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Electronic Structure of Silanes in the Semi-Empirical Equivalent Orbital Method

Vertical Ionization Potentials from the Data for SiH_4, Si_2H_6 and Silicon Band Structure

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The problem of the prediction of the valence IPs for silanes is considered. It is shown that the data on the silicon band structure combined with the photoelectron spectra of SiH_4, and Si_2H_6 permit to obtain the parameter scale, which includes all the nearest neighbour, second neighbour and the main third neighbour interaction parameters. Using the derived parameter scale the vertical ionization potentials of Si_3H_8, $SiH(SiH_3)_3$, $Si(SiH_3)_4$, the infinite polysilane valence band structure and the inner a_{1g} level for disilane are calculated. All the calculated levels are located above -20 eV and are expected to be measurable by the He (I) photoelectron spectroscopy.

Key words: Silicon band structure – Silanes – Vertical ionization potentials

1. Introduction

The progress in the photoelectron spectroscopy permits to investigate the valence ionization potentials (IP) of the molecules with the high accuracy. Therefore the theoretical calculations and predictions of the valence IPs with the similar accuracy are an actual problem now. It is known that the *ab initio* calculations cannot provide the desirable accuracy of about 0.1–0.2 eV. On the other hand the semi-empirical methods frequently provide the accuracy comparable with the experimental one. Of course the main problem of the semiempirical approach is the estimation of the parameters.

For the saturated compounds under consideration this problem seems to be solved in the best way using the Hall's equivalent orbital (EO) method [1, 2] because of the well known transferability of the EOs and the corresponding matrix elements of the Hartree-Fock Hamiltonian in the EO basis [12, 13]. The EO method relates directly the energy spectrum of the (saturated) system to its chemical constitution. Moreover one can outline both the interpretative advantages of the EO method and the simplicity of its application.

That is why there are many papers dealing with the application of this method to the interpretation of the photoelectron spectra of a number of different molecules [4–13]. Different methods have been used for the obtaining of the parameter scales

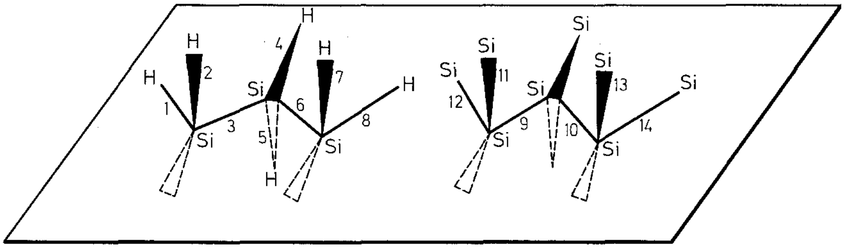

Fig. 1. Designation of interactions: $a=\langle 1|\mathscr{F}|1\rangle$, $b=\langle 1|\mathscr{F}|2\rangle$, $f=\langle 2|\mathscr{F}|5\rangle$, $g=\langle 2|\mathscr{F}|4\rangle$, $c=\langle 3|\mathscr{F}|3\rangle$, $d=\langle 1|\mathscr{F}|3\rangle$, $r=\langle 1|\mathscr{F}|6\rangle$, $s=\langle 2|\mathscr{F}|6\rangle$, $\beta_A=\langle 3|\mathscr{F}|5\rangle$, $\beta_t=\langle 9|\mathscr{F}|14\rangle$, $\beta_g=\langle 9|\mathscr{F}|13\rangle$, $\beta_w=\langle 12|\mathscr{F}|14\rangle$, $w=\langle 1|\mathscr{F}|8\rangle$, $\beta_p=\langle 11|\mathscr{F}|13\rangle$, $p=\langle 2|\mathscr{F}|7\rangle$, $\beta_m=\langle 12|\mathscr{F}|13\rangle$, $m=\langle 1|\mathscr{F}|7\rangle$

starting from the non-empirical calculation up to the statistical treatment of the spectra of the homologous series.

