Electronic structure of small GaAs clusters
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Electronic structure of small GaAs clusters

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The electronic structure of small Ga_x As_y clusters (x + y < 10) are calculated using the local density method. The calculation shows that even-numbered clusters tend to be singlets, as opposed to odd-numbered clusters which are open shell systems. This is in agreement with the experimental observations of even/odd alternations of the electron affinity and ionization potential. In the larger clusters, the atoms prefer an alternating bond arrangement; charge transfers are observed from Ga sites to As sites. This observation is also in agreement with recent chemisorption studies of ammonia on GaAs clusters. The close agreement between theoretical calculations and experimental results, together with the rich variation of electronic properties of GaAs clusters with composition makes GaAs clusters an ideal prototype system for the study of how electronic structure influences chemical reactivity.

I. INTRODUCTION

The understanding of the relationship between the geometrical and the electronic structure of a solid surface is of crucial importance for the understanding of many of its physical and chemical properties. In particular, it is known from chemisorption studies on metal and semiconductor surfaces that certain sites on the surface as well as facets can be much more reactive than others. These effects are caused by the fact that the local electronic structure of a surface can be very sensitive to the position of neighboring atoms.

Cluster science offers a particularly interesting area in which the correlation between reactivity and structure can be investigated. In a small cluster, the concentration of surface atoms is enhanced relative to bulk atoms. In addition, the surface of a small cluster provides several different chemisorption sites. The relative concentration of such sites is naturally much larger than what would be the case on, for example, a stepped surface.

Several recent experiments probing the sticking coefficient of simple molecules such as H_2 and NH_3 on small clusters have shown that the reactivity of a cluster can depend very sensitively on the cluster size. In addition, it has been shown that for a given composition of a cluster, there can exist several different isomers each of which can have a very different reactivity.

These types of experiments cannot be properly interpreted without detailed knowledge of the electronic and geometrical structure of the cluster. At present, such information can best be provided by theoretical calculations.

The exact numerical calculation of the electronic structure of molecules larger than dimers would be prohibitively time consuming even with present supercomputers. One must therefore develop some approximate schemes. Among the first principles approximations one can distinguish configuration interaction theory (CI) and density functional theory (DF). The two theories are formally exact but by restricting the number of configurations or choosing simplified exchange-correlation functionals practical approximate computational schemes result.

To date, most applications to solids, molecules, and atoms have shown that the different density functional approaches provide almost the same accuracy as CI but with a tremendous reduction in computational effort.

In the present paper detailed calculations of the electronic structure of small GaAs clusters will be presented and compared to recent experimental data.

The theoretical calculations are performed using the local density approximation (LDA). By minimizing the total energy, the equilibrium structure is obtained and the electronic structure calculated. The computational method, DMol^6 briefly described in Sec. II.

In Sec. III A an application to Ga_x As_y dimers is presented. For such small systems, conventional quantum chemistry methods such as the multiple CI theory can be applied. It is shown that the present LDA approach is as accurate as other high level methods.

In Sec. III B the electronic structure and geometry of various Ga_x As_y clusters of size range from x + y = 3–10 is presented. The emphasis is on the near x = y composition, which is the dominant composition observed in experiments.

In Sec. IV, the calculations are compared with recent experimental results. It is shown that even-numbered clusters have singlet electronic states and that the odd-numbered clusters are triplets. In the larger clusters, the atoms prefer an alternating bond arrangement where charges are transferred from the gallium atoms to the adjacent arsenic atoms.

II. THEORY

In this section, some theoretical details will be presented. In the first subsection, the local density approximation is discussed. In the second subsection, the numerical methods and procedure will be briefly introduced.

A. Theoretical formalism

Since its introduction, the density functional theory has emerged as an extremely efficient method for the first
principles calculation of the electronic structure of many-electron systems. Density functional theory is a formally exact method for the reduction of a complicated many-electron problem to a set of interacting one-electron equations. For a general many-electron problem the total energy and the electronic density in the system can be obtained by the solution of the following set of one-electron problems:

$$\left[-\nabla^2 + V_s(r) + \mu_{xc,\sigma}(r)\right] \psi_{k,\sigma}(r) = \epsilon_{k,\sigma} \psi_{k,\sigma}(r). \quad (2.1)$$

