

## Molecular Geometries by the Extended-Hückel Molecular Orbital Method: A Comment

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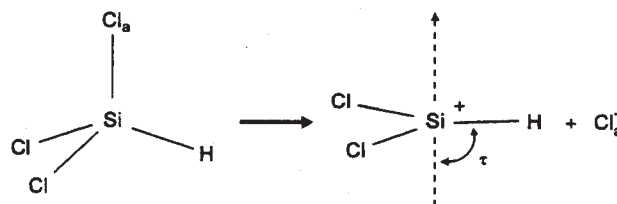
To obtain reliable potential energy curves for neutral molecules with the EHMO-ASED (extended-Hückel molecular orbitals-atom superposition and electron delocalization) method, it may be necessary to apply a self-consistent charge iteration procedure. We discuss the dissociation path  $\text{HSiCl}_3 \rightarrow \text{HSiCl}_2^+ + \text{Cl}^-$  as an example to illustrate this.

The extended-Hückel molecular orbital (EHMO) method<sup>1</sup> in its ASEd form (atom superposition and electron delocalization)<sup>2-4</sup> has proved to be a useful tool for combining the information of the extended-Hückel results with good geometry calculations for many organic and inorganic molecules<sup>5-9</sup> without losing the transparency and well-established prediction capabilities of the original method. The procedure has been successfully extended to infinite systems.<sup>5</sup> In our discussion of the electronic structure of the octasilasesquioxanes  $\text{X}_8\text{Si}_8\text{O}_{12}$  ( $\text{X} = \text{H}, \text{Cl}, \text{CH}_3$ ),<sup>6</sup> we analyzed the reaction path of the experimentally observed substitution reactions  $\text{Si-X} + \text{Y}' \rightarrow \text{Si-Y} + \text{X}'$  ( $\text{X} = \text{H}$  or  $\text{Cl}$ ;  $\text{Y} = \text{D}, \text{Cl}, \text{OSiMe}_3$ , different organic and metallorganic substituents,<sup>10</sup> and  $\text{Co}(\text{CO})_4$ ).<sup>9</sup> We explained in detail what happens when the Si-H bond is stretched, and we discussed that at a certain distance one has to decide between the formation of a  $\text{Si}^{\bullet}\cdots\text{H}^{\bullet}$  radical pair and the formation of an ion pair. A detailed molecular orbital analysis was presented.

We now illustrate on a typical example why it may be necessary to apply a self-consistent charge iteration procedure (SCC) to obtain reliable potential energy curves for neutral molecules with the EHMO-ASED method. The dissociation path  $\text{HSiCl}_3 \rightarrow \text{HSiCl}_2^+ + \text{Cl}^-$  illustrated in Scheme 1 is suitable for this purpose. To analyze this reaction path, we have varied independently the angle  $\tau$  and the Si-Cl and the Si-Cl<sub>a</sub> bond lengths. The index a marks the leaving Cl atom. It turned out that the Si-H bond length can be kept constant without losing information. The calculations have been carried out in three different ways: (A) by keeping the Coulomb terms  $H_{ii}$  constant, (B) the same as (A) but by adding an electrostatic term  $W(R)$ , and (C) by applying the self-consistent charge iteration procedure (SCC) to adjust the  $H_{ii}$  at each point. The SCC procedure is based on the charge dependence of the valence orbital ionization energies of the atoms which allows to iterate on the charges of all atoms in the molecule. For a detailed explanation we refer to refs 4, 11, and 12. The thus obtained minimum potential energy paths in the three-dimensional hypersurface are shown in Figure 1.