The purpose of the present paper is the application of the EO method to the prediction of the vertical IPs of the branched and linear silanes Si_nH_{2n+2} including polysilane. The experimental data are available for SiH_4 [19] and Si_2H_6 [17–18] but using the data for these molecules only one can not obtain a complete parameter scale. The main methodical advance of the present paper is the application of the data for crystalline silicon to the solution of the molecular problems [3]. We shall use the data for SiH_4 and Si_2H_6 too.

We had applied the analogous approach to the calculation of the photoelectron spectra of the higher linear and branched alkanes [3–5]. The application of the photoelectron data to CH_4, C_2H_6 together with the diamond valence band structure data leads to the agreement with the experiment within 0.1–0.2 eV.

The staggered geometry was accepted for all the molecules under consideration, and all the notations are taken from our previous paper [5].

2. Calculation of the Matrix Elements

2.1. Silicon

Let us calculate the Hartree-Fock Hamiltonian matrix elements in the EO basis. We shall take into account the nearest neighbour interaction element β_A(Si), all the second neighbour interactions β_g(Si) and β_t(Si) and the main[1] "through space" [21] interactions β_w(Si) and β_p(Si). Obviously in order to obtain the necessary parameters we have to use the silicon valence band characteristic levels. Moreover, it seems to be more convenient to use those levels the energy of which may be expressed in a simple analytical form in terms of the EO method parameters. These are the X_1, X_4, $L_{3'}$, $L_{2'}$, L_1 and Γ_1-levels. Here the edge of the valence band $\Gamma_{25'}$ was chosen as a zero point of the energy scale. Then, as it was shown recently [5], the corresponding energies are connected with the necessary parameters by the following equations:

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[1] These the through space interaction elements have to be more important, because the corresponding EOs lie in the same plane and therefore are expected to overlap considerably.

Table 1. The silicon valence band structure parameters (in eV)

$$\begin{aligned}
(\tfrac{1}{8})\varepsilon(X_4) &= 0.313 \pm 0.04 \\
(\tfrac{1}{4})\varepsilon(L_{3'}) &= 0.29 \pm 0.01 \\
(\tfrac{1}{8})\varepsilon(\Gamma_1) &= 1.56 \pm 0.08 \\
(\tfrac{1}{6})\{\varepsilon(L_{2'}) - \varepsilon(L_{3'})\} &= 1.35 \pm 0.08 \\
(\tfrac{1}{2})\varepsilon(L_1) &= 3.25 \pm 0.25
\end{aligned}$$

$$\begin{aligned}
&\beta_t - \beta_g + \beta_p = (\tfrac{1}{8})\varepsilon(X_4) \\
&\beta_t - \beta_g + 2\beta_p = (\tfrac{1}{4})\varepsilon(L_{3'}) \\
&-\{\beta_A + \beta_w\} - 2\beta_g = (\tfrac{1}{8})\varepsilon(\Gamma_1) \\
&-\{\beta_A + \beta_w\} = (\tfrac{1}{6})\{\varepsilon(L_{2'}) - \varepsilon(L_{3'})\} \\
&6\beta_t - 2\beta_g - \{\beta_A + \beta_w\} = (\tfrac{1}{2})\varepsilon(L_1)
\end{aligned} \tag{1}$$

We do not write and shall not use the expression for the X_1-level, because there are no experimental data at all on the energy of this level. The results of the recent UV-photoelectron and X-ray photoelectron data have been summarized in the paper by Cohen *et al.* [14]. The values of the right sides of the Eq.(1) calculated according to these data are listed in Table 1. The value $(\frac{1}{4})\varepsilon(L_{3'})$ obtained by the empirically adjusted OPW [15] and empirical pseudopotential methods [14] is also given in this table, because both these methods are known to reproduce the upper valence bands of a simple solid fairly reliably, the different data being in close agreement with each other. One can see from this table that the uncertainty for the right side of the last of the Eq.(1) is at least three times as large as that for any of the others, therefore one would not better use the expression for L_1-level in order to obtain the parameters. So there are four equations from which one obtains $\beta_g(\mathrm{Si}) = -0.11$, $\beta_t(\mathrm{Si}) = 0.24$, $\beta_p(\mathrm{Si}) = -0.03$ and $\beta_A(\mathrm{Si}) + \beta_w(\mathrm{Si}) = -1.35$ eV. One can see from the Fig. 1 that the parameters β_g, β_t and β_w include the resonance interactions only.

