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Polarity in semiconductor compounds

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The polarity in zinc-blende semiconductor compounds is calculated by extending Harrison's bond-orbital theory to a cluster model and the result is compared to values from previous calculations. We find that polarities from the cluster calculations differ significantly from those predicted by the bond-orbital model and that this difference cannot be accurately calculated by including bond metallization in first-order perturbation theory in the extended bond-orbital model. Cluster polarities are found to be 15%–30% lower than polarities predicted by the bond-orbital model, and comparable to a Brillouin-zone integration of the corresponding tight-binding Hamiltonian. Since bond-antibond interaction corrections to the energy enter in second-order perturbation theory, metallization corrections to the bond energies are found to be comparable whether calculated from a cluster model or using second-order perturbation theory in the extended bond-orbital model.

I. INTRODUCTION

Several definitions of polarity and ionicity of molecular and crystal bonds exist.[1–6] In binary semiconductors, polarity and ionicity provide a measure of the relative charge residing on the cation and anion sites in the lattice. As such, they can be related to the covalent and ionic contributions to the crystal bonding. In general, the unique assignment of the electronic charge to the cation and anion sublattices is ambiguous; however, in a tight-binding representation of the Hamiltonian, an unambiguous assignment of charge is possible. Here we choose to define the polarity in a compound AB as

$$\alpha_p = \frac{P(A) - P(B)}{P(A) + P(B)} , \tag{1}$$

where $P(A)$ is the probability that an electron in a bond is on the A site and $P(B)$ that it is on the B site. The polarity in Eq. (1) can be expressed in terms of the total net charge per cation and anion site in the crystal, Z_c and Z_a, respectively, through the relationship

$$\alpha_p = | Z_0 + Z_c | /4 = | Z_0 - Z_a | /4 , \tag{2}$$

where $Z_0 = 0$, 1, and 2 for group-IV, III-V, and II-VI compounds, respectively. This expression reduces to $\alpha_p = 0$ for the group-IV semiconductors. Equation (2) is the definition of polarity used in the bond-orbital (BO) model of Harrison[5] and is what Coulson *et al.*[2] and Falter *et al.*[6] refer to as *ionicity*. Phillips[3] defines a spectroscopic ionicity as

$$f_i^P = \frac{C^2}{C^2 + E_h^2} . \tag{3}$$

E_h and C in Phillips' ionicity are defined from the symmetric (real) and antisymmetric (imaginary) combination of the atomic pseudopotential of the constituent atoms. It is interesting to observe that Phillips' ionicity in Eq. (3) is related to the BO polarity by $f_i^P = \alpha_p^2$, if $C \propto V_3$ and $E_h \propto V_2$ are assumed [see Eq. (4) below]. However, the manner in which the covalent and ionic contributions to the bonding are determined differs substantially for the two methods.

II. EXTENDED BOND-ORBITAL POLARITY

Within the BO model, the polarity is given by

$$\alpha_p = \frac{V_3}{(V_2^2 + V_3^2)^{1/2}} , \tag{4}$$

where V_2 is the covalent energy, coupling two hybrids in a common bond, and V_3 is the polar energy, which is equal to half the difference between the cation and anion hybrid energy. In the extended bond-orbital (EBO) model, the matrix elements V_1^a and V_1^c, which couple hybrids on a common anion and cation, respectively, are treated in perturbation theory. Since the bond-bond and antibond-antibond interactions broaden the states into bands but do not shift the center of gravity of the valence and conduction bands, only the bond-antibond interactions need be included in the metallization corrections in the EBO model. Shifts to the energy levels enter in second-order perturbation theory, and the shifted bond energy e_b' is given by

$$e_b' = e_b + \sum_{i=a,c} 3 \left[\frac{| u_b^i |^2 | u_a^i |^2 | V_1^i |^2}{(e_b - e_a)} \right] . \tag{5}$$

Here, u_b^i and u_a^i are the coefficients on the ith (cation or anion) site of the respective bond and antibond state, and e_b and e_a are the respective bond and antibond energies from the bond-orbital model. Metallization shifts to the wave functions, and therefore polarities, enter in first-order perturbation theory. In the EBO, the probabilities that the valence electrons project on the anion and cat-

TABLE I. Polarity as a function of cluster size. Shown for comparison are the values from the bond-orbital (BO) model and the extended bond-orbital (EBO) model. Significant figures shown are intended to convey convergence information, not absolute significance of the polarity calculation.

