

RECONSTRUCTION OF THE (110) SURFACE OF III–V SEMICONDUCTOR COMPOUNDS *

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We have used ab initio quantum chemical methods to determine the structure of the clean (110) surface of the nine III–V compounds with III = B, Al or Ga, and V = N, P or As. The theoretical results for small clusters give geometries in good agreement with the experimental geometry for GaAs (the only case for which an experimental structure is available), supporting the use of such clusters in studying the reconstruction of the other systems. We find in all cases that the reconstruction of these (110) surfaces is determined by local valence hybridization forces on the surface atoms. To show the effects of these valence forces we have also carried out extensive calculations on the trihydrides of the above-mentioned elements, for which we have calculated bond distances, bond angles, and the variation of the total energy with bond angle, leading to inversion barriers for the trihydrides of column V elements.

1. Introduction

The reconstruction of semiconductor surfaces is of interest due to the importance of interfaces involving these semiconductors in practical applications. A knowledge of the microscopic structure of these surfaces is necessary for the determination of their electronic properties and for the study of the initial stages of chemisorption of various substances on these surfaces, even though the surface is in general not expected to have the same reconstruction before and after the chemisorption. In view of the importance of semiconductor surfaces it is not surprising that a great deal of work has been devoted to the study of these surfaces during recent years (see for instance refs. [1–4]).

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Of the various semiconductor surfaces, only the reconstruction of the (110) surface of GaAs, which has been studied extensively both experimentally [5–9] and theoretically [10,11], seems to be well understood at present. Therefore, we have decided to study the systematics of the reconstruction for compounds such as GaAs and to this end we have investigated the reconstruction of the (110) surface of various III–V compounds, where the column III element is either B, Al or Ga and the column V element either N, P or As. In order to establish trends in the reconstructions of the various compounds, we consider the zinc blende structure for all nine cases. Parts of this work have been published before [11].

To study the reconstruction we have applied the methods of quantum chemistry to appropriately chosen small clusters of atoms, which model the surface. From our results for GaAs(110) (see section 4), we conclude that such cluster models provide accurate reconstruction geometries. In section 2 we give a brief description of the theoretical methods, together with the strategy for obtaining adequate models of the surface.

We will show that the reconstruction of the various III–V surfaces can be understood on the basis of local valence considerations [8,12], as described in section 3. Indeed, in section 4 we shall find that the reconstruction of the (110) surface of the III–V compound XY ($X = \text{B, Al or Ga}$, $Y = \text{N, P or As}$) can be predicted fairly accurately solely from a knowledge of the behavior of the trihydrides. In section 5 the results for the reconstruction of the various compounds will be given and discussed. Section 6 contains a summary.

2. Theoretical methods

The methods used in these calculations are adaptations of well-established methods of quantum chemistry, which enable one to accurately calculate *ab initio* wavefunctions of molecules. These methods explicitly consider all electrons of the system and involve an exact evaluation of all one- and two-electron integrals required for the calculation of energies. Since these methods lead directly to total energies, they are especially well suited to determine accurate geometries of molecular systems. The application of these methods to semiconductors [13] and a comparison with other approaches [14] is available in the literature. Here we only comment on the main features of our approach.

At present the methods mentioned above are not capable of treating infinite systems. Therefore we start by creating a molecular cluster to mimic the surface chemical environment. In fig. 1 we show the (110) surface of GaAs. To obtain a model of this surface, we imagine that a portion of the surface is sliced out of the solid, leaving only surface atoms. Atoms at the edge of this cluster, which would have been connected to further atoms in the extended system, are connected to hydrogen atoms in the molecular cluster. The hydrogens are placed such that the bond angles of the extended system are preserved, but the distance of the hydrogen

