

Calculating the optical properties of defects and surfaces in wide band gap materials



Peter Deák

Bremen Center for Computational Materials Science, University of Bremen, PoB 330440, D-28834 Bremen, Germany

ARTICLE INFO

Keywords:

Defects
Hybrid functionals
Diamond
TiO₂
NV center
Water splitting

ABSTRACT

The optical properties of a material critically depend on its defects, and understanding that requires substantial and accurate input from theory. This paper describes recent developments in the electronic structure theory of defects in wide band gap materials, where the standard local or semi-local approximations of density functional theory fail. The success of the HSE06 screened hybrid functional is analyzed in case of Group-IV semiconductors and TiO₂, and shown that it is the consequence of error compensation between semi-local and non-local exchange, resulting in a proper derivative discontinuity (reproduction of the band gap) and a total energy which is a linear function of the fractional occupation numbers (removing most of the electron self-interaction). This allows the calculation of electronic transitions with accuracy unseen before, as demonstrated on the single-photon emitter NV(-) center in diamond and on polaronic states in TiO₂. Having a reliable tool for electronic structure calculations, theory can contribute to the understanding of complicated cases of light-matter interaction. Two examples are considered here: surface termination effects on the blinking and bleaching of the light-emission of the NV(-) center in diamond, and on the efficiency of photocatalytic water-splitting by TiO₂. Finally, an outlook is presented for the application of hybrid functionals in other materials, as, e.g., ZnO, Ga₂O₃ or CuGaS₂.

1. Introduction

Defects of semiconductors and insulators critically influence the optical properties, so understanding light-matter interaction requires fundamental knowledge about defect related electronic transitions. While the various forms of defect spectroscopy can supply a wealth of data, in most cases they do not allow the positive and unambiguous identification of particular defects as the origin of the observed spectral fingerprints. That is why one of the “founding fathers” of experimental defect physics, George D. Watkins, has teamed up with the quantum chemist, Richard P. Messmer in 1971, to start electronic structure calculations on defects [1,2]. Soon after that [3], defect theory has switched from semi-empirical quantum chemical methods to the local density approximation (LDA) of density functional theory (DFT). Despite of the well known underestimation of the band gap in LDA (and of the resulting uncertainty in defect level positions), in case of the traditional narrow band gap semiconductors both techniques have supplied similar results [4,5]. As the weight of research shifted from microelectronics to optoelectronics and photovoltaics, it has soon become clear that LDA or the semi-local generalized gradient approximation (GGA) just will not do for the defects of wide band gap materials applied in these areas [6,7]. After some years of searching, the hybrid functionals (mixing semi-local

and non-local exchange semi-empirically), have emerged as a useful alternative [8–10]. (Note that presently there is no ab initio total energy method which could be carried out accurately for supercell sizes required in defect calculations.) For years, the use of hybrid functionals have been controversial and they are often abused even today, so the first purpose of this paper to explain why and when hybrids are appropriate (Section 1). After establishing the proper criteria for choosing a hybrid functional, and as the second purpose of the paper, I will demonstrate the unprecedented accuracy which could be achieved in calculating defects in diamond and TiO₂ (Section 2). Relying on this accuracy, I will show how surface termination can influence light-matter interaction in the case of the single photon-emitter NV(-) center in diamond and in the photocatalytic water-splitting by TiO₂ (Section 3). Finally, some thought will be given to the applicability of hybrids in other materials, like ZnO and Ga-based semiconductors (Conclusion).

2. The rationale of hybrids and the performance of the HSE06 functional in Group-IV semiconductors and in TiO₂

For a long time, it has been assumed that the only error relevant for defect calculations with LDA or GGA is the underestimation of the band gap, and the calculated position of the defect-related gap levels can be

E-mail address: deak@uni-bremen.de.

<http://dx.doi.org/10.1016/j.physb.2017.06.024>

Received 20 April 2017; Received in revised form 29 May 2017; Accepted 6 June 2017

Available online 08 June 2017

0921-4526/ © 2017 Elsevier B.V. All rights reserved.

