CNDO methods all predict an increase in barrier in going from NH_2Cl to $N(CH_3)_2Cl$, while INDO–A and INDO–B predict a decrease. A barrier decrease would seem more likely because of steric hindrance in the pyramidal conformation due to the greater size of methyl groups as opposed to H atoms. (Compare NH_3 at 5.8 kcal/mol with $NH(CH_3)_2$ at 4.4 kcal/mol.)

While the CNDO method as parametrized by Mislow has been shown to have generally good predictive power, INDO–A seems to give more realistic results in the case of alkylamines and chloroalkylamines. It is for this reason that INDO–A has been chosen for the theoretical studies of these systems to be reported in subsequent papers.[21,22]

Calculational Details

One-center integrals for calculation of F^2 and G^1 values were obtained through use of Stevens' Independent Integrals Package[25] running on a Univac Series 70/46 computer.

Cartesian coordinates for the MO calculations were obtained through use of "COORD" (time sharing version)[26] running interactively on a DEC System 1050 computer.

The CNDO and INDO calculations were performed with a modified version of CNINDO[27] running on a Univac Series 70/46 computer.

Acknowledgment. The authors are grateful to the Worcester Area College Computation Center for a grant of computer time.

[25] R. M. Stevens, "Independent Integrals Package," Quantum Chemistry Program Exchange, Program No. 161.

[26] P. E. Stevenson and J. E. Merrill, "COORD (time sharing version)," Quantum Chemistry Program Exchange, Program No. 186.

[27] P. A. Dobosh, "CNINDO: CNDO and INDO Molecular Orbital Program (FORTRAN IV)," Quantum Chemistry Program Exchange, Program No. 141.

An *ab Initio* Study of the Role of d Orbitals in Chlorosilane

James M. Howell and John R. Van Wazer*

Contribution from the Department of Chemistry, Vanderbilt University,
Nashville, Tennessee 37235. *Received November 6, 1973*

Abstract: *Ab initio* LCAO–MO–SCF computations of the wave function of chlorosilane have been carried out in a moderately sized, uncontracted, Gaussian basis set with and without an appropriate manifold of d orbitals being allowed to the silicon and/or the chlorine atom. Electron-density difference plots show that conferring d character upon either the silicon or the chlorine has about the same effect on the detailed transfer of charge between the chlorine and silicon atoms, although the usual interpretation in terms of the contributing atomic orbitals leads to the conclusion that, when d character is allowed only to the silicon, there is a transfer of charge from the chlorine but, when it is allowed only to the chlorine, the effect is essentially just a polarization of this atom. The calculated variations in the orbital energies of the core electrons upon allowing or disallowing d character to the silicon or chlorine atoms are interpreted in terms of changes in the electrostatic potential in the core region.

Although a relatively important role has long been assigned[1] to d orbitals in the covalent chemistry of atoms of the third period, it has only been recently that the problem of d-orbital participation has been attacked quantitatively. Molecular optimization has shown[2,3] that the d contributions to the linear combination of atomic orbitals (LCAO) making up a self-consistent field (SCF) wave function involves 3d orbitals exhibiting radii which are approximately the same as those of the 3s and 3p orbitals instead of the much larger 3d radii obtained from promoting a 3s or 3p electron into a 3d orbital in an atomic calculation. Furthermore, even for coordination numbers five and six, an sp description is sufficient[4] for the molecular orbitals, and indeed LCAO–MO–SCF calculations[5,6] on molecules such as PF_5 illustrate that molecular-orbital charge distributions obtained using a linear combination of s, p, and d atomic orbitals differ only in fine details from those restricted to s and p orbitals for all of the constituent atoms including those of the third period.

An important role of d orbitals used in the description of atoms of both the second and third periods is as polarization functions,[7] with no net change occurring in the charge of the atom to which the d orbital has been allowed, since whatever electron density were to be gained by the d orbitals would be lost by the s and p orbitals of the same atom. The commonly discussed p_π–d_π electronic feedback[8–10] where the d orbitals on a third period atom accept charge from appropriate orbitals of neighboring atoms has been demonstrated in

[1] *E.g.*, L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, Chapter 7.

[2] J.-B. Robert, H. Marsmann, L. J. Schaad, and J. R. Van Wazer, *Phosphorus*, **2**, 11 (1972).

[3] J. R. Van Wazer and I. Absar, *Advan. Chem. Ser.*, **No. 110**, 20 (1972).

[4] R. E. Rundle, *J. Amer. Chem. Soc.*, **85**, 112 (1963); *Rec. Chem. Progr.*, **23**, 195 (1962); *Acta Crystallogr.*, **14**, 585 (1961); *Surv. Progr. Chem.*, **1**, 81 (1963); R. C. Hach and R. E. Rundle, *J. Amer. Chem. Soc.*, **73**, 4321 (1951).

[5] A. Strich and A. Viellard, *J. Amer. Chem. Soc.*, **95**, 5574 (1973); J. M. Howell and J. R. Van Wazer, *Inorg. Chem.*, in press; see also ref 6b; P. C. Van der Voorn and R. Drago, *J. Amer. Chem. Soc.*, **88**, 3255 (1966); P. C. Van der Voorn, K. F. Purcell, and R. Drago, *J. Chem. Phys.*, **433**, 3457 (1965).

[6] (a) A. Rauk, L. C. Allen, and K. Mislow, *J. Amer. Chem. Soc.*, **94**, 3035 (1972); (b) K. Issleib and W. Gründler, *Theor. Chim. Acta*, **8**, 70 (1967); (c) R. Hoffmann, J. M. Howell, and E. L. Mutterties, *J. Amer. Chem. Soc.*, **94**, 3047 (1972).