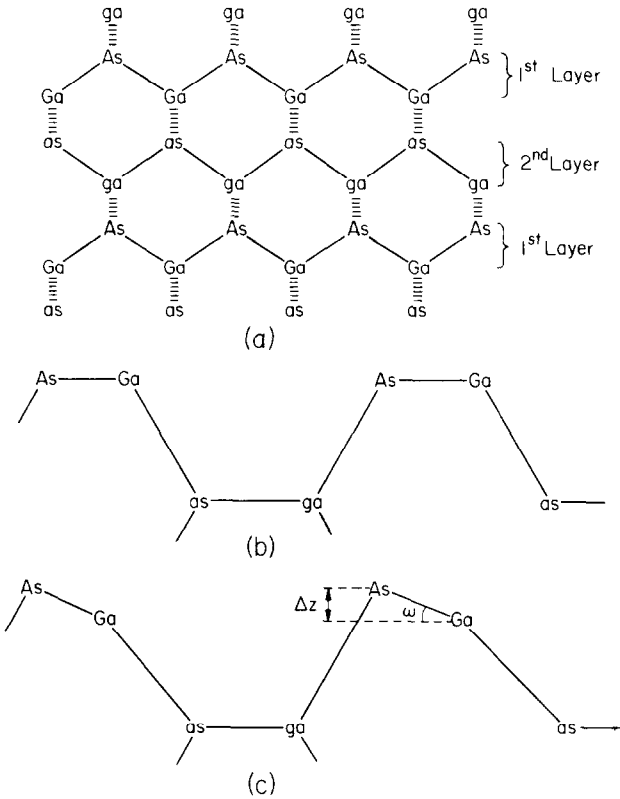


Fig. 1. The (110) surface of GaAs. Lower case symbols indicate subsurface atoms. (a) Top view; (b) side view of the projection in the $(1\bar{1}0)$ plane, unreconstructed; (c) side view of the projection in the $(1\bar{1}0)$ plane, after reconstruction. ω is the reconstruction angle, Δz is the surface strain.

atoms to their nearest neighbour surface atom is made to correspond to the same distance in the respective trihydrides. This procedure insures proper hybridization of the cluster atoms and prevents artificial dangling bonds at the edge of the cluster from interfering with real dangling bonds on the surface. Fig. 2 shows some of the models obtained with the above prescription for GaAs.

After approximating the surface by a finite cluster, we can apply the powerful techniques of molecular quantum mechanics to this cluster, to obtain a microscopic and quantitatively accurate model for the surface [15,16]. With these methods we can calculate the total energy of the cluster as a function of geometry and electronic configuration and so determine variationally the optimum geometry and electronic configuration.

To make this approach feasible for clusters containing heavy atoms, we have replaced the inner core electrons of these atoms with ab initio effective potentials

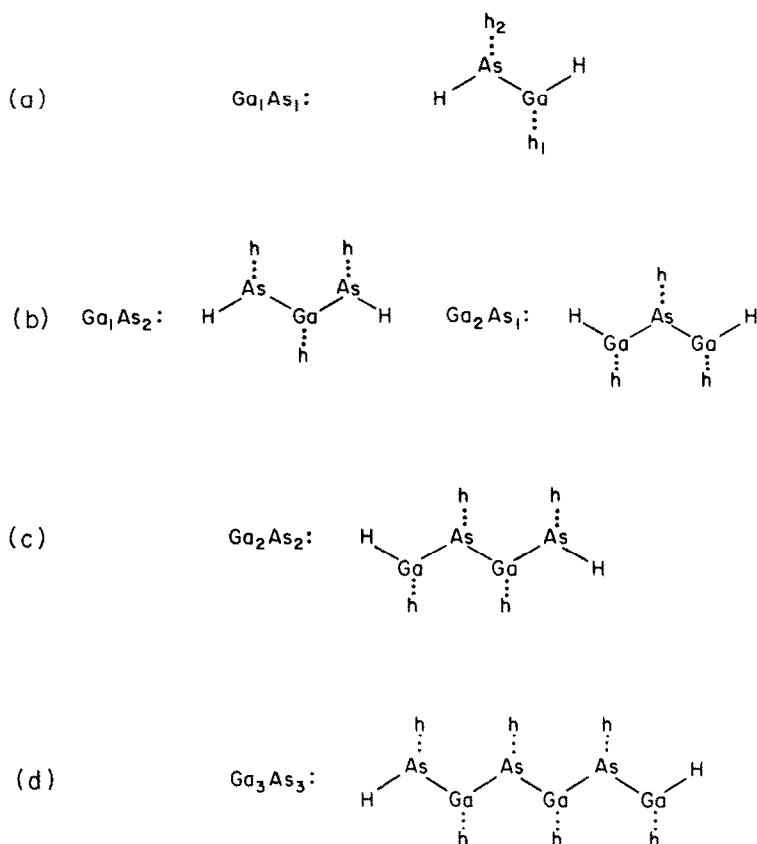


Fig. 2. Molecular models for the (110) surface of GaAs. Lower case letters indicate subsurface atoms.

[17]. These potentials are obtained in such a way that the atomic valence orbitals have the same energy and shape as the *ab initio* orbitals, and such that the Coulomb and exchange interactions as well as the long range behavior are the same as for the *ab initio* orbitals. This approach allows us to retain *ab initio* accuracy while considering large systems.

