

Title: In-silico determination of ground-state structures and physical properties of ternary nanoclusters based on a first-principles approach

Key words: Ternary clusters, first-principles, ground state structures

Executive Summary:

To search for the ground state structures of ternary clusters at quantum mechanical level unbiasedly (i.e., from an initial random configuration) is a hard-core computational task. These research tasks are rarely reported in the literature in the nanocluster research community due to its well-known technical difficulty. Our research objectives are to investigate the ground state structure of ternary Al-Ti-Ni cluster by using a home-grown, state-of-the-art computational scheme, in which a hybridized global minimum search algorithm (consists of basin hopping and genetic algorithm) is coupled to a density functional theory energy calculator. Obtaining the ground state structures for the ternary Al-Ti-Ni clusters constitute the first stage in our proposed research plan. The second stage involves in-silico measurements of the chemical order and electronic properties of these clusters using first-principles calculations, namely, density functional theory. The output of the research, apart from promised publications and trained human capital, will be a frontier algorithm that could identify ternary cluster at the first-principles level knowledge of the ground state structures of Al-Ti-Ni clusters. It will allow us to predict the physical properties, e.g., size-dependent thermal stability, chemical order, magnetic moment, vibrational and optical properties of Al-Ti-Ni cluster based on first-principles calculations. The capability to perform the search for ground state structures at the DFT level on ternary clusters is the most precious achievement of the proposed project. This is because currently there are relatively few research groups in the global research community are equipped with sufficient knowledge and computational algorithm to carry out such prediction and measurement. Our capability to make such kind of calculations can be showcased as a leading research frontier in the world. As a contrasting case to the current computational materials science research in Malaysia, in our neighbor countries, especially Thailand, Singapore and Vietnam, the research field is strongly supported at a national-wide level. The cost effectiveness in terms of publication per unit dollar spent, computational materials science is almost like an 'ultimate free lunch' for scientific publication and visibility. Malaysia is one of the slowest in recognizing the significance of computational materials science. The proposed research project is part of our earnest endeavor to establish a prolific research frontier, computational materials science, in Malaysia as a whole.

Problem statement:

A multicomponent cluster, made up of more than one type of chemical species, is basically a complicated, microscopic many-body system governed by the principles of quantum mechanics. Accurate and unambiguous determination of a ternary cluster's geometry, physical properties and ground state structures experimentally is practically a very difficult task due to the quantum nature and the nanoscale of the system. On the other hand, based on very general energetic principles, all the experimentally measurable physical properties of a nanocluster such as magnetic moment, vibrational modes, optical responses, thermal responses, chemical reactivity etc., are a strong function of its ground state. A sufficient knowledge of the ground state structures will permit one to extract all the desirable knowledge about the physical properties of the system via well-established total energy methods, such as the density functional perturbation theory. Hence, obtaining the ground state structures of a cluster is considered the first step, and the most crucial one, to accurately predict the physical properties inherent in it. Predicting the ground state structures of a ternary cluster at the first-principles level, e.g., via density functional theory (DFT), is known in the research community to be a very daunting task. Comparatively speaking, it is relatively easy, and quite routinely reported in the research front, to locate the ground states of a ternary system at the molecular dynamics, i.e. an empirical and non-quantum mechanical level. However, to search for the ground states at quantum mechanical level unbiasedly (i.e., from an initial random configuration), for clusters comprised of three distinctive atom types, involves an entirely different level of complication. It requires very demanding computational resources, a novel global minimum search strategy that must be incorporated via a practical means to evaluate the total energy (at quantum mechanical level) of a random cluster configuration. This research proposal intends to tackle such a hard-core problem, i.e., to determine, via an unbiased global minimal search approach, the ground state structures and physical properties of a specific type of ternary nanocluster, the Al-Ti-Ni system, based on density functional theory (which is a first-principle approach).

Hypothesis

- a. The ground states of a ternary cluster are in principle determined by the complex, non-local many-body quantum interactions acting among the constituent atoms and electrons.
- b. Cluster systems behave differently from bulk or molecular systems, and to accurately account for their behavior, especially the electronic structures, quantum mechanical effects must be taken into account.
- c. The Schrodinger equation of the many-body quantum system of a cluster can be reliably solved via the well-established first-principles approach, the density functional theory (DFT).
- d. In principle, the ground states exist and can be practically determined.

- e. The search for the quantum mechanical ground states of a ternary cluster can be computationally obtained with smart global minimization search algorithm.