[7] C. A. Coulson, *Nature (London)*, **221**, 1106 (1969).

[8] L. Pauling, *J. Phys. Chem.*, **56**, 361 (1952).

[9] H. H. Jaffé, *J. Phys. Chem.*, **58**, 185 (1954).

[10] D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

Table I. Some Overall Properties Calculated for Chlorosilane

		(3/95/95) basis set plus		
Property	No d's	d on Si	d on Cl	d on Si and Cl
Total energy (au)	−749.4829	−749.5767	−749.5032	−749.5888
Potential energy (au)				
Nuclear	+86.5223	+86.5223	+86.5223	+86.5223
One-electron	−1957.9463	−1958.2432	−1958.2700	−1958.5064
Two-electron	+372.3994	+372.7790	+372.7213	+373.0262
Kinetic energy (au)	+749.5417	+749.3652	+749.5231	+749.3691
Virial ratio	−1.99992	−2.00028	−1.99997	−2.00029
Binding energy[a] (eV)	9.00	11.56	9.56	11.89
Dipole moment[b] (D)	−0.889	−0.366	−0.246	+0.115
Charge[c] on H (e)	−0.061	+0.085	−0.077	+0.080
Charge on Si (e)	+0.308	−0.298	+0.408	−0.211
Charge on Cl (e)	−0.124	+0.043	−0.177	−0.029
Si–H overlap pop. (e)	0.689	0.810	0.696	0.811
Si–Cl overlap pop. (e)	0.610	0.863	0.651	0.890

[a] The binding energy is the difference between the sum of the total energies of the constituent atoms and the total molecular energy, with 1 au = 27.211 eV and no correction for molecular extracorrelation energy. The experimental binding energy (which includes correlation) is 14.0 eV (see ref 2 for method of calculation). [b] The experimental dipole moment is 1.28, according to L. O. Brockway and I. E. Coop, *Trans. Faraday Soc.*, **34**, 1429 (1938). A negative sign for the calculated dipole moment means that the negative end of the molecule is at the chlorine atom (1 au = 2.542 D). [c] The charge on an atom is obtained by subtracting the Mulliken gross population of that atom from its atomic number: R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 2338, 2343 (1955).

LCAO–MO–SCF calculations.[11–13] In this case, the occupancy of the s- and p-type orbitals of the third period atom remain relatively unchanged when d character is allowed to a pure sp representation. It is often difficult to differentiate cleanly between the polarization and the electron-acceptance roles of the d orbitals, since in practice these two effects are usually intermingled and may differ only in a formal sense.

The chlorosilane molecule, H_3SiCl, was chosen for the study presented herein since according to common chemical lore the greater electron-withdrawing ability of the chlorine as compared to the silicon atom should lead to considerable transfer of charge from the chlorine back to the silicon when d orbitals were allowed to the latter but to essentially no charge shift upon allowing d orbitals to the chlorine. The H_3SiCl molecule offers a good test of whether the results from *ab initio* LCAO–MO–SCF calculations do indeed bear out the usual concepts of the role of d orbitals in the chemistry of third-period atoms exhibiting tetrahedral coordination.

Calculational Details

The SCF calculations described herein were carried out on a CDC-6600 computer using a recently modified version of the POLYATOM program.[14] Following the practice employed in a number of our previous studies, we have used three s-type atom-optimized Gaussian exponents[15] to describe each hydrogen (H exponents: 4.239, 0.6577, 0.1483) and nine s plus five p, with or without a single d exponent for characterizing the silicon and the chlorine. (Si exponents: s type 7609.04, 1177.63, 275.750, 78.3797, 24.4594, 4.88498, 1.80323, 0.34339, and 0.126506; p type 78.3466, 18.3719, 5.46549, 1.66712, and 0.172716; d type[16] 0.35. Cl exponents: s type 13739.19, 2035,616, 482.1296, 136.5505, 41.56111, 9.61859, 3.54566, 0.881129, and 0.284524; p type 122.3800, 28.4600, 8.4250, 2.74342, and 0.37178; d type[16] 0.74.) All basis functions were uncontracted and the d set of Gaussian functions consisted of the usual five spherical-harmonic functions.

Planar electron-density maps were obtained from one program[17] and converted to a three-dimensional representation by another.[18] The Mulliken population analyses were calculated by a program written by I. Absar and the one-electron properties were obtained from a revised version of the Kortzeborn properties program.[19] The C_{3v} geometry of chlorosilane used in these calculations was obtained[20] from microwave spectroscopy: Si–H = 1.476, Si–Cl = 2.049 Å; ∠HSiCl = 109.0°.

Discussion

In order to identify the effects due to adding d orbitals, it seemed desirable to carry out four different calculations on chlorosilane. These consisted of having no d orbitals, *i.e.*, using a (3/95/95) basis set,[15] allowing a d set to the silicon (3/951/95), alternatively allowing d to the chlorine (3/95/951), or giving d character to both the silicon and the chlorine (3/951/951). Some of the results from these four calculations are summarized in Table I from which it can be seen that allowing a d manifold to the silicon was more effective in lowering the total energy than allowing it to the chlorine. Of

---

(11) H. Marsmann, L. C. D. Groenweghe, L. J. Schaad, and J. R. Van Wazer, *J. Amer. Chem. Soc.*, **92**, 6107 (1970).

(12) I. Absar and J. R. Van Wazer, *J. Amer. Chem. Soc.*, **94**, 2382 (1972).

(13) I. Absar and J. R. Van Wazer, *J. Amer. Chem. Soc.*, **94**, 6294 (1972).

