

## Cohesive energies of cubic III-V semiconductors

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Cohesive energies for twelve cubic III-V semiconductors with zinc-blende structure have been determined using an *ab initio* scheme. Correlation contributions, in particular, have been evaluated using the coupled-cluster approach with single and double excitations. This was done by means of increments obtained for localized bond orbitals and for pairs and triples of such bonds. Combining these results with corresponding Hartree-Fock data, we recover about 92% of the experimental cohesive energies. [S0163-1829(96)06328-X]

### I. INTRODUCTION

*Ab initio* calculations for ground-state properties of solids are most often performed currently within the density-functional theory (DFT) scheme. Typically the exchange and correlation contributions are calculated within the local-density approximation (LDA),<sup>1</sup> or, more recently, within the generalized-gradient approximation (GGA).<sup>2</sup> These methods yield quite good results for cohesive energies and other properties, but do not provide many-body wave functions; thus, a systematic improvement towards the exact result appears to be difficult. Hartree-Fock self-consistent-field (HF-SCF) calculations for solids, on the other hand, while lacking electron correlation as per its definition, have the merit of treating nonlocal exchange exactly and of supplying a good starting point for subsequent correlation calculations. One possibility suggested in the literature is to calculate correlation contributions on top of HF within LDA or GGA,<sup>3</sup> but the potential advantage through the availability of a many-body wave function is absent and the results do not seem to achieve a significant improvement over exchange-correlation (xc) DFT.

For finite systems such as atoms and molecules, accurate quantum-chemical methods such as configuration-interaction (CI) or coupled-cluster (CC) approaches have been developed for the determination of correlation energies. Infinite systems such as solids require the use of size consistent approximations for treating electron correlations such as coupled electron pair approximations (CEPA) or CC approaches. Because of the local character of the correlation hole one can expand the correlation energy in terms of local increments.<sup>4</sup> The idea is thereby to determine the required matrix elements by studying local excitations in clusters that are accessible to a full quantum-chemical treatment. A formal derivation of the method for an infinite periodic system can be found in Refs. 5 or 6 when the CEPA scheme is used. The derivation for the CC method is very similar; see, e.g., Ref. 7. The method of increments has previously been applied to ground-state properties (cohesive energies, lattice constants, and bulk moduli) of elementary semiconductors and has led to very good and reliable results.<sup>5</sup>

In the present paper we extend the method to polar semi-

conductors, especially to the twelve cubic III-V compounds. In order to assess the validity of the calculated correlation energies, we evaluate their differential contributions to the cohesive energies of these materials. For a comparison with experiment, however, we also need reliable SCF ground-state energies. In Sec. II we perform the SCF calculations using the program package CRYSTAL92.<sup>8</sup> In Sec. III we sketch the method of correlation-energy increments and report on computational details. The results are presented and discussed in Sec. IV. Conclusions follow in Sec. V.

### II. HARTREE-FOCK CALCULATIONS

For discussing the influence of electron correlation effects in solids, reliable SCF calculations are prerequisites. For the compounds that we are interested in, SCF calculations with the program package CRYSTAL88 have been performed by Causa, Dovesi, and Roetti.<sup>9</sup> However, small split-valence basis sets have been used in these calculations, and it is not clear how closely the results approach the HF limit.

Here, we want to supplement their results with our own calculations employing the scalar-relativistic energy-consistent pseudopotentials (PP) of Bergner *et al.* together with the corresponding atomic basis sets.<sup>10</sup> The cores replaced by the pseudopotentials are  $X^{3+}$  and  $X^{5+}$  for group 13 and 15, respectively, with two exceptions: 3-valence-electron pseudopotentials for the post-*d* elements gallium and indium have been found to underestimate the closed-shell repulsion of the underlying *d* shell on valence electrons of neighboring atoms;<sup>11,12</sup> we therefore performed the SCF calculations for Ga and In compounds with 13-valence-electron pseudopotentials,<sup>13</sup> explicitly treating the highest occupied *d* shell.

For the solids, we generated  $(4s4p1d)/[3s3p1d]$  Gaussian valence basis sets (Ga: from the atomic basis set<sup>13</sup>  $(8s6p7d)$  the very diffuse exponents are neglected in obtaining  $(7s4p6d)/[3s3p2d]$ ; In: from the atomic basis set<sup>13</sup>  $(6s6p6d)$  the very diffuse exponents are neglected in obtaining  $(4s4p5d)/[3s3p2d]$ ) as follows: starting from the energy-optimized atomic basis sets derived for the PP just mentioned,<sup>10,13</sup> the inner two (Ga: five) functions of *s* and *p* symmetry were contracted using atomic ground-state or-

TABLE I. Crystal-optimized basis sets for the III-V semiconductors. Of the  $s$  and  $p$  functions, only the two outer uncontracted exponents are listed. The inner contracted ones are chosen to be the same as in the original atom-optimized basis sets (Refs. 10,13).

