Contribution of d Orbitals in SiH SiH_2, SiH_3, and SiH_4

Jiro HIGUCHI, Shozo KUBOTA,* Toshio KUMAMOTO,** and Ikuo TOKUE***

Department of Chemistry, Faculty of Engineering, Yokohama National University, Minami-ku, Yokohama 233

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Semi-empirical calculations have been carried out for SiH_n ($n=1$, 2, 3, and 4) adopting the electron pair bond approximation using hybrid orbitals with d orbitals of Si determined by minimizing the energy of each ground state. The results are satisfactory as a whole for explaining the experimental data of these molecules. The contribution of d orbitals obtained is not very large, but it is important in discussing the energy levels and molecular structures of some low-lying electronic states. It is also shown that the maximum overlap method is not always adequate in determining hybrid orbitals including d orbitals.

Structures of some molecules containing second-row elements differ from those expected in molecules consisting of hydrogen and/or first-row elements. Examples can be found in such molecules as PCl_5 and SF_6, in which participation of the d orbitals of these rather heavy atoms in bonding is appreciable. This is because the d orbitals give a different angular effect from that of the s and p orbitals in bonding.

In the 3d orbital of second-row atoms, the energy is not so high as compared with those of the 3s and 3p valence electrons. Although the 4s and 4p extra-valence shell orbitals are also not high in energy, their mixing with the valence shell orbitals is expected to be very small in the low-lying electronic states.[1] Thus, for a discussion of the electronic properties of a molecule with second-row atoms, inclusion of the 3d orbital should not be completely ignored, although most calculations of these molecules have not always explicitly taken into account the effect of the d-character.

In the present work, a semi-quantitative calculation including the 3d orbitals has been carried out for the electronic structure of ground state for SiH, SiH_2, SiH_3, and SiH_4 which show some different properties from those of the corresponding CH_n molecules,[2-5] together with some excited states of SiH and SiH_2. In this case, the electron pair bond approximation was adopted since the valence bond method is rather useful in discussing the contribution of d orbital in bonding as compared with the molecular orbital method.

Hybrid Orbitals with d-Character

The spatial configurations of SiH, SiH_2, SiH_3, and SiH_4 were assumed to be of symmetry $C_{\infty v}$, C_{2v}, C_{3v}, and T_d, respectively, the coordinate system of these molecules being taken as shown in Fig. 1. For the first-row elements, the orthonormalized set of hybrid orbitals directed to each bond or non-bonding electron can uniquely be constructed from 2s, 2px, 2py, and 2pz orbitals taking the spatial configuration into consideration if a few external conditions such as equivalence of some orbitals are given. However, a similar set of hybrid orbitals including the d orbitals cannot uniquely be determined even if the same number of external conditions is given, and some additional parameters are necessary.

For SiH, SiH_2, SiH_3, and SiH_4 these hybrid orbitals can be expressed as follows:

SiH:

$$\left.\begin{aligned}\chi_l &= a_0\chi_s - b_0\chi_{p\sigma} + c_0\chi_{d\sigma}\\ \chi_b &= a_1\chi_s + b_1\chi_{p\sigma} + c_1\chi_{d\sigma}\\ \chi_\pi &= \quad b_\pi\chi_{p\pi} + c_\pi\chi_{d\pi}\end{aligned}\right\} \tag{1}$$

SiH_2:

$$\left.\begin{aligned}\chi_l &= a_0\chi_s + b_0\chi_{pz} + c_0\chi_{dz^2}\\ \left.\begin{matrix}\chi_{b1}\\ \chi_{b2}\end{matrix}\right\} &= a_1\chi_s + b_1\left[\pm\left(\sin\frac{\theta}{2}\right)\chi_{py} - \left(\cos\frac{\theta}{2}\right)\chi_{pz}\right]\\ &\quad + c_1\left[\frac{1}{2}\left(3\cos^2\frac{\theta}{2}-1\right)\chi_{dz^2} - \frac{1}{2}\left(3^{1/2}\sin^2\frac{\theta}{2}\right)\chi_{dx^2-y^2}\right.\\ &\quad \left.\mp\left(3^{1/2}\sin\frac{\theta}{2}\cos\frac{\theta}{2}\right)\chi_{dyz}\right]\end{aligned}\right\} \tag{2}$$

