The Modern VB Descriptions of CH_2, CH_2^+, SiH_2, and SiH_2^+

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Spin-coupled theory, which represents the modern form of valence bond theory, is used to investigate the (correlated) electronic structure of CH_2, SiH_2, CH_2^+, and SiH_2^+ in various states. The pictures that emerge for the bonding in these systems are remarkably similar to the classical ideas of covalent bonds constructed from sp^x-like hybrids and H(1s) orbitals, but there are also some important differences.

The spin-coupled valence bond approach to electronic structure is a modern *ab initio* technique which takes into account, from the outset, the chemically most important effects of electron correlation. It provides accurate descriptions of molecular processes, whilst retaining a chemically appealing representation of the wavefunction in terms of simple orbital pictures and in terms of the different ways of pairing-up the electron spins. This approach, which represents the modern form of valence bond theory, has been applied successfully to a wide range of problems. Recent applications of interest to organic chemists include studies of aromatic systems,[1] of 2,4-dimethylenecyclobutane-1,3-diyl,[2] of 1,3-dipoles,[3] and of methane[4] and methyl-lithium.[5]

In the present work we use spin-coupled theory to investigate the electronic structure of various states of methylene, silylene, and their cations. Calculations are carried out without preconceptions as to the form of the orbitals or as to the relative importance of the different modes of spin coupling. The descriptions that emerge are remarkably similar to Pauling's original picture of sp, sp^2, and sp^3 hybridization.[6] We present results for the $^3B_1$ and $^1A_1$ states of both CH_2 and SiH_2, and for the $^2A_1$ and $^2B_1$ states of both CH_2^+ and SiH_2^+.

Calculations.—In view of the availability of several recent reviews,[7] we provide here only a very brief description of the spin-coupled wavefunction. For a molecule with total spin S

$$\Psi_{SM} = \sum_{k=1}^{f_S^N} c_{S,k}\mathcal{A}(\psi_1{}^2\psi_2{}^2\cdots\psi_n{}^2\Theta^{2n}_{0,0;f}\varphi_1\varphi_2\cdots\varphi_N\Theta^N_{S,M;k}) \quad (1)$$

(and projection M) the wavefunction Ψ_{SM} can be written in the form[7a] shown in equation (1) where the n doubly occupied orthogonal orbitals ψ_μ describe the $2n$ core electrons and the N singly occupied non-orthogonal orbitals φ_μ describe the N valence electrons. The index k labels a particular mode of coupling together the spins of the N valence electrons in order to provide a resultant total spin of S. The $\Theta^N_{S,M;k}$ constitute a complete set of N-electron spin functions, with f_S^N members for each value of M, and we refer to the $c_{S,k}$ as spin-coupling coefficients. $\Theta^{2n}_{0,0;f}$, the last member of the set for $2n$ electrons coupled to a singlet, is the perfect-pairing spin function.

In the present study, we used basis sets for (Si/C/H) consisting of (12s 9p/10s 6p/5s) primitive Gaussians contracted to [6s 5p/5s 3p/3s].[8] These were augmented with polarization functions with exponents $d_{Si} = 0.388$, $d_C = 0.72$ and $p_H = 1.0$. We use the label TZVP for basis sets of this quality. Five components were used for the (spherical) d functions so that there are 31 basis functions for CH_2/CH_2^+ and 38 for SiH_2/SiH_2^+.

The core electrons are accommodated in doubly occupied molecular orbitals ψ_μ taken from appropriate restricted Hartree–Fock (RHF) calculations, and the valence orbitals φ_μ are expanded as completely general linear combinations of all the remaining molecular orbitals, regardless of symmetry or occupancy. All the spin-coupled orbitals φ_μ are fully optimized simultaneously with the spin-coupling coefficients $c_{S,k}$. In each case we use the complete set of Kotani or branching-diagram spin functions.[9]

There are no constraints on the overlaps between the spin-coupled orbitals, but each of them is orthogonal to any of the core orbitals. In the present work, we take into account the effects of electron correlation for the valence electrons, but not for the core electrons. We consider CH_2 and SiH_2 as molecules with six valence electrons, and their cations as systems with five valence electrons. The 'cores' for CH_2 and CH_2^+ consist of two electrons, essentially $C(1s^2)$, and for the silicon analogues they consist of ten electrons, essentially $Si(1s^22s^22p^6)$. Thus the spin-coupled orbitals for CH_2/CH_2^+ and SiH_2/SiH_2^+ are expanded in basis sets consisting of 30 and 33 MOs, respectively.

