

Branch-point energies and band discontinuities of III-nitrides and III-/II-oxides from quasiparticle band-structure calculations

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Using quasiparticle band structures based on modern electronic-structure theory, we calculate the branch-point energies for zinc blende (GaN, InN), rocksalt (MgO, CdO), wurtzite (AlN, GaN, InN, ZnO), and rhombohedral crystals (In₂O₃). For InN, CdO, ZnO, and also In₂O₃ the branch-point energies are located within the lowest conduction band. These predictions are in agreement with observations of surface electron accumulation (InN, CdO) or conducting behavior of the oxides (ZnO, In₂O₃). The results are used to predict natural band offsets for the materials investigated.

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When two semiconductors get in contact, their energy bands as well as the underlying wave functions in the interface region are subject to a remarkable influence due to the interface itself. While in a bulk material only nonevanescing states with real \mathbf{k} vectors appear and obey normalization conditions, the situation changes at surfaces and interfaces. There, wave functions that decay exponentially from one material into the other are also allowed. These so-called *virtual gap states* (ViGS) with eigenvalues generally within the gap and complex \mathbf{k} vectors give rise to a complex band structure.¹ The ViGS may be understood as a continuation of bulk valence-band (VB) and conduction-band (CB) states extending into the fundamental gap of a semiconductor. At a certain energy, called the branch-point energy (BPE) E_{BP} , these states change their character from predominantly VB-like (or donorlike) to mostly CB-like (or acceptorlike). Reaching from one material into the other such states transfer a net charge, the sign of which depends on the position of the Fermi level relative to the BPE. According to Tersoff² this charge transfer leads to an intrinsic interface dipole that tends to line up the energy bands in a way that the dipole itself vanishes. Therefore, E_{BP} serves as an energy reference level for the band alignment. In the case of a metal-semiconductor contact, this energy is frequently called *charge neutrality level*.²⁻⁴ Tersoff established a method to obtain the actual band lineup and therefore the relative energetical positions of the energy gaps by computing E_{BP} (or *effective midgap energy* in Ref. 2) for each of the involved semiconductors. It is based on the energy zero of the cell-averaged single-quasiparticle (QP) real-space Green's function, which can be decomposed into a VB and a CB part. At E_{BP} both parts contribute equally and the character of the states changes from VB- to CB-like.

A clear advantage of Tersoff's method is that it explains (in convincing agreement with experiments)² the band lineup just in terms of the bulk band structure, i.e., neglecting structural details of the actual interface—only the surface orientation enters. Unfortunately, from a practical point of view it is extremely difficult to converge the Green's function sufficiently with respect to the number of used \mathbf{k} points as well as CBs (at least for arbitrary orientations) to obtain values for E_{BP} , which are accurate within tenths of an eV. Furthermore,

Tersoff's method cannot be applied to systems where the BPE appears in the CB region, although there is experimental evidence that the BPE may also occur outside the gap within the bands. This is found for example for the wurtzite (wz) semiconductor InN.⁵ The BPE in the first CB has been identified as the origin of the electron accumulation at InN surfaces.⁶ Recently, also its temperature variance and its independence of surface orientation, bulk polytype, and doping have been demonstrated.^{7,8} For CdO also indications for E_{BP} above the CB minimum (CBM) ε_{CBM} exist.⁹ In this study we therefore focus on the group-III nitrides AlN, GaN, InN, the group-II oxides MgO, ZnO, and CdO as well as In₂O₃. They crystallize in different structures and possess different band-structure characteristics. In this study we use lattice parameters as obtained from structural relaxations within density functional theory (DFT) using local/semilocal approximations for exchange and correlation (XC).