SiH_3:

$$\left.\begin{aligned}\chi_n &= a_0\chi_s + b_0\chi_{pz} + c_0\chi_{dz^2}\\ \chi_{b1} &= a_1\chi_s + b_1[(\sin\beta)\chi_{px} - (\cos\beta)\chi_{pz}]\\ &\quad + c_1\left[\frac{1}{2}(3\cos^2\beta-1)\chi_{dz^2} + \frac{1}{2}(3^{1/2}\sin^2\beta)\chi_{dx^2-y^2}\right.\\ &\quad \left.- (3^{1/2}\sin\beta\cos\beta)\chi_{dxz}\right]\\ \left.\begin{matrix}\chi_{b2}\\ \chi_{b3}\end{matrix}\right\} &= a_1\chi_s + b_1\left[-\frac{1}{2}(\sin\beta)\chi_{px} \pm \frac{1}{2}(3^{1/2}\sin\beta)\chi_{py}\right.\\ &\quad \left.- (\cos\beta)\chi_{pz}\right] + c_1\left[\frac{1}{2}(3\cos^2\beta-1)\chi_{dz^2}\right.\\ &\quad - \frac{1}{4}(3^{1/2}\sin^2\beta)\chi_{dx^2-y^2} \mp (\sin^2\beta)\chi_{dxy}\\ &\quad \left.+ \frac{1}{2}(3^{1/2}\sin\beta\cos\beta)\chi_{dxz} \mp \frac{3}{2}(\sin\beta\cos\beta)\chi_{dyz}\right]\end{aligned}\right\} \tag{3}$$

SiH_4:

$$\left.\begin{aligned}\chi_{b1} &= (1/2)\chi_s + [(3/4)-c^2]^{1/2}\chi_{pz} + c\chi_{dz^2}\\ \chi_{b2} &= (1/2)\chi_s + [(3/4)-c^2]^{1/2}[(8^{1/2}/3)\chi_{px} - (1/3)\chi_{pz}]\\ &\quad + c[-(1/3)\chi_{dz^2} + (4/27^{1/2})\chi_{dx^2-y^2} - (8/27)^{1/2}\chi_{dxz}]\\ \left.\begin{matrix}\chi_{b3}\\ \chi_{b4}\end{matrix}\right\} &= (1/2)\chi_s + [(3/4)-c^2]^{1/2}[-(2^{1/2}/3)\chi_{px}\\ &\quad \pm (2/3)^{1/2}\chi_{py} - (1/3)\chi_{pz}] + c[-(1/3)\chi_{dz^2}\\ &\quad - (2/27^{1/2})\chi_{dx^2-y^2} \mp (2/3)\chi_{dxy} + (2/27)^{1/2}\chi_{dxz}\\ &\quad \pm (2^{1/2}/3)\chi_{dyz}]\end{aligned}\right\} \tag{4}$$

* Present address: Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai.

** Present address: Fujitsu System Laboratory of Information Processing, Fujitsu Limited, Ota-ku, Tokyo.

*** Present address: Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo.

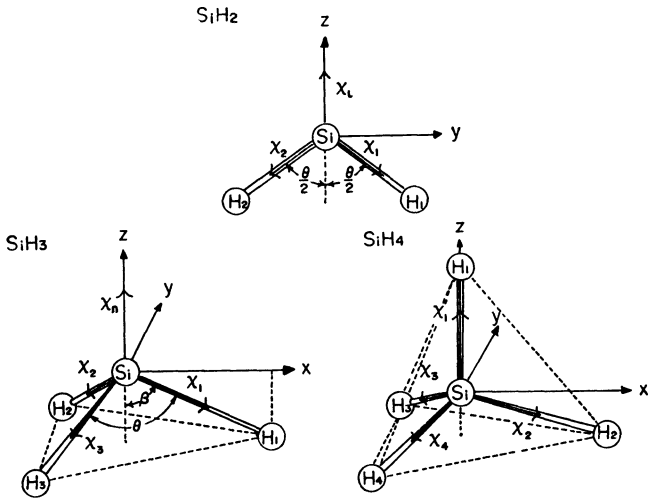

Fig. 1. Coordinate system and hybrid orbitals χ_i's in SiH_n (n=2, 3, and 4).

where l, n, and b denote lone pair, non-bonding and bonding, respectively.