		$s$	$s$	$p$	$p$	$d$
BN	B <sup>a</sup>	0.53	0.23	0.53	0.32	0.80
	N	0.706251	0.216399	0.808564	0.263	0.82
BP	B <sup>a</sup>	0.53	0.32	0.53	0.375	0.80
	P	0.331929	0.120819	0.41	0.16	0.80
BAs	B <sup>a</sup>	0.53	0.17	0.38	0.20	0.34
	As	0.294449	0.111896	0.254421	0.15	0.32
AlP	Al	0.170027	0.12	0.20	0.14	0.29
	P	0.331929	0.120819	0.227759	0.15	0.48
AlAs	Al	0.170027	0.12	0.20	0.15	0.29
	As	0.294449	0.12	0.254421	0.13	0.32
AlSb	Al	0.170027	0.105	0.212	0.143	0.29
	Sb	0.260956	0.100066	0.242631	0.083416	0.29
GaP	Ga	0.294700	0.14	0.396817	0.15	0.502918
	P	0.331929	0.120819	0.227759	0.15	0.48
GaAs	Ga	0.294700	0.15	0.396817	0.138	0.502918
	As	0.294449	0.111896	0.254421	0.107	0.32
GaSb	Ga	0.294700	0.15	0.396817	0.16	0.502918
	Sb	0.260956	0.100066	0.242631	0.083416	0.29
InP	In	0.176720	0.082360	0.200692	0.10	0.263986
	P	0.331929	0.120819	0.227759	0.13	0.48
InAs	In	0.176720	0.082360	0.200692	0.080578	0.263986
	As	0.294449	0.111896	0.254421	0.107	0.32
InSb	In	0.176720	0.082360	0.200692	0.080578	0.263986
	Sb	0.260956	0.100066	0.242631	0.083416	0.29

<sup>a</sup>The very diffuse  $d$  projector of the boron pseudopotential was neglected.

bital coefficients. The outer two  $s$  and  $p$  functions were left uncontracted. The most diffuse exponents of the atom have little effect in the solid, where, due to close packing, their role is taken over by basis functions of the neighboring atoms. Moreover, the use of basis functions that are too diffuse leads to numerical problems in CRYSTAL. Therefore we re-optimized the two outer  $s$  and  $p$  functions as well as an additional  $d$  polarization function for the solid. The crystal-optimized basis sets are listed in Table I.

Using the above basis sets, we determined SCF ground-state energies of the solid with CRYSTAL92.<sup>8</sup> When evaluating cohesive energies, we subtracted corresponding energies of free ground-state atoms obtained with the original atom-optimized sets,<sup>10,13</sup> using the quantum-chemical *ab initio* program MOLPRO94.<sup>14</sup> The results for the SCF cohesive energies at experimentally determined values of lattice constants<sup>15</sup> are listed in Table IV, and comparison is made to experimental cohesive energies corrected by the phonon zero-point energies  $\frac{9}{8}k_B\Theta_D$  (derived from the Debye model<sup>16</sup>) as well as by atomic spin-orbit splittings.<sup>17</sup> It is seen that binding energies, at the HF level, are between 50% and 70% of the experimental values leaving room for significant correlation contributions. The agreement with the previously published SCF cohesive energies<sup>9</sup> is very good for compounds containing B and Al, while small deviations of  $\sim 2\%$  of the cohesive energy are found for Ga and In com-

pounds. The stability of the results with quite different pseudopotentials and basis sets (Causa, Dovesi, and Roetti used PP's by Durand and Barthelat<sup>18</sup> and  $[2s2p1d]$  basis sets<sup>9</sup>) is gratifying to note, and we expect to be not very far from the basis-set limit of the SCF cohesive energy with our  $[3s3p1d]$  valence basis sets.

### III. CORRELATION EFFECTS

Calculating correlation effects using an expansion in terms of local increments<sup>4</sup> is formally similar to treating the hierarchy of  $n$ th-order atomic Bethe-Goldstone equations.<sup>19</sup> Here we only want to sketch the basic ideas and some important formulas (for more details see Refs. 5 and 6). The method relies on localized bond orbitals generated in a SCF reference calculation. One-bond correlation-energy increments  $\epsilon_i$  are obtained by correlating each of the localized orbitals separately while keeping the other ones inactive. In the present work we are using the coupled-cluster approach with single and double substitutions (CCSD). This yields a first approximation of the correlation energy

$$E_{\text{corr}}^{(1)} = \sum_i \epsilon_i, \quad (1)$$

which corresponds to the correlation energy of independent bonds.

