Electronic structure of \((\text{GaAs})_2\)

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Complete active space self-consistent field (CASSCF) followed by multireference singles + doubles CI (MRSDCI) calculations are carried out on \((\text{GaAs})_2\). Several isomers (rhombus, linear, trapezium) are considered as probable structures. The ground state of \((\text{GaAs})_2\) is found to be of \(\text{A}_1\) symmetry with an equilibrium structure of a rhombus \((r_c(\text{Ga-As}) = 2.68 \, \text{Å}, r_c(\text{As-As}) = 2.3 \, \text{Å})\). Analysis of the bonding orbitals reveals multiple bonding between the As atoms in the rhombus structure.

1. Introduction

The properties of mixed group III–V and other semiconductor cluster have received considerable attention in recent years [1–27]. Since the GaAs semiconductor is used in the fabrication of fast microelectronic devices, a significant amount of work has been done in studying the properties of GaAs material.

O'Brien et al. [5] have used the laser vaporization method to generate clusters of the general formula \(\text{Ga}_x\text{As}_y\) from a crystal of GaAs. Mass analysis of these clusters has revealed significant deviation from an expected binomial distribution for smaller clusters while larger clusters followed a binomial distribution. Furthermore, measured ionization potentials of \(\text{Ga}_x\text{As}_y\) clusters revealed considerable even–odd alternations. Photofragmentation patterns of \(\text{Ga}_x\text{As}_y^-\) exhibit dramatic contrast with analogous \(\text{Si}_x^-\) and \(\text{Ge}_x^-\) ions in that \(\text{Ga}_x\text{As}_y^-\) fragment into daughters containing fewer atoms compared to \(\text{Si}_x^-\) and \(\text{Ge}_x^-\) [6,22].

There are both experimental and theoretical studies on diatomic GaAs and its ions [9,10,15,16,20]. The results of earlier theoretical calculations on diatomic GaAs and GaAs\(^+\) [10,16,20] were found to be in accord with the observed spectra of these species [9,15].

The present author [28] enumerated systematically the possible isomers of \(\text{Ga}_x\text{As}_y\) using the Pólya theory of counting. The generating function thus obtained combined with a weighting for the Ga–As and As–As bond strengths yielded distributions for various formula consistent with the experimental observation of O’Brien et al. [5]. The author’s anticipation that isomers exist for \(\text{Ga}_x\text{As}_y\) was subsequently confirmed by Reent’s [14] experimental study on hydrogen halide etching of \(\text{Ga}_x\text{As}_y^-\) ions as a function of size. More recently Mandich and co-workers [21] found isomers for \(\text{In}_x\text{P}_y^-\) ions. In the earlier paper referred to above, the author [28] speculated that among the possible isomers for \((\text{GaAs})_2\), the most probable ground state geometry of \((\text{GaAs})_2\) would be a rhombus. The objective of this Letter is to put to test this speculation by making ab initio CASSCF/MRSDCI calculations on several isomers of \((\text{GaAs})_2\) with the aim of finding the ground state geometry, comprehending the nature of bonding and calculating the stability of the \((\text{GaAs})_2\) cluster.

2. Method of calculation

A complete active space self-consistent field (CASSCF) technique was used to generate orbitals for higher-order CI calculations. All calculations described here were made using relativistic effective core potentials (RECPs) which retained the outer \(4s^24p^1\) and \(4s^24p^3\) shells of Ga and As in the valence
space, respectively. These potentials have been tested before on several molecules including the diatomic GaAs molecule for which satisfactory agreement was found compared to all-electron calculations [20]. We employ (3s3p1d) valence Gaussian basis sets for both Ga and As and RECPS described before [20].

CASSCF calculations of the linear and rhombus structures were made in the $D_{2h}$ group while the corresponding calculations of the trapezium structure were made using the $C_{2v}$ symmetry. At the CASSCF level we did not allow excitations from the 4s orbitals of As and Ga, although their coefficients were allowed to change. All 4p orbitals of the separated atoms correlated in the $D_{2h}$ group into two $a_g$, two $b_{1u}$, two $b_{2u}$, two $b_{3u}$, two $b_{3u}$, one $b_{2g}$, and one $b_{1g}$ orbitals. Among these orbitals the second $b_{2g}$, the second $b_{3g}$, the second $b_{3u}$, $b_{2g}$ and $b_{1g}$ orbitals were found to be quite antibonding and thus less important. Omission of these orbitals from the active space brought down the configuration count to a manageable number for our codes. The resulting CASSCF active space consisted of two $a_g$, two $b_{1u}$, one $b_{2u}$, one $b_{2g}$ and one $b_{3u}$ orbitals. The eight outermost electrons of (GaAs)$_2$ were distributed in all possible ways among these orbitals. An alternative CASSCF which distributed twelve electrons (in this case only excitations from As(4s) orbitals were not allowed) among three $a_g$, three $b_{1u}$, one $b_{2u}$, one $b_{3g}$ and one $b_{3u}$ orbitals was also made. However, the geometries obtained using either methods did not differ much. Even the total energy was lowered by only 3 mhartree. Consequently, it is believed that the restricted-CASSCF yields a good set of orbitals for CI calculations.