The basis sets used in these calculations are double zeta or split valence (that is, two functions for each atomic valence orbital). The calculations on small models, containing only one column III and one column V surface atom, were performed with and without the use of d-polarization functions. It was found that in general the geometries were not sensitive to the use of these polarizations functions (see section 4), so that they were omitted in the calculations on larger clusters. Only when the column V atom is nitrogen do polarization functions become important. For GaAs it was found that electron correlation had little influence on the geom-

etry. Hence the calculations reported here are for closed shell Hartree–Fock wavefunctions.

3. Local valence picture

In this section we discuss the local valence forces that drive the reconstruction [8,12] (earlier discussions along such lines have been given in refs. [5] and [12]). This may best be done by considering the behavior of the individual column III and column V atoms on the (110) surface. In order to establish trends in the results for the different compounds, we assume that all III–V compounds considered in this paper have the zincblende structure, with nearest neighbour distances as given in table 1. For convenience we discuss below the behavior of the individual surface atoms for GaAs, but all the ideas are applicable to the other compounds as well.

The (110) surface of GaAs is shown in fig. 1. It consists of zig-zag chains of atoms, alternating Ga and As. Each surface atom has three ligands (fig. 1a), two of which are in the surface and one in the subsurface layer. Even for the unreconstructed surface (tetrahedral bond angles), generalized valence bond calculations for GaAs show that the two dangling bonds broken at the surface coalesce into one lone pair of electrons localized on the As center [23]. Thus the surface atoms closely resemble the normal trivalent atoms of each species: the surface Ga atom forms three covalent bonds to its nearest neighbours and thus no electrons in the fourth valence orbital; the surface As atom also forms three covalent bonds to its nearest neighbours and in addition has a (4s) lone pair. Therefore the chemical environment experienced by these surface atoms is similar to the environment experienced by these atoms in their respective trihydrides and the structure of the reconstructed surface should be closely related to that of the trihydrides.

Table 1
Nearest neighbour distances, in Å, for the III–V zincblende compounds studied in this work

III	V		
	N	P	As
B	1.565 ^{a)}	1.965 ^{b)}	2.068 ^{b)}
Al	1.964 ^{f)}	2.360 ^{c)}	2.451 ^{d)}
Ga	1.957 ^{f)}	2.360 ^{e)}	2.448 ^{e)}

a) Ref. [18].

b) Ref. [19].

c) Ref. [20].

d) Ref. [21].

e) Ref. [22].

f) Obtained by extrapolation.

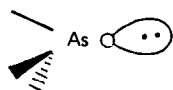


Fig. 3.

Consider therefore the trihydrides. The column III elements have a valence electronic configuration $(ns)^2(np)^1$. The trihydrides in this case are planar, involving sp^2 hybridization, with a bond angle of 120° . One expects therefore that the surface will reconstruct in such a way that the column III surface atom moves toward a planar geometry (average bond angle approximately 120°). The column V elements on the other hand have a valence configuration $(ns)^2(np)^3$. In this case the hydrogens will bind to the singly occupied p-orbitals, leading to pyramidal trihydrides with bond angles close to 90° . Because the different bond pairs must be orthogonal [24], the bond angles increase slightly, forcing the $(ns)^2$ lone pair to move slightly away from the ligands, as shown schematically for AsH_3 in fig. 3. Thus during reconstruction the column V element should move in such a way as to make the average bond angle around it smaller than the tetrahedral value of 109.47° . Results obtained for the various trihydrides are given in table 2. We see that the bond angle is 120° for trihydrides of column III elements, whereas for PH_3 and AsH_3 the bond angle is indeed close to 90° . For NH_3 the bond angle is sub-

Table 2

Optimum bond distance d and bond angle α , for the trihydrides of the column III and column V elements considered in this work; E_m is the calculated total energy at the optimum geometry ^{a)}

Trihydride	d -functions	Theory			Experiment ^{b)}	
		E_m (hartrees)	d (Å)	α	d (Å)	α
BH_3	No	-26.3749	1.200	120°		
BH_3	Yes	-26.3846	1.198	120°		
AlH_3	No	-243.5894	1.582	120°		
AlH_3	Yes	-243.6100	1.591	120°		
GaH_3	No	-3.6688	1.574	120°		
GaH_3	Yes	-3.6817	1.580	120°		
NH_3	No	-56.1688	1.018	113.8°		
NH_3	Yes	-56.1872	1.013	106.5°	1.012	106.7°
PH_3	No	-342.3996	1.412	97.0°		
PH_3	Yes	-342.4406	1.431	94.8°	1.420	93.3°
AsH_3	No	-7.6848	1.517	95.2°		
AsH_3	Yes	-7.7128	1.521	94.3°	1.511	92.1°

^{a)} The core energy of Ga or As is not included in the total energy of GaH_3 or AsH_3 .