In this equation, \( V_s(r) \) is the electrostatic potential at position \( r \). The spin is denoted by \( \sigma \). The effects of exchange and correlation is taken into account through the exchange correlation potential \( \mu_{xc,\sigma}(r) \) which is a functional of the electronic density \( \rho_\sigma(r) \) in the system. The electron density can be obtained from

$$\rho_\sigma(r) = \sum_{k,\sigma} |\psi_{k,\sigma}(r)|^2, \quad (2.2)$$

where the sum is over the lowest occupied states. In most practical applications one performs the local density approximation, i.e., one approximates \( \mu \) with the exchange correlation contribution for a homogeneous electron gas of density \( \rho(r) \). This approximation is obviously valid for slowly varying electron density systems. Applications have shown that even such inhomogeneous systems as atoms can be well described by the LDA.

Once the electron density distribution is calculated, the total energy can be obtained from

$$E^{\text{tot}} = \sum_{k,\sigma} \epsilon_{k,\sigma} + \sum_{\sigma} \int d^3r \rho_\sigma \left[ \epsilon_{xc,\sigma} - \mu_{xc,\sigma} - \frac{1}{2} V_s \right] + E^{\text{nuc}}, \quad (2.3)$$

where \( E^{\text{nuc}} \) is the repulsion between the nuclei in the system and \( V_s(r) \) is the electrostatic potential due to the electron charge distribution. In this equation \( d(\rho_\sigma(e_{xc,\sigma})/d\rho_\sigma = \mu_{xc,\sigma}. \) In the present application, an approximation for the exchange correlation potential derived by Hedin and Lundqvist is used.

B. Calculational details

The linear variational expansion of the single-particle molecular orbital

$$\psi_{k,\sigma}(r) = \sum_{l,\sigma} c_{k,l,\sigma} \phi_l(r) \quad (2.4)$$

is used to solve Eq. (2.1). Here \( \phi_l \) are atomic orbitals centered at each nucleus and \( c_l \) are the expansion coefficients. In the present work, accurate numerical atomic orbitals are used and integrations of the Hamiltonian matrix elements are made numerically. The Schrödinger equation is solved self-consistently on a set of discrete sampling points surrounding the molecule.

In DMol the grid is generated spherically around each nucleus (as atomic center) with increasing radial spacing. The spherical shells around different nuclei penetrate each other and no boundary faces are introduced. Gaussian quadrature rules are applied to the integrations over the spherical shells. In order to compensate the possible “double counting,” the integration weight on a grid node is split if the same spatial region is also sampled by another spherical shell of grid. By splitting the weights the grid is decomposed into each atomic center.

For each decomposed, spherical grid, the central region is densely sampled and the regions near the neighboring nuclei are relatively scarcely sampled. To eliminate the singular effects due to the nuclear cusp at an off-center nucleus, the weight is reduced for the grid nodes near this off-center nucleus. Meanwhile, this same region is also sampled by the spherical grid attached to that off-center nucleus with nearly fully weighed nodes. The proper splitting of the weights insures integrations over each decomposed grid to be precise. Details of this partitioning technique are given by Becke and Delley.

The partitioning of the molecular grid into atomic centers makes it convenient to use a multipolar expansion technique to facilitate the convergence of the SCF iterations. The multipolar components of the charge density \( \rho \) may be expressed as

$$\rho_{a,l,m}(s) = \int_{|s - s_0|} \rho_a(r) \rho(r) Y_{l,m}(r - R_a) d\Omega, \quad (2.5)$$

where \( Y_{l,m} \) is a spherical harmonic function of angular dependence \( (l, m) \), \( R_a \) is the position of the \( a \)th atomic center. The partitioning function \( \rho_a(r) \) satisfies the requirements \( \sum_a \rho_a(r) = 1 \) at every point \( r \). The integration is over the spherical shells centered at \( R_a \).

Since the off-center contribution to the charge density at a point \( r \) is effectively eliminated by the partitioning function \( \rho_a(r) \), the product \( \rho_a(r) \rho(r) \) is nearly spherically symmetric. The multipolar expansion of this decomposed charge density is expected to converge rapidly. Practically a maximum angular momentum of 2 or 3 provides good accuracy in our applications.

The Coulomb potential is treated in a similar way, i.e., first partitioned into individual atomic centers and then expanded in terms of spherical harmonics. The multipolar components of the Coulomb potential are related to the multipolar components of the charge density via the Green’s function defined by the Poisson’s equation. The use of a multipolar expansion technique greatly simplifies the evaluation of the Coulomb potential which is normally a multicenter integration.

