THEORETICAL STUDIES OF THE BONDING OF SULFUR TO MODELS OF THE (100) SURFACE OF NICKEL

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Electronic wavefunctions have been obtained as a function of geometry for a S atom bonded to Ni clusters consisting of 1 to 4 atoms designed to model bonding to the Ni(100) surface. Electron correlation effects were included using the generalized valence bond and configuration interaction methods. Modeling the (100) surface with four Ni atoms, we find the optimum S position to be 1.33 Å above the surface, in good agreement with the value (1.30 ± 0.10 Å) from dynamic LEED intensity calculations. The bonding is qualitatively like that in H₂S with two covalent bonds to one diagonal pair of Ni atoms. There is a S π pair overlapping the other diagonal pair of Ni atoms. [Deleting this pair the S moves in to a position 1.04 Å from the surface.] There are two equivalent such structures, the resonance leading to equivalent S atoms and a c(2 X 2) structure for the S overlayer. The Ni in the layer beneath the surface seems to have little effect (~0.03 Å) on the calculated geometry. Bonding the S directly above a single Ni atom leads to a much weaker bond ($D_e = 3.32$ eV) than does bonding in a bridge position ($D_e = 5.37$ eV).

1. Introduction

A first step in understanding the mechanisms of heterogeneous catalysis at transition metal surfaces is to understand the nature of the bonding of atoms and molecules to the surface.

Experimentally, geometric information is obtained by detailed analysis of low energy electron diffraction (LEED) intensities [1]. Because the theoretical analysis involves some severe approximations, these geometries cannot be described as purely experimental, however with high quality LEED intensities, it appears that the determination of geometric spacings of atomic overlayers to within ~0.1 Å is possible (in the direction perpendicular to the surface).

We are in the process of developing theoretical techniques for solving directly for
the geometries of chemisorbed species. Such theoretical procedures, if reliable, would be extremely valuable, since one could consider special surface defects (e.g., steps) and reaction intermediates, both of which are relevant for studying catalysis. Our theoretical model involves replacing the semi-infinite solid by a finite cluster. We feel that the chemisorptive bond is sufficiently localized that our description of the chemisorbed species is valid for the real metal, however detailed comparison to experiment would be valuable.

As a test of the theory, we have chosen to examine the geometries for S overlayers on the Ni(100) surface, a system which has been the object of extensive LEED studies and dynamic intensity calculations [1a].

We solve for the states of the finite clusters using the ab initio generalized valence bond (GVB) method [2a], which differs from the usual Hartree–Fock (HF) method in that it includes the dominant correlation effects necessary to describe bond formation.

In these calculations we explicitly include the 4s and 3d electrons of each Ni atom (ten electrons) and the 3s and 3p electrons of the S atom (six electrons), while the 18-electron Ar core of the Ni atom and the ten-electron Ne core of the S atom are replaced by effective potentials (see section 4).

In section 2, we discuss qualitatively the wavefunctions for the various clusters and compare the geometry predictions from the calculations with experimental results for the Ni(100) and Ni(110) surfaces, while Section 3 discusses the wavefunctions in more detail. Section 3 describes some of the details of the basis set and effective potentials used here, while Section 5 discusses the configuration interaction (CI) calculations.

A preliminary report of this work has been presented elsewhere [2b].

2. Qualitative description of the theoretical results

2.1.

2.1.1. NiS

We find that for the ground state of NiS, the Ni has the character of the Ni(4s)\(^1\)(3d)\(^9\) configuration, while the S has the character of the S(3s)\(^2\)(3p)\(^4\) configuration. The bonding is dominated by the sigma bond which may be described qualitatively as a Ni(4s) orbital paired up with a singly occupied S(3p\(\sigma\)) orbital. The quantitative shapes of these orbitals are given in fig. 1a, b; as expected from the relative electronegativities [3a] (1.8 for Ni, 2.5 for S) there is some charge transfer to the S atom (~0.38 electrons [4]). For the ground state of NiS the 3d hole of the Ni3d\(^9\) configuration is 3d\(\pi\). This orbital is paired with the 2p\(\pi\) hole of the S leading to a \(^3\Sigma^-\) ground state which is quite analogous to the ground states of O\(_2\) [5] and of NiO [6]. As indicated in fig. 1, the Ni3d orbitals are only slightly affected by the bond.
Fig. 1. The GVB orbitals of configuration $1b$ which corresponds to the $X^3\Sigma^-$ state of NiS. Unless otherwise noted, all plots have uniformly spaced contours of 0.05 a.u. Solid lines indicate positive contours, short dashes indicate negative contours, and long dashes indicate nodal lines. [Note that because an Ni(4s) orbital is much more diffuse than an Ni(3d) orbital, even a relatively small amount of 3d character appears very pronounced in the contour plots. Thus, the orbital in Fig. 1a, which appears to contain a large amount of 3d character, has <15% d character (from a Mulliken population analysis).] The same conventions are used for the other figures.
Table 1
Summary of results for bonding of sulfur to the Ni clusters

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Geometry</th>
<th>Model for</th>
<th>Distance above plane (Å)</th>
<th>(R_{NiS} ) (Å)</th>
<th>( D ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiS</td>
<td>Ni--S</td>
<td>–</td>
<td>1.91</td>
<td>1.91</td>
<td>3.32</td>
</tr>
<tr>
<td>Ni₂S</td>
<td>( \sqrt{2} a )</td>
<td>(110)</td>
<td>1.04</td>
<td>2.04</td>
<td>5.37</td>
</tr>
<tr>
<td>Ni₃S</td>
<td>Ni S Ni</td>
<td>–</td>
<td>1.07</td>
<td>2.06</td>
<td>3.89 ( a )</td>
</tr>
<tr>
<td>Ni₄S</td>
<td>( \sqrt{2} )</td>
<td>(100)</td>
<td>1.33</td>
<td>2.21</td>
<td>3.91 ( a )</td>
</tr>
</tbody>
</table>

\( a \) The NiS and Ni₂S calculations used a [3s, 1p, 2d/3s, 2p, 1d] basis, while a [2s, 1p, 1d/3s, 2p] basis was used for the Ni₃S and Ni₄S calculations. From comparisons of both types of calculations for Ni₂S we estimate that this basis leads to an error in \( D \), of 0.63 eV, but does not have a significant effect on the geometry. Thus, we have added 0.63 eV to the \( D \) values for the Ni₃S and Ni₄S calculations in order to compare with the NiS and Ni₂S calculations. (See footnote \( a \) of table 5.)

As indicated in table 1, the calculated bond distance is 1.91 Å which is substantially smaller than that of bulk Ni sulfides. (The bond length of the NiS molecule is not known experimentally.) The calculated bond energy is 3.32 eV which is in reasonable agreement with current experimental estimates \( 3.53 \pm 0.15 \) eV [7].

2.1.2. Ni₂S
As a first model for both the (100) and (110) surfaces we considered two Ni atoms separated by \( \sqrt{2} \) times the bulk separation [these atoms are second nearest
neighbor atoms of bulk Ni but correspond to neighboring Ni atoms on the (100) surface and in one direction on the (110) surface. Here we optimized the position of the S but with the Ni atoms fixed.

Qualitatively one can visualize the electronic configuration of Ni₂S as

\( \text{Ni}_2 \text{S GVB (2/PP)} \)

Fig. 2. Selected orbitals of the Ni₂S cluster.
where lines connect pairs of singly occupied bonding orbitals and the remaining
doubly occupied S(3p_x) orbital (pointing perpendicular to the plane) is denoted
with a circle containing two dots. (As discussed in section 3.2, the lowest state
corresponds to taking the 3d holes to be delta-like with respect to the NiS bond axes.)