Atomic Orbitals

In the calculation of molecular integrals, the atomic orbitals of Si used are the SCF–AO's (solutions of Hartree-Fock equation in the ^3P state) obtained by Watson and Freeman.[6] Since no 3d orbital is given in their paper, the following orbital was tentatively used:

$$\chi_{3d}^{Si} = 0.1571\chi_{3d}^{STO}(0.25) + 0.7607\chi_{3d}^{STO}(0.50) + 0.1651\chi_{3d}^{STO}(1.00) + 0.0561\chi_{3d}^{STO}(2.00) \quad (5)$$

where $\chi_{3d}^{STO}(\delta)$ is a Slater-type 3d AO with orbital exponent δ. The coefficients of these AO's are chosen so as to give a minimum energy of the ^1D state with electron configuration $3s^23p3d$ by using the above SCF–AO's. The orbital of hydrogen used (χ_H) is the Slater-type 1s AO with orbital exponent 1.00. All the internuclear distances between the silicon and hydrogen are taken to be 1.477 Å, which is the equilibrium distance of SiH_4 molecule.[7]

Method of Calculation

Since the molecular integrals used in semi-empirical valence bond calculations have not always been described with a unified formula, it will be necessary to clarify the definitions used. The procedure is briefly outlined in the following paragraphs. The Hamiltonian of SiH_n (n=1, 2, 3, 4) $\mathcal{H}$ can be expressed in atomic unit as

$$\mathcal{H} = \mathcal{H}_{Si} + \sum_{r=1}^{n}\mathcal{H}_{H(r)} + \sum_{p=1}^{14}\sum_{r=1}^{n}\mathcal{H}_{Si(p)-H(r)} + \sum_{r=s+1}^{n}\sum_{s=1}^{n-1}\mathcal{H}_{H(r)-H(s)} \quad (6)$$

where $\mathcal{H}_{Si}$ and $\mathcal{H}_{H(r)}$ are the atomic term of the Si which includes the 1st to the 14th electrons and that of the r-th hydrogen which includes the $(r+14)$-th electron, respectively, *i.e.*,

$$\mathcal{H}_{Si} = -\frac{1}{2}\sum_{p=1}^{14}\Delta_p - \sum_{p=1}^{14}\frac{14}{r_{Si-p}} + \sum_{p=q+1}^{14}\sum_{q=1}^{13}\frac{1}{r_{p-q}} \quad (p, q = 1\sim14) \quad (7)$$

and

$$\mathcal{H}_{H(r)} = -\frac{1}{2}\Delta_{(r+14)} - \frac{1}{r_{H(r)-(r+14)}} \quad (r = 1\sim n). \quad (8)$$

The $\mathcal{H}_{Si(p)-H(r)}$ and $\mathcal{H}_{H(r)-H(s)}$ are the interatomic interaction terms, *i.e.*,

$$\mathcal{H}_{Si(p)-H(r)} = \frac{1}{R_{Si-H(r)}} + \frac{1}{r_{p-(r+14)}} - \frac{1}{r_{Si-(r+14)}} - \frac{1}{r_{H(r)-p}} \quad (9)$$

and

$$\mathcal{H}_{H(r)-H(s)} = \frac{1}{R_{H(r)-H(s)}} + \frac{1}{r_{(r+14)-(s+14)}} - \frac{1}{r_{H(r)-(s+14)}} - \frac{1}{r_{H(s)-(r+14)}} \quad (10)$$

The treatment is based on the electron pair bond approximation without ionic structure using the hybrid orbitals (1)—(4). Using the Hamiltonian $\mathcal{H}$ (6), the total energy of SiH_n can approximately be expressed as

$$E_{SiH_n} = E_{Si} + \sum_{r=1}^{n}E_{H(r)} + \sum_{r=1}^{n}\sum_{p=1}^{14}(Q_{pr} + c_{p,(r+14)}R_{pr}) + (1-\delta_{1,n})\sum_{r=s+1}^{n}\sum_{s=1}^{n-1}\left(Q'_{rs} - \frac{1}{2}R'_{rs}\right)$$

$$c_{i,j} = \begin{cases} +1 & (i,j\text{: paired orbitals}) \\ -1/2 & (i,j\text{: non-paired orbitals}), \end{cases} \quad (11)$$

where E_{Si} is the energy concerning the Si atom only, $E_{H(r)}$ is the energy of the r-th atom, Q_{ij}'s and R_{ij}'s are the interatomic Coulomb and exchange integrals, respectively,[8] *i.e.*,

