THE DESCRIPTION OF CHEMICAL BONDING FROM AB INITIO CALCULATIONS

William A. Goddard III and Lawrence B. Harding
Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

INTRODUCTION

Concepts, such as hybridization and electronegativity, developed by Linus Pauling (1), Robert Mulliken (2), John Slater (3), and others in the 1930s have been very powerful in rationalizing and predicting molecular structure, bond energies, and some aspects of reactivity. The power of these concepts is exemplified in the classic exposition, Nature of the Chemical Bond, by Linus Pauling (4). In recent years experimental and theoretical studies of numerous radicals have provided an assembly of quantitative information concerning bond energies, excitation energies, relative ordering of states, and shapes of potential curves, much of which is not explained by the older ideas. However, it has recently become possible to abstract from ab initio calculations qualitative concepts that rationalize many of the observed properties in such a way as to allow quantitative predictions for related systems. Currently the basis and application of this approach is distributed over a number of papers (5–9). Here we draw these ideas together with applications to a number of related systems so as to indicate the utility and force of these methods.

For simplicity of presentation we use Si and its hydrides (SiH, SiH₂, SiH₃, SiH₄) as prototypes for outlining the various concepts. These ideas are then extended to other molecules by replacing Si with Be through F and Mg through Cl, and other related nontransition metal elements, and by replacing H with halogens such as F and Cl.

In the following discussion unless otherwise noted, experimental results are taken from (10) for atoms, from (11–13) for diatomic molecules, and from (14–16) for polyatomic molecules.

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SiHₙ MOLECULES

Ground State Silicon Atom

The ground state (³P) of atomic silicon has the configuration

\[(1s)^2(2s)^2(2p)^6(3s)^2(3p)^2\].

1. core valence electrons electrons

The wavefunction corresponding to Equation 1 is the Hartree-Fock (HF) wavefunction

\[\psi_{HF} = \mathcal{A}[\Phi_{core}(\phi_3\alpha)(\phi_3\beta)(\phi_{3p}\alpha)(\phi_{3p}\beta)],\]

2. where

\[\Phi_{core} = (\phi_{1s})(\phi_{1s})(\phi_{2s})(\phi_{2s})(\phi_{2p})(\phi_{2p})(\phi_{2p})(\phi_{2p})(\phi_{2p})(\phi_{2p}).\]

3. \(A\) is the antisymmetrizer or determinant operator, and each one-particle function is numbered in the sequence of its appearance [e.g. \(\phi_{3d}(1)\phi_{3d}(2)\)]. All orbitals in Equations 2 and 3 are understood to be optimized self-consistently. The core orbitals are very compact relative to the valence orbitals, and hence for geometries of chemical interest, differences in the shapes of molecular core orbitals are insignificant. For this reason, in the following discussion we will consider only the valence orbitals, although the core orbitals are present in the calculations. Thus Equation 2 becomes

\[\psi_{HF} = \mathcal{A}[(\phi_3\alpha)(\phi_3\beta)(\phi_{p3}\alpha)(\phi_{p3}\beta)] \]

4. where, for convenience, the \(n = 3\) quantum number has been suppressed and the spatial and spin functions have been separated.

Hartree-Fock wavefunctions, such as Equation 2, form the theoretical foundation for such useful concepts as the Aufbau model of atoms (17, 18) and orbital correlation diagrams for molecules (19); however, it has been shown repeatedly that HF wavefunctions are not adequate for describing the formation and dissociation of covalent bonds. The problem is that the two electrons associated with a particular bond generally associate with different fragments (radicals) as the bond is broken. In HF wavefunctions a bond pair consists of one doubly occupied orbital and hence will not, in general, lead to the correct dissociated radical species. The simplest wavefunction that removes this deficiency while retaining the proper spin symmetry and satisfying the Pauli principle is the generalized valence bond (GVB) wavefunction (20). In the GVB wavefunction each valence electron is allowed to have a different orbital, and every orbital is optimized self-consistently.
For the ground state of Si, the GVB wavefunction has the form
\[ \psi_{\text{GVB}} = \mathcal{A} \left\{ [\phi_i(1)\phi_i(2) + \phi_i(1)\phi_i(2)] \phi_{p_z}(3)\phi_{p_y}(4)\alpha(1)\beta(2)\alpha(3)\alpha(4)] \right\} = \mathcal{A} \left\{ [\phi_i\phi_i + \phi_i\phi_i] \phi_{p_z}\phi_{p_y}\alpha\beta\alpha\alpha \right\}, \]

where the orbitals are as shown in Figure 1. Here \( \phi_{p_z} \) and \( \phi_{p_y} \) are almost identical to the corresponding HF orbitals, but the HF 3s pair has been replaced by two singly occupied lobe orbitals (\( \phi_l \) and \( \phi_r \)). The lobe orbitals differ radically from the HF 3s orbital in that one, \( \phi_l \), is hybridized (poached) in the positive x direction, while the other, \( \phi_r \), is hybridized in the negative x direction. The result is that the motion of the two "3s electrons" is correlated such that they tend to stay apart while each remains close to the nucleus.

There are several important points to be made about the lobe orbitals of Equation 5. These orbitals can be written as
\[ \phi_l = (\phi_s + \lambda\phi_{p_x})(1 + \lambda^2)^{-1/2} \]
\[ \phi_r = (\phi_s - \lambda\phi_{p_x})(1 + \lambda^2)^{-1/2}, \]

These orbitals are shown in Figure 1. Long dashes indicate zero amplitude, solid lines and short dashes indicate positive and negative amplitude, with a spacing of 0.05 au of amplitude between various contours. The same convention is used for all other figures.

**Figure 1** Si(3P) orbitals. Long dashes indicate zero amplitude, solid lines and short dashes indicate positive and negative amplitude, with a spacing of 0.05 au of amplitude between various contours. The same convention is used for all other figures.
where \( \phi_{s} \) is nearly identical to the HF 3s orbital and \( \phi_{p_s} \) is nearly identical to the \( \phi_{p_x} \) and \( \phi_{p_y} \) orbitals of Equation 5. From Equation 6 it can be seen that the hybridization, or fractional \( p \) character, of a lobe orbital is simply \( \lambda^2/(1 + \lambda^2) \) and the overlap between the \( \phi_l \) and \( \phi_t \) orbitals is

\[
S_{lt} \equiv S = (1 - \lambda^2)/(1 + \lambda^2)
\]

or

\[
\lambda^2 = (1 - S)/(1 + S).
\]

For Si, \( \lambda = 0.376 \), and hence the \( l \) and \( t \) orbitals have an overlap of 0.752 and each consists of about 14.2\% \( p_x \) character.

Using Equation 6 we find that

\[
[\phi_l \phi_l + \phi_t \phi_t][2(1 + S^2)]^{-1/2} = [\phi_s \phi_s - \lambda^2 \phi_{p_x} \phi_{p_x}][1 + \lambda^2]^{-1/2}
\]

where the total wavefunction is normalized to unity. Thus the wavefunction in which one electron is always in \( \phi_l \) while the other is always in \( \phi_t \) is exactly equivalent to the wavefunction in which both electrons are in \( \phi_s \) part of the time [fraction = \( 1/(1 + \lambda^4) \)] and both are in \( \phi_{p_x} \) part of the time [fraction = \( \lambda^4/(1 + \lambda^4) \)]. The left side of Equation 8 is referred to as the GVB representation, and the orbitals (\( \phi_l \) and \( \phi_t \)) are referred to as GVB orbitals. The right side of Equation 8 is the natural orbital (NO) representation (of the GVB wavefunction) and the orbitals (\( \phi_s \) and \( \phi_{p_x} \)) are referred to as natural orbitals.

In order to satisfy the Pauli principle, a wavefunction of the form of Equation 8 must be combined with a singlet spin function, \( (\alpha \beta - \beta \alpha) \), and hence Equation 8 is referred to as singlet pairing of the two lobe orbitals. The alternative combination, Equation 9,

\[
(\phi_l \phi_l - \phi_t \phi_t) = (\phi_s \phi_{p_x} - \phi_{p_x} \phi_s)[(-2\lambda)/(1 + \lambda^2)]
\]

is referred to as triplet pairing since the Pauli principle requires a triplet spin function (e.g. \( \pi \alpha \)) to be associated with Equation 9.

Comparing the right sides of Equations 8 and 9, we see that triplet pairing of \( l \) and \( t \) forces the wavefunction to have only one electron in the \( s \) orbital while singlet pairing allows a much higher \( s \) occupation \( [1/(1 + \lambda^4)]^{-1/2} \). The valence \( s \) orbital penetrates the core region more effectively than does the \( p \) orbital and is consequently less shielded from the nuclear charge. Thus the \( s \) orbital is energetically more favorable than the \( p \) orbital, and, as a result, atomic states in which \( l \) and \( t \) are singlet-paired are much lower in energy (\( \sim 100 \) kcal) than those in which the lobes are triplet-paired.

