

Accurate defect levels obtained from the HSE06 range-separated hybrid functionalPeter Deák,^{1,*} Bálint Aradi,¹ Thomas Frauenheim,¹ Erik Janzén,² and Adam Gali³¹*Bremen Center for Comp. Mater. Sci., University of Bremen, P.O. Box 330440, D-28334 Bremen, Germany*²*Department of Physics, Chemistry, and Biology, Linköping University, SE-581 83 Linköping, Sweden*³*Department of Atomic Physics, Budapest University of Technology, Budafoki út 8., H-1111 Budapest, Hungary*

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Defect levels are a problem for standard implementations of density-functional theory and the error also influences the energetics. We demonstrate that the HSE06 functional, which describes the electronic structure of all group-IV semiconductors well (including Ge), gives highly accurate charge transition levels, too, if the defect wave function is host related—independent of localization. The degree of fulfilling the generalized Koopmans' theorem shows the reliability of the results and the highest-occupied eigenvalue always seems to give the correct vertical ionization energy.

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I. INTRODUCTION

Thermal or optical excitations of defects have a crucial influence on the functional properties of semiconductors and insulators, from electronics and optoelectronics to photovoltaics and photocatalysis. Theoretical prediction of levels in the gap is of paramount importance in identifying the defects, and its accuracy also influences the calculated formation and activation energies.^{1,2} The standard method for defect calculations is *ab initio* density-functional theory (DFT), applied to a supercell, in one of the standard implementations: the local density approximation or the (semilocal) generalized gradient approximation (GGA). The severe underestimation of the band gap in standard DFT causes significant uncertainties in the calculation of gap levels and the correct prediction of the electrical activity of defects in semiconductors mostly requires the application of appropriate corrections.^{1,3} While there is a general awareness about the “band-gap error” in the calculated position of gap levels, the consequences for the total energy, and so for the relative stability of various configurations, are often ignored even though they can be serious even in small band-gap materials (with small gap error) and hardly ignorable when the band gap is large.^{2,4} Taking quasiparticle corrections to the gap levels into account *a posteriori* in the total energy^{4–7} may help sometimes but not in general.² Problems of the standard implementation also affect the ionization energies. In case of an exact functional, the energy of the highest-occupied Kohn-Sham (KS) orbital should give the exact (vertical) ionization energy,⁸ or at least—if pseudopotentials are used—the ionization energy difference between the defect and the perfect solid (after proper potential alignment). This *generalized Koopmans' theorem* (gKT), which directly follows from Janak's, does not hold in standard DFT due to the positive curvature of the energy as a function of the fractional occupation number.⁹ While quasiparticle corrections to the defect levels are now possible, self-consistent many-body total energy calculations for supercells are as yet impractical. A possible substitute is the use of hybrid functionals which provide a much better description of the bulk electronics structure than standard ones (and at least as good a structure and thermochemistry). These essentially semiempirical func-

tionals seem to work consistently well for the bulk, if they are able to capture the dielectric screening in the given material.¹⁰ The question is, how reliable they are for defects.

Here we present calculations on various defects of group-IV semiconductors (from Ge, with a band gap of 0.7 eV to diamond with a gap of 5.5 eV) using the HSE06 range separated hybrid functional,¹¹ to test the capability of this method for predicting defect-level positions. Defect-to-conduction-band transitions of donors, valance-band-to-defect transitions of acceptors, as well as excitation of a defect itself are considered. The selected defects include shallow, deep and hyperdeep ones, the selection criterion having been the availability of reliable and accurate experimental data. The overall quantitative agreement between theory and experiment is good, showing that the HSE06 functional can describe defects with the same accuracy as it does the electronic structure of the bulk, in a wide range of band gaps and all sorts of impurities. (Study of defects in Ge is now also possible.) Within the uncertainty of the charge correction^{1,12} the gKT seems to be satisfied by the HSE06 results if the defect wave function is predominantly host derived. In these cases the calculated adiabatic ionization energies are within 0.1 eV of the experimental values. The latter is true *in all cases* for the vertical ionization energies obtained from the highest occupied eigenvalue.

II. COMPUTATION METHOD

Calculations have been carried out with the Vienna *ab initio* simulation package VASP 5.2, using the projector augmented wave method.¹³ Bulk properties have been calculated on the primitive cell with a $12 \times 12 \times 12$ Monkhorst-Pack-set,¹⁴ reduced by a factor of 2 in the Fock-exchange part.¹⁵ Convergence of the total energy has been achieved by setting the plane-wave cutoff for the wavefunction expansion (and for that of the charge density) to 420 (1260) eV for diamond, 320 (640) for Si and 420 (840) eV for Ge. Defect calculations have been carried out with these cutoffs in each material, except for first-row impurities in Si, where also 420 (840) eV was used. Spin-orbit splitting has not been taken into account. To avoid size effects as much as possible, a 512-atom supercell was used in the Γ approxima-

TABLE I. The fundamental gap (E_g), the first allowed optical transition at the Γ point, and the valence-band width for diamond, SiC, Si, and Ge.