(14) A modification by R. A. Gangi of the program POLYATOM written by D. B. Neumann, H. Basch, R. L. Kornegay, L. C. Snyder, J. W. Moskowitz, C. Hornback, and S. P. Liebmann. Version 2 of this program may be obtained from Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Ind. 47401.

(15) The usual description of a Gaussian basis set is employed in this paper in the order H/Si/Cl; *e.g.*, (3/95/951) means that three s-type exponents are used to described each hydrogen, nine s and five p for the silicon, and nine s, five p, and one d for the chlorine.

(16) I. Absar and J. R. Van Wazer, *Chem. Phys. Lett.*, **11**, 310 (1971).

(17) W. E. Palke, An Electron-Density Plot Program, later modified by T. H. Dunning at The California Institute of Technology and again changed by H. Marsmann and J. M. Howell in our laboratory.

(18) D. L. Nelson, "Perspective Plotting of Two-Dimensional Assays—PLOT3D, A Computer Program for a Digital Plotter," University of Maryland, Department of Physics and Astronomy, College Park, Md. 20742.

(19) R. N. Kortzeborn, "Expectation Values Over Mulliken Gaussian Wave Functions," Report RJ-577, IBM Research Laboratories, San Jose, Calif., June 12, 1969.

(20) C. Newman, J. K. O'Loane, S. R. Polo, and M. K. Wilson, *J. Chem. Phys.*, **25**, 855 (1956).

Table II. Orbital Energies and Mulliken Populations for the Valence Shell of H_3SiCl

Orbital[a]	Predominant character[b]	Energy[c] (au)	Gross atomic populations Si	H	Cl	Overlap population Si–H	Si–Cl
4e[d]	Cl $n_\perp$ + (Si–Cl)π^*	−0.3865	0.0098	0.2081	3.3656	0.0088	−0.0126
Δ_{Si}[e]		*−0.0120*[f]	*+0.3270*	*−0.0385*	*−0.2114*	*+0.0893*	*+0.0156*
Δ_{Cl}		*+0.0054*	*+0.0012*	*−0.0050*	*+0.0140*	*+0.0016*	*−0.0028*
$\Delta_{Si,Cl}$		*−0.0071*	*+0.3140*	*−0.0418*	*−0.1884*	*+0.0867*	*+0.1464*
9a	(Si–Cl)σ + Cl $n_\parallel$	−0.4393	0.5400	0.0636	1.2692	0.0172	0.2550
Δ_{Si}		*−0.0089*	*+0.0589*	*−0.0086*	*−0.0331*	*+0.0181*	*+0.0115*
Δ_{Cl}		*−0.0045*	*−0.0174*	*+0.0022*	*+0.0108*	*+0.0065*	*+0.0357*
$\Delta_{Si,Cl}$		*−0.0091*	*+0.0352*	*−0.0036*	*−0.0244*	*+0.0208*	*+0.0460*
3e	(Si–H)σ + (Si–Cl)π	−0.5156	1.7312	0.5937	0.4876	0.4521	0.1710
Δ_{Si}		*+0.0088*	*+0.2084*	*−0.0974*	*+0.0838*	*+0.0159*	*+0.0072*
Δ_{Cl}		*+0.0082*	*−0.0464*	*+0.0172*	*−0.0052*	*+0.0001*	*+0.0012*
$\Delta_{Si,Cl}$		*+0.0143*	*+0.1912*	*−0.0893*	*+0.0768*	*+0.0193*	*+0.0072*
8a	(Si–H)σ + (Si–Cl)σ^*	−0.7543	1.1861	0.1934	0.2338	0.2079	−0.0726
Δ_{Si}		*+0.0297*	*+0.0063*	*−0.0020*	*−0.0003*	*+0.0002*	*+0.0540*
Δ_{Cl}		*+0.0062*	*−0.0149*	*+0.0009*	*+0.0120*	*−0.0007*	*+0.0302*
$\Delta_{Si,Cl}$		*+0.0327*	*−0.0036*	*−0.0060*	*+0.0216*	*−0.0031*	*+0.0817*
7a	(Si–Cl)σ + Cl $n_\parallel$	−1.0865	0.2257	0.0021	1.7681	0.0026	0.2695
Δ_{Si}		*−0.0015*	*+0.0033*	*+0.0008*	*−0.0057*	*+0.0001*	*+0.0311*
Δ_{Cl}		*+0.0133*	*−0.0222*	*+0.0001*	*+0.0218*	*+0.0001*	*−0.0234*
$\Delta_{Si,Cl}$		*+0.0078*	*−0.0209*	*+0.0004*	*+0.0196*	*−0.0001*	*+0.0008*

[a] Note that the values listed for an e symmetry represent the sum of a degenerate pair; *i.e.*, they correspond to an occupancy of four electrons. [b] The major contribution(s) to the delocalized orbital, with $n_\perp$ and $n_\parallel$ referring to lone-pair electronic charge respectively oriented perpendicular to or along the Si–Cl bond axis. [c] 1 au = 27.211 eV. [d] The first line for each orbital presents the values calculated for the (3/95/95) basis set. [e] Δ_{Si} stands for the (3/951/95) minus the (3/95/95) values, Δ_{Cl} for the (3/95/951) minus the (3/95/95) values, and $\Delta_{Si,Cl}$ for the (3/951/951) minus the (3/95/95) values. [f] All differences are shown in italics.

course, allowing d character to both silicon and chlorine caused the largest decrease in total energy, with this decrease being only 7% smaller than the sum of the decreases in energy upon adding the d character separately to the silicon and chlorine.