In DMol, atomic orbitals that are exact numerical solutions of a neutral atomic systems are used as the basis functions. The use of such basis functions significantly reduce the size of the basis compared to Gaussian methods. For a molecule these basis functions fit naturally to the charge distribution in the regions near the nuclei and predict the right decomposition limit at infinite internuclear distances. To describe the intermediate regions, extended basis functions from positively charged atomic systems are added.

III. RESULTS

In this section, results for the electronic structures of Ga\(_{13}\)As\(_p\) clusters are presented. In the first part, the numeri-
veral accuracy of the density functional approach is shown by an application to dimers and comparison with the experiment and other high level quantum chemistry methods. In the second part, application of the present method is extended to clusters of larger size. All the computations included in this work are accomplished on a Silicon Graphics personal computer.

A. Gallium arsenide dimers

The accuracy of a molecular calculation depends on the quality of the basis set.

In the present work, two numerical basis sets are used. The first set includes all the occupied atomic orbitals of free Ga and As atoms and one additional function (from ionic Ga and As) for each of the 3d, 4s, and 4p orbitals, plus a 4d orbital as polarization function. This basis set is denoted DNP. The second set is obtained from the DNP by removing the extended 3d and 4d functions and freezing the core orbitals. This reduced basis set is denoted dn. The DNP set is used only for diatomic calculations. In the calculations for the clusters with 3 to 10 atoms (presented in the next subsection), the reduced set dn is used.

In Table I, DMol’s results for the gallium arsenide dimers are presented and compared with experiment and multiple CI calculations. We can see that the DNP set gives very accurate results for the equilibrium distance and vibrational frequency. For the reduced set, as a consequence of freezing the core orbitals, the bond lengths are increased by a few percent and the binding energy is decreased. In general, however, this reduced basis set gives a fairly good picture of the GaAs dimers.

The potential energy curves for the dimers As₂, GaAs, and Ga₂ are presented in Figs. 1 (a)–1 (c). The solid curves are obtained with the basis set DNP and the dashed curves are obtained with the basis set dn. The As₂ dimer is a singlet with a HOMO–LUMO gap of about 2 eV at its equilibrium separation 2.1 Å. It can be seen that the potential energy curve for As₂ [Fig. 1(a)] is relatively deep near the equilibrium distance. The other two dimers, GaAs and Ga₂, are triplets, each is shown with the energy curves of the two lowest-lying states as indicated in Figs. 1(b) and 1(c). These curves are relatively flat compared with As₂ (different energy scales are used to avoid confusion). The Ga₂ curves extend further to the right.

B. Small gallium arsenide clusters

The number of possible atomic arrangements of a cluster increases rapidly with cluster size. In order to systemize the search for the equilibrium structures of the different GaAs clusters, possible initial configurations must be defined as seeds for the LDA calculation and energy optimization. In the present case we started by considering clusters of stoichiometric composition, i.e., GaₙAsₙ₋₁. Recent UPS data suggests that these clusters are of closed shell type.

The search began by defining possible geometries using Polyta theory of counting and the geometries previously optimized for silicon clusters. For simplicity, all the bond lengths were fixed to the GaAs bulk values. This procedure defines several hundred different structures.

The electronic structure of these configurations was calculated using an extended Huckel method (EHT). Those geometries that came out as closed shell structures were first selected as seeds for geometry optimization. Comparisons of the EHT band structure with the LDA results for a given cluster geometry indeed show a very good qualitative agreement. In addition to these configurations we used a large number of open shell configurations as seeds. The seeds for the nonstoichiometric clusters were defined by substituting

<table>
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<tr>
<th>Dimers</th>
<th>( R_e (\text{Å}) )</th>
<th>( E_b (\text{eV}) )</th>
<th>( \omega_v (\text{cm}^{-1}) )</th>
<th>IP(eV)</th>
<th>EA(eV)</th>
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<td>GaAs(( ^{3} \Sigma^- ))</td>
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<td></td>
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<td>2.06±0.05</td>
<td>215</td>
<td>7.2±0.8</td>
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<td>LDF(DNP)</td>
<td>2.549</td>
<td>2.50</td>
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<td>1.82</td>
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<td>Ga₂(( ^{3} \Sigma^- ))</td>
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<tr>
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<td></td>
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and removing various atoms of the stoichiometric clusters. The different seed configurations were relaxed by DMol to find the local energy minima. The reduced basis set was used in this procedure. During the relaxation, the bond lengths and charge transfer changed about 5-30% and the total energy typically decreased a few tenths of an electron volt per atom. The geometry relaxation ended when the maximum energy gradient was smaller than 0.003 a.u. Only low order nondegenerate point groups were used to restrict the degrees of freedom in the geometrical relaxation.