	Method	E_g (eV)	$\Gamma_{25'} \rightarrow \Gamma_{2'}$ (eV)	VB width (eV)
Diamond	PBE	4.21	13.3	21.5
	Exptl. ^a	5.48	15.3	24.2
	HSE06	5.42	15.7	23.8
SiC(4H)	PBE	2.22		
	Exptl. ^a	3.23		
	HSE06	3.21		
SiC(3C)	PBE	1.37	6.1	15.3
	Exptl. ^{a,b}	2.36	7.4	17
	HSE06	2.25	7.7	17.1
Si	PBE	0.61	3.14	11.8
	Exptl. ^a	1.17	4.15	12.5
	HSE06	1.17	4.33	13.3
Ge	PBE	0.00		
	Exptl. ^a	0.74	0.90	13.0
	HSE06 ^c	0.84	0.88	13.9

^aReference 19.

^bReference 20.

^cWithout spin-orbit interaction.

tion for defect studies. Charged supercells were calculated assuming a jellium charge of opposite sign and the total energy was corrected by 65% of the monopole correction¹ since our supercells are all cubic, and the dielectric constants are high. (For the latter experimental values were used.) The average potentials between the perfect crystal and the defective supercell have been aligned using the method suggested in Ref. 3.

III. RESULTS

For lattice parameters, cohesive energy, and bulk moduli HSE06, with the fixed mixing ratio of 0.25/0.75 between Hartree-Fock and Perdew-Burke-Ernzerhof (PBE)¹⁸ exchange, and range separation at 4.81 Å, performs just as well as its predecessor HSE03,^{16,17} but gives even better band gaps for all group-IV semiconductors. As can be seen in Table I, however, this is not just a fortuitous compensation between the too large HF and the too small PBE band gap. HSE06 provides an overall improvement in the electronic structure over the semilocal PBE exchange functional—including higher excitations.

The quantity of primary interest here is, however, the energy of electronic transitions between defect levels or between the defect and the band edge of the perfect solid. We have recently demonstrated the high accuracy of HSE06 in the former, as shown in Table II.²² Comparison of the adiabatic and vertical transitions (with and without relaxation of the nuclei, respectively) to low-temperature photoluminescence data show that HSE06 gives a very good description of the relaxation effects as well.

TABLE II. HSE06 electronic transitions in the negative nitrogen+vacancy (NV^-) center in diamond [in (eV)]. Experimental data are from Ref. 21.

	Vertical		Adiabatic	
${}^3A_2 \rightarrow {}^3E$	Exptl.	HSE06	HSE06	Exptl.
$C_{512}:NV^-$	2.18	2.21	1.96	1.95

Transitions between a defect level and the band edges are usually calculated as the difference between the ionization energy of the defect and the electron affinity of the perfect crystal for donors, and between ionization energy of the crystal and the electron affinity of the defect for acceptors, since in defective supercells the valence- and conduction-band edges (VBM and CBM, respectively) of the bulk are not well defined. Ionization energies and electron affinities can be calculated self-consistently as total energy differences between two charge states. Using these Δ SCF values for the aforementioned ionization energy—electron affinity differences provides the so-called charge transition levels with respect to the CBM for donors and with respect to the VBM for acceptors. Based on the gKT,^{8,9} however, vertical transitions could be calculated directly as the difference, Δ KS, in the highest occupied Kohn-Sham levels between the defect and the crystal. The neutral defect has to be taken for the ionization energy and the negatively charged defect for the electron affinity.²³ While in case of local and semilocal exchange the curvature of the derivative of the energy with respect to the occupation number is positive, it is negative for the Hartree-Fock exchange. Therefore, a hybrid functional might show the correct linearity of the derivative and satisfy the gKT but it is not obvious that the mixing parameter chosen to reproduce the gap (and other bulk data) will be appropriate for that in case of an arbitrary defect.⁹ Therefore, we have applied both the Δ KS and the Δ SCF methods for calculating the vertical transitions, and compared the results to each other. For acceptors, both methods rely on the properties of the charged state and the KS energy also requires correction because of the potential of the image charges and the jellium.⁷ For a unit charge this should be about equal with the correction for the total energy, so the Δ KS and Δ SCF values of acceptors have been compared without any correction at all. Adiabatic transitions, calculated by the Δ SCF method with appropriate charge correction, are compared to measurements. Results are shown in Table III for donors and acceptors separately.

IV. DISCUSSION

For ten cases out of 12, the agreement of the adiabatic ionization energies is striking: within 0.1 eV. At the same time the gKT (agreement between Δ KS and Δ SCF) is also satisfied within the accuracy of the charge correction. The success cases extend to all three group-IV elemental semiconductors and for silicon they span the entire gap both for donors and acceptors. However, in each of these cases the defect state which gets ionized is more or less host related:

TABLE III. HSE06 charge transition levels of donors, $E(+/0)$, with respect to the CBM and of acceptors, $E(0/-)$, with respect to the VBM in (eV). For explanation, see text. Experimental data are from Ref. 24 and references therein.

