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Technical Report

MOLECULAR ORBITAL CALCULATION OF VANADIUM  
IN THE TUNGSTEN SITE OF  $\text{CaWO}_4$

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## ABSTRACT

Semiempirical MO calculations of vanadium in the tungsten site of  $\text{CaWO}_4$  crystals are presented. The two cases of  $[\text{VO}_4]^{3-}$  and  $[\text{VO}_4]^{4-}$  are considered. The true symmetry  $S_4$  of the tungsten site is used in the construction of the ICAO and ligand hybrid orbitals are constructed to accommodate the crystal structure. Small positive  $\Delta g$  shifts are predicted and possible accidental isotropy of the  $g$  tensor.



## CHAPTER I

### THEORETICAL BACKGROUND

The Schrödinger equation for a collection of  $k$  nuclei and  $N$  electrons in the Born-Oppenheimer approximation is:

$$H\Psi(\underline{r}_1\underline{r}_2\dots\underline{r}_N) = E\Psi(\underline{r}_1\underline{r}_2\dots\underline{r}_N) \quad (\text{I-1})$$

where the Hamiltonian is given in (I-2)

$$H = \sum_{i=1}^N \left\{ -\frac{\hbar^2}{2m} \nabla_i^2 - \sum_{j=1}^k \frac{Z_j e^2}{r_{ij}} \right\} + \sum_{i<i'}^N \frac{e^2}{r_{ii'}} \quad (\text{I-2})$$

In addition to the Born-Oppenheimer approximation which neglects the kinetic energy of the nuclei, we have neglected terms depending on the electron spin, the nuclear spin and the nuclear quadrupole moment. Even so the solution of Eq. (I-1) is impossible and only approximate numerical solutions can be obtained in the simple cases. The difficulty arises from the last term in Eq. (I-2) which expresses the electron-electron interaction. Without this term the Hamiltonian in Eq. (I-2) would become a sum of one-electron operators and the solutions of Eq. (I-1) would be in the form of a product of one-electron functions (or orbitals;) i.e.,

$$\Psi(\underline{r}_1\underline{r}_2\dots\underline{r}_N) = \psi_1(\underline{r}_1)\psi_2(\underline{r}_2)\dots\psi_N(\underline{r}_N) \quad (\text{I-3})$$

In the Self-consistent Field (SCF) approximation we keep the electron-electron interaction term but assume that the solution of Eq. (I-1) can be written in the form of a product of orbitals as in Eq. (I-3). Using this expression for

the solution and applying the variational principle to minimize the energy in (I-4)

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (\text{I-4})$$

we get the following N Hartree equations:

$$\left[ -\frac{\hbar^2}{2m} \nabla_i^2 - \sum_{j=1}^k \frac{Z_j e^2}{r_{ij}} + \sum_{\substack{i'=1 \\ i' \neq i}}^N \langle \psi_{i'}(2) | \frac{e^2}{r_{ii'}} | \psi_{i'}(2) \rangle \right] \psi_i(1) = E_i \psi_i(1) \quad i=1,2,3,\dots,N \quad (\text{I-5})$$

We interpret Eq. (I-5) as expressing the motion of the electron that occupies the  $i$ -th orbital, under the influence of the stationary nuclei (second term) and the fixed effective (average) field of the rest of the electrons which occupy the other orbitals (third term). The method used for solving the equations in (I-5) is by successive iterations. However this is still a formidable problem and therefore additional assumptions are introduced.

In the valence electron approximation we divide the electrons into two groups. The core electrons and the valence electrons. The core electrons are those found in closed atomic shells and are considered to interact with the rest of the electrons (the valence electrons) only through the screening of the corresponding nuclei. Therefore Eq. (I-5) simplifies into the following:

$$\left\{ -\frac{\hbar^2}{2m} \nabla_\mu^2 - \sum_{j=1}^k \frac{Z_j^* e^2}{r_{\mu j}} + \sum_{\substack{\mu'=1 \\ \mu' \neq \mu}}^{N_r} \langle \psi_{\mu'}(2) | \frac{e^2}{r_{\mu\mu'}} | \psi_{\mu'}(2) \rangle \right\} \psi_\mu(1) = E_\mu \psi_\mu(1) \quad \mu=1,2,\dots,N_r \quad (\text{I-6})$$

where  $Z_j^*$  is the effective nuclear charge of the  $j$ -th nucleus and  $N_r$  is the number of the valence electrons. Of course the only simplification that occurs in Eq. (I-6) with respect to Eq. (I-5) is in the number of the equations. The third term in Eq. (I-6) (as well as in Eq. (I-5)) varies with the index  $\mu$  because it expresses the potential energy of an electron in the  $\mu$ -th orbital due to the rest of the electrons which occupy the other orbitals and all orbitals are not the same. Nevertheless as an additional assumption we consider quite frequently that this variation is not great so that all valence electrons are considered to move under the same effective field.

Therefore we write one effective Hamiltonian for all valence electrons

$$H_{\text{eff}} = -\frac{\hbar^2}{2m} \nabla_{\underline{\mu}}^2 - \sum_{j=1}^k \frac{Z_j^* e^2}{r_{\underline{\mu}j}} + V(\underline{r}_{\underline{\mu}}) \quad (\text{I-7})$$

where  $V(\underline{r}_{\underline{\mu}})$  is the average value of the third term in (I-6) taken over all values of  $\mu'$ .

Thus the original many-electron problem has been reduced into a one-electron problem, namely the following.

$$H_{\text{eff}} \psi_{\mu}(\underline{r}_{\underline{\mu}}) = E_{\mu} \psi_{\mu}(\underline{r}_{\underline{\mu}}) \quad (\text{I-8})$$

#### SOLUTION OF THE ONE-ELECTRON PROBLEM

In order to solve Eq. (I-8) usually we approximate the molecular orbital  $\psi_{\mu}(\underline{r})$  by a linear combination of atomic orbitals (LCAO) centered at the different nuclei; i.e., we write

$$\psi_{\mu}(\underline{r}) \simeq \sum_{i=1}^n c_i \phi_i \quad (\text{I-9})$$

Then by using the variational method we minimize the expression (I-10)

$$E_{\mu} = \frac{\langle \psi_{\mu} | H_{\text{eff}} | \psi_{\mu} \rangle}{\langle \psi_{\mu} | \psi_{\mu} \rangle} \quad (\text{I-10})$$

where  $\psi_{\mu}$  is expressed by Eq. (I-9). This procedure gives the following equations:

$$\sum_{i=1}^n c_i (H_{ij} - ES_{ij}) = 0 \quad j=1,2,\dots,n \quad (\text{I-11})$$

For a nontrivial solution we must have

$$\det |H_{ij} - ES_{ij}| = 0 \quad i,j=1,2,\dots,n \quad (\text{I-12})$$

where by definition

$$H_{ii} \equiv \langle \phi_i | H_{\text{eff}} | \phi_i \rangle = \text{the Coulomb Integral}$$

$$H_{ij} \equiv \langle \phi_i | H_{\text{eff}} | \phi_j \rangle = \text{the Resonance Integral}$$

$$S_{ij} \equiv \langle \phi_i | \phi_j \rangle = \text{the Overlap Integral}$$

The selection of the proper atomic orbital  $\phi_i$  to be used in Eq. (I-9) rests on intuition and experience but the best coefficients  $c_i$ 's are determined rigorously by the variational method.

#### SIMPLIFICATION OF THE SECULAR DETERMINANT

The secular determinant (12) is usually quite cumbersome to solve. Its rank is equal to the number  $n$  of the AO used in the expansion (I-9), which is often twenty, thirty or forty. In order to factor out the secular determinant

it is convenient to use Group Theory to form combinations of the originally selected AO so that these combinations transform according to the irreducible representations (I.R.) of the group G of the symmetry transformations of the Hamiltonian  $H_{\text{eff}}$ . Then according to group theory the only nonzero matrix elements  $H_{ij}$  and  $S_{ij}$  occur between functions belonging to the same irreducible representation since the Hamiltonian operator and the identity operator transform according to the identity I.R. of the group G (see for example Heine "Group Theory"). The overlap integrals  $S_{ij}$  are called group overlap integrals when combinations of AO transforming according to the various I.R. are used. They are calculated by using SCF atomic orbitals like the ones given by Freeman and Watson or if the latter are not available Slater-type functions may be tried. For the Coulomb and resonance integrals either we try to calculate them directly from first principles or we approximate them by using experimental data concerning the ionization potential of free atoms and molecules.

The latter case is referred to as a semiempirical calculation.

CHAPTER II

SEMIEMPIRICAL MOLECULAR ORBITAL CALCULATION OF VANADIUM IN THE  
TUNGSTEN SITE OF  $\text{CaWO}_4$

In this chapter a semiempirical molecular orbital calculation of vanadium in the tungsten site of  $\text{CaWO}_4$  is tried.

