

# Bonding Forces and Energies on the Potential Energy Surface (PES) of the Optimized Gold Atomic Clusters by a Differentiation Step-Size ( $ds = \pm 0.01$ a.u.) via DFTB Method

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## Abstract

We have carried out the present ab initio study by using up-to-date computational concepts through our newly developed Numerical Finite-Difference analysis via the DFTB method. Significantly, to differentiate between zero (translational and rotational motion) and non-zero (vibrational motion) energy eigenvectors, we have accurately predicted with a differentiation step-size  $ds = \pm 0.01$  a.u. on the Potential Energy Surface (PES) of the re-optimized gold atomic structures  $Au_{3-58}$  at  $\Delta E = 0$ . With this small energy gap, we can see how the interaction of the different atomic motions was varied with  $3N$  and  $3N-6$  degrees of freedom, and also they are very independent of each other in gold atomic clusters. Moreover, the non-zero eigenvalues are quite stable whereas the values of the zero-eigen values are varying over several orders of magnitude.

**Keywords:** Gold Atomic Clusters; Density-Functional Tight-Binding (DFTB) approach; Finite-Difference Method; Force Constants (FCs); Energy Eigen Vectors

## Introduction

In general, nanoclusters are interesting because their physical, optical and electronic characteristics are strongly size dependent. Often changing the size by only one atom can significantly alter the physical chemical properties of the system, for that reasons, many new periodic tables can thus be envisioned classifying differently-sized clusters of the same material as new elements [1]. Potential applications are enormous, ranging from devices in nano-electronics and nano-optics to applications in medicine and materials [2].

The vibrational properties of clusters and small particles have been studied very intensively, and vital for understanding and describing the atomic interactions in the cluster [3, 4, 5, 6, 7, 8, 9]. Thermal properties like heat capacity and thermal conductivity as well as many other material properties are strongly influenced by the vibrational density of states (VDOS) [10, 11, 12, 13, 14, 15]. For this reason, a better understanding of the rules governing the vibrational properties of nanostructured materials is of high technological and fundamental interest. The vibrational properties play a major role in structural stability.

The structural determination of metal nanoparticles of their vibrational (phonon) density of states have been calculated by Huziel E. Saucedo and Ignacio L. Garzon. Specific heat capacity is an important thermodynamic property and is directly related to the structural stability, identification and energy of substances [9, 16]. Most recently, Huziel E. Saucedo and Ignacio L. Garzon calculated vibrational properties and specific heat of core-shell Ag-Au icosahedral nanoparticles [7].

Moreover, the big challenges were to differentiate in between translational, rotational motion and vibrational motion of energy eigen vectors, nevertheless, we have accurately predicted a differentiation step-size  $ds = \pm 0.01$  a.u. over a single point Potential Energy Surface (PES) that is after the re-optimization. With this small energy gap, one can see the interaction of the different atomic motions are very less and they are independent.

We use our numerical finite-difference approach along with the Density Functional Tight-Binding (DFTB) method. Overall, for a better understanding and to visualize, we have given an example of the re-optimized gold atomic cluster  $Au_{19}$  [17].

## Theoretical and Computational Procedure

The DFTB is based on the density functional theory of Hohenberg and Kohn in the formulation of Kohn and Sham [18, 19, 20]. In addition, the Kohn-Sham orbital's  $\psi_i(r)$  of the system of interest are expanded in terms of atom-centered basis functions  $\{\phi_m(r)\}$ ,

$$\psi_i(r) = \sum_m c_{im} \phi_m(r), \quad m = j. \quad (1)$$

While so far the variational parameters have been the real-space grid representations of the pseudo wave functions, it will now be the set of coefficients  $c_{im}$ . Index  $m$  describes the atom, where  $\phi_m$  is centered and it is angular as well as radially dependant. The  $\phi_m$  is determined by self-consistent DFT calculations on isolated atoms using large Slater-type basis sets. In calculating the orbital energies, we need the Hamilton matrix elements and the overlap matrix elements. The above formula gives the secular equations

$$\sum_m c_{im} (H_{mn} - \varepsilon_i S_{mn}) = 0. \quad (2)$$

Here,  $c_{im}$ 's are expansion coefficients,  $\varepsilon_i$  is for the single-particle energies (or where  $\varepsilon_i$  are the Kohn-Sham eigenvalues of the neutral), and the matrix elements of Hamiltonian  $H_{mn}$  and the overlap matrix elements  $S_{mn}$  are defined as

$$H_{mn} = \langle \phi_m | \hat{H} | \phi_n \rangle, \quad S_{mn} = \langle \phi_m | \phi_n \rangle. \quad (3)$$

They depend on the atomic positions and on a well-guessed density  $\rho(r)$ . By solving the Kohn-Sham equations in an effective one particle potential, the Hamiltonian  $\hat{H}$  is defined as

$$\hat{H}\psi_i(r) = \varepsilon_i\psi_i(r), \quad \hat{H} = \hat{T} + V_{eff}(r). \quad (4)$$

To calculate the Hamiltonian matrix, the effective potential  $V_{eff}$  has to be approximated. Here,  $\hat{T}$  being the kinetic-energy operator  $\sum(\hat{T} = -\frac{1}{2}\nabla^2)$  and  $V_{eff}(r)$  being the effective Kohn-Sham potential, which is approximated as a simple superposition of the potentials of the neutral atoms,

$$V_{eff}(r) = \sum_i V_j^0(|r - R_j|). \quad (5)$$

$V_j^0$  is the Kohn-Sham potential of a neutral atom,  $r_j = r - R_j$  is an atomic position, and  $R_j$  being the coordinates of the j-th atom.

