

Virtual synthesis of artificial molecules of In, Ga, and As with predesigned electronic properties using a self-consistent field method

Liudmila A. Pozhar,^{1,2,*} Alan T. Yeates,² Frank Szmulowicz,² and William C. Mitchel²

¹*Department of Chemistry, Western Kentucky University, 1906 College Heights Blvd, Bowling Green, Kentucky 42101, USA*

²*Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433, USA*

(Received 4 May 2006; published 8 August 2006)

A Hartree-Fock based (HF), multiconfiguration self-consistent field (MCSCF) method has been used to configure computationally several nonstoichiometric model pyramidal molecules of In, Ga, and As atoms with a predesigned electronic energy level structure. The geometry, structure, and composition of the molecules have been derived from those of the corresponding bulk lattices. Formation of the molecules under conditions mimicking vacuum and quantum confinement has been studied. The results prove that formation conditions affect the molecular parameters (such as the structure and bond length), thus causing significant effects (up to an order of magnitude) on the electronic properties of the molecules, including their charge and spin density distributions (CDDs and SDDs, respectively). The virtual (i.e., fundamental theory based, computational) synthesis of atomic-scale objects with predesigned physicochemical properties is a powerful method that can be used to develop electronic templates of artificial molecules, atomic clusters, small quantum dots (QDs), QD-based nanoheterostructures (NHSs), and other nanosystems of practical interest to guide their experimental realization.

DOI: [10.1103/PhysRevB.74.085306](https://doi.org/10.1103/PhysRevB.74.085306)

PACS number(s): 73.22.-f, 05.30.Fk, 36.40.Cg, 31.15.Ne

I. INTRODUCTION

Rapid progress¹ in fabrication of nanostructured materials based on artificial atomic clusters, molecules, small semiconductor QDs, and nanoheterostructures (NHSs) with characteristic dimensions reduced to nanometers has facilitated the development of 3D integrated circuits (ICs) and nanodevices with the enhanced capabilities and functionality through the use of quantum confinement effects. Further miniaturization of small semiconductor QDs and QD-based structures provides a foundation for realization of physical structures whose operation is defined by quantum coherence effects. Such structures not only possess a high density of IC elements in three dimensions (3D), but also facilitate the use of quantum-information processing principles to enable an orders-of-magnitude increase in information processing capabilities.² However, further progress in technology of quantum materials is limited by insufficient information on physicochemical, and in particular on electronic, properties of small atomic/molecular systems synthesized in quantum confinement that can be used to realize single quanta and to enable information exchange between quantum objects and devices. While experimental methods of acquiring such information on few-atomic systems are extremely demanding and inconclusive at present, reasonable evaluation of the properties of such systems can be obtained by theoretical means, in particular through a realistic modeling and/or virtual synthesis³ using the first-principle theoretical and computational methods.⁴ The key physical properties of the quantum objects, such as artificial molecules, and NHSs synthesized virtually can be directly related by theoretical means (through explicit analytical expressions) to the structure, composition, and spatial configuration of the quantum objects, and those of the “environment”^{5,6} interacting with such objects. In the case of small systems nucleating in quantum confinement, such as small QDs, artificial atoms, and mol-

ecules synthesized on surfaces, in subnanometer pores of porous membranes⁷ or within solid lattices, a full-scale realization of the first-principle computational approaches is quite feasible. More importantly, the data so obtained can be used in available analytical formulas⁵ to evaluate the corresponding charge transport coefficients and susceptibilities of the quantum objects that are difficult to measure experimentally, thus further guiding the practical use of quantum confinement effects and quantum-information processing principles.

A. Small pyramidal QDs of Ga and In with As: Existing studies

Since the early 1990s, a number of techniques have been established for experimental synthesis of small QDs of Ga, In, Al, and Ge with As and P atoms on surfaces/substrates of or embedded in GaAs, InGaAs, InGaP, AlGaAs, and other materials. Smaller QDs of several hundred atoms have been synthesized with a nanometer precision by the use of the “bottom-up” methods based on self-assembly or patterned growth that also include photolithography and etching steps.⁸ These small QDs grown on surfaces (self-assembly) or in confinement, such as that provided by nanometer-size V-shaped grooves or pyramidal recesses, are typically pyramidal, or otherwise possess tetrahedral symmetry. Modifications of the self-assembly method that use strain relaxation (with an initial deposition by MBE or MOCVD) also lead to a synthesis of pyramidal QDs. This latter technique is especially attractive as it does not require etching or patterning: pyramidal QDs grow naturally. At present, the smallest semiconductor compound pyramidal QDs (of about 150 to 200 atoms) have been realized using an organometallic CVD on patterned substrates and a pregrowth photolithography procedure that allows a precise control of the dot positions.⁹

Methods of theoretical description and computations of the equilibrium electronic structure in larger semiconductor

compound pyramidal QDs range from the first principle based, pseudopotential quantum statistical mechanical¹⁰ to half-heuristic methods (such as the effective mass, $\mathbf{k}\cdot\mathbf{p}$, tight binding, or envelop function approximations¹¹) developed for bulk semiconductors and equipped with adjustable parameters and heuristic assumptions to account, on average, for spatial inhomogeneity contributions. Even though these latter methods have been relatively adequate for larger QDs, they cannot provide details of the QD electronic level structure. In particular these methods, which include continuum treatment of interfaces and only linear strain effects, do not properly account for localization of the wave functions in some specific regions of the QDs, oversimplify the electron-hole Coulomb interactions, etc.

With a growing need in quantum computation facilities, miniaturization of ICs and electronic devices, and the development of various technologies to experimentally synthesize smaller and smaller QDs (most of which naturally or by design have the pyramidal shape^{8,9}), it has been understood that a theoretical description of such few-atomic systems has to provide information on their electronic structure in much greater detail. This realization has led to numerous studies of virtually synthesized artificial atoms and molecules using both the density functional theory (DFT)- and Hartree-Fock (HF)-based first principle statistical mechanical methods.

A very important difference between these fundamental theoretical methods and those used before is that the former allows a consideration of small QDs and atomic clusters as chemical entities, artificial molecules. Such molecules are stabilized by a collectivization of their valence electrons that is only possible by means of types of spatial arrangement of the electronic wave functions,¹² as compared to those typical for bulk systems, quantum wells and wires (QWWs), and larger QDs, and described by the classical valence theory (so-called “octet rule”). A direct consequence of the types of the valence properties is the existence and stability of numerous natural and artificial nonstoichiometric molecules extensively studied experimentally (see a detailed discussion in Ref. 12). However, this extremely important reality is not yet adequately addressed by the existing first-principle-based computational models of artificial molecules.¹³ In many cases, the analysis of the obtained computational results reflects only the octet rule considerations, and a number of steps (such as an addition or subtraction of electrons to/from an otherwise neutral cluster, or the use of hydrogen or metal atoms to tie up dangling bonds) are taken to ensure that such stable, virtually synthesized molecules are stoichiometrically “correct” from the octet rule standpoint.

B. Artificial molecules in quantum confinement

In this paper several nonstoichiometric, stable, neutral semiconductor pyramidal artificial molecules composed of ten Ga or In atoms with 4 As atoms are virtually designed by means of the first principle, restricted open shell HF (ROHF) based, complete active space self-consistent field (CASSCF), and MCSCF methods as realized by the GAMESS software package. The choice of these systems has been inspired by the existing demand for understanding of the electronic prop-

erties of the pyramidal artificial molecules that can serve as electronic templates of the existing and future “smallest QDs” realizable experimentally. This choice has been supported by the availability of other theoretical studies of similar, although smaller, clusters of Ga and As atoms^{14–18} using simpler computational methods. A comparison with the available computational data may help examine the reported tendencies in the electronic properties of the studied artificial molecules and their applicability to larger artificial molecules.

