

## Ab initio Effective Core Potential Calculations for Silane and Chlorosilanes

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The electronic structures of silane and chlorosilanes are studied by the SCF calculations using effective core potentials (ECP's). The results obtained with ECP's are in good agreement with corresponding all electron calculations demonstrating the reliability of ECP employed. The importance of polarization functions for the second row atoms is also evident in this study. The SCF calculations of silane and chlorosilanes are useful in qualitative understanding of many chemical properties since many trends are correctly obtained with the polarization functions included in basis sets of reasonable size.

### Introduction

As the number of atoms in the molecule increases, *ab initio* all electron (AE) calculations for molecules containing moderately heavy atoms become difficult even at the self-consistent field (SCF) level due to the large number of integrals involved. It is desirable to have methods which reduce computing time without losing too much advantages and accuracies of the *ab initio* calculations. Since most of the chemical properties of molecules depend mainly on the valence electronic structures of the constituent atoms, atomic cores may be replaced by the appropriate potential in such a manner that only valence electrons need to be explicitly treated in molecular orbital calculations without sacrificing accuracies. The above method is usually called *ab initio* effective core potential (ECP) method and suitable for the electronic structure calculations of heavy-atom-containing molecules since the computational savings can be significant for these molecules.

Among the various types of ECP methods developed so far<sup>1</sup>, the method based upon the shape consistent principle<sup>2,3</sup> is regarded as one of the most reliable methods. Recently Hay and Wadt (HW) generated ECP's for many atoms<sup>4</sup> using the shape consistent method developed by Christiansen *et al.*<sup>5</sup>. In this work, ECP's of HW are used for Si and Cl atoms in the study of the electronic structures of  $\text{Si}_{4-n}\text{Cl}_n$ , where  $n$  ranges from zero to four.

The silicon containing compounds exhibit chemical features that are quite dissimilar from the analogous carbon compounds. A partial list of examples include the instability of Si-H bonds, the absence of Si-Si multiple<sup>6</sup> bonds and the difficulty with which silane oligomers are prepared.<sup>6</sup> These differences arise, in part, from the different ways in which silicon and carbon s and p orbitals participate in chemical bonds. In addition, the silane and chlorosilanes are useful starting materials in microelectronics industry. The understanding of the properties of these compounds have some practical as well as the theoretical importances. The valence ionizations of the molecules,  $\text{SiH}_{4-n}\text{Cl}_n$  ( $n = 0-4$ ) have been studied by photoelectron spectroscopy<sup>7-12</sup> and the experimental data were interpreted almost exclusively with the aid of semiempirical methods.<sup>7-13</sup> The results of *ab initio* molecular orbital calculations are also available in the literature<sup>14-22</sup> mainly for the heat of formations and geometries. The study of  $\text{SiH}_{4-n}\text{Cl}_n$  molecules using ECP's provide an interesting comparison with AE and semiempirical calculations.

The important roles of d functions for second period atoms

contained in molecules are widely recognized, although there are some results claiming that s and p functions are sufficient for the molecular calculation.<sup>16,23</sup> Whether the effect of d function addition in the ECP calculation is equivalent or not to that in the AE calculation is also worthwhile to clarify.

In this work, we perform the SCF calculations using ECP's and results are analysed to shed some light on the following problems. The main goal is to test the general usefulness of the ECP parameters generated by Wadt and Hay<sup>4</sup> by comparing with similar AE calculations when available. We also look for the theoretical knowledge of the valence molecular orbitals of these molecules that can be useful for the interpretation of their photoelectron spectra. The role of d function in the molecular orbital calculations is studied at the SCF level by comparing calculations with and without d function on the second period atoms. The calculational methods are briefly described in the next section followed by that dealing with results and discussions of the computed values.