Donors	Vertical			Adiabatic		
	$E(+/0)$ wr. CBM	ΔKS^a	$\Delta\text{SCF}+0.65\text{MPC}$	Diff.	$\Delta\text{SCF}+0.65\text{MPC}$	Exptl.
$\text{C}_{512}:\text{P}_\text{C}$	-0.55	-0.58	0.03	-0.52	-0.58	0.06
$\text{Si}_{512}:\text{S}_{\text{Si}}$	-0.32	-0.27	-0.05	-0.26	-0.32	0.06
$\text{Si}_{512}:\text{S}_{\text{Si}}^+$	-0.55	-0.55	0.00	-0.54	-0.59	0.05
$\text{Si}_{512}:\text{Fe}_\text{i}$	-0.96	-0.66	-0.30	-0.49	-0.79	0.30
$\text{Si}_{512}:\text{Au}_{\text{Si}}$	-0.88	-0.84	-0.04	-0.75	-0.81	0.06
$\text{Si}_{512}:\text{C}_\text{i}$	-1.02	-0.86	-0.16	-0.75	-0.89	0.14
$\text{Ge}_{512}:\text{S}_{\text{Ge}}$	-0.36	-0.33	-0.03	-0.29	-0.28	-0.01

Acceptors	Vertical			Adiabatic		
	$E(0/-)$ wr. VBM	ΔKS^b	ΔSCF	Diff.	$\Delta\text{SCF}+0.65\text{MPC}$	Exptl.
$\text{C}_{512}:\text{B}_\text{C}$	0.18	0.22	-0.04	0.36	0.37	-0.01
$\text{Si}_{512}:\text{In}_{\text{Si}}$	0.12	0.10	0.02	0.15	0.15	0.00
$\text{Si}_{512}:\text{O}_{\text{Si}}$	0.88	0.93	-0.05	0.88	0.95	-0.07
$\text{Si}_{512}:\text{C}_\text{i}$	0.92	0.98	-0.06	1.00	1.05	-0.05
$\text{Ge}_{512}:\text{O}_{\text{Ge}}$	0.33	0.36	-0.03	0.34	0.32	0.02

^aN.B. The sum of the ΔKS vertical ionization energy and the relaxation energy of the charged state (difference of the adiabatic and vertical ΔSCF ionization energies) gives very good agreement with the experimental adiabatic ionization energy in every case.

^bN.B. For acceptors the ΔKS and ΔSCF values both need charge correction; see text.

either effective masslike (substitutional P and B in diamond, S and In in Si, S in Ge), or localized combinations of host sp^3 hybrids (substitutional Au and O in Si, O in Ge), while the acceptor state of C_i is a Si $3p$ orbital, strongly mixing with the CB. In contrast, for interstitial Fe and C, where the defect state has a dominant contribution from the localized Fe $3d$ orbital and from a pure C $2p$ lone pair, respectively, the accuracy is less: HSE06 gives a donor level position higher than the experimental value by about the same amount with what a pure PBE underestimates it. Curiously, in these two cases the error of the gKT is also about the same as the deviation from experiment. In fact, adding the relaxation energy of the ionized state (difference of the calculated adiabatic and vertical ionization energies in Table III) to the ΔKS vertical ionization energies yields almost exactly the measured adiabatic ionization energy also in these cases. This means that the ΔKS methods gives extremely good defect level positions in each and every case we have examined. The error for the Fe_i and C_i donors seems to be in the ΔSCF ionization energy. This could partly be due to the charge correction applied here, irrespective of the nature of the defect wave function, however, an error as large as 0.3 eV, cannot be accounted for by that alone. Apparently, the range separated hybrid functional can successfully mimic the exact DFT functional in every respect only for the sp^3 -bonded systems it has been parameterized for, providing defect level positions with an accuracy unheard of so far, and satisfying the gKT at the same time.²⁵ When the defect state to be ionized is not host derived, the ΔSCF ionization energy has a larger error (though not larger than GGA), while the ΔKS is still accurate.

V. CONCLUSION

In summary, we have shown that with its two fixed parameters, the HSE06 functional gives an excellent description of the electronic structure for both the perfect crystal and a wide range of the defects in group-IV semiconductors, provided the defect state is more host than impurity related, but irrespective of the localization. Monitoring the fulfillment of the generalized Koopmans' theorem appears to provide a convenient way to judge the reliability of the results. In case of discrepancy, the ΔKS ionization energy still appears to be accurate. Using that with the relaxation energy in the ionized state of donors also allows to avoid the necessity of charge correction. The correct description of the defect electronic structure gives confidence in the defect energetics obtained with HSE06. Since self-consistent total energy calculations by many-body methods are still impractical for supercells, screened exchange hybrids^{16,26-28} may very well serve as a substitute after careful testing for the given system. They even allow the study of defects in solids (such as Ge) which have no gap in the (semi-) local DFT approximations.

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*deak@bccms.uni-bremen.de

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