As shown in fig. 2, the two NiS sigma bonds (fig. 2a, b, c, d) are somewhat ionic,
much like those in diatomic NiS, leading to a total charge transfer to the S of 0.57
electrons [6]. The doubly occupied S(3s) orbital (fig. 2e) has built-in 3p character
resulting in hybridization away from the Ni–S bonds.

The calculated optimum NiS bond length has increased to 2.04 Å while the bond
energy of S to the Ni_2 complex has increased to 5.37 eV [neglecting the slight
attractive interaction between the Ni atoms of the free Ni_2 complex]. Thus, our cal-
culations indicate that bridging is more favorable than bonding directly above a sur-
face Ni atom. Comparing with the bond energy of NiS, 3.32 eV, suggests that
~0.64 eV of the bond energy of the NiS molecule is due to π bonding.

As discussed in section 2.2, the Ni_2S cluster is an appropriate model for the
registry of S on the (110) surface where the closest nonbonding Ni atoms are in the
next layer down. However, for the (100) surface there are two nearest neighbor Ni
atoms in the surface and one in the layer below close enough to affect the geo-
metry. We examined the effect of the second layer Ni atom using a Ni_3S cluster,
and the effect of the other two surface Ni atoms using a Ni_4S cluster.

2.1.3. Ni_3S

Adding a third Ni atom below the surface leads to the Ni_3S cluster. Qualita-
tively the bonding in Ni_3S involves Ni–S bonds to the two surface Ni atoms, as in
the Ni_2S calculation, while the Ni atom below the surface is nonbonding.

As discussed in section 3, we did not solve for the Ni_3S wavefunction in terms of
localized orbitals as in (1), but rather used the full C_2v symmetry of the molecule
leading to a wavefunction which may be qualitatively understood in terms of
bonding the S atom to the Ni_3 cluster in the following orientation:

As shown in fig. 3, the resulting wavefunction has a bond pair (fig. 3ab) with one
component (fig. 3a) which is basically a S(3p_y) orbital while the other component
(fig. 3b) corresponds qualitatively to Ni2(4s)–Ni4(4s). The other bonding orbital
(fig. 3c) is doubly occupied and corresponds to the bonding combination of a
S(3p_z) orbital and 4s character on all three Ni atoms. The 4s orbital of Ni5 (fig. 3d)
is nonbonding and has built-in 4p character so as to hybridize toward the bulk metal. The S(3s) orbital (fig. 3e) has hybridized slightly in the direction of Ni3.

Essentially, this wavefunction corresponds to two Ni-S bonds to Ni2 and Ni4, as in Ni2S, while Ni5 is nonbonding. Thus the geometry should be predominantly determined by the interactions between the sulfur and the surface Ni atoms (2 and 4). Indeed, the Ni3S cluster has an optimum geometry with the S 1.07 Å above the surface as compared with 1.04 Å for Ni2S, and we conclude that the second layer
Ni atom has only a very small effect on the geometry. The bond energy, on the other hand, decreases to 3.89 eV, since the bonding here involves disruption of metal–metal bonds for the Ni$_3$ cluster.

2.1.4. Ni$_4$S

Considering the four surface atoms interacting with the S for the (100) surface leads to the Ni$_4$S cluster. Qualitatively the electronic configuration of the Ni$_4$S cluster is:

The bonding orbitals (fig. 4a, b, c) are analogous to the bond orbitals of the Ni$_3$S cluster. The GVB pair (fig. 4a, b) involves one component (fig. 4a) which is essentially a S(3p$_y$) orbital while the other component (fig. 4b) corresponds approximately to Ni2(4s)–Ni4(4s). The other bonding orbital (fig. 4c) is essentially S(3p$_x$)-like, but has built in a bonding combination of Ni(4s) character on all four Ni atoms.

The 4s orbitals of the remaining two Ni atoms (fig. 4e, f) are high-spin coupled and have significant nonbonded repulsions with the doubly occupied S(3p$_x$) orbital. [As discussed in section 2.2, these orbitals are involved in bonds to adjacent S atoms for the full overlayer. Thus, we high-spin couple these orbitals to best approximate the repulsive effects between these orbitals and the S(3p$_x$) pair.]

The 4s orbitals of Ni1 and Ni3 have hybridized away from the sulfur orbitals to minimize their overlap with the S(3p$_x$) pair. (They must be orthogonal because of the Pauli principle.) This results in some stabilization of the S(3s) orbital by interaction with the 3d$^9$ cores of Ni1 and Ni3 (somewhat as for the 5σ orbital of CO upon bonding to Ni), however, the overall effect is repulsive and leads to an optimum geometry with the S atom 1.33 Å above the surface. (Compare with 1.04 Å for Ni$_2$S).

2.2. Comparison to experimental results

Fig. 5 shows the location of the S atom relative to the nearest neighbor Ni atoms for the (100) and (110) surfaces of Ni. Fig. 6 illustrates the bonding expected for c(2 × 2) overlayers on the (100) and (110) surfaces.
Fig. 4. Selected orbitals of the Ni₄S cluster.
Fig. 5. The geometry of the S atom and nearest neighbor Ni atoms for the Ni(100) and Ni(110) surfaces. Ni atoms in the plane of the paper are illustrated by light circles, while those below the paper are illustrated by dashed circles and the S atom is illustrated by a somewhat larger heavy circle. For the (110) surface, geometry A is suggested by our results, while geometry B is the registry with the surface assumed for calculation of LEED intensities [3a].

Fig. 6. The c(2x2) structure for S on Ni(100) and Ni(110) respectively. Circles represent surface Ni atoms, crosses represent S atoms, heavy lines represent Ni–S bonds, and dashed lines outline the unit cell.
2.2.1. The Ni(100) Surface

Ni atoms 2 and 4 of fig. 5 were included in the Ni$_2$S calculation. Adding Ni atom 5 leads to the Ni$_3$ cluster. However, as discussed in section 2.1.3, the effect of Ni atom 5 on the geometry is very small (0.03 Å), thus we included only the surface Ni atoms (1–4) in the Ni$_4$S calculation to determine the geometry. From fig. 6, one sees that Ni atoms 1 and 3 are involved in bonds to adjacent S atoms. These orbitals are expected to lead to nonbonded repulsions with the S orbitals, causing the S atom to be pushed up higher above the surface than for the Ni$_2$S complex. In the Ni$_4$S calculations (described in the previous section) this effect was approximated by coupling the 4s orbitals of Ni atoms 1 and 3 into a triplet state. The optimum geometry for the Ni$_4$S cluster has the S atom 1.33 Å above the surface in excellent agreement with the distance from LEED intensity analysis, 1.30 ± 0.10 Å [1a].

The bonding structure for (100) shown in fig. 6 has the corner and center S atoms related by a glide plane; consequently it leads to a p(2 × 2) structure. However, there is a degenerate structure with all the bound directions rotated by 90°; these two structures are expected to have a strong interaction (resonance), leading to all the S atoms being equivalent. Thus, including this resonance effect, the overall symmetry is c(2 × 2).

From fig. 6 we see that with a S in only half the four-fold sites each surface Ni atom has its 4s orbital involved in a Ni–S bond. Thus, this bonding picture suggests that the c(2 × 2) overlayer is particularly stable.