### Calculations

ECP's for Si and Cl atoms used in this study were generated by Wadt and Hay and the details concerning ECP's are referred to the original source.<sup>4</sup> The basis sets for Si and Cl atom are (3s3p/2s2p) contraction of pseudoorbitals of Wadt and Hay<sup>4b</sup> in which two innermost orbitals are contracted. The basis set for H atom is 21G with standard rescaling coefficients.<sup>24</sup> The values of d exponents for Si and Cl atom were 0.45 and 0.75, respectively.<sup>20</sup> The d functions consist of the usual five components of the spherical harmonic functions. For the assignment of orbital symmetries in  $\text{SiH}_2\text{Cl}_2$  molecule, the convention adopted for the orientation of the molecular axes is that two H atoms lie in the YZ plane. All calculations were performed using PSHONDO program.<sup>25,26</sup>

The calculations for  $\text{SiH}_{4-n}\text{Cl}_n$  ( $n = 0-4$ ) molecules were carried out at experimental geometries<sup>27-31</sup> with and without d functions on Si and Cl atoms. The results from these calculations include orbital energies for these molecules which can easily be compared with other calculational results and experimental valence ionization potentials (IP). For  $\text{SiH}_3\text{Cl}$ , we also performed calculations with d function only on Si or on Cl atom in order to investigate the effect of the inclusion of the d function on each atom. To test whether the ECP calculation can reproduce *ab initio* AE calculation results or not, we optimized the geometries of  $\text{SiH}_4$  and  $\text{SiCl}_4$ . We also partially optimized the geometry of  $\text{SiH}_3\text{Cl}$  by the following way. The bond length for Si-Cl is optimized with other variables fixed

and then the bond angle for H-Si-Cl is optimized with other variables fixed. All these results are analysed in detail in the following section.

## Results And Discussion

The experimental geometries<sup>27-31</sup> used in the present calculations for  $\text{SiH}_{4-n}\text{Cl}_n$  ( $n=0-4$ ) are listed in Table 1. The shortening of the Si-Cl bond is found experimentally to occur in going from  $\text{SiH}_3\text{Cl}$  to  $\text{SiH}_2\text{Cl}_2$  and again from  $\text{SiH}_2\text{Cl}_2$  to  $\text{SiHCl}_3$ . The Si-Cl bond length becomes slightly larger as molecule changes from  $\text{SiHCl}_3$  to  $\text{SiCl}_4$ . The change in the Si-Cl bond length in the  $\text{SiH}_{4-n}\text{Cl}_n$  ( $n=0-4$ ) as the number of chlorine atoms in molecules increases is not constant. The phenomena such as this are the so-called non-additive effects. This suggests that considering polyatomic molecules as systems containing non-interaction two-center bonds is not fully justified. In this molecular series, we can see from the Cl-Si-Cl bond angles that the interaction between the Si-Cl

bonds is repulsive as expected from the simple bond picture.

Table 2 lists some results from calculations for  $\text{SiH}_{4-n}\text{Cl}_n$  ( $n=0-4$ ) with and without d functions on Si and Cl atoms at experimental geometries summarized in Table 1. The total energies of all molecules naturally decrease when d functions are introduced into second period atoms. The calculated binding energy is the difference between the total molecular energy and the sum of total energies<sup>32</sup> of constituent atoms in the ground state. The experimental binding energies were obtained from the heat of formation<sup>34</sup> of each molecule by subtracting the sum of the heat of formation<sup>34</sup> of the constituent atoms.

In  $\text{SiH}_{4-n}\text{Cl}_n$  ( $n=0-4$ ), the experimental binding energy increase as the number of Cl atom in each molecule,  $n$ , becomes large. In calculations without d functions on second period atoms, binding energies decrease from  $n=0$  to  $n=3$  but increase from  $n=3$  to  $n=4$ . However, allowing d functions to second period atoms cause that the calculated binding energies become large and have the same trend as the experimental

Table 1. Experimental Geometries<sup>a</sup> of  $\text{SiH}_{4-n}\text{Cl}_n$  ( $n=0-4$ ) Molecules

n	Distance		Angle		Point group	Ref.
	d(Si-H)	d(Si-Cl)	$\angle\text{H-Si-H}$	$\angle\text{Cl-Si-Cl}$		
0	1.481		109.47		$T_d$	27
1	1.485	2.049	110.23		$C_{3v}$	28
2	1.480	2.033	110.30	109.70	$C_{2v}$	29
3	1.4655	2.0118		110.60	$C_{3v}$	30
4		2.019		109.47	$T_d$	31

<sup>a</sup>Distances in Å, angles in degree unit.

