Atomic and Electronic Properties of a 155 H_{2}S Cluster under Pressure

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ABSTRACT: This is an all-electron density functional study of a cluster with 155 H_{2}S molecules subjected to pressures between 0.2 and 681.2 GPa. For modeling pressure, the cluster was in a container made of 500 He atoms. As the pressure increased, the bond length between the atoms decreased. This decrease changed the atomic distribution of the cluster. Initially, the H_{2}S molecules interacted weakly through hydrogen bonds. Then, the pressure moved the H atoms along the axis connecting two sulfur atoms, with S–H bond lengths between 1.4 and 1.6 Å. At high pressures, the atomic distribution consisted of interleaved layers of H and S atoms. The energy density of states of the valence band had two sub-bands with an energy gap between them. The overlapping of the 2a_{1} molecular orbitals of the H_{2}S molecules determined the molecular orbitals in the low-energy sub-band. In this sub-band, the molecular orbital with the lowest energy has no nodes; at high pressures, it has non-zero values for all the internuclear regions of the cluster. The overlapping of the molecular orbitals 1b_{2}, 3a_{1}, and 1b_{1} of the H_{2}S molecules determined the orbitals in the high-energy sub-band. The energy band gap (lowest unoccupied molecular orbital−highest occupied molecular orbital) decreased with the pressure, from 5.3906 eV for 0.2 GPa to 0.4980 eV for 681.2 GPa, whereas the gap between the sub-bands decreased from 4.7729 eV for 0.2 GPa to 0.03 eV for pressures higher than 125.5 GPa. The present study provides, from first principles, an idea on the role of hydrogen atoms in the evolution of solid phases of H_{2}S with pressure, which is difficult to obtain from experiments.

INTRODUCTION

At high pressures, sulfur and lanthanum hydrides show superconductivity at temperatures above 200 K.\textsuperscript{1,2} Till now, these hydrides are the superconducting materials with the highest transition temperature to the superconducting state. Their discovery was the corollary of predictions that pure hydrogen or hydrogen-rich compounds could be superconductors with a high transition temperature.\textsuperscript{3,4}

Of the superconducting hydrides with a transition temperature higher than 200 K, the H_{2}S system has been attractive for its analysis in detail. It contains only two types of atoms: sulfur and hydrogen; both atoms have a low atomic number. In addition to this property, at low pressures, in this system, the solid phases are molecular with the H_{2}S molecule as the basic unit.

Although the solid phases of H_{2}S are crystalline, with translational symmetry, most of their properties depend on their local atomic order, which is determined by the interaction between the H_{2}S units that build the solid.

This local atomic order can be analyzed in clusters of H_{2}S, even when the cluster has only one molecule.

Small clusters with hundreds of H_{2}S units can be studied in detail using techniques of quantum mechanics. This study can be conducted even using the all-electron techniques because the sulfur and hydrogen atoms have a reduced number of electrons. With these techniques, it is possible to obtain the evolution of the local atomic order when the cluster is under pressure. The information obtained in these conditions can help to understand the properties of the H_{2}S system, including its superconducting behavior.

The study of the evolution, with pressure, of the local atomic order in clusters of the H_{2}S system, is fascinating because the properties of this system, under pressure, had been studied for many years.

The analysis of the H_{2}S system began at ambient pressure, where it presents the polymorphs I, II, and III at different temperatures.\textsuperscript{5} Experiments, at this pressure, with electron diffraction,\textsuperscript{6} nuclear magnetic resonance,\textsuperscript{7} X-ray diffraction, and neutron diffraction\textsuperscript{8} confirmed the existence of these polymorphs.

In the first experiments with solid H_{2}S under pressure, the P−V isotherms were measured from 0 to 1 GPa, generating a phase diagram.\textsuperscript{9} This diagram was extended using Raman spectroscopy, at pressures up to 23 GPa at room temperature\textsuperscript{10} and pressures up to 20 GPa at 30 K.\textsuperscript{11}

Because the pressure changes the atomic distribution, the solid phases of H_{2}S were analyzed with X-ray powder diffraction at room temperature and pressures up to 20 GPa.\textsuperscript{12} These experiments provided only the atomic distribution of the sulfur atoms because the diffraction of the hydrogen atoms is undistinguishable from the background. These experiments discovered polymorph IV of the solid H_{2}S.
which had previously been proposed from studies with Raman spectroscopy.13

Experiments at room temperature and pressures between 27 and 42 GPa showed the existence of polymorph V of solid H$_2$S. With the pressure, this polymorph transformed from yellow to black, which is said to be produced by the reduction of the energy band gap.14

Infrared spectroscopy studies, above 46 GPa, suggested that the H$_2$S molecules dissociated into H and S atoms.15 In these studies, the samples became opaque to radiation at pressures above 96 GPa, which the authors interpreted as metallization of the phases, produced by the interaction between the S atoms in the crystalline structure.