The equilibrium configuration of each cluster is chosen as the structure with the deepest local minimum. In view of the large number of initial structures, we feel confident that the configurations obtained lie very close to the true equilibrium geometries.

The binding energy, HOMO energy, band gap, and vertical EA and IP of the gallium arsenide clusters in their relaxed configurations are listed in Table II.

Clusters of \((x + y) = 4, 6, 8\), and 10 atoms are of closed shell singlet ground states and all, except for \(\text{Ga}_2\text{As}_4\), have band gaps larger than 1 eV at the lowest energy configuration. There is an apparent even/odd oscillation in electron affinity. The EA of \(\text{Ga}_2\text{As}_4\) is 2.8 eV, larger than expected from the oscillation trend but consistent with the relatively small band gap of 0.4 eV. More details about this cluster will be presented later.

There is no clear division between IP's of even- and odd-numbered clusters. These IP's are all calculated vertically on the relaxed configurations of neutral clusters; no geometry optimization is made for the positively charged clusters in the present work.

The structures we found the most stable for the gallium arsenide clusters are schematically plotted in Figs. 2(a)-2(j). We can see that these structures are close in shape to certain polyhedra. In particular, some polyhedral structures found stable for the silicon clusters were also found stable for the gallium arsenide clusters of the same size in our calculations.

A typical example is \(\text{Ga}_2\text{As}_5\). The lowest energy structure found for this isomer is a tetracapped trigonal prism (TTP), see Fig. 2(i), formed by decorating Ga atoms on the faces of a distorted trigonal prism with atoms on the vertices. By substitution of the atoms in the adjacent vertices, another configuration of nearly equal energy was found. The TTP structure was previously found to be the most stable for the \(\text{Si}_{10}\) cluster in the SA-LDA calculation.\(^{13}\)

The tetracapped octahedral (TO) structure [Fig. 2(j)] which was found to be almost equally stable for the \(\text{Si}_{10}\) cluster\(^{18}\) also resulted in a high binding energy for the \(\text{Ga}_2\text{As}_5\) cluster. A couple of different atomic arrangements with sim-

![Potential energy curves of diatomic molecules](image)

**FIG. 1.** Potential energy curves of diatomic molecules (a) \(\text{As}_2\) \((^1\Sigma_g^-)\), (b) \(\text{GaAs} (^1\Sigma_g^-)\) to the left and \(^1\Pi (\text{to the right})\), and (c) \(\text{Ga}_2\) \((^1\Sigma_g^-)\) to the left and \(^1\Pi (\text{to the right})\). The result of the basis set DNP is plotted in solid lines and the result of the basis set \(\text{dn} \) is plotted in dashed lines. See the text for details.