The true symmetry of the tungsten site is  $S_4$ . However, if one restricts himself to the four neighboring oxygen atoms, then the symmetry is higher, namely  $D_{2d}$ . The coordinate systems have been chosen according to Fig. 1. Notice that the coordinate systems on the oxygen atoms are left-handed. This facilitates the calculation of the group overlap integrals. The character table of the point group  $S_4$  is given in Table I. The atomic orbitals s, p, d are classified according to the I.R as well as the angular momentum operators  $\hat{L}_x$ ,  $\hat{L}_y$ ,  $\hat{L}_z$ . In the lower part of Table I the reduction of some direct products of I.R. is given.

TABLE I  
CHARACTER TABLE OF  $S_4$  POINT SYMMETRY GROUP

$S_4$	E	$C_2$	$S_4$	$S_4^3$	
$\Gamma_1$	1	1	1	1	s; $z^2$ ; $x^2 + y^2$ ; $\hat{L}_z$
$\Gamma_2$	1	1	-1	-1	z; $x^2 - y^2$ ; $xy$
E	2	-2	0	0	x, y; xz, yz; $\hat{L}_x$ , $\hat{L}_y$
$\Gamma_1 \times \Gamma_2$	1	-1	1	-1	= $\Gamma_2$
$\Gamma_1 \times E$	2	0	-2	0	= E
$\Gamma_2 \times E$	2	0	-2	0	= E
$E \times E$	4	0	4	0	= $2\Gamma_1 + 2\Gamma_2$



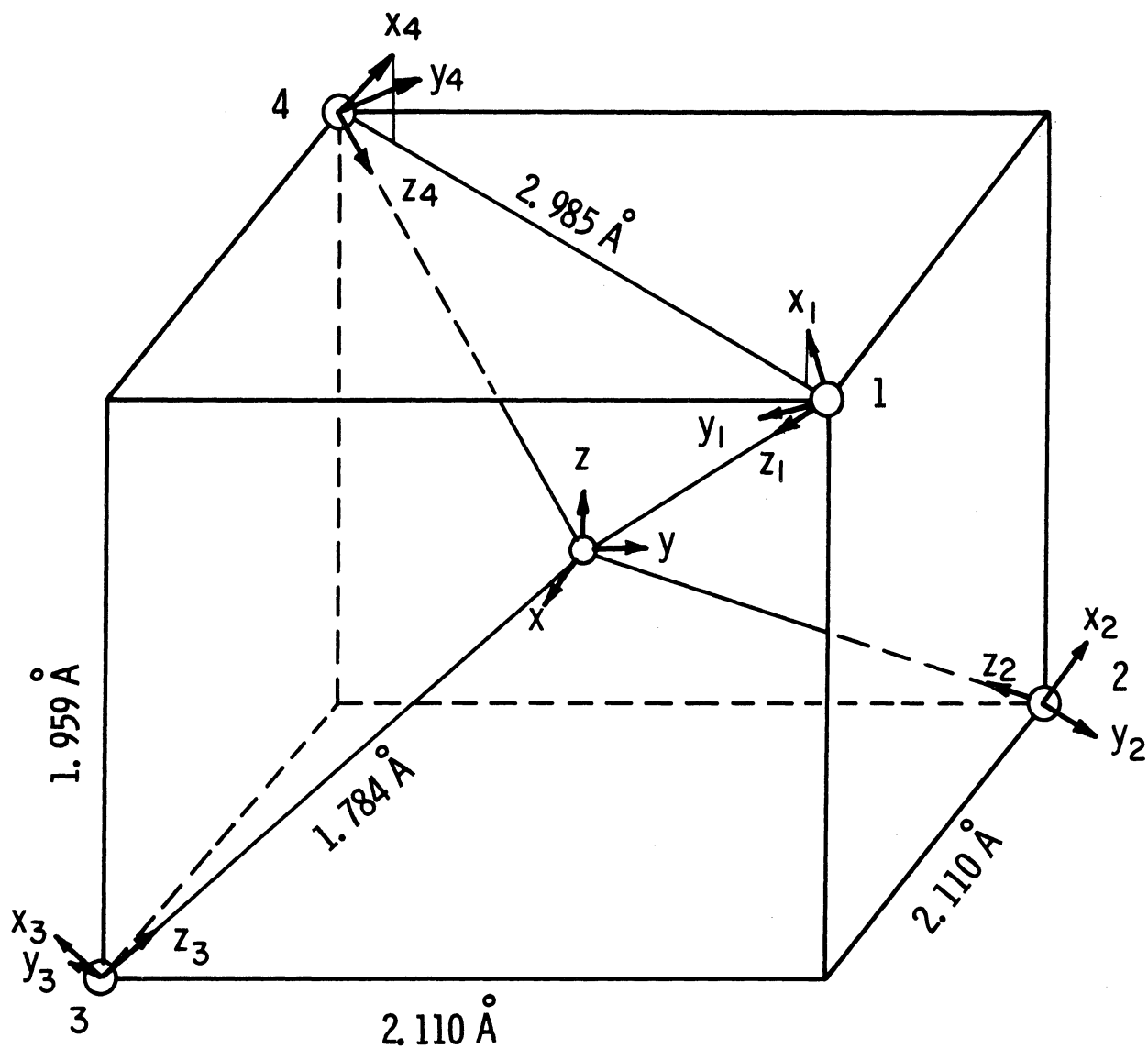
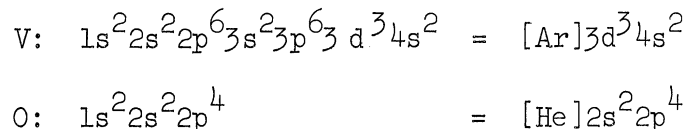


Fig. 1. Coordinate systems of vanadium and oxygen ions.

## SELECTION OF THE ATOMIC ORBITAL

Now the problem of which AO are to be used in the LCAO approximation is considered. The electronic configurations of the vanadium and oxygen atoms are as follows:



Since the vanadium  $3d$ ,  $4s$ , and  $4p$  AO's are energetically close as well as the oxygen  $2s$  and  $2p$  ones, it is reasonable to consider them as candidates in the expansion (II-1)

$$\psi_{\mu}(\underline{r}) = \sum_{i=1}^n c_i \phi_i \quad (\text{II-1})$$

Of course the greater the number  $n$  of the AO's used in (II-1) the better. However for practical reasons we try to limit this number as much as possible. Therefore we shall try to solve the problem of vanadium in the tungsten site using only the nine vanadium AO  $3d$ ,  $4s$ ,  $4p$  and the sixteen AO  $2s$ ,  $2p$  of the four neighboring oxygen atoms; i.e., we shall consider only the complex  $[\text{VO}_4]$ . Thus the molecular orbitals  $\psi_{\mu}(\underline{r})$  may be approximated by the (II-2).

$$\psi_{\mu}(\underline{r}) \approx \sum_{i=1}^{25} c_i \phi_i \quad (\text{II-2})$$

However, the approximation (II-2) is deficient in one important aspect, namely it does not take into consideration the surroundings of the complex  $[\text{VO}_4]$ . Thus one would be inclined to use the point symmetry group  $D_{2d}$  instead of the  $S_4$ . Furthermore the approximation (II-2) would result in the following

$\sigma$  oxygen hybrid bonding orbitals

$$\sin\theta_i(2s)_i + \cos\theta_i(2p)_i \quad i=1,2,3,4$$

whose hybridization angle  $\theta$  would be about  $25^\circ \pm 5^\circ$ , and the corresponding nonbonding orbitals

$$\cos\theta_i(2s)_i - \sin\theta_i(2p)_i$$

directed away from vanadium. What we intend to do, instead of the above program, is to incorporate the influence of the rest of the crystal in the construction of oxygen hybrid orbitals which will be combined afterwards according to the  $S_4$  point group.

Each of the oxygen atoms in the complex  $[VO_4]$  is at a distance of 1.78 Å from the vanadium atom and at 2.44 Å and 2.48 Å from two neighbor calcium atoms (see Fig. 2).

The vanadium atom and the two calcium atoms are the closest metal atoms and lie almost on a plane with the oxygen atom (oxygen atom about .25 Å off the plane defined by the vanadium and the calcium atoms).

