Technical science and innovation

Volume 2020 | Issue 3 Article 12

9-30-2020

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Recommended Citation
Zikrillaev, N.F.; Shakarov, F.Q.; and Khaqqulov, M. K. (2020) "NUMERICAL CALCULATION OF THE CHARGE STATE AND ELECTROSTATIC POTENTIAL OF A BINARY NANOCLUSTER STRUCTURE WITH SI2ZNS CELLS IN A CUBIC LATTICE OF CRYSTALLINE SILICON WITH A DIAMOND STRUCTURE," *Technical science and innovation*: Vol. 2020: Iss. 3, Article 12.
DOI: https://doi.org/10.51346/tstu-01.20.3-77-0076
Available at: https://btstu.researchcommons.org/journal/vol2020/iss3/12

**UDC 621.383.51**

# NUMERICAL CALCULATION OF THE CHARGE STATE AND ELECTROSTATIC POTENTIAL OF A BINARY NANOCLUSTER STRUCTURE WITH $SI_2ZNS$ CELLS IN A CUBIC LATTICE OF CRYSTALLINE SILICON WITH A DIAMOND STRUCTURE

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***Abstract:*** *Numerical calculation of electronic and atomic structures of complex systems of crystalline and transitional nano- and micro-sizes by using quantum physical methods will make it possible to forecast new properties of crystalline silicon with various concentrations of clusters of impurity atoms, structural arrangement at lattice sites and types of clusters. The quantum-chemical method was used to calculate the required characteristics of the cell, i.e. the charge state and electrostatic potential for the base matrix of Si (silicon) and silicon with an impurity cluster consisting of 3 tetrahedral cells type-* $Si_2ZnS$ *in the base lattice of Si. Calculation of the electrostatic potential of the base lattice of Si, and silicon with an impurity cluster of* $Si_2ZnS$ *in the Si lattice revealed a noticeable change in the potential intensity at the cell sites. In the cluster, charge transfer occurs from S (sulfur) atoms to Zn (zinc) atoms. Zn atoms at sites acquire a negative charge while S atoms acquire a positive charge. In fact, the numerical calculation confirms the hypothesis that instead of completing its structure to the most stable electronic configuration ...* $s^2p^6$*, in certain cases the chalcogen atom can also donate some of its electrons to form a quasi-stable configuration ...* $sp^3$*.*

***Key words:*** *Method of molecular mechanics, semi-empirical quantum-chemical method, calculations of the required characteristics of a node, charge state, cluster, silicon.*

**INTRODUCTION**. Numerical modeling of electronic and atomic structures of complex systems of molecular, crystalline and transitional nano- and micro-sized structures by quantum physical calculation technique is becoming widespread nowadays. This tendency was partially driven by the development of the corresponding mathematical apparatus and software. The properties of semiconductor nanoscale materials differ markedly from the properties of a bulk base material, represent mainly quantum nature and can adequately be described only using modern research methods based on density functional theory (DFT), i.e. method that is used for quantum calculation. Also, *ab initio* quantum mechanical methods and semi-empirical methods are widely implemented [1]. On the basis of these methods, programs have been developed that allow one to determine the properties of crystals with various chemical compositions and structures.

The paper is devoted to the numerical calculation of the charge state and electrostatic potential of a binary nanocluster structure with $Si_2ZnS$ cells in a cubic lattice of crystalline silicon with a diamond structure. A comparison of the charge state and electrostatic potential of the base silicon lattice with similar parameters and of a binary nanocluster structure with $Si_2ZnS$ cells is presented. In order to numerically calculate and study the electronic properties of atomic clusters, the authors had applied *ab initio* quantum mechanical method, in particular the restricted or unrestricted Hartree – Fock method (RHF/UHF) and semi-empirical method, in particular ZINDO/1 [2].

## 1. Methods of quantum mechanical study and numerical calculation of cluster structures.

Currently, in quantum chemistry, various versions of Hartree-Fock method, which is also called the molecular orbital method (MO LCAO), are most widely used. When calculating by method of molecular orbitals, a variation approach is used. In this case, the iteration is carried out until the energy of the system takes a minimum value [3]. At the same time, the minimum energy does not always correspond to the optimal geometry, and often the geometry deviates from the usual geometry that is generally accepted in the literature.