Ab initio molecular dynamics calculations, using periodic boundary conditions,16 suggested the transformation of polymorph V into a new H$_2$S solid: polymorph VI. This transformation explained the disappearance of the SH stretching bands in the region of 2300–2500 cm$^{-1}$ at pressures higher than 46 GPa.17 Polymorph VI appears at 65 GPa with a crystalline structure formed by layers of S atoms alternating with layers of H atoms.16 These calculations suggest that the S–S interactions in the sulfur layers generate the opacity to light that occurs at pressures above 96 GPa.15

Using solid-state calculations, Li et al.17 investigated the possible origin of the proposed metallic behavior in the H$_2$S system when subjected to pressure. Their calculations predicted new stable polymorphs of solid H$_2$S, including a superconductor at 80 K.

These results induced the experimental groups to search for this superconducting phase, in particular, to groups of experts in the analysis of superconducting hydrides.18 The experiments of these groups culminated in the discovery of superconductivity in the H$_2$S system at 203 K.2 It is interesting to note that this was the first experiment, which showed the existence of the metallic behavior of some of the solid phases of H$_2$S under pressure.

After this discovery, several groups tried to determine, from the experiments, the crystalline structure of the superconducting phase.19–23 So far, the proposed crystalline structures are not conclusive.

The present work describes ab initio, all-electron molecular calculations, using density functional theory (DFT), of a cluster containing 155 molecules of H$_2$S, which is subject to pressure. This study helps to understand the evolution, with the pressure, of the local atomic order in solid H$_2$S. For example, the changes that occur in the lengths of the S–S and S–H bonds. These changes are essential to understand the evolution of the crystalline structure and the electronic properties with pressure.

The study compares the changes observed, with the pressure, in the atomic and electronic distribution in the H$_2$S cluster, with those changes reported in the literature on solid H$_2$S, which were generated from experiments and calculations developed with techniques of quantum mechanics.

## RESULTS AND DISCUSSION

### Construction of the H$_2$S Cluster

The H$_2$S clusters were generated from H$_2$S crystallites constructing using the atomic sulfur distribution described by Strobel et al.,15 obtained from X-ray powder diffraction and Rietveld refinement. Sulfur atoms occupy the 8h Wyckoff sites with $x = 0.162$ in a tetragonal crystalline structure. The unit cell has the symmetry described by the space group $I4/mcm$ and lattice parameters $a = 7.37$ Å and $c = 6.07$ Å.

As the X-ray diffraction produced by the H atoms is too low, its contribution to X-ray diffraction patterns hides in the background. Therefore, Strobel et al. did not give the positions of the hydrogen atoms. In the reported structure, S–S distances have three different values: 3.890 Å (the most abundant), 3.546, and 3.377 Å.

The generated H$_2$S clusters had different dimensions. However, the results reported in the present work correspond to a cluster formed by 155 molecules of H$_2$S.

During the construction of the cluster, to obtain the hydrogen atom positions, two hydrogen atoms decorated each S atom with S–H bond lengths of 1.3 Å and an H–S–H angle of 180°. Then, with the sulfur atoms in fixed positions, the geometry of the cluster was optimized to its minimum energy.

After this optimization, the two H atoms associated with each sulfur atom appeared bonded to it with an average bond length of 1.38 Å, forming H–S–H angles of 94°. These values were like the S–H bond length and the H–S–H angle of the H$_2$S molecule, calculated with the same method and basis used for the calculations performed with the 155 H$_2$S cluster. After that, a new geometry optimization was performed, where the positions of S and H atoms changed until the cluster reached its minimum energy.

In the optimized geometry, the sulfur atoms formed H$_2$S molecules with S–H bond lengths of 1.38 Å, interacting with each other through hydrogen bonds. Most of these bonds had lengths of about 2.54 Å; the corresponding S–S distances were around 3.897 Å.

### Construction of the He Container

The pressure was modeled with a container made of a spherical shell of He atoms. The shell was constructed from a fullerene having 500 carbon atoms and a radius of 9.973 Å, where He atoms replaced the carbon atoms.

The initial average radius of the 155 H$_2$S cluster was 10.712 Å, which was larger than the radius of the He shell. Therefore, to bring the cluster to the container, the radius of the container was expanded to 13.962 Å after multiplying by 1.4, the initial coordinates of the He atoms. The origin of these coordinates was the center of the container.

For modeling pressure on the cluster, the radius of the He container was reduced. The radius of the shortest container, 7.480 Å, was 0.75 times the initial radius of the fullerene.

### Embedding the 155 H$_2$S Cluster into the 500 He Container

The H$_2$S cluster in the He container gave rise to the 155 H$_2$S–500 He system (Figure 1) which had 965 atoms (500 He, 155 S, and 310 H). This system was used to study the atomic distributions and the corresponding electronic properties of the 155 H$_2$S cluster as a function of pressure.

