

Revised *ab initio* natural band offsets of all group IV, II-VI, and III-V semiconductors

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Using an all-electron band structure approach, we have systematically calculated the natural band offsets between all group IV, III-V, and II-VI semiconductor compounds, taking into account the deformation potential of the core states. This revised approach removes assumptions regarding the reference level volume deformation and offers a more reliable prediction of the “natural” unstrained offsets. Comparison is made to experimental work, where a noticeable improvement is found compared to previous methodologies. © 2009 American Institute of Physics.

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The absolute band offset between semiconductors is one of the most fundamental properties in materials physics. It is a necessary quantity to assess charge transport and quantum confinement, and is of particular relevance to the design of solar cells, light emitting diodes, and other optoelectronic devices which feature an interface between two or more materials. The absolute band edge positions also have a role in determining material doping limits,^{1,2} in addition to electrochemical properties.³

X-ray photoemission spectroscopy (XPS) is often used experimentally to probe core states and hence provide a reference from which the alignment between the valence bands of two or more systems can be measured.⁴ Following the same procedure, theoretical calculations have been performed to obtain the “natural valence band offset” of two compounds at their respective equilibrium positions using the description^{5,6}

$$\Delta E_v(AX/BY) = \Delta E_{v,C'}(BY) - \Delta E_{v,C}(AX) + \Delta E_{C,C'}(AX/BY). \quad (1)$$

Here $\Delta E_{v,C}(AX) = E_v(AX) - E_C(AX)$ [the same for $\Delta E_{v,C'}(BY)$] is the energy difference between the valence band maximum (VBM) and core level at the equilibrium lattice constant and $\Delta E_{C,C'}(AX/BY) = E_{C'}(BY) - E_C(AX)$ is the core level energy difference between the two core levels in a relaxed (AX/BY) heterostructure, where a common energy reference exists.^{5,6} This is required as the energy levels of a periodic system are only defined with respect to an arbitrary constant.⁷ A similar procedure is employed in pseudopotential calculations where the core level is replaced by the averaged Coulomb potential energy.⁸ The calculated offsets are generally in good agreement with experimental observations when the same approach is used. For example, the calculated valence band offset $\Delta E_v(\text{ZnTe/CdTe})$ is -0.09 eV,⁵ whereas the XPS measurement obtained a value of -0.1 eV.⁹

However, the validity of the above approach is based on the assumption that the reference levels have zero absolute

deformation potential, and thus align between the bulk and heterostructures. This is justified when compounds AX and BY are lattice matched and there is no charge transfer between AX and BY in forming the heterostructure. However, for lattice mismatched systems, it is not established if this assumption is valid. In fact, recent theoretical work has shown that for almost all zinc-blende semiconductors, the absolute deformation potential of the core state ($a_C = d\epsilon_C/d\ln V$) is not negligible,^{10–12} thus, its effect has to be taken into account in calculating the natural valence band offset of two lattice mismatched systems.

In this paper we report the unstrained “natural” band offsets between all cubic group IV, II-V and II-VI semiconductors using a revised *ab initio* approach, without any approximation to the reference state, i.e., effects arising from the core level deformation potential are taken into account.^{11,12} We provide a succinct guide on how to perform such calculations and compare our comprehensive results to available experiment.

All calculations were performed at the experimental lattice constants^{13,14} using the local density approximation¹⁵ (LDA) including relativistic effects as implemented in the WIEN2K linearized augmented plane wave code.¹⁶ High cut-off energy for the basis functions and dense k -point sampling were used in each case to ensure fully converged results. We emphasize that the proposed approach is general and can be used with beyond-LDA methods including quasiparticle corrections.

In the following, we list the basic steps required to obtain the natural band offset between two isovalent and isostructural cubic semiconductors AX and BY, Fig. 1.