In the *ab initio* Hartree-Fock calculation, the experimentally determined parameters of the calculated molecule or cluster structure are not taken into account in the course of computer calculation. In fact, the issue of one-electron wave functions is considered, when the basis set is determined in advance for an approximate calculation by the method of molecular orbitals [3].

The Hartree-Fock method as the main calculation method that uses the Schrödinger function as a characteristic of the state of a quantum system, on the whole, can give an adequate answer about the quantum-mechanical parameters of the compound under study. For this, a complete account of the energy of motion of electrons, taking into account the correlation, and a representation of atomic orbitals, which would not contain errors in the basis set, should be made. At the moment, such calculations have been carried out only for the simplest molecular structures. Even the most successful approximations to Full CI (configuration interaction), such as CC or MCSCF, are applicable to molecules and systems that contain about 10 heavy atoms [4].

A rather attractive alternative to these methods is the method based on the use of density functional theory (DFT). Despite the fact that these methods often use rough approximations, in some cases and for most systems they give results at the level of accuracy inherent in the methods of combined clusters, or even sometimes exceed them in accuracy [5].

For a preliminary numerical calculation, a hypothetical binary nanocluster structure $Si_2ZnS$ was chosen. To carry out the calculations, we used the free Abinit software for density functional calculations, the non-commercial GAMESSPC software for semi-empirical calculations, as well as the free visualization programs ViewMol3D and Molekel. The Hyper Chem Lite 3.0.1 Evaluation program was also used to plot the molecule under study.

## 2. Theoretical justification that $Si_2ZnS$ structure could be formed in same circumstances.

The justification for proposing such a hypothesis was the following reasoning, based on the existing generally recognized concepts of the theory of the formation of chemical bonds and the analysis of the facts presented so far in this area of research.

During the formation of chalcogenides, the valence electrons of metals are transferred to chalcogenes with the corresponding extension of their electronic configuration $s^2p^4$ in the limiting case to $s^2p^6$. In alkali metals, the tendency of chalcogen atoms to form covalent groups among themselves is simultaneously manifested. An isolated sulfur atom has a configuration of electrons of valence states ... $s^2p^4$ and in compounds presumably tends to capture electrons and complete its structure to the most stable electronic configuration ... $s^2p^6$. However, in certain cases of chalcogen atoms, a part of the electrons can be given back with the formation of a quasi-stable configuration ... $sp^3$ [6].

A number of researchers drew attention in the past to the existence of binary compounds formed by elements equidistant from the elements of group IV of the Periodic Table, that presumable have the structure of sphalerite and wurtzite, close to the structure of diamond. Coordination number 4 corresponds to these structures for binary compounds. Like diamond, it can be assumed that the electron density along the directions of the spatial tetrahedron is maximum [7-11].

It is well known that metals of the zinc subgroup, which include cadmium, have rather high ionization potentials and their atoms do not completely donate their electrons; they can share them with neighboring non-metal atoms. In this case, four elongated electron clouds are formed around each atom, which, being located in the $sp^3$ configuration, arising due to the hybridization of *s*- and *p*-orbits, form four bonds directed to the vertices of a regular tetrahedron. In these compounds, the electron cloud is shifted from the atoms of the elements of group II to the atoms of the elements of group VI, i.e., to the chalcogenide; therefore, the bond in the chalcogenides of group II is ionic-covalent [12].

Recently, such compounds have found wider application in semiconductor technology. In particular, in [12], the prospects of using wide-gap $A^{II}B^{VI}$ semiconductors doped with *3d*-transition metal ions for the needs of spintronics and optoelectronics are considered.

Based on the above facts, we made the assumption that the formation of complexes of the type- $SiA_{II}^{2-}B_{VI}^{2+}$ with the participation of impurity atoms of II and VI groups of the Periodic Table and silicon atoms can occur in silicon single crystals [13].

Using the available quantum-chemical and molecular-dynamic methods, an elementary cell of the Si diamond lattice with four surrounding atoms located at the vertices of a regular tetrahedron embedded in a cube was built, as well as a crystal structure of a diamond-type lattice. For Si, the corresponding lattice parameters were set a = 5.43095 Å, d (A-B) = 2.35167 Å, and d (A-A) = 33.84026 Å.