Schematically, we will represent the wavefunction in Equation 8 as

\[
\text{(schematic representation of wavefunction)}
\]

where \( \bigcirc \) indicates a lobe orbital, a dot indicates one electron, and the line connecting the dots indicates singlet-pairing of the two orbitals. Similarly, we will
represent the ground state wavefunction of silicon, Equation 5, as

$$\text{Si}(3P)$$

11.

where $\bigcirc$ indicates the $p_z$ orbital and $\bigcirc$ indicates the $p_y$ orbital (pointing out of the plane of the paper).

**Low-Lying States of SiH**

Starting with the ground state orbitals of Si, Equation 11, and bonding an H to one of the singly occupied Si orbitals, we obtain two possible configurations: 1. bonding the H to an Si $p$ orbital leads to

$$\text{SiH}(2\Pi)$$

12.

which is symbolic for the wavefunction

$$\mathcal{A}[(\phi_p\phi_i + \phi_i\phi_p)(\phi_{p_x}\phi_{i_y} + \phi_{i_x}\phi_{p_y})\phi_p\alpha\beta\alpha\beta]$$

13.

and describes a $^2\Pi$ state, and 2. bonding the H to an Si lobe orbital ($l$) leads to

$$\text{SiH}(4\Sigma^-)$$

14.

which is symbolic for the wavefunction

$$\mathcal{A}[(\phi_l\phi_i + \phi_i\phi_l)(\phi_{p_x}\phi_{i_y} + \phi_{i_x}\phi_{p_y})\alpha\beta\alpha\beta]$$

15.

and describes a $^4\Sigma^-$ state. The three non-singlet-paired orbitals of Equation 14 can also be coupled to form two doublet states; however, since these orbitals are orthogonal, the state of highest spin ($^4\Sigma^-$) will be lowest in energy.

The actual optimum orbitals (at $R_o$) for the wavefunctions in Equations 12 and 14 are shown in Figures 2 and 3, respectively. That this qualitative description of the molecular states in terms of atomic orbitals is accurate is shown by the similarity between the molecular GVB orbitals (Figures 2 and 3) and the corresponding atomic GVB orbitals (Figure 1).

The simple GVB model discussed above predicts two low-lying states for SiH, the $^2\Pi$ state and the $^4\Sigma^-$ state. In order to better understand the relative energies of these two states we must examine in more detail the bonding schemes depicted in Equations 12 and 14. There is, of course, an intrinsic difference ($\sim 15$ kcal/mole) in the bond energy of an H to a $p$ orbital relative to the bond energy to a lobe orbital; however, the major differential effects involve the interaction of the H orbital with the orbitals not involved in the bond. Considering first the $^2\Pi$ state, Equation 12, the $\phi_H$ orbital, optimum for bonding to $\phi_{p_x}$, will overlap the two lobe orbitals, $\phi_l$ and $\phi_i$. The effect of the Pauli principle (or the determinant operator in Equation 13)
is to force \( \phi_H \) to be orthogonal to \( \phi_I \) and \( \phi_T \). This raises the total energy and hence decreases the bond energy. All orbitals readjust to minimize this effect, and, as seen in Figure 2, the major result is that the \( \phi_I \) and \( \phi_T \) orbitals rotate away from the bond pair. Thus, in the molecule, the angle of the lobe orbitals with respect to the \( z \) axis is 128° compared with an angle of 90° for the free atom (A. F. Voter, L. B. Harding, and W. A. Goddard, to be published).

Consider now the bonding scheme in the \( ^4\Sigma^- \) state of SiH, Equation 14. In the atom, \( \phi_I \) and \( \phi_T \) are singlet-paired, and the optimum orbitals have an overlap of 0.752, whereas in the molecule, the \( \phi_I \) orbital is singlet-paired with \( \phi_H \). Again, because of the Pauli principle, the \( \phi_T \) orbital of the molecule must become orthogonal to the \((\phi_I, \phi_H)\) bond orbitals, leading to an increase in the total energy of this state. This repulsive effect, which results from the unpairing of the \((\phi_I, \phi_T)\) orbitals, leads to a net bond energy much smaller than the intrinsic lobe orbital bond energy. In the optimized wavefunction the bonding and nonbonding orbitals have readjusted to minimize this repulsive interaction, leading to the GVB orbitals shown in Figure 3.
In conclusion, the atomic origins of the self-consistent GVB orbitals of both the $^2\Pi$ and $^4\Sigma^-$ states is clearly recognizable. In particular, the bond pair of the $^4\Sigma^-$ state involves an Si-centered orbital which is more lobe-like than the Si-centered bond orbital of the $^2\Pi$ state. Including all effects, the bonding of an H to a $p$ orbital of Si (forming the $^2\Pi$ state) is 70 kcal, while the bonding to a lobe orbital is 35 kcal. It should be emphasized, however, that the weakness of the lobe bond relative to the $p$ bond is due almost entirely to the energy required to uncouple the atomic $(l, T)$ pair.

**Low-Lying States of SiH$_2$**

Consider now the states of SiH$_2$ that result from bonding a hydrogen to the ground state of SiH, Equation 16,
Just as for SiH, we can form a strong bond to either the unpaired Si $p$ orbital or to one of the paired lobe orbitals. Bonding the H to the $p$ orbital leads to the $^1A_1$ state of SiH$_2$.

Bonding the H to a lobe orbital of Equation 16 leads to Equation 19.

In the optimum wavefunction, the orbitals comprising the two bond pairs will be equivalent, each having the character of roughly the average of a lobe bond and a $p$ bond, as depicted in Equation 20.

From Equation 16 the H–Si–H bond angle would be expected to be $128^\circ$. However, there are several important interactions to be considered. As the second H approaches the lobe orbital ($l$), the $\phi_l$ orbital will overlap not only $l$ but also $7$ and the other SiH bond pair. Because the wavefunction must satisfy the Pauli principle, these overlaps give rise to repulsive interactions. Of the two, the H–7 interaction will be more important (the $7$–$l$ angle is $104^\circ$ while the $l$–bond pair angle is $128^\circ$) and
thus these repulsions will reduce the bond angle from the expected 128°. In fact, the actual bond angle is 117° (20–22).

Above we found that bonding the hydrogen to a p orbital of Si leads to a stronger bond than bonding to a lobe orbital (due to the energy required to uncouple the atomic lobe pair). Similarly, for SiH₂ the strongest bond is obtained by bonding the H to the unpaired p orbital leading to a ¹A₁ ground state for SiH₂.

Low-Lying States of SiH₃ and SiH₄

Starting with the ground state (¹A₁) of SiH₂, Equation 18, we see that bonding a third H to SiH₂ should lead to a pyramidal molecule as shown in Equation 21,

\[ \text{Equation 21.} \]

Allowing all of the orbitals to readjust leads to three equivalent bond pairs, each having the character expected for the average of two p bonds and one lobe bond. Averaging the bond angles (92°, 109.7°, 109.7°) leads to a predicted bond angle of 104° for SiH₃.

It is important to note that the ground states of SiH and SiH₂ resulted from bonding to p orbitals and did not involve unpairing the two lobe orbitals of Si. In order to bond an H to SiH₂, however, it is necessary to unpair the lobe orbitals, and therefore we expect the H₂Si–H bond energy to be significantly weaker than the HSi–H energy.

Consider now how the character of the SiH₃ wavefunction changes as the molecule is distorted to a planar geometry. The nonbonding lobe orbital must remain orthogonal to the bond pairs and thus this orbital becomes a pₓ orbital at the planar geometry. Alternatively, the planar state can be considered to arise from bonding two hydrogens to the lobe orbitals of the ²Π ground state of SiH, Equation 16. The bond pairs, of course, readjust to become equivalent, and thus are each roughly the average of two lobe bonds and one p bond. As discussed above, the pyramidal molecule involves two p bonds and one lobe bond, and thus the barrier to inversion (∼10 kcal) in SiH₃ is directly related to the difference between p bonds and lobe bonds.

Starting with Equation 21 and bonding an H to the unpaired lobe orbital leads to tetrahedral SiH₄. Again, all the bond pairs readjust to minimize bond-bond repulsions, and to maximize bonding interactions, resulting in four equivalent bond pairs.

Summary

In the preceding discussion we constructed the lowest states of SiH₄ by bonding a hydrogen atom to the ground state of SiHₚ₋₁. In this model we first assumed that the orbitals of SiHₚ₋₁ remain unperturbed by additional hydrogen and then (after deciding on the optimal orbital pairing and geometry) we allowed for slight readjustments of the various orbitals.
A key feature in this qualitative description of SiHₙ is the use of optimized GVB orbitals, which allows a consistent, progressive description of each state. In the GVB description the correlated orbitals are hybridized even in the atom, and these orbitals are found to change quite continuously as a function of the number of bonds. With this simple model we were able to understand that 1. the ground state of SiH should be a 2Σ⁺ state and there should be a low-lying 4Σ⁻ excited state, 2. SiH₂ should also have two low-lying states, a 1A¹ ground state of bond angle ~90° and a 3B₁ excited state of bond angle ~117°, 3. SiH₃ should be pyramidal, and 4. the smallest bond energy in the series Dₙ-SiHₙ₋₁ should be D₄-SiH₂, since only in making this bond is it necessary to unpair the Si lobe orbitals.