$$Q_{pr} = \iint\chi^*_{Si(p)}(p)\chi^*_{H(r)}(r+14)\mathcal{H}_{Si(p)-H(r)} \times\chi_{Si(p)}(p)\chi_{H(r)}(r+14)d\tau_p d\tau_{r+14} \quad (12)$$

$$R_{pr} \simeq \iint\chi^*_{Si(p)}(p)\chi^*_{H(r)}(r+14)\mathcal{H}_{Si(p)-H(r)} \times\chi_{H(r)}(p)\chi_{Si(p)}(r+14)d\tau_p d\tau_{r+14} \quad (13)$$

$$Q'_{rs} = \iint\chi^*_{H(r)}(r+14)\chi^*_{H(s)}(s+14)\mathcal{H}_{H(r)-H(s)} \times\chi_{H(r)}(r+14)\chi_{H(s)}(s+14)d\tau_{r+14}d\tau_{s+14} \quad (14)$$

$$R'_{rs} \simeq \iint\chi^*_{H(r)}(r+14)\chi^*_{H(s)}(s+14)\mathcal{H}_{H(r)-H(s)} \times\chi_{H(s)}(r+14)\chi_{H(r)}(s+14)d\tau_{r+14}d\tau_{s+14}. \quad (15)$$

In Eq. (11), orthogonality among all the orbitals is assumed, except in the evaluation of R_{ij}'s with Eqs. (13) and (15). All the interactions with the inner shells of the Si atom are also included in the same way. The coefficients of the AO's in the hybrid orbitals (1)—(4) are determined so as to minimize the total energy of the corresponding ground state.

In the case of SiH, the treatment is similar to the restricted SCF-LCAO-MO method.[9] For the ground state:

$$^2\Pi: (\chi_l)^2[(\chi_b)(\chi_H)](\chi_\pi),^{10} \quad (16)$$

the coefficients of the AO's are determined by solving the following simultaneous equations:

$$\left.\begin{aligned}
&\left[H+Q-\frac{1}{2}R+2J_1-K_1+J_b-\frac{1}{2}K_b+J_{\pi+}-\frac{1}{2}K_{\pi+}\right]\chi_1 \\
&\quad=\varepsilon_{11}\chi_1+\frac{1}{2}\varepsilon_{1b}\chi_b \\
&\left[H+Q+R+2J_1-K_1+J_{\pi+}-\frac{1}{2}K_{\pi+}\right]\chi_b=\varepsilon_{1b}\chi_1+\varepsilon_{bb}\chi_b \\
&\left[H+Q-\frac{1}{2}R+2J_1-K_1+J_b-\frac{1}{2}K_b\right]\chi_{\pi+}=\varepsilon_{\pi\pi}\chi_{\pi+}
\end{aligned}\right\} \quad (17)$$

where

$$H=-\frac{1}{2}\Delta-\frac{14}{r_{Si}}+2J_{1s}-K_{1s}+2J_{2s}-K_{2s}+2J_{2p\sigma}-K_{2p\sigma}+2J_{2p\pi+}-K_{2p\pi+}+2J_{2p\pi-}-K_{2p\pi-} \quad (18)$$

$$J_k\chi_p(p)=\left[\int\chi_k^*(q)(1/r_{p-q})\chi_k(q)d\tau_q\right]\chi_p(p) \quad (19)$$

$$K_k\chi_p(p)=\left[\int\chi_k^*(q)(1/r_{p-q})\chi_p(q)d\tau_q\right]\chi_k(q) \quad (20)$$

$$Q\chi_p(p)=\left[\int\chi_H^*(15)\mathscr{H}_{Si(p)-H(1)}\chi_H(15)d\tau_{15}\right]\chi_p(p) \quad (21)$$

$$R\chi_p(p)=\left[\int\chi_H^*(15)\mathscr{H}_{Si(p)-H(1)}\chi_p(15)d\tau_{15}\right]\chi_H(p). \quad (22)$$