The energy due to the interelectronic repulsion (the two-electron potential energy) increases upon adding d orbitals, with the least increase being found for d on chlorine and the greatest for d on both the silicon and the chlorine. Conversely, the potential energy dealing with the attraction between the nuclei and the electrons (the one-electron potential energy) is found to decrease in the same manner upon allowing d character. These two observations as well as their reflection in the kinetic energy of the electrons indicate that supplying d character to chlorosilane causes the electrons to draw in toward the internuclear regions, with this effect being least for the d on the chlorine and the greatest for d on both the silicon and chlorine atoms. This surmise is in accord with the changes observed for both the Si–H and Si–Cl overlap populations.

Referring to the no-d case of Table I, the silicon appears to be electropositive to both the chlorine and hydrogen and the charge apportionment is about what would be expected from the often-quoted electronegativity values of 1.8 for Si, 2.1 for H, and 3.0 for Cl. It is interesting to note that the empirical relationsships[21,22] based on nuclear quadrupole coupling data connecting the ionic character of bonds with the difference in electronegativity between the bonded atoms lead to a much higher estimated charge on the silicon and chlorine atoms of chlorosilane than those presented for the (sp) calculation in Table I. However, the empirical relationships[23,24] based on dipole moments are reasonably satisfactory, with the best agreement in charge values (−0.05 for H, +0.39 for Si, and −0.24 for Cl) coming from the equation of Hannay and Smyth[24]—an equation which we have favored[25] for use in atomic-charge estimations.

Inclusion of d character on the silicon causes this atom to become negative with respect to both the hydrogen and chlorine. For all of the atoms, there is considerably less change in charge when allowing d character to the chlorine. In this latter case there is, not surprisingly, a shift of electrons away from the silicon with an equal gain in electronic charge by the chlorine and the three hydrogens taken as a group. With d character allowed to both the silicon and the chlorine, the results are intermediate, with the changes in gross charge upon allowing d character being approximately additive. Note that allowing d character to the chlorine has little effect on the overlap populations whereas they are increased considerably by allowing d atomic orbitals to the silicon, with the differences upon allowing d character being again nearly additive. These changes in the overall electronic populations are indicative that charge feedback is the major contributor when d is allowed to the silicon, whereas polarization and related effects dominate when d orbitals are afforded the chlorine atom.

The two quantities in Table I which may be compared to experiment are the binding energy and the dipole moment. The difference of *ca.* 2 eV between the experimental binding energy and that calculated for the case with d orbitals on both the silicon and the chlorine indicates that the correlation energy for this description of the H_3SiCl molecule is unusually small. As is often the case, the calculated dipole moment is lowered by

(21) B. P. Dailey and C. H. Townes, *J. Chem. Phys.*, **23**, 118 (1955).

(22) B. P. Dailey, *Discuss. Faraday Soc.*, No. **19**, 255, 274 (1955); W. Gordy, *ibid.*, No. **19**, 14 (1955).

(23) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(24) N. B. Hannay and C. P. Smyth, *J. Amer. Chem. Soc.*, **68**, 171 (1946).

(25) For example, see W. E. Morgan, W. J. Stec, R. G. Albridge, and J. R. Van Wazer, *Inorg. Chem.*, **10**, 926 (1971); R. Nordberg, H. Brecht, R. G. Albridge, A. Fahlman, and J. R. Van Wazer, *ibid.*, **9**, 2469 (1970).