### TABLE II. Results for the gallium arsenide clusters in the most stable structure.

<table>
<thead>
<tr>
<th>(x + y)</th>
<th>(\text{Ga}_x\text{As}_y)</th>
<th>Configurations</th>
<th>ptgrp</th>
<th>(E_s)</th>
<th>HOMO</th>
<th>(\Delta)</th>
<th>IP</th>
<th>EA</th>
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<td>(10)</td>
<td>(\text{Ga}_2\text{As}_4)</td>
<td>Tetracapped trigonal prism</td>
<td>(C_2)</td>
<td>2.65</td>
<td>6.0</td>
<td>1.7</td>
<td>8.0</td>
<td>2.4</td>
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<tr>
<td>(9)</td>
<td>(\text{Ga}_2\text{As}_4)</td>
<td>Tricapped trigonal prism</td>
<td>(C_2)</td>
<td>2.54</td>
<td>5.6</td>
<td>0.2</td>
<td>7.5</td>
<td>3.5</td>
</tr>
<tr>
<td>(8)</td>
<td>(\text{Ga}_2\text{As}_4)</td>
<td>Rhombic prism</td>
<td>(C_2)</td>
<td>2.54</td>
<td>5.1</td>
<td>0.4</td>
<td>7.3</td>
<td>2.8</td>
</tr>
<tr>
<td>(7)</td>
<td>(\text{Ga}_2\text{As}_4)</td>
<td>Capped prism</td>
<td>(C_2)</td>
<td>2.43</td>
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<td>0.3</td>
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<td>(6)</td>
<td>(\text{Ga}_2\text{As}_4)</td>
<td>Capped trigonal bipyramid</td>
<td>(C_{1h})</td>
<td>2.43</td>
<td>5.7</td>
<td>2.0</td>
<td>8.0</td>
<td>1.6</td>
</tr>
<tr>
<td>(5)</td>
<td>(\text{Ga}_2\text{As}_4)</td>
<td>Trigonal bipyramid</td>
<td>(C_{2v})</td>
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<td>1.2</td>
<td>8.0</td>
<td>1.9</td>
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<tr>
<td>(4)</td>
<td>(\text{Ga}_2\text{As}_4)</td>
<td>Planar rhombus</td>
<td>(D_{2h})</td>
<td>2.22</td>
<td>5.6</td>
<td>1.2</td>
<td>8.0</td>
<td>1.8</td>
</tr>
<tr>
<td>(3)</td>
<td>(\text{Ga}_2\text{As}_4)</td>
<td>Triangle</td>
<td>(C_{3v})</td>
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<td>5.3</td>
<td>0.5</td>
<td>8.1</td>
<td>2.1</td>
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<td>(C_{2v})</td>
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<td>0.2</td>
<td>7.8</td>
<td>1.9</td>
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\(^{13}\) J. Chem. Phys., Vol. 94, No. 12, 15 June 1991

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The search for energy minima of the Ga₂As₄ isomer started with the seeds obtained by removing one capping Ga atoms from the TTP or TO structures of the Ga₂As₅ isomer. The binding energies of the relaxed structures are about 2.5 eV. The most stable one is a distorted TTP [Fig. 2(h)].

The lowest energy structure for the Ga₂As₅ isomer is a rhombohedral structure with C₃ symmetry [Fig. 2(f)]. This structure is 0.14 eV/atom more stable than the bicapped octahedral structure [Fig. 2(g)], previously found to be the most stable for Si₈.

In this structure, the As atoms are located outside of the Ga atoms. This is an exception in the general trend observed in our results. The structure was obtained by relaxing a bicapped octahedral structure with two As atoms in the capped positions. For this seed geometry, the relaxation took an unusually long time (over 200 h) but finally the rhombohedral structure resulted. The efforts for different substitutions of atoms failed to reach a structure of comparably low energy.

Another point worth mentioning is that all the seed configurations we have tried for this isomer ended up with a band gap less than 1 eV, which is clearly smaller than that of the adjacent even-numbered isomers, Ga₄As₅ and Ga₃As₇, see Table III. Note that the trigonal antiprism structure for Ga₄As₄ listed in this table has a segregated arrangement of Ga and As atoms.

For the Ga₂As₅ isomer, the cubic structure with an alternating arrangement is unstable due to the static Jahn-Teller effects. The distorted descendants with lower order symmetry (e.g., C₂ᵥ) are still not energetically favored.

The lowest energy structure for the Ga₂As₅ isomer was obtained by relaxing a capped trigonal prism as the seed configuration. See Fig. 2(e).

The lowest energy structure for Ga₄As₇ was obtained by relaxing an edge capped trigonal prism [Fig. 2(d)], which is also the most stable structure for the Si₆ cluster. The (distorted) octahedral structures are less stable.

The lowest energy structure for the Ga₃As₇ isomer was obtained by relaxing a trigonal bipyramid [Fig. 2(c)]. A similar structure was previously found stable for Si₆.⁰⁹

The most stable structure for Ga₂As₅ was a planar rhombus in D₂h symmetry [Fig. 2(b)]. The rhombohedral structure we found agrees well in bond lengths and bond angles

TABLE III. Results for some even-numbered gallium arsenide clusters in different atomic arrangements. The units are eV/atom for the binding energy $E_b$ and eV for others. See captions for Table II.