Results

CH_2.—There has been much theoretical interest in predicting the small energy separation between the triplet ground state ($^3B_1$) and the first excited singlet state ($^1A_1$) of methylene. The most extensive calculations to date are those of Bauschlicher *et al.*;[10] they carried out CI calculations with very large basis sets (including g functions) and all single and double excitations out of a CASSCF reference wavefunction. This level of theory (second-order CI) was chosen because previous studies in a much smaller basis set had shown close agreement between the full CI and second-order CI estimates of the $^1A_1$–$^3B_1$ splitting.[11]

The $^3B_1$, $^1A_1$, and $^1B_1$ states of CH_2 have been considered previously using spin-coupled valence bond theory.[12] Direct comparison with the full CI result of Bauschlicher and Taylor[11] have shown that very compact spin-coupled VB wavefunctions can provide results of very high accuracy for the $^1A_1$–$^3B_1$ splitting. The form of the spin-coupled wavefunctions for these states has important consequences for the stereospecificity of the cycloaddition reaction of CH_2 with alkenes,[12] and further work is in progress on the potential energy surface for the $CH_2(^1A_1) + H_2 \longrightarrow CH_4$ insertion reaction.[13]

The calculations presented here for methylene use more extensive basis sets than in our previous work, and the geometries considered are slightly different, but the pictures that emerge are very similar indeed. These new calculations are included for completeness, so that we can compare more easily with CH_2^+, SiH_2 and SiH_2^+. Using the same geometries as