Note that the Van der Waals radius of the S atom is 1.85 Å [3b], whereas half the S–S distance for the c(2 × 2) structure is 1.76 Å. Thus, higher densities of S atoms on the surface are also unfavorable due to large nonbonded repulsions between adjacent sulfur atoms.

2.2.2. The (110) surface

For the (110) surface, LEED studies suggest that the S overlayer has a registry with the surface given by geometry B of fig. 5b. We have not carried out calculations that are appropriate to this particular registry with the surface. However, the Ni$_2$S cluster is appropriate to calculating the optimum geometry for a site of geometry A, since the closest nonbonded Ni atoms are in the next layer down (2.61 Å away for the experimental geometry) and should not significantly influence the geometry. Thus, for a registry with the surface given by geometry A we predict that the S atom should be 1.04 Å above the surface. This is in reasonable agreement with the distance, 0.93 ± 0.10 Å, found from the LEED analysis assuming geometry B.

As discussed in section 3.5, geometry B involves an Ni–Ni separation of $\sqrt{3}$ times the bulk separation, leading to an NiS bond length (2.35 Å) and an NiSNi angle (133.3°). This seems much less favorable than the geometry parameters calculated for geometry A, and Ni–S distance of 2.04 Å and NiSNi bond angle of 118.8°. Since the LEED intensity analysis is more sensitive to the distance above the surface than to the registry with the surface and since we obtain a reasonable
3. Further discussion of the wavefunctions

Before discussing the bonding of a sulfur atom to the various Ni clusters, we first consider the bonding in NiH and Ni₂ since these simple cases illustrate the basic characteristics of the bonding between Ni atoms and the bonding to a sulfur atom.

The Ni atom has two low-lying states 4s¹3d⁹(3D) and 4s²3d⁸(3F). Ignoring spin-orbit coupling effects, the ground state is 3D with the 3F state only 0.03 eV higher [9]. Thus, both states could play a role in the bonding. However, the Ni(4s) orbital is ~2½ times as large as the Ni(3d) orbitals (see fig. 7); thus the 4s orbital dominates the bonding. Bringing up an H atom to the 4s²3d⁸ state of Ni leads to repulsive interactions much as for the case of HeH. The 4s¹3d⁹ state of Ni, on the other

Fig. 7. Comparison of the 4s and 3d orbital sizes of the Ni atom.
hand, leads to a sigma bond between the Ni(4s) and H(1s) orbitals and, hence, an attractive potential curve as for H₂.

The remaining 3d⁹ configuration on the Ni then leads to \(^2\Sigma^+, \ ^2\Pi, \ \ ^2\Delta\) states depending on whether the singly occupied 3d orbital is taken as a 3dσ, 3dπ, or 3dδ orbital respectively. As discussed elsewhere [13], while the Ni configuration is basically 4s¹3d⁹, some 4s²3d⁸ character is introduced in certain states. The intra-atomic coupling between 4s¹3d⁹ and 4s²3d⁸ leads to a stabilization of the 4s¹3d⁹ configuration with a singly occupied 3dδ orbital. The net effect is the ordering \(^2\Delta < ^2\Pi < ^2\Sigma^+\) with \(^2\Delta 0.346 \text{ eV} \) below \(^2\Pi\) which in turn is 0.095 eV below \(^2\Sigma^+\) (at \(R_e\) for the \(X^2\Delta\) state) [12]. We find that these results are quite general for sigma bonds to the Ni(4s) orbital leading to an increased stability associated with having a 3d hole which is δ-like with respect to the bond axis.

From the discussion of NiH, it is not surprising that the bonding in Ni₂ [15] involves a 4s¹3d⁹ configuration on each Ni leading to a sigma bond between the 4s orbitals, and the lowest 3d occupation has both 3d holes taken in 3dF orbitals (other 3d orbital occupancies lead to numerous low-lying excited states).

For larger clusters of Ni atoms there is a possibility of bonding involving the 4s²3d⁸ configuration of the Ni atom. We illustrate this possibility for Ni₃ [14], where the central Ni atom can be taken as 4s¹3d⁹ or 4s²3d⁸ in character. For the 4s¹3d⁹ case (considering only the Ni(4s)-like orbitals), the bonding is analogous to that in linear H₃ [16] leading to resonance states of the form

\[ \sigma \quad \sigma \rightarrow \pi \quad \sigma \rightarrow \pi \quad \sigma \]  \(\text{(4)}\)

For the 4s²3d⁸ case the lowest state involves two sigma bonds:

\[ \sigma \rightarrow \sigma \quad \sigma \rightarrow \sigma \]  \(\text{(5)}\)

(Here the \(4s^2\) pair of the central Ni has been angularly correlated, leading to an sz lobe \(\sigma \rightarrow \sigma\) overlapping Ni1 and an sz lobe \(\sigma \rightarrow \sigma\) overlapping Ni2.)

Keeping the bond lengths equal, both (4) and (5) lead to linear geometries with \(R = 2.28 \text{ Å}\) for (4) and \(R = 2.36 \text{ Å}\) for (5). Using the optimum \(R\), the \(s^1d^9\) state (4) is the ground state. However, if the \(R\) is fixed at the bulk value of 2.49 Å the potential curves are as in fig. 8b. Here one sees that linear geometries favor \(s^2d^8\), while bent geometries favor \(s^1d^9\) [17]. (From examination of the orbitals we find that the sz and \(\bar{z}\)-like lobes of the central Ni in (5) remain oriented at 180° to each other as the molecule bends, leading to a decrease in the overlap of the bond pairs and a large increase in energy upon bending.) Thus, at the Ni–Ni–Ni bond angles involved in the Ni clusters considered here (90°), we expect that all Ni atoms have a \(4s^13d^9\) configuration. (The energies as a function of geometry for (4) and (5) are summarized in table 2.)
Ni₃ GEOMETRY VARIATION

(a) R VARIATION

(b) ANGLE VARIATION (R=2.49 Å)

Fig. 8. Energy of Ni₃ as a function of bond length and bond angle. The curves labeled $s^1d^9$ correspond to (4), while the curves labeled $s^2d^8$ correspond to (5). Fig. 8a corresponds to optimizing the Ni–Ni length for equal Ni–Ni bond lengths, while fig. 8b corresponds to varying the bond angle for a fixed Ni–Ni distance corresponding to the bulk separation (2.49 Å).
Table 2
Energies for GVB calculations on Ni3 as a function of geometry (always retaining equal bond lengths; as described in section 3, one state has s^1d^9 character on the central Ni while the other has s^2d^8 character)

<table>
<thead>
<tr>
<th>θ (deg)</th>
<th>R (a₀)</th>
<th>4.1 a₀</th>
<th>4.4 a₀</th>
<th>4.7 a₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>180 s^1d^9</td>
<td>-41.14976</td>
<td>-41.15143</td>
<td>-41.14397</td>
<td></td>
</tr>
<tr>
<td>s^2d^8</td>
<td>-41.13894</td>
<td>-41.14984</td>
<td>-41.14515</td>
<td></td>
</tr>
<tr>
<td>150 s^1d^9</td>
<td>-41.14398</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>s^2d^8</td>
<td>-41.13974</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120 s^1d^9</td>
<td>-41.14344</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>s^2d^8</td>
<td>-41.12270</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.1. NiS

Now we consider bonding a single Ni atom to S. The sulfur atom has a (1s)^2(2s)^2(2p)^6(3s)^2(3p)^4 configuration, leading to a 3p group state. Ignoring the core electrons and the (3s)^2 pair (since we find they are not involved in the bonding) leads to a (3p)^4 configuration which we represent as

![Diagram](6)

where ○ represents a 3px orbital perpendicular to the plane of the paper and □ represents a 3p orbital in the plane of the paper. Bringing up a single Ni atom (along the z axis) leads to formation of a sigma bond between the Ni(4s) and S(3p) orbital.