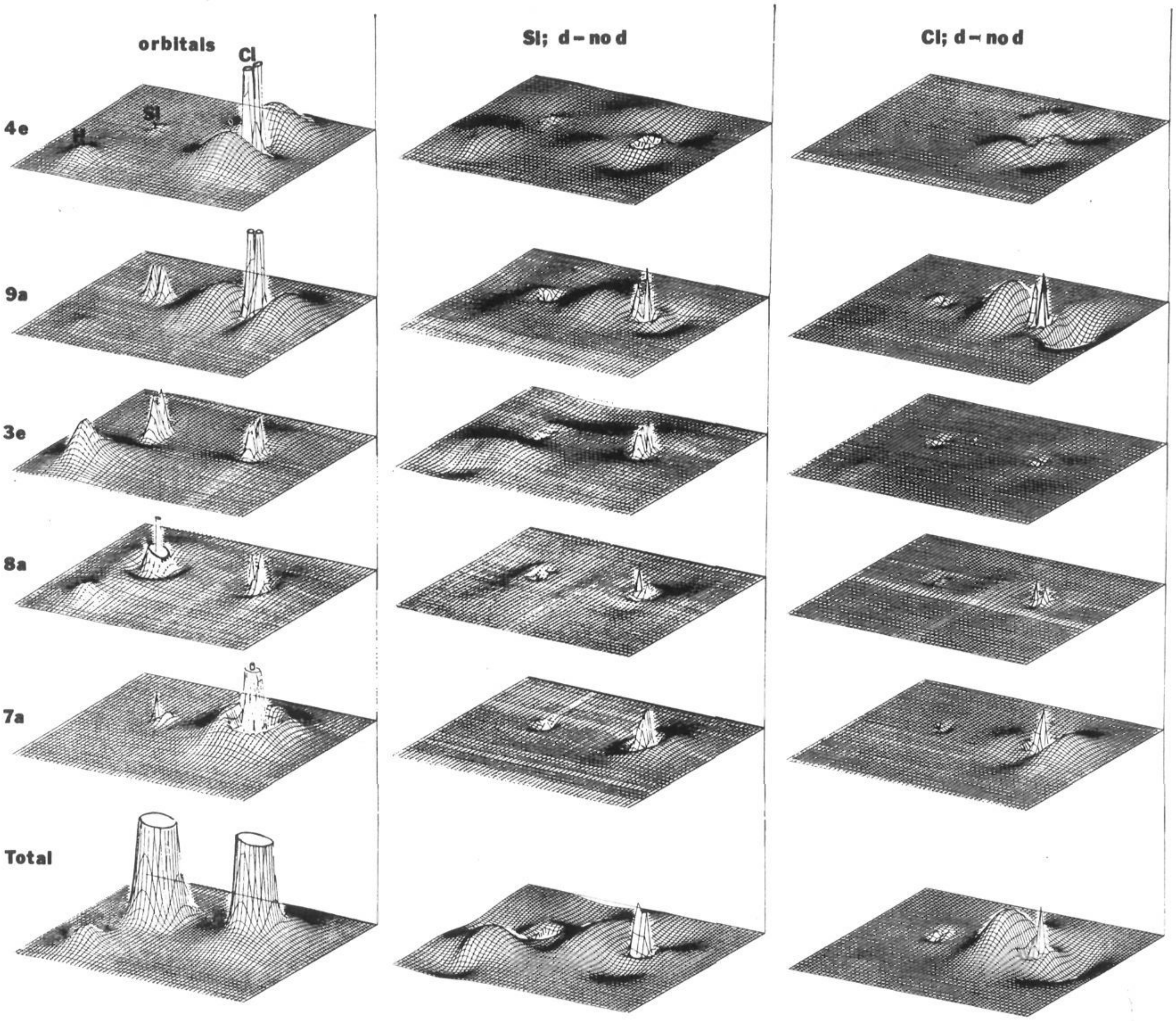


Figure 1. Electron-density plots for chlorosilane in the plane containing the Si–Cl bond and one of the hydrogen atoms. The left-hand plot shows the electron densities of the seven valence orbitals, with the diagrams for the e symmetry sets representing the degenerate pair. The remaining two plots, in which the perpendicular electron-density scale is magnified fivefold, represent electron-density difference plots corresponding to the addition of d character to the silicon (middle plot) and to the chlorine (right-hand plot).

the addition of d character to the molecule. Such a result is in accord with the deductions drawn above from the changes in the potential energies.

Chlorosilane has C_{3v} symmetry allowing a clear distinction to be made between orbitals of σ-like and π-like symmetry with respect to the Si–Cl bond. In discussing the results of these calculations, the terms σ, π, and δ will be employed as molecular quantum numbers, being referenced to the C_{3v} axis of the molecule. Since the molecule was set in the Cartesian coordinate system with the silicon at the origin and the chlorine on the positive z axis, the p_x and p_y orbitals for both the silicon and chlorine atoms must exhibit equal occupations, and they will be called the p_π and $p_{\pi'}$ atomic orbitals, respectively. Likewise, p_z will be denoted as p_σ, and d_{z^2} as d_σ. The occupation of d_{xz} must equal that of d_{yz}, and these correspond to the pair of d_π atomic orbitals for either the silicon or chlorine, while the $d_{x^2-y^2}$ and d_{xy} are also necessarily equally occupied and are designated as d_δ atomic orbitals.

In Table II the valence-orbital energies and Mulliken-population data are shown, along with a classification for the bonding characteristics, for each orbital. At the left of Figure 1 are displayed electron-density plots for the valence orbitals of H_3SiCl and the form that each orbital has taken will now be rationalized with the aid of the interaction diagram presented in Figure 2. At the left of Figure 2 are shown the appropriate valence-shell atomic orbitals of silicon while at the right are the orbitals of chlorine as well as the symmetry-adapted combination of the three hydrogen 1s atomic orbitals. The energy ordering and approximate spacing is derived from one-configuration atomic calculations on the individual atoms.

The lowest valence molecular orbitals, 7a, is derived primarily from the chlorine 3s slightly polarized toward the silicon 3s orbital (with which it is bonding) by the addition of some chlorine 3p character. The 8a orbital is derived from the mixing of the silicon 3s orbital with a combination of the three hydrogens. The high-lying silicon 3p orbital mixes in bonding relative to the hydrogens resulting in a polarization of the sp hybrid toward the hydrogens. Furthermore, there is a small contribution to the 8a orbital from the chlorine orbitals. In accord with their relative positions as shown in Figure 2 the higher lying chlorine 3p orbital mixes into the 8a

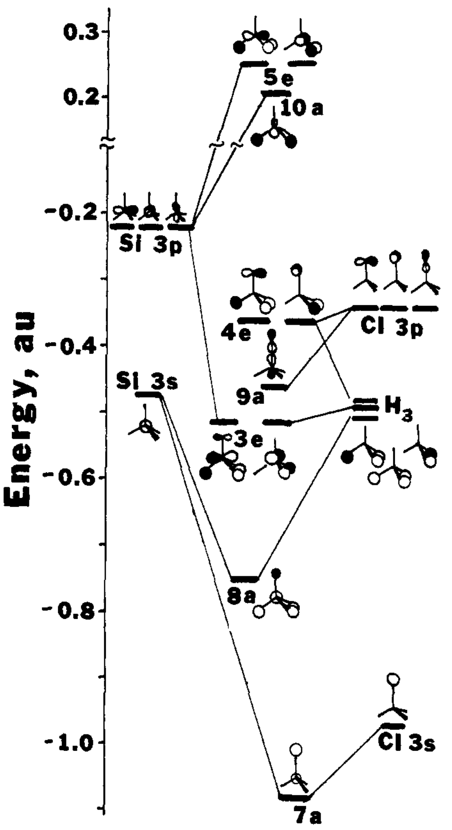


Figure 2. Molecular-orbital diagram showing the construction of the valence orbitals of H_3SiCl from the silicon and chlorine atoms and the set of three hydrogen atoms.

orbital in a bonding fashion while, on the other hand, the lower lying chlorine 3s orbital is incorporated antibonding relative to the silicon hybrid. In our calculations, the latter effect dominates so that there is a net antibonding interaction between the silicon and the chlorine. As shown in Figure 2, in accord with the density plots of Figure 1, the hybrid on chlorine is directed toward the lone-pair region.