Table 3. The Change in the Difference of Binding Energies<sup>a</sup> for  $\text{SiH}_{4-n}\text{Cl}_n$  ( $n=1-3$ )

Molecule	$\Delta^b E$ calculated via			
	Exp.	No d	d	MP4/6-31G**
$\text{SiH}_3\text{Cl}$	0.0869	-0.0261	0.0295	0.0064
$\text{SiH}_2\text{Cl}_2$	0.0129	-1.1805	-0.0396	0.0006
$\text{SiHCl}_3$	-0.0260	3.2808	-0.1033	-0.0613

<sup>a</sup>Energy in eV unit.

Table 2. Calculated Properties for  $\text{SiH}_{4-n}\text{Cl}_n$  ( $n=0-4$ ) with and without the d Functions on Si and Cl atom at Experimental Geometries

Properties	Basis set	n=0	n=1	n=2	n=3	n=4
Total energy (Hartree)	No d	-6.0334	-20.1987	-34.3594	-48.4522	-62.6655
	d	-6.0817	-20.2780	-34.4755	-48.6714	-62.8636
Binding energy <sup>a</sup> (eV)	No d	10.0628	9.5563	8.9268	6.4468	7.2476
	d	11.3778	11.7163	12.0843	12.4127	12.6380
	3-21G	9.6502	9.4118			7.8963
	3-21G*	12.2973	15.1823			
	3-21G	9.6153	9.2662			
	6-31G*	10.7820	11.2309			
	MP4/6-31G	13.1990	13.5239	13.9128	14.3023	14.6305
	Exp <sup>b</sup>	13.2262	13.8876	14.7356	15.6095	16.4314
Overlap on Si-H Si-Cl	No d	0.366	0.354	0.339	0.310	
	No d		0.253	0.260	0.301	0.255
	d	0.393	0.387	0.383	0.386	
	d		0.322	0.340	0.358	0.365
Charge on Si H Cl Si H HCl	No d	0.668	0.826	0.924	1.025	0.993
	No d	-0.167	-0.143	-0.117	-0.122	
	No d		-0.396	-0.345	-0.301	-0.248
	d	0.489	0.668	0.794	0.872	0.927
	d	-0.122	-0.109	-0.094	-0.077	
	d		-0.342	-0.303	-0.265	0.232
Dipole moment <sup>c</sup> (Debye)	No d		2.6875	2.7158	2.1100	
	d		1.8469	1.7508	1.0393	
	Exp		1.31	1.17	0.86	

<sup>a</sup>1 Hartree = 27.2117 eV. The 3-21G and 3-21G\* results taken from Ref.(14) and the 6-21G result taken from Ref.(19) and 6-31G\* result taken from Ref.(20). <sup>b</sup>Ref.(34). Zero point energy is not subtracted. <sup>c</sup>Experimental dipole moments taken from Ref.(33).

binding energies as shown in Table 2. Differences between experimental and calculated binding energies are reduced when allowing d functions to second period atoms. But, the magnitude of these differences are still large. This discrepancy is expected for any SCF calculations of these molecules since the correlation energies are important for the calculation of binding energies.

Calculations for  $\text{SiH}_4$  and  $\text{SiH}_3\text{Cl}$  with 3-21G and 3-21G\*

were performed by Luke.<sup>14</sup> Also Pople<sup>14</sup> carried out the calculation for  $\text{SiCl}_4$  with 3-21G basis. Although the results of ECP calculations cannot be compared directly with these AE calculations because AE results were obtained for each molecule at the optimized geometries with different basis sets, the results of AE calculations show the same trend as those of the corresponding ECP calculations as shown in Table 2.

Calculations for  $\text{SiH}_{4-n}\text{Cl}_n$  with 6-31G\*\* basis set were per-

**Table 4. Vertical Ionization Potentials (in eV) of  $\text{SiH}_{4-n}\text{Cl}_n$  ( $n=0-4$ ) from Calculations and Experiments. Calculated Values are Estimated Using Koopmans Theorem**