This leaves a single 3d hole on the Ni which, together with the two possible S atom configurations, leads to the ten configurations shown below as 1a to 5b [28]. Each of these configurations involves a sigma bond between Ni(4s) and S(3pσ) orbitals and the ordering of the states is controlled mainly by differences in the π bonding. In these diagrams, we indicate the Ni(3dπ) and S(3pπ) orbitals schematically [using the same notation for Ni dπ orbitals as was used in (6) for S pπ orbitals] and include the remaining Ni atom configuration in an abbreviated form (e.g., (dδ)^4(dσ)^3):

1a

(1a) (dδ)^4(dσ)^3 (4s) σ

\[ 3\Delta^- \]

1b

(1b) (dδ)^4(dσ)^3 (4s) σ

\[ 3\Sigma^- \]

\[ 1\Sigma^- \]

\[ 1\Delta^- \]
Thus, taking a Ni(3d\sigma) hole as in 1 and 2 leads to states X^3\Sigma^-, 1\Delta, 1\Sigma^+, 1\Sigma^-, 3\Delta, and 3\Sigma^+ which are analogous to the corresponding states of O_2 [7]. The 3d\sigma hole (as in 3) leads to the 2^1\Pi states and the 3d\delta hole (as in 4 and 5) leads to the 1^3\Pi and 1^1\Phi states.

The potential curves for these states of NiS (CI calculations based on the X^3\Sigma^- state of NiS, see section 5.1 for further discussion), are shown in fig. 9, while the CI energies used to construct the curves are shown in table 3.

By analogy to NiH, the states of the 3d\delta hole are expected to be stabilized rela-
Fig. 9. Potential curves for the states of NiS. The calculated points are at 3.4, 3.5, 3.8, 4.1, and 4.4 au, respectively. The numbers in parenthesis refer to the dominant configuration(s) for each state.

tive to the state of the 3dπ hole, which in turn are stabilized relative to the states of the 3dσ hole. This leads to the 4 and 5 states (which involve a 3dσ hole) being below the 3 states (which involve a 3dπ hole). However, as was the case for NiO [6], the states having a Ni 3dπ hole have additional π bonding, resulting in the 1 and 2 configurations being lowest. Thus 1,2 < 4,5 < 3. The ground state of NiS is the 3Σ− (1) state which has an electronic structure analogous to O2 [7]. The ordering of the remaining states is the same for the corresponding states of O2.

The orbitals of the X3Σ− state of NiS are shown in fig. 1. Looking at the sigma bond pair (fig. 1a, b) one sees that the Ni(4s)-like component (fig. 1a) has been distorted toward the sulfur [a situation typical of a somewhat ionic bond (toward the S)]. As for NiO [6], the doubly occupied π orbitals (fig. 1cf) have delocalized onto the opposite centers (leading to two three-electron bonds and the extra stability associated with the 3Σ− state). However, the doubly occupied S(3pₓ) orbital
Table 3
Energies for CI wavefunctions of NiS (subtract the quoted energy from −50.0 to get the total energy in hartrees)

<table>
<thead>
<tr>
<th>State a</th>
<th>R</th>
<th>3.4 a₀</th>
<th>3.5 a₀</th>
<th>3.8 a₀</th>
<th>4.1 a₀</th>
<th>4.4 a₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>3Φ(4, 5)</td>
<td>0.69700</td>
<td>0.70418</td>
<td>0.71071</td>
<td>0.70323</td>
<td>0.68905</td>
<td></td>
</tr>
<tr>
<td>23Π(4, 5)</td>
<td>0.69460</td>
<td>0.70200</td>
<td>0.70925</td>
<td>0.70229</td>
<td>0.68842</td>
<td></td>
</tr>
<tr>
<td>13Π(3)</td>
<td>0.68015</td>
<td>0.68739</td>
<td>0.69729</td>
<td>0.69346</td>
<td>0.68171</td>
<td></td>
</tr>
<tr>
<td>1Φ(4, 5)</td>
<td>0.68406</td>
<td>0.68293</td>
<td>0.70381</td>
<td>0.69930</td>
<td>0.68712</td>
<td></td>
</tr>
<tr>
<td>21Π(4, 5)</td>
<td>0.69015</td>
<td>0.69788</td>
<td>0.70658</td>
<td>0.70089</td>
<td>0.68803</td>
<td></td>
</tr>
<tr>
<td>11Π(3)</td>
<td>0.67077</td>
<td>0.67980</td>
<td>0.69353</td>
<td>0.69206</td>
<td>0.68192</td>
<td></td>
</tr>
<tr>
<td>3Σ+ (2)</td>
<td>0.64615</td>
<td>0.66069</td>
<td>0.68384</td>
<td>0.68653</td>
<td>0.67833</td>
<td></td>
</tr>
<tr>
<td>3Δ(1, 2)</td>
<td>0.64881</td>
<td>0.66311</td>
<td>0.68562</td>
<td>0.68783</td>
<td>0.67927</td>
<td></td>
</tr>
<tr>
<td>1Σ− (1)</td>
<td>0.65216</td>
<td>0.66181</td>
<td>0.6809</td>
<td>0.69000</td>
<td>0.68144</td>
<td></td>
</tr>
<tr>
<td>1Σ+ (2)</td>
<td>0.68965</td>
<td>0.69618</td>
<td>0.70303</td>
<td>0.69716</td>
<td>0.68468</td>
<td></td>
</tr>
<tr>
<td>1Δ(1, 2)</td>
<td>0.70338</td>
<td>0.70835</td>
<td>0.71115</td>
<td>0.70239</td>
<td>0.68804</td>
<td></td>
</tr>
<tr>
<td>X3Σ− (1) b</td>
<td>0.72086</td>
<td>0.72411</td>
<td>0.72204</td>
<td>0.70944</td>
<td>0.69236</td>
<td></td>
</tr>
</tbody>
</table>

a The numbers in parentheses indicate the dominant configuration(s) for each state.
b The potential curve for the X3Σ− state leads to $D_o = 3.32$ eV, $R_e = 1.91$ Å, and $\omega_e = 483$ cm⁻¹

(fig. 1f) has delocalized substantially more onto Ni than the doubly occupied Ni(3d₃z²) orbital (fig. 1c) did onto S, leading thus to some charge flow from S to Ni in the π system in response to charge flow from Ni to S in the sigma system. (The overall net charge transfer from the Mulliken populations is ~0.38 electron. For comparison the charge transfer in NiO is 0.55 electron.)

The potential curves in fig. 9 lead to $D_o = 3.32$ eV, $R_e = 1.91$ Å and $\omega_e = 483$ cm⁻¹ for the X3Σ− state. The only experimentally available information for NiS is $D_o = 3.53 \pm 0.15$ eV [7]. The calculated $R_e$ value, as expected, is substantially shorter than for bulk compounds (2.28, 2.34, 2.38, and 2.18 Å for Ni₃S₂, NiS₂, α-NiS and γ-NiS respectively) [1a].

3.2. Ni₂S

Bringing up two Ni atoms to (3) and considering only the 4s electrons of the Ni atoms leads to two sigma bonds to the sulphur as in H₂S.
Given (4) one expects the lowest Ni(3d) occupancy to correspond to taking the singly occupied Ni(3d) orbitals to be delta-like with respect to the Ni—S bond axis [19].