A crucial role of quantum confinement effects in shaping the electronic structure of artificial molecules is specifically addressed in this paper. Such an analysis is long overdue, as the ongoing experimental studies of similar Ga-As and In-As QDs (although larger in size, at present) are focused on quantum confinement/surface contributions to the electronic properties of the QDs. At the same time, the existing theoretical and computational models^{13–18} deal with artificial molecules virtually synthesized in the absence of any spatial constraints applied to the coordinates of the atoms forming the molecules (below called vacuum molecules), or external electromagnetic fields that affect their electronic structure.

In addition to experimentally studied quantum confinement effects, these effects can be instrumental in a selection of the most appropriate molecules among a number of spatial isomers that are often obtained in the course of the computational studies. One should note here, that surfaces on which artificial molecules may be experimentally synthesized contribute significantly to the nucleation process. From the cluster nucleation point of view, the surface structure details of atomic dimensions dramatically increase the probability of the heterogeneous nucleation scenario, as opposed to the corresponding homogeneous one, thus affecting the entire nucleation setup and providing for the “surface quantum contributions” to the electronic structure properties of the synthesized molecules.

While often closely resembling stable molecules nucleated in vacuum, artificial molecules synthesized, and stabilized in the presence of spatial constraints applied to the atomic positions (below called predesigned molecules) reveal the structure, composition, and electronic properties that differ dramatically from those of the similar vacuum molecules.^{3,19} Therefore, the development of computational models and means to mimic molecular synthesis in quantum confinement are necessary to establish theoretical/computational templates of the molecules and guidelines to help the further progress in experimental synthesis of nano-systems with the desirable electronic properties.

In Sec. II of this paper a simple systematic approach to the development of realistic models for the atomic structure and composition of such predesigned molecules and their vacuum counterparts is described. The electronic and magnetic properties of the artificial molecules so synthesized are discussed in detail. The obtained results and conclusions are discussed in Sec. III.

II. CASSCF/MCSCF DESIGN OF ARTIFICIAL MOLECULES

The MCSCF approximation used in this work to compute the equilibrium electronic energy level structure of artificial

molecules composed of Ga or In and As atoms is a sophisticated generalization of the restricted open-shell Hartree-Fock (ROHF) method²⁰ developed during the recent few decades and implemented as the GAMESS software package.²¹ Thus, the nonrelativistic Schrödinger equation written for a considered atomic system is solved using a solution (a combination of Slater determinants) of the corresponding Hartree-Fock equation as the zero-order approximation of the SCF determinant wave function of the molecule. Because the HF SCF determinant wave function is obtained in the Born-Oppenheimer approximation and includes the configuration interactions (CIs) only through the Pauli principle, it has to be further improved using the CASSCF method. In this variation procedure a “corrected” determinant wave function of the system is formed as a linear combination of all of the electronic orbitals corresponding to various configurations of the electrons distributed over available molecular orbitals. In principle, the CASSCF generates an “exact” determinant wave function of the system, but due to practical computational considerations the CAS is usually restricted to the necessary minimum set of active orbitals defining the electronic properties of the system. The CASSCF and “smaller” MCSCF procedures also take into consideration electronic correlations beyond those accounted for by the HF/ROHF procedure. The “larger” MCSCF, CI, and MP2 methods use and further improve upon the CASSCF determinant wave function so obtained, accounting for so-called “dynamic” electronic correlations.

Until recently,³ the above described total energy minimization procedure has been applied to the Schrödinger’s equation without any boundary conditions realized as spatial restrictions on the positions of the atoms comprising a studied system: the atoms could “move” until the minimum or a stationary point (if any) of the total energy is reached. Such a procedure may be a realistic model for molecules synthesized in vacuum in the absence of external fields, rather than for molecules synthesized on interfaces or in quantum confinement. The Coulomb interactions between electrons of the guest atoms and those of the host surface or confinement, and the excluded volume effects, are among the major driving forces shaping the geometry, structure, and composition of an artificial molecule emerging on the surface or in the confinement. In general, the quantum confinement may affect a course or inhibit/provoke chemical reactions, change a course and nature of thermodynamic processes (including nucleation) and the equilibrium conditions in confined systems, etc.^{22,5}

Therefore, the development of realistic computational models for artificial molecules nucleating on interfaces or in confinement has to account for any atomistic “environment” participating in the nucleation. This can be realized either by a complete computational replica of such an environment (that is, by accounting in the Schrödinger equation for the nucleating molecule for all of the electronic configurations and atomic positions of the atoms comprising the environment), or by the development of some predesigned setups that would model the major effects of the environment. Unfortunately, the complete recreation of the environment is computationally demanding and only feasible at present for the CI/CASSCF/MCSCF computations of systems composed of a few hundred atoms.

The remaining alternative is to develop sets of realistic spatial constraints applied to the positions of the atoms forming artificial molecules, and incorporate those as the boundary conditions into the procedure of solving the Schrödinger equation for the artificial molecules by the CI/CASSCF/MCSCF energy minimization method. Unfortunately, there is no guarantee that a chosen predesigned geometry, structure, and composition of the studied atomic cluster would permit the existence and uniqueness of the solution of the Schrödinger equation that would signify that the cluster realizes, indeed, a stable artificial molecule. Helpful hints, however, can be obtained from a comparison of the existing experimental data on and modeling the formation of small, few-atomic semiconductor element clusters. In particular, recent experimental studies of the Si(111)- 7×7 surface reconstruction and so-called “surface mediated magic clustering” of Ga, In, Al, and Ge by the use of the atomic resolution STM methods confirm that the surface structure defines the symmetry of these artificial molecules.²³ The STM images of the clusters recovered upon the use of the *ab initio* simulation packages are in a remarkable agreement with a honeycomb atomic structure model of the 6-atomic In or Ga clusters. The bond angles (slightly larger than 109.5° in the case of In and slightly smaller than 109.5° for Ga) and atomic positions derived by the application of this model suggest the tetrahedral symmetry of these small clusters induced by the surface structure. It has been found that local optimization of the chemical bonds is essential for the exceptional stability of such “magic” clusters. Experimental studies of small islands of Ge on the (111) surfaces of silicon,²⁴ Ga on the SiC (001) surfaces,²⁵ and InAs on the (113) surfaces²⁶ of GaAs reveal the pyramidal form of these larger clusters. These findings suggest that the corresponding elementary clusters from which the islands have grown can be of the pyramidal geometry.

Computational studies of small vacuum Ga, In, Ga-As, In-As, and other few-atomic clusters^{14–18,27} also often point out that the pyramidal geometry corresponds either to the minimum energy, or to a saddle point on the total energy surfaces of the clusters. Therefore, one is led to a conclusion that the symmetry elements of the zinc blende or wurtzite bulk lattices provide realistic setups for the geometry of the predesigned molecules.