On the other hand the overlap integrals between the atomic orbitals of the carbon and silicon atoms located at the same positions are quite equal. Then we have:

$$\beta_w(\mathrm{Si}) \approx \frac{\beta_g(\mathrm{Si})}{\beta_g(\mathrm{C})}\,\beta_w(\mathrm{C}) \approx \frac{\beta_t(\mathrm{Si})}{\beta_t(\mathrm{C})}\,\beta_w(\mathrm{C}) \approx -0.2\ \mathrm{eV}$$

and $\beta_A(\mathrm{Si}) \approx -1.15$ eV.

2.2. *Monosilane*

For monosilane one can write [1]:

$$\begin{aligned}
\varepsilon_{t_2} &= a - b \\
\varepsilon_{a_1} &= a + 3b
\end{aligned} \tag{2}$$

Table 2. Matrix elements of Hartree-Fock operator in the EO basis (in eV)

a(Si)	c(Si)	b(Si)	g(Si)	f(Si)	d(Si)	s(Si)	r(Si)	β_A(Si)	β_t(Si)
−13.88	−12.08	−1.43	−0.23	0.22	−1.29	−0.17	0.23	−1.15	0.24

β_g(Si)	β_w(Si)	β_p(Si)	w(Si)	p(Si)
−0.11	−0.20	−0.03	−0.20	−0.03

It has been pointed out [4] that it was not quite correct to use the first of these equations because of the Jahn-Teller splitting (about of 0.5 eV) of the threefold degenerate t_2-level [16]. So using the photoelectron spectroscopy data [19] we obtain $a+3b=18.16$ eV.

2.3. Disilane

Using the experimental data [18] and following [1] we obtain

$$\begin{aligned}\varepsilon_{e_g}&=a-b+f-g=-12.01\\ \varepsilon_{e_u}&=a-b-f+g=-12.91\\ \varepsilon_{a_{1u}}&=a+2b-f-2g=-16.50\end{aligned}\tag{3}$$

and

$$\begin{vmatrix} c-\varepsilon_{a_{1g}} & \sqrt{6}d \\ \sqrt{6}d & a+2b+f+2g-\varepsilon_{a_{1g}} \end{vmatrix}=0 \qquad \varepsilon_{a_{1g}}=-10.53\tag{4}$$

From the Eq.(3) and a_1-level of SiH_4 we have a(Si)$=-13.88$, b(Si)$=-1.43$, f(Si)$=0.22$, and g(Si)$=-0.23$ eV.

On account of the lack of the experimental value of the second valence a_{1g} level for disilane one could not obtain the c(Si) and d(Si) interaction elements from the determinant (4). Therefore let us estimate the interaction d(Si) indirectly. Using the LCAO approximation for EOs we obtain [4]:

$$d\approx(\tfrac{1}{2})\{\beta_A+b\}\tag{5}$$

(It may be pointed out that for the saturated hydrocarbons a similar equation holds with the very high accuracy of about 95%). Then using the vertical IP from the a_{1g} level we obtain c(Si)$=-12.08$ eV.

By analogy we have:

$$\begin{aligned}r&=(\tfrac{1}{2})\{f+\beta_t\}\\ s&=(\tfrac{1}{2})\{g+\beta_g\}\end{aligned}\tag{6}$$

Finally, taking into account the main contribution (from the atoms-second neighbours) for the through space [21] interactions we obtain [5] w(Si)$\approx\beta_w$(Si) and p(Si)$\approx\beta_p$(Si). The results of the consideration given above are summarized in Table 2.