<table>
<thead>
<tr>
<th>GaₙAsₙ</th>
<th>Configurations</th>
<th>pgrp</th>
<th>$E_b$</th>
<th>HOMO</th>
<th>$\Delta$</th>
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<tr>
<td>Ga₃As₇</td>
<td>Rhombic prism</td>
<td>C₁</td>
<td>2.54</td>
<td>5.1</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Bicapped octahedron</td>
<td>C₁</td>
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<td>5.4</td>
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<td></td>
<td>Square antiprism</td>
<td>C₁</td>
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<td>5.8</td>
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<td>Ga₃As₇</td>
<td>Capped trigonal bipyramid</td>
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<td>5.7</td>
<td>2.0</td>
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<td></td>
<td>Capped square pyramid</td>
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<td>2.40</td>
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<td></td>
<td>Bicapped tetrahedron</td>
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<td>2.30</td>
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<td>C₁</td>
<td>2.30</td>
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</tr>
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</table>

FIG. 2. Geometry of the most stable Ga₂As₅ isomers with near $x - y$ composition. The bigger circles represent As atoms and the smaller circles represent Ga atoms. Sticks are added between the balls intended to help for a three-dimensional perception, which do not necessarily represent a bond of any sort. The detailed geometries will be provided upon request. (a) Ga₄As₅, isosceles triangle; (b) Ga₅As₅, planar rhombus; (c) Ga₆As₅, trigonal bipyramid; (d) Ga₇As₅, edge capped trigonal prism; (e) Ga₈As₅, capped trigonal prism; (f) Ga₉As₅, rhombohedral; (g) Ga₊As₅, bicapped octahedron; (h) Ga₁₂As₁, TTP; (i) Ga₂₆As₁₂, tetracapped trigonal prism (TTP); (j) Ga₇As₇, tetracapped octahedron (TO).
with that obtained in a recent CASSCF/MRSDCI calculation. In addition, several three-dimensional configurations (within $C_{2v}$ symmetry) were tried but found less stable.

The most stable trimer was found to be GaAs$_2$ in an isosceles triangle [Fig. 2(a)].

The bond lengths in these clusters span a range from 2.2 to 2.8 Å. The As–As bond length does not vary much from a middle value 2.5 Å. By contrast, the Ga–Ga bond length varies from 2.4 to 2.8 Å. The variation of Ga–As bond length is intermediate. This is consistent with the potential energy curves of the corresponding dimers plotted in Fig. 1.

**IV. DISCUSSION**

Recent experiments on Ga$_x$As$_y$ clusters have shown that the electronic affinity (EA) of gallium arsenide clusters oscillates with the number of atoms ($x + y$); the even-numbered clusters tend to have smaller EA and the odd-numbered clusters have larger EA. Similar even/odd oscillation is also observed in the ionization potentials (IP). The observed oscillation of EA and IP with cluster size strongly suggests that the even-numbered neutral gallium arsenide clusters be of significant HOMO–LUMO separations and therefore of singlet ground states (except for the dimer GaAs which is known to have a triplet ground state).

In Table II, it can clearly be seen that the present calculation give support for this interpretation.

The reactivity of GaAs clusters with ammonia has also been studied. It was found that the largest reactivity was observed with equal numbers of Ga and As indicating that the atoms in GaAs clusters (of size 8 atoms and larger) may possibly be arranged in an alternating pattern with the Ga atoms losing electrons to the neighboring As atoms. The Lewis acid site thus formed at the cluster surface would allow a chemical bond between the ammonia molecule and the cluster surface.

This suggestion is also confirmed by the present calculation. The outermost sites are occupied by gallium atoms which are bound to neighboring arsenic atoms. Charges are transferred from the gallium atoms to the adjacent arsenic atoms. The tendency to alternating arrangements is clearly seen.

The close agreement between the calculated electronic properties and the experimental results shows that the electronic structure of Ga$_x$As$_y$ clusters can be conveniently described using the LDA theory. Ga$_x$As$_y$ clusters could therefore serve as very interesting model systems where it is possible to investigate how the details of the electronic structure influence the physical and chemical properties of the cluster. The LDA calculations are relatively straightforward to perform and very fast compared to other ab initio methods such as Hartree–Fock or CI. The simplicity of LDA allows relatively large clusters to be studied. At present, new LDA code is being developed employing a similar calculational technique as outlined in this paper but specifically designed to execute on parallel computers. This new program will allow the further detailed study and interpretation of various experiments on larger clusters.

**V. CONCLUSION**

The electronic structure of small GaAs clusters have been calculated using the local density approximation. Comparison with other theoretical calculations and experimental results for dimers show that the present approach provides very accurate results with a minimal computational effort. For larger GaAs clusters, the equilibrium geometries and electronic configuration has been calculated using total energy minimization. The results obtained is in agreement with experimental data.

**ACKNOWLEDGMENTS**

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