This conclusion has been further confirmed by computational design of In_3As , $\text{Ga}_{10}\text{As}_4$ and $\text{In}_{10}\text{As}_4$ almost-perfect pyramidal molecules from elemental zinc blende cube fragments of the GaAs and InAs bulk lattices formed of 14 Ga or In atoms at the cube vertices and the centers of the cube faces, and the 4 As atoms occupying the tetrahedral holes at $\frac{1}{4}$ of the cube body diagonals from the nearest cube vertices (see Refs. 3 or details). The covalent radii of In, As, and Ga in these lattices have been chosen equal to 1.44 Å, 1.18 Å, and 1.26 Å respectively, as given by experiment at 298.5 K (in the case of In and As) and 300 K (in the case of Ga). The ROHF total energy minimization procedure applied to the above described 18-atomic zinc blende lattice fragments reveals numerous “dangling bonds” that disappear when the extra 4 Ga or In atoms are removed, resulting in the pyramidal geometry of the stable molecules $\text{Ga}_{10}\text{As}_4$ and $\text{In}_{10}\text{As}_4$. In addition, a molecule where In atoms substitute Ga ones in

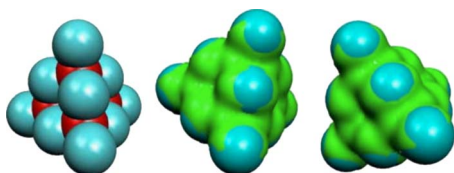


FIG. 1. (Color online) From left to right: the perfect pyramidal vacuum cluster $\text{Ga}_{10}\text{As}_4$ and the CDDs (green or gray surfaces) of the vacuum and predesigned $\text{Ga}_{10}\text{As}_4$ MCSCF triplets, respectively. The surfaces correspond to the fractions 0.03 of the respective maximum charge density values (not shown). Ga atoms are blue (light gray) and As red (dark gray); all dimensions are approximately to scale.

the otherwise Ga-based predesigned cluster has also been synthesized computationally. This substitution corresponds to assigning the Ga atomic covalent radii to In atoms, and results in the formation of the predesigned molecule $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$. The predesigned molecules so obtained have been further used to generate the corresponding vacuum molecules by relaxing the spatial constraints applied to the atomic positions in the predesigned clusters during the ROHF total energy minimization procedure. All of the ROHF-synthesized molecules have been further investigated by the CASSCF/MCSCF methods. The results of these studies are described and discussed below in detail.

A. CASSCF/MCSCF charge distributions of the studied artificial molecules

An application of the pyramidal configuration requirements described above and derived from the corresponding zinc blende lattice symmetry elements to spatially constrain positions of the atoms of the studied clusters has immediately led to the corresponding successful ROHF/CASSCF/MCSCF total energy minimization procedures. The ground states of these predesigned artificial molecules are triplets with the charge smoothly distributed over the molecular surfaces, thus signifying that there are no dangling bonds. After the relaxation of the spatial constraints applied to the atomic positions during the total energy minimization procedure, the corresponding ROHF/CASSCF/MCSCF vacuum counterparts of the predesigned molecules have been obtained. Their ground states are also triplets, and their structure and form are visually indistinguishable from those of the predesigned molecules (Figs. 1–3). This reflects the fact that the vacuum “optimization” of the atomic positions (i.e., the relaxation of the spatial constraint) leads to only small changes in atomic positions, approximately of the order of 10^{-2} Å (in a very few cases 0.09 Å).

The obtained results are in a good agreement with the available computational data on small $\text{Ga}_{13-n}\text{As}_n$ ($0 \leq n \leq 13$) clusters reviewed and studied in Ref. 15. These data have been obtained by the use of simpler ROHF-based methods (including a CASSCF one, with a relatively small set of basic functions), and are focused on the vacuum geometry and binding energies of the clusters. The corresponding direct optical transition energies (OTEs) and the ground state energies have not been specified. In particular, it has been

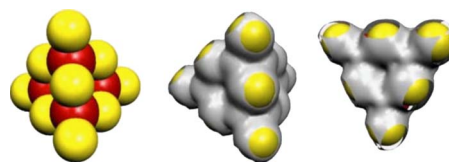


FIG. 2. (Color online) From left to right: the perfect pyramidal “natural” vacuum cluster $\text{In}_{10}\text{As}_4$ and the CDDs (gray surfaces) of the vacuum and predesigned $\text{In}_{10}\text{As}_4$ MCSCF triplets, respectively. The surfaces correspond to the fractions 0.04 and 0.06 of the maximum charge density values (not shown) for the vacuum and predesigned clusters, respectively. The In atoms are yellow (light gray) and As red (dark gray); all dimensions are approximately to scale.

found¹⁵ that among the clusters of 5, 6, and 13 atoms those with the higher ratio of As atoms to Ga atoms are more stable, and such smaller clusters possess the pyramidal form (see, also, Refs. 16–18). Accordingly, the ROHF/CASSCF/MCSCF results of the present work prove that all of the predesigned and vacuum clusters Ga_nAs_4 with $n > 10$ are unstable. Thus, among the larger than 13-atom clusters with 4 As atoms, only $\text{Ga}_{10}\text{As}_4$ ones are stable, and therefore realize the corresponding artificial molecules.

As mentioned above, the original predesigned pyramids have not been noticeably changed by the atomic position optimization. However, even such small changes in the atomic positions lead to significant changes in the electronic properties of the vacuum molecules as compared to those of the predesigned ones. As demonstrated below, these small changes also are sufficient to destroy or introduce the tetrahedral symmetry, which is reflected by the electronic energy level structures (ELs).

The minimum and maximum values of the CDDs and CDD surfaces of the vacuum and predesigned Ga-based molecules (Fig. 1) do not differ significantly. In both cases, the CDDs do not stretch far into the space beyond that occupied by the molecules, and the surfaces corresponding to the fractions over 0.04 of the respective maximum CDD values are entirely confined within the molecules. However, the dipole moments of these molecules differ almost four times (5.1437 D and 1.5827 D for the vacuum and predesigned molecules, respectively). This, of course, is caused by the loss of the computationally accurate tetrahedral symmetry during the atomic position optimization used to synthesize the vacuum Ga-based molecule.

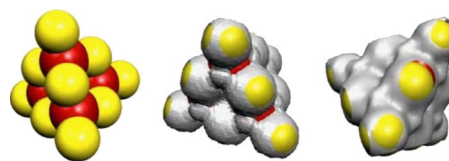


FIG. 3. (Color online) From left to right: the perfect pyramidal “artificial” vacuum cluster $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ and the CDDs (gray surfaces) of the vacuum and predesigned $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ MCSCF triplets, respectively. The surfaces correspond to the fractions 0.05 and 0.07 of the maximum charge density values (not shown) for the vacuum and predesigned clusters, respectively. The In atoms are yellow (light gray) and As red (dark gray); all dimensions are approximately to scale.

In the case of the “natural” In-based molecules (built using the In covalent radius specific to that of the In-As bulk lattice), discrepancies between the predesigned and vacuum molecules (Fig. 2) are larger than those between the corresponding Ga-based molecules. While the minimum and maximum CDD values of the natural In-based molecules do not differ significantly, their CDD surfaces do. In particular, the CDD of the predesigned molecule reaches much further into the space beyond the molecule. For example, the surface corresponding to the fraction 0.06 of the maximum CDD value is entirely confined in the space occupied by the vacuum molecule, while the corresponding surface of the predesigned molecule is outside of the predesigned molecule space. The dipole moment of this predesigned molecule is 5.8565 D, as opposed to the zero dipole moment of the corresponding vacuum molecule.

Interestingly, the “artificial” predesigned molecule $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$, where the In atoms are assigned the Ga atomic covalent radii (Fig. 3), does not disintegrate during the atomic position optimization, and the corresponding vacuum molecule does not closely resemble the natural vacuum $\text{In}_{10}\text{As}_4$ molecule. Instead, it realizes yet another pyramid that has its own structural and electronic characteristics significantly different from those of the corresponding natural vacuum molecule. The CDDs of the $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ molecules reach into the space outside of the molecules further than those of the natural $\text{In}_{10}\text{As}_4$ molecules. Thus, the surfaces corresponding to the fraction 0.05 of the maximum CDD values are outside the vacuum and predesigned $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ molecules, respectively, while the corresponding surfaces are confined inside the molecular space in the case of the respective natural In-based molecules. The dipole moments of the predesigned and vacuum molecules $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ are large, 5.2693 D and 10.0917 D, respectively.