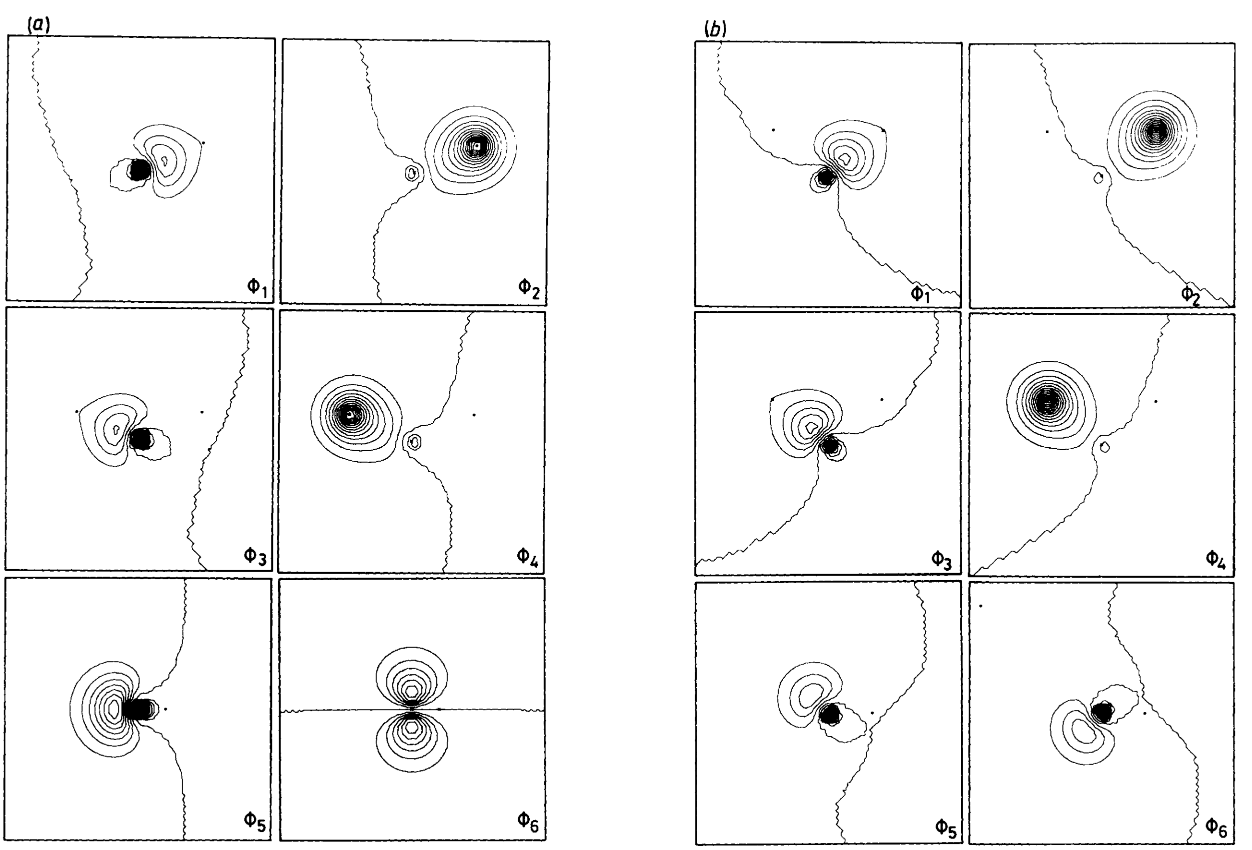

Figure 1. Contour plots of spin-coupled orbitals in CH_2: (*a*) the $^3B_1$ state, (*b*) the $^1A_1$ state. Orbitals φ_1–φ_4 are shown in the molecular plane (σ_v' mirror) and orbitals φ_5–φ_6 are shown in the σ_v mirror plane. Throughout this work we plot the square modulus of the orbitals, $|\varphi_\mu(r)|^2$, and the positions of the nuclei are denoted by crosses.

Bauschlicher and Taylor,[11] we first carried out single-configuration RHF calculations for the $^3B_1$ ($r_{CH} = 1.082$ Å, $\theta = 132.4°$) and $^1A_1$ ($r_{CH} = 1.117$ Å, $\theta = 102.4°$) states of CH_2. Spin-coupled calculations were then performed for the six valence electrons, with the two core electrons accommodated in the $1a_1$ molecular orbital, as indicated above. The complete spin spaces for six electrons consist of five functions for $S = 0$ and of nine for $S = 1$.

The spin-coupled orbitals φ_1–φ_6 are shown in Figure 1 for the $^3B_1$ and $^1A_1$ states of CH_2. For the triplet state, φ_1 is an sp^2-like orbital which overlaps most strongly (see Table 1) with φ_2, which is a distorted H(1s) function. Orbitals φ_3 and φ_4 are the counterparts in the second C–H bond. One of the non-bonding electrons occupies the remaining sp^2-like hybrid, which points away from the two hydrogen atoms. The sixth orbital closely resembles a C(2p) function, pointing perpendicular to the molecular plane. The dominant mode of spin coupling ($|c_{1,9}|^2 = 94.7\%$) corresponds to two C–H bonds and to triplet coupling of the spins of the two non-bonding electrons. We find that the spin-coupled wavefunction for the triplet state has the correct B_1 symmetry.

For the singlet state, φ_1 and φ_3 are now sp^3-like orbitals, which overlap most strongly (see Table 1) with the essentially H(1s) functions to which they point. The two remaining sp^3-like hybrids (φ_5 and φ_6) each accommodate one of the non-bonding electrons. As we would expect, the dominant mode of spin coupling ($|c_{0,5}|^2 = 98.8\%$) corresponds to two C–H bonds, with the spins of the two non-bonding electrons coupled to a singlet. We find that the spin-coupled wavefunction for this state has the correct A_1 symmetry. There are marked similarities to the spin-coupled description of methane.[4]

The energy lowering from the RHF to the spin-coupled description is much larger for the $^1A_1$ state than for the $^3B_1$ state (see Table 2). In spite of the constraint of 'strong orthogonality' on the orbitals, perfect-pairing GVB calculations[14] give rise to a description of $CH_2(^1A_1)$ which is fairly similar to that offered by the spin-coupled wavefunction. This is presumably because there is good spatial separation in this case between the different GVB orbital pairs.

The spin-coupled and RHF descriptions of the non-bonding electrons in the $^1A_1$ state of methylene are very different: in the RHF wavefunction, both of the non-bonding electrons occupy an sp^2-like hybrid in the plane of the molecule. However, it is now well-known that at least two configurations are necessary for a realistic molecular orbital theory description of this state. It is therefore not surprising that several misleading predictions arise from Woodward–Hoffmann type arguments, based only on the RHF orbitals: the form of the spin-coupled orbitals for the non-bonding electrons in $CH_2(^1A_1)$ has dramatic consequences for understanding the reactivity of this species.[12,13] The spin-coupled and RHF descriptions of the non-bonding electrons in $CH_2(^3B_1)$ are rather more similar.

Calculations were also carried out for the $^3B_1$ state at the equilibrium geometry of the $^1A_1$ state, and for the $^1A_1$ state at the equilibrium geometry of the $^3B_1$ state. The changes in hybridization that accompany reducing the angle in the triplet state or increasing the angle in the singlet state appear to have very little effect on the overlap between an sp^x-like hybrid on carbon and a distorted 1s function on hydrogen.