Approximately perpendicular to this plane and at a distance of 2.91 Å lies a tungsten atom. We make the assumption that the hybrid orbitals, which are constructed pointing towards the four metal atom, will result in the most stable situation. Since it is convenient to have these hybrid orbitals orthogonal to each other, we construct first the three orthogonal hybrid orbitals which are directed towards the vanadium atom and the two calcium atom as follows:

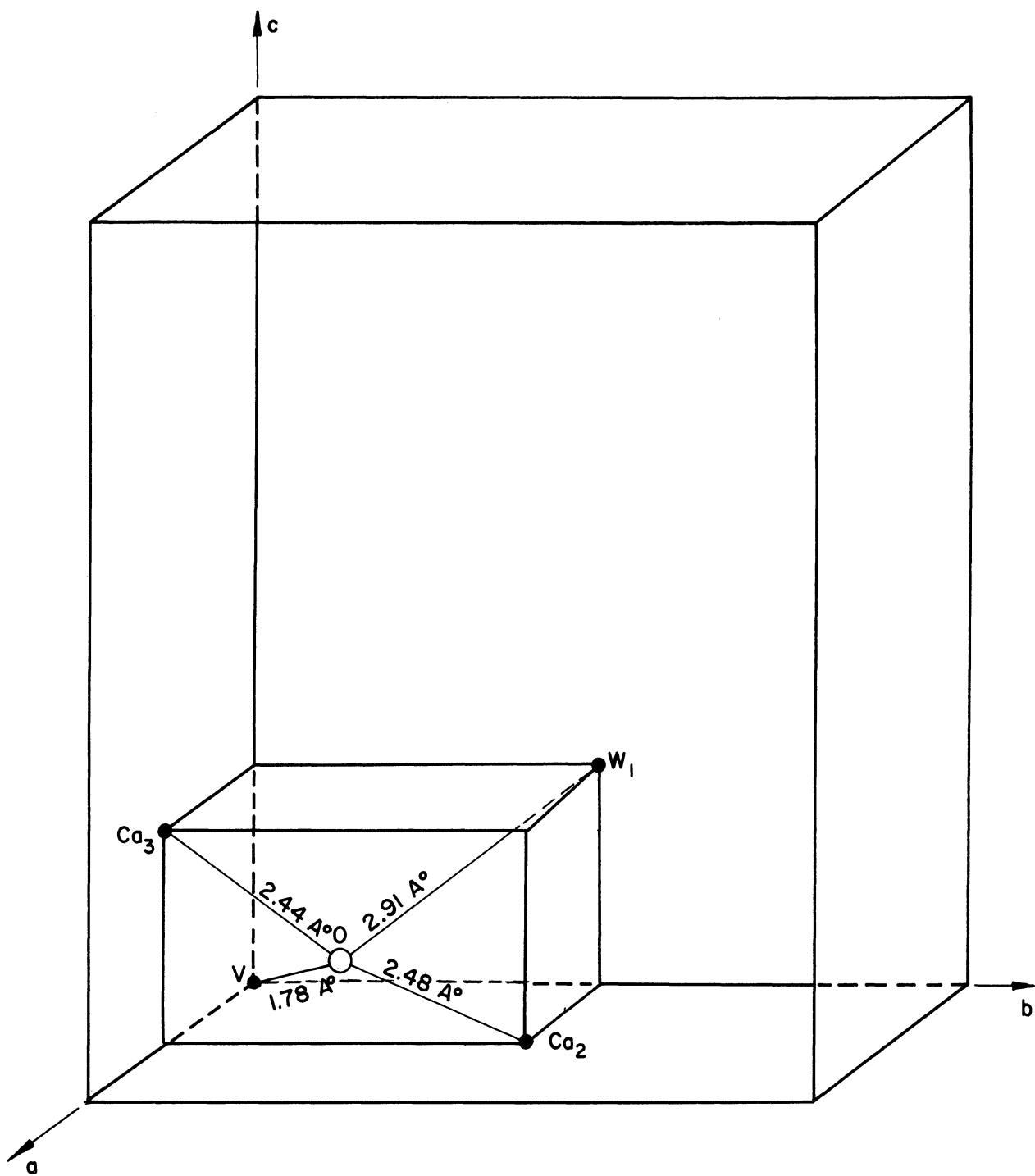


Fig. 2. Part of the unit cell showing the coordination of an oxygen atom.

$$\begin{aligned}
\phi_V &= .76473(2s) + .64435(2p)_V \\
\phi_{ca_2} &= .38671(2s) + .92220(2p)_2 \\
\phi_{ca_3} &= .49268(2s) + .87020(2p)_3
\end{aligned}
\tag{II-3}$$

Then we construct the orbital  $h$  which is orthogonal to the three orbitals in Eqs. (II-3) as follows:

$$h = .15133(2s) + .98848(2p)_{W_1} \tag{II-4}$$

The oxygen orbitals  $(2p)_V$ ,  $(2p)_2$ ,  $(2p)_3$  point towards the corresponding metal atoms. When checked the orbital  $h$  points quite close towards the direction of the  $W_1$ -site. To be more specific the direction angles of the  $h$  orbital are  $125^\circ$ ,  $53^\circ$ ,  $56^\circ$  and those of the  $W_1$ -site,  $116^\circ$ ,  $51^\circ$ ,  $50^\circ$ . The two directions form an angle of about  $10^\circ$ .

We take the orbitals in (II-3) and (II-4) as the proper ones to be used in (II-1). However, two of them, namely the  $\phi_{ca_2}$  and  $\phi_{ca_3}$  overlap very little with the vanadium orbitals and will be considered as nonbonding orbitals.

Thus referring to Fig. 1 the following orbitals (II-5) are to be used:

(a) the nine vanadium orbitals  $3d$ ,  $4s$ ,  $3p$

(b) the four  $\sigma$  orbitals

$$\sigma_i = .76473(2s)_i + .64435(2p)_i \quad i=1,2,3,4$$

(c) the four  $h$ -orbitals, which are almost  $\pi$ -orbitals,

$$\begin{aligned}
h &= .15133(2s) + (\alpha).52382(2p_x)_i - .81949(2p_y)_i \\
&\quad - .17957(2p_z)_i
\end{aligned}$$

where

$$\alpha = \begin{cases} 1 & \text{for } i=1,4 \\ -1 & \text{for } i=2,3 \end{cases} \tag{II-5}$$

Using the Character Table I for the  $S_4$  group and the transformation properties of the functions in (II-5) (see the Appendix) the combinations of orbitals which transform according to the I.R. of the  $S_4$  group are constructed. The results are summarized in Table II.

We observe that the symmetry arguments alone are not sufficient to determine the coefficients in the doubly degenerate irreducible representation E. This is because the  $S_4$  group is mathematically an abelian group with non-degenerate irreducible representations. The double degeneracy of the E I.R. which is shown in Table I is due to time reversal symmetry and not to the  $S_4$  point symmetry group.

TABLE II

COMBINATION OF AO TRANSFORMING ACCORDING TO THE I.R.'S OF THE  $S_4$  GROUP

I. R.	Metal	$\sigma$ -Ligand	$\pi$ -Ligand
$\Gamma_1$	$z^2; 4s$	$\Phi_1 = \frac{\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4}{2}$	$H_1 = \frac{h_1 + h_2 + h_3 + h_4}{2}$
$\Gamma_2$	$x^2 - y^2; xy; z$	$\Phi_2 = \frac{\sigma_1 - \sigma_2 - \sigma_3 + \sigma_4}{2}$	$H_2 = \frac{h_1 - h_2 - h_3 + h_4}{2}$
E	$\begin{pmatrix} \sin \alpha(xz) + \cos \alpha(yz) \\ \cos \alpha(xz) - \sin \alpha(yz) \end{pmatrix}$ $\begin{pmatrix} \sin \alpha'(y) + \cos \alpha'(x) \\ \cos \alpha'(y) - \sin \alpha'(x) \end{pmatrix}$	$\begin{pmatrix} \sin \beta\Phi_3 + \cos \beta\Phi_3' \\ \cos \beta\Phi_3 - \sin \beta\Phi_3' \end{pmatrix}$	$\begin{pmatrix} \sin \gamma H_3 + \cos \gamma H_3' \\ \cos \gamma H_3 - \sin \gamma H_3' \end{pmatrix}$

$$(1) \quad \Phi_3 \equiv \frac{\sigma_1 - \sigma_4}{\sqrt{2}}; \quad (3) \quad H_3 \equiv \frac{h_1 - h_4}{\sqrt{2}}$$

$$(2) \quad \Phi_3' \equiv \frac{\sigma_2 - \sigma_3}{\sqrt{2}}; \quad (4) \quad H_3' \equiv \frac{h_2 - h_3}{\sqrt{2}}$$

GROUP OVERLAP INTEGRALS

The group overlap integrals are calculated according to the standard techniques; see for example Reference 1 Chapter 7, Appendix I. The University of Michigan IBM 7090 computer was used. The following SCF radial functions were used.