The vacuum $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ molecule may serve as an example of an isomer of the natural vacuum molecule $\text{In}_{10}\text{As}_4$. Most likely, its existence (and that of other isomers discovered computationally in many reported cases) is caused by shortcomings of the available computational procedures. Specifically, the existing algorithms and software realizations of the first-principle theoretical methods provide means to determine only a local minimum value for the total energy of a considered system, and do not ensure finding the global one. Moreover, due to numerous, and often heuristic, approximations necessary to realize computationally the existing analytical methods, and a nonuniform convergence of the used minimization procedures, artificial minimum values of the total energy may be introduced and the “true” minimum energy values may be disregarded as saddle points, for example. This observation brings to the surface an importance of the use of additional fundamental considerations (such as a confinement symmetry-driven design suggested in this paper) that would help select the correct global minimum energy values and the corresponding molecular structure of a virtually synthesized molecule among a set of numerically realized candidates.

As applied to the case of the $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ molecules, this means that the predesigned $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ molecule may be realized in an appropriate confinement (such as that provided

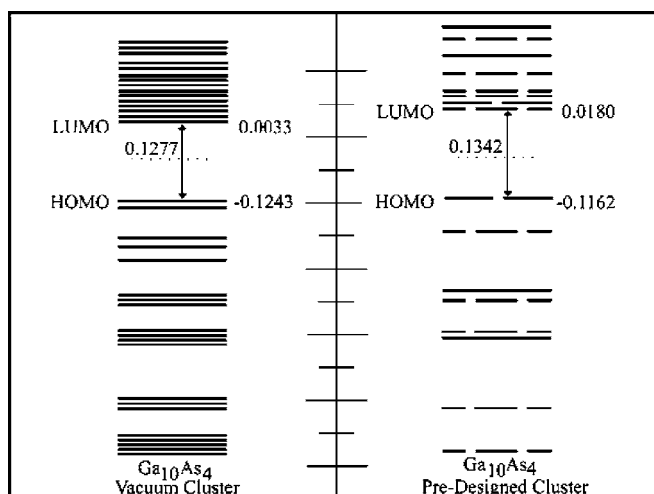


FIG. 4. The ELS of the vacuum and predesigned ROHF $\text{Ga}_{10}\text{As}_4$ triplets in the HOMO-LUMO regions. The electronic energy level values and the OTEs are in Hartree units. All separation distances are approximately to scale. The double- and triple-degenerate MOs of the predesigned molecule reflect its tetrahedral symmetry.

by the surrounding Ga bulk lattice, for example), and is likely to be a realistic model for similar small experimental In-based clusters nucleating on Ga surfaces or inside of the Ga bulk lattice. The vacuum $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ molecule, however, may not be stable if synthesized experimentally. This conclusion is made possible due to a comparison of the origins and properties of the vacuum $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ molecule and its natural counterpart, both of which emerged as a result of the well defined, symmetry-driven virtual synthesis procedure described above.

B. ROHF/CASSCF/MCSCF electronic properties of the synthesized molecules

To ensure a fast convergence of the CASSCF/MCSCF approximation procedures, the computations begin with the molecular orbitals (MOs) provided by the ROHF method using the largest available SBKJC basis function sets.²¹ The basis functions are applied on top of the effective core potential (ECP) that includes scalar relativistic contributions. The ROHF ELS fragments composed of about 30 MOs in the vicinity of the highest occupied and lowest unoccupied MOs (HOMOs and LUMOs, respectively) of the molecules virtually synthesized in this work are depicted in Figs. 4–6. With an exception of the natural In-based molecules, these data demonstrate a destruction of the tetrahedral symmetry of the predesigned molecules by the atomic position optimization: the ELSs of the vacuum molecules so obtained do not have doubly and triply degenerate MOs. The lifting of the degeneracy leads to the development of series of closely lying occupied MOs in the vacuum molecules. The predesigned molecules have smaller OTEs (the HOMO-LUMO energy differences). Notably, the ELS of the natural In-based predesigned molecule (Fig. 6) do not reflect the tetrahedral symmetry, despite the apparent pyramidal geometry of the

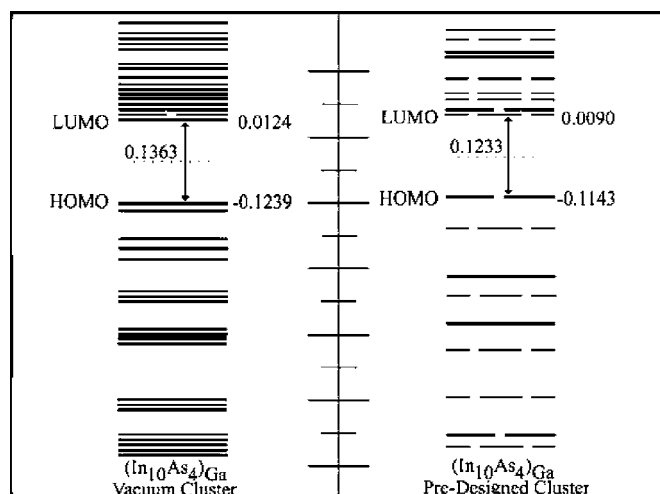


FIG. 5. The ELS of the vacuum and pre-designed ROHF $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ triplets in the HOMO-LUMO regions. The electronic energy level values and the OTEs are in Hartree units. All separation distances are approximately to scale. The double- and triple-degenerate MOs of the pre-designed molecule reflect its tetrahedral symmetry.

molecule. In fact, the corresponding vacuum cluster is more symmetric, featuring a number of doubly degenerate MOs. This confirms, once again, that the experimental covalent radius of the In atoms in the bulk In lattice used in the computations is not quite accurate.

A comparison of the pre-designed ROHF $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ triplet (Fig. 5) and its “parent” pre-designed ROHF triplets $\text{Ga}_{10}\text{As}_4$ and $\text{In}_{10}\text{As}_4$ (Figs. 4 and 6, respectively) leads to an important observation. It appears that the ELS of the pre-designed ROHF $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ triplet closely follows that of the pre-designed $\text{Ga}_{10}\text{As}_4$ triplet, while the electronic energy level values, the OTE and the value of the ground state energy are close to those of the pre-designed natural $\text{In}_{10}\text{As}_4$ triplet. Therefore, in the studied cases of small semiconductor com-

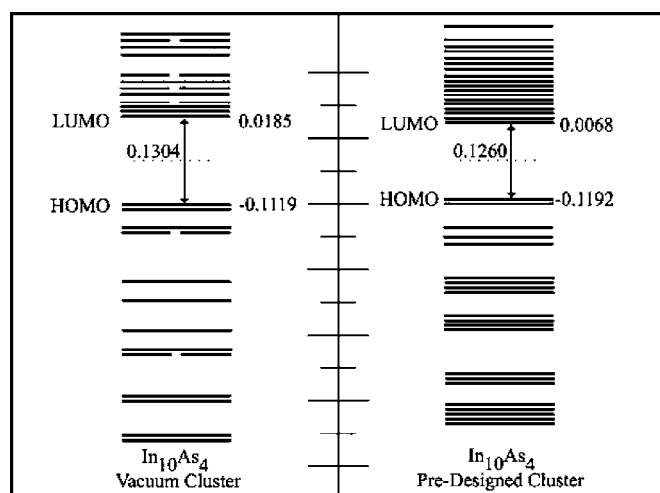


FIG. 6. The ELS of the vacuum and pre-designed natural ROHF triplets $\text{In}_{10}\text{As}_4$ in the HOMO-LUMO regions. The electronic energy level values and the OTEs are in Hartree units. All separation distances are approximately to scale.

pound clusters the atomic covalent radii define the ELS, while all of the relevant energy values are defined by the physical nature of the atoms.

This conclusion correlates with numerous experimental data (although obtained for much larger In-based clusters) mentioned in Sec. I and can be applied to evaluation of possible outcomes of virtual and experimental synthesis of artificial molecules in quantum confinement. Indeed, in the considered case the assignment of the Ga covalent radii to the In atoms reflects conditions of a strain-driven formation of an $\text{In}_{10}\text{As}_4$ cluster inside of the Ga bulk lattice or a similarly structured quantum confinement, and thus corresponds to a realistic experimental situation.