CH_2^+.—Early *ab initio* calculations on the CH_2^+ ion by Bender and Schaefer[15] predicted a bent $^2A_1$ ground state with θ

Table 1. Overlap integrals between the spin-coupled orbitals for the valence electrons of CH_2, CH_2^+, SiH_2, and SiH_2^+ (TZVP basis sets).

$CH_2(^3B_1)$		φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
	φ_1	1	0.80	0.49	0.17	0.42	0.00
	φ_2		1	0.17	−0.08	0.21	0.00
	φ_3			1	0.80	0.42	0.00
	φ_4				1	0.21	0.00
	φ_5					1	0.00
	φ_6						1
$CH_2(^1A_1)$		φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
	φ_1	1	0.80	0.32	0.12	0.19	0.19
	φ_2		1	0.12	−0.06	0.13	0.13
	φ_3			1	0.80	0.19	0.19
	φ_4				1	0.13	0.13
	φ_5					1	0.68
	φ_6						1
$CH_2^+(^2A_1)$		φ_1	φ_2	φ_3	φ_4	φ_5	
	φ_1	1	0.79	0.55	0.23	0.40	
	φ_2		1	0.22	−0.08	0.21	
	φ_3			1	0.79	0.40	
	φ_4				1	0.21	
	φ_5					1	
$CH_2^+(^2B_1)$		φ_1	φ_2	φ_3	φ_4	φ_5	
	φ_1	1	0.81	0.40	0.10	0.00	
	φ_2		1	0.10	−0.11	0.00	
	φ_3			1	0.81	0.00	
	φ_4				1	0.00	
	φ_5					1	
$SiH_2(^1A_1)$		φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
	φ_1	1	0.82	0.24	0.17	0.27	0.27
	φ_2		1	0.17	0.11	0.18	0.18
	φ_3			1	0.82	0.27	0.27
	φ_4				1	0.18	0.18
	φ_5					1	0.70
	φ_6						1
$SiH_2(^3B_1)$		φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
	φ_1	1	0.80	0.43	0.20	0.52	0.00
	φ_2		1	0.20	0.09	0.23	0.00
	φ_3			1	0.80	0.52	0.00
	φ_4				1	0.23	0.00
	φ_5					1	0.00
	φ_6						1
$SiH_2^+(^2A_1)$		φ_1	φ_2	φ_3	φ_4	φ_5	
	φ_1	1	0.80	0.46	0.23	0.53	
	φ_2		1	0.23	0.11	0.24	
	φ_3			1	0.80	0.53	
	φ_4				1	0.24	
	φ_5					1	
$SiH_2^+(^2B_1)$		φ_1	φ_2	φ_3	φ_4	φ_5	
	φ_1	1	0.77	0.35	0.05	0.00	
	φ_2		1	0.05	−0.02	0.00	
	φ_3			1	0.77	0.00	
	φ_4				1	0.00	
	φ_5					1	

Table 2. RHF and spin-coupled energies for CH_2, CH_2^+, SiH_2 and SiH_2^+ (TZVP basis sets). The geometries used are listed in the text.

		Energy/hartree	
	State	RHF	Spin-coupled
CH_2	$^3B_1$	−38.93 176	−38.96 689
	$^1A_1$	−38.88 969	−38.94 501
CH_2^+	$^2A_1$	−38.57 605	−38.61 013
	$^2B_1(^2\Pi)$	−38.56 868	−38.60 464
SiH_2	$^1A_1$	−290.02 127	−290.06 829
	$^3B_1$	−290.01 387	−290.04 279
SiH_2^+	$^2A_1$	−289.73 132	−289.76 128
	$^2B_1(^2\Pi)$	−289.68 565	−289.72 302