		Present Study		Other calculation			Experiment		
n=0	$\text{SiH}_4$								
Orb.	No d	d	No d <sup>a</sup>	d <sup>a</sup>	d <sup>b</sup>	E1 <sup>c</sup>	E2 <sup>d</sup>	E3 <sup>e</sup>	
1t <sub>2</sub>	13.2439	13.3011	12.97	13.20	12.67	12.67	12.6	12.82	
1a <sub>2</sub>	20.1965	19.7747	20.18	19.90	19.25	18.02	19.7	18.17	
n=1	$\text{SiH}_3\text{Cl}$								
Orb.	No d	d	No d <sup>f</sup>	d <sup>f</sup>	d <sup>g</sup>	E1 <sup>c</sup>	E2 <sup>d</sup>	E4 <sup>h</sup>	
2e	12.2779	12.3051	10.52	10.71	12.30	11.51	11.65	11.61	
3a <sub>1</sub>	14.1909	14.5392	11.95	12.20	14.40	12.9	13.51	13.4	
1e	14.8113	14.5583	14.03	13.64	14.50	13.8	13.99	13.7	
2a <sub>1</sub>	20.3979	19.8346	20.53	19.64	20.05	17.97	18.23	18.04	
1a <sub>1</sub>	29.9057	29.6036	29.57	29.35	30.01	23.7			
n=2	$\text{SiH}_2\text{Cl}_2$								
Orb.	No d	d	MNDO <sup>i</sup>	HFS <sup>j</sup>		E2 <sup>d</sup>			
3b <sub>1</sub>	12.6317	12.4820	12.31	12.08		12.09			
2b <sub>2</sub>	12.9555	12.8031	12.82	12.28		11.70			
1a <sub>2</sub>	13.3746	13.2167	13.12	12.53		13.53			
4a <sub>1</sub>	13.2412	13.2657	12.76	12.59		12.76			
1b <sub>2</sub>	15.2249	15.4100	15.32	14.54		14.20			
3a <sub>1</sub>	15.7583	15.4807	15.14	14.81		14.45			
2b <sub>1</sub>	16.1447	15.5597	15.43	15.40		14.60			
2a <sub>1</sub>	20.5394	19.8727	21.36	19.30		18.32			
1b <sub>2</sub>	30.1397	29.7152	25.19						
1a <sub>1</sub>	31.1819	30.5424	26.00						
n=3	$\text{SiHCl}_3$								
Orb.	No d	d	MNDO <sup>i</sup>	HFS <sup>j</sup>		E2 <sup>d</sup>			
1a <sub>2</sub>	13.2902	12.8956	13.31	12.03		11.94			
4a <sub>1</sub>	13.6059	13.0262	12.82	12.31		12.41			
43	13.5596	13.3473	13.21	12.32		12.41			
3e	14.1419	14.0167	13.61	12.81		13.07			
2e	16.3409	16.1901	16.19	14.86		14.75			
3a <sub>1</sub>	17.5162	16.3297	16.21	15.39		14.98			
2a <sub>1</sub>	21.9109	19.8700	21.63	18.64		18.14			
1e	30.8009	30.1859	25.75						
1a <sub>1</sub>	32.4282	31.4322	26.88						
n=4	$\text{SiCl}_4$								
Orb.	No d	d	MNDO <sup>i</sup>	HFS <sup>j</sup>		E5 <sup>k</sup>	E6 <sup>l</sup>		
1t <sub>1</sub>	13.7310	13.1242	13.71	12.04		12.03	12.12		
3t <sub>2</sub>	14.1555	13.9841	13.56	12.66		12.85	13.03		
1e	14.8440	14.4793	14.09	12.96		13.35	13.51		
2t <sub>2</sub>	17.1896	16.7189	16.97	15.15		15.13	15.27		
2a <sub>1</sub>	20.4061	19.7747	21.87	17.98		17.98	18.01		
1t <sub>2</sub>	31.2935	30.4472	26.27						
1a <sub>1</sub>	33.3262	32.0663	27.65						

\*Ref.(15). <sup>b</sup>Ref.(16) <sup>c</sup>Ref.(7). Symmetry of orbitals assigned by EHT calculation. <sup>d</sup>Ref.(8). Symmetry of orbitals assigned by CNDO/2 calculation. <sup>e</sup>Ref.(9). <sup>f</sup>Ref.(17). <sup>g</sup>Ref.(16). <sup>h</sup>Ref.(10). <sup>i</sup>Ref.(13). <sup>j</sup>Ref.(18). <sup>k</sup>Ref.(11). <sup>l</sup>Ref.(12).

formed by Ho *et al.*<sup>21</sup> using MP4 method at the optimized geometries in 6-31G\* basis set. Their binding energies are in better agreement with experimental binding energies than our ECP calculation with d functions since their calculations include correlation effects, which are important for binding energies, and since they use larger basis sets.