Table 3. The calculated vertical ionization potentials

Si_2H_6	Si_3H_8	$SiH(SiH_3)_3$	$Si(SiH_3)_4$
$18.52a_{1g}$	$10.17b_1$	$10.11e$	$10.04t_2$
	$10.80a_1$	$11.14a_1$	$12.22t_1$
	$11.83b_2$	$12.22a_2$	$12.62e$
	$12.36b_1$	$12.40e$	$12.74t_2$
	$12.42a_2$	$12.68e$	$13.70a_1$
	$12.71a_1$	$12.84a_1$	$17.38t_2$
	$13.10b_2$	$14.99a_1$	$18.77a_1$
	$15.77a_1$	$17.38e$	
	$17.38b_1$	$18.74a_1$	
	$18.67a_1$		

3. Calculation of the Silanes' Ionization Potentials

Using the parameters from the Table 2 we have calculated the vertical IPs for Si_3H_8, $SiH(SiH_3)_3$, $Si(SiH_3)_4$ and the second valence a_{1g}-level for Si_2H_6. The corresponding results are shown in Table 3.

We have calculated the valence band structure of the infinite polysilane too. In the EO method the dispersion curves for the cyclic $(SiH_2)_n$ chain may be obtained from the secular determinant:

$$\begin{vmatrix} H_{aa}-\varepsilon & H_{ab} & H_{ac} & H_{ac} & H_{ae} & H_{ae} \\ H_{ba} & H_{aa}-\varepsilon & H_{bc} & H_{bc} & H_{ac} & H_{ac} \\ H_{ca} & H_{cb} & H_{cc}-\varepsilon & H_{cd} & H_{ce} & H_{cf} \\ H_{ca} & H_{cb} & H_{dc} & H_{cc}-\varepsilon & H_{cf} & H_{ce} \\ H_{ea} & H_{ca} & H_{ec} & H_{fc} & H_{cc}-\varepsilon & H_{cd} \\ H_{ea} & H_{ca} & H_{fc} & H_{ec} & H_{dc} & H_{cc}-\varepsilon \end{vmatrix} = 0 \tag{7}$$

where

$$\begin{aligned} H_{aa} &= c + 2\beta_t \cos q \\ H_{cc} &= a + 2p \cos q \\ H_{ab} &= \beta_A + \beta_w \exp(iq) + \beta_A \exp(-iq) + \beta_w \exp(-i2q) \\ H_{ac} &= d + s \exp(iq) + \delta_m \exp(-iq) \\ H_{bc} &= s + d \exp(iq) + \delta_m \exp(i2q) \\ H_{ae} &= d + s \exp(-iq) + \delta_m \exp(iq) \\ H_{cd} &= b + 2k \cos q \\ H_{ce} &= g + g \exp(-iq) \\ H_{cf} &= f + f \exp(-iq) \end{aligned} \tag{8}$$

Here $q = kR_0$ is the scalar product of the wave vector k and the (one-dimensional) lattice period R_0.

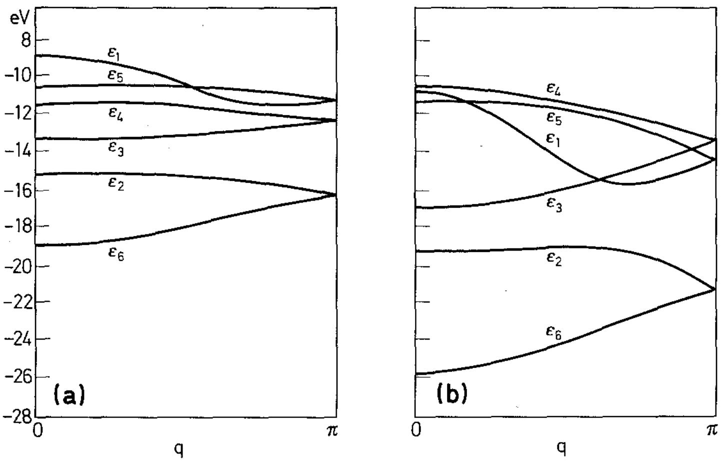

Fig. 2. a) polysilane, b) polyethylene valence band structure

Particularly for the zone center we have $q=0$ and

$$\begin{aligned}
\varepsilon_1 &= c+2\{\beta_t-\beta_A-\beta_w\} \\
\varepsilon_2 &= a+b-2\{g+f-p\} \\
\varepsilon_3 &= a-b+2\{g-f+p\} \\
\varepsilon_4 &= a-b+2\{f-g+p\} \\
\varepsilon_{5,6} &= (\tfrac{1}{2})\{H_{11}+H_{22}\} \pm \{(\tfrac{1}{4})(H_{11}-H_{22})^2+H_{12}H_{21}\}^{\frac{1}{2}}
\end{aligned} \tag{9}$$