The MOs of the considered six ROHF triplets $\text{Ga}_{10}\text{As}_4$, $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$, and $\text{In}_{10}\text{As}_4$ have been further used as an input for the corresponding CASSCF/MCSCF computations of the ground states of these artificial molecules. Four lowest CASSCF/MCSCF total energy states have been computed for every considered molecule. The largest available SBKJC basic function sets²¹ have been used. A choice of the complete active spaces (CASs) in most cases has been straightforward, as neither the CI procedure (the Davidson method) nor the two-particle charge density matrix calculations could produce meaningful results until the CASs have become large enough, involving 8 electrons and from 7 to 13 active MOs. The reason for these large CASs is provided by the tetrahedral symmetry and the nature of bonding in the considered nonstoichiometric molecules (see discussions in Sec. I and Ref. 12). Only in the case of the vacuum molecule $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ several CASs, from the smallest 2×4 to the large 8×10 one, have led to successful convergence of the CASSCF/MCSCF computational procedure, thus providing important information about the effects of the CAS choice on the values of the corresponding OTEs. This CAS flexibility of the vacuum molecule $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ does not agree with the physical nature of the molecule, and thus confirms again, that this molecule may be unstable if synthesized experimentally.

In Table I the obtained CASSCF/MCSCF computation results are summarized and compared to the respective ROHF data for all of the virtually synthesized molecules. All energy values listed in this table are calculated with the computational accuracy at least 10^{-12} Hartree, but only 6 or 4 digits after the dot are included in the listed data for simplicity.

In the case of the $\text{Ga}_{10}\text{As}_4$ molecules, the OTEs follow the tendencies suggested by the reported binding energies of smaller Ga-As clusters (see Refs. 15–18). Unfortunately, a similar information on small In-As clusters, apart from the molecule In_3As_3 ,³ is not available for a comparison.

As it can be seen from the results collected in Table I, the ROHF OTEs of all of the synthesized molecules are between 3.3 eV and 3.7 eV. A comparison of these values with the corresponding CASSCF/MCSCF ones leads to a confirmation of the well-known fact that the ROHF method does not allow accurate computations of the excited state energies, such as the LUMO, thus leading to a large error in the OTE evaluation. The CASSCF/MCSCF computations reveal a much more complicated picture where the MCSCF OTEs range from 0.8684 eV for the natural vacuum In-based molecules to 3.1813 eV for the artificial pre-designed one. The total energy minimum values of the vacuum molecules and

TABLE I. The ROHF and CASSCF/MCSCF energy spectrum data for the virtually synthesized predesigned and vacuum $\text{Ga}_{10}\text{As}_4$, $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$, and $\text{In}_{10}\text{As}_4$ molecules.

Artificial molecule	ROHF ground state (triplet) energy, $(-1) \times 1$ Hartree	ROHF direct optical transition energy, eV	MCSCF ground state (triplet) energy, $(-1) \times 1$ Hartree	MCSCF direct optical transition energy, eV	CAS (number of electrons \times MOs)
$\text{Ga}_{10}\text{As}_4$	2595.964256	3.6517	2596.026856	0.9312	8×13
$\text{Ga}_{10}\text{As}_4^a$	2595.987503	3.4749	2596.025906	2.3508	8×8
$[\text{In}_{10}\text{As}_4]_{\text{Ga}}$	1906.830250	3.3552	1906.883612	1.7803	8×10
$[\text{In}_{10}\text{As}_4]_{\text{Ga}}^a$	1906.845323	3.3334	1906.840516	6.5109	2×4
			1906.847588	3.6994	4×7
			1906.865828	1.0834	8×7
			1906.872776	3.1813	8×10
$\text{In}_{10}\text{As}_4$	1907.035049	3.4286	1907.077256	2.9964	6×9
$\text{In}_{10}\text{As}_4^a$	1906.961402	3.4232	1906.859968	0.8684	8×8

^aDenotes vacuum molecules.

those of their predesigned counterparts are within the expected accuracy of the CASSCF/MCSCF approximation, in agreement with the observation that the atomic positions in the vacuum molecules differ only slightly (10^{-2} Å, on average) from their respective positions in the corresponding predesigned molecules. The MCSCF OTEs of the vacuum triplets differ significantly from those of their predesigned counterparts, in agreement with experimental data widely used in semiconductor materials technologies and showing that even for large atomic clusters composed of thousands of atoms and thin films a small change in the covalent radii (due to the strain, for example) leads to a change up to 25% in the band gap values and other electronic properties of the clusters. The worst expected accuracy of the CASSCF/MCSCF approximation for the OTEs of medium-heavy atoms is from about 0.1 to²⁰ 0.2 eV and therefore, all of the differences between the MCSCF OTEs of the vacuum and predesigned molecules are well above possible errors introduced by the CASSCF/MCSCF approximation.

The obtained MCSCF OTE data demonstrate a crucial role played by a choice of the CAS in every particular case. Generally, for the semiconductor compound molecules studied here, small CASs do not allow the CASSCF/MCSCF procedures to converge, thus automatically suggesting the use of larger CASs. The reasons for this are manifold and originate from a complexity of the Coulomb interactions and their screening specific to the electronic structures of the considered molecules that have 50 valence and hundreds of deeper lying electrons. For such molecules even the deeply lying electronic orbitals provide significant contributions to the bonding, or physically, to the outer portions of the CDDs all of which are essential for the stability of the molecules. This phenomenon necessitates the development of new approaches¹² to description of the valence and bonding in nonstoichiometric molecules that should go beyond the classical valence theory with its octet rule.

The artificial vacuum molecule $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ appears to be the most CAS-tolerant, thus allowing an investigation of the effects of a CAS choice on the MCSCF ground state energy and OTE values. Generally, the nonlinearity of the ROHF/CASSCF/MCSCF approximations does not permit us to suggest simple correlations to describe such effects. The smallest CAS of the outer 2 electrons distributed over 4 active MOs provides the largest OTE value for the vacuum molecule $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$. The subsequent extensions of the CAS lead first to a decrease and then to an increase in the OTE values. The most appropriate CAS for this molecule is the 8×10 one (5 filled electronic energy levels in the HF HOMO region and 5 levels in the HF LUMO region), as it provides the lowest ground state energy. The OTE value computed using this CAS is 3.1813 eV. This choice of the most appropriate CAS for the vacuum molecule $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ is further supported by the observation that the smallest CASs of the other studied molecules involve 8 electrons and about 10 active MOs. The only exception is the natural predesigned molecule $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ for which CASs with 8 electrons do not lead to converging MCSCF procedures. The reason for this may originate from an already discussed possibility that the experimental value of the covalent radius of In used in virtual synthesis of this molecule is not sufficiently accurate to provide for the fine details of the electronic structure.

The obtained MCSCF data indicate that the electronic properties of small semiconductor compound molecules can be fine tuned to meet particular technological requirements. For example, in the Ga-based molecule case, the MCSCF OTEs are varied from about 0.9312 eV to 2.3508 eV with a very small variation in the positions of the atoms forming the molecules. Therefore, the carefully chosen geometry, structure, and composition of a quantum confinement can be instrumental for the formation of molecules with finally tuned, desirable electronic properties.

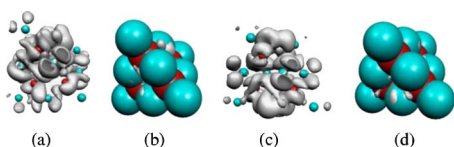


FIG. 7. (Color online) The SDD surfaces (gray) of the $\text{Ga}_{10}\text{As}_4$ molecules corresponding to fractions (cuts) of the respective maximum SDD values (not shown). (a) The vacuum molecule with the atomic dimensions reduced to reveal the structure of the surfaces inside the molecule: the cut 10^{-3} . (b) The same as in (a), but all dimensions are to scale. (c) The predesigned molecule with the atomic dimensions reduced: the cut 10^{-3} . (d) The same as in (c), but all dimensions are to scale. The SDD maximum value of the predesigned molecule is about 3 times larger than that of the vacuum one. The Ga atoms are blue (light gray), As red (dark gray).