For a given container radius, the positions of the He atom did not change, while those of S and H atoms varied until the entire system reached its minimum energy. For the container having a radius of 13.962 Å, after the energy minimization, the average radius of the external atoms of the cluster was 11.757 Å (Table 1). As a convention, the radius associated with the cluster was obtained by dividing by two the sum of the radius of the container and the average radius of the external atoms in the cluster. With this definition, the corresponding radius of the cluster was 12.860 Å, which gives a volume of 8908.1 Å$^3$ (Table 1).

The static pressure in the cluster due to the variation of the radius of the container was obtained by using eq 1.
Figure 1. One hundred and fifty-five H₂S molecules embedded in the container made with 500 He atoms.

Table 1. Dimension of Helium Containers and H₂S Clusters, the Outer Layer of the Cluster, Which Contains Only H Atoms; the Radius and Volume of the Cluster

| container radius (Å) | outer layer radius (Å) | num. H | cluster radius (Å) | cluster volume \(V(Å^3)\) |
|----------------------|------------------------|--------|--------------------|--------------------------|
| 13.962               | 11.7570                | 31     | 12.8597            | 8908.10                  |
| 12.965               | 10.9828                | 31     | 11.9739            | 7191.19                  |
| 11.968               | 10.0359                | 58     | 11.0018            | 5578.08                  |
| 10.971               | 9.2941                 | 46     | 10.1323            | 4357.28                  |
| 9.973                | 8.4974                 | 48     | 9.2353             | 3299.44                  |
| 9.475                | 8.0395                 | 58     | 8.7670             | 2822.58                  |
| 8.976                | 7.5581                 | 108    | 8.2670             | 2366.61                  |
| 8.477                | 7.1374                 | 133    | 7.8073             | 1993.38                  |
| 7.979                | 6.7710                 | 141    | 7.3748             | 1680.11                  |
| 7.480                | 6.3904                 | 141    | 6.9351             | 1397.17                  |

\[ P = -(\partial E/\partial V)_{N,T} \]  

\( \partial E \) is the variation of the total energy of the cluster, and \( \partial V \) is its variation in volume. \( N \) is the number of atoms, and \( T \) is the temperature.

The total energy of the cluster can be obtained using two different methods. First, calculating the energy of the container, \( E_{\text{500He}} \), and then subtracting it from the total energy of the system (Table 2). Second, obtaining this energy using all the H and S atoms in the cluster, \( E_{\text{155H2S}} \) (Table 2).

The energy values of the cluster using the two previous methods were different, with a difference that increases with pressure. Therefore, the total energy of the cluster, \( E_{\text{cluster}} \), was considered as the average value, \((E_{\text{total}} - E_{\text{500He}} + E_{\text{155H2S}})/2.0\), of the energy obtained using the two previous methods. For the lower pressures, \( E_{\text{total}} - E_{\text{500He}} \) was smaller than \( E_{\text{155H2S}} \), therefore, for these pressures, \( E_{\text{155H2S}} \) was approached as the energy of the cluster.

Figure 2 shows the total energy of the cluster, \( E_{\text{cluster}} \), versus cluster volume, \( V \), for the different diameters of the container. Because only ten \((E_{\text{cluster}} V)\) points were determined, they cannot be used alone to calculate the pressure at each point. It was necessary to find a continuous derivative function that described the evolution of the points. This function is granted to obtain pressure using eq 1.

The continuous derivative function was generated by fitting the set of \((E_{\text{cluster}} V)\) points with the sum of decreasing exponentials described by eq 2.

\[ E = E_0 + A_1 \exp(-V/t_1) + A_2 \exp(-V/t_2) \]  

with \( E_0 = -61,902.5(1) \text{ eV}, A_1 = 3662(99) \text{ eV}, t_1 = 0.28(1) \text{ Å}^3, A_2 = 252(6) \text{ eV}, \) and \( t_2 = 1.07(1) \text{ Å}^3 \) (the continuous curve in Figure 2).

Table 2. \( E_{\text{total}} \) is the Total Energy of the System, \( E_{\text{500He}} \) is the Energy That Considers Only the Atoms of He, and \( E_{\text{155H2S}} \) is the Energy That Considers Only the Atoms of S and H

| container radius (Å) | \( E_{\text{total}} - E_{\text{500He}} \) (hartree) | \( E_{\text{155H2S}} \) (hartree) | \( E_{\text{cluster}} \) (hartree) |
|----------------------|------------------------|--------------------------|--------------------------|
| 13.962               | -61 902.4113          | -61 902.3024            | -61 902.3024            |
| 12.965               | -61 902.5202          | -61 902.1781            | -61 902.1781            |
| 11.968               | -61 901.20316         | -61 901.4375            | -61 901.32066           |
| 10.971               | -61 897.86927         | -61 898.97083           | -61 898.42005           |
| 9.973                | -61 889.36279         | -61 892.45095           | -61 890.90687           |
| 9.475                | -61 881.79467         | -61 886.46617           | -61 884.13042           |
| 8.976                | -61 870.74835         | -61 877.54792           | -61 874.14814           |
| 8.477                | -61 855.71988         | -61 865.14814           | -61 860.43386           |
| 7.979                | -61 833.99097         | -61 846.82382           | -61 840.40739           |
| 7.480                | -61 797.15905         | -61 819.14895           | -61 808.15400           |

\( E_{\text{cluster}} \) is the energy associated with the cluster 155 H₂S.