SECOND-ROW ATOMS

From the previous section it is clear that the character of the atomic ground state wavefunctions plays a dominant role in molecular bonding. In this section we discuss briefly the ground states of the other second-row atoms, Na-Ar, as a prelude to a consideration of the hydrides of these atoms.

Again ignoring the core electrons, the ground state atoms have the following Hartree-Fock configurations:

Na: (3s)¹⁺, \( \alpha [ (\phi_s) \alpha ] = \alpha [ (\phi_{3s}) \alpha ] \)

Mg: (3s)², \( \alpha [ (\phi_s)^2 \alpha \beta ] = \alpha [ (\phi_{3s})^2 (\phi_{3p}) \alpha \beta ] \)

Al: (3s)²(3p)¹⁺, \( \alpha [ (\phi_s)^2 (\phi_{3p}) \alpha \beta ] \)

Si: (3s)²(3p)², \( \alpha [ (\phi_s)^2 (\phi_{3p})^2 \alpha \beta ] \)

P: (3s)²(3p)³, \( \alpha [ (\phi_s)^2 (\phi_{3p})^2 (\phi_{3p}) \alpha \beta ] \)

S: (3s)²(3p)⁴, \( \alpha [ (\phi_s)^2 (\phi_{3p})^2 (\phi_{3p}) \alpha \beta \alpha ] \)

Cl: (3s)²(3p)⁵, \( \alpha [ (\phi_s)^2 (\phi_{3p})^2 (\phi_{3p}) \alpha \beta \alpha \beta ] \)

Ar: (3s)²(3p)⁶, \( \alpha [ (\phi_s)^2 (\phi_{3p})^2 (\phi_{3p}) \alpha \beta \alpha \beta \alpha \beta ] \)

Correlating the 3s pair of P in the same way as for Si, Equation 5, leads to the wavefunction

\[ \alpha [ (\phi_s \phi_s + \phi_s \phi_s) \phi_{3p} \phi_{3p} \phi_{3p} \alpha \beta \alpha \alpha ] \]

\[ = \alpha [ (\phi_s^2 - \lambda^2 \phi_{3p}^2) \phi_{3p} \phi_{3p} \phi_{3p} \alpha \beta \alpha \alpha ] \]

\[ = \alpha [ \phi_{3p}^2 \phi_{3p} \phi_{3p} \phi_{3p} \alpha \beta \alpha \alpha ] - \lambda^2 \alpha [ \phi_{3p}^2 \phi_{3p} \phi_{3p} \phi_{3p} \alpha \beta \alpha \alpha ] \].

However, the second term of Equation 30c,

\[ \alpha [ \phi_{3p}^2 \phi_{3p} \phi_{3p} \phi_{3p} \alpha \beta \alpha \alpha ] \]

has three electrons in the \( \phi_{3p} \) orbital and hence, in order to satisfy the Pauli principle, this term must be zero. Thus, since all three 3p orbitals are singly occupied, the second term of Equation 30c will be exactly zero only if the correlating \( \phi_{3p} \) is identical to the singly occupied \( \phi_{3p} \). In fact, these two orbitals will not be exactly equal and hence there will be a small correlation effect. This will not, however, change the qualitative description of bonding discussed here.

\[ ^2 \text{ The second term of Equation 30c will be exactly zero only if the correlating } \phi_{3p} \text{ is identical to the singly occupied } \phi_{3p}. \]
GVB correlation of the 3s pair is eliminated\(^3\) and thus the GVB wavefunction of ground state P is identical to the HF wavefunction. Similarly for S, Cl, and Ar, the ground state GVB and HF wavefunctions are identical.

In both Mg and Al, the GVB wavefunction leads to lobe orbitals just as for Si. In Mg, since none of the 3p orbitals are occupied, the lobe pair can point in the \(x\), \(y\), or \(z\) directions leading to a GVB wavefunction of the form

\[
\mathcal{A}[(\phi_z^2 - \lambda^2 \phi_p^2 - \lambda^2 \phi_p^2 - \lambda^2 \phi_p^2)\alpha\beta].
\]

For Al the 3\(p_z\) orbital is singly occupied and hence the lobe orbitals can point in only the \(x\) or \(y\) directions. The resulting GVB wavefunction for ground state Al is

\[
\mathcal{A}[(\phi_z^2 - \lambda^2 \phi_p^2 - \lambda^2 \phi_p^2)\phi_p^2\alpha\beta].
\]

For Na, with only one valence electron, there are no corresponding correlation effects.

Schematically then, the simple GVB wavefunctions of the second-row atoms are as follows:\(^4\)

\[34.\]

\[35.\]

\[36.\]

\[37.\]

\[38.\]

\(^3\) It should be noted here that we are considering only the dominant angular correlation involving 3\(p\) orbitals. There are other less important correlations of the 3s pair, for example, radial correlation. However, in Si the angular correlation leads to two lobe orbitals on opposite sides of the atom, allowing effective bonding to an H; for P, S, Cl, and Ar, the correlation effects lead to no such separation.

\(^4\) For Mg and Al, the lobe pairs are actually correlated in more than one direction (see Equations 32 and 33). However, for simplicity in the diagrams we indicate only one of the possible correlations. It is understood in these cases that the actual GVB wavefunction is a superposition of two or three such configurations incorporating 3s correlation into all unoccupied \(p\) directions.
where, as before, a circle represents a \( p \) orbital out of the plane for all atoms except Na. Note also that the \( 3s \) pair has been omitted for P, S, Cl, and Ar.

SECOND-ROW HYDRIDES

Low-Lying States of \( MgH_n \)

Starting with the ground state of Mg, Equation 35, and bonding an H to one of the lobe orbitals leads to the ground state \( (^2\Sigma^+) \) of MgH,

\[
MgH(^{2}\Sigma^{+}) \quad \circ \bigcirc \bigcirc \bigcirc
\]

Since this bonding scheme is the only one attainable with ground state Mg, there will be no other bound states of MgH dissociating to ground state atoms.

Similarly, the ground state of MgH\(_2\) can be constructed by bonding an H to the unpaired lobe orbital of MgH. The result is a linear \( ^1\Sigma^+ \) ground state of Equation 43,

\[
MgH_2(^1\Sigma^+) \quad \circ \bigcirc \bigcirc \bigcirc
\]

Note that in making the first bond to Mg it was necessary to unpair the Mg lobe orbitals. Since the lobe orbitals overlap, unpairing them results in a significant increase in the total energy (62 kcal, for the free atom). The second MgH bond, however, is to an already unpaired lobe, and hence the second bond should be much stronger than the first, i.e.

\[
D_{H_2-Mg} \gg D_{Mg-H}. \quad 44.
\]

Since MgH\(_2\), Equation 43, has no more occupied orbitals available for bonding, MgH\(_3\) will not be a strongly bound molecule.

Higher Excited States of \( MgH_n \)

So far we have discussed only states of MgH and MgH\(_2\) that dissociate to ground state fragments. Considering in more detail the \( ^2\Sigma^+ \) state of MgH, Equation 42,
we note that one electron is not involved in the bond and therefore exciting this electron into a higher lying orbital will not disrupt the bond. The lowest unoccupied orbitals are the Mg 3pπ orbitals and so the lowest bound excited state of MgH will be the 2Π state,

\[ \text{MgH}(2\Pi) \]

45.

corresponding to exciting the nonbonding \( \pi \) orbital to a 3p orbital. This state dissociates to \( \text{Mg}(3P) \) rather than \( \text{Mg}(1S) \) and thus the MgH 2Σ⁺ \( \rightarrow \) 2Π excitation energy will be closely related to the atomic \( 1S \rightarrow 3P \) excitation energy. The potential curves for these states are shown schematically in Figure 4.

**Low-Lying States of AlH\(_n\)**

Starting with the ground state of Al, Equation 36, an H can bond either to the singly occupied \( p \) orbital, leading to the \( 1\Sigma^+ \) state,

\[ \text{AlH}(1\Sigma^+) \]

46.

or to one of the lobe orbitals, leading to the \( 3\Pi \) state,

\[ \text{AlH}(3\Pi) \]

47.

As with Si, the bond to the unpaired \( p \) orbital will be stronger than the bond to a
lobe orbital, and hence the ground state of AlH is the $^1\Sigma^+$ state. As with Si, interactions between the bond pair and the lobe pair in Equation 46 result in the lobe orbitals bending back to an angle of $\sim 128^\circ$ with respect to the bond axis.