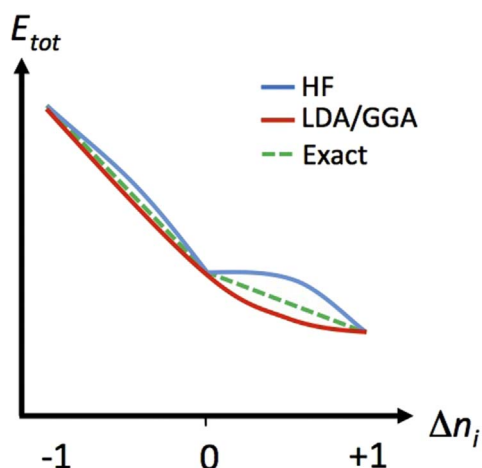


Fig. 1. Schematic representation of the total energy as a function of the change in the occupation number of the defect level.

corrected by the so-called “scissor-operator” [11]. It has been shown, however, that the scissor correction cannot always be applied [12] and, anyhow, the error in the gap level also influences the relative formation energy of different defect configurations or charge states [13,14]. This error often leads to false ground states which cannot be helped by additional GW [15] calculations.

The origin of the problems for defect calculations in the local and semi-local approximations are schematically depicted in Fig. 1. The exact DFT functional is a piecewise linear function of the occupation number with a derivative discontinuity at integer values. Due to Janak’s theorem, the linearity ensures that the position of the Kohn-Sham (KS) one-electron level of the defect is independent of its occupation, and equals exactly the ionization energy [16]. The latter is called the generalized Koopman’s theorem (gKT) [17]. In contrast, the LDA/GGA total energy lacks a derivative discontinuity and is a convex function of the fractional occupation numbers. The former is the reason for the much too small band gap, which often has the effect that actual gap levels are hidden in the bands and are incorrectly unoccupied (donors) or occupied (acceptors). The convex nature has two consequences: i) the defect level shifts upwards upon adding an electron and the gKT is not satisfied, and ii) delocalization of the defect state is favored. Since the localization of a defect state usually determines the position of the corresponding level in the gap directly, this error precludes accurate prediction of gap states. In addition, small polaron states (carriers trapped by strong local distortion of the lattice), which often occur in wide band gap materials, are usually missed.

Applying Hartree-Fock (HF) type non-local exchange in DFT brings back the derivative discontinuity and opens up the gap. However, the gap is strongly overestimated in that case and the total energy becomes a concave function between integer occupation numbers (see Fig. 1). As a consequence of the latter, the KS level of the defect shifts down upon occupation, the gKT is not fulfilled, and states are over-localized.

Hybrid functionals contain a semi-empirical mixture of GGA and HF exchange [18–20]. Their success in quantum chemistry has induced researchers to try them for solids, hoping also for a gap between those given by pure GGA and pure HF exchange. Indeed, it was found that the gap improves [8,9], although the optimal value of the mixing parameter α depends on the material and is connected to the dielectric screening [21–23]. Therefore, screened hybrid functionals [24,25], where the admixture of HF-exchange is phased out beyond a given screening length $2/\mu$, have attained special attention. The most often applied such functional, HSE06, was introduced originally on an entirely practical basis by Heyd, Scuseria and Ernzerhof [26]. In accordance with the argumentation of Ref. [27] for single bonds, and similarly to the unscreened PBE0 hybrid [20], the mixing parameter $\alpha = 0.25$ was found to be optimal also in HSE06. The screening parameter was then applied to fine-tune the band gaps.

Table 1

KS levels of selected donors and acceptors in Group-IV semiconductors with respect to the band edges (Δ KS), and the corresponding electronic transitions calculated as the difference of total energies at fixed geometry (Δ SCF) in eV [14,33].

