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An Unrestricted CNDO–MO Calculation of VCl_4

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The electronic structure of the tetrahedral molecule VCl_4 is investigated within the unrestricted CNDO–MO approximation. The Hartree-Fock equations have been solved using an unrestricted SCF method for open-shell configurations. An iterative procedure is used that employs a single spin-projection to insure a relatively pure doublet state. The metal and ligand valence orbitals have been varied in an attempt to minimize the total energy. Expanded 3*s* and 3*p* chlorine orbitals are indicated while the "optimum" vanadium orbitals $4s(\zeta_4 = 1.50)$, $4p(d^3p^2)$ and $3d(d^8)$ are obtained. Calculations assuming the unpaired electron occupies the $3a_1$, $2e$ and $4t_2$ molecular orbitals indicate that the $3a_1$ orbital is always the lone electron orbital. This result with the minimum total energy indicate that the $^2A_1$ state is the ground state configuration. Extended basis functions for the chlorine valence electrons are used to obtain this result.

Die Elektronenstruktur von tetraedrischem VCl_4 wird mittels einer CNDO–MO-Methode untersucht, bei der die HF-Gleichungen durch ein uneingeschränktes SCF-Verfahren für offene Schalen gelöst werden. Dies involviert ein iteratives Vorgehen mit einer einfachen Spinprojektion, so daß ein relativ reiner Dublettzustand resultiert. Sowohl die Metall- als auch die Liganden-Valenzorbitale sind variiert worden, um E_{ges} minimal zu machen. Die optimalen Vd-Zustände und Entwicklungen für die 3*s*- und 3*p*-Zustände werden angegeben. Die Rechnungen zeigen, daß das einsame Elektron immer im $3a_1$-Zustand sitzt, so daß die Grundkonfiguration von der Rasse $^2A_1$ ist.

Étude de la structure électronique de la molécule tétraédrique VCl_4 dans l'approximation CNDO–MO sans restriction de spin. Les équations de Hartree-Fock ont été résolues en utilisant une méthode SCF à couches ouvertes sans restriction. Le procédé itératif emploie une projection de spin afin d'assurer un état doublet relativement pur. Les orbitales de valence du métal et du ligand ont été modifiées afin d'essayer de minimiser l'énergie totale. On indique des orbitales étendues 3*s* et 3*p* pour le chlore, et l'on obtient des orbitales "optimales" pour le vanadium: $4s(\zeta_4 = 150)$, $4p(d^3p^2)$ et $3d(d^8)$. Des calculs montrent que des trois orbitales moléculaires $3a_1$, $2e$ et $4t_2$, l'électron célibataire occupe toujours la première. Ce résultat ainsi que celui sur l'énergie totale minimale indique que l'état $^2A_1$ est la configuration de l'état fondamental. Une base étendue pour les électrons de valence du chlore est utilisée pour obtenir ce résultat.

1. The Problem

Within the framework of the CNDO–MO scheme outlined by Dahl and Ballhausen [10] and Dahl and Johansen [11], an unrestricted [18] solution of the Hartree-Fock equations explicitly for open-shell electronic systems has been used to investigate VCl_4. Because the quartet and higher states can easily mix with the doublet ground state of VCl_4 in an open-shell calculation, we have employed a single spin-projection in each interation to remove the quartet contributions and leave a relatively pure doublet state.

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Calculations with the lone-electron assumed to occupy the $3a_1$, $2e$, and $4t_2$ orbitals have been performed. These correspond to the configurations $^2A_1$, ^2E, and $^2T_2$ respectively. For each state we have varied extensively the valence orbitals of vanadium (3*d*, 4*s*, and 4*p*) and chlorine (3*s* and 3*p*) in an attempt to minimize the total valence energy. We have also investigated the use of extended and minimum basis functions for the chlorine orbitals.

The VCl_4 molecule is assumed to be regularly tetrahedral with a V–Cl bond length of 2.14 Å [13] although the theory of Jahn and Teller [14] would suggest a lowering of symmetry if the resulting ground state were ^2E or $^2T_2$. No evidence for a static Jahn-Teller effect has been found in the vapor and solution phases, but a dynamic effect has been suggested [13, 15–17].

2. Description of Method

We shall confine ourselves to the differences between the restricted and unrestricted methods here since the method employed in the present calculations have been thoroughly described and discussed in Ref. [11].

The N-electron Hartree-Fock (HF) wave function is represented by a single Slater determinant:

$$\Psi = |\varphi_1^{c\alpha}, \varphi_1^{c\beta}, \ldots, \varphi_1^{\alpha}, \ldots, \varphi_p^{\alpha}, \varphi_1^{\beta}, \ldots, \varphi_q^{\beta}| \tag{1}$$

with φ_j^c, φ_k^α, and φ_m^β standing for the core, α-spin-valence and β-spin-valence MO respectively. The core orbitals are all assumed to be spin-paired and include the chlorine 1*s*, 2*s*, and 2*p* orbitals and the vanadium 1*s*, 2*s*, 2*p*, 3*s*, and 3*p* orbitals. These orbitals are assumed to be the same as in the free ground state atoms although we have used several basis sets to represent them. As in previous calculations, we have replaced the atomic orbitals (AO's) used to form the linear combination of atomic orbitals (LCAO) of the valence MO's with a set of orthonormal orbitals $\{\lambda_i\}$. The valence AO's for vanadium were the 3*d*, 4*s*, and 4*p* and for chlorine were the 3*s* and 3*p*. Thus we have the LCAO orthonormal valence MO's expressed in the form:

$$\varphi_i^k = \sum_{r=1}^{m} \lambda_r^k C_{ri}^k = \boldsymbol{\lambda}^k \boldsymbol{C}_j^k \qquad k = \alpha, \beta\,, \tag{2}$$

where $\boldsymbol{\lambda}^k$ is a row vector and $\boldsymbol{C}_i^k$ is a column vector. To a good approximation we thus have that all core and valence MO's form an orthonormal basis of dimension m.

With p orbitals φ_i^α occupied by electrons with α-spin and q orbitals φ_i^β occupied by electrons with β-spin, we can write the one-electron core operator

$$H^{c-k}(1) = T(1) + \sum_g V_g^k(1)\,, \tag{3a}$$

$$V_g^k(1) = -\frac{Z_g e^2}{r_{1g}} + \sum_{j \text{ on } g} (2J_j^{c-k} - K_j^{c-k})\,, \tag{3b}$$

where g numbers the various nuclei with charges $Z_g e$. $T(1)$ is the kinetic energy operator, and J_j^{c-k} and K_j^{c-k} are the spin-restricted Coulomb and exchange operators:

$$J_j^{c-k}\varphi^k(1)=\int\frac{e^2}{r_{12}}\varphi_j^c(2)\,\varphi_j^c(2)\,\mathrm{d}\tau_2\,\varphi^k(1)\,, \tag{4a}$$

$$K_j^{c-k}\varphi^k(1)=\int\frac{e^2}{r_{12}}\varphi_j^c(2)\,\varphi^k(2)\,\mathrm{d}\tau_2\,\varphi_j^c(1)\,, \tag{4b}$$

$$k=\alpha,\beta\,.$$

Following the method of Roothaan [12] for each set $\{\varphi_i^\alpha\}$ and $\{\varphi_i^\beta\}$ gives rise to the matrix equations to be solved:

$$\boldsymbol{F}^\alpha\boldsymbol{C}_i^\alpha=\varepsilon_i^\alpha\boldsymbol{S}\boldsymbol{C}_i^\alpha\,;\qquad \boldsymbol{F}^\beta\boldsymbol{C}_i^\beta=\varepsilon_i^\beta\boldsymbol{S}\boldsymbol{C}_i^\beta\,, \tag{5}$$

where the Fock matrices are given by $\boldsymbol{F}^k=\boldsymbol{H}^{c-k}+\boldsymbol{G}^k$. The matrix elements are defined by the following relations:

$$H_{rs}^{c-k}=\int\lambda_r^k(1)\,H^{c-k}(1)\,\lambda_s^k(1)\,\mathrm{d}\tau_1\qquad k=\alpha,\beta\,, \tag{6a}$$

$$S_{rs}=\int\lambda_r^k(1)\,\lambda_s^k(1)\,\mathrm{d}\tau_1\,, \tag{6b}$$

$$G_{rs}^k=\sum_{t,u}\{(P_{tu}^k+P_{tu}^f)\,[rs|tu]-P_{tu}^k[ru|ts]\}\qquad f=\alpha,\beta,\ f\neq k\,, \tag{6c}$$

$$[rs|tu]=\iint\lambda_r^k(1)\,\lambda_s^k(1)\frac{e^2}{r_{12}}\lambda_t^f(2)\,\lambda_u^f(2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2\qquad k=\text{or}\neq f. \tag{6d}$$

The unrestricted bond order matrices $\boldsymbol{P}^\alpha$ and $\boldsymbol{P}^\beta$ are defined by:

$$\begin{aligned}P_{tu}^\alpha&=\sum_{j=1}^{p}C_{tj}^\alpha C_{uj}^\alpha\,,\\ P_{tu}^\beta&=\sum_{j=1}^{q}C_{tj}^\beta C_{uj}^\beta\,.\end{aligned} \tag{7}$$

With the matrices $\boldsymbol{G}^\alpha$ and $\boldsymbol{G}^\beta$ defined by Eq. (6c), the bond order matrices are subject to the following restrictions [18–20]:

$$\begin{aligned}\boldsymbol{P}^\alpha\boldsymbol{S}\boldsymbol{P}^\alpha&=\boldsymbol{P}^\alpha\,;\qquad &\boldsymbol{P}^\beta\boldsymbol{S}\boldsymbol{P}^\beta&=\boldsymbol{P}^\beta\,,\\ \mathrm{tr}\,\boldsymbol{P}^\alpha&=p\,;&\mathrm{tr}\,\boldsymbol{P}^\beta&=q\,,\end{aligned} \tag{8}$$

where tr is the trace of the matrix. Since the MO's are assumed to be orthonormal, we have that the bond order matrices are restricted to be idempotent. McWeeny's [20] method is employed to insure the idempotency. The method due to Amos [19] is used to correct the traces.