In the next step we include the correlations of pairs of bonds. Only the nonadditive part  $\Delta\epsilon_{ij}$  of the two-bond correlation energy  $\epsilon_{ij}$  is needed:

$$\Delta\epsilon_{ij} = \epsilon_{ij} - (\epsilon_i + \epsilon_j). \quad (2)$$

Higher-order increments are defined analogously. For the three-bond increment, for example, one has

$$\Delta\epsilon_{ijk} = \epsilon_{ijk} - (\epsilon_i + \epsilon_j + \epsilon_k) - (\Delta\epsilon_{ij} + \Delta\epsilon_{jk} + \Delta\epsilon_{ik}). \quad (3)$$

The correlation energy of the solid is finally obtained by adding up all the increments with appropriate weight factors:

$$E_{\text{corr}}^{\text{solid}} = \sum_i \epsilon_i + \frac{1}{2} \sum_{\substack{ij \\ i \neq j}} \Delta\epsilon_{ij} + \frac{1}{6} \sum_{\substack{ijk \\ i \neq j \neq k}} \Delta\epsilon_{ijk} + \dots \quad (4)$$

It is obvious that by calculating higher and higher increments the exact correlation energy within CCSD is determined.

The procedure described above is only useful if the incremental expansion is well convergent, i.e., if increments up to, say, three-bond increments are sufficient, and if increments decrease rapidly with increasing distance between localized orbitals. These conditions were shown to be well met in the case of elementary semiconductors,<sup>5</sup> but have to be checked again for the polar compounds. Since (dynamical) correlation is a local effect, the increments should be fairly local entities at least for semiconductors and insulators. We use this property to calculate the correlation-energy increments in finite clusters. We select the clusters as fragments of the zinc-blende structure so that we can calculate all two-bond increments up to third nearest neighbors and all nearest-neighbor three-bond increments. The clusters are shown in Fig. 1. The bond length between the group 13 ( $X$ ) and the group 15 atom ( $Y$ ) is taken to be the same as in the solid at the experimental equilibrium lattice constant. The

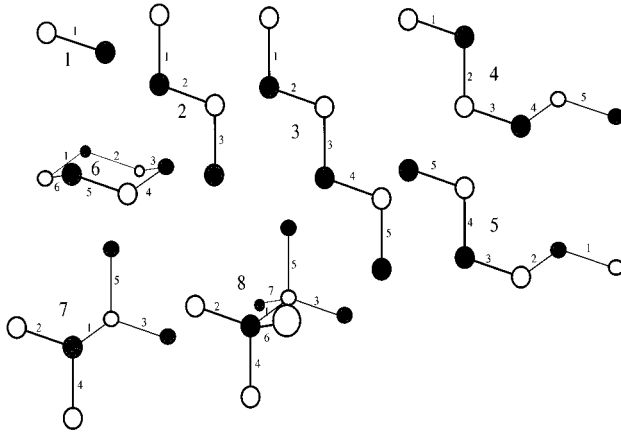


FIG. 1.  $X_n Y_n H_m$  clusters treated at the CCSD level. Big numbers designate clusters, small numbers the bonds in each cluster. H atoms are not drawn.

dangling bonds are saturated with hydrogens. The X-H and Y-H distances, respectively, were optimized in CCSD calculations for  $XYH_6$  clusters, yielding  $d_{BH}=1.187$  Å,  $d_{NH}=1.016$  Å,  $d_{AlH}=1.614$  Å,  $d_{PH}=1.408$  Å,  $d_{GaH}=1.621$  Å, and  $d_{AsH}=1.525$  Å; for In and Sb, we adopted the  $SnH_4$  distance (1.711 Å). Instead of constructing localized bond functions from the Bloch states derived using the CRYSTAL92 program, it is simpler to determine them from a cluster calculation. One merely has to show that, for a given increment, convergence is reached when the size of the cluster is sufficiently large. With this in mind we performed standard SCF calculations for each cluster and localized the bonds according to the Foster-Boys criterion<sup>20</sup> within the occupied valence space in  $C_1$  symmetry. Following the procedure described above we calculated the correlation-energy increments at the CCSD level [using the program package MOLPRO94 (Ref. 14)] successively correlating more and more of the localized X-Y bonds.