The objects of study were a Si lattice with a diamond structure with a hypothetical arrangement of S and Zn impurity atoms at the silicon lattice sites with the formation of the corresponding tetrahedral cells of the $Si_2ZnS$ type.

In the study of silicon cells with impurity atoms, the reference data on the lattice constants for $A^{II}B^{VI}$ compounds, in particular, for zinc sulfide ZnS, were taken into account.

## 3. Numerical calculation of the charge state and electrostatic potential of a cluster with $Si_2ZnS$ cells

In the method of molecular mechanics, atoms are considered as mechanical particles that interact with each other through some potential fields set empirically. The potential interaction energy depends on bond angles, bond lengths, torsion angles, and non-covalent interactions (including van der Waals forces, electrostatic interactions, and hydrogen bonds). In these calculations, the forces that act on atoms are represented as functions of the coordinates of the atoms [3].

The cost of performing a calculation using the Hartree-Fock method usually corresponds to the fourth power of the number of bases. This follows from the number of two-electron integrals required to create the Fock matrix. Semi-empirical methods reduce the cost of calculations by reducing the number of these integrals [3].

The required characteristics of a site (charge state) for the base lattice of Si and silicon with a cluster structure consisting of 3 tetrahedral sites $Si_2ZnS$ in the base lattice of Si were calculated using the method of molecular mechanics and the semiempirical quantum-chemical method, as shown in Fig. 1.