MRSDCI calculations were carried out following the CASSCF method. These calculations included all configurations in the CASSCF with coefficients $\geq 0.07$ as reference configurations. Subsequently, single and double excitations were allowed from these reference configurations which resulted in a configuration space of 234630 configurations for the $1A_g$ state of (GaAs)$_2$.

A critical comparison of geometries obtained using the CASSCF method and MRSDCI method revealed that there is not much change in the geometry of the ground state. Furthermore, CASSCF calculations showed that all other structures, states and isomers were much higher in energy. Hence MRSDCI calculations were restricted to the $1A_g$ state and the diatomic GaAs. The MRSDCI calculations of the diatomic GaAs were made to compute the energy required to separate (GaAs)$_2$ into two GaAs molecules.

For the singlet ground state of (GaAs)$_2$, a number of structures such as rhombus, trapezium, tetrahedron and linear were considered. Among these the rhombus structure was the lowest in energy for the $1A_g$ state.

All calculations described here were made using the author's [29] modified version of ALCHEMY II codes.

3. Results and discussion

Fig. 1 shows the optimized geometries including

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| Fig. 1. Geometries of isomers of (GaAs)$_2$. | 52 kcal/mole |
| 1$\Sigma_g^+$ | 104 kcal/mole |
| 0 kcal/mole |

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* The major authors of ALCHEMY II are B. Liu, B. Lengsfield and M. Yoshimine.
bond angles for the isomers of \((\text{GaAs})_2\) and their energy separations at the CASSCF level. As seen from fig. 1, the ground state of \((\text{GaAs})_2\) is of \(1A_g\) \((D_{2h})\) symmetry with an equilibrium geometry of a rhombus. Note that the As–As bond length is much shorter than the Ga–As bond length indicating multiple bonding between the arsenic atoms. This will be discussed further later using the MRSDCI orbital analysis.

There are several possible linear isomers such as Ga–As–As–Ga, Ga–As–Ga–As, As–Ga–Ga–As and As–As–Ga–Ga. The last two structures were eliminated because in these structures two Ga atoms are next to each other. Earlier calculations revealed that \(D_e(\text{Ga}_2)\) is only 1.2 eV \([17]\) while \(D_e(\text{As}_2)\) = 3.96 eV \([30]\). This means that structures which contain As–As and Ga–As bonds are likely to be more favorable than structures containing Ga–Ga bonds. The energy of Ga–As–Ga–As was found to be much higher since it has no As–As bonds. Hence among the linear isomers only the Ga–As–As–Ga was fully considered for geometry optimization. While partial multiple bonding between Ga atoms is possible, As–As bond strength is considerably stronger and thus Ga–As–As–Ga is more favorable than As–Ga–Ga–As.

A trapezoidal structure wherein the As atoms occupy the shorter side was considered. At the CASSCF level the trapezoidal structure was found to be at least 46 kcal/mol above the rhombus structure.

Electronic states of other possible spatial and spin symmetries were also considered. For example, fig. 1 shows a \(2B_{2u}\) state lying 104 kcal/mol above the \(1A_g\) ground state. Note that the high-spin multiplicity of this state weakens the As–As multiple bonding significantly elongating the As–As bond. The Ga–As bond is also weakened a bit as a consequence of the high-spin multiplicity and the weakening of the As–As bond.

As mentioned in section 2, more accurate MRSDCI calculations which included 234630 configurations were made to scale the accuracy of the CASSCF geometries and to compute the dissociation and atomization energies. Fig. 2 compares the CASSCF and MRSDCI geometries. As seen from fig. 2, the difference between the CASSCF and MRSDCI geometries is not substantial. Hence the predicted geometries for other structures in fig. 1 should be fairly accurate.

The energy for the following process which we denote by \(D_e((\text{GaAs})_2)\):

\[
(\text{GaAs})_2 \longrightarrow 2\text{GaAs},
\]