If the bond energies of all bonds for this molecular series remain exactly constant from one molecule to another, the increment  $\Delta E$  in the binding energy upon substitution of H by Cl will be a constant. Conversely, any change in  $\Delta E$  (denoted by  $\Delta^2 E$ ) is a direct measure of the non-additivity of bond energies. We have computed  $\Delta^2 E$  values from experimental and calculated binding energies. The results are listed in Table 3. The MP4 calculations using 6-31G\*\* at the optimized geometries in 6-31G\* reproduce the non-additive energy effects.<sup>21</sup> Our calculations without d functions on Si and Cl atoms give unreliable results in reproducing the non-additive effects. Our calculation with d functions do not agree with experiment but the agreement is far better than those without d function.

The study at the experimental geometry implies that the results of ECP calculations with and without d functions on second period atoms agree well with those of corresponding AE calculations and that the influence of d functions on second period atoms is similar in ECP calculations and in AE calculations. Clearly, d function for the second period atoms must be included to study the electronic structure of a molecule and to predict the correct trend in a molecular series such as  $\text{SiH}_{4-n}\text{Cl}_n$  ( $n=1-4$ ).

As one might expect from the often-quoted electronegativity values of 1.8 for Si, 2.1 for H and 3.0 for Cl, the Si atom in  $\text{SiH}_{4-n}\text{Cl}_n$  ( $n=1-4$ ) molecules appears to be electropositive relative to both H and Cl atoms as shown in Table 2. The net charge on each atom is reduced by the introductions of d functions to second period atoms indicating that there is a charge flow from Cl and H atoms to Si atom.

The dipole moments for the  $\text{SiH}_{4-n}\text{Cl}_n$  ( $n=0-4$ ) decrease upon adding d functions to second period atoms but do not change the directions as shown in Table 2. The effects of d function on the dipole moment are similar to those in the AE

calculations and in line with the change of charges. The dipole moments for the  $\text{SiH}_3\text{Cl}$  from the AE calculation<sup>14</sup> with 3-21G and 3-21G\* basis sets are 3.527 and 1.974 Debyes, respectively. Semkow *et al.*<sup>16</sup> performed AE calculation for  $\text{SiH}_3\text{Cl}$  using the bases 11s7p1d for Si and Cl, and 5s1p for H and obtained dipole moments of 1.93 and 2.65 Debye with and without polarization functions, respectively.

Table 4 contains the summary of the calculated orbital energies for  $\text{SiH}_{4-n}\text{Cl}_n$  ( $n=0-4$ ) with and without adding d function to the second period atoms and the comparison with other calculations and experimental IP's. These calculated orbital energies may be compared, assuming the validity of Koopmans' theorem, with experimentally observed vertical ionization energies.<sup>7-12</sup>

In  $\text{SiH}_4$ , the agreement between ECP and AE orbital energies with and without d function on Si atom is satisfactory. Semkow *et al.*<sup>16</sup> computed two sorts of IP's to estimate the orbital relaxation effects. In one calculation, IP's (column 5) were taken as the same as the negative of each orbital eigenvalue from the Koopmans' theorem. In the other calculation, IP's (column 6) were computed as the difference between the total energies of parent and ionized states. Calculated IP's in column 6 agree better with experimental IP's than those in column 5. If the orbital relaxation effects are included in the ECP calculations, agreement between ECP and experimental IP's will also be improved.

In  $\text{SiH}_3\text{Cl}$ , the top three AE IP's reported by Howell and Van Wazer<sup>17</sup> with and without d functions to second period atoms are lower than corresponding ECP IP's of the present study. But ECP IP's with d functions agree well with the corresponding AE IP's reported by Semkow *et al.*<sup>16</sup> which agree better with experimental IP's than those reported by Howell and Van Wazer<sup>17</sup> probably due to the basis set deficiency in the calculations by the latter. The ordering in orbital energies changes upon inclusion of the d functions in  $\text{SiH}_2\text{Cl}_2$  and  $\text{SiHCl}_3$ , in our calculation; a level exchange between 1a<sub>2</sub> and 4a<sub>1</sub> occurs in  $\text{SiH}_2\text{Cl}_2$  and a level exchange between 4a<sub>1</sub> and 4e occurs in  $\text{SiHCl}_3$ . Since we performed ECP calculations for these molecules at experimental geometries and the energy differences between the switched levels are small, we are not certain about the correct order of the levels in these molecules

