PHYSICAL REVIEW B **75**, 153204 (2007)

Limits of the scaled shift correction to levels of interstitial defects in semiconductors

P. Deák,[1] Th. Frauenheim,[1] and A. Gali[2]
[1]*Bremen Center for Computational Materials Science, Universität Bremen, Otto-Hahn-Allee 1, 28359 Bremen, Germany*
[2]*Department of Atomic Physics, Budapest University of Technology and Economics, Budafoki út 8, H-1111, Budapest, Hungary*

(Received 12 February 2007; published 20 April 2007)

The state-of-the-art method to calculate defect properties in semiconductors is density-functional theory (DFT) in a supercell geometry. Standard implementations of DFT, like the local density or the generalized gradient approximation, suffer from the underestimation of the band gap, which may lead to erroneous defect level positions. One possible remedy to this problem is the use of the scissor operator, originally introduced in the case of vacancies. Here we report a case study on interstitial hydrogen in silicon and silicon carbide, which shows that the scissor correction cannot always be applied successfully for interstitial defects and can cause significant errors, especially in wide-band-gap materials.

DOI: 10.1103/PhysRevB.75.153204 PACS number(s): 71.15.Mb, 71.55.Ht, 61.72.Bb, 61.72.Ji

Defect engineering, a key factor in the development of semiconductor technology, has relied, in the past decade, strongly on fundamental research, which was able to identify important defects through comparison of spectroscopic data with results of theoretical calculations. The state-of-the-art method for the latter is represented by *ab initio* supercell calculations of the electronic structure, using density-functional theory (DFT) in one of the standard implementations: local density or generalized gradient approximation (LDA/GGA). These methods provide a valence-band maximum (VBM) for semiconductors, which approximates the ionization energy reasonably well, but the conduction-band minimum (CBM) is substantially lower than the electron affinity. The resulting severe underestimation for the band gap causes significant uncertainties in the gap level of defects as well, the error usually increasing with delocalization. The reason for the gap error is the incomplete description of the electron self-interaction in standard DFT. First-principles corrections are computationally prohibitively costly for large systems, but recently, an approximate GW method has been developed[1] to calculate the necessary corrections to the LDA (or GGA) one-electron energies obtained in supercells. The corrected electronic structure reproduces the observed one quite nicely (alas, at considerable cost), but the corrections cannot be taken into account in the self-consistent total energy. Therefore, the recommended correction method for calculating the self-consistent electronic structure of defects (see, e.g., Ref. 2) is the use of the "scissor" operator,[3] which means a scaled shift with respect to the VBM. The scissor method assumes that the error is negligible for valence states and approximately constant for the conduction-band states.[4] In principle, the wave function of a defect can be expanded on the basis of the perfect crystalline states, and the amount of shifting for a particular level is determined by the weight of the conduction-band states in the expansion of the defect state. The shift necessary for the CBM to reproduce the experimental gap is, therefore, scaled by the sum of overlaps between the defect wave function and all CB states of the perfect crystal. The scissor operator was originally introduced for the case of the vacancy,[3] but, according to experience, it works reasonably well also for substitutional defects and even for split interstitials. However, by comparing the scissor corrections to those obtained with the GW method, in the following we will show that this is not the case for interstitial defects in the low electron density region of the crystal. For demonstration we will use the hydrogen interstitial in silicon (H_i). This is a very well-studied bistable defect,[5,6] with established configurations both in the high and low electron density regions of the crystal, providing an excellent probe to investigate the consequences of the gap error on the level position in different situations for the same atom. We will also use the case of hydrogen in the wide-band-gap semiconductor SiC to corroborate the result.

