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SEMIEMPIRICAL STUDIES OF INNER-CORE ENERGY LEVELS

IX. ESCA SHIFTS OF SILICON ATOMS IN VARIOUS CHEMICAL ENVIRONMENTS BY THE SCC-MO METHOD

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Summary

The semiempirical self-consistent charge molecular orbital (SCC-MO) method has been applied to a number of representative molecules involving Si atoms in various chemical environments. The calculated point charges were correlated with Si(2*p*) inner-core energy level shifts by using ground state potential, relaxation potential and transition potential models (GPM, RPM and TPM). The results are in good agreement with experimental data. Various contributions to the relaxation energy are briefly discussed.

Introduction

The ESCA chemical shifts of silicon atoms in various species have been investigated by a number of researchers [1—8] from the experimental and theoretical standpoints. Pursuing our interest in the electronic structure and properties of silicon compounds [9,10] we have carried out SCC-MO calculations of the energy level shifts of silicon inner-core electrons for representative substituted silanes. This is of some importance because X-ray PES probably gives the most direct experimental information about the charge distribution in molecules, and the SCC-MO method has substantially better performance in this context

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than other semiempirical schemes [11]. The effect of the final state (molecular ion) in the photoemission process is taken into account by using the equivalent core concept [12,13]. Additional computations based on the transition potential formalism [14] were executed for the sake of comparison. The best available experimental geometries were employed in the calculations. It was assumed that nuclei cannot undergo a fast change of the electronic distribution during photoionization, the geometries of the molecular ions thus being the same as those of the molecular ground states.

Computational method

The inner-shell energy levels are closely related to electrostatic potentials exhibited at the site of the ionized atom. The potential derived from the point charges has an especially simple and conceptualy attractive form. The concept was suggested first by Siegbahn et al. [15] and has proved very useful in discussing ESCA shifts. If the ground state electron distribution only is considered then the energy shifts are expressed as follows

$$\Delta BE_{\mathrm{A}} = k_1 Q_{\mathrm{A}} + k_2 M_{\mathrm{A}} + k_3 \tag{1}$$

where Q_{A} is the total valence electron density ascribed to the atom A in question and M_{A} is the Madelung term: $M_{\mathrm{A}} = \Sigma'_{\mathrm{B}} q_{\mathrm{B}}/R_{\mathrm{AB}}$. Here q_{B} is the formal effective charge of the atom *B*. A similar formula holds for transition potential approach:

$$\Delta BE_{\mathrm{A}} = k_1 Q_{\mathrm{A}}^{\mathrm{TP}} + k_2 M^{\mathrm{TP}} + k_3 \tag{2}$$

where $Q_{\mathrm{A}}^{\mathrm{TP}}$ is the density at the corresponding pseudo-atom. Following the equivalent core concept one obtains

$$BE_{\mathrm{A}} = k_1(\xi_{\mathrm{A}} Q_{\mathrm{A}} + \xi_{\tilde{\mathrm{A}}} Q_{\tilde{\mathrm{A}}}) + k_2(M_{\mathrm{A}} + M_{\tilde{\mathrm{A}}})/2 + k_3 \tag{3}$$

The atomic number of the equivalent core $\tilde{A}$ is given by $Z_{\mathrm{A}} + 1$ and ξ_{A} is $\xi_{\mathrm{A}} = (Z_{\mathrm{A}} - S_{\mathrm{A}})/n_{\mathrm{A}}$, where S_{A} is the screening constant, while n_{A} is the principal quantum number of the valence shell. In order to improve the quantitative agreement with experiment within the framework of the equivalent core model, we can increase the number of adjustable empirical parameters. Different weighting factors can be employed for the Q_{A} and $Q_{\tilde{\mathrm{A}}}$ charges and perhaps for the corresponding Madelung terms M_{A} and $M_{\tilde{\mathrm{A}}}$, and formula 3 then takes the following forms:

$$\Delta BE_{\mathrm{A}} = k_1 Q_{\mathrm{A}} + k_2 Q_{\tilde{\mathrm{A}}} + k_3(M_{\mathrm{A}} + M_{\tilde{\mathrm{A}}}) + k_4 \tag{4}$$

and

$$\Delta BE_{\mathrm{A}} = k_1 Q_{\mathrm{A}} + k_2 Q_{\tilde{\mathrm{A}}} + k_3 M_{\mathrm{A}} + k_4 M_{\tilde{\mathrm{A}}} + k_5 \tag{5}$$

The Clementi-Raimondi STO screening constants were employed in the computations which distinguish the orbital energies of 2*s* and 2*p* functions [16].