C. Spin density distributions of the virtually synthesized molecules

The CASSCF/MCSCF spin density distributions (SDDs) of the studied molecules are visualized in Figs. 7–9. As can be seen from the space-filled images, these SDDs are contained inside the space occupied by the molecules. The maximum values of the SDDs are relatively small, although those of the In-based molecules are larger than those of the Ga-based ones.

The CASSCF/MCSCF computations show that the SDDs of the predesigned molecules are slightly more evenly spread over the molecular spaces than the SDDs of the corresponding vacuum molecules. This observation indicates that the spatial constraints applied to the atomic positions help the collectivization of the electrons. Therefore, the molecules synthesized in quantum confinement may have enhanced magnetic properties, as compared to those of the corresponding vacuum molecules. However, in the cases considered in the present study the absolute values of the SDDs are very small. Therefore, these molecules are not expected to be of interest as a possible physical realization of the Q bit of quantum information, in contrast to similar molecules containing an added vanadium atom.²⁸

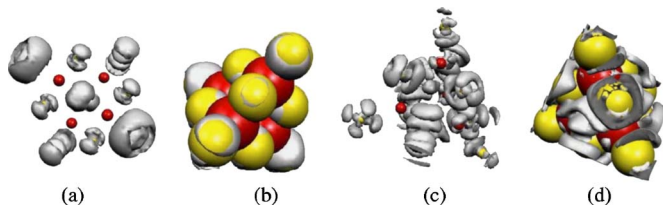


FIG. 8. (Color online) The SDD surfaces (gray) of the natural $\text{In}_{10}\text{As}_4$ molecules corresponding to fractions (cuts) of the respective maximum SDD values (not shown). (a) The vacuum molecule with atomic dimensions reduced: the cut 10^{-3} . (b) The vacuum molecule: the cut 10^{-4} ; all dimensions are to scale. (c) The predesigned molecule with atomic dimensions reduced: the cut 10^{-3} . (d) The predesigned molecule: the cut 10^{-4} ; all dimensions are to scale. The SDD maximum value of the predesigned molecule is about 3 times smaller than that of the vacuum one. The In atoms are yellow (light gray), As red (dark gray).

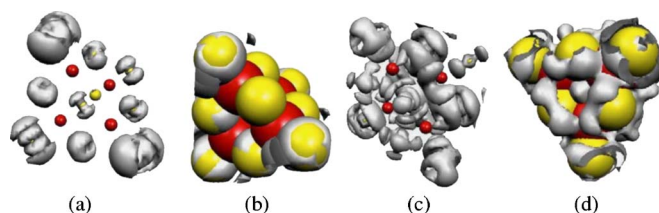


FIG. 9. (Color online) The SDD surfaces (gray) of the artificial $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ molecules corresponding to fractions (cuts) of the respective maximum SDD values (not shown). (a) The vacuum molecule with atomic dimensions reduced; the cut 10^{-3} . (b) The vacuum molecule; the cut 10^{-4} ; all dimensions are to scale. (c) The predesigned molecule with atomic dimensions reduced; the cut 10^{-3} . (d) The predesigned molecule; the cut 10^{-4} ; all dimensions are to scale. The SDD maximum value of the predesigned molecule is about 4 times smaller than that of the vacuum one. The In atoms are yellow (light gray), As red (dark gray).

III. CONCLUSIONS AND PROSPECTS

During the recent decades, the quantum statistical mechanical methods and their computational realizations are increasingly applied to the problem of synthesis of atomic clusters and artificial molecules with the predesigned electronic properties for the use in quantum electronics and quantum information processing. In the work reported here a powerful HF based, CASSCF/MCSCF method (as realized by the GAMES software package) has been successfully used to configure several stable small atomic clusters composed of 10 Ga or In atoms and 4 As atoms. These clusters serve as an example of some of the smallest QDs that can be realized experimentally. Preliminary investigations reveal that such nonstoichiometric clusters are stabilized via a covalent ligand bonding, as suggested in Ref. 12, and thus can be considered as artificial molecules. [Detailed studies of bonding in the virtually synthesized molecules are planned in the near future.] This conclusion is further supported by the available experimental data on the stability, ELS, and OTE of, and electronic binding in the experimentally realized small atomic clusters and larger pyramidal QDs discussed in Sec. I. In agreement with the presented theoretical results, these experimental data demonstrate that such experimentally designed objects are stable and possess distinctive quantum properties typical for atoms and molecules, including the quantized energy spectra and large OTEs.

The geometry, structure, and composition of the artificial molecules virtually designed in this study have been derived from that of the tetrahedral (pyramidal) symmetry elements of the GaAs and InAs semiconductor bulk lattices, and used in the computations in the form of spatial constraints applied to the atomic positions in the molecules. It has been demonstrated that such a symmetry based, systematic approach to the virtual design of artificial molecules provides a means to develop realistic computational models (templates) for artificial semiconductor compound molecules that may nucleate in quantum confinement or at interfaces, without a recreation of all of the atomistic scale details of the environment that shapes the nucleation. Among other capabilities, this approach has a potential to develop into one of the across-the-

scale modeling procedures that are very important for various applications in physics and technology.

One of the advantages of the symmetry-driven virtual design method reported and used in this study is a convenience to monitor a change in the properties of the pre-designed artificial molecules (exemplifying realistic results of the quantum confinement-driven nucleation) caused by a variation in the confinement structure as reflected by the corresponding changes in or relaxation of the spatial constraints applied to the atomic position. In the reported study, this capacity of the method has been used to compare the electronic properties of the pre-designed molecules to those of their vacuum counterparts obtained by the complete relaxation of the spatial constraints applied to the atomic positions. This comparison reveals the leading role of the quantum confinement effects (as modeled by the use of the spatial constraint) in shaping the electronic structure properties of the molecules synthesized in the confinement. In particular, it has been demonstrated that a small change in the covalent radii (i.e., bond lengths) of the atoms within an artificial molecule leads to a dramatic change in the electronic level structure and OTE, while having a little effect on the overall geometry, spatial structure, and total energy of the molecule. Although small, such changes in atomic positions lead to reshaping of the electronic energy level patterns, a degeneracy (or its lift) of the electronic energy levels, the development of the electronic level bands, etc.

Yet another important feature of the symmetry-based virtual design method is that the spatial constraints applied to the atomic positions may be used to model the strain-dominated nucleation effects that are often used in electronic materials technologies. Thus, a substitution of the Ga atoms by In ones in the pre-designed $\text{Ga}_{10}\text{As}_4$ molecule without a change in the Ga-driven spatial structure of this molecule permits to synthesize virtually a stable artificial pre-designed $[\text{In}_{10}\text{As}_4]_{\text{Ga}}$ molecule. A comparison of the electronic properties of this molecule to those of its Ga-based parent, and those of the natural In-based pre-designed molecule, has led to an important observation that is supported by the available experimental evidence and is likely to be correct for large classes of artificial nonstoichiometric molecules. Specifically, the electronic energy level structure of a small nonstoichiometric molecule is shaped by the environment in which the molecule nucleates (in the considered case, such an environment is modeled through the use of the geometry of the parent Ga molecule), while all of the energies and energy differences, such as the ground state energy and OTE (see Table I), are defined by the physical nature of the atoms comprising the molecule. In addition to practical implications of this observation discussed below, there is an important methodological one. In particular, an analysis of “inherent” features of the electronic properties of an artificial nonstoichiometric molecule may help identify the true stable

molecule among a set of its computational or unstable experimental isomers.