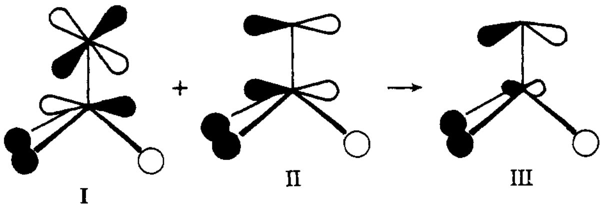
The highest filled molecular orbital of σ symmetry, 9a, consists primarily of the chlorine $3p_\sigma$ orbital stabilized by the higher lying silicon $3p_\sigma$ orbital. A small chlorine 3s component, antibonding to the silicon, serves to polarize the chlorine toward the lone-pair region.

We now turn to the π orbitals (of e symmetry) which occur in degenerate pairs. The lowest pair of the valence shell, the 3e set, is composed primarily of the silicon $3p_\pi$ orbitals bonding with the appropriate combinations of the three hydrogen 1s orbitals and is stabilized by the inclusion of a small amount of $3p_\pi$ orbitals. The next member of the e manifold, the 4e pair, consists of the highest filled orbitals of the molecule. As expected there is a nodal surface between the silicon and the chlorine resulting in an antibonding contribution to the (Si–Cl) overlap population. Of course, the next higher member of the e manifold (a virtual, unfilled orbital) will have one more nodal surface and is characterized as being an Si–H σ^* orbital. This σ^* orbital will be referred to below.

The effect of allowing d orbitals to the description of either the silicon or the chlorine is now discussed. Within the a manifold, only one d function will participate, d_σ. In the 7a orbital the d_σ orbital of silicon accepts a large amount of charge from the p_σ component of the chlorine and little from the chlorine 3s orbital thereby reducing the polarization of the chlorine hybrid, resulting in the (Si; d–no d) difference map of Figure 1 which shows a charge shift toward the chlorine lone-pair region. There is also the expected buildup of density at the silicon atom for this orbital upon allowing d character to the silicon. The (Si–Cl) overlap population of orbital 7a has increased, as shown in Table II, largely due to the increased delocalization of this highly polar molecular orbital. When d orbitals were allowed to the chlorine instead of the silicon, a difference map is produced which is clearly consistent with charge acceptance by the chlorine d_σ orbital bonding with the silicon hybrid: two peaks along the Si–Cl σ axis and two slight troughs perpendicular to the bond axis. Interestingly, the chlorine d_σ orbital causes (as does the silicon d_σ orbital) a polarization of charge toward the σ lone-pair region and this is again associated with a decrease in the participation of the chlorine $3p_\sigma$ orbital. A naive explanation for this is obtained by reasoning that the chlorine 3s component of orbital 7a was polarized toward the silicon partly because of the bonding interaction of the chlorine orbitals with the small concentration from silicon. However, when the silicon contribution to the orbital was reduced by means of the chlorine 3d orbitals accepting charge, so was the need for polarization. A decrease in the Si–Cl overlap population is noted in Table II due to an increase in the polarity of an already highly polar bond.

Orbital 8a shows the relatively small but expected results of charge being accepted into the $3d_\sigma$ orbitals of the silicon or the chlorine. In orbital 9a the effect of the silicon d_σ orbital is to build up charge in the Si–Cl bonding region. This is accomplished primarily by populating both the d_σ and the p_σ orbitals. The chlorine d_σ orbital accomplishes the same thing even more dramatically through polarization of the chlorine 3p orbital toward the silicon.

Turning now to d orbital participation in the e manifold, introduction of silicon d character causes a shift of density in the 3e orbitals from the hydrogens into the silicon atomic orbitals, mainly the d_δ set, and this in turn leads to a slight shift of electronic charge toward the chlorine, as shown in Figure 1. However, when the d character is allowed to the chlorine instead of the silicon there is a flow of charge primarily away from the silicon and toward the hydrogen atoms. This effect is noteworthy in that, although basis functions were added to the chlorine, the charge is seen to flow away from the chlorine toward the hydrogen atoms. This behavior may be attributed to the low-lying unoccupied (Si–H)σ^* bonds corresponding to the 5e pair of virtual orbitals. These orbitals are energetically lower than the chlorine d set with which they can mix to give the function shown schematically as I. This can then inter-



(1)

Table III. Chlorosilane Core-Orbital Energies and the Energy Shifts Caused by Introduction of d Character

Calcd	1a Cl "1s"	2a Si "1s"	3a Cl "2s"	4a Cl "$2p_\sigma$"	1e Cl "$2p_\pi$"	5a Si "2s"	6a Si "$2p_\sigma$"	2e Si "$2p_\pi$"
$\epsilon_{\text{no d}}$[a]	−104.8280	−68.9040	−10.5616	−8.02034	−8.0160	−6.2638	−4.3600	−4.3595
Δ_{Si}[b]	*−0.0266*[c]	*+0.0468*	*−0.0221*	*−0.0217*	*−0.0231*	*+0.0506*	*+0.0497*	*+0.0499*
Δ_{Cl}	*+0.0105*	*+0.0103*	*+0.0111*	*+0.0108*	*+0.0100*	*+0.0117*	*+0.0123*	*+0.0110*
$\Delta_{\text{Si,Cl}}$	*−0.0165*	*+0.0533*	*−0.0121*	*−0.0118*	*−0.0137*	*+0.0580*	*+0.0574*	+0.0569