A single Slater determinant wave function in the unrestricted Hartree-Fock method does not usually represent a pure spin state. Consequently we have employed a single spin projection in each iteration to remove the quartet state contribution and should leave a relatively pure doublet state. This is consistent with the results of Amos and Hall [19] who found that the contributions from spin states of higher multiplicity decrease rapidly. Sutcliffe [18] has obtained the following formulas for accomplishing the spin projection with overlap being included:

$$\begin{aligned} Q^\alpha &= P^\alpha - (P^\alpha S P^\beta S P^\alpha - \tfrac{1}{2} P^\alpha S P^\beta - \tfrac{1}{2} P^\beta S P^\alpha)/x\,, \\ Q^\beta &= P^\beta - (P^\beta S P^\alpha S P^\beta - \tfrac{1}{2} P^\alpha S P^\beta - \tfrac{1}{2} P^\beta S P^\alpha)/x\,, \end{aligned} \tag{9}$$

where Q^α and Q^β are the spin corrected matrices and

$$x = (s+1)(s+2) - \tfrac{1}{4}(p-q) - \tfrac{1}{2}(p+q) + \mathrm{tr}\, P^\alpha S P^\beta S \tag{10}$$

with $s = \frac{1}{2}$ for the removal of the quartet contributions. By checking intermediate projections for several calculations the first projection is found to be the most important since this corrects the bond order matrices obtained from the initially assumed input coefficients. This result is in accord with the results of Marshall [21] which indicate that a projection after the energy minimization is a poor approximation.

Although we have not calculated the total energy of the VCl_4 molecule, we have calculated the energy contribution due to the valence electrons:

$$E = \frac{1}{2}\left(\mathrm{tr}\, P^\alpha H^{c-\alpha} + \mathrm{tr}\, P^\beta H^{c-\beta} + \sum_i^p \varepsilon_i^\alpha + \sum_i^q \varepsilon_i^\beta\right). \tag{11}$$

If the bond distance V–Cl and the core orbitals are held constant, the variation of the total energy has been shown to be given by the variation of E when the valence AO's alone are varied [11]. The minimization of E has therefore been treated as the criterion for finding the optimum set of AO's.

Within the LCAO approximation we use symmetry adapted MO's for molecules of tetrahedral symmetry with the designations a_1, e, t_1, and t_2 [10]. In Eq. (2) we thus have that the AO's are symmetry adapted orbitals (SAO) formed with orthonormal AO's. Calculations assuming the unpaired electron occupies the $3a_1$, $2e$, and $4t_2$ molecular orbitals have been carried out.

3. Atomic Orbitals

The AO's used to construct the LCAO–MO's for the present calculation were taken, extrapolated or constructed from available tables of Slater type orbitals (STO). Most calculations were carried out with the core ground-state-free-atom HF wave functions of Clementi [22]. All of the $4p$ vanadium AO's were taken from the tables of Richardson, *et al.* [23] as were some of the double-zeta $3d(d^1\text{–}d^5)$ orbitals, given in Table 1. The remaining $3d$ orbitals (i.e., $d^6\text{–}d^{10}$) were obtained by extrapolating from the d^1 to d^5 orbitals. In Table 2 are given the $4s$ AO's of Becker and Dahl [8] with three additional orbitals which are denoted by $4s(\zeta_4)$. An arbitrary ζ_4 was chosen for the $4s(\zeta_4)$ orbital which is constructed to be orthogonal to the vanadium core orbitals given by Richardson, *et al.* [23]. The same procedure was used by Becker and Dahl [8] except the ζ_4 values were chosen systematically. Clementi's [22] HF orbitals were also used for the $3d$ and $4s$ vanadium orbitals and were found to give about the same orbital energies as the more approximate orbitals given in Tables 1 and 2.

Table 1. *Vanadium 3d orbitals*[a]

d^m	ζ_2	C_2	C_1
$3d(d^1)$	2.30	0.5560	0.5500
$3d(d^2)$	2.10	0.6050	0.5230
$3d(d^3)$	1.90	0.6550	0.4980
$3d(d^4)$	1.70	0.7060	0.4760
$3d(d^5)$	1.50	0.7520	0.4560
$3d(d^6)$	1.30	0.7939	0.4399
$3d(d^7)$	1.10	0.8321	0.4260
$3d(d^8)$	0.90	0.8648	0.4141
$3d(d^9)$	0.70	0.8907	0.4042
$3d(d^{10})$	0.50	0.9090	0.3956

[a] $n_1 = 3$, $\zeta_1 = 4.75$ and $n_2 = 3$.

Table 2. *Vanadium 4s orbitals*[a]

$d^n s^m$	ζ_4	C_4	C_3	C_2	C_1
$4s(d^3s^2)$	1.25	1.011517	−0.19137	0.07548	−0.02188
$4s(d^3s^1)$	1.41	1.02774	−0.25953	0.10090	−0.02919
$4s(\zeta_4)$	1.50	1.03731	−0.30166	0.11626	−0.03358
$4s(d^2s^2)$	1.60	1.05037	−0.35154	0.13408	−0.03869
$4s(\zeta_4)$	1.67	1.06115	−0.38830	0.14697	−0.04235
$4s(d^2s^1)$	1.75	1.07529	−0.43222	0.16208	−0.04666
$4s(\zeta_4)$	1.90	1.10740	−0.52000	0.19141	−0.05494

[a] $n_1 = 1$, $\zeta_1 = 22.395$, $n_2 = 2$, $\zeta_2 = 8.475$, $n_3 = 3$, $\zeta_3 = 3.850$ and $n_4 = 4$.