Besides the Green's function method several approximate treatments for the calculation of E_{BP} have been suggested. They basically follow Flores and co-workers^{3,10} who computed E_{BP} as the average of the midgap energies at the Γ , X , and L points of the Brillouin zone (BZ) for fcc crystals. Tersoff concluded^{2,11} from band-structure examinations that for diamond- and zinc-blende (zb)-structure crystals the BPE is simply given as $E_{BP} = \frac{1}{2}(\bar{\varepsilon}_{CBM} + \bar{\varepsilon}_{VBM})$, where $\bar{\varepsilon}_{VBM}$ is the energy of the (threefold degenerate) VB maximum (VBM) at Γ (without spin-orbit splitting) and $\bar{\varepsilon}_{CBM}$ is the energy of the off- Γ CBM usually located around X .

For the materials studied here, whose CBs in the vicinity of Γ are much lower in energy than in the outer part of the BZ, the latter method would give incorrect results. Therefore, a complete BZ average seems to be more appropriate. Modern electronic-structure calculations provide the energy eigenvalues at each desired \mathbf{k} point of the BZ. Cardona and Christensen¹² applied the concept of BZ averaging but only used the first of Baldereschi's special points to approximate the corresponding \mathbf{k} -point sum. More precisely, they calculated the BPE (they refer to it as midgap energy) by averaging the eigenvalues of the two highest VBs and the two lowest CBs at the first Baldereschi point. We basically follow the ideas of the previous approaches^{3,11,12} but perform the BZ average using QP energies computed at Γ -centered Monkhorst-Pack \mathbf{k} points,

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TABLE I. BPEs E_{BP} of semiconductors relative to the VBM derived from Eq. (1) together with fundamental gap values E_g from QP band structures. For comparison, available experimental values are also given. All values are in eV.

Semiconductor	E_g	E_{BP} (Theor.)	E_{BP} (Expt.)	ΔE_c	ΔE_v
wz-AlN	6.14	3.33		2.81	-3.33
wz-GaN	3.35	2.37	2.4 ^a	0.98	-2.37
zb-GaN	3.28	2.31		0.97	-2.31
wz-InN	0.71	1.58	1.64 ± 0.1 ^b 1.58 ± 0.1 ^c 1.83 ± 0.1 ^d	-0.87	-1.58
zb-InN	0.47	1.50	1.38 ± 0.1 ^c	-1.03	-1.50
rh-In ₂ O ₃	3.25	3.79		-0.54	-3.79
rs-MgO	7.49	5.42		2.07	-5.42
wz-ZnO	3.21	3.40		-0.19	-3.40
rs-CdO	0.68 (indirect)	2.45	1.30 ± 0.1 ^f	-1.77	-2.45

^aReference 1.

^bReference 5.

^cReference 6.

^dReference 8.

^eReference 7.

^fReference 9.

$$E_{BP} = \frac{1}{2N_{\mathbf{k}}} \sum_{\mathbf{k}} \left[\frac{1}{N_{CB}} \sum_i \varepsilon_{c_i}(\mathbf{k}) + \frac{1}{N_{VB}} \sum_j \varepsilon_{v_j}(\mathbf{k}) \right]. \quad (1)$$

Here, $N_{\mathbf{k}}$ is the number of points in the \mathbf{k} meshes. For materials with two atoms per unit cell [rocksalt (rs) or zb crystal structure] we include only the lowest CB ($N_{CB}=1$) and the two uppermost VBs ($N_{VB}=2$). In the case of wz crystals we correspondingly include the two lowest CBs and the four uppermost VBs. A scaling of the band numbers according to the number of valence electrons (without d electrons) in the primitive unit cell leads to 6 CBs and 12 VBs for In₂O₃ in the rhombohedral (rh) structure. Furthermore, we performed test calculations for the materials and crystal structures of interest here. N_{CB} is clearly determined by the huge dispersion of the lowest CB near Γ in all cases. Regarding N_{VB} , we exclude the third VB (in cubic crystals) because it shows a much larger \mathbf{k} dispersion throughout the BZ than the two uppermost ones. Consequently, the number of bands seems to introduce an uncertainty of the approach (1) of up to 0.2 eV. For AlN, GaN, InN, and ZnO there is quantitative agreement of the results for E_{BP} from Eq. (1) and the results of band alignment using hydrogen levels.⁴