Research Questions

- a. What are the quantum mechanical ground states of an Al-Ti-Ni cluster?
- b. What are the electronic structures, including the vibrational modes, chemical, reactivity, magnetic moment, optical responses of these clusters, and how the interplay of the atoms in the configuration influence these properties, according to the rules of quantum mechanics?
- c. Given their ground state structures, what are the thermal stability and melting points of these clusters?
- d. We are especially keen to investigate whether it is possible to obtain exotic magnetic properties in the Al-Ti-Ni clusters such as sudden enhancement of magnetic moment at certain magic numbers due to finite size effect as the composition of the clusters varies.

Literature Review

Nanoparticles or nanoclusters are viewed as fundamental building blocks of nanoscience and nanotechnology. The term 'nanocluster' is used to refer to a near monodispersed particle that is generally in the size of less than 10 nm or 100 Å [1]. Nanoclusters, due to quantum mechanical and finite size effects [2], are known to display surprisingly unexpected properties as compared to the bulk counterparts. Electrons in a nanocluster experience non-trivial confinement effect arising from the nanoscale geometry of the system. Nanoclusters research is currently the hottest multidisciplinary research front, being pursued by material scientists, physical chemists, condensed matter physicists and medical biologists due to their promising potential, ranging from advanced functional materials (nano-magnets), optics (quantum dots), bio-imaging (nano-magnets), drug delivery (carbon nanotubes) and catalysis (fuel cells). The wide range of applications is made possible due to the enormous variety of properties that arises from the many different structures of sizes and made of different type of atoms. Theoretical and computational studies of nanoclusters aim to study, understand, manipulate and predict the physical properties of finite (as opposed to periodic) atomic system comprising of a few up to several million atoms.

Many nanoclusters exhibit surprising properties otherwise unexpected. For example, metallic clusters are well known to have size-dependent melting temperatures that could be drastically lower than their bulk counterpart, as was reported by the ground-breaking finding in [3]. Many atoms are known to be non-magnetic, such as Pd and Rh, display large magnetic dipole moments when they are aggregated in cluster form due to accidental symmetry enhancement [3]. The magic polyicosahedral core-shell in metallic nanoalloy systems Ag-Ni and

Ag-Cu gives rise to a remarkable stability in their thermodynamic and electronic properties, resulting in melting points higher than their bulk counterparts [4].

Unbiased search for the ground state structures of a nanocluster is a very challenging task. Which research strategy to adopt in the ground state search depends primarily on the size, chemical composition, and the accuracy of the theoretical principle involved. For large clusters, empirical potential approach, e.g., molecular dynamics, is usually adopted due to its cheap computational cost. But the down side of this approach is that the results obtained relies heavily on the availability of the forcefields (a.k.a. potentials) of the relevant atomic species, as well as the accuracy of these forcefields in comparison to physical reality. On the other hand, if one insists that the ground state configuration must be accurate at the quantum mechanical level, the computational cost becomes a few orders higher. However, the motivation to calculate a cluster's ground states at quantum level is that it is theoretically more convincing, as the total energy is evaluated based on first-principles rather than from an empirically fitted potential. In addition, if one uses first-principles method as the energy calculator in the global minimum search algorithm, clusters comprised of any atom type can be calculated, as first-principle method, by definition, does not require any empirical input. Density functional theory (DFT) [5,6,7] is the most commonly used first-principles approach, which does not require the use of empirical potential specifically tailor-fitted for a particular atomic species. For a comprehensive review on nanoclusters and the search strategy for their ground state structures, we cite Refs. [8,9].

A common strategy to search for the ground state structures of a ternary cluster at DFT level essentially involves two independent ingredients, namely, an energy calculator and a global minimum search algorithm. In one of our recent publication [10], the technical procedure of such a search strategy was demonstrated in detail. In short, the two ingredients have to be implemented in the form of a software package that hybridizes the DFT calculations and the global search algorithm. A novel global search algorithm tailored for the purpose of locating the ground states of a cluster system has been introduced in one recent paper published by us (T. L. Yoon's group) in collaboration with our Taiwanese collaborators. The algorithm was dubbed EMBH [24]. This is our very own home-grown global minimum search algorithm which has gained peer recognition in a very renowned journal (Computer Physics Communications) and proven to work for monoatomic and binary cluster.

There is a large number of research articles regarding monoatomic and binary nanoclusters. However, research articles on ternary alloy clusters are scarce due to tremendous technical difficulties. The size of ternary nanoclusters reported in the literature at DFT level is usually small, e.g., less than 15 atoms, see for example, [11]. There has been some research works on very large ternary clusters of up to hundreds of atoms [13,14]. Nevertheless, these are evaluated using empirical approach, i.e., molecular dynamics, rather than DFT which is computationally too costly for such a large system. Recent examples of ternary cluster structure search at the DFT level include Fe-Co-Ni and Ag-Au-Pd [11, 12]. However, the current system we are interested in, the Al-Ti-Ni cluster, has been rare, except by the work of Erkoc who has published on the ground states of these system [15,16] as early as in 2002 and 2003. However,

the computational procedure reported in the paper is ambiguous and lacking in technical transparency. Their results are deemed not as reliable. In addition, the size of the Al-Ti-Ni system they investigated is limited to only 4 atoms. Other than Erkoc, no work on the ground state structures and properties of the Al-Ti-Ni system has been reported as far as we are aware of.