Minimum basis set orbitals to represent the AO's of chlorine are found to yield results which differ drastically from those obtained by using HF orbitals. Three types of minimum basis set orbitals and Clementi's HF orbitals were used for the chlorine AO's. In Table 3 are given the minimal basis set orbitals obtained by maximizing the overlap between Clementi's [22] HF orbitals and normalized minimal basis set orbitals which are Schmidt orthogonalized to the other orbitals of the same symmetry (e.g., Richardson, *et al.* [23]). The valence orbitals of Cl^+, Cl, and Cl^- which denote the electronic valence structures s^2p^4, s^2p^5, and s^2p^6 respectively were obtained by keeping the same ground state core orbitals and changing the 3*s* and 3*p* HF orbitals. This procedure is consistent with the results of Watson [24] which indicate that the core orbitals change only slightly with changes in the valence orbitals. With this procedure it is easier to see how the orbitals are changing since only one parameter changes in each of the valence orbitals. In all of the calculations the 3*s* and 3*p* orbitals were changed simultaneously. These orbitals are not found to represent the HF orbitals very well. These maximum overlap minimal basis functions are slightly more expanded than the basis set used by Becker and Dahl [8] obtained with the ζ values from Clementi and Raimondi [25] and a slight orbital expansion induced by considering a small negative charge $-\delta$ on the chlorine atom. The δ values from 0.0 to 1.0 should include the range considered for the maximum overlap functions.

Table 3. *Minimal basis sets for chlorine*

Maximum overlap	$\langle R^2 \rangle$				
Orbital	n_i	ζ_i	C_i	ζ_i	C_i
$1s$	1	16.4321	1.00000	16.3627	1.00000
$2s$	1	16.4321	−0.32921	16.3627	−0.33311
	2	5.8862	1.05280	5.9047	1.05402
$2p$	2	6.1758	1.00000	6.0370	1.00000
$3s(s^2p^4)$	1	16.4321	0.10707	16.3627	0.10565
	2	5.8862	−0.38500	5.9047	−0.37557
	3	2.4217	1.06485	2.3965	1.06166
$3p(s^2p^4)$	2	6.1758	−0.22687	6.0370	−0.22864
	3	2.0535	1.02541	2.0148	1.02580
$3s(s^2p^5)$	1	16.4321	0.10017	16.3627	0.09714
	2	5.8862	−0.35842	5.9047	−0.34431
	3	2.3358	1.05643	2.941	1.05206
$3p(s^2p^5)$	2	6.1758	−0.19947	6.0370	−0.19319
	3	1.9330	1.01970	1.8618	1.01849
$3s(s^2p^6)$	1	16.4321	0.09447	16.3627	0.09021
	2	5.8862	−0.33671	5.9047	−0.31727
	3	2.2639	1.04995	2.2028	1.04437
$3p(s^2p^6)$	2	6.1758	−0.16521	6.0370	−0.14318
	3	1.7734	1.01356	1.6265	1.01020

In Table 3 we also have the minimal basis set formed by constraining each orthonormal orbital to have the same average R^2, $\langle R^2 \rangle$, as its corresponding HF orbital. This criterion gives expanded orbitals that are more realistic in the overlap regions than either of the two other minimal basis sets.

Valence orbitals obtained from minimal basis sets are not expected to represent the HF orbitals of the free atoms but some insight can be gained by considering both types of orbitals in the LCAO–MO calculation. An attempt has been made to consider the various aspects of the MO calculation relative to which chlorine basis functions are used.

4. Results

I. *Search for Best Atomic Orbitals*

Even though it is possible to obtain minimum energies by varying the input AO's, some caution must be used in interpreting the results because of the approximations involved in the method. Since the vanadium atom ground state has the valence configuration d^3s^2, the HF orbitals for this state and the free atom chlorine were used in minimizing the total valence energy E with respect to the $4p$ vanadium orbital [23]. The minimum E was obtained with the $4p(d^3p^2)$ orbital in this and all other possible input combinations of AO's. In Fig. 1 are the orbital energies for this variation of the $4p$ orbitals.