Considering the ground state of AlH, the only orbitals available for bonding are the lobes. Bonding a hydrogen to one of the lobe orbitals of Equation 46 leads to

$$\text{AlH}_2(2\,A_1)$$

and allowing the bond to readjust (cf Equations 19 and 20 for SiH$_2$) leads to the $^2A_1$ state of AlH$_2$,

$$\text{AlH}_2(2\,A_1)$$

Again, as in SiH$_2$, Pauli principle repulsions between the two bond pairs and the singly occupied lobe orbital will decrease the AlH$_2$ angle from $128^\circ$ (the lobe-bond angle of AlH, Equation 46) to $\sim 117^\circ$.

The $^2A_1$ state of AlH$_2$ has one singly occupied, unpaired lobe orbital. Bonding a third hydrogen to this orbital leads to the planar ground state of AlH$_3$,

$$\text{AlH}_3(1\,A_1')$$

Since there are no additional valence orbitals available for bonding, a fourth H will not bond strongly to Equation 50.

Considering briefly the relative bond energies of the series $D_{\text{Al-H}}$, $D_{\text{HAI-H}}$, and $D_{\text{H}_2\text{Al-H}}$, the first and third bonds involve unpaired Al orbitals (a $p$ orbital in the first and a lobe in the third). In order to make the second bond, however, it was necessary to unpair the Al lobe orbitals, Equation 48. Thus the second bond energy will be at least 20 kcal smaller than either the first or the third.

**Higher Excited States of AlH$_n$**

In addition to the $^1\Sigma^+$ and $^3\Pi$ states of AlH, Equations 46 and 47, there are two other states that dissociate to ground state Al($^2P$). One is the $^1\Pi$ state which has the orbital occupation shown in Equation 47, but in which the two nonbonding orbitals, $\pi$ and $\pi_e$, are singlet-paired. The GVB wavefunctions for the $^3\Pi$ and $^1\Pi$ states are

$$\psi(3\Pi) = \mathcal{A}[(\phi_H\phi_H + \phi_H\phi_H)(\phi_H\phi_{\pi} - \phi_{\pi}\phi_H)x\alpha x\beta x\alpha]$$

$$\psi(1\Pi) = \mathcal{A}[(\phi_H\phi_H + \phi_H\phi_H)(\phi_H\phi_{\pi_e} + \phi_{\pi_e}\phi_H)x\beta x\beta]$$

51.
Using the same orbitals for these two states (this is, of course, an approximation) leads to a $^3\Pi \rightarrow ^1\Pi$ excitation energy of $2K_{l\pi}$, or about 40 kcal. The second additional state that dissociates to Al($^2P$) is the $^3\Sigma^+$ state, which has the same orbital occupancy as the $^1\Sigma^+$ state, Equation 46, but with the Al $p$ orbital triplet-coupled to the H orbital. The triplet-coupling results in a repulsive interaction and hence the $^3\Sigma^+$ state is not bound. The potential curves for these four states of AlH are shown in Figure 5.

Consider next the $^2A_1$ state of AlH$_2$, Equation 49. There is a low-lying, unoccupied $p\pi$ orbital (perpendicular to the plane of the page), and thus the lowest excited state is expected to correspond to exciting the nonbonding electron of the $^2A_1$ state into the $p\pi$ orbital, as in Equation 52,

\[
\text{AlH}(^2B_1) \quad 52.
\]

Now consider how the orbitals of these two states ($^2A_1$ and $^2B_1$) change as the bond angle is increased. The unpaired $\phi_i$ orbital of Equation 49 must remain orthogonal to the bond pairs (Pauli principle). Thus as the bond angle is increased to 180°, the $\phi_i$ orbital deforms continuously into a $p$ orbital at 180°, Equation 53,

\[
53.
\]

The energy of the $^2A_1$ state increases as it is distorted to a linear geometry (since the optimum angle is 117°).

As the $^2B_1$ state, Equation 52, is distorted toward a linear geometry, the nonbonding $p\pi$ orbital will not change significantly (it is orthogonal to the bond pairs
at all angles). Thus at a bond angle of 180° the $^2B_1$ state becomes Equation 54,

\[ \text{Equation 54} \]

with a $p\pi$ orbital out of the plane. For the $^2B_1$ state, since both bonds are to lobe orbitals, the optimum geometry is the linear one, Equation 54, just as in MgH$_2$. Thus the energy of the $^2A_1$ state increases as the molecule is made linear, while the energy of the $^2B_1$ state decreases.

At the linear geometry the two states, Equations 53 and 54, are components of the degenerate $^2\Pi$ state. The bending potential curves for these two states are shown in Figure 6.

Although AlH$_3$ has an empty $p\pi$ orbital, the excitation that corresponds to Equations 49–52 disrupts an AlH bond pair, giving the state

\[ \text{Equation 55} \]

which therefore will not be (strongly) bound with respect to AlH$_2 + H$.

**Higher Excited States of SiH$_n$**

The lowest states of the SiH$_n$ molecules we discussed earlier. Here we discuss some of the important higher-lying excited states.

In addition to the $^4\Pi$ and $^4\Sigma^-$ states of SiH, Equations 12 and 14, it is possible to construct several doublet states using the orbitals of Equation 14. Ignoring the bond pairs and taking the bond axis to be $z$, these states have wavefunctions of the form

\[ \text{Equation 56} \]

\[ \text{Equation 57} \]
SiH(2Δ⁺): \[ \mathcal{A} [\phi_1(\phi_{px}\phi_{py} - \phi_{px}\phi_{py})\alpha\beta] \];

SiH(2Σ⁺): \[ \mathcal{A} [\phi_1(\phi_{px}\phi_{py} + \phi_{px}\phi_{py})\alpha\beta] \];

SiH(2Σ⁻): \[ E_1\{\phi_1(\phi_{px}\phi_{py} - \phi_{px}\phi_{py})[\beta\alpha\alpha - \frac{1}{2}(\alpha\beta + \beta\alpha)]\} \].

Note that the 2Σ⁻, 2Δ⁻, and 2Σ⁻ states all have one electron in each of the three nonbonding orbitals, and that these states differ only in the way the three orbitals are coupled. There are three ways to couple three electrons, one leads to a quartet (\( S = \frac{3}{2} \)) state, while the other two lead to doublet (\( S = \frac{1}{2} \)) states. Of the doublet states, one, the 2Δ⁻ state, has the two p orbitals coupled into a singlet pair (low-spin), while the other (2Σ⁻) has the two p orbitals coupled into a triplet pair (high-spin). In both of the doublet states the T orbital is coupled to the \( p_x - p_y \) pair to lead to an overall doublet state.

Although all five states involve similar orbitals, the two-electron coulomb and exchange terms differ. Since the three orbitals are orthogonal, the state of highest multiplicity, 4Σ⁻, is the lowest in energy. The actual energy ordering of these states is \( 4Σ^- < 2Δ^- < 2Σ^- < 2Σ^+ \) (23).

As the SiH molecule is dissociated, the 4Σ⁻ and 2Σ⁻ states become components of Si(3P), while the 2Δ and 2Σ⁺ states lead to Si(1D). Thus a crossing of the 2Δ and 2Σ⁻ states occurs at some point along the potential curve.

One additional state dissociating to Si(3P) exists. This is the 4Π state, which has the same orbital occupation as the 2Π state, Equation 12, the difference being that the bond orbitals are triplet-paired, which leads to a repulsive potential curve. The potential curves for the above states are shown schematically in Figure 7.

Consider now the low-lying states of SiH₂. The first excited state of SiH₂ is the 3B₁ state, Equation 20. Equation 20 leads, however, to both a 3B₁ and a 1B₁ state depending upon whether the two nonbonding orbitals are coupled high-spin or...
low-spin. Using the same orbitals for both states, the singlet-triplet separation is

\[ \Delta E(1B_1 \rightarrow 3B_1) = 2K_{1,px} \]

or about 30 kcal\(^5\) (20).