We have studied H_i in a 64-atom silicon and in a 96-atom 4*H*-SiC supercell, relaxing atoms until the forces were below 0.02 eV/Å. These supercells are sufficiently big to accommodate the induced relaxation, but cannot prevent dispersion of the defect level. The level position of an isolated defect was, therefore, estimated by making a tight-binding fit to the defect band. The total energy and the forces were calculated within the local spin-density approximation (LDA).[7] We applied a plane-wave basis with an energy cutoff of 36 Ry, a 2^3 Monkhorst-Pack *k*-point set,[8] and either norm-conserving pseudopotentials (PPs) in the FHI96MD code[9] to calculate the scissor corrections (and to be comparable with earlier PP calculations) or the projector augmentation wave method within the VASP code[10] to calculate the GW corrections according to Ref. 1. (The two methods yield practically identical geometries and one-electron energies at the LDA level.) Convergence tests carried out with a 216-atom supercell and 64 Ry cutoff have shown that the energy levels are converged within 0.1 eV.

The LDA band gaps of silicon and 4*H*-SiC were calculated to be 0.56 and 2.18 eV, respectively. Comparing these to the low-temperature experimental band gaps of 1.17 and 3.26 eV gives the necessary rigid shifts of 0.61 and 1.08 eV, respectively, for the CBM states of the perfect systems. The scissor correction was obtained by multiplying these values by the overlap between the defect state and the CB states of the perfect supercell. The so obtained level positions, with respect to the VBM of the perfect crystal, were then compared to the quasiparticle (QP) energy difference between the defect level and the VBM, obtained by the parameter-free approximate GW method, as described in Ref. 1. For the perfect crystals, the calculated QP band gaps are 1.22 and 3.35 eV for Si and 4*H*-SiC, respectively, in good agreement with the experimental values.

In thermal equilibrium, H_i in silicon is only stable in its

TABLE I. Position of the CBM and the hydrogen-related one-electron levels with respect to the VBM of the perfect crystal in eV.

Level	LDA	LDA+scissor	LDA+GW
Si:CBM	+0.56	+1.17	+1.22
Si:BC(0)	+0.61	+1.14	+1.05
Si:AB(−)	−0.07	+0.37	+0.10
SiC:AB(−)	+0.50	+1.40	+0.62
SiC:CBM	+2.18	+3.26	+3.35

charged states: being at the bond center (BC) site in the positive charge state and near the tetrahedral (*T*) interstitial site in the negative charge state.[5] The neutral charge state is only metastable, but the (+|0) and (0|−) charge transition levels could still be deduced experimentally to be at CBM-0.18 and CBM-0.65 eV, respectively.[11] These values could be reasonably well reproduced by DFT-LDA calculations, assuming an *a posteriori* scissor correction of about the same magnitude at the BC and the *T* site.[12] Still, when the (+|−) transition levels of H_i (involving only correction near the *T* site, because there is no occupied level in the positive charge state) were compared in a wide range of semiconducting and insulating materials,[13] no correction at all appeared to be necessary even in very-wide-band-gap materials, although one expects the gap corrections to increase with the band gap, as the gap error does.

Our LDA calculation also puts H_i^+ in silicon at the BC position, with no occupied defect level in the gap. (The state corresponding to the three-center Si-H-Si bond is below the VBM.) The equilibrium of H_i^- we find, strictly speaking, to be at one of four equivalent antibonding (AB) positions, away from the *T* site along ⟨111⟩ by ~0.3 Å. The energy difference with respect to the *T* site is, however, small (0.03 eV) and, considering the zero-point energy, H_i^- can be regarded as being, on average, at the *T* site. The LDA electronic structure of H_i^- shows a fully occupied acceptor level near the VB, and the estimated level position of the isolated defect is slightly below the VBM. H_i^0 is most stable at the BC site, however, we find that the AB site is also a true local minimum (in accord with Refs. 14–16 but in contrast to Refs. 12, 17, and 18). The defect band of H_i^0 at the AB site mixes strongly with the VB, and the determination of the isolated defect level is not possible with a simple one-band tight-binding fit. In contrast, the defect band of H_i^0 at the BC site is disjunct from the CB, although the LDA level of the isolated defect is estimated to be slightly above the CBM.