All the calculations were carried out using the two sets of hybrid orbitals with and without d orbitals of Si atom. The most stable structure of the ground state of SiH_2,

$$^1A_1:\ (\chi_1)^2[(\chi_{b1})(\chi_{H(1)})][(\chi_{b2})(\chi_{H(2)})], \quad (23)$$

and that of SiH_3,

$$^2A_1:\ [(\chi_{b1})(\chi_{H(1)})][(\chi_{b2})(\chi_{H(2)})][(\chi_{b3})(\chi_{H(3)})](\chi_n), \quad (24)$$

were determined by changing the bond angle $\angle$HSiH only. For SiH and SiH_2, the excitation energies to the lower electronic states,

$$\left.\begin{aligned}
&^4\Sigma^-,\ ^2\Delta,\ ^2\Sigma^-,\ ^2\Sigma^+:\ [(\chi_b)(\chi_H)](\chi_\pi)^2(\chi_1) \quad (25)\\
&^2\Delta:\ (\chi_1)^2[(\chi_b)(\chi_H)](\chi_\delta) \quad (26)\\
&^2\Sigma^+:\ (\chi_1)^2[(\chi_b)(\chi_H)](\chi_\sigma^*) \quad (27)
\end{aligned}\right\}\ \text{for SiH}$$

and

$$\left.\begin{aligned}
&^3B_1,\ ^1B_1:\ [(\chi_{b1})(\chi_{H(1)})][(\chi_{b2})(\chi_{H(2)})](\chi_1)(\chi_n) \quad (28)\\
&^1A_1:\ [(\chi_{b1})(\chi_{H(1)})][(\chi_{b2})(\chi_{H(2)})](\chi_n)^2 \quad (29)
\end{aligned}\right\}\ \text{for } SiH_2$$

were also calculated using the hybrid orbitals of each ground state. In the vacant orbitals in the ground state, the χ_δ orbital of SiH was taken to be the 3dδ AO of Si, the χ_σ^* was the 3dσ-like orbital which is orthogonal to the χ_1 and χ_b, and the χ_n orbital of SiH_2 which is perpendicular to the molecular plane was assumed to be the 3px AO of Si.[11] In the case of the $^1A_1$ states of SiH_2, only the interaction between configurations (23) and (29) was taken into account so as to give the energies of the $^1\Delta_g$ and the $^1\Sigma_g^+$ states in the linear structure. The other states of SiH_n were calculated in the approximation of single configuration.

Results and Discussion

In the SiH radical, the $D^2\Delta$ and $E^2\Sigma^+$ states are not so high as compared with the lowest $^2\Delta$ and $^2\Sigma^+$ states, while those of the CH are expected to be high-energy excited states. However, no theoretical work has been done for these higher states. Therefore, the excitation energies have been calculated for the low-lying states with configurations (25)—(27). Using the hybrid orbitals determined for the ground state, the lower excited states with configuration (25) obtained are considerably high as compared with the experimental results [$\Delta E_{calc.}(^2\Delta)=5.81$ eV and $\Delta E_{calc.}(^2\Sigma^+)=6.90$ eV, while $\Delta E_{obs.}(^2\Delta)=3.01$ eV and $\Delta E_{obs.}(^2\Sigma^+)=3.84$ eV[12,13]]. This might be due to the fact that the distribution of σ electrons differs a great deal from that of the ground state where the hybridization ratios used in Eq. (1) were determined.[14] On the other hand, the calculated excitation energy of the higher $^2\Delta$ state with configuration (26) is 6.67 eV, in fair agreement with the observed value of the $D^2\Delta$ state [6.02 eV[12,13]]. The agreement might suggest the fact that the distribution of σ electrons in this $^2\Delta$ state does not differ much from that of the ground $^2\Pi$ state. Similarly, the observed higher $^2\Sigma^+$ state ($E^2\Sigma^+$) can be explained to be due to the excitation of one π electron from the ground state $^2\Pi$ into the 3d-like σ orbital (χ_σ^*). The results indicate that the contribution of d orbitals is important in discussing some observed lower electronic states of molecules with second-row atoms.

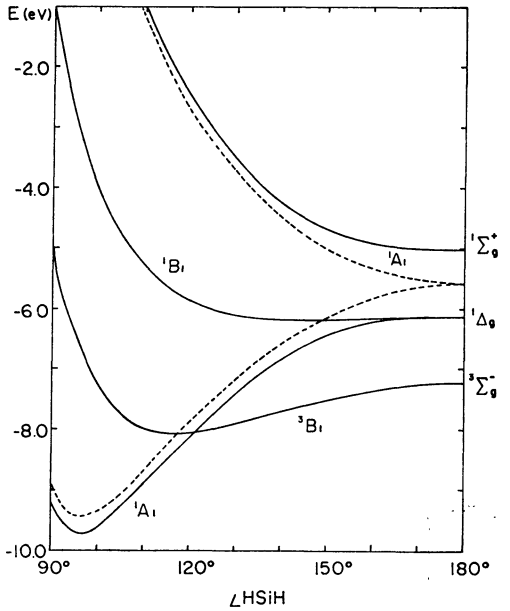

Fig. 2. Lower electronic states of SiH_2 calculated by including d orbitals. The dotted lines indicate the energies of the $^1A_1$ states without interaction between the lowest two configurations. The origin of energy is chosen to be $Si(^3P)+2H(^2S)$.