According to analysis of Hedin and Johansson [17] the relaxation energies are given by

$$E_{\mathrm{A}}^{\mathrm{r}} = \tfrac{1}{2}[V_{\mathrm{A}}(Z_{\mathrm{A}} + 1) - V_{\mathrm{A}}(Z_{\mathrm{A}})] \tag{6}$$

where $V_A(Z_A)$ and $V_A(Z_A + 1)$ are potentials exerted on the sites of the ionized atom A and the equivalent core $\tilde{A}$, respectively. In the point-charge approximation the relaxation energy E^r_A can be conveniently broken down into three contributions

$$E^r_A = E^r_A(\text{contr.}) + E^r_A(\text{flow}) + E^r_A(\text{mix.}) \tag{7}$$

Here

$$E^r_A(\text{contr.}) = 27.21\, Q_A(\xi_A - \xi_{\tilde{A}})/n \text{ eV} \tag{8a}$$

$$E^r_A(\text{flow}) = 7.2(M_{\tilde{A}} - M_A) \text{ eV} \tag{8b}$$

$$E^r_A(\text{mix.}) = 13.6\, \xi_{\tilde{A}}(Q_{\tilde{A}} - Q_A)/n \text{ eV} \tag{8c}$$

Similar expressions are easily derived for TP model. The first term (8a) obviously arises from the contraction of the valence orbitals of the host atom, since the positive charge is effectively increased. The charge flow relaxation term (8b) is a consequence of the electron density migration toward the positive hole. The mixed term (8c) reflects both the charge flow and contraction of atomic orbitals.

The results of the calculations are discussed in the next section.

Results and discussion

The correlated Si(2*p*) energy shifts measured relative to the TMS are summarized in Table 1, and it will be seen that the effect of CH_3 substitution is not well indicated by the GPM approach. The experimental binding energies increase along the series $Si(CH_3)_4 < SiH_3CH_3 < SiH_4$ while the opposite trend is predicted by eq. 1. It is instructive for this purpose to consider the effective

TABLE 1

COMPARISON BETWEEN THE CORRELATED Si(2*p*) ENERGY SHIFTS OBTAINED BY DIFFERENT GPM, RPM AND TPM APPROACHES AND EXPERIMENTAL DATA [a]

Compound	GPM eq. 1	TPM eq. 2	Equivalent core			Experimental
			eq. 3	eq. 4	eq. 5	
SiH_4	0.6	1.5	1.5	1.9	1.3	1.32
SiH_3CH_3	0.9	1.1	1.3	1.3	0.8	0.86
$Si(CH_3)_4$	1.7	0.9	1.1	0.6	0.1	0
SiH_3Cl	1.2	2.1	2.1	2.3	2.4	2.15
$SiCl_4$	2.5	3.3	3.2	3.1	4.2	4.43
SiH_3Br	0.9	1.6	1.6	1.8	2.0	2.12
$(CH_3)_3SiF$	2.5	1.4	1.5	1.2	0.9	1.13
$(CH_3)_3SiCl$	1.8	1.4	0.7	1.1	1.2	0.93
$(CH_3)_3SiBr$	1.6	1.2	1.2	0.9	0.9	0.95
$(CH_3)_3SiI$	1.5	1.1	1.1	0.8	1.0	0.75
SiF_4	6.1	6.8	6.8	6.7	6.5	6.45
$(SiH_3)_2O$	1.6	0.6	0.8	1.2	1.9	1.85
σ	1.1	0.7	0.7	0.6	0.2	

[a] In units of eV. The experimental values were taken from the refs. 3,4. The standard deviations are denoted by σ.

TABLE 2

THE EFFECTIVE CHARGES OF SILICON ATOMS IN THE STUDIED MOLECULES FOR THE GROUND STATE, HOLE STATE SIMULATED BY THE EQUIVALENT CORE, AVERAGE STATE DESCRIBED BY THE PSEUDO-ATOM APPEARING IN THE TP FORMALISM, AND THE CORRESPONDING MADELUNG TERMS [a]

Compound	q^{Gp}	q^{EC}	q^{TP}	M^{GP}	M^{EC}	M^{TP}
SiH_4	0.15	0.51	0.32	−0.10	0.33	0.12
SiH_3CH_3	0.21	0.46	0.32	−0.12	0.32	0.10
$Si(CH_3)_4$	0.38	0.38	0.35	−0.19	0.28	0.06
SiH_3Cl	0.27	0.55	0.41	−0.14	0.29	0.08
$SiCl_4$	0.53	0.67	0.60	−0.26	0.16	−0.05
SiH_3Br	0.21	0.50	0.35	−0.12	0.30	0.10
$(CH_3)_3SiF$	0.49	0.58	0.53	−0.32	0.13	−0.09
$(CH_3)_3SiCl$	0.38	0.45	0.41	−0.20	0.25	0.03
$(CH_3)_3SiBr$	0.35	0.43	0.38	−0.18	0.26	0.05
$(CH_3)_3SiI$	0.34	0.41	0.37	−0.17	0.27	0.05
SiF_4	1.13	1.33	1.23	−0.73	−0.21	−0.47
$(SiH_3)_2O$	0.31	0.58	0.44	−0.24	0.16	−0.05