was computed using the MRSDCI method. The \(D_e\) obtained this way for separating \((\text{GaAs})_2\) into two GaAs molecules is 2.5 eV. We consider this as a lower bound since higher-order correlation effects not included in the present calculations would increase the \(D_e\) further. Moreover, the CASSCF calculation of the GaAs diatomic was more complete compared to \((\text{GaAs})_2\) although the MRSDCI method is comparable. Allowing for a size consistency error of 0.5–0.75 eV for this, the \(D_e((\text{GaAs})_2)\) is predicted roughly as 3–3.25 eV. Since the d-correlation-corrected \(D_e(\text{GaAs})\) has been calculated before as 2 eV \([20]\), the total binding energy or the atomization energy of \((\text{GaAs})_2\) is calculated as 7–7.5 eV. Note that this value is only a lower bound due to various approximations and errors in electron correlations. The total binding energy of \((\text{GaAs})_2\) should be lower than the binding energy of Si4. Raghavachari \([23]\) calculated a binding energy of 10.7 eV for Si4 using a SCF/MP4 level of theory. Note that Si4 also has a \(1A_g\) ground state with an equilibrium geometry of a rhombus. Since \(D_0(\text{Si}_2)\) \([30]\), \(D_0(\text{Ge}_2)\) \([30]\) and \(D_0(\text{GaAs})\) \([20]\) are 3.21, 2.8 and 2.0 eV, respectively, we expect the total binding energy of \((\text{GaAs})_2\) to be roughly 2–3 eV below the binding energy of Si4. Hence our predicted value of 7–7.5 eV is reasonable.

The leading configurations in the MRSDCI wavefunction of the \(1A_g\) ground state are shown in table 1. As seen from this table, the dominant configura-
Table 1
Important configurations in the MRSDCI expansion contributing to the ground state of GaAs

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.904</td>
<td>1a_s 2a_s 3a_s 4a_s 1b_{1u} 2b_{1u} 3b_{1u} 1b_{2u} 2b_{2u} 1b_{3u} 1b_{2g} 1b_{1g}</td>
</tr>
<tr>
<td>-0.094</td>
<td>2 2 2 0 2 2 0 2 0 2 0 0 2</td>
</tr>
<tr>
<td>0.071</td>
<td>2 2 1 0 2 2 0 2 1 2 1 0 1</td>
</tr>
</tbody>
</table>

As seen from fig. 3, the 3a_s orbital is a strongly bonding orbital composed primarily of As(4p_x) and Ga(4s) (smaller contribution) with appropriate signs shown in fig. 3. The 2b_{1u} orbital is a bonding combination of As(4p_z), Ga(4s) and Ga(4p_z). The contribution of Ga(4p_z) is small. The 1b_{3g} orbital is made of Ga(4p_z) and As(4p_x) and is strongly bonding. The 1b_{3u} orbital is made of the 4p_x orbitals of all atoms. The contribution of As(4p_x) is larger than Ga(4p_z) to this orbital.

The above description of orbitals (fig. 3) then suggests As–As multiple bonding along the shorter diagonal of the rhombus. This multiple bonding interaction brings the two As atoms much closer compared to the distance between Ga and Ga or Ga and As. This is anticipated since the diatomic As_2 in its 1Σ_g^+ ground state exhibits triple bonding. In contrast, the two Ga atoms are non-bonding with respect to each other in (GaAs)_2. To offset for this, there is considerable bonding between Ga–As and As–As atoms (see fig. 3). Hence the rhombus structure is the most favorable structure to facilitate the type of orbital interactions in fig. 3 and to provide As–As multiple bonding. There is a partial Ga(4p_x)–As(4p_x) bonding also in the plane perpendicular to the rhombus in the 1b_{3u} orbital.

The above analysis and the geometry of (GaAs)_2 in fig. 2 are consistent with the equilibrium bond lengths of As_2 and GaAs. Earlier experimental and theoretical studies revealed that r_e(As_2) = 2.10 Å [30], r_e(GaAs) = 2.55 Å [20] and r_e(Ga_2) = 2.746 Å [31] in their ground states. The As–As bond length of 2.276 Å in the 1A_g state of (GaAs)_2 implies that there is some weakening of the triple bond in As_2 in the formation of (GaAs)_2. This is offset by the formation of four Ga–As bonds with bond lengths 2.678 Å, only 0.128 Å longer than the ground state r_e of GaAs. The total binding energy BE(Ga_2As_2) should then obey the following formula since Ga_2As_2 is roughly made of four partial Ga–As bonds and one partial As–As bond found in the corresponding dimers.
BE(Ga₂As₂) ≪ 4Dₓ(GaAs) + Dₓ(As₂).

Using the established Dₓs of GaAs and As₂ and allowing for the bond length changes in Ga₂As₂ (weakening of bond) it is estimated that BE(Ga₂As₂) < 9 eV. Since we have a lower bound from our calculations it is concluded that 7.5 < BE(Ga₂As₂) < 9 eV.

4. Conclusions

In this study we made CASSCF/MRSDCI calculations on several isomers of (GaAs)₂. The most stable structure for the ¹A₁ ground state was found to be a rhombus (rₓ(Ga–As)=2.681 Å, rₓ(As–As)=2.299 Å). Analyses of the highest occupied orbitals revealed multiple bonding between the As atoms, non-bonding interaction between the Ga atoms and bonding interaction between Ga and As atoms. The total binding energy of Ga₂As₂ with respect to the separated atoms was predicted to be between 7.5 and 9 eV.

Acknowledgement

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References