For the four low-lying states of SiH_2, the potential energy curves were calculated by including the d orbitals of Si as shown in Fig. 2. The dotted lines correspond to the energies without interaction between the lowest two $^1A_1$ configurations. The calculated equilibrium bond angle $\angle$HSiH in the ground state $^1A_1$ [96°] is in fair agreement with the observed result [92° [2]], while the value of the $^1B_1$ state [145°] is fairly larger than the expeimental [123° [2]]. The calculated energy difference between these states is 3.54 eV while the observed value is 1.93 eV. The disagreement is mainly due to the facts that the electron configuration is apparently different between these states and that

the hybrid orbitals used are determined for the energy of the $^1A_1$ state with configuration (23).

In the case without d orbitals, the bond angle ∠HSiH in each state is generally close to the result with d orbitals and that of the *ab initio* calculation (without d orbitals) by Wirsam.[15] For only the $^1B_1$ state, the bond angle obtained here is fairly large [about 30°] as compared with that of Wirsam, although the energy changes less than 0.5 eV in this vicinity. The difference between the results with and without the d orbitals is not very significant.

In both calculations, the ground state of SiH_2 is obtained as $^1A_1$, in contrast with $^3B_1$ of CH_2. The difference is not essentially due to the effect of the d orbitals, and can be explained by the following electronic properties: If the overalp integral between the valence v orbital (v means s, pσ, *etc.*) and the hydrogen 1s orbital is expressed by S_{vh}, the ratio of $S_{sh}/S_{p\sigma h}$ for SiH_n is fairly smaller than that of CH_n. Accordingly, the stabilization of the Si–H bond due to the inclusion of the s orbital is rather small as compared with that of the C–H bond. The separation between the lowest $^1A_1$ (or $^1B_1$) and $^3B_1$ states of SiH_2 is about three quarters of that of CH_2 near the linear structure.[16] Thus, the $^1A_1$ state of SiH_2 with nearly-rectangular bond angle is located lower than the $^3B_1$ state, in contrast with the case of CH_2.

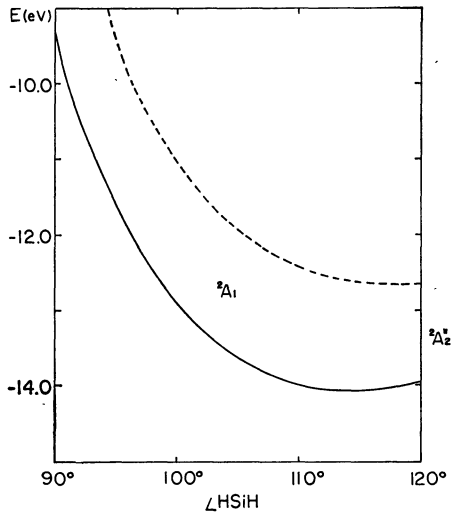

Fig. 3. Electronic energy of $^2A_1$ state of SiH_3 calculated by including d orbitals (full line) and that by disregarding d orbitals (dotted line). The origin of energy is chosen to be $Si(^3P)+3H(^2S)$.

The potential energy curve of the ground state of SiH_3 has been calculated as shown in Fig. 3. The most stable structure obtained is pyramidal (∠HSiH= 114°) by including the contribution of the d orbitals of Si, in consistent with the experimental result,[4] while it is nearly planar (∠HSiH=119°) by disregarding the d-character. The calculated bond angle is in close agreement with the value deduced by Sharp and Symons (113~114°).[17] This might show the facts that the pyramidal structure of SiH_3 is due to an appreciable contribution of the d orbital in the angular effect and that the inclusion of the d orbital is essentially necessary in the calculation of molecules with Si atom.