Table 5. The d Function Effects in  $\text{SiH}_3\text{Cl}$

Properties/Basis	No d	d on Si	d on Cl	d on Si and Cl
Total energy (Hartree)	-20.1987	-20.2637	-20.2162	-20.2780
Binding energy (eV)	9.5704	11.3403	10.0467	11.7305
Charge on Si	0.826	0.616	0.882	0.668
H	-0.143	-0.102	-0.153	-0.109
Cl	-0.396	-0.309	-0.424	-0.342
Overlap population on Si-H	0.354	0.385	0.356	0.387
Si-Cl	0.253	0.320	0.257	0.322
Dipole moment (Debye)	2.6875	2.3036	2.1770	1.8469
Orbital energy 2e (eV)				
3a <sub>1</sub>	-12.2779	-12.3650	-12.2072	-12.3051
1e	-14.1909	-14.4222	-14.3596	-14.5392
2a <sub>1</sub>	-14.8113	-14.6753	-14.6780	-14.5583
2a <sub>1</sub>	-20.3979	-19.8972	-20.3190	-19.8346
1a <sub>1</sub>	-29.9057	-29.8267	-29.6444	-29.6036

at the optimized geometries.

MNDO calculations<sup>13</sup> assign different orders of the levels for SiH<sub>2</sub>Cl<sub>2</sub>, SiHCl<sub>3</sub> and SiCl<sub>4</sub> from ECP calculations. HFS-DVM calculations<sup>18</sup> seem to agree better with experiments than ECP calculations, but the HFS-DVM method is specifically modified to yield better IP's.

In conclusion, ECP IP's agree reasonably well with AE IP's. When the relaxation effects and correlation effects on ionization are considered, we may expect that the agreement between ECP IP's and experimental IP's will be improved.

SiH<sub>3</sub>Cl molecule was studied by Howell and Van Wazer<sup>17</sup> using AE SCF method in order to identify the effects due to adding d orbitals on second period atoms. In order to investigate the same effects in SiH<sub>3</sub>Cl when ECP method is used, we performed two more calculations at experimental geometry in addition to two previous calculations with and without d functions on the second period atoms; a d function is added either on Si or on Cl atom. These results are summarized in Table 5. From Table 5, it can be seen that allowing a d function to Si atom was more effective in lowering the total energy than allowing a d function to Cl atom. Of course, allowing d functions to both Si and Cl atoms cause the largest decrease in the total energy. The Si atom appears to be electropositive to both H and Cl atoms in all four calculations. Addition of a d function to Si atom decreases the degree of charge separation but does not change the sign of charge on each atom in contrast to the results of Howell and Van Wazer.<sup>17</sup> Adding a d functions to Cl atom causes considerably less change in charge for all atoms. In this case, there is a charge transfer from the Si atom to the Cl and three H atoms. From the results of adding d functions to both Si and Cl atoms, it can be seen that the effects of d functions are approximately additive. The d function on Cl atom produces smaller change of overlap populations than that on Si atom, with the combined effect being again nearly additive. These changes in the overall electronic populations imply that charge transfer is the major contributor when a d function is allowed to Si atom,

Table 6. The Results of SiH<sub>3</sub>Cl Geometry Optimization

Properties	Basis	No d	d
Distance Si-H (Å)		1.473	1.462
Total energy (Hartree)		-6.0335	-6.0823
Binding energy (eV)		10.0839	11.4115
Charge on Si		0.671	0.490
H		-0.168	-0.122
Overlap population on Si-H		0.367	0.396
Orbital energy 1t <sub>2</sub> (eV)		-13.2711	-13.3718
1a <sub>1</sub>		-20.2455	-19.8890
Basis	d(Si-H)(Å)	Binding energy. (eV)	
No d	1.473	10.0839	
d	1.462	11.4115	
3-21G <sup>a</sup>	1.4865	9.6502	
3-21G <sup>**</sup>	1.4746	12.2973	
6-21G <sup>b</sup>	1.489	9.6153	
6-31G <sup>*c</sup>	1.475	10.7820	

<sup>a</sup>Ref.(14) <sup>b</sup>Ref.(19) <sup>c</sup>Ref.(20)

whereas polarization and related effects dominate when d functions are added to Cl atom.