Compound	BO	EBO	Cluster calculations 32 hybrids	 104 hybrids	 176 hybrids
AlP	0.524	0.487	0.418	0.420	0.421
GaP	0.500	0.457	0.377	0.381	0.383
InP	0.596	0.549	0.454	0.459	0.461
AlAs	0.523	0.473	0.385	0.389	0.391
GaAs	0.500	0.441	0.341	0.349	0.352
InAs	0.594	0.532	0.414	0.422	0.425
AlSb	0.462	0.405	0.311	0.317	0.319
GaSb	0.427	0.362	0.267	0.277	0.281
InSb	0.528	0.456	0.332	0.345	0.349
ZnS	0.650	0.614	0.550	0.551	0.551
CdS	0.708	0.671	0.602	0.603	0.603
HgS	0.688	0.642	0.550	0.552	0.553
ZnSe	0.669	0.624	0.544	0.546	0.547
CdSe	0.721	0.675	0.590	0.592	0.593
HgSe	0.699	0.644	0.529	0.535	0.537
ZnTe	0.671	0.625	0.534	0.538	0.539
CdTe	0.717	0.670	0.576	0.579	0.580
HgTe	0.685	0.627	0.499	0.508	0.511

ion sites, respectively, are given by

$$|u_b^{a'}|^2=\frac{1}{N}[|u_b^a|^2+3|u_a^a|^2(|H^c|^2+|H^a|^2)]\ ,$$
$$|u_b^{c'}|^2=\frac{1}{N}[|u_b^c|^2+3|u_a^c|^2(|H^c|^2+|H^a|^2)]\ , \tag{6}$$

where H^i ($i=a$ or c) is the matrix element of a bond with an adjacent antibond and is given by

$$H^i=\frac{u_b^i u_a^i V_1^i}{e_b-e_a}\ , \tag{7}$$

and N is the normalization factor.

Because $|u_b^c|^2$ is the probability that the electron in the bond resides on the cation site and $|u_b^a|^2$ is the probability that it resides on the anion site, once these are calculated, the polarity can be calculated directly from Eq. (1). Polarities calculated from the BO and EBO model for the group III-V and II-VI compounds are given in Table I.

III. CLUSTER POLARITY

In a recent paper,[7] we developed a cluster method to calculate vacancy formation energies in semiconductor compounds. There, an embedded-cluster method was used based on an extension of Harrison's bond orbital theory.[5] Following Harrison, the cluster Hamiltonian was expressed in a sp^3 hybrid basis with hybrid energies ε_h^c and ε_h^a, and only nearest-neighbor interactions were included. Site diagonal matrix elements were taken from Chen and Sher.[8] The method included metallic energy terms V_1^a and V_1^c, coupling hybrids on the same atom site, and the covalent interaction energy V_2 between nearest-neighbor hybrids pointing toward one another. We used a universal scaling law[9] for the covalent energy $V_2=-3.22\hbar/md^2$. The cluster was embedded in an infinite crystal composed of bond orbitals, and modifications to cluster eigenenergies were treated by coupling the cluster eigenstates to the extended crystal bond orbitals in second-order perturbation theory. From the cluster eigenstates, the electronic charge per atom site in the crystal can be obtained and is used here to define a cluster polarity.

In the cluster method, metallization interactions among the cluster orbitals are included explicitly in the cluster Hamiltonian. In addition, interactions among adjacent bond-bond and antibond-antibond are included in the cluster Hamiltonian. As a result, the cluster states are broadened into bands. The atom-centered clusters considered contain only complete bonds; no dangling hybrids at the cluster border are included. Because constructing the clusters in this manner eliminates dangling hybrid states, it is straightforward to compute metallization corrections to the cluster states that are due to interactions with bond orbitals outside the cluster. Shifts to the eigenenergies that result from the coupling to the antibond orbitals through a cation or anion at the cluster border are included through second-order perturbation theory, analogous to Eq. (5). The reason for including the coupling of the cluster to the medium in this way is to increase the rate of convergence as a function of cluster size.