Reliable bulk band structures are a crucial point for computing E_{BP} using Eq. (1) for the materials we are interested in. The common DFT treatment usually fails to predict energy bands comparable with experimental values¹³ as long as a local or semilocal approximation is used for the XC functional. For the nitrides and oxides DFT leads to large gap underestimations, especially due to its intrinsic lack of the excitation aspect as well as the unsatisfactory treatment of the shallow $3d$ or $4d$ electrons. The resulting band structures of zb-InN, wz-InN, and rs-CdO even correspond to that of zero-gap semiconductors with inverted CB and VB symmetries,^{14,15} for wz-ZnO a much too small gap^{15,16} occurs. In these cases the perturbation-theory treatment G_0W_0 of the QP effects¹³ within Hedin's GW approximation cannot sufficiently cure the deficiencies. Tersoff² just rigidly shifted the CBs to correct the gap, i.e., applied a scissors operator.¹³ Cardona and Christensen¹² avoided this scissors shift. Instead, they achieved an effective increase in E_{BP} by including the second CB in the computation procedure.

We choose the currently most reliable approach for the calculation of the QP band structures of these materials, as demonstrated for InN, ZnO, and In₂O₃,¹⁶⁻¹⁸ with an improved starting point for the iterative solution of the QP

equation. In the zeroth order eigenvalues and eigenfunctions of a generalized Kohn–Sham equation are computed with the spatially nonlocal HSE03 XC hybrid functional of Heyd *et al.*¹⁹ Although this approach is computationally quite demanding, we converge the results for E_{BP} with respect to the number of \mathbf{k} points by using similar BZ samplings as required for the computation of the density of states (DOS).

The three group-III nitrides AlN, GaN, and InN crystallize in the hexagonal wz or the cubic zb structure, while for the group-II oxides MgO, ZnO, and CdO the cubic rs or the wz structure is preferred. In the case of In₂O₃ there are two stable polymorphs: the rh and the bixbyite phase with body-centered cubic translational symmetry.¹⁸ Due to the high computational cost of the calculation using the nonlocal XC functional and the computation of the QP energies, we restrict ourselves to study only the rh phase of In₂O₃ instead of the bixbyite one with four times more atoms in the unit cell.¹⁸

In Table I the positions of the BPEs resulting from Eq. (1) are listed with respect to the VBM together with the fundamental gaps E_g computed within the HSE03+ G_0W_0 approach. Available experimental values for E_{BP} are given. For the zb polymorph of GaN (InN) we also compare with results from the Tersoff approach,² which yields $E_{BP}=2.31$ eV ($E_{BP}=1.86$ eV). This is in rough agreement with the values listed in Table I. As an interesting result we emphasize that for all of the studied materials, except AlN, GaN, and MgO, E_{BP} lies above the CBM. For both polytypes of InN this result is in very good agreement with recent measurements using different methods.^{5-8,20} One consequence of $E_{BP} > E_g$ is the observed electron accumulation at InN surfaces. For rs-CdO there is also experimental evidence for such an accumulation from x-ray photoemission spectroscopy.⁹

The BPE lying above the CBM for InN, CdO, In₂O₃, and ZnO is mainly a consequence of the low DOS close to the pronounced CBM. This is demonstrated in Fig. 1 for the QP band structures of zb-InN and rs-CdO. In both materials the CB exhibits the aforementioned strong dispersion near the BZ center with the energy at Γ being 4–5 eV lower than that in the outer regions of the BZ. Comparing both band structures it is obvious that the gap of rs-CdO is indirect (between Γ and L), while InN shows a direct gap at Γ . This is due to the fact that in the rs structure the pd repulsion is symmetry forbidden at Γ .¹⁵ Therefore, the L point of the VB band is about 1.12 eV higher in energy than the Γ point. The indirect