^{b)} Ref. [25].

stantially greater than 90° (106.5°), which is due to the shorter bond distance, resulting in a greater effect of orthogonality of bond pairs [24].

Combining the two results quoted above, one expects the reconstruction to be such that (see fig. 1c) the column III surface atom moves toward the subsurface, while the column V surface atom moves away from the unreconstructed surface. In this way the column III element moves toward a planar geometry (average bond angle close to 120°) and the column V surface atom moves toward a pyramidal geometry (average bond angle 94.3° , 94.8° and 106.5° for P, As and N, respectively). The surface strain, Δz , is defined as the z-projection (perpendicular to the unreconstructed surface) of the total displacement of the surface As relative to the surface Ga (see fig. 1c). The reconstruction angle ω corresponds to the angle between the unreconstructed (110) plane and the line connecting a surface Ga to a surface As, projected in the $(\bar{1}\bar{1}0)$ plane perpendicular to the surface plane (see fig. 1c).

4. The trihydrides

Since the trihydrides of the various elements considered in this study play an important role in describing and verifying the effects of the local valence forces, as described in the previous section, we give in this section the results of our calculations for these trihydrides.

In these calculations we have optimized the bond distance and bond angle assuming C_{3v} symmetry. This was done with closed shell Hartree–Fock wavefunctions, and the calculations were carried out with and without the use of d-polarization functions for the column III or column V element. The optimum geometries obtained in this way are given in table 2, together with the experimental results where those were available. We see that we do indeed obtain a bond angle of 120° for the trihydrides of the column III element and a bond angle close to 90° for PH_3 and AsH_3 , whereas the bond angle for NH_3 (106.5°) is considerably larger, as discussed above. Furthermore, in all cases where a comparison with experiment is possible, the agreement is good. Finally we notice that only in the case of NH_3 does the use of d-polarization functions have a large effect on the optimum geometry.

At the optimum bond distances we have determined the variation of the total energy as a function of the bond angle for the various trihydrides. The results of these calculations are shown in figs. 4–7, and will be used in the next section. Figs. 6 and 7 display the inversion barrier for the trihydrides of the column V elements. For the cases where d-polarization functions are used, these inversion barriers are 0.34 eV, 1.83 eV and 2.01 eV for NH_3 , PH_3 and AsH_3 , respectively.

5. Results and discussion

We have considered the following models for the (110) surface of the various III–V compounds: (i) the X_1Y_1 -model, consisting of one column III surface atom

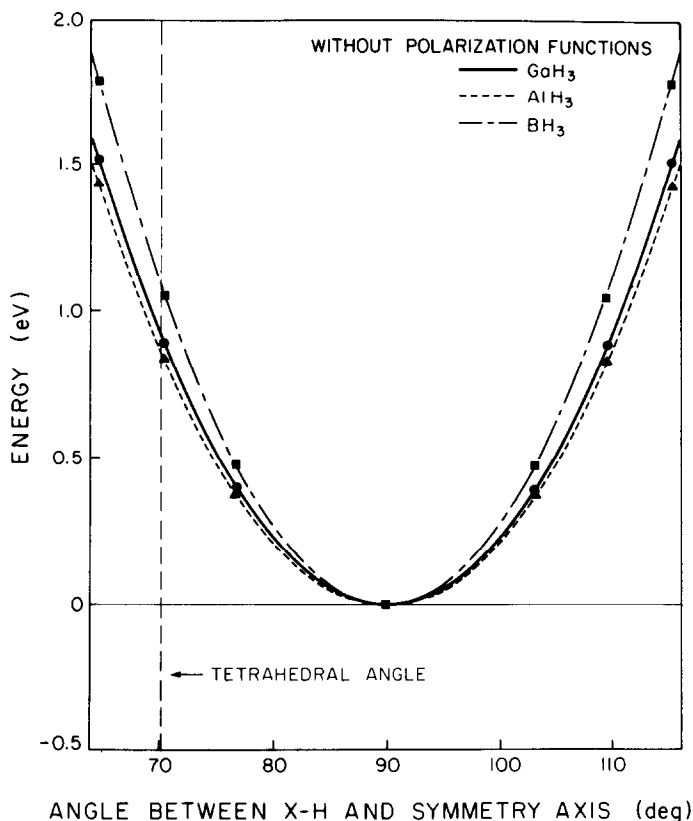


Fig. 4. Variation of the total energy as a function of bond angle for the trihydrides XH_3 of the column III elements B, Al and Ga. Without d-polarization functions.