As accounted for by the CASSCF/MCSCF method, the physics of the small nonstoichiometric molecules of semiconductor compound atoms configured in this work is shaped by a sensitive balance of the Coulomb interactions between hundreds of electrons of the Ga or In atoms, only a portion of which can be shared with the available four arsenic atoms. Some of these “extra” electrons occupy MOs derived from those of the available incomplete inner shells of the atoms comprising the molecule, but the rest of the electrons must be accommodated by the Ga or In atoms themselves. To achieve this effect, the entire electronic level structure of a nonstoichiometric molecule has to be configured in such a fashion that a large number of the outer MOs could participate in the electron sharing (covalent ligand bonding) and “stretching” the total electronic charge over a larger physical space. Not surprisingly, in all of the studied cases, the computational results show that 230 of the outer MOs have to be explicitly incorporated into computations. In agreement with the existing experimental observations, the above theoretical results show that a significant electronic charge is accumulated at the “surfaces” of these molecules, so that the molecules can act as a source of electrons. The development of a tractable and at the same time rigorous, fundamental quantum-theoretical description of bonding in and equilibrium electronic properties of nonstoichiometric semiconductor compound molecules is a challenging task that has to be addressed in the near future.

An important practical implication of the results obtained in this work is that the quantum confinement effects can be used to configure the ELSs and tune the OTEs of small nonstoichiometric semiconductor compound QDs within a wide range of values (up to several times in the cases studied here) to meet specific technological requirements. Examples of such molecules studied here (Table I) demonstrate that the gain/loss in the OTE values of similar small nonstoichiometric QDs synthesized in quantum confinement (with all of the atoms constrained) can be much larger than those currently realized (up to about 25%) through various technological improvements of the essentially surface-based nucleation procedures favored by the industry. Numerous fundamental challenges posed by small nonstoichiometric molecules of semiconductor compound atoms and their exceptional electronic properties suggest that experimental prototypes of the molecules designed in this work will be realized in the near future.

ACKNOWLEDGMENTS

L.A.P. acknowledges a support provided by the National Science Foundation (through the DMR No. 0340613), the National Research Council, and the Materials and Manufacturing Directorate of the Air Force Research Laboratory.

- *Corresponding author; email addresses: LPozhar@yahoo.com; Liudmila.Pozhar@wku.edu
- ¹*Optics of Quantum Dots and Wires*, edited by G. W. Bryant and G. S. Solomon (Artech House, Boston, 2005); N. Agraït, A. L. Yeyati and J. M. van Ruitenbeck, *Phys. Rep.* **377**, 81 (2003); J. P. Bird, R. Akis, D. K. Ferry, A. P. S. de Moura, Y. C. Lai, and K. M. Indlekofer, *Rep. Prog. Phys.* **66**, 583 (2003); D. K. Ferry, *Superlattices Microstruct.* **28**, 329 (2000); J. H. Davies, *The Physics of Low Dimensional Semiconductors* (Cambridge University Press, Cambridge, 1998).
- ²D. Crawley, K. Nikolic, and M. Rorshaw, *3-D Nanoelectronic Computer Architecture and Implementation* (Taylor & Francis/CRC Press, London, 2004).
- ³See, for example, L. A. Pozhar, A. T. Yeates, F. Szmulowicz, and W. C. Mitchel, *Europhys. Lett.* **71**, 380 (2005); L. A. Pozhar, A. T. Yeates, F. Szmulowicz, and W. C. Mitchel, *Mater. Res. Soc. Symp. Proc.* **829**, 49 (2005); **788**, 165 (2004); **790**, 169 (2004); G. W. Briant and W. Jaskolski, *ibid.* **789**, N13.2 (2004), and references therein.
- ⁴See, for example, B. Paulus, *Phys. Rep.* **428**, 1 (2006); *Quantum Theory of Real Materials*, edited by J. R. Chelikowsky and S. G. Louie (Kluwer, Boston, 1996); A. J. Freeman, *Annu. Rev. Mater. Sci.* **25**, 1 (1995); A. J. Freeman and E. Wimmer, *ibid.* **25**, 7 (1995); D. L. Smith and C. Mailhot, *Rev. Mod. Phys.* **62**, 173 (1990); B. O. Ross, *Adv. Chem. Phys.* **69**, 399 (1987), and references therein.
- ⁵L. A. Pozhar, cond-mat/0502476; L. A. Pozhar, *Mater. Res. Soc. Symp. Proc.* **789**, 49 (2004); L. A. Pozhar and K. E. Gubbins, *Phys. Rev. E* **56**, 5367 (1997); L. A. Pozhar, *ibid.* **61**, 1432 (2000); J. M. D. MacElroy, L. A. Pozhar, and S.-H. Suh, *Colloids Surf., A* **A187-A188**, 493 (2001); L. A. Pozhar, E. V. Kontar, and M. Z.-C. Hu, *J. Nanosci. Nanotechnol.* **2**, 209 (2002); L. A. Pozhar, V. F. de Almeida, and M. Z.-C. Hu, *Ceram. Trans.* **137**, 101 (2003).
- ⁶See also D. N. Zubarev, *Sov. Phys. Usp.* **3**, 320 (1960/61); D. N. Zubarev, *Nonlinear Statistical Thermodynamics* (Plenum Press, New York, 1974); S. V. Tyablikov, *Methods in the Quantum Theory of Magnetism* (Plenum Press, New York, 1967); N. N. Bogolyubov, *Introduction to Quantum Statistical Mechanics* (World Scientific, New Jersey, 1982); N. N. Bogolyubov, A. A. Logunov, A. I. Oksak, and I. T. Todorov, *General Principles of Quantum Field Theory* (Nauka, Moscow, 1987); N. N. Bogolyubov, *Selected Works*, edited by N. N. Bogolyubov, Jr., and A. M. Kurbatov (Gordon and Breach, New York, 1991); Yu. A. Tserkovnikov, *Dokl. Akad. Nauk SSSR* **143**, 832 (1962) [*Sov. Phys. Dokl.* **7**, 15 (1962/63)]; G. F. Mazenko, *Phys. Rev. A* **7**, 209 (1973); **7**, 222 (1973); **9**, 360 (1974); D. N. Zubarev and Yu. A. Tserkovnikov, *Tr. Mat. Inst. Steklova* **175**, 139 (1986) [Proceedings of the Steklov Institute of Mathematics **2**, 139 (1988)], etc., where the TTGF method was developed and applied to various problems of nonequilibrium statistical mechanics of bulk systems.
- ⁷F. Li, L. Zhang, and R. M. Metzger, *Chem. Mater.* **10**, 2470 (1998); O. Jessensky, F. Muller, and U. Gösele, *Appl. Phys. Lett.* **72**, 1173 (1999); R. R. Meyer, J. Sloan, R. E. Dunin-Borkowski, A. I. Kirkland, M. C. Novotny, S. R. Bailey, J. L. Hutchinson, and M. L. H. Green, *Science* **289**, 1324 (2000); P. S. Fodor, G. M. Tsoi, and L. E. Wenger, *J. Appl. Phys.* **91**, 8186 (2002).
- ⁸T. Fukui, S. Ando, Y. Tokura, and T. Toriyama, *Appl. Phys. Lett.* **58**, 2018 (1991); T. Fukui and S. Ando, *Superlattices Microstruct.* **12**, 141 (1992); Y. Nagamune, M. Nishioka, S. Tsukamoto, and Y. Arakawa, *Appl. Phys. Lett.* **64**, 2495 (1994); K. C. Rajkumar, K. Kaviani, J. Chen, P. Chen, and A. Madhukar, *ibid.* **60**, 850 (1992); A. Madhukar, K. C. Rajkumar, and P. Chen, *ibid.* **62**, 1547 (1993); K. C. Rajkumar, A. Madhukar, K. Rammohan, D. H. Rich, P. Chen, and L. Chen, *ibid.* **63**, 2905 (1993); K. C. Rajkumar, A. Madhukar, P. Chen, A. Konkar, L. Chen, K. Rammohan, and D. H. Rich, *J. Vac. Sci. Technol. B* **12**, 1071 (1994); R. L. Williams, G. C. Aers, P. J. Poole, J. Levebvre, D. Chithrani, and B. Lamontagne, *J. Cryst. Growth* **223**, 321 (2001); J. Levebvre, P. J. Poole, G. C. Aers, D. Chithrani, and R. L. Williams, *J. Vac. Sci. Technol. B* **20**, 2173 (2002); D. Chithrani, R. L. Williams, J. Levebvre, P. J. Poole, and G. C. Aers, *Appl. Phys. Lett.* **84**, 978 (2004).
- ⁹E. Kapon, E. Pelucchi, S. Watanabe, A. Malko, M. H. Baier, K. Leifer, B. Dwir, F. Michelini, and M.-A. Dupertuis, *Physica E (Amsterdam)* **25**, 288 (2004); F. Michelini, M.-A. Dupertuis, and E. Kapon, *Appl. Phys. Lett.* **84**, 4086 (2004); S. Watanabe, E. Pelucchi, B. Dwir, M. H. Baier, K. Leifer, and E. Kapon, *ibid.* **84**, 2907 (2004); M. H. Baier, S. Watanabe, E. Pelucchi, and E. Kapon, *ibid.* **84**, 1943 (2004); E. Pelucchi, S. Watanabe, K. Leifer, B. Dwir, and E. Kapon, *Physica E (Amsterdam)* **23**, 476 (2003).
- ¹⁰See, for example, L.-W. Wang, J. Kim, and A. Zunger, *Phys. Rev. B* **59**, 5678 (1999); J. Kim, L.-W. Wang, and A. Zunger, *ibid.* **57**, R9408 (1998); A. Zunger and L.-W. Wang, *Appl. Surf. Sci.* **102**, 350 (1996).
- ¹¹J.-Z. Zang and I. Galbraith, *Appl. Phys. Lett.* **84**, 1934 (2004); J.-Y. Marzin and G. Bastard, *Solid State Commun.* **92**, 437 (1994); M. Grundmann, O. Stier, and D. Bimberg, *Phys. Rev. B* **52**, 11969 (1995); T. Nakaoka, T. Saito, J. Tatebayashi, and Y. Arakawa, *ibid.* **70**, 235337 (2004); G. Alan, Y. M. Niquet, and C. Delerue, *Appl. Phys. Lett.* **77**, 639 (2000); H. Jiang and J. Singh, *Phys. Rev. B* **56**, 4696 (1997); T. Saito, J. N. Schulman, and Y. Arakawa, *ibid.* **57**, 13016 (1998); K. Chang and J.-B. Xia, *Solid State Commun.* **104**, 351 (1997).
- ¹²A. I. Boldyrev and L.-S. Wang, *J. Phys. Chem. A* **105**, 10759 (2001).
- ¹³See, for example, A. K. Singh, T. M. Briere, V. Kumar, and Y. Kawazoe, *Phys. Rev. Lett.* **91**, 146802 (2003); V. Kumar and Y. Kawazoe, *ibid.* **90**, 055502 (2003); J. Lu and S. Nagase, *ibid.* **90**, 115506 (2003), and references therein.
- ¹⁴E. F. Archiborg, A. St-Amant, S. K. Goh, and D. S. Marynick, *Chem. Phys. Lett.* **361**, 411 (2002); A. Costales, A. K. Kandalam, R. Franko, and R. Pandey, *J. Phys. Chem. B* **106**, 1940 (2002); P. P. Korambath and S. Karna, *J. Phys. Chem. A* **104**, 4801 (2000); P. P. Korambath, B. B. K. Singaraju, and S. P. Karna, *Int. J. Quantum Chem.* **77**, 563 (2000); P. Piquini, S. Canuto, and A. Fazio, *Nanostruct. Mater.* **10**, 635 (1998).
- ¹⁵H. K. Quek, Y. P. Feng, and C. K. Ong, *Z. Phys. D: At., Mol. Clusters* **42**, 309 (1997).
- ¹⁶S. Erkos and L. Turker, *Physica E (Amsterdam)* **5**, 7 (1999).
- ¹⁷J.-Y. Yi, *Phys. Rev. B* **61**, 7277 (2000); *Chem. Phys. Lett.* **325**, 269 (2000).
- ¹⁸H. H. Kwong, Y. P. Feng, and T. P. Boo, *Comput. Phys. Commun.* **142**, 290 (2001).
- ¹⁹G. W. Bryant and W. Jaskolski, *Mater. Res. Soc. Symp. Proc.* **789**, N3.10 (6p) (2004).
- ²⁰I. N. Levine, *Quantum Chemistry*, fifth edition (Prentice Hall,