On the other hand, an *ab initio* calculation by Wirsam[18] and an INDO calculation by Benson and Hudson[19] gave the pyramidal structure for the equilibrium geometry in spite of disregard of the d orbitals. Thus, one may conclude that there are two reasons for the pyramidal structure of SiH_3, in contrast with the nearly-planar structure of CH_3; it is due to the angular contribution of the d orbital of Si and that the stabilization of the Si–H bond due to the inclusion of the s orbital is rather small as compared with the case of the C–H bond.

In general, the energy lowering due to the inclusion of the d orbitals is not very large. The results for the ground states with equilibrium configuration are summarized in Tables 1 and 2. The stabilization energy per Si–H bond differs for the SiH_n molecules each other, this being mainly due to the fact that the contribution of the valence states of the Si atom concerned with each molecule is not quite the same. Actually, the energy lowering increases with decreasing the bond angle ∠HSiH. On the other hand, the contribution

Table 1. Calculated electronic energies in the equilibrium structure of SiH_n relative to the energy of $Si(^3P)+nH(^2S)$.

Hybridization		SiH	SiH_2	SiH_3	SiH_4
s-p-d	E(eV)	−4.64	−9.44	−14.05	−20.20
	∠HSiH	—	96°	114°	(109°28′)[a]
s-p	E(eV)	−3.92	−8.15	−12.66	−18.18
	∠HSiH	—	97°	119°	(109°28′)[a]
	ΔE (eV)	0.73	1.30	1.39	2.03

a) The assumed value.

Table 2. The s-, p-, and d-characters (in per cents) in the equilibrium structures of SiH_n.

		SiH		SiH_2		SiH_3		SiH_4	
	Hybridization	s-p-d	s-p	s-p-d	s-p	s-p-d	s-p	s-p-d	s-p
χ_{bl}	s-character	11.50	9.22	11.21	10.86	28.54	32.65	25.00	25.00
	p-character	83.01	90.78	83.70	89.14	68.03	67.35	71.13	75.00
	d-character	5.49	0.00	5.09	0.00	3.43	0.00	3.87	0.00
χ_l or χ_n	s-character	88.47	90.78	77.04	78.27	13.51	2.05	—	—
	p-character	11.09	9.22	22.81	21.73	85.91	97.95	—	—
	d-character	0.44	0.00	0.15	0.00	0.58	0.00	—	—
χ_π	p-character	99.72	100.00	—	—	—	—	—	—
	d-character	0.28	0.00	—	—	—	—	—	—

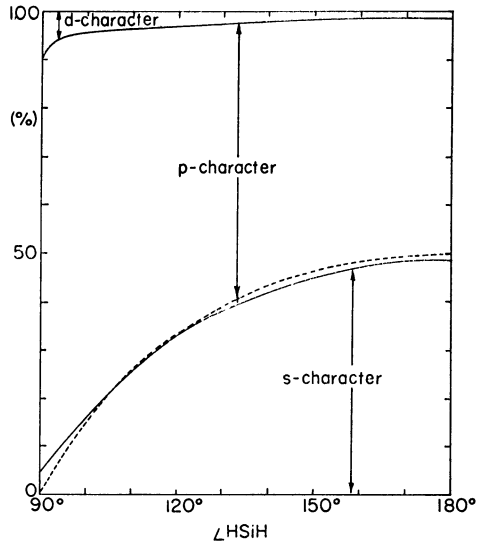

Fig. 4. The s-, p-, and d-characters in the bonding orbital χ_{bi} of SiH_2. The dotted line indicates the s-character calculated by disregarding d orbitals.

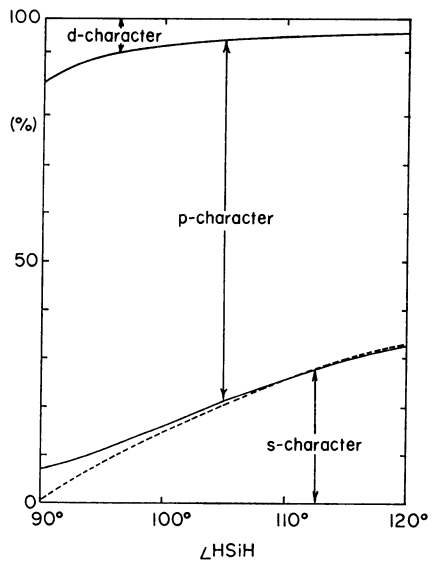

Fig. 5. The s-, p-, and d-characters in the bonding orbital χ_{bi} of SiH_3. The dotted line indicates the s-character calculated by disregarding d orbitals.

the ∠HSiH (Figs. 4 and 5). However, the energy of d-character of Si atom also increases with decreasing lowering is not exactly parallel with the d-character.