Increasing the bond angle of configuration 20 to 180° while keeping the \( \bar{t} \) orbital orthogonal to the bond pair (Pauli principle) leads to

Four states can be constructed using the two \( \pi \) orbitals of Equation 62,

\[
\begin{align*}
\text{SiH}_2(3\Sigma^-) & : \mathcal{A}[(p_xp_y - p_yp_x)\alpha\alpha], \\
\text{SiH}_2(1\Delta^-) & : \mathcal{A}[(p_xp_y + p_yp_x)\alpha\beta], \\
\text{SiH}_2(1\Delta^+) & : \mathcal{A}[(p_xp_y - p_yp_x)\alpha\beta], \\
\text{SiH}_2(1\Sigma^+) & : \mathcal{A}[(p_xp_y + p_yp_x)\alpha\beta].
\end{align*}
\]

Assuming the orbitals of all four states to be identical (and equivalent), the one-electron part of the energy expression for states 63–66 will be identical \((2h_{pp})\). The two-electron parts of the energy expressions are as follows;

\[
\begin{align*}
3\Sigma^- : J_{xy} - K_{xy}; \\
1\Delta^- : J_{xy} + K_{xy}; \\
1\Delta^+ : J_{xx} - K_{xy} = J_{xy} + K_{xy}; \\
1\Sigma^+ : J_{xx} + K_{xy} = J_{xy} + 3K_{xy},
\end{align*}
\]

where \( J_{xx} \), \( J_{xy} \), and \( K_{xy} \) are the usual coulomb and exchange integrals and we have made use of the equality of the \( 1\Delta^+ \) and \( 1\Delta^- \) energies to rewrite the \( 1\Sigma^+ \) energy. Since \( K_{xy} > 0 \), the \( 3\Sigma^- \) state is the ground state. As the bond angle is increased from the equilibrium nonlinear geometries to a linear geometry, the three states discussed earlier correlate as follows:

\[
\begin{align*}
3B_1 \rightarrow 3\Sigma^- \\
1B_1 \rightarrow 1\Delta^- \\
1A_1 \rightarrow 1\Delta^+.
\end{align*}
\]

\(^5\) Solving self-consistently for the \( 3B_1 \) state leads to a considerably larger \( K_{1,px} \) (28.7 kcal), while solving for the \( 1B_1 \) state leads to a smaller \( K \) (13.2 kcal). The value quoted here is for the average set of orbitals.
The correspondence between the $^1A_1$ and $^1\Delta^+$ states, Equation 73, may not be clear. Recall that the nonbonding orbitals $\ell$ and $\ell'$ of the $^1A_1$ state, Equation 18, must remain orthogonal to the bond orbitals as the bond angle is increased. Consequently, at $180^\circ$ these orbitals are $p$ orbitals bisecting the $x$ and $y$ axes (i.e. $\ell \rightarrow p_x + p_y$, $\ell' \rightarrow p_x - p_y$). Therefore the lone-pair part of the $^1A_1$ wavefunction, Equation 17b, becomes

\begin{align*}
\ell \rightarrow (p_x + p_y)(p_x - p_y) + (p_x - p_y)(p_x + p_y) = 2(p_x p_y - p_y p_x),
\end{align*}

and thus the $^1A_1$ state correlates with the linear $^1\Delta^+$ state.

Consider now the relative barriers to inversion of these states. First, at their respective equilibrium (nonlinear) geometries, the $^1A_1$ state is below the $^3B_1$ (see above). However, using the energy expressions of the corresponding linear states, Equations 67–70, we found the triplet to be the lowest state. Thus the inversion barrier of the $^3B_1$ state must be much lower than that of the $^1A_1$ state. Comparing now the $^3B_1$ and $^1B_1$ states, the only difference in the energy expressions of these two states is in the sign of the exchange integral, $K_{\ell p_x}$. In fact, assuming the orbitals of the two states to be identical, the $^3B_1 \rightarrow ^1B_1$ excitation energy is just $2K_{\ell p_x}$, Equation 61. At the linear geometry this excitation energy becomes $2K_{p_x p_y}$; thus, since $K_{\ell p_x} > K_{p_x p_y}$, the linear energy separation is less than the nonlinear value. Thus the $^1B_1$ inversion barrier is slightly less than the $^3B_1$. More qualitatively, in making the $^1A_1$ state linear, two $p$ bonds must be converted to lobe bonds, and hence a large barrier is expected. For the $^3B_1$ and $^1B_1$ states, only one $p$ bond must be converted to a lobe bond, and hence a much smaller barrier is expected. The $^1\Sigma^+$ state, Equation 66, will have a linear equilibrium geometry. Qualitative potential curves for these four states are shown in Figure 8.

![Figure 8](Schematic bending potential curves for SiH₂.)
Low-Lying States of $PH_n$

Starting with the ground state of $P$, Equation 38, and bonding an $H$ to any one of three equivalent, singly occupied $p$ orbitals leads to the $^3\Sigma^-$ state of $PH$,

$$PH(^3\Sigma^-)$$

Note that there is a doubly occupied 3s pair that is not shown in Equation 75.

Bonding an $H$ to a second $p$ orbital leads to the $^2B_1$ state of $PH_2$,

$$PH_2(^2B_1)$$

Because the two bonds involve perpendicular $p$ orbitals, we would expect a bond angle of approximately 90°. In fact, the bond angle is slightly larger, 92° (24), due to bond-bond repulsions (Pauli principle). Bonding an $H$ to the remaining singly occupied $p$ orbital of $PH_2$ leads to the pyramidal ground state of $PH_3$. Again the equilibrium bond angles are expected to be slightly larger than 90° (the observed angles are 92.2°).

All three bonds involve singly occupied phosphorous $p$ orbitals, and hence the three bond strengths should be comparable. There will, though, be a small, systematic change in the bond energies due to differences in the $p$-$p'$ exchange interactions as discussed in a later section. The result is that the bond strengths are in the order $D_p^\text{p-H} < D_{\text{HP-H}} < D_{\text{H}_2p-H}$.

Bonding a fourth $H$ to phosphorus requires the unpairing of the 3s pair. The energy of this unpairing is larger than the bond energy, and hence $PH_4$ is not expected to be (strongly) bound with respect to $PH_3$ plus $H$.

Higher Excited States of $PH_n$

Before discussing the higher excited states of phosphorous hydrides, we will first consider the low-lying excited states of atomic phosphorus having the same configuration [(3s)$^2$(3p)$^3$] as the ground state. There are two such states, $^2D$ and $^2P$, consisting of a total of eight spatially distinct components. Each of these component states involves either configurations such as Equation 38 or else of the form

$$\text{...}$$

in which one $p$ orbital is doubly occupied, one is singly occupied, and one is un-
occupied. Since one of the $p$ orbitals of Equation 77 is empty, the GVB description will involve a correlated 3s pair, as shown in Equation 78.$^6$

Consider now the states of PH that can be constructed using the orbitals of the ground state, Equation 75. There are four such states, just as with linear SiH$_2$; the $^3\Sigma^-$ state is lowest (ground state), followed by the $^1\Delta^\pm$ states, followed by the $^1\Sigma^+$ state.

The $^1\Delta^-$ state involves the same configuration as the $^3\Sigma^-$, Equation 75; however, the $^1\Delta^+$ and $^1\Sigma^+$ states are of the form

$$\begin{align*}
^1\Delta^+ \\
^1\Sigma^+ 
\end{align*}$$

Since there is an unoccupied $p$ orbital in both configurations, the GVB description leads to a correlated (3s) pair, Equation 80,$^7$

$$\begin{align*}
\text{\raisebox{0.5em}{.}} \\
\text{\raisebox{0.5em}{.}}
\end{align*}$$

Remember, the 3s pair is not shown in Equation 79, nor on the left side of Equation 80. As found in the $^2\Pi$ state of SiH, Figure 2, the lobe pairs of Equation 80 will be at an angle of about 128° with respect to the bond.

Now consider bonding an H to an excited state of phosphorus, Equation 78. Bonding to the singly occupied $p$ orbital leads to components of the $^1\Sigma^+$ and $^1\Delta^-$ states discussed above. (Thus, upon dissociation, these states lead to $^1D$ phosphorus.) Bonding to the lobe orbital of Equation 78 gives rise to the $^3\Pi$ and $^1\Pi$ states of PH,

$$\text{PH}^{(1,3\Pi)}$$

The lower of these two states, $^3\Pi$, is 84 kcal above the ground state; this large excitation energy results from two factors: 1. the necessity of unpairing the lobe orbitals of Equation 78, and 2. Equation 78 itself corresponds to an excited atomic

---

$^6$ This correlation is actually only important in the three components of the $^2P$ state and does not play a role in the $^2D$ states.

$^7$ This 3s correlation cancels in the $^1\Delta^+$ state (the minus combination in Equation 79).
state with respect to Equation 38. The potential curves for these states are shown in Figure 9.

Bonding an H to a lobe orbital of Equation 80 and allowing for orbital readjustments leads to the $^2A_1$ state of PH$_2$.

PH$_2(^2A_1)$:

As for SiH$_2$, the lobe-bond angle of PH is $\sim 128^\circ$; however, repulsions between the incoming H orbital and the now unpaired lobe orbital decrease the bond angle to about $118^\circ$. Increasing the bond angle of Equation 82 leads to one component of the $^2\Pi$ state of linear PH$_2$,

PH$_2(^2\Pi)$

The other component of the $^2\Pi$ state,
correlates with the $^2B_1$ ground state, Equation 76. Schematic potential curves for these two states are shown in Figure 10.