For hydrogen we chose Dunning's<sup>21</sup> double- $\zeta$  basis without a polarization function. Two different basis sets are used for the other elements. Basis A is of the same quality as for the SCF calculations of the preceding section:  $(4s4p)/[3s3p]$  (Ref. 10) valence basis sets energy optimized for the atoms, with  $d$  polarization functions optimized in CCSD calculations for  $XYH_6$  clusters (see Table II). Extended basis sets (B) have been generated by uncontracting the  $sp$  functions of basis A and by replacing the single  $d$

TABLE II. Polarization functions used in the basis sets for the CCSD calculations.

	Basis A, 1d		Basis B, 2d1f	
B	0.34	0.34	0.09	0.49
Al	0.29	0.29	0.10	0.35
Ga	0.23	0.23	0.10	0.36
In	0.12	0.12	0.04	0.32
N	0.82	0.82	0.23	1.09
P	0.48	0.48	0.16	0.56
As	0.32	0.32	0.12	0.47
Sb	0.19	0.19	0.07	0.40

TABLE III. Correlation-energy increments for GaAs (in a.u.), determined at the CCSD level using basis set A. For the numbering of the clusters and bonds involved, see Fig. 1.

	Source cluster/ bond orbitals	Increment	Weight factor for the solid
$\epsilon_i$	1/1	-0.019935	
	2/1	-0.018800	
	7/1	-0.018780	
	8/1	-0.018612	4
$\Delta\epsilon_{ij}$	2/1,2	-0.011748	
	7/1,2	-0.011445	
	8/1,2	-0.010962	6
	2/1,3	-0.003155	
	7/1,3	-0.003943	
	8/1,3	-0.004849	6
	8/2,3	-0.000843	12
	8/2,5	-0.000568	24
	3/1,4	-0.000205	6
	3/2,5	-0.000073	6
	4/1,4	-0.000158	24
	5/2,5	-0.000048	24
$\Delta\epsilon_{ijk}$	4/2,5	-0.000085	12
	5/1,4	-0.000109	12
	6/1,4	-0.000109	12
	8/1,2,4	0.001379	4
	8/1,3,5	0.000254	4
	8/1,2,3	0.000022	12
	8/1,2,5	0.000124	24

function by a  $2d1f$  polarization set. The latter was obtained by adding a second more diffuse  $d$  function to the one of basis A and by optimizing the  $f$  exponent in CCSD calculations for the  $XYH_6$  clusters (see Table II).

We have checked the convergence of the incremental expansion for all polar substances and will discuss it here for GaAs. As can be seen from Table III, the increments decrease quite rapidly with increasing distance of the bonds. The nearest-neighbor two-bond increments contribute 51% of the correlation energy of GaAs, all next-nearest neighbors 13%, and the third-nearest ones only 6%. After these increments we truncate the expansion because the fourth-nearest neighbors' contribution is only 0.5%. Note that the integrated truncation error decreases with  $r^{-3}$ , because the interaction is van der Waals-like  $r^{-6}$  and the number of pairs of bonds grows like  $r^2$ .

The convergence with respect to the number of bonds correlated simultaneously in the incremental expansion is also quite satisfactory. For GaAs again, the one-bond increment contributes 38% of the correlation energy, the two-bond increments are very important (70%) but yield a correlation energy too large in magnitude, while the three-bond increments reduce it by 8%. An estimate of the nearest-neighbor four-bond increments and next-nearest-neighbor three-bond increments is  $\sim 0.5\%$ . Thus, the overall error due to truncations in the incremental expansion is less than 1% of

TABLE IV. Cohesive energies per unit cell (in a.u.), at different theoretical levels (cf. text). Deviations from experimental values (in percent) are given in parentheses. For comparison, literature data from DFT calculations are also reported.

	HF		HF+corr Basis A		HF+corr Basis B		LDA (Ref. 3)		GGA (Ref. 3)		Expt.
BN	0.335	(67%)	0.451	(90%)	0.455	(91%)	0.609	(122%)	0.505	(101%)	0.500
BP	0.230	(60%)	0.325	(85%)	0.344	(90%)					0.382
BAs	0.202		0.303		0.315						
AIP	0.198	(64%)	0.269	(87%)	0.292	(94%)	0.371	(120%)	0.308	(100%)	0.309
AlAs	0.173	(59%)	0.246	(84%)	0.264	(90%)					0.294
AlSb	0.146	(60%)	0.223	(92%)	0.232	(95%)					0.243
GaP	0.147	(53%)	0.221	(81%)	0.246	(91%)					0.271
GaAs	0.130	(53%)	0.207	(84%)	0.228	(93%)	0.285	(116%)	0.229	(93%)	0.246
GaSb	0.109	(49%)	0.183	(82%)	0.198	(89%)					0.223
InP	0.142	(57%)	0.205	(82%)	0.234	(94%)					0.250
InAs	0.129	(54%)	0.194	(81%)	0.219	(92%)					0.239
InSb	0.117	(55%)	0.182	(85%)	0.201	(94%)					0.213

the correlation energy, the same accuracy as was reached for the elementary semiconductors.<sup>5</sup>