In the present calculation, the contribution of d orbital is not very great but should not be completely disregarded. The d-character in the lone pair and the non-bonding orbitals is very small as compared with that of the bonding orbitals (Table 2). This is understandable from the fact that the hybridization of the d orbitals mainly contributes to the bonding energy. For SiH_2 and SiH_3, the maximum value of d-character in the lone pair and the non-bonding orbitals (0.22 and 0.59%, respectively) appeared near bond angles of 110 and 113°, respectively, while the d-character of the bonding orbitals increases with decreasing the bond angle (Figs. 4 and 5). For SiH_4, the relation where

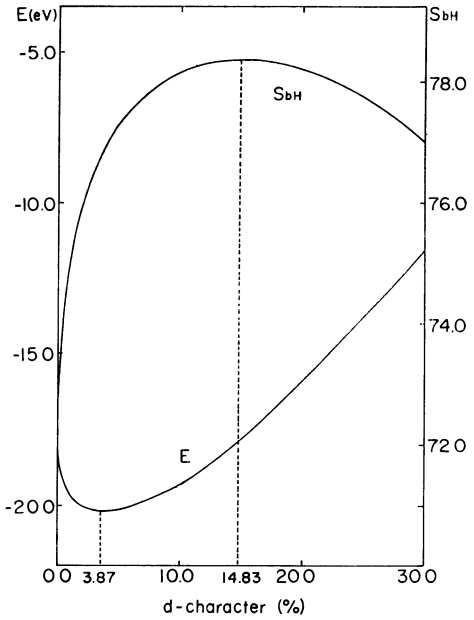

Fig. 6. Effect of d-character for the electronic energy (E) and the overlap integral between χ_{bi} and $\chi_{H(i)}$ [S_{bh}] in SiH_4. The origin of energy is chosen to be $Si(^3P)+4H(^2S)$.

the d-character is equal to the decrease in the p-character due to the inclusion of the d orbitals is exactly satisfied [*cf.* Eq. (4)]. This is also roughly valid for the other SiH_n radicals (Table 2, Figs. 4 and 5).

The maximum value of energy lowering for SiH_4 due to the inclusion of the d orbitals of Si has been obtained to be 2.03 eV at the d-character of 3.87% in the bonding orbital χ_{bi}. On the other hand, the maximum overlapping between the χ_{bi} and the $\chi_{H(i)}$ appeared at the d-character of 14.83% as shown in Fig. 6. This discrepancy may be explained as follows: the stabilization of the Si–H bond due to the exchange energy between the χ_{bi} and the $\chi_{H(i)}$ may increase with increasing the value of the corresponding overlap integral. However, the total energy increases beyond a certain value of the d-character, since the energy of d orbital is rather high as compared with the other valence orbitals of Si. This might suggest the fact that the maximum overlap method[20] is not always adequate in determining the hybrid orbitals with d orbitals.

The present work includes several approximations and assumptions. The atomic orbitals used may not be completely adequate for all the states. Actually, the determination of the 3d orbital is rather tentative but may be allowed for the present purpose. This may be recognized from the fact that the energy levels of Si atom calculated using the present AO's are generally satisfactory in a semi-quantitative sense except that the order of the $^3D(3s^23p3d)$ and $^3P(3s^23p3d)$ states is the reverse of that given in Moore's table.[21] Therefore, the experimental values are not included in the present calculation, although a better result might be obtained by using such values.

The result obtained for the ground state of SiH_n is generally satisfactory as compared with those of other calculations.[15,18,19,22,23] This is partly due to the facts

that the approximation for the exchange integrals (12) and (14) are fairly permissible, as has already been shown by the calculations of CH[9] and CH_2,[24] and that the contribution of ionic structures is not great in the ground states of the molecules. As far as the hybrid orbitals determined for the ground state are used in the approximation of single configuration, the results for the excited states are not so good as in the ground state. However, better results can be expected in a similar treatment if the hybrid orbitals are obtained so as to minimize the energy of the state in question or if the interaction with some other electronic configurations are included.

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11) Exactly speaking, the following orbital should be used:
$$\chi_n = (1-c_n^2)^{1/2}\chi_{px} + c_n\chi_{dxz}.$$
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