[a] The first line for each orbital presents the values calculated for the (3/95/95) basis set. Energies given in au. [b] Δ_{Si} stands for the (3/951/95) minus the (3/95/95) values, Δ_{Cl} for the (3/95/951) minus the (3/95/95) values, and $\Delta_{\text{Si,Cl}}$ for the (3/951/951) minus the (3/95/95) values. [c] All differences are shown in italics.

act with the 3e set, a member of which is shown as II, to give a composite function, III, where there is a stabilizing interaction between the silicon p orbital and the chlorine d orbital to yield a decrease in the silicon density and an increase in the electronic charge on the hydrogens.

The 4e set which primarily encompasses the chlorine lone pairs perpendicular to the Si–Cl bond axis undergoes similar perturbation by the d orbitals with the silicon d_π orbitals accepting large amounts of charge with the (Si–Cl) overlap population being accordingly increased. The participation by the chlorine d orbitals within the 4e set is small, relative to that of silicon, because the silicon d_π orbitals can bond effectively with both the hydrogens and the chlorine lone-pair orbitals simultaneously while the chlorine d_π orbitals can bond only with silicon which, in the sp calculation has very little density in the 4e set (Table II and Figure 2). In fact we note that the incorporation of chlorine d orbitals appears to be governed by considerations of charge reorganization as opposed to bond formation since the chlorine d orbitals are incorporated antibonding relative to the silicon p orbitals.

Since we have C_{3v} symmetry, the σ and π systems are unambiguously separated and we may divide up the effects of each of the d orbital sets in terms of the σ and π manifolds. Although the silicon d orbitals accept much more charge in the π orbitals than in the σ (0.5354 e *vs.* 0.0685 e), the increase in the (Si–Cl) overlap population is comparable: 0.1632 e for the π system and 0.1150 for the σ. The chlorine d orbitals, as expected, accept charge more effectively in the σ manifold, 0.0446 e, than in the π, 0.0088. The (Si–Cl) overlap population is strengthened in the σ orbitals, 0.0425 e, and weakened slightly in the π set, −0.0016 e.

The d_π orbitals of the silicon are more efficient than those of chlorine in accepting charge even though they probably lie higher in energy than those of chlorine. There are two possible reasons for this: of the electron donating functions, the chlorine lone pairs with which the silicon d orbitals interact lie higher in energy and thus are more available for interaction than the (Si–H) orbitals; and secondly the 4e set is more localized to the chlorine than is the 3e set to the silicon which will also favor delocalization by the silicon d orbitals.

In summary, it should be noted from the second and third columns of Figure 1 that, in the Si–Cl portion of the chlorosilane molecule, allowing d character to either the silicon or chlorine atoms has the same general effect with respect to the redistribution of charge in each molecular orbital. However, when d character is allowed to the silicon, there are additional charge-transfer effects involving the hydrogens, which are the other nearest neighbor atoms of the silicon. Even though both the mathematical- and common-language descriptions imply a different behavior upon supplying d functions to silicon as opposed to chlorine, it is clear from Figure 1 that the overall process is simply one of reducing molecular charge-polarization in the molecule.

Inner Orbitals and the Electric Potential. Table III presents the calculated energy shifts that occur in the core orbitals when the d orbitals are introduced into the calculation. The shifts caused by the silicon d orbitals appear to be in agreement with simple electrostatic arguments that increasing the electron density about the silicon nucleus at the expense of the chlorine atom will cause the silicon core orbitals to increase in energy and those of the chlorine to decrease. However, a problem arises when the effect of the chlorine d orbitals are considered; both the silicon and the chlorine core orbitals increase in energy, even though the silicon has become more positive in the Mulliken analysis.

To investigate this further, the electrostatic potential due to the various molecular orbitals was calculated at the silicon and chlorine nuclei. When summed over all of the molecular orbitals, a good correlation was observed between the shifts in the (total) electrostatic potential occasioned by the introduction of the d orbital sets and the concomitant shifts in the core-orbital energies. Thus, for the basis sets employed herein, the introduction of d orbitals to the silicon causes the energy of each silicon-core molecular orbital to rise by about 0.050 au, while the electrostatic potential at the silicon increases by 0.045 au/e and, when chlorine d orbitals are introduced, each silicon core-orbital energy increases by *ca.* 0.011 au, with the electrostatic potential at the silicon increasing by 0.010 au/e. Likewise, d orbitals to the silicon causes the energy of each chlorine core molecular orbital to drop by *ca.* 0.024 au, while the electrostatic potential decreases by 0.027 au/e, whereas d orbitals to the chlorine causes an increase in chlorine core-orbital energy of *ca.* 0.011 au as compared to an increase of 0.009 au/e in the electrostatic potential.