Figure 2. Total energy of the 155 H₂S cluster as a function of its volume for different container radii.

was necessary to find a continuous derivative function that described the evolution of the points. This function is granted to obtain pressure using eq 1.

The continuous derivative function was generated by fitting the set of \((E_{\text{cluster}} V)\) points with the sum of decreasing exponentials described by eq 2.

\[ E = E_0 + A_1 \exp(-V/t_1) + A_2 \exp(-V/t_2) \]  

with \( E_0 = -61,902.5(1) \text{ eV}, A_1 = 3662(99) \text{ eV}, t_1 = 0.28(1) \text{ Å}^3, A_2 = 252(6) \text{ eV}, \) and \( t_2 = 1.07(1) \text{ Å}^3 \) (the continuous curve in Figure 2). The parameters \( E_0, A_1, t_1, A_2, \) and \( t_2 \) were optimized using the mean square error method. The derivative of this curve at each point provides the corresponding pressure value (Table 3).

Evolution of the Atomic Distribution of the 155 H₂S Cluster with Pressure. After embedding the cluster into the container and optimizing the geometry of the system, the pressure in the cluster was 0.2 GPa (Table 3). At this pressure, almost all S–S distances were in the distribution centered at 3.76 Å. A few S–S distances distributed around 3.42 Å (Figure 3A, Table 4).

At 0.2 GPa, the H₂S molecules interacted with each other via weak hydrogen bonds, with bond lengths distributed around 2.40 Å (Table 4, Figure 4A). The H₂S molecules on the surface of the cluster favored the interaction between the H and He atoms. At this pressure, the surface of the cluster contained approximately 10% of all the H atoms (Table 1).

The distances S–S decreased when the pressure in the cluster increased to 5.6 GPa (Table 4). This decrease reflects
bonds had a distribution centered at 1.96 Å (Table 4). Continued until 17.5 GPa, where the lengths of the hydrogen molecules, from 2.40 to 2.11 Å (Table 4). This trend distributed around 1.38 and 1.96 Å, whereas the angles $S$ between two sulfur atoms. The length of the $S$–$H$ bonds was distributed around 177°. During polymerization, a stronger interaction between the $H_2S$ units replaced the hydrogen bond. The transformation of the hydrogen bonds was like the symmetrization of the hydrogen bond reported for ice and boehmite under pressure.\(^{26,27}\)

This polymerization can be the precursor of the reported polymeric phases with symmetry $Pmcm_1$ and $P1$.\(^{16}\) These phases were found at high pressures using quantum mechanical calculations with periodic boundary conditions.\(^{16}\)

The degree of polymerization of the $H_2S$ units increased with pressure. At 47.5 GPa, most of the $H_2S$ units polymerized and cross-linked. At this pressure, the $S$–$S$ distances distributed around 3.03 and 2.67 Å (Table 4). For the $S$–$S$ distances centered around 3.03 Å, one H atom located between the two sulfur atoms, with $S$–$H$ bond lengths distributed around 1.37 and 1.74 Å (Table 4), and the $S$–$H$–$S$ angle distributed around 166°. The analysis of the atomic distribution shows that the short distances $S$–$S$ (2.67 Å) corresponded to the interaction $S$–$S$ without any atom of hydrogen between the atoms of sulfur.

This polymerization explains the behavior that Sakashita et al.\(^{15}\) observed at 46 GPa and interpreted as dissociation of the $H_2S$ molecules.

At 76 GPa, the polymerization SHS was almost complete. Distances $S$–$S$ were distributed around 2.94 Å, with one $H$ between the atoms of $S$. The respective angle $S$–$H$–$S$ distributed around 166°; the length of the $S$–$H$ bond centered around 1.38 and 1.61 Å. At this pressure, the length of the $S$–$S$ bond (without $H$ between the $S$ atoms) contracted to 2.57 Å. The respective infrared spectrum disappeared because the $H_2S$ units lost their molecular nature.