X and one column V surface atom Y (fig. 2a); and (ii) the X_2Y_2 -model, consisting of two column III and two column V surface atoms (fig. 2c). In the case of GaAs we also considered the Ga_3As_3 -model (fig. 2d). The surface reconstruction was obtained by carrying out the following geometric variations (fig. 1c): the position of the (virtual) subsurface atoms was kept fixed and the surface atoms were allowed to move in the $(1\bar{1}0)$ plane through their unrelaxed positions in such a way that the distance to the subsurface nearest neighbour remained constant. For each model we calculated the following quantities: (i) the surface strain Δ , (ii) the reconstruction angle ω , (iii) the average bond angles α_x and α_y around the surface cation and anion respectively, (iv) the energy lowering ΔE per pair of surface atoms upon reconstruction, and (v) the energy lowering ΔE^* per pair of surface atoms as obtained from their respective trihydrides (see below). The results of our calculations are summarized in tables 3–5.

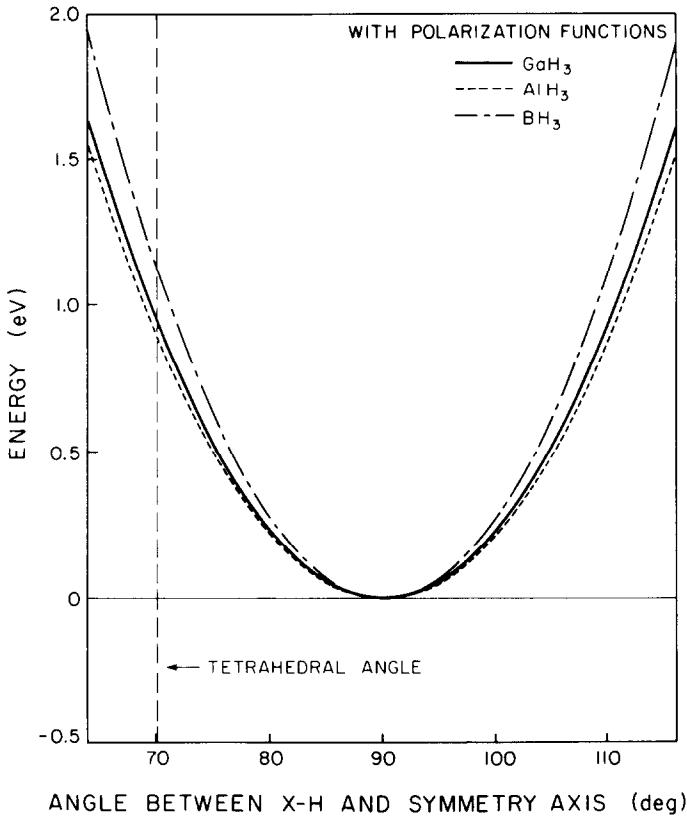


Fig. 5. Variation of the total energy as a function of bond angle for the trihydrides XH_3 of the column III elements B, Al and Ga. With d-polarization functions.

In table 3 we give Δ , ω , α_x and α_y for the various models considered for GaAs, as well as experimental results. We see that the results for each of these models ($\Delta = 0.66$ to 0.67 \AA) agree well with the experimental results for the top layer relaxation ($0.65 < \Delta < 0.70 \text{ \AA}$), obtained from LEED data. Our top layer relaxations agree also with those obtained by Chadi [26], using a semi-empirical total energy minimization. Both the LEED data and Chadi's approach lead to further changes in the geometry which we have not considered. These additional changes consist of a contraction of the top layer toward the subsurface and/or subsurface relaxations. However, in all cases the top layer relaxation is determined first, after which further changes in the geometry are considered without changing the top layer relaxation. So our results are indeed in good agreement with the experimental results as well as with the results of Chadi. We believe that the top layer relaxation is the dominant effect and other geometry changes are of secondary importance.