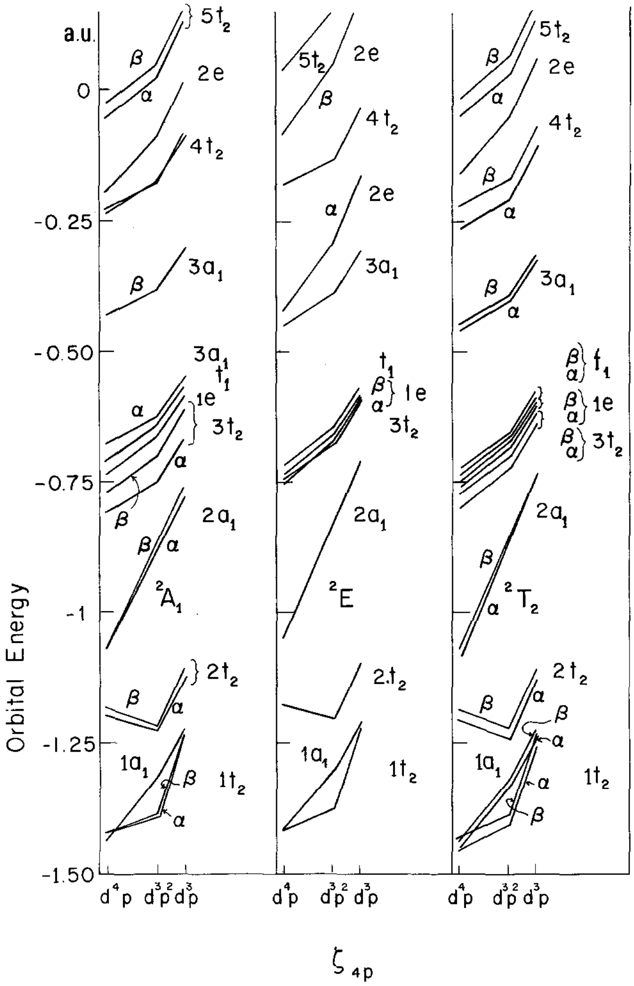

Fig. 1. Orbital energies in a.u. = 27.21 eV obtained with HF atomic ground state orbitals for vanadium and chlorine as a function of the V(4p) parameter ζ_{4p} with the lone-electron assumed to occupy the MO's $3a_1(^2A_1)$, $2e(^2E)$ and $4t_2(^2T_2)$

With the $4p(d^3p^2)$ orbital and the remaining orbitals held constant we varied the $3d$ orbitals to obtain E as illustrated in Fig. 2. The $3d(d^8)$ orbital which gives the minimum E is slightly more extended than might be expected from the atomic ground state, therefore we have also minimized the energy with the $3d(d^5)$ orbital. The two $4d$ orbitals of Richardson, *et al.* [23] were substituted for the $3d$ orbitals with the resulting energies shown in Fig. 2. A minimum energy for the $4d(\zeta_2 = 1.0)$ orbital suggests that the $4d$ orbitals should probably be included in a more elaborate calculation.

Unlike the $3d$ and $4p$ orbitals, the $4s$ orbitals change with the assumed occupied orbital to obtain the minimum E values. In general the ζ_4 varies within the range 1.5 to 1.75 for the $4s$ orbital and has a dramatic effect on the orbital

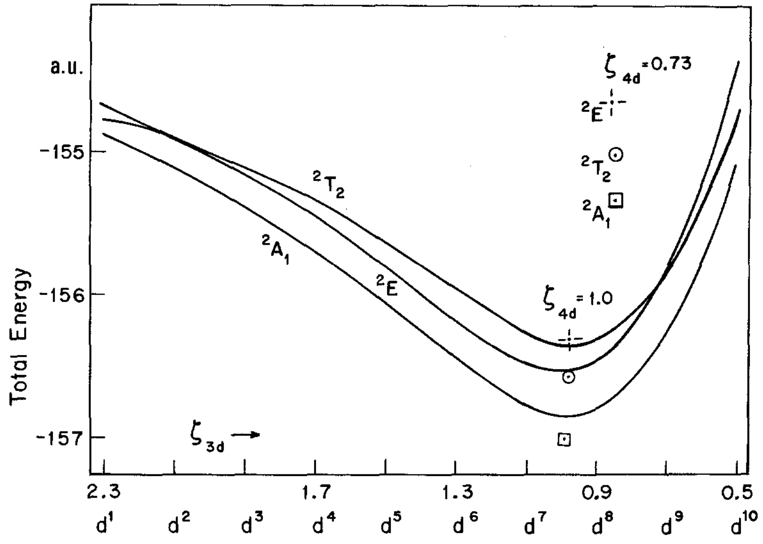

Fig. 2. Total valence energy E in a.u. = 27.21 eV as a function of the V(3*d*) parameter ζ_{3d} (or orbital d^1–d^{10}). HF atomic orbitals were used for the atomic ground states except for the $4p(d^3d^2)$ vanadium orbital and the varied V(3*d*) orbital. The results obtained with V(4*d*) orbitals substituted for V(3*d*) orbitals with all other orbitals the same are also illustrated

Table 4. *Molecular orbitals for* VCl_4, *corresponding to the orbitals* $3d(d^8)$, $4s(\zeta_4 = 1.50)$, $4p(d^3p^2)$, *and* $Cl(s^2p^6)$