- New Jersey, 2000); A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry* (McGraw Hill, New York, 1989); *Ab Initio Methods in Quantum Chemistry. Part II* edited by K. P. Lawley (Wiley & Sons, New York, 1987); B. O. Ross, *Adv. Chem. Phys.* **69**, 399 (1987); C. C. J. Roothaan, *Rev. Mod. Phys.* **32**, 179 (1960).
- ²¹M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.* **14**, 1347 (1993); <http://www.msg.ameslab.gov/GAMESS/GAMESS.html>
- ²²L. A. Pozhar, *Phys. Rev. E* **61**, 1432 (2000); L. A. Pozhar and K. E. Gubbins, *ibid.* **56**, 5367 (1997); J. K. Percus, L. A. Pozhar, and K. E. Gubbins, *ibid.* **51**, 261 (1995); L. A. Pozhar, K. E. Gubbins, and J. K. Percus, *ibid.* **48**, 1819 (1993); L. A. Pozhar and K. E. Gubbins, *J. Chem. Phys.* **99**, 8970 (1993).
- ²³H. H. Chang, M. Y. Lai, J. H. Wei, C. M. Wei, and Y. L. Wang, *Phys. Rev. Lett.* **92**, 066103 (2004); J.-F. Jia, X. Liu, J.-Z. Wang, J.-L. Li, X. S. Wang, Q.-K. Xue, Z.-Q. Li, Z. Zhang, and S. B. Zhang, *Phys. Rev. B* **66**, 165412 (2002); M. Y. Lai and Y. L. Wang, *ibid.* **64**, 241404(R) (2001); R. Biswas and Y.-P. Li, *Phys. Rev. Lett.* **82**, 2512 (1999); S. B. Zhang and D. J. Chadi, *Phys. Rev. B* **42**, 7174 (1990).
- ²⁴O. P. Pchelyakov, Yu. B. Bolkhovityanov, A. V. Dvurechenskii, L. V. Sokolov, A. I. Nikiforov, A. I. Yakimov, and B. Voigtländer, *Semiconductors* **34**, 1229 (2000).
- ²⁵K. Jeganathan, M. Shimizu, T. Ide, and H. Okumura, *Phys. Status Solidi B* **240**, 326 (2003).
- ²⁶Y. Temko, T. Suzuki, P. Kratzer, and K. Jacobi, *Phys. Rev. B* **68**, 165310 (2003).
- ²⁷See, for example, G. S. H. Lee, D. C. Craig, I. Ma, M. L. Scudder, T. D. Bailey, and I. G. Dance, *J. Am. Chem. Soc.* **110**, 4863 (1988).
- ²⁸L. A. Pozhar, A. T. Yeates, F. Szmulowicz, and W. C. Mitchel, *Mater. Res. Soc. Symp. Proc.* **830**, D6-12.1 (2005); L. A. Pozhar, A. T. Yeates, F. Szmulowicz, and W. C. Mitchel, *ibid.* **891**, EE02-04.1 (2006).