Oxygen

$$\begin{aligned} R(2s) &= .5459\phi_2(1.80) + .4839\phi_2(2.80) \\ R(2p) &= .6804\phi_2(1.55) + .4038\phi_2(3.45) \end{aligned} \tag{II-6}$$

Vanadium

$$\begin{aligned} R(3d) &= .5243\phi_3(1.8289) + .4989\phi_3(3.6102) \\ &\quad + .1131\phi_3(6.8020) + .0055\phi_3(12.4322) \\ R(4s) &= R(4p) = .0677\phi_3(9.3319) - .0971\phi_3(5.1562) \\ &\quad - .0246\phi_3(3.5078) + .0441\phi_4(3.8742) \\ &\quad + .3607\phi_4(1.8764) + .6090\phi_4(1.1462) \\ &\quad + .1487\phi_4(.7800) \end{aligned} \tag{II-7}$$

where

$$\phi_n(\mu) \equiv \sqrt{\frac{(2\mu)^{2n+1}}{(2n)!}} r^{n-1} e^{-\mu r}$$

The following nonzero overlap integrals were found:

$$\begin{aligned} G_{\Gamma_1}(z^2, \phi_1) &= .02022; & G_{\Gamma_2}(x^2-y^2, H^2) &= -.15657 \\ G_{\Gamma_1}(z^2, H_1) &= .09518; & G_{\Gamma_2}(xy, \phi_2) &= .25564 \\ G_{\Gamma_1}(4s, \phi_1) &= .67470; & G_{\Gamma_2}(xy, H_2) &= -.05509 \\ G_{\Gamma_1}(4s, H_1) &= .04082; & G_{\Gamma_2}(z, H_2) &= .18355 \end{aligned} \tag{II-8}$$

$$\begin{aligned}
G_E(xz, \varphi_3) &= G_E(xz, \varphi_3') = G_E(yz, \varphi_3) = -G_E(yz, \varphi_3') = .16792 \\
G_E(y, \varphi_3) &= G_E(y, \varphi_3') = G_E(x, \varphi_3) = -G_E(x, \varphi_3') = .37166 \\
G_E(xz, H_3) &= -G_E(yz, H_3) = -.02774 \\
G_E(xz, H_3') &= G_E(yz, H_3) = .07510 \\
G_E(y, H_3) &= -G_E(x, H_3) = .14880 \\
G_E(y, H_3') &= G_E(x, H_3) = -.19477
\end{aligned}
\tag{II.8}$$

#### RESONANCE (or Exchange) INTEGRALS

In the semiempirical calculations we approximate the Coulomb integrals by experimental data and the resonance integrals by the following relation (II-9)

$$H_{ij} = -FG_{ij} \sqrt{H_{ii}H_{jj}} \tag{II-9}$$

where F is a constant between 1.67 and 2.00. The  $G_{ij}$  is the group overlap integral between the i-th and j-th orbitals. In the following, F will be taken equal to 2.00 according to common practice.

#### COULOMB INTEGRALS

The results of any semiempirical calculation depend crucially on the Coulomb integrals  $H_{ii}$  used in the Secular Equation (II-10)

$$|H_{ij} - ES_{ij}| = 0 \tag{II-10}$$

On the other hand the Coulomb integrals  $H_{ii}$ , which are approximated as



valence-state ionization potentials (VSIP), depend again crucially on the charges and the electronic configurations of the atoms. Therefore it seems that one is faced with an ambiguous problem. The way out of this ambiguity is to use the trial and error method in connection with some monitoring device. The most commonly used monitoring device is the "charge self-consistency"; i.e., (a) we assume a certain electronic charge and configuration (b) we estimate the corresponding VSIP (c) the secular equation is solved (d) the charge and configurations is calculated from the solution and (e) we stop when agreement between assumed and calculated values is reached.

Any overlap charge is divided in half between metal and ligand orbitals according to Mulliken's<sup>4</sup> suggestion.

To start the calculation we assume a charge of minus three for the complex  $[VO_4]$  which makes it isoelectronic with the complex  $[WO_4]^{2-}$  with 32 electrons. We expect most of this charge to be located in the periphery of the complex leaving the vanadium atom almost neutral. Thus each oxygen atom will have a charge in the vicinity of  $-.75$ . From previous calculations<sup>5</sup> the following VSIP of the  $\sigma$  and  $h$  oxygen orbitals are deduced:

$$\begin{aligned} \text{VSIP(Oxygen } \sigma) &= -77000 \text{ cm}^{-1} \\ \text{VSIP(Oxygen } h) &= -49500 \text{ cm}^{-1} \end{aligned} \tag{II-11}$$

These VSIP are held fixed in the following trial and error calculation. In general form the calculation runs as follows:

Assumed vanadium configuration:  $d^d s^s p^p$

Assumed vanadium charge:  $q = 5-d-s-p$

Assumed electronic charge:  $n = 5-q = d+s+p$

a) The Case of 3d VSIP

The assumed configuration  $3d^d 4s^s 4p^p$  is split into components corresponding to the configurations  $3d^n$ ,  $3d^{n-1} 4s$  and  $3d^{n-1} 4p$  as follows:

$$\text{Conf. } 3d^d 4s^s 4p^p = (1-s-p)\text{Conf} 3d^n + s\text{Conf} 3d^{n-1} 4s + p\text{Conf} 3d^{n-1} 4p$$

Then the VSIP of the 3d electron is given by the following expression

$$3d\text{VSIP} = (1-s-p)(3d\text{VSIP of } 3d^n) + s(3d\text{VSIP of } 3d^{n-1} 4s) + p(3d\text{VSIP of } 3d^{n-1} 4p) \quad (\text{II-12})$$

Generally  $n$  is not an integer. However, available estimations for the various VSIP's exist only for integer values of  $n$ . In Table III the values given<sup>3</sup> for vanadium by A. Viste and H. Basch are listed. The strong dependence of the VSIP's on the vanadium charge and configuration is obvious from the Table III.

In order to be able to use formula (II-12) in the cases where the electronic charge  $n$  is not an integer we interpolate the VSIP's assuming at most a quadratic dependence on the charge  $q$ . Therefore for every configuration we have an expression of the form

$$\text{VSIP}(q) = Aq^2 + Bq + C \quad (\text{II-13})$$

Table IV gives the calculated values of  $A$ ,  $B$ ,  $C$  for the corresponding transitions of Table III. Whenever the VSIP's for only two integer values  $n$  of a certain configuration are known, the coefficient  $A$  of the quadratic dependence is taken from the preceding configuration. Also, whenever the VSIP of a single integer value is known then both the coefficients  $A$  and  $B$  are

TABLE III

VALENCE-STATE IONIZATION POTENTIALS FOR VANADIUM IN  $\text{KCM}^{-1}$ 

Transition Involves	Vanadium Charge Change		
	0 $\rightarrow$ +1	+1 $\rightarrow$ +2	+2 $\rightarrow$ +3
3d electron	(3d <sup>5</sup> $\rightarrow$ 3d <sup>4</sup> )-31.4 (3d <sup>4</sup> 4s $\rightarrow$ 3d <sup>3</sup> 4s)-51.4 (3d <sup>4</sup> 4p $\rightarrow$ 3d <sup>3</sup> 4p)-61.4	(3d <sup>4</sup> $\rightarrow$ 3d <sup>3</sup> )(-115.2) (3d <sup>3</sup> 4s $\rightarrow$ 3d <sup>2</sup> 4s)(-152.4) (3d <sup>3</sup> 4p $\rightarrow$ 3d <sup>2</sup> 4p)(-162.7)	(3d <sup>3</sup> $\rightarrow$ 3d <sup>2</sup> )-230.6 (3d <sup>2</sup> 4s $\rightarrow$ 3d4s)-281.4
4s electron	(3d <sup>4</sup> 4s $\rightarrow$ 3d <sup>4</sup> )-51.0 (3d <sup>3</sup> 4s <sup>2</sup> $\rightarrow$ 3d <sup>3</sup> 4s)-60.4 (3d <sup>3</sup> 4s4p $\rightarrow$ 3d <sup>3</sup> 4p)(-70.6)	(3d <sup>3</sup> 4s $\rightarrow$ 3d <sup>3</sup> )-113.7 (3d <sup>2</sup> 4s <sup>2</sup> $\rightarrow$ 3d <sup>2</sup> 4s)(-131.9) (3d <sup>2</sup> 4s4p $\rightarrow$ 3d <sup>2</sup> 4p)(-136.7)	(3d <sup>2</sup> 4s $\rightarrow$ 3d <sup>2</sup> )-193.5
4p electron	(3d <sup>4</sup> 4p $\rightarrow$ 3d <sup>4</sup> )-27.7 (3d <sup>3</sup> 4p <sup>2</sup> $\rightarrow$ 3d <sup>3</sup> 4p)(-36.8) (3d <sup>3</sup> 4s4p $\rightarrow$ 3d <sup>3</sup> 4s)(-36.4)	(3d <sup>3</sup> 4p $\rightarrow$ 3d <sup>3</sup> )-80.6 (3d <sup>3</sup> 4s4p $\rightarrow$ 3d <sup>2</sup> 4s)-94.7	(3d <sup>2</sup> 4p $\rightarrow$ 3d <sup>2</sup> )(-148.4)

Note: Parentheses around the values indicate a result obtained by interpolation.

taken from the preceding configuration. It is obvious that the obtained curves in the latter two cases are less reliable but that is the best we can do for the present time.