Symmetry		Eigenvalue (eV)	Eigenvectors				
a_1			s	σ_s	σ_p		
	α	−19.3690	0.26094	0.10761	0.95934		
		−34.1982	0.53626	0.81017	−0.23674		
		−45.8175	0.80270	−0.57623	−0.15370		
	β	−12.3361	0.39082	0.14146	0.90953		
		−30.7610	0.72873	0.55610	−0.39962		
		−41.7242	−0.56232	0.81899	0.11425		
e			d	π			
	α	2.8666	0.97602	−0.21769			
		−21.2594	0.21769	0.97602			
	β	2.8660	0.97605	−0.21755			
		−21.2738	0.21755	0.97605			
t_2			p	d	σ_p	σ_s	π_p
	α	13.7571	0.08569	0.85845	−0.35242	−0.34214	−0.12028
		− 0.0184	−0.60575	0.17652	0.24422	−0.20862	0.70621
		−23.2547	−0.05734	0.19125	0.83531	−0.23487	−0.45523
		−45.9274	0.41354	0.40279	0.31252	0.67125	0.34425
		−50.5148	0.67188	−0.18192	0.14406	−0.57765	0.40132
	β	14.0583	0.09073	0.85069	−0.37149	−0.33925	−0.12245
		0.0552	−0.60375	0.39057	0.25346	−0.21363	0.69948
		−22.1565	−0.03472	0.21326	0.83337	−0.22184	−0.45781
		−45.6217	0.42131	0.40064	0.28914	0.67251	0.35512
		−50.5143	0.66973	−0.18443	0.14014	−0.58119	0.40003
t_1			π				
	α	−20.3110	1.00000				
	β	−20.3261	1.00000				

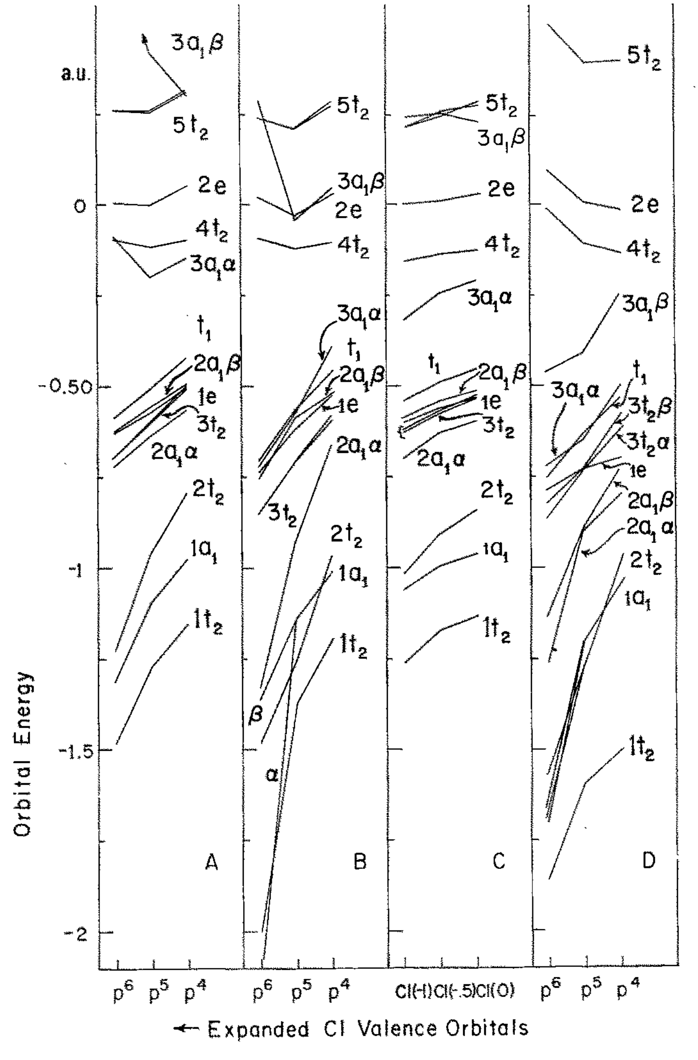

Fig. 3. $^2A_1$ orbital energies in a.u. = 27.21 eV obtained with the atomic orbitals $3d(d^5)$, $4s(\zeta_4 = 1.67)$, $4p(d^3p^2)$ and varied chlorine orbitals are given in parts (A), (B), and (C). All core orbitals were of the atomic ground state HF type. Chlorine valence orbitals were taken from the (A) $\langle R^2 \rangle$ minimal basis set, (B) HF basis set and (C) Cl($-\delta$) minimal basis set. In (B) are given the minimum E results with the $3d(d^5)$ orbital. Part (D) illustrates the minimum E results obtained with the orbitals $3d(d^8)$, $4s(\zeta_4 = 1.50)$, $4p(d^3p^2)$ and chlorine HF valence orbitals. The core orbitals are the same as in parts (A), (B), and (C)

energies. "Optimum" valence orbitals for vanadium were found to be $4s(\zeta_4 = 1.50)$, $4p(d^3p^2)$, and $3d(d^8)$. In Table 4 and Fig. 3 D are given the results for this calculation. As has been the case for other calculations, the Cl$^-$ ion valence orbitals give the lowest E values. With the $3d(d^5)$ orbital the minimum E was obtained with the $4s(\zeta_4 = 1.67)$, $4p(d^3p^2)$ and Cl$^-$ valence orbitals. The orbital energy results for this set of AO's are illustrated in Fig. 3 B. The dramatic effect of the 4s orbitals on the system of MO's comes to light on comparing Fig. 3B and D. If the 4s $\zeta_4 = 1.6$ is used instead of the $\zeta_4 = 1.5$ for the $3d(d^8)$ "optimum" results, the order of the orbitals is very similar to the $3d(d^5)$ results in Fig. 3B including the low lying $1a_1\alpha$ orbital and the $3a_1\alpha$ orbital lying slightly below the t_1 orbital although the energy E is higher than the "optimum" result by about 0.4 atomic units (11.0 eV).