- (i) *Bulk compounds AX and BY.* The initial step is to perform separate bulk calculations for the compounds AX and BY at their averaged volume. From this we can determine the energy separation $\Delta E_{v,C}^{(av)}$ between the core level eigenvalues and the Γ_{8v} VBM state. In our calculations, we use the average of the cation and anion 1s core levels. The final result is not sensitive (within 0.05 eV) to the reference level employed. From this step, we have

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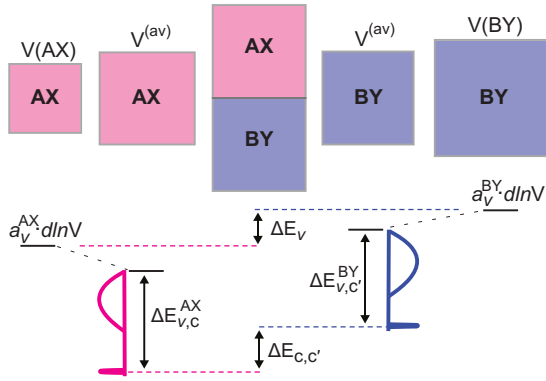


FIG. 1. (Color online) Illustrated steps involved for the revised natural valence band offset calculation using a core level reference.

$$\Delta E_{v,\text{core}}^{(av)}(AX/BY) = \Delta E_{v,C'}^{(av)}(BY) - \Delta E_{v,C'}^{(av)}(AX). \quad (2)$$

- (ii) *Heterostructure alignment.* To align the AX and BY reference levels between the isolated systems, we perform an explicit calculation combining both materials. This is usually done by forming an unrelaxed $(AX)_n(BY)_n$ superlattice along the (001) direction at the average lattice constant, with the atoms at the ideal zinc-blende positions. The slab thickness is checked. For our purpose, $n=6$ is sufficient and offers convergence to within 0.01 eV. The choice of superlattice direction is also found to be small, with a con-

verged (110) superlattice differing by 0.01 eV or less. The difference in the core levels ($\Delta E_{C,C'}$) between the center (bulklike region) of each half of the superlattice then is derived.

$$\Delta E_{C,C'}^{(av)}(AX/BY) = E_{C'}(BY) - E_C(AX). \quad (3)$$

This provides the band offset $\Delta E_v^{(av)}(AX/BY)$ at their averaged lattice constants.

$$\Delta E_v^{(av)}(AX/BY) = \Delta E_{v,\text{core}}^{(av)}(AX/BY) + \Delta E_{C,C'}^{(av)}(AX/BY). \quad (4)$$

For lattice matched systems, this is the same procedure adopted in previous calculations.⁵

- (iii) *Valence band deformation.* To obtain the natural band offset, i.e., the offsets when the compounds are at their respective equilibrium lattice constants, we need to account for changes in the VBM state under a hydrostatic volume deformation (a_v^{VBM}). This is obtained by calculating a series of absolute uniaxial deformation potentials for the core state and performing an angular average.¹² From the calculated hydrostatic absolute deformation potential of the core state, the deformation potential of the VBM state can be easily obtained.^{12,17} Using this approach, we have recently reported the absolute volume deformation potentials of all group IV, III-V, and II-VI semiconductors.¹⁸