Relevance to Government Policy, if any

Our proposed project is advancing one of the prioritised research areas as stated in the policy of 'MALAYSIA'S S&T POLICY FOR THE 21st CENTURY', namely, advanced materials, which are an integral part in any new energy source research. The scope and scale of our proposal, which is computational-cum-theoretical in nature, is perfectly in line with the criteria mentioned in the policy: 'Specific areas must be selected based on relevance, a demonstrated need, the availability of a natural advantage and constraints of manpower and budget allocation.

Objectives

To obtain and analyze the Al-Ti-Ni nanoclusters at the accuracy of quantum mechanical level, and hence predicting their structural, stabilities and electronic properties in-silico.

Methodology

To determine the ground states of the ternary Al-Ti-Ni clusters, a broad configuration search for cluster structures is to be performed by initializing the cluster in a random configuration. The search is to be implemented using a specially designed package comprised of a global minimum search algorithm component that is synergistically coupled to an energy calculator component. In the present case, the DFT package, Gaussian 03 (G03) [18] is used as the energy calculator. There are a few variants for the global minimum search algorithm in our computational arsenal. These include parallel tempering multicanonical basin hopping with genetic algorithm (PTMBHGA) [17] and Extended Modified Basin Hopping (EMBH) [24]. The computational packages PTMBHGA-G03 [17], EMBH-G03 [24] are well established methodologies published by our group in collaboration with the Taiwanese NCU group, which are versatile tools that are developed with the specific purpose to locate ground state structures of cluster systems. A similar algorithm but with some technical variation in the details of the search strategy has also been published by our own group in the search for the Hf clusters [10]. The accumulated experience we have gathered from the computational arsenal [10,17,24] published by our own group and our Taiwanese collaborators will be deployed in the search for the ground state structures of the ternary clusters. The methodology presented in the following is an adaption (with some possible modifications) of our own published methodology. All the required computational codes to implement the global minimum search algorithm (PTMBHGA-G03, EMBH-G03) have already been developed by or available to our group.

Basin Hopping (BH) technique was first proposed by Wales and Doye [19] and Li and Scheraga [26] to locate the optimized energy value for potential energy function with a funnel landscape. For the present case of the Al-Ti-Ni ternary cluster, the BH method will be implemented by choosing an appropriate modified confinement radius R_{d*} , and is written as

$$R_{d*} = \alpha \left[1 + \left(\frac{3n}{4\sqrt{2}} \right)^{\frac{1}{3}} \right] r_0,$$

where α is a tunable scaling parameter, n the total number of atoms in cluster and r_0 refers to nearest-neighbour distance between atoms. Based on the literature we had reviewed [20], it was noted that a well encapsulated cluster is required to boost the convergence efficiency of the global optimization procedure. This can be computationally implemented by scaling the factor α from 1.0 to a finely tuned value (< 1.0). However, the optimization could possibly fail if the factor α is scaled excessively, as a value of α that is too small will render the space confining the BH algorithm to shrunk violently, leading to divergence.

A two-stage procedure will be required in order to obtain the optimized structures for the Al-Ti-Ni clusters. At the first stage, two conventional optimization algorithms, i.e. BH [21, 22] and genetic algorithm (GA) will be applied to generate the low-lying structures (LLS) in the density functional theory potential (DFT) energy surface (PES). Initially, 20 configurations of structures are randomly generated. Each of these configurations (also known as candidates) is locally minimized by using Monte Carlo BH for a total of 100 BH steps. BH makes use of the limited-memory Broyden-Fletcher-Goldfarb-Shanno algorithm (L-BFGS) as the local energy minimization algorithm to minimize the potential energy of cluster structures. In each BH steps, these configurations are subjected to either the angular move or random displacement (ARMD) genetic-like operation [23] or cut-and-splice genetic operator (GO) [22]. ARMD is a random move method used by Monte Carlo BH to adjust the positions of the cluster structure to give birth to a new configuration. Cut-and-splice GO is a technique in GA that employs a mating operator to generate new structure configurations from a previous structure. The new cluster structures that are generated by either ARMD or cut-and-splice operator in each BH step is relaxed and its total energy is evaluated by using a first-principles energy calculator, G03. The DFT calculations will be carried out by using the Slater, Vosko, Wilks, and Nusair (SVWN) exchange-correlation functional and 3-21G Pople basis set, where SVWN is an exchange correlation functional equivalent to local spin density approximation (LSDA) in G03. Next, these 20 candidates, which were generated from the previous 100 BH steps, will play the role as the first-generation “parents” to breed the “offspring” by using the cut-and-splice operator. To generate a next generation, five candidates with the lowest fitness value are removed and the remaining of the 15 candidates will once again subjected to ARMD or cut-and-splice operator to generate five new “offspring”, replacing those candidates already been discarded so that the number of candidates in the GA population is maintained at 20. An “offspring” is optimized with 100 BH steps for each generation and is continued for 5 generations. After that, 100 BH steps are performed on these 20 individuals independently to guarantee the cluster structures with