TABLE IV

COEFFICIENTS OF THE INTERPOLATION TRINOMIAL  $Aq^2+Bq+C$  FOR THE VARIOUS VANADIUM CONFIGURATIONS

VSIP	Starting Configuration	A	B	C
3d	$3d^5$	-15.8	-68.0	-31.4
3d	$3d^4 4s$	-14.0	-87.0	-51.4
3d	$3d^4 4p$	-14.0	-87.3	-61.4
4s	$3d^4 4s$	- 8.6	-54.1	-51.0
4s	$3d^3 4s^2$	- 8.6	-62.9	-60.4
4s	$3d^3 4s4p$	- 8.6	-57.5	-70.6
4p	$3d^4 4p$	- 7.5	-45.4	-27.7
4p	$3d^3 4p^2$	- 7.5	-50.8	-36.8
4p	$3d^3 4s4p$	- 7.5	-50.8	-36.4

b) Cases of 4s and 4p VSIP's

These cases are similar to the previous one of the 3d VSIP with the difference that when the assumed configuration  $3d^d 4s^s 4p^p$  is decomposed to its components the results depend on what electronic orbital we have in mind. For example for the VSIP of a 4s electron the assumed configuration should be decomposed in contributions from the configurations  $3d^4 4s$ ,  $3d^3 4s^2$  and

and  $3d^3 4s 4p$ . Thus the obtained result is

$$\text{Conf. } 3d^d 4s^s 4p^p = (2-s-p)\text{Conf} 3d^4 4s + (s-1)\text{Conf} 3d^3 4s^2 + p\text{Conf} 3d^3 4s 4p \quad (\text{II-14})$$

Similarly when the VSIP of the  $4p$  electron is involved the configurations that should be considered are the  $3d^4 4p$ ,  $3d^3 4p^2$  and  $3d^3 4s 4p$ .

Thus we have instead

$$\text{Conf} 3d^d 4s^s 4p^p = (2-s-p)\text{Conf} 3d^4 4p + (p-1)\text{Conf} 3d^3 4p^2 + s\text{Conf} 3d^3 4s 4p \quad (\text{II-15})$$

#### RESULTS OF THE CHARGE-SELFCONSISTENT CALCULATION

By trial and error the following vanadium configuration has been found to give charge self-consistent results:

$$\begin{array}{ccc} 3.8281 & .4394 & .5744 \\ (3d) & (4s) & (4p) \end{array} \quad (\text{II-16})$$

Assuming this configuration the VSIP's for the vanadium atomic orbitals are found as follows.

$$\begin{aligned} 3d \text{ VSIP} &= -[-.0138(42.5) + .4394(65.5) + .5744(75.5)] = -71.6 \text{ Kcm}^{-1} \\ 4s \text{ VSIP} &= -[.9862(59.8) - .5606(70.6) + .5744(79.9)] = -65.3 \text{ Kcm}^{-1} \\ 4p \text{ VSIP} &= -[.9862(35.1) - .4256(45.0) + .4394(44.6)] = -35.0 \text{ Kcm}^{-1} \end{aligned} \quad (\text{II-17})$$

We have taken already as VSIP's for the  $\sigma$  and  $h$  oxygen hybrid orbitals  $-77.0 \text{ Kcm}^{-1}$  and  $-49.5 \text{ Kcm}^{-1}$  correspondingly.

Approximating the Coulomb integrals  $H_{ii}$  with the above VSIP's four secular equations are solved, one for each of the irreducible representations of the  $S$  point group. The results are given in the following Table V and Fig. 3.

TABLE V

EIGENVALUES AND EIGENFUNCTIONS OF THE COMPLEX  $[\text{VO}_4]^{3-}$ 

$\text{cm}^{-1}$		
+76893	$\Gamma_1$	$-.0479z^2 - 1.2652s + 1.2147\phi_1 + .0850H_1$
+26974	E	$-.2577xz - .2320yz - .9126y - .7404x + .9116\phi_3 + .0878\phi_3' + .0075H_3 - .3657H_3'$ $-.2320xz + .2577yz - .7404y + .9126x - .0878\phi_3 + .9116\phi_3' + .3657H_3 + .0075H_3'$
-28404	$\Gamma_2$	$-.1961x^2 - y^2 + .1252xy + .9128z + .0791\phi_2 - .5971H_2$
-45315	$\Gamma_2$	$.2640x^2 - y^2 + .5629xy + .4053z - .4688\phi_2 + .6015H_2$
-45641	E	$.4524xz + .1653yz - .0863y + .0024x - .2825\phi_3 - .0971\phi_3' + .1321H_3 - .8943H_3'$ $-.1653xz + .4524yz - .0024y - .0863x - .0971\phi_3 + .2825\phi_3' - .8943H_3 - .1321H_3'$
-47689	$\Gamma_1$	$-.2754z^2 + .03238 - .0508\phi_1 + .9855H_1$
-50849	$\Gamma_2$	$.2686x^2 - y^2 - .6415xy + .1958z + .6126\phi_2 + .5226H_2$
-62451	E	$-.6052xz + .2756yz + .3394y - .1479x + .1253\phi_3 + .3604\phi_3' + .2912H_3 - .2361H_3'$ $+ .2756xz + .6052yz - .1479y - .3394x - .3604\phi_3 + .1253\phi_3' + .2361H_3 + .2912H_3'$
-72465	$\Gamma_1$	$.9652z^2 - .0306s - .0113\phi_1 + .1843H_1$
-73729	$\Gamma_2$	$-.920x^2 - y^2 + .0059xy + .0122z + .0348\phi_2 + .2711H_2$
-89339	E	$.5058xz + .1908yz + .0891y + .0339x + .6148\phi_3 + .2779\phi_3' - .0008H_3 + .0358H_3'$ $-.1908xz + .5058yz - .0339y + .0891x + .2779\phi_3 - .6148\phi_3' + .0358H_3 + .0008H_3'$
-89640	$\Gamma_2$	$.0061x^2 - y^2 + .5740xy + .0005z + .6838\phi_2 - .0239H_2$
-100007	$\Gamma_1$	$.0212z^2 + .4895s + .6015\phi_1 + .0062H_1$