In these calculations we fixed the Ni—Ni distance at \( \sqrt{2}a \) (where \( a \) is the nearest neighbor distance 2.49 Å in Ni metal) as appropriate for next nearest neighbors on the Ni(100) and Ni(110) surfaces. We then varied the NiS distance (retaining \( C_{2v} \) symmetry). The resulting potential curve is shown in fig. 10, while the energies used

![Ni2S geometry optimization](image)

**Fig. 10. Ni2S geometry optimization. The calculated points are indicated.**

Table 4

<table>
<thead>
<tr>
<th>( D (\text{Å}) )</th>
<th>Energy ( \text{E} (\text{hartree}) )</th>
</tr>
</thead>
<tbody>
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<td>2.4567</td>
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</tr>
<tr>
<td>2.2000</td>
<td>-91.28880</td>
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<tr>
<td>1.9700 (^b)</td>
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<td>-91.28995</td>
</tr>
<tr>
<td>1.5000</td>
<td>-91.28179</td>
</tr>
</tbody>
</table>

\(^a\) The basis set is \([3s, 1p, 2d/3s, 2p, 1d]\) (see section 3).

\(^b\) This is the minimum from a fit to the other 4 points.

\(^c\) The optimum geometry is with the S 1.04 Å above the surface, which corresponds to a Ni—S distance of 2.04 Å and a NiSNi angle of 118.8°. The bond energies \( (D_{e}) \) for GVB and CI wavefunctions are 5.27 eV and 5.37 eV, respectively. (The Ni$_{2}$ energy is taken as twice the HF energy of the Ni atom.)

\(^d\) GVB(2/pp) calculations
to construct the curve are tabulated in table 4. The optimum geometry from the potential curve corresponds to a distance above the surface of 1.04 Å which leads to a Ni–S bond length of 2.04 Å and a NiSNi angle of 118.8°.

Thus the NiS distance is 0.13 Å longer than for NiS, a reasonable result given that the ground state of NiS involved important π bonding effects not present in the case of Ni₂S.

Normally in bonding to sulfur one expects bond angles only slightly larger than 90° (e.g., 92.5° in H₂S [20]). However, there are two factors which tend to lead to a larger bond angle for Ni₂S than for H₂S: (i) The Ni(4s) orbital is much larger than a H(1s) orbital leading thus to larger orthogonality constraints (the orbitals of the two bond pairs must become orthogonal because of the Pauli principle). These effects are minimized by increasing the bond angle. (ii) The NiS bond is more ionic than an HS bond, leading to an increased overlap of the Ni(4s) orbitals and favoring an even larger bond angle.

In addition, the optimum bond angle in our Ni₂S complex represents to some extent a compromise between bond angle and bond length at the fixed Ni–Ni separation used (e.g., a small bond angle of 92.5° would lead to a Ni–S distance of 2.43 Å, much too large for a NiS bond).

Selected orbitals of Ni₂S (at the optimum geometry) are shown in fig. 2 where one sees that: (i) The Ni–S sigma bonds are very similar to the corresponding bond orbitals for NiS shown in fig. 1; and (ii) the S(3s) pair has built-in 3p, character in such a way as to move away from the bond pairs. These orbitals were used to construct a small CI wavefunction (see section 5.2) over the occupied orbitals of the GVB wavefunction. This CI wavefunction leads to a $D_\text{e}$ of 5.37 eV [as compared with 5.27 eV for the GVB(2/PP) wavefunction]. Comparing to the bond energy for NiS (3.32 eV) indicates that S has a strong tendency to bridge two Ni atoms for Ni–Ni separations of $\sqrt{2}a$, as on the Ni(100) and Ni(110) surfaces [23].

3.3. Ni₃S

We first consider an alternative form of the wavefunction for Ni₃S which is more appropriate to four-fold bonding sites on Ni(100). For the case of Ni₂S, the (GVB(2/PP) wavefunction (7) corresponds to localized bond pairs which are represented in terms of natural orbitals as

$$\left(\phi_\lambda - \lambda\phi_{\lambda}^*\right)\left(\phi_\rho - \lambda\phi_{\rho}^*\right),$$

where $\phi_\lambda$ is the mirror image of $\phi_\rho$ and $\phi_{\lambda}^*$ is the mirror image of $\phi_{\rho}^*$, respectively. An alternative way to correlate this wavefunction using symmetry orbitals is

$$\left(a_1 - \lambda a_1^2\right)\left(b_2^2 - \lambda b_2^2\right),$$

where

$$a_1 = \phi_\lambda + \phi_\rho, \quad b_2 = \phi_\lambda - \phi_\rho, \quad 2a_1 = \phi_\lambda^* + \phi_\rho^*, \quad 2b_2 = \phi_\lambda^* - \phi_\rho^*.$$
For Ni₂S the wavefunction (8) leads to a lower energy than (9). However, for S in a four-fold site on the Ni(100) surface, the presence of the other nearby Ni atoms restricts the correlation effects, leading to a wavefunction of the form (9) being lower [22]. Thus, we show the orbitals of (9) in fig. 11 for comparison to the
orbitals of the Ni$_2$S and Ni$_4$S clusters to be discussed next.

The orbitals shown in fig. 11 may be interpreted in terms of bonding the sulfur atom to the Ni$_2$ cluster in the following orientation:

\[ \text{(10)} \]

The S(3p$_z$) orbital (fig. 11a) is then singlet paired with the a$_1$ combination of the Ni(4s) orbitals (fig. 11b) and the S(3p$_y$) orbital (fig. 11c) is singlet paired with the b$_2$ combination of the Ni(4s) orbitals (fig. 11d), leading to the bond pairs shown in fig. 11. We also show the 1a$_1$ orbital of (9) (fig. 11e), since it is appropriate to cases where this orbital is not correlated.

Considering only the Ni(4s) electrons, the bonding in the Ni$_3$ cluster may be thought of as:

\[ \text{(11)} \]

Using symmetry for the GVB wavefunction leads to

\[ (1a_1^2 - \lambda 2a_1^2) \ b_2^3. \] \quad \text{(12)}

The orbitals of this wavefunction are shown in fig. 12 where one sees that the bond pair corresponds to a component localized mainly on Ni5 and a component localized mainly on Ni2 and Ni4, while the singly occupied orbital corresponds to the antibonding combination of Ni2(4s) and Ni4(4s) [23].

Given the structure of Ni3, bonding a S atom leads to three principal resonance structures:

\[ \text{(13)} \]

\[ \text{(14)} \]

\[ \text{(15)} \]

We find that the dominant configuration is (15) which involves disruption of the Ni–Ni bond leading to formation of two Ni–S bonds. [For the actual solid, the Ni5(4s) orbital of (15) is able to form bonds to other Ni atoms leading to less dis-
rupture of metal-metal bonds and further favoring (15).] The GVB wavefunction for (15) is

$$1a_1^2(1b_2^2 - \lambda 2b_3) 1b_1^2 2a_1^1.$$  \hspace{1cm} (16)

Here the $1a_1^2(1b_2^2 - \lambda 2b_2^2)$ part of the wavefunction is analogous to the wavefunction (9) for the bond pairs of Ni$_2$S except that the $1a_2^2$ pair is not correlated. The $2a_1$ orbital is predominately a 4s orbital on Ni5 and the $1b_1^2$ pair corresponds to a S$(3p_x)$ pair.