Starting with the $^2A_1$ state of PH$_2$, Equation 82, and bonding a third H leads to the planar $^1A'$ state of PH$_3$,

$$\text{PH}_3(^1A')$$

The energy difference between this planar state and the pyramidal ground state of PH$_3$ is the barrier to inversion. Recall that pyramidal PH$_3$ involves three $p$ bonds to the ground state of phosphorus. The planar state, however, involves one $p$ bond and two lobe bonds to an excited state of phosphorus. Thus the inversion barrier of PH$_3$ is expected to be much larger than that of SiH$_3$, where the barrier was just the difference between a lobe bond and a $p$ bond ($\sim 10$ kcal). The actual barrier in PH$_3$ is approximately 37 kcal (25–27).

**Low-Lying States of SH$_n$**

Starting with the ground state of sulfur, Equation 39, and bonding an H to one of the two singly occupied $p$ orbitals leads to the $^2\Pi$ ground state of SH,

$$\text{SH}(^2\Pi)$$

---

8 Recall that the 3s pair of Equation 76, not shown, must remain orthogonal to the bond pairs as the bond angle is increased, and thus correlates with a $px$ pair of the linear molecule.
Bonding a second H gives rise to the $^1A_1$ state of SH$_2$,

\[
\text{SH}_2(^1A_1)
\]

Because both bonds are to \( p \) orbitals, the bond angle should be 90°; however, bond-bond repulsions lead to the slightly larger angle of 92°.

In order to bond a third H to sulfur, it is necessary to unpair the 3s electron pair. The 3s pair of S, though, is not highly correlated (as it is in Mg, Al, and Si) and thus the energy required to uncouple the pair is larger than the resulting bond energy. Hence, SH$_3$ is not expected to be (strongly) bound with respect to SH$_2$ plus H.

**Higher Excited States of SH$_n$**

Using the ground state configuration of atomic sulfur, $(3s)^2(3p)^4$, we can construct two excited states ($^1D$ and $^1S$) in addition to the $^3P$ ground state. There are six spatially distinct components of these states, three of the form shown in Equation 39 and three of the form

\[
\text{SH}_2
\]

Since Equation 88 involves an unoccupied \( p \) orbital, the GVB description leads to a correlated (3s) pair,

\[
\text{SH}(2\Sigma^+)
\]

Bonding an H to one of the lobe orbitals of Equation 89 yields the $2\Sigma^+$ state of SH,

\[
\text{SH}_2(1\Sigma_g^+)
\]

This state is very high lying (~84 kcal above the $^2\Pi$) since it requires both an excited state of sulfur and the unpairing of the (3s) lobe orbitals. Schematic potential curves for these states are shown in Figure 11.

Bonding an H to the unpaired lobe orbital of Equation 90 leads to the linear $1\Sigma_g^+$ state of SH$_2$,
This configuration correlates with the \( ^1A_1 \) ground state when the bond angle is decreased. Thus inversion of the \( ^1A_1 \) state of \( \text{SH}_2 \) proceeds through a state in which both \( p \) bonds of the \( ^1A_1 \) state are replaced with lobe bonds, and in which an excited state of atomic sulfur is employed.

**The States of \( \text{CIH}_n \)**

The ground state of \( \text{Cl} \), Equation 40, includes one singly occupied \( p \) orbital. Bonding an \( \text{H} \) to this orbital yields the \( ^1\Sigma^+ \) ground state of \( \text{HCl} \),

\[
\text{HCl}(^1\Sigma^+)
\]

As there are no additional orbitals available for bonding, \( \text{ClH}_2 \) is not expected to be bound, nor are any low-lying bound excited states of \( \text{ClH} \) expected.

**FIRST-ROW HYDRIDES**

The principles (of bonding) discussed in the previous sections apply also to the hydrides of corresponding atoms of other rows of the periodic table. For hydrides of atoms below the second row, the qualitative description of bonding is identical to that of the second-row hydrides. For the first-row hydrides, however, some of the qualitative aspects of bonding are different. In this section we first discuss the origin of the differences, and then the implications of these differences, taking the \( \text{CH}_n \) and \( \text{NH}_n \) series as examples.

**Bond-Bond Repulsions**

In the simplest description, bonding two \( \text{H} \) atoms to two singly occupied \( p \) orbitals would lead to a bond angle of \( 90^\circ \). For second-row atoms, Pauli principle repulsions between the bond pairs increase these angles slightly to \( 91-93^\circ \). Assuming covalent
Table 1  Summary of bond lengths and angles of the hydrides of the first, second, and third rows of the periodic table

<table>
<thead>
<tr>
<th>GVB Diagram</th>
<th>State</th>
<th>Molecule</th>
<th>$\theta$ (Obs)$^a$ (degrees)</th>
<th>$\theta$ (Est)$^{b, c}$ (degrees)</th>
<th>Bond length Å</th>
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<td></td>
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<td>MgH</td>
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<td></td>
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* Angles in parentheses are estimated.
* Estimated angles based on simple model discussed in text (allowing no readjustment of orbitals).
bonds, this repulsive interaction depends upon the overlap (squared) of the two H orbitals. For SiH$_2(^1A_1)$, PH$_2(^2B_1)$, and SH$_2(^1A_1)$ the H–H distances for two bonds at 90° are 2.148, 2.010, and 1.878 Å. However, for the corresponding first-row hydrides, CH$_2$, NH$_2$, and OH$_2$, the bond lengths are ~30% shorter, and hence the H–H distances have decreased to 1.5712, 1.448, and 1.352 Å. This difference in H–H distances leads to an increase in the H–H overlap, for example, from 0.252 for SH$_2$ to 0.445 for OH$_2$. As a result, the optimum bond angles for the first-row compounds are significantly larger [102° for CH$_2(^1A_1)$, 103° for NH$_2(^2B_1)$, and 104° for OH$_2(^1A_1)$] than those of their second-row counterparts. Note that for all three molecules, the simplest description of the bonding involves two perpendicular $p$ orbitals and hence leads to predicted bond angles of 90°.

Recall for SiH($^2\Pi$), Equation 16, the angle between the lobe orbitals and the bond is 128° (corresponding to an angle between the two lobes of 104°). Thus bonding an H to a lobe of SiH($^2\Pi$) and averaging the two bond pairs would be expected to lead to an angle of 116° between the remaining lobe and each of the bonds. In fact the actual angle is some what larger (121°), which indicates that the dominant repulsive overlap is between the bond pairs and the lobe orbital, rather than between the two bond pairs. (Had the bond pair–bond pair repulsion been dominant, the readjustment would have been to increase the bond angle, thus decreasing the bond-lobe angles.)

For CH($^2\Pi$) the bond-lobe angle is also 128° (6, 28), and thus bonding an H to a lobe orbital of CH($^2\Pi$) would also be expected to lead to a bond-lobe angle of 116°. In this case, however, the actual angle is somewhat smaller (113.5°), which indicates that for the first-row compound the bond-bond repulsions are dominant. Thus the bond angle of CH$_2(^3B_1)$ is 133° (360 – 227), slightly larger than expected on the basis of the CH($^2\Pi$) bond-lobe angles. Similarly for BH($^1\Sigma^+$), the bond-lobe angles are 126° (5, 7), while bonding an H to one of the lobes leads to a bond angle of 131°. Thus, for both CH$_2$ and BH$_2$ the bond angles are ~5° larger than the corresponding CH and BH bond-lobe angles.

In summary, for first-row hydrides, bond-bond repulsions lead to a 12–15° increase in the bond angle between the p-like bonds and to a 5° increase for the case involving one p-like and one lobe-like bond. This effect is much larger for first-row hydrides than for hydrides of any of the lower rows simply because of the smaller bond lengths in the first-row hydrides. A detailed comparison of bond lengths and bond angles for first-, second-, and third-row hydrides is given in Table 1.

**Relative Strengths of Bonds to Lobe and p Orbitals**

A second factor distinguishing the first-row atoms from the others is that the sizes of the s and p orbitals are comparable for the first row, whereas for lower rows the s orbitals are significantly smaller than the p orbitals. The comparison of sizes is shown in Figure 12 where the valence s and p orbitals are compared for the B, C, and N columns of the first four rows of the periodic table.

The origin of this difference is as follows: for first-row atoms, the valence 2s orbital penetrates the 1s core more effectively than does the 2p orbital. Balancing this effect, however, is the constraint that the 2s orbital must remain orthogonal
Line plots of Hartree-Fock atomic orbitals. The X’s indicate the atomic covalent radii.

to the 1s orbital. No such constraint exists for the 2p orbitals. For atoms from the lower rows, the valence s orbital still penetrates the core more effectively than do the valence p’s; however, in these atoms, both the valence s and the valence p orbitals are subject to orthogonality constraints (involving core orbitals). The result is that for atoms of the second row (and below) the valence s orbital is significantly more contracted than the valence p orbital, whereas for first-row atoms, the penetration and orthogonality effects nearly cancel. Thus there is a smaller difference between the valence s and p sizes of the first row than for any of the lower rows. This similarity in size of the first-row 2s and 2p orbitals leads to an increased importance of 2s-2p, or lobe, correlation, and thus a decreased overlap between the two lobe orbitals. For example, for Al, the overlap between the l and 7 lobes is 0.74 (J. P. Dwyer and W. A. Goddard III, unpublished results), whereas for B this overlap is 0.68 (7). Thus for first-row compounds, bonds to lobe orbitals are significantly more favorable (relative to p bonds) than for other rows.
Low-Lying States of $CH_n$

The lowest states of CH arise from bonding an H to either a carbon p orbital, forming the $^2\Pi$ ground state, Equation 12, or to a lobe orbital forming the $^4\Sigma^-$, $^2\Delta$, and $^2\Sigma^-$ states, Equation 14. The ordering of these states is identical to that found for SiH; however, the corresponding excitation energies differ considerably in magnitude. For example, the lowest ($^4\Sigma^-$) of the lobe-bonded states of CH lies 17 kcal (29, 30) above the ground ($p$-bonded) state. This is less than half the corresponding excitation energy of SiH, as expected from the above analysis.