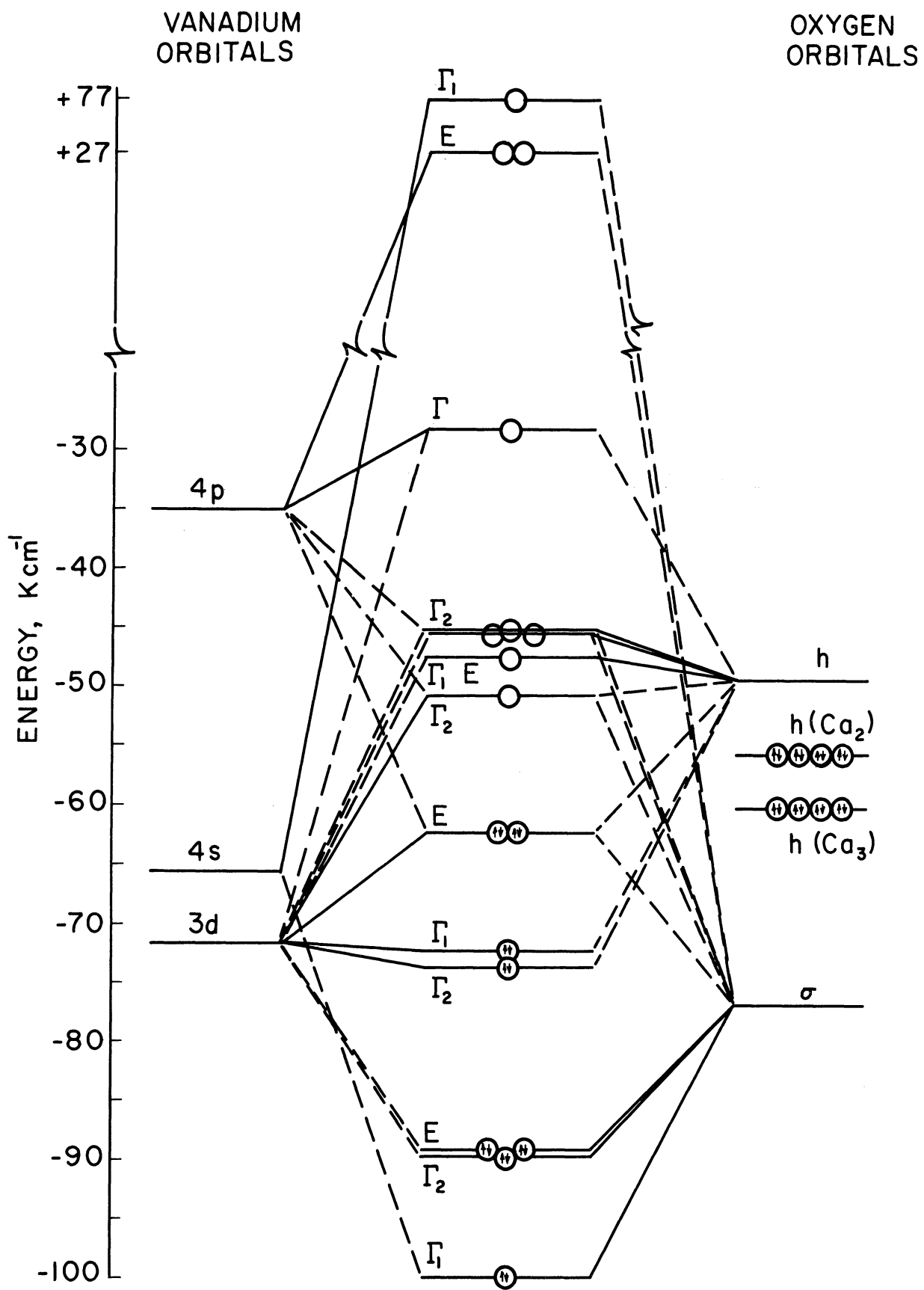


Fig. 3. Charge self-consistent MO calculation of vanadium in the Tungsten site of  $\text{CaWO}_4$ .

Using the eigenfunctions of Table V and the overlap integrals in (II-8) the output configuration is calculated and matches exactly the assumed configuration

$$\begin{array}{ccc} 3.8281 & .4394 & .5744 \\ 3d & 4s & 4p \end{array}$$

To be more specific the following distribution of electronic charge is found:

TABLE VI  
DISTRIBUTION OF THE METAL ELECTRONIC CHARGE AMONG THE AO

I.R	Orbital	Electronic charge
$\Gamma_1$	$3z^2-r^2$	.9490
	4s	.4394
$\Gamma_2$	$x^2-y^2$	.8849
	xy	.4299
	z	.0008
E	xz	.7822
	yz	.7822
	y	.2868
	x	.2868

The total electronic charge is 4.8419 corresponding to a net vanadium charge of

$$q = +.1581 \quad (\text{II-18})$$

On the right hand side of Fig. 3 in addition to the  $\sigma$  and  $h$  oxygen hybrid



orbitals the oxygen nonbonding orbitals which are directed towards the neighboring calcium atoms are shown. Their energies are calculated from the same values of the oxygen 2s and 2p VSIP which were used in calculating the  $\sigma$  and h orbitals, namely  $2pVSIP = -48.4 \text{ Kcm}^{-1}$  and  $2sVSIP = -97.3 \text{ Kcm}^{-1}$ .

#### HIGHEST OCCUPIED ORBITAL

The assumed charge on the complex  $VO_4$  and  $-3$  corresponding to a total number of 32 electron. We start filling the levels in Fig. 3 from the bottom going up until the number of electrons is exhausted. The highest filled level is the  $h(Ca_2)$ . However, the levels  $h(Ca_2)$  and  $h(Ca_3)$  are considered as nonbonding and therefore do not enter in the interactions of the vanadium center. For the latter the highest filled level is the doubly degenerate level E at  $-62.5 \text{ Kcm}^{-1}$ .

## CHAPTER III

### EPR PROPERTIES OF THE COMPLEX $[\text{VO}_4]$

According to the results obtained in the previous chapter no EPR signal is expected from the complex  $[\text{VO}_4]^{3-}$  because all electrons are paired. This is in agreement with the experimental fact that the crystals of  $\text{CaWO}_4:\text{V}$  do not show any EPR signal. However, after x-irradiation many EPR lines are observed<sup>6</sup> bearing the signature of the vanadium hyperfine interaction. In particular an intense set of eight lines is observed<sup>6</sup> which shows an isotropic  $g$  value of 2.0245 and a hyperfine separation of 19 to 21 gauss. Both of these properties are a little unusual for vanadium and the possibility of identifying the complex  $[\text{VO}_4]$  as the source of this EPR signal need to be considered. Obviously the x-irradiation produces unpaired spins giving the EPR signal. We distinguish the following possibilities:

- a) An electron is knocked out of the vanadium center by the x-rays. This leaves a hole in the highest occupied level. When examined the EPR properties of this hole are found far from being the isotropic tensor.
- b) An electron is excited from the level E to a higher level. This gives spin zero or one contrary to the observed effective spin of  $1/2$ .
- c) An electron is added to the vanadium center. In this case the calculated  $g$  values are found as follows when the eigenvalues and eigenfunctions of Table V are used:

$$g_{11} = 2.010$$

(III-1)

$$g_1 = 2.003$$

#### COMMENTS

Only in the last case do we have some resemblance with the observed set of the eight strong lines; namely (a) the calculated  $g$  values are greater than 2 (b) the extra electron in the  $\Gamma_2$  level spends less than 42% of its time in the vanadium neighborhood in accordance, perhaps, with the observed small hyperfine interaction. However, the numerical results are fair because they show a pronounced anisotropy which is compatible with the symmetry of the tungsten site but not in agreement with the experimental values. In addition the calculated values for the  $\Delta g$ 's are small. Probable inadequacies of calculation may be due to the following reasons:

a) The complex  $[\text{VO}_4]$  is not in vacuum but in the  $\text{CaWO}_4$  crystal.

Therefore the VSIP may be altered by a type of Madelung potential.

b) With the extra electron in the  $\Gamma_2$  orbital the charge of the complex has been altered and consequently the VSIP's have changed too. The alteration may be due either to the addition of a completely new electron to the complex bringing its charge up to -4 or to the transfer of one electron from the lone pairs of the nonbonding orbitals to the  $\Gamma_2$  molecular orbital. The latter transfer leaves the overall charge of the complex unchanged but redistributes the electronic cloud so that an excited state results. In any case due to the necessity of charge neutrality the extra

negative charge of the vanadium center has to be compensated by a positive charge in the neighborhood.

We consider the case (b) in which extra negative charge is added to vanadium. The usual formula<sup>7</sup> for nondegenerate ground state is used; i.e.,

$$g_{ij} = 2(\delta_{ij} - \lambda \Lambda_{ij}) \quad (\text{III-2})$$

where

$$\Lambda_{ij} = \sum_{n \neq 0} \frac{\langle 0 | \hat{L}_i | n \rangle \langle n | \hat{L}_j | 0 \rangle}{E_n - E_0} \quad (\text{III-3})$$

However an extra difficulty arises from the fact that the ground state  $|0\rangle$  and the excited states  $|n\rangle$ , which are Slater determinants, consist of wave functions having both metal and ligand parts. Thus in one of the matrix elements, for example the  $\langle 0 | \hat{L}_i | n \rangle$  only ligand-ligand and metal-metal contributions need to be taken thinking of it as being the matrix element due to the spin-orbit coupling (There is a  $1/r^3$  dependence in the spin-orbit coupling constant). In this case the other matrix element  $\langle n | \hat{L}_j | 0 \rangle$  has to be due to the Zeeman interaction and the contributions from metal-ligand and ligand-metal should be taken in addition to the others. For more details see the example References 5 and 8. In Fig. 4 the coupling of the  $\Gamma_2$  I.R. is shown by the singular momentum operators. As for the one-electron spin-orbit coupling constant the value of  $-150\text{cm}^{-1}$  is used. From the spectroscopic data the corresponding values of  $V^\circ$  and  $V^+$  are  $-158\text{cm}^{-1}$  and  $-136\text{cm}^{-1}$ . Actually for the parts coming from the ligand contribution a higher constant should be used. However, by using  $180\text{cm}^{-1}$  for the ligand-ligand evaluations of the spin-orbit matrix elements no