As the pressure increased, this atomic distribution remained nearly constant, even at 125.5 GPa. At this pressure, the $S$–$S$ contracted to values of 2.85 and 2.47 Å, whereas the lengths of the $H_2S$ bonds did not change (Table 4). The contraction of the distances $S$–$S$ with an atom of $H$ in the middle had three effects. First, the angles $S$–$H$–$S$ decreased from 166 to 145°. Second, some $H$ atoms were displaced, favoring the $H$–$H$ interaction. The shortest distance between the displaced $H$ atoms (Figure 5D) was similar to that observed in molecular hydrogen (0.75 Å). However, the $H$ atoms continued to interact with the corresponding $S$ atoms. Third, the displace-

### Table 3. Calculated Pressure on the 155 $H_2S$ Cluster Produced by the Containers with Different Radii

| container radius (Å) | $E_{\text{cluster}}$ (hartree) | cluster volume $V$ (Å$^3$) | pressure (GPa) |
|----------------------|-------------------------------|-----------------------------|--------------|
| 13.962               | $-61.902.30234$               | 8908.10                     | 0.2          |
| 12.965               | $-61.902.17819$               | 7191.19                     | 1.2          |
| 11.968               | $-61.901.32026$               | 5578.08                     | 5.6          |
| 10.971               | $-61.898.42005$               | 4357.28                     | 17.5         |
| 9.973                | $-61.890.90687$               | 3299.44                     | 47.5         |
| 9.475                | $-61.884.13042$               | 2822.58                     | 76.0         |
| 8.976                | $-61.874.14814$               | 2366.61                     | 125.5        |
| 8.477                | $-61.860.43386$               | 1993.38                     | 208.3        |
| 7.979                | $-61.840.40739$               | 1680.11                     | 361.7        |
| 7.480                | $-61.808.15400$               | 1397.17                     | 681.2        |

### Table 4. Center of the Distribution of $S(H)$–$S$ ($S$–$S$ Distance with One $H$ in between), $S$–$S$, $S$–$H$, and $SH$–$S$ Bond Lengths as a Function of Pressure

| pressure (GPa) | $S(H)$–$S$ (Å) | $S$–$S$ (Å) | $S$–$H$ (Å) | $SH$–$S$ (Å) | $S$–$H$–$S$ angle (degree) |
|---------------|----------------|-------------|-------------|---------------|----------------------------|
| 0.2           | 3.76           | 3.42        | 1.36        | 2.40          |                            |
| 1.2           | 3.66           | 3.31        | 1.36        | 2.39          |                            |
| 5.6           | 3.48           | 3.22        | 1.37        | 2.11          |                            |
| 17.5          | 3.24           | 2.87        | 1.38        | 1.96          | 177                        |
| 47.5          | 3.03           | 2.67        | 1.37        | 1.74          | 166                        |
| 76.0          | 2.94           | 2.57        | 1.38        | 1.61          | 166                        |
| 125.5         | 2.85           | 2.47        | 1.41        | 1.64          | 145                        |
| 208.3         | 2.77           | 2.37        | 1.41        | 1.65          | 125–130                    |
| 361.7         | 2.57           | 2.16        | 1.41        | 1.57          | 120–130                    |
| 681.2         | 2.40           | 2.03        | 1.37        | 1.58          | 100–110                    |

Figure 3. $S$–$S$ pair distribution function for different pressures. (A) 0.2, (B) 17.5, (C) 125.5, and (D) 361.7 GPa.

Figure 4. $S$–$H$ pair distribution function for different pressures. (A) 0.2, (B) 17.5, (C) 125.5, and (D) 361.7 GPa.
ment of H atoms increased the number of S–S bonds in the system (Figure 3C). The number of H atoms on the surface of the 155 H₂S cluster also increased. The number was approximated triple (108 H atoms) than for the low pressures (Table 1).

The number of displaced H atoms increased with pressure (Figure 3D) because the S–S distances contracted (Figure 3D). At 208.3 GPa, the S–S distances were distributed around 2.77 and 2.37 Å. The lengths of the S–H bond did not change (Table 4), but the displacement of H atoms favored the H–H interactions and changed their distribution. At 208.3 GPa, the hydrogen and sulfur atoms ordered into a layer of 133 H atoms on the cluster surface; then, a concentric layer of 94 S atoms mixed with 8 H atoms and another, more in-depth, concentric layer of 90 atoms of H. In the region of smaller cluster radii, the S and H atoms were mixed.

The previous trend continued for higher pressures (Table 4). At the highest pressure, the S–S distances had values of the same magnitude that the S–S bond lengths in the chains of 8 sulfur atoms formed at room temperature in pure sulfur. These values are also similar to those of S–S bond lengths in sulfur under high pressures and in superconducting sulfur.

However, it should be noted that the sulfur atoms did not segregate to build sulfur clusters. They always interacted with a distribution of H atoms. This result is consistent with the phase diagram and symmetrization in solid D₂S obtained with micro-Raman spectroscopy.

At high pressures, 361.7 and 681.2 GPa, in the cluster, approximately 45% (Table 1) of all the H atoms (141 in total) were on the surface of the cluster. To these atoms followed an inner layer of 94 S atoms and then a layer that had 90 atoms of H. For very internal diameters in the cluster, the H and S atoms were mixed.

Pressures above 100 GPa favored the formation of a laminar structure. In the present case, the container of He was a spherical shell. Therefore, the generated layers had spherical symmetry.

A container in the shape of a parallelepiped would result in the formation of alternative flat sheets made of H or S atoms, as reported for phase VI of solid H₂S at high pressures, obtained with molecular dynamics calculations using periodic boundary conditions.