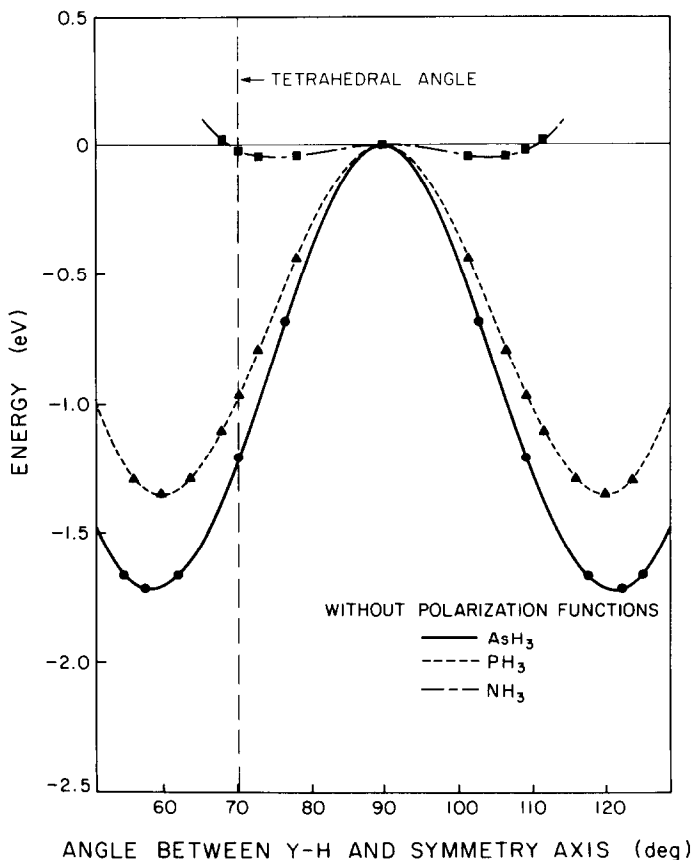


Fig. 6. Variation of the total energy as a function of bond angle for the trihydrides YH_3 of the column V elements N, P and As. Without d-polarization functions.

Furthermore, the subsurface relaxations obtained from the LEED data must be viewed with caution [6]. This is because the second layer atoms are allowed to move only in the direction perpendicular to the unreconstructed surface, which leads to changes in the bond length between second and third layer atoms. For instance, the results of Meyer et al. [9] lead to bond length changes of 0.09%, 0.24%, -4.05%, 0.12%, 1.98% and -2.02% for $\text{Ga}_1\text{-As}_1$, $\text{Ga}_1\text{-As}_2$, $\text{As}_1\text{-Ga}_2$, $\text{Ga}_2\text{-As}_2$, $\text{Ga}_2\text{-As}_3$ and $\text{As}_2\text{-Ga}_3$, respectively. Here the subscript indicates the layer for the various atoms. We see that the changes in bond length between second and third layer atoms are greater than those among second layer atoms and of the same order of magnitude as those between first and second layer atoms.

The good agreement found above indicates that these small models do indeed represent the surface adequately, as is also evident from the fact that the results

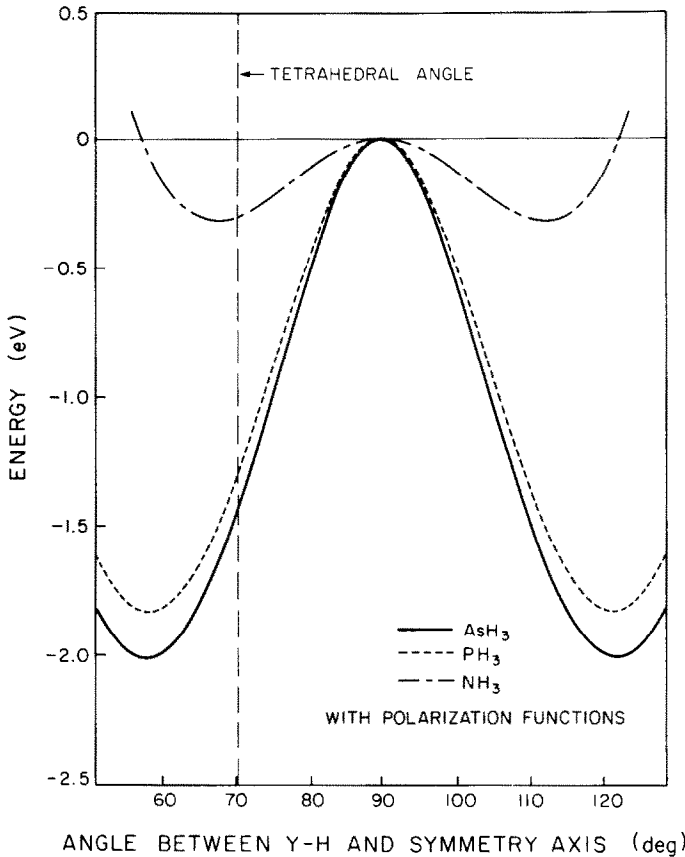


Fig. 7. Variation of the total energy as a function of bond angle for the trihydrides YH_3 of the column V elements N, P and As. With d-polarization functions.

