattice parameters. For Ti$_3$INA$_3$, uncorrected PBE gives somewhat stronger binding along the a and b axes, where there is a significant contribution from weak CH···N hydrogen bonds between the INA groups of different units (indicated in Figure 1b), although the minimum is still too shallow comparing to the vdw-corrected curves and the lattice parameters are overestimated. Along the c-axis the behavior of uncorrected PBE is similar to that observed for Ti$_2$cat$_2$. For both Ti$_2$cat$_2$ and Ti$_3$INA$_3$, PBE+TS-vdW gives deep minima and lattice parameters in good agreement with experiment, if slightly underestimated along all crystal axes. The slight underestimation of the lattice parameters may be a result of overestimation of the static polarizability by PBE. Using a C$_6$ of 220 Hartree-Bohr$^6$ for Ti leads to a significant reduction in the binding energy comparing to standard TS. However, the geometry is largely unaffected.

Using the iterative Hirshfeld procedure to obtain more realistic dispersion coefficients is expected to have a drastic effect for metal-oxide surfaces and other systems comprising a significant portion of metal cations. The success of PBE+TS-vdW in obtaining the geometry of Ti$_2$cat$_2$ and Ti$_3$INA$_3$ demonstrates yet again the viability of the TS correction scheme for large systems, comprising several hundred atoms.
Figure 1: Schematic illustration of the crystal structures of a) Ti$_2$cat$_2$ and b) Ti$_3$INA$_3$ (Ti-cyan, O-red, C-gray, N-blue, H-white)

Figure 2: Schematic illustrations of a) INA, b) TiO$_2$, c) IPA and d) catechol
Figure 3: QP HOMO and LUMO energies, calculated based on PBE and PBEh with increasingly large basis sets, compared to experimental IP and EA for: a) and b) TiO$_2$, c) IPA, d) catechol
Figure 4: DFT and QP HOMO and LUMO energies, calculated with PBE combined with an increasingly large fraction of exact exchange, and with a tier 4 basis set, compared to experimental IP and EA for: a) and b) TiO$_2$, c) IPA, d) catechol. The unfilled markers are for HF. The corresponding ΔSCF values obtained at the DFT level with a tier 2 basis set are also shown.
Figure 5: DFT and QP spectra of (TiO₂), broadened by a 0.25 eV Gaussian to simulate experimental resolution, compared to gas phase UPS³⁹
Figure 6: DFT and QP spectra of catechol, broadened by a 0.35 eV Gaussian to simulate experimental resolution, compared to gas phase UPS. Also shown are visualizations of the frontier orbitals of catechol, obtained with PBEh.
Figure 7: a) DFT and QP spectra of INA, broadened by a 0.5 eV Gaussian to simulate experimental resolution, compared to the UPS of a monolayer of INA on TiO$_2$(110)$_5$.\textsuperscript{50} The computed spectra are shifted to align the HOMO level with experiment. b) A close-up of the first peak. c) Visualizations of the frontier orbitals of INA, obtained with PBE+35%Exx.
Table 1: GW corrections to the DFT energies $[E(QP) - E(DFT)]$ of the frontier orbitals of INA for different fractions of exact exchange

<table>
<thead>
<tr>
<th>Orbital</th>
<th>GW@PBE</th>
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Figure 8: Level alignment of catechol, IPA, and Ti$_2$cat$_2$ with and without IPA, obtained using a) PBE, b) PBEh, c) GW@PBE, and d) GW@PBEh
Figure 9: Frontier orbitals of Ti$_2$cat$_2$ without IPA, obtained with PBEh
Figure 10: DFT and QP spectra of Ti$_2$cat$_2$, with and without IPA, broadened by a 0.5 eV Gaussian to simulate experimental resolution, compared to the UPS of a monolayer of catechol on TiO$_2$(110), taken at two polarizations.$^{53}$ The computed spectra are shifted to align the HOMO level with experiment.
Figure 11: Level alignment of INA, IPA, and Ti$_3$INA$_3$ with and without IPA, obtained using a) PBE, b) PBE+35%Exx, c) GW@PBE, and d) GW@PBE+35%Exx.
Figure 12: Frontier orbitals of Ti$_3$NA$_3$ without IPA, obtained with PBE and PBE+35%Exx: a) orbital associated with INA a orbital, b) orbital associated with INA b orbital, c) PBE HOMO-6, d) PBE+35% Exx HOMO-6, e) orbital associated with TiO$_2$ LUMO, and f) orbital associated with INA LUMO
Figure 13:
Ordering of the frontier orbitals of Ti$_3$INA$_3$ with DFT and GW, as obtained with PBE vs.
PBE+35%Ex. The energy levels of orbitals associated with INA orbital a are marked in green, the energy levels of orbitals associated with INA orbital b are marked with red, and orbitals associated with the IPA HOMO are marked in blue.
Figure 14: DFT and QP spectra of Ti$_3$INA$_3$, with and without IPA, broadened by a 0.5 eV Gaussian to simulate experimental resolution, compared to the UPS of a monolayer of INA on TiO$_2$(110). The computed spectra are shifted to align the HOMO level with experiment.
Figure A1: Geometries of a) Ti$_2$cat$_2$ and b) Ti$_3$INA$_3$, obtained using PBE+TS-vdW for isolated clusters (green) and for the full unit cells (red), superimposed on the experimental structure$^{27}$ (blue).
Figure A2: Binding energy curves along the crystal axes of Ti$_2$Ca$_2$, obtained with and without the TS-vdW correction, compared to the experimental lattice parameters.\textsuperscript{27}
Figure A3: Binding energy curves along the crystal axes of Ti$_3$INA$_3$, obtained with and without the TS-vdW correction, compared to the experimental lattice parameters.\textsuperscript{27}
32. X. Ren, P. Rinke, V. Blum, J. Wieferink, A. Tkatchenko, A. Sanfilipo, K. Reuter, and M. Scheffler, to be published.
42. A similar comparison for INA is not conducted here because experimental values for its IP and/or EA are presently unavailable.
43. N. Marom, X. Ren, J. E. Moussa, J. R. Chelikowsky, and L. Kronik, To be published.
47. We note that tuning the fraction of exact exchange and using a simple hybrid functional as a mean field starting point often improves upon semi-local DFT, however, it has the limitation that there is no system specific definition of screening. In this respect, the Coulomb-hole plus screened-exchange (COHSEX) approach may be a better albeit more expensive starting point.
49. N. Marom, M. Kim, and J. R. Chelikowsky, To be published.