the lowest energy value are obtained from the above procedure. Finally, the lowest-energy configuration is found from these 20 individuals.

In the second stage, the cluster's configuration with lowest energy that was obtained from the first stage is once again subjected to the PTMBHGA-G03 procedure. To this end, Monte Carlo BH is applied on this individual for 100 BH steps. Similar to the procedure in the first stage, this individual is subjected to either the techniques from Monte Carlo BH or GA to form new configurations. Total energies and structures of the clusters generated were calculated using Becke three-parameter, Lee-Yang-Parr (B3LYP) exchange correlation functional and the 6-311G* basis set in G03. Vibrational frequency for each of these individuals generated in each BH step will be calculated using the 'ultrafine grid' functionality in G03. These frequency calculations are conducted to ensure that the optimized structures are local minima instead of transition structures that display negative frequencies. The resultant structures at this stage are then subjected to a 100-step BH local minimization. Finally, a unique cluster with lowest energy at the end of the 100-step BH procedure is identified as the ground state structure.

The physical and electronic properties of the resultant ground state structures are then evaluated and calculated by using density functional perturbation theory (DFTP) that are available in the Gaussian 03 code.

The calculations as proposed above will be implemented using existing or to-be-purchased massively parallelized, Linux based, computer clusters in the school of physics and school of computer science, USM.

Novel Theories/New findings/Knowledge

1. A frontier algorithm that could identify ternary cluster at the first-principles level
2. Knowledge of the ground state structures of Al-Ti-Ni cluster
3. Prediction and in-silico measurements of the physical properties, e.g., size-dependent thermal stability, chemical order, magnetic moment, vibrational and optical properties of Al-Ti-Ni cluster based on first-principles calculations.

Specific or Potential Applications

According to [25], graphene decorated with small binary Ti-Al clusters is a feasible alternative to the next-generation hydrogen storage system, which requires a gravimetric content of at least 7.5 wt%, and an adsorption energy of 0.2–0.6 eV per H₂. It has been shown in [25] that hydrogen adsorption in bimetallic Ti-Al clusters supported on graphene enhances its hydrogen gravimetric content up to 3.2–3.6 wt%. A controlled introduction of a third element Ni into the Ti-Al binary cluster could strongly functionalise the parent Ti-Al cluster. Decorating graphene

with such a ternary Al-Ti-Ni cluster opens up the possibility of enhancing its hydrogen gravimetric content to make it a promising candidate for the next-generation hydrogen storage.

Impact on society, Economy and Nation:

The successful establishment of a research team that can model, predict and 'measure' properties of materials at the atomic level not by actually carrying out real experiments, but by using the sole computational power coupled with state-of-the-arts computational technology will definitely be a benefit to a developing country like Malaysia. Computational materials science is the most obvious research approach to complement real experiments which are conventionally carried out in our local research labs without a significant theoretical component. Properties of materials that are impossible or not feasible to be carried out in practice (perhaps due to the difficulty caused by technical or financial reasons) can be predicted and 'measured' in simulations without much cost. In principle any functional materials, not limited only to the systems proposed here, can be simulated. These advanced materials could have very great potential in high-end technological applications. In the context of a developing country like Malaysia who is stuck at the bottle neck of a middle-income country, lack of financial support for experimental research is a real issue. But if armed with atomistic computational simulation, the advanced knowledge of these functional materials can be accessed even without the need to set up real experiments. The cost effectiveness in terms of knowledge gain per unit dollar spent, computational materials science is almost the 'ultimate free lunch'. This is also a research field that can publish relatively easily. Other developing countries which understand the pragmatic advantages of computational materials science have already invested heavily in this field. For example, Thailand has a very active computational materials science research, so is Vietnam, Algeria and many south American countries. Malaysia is one of the slowest in recognizing the significance of computational materials science.

Intellectual Property

Note: This is a theoretical cum computational research project on fundamental physics that produces universal knowledge that cannot be filed for IP.

Equipment

Cluster Computers in USM Physics School

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