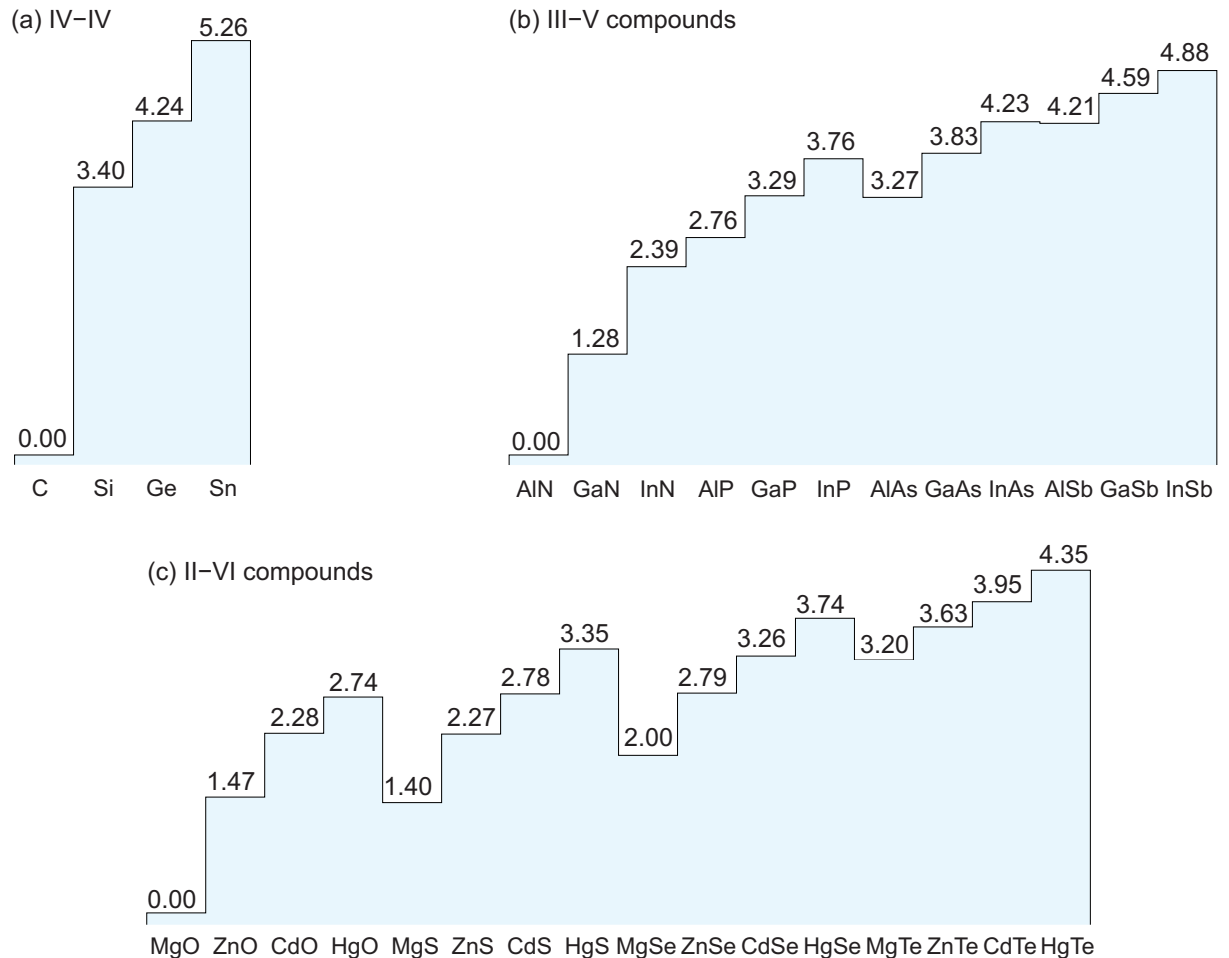


FIG. 2. (Color online) *Ab initio* natural valence band offsets of all diamond group IV and zinc-blende II-VI and III-V semiconductors.

Once a_v^{VBM} is known for both AX and BY , the final natural band offsets $\Delta E_v(AX/BY)$ can be directly obtained from

$$\Delta E_v(AX/BY) = \Delta E_v^{(av)}(AX/BY) + a_v^{\text{VBM}}(AX)d\ln V(AX) + a_v^{\text{VBM}}(BY)d\ln V(BY), \quad (5)$$

where $d\ln V = \Delta V/V$ is the relative volume difference between the equilibrium structures of AX and BY and their average.

The results of this methodology, systematically applied to a range of diamond and zinc-blende semiconductor systems, are shown in Fig. 2. To enforce the transitivity relation, i.e., from the calculated offsets between (AX/BY) and (BY/CZ) , the offset between (AX/CZ) can be inferred, the final offsets presented in Fig. 2 are obtained from a least-squares fit over a number of direct and transitive pairs, with a standard deviation of ± 0.1 eV.

The general chemical trends obtained from the calculated offsets follow established expectations: (i) the VBM energies *increase* with increasing anion atomic number due to lower binding energy of the anion p states; (ii) the VBM energies increase with increasing cation atomic number because the larger bond length reduces the cation p -anion p coupling, increasing the bonding VBM energies, and the additional effect of increased cation d -anion p coupling.

The calculated offsets using the revised approach address a number of long-standing anomalies between theory and experiment. For (GaAs/InAs) the predicted offset is increased from 0.06 eV in the previous calculation⁵ to 0.50 eV, in good agreement with deep level transient spectroscopy measurements of 0.46 eV.¹⁹ For (GaN/InN) the predicted offset increases from 0.2–0.3 (Ref. 5 and 20) to 1.11 eV, more in line with experimental estimations of 0.9–1.1 eV.^{21–23} For InN, one should keep in mind the difficulty in growing high quality films, which contributes to the wide range of measurements reported for the (AlN/InN) offset from 1.5 (Ref. 24) to 3.1 eV,²⁵ and our theory predicts 2.39 eV, midway between the two extremes.

In conclusion, we have reported the natural valence band offsets for the majority of elemental and binary semiconductors, calculated using an approach which removes the vol-

ume dependence of the reference state. These predictions will be of benefit in assessing material applicability for device applications, and assisting experimental interpretation of device performance.

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