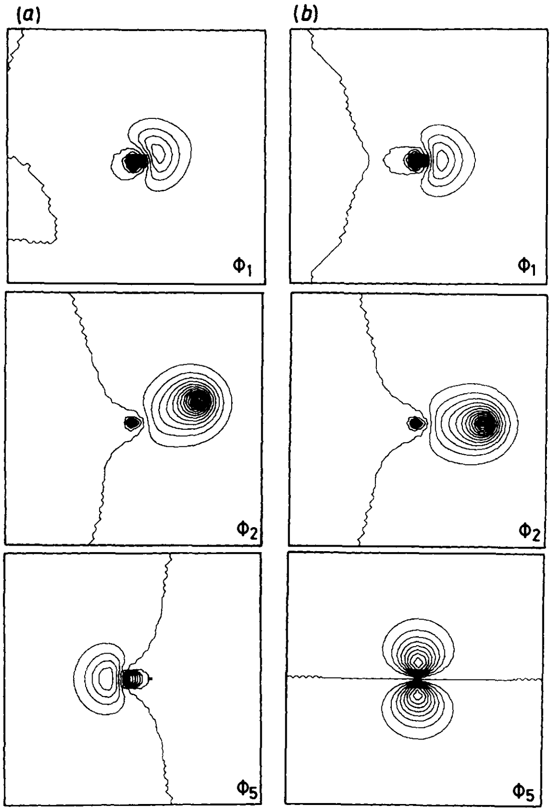

Figure 2. Spin-coupled orbitals φ_1, φ_2, and φ_5 in CH_2^+: (*a*) the $^2A_1$ state, (*b*) the $^2\Pi$ state ($^2B_1$ in C_{2v} symmetry). The contour plots are analogous to those in Figure 1.

ca. 140°, and a low-lying linear $^2\Pi(^2B_1)$ excited state. The geometry of the ground state is consistent with a re-interpretation of the experimental work of Herzberg[16] in terms of the subsequently determined bent geometry of CH_2. Motivated by interest in the $C^+ + H_2$ ion–molecule reaction, potential energy surfaces have now been calculated for low-lying states of CH_2^+ using a variety of *ab initio* techniques.[17–20] The total reaction cross section for $C^+(^2P) + H_2 \longrightarrow CH^+ + H$ has been measured by a number of groups.[21] The previous spin-coupled calculations[20] used rather more modest basis sets than in the current work, and implemented the core–valence separation in a different way.

We first carried out RHF calculations for the $^2A_1$ and $^2B_1$ ($^2\Pi$) states of CH_2^+ using geometries $r_{CH} = 1.12$ Å, $\theta = 141°$ and $r_{CH} = 1.10$ Å, $\theta = 180°$, respectively. Symmetry-equivalencing was necessary for the excited state in order to describe correctly the Π symmetry. Spin-coupled calculations were then performed for the valence electrons, including all five spin functions for $N = 5$ and $S = \frac{1}{2}$. The calculated energies are reported in Table 2.

The unique spin-coupled orbitals (φ_1, φ_2, and φ_5) are shown in Figure 2(*a*) for the non-linear ground state. Orbital φ_1 is a distorted sp^2-like hybrid on C and has an overlap of 0.79 (see Table 1) with orbital φ_2, which is essentially a distorted H(1s) function. The dominant mode of spin-coupling ($|c_{\frac{1}{2},5}|^2 = 97.8\%$) corresponds to singlet coupling of these two electrons, so that φ_1 and φ_2 describe a C–H bond. Orbitals φ_3 and φ_4 are the counterparts in the other C–H bond, and may be trans-