converge rapidly with cluster size ($\Delta z = 0.660 \text{ \AA}$ for the Ga_1As_1 -model and 0.669 \AA for the Ga_3As_3 -model). This demonstrates that the surface reconstruction is determined mainly by the local properties of the surface, as is also clear from the fact that the angles α_x and α_y are very close to the values we expect from the consideration of the local valence forces (119.4° versus 120° for α_x and 94.9° versus 94.3° for α_y). Finally, it is clear from the results given in table 3 that in the case of GaAs the use of d-polarization functions has little effect on the geometry.

Having established that in the case of GaAs the small models used in our calculations do indeed represent the surface adequately, we proceed to apply the same methods to small models representative of the other III-V compounds. In these cases no experimental data are available, but on the basis of the above results for GaAs we expect the calculations for the other compounds to be accurate as well.

Table 3

Results for the reconstruction of GaAs(110); Δ is the surface strain, ω is the reconstruction angle, α_x is the average angle around the surface Ga, α_y is the average angle around the surface As

A. Theoretical results					
Model	d-functions	Δ (Å)	ω	α_x	α_y
Ga ₁ As ₁	No	0.660	26.8°	119.3°	95.1°
	Yes	0.674	27.5°	119.4°	94.9°
Ga ₂ As ₂	No	0.665	27.2°	119.4°	95.1°
	Yes	0.679	27.8°	119.5°	94.9°
Ga ₃ As ₃	No	0.669	27.3°	119.4°	95.1°

B. Experimental results			
Reference	Year	Δ (Å)	ω
[5]	1976	$0.64 \leq \Delta \leq 0.81$	$27^\circ \leq \omega \leq 34.8^\circ$
[6]	1978	0.650	27.21°
[7]	1978	0.700	26.35°
[8]	1978	0.650	28.51°
[9]	1979	0.650	27.34°

For each case where several cluster sizes have been considered, we find a rapid convergence of the results with cluster size, as shown in table 4. Similarly we have investigated the effect of the use of d-polarization functions for the X₁Y₁-model of each compound, also shown in table 4; only in the case where N is the anion do d-polarization functions have a large effect on the geometry. Consequently for larger models we have used d-polarization functions only for cases involving N.

In table 5 we show the most accurate results obtained for the various models. We see that the arguments presented in section 3 are indeed borne out by the calculations: the average bond angle α_x around the column III element is in all cases close to the value of 120° expected from a consideration of the trihydrides, whereas the average bond angles α_y around N, P or As are always close to the trihydride values of 106.5°, 94.8° and 94.3°, respectively. Furthermore the results in table 5 show certain trends. Consider for instance the arsenides. In this group the results for AlAs and GaAs are very similar, but the results change for BAs. This is probably due to the smaller size of the B atom and the shorter bond distance in BAs compared to AlAs and GaAs. Similarly, for the phosphides, the results for AlP and GaP are very similar, but BP is different. In addition, as a group the phosphides are slightly different from the arsenides. This indicates that the reconstruction is dominated by the anion, although the cation also has an effect. This conclusion is confirmed by the results for the nitrides, which as a group differ from the arsenides

Table 4

Effects of cluster size and d-polarization functions on the theoretical results for the reconstruction; E_{\dagger} is the total energy of the cluster at the optimum geometry ^{a)}