Variations in E on changing the chlorine valence orbitals from the s^2p^4 state to the s^2p^5 state functions are on the order of 1. atomic units (27.21 eV) while changes from s^2p^5 to s^2p^6 are of the order of 7.–8. atomic units. Even though this drastic drop in E would suggest the use of more expanded orbitals, the increased overlap from these AO's would give a greater uncertainty in the results.

II. Molecular Orbitals and Ground State

By carrying out calculations with the unpaired electron assumed to occupy the $3a_1$, $2e$, and $4t_2$ orbitals we have found that the lone electron occupies the $3a_1$ MO if *all* of the chlorine AO's are taken from Clementi's [22] HF orbitals. The stability of the $3a_1$ orbital arises from the strong participation of the 4s and 4p metal orbitals in the bonding molecular orbitals. As was pointed out by Becker and Dahl [8], this strong participation is an inevitable result of the Schmidt orthogonalization used in this type of CNDO–MO calculation.

The minimum total valence energy for the three possible lone electron MO cases indicate the following order of filling for all of the MO's:

$$\begin{aligned} &1t_2 < 2t_2\alpha \gtrsim 1a_1\alpha \gtrsim 2t_2\beta < 1a_1\beta < 2a_1\alpha < 2a_1\beta \\ &\quad < 3t_2 < 1e < t_1 \gtrsim 3a_1\alpha < 3a_1\beta < 4t_2 < 2e < 5t_2 \,. \end{aligned} \tag{12}$$

This order is not unambiguous, but the shifts that take place are easily related to which MO the lone electron is assumed to occupy. The order given is obtained for the ground state $^2A_1$ case given in Table 4. For the minimum E for the ^2E case the only changes are the removal of the splitting of the $a_1\alpha$ orbitals and placing these orbitals in the same order as for the $a_1\beta$ orbitals. The other change for this case is the lowering of $2e\alpha$ orbital energy below the $4t_2$ level. In the $^2T_2$ case the only change is in the a_1 orbital spin splitting as for the ^2E case given above.

Although there are some shifting of the MO's in the various calculations, the general characteristics are illustrated by Fig. 1. For the $^2A_1$ calculations there is always some splitting of the a_1 and t_2 levels for the α- and β-spin electrons while the e symmetry levels are approximately the same for both spins. With the ^2E calculations the only appreciable splitting is with the e levels. In the $^2T_2$ results there is some splitting for almost all of the levels. Generally the orbital energies are fairly constant for all of the orbitals except for the orbital which is assumed to contain the lone electron. This energy is lowered for the α-spin orbital leaving the β-spin virtual orbital energy almost unchanged. The greatest change is always found in the ^2E case where there is a slight raising of the β-spin orbital energy.

The amount of separation between the corresponding α and β orbital energies is a physical and computational consequence manifested by which SAO or SAO's have the highest probability(s) of containing the lone electron. For the $^2A_1$ and

^2E computations the lone electron occupies a MO which is dominated by one SAO. As expected the ^2E results indicate a one electron MO with V(4*d*) characteristics, but unexpectedly the $^2A_1$ has pairing of α and β spin electrons in SAO's which are mainly V(4*s*) and Cl(σ_s) in character and a one electron MO which is predominantly the SAO Cl(σ_p). Consequently the lone electron orbital and its virtual orbital counterpart should have orbital energies that differ by approximately the coulomb integral between the dominant SAO's divided by the degeneracy. Computationally this is a result of Eq. (6c). Physically the lone electron in an SAO gains the stabilizing nuclear interactions, but is does not become destabilized by another electron in the same SAO. This results in a lowering of the orbital energy of the lone electron.

For the $^2T_2$ case we have a different situation. Here the additional electron is not in any one SAO, but it is fairly evenly distributed over all five SAO's of T_2 symmetry. Consequently the α-spin orbital energies are all lowered slightly instead of the larger single change found for the previous two cases. The minimum *E* results yields a maximum charge density for the lone electron of 0.39 in the Cl(π_p) SAO and a minimum of 0.10 in the V(3*d*) SAO.

III. Basis Sets

All of the results given thus far have been obtained with Clementi's [22] HF orbitals for all the core and chlorine valence orbitals. The vanadium valence orbitals were not necessarily extended basis orbitals but the results change only slightly by using non-HF orbitals. This effect was not found to be true for the chlorine valence orbitals as is illustrated in Figs. 3A and C. For the results in Figs. 3A, B, and C we have kept all of the vanadium orbitals and the core orbitals for chlorine the same but have varied the chlorine valence orbitals over the same electronic structures with different basis sets. If the HF orbitals are assumed to give the "best" possible MO picture of a complex, then several factors are apparent in Fig. 3 which should be taken into consideration when more approximate basis functions are used. In Fig. 3A the results obtained with the $\langle R^2 \rangle$ minimal basis valence orbitals indicate orbital energies for the filled orbitals which are in better agreement with the HF results in Fig. 3B than the results obtained with Cl($-\delta$) minimal basis set of Becker and Dahl [8] as illustrated in Fig. 3C. However, in Fig. 3C we have better agreement with the order of filling of the MO's than in Fig. 3A. The maximum overlap minimal basis set gives intermediate results to those illustrated in Figs. 3A and C. As expected the HF orbitals give the lowest total valence energy and the $\langle R^2 \rangle$ basis set gives the lowest *E* for the minimal basis sets.