When d functions are allowed to Si and/or Cl atom, dipole moment decrease in magnitude but does not change the direction of dipole. The change in the dipole moments do not necessarily parallel those in charge in these cases as can be seen by comparing No d case with d on Cl in Table 5. The detailed shape of the charge distribution among the atomic orbitals of a given atom also contribute significantly to the dipole moment and the net charge alone is not the only factor for the dipole moment even at the same nuclear geometries.

The change in orbital energies upon addition of d functions to the second period atom have the same trend as the results of Howell and Van Wazer.<sup>17</sup> The top three valence orbital energies are significantly lower than those reported by Howell and Van Wazer<sup>17</sup> probably due to the different geometries and basis sets used in the calculations and not due to the intrinsic differences between AE and ECP calculations.

In order to investigate the effects of d functions on the molecular geometries, we optimized the geometries of SiH<sub>4</sub> and SiCl<sub>4</sub> with and without d functions on the second period atoms. Also we optimized the geometry for the SiH<sub>3</sub>Cl molecule in the following manner. First, the bond length, d(Si-Cl), was optimized with other variables fixed at the experimental values and then the bond angle, ∠H-Si-Cl, was optimized with d(Si-Cl) fixed at the previously optimized value and d(Si-H) fixed at the experimental value.

Table 7. The Results of SiH<sub>3</sub>Cl Geometry Optimization

Properties	Basis	No d	d	
Distance Si-Cl (Å)		2.163	2.040	
Angle H-Si-Cl (Degree)		107.5	108.7	
Total energy (Hartree)		-20.2032	-20.2781	
Binding energy (eV)		9.6930	11.7981	
Charge on Si		0.835	0.667	
H		-0.138	-0.110	
Cl		-0.420	-0.338	
Overlap population on Si-H		0.351	0.338	
Si-Cl		0.249	0.299	
Dipole moment (Debye)		3.2571	1.8022	
Orbital energy 2e (eV)		-12.1527	2e -12.3079	
3a <sub>1</sub>		-13.6848	1e -14.5691	
1e		-14.7134	3a <sub>1</sub> -14.5746	
2a <sub>1</sub>		-20.4795	2a <sub>1</sub> -19.8292	
1a <sub>1</sub>		-29.1964	1a <sub>1</sub> -29.6526	
Basis	d(Si-Cl)	d(Si-H)	∠HSiH	Binding energy.(eV)
No d	2.163	1.485	111.37	9.6930
d	2.040	1.485	110.23	11.7312
3-21G <sup>a</sup>	2.191	1.475	111.78	9.4118
3-21G <sup>**</sup>	2.056	1.467	110.47	15.1823
6-21G <sup>b</sup>	2.187	1.477	111.6	9.2662
6-31G <sup>*c</sup>	2.067	1.468	108.31	11.2309

<sup>a</sup>Ref.(14) <sup>b</sup>Ref.(19) <sup>c</sup>Ref.(20)

Table 6 contains the results for  $\text{SiH}_4$ . Allowing d function to Si atom caused the shortening in the bond length,  $d(\text{Si-H})$ , as large as 0.011 Å and the increase in the binding energy as much as 1.327 eV. The effects of d function is not small even in the molecule which contains only one second period atom such as  $\text{SiH}_4$ . Although the calculated binding energy is similar to the AE value, the optimized bond length is short by as much as 0.01 Å. It is probable that the ECP's generated by Wadt and Hay are slightly more attractive than the AE potentials.

Table 7 displays the results for  $\text{SiH}_3\text{Cl}$ . When d functions are allowed to Si and Cl atom, the Si-Cl bond length,  $d(\text{Si-Cl})$ , becomes shorter by 0.123 Å, and the bond angle,  $\angle\text{H-Si-Cl}$ , smaller by 1.2 degree, and the binding energy increases by about 2 eV. The optimized bond length for  $d(\text{Si-Cl})$  by ECP method is shorter by about 0.02 Å than the comparable AE results again indicating that ECP generated by Wadt and Hay may slightly underestimate the repulsive part. Changes in dipole moments and charge separations are essentially the same as those computed at the experimental geometry. (Table 2) A slightly better agreement with experiment is obtained at the optimized geometry with d functions included.