We show the orbitals corresponding to (16) in fig. 3. Here one sees that the bond pair is similar to the $b_2^2$ pair in (9) and has one component (fig. 3a) which is basically S$(3p_y)$-like, while the other component (fig. 3b) corresponds to the $b_2$ combination of 4s functions on Ni2 and Ni4. The doubly occupied $1a_1$ orbital (fig. 3c) has slightly less bonding character than for Ni$_2$S, largely as a result of orthogonality constraints with the $2a_1$ singly occupied orbital (fig. 3d), which is mainly a 4s orbital on Ni5 but with substantial hybridization away from the Ni–S bonds.
Putting these effects together, orthogonality constraints between the 4s orbital of Ni5 and the bond pairs are expected to increase slightly the distance of the S above the surface, but this effect should be partially counterbalanced by the small, attractive interaction between the S(3s) pair and the 3d⁹ core of Ni5. These considerations suggest that the Ni₃S cluster should lead to a geometry with the sulfur atom slightly further above the surface than for the Ni₂S cluster. Indeed, we find that the optimum distance above the surface for the Ni₃S cluster is 1.07 Å, only 0.03 Å larger than the optimum distance (1.04 Å) for the Ni₂S cluster. We conclude that the effect of Ni5 (the second layer Ni) on the geometry is negligible and the geometry of the S atom should be determined mainly by the four nearest neighbor atoms in the surface. Table 5 summarizes the Ni₃S geometry optimization.

### 3.4. Ni₄S

In section 2.1.4, we noted that for the Ni₄S cluster the S(3s) pair is stabilized by interaction with the 3d⁹ cores of Ni atoms 1 and 3, leading to incorporation of S(3p₂) character so as to hybridize toward the surface. [Here the S(3s) orbital energy is 2.12 eV more negative than for the atom as compared to 0.43 eV more negative in the case of the Ni₃S cluster.]

The hybridization of the S(3s) orbital toward the surface leads to correlation effects for the NiS bond pairs being substantially less important in the z direction.

<table>
<thead>
<tr>
<th>D (a₀)</th>
<th>Energy b</th>
<th>HF</th>
<th>GVB(1/pp)</th>
<th>CI c</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.457</td>
<td>0.77815</td>
<td>0.78581</td>
<td>0.79435</td>
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</tr>
<tr>
<td>2.000</td>
<td>0.78701</td>
<td>0.79383</td>
<td>0.79999</td>
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</tr>
<tr>
<td>1.800</td>
<td>0.78665</td>
<td>0.79312</td>
<td>0.79840</td>
<td></td>
</tr>
<tr>
<td>1.600</td>
<td>0.78335</td>
<td>0.78948</td>
<td>0.79418</td>
<td></td>
</tr>
</tbody>
</table>

a These calculations use the [2s, 1p, 1d/3s, 2p] basis. For Ni₂S this basis leads to an error of 0.343 eV from removal of S d functions and an error of 0.283 eV from the single zeta contraction of the Ni(3d) basis functions.

b Subtract the quoted value from −131.0 to get the total energy in hartree.

c The optimum geometry is with the S 1.07 Å above the surface, which corresponds to a Ni−S distance of 2.06 Å and a NiSNi angle of 117.2°. The $D_e$ value is 3.261 eV.

For purposes of comparing to the Ni₂S and NiS calculations which use the larger [3s, 1p, 2d/3s, 2p, 1d] basis one should add the total error for the smaller basis a (0.625 eV) leading to a $D_e$ of 3.886 eV.
than in the $y$ direction \[24\] resulting in NiS bond pairs of the form

$$1a_1^2(1b_2^2 - \lambda 2b_2^2)$$ \hspace{1cm} (17)

(analogous to the description of the NiS bond pairs in Ni$_3$S). Combining these orbitals with the Ni1 and Ni3 4s orbitals ($2a_1^1 2b_1^1$) and the S(3p$_x$) pair ($1b_1^2$) leads to a total wavefunction \[25\]

$$1a_1^2(1b_2^2 - \lambda 2b_2^2) 1b_1^2 2a_1^1 2b_1^1.$$ \hspace{1cm} (18)

The orbitals of (18) are shown in fig. 4. Examining first the bond pair (fig. 4a, b) we see that one component (fig. 4a) is essentially a S(3p$_y$) orbital, while the other component (fig. 4b) corresponds to the $b_2$ combination of 4s orbitals on Ni2 and Ni4. The 1a$_1^2$ pair (fig. 4c) is mainly S(3p$_z$)-like, but has Ni–S bonding character on all four Ni atoms. The S(3s) orbital (fig. 4d) has built in a small amount of 3d$\sigma$ character on all four Ni atoms, somewhat analogously to the small incorporation of 3d$\sigma$ character for the 5$\sigma$ orbital of CO bonded to Ni. Thus the a$_1$ bonding pair and the S(3s) pair have the four-fold symmetry of the Ni$_4$S cluster, whereas the b$_2$ bond pair is localized (involving bonding to Ni2 and Ni4).

The Ni1 and Ni3 4s orbitals show antibonding character on the sulfur due to orthogonality constraints with the sulfur orbitals. These effects seem to be more important than stabilization of the S(3s) pair, leading to an optimum geometry

**Ni$_4$S GEOMETRY OPTIMIZATION**

![Ni$_4$S geometry optimization graph](image-url)

Fig. 13. The Ni$_4$S geometry optimization. The calculated points are indicated.
Table 6
Ni₄S geometry optimization; D is the distance from the S to the Ni₄ plane

<table>
<thead>
<tr>
<th>D (Å)</th>
<th>Energy a, b (hartree)</th>
</tr>
</thead>
<tbody>
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</tr>
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<td>2.6</td>
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</tr>
<tr>
<td>2.4</td>
<td>-172.35079</td>
</tr>
</tbody>
</table>

a The optimum geometry has the S atom 1.33 Å above the surface, which leads to a Ni—S distance of 2.21 Å and a NiSNi angle of 105.6°. The Do value is 3.28 eV.
b GVB(1/pp) calculations.

with the S 1.33 Å above the surface as compared with 1.04 Å for the Ni₂S cluster.

In fig. 6 we show the overall bonding pattern for the c(2 × 2) structure on the surface. The localized orbitals shown in fig. 6 correspond to the b₂ bond pair of our Ni₄S cluster. Including these bonds, the S atoms are related by a glide plane and the overlayer is actually of p(2 × 2) symmetry. However, the overlayer structure shown is degenerate with an equivalent structure where all the bond pairs are rotated by 90°. For the portion of the overlayer included in our Ni₄S calculation, these two structures are actually of different symmetry (b₁ and b₂) and thus do not couple to each other. However, if the total overlayer is considered, these structures are both of a₁ symmetry and do overlap. Thus, they interact strongly (resonate) leading to all S atoms on the surface being equivalent and the total symmetry of the overlayer is c(2 × 2).

The energies of the Ni₄S cluster as a function of geometry are shown in table 6.

3.5. Comparison of bonding geometries for the (110) surface

In fig. 5 we compare the bonding position currently suggested for S on Ni(110) from analysis of the LEED intensity data [1a] (geometry B) with the position calculated using our Ni₂S model (geometry A). For geometry A the S is bridged across Ni atoms 1 and 2 which are separated by \(\sqrt{2}a\) (as in our Ni₂S calculations). Here, there are two second nearest neighbors below the surface (Ni atoms 3 and 4), but they are 2.609 Å from the S and should not interact strongly with the S atom. We thus conclude that our Ni₂S calculations should be a good model for this surface, and we find that the calculated distance above the surface (1.04 Å) for the Ni₂S model is in reasonable agreement with the distance (0.93 ± 0.1 Å) from the LEED analysis assuming geometry B [1a]. (We assume here that the distance above the surface influences the fit to the LEED data more strongly than differences in the registry with the surface [8].)