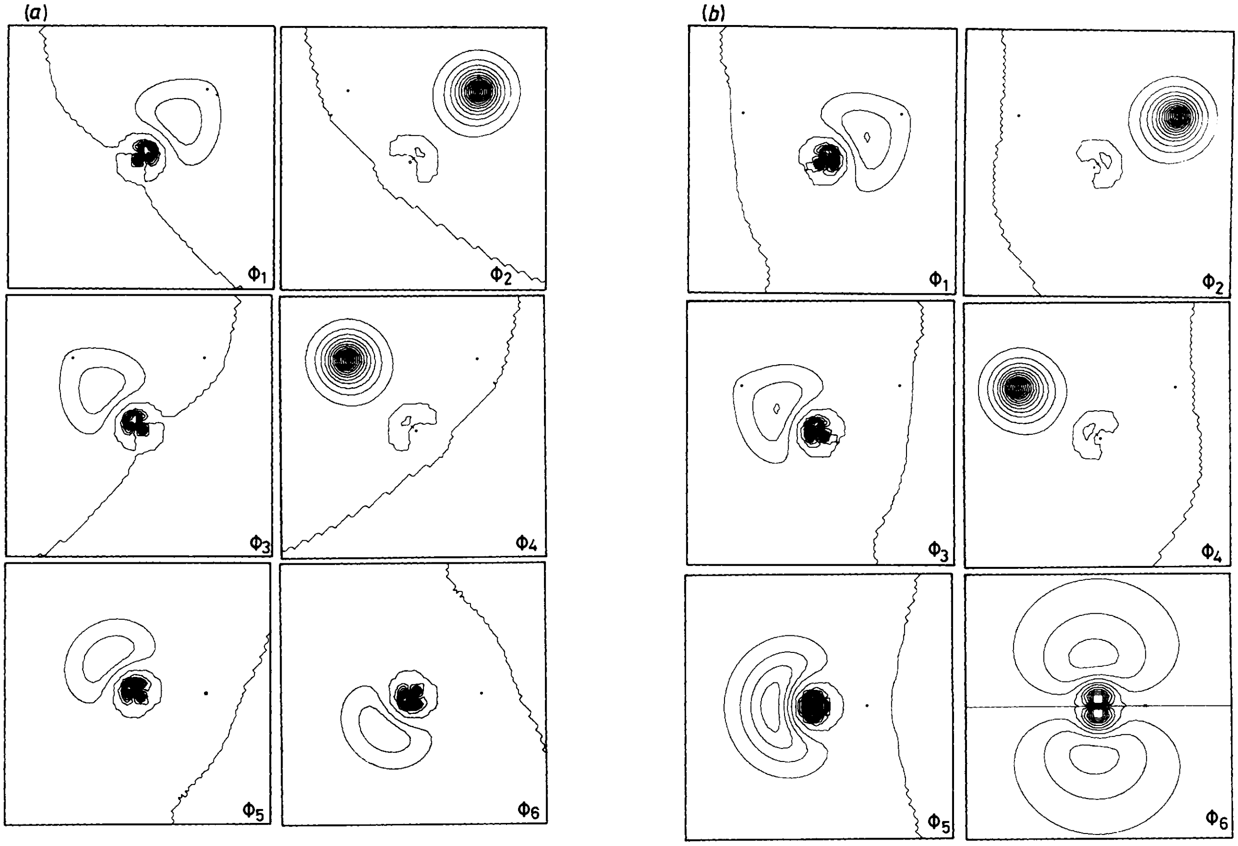

Figure 3. Spin-coupled orbitals in SiH_2: (*a*) the $^1A_1$ state, (*b*) the $^3B_1$ state. The contour plots are analogous to those in Figure 1. In the case of the 3p-type orbital for the $^3B_1$ state, we plot $\varphi_\mu(r)$ instead of $|\varphi_\mu(r)|^2$, so as to emphasize more clearly the nodal structure.

formed into φ_1 and φ_2 by operations of the C_{2v} point group. Orbital φ_5 is the third sp^2-like hybrid, coplanar with the others but pointing away from the H atoms, and it describes the non-bonding electron. We find that the overall spin-coupled wavefunction has $^2A_1$ symmetry.

The unique spin-coupled orbitals (φ_1, φ_2, and φ_5) for the linear excited state are shown in Figure 2(*b*). Orbitals φ_2 and φ_4 are distorted 1s functions on the hydrogen atoms, as before, but φ_1 and φ_3 are now essentially sp-like hybrids on carbon. The overlap between φ_1 and φ_2 is 0.81 (see Table 1), and the dominant mode of spin-coupling has $|c_{\frac{1}{2},5}|^2 = 95.2\%$, so that there are two C–H bonds. In this case, the non-bonding electron occupies a C(2p) orbital pointing perpendicular to the molecular axis, and the overall wavefunction has the expected $^2B_1$ (or $^2\Pi$) symmetry.

SiH_2.—Silylene, SiH_2, which has been the subject of much theoretical interest because of its relationship to methylene, differs in the ordering of the singlet and triplet states. Although the $^1A_1$ ground state was fairly well characterized experimentally more than twenty years ago,[22] it was only fairly recently that the $^3B_1$–$^1A_1$ splitting was accurately determined[23] (21 ± 0.7 kcal mol^{-1}). The most reliable theoretical estimate of this splitting, 20.4 kcal mol^{-1}, comes from the work of Bauschlicher *et al.*[10] who used second-order CI wavefunctions with extremely large basis sets.

For each spin multiplicity, spin-coupled calculations were carried out for the six valence electrons, with the ten 'core' electrons accommodated in doubly occupied molecular orbitals obtained from single configuration RHF calculations on each state. The geometries employed were $r_{SiH} = 1.516$ Å and $\theta = 92.3°$ for the $^1A_1$ ground state,[22] and $r_{SiH} = 1.524$ Å and $\theta = 118.0°$ for the $^3B_1$ excited state.[24]

The spin-coupled orbitals φ_1–φ_6 for the triplet state of SiH_2 are shown in Figure 3(*a*) and resemble closely those for $CH_2(^3B_1)$. The dominant mode of spin-coupling, with $|c_{1,9}|^2 = 98.1\%$, corresponds to two Si–H bonds and to triplet coupling of the spins of the two non-bonding electrons. The spin-coupled orbitals for the singlet state of SiH_2 [see Figure 3(*b*)] also resemble closely those for the analogous state in CH_2. As we would expect, the dominant mode of spin-coupling is the perfect-pairing function, with $|c_{0,5}|^2 = 99.5\%$, corresponding to two Si–H bonds and to singlet coupling of the spins of the non-bonding electrons.