[a] Charges in units of $|e|$, the Madelung terms in units eV.

charges of the silicon atoms shown in Table 2. The positive charge q^{GP} decreases in the above series in an additive manner. Some support for the estimated charge changes is offered by the ab initio calculations performed by Schaefer et al. employing the relatively flexible basis sets [18]. The effective charges of Si atoms in SiH_3CH_3 and SiH_4 were 0.86 and 0.80 (in $|e|$), respectively, reflecting a somewhat higher CH_3 group electronegativity compared to that of the hydrogen atom. The ab initio and SCC-MO atomic formal charges are not directly comparable, but the relative differences are virtually the same. Application of the simple rule of thumb according to which a larger positive charge means a smaller electron repulsion at the host atom, so leading to higher binding energies, suggests that TMS should have the largest binding Si(2*p*) energy; this is contrary to observation, indicating that relaxation has a dominating influence. The same result was found for the series $Ge(CH_3)_4 \rightarrow GeH_4$ [19]. Methods which specifically consider the effects of charge reorganization (eqs. 2—5) lead to the correct ordering of Si(2*p*) levels. Quantitative agreement with the experimental data is achieved, however, only with a five-parameter formula (eq. 5). It is noteworthy that q^{EC} and M^{EC} for the equivalent core both exhibit increase in the right direction (Table 2). Interestingly, the charges q^{GP} and q^{EC} are equal in TMS, which means that the charge flow toward the positive hole completely compensates for the loss of the inner electron. Analysis of the relaxation energies is illuminating. Consideration of the data in Table 3 reveals that both equivalent core and transition potential relaxation energies show substantial decreases in the series $Si(CH_3)_4 \rightarrow SiH_4$ in qualitative agreement with experiment. The term $E^{\mathrm{r}}_{\mathrm{Si}}$(mix.) is responsible for this trend since the sum of $E^{\mathrm{r}}_{\mathrm{Si}}$(contr.) and $E^{\mathrm{r}}_{\mathrm{Si}}$(flow) is practically zero because of their opposite signs. Replacement of CH_3 group in the TMS by the halides (F, Cl, Br, I) should stabilize the Si(2*p*) level, and this is reflected by all the formulae (eqs. 1—5). However, neither of them agrees with the experimental results that the B.E.'s in $(CH_3)_3SiCl$ and $(CH_3)_3SiBr$ are about the same. The differences in this

TABLE 3

VARIOUS CONTRIBUTIONS TO THE RELAXATION ENERGY ESTIMATED BY THE EQUIVALENT CORE AND TRANSITION POTENTIAL METHODS (IN eV)

Compound	E^{r}_{Si}(contr.)		E^{r}_{Si}(flow)		E^{r}_{Si}(mix.)		E^{r}_{Si}(total)	
	EC	TP	EC	TP	EC	TP	EC	TP
SiH_4	3.8	3.8	−3.1	−3.1	4.6	4.4	5.3	5.1
SiH_3CH_3	3.7	3.7	−3.2	−3.3	5.5	5.3	6.0	5.7
$Si(CH_3)_4$	3.6	3.6	−3.4	−3.6	7.2	7.2	7.4	7.2
SiH_3Cl	3.7	3.7	−3.1	−3.1	5.2	4.9	5.8	5.5
$SiCl_4$	3.4	3.4	−3.1	−3.1	6.2	5.8	6.5	6.1
SiH_3Br	3.7	3.7	−3.0	−3.0	5.2	4.9	5.9	5.6
$(CH_3)_3SiF$	3.5	3.5	−3.3	−3.3	6.6	6.2	6.8	6.4
$(CH_3)_3SiCl$	3.6	3.6	−3.2	−3.2	6.7	6.4	7.1	6.8
$(CH_3)_3SiBr$	3.6	3.6	−3.2	−3.2	6.7	6.4	7.1	6.8
$(CH_3)_3SiI$	3.6	3.6	−3.1	−3.2	6.7	6.4	7.2	6.8
SiF_4	2.8	2.8	−3.7	−3.7	5.9	5.5	5.0	4.6
$(SiH_3)_2O$	3.6	3.6	−2.9	−2.7	5.3	5.0	6.0	5.9

series are very small, and it seems that the point-charge electrostatic potential is too crude to reproduce them. The Si(2*p*) energy levels in tetrachlorosilane and tetrafluorosilane are well described, particularly by the approaches involving relaxation effects. The Si atom in SiF_4 assumes a very high formal charge of 1.13 $|e|$ which means that, loosely speaking, there is a positive "hole" in its valence shell in the ground state. Needless to say, SiF_4 possesses the most stable Si(2*p*) level. Although physical meaning should not be attached to absolute values of formal charges presented in Table 2, survey of the data shows that they provide a fairly consistent pattern closely related to that expected from chemical intuition. It is of interest that the transition potential charges q^{TP} are almost exactly equal to arithmetical means of q^{GP} and q^{EC}. The same conclusion holds for the corresponding Madelung terms. Hence we can make the approximations

$$q^{TP} \simeq (q^{GP} + q^{EC})/2 \text{ and } M^{TP} \simeq (M^{GP} + M^{EC})/2 \tag{9}$$