The potential energy curve A leads directly to a dissociation of the  $\text{HSiCl}_3$  molecule to  $\text{HSiCl}_2^+ + \text{Cl}^-$ . However,  $\text{HSiCl}_3$  is known as a stable molecule. The reason why A is wrong is easily understood by considering the left side of the correlation diagram in Figure 2. It shows that the filled 3p orbitals of  $\text{Cl}_a^-$  remain at approximately the same energy as the corresponding nonbonding orbitals in the molecule. However, the ionization energy of the free  $\text{Cl}^-$  ion is 3.6 eV. If SCC is applied, curve C results, which looks good and has the minimum at 1.99 Å, close to the experimental value of 2.012 Å.<sup>13</sup> The right side of

SCHEME 1<sup>a</sup>



<sup>a</sup> The coordinates varied independently in the calculations are the Si-Cl<sub>a</sub> and the two Si-Cl bond lengths and the angle  $\tau$  which refers to the two Cl and the H atoms. The Si-H bond length was kept constant at 1.466 Å.<sup>13</sup>

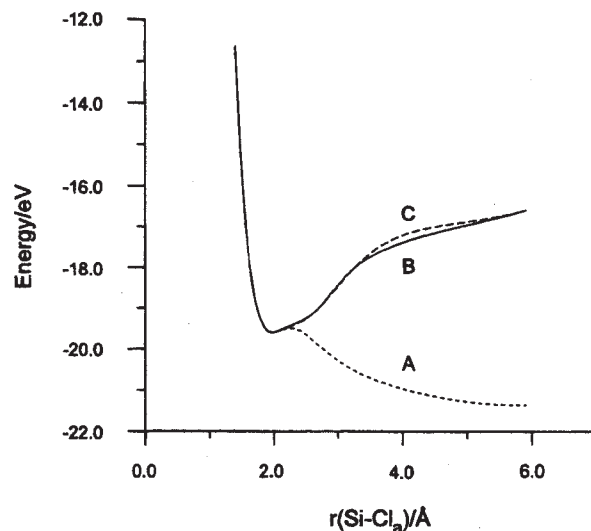
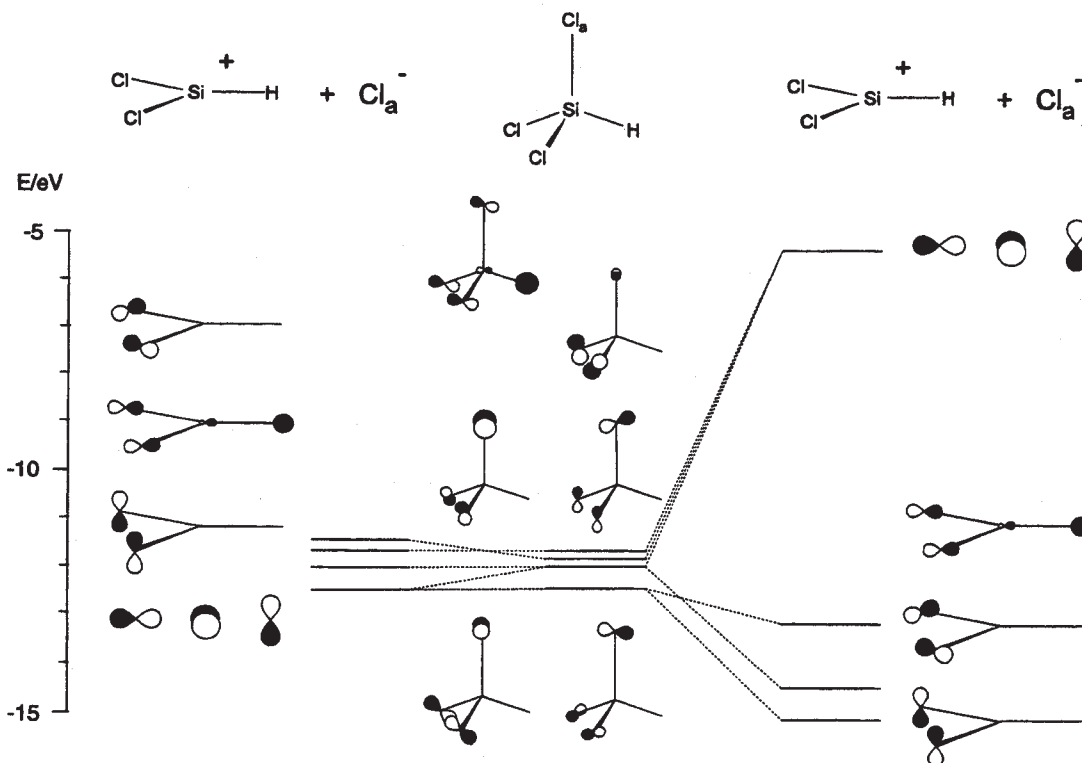