The short-range interactions can be approximated by simple pair potentials, and the total energy of the compound of interest relative to that of the isolated atoms is then written as,

$$E_{tot} = \sum_i \varepsilon_i - \sum_j \sum_{m_j}^{occ} \varepsilon_{jm_j} + \frac{1}{2} \sum_{j \neq j'} U_{jj'}(|R_j - R_{j'}|), \quad \varepsilon_B \equiv \sum_i \varepsilon_i - \sum_j \sum_{m_j}^{occ} \varepsilon_{jm_j} \quad (6)$$

Here, the majority of the binding energy ( $\varepsilon_B$ ) is contained in the difference between the single-particle energies  $\varepsilon_i$  of the system of interest and the single particle energies  $\varepsilon_{jm_j}$  of the isolated atoms (atom index j, orbital index  $m_j$ ),  $U_{jj'}(|R_j - R_{j'}|)$  is determined as the difference between  $\varepsilon_B$  and  $\varepsilon_B^{SCF}$  for diatomic molecules (with  $E_B^{SCF}$  being the total energy from parameter-free density functional calculations). In the present study, only the 5d and 6s electrons of the gold atoms are explicitly included, whereas the rest are treated within a frozen-core approximation [18, 20, 21].

### The Structural Re-Optimization Process

In our case, we have calculated the numerical first-order derivatives of the forces ( $F_{i\alpha}, F_{j\beta}$ ) instead of the numerical-second-order derivatives of the total energy ( $E_{tot}$ ). In principle, there is no difference, but numerically the approach of using the forces is more accurate,

$$\frac{1}{M} \frac{\partial^2 E_{tot}}{\partial R_{i\alpha} \partial R_{j\beta}} = \frac{1}{M} \frac{1}{2ds} \left[ \frac{\partial}{\partial R_{i\alpha}} (-F_{j\beta}) + \frac{\partial}{\partial R_{j\beta}} (-F_{i\alpha}) \right] \quad (7)$$

Here,  $R_{i\alpha}, R_{j\beta}$  are the nuclei coordinates, F is a restoring forces which is acting upon the atoms,  $ds$  is a differentiation step-size and  $M$  represents the atomic mass, for the homonuclear case. The complete list of these Force Constants (FCs) is called the Hessian H, which is a  $(3N \times 3N)$  matrix.

### Results and Discussion

in order to fully exploit the potential applications of cluster based nanomaterials, it is necessary to gain full control of the cluster size, shape and structure. Nevertheless, in this article, we present an in-depth study to select the very accurate differentiation step-size ( $ds$ ) with respect to the bond length fluctuations over the potential energy surface (PES), and how one must be careful to extract the vibrational frequency and the translational, rotational frequency of the re-optimized neutral gold cluster at  $\Delta E = 0$ . Here, we have given an example of a cluster.

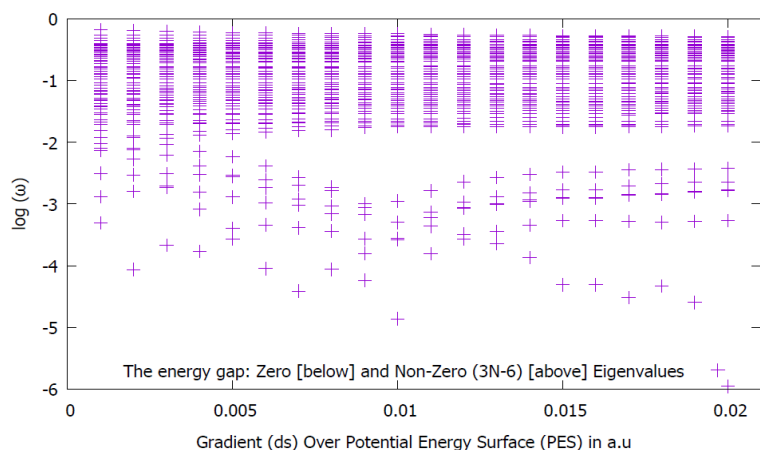
At first, we tried to find a scheme which will allow to discriminate between the Hessian eigenvalues which correspond to the vibrational eigenvectors and the Hessian eigenvalues which correspond to translational and rotational motion of the atoms in the clusters. For all the cluster structures, ( $Au_N, N = 3 - 58$ ) this was simply done by comparing the eigenvalues, it was possible to numerically distinguish between zero eigenvalues - translation and rotation and non-zero-eigenvalues - vibration [22]. Here, we have given an example of a cluster ( $Au_N, N = 19$ ).