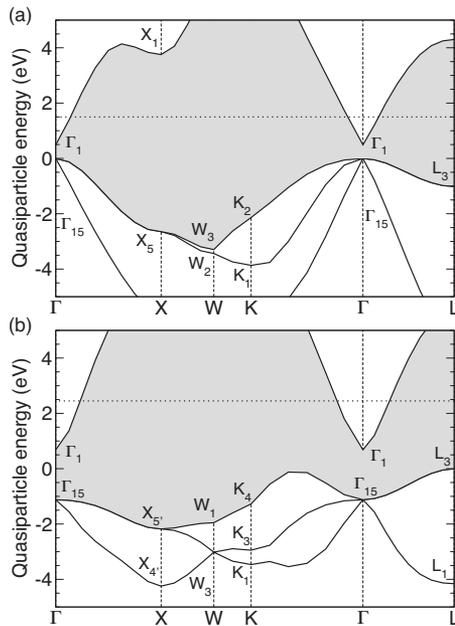


FIG. 1. QP band structure of (a) zb-InN and (b) rs-CdO calculated within the HSE03+ G_0W_0 approach. The dotted line indicates the BPE Eq. (1) and the VBM has been used as energy zero.

gap between Γ and L is found to be 0.68 eV, in good agreement with the experimental value of 0.84 eV.²¹

For the three nitrides AlN, GaN, and InN we note that the BPEs computed within the tight-binding method or a pseudopotential approach are very close to the ones derived from QP calculations: Mönch¹ and Robertson and Falabretti²² computed values of 2.97/3.97 eV for AlN, 2.37/2.88 eV for GaN, and 1.51/1.87 eV for InN, which agree well with our values in Table I. This fact and the excellent agreement with experimental values for wz-GaN¹ as well as wz- and zb-InN⁵⁻⁸ suggest a high predictive power for E_{BP} of the studied oxides (see Table I). For wz-ZnO the BPE agrees within 0.2 eV with the CBM. This might be an indication why ZnO can be used as transparent conducting oxide (TCO) at least after doping with Al. For In₂O₃ the distance between E_g and E_{BP} is slightly larger with about 0.5 eV, but also in this case doping, e.g., with Sn, does enable this material to act as a TCO. In any case, our prediction for E_{BP} is in agreement with the standard picture of In₂O₃ being a degenerate semiconductor.

As mentioned in the Introduction the BPE can be used as a universal energy level of reference to align the energy bands of different semiconductors. With the values from Table I, we obtain band lineups as presented in Fig. 2 for the equilibrium polymorphs of the studied compounds. The relative positions of the band extrema ε_{CBM} and ε_{VBM} with respect to E_{BP} can be interpreted as natural band discontinuities ΔE_c and ΔE_v . Our predictions for relative ΔE_v between the nitrides agree with other calculations^{4,23} with respect to sign and order of magnitude. Concluding from Fig. 2 all combinations of the three oxides rs-MgO, wz-ZnO, and rs-CdO should result in type-I heterostructures, and also the combination of InN and In₂O₃ should give rise to type-I heterointerfaces with interesting consequences for two dimensional electron gases.

In conclusion, using modern QP calculations we have demonstrated that high unintentional n -type conductivity of nominally undoped InN, CdO, ZnO, and In₂O₃ surfaces may

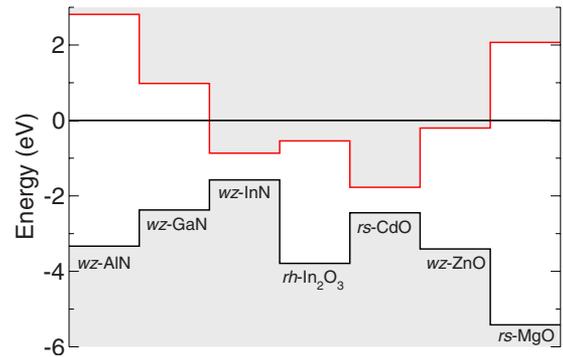


FIG. 2. (Color online) CB and VB edges for nitrides and oxides in various crystallographic structures. The BPEs are used for alignment. The values for E_g and E_{BP} are taken from QP calculations.

occur due to the low Γ point CB minima lying significantly below the BPE. The band lineup by means of the BPE has been used to predict natural band offsets for group-II oxides, group-III nitrides, and In₂O₃.

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