For both states of SiH_2, the only significant difference in the form of the silicon hybrids from those in CH_2 arise from their 3s/3p parentage, as opposed to 2s/2p: the orbitals are larger and show additional nodal structure. In addition, the distortion of the H(1s) orbitals appears to be slightly larger for CH_2 than for SiH_2, consistent with the change in electronegativity from carbon to silicon. Nevertheless, the overlap integrals between the silicon sp^x hybrids and the hydrogen orbitals (see Table 1) are much the same as for methylene. Calculations were also carried out for the $^1A_1$ ground state of SiH_2 with the bond angle increased to the corresponding value in CH_2 (102.4°). The overlaps between the sp^x-like hybrids and the hydrogen orbitals to which they point were essentially unchanged.

At the RHF level, the predicted $^3B_1$–$^1A_1$ splitting in this basis set is 4.6 kcal mol^{-1}. The electron correlation effects taken into account by the spin-coupled method lower the singlet state relative to the triplet state and increase our predicted splitting to 16.0 kcal mol^{-1}. As indicated previously, more accurate values require much larger basis sets, as well as more complete treatments of electron correlation.

It is interesting to ask how consistently the spin-coupled method treats the two different spin multiplicities. With this in

Table 3. Comparison of spin-coupled results for SiH_2 with the full CI calculations of Bauschlicher and Taylor ref. 24[a].

	$^1A_1$–$^3B_1$ splitting/ kcal mol^{-1}
RHF	5.5
Spin-coupled	17.1
Second-order CI	18.2
Full CI	18.4

[a] All the calculations use the same geometries[30] and basis set ([6s4p1d] on Si).

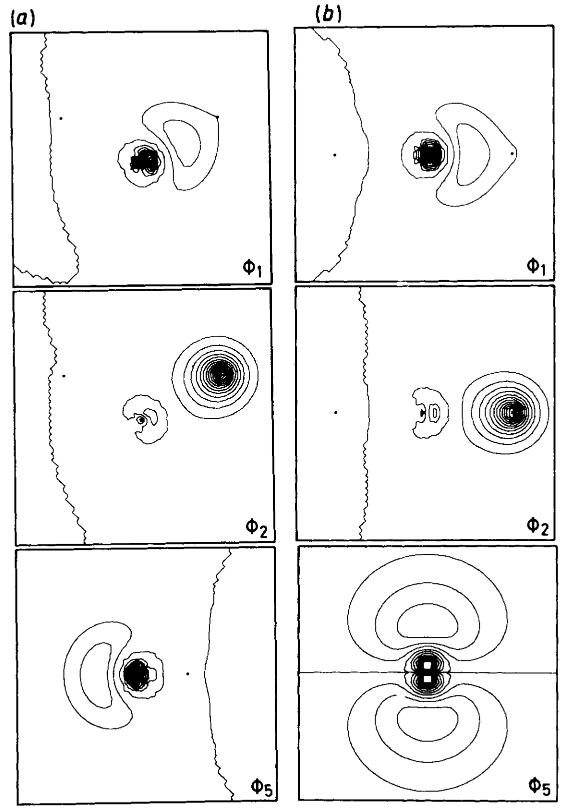

Figure 4. Spin-coupled orbitals φ_1, φ_2, and φ_5 in SiH_2^+: (*a*) the $^2A_1$ state, (*b*) the $^2\Pi$ state ($^2B_1$ in C_{2v} symmetry). The contour plots are analogous to those in Figure 1. In the case of the 3p-type orbital for the $^2B_1$ state, we plot $\varphi_\mu(r)$ instead of $|\varphi_\mu(r)|^2$, so as to emphasize more clearly the nodal structure.

mind, additional calculations were carried out using the same geometries and basis set ([6s4p1d] on Si) as employed by Bauschlicher and Taylor[24] in a full CI treatment. The results are collected in Table 3 and suggest that the spin-coupled method does indeed provide a balanced treatment of this problem. Our estimate of the splitting could be brought closer to the full CI result by including additional spin-coupled configurations in a non-orthogonal CI treatment, but experience indicates that this further step would not significantly modify our physical picture.