Examination of the contributions of each molecular orbital to the electrostatic potential shows that sizable shifts in potential at the silicon and the chlorine nuclei, due to introduction of either silicon or chlorine d orbitals, occur only in the valence shell. Indeed, it is found that the highest occupied set of molecular orbitals, 4e, is primarily responsible for the shifts in electrostatic potential at either the silicon or chlorine nuclei when silicon d orbitals are added to the basis set. However, when the d character is given to the chlorine, the charge shifts in the 9a orbital are predominant in the electrostatic potential at the silicon nucleus. This is easily understood by reference to Figure 1. Silicon d orbitals shift large amounts of charge in the chlorine π-like lone-pair molecular orbitals, 4e, closer to the silicon causing an increase in the potential at the silicon nuclear position and a decrease at the chlorine. This is in accord with the Mulliken population analysis. On the other hand, while the chlorine does accept some charge from the silicon, accounting for the increased potential of the chlorine nucleus, its dominant effect is to redistribute the n_σ orbital, 9a, again bringing charge into the internuclear region closer to the silicon, thereby causing the increase in the potential at the silicon. In conclusion, while the silicon loses density to the chlorine d orbitals, it experiences a higher potential due to the chlorine d orbitals bringing chlorine lone-pair charge into the (Si–Cl) area.

An effect observed both experimentally for binding energies and theoretically for orbital energies is that the core electronic energies of a particular atom will shift by the same amount in response to a change in molecular environment.[26] For instance in this study, it was found that the energies of all of the core orbitals of silicon shifted by about the same amount when a given set of d orbitals was introduced. Similarly the chlorine core orbitals shifted by an approximately constant, although different amount. This has been interpreted as indicating that all the core orbitals on a given atom are subject to about the same overall change in the electrostatic potential in the core region. This was investigated by calculating the electrostatic potential in the chlorosilane molecule at a distance from either the silicon or chlorine nucleus corresponding to the radius which maximizes the value of ψ^2 for the chosen inner orbital in the respective ground-state atom. These calculations were carried out for four points around each of these two atoms—points lying in a plane passing through the silicon and the chlorine nuclei and one of the hydrogen nuclei of H_3SiCl. Not surprisingly, the potentials calculated for each of these four points, equidistant from the chosen atomic nucleus, were not very different from each other. However, for both the silicon and chlorine atoms, the orbital-radius electrostatic potential was consistently found to be the largest for the point in the Si–Cl bonding region. The shifts in potential were found to be about the same in every direction around the silicon nucleus, as would be expected from the fact that the silicon accepts charge from the hydrogen atoms as well as from the chlorine. On the other hand, the shifts in the potential about the chlorine atom caused by introduction of chlorine d orbitals are distinctly anisotropic, in accord with the role of charge rearrangement played by the chlorine d functions. Indeed, the extreme situation was found for the chlorine "2s" orbital, for which upon allowing chlorine d character the potential increased at the Si–Cl bond axis while decreasing at the other points.

An average value, $\Delta\bar{V}$, for the difference in electrostatic potential (in au/e) between the d and no-d calculations was estimated from the data discussed in the preceding paragraph for the sphere (centered on the respective nucleus) corresponding to the maximum electron density of the chosen inner orbital of the ground-state atom. As shown in Table IV the small differences observed between the "1s," "2s," and "2p" inner-orbital energy shifts, $\Delta\epsilon$, are quite closely paralleled by the differences in the respective values of $\Delta\bar{V}$. Thus, it would seem that, if the electrostatic potential were truly averaged over the spatial distribution of the respective core orbital, instead of by the rather crude process used to obtain $\Delta\bar{V}$, the perturbations in the energy of each core orbital of a given atom attributable to changes in its molecular environment might well be exactly proportional to the commensurate properly averaged electrostatic potential. These ideas are important to the understanding of chemical shifts in core-electron spectroscopy (ESCA).

Table IV. Changes in Core-Orbital Energies and in the Respective Average Orbital-Radius Electrostatic Potentials upon Allowing d Character to Chlorosilane

d character on	Core orbital	Silicon atom		Chlorine atom	
		$\Delta\epsilon$[a]	$\Delta\bar{V}$[b]	$\Delta\epsilon$	$\Delta\bar{V}$
Si	1s	0.0468	0.0459	−0.0266	−0.0270
	2s	0.0506	0.0490	−0.0221	−0.0235
	2p	0.0498[c]	0.0484	−0.0226[c]	−0.0244
Cl	1s	0.0103	0.0099	0.0105	0.0102
	2s	0.0117	0.0111	0.0111	0.0104
	2p	0.0114[c]	0.0103	0.0103[c]	0.0104
Si and Cl	1s	0.0533	0.0524	−0.0165	−0.0172
	2s	0.0580	0.0561	−0.0121	−0.0138
	2p	0.0570[c]	0.0553	−0.0131[c]	−0.0146

[a] $\Delta\epsilon$ is the difference in the orbital energy (in au) between the d and no-d calculations. [b] $\Delta\bar{V}$ is the average difference in electrostatic potential (in au/e) between the d and no-d calculations, with the averaging being an approximation to that carried out over the sphere (centered on the respective nucleus) corresponding to the maximum electron density in the ground-state atom. [c] An average of the "$2p_\sigma$" plus twice the "$2p_\pi$" values.

Acknowledgments. We wish to thank the Air Force Office of Scientific Research, Air Force Systems Command, United States Air Force under AFOSR contract No. AFOSR-72-2265 for partial financial support of this work. We also wish to thank Dr. Raymond Gangi for supplying the POLYATOM program to us.

---

(26) C. S. Fadley, S. B. M. Hagstrom, M. P. Klein, and D. A. Shirley, *J. Chem. Phys.*, **48**, 3779 (1968); W. J. Stec, W. E. Morgan, R. G. Albridge, and J. R. Van Wazer, *Inorg. Chem.*, **11**, 219 (1972); T. A. Carlson, *Phys. Today*, **25**(1), 39 (1972).