The order of orbital energies of  $3a_1$  and  $1e$  molecular orbitals changes upon allowing d functions to the second period atoms. The difference in experimental IP between these two levels is 0.3–0.9 eV. The  $1e$  level is lower than  $3a_1$  level by about 1.0 eV in the calculation without d functions. ECP calculations without d functions at several bond lengths,  $d(\text{Si-Cl})$ , produce the same ordering in orbital energy level but those with d functions show the level exchange between  $1e$  and  $3a_1$ , as bond length,  $d(\text{Si-Cl})$ , change from  $d=2.049$  to  $d=2.040$  Å. The reliable orderings of these energy levels will certainly require the full optimization of the geometry and probably become definitive only when the large basis set calculations which incorporate correlation effects as well as the relaxation

Table 8. The Results of  $\text{SiCl}_4$  Geometry Optimization

Properties	No d	d
Distance Si-Cl (Å)	2.122	2.006
Total energy (Hartree)	-62.5681	-62.8639
Binding energy (eV)	7.6718	12.6472
Charge on Si	1.070	0.935
Cl	-0.267	-0.234
Overlap population on Si-Cl	0.238	0.370
Orbital energy $1t_1$ (eV)	-13.7446	-13.1079
$3t_2$	-14.0004	-13.9977
$1e$	-14.5882	-14.5093
$1t_2$	-16.6155	-16.7733
$2a_1$	-20.2591	-19.7856
$1t_2$	-30.8690	-30.4798
$1a_1$	-32.3928	-32.1561
Basis	$d(\text{Si-Cl})(\text{Å})$	Binding energy. (eV)
No d	2.122	7.6718
d	2.006	12.6472
3-21G*	2.1232	7.8963

\*Ref.(14)

effects are employed.

Table 8 lists the results of geometry optimization for  $\text{SiCl}_4$ . The d functions to the second period atoms again shorten the bond length,  $d(\text{Si-Cl})$ , by as large as 0.116 Å and increase the binding energy by as much as 4.975 eV. Unfortunately, the comparisons with AE calculations are not available for this molecule.

In summary, we have demonstrated that the numerical results obtained using ECP are essentially the same as those from AE calculations although computational times required for ECP calculations for molecules such as  $\text{SiCl}_4$  are less than one tenth of those for AE calculations. The ECP used in this study might be slightly attractive but sufficiently accurate enough for most purposes. If the discrepancies between ECP and AE calculations substantially increase for heavier atoms, the further improvement in the generating mechanism of ECP will be worthwhile. The study in this direction as well as the further testing of ECP are in progress. The importance of the polarization function and the basis set of the reasonable size is also evident in the present study. The reliable interpretation of the photoelectron spectra will require substantially more sophisticated approach than the present scheme.

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## A Nonlinear Theory for the Brusselator Near the Critical Point Caused by Diffusion

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A nonlinear theory is presented for the fluctuations of intermediates in the Brusselator near the critical point caused by diffusion. The method used is the two time scaling method different from the conventional method in the sense that a slight nonlinear effect is included in the initial time region where the linear approximation is conventionally valid. The result obtained by the nonlinear theory shows that fluctuations close to the critical point approach the value of a stable steady state or deviate infinitely from an unstable steady state, as time goes to infinity, while the linear theory gives approximately time-independent fluctuations. A brief discussion is given for the correlation at a time between fluctuating intermediates when the system approaches a stable steady state.

### Introduction

Recently, much attention<sup>1-6</sup> has been given theoretically and experimentally to chemical reactions with instability since Lotka<sup>7</sup> proposed in 1920 a simple model of autocatalytic chemical reactions which show sustained oscillations in the concentration of the autocatalytic species when open to a flow of matter through the system. Bray<sup>8</sup> discovered this kind of sustained oscillation in an inorganic redox reaction. In 1952, Turing<sup>9</sup> showed that stable spatial patterns can be obtained

when chemical reactions are coupled to the process of diffusion. Thus, he laid the foundation for a biochemical theory of morphogenesis. More recently a famous reaction, called the Belousov-Zhabotinsky reaction, which shows temporal oscillations and spatial patterns has been intensively studied by many authors.<sup>5-6, 10-11</sup>

The model, one of the models with chemical instability, to be considered in this paper is the Brusselator<sup>1</sup>, which was invented and carefully studied by Prigogine and his coworkers in the Brussels school. The reaction mechanism for the