Starting with the $^2\Pi$ state of CH, the lowest states of CH$_2$ are obtained by bonding an H to either a p orbital ($^1A_1$ state) or a lobe orbital ($^3B_1$ state). Recall, for SiH$_2$, Equations 13 and 20, the ground state is $^1A_1$ with the $^3B_1$ state lying 18 kcal higher. Comparing CH$_2$ with SiH$_2$, there are two important factors in CH$_2$ that favor the $^3B_1$ state relative to the $^1A_1$. First, the bonds of the $^1A_1$ state involve perpendicular p orbitals and hence will favor small bond angles, $\sim 90^\circ$; the bonds in the $^3B_1$ state favor larger angles, $\sim 128^\circ$ (see above). For first-row compounds, the importance of bond-bond repulsions (which are, of course, largest at small bond angles) leads to a significant increase in the energies of states that involve small bond angles, relative to those with larger angles. This effect increases the energy of the $^1A_1$ state relative to the $^3B_1$ state. The second factor is that bonds to lobe orbitals are more comparable (energetically) to bonds to p orbitals for first-row atoms than for the Si row. The $^3A_1$ state involves two bonds to p orbitals while the $^3B_1$ state involves one p bond and one lobe bond. Thus this effect also lowers the energy of the $^3B_1$ relative to the $^1A_1$.

The net result is that the ordering of the first two states of CH$_2$ is inverted with respect to SiH$_2$. Thus the ground state of CH$_2$ is the $^3B_1$ state, which lies 9 kcal (29, 31–34) below the $^1A_1$ state, while for SiH$_2$ the $^3B_1$ state is 18 kcal above $^1A_1$.

Starting with the $^3B_1$ ground state of CH$_2$, there are two possibilities for bonding a third hydrogen, the unpaired lobe orbital or the $p\pi$ orbital. Again, due to the importance of bond-bond interactions, the lowest configuration will be the one with the largest bond angles. Bonding to the lobe leads to planar CH$_3$ ($120^\circ$ bond angles), while bonding to the $p\pi$ orbital leads to two $90^\circ$ bond angles. Thus the lowest energy configuration for CH$_3$ is planar, whereas for SiH$_3$ it is pyramidal. Because of the ability of $^3B_1$ CH$_2$ to bond an H to either the lobe or p orbital, the force constant for pyramidal distortion of CH$_3$ is quite small (35).

Low-Lying States of $NH_n$

The ground state of N, Equation 38, consists of three singly occupied p orbitals. Bonding an H to one of these leads directly to the $^3\Sigma^-$ state of NH. No other ground states of NH correlate with the ground state atoms (36). As discussed for PH, there are four excited states of NH correlating with the lowest excited state of N($^2D$). Two of these, $^1\Delta$ and $^1\Sigma^+$, involve a bond to a $p$ orbital of N, while the remaining two, $^3\Pi$ and $^3\Pi$, involve bonds to lobe orbitals of N. There are two important considerations in comparing these states of NH to those of PH; 1. the increased importance of lobe bonds in N, and 2. the relative magnitudes of the $^4S \rightarrow ^2D$
excitation in N (55 kcal) and P (32 kcal). These two effects nearly cancel for the Π states, which leads to $^3\Sigma^\text{-} \rightarrow ^3\Pi$ excitation energies of 85 kcal and 83 kcal for NH and PH, respectively.

Starting with the $^3\Sigma^\text{-}$ state of NH and bonding an H to one of the two singly occupied $\pi^*$ orbitals leads to the $^2B_1$ state of NH$_2$. Bond-bond repulsions increase the bond angle to 103°, compared with an optimum angle of 92° for PH$_2$. Increasing the bond angle of this state leads to the $^2\Pi$ state of linear NH$_2$, Equation 84. The barrier to inversion in NH$_2$($^2B_1$) should be much less than that of PH$_2$, both because bond-bond repulsions favor a linear geometry (more important in NH$_2$) and because the wavefunction at 180° involves two bonds to lobe orbitals (more favorable in NH$_2$). In fact, the barrier in NH$_2$ is 34 kcal (37), while the barrier in PH$_2$ is ~65 kcal.

Similarly, comparing NH$_3$ and PH$_3$, the barrier to inversion in the first-row compound (6 kcal) is much smaller than that of the second-row compound (~37 kcal).

**HALIDES (AX$_n$, X = F, Cl, . . .)**

Since the valence shell of fluorine and other halogens ($ns^2np^5$) contains only one singly occupied orbital, we expect the compounds AX$_n$ to be qualitatively similar to the corresponding AH$_n$ molecules. There are, however, two important differences to be considered; the large electronegativity of the halogens and the interaction of the doubly occupied valence orbitals of the halogen with adjacent centers. In this section we discuss briefly the implications of these effects on the electronic structure of simple halides, using the CX$_n$ series to illustrate the concepts.

Bonding the singly occupied 2p orbital of an F to a p orbital of atomic C leads directly to the $^2\Pi$ ground state of CF,

\[ \text{CF}^{(2\Pi)} \]

Similarly, bonding to a lobe orbital of C leads to the $^4\Sigma^\text{-}$ state,

\[ \text{CF}^{(4\Sigma^\text{-})} \]

For CH$_3$, the bond energy of the $^2\Pi$ state is 80 kcal, while that of the $^4\Sigma^\text{-}$ state is only slightly less, 63 kcal, and hence the CH($^2\Pi - ^4\Sigma^\text{-}$) separation is 17 kcal. Consider now the effect of replacing the covalent bond of C–H with a highly ionic bond polarized away from the carbon. In order to ascertain the effect we consider the idealized structure C$^+$F$^-$ and estimate the bond energy of this species using the approximate relationship,

\[ D_{\text{ion}}(C^+F^-) = \text{EA}(F) - \text{IP}(C) + 1/R, \]
where EA(F) is the electron affinity of atomic fluorine, IP(C) is the ionization potential of carbon, and R is the internuclear distance. An important point here is that the IP(C) depends on the molecular state. For example, in this idealized model the $^2\Pi$ state of CF is described as $C^+(2s^22p^1)F^-(2s^22p^6)$, while the $^4\Sigma^-$ state is of the form $C^+(2s^12p^2)F^-(2s^22p^6)$. Thus the appropriate ionization potentials are $IP_{2\Pi}(C) = 260$ kcal for the $^2\Pi$ state and $IP_{4\Sigma^-}(C) = 383$ kcal for the $^4\Sigma^-$ state. Substitution into Equation 95 (using $R = 1.27$ Å) leads to the following bond energies,

$$D_{\text{ION}}(^2\Pi) = 78 - 260 + 261 = 79 \text{ kcal}$$

$$D_{\text{ION}}(^4\Sigma^-) = 78 - 383 + 261 = -43 \text{ kcal}.$$  

Thus the ionic bond energy of the $^2\Pi$ state is comparable to the covalent (CH) bond energy, 80 kcal. These two idealized structures overlap considerably, and hence the actual wavefunction will be a combination of the two, which leads to a bond energy lower than either. The actual bond energy of CF($^2\Pi$) is 127 kcal.

Considering now the $^4\Sigma^-$ state, the estimated ionic bond energy is much less favorable (in fact, it is negative). Therefore, we do not expect a significant contribution of the ionic structure in the optimum wavefunction. In fact, the bond energy of CF($^4\Sigma^-$) is $\sim 63$ kcal (W. J. Hunt, P. J. Hay, and W. A. Goddard III, unpublished results), quite close to that of the covalent molecule CH($^4\Sigma^-$), 53 kcal.

Consider now bonding a second F to C to form CF$_2$. Starting with the $^2\Pi$ state of CF, Equation 93, there are again two possibilities, one, CF$_2(^1A_1)$, in which the second bond is to the unpaired $p$ orbital of CH, and the other, CF$_2(^3B_1)$, in which the bond is to a lobe orbital. Recall that for the hydride, these two states are of comparable energies (the $^3B_1$ state is 9 kcal below the $^1A_1$). For CF$_2$ the second F will bond much more strongly to a $p$ orbital than to a lobe (as found for CF), and hence the ground state of CF$_2$ is the $^1A_1$ state. In fact, the CF$_2(^3B_1)$ lies $\sim 46$ kcal above the $^1A_1$ state (38).