### A Differentiation Step-Size on the Potential Energy Surface (PES)

We found that the a differentiation step-size [ $ds = \pm 0.01$  a.u.] at the equilibrium coordinate values of the optimized clusters, which has been implemented within the scheme developed by M. Dvornikov [23] along with the DFTB method, which is a reasonable value and allowed to discriminate between the translational, rotational motion (Zero eigenvalues) and the vibrational motion (Non-Zero-eigenvalues) of the atoms of the Hessian eigenvalues. The desired set of system eigenfrequencies ( $3N - 6$ ) is obtained by a diagonalization of the symmetric positive semidefinite Hessian matrix. The vibrational frequency of the optimized neutral gold cluster which will be useful to predicts many properties.

Consider that if the whole problem was solved analytically, six out of the 3N eigenvalues were exactly zero. Moreover, the non-zero eigenvalues have to be positive, because by assumption, the structures correspond to minima on the PES. However, since the energy calculations as well as the differentiation and the diagonalization are realized through numerical algorithms, the zero eigenvalues will not exactly be equal to zero. But still, they should be very small compared to the non-zero eigenvalues [22].

We found, that reasonable step-size should be in the proximity of  $ds = 0.01$  atomic units. For all the clusters upto 58 from 3, i.e. clusters which are optimized up to high accuracy, smaller values of  $ds$  lead to zero-eigenvalues which are even closer to zero. However, if one applies such a very small step-sizes ( $ds = \pm 0.001$  a.u.) on bigger structures, the resulting Hessian might not longer



**Figure 1 :** Au<sub>19</sub> (C<sub>1</sub>): The energy gap in between Zero [below] and Non-Zero (3N-6) [above] Eigen Values at  $\Delta E = 0$

be positive semidefinite and the results might become inaccurate. Most importantly, not only that it is not at all possible to have any type of internuclear interactions, even the outer surface attraction or repulsive forces upon each of the atoms. That means, there will be no vibration at all, therefore, we can not extract any kind of future in the clusters. In addition to that it would not be possible at all to numerically discriminate between the zero and the non-zero eigenvalues anymore (see Figure 1). Our new strategy proceeds on the assumptions, that the numerically optimized structures are almost exact, that the Hessian changes very little around the minimum and that the differentiation scheme works in principle.

## Bonding Forces and Energies

If the energy absorbed when bond breaks, at the same time, the energy released when bond forms. When increase the bond length then bond strength will become weaker but if we bring closer the bond length to each other, as a result, the bond strength will become stronger. We can observe attraction with a shared electrons as well as repulsion due to nuclei and electron shell. With a differentiation step-size  $ds = \pm 0.01$  atomic units, the forces in the atom are repulsions between electrons and attraction between electrons and protons. The neutrons play no significant role. Mainly, the Coulomb forces are occurred due to attraction between electrons and nuclei, repulsion between electrons and between nuclei. The force between atoms is given by a sum of all the individual forces, and the fact that the electrons are located outside the atom and the nucleus in the center.

In our case, when two atoms come very close, the force between them is always repulsive, because the electrons stay outside and the nuclei repel each other. Unless both atoms are ions of the same charge (e.g., both negative) the forces between atoms is always attractive at large internuclear distances  $r$ . Since

the force is repulsive at small  $r$ , and attractive at small  $r$ , there is a distance at which the force is zero. This is the equilibrium distance at which the atoms prefer to stay. The interaction energy is the potential energy between the atoms. It is negative if the atoms are bound and positive if they can move away from each other. The interaction energy is the integral of the force over the separation distance, so these two quantities are directly related. The interaction energy is a minimum at the equilibrium position. This value of the energy is called the bond energy, and is the energy needed to separate completely to infinity (the work that needs to be done to overcome the attractive force.) The strongest the bond energy, the hardest is to move the atoms, for instance the hardest it is to melt the solid, or to evaporate its atoms. By the way, spin-orbit couplings effects are in part included indirectly through the short-ranged pair potentials.

## Conclusion

In conclusion, on Au<sub>19</sub> atomic cluster, the non-zero eigenvalues are quite stable whereas the values of the zero-eigenvalues are varying over several orders of magnitude. Nevertheless, Figure 1 shows that how exactly it differs with the  $\log(\omega)$  values with respect to  $ds$  values. To be noticed that the negative sign occur due to the log term. Over all, we have confirmed that for a small differentiation step-size ( $ds$ ) around 0.01 a.u., the results are magnificently active to variations in  $ds$ . Therefore, we have strongly chosen  $ds = \pm 0.01$  a.u. in the present calculations.

In conclusion, we strongly confirm that our approach with the numerical finite-difference method will be much helpful to extract the very accurate and the existing stored energy in terms of the vibrational spectrum for any type of metallic atomic clusters and make use of it for the different technological applications. And it can be compared with the theoretical as well as the experimental results.

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