Table I compares the results of the two correction procedures, mentioned in the Introduction, for H_i^0 at the BC site and H_i^- at the AB site. As can be seen, the GW correction shifts the donor level of H_i^0 at BC by 0.44 eV, 2/3 of the CBM correction, 0.66 eV. The scissor correction, 0.53 eV for the defect level, compared to the necessary correction for the CBM, 0.61 eV, gives a reasonably good approximation to that. In contrast, the deviation is rather big for the acceptor level of H_i^- at AB. While the GW correction is only 0.17 eV, the scissor gives 0.44 eV, almost as high as for the donor state at BC. To examine the effect of a larger gap and a larger gap error, we also calculated H_i in 4*H*-SiC. In accordance with earlier LDA calculations,[19–22] the BC site is not the most stable one even for H_i^0 in SiC, but the stable state of H_i^- is at an AB site behind a silicon atom. The corresponding LDA acceptor level is at 0.5 eV above the VBM. As can also be seen in Table I, the scissor correction for H_i^0 in Si and SiC at the AB site is almost in proportion to the increase in the gap error, while the GW correction remains very similar to the case of silicon. Apparently, there is a general, non-material-specific discrepancy between the scissor and the GW correction at play here.

The explanation lies in the different nature of the defect state at BC and AB. At BC it is essentially an antibonding combination of the sp^3 hybrids on the silicon neighbors of H_i (with a node on the hydrogen atom), i.e., clearly conduction-band derived and delocalized. The defect state near *T* is the arch example of a hydrogenic effective-mass state. Since the crystalline electron density around *T* is small, the Coulomb potential is weakly screened, so the state is strongly localized. (Indeed, paramagnetic resonance data show a 30-times stronger localization at *T* than at BC.[5]) This is the reason why GW gives a much smaller correction for the defect state at *T* than at BC. However, the sum of overlaps with the CB states in the former case is almost as high (0.72) as in the latter (0.87), leading to a large shift by the scissor correction in both cases. This is, of course, to be expected, because in the interstitial "hole" in the diamond lattice (where the electron density is small), only CB states can be used to expand even an essentially valence state, such as the 1*s* state of the hydrogen atom.

The same problem should occur in any case when a defect resides in a low electron density region of the crystal, where the VB states of the perfect crystal do not provide an adequate basis for expanding a strongly localized defect state. For such cases, the scissor operator provides a strong overcorrection. It should be emphasized, however, that in the high electron density regions of the crystal, the necessary correction might be rather large and given correctly by the scissor method. The case of the hydrogen interstitial clearly demonstrates that the consequences of the gap error might vary strongly in different configurations of the same impurity atom. Since the error in the one-electron levels should affect the total energy, this might seriously impinge on the calculated diffusion routes, charge transition levels, and the relative stability of substitutional and interstitial configurations.

The question of using or not using a correction can be critical in wide-band-gap semiconductors like 4*H*-SiC. If the defect level is deep in the gap (small coupling to VB and CB states), the error in the total energy can be estimated, in a first approximation, by the correction to the one-electron level, multiplied by its occupation number. Using this procedure with the scissor correction, we have reported earlier a high-lying (+|−) charge transition level for H_i^- at VBM +2.4 eV in 4*H*-SiC.[21] The present GW result indicates that this was in error, and the (+|−) level is only at about VBM+1.4 eV. Through the formation energy of H_i^-, its binding energy to dopants is also influenced. Based on the scissor correction, we have reported[23] the binding energy of H_i^- to the nitrogen donor to be ≈2.0 eV, while the GW correction obtained here indicates a binding energy of only

≈0.4 eV (with a much lowered equilibrium concentration of hydrogen in *n*-type samples, as a consequence).

Finally, we note that the small correction given by the GW method for H_i^- at the AB site of silicon is consistent with Ref. 13 but is not sufficient to push the LDA $(0|-)$ transition level up to the experimentally observed position. The difference can partly be attributed to a necessary charge correction,[24] but we believe that this is also connected to the overestimation of the formation energy of H_i^0 at AB, due to neglecting the vibrational coupling despite the strongly anharmonic potential for the electrons.[25]

P.D. acknowledges a discussion with Ch. Van de Walle, some time ago, which initiated this study. The authors wish to thank the help of J. Furthmüller in the GW calculations. Discussions with K. Bonde-Nielsen are appreciated. The support of the German-Hungarian bilateral research fund, 436 UNG 113/167/0-1, is also acknowledged.