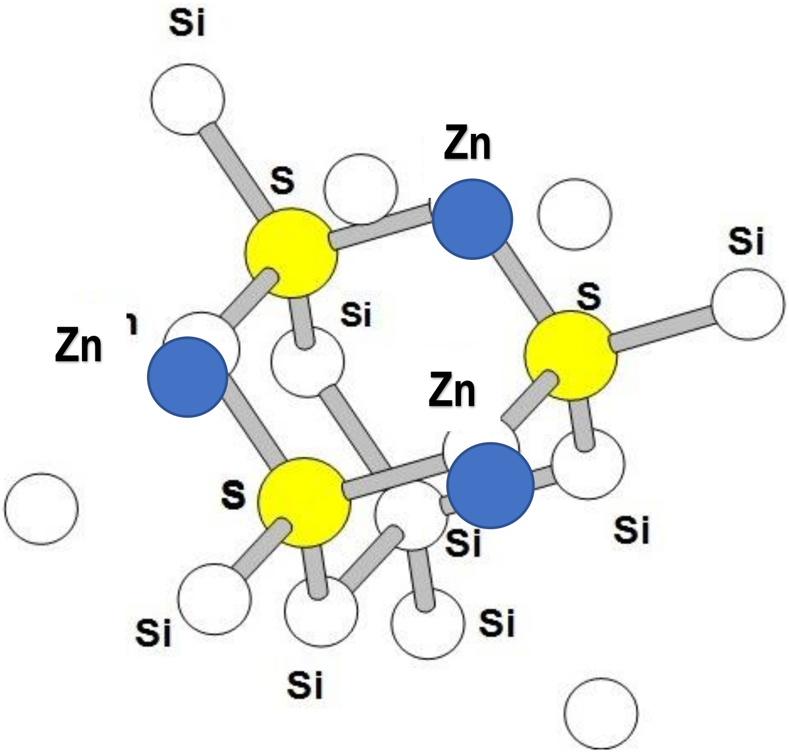

**Fig. 1**. Si lattice with $Si_2ZnS$-type cells.

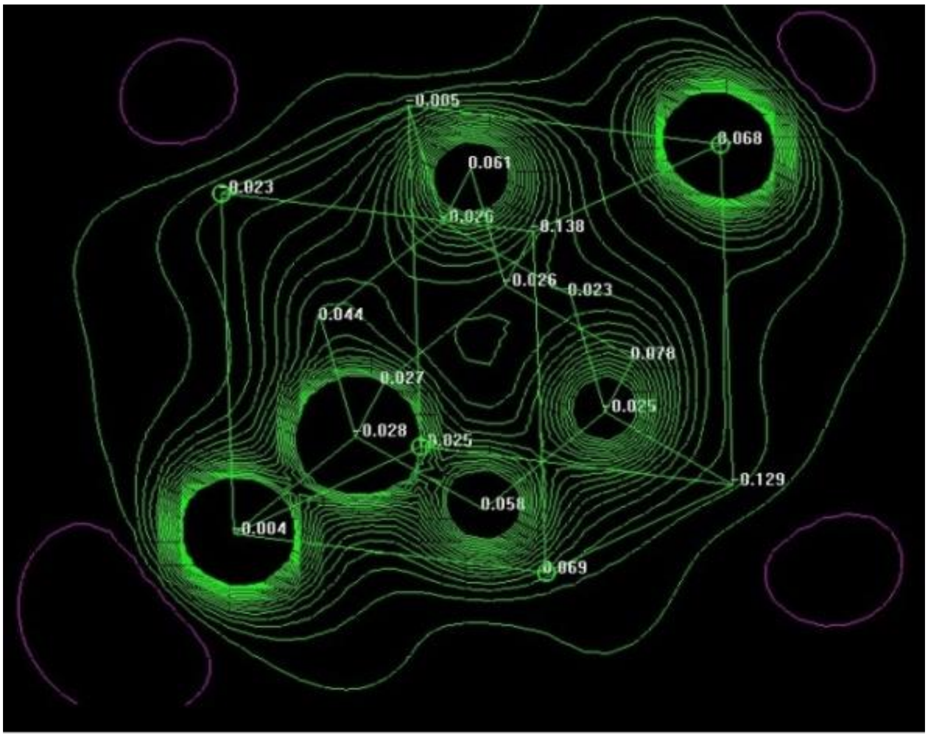

**Fig.2.** Charge state of the base lattice of Si

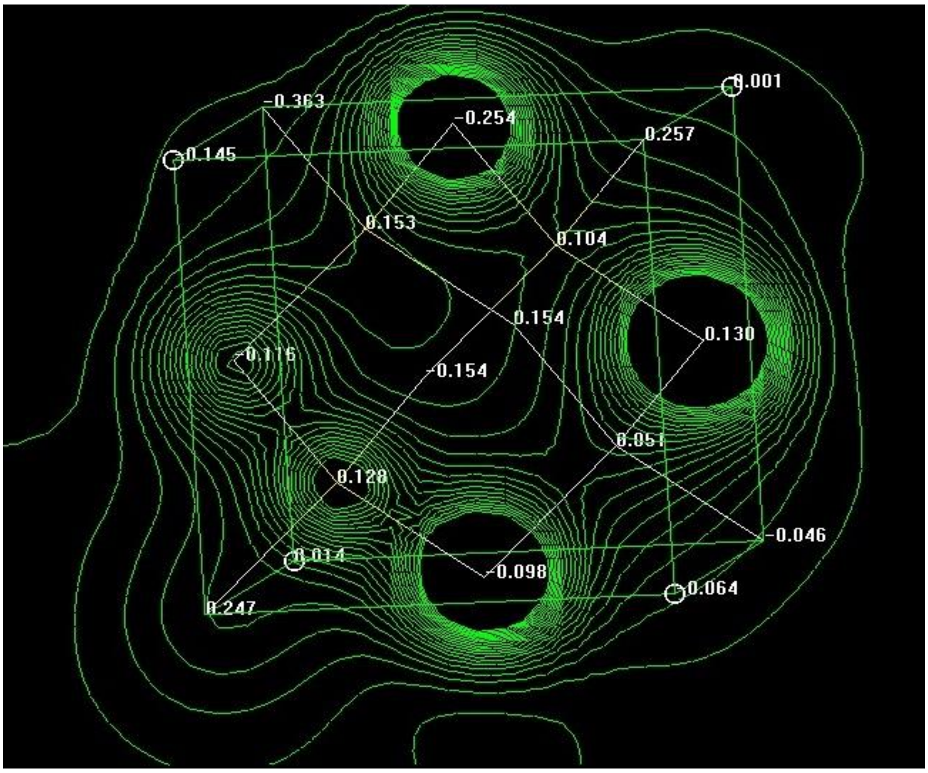

**Fig. 3.** Charge state in the Si lattice with $Si_2ZnS$ cells

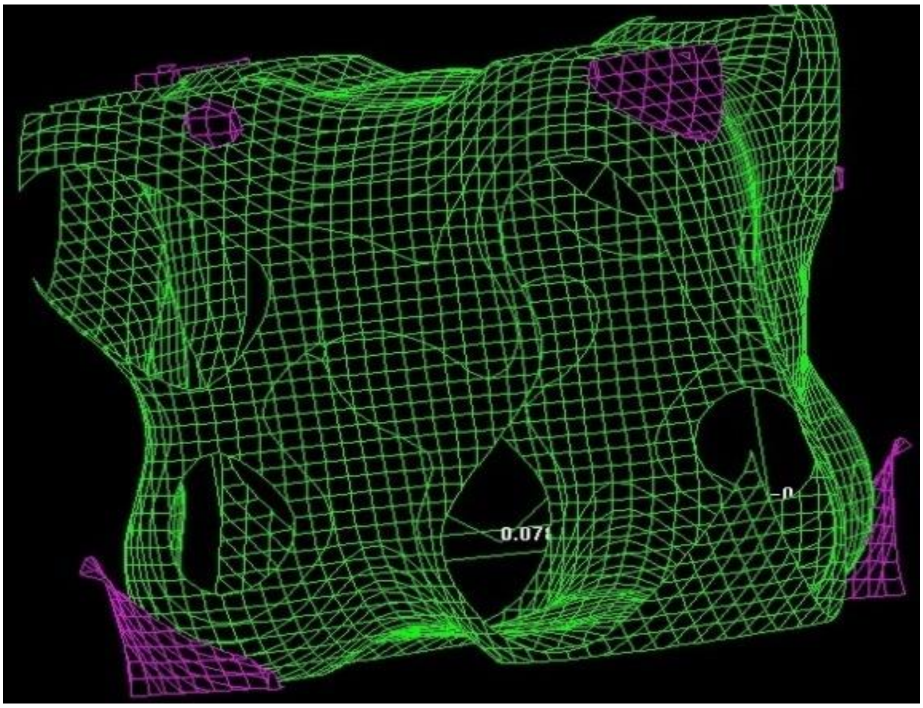

**Fig.4.** 3d-image of electrostatic potential in Si lattice

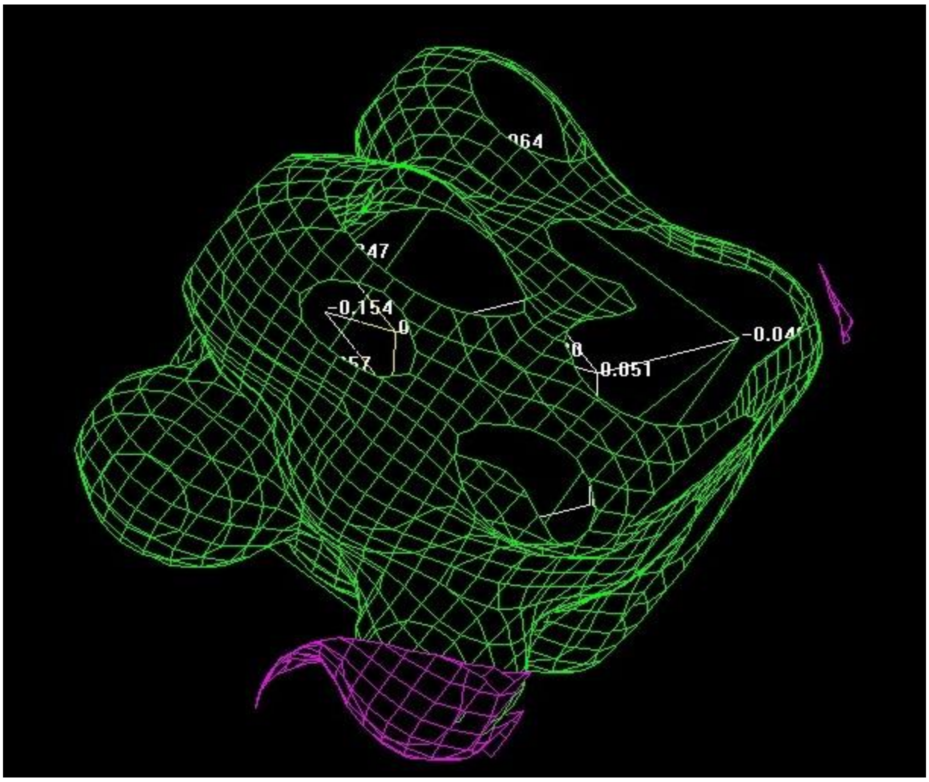

**Fig.5.** 3d-image of electrostatic potential of Si lattice with $Si_2ZnS$ cell.

It should be noted that these charges represent the difference between the positive charge of the nucleus and the charge of the electrons. The charge is "zero" for a neutral system, a positive real number for a cation and a negative real number for an anion [3].