SiH_2^+.—The electronic spectrum of SiH_2^+ has been recorded in the range 567–659 nm by Sarre and co-workers[25] using laser photofragment spectroscopy, and has been assigned as $A^2\Pi \longleftarrow X^2A_1$. It was not possible in their work to obtain a full set of molecular parameters, because relatively few lines were resolved, but rotational constants were sufficiently well determined to suggest a bond length for the ground state of 1.49 ± 0.01 Å with an angle of 119 ± 0.5°. These values are in good agreement with the predictions of various *ab initio* calculations.[26–28] The total reaction cross section for the process $Si^+(^2P) + H_2 \longrightarrow SiH^+ + H$ has been measured by Elking and Armentrout.[29]

We first carried out an RHF calculation for the $^2A_1$ ground state of SiH_2^+ using $r_{SiH} = 1.49$ Å and $\theta = 119°$. Spin-coupled calculations were then performed for the five valence electrons, including all five spin functions for $N = 5$ and $S = \frac{1}{2}$. The energies are reported in Table 2 and the unique spin-coupled orbitals (φ_1, φ_2, and φ_5) are shown in Figure 4(*a*). The orbital picture is analogous to that in the ground state of CH_2^+. In the present case, φ_1 and φ_2 have an overlap of 0.80 (see Table 1), so that the overwhelmingly dominant mode of spin-coupling ($|c_{\frac{1}{2},5}|^2 = 100\%$) corresponds to two Si–H bonds. We find that the overall spin-coupled wavefunction has $^2A_1$ symmetry.

Analogous calculations were carried out for linear SiH_2^+, using a bond length of $r_{SiH} = 1.45$ Å, with no attempt at geometry optimization. The spin-coupled orbitals turn out to be similar to those in linear CH_2^+ [see Figure 4(*b*)]. In the present case, the overlap integral between φ_1 and φ_2 is 0.77 (see Table 1), and the dominant mode of spin-coupling ($|c_{\frac{1}{2},5}|^2 = 94.0\%$) corresponds to two Si–H bonds. The preference for a non-linear geometry appears to be more marked than was the case for CH_2^+ (see Table 2), although our predicted energy difference might be reduced slightly by optimization of the Si–H bond length. The efficient optimization of molecular geometries requires the availability of first and second derivatives of the energy with respect to nuclear displacements; work is in hand to include such derivatives in the spin-coupled method.

Conclusions

The descriptions that emerge here for the behaviour of the correlated valence electrons in various states of CH_2, CH_2^+, SiH_2, and SiH_2^+ are remarkably similar to the classical VB picture of sp, sp^2, and sp^3 hybridization. In each case we can identify two equivalent directed covalent bonds formed by the overlap of an sp^x-like hybrid on the heavy atom and a distorted 1s orbital on hydrogen, with singlet coupling of the associated spins. The non-bonding electrons are also accommodated in sp^x-like orbitals or in p orbitals, depending on the overall spatial symmetry of the wavefunction.

The differences between the spin-coupled orbitals for CH_2/CH_2^+ and for SiH_2/SiH_2^+ appear to be related very simply to the parentage of the sp^x-like orbitals (2s/2p *versus* 3s/3p) and to the change in electronegativity, which effects the degree of distortion of the H(1s) orbital. In general, replacing C by Si in these molecules has the effect of increasing further the importance of the dominant mode of spin coupling.

There are, however, some significant differences from the classical VB descriptions of these molecules. In particular, all of the orbitals show some distortion towards neighbouring centres. In addition, although each bonding sp^x-like orbital overlaps most strongly (*ca.* 0.8) with the H(1s) orbital to which it points, all of the spin-coupled orbitals overlap with one another (unless they are orthogonal by symmetry). The overlap integrals between bonding hybrids on the same centre are in the range 0.24–0.55. The overlaps between the sp^x-like hybrids and the hydrogen orbitals appear to be relatively insensitive to changes in bond angle.

A further very important difference from the classical VB description of these molecules is of course the accuracy of the spin-coupled wavefunction, which consistently yields energies significantly better than those from RHF calculations in the same basis set. In the case of the neutral molecules, the electron correlation effects taken into account by the spin-coupled wavefunction stabilize the $^1A_1$ state much more than the $^3B_1$

state, reflecting the particular inadequacies of single-configuration RHF descriptions for these singlet states. This has the effect of decreasing the predicted $^1A_1$–$^3B_1$ splitting for CH_2 but of increasing the corresponding value for SiH_2, because of the different orderings of these two states. Comparisons with full CI calculations for CH_2 and SiH_2 suggest that the spin-coupled approach provides balanced treatments of these singlet and triplet states.

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