Starting with CF$_2(^1A_1)$ and bonding a third F, there is only one choice, a bond to a lobe orbital of CF$_2$. This third bond then will be much weaker than either of the first two, since the lobe orbitals of CF$_2$ must be unpaired, and since the bond involves a lobe of C rather than a $p$ orbital (hence ionic character will not be an important factor). The result is pyramidal CF$_3$, thereby maximizing the carbon $p$ character in the bonds. This is in contrast to CH$_3$, which, as discussed above, is planar.

In summary, the IP of a valence $p$ orbital is always much smaller than that of a valence $s$. Consequently, in considering bonding between two atoms of very different electronegativities (such as C and F), bonds involving a $p$ orbital of the less electronegative atom will be much more stable than those involving lobe orbitals (due to the incorporation of ionic character in the $p$ orbital bond). Thus, comparing the CH$_n$ molecules to the CF$_n$ series, the large difference in electronegativities of H and F lead to important differences in the electronic structure and geometries of these species.

Consider now the remaining halogens, Cl, Br, I, . . . . An important difference between F and all of the lower halogens is that bond distances become much longer as we move down the row. Consequently, the $1/R$ term of Equation 95 is not nearly
as favorable. Thus, even for Cl, which has a higher electron affinity than F, ionic bonding character will not be as important. As a result, for Cl, Br, etc., the bond strengths relative to \( p \) and lobe orbitals are more comparable. In addition, the total bond strength of, for example, the \( ^2\Pi \) state of \( CX \) becomes much smaller (128, 95, 67, and 50 kcal for CF, CCl, CBr, and Cl, respectively). Similarly the \( ^2\Pi - ^4\Sigma^- \) separation will decrease along this series.

For \( CX_2 \), as the importance of ionic bonding decreases, the energy of the \( ^1A_1 \) state will increase relative to the \( ^3B_1 \) state. For example, the \( ^1A_1 - ^3B_1 \) separation of CCl\(_2\) is only 13 kcal, compared with a separation of 46 kcal for CF\(_2\) (38). In fact, for CBr\(_2\) or Cl\(_2\), the \( ^3B_1 \) state may well be the ground state. Replacing the electronegative halogen with an electropositive alkali should reverse these trends, favoring \( ^4\Sigma^- \) CNa and \( ^3B_1 \) CNa\(_2\).

Consider now replacing the carbon in the \( CX_n \) series with one of its lower-row analogues, Si or Ge. There are two important differences to be considered; 1. the absolute IP's are much smaller (for example, IP\(_p\) = 260, 188, and 182 kcal for C, Si, and Ge, respectively), and 2. the bond lengths become larger [\( R_e(C-F) = 1.272, R_e(Si-F) = 1.601 \)]. Taking CF-SiF as a specific comparison, substitution into Equation 95 leads to an ionic bond strength for the \( ^2\Pi \) state of SiF of 97 kcal, whereas the observed bond strength is 129 kcal. For comparison, the corresponding covalent bond strength of SiH is 71 kcal, which indicates that the ionic SiF bond energy is larger than the covalent bond energy. Recall that for CF the ionic and covalent bond energies were approximately equal. Thus we see that the large decrease in the atomic ionization potentials of the lower rows of the periodic chart leads to an increased importance of ionic character in the halides of these elements. Consequently, the bonding in second-row halides will be similar to that discussed for the \( CX_n \) series.

### BOND ENERGIES

In the preceding sections we presented an orbital description of the electronic structure of simple hydrides and halides. In this section we discuss the trends in bond energies that can be understood in these terms.

Consider the ground states of \( P(4S) \), \( PH(3\Sigma^-) \), \( PH_2(2\Sigma^+) \), and \( PH_3(1A) \) (see Equations 38, 75, and 76). Each bond in this series involves a singly occupied \( 3p \) orbital of phosphorus. Thus one might expect the three bond energies to be comparable, possibly decreasing slightly due to bond-bond repulsions. In fact, the trend should be in the opposite direction, \( D(P-H) < D(HP-H) < D(H_2P-H) \), with an increase of \( \sim 5 \) kcal per H. In order to understand this trend we must consider the \( p-p' \) exchange interactions in each of these molecules.

If we assume each bond pair to be purely covalent, the energies of these molecules have the form

\[
E[P(4S)] = E_0(P) - K_{xy} - K_{xz} - K_{yz} \quad 98.
\]

\[
E[PH(3\Sigma^-)] = E_0(PH) - K_{xy} - \frac{1}{2}K_{xz} - \frac{1}{2}K_{yz} \quad 99.
\]
Table 2  Estimated bond energies and heats of formation (kcal/mole) of $AH_n$ species

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>P</th>
<th>As</th>
<th>Sb</th>
<th>O</th>
<th>S</th>
<th>Se</th>
<th>Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_{\text{el}}(A)$</td>
<td>112.5 ± 1</td>
<td>79.18 ± 0.05</td>
<td>72.04</td>
<td>62.63</td>
<td>58.989 ± 0.03</td>
<td>66.14 ± 0.5</td>
<td>54.11</td>
<td>47.0</td>
</tr>
<tr>
<td>$\Delta H_{\text{el}}(AH_n)$</td>
<td>-9.30 ± 0.1</td>
<td>7.0 ± 0.4</td>
<td>17.70</td>
<td>36.625</td>
<td>-57.103</td>
<td>-4.18 ± 0.15</td>
<td>8.05</td>
<td>24.8</td>
</tr>
<tr>
<td>$K_{pp}$</td>
<td>18.32</td>
<td>10.84</td>
<td>10.29</td>
<td>8.88</td>
<td>22.57</td>
<td>12.93</td>
<td>12.34</td>
<td>12.08</td>
</tr>
<tr>
<td>$D(A-H)$</td>
<td>101.39</td>
<td>81.11</td>
<td>74.89</td>
<td>64.74</td>
<td>115.32</td>
<td>90.03</td>
<td>77.75</td>
<td>69.75</td>
</tr>
<tr>
<td>$D(AH)$</td>
<td>83.07</td>
<td>70.27</td>
<td>64.60</td>
<td>55.86</td>
<td>104.04</td>
<td>83.56</td>
<td>71.58</td>
<td>59.71</td>
</tr>
<tr>
<td>$D(H-AH)$</td>
<td>92.23</td>
<td>75.69</td>
<td>69.75</td>
<td>60.30</td>
<td>115.32</td>
<td>90.03</td>
<td>77.75</td>
<td>65.75</td>
</tr>
<tr>
<td>$D(H-AH)$</td>
<td>101.39</td>
<td>81.11</td>
<td>74.89</td>
<td>64.74</td>
<td>115.32</td>
<td>90.03</td>
<td>77.75</td>
<td>65.75</td>
</tr>
<tr>
<td>$\Delta K_{pp}$</td>
<td>40.47</td>
<td>36.49</td>
<td>40.96</td>
<td>49.74</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$\Delta H_{\text{el}}(AH)_{\text{CALC}}$</td>
<td>40.8 ± 3</td>
<td>30.6 ± 23</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

* Based on lowest two $LS$ states after averaging over $J$ state

\[ E[PH_2(2B_1)] = E_0(PH_2) - \frac{1}{2}K_{xy} - \frac{1}{2}K_{xz} - \frac{1}{2}K_{yz} \]

where we have considered explicitly only the one center p-p' exchange integrals. Assuming the exchangeless bond energies, $D_{\text{PH}}$, to be constant (neglecting bond-bond interactions) leads to the predicted bond energies,

\[ D(H_2P-H) = D_{PH} \]

\[ D(HP-H) = D_{PH} - \frac{1}{2}K_{xy} \]

\[ D(P-H) = D_{PH} - \frac{1}{2}K_{xz} - \frac{1}{2}K_{yz}. \]

Using the experimental atomization energy for the saturated $AH_3$ molecules and exchange integrals derived from atomic spectra leads to the predicted bond energies of Table 2. In most cases the predicted energies are probably more accurate than the current experimental data.

A similar analysis for the $OH_n$, $SH_n$, . . ., series leads to

\[ D(HA-H) = D_{PH} \]

\[ D(AH) = D_{PH} - \frac{1}{2}K_{xy}. \]

The numerical results are also given in Table 2. Again, all predictions are within experimental error limits except for $D(O-H)$, which is 3 kcal high.

The above analysis can be extended to include bonds to lobe orbitals, which leads to relationships between excitation energies and inversion barriers of the various hydrides. This analysis, though, is beyond the scope of the present review.

SUMMARY

The qualitative orbital view of molecules derived from ab initio (generalized valence bond) calculations of atoms leads to simple concepts relating to geometries, bond energies, and ordering of electronic states, which can be used for semiquantitative predictions.
ACKNOWLEDGMENT

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