Non-covalent electrostatic interactions were calculated using dipole-type interactions or partial atomic charges. The calculation took into account the dielectric constant epsilon, which adjusts the magnitude of the interaction of charges (and electrostatic potential) [3].

Calculation of the electrostatic potential of the base Si lattice, as shown in Fig. 2 and silicon with an impurity cluster consisting of 3 tetrahedral $Si_2ZnS$ cells in the Si base lattice, as shown in Fig. 3, revealed a noticeable change in the potential intensity at the cell sites. In the cluster, charge transfer occurs from S atoms to Zn atoms. As shown in Fig. 3, the Zn atoms in the sites acquire a negative charge, and the S atoms acquire a positive charge, as a result of which the ionic component of the interatomic bond arises, which leads to a deviation of the angles and bond lengths from the correct geometric ones. In practice, the numerical calculation confirms the hypothesis that instead of completing its structure to the most stable electronic configuration ... $s^2p^6$, in certain cases the chalcogen atom can also donate some of its electrons to form the quasi-stable configuration ... $sp^3$ [14].

In the model calculation, the electrostatic potential field is depicted as a function of the distribution of the electron charge around the nucleus and the nuclear charge. It should be especially noted that the calculation of the charge states of a molecule is carried out without taking into account changes in the geometry of its structure (interatomic distances in the molecule). Carrying out the geometry optimization procedure leads to significant time losses and leads to significant and ineffective use of computer resources. In many cases, after optimization, the total energy of the system rises. In such cases, it is necessary to calculate the charge state and other parameters of molecular structures for the initially constructed correct geometric structure [15].

At the same time, the program also allows you to obtain a map of potential energy, since there are options for choosing an image of an electrostatic potential, a charge state, a potential energy surface both on a plane and in a spatial image.

For systems with a large number of calculated molecules or atoms, it is often necessary to use parallel computations or more time. It should also be noted that when choosing different methods for calculating the electrostatic potential map and the values of the charge state, we get different ones most of the time the convergence between them is not good enough. In fig. Figures 4 and 5 show the electrostatic potentials of the Si lattice and the Si lattice with $Si_2ZnS$ cells, respectively, in the *3d* dimension, obtained after the completion of semi-empirical calculations by the ZINDO-S method.

It should be noted that the electrostatic potential is calculated as the potential energy of interaction of a unit of positive charge with molecular energy.

**CONCLUSION.** In conclusion, it can be noted that the Schrödinger equation in the approach of the semi-empirical method was solved for atoms and structures using known approximations and simplifications.

Calculation of the electrostatic potential of the base lattice of Si and silicon with an impurity cluster consisting of 3 tetrahedral $Si_2ZnS$ cells in the base Si lattice revealed a noticeable change in the potential intensity at cell sites. In the cluster, charge transfer occurs from S atoms to Zn atoms. Calculations showed that the Zn atoms at the sites acquire a negative charge, and the S atoms acquire a positive charge, as a result of which the ionic component of the interatomic bond arises, which leads to a deviation of the angles and bond lengths from the correct geometric ones. In practice, the numerical calculation confirms the hypothesis that instead of completing its structure to the most stable electronic configuration ... $s^2p^6$, in certain cases the chalcogen atom can also donate some of its electrons to form a quasi-stable configuration ... $sp^3$. Also, due to the appearance of the ionic component of the bond, a noticeable change is formed in the form of the electrostatic potential of the structure with the $Si_2ZnS$ cell, which is caused by a change in the potential energy of the cell due to the appearance of a strong Coulomb field inside the cell.

The performed model calculation of the lattice parameters, charge state, and electrostatic potential in the silicon lattice of the diamond structure with a $Si_2ZnS$ cell makes it possible to predict in the future new properties of crystalline silicon with different concentrations, structural arrangement at lattice sites and types of clusters of impurity atoms.

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