Molecular dynamical calculations for 500 fs in the 155 H₂S–500 He system at 100 K, under pressures of 125.5 and 361.7 GPa, showed that the laminar atomic distribution was stable.

Evolution of the Electronic Structure of the 155 H₂S Cluster with Pressure. Energy Density of States. The electronic structure of the H₂S molecule determined the electronic structure of the 155 H₂S cluster.

For the valence electrons in the H₂S molecule, bonding molecular orbital 2a₁ is the one with the lowest energy, −20.6643 eV (Figure 6A). It is at 140.1142 eV above the highest energy of the core electrons.

In the cluster with 155 H₂S molecules, at 0.2 GPa, the energy associated with the lowest occupied molecular orbital of the valence band (LOMOVB) was −22.3433 eV (Table 5, Figure 6B). This energy is 136.9195 eV above the highest energy of the core electrons.

At a pressure of 0.2 GPa in the cluster, the energy gap, the energy difference between the HOMO and the lowest unoccupied molecular orbital (LUMO) energies, was 5.3906 eV (Table 5). This gap was smaller than the corresponding energy gap for an isolated H₂S molecule (7.8342 eV). As the
pressure increased, the LUMO energy decreased exponentially, whereas the HOMO energy increased exponentially (Figure 7, Table 5). These changes in energy resulted in an exponential decrease in the energy band gap (Figure 8, Table 5).

The increase in pressure also modified the energy density of states. For example, the energy gap between sub-bands decreased exponentially (Figure 8, Table 5). Clusters with more H₂S molecules would produce a better definition of this gap at high pressures.

The experimental band gap reported for solid H₂S under a pressure of 0.3 GPa is 4.8 eV, which is less than the band gap obtained for the cluster of 155 H₂S molecules, 5.3906 eV, at 0.2 GPa but approaches the energy gap between the sub-bands, 4.7729 eV, at this pressure. The experimental value of the reported energy gap for solid H₂S under a pressure of 29 GPa is 2.7 eV, which is less than the value of 3.6844 eV obtained for the band gap of the cluster at 47.5 GPa and similar to the energy gap between the sub-bands, 2.86 eV, at this pressure.

**Spatial Distribution of the Molecular Orbitals with Pressure.** The spatial distribution of the molecular orbitals of the 155 H₂S cluster correlates with the spatial distribution of the H₂S molecule.

For the valence electrons in the H₂S molecule, bonding molecular orbital 2a₁ (Figure 9A) has the lowest energy (−20.6643 eV, Figure 6A). Its composition analysis of Mulliken shows that the atomic orbital 1s of the hydrogen atoms contribute to 19.46%. The atomic orbitals of the sulfur atom contribute with the following values: 2s, 76.28%; 2pₓ, 2.84%; 2pᵧ, 4.24%. This molecular orbital is distributed, without nodes, throughout the space of the H₂S molecule.

The molecular orbital with the next higher energy (−12.3866 eV, Figure 6A) is bonding molecular orbital 1b₂ (Figure 9B). This orbital is a mixture of the 2pₓ and 2pᵧ atomic orbitals of sulfur and the antisymmetric linear combination of the atomic orbital 1s of the two H atoms. The molecular orbital with the next higher energy (−9.7934 eV, Figure 6A) is antibonding orbital 3a₁ (Figure 9C). This molecular orbital is a mixture of the 2s, 2pₓ, and 2pᵧ atomic orbitals of the sulfur with the atomic orbital 1s of the H atoms. Nonbonding (“lone pair”) molecular orbital 1b₁, with the highest energy (−7.2246 eV, Figure 6A), is the HOMO (Figure 9D), formed with the atomic orbitals 2pᵧ of the sulfur atom.

The DFT calculations showed that the molecular orbitals that describe the valence electrons of the H₂S molecule were

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**Table 5. One hundred and fifty-five H₂S Cluster: Energy of LOMOV, Energy Gap between Sub-Bands (Inner Gap), Energy of the HOMO, Energy of the LUMO, and Energy Band Gap, as a Function of Pressure**

| pressure (GPa) | LOMOV (eV) | inner gap (eV) | HOMO (eV) | LUMO (eV) | band gap (eV) |
|---------------|------------|----------------|----------|----------|--------------|
| 0.2           | −22.3433   | 4.7729         | −6.0763  | −0.6857  | 5.3906       |
| 1.2           | −22.3297   | 5.0885         | −6.1607  | −0.7075  | 5.4532       |
| 5.6           | −22.5038   | 5.3409         | −6.3784  | −0.7701  | 5.6083       |
| 17.5          | −23.5324   | 4.2477         | −6.2586  | −1.0313  | 5.2273       |
| 47.5          | −25.4372   | 2.8600         | −5.2491  | −1.5647  | 3.6844       |
| 76.0          | −26.9828   | 1.7524         | −4.7293  | −2.0272  | 2.7021       |
| 125.5         | −29.0264   | 0.7184         | −4.2423  | −3.1837  | 1.0586       |
| 208.3         | −31.3285   | 0.0200         | −4.0354  | −0.3056  | 0.9768       |
| 361.7         | −34.2619   | 0.0301         | −3.7633  | −3.2518  | 0.5115       |
| 681.2         | −38.6184   | 0.0299         | −3.6327  | −3.1347  | 0.4980       |

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**Figure 7.** Energy of the HOMO and the LUMO as a function of the pressure.