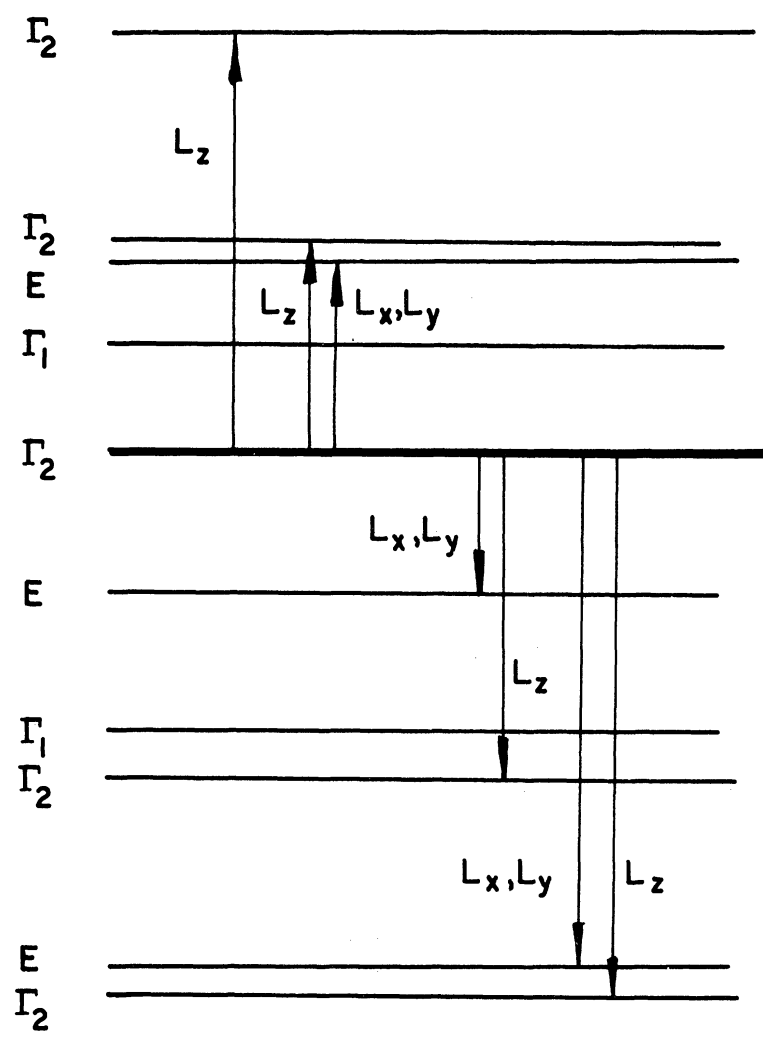


Fig. 4. Coupling of the  $\Gamma_2$  I.R. by the angular momentum operators.

effect of importance is observed.

CHARGE-SELFCONSISTENT CALCULATION WITH THE EXCITED  $\Gamma_2$  LEVEL OCCUPIED BY AN EXTRA ELECTRON

The calculation for the complex  $[\text{VO}_4]^{4-}$  follows the same steps as that of  $[\text{VO}_4]^{3-}$ . We start by fixing the values of oxygen (2p) VSIP  $\approx -16 \text{ Kcm}^{-1}$  and (2s)VSIP  $\approx -70 \text{ Kcm}^{-1}$ . The higher VSIP are due now to the approximate -1 charge that each of the oxygen atoms is suppose to have. Various vanadium configurations are tried. Self-consistency is obtained for the following configuration

$$\begin{array}{ccc} 4.6718 & .4967 & .0102 \\ 3d & 4s & 4p \end{array} \quad (\text{III-4})$$

The total electronic charge is  $n = 5.1788$  corresponding to a net vanadium charge of  $q = -.1788$ .

The VSIP corresponding to this configuration are as follows:

$$\begin{aligned} E_d &= -[.4390(19.7)+.4968(36.3)+.0102(46.2)] = -28.22 \\ E_s &= -[1.4930(41.6)-.5032(49.4)+.0102(60.6)] = -37.87 \quad (\text{III-5}) \\ E_p &= -[1.4930(19.8)-.9898(27.9)+.4965(27.5)] = -15.61 \end{aligned}$$

The above results are obtained in this case by extrapolating the quadratic fit of Table IV in the region of negative vanadium charge and are less reliable than before. Specially it was felt that the (2p)VSIP value should be increased a little. Summarizing, the following VSIP values were used, which gave the above mentioned configuration (III-4).

$$\begin{aligned} (4p)\text{VSIP} &= -5.93 \text{ Kcm}^{-1} & (h)\text{VSIP} &= -16.2 \text{ Kcm}^{-1} \\ (3d)\text{VSIP} &= -28.3 \text{ Kcm}^{-1} & & \\ (4s)\text{VSIP} &= -37.7 \text{ Kcm}^{-1} & (\sigma)\text{VSIP} &= -38.1 \text{ Kcm}^{-1} \end{aligned} \quad (\text{III-6})$$

Except for the increase in the (4p)VSIP of the order of 1 ev. the calculation is rigorously charge self-consistent. The distribution of the electronic charge is as follows:

TABLE VII

DISTRIBUTION OF THE METAL ELECTRONIC CHARGE AMONG THE AO

I.R	Orbital	Electronic charge
$\Gamma_1$	$3z^2-r^2$	.9780
	4s	.4968
$\Gamma_2$	$x^2-y^2$	.9493
	xy	.9574
	z	
E	xz	.8935
	yz	.8935
	y	.0053
	x	.0053

The calculated g values are:

$$g_{11} = 2.0700$$

$$g_{\underline{1}} = 2.0608 \quad (\text{III-7})$$

We observe that the g tensor is almost isotropic but the absolute values are greater this time than the observed one.

At this point we observe by mere arithmetic that if all VSIP are made deeper by a factor of 2.528 the following values are obtained for the g tensor.

$$g_{11} = 2.0268 \text{ and } g_{\underline{1}} = 2.0231$$

These values are just above and below the observed  $g$  value of 2.0245.

The above mention reduction involves energies of the order of  $50 \text{ Kcm}^{-1}$  for the vanadium 3d and 4s VSIP's.

A rough calculation shows that a positive unit charge located at the site of a neighboring calcium atom lowers the potential energy of an electron at the tungsten site by about  $30 \text{ Kcm}^{-1}$ . Similarly a positive unit charge at a distance of  $1.784 \text{ \AA}$  which is the vanadium-oxygen distance creates a lowering of about  $65 \text{ Kcm}^{-1}$ .

From these magnitudes we observe that perhaps the final answer to the problem lies in the way the extra negative charge which is located at the vanadium site is compensated by the crystal.

The results are summarized in Fig. 5 and Table VIII.



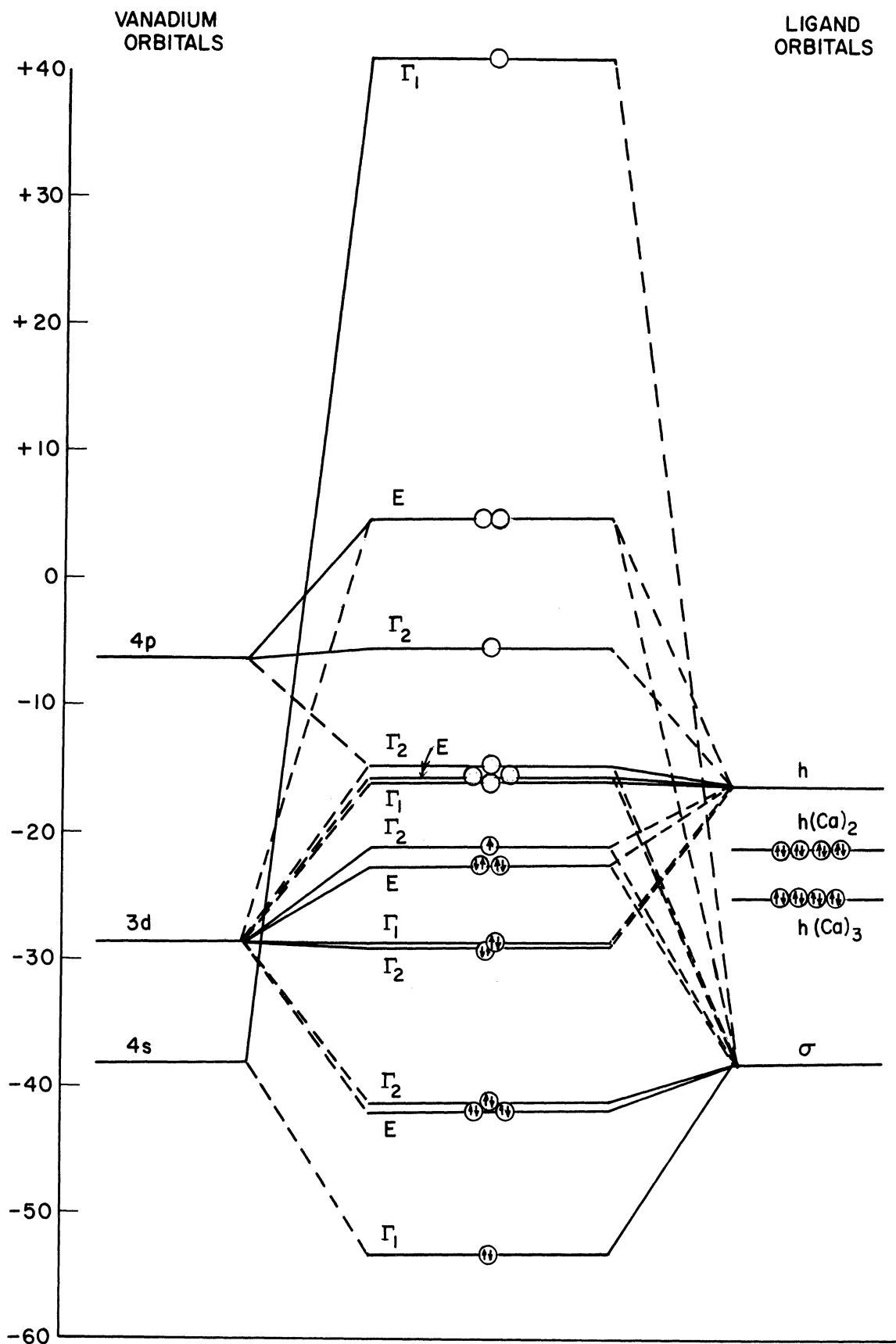


Fig. 5. MO calculation of the complex  $[\text{VO}_4]^{4-}$ .