Thus only one of RPM or TPM calculations need be performed and the relevant entities of the counterpart approach can be estimated by use of eq. 9.

The various contributions to the relaxation energies and the total values of the latter indicated by the equivalent core and transition potential methods are very similar. The estimated average relaxation energy for the Si(2*p*) level is about 6 eV, which is significantly lower than the relaxation energies of 1*s* electrons of the first row atoms. The scatter of the E^{r}_{Si} values around the average energy is roughly within the limits of ±1 eV. This is sometimes of importance, as illustrated by the $Si(CH_3)_4 \rightarrow SiH_4$ series (vide supra). Not suprisingly, the smallest relaxation effect appears in SiF_4 due to the low E^{r}_{Si}(contr.) term. This is a consequence of the positive "hole" in the Si valence shell. Otherwise the E^{r}_{Si}(contr.) term is practically constant at a value of ~3.6 eV. The E^{r}_{Si}(flow) contribution is also fairly constant, while the largest variation is found in the mixed term E^{r}_{Si}(mix.) because it reflects both the charge migration and orbital contraction effects. Since the E^{r}_{Si}(contr.) and E^{r}_{Si}(flow) terms almost cancel each other, E^{r}_{Si}(mix.) is roughly equal to the total relaxation energy in most cases. It is of interest to relate the contributions of various atoms in a molecule to the E^{r}_{Si}(flow) term. The corresponding values in SiH_3—CH_3 are:

$E^{r}_{Si}(\text{flow})_C = -0.7$ eV

$3\ E^{r}_{Si}(\text{flow})_{H_C} = -0.5$ eV

$3\ E^{r}_{Si}(\text{flow})_{H_{Si}} = -2.0$ eV

where the lower index on the right hand side signifies the atom taking part in the electron charge reorganization processes. It appears that the atoms directly bonded to the ionized Si atom each contribute −0.7 eV to the flow charge term. Hydrogen atoms attached to carbon are less important, exhibiting an effect of −0.17 eV (per H_C). The total relaxation energy of methylsilane (6.0 eV) can be compared with the ab initio estimate of 8 eV [20]. The semiempirical value seems to be too low, but it should be remembered that ab initio estimates of relaxation energies depend strongly on the quality of the basis set used. We are confident that the SCC-MO relaxation energies given in Table 3 are reasonable, although scaling against the accurate ab initio results is desirable.

The role of *d*-orbitals in bonding of second row atoms is a much debated question. It is well established by now that their importance diminishes as the description of inner-shell orbitals becomes more refined. Schaefer et al. [18] found that *d*-orbitals populations in SiH_4 and SiH_3—CH_3 are only 0.1 $|e|$, but this may increase with the increase of the electronegativity of substituents in conjunction with higher p_π—d_π back bonding ability. However, Perry and Jolly [21] studied the X-ray PES spectra in the valence region for SiH_4, SiH_3CH_3, $Si(CH_3)_4$, SiH_3Cl and SiF_4 and found that the experimental data can be rationalized without substantial participation of silicon *d*-orbitals. We used only an *s*, *p* basis set for the SCC-MO computations and the resulting ESCA shifts are in satisfactory agreement with observed values. The employment of *d*-orbitals in such an approximate method is not justified, particularly if they are not specially parametrized to fit the X-ray PES experimental data. Finally, it should be mentioned that 2*p* levels of Si were examined for SiH_4, $SiCl_4$ and SiF_4 by Hartmann and Szargan using SCF-Xα-SW method [22]. Their results are not in very good agreement with experiment, the deviations being 1.1 eV, 1.9 eV and 3.6 eV for SiH_4, $SiCl_4$ and SiF_4, respectively.

To conclude, the present results indicate that the semiempirical SCC-MO method used in conjunction with an electrostatic model involving the final state effect (via RPM or TPM approaches) provide a fair description of the inner-core energy shifts of silicon atoms in various chemical environments. Since the results for sulfur ESCA shifts are in good accordance with experimental data [23], it follows that the SCC-MO method is a useful tool in studying changes of inner-shell energy levels of the second row atoms.

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