Model	d-functions	Δ (Å)	ω	α_x	α_y	E_{\dagger} (hartrees)
B ₁ N ₁	No	0.222	17.8°	117.9°	105.6°	-81.4029
	Yes	0.276	21.7°	118.7°	103.5°	-81.4407
B ₁ P ₁	No	0.495	26.0°	119.2°	96.8°	-367.6309
	Yes	0.517	27.1°	119.4°	96.2°	-367.6792
B ₁ As ₁	No	0.542	26.8°	119.3°	96.1°	-32.9157
	Yes	0.554	27.4°	119.4°	95.8°	-32.9507
B ₂ As ₂	No	0.541	27.0°	119.4°	96.3°	-64.6898
Al ₁ N ₁	No	0.207	14.2°	117.3°	108.3°	-298.6267
	Yes	0.295	19.3°	118.3°	105.5°	-298.6690
Al ₂ N ₂	Yes	0.303	20.8°	118.7°	105.8°	-596.2259
Al ₁ P ₁	No	0.595	25.4°	119.1°	96.2°	-584.8594
	Yes	0.627	26.9°	119.3°	95.6°	-584.9191
Al ₂ P ₂	No	0.594	25.7°	119.1°	96.5°	-1168.6005
Al ₁ As ₁	No	0.662	26.7°	119.3°	94.9°	-250.1461
	Yes	0.673	27.4°	119.4°	94.9°	-250.1947
Al ₂ As ₂	No	0.667	27.2°	119.4°	95.0°	-499.1758
Ga ₁ N ₁	No	0.231	14.9°	117.2°	106.9°	-58.6899
	Yes	0.315	19.4°	118.1°	104.0°	-58.7244
Ga ₁ P ₁	No	0.601	25.6°	119.1°	96.2°	-344.9402
	Yes	0.632	27.0°	119.4°	95.5°	-344.9890
Ga ₂ P ₂	No	0.606	26.1°	119.2°	96.2°	-688.7608
Ga ₁ As ₁	No	0.660	26.8°	119.3°	95.1°	-10.2281
	Yes	0.674	27.5°	119.4°	94.9°	-10.2661
Ga ₂ As ₂	No	0.665	27.2°	119.4°	95.1°	-19.3395
	Yes	0.679	27.8°	119.5°	94.9°	-19.4138
Ga ₃ As ₃	No	0.669	27.3°	119.4°	95.1°	-28.4510

a) The core energy of Ga or As is not included in the total energy of clusters containing these atoms.

and the phosphides, but with similar trends apparent within the group.

In order to further test the ideas presented in section 3, we have also estimated the energy lowering per pair of surface atoms using the data from the trihydrides. To illustrate how this was done we consider again GaAs. From table 5 we find that on the reconstructed surface the average bond angle around the Ga atom is 119.5°, whereas for the unreconstructed surface it is 109.5°. From fig. 5 we find that this change in geometry corresponds to an energy difference of 0.86 eV for GaH₃. Similarly, on the reconstructed surface the average angle around the As atom is 94.9° whereas on the unreconstructed surface the angle is 109.5°. From fig. 7 we obtain an energy lowering of 0.58 eV for AsH₃. The sum of these two energy lowerings, $\Delta E^* = 1.44$ eV, gives an estimate for the energy lowering in good agreement

Table 5

Summary for the reconstruction of the various III–V compounds; in each case we have used the largest cluster common to the various cations for the same anion, ΔE is the energy change upon reconstruction ($\Delta E = 0$ for tetrahedral), ΔE^* is the energy change predicted by the use of the trihydride potential curves

Compound	Δ (Å)	ω	α_x	α_y	ΔE (eV)	ΔE^* (eV)
GaAs	0.679	27.8°	119.5°	94.9°	1.32	1.44
AlAs	0.673	27.4°	119.4°	94.9°	1.19	1.39
BAAs	0.554	27.4°	119.4°	95.8°	1.50	1.59
GaP	0.632	27.0°	119.4°	95.5°	1.21	1.39
AlP	0.627	26.9°	119.3°	95.6°	1.14	1.35
BP	0.517	27.1°	119.4°	96.2°	1.47	1.55
GaN	0.315	19.4°	118.1°	104.0°	0.77	0.76
AlN	0.303	20.8°	118.7°	105.8°	1.11	0.77
BN	0.276	21.7°	118.7°	103.5°	1.11	0.95

with the calculated value, $\Delta E = 1.37$ eV. From table 5 we see that ΔE^* is generally about 10% greater than ΔE (exceptions are AlN and BN). The correspondence between ΔE and ΔE^* confirms again that the reconstruction is determined by local valence forces as described in section 3.

Another point of interest is the fact that the results for AlP, AlAs, GaP and GaAs are all very similar, so that AlP could have been used as a model for calculations on GaAs. For all-electron *ab initio* calculations this leads to a great reduction in the cost of the calculations.

6. Summary

We have shown that the (110) surface of III–V semiconductors may be accurately modelled by appropriate small clusters. Application of quantum chemical techniques then leads to an accurate microscopic description of these surfaces.

We find that the reconstruction of the (110) surface of III–V semiconductors can be understood on the basis of local valence considerations: the cation assumes a more or less planar geometry on the reconstructed surface, while the anion assumes a more or less pyramidal geometry. The details of the reconstruction seem to be dominated by the anion.

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