The bond polarity of a specific bond j in the cluster is calculated by summing over the contributions to the specific orbitals j_c and j_a on the cation and anion site, respectively, for all the spin-degenerate occupied states n in the cluster. Thus the total probability that the valence electrons project onto the anion and cation hybrids of the jth cluster bond is given by

TABLE II. Comparison of polarities from various calculations. Cl is the cluster containing 176 hybrid orbitals; BZ is the Brillouin-zone integration of LCAO Hamiltonian as discussed in text; BO is the bond orbital model of Harrison (Ref. 5); f_I^P from Phillips' ionicity (Ref. 3); expt, from the experiment-deduced ionicity scale of Falter *et al.* (Ref. 6).

Compound	α_p (Cl)	α_p (BZ)	α_p (BO)	f_I^P	f_I (expt)[a]
AlP	0.42	0.44	0.52	0.31	0.33
GaP	0.38	0.40	0.50	0.33	0.31
InP	0.46	0.48	0.60	0.42	0.32
AlAs	0.39	0.41	0.52	0.27	0.31
GaAs	0.35	0.37	0.50	0.31	0.30
InAs	0.42	0.44	0.59	0.36	0.30
AlSb	0.32	0.34	0.46	0.25	0.30
GaSb	0.28	0.30	0.43	0.26	0.29
InSb	0.35	0.37	0.53	0.32	0.29
ZnS	0.55	0.56	0.65	0.62	0.60
CdS	0.60	0.61	0.71	0.69	
HgS	0.55	0.57	0.69	0.79	
ZnSe	0.55	0.56	0.67	0.63	0.59
CdSe	0.59	0.61	0.72	0.70	
HgSe	0.54	0.55	0.70	0.68	
ZnTe	0.54	0.55	0.67	0.61	0.57
CdTe	0.58	0.59	0.72	0.72	0.58
HgTe	0.51	0.53	0.69	0.65	0.53

[a] The ionicity definition of Falter *et al.* is the same as Harrison's polarity and differs from Phillips' ionicity.

$$Q_j^i = \sum_n 2\,|\,u^i(j,n)\,|^2 \tag{8}$$

for $i=$ anion and cation, respectively. Here $u^i(j,n)$ is the wave-function coefficient of the nth eigenstate on the jth bond and the ith (cation or anion) site. The polarity of the jth cluster bond is then given by

$$\alpha_{pj} = 1 - Q_j^c = Q_j^a - 1 \ . \tag{9}$$

To define the cluster polarity, we average the polarity of all inner bonds of the cluster (that is, cluster bonds not adjacent to the cluster edge). Thus we include only bonds for which the coupling to adjacent bonds and antibonds at both bond ends can be treated explicitly within the cluster Hamiltonian.

Polarities calculated from three sizes of atom-centered clusters are shown in Table I. The clusters containing 32, 104, and 176 hybrid orbitals contain 2, 3, and 4 shells of neighbors about the central atom. Polarities were calculated for both cation- and anion-centered clusters, and an average polarity of the two is quoted. For the largest cluster size considered, the fluctuation of the polarities from one inner shell to another varied by an average of less than 2%, and polarities from the cation- and anion-centered clusters agreed within an average of less than 1%.

One further calculation of the polarity has been considered. The linear combination of atomic orbitals (LCAO) Hamiltonian in an *sp* atomic basis[10] (as compared to the hybrid basis in the cluster Hamiltonian above) was constructed, and the Brillouin-zone integration performed using 10 special k points.[11] A universal scaling law for off-diagonal covalent matrix elements has been assumed,[9] corresponding to those used in the BO and cluster calculation. The integrated charge density per cation and anion site was calculated and used to compute the effective polarity as defined by Eq. (1). Values for the effective polarities from the full Brillouin-zone integration of the tight-binding Hamiltonian α_p (BZ) are shown in Table II. Also shown for comparison are ionicities as calculated by Phillips,[3] those deduced from experiment by Falter *et al.*,[6] and polarities from the BO and cluster calculations.

IV. DISCUSSION

Polarities calculated from the BO and EBO models, as shown in Table I, differ substantially (5 to 15%), indicating the importance of the metallization corrections to the BO polarities. The polarities are lowered when metallization corrections are included, because this interaction admixes antibond states (whose charge shifts are opposite to those of the bonding states) into the occupied bond states. The modification is large because the polarity is a property of the wave function, which is affected in first-order perturbation theory by the metallization correction terms.