Figure 1. Minimum potential energy path of the three-dimensional energy hypersurface as a function of the internuclear distance Si-Cl<sub>a</sub>. (A)  $E(R)$  has been calculated by keeping all parameters constant. (B) The same as (A) plus the electrostatic term  $W(R)$ . (C) The SCC procedure has been applied at each point.

the correlation diagram in Figure 2 shows the reason why the potential energy curve C is so much better than A. At an Si<sup>•</sup>·Cl<sub>a</sub> distance of 6 Å the 3p(Cl<sub>a</sub>) orbitals are at about -5 eV, and also the 3s(Cl<sub>a</sub>) orbital rises to higher energy. This is physically correct and a consequence of the design of the SCC procedure.

Analysis of the orbitals is often easier if the Coulomb integrals are kept constant along the reaction path, and the SCC calculations can be time-consuming. Electrostatic forces within the EHMO procedure have been described many years ago<sup>14</sup> and have been discussed recently in a computational study on the formation of metal oxide diatomics and clusters.<sup>15</sup> One can therefore try to obtain reasonable potential energy curves by

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**Figure 2.** Correlation diagram for the reaction path  $\text{HCl}_2\text{Si}-\text{Cl}_a \rightarrow \text{HCl}_2\text{Si}^+ + \text{Cl}_a^-$ . Left: all parameters were kept constant. Right: the SCC procedure has been applied at each point.

adding the electrostatic interaction term

$$W(R) = -\frac{Q_X Q_Y}{4\pi\epsilon} \int_{d_0}^R \frac{dr}{r^2} = -\frac{Q_X Q_Y}{4\pi\epsilon} \left( \frac{1}{d_0} - \frac{1}{R} \right), \quad R \geq d_0$$

$Q_X$  and  $Q_Y$  are the total EHMO charges of the fragments  $X$  and  $Y$ , respectively, obtained from Mulliken population analysis.<sup>16</sup>  $d_0$  is the sum of the orbital radii calculated from the Slater exponents (see eqs 13 and 14 in ref 2), and  $\epsilon$  is the permittivity chosen as vacuum permittivity  $\epsilon_0$  in our calculations. The potential energy curve B, which has been obtained by adding  $W(R)$  to the EHMO-ASED energy  $E(R)$ , nearly coincides with C at short and at long distances. Both potential curves converge correctly at infinite  $r(\text{Si}-\text{Cl}_a)$ . This means that if little computational effort is important, one can try the simple electrostatic approach. Analysis of the orbitals along the reaction pathway will always help to decide whether the calculations are physically reliable or whether a more involved procedure is advisable.

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## Appendix

The molecular orbital calculations have been carried out by the EHMO-ASED procedure explained in ref 2 with the ICONC&INPUTC Fortran Program.<sup>4</sup> The parameters used are listed in Table 1.  $N$  stands for the number of valence electrons,  $n_s$  and  $n_p$  are the principal quantum numbers of the  $s$  and  $p$  orbitals, respectively,  $\zeta_s$  and  $\zeta_p$  are the Slater exponents, and  $H_{pp}$  and  $H_{ss}$  are the Coulomb integrals, which have been obtained by charge iteration at equilibrium geometry with the parameters

**TABLE 1: EHMO Parameters**

atom	$N$	$n_s$	$\zeta_s$	$H_{ss}/\text{eV}$	$n_p$	$\zeta_p$	$H_{pp}/\text{eV}$
Si	4	3	1.7	-19.57	3	1.7	-11.67
Cl	7	3	2.18	-23.78	3	1.73	-12.44
H	1	1	1.3	-11.57			

given in refs 4 and 11. Curve C in Figure 1 was obtained by applying charge iteration at each geometry. Standard  $\kappa = 1.0$  and  $\delta = 0.35 \text{ \AA}^{-1}$  were applied, with the exception of the Si-H bond for which  $\kappa = 0.75$  was used.

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