Geometry B has the S bridged across Ni atoms separated by \(\sqrt{3}a\). One can imagine two bonding arrangements consistent with this geometry: (i) a bonding
arrangement where the S atom forms two sigma bonds to Ni atoms separated by \( \sqrt{3}a \) (e.g., 2 and 4) as in our Ni$_2$S model; (ii) a situation in which the S atom bonds to the atom directly beneath it in the layer beneath the surface (i.e., to Ni5) as in our NiS calculations.

(i) leads to a Ni–S distance of 2.35 Å which is considerably larger than the optimum Ni–S distance we find for Ni$_2$S and leads to a NiSNi bond angle of 133.3° which seems unreasonably large. In addition there should be strong nonbonded repulsions from Ni5 (2.17 Å from the S) and Ni1 and Ni3 (2.35 Å from the S).

(ii) leads to a reasonable Ni–S distance (2.17 Å) but suffers from the fact that there are four nearest neighbor atoms (1, 2, 3, and 4) only 2.35 Å away which should lead to strong nonbonded repulsions. In addition, we find that bridged bonding should be stronger.

With either type of bonding we would expect geometry B to be less favorable than geometry A. (A also leads to reasonable Ni–S bond lengths and minimal nonbonded repulsions.)

The assumption is often made that an adsorbed atom will occupy a position similar to that which would be occupied by a metal atom in the next layer up. However, for S we find that the character of the atomic orbitals (two singly occupied 3p orbitals oriented at 90° to each other) leads to a strong preference for forming two bonds to next nearest neighbor Ni atoms. Thus, the chemical nature of the adsorbed atom may play a role in determining the bonding site and in the case of the Ni(110) surface may result in a structure different from that obtained with a "hard sphere model".

4. Calculation details

The effective potential used for the Ni atom has been previously reported [26]. (This potential replaces the 18 electron Ar-core of the Ni atom.) The Ni basis set was taken from the set optimized for the third row atoms by Wachters [27]. All five d primitives of each type were used but only the outer four s functions were needed for describing the coreless Hartree–Fock orbital [30]. In addition, a single set of p functions \( \alpha = 0.12 \) was added to describe polarization effects involving the 4s orbital.

Two contractions of this basis set were used. The first is identical to that used in ref. 11 and has the tightest two s primitives and the tightest four d primitives contracted together based on the 4s$^2$3d$^8$(3F) state of the Ni atom. This basis then has three contracted s functions and two contracted d functions of each type and is denoted [3s, 1p, 2d]. This basis set was used for the NiS and Ni$_2$S calculations.

For the larger Ni$_3$S and Ni$_4$S calculations we contracted the basis to [2s, 1p, 1d]. Since the states considered here have the 4s$^1$3d$^9$ configuration on Ni, the contraction used was based on a (symmetry restricted) HF calculation for the 4s$^1$3d$^9$ state of the Ni atom [15]. The tightest three s functions were contracted together
Table 7
The nickel basis set

<table>
<thead>
<tr>
<th>α</th>
<th>[3s, 1p, 2d]</th>
<th>[2s, 1p, 1d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
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<td>0.07894</td>
</tr>
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<td></td>
<td>0.918169</td>
<td>0.93226</td>
</tr>
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<td></td>
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<td></td>
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<td>1.00000</td>
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<tr>
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<tr>
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Note: The energy of the \(^3\text{D}(4s^13d^9)\) state of the Ni atom using this basis is -40.4943 \(\hbar\).

Table 8
The sulfur basis set and effective potential

<table>
<thead>
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<th>α</th>
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</thead>
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<tr>
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<td>1.0000</td>
</tr>
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</table>

Effective potential
\(V_q = \sum_k C_k r^n k e^{-\xi k r^2}\)

<table>
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<th>n</th>
<th>(n)</th>
<th>(\xi)</th>
<th>c</th>
</tr>
</thead>
<tbody>
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<td>5.5929</td>
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<td></td>
<td>0</td>
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<tr>
<td>(V_{p-d})</td>
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<td></td>
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<tr>
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<tr>
<td></td>
<td>-1</td>
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</tr>
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</table>

Note: The energy of the \(^3\text{P}\) ground state of the S atom is -10.1090 \(\hbar\) using the basis set and potential.
while the fourth was left free and all five d functions were contracted to a single d function. This contraction of the Ni basis led to energies about 0.3 eV higher for Ni$_2$S than with the [3s, 1p, 2d] basis. These two contractions of the Ni basis set are given in table 7.

For the sulfur atom we used an effective potential to replace the ten electron Ne core leaving only the 3s and 3p electrons [31]. The basis set used for S was based on the (11s, 7p) primitive set of Huzinaga [30]. The outer four s functions of this basis were used with the inner two contracted together based on the $^3P$ state of the S atom. The p primitive basis consisted of three functions of each type where the outer two are those given by Huzinaga, while the third was obtained by taking the geometric mean of the third and fourth primitives given by Huzinaga. The inner two of the resulting three primitives were contracted together based on the $^3P$ state of the S atom. The resulting basis is [3s,2p]. For NiS and Ni$_2$S, we also added to the S a single set of d functions $\alpha = 0.532$. (The value of the exponent was optimized for S$_2$ [1]). The d functions were not found to be especially important (energy contribution 0.3 eV for Ni$_2$S) and were omitted for the Larger Ni$_3$S and Ni$_4$S calculations. The basis set and effective potential for S are given in table 8.

5. Details of the CI calculations

5.1. NiS

The starting point for the basis was the GVB orbitals of configuration $1b$ (10 orbitals including the natural orbitals of the bond pair and the S (3s)-like orbital). Because configuration $1b$ is only one of two degenerate configurations (i.e., $1a$ and $1b$) which together describe the $X^3\Sigma^-$ state of NiS, the $\pi_x$ and $\pi_y$ orbitals from the calculation were not equivalent as is evident from fig. 1. In order to generate an equivalent set of orbitals for the CI, the $\pi_x$ orbitals were rotated and averaged with the $\pi_y$ orbitals and the resulting set of two functions was used in both directions.

To provide sufficient flexibility to describe the electronic states of NiS, additional orbitals (suitably orthogonalized to the occupied orbitals) referred to as virtual orbitals, were added which correspond to the more diffuse components of the Ni$(3d\pi_x)$, Ni$(3d\pi_y)$, S$(3p\pi_x)$, Ni$(3d\delta_{xy})$, and Ni$(3d\delta_{xy}x^2y^2)$-like functions. The resultant basis consisted of 16 functions.