where

$$\begin{aligned}
H_{11} &= c+2\{\beta_A+\beta_t+\beta_w\} \\
H_{22} &= a+b+2\{g+f+p\} \\
H_{12} &= 2\sqrt{2}\{d+s\}
\end{aligned} \tag{10}$$

The corresponding curves are given on the Fig. 2 where the valence band structure of the polyethylene chain $(CH_2)_n$ is shown for comparison too.

4. Comparison of the Alkanes and Silanes Spectra

It is interesting to discuss the main qualitative features of the calculated IPs for silanes in comparison with those for the saturated hydrocarbons [5]. It is seen from the comparison of the corresponding parameter scales that all the off-diagonal matrix elements for silanes are smaller than those for alkanes. Therefore, the differences between the first and the inner levels are smaller too. The expected value of the effective Hamiltonian on the silicon sp^3-hybrid orbital is about 4.4 eV smaller than that for the carbon sp^3-orbital. Accordingly, the diagonal matrix elements a and c are smaller for the silicon compound on the values about 2.1 and 4.3 eV.

The decrease of the diagonal elements leads to all the corresponding levels growing higher, the uppermost levels being those for which the contribution of the

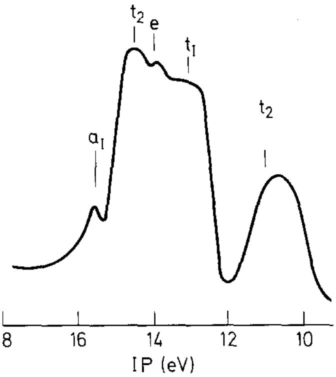

Fig. 3. The photoelectron spectrum of $Si(CH_3)_4$ [20]

Si–Si EOs predominates. All these alterations in the level ordering are expressively seen on the example of the polysilane band structure, where the subband ordering of the highest levels essentially differs from that for polyethylene.

In consequence with the parameter scale change mentioned all the calculated energy levels are located above -20 eV i.e. in the He(I) photoelectron spectroscopy region.

5. On the Reliability of the Parameter Scale

Presently no photoelectron spectroscopy data on the mentioned silicon compounds are available and the data from the Table 3 and Fig. 2 have a predictive character. However an examination of the reliability of these data (i.e. the parameter scale from the Table 2) can be done indirectly on the example of the organosilicon compounds using the parameters for alkanes [5] and silanes and expressing the lacking parameters in terms of the mentioned ones. One can do this by the most simple way using the LCAO form of EOs and applying the EHM (or CNDO) ideology for the expression of the matrix elements. So we obtain

$$c(\mathrm{Si{-}C}) = (\tfrac{1}{2})\{c(\mathrm{Si{-}Si}) + c(\mathrm{C{-}C})\}$$

$$\beta_{\mathrm{A}}^{\mathrm{Si}}(\mathrm{Si{-}C}) = (\tfrac{1}{2})\{\beta_A(\mathrm{Si}) + \beta_A(\mathrm{C})\} + \varDelta$$

(where $\varDelta = (\tfrac{1}{8})\{I_s(\mathrm{Si}) - I_s(\mathrm{C})\} - (\tfrac{1}{8})\{I_p(\mathrm{Si}) - I_p(\mathrm{C})\}$) and so on. Here I_s, I_p are the atomic valence ionisation potentials. In Fig. 3 the vertical IPs for $Si(CH_3)_4$ are presented. This is the only molecule of the similar size as the silanes under consideration for which the high resolution photoelectron spectrum is measured [20]. The disagreement between the theoretical and experimental data is about 0.1 eV. Together with the previous results for saturated hydrocarbons this is an evidence in favour of the reliability of the present approach.

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