The cluster polarities show an even further reduction (15 to 35% as compared to the BO polarities), as illustrated in Table I. Differences between the EBO and the cluster polarities arise from several sources. First, in the EBO model, the effects of the bond-antibond interaction are included in first-order perturbation theory; in the cluster calculation, however, the bond-antibond interaction within the cluster is computed explicitly in the diagonalization and, therefore, is treated to all orders of perturbation theory. Second, the bond-bond and antibond-antibond interactions are also explicitly included in the cluster calculation. While the bond-bond interactions broaden the bonding states into bands, bond-bond coupling does not, by itself, affect the bond polarity, as it admixes states of equal polarization. However, it has an indirect effect because it splits the bonding and antibonding states, bringing some closer together and separating others. This indirect effect is automatically included in the cluster calculation. From Table II, one sees that the polarity calculated from the BO model is larger than the polarity (or ionicity) determined from the other methods shown and that the larger polarity results from neglecting the important bond-antibond coupling.

The calculated cluster polarity varies by less than 5% from the smallest to the largest cluster size considered here. The apparent near convergence of the polarity with cluster size for even the smallest (32-hybrid) cluster indicates that the polarity modifications are not long range; they arise from the direct incorporation of adjacent hybrid-hybrid interaction into the cluster diagonalization, rather than through perturbation theory. The relative shifts between the polarities calculated from the simple bond-orbital model and those found in the 176-hybrid cluster follow the trends in $V_1^{c,a}$ for the constituent atoms; larger shifts occur as the cation and anion row numbers in the periodic table increase.

We emphasize that while the treatment of the bond-antibond interaction to all orders within a cluster calculation is important in calculating the corrections to the compound polarity, the corrections to the energy are adequately predicted by second-order perturbation theory within the EBO model. As a typical example, the correction to the BO bonding energy of AlAs is 3.2% when treated in second-order perturbation theory in the EBO, and it is 3.5% when treated within a 176-hybrid cluster model. Thus a cluster calculation adds little to simple second-order perturbation corrections to the BO energies from metallization.

The modified polarities calculated from the clusters are the appropriate polarities to use in calculating many physical properties. These lowered polarities may have significant consequences. For example, the polarity difference between CdTe and HgTe goes from approximately 4% for the BO model to approximately 12% for the large-cluster model. This change will substantially affect predictions about the influence of electron-electron interactions on the excess enthalpy of $Hg_{1-x}Cd_xTe$ alloys, on the polar optical-phonon shifts in alloys, and generally on all properties that are sensitive to lattice polarization. However, a warning should be given. It is inappropriate, in general, to use the modified polarity to define an effective V_3, V_3^{eff} and then reinsert that V_3^{eff} back into BO expressions—for example, to calculate bond energies. We have demonstrated that the bond energy is well approximated by simple bond-orbital values corrected in perturbation theory, i.e., an EBO value.

As shown in Table II, polarities from the cluster calculation and Brillouin-zone integration of the LCAO Hamiltonian yield values in excellent agreement with each other, indicating that the charge density of the inner cluster bonds is nearly converged to the periodic crystal results. The small difference in these calculations reflects cluster size effects as well as the neglect of matrix elements coupling nonbonding hybrids on adjacent sites in the cluster calculation. The numerical polarity values deduced by Falter[6] from experimentally measured transverse effective charges and the macroscopic dielectric constant agree closely with Phillips' ionicity values and the cluster polarity, as seen in Table II. The agreement between the values of Falter and Phillips is curious because they define ionicity differently.

The extension of the BO model to a cluster has been found to yield information on the effects of bond-antibond interaction, the wave functions and, therefore, bond polarities. We have demonstrated that while the bond-orbital-model predictions of bond energies are subject to small metallization corrections by second-order perturbation theory, polarity is not. Polarity is influenced by higher-order corrections. Accurate calculation of polarity within this model requires either taking account of an extended cluster or using a Brillouin-zone integration. The cluster method will have distinct advantages when treating problems like impurities or alloys where lattice periodicity is lost.

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