The configurations were generated using a procedure analogous to that which had been used for O$_2$ by Moss and Goddard [5a]. The first step was to select a set of reference configurations corresponding to the dominant configurations for the states of interest (in this case configurations $1a$–$5b$). This configuraiton list then defined a set of generating configurations which consisted of products of single excitations within subsets corresponding to: (i) the natural orbitals of the GVB bond pair, (ii) the Ni$(3d\pi_x)$ and S$(3p\pi_x)$ orbitals, and (iii) the Ni$(3d\pi_y)$ and S$(3p\pi_y)$
Table 9
Generating configurations for the NiS CI

<table>
<thead>
<tr>
<th></th>
<th>Ni(3dσ)</th>
<th>σ</th>
<th>σ⁺ᵃ</th>
<th>Ni(3dπₓ)</th>
<th>S(3pπₓ)</th>
<th>Ni(3dπᵧ)</th>
<th>S(3pπᵧ)</th>
<th>Ni(3dδₓᵧ)</th>
<th>Ni(3dδₓ₂₋ᵧ₂)</th>
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<td>A1</td>
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<td>2</td>
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<td>B1</td>
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</table>

ᵃ σ and σ⁺ are the natural orbitals of the sigma bond pair.
ᵇ The parentheses indicate that we take products of the configurations in the left parentheses with those in the right parentheses (e.g., for the A1 case there are 2 × 6 = 12 configurations).
Table 10
Generating configurations for the Ni$_2$S CI calculation

<table>
<thead>
<tr>
<th>la$_1$</th>
<th>2a$_1$</th>
<th>1b$_2$</th>
<th>2b$_2$ $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
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<td>2</td>
<td>0</td>
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<tr>
<td>1</td>
<td>1</td>
<td>1</td>
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</tr>
</tbody>
</table>

$^a$ These orbitals correspond to the bond orbitals of Ni$_2$S projected on C$_{2v}$ symmetry.

$^b$ See footnote b of table 9.

orbitals. Single excitations from the generating configurations into the space of the above six orbitals generates all the important configurations for the states of interest. However, we also allow all single excitations from the generating configurations into the full virtual space in order to ensure inclusion of readjustment effects necessary to allow a consistent treatment of all the states.

We show the generating configurations for the NiS CI in table 9 (based on C$_{2v}$ symmetry). The resultant CI consisted of (130,232), (92,208), (122,326), (92,324), (158,392) and (158,626) \{(spatials, spin eigenfunctions)\} for the $^1$A$_1$, $^1$A$_2$, $^3$A$_1$, $^3$A$_2$, $^1$B$_1$ and $^3$B$_1$ CI calculations, respectively.

5.2. Ni$_2$S

The GVB calculations were carried out in C$_3$ symmetry (retaining the molecular plane) which led to localized bond pairs as in (8). However, in the CI we did not use these orbitals but rather used orbitals corresponding to (9) which have the full C$_{2v}$ symmetry of the molecule and are generated by projecting the localized orbitals of (8) onto the wavefunction (9). In addition, the remaining occupied orbitals (which were essentially of C$_{2v}$ symmetry) were projected, leading to a total of 16 basis functions.

The configurations were generated in a manner analogous to the NiS CI using the generating configuration shown in table 10.

The CI calculations were carried out only at the optimum geometry found from the GVB calculations. Since we found the CI energy to be only $\sim$0.1 eV below the GVB energy (at this R), we concluded that CI effects would have only negligible effects on the geometry.

5.3. Ni$_3$ and Ni$_3$S

For Ni$_3$ the CI basis consisted of the orbitals of (12) plus all the occupied $a_2$ and $b_1$ orbitals (which were included to allow readjustment effects involving reorientation of the 3d holes of the Ni atoms). The generating configurations used are given in table 11.
Table 11
Generating configurations for the Ni$_3$ and Ni$_3$S CI calculations

<table>
<thead>
<tr>
<th></th>
<th>1a$_1$</th>
<th>2a$_1$</th>
<th>1b$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_3$</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni$_3$S</td>
<td>2 1</td>
<td>2 0</td>
<td></td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
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<td></td>
</tr>
</tbody>
</table>

$^a$ These configurations correspond to wavefunction (12).

$^b$ These configurations correspond to wavefunction (16).

$^c$ See footnote b of table 9.

For Ni$_3$S the CI basis consisted of the orbitals of (16) plus the S(3s)-like orbital, additional virtuals having the character of the more diffuse components of the S(3p$_x$) and S(3p$_y$)-like functions, and all the occupied a$_2$ and b$_1$ orbitals (which were included to allow readjustment of the 3d holes for the Ni atoms, as for the Ni$_3$ calculation). The generating configurations are given in table 11. As can be seen from the energies in table 5, the energy lowering from GVB to CI is comparable to that from HF to GVB.

References

[4] This is from Mulliken populations. Generally, these populations indicate a greater charge transfer than would be indicated, for example, by the dipole moment. Thus, the populations although indicative of charge transfer should not be taken too literally.
[8] For example, for S on Ni(111) there are two possible three-fold sites. The LEED intensities are quite similar for these two sites but change significantly if the distance to the surface is changed [1a].
[9] The quoted atomic separations are obtained by taking a weighted average over the spectral levels corresponding to a given L and S (spin-orbit interactions are not included in our calculations). The values are from ref. [10].
In these calculations we have used the [3s, 1p, 2d] contraction of the Ni basis (see section 4) for the central Ni atom in conjunction with the MEP. For the other two Ni atoms, we have used an effective potential which replaces the 18 electron Ar core and a weighted average over the various 3d$^9$ configurations (referred to as the d-averaged potential [15]). The reamining 4s orbital is then expanded in an sp basis identical to that used on the central Ni atom.

T.H. Upton and W.A. Goddard III, unpublished results.

Here we are referring to a linear geometry with equal bond lengths.

For (5) the GVB (2/PP) wavefunction was used. However, for (4) the perfect pairing approximation (see ref. [2]) is not applicable and we used the SOGVB method [F.W. Bobrowicz, Ph.D. Thesis, California Institute of Technology (1974)] which retains strong orthogonality but relaxes the perfect pairing restriction.

Configurations 1a to 5b are analogous to the group I configurations of NiO [6].

There are two possible choices for the delta-like orbitals on each Ni. Their energies are within ~0.04 eV and we chose to solve self-consistently for the case where each Ni 3d$^6$ hole is asymmetric with respect to the molecular plane, since this choice simplifies the SCF calculations.


The Ni and Ni$_2$ clusters (which correspond to the NiS and Ni$_2$S clusters) have zero bond energy. Thus, effects arising from disruption of metal-metal bonds are not included. These effects should be more important for the bridged case and comparisons of the NiS and Ni$_2$S bond energies is expected to overestimate the favorability of bridged sites over linear sites.

For Ni$_2$S we find that (8) is 0.083 eV below (9). For (9) the correlation energies due to the $a_1$ and $b_2$ pairs are 0.26 eV and 0.19 eV, respectively. For Ni$_3$S and Ni$_4$S the $b_2$ pairs have comparable correlation energies but the $a_1$ pairs contribute only 0.12 eV and 0.12 eV for Ni$_3$S and Ni$_4$S, respectively.

The 3d holes for Ni$_2$ and Ni$_4$ were taken in orbitals of the form $xz + yz$ and $xz - yz$ which are thus delta-like with respect to the bond axes while the 3d hole for Ni$_5$ was taken in a $3d_{xy}$ orbital (which represents a compromise between delta character with respect to the two bond axes).

We show here the orbitals which involve the Ni$(4s)$ orbitals and the orbitals of the S$(3p^4)$ configuration. The remaining 3d occupation is the same as for the Ni$_3$ cluster [25].

The Ni(3d) holes for Ni atoms 2 and 4 (involved in Ni−S bonds) were taken to be delta-like with respect to the NiS bond axis and asymmetric with respect to the $yz$ plane (containing Ni$_2$, Ni$_4$, and the S) which is the same orientation as for the $b_2$ calculation. The Ni(3d) holes for Ni$_1$ and Ni$_3$ were taken in $3d_{yz}$ orbitals which are delta-like with respect to the x axis, which passes through Ni$_1$ and Ni$_3$.

The numerical potential is reported in ref. [14]. See also the discussion inf ref. [13].


R.A. Bair and W.A. Goddard III, unpublished results.

S. Huzinaga, unpublished.