The next point we have to check is the transferability of the increments from clusters to the solid. We test the sensitivity of the chemical surroundings by determining the increments in different clusters. The change from GaAsH<sub>6</sub>, where the Ga-As bond is surrounded only by hydrogens, to Ga<sub>4</sub>As<sub>4</sub>H<sub>18</sub>, where the inner Ga-As bond has the same neighbors as in the solid, is 0.005 a.u. for the one-bond increment. The differences in the nearest-neighbor two-bond increments are  $-0.005$  a.u., so that the main errors due to lack of transferability cancel. The tendency for individual (one- and two-bond) errors to be of different sign is seen in all III-V compounds. We estimate an upper limit for the transferability error to 1% of the correlation energy.

Thus, we end up with a total error of 2% for approximations inherent in our use of the incremental expansion of the correlation energy. Not included are shortcomings of one- and many-particle basis sets in the determination of individual increments; the largest part of this remaining error is probably due to limitations of the one-particle basis set and will be discussed in Sec. IV.

#### IV. RESULTS AND DISCUSSION

Applying the method of increments as described in Sec. III we determined correlation contributions to cohesive energies for all twelve cubic III-V semiconductors. The increments were always taken from the largest possible cluster (cf. Table III and Fig. 1) and multiplied by the weight factors appropriate for the zinc-blende structure. The correlation contributions to the cohesive energies were obtained as  $E_{\text{coh}}^{\text{corr}} = E_{\text{solid}}^{\text{corr}} - \sum_i E_{\text{atom},i}^{\text{corr}}$  per unit cell. The results for the two different basis sets are shown in Table IV. For basis set A we obtain an average of 86% of the experimental cohesive energies, which amounts to  $\approx 67\%$  of the ‘‘experimental’’ correlation contributions to the cohesive energies (defined here as the differences between the experimental cohesive energies and the corresponding SCF values). The larger basis set

B yields a substantial improvement,  $\approx 82\%$  of the correlation contributions to the cohesive energies. Overall we obtain with basis B an average of 92% of the cohesive energy with only small fluctuations for the different materials. In earlier calculations for the elementary semiconductors,<sup>5</sup> we obtained  $\approx 94\%$  of the cohesive energy. The deviation may be due, in part, to the different correlation treatment. For the elementary semiconductors we used a coupled-electron-pair approximation (CEPA-0). It is well known that CEPA-0 yields larger correlation contributions than the CCSD approach; in test calculations we found a deviation of  $\approx 1\%$ . If the basis set, especially the polarization set, is enlarged even more, e.g., to  $3d2f1g$ , a further increase of the correlation effects can be expected. In test calculations for GaAs, where the one-bond increment and the nearest-neighbor two-bond increments were determined with this extended basis set, we obtained an increase of 10% of the correlation contribution to the cohesive energy.

For comparison, we have also listed in Table IV results from the literature, which have been obtained with other methods. LDA (Ref. 3) overestimates the cohesive energies by  $\approx 20\%$ , GGA is at the same level of accuracy or slightly better than our results. In contrast to these methods, our approach lends itself to systematic improvement; moreover, a detailed insight into the nature of the correlation effects becomes possible.

#### V. CONCLUSIONS

We have determined cohesive energies of twelve cubic III-V semiconductors, both at the SCF and the CCSD levels. The SCF results have been obtained with the CRYSTAL92 code using relativistic energy-consistent pseudopotentials and  $[3s3p1d]$  Gaussian valence basis sets. Electron correlations are described at the CCSD level with the method of local increments, using the same pseudopotentials in cluster calculations with the *ab-initio* program MOLPRO94. Increasing cluster and basis-set size, this approach allows for a systematic improvement of accuracy towards the fully corre-

lated solid-state limit. The results show that the method works well for polar III-V semiconductors with zinc-blende structure: the calculated cohesive energies are  $92 \pm 3\%$  of the experimental values using an uncontracted ( $4s4p2d1f$ ) valence basis set. Work is underway in our laboratory to apply the method to other ground-state properties of the III-V compounds.

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