---

[1] J. Furthmüller, G. Cappellini, H. C. Weissker, and F. Bechstedt, Phys. Rev. B **66**, 045110 (2002).
[2] C. W. M. Castleton, A. Höglund, and S. Mirbt, Phys. Rev. B **73**, 035215 (2006).
[3] G. A. Baraff and M. Schlüter, Phys. Rev. B **30**, 1853 (1984).
[4] It should be noted that, contrary to popular belief, this is only true in the same dispersion branch. For example, the indirect band gap—i.e., the position of the first CB branch with respect to the VBM—is underestimated by about 0.7 eV in silicon, while the direct gap at the zone center, i.e., the position of the fourth CB branch, by 1.7 eV (Ref. 26).
[5] S. K. Estreicher, Mater. Sci. Eng., R. **14**, 319 (1995).
[6] C. A. J. Ammerlaan, in *Silicon. Evolution and Future of a Technology*, edited by P. Siffert and E. Krimmel (Springer-Verlag, Berlin, 2004), Vol. 217, p. 261.
[7] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[8] H. J. Monkhorst and J. K. Pack, Phys. Rev. B **13**, 5188 (1976).
[9] M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, Comput. Phys. Commun. **107**, 187 (1997).
[10] G. Kresse and J. Hafner, Phys. Rev. B **49**, 14251 (1994); G. Kresse and J. Furthmüller, *ibid.* **54**, 11169 (1996); G. Kresse and D. Joubert, *ibid.* **59**, 1758 (1999).
[11] K. B. Nielsen, L. Dobaczewski, S. Sogård, and B. B. Nielsen, Phys. Rev. B **65**, 075205 (2002).
[12] C. Herring, N. M. Johnson, and C. G. Van de Walle, Phys. Rev. B **64**, 125209 (2001).
[13] C. G. Van de Walle and J. Neugebauer, Nature (London) **423**, 626 (2003).
[14] S. Estreicher, Phys. Rev. B **36**, 9122 (1987).
[15] P. Deák, L. C. Snyder, and J. W. Corbett, Phys. Rev. B **37**, 6887 (1987).
[16] R. Jones, Physica B **170**, 181 (1991).
[17] C. G. Van de Walle, Y. Bar-Yam, and S. T. Pantelides, Phys. Rev. Lett. **60**, 2761 (1988).
[18] N. M. Johnson, C. Herring, and C. G. Van de Walle, Phys. Rev. Lett. **73**, 130 (1991).
[19] C. H. Chu and S. K. Estreicher, Phys. Rev. B **42**, 9486 (1990).
[20] B. Aradi, A. Gali, P. Deak, J. E. Lowther, N. T. Son, E. Janzen, and W. J. Choyke, Phys. Rev. B **63**, 245202 (2001).
[21] P. Deák, A. Gali, and B. Aradi, Mater. Sci. Forum **353-356**, 421 (2001); in *Silicon Carbide–Recent Major Advances*, edited by W. J. Choyke, H. Matsunami, and G. Pensl (Springer-Verlag, Berlin, 2003), Chap. 3.
[22] M. Kaukonen, C. J. Fall, and J. Lento, Appl. Phys. Lett. **83**, 923 (2003).
[23] A. Gali, P. Deák, N. T. Son, and E. Janzén, Appl. Phys. Lett. **83**, 1385 (2003).
[24] Due to the strong localization of the defect state, the Makov-Payne correction (Ref. 27) seems to be applicable.
[25] P. Deák, T. Frauenheim, J. E. Lowther, and A. Gali (unpublished).
[26] P. Deák *et al.*, J. Phys.: Condens. Matter **17**, S2141 (2005).
[27] G. Makov and M. C. Payne, Phys. Rev. B **51**, 4014 (1995).