Donors			Acceptors		
$E(+/0) - E_{CB}$	Δ KS	Δ SCF	$E_{VB} - E(0/-)$	Δ KS	Δ SCF
$C_{512}:P_C$	0.6	0.6	$C_{512}:B_C$	0.3	0.4
$Si_{512}:S_{Si}$	0.3	0.3	$Si_{512}:In_{Si}$	0.2	0.2
$Si_{512}:S_{Si}^+$	0.6	0.6	$Si_{512}:O_{Si}$	0.9	1.0
$Si_{512}:C_i$	1.0	0.9	$Si_{512}:C_i$	1.0	1.0
$Ge_{512}:S_{Ge}$	0.4	0.3	$Ge_{512}:O_{Ge}$	0.4	0.4

Nowadays $\mu = 0.20$ is usually set, resulting in the best band gap for a large number of semiconductors. It should be noted, however, that HSE06 usually works best for medium-sized gaps (medium screening) but not for wide band gap insulators (weak screening), and breaks down in metals [28–31]. It appears quite obvious that screening cannot be universally described by this simple two-parameter approximation even in bulk materials, let alone in low-dimensional systems [32].

As explained above, getting the correct band gap is not sufficient to mimic the exact functional: for that the linearity of the total energy with fractional occupation numbers is also required, i.e., the fulfillment of the gKT. In principle, error compensation between the convex LDA/GGA and the concave HF exchange functional can lead to that. In particular, it was found that the standard parameters of HSE06 satisfy the gKT in Group-IV semiconductors [14,33]. Table 1. shows a comparison of the KS-level of defects with respect to the band edges (Δ KS), to the corresponding vertical electronic transition (optical internal ionization) of the defect, calculated via total energy differences (Δ SCF). As can be seen, the values are equal within the accuracy of the applied correction method for the interaction of artificially repeated charges in the periodic description of the ionized system.

In addition, HSE06 reproduces not only the minimum band gap but also higher transitions and the valence band width, as shown in Table 2, where it can be seen that HSE06 provides a good description of the ground state properties as well. We see that the correct band gap and the fulfillment of the gKT means that HSE06 is, for these materials, a good approximation of the exact functional. Accordingly, the calculated adiabatic (thermal) charge transition levels are in excellent agreement with experiment. This is demonstrated in Table 3 for defects in diamond [33,34]. Similar accuracy could be achieved at internal electronic transitions of nitrogen-related defects (Table 4).

While the improvement brought about by HSE06 is only quantitative in Group-IV semiconductors (except for germanium, where GGA does not give a gap at all), it is of fundamental nature in TiO_2 , which is a highly polarizable transition metal oxide with a low temperature optical band gap of 3.0 eV in the rutile, and 3.4 eV in the anatase modification (for refs. see [35]). Due to significant electron-phonon interaction, the optical gap is substantially lower than the single-particle gaps, 3.4 and 3.6 eV, respectively (for a discussion see Ref. [36]), and GGA underestimates those by about 50%. Therefore, the defect level associated with the most important intrinsic defect, the oxygen vacancy, remains hidden in the conduction band, and GGA calculations have predicted – erroneously – a shallow effective mass state for this defect. Even more disturbing was the fact that GGA calculations predicted that Nb or Al substitution of a Ti atom would lead to shallow donors or acceptors, respectively, while there is experimental evidence that Nb is a deep donor in rutile and Al is a deep acceptor in anatase, but not vice versa.

As it turns out, HSE06 can reproduce the single-particle band gaps in the two modifications on par with GW calculations [36], and fulfills the gKT [37], as shown in Table 5. Note that the applied charge correction procedure was somewhat less accurate here. As a consequence, the donor level of Nb_{Ti} , at a concentration of $\sim 1\%$, was calculated to be at $E_C - 1.0$ eV, in good agreement with the infrared

Download English Version:

<https://daneshyari.com/en/article/8161031>

Download Persian Version:

<https://daneshyari.com/article/8161031>

[Daneshyari.com](https://daneshyari.com)