**Figure 8.** Energy band gap (difference between LUMO energy and HOMO energy) and the energy gap (inner gap) between the sub-bands in the valence band, as a function of the pressure.

**Figure 9.** Isosurface (iso = 0.01) of the molecular orbitals of the valence electrons of the H₂S molecule. (A) Molecular orbital 2a₁, energy \( E = -20.6643 \) eV; (B) molecular orbital 1b₂, energy \( E = -12.3866 \) eV; (C) molecular orbital 3a₁, energy \( E = -9.7934 \) eV; (D) molecular orbital 1b₁ (HOMO), energy \( E = -7.2246 \) eV.
the basis for constructing the molecular orbitals of the valence band of the 155 H$_2$S cluster (Figure 6).

In this cluster, the bonding molecular orbital $2a_1$ of the H$_2$S molecules determined the molecular orbitals of the low-energy sub-band of the cluster. All molecular orbitals in this sub-band have a reduced number of nodes (Figure 10). Of these, at high pressures, the LOMOVB is a bonding molecular orbital with non-zero values in all the internuclear regions of the cluster (Figure 10A).

With pressure, the overlapping of the molecular orbitals $1b_2$, $3a_1$, and $1b_1$ of the H$_2$S molecules determined the spatial distribution of the molecular orbitals of the high energy sub-band of the 155 H$_2$S cluster. In this sub-band, the molecular orbitals have nodes (Figure 11) even at the highest pressure. As an example, Figure 12 shows the evolution of the HOMO with pressure.

This bonding molecular orbital was a mixture of the 1s atomic orbital of the hydrogen atoms and the atomic orbitals 2s, 2p$_x$, 2p$_y$, and 2p$_z$ of the sulfur atoms. The composition analysis of Mulliken gave the following percentages of these atomic orbitals. For a pressure of 0.2 GPa, 19.49% of the 1s of the hydrogen atoms, 76.82% of the 2s, 0.33% of the 2p$_x$, 0.63% of the 2p$_y$, and 2.73% of the 2p$_z$ of the sulfur atoms. This composition is similar to that of an isolated H$_2$S molecule.

For the pressure of 361.7 GPa, the composition analysis of Mulliken of the LOMOVB was 11.33% of the 1s atomic orbital of the hydrogen atoms, 87.80% of the 2s, 0.44% of the 2p$_x$, −0.40% of the 2p$_y$, and 0.83% of the 2p$_z$ atomic orbitals of the sulfur atoms.
These results show that the LOMOVB is predominantly the mixture of the 1s atomic orbitals of the hydrogen atoms, with the 2s atomic orbitals of the sulfur atoms. Table 6 shows the evolution of the composition of this molecular orbital with pressure. It provides the number of atomic orbitals that contribute, above a threshold (in %), to the molecular orbital.

For 0.2 GPa, the molecular orbital located in a small number of H2S molecules. Therefore, 32 atomic orbitals were enough to generate 98% of it. At 17.5 GPa, to obtain this percentage of the molecular orbital, the number of atomic orbitals was 603. This number indicates that more and more H2S entities contribute to the LOMOVB as the pressure increased. These results agree with the spatial distribution of this molecular orbital as a function of the pressure, which is shown in Figure 13.

Table 7 shows the increase, with pressure, in the number of atomic orbitals that overlap during the generation of the LOMOVB. For example, for the pressure of 0.2 GPa, the overlap contributed 34.11%, whereas for the pressure of 76.0 GPa, the contribution was 60.57%. The overlap of 34.11% corresponds, basically, to the superposition of the atomic orbitals during the construction of bonding molecular orbital 2a1 of the almost isolated 155 H2S molecules. The difference between these values (26.46%) corresponds to the overlap of the atomic orbitals that describe the internuclear contributions of the molecular orbital.