TABLE VIII

EIGENVALUES AND EIGENFUNCTIONS OF THE COMPLEX  $[\text{VO}_4]^{4-}$ 

Energy $\text{cm}^{-1}$	I.R.	Eigenfunctions
+41218 (104199)	$\Gamma_1$	$-.0485z^2 - 1.2432s + 1.2390\phi_1 + .0869H_1$
+5167 (13063)	E	$-.2869xz + .0014yz - 1.2200y + .0698x + .4268\phi_3 + .4698\phi_3' + .2080H_3 - .2150H_3'$ $+ .0014xz + .2869yz + .0698y + 1.2200x - .4698\phi_3 + .4268\phi_3' + .2150H_3 + .2080H_3'$
-5170 (-13071)	$\Gamma_2$	$-.0738(x^2 - y^2) - .0378xy + 1.0123z + .0178\phi_2 - .2895H_2$
-14515 (-36693)	$\Gamma_2$	$.3081(x^2 - y^2) + .2286xy + .1044z - .1270\phi_2 + .9595H_2$
-15493 (-39167)	E	$.2980xz + .0896yz - .0300y + .0127x - .1406\phi_3 - .0676\phi_3' + .0984H_3 - .9720H_3'$ $- .0896xz + .2980yz - .0127y - .0300x - .0676\phi_3 + .1406\phi_3' - .9720H_3 - .0984H_3'$
-15739 (-39787)	$\Gamma_1$	$-.2001z^2 + .0337s - .0522\phi_1 + .9966H_1$
-20928 (-52907)	$\Gamma_2$	$.0823(x^2 - y^2) - .9266xy - .0029z + .6188\phi_2 + .1776H_2$
-22380 (-56576)	E	$-.5669xz + .6598yz + .0783y - .0953x - .0400\phi_3 + .5373\phi_3' + .2032H_3 - .0801H_3'$ $.6598xz + .5669yz - .0953y - .0783x - .5373\phi_3 - .0400\phi_3' + .0801H_3 + .2032H_3'$
-28490 (-72023)	$\Gamma_1$	$.9837z^2 - .0244s + .0042\phi_1 + .1079H_1$
-28734 (-72639)	$\Gamma_2$	$.9586(x^2 - y^2) + .0134xy + .0126z - .0136\phi_2 - .1719H_2$
-41138 (-103996)	$\Gamma_2$	$.00003(x^2 - y^2) + .4014xy + .0002z + .8189\phi_2 - .0016H_2$
-41595 (-105151)	E	$.3532xz - .1614yz - .1438y + .0658x + .3193\phi_3 + .8440\phi_3' + .0286H_3 - .0147H_3'$ $.1614xz + .3532yz - .0658y - .1438x + .8440\phi_3 - .3143\phi_3' - .0147H_3 - .0286H_3'$
-53148 (-134358)	$\Gamma_1$	$.0057z^2 + .5432s + .5496\phi_1 - .0024H_1$

Note: The numbers in parenthesis correspond to the case where all the VSIP have been divided by the factor 2.528.

## CHAPTER IV

### CONCLUSIONS AND REMARKS

The results obtained in the Chapters III and IV point decidedly in identifying the complex  $[\text{VO}_4]$  as the source of the set of the eight intense lines. During the trial and error method all calculations were giving positive  $\Delta g$  shifts with values varying from .002 to .080. The complex  $[\text{VO}_4]^{4-}$  seems to satisfy better the charge self-consistency and the isotropy of the  $g$  tensor although not both of them simultaneously. However, one may find many reasons for changing the extrapolated VSIP's, as we did, in the case of the  $[\text{VO}_4]^{4-}$ , in order to accommodate both the isotropy of tensor and the charge self-consistency. It is felt that further calculations at this point will not help much. On the contrary more experimental results are needed. For example a serious objection that one might have for the scheme of  $[\text{VO}_4]^{4-}$  is the two extra negative charges of this complex as compared to  $[\text{WO}_4]^{2-}$ . Even in the milder case of  $[\text{VO}_4]^{3-}$ , charge compensation is required which, if the sample is pure  $\text{CaWO}_4$  with vanadium only as an impurity, must come from vanadium itself.

Thus one can picture the complex  $[\text{VO}_4]^{3-}$  adjacent to a  $\text{V}^{3+}$  which occupies a calcium site. Then a very appealing scheme is the following: By x-irradiation a lone pair occupying the nonbonding orbitals  $h(\text{Ca}_2)$  or  $h(\text{Ca}_3)$  is broken up. One of the electrons is transferred to the  $\Gamma_2$  MO giving the above mentioned EPR signal and the other electron is attracted

by the adjacent vanadium reducing it to  $V^{2+}$ . Therefore the total charge of the complex is actually decreased to  $[VO_4]^{2-}$  and the adjacent vanadium has an odd number of electrons which should produce an EPR signal characteristic of ionic vanadium.

Furthermore this signal should be anisotropic having some relation with the broken lone pair. Referring to Fig. 3 it seems that the  $h(Ca_2)$  lone pairs are more likely to be affected by the x-irradiation since they lie higher in energy than the  $h(Ca_3)$  ones. On the other hand the  $h(Ca_3)$  are closer to the calcium sites that presumably the vanadium impurity occupies.

Perhaps it is significant that such anisotropic spectra characteristic of ionic vanadium have been reported.<sup>6</sup> A further experimental study of these spectra, specially their angular properties with respect to orbitals  $h(Ca_2)$  and  $h(Ca_3)$  seems to be highly desirable.

Finally in Chapter III we saw that a reduction of the estimated VSIP by a factor 2.528 would bring the  $g$  values in the right position. This reduction amounts in using the following VSIP's.

$$\begin{aligned}
 4p\text{VSIP} &= -15.0 \text{ Kcm}^{-1} & \text{VSIP} &= -41.0 \text{ Kcm}^{-1} \\
 4s\text{VSIP} &= -95.0 \text{ Kcm}^{-1} & \text{VSIP} &= -96.2 \text{ Kcm}^{-1} & \text{(IV-1)} \\
 3d\text{VSIP} &= -71.6 \text{ Kcm}^{-1}
 \end{aligned}$$

We notice that according to the above model in which a lone pair is split we can accomplish two things. First bring an electron to the orbital which gives the EPR signal of the strong lines and second reduce the overall charge of the complex to -2 so that the VSIP are lowered as required

to produce the observable g values. In fact both the  $\sigma$  VSIP and  $4s$ VSIP in (IV-1) are lower than in the case of the  $[\text{VO}_4]^{3-}$ . The  $4s$  and  $3d$  interchange order probably because the  $\Gamma_2$  orbital adds electronic charge to the  $3d$  orbitals  $x^2-y^2$  and  $xy$ . Similarly charge is added to the  $h$  and  $4p$  orbitals accounting perhaps for the relative increase in these VSIP's.

APPENDIX

TRANSFORMATION OF AO BY THE  $S_4$  GROUP  
(Coordinates and Indices as in Fig. 1)

$S_4$	E	$C_2$	$S_4$	$S_4^3$
$\sigma_1$	$\sigma_1$	$\sigma_4$	$\sigma_2$	$\sigma_3$
$\sigma_2$	$\sigma_2$	$\sigma_3$	$\sigma_4$	$\sigma_1$
$\sigma_3$	$\sigma_3$	$\sigma_2$	$\sigma_1$	$\sigma_4$
$\sigma_4$	$\sigma_4$	$\sigma_1$	$\sigma_3$	$\sigma_2$
$x_1$	$x_1$	$x_4$	$-x_2$	$-x_3$
$x_2$	$x_2$	$x_3$	$-x_4$	$-x_1$
$x_3$	$x_3$	$x_2$	$-x_1$	$-x_4$
$x_4$	$x_4$	$x_1$	$-x_3$	$-x_2$
$y_1$	$y_1$	$y_4$	$y_2$	$y_3$
$y_2$	$y_2$	$y_3$	$y_4$	$y_1$
$y_3$	$y_3$	$y_2$	$y_1$	$y_4$
$y_4$	$y_4$	$y_1$	$y_3$	$y_2$
$x$	$x$	$-x$	$y$	$-y$
$y$	$y$	$-y$	$-x$	$x$
$z$	$z$	$z$	$-z$	$-z$

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