Although it would be assumed that some useful information could be obtained by using some type of minimal basis set functions for the chlorine valence orbitals, all of the possible information is found to be ambiguous. By making the assumption as to which of the three possible MO's the lone electron occupies we have found that the electron ends up in the assumed MO. As mentioned before, the lone electron always ends up in the $3a_1\alpha$ MO with HF orbitals. Also it appears that the $^2T_2$ state has the minimum *E* with the minimal basis sets in contrast to the $^2A_1$ state obtained with the HF orbitals. The $^2T_2$

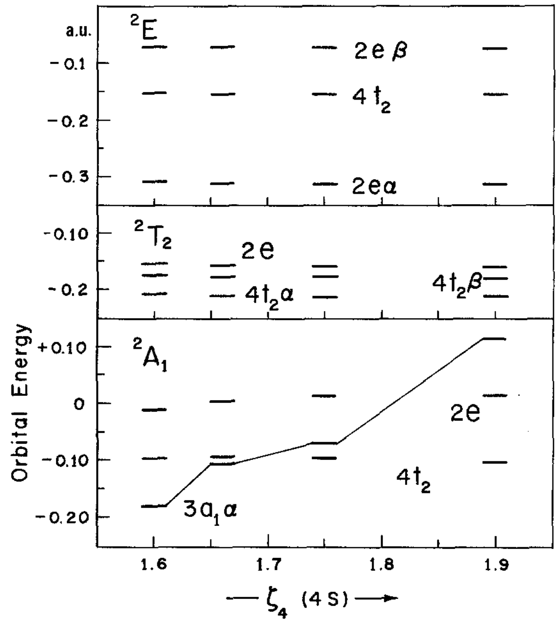

Fig. 4. Orbital energies in a.u. = 27.21 eV for the lowest virtual orbitals and the lone-electron orbital as a function of $4s(\zeta_4)$ for the three possible cases. All of the chlorine orbitals are from the $Cl(s^2p^6)$ maximum overlap basis set with the $3d(d^8)$, $4p(d^3p^2)$ and HF core orbitals for vanadium

state is also the state found by Becker and Dahl with all of the orbitals being taken from minimal basis sets.

In Fig. 4 we have the orbital energies for the lone-electron and the lowest virtual orbitals for the three assumed possibilities. Variation of the ζ_4 for the vanadium 4s orbital is used with the $4p(d^3p^2)$ and $3d(d^8)$ orbitals. Also we used all of the maximum overlap minimal basis set chlorine orbitals given in Table 3 for the s^2p^6 configuration. The results illustrated in Fig. 4 are typical of all the calculation involving minimal basis sets for the chlorine valence orbitals. A minimum E is obtained for a $\zeta_4 = 1.67$ for the $^2A_1$ case and a $\zeta_4 = 1.75$ for the ^2E and $^2T_2$ cases given in Fig. 4. However for these calculations it is the ^2E state with the lowest E.

5. Conclusions

The unambiguous results obtained with HF chlorine orbitals suggest that the Jahn-Teller effect would not be found for the VCl_4 complex since the lone-electron occupies the non-degenerate $3a_1$ orbital. Experimental results have been interpreted to suggest both the absence [16] and presence [26] of the effect although there is the difficulty of contaminants such as $VOCl_3$. Theoretical investigations [6, 27–29] for the Jahn-Teller effect of VCl_4 are based on the assumption that the unpaired electron occupies a degenerate *e*-symmetry MO predicted by simple ligand field theory which is apparently not applicable to this system. It is anticipated that the MnO_4^{-2} and CrO_4^{-3} complexes will be investigated to see if the ligand field results are restored as they should be.

Although the absence of an electron paramagnetic resonance for VCl_4 in heptane solutions is interpreted as resulting from very short relaxation times [30], the results reported here indicate a very small Fermi contact interaction since the unpaired electron occupies an orbital which is primarily of $Cl(\sigma_p)$ character and the $V(s)$ electrons are predominantly paired. Slight distortions of the tetrahedral structure and other host-lattice effects explain the appearance of the eight hyperfine components observed in solid state experiments. The ^{51}V in VCl_4 has been studied in a $TiCl_4$ matrix below 9 °K [31] and in Kr and Xe matrices [32].

In light of the results of Becker and Dahl [7] and those reported here it seems apparent that the equivalence restriction is invalid for at least the VCl_4 complex. Also it is apparent that the order of filling of the MO levels for this complex are not the same as those obtained from ligand field theory. The AO's used in the calculations are not assumed to be the best possible choice, but within the framework of the CNDO–MO procedures they should be adequate. Contrary to the popular practice of using minimal basis sets for the AO's in MO calculations, we have found that chlorine orbitals from these sets were not adequate to be used in this calculation although the vanadium minimal basis sets give results that are consistent with the HF basis sets (where comparisons can be made).

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