Table 6. 155 H2S Cluster: The Population of the LOMOVB

| pressure (GPa) | % >0.1% | N | % >0.01% |
|---------------|---------|---|---------|
| 0.2           | 98.32   | 32| 99.75   | 81 |
| 1.2           | 97.37   | 42| 99.53   | 107|
| 5.6           | 86.63   | 115| 97.91  | 429|
| 17.5          | 83.03   | 172| 97.73  | 603|
| 47.5          | 82.46   | 214| 97.94  | 714|
| 76.0          | 82.13   | 195| 97.89  | 733|
| 125.5         | 83.62   | 183| 98.02  | 774|
| 208.3         | 83.61   | 196| 98.08  | 812|
| 361.7         | 85.11   | 239| 98.22  | 958|
| 681.2         | 88.00   | 272| 98.57  | 1026|

*The number (N) of atomic orbitals that generate it, for different population thresholds absolute values, as a function of pressure.*

| pressure (GPa) | atomic (%) | overlap (%) |
|---------------|------------|-------------|
| 0.2           | 64.21      | 34.11       |
| 1.2           | 61.88      | 36.80       |
| 5.6           | 55.43      | 42.48       |
| 17.5          | 47.71      | 50.02       |
| 47.5          | 40.55      | 57.39       |
| 76.0          | 37.32      | 60.57       |
| 125.5         | 35.75      | 62.27       |
| 208.3         | 33.64      | 64.44       |
| 361.7         | 34.20      | 64.02       |
| 681.2         | 38.40      | 60.17       |

CONCLUSIONS

To model the pressure on a cluster that has 155 H2S molecules; the cluster was embedded in a container made of a spherical shell of 500 He atoms. The reduction in the diameter of the container was enough to model the pressure on the cluster between 0.2 to 681.2 GPa. The size of the system, the cluster and the container (500 He, 155 S and 310 H), allowed a DFT study, ab initio, and all-electron of the atomic distribution and electronic properties of the cluster as a function of pressure.

The atomic distribution of the 155 H2S molecules in the cluster changed with the pressure. At low pressures, the H2S molecules interacted with each other through a hydrogen bond, with a bond length of 2.40 Å. As the pressure increased, a strong interaction replaced the hydrogen bond. This interaction had H–S bond lengths between 1.40 and 1.64 Å with the H atoms between two sulfur atoms. At higher pressures, the H atoms moved from the axis connecting the respective sulfur atoms, generating intercalated layers of pure H and pure S in the 155 H2S cluster, with strong interactions between all the atoms.

The energy density of states had two sub-bands in the valence band, with an energy gap between them that decreased with pressure. The sub-band of low energy corresponded to the molecular orbitals of the cluster generated by the overlap of the bonding molecular orbital 2a1 of the H2S molecules. The high-energy sub-band corresponded to the molecular orbitals of the cluster generated by the overlap of the molecular orbitals 1b2, 3a1, and 1b1 of the H2S molecules. All molecular orbitals of the cluster in this sub-band have nodes.

The molecular orbitals of the cluster in the sub-band at low energies have a reduced number of nodes. The molecular orbital with the lowest energy, the LOMOVB, has no nodes; at high pressures, it has non-zero contribution in all the internuclear regions of the cluster. This molecular orbital is predominantly the mixture of the atomic orbital 1s of the hydrogen atoms, with the atomic orbitals 2s of the sulfur atoms.

The energy band gap, the difference between the LUMO and the HOMO energies, decreased exponentially with the pressure from 5.3906 eV for 0.2 GPa to 0.4980 eV for 681.2 GPa. The energy gap between sub-bands decreased from 4.7729 eV for 0.2 GPa to 0.03 eV for pressures greater than 125.5 GPa.

The present study provides, from first principles, an idea on the role of the hydrogen atoms in the evolution of the solid phases of H2S with the pressure, which is difficult to obtain from experiments.

METHOD

The total energies of the H2S system were calculated using DFT. In this theory, a single determinant of molecular orbitals represents the electron wave function. The orbitals were generated using basis set 6-31g and self-consistently solving the DFT Kohn–Sham one-electron equations. The generalized gradient functional B3LYP modeled the energy of exchange–correlation. Dispersion correction was added to the functional.

Molecular dynamics calculations were performed on the system using the microcanonical ensemble (NVE), with an integration time step of 0.3 fs, and the velocity rescaling
thermostat. The rescaling time was much longer than the desired simulation time (500 fs).40,41

Some calculations were made using the functionals LC-PBE52 and LC_PBE053 to see if the results did not depend on the exchange correlation model associated with the functional. Some calculations were repeated using basis set 6-31g*66, which includes polarization functions in the hydrogen and sulfur atoms. The results were not different from those obtained with basis set 6-31g.

TeraChem54,55 was the code that was used to perform the molecular calculations. Algorithm L-BFGS56 generated the atomic distribution of the system with minimum energy, with the following convergence conditions: an energy threshold of 10−6 hartree, a maximum step of 10−3 Bohr, an rms step of 10−3 Bohr, a maximum gradient of 10−4 hartree/Bohr, and an rms gradient of 10−4 hartree/Bohr. For the calculations, we used two workstations: one with 4 Nvidia Tesla Kepler K80 GPU cards and another one with 3 Nvidia Tesla V100 GPU cards.

The VMD code57 was used to analyze orbitals and pair distribution functions and to inspect the distribution of the atoms in the cluster.

The code MULTIWFM (V. 3.5)34 was used to perform the analysis of the composition of Mulliken.35

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Notes

The author declares no competing financial interest.

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